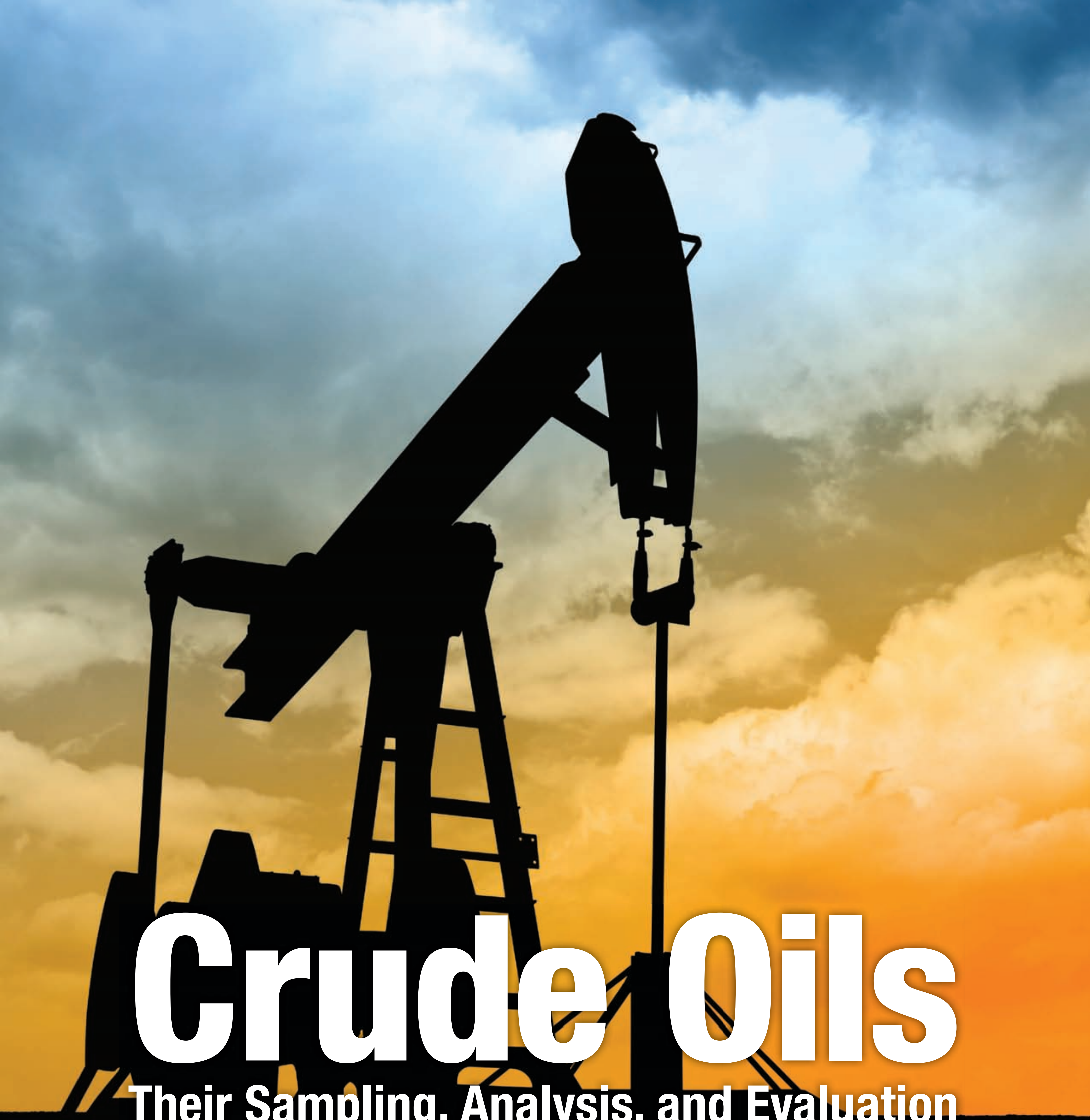


Crude Oils

Their Sampling, Analysis, and Evaluation

Harry N. Giles and Clifford O. Mills

ASTM
INTERNATIONAL
Standards Worldwide

Crude Oils: Their Sampling, Analysis, and Evaluation

Harry N. Giles and Clifford O. Mills

ASTM Stock Number: MNL68

INTERNATIONAL
Standards Worldwide
ASTM International
100 Barr Harbor Drive
PO Box C700
West Conshohocken, PA 19428-2959

Printed in U.S.A.

Library of Congress Cataloging-in-Publication Data

Giles, Harry N.
Crude oils: their sampling, analysis, and evaluation/Harry N. Giles and Clifford O. Mills.
p. cm.
Includes bibliographical references and index.
ISBN: 978-0-8031-7014-8
1. Petroleum—Analysis. I. Mills, Clifford O. II. Title.
TP691.G545 2010
665.5—dc22 2010031882

Printed in Newburyport, MA
November, 2010

Foreword

THIS PUBLICATION, Crude Oils: Their Sampling, Analysis, and Evaluation, was sponsored by ASTM committee D02 on Petroleum Products and Lubricants. The authors are Harry N. Giles, Consultant, 2324 N. Dickerson Street, Arlington, Virginia 22207 and Clifford O. Mills, Consultant, 1971 E. Tower Road, Ponca City, Oklahoma 74604. This is Manual 68 in the ASTM International manual series.

Acknowledgments

This manual is based on the ASTM International Technical and Professional Training Course of the same name that has been taught by the authors at several locations worldwide numerous times since 2005. This manual would not have been possible without the support and encouragement of many of our colleagues and participants in the course. We are grateful to many individuals and companies for providing us some of the material included herein. We appreciate their willingness to share this information because it makes our task easier illustrating some of the topics. The following individuals and companies provided some of the material included in this course: Baker Hughes and Larry Kremer; Canadian Crude Quality Technical Association and Andre Lemieux; Chevron Energy Technology Company and Anne Shafizadeh; Crude Oil Quality Association; DynMcDermott Petroleum Operating Co.; Google and the WorldWideWeb; Intertek; KBW Process Engineers; Koehler Instruments; Arden Strycker, Northrop Grumman Mission Systems; Patrice Perkins, PetroTech Intel; Professor G. Ali Mansoori, University of Illinois–Chicago; Professor Bahman Tohidi, Institute of Petroleum Engineering; Heriot-Watt University; Dan Villalanti, Triton Analytics; Anne Brackett Walker, W. L. Walker Co.; and David Fish, Welker Engineering. We apologize if we neglected to mention someone that has assisted us; this is not intentional. Dr. Arden Strycker of Northrop Grumman Mission Systems kindly reviewed the manuscript and provided many valuable comments that helped us improve the contents. We also thank the staff at ASTM International, who helped in making the course a reality, and the members of the Publications Department for their guidance, support, and, most of all, their patience during the preparation of this manual.

Harry N. Giles
Arlington, VA

Clifford O. Mills
Ponca City, OK

Contents

Glossary of Terms

Additives–Substance added to a crude oil stream in relatively minor amounts to facilitate its production and transportation and minimize adverse effects on equipment. These include pour point depressants, drag reducing agents, demulsifiers, and corrosion inhibitors.

API gravity–A special function of relative density (specific gravity) 60/60°F, represented by:

$$° API = 141.5/(\textit{specific gravity } 60/60°F) - 131.5$$

[ASTM D1298]

Assay–A combination of physical and chemical data that uniquely describe a crude oil.

Bitumen–A category of crude oil that is black, highly viscous, and semisolid at normal temperatures, will not flow without dilution, and generally has an API of less than 10°.

Challenging (or challenged) crude–See *Opportunity crude*.

Compatibility–The capacity of two or more crude oils to be commingled without asphaltenes or waxes precipitating or flocculating out of the mixture.

Condensate–Liquid mixture usually recovered from natural gas consisting primarily of hydrocarbons from approximately C_6–$C_{12\text{-}15}$, and having an API gravity greater than 45°. The mixture may also contain hydrogen sulfide, thiols, carbon dioxide, and nitrogen. Some consider condensate to be a light, sweet crude oil. Other terms include *gas condensate, natural gas liquids, lease condensate, and natural gasoline*.

Contaminant–Any material added to a crude oil stream that is not naturally occurring or exceeds the concentration normally present.

Crude oil–Naturally occurring hydrocarbon mixture, generally in a liquid state, which may also contain compounds of sulfur, nitrogen, oxygen, metals, and other elements. [ASTM D4175]

Degradation–A lessening in quality of a crude oil stream commonly resulting from mixing of another stream of poorer quality. Degradation of a crude oil can also result from biological activity.

Differentiation–Natural development of a density differential from top to bottom in a storage container. *Cf. Stratification*.

Impurity–Nonhydrocarbons naturally occurring in crude oil. These typically include sediment; water; salts; organic acids; heteroatomic compounds of sulfur, nitrogen, and oxygen; and metals–particularly nickel and V.

Incompatibility–Agglomeration or flocculation of asphaltenes, waxes, or both from a mixture of two or more crude oils. *Cf. Compatibility*.

Opportunity crude–A crude oil priced below market value. An opportunity crude may be production from a new field with little or no processing history, a distressed cargo, or a crude oil with a known history that reduces refinery profitability. This latter can result from the crude having a high total acid number, sulfur content, and/or metals, problematic contaminants, or is difficult to upgrade or has unattractive yields.

Referee test method–An analytical method designated in testing protocols to be used in case of disputes.

Relative density (specific gravity)–The ratio of the mass of a given volume of liquid at a specific temperature to the mass of an equal volume of pure water at the same or different temperature. Both reference temperatures must be explicitly stated. [ASTM D1298]

Representative sample–A portion extracted from a total volume that contains the constituents in the same proportion as are present in the total volume. [ASTM D4057]

Sampling–All the steps required to obtain an aliquot representative of the contents of any tank, pipe, or other system and to place the sample into a suitable laboratory sample container. [ASTM D6470]

Slop oil–A combination of off-specification fuel, water, refinery wastes, and transmix. Slop oil is usually processed in the generating refinery but is occasionally exported or shipped domestically for use as an inexpensive feedstock for processing in atmospheric units.

Stability–The ability of a crude oil when produced, transported, and/or stored to endure without physical or chemical change, such as flocculation or precipitation of asphaltenes and/or waxes.

Stratification–The intentional layering of different crudes oils in a storage container taking advantage of differences in their density. *Cf. Differentiation*.

Synthetic crude oil–Stream derived by upgrading oil-sands bitumen and extra-heavy crude oil. Upgrading processes include hydroprocessing and coking to yield a more fungible, lighter, less viscous stream.

Transmix–Transportation mixture is the material present at the interface between different quality crude oils batched in a common carrier pipeline system. Generally, at a terminal, the mixture will be relegated to the lower quality crude oil.

1

Introduction

This manual is intended for whoever is involved with sampling and analysis of crude oils after they are produced and stabilized; essentially the mid- and downstream sectors of the industry. They will be the operators of pipelines and tankers that transport the crude oil, the terminals that temporarily store it, laboratory personnel that are responsible for its characterization, refiners that eventually process it, and traders responsible for its sale or acquisition.

Crude oils are a highly complex combination of hydrocarbons; heterocyclic compounds of nitrogen, oxygen, and sulfur; organometallic compounds; inorganic sediment; and water. More than 600 different hydrocarbons have been positively identified in crude oil, and it is likely that thousands of compounds occur, many of which probably will never be identified. In a study sponsored by the American Petroleum Institute (API) in the 1960s, nearly 300 individual hydrocarbons were identified in Ponca City, Oklahoma, crude oil [1,2]. In another API project beginning in the 1950s, some 200 individual sulfur compounds were identified in a 20-year systematic study of four crude oils [3]. In the ensuing 50+ years, hundreds, and perhaps thousands, of other hydrocarbons and sulfur compounds have been "identified" using increasingly more sophisticated instrumentation. Not only is the composition of crude oil highly complex, it is also highly variable from field to field, and even within a given field it is likely to exhibit inhomogeneity from reservoir to reservoir. Physical and chemical characterization of this complex mixture is further complicated for the analyst by the fact that crude oils are not pure solutions but commonly contain colloidally suspended components, dispersed solids, and emulsified water.

Compared with refined products such as gasoline and aviation turbine fuel, there is relatively little in the literature on the analysis and characterization of crude oils. Indeed, for many years, there were relatively few ASTM methods specific to crude oils, although several ASTM methods had been adapted for their analysis. This situation may have resulted, at least in part, from the historical tendency of refinery chemists to independently develop or modify analytical methods specific to their needs and, subsequently, for the methods to become company proprietary. In recent years, the unique problems associated with sampling and analysis of crude oils have received more attention, and more methods for determining selected constituents and characteristics of crude oils have been standardized.

A series of articles [4-9] illustrates the diversity of crude oil assay practices used by major refiners in the United States and Austria. The dissimilarity of published results [10] and as provided by several companies on their Web sites [11] is a reflection of this independent development of analytical schemes, although standardized approaches to crude oil analysis have been published [12-15]. Despite the complexity of crude oil composition and the diversity of analytical methodology, probably more crude oil analyses are routinely performed on a daily basis using inherently similar methods than are analyses on any single refined petroleum product except, possibly, gasoline.

The overriding issue when performing comprehensive crude oil assays is economics. Crude oils are assayed to determine (*a*) the slate of products that can be produced with a given refinery's process technology, (*b*) the processing difficulties that may arise as a result of inherent impurities and contaminants, and (*c*) the downstream processing and upgrading that may be necessary to optimize yields of high-value specification products. Today, analytical data are typically stored in electronic databases that can be accessed by computer models that generate refinery-specific economic valuations of each crude oil or crude slate; that is, a mixture of crude oils processed together. Linear programming (LP) models are available from several commercial vendors, but several companies have developed their own models to meet the needs of their specific refinery configurations.

Analyses are also performed to determine whether each batch of crude oil received at a terminal or the refinery gate meets expectations. Can the crude oil be commingled into a common stream pipeline system, or does it need to be batched? Does the crude receipt match the database assay so that the projected economic valuations and operational strategies are valid? Has any unintentional contamination or purposeful adulteration occurred during gathering, storage, or transport of the crude oil that may increase the processing cost or decrease the value of the refined products? The information needed to answer these questions is often refinery-specific–a function of the refinery's operating constraints and product slate–and, almost certainly, has considerable financial consequences.

To obtain the desired information, two different analytical schemes are commonly used; namely, an inspection assay and a comprehensive assay. Inspection assays usually involve determination of a few key whole crude oil properties such as API gravity, sulfur content, and pour point–principally as a means of determining if major changes in a crude oil stream's characteristics have occurred since the last comprehensive assay was performed. Additional analyses may be performed to help ensure that the quality of the cargo or shipment received is that which is expected; to ascertain the quantity of impurities such as salt, sediment, and water; and to provide other critical refinery-specific information. Inspection assays are routinely performed on all shipments received at a terminal or refinery. On the other hand, the comprehensive assay is complex, costly, and time-consuming and is normally performed only when a new field comes on stream for which a company has an equity interest, a crude that has not previously been processed arrives at a refinery, or when the inspection assay indicates that significant changes in the stream's composition have occurred. Except for these circumstances, a comprehensive assay of a particular crude oil stream may not be updated for several years.

Moreover, many major pipeline companies require a comprehensive assay when accepting a new crude oil stream for transportation in their system on a common stream basis. Thereafter, an inspection assay is used for checking the quality of shipments.

BRIEF HISTORY OF CRUDE OIL EXPLOITATION AND USE

Herodotus, the ancient Greek historian, recorded about 440 BCE that the Mesopotamians in 40th century BCE used bitumen to caulk their ships and as an adhesive [16]. This is thought to be the first recorded use of petroleum by a civilization. Herodotus also recorded that beginning about 1000 BCE, the ancient Egyptians used crude oil or a derivative in their mummification process. The term "mummy" is derived from the Persian word "mummeia," meaning pitch or asphalt. Many ancient civilizations including those of the Persians and Sumerians used bitumen for medicinal purposes, a practice also known to have been used by pre-Columbian cultures in the Americas. Further documentation of the medicinal uses of petroleum was provided by Georgius Agricola, the 16th century German physician and scientist in his *De Natura Fossilium* [17]. In that, he reported that "It is used in medicine ... Spread on cattle and beasts of burden it cures mange and Pliny writes that the Babylonians believed it to be good for jaundice ... They also believed it to be a cure for leprosy (and) it is used as an ointment for the gout." In this latter respect, it has been reported by several writers that, in 1539, oil in some form was exported from Venezuela to Spain for use in treating gout suffered by the Holy Roman emperor Charles V. In his "Travels," Marco Polo wrote of its use in the 13th century in the Caspian Sea region to treat mange in camels and as a therapeutic ointment for various skin conditions in humans [18]. From the writings of Agricola and others on the medicinal virtues of petroleum, it is no wonder that centuries later "snake oil" salesmen were so successful in marketing their concoctions—many of which contained crude oil or some derivative.

The earliest known oil wells were drilled in China in 347 CE to depths of as much as 240 m using bits attached to bamboo shafts. In 1594, a well was hand dug near Baku, Azerbaijan to a depth of 35 m [19]. Hand dug wells continued to be used in Azerbaijan until the mid-19th century for recovery of crude oil [18].

The "modern" history of petroleum perhaps dates from 1846 when Abraham Gesner developed a process for extracting what he termed "keroselain" from coal [20]. In 1853, Ignacy Lukasiewicz, a Polish pharmacist, made improvements to Gesner's process and used it to distill kerosene from seep oil [21]. In 1854, Benjamin Silliman, a chemist and professor of science at Yale University, became the first person known to fractionate petroleum by distillation. This was followed in 1855 by his "Report on the Rock Oil, or Petroleum, from Venango Co., PA, with special reference to its use for illumination and other purposes" [22]. In this, he documented that half of the crude oil he studied could be economically exploited as an illuminant and that much of the remaining byproducts had commercial value.

The first commercial oil discovery in North American was made in 1858 in Ontario, Canada, when a 3-m deep hand dug pit encountered a pool of crude oil. This predated by one year the more famous well drilled by "Colonel" Edwin Drake near Titusville, Pennsylvania, to a depth of 21 m. Following Drake's success, Silliman's report became an important document in promoting commercial development at Titusville, which is located in Venango County.

