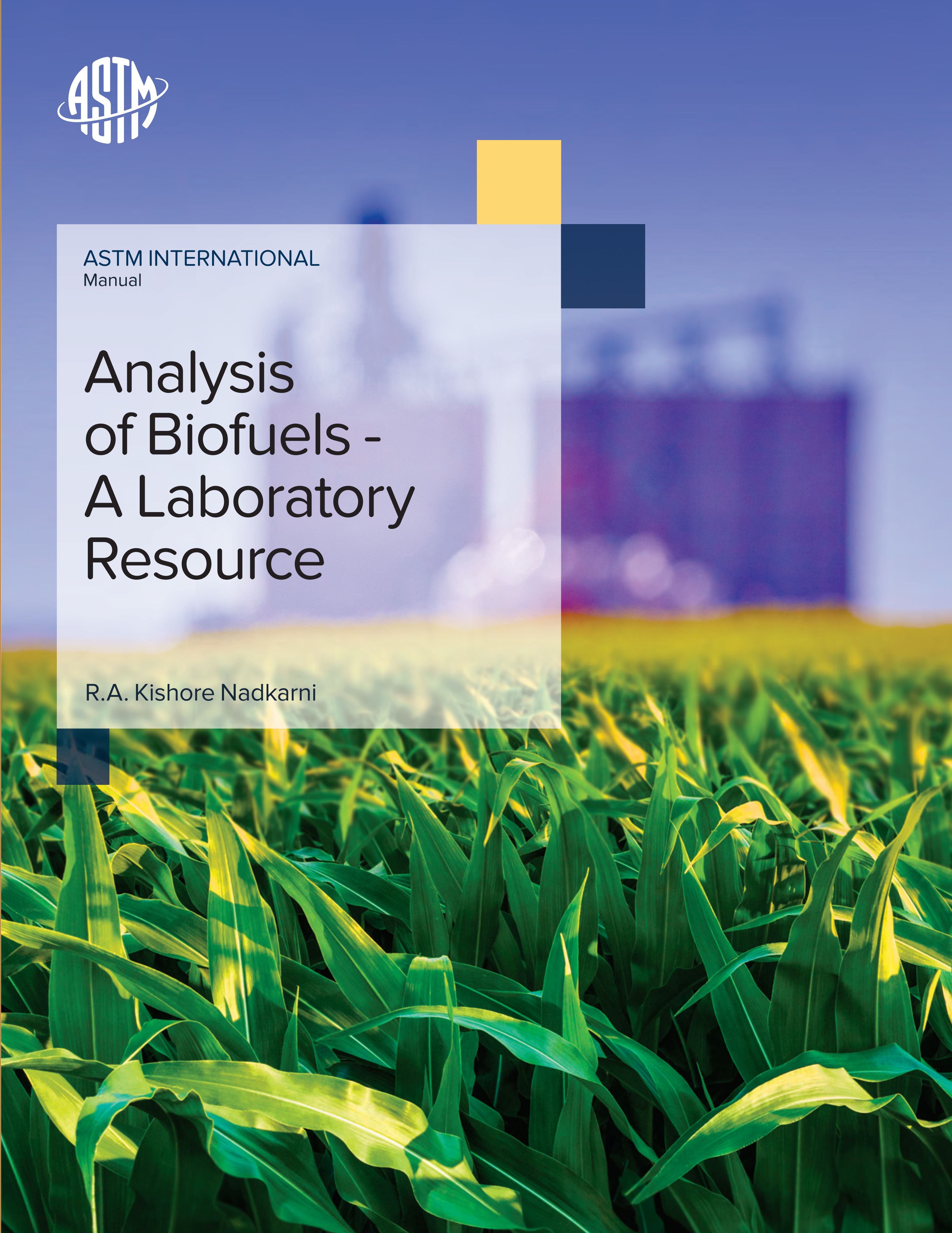

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Analysis of Biofuels - A Laboratory Resource

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Foreword

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UOP Methods

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Note: Rows in bold type are ASTM biofuels specifications; NA = not available.

[a] Test method standards specifically developed for the analysis of biofuels.

Chapter 1 | Introduction to Biofuels and Overview of Analysis Methods

As the crude oil stocks around the world slowly dwindle and the price of crude oil and gasoline at the pump skyrocket, serious attention is being given to developing alternate fuels for internal combustion engines. The more prominent among these alternative fuels are the ones derived from biomass, of which there is an abundance in a majority of oil-consuming countries. With encouragement from U.S. state and federal governments, a big push is on the way to commercialize biofuels. Worldwide investment in biofuels rose from $5 billion in 1995 to $38 billion in 2005 and topped $100 billion by 2010. According to the National Biodiesel Board, more than 170 companies in the United States are actively marketing biodiesel. ASTM International is working toward standardizing or developing test methods for the characterization of these biofuels and biolubes.

Challenges of Alternative Energy Sources

Given the world's ever expanding requirements for energy, alternate sources are being investigated around the globe. Among the possible alternate resources for crude oil are coal, oil shale, wind, solar, nuclear, ocean, and so on. Currently, interest is focused primarily on biofuels. Chief among the entities developing biofuels are the United States, Brazil, and the European Union (EU).

In 2010, worldwide biofuel production reached 28 billion gallons, up 17 % from 2009, and biofuels provided 2.7 % of the world's fuels for road transport. Global ethanol fuel production reached 23 billion gallons in 2010, with the United States and Brazil as the world's top producers; together they account for 90 % of global production. The world's largest biodiesel producer is the EU, accounting for 53 % of all biodiesel production in 2010. As of 2011, mandates for blending biofuels exist in 31 countries at the national level and in 29 states or provinces. The International Energy Agency (IEA) has a goal for biofuels to meet more than a quarter of the world's demand for transportation fuels by 2050 to reduce dependence on petroleum and coal [1].

Biomass is the source of all biofuels, which can be simply defined as any plant or animal material of recent origin, as opposed to plant or animal material that over millions of years has transformed into crude oil, tar sands, coal, oil shale, natural gas, or other petroleum product. For example, wood—used by humans for heating since the earliest days of civilization—is a biomass in its simplest form. Cotton fiber biomass has been used for tens of thousands of years for making clothes for humans [2]. Although numerous technologies are under development for converting biomass to fuels and chemicals, they all follow the same basic procedure (Table 1.1).

Biofuel contains energy from geologically recent carbon fixation. These fuels are produced from living organisms. Examples of carbon fixation occur in plants and microalgae. These fuels are made from biomass conversion of living organisms such as plants or plant-derived materials. The biomass can be converted to convenient energy containing substances in three different ways: thermal, chemical, or biochemical conversions. The fuel from biomass conversion can be in solid, liquid, or gas form [1].

During 2006 trilateral discussions, leaders from Brazil, the EU, and the United States affirmed their belief that the market for biofuels is viable, that it will continue to grow within the regions, and that the international trade in biofuels will increase significantly by the end of the decade. To support the global trade of biofuels, all three entities agreed to promote, whenever possible, the compatibility of biofuel-related standards in their respective regions. The group also concluded that the lack of a single international standard was not a hindrance in the marketplace. Subsequently, the International Biofuels Forum a government initiative among Brazil, China, the EU, India, South Africa, and the United States—was launched in March 2007 to promote the sustained use and production of biofuels around the globe [3]. This group classified biodiesel and bioethanol specifications into three categories (Tables 1.2 and 1.3).

It appears that bioethanol specifications are more closely aligned among the three regions than biodiesel specifications. This is because bioethanol is a single chemical compound, whereas biodiesel is not a single chemical entity; it is derived from several types of feedstocks that may translate into variations in the performance characteristics of the finished fuel. Also, in biodiesel production, fatty acid methyl esters (FAMEs) and fatty acid ethyl esters are two chemically different mixtures, making it a challenge to develop a common standard that can address the complex fuel and engine requirements.

President George W. Bush signed the Energy Policy Act of 2005 (PL 109-58), which set minimum use requirements for

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TABLE 1.1 Basic Processes for Production of Biofuels

Biomass Feedstock	Transformation Process	Final Product
Algae, corn, sugarcane bagasse, switchgrass, tallow, wood	Catalysis, chemical extraction, combustion, enzymes, fermentation, pyrolysis	Biodiesel, butanol, ethanol, ethylene, syngas, heat

From [2].

TABLE 1.2 Classification of Various Biodiesel Specifications

Category A (Similar)	Category B (Significant Differences)	Category C (Fundamental Differences)
Sulfated ash	Phosphorus content	Sulfur content
Alkali and alkaline Earth metal content	Carbon residue	Cold climate operability
Free glycerol content	Total glycerol content	Cetane number
Copper strip corrosion	Ester content	Oxidation stability
Methanol and ethanol content	Distillation temperature	Monoglycerides, diglycerides, and triacylglycerides
Acid number	Flash point	Density
	Water and sediment content	Kinematic viscosity
		Iodine number
		Linolenic acid content
		Polyunsaturated methyl ester

TABLE 1.3 Classification of Various Bioethanol Specifications

Category A (Similar)	Category B (Significant Differences)	Category C (Fundamental Differences)
Color	Ethanol content	Water Content
Appearance	Acidity	
Density	Phosphorus content	
Sulfate content	pHe	
Copper content	Gum/evaporation residue	
Iron content	Chloride content	
Sodium content		
Electrolytic conductivity		
Sulfur content		

renewable fuels such as ethanol and biodiesel. It established a Renewable Fuel Standard (RFS) and mandated the production of 4 billion gallons of renewable fuels (ethanol and biodiesel) in 2006, increasing to 7.5 billion gallons by 2012. The U.S. Environmental Protection Agency (EPA) issued a final ruling implementing RFS on May 1, 2007. President Bush had called for the scope of the RFS to be expanded to an Alternative Fuels Standard (AFS) to include not only corn-based and cellulose-based ethanol and biodiesel but also methanol, butanol, and other alternative fuels. It is likely that at least 15 % of President Bush's target for a 10 % reduction in U.S. gasoline usage by 2017 will be met by the AFS. An energy bill signed by President Bush in December 2007 required 500 million gallons of biomass-based diesels to be introduced into the diesel pool by 2009, with a phased increase to 1 billion gallons by 2012 and 36 billion gallons by 2022. The EPA issued a final rule implementing RFS on May 1, 2007 [4].

The second version of the national Renewable Fuel Standard (RFS2) was passed by the U.S. Congress, requiring more than 1 billion gallons of biomass-based diesel be used in the U.S. diesel fuel pool by 2012. These state and anticipated federal mandated volumes specific to biodiesels have caused a dramatic increase in production capacity and overall product volumes for biodiesel [5].

The original RFS targets were surpassed by increased use of biofuels. In his January 23, 2007, State of the Union address, President Bush called for a 20 % reduction in gasoline consumption by 2017 (the so-called "twenty in ten" plan). This plan would increase the use of renewable and alternative fuels to 35 billion gallons by 2017, nearly five times the 2012 level required under the Energy Policy Act of 2005. Several bills were introduced in the U.S. Congress to increase biofuel production and consumption.

Biodiesel and ethanol fuel are the two most important alternate fuels to conventional petroleum-derived fuels. Biodiesel is a renewable source of energy. In the United States, biodiesel is comprised of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated as B100. Biodiesel is registered with the EPA as a fuel and a fuel additive under Section 211(b) of the Clean Air Act. Biodiesel blends can be used in many applications that utilize petroleum middle distillate (i.e., diesel fuel) products, such as on- and off-road diesel, home heating oil, boiler fuel, marine diesel fuel, and nonaviation gas turbine fuel. Biodiesel is most commonly used as a blend (B5) with conventional petroleum diesel in the existing equipment that more traditionally has operated solely on petroleum diesel. Blends in the range of B6 to B20 are also in regular usage with heavier duty diesel trucks and buses. Biodiesel is not suitable for use in gasoline engines; it is strictly intended for use in diesel engines [5].

In November 2014, the EPA announced that it was unable to decide on rule setting levels for the amount of biofuel it would require to be blended into conventional vehicle fuels for 2015 and 2016. The agency did not take up the RFS rule until 2015, when it sought to set levels for 2015 and 2016. The decision not to decide was the latest setback in a long line of economic, legal, and logistical hurdles the EPA has faced since it started requiring increased levels of ethanol to be incorporated into vehicle fuel under the energy laws passed in 2005 and 2007 [6].

By the end of 2015, the price of crude oil had collapsed more than 60 %, from more than a $100 a barrel to less than about $45 a barrel, the lowest price since the 2009 recession. Even in New York City, where gas prices are among the highest in the continental United States, regular gasoline could be found for around $2 a gallon as compared to about $4 or more a gallon earlier in 2014.

In July 2015, the American Automobile Association predicted that continued sliding oil prices would bring $2 a gallon gasoline back to U.S. filling stations later that same year. At the time of this writing, U.S. crude oil prices have fallen 20 % since June 2015 due to a glut of gasoline from shale fracking.

Biobased products are broadly defined as nonfood, nonfeed industrial products derived wholly or significantly in part from renewable plant, animal, marine, or forestry materials. Many biobased products have successfully entered the marketplace and have added value to agricultural materials beyond the traditional food, animal feed, and fiber markets. In addition to relieving dependence on imported petroleum, biobased products are important for many reasons from the perspective of the U.S. Department of Agriculture (USDA) [7].

Many governments around the globe have undertaken aggressive mandates to incorporate bioenergy into their transportation fuels in the hopes of limiting the world's overwhelming dependence on gasoline and diesel to move people and goods. Although biofuels account for only about 2.5 % of transportation fuel today, the EU expects renewable energy—primarily biofuels—to account for 10 % of its transportation fuel by 2020. In the United States, the biofuel goal is about 12 % by early in the next decade. The IEA envisions using biofuels to supply as much of 27 % of the world's transportation needs by mid-century [8,9].

Ethanol as an Automotive Biofuel

Ethanol has been used as a motor fuel in the United States since Henry Ford launched his famous Model T in 1908, making it capable of running on gasoline, ethanol, or a mixture of both. It has been widely used in the United States for many years as a gasoline extender and octane enhancer. The relatively cheap price of gasoline marginalized ethanol until the Arab oil embargo in the 1970s, when the U.S. Congress began giving oil companies tax credits for every gallon of ethanol they blended into gasoline. At that time, gasoline producers blended up to 10 volume percent ethanol with 90 % gasoline (a product known as gasohol at that time) to extend gasoline supplies. When oil prices began to fall in the late 1980s, U.S. dependence on imported oil began to grow, and ethanol was again relegated to little more than a blending component for some gas in the Midwest. However, Middle Eastern conflicts have again renewed interest in bioethanol and other alternative fuels, which are back at the forefront of the energy debate [9,10].

Nearly 40 years ago, a group of businessmen saw the potential of bioethanol made from sugarcane as a transportation fuel and created a national program promoting its use. Today, there are more than 300 bioethanol plants in Brazil. Roughly the size of the contiguous United States, Brazil has become a major player in bioethanol and biodiesel, most of which is currently produced in the state of Sao Paulo in the south. In March 2007, Brazilian president Luiz Inacio Lula da Silva and U.S. president George W. Bush signed a memorandum of understanding for establishing an energy partnership to encourage bioethanol and biodiesel use throughout North and South America. Today, the United States and Brazil together produce about 70 % of the world's bioethanol, but they manufacture and use it in different ways. For example, U.S. bioethanol is made from cornstarch, which involves a slightly more complicated process. Enzymes are needed to convert starch to glucose, which is then fermented. This extra step means the Brazilian method is more efficient and less expensive [10].

Bioethanol is an alcohol made by fermentation, mostly from carbohydrates produced in sugar or starch crops such as corn, sugarcane, or sweet sorghum. Cellulosic biomass, derived from nonfood sources such as trees and grasses, is also being developed as a feedstock for ethanol production [1].

Ethanol is hygroscopic and attracts moisture from the air. In the United States, this moisture has been considered a problem because it can lead to corrosion in fuel pipelines, storage tanks, and in car engines. In Brazil, hydrated bioethanol seems to be working fine. Overall, some 28 % of automobiles in Brazil are capable of running on one of these bioethanol options. Bioethanol is used for 12.6 % of transportation fuel in Brazil and 3.5 % in the United States [10].

Ethanol fuel—biologically produced alcohols (most commonly ethanol and less commonly propanol and butanol)—is produced by the action of microorganisms and enzymes through the fermentation of sugars or starches (easiest) or from cellulose (more difficult). Biobutanol (also called biogasoline) is often touted as a replacement for gasoline because it can be used directly in a gasoline engine (in a similar way to using biodiesel in diesel engines) [1].

Ethanol fuel is the most common biofuel worldwide, particularly in Brazil. Alcohol fuels are produced by the fermentation of sugars derived from wheat, corn, sugar beets, sugarcane, molasses, and any sugar or starch from which alcoholic beverages, such as whiskey, can be made (such as potato and fruit waste, etc.). The ethanol production methods used are enzyme digestion (to release sugars from stored starches), fermentation of sugars, distillation, and drying. The distillation process needs a significant energy input for generating heat [1].

Any car will burn gasoline mixed with a small amount of ethanol. But cars must be equipped with special equipment to burn fuel that is more than about 10 % ethanol. Nearly all U.S. gasoline now contains 10 % ethanol, and the United States produces more than half of the world's ethanol. Over the years, U.S. production of corn kernel-based ethanol has grown to 14 billion gal per year, but celluosic ethanol production has stayed flat at less than 10 million gal annually. At present, a subsidy program specifically for ethanol made from cellulosic materials—corn stover, wood chips, switchgrass, and other nonfood materials—remains in place [11].

In April 2012, the EPA moved to allow higher levels of ethanol (15 %) to be added to gasoline sold for motor vehicles. This is called E15 motor fuel and is limited to use in model year 2001 and newer vehicles.

Ethanol can be used in gasoline engines as a replacement for gasoline or mixed with gasoline to any percentage. Most existing automobile engines can run on blends of up to 15 % bioethanol with gasoline. Ethanol has a smaller energy density than that of gasoline. This means it takes more fuel (volume and mass) to produce the same amount of energy. An advantage of ethanol is that it has a higher octane rating than that of the ethanol-free gasoline available at roadside gas stations; this allows an increase in an engine's compression ratio for increased thermal efficiency.

In high-altitude locations, some states mandate a mix of gasoline and ethanol as a winter oxidizer to reduce atmospheric pollution emissions [1].

All motor vehicles sold in the United States have been designed and engineered to allow the use of up to 10 % ethanol (E10). Flex-fuel vehicles (FFVs) are capable of running either on gasoline or a blend of gasoline and up to 85 % ethanol. The cost of converting a vehicle into a FFV is negligible (about $100 as of this writing), and involves minor fuel and ignition system changes. At the moment, however, only a tiny percentage of motor vehicles on the road have been converted to FFVs. Part of the problem is the availability of E85 fueling stations, which are few and far between even in the Midwestern states, where corn-based ethanol primarily is produced. It costs about $60,000 to retrofit an existing gas station to offer E85 [12].

The majority of ethanol in the United States is made from corn, but it can also be produced from a variety of other feedstocks. According to the U.S. National Renewable Energy Laboratory, more than 80 % of the first-generation corn ethanol used as a fuel is made by a dry milling process in which the entire corn kernel is ground into flour referred to as "meal." Ethanol can be produced by a dry mill process or a wet mill process. The first is the most widely used process; the starch portion of the corn is fermented into sugar and then distilled into ethanol. Water, enzymes, and ammonia are added to form a slurry for conversion of the starch to dextrose. The mixture is processed at high temperatures to reduce the bacteria levels and is then cooled in fermenters prior to the addition of yeast, which will convert sugar to ethanol and carbon dioxide. This entire process takes from 40 to 50 h, during which time the mash is kept cool and agitated in order to facilitate yeast activity. After the fermentation is complete, the mixture is transferred to distillation columns, where the ethanol is removed and dehydrated to near 200 proof, using a molecular sieve system. A denaturant (such as gasoline) is added to render the product undrinkable, after which it is quality certified for shipment to gasoline retailers or terminals. The residual solid material is processed into livestock feed [2].

An emerging player in ethanol manufacturing is palm oil as a source for chemicals and fuel. Some 63 million metric tons of palm oil is harvested annually from tropical plantations, 87 % of it coming from Malaysia and Indonesia, where palm plantations cover 41 million acres. Annual production is expected to rise about 15 % by 2025 to more than 70 million metric tons. The palm oil yield of 2.5 metric tons per acre is twice that of coconut oil and 10 times that of soybean oil. Palm oil is derived from the flesh and kernel of the fruit of oil palms. But palm oil's large-scale use has environmental costs. In Southeast Asia, it is the leading driver of deforestation [13].

Thailand's state-owned group of oil and petrochemical companies (PTT) is a driving force in trying to make that country into a global leader in biobased chemicals. As the world's top exporter of cassava (a starchy root grown in the tropics) and the number two exporter of sugar, Thailand is well-suited for this task. Along with several chemical companies, PTT is involved in Thaioil Ethanol, which operates three ethanol plants in Thailand that use sugarcane molasses and cassava as raw materials [14].

In June 2015, the EPA proposed requiring 16.3 billion gal of ethanol equivalent to be blended into gasoline and diesel in 2015 and 17.4 billion gal in 2016. The EPA said that it would review public comments and finalize the RFS rule by the court-ordered deadline of November 30, 2015 [15]. In December 2015, the EPA announced its final rule on how much corn ethanol and advanced biofuel will be blended in the U.S. fuel supply in 2016. The EPA's rule finalizes higher volumes of renewable fuel than those that the agency proposed earlier. The agency's blend requirements for renewable fuels in 2016 is 68.55 billion L, which is lower than the target set by Congress in the 2007 Energy Independence and Security Act. In comparison, the standard for 2015 was 64.09 billion L [16].

Other bioalcohols in use as fuels are methanol and butanol. Methanol currently is produced from natural gas, a nonrenewable fossil fuel. It can also be produced from biomass as bioethanol. Butanol (C_4H_9OH) is formed by acetone, butanol, and ethanol fermentation, and experimental modifications of the process show potentially high net energy gains with butanol as the only liquid product. Butanol will produce 25 % more energy per unit volume than ethanol and allegedly can be burned "as is" in existing gasoline engines. When burned, it also produces far lower greenhouse gas emissions. It is less corrosive and less water soluble than ethanol and could be distributed within existing infrastructures [1,17]. The specification ASTM D7862 has been issued for butanol for use in fuels (see Chapter 2).

An alternative to ethanol as a biofuel is isobutyl alcohol (IBA). It has a greater energy density and a smaller propensity for corroding fuel systems. These factors allow IBA to be blended into gasoline at up to 16 % by volume, compared with ethanol's limit of about 10 % by volume for standard engines. To maintain gasoline's optimal vapor pressure, refiners adding ethanol need to counter its high vapor pressure by removing other volatile components, such as light naphtha, which then go to less profitable markets. With its lower vapor pressure, IBA avoids the need to perform this step. Additionally, a gallon of IBA has more renewable carbon than a gallon of ethanol, enabling refiners to more effectively meet regulatory requirements for renewable fuel use.

Biodiesel as an Automotive Diesel Fuel

The term "biodiesel" refers to monoalkyl esters of fatty acids—typically FAMEs that are produced from vegetable oil, animal fat, or from waste cooking oil in a chemical reaction known as transesterification. In the United States, soybean oil is the major feedstock; rapeseed oil is used in Europe, and palm oil is a large player in other regions of the world. Although there are some users of 100 % biodiesel (or B100) as a fuel, the properties of B100 are considerably different from those of conventional diesel fuel or heating oil. Therefore, it is much more common to use biodiesel as a blend with petroleum diesel at levels ranging from 2 % (B2) to 20 % (B20) by volume [18].

Biodiesel typically is produced by a transesterification reaction of a vegetable oil or animal fat with an alcohol (such as methanol or ethanol) in the presence of a catalyst to yield monoalkyl esters and glycerin. This process occurs via a sequence of three reversible reactions in which the triglyceride molecules are converted in a step-by-step process into diglycerides, monoglycerides, and glycerol. This reaction leads to a mixture of glycerol and alkyl esters of fatty acids, with physical and chemical properties similar to diesel fuel derived from petroleum. The finished biodiesel derives approximately 10 % of its mass from the reacted alcohol. The alcohol used in the reaction may or may not come from renewable resources. A biodiesel blend is a mixture of biodiesel fuel with petroleum-based diesel fuel and is designated BXX, where XX is the volume percent of the biodiesel [19].

Once synthesized, the biodiesel is submitted to a purification process. The advantage of using short-chain alkyl esters is that they exhibit lower viscosity than vegetable oils by an order of magnitude. These lower viscosities are much closer to those exhibited by petroleum-derived diesel fuel. The use of short-chain alkyl esters eliminates operating problems such as the formation of deposits within the engine [18].

Biodiesel is produced from a variety of vegetable oils and animal fats, with soy being the predominant source in the United States. The oil is obtained by first cleaning, cracking, and conditioning the beans, which are subsequently compressed into flakes. As demand increases, it is likely that a variety of other sources (including canola, palm, jatropha, and used kitchen oil) will be utilized. This brings increased quality concerns about parameters—including oxidative stability, low-temperature handling and operability, resistance to phase separation, batch-to-batch consistency, biological growth, and additive response [20]. According to the National Biodiesel Board, more than 170 companies in the United States are actively marketing biodiesel.

For producing biodiesels, a fat or oil is reacted with an alcohol (e.g., methanol) in the presence of a catalyst to produce glycerin and methyl esters, or biodiesel. The first step simply removes dirt, charred food, water, or other contaminants that could interfere with the reaction process. The methanol is charged in excess to help in quick conversion and is recovered for reuse. The catalyst used in the process usually is sodium or potassium hydroxide, which is premixed with methanol. In this step, the mixture undergoes a transesterification reaction that converts lipids to biodiesel and glycerol. If the feedstock oil has a high acid content, acid-catalyzed esterification can be used to react fatty acids with alcohol to produce biodiesel, but this process is much rarer. In either case, the reaction produces not only biodiesel but also by-products such as soap, glycerol, excess alcohol, and trace amounts of water. All of these by-products must be removed to meet fuel standards prior to sale [2].

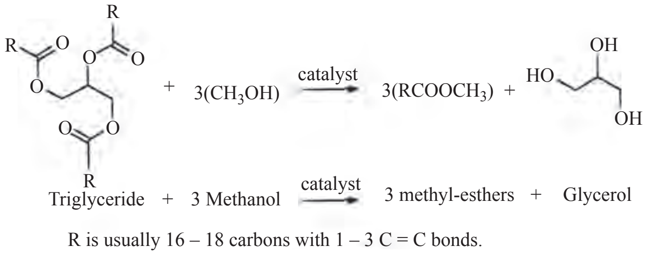
Soybean oil is the largest source of biodiesel in the United States; however, oil from other plants is sometimes used. Soybeans primarily are grown as a high-protein animal feed because they are 80 % high protein meal and only 20 % oil. Other major sources are animal fats or tallow (beef, pork, poultry) and used restaurant frying oils. All these oils and fats are produced as minor by-products of growing food or animal feed or, in the case of the used cooking oil, as a second-use by-product. Beef, hogs, and chickens are grown for human consumption and yield only around 10 % fat. Among other novel sources of biofuels are canola, palm, jatropha plants, algae, enzymatic production of triglycerides from cellulose, use of microorganisms for direct production of methyl esters from sugar, and even production of biodiesel from municipal sludge. Some of these so-called second- or third-generation biodiesel routes can provide a biodiesel that has superior cold flow properties and stability even compared to petroleum-based diesel, while keeping the already beneficial biodegradability, high cetane, improved lubricity, and emission reductions associated with current first-generation biodiesel produced from traditional fats and oils by transesterification of the methyl and ethyl esters. Over time, it is expected that biodiesel processing and the finished product will improve and that its usage rate ultimately will be driven by economics and market forces but also by requirements to meet mandates on carbon dioxide to ameliorate climate change. The need to meet sustainability goals will also likely play a role in the future of biodiesel [5]. See Fig. 1.1, which depicts the reactions of vegetable oil to form methyl esters [19].

Conventionally, biodiesel is produced through a transesterification reaction of a natural oil triglyceride (animal fat or vegetable oil) with a short-chain alcohol (typically methanol) in the presence of a catalyst (usually sodium hydroxide [NaOH] or potassium hydroxide [KOH]). The reaction occurs stepwise with one fatty acid chain being removed from the glycerin backbone first (forming one monoalkyl ester and a diglyceride), the second fatty acid removed next (forming two molecules of monoalkyl esters and a monoglyceride), and last, reaction of the third fatty acid. The resulting products are three monoalkyl esters (biodiesel) and glycerin. Glycerin is removed as a coproduct and can be upgraded to a valuable pharmaceutical grade. The reaction is as follows [5].

100 lb triglyceride (soybean oil) + 10 lb alcohol (methanol) = 10 lb glycerin + 100 lb monoalkyl esters (biodiesel)

The resulting mixtures of FAME have chemical and physical properties similar to those of conventional diesel fuel. It is not clear whether diesel engines or boilers are fully compatible with B100. Therefore, it is much more common to use biodiesel as a blend with petroleum diesel at levels ranging from 2 % (B2) to 20 % (B20) by volume. Diesel engines can run on B100; however, most of the testing in the United States has been done on blends of biodiesel and low sulfur diesel. Testing done on the biodiesel fuel mixture shows that this fuel produces lower emissions of particulate matter,

FIG. 1.1 Reactions of vegetable oil to form methyl esters.



hydrocarbons, and carbon monoxide compared with the conventional diesel fuel. Nitrogen oxide (NO_x) emissions can be slightly higher than with conventional diesel, unless the fuel system injection timing is optimized for B20 [19].

Almost all of the biodiesel used in the United States is of the S15 grade. Natural vegetable oil feedstocks have virtually no sulfur (usually less than 1 or 2 mg/kg), but some animal fats or yellow grease-based biodiesel may have sulfur content slightly higher than 15 mg/kg due to the presence of hair or hide materials from the animal fat rendering process or from frying foods high in sulfur, such as onion rings [5].

Biodiesel (B100) has good lubricity properties and essentially contains no sulfur or aromatics. However, it has a relatively high pour point, which could limit its use in cold weather. Biodiesel is biodegradable, but that property may lead to increased biological growth during storage. Biodiesel is also more susceptible to oxidative degradation than petroleum diesel [19].

Table 1.4 shows how biodiesels produced this way are distinguished from petroleum-derived diesel by following test protocols suggested by the ASTM Biodiesel Task Force [5].

There are differences between biodiesel and petroleum-derived diesel. For biodiesels, the cetane number test method ASTM D613 must be used; the calculated cetane index ASTM D4737 cannot be used because it is based on historical data for the distillation curve of petroleum diesel and is not applicable to biodiesel. Biodiesels lack a "distillation curve" because petroleum diesel contains hundreds of compounds boiling at differing temperatures, while biodiesel contains only a few compounds—primarily C16 to C18 carbon chain-length alkyl esters along with minor variations in carbon double bonds. These compounds all boil at approximately the same temperature.

TABLE 1.4 Differentiation of Biodiesel from Petroleum-Derived Diesel

Rationale for Test	Test Method	Measurement
Conversion of fat or oil to monoalkyl esters	ASTM D6584	Total glycerin
Removal of unbound glycerin	ASTM D6584	Free glycerin
Removal of catalyst used in biodiesel production	ASTM D874 EN 14538	Sulfated ash Levels of combined Na^+ K
Removal of alcohol, usually methanol	EN 14110 ASTM D93	Methanol by gas chromatography (GC) High flash point value
Absence of fatty acids	ASTM D664	Acid number

Some examples of properties of biodiesels from different sources are given in Table 1.5 [21].

Another difference is that the molecular weight and composition of biodiesel also account for its high flash point. Howell lists additional differences between biodiesel and petroleum-based diesel: ASTM D4530 carbon residue, ASTM D482 ash versus ASTM D874 sulfated ash, limits on ASTM D93 flash point, ASTM D1160 vacuum distillation, ASTM D613 cetane number limit, BS EN 14538 sodium (Na) plus potassium (K) plus calcium (Ca) plus magnesium (Mg) levels, ASTM D4951 phosphorus limit at 10 mg/kg, BS EN 14112 oxidation stability, and cold soak filterability [5].

Of prime importance to vehicle original equipment manufacturers (OEMs) and consumers is that the increased use of biodiesel does not damage their hardware or compromise performance. In an effort to meet these requirements, various standards have been introduced. In the United States, B100 must meet ASTM D6751 or the European EN 14214 specifications, and new limits on Na, Ca, K, and Mg for biodiesel blends have been added to ASTM D6751.

Most heavy duty engine manufacturers approve the use of biodiesel blends up to 5 % in their engines without voiding warranties so long as the biodiesel meets ASTM D6751 specifications. Some OEMs have gone a little farther, allowing 20 % to 30 % biodiesel in certain engines. However, many diesel fuel injection equipment manufacturers are concerned about the impact of the wide range of FAME sources on finished fuel characteristics, most notably oxidation stability in ultra-low-sulfur diesel blends. In Europe, the agreed position limits mixtures to a maximum of 5 % FAMEs (meeting the EN 14214 standard) and with unadulterated diesel fuel (meeting the EN 590 standard). The final B5 product must also comply with EN 590 at the pump to remove risks in the distribution system [4].

Biodiesel remains the only advanced biofuel in commercial production across the country. The level of biodiesel to be included in U.S. diesel fuel markets was set at 800 million gal in 2011 and was increased to 1 billion gal in 2012. In September 2012, the EPA announced that it would boost the biodiesel volume requirements to 1.28 billion gal in 2013. The EPA estimates that biomass-based diesel reduces the greenhouse gas emissions by more than 50 % when compared with petroleum diesel.

Green diesel is produced by hydrocracking biological oil feedstocks, such as vegetable oils and animal fats. Hydrocracking

TABLE 1.5 Properties of Diesel and Biodiesel

Property	Diesel	Beef Tallow	Beef Tallow Biodiesel	Soybean Oil	Soybean Biodiesel	Sunflower Oil	Sunflower Biodiesel
Density, g/cc at 20°C	0.88519		0.86470	0.92037	0.88230	0.92080	0.88654
Flash point, °C	67		158	332	150		166
Cloud point, °C	2	43	15	−2	0	1	4
Pour point, °C	−12	22	3	−14	−6	−18	−9
Copper strip corrosion	1a	1b	1a	1b	1a	1a	1a
Heating value, kJ/kg	42,800		42,365		41,685		41,330

is a refinery method that uses elevated temperatures and pressure in the presence of a catalyst to break down larger molecules found in vegetable oils into shorter hydrocarbon chains used in diesel engines. Green diesel is also called renewable diesel, hydrotreated vegetable oil, or hydrogen-derived renewable diesel. Green diesel has the same chemical properties as petroleum-based diesel fuel. It does not require new engines, pipelines, or infrastructure to distribute and use, but it has not been produced at a cost competitive with petroleum diesel [1].

Sources of Biofuels

Biofuels and biodiesels derived from plant or animal origins have been looked at as alternatives to gasoline and diesel procured from crude oil refining. In the United States, EU, and Brazil in particular, considerable efforts are underway to commercialize such petroleum substitute products. Feedstocks for biofuels include animal fats, vegetable oils, soy, rapeseed, jatropha, mahua, mustard, flax, sunflower, palm oil, hemp, field pennycress, *Pongamia pinnata*, and algae.

The U.S. Department of Energy (DOE) has issued many research grants to create the required technology. Some of the biofuels supported by these grants are shown in Table 1.6 [2].

Biofuels derived from food sources such as edible corn, sugar, starch, or vegetable oil are considered as first-generation biofuels, and those coming from a variety of feedstocks such as lignose or municipal waste are considered as second-generation biofuels. Third-generation biofuels are typically microbial, using carbon dioxide as their feedstock, and are much more carbon neutral [22].

Second-generation biofuels made from lignocellulosic feedstocks can be produced from either a biochemical or a thermochemical process. The biochemical process uses enzymes and microorganisms to convert cellulose and hemicellulose to sugars prior to fermentation to produce ethanol. A biological, physical, chemical, or a combination pretreatment process is required to expose the cellulose and hemicellulose for subsequent enzymatic hydrolysis. The pretreatment process is a major cost component of the overall process. A key goal for the efficient production of lignocellulosic ethanol is that all C5 (pentose) and C6 (hexose) sugars released during the pretreatment and hydrolysis steps are fermented into ethanol. The thermochemical processes employ pyrolysis/gasification technologies to produce a synthesis gas ($CO + H_2$) from which a wide range of long-carbon-chain biofuels such as synthetic diesel, aviation fuel, or ethanol can be reformed using the Fischer-Tropsch conversion [2].

TABLE 1.6 Biofuels Programs Supported by the U.S. Department of Energy

Fuel	Source	Benefits
Grain/sugar ethanol	Corn, sorghum, sugarcane	High-octane fuel for gasoline blends; made from a widely available renewable source
Biodiesel	Vegetable oils, fats, greases	Reduces emission; increases diesel fuel lubricity
Green diesel and gasoline	Oils and fats blended with crude oil	Superior feedstock for refineries; low-sulfur fuels
Cellulosic ethanol	Grass, wood chips, agricultural residues	High-octane fuel for gasoline blends; only viable scenario to replace 30 % of U.S. petroleum use
Butanol	Corn, sorghum, wheat, sugarcane	Low-volatility, high-energy density, water-tolerant alternate fuel
Pyrolysis liquids	Any lignocellulosic biomass	Offers refinery feedstocks, fuel oils, and a future source of aromatics or phenols
Syngas liquids	Various biomass and fossil fuel sources	Integrate biomass source with fossil fuel sources; high-quality diesel or gasoline
Diesel/jet fuel from algae	Microalgae from aquaculture	High yield per acre and an aquaculture source of biofuels; could be employed for CO_2 capture and reuse
Hydrocarbons from biomass	Biomass carbohydrates	Generate synthetic gasoline, diesel fuel, and other petroleum products

Source: Collins [2].

In 2004, the DOE identified a set of biomass-derived compounds best suited to replace petroleum-derived chemicals. Table 1.7 is extracted from the source to limit only to fuel-related chemicals [23]. Other platform chemicals that are doing well or that are poised to do well as feedstock chemicals include ethanol, butanediols, acetic acid, acrylic acid, adipic acid, lactic acid, farnesene, p-xylene, isobutanol, fatty acid esters, isoprene, furfurals, y-valerolactone, triacetic acid lactone, and isosorbide. The scorecard grade in Table 1.7 is based on assessments by biobased chemical experts and compiled by *Chemical & Engineering News* (Washington, DC). Grades are: A = being commercialized, B = significant activity, C = actively pursued by researchers, and D = limited activity.

Biomass as a term is defined by ASTM Committee E48 as follows. The scope of the committee is defined as, “The promotion

TABLE 1.7 Status of Biomass-Derived Technology for Replacement of Petroleum Derived Chemicals as Fuel Components

DOE’s Top Choices	Source	Key Uses and Products	Status	Bio-Scorecard Grade
Glycerol	Chemical or enzymatic transesterification of vegetable oils	Polyesters, butanol, soaps, cosmetics, etc.	Currently active	B
Sorbitol	Hydrogenation of glucose from corn syrup, bacterial fermentation	Fuel ingredients, sweeteners, etc.	Currently active	B
Levulinic acid	Acid-catalyzed dehydration of sugars	Fuel ingredients, solvents, etc.	No activity at present	C

Excerpted from Ref. [23].

of knowledge and the development of standards for bioenergy and industrial chemicals from biomass. The focus of the committee shall be on bioenergy and industrial chemicals from biomass, from characterization through manufacturing."

- Biomass (ASTM E1126)—"Total weight of living matter in a given volume. When considered as an energy source, biomass is further subdivided into: (1) primary biomass, rapidly growing plant material that may be used directly or after a conversion process for the production of energy, and (2) secondary biomass, biomass residues remaining after the production of fiber, food, or other products of agriculture, or biomass by-products from animal husbandry or food preparation that are modified physically rather than chemically. Examples include waste materials from agriculture or forestry industries (manure, sewage, etc.) from which energy may be produced. The above distinction noted between primary and secondary biomass is based on economic factors; these are defined differently in ecological science."
- Biomass (ASTM E1126, ASTM E1218)—"Any material, excluding fossil fuels, which is or was a living organism that can be used as a fuel directly or after a conversion process. Peat is not a biomass."
- Biomass (ASTM E1705)—"Material derived from living or recently living (non-fossil) sources. Sometimes referred to as renewable organic material. Examples of biomass include whole or parts of plants, trees, aquatic organisms, animals, algae and microorganisms."

A discussion of ASTM standards for biotechnology issued by Committee E48 is included in Chapter 7. See other terminology related to biofuels in Table 1.7.

Cellulosic Ethanol

Another alternate to gasoline is a renewable fuel substitute such as cellulosic ethanol made from a wide variety of plants, including poplar trees, switchgrass, and cornstalks. Some experts estimate that it will take 15 to 20 years before cellulosic ethanol becomes competitive. Studies suggest that cellulosic ethanol could yield at least four to six times the energy expended to produce it. The DOE estimates that the United States could produce more than 1 billion tons of cellulosic material annually for ethanol production, from switchgrass grown on marginal agricultural land to wood chips and other waste produced by the timber industry. In theory, that material could produce enough ethanol to substitute for about 30 % of the country's oil consumption [24]. Some other possible vegetation biosources suggested for conversion to liquid fuels are woody plants (including paper waste and yard trimmings), perennial grasses (such as miscanthus), plants for arid lands (such as agave), plants resistant to salt (such as prairie cordgrass), plants with an extended growth range (such as miscane, a miscanthus-sugarcane hybrid), and plants resistant to parasites (such as switchgrass and mascanthus) [7].

In mid-2014, the EPA raised the number of biofuels that are officially considered cellulosic under the national renewable fuel standard program. The move may help address the inability of fuel blenders to obtain enough cellulosic biofuels to meet renewable fuel targets set by the 2007 Energy Independence and Security Act. A final rule from the EPA makes several changes in what is defined as a cellulosic fuel. It defines corn kernel fiber as a crop residue, making it count as cellulosic material for producing ethanol. The rule also defines methane from landfills, sewage treatment facilities, and other sources as cellulosic biofuel—if the methane is compressed or liquefied and used as a transportation fuel or to generate electricity [8].

Algae, a third-generation biofuel feedstock, presents one of the most attractive renewable fuel opportunities. Algae's potential arises from its high biomass yield, its ability to grow in a range of environments, and its effectiveness as a bioremediation agent for carbon dioxide (CO_2) sequestration and waste water treatment. Microalgae are the fastest growing photosynthesizing organisms and can complete an entire growing cycle every few days. Under optimum growing conditions, microalgae are reported to produce up to 15,000 gal of oil/hector/year. Algae can be grown under conditions that are unsuitable for conventional crop production, thus ensuring that there is no competition with food crops for land and also solving the "food versus fuel" dilemma. Apart from biodiesel, algae can also be processed to make other biofuels such as ethanol, methane, hydrogen, and natural gas. Although there are advantages for it use as an alternate fuel feedstock, there are also many drawbacks to large-scale development of algae as a fuel source. These include algae strain selection, land requirements, cost of nutrients, contamination of algae cultivation, cost of algae cultivation, cost of algae harvesting, and efficient and cost-effective oil extraction from algae [25].

Aviation Biofuels

Replacing petroleum-based aircraft fuels is an obvious pathway to consider as alternative nonpetroleum-based fuels gain hold in other applications. Fuel costs are a huge cost factor in airline operations. For example, in 2014, United Airlines alone spent $11.7 billion on 3.2 billion gal of jet fuel. The U.S. Air Force (USAF) is considering a jet fuel composed of no more than 50 % petroleum. The commercial aviation industry also appears to be getting behind the synthetic fuels. The rationale in both cases is to make sure that the fuel is always available, to use less of it, and to consider environmental concerns, particularly greenhouse gas emissions. It is estimated that the USAF uses about 52.5 % of all fossil fuel purchased by the federal government. Corn produced fuel is not suitable for aviation because it does not have enough Btus for jet fuel. An Air Force B-52 bomber undertook a successful test flight using a blend of jet fuel and fuel produced from natural gas. Sasol of South Africa and Shell Oil Products have been certified to supply fuel blends for tests. [26].

In July 2012, the Great Green Fleet (which included half a dozen U.S. Navy ships and associated aircraft) gathered off the coast of Hawaii to successfully demonstrate military use of biofuels on a large scale (rather than in one-off experiments). The fleet sailed on a blend of traditional petroleum fuel and biofuels prepared from algae and cooking oils. The exercise was technically successful, but the future remains cloudy because the U.S. Congress has included language in the defense bill of that fiscal year to prohibit the military from spending money on biofuel research until the price of biofuel drops down to the level of traditional petroleum-based fuel. The main drivers behind the military's desire to explore biofuels are rapidly rising energy costs. The U.S. Department of Defense (DOD) estimates that, for every 25-cent rise in the cost of a gallon of fuel, the department spends an extra $1 billion for its fuel. As the single largest consumer of petroleum fuel worldwide, the military could be a large market for biofuels. The DOD has a legislative mandate to use 20 % renewable fuels by 2015. After the Hawaii naval exercise, the Navy is hoping to deploy a multivessel carrier strike group fueled by alternative sources of power, including biofuels and nuclear energy, by 2016 [27].

Three different alternative aircraft fuel possibilities have also been considered: synthetic fuels, biofuels, and other alternative fuels. Synthetic kerosine can be made from coal, natural gas, or other hydrocarbon resources, and it can be produced by first turning the resource into gases, which are then recombined to form hydrocarbon liquids. Synthetic kerosine can be tailored to have properties similar to petroleum kerosine and can be thought of as a drop-in replacement. These can be produced by the Fischer-Tropsch process using natural gas, coal, or any carbon-based material, including plant crops, direct coal liquefaction, and biofuels with refinery-based upgrading to jet fuel. One of the challenges of using current biofuels in commercial aircraft is their propensity to freeze at normal operating cruise fuel temperatures. Another challenge is biofuel's lack of long-term fuel storage and thermal stability. Currently, it is advised that the product be used within six months of manufacture [28].

U.S. commercial airline companies also have the same goal of securing a reliable and competitive fuel supply for their fleets. The International Air Transport Association (IATA) estimates that the airline industry's carbon footprint can be reduced by 89 % if biofuels are used. U.S. airlines consume 18 billion gal of jet fuel annually—approximately 10 % of the total U.S. fossil fuel usage—at a cost of $50 billion, or 25 % to 35 % of their operating costs. The price of biofuels is the dilemma right now. When Alaska Airlines debuted its first commercial biofuel-powered flight in late 2011, it paid six times the cost of traditional jet fuel. United Airlines' biofuel was four times as costly. Even Boeing is investing in biofuel research, hoping that when the cost of fuel decreases, airlines will have more capital to purchase more aircraft [29]. United is coordinating sustainable biofuel research programs in the United States, Australia, China, Brazil, Japan, and the United Arab Emirates.

Continental Airlines conducted the first experimental flight of a U.S. jetliner powered by biofuel made from plants in January 2009. A Boeing 737-800 that carried no passengers was in the air for 1 h and 45 min out of Bush Intercontinental Airport in Houston, TX. It was the first commercial airliner to use algae as a fuel source. One engine ran on a mixture of biofuel made from algae, jatropha plants, and jet fuel, and the other was powered only by jet fuel [30]. In December 2008, Air New Zealand flew a passenger jet powered with a combination of diesel fuel and oil from jatropha plants from Auckland [31]. Less than three years later, the first regular scheduled commercial route from Hamburg to Frankfurt, Germany, started a six-month trial, taking flight with one engine operating on a 50 % biofuel component consisting of jatropha, camelina, and animal fats [32].

In November 2011, United Airlines debuted its first commercial flight using biofuel (a blend of 40 % algae-based fuel and 60 % regular jet fuel) on a Continental-operated Boeing 737-800 from Houston to Chicago. The algae were grown in fermentation vessels and were fed a range of sugars, including sugarcane, corn, and cellulosic sugars [31].

Between 2009 and 2011, research-scale production of biobased jet fuel had been used primarily for test flights. Based on these data, ASTM certified fuels made from hydrotreated esters and fatty acids (HEFAs) as drop-in replacements for conventional jet fuel in July 2011. Passenger planes can now run on a blend of up to 50 % biofuel. The only other way biomass can become a component of certified jet fuel is to convert it into synthesis gas and use the Fischer-Tropsch reaction to create the fuel. This process was used in Germany to convert coal to liquid fuels during World War II and is still used today in South Africa. The IATA estimates the global market for jet fuels represents a 10 % slice of all transportation fuels, or approximately 64 billion gal per year [33].

ASTM D7566 for aviation turbine fuel containing synthetic hydrocarbons now includes an annex with requirements for synthetic fuel components manufactured from HEFAs produced from various feedstocks. ASTM D7566 enables the use of such fuel components without compromising safety. Fuels made from camelina, jatropha, and algae can offer as much as an 85 % reduction in net carbon emissions compared to petroleum fuels. The 2013 edition of ASTM D7566 prescribes performance requirements for HEFA aviation fuel-blending components, which can be manufactured from a variety of feedstocks such as the inedible plants camelina and jatropha, algae, coconut or vegetable or other oils, chicken fat, and more. The standard already specified blend components produced through Fischer-Tropsch synthesis [34].

On the other hand, the traditionally used standard specification ASTM D1656 for aviation turbine fuels now includes a parameter for detecting low levels of FAMEs in jet fuels. ASTM D1655 has been used for a very long time for ensuring quality control and safe distribution of jet fuel. The same distribution systems (e.g., shipping containers, pipelines, etc.) are used for jet fuel as for biodiesel. After biodiesel is transported through a distribution system, there is a possibility that traces of FAMEs may be picked up by jet fuel that later uses the same distribution system. The initial response to the introduction of biodiesels into the marketplace was to maintain an undetectable level of FAMEs contamination in jet fuel. Due to the costs associated with that requirement and the rising presence of biofuels worldwide, industry experts studied whether the level of allowable FAMEs in jet fuel could be increased without compromising safety or adversely affecting aircraft operation. As a result, the current revision of ASTM D1655 safely increases the allowable cross-contamination of FAMEs in jet fuel from 5.0 to 50 ppm. No discernible negative impact on jet fuel product quality was observed up to 400 ppm of biodiesel. A potential future revision could further increase the standard to allow 100 ppm biodiesel. The test method used for determining the trace quantities of FAMEs in jet fuel is International Petroleum (IP) 585-10 or IP 590-10 [35].

Biolubricants

Along with the progress for biofuels, oil marketers and additive manufacturers as well as the major OEMs are working to develop lube products capable of dealing with some of the unique challenges biofuels bring to the game. Gear oils, metal working fluids, greases, and hydraulic oils have all been formulated with biolubricant stocks, some from animal sources but most from plant-based materials. Biolubricant base stocks are very diverse in themselves. High oleic sunflower oil, soybean oil, and genetically engineered plant oils are a few of the many choices available. Biolube base stocks also have attractive properties such as a relatively high viscosity index, inherent friction reduction, and good load-carrying capabilities. However, at the moment, there is no engine oil formulation meeting current American Petroleum Institute/International Lubricants Standardization and Approval Committee specifications that is based on biolubes. Engine oils, representing the biggest segment of the 2.5 billion gal U.S. lubricant market, are a tempting target for biolube manufacturers and marketers. There are major challenges in both gasoline- and diesel-powered engines, which will eventually be solved [36].

Many products, including lubricants, have been officially designated by the U.S. government and must be given first preference for purchase by federal agencies, thus creating a tremendous market pull for the new products through the purchasing power of the federal government. The USDA has supported the University of Northern Iowa National Agriculture-Based Lubricants Center for more than a decade, resulting in a commercial line of industrial lubricants that are used by the trucking and rail industries for improved performance in place of their petroleum-based counterparts. These products offer advantages that include better adherence to metals, good lubricity, and a higher viscosity index. Human health and safety advantages include low toxicity and high flash and fire points. These products are total loss lubricants; therefore, biodegradability in the environment is an important property. The USDA's Agricultural Research Service (ARS) has developed an efficient process to produce novel biobased functional fluids based on estolides, which are high molecular weight derivatives of fatty acids. ARS technology has resulted in products with excellent lubricity, cold temperature, and oxidative stability properties, and they are biodegradable in the environment [37].

Products that are designated as biobased are posted on the BioPreferred Web site (www.biopreferred.gov/BioPreferred) that federal agencies and others can use as a reference when making purchasing decisions. More than 5,100 products are eligible for preferred procurement under the six categories. Examples of functional fluids that have been designated as such are listed in Table 1.8 [33].

TABLE 1.8 Examples of Functional Fluids Designated with Minimum Biobased Content

Designated Items	Minimum Biobased Content, %
Two-cycle engine oils	34
Chain and cable lubricants	77
Firearm lubricants	49
Fluid-filled transformers—synthetic ester-based	66
Fluid-filled transformers—vegetable oil-based	95
Forming lubricants	68
Gear lubricants	58
Greases	75
Greases—food grade	42
Greases—multipurpose	72
Greases—rail track	30
Greases—truck	71
Heat transfer fluids	89
Hydraulic fluids—mobile equipment	44
Metalworking fluids—general-purpose soluble, semisynthetic, and synthetic oils	57
Metalworking fluids—high performance soluble, semisynthetic, and synthetic oils	40
Metalworking fluids—straight oils	66
Penetrating lubricants	68
Turbine drip oils	87

To obtain a label saying the product is biobased, validation must be obtained from a certified laboratory using ASTM D6866. The USDA has set a 25 % minimum biobased content as the entry level for the label. ASTM D6866 uses radiocarbon analysis to determine if a product meets minimum biobased content. The standard distinguishes carbon content in biomass-based products from carbon content in fossil-based products. Because biomass contains a known amount of radiocarbon (or C-14), carbon from biomass can be differentiated from products that do not contain C-14. Inorganic carbon, noncarbon materials, and product weight are not taken into consideration for calculating the percent of biobased content. The standard does not measure product biodegradability; therefore, other tools such as life cycle analysis need to be used to describe environmental and economic benefits [36].

Vegetable fluids are great biodegradable lubricants. They are processed from renewable resources and are extremely biodegradable (more than 80 %). The drawbacks of vegetable oils for a high-performance multipurpose lubricant are thermal stability and lower temperature performance. The pour point of canola oil is –15°C. This property is unacceptable for lubricants used in low-temperature applications. The lubricant would become a wax and fail to sufficiently lubricate. In order to extend the low-temperature performance of canola oil, other base fluids can be blended into it. The addition of polyalpha olefin of 4 cst kinematic viscosity would improve the low-temperature performance of the fluid, but the biodegradability would be reduced [38].

BQ-9000 Quality Management System Laboratory Requirements

The National Biodiesel Accreditation Program, BQ-9000, is a voluntary program for the accreditation of U.S. and Canadian producers and marketers of biodiesel fuel. It aims to ensure that biodiesel is produced and maintained at the biodiesel industry standard and combines the ASTM D6751 standard with a quality management program that monitors storage, sampling, testing, blending, shipping, and distribution [5].

The National Biodiesel Accreditation Commission, an autonomous committee of the National Biodiesel Board, Jefferson City, MO, has prepared this document for use in a cooperative and voluntary program for the certification of laboratories. Compliance is a minimum requirement for the certification process. This document is very similar to International Organization for Standardization (ISO) 9000 (and in particular ISO 17025 and ASTM D6792) quality management systems widely used throughout the world for oil industry laboratory and plant registrations.

The requirements include documented quality policy, a quality manual, document control, control and retention of records, management responsibility, internal quality system audit, quality management review, sample management, data and record management, calibration and maintenance, quality control, proficiency testing, corrective and preventive actions, and customer complaints.

Terminology

Terminology specific to biofuel specifications and usage is included in Table 1.9. Most of the terminology is excerpted from relevant ASTM standards. A number of alternate but similar definitions for biomass are given in various ASTM standards and often confuse the issue as to what is a definitive definition (Table 1.10).

Balloting is underway in ASTM Committee E48 to incorporate a new definition of biomass but that also includes some portions of the definition currently given in ASTM E1705:

> Biomass, n—Material comprised of living or recently living (non-fossil) matter.
>
> *Discussion*: Sometimes referred to as renewable organic material; examples of biomass include whole or parts of plants, trees, aquatic organisms, animals, algae, and microorganisms.
>
> *Discussion*: When considered as an energy source, biomass may be further subdivided into: (1) primary biomass—rapidly growing plant materials that may be used directly or after a conversion process for the production of energy, and (2) secondary biomass—biomass residues remaining after the production of fiber, food, or other products of agriculture, or biomass by-products from animal husbandry or food preparation that are modified physically rather than chemically. Examples include waste materials from agriculture, forestry industries, and some municipal operations (manure, saw dust, sewage, etc.) from which energy may be produced.

Overview of Analysis Methods

The significance of the tests used to characterize biofuels (or any product, for that matter) has to do with the specific usage to which a particular product is put and how effective the product will be in that task. Howell [5] and Nadkarni [39] have described in detail the significance of various tests used in the analysis of petroleum products and lubricants. A list of ASTM test method standards used in characterizing biofuels is given in Tables 3.1, 4.1, 5.1, and 6.1 in Chapters 3, 4, 5, and 6, respectively, of this volume. Most of the test methods in this list originated from the efforts to characterize petroleum products and lubricants over the last century, and only lately have they been adopted for use in the biofuels area. As such, it is not completely clear how many of these tests are actually valid for biofuels or whether the biofuel matrix produces the same degree of precision of analysis as those of traditional petroleum products and lubricants. On the other hand, there are several test methods that apply to biofuels without any modifications being necessary. Several other test methods have been specifically written for biofuels.

The problem of appropriate test methods for the analysis of biofuels has long been recognized. At an ASTM Biofuels Workshop held in Miami, FL, in June 2007, several speakers pointed out a host of test methods that do not include biofuels in their scope and that have no precision data for biofuels. In addition, it cannot be confidently said that the petroleum-based test methods are fully applicable, without any modifications, to the analysis of biofuels. The situation has improved in the last few years with new test methods developed for biofuels, but there still are a large number of test methods for which their applicability to biofuels has not been proven.

The properties of commercial biodiesel fuel depend upon the refining practices used and on the nature of the renewable lipids from which the fuel is produced. As discussed earlier in this chapter, biofuel can be produced from a variety of vegetable oils or animal fats having similar volatility characteristics and combustion emissions with varying cold flow properties.

The following paragraphs excerpted from ASTM D975 Appendix X7 are pertinent in this respect of the choice of test methods for characterizing alternate fuels to petroleum-based fuels.

> X7.6 Because the composition and properties of new fuels may vary, the particular path to a specification for a new fuel may vary. Some current alternative fuels are similar to traditional petroleum-refined diesel fuel while others are chemically and physically different. Future fuels may vary even more.
>
> X7.7 Three areas for consideration when reviewing new fuels alignment with existing standards or developing new standards are: test methods, chemical and physical limitations of fuels in existing specifications, and chemical and physical limitations appropriate for new fuels. The test methods that have been developed for existing compression ignition engine fuels may or may not be appropriate for a new fuel. Guidance on materials used to develop a test method, and its applicability, can generally be found in a test method's scope and precision statements. The test method may also work for other materials.
>
> X7.8 Applicability of the test method to materials outside its scope may be established by the subcommittee responsible for the method. Also, Subcommittee D02.EO, during the specification development process, may determine

TABLE 1.9 Terminology Used in Biofuels

Term	Explanation	ASTM Standard
B6 to B20	Fuel blend consisting of 6 to 20 volume percent biodiesel conforming to the requirements of ASTM D6751 with the remainder being a light middle or middle distillate grade diesel fuel and meeting the requirements of this specification. The abbreviation Bxxx represents a specific blend concentration in the range B6 to B20, where xx is the percent volume of biodiesel in the fuel blend.	ASTM D7467
Biodiesel	Fuel comprised of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated B100. Biodiesel is typically produced by a reaction of vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst to yield monoesters and glycerin. The finished biodiesel derives approximately 10 % of its mass from the reacted alcohol. The alcohol used in the reaction may or may not come from renewable resources. The fuel typically may contain up to 14 different types of fatty acids that are chemically transformed into fatty acid methyl esters (FAME). Biodiesel as defined here is registered with the EPA as a fuel and a fuel additive under Section 211(b) of the Clean Air Act. There is, however, other usages of the term biodiesel in the marketplace. Due to its EPA registration and the widespread commercial use of the term biodiesel in the U.S. marketplace, the term biodiesel is maintained for this specification.	ASTM D396: ASTM D975, ASTM D7467; ASTM D7501 ASTM D5771; ASTM D6751; ASTM D7371 ASTM D6751
Biodiesel (B100)	Fuel comprised of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats.	ASTM D6584
Biodiesel blend	A blend of biodiesel fuel with petroleum-based diesel fuel designated as BXX, where XX is the volume percent of biodiesel.	ASTM D975; ASTM D7371
Biodiesel fuel	Synonym for biodiesel.	ASTM D6751
Biofuel	Fuel comprised of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated as B100 in ASTM D975. A liquid fuel derived from a biological source, specifically excluding fuels derived from petroleum and related to fossil fuel sources. Some examples of biofuels are ethanol derived from sugarcane, corn, or grains, biodiesel (fatty acid methyl esters), "raw" vegetable oils, hydrogenated vegetable oils, Fischer Tropsch fuels derived from biomass but not from natural gas or coal.	
Biomass	Biological material, including any material other than fossil fuels which is or was a living organism or component or product of a living organism.	ASTM D5864; ASTM D6469; ASTM D7719
BXX blend	Fuel blend consisting of up to 20 volume percent biodiesel designed as up to B20 conforming to the requirements of ASTM D6751 with the remainder being a light middle or middle distillate grade diesel fuel and meeting the requirements of the test method. The abbreviation BXX represents a specific blend concentration in the range B2 to B20, where XX is the percent volume of biodiesel in the fuel blend.	ASTM D7501
Char	Fine carbonaceous powder that is separated from the vapors of biomass during pyrolysis. Pyrolysis liquid biofuel contains uniformly suspended char.	ASTM D7544
Denaturants	Materials added to ethanol to make it unsuitable for beverage use under a formula approved by a regulatory agency to prevent the imposition of beverage alcohol tax.	ASTM D4806
Denatured fuel ethanol	Fuel ethanol made unfit for beverage use by addition of denaturants under a formula approved by a regulatory agency to prevent the imposition of beverage alcohol tax.	ASTM D4806: ASTM D6423; ASTM D7653
Diesel fuel	Middle petroleum distillate fuel.	ASTM D6751
Diesel fuel oil	A petroleum-based diesel fuel as described in ASTM D975. Any petroleum liquid suitable for the generation of power by combustion in compression ignition (diesel) engines. Different grades are characterized primarily by viscosity ranges and by minimum cetane numbers.	ASTM D7806
ETBE	Ethyl tertiary-butyl ether, a chemical compound $CH_3CH_2OC(CH_3)_3$.	
Ethanol	Ethyl alcohol C_2H_5OH.	
Ethanol flex fuel	Mid-level ethanol fuel blends for use in flexible-fuel vehicles with ethanol concentrations greater than those suitable for conventional-fuel vehicles and less than the minimum ethanol content specification limits of ASTM D5798.	ASTM D7794
Ethanol fuel blend	A high concentration ethanol-based fuel for flexible-fuel spark-ignition engines and vehicles.	ASTM D7794
FAME	A biodiesel composed of long-chain fatty acid methyl esters derived from vegetable or animal fats. Used as a component in automotive diesel fuel and the potential source of contamination in aviation turbine fuel due to multi-fuel tankers and pipelines.	ASTM D7806 ASTM D7797
Free glycerin	A measure of the amount of glycerin remaining in the fuel.	ASTM D6751

(Continued)

TABLE 1.9 Terminology Used in Biofuels (*Continued*)

Term	Explanation	ASTM Standard
Fuel ethanol	Blend of ethanol and hydrocarbons of which the ethanol portion is nominally 75 to 85 volume percent denatured ethanol (i.e., Ed75–Ed85); a grade of undenatured ethanol with other components common to its production (including water) that do not affect the use of the product as a component for automotive spark-ignition engine fuels.	ASTM D4806; ASTM D5798; ASTM D6423; ASTM D7563
Gasoline	A volatile mixture of liquid hydrocarbons, generally containing small amounts of additives, suitable for use as a fuel in spark-ignition, internal combustion engines.	ASTM D4814
Gasoline–alcohol blend	A spark-ignition engine fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass % oxygen or more than 0.15 mass % oxygen, if methanol is the only oxygenate) of one or more alcohols.	ASTM D4806; ASTM D4814
Gasoline-ethanol blend	A fuel consisting primarily of gasoline along with a substantial amount (> 0.35 mass % oxygen) of denatured ethanol.	ASTM D4806
Gasoline-oxygenate blend	A spark-ignition engine fuel containing primarily gasoline with one or more oxygenates.	ASTM D323
Grade S15 B100	A grade of biodiesel meeting ASTM D6751 and having a sulfur specification of 15 mg/kg maximum.	ASTM D6751
Grade S500 B100	A grade of biodiesel meeting ASTM D6751 and having a sulfur specification of 500 mg/kg maximum.	ASTM D6751
Hydrocarbon oil	Homogenous mixture of solution with elemental composition primarily of carbon and hydrogen and also containing sulfur consistent with the limits given in ASTM D975, oxygen or nitrogen from residual impurities and contaminants and excluding added oxygenated materials, such as alcohols, esters, ethers, and triglycerides.	ASTM D975
Methanol	Methyl alcohol CH_3 OH	
Methyl tertiary butyl ether (MTBE)	Chemical compound $(CH_3)_3COCH_3$.	
Middle distillate fuel	Kerosine and gas oils boiling between approximately 150°C and 400°C at normal atmospheric pressure and having a closed-cup flash point (ASTM D93) above 38°C.	ASTM D6751
Mid-level ethanol fuel blend	An automotive spark-ignition engine fuel with an ethanol concentration greater than those suitable for conventional-fuel vehicles and less than the minimum ethanol content limit of ASTM D5798. Mid-level ethanol fuel blends are often referred to as EXX where XX represents the nominal percentage of denatured fuel ethanol.	ASTM D7794
Monoglyceride	A partially reacted fat or oil molecule with one long chain alkyl ester group on a glycerin backbone.	
Oxygenate	An oxygen–containing, ashless, organic compound, such as an alcohol or ether, which can be used as a fuel or fuel supplement.	ASTM D2699; ASTM D2700;ASTM D4806; ASTM D4814; ASTM D5845; ASTM D5983; ASTM D4953; ASTM D6277; ASTM D7618
Product methanol	The methanol produced for the purpose of blending with the spark ignition fuel. Its purity must be known prior to blending.	WK 39644
Pyrolysis liquid biofuel	A liquid product from the pyrolysis of biomass. Pyrolysis is achieved by chemical decomposition of organic materials by heating in the absence of oxygen, followed by the rapid condensation of its vapors. Pyrolysis liquid biofuel is comprised of a complex mixture of decomposition products of ligno-cellulosoic biomass including highly oxygenated organic compounds. It is produced from the pyrolysis of the biomass, followed by the rapid condensation of its vapors. Solid particles contained within the pyrolysis liquid biofuel are called pyrolysis solids and consist of ash and char.	ASTM D7544, ASTM D7579
Renewable fuel	A fuel derived from a sustainable or biological source. Some examples of renewable fuels are biofuels and fuels such as hydrogen manufactured by electrolysis of water using electricity generated by wind or solar power.	[26]
Synthesized hydrocarbons	Hydrocarbons derived from alternative sources such as coal, natural gas, biomass, and hydrogenated fats and oils by processes such as gasification, Fischer-Tropsch synthesis, and hydroprocessing.	ASTM D7566
Total glycerin	The sum of the free glycerin and the glycerin portion of any unreacted or partially reacted oil or fat.	ASTM D6751
Triglyceride burner fuel	Any triglyceride including recycled and unused cooking oil, greases, animal fats, and naturally occurring constituents of triglycerides including mono- and diglycerides, and free fatty acids, suitable for the generation of heat by combustion in a furnace or firebox as a vapor or a spray or a combination of both with little or no preconditioning other than preheating.	ASTM D7666

TABLE 1.10 ASTM Definitions of "Biomass"

ASTM Standard	ASTM Committee	Biomass Definition	Discussion
ASTM E1218	E47	The dry weight of living matter present in a population and expressed in terms of a given area or volume (e.g., mg algae per liter). Because biomass is difficult to measure accurately, surrogate measures of biomass, such as cell counts, are typically used in this test.	
ASTM E1705	E48	Any material, excluding fossil fuels, which is or was a living organism that can be used as a fuel directly or after a conversion process. Peat is not a biomass.	
ASTM E1706	E48	Material comprised of living or recently living (nonfossil) matter.	
ASTM E2523; ASTM E2694	E34	Any matter that is or was a living organism or excreted from a microorganism.	
ASTM D1129; ASTM D6161; ASTM D7687	D19 D02	Any material that is or was a living organism or excreted from a microorganism.	
ASTM D5864; ASTM D6006; ASTM D6139; ASTM D6384; ASTM D6469	D02	Biological material including any material other than fossil fuels that is or was a living organism or component or product of a living organism.	Products of living organisms include those materials produced directly by living organisms as metabolites (e.g., ethanol, various carbohydrates and fatty acids), materials manufactured by processing living organisms (e.g., pellets manufactured by shredding and pelletizing plant material), and materials produced by processing living organisms, their components or metabolites (e.g., transesterified oil; also called biodiesel).
ASTM D7719	D02	Plant material, vegetation, or agricultural waste used as a fuel or energy source.	
ASTM D6813	D02	Any material, excluding fossil fuels, that is or was a living organism that can be used as a fuel. Peanut hulls, agricultural waste, corn and other grains, and sugar are all examples of biomass.	

that a test method is applicable for specification purposes, even if the material is not in the test method's scope. Chemical and physical limits set in existing standards may or may not be appropriate to the new fuel or components. The new material may also require chemical or physical limits that are not appropriate to fuels in existing standards. These along with other considerations may indicate the need for separate new specifications. Although each case will require a separate evaluation, logic suggests that the fewer chemical and physical differences there are between the new fuel and the traditional petroleum-based fuel, the fewer differences in test methods and chemical or physical limits will be needed.

A Note on Test Methods

Biofuels increasingly are becoming important alternatives to traditional fossil fuel-based energy sources. Although a number of biofuel specifications have been formalized, the analytical test methods quoted in these specifications remain largely untested for many of these matrices. These test methods were originally devised for the analysis of petroleum and petroleum products, and their utility and precision for application to biofuels is largely unknown. This chapter summarizes current information about the test methods for analysis of oxygenated fuels, biodiesel, fuel ethanol, and certain synthetic biofuels. It is hoped that this information will be useful to product specification writers as well as to laboratory users. Areas where further work needs to be carried out for definitive elemental analysis of biofuels and oxygenated fuels are also identified.

A number of test methods described in this book have international counterparts in the ISO, IP, German Institute of Standardization (Deutsches Institut für Normung or DIN), or in Japanese Industrial Standards (JIS) [40]. These are listed in Chapters 3, 4, and 5. No claim is being made that all details in ASTM and non-ASTM standards are exactly the same. However, it is expected that, if properly followed, both sets of test methods should give statistically equivalent results. In an increasingly global marketplace, it is important to be cognizant of such equivalency for commerce among different regions of the world. A number of these specified test methods have been reviewed with regard to their applicability to biofuels characterization [41].

Several tests are common in the Brazilian, EU, and ASTM specifications for biodiesels. Many of these tests are technically equivalent. Some examples of this equivalency are given in Table 1.11.

- Copper in ASTM D4806 for denatured fuel ethanol is required to be determined by ASTM D1688A, an atomic absorption spectrometry (AAS) method for the determination of copper in water. However, hardly any oil industry laboratories use this test method. The analysis of ethanol-fuel samples in the ASTM

TABLE 1.11 Comparative Test Methods Used in Biodiesel Specifications

Analysis	Brazil (007/2008)	EU (EN 14214)	ASTM D6751
Sulfated ash	NBR 984; ISO 3987; ASTM D874	ISO 3987	ASTM D874
Na + K	EN 14108	EN 14108	EN 14538
Ca + Mg	EN 14109	EN 14109	
Phosphorus	EN 14107; ASTM D4851	EN 14107; EN 14538	ASTM D4951
Sulfur	ASTM D5453	ISO 20846; ISO 20884	ASTM D5453; ASTM D4294

Proficiency Testing Program (PTP) show no laboratory detecting copper in this product, which means that the copper levels in ethanol fuel are below the detection limit of the cited test method. Therefore, it would be useful to develop an inductively coupled plasma atomic emission spectrometry (ICP-AES) method for this analysis, which is more sensitive than the AAS technique and can determine copper as well as several other metals simultaneously. A method draft has been documented, but no interlaboratory study (ILS) has been conducted.

- Phosphorus determination is required by ASTM D6751 for biodiesel blends using ASTM D4951. This is an ICP-AES test method widely used in the oil industry for the analysis of additives and lubricating oils. These matrices have much higher phosphorus levels than biofuels; hence, the test method is incapable of determining very low levels of phosphorus in biofuels.
- Ca + Mg and Na + K are to be determined by EN 14538 as required in ASTM D6751 for biodiesel blends. This test method uses ICP-AES for the determination, although it is not clear why Ca + Mg and Na + K are reported as sums of these individual elements because, in reality, the method determines each element individually. Based on the data obtained in the ASTM PTP, cross-checks for biodiesel following reproducibility were calculated. Repeatability could not be calculated because the PTP cross-check only collects a single determination from each laboratory. Extremely high test performance indices (TPIs) calculated from this reproducibility data casts serious doubt on the reliability of the EN 14538 test method. The specified test method may not represent the real-world precision in the laboratories. Hence, it would be preferable to replace the EN test method with a new ASTM standard following a new ILS. Table 1.12 summarizes the data from three biodiesel ASTM PTPs for the year 2013. The same pattern is observed in these cross-checks in earlier years. In spite of the large number of laboratories participating (about 35 for each cycle), many results have been rejected as statistical outliers (about 10 for each analysis in each cycle). The resultant mean ± standard deviation values are essentially meaningless, with 100 % or more variability in each case. The calculated TPI values are ridiculously high—to the point of being unbelievable, particularly for Ca + Mg analysis. Given the wide range of individual results, it is impossible to believe that such results are credible. Either the EN 14538 ILS for determining the precision was not properly conducted or was not statistically properly validated (or both)—hence, the need for a new ICP-AES standard for this analysis.

TABLE 1.12 ASTM Cross-Check Results for Metals in Biodiesel Sample

Analysis	Ca + Mg	Na + K
EN 14538 reproducibility	0.149 X + 1.186	0.191 X + 0.941
BIOD1304	0.04 ± 0.06 (34)	0.19 ± 0.24 (36)
- [TPI]	[7.00]	[1.48]
- Data outliers	14	11
BIOD 1308	0.05 ± 0.07 (35)	0.10 ± 0.14 (33)
- [TPI]	[6.26]	[2.46]
- Data outliers	12	13
BIOD 1312	0.03 ± 0.05 (37)	0.13 ± 0.20 (39)
- [TPI]	[8.50]	[1.76]
- Data outliers	12	10

Note: Where X is the average of two determinations in mg/kg. The results are expressed as mean value ± standard deviation (number of valid results).

- Ethanol and methanol are determined by ASTM D5501, based on gas chromatographic separation of the components and flame ionization detection. However, the test method covers 93 to 97 mol % ethanol and does not determine E85. Hence, the scope of the method needs to be extended.
- Aromaticity: Hydrocarbon types in liquid petroleum products, including oxygenated fuels, are determined using fluorescent indicator absorption ASTM D1319. Aromatics, olefins, and saturates are distinguished and quantitated by this test method. Separate precision values have been calculated for oxygen-free and oxygenate containing samples. The latter precision includes samples of oxygenate blended (e.g., methyl tertiary butyl ether [MTBE] and ethanol) gasoline fuels with a concentration range of 13 to 40 volume percent aromatics, 4 to 33 volume percent olefins, and 45 to 68 volume percent saturates.

Hydrocarbon Types	Range vol %	Repeatability vol %	Reproducibility vol %
Aromatics	13–40	1.3	3.7
Olefins	4–33	$0.26\ X^{0.6}$	$0.82\ X^{0.6}$

Note: Where X is the average of two results.

The results as obtained by ASTM D1319 for ethanol blends need to be corrected for the ethanol content because the ethanol becomes part of the eluent fluid and is not seen in the analysis.

- Ash and sulfated ash are determined by ASTM D482 and ASTM D874, respectively, which are widely used in the oil industry for the analysis of lubricants. Although the scopes of these two test methods do not include biofuels, it is expected that the tests will be applicable to these matrices. However, because there is very little inorganic matter in biofuels, most of the time these test methods do not produce weighable amounts of ignition residues.

- Inorganic sulfate and chloride are determined in biofuels using ASTM D7318, ASTM D7319, and ASTM D7328. These test methods were specifically developed for fuel ethanols. In practice, it appears that the latter two ion chromatographic test methods (ASTM D7319 and ASTM D7328) are more widely used than the potentiometric titration method (ASTM D7318).
- Acid number or acidity determinations are required by ethanol specification ASTM D4806, biodiesel specification ASTM D6751, and ethanol fuel specification ASTM D5798. The two test methods specified for acidity are ASTM D664 and ASTM D1613. Of these two, ASTM D664 B was specifically developed for biofuels, but ASTM D1613 seems to be an incorrect choice for biofuels because the method is meant to analyze paint, varnishes, lacquer, and related products.
- Sulfur is one of the important criteria in the analysis of biofuels given its relevance in environmental impact. The most widely used test methods in this area are ASTM D2622 for wavelength dispersive X-ray fluorescence (WD-XRF), ASTM D7039 for monochromatic wavelength dispersive X-ray fluorescence (MWD-XRF), and ASTM D5453 for ultraviolet-fluorescence (UVFL). Discussion of this issue is adequately covered in Chapter 5 of this book and will not be repeated here.
- Cloud point is determined using ASTM D2500 as a referee method and ASTM D5773 and ASTM D7397 as alternate test methods in biodiesel specification ASTM D6751. All these methods have been tested on their applicability to the analysis of biofuels.
- Glycerin (both free and bonded content) reflects biodiesel quality. This is determined in B100 methyl esters by gas chromatography (GC) using ASTM D6584. However, this procedure is not applicable to vegetable oil and esters obtained from lauric oils, such as coconut oil and palm kernel oil.
- Biodiesel content of diesel fuel oil is determined using mid-infrared spectroscopy with an attenuated total reflectance sample cell (ASTM D7371). The method is applicable to concentrations from 1 to 20 volume percent. This procedure is applicable only to FAMEs. Biodiesel in the form of fatty acid ethyl ester will cause a negative bias. The hydrocarbon composition of a diesel fuel has a significant impact on the calibration model. Therefore, a robust calibration model is important so that the diesel fuel in the biodiesel fuel blend is represented in the calibration set.
- Metals are included in a few of the biofuels specifications, but their concentration levels are too low to obtain a meaningful analysis. These elements include calcium + magnesium, copper, lead, sodium + potassium, and phosphorus. Based on the ASTM proficiency testing programs, most of the time none of these elements are quantified. See Chapter 6 in this volume for further details.

Analytical tests may be classified as physical test methods, chemical analysis tests, elemental analysis tests, and environmental tests and are included in Chapters 3, 4, 5, and 6, respectively, of this book. In some cases, the classification is somewhat arbitrary and arguable. For example, test methods for the determination of water could be included as physical test methods if done by distillation or centrifugation (ASTM D95, ASTM D473, ASTM D1796, or ASTM D2709), or they can be included under chemical test methods if done by Karl Fischer titrations (ASTM D6304, WK 41558). Again, a best effort has been made to place them in their proper classification.

In each of these chapters, the test methods for a similar parameter are grouped together (e.g., all pour point test methods appear together in Chapter 3 on physical test methods; all sulfur test methods for elemental analysis are together in Chapter 5, etc.). Each test method cited includes details as to its significance, its scope in the petroleum products and biofuels areas, a summary of the test method, and details about the precision of the test method, particularly for biofuels where available. Table 1.13 lists where the test methods have specifically spelled out their applicability to biofuels and where they have not. This is contingent upon chemists in this area testing those methods where, to

TABLE 1.13 Applicability of Test Methods to Biofuels

Scope Includes Biofuels Analysis		Scope Does Not Include Biofuels Analysis	
Test Method	**Analysis**	**Test Method**	**Analysis**
ASTM D86	Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure		
ASTM D664 B[a]	Acid Number	ASTM D56	Tag Closed Cup Flash Point
ASTM D2500	Cloud Point	ASTM D95	Water by Distillation
ASTM D2622	Sulfur by WD-XRF	ASTM D97	Pour Point
ASTM D3828	Flash Point by Small Scale Closed Cup Tester	ASTM D381	Gum Content in Fuels
ASTM D4294	Sulfur by ED-XRF	ASTM D473	Sediment by Extraction
ASTM D4815	Alcohols by GC	ASTM D482	Ash
ASTM D5191	Vapor Pressure	ASTM D874	Sulfated Ash
ASTM D5453	Sulfur by UVFL	ASTM D974	Acid-Base Number by Colorimetric Titration
ASTM D5501[a]	Ethanol in Denatured Fuel Ethanol by GC	ASTM D1160	Distillation at Reduced Pressure

(Continued)

TABLE 1.13 Applicability of Test Methods to Biofuels (*Continued*)

Scope Includes Biofuels Analysis		Scope Does Not Include Biofuels Analysis	
Test Method	**Analysis**	**Test Method**	**Analysis**
ASTM D5622	Total Oxygen by Reductive Pyrolysis	ASTM D1266	Sulfur by Lamp Method
ASTM D5623	Sulfur by GC Sulfur Selective Detection	ASTM D1298	Density by Hydrometer
ASTM D5771	Cloud Point	ASTM D1319	Hydrocarbon Types
ASTM D5772	Cloud Point	ASTM D1500	ASTM Color
ASTM D5845[a]	Alcohols in Gasoline by IRS	ASTM D1552	Sulfur by High Temperature Combustion
ASTM D6079	Lubricity by HFRR	ASTM D1796	Water and Sediment by Centrifuge Method
ASTM D6423[a]	pHe of Ethanol and Fuel Ethanol	ASTM D2624	Electrical Conductivity
ASTM D6584[a]	Glycerides in B100 by GC	ASTM D2709	Water and Sediment by Centrifuge
ASTM D6773	Cloud Point	ASTM D2896	Base Number
ASTM D6890	Ignition Delay and DCN	ASTM D3231	Phosphorus in Gasoline
ASTM D6920	Sulfur by Electrochemical Detection	ASTM D3237	Lead in Gasoline by AAS
ASTM D7039	Sulfur by MWD-XRF	ASTM D3242	Acidity of Aviation Turbine Fuels
ASTM D7318[a]	Inorganic Sulfate in Ethanol	ASTM D3341	Lead in Gasoline by ICI Method
ASTM D7319[a]	Sulfate and Chloride by IC	ASTM D4308	Electrical Conductivity
ASTM D7321[a]	Particulate Contamination in Biodiesel	ASTM D4539	Filterability by LTFT
ASTM D7328[a]	Sulfate and Chloride by IC	ASTM D4629	Nitrogen by Chemiluminescence
ASTM D7347[a]	Olefins in Fuel Ethanol by SCFC	ASTM D4737	Calculated Cetane Index
ASTM D7371[a]	FAME in Biodiesel by IR	ASTM D4739	Base Number
ASTM D7398[a]	Boiling Range of FAME	ASTM D4951	Additive Elements by ICP-AES
ASTM D7462[a]	Oxidation Stability of Biodiesel	ASTM D5059	Lead in Gasoline by XRF
ASTM D7501[a]	CSFT of Biodiesel	ASTM D6450	Flash Point by CCCFP
ASTM D7576[a]	Aromatics in Ethanol Fuels by GC	ASTM E203	Water by KF Titration
ASTM D7579[a]	Pyrolysis Solids	ASTM E1064	Water in Organic Liquids by Coulometric KF Titration
ASTM D7591[a]	Glycerin in Biodiesel Blends		
ASTM D7689	Cloud Point by Mini Method		
ASTM D7717[a]	Preparation of Blendstocks for Analysis		
ASTM D7795	Acidity in Ethanol and Ethanol Blends by Titration		
ASTM D7796[a]	ETBE by Gas Chromatography		
ASTM D7797[a]	FAME in Aviation Turbine Fuels by IR		
ASTM D7806[a]	FAME of Biodiesels by mid-IR		
ASTM D7861[a]	FAME in Diesel Fuel by LVF Array Based Mid-IRS		
ASTM D7875[a]	Butanol and Acetone Content for Blending with Gasoline by GC		
ASTM D7963[a]	Contamination Level of FAME in Fuels by Flow Analysis by FTIR and Rapid Screening		
ASTM D7920[a]	Product Methanol and Methanol Blended in Gasoline by GC		
ASTM D7923[a]	Water in Ethanol Blends by KF Titration		
EN 14103[a]	Ester and Linolenic Ester Methyl Ester in FAME		
EN 14105[a]	Monoglycerides in Biodiesel Blend Stocks		
EN 14110[a]	Methanol Content of FAME		
EN 14112[a]	Oxidation Stability		
EN14538[a]	Metals in Biofuels		
EN 15751[a]	Oxidation Stability		
EN 15779[a]	Polyunsaturated Fatty Acid Methyl Esters in Biodiesels		
ISO 13032[a]	Sulfur in Gasoline-FAME by ED-XRF		

Note: WD-XRF = wavelength dispersive X-ray fluorescence; ED-XRF = energy dispersive X-ray fluorescence; GC = gas chromatography; UV-FL = ultraviolet fluorescence; IRS = infrared spectroscopy; HFRR = high frequency reciprocating rig; DCN = derived cetane number; MWD-XRF = monochromatic wavelength dispersive X-ray fluorescence; IC = ion chromatography; SCFC = super critical fluid chromatography; IR = infrared; FAME = fatty acid methyl ester; CSFT = cold soak filtration test; ETBE = ethyl tert-butyl ether; LVF = linear variable filter; FTIR = Fourier transform infrared spectroscopy; KF = Karl Fischer; AAS = atomic absorption spectrometry; ICI = iodine chloride; LTFT = low temperature flow test; ICP-AES = inductively coupled plasma atomic emission spectroscopy; XRF = X-ray fluorescence; CCCFP = continuously closed cup flash point.

[a] These test methods were specifically developed for biodiesels and fuel ethanol products.

date, their applicability to biofuels has not been specifically proven.

TABLE 1.14 Biofuel Standard Reference Materials Available from NIST

SRM #	Description	Analysis
1837	Gasoline	Methanol and butanol
1838	Gasoline	Ethanol
1839	Gasoline	Methanol
2286	Reference gasoline	Ethanol (nominal 2.0 wt. % oxygen)
2287	Reference gasoline	Ethanol (nominal 3.5 wt. % oxygen)
2294	RFG (nominal 11 % MTBE)	Sulfur (40.9 mg/kg)
2295	RFG (nominal 15 % MTBE)	Sulfur (0.3080 %)
2296	RFG (nominal 13 % MTBE)	Sulfur (40.0 mg/kg)
2297	RFG (nominal 10 % Ethanol)	Sulfur (303.7 mg/kg)
2773	B100 biodiesel (animal-based)	Sulfur (7.39 mg/kg)
2377	FAME in 2,2,4-trimethylpentane	
2272	B100 biodiesel (soy-based)	
8491	Sugarcane bagasse whole biomass feedstock	
8492	Eastern cottonwood whole biomass feedstock	
8493	Monterey pine whole biomass feedstock	
8494	Wheat straw whole biomass feedstock	
8495	Northern softwood	
8496	Eucalyptus hardwood	

Standard Reference Materials

Standard reference materials (SRMs) play a vital role in evaluating new analytical test methods, assessing the laboratory capability for performing the tests with required precision and accuracy, and for routine quality assurance of the data generated in the laboratories. Often SRMs are also used as the calibrating materials.

In fossil fuel (petroleum products, coal, and coke) analysis, several standard reference materials are available commercially or from the National Institute of Standards and Technology (NIST). They are widely used in the oil industry in ascertaining the accuracy and precision of a given test method. With the advent of biofuels, NIST has undertaken the task of certifying and issuing such standard reference materials for use.

NIST is perhaps the leading source of extremely reliable SRMs in a variety of matrices. NIST certifies each SRM based on replicate analysis values obtained by at least two independently based methods. There are other national bodies in the United Kingdom, Germany, and elsewhere that also produce similar SRMs. In addition, some commercial companies supply reference materials, although their certified values do not undergo the rigorous scrutiny that NIST undertakes.

NIST SRMs useful for analysis of biofuels are listed in Table 1.14. It would be highly desirable to have additional SRMs available for other analyses. Always consult the NIST Web page for the availability of these and other SRMs. Such appropriate SRMs should be used for calibration or quality control (or for both) in laboratory analysis. When a suitable SRM is not available, an appropriate reference material traceable to the SI unit of mass fraction should be used.

Another source for reference materials are industry round-robins such as the ASTM proficiency testing programs conducted by the D02 Committee. (See Chapter 8 on ASTM proficiency testing programs.) At present, biodiesel and fuel ethanol sample materials are used in these cross-checks three times a year (April, August, and November for biodiesels, and April, August, and December for fuel ethanol), and usually about 80 and 100 laboratories take part in these cross-checks, respectively. However, the use of these analyzed samples as reference materials needs to be considered with caution. These are consensus values and not certified values. Experience in these programs has shown that a large degree of uncertainty is associated with the calculated mean values. Hence, such materials are better suited as quality control materials rather than as primary reference standards. It is strongly suggested that the laboratories involved in such analyses make use of these SRMs to validate their laboratory and test method capabilities.

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Abstract

A brief history and development of biofuels is given, with an emphasis on work occurring in the United States and Brazil. Ethanol fuel, biodiesel, biolubricant, and aviation biofuels are discussed. Terminology used in the biofuels standards is explained. An overview of analytical test methods used for biofuels is provided.

Keywords

aviation biofuel, biofuels, biodiesel, biolubricant, BQ 9000 quality management, cellulosic ethanol, fuel ethanol

Chapter 2 | Biofuels Product Specifications

Biofuel Product Specifications

There are about a dozen biofuel product specifications in the ASTM literature. Many are based on and modified from traditional petroleum-based products. Thus, often the same analytical properties are determined for characterizing the biofuels as those used for petroleum-based hydrocarbon liquids. In this chapter, each of these product specifications are discussed as they relate to biofuels, and ASTM specifications are detailed. These specifications are meant for use by purchasing agencies in formulating specifications to be included in contracts for purchase of products and for the guidance of consumers of these products in selecting materials most suitable for their needs. Table 2.1 gives a list of currently available ASTM specifications relating to biofuels. The significance of including the tests for a particular product and other related information are also discussed where available.

The product specifications should be checked before their use to ensure that they are the most current specifications because many of them are revised on a frequent basis (e.g., ASTM D396, ASTM D975, ASTM D4814, etc.). Biofuels can be classified roughly by their usage or compositional characteristics.

- Traditional petroleum-based fuels mixed with biodiesels: ASTM D396 (fuel oil), ASTM D975 (diesel fuel oil), ASTM D6751 (biodiesel fuel blend stock), and ASTM D7467 (diesel fuel oil-biodiesel blend). Test properties for these products follow traditional petroleum-based products.
    - The properties of commercial biodiesel fuel depend on the refining practices used and the nature of the renewable lipids from which it is produced. For example, biodiesel can be produced from various vegetable oils or animal fats that produce similar volatility characteristics and combustion emissions with varying cold flow properties.
    - In all cases, biodiesels or biodiesel blends (up to B5 in ASTM D975 and B6 to B20 in ASTM D7467) are used in the same equipment as conventional diesel fuels, often without modifications or restrictions. Therefore, the same general fuel requirements and considerations for engines and equipment with conventional diesel fuel also apply to the use of biodiesel and biodiesel blend equipment.
- Traditional petroleum-based gasoline mixes: ASTM D4814 (gasoline). Test properties for these materials are the same as those used for traditional petroleum-based fuels.
- Ethanol/methanol-based fuels: ASTM D4806 (denatured fuel ethanol), ASTM D5797 (fuel methanol M70-M85), ASTM D5798 (ethanol fuel blends), and ASTM D7794 (mid-level ethanol fuel blends). Test properties for these alcohols are borrowed from petroleum-based fuels, and their applicability to new materials may or may not be known.
    - The primary fuel ethanol specifications are ASTM D4806 and ASTM D5798. ASTM D4814 covers the basic automotive fuels used in spark-ignition engines. Examples of these are gasolines and their blends with oxygenates, including gasoline containing up to 10 volume percent ethanol (i.e., E10). ASTM D4806 covers nominally anhydrous denatured fuel ethanol intended to be blended with gasoline at 1 to 10 volume percent ethanol for use as spark-ignition engine fuel. ASTM D5798 covers nominally 75 to 85 volume percent denatured fuel ethanol and 15 to 25 additional volume percent hydrocarbons for use in ground vehicles with automotive spark-ignition engines (ASTM E85).
- Miscellaneous other biofuels: ASTM D7544 (pyrolysis liquid biofuel) and ASTM D7666 (triglyceride burner fuel). Test properties for these synthetic products may or may not have been tested on these products.

ASTM Specification D396-14a

This is a specification for fuel oils intended for use in various types of fuel-oil-burning equipment under various climatic and operating conditions, and it includes biodiesel blend specifications up to 5 % by volume (B-5). It divides fuel oils into grades based upon the types of burners for which they are suitable. It places limiting values on several of the properties of the oils in each grade. The properties selected for limitation are those that are believed to be of the greatest significance in determining the performance characteristics of the oils in the types of burners in which they are most commonly used.

Because of the methods used in their production, fuel oils fall into two broad classifications: distillates and residuals. The

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TABLE 2.1 List of ASTM Standards Referred to in This Chapter (Product Specifications)

ASTM Standard	Description
ASTM D396–14a	*Standard Specification for Fuel Oils*
ASTM D975–14a	*Standard Specification for Diesel Fuel Oils*
ASTM D4806–14	*Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel*
ASTM D4814–14b	*Standard Specification for Automotive Spark-Ignition Engine Fuel*
ASTM D5797–13	*Standard Specification for Fuel Methanol (M70–M85) for Automotive Spark-Ignition Engines*
ASTM D5798–14	*Standard Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines*
ASTM D5983–13	*Standard Specification for Methyl Tertiary-Butyl Ether (MTBE) for Downstream Blending for Use in Automotive Spark-Ignition Engine Fuel*
ASTM D6751–14	*Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels*
ASTM D7467–13	*Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20)*
ASTM D7544–12	*Standard Specifications for Pyrolysis Liquid Biofuel*
ASTM D7666–12	*Standard Specification for Triglyceride Burner Fuel*
ASTM D7794–12	*Standard Practice for Blending Mid-Level Ethanol Fuel Blends for Flexible-Fuel Vehicles with Automotive Spark-Ignition Engines*
ASTM D7862–13	*Standard Specification for Butanol for Blending with Gasoline for Use as Automotive Spark-Ignition Engine Fuel*

distillates consist of overhead or distilled fractions. The residuals are bottoms remaining from the distillation or blends of these bottoms with distillates. In this specification, Grades No. 1 and No. 2 are distillates and Grades from No. 4 to No. 6 are usually residual, although some heavy distillates can be sold as Grade No. 4. These grades can be described as follows:

- + *Grades No. 1 S5000, No. 1 S500, No. 2 S5000, and No. 2 S500* are middle distillate fuels for use in domestic and small industrial burners. The first two are particularly adapted to vaporizing type burners in which the oil is converted to a vapor by contact with a heated surface or by radiation, or where storage conditions require low pour point fuel. High volatility is necessary to ensure that the evaporation proceeds with a minimum of residue. Grades No. 2 S5000 and No. 2 S500 are also middle distillates but are somewhat heavier than Grades No. 1 S5000 and No. 1 S500. They are intended for use in atomizing type burners that spray the oil into a combustion chamber where the tiny droplets burn while in suspension. These grades of oil are used in most domestic burners and in many medium-capacity commercial/industrial burners where ease of handling and ready availability sometimes justify higher cost over the residual fuels.

  In both No. 1 and No. 2 grades, the low sulfur grade S500 may be specified by federal, state, or local regulations and can result in reduced deposits on ferrous heat exchanger surfaces compared to Grade S5000 when burned under similar conditions.
- + *Grades No. 4 (Light) and No. 4* are heavy distillate fuels or middle distillate/residual fuel blends used in commercial/industrial burners equipped for this viscosity range. The first one is intended for use both in pressure-atomizing commercial/industrial burners not requiring higher cost distillates and in burners equipped to atomize oils of higher viscosity. Its permissible viscosity range allows it to be pumped and atomized at relatively low storage temperatures. Grade No. 4 is usually a heavy distillate/residual fuel blend but can be a heavy distillate fuel meeting the specification viscosity range. It is intended for use in burners equipped with devices that atomize oils of higher viscosity than domestic burners can handle. In all but extremely cold weather, it requires no preheating for handling.
- + *Grades No. 5 (Light), No. 5 (Heavy), and No. 6* are residual fuels of increasing viscosity and boiling range used in industrial burners. Preheating is usually required for handling and proper atomization. Grade No. 5 (Light) is residual fuel of intermediate viscosity for burners capable of handling fuel more viscous than Grade No. 4 without preheating. Preheating may be necessary in some types of equipment for burning and in colder climates for handling. Grade No. 5 (Heavy) is a residual fuel more viscous than Grade No. 5 (Light), and it is intended for use in similar service. Preheating may be necessary in some types of equipment for burning and in colder climates for handling. Grade No. 6, sometimes referred to as Bunker C, is a high-viscosity oil used mostly in commercial and industrial heating. It requires preheating in the storage tank to permit atomizing. The extra equipment and maintenance required to handle this fuel usually precludes its use in small installations.
- + *Blends with biodiesel*: If biodiesel is a component of any fuel oil, it needs to meet the requirements of ASTM D6751. Fuel oil containing up to 5 volume percent biodiesel shall meet the requirements of the appropriate Grade No. 1 or No. 2 fuel as listed in Table 2.2. ASTM EN 14078 is used for determining the volume percent biodiesel in a biodiesel blend. Fuel oils containing more than 5 volume percent biodiesel component and biodiesel blends with Grades No. 4, 5, or 6 are not included in this specification.

The latest revision of the specification, ASTM D396-15a, makes provisions for the inclusion of up to 20 % biodiesel by volume for all sulfur grades of No. 1 and No. 2 fuel oil of ASTM D396. These Grades 1 and 2 cover fuels for domestic use (i.e., home heating) and for small industrial burners. Over the last eight years, various organizations have collected and examined data for use of up to 20 % biodiesel in fuel oils. This limit is now being included in the standard specification. The new grade of B6-B20 could have a significant impact on the heating oil industry while also helping to meet growing consumer and regulatory demand for cleaner-burning low-carbon fuels [1].

Various grades of fuel oil must conform to the limiting requirements shown in Table 2.2. Modifications of limiting requirements to meet special operating conditions agreed upon among the purchaser, the seller, and the supplier shall fall within the limits specified for each grade.