Thereafter, developments in the petroleum industry spread worldwide but were most prevalent in North America and in the Caspian Sea region. Many significant developments in the exploitation and use of crude oil took place in Azerbaijan and Russia in the mid- to late 19th century. Azerbaijan is the oldest known oil-producing region in the world, and it was there that Russian engineer F. N. Semyenov drilled the first modern oil well in 1848. The first offshore well was also drilled in the Azerbaijan area of the Caspian Sea at the end of the 19th century [23]. Ludvig and Robert Nobel, brothers of Alfred, the inventor of dynamite and benefactor of his namesake Nobel Prize, were responsible for considerable development of Azerbaijan's petroleum resources and for several technological advances. Beginning in 1877, they had a fleet of tankers, several railway tank cars, and a pipeline built for transporting crude oil. The brothers introduced the use of tanks to store crude oil, rather than in the commonly used open vessels and pits [24]. This practice resulted in large losses through evaporation and oil penetrating into the ground and significant ecological damage that persisted for decades. By 1900, Azerbaijan was the world's largest producer of crude oil.

Totten provides a comprehensive timeline of the important events in the history of the petroleum industry from ancient times to the present [19]. Table 1 provides a summary of some of the highlights in ancient and modern exploitation and use of crude oil.

Zayn Bilkadi, in his introduction to *Babylon to Baku* [25], accurately portrayed the importance of petroleum in today's world.

> There is one natural material which touches almost every facet of our lives; it assists us to travel long distances, it is an ingredient in many of our medicines, it is used in the manufacture of our clothes and in the microchips we build into our computers. In fact, it is essential to our daily existence.

That material is, of course, crude oil.

A few of the superlatives that can be attributed to crude oil are

- Volume produced each day worldwide is sufficient to fill a string of railroad tank cars over 2100 km in length
- Basis of world's first trillion dollar industry
- World's most actively traded commodity
- Largest single item in balance of payments and exchanges between nations
- Employs most of world's commercial shipping tonnage
- More than 1 million km of pipelines are dedicated to its transportation

STRATEGIC IMPORTANCE OF CRUDE OIL

Early in the 20th century, Winston Churchill successfully argued that the British Navy should switch from coal to petroleum to power its warships [26]. In 1907, the *Oil & Gas Journal* in an article titled "When Will the United States Navy Wake Up!" reported on the British Admiralty converting its warships from use of coal to crude oil as fuel [27]. The article went on to state that "Japan is also aware of the fact that coal is so scarce in (the Pacific Ocean) that the use crude oil as fuel is absolutely imperative to insure success or

TABLE 1—Historical highlights in exploitation and use of crude oil.

Year	Event
40th century BCE	Mesopotamians use bitumen to caulk ships and as an adhesive
1000–300 BCE	Egyptians use a derivative of crude oil in mummification
2500 BCE–1400 CE	Crude oil used for medicinal purposes by many Eurasian and western hemisphere cultures
347 CE	Wells drilled in China to depth of 240 m using bits attached to bamboo shafts
13th century CE	Marco Polo in his "Travels" records it being used to treat mange in camels and as a therapeutic ointment by humans in the Caspian Sea region
1539	Exported from Venezuela to Spain to treat gout in HRE Charles V
1594	Well hand dug in Azerbaijan to depth of 35 m
1846	Gessner develops process for extracting "keroselain" from coal
1853	Lukasiewicz distills kerosene from seep oil
1855	Silliman publishes his "Report on the Rock Oil, or Petroleum, from Venango Co., PA ...." This is the first known crude oil "assay."
1859	"Col." Drake drills successful well at Titusville, PA
1863	2" diameter cast iron pipeline built at Titusville to transport crude oil 2 ½ mi
1873–1890	Nobel brothers develop Azerbaijan's petroleum resources and implement numerous technological advances related to production, storage, and transportation
1886	Benz patents "carriage with gasoline engine"
1891	Thermal cracking process patented by Russian engineer V. Shukhov
1892	Patent issued in Germany for internal compression (diesel) engine
1914–1918	Large scale demand created for petroleum products – mostly gasoline
1936	Catalytic cracking process developed by Eugene Houdry of Sun Oil Co.
1942–1943	The "Big Inch" a 24" diameter pipeline built to transport crude oil from East Texas to refineries at Linden, NJ and Philadelphia

victory (in naval operations)." The article noted that U.S. Navy Department "reports demonstrated conclusively the superiority of crude oil over coal as a fuel." In 1910, with passage of the Picket Act and support of President William Howard Taft, the United States withdrew oil-bearing lands in California and Wyoming as sources of fuel for the U.S. Navy. These later became known as Naval Petroleum Reserves. In this case, the crude oil–when needed–would be used to produce Navy Special Fuel Oil–a heavy fuel oil analogous to No. 5 burner fuel–rather than for direct burning.

In 1919, a German patent was issued to Deutsche Erdöl AG for underground storage of petroleum in caverns in salt beds [28]. At that time, it is likely that little attention was given to its strategic potential–present or future. The first known use of this technology was in 1950, when a solution-mined cavern in salt was used for operational storage of propane and butane in the Keystone Field in western Texas.

In the years leading up to World War II, several countries, including Sweden and Britain, began stockpiling refined products such as aviation gasoline–but apparently not crude oil. After its entry into World War II, some senior U.S. politicians recognized the strategic importance of crude oil. In December 1943, Secretary of the Interior Harold Ickes wrote an article "We're Running out of Oil" in which he warned "if there should be a World War III it would have to be fought with some else's petroleum, because the United States wouldn't have it." [29,30]. In 1944, Ickes called for the stockpiling of crude oil, but no action was taken. Then in 1952, President Harry S Truman's Minerals Policy Commission advocated a strategic oil supply. After the Suez Crisis in 1956, Britain began storing crude oil and refined products in solution-mined caverns in salt, and President Eisenhower recommended creation of a reserve in the United States. In support of Presidents Truman and Eisenhower, the U.S. National Petroleum Council submitted reports promoting the practicality of petroleum reserves.

The large-scale creation of petroleum stockpiles began in the late 1960s. From 1967 to 1972, France, Germany, Japan, and others commenced stockpiling crude oil and refined products in aboveground tanks, underground caverns, and tank ships. The United States did not begin stockpiling crude oil until after the Arab Oil Embargo of 1973−1974 when it created the Strategic Petroleum Reserve. From 1980 through the present, there has been a global proliferation of stockpiles [31]. Among the major countries currently having or currently developing crude oil stockpiles are Austria, France, Germany, India, Japan, the Netherlands, Spain, People's Republic of China, Republic of Korea, and the United States. In 2008, the U.S. Energy Information Administration estimated that over 4 billion barrels of petroleum reserves existed worldwide, with crude oil comprising somewhat more than half of the total.

Developments in Analysis of Crude Oil

Benjamin Silliman, professor of chemistry at Yale University, is probably the father of crude oil analytical chemistry. In late 1854, he was sent three barrels of "rock oil" skimmed from Oil Creek in Venango County, Pennsylvania. Over the next 5 months he conducted several tests during which he developed a technique that today is known as fractional distillation. Using this, he "refined" the rock oil and separated it into eight fractions. In his report, Silliman described the general properties of the oil and those of the fractions he had distilled and collected. He determined the boiling range of each and their specific gravity [22]. This likely is the first assay of a crude oil every published.

Silliman's report was followed just 1 year later by a report that dealt with the "artificial destructive distillation" and characterization of "Burmese Naphtha, or Rangoon Tar" [32]. In this, it was noted that the material "contains indeed so great a variety of substances, and some of them in so exceedingly minute a proportion, that even the large amount of material at our disposal was insufficient for the complete examination of several constituents, the presence of which we had succeeded in establishing beyond a doubt." In the course of the investigation, several aromatic compounds were separated and studied in great detail.

By the end of the 19th century, great strides had been made in determining the composition of crude oil, mostly by Russian scientists and engineers involved in its refining.

> It was clear that crude oil was a greatly varying mixture of widely different hydrocarbons, a mixture of straight-chain paraffins (sometimes with short side chains), of aromatic hydrocarbons deriving from benzene, and cyclic hydrocarbons or naphthenes having a ring structure with five or six carbon atoms as nucleus. Besides these saturated hydrocarbons there might also be present small quantities of unsaturated olefins, sulphur, nitrogen and oxygen compounds, which gave each crude a special character and compelled the refiner to take its composition into account [33].

Beginning in 1924, API began supporting several research projects on the heteroatomic composition of crude oil. The first two of these, initiated in 1926, were to isolate and study sulfur and nitrogen compounds. This was followed in 1927 by a project on the metallic constituents of crude oil [34]. These and several other studies that continued into the 1960s used separation, analysis, and compound identification techniques, some of which might seem primitive by modern standards, yet they succeeded in separating and identifying over 600 individual hydrocarbons and over 200 individual sulfur compounds. Unquestionably, these studies have been fundamentally important in our understanding of the origin, chemistry, and geochemical history of crude oil.

In the last 40 years, advances in instrumentation have allowed the petroleum chemist to separate and identify crude oil components that are characterized as "novel" by some investigators [35]. However, these are present in such infinitesimally small concentrations that they do not have even a trivial effect on refining or product quality, yet they may provide important insight into the origin of petroleum and its transformation in the reservoir. These techniques include gas chromatography (GC), mass spectrometry (MS), atomic absorption and inductively coupled plasma (ICP) spectrometry, and numerous multihyphenated techniques such as GC-MS, atomic emission spectrometry (AES)-ICP, and ICP-MS, among others [36].

2

Sampling

The basic objective of sampling is to obtain a small portion ("spot" sample) for analysis that is truly representative of the material contained in a large bulk container, vessel, or pipeline shipment. Often, the spot sample may be as little as one part in greater than ten million. Frequently, a series of spot samples may be collected and composited for analysis, which can help to minimize randomness and nonhomogeneity and make for a somewhat more representative sample. Samples to be composited must be thoroughly mixed and volumetrically proportional.

Crude oil to be sampled may be in static storage in an above- or underground tank or a marine vessel, or it may be flowing through a pipeline or vessel offloading line. For static storage, samples are collected manually using several different devices. For streams flowing in a pipeline, automatic sampling methods are used. In establishing a sampling protocol, the analytical tests to be performed will dictate the volume of sample needed, type(s) of container(s) to be used, and precautions necessary to preserve sample integrity. The latter consideration is especially important for samples to be collected for vapor pressure determination or measurement of hydrogen sulfide (H_2S) content.

The importance of adhering to a rigorous sampling protocol to ensure that samples are representative of the bulk material cannot be overemphasized. Representative samples are required for the determination of chemical and physical properties used to establish standard volumes and compliance with contractual specifications. Maintaining compositional integrity of these samples from the time of collection until they are analyzed requires care and effort.

Moreover, it is critically important that the sampling procedure does not introduce any contaminant into the sample or otherwise alter the sample so that subsequent test results are affected. Procedures for collection and handling of samples for H_2S determination are especially critical because of the highly reactive nature and volatility of this compound. Appendix 1 provides recommended procedures suitable for collection and handling of samples for determination of H_2S in crude oil. These were developed by the U.S. Department of Energy's Strategic Petroleum Reserve in support of its crude oil assay program and underwent rigorous field and laboratory testing [37]. With proper handling, samples do not exhibit detectable loss of their H_2S for a minimum of 10 days.

MANUAL SAMPLING

ASTM D4057: Practice for Manual Sampling of Petroleum and Petroleum Products[1,2] provides procedures for manually obtaining samples, the vapor pressure of which at ambient conditions is below 101 kPa (14.7 psi), from tanks, pipelines, drums, barrels, and other containers. This practice addresses, in detail, the various factors that need to be considered in obtaining a representative sample. These considerations include the analytical tests to be conducted on the sample, the types of sample containers to be used, and any special instructions required for special materials such as crude oils to be sampled. Test Method D5854 provides additional guidance for sample mixing and handling. In many liquid manual sampling applications, it must be kept in mind that the material to be sampled contains a heavy component (e.g., free water) that tends to separate from the main component. Unless certain conditions can be met to allow for this, an automatic sampling system as described in ASTM D4177 is highly recommended.

Apparatus

Sample containers come in various shapes, sizes, and materials. To be able to select the right container for a given application, one must have knowledge of the material to be sampled to ensure that there will be no interaction between the sampled material and the container that would affect the integrity of the other. Additional considerations in the selection of sample containers are the type of mixing required to remix the contents before transferring the sample from the container and the type of laboratory analyses that are to be conducted on the sample. For most samples, the container must be large enough to contain the required sample volume without exceeding 80% of the container capacity. The additional capacity is required for thermal expansion of the sample and to enhance sample mixing efficiency.

SAMPLE MIXING SYSTEMS

The sample container should be compatible with the mixing system for remixing samples that have stratified to ensure that a representative sample is available for transfer to an intermediate container or the analytical apparatus. This is especially critical when remixing crude oil samples to ensure a representative sample. When separation of entrained constituents such as sediment and water is not a major concern, adequate mixing may be achieved by such methods as shaking (manual or mechanical) or use of a shear mixer. However, manual and mechanical shaking of the sample container are not recommended methods for mixing a sample for sediment and water analysis. Tests have shown it is difficult to impart sufficient mixing energy to mix and maintain a homogeneous representative sample.

SAMPLE TRANSFERS

The number of intermediate transfers from one container to another between the actual sampling operation and testing

---

[1] Appendix 2 lists the ASTM and other standards referenced in this manual.

[2] Appendix 3 provides *excerpts* from the Scope and certain other sections for most of the ASTM standards cited in this manual.

should be minimized to the maximum extent possible. The loss of light hydrocarbons as the result of splashing, loss of water due to clingage, or contamination from external sources, or a combination thereof, may distort test results. The more transfers between containers, the greater the likelihood one or more of these problems may occur.

SAMPLE STORAGE

Except when being transferred, samples should be maintained in a closed container to prevent loss of light components. Samples should be protected during storage to prevent weathering or degradation from light, heat, or other potentially detrimental conditions. Refrigerated storage at approximately 5°C will help preserve compositional integrity when samples are stored for protracted periods.

SPECIAL PRECAUTIONS

Crude oil almost invariably contains sediment and water, which will rapidly settle out, and may contain H_2S, an extremely toxic gas. Sampling of tanks through a stand pipe that is not slotted or perforated will not yield a representative sample. When crude oil is to be tested for vapor pressure, care must be exercised in sample collection and handling, and reference should be made to ASTM D5842.

AUTOMATIC SAMPLING

ASTM D4177: Practice for Automatic Sampling of Petroleum and Petroleum Products covers information for the extraction of representative samples of petroleum from a flowing stream and storing them in a sample receiver. Several precautions must be observed in the use of automatic systems when sampling crude oil. Free and entrained water must be uniformly dispersed at the sample point. The sample must be maintained in the sample receiver without altering the sample composition. Venting of hydrocarbon vapors during receiver filling and storage must be minimized. A properly designed, installed, tested, and operational automatic sample system is to be preferred to manual sampling and is more likely to provide a representative test specimen that can be delivered into the analytical apparatus.

SAMPLING FOR VAPOR PRESSURE DETERMINATION

ASTM D5842: Practice for Sampling and Handling of Fuels for Volatility Measurements covers procedures and equipment for obtaining, mixing, and handling representative samples of volatile fuels. Although directed to products such as gasoline and reformulated fuels, the guidance provided is also useful in sampling and handling of crude oils and condensates.

Vapor pressure is extremely sensitive to evaporation losses and to slight changes in composition. The precautions required to ensure the representative character of the sample are numerous and depend on the tank, carrier, container, or pipe from which the sample is being obtained; the type and cleanliness of the sample container; and the sampling procedure that is used. For example, ASTM D323 requires that the sample shall be taken in 1-L containers filled 70–80 %. The sample container and its contents have to be cooled to a temperature of 0–1°C before the container is opened. With crude oils with a pour point greater than 1°C, this requirement can affect results. Directions for sampling cannot be made explicit enough to cover all cases, and extreme care and good judgment are necessary.

MIXING AND HANDLING OF SAMPLES

ASTM D5854: Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products covers the handling, mixing, and conditioning procedures that are required to ensure that a representative sample is delivered from the primary sample container or receiver into the analytical test apparatus or into intermediate containers. This practice also provides a guide for selecting suitable containers for crude oil samples for various analyses.

Further guidance and precautions to be observed in sampling for specific tests such as water determination and measurement of vapor pressure are provided in discussion of the relevant test methods elsewhere in this manual.

Sample Containers

No single container type will meet requirements of all sampling operations or restrictions necessary to ensure sample compositional integrity for different tests. Sample containers must be clean and free from all substances that might contaminate the material being sampled, such as water, dirt, washing compounds, naphtha or other solvent, soldering fluxes, acid, rust, and oil. Table 1 provides a guide for selecting the sample container most suitable for various crude oil analyses. It is impossible to cover all sampling container requirements; therefore, when questions arise as to a container's suitability for a given application, experience and testing should be relied upon. Regardless of the container type, before a sample is transferred from one container to another, a homogenous mix must be created and maintained until the transfer is complete. Even "new" containers should be inspected for cleanliness before use.

Sample Mixing Methods

Sample mixing methods can be divided into three general categories of power mixing, shaking, and no mixing. These categories vary greatly in severity depending on the equipment used, the type of analytical test to be conducted, and the characteristics of the sample. Further, power mixers are of two subtypes–insertion and closed loop. Overmixing with power mixers may create an oil and water emulsion that will affect the accuracy of certain analytical tests. Power mixers may entrain air into the sample that could affect certain analytical tests. Loss of vapor normally associated with rise in temperature may also occur, which could affect test results for water, Reid vapor pressure (RVP), and density. Shaking simply involves manually or mechanically shaking the sample container to redisperse separated constituents such as sediment and water. If a sample is known to be homogeneous, no mixing is required; however, this is rarely the case with crude oils. Nevertheless, samples should not be mixed when the analytical tests to be conducted may be affected by air, which could be introduced by power mixing or shaking. When the results will be affected by interference from extraneous material such as water and sediment, the sample should not be shaken. Table 2 lists the recommended mixing procedure to be used before a sample is transferred from a container for certain crude oil tests.