As fuel oil specifications become more stringent and contaminants and impurities become more tightly controlled, even greater

TABLE 2.2 Product Specifications for Fuel Oils per ASTM D396-14a

Property	ASTM Test Method	Fuel Oil Grade	Limits
Flash point, °C	ASTM D93 A	No. 1 S500, No. 1 S5000, No. 2 S500, No. 2 S5000, No. 4 light	38
	ASTM D93 B	No. 4, No. 5 light, No. 5 heavy	55
		No. 6	60
Water and sediment, % vol max	ASTM D2709	No. 1 S500, No. 1 S5000, No. 2 S500, No. 2 S5000	0.05
	ASTM D95 + ASTM D473	No. 4 light, No. 4	0.50
		No. 5 light, No. 5 heavy	1.00
		No. 6	2.00
Distillation temp., °C	ASTM D86	No. 1 S500, No. 1 S5000	215
10 % vol recovered max		No. 2 S500, No. 2 S5000	282
90 % vol recovered min		No. 1 S500, No. 1 S5000	288
90 % vol recovered max		No. 2 S500, No. 2 S5000	338
Kinematic viscosity at 40°C, mm²/s, min–max	ASTM D445	No. 1 S500, No. 1 S5000	1.3–2.4
		No. 2 S500, No. 2 S5000	1.9–4.1
		No. 4 light	1.9–5.5
		No. 4	>5.5–24
Kinematic viscosity at 100°C mm²/s, min–max	ASTM D445	No. 5 light	5.0–8.9
		No. 5 heavy	9.0–4.9
		No. 6	15.0–50
Ramsbottom carbon residue on 10 % distillation residue, % mass, max	ASTM D524	No. 1 S500, No. 1 S5000	0.15
		No. 2 S500, No. 2 S5000	0.35
Ash, mass %, max	ASTM D482	No. 4 light	0.05
		No. 4	0.10
		No. 5 light, No. 5 heavy	0.15
Sulfur, mass %, max[a]	ASTM D129	No. 1 S5000, No. 2 S5000	0.5
	ASTM D2622	No. 1 S500, No. 2 S500	0.05
Copper strip corrosion rating, max	ASTM D130	No, 1 S500, No. 1 S5000, No. 2 S500, No. 2 S5000	No. 3
Density, at 15°C, kg/m³	ASTM D1298	No. 4 light	>876
		No. 1 S500, No. 1 S5000	max 850
		No. 2 S500, No. 2 S5000	max 876
Pour point, °C, max	ASTM D97	No. 1 S500, No. 1 S5000	−18
		No. 2 S500, No. 2 S5000, No. 4 light, No. 4	−6

[a] ASTM D2622 is the referee test method. Other test methods allowed to be used are ASTM D129, ASTM D1266, ASTM D1552, ASTM D4294, ASTM D5453, ASTM D7039, or ASTM D7220 (or a combination thereof).

care needs to be taken in collecting and storing samples for quality assessment. Appropriate manual and automatic methods of sampling are covered in ASTM D4057 and ASTM D4177, respectively. Refer to ASTM D4306 for aviation fuel container selection for tests sensitive to trace contamination. ASTM D5854 gives procedures on container selection and sample mixing and handling. For volatility determination of a sample, refer to ASTM D5842 for special precautions recommended for representative sampling and handling instructions.

Residual fuel oil supplied to meet regulations requiring low sulfur content can differ from the grade previously supplied. It may be lower in viscosity (and fall into a different grade number). It must be fluid at a given temperature; ASTM D97 need not accurately reflect pour point, which can be expected after a period of storage. It is suggested that the purchaser and supplier discuss the proper handling and operating techniques for a given low-sulfur residual fuel oil in the installation where it is to be used.

ASTM Specification D975-14a

This specification covers seven grades of diesel fuel oils suitable for various types of diesel engines. Some grades as specified may contain up to 5 % biodiesel. These grades are described as follows:

- + *Grade No. 1-D S15* is a special-purpose light middle-distillate fuel for use in diesel engine applications requiring a fuel with 15 ppm sulfur (maximum) and higher volatility than that provided by Grade No. 2-D S15 fuels. Fuels within this grade are suitable for use in (1) high-speed diesel engines and diesel engine applications that require ultra-low sulfur fuels, (2) applications necessitating frequent and relatively wide variations in loads and speeds, and (3) applications where abnormally low operating temperatures are encountered.

- *+ Grade No. 1-DS500* is a special-purpose light middle distillate fuel for use in diesel engine applications requiring a fuel with 500 ppm sulfur (maximum) and higher volatility than that provided by Grade No. 2-D S500 fuels. Fuels within this grade are suitable for use in (1) high-speed diesel engines that require low sulfur fuels, (2) applications necessitating frequent and relatively wide variations in loads and speeds, and (3) applications where abnormally low operating temperatures are encountered.
- *+ Grade No. 1-D S5000* is a special-purpose light middle distillate fuel for use in diesel engine applications requiring a fuel with 5,000 ppm sulfur (maximum) and higher volatility than that provided by Grade No. 2-D S5000 fuels. Fuels within this grade are suitable for use in high-speed diesel engines necessitating frequent and relatively wide variations in loads and speeds and for use in cases where abnormally low operating temperatures are encountered.
- *+ Grade No. 2-D S15* is a general-purpose middle distillate fuel for use in diesel engine applications requiring a fuel with 15 ppm sulfur (maximum). It is especially suitable for use in applications with conditions of varying speed and load. Fuels within this grade are appropriate for use in (1) high-speed diesel engines that require ultra-low sulfur fuels, (2) applications necessitating relatively high loads and uniform speeds, or (3) diesel engines not requiring fuels having higher volatility or other properties specified in Grade No. 1-D S15.
- *+ Grade No. 2-D S500* is a general-purpose middle distillate fuel for use in diesel engine applications requiring a fuel with 500 ppm sulfur (maximum). It is especially suitable for use in applications with conditions of varying speed and load. These fuels are appropriate for use in (1) high-speed diesel engine applications that require low sulfur fuels, (2) applications necessitating relatively high loads and uniform speeds, or (3) diesel engines not requiring fuels having higher volatility or other properties specified in Grade No. 1-D S500.
- *+ Grade No. 2-D S5000* is a general-purpose middle distillate fuel for use in diesel engine applications requiring a fuel with 5,000 mg/kg sulfur (maximum), especially in conditions of varying speed and load. These fuels are suitable for use in (1) high-speed diesel engines in applications necessitating relatively high loads and uniform speeds or (2) diesel engines not requiring fuels having higher volatility or other properties specified in Grade No. 1-D S5000.
- *+ Grade No. 4-D* is a heavy distillate fuel, or a blend of distillate and residual fuel oil, for use in low- and medium-speed diesel engines in applications involving predominantly constant speed and load.

The grades of diesel fuel oils described here shall be hydrocarbon oils, except as provided in the alternate fuel section of ASTM D975-14a, with the addition of chemicals to enhance performance, if required, conforming to the detailed requirements shown in the standard (which will be outlined later in this chapter). Additives generally are included in finished diesel fuel to improve performance properties such as cetane number, lubricity, cold flow, and so on.

FUEL BLENDS WITH BIODIESEL

If biodiesel is a component of any diesel fuel, the biodiesel shall meet the requirements of ASTM D6751. Diesel fuel oil containing up to 5 volume percent biodiesel shall meet the requirements for the appropriate Grade No. 1-D or No. 2-D fuel. ASTM D7371 shall be used for the determination of the volume percent biodiesel in a biodiesel blend. ASTM EN 14078 may also be used. The referee method is ASTM D7371. Diesel fuels containing more than 5 volume percent biodiesel component or biodiesel blends with No. 4-D fuel are not included in this specification.

ASTM D4806-14

This specification is for denatured fuel ethanol for blending with gasolines for use as automotive spark-ignition engine fuel. Nominally, it covers anhydrous denatured fuel ethanol intended to be blended with unleaded or leaded gasolines at 1 to 10 volume percent for use as automotive spark-ignition engine fuel covered by ASTM D4814 (see next section). Performance requirements for this product as specified in ASTM D4806 are listed in Table 2.3.

TABLE 2.3 Performance Requirements for Denatured Fuel Ethanol per ASTM D4806-14

Property	Limit	Test Method
Ethanol, volume %, min	92.1	ASTM D5501
Methanol, volume %, max	0.5	ASTM D5501
Solvent washed gum, mg/100 mL, max	5.0	ASTM D381
Water, volume % (mass %), max	1.0 (1.26)	ASTM E203 or ASTM E1064
Inorganic chloride, mass ppm (mg/L), max	10 (8)	ASTM D7319 or ASTM D7328
Copper, mg/kg, max	0.1	ASTM D1688
Acidity (as acetic acid), mass % (mg/L), max	0.007 (56)	ASTM D1613
pHe	6.5 to 9.0	ASTM D6423
Sulfur, mass mg/kg, max[a]	30	ASTM D2622, ASTM D3120, ASTM D5453, or ASTM D7039
Existent Sulfate, mass mg/kg, max	4	ASTM D7318, ASTM D7319, or ASTM D7328

[a] ASTM D2622, ASTM D3120, ASTM D5453, or ASTM D7039 are allowed to be used. The State of California only allows the use of ASTM D5453; the U.S. Environmental Protection Agency allows ASTM D3120, ASTM D5453, or ASTM D7039 as long as these alternative test methods are correlated with ASTM D2622.

Manufacturers, importers, and others denaturing fuel ethanol shall avoid ethanol (e.g., improperly recycled ethanol) or denaturants contaminated by silicon-containing materials, or both. Silicon contamination of gasoline-oxygenate blends has led to fouled vehicle components (e.g., spark plugs, exhaust oxygen sensors, catalytic converters) requiring parts replacement and repairs [1]. ASTM Test Method D7757 should be used to check the concentration of silicon in gasoline.

Scopes of some of the test methods listed in Table 2.3 do not include denatured fuel ethanol. The precision of those test methods can differ from the reported precisions when testing denatured fuel ethanol.

TEST METHODS

The test methods listed in Table 2.2 are used for the characterization of fuel oils. Several of the tests have alternate methods allowed for the determination of the same parameter. See Table 2.4 for discussion of such allowed variations. Specifications for diesel fuel oils per ASTM Specification D975 are given in ASTM Specification D4814–14b.

ASTM Specification D4814–14b

This is a specification for automotive spark-ignition engine fuel for ground vehicles. The spark-ignition engine fuels covered in this specification are gasoline and its blends with oxygenate, such as alcohols and ethers. This standard is interpreted to cover all gasoline/ethanol blends where ethanol is not the primary fuel component. This specification does not apply to the fuels that contain oxygenates as the primary components, such as fuel methanol (M85). Revision of this specification is being considered for gasoline-ethanol blends containing up to 15 % by volume ethanol.

Tests applicable to gasoline are not necessarily applicable to its blends with oxygenates. Consequently, the test fuel must first be identified as to its oxygenate type and content. ASTM D4815 and ASTM D5599 provide procedures for determining oxygenate concentration in mass percent. The limits in Table 2.6 are placed on all types of volatility classes of ASTM D4814 gasoline fuels.

See the note in the earlier section on ASTM D4806 regarding the silicon impurities in gasoline [1].

ASTM Specification D5797–13

This specification covers a fuel blend, nominally 70 % to 85 % methanol and 30 % to 14 % hydrocarbons, for use in ground vehicles with automotive spark-ignition engines. The requirements for fuel methanol are specified in Table 2.7. The appropriateness of ASTM test methods has not been demonstrated for use with M70–M85.

ASTM Specification D5798–14

This specification covers the requirements for automotive fuel blends with ethanol and gasoline for use in ground vehicles equipped with flexible-fuel spark-ignition engines. Fuel produced to this specification contains 51 to 83 volume percent ethanol. Sometimes it is referred to as “ethanol flex-fuel.” The vapor pressure of ethanol fuel blends is varied for seasonal climatic changes. It is increased at lower temperatures to ensure adequate flexible-fuel operability. This specification formerly covered fuel ethanol (Ed70–Ed85) for automotive spark-ignition engines. The nomenclature “fuel ethanol” has been changed to “ethanol fuel blends” to distinguish this product from denatured fuel ethanol (ASTM D4806).

TABLE 2.4 Alternate Methods Allowed for Fuel Oil Specification ASTM D396-14a

Analysis	Primary Test Method	Allowed Alternates
Flash point	ASTM D93 A for grades No. 1 S5000 and S500, No. 2 S5000 and S500, and No. 4 (light) ASTM D93 B for grades No. 4, No. 5 (light and heavy), and No. 6	ASTM D3828 for grades No. 1 S5000 and S500, No. 2 S5000 and S500, and No. 4 (light) ASTM D56 for grades No. 1, No. 1 low sulfur, No. 2, and No. 2 low sulfur, if the flash point is below 93°C and the viscosity is below 5.5 mm^2/s at 40°C.
Pour point	ASTM D97	ASTM D5949, ASTM D5950, ASTM D5985, ASTM D6749, and ASTM D6892 for all grades as alternative test methods.
Water and sediment	ASTM D2709 for grades No. 1 S5000 and S500, No. 2 S5000 and S500 ASTM D95 and ASTM D473 for grade Nos. 4, 5, and 6	
Density	ASTM D1298	ASTM D4052 as an alternate
Distillation	ASTM D86 for grade Nos. 1 and 2	ASTM D2887 as an alternate
Sulfur	ASTM D129 for >0.1 mass % for grades No. 1 and No. 2 S5000, No. 4 (light), No. 5 (heavy), and No. 6	ASTM D1266 for 0.01 to 0.4 mass % for Nos. 1 and 2 S500 ASTM D1552 for >0.06 mass % for Nos. 1 and 2 S5000, No. 4 (light), No. 4, No. 5 (light and heavy), and No. 6 ASTM D2622 for 0.0003 to 5.3 mass % for all grades ASTM D4294 for 0.0150 to 5.00 mass % for all grades ASTM D5453 for 0.0001 to 0.8 mass % for all grades ASTM D7039 for 0.0004 to 0.0017 mass % for S500 grade
Biodiesel content	ASTM D7371	ASTM D7861

TABLE 2.5 Product Specifications of Diesel Fuel Oils per ASTM D975-14a

Property	Test Method	Grades	Limits
Flash point, °C	ASTM D93	No. 1-D S15, No. 1-D S500, No. 1-D S5000	38
		No. 2-D S15, No. 2-D S500, No. 2-D S5000	52
		No. 4-D	55
Distillation temperature, °C 90 % vol recovered	ASTM D86 Min	No. 2-D S15, No. 2-D S500, No. 2-D S5000	282
	ASTM D86 Max	No. 1-D S15, No. 1-D S500, No. 1-D S5000	288
		No. 2-D S15, No. 2-D S500, No. 2-D S5000	338
Kinematic viscosity, mm^2/s at 40°C	ASTM D445 Min	No. 1-D S15, No. 1-D S500, No. 1-D S5000	1.3
	ASTM D445 Max	No. 2-D S15, No. 2-D S500, No. 2-D S5000	1.9
		No. 4-D	5.5
		No. 1-D S15, No. 1-D S500, No. 1-D S5000	2.4
		No. 2-D S15, No. 2-D S500, No. 2-D S5000	4.1
		No. 4-D	24.0
Ash, mass %, max	ASTM D482	All grades except 4-D	0.01
		Grade 4-D	0.10
Sulfur, mg/kg, max	ASTM D5453	No. 1-D S 15, No. 2-D S15	15
Sulfur, mass %, max	ASTM D2622	No. 1-D S500, No. 2-D S500	0.05
Sulfur, mass %, max	ASTM D129	No. 1-D S5000, No. 2-D S5000	0.50
		No. 4-D	2.00
Cetane number, min	ASTM D613	All grades except No. 4-D	40
		No. 4-D	30
Ramsbottom carbon residue on 10 % distillation residue, % mass, max	ASTM D524	No. 1-D 15, No. 1-D 500, No. 1-D 5000	0.15
		No. 2-D S15, No. 2-D S500, No. 2-D S5000	0.35
All Grades			
Water and sediment, % vol. max	ASTM D2709 or ASTM D1796	0.05	
Cu strip corrosion rating, max	ASTM D130	No. 3	
Cetane index, min	ASTM D976–80	40	
Aromaticity, % vol max	ASTM D1310	35	
Lubricity HFRR at 60°C, micron, max	ASTM D6079/ASTM D7688	520	
Conductivity pS/m	ASTM D2624/ASTM D4308	25	
Biofuel content	ASTM D7371/ASTM D7861		

Note: HFRR = high-frequency reciprocating rig.

TABLE 2.6 Analytical Limits for Gasoline Fuel Testing per ASTM D4814-14b

Analysis	Test Limits	Test Method
Lead, max, g/L (g/U.S. gal)	Unleaded: 0.013 (0.05) Leaded:1.1 (4.2)	ASTM D3341 or ASTM D5059; ASTM D3237
Copper strip corrosion, max	No. 1	ASTM D130, 3 h at 50°C
Silver strip corrosion, max	1	Annex A1 in ASTM D4814
Solvent washed gum, mg/100 mL, max	5	ASTM D381, air jet apparatus
Sulfur, max, mass %	Unleaded: 0.0080 Leaded: 0.15	ASTM D1266, ASTM D2622, ASTM D3120, ASTM D5453, ASTM D6920, or ASTM D7039
Oxidation stability, min, minutes	240	ASTM D525
Oxygenates		ASTM D4815, ASTM D5599, or ASTM D5845

TABLE 2.7 Requirements for Fuel Methanol (M70–M85)

Properties	Test Method	Class 1	Class 2	Class 3
Methanol + higher alcohols, min. volume %	Annex A1 of ASTM D5797	84	80	70
Hydrocarbon/aliphatic ether, volume %	ASTM D4815	14–16	14–20	14–30
Vapor pressure, kPa (psi)	ASTM D4953, ASTM D5190, or ASTM D5191	48–62 (7.0–9.0)	62–83 (9.0–12.0)	83–103 (12.0–15.0)
Lead, max, mg/L	ASTM D5059	2.6	2.6	3.9
Phosphorus, max, mg/L	ASTM D3231	0.2	0.3	0.4
Sulfur, max, mg/kg	ASTM D1266, ASTM D2622, ASTM D3120, or ASTM D5453	160	200	300
All Classes				
Higher alcohols, max, volume %	Annex A1 of ASTM D5797	2		
Acidity as acetic acid, max, mg/kg	ASTM D1613	50		
Solvent washed gum, max, mg/100 mL	ASTM D381	5		
Unwashed gum, max, mg/100 mL	ASTM D381	20		
Total chlorine as chlorides, max, mg/kg	ASTM D4929 B	2		
Inorganic chloride, max, mg/kg	ASTM D512 C; Annex A3 in ASTM D5797	1		
Water, max, mass %	ASTM E203	0.5		
Appearance	–	Visibly free of suspended or precipitated contaminants (clear and bright)		

The ethanol fuel blend performance requirements are given in Table 2.8. Most of the requirements cited are based on the best technical information available. Requirements for sulfur, phosphorus, and lead are based on the use of gasoline defined in ASTM D4814 and on the understanding that the control of these elements will affect the catalyst lifetime.

TABLE 2.8 Requirements for Ethanol Fuel Blends per ASTM D5798-14

Properties	Test Method	Limits
Vapor pressure, kPa (psi)	ASTM D4953, ASTM D5190, or ASTM D5191	Class 1: 38–62 (5.5–9.0) Class 2: 48–65 (7.0–9.5) Class 3: 59–83 (8.5–12.0) Class 4: 66–103 (9.5–15.0)
Ethanol, volume %	ASTM D5501	51–83
Water, max, mass %	ASTM E203 or ASTM E1064	1.0
Methanol. max, volume %	ASTM D5501	0.5
Sulfur, max, mg/kg	ASTM D5453 or ASTM D7039	80
Acidity (as acetic acid), max, mass % (mg/L)	ASTM D1613	0.005 (40)
Solvent washed gum, max, mg/100 mL	ASTM D381	5
Unwashed gum, max, mg/100 mL	ASTM D381	20
pHe	ASTM D6423	6.5 to 9.0
Inorganic chloride, max, mg/kg	ASTM D7319 or ASTM D7328	1
Copper, max, mg/L	ASTM D1688	0.07

ASTM D5983-13

This specification covers fuel-grade methyl tertiary-butyl ether (MTBE) utilized in commerce, terminal blending, or downstream blending with fuels for spark-ignition engines. Other MTBE grades may be available for blending that are not covered by this specification. Performance requirements for MTBE are given in Table 2.9 per ASTM D5983. The scope of some of the test methods listed in ASTM D5983 does not include MTBE. The precision of those test methods may differ from the reported precision given in the standard test methods when testing MTBE.

TABLE 2.9 Requirements for MTBE per ASTM D5983-13

Property	Test Method	Limits
Appearance	–	Clear and bright
Color, saybolt, min	ASTM D156	+ 5
Sulfur, max, mg/kg	ASTM D4045	300
Solvent washed gum, max, mg/100 mL	ASTM D381 with air-jet apparatus	5.0
Copper strip corrosion, max	ASTM D130 at 3 h at 50°C	1
MTBE, min, mass %	ASTM D5441	95.0
Methanol, max, mass %	ASTM D5441	0.5
Vapor pressure, max, kPa	ASTM D4953	62
Water, max, mass %	ASTM E203 or ASTM E1064	0.10
API gravity at 15.6°C or Density at 15°C, kg/L	ASTM D1298 or ASTM D4052	Report

ASTM D6751-14

This ASTM specification is for biodiesel fuel blend stock (B100) for middle distillate fuels. It is classified very similarly to its non-biodiesel counterpart ASTM D975 for diesel fuel oils. Its grades are described as follows:

- + *Grade No. 1-B S15* is a special-purpose biodiesel blendstock intended for use in middle distillate fuel applications that can be sensitive to the presence of partially reacted glycerides, including those applications requiring good low-temperature operability and a fuel blend component with 15 mg/kg sulfur (maximum).
- + *Grade No. 1-B S500* is the same as Grade No. 1-B S15 except with a maximum sulfur content of 500 mg/kg.
- + *Grade No. 2-B S15* is a special-purpose biodiesel blendstock intended for use in middle distillate fuel applications that require a fuel blend component with 15 mg/kg sulfur (maximum).
- + *Grade No. 2-B S500* is the same as Grade No. 2-B S15 but with a maximum sulfur content of 500 mg/kg.

ASTM D6751 is also used wholly or in parts in many countries around the world, including Brazil, Greece, Malaysia, the Philippines, and Singapore. In the United States, at least 35 states require their biodiesel fuel to meet ASTM specifications.

ASTM D6751 continues to be the foundational quality standard for a biodiesel industry whose U. S. sales have risen from less than 20 million gal in 2001 to more than 1.6 billion gal in 2013. The latest version of ASTM D6751-15a includes a modification of B100 to include specifications for stability, sodium/potassium, calcium/magnesium, and to reduce the acid number; an addition of controls for minor biodiesel components to ensure the fuel would perform as expected with new ultra-low sulfur diesel fuel in cold weather; an addition of a second grade of biodiesel that had tighter specifications for minor components; and an addition of ASTM D7668 as an alternative to standard ASTM D613 for determining cetane number. The improvements to ASTM D6751 and growth of the industry have also resulted in major revisions to ASTM standards for home heating oil and jet fuels. The maximum amount of biodiesel allowed in the ASTM D1655 jet fuel standard was raised from 5 to 50 ppm, with a planned increase to 100 in roughly two years. The increase gives pipeline companies the flexibility to consider transporting biodiesel blends in pipelines that also carry jet fuel while maintaining its quality [2].

An important feature of this specification is that it is not a fuel specification but is for a fuel blendstock that can be used up to 20 volume percent. To protect the performance and durability of combustion equipment, ASTM D6751 places limits on impurities that can remain from the biodiesel production process. These include methanol, glycerin (a by-product), unconverted and partly converted feedstock, and the sodium plus potassium that may remain from the caustic used to catalyze the transesterification reaction. Methanol is one of the reactants used to produce biodiesel. To drive the reaction to completion, it is typical to use 4:1 excess methanol; hence, methanol must be removed from the product. Methanol above about 0.2 weight percent is known to be incompatible with some automotive fuel system elastomers and metals. ASTM D6751 indirectly controls the amount of methanol in the end product by limiting its flash point, as measured by a Pensky Martens Closed Cup Tester (ASTM D93), to above 130°C. Alternatively, if the product has an ASTM D93 flash point of 93°C, it must be accompanied by measuring the methanol content of the product using ASTM Test Method EN 14110 and having the methanol content below 0.2 %. That ensures that the biodiesel is in a nonhazardous category for transportation purposes [3].

The specification ASTM D6751 prescribes the required properties of diesel fuels at the time and place of delivery. The biodiesel specified shall be monoalkyl esters of long-chain fatty acids derived from vegetable oils and animal fats. A considerable amount of experience exists in the United States with a 20 % blend of biodiesel, primarily produced from soybean oil, with 80% diesel fuel (B20). Experience with biodiesel produced from animal fats and other oils is similar. Experience with B20 and lower blends in other applications is not as prevalent. Although biodiesel (B100) can be used, blends of more than 20 % biodiesel with diesel oil (B20) should be evaluated on a case-by-case basis until further experience is available. The user should consult the equipment manufacturer or owner's manual regarding the suitability of using biodiesel or biodiesel blends in a particular engine or application.

Glycerin is a by-product of the transesterification reaction. Glycerin is a viscous liquid that can separate from the B100 or blends to form deposits at the bottom of the fuel storage tanks and can cause fuel filter plugging. High levels of glycerin can also lead to fuel injector deposits. To prevent these operational problems, ASTM D6751 limits free glycerin content to 0.020 weight percent maximum. High levels of unconverted or partly converted feedstocks (vegetable oil, waste cooking oil, or animal fat) are known to cause similar problems (as mentioned earlier) in diesel engines. These materials contain mono-, di-, and triglycerides (or more properly, acyl glycerides) and are limited to 0.240 weight percent as total glycerin [2,3].

Most biodiesel production schemes use sodium hydroxide (NaOH) or potassium hydroxide (KOH) to catalyze the transesterification reaction. ASTM D6751 limits Na + K to 5 mg/kg maximum as determined by test method EN 14538. Additionally, biodiesel can become contaminated with calcium (Ca) and magnesium (Mg) from the use of hard water to extract impurities. ASTM D6751 also limits Ca + Mg content to 5 mg/kg as determined by test method EN 14538. This is an inductively coupled plasma atomic emission spectroscopy method and can simultaneously determine several trace elements in the product [3].

The biodiesel specifications shall conform to the detailed requirements shown in Table 2.10.

ASTM Specification D7467-13

This specification covers fuel blend grades of 6 to 20 volume percent biodiesel with the remainder being a light middle or middle distillate diesel fuel ASTM D975 Grades No. 1-D and No. 2-D, collectively designated as B6 or B20. These grades are suitable for various types of diesel engines for use as on- or off-road diesel.

TABLE 2.10 Requirements of Biodiesel (B100) Blendstocks per ASTM D6751-14

Property	Test Method	Grade No. 1-B S15	Grade No. 1-B S500	Grade No. 2-B S15	Grade No. 2-B S500
Sulfur, mg/kg, max	ASTM D5453[a]	15	500	15	500
Cold soak filterability, s, max	ASTM D7501	200	200	360	360
Monoglyceride, mass %, max	ASTM D6584[b]	0.40	0.40		
Requirements for all grades					
Ca + Mg, mg/kg, max		EN 14538[c]	5		
Na + K, mg/kg, max		EN 14538[c]	5		
Flash point, °C, min		ASTM D93[d]	93		
Alcohol					
—mass % max		EN 14110	0.2		
—flash point, °C, min		ASTM D93[d]	130		
Water and sediment, vol. %, max		ASTM D2709[e]	0.050		
Kinematic viscosity at 40°C, mm^2/s,		ASTM D445	1.9–6.0		
Sulfated ash, mass %, max		ASTM D874	0.020		
Copper strip corrosion, max		ASTM D130[f]	No. 3		
Cetane number, min		ASTM D613[g]	47		
Cloud point, °C		ASTM D2500[h]	Report		
Carbon residue, mass %, max		ASTM D4530[i]	0.050		
Acid number, mg/kg, max		ASTM D664[j]	0.50		
Free glycerin, mass %, max		ASTM D6584[k]	0.020		
Total glycerin, mass %, max		ASTM D6584[k]	0.240		
Phosphorus, mass %, max		ASTM D4951[l]	0.001		
Distillation temperature, 90% recovered, max		ASTM D1160[m]	360		
Oxidation stability, h, min		EN 15751[n]	3		

[a] ASTM D7039 may also be used. Other test methods may also be suitable for determining sulfur up to 0.05 % sulfur in biodiesel fuels, such as ASTM D1266, ASTM D2622, ASTM D3120, and ASTM D4294, but may provide falsely high results. Their precision and bias with biodiesels is not known. ASTM D5453 shall be the referee test method.

[b] ASTM D6584, EN 14105, and AOCS Standard Procedure Ck 2-09 may be used for determining monoglycerides. ASTM D6584 shall be the referee test method.

[c] ASTM UOP 391 was allowed at one time to be used as an alternative for EN 14538. However, it cannot be used any longer because the reagents needed for this test are no longer available. EN 14538 shall be the referee test method.

[d] ASTM D3828 or ASTM D6450 can also be used as alternative test methods for ASTM D93 flash point test method. The precision and bias of these alternative test methods are not known at present. ASTM D93 shall be the referee test method.

[e] ASTM D1796 may also be used in place of ASTM D2709 for determining water and sediment. The latter will be the referee test method. The precision and bias of both these test methods with biodiesel is not known.

[f] Copper strip corrosion test will be carried out at 50°C for 3 h.

[g] ASTM D6890 may also be used in place of ASTM D613 for determining cetane number. The latter test method is considered as the referee test method.

[h] ASTM D5771, ASTM D5772, ASTM D5773, or ASTM D7397 or AOCS Standard Procedure Ck 2-09 may also be used as alternative tests for ASTM D2500 for cloud point. ASTM D3117 may also be used because it is closely related, although its precision and bias for biodiesel is not known. ASTM D2500 shall be the referee test method.

[i] A 100 % sample shall replace the 10 % residual, with percent residue in the original sample reported using the 10 % residual calculation. ASTM D189 or ASTM D524 may also be used. ASTM D4530 shall be the referee test method.

[j] ASTM D3242 or ASTM D974 may also be used for acid number determination. ASTM D664 shall be the referee test method.

[k] AOCS Standard Procedure Ck 2-09 may also be used for determination of total or free glycerin. ASTM D6584 shall be the referee test method.

[l] Although ASTM D4951 is specified as the test method for determining phosphorus in this specification, the method quoted is not capable of determining this low level (10 mg/kg) of phosphorus in a sample.

[m] ASTM D7344 or ASTM D7345 can be used as alternative methods to ASTM D1160 referee method.

[n] EN 14112 may also be used as an alternate to the determination of oxidation stability by EN 15751. However, the latter test method shall be considered the referee test method.

The biodiesel component of the blend shall conform to the requirements of ASTM D6751.

The fuel sulfur grades are described as follows:

- + Grade B6 to B20 S15—A fuel with a maximum of 15 mg/kg sulfur
- + Grade B6 to B20 S500—A fuel with a maximum of 500 mg/kg sulfur
- + Grade B6 to B20 S5000—A fuel with a maximum of 5000 mg/kg sulfur

The properties of commercial B6 to B20 blends depend on the refining practices used and on the nature of the distillate fuel oils and biodiesel from which they are produced. Distillate fuel oils, for example, may be produced within the boiling range of 150 to 400°C and have many possible combinations of various properties, such as volatility, ignition quality, viscosity, and other characteristics. Biodiesel, for example, can be produced from a variety of animal fats or vegetable oils that produce similar volatility characteristics and combustion emissions with varying cold flow properties.

Required properties of B6 to B20 biodiesel blends are given in Table 2.11. The referee test method and alternate test methods for sulfur determination, the range over which each test method applies, and the corresponding fuel grade are given in Table 2.12.

ASTM D7544-12

This is a specification for pyrolysis liquid biofuel produced from biomass intended for use in various types of industrial fuel-burning equipment under various climatic and operating conditions. These grades are described as follows:

- + *Grade G* is intended for use in industrial burners equipped to handle the pyrolysis liquid biofuels meeting the requirements listed for Grade G in Table 2.13. This grade biofuel is not intended for use in residential heaters, small commercial boilers, engines, or marine applications.

TABLE 2.11 Requirements for B6 to B20 Biodiesel Blends

Property	Test Method	B6 to B20 S15	B6 to B20 S500	B6 to B20 S5000
Acid number, mg KOH/g, max	ASTM D664	0.3	0.3	0.3
Viscosity, mm^2/s at 40°C	ASTM D445	1.9–4.1	1.9–4.1	1.9–4.1
Flash point, °C, min	ASTM D93[a]	52	52	52
Cloud Point, °C, LTFT/CFPP, °C, max	ASTM D2500 ASTM D4539 ASTM D6371	[b,c]	[b,c]	[b,c]
Sulfur, mg/kg Sulfur, mass %, max Sulfur, mass %, max	ASTM D5453 ASTM D2622 ASTM D129	15	0.05	0.50
Distillation temperature, °C, 90 % vol recovered, max	ASTM D86	343	343	343
Ramsbottom carbon residue, on 10 % bottoms, max	ASTM D524	0.35	0.35	0.35
Cetane number, min	ASTM D613[d]	40	40	40
Aromaticity, % vol, max	ASTM D1319[e]	35	35	
Ash, mass %, max	ASTM D482	0.01	0.01	0.01
Water and sediment, volume %, max	ASTM D2709	0.05	0.05	0.05
Copper corrosion, 3 h at 50°C, max	ASTM D130	No. 3	No. 3	No. 3
Biodiesel content, % (V/V)	ASTM D7371[f]	6–20	6–20	6–20
Oxidation stability, h, min[g]	EN15751	6	6	6
Lubricity, HFRR at 60°C, micron, max	ASTM D6079	520	520	520

Note: LTFT = low temperature flow test; CFPP = cold filter plugging point.

[a] ASTM D3828 or ASTM D6450 can also be used as alternative test method for ASTM D93 (flash point). The precision and bias of these alternative test methods are not known at present. ASTM D93 shall be the referee test method.

[b] ASTM D5771, ASTM D5772, ASTM D5773, or ASTM D7397, or AOCS Standard Procedure Ck 2-09 may also be used as alternative tests for ASTM D2500 (cloud point). ASTM D3117 may also be used because it is closely related, although its precision and bias for biodiesel are not known. ASTM D2500 shall be the referee test method.

[c] It is unrealistic to specify low temperature properties that will ensure satisfactory operation at ambient conditions. See Table 1 of ASTM D7467 for details.

[d] ASTM D6890 may also be used in place of ASTM D613 for determining cetane number. The latter is considered as the referee test method.

[e] ASTM D1319 provides an indication of the aromatic content of the fuels. For the fuels with a maximum final boiling point of 315°C, this test method is a measurement of aromatic content of the fuel. Grade S5000 does not have an aromatic content.

[f] ASTM D7371 is used for biodiesel content. EN 14078 may also be used. ASTM Test method D7861 can also be used as an alternative test method. In case of dispute, ASTM D7371 is considered as the referee test method.

[g] ASTM D1319 provides an indication of the aromatic content of the fuels. For the fuels with a maximum final boiling point of 315°C, this test method is a measurement of aromatic content of the fuel. Grade S5000 does not have an aromatic content.

TABLE 2.12 Alternate Sulfur Test Methods for Biodiesel Blends

Sulfur Test Method	Range	Fuel Grades
ASTM D129 (referee)	>0.1 mass %	S5000
ASTM D1266	0.0005 to 0.4 mass %	S500
ASTM D1552	>0.06 mass %	S5000
ASTM D2622 (referee for S500 grade)	0.0003 to 5.3 mass %	All grades
ASTM D3120	3.0 to 100 mg/kg	S15, S500[a]
ASTM D4294	0.0150 to 5.00 mass %	S5000
ASTM D5453 (referee for S15 grade)	1 to 8,000 mg/kg	All grades

[a] S500 grade must be diluted before testing.

TABLE 2.13 Requirements for Pyrolysis Liquid Biofuels (ASTM D7544-12)

Property	Test Method	Grade G	Grade D
Gross heat of combustion, MJ/kg, min	ASTM D240	15	15
Water, % mass, max	ASTM E203	30	30
Pyrolysis solids, % mass, max	ASTM D7579	2.5	0.25
Kinematic viscosity at 40°C, mm^2/s, max	ASTM D445	125	125
Density at 20°C, kg/dm^3	ASTM D4052	1.1–1.3	1.1–1.3
Sulfur, % mass, max	ASTM D4294	0.05	0.05
Ash, % mass, max	ASTM D482	0.25	0.15
pH	ASTM E70	Report	Report
Flash point, °C, min	ASTM D93 B	45	45
Pour point, °C, max	ASTM D97	−9	−9

- + *Grade D* is intended for use in commercial/industrial burners requiring lower solids and ash content and in those that are equipped to handle the pyrolysis liquid biofuels meeting the requirements listed in Table 2.13 for Grade D. This grade of biofuel is not intended for use in residential heaters, engines, or marine applications not modified to handle these types of fuels.

The pyrolysis liquid biofuel specified in ASTM D7544 shall remain uniform in medium-term storage and not separate by gravity into layers. Long-term storage or equipment downtime can necessitate circulation of pyrolysis liquid biofuel in-tank to prevent such separation. If minor separation occurs during medium-range storage, mild agitation or product circulation should reverse such separation.

The various grades of pyrolysis liquid biofuel shall conform to the detailed requirements given in Table 2.13. The properties selected for limitation are those that are believed to be of the greatest significance in obtaining acceptable performance of the burner.

ASTM D7666-12

This specification covers two grades of burner fuel consisting of triglycerides, including monoglycerides, diglycerides, and free fatty acids and is distinguished by the pour point. The grade designation "TBF" identifies them as triglyceride burner fuels. The triglyceride burner fuels are intended for use in commercial or industrial air or steam-atomized fuel-oil-burning equipment manufactured from materials compatible with fuels having an acid number as specified in Table 2.14 and under various climatic and operating conditions for the purposes of heat generation. The fuels specified herein are not intended for blending with conventional fuel oils for this purpose. They are not intended for use in burners <0.32 GJ/h (0.3 by 10^6 Btu/h) such as residential burners or small-pressure atomization burners, nor are they intended for use in internal combustion engines or marine applications.

Triglyceride burner fuel (TBF) is defined as any triglyceride—including recycled and unused cooking oil, greases, animal fats, and naturally occurring constituents of triglycerides, including monoglycerides, diglycerides, and free fatty acids—suitable for the generation of heat by combustion in a furnace or a firebox as a vapor or a spray or a combination of both with little or no preconditioning other than preheating. The triglyceride burner fuel shall be homogenous, consisting primarily of triglycerides and naturally

TABLE 2.14 Requirements for Triglyceride Burner Fuels per ASTM D7666-12

Property	Test Method	Grade TBF 5	Grade TBF 6
Pour point, °C	ASTM D97[a]	>21	>21
Flash point, °C, min	ASTM D93 B[b]	93	93
Water and sediment, % vol, max	ASTM D1796[c]	2.0	2.0
Kinematic viscosity at 100°C, mm^2/s	ASTM D445[d]	Report	Report
Density, kg/m^3 at 15°C	ASTM D1298[e]	Report	Report
Titer, °C	ASTM D1982	Report	Report
Acid number, mg KOH/g, max	ASTM D664[f]	30.0	30.0
Ash, wt %, max	ASTM D482[g]	0.15	0.15
Sulfur, wt. %	ASTM D4294[h]	Report	Report
Insolubles, % mass	ASTM D128	2	2
Gross heating value, MJ/kg, min	ASTM D240	36.1	36.1

[a] ASTM D5949, ASTM D5950, or ASTM D6892 may alternatively be used with the same limits. ASTM D97 shall be the referee method in case of disputes.

[b] For both grades, ASTM D3828 may alternatively be used with the same limits. ASTM D93 B shall be the referee method in case of disputes.

[c] ASTM D2709 or ASTM D4007 may be used with the same limit. For non-emulsified samples, ASTM D95 and ASTM D473 may also be used with the same limits. ASTM D1796 shall be the referee test method in case of disputes.

[d] For quality control, dynamic viscosity by ASTM D7042 may be used.

[e] ASTM D1298, ASTM D4052, ASTM D5355, or ASTM D7042 may be used as the alternative tests for measuring density.

[f] ASTM D974 or ASTM D3339 may be used with the same limits as the referee ASTM D664 for acid number.

[g] ASTM D5347 may be used with the same limits as referee ASTM D482 for measurement of ash.

[h] ASTM D1266, ASTM D1552, ASTM D2622, ASTM D5185, or ASTM D5453 may be used as alternate test method to ASTM D4294 for measurement of sulfur with the same limits.

occurring constituents of triglycerides and shall conform to the limiting requirements given in Table 2.14. The properties listed in this table are of greatest significance in obtaining acceptable performance of the burner.

- + *Grade TBF 5* is a burner fuel comprised of commercial recycled and unused cooking oils, greases, and rendered animal fats that have a pour point below 21°C in accordance with ASTM D97. This grade is intended for use in industrial burners and commercial boilers supplied with devices that use steam or compressed air to atomize fuel oil of higher viscosity. Preheating may be necessary for burning this fuel in some types of equipment and in colder climates for ease of handling.
- + *Grade TBF 6* is a burner fuel made up of commercial recycled and unused cooking oils, greases, and rendered fats that have a pour point equal to or higher than 21°C in accordance with ASTM D97. This grade is intended for use in industrial burners and commercial boilers supplied with devices that use steam or compressed air to atomize fuel oil of higher viscosity. The use of this grade may require preheating in the storage tank to permit pumping. Additional preheating at the burner may be necessary to permit satisfactory atomization. The extra equipment and maintenance required to handle this fuel grade may preclude its use in small or unattended installations or in both.

Triglyceride burner fuels shall remain homogenous and uniform in storage and shall not separate by gravity or aging into layers under normal operating conditions. Prolonged storage or equipment downtime may necessitate circulation of the fuel oil in the tank to prevent such separation. The triglyceride burner fuel shall be free of solid or fibrous matter that could cause system handling or maintenance problems.

ASTM D7794-12

This is a practice for blending mid-level ethanol fuels for flexible-fuel vehicles with automotive spark-ignition engines. These have ethanol concentrations greater than those suitable for conventional-fuel vehicles and less than the minimum ethanol content specification limits of ASTM D5798. These mid-level ethanol fuel blends are only suitable for use in ground flexible-fuel vehicles equipped with spark-ignition engines. Flexible-fuel engines are designed to operate on gasoline or gasoline-ethanol blends that meet the requirements of ASTM D4814, ethanol fuel blends that meet the requirements of ASTM D5798, or any combination of these. In the United States, these vehicles are certified by the U. S. Environmental Protection Agency as emission compliant with these types of fuels.

The mid-level ethanol fuel blend shall be blended from either (1) or (2):

1. Denatured fuel ethanol conforming to the requirements of ASTM D4806 with a reduced limit on inorganic chloride content that will ensure no more than 1 mg/kg inorganic chloride in the finished fuel and from spark-ignition engine fuel conforming to ASTM D4814 (often at a distribution terminal or bulk plant)
2. Ethanol fuel blends conforming to ASTM D5798 and from spark-ignition engine fuel conforming to ASTM D4814 (often at a retail site)

This practice provides procedures for blending automotive spark-ignition engine fuels with ethanol concentrations greater than those suitable for conventional-fuel vehicles and less than the minimum ethanol content limit of ASTM D5798. It addresses in detail the various factors that need to be considered when blending. These considerations include selection of fuel components for blending and general handling information. Use of butanol as a fuel is described in ASTM's, "Update: A Promising Future for Butanol" [4].

ASTM D7862-13

This specification covers butanol intended to be blended with gasoline at 1 to 12.5 volume percent for use as an automotive spark-ignition engine fuel. Butanol contains 22 mass percent oxygen. The mass percent of oxygen of a butanol blend with gasoline depends on the volume percent of butanol blended, the density of the butanol isomer, and the density of the base blendstock. In the United States, the maximum limit on blending is not a performance limit but a current regulatory limit. Butanol has several benefits as a blending agent in gasoline. It is compatible with existing vehicles and refueling infrastructure, and it also offers a high blending value due to its low vapor pressure, high octane number, and favorable distillation properties [4].

Isobutanol is expected to be blended into gasoline for use in automobiles, all-terrain vehicles, boats, lawn mowers, and snow blowers. It is also used in many chemical applications that include

TABLE 2.15 Requirements for Butanol per ASTM D7862-13

Property	Limit	Test Method
Butanol, vol % min	96.0	ASTM D7875 or Annex of ASTM D7862
1-Butanol, vol %	Report	ASTM D7875
2-Butanol, vol. %	Report	ASTM D7875
2-Methyl-1-propanol, vol %	Report	ASTM D7875
Methanol, vol % max	0.4	ASTM D7875
Water, vol % max	1.0	ASTM E203 or ASTM E1064
Acidity (as acetic acid), mass % (mg/L), max	0.07 (56)	ASTM D1613
Inorganic chloride, mg/kg (mg/L), max	8 (6)	ASTM D7319
Solvent washed gum, mg/100 mL, max	5.0	ASTM D381 (air jet apparatus)
Sulfur, mg/kg, max	30	ASTM D2622 or ASTM D5453[a]
Existent sulfate, mg/kg, max	4	ASTM D7319
Appearance	[b]	

[a] In the United States, ASTM D3120 or ASTM D5453 are also allowed for sulfur.

[b] Part of workmanship; visually free of sediment and suspended matter; clear and bright at the ambient temperature.

paints and coatings; 1-butanol is an intermediate for coatings and textiles, while isobutyl alcohol is mainly used as a solvent.

Butanol manufacturers are cautioned to avoid contamination by silicon-containing materials. Silicon contamination of gasoline-oxygenate blends has led to fouled vehicle components (e.g., spark plugs, exhaust oxygen sensors, catalytic converters), requiring part replacement and repairs. Suppliers shall also avoid butanol contaminated with acetone. Acetone contamination of gasoline-oxygenate blends can degrade elastomers used in fuel system components as well as paint or clearcoat finishes used on vehicles (or both).

The specification ASTM D7862 given in Table 2.15 covers three butanol isomers: 1-butanol, 2-butanol, and 2-methyl-1-propanol. ASTM D7862 specifically excludes 2-methyl-2-propanol (i.e., tert-butanol) because it has different physical properties such as melting point and water miscibility than the other three isomers. The standard for actual assay of butanol and acetone can be found in ASTM D7875, described in Chapter 4.

References

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[2] ASTM, “Making Way for Biodiesel,” *ASTM Standardization News*, Vol. 43, No. 3, 2015, p. 44.

[3] Howell, S., “Biofuel for a Changing World,” *ASTM Standardization News*, Vol. 43, No. 3, 2015, p. 64.

[4] ASTM, “Update: A Promising Future for Butanol,” *ASTM Standardization News*, Vol. 43, No. 1, 2015, p. 40.

Abstract

There are about a dozen ASTM product specifications that relate to biofuels. These are summarized in this chapter and the specified parameters are discussed.

Keywords

biofuel specifications, biodiesel specifications, butanol fuel specification, fuel ethanol specifications, gasoline specifications, MTBE specifications, pyrolysis liquid biofuel specification, triglyceride burner fuel specifications

Chapter 3 | Physical Test Methods for Biofuels

As biodiesel, fuel ethanol, and certain synthetic biofuels become increasingly utilized, the test methods for petroleum products are being used for the new materials. A majority of these tests were designed for petroleum products. Some of the test methods for gasoline may not be applicable to oxygenated fuels or the precision of the test methods may be different for gasoline-based and biofuel-based products. Sometimes there is not sufficient data to extrapolate from tests that have been performed on biodiesel and ethanol fuel to other biofuels and oxygenated fuels of different compositions. Several of the newer ASTM test methods have been specifically designed for biofuels or ethanol fuels.

Not all test methods required in these product specifications are included in their respective product-specific proficiency testing programs (PTPs) by ASTM because not all tests are performed by these industry's laboratories. Many of the test methods in the biofuel specifications may have to have their scopes updated, and their precision statements need to be reevaluated to be certain that they apply to biodiesel and fuel ethanol products. This will involve conducting a large number of interlaboratory studies to arrive at new precision estimates for these test methods and to evaluate the modifications, if any, as they relate to the original test methods. Thus, until all biofuel specification tests are fully evaluated, the PTP process and its resulting data serve as an indicator as to whether the tests may be applicable to biofuel matrices with the same degree of precision as for other typical petroleum products in the marketplace. This is a tall order to complete.

In Chapters 3 through 6, the tests used for biofuels are roughly divided into physical, chemical, elemental, and environmental test methods. Each test method is briefly described in terms of its scope, analytical principles, interferences (if any), and its precision estimates. The experience of these tests through ASTM PTP programs is discussed in Chapter 7.

Physical tests for biofuels include those listed in Table 3.1. Their international equivalents are listed in Table 3.2.

Appearance

Turbidity, phase separation, or evidence of precipitation normally indicates contamination of the fuel. The test is done by observing a sample placed in a clean glass test tube or a beaker and watching for any such indication.

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ASTM D189, ASTM D524, and ASTM D4530, Carbon Residue of Petroleum Products

SIGNIFICANCE

Three test methods are available for the determination of carbon residue in petroleum products: ASTM D189, ASTM D524, and ASTM D4530. Within the context of these three methods, the term "carbon residue" is used to designate the carbonaceous residue formed after evaporation and pyrolysis of a petroleum product under the conditions specified in these test methods. The residue is not composed entirely of carbon but is a coke that can be further changed by pyrolysis. The carbon residue values obtained by these three test methods may or may not be the same numerically. Approximate correlations have been developed among these tests but need not apply to all materials that can be tested (see Fig. 3.1).

Carbon residue of a fuel is a measure of the carbonaceous material left after all the volatile components are vaporized in the absence of air. It is a rough approximation of the tendency of a fuel to form deposits in vaporizing burners, such as pot-type and sleeve-type burners, where the fuel is vaporized in an air-deficient atmosphere. Although not directly correlating with engine deposits, this property is considered an approximation. It is considered one of the most important biodiesel quality criteria because it is linked with many other parameters. For fatty acid methyl esters (FAMEs), carbon residue correlates with the respective amounts of glycerides, free fatty acids, soaps, and the remaining catalyst or contaminants. Moreover, this parameter is influenced by high concentrations of polyunsaturated FAMEs and polymers. For these reasons, the amount of carbon residue is limited in biodiesel specifications [1].

Region	Limits	Test Method(s)
Brazil	0.10 % m/m max	ISO 10370/ASTM D4530
European Union	0.30 % m/m max	ISO 10370
United States	0.050 % m/m max	ASTM D4530

Although biodiesel is in the distillate boiling range, most biodiesels boil at approximately the same temperature, and it is difficult to leave a 10 % residual sample upon distillation. Hence, a

TABLE 3.1 ASTM Physical Testing Standards Used for Biofuels

ASTM Standard	Description
ASTM D56	Flash Point by Tag Closed Cup Tester
ASTM D86	Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure
ASTM D93	Flash Point by Pensky-Martens Closed Cup Tester
ASTM D95	Water in Petroleum Products and Bituminous Materials by Distillation
ASTM D97	Pour Point of Petroleum Products
ASTM D130	Corrosiveness to Copper from Petroleum Products by Copper Strip Test
ASTM D156	Saybolt Color of Petroleum Products
ASTM D189	Conradson Carbon Residue of Petroleum Products
ASTM D240	Heat of Combustion of Liquid Fuels by Bomb Calorimeter
ASTM D445	Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)
ASTM D473	Sediment in Crude Oils and Fuel Oils by the Extraction Method
ASTM D524	Ramsbottom Carbon Residue of Petroleum Products
ASTM D613	Cetane Number of Diesel Fuel Oil
ASTM D976	Calculated Cetane Index of Distillate Fuels
ASTM D1160	Distillation of Petroleum Products at Reduced Pressure
ASTM D1298	Density, Relative Density, or American Petroleum Institute (API) Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
ASTM D1310	Flash Point and Fire Point of Liquids by Tag Open-Cup Apparatus
ASTM D1500	ASTM Color of Petroleum Products (ASTM Color Scale)
ASTM D1796	Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure)
ASTM D1982	Titer of Fatty Acids
ASTM D2500	Cloud Point of Petroleum Products
ASTM D2624	Electrical Conductivity of Aviation and Distillate Fuels
ASTM D2709	Water and Sediment in Middle Distillate Fuels by Centrifuge Method
ASTM D2887	Boiling Range Distribution of Petroleum Fractions by Gas Chromatography
ASTM D3828	Flash Point by Small Scale Closed Cup Tester
ASTM D4052	Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
ASTM D4308	Electrical Conductivity of Liquid Hydrocarbons by Precision Meter
ASTM D4530	Determination of Carbon Residue (Micro Method)
ASTM D4539	Filterability of Diesel Fuels by Low-Temperature Flow Test
ASTM D4737	Calculated Cetane Index by Four Variable Equation
ASTM D4953	Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)
ASTM D5190	Vapor Pressure of Petroleum Products (Automatic Method)
ASTM D5191	Vapor Pressure of Petroleum Products (Mini Method)
ASTM D5771	Cloud Point of Petroleum Products by (Optical Detection Stepped Cooling Method)
ASTM D5772	Cloud Point of Petroleum Products (Linear Cooling Rate Method)
ASTM D5773	Cloud Point of Petroleum Products (Constant Cooling Rate Method)
ASTM D5949	Pour Point of Petroleum Products (Automatic Pressure Pulsing Method)
ASTM D5950	Pour Point of Petroleum Products (Automatic Tilt Method)
ASTM D5985	Pour Point of Petroleum Products (Rotational Method)
ASTM D6079	Evaluating Lubricity of Diesel Fuel by High Frequency Reciprocating Rig
ASTM D6371	Cold Filter Plugging Point of Diesel and Heating Fuels
ASTM D6450	Flash Point by Continuously Closed Cup Tester
ASTM D6468	High Temperature Stability of Middle Distillate Fuels
ASTM D6749	Pour Point of Petroleum Products (Automatic Air Pressure Method)
ASTM D6890	Determination of Ignition Delay and Derived Cetane Number of Diesel Fuel Oils by Combustion in a Constant Volume Chamber
ASTM D6892	Pour Point of Petroleum Products (Robotic Tilt Method)

(Continued)

ASTM Standard	Description
ASTM **D7042**	Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)
ASTM **D7321**[a]	Particulate Contamination of Biodiesel B100 and Blend Stock Biodiesel Esters and Biodiesel Blends by Laboratory Filtration
ASTM **D7344**	Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure (Mini Method)
ASTM **D7345**	Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure (Micro Distillation Method)
ASTM **D7397**	Cloud Point of Petroleum Products (Miniaturized Optical Method)
ASTM **D7501**[a]	Determination of Fuel Filter Blocking Potential of Biodiesel (B100) Blend Stock by Cold Soak Filtration Test
ASTM **D7579**[a]	Pyrolysis Solid Content in Pyrolysis Liquids by Filtration of Solids in Methanol
ASTM **D7688**	Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig (HFRR) by Visual Observation
ASTM **D7689**	Cloud Point of Petroleum Products (Mini Method)
ASTM **D7717**[a]	Practice for Preparing Volumetric Blends of Denatured Fuel Ethanol and Gasoline Blendstocks for Laboratory Analysis

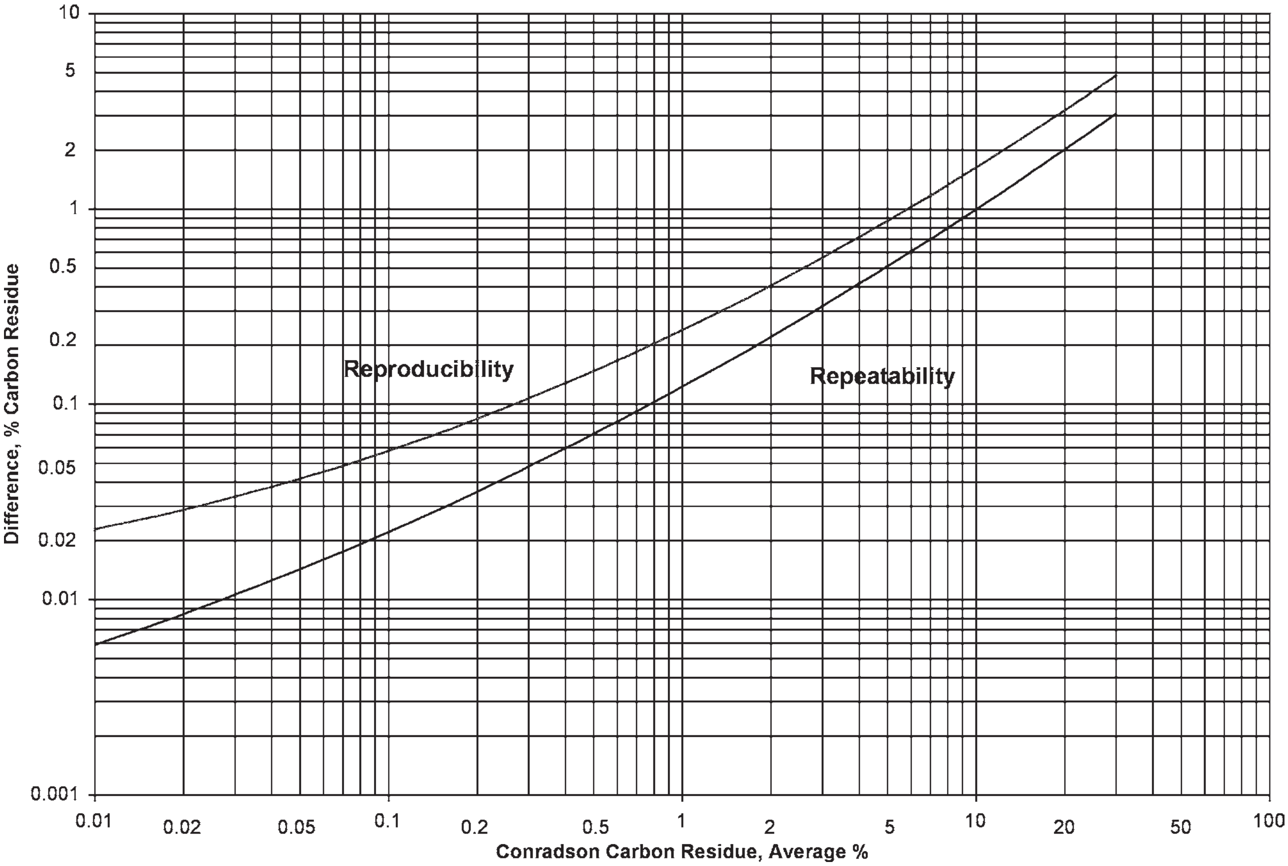
[a] These test methods were specifically developed for the analysis of biofuels.

TABLE 3.2 International Equivalents for Physical Tests for Biofuels

Analysis	ASTM	IP	ISO	DIN	JIS
Tag Flash Point	ASTM **D56**			51411	K 2580
Distillation	ASTM **D86**	123	3405	51751	K 2254
PMCC Flash Point	ASTM **D93**	34	2719	51758	K 2265
Water by Distillation	ASTM **D95**	74	3733	51582	K 2275
Pour Point	ASTM **D97**	15	3016	51597	K 2269
Copper Corrosion	ASTM **D130**	154	2160	51759	K 2513
Saybolt Color	ASTM **D156**			51411	K 2580
Conradson Carbon Residue	ASTM **D189**	13	6615	51551	K 2270
Heat of Combustion	ASTM **D240**	12			
Gum in Fuels by Jet Evaporation	ASTM **D381**	131	6246	51754	K 2258
Kinematic Viscosity	ASTM **D445**	71-1	3104	51562	K 2283
Sediment in Crude and Fuel Oils	ASTM **D473**	53	3735	51789	
Ramsbottom Carbon Residue	ASTM **D524**	14	4262		
Cetane Number of Diesel Fuel Oil	ASTM **D613**	41	5165		K 2280
Oxidation Stability	ASTM **D942**	142		51808	
Distillation at Reduced Pressure	ASTM **D1160**		6616		
Density	ASTM **D1298**	160	3675	51757H	K 2249H
ASTM Color	ASTM **D1500**	196	2049	51578	K 2580
Sediment and Water	ASTM **D1796**	75	3734	51793	
Oxidation Stability	ASTM **D2274**	388	12205		
Cloud Point	ASTM **D2500**	219	3015	51597	K 2269
Electrical Conductivity	ASTM **D2624**	274	6297	51412 T2	
Boiling Range by GC	ASTM **D2887**	321	3924		K 2254
Seta Flash Point	ASTM **D3828A**	524	3680		
	ASTM **D3828B**	523	3679		
Density	ASTM **D4052**	365	12185	51757D	K 2249D
Microcarbon Residue	ASTM **D4530**	398	10370		
Vapor Pressure (Mini Method)	ASTM **D5191**	394			
Lubricity of Diesel Fuels by HFRR	ASTM **D6079**		12156		
Cold Filter Plugging Point of Diesel and Heating Fuels	ASTM **D6371**	309	EN 116		
Lubricity of Diesel Fuels by HFRR Visual Observation	ASTM **D7688**		12156		

Note: DIN = Deutsches Institut für Normung (German Institute for Standardization); GC = gas chromatography; HFRR = high-frequency reciprocating rig; IP = International Petroleum; ISO = International Organization for Standardization; JIN = Japanese Industrial Standard; PMCC = Pensky-Martens closed cup.
Excerpted from Ref. [1].

FIG. 3.1 Precision of ASTM D189 for the determination of Conradson carbon residue.



100 % sample is used to replace the 10 % residual sample, with the calculation executed as if it were the 10 % residual. To obtain a measurable value of carbon residue in the lighter distillate fuel oils, it is necessary to distill the oil to remove 90 % of it, in accordance with Section 9 of ASTM D524, and then to determine the carbon residue concentrated in the remaining 10 % of the bottom. ASTM D524 is used for this analysis.

Similarly, provided amyl nitrate is absent (or if it is present, provided the test is performed on the base fuel without additive), the carbon residue of diesel fuel correlates with combustion chamber deposits. The carbon residue value of motor oil (although at one time regarded as indicative of the amount of carbonaceous deposits a motor oil would form in the combustion chamber of an engine) is now considered to be of doubtful significance due to the presence of additives in many oils. For example, an ash-forming detergent additive may increase the carbon residue value of oil yet will generally reduce its tendency to form deposits. The carbon residue of gas oil is useful as a guide in the manufacture of gas from gas oil, while the carbon residue value of crude oil residua, cylinders, and bright stocks are useful in the manufacture of lubricants.

Ash-forming constituents, such as those defined by ASTM D482, or nonvolatile additives present in the sample will add to the carbon residue value and will be included as part of the total carbon residue value reported.

SCOPE

These procedures are applicable to most petroleum products but have not been tested for precision and bias specifically on biofuels. However, some of them are quoted in ASTM specifications for biofuels (e.g., ASTM D396, ASTM D975, ASTM D6751, and ASTM D7467).

Product Specification	Test Method	Specification Limits
ASTM D396—No. 1 S500, No. 1 S5000	ASTM D524	0.15 % max
—No. 2 S500, No. 2 S5000		0.35 % max
ASTM D975—No. 1-D 15, No. 1-D500, No. 1-D 5000		0.15 % max
—No. 2-D S15, No. 2-D S500, No. 2-D S5000		0.35 % max
ASTM D6751	ASTM D4530	0.050 % max
ASTM D7467	ASTM D524	0.35 % max

ASTM D189, Conradson Carbon Residue

This test method covers the determination of the amount of carbon residue left after evaporation and pyrolysis of an oil, and it is intended to provide some indication of relative coke-forming propensities.

The method is generally applicable to relatively nonvolatile petroleum products that partially decompose on distillation at atmospheric pressure. Petroleum products containing ash-forming constituents will have an erroneously high carbon residue depending upon the amount of ash formed.

A weighed quantity of sample is placed in a crucible and subjected to destructive distillation. The residue undergoes cracking and coking reactions during a fixed period of severe heating. At the end of the specified heating period, the test crucible containing the carbonaceous residue is cooled in a desiccator and weighed. The residue remaining is calculated as a percentage of the original sample and is reported as Conradson carbon residue. Test precision of ASTM D189 should be within limits shown in Figs. 3.2–3.4 depict the correlation between Conradson carbon and Ramsbottom carbon results and the correlation between Conradson carbon and micro carbon residue tests, respectively.

ASTM D524, Ramsbottom Carbon Residue

This test method generally is applicable to relatively nonvolatile petroleum products that partially decompose on distillation at atmospheric pressure. The values obtained by this method are not numerically the same as those obtained by ASTM D189 or ASTM D4530. In this test method, the sample is weighed into a special glass bulb having a capillary opening, and it is placed in a muffle furnace maintained at about 550°C. All volatile material is evaporated out of the bulb, and the heavier residue remaining in the bulb undergoes cracking and coking reactions. After a specified heating period, the bulb is removed from the bath, cooled in a desiccator, and again weighed. The residue remaining is calculated as a percentage of the original sample and is reported as the Ramsbottom carbon residue. The test precision is given in Fig. 3.5.

ASTM D4530, Carbon Residue (Micro Method)

This procedure is a modification of the original ASTM D189 and apparatus for carbon residue for petroleum products. It covers the determination of the amount of carbon residue formed after evaporation and the pyrolysis of petroleum materials under certain conditions. It is intended to provide some indication of the relative coke-forming tendency of such materials. The test results are equivalent to the Conradson carbon residue test, ASTM D189

FIG. 3.2 Correlation between ASTM D189, *Standard Test Method for Conradson Carbon Residue of Petroleum Producs*, and ASTM D524, *Standard Test Method for Ramsbottom Carbon Residue of Petroleum Products*.

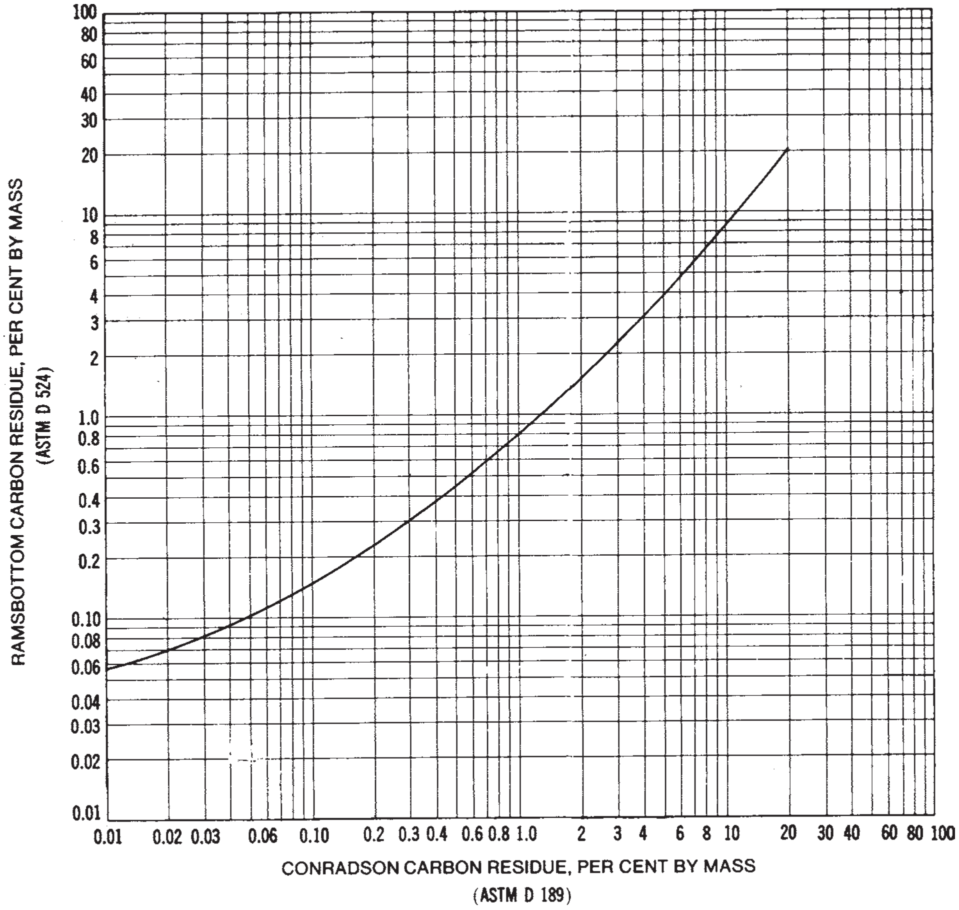


FIG. 3.3 Correlation between ASTM D189, *Standard Test Method for Conradson Carbon Residue of Petroleum Product,* and ASTM D4530, *Standard Test Method for Determination of Carbon Residue (Micro Method).*

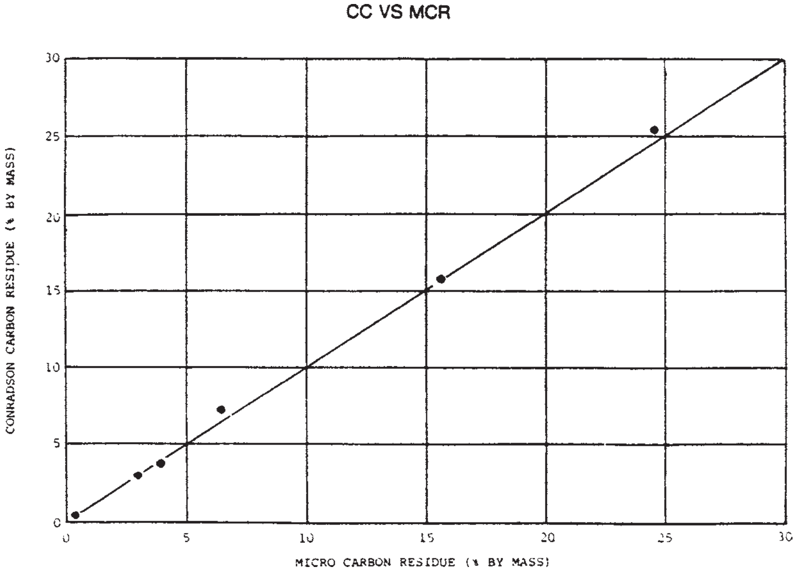
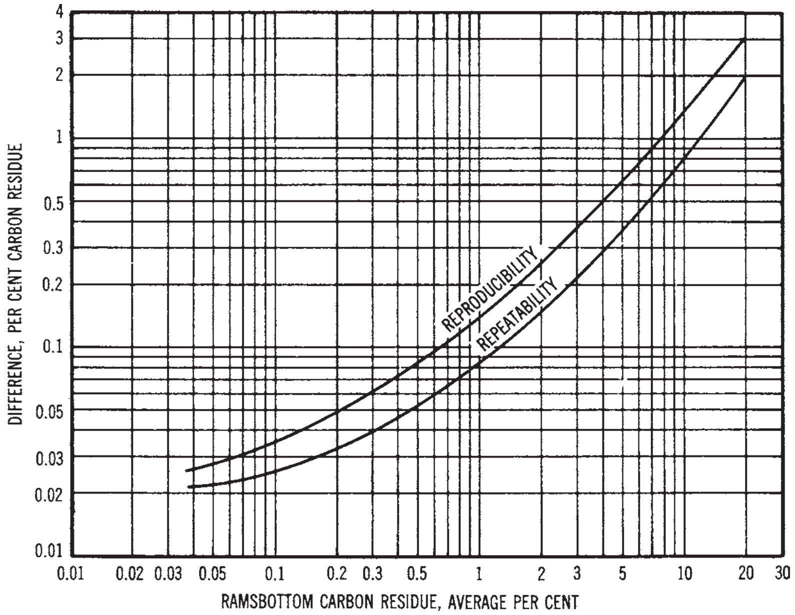


FIG. 3.4 Precision of ASTM D524, *Standard Test Method for Ramsbottom Carbon Residue of Petroleum Products.*

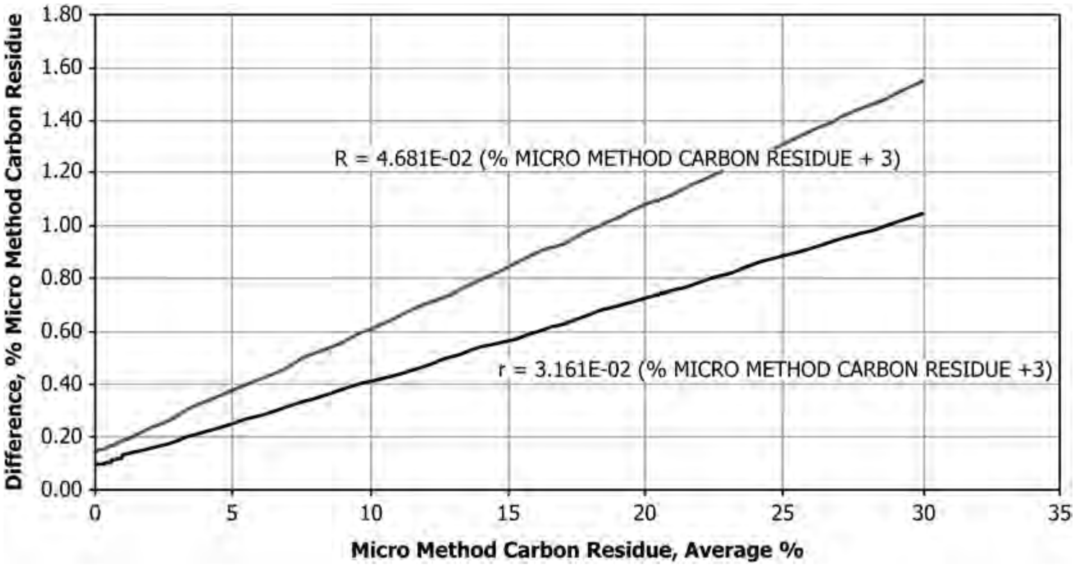


(see Fig. 3.5). This test method offers the advantages of better control of test conditions, smaller samples, and less operator attention compared to ASTM D189—to which it is equivalent.

In this procedure, a weighed quantity of sample is placed in a glass vial and heated to 500°C under an inert (nitrogen) atmosphere in a controlled manner for a specific time. The sample undergoes coking reactions, and the volatiles formed are swept away by the nitrogen flow. The carbonaceous residue remaining is reported as a percentage of the original sample as "carbon residue (micro)." When the test results are expected to be below 0.10 % (m/m), the sample can be distilled to produce a 10 % volume/volume bottom prior to performing the test. The test precision has been found to be as follows (also shown in Fig. 3.5):

Repeatability	$0.0770 \times X^{0.66}$
Reproducibility	$0.2451 \times X^{0.66}$

FIG. 3.5 Precision of ASTM D4530, *Standard Test Method for Determination of Carbon Residue (Micro Method).*



ASTM D976, ASTM D4737, and ASTM D6890, Cetane Number, Cetane Index, and Derived Cetane Number of Distillate Fuels

SIGNIFICANCE

Cetane number is a measurement of the ignition quality of a fuel, and it influences white smoke and combustion roughness. The cetane number requirements depend on engine design, size, nature of speed and load variations, and on starting and atmospheric conditions. An increase in cetane number over values actually required does not materially improve engine performance. A high cetane number is associated with rapid engine starting and smooth combustion. A low cetane number causes deterioration in this behavior and causes higher-exhaust gas emissions of hydrocarbons and particulates. Accordingly, the cetane number specified should be as low as possible to ensure maximum fuel availability. In general, biodiesel has slightly higher cetane numbers than fossil fuel-derived diesel. The cetane number rises with increasing length of fatty acid chain and ester groups, although it is inversely related to the number of double bonds. The cetane number of pure biodiesel (B100) is dependent on the distribution and availability of fatty acids within the oils used in the initial esterification reaction.

Measuring the quantity of FAMEs and linolenic methyl esters within B100 allows for an accurate calculation of the cetane number of a biofuel. It is determined using ASTM D976. FAME concentration is measured by gas chromatography (GC) method EN 14103 and requires a split/splitless or programmable temperature vaporizing injector to introduce the fuel samples onto the column. Accurate, sensitive detection and quantification of the FAME concentration is best achieved on a polar GC column capable of separating the esterified fatty acids and lenolenic methyl esters. GC analysis of a biodiesel sample should provide verification that FAME levels within the sample exceed 96.5 % m/m, with the level of linolenic methyl esters being <12 % m/m. This GC method is suitable for the separation of B100 samples containing FAMEs of chain lengths from C14 to C24 [2].

Cetane number is assessed by comparing the ignition delay of a diesel fuel with that of mixtures of hexadecane ($C_{16}H_{34}$) and isocetane (2,2,4,4,6,8,8-heptamethylnonane [$C_{16}H_{34}$]). The regulatory requirements for the cetane number of a diesel fuel are legislated by EN 590 and ASTM D975 [2].

The cetane number of diesel fuel is regulated in the European Union (EU) at >51, in the United States at >40, and in Brazil at >42. It is determined by test methods ISO 5165 or ASTM D613 in Brazil, ISO 5165 in the EU, and ASTM D613 in the United States. The cetane number is feedstock dependent and is governed by national regulations for diesel. Hence, an alignment of national regulations appears very difficult, and perhaps commercial agreements might be the best approach for this parameter [1].

SCOPE

Cetane number is a requirement in product specifications of diesel fuel Grades No. 1-D S15, No. 1-D S500, No. 2-D S15, and 2-D S500. Grades 1-D S5000, No. 2-D S5000, and No. 4-D do not have an aromatic content requirement so this test method should not be used as a surrogate for aromatic content. The calculated cetane index, ASTM D976 (as follows) or ASTM D4737 (the preferred test method), may not be used to approximate the cetane number with biodiesel or its blends. There are no substantiating data to support the calculation of cetane index with biodiesel or its blends.

Biofuel product specifications for biodiesel (B100) blendstock (ASTM D6751) and B6 to B20 biodiesel blends (ASTM D7467) limit the cetane number levels to 47 and 40, respectively.

ANALYSIS

This test method covers the determination of the rating of diesel fuel in terms of an arbitrary scale of cetane numbers using a standard single-cylinder, four-stroke cycle, variable compression ratio, indirect injected diesel engine. The cetane number scale covers the range from zero to 100, but typical testing is in the range of 30 to 65 cetane numbers.

The cetane number of a diesel fuel oil is determined by comparing its combustion characteristics in a test engine with those for blends of reference fuels of known cetane number under standard operating conditions. This is accomplished using the bracketing handwheel procedure that varies the compression ratio handwheel reading for the sample and each of the two bracketing reference fuels to obtain a specific ignition delay, permitting the interpolation of cetane number in terms of handwheel reading.

PRECISION

Based on an interlaboratory study (RR-D02-1303), the following precision has been obtained (Table 3.3). The repeatability precision limits are based on the ASTM National Exchange Group (NEG) monthly sample testing program from mid-1978 through 1987. During this period, each exchange sample was rated twice on the same day by the same operator on one engine in each of the member laboratories. The reproducibility precision limits are based on the combined NEG monthly sample testing program data from mid-1978 through mid-1992, the Energy Institute's monthly sample data from 1988 through mid-1992, and on the Institue Francais de Petrole monthly sample data for 1989 through early 1992.

CETANE INDEX

ASTM D976 is used to calculate the cetane index formula, which represents a means for directly estimating the ASTM cetane number of distillate fuels from American Petroleum Institute (API) gravity and mid-boiling point. The index value, as compared with the formula, is termed the calculated cetane index. The calculated cetane index is not an optional method for expressing the ASTM cetane number. It is a supplementary tool for estimating cetane number when used with due regard for its limitations. The calculated cetane index formula is particularly applicable to straight-run fuels, catalytically cracked stocks, and blends of the two.

The calculated cetane index, as described in this test method, is recognized by the U.S. Environmental Protection Agency as an alternative method to meet the U.S. federal diesel aromatics limit for diesel fuels containing less than 500 mg/kg sulfur.

TABLE 3.3 Cetane Number Precision Limits per ASTM D613

Average Cetane Number Level	Repeatability	Reproducibility
40	0.8	2.8
44	0.9	3.3
48	0.9	3.8
52	0.9	4.3
56	1.0	4.8

Note: Values for cetane numbers intermediate to those listed here may be obtained by linear interpolation.

ANALYSIS

For calculating this index, data are obtained by the following test methods:

API gravity	ASTM D287, ASTM D1298, or ASTM D4052
Mid-boiling point temperature	ASTM D86
Density	ASTM D1298 or ASTM D4052

PRECISION

Correlation of index values with ASTM cetane number is dependent to a great extent upon the accuracy of the determination of both API gravity and mid-boiling point. Within the range from 30 to 60 cetane numbers, the expected correlation of the calculated cetane index with the ASTM cetane number will be somewhat less than ±2 cetane numbers for 75 % of the distillate fuels evaluated. Errors in correlation may be greater for fuels whose cetane numbers are outside this range.

ASTM D4737

The calculated cetane index by four variables equation provides a means for estimating the ASTM cetane number (ASTM D613) of distillate fuels from density and distillation recovery temperature measurements. This is not an optional method for expressing the ASTM cetane number. It is a supplementary tool for estimating cetane number when a result by ASTM D613 is not available and if a cetane improver is not used. As a supplementary tool, this result must be used with due regard for its limitations.

The calculated cetane index by four-variables equation is useful for estimating the ASTM cetane number when a test engine is not available for determining this property directly and when a cetane improver is not used. It may be conveniently utilized for estimating cetane number when the quantity of sample available is too small for an engine rating.

SCOPE

This test method is applicable to the following diesel fuels. Biodiesel blends are excluded from this test method because they were not part of the data sets used to develop either Procedure A or Procedure B.

	Procedure A	Procedure B
Specifications	ASTM D975, Grades No. 1-D S15, No. 1-D S500 No. 1-D S5000, No. 2-D S15, No. 2-D S5000, No. 4-D	ASTM D975, Grade No. 2-D S500

The cetane number specification limits for these fuels are as follows:

Specification	Grades	Minimum Limit
ASTM D975	All grades except No. 4-D	40
	No. 4-D	30
ASTM D6751		47
ASTM D7467	All grades	40

PRECISION

Within the range from 32.5 to 56.5 cetane numbers, the expected correlation of the calculated cetane index with the ASTM cetane number will be less than ±2 cetane numbers for 65 % of the distillate fuels evaluated. Errors in correlation may be greater for fuels whose cetane numbers are outside this range.

DERIVED CETANE NUMBER

This is measured by ASTM D6890. This automated laboratory test method covers the quantitative determination of the ignition characteristics of conventional diesel fuel oil, oil-sands-based fuels, blends of fuels containing biodiesel material, and diesel fuel oils containing cetane number improver additives, and it is applicable to products typical of ASTM D975 Grades No. 1-D and 2-D regular and low-sulfur diesel fuel oils. This test method measures the ignition delay and utilizes a constant volume combustion chamber with direct fuel injection into heated, compressed air. An equation correlates an ignition delay determination to cetane number by ASTM D613, resulting in a derived cetane number (DCN). This test method covers the ignition delay range from 3.1 to 6.5 ms (64 to 33 DCN). There is no information about how DCNs outside the 33 to 64 range compare to ASTM D613 cetane numbers.

ANALYSIS

A small specimen of diesel fuel oil is injected into a heated, temperature-controlled, constant-volume chamber that previously has been charged with compressed air. Each injection produces a single-shot, compression ignition combustion cycle. Ignition delay (ID) is measured using sensors that detect the start of the fuel injection and the start of the significant combustion for each cycle. A complete sequence comprises 15 preliminary cycles and 32 further cycles. The ID measurements for the last 32 cycles are averaged to produce the ID result. An equation converts the ID result to cetane number by ASTM D613. This test requires a sample of approximately 100 mL and a test time of approximately 20 min on a fit-for-use instrument.

PRECISION

Based on an interlaboratory study conducted in 2002 (RR-D02-1602), the following precision limits were obtained.

	ID (ms)	DCN
Repeatability	0.0500 × (ID – 2.5)	0.0132 × (DCN + 18)
Reproducibility	0.0792 × (ID – 1.1)	0.0385 × (DCN + 18)

Reduced Temperature Properties

The cloud point and pour point of a fuel are good measures for determining low temperature operability for a batch of fuel oil. It is especially important to consider these fuels properties if the heating oil will be subjected to low ambient temperatures at time of use. Fuel temperatures can fluctuate markedly in small, residential, outdoor above-ground tanks compared with indoor, basement tanks or underground tanks. A decrease or stoppage of fuel flow can occur in small transfer lines used for residential heating applications because the fuel line temperature will fluctuate with ambient temperature faster than will bulk tank contents. Fuel oil purchased during the summer, but not used until the cold heating season arrives, can be a serious source of problems. This is because when these fuels are produced they are intended for use during the warm season and thus typically have higher cloud and pour points than fuels produced for use during the cold season. Fuels can be produced for use at low temperatures with lower cloud and pour points by blending with low paraffin fuels, such as kerosine or No. 1 fuel, and additives—or a combination thereof—to improve the temperature operability. The key to effective treatment is routine monitoring of incoming and stored fuels and testing of the treated fuels. Some pipeline companies or local specifications have included requirements for both cloud and pour points for certain grades of fuel oil. Available cloud point test methods are discussed as follows and the pour point test methods are detailed later in this chapter.

The presence of biodiesel in the fuel may also affect cold flow properties and operations in part due to higher viscosity, higher cloud point, or the inclusion of other compounds that adversely affect cold flow operations. There are two different cold temperature performance concerns: handling and operability. Handling, including filterability, is the ability to store, blend, and pump B100 or the resulting blend. Operability refers to the use of the diesel blend in a vehicle's fueling system. As shown in Table 3.4, the cold flow properties of biodiesel vary with the fatty acid composition of the feedstocks. Typical values for biodiesels produced from various feedstocks are shown in Table 3.4. However, some biodiesel is produced from multiple biodiesel feedstocks. The cold flow properties of any biodiesel being blended must be understood, especially when biodiesel is blended into a diesel base stock at terminal locations where options to correct the cold temperature performance may be limited.

The second factor influencing the cold temperature performance of biodiesel is the presence of impurities that can promote the formation of precipitates and deposits. Two main impurities are saturated monoglycerides and sterol glucosides. Precipitation from B100 is thought to be associated with the presence of sterol glucosides, although precipitation from diesel blends is more often linked to the presence of saturated monoglycerides [3].

Biodiesel from most common feedstocks has inferior cold flow properties compared to conventional diesel fuels. Blends with

TABLE 3.4 Typical Handling Properties for Biodiesel Manufactured from Different Feedstocks

Feedstock	Cloud Point, °C	CFPP, °C	Viscosity, cSt at 40°C
Canola/rapeseed	−3	−13	4.4
Sunflower	+3	−3	4.4
Soybean	+1	−4	4.0
Coconut	0	−4	2.7
Palm	13	12	4.6
Tallow	16	14	4.8

From [4].

as little as 10 vol % biodiesel content typically have significantly higher cloud point (CP), pour point (PP), and cold filter plugging point (CFPP) than the No. 2 grade diesel fuel. Although PP and CFPP may be lowered by treating with cold flow improver additives, these additives do not reduce CP by more than 3 to 5°C. When stored in moderate temperature climates, biodiesel should be periodically monitored during cooler months. Dunn has examined the use of automated ASTM test methods to reliably monitor these properties [5]. Automated instruments have a number of advantages over manually operated apparatuses, namely small sample volumes, consistency, speed of analysis, and accuracy of results. The samples were also analyzed by subambient differential scanning calorimetry performed at various heating and cooling scan rates for comparison with cold flow property results [5].

Results from a variety of biodiesels in the aforementioned study indicate that automated cloud points of neat and blended biodiesel samples deviated from manual cloud points by an average of +1.6°C. Automated cloud point analysis generally yielded higher temperatures than manual results. Similarly, automated pour points of neat and blended biodiesel samples deviated from corresponding manual pour points by an average of +2.7°C. Automated measurements yielded higher results than manual ones. CFPP of neat and blended biodiesel samples deviated from corresponding manual CFPP results by an average of −1°C. Regression analysis suggested a near-linear correlation for CFPP versus cloud point data [5].

The melting point of biodiesel products depends on chain length and degrees of unsaturation, with long-chain saturated fatty acid esters displaying particularly unfavorable cold temperature behavior. The following controls are used in biofuel-producing regions of the world.

	Cloud Point		CFPP	
Region	**Limit**	**Test Method**	**Limit**	**Test Method**
Brazil	None	Not Applicable	National specifications	ASTM D6371
European Union	National specifications	ISO 23015	National specifications	EN 116
United States	Report	ASTM D2500	None	ASTM D6371

ASTM D2500, ASTM D5771, ASTM D5772, ASTM D5773, ASTM D7397, and ASTM D7689, Cloud Point of Petroleum Products

SIGNIFICANCE

Cloud point defines the temperature at which a cloud or haze of wax crystals appears in the oil under prescribed test conditions that generally relate to the temperature at which wax crystals begin to precipitate from the oil in use. The cloud point of a petroleum oil is an index of the lowest temperature of its utility for certain applications. Cloud point is the temperature at which a cloud of wax crystal first appears in a liquid when it is cooled under conditions prescribed in this test method. This test method covers only petroleum oils that are transparent in layers 38 mm (1.5 in.) in thickness and with a cloud point below 49°C (120°F).

To many observers, the cluster of wax crystals looks like a whitish or milky cloud—hence the name of the test method. The cloud appears when the temperature of the specimen is low enough to cause wax crystals to form. For many specimens, the crystals first form at the lower circumferential wall of the test jar where the temperature is lowest. The size and position of the cloud or cluster at the cloud point varies depending upon the nature of the specimen. Some samples will form large, easily observable clusters, while others are barely perceptible. Upon cooling to temperatures lower than the cloud point, clusters of crystals will grow in multiple directions.

The purpose of the cloud point method is to detect the presence of wax crystals in the specimen; however, trace amounts of water and inorganic compounds may also be present. The intent of the cloud point method is to capture the temperature at which the liquids in the specimen begin to change from a single liquid phase to a two-phase system containing solid and liquid. It is not the intent of this test method to monitor the phase transition of the trace components, such as water.

It is generally observed that the cloud point temperature of a fuel oil is higher than its pour point by several degrees Celsius. Fuel oils stored at or below their cloud point temperature can have suspended wax crystals that may cause operability problems due to plugging. Examples are when fuels are pumped through small openings or passageways, that is, oil-line filters, burner nozzles, and pump strainers. The plugging is reversible when the fuel is warmed. Biodiesel generally has a higher cloud point than petroleum-based diesel fuel. The cloud point of biodiesel and its impact on the cold flow properties of the resulting blend should be monitored by the user to ensure trouble-free operation in cold climates. See Appendix X4 of ASTM D975.

The cloud point test method is included in ASTM D6751 and ASTM D7467 for biodiesel blends. ASTM D3117 could also be used because it was closely related. However, that test method has now been withdrawn from publication.

Specification	Test Method	Limits
ASTM D6751	ASTM D2500; alternate test methods ASTM D5771, ASTM D5772, ASTM D5773, ASTM D7397, ASTM D7689	Report
ASTM D7467	ASTM D2500; alternate test methods ASTM D5771, ASTM D5772, ASTM D5773, ASTM D7397, ASTM D7689	Report

Cloud points are usually determined using the manual test method ASTM D2500 or the automatic test methods ASTM D5771, ASTM D5772, ASTM D5773, ASTM D7397, or ASTM D7689. In case of disputes, ASTM D2500 will be the referee method. The five automatic methods are alternatives to the manual ASTM D2500 method for use with automatic apparatus. When specifications quote ASTM D2500, do not substitute these methods without obtaining comparative data and customer agreement. All five automatic test methods are more precise than manual ASTM D2500. All methods cover the range from −60 to +49°C, with a temperature resolution of 0.1°C.

In ASTM D2500, the sample is first heated to a temperature above the expected cloud point, then cooled at a specified rate, and examined periodically. The temperature at which haziness is first observed at the bottom of the test jar is recorded as the cloud point.

Other alternate cloud point test methods are as follows:

ASTM	IP	Instrument	Range, °C	ASTM Research Report
ASTM D5771	444	ISL	−60 to +49	RR-D02-1373; -1508; -1524; -1740
ASTM D5772	445	Herzog	−60 to +49	RR-D02-1373; -1509; -1524
ASTM D5773	446	Phase Technology	−60 to +49	RR-D02-1373; -1510; -1524
ASTM D7397	–	Phase Technology	−60 to +20	RR-D02-1627
ASTM D7689	–	ISL	−50 to +6	RR-D02-1726

ASTM D5771, Optical Detection Stepped Cooling Method

After inserting the specimen into the apparatus and initiating the program, the specimen is cooled incrementally according to the cooling profile listed. The specimen is continuously monitored by a reflective optical system for the formation of a crystalline structure. When the crystallization of the wax in the specimen is detected by the optical system, the temperature is recorded to within 0.1°C resolution. The specimen is then heated to facilitate the start of the next test.

ASTM D5772, Linear Cooling Rate Method

After insertion of the specimen into the apparatus and initiation of the program, the specimen is heated and then linearly cooled at a specified rate. The specimen is continuously monitored by an opposing optical light barrier for the crystal structure formation. When the crystallization of the wax in the specimen is detected by the optical barrier, the temperature is recorded with a resolution of 0.1°C. The specimen is then heated to the original starting temperature.

ASTM D5773, Constant Cooling Rate Method

A specimen is cooled by a Peltier device at a constant rate of 1.5 ± 0.1°C/min while continuously being illuminated by a light source. The specimen is continuously monitored by an array of optical detectors for the first appearance of a cloud of wax crystals. The detectors are sufficient in number to ensure that any solid phase hydrocarbon crystals that may form are detected. The temperature at which the appearance of a cloud of wax crystals is first detected in the specimen is recorded to a 0.1°C resolution. When the recorded temperature is rounded to the next lower integer temperature, it is designated as the ASTM D2500/IP 219 equivalent cloud point per ASTM D5773.

ASTM D7397, Miniaturized Optical Method

A specimen is cooled by a Peltier device in a miniaturized specimen receptacle at a rate of 30 ± 5°C/min while continuously being illuminated by a light source. The specimen is continuously monitored by an optical detector for the first appearance of a cloud of wax crystals. Once the crystals are first detected, as manifested by an increase in scattered light level received by the optical detector, the specimen is warmed at a rate of 15 ± 5°C/min. As soon as all the crystals are re-dissolved into the liquid specimen, warming is halted and the specimen is cooled again—but this time at a slower rate of 6 ± 3°C/min. When crystals first appear under this slower cooling rate, the temperature of the specimen is recorded to 0.1°C resolution as the cloud point. When the recorded temperature is rounded to the next lower integer temperature, it is designated as the ASTM D2500/IP 219 equivalent cloud point per ASTM D5773.

ASTM D7689, Mini Method

A specimen is inserted into an automatic instrument, and the program is started for heating the test specimen, if necessary, to a starting temperature and then cooled by a prescribed rate. The test specimen is continuously monitored with opposing light emitter and optical receiver for the appearance of hydrocarbon crystals. When the crystallization in the specimen is detected by the optical system, the temperature is recorded to within a 0.1°C resolution. The specimen is then heated to facilitate the start of the next test.

The precisions of these six test methods for cloud point determination are given in Table 3.5.

ASTM D6371, CFPP of Diesel and Heating Fuels

SIGNIFICANCE

The CFPP of a diesel or heating fuel is suitable for estimating the lowest temperature at which a fuel will give trouble-free flow in certain fuel systems. For diesel fuels used in European light-duty trucks, the results are usually close to the temperature of failure in service except when the fuel system contains, for example, a paper filter installed in a location exposed to the weather or if the filter plugging temperature is more than 12°C below the cloud point value. Domestic heating installations are usually less critical and often operate satisfactorily at temperatures somewhat lower than those indicated by the test results. The difference in the results obtained from the sample as received and after heat treatment at 45°C for 30 min can be used to investigate complaints of unsatisfactory performance under low-temperature conditions.

TABLE 3.5 Precision of Cloud Point Test Methods

Method	Repeatability, °C	Reproducibility, °C	Bias vs. ASTM D2500, °C
ASTM D2500—Petroleum Products	2	4	–
—Biodiesel Blends	2	3	–
ASTM D5771—Petroleum Products	2.2	3.9	−0.56
—Biodiesel Blends	1.2	2.7	
ASTM D5772—Petroleum Products	1.3	3.3	−0.67
—Biodiesel Blends	0.7	2.2	
ASTM D5773—Petroleum Products	1.3	2.5	−0.03
—Biodiesel Blends	0.017 × (27 − X)	0.063 × (27 − X)	
ASTM D7397—Petroleum Products	0.26E-01 × (31.0–X)	0.34E – 01 × (31.0 − X)	−0.49
ASTM D7689—Petroleum Products	0.0206 (30°C – X)	0.0561 (30°C – X)	

Note: Where X is the cloud point; ASTM D2500, RR-D02-1444 and -1524.

ANALYSIS

ASTM D6371 is used for measuring the CFPP of distillate fuels, including those containing a flow-improving or other additive intended for use in diesel engines and domestic heating installations. Either a manual or automated apparatus can be used in this test. A sample is cooled under specified conditions and at intervals of 1°C is drawn into a pipette under a controlled vacuum through a standardized wire mesh filter. As the sample continues to cool, the procedure is repeated for each 1°C below the first test temperature. The testing is continued until the amount of wax crystals that have separated out of the solution is sufficient to stop or slow down the flow so that the time taken to fill the pipette exceeds 60 s or until the fuel fails to return completely to the test jar before the fuel has cooled by a further 1°C. The indicated temperature at which the last filtration was commenced is recorded as the CFPP.

PRECISION

Based on an interlaboratory study conducted by the Energy Institute (London) involving 46 laboratories and five samples ranging in CFPP values from 0 to −33°C, repeatability and reproducibility for this test method were found to be 1.76°C repeatability and 0.102(25 – X)°C reproducibility, where X is the average of two results. There is no relative bias between manual and automated apparatus (see RR-D02-1452).

ASTM D7501, Cold Soak Filterability of Biodiesel (B100) Blend Stock

SIGNIFICANCE

Some substances that are soluble or appear to be soluble in biodiesel (B100) at room temperature will, upon cooling to temperatures above the cloud point or standing at room temperature for extended periods, come out of solution. This phenomenon has been observed in both B100 and BXXX blends. These substances can cause filter plugging. This test method provides an accelerated means of assessing the presence of these substances in B100 and their ability to plug filters; B100 biodiesel fuels that give short filtration times are expected to give satisfactory operation of BXX blends at least down to the cloud point of the biodiesel blends.

SCOPE

This test method can be used in specifications as a means of controlling levels of minor filter plugging components in biodiesel and biodiesel blends. This test method covers the determination by filtration time after cold soak of the suitability for a biodiesel (B100) blend stock that meets all other requirements of ASTM D6751 and that has a cloud point below 20°C to provide adequate performance to at least the cloud point of the finished blend.

ANALYSIS

In this test method, 300 mL of biodiesel (B100) is stored at 4.5 ± 0.5°C for 16 h, allowed to warm to 25 ± 1°C, and then is vacuum filtered through a single 0.7-μm glass fiber filter at controlled vacuum levels of ~70 to 85 kPa. The filtration time is reported in seconds.

PRECISION

Based on an interlaboratory study that included samples with mean cold soak filtration test results from 77.5 to 188.6 (RR-D02-1672), the following precision for this test method was obtained: repeatability 0.2959 (X − 4.5000E+01) and reproducibility 0.5387 (X − 4.5000E+01). This translates into availability for use in specification limits within the range of 120 and 400 s as shown in Table 3.6.

TABLE 3.6 Precision Ranges for ASTM D7501 Cold Soak Filtration Test Biofuel Specifications

Time, s	80	120	150	200	240	280	320	360	400
Repeatability	10	22	34	46	58	70	81	93	105
Reproducibility	19	40	62	83	105	127	148	170	191

ASTM D1500, ASTM Color of Petroleum Products

SIGNIFICANCE

Determination of petroleum product color is used mainly for manufacturing control purposes and is an important quality characteristic because color is readily observed by the user of the product. In some cases, the color may serve as an indicator of the degree of refinement of the material. When the color range of a particular product is known, a variation outside the established range may indicate possible contamination with another product. However, color is not always a reliable guide for product quality and should not be used indiscriminately in product specifications.