SAMPLE CHAIN OF CUSTODY

Chain-of-custody procedures are a necessary element in a program to ensure one's ability to support data and conclusions adequately in a legal or regulatory situation. ASTM D4840: Guide for Sample Chain-of-Custody Procedures contains a

TABLE 1—Summary of Container Materials for Crude Oils (ASTM D5854)

	Type of Analysis										
	Density	Chloride	Hydro-Carbon Distribution	Neutralization Number	Pour Point	Salt	S and W	Sulfur	Trace Metals	Vapor Pressure	Viscosity
Hard borosilicate glass											
Immediate use	S	P	NP	P	S	S	S	P	P	S	S
Storage—6 months	S	P	NP	P	S	S	S	P	P	S	S
Reuse	S	P	NP	P	S	S	S	P	S	S	S
Stainless steel											
Immediate use	S	S	S	S	S	S	S	S	S	S	S
Storage—6 months	S	S	S	S	S	S	S	S	S	S	S
Reuse	S	S	S	S	S	S	S	S	S	S	S
Epoxy-lined steel											
Immediate use	P	S	S	S	S	S	P	S	S	S	S
Storage—6 months	P	S	S	S	S	S	P	S	S	S	S
Reuse	S	S	S	S	S	S	S	S	S	S	S
Tin-plated soldered steel (Superclean only)											
Immediate use	S	S	S	S	S	S	S	S	NR	S	S
Storage—6 months	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Reuse	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Polytetrafluoroethylene, Perfluoroalkoxy or Fluorinated ethylene propylene											
Immediate use	S	S	NP	S	S	S	S	S	P	S	S
Storage—6 months	NR	NR	NP	NR	NR	NR	NR	NR	NR	NR	NR
Reuse	S	S	NP	S	S	S	S	S	S	S	S
High-density linear polyethylene											
Immediate use	S	S	NP	S	S	S	S	S	P	S	S
Storage—6 months	S	NR	NP	NR	NR	NR	NR	NR	NR	NR	NR
Reuse	S	NR	NP	NR	NR	NR	NR	NR	NR	NR	NR

Note 1—The containers listed in this summary should not be used without consulting the appropriate paragraphs of this practice for detail advice.
Note 2—Where REUSE is indicated, containers should be cleaned in accordance with 6.7 prior to reuse.
Note 3 Legend:
NR = not recommended
NP = not practical
P = preferred
5 = suitable

TABLE 2—Summary of Recommended Mixing Procedures for Crude Oils

Test Purpose	Recommended Mixing Procedure	
	Power	None
Density	X	
Sediment and water	X	
Vapor pressure		X
Sulfur by X ray		X
Other tests	Note 1	Note 1

Note 1 = Refer to specific analytical test procedure.

comprehensive discussion of potential requirements for a sample chain-of-custody program and describes the procedures involved. The purpose of these procedures is to provide accountability for and documentation of sample integrity from the time samples are collected until they are disposed of.

SAMPLE ARCHIVE

Samples, or representative portions thereof, should be maintained in a sample archive for a minimum of 45 days, although the time requirement can be from 30 to 180 days. Archived samples may be needed in case of disputes, should additional data become necessary, or to conform to contractual requirements or environmental or governmental regulations.

SUMMARY

In any sampling operation, whether manual or automatic, it must be kept in mind that crude oils are not homogeneous. They contain sediment and water that can settle out and asphaltenes and waxes that can flocculate or precipitate out under certain conditions. In pipeline shipments, different crudes will commonly be batched, and some mixing will take place between the heads and tails of these. When crude oils are discharged into a storage tank, there will frequently be a tank heel that may be of different quality. During storage in a tank, crudes oils–even a single crude–can differentiate and exhibit a density differential from top to bottom. Also, sediment and water present in the incoming crude oil will settle during storage. Conversely, sediment and water already present in a tank heel can be resuspended by the turbulence created when further crude oil is pumped in. Crude oil can also exhibit a density differential from one side of a tank to the opposite because of heating by the Sun’s rays. At a terminal, when storage capacity is at a premium, operators may intentionally layer similar quality crudes in a tank. Collection of a representative sample may be impeded by the presence of deadwood in ship’s compartments and tank stand pipes that are not slotted or perforated. In sampling a pipeline, flow must be turbulent and not laminar. With dense or viscous crude oils, this can become problematic.

In conclusion, it was accurately said “Sampling is truly an art. Failure to use proper techniques can cost companies huge sums of money daily. Sampling is too critical to be left to guess work, old outdated methods, or unproven techniques” [38].

3

Inspection Assays

INTRODUCTION

The testing of crude oils to determine their quality and to assess refining characteristics generally involves two sequential but complimentary series of tests. An inspection analysis as described in this chapter is performed initially to determine a few to numerous whole crude oil properties. This is followed by a detailed comprehensive analysis described in the next chapter that involves distillation of the crude oil into several fractions or cuts that are analyzed to determine their suitability for use or blending into a host of refined products.

Inspection assays comprise a relatively limited number of tests generally restricted to the whole crude oil. On the basis of published data, there is little agreement as to what constitutes an inspection assay. Because the data are primarily for intracompany use, there is little driving force for a standard scheme. At a bare minimum, American Petroleum Institute (API) gravity and sulfur, sediment, and water content are usually determined, although it is useful to also know the pour point, which provides some basic perception of the crude oil's fluidity and composition. A more detailed inspection assay might consist of the following tests: API gravity (or density or relative density), total sulfur content, pour point, viscosity, carbon residue, salt content, total acid number (neutralization number), and water and sediment content. Individual shippers and refiners may substitute or add tests (e.g., trace metal or organic halide tests) that may be critical to their operations. Combining the results from these few tests and high-temperature simulated distillation data of a current crude oil batch with the archived data from a comprehensive assay, the process engineer will be able to estimate generally the product slate that the crude will yield and any extraordinary processing problems that may be encountered.

In the early 1990s, the API formed an Ad Hoc Crude Oil Quality Task Force. The report of this task group recommends a set of crude oil quality testing procedures that, if adopted by a shipper or refiner, would help ensure the quality of crude oil from the wellhead to the refinery [39]. These procedures include tests for API gravity, sediment and water content, organohalide compounds, salt, sulfur, and neutralization number, among others. Although not a standard, it is an important aid to members of the petroleum industry in protecting the quality of common stream crude petroleum from contamination by foreign substances or crude petroleum of unspecified makeup. The report is also a useful guide for an inspection program using mostly standardized procedures widely accepted in the industry for monitoring the quality of mercantile commodity.

It is important to note that, in the following discussion of test methods, "crude oil" may not be included in the title or even in the scope. However, many test methods have been adapted to and are widely used and accepted for crude oil analysis.

API GRAVITY AND DENSITY

Accurate determination of the density or API gravity of crude oil is necessary for the conversion of measured volumes to volumes at the standard temperature of 15.56°C (60°F) using ASTM D1250: Petroleum Measurement Tables. API gravity is a special function of relative density (specific gravity) represented by the following:

$$\text{API gravity, degrees} = \left(\frac{141.5}{\text{specific gravity } 60/60^\circ\text{F}}\right) - 131.5 \tag{1}$$

No statement of reference temperature is required because 60°F is included in the definition. Fig. 1 depicts the relationship between the two. A specific gravity of 1.00–that of water–equates to an API gravity of 10.0.

API Gravity History

In 1916, the U.S. National Bureau of Standards adopted the Baumé scale as the standard for measuring the specific gravity of liquids less dense than water. The Baumé scale, developed in 1768, used solutions of sodium chloride (NaCl) in water for degree calibration. When adopted, a large margin of error was unintentionally introduced as later found in investigation by the U.S. National Academy of Sciences. This resulted in hydrometers in the United States being manufactured with a modulus of 141.5 rather than the correct Baumé scale modulus of 140. By 1921, the scale was so firmly established that API created the API gravity scale, which recognized the scale being used by the industry [40].

Density and API gravity are also factors indicating the quality of crude oils. Generally, the heavier (lower the API gravity) the crude oil the greater the quantity of heavier components that may be more refractory and require greater upgrading or more severe cracking to produce salable products. Conversely, the lighter the crude oil the greater the quantity of easily distillable products. Crude oil prices are frequently posted against values in kilograms per cubic metre (kg/m^3) or in degrees API. However, this property alone is an uncertain indication of quality and must be correlated with other properties.

The relative density (specific gravity) or density of a crude oil may also be reported in analyses. Relative density is the ratio of the mass of a given volume of liquid at a specific temperature to the mass of an equal volume of pure water at the same or a different temperature. Both reference temperatures must be explicitly stated. Density is simply the mass of liquid per unit volume at 15°C, with the standard unit of measurement being kg/m^3.

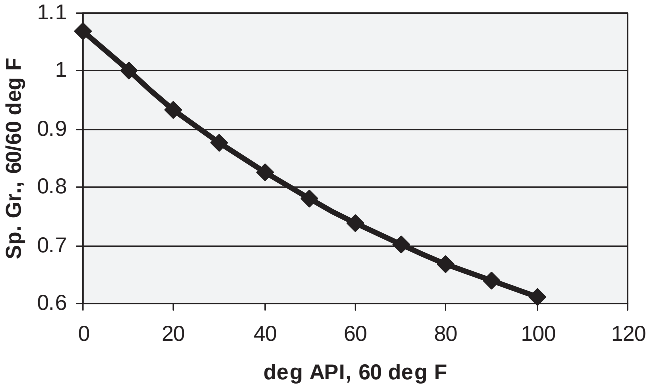


Fig. 1—Relationship between specific gravity and API gravity.

Measurement by Hydrometer

API gravity, or density or relative density, can be determined easily using one of two hydrometer methods [ASTM D287: Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method), or ASTM D1298: Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method]. A third hydrometer method (ASTM D6822: Test Method for Density, Relative Density, and API Gravity of Crude Petroleum and Liquid Petroleum Products by Thermohydrometer Method) is more applicable to field applications in which limited laboratory facilities are available.

Measurement by Digital Density Analyzer

Many laboratories are now using an instrumental method (ASTM D5002: Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer) rather than the hydrometer methods. This method requires a considerably smaller sample than the hydrometer methods.

Density or API gravity as determined by the hydrometer methods is most accurate at or near the standard temperature of 15.56°C (60°F). The results of all four of the test methods will be affected by the presence of air or gas bubbles and sediment and water and by the loss of light components. For volatile crude oils [i.e., those with a Reid vapor pressure (RVP) of >50 kPa] it is preferable to use a variable volume (floating piston) sample container to minimize loss of light components. In the absence of this apparatus, extreme care must be taken to minimize losses, including the transfer of the sample to a chilled container after sampling. It is also preferable to mix the sample in its original closed container to minimize loss of light components.

For crude oils having a pour point greater than 10°C, or a cloud point or wax appearance temperature (WAT) greater than 15°C, the sample should be warmed to 9°C above the pour point, or 3°C above the cloud point or WAT, before mixing. As discussed in a subsequent chapter, IP389 determination of WAT of middle distillate fuels by differential thermal analysis (DTA) or differential scanning calorimetry (DSC) will provide an indication of the WAT.

BITUMEN AND EXTRA-HEAVY CRUDE OILS

The presence of water, solids, and air bubbles–all of which can be difficult to remove from these materials before analysis–makes accurate determination of their density more difficult than for lighter crude oils. Sediment and water do not readily settle out, and air bubbles are not easily seen.

Pycnometers are suitable for measurement of density of these materials. ASTM D1480: Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer describes two procedures for the measurement of the density of materials that are fluid at the desired test temperature. In addition to ASTM D5002, ASTM D4052: Test Method for Density and Relative Density of Liquids by Digital Density Meter has also been used for determining density of bitumens and heavy crude oils. In using digital density meters, air bubbles can result in unstable readings, and heating the sample before analysis can help to eliminate them.

Determination of the density of semi-solid and solid bituminous materials and materials having a density greater than 1.00 (API <10.0°) is beyond the scope of this manual.

SULFUR CONTENT

The sulfur content of a crude oil, which may vary from less than 0.1 to over 5 mass percent, is one of its most important quality attributes. Sulfur compounds are some of the most egregious nonhydrocarbon materials present in crude oils. They contribute to corrosion of refinery equipment and poisoning of catalysts, cause corrosiveness in refined products, and contribute to environmental pollution through emission of sulfur oxides from combustion of fuel products. Sulfur compounds may be present throughout the boiling range of crude oils, although, as a rule, they are more abundant in the heavier fractions. In some crude oils, thermally reactive sulfur compounds can decompose on heating to produce hydrogen sulfide, which is highly toxic and very corrosive. Consequently, in reporting the hydrogen sulfide content of a crude oil, it is important to distinguish between that which is dissolved and that which is evolved on heating or distillation. The thiols (mercaptans) typically present in a crude oil can impart a foul odor, depending on the species. Butanethiol, a compound naturally present in many crude oils, is one of the odorants commonly used in natural gas. The fetid smell in the secretion ejected by skunks is also due, in part, to this compound. Ethanethiol is another odorant commonly used in natural gas and liquefied petroleum gases (propane and butane).

Until relatively recently, one of the most widely used methods for determination of total sulfur content has been combustion of a sample in oxygen to convert the sulfur to sulfur dioxide, which is collected and subsequently titrated iodometrically or detected by nondispersive infrared (IR) spectroscopy. This is commonly referred to as the Leco technique, but in its standard form is ASTM D1552: Test Method for Sulfur in Petroleum Products (High-Temperature Method). In IR detection, the most commonly used form of measurement, a sample is weighed into a boat, which is then inserted into the furnace and combusted. Although the scope of the method indicates it is applicable to samples boiling above 177°C, it has been widely used for the analysis of crude oils. Loss of light components during the weighing and transfer process could be expected to affect results. A much older method involving combustion in an oxidation bomb with subsequent gravimetric determination of sulfur as barium sulfate [ASTM D129: Test Method for Sulfur in Petroleum Products (General Bomb Method)] is not as accurate as the high-temperature method, partially because of interference from the sediment inherently present in crude oil.

These older techniques have now largely been replaced by two instrumental methods: ASTM D2622: Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry and ASTM D4294: Test Method for Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy.

A fundamental assumption in ASTM D2622 is that the sample and standard matrices are well matched. When the elemental composition of the sample differs significantly from that of the standard, errors in the sulfur determination can result. For crude oils, this matrix mismatch is usually the result of differences in the carbon-hydrogen ratio. Presence of interfering heteroatomic species is less likely to be a contributing factor. This test method provides rapid and precise measurement of total sulfur with a minimum of sample preparation. However, the equipment tends to be more expensive than for alternative test methods, such as ASTM D4294.

In the round-robin studies used to develop precision data for ASTM D2622 and ASTM D4294, the highest level of sulfur in a sample was 4.6 mass percent. Samples containing more than 5.0 mass percent should be diluted to bring the sulfur concentration of the diluted material within the scope of the test method. However, samples that are diluted can have higher errors than nondiluted samples.

As with ASTM D2622, a fundamental assumption in ASTM D4294 is that the sample and standard matrices are well matched. Moreover, spectral interferences may arise from the presence of silicon, calcium, and halides–elements commonly present in the inorganic sediment inherently present in crude oils. In modern instruments, these may be compensated for with the use of built-in software. ASTM D4294 also provides rapid and precise measurement of total sulfur with a minimum of sample preparation, and the instrumentation is less costly than that for ASTM D2622. Of the two methods, ASTM D4294 has slightly better repeatability and reproducibility and is also adaptable to field applications.

Sediment, water, and waxes commonly present in crude oil samples can settle onto the Mylar™ film sealing the test cell and interfere in sulfur determination by both of the X-ray methods. Before analysis, water and particulates should be removed from the sample by centrifugation or settling, but care must be taken that sample integrity is not compromised.

ASTM D7343 Optimization, Sample Handling, Calibration, and Validation of X-ray Fluorescence Spectrometry Methods for Elemental Analysis of Petroleum Products and Lubricants provides information relating to sampling, calibration, and validation of X-ray fluorescence instruments applicable to determination of sulfur by ASTM D2622 and D4294. This practice includes sampling issues such as the selection of storage vessels, transportation, and subsampling. Treatment, assembly, and handling of technique-specific sample holders and cups are also included. Technique-specific requirements during analytical measurement and validation of measurement are described.

Hydrogen Sulfide and Thiols or Mercaptans

Hydrogen sulfide (H_2S) is a highly toxic and corrosive gas that occurs naturally in some but not all crude oils. H_2S can be formed by thermal decomposition of elemental sulfur and thiols, and even crude oils that do not contain the compound naturally may produce the gas on heating or during distillation. Reservoir "souring" by H_2S may occur from reduction of bisulfite chemicals used as oxygen scavengers, thermal decomposition of sulfur compounds, or dissolution of iron sulfide. H_2S is also known to be produced by action of sulfate-reducing bacteria (SRB) in storage tanks, in the legs of offshore production platforms used for storage, and in the dead legs of pipelines. Studies have shown that the H_2S present in some crude oil reservoirs has unequivocally resulted from SRB activity [41]. Sulfate reduction in the reservoir by SRB introduced with water used for enhanced oil recovery is now widely accepted as the most significant mechanism contributing to formation of H_2S in crude oils [42].

In analyses, it is important to report H_2S as dissolved (existent; that which is naturally present) or evolved (potential; that which results from decomposition of sulfur compounds on heating or distillation). Elemental sulfur and many thiols will decompose when heated and form H_2S.

Thiols or mercaptans are considerably more prevalent in crude oils than H_2S. They are the least stable sulfur compounds and many decompose on heating to form H_2S. This reaction can begin at less than 100°C, with maximum evolution at approximately 200°C [43]. Thiols may be distributed across a wide boiling range, extending from the lightest fraction well into vacuum gas oil, and can give rise to evolution of H_2S across much the same boiling range. Free sulfur is known to occur in crude oils and it will also decompose on heating to form H_2S.

These components are commonly determined by nonaqueous potentiometric titration with silver nitrate (UOP 163: Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration). The presence of free sulfur in samples complicates interpretation of the titration curves. A newer test method developed specifically for fuel oils may prove applicable to crude oils with further testing (IP 570 Determination of Hydrogen Sulfide in Fuel Oils—Rapid Liquid Phase Extraction Method). The test method is automatic, suitable for laboratory or field use, and provides results in approximately 15 min. Crude oils were not included in the interlaboratory study that developed the method's precision data, and a new round robin will need to be conducted to obtain these.

H_2S is very volatile and highly reactive, and unless precautions are taken in the collection and preservation of samples, results will not be representative (Appendix 1). A test kit has been developed that is very useful for rapidly determining H_2S concentration in liquid samples in the field [44]. This kit has an accuracy of approximately ±20 % for H_2S. A commonly used field technique for determining H_2S concentration in head space gases is the so-called "Dräger" tube, keeping in mind that concentration in the head space cannot be equated to liquid concentration. This is especially applicable to marine cargoes as reported in the International Safety Guide for Oil Tankers and Terminals. "It is important to distinguish between concentrations of H_2S in the atmosphere, expressed in ppmv, and concentrations in liquid petroleum expressed in ppmw. For example, a crude oil containing 70 ppmw H_2S has been shown to give rise to a concentration of 7,000 ppmv in the gas stream" [45].

WATER AND SEDIMENT

The water and sediment content of crude oil results principally from production and transportation practices. Water, with its dissolved salts, may occur as easily removable suspended droplets or as an emulsion. The sediment dispersed in crude oil may be comprised of inorganic minerals from the production horizon or from drilling fluids, as well as scale and rust from pipelines and tanks used for oil transportation and storage. Usually water is present in far greater amounts than sediment, but, collectively, it is unusual for them to exceed 1 % (v/v) of the crude oil on a delivered basis. Water and sediment can foul heaters, distillation towers, and exchangers and can contribute to corrosion and to deleterious product quality. Also, water and sediment are principal components of the sludge that accumulates in storage tanks and must be disposed of periodically in an environmentally acceptable manner.

Further, water bottoms in storage tanks can promote microbiological activity and, if the system is anaerobic, production of corrosive acids and H_2S can result. This is not usually a problem with crude oils because stocks are normally rotated on a regular basis. Nevertheless, anaerobic degradation of crude oil stocks and production of H_2S has been known to happen, and the operator must be aware of the potential for this occurring and the analyst must take this into consideration in evaluating results.

Knowledge of the water and sediment content is also important in accurately determining net volumes of crude oil in sales, taxation, exchanges, and custody transfers. When a significant amount of free water is present in a marine cargo, identification of its probable source should be a major consideration. Guidelines that include basic sampling, testing, and analytical procedures and interpretation and presentation of results for this process have been published by API in their *Manual of Petroleum Measurement Standards* [46].

Several test methods exist for the determination of water and sediment in crude oil. Some of these are specific to water alone, others to sediment alone, and one other to a combination of sediment and water.

Water

Techniques for measuring water content are heating under reflux conditions with a water immiscible solvent that distills as an azeotrope with the water (ASTM D4006: Test Method for Water in Crude Oil by Distillation), potentiometric titration (ASTM D4377: Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration), or the more generally preferred coulometric titration (ASTM D4928: Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration). The latter two Karl Fischer methods include a homogenization step designed to redisperse any water that has separated from the crude oil while the sample has been stored. Because the two Karl Fischer methods are quite similar, it has been proposed that they be combined into a single method with two parts–one for potentiometric titration and the second for coulometric titration. Water may also be determined by centrifugation, as discussed in the following subsection on water and sediment.

The precision of the distillation method, especially at low levels, can be affected by water droplets adhering to surfaces in the apparatus and therefore not settling into the water trap to be measured. To minimize the problem, all apparatus must be chemically cleaned at least daily to remove surface films and debris, which hinder free drainage of water in the test apparatus. At the conclusion of the distillation, the condenser and trap should be carefully inspected for water droplets adhering to surfaces. These should then be carefully dislodged using a tetrafluoroethylene (TFE) pick or scraper and transferred to the water layer.

For both of the Karl Fischer methods, thiols and sulfides (S^- and H_2S) are known to interfere, but at levels of less than 500 µg/g (ppm) the interference from these compounds is insignificant except at low water levels (<0.02 mass percent). If thiol and H_2S contents are accurately known and water levels are very low, corrections can be approximated for the interfering compounds. The interference from thiol sulfur follows the theoretical stoichiometry of 1 to 0.28; that is, 1,000 µg/g (ppm) of thiol sulfur can generate a response equivalent to 280 µg/g (ppm) water. The interference from H_2S sulfur follows the theoretical stoichiometry of 1 to 0.56; that is, 1,000 µg/g (ppm) of H_2S sulfur can generate a response equivalent to 560 µg/g (ppm) water. However, the validity of correcting measured water contents for known thiol/sulfide levels has not been rigorously determined and corrections should be made with caution.

Because of the relatively small sample size involved in the two Karl Fischer methods, in transferring samples by syringe it is important that no air bubbles be present. Heavy and viscous oils can be difficult to measure by syringe, and sample aliquots should be drawn by mass rather than volume.

Sediment

An accurate method for sediment entails extraction with hot toluene in a refractory thimble (ASTM D473: Test Method for Sediment in Crude Oils and Fuels Oils by the Extraction Method). A somewhat less time-consuming method of determining sediment involves dissolving a sample in hot toluene and filtering the solution under gravity through a membrane filter (ASTM D4807: Test Method for Sediment in Crude Oil by Membrane Filtration). Fig. 2 is a photomicrograph of sediment recovered from a crude oil by extraction and membrane filtration. Most of the grains are less than approximately 20 µm in their largest dimension.

In assays, sediment values are commonly reported as volume percent, rather than in mass percent as determined by these methods. A major portion of the sediment is probably sand (silicon dioxide, which has a density of 2.32 g/mL) with lesser amounts of other materials having somewhat lower densities arbitrarily assumed to be 2.0 g/mL. To obtain a value in volume percent for the sediment, divide the mass

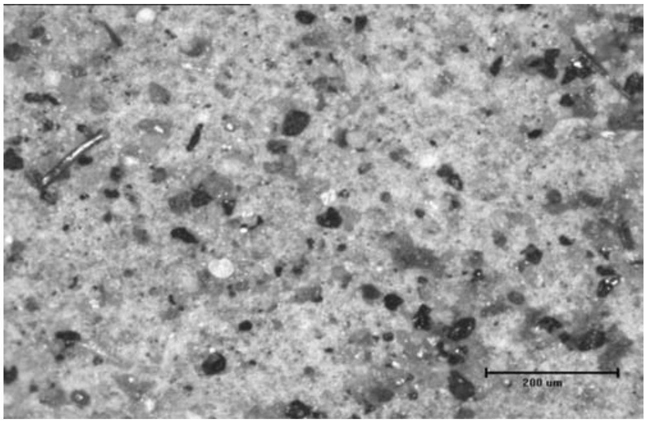


Fig. 2—Photomicrograph in plain transmitted light of sediment recovered from a crude oil by extraction and membrane filtration (Courtesy of Baker Hughes).

percent sediment by 2.0 and multiply by the relative density of the crude oil according to the following equation:

$$S_v = \frac{S}{2.0} \times \text{relative density of oil} \qquad (2)$$

where:

S_v = the sediment content of the sample as a percentage by volume and

S = the sediment content of the sample as a percentage by mass.

This calculation is for convenience only, and the precision and bias have not been established.

Excessive reuse of thimbles in ASTM D473 is to be avoided because, over time, the pores become clogged with inorganic material resulting in falsely high results. Also, the use of toluene in laboratories is coming under increasing scrutiny by safety and health groups, and a future ban on its use is not inconceivable. No alternative solvent has been identified to date, although some laboratories are known to use Varsol™ and aviation turbine (jet) fuel in lieu of toluene.

Sediment and Water

Centrifugal separation of the water and sediment [ASTM D4007: Test Method for Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure)] is rapid and relatively inexpensive, but the amount of water detected is almost invariably lower than the actual water content. This can result from inaccuracy in reading the interface between oil and water and emulsified water not being totally separated.

ASTM D96: Test Method for Water and Sediment in Crude Oil by Centrifuge Method (Field Procedure) covers the determination of sediment and water in crude oil during field custody transfers. This method may not always provide the most accurate results, but it is considered the most practical method for field determination of sediment and water. The method is still widely used although it was withdrawn with no replacement by ASTM in 2000. A technically equivalent version of the method is available as Chapter 10.4 in the API *Manual of Petroleum Measurement Standards*.

For all of the methods for sediment and water determination, sample homogenization is critically important and analyses must be conducted immediately after mixing to preclude settling. Loss of light ends will also affect results, and care must be exercised during mixing so that the temperature does not rise more than 10°C.

SALT CONTENT

The salt content of crude oil is highly variable and, as with water and sediment, results principally from production practices used in the field and, to a lesser extent, from its handling aboard tankers bringing it to terminals. The bulk of the salt present will be dissolved in coexisting free and emulsified water and can be removed in desalters, but small amounts of salt may be dissolved in the crude oil itself and present as a crystalline solid. Salt may be derived from reservoir or formation waters or from other waters used in secondary recovery operations. Aboard tankers, nonsegregated ballast water of varying salinity may also be a source of salt contamination.

Salt in crude oil may be deleterious in several ways. Even in small concentrations, salts will accumulate in distillation towers, heaters, and exchangers, leading to fouling that requires expensive cleanup. More importantly, during flash vaporization of crude oil, certain metallic salts, especially magnesium chloride, can be hydrolyzed to hydrochloric acid according to the following reaction:

$$\mathrm{MgCl_2 + H_2O \rightarrow 2\ HCl + MgO} \qquad (3)$$

The hydrochloric acid evolved is extremely corrosive, necessitating the injection of a basic compound, such as ammonia, into the overhead lines to minimize corrosion damage. Salts and evolved acids can also contaminate overhead and residual products, and certain metallic salts can deactivate catalysts. A thorough discussion of the effects of salt on crude processing is included in a manual on impurities in petroleum [47].

For many years the salt content has been routinely determined by comparing the conductivity of a solution of crude oil in a polar solvent to that of a series of standard salt solutions in the same solvent [ASTM D3230: Test Method for Salts in Crude Oil (Electrometric Method)]. This test method provides an approximate measure of the chloride content of the crude oil being tested on the basis of measurement of its conductivity. The chloride content is obtained by reference to a calibration curve prepared using a given mixture of salts. Because conductivity varies with varying salt composition, unless the composition of salts in the sample being tested is the same as the calibration mixture, results will be affected. Also, temperature and other conductive materials such as sediment and water present in the crude oil sample will affect results. These factors contribute to the relatively poor precision of the method.

With crude oils having a viscosity in excess of approximately 700 cSt at ambient laboratory conditions, it can be very difficult to transfer the test sample using a pipet as required by ASTM D3230. With highly viscous oils, a 10-mL graduated cylinder is a practical alternative, provided it is used to transfer the crude oil and neutral oil. However, precision of the method is based only on use of a 10-mL pipet and may not apply when using a 10-mL graduated cylinder.

ASTM D6470: Test Method for Salt in Crude Oils (Potentiometric Method) is less affected by salt composition and has considerably better precision than the older method. H_2S and thiols interfere in the determination of salts by potentiometric titration, and a step is provided in this test method for eliminating these before determination.

As with many test methods, sample homogenization is critically important in salt determination. Waxy samples and those solid at room temperature must be heated to 3°C above their pour point to facilitate test sample withdrawal. A nonaerating high-speed shear mixer is suitable for small laboratory sample containers up to approximately 500 mL. However, it is important that the temperature not be allowed to rise more than 10°C during mixing, otherwise excessive loss of light ends can occur or the dispersion can become unstable.

The results of ASTM D3230 are in pounds per thousand barrels (PTB), the common industry reporting factor. Those of ASTM D6470 are in milligrams per kilogram (mg/kg), in conforming to metric practice. Conversion between the two is accomplished using the following simple formulas:

$$\mathit{Salt}, \mathrm{mg/kg} = X/d \qquad (4)$$

$$\mathit{Salt}, \mathrm{mg/kg} = 2.853\ Y/d \qquad (5)$$

where:

X = measured concentration, mg/m^3,

Y = measured concentration, PTB, and

d = specimen density at 15°C, kg/m^3.

Regardless of the method used, it is necessary to use other methods (e.g., atomic absorption, inductively coupled argon plasma spectrophotometry, or ion-chromatography) to determine the composition of the salts present.

FLUIDITY—POUR POINT AND VISCOSITY

Pour point and viscosity determinations of crude oils are performed principally to ascertain their handling characteristics at low temperatures. However, there are some general relationships about crude oil composition that can be derived from pour point and viscosity data. Commonly, the lower the pour point of a crude oil the more naphthenic or aromatic it is, and the higher the pour point the more paraffinic it is. There are numerous exceptions to this rule of thumb, and other data must be used to verify a crude oil's character. Viscosity is also affected by the aromaticity or paraffinicity of the sample. Those crude oils with a greater concentration of paraffins generally have a lower viscosity than crude oils having a relatively large proportion of aromatic and naphthenic compounds.

Pour point is determined by cooling a preheated sample at a specified rate and examining its flow characteristics at intervals of 3°C. ASTM D97: Test Method for Pour Point of Petroleum Products is the most widely used procedure for this measurement, although crude oils are not mentioned in the method's Scope. An alternative procedure specifically for testing the pour point of crude oils is described in ASTM D5853: Test Method for Pour Point of Crude Oils.

Both test methods use the same apparatus but differ in the test procedures and the lower limit of determination. In ASTM D97, a single value is determined in defining pour point, whereas in ASTM D5853, maximum (upper) and minimum (lower) pour point values may be measured. The maximum (upper) pour point is defined as the temperature obtained after the test specimen has been subjected to a prescribed treatment designed to enhance gelation of wax crystals and solidification of the test specimen. The minimum (lower) pour point temperature is that obtained after the test specimen has been subjected to a prescribed treatment designed to delay gelation of wax crystals and solidification of the test specimen. The maximum and minimum pour point temperatures provide a temperature window in which a crude oil, depending on its thermal history, might appear in the liquid and solid state. The test method is especially useful for the screening of the effect of wax interaction modifiers (pour point depressants) on the flow behavior of crude oils. However, in practice few laboratories using ASTM D5853 are determining the minimum pour point on the basis of published data. Further, ASTM D97 has no defined lower limit of applicability, whereas ASTM D5853 only covers determination down to −36°C.

The pour point of crude oils is very sensitive to trace amounts of high melting waxes, and meticulous care must be exercised to ensure waxes present are completely melted or homogeneously dispersed. Crude oils stored below their cloud point will deposit waxes. The wax coming out of solution will preferentially be the high melting wax, which is the type that has the most pronounced influence on pour point temperature. This wax is also the most difficult to redissolve or homogeneously disperse in the crude oil. Heating the crude oil to 20°C above the expected pour point will usually result in the wax going back into solution, but caution must be observed to avoid loss of light ends. An accurate determination of the temperature to which a sample must be heated to redissolve all wax may require measurement of its wax disappearance temperature (WDT). Further discussion of this is provided in the succeeding chapter on crude oil compatibility and stability.

Viscosity is determined by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer [ASTM D445: Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)]. Although the preferred unit of kinematic viscosity is millimeter squared per second (mm^2/s), many older analyses report it in centistokes (cSt). These units are equivalent, with 1 mm^2/s equaling 1 cSt.

ASTM D7279: Test Method for Kinematic Viscosity of Transparent and Opaque Liquids by Automated Houillon Viscometer is beginning to be used in several petroleum laboratories in addition to ASTM D445. The test method is applicable to material having a viscosity of 2–1500 cSt at 20–150°C, and requires only approximately 1 mL of sample. The method is rapid and provides results in approximately 15 min, making it especially useful in determining viscosity of blends. Although the Scope of the method only refers to "fresh and used lube oils", it is increasingly being used for crude oils.

At one time, the petroleum industry measured viscosity by means of the Saybolt viscometer and expressed values in units of Saybolt Universal Seconds (SUS) or Saybolt Furol Seconds (SFS). This practice is now largely obsolete in the industry. ASTM D2161: Practice for Conversion of Kinematic Viscosity to Saybolt Universal Viscosity or to Saybolt Furol Viscosity establishes equations that may be used for calculating kinematic viscosities from SUS and SFS data that appear in older literature.

By determining viscosity at two temperatures such as 25°C and 40°C, viscosity at any other temperature over a limited range may be interpolated or extrapolated using viscosity-temperature charts (ASTM D341: Viscosity-Temperature Charts for Liquid Petroleum Products). It must be kept in mind that these charts are not linear. Also, the lowest temperature at which viscosity is determined should be at least 5°C higher than the pour point. Otherwise, the crude oil may not exhibit Newtonian behavior.

For waxy crude oils and those with a pour point greater than approximately 25°C and very viscous material such as bitumen, it is best to determine viscosity at three temperatures to ensure the material is Newtonian at the test temperature. For these types of material, the lowest temperature at which viscosity is measured may need to be 20°C higher than the pour point.

A common source of error in determining viscosity when using test method ASTM D445 is the presence of particulates lodged in the capillary bore. If sediment is present, which is commonly the case with crude oils, samples should first be filtered or centrifuged. Samples should also be air free. Homogenization can introduce air bubbles that will affect test results, and it may be necessary to allow samples to stand for a period of time to allow entrained air to disperse. Temperature control is critically important in obtaining accurate and precise viscosity measurements.

VAPOR PRESSURE

Vapor pressure is an important physical property of crude oils impacting shipping, storage, and refinery handling practices. The greater the vapor pressure of a crude oil, the greater the potential for atmospheric emission of hydrocarbons and other volatile compounds such as H_2S. With the increasingly more stringent environmental limitations on emission of these compounds, it is important that the vapor pressure be known so that crude oil stocks can be stored and handled in an appropriate manner.

ASTM D323: Test Method for Vapor Pressure of Petroleum Products (Reid Method) is the oldest of the several methods used for determining vapor pressure of crude oils. The RVP differs from the true vapor pressure of the sample under test because of some small sample vaporization and the presence of water vapor and air in the sample chamber used in the test. ASTM D323 is not an easy test to perform and it is time-consuming. However, an automatic vapor pressure instrumental method did not become standardized until 1991 with the publication of ASTM D5191: Test Method for Vapor Pressure of Petroleum Products (Mini Method). No crude oil samples were included in the interlaboratory study to determine the precision of this method. Hence, its use for crude oil vapor pressure measurement is specifically outside of the method's Scope, yet the method is routinely used for the determination of crude oil vapor pressure by several laboratories.

ASTM D323 and ASTM D5191 provide different measures of vapor pressure that are affected by the different test conditions, and ASTM D323 generally provides results that are somewhat higher than those of ASTM D5191. The latter technique also does not take into account dissolved water in the sample in determining total pressure. Moreover, the two methods are restricted to samples collected from a nonpressurized source such as a storage tank or oil tanker.

ASTM D323 and ASTM D5191 prescribe that sampling is to be done in accordance with ASTM D4057. Normally, 1-L containers filled between 70 and 80 % of capacity with sample are used for vapor pressure determination. However, samples taken in containers of sizes other than those prescribed in Practice D4057, such as 250 mL, can be used if it is recognized that the precision could be affected. In the case of referee testing, the 1-L sample container shall be mandatory. Regardless of the size of sample container used, it shall not be filled beyond 80 % of its capacity.