In the case of ethanol biofuels, color is not listed in the EN or ASTM specifications, but there is a requirement to add an orange dye in the Brazilian (ANP) specification for anhydrous ethanol. ANP does not require the use of dyes for exported ethanol. The European Committee for Standardization (CEN) and ASTM specifications permit the addition of dyes and chemical markers (see CEN 15376 and ASTM D4806). Ethanol may have a natural yellow color that derives from the presence of proteins. It is not anticipated that this will cause problems for the petroleum or automotive industry, but a color scale is being investigated by CEN to quantify the issue [1].

There are several test methods for the determination of color of petroleum products based on different rating scales. Of these, ASTM D1500 covers the visual determination of the color of a wide variety of petroleum products such as lubricating oils, heating oils, diesel fuel oils, and petroleum waxes. ASTM D156 is applicable to refined products that have an ASTM color lighter than 0.5.

ANALYSIS

In this test method, using a standard light source, a liquid sample is placed in the test container and compared with colored glass disks ranging in value from 0.5 to 8.0. When an exact match is not found and the sample color falls between two standard colors, the higher of the two colors is reported.

PRECISION

The test precision is given as repeatability: 0.5, and reproducibility: 1.0. The approximate correlation between among color scales is given in Fig. 3.6.

ASTM D156, Saybolt Color of Petroleum Products

SIGNIFICANCE

The Saybolt color test method (ASTM D156) is an empirical definition of the color of a clear petroleum liquid based on a scale of −16 (darkest) to +30 (lightest). The number is derived by finding the height of a column of the sample that, when viewed through the length of the column, visually matches one of three glass standards.

SCOPE

This test method covers the determination of the color of refined oils such as undyed motor and aviation gasoline, jet propulsion fuels, naphtha and kerosine, and, in addition, petroleum waxes and pharmaceutical white oils. For determining the color of petroleum products darker than Saybolt color −16, see ASTM D1500.

ANALYSIS

In this test method, the height of a column of sample is decreased by levels corresponding to color numbers until the color of the sample is unmistakably lighter than that of the standard. The color number above this level is reported, regardless of whether the sample was darker, questionable, or a match at the higher level.

PRECISION

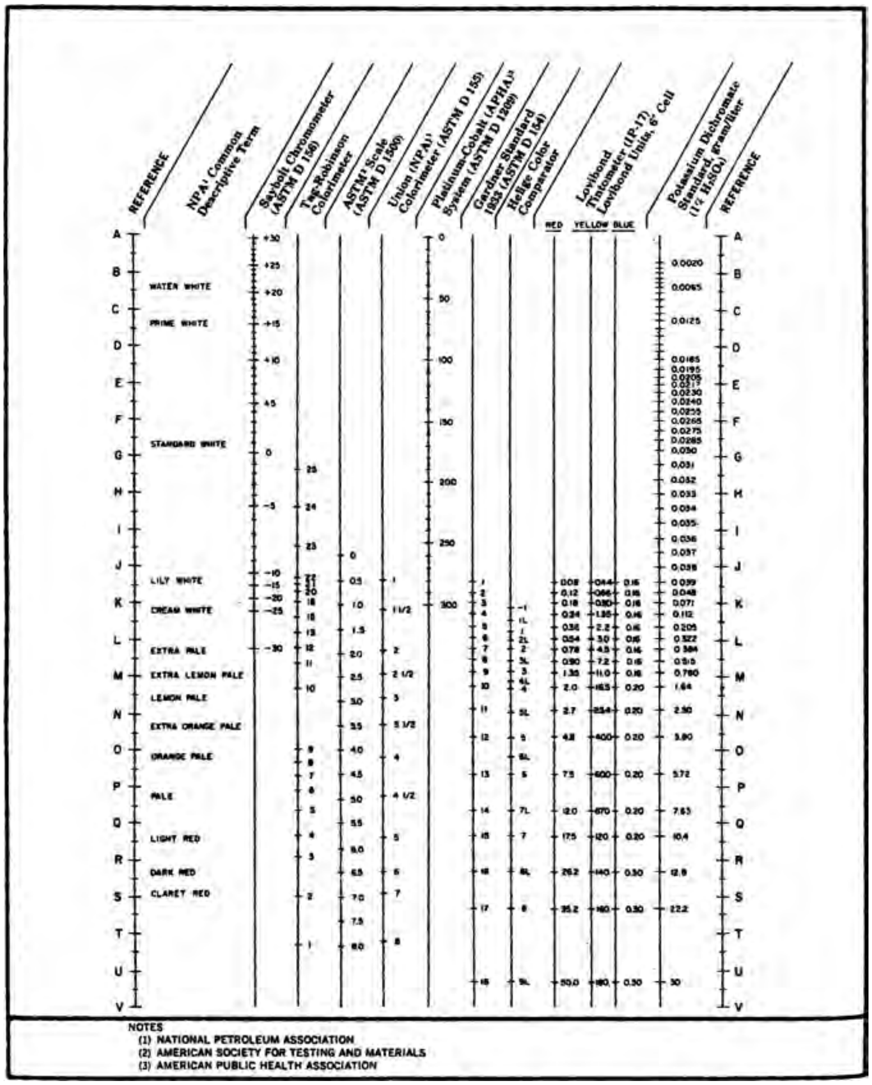
The precision of the method is given as repeatability, one color unit, and reproducibility, two color units.

ASTM D2624 and ASTM D4308, Electrical Conductivity of Aviation and Distillate Fuels

SIGNIFICANCE

An important consideration in the safe handling characteristics of any fuel is conductivity. The risk associated with explosions due to static electrical discharge depends on the amount of hydrocarbon and oxygen in the vapor space and on the energy and the duration of a static discharge. Conductivity is known to be highly dependent on temperature. The ability of a fuel to dissipate a charge that

FIG. 3.6 Comparison of color scales.



NOTES
(1) NATIONAL PETROLEUM ASSOCIATION
(2) AMERICAN SOCIETY FOR TESTING AND MATERIALS
(3) AMERICAN PUBLIC HEALTH ASSOCIATION

has been generated during pumping and filtering operations is controlled by its electrical conductivity, which depends upon its ionic species content. If conductivity is high enough, charges dissipate fast to prevent their accumulation and to avoid dangerously high potentials in a receiving tank. These test methods cover the determination of the electrical conductivity of aviation and distillate fuels with and without a static dissipater additive. Two methods are available for field tests of fuel conductivity: (1) portable meters for direct measurements in tanks or the field or the laboratory measurements of fuel samples and (2) in-line meters for continuous measurement of fuel conductivity in a fuel distribution system. For specification purposes, the conductivity measurements should be made with the portable meters.

SCOPE

ASTM D2624 and ASTM D4308 are allowed for all grades of No. 1 and No. 2 diesel fuels (ASTM D975) at a level of 25 pS/m. There are no conductivity requirements for No. 4 diesel fuel. For conductivities below 1 pS/m, ASTM D4308 is preferred.

ASTM D2624

A voltage is applied across two electrodes in the fuel, and the resulting current is expressed as a conductivity value. With the portable meters, the current measurement is made almost instantaneously upon the application of the voltage. This test method can measure conductivities from 1 to 2,000 pS/m. This test may be conducted with a portable meter or with continuous in-line metering. The following precision was obtained for measuring electrical conductivity using different models of meters (Table 3.7). The precision is also shown in Fig. 3.7 for both repeatability and reproducibility.

ASTM D4308

This test method applies to the determination of the "rest" conductivity of aviation fuels and other similar low-conductivity hydrocarbon liquids in the range of 0.1 to 2,000 pS/m. Rest conductivity is defined as the reciprocal of the resistance of uncharged fuel in the absence of ionic depletion or polarization. It is the electrical

FIG. 3.7 Precision of ASTM D2624, *Standard Test Methods for Electrical Conductivity of Aviation and Distillate Fuels.*

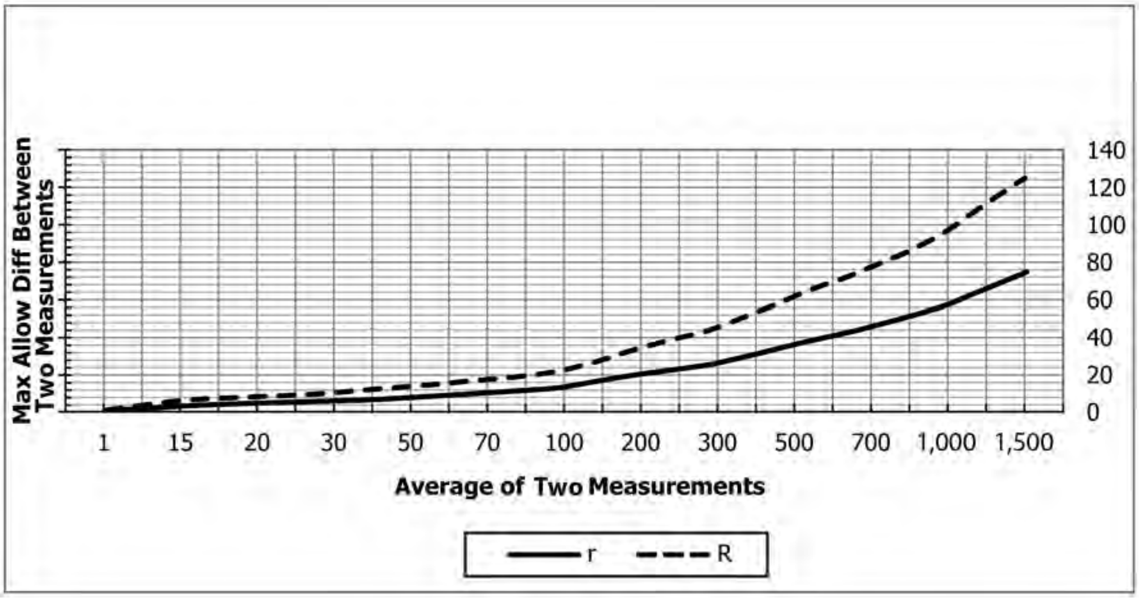


TABLE 3.7 Precision Estimates for ASTM D2624 Conductivity Measurements

	Models[a]		Models[b]		Models[c]	
Conductivity, pS/m	r	R	R	R	r	R
1	1	1	0	0	1	1
15	6	3	2	2	6	6
20	7	4	2	2	7	7
30	9	6	3	3	8	8
50	13	10	5	5	10	10
70	15	13	7	7	12	12
100	19	17	9	9	15	15
200	29	32	17	16	21	21
300	37	45	23	22	26	26
500	51	69	36	34	33	33
700	62	92	47	46	39	39
1,000	77	125	64	61	47	37
1,500	98	177	89	86	57	57

[a] Emcee Models 1150, 1151, 1152, and 1153.
[b] Maihak Model MLA 900.
[c] D-2 Incorporated Model JF-1A-HH.

conductivity at the initial instant of current measurement after a DC voltage is impressed between electrodes. The test method can be used in the field or in a laboratory. This test method can supplement ASTM D2624, which is limited to fuels containing static dissipater additives.

In this test method, a sample of liquid hydrocarbon is introduced into a clean conductivity cell that is connected in series to a battery voltage source and a sensitive DC ammeter. The conductivity—automatically calculated from the observed peak current reading DC voltage and cell constant using Ohm's law—appears as a digital value in either a manual or automatic mode of meter operation. Precision of this test method is given in Fig. 3.8.

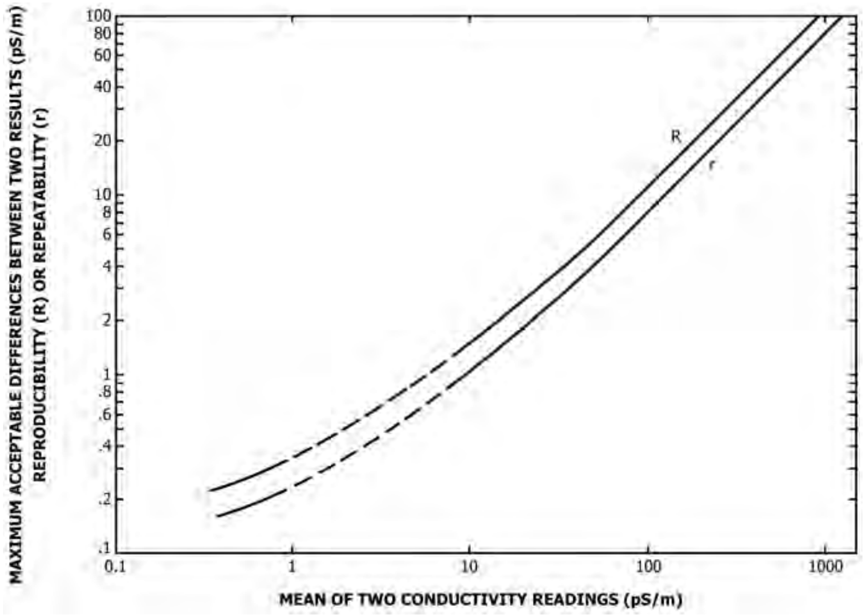
ASTM D130, Corrosion of Petroleum Products Using Copper Strip Test

SIGNIFICANCE

This test indicates the presence or absence of materials that could corrode copper, brass, and bronze components of a fuel system. Most sulfur compounds in petroleum are removed during refining. However, some residual sulfur compounds can have a corroding action on various metals. This effect is dependent on the types of sulfur compounds present. The presence of acids or sulfur-containing compounds can tarnish the copper strip, thus indicating the possibility for corrosion. Fuels must pass the copper strip corrosion test to minimize corrosion in fuel systems due to sulfur compounds in the fuel. Some fuels corrode fuel system metals other than copper, but there are no ASTM test methods to evaluate corrosion of these metals. Depending on the type and concentration of oxygenate, gasoline-oxygenate blends can corrode metals such as zinc, magnesium, aluminum, steel, and terne. However, at this time, there is no test method with a known correlation to field performance. Consequently, additional corrosion tests are needed. The following limits are placed in biodiesel specifications for the copper corrosion test.

Brazil	Class 1	ABNT NBR 14539/ISO 2160/ASTM D130
European Union	Class 1	ISO 2160
United States	Class 3	ASTM D130

FIG. 3.8 Precision of ASTM D4308, *Standard Test Method for Electrical Conductivity of Liquid Hydrocarbons by Precision Meter.*



Reactive sulfur compounds present in automotive spark-ignition engine fuel under some circumstances can corrode or tarnish silver alloy fuel gauge in-tank solder units. To minimize the failure of silver alloy in-tank sender units by corrosion or tarnish, fuels must pass the silver strip corrosion test.

SCOPE

This property is specified only for Nos. 1 and 2 distillate fuel oils in ASTM D396. ASTM D130, a 3-h test at a minimum control temperature of 50°C, is used for this determination in the corrosion testing of gasolines. Other specifications (ASTM D975, ASTM D4814, ASTM D5983, ASTM D6751, and ASTM D7467) also contain copper corrosion ASTM D140 test limits.

As a pass-fail test, normal statistical calculations of precision under ASTM D6300 cannot be applied for this test.

ASTM D1298, ASTM D4052, and ASTM D7042, Density of Petroleum Products

SIGNIFICANCE

Density is a fundamental physical property. However, by itself it is of little significance as an indication of the burning characteristics of fuel oil. But when used in conjunction with other properties, it is of value in mass-volume relationships and in calculating the specific energy (heating value) of an oil. Accurate determination of the gravity of petroleum and its products is necessary for the conversion of measured volumes to those at the standard temperature of 60°F (15.56°C). Gravity is a factor governing the quality of crude oils. However, the gravity of a petroleum product is an uncertain indication of its quality. When correlated with other properties, gravity can be used to give approximate hydrocarbon composition and heat of combustion.

The densities of biodiesels are generally higher than those of fossil diesel fuels. The values depend on their fatty acid composition as well as on their purity. Density increases with decreasing chain length and increasing number of double bonds, or it can be decreased by the presence of low-density contaminants such as methanol [1]. The following limits are placed on biodiesels for density.

Region	Limits	Test Method(s)
Brazil	Report at 20°C	NBR 7148/14065; ASTM D1298; ASTM D4052
European Union	860–900 kg/m^3 at 15°C	ISO 3675/12185
United States	Report	Not applicable

The density of biodiesel meeting the specifications in ASTM D396 and ASTM D975 falls between 0.86 and 0.90, with typical values falling between 0.88 and 0.89. Because the densities of petroleum-based diesels and biodiesels are similar, a separate specification for biodiesel is not necessary. The density of raw oils and fats can be similar to biodiesel, and the use of density as an expedient check of fuel quality may not be as useful for biodiesel as it is for petroleum-based diesel fuel [6].

SCOPE

The following specifications contain limits on the density values.

Product Specifications	Test Method	Density Value Limits
ASTM D396—No. 4 Light	ASTM D1298	>876
—No. 1 S500, No. 1 S5000		850 max
—No. 2 S500, No. 2 S5000		876 max

ASTM D5983	ASTM D1298 or ASTM D4052	Report
ASTM D7544	ASTM D4052	1.1–1.3
ASTM D7666	ASTM D1298	Report

Although several test methods are available for density determination, two principal test methods used for petroleum products and lubricants are ASTM D1298 and ASTM D4052. ASTM D7042 is also available as an alternate test method.

ASTM D1298

This test method covers the laboratory determination (using a glass hydrometer in conjunction with a series of calculations) of the density, relative density, or API gravity of a petroleum product normally handled as a liquid and having a Reid vapor pressure (RVP) of 101.325 kPa (14.696 psi) or less. Values are determined at existing temperatures and converted to 15°C or 60°F by means of a series of calculations and international standard tables. In this test method, the sample is brought to a specified temperature and transferred to a hydrometer cylinder at approximately the same temperature. The appropriate hydrometer is lowered into the sample and allowed to settle. After temperature equilibrium has been reached, the hydrometer scale is read, and the temperature of the sample is noted. If necessary, the cylinder and its contents may be placed in a constant temperature bath to avoid excessive temperature variation during the test.

ASTM D4052

This test method uses an automated digital density meter. It covers the determination of the density or relative density of petroleum distillates and viscous oils that can be handled in a normal fashion as liquids at test temperatures between 15 and 35°C. Its application is restricted to liquids with vapor pressures below 600 mm Hg (80 kPa) and to viscosities below about 15,000 cSt (mm^2/s) at the temperature of the test. The scope of this method is restricted to samples with a vapor pressure of <11.6 psi. Gasoline and E10 blends frequently have vapor pressures of >11.6 psi. Some examples of products that can be tested using this procedure include gasoline, gasoline-oxygenate blends, diesel fuel, jet fuel, base stocks, waxes, and lubricating oils. This test method should not be applied to samples so dark in color that the absence of air bubbles in the sample cell cannot be established with certainty. Ruggedness of test data is available from cross-check data and other round-robins (Table 3.8). The reproducibility of ASTM D4052 for density is given as 0.0005, based on pure compounds only. There were no petroleum mixtures in that study.

In this test method, a small volume (approximately 0.7 mL) of liquid sample is introduced into an oscillating sample tube, and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density, relative density, or API gravity of the sample. Both manual and automated injection techniques are used. The precision of test methods ASTM D1298 and ASTM D4052 are given in Tables 3.9 and 3.10, respectively, based on interlaboratory studies (RR-D02-1387; RR-D02-1734).

TABLE 3.8 Analysis of Gasolines (>11.6 psi) in ASTM Gasoline Proficiency Testing Programs

Samples	ASTM D5191: RVP	ASTM D4052: Density
RFG 0701	7.17	0.7483 ± 0.0011 (88)
MG 0504	7.79	0.7367 ± 0.0015 (93)
MG 0404	11.76	0.7353 ± 0.0021 (71)
MG 0512	12.09	0.7281 ± 0.0020 (97)
RFG 0603	12.71	0.7352 ± 0.0010 (77)
RFG 0703	13.09	0.7281 ± 0.0018 (94)
MG 0604	13.80	0.7327 ± 0.0028 (93)
RFG 0705	14.19	0.7293 ± 0.0017 (90)
RFG 0607	14.83	0.7248 ± 0.0013 (83)
MG 0304	15.13	0.7313 ± 0.0025 (70)
RFG 0704	15.31	0.7208 ± 0.0016 (91)

Note: Density results are expressed as mean value ± reproducibility (number of replicates); MG = motor gasoline; RFG = reformulated gasoline. RVP = Reid vapor pressure.

TABLE 3.9 Precision of ASTM D1298

Product	Temperature Range	Units	Repeatability	Reproducibility
Transparent	−2 to 24.5°C	Density	0.0005	0.0012
Nonviscous	29 to 76°F	Specific gravity	0.0005	0.0012
	42 to 78°F	API gravity	0.1	0.3
Opaque	−2 to 24.5°C	Density	0.006	0.0015
	29 to 76°F	Specific gravity	0.0006	0.0015
	42 to 78°F	API gravity	0.2	0.5

TABLE 3.10 Precision of ASTM D4052

Sample Types	Range	Testing Condition	Repeatability	Reproducibility
Gasoline and RFG	0.71–0.78	Manual Manual or auto	0.00045 0.00031	0.00195 − 0.0344 (D − 0.75)
Distillates, base stocks, and lube oils	0.80–0.88	Manual or auto	0.00011	0.00050
Gasoline and RFG	51–66	Manual or auto	0.063	0.60 + 0.037 (G − 60)
Distillates, base stocks, and lube oils	29–45	Manual or auto	0.022	0.128

Note: D = density or relative density value obtained; G = API gravity value obtained; RFG = reformulated gasoline.

(Measurement of density using a Stabinger viscometer [ASTM D7042] is discussed later in this chapter in the kinematic viscosity section.)

Density of Biodiesels Using a Digital Density Meter

Characterization of the density of biodiesels obtained from soybean, sunflower, canola, and beef tallow in relation to temperature in the range of 15 to 40°C was studied by Santo Filho et al. [7]. The density from all the samples investigated showed a linear behavior with respect to temperature. A Mettler-Toledo DA-310 digital density meter was used. The results obtained from these measurements are given in Table 3.11.

In places where it is difficult to acquire diesel oil, some oil producers mix plant oil with diesel oil as fuel for trucks. Diesel engine oils are not prepared for high-viscosity oils. The use of pure vegetable oils, which are highly viscous compared to diesel oil, cause major problems such as saponification and reduced engine life. Santo Filho et al. [8] combined a diesel fuel mixture with plant triglyceride in the proportion and range of about 5 % to 20 %. The samples were measured with a density meter at temperatures varying between 18 and 25°C as well as at 15°C. Afterward, the uncertainties of measurement were calculated, and the density change with respect to temperatures with density variation curves was shown. Vegetable oils show much higher density values than those required in ASTM standards for diesel fuel. According to the authors, the observations about volume, density, mass, and heating power are enough to justify several adjustments in the feed system of diesel engines so that they can use vegetable oil [8].

Density measurements have long been used to monitor petrochemical distillation. Measuring the density or specific gravity of biodiesel has been reported to be the preferred method of blending biodiesel fuel for accuracy and ease of use. Sparks et al. [9] investigated the application of microelectromechanical systems technology to fuel monitoring quality control and to blending. The microfluidic sensor has on-chip density/specific gravity, temperature, and viscosity measurement capabilities. The ability to differentiate among gasoline, ethanol, diesel, biodiesel, butanol, Fischer-Tropsch fuel, water, and air contamination with a density measurement and, in some cases, a viscosity measurement was demonstrated. Using gravimetric measurements based on fluid density, concentrations of fuel blends such as ethanol-gasoline can be measured. Contamination levels of water can also be measured in this manner. The density of fuel over temperature can be made with this sensing technology and applied to custody transfer. Potential microfluidic clogging issues are addressed by filtration and by adding the capability of sensing flow through the sensor. Measuring fluids under high flow rates is accommodated with a bypass design [9].

TABLE 3.11 Variance of Biodiesel Density with Temperature

Soybean Biodiesel		Sunflower Biodiesel	Beef Tallow Biodiesel	Canola Biodiesel	Diesel Oil
°C	Density	Density	Density	Density	Density
15	0.88595	0.88654		0.88219	0.83824
16	0.88521	0.88579			
17	0.88448	0.88508	0.86696		
18	0.88375	0.88435	0.86618		
19	0.88303	0.88363	0.86547		
20	0.88230	0.88288	0.86473	0.87852	0.83475
25	0.87865	0.87931	0.86112	0.87484	0.83126
30	0.87497	0.87563	0.85741	0.87120	0.82779
35	0.87135	0.87201	0.85376	0.86757	0.82433
40	0.86767	0.86836	0.85008	0.86394	0.82086

Note: All values of density are expressed as g/cm^3.

ASTM D86 and ASTM D1078, Distillation of Petroleum Products

SIGNIFICANCE

Distillation (volatility) properties of petroleum products are indicative of their performance. The distillation of hydrocarbons has an important effect on their safety and performance, especially in the case of fuels and solvents. Volatility is the major determinant resulting from the tendency of a hydrocarbon mixture to produce potentially explosive vapors. Distillation characteristics are critically important for both automotive and aviation gasolines, affecting starting and warm-up, and for the tendency to vapor lock at high operating temperature or at high altitude, or both. The presence of high boiling point components in these and other fuels can significantly affect the degree of formation of solid combustion deposits. The empirical results obtained in distillation methods have been found to correlate with automotive equipment performance factors and with volatility characteristics of the sample. Distillation data of petroleum products can be used in engineering calculations to design distillation equipment, to prepare appropriate blends for industrial purposes, to determine compliance with regulatory rules, to determine the suitability of the product as feed to a refining process, or for a host of other purposes. The boiling range is directly related to viscosity, vapor pressure, heating value, average molecular weight, and many other chemical, physical, and mechanical properties. Any of these properties can be a determining factor in the suitability of the product for its intended application. Petroleum product specifications often include distillation limits based on the data obtained by these test methods. There are several ASTM test methods for this analysis; precision data are available for some of them for biofuels. Two principal distillation test methods are ASTM D86 and ASTM D1078. They differ only in heating rates and flask sizes used. ASTM D86 is used for heavier fluids with a dry point >140°C.

Biodiesel exhibits a series of close boiling points rather than a distillation curve as exhibited by petroleum-based diesel fuel. The fatty acid chains in the raw oils and fats from which biodiesel is produced mainly are composed of straight-chain hydrocarbons with 16 to 18 carbons that have similar boiling temperatures. The atmospheric boiling point of biodiesel generally ranges from 330 to 357°C; thus, the specification value of 360°C is not problematic. This specification was incorporated as an added precaution to ensure that the fuel has not been adulterated with high boiling contaminants [6].

Definitions of terms used:

- *Initial Boiling Point*—The thermometer reading that is observed at the instant that the first drop of condensate falls from the lower end of the condenser tube.
- *End Point or Final Boiling Point*—The maximum corrected thermometer reading obtained during the test. This usually occurs after the evaporation of all liquid from the bottom of the flask. The term "maximum temperature" is a frequently used synonym.
- *Dry Point*—The thermometer reading that is observed at the instant the last drop of liquid evaporates from the lowest point in the flask. Any drops of film or liquid on the side of the flask or on the thermometer are disregarded.
- *Decomposition Point*—The thermometer reading that coincides with the first indications of thermal decomposition of the liquid in the flask. Characteristic indications of thermal decomposition are an evolution of fumes and erratic thermometer readings that usually show a decided decrease after any attempt is made to adjust the heat.
- *Percent Recovered*—The volume in mL of condensate observed in the receiving graduate in connection with a simultaneous thermometer reading.
- *Percent Recovery*—The maximum percent recovered.
- *Percent Total Recovery*—The combined percent recovery and residue in the flask.
- *Percent Loss*—One hundred minus the percent total recovery.
- *Percent Residue*—The percent total recovery minus the percent recovery, or the volume of residue in mL if measured directly.
- *Percent Evaporated*—The sum of the percent recovered and the percent loss.

ASTM D86

This is one of the oldest test methods under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants. It is used for the distillation of petroleum products at atmospheric pressure. This method covers the distillation of light and middle distillates, automotive spark-ignition engine fuels with or without oxygenates, aviation gasolines, aviation turbine fuels, biodiesel blends up to 20 %, marine fuels, special petroleum spirits, naphthas, kerosines, white spirits, Grades 1 and 2 burner fuels, distillate fuel oils, and similar petroleum products. It is included in the product specifications for ASTM D396, ASTM D975, and ASTM D7467. The method, however, is not applicable to products containing appreciable quantities of residual material.

ANALYSIS

In this test method, a 100-mL sample is distilled (manually or automatically) under prescribed conditions appropriate to its nature. Thermometer readings and volumes of condensate are systematically recorded and, from these data, the results are calculated and reported as any or all of the aforementioned characteristics. At the conclusion of the distillation, the observed vapor temperature can be corrected for barometric pressure.

PRECISION

The precision of ASTM D86–11b is given in Table 3.12. An interlaboratory study was conducted in 2008 involving eleven different laboratories submitting 15 data sets and 15 different samples of ethanol-fuel blends containing 25, 50, and 75 volume percent ethanol. Based on these data (RR-D02-1694), the repeatability limits of these samples are comparable to or within the published repeatability of the method. Thus, it can be concluded that ASTM D86 is applicable to ethanol-fuel blends such as Ed75 and Ed85 (ASTM D5798) or to other ethanol-fuel blends with greater than 10 % volume ethanol.

The precision was derived from a 2005 interlaboratory study (RR-D02-1621) in which 16 laboratories participated and analyzed sample sets composed of specification-grade diesel with a B5 and B20 biodiesel, specification-grade heating oil, aviation turbine fuels, marine fuels, mineral spirits, and toluene. The temperature range covered was from 145 to 365°C.

ASTM D95

This test method is used for the determination of water in the range from 0 to 25 percent volume in petroleum products, tars, and other bituminous materials by distillation method. The material to be tested is heated under reflux with a

TABLE 3.12 Precision Estimates of ASTM D86 Automated Distillation Test Method

Percent Evaporated	Boiling Point Range, °C	Repeatability	Reproducibility
Group 1, 2, and 3 Samples			
IBP	20–70	3	5
5 %	25–100	1.5 + 2.8(0.43Sc + 0.24)	2.5 + 2.8 (0.43Sc + 0.24)
10 % to 80 %	35–245	1.0 + 2.8(0.43Sc + 0.24)	2.0 + 2.8(0.43Sc + 0.24)
90 %	110–245	2.0 + 2.8(0.43Sc + 0.24)	3.0 + 2.8(0.43Sc + 0.24)
95 %	110–245	2.0 + 2.8 (0.43Sc + 0.24)	3.5 + 2.8(0.43Sc + 0.24)
FBP	135–260	3.5	7
Group 4 Samples			
IBP	145–220	0.02T	0.055T
10 %	160–265	0.009T	0.022T
50 %	170–295	1.0	3.0
90 %	180–340	0.004T	0.015T
95 %	260–340	0.015 (T–140)	0.042 (T–140)
FBP	195–365	2.2	7.1

Note: Where Sc is slope or rate of change of temperature in °C calculated using Annex A4.10.1; where T is the recovered temperature within the valid range prescribed; IBP = initial boiling point; FBP = final boiling point.

TABLE 3.13 Precision of ASTM D95 Distillation Test Method for Water

Water Collected, mL	Repeatability	Reproducibility
0.0–1.0	0.1 mL	0.2 mL
1.1–25	0.1 mL or 2 % of the mean, whichever is greater	0.2 mL or 10 % of the mean, whichever is greater

water-immiscible solvent, which co-distills with the water in the sample. Condensed solvent and water are continuously separated in a trap—the water settling in the graduated section of the trap and the solvent returning to the still. The precision of this test method was found to be as follows (Table 3.13).

ASTM D1160

This test method is used for the determination of the distillation characteristics of petroleum products and fractions that can be partially or completely vaporized at a maximum liquid temperature of 400°C and that may decompose if distilled at atmospheric pressure. Both manual and automatic distillation procedures are included. The referee method is the manual method at a mutually agreed upon pressure. Many engineering design correlations have been developed based on data obtained by this test method. These correlative methods have been used extensively in current engineering practices. ASTM D1160 is cited in biofuel specifications ASTM D6751 and ASTM D7467, with a maximum distillation temperature for 90 % recovery as 360°C and 343°C, respectively. Like ester content, this parameter is considered as an important tool for determining the presence of other substances and, in some cases, for meeting the legal definition of biodiesel (i.e., monoalkyl esters). This parameter was added to the specification to make sure that unscrupulous blenders did not adulterate B100 with heavy petroleum components. This contamination would not be detected by any other requirement in the specification.

ANALYSIS

In this test method, a sample is distilled at an accurately controlled pressure between 0.13 and 6.7 kPa (1 and 50 mm of Hg) under conditions designed to provide approximately one theoretical plate fractionation. Data are obtained from the initial and final boiling points, and a distillation curve relating volume percent distilled and atmospheric equivalent boiling point temperature can be prepared. The precision of this test method for general petroleum liquids is given in Table 2 of ASTM D1160-06 (RR-D02-1206). Precision for biodiesel analysis based on a 2012 interlaboratory study (RR-D02-1766) that involved nine laboratories using automatic and manual ASTM D1160 instruments analyzing eleven blind samples of eight specification-grade biodiesels derived from soy, canola, tallow, yellow grease, two mixed blends of biodiesel (soy and tallow), and a mustard oil is as follows:

Biodiesel Precision, °C	IBP	5 to 50 % Recovered	60 to 95 % Recovered	FBP	Range
Repeatability	39	2.1	2.1	24	274–400
Reproducibility	89	5.55	4.64	68	274–400

ASTM D7344 and ASTM D7345 are considered as the alternate test methods to the ASTM D1160 referee test method for these products. The scope and precision of these methods for biodiesel are considered as similar.

90% Recovered, °C	Repeatability		Repeat-ability	Reproducibility		Reproducibility
	ASTM D7344	ASTM D7345	ASTM D1160	ASTM D7344	ASTM D7345	ASTM D1160
360	3.3	1.6	2.1	4.5	6.3	4.64

ASTM D7344, Distillation of Petroleum Products at Atmospheric Pressure (Mini Method)

SIGNIFICANCE

The distillation (volatility) characteristics of hydrocarbons have an important effect on their safety and performance, especially in the case of fuels and solvents. The boiling range gives information on the composition, properties, and behavior of the fuel during storage and use. Volatility is the major determinant of the tendency of a hydrocarbon mixture to produce potentially explosive vapors.

The distillation characteristics are equally important for both automotive and aviation gasolines and affect start-up, warm-up, and those fuels' tendency to vapor lock at high operating temperatures or high altitudes, or both. The presence of high boiling point components in these and other fuels can significantly affect the degree of formation of solid combustion deposits.

SCOPE

This test method covers the procedure for the determination of the distillation characteristics of petroleum products in the range of 20 to 400°C using a miniaturized automatic distillation apparatus. This test method is applicable to various petroleum products, including diesel and biodiesel.

ANALYSIS

This apparatus uses a heat source, specimen cup, stainless steel distillation column, temperature measuring device, a thermoelectrically controlled condenser and receiver system, a thermoelectrically controlled sample introduction and dosing system, and a system to measure and automatically record the vapor temperature, the associated percent recovered volume in the receiver, the condenser temperature, and the barometric pressure. The sole source of this apparatus is Grabner Instruments (Vienna, Austria).

PRECISION

Although originally intended for various petroleum products, the test method now also includes biodiesel samples. Based on a

TABLE 3.14 Precision of ASTM D7344 for Biodiesels

Recovery, %	Repeatability	Reproducibility	Range, °C
IBP	0.66 (X − 50)	0.66 (X − 50)	155–245
5	29.4	36.9	290–320
10	19.5	26.5	305–335
20	12.8	19.4	325–350
30	5.35	7.99	330–360
40 to 95	0.0736 (X − 315)	0.1 (X − 315)	335–370
FBP	0.395 (X − 345)	0.825 (X − 345)	345–370

2012 interlaboratory study that included nine participating laboratories using various ASTM D1160 apparatus, and eleven participating laboratories using ASTM D7344 apparatus, blind replicates of eleven sample sets composed of eight specification-grade biodiesels (derived from soy, canola, tallow, and yellow grease), two mixed blends of biodiesel (soy and tallow), and a mustard oil were analyzed. The distillation range was from 274 to 400°C. The precision obtained from this study is summarized in Table 3.14.

The scope and precision of ASTM D7344 was approved for biodiesel (B100) in 2014. A precision comparison is shown here:

Typical Precision at 90 % Recovered (Valid Range 335 to 370°C)

90 % Recovered, °C	Repeatability ASTM D7344	Reproducibility ASTM D7344	Repeatability ASTM D1160	Reproducibility ASTM D1160
360	3.3	4.5	2.1	4.64

With regard to any relative bias between ASTM D1160 and ASTM D7344, the latter standard contains the following statement: "For T90 %—Test material property differences cannot be reliably distinguished by either Test Method D7344 or Test Method D1160, or both."

Because the typical biodiesel blendstock (B100) has a relatively narrow boiling range temperature (approximately 40°C), the statistical observation of each test method mean is relatively difficult to achieve at any given percent recovered because it essentially is masked by the detection capability (noise) of the test method as well as by the incumbent reproducibility of each test method. An ASTM D6708 comparison shows the means are within the reproducibility of both methods and a between-methods adjustment of approximately 2°C at 353°C, which is the temperature near the estimated average boiling point at 90 % for ASTM D1160. In any case, the proposed relative bias is less than the reproducibility of either method. Based on the aforementioned discussions, it was decided to allow ASTM D7344 as an alternate method for ASTM D1160. When using ASTM D7344, the observed bias should be corrected by adding 3°C to the temperature result before comparing that result to the Table 1 requirement, and the ASTM D7344 values should be reported as "bias corrected." ASTM D1160 is the referee test method.

ASTM D7345, Distillation of Petroleum Products at Atmospheric Pressure (Micro Distillation Method)

SIGNIFICANCE

See the earlier discussion of ASTM D7344.

SCOPE

See the earlier discussion of ASTM D7344.

ANALYSIS

A sample specimen is transferred into a distillation flask, which is then placed into position on the automatic apparatus, and heat is applied to the bottom of the distillation flask. The automatic apparatus measures and records specimen vapor and liquid temperatures and pressure in the distillation flask as the sample gradually distills under atmospheric pressure conditions. Automatic recordings are made throughout the distillation, and the data are stored in the apparatus memory. At the conclusion of the distillation, the collected data are treated by the data processing system, converted to distillation characteristics, and corrected for barometric pressure. The sole supply source for this apparatus is ISL/PAC (Verson, France).

PRECISION

The original test method had precision statements for various petroleum products. This has now been extended to include biodiesel based on a 2012 interlaboratory study that included nine laboratories using various ASTM D1160 apparatus and 12 laboratories using ASTM D7345 apparatus and analyzing blind replicates of 11 sample sets comprised of eight specification-grade biodiesels (derived from soy, canola, tallow, and yellow grease), two biodiesel mixed blends (soy and tallow), and a mustard oil. The distillation range was from 274 to 400°C. The following precision was obtained.

Biodiesel Precision, °C	IBP	5–95 % Recovered	FBP	Range, °C
Repeatability	2.73	0.0227 (X − 290)	3.0	300–400
Reproducibility	6.5	0.0898 (X − 290)	6.7	300–400

Note: Where X is the average of two determinations.

ASTM D4539, Filterability of Diesel Fuels by Low Temperature Flow Test

SIGNIFICANCE

The low temperature flow test (LTFT) results are indicative of the low temperature flow performance of fuel in some diesel vehicles. ASTM D4539 is especially useful for the evaluation of fuels containing flow improver additives. This test can be used to supplement other measurements of diesel fuel low temperature behavior such as ASTM D97 pour point, ASTM D2500 cloud point, or ASTM D3117 wax appearance point.

ANALYSIS

In this test method, the temperature of a series of test specimens of fuel is lowered at a prescribed cooling rate. At the commencing temperature and at each 1°C interval thereafter, a separate specimen from the series is filtered through a 17-μm screen until a minimum LTFT pass temperature is obtained. The minimum LTFT pass temperature is the lowest temperature, expressed as a multiple of 1°C, at which the test specimen can be filtered in 60 s or less. Alternatively, a single specimen may be cooled as described earlier and tested at a specified temperature to determine whether it passes or fails at that temperature.

PRECISION

Based on an interlaboratory study involving temperatures from –10 to –25°C, repeatability and reproducibility of this test are estimated as 2°C and 4°C, respectively. No statement of bias can be made for this test method.

ASTM D56, ASTM D92, ASTM D93, ASTM D1310, ASTM D3828, and ASTM D6450, Flash Point of Petroleum Products

SIGNIFICANCE

Flash point of fuel oil is an indication of the maximum temperature at which it can be stored and handled without a serious fire hazard. The lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg) at which application of a test flame causes the vapor of a sample to ignite under specified test conditions is considered its flash point. The sample is deemed to have flashed when a large flame appears and instantaneously propagates itself over the surface of the sample. Occasional appearance of a blue halo or an enlarged flame close to the actual flash point is not considered a true flash point.

Flash point measures the tendency of a sample to form a flammable mixture with air under controlled laboratory conditions. Flash point data are used in shipping and safety regulations to define “flammable” and “combustible” materials. Flash point data can also indicate the possible presence of highly volatile and flammable components in a relatively nonvolatile or nonflammable material.

The flash point of a petroleum-based diesel fuel is only about half the value of that for biodiesel, representing an important safety asset for the latter. The flash point of pure biodiesel is considerably higher than the prescribed limits, but it can decrease rapidly with an increasing amount of residual alcohol. Because these two aspects are strictly correlated, the flash point can be used as an indicator of the presence of methanol in the biodiesel. Flash point is used as a regulation for categorizing the transport and storage of fuels, with different thresholds from region to region, so aligning the biodiesel standards would possibly require a corresponding alignment of regulations. The current limits are as follows [1].

Region	Limit	Standard
Brazil	100°C	ABNT NBR 14598/ISO 3679/ASTM D93
European Union	120°C	ISO 3679
United States	93°C[a]	ASTM D93

[a] 130°C only if methanol is not measured directly.

Not all flash point test methods give the same results because flash point values are a function of the apparatus design, the conditions under which the apparatus is used, and the operational procedure carried out. No valid general correlation among different flash point test methods can be predicted.

Erroneously high flash points can be obtained when precautions are not taken to avoid the loss of volatile material. Samples should not be stored in plastic bottles because the volatile material may diffuse through the walls of the container. The containers should not be opened unnecessarily. The samples should not be transferred between containers unless the sample temperature is at least 20°F (11°C) below the expected flash point. Flash point should not be confused with autoignition temperature (ASTM E659), which measures spontaneous combustion with no external source of ignition.

The minimum permissible flash point is usually regulated by federal, state, or municipal laws and is based on accepted practice in handling and use. The flash point as specified is not directly related to engine performance. It is, however, of importance in connection with legal requirements and safety precautions involved in fuel handling and storage, and it normally is specified to meet insurance and fire regulations. The flash point for biodiesel has been set at 93°C (200°F) minimum, so biodiesel falls under the nonhazardous category in National Fire Protection Association codes. An excellent handbook on flash point determination is available from White and Montemayor [10].

ANALYSIS

There are several ASTM flash point test methods available for the analysis of petroleum products and lubricants:

ASTM D56	Tag Closed Cup Tester
ASTM D92	Cleveland Open Cup Tester
ASTM D93	Pensky-Martens Closed Cup Tester
ASTM D1310	Tag Open Cup Tester
ASTM D3278	Small Scale Closed Cup Tester
ASTM D3828	Small Scale Closed Tester
ASTM D6450	Continuously Closed Cup Tester
ASTM D7094	Modified Continuously Closed Cup Tester

Of these, ASTM D93 Procedures A and B are the preferred test methods of choice for this determination in fuels where this quality is specified: ASTM D396, ASTM D975, ASTM D6751, ASTM D7467, ASTM D7544, and ASTM D7666. For all grades of diesel fuel oils (ASTM D396, ASTM D6751, ASTM D7467, and ASTM D7666), ASTM D3828 may be used as an alternate with the same limits. ASTM D56 is also an alternate test method for some grades (e.g., ASTM D395). ASTM D6450 can also be used as an alternative to ASTM D93 for specifications ASTM D6751 and ASTM D7467.

Specification	Flash Point Test Method	Alternative Test Method
ASTM D396	ASTM D93	ASTM D56; ASTM D3828
ASTM D975	ASTM D93	
ASTM D6751	ASTM D93	ASTM D3828; ASTM D6450
ASTM D7467	ASTM D93	ASTM D3828; ASTM D6450
ASTM D7544	ASTM D93	
ASTM D7666	ASTM D93	ASTM D3828

TABLE 3.15 Comparison of Flash Point Test Methods for Biofuels

	Procedure A	Procedure B	Procedure Cloud Point
Samples	Distillate fuels, diesel, biodiesel blend, kerosine, heating oil, turbine fuels, new and used lube oils	Residual fuel oils, cutback residue, used lube oils, petroleum liquids with solids, etc.	Biodiesels
Heating rate	5–6°C/min.	1–1.6°C/min.	3 ± 0.5°C/min
Stirrer speed	90–120 rpm	250 ± 10 rpm	90 to 120 rpm
Precision	r = 0.029 X R = 0.071 X	r = 2 to 5°C R = 6 to 10°C	r = 8.4°C R = 14.7°C
Research report	RR-S15-1008		RR-D02-1683

Note: Where X is the result in °C.

A comparison of various flash point test methods used for biofuels is given in Table 3.15.

ASTM D93, Pensky-Martens Closed Cup Tester

This method is used for the analysis of fuel oils, lube oils, suspension of solids, liquids that tend to form a surface film under test conditions, and other liquids. The temperature range measured is between 40 and 360°C by a manual or automatic Pensky-Martens closed cup (PMCC) tester. The flash point of biodiesels can be determined by an automatic PMCC tester in the range of 60 to 190°C. In this test method, a brass cup of specified dimensions, filled to the inside mark with the test specimen (about 75 mL), and fitted with a cover of specified dimensions, is heated at a slow, constant rate with continual stirring. An ignition source is directed into the test cup at regular intervals with simultaneous interruption of the stirring until a flash is detected. The flash point is the lowest temperature at which the vapor above the sample ignites. There are three procedures allowed that differ in their heating rate and in the stirrer speed of the sample.

ASTM D56, Tag Closed Cup Tester

This test method covers the determination of the flash point, by Tag closed cup tester, of liquids with a viscosity of <5.5 cSt at 104°F (40°C) or <9.5 cSt at 77°F (25°C) and a flash point <200°F (93°C), except cutback asphalts (which tend to form a surface film) and materials that contain suspended solids. For other liquids, ASTM D93 should be used.

The specimen is placed in the cup of the tester and, with the lid closed, heated at a slow constant rate. An ignition source is directed into the cup at regular intervals. The flash point is taken as the lowest temperature at which the application of the ignition source causes the vapor above the sample to ignite. The following precision for this test method has been obtained.

Flash Point	Repeatability	Reproducibility
<60°C (140°F)	1.2°C (2.0°F)	4.3°C (8°F)
≥60°C (138.2°F)	1.6°C (3.0°F)	5.8°C (10°F)

ASTM D1310, Tag Open Cup Flash Point Apparatus

This test method covers the determination of flash and fire points of liquids having flash points between –18 and 165°C and fire points up to 325°C using a Tag open cup apparatus. The specimen is placed in the cup of a Tag open cup apparatus and heated at a slow, but constant, rate. A small test flame is passed at a uniform rate across the cup at specified intervals until a flash occurs. Based on an interlaboratory study (RR-D01-1002), the following precision was obtained.

Flash Point Range	Repeatability	Reproducibility
0 and 200°F (–18 and 93°C)	4°F (2°C)	7°F (4°C)
200 and 325°F (93 and 165°C)	9°F (5°C)	12°F (7°C)
Viscous heavily pigmented materials	9°F (5°C)	24°F (13°C)

ASTM D3828, Small Scale Closed Cup Tester

This test method covers procedures for the determination of the flash point by a Setaflash® closed tester. The procedures may be used to determine the actual flash point temperature of a sample or whether a product will or will not flash at a specified temperature (flash/no flash). This test method covers flash points in the range of –30°C to 300°C for petroleum products and biodiesel liquid fuels. When used in conjunction with an electronic thermal flash detector, the test method is also suitable for flash point tests on biodiesels such as FAMEs.

- *Method A: Flash/No Flash Test*—A portion of a sample is introduced by a syringe into the cup of the selected apparatus that is set and maintained at the specified temperature. After a specific time, an ignition source is applied and an observation made as to whether or not a flash occurred.
- *Method B: Finite (or Actual) Flash Point*—This method essentially repeats Method A for a number of times and, by changing the test temperature and test specimen a number of times, determines the flash point. A portion of a sample is introduced into the cup of

the selected apparatus that is maintained at the expected flash point. After a specified time, an ignition source is applied and the observation made as to whether or not a flash occurred.

The test specimen is removed from the cup, the cup cleaned, and the cup temperature adjusted 9°F (5°C) lower or higher, depending on whether or not a flash occurred previously. A fresh test specimen is introduced and tested. This procedure is repeated until the flash point is established within 9°F (5°C). The procedure is then repeated at 2°F (1°C) intervals until the flash point is determined to the nearest 2°F (1°C). If improved accuracy is desired, the procedure is repeated at 1°F (0.5°C) intervals until the flash point is determined to the nearest 1°F (0.5°C).

For all products (except biodiesels) for test temperatures up to and including 100°C, the test time is 1 min and the specimen volume is 2 mL. For all products (except biodiesels) for test temperatures above 100°C, the test time is 2 min and the specimen volume is 4 mL. The following precision is obtained for this test method. For biodiesels, the test time is 1 min and the specimen volume is 2 mL.

Range	Repeatability	Reproducibility
20 to 70°C	0.5°C	0.03 (M + 29)°C
Above 70°C	0.022 $M^{0.9}$ °C	0.083 $M^{0.9}$ °C
FAME	1.9°C	15°C

Note: Where M is the mean of the two results.

ASTM D6450, Continuously Closed Cup Tester

This is a dynamic test method and depends on the definite rates of temperature increase. The test method covers the determination of the flash point of fuel oils, lube oils, solvents, and other liquids by continuously closed cup tester. The test method utilizes a closed but unsealed cup with air injected into the test chamber. This method is suitable for testing samples with a flash point from 10 to 250°C. Flash points below 10°C and above 250°C can be ascertained; however, the precision has not been determined at these temperatures.

In this test method, the lid of the chamber is regulated to a temperature of at least 18°C below the expected flash point. A 1-mL test specimen is introduced into the sample cup, and a temperature of at least 18°C below the expected flash point for both the specimen and cup is ensured (by cooling, if necessary). The cup is then raised and pressed onto a lid of specified dimensions to form a continuously closed but unsealed test chamber with an overall volume of 4 mL. The lid is heated at a prescribed constant rate. An arc of defined energy is discharged inside the test chamber at regular intervals. After each ignition, 1.5 mL of air is introduced into the test chamber to provide the necessary oxygen for the next flash test. After each arc, the instantaneous pressure increase above the ambient barometric pressure inside the test chamber is monitored. When the pressure increase exceeds a defined threshold, the temperature at that point is recorded as the uncorrected flash point.

This test method has a precision of 1.9°C repeatability and 3.1°C reproducibility. The bias of this test method has not been determined.

ASTM D240, Heat of Combustion of Liquid Hydrocarbon Fuels

SIGNIFICANCE

This test method is applicable for liquid hydrocarbon fuels ranging in volatility from that of light distillates to that of residual fuels. Under normal conditions, this test method is directly applicable to such fuels as gasolines, kerosines, Nos. 1 and 2 fuel oils, Nos. 1-D and 2-D diesel fuels, and Nos. 0-GT, 1-GT, and 2-GT gas turbine fuels, under ASTM D7544 and ASTM D7666. It is a measure of the energy content of pyrolysis liquid biofuel. As a reference, pyrolysis liquid has approximately half the heat of combustion on a volumetric basis compared to that of No. 2 fuel oil (ASTM D396). The heat of combustion is an important basis for quantifying monetary value and for equipment selection or design, or both. Knowledge of this value is essential when considering thermal efficiency equipment for producing either power or heat.

ANALYSIS

The heat of combustion is measured using ASTM D240 by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during, and after combustion, with proper allowance for thermochemical and heat transfer corrections. Either isothermal or adiabatic calorimeter jackets can be used. This test method has a repeatability of 0.13 MJ/kg and a reproducibility of 0.40 MJ/kg (RR-D02-38).

ASTM D6468, High Temperature Stability of Distillate Fuels

SIGNIFICANCE

ASTM D6468 provides an indication of the thermal oxidative stability of distillate fuels when heated to high temperatures that simulate those that may occur in some types of recirculating engine or burner fuel delivery systems. Results have not been substantially correlated to engine or burner operation. The test method can be useful for investigating operational problems related to fuel thermal stability. When the test method is used to monitor the manufacture or storage of fuels, changes in filter rating values can indicate a relative change in inherent stability. Storage stability predictions are more reliable when correlated to longer-term storage tests such as ASTM D4625 or to other lower temperature, long-term tests.

SCOPE

This test method is suitable for all No. 1 and No. 2 grades in ASTM D396, ASTM D975, ASTM D2880, and ASTM D3699, and for grades DMX and DMA in ASTM D2069. It is also suitable for similar fuels meeting other specifications. However, this test method is not suitable for a flash point, as determined by ASTM D56, ASTM D93, or ASTM D3828, less than 38°C. This test method is also not suitable for fuels containing residual oils.

ANALYSIS

This test method uses a filter paper with a nominal porosity of 1 µm, which will not capture all of the sediment formed during aging but will allow differentiation over a broad range. Reflectance ratings are also affected by the color of the filterable insolubles, which may not correlate to the mass of the material filtered from the aged fuel sample. Therefore, no quantitative relationship exists between the pad rating and the gravimetric mass of filterable insolubles.

In this test method, two 50-mL volumes of filtered middle distillate fuel are aged for 90 or 180 min at 150°C in open tubes with air exposure. After aging and cooling, the fuel samples are filtered, and the average amount of filterable insolubles is estimated by measuring the light reflectance of the filter pads. The 100 % and 0 % extremes of the reflectance ratings are defined by an unused filter pad and a commercial black standard, respectively.

PRECISION

The following precision for this test method is obtained (RR-D02-1463).

Aging Time	Repeatability	Reproducibility
90 min	22.42–0.2130 X	44.04–0.4281 X
180 min	22.55–0.2145 X	34.11–0.3034 X

Note: Where X is the average of two results in percentage reflectance.

ASTM D445 and ASTM D7042, Kinematic Viscosity of Transparent and Opaque Liquids

SIGNIFICANCE

It is advantageous to specify viscosity for some engines as a minimum limit because of power loss due to injection pump and injector leakage. Maximum viscosity, on the other hand, is limited by considerations involved in engine design and size and by the characteristics of the injector system. The kinematic viscosity of biodiesel is higher than that of fossil diesel and, in some cases, at low temperatures becomes very viscous or even solid. High viscosity affects the volume flow and injection spray characteristics in the engine and at low temperatures may compromise the mechanical integrity of injection pump drive systems (when used as standalone B100 diesel fuel). The upper limit for the viscosity of biodiesel (6.0 mm^2/s at 40°C) is higher than the maximum allowable viscosity in ASTM D975 Grades 2-D and 2-D low sulfur (4.1 mm^2/s at 40°C). Blending biodiesel with diesel fuel close to its upper limit could result in a biodiesel blend with viscosity above the upper limits contained in ASTM D975.

Viscosity of a triglyceride burner fuel (TBF) material is more significant than that of conventional petroleum-based fuel oil. Viscosity indicates both the relative ease with which the fuel will flow, or can be pumped, and the ease of atomization. To obtain viscosity over an extended temperature range, viscosity may be measured at temperatures other than the one given in the specification. The viscosity of both TBF 5 and TBF 6 fuel oils can change significantly with relatively small differences in the range of temperatures at which the burner operates.

Many petroleum products are used as lubricants for bearings, gears, compressor cylinders, hydraulic equipment, and so on. The proper operation of the equipment depends upon the proper kinematic viscosity or on the viscosity (sometimes called the dynamic viscosity) of the liquid. Thus, the accurate measurement of kinematic viscosity and viscosity is essential to many product specifications. The kinematic viscosity of many petroleum fuels is important for their proper use—for example, for the flow of fuels through pipe lines, injection nozzles, and orifices, and for the determination of the temperature range for proper operation of the fuel in burners. Viscosity of oil is a measure of its resistance to flow. In fuel oil, it is highly significant because it indicates the relative ease with which the oil will flow or can be pumped as well as the ease of atomization.

The following kinematic viscosity limits are set for biodiesel specifications.

Region	Limits	Test Method
Brazil	Report	NBR 10441; ISO 3104; ASTM D445
European Union	3.5–5.0 mm^2/s at 40°C	ISO 3104
United States	1.9–6.0 mm^2/s at 40°C	ASTM D445

Note: This property is determined by ASTM D445 and the alternative, ASTM D7042.

Santo Filho et al. [11] have studied the variation of biodiesel viscosity with temperature from a metrological point of view. Several biodiesel types from soybean, sunflower, corn, castor bean, and animal fat were studied. All the biodiesel types were obtained by a transesterification reaction with methanol in the presence of an alkaline base as a catalyst. This study showed the behavior of the biodiesel viscosity in a temperature range of 20 to 40°C and also how its composition influenced the viscosity [11]. Differences in the FAMEs concerning the number of carbon atoms, saturated and unsaturated carbon chains, the number of carbon-carbon double bonds in the chain, or the presence of organic functional radicals bonded to the carbon chain can alter the viscosity, affecting the spray behavior upon injection in the combustion chamber of the engine. The shape of the spray and the droplet size are responsible for the efficiency of the combustion process. The viscosity of fluid mineral oils, vegetable oils, diesel oil, biodiesel, and so on varies with temperature, diminishing as the temperature is elevated.

ASTM D445

This test method covers the determination of the kinematic viscosity of liquid petroleum products, both transparent and opaque, by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity can be obtained by multiplying the measured kinematic viscosity by the density of the liquid. This test method is primarily intended for application to liquids for which the shear stress and shear rates are proportional. This test method also includes the determination of the kinematic viscosity of fuel oils that often exhibit non-Newtonian properties. The range of kinematic viscosities covered by this test method is from 0.2 to 300,000 mm^2/s at all temperatures.

SCOPE

ASTM D445 is quoted in several specifications of petroleum products and lubricants. See Table 3.16 for biofuel-related specifications.

Kinematic viscosity is a measure of the resistive flow on a fluid under gravity, with the pressure head being proportional to the density, p, of the fluid: for gravity flow under a given hydrostatic head, the pressure head of a liquid is proportional to its density, p. For any particular viscometer, the time of flow of a fixed volume of fluid is directly proportional to its kinematic viscosity, $v = n/p$, where n is the dynamic viscosity coefficient. The kinematic viscosity coefficient has the dimension L^2/T, where L is a length, and T is a time. The cgs unit of kinematic viscosity is one centimetre squared per second and is called one stokes (symbol St).The SI unit of kinematic viscosity is one metre squared per second and is equivalent to 104 ST. Frequently, the centistokes (symbol cSt) is used ($1\ cSt = 10^{-2} St = 1\ mm^2/s$).

ANALYSIS

In this test, the time is measured in seconds for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer. Two such determinations are needed from which to calculate a kinematic viscosity result that is the average of two acceptable determined values.

The test precision of ASTM D445 is given in Table 3.17. Specifically, biofuels have not been evaluated in this fashion.

Analysis of a large set of data, including both automated and manual viscometers over the temperature range of 40 to 100°C, shows that the reproducibility of automated viscometer data is not statistically significantly different than the reproducibility of manual viscometer data. It is also shown that there is no bias of the automated data in comparison to the manual data (RR-D02-1498).

TABLE 3.16 Biofuel Specifications for Kinematic Viscosity

Product Specification	Product Grade	Limits, mm^2/s
ASTM D396	No. 1 S500 and No. 1 S5000	1.3–2.4
	No. 2 S500 and No. 2 S5000	1.9–4.1
	No. 4 Light	1.9–5.5
	No. 4	>5.5–24.0
ASTM D975	No. 1-D S15, No. 1-D S500, No. 1-D S5000	1.3–2.4
	No. 2-D S15, No. 2-D S500, No. 2-D S5000	1.9–4.1
	No. 4-D	5.5–24.0
ASTM D6751	All grades	1.9–6.0
ASTM D7467	All grades	1.9–4.1
ASTM D7544	All grades	125 max
ASTM D7666	All grades	Report

TABLE 3.17 Precision of Kinematic Viscosity ASTM D445

	Determinability		Repeatability		Reproducibility	
Base oils at 40 and 100°	0.0020y	(0.20%)	0.0011x	(0.11%)	0.0065x	(0.65%)
Formulated oils at 40 and 100°C	0.0013y	(0.13%)	0.0026x	(0.26%)	0.0076x	(0.76%)
Formulated oils at 150°C	0.015y	(1.5%)	0.0056x	(0.56%)	0.018x	(1.8%)
Petroleum wax at 100°C	0.0080y	(0.80%)	$0.0141x^{1.2}$		$0.0366x^{1.2}$	
Residual fuel oils at 80 and 100°C	0.011 (y+8)		0.013 (x+8)		0.04 (x+8)	
Residual fuel oils at 50°C	0.017y	(1.7%)	0.015x	(1.5%)	0.074x	(7.4%)

Note: Where y is the average of determinations being compared; x is the average of results being compared.

ASTM D7042

This test method is called Stabinger viscosity and the instrument is available from Anton Paar Gmbh in Austria. This test method provides concurrent measurements of dynamic viscosity and density of liquid petroleum products, both transparent and opaque. The kinematic viscosity can be calculated by dividing the dynamic viscosity by density obtained at the same temperature. This test method is intended for liquids that follow Newtonian behavior (i.e., those for which primarily the shear stress and shear rate are proportional).

In this test method, a specimen is introduced into the measuring cells, which are at a closely controlled and known temperature. The measuring cell consists of a pair of rotating concentric cylinders and an oscillating U-tube. The dynamic viscosity is determined from the equilibrium rotational speed of the inner cylinder under the influence of shear stress of the test specimen and an eddy current brake in conjunction with adjustment data. The density is determined by oscillation frequency of the U-tube in conjunction with adjustment data. The kinematic viscosity is calculated by dividing the dynamic viscosity by density.

The method has no bias against ASTM D445 for kinematic viscosity or ASTM D4052 for density. Precision for the test method is given in Table 3.18.

ASTM D6079 and ASTM D7688, Lubricity of Diesel Fuels

SIGNIFICANCE

Diesel fuel injection equipment has some reliance on the lubricating properties of diesel fuel. Shortened life of engine components, such as diesel fuel injection pumps and injectors, has sometimes been ascribed to a lack of lubricity in a diesel fuel. The trend of

TABLE 3.18 Precision of Stabinger ASTM D7042

Property	Repeatability at 40°C	Repeatability at 100°C	Reproducibility at 40°C	Reproducibility at 100°C
Kinematic Viscosity of Base Oils	0.00094 X	0.0003472 (X + 5)	0.00584 X	0.002889(X + 5)
Kinematic Viscosity of Diesel fuels	0.782E-02X$^{0.778}$	NA	0.3374E-01X$^{0.778}$	NA
Density of Base Oils	0.00030	0.00033	0.00147	0.00131
Density of Diesel Fuels	0.14E-02 × (1.03–X)	NA	0.7E-02(1.03–X)	NA

Note: X is the average of results being compared; See ASTM D7042 for additional data on precision of other petroleum products; NA = not available.

high-frequency reciprocating rig (HFRR) test results to diesel injection system pump component distress die to wear has been demonstrated in pump rig tests for some fuel/hardware combinations where boundary lubrication is believed to be a factor in the operation of the component. The wear scar generated in the HFRR test is sensitive to contamination of the fluids and test materials, the temperature of the test fuel, and to the ambient relative humidity. Lubricity evaluations are also sensitive to trace contaminants acquired during test fuel sampling and storage. The Scuffing Load Ball on Cylinder Lubricity Evaluator, ASTM D6078, is also used for evaluating diesel fuel lubricity. However, no absolute correlation has been developed between these two test methods.

The HFRR method may be used to evaluate the relative effectiveness of diesel fuels for preventing wear under the prescribed test conditions. Correlation of HFRR test results with field performance of diesel fuel injection systems has not yet been determined. This test method is designed to evaluate boundary lubrication properties. Even though viscosity effects on lubricity in this test method are not totally eliminated, they are minimized.

SCOPE

ASTM D6079 or ASTM D7688 is used for measuring the lubricity of fuel oils. ASTM D6079 is considered the referee method. Both test methods are applicable to middle distillate fuels such as Grades No. 1-D S15, S500, and S5000, and Grades No. 2-D S15, S500, and S5000 diesel fuels, in accordance with ASTM D975 and to other similar petroleum-based fuels that can be used in diesel engines. This test method is applicable to biodiesel blends; B5 was included in the interlaboratory study.

Blending biodiesel fuel with petroleum-based compression-ignition fuel typically improves fuel lubricity. No specification is needed for biodiesel lubricity because values are lower than a 300-µ wear scar diameter using HFRR with B100 [1].

ASTM D6079

In this test method, a 2-mL test specimen of fuel is placed in the test reservoir of an HFRR. A vibrator arm holding a nonrotating steel ball and loaded with a 200-g mass is lowered until it contacts a test disk completely submerged in the fuel. When the fuel temperature has stabilized, the ball is rubbed against a disk with a 1-mm stroke at a frequency of 50 Hz for 75 min. The test fuel temperature is maintained at 60°C and the ambient relative humidity is maintained between 30 % and 85 %. At the conclusion of the test, the upper specimen holder is removed from the vibrator arm and cleaned. The image of the wear scar is captured using a microscope digital camera, and the dimensions of the major and minor axes of the wear scar are measured and recorded.

Based on an interlaboratory study (ASTM RR-D02-1718), a repeatability of 50 µm and a reproducibility of 80 µm have been established for this test method. This study was conducted in 2008 and involved ten laboratories analyzing six fluids in four replicates each (Grade No. 1-D, Grade No. 2-D, additized, and a biodiesel blend).

ASTM D7688

This test method is conducted exactly as ASTM D6079 except, at the very end, the dimensions of the major and minor axes are measured under 100× magnification and recorded instead of using a microscope digital camera as in the case of ASTM D6079. The same interlaboratory study as noted earlier was used to determine the precision of ASTM D7688 and results had 70 µm repeatability and 90 µm reproducibility.

Luminosity

SIGNIFICANCE

When pure methanol burns, it produces a blue, smokeless, nonluminous flame that is nearly invisible in daylight. Thus, it is difficult to know when a fire exists and when to fight such a fire. A desirable property of M70–M85 fuel is that it maintains a clearly visible flame throughout the duration of a burn. To make a methanol flame visible, materials such as aromatic hydrocarbons are added to methanol. In general, it has been established that unleaded gasoline having greater than 30 volume percent aromatics content when used as the hydrocarbon portion of M70–M85 will result in an M70–M85 fuel that will meet a requirement of a clearly visible flame throughout most of a burn. However, the luminosity performance is dependent on the types of aromatics present in the hydrocarbon portion.

Appendix X2 of ASTM D5797 contains a suggested procedure for measuring the luminosity of M70–M85 fuel. However, a lack of suitable criteria for establishing the relevancy of the procedure makes it unusable as the basis of a specification.

ASTM D7321, Particulate Contamination of Biodiesel B100 Blend Stock

SIGNIFICANCE

The mass of particulates present in a fuel is a significant factor, along with the size and the nature of the individual particles, in the rapidity with which a fuel system can filter and other small orifices in fuel system can become plugged. Total contamination is defined as the amount of insoluble material retained after filtration of a fuel sample under standardized conditions. It is limited to 24 mg/kg in an EU specification for both biodiesel and fossil diesel fuels. The total contamination parameter has become an important quality criterion because biodiesel with a high concentration of insoluble impurities tends to cause blockage of fuel filters at filling pumps and vehicles. Fuel injection equipment suppliers are concerned for the premature wear of the injection system components. Some cases of high contaminants have already been seen in Europe. High concentrations of soaps and sediments mainly are associated with these phenomena [12].

SCOPE

This test method provides a means of assessing the mass of particulates present in a fuel sample. This test method can be used in specifications and purchase documents as a means of controlling particulate contamination levels in the fuels purchased. It also covers the determination of the mass of particulate contamination in B100 biodiesel in accordance with ASTM D6751 and in BXX blends that are prepared against all No. 1 and No. 2 grade fuels allowed within ASTM D396 and ASTM D975.

ANALYSIS

In ASTM D7321, a measured volume of about 400 mL of biodiesel ester (B100) or about 800 mL of biodiesel blend (BXX) is vacuum filtered through one 0.7-μm glass fiber filter. When the contamination is high or of a nature that induces slow filtration rates, two or more filtrations (using a fresh test filter each time) may be required to complete filtration in a reasonable time. After the filtration has been completed, the test filter is washed with solvent, dried, and weighed. The particulate contamination level is determined by subtracting the blank filter mass before filtration from the mass gained by the test filter, and it is reported as g/m^3 or its equivalent in mg/L.

PRECISION

Based on an interlaboratory study (RR-D02-1713), the precision of this test method was found to have a repeatability of 0.9192 by $X^{0.50}$ and a reproducibility of 1.4625 by $X^{0.50}$ for B100 and BXX filtrations, where X is the average of the results being compared.

ASTM D97, ASTM D5949, ASTM D5950, ASTM D5985, ASTM D6749, and ASTM D6892, Pour Point of Petroleum Products

SIGNIFICANCE

Pour point is an indication of the lowest temperature at which a fuel oil is capable of flowing under very low forces. Flow characteristics, like pour point, can be critical for the correct operation of lubricating oil systems, fuel systems, and pipeline operations. Petroleum blending operations require precise measurement of the pour point. The pour point is prescribed in accordance with the conditions of storage and use. Higher pour point fuels are permissible where heated storage and adequate piping facilities are provided. An increase in pour point can occur when residual fuel oils are subjected to cyclic temperature variations that can occur in the course of storage or when the fuel is preheated and returned to storage tanks.

SCOPE

A number of biofuel-related products have pour point as a quality test in their specifications (Table 3.19).

ANALYSIS

Pour points are usually determined using manual ASTM D97 or automated ASTM D5949, ASTM D5950, ASTM D5985, ASTM D6749, or ASTM D6892.

Test Method	Technology
ASTM D5949	Automatic Pressure Pulsing
ASTM D5950	Automatic Tilt Method
ASTM D5985	Rotational Method
ASTM D6749	Automatic Air Pressure Method
ASTM D6892	Robotic Tilt Method

None of these pour point test methods are intended for use with testing crude oils nor has their applicability been verified for residual fuels. The precisions of various pour point test methods are given in Table 3.20.

TABLE 3.19 Pour Point Limits in Biofuel-Related Product Specifications

Product	Grade	Max Limits, °C
ASTM D396	No. 1 S500 and No. 1 S5000	−18
	No. 2 S500, No. 2 S5000, No. 4 Light, No. 4	−6
ASTM D7544	All grades	−9
ASTM D7666	All grades	<21

Note: ASTM D97 is the primary and ASTM D5949, ASTM D5950, ASTM D5985, ASTM D6749, and ASTM D6892 are alternate allowed test methods for pour point determination.

TABLE 3.20 Precision of Pour Point Test Methods for Petroleum Products

Test Method	Repeatability	Reproducibility	ASTM Research Report
ASTM **D97**[a]	6	9	RR-D02-1499
ASTM **D97**[b]	3	9	NA
ASTM **D5949**[c]	Model 70V: 1.6/2.2 Models 30, 50, 70: 2.9/4.1	Model 70V: 3.2/3.8 Models 30, 50, 70: 6.2/6.3	RR-D02-1312 and -1499
ASTM **D5950**[c]	3.9/2.7	6.1/4.5	RR-D02-1312 and -1499
ASTM **D5985**	2.3	8.7	RR-D02-1312
ASTM **D6749**[c]	2.5/1.1	3.1/2.2	RR-D02-1499
ASTM **D6892**[c]	3.2/1.8	3.6/2.3	RR-D02-1499

Note: NA = not available.
[a] Precision for lubricating oils.
[b] Precision for middle distillates and residual fuels.
[c] Two precision figures are given for measurements at 1 and 3°C intervals, respectively.

ASTM D97

After preliminary heating, the sample is cooled at a specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which movement of the specimen is observed is recorded as the pour point.

ASTM D5949

This test method covers the determination of pour point of petroleum products by an automatic instrument that applies a controlled burst of nitrogen gas onto the specimen surface while the specimen is being cooled and detects movement of the surface of the test specimen with an optical device. This test method includes the range of temperatures from −57 to +51°C. Test results from this method can also be determined at 1 and 3°C testing intervals; however, precision data at these testing intervals are not available.

In this test method, after inserting the test specimen into the automatic pour point apparatus and initiation of the test program, the test specimen is heated and then cooled by a Peltier device at a rate of 1.5 ± 0.1°C/min. At temperature intervals of 1 or 3°C, depending on the selection made by the user, a moving force in the form of a pressurized pulse of nitrogen gas is imparted onto the surface of the specimen. Multiple optical detectors are used in conjunction with a light source to monitor movement of the surface of the specimen. The lowest temperature at which movement of the specimen surface is observed upon application of a pulse of nitrogen gas is recorded as the pour point (ASTM **D5949**).

ASTM D5950

This test method covers the determination of the pour point of petroleum products by an automatic instrument that tilts the test jar during cooling and detects movement of the surface of the test specimen with an optical device. This test method includes the range of temperatures from −66 to +51°C. Test results from this method can be determined at 1 or 3°C intervals.

In this test method, after preliminary heating, the test specimen is inserted into the automatic pour point apparatus. After starting the program, the specimen is cooled according to the cooling profile listed in the test method and examined in either 1 or 3°C intervals. The lowest temperature at which movement of a specimen is detected, by the automatic equipment, is displayed as the pour point.

ASTM D5985

ASTM **D5985** covers the determination of pour point of petroleum products by an automatic instrument and continuously rotates the test specimen against a suspended detection device during cooling of the test specimen. This test method includes the range of temperatures from −57 to +51°C and determines the no-flow point of petroleum products by detecting the crystal structure or viscosity increase, or both, in the sample that is sufficient to impede flow of the specimen.

In this test method, after inserting the test specimen into the automatic pour point apparatus and initiation of the program, the test specimen is heated and then cooled by maintaining a constant temperature differential between the cooling block and the sample. The test specimen is continuously tested for flow characteristics by rotating the test specimen cup at approximately 0.1 rpm against a stationary, counterbalanced, sphere-shaped pendulum. The temperature of the test specimen at which a crystal structure or a viscosity increase, or both, within the test specimen causes the displacement of the pendulum and is recorded with a resolution of 0.1°C. The test specimen is then heated to the original starting temperature.

ASTM D6749

This test method covers the temperature range from −57 to +51°C. Test results from this method can be obtained at either 1 or 3°C intervals. After inserting the test jar containing the specimen into the automatic pour point apparatus and initiating the test program, the specimen is automatically heated to the designated temperature and then cooled at a controlled rate. At temperature intervals of 1 or 3°C, depending on the selection made by the user prior to the test, a slightly positive air pressure is gently applied onto the surface of the specimen which is contained in an airtight test jar equipped with a communicating tube. Because one end of the communicating tube is inserted into the specimen while the other end is maintained at atmospheric pressure, a small amount of downward movement or deformation of the specimen surface as a result of the application of the air pressure is observed by means of upward movement of the specimen in the communicating tube. This upward movement of the specimen is detected by a pressure sensor that is installed at the atmospheric end of the communicating tube. The lowest temperature at which deformation of the specimen is observed upon application of air pressure is recorded as the end point.

ASTM D6892

This test method covers the temperature range from −57 to +51°C. Test results by this method can be obtained at either 1 or 3°C intervals. In this test method, the automatic instrument tilts the test jar to detect surface movements of the test specimen with an optical device after being removed from a regulated, stepped-bath cooling jacket. After insertion of the specimen into the automatic pour point apparatus and initiation of the test program, the specimen is heated and then cooled according to a prescribed profile. The surface of the specimen is examined periodically for movement using an optical camera system mounted on top of the specimen test jar while tilting the specimen test jar. The test jar is removed from the jacketed cooling chamber prior to each examination. The lowest temperature, when movement of the surface of the specimen is detected, is recorded as the pour point.

ASTM D7579, Pyrolysis Solids in Pyrolysis Liquids by Filtration

SIGNIFICANCE

Pyrolysis liquid biofuel is a liquid product from the pyrolysis of biomass, followed by the rapid condensation of the vapors. It is comprised of a complex mixture of lignocellulosic biomass decomposition products, including highly oxygenated organic compounds. It can be produced to various char concentrations. Increasing pyrolysis solid content (consisting of solid particles of ash and char) can negatively affect the pyrolysis liquid biofuel handling, atomization, and storage stability. The specification for pyrolysis liquid biofuel, ASTM D7544, includes this test method. Grade G and Grade D have a max pyrolysis solids limit of 2.5 and 0.25 mass percent, respectively.

ANALYSIS

ASTM D7579 describes a filtration procedure for determining the pyrolysis solids content of pyrolysis liquid. In this test method, a pyrolysis liquid sample is dissolved in methanol and dichloromethane 1:1 solution, which is then filtered through a vacuum filter system. After filtering, the filtrand is washed with a solvent until the filtrate is clear. The filter is removed, dried, and weighed.

PRECISION

The repeatability of this test method has been found to be 0.1303 times weight percent, where X is the average of results (RR-D02-1664). No estimate of reproducibility is available.

Thermogravimetric Analysis

Animal livestock wastes are looked upon as an opportunity to utilize additional resources that are basically waste products into useful energy sources. Manure can be used as a feedstock for various thermochemical conversion processes such as pyrolysis and gasification as well as liquefaction. In order to apply these processes, the manure must be properly characterized for volatile matter (VM) and ash contents. Cantrell, Martin, and Ro [13] have used thermogravimetric analysis (TGA) for the rapid assessment of VM and ash content in swine, dairy, rabbit, and poultry manures. The TGA assessment of VM in manures was the same as those found by ASTM D3175 in the 47 % to 78 % mass range. The ash results were also similar to those found by ASTM D3174 in the range from 4 to 47 mass percent. The TGA ash determination should occur above 600°C with the following conditions: zero grade air at 2 to 4 furnace volumes/min, heating rate of 11°C/min, temperature range of 110 to 950°C, and isothermal hold at 950°C for 10 min. The VM determination by TGA should follow the ASTM D3175 method. Some typical results obtained by traditional ASTM methods and the proposed TGA method are given in Table 3.21 [13].

The TGA technique offered a more complete oxidation and devolatilization of manure samples, especially those with greater ash content, due to the small sample size that is amenable to uniform temperature distribution. However, the precision of TGA values would need to be improved by more replications and established sample loading methods. The TGA determination of volatile matter in manure should follow ASTM D3175. This requires the flow rate of nitrogen to be between two and four furnace exchanges per minute. The TGA determination of ash should occur above 600°C with preference for the details listed earlier.

ASTM D1982, Titer of Fatty Acids

SIGNIFICANCE

The titer of a fat is the temperature at which it solidifies. The higher the titer, the harder the fat. Traditionally, titer is used to determine whether an animal fat is considered tallow (titer is higher than 40°C) or grease (titer below 40°C), but it may also be useful in determining the operating temperature range of TBFs. Saturated fatty acids solidify at a higher temperature than unsaturated fatty acids.

SCOPE

Triglyceride burner fuel (ASTM D7666) contains this property with the limit as "report."

TABLE 3.21 Thermogravimetric Analysis Determination of Volatile Matter and Ash in Livestock Manure

		Ash, mass %		VM, mass %	
Manure	**Description**	**ASTM D3174**	**TGA**	**ASTM D3175**	**TGA**
Swine	Flushed effluent Separated solids sludge	31.92 ± 0.73 46.90 ± 0.74	33.41 ± 1.23 48.56 ± 3.69	89.86 90.07 ± 1.57 88.84 ± 0.93	84.96 ± 3.18 86.14 ± 4.61 88.98 ± 1.18
Dairy	Scraped influent Separated solids	13.75 ± 1.19	17.00 ± 3.91	79.97 ± 1.23 81.32 ± 0.86	79.95 ± 2.02 80.31 ± 0.84
Poultry	Soiled litter	22.29 ± 0.05	24.76 ± 1.04	78.83 ± 7.91	80.39 ± 3.73

ANALYSIS

ASTM D1982 measures the solidification temperature of a titer of a sample containing both unsaturated and saturated fatty acids by cooling the specimen and measuring the temperature at which solidification occurs. Water present in the sample will raise the titer, so provisions are made in the test method to remove traces of moisture. A sample is heated on a hot plate to 130°C to remove traces of moisture before it is filled in a test tube and heated in a water bath to a temperature 15 to 20°C below the expected titer point. The sample in the test tube is stirred until the temperature remains constant for 30 s or begins to rise in less than a 30-s interval. The titer point is the highest temperature indicated by the thermometer during the rise.

PRECISION

Duplicate determinations by the same operator should agree within 0.2°C.

ASTM D4953, ASTM D5190, and ASTM D5191, Vapor Pressure of Petroleum Products

SIGNIFICANCE

Vapor pressure is an important physical property of liquid spark-ignition engine fuels. It provides an indication of how a fuel will perform under different operating conditions, such as whether it will cause vapor lock at high ambient temperature or at high altitude, or if it will provide easy starting at low ambient temperature.

The addition of volatile hydrocarbons improves cold startability. The addition of too much volatile hydrocarbon can cause hot fuel handling problems. During winter, when blending with gasoline as the hydrocarbon portion, a higher hydrocarbon content may be necessary to obtain the required volatility. High vapor pressures are required in the winter for cold starting, and lower vapor pressures are needed in the summer to prevent hot fuel handling problems. Excessive vapor pressure for a given ambient condition can contribute to evaporative emissions. Petroleum product specifications generally include vapor pressure limits to ensure products of suitable volatility performance. Vapor pressure of fuels is regulated by various government agencies. Lower and upper limits on vapor pressure for three volatility classes are used to define the acceptable range of the volatile components to ensure proper vehicle performance.

Product Specification	Grades	Limits, kPa (psi)
ASTM D5797	Class 1	48–62 (7.0–9.0)
	Class 2	62–83 (9.0–12.0)
	Class 3	83–103 (12.0–15.0)
ASTM D5798	Class 1	38–62 (5.5–9.0)
	Class 2	48–65 (7.0–9.5)
	Class 3	59–83 (8.5–12.0)
	Class 4	66–103 (9.5–15.0)
ASTM D5983	–	62 max

Note: Three test methods—ASTM D4953, ASTM D5190, or ASTM D5191—are allowed for this determination in petroleum products.

ASTM D4953

This test method is a modification of Reid vapor pressure, ASTM D323. It is applicable to gasolines and gasoline-oxygenate blends with a vapor pressure of 35 to 100 kPa. This test method contains two procedures for determining vapor pressure. The liquid chamber of the vapor pressure apparatus is filled with a chilled sample and connected to the vapor chamber at 100°F. The apparatus is immersed in a bath of 100°F until a constant pressure is observed. The pressure reading is suitably corrected as the vapor pressure of the specimen.

In Procedure A, the same apparatus and essentially the same procedure as in ASTM D323 is utilized with the exception that the interior surfaces of the liquid and vapor chambers are maintained completely free of water. Procedure B utilizes a semiautomatic apparatus with the liquid and vapor chambers identical in volume to those used in Procedure A. The apparatus is suspended in a horizontal bath and rotated while attaining equilibrium. Either a Bourdon gage or pressure transducer can be used with this procedure. The interior surfaces of the liquid and vapor chambers are maintained free of water.

PRECISION

Based on an interlaboratory study involving 14 types of hydrocarbons and hydrocarbon-oxygenate blends and a total of 60 laboratories (RR-D02-1286), the precision of these two procedures was found as follows.

Procedure	Repeatability, kPa	Reproducibility, kPa
A	3.65	5.52
B with gage	4.00	5.38
B with transducer (Herzog)	2.14	2.90
B with transducer (Precision Scientific)	3.58	4.27

ASTM D5190

This test method is used for the determination of the total vapor pressure of air-containing, volatile petroleum products. It is suitable for testing samples with boiling points above 0°C that exert a vapor pressure between 7 and 172 kPa at a vapor to liquid ratio of 4:1. This method is suitable for testing gasolines that contain oxygenates. No account is made of dissolved water in the sample. This test method can be used for the calculation of a dry vapor pressure equivalent (DVPE) by means of a correlation equation. The calculated DVPE very closely approximates the dry vapor pressure that would be obtained on the same material when tested in accordance with ASTM D4953. This test method is more precise than ASTM D4953.

ANALYSIS

In this test method, the chilled sample cup of the automatic vapor pressure instrument is filled with a chilled sample and is coupled to the instrument inlet fitting. The sample is then automatically forced from the sample chamber to the expansion chamber where it is held until thermal equilibrium at 100°F is reached. In this process, the sample is expanded to five times its volume (4:1 vapor liquid ratio). The vapor pressure is measured by a pressure transducer. The measured vapor pressure is automatically converted to a DVPE value by the instrument.

PRECISION

Based on an interlaboratory study involving 14 types of hydrocarbons and hydrocarbon-oxygenate blends and a total of 60 laboratories, the following precision was obtained for this test method (RR-D02-1286).

Repeatability	2.48 kPa
Reproducibility	3.45 kPa

ASTM D5191

This is a more precise test method than ASTM D4953, uses a small sample size (1–10 mL), and requires about 7 min to complete. This test method is used for the determination of the total vapor pressure of air-containing, volatile petroleum products, including automotive spark-ignition engine fuels with or without oxygenates. It is suitable for testing samples with boiling points above 0°C that exert a vapor pressure between 7 and 172 kPa at a vapor to liquid ratio of 4:1. This test method is suitable for testing gasolines that contain oxygenates. No account is made of dissolved water in the sample. This test method can be used for the calculation of a DVPE by means of a correlation.

ANALYSIS

In this test method, a known volume of chilled, air-saturated sample is introduced into a thermostatically controlled, evacuated test chamber, or into a test chamber with a moveable piston that expands the volume after sample introduction, the internal volume of which is five times that of the total test specimen introduced into the chamber. After introduction into the test chamber, the test specimen is allowed to reach thermal equilibrium at the test temperature 37.8°C (100°F). The resulting rise in pressure in the chamber is measured using a pressure transducer sensor and indicator. Only total pressure measurements (sum of the partial pressure of the sample and the partial pressure of the dissolved air) are used in this test method, although some instruments can measure the absolute pressure of the sample as well. The measured total vapor pressure is converted to a DVPE by use of a correlation equation.

PRECISION

An interlaboratory study conducted included 11 laboratories and 15 different samples of ethanol-fuel blends containing 25, 50, and 75 volume percent ethanol. Based on that data, it is concluded that ASTM D5191 can be used for ethanol-fuel blends, such as Ed75 and Ed85 (ASTM D5798) and other ethanol-fuel blends with greater than 10 volume percent ethanol (RR-D02-1694). The precision of this test method has been found to be as follows (RR-D02-1619).

Container Size	Repeatability	Reproducibility
250 mL	1.47 kPa (0.21 psi)	2.75 kPa (0.40 psi)
1 L	0.006 (DVPE + B)	0.01014 (DVPE + B)

Note: Where DVPE is lPa (psi) as determined by Equation 1 in ASTM D5191 and B = 160 kPa (23.2 psi).

Water in Petroleum Products

SIGNIFICANCE

Water content in high quantities leads to lower overall viscosity and heat of combustion of pyrolysis liquid biofuel. Water content reduces the flame temperatures of pyrolysis liquid, which contributes to lower nitrogen dioxide emissions during combustion. Water content higher than given in the specification limit can cause phase separation, leading to a nonhomogenous mixture. Water is introduced into biodiesel during the final washing step of the production process and has to be reduced by drying. However, even very low water contents achieved directly after production do not guarantee that biodiesel fuels will still meet the specifications during combustion. Because biodiesel is hygroscopic, it can absorb water in a concentration of up to 1,000 mg/kg during storage. Once the solubility limits is exceeded (at about 1,500 mg/kg of water in fuels containing 0.2 % methanol), water separates inside the storage tank and collects at the bottom. Free water promotes biological growth, so that sludge and slime formation thus induced may cause blockage of fuel filters and fuel lines. Moreover, high water contents are also associated with hydrolysis reactions, partly converting biodiesel to free fatty acids, also linked to fuel filter blocking. Finally, corrosion of chromium and zinc parts within the engine and injection systems have been reported. Lower water concentrations, which pose no difficulties in pure biodiesel fuels, may become problematic in blends with fossil diesel because phase separation is likely to occur. For these reasons, maximum water content is included in biodiesel specifications.

Region	Water and Sediment Limit	Test Method	Water Limit	Test Method
Brazil	0.05 % vol max	ASTM D2709	None	None
European Union	None	None	500 mg/kg max	ISO 12937
United States	0.050 % vol max	ASTM D2709	None	None

SCOPE

There are a large number of ASTM test methods for the determination of water in petroleum products and lubricants. Many of these products have water as a criterion in their specifications. Out of these, water specification is required in the following biofuel-related products (Table 3.22). However, in most of cases, the precision is based on the experience of analyzing petroleum products, not biofuels.

TABLE 3.22 Biofuels Specifications for Water and Sediment Content

Biofuels Product Specification	Product Grade	Test Method	Limits, % vol max
ASTM D396	No. 1 S500, No. 1 S5000, No. 2 S500, No. 2 S5000	ASTM D2709	0.05
	No. 4 light, No. 4	ASTM D95 + ASTM D473	0.50
	No. 5 light, No. 5 heavy	ASTM D95 + ASTM D473	1.00
	No. 6	ASTM D95 + ASTM D473	2.00
ASTM D975	All grades	ASTM D2709 or ASTM D1796	0.05
ASTM D4806		ASTM E203 or ASTM E1064	1.0
ASTM D5797	All classes	ASTM E203	0.5
ASTM D5798		ASTM E203 or ASTM E1064	1.0
ASTM D5983		ASTM E203 or ASTM E1064	0.10
ASTM D6751	All grades	ASTM D2709	0.050
ASTM D7467	All grades	ASTM D2709	0.05
ASTM D7544	All grades	ASTM E203	30
ASTM D7666	All grades	ASTM D1796	2.0
ASTM D7862		ASTM E203 or ASTM E1064	1.0

Of these, ASTM D95, ASTM D473, ASTM D1796, and ASTM D2709 are based on physical separation—such as using centrifugation; the other two test methods ASTM E203 and ASTM E1064 are based on potentiometric titrations and are discussed in the next chapter (on chemical analysis).

Water and Sediment

Water can be found at some concentrations in all marketable fuels. Water can either be a separate phase (i.e., free water) or dissolved in the fuel. The amount of water that will dissolve in fuel is dependent on the temperature and chemical composition (including all blend components, additives, and impurities) of the fuel.

Sediment, otherwise known as particulates, can be found in virtually all marketplace fuels. These particulates come from a variety of sources, including piping, storage tanks, microbial contamination, fuel degradation products, and exposure to airborne particles during fuel transportation and handling. Engine/vehicle filtration systems are designed based on the expectation that fuel introduced to the engine's fuel tank will meet certain cleanliness levels.

Sediment or particulates in fuel can be measured in two fundamentally different ways: (1) mass of the total sediment or particulates per units volume or (2) particle size and count per unit volume. ASTM has developed a particle size rating procedure that describes particle size and related count information (ASTM D7619).

Appreciable amounts of water and sediment in a fuel oil tend to cause fouling of facilities for handling it and cause trouble in burner mechanisms. Sediment may accumulate in storage tanks and on filter screens or burner parts, resulting in obstruction of oil flow from the tank to the burner. Water in distillate fuels can cause corrosion of tanks and equipment, and it can produce emulsions in residual fuels. (See Table 2.4 for the tests allowed for this determination in various grades of fuel oils.)

Similar to fuel oils, water and sediment in triglyceride burner fuels (TBFs) tend to cause fouling of fuel-handling facilities and cause trouble in burner mechanisms. Sediment is likely to accumulate in storage tanks and on strainer screens or burner parts, resulting in obstruction of the oil flow from the tank to the burner. Water in the TBF can cause corrosion of the tanks and equipment, and it may cause an interphase layer. The presence of water in a burner fuel can also cause spattering in a burner flame and lead to damage of burner nozzles. Excessive water in TBF can extinguish the flame, leading to a flame-out.

Brazilian and U.S. biodiesel specifications combine water content and sediment in a single parameter, whereas European specifications treat water as a separate parameter with the sediment being treated under the total contamination property.

Water and Sediment in Middle Distillate Fuels

ASTM D473

ASTM D473 determines sediment in oils in the range from 0.01 to 0.40 mass percent by extracting the sample in hot toluene until the residue reaches a constant mass. In the sediment range of 0 to 0.4 %, the repeatability is 0.017 + 0.255X, and the reproducibility 0.033 + 0.255X, where X is the average percent of sediment result.

ASTM D1796

This test method is used for the determination of water and sediment from 0 to 30 % volume in fuel oils by the centrifuge method. With some types of the fuel oils, such as residual fuel oils or distillate fuel oils containing residual components, it is difficult to obtain water or sediment contents with this test method. In such cases, ASTM D95 or ASTM D473 may be used. Also, this test method may not be suitable for products that contain alcohols that are soluble in water. In such cases, ASTM D6304 may be used.

In this test method, equal volumes of fuel oil and water-saturated toluene are placed in each of the two cone-shaped centrifuge tubes. The solutions are maintained at 60 ± 1°C and spun for 10 min at a speed between 500 and 800 rcf. After centrifugation, the volume of the higher-density water and sediment layer at the bottom of the tube is read. The precision of this test method is depicted in Fig. 3.9.

ASTM D2709

ASTM D2709 is used as an indication of water and sediment in fuels having viscosities at 40°C in the range of 1.0 to 4.1 cSt and

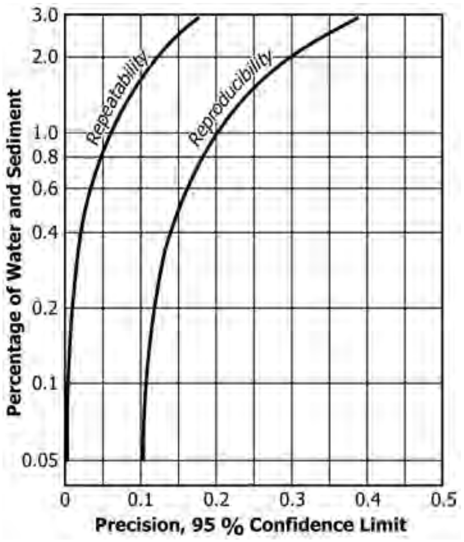


FIG. 3.9 Precision of ASTM D1796, *Standard Test Method for Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure)*.

densities in the range of 770 to 900 kg/m^3. Diesel fuel should never contain free water at the time it is introduced into a vehicle or equipment fuel tank, but such a result can be difficult to achieve when "warm" fuel, saturated with dissolved water, cools. Under those circumstances, free water (or ice at temperatures below 0°C) separates from the fuel.

Fuels corresponding to ASTM D975 Grades 1D and 2D, ASTM D2880 Grades 0-GT and 1-GT, and ASTM D3690 Grades 1-K and 2-K will usually fall in this viscosity and density range. ASTM D1796 is intended for higher viscosity fuels oils.

The ASTM D2709 centrifuge test method for the determination of free water and sediment provides a cost-effective screening procedure to determine relatively high levels of free water and sediment, but it cannot measure dissolved water. In contrast, the ASTM D6304 and ASTM E1064 test methods measure total water content (the sum of dissolved and free water).

In ASTM D2709, a 100-mL sample of fuel is centrifuged at a relative centrifugal force of 800 for 10 min at 21 to 32°C in a centrifuge tube readable to 0.005 mL and measurable to 0.01 mL. After centrifugation, the volume of water and sediment that has settled into the tip of the centrifuge is read to the nearest 0.005 mL and reported as the volumetric percent water and sediment by centrifuge. This test method has a precision of 0.014 volume percent repeatability and 0.041 volume percent reproducibility (RR-D02-1308).

Within a typical time span between production and use, biodiesel blends of FAME with petroleum diesel such as B5 and B20 are used by consumers within a few weeks of blending. However, many large industrial installations may store a biodiesel blend for many months before use. Exposure to air over months of storage can lead to natural oxidation of the biodegradable FAME. The by-products formed can precipitate and form a rancid gel-like mass in the storage tank. Upon use, the precipitate can accumulate on filters or may cause sticking of fuel pump parts. Some short-term stability tests are performed using ISO 14112 for FAME, ASTM D2274 for distillate fuel oil, and ASTM D4625 for middle distillate fuel storage stability at 43°C. McGinnis and Peyton have undertaken a detailed study of the sediment formed from a biodiesel B20 blend [14]. The gel-like sediment was formed in a blend of soy-based FAME and ULSD, which was stored under ASTM D4625 conditions without any antioxidant. However, no sediment formed in B100 without antioxidant addition or in B5 and B20 blends dosed with an antioxidant. GC and GC mass spectrometry analysis indicates that the majority of the sediment consists of a wide variety of polar oxygenated compounds, varying considerably in molecular weight, formed from oxidative addition and degradation by-products, as well as higher molecular weight oligomers.

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Abstract

There are about 55 test methods determining physical properties of biofuels. These are discussed with reference to their test significance, principle of analysis, and the test method precision.

Keywords

biofuels, physical test for biofuels

Chapter 4 | Chemical Analysis Test Methods for Biofuels

A number of chemical test methods are used for the characterization of biofuels. These are listed in Table 4.1, and the international equivalent of some of these test methods from the United Kingdom, the International Organization for Standardization (ISO), International Petroleum (IP), Germany (DIN), and Japan (JIS) are listed in Table 4.2. Similar to physical test methods, most of these have been inherited from applications for petroleum products, and their precision specifically for biofuels mostly is not known. More recently, several chemical test methods have been specifically developed for biofuels. See Table 4.1.

ASTM D7717, Preparation of Volumetric Blends of Denatured Fuel Ethanol and Gasoline Blendstocks for Laboratory Analysis

SIGNIFICANCE

ASTM D7717 provides instructions on making a volumetric blend of denatured fuel ethanol with gasoline blendstocks, such as reformulated gasoline blendstock for oxygenate blending or a conventional gasoline blendstock for oxygenate blending. Typically, denatured fuel ethanol is added to gasoline blendstocks after production. For laboratories to test a sample that is similar to the finished fuel available in the market, it is important to provide a laboratory practice that standardizes the preparation of a blend of denatured fuel ethanol and gasoline blendstock.

The laboratory blend shall be prepared volumetrically to yield a fuel similar to that produced for consumer use. When applicable, the blends shall meet requirements of CFR 40.80, Subpart D—Reformulated Gasoline.

SUMMARY

A specific measured volume of denatured fuel ethanol is blended with a gasoline blendstock to achieve a final blend of a predetermined percentage of denatured fuel ethanol. The blend shall be prepared with all components and the apparatus chilled. The total volume of the blend prepared is dependent upon the volume needed to complete the required testing.

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ASTM D664, ASTM D974, ASTM D2896, ASTM D3242, ASTM D3339, and ASTM D4739, Acid and Base Numbers

SIGNIFICANCE

Due to the presence of even small quantities of low-molecular weight organic acids—such as acetic acid in denatured fuel ethanol—are highly corrosive to many metals. Similarly, very dilute solutions of low-molecular weight organic acids, such as formic acid in M70–M85 fuels, are highly corrosive to many metals. It is therefore necessary to keep such acids at a very low level.