The current precision statements in ASTM D5191 were derived from a 2003 Interlaboratory Study (ILS) using samples in 250-mL and 1-L clear glass containers. The differences in precision results obtained from 250-mL and 1-L containers were found to be statistically significant, whereas there was no statistically observable bias detected between 250-mL and 1-L containers. Tables 2 and 3 and Figs. 1 and 2 in ASTM D5191 provide more specific details on precision differences as a function of container size.

ASTM D6377: Test Method for Determination of Vapor Pressure of Crude Oil: $VPCR_x$ (Expansion Method) covers determination for vapor-liquid ratios of from 4:1 to 0.02:1. When the vapor pressure measurement is done for a 4:1 ratio at 37.8°C, the observed vapor pressure can be compared to the vapor pressure obtained by ASTM D323. A vapor-liquid ratio of 0.02:1 mimics closely the situation of an oil tanker and approaches the true vapor pressure. This method may be used for analyzing samples from a pressurized source such as a pipeline collected using a floating piston cylinder in accordance with ASTM D3700. This method is also useful for samples that will boil at normal atmospheric pressures and ambient temperatures. When collecting samples from pressurized systems, sampling may be done in accordance with ASTM D4177 rather than ASTM D4057. When using a floating piston cylinder, it is advisable to use a gas such as argon as the back pressure agent rather than air, nitrogen, or helium. The larger molecular size of argon molecules relative to the other gases helps minimize leakage across the O-ring seals on the floating piston cylinder and integrity of the sample can be maintained for a longer period. When a floating piston cylinder has been used for sample collection, chilling and air saturation of the sample are not required before the vapor pressure measurement.

The extreme sensitivity of vapor pressure measurements to evaporative losses and the resultant changes in composition require the utmost precaution and the most meticulous care in the collection and handling of samples, regardless of the test method to be used. Moreover, vapor pressure determination is required to be performed on the first specimen withdrawn from the sample container. The remaining sample in the container is not to be used for a second vapor pressure determination because results will be affected by the additional handling. The effect of taking more than one test specimen from the same sample container was evaluated as part of the 2003 ILS study previously mentioned. A precision effect was observed between the first and second replicates taken from the 1-L and 250-mL containers evaluated.

The procedures for sampling and vapor pressure determination of crude oil are complex, especially if the crude oil has a pour point greater than 0–1°C or if its vapor pressure is greater than the ambient atmospheric pressure.

ASTM Manual 51 Distillation and Vapor Pressure Measurement in Petroleum Products includes detailed discussion of the several ASTM test methods used to measure vapor pressure of crude oil (i.e., D323, D5191, and D6377) [48]. This will provide the analyst a better understanding of the details of each method and how they apply to determination of this parameter. A separate, complimentary chapter provides a more in-depth discussion of the importance of crude oil vapor pressure measurements as they relate to determining regulatory compliance.

TOTAL ACID NUMBER

The acids present in crude oil contribute to increased rates of corrosion in the refinery and can contribute to instability in refined products. Surface activity imparted by acids can also make for difficulty in desalting of crude oils. Total acid number, as determined by ASTM D664: Test Method for Acid Number of Petroleum Products by Potentiometric Titration, provides an indication of the acid content of a crude oil. Test results will also indicate the presence of remnant inorganic acids such as hydrochloric acid and hydrofluoric acid used in production well workover operations. Organic acids such as acetic acid (CH_3COOH) and formic acid ($HCOOH$) are sometimes used in acidizing wells particularly for high-temperature applications. If not neutralized, they too will be determined in the analysis. Salts of heavy metals may have acidic characteristics and react during the determination of the acid number. The method does not differentiate acid species (e.g., carboxylic, naphthenic, or inorganic) and does not provide any indication of relative acid strength. Although no general correlation is known between acid number and the corrosive tendency of oils toward metals, knowledge of the acid number is important in planning for injection of neutralizing agents in refinery streams or reducing the acid content to an acceptable level by other means such as dilution with lower acid streams. Acid number data can also be useful when selecting metallurgy for new or replacement units.

Historically, crude oils with an acid number of less than 0.5 mg potassium hydroxide (KOH)/g have been considered acceptable for processing by most refineries without the use of a neutralizing agent. Some refineries have the metallurgy that allows them to process streams with an acid number of up to approximately 1.0 mg KOH/g. Several crude oils being produced today have acid numbers well above 1.0 mg KOH/g. These high-acid crudes (HACs), which are generally heavy, may be traded at a discount price relative to other similar quality crude oils or may be difficult to market.

Use of ASTM D664 for determining acid number of heavy crude oils and bitumens such as produced from Canadian oil sands can be problematic. Among the problems encountered in analysis of such streams are interference from a moderately high water content (>0.5%), incomplete solubility of the sample in the mixture of toluene and propan-2-ol, and precipitation of asphaltenes. Proposed modifications to ASTM D664 were shown in a small three-laboratory ILS to yield considerably improved reproducibility in analysis of a bitumen with a mean acid number of 3.30 mg KOH/g [49].

CARBON RESIDUE

Carbon residue is a useful measure of the amount of material left after evaporation and pyrolysis and provides some indication of the relative coke-forming propensity of crude oil. The residue formed is not composed entirely of carbon but is a coke, the composition of which can be changed by further pyrolysis. The term continues to be used in test methods in deference to its wide common usage. Two methods have historically been used for determination of carbon residue. These are ASTM D189: Test Method for Conradson Carbon Residue of Petroleum Products and ASTM D524: Test Method for Ramsbottom Carbon Residue of Petroleum Products. No exact correlation of the results obtained by these two test methods exists because of the empirical nature of the two test methods. However, an approximate correlation has been derived (Fig. 3). Caution should be exercised in the application of this approximate relation to samples having low carbon residues.

ASTM D4530: Test Method for Determination of Carbon Residue (Micro Method) has been correlated to Test Method D189 in a cooperative program (Fig. 4). This established that the data generated by ASTM D4530 are statistically equivalent to the Conradson residue test (ASTM D189), except for better precision in the Micro Method residue test. The method also offers the advantages of better control of test conditions, smaller samples, and less operator attention.

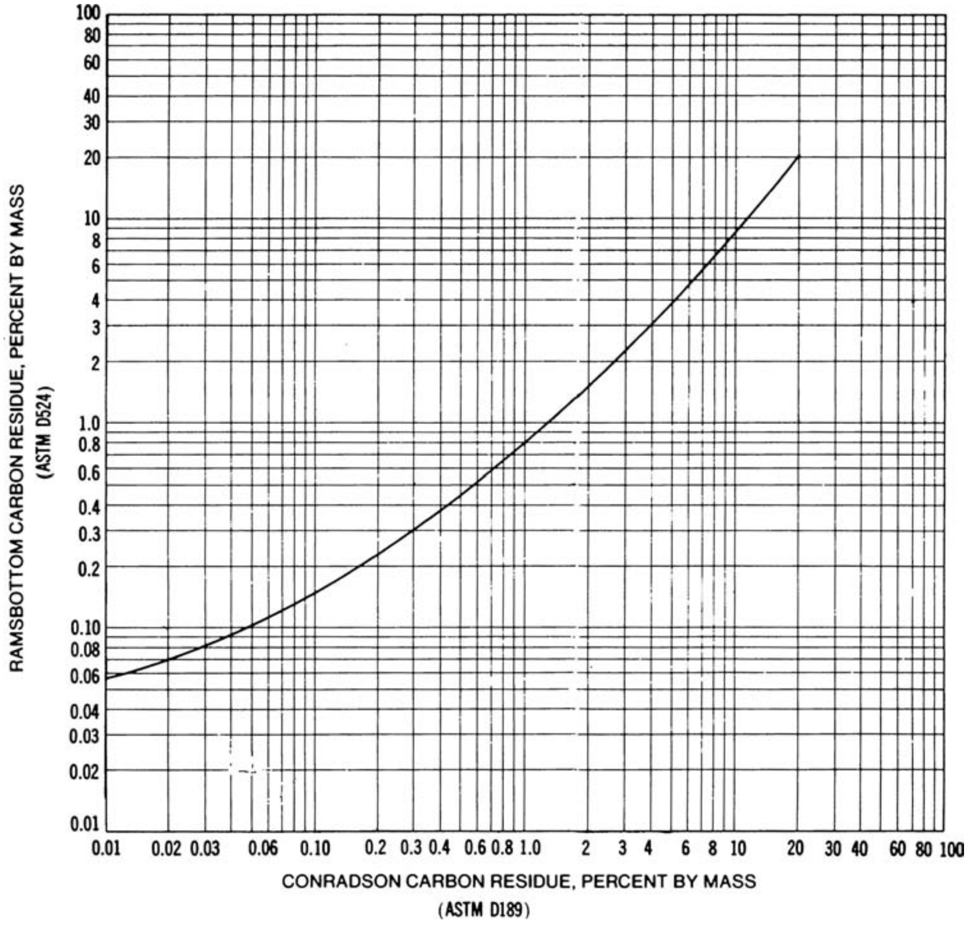


Fig. 3—Correlation of Conradson (D189) and Ramsbottom (D524) carbon residue tests.

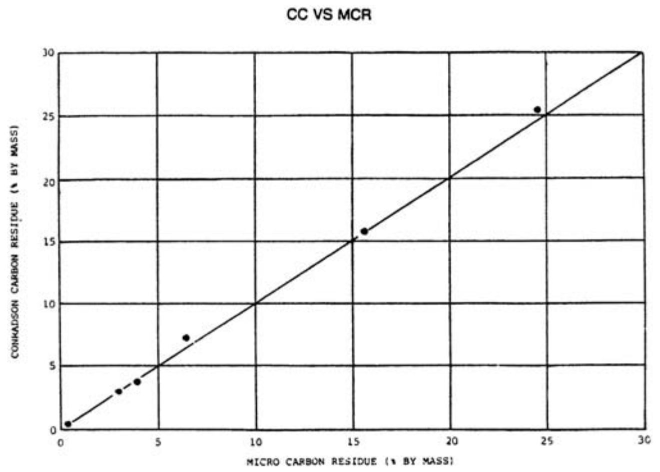


Fig. 4—Correlation of Conradson (D189) and carbon residue (Micro) (D4530) tests.

CHARACTERIZATION FACTOR

One of the most widely used indexes of composition is the Universal Oil Product (UOP) Characterization or Watson K-factor, which was originally defined as the cube root of the average molal boiling point in °R absolute (Rankine) temperature divided by the specific gravity, at 60/60°F [50]. Determination of the UOP characterization factor has conveniently been related to viscosity and API gravity and a nomograph for this purpose is provided in UOP Method 375: Calculation of UOP Characterization Factor and Estimation of Molecular Weight of Petroleum Oils (Fig. 5).

For a given carbon number, the boiling point and specific gravity increase in the order paraffins→naphthenes→aromatics, with specific gravity exhibiting a relatively greater increase than boiling point. Consequently, oils with a high paraffin content have $K \geq 12.0$, with lower values indicating progressively more aromatics [51]. These values provide a general rule of thumb on product yields; the paraffin base crude oils will give the highest gasoline yields, whereas the aromatic base feedstocks will be the most refractory and require a greater degree of upgrading.

It must be kept in mind that the Watson K-factor was developed in the 1930s. With the considerably more detailed data available today, it is easy to demonstrate that the relationship between K-factor and chemical character of a crude oil is approximate at best, and other data must be used in making a definitive characterization. Fig. 6 compares paraffin content versus K-factor for 178 crude oils, whereas Fig. 7 compares naphthene content versus K-factor for the same group. As can be seen, there is only an approximate

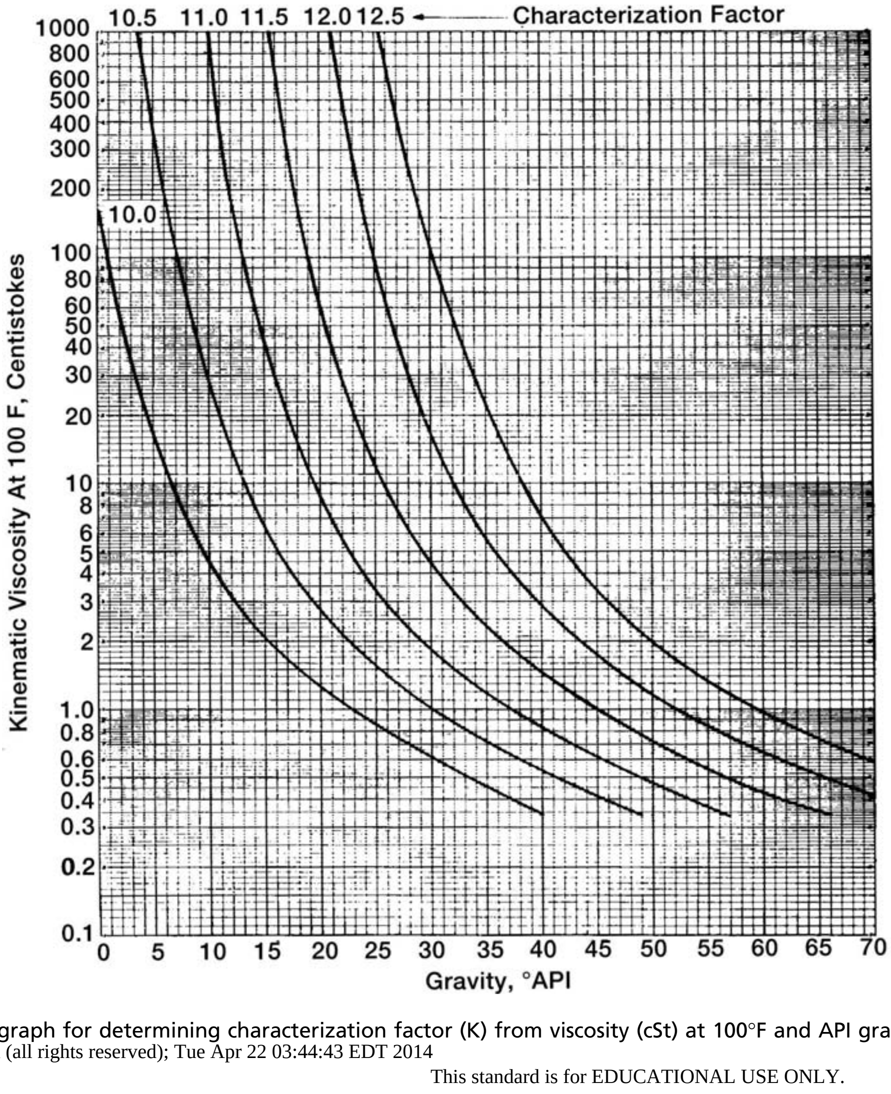


Fig. 5—Nomograph for determining characterization factor (K) from viscosity (cSt) at 100°F and API gravity (UOP 375).

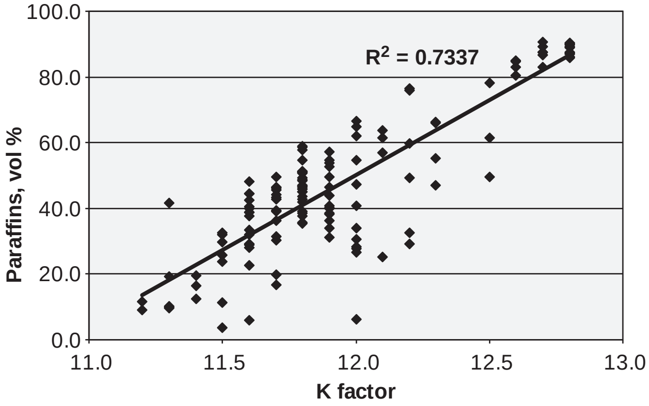


Fig. 6—K-factor versus paraffin content of 178 crude oils.

relationship between the two factors. Moreover, across the boiling range of a crude oil, chemical character can shift quite dramatically between fractions. This is well illustrated in Figs. 8 and 9 for two crude oils having the same K-factor and nearly the same API gravity. Despite these obvious shortcomings, the K-factor is determined and reported on virtually every detailed crude oil assay.

Other parameters used to characterize petroleum, including refractivity intercept, viscosity gravity constant, and carbon-to-hydrogen weight ratio, are discussed by Riazi [52].

TRACE ELEMENTS

Knowledge of the trace element constituents in crude oil is important because they can have an adverse effect on petroleum refining, product quality, and the environment. Among the problems associated with trace elements are catalyst poisoning in the refinery and excessive atmospheric emissions in combustion of fuels. Elements such as iron, arsenic, and lead are catalyst poisons. Vanadium compounds can cause refractory damage in furnaces, and sodium compounds have been found to cause superficial fusion on fire brick [53]. Some organometallic compounds are volatile, which can lead to contamination of distillate fractions and a reduction in their stability or malfunctions of equipment when they are combusted [54]. Concentration of the nonvolatile organometallics in heavy products such as premium coke can have a significant impact on price, marketability, and use. Knowledge of trace element concentrations is also useful in exploration in correlating production from different wells and horizons in a field [55].

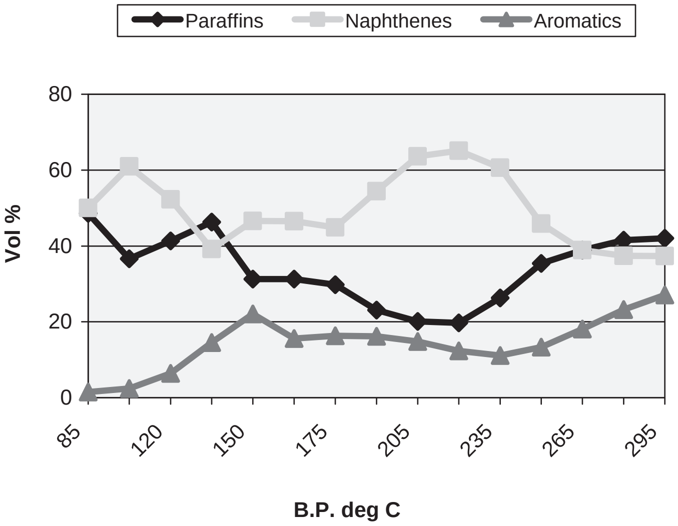


Fig. 8—Variation in paraffin, naphthene, and aromatic content for a 31.0° API West African crude oil with K = 11.9.

Nickel and vanadium nearly invariably are the most abundant trace element constituents of crude oil. However, until recently, relatively little systematic analytical work had been carried out on many other trace elements. With heightened environmental awareness and susceptibility of many catalysts to poisoning or deactivation by trace metals, more work is being done on determining their presence in crude oils. Published reports indicate that over 30 trace metals definitively occur in crude oils [56,57]. An extensive review of the literature published through 1973 provides information on the occurrence and concentration of 45 trace elements [58]. Using highly sophisticated techniques such as neutron activation analysis and with the greatly improved sensitivity of modern detectors, it is likely that even more elements will be found, but probably in sub-parts-per-billion concentrations.

In handling of crude oils, several trace metals are of considerable interest because of their potential impact on the environment resulting from atmospheric emissions when fuels are burned, or from discharge of process streams or disposal of wastes. In the Netherlands, in support of the North Sea Action Plan to reduce emissions, a detailed study of crude oils imported into the country was conducted in

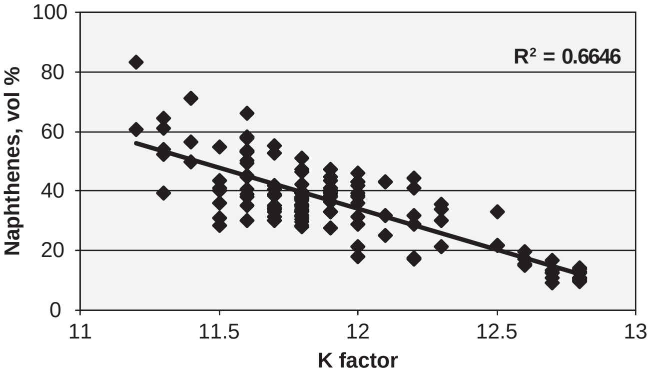


Fig. 7—K-factor versus naphthene content for 178 crude oils.

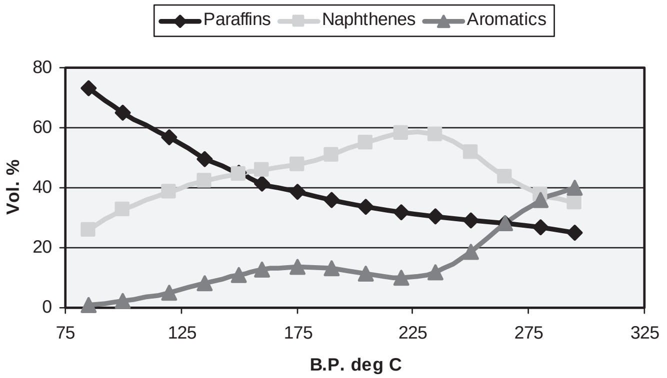


Fig. 9—Variation in paraffin, naphthene, and aromatic content for a 30.7° API Gulf of Mexico crude oil with K = 11.9.

the 1990s [59]. The study found that cadmium, zinc, and copper were not indigenous to the crude oils studied but were the result of contamination by associated water and/or particles from the producing wells. Chromium was found to be indigenous for the most part and associated with the hydrocarbon matrix. Some inorganic chromium was thought to be present as a contaminant. The study was unable to determine the origin of arsenic found in the crude oils, but it was considered to probably be a contaminant. The intention to study mercury was abandoned because a reliable analysis technique was not found at the time of the study.

Two metals currently of considerable environmental concern are mercury and selenium, both of which occur naturally in crude oil at varying concentrations. Mercury is of concern as an air and water pollutant, and selenium is of concern as a water pollutant.

There is substantial evidence indicating that mercury can occur in crude oil as volatile, dissolved, and particulate (suspended) species–all of which differ considerably in their chemical structure and behavior. Supporting the presence of volatile species, elemental mercury has been found condensed in cooler regions in refinery distillation towers and in cryogenic heat exchangers that liquefy petroleum gases. Further, replicate laboratory analyses on the same sample have found decreases in concentration over time [60]. Mercury has also been found in sludge that accumulates in strategic stockpiles of crude oil, clearly indicating the occurrence of particulate or suspended species [61]. Finally, mercury can be present in various petroleum distillation fractions across a broad boiling range.

Mercury is among the most difficult of the metals present in crude oils to accurately determine, and its concentration is generally at low parts-per-million to parts-per-billion levels. In a study of 103 crude oils from the United States, Europe, Africa, and Asia, total mercury concentrations ranged from 0.02 to 10 ng/g [61]. This is about an order of magnitude lower than anticipated based on historical data.

Contamination is a significant issue whenever samples contain the target analyte at such low levels. ASTM D7482: Practice for Sampling, Storage, and Handling of Hydrocarbons for Mercury Analysis covers the types of and preparation of containers most suitable for the handling of hydrocarbon samples for the determination of total mercury. This practice was developed for sampling streams where the mercury speciation is predominantly elemental mercury (Hg(0)) present as a mixture of dissolved Hg(0) atoms, adsorbed Hg(0) on particulates, and suspended droplets of metallic mercury.

UOP 938 Total Mercury and Mercury Species in Liquid Hydrocarbons is widely used for determining total mercury content of crude oils. The method is applicable to samples containing 0.1 to 10,000 ng/mL. An appendix provides a procedure that can be used to differentiate between elemental mercury, organic nonionic mercury, and ionic (inorganic and organic) mercury species.

ASTM D7622: Test Method for Total Mercury in Crude Oil Using Combustion and Direct Cold Vapor Atomic Absorption Method with Zeeman Background Correction, and ASTM D7623: Total Mercury in Crude Oil Using Combustion-Gold Amalgamation and Cold Vapor Atomic Absorption Method provide two other methods for determination of total mercury in crude oil. This latter test method uses the same instrumentation as that used in UOP 938. ASTM D7622 is applicable to samples containing from 5.0 to 350 ng/mL of mercury, whereas ASTM D7623 is applicable to samples containing between 5 and 400 ng/mL of mercury.

Selenium has become a priority pollutant because of its high toxicity to aquatic wildlife. In refineries, it partitions into wastewater streams and can be discharged from treatment plants into the environment where it rapidly bioaccumulates.

As with mercury, selenium can be present as different species that behave differently and complicate identification and remediation. Selenate [Se(VI)], selenite [Se(IV)], selenide [Se(-II)], colloidal selenium (Se°), and selenocyanate ($SeCN^-$) have all been observed in wastewaters [62]. In this study, which comprised 16 different crude oils, a large variability was observed in the total concentration of selenium in the samples (<10 to 960 $\mu g\ kg^{-1}$).

Several trace metals are now customarily included in crude oil analyses. Among these are calcium, copper, iron, mercury, nickel, selenium, sodium, and vanadium. The suite of elements determined will be dictated by refinery processes, product slate, regulation, and environmental considerations. Several analytical methods are available for the routine determination of many trace elements in crude oil. Among the techniques used for trace element determinations are flameless and flame atomic absorption spectrophotometry (AAS) (ASTM D5863: Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry) and inductively coupled argon plasma spectrophotometry [ASTM D5708: Test Method for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively-Coupled Plasma (ICP) Atomic Emission Spectrometry]. Some of these techniques allow direct aspiration of the samples (diluted in a solvent) instead of the time-consuming sample preparation procedures such as wet ashing (acid decomposition) or flame or dry ashing (removal of volatile/combustible constituents). A modified version of ASTM D5185: Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry is being used by some laboratories for the determination of elements such as lead and phosphorus in crude oils.

Inductively coupled plasma–atomic emission spectrometry (ICP-AES) is one of the more widely used analytical techniques in the oil industry for multielement analysis. The advantages of using an ICP-AES analysis include high sensitivity for many elements, relative freedom from interferences, linear calibration over a wide dynamic concentration range, single or multielement capability, and ability to calibrate the instrument on the basis of elemental standards irrespective of their elemental chemical forms within limits such as solubility and volatility assuming direct liquid aspiration. Thus, the technique has become a method of choice in many oil industry laboratories for metal analysis. ASTM D7260: Practice for Optimization, Calibration, and Validation of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for Elemental Analysis of Petroleum Products and Lubricants summarizes the protocols to be followed during calibration and verification of instrument performance. With the low levels at which many elements of interest are present, these protocols are of the utmost importance in obtaining accurate data.

Despite the advantages of ICP-AES, several laboratories continue to use AAS because detection limits are often better. X-ray fluorescence spectrophotometry is also sometimes used, although matrix effects can be a problem. The method to be used is generally a matter of individual preference and instrumentation availability.

Many advances have been made in techniques for trace and ultratrace sample preparation and elemental analysis including AAS, ICP-MS, isotope dilution mass spectrometry, and other multihyphenated methods. Several of these are discussed in ASTM STP 1468 [36].

Sample Preparation for Elemental Analysis

The test methods used for analysis of crude oils for their elemental metals content use various analytical techniques. Some of these test methods require little or no sample preparation, some others require only simple dilution, and others require elaborate sample decomposition before the sample is analyzed for its elemental content. ASTM D7455: Practice for Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis covers alternative ways of preparing a sample for elemental analysis. The means of preparation of samples may vary from no special steps to extensive procedures dependent on the sample matrix and the measurement technique to be used. Adoption of uniform practices for sample preparation is beneficial in standardizing the procedures and obtaining consistent results among laboratories. This becomes especially important in cases of dispute, such as in contract compliance, and because of environmental, industrial hygiene, and regulatory concerns.

MICROWAVE DIGESTION

The traditional method of digestion/ashing of samples for trace element analysis as described in ASTM D5708 is time-consuming, and up to 24 h may be necessary to decompose heavy or bituminous material. Moreover, during the process, elements of interest may be lost by spattering and foaming, the risk of contamination is ever present, and the sample may not be totally decomposed. Microwave digestion of samples has become commonplace in many laboratories worldwide as an excellent alternative means for rapidly decomposing even refractory samples and with essentially no loss of elements of interest during the process or contamination.

This technique involves high-pressure dissolution in sealed vessels at elevated temperatures to attain rapid sample decomposition and analyte dissolution [63]. Basically, the sample is sealed in a Teflon™ vessel with a combination of nitric acid (HNO_3), hydrochloric acid (HCl), and hydrogen peroxide (H_2O_2) and digested for approximately 1 h at approximately 200°C. The result in a precipitate-free, clear yellow solution that can be diluted and run directly by AAS. If the sample is to be analyzed by ICP-MS, it may be necessary to evaporate the excess HNO_3 before dilution and analysis.

NITROGEN CONTENT

The nitrogen constituents in crude oils are divided into two major classes–basic and nonbasic. Basic nitrogen constituents include such compounds as pyridines and quinolines, and the nonbasic constituents are typified by carbazoles, indoles, and pyrroles [34]. The classification of nitrogen compounds as basic or nonbasic is based on whether they can be titrated with perchloric acid in a 50:50 solution of glacial acetic acid and benzene. Compounds extracted by acids are basic; the compounds that cannot be extracted are nonbasic [64]. In general, basic compounds account for approximately 30% of the total nitrogen present.

Like sulfur, nitrogen concentration increases with increasing boiling point, but unlike sulfur, usually only trace quantities of nitrogen are found in the fractions boiling below approximately 343°C. API Research Project 52 identified numerous nitrogen compounds present in crude oils and reported on many of the problems they cause in refining and with product quality [65]. As a group, they can contaminate refinery catalysts sometimes when even trace quantities are present in feedstocks. Nitrogen compounds also contribute to refined product instability, are responsible for formation and precipitation of gums in some fuels, and become an environmental pollutant when fuels are burned because of emission of oxides of nitrogen (NO_x). Further, they tend to be the most difficult class of compounds to hydrogenate and are of increasing concern to refiners. The nitrogen content remaining in the product from a hydrotreater is a measure of the effectiveness of the hydrotreating process.

Three test methods are available for the determination of total nitrogen. ASTM D3228: Test Method for Total Nitrogen in Lubricating Oils and Fuel Oils by Modified Kjeldahl Method is a manual method rarely used for analysis of crude oils. The test method is time-consuming and involves hazardous substances such as sulfuric acid and mercuric oxide. During the test procedure, H_2S is evolved and mercuric sulfide is produced. Moreover, it is not applicable to nitrogen present in heterocyclic compounds, in which case lower results will be obtained compared with the actual total nitrogen concentration.

The two methods commonly used for determination of total nitrogen in crude oils both involve chemiluminescent detection. ASTM D4629: Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection covers determination of trace quantities of nitrogen in the range 0.3 to 100 mg/kg. This test method has been successfully applied in interlaboratory studies to samples with higher concentrations by dilution to bring the concentration to within the range covered by the test method's Scope and, as such, is frequently used for determination of total nitrogen content of crude oils having a wide range in concentration. ASTM D5762: Test Method for Nitrogen in Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence covers determination of total nitrogen at concentrations of 40–10,000 mg/kg.

Because some nitrogen compounds are volatile and to prevent contamination, it is advisable that samples be analyzed as soon as possible after their collection. ASTM D7455 discussed earlier in the section on trace metals provides information relevant to sample preparation for their nitrogen determination.

There are no standard test methods for determining basic nitrogen in crude oil. It usually suffices to determine total nitrogen and assume that approximately 30% is basic in character. This ratio appears to be approximately constant throughout the boiling range of a crude oil.

Instrumental fast neutron activation analysis has been used to directly determine nitrogen in crude oils in the range of 0.014–0.490 % [66]. This provides an accurate and rapid means of determining nitrogen, but few laboratories have the requisite instrumentation. Identification and distribution of nitrogen compounds in middle distillate fuels derived from crude oils from several sources has also been done by gas chromatography (GC)/MS [67]. This technique also does not lend itself to routine laboratory determinations of the nitrogen concentration of crude oil.

ORGANIC HALIDES

Organic halides do not occur naturally in crude oils. They–mainly chloride species–are among the most egregious contaminants, and their presence commonly results from solvents used in cleaning operations at production sites and in pipelines and tanks. Their presence may also result from illicit disposal of waste solvents. These compounds are potentially damaging to refinery processes. For example, HCl can be produced in hydrotreating or reforming reactors, after which the highly corrosive acid can accumulate in condensing regions of the refinery. Large or unexpected concentrations of the resulting acids cannot be effectively neutralized, and damage can result. Organic halide species can also poison catalysts in reformers and adversely affect gasoline yields.

After enactment of the Resource Conservation and Recovery Act (RCRA) in 1976, there have been numerous reports of incidents involving the presence of organic halides in crude oil feedstocks and their consequences. In 1981, in an article in *Oil Daily*, it was noted that "the consequences of organically-combined chlorine in crude are by no means trivial" [68]. A report by the U.S. General Accounting Office disclosed 40 cases of crude oil contamination that occurred between 1981 and 1989, most involving disposal of organic chlorides into crude oil [69]. In 2000, it was reported that "a series of sudden tube leaks in ... overhead exchangers of a crude tower of a major Gulf Coast refinery was attributed to repeated contamination of the crude charge with organic chlorides" [70]. In this latter case, a single supplier had repeatedly dumped contaminated crude oil containing from 3 to 3,000 mg/L organic chlorides into one of the refinery's pipelines over a 10-month period. To combat organic chloride contamination, one major crude oil common carrier pipeline instituted a program that resulted in a significant reduction in incidents in its system [71]. Despite these widely publicized incidents, the use of halogenated solvents continues to be promoted for removing wax buildup in pipelines [72].

Total organic halide content of the naphtha fraction can be effectively determined using ASTM D4929: Test Method for Determination of Organic Chloride Content in Crude Oil. In performing the test, it is imperative that the sample be distilled to obtain a naphtha fraction before chloride determination as described in the test method to eliminate potential interference by inorganic salts. Other titratable halides such as hydrogen bromide (HBr) and hydrogen iodide (HI) will also give a positive response. Some commonly encountered organic chloride compounds such as dichloromethane have a relatively low boiling point and can be lost before analysis because of exposure. Consequently, it is important that samples be analyzed as soon as possible after collection. ASTM D7455 discussed earlier in the section on trace metals provides information relevant to sample preparation for organic chloride determination. Table 1 lists some of the organochloride compounds commonly used as solvents, cleaning agents, and in industrial processes and their boiling points.

ASPHALTENES

By definition, asphaltenes are wax-free material insoluble in *n*-heptane, but soluble in hot toluene. In classical references, benzene is used rather than toluene; however, because of its known carcinogenicity, it has largely been banned in laboratories. Other solvents such as *n*-pentane or *n*-hexane may be used in the determination, but the quantity and properties of the separated material will differ from that obtained using *n*-heptane [73]. Fig. 10 depicts this variation in relative terms in the mass percent of asphaltenes that will precipitate from a given crude oil as a function of the carbon number of the n-alkane precipitant from n-C_3 through n-C_{10}.

Asphaltenes are the organic molecules of highest molecular mass and carbon-hydrogen ratio normally occurring in crude oil. They are highly aromatic in character, and their composition normally includes a disproportionately high quantity of the sulfur, nitrogen, and metals present in crude oil. If the colloidal suspension of these molecules is disturbed through excess stress or incompatibility, they can give rise to problems during storage and handling.

When crude oil is produced from the reservoir, the depressurization that occurs can result in flocculation of asphaltenes [74–76]. Further flocculation can take place during transportation and in refinery processing where the precipitates can foul pipelines, preheat trains, and result in desalter upsets (Fig. 11). In desalter units, asphaltene precipitates can stabilize emulsions, resulting in an increase in the solids and oil carried under to the wastewater treatment facility. Asphaltenes can stabilize emulsions and result in excessive salts and water being carried over to other refinery units where they can foul equipment and contaminate products.

Asphaltene flocculation and its causes have been the subject of considerable study, as well summarized by James G. Speight [77] and discussed in papers related to the DeepStar Project [78]. G. A. Mansoori and his collaborators at the University of Illinois at Chicago have devoted considerable study to deposition of heavy organic material during crude oil production and refinery processing and to characterization of the deposits [79–81].

Another common cause of destabilization and precipitation is the blending of incompatible crude oils, such as one that is paraffinic with one that is more asphaltenic or aromatic in character [82,83]. Asphaltenes are also the last molecules in a product to combust completely; thus, their occurrence may be one indicator of black smoke propensity.