Acid number is used to determine the level of free fatty acids or processing acids that may be present in biodiesel or triglyceride burner fuels. Biodiesels with a high acid number have been shown to increase fueling system deposits and may increase the likelihood for corrosion and filter-plugging potential. Burner materials such as copper, brass, bronze, or light-gage carbon steel may have reduced service life due to corrosion when exposed to triglyceride burner fuels.

Acid number measures a different phenomenon for biodiesel than for petroleum-based diesel fuel. The acid number for biodiesel measures free fatty acids or degradation by-products not found in petroleum-based diesel fuel. Increased recycle temperatures in new fuel system designs may accelerate the fuel degradation, which could result in high acid values and increased filter-plugging potential. If mineral acids are used in the production process, their presence as acids in the finished fuels is also measured with the acid number. It is influenced on one hand by the type of feedstock used for fuel production and its degree of refinement. On the other hand, acidity can be generated during the production process. Acidity characterizes the degree of fuel aging during storage because it increases gradually due to degradation of biodiesel. Because of the possibility of the corrosive effect, the acidity is limited in biodiesel specifications.

Region	Limit	Test Method(s)
Brazil	0.80 mg KOH/g max	ABNT NBR 14448/EN 14104
European Union	0.50 mg KOH/g max	EN 14104
United States	0.50 mg KOH/g max	ASTM D664

Note: ABNT = Brazilian National Standards Organization (Associação Brasileira de Normas Técnicas); KOH = potassium hydroxide.

TABLE 4.1 List of ASTM Standards for Chemical Analysis of Biofuels

ASTM Standard	Description
ASTM D95	Water in Petroleum Products and Bituminous Materials by Distillation
ASTM D128	Analysis of Lubricating Grease
ASTM D381	Gum Content in Fuels by Jet Evaporation
ASTM D482	Ash from Petroleum Products
ASTM D525	Oxidation Stability of Gasoline (Induction Period Method)
ASTM D664 B[a]	Acid Number of Petroleum Products by Potentiometric Titration
ASTM D874	Sulfated Ash from Lubricating Oils and Additives
ASTM D974	Acid and Base Number by Color-Indicator Titration
ASTM D1319	Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption
ASTM D1541	Total Iodine Value of Drying Oils and Their Derivatives (withdrawn 2006)
ASTM D1613	Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products
ASTM D1959	Iodine Value of Drying Oils and Fatty Acid (withdrawn 2006)
ASTM D2896	Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration
ASTM D3227	(Thiol Mercaptan) Sulfur in Gasoline, Kerosine, Aviation Turbine, and Distillate Fuels (Potentiometric Method)
ASTM D3339	Acid Number of Petroleum Products by Semi-Micro Color Indicator Titration
ASTM D4739	Base Number Determination by Potentiometric Hydrochloric Acid Titration
ASTM D4815	Determination of MTBE, ETBE, TAME, DIPE, Tertiary-Amyl Alcohol and C1 to C4 Alcohols in Gasoline by Gas Chromatography
ASTM D5441	Analysis of Methyl Tert-Butyl Ether (MTBE) by Gas Chromatography
ASTM D5501[a]	Determination of Ethanol and Methanol Content in Fuels Containing Greater than 20 % Ethanol by Gas Chromatography
ASTM D5599	Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection
ASTM D5845[a]	Determination of MTBE, ETBE, TAME, DIPE, Methanol, Ethanol, and Tert-Butanol in Gasoline by Infrared Spectroscopy
ASTM D6423[a]	Determination of pHe of Denatured Fuel Ethanol and Ethanol Fuel Blends
ASTM D6584[a]	Determination of Total Monoglycerides, Total Diglycerides, Total Triglycerides, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography
ASTM D7318[a]	Existent Inorganic Sulfate in Ethanol by Potentiometric Titration
ASTM D7319[a]	Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography
ASTM D7328[a]	Determination of Existent and Potential Inorganic Sulfate and Total Inorganic Chloride by in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection
ASTM D7347[a]	Determination of Olefin Content of Denatured Ethanol by Supercritical Fluid Chromatography
ASTM D7371[a]	Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid-Infrared Spectroscopy (FTIR-ATR-PLS Method)
ASTM D7398[a]	Boiling Range Distribution of Fatty Acid Methyl Esters (FAME) in the Boiling Range from 100 to 615°C by Gas Chromatography
ASTM D7462[a]	Oxidation Stability of Biodiesel (B100) and Blends of Biodiesel with Middle Distillate Petroleum Fuel (Accelerated Method)
ASTM D7545	Oxidation Stability of Middle Distillate Fuels—Rapid Small Scale Oxidation Test (RSSOT)
ASTM D7576[a]	Determination of Benzene and Total Aromatics in Denatured Fuel Ethanol by Gas Chromatography
ASTM D7591[a]	Determination of Free and Total Glycerin in Biodiesel Blends by Anion Exchange Chromatography
ASTM D7717[a]	Practice for Preparing Volumetric Blends of Denatured Fuel Ethanol and Gasoline Blendstocks for Laboratory Analysis
ASTM D7754[a]	Determination of Trace Oxygenates in Automotive Spark-Ignition Engine Fuel by Multidimensional Gas Chromatography
ASTM D7795[a]	Acidity in Ethanol and Ethanol Blends by Titration
ASTM D7796[a]	Ethyl Tert-Butyl Ether (ETBE) by Gas Chromatography
ASTM D7797[a]	Determination of the Fatty Acid Methyl Esters Content of Aviation Turbine Fuel Using Flow Analysis by Fourier Transform Infrared Spectroscopy–Rapid Screening Method
ASTM D7798[a]	Boiling Range Distribution of Petroleum Distillates with Final Boiling Points up to 538°C by Ultra Fast Gas Chromatography (UF-GC)
ASTM D7806[a]	Determination of Fatty Acid Methyl Ester (FAME) Content of a Blend of Biodiesel and Petroleum-Based Diesel Fuel Oil Using Mid-Infrared Spectroscopy
ASTM D7875[a]	Determination of Butanol and Acetone Content of Butanol for Blending with Gasoline by Gas Chromatography
ASTM D7963	Determination of Contamination Level of Fatty Acid Methyl Esters in Middle Distillate and Residual Fuels Using Flow Analysis by Fourier Transform Infrared Spectroscopy—Rapid Screening Method
ASTM D7920[a]	Determination of Fuel Methanol (M99) and Methanol Fuel Blends (M10 to M99) by Gas Chromatography

(Continued)

ASTM Standard	Description
ASTM D7861[a]	FAME in Diesel Fuel by Linear Variable Filter Array Based Mid-IR (WK 24421)
ASTM D7923[a]	Water in Ethanol Blends (WK 41558)
ASTM E70	pH of Aqueous Solutions with the Glass Electrode
ASTM E203	Water Using Volumetric Karl Fischer Titration
ASTM E1064	Water in Organic Liquids by Coulometric Karl Fischer Titration
EN 14078[a]	Determination of Fatty Acid Methyl Ester (FAME) Content in Middle Distillates by Infrared Spectrometry
EN 14103[a]	Determination of Ester and Linolenic Acid Methyl Ester Contents in FAMEs
EN 14105[a]	Determination of Free and Total Glycerol and Mono-, Di-, and Triglyceride Contents of FAMEs
EN 14110[a]	Determination of Methanol Content of FAMEs
EN 14112[a]	Determination of Oxidation Stability (Accelerated Oxidation Test) of FAMEs
EN 15751[a]	Determination of Oxidation Stability of FAME Fuel and Blends with Diesel Fuel by Accelerated Oxidation Method
EN 15779[a]	Determination of Polyunsaturated Fatty Acid Methyl Esters (FAMEs) by Gas Chromatography

[a] These test methods were specifically developed for the analysis of biofuels.

TABLE 4.2 Equivalent Test Methods for Chemical Analysis of Biofuels

Analysis	ASTM	IP	ISO	DIN	JIS
Solvent Washed Gum	ASTM D381	131	6246	51784	K 2261
Ash	ASTM D482	4	6245		K 2272
Oxidation Stability	ASTM D525	40	7536	51780	
Cetane Number	ASTM D613	41	5165		K 2280
Acid Number	ASTM D664	177	6619		K 2501
Sulfated Ash	ASTM D874	163	3987	51575	K 2272
Acid Number	ASTM D974	139	6618	51558T1	K 2501
Hydrocarbon Types	ASTM D1319	156	3837	51791	K 2536
Boiling Range by Gas Chromatography	ASTM D2887	406	3924		K 2254
Base Number	ASTM D2896	276	3771		K 2501
Mercaptan Sulfur	ASTM D3227	342	3012		K 2276
Acid Number	ASTM D3242	354		51558T3	
Acid Number	ASTM D3339	431	7537		
Base Number	ASTM D4739	417	6619		K 2501
Oxygenates in Gasoline by Gas Chromatography	ASTM D5599	408			
FAME in Aviation Turbine Fuels	ASTM D7797	583			

Excerpted from [1]

The two test methods ASTM D664 and EN 14104 are not technically equivalent.

The acid number of biodiesel has been determined by volumetric titration with potentiometric and colorimetric detection [2,3].

ASTM D974 and EN 14104 note the use of indicators for the determination of the end point (p-naphtholbenzein and phenolphthalein, respectively), but some studies have shown that the use of acid-base indicators can lead to an increase of about 10 % to 20 %

Parameter	ASTM D664	EN 14104
Scope	Petroleum products and lubricants	FAME
Method	Dissolve the sample in a mixture of toluene, isopropanol, and water. Titrate with alcoholic KOH to the end point of a glass indicating electrode.	Dissolve the sample in diethyl ether and ethanol. Titrate with KOH in ethanol to a phenolphthalein indicator end point.
Report	To three significant figures	To three significant figures
Repeatability	0.07 at 0.5 mg KOH/g	0.02 mg KOH/g
Reproducibility	0.21 at 0.5 mg KOH/g	0.06 mg KOH/g

Note: KOH = potassium hydroxide.

in the real value of the acid number of the samples [4]. Additionally, a mixture of toluene, 2-propanol, and water as solvent may contribute to an increase in the acid number results [3]. The determination of acid number by potentiometric titrations has many advantages over traditional colorimetric titrations, such as the analysis of colored samples, less error in the end-point detection, and the possibility of making the titration automatically [3].

Recently, the acid number test method for potentiometric titration (ASTM D664) was modified as Part B specifically for biodiesels. The main change consisted of reducing the titrant concentration by a factor of ten as well as the type of solvent used.

The base number of new and used petroleum products, particularly lubricants, is routinely determined in lubricant laboratories. The relative amounts of basic constituents present as additives in lubricants can be determined by titrating with acids. ASTM D974, ASTM D2896, and ASTM D4739 are used for this determination. Different base number methods may give different results for the same sample. The test method should not be arbitrarily changed because the new values may not be compatible with the historical data. ASTM D2896 remains the preferred test method for base number due to its superior precision, definitive end point, and large historical database.

SCOPE

Acid number test method ASTM D664B was developed for biodiesel analysis. The applicability of other acid number test methods (ASTM D974, ASTM D3242, and ASTM D3339) has not been specifically demonstrated for biofuels. The applicability of base number ASTM D974, ASTM D2896, or ASTM D4739 also has not been demonstrated specifically for biofuels.

Specification	Test Method	Alternative Test Methods	Acid Number, mg KOH/g	Base Number, mg KOH/g
ASTM D6751	ASTM D664	ASTM D974 or ASTM D3242	0.50	NA
ASTM D7467	ASTM D664		0.3	NA
ASTM D7666	ASTM D664	ASTM D974 or ASTM D3339	30.0	NA

Note: NA = no specification limits.

Goncalves et al. [5] have tested acid number determination of biodiesel by potentiometric titration using different methods. Three different matrices—soy/animal fat, castor oil, and palm oil—were used along with three different analytical methods based on automatic volumetric titration with potentiometric detection. One method tested was ASTM D664 B, and the other two were similar in format but changes were made in the solvent (2-propanol by a mixture of toluene, 2-propanol, and water with a volumetric ratio of 100:99:1) or in the filling solution (lithium chloride potassium chloride) of the combined glass electrode used in the detection. Basically, it was observed that there was a difference of about 3.1 % between the acid numbers obtained by the three methods. ASTM D664 B had a repeatability of 4.4 % for soy/animal fat biodiesel, 3.9 % for castor biodiesel, and 9.8 % for palm biodiesel [5].

The three variations produced results with some differences among them. For the soy/animal biodiesel, there was a difference of 2.3 % between the acid numbers determined by Methods 1 and 2, and 6.4 % between Methods 1 and 3. For the castor biodiesel, the difference was 3.2 % between Methods 1 and 2 and 1.0 % between Methods 1 and 3. The palm biodiesel had a difference of 1.5 % and 4.3 % between Methods 1 and 2 and between Methods 1 and 3, respectively. In general, a difference of 3.1 % was observed between the acid numbers obtained from different methods. For all of the biodiesels, the acid number showed a little bias, Method 2 always presented the lowest value, and Method 3 had the highest results [5].

The definitions of terms used are as follows:

- *Acid number* is the quantity of base, expressed in milligrams of KOH per gram of sample that is required to titrate a sample in the solvent to a green/green-brown end point using p-naphtholbenzein indicator solution in ASTM D974 or from its initial meter reading to a meter reading corresponding to a freshly prepared nonaqueous buffer solution or a well-defined inflection point as specified in ASTM D664. The acid numbers obtained by test methods ASTM D664, ASTM D974, or ASTM D3339 may or may not be numerically the same.
- *Base number* is the quantity of a specified acid, expressed in terms of the equivalent number of milligrams of KOH per gram of sample, required to titrate a sample to a specified end point using a specified detection system. Three test methods can be used for this analysis: ASTM D974, ASTM D2896, and ASTM D4739. The results obtained by these three test methods for base number may or may not be numerically the same.

ASTM D664 B

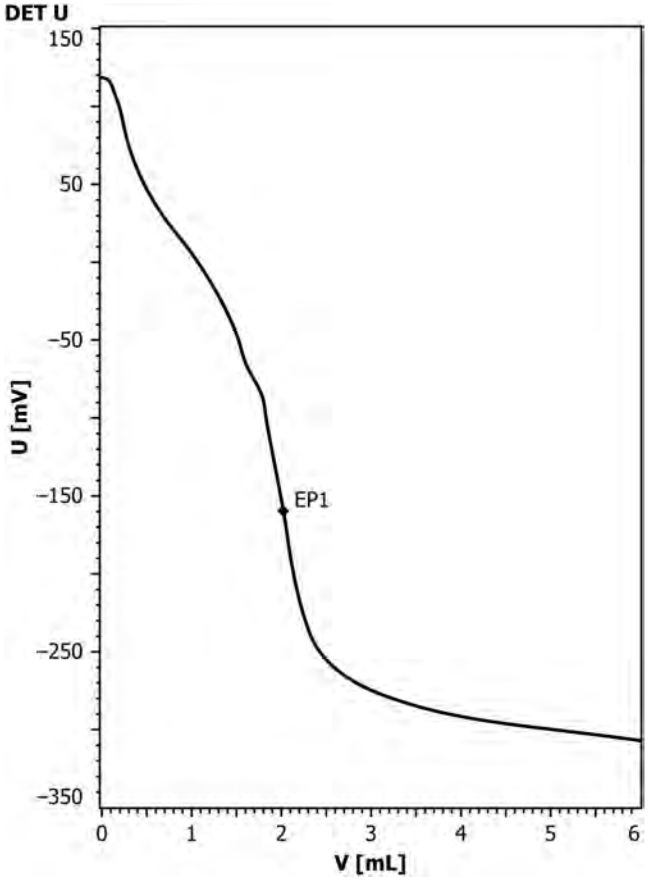
This test method was specifically developed for the analysis of biodiesel and biodiesel blends with low acidity and slightly different solubility and requires the use of an automatic titrator with an automatic end-point-seeking capability. The sample is dissolved in a mixture of toluene and isopropyl alcohol (IPA) containing a small amount of water and titrated potentiometrically with an alcoholic KOH solution using a glass-indicating electrode and a reference electrode or combination electrode. The meter readings can be plotted manually or automatically against the respective volumes of the titrating solution, and the end points are taken only at well-defined inflections in the resulting curve. When no definite inflections are obtained, the end points are taken at meter readings corresponding to those found for freshly prepared nonaqueous acidic and buffer solutions. See Fig. 4.1 for an example of a titration curve of a biodiesel sample.

Multiple titration inflection points are often found during this analysis that are associated with organic acids that form over time due to the oxidation of biodiesel over prolonged periods of storage. The volume of titrant for the last well-defined end point should be used to calculate total acidity.

ASTM D974

This test method requires the sample to be dissolved in a mixture of toluene and IPA containing a small amount of water, and the resulting single-phase solution is titrated at room temperature with a standard alcoholic base or alcoholic acid solution,

FIG. 4.1 Titration curve of a biodiesel sample by ASTM D664, *Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration.*



respectively, to the end point indicated by color change of the added p-naphtholbenzein solution (orange in acid and green-brown in base). For determining base number, the titration is carried out using standard dilute hydrochloric acid and titrated until the green-brown color changes to orange.

ASTM D2896

This test method is used to determine the base number of petroleum products by titration with perchloric acid in glacial acetic acid. Two procedures under this test method use different titration solvent volumes and sample weights. The sample is dissolved in an essentially anhydrous mixture of chlorobenzene and glacial acetic acid and titrated with perchloric acid in glacial acetic acid using a potentiometric titrimeter. A glass-indicating electrode and reference electrode are used. The end point is taken at the inflection in the resulting titration curve. Procedure A uses 120 mL and Procedure B uses 60 mL of titration solvent. Additionally, the two procedures use different equations for the calculation of appropriate sample weights.

ASTM D3242

ASTM D3242 determines acidity in aviation turbine fuel in the range from 0.000 to 0.100 mg KOH/g. In this test method, the sample is dissolved in a mixture of toluene and IPA containing a small amount of water. The solution is then titrated at room temperature under a nitrogen atmosphere with standard KOH in IPA from orange to the stable green color of the added p-naphtholbenzein indicator.

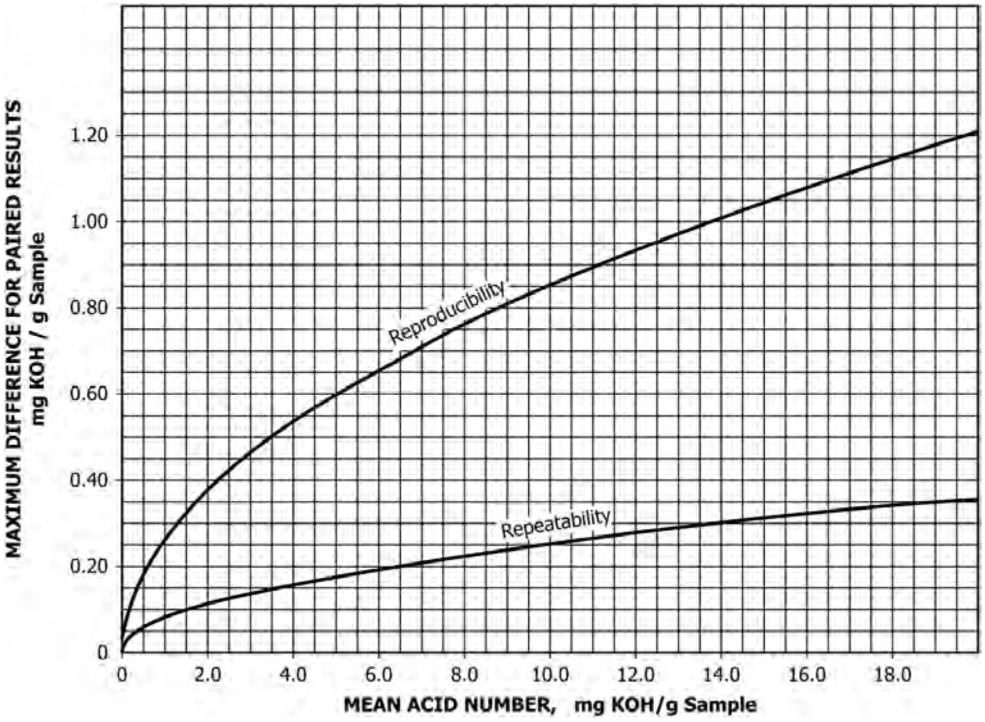
ASTM D3339

This test method requires the sample to be dissolved in a solvent mixture of toluene, IPA, and a small amount of water. The solution is then titrated at room temperature under a nitrogen atmosphere with standard KOH in IPA to the stable green color of the added p-naphtholbenzein indicator. This method requires substantially less sample than is required in ASTM D664 or ASTM D974. The results obtained using this method have been found to be numerically the same as those obtained by ASTM D3339. (See Fig. 4.2 for the repeatability and reproducibility using this test method.)

ASTM D4739

ASTM D4739 covers the determination of basic constituents of petroleum products and new and used lubricants. It shall be used exclusively for the purpose of tracking base number loss as oil

FIG. 4.2 Precision of ASTM D3339, *Standard Test Method for Acid Number of Petroleum Products by Semi-Micro Color Indicator Titration*.



proceeds in service. In many cases, base number test methods ASTM D2896 and ASTM D4739 will provide different results. In this test method, a sample is dissolved in a mixture of toluene, isopropanol, chloroform, and a small amount of water and titrated potentiometrically with alcoholic hydrochloric acid solution. An example of the titration curves obtained using ASTM D4739 for acid number determination is shown in Fig. 4.3. The test results of this procedure are obtained by a titration mode of fixed increment

FIG. 4.3 Titration curves of acid number by ASTM D4739, *Standard Test Method for Base Number Determination by Potentiometric Hydrochloric Acid Titration*.

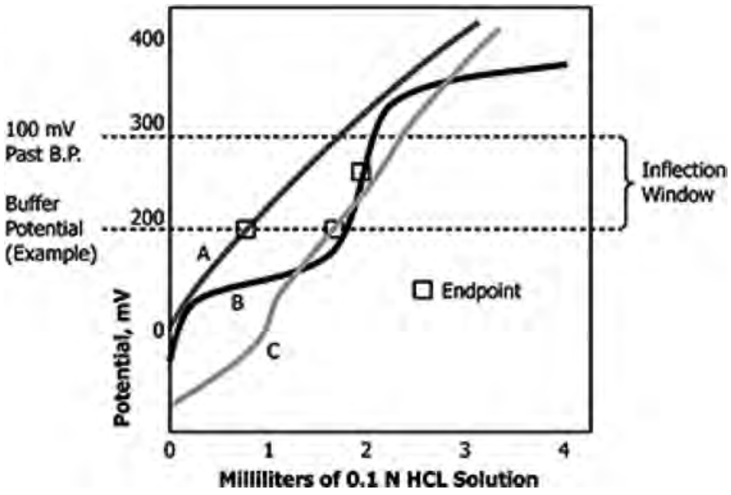


TABLE 4.3 Comparison of ASTM Test Methods for Acid Number Determination

Area	ASTM D664	ASTM D974	ASTM D3339	ASTM D4739
Significance	Determines acidic constituents. Indicates relative changes in oil under oxidizing conditions but cannot predict corrosion behavior.	Same as in ASTM D664.	Same as in ASTM D664. Mainly used for small amounts of sample from oxidation test method ASTM D943.	Same as in ASTM D664.
Scope	Fresh and used oils. Results may not be same as by ASTM D974 or ASTM D3339.	Fresh and used oils. Results same as by ASTM D3339 but not as by ASTM D664.	Fresh or used oils for very small samples. Results same as by ASTM D3339 but not as by ASTM D664.	Fresh and used oils. Results may not be same as those obtained by ASTM D664, ASTM D974, or ASTM D3339.
Procedure	Sample is dissolved in toluene + IPA + water. Titrated potentiometrically with alcoholic KOH. Inflection or buffer end points.	Same as in ASTM D664 except p-naphtholbenzein used as color indicator.	Same as in ASTM D664.	Sample is dissolved in toluene + IPA + chloroform + water. Titrated potentiometrically with alcoholic KOH. Inflection or buffer end points.
Limitations	Used oils change in storage. Representative sampling is difficult with sediment in used oils.	Difficulty with highly colored oils. (Use ASTM D664 instead.) Used oils change in storage. Representative sampling is difficult with sediment in used oils.	Same as in ASTM D974.	Same as in ASTM D664.
Precision	See Table 4.5.	See Table 4.5.	See Table 4.5.	See Table 4.5.

and fixed time additions of the titrant. ASTM D2896 is considered a better base number method than ASTM D4739 because it titrates both weak and strong bases. Historically, for both new and used lubricants, ASTM D2896 gives a higher value for base number than ASTM D4739.

A comparison of multiple test methods for determining acid numbers and base numbers is given in Tables 4.3 and 4.4, respectively.

PRECISION

Precision for acid and base number methods is given in Table 4.5. The estimates for ASTM D664 B are for biodiesel samples. The rest of the precision estimates are for fresh and used lubricating oils and additives. At present, for these test methods, no such information is available for biofuels.

Precision for ASTM D2896 and ASTM D4739 is given in Table 4.6.

TABLE 4.4 Comparison of ASTM Test Methods for Base Number Determination

Area	ASTM D974	ASTM D2896	ASTM D4739
Significance	Determines organic and inorganic bases, amino compounds, salts of weak acids, basic salts of polyacidic bases, and heavy metal salts.	Same as in ASTM D974.	Same as in ASTM D974.
Scope	Fresh and used oils	Fresh and used oils	Fresh and used oils
Procedure	Sample is dissolved in toluene + IPA and titrated with alcoholic hydrochloric acid (HCl). Uses p-naphtholbenzein as color indicator.	Sample is dissolved in chlorobenzene + glacial acetic acid and titrated with perchloric acid in glacial acetic acid. Uses potentiometric titrator. Fast equilibration. Continuous addition of titrant. Inflection end point.	Sample is dissolved in IPA + chloroform + toluene + 5 % water and titrated with alcoholic HCl. Uses potentiometric titrator. Slow equilibration. Fixed additions of titrant. Inflection or buffer end point.
Limitations	Not suitable for measuring components of many basic additive type lube oils. Dark colored oils cannot be analyzed by this method.	With strongly overbased oil additives and nitrogenous polymeric compounds higher results may be obtained.	Chloroform is a suspected carcinogen. Method cannot be used for samples with base numbers higher than 70.
Advantages		Gives better precision. Gives good titration breaks. Results are not dependent on sample weights. Good agreement with calculated results even with overbased oils. Complete titration of weak bases is obtained.	Gives better precision. Gives well-defined inflection breaks. Easy to dissolve the samples.
General		Results obtained are similar to those obtained by ASTM D664 for many materials but usually higher. No constant correlation between ASTM D664 and ASTM D2896 for all products but consistent for same product.	Results obtained are similar to those obtained by ASTM D664 for many materials but usually higher. No constant correlation among ASTM D664, ASTM D2896, or ASTM D4739 for all products but consistent for same product.
Precision	See Table 4.5	See Table 4.5	See Table 4.5

TABLE 4.5 Precision for Acid and Base Numbers in Lubricating Oils

Test Method	ASTM D664B[a]	ASTM D974			ASTM D3242	ASTM D3339
Range		0.00–0.1; 0.1–0.5; 0.5–2.0			0.001 to 0.100	0.05 to 20.0
Repeatability	$0.264 \times 10^{-1}\ X^{0.4}$	0.03	0.05	0.10	$0.0132\ X^{0.5}$	$0.08\ (X)^{0.5}$
Reproducibility	$0.177\ X^{0.4}$	0.04	0.08	15 %	$0.0406\ X^{0.5}$	$0.27\ (X)^{0.5}$
Bias	Not known	Not known			Not known	Not known

Note: Where X is the average of two results. [a]RR-D02-1727 (2009).

TABLE 4.6 Precision for Base Number Test Methods

Test Method	Samples	Range	Repeatability	Reproducibility	Research Report
ASTM D2896 Procedure A	All oils with forward titration	6 to 70	3 % of mean	7 % of mean	RR-D02-1011
	Used oils with back titration	5 to 27	24 % of mean	32 % of mean	
ASTM D2896 Procedure B	All oils with forward titration		5 % of mean	7 % of mean	RR-D02-1237
ASTM D2896 Alternative Solvents X2	Fresh and used oils	0.5 to 400	6.2 % of mean	16.2 % of mean	RR-D02-1345
ASTM D4739	Fresh oils	Up to 250	$0.11\ (X + 0.0268)^{0.79}$	$0.42\ (X + 0.0268)^{0.79}$	RR-D02-1217
ASTM D4739	Used oils		$0.22\ X^{0.47}$	$1.53\ X^{0.47}$	RR-D02-1638

Note: Where X is the average of two results.

ASTM D1613, Acidity in Volatile Solvents

SIGNIFICANCE

In Europe, acidity is a concern for ethanol manufactured from wine alcohol because of the complex acids that may be produced. This is why the pHe method (ASTM D6423) was developed. The acidity titration correlates with buffering strength rather than acetic acid content. Very dilute aqueous solutions of low-molecular weight organic acids such as acetic acid are highly corrosive to many metals. It is therefore necessary to keep such acids at a very low concentration. Acidity of butanol blended with gasoline for use as automotive spark-ignition engine fuel is measured by ASTM D1613 and is reported as acetic acid mass percent.

ASTM D1613 covers the determination of total acidity as acetic acid, in concentrations below 0.05 %, in organic compounds and hydrocarbon mixtures used in paint, varnish, and lacquer solvents and diluents. It is known to be applicable to such mixtures as low- molecular weight saturated and unsaturated alcohols, ketones, ethers, esters, hydrocarbon diluents, naphtha, and other light distillate petroleum fractions.

The maximum specification for acidity in the United States (0.0074 mass percent) is slightly higher than that for the European Union (EU) (0.007 mass percent). Brazil's specification is roughly half of this value (0.0038 mass percent) due to the higher concentration of ethanol in their gasoline blends [6].

ANALYSIS

Test methods for measuring acidity for the United States (ASTM D1613), the EU (EN 15491), and Brazil (NBR 9866) are all quite similar, involving a water-ethanol titration, and should produce quite similar results. The Brazilian National Standards Organization (ABNT) method may have a slight bias because a different indicator is used in the titration [6]. This test method can give erroneously high acidity results in ethanol due to dissolved carbon dioxide (CO_2) interference.

In this test method, the specimen is mixed with either an equal volume of water or an equal volume of alcohol and then is titrated with an aqueous sodium hydroxide (NaOH) solution to the phenolphthalein end point.

INTERFERENCE

It has been observed that in a CO_2-rich laboratory environment, such as those in an ethanol-from-corn manufacturing facility, a 0.5 % CO_2 level or greater can cause a positive interference (higher results) when using this test method. If the laboratory has this level of CO_2 or greater, it is recommended that proper precautions should be taken to minimize the CO_2 interference.

PRECISION

Based on an interlaboratory study (RR-D01-1041), the following precision is expected.

Repeatability	0.0003 % absolute
Reproducibility	0.0005 % absolute

ASTM D7795, Acidity in Ethanol and Ethanol Blends

SIGNIFICANCE

Because ASTM D1613 was approved only for paint, varnish, and similar materials, a comparable method was developed to analyze ethanol blends with gasoline. Also, although ASTM D1613 allowed for purging of samples to remove interfering dissolved carbon dioxide, it did not explicitly require this step, which could lead to erroneously high results, in addition, results changed over time as the product naturally off-gassed carbon dioxide. Based on experimentation, the optimum purge conditions were determined to be a rate of 400 mL/min for 120 s.

This test method measures acidity as acetic acid in ethanol or ethanol blends with gasoline ranging from E95 to E30 quantitatively. Denatured fuel ethanol may contain additives such as corrosion inhibitors and detergents as well as contaminants from manufacturing that can affect the acidity of finished ethanol fuel. Very dilute aqueous solutions of low molecular mass organic acids such as acetic acid are highly corrosive to many metals. It is important to keep such acids at a very low level.

Acceptable levels of acidity in ethanol or ethanol blends can vary with different specifications but in general is below 200 mg/kg. Knowledge of the acidity can be required to establish whether the product quality meets a specification.

ANALYSIS

Commonly available grades of denatured ethanol (such as in ASTM D4806) and ethanol blends with gasoline ranging from E95 to E30 may be directly analyzed by this test method without any sample preparation. Two procedures are used: the referee method with potentiometric titration and another with color end-point titration.

In these procedures, the samples are purged with nitrogen prior to and during titration for the elimination of carbon dioxide, and then a known amount of ethanol or ethanol blend sample is analyzed potentiometrically using a monotonic or dynamic end-point titrant addition as specified in Test Method A, or by color end-point titration as specified in Test Method B, using a base NaOH solution. Acid content is calculated as milligrams of acetic acid per kilogram of sample.

INTERFERENCE

Basic solutions will absorb carbon dioxide from the air to produce carbonate ions in the titrant and will change the concentration of the titrant. Care should be taken to minimize exposure of basic titrants to the air as much as possible. Verify the concentration of the titrant (i.e., standardize the titrant against standard potassium hydrogen phthalate) frequently enough to detect concentration changes of 0.0005 M and especially if prolonged exposure to the air occurs. Minimize the exposure of ethanol or ethanol blend samples to the air to avoid contamination from carbon dioxide.

PRECISION

Based on a limited interlaboratory study among three laboratories analyzing 18 samples each by both Test Methods A and B (RR-D02-1754), the following repeatability was obtained in 2011. The levels of acidity varied from about 10 to 265 mg/kg.

Potentiometric Titration	$0.78\ X^{0.5}$
Colorimetric Titration	$0.023\ (X + 200)$

In a follow-up interlaboratory study (ILS), seven laboratories analyzed three blends of gasoline with ethanol, E30, E60, and denatured ethanol. These blends were measured pure and with an addition of a known acetic acid spike of 100 and 200 mg/kg. The levels of acidity tested ranged from 8.5 to 268 mg/kg for potentiometric titration and 10.5 to 265 mg/kg for color end-point titration. The results obtained in this ILS are given in Table 4.7 (WK#44531).

It is not clear from the ILS report whether any statistical outliers have been deleted from the final calculations. Even a casual

TABLE 4.7 Interlaboratory Study Results for Acidity in Fuel Ethanol Potentiometric Titration (Method A)

Lab	E30	E30 + 100	E30 + 200	E60	E60 + 100	E60 + 200	E98	E98+ 100	E98+ 200
1	5.0; 5.1	97.7; 97.1	192.2; 193.8	7.8; 6.7	100.2; 100.5	200.6; 196.6	9.1; 6.7	102.6; 99.3	194.6; 195.6
2	6.0; 5.8	106.5; 104.8	248.5; 266.2	8.3; 8.8	106.2; 107.5	205.0; 206.5	12.4; 12.4	107.2; 115.5	206.8; 206.5
3	5.3; 5.3	99.3; 101.4	195.2; 198.1	6.5; 7.2	101.7; 101.6	196.8; 202.8	7.5; 9.7	102.1; 102.3	198.1; 203.3
8	5.0; 4.9	95.5; 93.9	186.0; 187.7	7.4; 6.8	97.8; 96.7	185.8; 187.6	10.1; 10.7	99.3; 99.3	191.6; 189.5
9	5.0; 5.2	100.5; 99.9	197.4; 197.7	6.7; 6.6	101.8; 102.7	196.5; 197.4	6.5; 6.7	102.3; 101.4	195.3; 196.7
10	5.3; 5.3	100.4; 100.9	198.7; 198.9	7.6; 7.3	107.1; 103.3	199.1; 199.1	9.2; 9.1	106.1; 101.8	207.2; 199.4
12	4.7; 4.9	47.3; 38.7	51.4; 40.7	6.4; 6.6	104.5; 104.6	200.5; 201.0	6.2; 3.7	103.1; 103.3	200.0; 200.1
Color indicator titration (Method B)									
4	7.6; 8.0	100.3; 105.2	192.9; 193.4	13.1; 13.5	103.7; 103.4	197.0; 194.6	16.6; 20.9	103.7; 103.9	193.1; 196.5

(Continued)

TABLE 4.7 *(Continued)*

Lab	E30	E30 + 100	E30 + 200	E60	E60 + 100	E60 + 200	E98	E98+ 100	E98+ 200
5	18.0; 12.2	134.9; 112.3	208.0; 192.8	21.8; 20.0	88.6; 117.6	192.0; 218.2	26.0; 33.3	120.4; 110.3	189.4; 218.9
6	11.0; 11.0	115.0; 110.0	200.9; 200.9	20.0; 24.0	117.0; 115.0	206.7; 206.7	25.0; 25.0	113.0; 112.0	202.9; 202.9
7	11.5; 11.0	113.0; 113.6	202.1; 208.7	20.5; 20.0	120.5; 119.1	213.7; 212.2	26.0; 30.0	119.1; 118.6	211.2; 213.7
11	9.5; 10.8	105.4; 102.7	190.7; 192.6	17.2; 18.9	107.8; 107.2	193.7; 194.4	19.5; 19.3	105.7; 105.9	194.3; 191.1
13	16.0; 11.0	112.6; 111.0	207.2; 200.9	16.3; 24.0	123.4; 115.0	217.8; 206.9	22.2; 25.0	119.4; 112.0	216.2; 202.9
14	10.1; 20.1	109.8; 106.1	162.5; 186.3	19.8; 17.5	123.9; 115.3	213.5; 227.8	19.8; 17.7	119.8; 120.1	215.7; 217.1

perusal of Table 4.7 shows very clear potential outliers and wide divergence between the results for Methods A and B for the same samples. The precision of the method is calculated as:

ASTM D7795	Repeatability	Reproducibility
Method A (Potentiometric)	$0.1965\ X^{0.67}$	$0.4796\ X^{0.67}$
Method B (Colorimetric)	$2.5127\ X^{0.4189}$	$3.4181\ X^{0.4189}$

Note: Where X is the average of two determinations.

Based on these precision estimates, the following deviations will be observed at 10 and 100 mg/kg acidity, which are quite unacceptable in commerce and given the variability between the two methods for the same parameter.

	Repeatability		Reproducibility	
Acidity, mg/kg	Method A	Method B	Method A	Method B
10	0.92	6.59	2.24	8.97
100	4.30	17.3	10.5	23.5

The ASTM D6708 statistical analysis of the comparative data shows that Method B gives higher results for acidity than Method A (about 10 mg/kg). Repeatability of Method B is 5 times higher and reproducibility 2.6 times higher than that of Method A. An F-test for variance also shows the precisions of two methods are significantly different. Potentiometric data are preferred.

Alcohol

SIGNIFICANCE

The reason for controlling the alcohol content of a fuel is to limit the level of unreacted alcohol remaining in the finished fuel. This can be measured directly by the volume percent of alcohol or indirectly through a high flash point value. The flash point specification, when used for alcohol control for biodiesel, is intended to be 100°C minimum, which has been correlated to 0.2 volume percent alcohol. Typical values are above 160°C. The flash point specification has been set at a 130°C minimum to ensure an actual value of 100°C minimum due to the high variability with flash point test method ASTM D93 as the flash point approaches 100°C.

All three ethanol-producing regions in the world describe ethanol and higher alcohol content parameters differently. ASTM specifies a minimum ethanol content (93.9 volume percent), and ABNT specifies a minimum content only for ethanol that is not produced by the fermentation of sugarcane (99.6 volume percent). The Center for European Normalization (CEN) specifies a minimum ethanol plus higher alcohol (C3–C5) content at 98.8 volume percent. ABNT specifies a total alcohol content minimum limit at 99.6 volume percent. All specify the ASTM D5501 gas chromatographic test method for ethanol measurement. Brazil only applies it to ethanol not produced by the fermentation of sugarcane. For sugarcane-based ethanol, Brazil uses density because the product contains very little other alcohol. The EU does not directly specify ethanol but instead specifies ethanol + C3–C5 alcohols and methanol limits [6].

Methanol and ethanol can cause fuel system corrosion, low lubricity, and adverse effects on injectors due to its high volatility, and both are harmful to some materials in fuel distribution and vehicle fuel systems. Both methanol and ethanol affect the flash point of esters. For these reasons, methanol and ethanol are controlled in the specifications.

Region	Limit, % m/m	Test Method(s)
Brazil	0.50	NBR 15343; EN 14110
European Union	0.20	EN 14110
United States	0.2	EN 14110

Both the ASTM and CEN specifications have precise limits on methanol but not Brazil. The CEN specification (1.0 volume percent max) is twice that of the ASTM limit (0.53 volume percent max), but this is due to the maximum quantity of ethanol permitted in the finished blend with gasoline—5 volume percent for the EU and 10 volume percent for the U.S. test method. ASTM D5501 is used in the United States for methanol content, and EC/2870/2000 Method III is used in the EU. Both are gas chromatographic test methods [6].

ASTM D4815, Alcohols and Ethers in Gasoline

SIGNIFICANCE

Ethers, alcohols, and other oxygenates can be added to gasoline to increase octane number and to reduce emissions. Type and concentration of various oxygenates are specified and regulated to ensure acceptable commercial gasoline quality. Drivability, vapor pressure, phase separation, exhaust, and evaporative emissions are some of the concerns associated with oxygenated fuels. ASTM D4815 is applicable to quality control in the production of gasoline and for the determination of deliberate or extraneous oxygenate additions or contamination. It covers the determination of ethers and alcohols in gasoline by gas chromatography (GC). Specific compounds determined are methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), di-isopropyl ether (DIPE), methanol, ethanol, isopropanol, n-propanol, isobutanol, tert-butanol, sec-butanol, n-butanol, and tert-pentanol.

SCOPE

Individual ethers are determined from 0.20 to 20.0 mass percent. Individual alcohols are determined from 0.20 to 12.0 mass percent. At concentrations <0.20 mass percent, it is possible that hydrocarbons may interfere with several ethers and alcohols. Alcohol-based fuels such as M-85 and E-85, MTBE product, ethanol product, and denatured alcohol are specifically excluded from this test method. The methanol content of M-85 fuel is considered beyond the operating range of the system. Benzene, although detected, cannot be quantified by this test method and must be analyzed by alternate methodology, such as ASTM D3606.

ASTM D4814 for automotive spark-ignition engine fuel contains limits on oxygenate content as measured by ASTM D4815, ASTM D5599, or ASTM D5845.

ANALYSIS

In this test method, an appropriate internal standard, such as 1,2-dimethoxyethane, is added to the sample, which is then introduced into a gas chromatograph equipped with two columns and a column switching valve. The sample first passes onto a polar 1,2,3-tris-2-cyanoethoxyproppane column, which elutes lighter hydrocarbons to vent and retains the oxygenated and heavier hydrocarbons. After methylcyclopentane, but before DIPE and MTBE elute from the polar column, the valve is switched to backflush the oxygenates onto a wall-coated open tubular (WCOT) nonpolar column. The alcohols and ethers elute from the nonpolar column in the order of their boiling points and before elution of any major hydrocarbon constituents. After benzene and TAME elute from the nonpolar column, the column switching valve is switched back to its original position to backflush the heavy hydrocarbons. The eluted components are detected by a flame ionization or thermal conductivity detector. The detector response is proportional to the component concentration. The recorded peak areas are measured, and the concentration of each component is calculated with reference to the internal standard.

See Fig. 4.4 for a representative gas chromatogram of an analysis of oxygenates in gasoline and Fig. 4.5 for a chromatogram showing hydrocarbon interference. In Fig. 4.4, the gasoline used had 10 volume percent olefins. Each alcohol and ether was added at 0.1 mass percent into the 10 volume percent olefin gasoline, and the resulting chromatogram was compared with that obtained with no ethers or alcohols added.

PRECISION

The precision of this test method is shown in Table 4.8 from RR-D02-1296.

FIG. 4.4 Analysis of oxygenates in gasoline by ASTM D4815, *Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE,Tertiary-Amyl Alcohol and C1 to C4 Alcohols in Gasoline by Gas Chromatographys*.

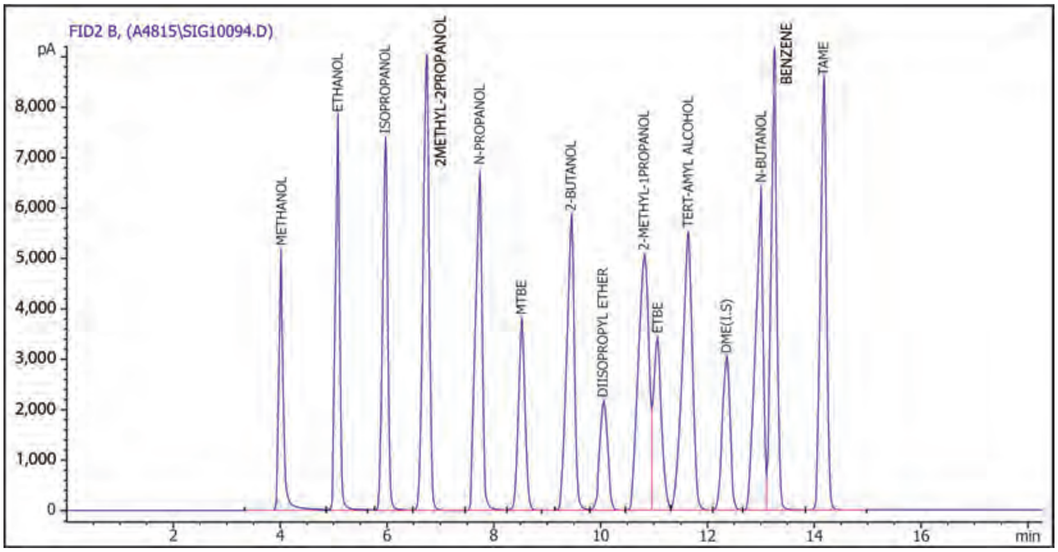


FIG. 4.5 Chromatogram showing hydrocarbon interference in analysis of oxygenates in gasoline using ASTM D4815, *Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE,Tertiary-Amyl Alcohol and C1 to C4 Alcohols in Gasoline by Gas Chromatography.*

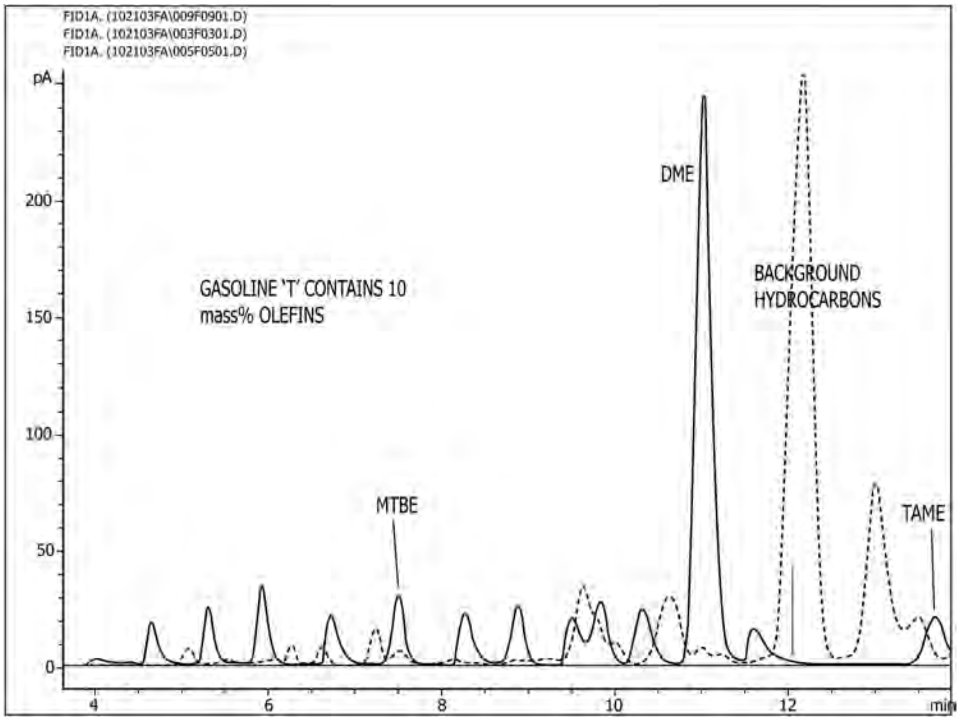


TABLE 4.8 Precision of ASTM D4815 for Oxygenates in Gasoline

Component	Repeatability	Reproducibility
Methanol	0.09 $X^{0.59}$	0.37 $X^{0.61}$
Ethanol	0.06 $X^{0.61}$	0.23 $X^{0.57}$
Isopropanol	0.04 $X^{0.56}$	0.42 $X^{0.67}$
tert-Butanol	0.04 $X^{0.56}$	0.19 $X^{0.67}$
n-Propanol	0.003 $X^{0.57}$	0.11 $X^{0.57}$
MTBE	0.05 $X^{0.56}$	0.12 $X^{0.67}$
Sec-Butanol	0.003 $X^{0.61}$	0.44 $X^{0.67}$
DIPE	0.08 $X^{0.56}$	0.42 $X^{0.67}$
Isobutanol	0.08 $X^{0.56}$	0.42 $X^{0.67}$
ETBE	0.05 $X^{0.82}$	0.36 $X^{0.76}$
tert-Pentanol	0.04 $X^{0.61}$	0.15 $X^{0.57}$
n-Butanol	0.06 $X^{0.61}$	0.22 $X^{0.57}$
TAME	0.05 $X^{0.70}$	0.31 $X^{0.51}$
Total oxygen	0.02 $X^{1.26}$	0.09 $X^{1.27}$

Note: Where X is the mean mass percent of the component.

ASTM D5845, Alcohols and Ethers in Gasoline by Infrared Spectroscopy

SIGNIFICANCE

See earlier discussion.

SCOPE

ASTM D5845 covers the determination of methanol, ethanol, tert-butanol, MTBE, ETBE, TAME, and DIPE in gasoline by infrared spectroscopy. The range of analysis for these components is:

Methanol	0.1 to 6 mass %
Ethanol	0.1 to 11 mass %
tert-Butanol	0.1 to 14 mass %
DIPE, MTBE, ETBE, and TAME	0.1 to 20 mass %

This test method is quoted along with ASTM D4815 and ASTM D5599 for the determination of oxygenates in ASTM D4814.

ANALYSIS

This test method is faster, simpler, less expensive, and more portable than the current methods. In ASTM D5845, a sample of gasoline is introduced into a liquid sample cell. A beam of infrared light (IR) is imaged through the sample onto a detector, and the detector response is determined. Regions of the IR spectrum are selected for use in the analysis by either placing highly selective bandpass filters before or after the sample or by mathematically selecting the region after the whole spectrum is obtained. A multivariate mathematical analysis is carried out that converts the detector response for the selected regions in the spectrum of an unknown to a concentration for each component.

PRECISION

Based on an interlaboratory study, Table 4.9 shows the precision levels obtained for this test method (RR-D02-1374).

TABLE 4.9 Precision of ASTM D5845 by Infrared Spectroscopy

Oxygenate	Repeatability	Reproducibility
MTBE	0.13	0.98
TAME	0.13	1.36
ETBE	0.15	0.77
Ethanol	0.13	0.59
Methanol	0.07	0.37
tert-Butanol	0.10	0.59
DIPE	0.14	0.79
Total oxygen	0.05	0.30

ASTM D482, Ash in Petroleum Products

SIGNIFICANCE

The quantity of noncombustible material in oil is considered as ash. Ash-forming material can be present in fuel oil in two forms: (1) abrasive solids and (2) soluble metallic soaps. Abrasive solids contribute to injector, fuel pump, piston, burner pump, valve, and ring wear and also to engine deposits. They can decrease fuel efficiency by fouling heat exchange surfaces. Soluble metallic soaps have little effect on wear but can contain elements that produce corrosion and deposits on boiler heater surfaces and can contribute to engine deposits. Excessive amounts can indicate the presence of materials that can cause high wear of burner pumps and valves and can contribute to deposits on boiling heating surfaces. Excessive amounts of ash also may necessitate particulate collection equipment for compliance with national or local air emission regulations. Ash in a petroleum product can result from oil- or water-soluble metallic compounds or from extraneous solids such as dirt and rust. This method is not valid for petroleum products containing ash-forming additives—including certain phosphorus compounds, for lubricating oils containing lead, or for used engine crankcase oils. In certain types of samples (e.g., distillate oils), all of the ash-forming metals may not be quantitatively retained in the ash. In all such cases, the sulfated ash procedure ASTM D874 should be used.

This test method's scope does not include nonpetroleum products. A separate test method, ASTM E1755, used for the determination of ash in biomass is very similar to ASTM D482.

The quantity of maximum ash allowed in fuel products is specified in ASTM D396, ASTM D975, ASTM D7467, ASTM D7544, and ASTM D7666 (Table 4.10). All values are in mass percent maximum.

All three biofuel-producing regions of the world use similar and equivalent test methods for ash and sulfated ash determinations.

Region	Limit	Test Method(s)
Brazil	Limit 0.02 % m/m max	NBR 984; ISO 3987; ASTM D874
EU	Limit 0.02 % m/m max	ISO 3987
United States	Limit 0.02 % m/m max	ASTM D874

TABLE 4.10 Specification Limits for Ash Content of Biofuels

Product	Grade	Ash, mass % max
ASTM D396 Fuel Oil	No. 4 Light	0.05
	No. 4	0.10
	No. 5 Light	0.15
	No. 5 Heavy	0.15
ASTM D975 Diesel Fuel Oil	All grades except 4-D	0.01
	Grade 4-D	0.10
ASTM D7467 Biodiesel Blend	All grades	0.01
ASTM D7544 Pyrolysis Biofuel	Grade G	0.25
	Grade D	0.15
ASTM D7666 Triglyceride Burner Fuel	All grades	0.15

ANALYSIS

ASTM D482 is used to estimate this quality. In this test method, a sample in a suitable vessel is ignited and burned and then later is oxidized in a muffle furnace at 775°C until only ash and carbon remain and constant residual weight is achieved. During combustion, all organic matter and volatile components such as sulfur, nitrogen, and chlorine are oxidized, and only metal oxides are left in the residue. The ash content of the original sample is calculated from the difference between the initial and residue weights.

PRECISION

The precision of ash determination based on petroleum products is found to be as follows. (This does not necessarily apply to biofuels, which usually contain extremely small quantities of ash, if any at all.)

Ash, mass %	Repeatability	Reproducibility
0.001 to 0.079	0.003	0.005
0.080 to 0.180	0.007	0.024

ASTM D874, Sulfated Ash from Lubricating Oils and Additives

SIGNIFICANCE

Sulfated ash is the residue remaining after the sample has been carbonized and the residue subsequently treated with sulfuric acid and heated to constant weight. The sulfated ash may be used to indicate the concentration of known metal-containing additives in new oils. When phosphorus is absent, barium, calcium, magnesium, sodium, and potassium are converted to their sulfates and tin (stannic) and zinc to their oxides. Sulfur and chlorine do not interfere but, when phosphorus is present with metals, it remains partially or wholly in the sulfated ash as metal phosphates. Because zinc sulfate slowly decomposes to its oxide at the ignition temperature specified in the method, samples containing zinc may give variable results unless the zinc sulfate is completely converted to the oxide. Magnesium does not react the same as other alkali metals in this test. If magnesium additives are present, the data should be interpreted with caution. Samples containing molybdenum may give low results because molybdenum compounds may not be fully recovered at the temperature of ashing.

A product's sulfated ash comes from three sources contained in a biodiesel product: (1) abrasive solids, (2) soluble metallic soaps, and (3) unremoved catalysts. Abrasive solids and unremoved catalysts can contribute to injector, fuel pump, piston, and ring wear and also to engine deposits. Soluble metallic soaps have little effect on wear but may contribute to filter plugging and engine deposits.

Fuel specifications have the following limits and test methods for this analysis. These test methods are technically similar.

Region	Limit	Test Method(s)
Brazil	0.02 % m/m max	ABNT NBR 984/ISO 3987/ASTM D874
European Union	0.02 % m/m max	ISO 3987
United States	0.020 % m/m max	ASTM D874

SCOPE

Application of this method to sulfated ash levels below 0.02 % is restricted to oils containing ashless additives. The lower limit of the method is 0.005 % sulfated ash. This method is not intended for the analysis of used engine oils or oils containing lead. Neither is it recommended for the analysis of nonadditive lubricating oils, for which ASTM D482 should be used. Because of various interelement interferences, it has been observed that the experimentally obtained sulfated ash values may differ from the sulfated ash values calculated from elemental analysis. The formation of such nonsulfated species is dependent on the temperature of ashing, time ashed, and on the composition of the metal compounds present in the oils. Hence, sulfated ash requirements generally should not be used in product specifications without a clear understanding between the buyer and the seller regarding the unreliability of the sulfated ash value as an indicator of total metallic components. Nadkarni, Ledesma, and Via have discussed this issue in detail [7]. Fig. 4.6 shows an X-ray diffraction pattern for a sulfated ash residue of a lubricating oil. A number of nonstoichiometric and nonoxide molecules are evident throughout the spectrum, indicating that, even after full combustion, there are other metal nonoxide species present in the residue.

Because biofuels generally have very low levels of metals present in them, resulting sulfated ash levels are also very low to the point of being below detection limits. Only ASTM D6751 lists sulfated ash as a quality parameter at 0.020 mass percent maximum in all grades.

ANALYSIS

The sample is ignited and burned until only ash and carbon remain. After cooling, the residue is treated with sulfuric acid and heated at 775°C until oxidation of carbon is complete. The ash is then cooled, retreated with sulfuric acid, and heated at 775°C to constant weight. Given the absence of significant amounts of metals in biofuels, it is unlikely that a quantitative amount of sulfated ash can be measured in this analysis.

PRECISION

The following test precision is obtained for lubricating oils and additives (Table 4.11).

ASTM D7576, Benzene and Total Aromatics in Denatured Fuel Ethanol by Gas Chromatography

SIGNIFICANCE

Regulations in some jurisdictions, such as in California, limit the concentration of benzene and total aromatic content of denatured fuel ethanol in order to reduce the ozone reactivity and toxicity of automotive evaporative and exhaust emissions. Results from this

FIG. 4.6 X-ray diffraction pattern of sulfated ash residue from a lubricating oil (ASTM D874).

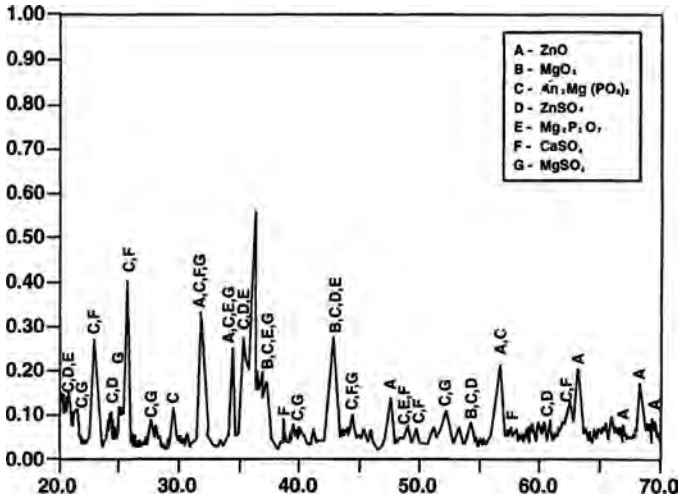


TABLE 4.11 Precision of Sulfated Ash Test for Lubricating Oils and Additives

Sulfated Ash Range, mass %	Repeatability	Reproducibility	ASTM Research Report
0.005 to 0.10	0.047 $X^{0.85}$	0.189 $X^{0.85}$	RR-D02-1597
0.11 to 25	0.060 $X^{0.75}$	0.142 $X^{0.75}$	RR-D02-1597
0.8 to 1.6[a]	0.08068 $X^{1.40}$	0.1563 $X^{1.40}$	RR-D02-1625

Note: Where X is average of two results. [a]For American Petroleum Institute Proposed Category (API PC) 10 oils.

test method may be used to assess product quality and to meet new fuel regulations.

ANALYSIS

ASTM D7576 determines total aromatics by adding the concentrations of benzene, toluene, ethylbenzene, 0-xylene, m-xylene, p-xylene, and C_9 and heavier aromatics. The aromatic hydrocarbons are separated without interferences from other hydrocarbons in denatured fuel ethanol. Nonaromatic hydrocarbons having a boiling point greater than that of n-dodecane can cause interferences with the determination of the C_9 and heavier aromatics. For the C_8 aromatics, p-xylene and m-xylene co-elute while ethylbenzene and o-xylene are separated. The C_9 and heavier aromatics are determined as a single group.

This test method utilizes a two-column chromatographic system equipped with a column switching valve and a flame ionization detector. An internal standard, such as 2-hexanone, is used. Figs. 4.7 and 4.8 are the chromatograms of aromatics in denatured fuel ethanol from Analysis 1 and Analysis 2 obtained by ASTM D7576.

FIG. 4.7 Aromatics in denatured fuel ethanol, Analysis No.1, by ASTM D7576, *Standard Test Method for Determination of Benzene and Total Aromatics in Denatured Fuel Ethanol by Gas Chromatography.*

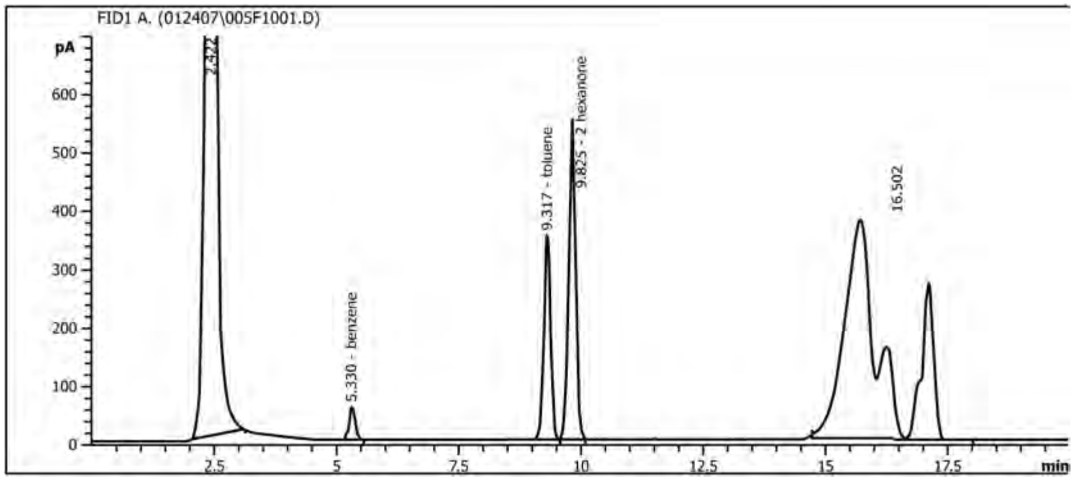


FIG. 4.8 Aromatics in denatured fuel ethanol, Analysis No. 2, by ASTM D7576, *Standard Test Method for Determination of Benzene and Total Aromatics in Denatured Fuel Ethanol by Gas Chromatography.*

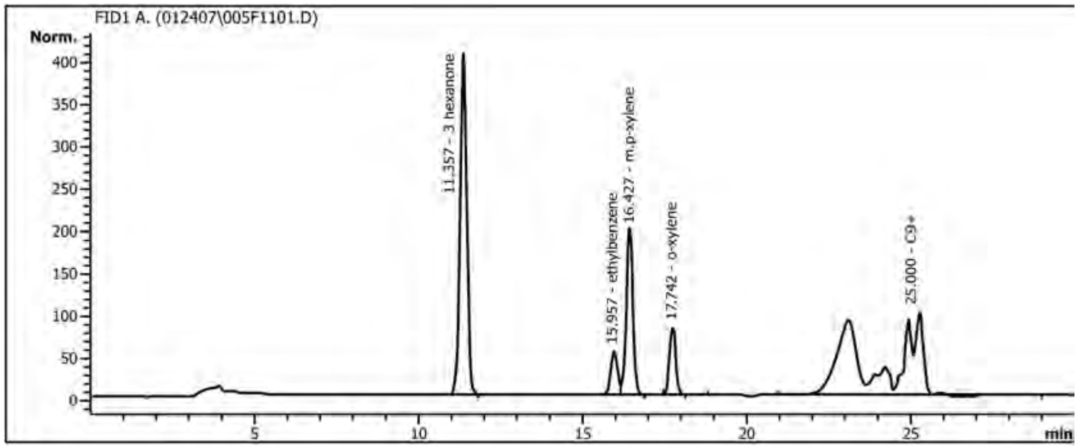


TABLE 4.12 Precision of ASTM D7576 for the Determination of Benzene and Total Aromatics in Fuel Ethanol

Component	Range, vol %	Repeatability	Reproducibility
Benzene	0.01–0.06	$0.237\ X^{0.359}$	0.142 (X + 0.03)
Total aromatics	0.25–2.10	0.038 X	0.120 (X + 0.5)

Note: Where X is the average vaue of the results.

SCOPE

This test method covers the following concentration ranges: benzene 0.01 to 0.06 volume percent and total aromatics 0.25 to 2.10 volume percent.

PRECISION

The precision is based on an interlaboratory study conducted in 2007 involving seven sets of denatured fuel ethanol samples and five laboratories. The benzene content of these samples ranged from 0.00 to 0.06 volume percent nominal, and the total aromatic content ranged from 0 to 2.2 volume percent nominal. The precision given in Table 4.12 was obtained.

ASTM D2887, Boiling Point Distribution by Gas Chromatography

SIGNIFICANCE

The determination of the boiling range distribution of petroleum fractions by gas chromatography is a rapid analytical tool that may be used to replace conventional distillation methods for control of refining operations and specification testing. Data derived by this test method essentially are equivalent to those obtained by true boiling point distillation (Method ASTM D2892). They are not equivalent to results from low-efficiency distillations, such as those obtained with ASTM D86 or ASTM D1160. The method is applicable to petroleum products and fractions with a final boiling point of 538°C (1,000°F) or lower at atmospheric pressure as measured by this method. The method is not designed for use with gasoline samples or gasoline components. These samples must be analyzed by ASTM D3710. The method is limited to samples having a boiling range greater than 55°C (100°F) and having a vapor pressure sufficiently low to permit sampling at ambient temperature.

A correlation of 17 % oil volatility by gas chromatography standard deviation (GC-SD) methods (ASTM D2887 or ASTM D5480) has been found equivalent to 21.5 % volatility by the Noack method. This test method is included in ASTM D396.

ASTM D2887 is allowed to be used as an alternate test method for ASTM D86 in some gasoline and diesel product specifications. The following definitions are used in this context:

- *Initial Boiling Point*—The point at which a cumulative area count equal to 0.5 % of the total area under the chromatogram is obtained.
- *Final Boiling Point*—The point at which a cumulative area count equal to 99.5 % of the total area under the chromatogram is obtained.

ANALYSIS

The boiling range distribution determination by distillation is simulated by the use of GC. A nonpolar packed or open tubular (capillary) GC column is used to elute the hydrocarbon components of the sample in order of increasing boiling point. The sample is introduced into a gas chromatographic column that separates hydrocarbons in boiling point order. The column temperature is raised at a reproducible linear rate, and the area under the chromatogram is recorded throughout the run. Boiling temperatures are assigned to the time axis from a calibration curve, obtained under the same conditions by running a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data, the boiling range distribution may be obtained.

PRECISION

The precision shown in Table 4.13 is obtained for this test method based on an interlaboratory study that involved analysis of nine

TABLE 4.13 Precision of ASTM D2887 Distillation Test Method

% Off	Range of Results, °C	Repeatability, °C	Reproducibility, °C
IBP	112–213	0.011 X	0.066 X
5 %	133–286	0.0032 (X + 100)	0.015 (X + 100)
10–20 %	139–341	0.8	0.015 (X + 100)
30 %	161–368	0.8	0.013 (X + 100)
40 %	171–370	0.8	4.3
50–90 %	182–426	1.0	4.3
95 %	241–437	1.2	5.0
FBP	274–475	3.2	11.8

Note: Where X is the average of two results in °C. IBP = initial boiling point; FBP = final boiling point.

samples among 19 laboratories using both packed and open tubular columns (RR-D02-1406).

ASTM D7798, Boiling Range Distribution of Petroleum Distillates by Ultra Fast Gas Chromatography

SIGNIFICANCE

The boiling range distribution of petroleum distillate fractions provides an insight into the composition of feedstocks and products related to petroleum refining processes. A major advantage of the fast analysis time obtained from this test method is increasing product throughput and reduced laboratory time by a factor of at least three. This gas chromatographic determination of boiling range can be used to replace conventional distillation methods for product specification testing with the initial agreement of interested parties.

SCOPE

This test method covers the determination of the boiling range distribution of petroleum products and biodiesel formulations, B5, B10, and B20. It is applicable to petroleum distillates having a final boiling point not greater than 538°C or lower at atmospheric pressure as measured by this test method. The difference between the initial boiling point and the final boiling point shall be greater than 55°C.

This test method is not applicable for analysis of petroleum containing low-molecular weight components such as naphthas, reformates, gasoline, and full-range crude oils. Materials containing heterogeneous mixtures (e.g., alcohols, ethers, acids, or esters, except biodiesels) or residues are not to be analyzed by this test method.

Boiling range distributions obtained by this test method are essentially equivalent to results obtained by true boiling point distillation (such as ASTM D2892). They are not equivalent to results from low-efficiency distillation, such as those obtained with ASTM D86 or ASTM D1160.

ANALYSIS

This test method uses the principles of simulated distillation methodology as well as gas chromatographic components that allow the entire analysis from sample to sample to occur in 5 min or less. In these instruments, the column is heated directly (by the supplying heat column instead of an oven) at rates 10 to 15 times that of a conventional gas chromatograph; thus, the analysis time is reduced from sample to sample. A nonpolar capillary GC column is used to separate the hydrocarbon components of the sample and to cause them to elute in order of increasing boiling point.

Depending on the analyzer and the column used, a sample aliquot is diluted with a viscosity-reducing solvent or introduced neat into the GC system. Sample vaporization is provided by separate heating of the point of injection or in conjunction with column oven heating. The column temperature is raised at a reproducible rate to effect separation of the hydrocarbon components in order of increasing boiling point. The elution of sample components is quantitatively determined using a flame ionization detector. The detector signal is recorded as area slices for consecutive retention time intervals during the analysis.

TABLE 4.14 Repeatability Standard Deviation Results of a Gas Oil Analysis Using ASTM D7798

% off	Average Result, °C	Standard Deviation	Repeatability Limit
IBP	110	1	2.77
5	149.09	1.32	3.6564
10	174.58	0.47	1.3019
15	200.19	1.26	3.4902
20	223.16	1.72	4.7644
25	242.57	1.61	4.4597
30	259.37	1.16	3.2132
35	275.13	0.81	2.2437
40	289.75	0.53	1.4681
45	302.25	0.53	1.4681
50	310.45	0.47	1.3019
55	321.62	0.38	1.0526
60	331.68	0.15	0.4155
65	343.25	0.42	1.1634
70	354.28	0.39	1.0803
75	366.42	0.36	0.9972
80	379.26	0.35	0.9695
85	392.61	0.23	0.6371
90	408.81	0.33	0.9141
95	438.88	0.33	0.9141
FBP	482.7	0.92	2.5484

Retention times of known normal paraffin hydrocarbons, spanning the scope of the test method (C_5–C_{44}) are determined and correlated to their boiling point temperatures. The normalized cumulative corrected sample area for each consecutive recorded time interval is used to calculate the boiling range distribution. The boiling point temperature at each reported percent off increment is calculated from the retention time calibration.

PRECISION

The repeatability standard deviation of analysis of a reference gas oil is shown in Table 4.14 based on four replicates from a single instrument.

ASTM D7398, Boiling Range Distribution of Fatty Acid Methyl Esters by Gas Chromatography

SIGNIFICANCE

The boiling range distribution of FAMEs provides an insight into the composition of products related to the transesterification process. This gas chromatographic determination of boiling range can be used to replace conventional distillation methods for product specification testing with the initial agreement of interested parties. Biodiesel FAMEs exhibit a boiling point rather than a distillation curve. The fatty acid chains in the raw oils and fats from which biodiesel is produced are mainly composed of straight-chain hydrocarbons with 16 to 18 carbons that have similar boiling temperatures. The atmospheric boiling point of biodiesel generally ranges from 330 to 357°C. The ASTM D6751 value of 360°C maximum at 90 % off by ASTM D1160 was incorporated as a precaution to ensure that the fuel has not been adulterated with high boiling contaminants. ASTM D7398 covers the determination of the boiling range distribution of FAMEs. This test method is applicable to FAMEs (biodiesel B100) having an initial boiling point greater than 100°C and a final boiling point less than 615°C at atmospheric pressure. This test method can also be applicable to blends of diesel and biodiesel (B1 through B100). ASTM D7398 is not applicable for analysis of petroleum-containing low-molecular weight components such as naphthas, reformates, gasoline, and crude oil.

Boiling range results obtained by this test method are not equivalent to results obtained from low-efficiency distillation such as those obtained with ASTM D86 or ASTM D1160, especially the initial and final boiling points.

ANALYSIS

A sample aliquot is diluted with a viscosity-reducing solvent and introduced into the GC system. The solvent should be apolar and not interfere with measurement of the sample in the 100 to 615°C range. Sample vaporization is provided by separate heating of the point of injection or in conjunction with column oven heating. The column oven temperature is raised at a reproducible linear rate to effect separation of the FAME components in order of increasing boiling point relative to an n-paraffin calibration mixture. The elution of sample components is quantitatively determined using a flame ionization detector. The detector signal integral is recorded as area slices for consecutive retention time intervals during the analysis. Retention times of known normal paraffin hydrocarbons spanning the scope of the test method (C_5 to C_{60}) are determined and correlated to their boiling point temperatures. The normalized cumulative corrected sample areas for each consecutive recorded time interval are used to calculate the boiling range distribution. The boiling point temperature at each reported percent off increment is calculated from the retention time calibration. The retention time versus boiling point curve is calibrated with normal paraffin hydrocarbons because these boiling points are well defined. A mixture of FAMEs is analyzed to check column resolution. A triglyceride is analyzed to verify the system's ability to detect untreated oil.

PRECISION

Based on an interlaboratory study (RR-D02-1729), the precision of this test method has been found to be 0.8°C repeatability and 6.8°C reproducibility for T90. This test method requires further standardization. The current degrees of freedom for reproducibility are too low; hence, ASTM D02.CS 94 has recommended that this test method should not be used for commerce.

ASTM D7875, Butanol and Acetone Content of Butanol

SIGNIFICANCE

Butanol is approved for blending with gasoline in accordance with ASTM D7862. This test method is used to determine the percentage of butanol (purity) of the butanol for blending with gasoline and identifies and quantifies acetone, ethanol, and methanol but does not purport to identify all individual components that may be present in butanol for gasoline blending. The concentration ranges of components determined by this test method are:

Butanol	95 to 99.9 % by mass
Acetone	0.02 to 1.5 % by mass
Ethanol	0.02 to 1.5 % by mass
Methanol	0.02 to 1.5 % by mass

Water cannot be determined by this test method and shall be measured by a procedure such as ASTM D1364, and the results used to correct the chromatographic values. This test method is inappropriate for impurities that boil at temperatures higher than 225°C or for impurities that cause poor or no response in a flame ionization detector, such as water.

ANALYSIS

A representative aliquot of the butanol sample is introduced into a gas chromatograph equipped with a polydimethylsiloxane-bonded phase capillary column. Helium carrier gas transports the vaporized aliquot through the column where the components are separated by the chromatographic process. Components are sensed by a flame ionization detector as they elute from the column. The detector signal is processed by an electronic data acquisition system. The butanol, acetone, ethanol, and methanol components are identified by comparing their retention times to the ones identified by analyzing standards under identical conditions. The concentrations of all components are determined in mass percent area by normalization of the peak areas.

PRECISION

Only a repeatability estimate is available for this test method based on limited laboratory results from a single laboratory. Reproducibility or bias has not been determined for this test method.

Component	Range, mass %	Repeatability, mass %
2-Methyl-1-propanol	95 to 99.9	0.205
1-Butanol	95 to 99.9	0.350
2-Butanol	95 to 99.9	0.366
Acetone	0.02 to 1.5	0.000185X1/2
Methanol	0.02 to 1.5	0.000199X1/2
Ethanol	0.02 to 1.5	0.000202X1/2

Ester Content of Biodiesels

Faria et al. [8] have described a method for the determination of ester content in different kinds of biodiesel found in Brazil. Because Brazil uses a variety of crop materials as feedstock—soybean, castor oil, animal fat, palm oil, and so on—existing international methods are not necessarily applicable to biodiesel samples from all sources. A new Brazilian standard method, ABNT NBR 15764, has been developed using gas chromatography and a mixture of esters as an external standard. A small amount of a sample is diluted in 10 mL of chloroform, and 0.5 μL is injected in the gas chromatograph using an automatic sampler. GC-MS is used to identify all esters present in the sample. After the sample identification, quantification is carried out using a gas chromatograph equipped with a flame ionization detector.

ASTM D7806, Fatty Acid Methyl Ester Content of a Biodiesel Blend and Petroleum-Based Diesel Fuel Oil

SIGNIFICANCE

Biodiesel is a fuel commodity primarily used as a value-added blending component with diesel fuel. This test method is fast and simple to run, and it is applicable to quality control in the production and distribution of diesel fuel and biodiesel blends containing FAMEs. It is applicable to concentrations from 1 to 30 volume percent. This test method is not appropriate for the determination of the concentration of biodiesel that is in the form of fatty acid ethyl esters (FAEEs).

ANALYSIS

In ASTM D7806, a sample of diesel fuel or biodiesel blend is introduced into a liquid sample cell having a specified path length. A beam of IR light is imaged through the sample onto a detector, and the detector response is determined. Wavelengths of the absorption spectrum that correlate highly with biodiesel or interferences are selected for analysis. Mathematical analysis converts the detector response for the selected areas or peaks of the spectrum of the unknown to a concentration of biodiesel. Either a Fourier transform mid-IR spectrometer or a filter-based mid-IR spectrometer may be used for this analysis.

The primary spectral interferences are vegetable oils or animal fats or both. Samples containing undissolved water will result in erroneous results. Cloudy or water-saturated samples should be filtered through a dry filter paper until clear and prior to their introduction into the instrument sample cell.

PRECISION

Only repeatability data are available at present. Based on a limited scale interlaboratory study, the repeatability has been found to be X ± 0.3 volume percent for Fourier transform infrared spectroscopy (FTIR) instruments using linear regression and X ± 0.34 volume percent for filter instruments using linear regression, where X is the biodiesel concentration determined.

EN 14103, Ester and Linolenic Ester Methyl Ester Content in Fatty Acid Methyl Esters

The scope of this method verifies that the ester content of FAMEs is greater than 90 % and the linolenic ester content is between 1 % and 15 % (m/m). The ester content is integrated as C6:0 to C24:1 using a column oven programmed run. Linolenic acid ester is also determined and reported separately. The internal standard has been changed from C17:0 to C19:0 to allow this method to be used for biodiesel from an animal source. Because C17:0 FAME is present as a component itself in samples containing animal sources, using it as an internal standard would lead to biased results. Other changes include the use of toluene as the solvent instead of heptane.

EN 15779, Fatty Acid Methyl Ester Content of Biodiesels Using Gas Chromatography

Algae are gaining interest as a potential source for biodiesel. Together with *Jathropa* shrubs, algae form one of the most interesting alternative diesel sources that do not interfere with the food chain. However, polyunsaturated fatty acid methyl esters (PUFAs) are more prominent in marine-based sources than in land-based crops. These PUFAs exhibit lower oxidation stability and are more susceptible to polymerization reactions, which may ultimately contribute or even lead to engine fouling and fuel line or filter blocking.

ASTM EN 15779 is mandated for the determination of PUFAs between 0.6 and 1.5 % (m/m). The maximum allowable concentration according to EN 14214 is 1.0 %. In a repeatability study, 1 % PUFA (0.25 % each component) was added to an unknown biodiesel sample. The data demonstrate low levels of C22:5 and C22:6 in the sample (0.02 and 0.07 %, respectively). Each analysis is based on eight replicate analyses [8].

Sample	C20:4	C20:5	C22:5	C22:6	Total PUFA
Average %	0.25	0.25	0.27	0.32	1.09
SD %	0.00	0.00	0.00	0.00	0.00
0.15 RSD %	0.23	0.09	0.30	0.29	0.15
Sample	n.d.	n.d.	0.02	0.07	0.09

SD = standard deviation. RSD = relative standard deviation.

ASTM D7371, Fatty Acid Methyl Ester Content of Diesel Fuel Oil Using Mid-Infrared Spectroscopy

SIGNIFICANCE

Biodiesel is a blendstock commodity primarily used as a value-added blended component with diesel fuel. This test method is applicable for quality control in the production and distribution of diesel fuel and biodiesel blends containing FAME.

SCOPE

ASTM D7371 covers the determination of the FAME biodiesel content in diesel fuel oils. It is applicable to concentrations from 1 to 20 volume percent. Using the proper attenuated total reflectance (ATR) sample accessory, the range may be expanded from 1 to 100 volume percent; however, the precision is not available above 20 volume percent. This procedure is only applicable to FAMEs. Biodiesel in the form of FAEEs will cause a negative bias.

ANALYSIS

A sample of diesel fuel, biodiesel, or biodiesel blend is introduced into a liquid ATR sample cell. A beam of IR light is imaged through the sample onto a detector, and the detector response is determined. Wavelengths of the absorption spectrum that correlate highly with biodiesel or interferences are selected for analysis. A multivariate mathematical analysis converts the detector response for the selected areas of the spectrum from an unknown to a concentration of biodiesel.

This test method uses a Fourier transform mid-IR spectrometer with an ATR sample cell. The absorption spectrum is used to calculate a partial least squares (PLS) calibration algorithm. The hydrocarbon composition of diesel fuel has a significant impact on the calibration model. Therefore, for a robust calibration model, it is important that the diesel fuel in the biodiesel fuel blend is represented in the calibration set. There are also interferences from water vapor, FAMEs, and undissolved water in this analysis. (See ASTM D7371 for a discussion of these interferences.)

Experience has shown that biodiesels (FAMEs) made from various base stock materials have very similar absorbance in the spectral region used in this test method. The precision of this test method, given here, was developed using soy-derived biodiesel for calibration and validation standards. ASTM RR-D02-1624 illustrates that other feedstock (animal fat, canola oil, *Jatropha* oil, palm oil, rapeseed, and yellow grease) methyl esters are very similar to soy methyl esters, with yellow grease methyl esters being the most different. See Figs. 4.9 and 4.10 for illustrations of IR spectra of 0.29 %, 9.72 %, and 19.45 % biodiesel in diesel fuel.

PRECISION

Based on an interlaboratory study involving five laboratories and 16 samples covering the range from 1 to 20 volume percent biodiesel, the following precision values were obtained (RR-D02-1624).

Repeatability	0.01505 (X + 14.905) vol/vol %
Reproducibility	0.04770 (X + 14.905) vol/vol %

Note: Where X is the biodiesel concentration determined.

EN 14078, Determination of Fatty Acid Methyl Ester Content of Middle Distillates by Infrared Spectroscopy

SIGNIFICANCE

This standard specifies a test method for the determination of FAME content of diesel fuel or domestic heating fuel by mid-IR

FIG. 4.9 Infrared spectra of biodiesel in diesel fuel (full region) by ASTM D7371, *Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method).*

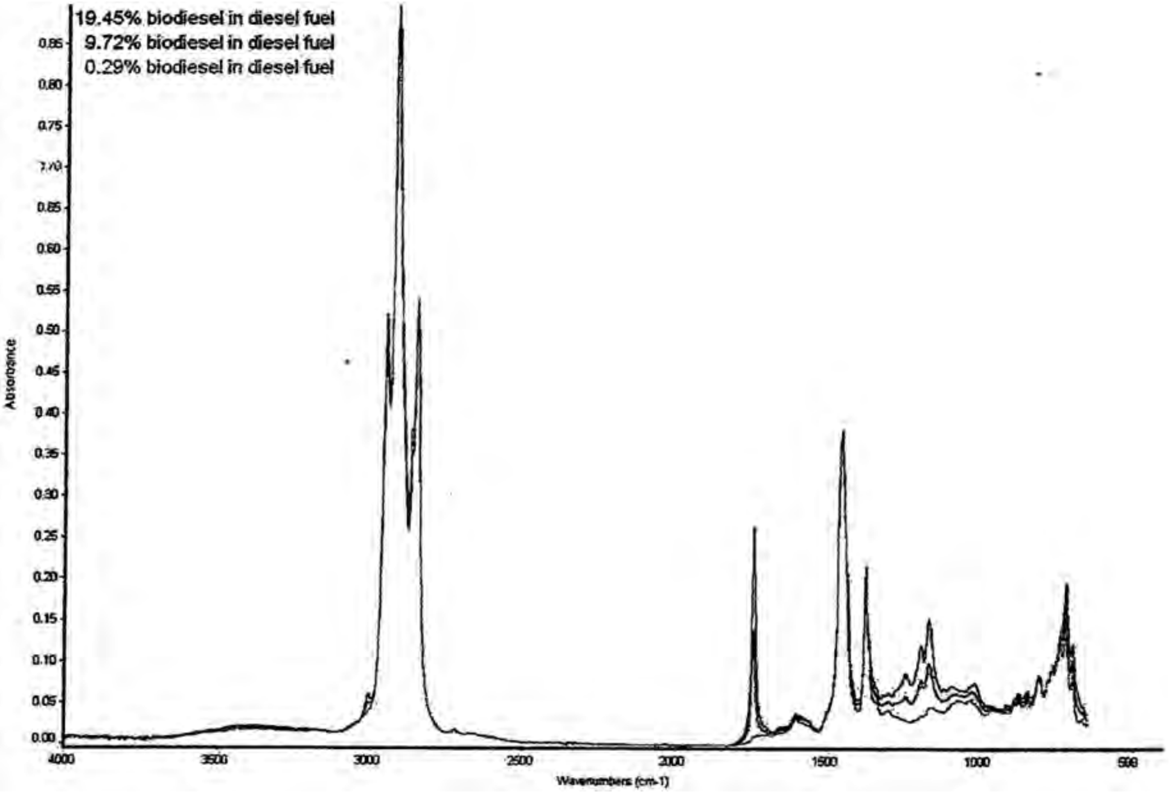
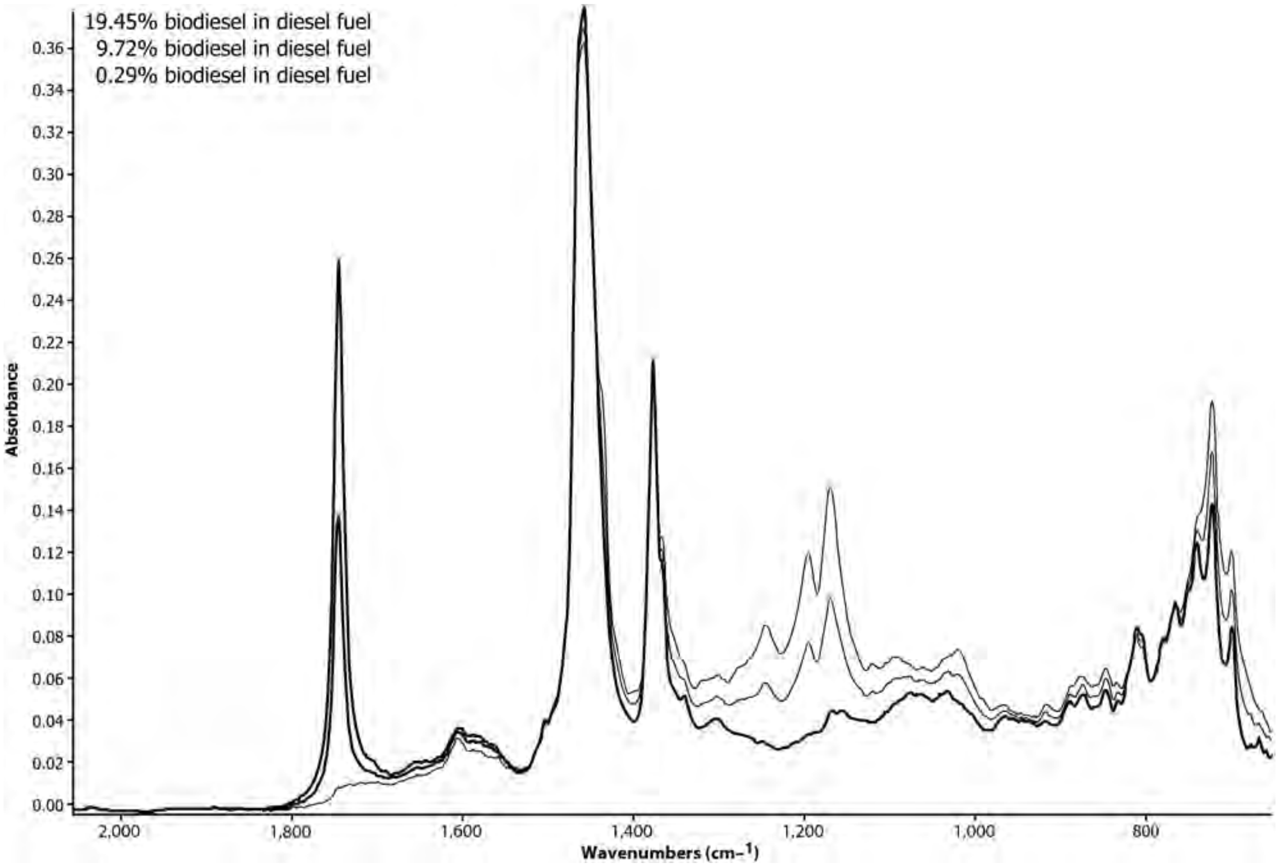


FIG. 4.10 Infrared spectra of biodiesel in diesel fuel (Regions 1 and 2) by ASTM D7371, *Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method)*.



spectrometry, which applies to ranges of FAME content: Range A for FAME content of from approximately 0.05 volume percent to 3 volume percent, and Range B for FAME content from approximately 3 volume percent to 20 volume percent. In principle, higher FAME contents can also be analyzed if diluted. This test method was verified to be applicable to samples containing FAMEs conforming to EN 14214 or EN 14213. Reliable quantitative results are obtained only if the samples do not contain any significant amounts of other interfering components, especially esters and other carbonyl compounds that possess absorption bands in the spectral region used for quantifying FAMEs. If such interfering components are present, this test method is expected to give higher results.

ANALYSIS

The mid-IR absorption spectrum of a test portion of a sample that has been diluted as appropriate with FAME-free solvent is recorded. The absorbance at the peak maximum of the typical absorption band for esters at about 1745 ± 5 cm^{-1} is measured. Initially, the calibration as well as evaluation of the data will be carried out as grams of FAME per liter. For converting g/L to the reporting unit % vol/vol, a fixed density of FAME of 888.3 kg/m^3 at 15°C is used.

Two measurement ranges (A and B) are chosen for which specific adjustments for the calibration and dilution need to be followed. Measurement preferably without dilution for Range A and a shorter path length of the measurement cell for Range B. In particular, the lower determination, Range A, is challenging. All the details of the method must be carried out exactly as specified to obtain improved precision. Based on the absorbance measured at the maximum of the peak of the absorption band, the FAME content is calculated by means of a calibration function that has been determined by measuring calibration solutions for which the FAME content is known.

PRECISION

Based on an European interlaboratory study involving a matrix of various diesel fuels with both low and high FAME contents, as well as three domestic heating oils, the following precision was obtained.

Measurement Range and Type of Product	Repeatability, % v/v	Reproducibility, % v/v
Middle distillate Range A	0.0126 X + 0.0079	0.0499 X + 0.0231
Middle distillate Range B	0.0166 X − 0.0195	0.0793 X − 0.0413
Domestic heating oil with FAME content of approx. 0.06 % v/v	0.004	0.015

Note: Where X is the average of the two results being compared.

Rapid Analysis of Biofuels and Biofuels Blends with Fourier Transform Infrared Spectroscopy

FTIR spectroscopy is particularly well-suited to the measurement of several important fuel parameters such as the rapid determination of critical impurities at sub-percent levels in both biodiesel and bioethanol. The concentration of biodiesel in diesel fuel—whether it is a desirable blend component or a contaminant—can be accurately quantified by FTIR at concentrations as low as tens of ppm. The specific biological origin of biodiesel affects its properties, and FTIR analysis allows discrimination among biodiesel samples from various feedstocks such as palm, soy, and rapeseed. An analysis summary of 60 mixtures of ethanol with water (0–1 % mass), methanol (0–1 % mass), 1-propanol (0–1.7 % mass), 1-propanol (0–1.7 % mass), 1-pentanol (0–1.7 % mass), and petroleum spirit (0–7 % mass) was analyzed by this technique. The summary of analyses shown in Table 4.15, along with the product specifications for ethanol in ASTM D4806 and EN 15376, shows achievable detection limits within the specification limits [9].

FTIR is also well-suited for the determination of biodiesel content of diesel fuel. The FAMEs in biodiesel have a strong absorption band from a carbonyl group that is free from interference by the mineral diesel matrix. Two standard test methods based on this chemistry are available: ASTM D7371 and EN 14078. The former uses an ATR measurement that trades a more involved calibration procedure for slightly improved ease of measurement, while the latter uses a straightforward transmission measurement to calibrate and allows excellent sensitivity for low concentrations. Transmission measurements similar to EN 14078 can be used to check for the presence of trace amounts of FAMEs in fuel that should be FAME-free. ISO 8217 (2010) recommends that the marine distillate fuels should not contain FAMEs with a concentration limit of 0.1 %. FTIR is easily capable of measuring this concentration, and detection limits of tens of ppm can be obtained when a representative reference spectrum of uncontaminated fuel is available for subtraction [9].

As mentioned earlier, FTIR can clearly distinguish among biodiesel sources based on the spectrum corresponding to alkene functional groups. The intensity increases in the order palm < rape < soy. This observation is consistent with the data shown here that were derived from tabulated chain distributions for these oils. Thus, FTIR spectroscopy can provide a very quick way to check the provenance of a biodiesel sample [9].

Parameter	Palm	Rape	Soy
Average chain length	13.3	19.0	17.9
Average double bonds per chain	0.18	1.04	1.44
Fraction of unsaturated bonds	1.4 %	5.5 %	8.0 %

ASTM D7963, Fatty Acid Methyl Esters in Middle Distillate and Residual Fuels Using Flow Analysis by Fourier Transform Infrared Spectroscopy–Rapid Screening Method

SIGNIFICANCE

Government requirements to add FAMEs to diesel fuel have had the unintended side effect of leading to potential FAME contamination of fuels in multifuel transport facilities, such as cargo tankers and pipelines, and to industry-wide concerns. This has led to a requirement to measure contamination levels in diesel and other fuels to assist custody transfer issues.

Analytical methods have been developed with the capability of measuring down to <5-mg/kg levels of FAMEs in aviation turbine fuel (AVTUR); however, these are complex and require specialized personnel and laboratory facilities. The ASTM D7963 rapid screening method has been developed for use in the supply chain by non-specialized personnel to cover the range of 20 to 200,000 mg/kg. A similar procedure, ASTM D7797, is available for AVTUR in the range of 20 to 150 mg/kg. Both of these procedures use the same apparatus with a specific model developed for AVTUR.

ANALYSIS

This test method describes a rapid screening method using flow analysis by FTIR with partial least squares (PLS-1) processing for the quantitative determination of the FAME contamination of middle distillates in the range of 20 to 1,000 mg/kg and for middle distillates and residual fuels, following dilution, for levels above 0.1 %. This test method detects all FAME components, with peak IR absorbance at approximately 1749 cm^{-1} and C_8 to C_{22} molecules as specified in standards such as ASTM D6751 and EN 14214. The accuracy of the method is based on the molecular mass of C_{16} to C_{18} FAME

TABLE 4.15 Ethanol Analysis Using Fourier Transform Infrared Spectroscopy Versus Ethanol Specifications

Parameter	ASTM D4806	EN 15376	FTIR LOD
Water	1.0 % vol (1.3 % mass)	0.3 % mass	0.15 % mass
Methanol	0.5 % vol (0.5 % mass)	1.0 % mass	0.12 % mass
C_3–C_5 alcohols	NA	2.0 % mass	0.48 % mass
Gasoline denaturant	1.96–5 % vol (~25 % mass)	NA	0.7 % mass

Note: NA = not available; LOD = limits of detection.
From Ref. [9].

species. The presence of other FAME species with different molecular masses could affect the accuracy.

The test specimen is automatically analyzed by an FTIR spectrometer, in a 2-mm effective path-length flow-through cell, before and after flowing through a cartridge containing a sorbent designed to have a relatively long residence time for FAMEs. The spectroscopic absorbance differences of the IR spectra between the measurements are processed in conjunction with a PLS-1 model to determine the presence and amplitude of the carbonyl peak of FAME at approximately 1749 cm^{-1}. The flow analysis by FTIR enables the effects of potential interferences to be removed by using their relative retardance times through the sorbent in conjunction with their absorbance at specific wavelengths. Test time typically is less than 20 min.

PRECISION

No estimate of repeatability or reproducibility is available at present. However, based on a limited study at a single laboratory comprising three analyzers and three operators across 13 samples containing a known concentration of FAMEs in the range of 0 % to 20 %, the following precisions were given.

$\text{Repeatability} = 0.2933 \times (\text{FAME})^{0.8302}$

$\text{Reproducibility} = 1.5 \times (0.3508 \times (\text{FAME})^{0.8302}$

ASTM D7797, Fatty Acid Methyl Ester Content of Aviation Turbine Fuel by Fourier Transform Infrared Spectroscopy

SIGNIFICANCE

The present and growing international governmental requirements to add FAMEs to diesel fuel have had the unintended side effect of leading to potential FAME contamination of jet engine fuel in multifuel transport facilities, such as cargo tankers and pipelines, and to industry-wide concerns. Analytical methods have been developed with the capability of measuring down to <5 mg/kg levels of FAME. However, these are complex and require specialized personnel and laboratory facilities. This rapid screening method, ASTM D7797, has been developed for use in the supply chain by nonspecialized personnel to cover the range of 20 to 150 mg/kg of FAMEs.

SCOPE

The specifications falling within the scope of this test method are ASTM D1655 and Defense Standard 91-91. This test method detects all FAME components, with peak IR absorbance at approximately 1,749 cm^{-1} and C_8 to C_{22} molecules as specified in ASTM D6751 and EN 14214. The accuracy of the method is based on the molecular weight of C16 to C18 FAME species. The presence of other FAME species with different molecular weights could affect the accuracy. Additives such as antistatic agents and antioxidation and corrosion inhibitors are measured with FAMEs by the FTIR spectrometer. However, the effects of these additives are removed by the flow analysis processing. FAME concentrations from 150 to 500 mg/kg and below 20 mg/kg can be measured, but the precision could be affected.

ANALYSIS

This test method specifies a rapid screening method using flow analysis by FTIR spectroscopy with PLS-1 processing for the determination of FAME content of AVTUR fuel in the range of 20 to 150 mg/kg. A test specimen of AVTUR fuel is automatically analyzed by an FTIR spectrometer in a 2-mm effective path-length flow-through cell before and after flowing through a cartridge containing a sorbent designed to have a relatively long residence time for FAMEs. The spectroscopic absorbance differences of the IR spectra among the measurements are processed in conjunction with a PLS-1 model to determine the presence and amplitude of the carbonyl peak of FAMEs at approximately 1,740 cm^{-1}. The typical test time is 20 min. The flow analysis by FTIR enables the effects of potential interferences to be removed by using their relative retention times through the sorbent in conjunction with their absorbance at specific wavelengths.

PRECISION

Based on a 2009 interlaboratory study using nine laboratories and a sample set of 13 AVTUR samples blended with known amounts of FAMEs, the following precision was obtained for this analysis.

Repeatability = 0.01921 (X + 150)

Reproducibility = 0.02184 (X + 150)

Note: Where X is the average of two results being compared in mg/kg.

Analysis of Synthetic Jet Fuel Blend with Mid-Infrared Spectroscopy

A portable mid-IR analyzer was evaluated by Wilks as a possible tool for analyzing the blend ratio of synthetic jet fuels. Both commercial Jet A and military spec JP-8 fuels were blended with different levels of synthetic jet fuel, and calibrations were generated on an analyzer. It was possible to calibrate using Jet A fuel and predict the synthetic blend ratio on JP-8 fuel, so the calibration was robust enough to compensate for different fuel types [10].

ASTM D7861, FAMEs in Diesel Fuels by Linear Variable Filter Array Based on Mid-Infrared Spectroscopy

SIGNIFICANCE

The instrumentation for this test is portable and low in cost compared to ASTM D7371 for biodiesel blend determination in diesel fuels. Linear variable filter (LVF)-array IR spectrometers can be made with no moving parts, so they are conducive to field testing. The method of calibration used for this analysis involves a univariate calibration that requires less time and cost input. There has been much interest in a field test type of method as a screening tool for biodiesel in diesel fuel now that up to 5 % biodiesel is allowed undisclosed in ASTM D975 diesel fuels. This test method can be used to determine that the biodiesel content of a diesel sample is either not below the minimum allowable limit or that it does not exceed the maximum allowable limit.

SCOPE

This test method determines FAMEs or biodiesel in diesel fuel oils. FAMEs can be quantitatively determined from 1.0 to 30.0 volume percent. This test method uses linear variable filter array based on mid-IR spectroscopy and a horizontal attenuated total reflectance (HATR) crystal as well as a univariate calibration for monitoring FAME concentrations. Univariate calibration is a process for creating a calibration model in which a single measured variable (e.g., the absorbance at a particular wavelength) is correlated with the concentration or property values for a set of calibration samples.

ANALYSIS

A sample of diesel fuel or biodiesel blend is placed onto an HATR crystal. Infrared light is imaged through the sample, then through the LVF and, finally, onto a detector array. The LVF separates the infrared light into specific wavelengths so that the response of the detector array generates an infrared spectrum. Spectral corrections are performed to eliminate interferences caused by diesel and biodiesel variations. A wavelength region of the absorption spectrum that correlates with biodiesel is selected for analysis. The area of the selected region is determined. A calibration curve converts the selected area of an unknown sample to a biodiesel concentration.

INTERFERENCES

The hydrocarbon composition of diesel fuels can affect the accuracy of the calibration. When possible, it is advised that diesel fuels used in the calibration be similar to the unknown samples to be analyzed. Samples containing undissolved water or particulates (or both) will result in erroneous results. Cloudy or water-saturated samples should be filtered through a qualitative filter paper until clear, prior to their introduction onto the instrument sample crystal. The primary spectral interferences are vegetable oils or animal fats (or both). Other means of analysis or separate calibrations may be required if the fuel is suspected to be contaminated with vegetable oils or animal fats. Due to inherent variability in linear variable filters, calibrations cannot be transferred among instruments. Each instrument must be calibrated separately prior to use. This test method is not appropriate for FAEEs. It will cause a negative bias.

PRECISION

Based on an interlaboratory study conducted in 2011 that included 12 laboratories testing 27 different diesel blends, the following precisions were obtained (RR-D02-1795). The three different diesels were a Fischer-Tropsch diesel (10 % aromatics), along with a diesel with 21.2 % aromatics and one with 29.0 % aromatics. Three different biodiesel types (soybean, canola, and waste vegetable oil) were also in the interlaboratory study, where two different types (soybean and yellow grease) were used in the most recent ASTM D7371 study (RR-D02-1624) and 16 samples with 4 different diesel types were tested. The four different diesels were a Fischer-Tropsch diesel (0 % aromatics), an ultra-low-sulfur diesel (ULSD) research fuel, a ULSD with approximately 20 % aromatics, and a ULSD with approximately 30 % aromatics. The precision from the ASTM D7861 interlaboratory study was slightly better than that of ASTM D7371.

	ASTM D7861	ASTM D7371
Repeatability	0.011 (X + 6.485) vol %	0.01505 (X + 14.905) vol %
Reproducibility	0.043 (X + 6.485) vol %	0.04770 (X + 14.905) vol %

Where X is the average of two determinations. Examples of calculation of precision are shown here:

Concentration, vol. %	Repeatability		Reproducibility	
	ASTM D7861	ASTM D7371	ASTM D7861	ASTM D7371
1.0	0.08	0.24	0.32	0.76
5.0	0.13	0.30	0.49	0.95
10.0	0.18	0.37	0.71	1.19
15.0	0.24	0.45	0.92	1.43
20.0	0.29	0.53	1.14	1.66
25.0	0.35		1.35	
30.0	0.40		1.57	

Raman Spectroscopy for Analysis of Biodiesel

Mattley has demonstrated application of Raman spectroscopy to the analysis of biodiesel and petroleum-based fuels [11]. With no requirement for sample preparation and the ability to identify and quantify materials using robust, handheld, portable instrumentation, Raman has found many uses in a range of industries. In the case of fuels, Raman spectra contain a wealth of spectral features due to the presence of different types of hydrocarbons, resulting in a unique Raman fingerprint based on composition and chemical structure. Corn oil biofuel and petroleum-based diesel were compared by their Raman spectra. Although these spectra share some common features due to the hydrocarbon content of the samples, there are also a number of spectral differences observed in the fingerprint region from 500 to 2,000 cm^{-1}. Even though both samples are suitable for use as fuel in diesel engines, they have distinct Raman spectra that distinguish the biodiesel fuel (corn oil) from the petroleum-based diesel fuel. Specifically, the presence of peaks for stearate (a form of fatty acid found in animal and vegetable fats and oils) in the region from 1,600 to 1,800 cm^{-1} are specific for corn oil and are not observed in the Raman spectrum for petroleum-based diesel oil. These peaks, along with the other spectral differences, allow for easy discrimination of these fuels.

Distillation of Petroleum Products

SIGNIFICANCE

A distillation test is used to show the volatility of a fuel and the ease with which it can be vaporized. The fuel volatility requirements depend on engine design, size, nature of speed and load variations, and starting and atmospheric conditions. For engines in services involving rapidly fluctuating loads and speeds, such as in bus and truck operation, the more volatile fuels can provide the best performance, particularly with respect to smoke and odor. The biodiesel portion of the B6 to B20 blends may also provide smoke and odor improvement. However, the best fuel economy generally is obtained from the heavier types of fuels because of their higher heat content. This test is of greater significance for oils that are to be burned in vaporizing-type burners rather than for the atomizing type. ASTM D86 or ASTM D2887 may be used for this analysis. ASTM D7345 can also be used as an alternative method with the same limits. ASTM D86 is the referee test method.

Biodiesel exhibits a boiling point rather than a distillation curve. The fatty acid chains in the raw oils and fats from which biodiesel is produced are mainly comprised of straight-chain hydrocarbons with 16 to 18 carbons that have similar boiling temperatures. The atmospheric boiling point of biodiesel generally ranges from 330 to 357°C; thus, the specification value of 360°C for biodiesel is not problematic. This specification was incorporated as an added precaution to ensure that the fuel has not been adulterated with high boiling contaminants.

ASTM D5501, Ethanol in Denatured Fuel Ethanol by Gas Chromatography

SIGNIFICANCE

The ethanol content of denatured fuel ethanol is important to know in determining the blend ratios for adding denatured fuel ethanol into the finished gasoline. The ethanol content of denatured fuel ethanol will vary based on levels of denaturant, water, and the minor components common to ethanol production. Fuel ethanol is required to be denatured with gasoline in accordance with ASTM D4806. State and federal laws specify the concentration of ethanol in gasoline blends.

SCOPE

ASTM D5501 covers the determination of ethanol content of denatured fuel ethanol by GC. Ethanol is determined from 93 to 97 mass percent and methanol from 0.1 to 0.6 mass percent. This method does not identify and quantify methanol but does purport to identify all individual components that make up the denaturant. Water cannot be measured by this test method, but it can be measured by procedures such as ASTM D1364. This test method is inappropriate for impurities that boil at temperatures above 225°C or for impurities that cause poor or no response in a flame ionization detector, such as water.

Biofuel product specifications include ASTM D4806 for an ethanol limit of 92.1 volume percent min and ASTM D5798 for an ethanol limit of 51 to 83 volume percent.

Fusel oils are alcohol contaminants (primarily C5) formed during the ethanol manufacturing process. An insignificant amount of fusel oil is expected to be found in E85 and E95 fuels. A ruggedness test conducted on commercial E95 samples produced the results given in Table 4.16. Ethanol was determined using ASTM D5501. All other species were determined by a two GC column method [12].

ANALYSIS

In this test method, a fuel ethanol sample is injected into a gas chromatograph equipped with a methyl silicone-bonded phase-fused silica capillary column. Helium carrier gas transports the vaporized aliquot through the column where the components are separated. They are revealed by a flame ionization detector as they elute from the column. The detector signal is processed by an electronic data acquisition system. The identification of all components is done by comparing their retention times with those of the standards, and concentration is calculated by using normalized peak areas. An example of a sample chromatogram showing the separation of methanol and ethanol using ASTM D5501 is shown in Fig. 4.11.

PRECISION

No significant difference was found between the ethanol or methanol content obtained by this test method and the expected content based on their concentration added to the samples. The precision of the method is as follows:

Component	Range, mass %	Repeatability	Reproducibility
Ethanol	93–97	0.21	0.53
Methanol	0.01–0.6	$0.01859 \times X^{0.5}$	$0.01172 \times X^{0.5}$

Note: Where X is the mass percent of the component being determined.

TABLE 4.16 Fuel Oils: Commercial E95 Samples

Component	Sample 1	Sample 2	Sample 3	Sample 4
Methanol	0.038; 0.037	0.059; 0.057	0.019; 0.018	0.038; 0.039
Ethanol	95.67; 95.65	95.98; 95.93	98.58; 98.68	96.09; 97.13
n-Propanol	0.104; 0.105	0.087; 0.086	0.043; 0.042	0.083; 0.084
i-Butanol	0.054; 0.055	0.040; 0.039	0.049; 0.048	0.050; 0.051
n-Butanol	0.002; 0.002	0.002; 0.002	0.002; 0.002	0.001; 0.001
3-Methyl-1-butanol	0.134; 0.133	0.114; 0.115	0.125; 0.124	0.150; 0.151
2-Methyl-1-butanol	0.252; 0.251	0.156; 0.154	0.121; 0.120	0.162; 0.163

Note: All results are in mass percent.

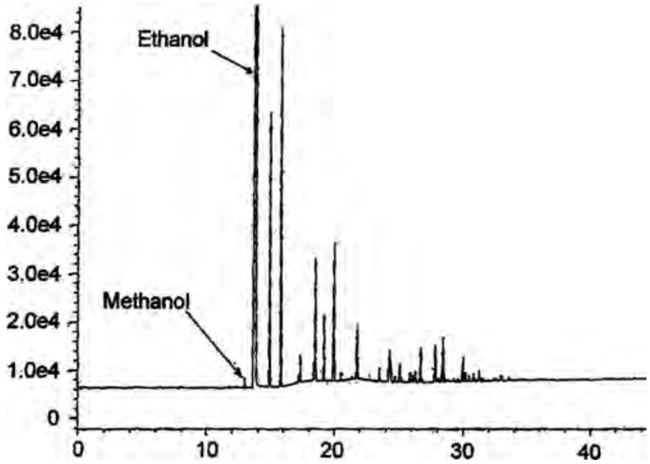


FIG. 4.11 Gas chromatogram of methanol and ethanol using ASTM D5501, *Standard Test Method for Determination of Ethanol and Methanol Content in Fuels Containing Greater Than 20 % Ethanol by Gas Chromatography.*

ASTM D7318, ASTM D7319, and ASTM D7328, Inorganic Sulfate and Chloride in Ethanol

SIGNIFICANCE

Ethanol is used as a blending agent added to gasoline. The contaminants of ethanol fuel with salt anions such as chloride and sulfate can affect engine performance because salts and sediments that are formed can block the nozzles and induce corrosion in the vehicle components in contact with the fuel. Sulfates are indicated in filter-plugging deposits and fuel injector deposits. When fuel ethanol is burned, sulfates may contribute to sulfuric acid emissions. Ethanol acceptability for use depends on its sulfate content. Sulfates and chlorides can be found in filter-plugging deposits and fuel injector deposits. The acceptability for use of the fuel components and the finished fuels depends on the sulfate and chloride content.

Low concentrations of inorganic (ionic) chloride ions are corrosive to many metals. It is desirable to minimize inorganic chloride compounds in fuel ethanol. An inorganic chloride limit of 1 mg/kg maximum has been found to be adequate in protecting fuel system components.

Both the ABNT and ASTM specifications have a limit of 4 mg/kg maximum sulfates; however, the Brazilian specification is for hydrous ethanol. Anhydrous ethanol is made from hydrous ethanol, so the specification would also apply to anhydrous ethanol. CEN has no such limit.

The method is applicable to hydrous and anhydrous denatured ethanol to be used in motor fuel applications. Chassaniol has discussed the applications of ion chromatography in the analysis of petroleum products [13].

SCOPE

ASTM D7566 allows a maximum of 1-mg/kg of halogens using ASTM D7359. This is an ASTM Committee D16 test method, and there is no equivalent method in the D02 Committee. This test method determines fluorine, chlorine, and sulfur in aromatic hydrocarbons and their mixtures by oxidative pyrolysis combustion followed by ion chromatographic separation and conductivity detection. Applicability of this test method for biofuels is not known.

Ethanol fuel specification ASTM D4806 allows a maximum of 10 mg/kg or 8 mg/L, and ASTM D5798 allows a maximum of 1 mg/kg inorganic chloride content.

Some definitions specific to these analyses are as follows:

- *Existent Inorganic Sulfate*—Inorganic sulfate species actually present in the sample at the time of analysis with no oxidation treatment. Specifically in this test method, inorganic sulfate is present as sulfate in ethanol (ASTM D7318, ASTM D7319, and ASTM D7328).
- *Inorganic Chloride*—Chloride present as hydrochloric acid, ionic salts of this acid, or mixtures of these (ASTM D7319 and ASTM D7328).
- *Inorganic Sulfate*—Sulfate species (SO_4^{-2}) present as sulfuric acid, ionic salts of this acid, or as mixtures of these (ASTM D7318, ASTM D7319, and ASTM D7328).
- *Potential Sulfate*—Inorganic sulfate species present after the sample has been reacted with an oxidizing agent (ASTM D7319 and ASTM D7328).

ANALYSIS

There are three procedures available for this analysis based on potentiometric titration or ion chromatography. These test methods are:

ASTM D7318	Total Inorganic Sulfate by Potentiometric Titration
ASTM D7319	Total and Potential Sulfate and Inorganic Chloride by Direct Injection Suppressed Ion Chromatography
ASTM D7328	Total and Potential Inorganic Sulfate and Total Inorganic Chloride by Ion Chromatography Using Aqueous Sample Injection

These test methods were specifically developed for use in the analysis of ethanol fuels. However, since their publication, it has been observed that ion chromatographic ASTM D7319 and ASTM D7328 are much more widely used in industry laboratories than the potentiometric titration ASTM D7318. The equivalents of these ASTM test methods are NBR 10894 in Brazil and prEN 15492 in the European Union.

Gandhi [14] has shown some data on comparative analysis of ethanol for chloride and sulfate (Table 4.17) using a tri-chamber method and a continuous method (ASTM D7319 and ASTM D7328). The system has been shown to be stable even after 1,500 injections of a denatured ethanol sample fortified with sulfate and hydrogen peroxide. The retention times (for column performance), repeatable area counts (for suppressor performance), and consistent concentration values (for calibration stability) were found to be reliable, rugged, and dependable over 1,500 injections:

Sulfate Concentration, mg/kg	5.607 ± 0.2744 (4.89 % RSD)
Area Counts, mV/s	123.634 ± 0.5744 (0.4646 % RSD)
Retention Time, min	12.54 ± 0.0267 (0.2128 % RSD)

ASTM D7318

This method is applicable to hydrous ethanol, anhydrous ethanol, and anhydrous denatured ethanol (which is added as a blending agent with spark-ignition fuels). This test method covers a potentiometric titration procedure for determining the existent inorganic sulfate content of ethanol. The range of determination is 1.0 to 20 mg/kg existent inorganic sulfate. An ethanol sample is titrated in ethanolic medium with a standard lead nitrate solution. Lead sulfate precipitate is formed during the titration. Perchloric acid is added to remove possible interference from carbonate. The end point is signaled by an increase in lead ion activity as measured by a lead-selective electrode.

PRECISION

The precision for existent inorganic sulfate is as follows (RR-D02-1615):

Repeatability	$0.1711 (X + 0.1301)^{0.2678}$
Reproducibility	$0.5807 (X + 0.1301)^{0.2678}$

Note: Where X is the average result of two determinations.

Because there are no generally accepted reference materials for this property, bias of this method cannot be determined.

ASTM D7319

This test method covers a direct ion chromatographic procedure for determining existent and potential inorganic sulfate and total inorganic chloride in hydrous and anhydrous denatured ethanol and butanol to be used in motor fuel applications. It is intended for the analysis of ethanol and butanol samples containing between 1.0 and 20 mg/kg of existent or potential inorganic sulfate and 1.0 to 50 mg/kg of inorganic chloride. 1-Butanol, 2-butanol, and isobutanol are included in the testing of this method, but tertiary butanol is not included.

TABLE 4.17 ASTM Round-Robin Data for Chloride and Sulfate in Ethanol

Analyte	Concentration, mg/kg	Tri-Chamber r	Tri-Chamber R	Continuous r	Continuous R
Total chloride	1.0	0.07	0.42	0.07	0.42
	20.0	0.56	3.40	0.56	3.40
	50.0	1.06	6.45	1.06	6.45
Total sulfate	1.0	0.09	1.22	0.25	1.60
	4.0	0.20	2.86	0.61	3.99
	20.0	0.55	7.73	1.77	11.54
Potential sulfate	1.0	0.13	0.97	0.27	1.43
	4.0	0.33	2.55	0.71	3.73
	20.0	1.01	7.80	2.16	11.32

Note: Where r is repeatability and R is reproducibility. From [14].

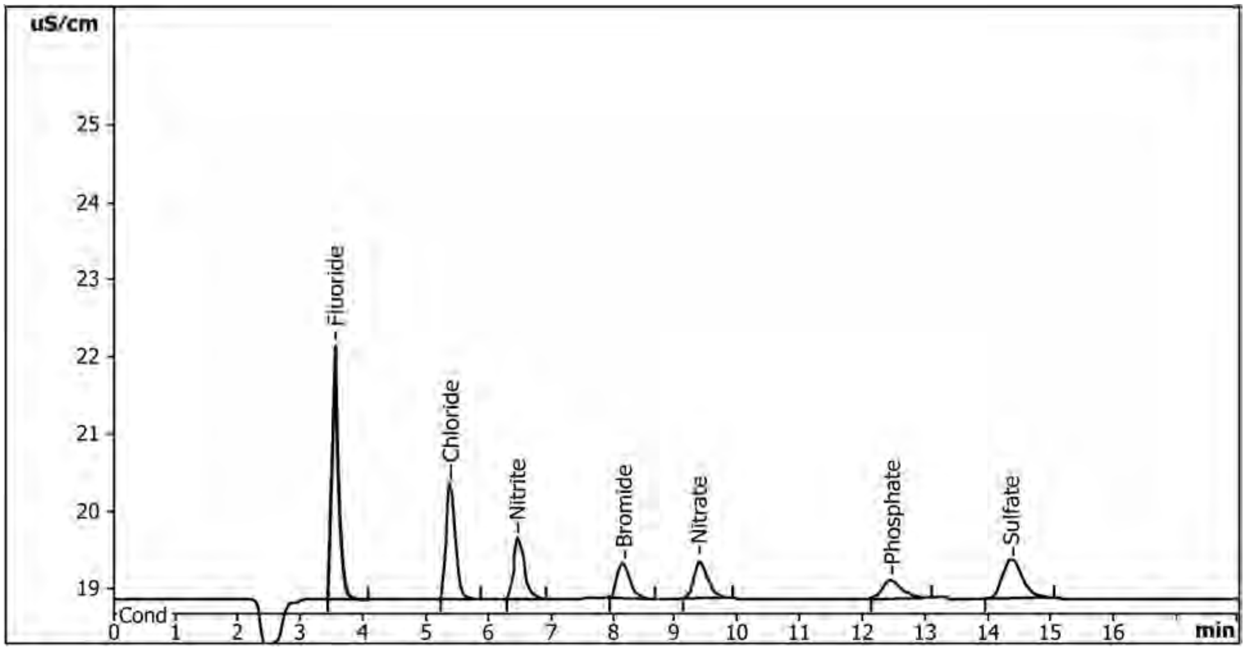
In this test method for existent inorganic sulfate and total chloride, a small volume of an ethanol or butanol sample is directly injected into a suitable configured ion chromatograph in accordance with manufacturers' recommendations for this test method. For potential sulfate, 0.5 mL of 30 % hydrogen peroxide solution is added to 9.5 mL of the ethanol or butanol sample and then injected into the ion chromatograph. Ions are separated based on their affinity for exchange sites of the resin with respect to the resin's affinity for the eluent. The suppressor increases the sensitivity of the test method by increasing the conductivity of the analyte and decreasing the conductivity of the eluent. It also converts the eluent and analytes to corresponding hydrogen forms of anions. Anions are quantified by integrating their responses compared with an external calibration curve. The calibration standards are prepared in an aqueous matrix. The use of acid suppression technology is more significant for the precision of sulfate measurement than for chloride. The sulfate precision will be worse if acid suppression is not used. A similar method for chloride determination can be found in EN 15492 for total chloride.

Because butanol has limited solubility in water, the samples should not be diluted with water prior to analysis. In addition, any remnant water from the sample delivery device or glassware may lead to low recoveries of sulfate and chloride. Unintended water contamination of the sample should be avoided. Added water can lead to phase separation of the sample. Chloride and sulfate ions can migrate to the water-dominant phase and lower the recovery from the butanol. A typical ion chromatogram of a solution containing 1 mg/L of various anions in water is shown in Fig. 4.12.

INTERFERENCES

Interferences can be caused by substances with similar ion chromatographic retention times, especially if they are in high concentration compared to the analyte of interest. Sample dilution can be

FIG. 4.12 Ion chromatogram of anionic species by ASTM D7319, *Standard Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography.*



used to minimize or resolve most interference problems. A water dip (system void or negative peak) can cause interference with some integrators. Usually, water dip should not be a problem for chloride and sulfate determinations because their peaks are far away from the water dip. Given the trace amounts of chloride and sulfate determined in this test method, interferences can be caused by contamination of glassware, eluent, reagents, and so on. Hence, great care should be kept to ensure that the contamination is kept to a minimum.

PRECISION

Based on ASTM RR-D02-1614, the following precision is expected for results by ASTM D7319 for ethanol and butanol (Table 4.18).

Because there is no generally accepted reference material for this analysis, no statement regarding the bias of this method can be made.

ASTM D7328

This method can measure between 0.55 and 20 mg/kg of existent inorganic sulfate, 4.0 to 20 mg/kg of potential inorganic sulfate, and 0.75 to 50 mg/kg of total inorganic chloride in hydrous and anhydrous denatured ethanol to be used in motor fuel applications. For existent inorganic sulfate and chloride, a small volume of a sample is evaporated to dryness and reconstituted to the initial sample volume with deionized water. Then it is injected into an ion chromatograph consisting of appropriate ion

TABLE 4.18 Precision for Chloride and Sulfate Determination of Alcohols

Analysis	Matrix	Applicable Range, mg/kg	PLOQ Estimate, mg/kg	Repeatability	Reproducibility
Total chloride	Ethanol	0.75–50	0.75	$6.851^{-2}\ X^{0.7000}$	$0.4172\ X^{0.7000}$
	Butanol	0.1–31.6	0.56	$9.55^{-3}\ (X + 16)$	$0.03073 \times (X + 16)$
Existent inorganic sulfate	Ethanol	1.0–20	0.01	$0.09030 \times (X + 10^{-04})^{0.623}$	$1.2291 \times (X + 1.00^{-4})^{0.6230}$
	Butanol	0.3–12.1	1.1	$0.01134 \times (X +25)$	$0.04898 \times (X + 25)$
Potential sulfate	Ethanol	1.0–20	0.01	$0.09645 \times (X + 0.59494)^{0.8642}$	$0.9408 \times (X +0.59494)^{0.8642}$
	Butanol	0.3–11.7	0.61	$0.01516 \times (X + 11)$	$0.08221 \times (X + 11)$

Note: Where X is the average of two determinations; PLOQ = pooled limit of quantitation.

TABLE 4.19 Precision of ASTM D7328 for Chloride and Sulfate

Analysis	Range, mg/kg	PLOQ, mg/kg	Repeatability	Reproducibility
Total chloride	0.75–50	0.75	0.02078 (X + 10.0709)	0.1173 (X + 10.0709)
Existent inorganic sulfate	0.55–20	0.55	$0.2319\ (X + 1.00^{-04})^{0.5000}$	$1.0963(X + 1.00^{-04})^{0.5000}$
Potential sulfate	4.0–50	4.0	$0.1763\ X^{0.4000}$	$1.0505\ X^{0.4000}$

Note: Where X is the average of two determinations; PLOQ = pooled limit of quantitation.

exchange columns, a suppressor, and a conductivity detector. For potential sulfate, a small volume of the sample is evaporated to dryness and reconstituted to the initial sample volume with 0.90 % hydrogen peroxide solution in water and injected into an ion chromatograph.

Similar methods for chloride and sulfate determinations can be found in ASTM D5827 for engine coolant and for ethanol in ISO/CEN 15492.

INTERFERENCES

See those listed under ASTM D7319.

PRECISION

See Table 4.19 as well as RR-D02-1611. Because no generally accepted reference materials are available for this analysis, no statement regarding the bias of this test method can be made.

ASTM D1541 and ASTM D1959, Iodine Number

SIGNIFICANCE

The iodine number (also referred to as the iodine index or iodine value) reflects the stability to oxidation. The iodine number is directly related to the number of double bonds present in the biodiesel fuel, which in turn depends on the origin of the vegetable oil used. According to ASTM D1959, when the iodine number is determined in oils and fats containing conjugated double bonds, the result is not a measure of total unsaturation but instead it is an empirical value that is only reflective of total unsaturation. ASTM D1541 is used to obtain the total iodine number of biodiesel samples containing conjugated double bonds.

The iodine number is expressed in grams of iodine per 100 g of the sample. A relatively high carbon double bond content in the biodiesel will yield a high iodine number. However, the iodine number does not distinguish structural differences in the fatty acid component of the biodiesel. Biodiesel containing relatively high concentrations of unsaturated fatty components is more susceptible to oxidative degradation. Storage time, exposure to light and air, exposure to relatively high temperatures, fatty acid concentration, water content, and the presence of certain contaminants accelerate biodiesel degradation and polymerization [15]. Biodiesels with iodine numbers higher than 135 g/100 g would make the biodiesel unsuitable as a fuel. The removal of unsaturates through processes such as hydrogenation would result in an increase in viscosity and a reduction in cold temperature flowability. On the other hand, the higher the level of unsaturation of the oil, the lower the oxidation stability of the resulting biodiesel [16].

ANALYSIS

Presently, Cd 1-25 of the American Oil Chemists' Society, a procedure for oils and fats, is the method used for the determination of iodine number. Known as the Wijs method, it is based on the reagent iodine monochloride dissolved in glacial acetic acid to produce a 0.1-mol/L solution. This procedure can also be used for the determination of the iodine number of biodiesel because the unsaturation in the alkyl esters is the same as the original fat. The determination of the iodine number in biodiesel by redox titration with a solution of sodium thiosulfate is described in EN 14111 and follows the Wijs method for oils and fats.

Despite the excellence of the Wijs method, the use of Wijs solution requires careful handling and is relatively expensive in cost. Hence, a new method is proposed for oils and fats that is based on the work of Margosches, Hinner, and Friedmann [17]. This method uses the ethanol solutions of the fats and the reagent iodine and utilizes the aqueous thiosulfate solution as a titrant. It is also faster, taking only about 10 min (versus more than an hour for the Wijs procedure).

RESULTS

Iodine numbers obtained for several biodiesel samples by comparing results from the Wijs method and the proposed method are shown in Table 4.20. The T-test calculations show complete agreement between the two sets of results. Based on the F-test, there is an agreement in the precision of the two procedures. The data in Table 4.20 clearly show that the iodine number is not only indicative of the quantity of double bonds but can also be used as a parameter for differentiating among the vegetable, animal, and blend biodiesels.

A potentiometric titration from palm oil has been developed as an alternative technique for the biodiesel matrix. Potentiometric titration was found to be more precise than volumetric titration with a color end point. Based on the analyses, results with potentiometric and volumetric titrations were comparable. However, solvents used to dissolve the biodiesel sample and the reaction temperatures have shown significant differences, indicating the influence of these variables in the

TABLE 4.20 Comparison of Two Methods for Iodine Values in Biodiesel

Biodiesel Sample	Wijs Method	Margosches, Hinner, and Friedmann Method
Soya	129.6 ± 0.6	128.5 ± 1.5
Corn	113.5 ± 1.0	112.2 ± 1.6
Sunflower	128.2 ± 1.9	128.3 ± 2.4
Beef tallow	45.5 ± 0.9	47.0 ± 1.2
Castor	71.0 ± 1.2	70.7 ± 1.8
Canola	92.4 ± 1.6	91.1 ± 2.5
Swine lard	57.8 ± 1.5	60.3 ± 2.0
Cotton	108.5 ± 0.8	108.4 ± 2.0
Soya + cotton	123.5 ± 1.3	124.4 ± 1.0
Swine lard + soya	86.2 ± 2.5	88.4 ± 1.6

Note: Iodine values are expressed as grams of iodine per 100 g of the sample. Each determination was done in five replicates.

determination of iodine values. For temperature, there was a tendency to increase the iodine value in the measurements at 37°C. However, the results at 26°C compare well with the iodine numbers obtained by other ASTM, EN, DIN, or Association of Official Chemical Societies (AOCS) test methods [16].

No. of Analysis	Titration Technique	Solvent	Iodine Value, g/100 g	% RSD
1	Volumetric	Carbon tetrachloride	61.97	0.54
2	Volumetric	Carbon tetrachloride	63.89	1.03
3	Volumetric	Cyclohexane/Acetic acid	61.46	0.41
4	Volumetric	Cyclohexane/Acetic acid	63.28	0.25
5	Potentiometric	Carbon tetrachloride	63.201	0.044
6	Potentiometric	Carbon tetrachloride	62.782	0.322
7	Potentiometric	Cyclohexane/Acetic acid	61.707	0.285
8	Potentiometric	Cyclohexane/Acetic acid	63.186	0.244

ASTM D6584, Total Glycerides and Glycerin in B-100 Biodiesels

SIGNIFICANCE

Free and bonded glycerin content reflects the quality of biodiesel. A high content of free glycerin may cause problems during storage, or in the fuel system, due to separation of the glycerin. High total glycerin content can lead to injector fouling and may also contribute to the formation of deposits at injection nozzles, pistons, and valves. Free glycerol in FAMEs is dependent on the production process, and high values may result from insufficient separation or washing of the ester product. The glycerol may separate in storage once its solvent methanol has evaporated. Free glycerol separates from the biodiesel and falls to the bottom of the storage or vehicle fuel tank, attracting other polar components such as water, monoglycerides, and soaps. These can lodge in the vehicle fuel filter and can result in damage to the vehicle fuel injection system. High free glycerol levels can also cause injector coking. For these reasons, free and total glycerol are limited in biodiesel specifications [6].

Region	Free Glycerol Limit	Total Glycerol Limit	Test Method(s)
Brazil	0.02 % m/m max	0.38 % m/m	NBR 15341/EN 14105/14106
European Union	0.02 % m/m max	0.25 % m/m	EN 14105/14106
United States	0.020 % m/m max	0.24 % m/m	ASTM D6584

SCOPE

ASTM D6584 covers the quantitative determination of total monoglyceride, total diglyceride, total triglyceride, and free and total glycerin in B-100 methyl esters by GC. The range of quantitation for monoglyceride is 0.009 to 0.7786 mass percent; for diglycerides, it is 0.092353 to 0.54475 mass percent; and for triglycerides, it is 0.00092857 to 1.3881 mass percent. The range of quantitation for free glycerin is 0.0005714 to 0.019533 mass percent and for total glycerin from 0.0090714 to 0.42767 mass percent. This procedure is not applicable to vegetable oil methyl esters obtained from lauric oils, such as coconut oil and palm kernel oil.

Biodiesel B100 blendstock (ASTM D6751) allows free and total glycerin content to a maximum of 0.020 and 0.240 mass percent, respectively, for all grades. AOCS Standard Procedure Ck 2-09 may also be used for the determination of total or free glycerin. ASTM D6584 shall be the referee test method.

ANALYSIS

The sample is analyzed by GC after silylating with N-methyl-N-trimethylsilyl trifluoroacetamide. Calibration is achieved by the use of two internal standards and four reference materials. Mono-, di-, and triglycerides are determined by comparing to monoolein, diolein, and triolein standards, respectively. Average conversion factors are applied to mono-, di-, and triglycerides to calculate the bonded glycerin content of the sample. See Figs. 4.13–4.19 for chromatograms of canola-based, soy-based, mixed feedstocks-based, and palm-based B100 biodiesel samples obtained using ASTM D6584.

PRECISION

The precision of this test method was determined based on a 2012 interlaboratory study that involved 11 laboratories and 14 B-100 biodiesel samples from a variety of sources (RR-D02-1756).

Parameter	Repeatability	Reproducibility
Total glycerin	$0.76E^{-01} \times TG^{0.73}$	$0.29 \times TG^{0.73}$
Free glycerin	$0.195E^{-01} \times FG + 0.0001^{0.27}$	$0.246E^{-01} \times FG + 0.0001^{0.27}$
Total monoglyceride	$0.78E^{-01} \times M^{0.62}$	$0.46 \times M^{0.62}$
Total diglyceride	$0.344 \times D^{0.93}$	$0.784 \times D^{0.93}$
Total triglyceride	$0.12 \times T^{0.687}$	$1.08 \times T^{0.687}$

Note: Where TG, FG, M, D, and T are the calculated results for total glycerin, free glycerin, total monoglyceride, total diglyceride, and total triglyceride, respectively, expressed as mass percent content in the sample.

FIG. 4.13 Reference chromatogram of glycerides by ASTM D6584, *Standard Test Method for Determination of Total Monoglycerides, Total Diglycerides, Total Triglycerides, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography.*

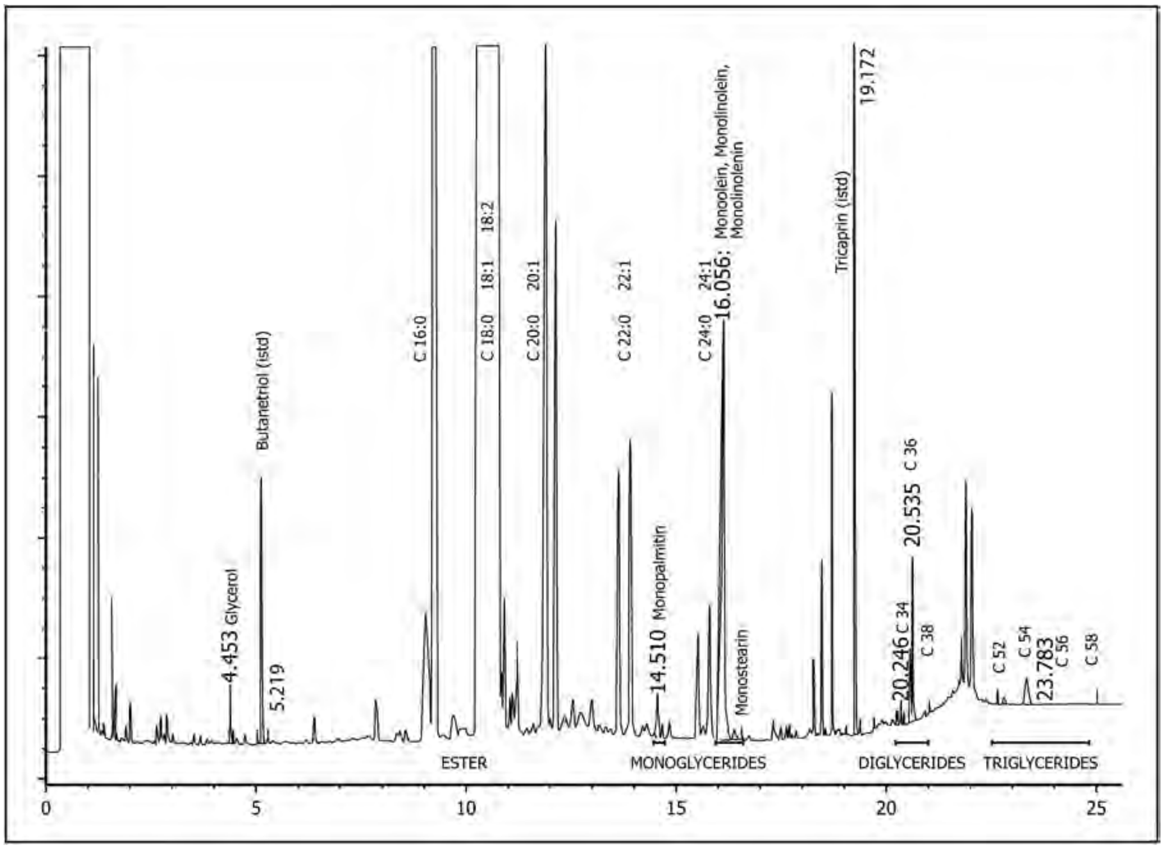


FIG. 4.14 Overlay of canola-based B100 and monoglyceride standard solution by ASTM D6584, *Standard Test Method for Determination of Total Monoglycerides, Total Diglycerides, Total Triglycerides, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography.*

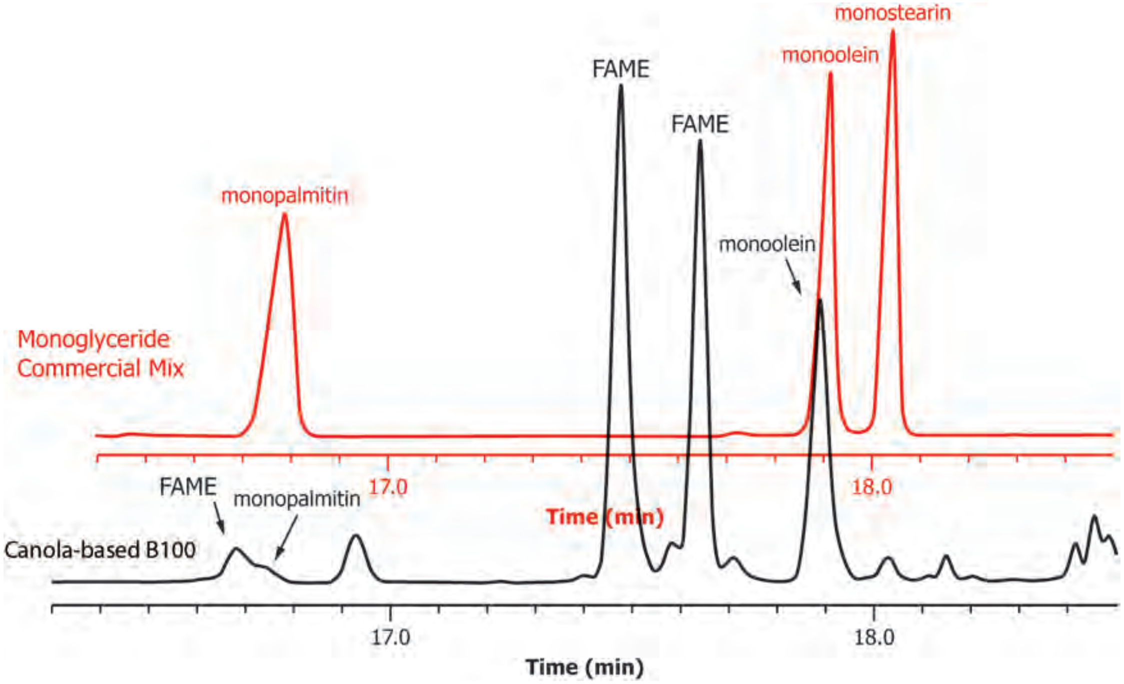


FIG. 4.15 Overlay of soy-based B100 and monoglyceride standard solution by ASTM D6584, *Standard Test Method for Determination of Total Monoglycerides, Total Diglycerides, Total Triglycerides, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography.*

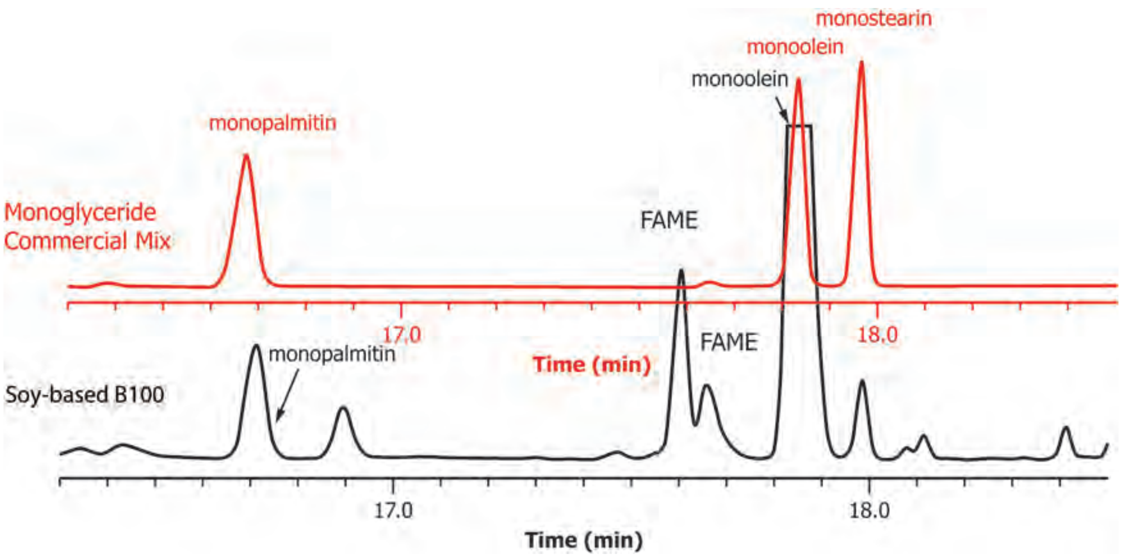
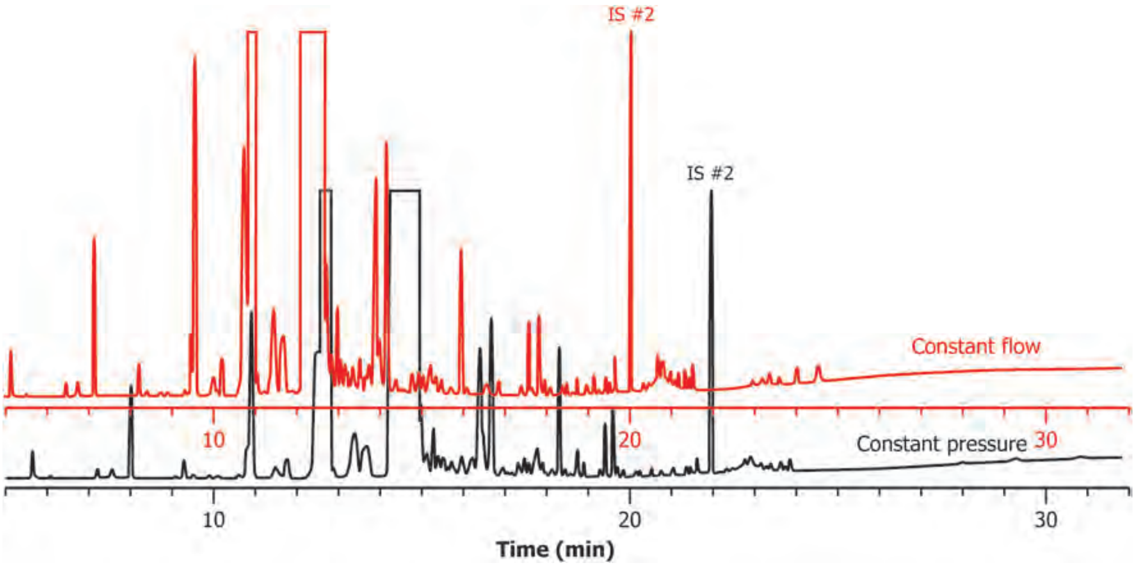


FIG. 4.16 Overlay of B-100 sample derived from mixed feedstocks by ASTM D6584, *Standard Test Method for Determination of Total Monoglycerides, Total Diglycerides, Total Triglycerides, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography.*



EN 14105, Free and Total Glycerol and Glycerides in Fatty Acid Methyl Esters

SIGNIFICANCE

Fats and oils consist of high concentrations of triacyl glycerides that are based on a tri-ol (glycerine) backbone with three fatty acid side chains. Addition of NaOH causes hydrolysis of the ester bonds between the glycerol and the fatty acid chains. Glycerine is therefore the major by-product of the reaction. Fortunately, the glycerine component is significantly denser than the fatty acid esters and can be separated by gravity. A low concentration of glycerine is required to ensure good cold weather performance and to prevent injector port deposits from reducing engine efficiency. The levels of glycerine are carefully regulated in EN 14105 and ASTM D6751.

Saturated monoglycerides have been identified as among the problem areas for biodiesel blended diesel fuels. The saturated monoglyceride content of biodiesel will depend on the manufacturing steps taken to reduce the concentration (e.g., distillation,

FIG. 4.17 Example of a canola-based B-100 chromatogram obtained by ASTM D6584, *Standard Test Method for Determination of Total Monoglycerides, Total Diglycerides, Total Triglycerides, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography.*

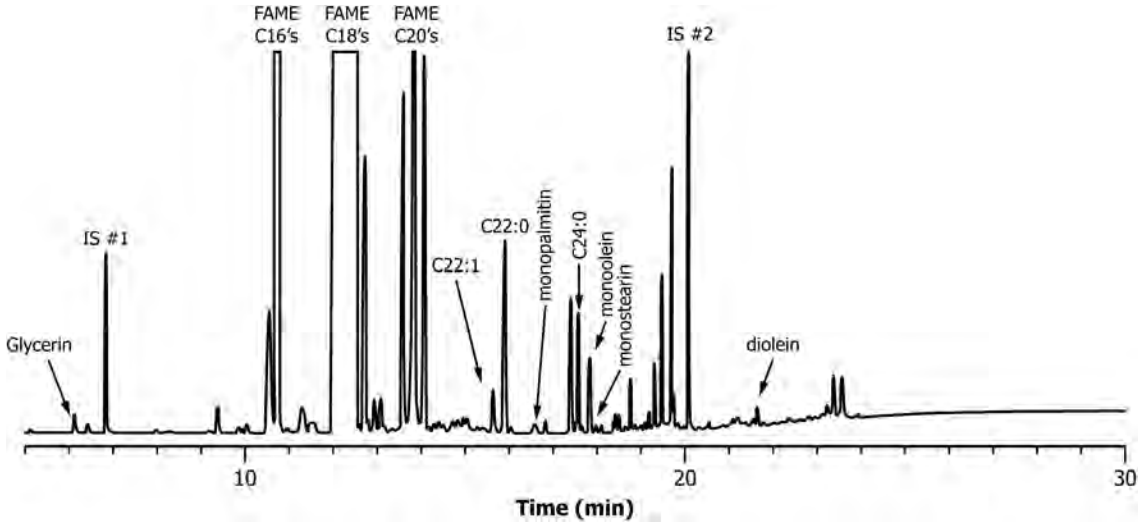
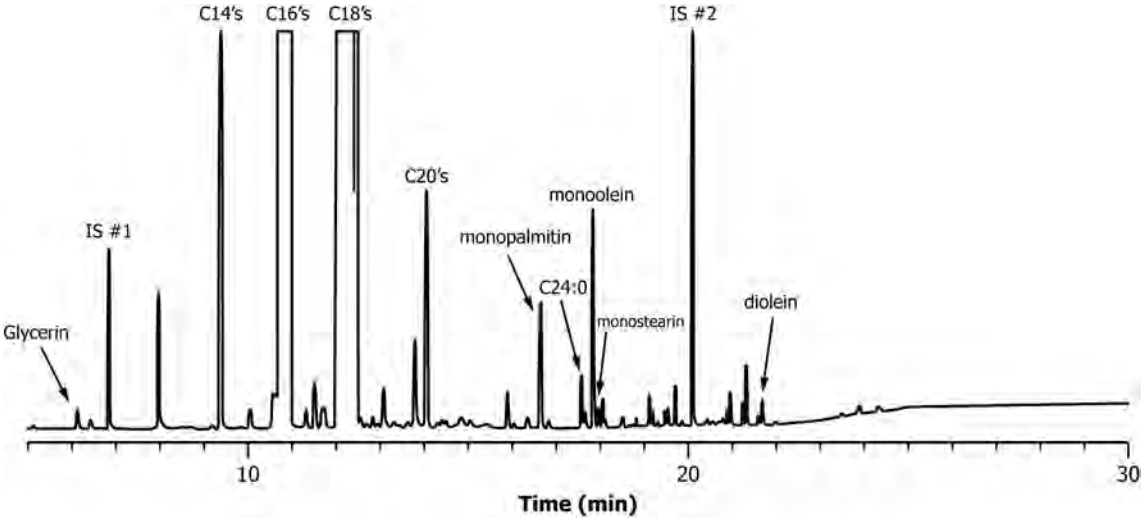


FIG. 4.18 Example of a palm-oil-based B-100 chromatogram obtained by ASTM D6584, *Standard Test Method for Determination of Total Monolycerides, Total Diglycerides, Total Triglycerides, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography.*



settling). Monoglycerides have poor solubility in diesel fuel and their solubility is temperature dependent [18].

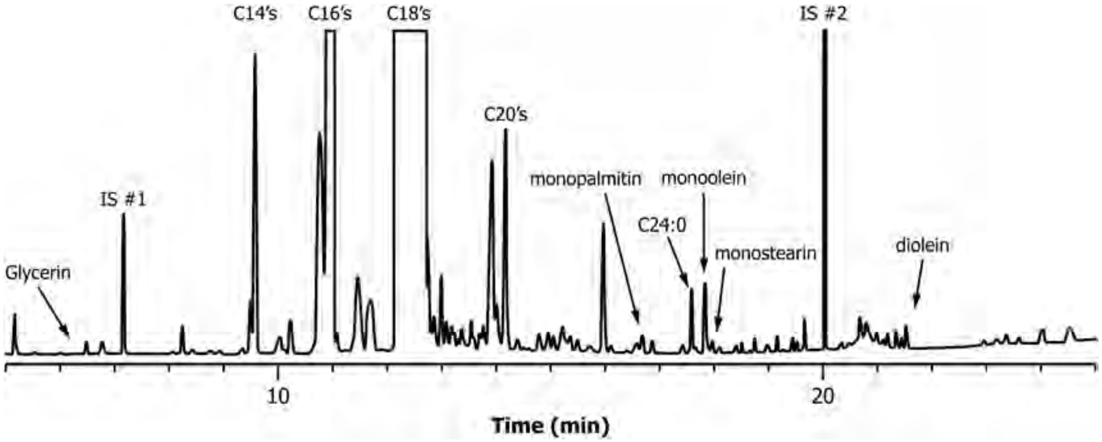
ANALYSIS

Gas chromatographic analysis of the concentration of total glycerine requires a nondiscriminative cold injection system that can transfer volatile and heavy sample components to the column. A 5 % phenyl polysilphenylene-siloxane stationary phase coupled with a flame ionization detector is used for the accurate quantitation of the glycerine and glycerides contained in the sample. A total glycerine level of 0.25 % m/m is permitted under EN 14214, and the analysis must be capable of detecting levels of total glycerine between 0.05 % and 0.5 % m/m.

Under the conditions described, the quantification limits are 0.01 mass percent for free glycerol and 0.10 mass percent for all glycerides. This method is suitable for FAMEs prepared from rapeseed, sunflower, soybean, palm, animal oils and fats, and mixtures of these. It is not suitable for fats produced from or containing coconut and palm kernel oil derivatives because of the overlapping of different glyceride peaks.

This test method is similar to ASTM D6584 (discussed earlier). It determines the free and total glycerol and residual mono-, di-, and

FIG. 4.19 Example of a mixed feedstock-based B-100 chromatogram obtained by ASTM D6584, *Standard Test Method for Determination of Total Monoglycerides, Total Diglycerides, Total Triglycerides, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography*.



triglyceride content in FAMEs prepared from rapeseed, sunflower seed, soybean, palm, animal oils, fats, and their mixtures. The sample is analyzed after silylating with N-methyl-N-(trimethylsilyl) trifluoroacetamide. After derivatization, the sample is injected directly onto the polydimethylsiloxane column. Quantitation of glycerol is performed against 1,2,4-butanetriol as an internal standard. Mono-, di-, and triglycerides are evaluated against new individual internal standards for each glyceride category. The method requires column performance criteria calculated for every analysis.

PRECISION

The following precision limits are based on a European interlaboratory study conducted in 2008 involving 16 laboratories—with each having carried out two determinations on each sample.

Compound	Repeatability	Reproducibility
Free glycerol	0.1615 X + 0.0003	0.1833 X + 0.0061
Monoglycerides	0.0787 X + 0.0059	0.1867 X + 0.0654
Diglycerides	0.0989 X + 0.0042	0.1885 X + 0.0289
Triglycerides	0.0469 X + 0.0128	0.3180 X + 0.0520
Total glycerol	0.1092 X − 0.0034	0.1902 X + 0.0115

Note: Where X is the mean value of the two results being compared.

ASTM D7591, Free and Total Glycerin in Biodiesel Blends

SIGNIFICANCE

Petroleum-based diesel may be blended with biodiesel. High levels of free glycerin in biodiesel can cause injector deposits ("gel effects") as well as clog fuel systems. High levels of unreacted glycerides can cause injector deposits, can adversely affect cold weather operation, and can result in filter plugging. The free glycerin method is used to determine the level of glycerin in the fuel. High levels of free glycerin can cause injector deposits as well as clogged fueling systems and can result in a buildup of free glycerin in the bottom of storage and fueling systems. The total glycerin method is used to determine the level of glycerin in the fuel, including the free glycerin and the glycerin portion of any unreacted or partially reacted oil or fat. Low levels of total glycerin ensure that high conversion of the oil or fat into its monoalkyl esters has taken place.

SCOPE

ASTM D7591 is applicable for determining free and total glycerin content of biodiesel (B100) and blends (B0 to B20) with diesel fuel oils defined by ASTM D975 Grades 1-D, 2-D, and low-sulfur 1-D and 2-D as well as ASTM D6751 (for B100 feedstocks). It is intended for the analysis of biodiesel and blend samples containing between 0.5 to 50 mg/kg glycerin.

ANALYSIS

- *Free Glycerin*—A small volume of an extract of the blend sample is directly injected into an ion chromatograph consisting of an appropriate ion exchange column and into an electrochemical detector. Glycerin is separated based on its affinity for ion exchange sites for the eluent. An electrochemical detector is used for the detection of glycerin. It is quantified by peak area, based on an external calibration curve, and is reported as mg/kg. Calibration standards are prepared from commercially available glycerin (99 + % pure) in an aqueous solution.
- *Total Glycerin*—A small volume of an extract of a saponized blend sample is directly injected into an ion chromatograph, consisting of an appropriate ion exchange column, and into an electrochemical detector. Glycerin is separated based on its affinity for ion exchange sites of the resin with respect to the resin's affinity for the eluent. An electrochemical detector is used for the detection of glycerin. It is quantified by peak area based on an external calibration curve and is reported as mg/kg. Calibration standards are prepared from commercially available glycerin (99 + % pure) in an aqueous solution.

TABLE 4.21 Precision of ASTM D7591 for Free and Total Glycerin

	Free Glycerin		Total Glycerin	
Biodiesel Blends	**Repeatability**	**Reproducibility**	**Repeatability**	**Reproducibility**
B100	$0.19E{-}01\ X^{0.8}$	$0.2537\ X^{0.8}$	$0.117\ X^{1.4}$	$0.8274\ X^{1.4}$
B1 to B6 blends	$1.8960\ X^{1.5}$	$2.9337\ X^{1.5}$	5.079E−02 X	9.856E−02 X
B7 to B10 blends	$4.289E{-}06\ X^{-0.3}$	$9.373E{-}06\ X^{-0.3}$	$0.2798\ X^{1.5}$	$0.7850\ X^{1.5}$
B10 to B20 blends	8.863E−02 X	2.645E−02 X	$1.243\ X^{1.3}$	$2.422\ X^{1.3}$

Note: Where X is the average of results in mass percent.

PRECISION

Based on an interlaboratory study (RR-D02-1737) conducted in 2009 in which eleven laboratories participated in analyzing eleven diesel and biodiesel samples, the precision was calculated as summarized in Table 4.21.

Fatty Acid Methyl Esters in Biodiesel Using IP 599 Test Method

The IP 599 test method determines FAMEs in aviation turbine fuel by GC using heart-cut and refocusing. An application note from PAC Instruments indicates that the analyzer provides a unique GC analyzer, combining clean-switching and refocusing. It provides accurate quantitative data on individual and total FAME components in the range of C16 to C18, with the option to analyze C14 FAMEs. The method is specified for the range of approximately 3.5 to 116 mg/kg FAMEs. This is adequate to meet the 5 mg/kg lower limit defined in Defense Department Standards 91-91 and ASTM D1655. The Energy Institute (London) conducted an interlaboratory study among eight laboratories from Europe and Canada analyzing samples by this method. The precision calculated exceeds the known precisions obtained by IP 583 (IR method), IP 585 (GC-MS method), and IP 590 (high-performance liquid chromatography [HPLC] method). Additionally, the FAME in the AVTUR analyzer is easy to use due to the absence of sample preparation or complex multicomponent calibrations [19].

ASTM D1319, Hydrocarbon Types in Liquid Petroleum Products

SIGNIFICANCE

The determination of hydrocarbon types—aromatics, olefins, and saturates—in petroleum fractions is important in characterizing the quality of petroleum fractions as gasoline blending components, as feeds to catalytic reforming processes, as products from thermal and catalytic cracking, and as blending components for motor and aviation fuels. Hydrocarbons are deliberately added to methanol fuel blends to provide improved cold startability and cold-start and warm-up drivability. The addition of hydrocarbons also contributes to flame visibility (luminous flame), nonexplosive air-fuel mixtures in storage tanks (rich mixture vapor space), and to denaturation (malodorant and taste deterrent). The hydrocarbon portion of the fuel must be unleaded. The hydrocarbon should be stable, noncorrosive, and in the boiling range of spark-ignition engine fuel as specified in ASTM D4814. Analysis from this test method uses the information in ASTM D1655 as a quality measure.

SCOPE

Aromaticity of fuels is measured using ASTM D1319. For fuels with a maximum final boiling point of 315°C, this method is a measurement of the aromatic content of the fuel. Increases in aromatic content of fuels over specified limits can have a negative impact on emissions. This test method is used for fuel Grades No. 1-D S15, No. 1-D S500, No. 2-D S15, and No. 2-D S500 and is required by 40 CFR Part 80. Grades No. 1-D S5000, No. 2-D S5000, and No. 4-D do not have an aromatic content requirement.

ASTM D7467 for biodiesel blends specifies a limit of 35 volume percent maximum for all grades as the aromaticity level determined by ASTM D1319. For fuels with a maximum final boiling point of 315°C, this test method is a measurement of aromatic content. Grade S5000 does not have an aromatic content limit.

ANALYSIS

There are a number of ASTM test methods for the determination of hydrocarbons in petroleum products such as gasoline and diesel (Table 4.22). Most of these test methods involve gas chromatographic separation of individual hydrocarbons.

Of these, only ASTM D1319 is quoted in the biodiesel blend specification ASTM D7467. This test method is intended for use with a full boiling range of 5 to 99 volume percent aromatics, 0.3 to 55 volume percent olefins, and 1 to 95 volume percent saturates in petroleum fractions that distill below 315°C. In this test method, a small amount of sample is introduced into a special glass adsorption column packed with activated silica gel. A small layer of silica gel contains a mixture of fluorescent dyes. When the sample has been adsorbed on the gel, alcohol is added to desorb the sample down the column. The hydrocarbons are separated according to their affinities into three types. The fluorescent dyes also react selectively with the hydrocarbon types and make the boundary zones visible under ultraviolet light. The volume percentage of each hydrocarbon type is calculated from the length of each zone in the column.

Samples containing dark-colored components that interfere with reading the chromatographic bands cannot be analyzed. The

TABLE 4.22 ASTM Test Methods for Hydrocarbon Analysis of Petroleum Products

Test Method	Analysis
ASTM D1319	Hydrocarbon types in liquid petroleum products by fluorescent indicator adsorption
ASTM D2007	Characteristic groups in rubber extender and processing oils and other petroleum derived oils by clay-gel absorption chromatography
ASTM D2425	Hydrocarbon types in middle distillates by mass spectrometry
ASTM D2427	Hydrocarbon types in gasoline by gas chromatography
ASTM D2505	Ethylene, other hydrocarbons, and carbon dioxide in high-purity ethylene by gas chromatography
ASTM D2549	Aromatics and nonaromatic fractions of high-boiling oils by elution chromatography
ASTM D2786	Hydrocarbon type analysis of gas-oil saturate fractions by high ionizing voltage mass spectrometry
ASTM D2789	Hydrocarbon types in low olefin gasoline by mass spectrometry
ASTM D3239	Aromatic type analysis of gas-oil aromatic fractions by high ionizing voltage mass spectrometry
ASTM D5443	Hydrocarbon types by multidimensional gas chromatography
ASTM D6379	Aromatic hydrocarbon types in aviation fuels and petroleum distillates with HPLC with refractive index detection
ASTM D6591	Aromatic hydrocarbon types in middle distillates by HPLC with refractive index detection
ASTM D6839	Hydrocarbon types in spark-ignition engine fuels by gas chromatography
ASTM D7419	Total aromatics and total saturates in lube basestocks by HPLC and refractive index detection
ASTM D7753	Hydrocarbon types and benzene in light petroleum distillates by gas chromatography
ASTM D7754	Trace oxygenates in automotive spark-ignition engine fuel by multidimensional gas chromatography

oxygenated blending components methanol, ethanol, MTBE, TAME, and ETBE do not interfere with the determination of hydrocarbon types at concentrations normally found in commercial blends. These oxygenated components are not detected because they elute with alcohol desorbent.

PRECISION

Based on an interlaboratory study (RR-D02-1361), the precision found for this test method is summarized in Table 4.23. One precision is applicable to unleaded fuels that do not contain oxygenated blending components. The second precision applies to oxygenate blended (e.g., MTBE, ethanol) automotive spark-ignition fuel samples with a concentration range of 13 to 40 volume percent aromatics, 4 to 33 volume percent olefins, and 45 to 68 volume percent saturates.

ASTM D128, Insolubles in Petroleum Products

SIGNIFICANCE

Impurities such as mineral grit, cellulosic fiber, or polymeric materials within most rendered material are known to cause operational issues in industrial burners if not pretreated. Mineral grit results in ash formation and so will be reflected in the measure of ash, but insoluble constituents such as cellulosic and polymeric materials that do not contribute to significant ash formation may also cause operational problems. In analysis of grease, "insolubles" are considered as the material remaining after the acid hydrolysis, water extraction, and solvent extraction of soap-thickened greases. It consists of such materials as graphite, molybdenum disulfide, insoluble polymers, and so forth.

TABLE 4.23 Precision of ASTM D1319 for Hydrocarbon Analysis

Oxygenate-Containing Samples			
Component	**Range, Volume %**	**Repeatability, Volume %**	**Reproducibility, Volume %**
Aromatics	13–40	1.3	3.7
Olefins	4–33	$0.26\ X^{0.6}$	$0.82\ X^{0.6}$
Saturates	45–68	1.5	4.2
Oxygenate-Free Samples[a]			
Aromatics	5–99	0.7–0.3	1.5–0.7
Olefins	1–55	0.4–2.0	1.7–8.5
Saturates	1–95	0.3–0.3	1.1–2.4

Note: Where X is the volume percent of olefins.

[a] See detailed data on precision in Table 3 of ASTM D1319-10.

SCOPE

ASTM D128 is suitable for Grade TBF5 and TBF6 (ASTM D7666) fuels. Developed for the determination of insoluble material in fats used in grease, the test is ultimately conducted at 65°C, and it measures the mass percent of insoluble material. The limit of 2 % is the American Fats and Oils Association specification for insolubles in tallow and greases. Users of triglyceride burner fuels should consider the quantity of insoluble components very carefully because 2 % of all fuel used can amount to significant quantities of materials that must be removed from storage tanks and disposed of.

ANALYSIS

In this test method, a sample containing insolubles is heated with dilute hydrochloric acid until all soap lumps have disappeared and the upper layer is clear. The filter contents are washed with n-hexane and then with alcohol. The residue remaining on the Gooch crucible is dried at 120°C and weighed to be reported as percent insolubles.

PRECISION

No precision data are available for this test method.

ASTM D3227, Mercaptan Sulfur in Petroleum Products

SIGNIFICANCE

Mercaptan sulfur has an objectionable odor, an adverse effect on fuel system elastomers, and is corrosive to fuel system components. ASTM D7566 allows a maximum of amount of 0.003 mass percent of mercaptan sulfur in the product.

SCOPE

This test method has been applied for the analysis of gasoline, diesel, kerosine, aviation turbine fuel, and distillate fuels. The precision of this analysis for biofuels is not known.

ANALYSIS

In this test method, the sample is dissolved in an alcoholic sodium acetate titration solvent and potentiometrically titrated with silver nitrate solution. Under these conditions, the mercaptan sulfur is precipitated as silver mercaptide, and the end point is shown by a large change in cell potential between a glass reference electrode and a silver/silver sulfide indicating electrode. Examples of mercaptan sulfur titration curves obtained by ASTM D3227 are shown in Fig. 4.20.

PRECISION

Fig. 4.21 shows the precision curves that can be contained using ASTM D3227 for mercaptan sulfur. The following precision estimates are given in ASTM D3227.

Repeatability	0.00007 + 0.027X
Reproducibility	0.00031 + 0.042X

Note: Where X is the average of duplicate results.

Methanol

SIGNIFICANCE

In small quantities, methanol can be produced in the ethanol production process. Methanol at high concentrations can be corrosive to components of the fuel system and has a greater effect on increasing vapor pressure than does ethanol. The limit in ethanol fuel is set to prevent methanol corrosion and the incremental effect

FIG. 4.20 Examples of mercaptan sulfur titrations in ASTM D3227, *Standard Test Method for (Thiol Mercaptan) Sulfur in Gasoline, Kerosine, Aviation Turbine, and Distillate Fuels (Potentiometric Method).*

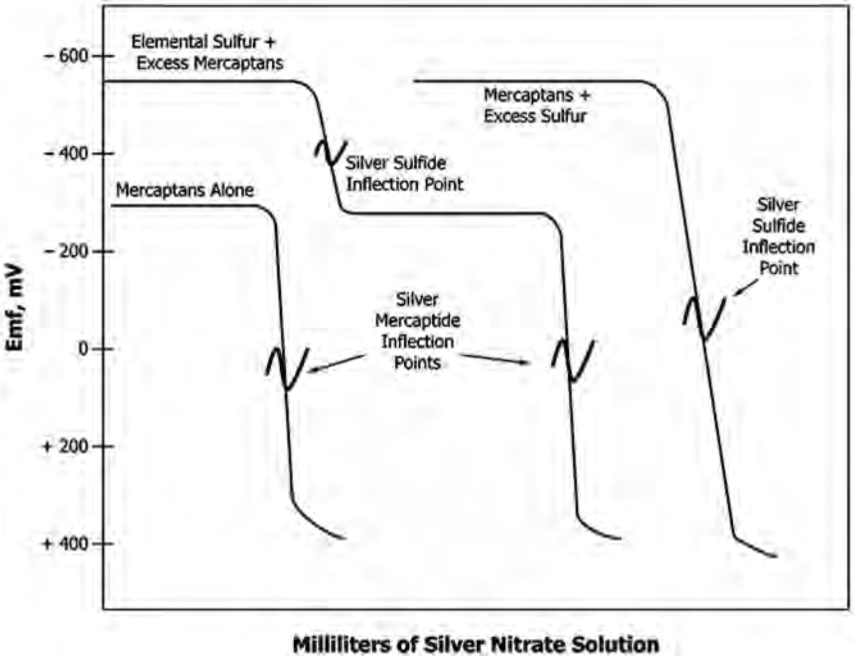
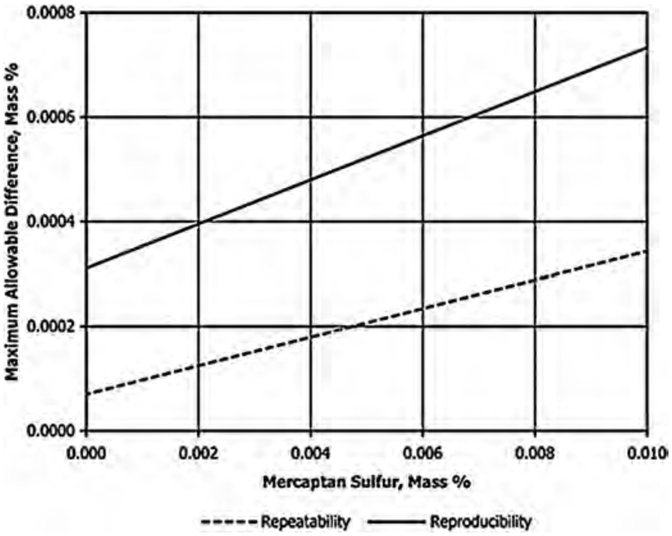


FIG. 4.21 Precision curves for mercaptan sulfur using ASTM D3227, *Standard Test Method for (Thiol Mercaptan) Sulfur in Gasoline, Kerosine, Aviation Turbine, and Distillate Fuels (Potentiometric Method).*



on vapor pressure. The limit is also to prevent methanol from being used as a denaturant.

Region	Limit	Test Method(s)
Brazil	0.50 % m/m	ABNT NBR 15343/EN 14110
European Union	0.20 % m/m	EN 14110
United States	0.2 % m/m or flash point 130°C	EN 14110

The methanol content of M70–M85 is a crucial parameter because it affects the capability of the fuel metering system of the M70–M85 vehicle to establish the proper air–fuel ratio for optimum vehicle operation. This is much less of a concern for multi-fuel-capable vehicles than for dedicated M70–M85 vehicles. Methanol content affects the lubrication properties of the fuel as well as the water tolerance of the M70–M85.

ASTM D5797 for fuel methanol (M70–M85) requires a test method to analyze methanol in the concentration range of 10 % to 99.8 %. The Methanol Institute reports that, in the coming years, methanol (produced from abundant natural gas) will be made available in appreciable amounts. This methanol will be available for inclusion in the gasoline pool.

ASTM D7920, Fuel Methanol and Methanol Fuel Blends by Gas Chromatography

SCOPE

This test method covers the determination of methanol content of M10–M99 in spark-ignition blend fuels, including product fuel methanol (M99) by GC. It is designed to measure not only the methanol in blended gasoline but also the impurities in the product methanol (M99) itself in the range of 5 to 1,000 ppm. However, not all impurities are measured or detected by this method. Water cannot be determined by this test method and shall be measured by a separate procedure, and the result will be used to correct the concentration determined.

ANALYSIS

The method uses a heart-cut technique where the component of interest is transferred from a nonpolar column to a polar column. Heart-cut is a technique that uses a switching device to which the following five components are connected:

1. A primary column, usually nonpolar, that spans from the inlet to the device
2. An analytical column, usually polar, that spans from the device to the analytical detector
3. A restrictor or tubing of small diameter that connects from the device to a second detector whose function is to serve as the monitor detector
4. An external pressure device that controls the pressure at the point where the two columns coincide
5. A solenoid that directs the pressure to the two points of the device

By switching the applied pressure, the components eluting from the primary column can either be sent to the monitor detector or to the analytical column where further separation occurs; thus, the compounds of interest elute at the analytical detector.

The sample is injected into a gas chromatograph where the components are separated in the primary column and subsequently eluted through the restrictor and detected by the monitor detector. The methanol is identified and the heart-cut window is determined. The instrument settings are set to transfer methanol from the primary column to the analytical column. A further separation takes place in the analytical polar column suitable for the polarity of methanol. After elution from the secondary column, methanol is analyzed by the analytical detector. Product methanol is analyzed by the primary column only without the execution of a heart-cut. Analysis is made in the monitor detector (Fig. 4.22).

EN 14110 uses headspace chromatography to accurately assess the methanol contamination and can be coupled with polar and nonpolar stationary-phase chromatography, typically a 100 % dimethyl polysiloxane phase. When coupled with a flame ionization detector, the system is capable of measuring the levels of methanol contamination between 0.001 % and 0.5 % m/m, which satisfies the regulatory limits set in EN 14214 [20].

PRECISION

A temporary repeatability standard deviation was obtained by analyzing methanol samples blended with gasoline as well as product methanol using helium and hydrogen as carriers (Table 4.24). A full interlaboratory study is to be completed.

EN 14110, Methanol Content of Fatty Acid Methyl Esters

SIGNIFICANCE

This method is used for determining methanol content of FAMEs for use as diesel fuel and domestic heating fuel. The method is applicable for a concentration range from 0.01 to 0.5 mass percent methanol. The method is not applicable to mixtures of FAMEs that contain other low boiling components.

TABLE 4.24 Temporary Precision of Methanol Determination Using Heart-Cut Gas Chromatography

Helium Carrier				
Methanol Blended Gasoline	**Sample 1**	**Sample 2**	**Sample 3**	
Average, vol %	71.43	89.13	85.28	
Std. deviation	0.30	0.31	0.07	
Repeatability	0.54	0.99	0.19	
Hydrogen Carrier				
Methanol Blended Gasoline	**Sample 4**	**Sample 5**	**Sample 6**	**Sample 7**
Average, vol %	87.11	85.25	85.49	99.33
Std. deviation	0.20	0.30	0.06	0.10
Repeatability	0.16	1.31	0.18	0.27
Product Methanol	**Hydrogen Carrier**	**Helium Carrier**		
Average, vol. %	98.68	98.17		
Std. deviation	0.01	0.17		
Repeatability	0.02	0.41		

ANALYSIS

The sample is heated at 80°C in a hermetically sealed vial to allow desorption of contained methanol into the gas phase. When equilibrium is reached, a defined part of the gas phase is injected into a gas chromatograph, where methanol is detected with a flame ionization detector. Methanol is normally the only peak in the chromatogram. The amount of methanol is calculated by reference to an external calibration. Methanol can also be determined after the addition of an internal standard to the sample before heating, followed by calculation with the use of an internal calibration factor. If only manual equipment is available, then only internal standard calibration should be used.

PRECISION

The following precision was obtained based on a 1999 European interlaboratory study. In this study, Procedures A (with automatic headspace system) and B (with manual procedure) were both studied and no significant differences were observed between the two procedures for the methanol concentration range of 0.01 to 0.20 mass percent.

The samples used included FAMEs prepared from rapeseed oil, sunflower oil, and their mixtures.

Repeatability	0.056 X + 0.001
Reproducibility	0.221 X + 0.003

Note: Where X is the mean of two results.

ASTM D7796, Analysis of Ethyl Tert-Butyl Ether by Gas Chromatography

SIGNIFICANCE

The presence of impurities in an ETBE product can have a deleterious effect upon the value of ETBE as a fuel additive. Oxygenate and olefin contents are of primary concern. This test method provides information about the composition of the ETBE product that is useful in the evaluation of process operating control, in the valuation of the product, and for regulatory purposes.

SCOPE

ASTM D7796 covers the determination of the purity of ETBE by GC with a flame ionization detector. This technique is sensitive to the contaminants commonly found in ETBE. It provides a procedure to measure impurities in ETBE—such as C_4 to C_{12} olefins, methyl, isopropyl and tert-butyl alcohols, methyl sec-butyl and methyl tert-amyl ethers, acetone, and methyl ethyl ketone. Impurities are determined to a minimum concentration of 0.02 mass percent. Most of the impurities in ETBE are resolved by this test method; however, some co-elution is encountered. This test method is not applicable for the determination of ETBE in gasoline. In addition, water cannot be determined by this method.

ASTM D7796 is inappropriate for impurities that boil at temperatures higher than 180°C or for impurities that cause poor or no response in a flame ionization detector (such as water).

ANALYSIS

In this test method, a representative aliquot of ETBE product sample is introduced into a gas chromatograph equipped with a methyl silicone bonded phase fused silica open tubular column. Helium carrier gas transports the vaporized aliquot through the column where the components are separated by the chromatographic process. Components are sensed by a flame ionization detector as they elute from the column. The detector signal is processed by an electronic data acquisition system or by an integrating computer. Each eluting component is identified by comparing its retention time to those established from analyzing standards under identical conditions.

The concentration of each component in mass percent is determined by normalization of the peak areas after each peak area has been corrected by a detector response multiplication factor and the water content of the sample. The detector response factors are determined by analyzing prepared standards with concentrations similar to those encountered in the sample.

Cyclopentane and 2,3-dimethylbutane have been observed to co-elute with MTBE. However, these impurities are not commonly found in MTBE, and MTBE is typically present in very low concentrations in ETBE.

PRECISION

A proper interlaboratory study has not been undertaken for this test method. A preliminary repeatability was obtained by analyzing two samples of ETBE in a single laboratory 12 times, and these results are included in the test method.

ASTM D5441, Purity of Methyl Tert-Butyl Ether by Gas Chromatography

SIGNIFICANCE

The presence of impurities in an MTBE product can have a deleterious effect upon the value of MTBE as a gasoline additive. Oxygenate and olefin contents are of primary concern. This test method provides information about the composition of an MTBE product that is useful in the evaluation of process operating controls, in the valuation of the product, and for regulatory purposes.

SCOPE

ASTM D5441 covers the determination of the purity of MTBE by GC with a flame ionization detector. It is a technique that is sensitive to the contaminants commonly found in MTBE and is widely used. ASTM D5441 provides a procedure for measuring impurities in MTBE such as C_4 to C_{12} olefins, methyl, isopropyl and tert-butyl alcohols, methyl sec-butyl and methyl tert-amyl ethers, acetone, and methyl ethyl ketone. Impurities are determined to a minimum concentration of 0.02 mass percent. This test method is not applicable for the determination of MTBE in gasoline. Nor can water be determined by this test method.

ANALYSIS

A majority of the impurities in MTBE are resolved by the test method; however, some co-elution is encountered. Cyclopentane and 2,3-dimethylbutane have been observed to co-elute with MTBE. However, these compounds are not commonly found as impurities in MTBE. This test method is inappropriate for impurities that boil at temperatures higher than 180°C or for impurities that cause poor or no response in a flame ionization detector (such as water).

TABLE 4.25 Precision of ASTM D5441 for Selected Impurities in Methyl Tert-Butyl Ether

Component	Range, mass %	Repeatability	Reproducibility
Methanol	0.0113–0.3719	$0.0181\ X^{0.25}$	$0.0994\ X^{0.25}$
Isobutylene/1-butene	0.0168–0.1356	$0.0998(X + 0.0049)$	$0.3199\ (X + 0.0049)$
Isopentane	0.0561–1.9290	$0.0390\ X^{0.6667}$	$0.1646\ X^{0.6667}$
Trans-2-pentene	0.0128–0.5003	$0.0084\ X^{-0.0036}$	$0.0630\ X^{0.2678}$
Tert-butanol	0.4741–0.8763	0.016	0.132
Cis-2-pentene	0.0970–0.5089	$0.0401\ X^{0.5}$	$0.1092\ X^{0.5}$
2-methyl-2-butene	0.0144–0.4391	$0.0122\ X^{0.0994}$	$0.0799\ X^{0.3818}$
Methyl tert-butyl ether	93.23–97.87	$0.0448\ (0.00X)^{-18}$	$0.2932\ (0.00X)^{-18}$
Sec-butyl methyl ether	0.0200–0.4821	$0.0065\ X^{0.0123}$	$0.1606\ X^{0.4424}$
Tert-amyl methyl ether	0.4961–0.7072	0.019	0.124
2,4,4-trimethyl-1-pentene	0.0852–1.0150	$0.0388(X + 0.0415)$	$0.2523\ (X + 0.0415)$

Note: Where X is the mean of the values being compared.

In this test method, a representative aliquot of MTBE product sample is introduced into a gas chromatograph equipped with a methyl silicone bonded phase fused silica open tubular column. Helium carrier gas transports the vaporized aliquot through the column where the components are separated by the chromatographic process. Components are sensed by a flame ionization detector as they elute from the column. The detector signal is processed by an electronic data acquisition system or by an integrating computer. Each eluting component is identified by comparing its retention time to those already established by analyzing standards under identical conditions.

The concentrations of each component in mass percent are determined by normalization of the peak areas after each peak area has been corrected by a detector response multiplication factor. The detector responsive factors are determined by analyzing prepared standards with concentrations similar to those encountered in the sample.

PRECISION

Precision values given in Table 4.25 were obtained for this test method based on an interlaboratory study (RR-D02-1306).

ASTM D7347, Olefins in Denatured Ethanol by Supercritical Fluid Chromatography

SIGNIFICANCE

Olefinic hydrocarbons that may be present in denatured ethanol have been demonstrated to contribute to petrochemical reactions in the atmosphere, and this can result in the formation of smog in susceptible urban areas. The California Air Resources Board has specified a maximum allowable limit of total olefins in spark-ignition engine fuel. Denatured ethanol will be added as an oxygenate additive and will contain olefinic species contributing to the total olefins present in spark-ignition engine fuel.

This test method is automated, does not require any sample preparation, and has a relatively short analysis time of approximately 20 min. The application range of the method is from 0.1 to 1.0 mass percent total olefins.

ANALYSIS

A small aliquot of the denatured ethanol sample is injected onto a set of three analytical chromatographic columns connected in a series. The sample is transported through the columns using supercritical carbon dioxide as the mobile phase. The first column is packed with polyvinyl alcohol; the second in the series is packed with high surface area silica gel particles; and the third column is packed with silica particles coated with strong cation exchange material loaded with silver ions.

Two six-port switching valves are used to direct the different classes of components through the chromatographic system to the detector. A flame ionization detector is used for quantitation. Calibration is based on the area of chromatographic signal for olefins, relative to standard reference materials, that contains a known mass percent of total olefins corrected for density.

PRECISION

Based on an interlaboratory study involving five denatured alcohols run in duplicate in five laboratories, the following repeatability was obtained for this test method (RR-D02-1640). The reproducibility of the method has not yet been determined.

Repeatability	r = 0.052 (X + 1), where X is the calculated result in mass percent

Oxidation Stability

Vegetable oils are protected from oxidation by natural antioxidants; however, during the conversion process to biodiesels, they are removed. Hence, biodiesel is not stable, and it oxidizes by contact with air. Thus, it has a limited storage time. Factors such as elevated temperatures and the presence of metals facilitate the oxidation. Oxidation of biodiesel in contact with air results in the formation of hydroperoxides. Thus, the extent of the degree of oxidation can be characterized by the peroxide value, which can be determined using ASTM D3703. Hydroperoxides lead to decomposition into low-molecular weight (aldehydes, ketones, and acids) and high-molecular weight polymeric material gum. The resulting oxidation products can damage vehicle motors. That is why oxidation stability is an important quality criterion for biodiesel and it must be regularly determined during the production and storage processes. This problem is avoided by the addition of natural antioxidants such as tocopherols or synthetics such as tert-butyl-hydroquinone, butylated hydroxytoluene, propyl gallate, and pyrogallol [21].

Over the years, a number of methods have been developed for determining the oxidation stability of oils and fats. These methods are based on the rate of oxygen absorption by oils and fats (in a liquid state) that have been placed in contact with air. Oxygen absorption may be measured directly using the Warburg apparatus or indirectly by determining peroxides or the products dissociated from them during oxidation.

Oxidation stability is a physical property of liquid fuels used to describe their aging behavior during transport and storage. In biodiesel and its blends with diesel, oxidation of fuel can result in acid formation and polymer solids that can plug filters and leave problematic deposits throughout the fuel supply system. ASTM D2274 is the most frequently used method for characterizing the aging behavior of diesel by determining the polymer (sludge) content of artificially aged fuel [22].

Oxidation stability varies considerably with its feedstock, its harvest, the process used to make the biodiesel, and the blend ratio used with petroleum-based diesel. It also appears that the exact chemical processes used to convert the raw feedstock into a FAME play a critical role in the quality and stability of FAMEs and the "trace constituents" that are left in the biodiesel. The extent of the challenge becomes evident when one considers the variety of feedstocks used to produce biodiesel: rapeseed (in Europe), palm oil, soybean oil, used fat, animal fat, and much more. Although antioxidant additives exist, present-day efforts at pairing a biodiesel fuel with the best additive are frequently a matter of trial-and-error experimentation and testing [22].

Of the indirect methods of determination, the active oxygen method (AOM) is the oldest, and it is based on the determination of the peroxide value in line with the progress of the aeration of the sample at 98.7°C. It specifies the time that elapses until a peroxide value of 100 mmol (active oxygen per 2 kg) has been reached. The Swift Stability Test has been derived from this method. These determinations are very time-consuming and cannot be automated.

Standard	Organization	Analysis
ASTM D525	ASTM	Oxidation Stability of Gasoline
ASTM D7462	ASTM	Biodiesel and Biodiesel Blends
ASTM D7545	ASTM	Middle Distillates Fuels by RSSOT
EN 14112	ISO	FAME
EN 15751	ISO	FAME Fuels and Blends with Diesel

ASTM D525, Oxidation Stability of Gasoline

SIGNIFICANCE

Oxidation is a major chemical process that causes the formation of adherent and filterable insolubles. Any substances, such as copper or chromium, that catalyze oxidation reactions will cause more rapid or greater quantities of insoluble material, or both, to form. ASTM D525 for oxidation stability covers the stability of gasoline in finished form only and under accelerated oxidation conditions. The induction period (defined as the time elapsed between the placing of the pressure vessel in the bath and the break point at

100°C) may be used as an indication of the tendency of motor gasoline to form gum in storage. It should be recognized, however, that the correlation with the formation of gum in storage may vary markedly under different storage conditions and with different gasolines.

SCOPE

ASTM D4814, for gasoline fuels, has a minimum oxidation stability of 240 min. ASTM D7467, for B6 to B20 biodiesel, blends the oxidation stability test method in EN 15751 and a minimum limit of 6 h for all grades.

ANALYSIS

The sample is oxidized in a pressure vessel initially filled at 15 to 25°C with oxygen pressure at 690 to 705 kPa and heated at a temperature between 98 and 102°C. The pressure is recorded continuously or read at stated intervals until the break point is reached (defined as the point in the pressure-time curve that is preceded by a pressure drop of exactly 14 kPa within 15 min and succeeded by a drop of not less than 14 kPa in 15 min). The time required for the sample to reach this point is the observed induction period at the temperature of test from which the induction period at 100°C can be calculated.

PRECISION

This test method has a repeatability of 5 % and a reproducibility of 10 %. No statement of bias can be made.

ASTM D7462, Oxidation Stability of Biodiesel and Biodiesel Blends

SIGNIFICANCE

Due to their chemical composition, biodiesel fuels are more sensitive to oxidative degradation than fossil diesel fuels. This is especially true for fuels with a high content of di- and higher unsaturated esters because the methylene groups adjacent to double bonds have turned out to be particularly susceptible to radical attack as the first step of fuel oxidation. The hydroperoxides so formed may polymerize with other free radicals to form insoluble sediments and gums, which are associated with fuel filter plugging and deposits within the injection system and the combustion chamber [6]. Where the oxidative stability of biodiesel is considered insufficient, antioxidant additives might have to be added to ensure the fuel will still meet the specifications. EN ISO 14112 is specified in all three regions of biodiesel production, and the limit is a 6-h minimum in Brazil and the EU and a 3-h minimum in the United States.

ASTM D7462 covers a measurement of the oxidation stability of biodiesel (B100) blendstock as specified in ASTM D6751 and blends of biodiesel with middle distillate petroleum fuels, including B6 to B20, as specified in ASTM D7467 under specified oxidizing conditions at 95°C. Specifically, the oxidation stability is assessed by the formation and measurement of insoluble degradation materials.

Biodiesel B100, composed of alkyl esters, can have good solubility for some products of oxidative degradation. Thus, some B100 samples could undergo significant degradation but show little or no sediment formation. By contrast, many petroleum diesel fuels have relatively poor solubility for products of oxidative degradation, so Bxx blends, such as B20, could show higher sediment levels.

Grades No. 1 and No. 2 in ASTM D396 or ASTM D975 currently allow up to 5 % biodiesel (meeting ASTM D6751). This method is preferred for testing fuels that may contain biodiesel blendstock, rather than ASTM D2274, due to the incompatibility of biodiesel blendstock with the membrane filters specified in ASTM D2274.

This test method may not provide a prediction of the quantity of insolubles that will form in field storage over any given period of time. The amount of insolubles formed in such field storage is subject to the specific storage conditions, which are too variable for this test method to predict accurately. This test method yields results more rapidly than ASTM D4625, the 43°C bottle test. However, as a result of the significantly elevated temperature and the pure oxygen atmosphere, the nature and the amount of insolubles may deviate to a greater extent than those in ASTM D4625 that are formed in field storage.

ANALYSIS

A 350-mL volume of filtered sample is aged at 95°C for 16 h while oxygen is bubbled through the sample at a rate of 3 L/h. After aging, the mixture is cooled to approximately room temperature before filtering to obtain the filterable insolubles quantity. The interior of the oxidation cell is also washed with hydrocarbon solvent to remove any filterable insolubles and any liquid that can be removed by the solvent. These washings are also filtered and included as filterable insolubles. Adherent insolubles are then removed from the oxidation cell and associated glassware with trisolvent (high-purity acetone + methanol + toluene in 1:1:1 ratio). The trisolvent is evaporated to obtain the quantity of adherent insolubles. The sum of the filterable and adherent insolubles, expressed as milligrams per 100 mL, is reported as total insolubles.

PRECISION

No interlaboratory study has been completed yet to obtain the precision for this test method.

ASTM D7545, Oxidation Stability of Middle Distillate Fuels by Rapid Small Scale Oxidation Test

SIGNIFICANCE

The induction period obtained through this test method may be used as an indicator of the oxidation and storage stability of middle distillate fuel. Compared to some other oxidation and storage stability tests, this method uses a small sample and gives a result in a short period of time.

SCOPE

This test method covers middle distillate fuels, such as diesel fuels and heating oils, with up to 100 % biodiesel, under accelerated oxidation conditions, by an automatic instrument. This test method is designed for products complying with ASTM D975 on diesel fuel, Grades No. 1D and 2D; ASTM D396 on burner fuel, Grades No. 1 and No. 2; ASTM D6751 on biodiesel, B100; and ASTM D7467 on diesel fuel oil, B6 to B20. The Rapid Small Scale Oxidation Test method is quicker than other actual methods evaluating the oxidation stability of biodiesel, petroleum middle distillates, and blends.

ANALYSIS

A 5-mL sample is introduced into a pressure vessel that is then charged with oxygen to 700 kPa at ambient temperature. The test is initiated by starting the heater and warming the pressure vessel to a temperature of 140°C. This initiates a fast oxidation—the results of which are determined by the time needed to achieve a pressure drop of 10 % in the system. Testing has confirmed that the time needed to achieve the 10 % drop in pressure is directly related to the sample's oxidation stability. The pressure is recorded continuously until the break point is reached. Alternatively, the test may be terminated when a minimum specification temperature is reached. The PetroOXY apparatus from Petrotest is used for biodiesel in the ASTM D7545 oxidation stability test. It is also the same apparatus and technique used in ASTM D7525 for oxidation stability of gasoline [22].

PRECISION

A formal interlaboratory study has not yet been completed. A preliminary study shows a repeatability of 3.2 min as the interim precision.

EN 14112, Oxidation Stability of Fatty Acid Methyl Esters

SIGNIFICANCE

See EN 15751.

ANALYSIS

A stream of purified air is passed through the sample, which has been brought to 110°C. The vapors released during the oxidation process, together with the air, are passed into a flask containing distilled or demineralized water and containing an electrode for measuring the conductivity. The electrode is connected to a measuring and recording device. It indicates the end of the induction period when the conductivity begins to increase rapidly. This accelerated increase is caused by the dissociation of volatile carboxylic acids produced during the oxidation process and absorbed in the water.

An instrument called a Rancimat is available for this analysis from Metrohm AG. The results can be calculated manually or automatically with this instrument.

PRECISION

The following precision was obtained based on a European interlaboratory study carried out in 2000 involving eight laboratories and eight samples of rapeseed, sunflower oil, frying oil FAME, and palm oil at a test temperature of 110°C.

Repeatability	0.09 X + 0.16
Reproducibility	0.26 X + 0.23

EN 15751, Oxidation Stability of Fatty Acid Methyl Ester Fuels and Their Blends with Diesels

SIGNIFICANCE

The induction period as measured in the oxidation stability test is used as an indication of the resistance of fuel to gum formation in storage. Experience indicates that fuels with an induction period equal to or greater than that shown earlier in Table 2.5 generally have acceptable short-term storage stability. However, correlation of the induction period with the formation of gum in storage can vary markedly under different storage conditions and with different fuels.

Products of oxidation in biodiesel can take the form of various acids or polymers, which, if in high enough concentration, can cause fuel system deposits and lead to filter clogging and fuel system malfunctions. Additives designed to retard the formation of acids and polymers can significantly improve the oxidation stability performance of biodiesel.

It is recommended that EN 15751 be utilized for measurement of biodiesel oxidation stability because EN 14112 may be withdrawn in the future as an option for testing biodiesel and biodiesel blends. EN 15751 is based on EN 14112, which was specifically adapted for the determination of oxidation stability of FAMEs. The modification allows the determination of oxidation stability for pure FAME and diesel/FAME blends at various levels. In this method, the oxidation process is split into two phases. The first phase (the induction period) is characterized by slow reaction of oxygen during which peroxides are formed. The second phase (tainted odor and flavor phase) is characterized by rapid reaction in which peroxides are not only formed but these peroxides are then dissociated under the influence of the high temperature. During this phase, products such as aldehydes, ketones, and low fatty acids are formed. These products give rise to deviant odor and flavor.

ANALYSIS

The method is a conductimetric determination of volatile acid dissociation products (mainly formic acid and acetic acid) produced during oxidation. The determination can also be done by an automatic potentiometric titration. From the conductivity curve, an induction time is determined in line with the induction time obtained using the AOM, provided that the determinations are carried out at the same temperature. The curves can have very different shapes.

In this test, a stream of purified air is passed through the sample, which has been brought to a specific temperature (usually 110°C). The vapors released during the oxidation process, together with the air, are passed into a flask containing demineralized or distilled water with an electrode for measuring conductivity. The electrode is connected to a measuring and recording device that indicates the end of the induction period when the conductivity begins to increase rapidly. This accelerated increase is caused by the dissociation of volatile carboxylic acids produced during the oxidation process and absorbed in the water. The measurement may be terminated when (1) the signal has reached 100 %

of the recorded scale, usually 200 uS/cm, or (2) when the conductivity curve flattens again after exceeding the induction period. Care should be taken that the test is not terminated before the curve has flattened sufficiently to fit an accurate second tangent.

Two commercial instruments are available for this analysis: Rancimat Model 73 or higher (from Metrohm AG) and the OSI Instrument (from Omnion, Inc.).

PRECISION

The following precision was obtained based on an interlaboratory study carried out on 10 samples that was conducted in 2007 in Europe with the participation of 12 laboratories.

Repeatability	0.22027 + 0.04344 X
Reproducibility	0.37269 + 0.19038 X

Note: Where X is the mean of two results.

Oxidation Stability Using Pressure Differential Scanning Calorimetry

In addition to the ASTM standards mentioned earlier, a new approach for measuring oxidation stability of biodiesel has been using pressure differential scanning calorimetry. In experiments with palm and soy biodiesels, it was found that oxidation onset temperature (OOT) is more suitable than oxygen induction time for oxidation studies of palm biodiesels. Considering the biodiesel type, antioxidant addition, and pressure, the most important factor on the OOT is the biodiesel type. The onset shows a clear dependence on the pressure and, to a lesser extent, on the antioxidant addition. The relative oxidation stabilities of soy and palm biodiesels with and without the addition of Baynox are significantly different. The results from nonisothermal thermogravimetry show an increase in thermal stability with the antioxidant addition. Although it could not be related to the oxidation stability. The low temperature differential scanning calorimetry results show that the crystallization temperatures and the cold filter plugging point are related to the unsaturated ester content, which is also indicated by the iodine value. No effect of an antioxidant was observed in the crystallization [23].

ASTM D5599, Oxygenates in Gasoline by Gas Chromatography

SIGNIFICANCE

In gasoline blending, the determination of organic oxygenated compounds is important. Alcohols, ethers, and other oxygenates are added to gasoline to increase the octane number and to reduce tailpipe emissions of carbon monoxide. They must be added in the proper concentration and ratios to meet regulatory limitations and to avoid phase separation and problems with engine performance or efficiency. ASTM D5599 provides sufficient oxygen-to-hydrocarbon selectivity and sensitivity to allow determination of oxygenates in gasoline samples without interference from the bulk hydrocarbon matrix.

SCOPE

ASTM D5599 covers a GC procedure for the quantitative determination of organic oxygenated compounds in gasoline having a final boiling point not greater than 220°C and in oxygenates having a boiling point limit of 130°C. It is applicable when oxygenates are present in the 0.1 % to 20 % by mass range. This test method is intended to determine the mass concentration of each oxygenate compound present in a gasoline sample. This requires knowledge of the identity of each oxygenate being determined. However, the oxygen selective detector used in this test method exhibits a response that is proportional to the mass of oxygen. Therefore, it is possible to determine the mass concentration of oxygen contributed by any oxygenated compound in the sample, whether or not it is identified. Total oxygen content in a gasoline sample may be determined from the summation of the accurately determined individual oxygenated compounds. The summed area of other uncalibrated or unknown oxygenated compounds that are present may be converted to a mass concentration of oxygen and summed with the oxygen concentration of the known oxygenated compounds.

ANALYSIS

An internal standard of a noninterfering oxygenate (for example, 1,2-dimethoxyethane) is added in quantitative proportion to the gasoline sample. A representative aliquot of the sample and the internal standard is injected into a gas chromatograph equipped with a capillary column operated to ensure the separation of oxygenates. Hydrocarbons and oxygenates are eluted from the column, but only oxygenates are detected with the oxygen selective flame ionization detector.

Calibration mixtures are used for determining the retention times and relative mass response factors of oxygenates of interest. The peak area of each oxygenate in the gasoline is measured relative to the peak area of the internal standard. A quadratic least square fit of the calibrated data of each oxygenate is applied, and the concentrations of each oxygenate are calculated. A chromatogram of a blend of oxygenates is shown in Fig. 4.22.

PRECISION

The precision shown in Table 4.26 is based on an interlaboratory study involving 10 laboratories measuring 13 oxygenates and total oxygen in 12 gasoline samples (RR-D02-1359).

ASTM D7754, Oxygenates in Fuels by Multidimensional Gas Chromatography

SIGNIFICANCE

The analysis of trace oxygenates in automotive spark-ignition engine fuel has become routine in certain areas to ensure compliance whenever oxygenated fuels are used. In addition, test methods to measure trace levels of oxygenates in automotive spark-ignition engine fuel are necessary to assess product quality.