ASTM D6560: Test Method for Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products covers a procedure for their determination. The test method requires that the crude oil first be topped to an oil temperature of 260°C before analysis. However, many laboratories are performing the test without first topping the sample. Analyses of topped and untopped samples of the same crude oil have shown that the results can differ

TABLE 1—Common Organic Chloride Compounds

Compound	Boiling Point, °C
Dichloromethane (methylene chloride)	40
Trichloromethane (chloroform)	62
Tetrachloromethane (carbon tetrachloride)	77
1,2-Dichloroethane (ethylene dichloride)	84
1,1,1-Trichloroethane (trichloroethylene)	87
Tetrachloroethylene (perchloroethylene)	121

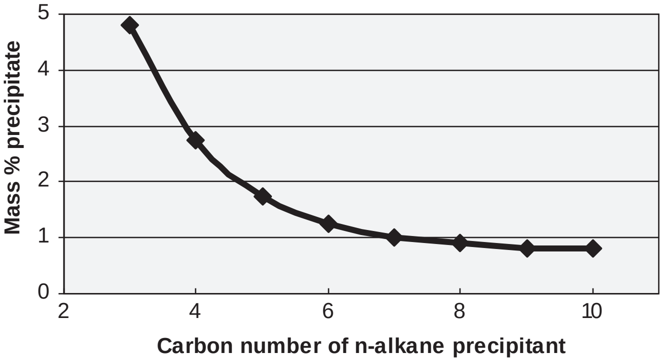


Fig. 10—Variation in asphaltene yield as function of carbon number of precipitant (values of precipitate are relative and not absolute).

significantly, although without a systematic bias. ASTM D3279: Test Method for *n*-Heptane Insolubles is similar in scope to ASTM D6560 and is useful in quantifying the asphaltene content of crude oils. The test sample is first topped to a temperature of 343°C or higher before analysis. On the basis of results of the ASTM Interlaboratory Crosscheck Program on #6 Fuel Oil and a limited interlaboratory study in Europe on bitumen samples, the two test methods give similar results and there is no systematic bias.

BOILING POINT DISTRIBUTION

Boiling point distribution provides insight into the composition of crude oil and an estimation of the quantity of products likely to be yielded in refinery processes. These data are also used to evaluate new crudes, to confirm crude quality, and to provide essential data for optimization of refinery processes. Historically, these data have been obtained by a physical or true boiling point distillation, a lengthy process that requires a relatively large volume of sample and to be discussed in the following chapter in more detail. Simulated distillation using GC can be used to rapidly determine this parameter without the need for a conventional physical distillation. The ability to rapidly and reliably determine product yields has important economic considerations. New crude oils can be rapidly evaluated, cargo receipts can be quickly screened to determine if they have been spiked or topped, decisions can be made on purchase of "opportunity" crude oils or distressed cargoes, and a rapid assessment can be made of whether a particular blend will produce a desired product slate.

ASTM D2887: Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography, originally approved in 1973, was the first standardized GC method for determining boiling range distribution of petroleum. However, the test method is restricted to petroleum products and fractions in the range of 55–538°C, which limits its usefulness for crude oils. ASTM D5307: Test Method for Determination of the Boiling Range Distribution of Crude Petroleum by Gas Chromatography covers determination of the boiling range distribution of water-free crude oil, but still only up to 538°C, which corresponds to n-C_{43}. Material boiling above 538°C is reported as residue. Most crude oils have a final boiling point well above 538°C, limiting the application of these two test methods. Both test methods have nevertheless been shown to be equivalent to ASTM D2892: Distillation of Crude Oil (15-Theoretical Plate Column) and are considerably faster and require much less sample than the physical distillation method. Consequently, these GC simulated distillation methods can be used in lieu of ASTM D2892 to rapidly obtain an estimate of refinery yields.

ASTM D7169: Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography, a method commonly abbreviated HTSD, extends the boiling range distribution through a temperature of 720°C. This temperature corresponds to the elution of n-C_{100}. The amount of residue (or sample recovery) is determined using an external standard. The extended range of this test method is important to the refinery engineer because several heavy crude oils available in today's market have a substantial amount of residue boiling well beyond 538°C.

Carbon disulfide is used as a solvent to dilute the sample and its presence results in an unreliable boiling point distribution in the interval of C_4–C_8 (0–126°C). A separate, higher resolution GC analysis of the light-end portion of the sample may thus be necessary to obtain a more accurate characterization of the boiling point curve in this interval. An appendix to the test method provides a suggested light-end analysis procedure for more accurately characterizing

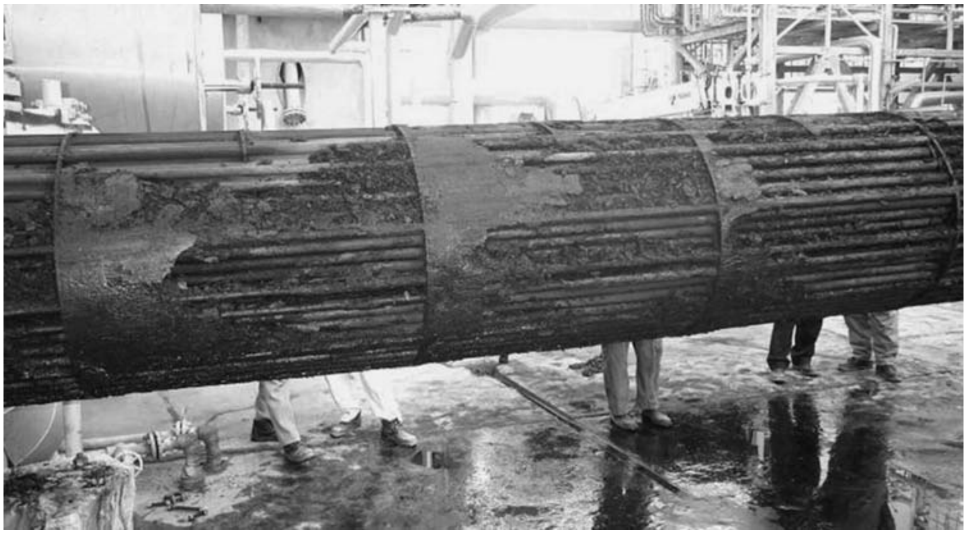


Fig. 11—Refinery heat exchanger fouled by asphaltenes (Courtesy of Professor G. A. Mansoori).

the boiling curve in the region C_4–C_8. Fig. 12 shows typical uncorrected and corrected distillation curves for a crude oil analyzed by this test method and using the suggested light-end analysis procedure.

Determination of boiling point distribution by HTSD is useful for rapidly obtaining information on the potential mass percent yield of products. These data provide refiners the ability to quickly evaluate crude oils and to select those with economic advantages and more favorable refining margins [84]. The information it provides can be input to linear programming (LP) models and used in establishing operations conditions in the refinery. Data on the boiling point distribution also serve as a rapid method for screening for the presence of diluents or residuum, constituting what is commonly referred to as "dumbbell crude."

Further discussion on application of GC to determination of boiling point distribution can be found in ASTM Manual 51 [48]. This includes important considerations such as instrument requirements, column selection, carrier gas, analysis software, data interpretation, and a comparison to physical distillation. However, GC-simulated distillation does not provide any material for quality assessments. This requires that samples be fractionated by conventional physical or potstill distillation methods, which are described in the next chapter.

OTHER TESTS

Other properties that are generally determined on a more limited basis include, but are not limited to, the following.

Methanol

Methanol, as with organic halides, does not occur naturally in crude oils but is introduced artificially to prevent formation of gas hydrates–large matrixes of methane and water that can block or impede flow in pipelines. Use of methanol as a hydrate inhibitor occurs mostly in production of crude oils from deep waters such as the Outer Continental Shelf of the Gulf of Mexico, offshore West Africa, and in areas of the North Sea. It may also be used in cold climates to assist in thawing pumps and pipelines. With the growing number of subsea wells in ever deeper water, the use of methanol is likely to increase, posing a growing problem for refiners. For crude oil produced from the Gulf of Mexico, methanol contamination commonly occurs after hurricanes after production restarts and until pipelines have been warmed by the produced oil. Because the methanol is water miscible, it gets carried with water present in the crude oil to the refinery where it comes out in the water effluent from the desalter unit. When it reaches the wastewater treatment system, it can drastically upset the balance of the system. The bacteria used in the plant to digest oily components prefer the methanol, leaving hydrocarbons and some other toxic substances untreated. Large incursions of methanol can lead to a "bug kill" that effectively deactivates the system. Either of these situations can result in discharge of pollutants and environmental excursions that exceed permitted levels. Increasingly, refiners are setting limits on the content of methanol they receive, generally a maximum of 50 parts per million (ppm).

Methanol that partitions into the crude oil phase can lower its apparent WAT, complicating accurate determination of this characteristic [85].

Currently, there is no standard test method for determining methanol in crude oils containing water. ASTM D7059: Test Method for Determination of Methanol in Crude Oil by Multidimensional Gas Chromatography is applicable only to crude oils containing a maximum of 0.1 % (v/v) water. As such, it is not applicable to analysis of most production quality crude oil streams that commonly contain 0.25–1.0 % (v/v) water. Several instrument manufacturers

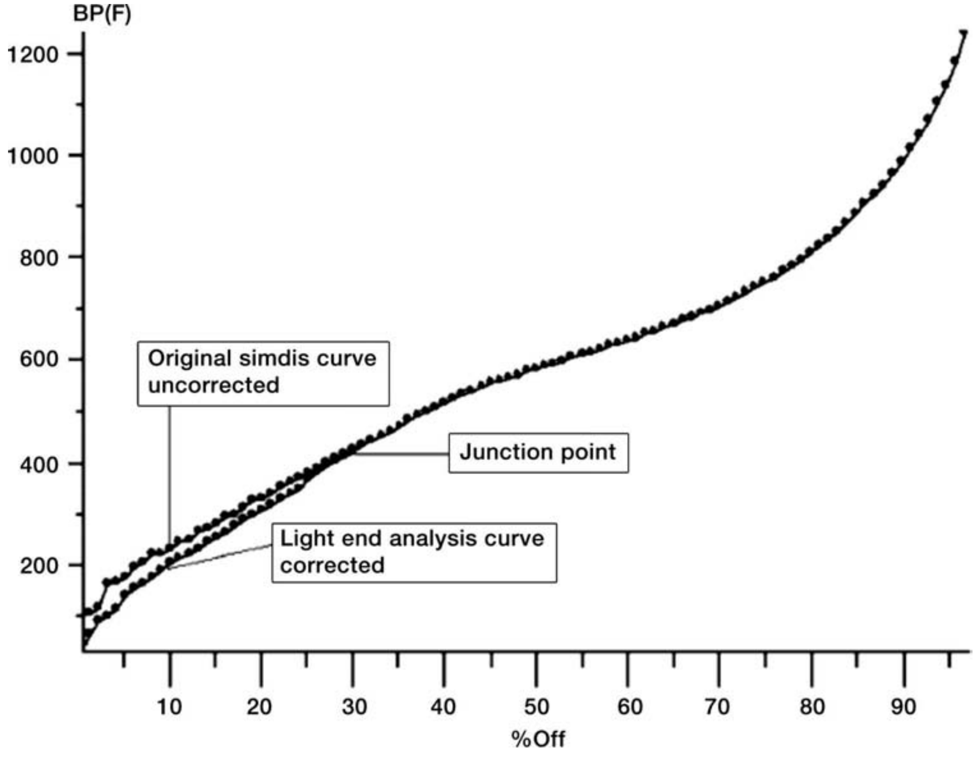


Fig. 12—Corrected and uncorrected D7169 distillation curves.

have worked on development of suitable analytical methods. A prototype online GC system for real-time measurement of methanol in a crude oil stream was tested by a crude oil pipeline company at one of its onshore Gulf of Mexico terminals, but the system did not have the necessary capabilities or ruggedness. In the absence of a standard test method, methanol can be determined by washing a sample with water, then analyzing the eluate by GC. This method is time-consuming and does not allow for continuous monitoring of a stream. This latter is an important consideration because methanol is typically disposed of in batches from offshore operations rather than on a continuous basis and arrives at refineries in slugs over a short period of time [86].

Near-IR analysis may provide a rapid and more accurate means of determining methanol in crude oil. Test results have shown a moderately good correlation ($R^2 = 0.92$) in comparing results measured by this technique with known amounts of methanol over a concentration range of 50–500 ppm mass added to previously washed crude oil samples [87].

Ash

Ash present in crude oil results from the presence of noncombustible extraneous solids such as co-produced sediment, pipeline scale, and rust. Normally there is a close correlation between a crude oil's ash content and its sediment content. In use of crude oil as a fuel, it is important to know its ash content because this can be related directly to particulate emissions. ASTM D482: Test Method for Ash from Petroleum Products covers the determination of this property. Ash results are rarely published in assays unless the crude oil is to be used directly as fuel.

Waxes

Waxes are a complex mixture of mostly normal- and iso-alkanes having chain lengths of greater than approximately 30 carbon atoms. As a group, they contribute to several problems in crude oil production, transportation, storage, and handling. Among these, they congeal in pipelines and other production equipment, which restricts flow, and they agglomerate and contribute to sludge buildup in tanks. UOP 46 Wax Content of Petroleum Oils and Asphalts is a widely used method for estimating the wax content of crude oil. This test involves dissolving an asphalt-free sample in dichloromethane then cooling the solution to −30°C. The precipitated waxes are recovered by filtration and the mass is determined. The method is complex and involves use of some toxic and hazardous chemicals.

Among other methods that have been used for determination of wax content are GC, pulsed nuclear magnetic resonance (NMR), and density measurements. GC and pulsed NMR are reported to have poor accuracy and low repeatability, and the density measurement technique apparently requires specialized equipment [88].

Flash Point

Flash point is defined as the lowest temperature at which application of an ignition source causes the vapors of a specimen of the sample to ignite. The temperature is a measure of the tendency of crude oil to form a flammable mixture with air and is used in shipping and safety regulations to define flammable and combustible materials. Two methods are usually used for its determination–ASTM D56: Flash Point by Tag Closed Cup Tester or ASTM D93: Flash Point by Pensky-Martens Closed Cup Tester–depending on crude oil properties. Flash point is infrequently determined on crude oils because most have flash points less than 5°C.

TABLE 2—Crude Oil Inspection Assay Properties

Property	ASTM Referee Test Method
API, relative density, or specific gravity	D1298 or D5002
Pour point	D97 or D5853
Nitrogen, total, mass percent	D5762
Sulfur, total, mass percent	D4294
Viscosity, cSt at 25°C and 40°C	D445
Water, volume percent	D4928
Sediment, mass percent	D473
Salt, ppm	D6470
Total acid number, mg KOH/g	D664
Organic chlorides, ppm	D4929
Hydrogen sulfide and mercaptans, ppm	UOP 163
Vapor pressure, kPa @ 37.8°C	D323 or D6377
Trace metals, ppm	D5708 or D5863
Carbon residue, mass percent	D4530
Asphaltenes, mass percent	D6560
Methanol, ppm	Gas chromatography or infrared spectroscopy
Boiling range distribution	D7169

REFEREE TEST METHODS

When two or more test methods are available for determining a property, one is customarily designated as the referee or primary method in testing protocols. This provides for resolving disputes in cases in which two methods yield different results on the same material. The methods listed in Table 2 are those generally accepted as referee methods for determination of the property. In some cases, two test methods are listed for the same property because their respective scopes differ or the methods provide equivalent results. In these cases, it is important that the purpose of the analysis and the nature of the material are clearly understood in selecting a suitable referee method and that it be agreed upon by interested parties.

The inspection assay tests discussed in the preceding sections are unquestionably not exhaustive but are the ones most commonly used. These tests will provide the analyst and refiner with data on a crude oil's handling characteristics, some of the impurities and contaminants that are present, evidence of spiking or topping, and a general idea of the products that may be recoverable.

A summary of these inspection test methods is provided in Table 2. However, these tests will not provide the data essential for determining whether a given crude oil or blend of crude oils will yield an economically attractive product slate. This requires that a comprehensive assay be performed, as described in the following chapter.

4

Comprehensive Assays and Fraction Evaluations

TRUE BOILING POINT DISTILLATION

In addition to the whole crude oil tests performed as part of the inspection assay, a comprehensive or full assay requires that the crude oil be fractionally distilled and the fractions characterized by appropriate tests. This characterization is necessary to enable the refiner to assess the quantity and quality of products recoverable from a given crude oil and to determine if that product slate economically satisfies the market requirements of a particular refinery. Refiners tailor a comprehensive assay to their individual needs, and the number of cuts or fractions taken may vary from as few as 4 to 24 or more. The following ten fractions provide the basis for a moderately thorough evaluation:

C_2–C_4	Gas
C_5–79°C	Light naphtha
79–121°C	Medium naphtha
121–191°C	Heavy naphtha
191–277°C	Kerosine
277–343°C	Distillate fuel oil
343–455°C	Light vacuum gas oil (LVGO)
455–566°C	Heavy vacuum gas oil (HVGO)
343°C+	Atmospheric (long) residuum
566°C+	Vacuum (short) residuum

Commonly, from 5 to 50 L of crude oil are needed for a comprehensive assay, depending on the number of cuts to be taken and the tests to be performed on the fractions. Fractionation of the crude oil begins with a true boiling point (TBP) distillation using a fractionating column having an efficiency of 14–18 theoretical plates and operated at a reflux ratio of 5:1. ASTM D2892: Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column) details procedures for the production of a liquefied gas fraction, various distillate cuts, and an atmospheric residuum. The distillation may be used for all fractions up to a maximum cutpoint of approximately 400°C atmospheric equivalent temperature (AET) provided reduced pressure is used to avoid cracking. The quantity of sample to be distilled will be dependent on the number of cuts to be made and the volume of the various fractions needed for subsequent analyses. The mass and density of each cut or fraction are obtained and distillation yields by mass are calculated from the mass of all fractions, including the liquefied gas cut and the residue. Distillation yields by volume of all fractions and the residue are calculated from mass and density. From these data, curves corresponding to TBP in mass or volume percent, or both, versus AET are plotted. The method does not prescribe specific cutpoint temperatures, which are to be agreed upon by interested parties before beginning the distillation. The fractions yielded can be analyzed as produced or combined to produce samples specific to what is needed for analytical studies and engineering and product quality evaluations.