FIG. 4.22 Chromatogram of an oxygenate blend using ASTM D5599, *Standard Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective Flame Ionization Detection.*

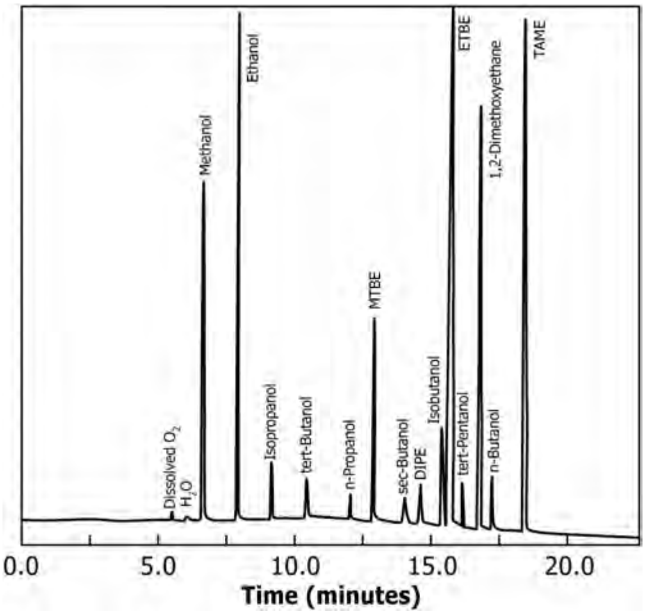


TABLE 4.26 Precision of ASTM D5599 for Oxygenates in Gasoline

Component	Range, mass %	Repeatability	Reproducibility
Methanol	0.20–1.00	$0.07\ X^{0.49}$	$0.25\ X^{0.86}$
Ethanol	1.00–12.00	$0.03\ X^{0.92}$	$0.27\ X^{0.80}$
Isopropanol		$0.04\ X^{0.54}$	$0.21\ X^{0.71}$
tert-Butanol		$0.05\ X^{0.65}$	$0.20\ X^{0.80}$
n-Propanol		$0.04\ X^{0.35}$	$0.17\ X^{0.88}$
MTBE	0.20–20.00	$0.05\ X^{0.58}$	$0.10\ X^{0.95}$
sec-Butanol		$0.03\ X^{0.54}$	$0.17\ X^{0.73}$
DIPE	1.00–20.00	$0.05\ X^{0.65}$	$0.16\ X^{0.71}$
Isobutanol		$0.03\ X^{0.79}$	$0.19\ X^{0.83}$
ETBE	1.00–20.00	$0.04\ X^{0.86}$	$0.25\ X^{0.79}$
tert-Pentanol		$0.05\ X^{0.41}$	$0.18\ X^{0.55}$
n-Butanol		$0.06\ X^{0.46}$	$0.22\ X^{0.30}$
TAME	1.00–20.00	$0.04\ X^{0.58}$	$0.24\ X^{0.69}$
Total oxygen		$0.03\ X^{0.93}$	$0.13\ X^{0.83}$

Note: Where X is the mean mass percent of the component.

SCOPE

This test method is used for the determination of oxygenates. The concentration range of oxygenates covered in the interlaboratory study was from 10 to 200 mg/kg. Oxygenates that are analyzed are:

MTBE
DIPE
ETBE
Methanol
TAME
i-Propanol
i-Butanol
sec-Butyl alcohol
n-Propanol
n-Butanol
tert-Butyl alcohol
tert-Pentanol

Ethanol usually is not measured as a trace oxygenate because it can be used as the main oxygenate compound in finished automotive spark-ignition fuels, such as reformulated automotive spark-ignition engine fuel. Additionally, this test method is also suitable for the measurements of the C5 isomeric alcohols (2-methyl-1-butanol, 2-methyl-2-butanol) present from the fermentation of alcohol.

The ethanol blending concentration for which this test method applies ranges from 1 % to 15 % by volume. Higher concentrations of ethanol co-elute with methanol in the analytical column. Refer to the test method for handling such samples with higher levels of ethanol.

ANALYSIS

This test method uses multidimensional GC with 1,2-dimethoxy ethane (DME) as the internal standard. A sample with the addition of the internal standard is introduced into a gas chromatograph equipped with two columns and a four-port switching valve. The sample first passes onto an apolar polydimethylsiloxane WCOT column that performs a pre-separation of the trace oxygenates and elutes unwanted high boiling hydrocarbons to vent. Oxygenates and DME are transferred to the analytical oxygen selective column by the switching valve. While oxygenates and the DME are eluting from the analytical column, the inlet's carrier gas is used to elute the hydrocarbons from the pre-column to yield a stable baseline for the next analysis. The eluted components are detected by one or two flame ionization detectors.

PRECISION

Based on an interlaboratory study involving five laboratories and six gravimetrically spiked automotive spark-ignition fuel samples at varied concentration levels within the range of the method analyzed in duplicate, the precision shown in Table 4.27 was obtained.

TABLE 4.27 Precision of ASTM D7754 for Oxygenates

Component	Concentration Range, ppm	Repeatability, ppm	Reproducibility, ppm
ETBE	13–1759	$0.1503\ X^{0.8876}$	$0.3221\ X^{0.8876}$
MTBE	18–1717	$0.2548\ X^{0.8476}$	$0.5809\ X^{0.8476}$
DIPE	13–1703	$0.2678\ X^{0.7085}$	$2.3323\ X^{0.4916}$
TAME	13–1842	$0.2545\ X^{0.7467}$	$0.3736\ X^{0.7467}$
Methanol	12–1881	$0.1272\ X^{0.9217}$	$0.2045\ X^{0.9217}$
n, i-Propanol	19 - 1904 each	$0.1173\ X^{0.9183}$	$0.1720\ X^{0.9183}$
t, s, i-Butanol	19–1891 each	$0.003845\ X^{1.3463}$	$0.008489\ X^{1.3463}$
n-Butanol	12–1952	$1.4747\ X^{0.4455}$	$3.4596\ X^{0.4455}$
t-Pentanol	13–1958	$0.4487\ X^{0.6306}$	$0.9752\ X^{0.6306}$

Note: Where X is the value obtained from analysis in ppm.

ASTM D6423, The pHe of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol

SIGNIFICANCE

The pHe is a measure of the acid strength of ethanol-hydrocarbon blends defined by this apparatus and procedure. The acid strength, as measured by pHe, is a good predictor of the corrosion potential of ethanol fuels. It is preferable to total acidity because total acidity does not measure acid strength, it overestimates the contribution of weak acids (such as carbonic acid), and it may underestimate the corrosion potential of low concentrations of strong acids (such as sulfuric acid). A pHe value for alcohol solutions is not comparable to pH values of water solutions. The values of pHe measured will depend somewhat on the fuel blend, the stirring rate, and the time the electrode is in the fuel. When the pHe of ethanol used as a fuel for automotive spark-ignition engines is below 6.5, fuel pumps can malfunction as a result of film forming between the brushes and commutator, fuel injectors can fail from corrosive wear, and excessive cylinder engine wear can occur. When the pHe is above 9.0, fuel pump plastic parts can fail. The adverse effects are less when ethanol is used at 10 volume percent in a blend with gasoline.

SCOPE

This test method covers a procedure to determine a measure of the acid strength of high ethanol content fuels. These include denatured fuel ethanol and ethanol fuel blends. The test method is applicable to denatured fuel ethanol as described in ASTM D4806 and to ethanol fuel blends as described in ASTM D5798 containing ethanol at nominally 51 % by volume or more. The specification limits for pHe for ethanol in the United States (6.5–9.0) and Brazil (6.0–8.0) are very similar in appearance. However, the Brazilian specification is only for hydrous ethanol. It is doubtful if the two procedures would give equivalent results because of the equipment used. The U.S. test method is ASTM D6423, and the Brazilian test method is NBR 10891. The CEN specification excludes pHe due to the problems associated with repeatability of the ASTM procedure when the ASTM specified equipment was not used [6].

In general, a glass electrode is used for determining the pH aqueous media. Both ASTM D6423 and Brazil's ABNT/NBR 10891 use aqueous buffer solutions for calibration of pH meters. However, this change from aqueous to ethanol medium produces variations on diverse potentials, which contribute to the pH measurement. Thus, the values obtained do not represent the concentration of hydrogen ion activity from that nonaqueous medium [24].

Another problem that can come from the pH measurement using a glass electrode in ethanol is the dehydration of the glass membrane. The surface of the glass electrode should be hydrated before using it as a pH electrode because nonhygroscopic glasses do not show a response to pH measurement and they also lose their sensibility to pH response with the membrane dehydration. Therefore, in this case, the effect is reversible, and the response of the electrode to pH is recovered when the electrode is dipped in water [24].

Da Silva et al. [24] studied the problem of using a glass electrode in anhydrous ethanol and ethanol-water solutions for measuring pH values and have shown that this property depends on the solution composition, the contact time with the solution, the utilized temperature, and the type of electrolyte used. It was also observed that the behavior of the glass electrode differs from an acid medium to an alkaline medium. These studies provided correction factors for pH values from 2 to 12, allowing the realization of proper measurements of the hydrogen ion activity in the ethanol-water and anhydrous ethanol solutions. However, these correction factors cannot be applied to the fuel ethanol. Alternatively, a new method was developed for the correction of the pH values, which can be applied in hydrous and anhydrous ethanol solutions. In this approach, a correction curve in the same ethanol-water composition from the fuel ethanol sample is built because the proportion of the ethanol-water is the most influential factor in the pH measurement. Two samples of anhydrous ethanol fuel and a hydrated ethanol fuel obtained from a Brazilian ethanol producer showed the following results. Each sample contained 0.543 % and 6.01 % water, respectively. The analyses were done using the ASTM D6423 procedure and with the correction curve proposed in this work. In both cases analyses were done in triplicate [25].

	ASTM D6423		Proposed Method	
Sample	pH	Standard Deviation	pH	Standard Deviation
Anhydrous ethanol fuel	7.02	0.08	7.55	0.01
Hydrated ethanol fuel	7.72	0.09	7.76	0.01

The pH values obtained using ASTM D6423 presented a higher standard deviation and different values when compared to the proposed modification. These differences can be related to the electrolyte addition, which has contributed to obtaining lower standard deviations as well as more precise values.

ANALYSIS

The sample is analyzed at room temperature using a specified (Orion) electrode system and a pH meter with an input impedance of >10^{12} ohms. Meters designed for use with an ion-specific electrode normally meet this criterion. Readings are taken at exactly 30 s because the meter reading will change throughout the analysis due to glass electrode voltage drift caused by dehydration of the glass-electrode membrane. Because alcohol dehydrates the glass-electrode membrane, the time spent soaking in the alcohol solution should be minimized. The electrode is soaked in a water-based pH 7 buffer between readings to prepare it for the next sample. This rehydrates the glass electrode, a necessary step in preserving the electrode's response characteristics.

The EU believes that more water and denaturant are needed to make ASTM D6423 workable. This test method has been found to work with undenatured ethanol, denatured ethanol, E10, and E85 with very low water levels [6].

PRECISION

Based on an interlaboratory study conducted in 2014, the following precision estimates were found.

Repeatability =	0.3963 $(10.2301-X)^{0.1584}$ pHe
Reproducibility =	0.9078 $(10.2301-X)^{0.1584}$ pHe

Note: Where X is the pHe value determined by following ASTM D6423.

ASTM E70, The pH of Aqueous Solutions with the Glass Electrode

SIGNIFICANCE

Because pH is an accurate measurement of the hydrogen ion concentration, it is widely used for the characterization of aqueous solutions; pH measurement is one of the main process control variables in the chemical industry. In general, this test method will give an accurate measure of hydrogen ion activity if the pH lies between 2 and 12 and the concentration of electrolytes or nonelectrolytes does not exceed 0.1 mol/L.

PRECISION

In an interlaboratory study conducted in 1973, repeatability was found to be 0.02 and reproducibility to be 0.11 pH unit.

Borges et al. studied pH measurement in bioethanol by using different electrodes and different international standards [25]. A certified reference material of bioethanol from sugarcane (approximately 99.6 % ethanol content) was used with two commercial pH electrodes having different internal filling electrolytic solutions. One electrode had potassium chloride as is specified in ASTM D6423. The other used lithium chloride as specified in the Brazilian standard (ABNT NBR 10891) and the European standard (EN 15490). This study has shown that there are significant differences among the pH values (more than 1 pH unit) measured by the different electrodes related to the internal filling solution. The authors suggest that it is therefore necessary to harmonize these three standards for pH measurements in bioethanol as a fuel both for quality control and international trade.

ASTM D381, Solvent-Washed Gum in Jet Fuels

SIGNIFICANCE

This test measures the amount of residue after evaporation of the fuel and following a heptane wash. The heptane wash removes the heptane-soluble, nonvolatile material such as additives, carrier oils used with additives, and diesel fuels. Solvent-washed gum consists of heptane-insoluble gum. Unwashed gum consists of fuel-insoluble gum and fuel-soluble gum. The fuel-insoluble portion can clog fuel filters. Both can be deposited on surfaces when the fuel evaporates.

This test method covers the existent gum content of aviation fuels and the gum content of motor gasolines or other volatile distillates in their finished form, including those containing alcohol and ether-type oxygenates and deposit control additives.

Solvent-washed gum content can contribute to deposits on the surface of carburetors, fuel injectors, intake manifolds, ports, valves, and valve guides. The impact of solvent-washed gum from pure alcohol such as ethanol on malfunctions of modern engines is not well-established, and the current specification limit is historic rather than the result of recent correlative studies. It depends on where the deposits form, the presence of other deposit precursors (such as airborne debris, blow-by, exhaust gas recirculation gases, and oxidized engine oil), and on the amount of deposits. Essentially, the test method is used to detect the presence of high boiling, heptane-insoluble impurities.

The true significance of this test method for determining gum in motor gasoline is not firmly established. A large amount of gum can cause induction-system deposits and sticking of intake valves. This test by itself is not correlative to induction system deposits. It is applied to motor gasolines to measure the oxidation products formed in the sample prior to or during the comparatively mild conditions of the test procedure. Because many motor gasolines are purposely blended with nonvolatile oils or additives, the heptane extraction step is necessary to remove these from the evaporation residue so that the deleterious material gum may be determined. With respect to aviation turbine fuels, large quantities of gum are indicative of contamination of fuel by higher boiling oils or particulate matter and generally reflect poor handling practices in distribution downstream of the refinery.

The difference between the unwashed and solvent-washed gum content values can be used to assess the presence and amount of nonvolatile material in the fuel. Additional analytical testing is required to determine if the material is additive, carrier oil, diesel fuel, and so forth. The unwashed gum content limit in M70–M85 fuel (ASTM D5797) is intended to limit high-boiling contaminants, such as diesel fuel, that can affect engine performance yet to allow the proper dosage of deposit-control additives with carrier oils normally added to the hydrocarbon portion of the fuel methanol (M70–M85).

The three ethanol-producing regions of the world use different test procedures—although they try to determine the residue remaining after the ethanol is evaporated. The different procedures make it difficult to compare the specification maximum values of 5.3 mg/100 mL for the United States, 10 mg/100 mL for the EU, and 5.0 mg/100 mL for Brazil. The test methods used are ASTM D381 for the United States, NBR 8644 in Brazil, and a procedure from Annex II of ECD/2870/2000 in the EU. The first two procedures are similar except that the United States measures heptane-washed gum and Brazil measures unwashed gum. The EU measures an unwashed residue similar to Brazil but under different conditions [6].

SCOPE

This test method covers the determination of existent gum content of aviation fuels and the gum content of motor gasoline or other volatile distillates in their finished form. Provisions are made for the determination of the heptane insoluble portions of the residue of the nonaviation fuels. This test is included in ASTM D4806, ASTM D4814, ASTM D5797, ASTM D5798, and ASTM D5983. The product specification limits are given in Table 4.28.

TABLE 4.28 Product Specifications for Solvent-Washed Gum (ASTM D381)

Product	Specification	Limits, mg/100 mL, max
Denatured fuel ethanol	ASTM D4806	5.0
Gasoline fuels	ASTM D4814	5.0
Gasoline fuel blend	ASTM D5797	5; 20 (unwashed gum)
Ethanol fuel blend	ASTM D5798	5; 20 (unwashed gum)
Fuel-grade MTBE	ASTM D5983	5.0

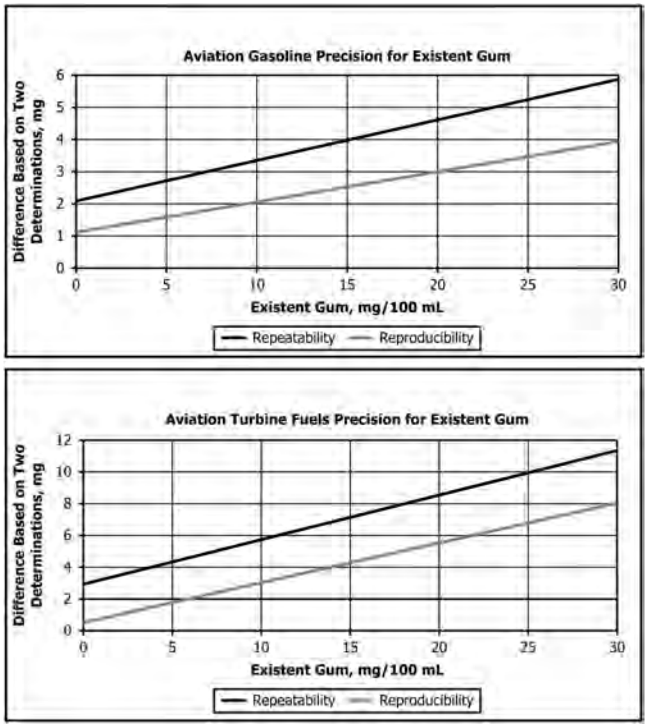
ANALYSIS

In this test, 50 ± 0.5 mL of fuel is evaporated under controlled conditions of temperature and flow of air or steam. For aviation gasoline and aircraft turbine fuel, the resulting residue is weighed and reported. For motor gasoline, the residue is weighed before and after extracting it with n-heptane, and the results are reported as milligrams per 100 mL.

PRECISION

Precision statements for ASTM D381 were developed using data from an interlaboratory study of 14 finished motor gasolines, which included two samples containing 10 volume percent ethanol and five samples containing 15 volume percent MTBE, as well as deposit control additives (RR-D02-1466 [1997]). Both precisions are depicted graphically in Fig. 4.23.

FIG. 4.23 Precision of existent gum by ASTM D381, *Standard Test Method for Gum Content in Fuels by Jet Evaporation*.



Parameter	Repeatability	Reproducibility
Existent gum (aviation gasoline)	1.11 + 0.095 X	2.09 + 0.126 X
Existent gum (aviation turbine fuel)	0.5882 + 0.2490 X	2.941 + 0.2794 X
Unwashed gum	$0.997\ X^{0.4}$	$1.928\ X^{0.4}$
Solvent-washed gum	$1.298\ X^{0.3}$	$2.494\ X^{0.3}$

Note: Where X is the average of the results being compared.

Water in Petroleum Products and Biofuels

SIGNIFICANCE

The solubility of hydrocarbons in fuels decreases with lowering temperature and increasing water content. Separation of the hydrocarbon from the fuel will adversely affect cold starting and driveability, luminosity, and taste deterrence. Water may affect the calibration of some types of composition sensors of flexible-fuel vehicles. Water also reduces the energy content of the fuel and thus adversely affects fuel economy and power. Because some degree of water contamination is practically unavoidable in transport and handling, and because the fuel methanol is miscible with water, the water content of fuel methanol or ethanol is limited to reduce the potential for problems.

Blends of fuel ethanol and hydrocarbons have a limited solvency for water that is dependent upon the ratio of ethanol to hydrocarbons. Workmanship is important during the blending, storage, and transportation of fuel to avoid water contamination. High levels of water may cause haze or phase separation in ethanol and hydrocarbon blends and lead to freezing problems at low temperatures. Haze has been associated with corrosion and filter plugging due to the ability of water to dissolve salts.

If biodiesel is present in the fuel, water can have a more pronounced effect on the diesel fuel. Water is more soluble in a biodiesel blend as compared to a fuel with no biodiesel. Dissolved water in biodiesel can hydrate (or add water molecules to) the FAME molecules. The properties of hydrated FAMEs are different from those of nonhydrated FAMEs. Dissolved water in biodiesel, usually in combination with other contaminants, can also lead to hydrolysis of biodiesel, where the molecule is degraded or broken apart, which can allow further reaction with other compounds to form salts, soaps, or peroxides [17].

Water content among three biofuel-producing international regions is difficult to agree upon because it is based upon the ethanol content of the gasoline-ethanol blend that the individual countries use. The lower water limit in Europe is to protect the motorist from the negative impact on vehicles due to the higher risk of phase separation at their lower ethanol levels. The amount of ethanol used in gasoline is tied to each country's regulatory framework [6]. Karl Fischer titration for biofuels is described by ISO 12937, and this standard is required in ISO 14204.

SCOPE

Most of the biofuel-related ASTM specifications contain analysis for water or for water plus sediment content. See Table 4.29.

TABLE 4.29 Determination of Water in Biofuel Specifications

Specification	Analysis	Test Method	Limits
ASTM D396	Water and sediment	ASTM D2709; ASTM D95 + ASTM D473	0.05 to 2.00 % max
ASTM D975	Water and sediment	ASTM D2709 or ASTM D1796	0.05 % max
ASTM D4806	Water	ASTM E203 or ASTM E1064	1.0 (1.26) % max
ASTM D5797	Water	ASTM E203	0.5 mass % max
ASTM D5798	Water	ASTM E203 or ASTM E1064	1.0 mass % max
ASTM D5983	Water	ASTM E203 or ASTM E1064	0.10 mass % max
ASTM D6751	Water and sediment	ASTM D2709 or ASTM D1796	0.050 % max
ASTM D7467	Water and sediment	ASTM D2709	0.05 % max
ASTM D7544	Water	ASTM E203	30 mass % max
ASTM D7666	Water and sediment	ASTM D1796 or ASTM D2709	2.0 % max
ASTM D7862	Water	ASTM E203 or ASTM E1064	1.0 % max

ANALYSIS

There are a large number of ASTM test methods available for this determination (Table 4.30). Most of them have not necessarily been applied for determining precision specific to biofuels. Additional test methods for water (and sediment) determination are described in Chapter 3 on physical test methods.

Water content in most fuels or biofuels is determined using Karl Fischer titration, either potentiometrically or coluometrically. ASTM E203 describes the modifications required to run the test in the presence of alcohols. Relative density or specific gravity (determined by ASTM D1298 or ASTM D4052) is required to convert the Karl Fischer water results from ASTM E203 or ASTM E1064 test methods from a mass percent to a volume percent basis. The United States has a 1.0 volume percent maximum limit, but the actual water levels are more commonly 0.6 to 0.7 volume percent. The EU has a 0.24 volume percent maximum limit. Brazil has no water specification but, by calculation, water is in the range of 0.4 volume percent. [6].

TABLE 4.30 Determination of Water in Petroleum Products

Manual–Colorimetry	Potentiometric Titration	Coulometric Titration
ASTM D890	ASTM D1348	ASTM D1123 B
ASTM D1123 A	ASTM D1364	ASTM D1533 B
ASTM D1364	ASTM D1533 A and C	ASTM D3401 A
ASTM D1568	ASTM D1631	ASTM D4672 B
ASTM D2072	ASTM D1744	ASTM D4928
ASTM D6986	ASTM D3401 B	ASTM D6304
ASTM D7546	ASTM D4017	ASTM D7375
	ASTM D4377	ASTM E1064
	ASTM D4672 A	ASTM D7923 A
	ASTM D7923 B	
	ASTM E203	
	ASTM F1214	

Excerpted from [1].

In most cases of Karl Fischer titration applied in the biodiesel field, the sample can be directly injected into the Karl Fischer solution, and xylene can also be injected in order to improve biodiesel solubility. However, because many biodiesel fuels contain additives or impurities that can undergo reactions during titration, they should not be injected directly. Also, the oily property of biodiesel contaminates the Karl Fischer solution when directly injected, increasing the number of times this solution should be replaced. Instead, the sample's water content has to be driven off using a Karl Fischer oven and transferred to the Karl Fischer coulometer titration cell in a flow of carrier gas. Using these apparatuses, this process can also be fully automated; consequently, in addition to better accuracy on moisture determination, faster results can be obtained.

Work done specifically on the determination of water in biodiesel by coulometric Karl Fischer titration by Vicetim et al. shows the influence of varying parameters in the procedure on the final water results. Several parameters were investigated, and three of them were optimized according to experimental design. The highest accuracy for moisture determination with a relative standard deviation of 1.48 % was achieved when the Karl Fischer titrator was operated with an electrode without a diaphragm, a sample mass of 4 g, and an oven temperature set to 170°C. Other parameters such as carrier gas flux and extraction time presented minimal or no effects for improving the accuracy of moisture determination. Under these conditions, seven total moisture analyses were performed, totaling 21 differences between the two results. The mean moisture content in this soybean biodiesel sample was 0.05941 % and the relative standard deviation was 1.48 %. No difference exceeded the value R = 0.0046, thus showing that the optimized method was considered repetitive according to ISO 12937 [26].

ASTM D6304

ASTM D6304 is a widely used coulometric titration test method for petroleum products and lubricants. It covers the determination of water in the range of 10 to 25 000 mg/kg entrained water in petroleum products and hydrocarbons using automated instruments. This test method is applicable to additives, lubricating oils, base oils, automatic transmission fluids, hydrocarbon solvents, and other petroleum products. By proper choice of sample size, this test method may be used for the determination of water from mg/kg to percent level concentrations. The normal chemical interferences in Karl Fischer titrations also apply to this test method (e.g., mercaptan, sulfide, sulfur, etc.).

ANALYSIS

The sample injection in the titration vessel can be done volumetrically or gravimetrically. The instrument automatically titrates the sample with commercially available Karl Fischer reagents. Iodine for the Karl Fischer reaction is generated coulometrically at the anode. When all of the water has been titrated, excess iodine is detected by an electrochemical end point detector and the titration is terminated. Based on the stoichiometry of the reaction, 1 mol of iodine reacts with 1 mol of water; thus, the quantity of water is proportional to the total integrated current according to Faraday's law, and it displays the result at the end of the titration. Viscous samples can be analyzed by using a water evaporator accessory that heats the sample in the evaporation chamber, and then the vaporized water is carried into the Karl Fischer titration cell by a dry inert carrier gas.

PRECISION

Based on an interlaboratory study (RR-D02-1436), the precision of this test method is given as follows.

Injection	Volumetric	Gravimetric
Repeatability	$0.08852\ X^{0.7}$	$0.03813\ X^{0.6}$
Reproducibility	$0.5248\ X^{0.7}$	$0.4243\ X^{0.6}$

ASTM D7923

This test method covers the determination of water from 0 to 1.6 mass percent in blends of ethanol, hydrocarbon, and corresponding blends. It is intended for measuring water content of gasoline or other hydrocarbon blendstock, denatured fuel ethanol (ASTM D4806), and ethanol fuel blends (ASTM D5798 and ASTM D7794).

ANALYSIS

There are two procedures: Procedure A using coulometric Karl Fischer titration and Procedure B using volumetric Karl Fischer titration. In the titrations, iodine is consumed by water in a 1:1 molar ratio in the presence of sulfur dioxide, organic base, and methanol or other alcohols. The coulometric procedure generates iodine from iodide by anodic oxidation while the iodine is already present in the volumetric Karl Fischer reagents.

INTERFERENCES

A number of functional groups are known to interfere with Karl Fischer titrations. In hydrocarbons, the most common interferences are mercaptans and sulfides. In ethanol, aldehydes and ketones are known to interfere with the Karl Fischer reagent. Some interferences can be mitigated with the use of applicable reagents. For fuel-grade ethanol and gasoline in areas with stringent environmental regulations, the magnitude of the interference should be negligible under most circumstances.

PRECISION

Based on a study involving 12 laboratories analyzing 12 samples each in duplicate by coulometric Procedure A, and eight laboratories analyzing 14 samples each in duplicate by volumetric titration Procedure B, the following precision was obtained.

Procedure	Repeatability	Reproducibility
A (Coulometric)	$2.216\ E\text{-}02 * X^{0.5746}$ mass %	$3.356\ E\text{-}02 * X^{0.5746}$ mass %
B (Volumetric)	$2.495\ E\text{-}02 * (X + 0.0002)^{0.3144}$ mass %	$4.282\ E\text{-}02 * (X + 0.0002)^{0.3144}$ mass %

Note: Where X is the calculated result for percentage of water expressed as mass percent.

ASTM E203

ASTM E203 discusses organic compounds in which water may be determined directly and compounds in which water cannot be determined directly but in which interferences may be eliminated by suitable chemical reactions.

PROCEDURE

The sample containing a maximum of 100 mg of water is dissolved in a suitable liquid and titrated with a Karl Fischer reagent that contains iodine, sulfur dioxide, organic base, and a solvent (typically an alcohol such as methanol, ethylene glycol, or 2-methoxyethanol). The titration end point is determined potentiometrically with a platinum electrode that senses a sharp change in cell resistance when the iodine is reduced by sulfur dioxide in the presence of water. There are a number of chemicals that will interfere with the titration.

PRECISION

Based on interlaboratory studies conducted by ASTM D01 paint and ASTM D01.35 solvents committees, the following precision was obtained.

	Pyridine-Based Reagents	Pyridine-Free Reagents
Repeatability	0.008 %	0.010 %
Reproducibility	0.027 %	0.078 %

ASTM E1064

This test method is based on the Karl Fischer reaction for determining water—the reduction of iodine by sulfur dioxide in the presence of water to form sulfur trioxide and hydroiodic acid. The reaction becomes quantitative only when pyridine and methyl alcohol are present. Unlike the usual Karl Fischer reagents that include iodine, the coulometric technique electrolytically generates iodine, with 10.71° C of generating current corresponding to 1 mg of water in accordance with Faraday's law. This method specifically allows the use of Photovolt and Mitsubishi coulometric instruments.

SCOPE

The coulometric technique is especially suited for determining low concentrations of water in organic liquids that would yield small titers by the Karl Fischer volumetric procedure. The precision and accuracy of the coulometric technique decreases for concentrations of water much greater than 2.0 % because of the difficulty in measuring the small size of sample required. The test method assumes 100 % efficiency of coulombs in iodine production. Provision is made for verifying this efficiency. Interfering substances are the same as those that are encountered in the conventional Karl Fischer titration and include free halogens, ketones, aldehydes, most acids, and oxidizing or reducing agents.

PRECISION

The following precision has been found for this test method.

	Repeatability	Reproducibility
% RSD	3.9	17.1
Two averages should not differ by more than (% relative):	5.8	20.4

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Abstract

There are about 50 chemical analysis test method used for the characterization of biofuels. They are summarized in this chapter, including significance of the tests, principles underlying the analysis, and test method precision.

Keywords

chemical analysis, biofuels

Chapter 5 | Elemental Analysis Test Methods for Biofuels

Inorganic elements play an important role in the use of petroleum products, fuels, and lubricants in the industry. Similar to other petroleum products and lubricants, biofuels also have some inorganic elements as constituents of their composition. However, the elemental concentrations in biofuels are not as high as in many petroleum products and especially as in lubricants. Discussions on the determination of inorganic elements in petroleum products are available in the proceedings of two ASTM symposiums [1,2]. A review of spectroscopic elemental analysis of biofuels and biolubes is also available [3]. More recently, a comprehensive treatise on this subject has been published by Nadkarni [4]. ASTM WK 27610 reviews the elemental analysis test methods for all biodiesel and ethanol fuel specifications [3,5–7].

A list of the test methods used for elemental analysis is given in Table 5.1. Similar to physical or chemical test methods, most of these elemental test methods originated for use in analyzing petroleum products and lubricants, and their precision specifically for biofuels is not always available. Additionally, a few new test methods have been specifically developed for elemental analysis of biofuels.

Some of the elemental test methods have their counterparts from other standards writing organizations. These are summarized where available in Table 5.2. Although the international standards are not exactly identical to each other, if appropriately followed, they should yield equivalent results to their ASTM counterparts. Similar to the chromatographic methods of analysis for organic components in petroleum products and lubricants (Chapter 3), research on elemental analysis of these matrices continues to use a diverse variety of elemental analysis techniques, and a large amount of information is thus available in the literature.

EN 14538, Calcium, Potassium, Magnesium, and Sodium Content of Fatty Acid Methyl Esters

SIGNIFICANCE

These alkali and alkaline earth elements may be present in biodiesel as abrasive solids or soluble metallic soaps. Abrasive solids can contribute to injector, fuel pump, piston, and ring wear, as well as to engine deposits. Soluble metallic soaps have little effect on wear, but they may contribute to filter plugging and engine deposits. Sodium and potassium are associated with the formation of ash within the engine; calcium soaps are responsible for injection pump sticking. High levels of calcium, magnesium, sodium, and potassium compounds may also be collected in exhaust particulate removal devices and are not typically removed during passive or active regeneration. They can create increased back pressure and reduced time to service maintenance because ash accumulates on the catalyst [5].

Metal ions are introduced into the biodiesel fuel during the production process. Whereas alkali metals come from catalyst residues, alkaline earth metals may originate from hard washing water.

In reality, there is very little calcium or magnesium in the diesel fuel or gasoline at a refinery with modern processing practices. There could be calcium or magnesium in either fuel if they were contaminated by groundwater (which usually contains these metals) or by engine lube oils (from basic detergents in engine oil). This is occasionally observed in contaminated fuel samples from the field, but it is not a fuel specification issue for either gasoline or diesel fuel. Caustic soda is a key processing aid in the desulfurization of gasoline, and the presence of trace amounts of sodium or potassium could originate from this step.

SCOPE

The biodiesel blend stock (B100) for middle distillate fuels (ASTM D6751) includes these four elements with a maximum limit of 5 mg/kg. Due to the biodiesel in B6 to B20 blends, the concentration of these metals should be less than 1 to 2 ppm, making accurate measurement difficult. There are also no controls for these metals in ASTM D975 at present and no available database for the potential contributions of these metals from petroleum-based diesel fuel. The following limits are set in biodiesel specification standards.

Region	Na + K	Test Method	Ca + Mg	Test Method
Brazil	10 mg/kg max	EN 14108/14109	Report	EN 14538
European Union	5 mg/kg max	EN 14108/14109	5 mg/kg max	EN 14538
United States	5 mg/kg max	EN 14538	5 mg/kg max	EN 14538

DOI: 10.1520/MNL772015001105

TABLE 5.1 List of ASTM Test Methods for Elemental Analysis for Biofuels

ASTM Standard	Description
ASTM D129	Sulfur in Petroleum Products (General High Pressure Decomposition Device Method)
ASTM D482	Ash from Petroleum Products
ASTM D874	Sulfated Ash from Lubricating Oils and Additives
ASTM D1266	Sulfur in Petroleum Products (Lamp Method)
ASTM D1552	Sulfur in Petroleum Products by High Temperature Combustion and IR Detection
ASTM D2622	Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry
ASTM D3120	Trace Quantities of Sulfur in Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry
ASTM D3227	(Thiol Mercaptan) Sulfur in Gasoline, Kerosine, Aviation Turbine, and Distillate Fuels (Potentiometric Method)
ASTM D3228	Total Nitrogen in Lubricating Oils and Fuel Oils by Modified Kjeldahl Method
ASTM D3231	Phosphorus in Gasoline
ASTM D3237	Lead in Gasoline by Atomic Absorption Spectrometry
ASTM D3341	Lead in Gasoline—Iodine Monochloride Method
ASTM D4045	Sulfur in Petroleum Products by Hydrogenolysis and Rateometric Colorimetry
ASTM D4294	Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry
ASTM D4628	Analysis of Barium, Calcium, Magnesium, and Zinc in Unused Lubricating Oils by Atomic Absorption Spectrometry
ASTM D4629	Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection
ASTM D4927	Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-ray Fluorescence Spectroscopy
ASTM D4929 B	Determination of Organic Chloride Content in Crude Oil
ASTM D4951	Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry
ASTM D5059	Lead in Gasoline by X-ray Spectrometry
ASTM D5185	Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
ASTM D5291	Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants
ASTM D5453	Determination of Total Sulfur in Light Hydrocarbons, Spark-Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence
ASTM D5622	Determination of Total Oxygen in Gasoline and Methanol Fuels by Reductive Pyrolysis
ASTM D5623	Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection
ASTM D5762	Nitrogen in Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence
ASTM D6920	Total Sulfur in Naphthas, Distillates, Reformulated Gasolines, Diesels, Biodiesels, and Motor Fuels by Oxidative Combustion and Electrochemical Detection
ASTM D7039	Sulfur in Gasoline, Diesel Fuel, Jet Fuel, Kerosine, Biodiesel, Biodiesel Blends, and Gasoline-Ethanol Blends by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry
ASTM D7318[a]	Existent Inorganic Sulfate in Ethanol by Potentiometric Titration
ASTM D7319[a]	Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography
ASTM D7328[a]	Determination of Existent and Potential Inorganic Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection
ASTM D7757[a]	Silicon in Gasoline and Related Products by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry
EN 14538[a]	Determination of Ca, K, Mg and Na Content of FAME by Optical Emission Spectral Method with Inductively Coupled Plasma
WK 21755[a]	Ca + Mg and Na + K by Combustion Followed by ICP-AES (Not Published)
ISO 13032[a]	Determination of Low Concentration of Sulfur in Automotice Fuels Using Energy Dispersive X-ray Fluorescence Spectrometric Method
ASTM UOP 391	Trace Metals in Petroleum Products or Organics by AAS

[a] These test methods were specifically developed for the analysis of biofuels.

TABLE 5.2 International Equivalents of Elemental Analysis Methods for Biofuels

Analysis	ASTM	IP	ISO	DIN	JIS
Sulfur by Bomb Method	ASTM D129	61		51577	
Ash	ASTM D482	4	6245		K 2272
Sulfated Ash	ASTM D874	163	3987	51575	K 2272
Sulfur by Lamp	ASTM D1266	107			
Sulfur by WD-XRF	ASTM D2622			51400T6	K 2541
Sulfur by Oxidative Microcoulometry	ASTM D3120		16591		
Mercaptan Sulfur	ASTM D3227	342	3012		K 2276
Lead by AAS	ASTM D3237	428			
Lead by ICl Method	ASTM D3341	270	3830	51769 T2	K 2255
Metals by ED-XRF	ASTM D4294	336	8754		
Metals by AAS	ASTM D4628	308		51391T1	
Nitrogen by Chemiluminescence	ASTM D4629	379			
Metals by WD-XRF	ASTM D4927	407		51391T2	

Note: Excerpted from Ref. [8]. AAS = atomic absorption spectrometry; ED-XRF = energy-dispersive X-ray fluorescence analysis; ICl = iodine monochloride; WD-XRF = wavelength-dispersive X-ray fluorescence.

ANALYSIS

In the test method EN 14538, an exactly weighed test portion is diluted with kerosine using a 1:1 weight ratio. The resulting solution is directly injected into the plasma of an inductively coupled plasma atomic emission spectrometry (ICP-AES). The interference-free wavelengths recommended for analysis are:

Calcium	422.673 (or 317.933, 393.366, 396.847) nm
Magnesium	279.553 (or 285.213) nm
Sodium	588.995 (or 589.592) nm
Potassium	769.897 (or 766.490) nm

For reference and calibration purposes, calibration samples with known amounts of the elements under investigation in the range of 0.5 to 10 mg/kg are used. The sums of the content of calcium and magnesium and sodium and potassium are reported.

PRECISION

The following repeatability and reproducibility have been found for this test method.

Elements	Repeatability	Reproducibility
Ca + Mg	0.023 X + 0.271	0.149 X + 1.186
Na + K	0.020 X + 0.193	0.191 X + 0.941

Note: Where X is the mean of the two results.

In a separate ASTM interlaboratory study, six biodiesel samples used in the D02.CS 92 Proficiency Testing Program (PTP) were analyzed for these four elements using a method identical to EN 14538. Only a single sample was analyzed in each laboratory so the repeatability cannot be calculated per ASTM D6300 protocol. However, the reproducibility found for this analysis was (Ca + Mg) = 2.8 $X^{0.6}$ and (Na + K) = 1.3 $X^{0.5}$, where X is the mean of two results. The reproducibility of EN 14538 is somewhat superior than the one found here. We believe, however, that the ASTM interlaboratory study reproducibility value is more realistic because this calculation is based on data from 42 laboratories collected over a period of two years. No information is available on the details of the Center for European Normalization (CEN) crosscheck to arrive at their precision calculations.

Results from all ASTM PTPs for biodiesel also indicate very poor quality data using the EN 14538 test method. As examples in Table 5.3 show, there is no value whatsoever in such ineffective analysis, where the standard deviation is equal to or higher than the mean value.

The biodiesel specification ASTM D6751 includes ASTM UOP 391 as an alternate suggested test method for the aforementioned metal analysis instead of EN 14538. The test method consists of wet ashing of an organic material with fuming sulfuric acid that is ignited and ashed at 538°C. The residue is then dissolved with aqua regia and, after evaporation, is dissolved in dilute hydrochloric acid containing scandium as an internal standard. In ASTM UOP 389, the trace elements are determined by ICP-AES, and in ASTM UOP 391 they are determined by atomic absorption spectrometry (AAS).

The fuming sulfuric acid required for dissolution of the sample must be of ultra-high purity with no trace elements. Although it was at one time available from VWR Corp, this reagent has now

TABLE 5.3 Determination of Calcium Plus Magnesium (Ca + Mg) and Sodium Plus Potassium (Na + K) in Biodiesels

Biodiesel Sample	Ca + Mg, mg/kg	Na + K, mg/kg
BIOD 1204	0.05 ± 0.08 (33)	0.31 ± 0.38 (33)
BIOD 1208	0.07 ± 0.10 (31)	0.53 ± 0.51 (34)
BIOD 1304	0.04 ± 0.06 (34)	0.19 ± 0.24 (36)
BIOD 1308	0.05 ± 0.07 (35)	0.10 ± 0.14 (33)
BIOD 1311	0.03 ± 0.05 (37)	0.13 ± 0.20 (39)

Note: All results are expressed as robust mean ± robust standard deviation (number of valid results).

been discontinued. Therefore, this test method can no longer be used for such analysis.

Inductively Coupled Plasma Atomic Emission Spectrometric Determination of Trace Metals in Fuel Ethanol

This proposed test method would allow several trace elements (copper, lead, phosphorus, etc.) to be determined in fuel ethanol and would replace other currently allowed test methods (ASTM D1688 for copper, ASTM D5059 for lead, and ASTM D3231 or ASTM D4951 for phosphorus). A sample is evaporated to a small volume to remove most of its volatile components. The residue is reconstituted with deionized water or dilute nitric acid, and the trace elements are determined with ICP-AES. Aqueous calibration standards are used. Alternatively, the sample may be directly nebulized into the ICP-AES torch and the elements determined.

The elements that would be determined by this proposed test method are calcium (Ca), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), phosphorus (P), potassium (K), sodium (Na), and sulfur (S). Estimated detection limits would vary from 5 to 50 mg/kg. Although proposed some time ago, ASTM D02 has not completed this ILS.

Agilent: 5991-0771EN (2012), Metals in Biofuels by Microwave Plasma Atomic Emission Spectrometry

The presence of metals and metalloids in petrochemical products can influence the performance of engines and can contribute to shortening the life of the machinery. The presence of metals may deteriorate the fuel quality by oxidative decomposition reactions. Additionally, some elements act as a catalyst poison, contributing to increases in the amount of toxic gases and particulate matter emitted by the vehicles. Some elements can be naturally present in ethanol as a result of the soil composition where sugarcane has grown. Alternatively, these elements can be introduced into the fuel during its production, storage, or transport (or combinations thereof). Thus, after fuel combustion, these elements can significantly increase air pollution.

Some examples of the use of atomic spectroscopy for the analysis of biofuels are given in references using flame AAS (FAAS) for biodiesel [9], FAAS for ethanol [10], electrothermal vaporization (ETV) ICP-AES for ethanol [11], and so on. Microwave plasma atomic emission spectrometry (MP-AES) has been suggested as an alternative to ICP-AES for metal analysis. Its use for the determination of silicon (Si) in gasoline and diesel has been mentioned earlier in this chapter [12].

Additionally, this technique has been demonstrated for the determination of chromium (Cr), nickel (Ni), Pb, and vanadium (V) in ethanol fuel using an Agilent 4100 MP-AES instrument [12]. Ethanol fuel samples were diluted tenfold with nitric acid. Aqueous element standards containing 10 % ethanol were used. Based on spiked recovery analyses, between 92 % and 108 % recoveries were obtained indicating low intensity of matrix effects commonly caused by organic compounds and concomitant elements such as Cu, Na, and Fe. See Table 5.4.

TABLE 5.4 Recovery Studies of Spiked Ethanol Fuel Samples

Element	Wavelength, nm	Added, µg/L	Found, µg/L	Recovery, %
Chromium	425.433	20	21.2 ± 1.2	106
		100	95.1 ± 1.2	95
		500	460 ± 30	92
Nickel	352.454	100	95.3 ± 0.8	95
Lead	405.781	400	430 ± 10	108
		1000	990 ± 10	99
Vanadium	437.923	20	19.8 ± 1.6	99
		100	98.4 ± 1.4	98
		500	460 ± 20	92

From Ref. [12].

SCOPE

This proposed test method provides an easy and reliable measurement to ensure that these biofuels meet the appropriate quality standards prior to blending. The MP-AES technique is especially useful for measurements in remote regions where gas supplies are problematic because the instrument needs only nitrogen gas that can be generated in the laboratory. This test method covers the determination of metals and metalloids in biodiesel or ethanol. The specific elements that can be determined include Ca, Cr, Cu, Pb, Mg, Ni, P, K, Si, Na, and V. This test method uses soluble metals for calibration and does not purport to quantitatively determine insoluble particulates. Analytical results are particle size dependent, and low results are obtained for particles larger than a few micrometres.

Test times are approximately a few minutes per test specimen, and detectability for most elements is in the low mg/kg range.

INTERFERENCES

Spectral interferences can usually be avoided by judicious choice of analytical wavelengths. When spectral interferences cannot be avoided, the necessary corrections should be made using the computer software supplied by the instrument manufacturer. Differences in the viscosities of the test specimen solution and standard solutions can cause differences in solution uptake rates. These differences can adversely affect the accuracy of the analysis. The effects can be reduced by using a peristaltic pump to deliver solutions to the nebulizer or by the use of internal standardization (or both), with mass flow control on the nebulizer gas line for more reliable flow. Particulates can plug the nebulizer, thereby causing low results. Use of a total dissolved solids nebulizer helps to minimize this effect. Also, the specimen introduction system can limit the transport of particulates, and the plasma can incompletely atomize particulates, thereby causing low results.

ANALYSIS

Bioethanol samples are diluted 1:10 with aqueous dilute nitric acid, and diesel or biodiesel samples are diluted 1:10 with an organic solvent such as ethanol, xylene, monoisobutyl ketone, Di-isobutyl ketone, white spirit, or narrow cut kerosine and are mixed well. The diluted samples are directly introduced into the microwave plasma atomic emission spectrometer. Measurements of emission intensity at the appropriate wavelength for each element are then compared with measurements made under the same conditions on a standard reference elemental solution.

PRECISION

An actual interlaboratory study for demonstrating the precision of the proposed technique has not yet taken place.

Inductively Coupled Plasma Mass Spectrometric Determination of Trace Metals in Biofuels

Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful technique for the determination of trace elements in petroleum products and fuels. It is superior to ICP-AES in its sensitivity. Hwang reviewed the applications of ICP-MS technique for the determination of multiple trace elements in biodiesel and bioethanol [13]. Lachas et al. compared several sample preparations (including wet ashing and microwave extraction) for trace element analysis in milligram sample sizes of biomass samples using ICP-MS. The accuracy and sensitivity of the measurements improved when the dilution rate was decreased from 5,000 to 1,000 and to 500 [14]. Baernthaler et al. developed a reliable ashing method to accurately determine both major and minor ash-forming elements in solid biofuels using ICP-MS. Wood and bark, straw, and olive residues were analyzed using several digestion and analytical methods [15]. The digestion methods included wet and dry ashing with different acid mixtures. Analytical techniques surveyed included FAAS, graphite furnace AAS, cold vapor AAS, ICP-AES, ICP-MS, and X-ray fluorescence.

Saint'Pierre et al. used an ignition delay electrothermal vaporization inductively coupled plasma mass spectrometry (ID-ETV-ICP-MS) technique to determine several trace elements in a fuel alcohol sample [16]. The ID proved to be a robust, fast, and simple calibration technique for the analysis of fuel ethanol. Later, Saint'Pierre et al. developed a flow injection system, coupling it to an ultrasonic nebulizer for direct introduction of fuel ethanol for trace elements analysis by ICP-MS [17]. External calibration versus aqueous solutions, matrix matching, and ID were compared. Both ID and calibration with aqueous solutions improved speed, precision, sensitivity, and agreement with the results obtained by ETV-ICP-MS. Saint'Pierre et al. also presented the use of many sample preparation and sample introduction systems with an ICP-MS for the analysis of biofuels and petroleum fuels [18]. Woods and Fryer used an ICP-MS fitted with an octopole reaction system (ORS) to directly measure the inorganic contents of several biodiesel materials [19]. Following the sample's dilution with kerosine, the biofuel was analyzed directly. The ORS effectively removed matrix- and plasma-based spectral interferences to enable measurement of all important analytes, including sulfur, at levels below those possible by ICP-AES.

ASTM D5291, Carbon and Hydrogen in Petroleum Products

SIGNIFICANCE

Carbon, hydrogen, and nitrogen analyses are useful in determining the complex nature of sample types. These results can be used to estimate the processing and refining potentials and yields in the petrochemical industry. Hydrogen to carbon ratio is useful for assessing the performance of upgrading processes. ASTM D7566 allows a maximum of 99.5 mass percent carbon-hydrogen for hydroprocessed synthetic paraffinic kerosine. ASTM D5291 is specified for carbon-hydrogen determination in ASTM D7566.

ANALYSIS

Four procedures included in ASTM D5291 use combustion followed by infrared (IR) detection, gas chromatographic separation, or thermal conductivity detection. Each procedure is based on specific commercial instrumentation.

PRECISION

Precision obtainable by ASTM D5291 is summarized in Table 5.5. The samples included in this study were not biofuels.

ASTM D4929B, Organic Chloride Content of Crude Oil

SIGNIFICANCE

Chloride ions even at low concentrations in denatured fuel ethanol are corrosive to many metals. Similarly, ionic (i.e., inorganic)

TABLE 5.5 Precision of ASTM D5291 for Carbon and Hydrogen

Element	Concentration Range, mass %	Procedure	Repeatability	Reproducibility
Carbon	75–87	A–C	X + 48.48 (0.0072)	X + 48.48 (0.018)
		D	0.5644	1.4671
Hydrogen	9–16	A–C	$X^{0.5}$ × 0.1162	$X^{0.5}$ × 0.2314
		D	0.5905	1.9089

Note: Where X is the average of two determinations in mass percent.

and organic chlorines are corrosive to many metals. It is desirable to minimize these compounds in fuel methanol and fuel ethanol. Total chlorine as a chloride maximum limit of 2 mg/kg has been found to be inadequate in protecting some fuel system components. An inorganic chloride maximum limit of 1 mg/kg is specified in ASTM D5797 to provide additional protection.

SCOPE

ASTM D4929 B determines organic chloride above 1 mg/kg levels in crude oils using distillation followed by microcoulometric determination of chloride. The precision or the applicability of the method for biofuels is not known.

ANALYSIS

Crude oil is distilled to obtain the naphtha cut at 204°C based on the distillation of petroleum products (ASTM D86). The naphtha cut is washed successively with a caustic (repeatedly when necessary) and water to remove hydrogen sulfide and inorganic chlorides, respectively. The washed naphtha fraction is injected into an oxidative furnace in a flowing stream of gas containing about 80 % oxygen and 20 % inert gas, such as argon, helium, or nitrogen. The gas and the sample flow through a combustion tube maintained at about 800°C. The resultant chlorides and oxychlorides are coulometrically titrated with silver nitrate. The silver ions thus consumed are coulometrically replaced. The total current required to replace the silver ions is a measure of the chlorine present in the injected sample. The reactions taking place in this titration are:

$$\mathrm{Cl^- + Ag^+ \rightarrow AgCl(s)}$$
$$\mathrm{Ag^0 \rightarrow Ag^+ + e^-}$$

Hydroiodic and hydrobromic acids will also titrate and give a positive response. They do not react in the titration cell; an approximately 50 % microequivalent response is detected. A total sulfur concentration of up to 10,000 times the chlorine level can be tolerated.

Based on an interlaboratory study (RR-D02-1293), the precision of this test method for crude oils has been found to be 1.01 $(X - 0.17)^{0.467}$ as repeatability and 1.32 $(X - 0.17)^{0.467}$ as reproducibility, where X is the average of two determinations.

ASTM D1688A, Copper in Water by Atomic Absorption Spectrometry

SIGNIFICANCE

Copper is a very active oxidation catalyst for the low-temperature oxidation of hydrocarbons. It has been shown that copper concentrations higher than 0.012 mg/kg in commercial gasolines can significantly increase the rate of gum formation. Maximum copper content of 0.1 mg/kg is allowed in ASTM D4806 and 0.07 mg/L in ASTM D5798. The EU limit also is 0.1 mg/kg and Brazil's is 0.07 mg/kg.

Brazil has questioned whether this parameter is still required because originally it was intended to prevent copper contamination from production facilities using copper tubes and stills. However, CEN believes that it is necessary because ethanol may enter the fuel chain from whiskey distillers when it is unfit for human consumption. Copper stills are commonly used in liquor manufacture. An ICP-AES test method for measuring Cu, Na, Fe, and P would be useful [20].

ANALYSIS

Copper in denatured fuel ethanol is determined using a modified ASTM D1688, Procedure A, per ASTM D4806 and ASTM D5798 for fuel ethanol. The modifications consist of mixing reagent-grade ethanol in place of water as the solvent or the diluent for the preparation of reagents and standard solutions. However, this must not be done to prepare the stock copper solution described in ASTM D1688, Procedure A. Because a violent reaction can occur between the acid and the ethanol, water must be used as specified in the acid solution part of the procedure to prepare the stock copper solution. Ethanol should be used for the rinse and final dilution only. The measurement is made using atomic absorption spectrometry for copper.

Test methods used in Brazil (NBR 10893) and by the EU (EN 15488) should give comparable results to those obtained by ASTM D1688 A.

PRECISION

The precision of this modified method has not been determined for the ethanol-fuel matrix, but it is expected to be similar to the precision of ASTM D1688, Procedure A. ASTM PTP crosschecks for fuel ethanol in the last three years show no laboratory detecting copper in these samples, which means copper levels are below the detection limit of the cited test method. Hence, it would be useful to develop an ICP-AES test method for this analysis. The ICP-AES technique is usually far more sensitive than other trace element measurement test methods, such as AAS. There is little point in keeping the copper specification in ethanol fuel products because the test method quoted is not capable of detecting copper at the level it may be present in the fuel. It is questionable if there is any detectable copper in the fuel; this requirement is apparently a carryover from earlier days when copper pipes were used in synthesis, which is not the case today.

ASTM D3237, ASTM D3341, and ASTM D5059, Lead in Gasoline and Diesel Fuels

SIGNIFICANCE

Most modern gasoline-powered vehicles are equipped with exhaust catalytic converters to control emissions of hydrocarbons, carbon monoxide, and oxides of nitrogen. Most fuel methanol fuel vehicles are also equipped with exhaust catalysts that control emissions of formaldehyde as well as the regulated emissions. Lead compounds deactivate these catalysts and are limited to trace amounts to prevent this problem. With the phase-out of lead in gasoline over the last three decades, the importance of the determination of added lead in gasoline has decreased. However, it is still necessary to measure the trace levels of lead as required by U.S. regulations for lead-free gasoline. These test methods can be used to ensure compliance of trace lead in gasoline as required by U.S. regulations for lead-free gasoline.

ANALYSIS

There are several test methods for the determination of lead in petroleum products given the earlier importance of lead levels. Of these, three test methods are quoted in biofuel specifications.

Specification	Lead Level	Test Method
Gasoline Fuel ASTM D4815	Unleaded: 0.13 g/L (0.05 g/gal) Leaded: 1.1 g/L (4.2 g /U.S. gal)	ASTM D3237; ASTM D3341; ASTM D5059
Fuel Methanol ASTM D5797	Class 1: 2.6 mg/L Class 2: 2.6 mg/L Class 3: 3.9 mg/L	ASTM D5059

ASTM D3237

This test method is applicable in the range of 2.5 to 25 mg/L of lead. It compensates for variations in gasoline composition and is not affected by the type of lead alkyls in the sample. In this test method, the gasoline sample is diluted with methyl isobutyl ketone, and the alkyl lead components are stabilized by reaction with iodine and a quaternary ammonium salt. The lead content of the sample is determined by flame atomic absorption spectrometry measured at the wavelength of 283.3 nm, using the standards prepared from reagent-grade lead chloride. All alkyl lead compounds give an identical response. This test method has a repeatability of 1.3 mg/L and a reproducibility of 2.6 mg/L (RR-D02-1376).

ASTM D3341

This test method is applicable in the range of 0.026 to 1.3 g/L of lead. A known volume of the sample is diluted with heavy distillate and shaken with an aqueous iodine monochloride reagent. Any tetra-alkyl lead compounds present are converted to dialkyl lead compounds and are extracted into the aqueous phase. The separated aqueous extract is evaporated to a low volume to decompose free iodine monochloride. Any organic matter present is removed by oxidation with nitric acid, which also converts dialkyl lead compounds to inorganic lead compounds. The residue is dissolved in water and buffered at pH 5 using sodium acetate–acetic acid buffer. The lead content of the solution is determined by titrating with ethylenediaminetetraacetic acid using xylenol orange as an indicator.

This test method has a repeatability of 0.00365 + 0.0073X and a reproducibility of 0.0135 + 0.027X, where X is the average results in g Pb/L at 15.5°C.

ASTM D5059

The three parts of this test method cover the determination of lead in gasoline in the range of 0.0026 to 1.32 g lead/L. They compensate for the normal variation in gasoline composition and are independent of lead alkyl type present. At one time, the three parts of this test method had different ASTM designations:

Current Test Method	Former Test Method
Procedure A	ASTM D2599, Section 5–9
Procedure B	ASTM D2599, Section 10–14
Procedure C	ASTM D3229, Section 15–19

- **Procedure A**—One volume of sample is mixed with an equal volume of bismuth internal standard solution. The mixture is placed in an X-ray beam, and radiations at 1.75 A^0 for lead and 1.144 A^0 for bismuth are measured. By comparing the ratio of intensities to that of known standards, the lead content of gasoline is calculated.
- **Procedure B**—The ratio of net X-ray intensity of lead radiation to the net intensity of the incoherently scattered tungsten radiation is obtained on a portion of the sample. By comparing this to the intensity of a known lead standard, the lead content of gasoline is calculated.
- **Procedure C**—This test method is the same as Procedure A, but an additional background radiation at 1.194 A^0 is also measured. A blank made with isooctane and a bismuth internal standard are run using the same procedure. The lead content of gasoline is calculated based on comparing the ratio of lead to bismuth radiation intensities to that of known standards, after subtracting the blank ratio.

The precision of ASTM D5059 has been found to be as follows:

Procedure	Repeatability	Reproducibility
Procedure A	0.008 + 0.008 X	0.027 + 0.030 X
Procedure B	0.004 + 0.015 X	0.010 + 0.039 X
Procedure C	0.007 + 0.14 X	0.018 + 0.15 X

Note: Where X is the average result expressed in g lead/L at 15°C in Procedures A and B, and in g lead/U.S. gal at 15.5°C in Procedure C.

ASTM D4629, ASTM D5291, and ASTM D5762, Nitrogen in Petroleum Products

SIGNIFICANCE

Nitrogen oxide emission regulations have been imposed on certain combustion facilities as a function of the nitrogen content of the fuel. For the purposes of these regulations, distillate fuels, low- and high-nitrogen residual fuels have been defined by their nitrogen content. Installations are required to meet different emission standards according to the classification of the fuel being used.

When regulations require such a distinction to be made, fuel nitrogen specifications can be needed in the contractual agreement between the purchaser and the supplier.

Many nitrogen compounds even at trace levels in feedstocks can contaminate refinery catalysts. They tend to be the most difficult class of compounds to hydrogenate, so the nitrogen content remaining in the product of a hydrotreater is a measure of the effectiveness of the hydrotreating process. ASTM D7566 allows a maximum limit of 2 mg/kg nitrogen.

ANALYSIS

There are several ASTM test methods for the determination of nitrogen in liquid petroleum products:

ASTM Test Method	Analytical Technique
ASTM D3228	Kjeldahl Digestion and Acid Titration
ASTM D4629	Oxidative Combustion and Chemiluminescence Detection
ASTM D5291	Combustion, Gas Separations, and Thermal Conductivity Detection
ASTM D5762	Boat Inlet Combustion and Chemiluminescence Detection

Of these, ASTM D4629 is the only one quoted in biofuel specifications, although there is no precision known for this test method for biofuels. Originally, this method was developed for the determination of trace amounts of nitrogen in fuels and additive products, and until other modern instrumental test methods came along, was the only instrumental test method for nitrogen determination in petroleum products [21].

ASTM D4629

This test method is applicable to liquid hydrocarbons boiling in the range from approximately 50 to 400°C, with viscosities between approximately 0.2 and 10 cSt at room temperature. It is applicable to naphthas, distillates, and oils containing 0.3 to 100 mg/kg total nitrogen.

ANALYSIS

In this test method, a sample of liquid petroleum hydrocarbon is injected into a stream of inert gas (helium or argon). The sample is vaporized and carried to a high-temperature zone where oxygen is introduced and organic and bound nitrogen is converted to nitrogen oxide (NO). The NO contacts ozone and is converted to excited nitrogen oxide (NO_2^*). The light emitted as the excited NO_2^* decays is detected by a photomultiplier tube and the resulting signal is a measure of the nitrogen content of the sample. Based on interlaboratory studies (RR-D02-1199 and -1527), the precision of this test method has been determined to be 0.1825 $X^{0.5149}$ repeatability and 0.8094 $X^{0.5149}$ as the reproducibility, where X is the average of two test results.

ASTM D5762

This test method covers the determination of nitrogen in liquid hydrocarbons, including petroleum process streams and lubricating oils in the concentration range from 40 to 10,000 mg/kg.

ANALYSIS

In this test method, a sample is placed on a sample boat at room temperature. The sample and the boat are advanced into a high-temperature combustion tube where the nitrogen is oxidized to nitric oxide (NO) in an oxygen atmosphere. The NO contacts ozone and is converted to excited nitrogen dioxide (NO_2). The light emitted as the excited NO_2 decays is detected by a photomultiplier tube, and the resulting signal is a measure of the nitrogen contained in the sample.

PRECISION

Based on an interlaboratory study (RR-D02-1507), the following precision was found for this test method. No bias was found analyzing a National Institute of Standards and Technology Standard Reference Material (NIST SRM).

Repeatability	0.087 by X mg/kg
Reproducibility	0.266 by X mg/kg

Note: Where X is the average of the two test results.

ASTM D5622, Total Oxygen in Gasoline and Methanol Fuels

SIGNIFICANCE

The presence of oxygen-containing compounds in gasoline can promote more complete combustion, which reduces carbon monoxide emissions. The Clean Air Act of 1992 stipulated that gasoline sold within certain geographically specified areas contain a minimum amount of oxygen (presently 2.7 mass percent) during certain periods of the year. This requirement can be met by blending compounds such as methyl tertiary butyl ether, ethyl tertiary butyl ether, and ethanol into gasoline.

SCOPE

This test method covers the quantitative determination of total oxygen in gasoline and methanol fuels by reductive pyrolysis. This test method complements ASTM D4815, which covers the determination of several specific oxygen-containing compounds in gasoline.

ANALYSIS

In this test method (ASTM D5622), a sample of gasoline is pyrolyzed in a carbon-rich environment. A fuel sample is injected by syringe into a 950 to 1300°C high-temperature tube furnace that contains metallized carbon. Oxygen-containing compounds are pyrolyzed, and the oxygen is quantitatively converted into carbon monoxide. A carrier gas such as nitrogen, helium, or a helium-hydrogen mixture sweeps the pyrolysis gases into any of the four downstream systems of reactors, scrubbers, separators, and detectors for the determination of the carbon monoxide content, and hence, of the oxygen in the original fuel sample.

PRECISION

Based on an interlaboratory study, the precision of this test method has been found to be as follows.

Oxygen Content, mass %	Repeatability	Reproducibility
1.0 to 5.0	0.06 %	0.26 %
40 to 50	0.81 %	0.81 %

ASTM D3231 and ASTM D4951, Phosphorus in Petroleum Fuels

SIGNIFICANCE

Phosphorus is a natural element present in all plants and animals (usually as phospholipids), and it is also found in vegetable oils. It can affect the conversion rates in diesel exhaust catalytic converters used to control emissions. Similar to lead, phosphorus deactivates exhaust catalysts and is limited to trace amounts in fuels. Catalytic converters are becoming more common on diesel-powered equipment as emission standards are tightened, so low phosphorus levels will be of increasing importance. Biodiesel produced from U.S. sources has been shown to have low phosphorus content (below 1 mg/kg), and the specification value of 10 mg/kg maximum is not problematic. Biodiesel from other sources may or may not contain higher levels of phosphorus [8], and this specification was added to ensure that all biodiesel, regardless of the source, has a low phosphorus content. The following phosphorus limits are included in biodiesel specifications.

Only the EU has a phosphorus limit on ethanol, and it is based on data from the ethanol producers. Phosphorus may be an issue if ethanol is produced from nontraditional feedstocks and processes. The source of phosphorus may be fertilizers and nutrients used in the fermentation process or may be from the feedstock [20].

Region	Limits	Test Method(s)
Brazil	10 mg/kg report	EN 14107/ASTM D4951
European Union	10.0 mg/kg max	EN 14107
United States	10 mg/kg max	ASTM D4951

SCOPE

The following limits are set in biofuels specifications for phosphorus content.

Specification	Phosphorus Level	Test Method
ASTM D5797	Class 1 (0.2), Class 2 (0.3), Class 3 (0.4) mg/L	ASTM D3231
ASTM D6751	0.001 mass %	ASTM D4951

ANALYSIS

There are several test methods for the determination of phosphorus in petroleum products. Only two of them are prescribed in biofuel specifications.

ASTM Test Method	Matrix	Technique
ASTM D3231	Gasoline	Colorimetric
ASTM D1091	Lubricating oils	Colorimetric
ASTM D4047	Lubricating oils	Colorimetric
ASTM D4927	Additives	WD-XRF
ASTM D4951	Additives	ICP-AES
ASTM D5185	Lubricating oils	ICP-AES
ASTM D7040	Lubricating oils	ICP-AES
ASTM D7111	Middle distillate fuels	ICP-AES

The test method given in ASTM D6751 for biodiesel is the ICP-AES, ASTM D4951; however, it is impossible to determine a 10 ppm level of phosphorus by this test method. ASTM D4951 is intended for the analysis of lubricants and additives that contain far higher levels of phosphorus and other metals compared with biodiesel. Perhaps the ASTM D7111 ICP-AES test method for middle distillate fuels would be a better choice.

ASTM D3231

This test method is applicable for the determination of phosphorus in the range from 0.2 to 40 mg/L. The organic matter in the sample is decomposed by ignition in the presence of zinc oxide. The residue is dissolved in sulfuric acid and reacted with ammonium molybdate and hydrazine sulfate. The absorbance of molybdenum blue complex is measured at 820 nm in a 5-mm cell in a spectrophotometer and is proportional to the phosphorus concentration in the sample.

PRECISION

Precision is as follows.

Phosphorus Range, mg/L	Repeatability	Reproducibility
0.2–1.3	0.05	0.13
1.3–40	7 % of the mean	13 % of the mean

ASTM D7757, Silicon in Gasoline and Diesel

SIGNIFICANCE

Silicone oil (as siloxanes) defoamer can be added to coker feedstocks to minimize foaming in the coker. During combustion, these compounds decompose to form silicon dioxide, which can produce a coating layer on the catalyst element of the exhaust system and significantly increase air pollution. Residual silicon in the coker naphtha can adversely affect downstream catalytic processing of the naphtha [22].

Regulation in this field is increasingly common, and recent legislation in Brazil has established the maximum concentration of silicon plus aluminum as 80 mg/kg [23].

Finished gasoline and ethanol-fuel blends can come into contact with silicon in a number of ways. Waste hydrocarbon solvents such as toluene can be added to gasoline. Such solvents can contain soluble silicon compounds. Silicon-based antifoam agents can be used in ethanol plants, which then pass silicon on to the finished ethanol-fuel blend. Silicon contamination of gasoline, denatured ethanol, and their blends has led to fouled vehicle components (e.g., spark plugs, exhaust oxygen sensors, catalytic converters) requiring replacement of parts and repairs. Hence, manufacturers and blenders of fuel ethanol (Ed75–Ed85) have been advised to avoid ethanol or denaturants and hydrocarbon blend components contaminated with silicon-containing materials such as recycled toluene previously used in cleaning semiconductors [24].

ANALYSIS

ASTM D7757 determines silicon compounds in naphtha, gasoline, reformulated gasoline (RFG), gasoline-oxygenate blends, denaturants, hydrocarbon blend components, denatured fuel ethanol, or toluene. This test method is based on monochromatic wavelength-dispersive X-ray fluorescence spectroscopy. This dynamic range is 3 to 100 mg/kg, and the pooled limit of quantitation is 3 mg/kg at a 600-s counting time.

PRECISION

This test method has been used to analyze gasoline fuels and fuel ethanol blends. Based on an interlaboratory study involving seven laboratories analyzing 24 silicon-doped samples—including six gasolines, four gasolines with 10 % ethanol, two naphthas, two toluene samples, and four E85 and six E100 samples, the following precision was obtained (RR-D02-1735).

Repeatability	$0.5582\ X^{0.5471}$
Reproducibility	$1.0535\ X^{0.5471}$

Note: Where X is the average of duplicate determinations.

Use of microwave plasma atomic emission spectrometry (MP-AES) has been proposed as a sensitive method for trace amounts of silicon in diesel and biodiesel [25]. In this method, an Agilent 4100 MP-AES spectrometer is used. This produces a robust and stable plasma utilizing magnetically coupled microwave energy. A nitrogen gas generator feeds the microwave plasma, and no additional gas source is required to run the instrument. Three sample preparation procedures were evaluated: microwave-assisted digestion, micro-emulsion preparation in n-propanol, and dilution in ethanol. A closed-vessel microwave oven equipped with 45-mL PFA vessels was used for the digestion of diesel and biodiesel samples in 50 % nitric acid plus 30 % hydrogen peroxide.

All three preparation procedures evaluated provided adequate sensitivity. The accuracy of all three procedures was developed using spiked studies with both sample matrices. Results of this study are given in Table 5.6 and show all recoveries were between 80 % and 102 %.

Thus, accurate silicon determinations were successfully carried out simply by diluting the samples in ethanol and using external calibration with aqueous solutions.

Sulfur in Petroleum Products and Fuels

SIGNIFICANCE

The limit on sulfur content in fuels is included to protect against engine wear, deterioration of engine oil, and corrosion of exhaust system parts. Limits on sulfur concentration in a fuel can be required for special uses in connection with heat treatment, nonferrous metal, glass, and ceramic furnaces, or to meet regulatory legislation or regulations. The effect of sulfur content on engine wear and deposits appears to vary considerably in importance and depends largely on operating conditions. Fuel sulfur can affect engine wear, deterioration of engine oil, corrosion of exhaust system parts, exhaust catalyst deactivation, and emission control system performance. To ensure maximum availability of fuels, the permissible sulfur content should be specified as high as practicable, consistent with maintenance considerations.

The U.S. Environmental Protection Agency's (EPA's) Federal Tier 2 Motor Vehicle and Emission Standards and Gasoline Sulfur Control Requirements establish sulfur standards for refineries and importers producing reformulated gasoline, reformulated blendstock for oxygenate blending, and conventional gasoline. The EPA has established gasoline sulfur controls to support vehicle emission standards. Sulfur contaminates the catalytic converter necessary

TABLE 5.6 Spike Experiments for Silicon by MP-AES Technique

Sample	Silicon Emission Line, nm	Digestion		Ethanol Dilution		Micro-Emulsion	
		Added	Recovered	Added	Recovered	Added	Recovered
Biodiesel	251.611	3.0	3.05 ± 0.07	0.5	0.45 ± 0.03	1.0	0.89 ± 0.05
				1.0	0.99 ± 0.09		
	288.158	3.0	3.05 ± 0.01	0.5	0.40 ± 0.04	1.0	0.89 ± 0.06
				1.0	1.02 ± 0.17		
Diesel	251.611	3.0	3.09 ± 0.10	0.5	0.47 ± 0.01	1.0	0.96 ± 0.03
				1.0	0.91 ± 0.01		
	288.158	3.07 ± 0.15		0.5	0.46 ± 0.01	1.0	0.96 ± 0.04
				1.0	0.95 ± 0.01		

From Ref. [13].

for reducing emissions of hydrocarbon, carbon monoxide, and nitrogen oxide. The limit for sulfur in EU regulations is 10 mg/kg maximum.

California specifies that compliance with the California sulfur standard for denatured ethanol shall be determined using ASTM D5453-93. The EPA allows ASTM D3120-06e1, ASTM D5453-08a, or ASTM D7039-07 for measuring sulfur in gasoline as long as these alternative test method results are correlated to the EPA-designated test method, ASTM D2622-05, when determining compliance with federal EPA sulfur standards. Table 5.7 shows the referee and alternate test methods for sulfur, the range over which each test method applies, and the corresponding fuel grades of diesel fuel oils.

In 2014, the EPA published its Tier 3 motor vehicle emission and fuel standards [26]. Starting in 2017, Tier 3 sets new vehicle emissions standards and lowers the sulfur content of gasoline, considering the vehicle and its fuel as an integrated system. The change is expected to help the mechanisms in an automobile do a better job of capturing the pollutants that lead to smog, which triggers asthma attacks and respiratory diseases [27]. However, the petroleum industry has argued against this rule because of concerns over cost burden to the oil companies. A study produced by the American Petroleum Institute estimates the new rules would require upgrades at refineries across the country that could cost a combined $10 billion, with annual compliance costs of $2.4 billion—or up to 9 cents per gallon of gasoline [27]. However, the EPA contends that the changes would cost no more than a penny per gallon, on the average, once the standards are fully in place.

The Tier 3 gasoline standards will reduce sulfur levels by more than 60 %, down from 30 to 10 mg/kg. Volatile organic compounds and nitrogen oxides will be reduced by 80 %, and toxic air pollutants such as benzene will be reduced by as much as 30 %, according to the EPA. The Tier 3 gasoline sulfur standards are similar to levels already achieved in California, Europe, Japan, South Korea, and several other countries.

Sulfur content of fuel oil can be limited for special uses in connection with heat treatment, nonferrous metal, glass, and ceramic furnaces, or to meet federal, state, or local legislation or regulations. The effect of sulfur content on engine wear and deposits appears to vary considerably in importance and depends largely on operating conditions. Fuel sulfur can affect emission control

TABLE 5.7 Sulfur Test Methods Quoted in Biofuels Product Specifications

Product Specification	Product Grade	Sulfur Test Method	Alternate Sulfur Test Method	Specification Limits, mass %, max
ASTM D396 (Fuel Oil)	No.1 and No. 2 S 5000	ASTM D129	See Table 2.4	0.5
	No. 1 and No. 2 S 500	ASTM D2622		0.05
ASTM D975 (Diesel Fuel Oil)	No. 1 and No. 2 D-S5000	ASTM D129		0.50
	No. 4-D	ASTM D2622		2.00
	No. 1 and No. 2 D-S 500	ASTM D5453		0.05
	No. 1 and No. 2 D-S 15			15 ppm
ASTM D4806 (Fuel Ethanol)		ASTM D2622	ASTM D3120; ASTM D5453; ASTM D7039	30 ppm
ASTM D4814 (Gasoline)	Unleaded	ASTM D1266	ASTM D2622; ASTM D3120; ASTM D5453; ASTM D6920; ASTM D7039	0.0080
	Leaded	ASTM D1266	Same as above	0.15
ASTM D5797 (Fuel Methanol)	Class 1	ASTM D1266	ASTM D2622; ASTM D3120; ASTM D5453	160 ppm
	Class 2	ASTM D1266	Same as above	200 ppm
	Class 3	ASTM D1266	Same as above	300 ppm
ASTM D5798 (Ethanol Fuel)		ASTM D5453	ASTM D7039	80 ppm
ASTM D5983 (MTBE)		ASTM D4045		300 ppm
ASTM D6751 (B100)	No. 1-B and 2-B S15	ASTM D5453	ASTM D7039	
	No. 1-B and No. 2-B S500	ASTM D5453	ASTM D7039	15 ppm
				500 ppm
ASTM D7467 (Biodiesel)	S15	ASTM D5453		
	S500	ASTM D2622		15 ppm
	S5000	ASTM D129		0.05
				0.50
ASTM D7544 (Pyrolysis Biofuel)	Grades G and D	ASTM D4294		0.05
ASTM D7666 (Triglyceride)	Grades TBF 5 and 6	ASTM D4294	ASTM D1266, ASTM D1552, ASTM D2622, ASTM D5185, ASTM D5453	Report

Note: MTBE = methyl tertiary butyl ether; TBF = triglyceride burner fuel.

systems' performance, and various limits on sulfur have been imposed for environmental reasons. B100 is essentially sulfur-free. To ensure maximum availability of fuels, the permissible sulfur content should be specified as high as is practicable, consistent with maintenance considerations. Nadkarni has extensively discussed the chemistry and analysis of fossil fuel products for sulfur by the multiple techniques available [28].

SCOPE

All biofuels have sulfur as one of their specification limits. The maximum limits vary from low mg/kg levels to several thousand mg/kg levels. See Table 5.7 for different sulfur test methods for different biofuels.

ANALYSIS

Many test methods, including those for sulfur determination, have been simply picked from a slate for petroleum analysis and included in biofuel applications. Most petroleum test methods do not include biofuels in their scope. Most of the test methods for sulfur determination fall into this second category. It is not clear that biofuels behave the same way toward petroleum test methods regarding their precision and accuracy. See Nadkarni for an evaluation and status of the present challenges facing analysis of biofuels [28,29].

The three test methods for sulfur included in the biofuel specifications are ASTM D129, ASTM D2622, and ASTM D5453. (ASTM D2622 is equivalent to EN 15485, and ASTM D5453 is considered to be equivalent to EN 15486.) Of these, the first test method is antiquated and rarely used in modern industry laboratories. Moreover, it is limited to samples of low volatility and to those containing at least 0.1 mass percent sulfur. Thus, it is the wrong choice for biofuels with specification limits of <0.05 mass percent sulfur. ASTM D2622 or ASTM D4294 are wavelength- and energy-dispersive X-ray fluorescence methods, respectively. They are widely used in the oil industry for sulfur determination in diverse petroleum product matrices. However, one major drawback of these methods for use in biofuels analysis is their oxygen content, which can seriously affect the sulfur results. ASTM D7039 is an X-ray fluorescence method based on the monochromatic wavelength-dispersive technique. It has not been extensively studied for application to biofuels, but preliminary data show that it will no doubt be useful for such analysis. Based on an extremely limited study conducted by the Alberta Research Council, the following precision estimates were obtained for biofuels. However, these data should be treated with caution because they are based on no more than one or two samples of each type [30].

Samples	No. of Samples	Range, mg/kg	Repeatability	Reproducibility
Biodiesel blends	2	4–17	0.53 $X^{0.5}$	0.77 $X^{0.5}$
Ethanol	1	1.7–3.1	0.47	1.4

Similarly, the agreement between ASTM D5453 and ASTM D7039 results for sulfur in ASTM's ethanol fuel Interlaboratory Crosscheck Program (ILCP) are also excellent. All results are in mg/kg.

Samples	ASTM D5453	ASTM D7039
ASTM ILCP EtOH 1008	1.31 ± 0.36 (41)	1.08 ± 0.23 (10)
ASTM ILCP EtOH 1012	3.61 ± 0.91 (43)	3.31 ± 0.34 (9)

In other major biodiesel-producing regions, sulfur methods equivalent to ASTM D5453 and ASTM D4294 are included in their specifications.

• Brazil	ASTM D5453 (ANP 42)
• EU	ISO 20884 and ISO 20846 (EN 14214)

Based on the sulfur level present in a product, different test methods should be used based on the scope and interferences in the analysis. A number of alternate tests can be used for this determination. (See Table 2.3 for alternate ASTM sulfur test methods available for the analyses of petroleum products and lubricants, and by extension to biofuels.) ASTM D5453 should be used with biodiesel. Use of other test methods may provide falsely high results when analyzing B100 with extremely low sulfur levels (less than 5 mg/kg); XRF test methods for sulfur give falsely high results due to the presence of the oxygen in the biodiesel. Sulfur results using ASTM D2622 were more accurate with B20 samples than with B100 samples due to the lower oxygen content of B20.

ASTM D129

This was the first test method for sulfur determination in petroleum products and was issued by ASTM Committee D02 back in 1922. It is mainly used for high levels of sulfur in the samples. It is applicable to petroleum products, including lubricating oils containing additives, additive concentrates, and lubricating greases that cannot be burned completely in a wick lamp. The test method is applicable to any petroleum product containing at least 0.1 mass percent sulfur and sufficiently low in volatility that it can be weighed accurately in an open sample boat. ASTM D129 is the wrong choice for analyzing biofuels with specification limits of <0.05 mass percent sulfur, and it has not been validated for any level of sulfur in biofuels or oxygenated fuels.

SCOPE

This test method is not applicable to samples containing elements that leave residues (other than barium sulfate, which is insoluble in dilute hydrochloric acid) and that would interfere in the precipitation step. These interfering elements include Fe, Al, Ca, Si, and Pb, which are sometimes present in greases, lube oil additives, or additive oils. Other acid-insoluble materials that interfere are silica, molybdenum disulfide, asbestos, mica, and so on. This test method is not applicable to used oils containing wear metals and lead or silicates from contamination. The sample types that are excluded here can be analyzed using ASTM D1552.

ANALYSIS

In this test method, a sample is oxidized by combustion in a high-pressure decomposition device containing oxygen under pressure. To aid the combustion, a small portion of white oil is added to the combustion boat. The sulfur, as sulfate in the high-pressure decomposition device washings, is determined gravimetrically as barium sulfate.

PRECISION

The following precision was obtained based on an interlaboratory study (RR-D02-1278).

Sulfur, mass %	Repeatability	Reproducibility
0.1 to 0.5	0.04	0.05
0.5 to 1.0	0.06	0.09
1.0 to 1.5	0.08	0.15
1.5 to 2.0	0.12	0.25
2.0 to 2.5	0.18	0.27

ASTM D1266

This test method covers the determination of total sulfur in liquid petroleum products in concentrations from 0.01 to 0.4 mass percent. A modification of the basic procedure can determine sulfur at concentrations as low as 5 mg/kg. The comparable lamp method for the determination of sulfur in liquefied petroleum gas is ASTM D2784. For the determination of sulfur in heavier petroleum products that cannot be burned in a lamp, the pressure decomposition method (ASTM D129), the quartz tube method (IP 63), or the high-temperature method (ASTM D1552) can be used.

SCOPE

The direct burning procedure is applicable to the analysis of materials such as gasoline, kerosine, naphtha, and other liquids that can be burned completely in a wick lamp. The blending procedure is applicable to the analysis of gas oils and distillate fuel oils, naphthenic acids, alkyl phenols, high sulfur content petroleum products, and many other materials that cannot be burned satisfactorily by the direct burning procedure.

Phosphorus compounds normally present in commercial gasoline do not interfere. A correction is given for the small amount of acid resulting from the combustion of the lead anti-knock fluids in gasoline. Appreciable concentrations of acid-forming or base-forming elements from other sources interfere when the titration procedure is used because no correction is provided in these cases.

ANALYSIS

In this test method, a sample is burned in a closed system using a suitable lamp and an artificial atmosphere composed of 70 % carbon dioxide and 30 % oxygen to prevent formation of nitrogen oxides. The resultant oxides of sulfur are absorbed and oxidized to sulfuric acid by means of a hydrogen peroxide solution that is then flushed with air to remove dissolved carbon dioxide. Sulfur as sulfate in the absorbent is determined acidimetrically by titration with a standard sodium hydroxide solution or gravimetrically by precipitation as barium sulfate ($BaSO_4$). Alternatively, the sample may be burned in air, the sulfur as sulfate in the absorbent being determined by precipitation as $BaSO_4$ for weighing. In the absence of acid-forming or base-forming elements, other than sulfur, results by the volumetric and gravimetric finishes are equivalent within the precision limits of the method. For sulfur contents below 0.01 mass percent, it is necessary to determine the sulfate content in the absorber solution turbidimetrically as $BaSO_4$.

PRECISION

The precision of this test method is given as repeatability 0.005 and reproducibility 0.010 + 0.025X, where X is the sulfur content in mass percent. When using the turbidimetric method for trace amounts of sulfur, the following precision is expected.

Sulfur Content, mg/kg	Repeatability	Reproducibility
5 to 80	0.116 × X	–
5 to 125	–	0.145 × X
Over 80 to 280	(0.01 × X) + 8.5	–
Over 125 to 280	–	(0.508 × X) – 45.4

Note: Where X is the sulfur concentration in mg/kg.

ASTM D1552, Sulfur in Petroleum Products by High Temperature Combustion and Infrared or Thermal Conductivity Detection

SCOPE

Originally, this test method covered three procedures for the determination of total sulfur in petroleum products, including lubricating oils containing additives and in additive concentrates. This test method is applicable to liquids boiling above 177°C and containing not less than 0.06 mass percent sulfur. Petroleum coke containing up to 8 mass percent sulfur can be analyzed by this test method.

ANALYSIS

Two out of these three procedures used iodate detection, one using an induction furnace, the other a resistance furnace. However, both iodate procedures were discontinued in 2015 because of lack of interest on the part of the industry. The third procedure uses IR detection following pyrolysis in a resistance furnace.

The sample is weighed and placed into a furnace at a temperature and oxygen atmosphere sufficient to combust the entire sample and oxidize sulfur to sulfur dioxide (SO_2), typically between 1150 and 1450°C. Most sulfur present is combusted to SO_2, which is then measured with an infrared or a thermal conductivity detector after moisture and dust are removed by a trap. Apparatuses utilizing a thermal conductivity detector may require the sample gas product to pass an oxygen scrubber and purge/traps to allow passing of contaminants prior to measuring SO_2. The IR system can tolerate somewhat higher concentrations. Nitrogen, when present in excess of 0.1 mass percent, may interfere with the iodate systems; the extent of such interference may be dependent on the type of nitrogen compound as well as on the combustion conditions. Nitrogen does not interfere with the IR system. The alkali

TABLE 5.8 Precision of ASTM D1552 for Petroleum Products

Sulfur Range, mass %	Repeatability		Reproducibility	
	Iodate	IR	Iodate	IR
0.0 to 0.5	0.05	0.04	0.08	0.13
0.5 to 1.0	0.07	0.07	0.11	0.21
1.0 to 2.0	0.10	0.09	0.17	0.27
2.0 to 3.0	0.16	0.12	0.26	0.38
3.0 to 4.0	0.22	0.13	0.40	0.44
4.0 to 5.0	0.24	0.16	0.54	0.49
Petroleum coke	0.05 X		0.22 X	

Note: Where X is the average of two test results. The bias of this test method has not been determined.

and alkaline earth metals, as well as Zn, P, and Pb, do not interfere with either system.

PRECISION

Based on an interlaboratory study (RR-D02-1231), the precision shown in Table 5.8 was obtained for the analysis of petroleum products and petroleum coke by iodate and IR methods. The precision of this test method for biofuels analysis is not known.

The precision of the revised ASTM D1552-15 test method was found to be as follows based on a new interlaboratory study (RR-D02-XXXX).

Repeatability	$0.6792e^{2}02\ X^{0.5493}$
Reproducibility	$0.1830\ X^{0.5493}$

Note: Where X is the average of the two sulfur results in mass percent.

This translates into following examples of specific levels of sulfur.

Sulfur, mass %	Repeatability	Reproducibility
0.1	0.02	0.05
1.0	0.07	0.18
5.0	0.16	0.44
10.0	0.24	0.65
20.0	0.35	0.95
30.0	0.43	1.19

ASTM D2622, Sulfur in Petroleum Products Using Wavelength Dispersive X-Ray Fluorescence Spectroscopy

This is probably the most important test method for the determination of sulfur in liquid fossil fuels, and it is widely used throughout the industry. The method has been very thoroughly studied in industry laboratories. ASTM D2622 covers the determination of total sulfur in petroleum and petroleum products that are single-phase and either liquid at ambient temperatures, liquefiable with moderate heat, or soluble in hydrocarbon solvents. These materials can include diesel fuel, jet fuel, kerosine, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasohol, and biodiesel. This test method is quoted in biodiesel specifications ASTM D975 and ASTM D4806 (see Table 5.6).

B100 is essentially sulfur-free, although some animal fat-based biodiesel has been found with up to 100 mg/kg sulfur (a result of hides and hair from the animal fat-rendering process), and some yellow grease-based biodiesel has been found with similar levels (a result of frying foods high in sulfur, such as onion rings). ASTM D5453 (discussed later in this chapter) is the best choice for sulfur determination of biodiesel. Use of other test methods may give falsely high results when analyzing B100 with extremely low sulfur (<5 mg/kg) levels. The results from ASTM D2622 were more accurate with B20 than with B100 due to the lower oxygen content of B20.

SCOPE

The test method is applicable to samples in the range of 3 mg/kg to 4.6 mass percent sulfur. Samples containing even higher levels of sulfur can be diluted to bring the sulfur concentration of the diluted material within the scope of the test method. Samples that are diluted can have higher errors than indicated in the precision given for nondiluted samples. Volatile samples such as high vapor pressure gasolines or light hydrocarbons may not meet the stated precision because of the selective loss of the light materials during the analysis. A fundamental assumption of this test method is that the standard and sample matrices are well matched or that the matrix differences are accounted for. Matrix mismatch can be caused by the carbon-to-hydrogen ratio differences between samples and standards or by the presence of other interfering heteroatoms or species (Table 5.9).

One way of minimizing or eliminating such interferences is to dilute the sample with blank sulfur solvent to reduce the

TABLE 5.9 Concentration of Interfering Species in ASTM D2622 and ASTM D4294 Determination of Sulfur

Interfering Species	Mass % Tolerated in ASTM D2622	Mass % Tolerated in ASTM D4294
Phosphorus	0.3	0.3
Zinc	0.6	0.6
Barium	0.8	0.8
Lead	0.9	0.9
Calcium	1	1
Chlorine	3	3
Oxygen	2.8	–
FAME	25	5
Ethanol	8.6	8.6
Methanol	6	6

Note: FAME = fatty acid methyl ester.

interferent concentration below the values given here to mitigate the effect of interference.

ANALYSIS

In this test method, the sample is placed in the X-ray beam, and the peak intensity of the sulfur K alpha line at 0.5373 nm is measured. The background intensity, measured at a recommended wavelength of 0.5190 nm (0.5437 for a rhodium target tube) is subtracted from the peak intensity. The resultant net counting rate is then compared to a previously prepared calibration curve or equation to obtain the concentration of sulfur in mg/kg or mass percent. Usually a high-purity di-n-butyl sulfide with certified sulfur content is used as a calibration standard in this procedure. It is essential to know the sulfur content of the di-n-butyl sulfide—not just the purity—because impurities may also be sulfur-containing compounds.

There are significant interferences in this test method. When the elemental composition (excluding sulfur) of the sample differs from the standards, errors in the sulfur determination can result. For example, differences in the carbon-to-hydrogen ratio of the sample and in the calibration standard (usually a pure organic sulfur compound) introduce errors. Some other interferences and action levels are listed in Table 5.9. In such cases, the sample should be diluted with a blank sulfur solvent to reduce the interferent concentration below the value given in the table to mitigate the effect of this interference.

The main problem in using the XRF test methods for sulfur determination in biofuels is the presence of oxygenates. It is estimated that, in the ASTM D2622 WD-XRF test method, up to 2.8 mass percent of oxygen, 25 mass percent of FAME, 8.6 mass percent of ethanol, and 6 mass percent of methanol can be tolerated. Fuels containing large amounts of ethanol or methanol have a high oxygen content, which leads to significant absorption of sulfur K alpha radiation and results in low sulfur results. Such fuels can, however, be analyzed using this test method provided that either correction factors are applied to the results (when calibrating with white oil) or that the calibration standards are prepared to match the matrix of the samples.

In general, petroleum products with compositions that vary from white oil used in calibrant solutions can be analyzed with standards from base materials that are of the same or similar composition. Thus, a gasoline sample may be simulated by mixing isooctane and toluene in a ratio that approximates the expected aromatic content of the samples to be analyzed. Standards made from this simulated gasoline can produce results that are more accurate than results obtained using white oil standards.

In one interlaboratory study, among other petroleum samples, one sample each of B5, B100 biodiesels, E85 gasohol, gasolines with 13 % ethyl tert-butyl ether (ETBE), and gasoline with 5 % ethanol were analyzed with satisfactory results using ASTM D2622. These samples contained sulfur levels between 18 and 232 mg/kg [31]. In an earlier ILS conducted in 2002, among a large number of gasoline and diesel samples, two biodiesels and one soy biodiesel were analyzed by various test methods for sulfur [32]. Both these studies clearly show that, with proper interference calibration, ASTM D2622 is capable of determining trace amounts of sulfur in biofuels.

In a limited study conducted by the Alberta Research Council, a sample of fuel ethanol was analyzed by 31 laboratories to obtain a value of 1.6879 ± 0.4837 mg/kg to demonstrate the ability of this test method to analyze ethanol samples with extremely low sulfur values [30].

In the 2007 ASTM interlaboratory study for establishing the precisions of current versions of ASTM D2622 [31] and ASTM D4294 [30], 27 samples were analyzed among 15 and 25 laboratories, respectively. Of these sample, four were biodiesels and ethanol fuels. Each sample was analyzed in duplicate by each laboratory [33]. Most laboratories produced consistent results (Table 5.10).

Based on the aforementioned study, the following precision estimates have been calculated for all samples and for biofuels and are shown in Table 5.11.

PRECISION

A major interlaboratory study conducted for obtaining the precision and bias of this test method used 27 samples, including gasolines, distillates, biodiesel, residual oils, and crude oils [33]. The sulfur concentration range was 0.1 mg/kg to 4.6 mass percent. A pooled limit of quantitation of approximately 3 mg/kg sulfur was obtained for all sample types. Overall repeatability and reproducibility found for gasoline and diesel were as follows:

TABLE 5.10 Replicate Analysis of Sulfur in Biofuels by X-ray Fluorescence Methods

Product	ASTM D2622	ASTM D4294
B100 biodiesel	12.99 ± 1.53 (28)	18.41 ± 5.81 (23)
B20 biodiesel	65.46 ± 2.75 (28)	75.90 ± 8.45 (23)
E85 gasohol	6482.0 ± 152.4 (27)	6634.8 ± 257.9 (24)
E5 gasohol	22.217 ± 521.8 (26)	22.415 ± 348 (21)

Note: All results are in mg/kg. The results are expressed as mean ± standard deviation (number of results).

TABLE 5.11 Precision of X-ray Fluorescence Test Methods for Biofuels

Sample Types	ASTM D2622 Repeatability	ASTM D2622 Reproducibility	ASTM D4294 Repeatability	ASTM D4294 Reproducibility
All samples	$0.1462\ X^{0.8015}$	$0.4273\ X^{0.8015}$	$0.4347\ X^{0.6446}$	$1.9182\ X^{0.6446}$
Gasoline	$0.5006\ X^{0.4377}$	$1.4533\ X^{0.4377}$	$1.4477\ X^{0.3661}$	$7.1295\ X^{0.3661}$
Diesel	$0.1037\ X^{0.8000}$	$0.3586\ X^{0.8000}$	$1.6658\ X^{0.3300}$	$8.9798\ X^{0.3300}$

Note: Where X is the mean of duplicate determinations.

$\text{Repeatability} = 0.1462\ (X^{0.8015})\ \text{mg/kg}$
$\text{Repeatability} = 0.1462\ (Y \times 10\,000)^{0.8015})/10{,}000\ \text{mass \%}$
$\text{Reproducibility} = 0.4273\ X^{0.8015}\ \text{mg/kg}$
$\text{Reproducibility} = (0.4273\ (Y \times 10\,000)^{0.8015})/10{,}000\ \text{mass \%}$

Where X and Y are the sulfur concentrations in mg/kg and mass percent total sulfur, respectively.

BIAS

Based on the analysis of ten NIST SRMs, there was no significant bias among the certified values and the results obtained in the ILS for any SRM or sample type within measured reproducibilities, especially after the carbon-to-hydrogen ratio corrections were applied. See Table 5.12 for a comparison of the results obtained on NIST SRMs in this ILS.

The precision given here for all samples (inclusive) is detailed by product and instrument types in Table 5.13. The power of the X-ray fluorescence source can affect the precision of results measured by this method. In this context, instruments having >1,000 W sources are defined as high power, while those having <1,000 W sources are defined as low power.

There have been reports from some testing facilities that iron sulfide corrosion particles interfere with the analysis of ultra-low sulfur diesel (ULSD), particularly using XRF methods such as ASTM D2622, but not with ASTM D5453. Iron sulfide is nonvolatile and insoluble. With the combustion technique ASTM D5453, even if the particles did somehow enter into the syringe, they would not be converted to a volatile form so that the sulfur in iron sulfide would be analyzed. With the XRF technique, the insoluble particles would fall to the analytical viewing surface, making the sulfur concentration in the fuel appear higher than in reality. This issue has become more noticeable due to the significant decrease in sulfur content and because the ULSD tanks are being circulated more than conventional diesel tanks to improve sample homogeneity. The circulation could potentially stir up the fine particulates such as iron sulfide (rust) from tank bottoms.

ASTM D3120, Sulfur in Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

SIGNIFICANCE

This test method covers the determination of sulfur in the range from 3.0 to 1,000 mg/kg in light liquid hydrocarbons and fuels with oxygenates boiling in the range from 26 to 274°C. Other materials falling within the stated distillation range but having sulfur concentrations above 1,000 mg/kg may be tested using appropriate dilutions to bring them within the specified limit. The dilution with isooctane may result in a loss of precision in the analysis. Additionally, sample types that may be outside the specified distillation range, such as diesels and biodiesels, may be analyzed by this test method.

Preliminary data have shown that this test method is also applicable to the determination of sulfur in denatured fuel ethanol (ASTM D4806), automotive spark-ignition engine fuel (ASTM

TABLE 5.12 Comparison of NIST SRM Data and ASTM ILS Measured Results

NIST SRM #	Matrix	Sulfur NIST Value, mg/kg	C/H Mass Ratio	Average Measured Sulfur Found in ILS, mg/kg	Average C/H Corrected Sulfur Found in ILS, mg/kg	Corrected Bias, mg/kg Sulfur	Relative Corrected Bias, %
2298	Gasoline	4.7	5.47	6.0	6.0	1.3	27.66
2723 a	Diesel	11.0	5.99	10.1	10.2	−0.8	−7.27
2299	Gasoline	13.6	6.17	14.2	14.3	0.7	5.15
2296	Gasoline	40.0	6.42	40.2	40.6	0.6	1.50
2770	Diesel	41.6	5.75	42.1	42.4	0.8	1.92
2724 b	Diesel	426.5	7.18	420.9	426.4	−0.1	−0.02
2722	Crude Oil	2,103	7.22	2,054	2,105	2	0.10
1619 b	Residual fuel oil	6,960	8.80	6,448	6,804	−156	−2.24
2721	Crude oil	15,830	7.17	15,994	16,217	387	2.44
1620 c	Residual fuel oil	45,610	7.93	44,424	46,535	935	2.05

TABLE 5.13 Precision Values for Sulfur by ASTM D2622 Test Method

NIST SRM #	Repeatability	Reproducibility
Gasolines: 2298, 2296, 2299; gasoline with 5 % ethanol; unleaded regular gasoline	$0.5006\ X^{0.4377}$ mg/kg $(0.5006\ (Y \times 10{,}000)^{0.4377})/10{,}000$ mass %	$1.4533\ X^{0.4377}$ mg/kg $(1.4533\ (Y \times 10{,}000)^{0.4377})/10{,}000$ mass %
Diesels: 2723 a, 2770, 2724 b, diesel, B-5 diesel	$0.1037\ X^{0.8000}$ mg/kg $(0.1037\ (Y \times 10{,}000)^{0.8000})/10{,}000$ mass %	$0.3856\ X^{0.8000}$ mg/kg $(0.3856\ (Y \times 10{,}000)^{0.8000})/10{,}000$ mass %
High-power instruments	$0.08681\ X^{0.8383}$ mg/kg $(0.08681 \times (Y \times 10{,}000)^{0.8383})/ 10{,}000$ mass %	$0.3086\ X^{0.8383}$ mg/kg $(0.3086 \times (Y \times 10{,}000)^{0.8383})/10{,}000$ mass %

TABLE 5.14 Ruggedness Study for Analysis of Ethanol Fuels Using ASTM D3120

Sample	N	Sulfur Found, mg/kg	Standard Deviation	% RSD	Repeatability (SD × 2.77)
Gasoline EM87	18	17.75	0.358	2.02	0.991
Gasoline EM87 + 10 % ethanol	18	15.40	0.176	1.014	0.487
Pure ethanol	20	0.192	0.156	81.3	0.433
Ethanol + Spike 1.42	10	1.37	0.06	4.39	0.167
Ethanol + Spike 2.25	15	2.18	0.09	4.13	0.248

D4814), Ed75–Ed85 (ASTM D5798), or to gasoline-oxygenate fuel blends with greater than 10 % ethanol. However, the precision of analysis of such materials has not yet been determined.

A ruggedness study conducted in one laboratory using this test method for biofuels produced the following results. Samples of gasoline, gasoline with 10 % ethanol, pure ethanol, and ethanol spiked with sulfur at two different levels were analyzed using a Mitsubishi TOX-100 instrument. The instrument was calibrated in the range of 0.000 to 1.515 mg/L of sulfur prepared from a stock solution of 101 mg/L of sulfur. The calibration was done at four levels of sulfur concentration: 0.252, 0.505, 1.010, and 1.515 ng. Each measurement was repeated three times. A correlation (R2) of 0.9994 with a y of 0.8117x + 0.0067 was found. Recoveries of two spiked samples were 96.5 and 97.0 %, respectively. The results obtained in this study are shown in Table 5.14 [34].

ANALYSIS

In this test method, a liquid sample is introduced into a pyrolysis tube maintained at a temperature between 900 and 1,200°C that has a flowing stream of gas containing 50 % to 80 % oxygen and 20 % to 50 % inert gas (such as argon, helium, etc.). Oxidative pyrolysis converts the sulfur to sulfur oxide, which then flows into a titration cell where it reacts with triiodide ion present in the electrolyte. The triiodide ion consumed is coulometrically replaced, and the total current required to replace it is a measure of the sulfur present in the sample. The reaction occurring in the titration cell as sulfur dioxide enters is:

$$I_3 + SO_2^- + H_2O \rightarrow SO_3 + 3I^- + 2\,H^+$$

The triiodide ion consumed in the aforementioned reaction is generated coulometrically per this formula:

$$3\,I^- \rightarrow I_3 + 2e^-$$

These microequivalents of triiodide ion are equal to the number of microequivalents of titratable SO_2 ion entering the titration cell.

This test method is applicable in the presence of total halide concentrations of up to ten times the sulfur level and total nitrogen concentrations of up to one thousand times the sulfur level. Stringent techniques should be applied to eliminate all possible sources of sulfur contamination to attain the quantitative detectability capable with this test method. ASTM D1320 is not applicable in the presence of total heavy metal (e. g., Ni, V, Pb, etc.) concentrations in excess of 500 mg/kg.

The configuration of the pyrolysis tube and furnace may be constructed as is desirable as long as the operating parameters are met. Dibenzothiophene, n-butyl sulfide, or thianaphthene (benzothiophene) diluted in toluene, xylene, or isooctane can be used as the sulfur calibration standards. The concentration ranges used for calibration solutions are 10, 50, and 500 µg/mL. A correction for chemical impurity can be applied to the solutions if deemed necessary. Not all of the sulfur in the sample exits the oxidation zone of the furnace as titratable SO_2. In the strongly oxidative conditions of the pyrolysis tube, some of the sulfur is also converted to sulfur trioxide (SO_3), which does not react with the titrant. Accordingly, sulfur standards appropriate to the sample's boiling range and sulfur type are recommended to guarantee adequate calibration. Recoveries less than 75 % are to be considered suspect. In such cases, it is recommended the operator check that the coulometric system, measuring parameters, and operating techniques are in proper order. If the apparatus is being operated properly, recoveries between 75 % to 90 % are to be expected.

PRECISION

Based on separate interlaboratory studies, the following precisions and bias were found for this test method (Table 5.15). These studies are documented in ASTM research reports RR-D02-1036, RR-D02-1546, and RR-D02-1547.

TABLE 5.15 Precision of Coulometric Method ASTM D3120 for Sulfur Determination

Study	PLOQ	Repeatability	Reproducibility
RR-D02-1036		$0.2802\ X^{0.7901}$	$0.5793\ X^{0.7901}$
RR-D02-1546 and RR-D02-1547	Gasoline: 3 ppm	Gasoline: $0.03194\ (X + 7.4502)^{1.3226}$	Gasoline: $0.1470\ (X + 7.4502)^{1.3226}$
	Diesel: 5 ppm	Diesel: 0.08520 (X + 0.65758)	Diesel: 0.5152 (X + 0.65758)

Note: Where X is the average of duplicate results in µg/g. PLOQ = pooled limit of quantitation.

Three NIST SRMs were analyzed to determine the bias. Gasoline SRMs 2298 (1.6 µg/g sulfur) and 2299 (13.6 µg/g sulfur), and diesel SRM 2723a (10 µg/g sulfur) were used. There was no significant bias for SRMs 2299 and 2723a. However, there was a bias of −1.25 for SRM 2298.

ASTM D4045, Sulfur in Fuels by Hydrogenolysis and Rateometric Colorimetry

This test method is based on the work developed by Drushel [35] and is similar to ASTM D4468 for the determination of hydrogen sulfide in fuel oils. ASTM D4045 is quoted in ASTM D5983 for MTBE at 300 mg/kg maximum content.

SCOPE

This test method covers the range of sulfur from 0.02 to 10 mg/kg. It can be extended to higher concentration by dilution of the sample. It is applicable to liquids whose boiling points are between 30 and 371°C. Materials that can be analyzed include naphtha, kerosine, alcohol, steam condensate, various distillates, jet fuel, benzene, and toluene.

ANALYSIS

In this test method, a liquid sample is injected at a constant rate into a flowing hydrogen stream in a hydrogenolysis apparatus. The sample and hydrogen are pyrolyzed at a temperature of 1,300°C or above to convert sulfur compounds to hydrogen sulfide. Readout is by the rateometric detection of the colorimetric reaction of hydrogen sulfide (H_2S) with lead acetate. Condensable components are converted to gaseous products, such as methane, during hydrogenolysis. Di-n-butyl sulfide is used as the calibrant.

To prevent the adsorption impediment of H_2S in the trace sulfur analyzer using this method, a specially prepared pure ceramic tube has been developed to be the only usable reactor for the hydrogenolysis procedure. However, a conventional ceramic tube becomes unstable by inhibiting the H_2S adsorption on the basic impurities by a substitute adsorption of CO_2 that can be introduced continually with hydrogen in the ceramic reactor. Applying the oxyhydro procedure to reduce the carbon deposit in the analysis of kerosine, a large overestimation error occurred in the determination of a single ppb of sulfur using even the specially prepared pure ceramic tube. The overestimation error was completely eliminated.

By continuous introduction of CO_2 with hydrogen, even using conventional ceramic reactors and by following procedures to suppress noise from the system, the original limit of detection of 25 ppb of sulfur for the analyzer was improved to 0.3 ppb. However, the practical limit of detection or accuracy must be determined for each instrument [36,37].

PRECISION

Per an interlaboratory study that was conducted (RR-D02-1405), the following precision for this test method has been determined. Bias of this test method is not known.

Repeatability	$0.16\ X^{0.5}$
Reproducibility	$0.26\ X^{0.5}$

Note: Where X is the average value of two results in mg/kg.

ASTM D4294, Sulfur in Gasoline and Diesel Using Energy Dispersive X-Ray Fluorescence Spectroscopy

SCOPE

This is a widely used XRF test method for sulfur at both low and high concentration levels. It is a widely used, less expensive alternative to ASTM D2622 instrumentation—although at very low levels of sulfur, its precision is not very good. It is applicable to the analysis of petroleum and petroleum products that are single-phase and either liquid at ambient conditions, liquefiable with moderate heat, or soluble in hydrocarbon solvents. These materials can include diesel fuel, jet fuel, kerosine, other distillate oils, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasohol, biodiesel, and similar petroleum products. The scope of the method is 17 mg/kg to 4.6 mass percent. An estimated pooled limit of quantitation is 16 mg/kg. However, because the instruments covered by this test method can vary in sensitivity, the applicability of the test method at sulfur concentrations below approximately 20 mg/kg must be determined on an individual basis. Samples containing more than 4.6 mass percent sulfur can be diluted to bring the sulfur concentration of the diluted material within the scope of this test method. Samples that are diluted can have higher errors than undiluted samples. Volatile samples, such as high vapor pressure gasolines or light hydrocarbons, may not meet the stated precision because of selective loss of light materials during the analysis. A fundamental assumption in this test method is that the standard and sample matrices are well matched or that the matrix differences are accounted for. Matrix mismatch can be caused by carbon-to-hydrogen ratio differences between samples and standards or by the presence of other heteroatoms.

ANALYSIS

In this test method, a sample is placed in the beam emitted from an X-ray tube, the resultant characteristic X-radiation is measured, and the accumulated count is compared with counts from previously prepared calibration samples to obtain the sulfur concentration in mass percent or mg/kg (or in both). A minimum of three groups of calibration samples are required to span the concentration range.

INTERFERENCES

Spectral and matrix interferences generally are encountered in X-ray fluorescence analysis. Spectral interferences are caused by the closeness of the X-ray characteristic lines of the elements present in a sample and the limited detector ability to completely resolve them. As a result, the lines produce spectral peaks that overlap with each other. Spectral interferences may arise from samples containing lead alkyls, Si, P, Ca, K, halides, and catalyst particles present at concentrations greater than one-tenth of the measured concentration of sulfur—or more than a few hundred mg/kg. The manufacturer's operating guide should be followed to compensate for the interferences.

Matrix effects are caused by concentration variations of the elements in a sample. These variations directly influence X-ray absorption and change the measured intensity of each element. For example, performance-enhancing additives, such as oxygenates in gasoline, may affect the apparent sulfur reading. Other matrix-related interferences may arise from heavy metal additives, lead alkyls, and elements such as Si, P, Ca, K, and the halides, especially if present in concentrations greater than one-tenth of the measured concentration of sulfur, or more than a few hundred mg/kg. These types of interferences are always present in XRF analysis and are completely unrelated to spectral interferences.

The interferences mentioned here may be compensated for in contemporary instruments with the use of built-in software for spectral deconvolution or overlap correction and inter-element correction by multiple regression or by other mathematical methods. In general, petroleum materials with compositions that vary from oils as specified in the method may be analyzed with standards made from base materials that are of the same, or similar, composition. Thus, gasoline may be simulated by mixing isooctane with toluene in a ratio that approximates the true aromatic content of the samples to be analyzed. Standards made up from this simulated gasoline will produce results that are more accurate than results obtained using white oil.

For white oil-based standards, in the ED-XRF test method ASTM D4294, the following corrections are required:

Sulfur (in M85), mass % = sulfur, mass %/0.59
Sulfur (in M100), mass % = sulfur, mass %/0.55

In the case of petroleum materials that contain suspended water, it is recommended that the water be removed before testing or that the sample be thoroughly homogenized and immediately tested. The interference is greatest if the water creates a layer over the transparent film because it will attenuate the X-ray intensity for sulfur. One way to accomplish the removal of water is to centrifuge the sample first under ambient sealed conditions, taking care that the sample integrity is not compromised.

PRECISION

A large ILS (RR-D02-1635) conducted to obtain the precision of this method included 27 samples such as distillates, gasoline with or without oxygenates, kerosine, diesel, biodiesel E-85, residual oils, and crude oils. The sulfur concentrations ranged from 1 mg/kg to 4.6 mass percent [33]. The following precisions were found for all materials:

Repeatability: $0.4347\ X^{0.6446}$ mg/kg
Repeatability: $(0.4347\ (Y \times 10\ 000)^{0.6446})/10{,}000$ mass %
Reproducibility: $1.9182\ X^{0.6446}$ mg/kg
Reproducibility: $(1.9182\ (Y \times 10\ 000)^{0.6446})/10{,}000$ mass %

BIAS

Based on the NIST SRMs analyzed in this ILS, there did not appear to be any significant bias between the values certified by NIST and those obtained in this crosscheck (Table 5.16). Additional separate precision statements for gasolines and diesels are given in Table 5.17.

Although per its scope statement, this test method is not meant for measuring sulfur less than 150 mg/kg in gasoline or diesel samples, it appears to be widely used in the oil industry in

TABLE 5.16 Analysis of NIST SRMs by ASTM D4294 Interlaboratory Study

NIST SRM #	Matrix	Sulfur, NIST mg/kg	Sulfur Found, mg/kg	Apparent Bias mg/kg Sulfur	Relative Bias, %
2296	RFG	40.0	46.3	+6.3	+15.6
2299	RFG	13.6	18.1	+4.5	+33.1
2770	Diesel	41.6	49.4	+7.8	+18.8
2724 b	Diesel	426.5	430.8	+4.3	+1.01
2721	Crude oil	15.832	16.118	+288	+1.82
2722	Crude oil	2,104	2,082	−21	−1.00
1619 b	Residual fuel oil	6,960	6,654	−306	−4.40
1620 c	Residual fuel oil	45,610	45,801	+191	+0.42

TABLE 5.17 Precision for Fuel Analysis Using ASTM D4294 for Sulfur

Samples	Repeatability	Reproducibility
Diesel: NIST 2770, 2724b, diesel, B-5 diesel	$1.6658\ X^{0.3300}$ mg/kg $(1.6658\ (Y \times 10{,}000)^{0.3300}/\ 10{,}000$ mass %	$8.9798\ X^{0.3300}$ mg/kg $(8.9798\ (Y \times 10{,}000)^{0.3300}/\ 10{,}000$ mass %
Gasoline: RFG, gasoline with 13 % ETBE, gasoline with 5 % ethanol, E-85	$1.4477\ X^{0.3661}$ mg/kg $(1.4477\ (Y \times 10{,}000)^{0.3661}/\ 10{,}000$ mass %	$7.1295\ X^{0.3661}$ mg/kg $(7.1295\ (Y \times 10{,}000)^{0.3661}/\ 10{,}000$ mass %

spite of its poor reproducibility—as seen in the ASTM Interlaboratory Crosscheck Programs (ILCPs). The reason for its widespread use is probably the low cost of purchase and maintenance of the instrumentation used in this test method. Table 5.18 compares the results obtained for several typical samples of petroleum products analyzed by three major methods used in oil industry laboratories: ASTM D2622 WD-XRF, ASTM D4294 ED-XRF, and ASTM D5453 UVFL. In spite of the large number of laboratories using ASTM D4294, poor reproducibility—sometimes approaching 100 % or more of the mean value—makes this analysis of very little use, especially in settling quality disputes between a buyer and a seller or in regulatory affairs. These false positive results can indicate that the product is exceeding the regulatory mandatory sulfur limits. Because of such poor data quality, the EPA did not include ASTM D4294 as one of the preferred methods for determining sulfur in fuels of the future. Again, at a below 30 mg/kg sulfur level, ASTM D5453 has the best precision among the three test methods compared here, and there is good equivalence between the results from ASTM D2622 and ASTM D5453.

When the sulfur levels are in the mass percent range, ASTM D4294 produces results just as good as those of other credible test methods. See the results for the ASTM ILCP in Table 5.19.

However, at very low levels of sulfur, ASTM D4294 produces high-biased, false positive results. Note the good agreement between the ASTM D2622 and ASTM D5453 results in Table 5.20 versus the erroneous very high results with extremely poor precision obtained with ASTM D4294 for these four matrices.

Calculated precisions at various sulfur levels are given in Table 5.21 for ASTM D2622 and ASTM D4294. The precision of

TABLE 5.18 Comparison of Test Methods for Sulfur Determination in Petroleum Products

ASTM Sample	ASTM D2622 WD-XRF	ASTM D4294 ED-XRF	ASTM D5453 UVFL
JF 9811	6.1 ± 15.8 (34)	34 ± 83 (81)	2.85 ± 1.8 (16)
MG 9812	184 ± 39 (27)	195 ± 111 (52)	165 ± 68 (16)
MG 9904	96 ± 24 (30)	105 ± 94 (49)	79 ± 39 (15)
MG 0208	13.4 ± 4.8 (36)	31 ± 21 (39)	11.7 ± 1.9 (22)
RFG 9811	218 ± 39 (69)	235 ± 75 (42)	214 ± 68 (20)
RFG 9902	67 ± 24 (73)	72 ± 66 (39)	65 ± 20 (25)
RFG 9904	30 ± 19 (71)	42 ± 69 (39)	29 ± 7 (24)
RFG 9905	99 ± 27 (74)	114 ± 100 (44)	89 ± 22 (25)
RFG 9906	17 ± 17 (66)	29 ± 58 (31)	14 ± 4 (22)
RFG 0307	16.8 ± 3.5 (58)	31 ± 18 (28)	15.0 ± 2.7 (40)
RFG 0404	416 ± 16 (58)	438 ± 20 (35)	411 ± 30 (48)
DL 9810	441 ± 52 (63)	456 ± 102 (143)	440 ± 91 (16)
DL 9902	466 ± 53 (64)	487 ± 75 (142)	471 ± 152 (20)
DL 0202	32.6 ± 6 (80)	44 ± 43 (137)	32.0 ± 4.7 (45)

Note: All results are in mg/kg sulfur. Values are expressed as mean value ± reproducibility (number of valid results). JF = jet fuel; MG = motor gasoline; RFG = reformulated gasoline; DL = diesel fuel.

TABLE 5.20 ASTM Crosschecks for Low Levels of Sulfur

Sample	ASTM D2622 Results	ASTM D4294 Results	ASTM D5453 Results
MG 0312	6.3 ± 3.1 (24)	27 ± 31 (39)	3.74 ± 0.85 (37)
DL 0402	9.3 ± 4.3 (67)	26 ± 23 (91)	8.22 ± 1.86 (61)
JF 0403	9.6 ± 2.8 (60)	26 ± 20 (94)	9.0 ± 1.5 (56)
RFG 0403	10.8 ± 4.2 (60)	28 ± 19 (24)	9.31 ± 1.42 (54)

Note: All results are expressed as ppm ± standard deviation (# of valid results).

TABLE 5.19 Determination of Sulfur at Higher Concentrations

ASTM Sample	ASTM D2622 WD-XRF	ASTM D4294 ED-XRF	ASTM D4951 ICPAES	ASTM D5453 UVFL
CO 0403	1.008 ± 0.019 (14)	1.042 ± 0.038 (76)		
CO 0711	0.1978 ± 0.0072 (18)	0.202 ± 0.010 (73)		
CO 0803	0.2003 ± 0.0092 (23)	0.2025 ± 0.0065(82)		
CO 0807	2.722 ± 0.126 (19)	2.832 ± 0.098 (89)		
CO 0811	0.9319 ± 0.0363 (25)	0.9487 ± 0.0324(89)		
CO 0903	0.4227 ± 0.0152 (27)	0.4237 ± 0.0132(92)		
CO 0907	0.0645 ± 0.0314 (21)	0.0864 ± 0.0159(70)		
GO 0404		1.856 ± 0.069(6)	1.831 ± 0.148(7)	
GO 0312		1.832 ± 0.060 (8)	1.758 ± 0.038(4)	
GG 0403	0.2089 ± 0.0055(12)	0.2057 ± 0.0098(22)		
RFG 0404	0.0416 ± 0.0016(58)	0.0438 ± 0.0022(35)		0.0411 ± 0.003(48)
MG 0404	0.0271 ± 0.011 (30)	0.0276 ± 0.004(51)		0.0258 ± 0.003(39)
RFG 0312	0.0238 ± 0.0013 (63)	0.0258 ± 0.0029(38)		0.0230 ± 0.002(44)

Note: All values are expressed in mass percent as average value ± standard deviation (number of valid results). UVFL = ultraviolet-fluorescence; CO = crude oil; GO = gear oil; GG = general gas oil; RFG = reformulated gasoline; MG = motor gasoline.

TABLE 5.21 Calculated Precision of X-ray Fluorescence Test Methods for Sulfur

	ASTM D2622		ASTM D4294	
Sulfur Concentration, mg/kg	**Repeatability**	**Reproducibility**	**Repeatability**	**Reproducibility**
3	0.4	1.0		
5	0.5	1.6		
10	0.9	2.7		
25	1.9	5.6	3.4	15
50	3.4	9.8	5.4	24
100	5.9	17.1	8.5	37
500	21	62	24	105
1,000	37	108	37	165
5,000	135	394	105	465
10,000	235	687	165	727
46,000	798	2,333	440	1,943

ASTM D2622 is superior at lower levels of sulfur concentrations compared to that of ASTM D4294.

ISO 13032, Low Sulfur Content of Automotive Fuels Using Energy-Dispersive X-ray Fluorescence

SIGNIFICANCE

This test method determines sulfur in gasoline containing up to 3.7 mass percent oxygen (including those blended with ethanol up to 10 volume percent) and diesel fuels (including those containing up to about 3 volume percent FAME) that have sulfur contents ranging from 8 to 50 mg/kg. This standard is not applicable to leaded automotive gasolines, lead replacement gasolines containing greater than 8 mg/kg of lead, or to products and feedstocks containing lead, silicon, phosphorus, calcium, potassium, or halides at concentrations greater than one-tenth of the concentration of sulfur measured or more than 10 mg/kg, whichever is greater.

ANALYSIS

A test portion of the sample, in a cup fitted with an X-ray transparent window, is placed in a beam of exciting radiation from an X-ray tube. The exciting radiation may be either direct or indirect (via a polarizing or secondary target). The intensity of the sulfur K characteristic X-radiation is measured, and the accumulated count is compared with a calibration curve constructed from sulfur standards covering the range of sulfur contents under examination.

PRECISION

The following precision values have been found for this test method.

Repeatability	0.005X + 1.07
Reproducibility	0.016X + 3.70

Note: Where X is the average (in mg/kg) of the two results being compared.

ASTM D4951 and ASTM D5185, Metal Analysis in Lubricating Additives and Oils Using Inductively Coupled Plasma Atomic Emission Spectrometry

SCOPE

These two test methods are widely used in the oil industry for the determination of several metals and some nonmetals in lubricating additives and oils, base oils, used oils, and similar fluids. ASTM D4951 is capable of determining nine elements, and ASTM D5185 is capable of determining about 21 elements simultaneously. Of these, two elements of interest in biofuels analysis are phosphorus and sulfur.

ASTM D6751 and ASTM D7467 quote these two methods for phosphorus and sulfur. The phosphorus level in biodiesel ASTM D6751 is a maximum amount of 10 mg/kg. In this context, ASTM D4951 is an inappropriate test method to determine 10 mg/kg maximum of phosphorus because the lower limit of phosphorus determination by this method is 500 mg/kg. Consequently, in all ASTM Proficiency Testing Programs for biodiesel, no phosphorus content has been detected by any participating laboratories using this test method.

ANALYSIS

In both of these test methods, a sample portion is weighed and diluted by mass with mixed xylenes or other solvents. An internal standard is added to the solution. The solutions are introduced into the plasma of the ICP-AES instrument by free aspiration or by an optional peristaltic pump. By comparing emission intensities of elements in the test specimen with the emission intensities measured with the calibration standards and by applying the appropriate internal standard correction, the concentration of the element in the sample is calculated.

TABLE 5.22 Precision for Phosphorus and Sulfur Using ICP-AES Test Methods

Test Method ASTM D4951

Element	Matrix	Range, mass %	Repeatability	Reproducibility
Phosphorus	Oil	0.05–0.12	0.0264 X	0.101 X
	Additive	0.7–1.3	0.0313 (X + 0.294)	0.115 (X + 0.294)
Sulfur	Oil	0.3–0.8	0.016	0.061
	Additive	3.0–3.2	0.14	0.372

Test Method ASTM D5185

Element	Matrix	Range, mass %	Repeatability	Reproducibility
Phosphorus	Oils and used oils	10–1,000	1.3 $X^{0.58}$	4.3 $X^{0.50}$
Sulfur	Oils and used oils	900–6,000	0.49 $X^{0.81}$	1.2 $X^{0.75}$

Note: X is the mean concentration in mass %; X is the mean concentration in mg/kg.

PRECISION

ASTM D4951 and ASTM D5185 show the following precisions based on various interlaboratory crosschecks utilizing additives, lubricating oils, base oils, and used oils (Table 5.22). None of these data are based on the analysis of biofuels.

ASTM D5453, Sulfur in Fuels and Oils by Combustion-Ultraviolet Fluorescence

This is a widely used test method for the determination of low amounts of sulfur in diverse petroleum products and fuels. It is an EPA and California Air Resources Board (CARB) approved test method for such analysis. ASTM D5453 covers the determination of total sulfur (1 to 8,000 mg/kg range) in liquid hydrocarbons, boiling in the range from approximately 25 to 400°C with viscosities between approximately 0.2 and 20 cSt at room temperature. This test method is applicable to petroleum products such as naphthas, distillates, engine oil, ethanol, FAME, and engine fuel such as gasoline, oxygen-enriched gasoline (ethanol blends E-85 and M-85), RFG, diesel, biodiesel, diesel/biodiesel blends, and jet fuel. It is a mandated specification or an alternate specification test method for a number of biofuels.

In one study, data from a round-robin conducted by Western States Petroleum Association in 2000 were analyzed. Nine industry laboratories plus the CARB laboratory participated in this round-robin. Thirteen samples were used, each analyzed in triplicate by each laboratory. Ten of the materials were denatured fuel ethanol for blending with gasoline for use as automotive spark-ignition engine fuel conforming to ASTM D4806 specifications, containing from 1.5 to 42 mg/kg sulfur. Two samples were isooctane-based materials with controlled amounts of sulfur (two at 20 mg/kg and one blank). Overall, the repeatability and reproducibility found in this round-robin were worse than those given in the ASTM D5453 test method for sulfur concentrations less than 17 mg/kg. At 1.5 mg/kg, it is more than twice the published repeatability, but it is 26 % less at 40 mg/kg. The estimated reproducibility is also worse than the published reproducibility for concentrations less than 10 mg/kg sulfur. It is not quite twice the published reproducibility at 1.5 mg/kg, but it is 38 % less at 40 mg/kg sulfur. (See ASTM RR- D02-1633.)

In another study, an ASTM RFG 0607 sample was blended with 0 % to 90 % varying amounts of ethanol. The data in Table 5.23 show close agreement between the averages measured and the expected sulfur values. The ethanol diluent was found to contain about 3 mg/kg total sulfur.

In another study, several organic compounds containing sulfur–oxygen bonds were analyzed at about a 100 mg/kg sulfur level in aqueous solutions in five replicates [38]. Results and recoveries are reported in Table 5.24.

TABLE 5.23 Sulfur Determination in Gasoline/Ethanol Mixtures Using ASTM D5453

% Ethanol	Average Measured Sulfur, mg/kg	Expected Sulfur Concentration, mg/kg
0	33.7	
2	33.4	33.0
5	32.5	32.0
10	30.6	30.3
20	27.9	27.0
30	24.7	23.6
40	21.4	20.2
50	18.3	16.9
60	15.2	13.5
70	11.5	10.1
80	9.1	6.7
90	5.7	3.4
100	3.4	0.0

Note: Halogens in amounts less than 0.35 mass percent do not interfere in this determination. The pooled limit of quantitation was found to be less than 1.0 and less than 5.0 mg/kg sulfur.

TABLE 5.24 Recovery of Sulfur–Oxygen Compounds

Compound	Expected Sulfur Concentration, mg/kg	Sulfur Concentration Found, mg/kg	Percent Recovery
2-thiophene carboxylic acid	125	110	88
Sodium sulfate	105	99	94
Benzene sulfinic acid	124	110	89
2-methyl-2-propene-1-sulfonic acid	115	113	98
Benzene sulfonic acid	108	86	80

ANALYSIS

In this test method, a liquid hydrocarbon sample is either directly injected or placed in a sample boat. The sample or boat (or both) is inserted into a high-temperature quartz combustion tube where the sulfur is oxidized to sulfur dioxide in an oxygen-rich atmosphere. The combustion tube must have side arms for the introduction of oxygen and carrier gas. Water produced during the sample combustion is removed, and the sample combustion gases are next exposed to ultraviolet (UV) light. The SO_2 absorbs the energy from the UV light and is converted to excited sulfur dioxide (SO_2*). The fluorescence emitted from the excited SO_2* as it returns to a stable state, SO_2, is detected by a photomultiplier tube and the resulting signal is a measure of the sulfur contained in the sample [36].

$$R-S+O_2\,@1{,}050^\circ C \rightarrow SO_2+CO_2+H_2O+\text{combustion products}$$

$$SO_2+hv \rightarrow SO_2^* + hv^1$$

Dibenzothiophene, butyl sulfide, or thianaphthene dissolved in toluene, xylene, isooctane, or other appropriate solvents may be used as calibration standards.

A direct injection inlet system can also be utilized that is capable of allowing the quantitative delivery of the material to be analyzed into an inlet carrier stream, which directs the sample into the oxidation zone at a controlled and repeatable rate. A syringe drive mechanism that discharges the sample from the microliter syringe at a rate of approximately 1 µL/s is required. A boat inlet system with an extended combustion tube provides a seal to the inlet of the oxidation area and is swept by a carrier gas. The system provides an area to position the sample-carrying mechanism (i.e., the boat) at a retracted position removed from the furnace. The boat drive mechanism fully inserts the boat into the hottest section of the furnace inlet. Thus, a drive mechanism that advances and withdraws the sample boat into and out of the furnace at a controlled and repeatable rate is required.

Based on the expected sulfur concentration in the sample, one of the three calibration curves should be used (Table 5.25).

TABLE 5.25 Typical Sulfur Calibration Ranges and Standard Concentrations

Curve I Sulfur, ng/µL	Curve II Sulfur, ng/µL	Curve III Sulfur, ng/µL
0.50	5.00	100.00
1.00	25.00	500.00
2.50	50.00	1,000.00
5.00	100.00	
10.00		
Injection size: 10–20 µL	Injection size: 5–10 µL	Injection size: 5 µL

Another study involved analysis of an ASTM biodiesel sample (BIOD 0704) in the ILCP. Forty-four laboratories analyzed this sample using ASTM D5453. Only four laboratories had results outside the three-sigma range of the stated ASTM D5453 reproducibility. The "recalculated" reproducibility is less than 2 mg/kg from reproducibility in ASTM D5453 at the 7.5 mg/kg level. Some cross-check results indicate that further improvement in ASTM D5453 operation is necessary when analyzing biodiesels to improve the precision (Table 5.26).

Thus, based on these multiple studies, it appears clear that ASTM D5453 is capable of accurately determining sulfur in biofuels at low levels of sulfur. However, as the sulfur levels fall toward 1 mg/kg or below, the precision of analysis has worsened, resulting in lower test performance indexes (TPIs). Perhaps the authors of these test methods for sulfur need to take a fresh look at improving the precision of the methods at these low levels. This is true not only for ASTM D5453 but also for ASTM D2622 and ASTM D7039, the most important test methods for sulfur in biofuels as well as for other petroleum products.

The major benchmark ILS mentioned earlier in the chapter included a few biodiesel samples. The data in Table 5.27 show that all three test methods produce reproducible sulfur results for the biodiesel matrix.

INTERFERENCES

Nitric oxide produced by combustion of nitrogen compounds in the sample will fluoresce but at a reduced brightness compared to SO_2. This will falsely increase detected sulfur result. The rejection ratio for N-O in a UV-fluorescence detector is greater than 100:1, or possibly 50:1. Thus, for every 50 mg/kg of nitrogen, sulfur will increase by 1 mg/kg. Usually, most hydrocarbon samples do not have a high enough nitrogen content to make this interference a concern. Another interferent is moisture, which quenches fluorescence reaction; when condensed, it will absorb SO_2. Either using a membrane dryer or keeping the sample path heated reduces humidity and prevents water from condensing. After increasing for the first several injections, the moisture content stabilizes. This

TABLE 5.26 Reproducibility of ASTM D5453 in ASTM ILCP Crosschecks

Biodiesel ILCP	Mean ± SD (Valid Results)	ASTM D5453 Reproducibility	Reproducibility of These Data
BIOD 0511	1.3 ± 0.7 (11)	0.7	1.8
BIOD 0604	1.2 ± 0.4 (17)	0.7	1.1
BIOD 0608	6.1 ± 1.5 (21)	2.2	3.8
BIOD 0611	1.5 ± 0.5 (21)	0.7	1.3
BIOD 0704	7.5 ± 1.6 (44)	2.6	4.5
BIOD 0804	2.97 ±1.01 (50)	1.31	2.80
BIOD 0808	5.31 ± 0.77 (56)	2.03	2.13
BIOD 0811	3.44 ± 0.69 (62)	1.46	1.91
BIOD 1111	1.10 ± 0.38 (62)	0.62	1.05
BIOD 1204	0.56 ± 0.32 (62)	0.38	0.89
BIOD 1208	0.51 ± 0.35 (52)	0.97	0.36
BIOD1211	1.23 ± 0.38 (61)	0.68	1.05
BIOD 1304	0.46 ± 0.31 (58)	0.32	0.86
BIOD 1308	0.42 ± 0.34 (54)	0.30	0.94
BIOD 1311	8.31 ± 1.03 (65)	2.84	2.85
BIOD 1404	0.85 ± 0.43 (65)	0.51	1.19
BIOD 1408	0.41 ± 0.33 (61)	0.30	0.91
BIOD 1411	3.62 ± 0.55 (74)	1.52	1.52
BIOD 1504	2.05 ± 0.49 (71)	0.99	1.36
ETOH 0804	2.75 ± 0.63 (33)	1.24	1.75
ETOH 0808	2.62 ± 0.71 (29)	1.19	1.97
ETOH 0812	1.64 ± 0.36 (28)	0.84	1.00
ETOH 1104	1.29 ± 0.32 (46)	0.70	0.89
ETOH 1108	2.17 ± 0.53 (52)	1.04	1.47
ETOH 1204	1.51 ± 0.40 (49)	0.79	1.11
ETOH 1208	1.91 ± 0.57 (46)	0.94	1.58
ETOH 1212	1.79 ± 0.54 (50)	0.90	1.50
ETOH 1304	2.22 ± 0.48 (49)	1.05	1.33
ETOH 1308	2.57 ± 0.50 (50)	1.18	1.39
ETOH 1312	2.56 ± 0.45 (51)	1.17	1.25
ETOH 1404	1.74 ± 0.44 (46)	0.88	1.22
ETOH 1408	2.09 ± 0.50 (42)	1.01	1.39
ETOH 1412	2.19 ± 0.41 (48)	1.04	1.14
ETOH 1504	1.84 ± 0.48 (46)	0.92	1.33

Note: SD = standard deviation.

TABLE 5.27 Sulfur in Biodiesels by Alternate Test Methods

Sample	ASTM D2622	ASTM D3120	ASTM D5453	ASTM D6920
D11 biodiesel	NA	11.9 ± 3.3	11.0 ± 2.3	9.18 ± 2.92
D12 biodiesel	NA	27.5 ± 4.3	29.0 ± 4.4	26.1 ± 6.9
D14 soy biodiesel	NA	NA	0.82 ± 0.82	1.06 ± 0.84

Note: All results are in mg/kg sulfur; NA = not available.

quenching effect will reduce overall detector sensitivity but the linearity is not affected. Chlorine will fluoresce but has a rejection ratio of approximately 8,000:1. Carbon dioxide can potentially quench fluorescence reaction, but experiments have shown no evidence of this effect on this analysis.

It has been reported in testing of ULSD samples that there could be some interference caused by an iron sulfide corrosion product in the diesel sample. This causes a false high reading when using the ASTM D2622 WD-XRF method but not when using ASTM D5453. Iron sulfide is not volatile. Hence, even if the particles did get into the syringe, they would not be converted to a volatile form so that sulfur in the sulfide can be analyzed. But with the XRF analysis, the insoluble particles would accumulate in the X-ray cup on the face of the analytical surface, making the sulfur reading higher than it actually is. The issue is now more noticeable due to significant decreases in sulfur content and also because ULSD tanks are being circulated more than conventional diesel tanks to improve sample homogeneity. The circulation could potentially stir fine particles from tank bottoms, such as iron sulfide rust [38].

In an Alberta Research Council study, a set of 30 samples was analyzed using ASTM D5453 and ASTM D7039. The set included ULSD, gasolines, aviation gasoline, fuel oils, biodiesels, and aviation turbine fuel. A statistically observable bias with all results combined over several calibration curves (0 to 400 mg/kg nominal) was detected. However, no statistically observable bias using independent t-tests for three samples greater than 200 mg/kg nominal sulfur was observed. The conclusion was that ASTM D5453 and ASTM D7039 should be considered as practically equivalent over all sample types studied between 0 to 100 mg/kg if ASTM D7039 is calibrated using one equation for the aforementioned range [30].

PRECISION

A number of ASTM research reports have documented the applicability of this technique to various petroleum products:

RR-D02–1307 (1992)	Multiple matrices
RR-D02–1456 (1999)	UVFl–XRF equivalence study
RR-D02–1465 (1997)	Gasoline and RFG
RR-D02–1475 (1998)	Low-level gasoline, diesel, and biodiesel
RR-D02–1547 (2000–2001)	Low-level gasoline and diesels
RR-D02–1633 (2008)	Biofuels

Overall, based on these round-robins, the following precisions have been calculated.

Sulfur Concentration, mg/kg	Repeatability	Reproducibility
<400	$0.1788\ X^{0.75}$	$0.5797\ X^{0.75}$
>400	0.02902 X	0.1267 X

Note: Where X is the average of two test results.

BIAS

There were several NIST SRMs analyzed by this method, and no significant bias was found for any of the tested standards: gasoline

SRMs 2298 (4.6 mg/kg) and 2299 (13.6 mg/kg) and diesel SRM 2723a (10 mg/kg).

In one study, Kowalewska and Laskowska compared the analytical performance of ASTM D2622 and ASTM D5453 for the determination of sulfur in modern automotive fuels, biofuels, and biocomponents [39]. They concluded that a simplified standard addition method turns out to be efficient in overcoming the multiplicative effect of absorption by the main components of the matrix (C, H, and O) in ASTM D2622, but it does not correct nitrogen influence on UV determination that is an effect of additive character.

ASTM D6920, Sulfur in Gasoline and Diesels by Oxidative Combustion and Electrochemical Detection

This test method is seldom used in oil industry laboratories; however, it is quoted in some biofuel specifications as an alternate test method for sulfur. The EPA had designated it as the method of choice for determining low levels of sulfur in gasoline and diesel. But after concerted efforts by the oil industry proving that this test method was the least precise among the test methods available for sulfur determination, the EPA withdrew its approval.

SCOPE

This test method covers the determination of total sulfur in liquid hydrocarbons, boiling in the range from approximately 25 to 400°C, with viscosities between approximately 0.2 and 10 cSt at room temperature. The test method is applicable to naphthas, distillates, and motor fuels such as gasolines, reformulated gasolines, gasohols, diesels, and biodiesels containing approximately 1 to 100 mg/kg total sulfur in gasoline type products and approximately 1 to 40 mg/kg sulfur in diesel-type products. Based on an interlaboratory study, the pooled limit of quantitation of this test method is 3 mg/kg for gasoline and less than 0.5 mg/kg for diesel samples.

ANALYSIS

In this test method, the sample is injected at a controlled rate into a stream of inert gas (helium or argon) or inert gas mixed with oxygen. The sample is vaporized and carried into a high-temperature zone (>900°C) where oxygen is introduced. Sulfur compounds present in the test specimen are converted to sulfur dioxide that is reacted with the sensing electrode in a three-electrode electrochemical cell. This reaction produces a measurable current that is directly proportional to the amount of sulfur in the original sample material. The reactions that occur are as follows:

$$\text{Combustion @} > 900^\circ\text{C:}\quad R-S+O_2 \rightarrow CO_2+H_2O+SO_2+\text{oxides}$$

$$\text{Detection:}\quad SO_2+2H_2O \rightarrow H_2SO_4+2\,H^+ +2e^-$$

Virtually all sulfur compounds will be detected by this technique. The detector response for this technique within the scope of this test method is linear with sulfur concentration. Moisture produced during the combustion step can interfere if not removed prior to the detector. Equivalent amounts of nitrogen in the sample may also interfere. Dibenzothiophene is used as the sulfur calibrant in this technique [40].

PRECISION

Precision and bias, based on an interlaboratory study that included 16 laboratories that analyzed 16 samples each of gasoline and diesel in duplicate (RR-D02-1547), were found to be as follows.

	Gasoline	Diesel
Total sulfur, mg/kg	3 to 100	1 to 40
Repeatability	$0.3395\ X^{0.7739}$	$0.1960\ (X + 0.61789)^{0.9022}$
Reproducibility	$1.6384\ X^{0.7739}$	$1.3028\ (X + 0.61789)^{0.9022}$
Bias	None	None

Note: Where X is the average of two results in mg/kg.

Based on the analysis of NIST SRMs, there was no significant bias for the test method on either instrument between the results from this test method and the NIST-certified values for diesel SRM 2723a. For gasoline SRM 2299 containing 13.6 mg/kg sulfur there was no bias; however, for gasoline SRM 2298 containing 4.6 mg/kg total sulfur, there was a bias of −0.78 mg/kg for the test method on both the instruments.

ASTM D7039, Sulfur in Gasoline and Diesel Fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry

This test method is based on the monochromatic wavelength dispersive X-ray fluorescence (MWD-XRF) technique. It has had singular success in accurately analyzing trace quantities of sulfur in gasoline, naphtha, diesel, jet fuel, kerosine, biodiesel, ethanol, and gasoline-ethanol blends. It is a test method for sulfur in ASTM D4806 for ethanol fuels. Its analysis range is from 0.5 to 2875 mg/kg sulfur. The pooled limit of quantitation is 1.9 mg/kg. Volatile samples such as high-vapor-pressure gasoline or light hydrocarbons might not meet the stated precision because of the evaporation of light components during the analysis. Gasoline samples containing oxygenates may be analyzed by this test method provided the matrix of the calibration standards is either matched to the sample matrices or the matrix correction described in the test method is applied to the results. Fuels containing sulfur above 3,000 mg/kg can be analyzed after dilution with the appropriate solvent. However, the precision and bias of the diluted samples may not be the same as that given in the test method. When the elemental composition of the sample differs significantly from the calibration standards used to prepare the calibration curve, the cautions and recommendations given in the test method should be carefully observed [41,42].

ANALYSIS

In this test method, two doubly curved crystal optics are used to provide monochromatic excitation. An X-ray beam, with a wavelength suitable to excite the K-shell electrons of sulfur, is focused onto a test specimen contained in a sample cell. The fluorescent K alpha radiation at 0.5373 nm emitted by sulfur is collected by a fixed monochromator (analyzer). The intensity counts per second of sulfur X-rays are measured using a suitable detector and converted to the concentration of sulfur in the test specimen using a calibration equation. Excitation by monochromatic X-rays reduces background, simplifies matrix correction, and increases the signal to background ratio compared to polychromatic excitation used in conventional WD-XRF techniques [42]. Di-n-butyl sulfide is used as the calibration standard.

In this MWD-XRF test method (ASTM D7039), a matrix correction factor can be used to correct for bias resulting from differences in matrices of calibrants and test samples due to hydrogen, carbon, and oxygen. For general analytical purposes, the matrices of test sample and calibrant are considered to be matched when the calculated correction factor is within the 0.98 to 1.04 range. No matrix correction is required in this range. For most testing, matrix correction can be avoided with a proper choice of calibrants. Gasoline samples containing oxygenates may be analyzed with this test method if the matrix of the calibration standards is either matched to the sample matrices or the matrix correction given in the method is applied to the results. Gasolines with oxygenates up to 2.3 mass percent oxygen (i.e., 12 mass percent MTBE) can be tolerated for the test samples with the same carbon/hydrogen ratio as the calibrants.

Differences between the elemental composition of test samples and the calibration standards can result in biased sulfur determinations. For diesels and gasolines within the scope of this test method, the only important elements contributing to bias resulting from differences in the matrices of calibrants and test samples are hydrogen, carbon, and oxygen. A matrix correction factor, C, can be used to correct this bias. For general analytical purposes, the matrices of test samples and the calibrants are considered to be matched when the calculated correction factor C is within 0.98 to 1.04. No matrix correction is required within this range. A matrix correction is required when the value of C is outside the range of 0.98 to 1.04. For most testing, matrix correction can be avoided with a proper choice of calibrants. For example, a calibrant with 86 mass percent carbon and 14 mass percent hydrogen can cover non-oxygen-containing samples with carbon-to-hydrogen ratios from 5.4 to 8.5. For gasolines and oxygenates, up to 2.3 mass percent oxygen (i.e., 12 mass percent MTBE) can be tolerated for test samples with the same carbon-to-hydrogen ratio as the calibrants.

To minimize any bias in the results, calibration standards prepared from sulfur-free base materials of the same or similar elemental composition as the test sample should be used. When diluting samples, diluent with an elemental composition the same or similar to the base material should be used for preparing the calibration standards. A base material for gasoline can be approximately simulated by mixing isooctane and toluene in a ratio that approximates the expected aromatic content of the samples to be analyzed. Fuels containing oxygenates may be analyzed using calibration standards containing the same amount of the same oxygenate in the test fuel.

PRECISION

The limit of detection for a single analyzer was found to be 0.36 mg/kg. In a limited study conducted at Alberta Research Council, a sample of fuel ethanol was analyzed by 31 laboratories to obtain a value of 1.6879 ± 0.4837 mg/kg to demonstrate the ability of this test method to analyze ethanol samples with extremely low sulfur values [43]. In the last ILS conducted in 2011, the following precisions were obtained that are considered as final.

Sample range = 1.10 to 2822.1 mg/kg
PLOQ = 3.2 mg/kg
Repeatability = $0.4998\ X^{0.54}$
Reproducibility = $0.7384\ X^{0.54}$

Results for NIST SRMs analyzed in an interlaboratory study to measure the precision values resulted in the data in Table 5.28. No statistically significant bias was observed for this test method using an NIST SRM 1616b kerosine sample.

In an interlaboratory study, the Alberta Research Council investigated the precision of ASTM D7039. Twenty-one laboratories analyzed 23 samples comprised of gasoline, ethanol, aviation gasoline, fuel ethanol, biodiesel, kerosine, fuel oil, additive, and crude oil for their sulfur content using ASTM D7039 instruments. The results of using ASTM D5453 and ASTM D7039 are given in Table 5.29, and the two sets of results are in good agreement with each other. The precisions obtained in this study are shown in Table 5.30 [43].

TABLE 5.28 Analysis of NIST Fuel Standard Reference Materials by MWD-XRF

NIST SRM	Certified Value, mg/kg	Measured Value, mg/kg	Measured Bias, mg/kg	Relative Measured Bias, %
Gasoline 2298	4.7 ± 1.3	4.6 ± 1.2	0.1	2.1
Gasoline 2299	13.6 ± 1.5	11.6 ± 0.6	−2.0	
Diesel 2723a	11.0 ± 1.1	11.1 ± 1.2	−0.1	−0.9
Diesel 2724b	426.5 ± 57	431 ± 16	−5.0	−1.2
Kerosine 1616a	146.2 ± 1.8	149 ± 2.50	2.8	

TABLE 5.29 Analysis for Sulfur in Biofuels Using Alternate Test Methods

Biofuel Sample	ASTM D5453	ASTM D7039
Soybean oil ester B100–biodiesel	1.1; 0.7	0.9; 1.0
Ethanol blended gasoline	23.1; 23.9	24.0; 23.1
Ethanol blended gasoline	36.3; 38.7	35.6; 35.4
BIOD B20/ULSD canola FAME	5.3; 5.0	5.8; 5.8
BIOD B100 canola FAME	2.7; 2.0	2.6; 3.0

Note: All results are in mg/kg of sulfur determined in duplicate.

TABLE 5.30 Precision Obtained for ASTM D7039 in an Alberta Research Council Study

Parameter	Ultra-Low Sulfur Diesel	Motor Gasoline
Repeatability	0.53 $X^{0.5}$	0.2704 $X^{0.77}$
Reproducibility	0.77 $X^{0.5}$	0.478 $X^{0.77}$
Sulfur range, mg/kg	4 to 17	4 to 1900
Total number of samples	4	13

Note: Where X is the average of two determinations in mg/kg.

TABLE 5.31 Determination of Sulfur in Biofuels Using XRF Test Methods

Samples	ASTM D2622 WD-XRF	ASTM D4294 ED-XRF	ASTM D7039 MWD-XRF
B100 biodiesel	12.99 ±1.53 (28)	18.41 ± 5.81 (23)	
B2 biodiesel	65.46 ± 2.75 (28)	75.90 ± 8.45 (23)	
E85 ethanol blend	6482.0 ± 152.4 (27)	6634.8 ± 257.9	
E5 ethanol blend	22217 ± 521.8 (26)	22415 ± 348 (21)	
ETOH 1008		**ASTM D5453 UV-FLR** 1.31 ± 0.36 (41)	1.08 ± 0.23 (10)
ETOH 1012		3.61 ± 0.91 (43)	3.31 ± 0.34 (9)

Note: All results are in mg/kg of sulfur. The data are expressed as average value ± standard deviation (number of results).

Some more comparisons of the three major sulfur test methods on biofuels are shown in Table 5.31. All three test methods produced equivalent results. These data are from ASTM CS 92 ILCP reports.

ASTM D5623, Sulfur Species by Gas Chromatography

SIGNIFICANCE

Frequently, the knowledge of individual sulfur compounds present in a product is more useful than the total amount of sulfur present. Often sulfur compounds are odorous, corrosive to equipment, and inhibit or destroy catalysts used in downstream processing. The ability to speciate sulfur compounds in various petroleum liquids is useful for controlling sulfur compounds in finished petroleum products and is frequently more important than knowledge of the total sulfur content alone.

This test method covers the determination of volatile sulfur compounds in light petroleum liquids. ASTM D5623 is applicable for distillates, gasoline motor fuels, including those containing oxygenates, and other petroleum liquids with a final boiling point of approximately 230°C or lower at atmospheric pressure. Generally, this test method can determine individual sulfur species at levels of 0.1 to 100 mg/kg. It does not purport to identify all individual sulfur compounds present. Also, some sulfur compounds (such as hydrogen sulfide and mercaptans) are reactive, and their concentration in samples may change during sampling and analysis. Total sulfur content of the sample can be calculated from the sum of the individual compounds determined. However, this is not the preferred test method for the determination of total sulfur in a petroleum sample.

ANALYSIS

The sample is analyzed by GC with an appropriate sulfur selective detector. Calibration is done by an appropriate internal or external standard. All sulfur compounds are assumed to produce an equivalent response as sulfur. As sulfur compounds elute from the GC column, they are quantified by a sulfur selective chemiluminescence detector that produces a linear and equimolar response to sulfur compounds. The following precision for this test method has been obtained (RR-D02-1335).

Standardization	Compound	Range	Repeatability	Reproducibility
Internal	Single component	1 to 100	0.11 X	0.42 X
	Total sulfur	10 to 200	0.12 X	0.33 X
External	Single component	1 to 100	0.31 X	0.53 X
	Total sulfur	10 to 200	0.24 X	0.52 X

Note: All values are in mg/kg, where X is the mean of duplicate determinations.

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Abstract

There are about 40 test methods for elemental analysis of biofuels. These are described in this chapter, giving information on the significance of these tests in biofuels, the analytical principals involved, and the precision estimates of the test methods.

Keywords

elemental analysis, biofuels

Chapter 6 | Environmental Analysis Test Methods for Biofuels

In addition to the chemical, elemental, and physical tests described so far in this book, some miscellaneous tests are applicable to biofuels that may be considered environmental or ecological in nature. One group of such tests is meant to estimate biodegradability and renewable content of test fuels or microbial contamination. Biofuel specifications usually do not contain specific biodegradation or renewable content limits per se. Over the last two decades, numerous standard testing methods and computer-based predictive models have been developed to help assess the environmental persistence, biodegradation, and toxicity of materials. Most of these methods have been developed for simple, soluble, and nonvolatile substances. In contrast, most fuels and lubricant products are not defined as such but rather are mixtures (simple and complex) of organic molecules, often relatively insoluble in water or volatile (or both). Also, additives can introduce metals and other inorganic compounds into the mixture. Nevertheless, the same standard methods were and are used to test these products. This often produces misleading results and interpretations. Characteristics such as water solubility, vapor pressure, dissociation constant, and sorption can render a specific test method inappropriate for many of these materials. In many cases, the results of different test methods for the same basic characteristics (e.g., biodegradation) cannot be directly compared [1].

Traditional lubricants used in machinery are usually toxic and are not readily biodegradable due to the poor biodegradability of their base oils. To preserve environmental and ground water systems, there has been an increasing interest in using environmentally acceptable (EA) lubricants in environmentally sensitive industries such as construction, forestry, and agriculture. These EA lubricants are less toxic and readily biodegradable products. Currently, many EA lubricants have been formulated with renewable oils such as rapeseed, sunflower, corn, soybean, canola, and synthetic esters [2].

The biodegradability of lubricants allows them to break down in the environment, reducing negative effects from leaks and spills. They can be nontoxic, meaning they will not harm operators, animals, or plants that come in contact with the fluid. Furthermore, they are renewable. One of the main reasons for concern about lubricants' environmental safety is that many industrial lubricants find their way into the environment. The National Oceanic and Atmospheric Administration estimates that more than 700 million gal of petroleum oil enter the environment each year—more than half of which is released through irresponsible and illegal disposal.

Biodegradation

Biodegradation is a natural process caused by the action of microorganisms in the presence of oxygen, nitrogen, phosphorus, and trace minerals. Organic pollutants can support microbial growth and are converted into a series of oxidation products that ultimately end with carbon dioxide and water. Inherent biodegradability of a lubricant depends to a large extent upon its molecular structure and composition [2]. Typically, straight-chain aliphatic compounds (i.e., alkanes) are easily degraded; however, aromatic compounds are degraded very slowly and are toxic. Polymeric materials are among the most resistant to microbial attack. Oils derived from renewable resources are more biodegradable than petroleum-based oils. In addition, the water solubility (or dispersibility) of lubricant products, their molecular size, pH of the solution, types of materials, temperature, total dissolved solids, and their toxicity all affect their biodegradability. Among these, it is strongly believed that molecular structure and toxicity may play the most significant role in the biodegradation of lubricants [2]. Some terms used in this context are explained in Table 6.1.

Biodegradation is the biologically mediated transformation of a material. The microorganisms that accomplish the biodegradation are very important to the nature of the result. Generally, the interest in studying biodegradation is for using the results to predict the environmental fate of a chemical. Thus, the microorganisms used in laboratory tests are mixtures of species collected from particular environments. For a variety of reasons, sewage sludge has become the standard source of mixed inoculum for introduction into laboratory biodegradation test systems.

In the aquatic environment, bacterial numbers are lower than in sewage, and there are also low concentrations of a variety of chemicals and nutrients. In standardized testing, the organisms are constrained within a small volume and are presented with a high concentration of the test material as the sole source of carbon. Those organisms capable of degrading the chemical will use it as a source of carbon for new cells and energy. Pre-exposure to petroleum products can result in a 1 % to 10 % increase in the total population of petroleum-degrading microorganisms. The rate of this

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TABLE 6.1 Terminology Used in Biodegradation Tests

Term	Explanation	Standard
Aerobic	Taking place in the presence of oxygen.	ASTM D6006
Anaerobic	Taking place in the absence of oxygen.	ASTM D6006
Biodegradation	The transformation of a material resulting from the complex enzymatic action of microorganisms (e.g., bacteria, fungi). It usually leads to the disappearance of the parent structure and to the formation of smaller chemical species, some of which are used for cell metabolism. Although typically used in reference to microbial activity, it may also refer to general metabolic breakdown of a substance by any living organism.	
Inherent biodegradability	Classification of chemicals for which there is unequivocal evidence of biodegradation (primary or ultimate) in any test of biodegradability.	
Inoculum	Living spores, bacteria, single-celled organisms, or other live materials that are introduced into a test medium.	ASTM D6384
Primary biodegradation	Degradation of the test substance resulting in a change in its physical or chemical properties, or in both.	ASTM D6006
Ultimate biodegradation	Degradation achieved when a substance is totally utilized by microorganisms resulting in the production of carbon dioxide (and possibly methane in the case of anaerobic biodegradation), water, inorganic compounds, and new microbial cellular constituents (biomass or secretions, or both).	ASTM D6006

biodegradation reflects the growth rates of those particular organisms under the conditions of the test. The test results are used to classify the persistence of the material and to estimate its half-life in the environment [1].

Certain environmental conditions (e.g., availability of oxygen) greatly influence the types of organisms and their metabolic pathways. Standardized tests exist for aerobic and anaerobic conditions in the major environmental compartments (freshwater, marine water, sediments, and soils). In some cases, simulation tests are intended to replicate the natural conditions of the organisms, their environment, and their exposure to the chemical [3]. The main terms used to describe biodegradation—primary and ultimate—distinguish between two extents of biodegradation. "Primary" refers to the initial transformation from the parent material, and "ultimate" refers to mineralization of the material. The rate is described by the terms inherent and ready. In general, to be classified as "inherently" biodegradable, there must be unequivocal evidence of biodegradation by any test method. The Organization for Economic Cooperation and Development (OECD) methods require 20 % degradation for this classification. "Ready" biodegradability is a regulatory classification originating in the European Union that has very specific criteria. See Hinman for further discussion of this classification [1].

There are two commonly used designations for biodegradability: "readily" and "inherently." Readily biodegradable is defined as breaking down very rapidly in the environment by a prescribed amount in a specific time frame. Inherently biodegradable is misleading to the unknowing because it means the substance has the propensity to break down with no defined amount or time frame. Thus, an inherently biodegradable product breaks down very slowly over time, usually in terms of years. These type of products can persist in the environment for several years, continuing to cause substantial damage. They require long-term remediation due to their environmental persistence. Typically, these products are petroleum-based, such as conventional lubricants [4].

Certain standardized tests have been developed for regulatory purposes to evaluate the rate and extent of biodegradation. See Table 6.2 [5]. A number of biodegradation tests are available and differ mainly in the method of analysis. The different assays give different results. The analytical methods dictate details of the procedures and result in different applicabilities for each test. Generally, the disappearance of dissolved organic carbon is more rapid than the utilization of oxygen or the production of carbon dioxide. Standard tests for biodegradation have been issued by several organizations such as ASTM, OECD, the European

TABLE 6.2 Examples of Biodegradation Tests

Attribute	Categories	Measurement	Properties
Extent of biodegradation	Ultimate	Oxygen, carbon dioxide, methane	Measures total conversion to inorganic forms; mineralization
	Primary	Specific analysis	Based on analysis of specific chemical or chemical class; abiotic losses controlled
	Removal	Specific analysis	Primary biodegradation; both abiotic and biodegradation
Ease of biodegradation	Ready	Oxygen, carbon dioxide, dissolved organic carbon (DOC)	Regulatory definition of "rapid" biodegradation; uses <30 mg/L nonadapted inoculum; reaches minimum 60 % degradation to oxygen, carbon dioxide, or 70 % removal of DOC in 28 days; must go from 10 % to the pass level (60 % or 70 %) in 10 days
	Inherent	Oxygen, carbon dioxide, methane, DOC, specific analysis	Enhanced conditions to show possibility of eventually biodegrading; generally a high biomass adapted inoculum
	Simulation	Specific analysis	Reflects actual environmental behavior; difficult to simulate most exposure situations

From Ref. [5].

TABLE 6.3 Examples of Relevant Biodegradation Test Methods

Test	Standard /Reference	Environment	Biodegradation Extent	Biodegradation Rate
DOC Die-Away	OECD 301 A; EC C-4A; ISO 7827	Aquatic	Ultimate Primary	Ready
Modified Sturm Method	OECD 301 B; EC C4-A; ASTM D5864; ISO 9439; EPA 835.3110	Aquatic	Ultimate	Ready
Gledhill Method	ASTM D6139	Aquatic	Ultimate	Ready
MITI (I and II)	OECD 301 C; EC C4-F(I); OECD 302 C(II); EPA 835.3110	Aquatic	Ultimate	Ready
Closed Bottle	OECD 301 D; EC C4-D; ASTM E1720; ISO 10707; EPA 835.3110	Aquatic	Ultimate	Ready
2-Phase Closed Bottle	ISO 10708	Aquatic	Ultimate	Ready
Modified Screening	OECD 301 E; EC C4-B; ISO 7827	Aquatic	Ultimate	Ready
Respirometry	OECD 301 F; EC C4-D; ISO 9408; EPA 835.3110	Aquatic	Ultimate Primary	Ready Inherent
Sea Water	OECD 306	Aquatic–Marine	Ultimate	Inherent
Zahn-Wellens/EMPA	OECD 302 B; ISO 9888; EPA 835.3200	Aquatic	Ultimate Primary	Inherent
Sludge–Semicontinuous (Mod. semi-continuous activated sludge [SCAS])	OECD 302 A; ASTM E1625; ISO 9887; EPA 835.3210; EPA 835.5045	Aquatic	Ultimate Primary Removal	Inherent
Sludge – Continuous (Coupled Units)	OECD 303 A; ISO 11733	Aquatic	Ultimate Simulation	Inherent
Soil	OECD 304 A; ISO 14239; EPA 835.3300	Soil	Ultimate Simulation	Inherent
Biogas Generation–Anaerobic	ECETOC TR 28; ISO 11734	Aquatic	Ultimate Primary	Inherent
2-Stroke Oil	CEC L-35-A-94	Aquatic	Primary	Inherent
CO_2 Generation in Sealed Vessels	ISO 14593; CONCAWE Rpt. No. 99/59; Battersby 1997; EPA 835.3120	Aquatic	Ultimate	Inherent
Porous Pot Test	ASTM E1798	Aquatic	Ultimate Simulation	Inherent
Shake-Flask Die-Away Test	ASTM E1279; EPA 835.3170+	Aquatic–Surface Water	Primary	Inherent

From Ref. [5].

Commission (EC), the International Organization for Standardization (ISO), and the U.S. Environmental Protection Agency (EPA). Hinman has provided an extensive list of commonly used standardized tests, the general characteristics of the tests, and their general applicability [5]. A summary of these tests is given in Table 6.3 [5]. In the United States, government authorization for the manufacture of new chemicals is regulated under the Toxic Substances Control Act (TSCA), which requires a premanufacturing notification be submitted for EPA review before full-scale manufacture of the material. In Canada, the New Substances Provisions of the Canadian Environmental Protection Act performs an equivalent role. In the European Union, Council Directive 67/548/EEC-Classification, Packaging, and Labeling of Dangerous Substances drives the premarketing notification process. Of the many tests required for these notifications, those for biodegradation testing are listed in Table 6.4 [5].

Comparing the results from different test methods for the same or similar materials can be problematic. The “percent biodegradation” is very dependent upon what type of biodegradability was tested. As a result of this and various complications resulting from the use of inappropriate tests for the physical characteristics of the material, the comparison of biodegradability among materials is only quantitative if they are tested in the same test systems using the same inoculum prepared at the same time. The major use of biodegradation tests is to provide an estimate of the potential of a material to degrade in the environment [1].

In general, hydrocarbons are biodegradable in varying degrees. Fuels and lubricants are mixtures with some components having low water solubility that often limits the concentration in solution and thus their availability to the microorganisms. The aromatics tend to be slightly more water-soluble and give “better” results in standardized tests than the paraffins. Among the paraffins, the linear hydrocarbons are considered more biodegradable than the branched hydrocarbons. This results from microbial oxidation of one end of the linear molecule to a carboxylic acid. The metabolic processes in nearly all organisms can easily degrade the resulting fatty acid. The presence of branching hinders degradation to some extent [5].

A partial list of available ASTM biodegradation tests for various classes of petroleum products and lubricants is given in Table 6.5. The EPA tests for biodegradability are given in Table 6.6. At present, there are no published ASTM or other tests for biodegradation for biofuels. Of the ASTM test methods listed in Table 6.5, at least three are applicable to lubricant and grease testing. These test methods measure the ultimate biodegradation of the lubricants. The evolved carbon dioxide (CO_2) methods work by collecting the evolved CO_2 from the biological breakdown of the lubricant. At the completion of the test, the CO_2 evolved is compared to the theoretical CO_2 that can be produced from the biological breakdown and reported as the percentage of biodegradation. ASTM D6731 works by collecting the oxygen consumed from the biological breakdown of the lubricant. The oxygen consumed is compared to the amount

TABLE 6.4 Classification of Biodegradation Tests

Characteristics	USA-TSCA	European Union	Canada
Ready biodegradation	835.3110	OECD 301	OECD 301
		OECD 310	OECD 310
		OECD 311	OECD 311
Inherent biodegradation	835.3100	OECD 302	OECD 302
	835.3120	OECD 304	OECD 304
	835.3200		
	835.3400		
	835.5045		
Simulation biodegradation		OECD 303	
		OECD 309	

From Ref. [5].

TABLE 6.5 International Biodegradation Tests for Petroleum Products and Lubricants

ASTM	ISO	OECD
ASTM D5846, Biodegradability by Modified Sturm Test		
ASTM D5864, Aerobic Aquatic Biodegradation of Lubricants or Their Components	ISO 7827, Aqueous Medium of the "Ultimate" Aerobic Biodegradability of Organic Compounds—Dissolved Organic Carbon	OECD 301, Ready Biodegradability OECD 301B, CO_2 Evolution Test (the Modified Sturm Test) OECD 301C, Modified MITI Test
ASTM D6006, Guide for Assessing Biodegradability of Hydraulic Fluids	ISO 9408, Ultimate Aerobic Biodegradability of Organic Compounds in Aqueous Medium	OECD 302, Inherent Biodegradability
ASTM D6139, Aerobic Aquatic Biodegradation of Lubricants or Their Components	ISO 9439, Ultimate Aerobic Biodegradability of Organic Compounds in Aqueous Medium	OECD 304, Inherent Biodegradability in Soil
ASTM D6384, Terminology Relating to Biodegradability and Ecotoxicity of Lubricants	ISO 9887, Aerobic Biodegradability of Organic Compounds in an Aqueous Medium—SCAS Test	OECD 306, Biodegradability in Seawater
ASTM D6731, Aerobic, Aquatic Biodegradability of Lubricants or Components in a Closed Respirometer	ISO 9888, Ultimate Aerobic Biodegradability of Organic Compounds in Aqueous Medium—Static Test	OECD 309, Aerobic Mineralization in Surface Water—Simulation Test
ASTM D6866, Renewable Content of Samples Using Radiochemical Analysis		
ASTM E1279, Biodegradation by a Shake-Flask Die-Away Method	ISO 10634, Preparation and Treatment of Poorly Water-Soluble Organic Compounds for Biodegradability in an Aqueous Medium	OECD 310, Ready Biodegradability—CO_2 in Sealed Vessels
ASTM E1625, Biodegradability of Organic Chemicals in Semi-Continuous Activated Sludge (SCAS)	ISO 10707, Ultimate Aerobic Biodegradability of Organic Compounds in an Aqueous Medium by Closed Bottle Test	OECD 311, Ready Anaerobic Biodegradability in Diluted Anaerobic Sewage Sludge
ASTM E1720, Ready and Ultimate Biodegradability of Organic Chemicals in a Sealed Vessel CO_2 Production Test	ISO 10708, Ultimate Aerobic Biodegradability of Organic Compounds in an Aqueous Medium in a Two-Phase Closed Bottle Test	
ASTM E1798, Assessing Treatability or Biodegradability, or Both, of Organic Chemicals in Porous Pots	ISO 11266, Guidance for Laboratory Testing for Biodegradation of Organic Chemicals in Soil Under Aerobic Conditions	
ASTM E2170, Anaerobic Biodegradation Potential of Organic Chemicals Under Methanogenic Conditions	ISO 11733, Elimination and Biodegradability of Organic Compounds in an Aqueous Medium (Activated Sludge Simulation Test [ASST])	
	ISO 11734, Ultimate Anaerobic Biodegradability of Organic Compounds in Digested Sludge	
	ISO 14593, Ultimate Aerobic Biodegradability of Organic Compounds in Aqueous Medium	
	ISO/TR 15462, Selection of Tests for Biodegradability	
	ISO 16221, Determination of Biodegradability in the Marine Environment	

TABLE 6.6 U.S. EPA Biodegradability Tests for Petroleum Products and Lubricants

US EPA	Subject
835.3100	Aerobic Aquatic Biodegradation
835.3110	Ready Biodegradability
835.3120	Sealed-Vessel Carbon Dioxide Production Test
835.3170	Shake-Flask Die-Away Test
835.3180	Sediment/Water Microcosm Biodegradation Test
835.3210	Modified SCAS Test
835.3300	Soil Biodegradation
835.3400	Anaerobic Biodegradability of Organic Chemicals

of the theoretical oxygen that should be consumed by the breakdown or the oxidation of the test lubricant. The amount collected is reported as a percentage of the total biodegradation. For all of these methods, it is important to obtain accurate elemental analysis of the test material in order to have a relevant test result [6].

The ASTM test methods are very similar to each other and simulate the biodegradation process used in a waste treatment facility. But they have a long testing time (28 days). Additionally, these tests also have very poor precision due to the various and multiple inoculum sources. A problem with inoculums is that although one may get it from the same source, differences in the microorganism population can vary from batch to batch [2].

In-Sik Rhee has developed a new way to determine biodegradability of lubricants using a biokinetic model [7]. Currently available ASTM and OECD test methods take a long time (28 days), and special biological knowledge is required. To resolve this problem, a biokinetic model was developed based on the composition of lubricants. The advantage of this biokinetic model is that it can predict the biodegradability of lubricants within a day without the use of microorganisms. The new test method (ASTM D7373) has excellent correlation with the aerobic closed respirometer test, ASTM D6731.

ASTM D5846, Universal Oxidation Test for Hydraulic and Turbine Oils Using the Universal Oxidation Test Apparatus

This test was developed for evaluating the oxidation stability of petroleum-based hydraulic oils and oils for steam and gas turbines. It has also been used to evaluate the oxidation stability of fluids made with synthetic base stock and in-service oils.

SIGNIFICANCE

Degradation of hydraulic fluids and turbine oils, caused by oxidation or thermal breakdown, can result in the formation of acids or insoluble solids and render the oil unfit for further use. This test method can be used to estimate the relative oxidation stability of petroleum-based oils. The correlation between results of this test and the oxidation stability in use can vary markedly with service conditions and with various oils.

ANALYSIS

An oil sample is contacted with air at 135°C in the presence of copper and iron metals. The acid number and spot-forming tendency of the oil are measured daily. The test is terminated when the oxidation life of the oil has been reached. The oil is considered to be degraded when either its acid number (measured by test methods ASTM D974 or ASTM D664) has increased by 0.5 mg KOH/g over that of new oil or when the oil begins to form insoluble solids so that when a drop of oil is placed onto a filter paper it shows a clearly defined dark spot surrounded by a ring of clear oil.

PRECISION

Based on two interlaboratory studies, the following precisions have been obtained for antiwear hydraulic oils as well as steam and gas turbine oils. No information is available for biofuels or biolubricants.

Oils	Repeatability	Reproducibility
Antiwear hydraulic oils	0.0614 X	0.0918 X
Steam and gas turbine oils	0.0486 X	0.1400 X

Note: Where X is the average of two results.

ASTM D5864, Aerobic Aquatic Biodegradation of Lubricants or Their Compounds

This test method is a version of the OECD 301 B Modified Sturm Test that closely simulates wastewater biodegradation conditions. It was designed to determine the degree of aerobic aquatic biodegradation of lubricants upon exposure to inoculum under laboratory conditions. In this test, the biodegradability of a lubricant is expressed as a percentage of maximum carbon conversion under well-controlled conditions for a period of 28 days.

SIGNIFICANCE

This test method covers the determination of the degree of aerobic aquatic biodegradation of fully formulated lubricants or their components upon exposure to an inoculum under laboratory conditions. It is intended to specifically address the difficulties associated with testing water-insoluble materials and the complex mixtures found in many lubricants. This test method is designed to be applicable to all lubricants that are not volatile and are not inhibitory at the test concentration of the organisms present in the inoculum.

SCOPE

In this test method, the degree of aquatic biodegradation of a lubricant or components of a lubricant is measured by the amount of evolved carbon dioxide upon exposure of the test material to an inoculum. The plateau level of carbon dioxide evolution in this test method will suggest the degree of biodegradability of the lubricant. Test substances that achieve a high degree of biodegradation in this test may be assumed to easily biodegrade in many aerobic aquatic environments.

ANALYSIS

Biodegradation of a test material is measured by collecting and measuring the carbon dioxide produced when the lubricant or component is exposed to microorganisms under controlled aerobic conditions. This value is then compared to the theoretical amount of CO_2 that could be generated if all of the carbon in the test material were converted to CO_2, which is a product of aerobic microbial metabolism of carbon-containing substances and so is a direct measure of the test substance's ultimate biodegradation. CO_2 production is quantified by trapping it in a barium hydroxide solution and titrating the solution to calculate the amount of CO_2 absorbed.

The carbon content of the test substance is determined by ASTM D5291 or an equivalent method, and the theoretical carbon dioxide is calculated from the measurement. It is necessary to directly measure the carbon content of the test substance instead of calculating this number because of the complexity of the mixture of compounds present in the lubricants. Biodegradability is expressed as a percentage of theoretical CO_2 production.

PRECISION

Based on an interlaboratory study, the following precision was obtained (RR-D02-1584).

Repeatability $0.4124 \times [X \times (100 - X)]^{0.5}$
Reproducibility $0.8516 \times [X \times (100 - X0]^{0.5}$
(Where the X is the average value obtained.)

ASTM D6006, Assessing Biodegradability of Hydraulic Fluids

SIGNIFICANCE

This guide discuss the ways to assess the likelihood that a hydraulic fluid will undergo biodegradation if it enters an environment that is known to support biodegradation of some substances. This information can be used in making or assessing claims of biodegradability of a fluid formula. The tests discussed in this guide take a minimum of three to four weeks.

SUMMARY

This guide gives two kinds of information that relates to the testing of hydraulic fluids for biodegradability: general information on biodegradability and specific information on the methods, advantages, and disadvantages of several of the biodegradation tests frequently used for hydraulic fluids. These test methods include those listed in Table 6.7.

TABLE 6.7 Test Methods for Assessing Biodegradability of Hydraulic Fluids

Environmental Conditions	Standards Organization	Test Method
Aerobic aquatic	OECD	301B Modified Sturm Test
	OECD	301F Manometric Respirometry Test
	U.S. EPA	Shake-Flask Test
	ISO	9439
	ASTM	D5864
	CEC	L-33-A-94
Aerobic marine	OECD	306
Aerobic soil	U. S. FDA	Aerobic Biodegradation in Soil
	OECD	304A
Anaerobic	U. S. EPA	Anaerobic Biodegradation
	ECETOC	Evaluation of Anaerobic Biodegradation
	ASTM	E1196
	ASTM	D5210

Further information on the environmental impact of hydraulic fluids, particularly for biodegradation, is given in ASTM D6046.

ASTM D6046, Classification of Hydraulic Fluids for Environmental Impact

This classification covers all unused, fully formulated hydraulic fluids in their original form. It establishes categories for the impact of hydraulic fluids on different environmental compartments, as shown in Table 6.8. In this classification, among the aspects of environmental impact included are environmental persistence of which biodegradability is one component and acute ecotoxicity.

The test procedures used to establish the categories are laboratory standard tests and are not intended to simulate the natural environment. The classification of hydraulic fluids for environmental persistence is defined by the hydraulic fluid's biodegradability as measured in tests for either ultimate or primary

TABLE 6.8 Overview of Extended Classification

Environmental Compartment	Environmental Persistence	Ecotoxicity	Bioaccumulation
Fresh water	Pw	Tw	Bw
Marine	Pm	Tm	Bm
Soil	Ps	Ts	Bs
Anaerobic	Pa	Ta	Ba

biodegradation. Further discussion of this classification can be found in the ASTM D6046 standard.

ASTM D6139, Aerobic Aquatic Biodegradation of Lubricants or Their Components Using the Gledhill Shake Flask

This biodegradation test is a version of the EPA's (Gledhill) Shake Flask Test, and it is very similar to the ASTM D5864 biodegradation test except for the agitating of the solution. Currently, this test method is utilized to determine the environmental property by regulatory agencies such as the EPA.

SIGNIFICANCE

Results from this CO_2 evolution test method suggest—within the confines of a controlled laboratory setting—the degree of ultimate aerobic aquatic biodegradability of a lubricant or of the components of a lubricant. Materials that achieve a high degree of biodegradation when undergoing this test may be assumed to easily biodegrade in many aerobic aquatic environments. (See the caveats given in the test method for this analysis.)

SCOPE

This test method covers the determination of the degree of aerobic aquatic biodegradation of fully formulated lubricants or their components on exposure to an inoculum under controlled laboratory conditions. This test method is an ultimate biodegradation test that measures CO_2 evolution. This test method is specifically intended to address the difficulties associated with testing water-insoluble materials and complex mixtures such as are found in many lubricants. This test method is designed to be applicable to all nonvolatile lubricants or their components that are not toxic and not inhibitory at the test concentration to the organisms present in the inoculum.

SUMMARY

See the aforementioned ASTM D5864. The precision or bias of this test method has not been determined.

ASTM D6731, Biodegradability of Lubricants in a Closed Respirometer

This test method is a version of OECD 301 F, the Manometric Respirometry Test, known as the modified biochemical oxygen demand test. It was designed to determine the degree of biodegradability of lubricants or their components in an aerobic aqueous medium on exposure to an inoculum under laboratory conditions.

SIGNIFICANCE

See the aforementioned ASTM D5864.

SCOPE

See the aforementioned ASTM D5864.

SUMMARY

Biodegradation of the test material is determined by measuring the oxygen consumed when the lubricant or component is exposed to microorganisms under controlled aerobic aquatic conditions. This value is then compared to the theoretical amount of oxygen that is required to oxidize all of the elements (i.e., carbon, hydrogen, nitrogen, etc.) in the test material. This test method mixes the test material with aerobic microorganisms in a closed respirometer containing a defined aquatic medium and measures the material's biodegradation by following the decrease in oxygen in the respirometer. A reference material known to biodegrade, such as low erucic acid rapeseed oil or canola oil, is run alongside the test material to confirm that the inoculum is viable and capable of biodegrading suitable material under test conditions.

The inoculated medium is stirred in a closed flask, and the consumption of oxygen is determined either by measuring the amount of oxygen required to maintain a constant gas volume in the respirometer flask or by measuring the change in volume or pressure (or a combination of the two) in the apparatus. Evolved CO_2 is absorbed in an alkaline trap solution or another CO_2 absorbing system suspended within the test vessel, typically in the vessel's head space. Biodegradation is followed over a specific period by determining the consumption of oxygen. Normally the test duration is 28 days; however, the test may be terminated if oxygen consumption has plateaued. The test duration may also be extended if the system's integrity is maintained and the inoculum in the blank systems is viable. The precision or bias of this test method has not been determined.

ASTM D6866, Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis

SIGNIFICANCE

In the United States, presidential orders and public laws require federal agencies to develop procedures to identify, encourage, and produce products derived from biobased, renewable, sustainable, and low environmental impact resources so as to promote the market infrastructure necessary to induce greater use of such resources in commercial, nonfood products.

ANALYSIS

The two test methods in this standard are applicable to any product containing carbon-based components that can be combusted in the presence of oxygen to produce carbon dioxide gas. The overall analytical method is also applicable to gaseous samples, including flue gases from electrical utility boilers and waste incinerators.

Method A has been deleted from the current editions of ASTM D6866 due to the inapplicability of this low-precision method for biobased analysis. The method utilized liquid scintillation counter (LSC) and CO_2 absorption into a cocktail vial. Error was cited as ±15 % absolute due to technical challenges and low radiocarbon counts. Empirical evidence now indicates error may be ±20 % or higher in routine use.

Method B utilizes accelerator mass spectrometry (AMS) along with isotope ratio mass spectrometry techniques to quantify the biobased content of a given product. Instrumental error can be within 0.1 % to 0.5 % (1 RSD), but empirical studies indicate a total uncertainty of up to ±3 % absolute. Sample preparation methods include the production of CO_2 within a vacuum manifold system where it is ultimately distilled, quantified in a calibrated volume, transferred to a quartz tube, and torch sealed. The CO_2 is then delivered to an AMS facility for final processing and analysis.

Method C uses LSC techniques to quantify biobased content of a product using sample carbon that has been converted to benzene. This test method determines the biobased content of a sample with a maximum total error of ±3 % absolute.

Test Methods B and C directly discriminate between product carbon resulting from contemporary carbon input and that derived from fossil-based input. A measurement of a product's $^{14}C/^{12}C$ content is determined relative to the modern carbon-based oxalic acid radiocarbon (see National Institute of Standards and Technology Standard Reference Material 4990c).

PRECISION

The estimates of specific precision or bias for these methods are not known. The results are considered acceptable if it can be shown that the data are traceable to the primary standards and fall within the uncertainties quoted in the methods.

ASTM D7373, Predicting Biodegradability of Lubricants Using a Biokinetic Model

This biokinetic model was developed based on fundamental microbiology theory and the compositional analysis of lubricants and does not need any biodegradation test apparatus and inoculums. It can predict the biodegradability of a lubricant within a day [2,7].

SIGNIFICANCE

This procedure is able to predict the biodegradability of lubricants within a day without dealing with microorganisms. Excellent correlation is established between the test results and the conventional biodegradation test methods such as ASTM D5864 and ASTM D6731 discussed earlier.

SUMMARY

A weighed amount of sample is charged to the top of a gas chromatographic column packed with activated bauxite and silica gel. To elute nonaromatics, n-pentane is added to the column. When all nonaromatics are eluted, a nonpolar aromatics fraction is eluted by additions of an equal mixture of toluene and n-pentane. The ester fraction is eluted by additions of diethyl ether. The polar aromatics are then eluted by chloroform and ethyl alcohol. The solvents are completely removed by evaporation, and the residues are weighed and calculated as the nonaromatics, nonpolar aromatics, ester fractions, and polar aromatics of the sample. The effective composition to biodegradation (ECB) is calculated based on the amount of nonaromatics and ester fractions with their material ECB coefficients. The biodegradability of a lubricant is then calculated using the biokinetic model.

PRECISION

The following precisions were obtained based on an interlaboratory study involving eleven base oils and four laboratories.

Repeatability	1 %
Reproducibility	3.8 %

A comparison of results, using the ASTM D6731 and the ASTM D7373 biokinetic model methods on several types of biobased lubricants, shows remarkable equivalency between the two sets of results (Table 6.9). The results clearly show that the biokinetic model (ASTM D7373) has excellent correlation ($r^2 = 0.99$) with results obtained from the ASTM D6731 biodegradation test. Additionally, the new method reduces the testing time from 28 days to 1 day and can easily predict the biodegradability of fluids without handling microorganisms [2,7].

MICROBIAL CONTAMINATION

Biofuel specifications for diesel fuel oil ASTM D975, ASTM D4814, ASTM D7544, and ASTM D7794 mention microbial contamination in the specifications, although no hard and fast limits are set for this property. Uncontrolled microbial contamination in fuel systems can cause or contribute to a variety of problems, including increased corrosivity and decreased stability, filterability, and

TABLE 6.9 Comparison of Biodegradability Test Methods ASTM D6731 and ASTM D7373

Base Oil	Identification	ASTM D6731	ASTM D7373
Biobased oil	Tractor hydraulic fluid	65.3	67
Mineral oil	Hydraulic fluid	38	35
Poly alpha olefins 2cSt	Base oil	65.3	67
Biobased oil	Hydraulic fluid	78	77
Water-insoluble polypropylene glycol		7	13
Mineral oil	Gear oil	31.7	34
Mineral oil	Tractor hydraulic fluid	33	35
Biobased oil	Hydraulic fluid	83.9	83
Blended biobased oil	Hydraulic fluid	50	53
PAO 4 cSt	Base oil	57.4	53
Hydrocarbon-soluble polybutylene glycol		61	62

caloric value. Microbial processes in fuel systems can also cause or contribute to system damage. This can lead to corrosion, odor, filter plugging, decreased stability, and to deterioration of fuel/water separation characteristics. In addition to system component damage, off-specification fuel can result. Because the microbes contributing to the problems are not necessarily present in the fuel itself, no microbial quality criteria for fuels is recommended. However, it is important for personnel responsible for fuel quality to understand how uncontrolled microbial contamination can affect fuel quality.

ASTM Guide D6469 provides personnel with limited microbiological background and an understanding of the symptoms, occurrences, and consequences of microbial contamination. This guide also suggests means for detecting and controlling microbial contamination in fuels and fuel systems. ASTM **D6469** applies primarily to gasoline, aviation, boiler, industrial gas turbine, diesel, marine, and furnace fuels. Even so, the principles discussed therein also generally apply to crude oil and all liquid petroleum fuels. This guide provides information addressing the conditions that lead to fuel microbial contamination and biodegradation as well as the general characteristics of and strategies for controlling microbial contamination. ASTM Manual 47, *Fuel and Fuel System Microbiology,* includes a compilation of ASTM guides, practices, and methods that can be used to facilitate the microbial contamination detection and biodeterioration diagnosis. Good housekeeping, especially keeping the fuel dry, is critical.

A recently proposed ASTM standard will provide a screening process to determine microbial contamination in fuel. This work is sponsored by Subcommittee D02.SC 14 on Stability and Cleanliness of Liquid Fuels. Workers involved in fueling vehicles and aircraft will use this standard (currently ASTM WK 48076), *New Test Method for Screening of Fuels and Fuel Associated Aqueous Specimens for Microbial Contamination by Lateral Flow Immunoassay*, to test levels of microbial contamination before beginning the fueling process, thus avoiding the costs of decontaminating vehicle fuel tanks. The test described in the proposed standard provides a semiquantitative indication of the presence or absence of substantial levels of microbial contamination in fuel system samples. Testing in accordance with the proposed standard will provide preliminary information that will indicate whether more quantitative testing is needed.

Although microbial damage is well documented, the relationship between contamination and damage is very complex. Microbes detected in fuel samples are generally dormant but have the potential to become revitalized when conditions permit. Nearly all contaminating microbes are found on system surfaces such as tanks and pipeline walls rather than in fuel samples. Although the population density of contaminants is much greater in fuel-associated water than in fuel samples, it can be quite challenging to obtain samples that contain fuel-associated water. This standard is expected to serve as a tool for addressing that problem.

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Abstract

There are several test methods that can be classified as environmental tests for biofuels and petroleum products. These are discussed in this chapter in context of their significance, principle of analysis, and test precision where available.

Keywords

biofuels, environmental test methods

Chapter 7 | Test Methods for Bioenergy from Biomass

ASTM Committee E48 has jurisdiction over bioenergy and industrial chemicals. In that capacity, some standards have been issued by this committee. Most of these are similar to techniques based on chemical or physical test methods used in ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants or ASTM Committee D05 on Coal and Coke. A list of the standards issued by ASTM Committee E48 related to bioenergy from biomass is given in Table 7.1.

Standard terminology used in the context of this chapter is listed in Table 7.2. The terminology is excerpted from ASTM Standard E1705. All these definitions were under ASTM E1126, Terminology Relating to Biomass Fuels, which was withdrawn in 2003.

ASTM E870, Standard Test Methods for Analysis of Wood Fuels

These test methods cover the proximate and ultimate analysis of wood fuels and the determination of gross caloric value of wood fuels sampled and prepared by prescribed test methods and analyzed according to ASTM established procedures. Test methods as herein described may be used to establish the rank of fuels, to show the ratio of combustible to incombustible constituents, to provide the basis for buying and selling, and to evaluate for beneficiation or for other purposes.

Proximate analysis is considered as an assay of the moisture, ash, volatile matter, and fixed carbon as determined by prescribed test methods. Other constituents such as sulfur and phosphorus are not included.

Ultimate analysis is considered as the determination of carbon and hydrogen in the material, as found in the gaseous products of its complete combustion; the determination of sulfur, nitrogen, and ash in the material as a whole; and the calculation of oxygen by difference.

Test methods used for these analyses are listed in Table 7.3. The precision and bias of these test methods described herein are contained in these individual test methods. These test methods are described here.

Two other parameters that are included in proximate and ultimate analyses are fixed carbon and oxygen. Both of these parameters are obtained by calculations.

TABLE 7.1 Bioenergy Standards Issued by ASTM Committee E48

Committee E48 Standard	Subject	Similar Committee D02 Standard	Similar Committee D05 Standard
ASTM E870	Analysis of Wood Fuels		
ASTM E871	Moisture in Particulate Wood Fuels		ASTM D2961; ASTM D3173; ASTM D3302
ASTM E872	Volatile Matter in Particulate Wood Fuels		ASTM D3175
ASTM E873	Bulk Density of Densified Particulate Biomass Fuels		ASTM D6347
ASTM E1358	Moisture in Particulate Wood Fuels		ASTM D2961; ASTM D3173; ASTM D3302
ASTM E1534	Ash in Particulate Wood Fuels	ASTM D482	ASTM D3174
ASTM E1690	Ethanol Extractives in Biomass		
ASTM E1721	Acid-Insoluble Residue in Biomass		
ASTM E1755	Ash in Biomass	ASTM D482	ASTM D3174
ASTM E1756	Total Solids in Biomass		
ASTM E1757	Preparation of Biomass for Compositional Analysis		
ASTM E1758	Carbohydrates in Biomass by High Performance Liquid Chromatography (HPLC)		
ASTM E1821	Carbohydrates in Biomass by Gas Chromatography (GC)		

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TABLE 7.2 Terminology Related to Biotechnology Used in This Chapter

Term	Definition
Bagasse	Residue remaining after extraction of a sugar-containing juice from plants such as sugarcane.
Bioconversion	A general term describing the use of biological systems to transform one compound into another. Examples are digestion of organic wastes or sewage by microorganisms to produce methane.
Biofuel	Biomass-derived fuel.
Biomass	Any material, excluding fossil fuels, which is or was a living organism that can be used as a fuel directly or after a conversion process. Peat is not a biomass.
Biomass fuel	Fuel derived from biomass.
Corn stover	Stalks of the maize plant.
Denatured fuel ethanol	Fuel ethanol to which chemicals (denaturants) have been added to make the ethanol unfit for human consumption in accordance with the regulations of the Bureau of Alcohol, Tobacco, Firearms, and Explosives of the U.S. Department of Justice.
Densified particulate biomass fuels	A fuel made by mechanical compression of biomass to increase the bulk density and to press the fuel into specific shapes, such as pellets and briquettes. The fuel can have a maximum volume of 16.39 cm^3 such that the largest dimension is 7.62 cm.
Distillate	The overhead product of distillation, such as ethanol liquid from the top of a beer still (ASTM E1344).
Ethanol extractives	Residue remaining after evaporation of the ethanol solvent. These are materials that are removed from the biomass by extraction with 190 proof ethanol. (ASTM E1690)
Fermentation	Decomposition of organic compounds by microorganisms to fuels and chemicals such as alcohols, acids, and energy-rich gases.
Fermentation fuel	A fuel produced by the fermentation of biomass.
Fuel alcohol	Ethyl, methyl, or higher alcohols with impurities (including water but excluding denaturants) produced for use as a fuel alone or as an addition to other fuels, such as gasoline.
Fuel ethanol	Ethanol with impurities (including water but excluding denaturant).
Municipal solid waste (MSW)	The refuse material collected from urban areas in the form of organic matter, glass, plastics, waste paper, and so on, not including human wastes.
Particulate wood fuel	Any wood fuel with a maximum particle volume of 16.39 cm^3 such that the largest dimension is 7.62 cm.
Refuse derived fuel (RDF)	Fuel processed from industrial waste, municipal waste, garbage, or sewage sludge.
Refuse derived fuel 3 (RDF 3)	As defined by ASTM Committee E-38 on Resource Recovery, RDF-3 is a shredded fuel derived from municipal solid waste (MSW) that has been processed to remove metal, glass, and other inorganics. The material has a particle size such that 95 % weight passes through a 2-in. square mesh screen.
Renewable energy resources	Sources of energy that are regenerative or virtually inexhaustible, such as solar, wind, ocean, biomass, municipal wastes, and hydropower energy. Geothermal energy is sometimes also included in the definition of this term.
Stover	Dried stalks and leaves of a crop remaining after the grain has been harvested.
Syngas	Synthetic gas resulting from incomplete combustion or pyrolysis of organic material to primarily carbon monoxide and hydrogen.
Wood fuel	Fuel derived from biomass composed of woody trees or shrubs.

TABLE 7.3 Test methods used in proximate and ultimate analysis of wood fuels

ASTM Standard Test Method	Analysis
ASTM E871	Moisture
ASTM D1102; ASTM E1534	Ash
ASTM E872	Volatile Matter
ASTM E777	Carbon and Hydrogen
ASTM E775	Sulfur
ASTM E778	Nitrogen
ASTM E711	Gross Calorific Value

- The fixed carbon is a calculated value as the resultant of the summation of the percentage of moisture, ash, and volatile matter subtracted from 100. All percentages shall be on the same moisture reference base.
- The oxygen is calculated as the resultant of the summation of the percentages of carbon, hydrogen, sulfur, nitrogen, and ash subtracted from 100. All percentages shall be on the same moisture reference base.

ASTM E871, Moisture Analysis of Particulate Wood Fuels

SIGNIFICANCE

This test method covers the determination of total weight basis in the analysis sample of particulate wood fuel, which may be sander dust, sawdust, pellets, green tree chips, hogged fuel, or other type of particulate wood fuel having a maximum particle volume of 16.39 cm^3. It is used for calculating other analytical results on a dry basis. Moisture, when determined as herein described, may be used to indicate yield on processes, to provide the basis for purchasing and selling, or to establish burning characteristics.

ANALYSIS

Collect increments regularly, systematically, and with such frequency that the entire quantity of wood sampled will be represented proportionally in the gross sample. The quantity of the sample shall be large enough to be representative but not less than 10 kg. The samples collected from the surface of the pile are, in general, unreliable because of the exposure to the environment.

A minimum of 50 g of sample in a container is dried in the oven for 16 h at 103 ± 1°C. After weighing the sample, the heating procedure is repeated for 2 h. The weighing and reheating is continued until the total weight change among weight values varies less than 0.2 %.

PRECISION

Repeatability: 0.5 %; reproducibility: 1 %.

ASTM E1358, Moisture Content of Particulate Wood Fuels Using A Microwave Oven

SIGNIFICANCE

This test method provides a rapid determination of moisture in particulate wood fuels in several minutes. It is an alternative to ASTM E871, which requires a minimum of 18 h. This method is applicable to situations such as the spot check of the moisture delivered by truck where a quick indication of the moisture of wood delivered is desirable.

ANALYSIS

Determine the weight of three sheets of standard paper towels placed on top of each other. Place a 50-g sample of wood on top of the paper towels. Place the sample in the microwave oven and heat on full power using the prescribed schedule. Remove the sample and towels from the oven after each heating interval, weigh, and stir. When the mass change among successive weighing is less than 0.5 g, record this mass.

PRECISION

Repeatability: 1 %; reproducibility: 1.5 %.

ASTM E872, Volatile Matter of Particulate Wood Fuels

SIGNIFICANCE

This test method determines the percentage of gaseous products, exclusive of moisture vapor, in the analysis sample of particulate wood fuel that is released under the specific conditions of this test. The particulate wood fuel may be sander dust, sawdust, pellets, green tree chips, hogged fuel, or other type of particulate wood fuel having a maximum particle volume of 16.39 cm^3. The volatile matter, when determined as herein described, may be used to indicate yields on processes to provide the basis for purchasing and selling or to establish burning characteristics.

ANALYSIS

Collect increments regularly, systematically, and with such frequency that the entire quantity of wood sampled will be represented proportionally in the gross sample. The quantity of the sample shall be large enough to be representative but not less than 10 kg. The samples collected from the surface of the pile are, in general, unreliable because of the exposure to the environment.

Volatile matter is determined by establishing the loss in weight resulting from heating wood under rigidly controlled conditions. The measured weight loss, corrected for moisture as determined by ASTM E871, establishes the volatile matter content. Approximately 1 g of sample is taken for analysis. The sample is heated in a crucible to 950 ± 20°C in a muffle furnace for a period of exactly 7 min. After removing from the furnace and cooling to room temperature in a desiccator, the sample is reweighed.

PRECISION

Repeatability: 0.3 %; reproducibility: 1.0 %.

ASTM E873, Bulk Density of Densified Particulate Biomass Fuels

SIGNIFICANCE

The test procedure described in this test method can be used to determine the bulk density (or bulk-specific weight) of any densified particulate biomass fuel meeting the particle volume of 16.39 cm^2 requirements specified in this test method.

ANALYSIS

Collect increments regularly, systematically, and with such frequency that the entire quantity of pellets sampled will be represented proportionally in the gross sample. The quantity of the sample shall be large enough to be representative but not less than 45.45 kg. The samples collected from the surface of the pile are, in general, unreliable because of the exposure to the environment.

A box of specified size is filled to a specified height with the sample, the box is dropped five times to settle its contents, and then the box is weighed.

There are no precision or bias estimates available.

ASTM E1534, Ash Content of Particulate Wood Fuels

SIGNIFICANCE

The ash content determines the weight of the noncombustible part of a particulate wood fuel that oxidizes during a combustion process but releases no energy.

ANALYSIS

Ash content is determined by establishing the weight loss of the sample when heated under rigidly controlled conditions of temperature, time, sample weight, and equipment specifications. In this test method, a 2-g sample of the wood is placed in a silica or porcelain crucible and slowly heated in a muffle furnace to a temperature of 580 to 600°C. The crucible is removed from the furnace, cooled, and weighed. Repeat the heating for 30-min periods until the weight of the ash and crucible after cooling is constant to within 0.2 mg.

PRECISION

Repeatability 0.5 %; reproducibility 1.0 %.

ASTM E1755, Ash in Biomass

SIGNIFICANCE

The ash content is an approximate measure of the mineral content and other inorganic matter in biomass. The ash content is used in conjunction with other assays to determine the total composition of biomass samples. This test method covers the determination of ash, expressed as the mass percent of residue remaining after dry oxidation at 575 ± 25°C, of hard and soft woods, herbaceous materials (such as switchgrass and sericea), agricultural residues (such as corn stover, wheat straw, and bagasse), wastepaper (such as office waste, boxboard, and newsprint), acid- and alkaline-pretreated biomass, and the solid fraction of fermentation residues. All results are reported relative to the 105°C oven-dried mass of the sample.

ANALYSIS

All samples should be ground or milled to reduce the size of the large pieces to less than 1 mm in diameter. The sample is then redried at 105°C prior to testing. Prepared biomass can be used in place of 105°C dried material, but the mass of the material must be corrected for its moisture content by using ASTM E1756 prior to calculating the ash content.

In this procedure, approximately 0.5 to 1.0 g of a test specimen is weighed into a tared pan or a crucible. It is heated in a muffle furnace at 575 ± 25°C for a minimum of 3 h or until all the carbon is eliminated. After cooling, the crucible with the residue is weighed. The ashing is repeated for 1-h periods until the mass after cooling is constant to within 0.3 mg, and the ash content is calculated.

PRECISION

From an interlaboratory study based on analysis of samples of hybrid poplar in five different laboratories, the following precision was obtained.

- Repeatability: 2.67 % of the average
- Reproducibility: 8.93 % of the average

ASTM E1690, Ethanol Extractives in Biomass

SIGNIFICANCE

Ethanol extractives are any materials found in biomass that are soluble in ethanol. They are not considered to be part of the structural components of biomass and should be removed prior to any chemical analysis of the sample. The prolonged extraction removes nonstructural material that can include waxes, fats, resins, tannins, sugars, starches, and pigments. Removing hydrophobic materials from the biomass makes it easier to wet the material for the analysis of structural components. This test method yields results comparable to ASTM D1107.

This test method covers the determination of ethanol-soluble extractives, expressed as a percentage of the oven-dried biomass, of hard and soft woods, herbaceous materials (such as switchgrass and sericea), agricultural residues (such as corn stover, wheat straw, and bagasse), and wastepaper (such as office waste, boxboard, and newsprint). All results are reported to the oven-dried weight of the sample. This test method may not be suitable for hard and soft wood samples that include bark or those with more than 10 % extractable materials.

ANALYSIS

A quantity of biomass is filled in a Soxhlet thimble, placed in a Soxhlet apparatus, and is refluxed using at least 160 mL of 190 proof ethanol. The material is heated at reflux for at least 24 h. When the extraction time is complete, the sample is transferred to a Buchner funnel. Any residual solvent is removed by vacuum filtration, and the sample is washed thoroughly with 190 proof ethanol, collecting all of the filtrate.

The biomass is allowed to dry in the Buchner funnel while it is still attached to the vacuum system. The filtrates are combined, and the solvent is removed using a rotary evaporator with 75 to 100 torr vacuum and a water bath temperature of 45 ± 5°C to heat the flask during evaporation. The flask is placed in a vacuum oven at 40 ± 1°C for 24 ± 1 h after all visible solvent is removed by the rotary evaporator. After cooling the flask in a desiccator, it is weighed to determine the weight of the residue.

Prolonged heating of the extractive residue may result in a low bias for the reported results because of the evaporation of semivolatile constituents. Insufficient heating or using inadequate vacuum can bias the results high because of incomplete removal of ethanol solvent.

PRECISION

Based on a single laboratory analysis, the following repeatability was observed.

Material	Standard Deviation	Coefficient of Variation
Hybrid poplar	0.15 %	0.76 %
NIST 8494 wheat straw	0.20 %	1.6 %
NIST 8493 *Pinus radiata*	0.20 %	8.0 %

ASTM E1721, Acid-Insoluble Residue in Biomass

SIGNIFICANCE

Biomass is composed largely of the following: cellulose, a polymer of glucose; hemicellulose, a complex polymer, the main chain of which consists of xylans or glucomannans; and lignin, a complex phenolic polymer. The lignin is mostly insoluble in mineral acids, unlike the other cell wall components of biomass. For this reason, lignin can be analyzed gravimetrically after hydrolyzing the cellulose and hemicellulose fractions with sulfuric acid. This test method covers determination of the acid-insoluble residue of hard and soft woods, herbaceous materials (such as switchgrass and sericea), agricultural residues (such as corn stover, wheat straw, and bagasse), wastepaper (such as office waste, boxboard, and newsprint), acid- and alkaline-pretreated biomass, and the solid fraction of fermentation residues.

The residue collected contains the acid-insoluble lignin and any condensed proteins from the original sample. An independent nitrogen analysis would be required to determine the acid-insoluble lignin content separate from the condensed protein fraction and is outside the scope of this test method.

A portion of the lignin in some biomass samples will remain soluble during this procedure. The total lignin in a biomass sample includes both acid-insoluble lignin and lignin in the acid-insoluble residue.

All results are reported relative to the 105°C oven-dried weight of the sample. The result of acid-insoluble residue analysis is used in conjunction with other assays to determine the total composition of a biomass sample.

DEFINITIONS

- *Acid-Insoluble Residue*—The solid residue, corrected for acid-insoluble ash, retained on a medium-porosity filter crucible after the primary 72 % and secondary 4 % sulfuric acid hydrolysis described in this test method. The material is primarily acid-insoluble lignin and any condensed proteins.
- *Prepared Biomass*—Material that has been treated in accordance with ASTM E1757 in order to raise the total solids content above 85 % based on an oven-dried solids weight.

ANALYSIS

A 0.3-g sample is placed in a test tube and treated with 3 mL of sulfuric acid and thoroughly mixed. The test tube is placed in a water bath controlled to 30°C and hydrolyzed for 2 h. At the end of this time, the sample with added water is placed in an autoclave for 1 h at 121°C. After cooling, the hydrolysis solution is vacuum filtered through a filtering crucible. The residue is washed, dried, and weighed. It is ignited at 575°C in a muffle furnace for a minimum of 3 h. The residue is cooled and weighed.

The results of acid-insoluble residue analysis are affected by the incomplete hydrolysis of biomass. The results will be biased high unless the sample is hydrolyzed completely. The results are affected by the timing of the acid digestion steps. The insoluble residue will dissolve slowly into solution in an irreproducible manner. The timing within this test method must be followed closely.

PRECISION

Repeatability is 0.41 % standard deviation and 1.59 % coefficient of variation. Reproducibility is 2.37 % standard deviation and 9.92 % coefficient of variation.

ASTM E1756, Total Solids in Biomass

SIGNIFICANCE

The total solids content is used to adjust the mass of the biomass so that all analytical results may be reported on a moisture-free basis. Moisture is a ubiquitous and variable component of any biomass sample. Moisture is not considered a structural component of biomass and can change with storage and handling of biomass samples. The determination of the total solids content allows for the correction of biomass samples to an oven-dried solid mass that is constant for a particular sample. Total solids content may be determined by overnight drying at 105°C in a convection oven or with a loss-on-drying moisture analyzer. Materials suitable for this procedure include samples prepared in accordance with ASTM E1757 and extractive-free material prepared in accordance with ASTM E1690. This procedure is not suitable for biomass samples that visibly change on heating to 105°C—for example, unwashed acid-pretreated biomass still containing free acid. Some materials that contain large amounts of free sugars or proteins will caramelize or brown under direct infrared heating elements used in Test Method B. Total solids in these materials should be determined by Test Method A. For particulate wood fuels, ASTM E871 should be used.

ANALYSIS

There are two procedures that can be used for this determination.

- Procedure A—This test method is suitable for either prepared biomass samples or extractive-free material and involves drying the samples at 105 ± 3°C in a drying oven for at least 3 h but not longer than 72 h.
- Procedure B—This test method is suitable for either prepared biomass samples or extractive-free material and uses an automated moisture analyzer. This procedure is not suitable for materials with bulk densities less than 0.1 g/cm^3. In this procedure, the analyzer is also programmed to heat the sample to 105°C.

PRECISION

Based on analysis of samples in duplicate by the same operator, the following precision estimates were observed.

- Test Method A: 0.55 % for hybrid poplar samples
  1.35 % for washed, lyophilized fermentation residues
- Test Method B: 0.56 % for hybrid poplar samples
  0.89 % for switchgrass samples

ASTM E1757, Preparation of Biomass for Compositional Analysis

SIGNIFICANCE

This practice covers a reproducible way to convert hardwoods, softwoods, herbaceous materials (such as switchgrass and sericea), agricultural residues (such as corn stover, wheat straw, and bagasse), wastepaper (such as office waste, boxboard, and newsprint), feedstocks pretreated to improve suitability for fermentation, and fermentation residues into a uniform material suitable for compositional analysis.

This practice is not intended for materials that will pass through a 20-mesh sieve or that cannot be dried by the described methods to a total solids content of greater than 85 % based on an oven-dried weight. This practice will separate the milled material into two fractions, a –20/+80 mesh fraction and a –80 mesh fraction. Extraneous inorganic materials will accumulate in the –80 mesh fraction, and it should be analyzed independently from the –20/+80 mesh fraction. Weighted results from the two fractions can then be combined to obtain results for the materials on an "as received" basis.

Milling and sieving actions both produce large amounts of dust. This dust can be a nuisance hazard and irritant. There are three preparation methods.

- Preparation Method A—This method is suitable for the preparation of large quantities (>20 g) of field-collected samples into a form appropriate for compositional analysis. In this procedure, the sample is air-dried, milled to pass through a 2-mm screen, and shaken for 15 min. This process is repeated until all of the milled material will pass through the 20-mesh sieve.
- Preparation Methods B and C—These test methods are suitable for very moist feedstocks, samples that would not be stable during prolonged exposure to ambient conditions, or for drying materials when room conditions deviate from the ambient conditions described in this procedure. Test Method C is suitable for very wet biomass that is at risk for mold growth during drying, for wet pretreated biomass or fermentation residues (sludges) that might degrade if allowed to stand for prolonged periods, or for drying biomass when the prevailing conditions do not meet the ambient conditions defined in the procedure. Test Method C is also suitable for handling materials that are heat-sensitive and that would degrade if subjected to the drying oven in Test Method B. These test methods are also suitable for handling small samples of biomass (<20 g). The drying step is done in a convection oven at 45°C (Test Method B) or by lyophilization (Test Method C).

ASTM E1758, Carbohydrates in Biomass by High Performance Liquid Chromatography

SIGNIFICANCE

The carbohydrates making up a major portion of biomass samples are polysaccharides constructed primarily of glucose, xylose, arabinose, galactose, and mannose subunits. The polysaccharides present in a biomass sample can be hydrolyzed to their component sugar monomers by sulfuric acid in a two-stage hydrolysis process. These monosaccharides can then be quantified by ion-moderated partition high performance liquid chromatography (HPLC). The results are reported as mass percent of each sugar on a 105°C dried mass basis. Sample materials suitable for this procedure include hardwoods, softwoods, herbaceous materials (such as switchgrass and sericea), agricultural residues (such as corn stover, wheat straw, and bagasse), wastepaper (such as office waste, boxboard, and newsprint), acid or alkaline-pretreated biomass (washed free of any residual acid or alkali), and the solid fraction of fermentation residues.

The mass percentage of sugar content is used in conjunction with other assays to determine the total composition of biomass samples. Samples with high protein content may result in the mass percentage of sugar values being biased low as a consequence of protein binding with monosaccharides. Test specimens not suitable for analysis by this procedure include alkaline- and acid-pretreated biomass samples that have not been washed. Unwashed pretreated biomass samples containing free acid or alkali may change visibly during heating.

ANALYSIS

Hewlett Packard 1090 HPLC or equivalent with refractive index detector with Biorad HPLC columns HPX 87C or HPX 87P or equivalent are used for this analysis.

PRECISION

Replicate testing of glucose in a hybrid poplar in laboratories using HPX 87P obtained 1.90 % standard deviation and 3.95 % coefficient of variation.

ASTM E1821, Carbohydrates in Biomass by Gas Chromatography

SIGNIFICANCE

This test method is a reproducible way to quantitatively determine the lignocellulosic materials, their kind, and the amount of structural carbohydrates in them made from arabinose, xylose, mannose, galactose, and glucose. This is achieved by first hydrolyzing the carbohydrates to their constituent monosaccharides. Subsequent derivatization produces the corresponding alditol acetates that are quantified using capillary GC. The structural carbohydrate content is used in conjunction with other assays to determine the total composition of biomass samples.

Sample materials suitable for this procedure include hardwoods, softwoods, herbaceous materials (such as switchgrass and sericea), agricultural residues (such as corn stover, wheat straw, and bagasse), wastepaper (such as office waste, boxboard, and newsprint), acid- or alkaline-pretreated biomass (washed free of any residual acid or alkali), and the solid fraction of fermentation residues.

The options for the type of samples to be analyzed in this procedure are:

- Prepared biomass samples: (1) air-dried material; (2) 45°C dried material; and (3) freeze-dried material
- Extractive-free sample

This standard method generally is not suitable for samples that contain soluble, nonstructural carbohydrates unless they are removed prior to the analysis.

INTERFERENCES

The results of structural carbohydrate analysis are affected by incomplete hydrolysis of biomass or hydrolysis conditions that are too severe. Incomplete hydrolysis will bias the results low because dimeric and oligomeric carbohydrates are not quantified. Hydrolysis conditions that are too severe degrade the liberated monosaccharides into materials that are not quantified by this procedure, again biasing the results low.

Incomplete neutralization and removal of acetic acid from the methylene chloride extract prior to GC analysis can result in a ghost peak appearing in the chromatogram or in carryover of monosaccharaides from one injection to the next, leading to erroneous quantitation.

Test specimens not suitable for this analysis include alkaline- and acid-pretreated biomass samples that have not been washed. Untreated pretreated biomass samples containing free acid or alkali may change visibly on heating. Materials containing nonstructural carbohydrates are also unsuitable for this procedure because nonstructural carbohydrates may undergo degradation to materials that are not quantified in this procedure.

ANALYSIS

A complete sequence of analysis includes pretreatment of specimens with 12 M sulfuric acid; dilution and autoclaving of specimens and loss factor sample solutions; filtration of insoluble from hydrolyzates and loss factor sample solutions; derivatization of monosaccharides in GC calibration standards, loss factor calibration solution, loss factor sample solution, and in hydrolyzates specimens; GC analysis of derivatized GC calibration standards, loss factor calibration solution, loss factor sample solutions, and hydrolysate specimens; and finally, calculation of anhydrosugar contents.

PRECISION

The data for these calculations have not yet been completed.

Abstract

There are about a dozen ASTM standards that apply to bioenergy materials issued by ASTM E48 Committee. These are summarized here regarding the test significance, test summary, and test precision, where available.

Keywords

bioenergy, analysis methods

Chapter 8 | ASTM Proficiency Testing Programs for Biofuels[1]

Proficiency testing programs (PTPs) play an important role in maintaining the quality of data produced in a laboratory. PTPs are useful statistical quality assurance tools to monitor the strengths and weaknesses of a laboratory's performance. Many laboratory accreditation agencies require laboratory participation in such programs. Two significant PTPs sponsored by ASTM Committee D02 on Petroleum Products and Lubricants have been those on biodiesel and fuel ethanol that were launched in the past few years.

ASTM Proficiency Testing Programs

A PTP can be defined as a testing program where identical samples are sent to participating laboratories where they are analyzed using standard test methods and the results reported for statistical treatment. PTPs, also known as crosschecks, check schemes, and round-robins, provide an expedient means of assessing the performance bias of one laboratory relative to other laboratories with the same industrial focus.

Several papers have been published describing the details of ASTM Committee D02's proficiency testing programs [1–8]. A brief summary follows. In general, ASTM PTPs are designed to provide participating laboratories (who pay a fee to participate) with a way to periodically compare their level and consistency of testing with that of other participating laboratories utilizing ASTM standard test methods. Participants receive sample material and specific instructions for performing the tests. Each laboratory electronically records and submits its test data from a program trial to ASTM for processing into an overall statistical summary report.

Robust statistics are used to calculate the data mean and standard deviation [9]. The use of robust statistics versus conventional statistics limits the data rejected as outliers given the wide diversity of laboratories involved and sometimes the wide range of results received. However, because of the use of robust statistics, for a number of program tests, the reproducibility of the data generated from these crosschecks is worse than the expected reproducibility estimates published in the ASTM standard test methods. In spite of a sometimes wide range of results reported, no outliers are rejected, resulting in overall poor precision. The Anderson-Darling (AD) statistic is used to test if a sample of data came from a population with a specific distribution. Essentially, for all ASTM PTP test data generated, the AD statistical application performs a "goodness of fit" or "normalcy" test to determine if the data are from a normal distribution. The PTP test data population is tested against normal behavior and measurement resolution adequacy using the AD statistic. Gross violations (AD >1.0) are flagged and a comment is added to the data tables stating that the data should *not* be interpreted using conventional normal distribution based probabilities.

It is suspected that some of the factors contributing to this poor reproducibility are due to laboratories not correctly following the test method details or not performing adequate and frequent calibrations and routine quality control (or to both). One final information tool found useful is that for each test a calculation of the test performance index (TPI) is performed and reported. This calculation is defined as the ratio of test method reproducibility divided by the robust reproducibility of the PTP data set. Index criteria for deciding what the TPI means are as follows, as excerpted from ASTM Standard Guide D7372 (Table 8.1).

TPI values in the range <0.8 to 1.2 should lead all laboratories to consider their own contribution to the relatively poor performance by the industry group. The subcommittee responsible for the test should also review if the published precision reflects reality. Whether improvement in the test methods used in a PTP is needed or not can be judged from the TPI. Some TPIs are satisfactory, but many are not, indicating (1) improvement in the laboratory performance is needed, (2) test method improvement is needed, (3) alternate test methods need be investigated, or (4) product specification limits need to be reviewed to be in conformance with the expected test variability (or any combination of these factors).

ASTM final statistical summary reports are provided to each participating laboratory who submitted data for the trial. Each laboratory's data are coded with only the participant knowing its own laboratory identification code. The various standards-writing subcommittees of Committee D02 also receive these anonymous data reports as a review of the status of their test methods to determine if any revisions to the method are warranted.

Because of electronic enhancements, the entire cycle of data reporting and the publishing of the final report is done electronically, thus reducing the turnaround time of final reports for the

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[1] Some text in this chapter is excerpted from and updated from Reference 8.10.

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TABLE 8.1 Implications of Test Performance Indexes

Test Performance Index	Implications
>1.2	The performance of the group providing data is probably satisfactory relative to the corresponding ASTM published precision.
0.8 to 1.2	The performance of the group providing data may be marginal and each laboratory should consider reviewing the test method procedures to identify opportunities for improvement.
<0.8	The performance of the test method as practiced by the group is not consistent with the ASTM published precision and laboratory method and performance improvements should be investigated by all the laboratories.

data submission deadline. Typically, all final summary reports for each test trial are delivered within 30 days of the data submission deadline. This enables the participants to quickly take all corrective actions necessary that immediately impact or affect their quality assurance activities.

Each laboratory analyzes the crosscheck sample only once—except for the ultra-low sulfur diesel (ULSD) program where it is analyzed in duplicate because of the request from the U.S. Environmental Protection Agency. Most programs are conducted three times a year, with the exception of the reformulated gasoline and ULSD programs, which are conducted monthly.

The potential benefits of participating in a PTP exercise are multiple:

- It provides a laboratory with a means to measure its competence against industry laboratories.
- It provides a consistent foundation of performance that customers and data users can rely on.
- It monitors the strengths and weaknesses of a laboratory's test performance.
- It provides a quality control tool for long-term performance.
- It provides a material with assigned mean values and variance limits that can later be used for laboratory quality control.
- It provides information to the sponsoring standards-writing subcommittees on how well their test methods are performing in the "real world" to measure product properties of interest with sufficient precision and accuracy.
- Participation in a PTP satisfies laboratory accreditation requirements for many organizations (e.g., American Association for Laboratory Accreditation, American Petroleum Institute [API], American Chemistry Council, etc.).

The final statistical summary report contains the number of valid data points, each laboratory's (coded for anonymity) test results, their deviations from the mean value, flagged outliers, and other pertinent information. It contains a summary box giving robust mean, robust standard deviation, the crosscheck reproducibility versus the test method reproducibility, an Anderson-Darling statistic, and calculated TPI value (Fig. 8.1). Because only a single aliquot is analyzed, only reproducibility can be calculated, not repeatability, except for the ULSD program where duplicate samples are analyzed by each laboratory and a repeatability value is reported. The summary report also contains Z-scores for each laboratory. This is a standardized and dimensionless measure of the difference between an individual result in a data set and the robust mean of the data set. This score is expressed in units of standard deviation of the data set by dividing the actual difference between the lab result and the robust mean by the robust standard deviation of the overall data set.

$$\text{Lab Z-Score} = \frac{(\text{Lab Result} - \text{Robust Mean})}{\text{Overall Robust Standard Deviation}}$$

The sign (+ or –) preceding the Z-score reflects the magnitude of the relative bias of the individual result versus the robust mean of the sample group. The sign and the magnitude of the mean Z-score for a series over a selected time period are an indication of the long-term relative bias. The significance of bias increases as the Z-Score mean moves farther away from zero.

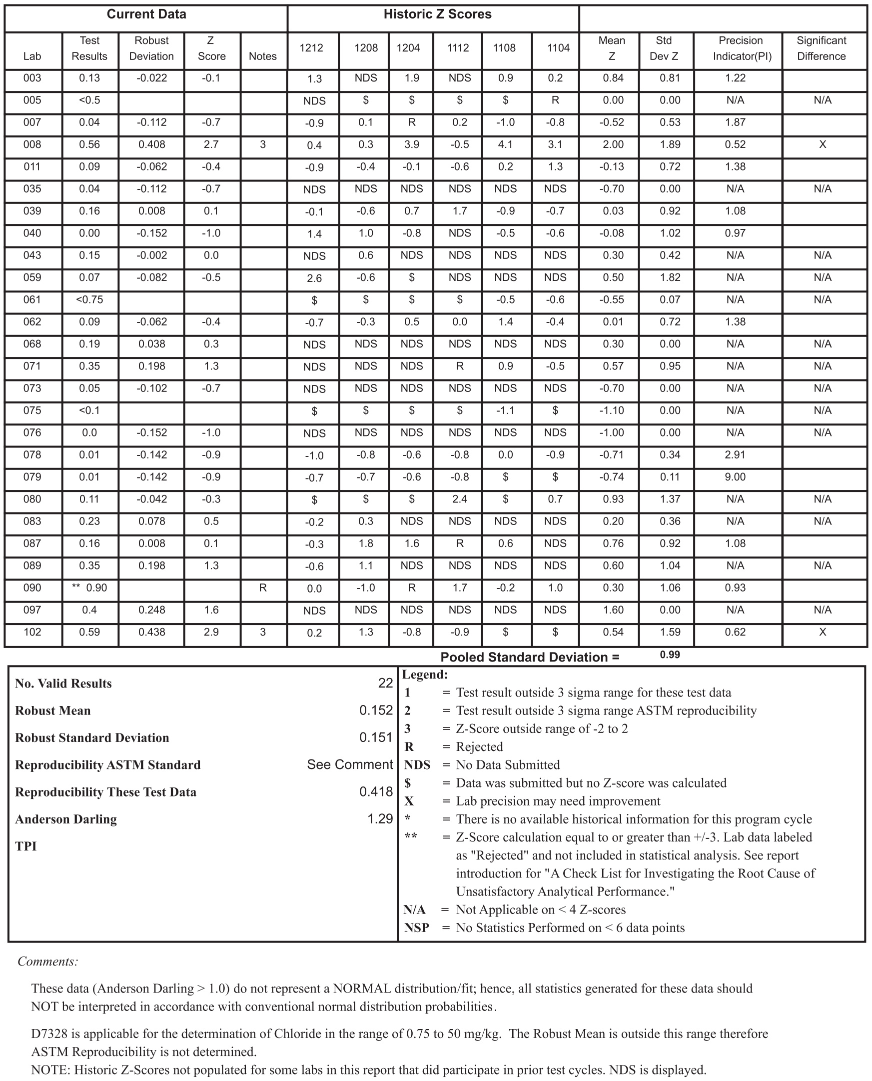
Additionally, each report contains a chart plotting test results by laboratory code for each test (e.g., Fig. 8.2 for sulfur determination by ASTM D5453 in analysis of ETOH 1304 sample) and a histogram distribution of the results about the sample mean (e.g., Fig. 8.3 of pHe determination by ASTM D6423 in ETOH 1304 sample). Other figures demonstrate different histogram patterns, such as Fig. 8.4 of flash point determination by ASTM D93 C in a sample of biodiesel (BIOD) 1308 and Fig. 8.5 of methanol content by gas chromatography ASTM D5501 in a sample of ETOH 1308. Not all the histograms are in normal or in ideal bell shape, indicating uneven and biased distribution of the data.

In cases where the same parameter is determined using multiple test methods, a box and whisker plot is provided to compare alternate methods for the same analysis (e.g., Fig. 8.6 showing acid number determination by ASTM D664 and ASTM D974 in a sample of BIOD 1308, Fig. 8.7 showing results for carbon residue by ASTM D189 and ASTM D4530 in a sample of BIOD 1308, and Fig. 8.8 showing the results of flash point determination in a sample of BIOD 1308). Ideally, in all these examples, the mean of the results for a sample using alternate tests should be equivalent. This may or may not be the case in these real examples. Precisions of individual test methods purportedly determining the same parameter may also be quite different. Thus, a best test method chosen for an analysis should take this history into account.

A number of D02 Committee statistical standards are utilized in processing the large amount of data produced in this program (Table 8.2).

Thus, the PTPs offer a way for those involved in laboratory operations, writers of product specifications, and those involved in development of precision statements for the test methods to gain insights into performance in the operations of the real world. ASTM D7372, *Standard Guide for Analysis and Interpretation of Proficiency Test Program Results*, can be used to evaluate the performance of a laboratory or a group of laboratories participating in any of the 28 proficiency testing programs involving petroleum products and lubricants.

FIG. 8.1 Analytical data report page for ASTM D7328, *Determination of Total Inorganic Chloride in ETOH 1304 Sample*.



Current Data					Historic Z Scores									
Lab	Test Results	Robust Deviation	Z Score	Notes	1212	1208	1204	1112	1108	1104	Mean Z	Std Dev Z	Precision Indicator(PI)	Significant Difference
003	0.13	-0.022	-0.1		1.3	NDS	1.9	NDS	0.9	0.2	0.84	0.81	1.22	
005	<0.5				NDS	$	$	$	$	R	0.00	0.00	N/A	N/A
007	0.04	-0.112	-0.7		-0.9	0.1	R	0.2	-1.0	-0.8	-0.52	0.53	1.87	
008	0.56	0.408	2.7	3	0.4	0.3	3.9	-0.5	4.1	3.1	2.00	1.89	0.52	X
011	0.09	-0.062	-0.4		-0.9	-0.4	-0.1	-0.6	0.2	1.3	-0.13	0.72	1.38	
035	0.04	-0.112	-0.7		NDS	NDS	NDS	NDS	NDS	NDS	-0.70	0.00	N/A	N/A
039	0.16	0.008	0.1		-0.1	-0.6	0.7	1.7	-0.9	-0.7	0.03	0.92	1.08	
040	0.00	-0.152	-1.0		1.4	1.0	-0.8	NDS	-0.5	-0.6	-0.08	1.02	0.97	
043	0.15	-0.002	0.0		NDS	0.6	NDS	NDS	NDS	NDS	0.30	0.42	N/A	N/A
059	0.07	-0.082	-0.5		2.6	-0.6	$	NDS	NDS	NDS	0.50	1.82	N/A	N/A
061	<0.75				$	$	$	$	-0.5	-0.6	-0.55	0.07	N/A	N/A
062	0.09	-0.062	-0.4		-0.7	-0.3	0.5	0.0	1.4	-0.4	0.01	0.72	1.38	
068	0.19	0.038	0.3		NDS	NDS	NDS	NDS	NDS	NDS	0.30	0.00	N/A	N/A
071	0.35	0.198	1.3		NDS	NDS	NDS	R	0.9	-0.5	0.57	0.95	N/A	N/A
073	0.05	-0.102	-0.7		NDS	NDS	NDS	NDS	NDS	NDS	-0.70	0.00	N/A	N/A
075	<0.1				$	$	$	$	-1.1	$	-1.10	0.00	N/A	N/A
076	0.0	-0.152	-1.0		NDS	NDS	NDS	NDS	NDS	NDS	-1.00	0.00	N/A	N/A
078	0.01	-0.142	-0.9		-1.0	-0.8	-0.6	-0.8	0.0	-0.9	-0.71	0.34	2.91	
079	0.01	-0.142	-0.9		-0.7	-0.7	-0.6	-0.8	$	$	-0.74	0.11	9.00	
080	0.11	-0.042	-0.3		$	$	$	2.4	$	0.7	0.93	1.37	N/A	N/A
083	0.23	0.078	0.5		-0.2	0.3	NDS	NDS	NDS	NDS	0.20	0.36	N/A	N/A
087	0.16	0.008	0.1		-0.3	1.8	1.6	R	0.6	NDS	0.76	0.92	1.08	
089	0.35	0.198	1.3		-0.6	1.1	NDS	NDS	NDS	NDS	0.60	1.04	N/A	N/A
090	** 0.90			R	0.0	-1.0	R	1.7	-0.2	1.0	0.30	1.06	0.93	
097	0.4	0.248	1.6		NDS	NDS	NDS	NDS	NDS	NDS	1.60	0.00	N/A	N/A
102	0.59	0.438	2.9	3	0.2	1.3	-0.8	-0.9	$	$	0.54	1.59	0.62	X

Pooled Standard Deviation = 0.99

No. Valid Results	22
Robust Mean	0.152
Robust Standard Deviation	0.151
Reproducibility ASTM Standard	See Comment
Reproducibility These Test Data	0.418
Anderson Darling	1.29
TPI	

Legend:
1 = Test result outside 3 sigma range for these test data
2 = Test result outside 3 sigma range ASTM reproducibility
3 = Z-Score outside range of -2 to 2
R = Rejected
NDS = No Data Submitted
$ = Data was submitted but no Z-score was calculated
X = Lab precision may need improvement
***** = There is no available historical information for this program cycle
****** = Z-Score calculation equal to or greater than +/-3. Lab data labeled as "Rejected" and not included in statistical analysis. See report introduction for "A Check List for Investigating the Root Cause of Unsatisfactory Analytical Performance."
N/A = Not Applicable on < 4 Z-scores
NSP = No Statistics Performed on < 6 data points

Comments:

These data (Anderson Darling > 1.0) do not represent a NORMAL distribution/fit; hence, all statistics generated for these data should NOT be interpreted in accordance with conventional normal distribution probabilities.

D7328 is applicable for the determination of Chloride in the range of 0.75 to 50 mg/kg. The Robust Mean is outside this range therefore ASTM Reproducibility is not determined.
NOTE: Historic Z-Scores not populated for some labs in this report that did participate in prior test cycles. NDS is displayed.

ASTM International has been a pioneer in PTP programs for a number of years. The most prominent among such programs is the one sponsored by ASTM Committee D02 on Petroleum Products and Lubricants, entitled the ASTM Interlaboratory Crosscheck Program (ILCP). This program was initiated in 1993 and now covers 28 products spanning virtually all products produced or analyzed in the oil industry (or both). More than 3,300 laboratories worldwide are participating in these programs; of these, more than 57 % are non-U.S.-based.

Biofuel Proficiency Testing Programs

Biofuel PTP programs [10] were added to the scope of Committee D02's PTPs. The biodiesel PTPs began in 2005 and now involve 118 labs and about 30 test methods. The fuel ethanol program was started in 2007 and now involves 115 labs and 14 test methods. Each program is conducted three times a year: April, August, and November for biodiesel, and April, August, and December for fuel ethanol. The cost of each program (in 2015) was $689 and $717 per year per participant, respectively. In recent years, the most significant growth in the PTPs for petroleum products has been in these two programs. The status of these two programs is given in Table 8.3. However, it should be noted that in spite of the seemingly substantial number of total labs participating in these two programs, the actual data returned for individual tests in these programs are far less. The tests used in these two ILCPs are included in Table 8.4.

Most of the tests in each program appear in the biofuel specifications for each product (Table 8.4). Some of the tests selected from the specifications are not appropriate for the

FIG. 8.2 S-chart for sulfur determination by test method ASTM D5453 in ETOH 1304 sample.

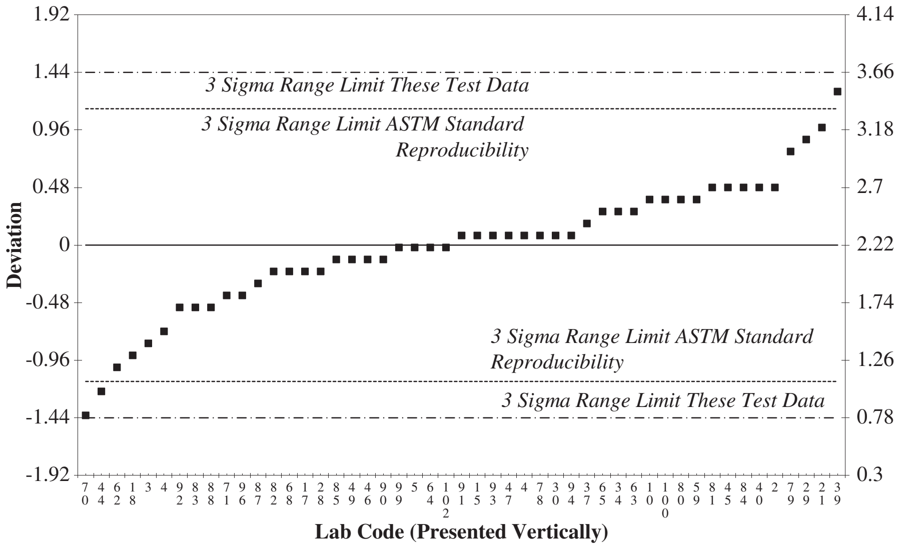
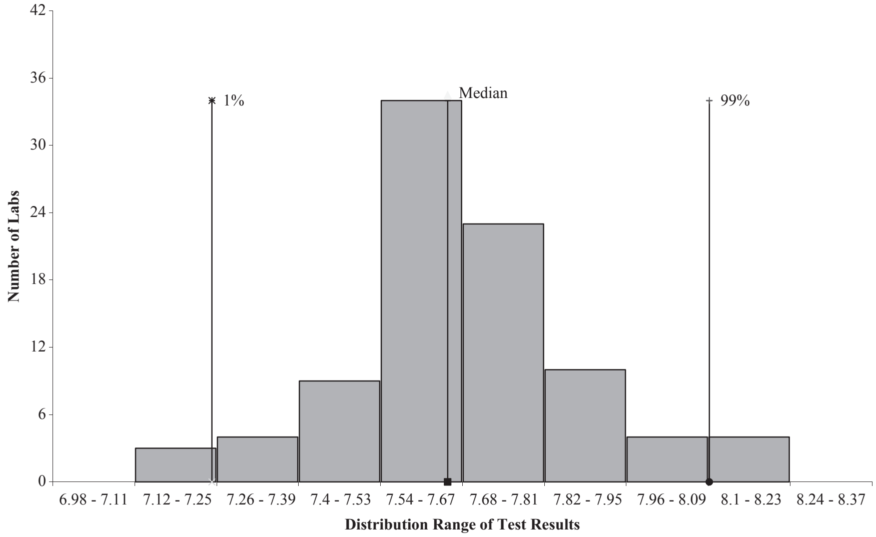


FIG. 8.3 Histogram of pHe determination results using test method ASTM D6423 in ETOH 1304 sample.



specific analysis desired on the biofuel. Not all laboratories report results for each of these program tests. Laboratory participants are allowed the freedom to report the results for those tests they typically perform and that they are capable of carrying out. Table 8.5 summarizes the data for fuel ethanol test trials, and Table 8.6 summarizes the data for biodiesel test trials, in both cases from 2012 through 2014.

Several of the analyses can be done using alternate test methods where available. Generally, the alternate test methods give equivalent results within their individual test method variability (see Table 8.7 for biodiesel and Table 8.8 for fuel ethanol). Some of the data are shown as box and whisker graphs in Figs. 8.6–8.8 for acid number (ASTM D664 and ASTM D974), carbon residue (ASTM D189 and ASTM D4530), and for flash point (ASTM D93A, ASTM D93C, and ASTM D3828), respectively, for sample BIOD 1308.

As mentioned earlier, TPI is a way of measuring not only a laboratory's proficiency but also as a way of checking on how well the industry as a group is performing, including how well the selected test method is suited for the desired analysis. These data are summarized in Table 8.9 for the six trials conducted in 2013 for both biofuels.

As one can easily interpret from this table, a number of tests required in the product specifications for both biodiesel fuel and fuel ethanol have not produced satisfactory precision (i.e., >1.00 TPI). In addition, a large number of tests are not being conducted by

FIG. 8.4 Histogram of flash point determination results using test method ASTM D93 Procedure C in BIOD 1308 sample.

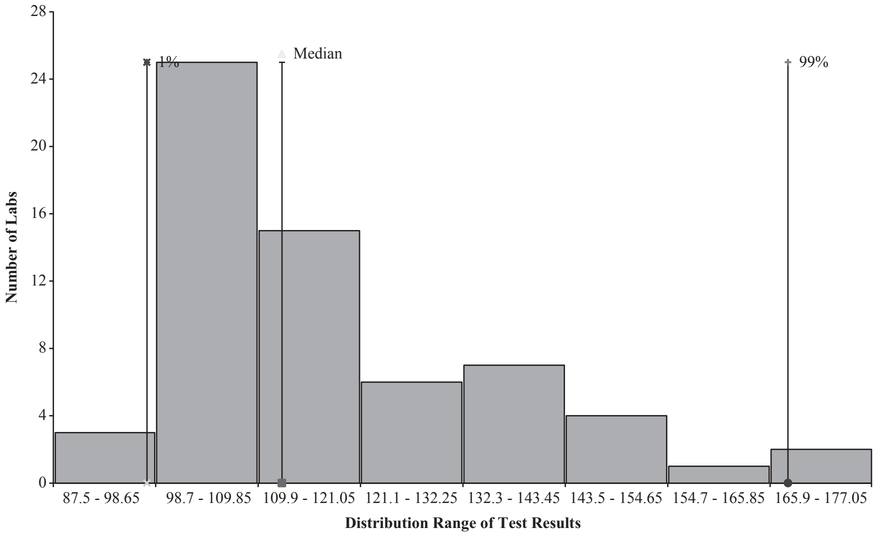
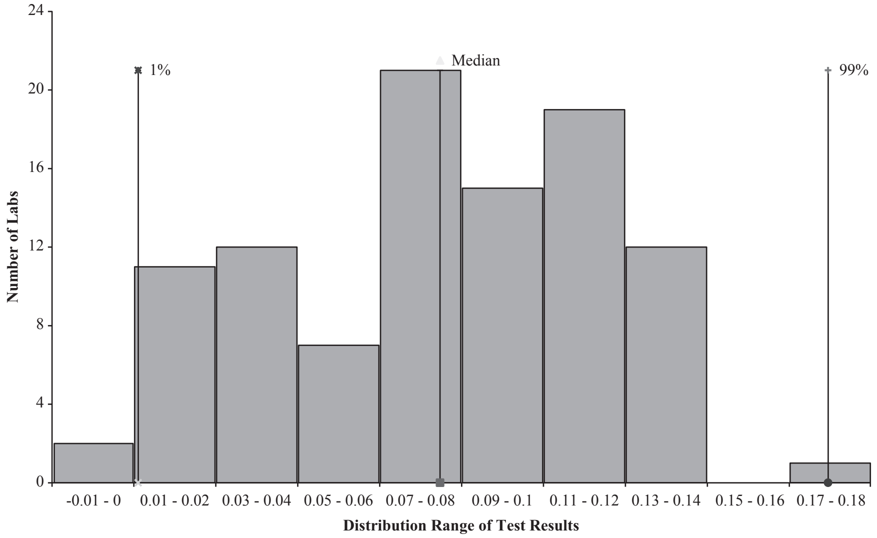
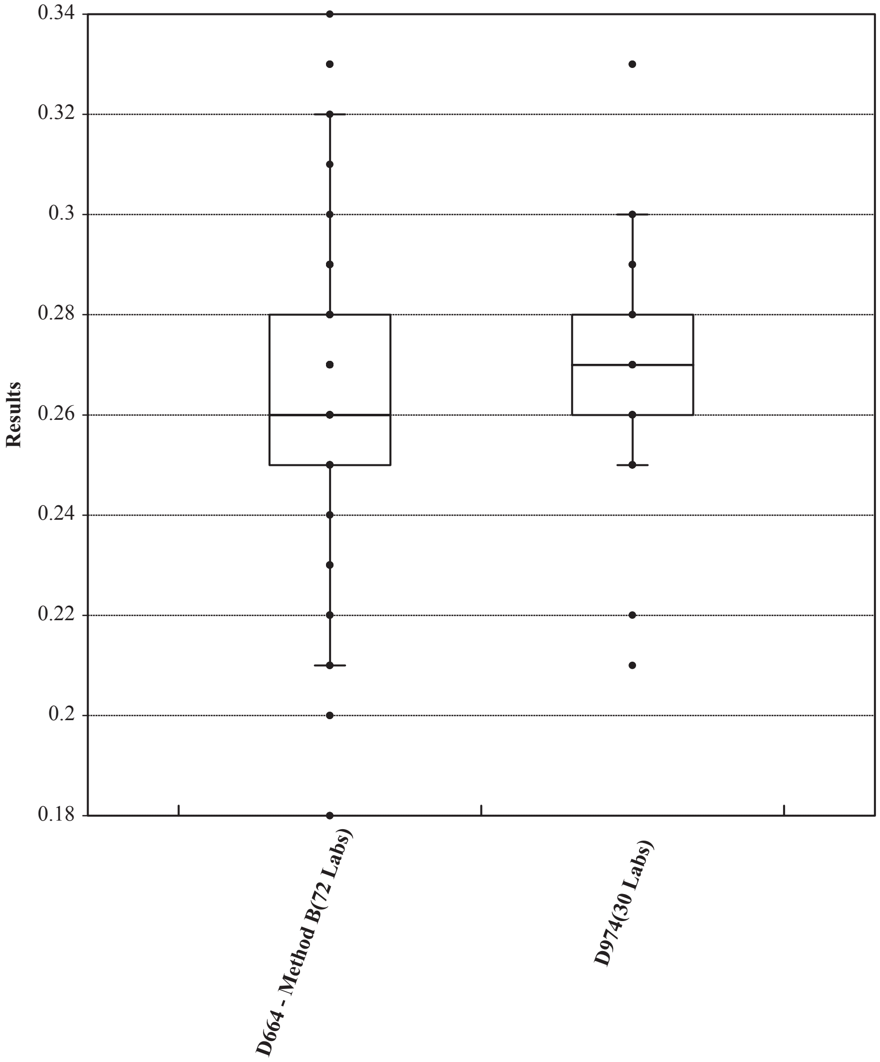


FIG. 8.5 Histogram of ethanol/methanol results using test method ASTM D5501 in ETOH 1308 sample.



many laboratories. It would be interesting to find out how the product batches are certified as meeting the product specification requirements when these tests are not being carried out by many of the production laboratories participating in the PTP. More importantly, it is recognized that many of the tests required in the product specifications do not have biofuels as applicable in their scopes and no precision data for biofuels are given for such analyses. Thus, how would the product quality disagreements be resolved, especially since this requires reproducibility data per ASTM D3244, *Practice for Utilization of Test Data to Determine Conformance with Specifications*, or its equivalent ISO 4259 standard? Some of these tests are conducted by a large number of laboratories; however, no TPI can be calculated because of the lack of a reproducibility value or calculation provided in the test methods (e.g., ASTM D445 kinematic viscosity, ASTM D874 sulfated ash, ASTM D4951 phosphorus, ASTM D482 ash, etc.). For a large number of tests, however, the TPIs leave much to be desired (Table 8.9). This could be because the laboratories do not have enough experience in conducting these tests, the tests need modifications to suit the biofuel matrix, or the test method reproducibility used in calculating the TPI is not valid for this matrix. Also, some designated tests are completely wrong for the required analyses (e.g. ASTM D4951, inductively coupled plasma atomic emission spectrometry method for metals is meant for additives and lubricating oils at a high level of phosphorus not for trace quantities present in biodiesel; the same is true for ASTM D1688 for copper in fuel ethanol).

FIG. 8.6 Box and whisker graph of acid number results in BIOD 1308 sample.

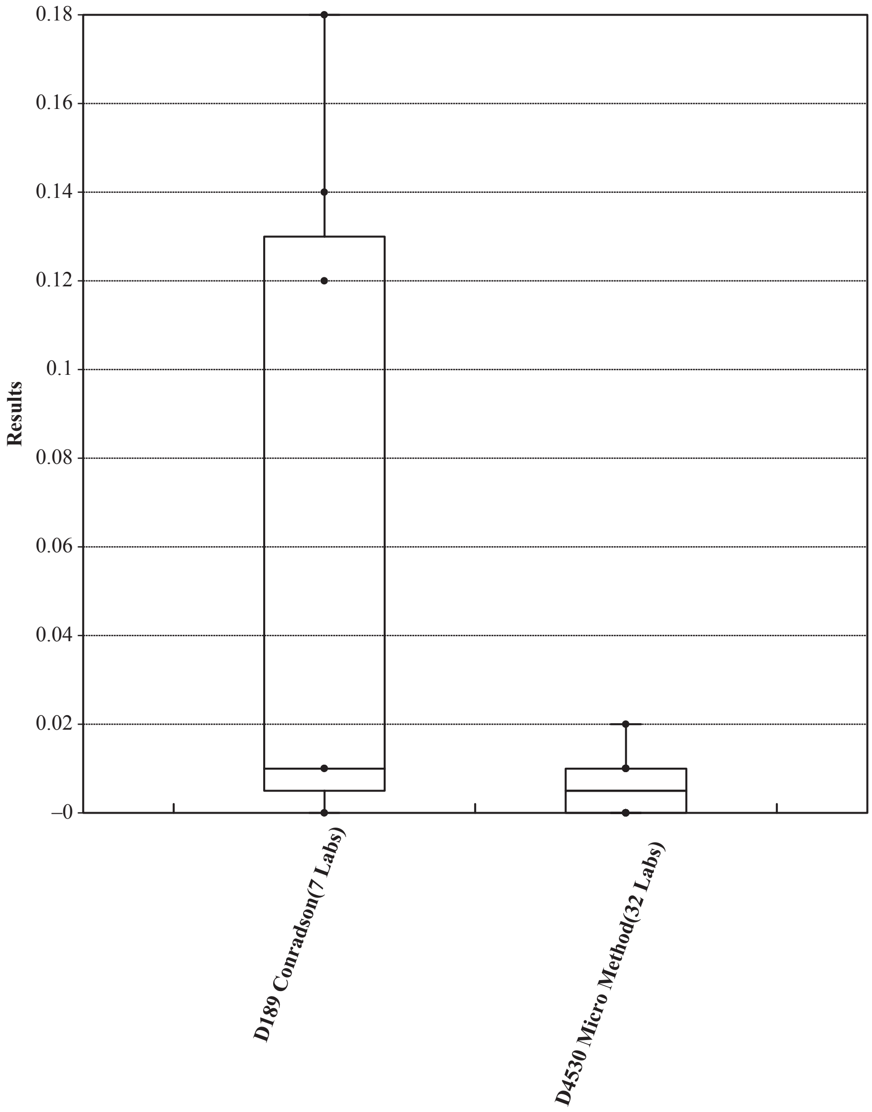


Overall ranges of TPIs obtained over the years of the biofuels programs are qualitatively summarized in Table 8.10. Several tests can use improvement in them for biofuels analysis.

In Figs. 8.1–8.8, data generated in this program are shown as examples of charts produced. The examples are typical of those obtained for biodiesel and ethanol fuel samples routinely analyzed in this program. Fig. 8.1 shows a page of the results from all participating laboratories for the April 2013 cycle of ethanol fuel for total inorganic chloride using ASTM D7328. Fig. 8.2 depicts the results of sulfur by ASTM D5453 in an ethanol fuel sample analyzed in April 2013. Fig. 8.3 shows the distribution of results for pHe by ASTM D6423 using a histogram. The histogram is reasonably close to a normal bell-shaped curve. Although most of the histograms for all test analyses look satisfactory, scrutiny of individual diagrams shows some unsatisfactory results—such as abnormal distribution of data and worrisome trends in the data sets. In Fig. 8.4 of flash point determination using the ASTM D93 Procedure C of a biodiesel sample from August 2013, some laboratories are getting very high or very low results. Similarly, Fig. 8.5 shows a wide variation in the results distribution for methanol content as determined by ASTM D5501 in an ethanol fuel sample of August 2013. The histogram is in a very poor shape, far from a normal distribution. These laboratories need to check whether they are doing something different than the rest of the laboratories and take corrective actions where necessary.

Figs. 8.7 and 8.8 show the data from biodiesel samples analyzed in August 2013, comparing the alternate test methods used for determination of acid number by ASTM D664 and ASTM D974 for the determination of carbon residue by ASTM D189 and ASTM D4530 and the determination of flash point by ASTM D93 Procedures A and C, and ASTM D3828. These box and whisker graphs are meant to provide a cross reference of test data generated from different procedures and methods that measure the same test parameter. The box and whisker graph separates the test data by standard, with the shaded box representing the middle 50 % of test data centered around the median. The horizontal

FIG. 8.7 Box and whisker graph of carbon residue results in BIOD 1308 sample.



line within the box represents the median of the reported data. The whisker length has been adjusted to the last data point that falls within 1.5 times the difference between the upper and lower value of the shaded box. Data points above or below the whisker are included, unless the data is off the "Y" axis scale. Data that would be plotted off the graph are indicated with an arrow. Outlier data are not included in this graph. The "Y" axis scale represents the absolute value; the "X" axis scale provides an identification of the test method and number of reporting data points. In these particular cases, the alternate test methods used for these analyses by different laboratories have given results within the reproducibility of the methods.

In these box and whisker examples, acid number results overlap for each of the test methods, although the precision of each test method is quite different. In the example of carbon residue determination, the means are about the same, but there is a wide disparity between the precisions obtained for the ASTM D189 and ASTM D4530 test methods for the determination of carbon residue. Finally, in the case of flash point determination, three test methods have produced significantly different mean results as well as a wide spread of the results.

In summary, there are many advantages in participating in the ASTM Proficiency Testing Program, particularly for new matrices such as biofuels. The biggest take-home advantage is that two parties gain from the ASTM Proficiency Testing Program. The first party is the participating laboratory who can readily identify and correct their testing weaknesses, if necessary, and ultimately improve their overall quality assurance. The second party is the ASTM standardization authorities who are responsible for the technical credibility and use of the published ASTM product specifications and supporting test methods. Through both ASTM processes, the standards for the industry are being improved to best serve the new marketplace needs through utilizing new product matrices.

FIG. 8.8 Box and whisker graph of flash point results in BIOD 1308 sample.

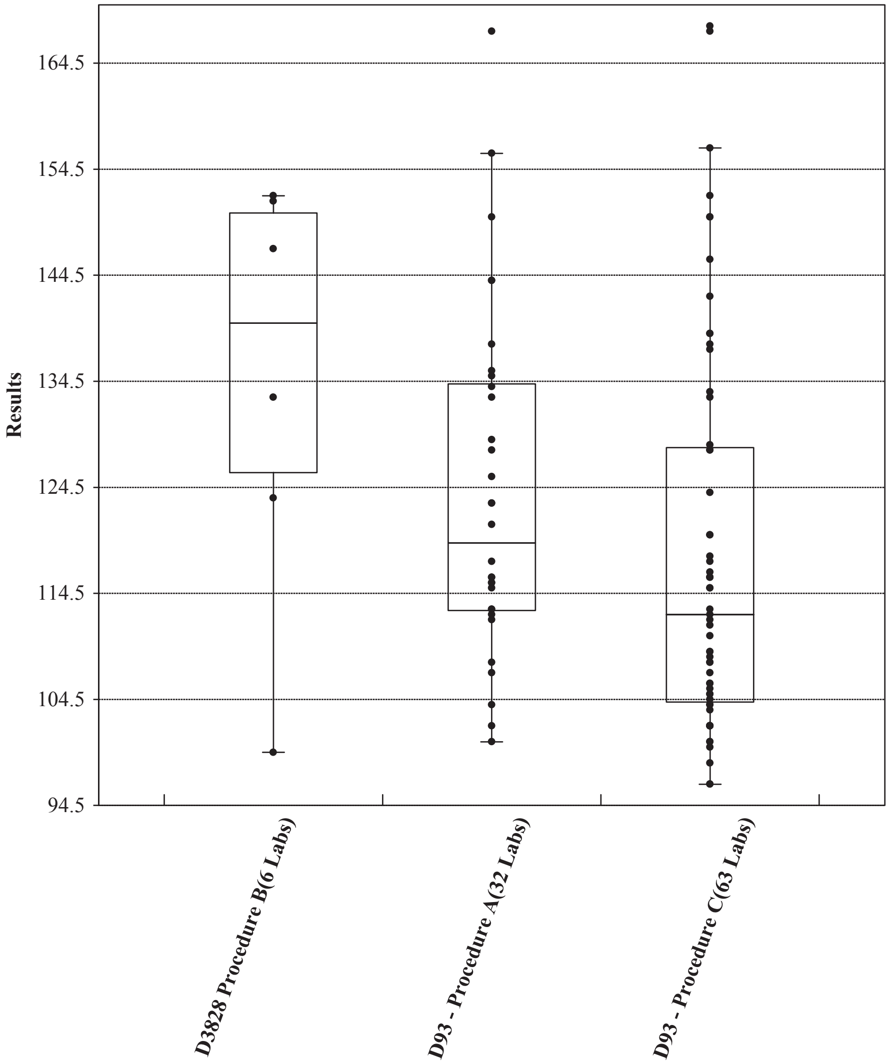


TABLE 8.2 D02 Committee Statistical Standards Utilized in Coordinating Subcommittee 92 (CS 92) Proficiency Testing Programs

D02 Standard	Subject
ASTM D3244	Practice for Utilization of Test Data to Determine Conformance with Specifications
ASTM D6259	Practice for Determination of a Pooled Limit of Quantitation for a Test Method
ASTM D6299	Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
ASTM D6300	Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants
ASTM D6617	Practice for Laboratory Bias Detection Using Single Test Result from Standard Material
ASTM D6708	Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material
ASTM D6792	Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories
ASTM D7372	Guide for Analysis and Interpretation of Proficiency Test Program Results
ASTM D7778	Guide for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
ASTM D7915	Practice for Application of Generalized Extreme Studentized Deviate (GESD) Technique to Simultaneously Identify Multiple Outliers in a Data Set

TABLE 8.3 Current Status of ASTM Biofuels Proficiency Testing Programs

Year	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Biodiesel (April, August, November)	40	51	88	118	126	121	119	119	120	131	123
Ethanol Fuel (April, August, December)	-	-	51	80	81	93	110	116	120	119	115

TABLE 8.4 Tests Used in Biofuels Interlaboratory Crosscheck Program

Analysis	Biodiesel ILCP	Fuel Ethanol ILCP
Acidity	ASTM D664; ASTM D974	ASTM D1613
Ash	ASTM D482	
Carbon Residue	ASTM D4530; ASTM D189	
Cloud Point	ASTM D2500; ASTM D3117; ASTM D5771; ASTM D5773	
Cold Filter Plugging Point	ASTM D6371	
Cold Soak Filtration	ASTM D7501	
Copper		ASTM D1688 A
Copper Corrosion	ASTM D130	
Density	ASTM D1298; ASTM D4052	ASTM D4052
Distillation	ASTM D1160	
Ethanol/Methanol		ASTM D5501
Flash Point	ASTM D93; ASTM D3828	
Glycerin	ASTM D6584	
Inorganic Chloride		ASTM D7319; ASTM D7328
Kinematic Viscosity	ASTM D445; ASTM D7042	
Lubricity	ASTM D6079	
Metals (Ca, Na, K, Mg)	EN 14538	
Methanol	EN 14110	
Oxidation Stability	EN 14112	
Particulate Contamination	ASTM D7321	
pHe		ASTM D6423
Phosphorus	ASTM D4951	
Solvent Washed Gum		ASTM D381
Sulfate		ASTM D7318; ASTM D7319; ASTM D7328
Sulfated Ash	ASTM D874	
Sulfur	ASTM D5453; ASTM D1266; ASTM D6428, ASTM D7039	ASTM D5453; ASTM D7039
Thermal Stability	ASTM D6468	
Water by Karl Fisher	ASTM D6304	ASTM E203; ASTM E1064
Water and Sediment	ASTM D2709	

TABLE 8.5 Proficiency Testing Analysis of Fuel Ethanol

Period Analysis	Test Method	1204	1208	1212
Acidity	ASTM D1613	0.000117 ± 0.00046 (76)	0.01318 ± 0.0066 (78)	0.00406 ± 0.00109 (83)
Gum	ASTM D381	0.18 ± 0.30 (40)	0.59 ± 0.55 (36)	0.27 ± 0.34 (40)
Density	ASTM D4052	0.7915 ± 0.00038 (76)	0.7927 ± 0.00028 (71)	0.7946 ± 0.00043 (83)
Ethanol	ASTM D5501	98.13 ± 0.168 (82)	96.81 ± 0.326 (79)	96.42 ± 0.28 (84)
Methanol	ASTM D5501	0.010 ± 0.008 (68)	0.233 ± 0.110 (84)	0.082 ± 0.054 (90)
pHe	ASTM D6423	6.96 ± 1.041 (88)	7.584 ± 0.146 (76)	7.593 ± 0.197 (84)
Sulfur	ASTM D5453	1.51 ± 0.40 (49)	1.91 ± 0.57 (46)	1.79 ± 0.54 (50)
Sulfur	ASTM D7039	1.19 ± 0.43 (20)	1.38 ± 0.44 (17)	1.34 ± 0.46 (19)
Sulfate	ASTM D7319	0.17 ± 0.14 (32)	0.11 ± 0.12 (30)	—
Sulfate	ASTM D7328	0.213 ± 0.206 (21)	0.263 ± 0.271 (24)	0.364 ± 0.302 (21)
Chloride	ASTM D7319	0.03 ± 0.06 (33)	0 ± 0 (23)	—
Chloride	ASTM D7328	0.043 ± 0.055 (8)	0.099 ± 0.095 (20)	0.229 ± 0.209 (19)
Water	ASTM E1064	0.0191 ± 0.0052 (80)	0.2282 ± 0.0103 (71)	1.025 ± 0.0276 (69)
Water	ASTM E203	0.0185 ± 0.0054 (17)	0.2272 ± 0.0234 (16)	1.011 ± 0.0415 (18)
Period Analysis	**Test Method**	**1304**	**1308**	**1312**
Acidity	ASTM D1613	0.00414 ± 0.0011 (85)	0.00436 ± 0.00098 (92)	0.00433 ± 0.00092 (92)
Gum	ASTM D381	0.37 ± 0.37 (42)	0.21 ± 0.31 (36)	0.20 ± 0.28 (41)
Density	ASTM D4052	0.7945 ± 0.0004 (77)	0.7946 ± 0.0004 (86)	0.7946 ± 0.00042 (84)
Ethanol	ASTM D5501	96.82 ± 0.19 (88)	96.76 ± 0.21 (98)	96.75 ± 0.196 (95)
Methanol	ASTM D5501	0.071 ± 0.037(92)	0.079 ± 0.044 (100)	0.077 ± 0.043 (98)
pHe	ASTM D6423	7.672 ± 0.181(91)	7.384 ± 0.233 (94)	7.358 ± 0.258 (94)
Sulfur	ASTM D5453	2.22 ± 0.48 (49)	2.57 ± 0.50 (50)	2.56 ± 0.45 (51)
Sulfur	ASTM D7039	1.56 ± 0.55 (18)	1.89 ± 0.47 (24)	2.26 ± 0.39 (19)
Sulfate	ASTM D7319	0.17 ± 0.17 (34)	—	0.60 ± 0.31 (46)
Sulfate	ASTM D7328	0.309 ± 0.293 (25)	0.784 ± 0.563 (25)	0.723 ± 0.314 (25)
Chloride	ASTM D7319	0.13 ± 0.14 (30)	—	0.08 ± 0.11 (34)
Chloride	ASTM D7328	0.152 ± 0.151 (22)	0.188 ± 0.177 (22)	0.145 ± 0.132 (19)
Water	ASTM E1064	0.9153 ± 0.0247 (80)	0.9733 ± 0.0316 (86)	0.9763 ± 0.0312 (85)
Water	ASTM E203	0.9057 ± 0.0286 (17)	0.9636 ± 0.0319 (17)	0.9679 ± 0.0480 (20)
Period Analysis	**Test Method**	**1404**	**1408**	**1412**
Acidity	ASTM D1613	0.00195 ± 0.00063 (95)	0.00175 ± 0.00057 (86)	0.00185 ± 0.00066 (89)
Gum	ASTM D381	0.30 ± 0.38 (45)	0.27 ± 0.36 (40)	0.31 ± 0.40 (40)
Density	ASTM D4052	0.7935 ± 0.00046 (84)	0.7922 ± 0.00039 (81)	0.7921 ± 0.0004 (84)
Ethanol	ASTM D5501	97.45 ± 0.204 (94)	97.93 ± 0.207 (96)	97.88 ± 0.24 (98)
Methanol	ASTM D5501	0.024 ± 0.012 (90)	0.007 ± 0.007 (84)	0.008 ± 0.010 (86)
pHe	ASTM D6423	6.499 ± 0.50 (96)	7.223 ± 0.339 (95)	7.015 ± 0.230 (95)
Sulfur	ASTM D5453	1.74 ± 0.44 (46)	2.09 ± 0.50 (42)	2.19 ± 0.41 (48)
Sulfur	ASTM D7039	1.50 ± 0.38 (18)	1.51 ± 0.53 (22)	1.67 ± 0.45 (20)
Potential Sulfate	ASTM D7319	2.32 ± 0.83 (17)	1.36 ± 0.52 (18)	1.36 ± 0.68 (26)
Sulfate	ASTM D7319	2.16 ± 0.91 (55)	1.10 ± 0.43 (48)	1.07 ± 0.44 (56)
Sulfate	ASTM D7328	1.818 ± 0.568 (25)	1.10 ± 0.397 (25)	1.20 ± 0.46 (25)
Chloride	ASTM D7319	0.13 ± 0.17 (37)	0.09 ± 0.09 (33)	0.10 ± 0.11 (43)
Chloride	ASTM D7328	0.145 ± 0.126 (26)	0.168 ± 0.144 (24)	0.156 ± 0.129 (21)
Water	ASTM E1064	0.5541 ± 0.0196 (81)	0.1857 ± 0.0114 (88)	0.1809 ± 0.0068 (77)
Water	ASTM E203	0.5526 ± 0.0207 (25)	0.1883 ± 0.0152 (21)	0.1847 ± 0.0097 (26)

Note: All results are expressed as mean value ± robust standard deviation (number of valid results). No copper by ASTM D1688 per ASTM D4806 was detected in any of these programs. No inorganic sulfate by potentiometric lead titration ASTM D7318 was detected in any of these programs.

TABLE 8.6 Proficiency Testing Analysis of Biodiesel

Period Analysis	Test Method	1204	1208	1211
IBP	ASTM D1160	302.6 ± 40.6 (14)	269.1 ± 86.1 (12)	303.9 ± 48.5 (13)
	Auto Manual	301.6 ± 38.6 (12)	290.3 ± 55.4 (11)	329.5 ± 14.7 (11)
5 % Distill.	ASTM D1160	346.8 ± 2.2 (13)	346.3 ± 1.7 (11)	346.9 ± 1.1 (12)
	Auto Manual	337.2 ± 18.0 (12)	346.6 ± 3.8 (9)	346.7 ± 2.1 (9)
10 % Distill.	ASTM D1160	347.6 ± 1.4 (13)	347.5 ± 1.2 (11)	348.1 ± 0.9 (12)
	Auto Manual	345.5 ± 9.1 (10)	347.1 ± 1.2 (8)	347.4 ± 1.1 (9)
20 % Distill.	ASTM D1160	348.2 ± 1.0 (13)	348.2 ± 0.9 (11)	349.2 ± 0.9 (12)
	Auto Manual	347.4 ± 6.9 (10)	348.2 ± 1.1 (8)	347.9 ± 1.1 (9)
30 % Distill.	ASTM D1160	349.0 ± 1.2 (13)	348.9 ± 1.0 (11)	349.4 ± 1.1 (13)
	Auto Manual	344.4 ± 8.8 (11)	349.3 ± 1.5 (8)	348.2 ± 1.2 (9)
40 % Distill.	ASTM D1160	349.6 ± 1.2 (13)	349.4 ± 1.2 (11)	350.4 ± 0.8 (12)
	Auto Manual	349.1 ± 7.2 (10)	349.8 ± 1.3 (8)	348.7 ± 1.3 (9)
50 % Distill.	ASTM D1160	350.1 ± 1.2 (13)	350.1 ± 1.0 (11)	350.8 ± 1.0 (13)
	Auto Manual	349.5 ± 6.8 (10)	350.2 ± 1.5 (8)	349.1 ± 1.5 (9)
60 % Distill.	ASTM D1160	350.7 ± 1.1 (13)	350.7 ± 0.9 (11)	351.4 ± 1.3 (13)
	Auto Manual	350.5 ± 6.8 (10)	351.6 ± 2.5 (9)	350.0 ± 1.9 (9)
70 % Distill.	ASTM D1160	351.2 ± 1.0 (13)	351.1 ± 0.9 (11)	352.0 ± 1.4 (13)
	Auto Manual	350.8 ± 7.3 (10)	351.4 ± 1.2 (8)	350.9 ± 1.8 (9)
80 % Distill.	ASTM D1160	351.6 ± 0.9 (13)	351.5 ± 1.2 (11)	352.6 ± 1.4 (13)
	Auto Manual	351.6 ± 7.3 (10)	352.9 ± 2.4 (9)	351.9 ± 2.4 (9)
90 % Distill.	ASTM D1160	353.0 ± 0.9 (13)	352.8 ± 1.3 (11)	353.7 ± 1.7 (13)
	Auto Manual	353.1 ± 7.8 (10)	353.3 ± 1.6 (8)	352.7 ± 2.7 (9)
95 % Distill.	ASTM D1160	354.4 ± 1.2 (12)	354.6 ± 3.0 (10)	3556.1 ± 2.1 (11)
	Auto Manual	355.4 ± 6.3 (10)	355.3 ± 1.5 (8)	355.6 ± 1.4 (9)
FBP Distill.	ASTM D1160	366.8 ± 19.0 (14)	371.3 ± 18.6 (10)	374.9 ± 22.7 (12)
	Auto Manual	370.4 ± 14.2 (10)	364.9 ± 10.3 (9)	377.7 ± 16.3 (10)
API Gravity	ASTM D1298	28.36 ± 0.11 (19)	28.27 ± 0.10 (14)	28.43 ± 0.07 (19)
Density	ASTM D1298	0.8848 ± 0.00045 (32)	0.88493 ± 0.00059 (28)	0.88431 ± 0.00045 (29)
Density	ASTM D4052	0.8851 ± 0.00013 (48)	0.88527 ± 0.00016 (48)	0.88439 ± 0.00015 (46)
Carbon Residue	ASTM D189	0.010 ± 0.012 (11)	0.022 ± 0.026 (5)	0.010 ± 0.000 (4)
Carbon Residue	ASTM D4530	0.004 ± 0.006 (31)	0.007 ± 0.009 (34)	0.005 ± 0.006(37
Cloud Point	ASTM D2500	0.4 ± 1.2 (60)	0.5 ± 1.1 (53)	1.3 ± 1.2 (59)
Cloud Point	ASTM D5771	0.25 ± 0.56 (7)	0.44 ± 0.43 (7)	1.35 ± 0.50 (7)
Cloud Point	ASTM D5773	0.42 ± 0.43 (25)	0.18 ± 0.26 (21)	1.14 ± 0.24 (22)
Flash Point	ASTM D3828B	172.4 ± 7.8 (7)	NA	162.3 ± 11.6 (7)
Flash Point	ASTM D93 A	167.5 ± 5.81 (36)	174.7 ± 4.91 (26)	141.4 ± 12.2 (31)
Flash Point	ASTM D93 C	165.7 ± 6.19 (44)	174.6 ± 5.08 (46)	140.2 ± 14.2 (53)
KV @ 40°C	ASTM D445	4.080 ± 0.0141 (51)	4.057 ± 0.026 (56)	4.10 ± 0.019 (55)
KV @ 40°C	ASTM D7042	4.0749 ± 0.0296 (6)	4.071 ± 0.052 (10)	4.122 ± 0.0339 (9)
Ash	ASTM D482	0.000 ± 0.000 (20)	0.000 ± 0.0000 (21)	0.0003 ± 0.0005 (22)
SASH	ASTM D874	0.0005 ± 0.0007 (34)	0.0008 ± 0.0008 (28)	0.0004 ± 0.0006 (30)
Sulfur	ASTM D5453	0.56 ± 0.32 (62)	0.51 ± 0.35 (52)	1.23 ± 0.38 (61)
Lubricity-HFRR	ASTM D6079	159.8 ± 8.488 (25)	170.58 ± 14.86 (23)	164.88 ± 11.96 (25)
Lubricity-HFRR	ASTM D7688	159.07 ± 15.8 (6)	158.6 ± 8.765 (5)	169.95 ± 18.81 (6)
Water	ASTM D6304A	183.5 ± 38.9 (74)	282.0 ± 31.8 (73)	229.6 ± 22.5 (76)
CFPP	ASTM D6371	−3.6 ±1.1 (43)	−3.4 ± 1.2 (40)	−2.8 ± 1.4 (43)
Thermal Stability	ASTM D6468	99.0 ± 0.8 (12)	98.7 ± 1.0 (10)	97.5 ± 2.0 (11)

(Continued)

TABLE 8.6 *(Continued)*

Period Analysis	Test Method	1204	1208	1211
Free Glycerin	ASTM D6584	0.0077 ± 0.0014 (60)	0.0016 ± 0.0012 (60)	0.0046 ± 0.0010 (62)
Total Glycerin	ASTM D6584	0.1092 ± 0.0106 (63)	0.0927 ± 0.0266 (66)	0.1322 ± 0.0116 (67)
Diglyceride	ASTM D6584	0.0781 ± 0.0196 (64)	0.1141 ± 0.0121 (67)	0.0121 ± 0.0131 (57)
Monoglyceride	ASTM D6584	0.3399 ± 0.0314 (63)	0.3657 ± 0.0424 (64)	0.4512 ± 0.0422 (65)
Triglyceride	ASTM D6584	0.0153 ± 0.0180 (62)	0.0157 ± 0.0150 (61)	0.0577 ± 0.0186 (67)
Acid Number	ASTM D664 B	0.097 ± 0.022 (62)	0.313 ± 0.031 (66)	0.213 ± 0.028 (69)
Acid Number	ASTM D974	0.099 ± 0.019 (23)	0.316± 0.014 (23)	0.215 ± 0.013 (23)
Particulates	ASTM D7321	2.17 ± 1.66 (16)	3.98 ± 3.53 (24)	1.36 ± 1.46 (27)
CSFT	ASTM D7501	90.7 ± 15.8 (52)	123.6 ± 39.3 (53)	93.6 ± 14.5 (58)
Methanol	EN14110A	0.030 ± 0.009 (15)	0.003 ± 0.005 (14)	0.074 ± 0.013 (21)
Methanol	EN14110B	0.029 ± 0.005 (22)	0.000 ± 0.000 (26)	0.084 ± 0.016 (25)
Oxidation Stability	EN14112	5.16 ± 0.64 (67)	6.40 ± 0.57 (61)	7.45 ± 0.76 (67)
Ca + Mg	EN14538	0.05 ± 0.08 (33)	0.07 ± 0.10 (31)	0.06 ± 0.09 (33)
Na + K	EN 14538	0.31 ± 0.38 (33)	0.53 ± 0.51 (34)	0.06 ± 0.10 (31)
Period Analysis	**Test Method**	**1304**	**1308**	**1311**
IBP	ASTM D1160	321.1 ± 25.9 (16)	316.0 ± 24.1 (16)	263.2 ± 57.1(17)
	Auto Manual	299.5 ± 42.0 (13)	299.6 ± 58.6 (13)	254.3 ± 48.2 (13)
5 % Distill.	ASTM D1160	346.6 ± 9.5 (16)	346.4 ± 1.9 (14)	341.7 ± 3.2 (15)
	Auto Manual	341.5 ± 8.7 (13)	344.7 ± 4.3 (11)	341.2 ± 1.9 (12)
10 % Distill.	ASTM D1160	347.6 ± 1.2 (16)	347.4 ± 1.2 (14)	344.9 ± 1.7 (15)
	Auto Manual	345.3 ± 4.9 (13)	345.6 ± 3.2 (11)	343.1 ± 2.5 (13)
20 % Distill.	ASTM D1160	348.4 ± 1.2 (16)	348.2 ± 1.5 (16)	346.7 ± 1.4 (15)
	Auto Manual	346.7 ± 3.5 (13)	346.9 ± 1.6 (10)	344.5 ± 3.2 (13)
30 % Distill.	ASTM D1160	349.0 ± 0.9 (15)	349.1 ± 1.3 (16)	347.7 ± 1.3 (15)
	Auto Manual	347.1 ± 3.4 (13)	348.1 ± 1.6 (10)	345.5 ± 2.7 (13)
40 % Distill.	ASTM D1160	349.6 ± 0.6 (15)	349.9 ± 1.5 (16)	348.4 ± 1.4 (15)
	Auto Manual	348.5 ± 2.3 (12)	348.6 ± 1.9 (10)	345.6 ± 4.3 (14)
50 % Distill.	ASTM D1160	350.2 ± 0.7 (15)	350.2 ± 1.6 (16)	349.5 ± 1.6 (15)
	Auto Manual	349.4 ± 1.5 (12)	349.4 ± 1.9 (10)	346.6 ± 4.2 (14)
60 % Distill.	ASTM D1160	350.7 ± 0.6 (15)	350.9 ± 1.6 (16)	350.2 ± 1.6 (15)
	Auto Manual	350.0 ± 1.9 (12)	349.9 ± 2.2 (10)	347.9 ± 3.1 (14)
70 % Distill.	ASTM D1160	352.4 ± 0.6 (15)	351.4 ± 1.4 (16)	351.2 ± 1.4 (15)
	Auto Manual	350.8 ± 2.0 (12)	350.5 ± 2.5 (10)	348.5 ± 3.7 (14)
80 % Distill.	ASTM D1160	352.4 ± 0.6 (15)	352.2 ± 1.5 (16)	352.2 ± 1.4 (15)
	Auto Manual	351.6 ± 1.8 (12)	351.3 ± 2.1 (10)	349.8 ± 3.4 (14)
90 % Distill.	ASTM D1160	353.8 ± 0.9 (15)	353.8 ± 2.1 (16)	353.7 ± 2.0 (16)
	Auto Manual	352.1 ± 3.0 (14)	353.0 ± 2.7 (10)	351.3 ± 3.6 (14)
95 % Distill.	ASTM D1160	355.1 ± 2.3 (17)	356.1 ± 3.3 (14)	355.3 ± 3.4 (16)
	Auto Manual	354.3 ± 2.4 (12)	354.6 ± 4.1 (10)	352.2 ± 5.3 (13)
FBP Distill.	ASTM D1160	378.4 ± 24.3 (18)	379.0 ± 22.5 (15)	362.5 ± 9.1 (15)
	Auto Manual	361.1 ± 10.3	363.7 ± 23.3 (11)	359.1 ± 8.1 (12)
API Gravity	ASTM D1298	28.41 ± 0.08 (21)	28.38 ± 0.08 (20)	29.14 ± 0.06 (25)
Density	ASTM D1298	0.8844±0.00043 (31)	0.8845±0.00052 (32)	0.8804 ± 0.00051 (29)
Density	ASTM D4052	0.88463±0.00019 (54)	0.8848±0.00016 (58)	0.8807 ± 0.00018 (64)
Carbon Residue	ASTM D189	0.011 ± 0.011 (9)	0.066 ± 0.088 (7)	NA
Carbon Residue	ASTM D4530	0.009 ± 0.009 (37)	0.005± 0.006 (32)	0.003 ± 0.005(33

(Continued)

TABLE 8.6 *(Continued)*

Period Analysis	Test Method	1204	1208	1211
Cloud Point	ASTM D2500	0.4 ± 0.1 (59)	0.6 ± 0.9 (63)	2.3 ± 1.2 (61)
Cloud. Point	ASTM D5771	0.91 ± 0.79 (8)	0.87 ± 0.63 (9)	2.31 ± 0.57 (13)
Cloud. Point	ASTM D5773	0.42 ± 0.49 (28)	0.50 ± 0.39 (27)	2.45 ± 0.79 (26)
Flash Point	ASTM D3828B	150.9 ± 14.3 (8)	136.0 ± 19.7 (6)	NA
Flash Point	ASTM D93 A	144.4 ± 10.96 (26)	122.8 ± 15.7 (32)	162.4 ± 4.17 (27)
Flash Point	ASTM D93 C	134.8 ± 8.5 (57)	116.6 ± 16.7 (63)	162.3 ± 4.1(58)
KV @ 40°C	ASTM D445	4.0786 ±0.0171(53)	4.0831±0.0168 (54)	4.1607 ± 0.0163 (58)
KV @ 40°C	ASTM D7042	4.0935 ± 0.0212 (8)	4.0975±0.0105(7)	4.176 ± 0.022(8)
Ash	ASTM D482	0.0003±0.0005 (23)	0.000± 0.000 (23)	0.0003 ± 0.0005 (24)
SASH	ASTM D874	0.0005±0.0007 (31)	0.0004±0.0007 (29)	0.0003 ± 0.0005 (30)
Sulfur	ASTM D5453	0.46 ± 0.31 (58)	0.42 ± 0.34 (54)	8.31 ± 1.03 (65)
Lubricity-HFRR	ASTM D6079	161.538±9.364 (26)	157.4 ± 13.9 (27)	202.1 ± 29.6(27)
Lubricity-HFRR	ASTM D7688	150.50 ± 17.59 (8)	155.0 ± 6.06 (8)	221.83 ± 84.37 (6)
Water	ASTM D6304A	242.3 ± 38.4 (80)	393.1 ± 52.0 (86)	252.1 ± 28.1 (87)
CFPP	ASTM D6371	−3.0 ± 1.1 (46)	−3.9 ± 1.2 (45)	−0.8 ± 1.1 (48)
Thermal Stability	ASTM D6468	98.0 ± 1.8 (13)	98.0 ± 2.4 (13)	98.6 ± 0.7 (15)
Free Glycerin	ASTM D6584	0.0023±0.0012 (62)	0.0107±0.0022 (64)	0.0144 ± 0.0051 (78)
Total Glycerin	ASTM D6584	0.1071±0.0094 (72)	0.1438±0.0169 (68)	0.0428 ± 0.00119 (74)
Diglyceride	ASTM D6584	0.0445±0.0126 (66)	0.2312±0.0425 (64)	0.0007 ± 0.0011 (60)
Monoglyceride	ASTM D6584	0.3728±0.0355 (69)	0.308±0.0373(64)	0.1028 ± 0.041 (75)
Triglyceride	ASTM D6584	0.0044±0.0065 (57)	0.1706±0.0837 (66)	0.0000 ± 0.0000 (54)
Acid Number	ASTM D664	0.274 ± 0.033 (72)	0.262± 0.030 (72)	0.321 ± 0.037(84
Acid Number	ASTM D974	0.283 ± 0.020 (29)	0.270 ± 0.021(30)	0.316 ± 0.025(29
Particulates	ASTM D7321	1.56 ± 1.56 (28)	2.82 ± 2.00 (30)	3.28 ± 2.85 (25)
CSFT	ASTM D7501	92.1 ± 13.8 (55)	89.5 ± 13.2 (60)	90.7 ± 10.4 (64)
Methanol	EN14110A	0.068 ± 0.014 (16)	0.112 ± 0.026(15)	0.009 ± 0.005(26
Methanol	EN14110B	0.072 ± 0.013 (26)	0.129 ±0.021 (24)	0.010 ± 0.000(12
Oxidation Stability	EN14112	5.81 ± 0.78 (70)	7.13 ± 0.72 (68)	7.32 ± 0.63 (75)
Ca + Mg	EN14538	0.04 ± 0.06 (34)	0.05 ± 0.07 (35)	0.03 ± 0.05 (37)
Na + K	EN 14538	0.19 ± 0.24 (36)	0.10 ± 0.14 (33)	0.13 ± 0.20 (39)
Period Analysis	**Test Method**	**1404**	**1408**	**1411**
IBP	ASTM D1160	258.7 ± 35.9 (15)	324.2 ± 22.9 (18)	313.1 ± 15.7 (16)
	Auto Manual	266.8 ± 48.9 (17)	310.7 ± 48.0 (13)	306.5 ± 29.0(13)
5 % Distill.	ASTM D1160	345.2 ± 1.7 (13)	347.0 ± 1.4(16)	337.3 ±1.2 (16)
	Auto Manual	341.9 ± 5.3 (16)	346.2 ± 1.4 (11)	336.6 ± 4.0 (13)
10 % Distill.	ASTM D1160	347.2 ± 1.6 (13)	347.8 ± 1.5 (17)	339.4 ± 1.6 (16)
	Auto Manual	344.8 ± 3.1 (15)	346.8 ± 1.3 (11)	338.0 ± 3.3 (13)
20 % Distill.	ASTM D1160	348.3 ± 0.9 (12)	348.1 ± 0.9 (16)	341.5 ± 1.3 (16)
	Auto Manual	346.9 ± 2.9 (15)	347.5 ± 1.5 (12)	340.0 ± 3.4 (12)
30 % Distill.	ASTM D1160	349.2 ± 1.2 (13)	348.8 ± 1.0 (17)	343.3 ± 1.2 (16)
	Auto Manual	347.6 ± 2.9 (15)	348.2 ± 1.6 (12)	341.5 ± 3.4 (13)
40 % Distill.	ASTM D1160	349.8 ± 1.2 (14)	349.6 ± 1.0 (17)	344.5 ± 0.7 (16)
	Auto Manual	348.4 ± 3.4 (15)	348.7 ± 1.4 (12)	343.4 ± 3.4 (13)
50 % Distill.	ASTM D1160	350.3 ± 0.9 (13)	350.0 ± 0.9 (16)	346.1 ± 0.8 (16)
	Auto Manual	349.5 ± 2.7 (15)	349.1 ± 1.6 (12)	344.8 ± 3.0 (13)

(Continued)

TABLE 8.6 *(Continued)*

Period Analysis	Test Method	1204	1208	1211
60 % Distill.	ASTM D1160	351.2 ± 0.8 (14)	350.4 ± 0.6 (15)	347.6 ± 1.1 (16)
	Auto Manual	349.4 ± 3.9 (16)	349.7 ± 1.4 (12)	346.5 ± 3.3 (13)
70 % Distill.	ASTM D1160	351.7 ± 1.1 (15)	351.5 ± 1.3 (17)	349.1 ± 1.0 (16)
	Auto Manual	350.6 ± 3.1 (16)	350.3 ± 0.9 (12)	347.5 ± 3.8 (13)
80 % Distill.	ASTM D1160	352.2 ± 1.0 (15)	351.8 ± 0.9 (15)	350.7 ± 1.2 (16)
	Auto Manual	351.4 ± 3.2 (16)	351.3 ± 1.4 (12)	349.3 ± 3.5 (13)
90 % Distill.	ASTM D1160	353.8 ± 1.4 (15)	353.2 ± 1.1 (16)	353.0 ± 1.1 (16)
	Auto Manual	352.5 ± 3.6 (17)	352.5 ± 1.4 (12)	351.5 ± 3.3 (12)
95 % Distill.	ASTM D1160	356.9 ± 2.7 (15)	356.3 ± 2.3 (17)	354.0 ± 1.1 (16)
	Auto Manual	354.7 ± 5.5 (16)	354.2 ± 1.4 (13)	352.6 ± 3.6 (14)
FBP Distill.	ASTM D1160	371.9 ± 20.2 (13)	385.2 ± 25.3 (17)	359.2 ± 4.9 (14)
	Auto Manual	364.1 ± 9.8 (14)	370.8 ± 16.8 (13)	357.7 ±7.2 (13)
API Gravity	ASTM D1298	28.44 ± 0.06 (21)	28.37 ± 0.10 (24)	30.04 ± 0.11 (19)
Density	ASTM D1298	0.8841 ± 0.0004(25)	0.8846 ± 0.00051 (34)	0.8755 ± 0.00055(32)
Density	ASTM D4052	0.8844 ± 0.0001 (62)	0.8849 ± 0.00009 (61)	0.8757 ± 0.00012(75)
Carbon Residue	ASTM D189	0.022 ± 0.027 (10)	0.006 ± 0.006 (7)	0.000 ± 0.000 (9)
Carbon Residue	ASTM D4530	0.005 ± 0.006 (34)	0.003 ± 0.005 (29)	0.000 ± 0.000 (46)
Cloud Point	ASTM D2500	0.3 ± 1.0 (62)	0.2 ± 0.9 (64)	11.4 ± 1.2 (68)
Cloud. Point	ASTM D5771	0.50 ± 0.51 (13)	0.89 ± 0.26 (9)	10.6 ± 0.69 (10)
Cloud. Point	ASTM D5773	0.29 ± 0.34 (25)	0.42 ± 0.24 (26)	12.01 ± 0.70 (26)
Flash Point	ASTM D3828B	146.1 ± 14.2 (8)	168.6 ± 10.5 (8)	156.1 ± 5.0 (4)
Flash Point	ASTM D93 A	119.03 ± 10.48 (34)	168.59 ± 5.38 (31)	145.5 ± 7.07 (39)
Flash Point	ASTM D93 C	117.00 ± 11.95 (59)	168.24 ± 5.16 (60)	144.1 ± 7.5 (68)
KV @40°C	ASTM D445	4.1181 ± 0.0163 (55)	4.0735 ± 0.0229 (59)	4.4694 ± 0.0164 (65)
KV @ 40°C	ASTM D7042	4.1388 ± 0.0358 (9)	4.0887 ± 0.0249 (11)	4.4747 ± 0.0192 (10)
Ash	ASTM D482	0.0003 ± 0.0005 (29)	0.0000 ± 0.0000 (29)	0.0000 ± 0.0000(35)
SASH	ASTM D874	0.0005 ± 0.0008 (33)	0.0003 ± 0.0005 (29)	0.0003 ± 0.0005 (45)
Sulfur	ASTM D5453	0.85 ± 0.43 (65)	0.41 ± 0.33 (61)	3.62 ± 0.55 (77)
Sulfur	ASTM D7039	0.46 ± 0.38 (16)	0.18 ± 0.29 (18)	3.02 ± 0.64 (17)
Lubricity-HFRR	ASTM D6079	165.2 ± 11.8 (28)	160.5 ± 20.2 (26)	188.2 ± 18.3 (25)
Lubricity-HFRR	ASTM D7688	179.68 ± 53.4 (7)	164.0 ± 4.741 (5)	186.4 ± 26.1 (7)
Water	ASTM D6304A	0.0 ± 0.0 (73)	0.1 ± 0.0 (61)	0.0 ± 0.0 (76)
	ASTM E203			0.0143 ± 0.0024 (19)
CFPP	ASTM D6371	−3.9 ± 0.9 (50)	−3.5 ± 1.0 (43)	8.6 ± 0.8 (49)
Thermal Stability	ASTM D6468	98.3 ± 1.0 (17)		99.0 ± 0.0 (15)
Free Glycerin	ASTM D6584	0.0111 ± 0.0042 (75)	0.0061 ± 0.0014 (65)	0.0101 ± 0.0018 (73)
Total Glycerin	ASTM D6584	0.1657 ± 0.0271 (76)	0.1086 ± 0.0127 (66)	0.0292 ± 0.0059 (73)
Diglyceride	ASTM D6584	0.2752 ± 0.0703 (74)	0.1022 ± 0.0239 (69)	0.0100 ± 0.0092 (73)
Monoglyceride	ASTM D6584	0.3380 ± 0.0521 (72)		0.0682 ± 0.0181 (73)
Triglyceride	ASTM D6584	0.2298 ± 0.1143 (75)		0.0004 ± 0.0007 (73)
Acid Number	ASTM D664B	0.309 ± 0.029 (79)	0.261 ± 0.032 (80)	0.264 ± 0.030 (83)
Acid Number	ASTM D974	0.319 ± 0.023 (27)	0.269 ± 0.033 (28)	0.253 ± 0.015 (24)
Particulates	ASTM D7321	2.80 ± 2.14 (33)	1.94 ± 1.86 (31)	3.93 ± 3.51 (35)
CSFT	ASTM D7501	91.1 ± 14.0 (67)	90.8 ± 14.0 (63)	107.4 ± 17.4 (64)
Ester	EN14103			95.86 ± 3.29 (22)

(Continued)

TABLE 8.6 *(Continued)*

Period Analysis	Test Method	1204	1208	1211
Linolenic Acid Methyl Ester	EN 14103			0.46 ± 0.07 (21)
Methanol	EN14110A	0.114 ± 0.015 (29)	0.034 ± 0.007 (13)	0.056 ± 0.006(29
Methanol	EN14110B	0.096 ± 0.035 (21)	0.034 ± 0.011 (35)	0.054 ± 0.010(17
Oxidation Stability	EN14112	8.57 ± 1.49 (73)	7.67 ± 0.92 (58)	48.08 ± 6.31 (49)
Ca + Mg	EN14538	0.06 ± 0.08 (39)	0.05 ± 0.07 (34)	0.00 ± 0.00 (50)
Na + K	EN 14538	0.42 ± 0.45 (41)	0.22 ± 0.26 (35)	0.08 ± 0.12 (50)
FAME	EN 15751			54.23 ± 3.42 (25)

Note: All results are expressed as mean value ± robust standard deviation (no. of valid results); No phosphorus by ASTM D4951, sulfur by ASTM D6428, or water and sediment by ASTM D2709 were detected in any of these samples; CFPP = cold filter plugging point; CSFT = cold soak filtration test; FAME = fatty acid methyl ester; FBP = final boiling point; HFRR = high frequency reciprocating rig; IBP = initial boiling point; KV = kinematic viscosity; SASH = sulfated ash.

TABLE 8.7 Analysis of Biodiesels by Alternate Test Methods

Analysis	Test Method	BIOD 1304	BIOD 1308	BIOD 1311
Carbon Residue, m %	ASTM D189	0.011 ± 0.011 (9)	0.066 ± 0.088 (7)	NA
	ASTM D4530	0.009 ± 0.009 (37)	0.005 ± 0.006 (32)	0.003 ± 0.005 (29)
Cloud Point, °C	ASTM D2500	0.4 ± 0.1 (59)	0.6 ± 0.9 (63)	2.3 ± 1.1 (55)
	ASTM D5771	0.91 ± 0.79 (8)	0.87 ± 0.63 (9)	2.31 ± 0.57 (13)
	ASTM D5773	0.42 ± 0.49 (28)	0.50 ± 0.39 (27)	2.48 ± 0.80 (25)
Flash Point, °C	ASTM D93 A	144.4 ± 10.96 (26)	122.8 ± 15.7 (32)	161.8 ± 3.79 (24)
	ASTM D93 C	134.8 ± 8.5 (57)	116.6 ± 16.7 (63)	162.4 ± 4.1 (56)
	ASTM D3828	150.9 ± 14.3 (8)	136.0 ± 19.7 (6)	NA
Kinematic Viscosity, cSt	ASTM D445	4.079 ± 0.017 (53)	4.083 ± 0.017 (54)	4.160 ± 0.016 (53)
	ASTM D7042	4.094 ± 0.0212 (8)	4.098 ± 0.0105 (7)	4.181± 0.031 (8)
Density	ASTM D1298	0.8844 ± 0.0004 (31)	0.8845 ± 0.0005 (32)	0.8804 ± 0.0005 (27)
	ASTM D4052	0.8846 ± 0.0002 (54)	0.8848 ± 0.0002 (58)	0.8807 ± 0.0002 (57)
Acid Number	ASTM D664	0.274 ± 0.033 (72)	0.262 ± 0.030 (72)	0.321 ± 0.036 (77)
	ASTM D974	0.283 ± 0.020 (29)	0.270 ± 0.021 (30)	0.315 ± 0.025 (27)

Note: Results are shown as mean value ± standard deviation (number of valid results); NA = there were insufficient number of data points to perform this calculation.

TABLE 8.8 Analysis of Fuel Ethanol by Alternate Test Methods

Analysis	Test Method	ETOH 1304	ETOH 1308	ETOH 1312
Sulfur, mg/kg	ASTM D5453	2.22 ± 0.48 (49)	2.57 ± 0.50 (50)	2.56 ± 0.45 (51)
	ASTM D7039	1.56 ± 0.55 (18)	1.89 ± 0.47 (24)	2.26 ± 0.39 (19)
Sulfate, mg/kg	ASTM D7319	0.17 ± 0.17 (34)	0.784 ± 0.563 (25)	0.60 ± 0.31 (46)
	ASTM D7328	0.309 ± 0.292 (25)		0.723 ± 0.314 (25)
Chloride, mg/kg	ASTM D7319	0.13 ± 0.14 (30)	0.188 ± 0.177 (22)	0.08 ± 0.11 (34)
	ASTM D7328	0.152 ± 0.151 (22)		0.723 ± 0.314 (25)
Water, mg/kg	ASTM E203	0.9057 ± 0.0286 (17)	0.9636 ± 0.0319 (17)	0.9679 ± 0.048 (20)
	ASTM E1064	0.9153 ± 0.0247 (80)	0.9733 ± 0.0316 (86)	0.9763 ± 0.0312 (85)

Note: Results are shown as mean value ± standard deviation (number of valid results).

TABLE 8.9 Comparison of Industry Precision in Biofuels Analysis

		Biodiesel TPI			Ethanol TPI		
Analysis	**Test Method**	**1304**	**1308**	**1311**	**1304**	**1308**	**1312**
Cloud Point	ASTM D2500,	1.33	1.60	1.33			
	ASTM D5771,	1.23	1.54	1.71			
	ASTM D5773	1.84	2.31	1.13			
API Gravity	ASTM D1298	2.27	2.27	2.94			
Density		1.26	1.04	1.04			
Distillation, Auto	ASTM D1160	0.94	0.79				
+20 %		0.94	0.79				
+50 %		1.53	0.61	0.65			
+90 %		1.28	0.59	0.47			
Distillation, Manual							
+20 %		0.36	0.89				
+50 %		0.79	0.55	0.50			
+90 %		0.25	0.47	0.97			
Flash Point	ASTM D3828B	0.19	0.13	NA			
Flash Point	ASTM D93 A	0.34	0.20	1.09			
	ASTM D93 C	0.63	0.32	1.29			
Carbon Residue	ASTM D189	0.80	0.19	NA			
Carbon Residue	ASTM D4530	5.64	8.29	10.1			
Sulfur	ASTM D5453,	0.37	0.32	0.99	0.79	0.85	0.94
	ASTM D7039			0.56			1.06
Lubricity HFRR	ASTM D6079	3.08	2.08	1.02			
Lubricity HFRR	ASTM D7688	1.85	5.36	NA			
Particulate Contamination	ASTM D6217	1.81	2.55	1.99			
Karl Fischer Water	ASTM D6304A	0.11	0.11	0.15			
CSFT	ASTM D7501	NA	0.66	0.85			
CFPP	ASTM D6371	0.97	0.88	0.93			
Free Glycerin	ASTM D6584	1.73	1.93	0.99			
Total Glycerin	ASTM D6584	2.50	1.78	1.01			
Total Diglycerides	ASTM D6584	12.07	3.95				
Total Monoglycerides	ASTM D6584	3.18	2.65	1.07			
Total Triglycerides	ASTM D6584	2.67	1.48				
Acidity	ASTM D974	1.45	1.38	NA			
Acidity	ASTM D1613				0.16	0.18	0.20
Ethanol	ASTM D5501				1.01	0.92	0.98
Methanol	ASTM D5501				0.30	0.27	0.28
Methanol	EN14110A	0.46	0.55				
Methanol	EN14110B	0.53	0.39	0.36			
Oxidation Stability	EN 14112	0.81	1.05	1.21			
Ca + Mg	EN 14538	7.00	6.26	7.00			
Na + K	EN 14538	1.48	2.46	1.31			
Thermal Stability	ASTM D6468	0.42	0.32	0.82			
Solvent Washed Gum	ASTM D381				1.81	1.81	1.97
pHe	ASTM D6423				1.04	0.81	0.73
Total Sulfate	ASTM D7328				0.75	0.62	1.07
Water	ASTM E203				0.34	0.31	0.20
Water and Sediment	ASTM D2709	NA	13.67	NA			

Note: NA = TPI could not be calculated due to the lack of test method reproducibility value or calculation as the test pertains to biofuels as a product, or there were insufficient number of data points to perform this calculation.

TABLE 8.10 Range of Test Performance Indexes Obtained for Biofuels Analysis

TPI	Indication[a]	Biodiesel ILCP	Fuel Ethanol ILCP
<0.8	Needs Improvement	ASTM D3828B and ASTM D93 Flash Point; ASTM D5453 Sulfur; ASTM D6304A KF Water; EN 14110 Methanol; ASTM D1160 Distillation-Manual; ASTM D6468 Thermal Stability; EN 14110 Methanol	ASTM E203 Water; ASTM D1613 Acidity; ASTM D5501 Methanol; EN 14110 Methanol
0.8–1.2	Adequate but can use improvement	ASTM D189 Carbon Residue; ASTM D1160 Distillation-Auto; ASTM D6371 CFPP; ASTM D7501 CSFT	ASTM D6423 pHe ASTM D5453 Sulfur; ASTM D5501 Ethanol; ASTM D7328 Sulfate
>1.2	Satisfactory	ASTM D2500, ASTM D5771, and ASTM D5773 Cloud Point; ASTM D6079 and ASTM D7688 HFRR; ASTM D664 and ASTM D974 TAN; ASTM D4530 Microcarbon Residue; ASTM D6217 Particulate Contamination; EN 14538 Metals; ASTM D6584 Glycerin	ASTM D381 Solvent Washed Gum
Not Determined or Not Enough Labs		ASTM D3117 Cloud Point; ASTM D6890 Ignition Delay	ASTM D7318 Sulfate
No ASTM Reproducibility Value Available		ASTM D189 Carbon Residue; ASTM D445 Kinematic Viscosity; ASTM D4539 LTFT; ASTM D482 Ash; ASTM D4951 Phosphorus; ASTM D6468 Thermal Stability; ASTM D874 Sulfated Ash; ASTM D6890 Ignition Delay	ASTM D7319 Chloride; ASTM E1064 Water; ASTM D1688 Copper

[a] See the earlier text for explanation.

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Abstract

There are two proficiency testing programs conducted by Committee D02 for biofuels: Biodiesel and Fuel Ethanol. These programs are discussed, and data from recent programs are used to illustrate the efficacy of the programs.

Keywords

proficiency testing programs, biodiesel, fuel ethanol

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Review:

Analysis of Biofuels: A Laboratory Resource by R.A. Kishore Nadkarni presents an authoritative and essential review of biofuels technology, a vitally important technology area of increasing importance. Topical areas that are expertly covered include: product specifications and an up-to-date overview of test methods for physical and chemical analysis, environmental analysis, and bioenergy from biomass. In addition, ASTM proficiency testing programs for biofuels are detailed. This book assuredly will be an invaluable working reference for practitioners in the fuels technology area.

–George E. Totten, Ph.D., Portland State University, Portland, OR, USA

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