The sample to be distilled must have been obtained in accordance with ASTM Practice D4057 or D4177 and must be received in a sealed container and show no evidence of leakage. Before opening the sample, it must be cooled to between 0 and 5°C. If, on opening, it appears waxy or too viscous to handle, the temperature should be raised to 5°C above its pour point. After thorough mixing, the sample's water content is to be determined. If the water content exceeds 0.3 % volume, the sample should be dehydrated before fractional distillation. Attempts to distill "wet" crude oil samples in glass columns can result in "bumping" and breakage of the glassware, posing a potential fire hazard. Moreover, the presence of water will affect the accuracy of distillation yields in the naphtha range. These effects are more pronounced for heavy crude oils containing low amounts of hydrocarbons boiling below 100°C. A suitable practice for dehydration of wet crude oils is described in an appendix to ASTM D2892.

Beyond an AET of 400°C, it is necessary to continue the distillation at further reduced pressures under conditions that provide approximately a one-theoretical plate fractionation. ASTM D5236: Test Method for Distillation of Heavy Hydrocarbon Mixtures (Vacuum Potstill Method) enables the distillation to be continued to a temperature of up to approximately 565°C AET at a pressure of 0.013 kPa. This test method details the procedures for the production of distillate fractions in the gas oil and lubricating oil range as well as the production of standard residue and provides for the determination of standard distillation curves to the highest AET possible by conventional distillation. The maximum achievable AET is dependent on the heat tolerance of the charge. It will be significantly lower for heat-sensitive samples and might be somewhat higher for nonheat-sensitive material.

As with ASTM D2892, the mass and density of each cut or fraction are obtained and distillation yields by mass are calculated from the mass of all fractions and the residue. Distillation yields by volume of all fractions and the residue are calculated from mass and density. From these data, distillation curves in mass or volume percent, or both, versus

AET are plotted. The method does not prescribe specific cutpoint temperatures, which are to be agreed upon by interested parties before beginning the distillation. The fractions yielded can be analyzed as produced or combined to produce samples specific to what is needed for analytical studies and engineering and product quality evaluations.

The sample to be distilled using ASTM D5236 can be the residue from ASTM D2892, or it can be a heavy crude oil obtained in accordance with ASTM Practice D4057 or D4177. The latter must be received in a sealed container and show no evidence of leakage. On opening, if the sample looks waxy or is solid, it should be warmed to liquefy it and be thoroughly mixed before proceeding with the distillation. If, upon examination, there is evidence of water present in the sample (>0.1 % volume) a preliminary distillation should be performed as described in the test method Annex.

This test method can also be used for heavy crude oils with initial boiling points greater than 150°C, but distillation curves and fraction qualities are not comparable to what would be obtained on similar material using ASTM D2892.

In graphing boiling point data from ASTM D2892 and D 5236 on a single continuous curve, there will be an offset at the switchover point between the two sets of data. Several factors are responsible for this "mismatch." First, ASTM D2892 uses a 15-theoretical plate column, whereas ASTM D5236 uses a 1-theoretical plate column. This affects the separation efficiency of the two methods. Also, the "overlap" at each cutpoint for ASTM D2892 is only approximately 15–20°C, whereas for ASTM D5236, the overlap can be 50–70°C. Graphing the data for the two methods will produce a curve similar to that depicted in Fig. 1. Further discussion of yield curves is provided in Chapter 3 of Manual 51 from which the graph is taken [48]. Fortunately, many of the computer crude oil data management programs available today and widely used will produce a smooth boiling point curve that reasonably approximates the theoretical TBP curve for a particular crude oil.

Using ASTM D1160: Test Method for Distillation of Petroleum Products at Reduced Pressure, samples are distilled at reduced pressure under conditions designed to provide approximately a one-theoretical plate separation. The test uses only a 200-mL charge and all distilled material is collected in a single receiver. Thus, unlike ASTM D2892 and D5236, the method does not provide material that can be characterized. Results are strictly limited to providing data from which the initial boiling point, the final boiling point, and a distillation curve relating volume percent distilled and atmospheric equivalent boiling point temperature can be prepared. Moreover, the method is only useful up to a maximum liquid temperature of approximately 400°C at a pressure of 0.13 kPa (640°C AET).

A detailed discussion of these three ASTM methods used for crude oil distillation is provided in the ASTM MNL51 cited earlier in the discussion on vapor pressure [48]. This includes their field of application; important parameters; comments on terminology, precision, and accuracy; and a comparison of ASTM D2892 and D5236.

Fig. 2 graphically depicts typical boiling range curves for a heavy (22°API) and a light (38°API) crude oil.

Wiped-wall or thin-film molecular stills have short residence times mimicking those in refinery distillation units. Consequently, they can be used to separate higher boiling fractions under conditions that minimize cracking of thermally labile constituents that would otherwise occur with ASTM D5236 in which residence times are longer. However, in wiped-wall stills, cutpoints cannot be directly selected because vapor temperature in the distillation column cannot be measured accurately under operating conditions. Instead, the wall (film) temperature, pressure, and feed rate that will produce a cut equivalent to a ASTM D1160 or D5236 fraction with a given endpoint are determined from in-house correlations developed by matching yields between the wiped-wall distillation and the ASTM D1160 or D5236 distillation. ASTM D7169 should be useful in determining cutpoints of the higher boiling fraction material recovered by wiped-wall distillation. Despite this indirect approach, wiped-wall stills are often used because they allow higher endpoints to be attained than with ASTM D1160 or D5236 and can easily provide large quantities of material for characterization.

After fractionation of the crude oil, each of the fractions is analyzed to determine one or more of its physical and/or chemical characteristics depending on the needs of the analyst or refiner. In the following discussion, the properties or

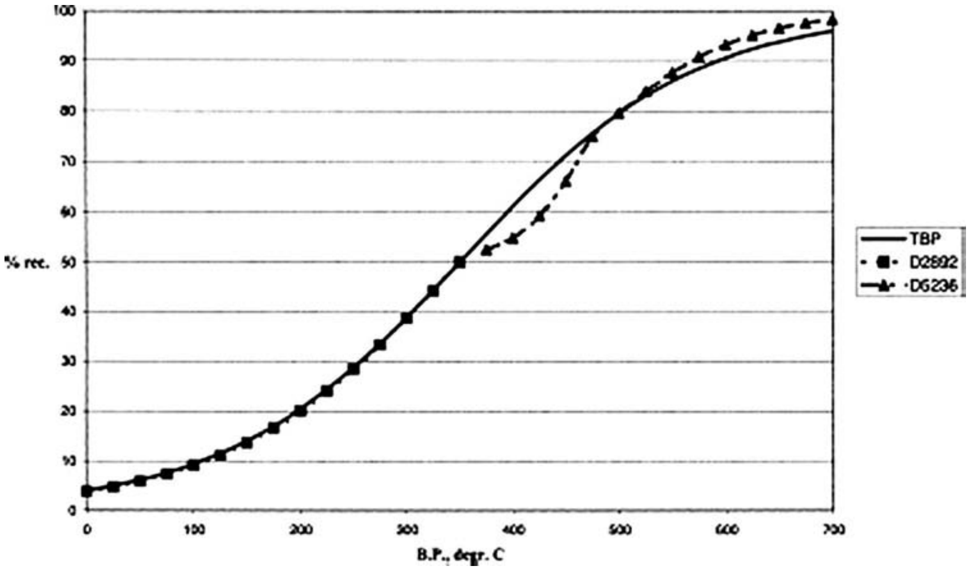


Fig. 1—Combined ASTM D2892 and D5236 boiling point curves.

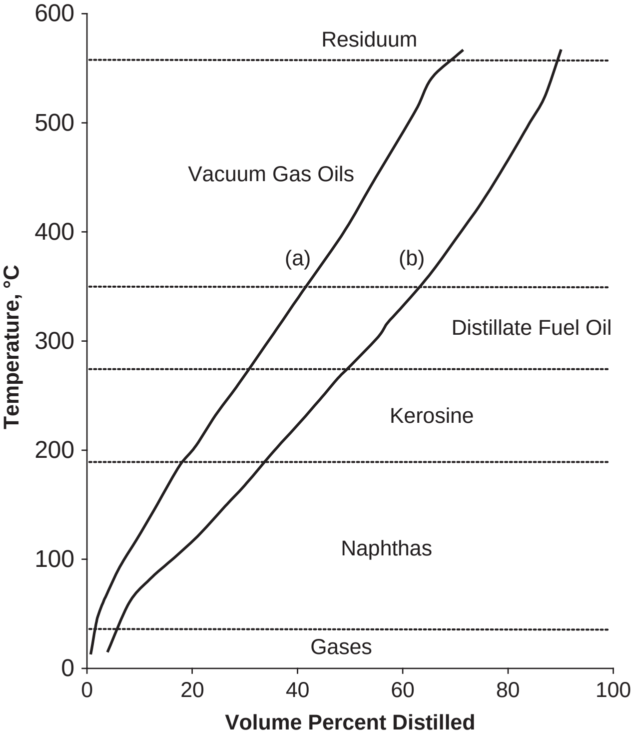


Fig. 2—True boiling point (TBP) distillation curves for (*a*) a heavy (22°API) crude oil, and (*b*) a light (38°API) crude oil.

constituents generally measured in a detailed analysis of each of the above ten fractions are listed. All of the various tests that could be performed on each of the fractions are too numerous to be included here. Other publications provide in-depth discussion on analysis and characterization of the various petroleum fractions and the products they comprise [89–92]. Table 1 summarizes this comprehensive assay format and indicates representative test methods for determining the properties. As with Table 3.2, the methods listed are those generally accepted as referee methods for determination of the property.

Numerous standard test methods are available for the determination of the properties and constituents of the distillate and residual fractions described. These test methods will not be enumerated in the following discussion because they are described in detail in the references just cited [89–92]. Although not listed in the table or succeeding discussion, volume and mass percent yields are an integral part of the analysis. These provide critical information on the quantity of product yields, allow calculation of mass balances, and permit the analyst or refiner to reformat data using linear programming (LP) models and empirically derived correlations to obtain characteristics of fractions suitable to their individual needs.

GAS

Typically, the gas or debutanization fraction is analyzed by high-resolution gas chromatography for quantitative determination of individual C_2–C_4, and total C_5+ hydrocarbons. Relative density (specific gravity) can be calculated from the compositional analysis.

NAPHTHA FRACTIONS

Density or specific gravity, total sulfur, mercaptan sulfur, hydrogen sulfide, and organic halides are typically determined on these fractions. Because these fractions, and especially the light naphtha fraction, are important as a petrochemical feedstock and as a gasoline blending component or reformer feedstock, it is likely that they would also be analyzed by high-resolution gas chromatography for quantitative determination of their paraffin, isoparaffin, aromatic, and naphthene (cycloparaffin) components (PIAN analysis; ASTM D5134 Test Method for Detailed Analysis of Petroleum Naphthas through *n*-Nonane by Capillary Gas Chromatography). The Scope of this test method limits it to determination of hydrocarbons eluting through *n*-nonane [boiling point (bp) 150.8°C]. However, through judicious selection of columns and operating conditions, some laboratories have extended this method to *n*-dodecane (bp 216°C). This test method is applicable to olefin-free (<2 % olefins by liquid volume) liquid hydrocarbon mixtures and is not suitable for naphthas derived from some synthetic crude oil streams such as produced from oil sands.

Octane numbers would also be determined for these fractions if they are to be included as a gasoline-blending component. Historically, octane numbers are determined using special engines that require relatively large volumes of sample. Today, many companies are now using semi-micro methods that require considerably less sample than the engine test methods for determination of octane numbers [93]. Other laboratories use PIAN data to calculate octane numbers [5]. Detailed hydrocarbon composition such as obtained by PIAN analysis is also used as input in the mathematical modeling of refinery processes. For the heavy naphtha fraction, aniline point would also normally be determined.

Included in the information that can be derived from the PIAN analysis are the concentrations of benzene, benzene precursors (compounds that ultimately form benzene in a refinery's reforming unit), ethyl benzene, toluene, and xylene (B-E-T-X). These data are important because of environmental regulations limiting the maximum concentration of benzene in reformulated gasoline and because of the importance of these compounds as petrochemical feedstocks and intermediates.

KEROSINE

Typically, density or specific gravity; total sulfur; mercaptan sulfur; hydrogen sulfide; organic halides; aniline point; total acid or neutralization number; naphthalene content; smoke point; total nitrogen; viscosity; and pour, cloud, and freezing points would be determined for this fraction and a cetane index calculated. Other tests that might be performed, depending on the intended end use of the fraction, are flash point, corrosiveness, and thermal stability.

As discussed earlier in the section on sulfur content, thermally reactive sulfur compounds such as mercaptans may be present in crude oils. On heating or distillation, these can decompose to form hydrogen sulfide, giving rise to its presence in the naphtha and kerosine fractions.

DISTILLATE FUEL OIL

Tests of the distillate fuel oil fraction, which includes material used to produce aviation turbine fuel, normally include determination of density or specific gravity; total sulfur; aniline point; total acid number; naphthalene content; smoke point; total nitrogen; viscosity; cloud, freeze, and pour points; and calculation of cetane index. Thermal stability and corrosiveness may also be determined in more thorough evaluations. Measurement of refractive index is also useful in

TABLE 1—Crude Oil Comprehensive Assay Format

Property	ASTM Representative Test Methods	Whole Crude	C_2–C_4 Gases	C_5–79°C Light Naphtha	79°C–121°C Medium Naphtha	121°C–191°C Heavy Naphtha	191°C–277°C Kerosine	277°C–343°C Distillate Fuel Oil	343°C–455°C Light Vacuum Gas Oil	455°C–566°C Heavy Vacuum Gas Oil	≥343°C Atmospheric Residuum	≥566°C Vacuum Residuum
Volume and mass percent yields	**D2892 and D5236**		**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**
°API, density, specific gravity	**D5002**	**X**		**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**
Sulfur, total, mass percent	**D4294**	**X**		**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**
Sediment, mass percent	**D473**	**X**										
Water, volume percent	**D4928**	**X**										
Salt, mass percent	**D6470**	**X**										
Nitrogen, total, mass percent	**D5762**	**X**					**X**	**X**	**X**	**X**	**X**	**X**
Nitrogen, basic, mass percent	**D2896**								**X**	**X**	**X**	**X**
Carbon residue, mass percent	**D4530**	**X**							**X**	**X**	**X**	**X**
Pour point	**D5853**	**X**					**X**	**X**	**X**	**X**	**X**	
Metals: Ni, V, Fe, Cu	**D5708**	**X**									**X**	**X**
Organic chlorides, total, ppm	**D4929**	**X**		**X**	**X**	**X**	**X**					
UOP K-factor	**UOP 375**	**X**										
Vapor pressure, kPa at 37.8°C	**D323 or D6377**	**X**										
Acid number, mg KOH/g	**D664**	**X**					**X**	**X**	**X**	**X**	**X**	**X**
H_2S and mercaptans, ppm	**UOP 163**	**X**		**X**	**X**	**X**	**X**					
Paraffins, isoparaffins, aromatics, naphthenes (PIAN)	**D5134**	**B-T-E-X**	**X**	**X**	**X**	**X**						

Viscosity, cSt, at 25°C	**D445**	X					X					
40°C		X					X	X				
55°C								X	X	X	X	
80°C									X	X	X	X
100°C												X
120°C												X
High-temperature simulated distillation	**D7169**	X										
Hydrogen and carbon, mass percent	**D5291**								X	X	X	X
Refractive index at 20°C	**D1218**						X	X				
Research and motor octane numbers	**Calculation from PIAN data**			X	X	X						
Asphaltenes, mass percent	**D6560**									X	X	X
Aniline point	**D611**					X	X	X	X	X		
Cetane index	**D976**						X	X	X			
Naphthalenes, volume percent	**D1840**						X	X				
Smoke point, mm	**D1322**						X	X				
Freezing point	**D2386**						X					
Cloud point	**D5773**						X	X	X	X		
Penetration	**D5**											X
Softening point	**D36**											X

correlative methods, especially in LP models, for determination of the gross composition of this fraction.

VACUUM GAS OIL FRACTIONS

Density or specific gravity, total sulfur, total nitrogen, aniline point, viscosity, acid number, cloud and pour points, and carbon residue would normally be determined on these fractions. Cetane index would be determined on the LVGO if the material is to be used as diesel fuel oil blending stock. If the HVGO is to be used as catalytic cracker feedstock, asphaltenes, nickel and vanadium, and hydrogen and carbon contents would also be determined. Lube stock evaluations would include determination of wax content. Basic nitrogen is also typically determined on these fractions. However, in general, the ratio of basic to total nitrogen is on the order of 0.3:1 for many crude oils and virgin stocks [34]. The types of nitrogen compounds present in various crude oils appear to be essentially the same, although the actual amounts may vary considerably [94]. Consequently, for most assays it is sufficient to determine total nitrogen and to assume that approximately one third is basic in character.

RESIDUUM

Tests of the residuum fractions usually include density or specific gravity, total sulfur, total and basic nitrogen, acid number, viscosity, trace metals, asphaltenes, and carbon residue. Hydrogen/carbon ratio and pour point determinations on the atmospheric (long) and vacuum (short) residua are also important. Refiners are increasingly minimizing production of material that formerly went into heavy fuels such as No. 6 and bunker oil as markets for these products diminish.

Determination of the properties of asphalt, such as penetration (ASTM D5: Test Method for Penetration of Bituminous Materials), softening point [ASTM D36: Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus)], and viscosity would also be included in some assays. However, penetration and softening point tests were developed in an era of less traffic and significantly lower pavement loadings and are no longer suitable for evaluating asphalt to be used as a binder. Newer "Performance Grade" tests such as Dynamic Shear Rheometer, Rolling Thin Film Oven, and Direct Tension Test have been developed [95].

In the preceding discussion, the properties listed for each fraction and for the whole crude oil assay are not exhaustive but are illustrative of those used to evaluate quality. As noted earlier, refiners tailor their analytical scheme to their particular crude oil and product slates, although one refiner is reported to have said, "The best crude oil assay is a 100,000 bbl run through my refinery" [96]. Although this opinion carries some validity, the assay tests presented here provide data that are sufficient for most refiners to evaluate crude oil streams.

With the proliferation of computer LP models and their associated assay libraries [9], many refiners no longer need to perform comprehensive assays as frequently as in the past. Often, an inspection assay is all that is required for them to plan for changes in processing that will be necessitated by varying levels of impurities or small changes in crude oil composition resulting from changes in the production commingled to make up the crude oil stream. Most importantly, an inspection assay can be completed much more rapidly than a comprehensive assay and requires considerably less material. Collectively, these can result in savings in analysts' time and shipping and handling expenses.

The quality of cargoes arriving at refineries may not conform to what is known or expected for that stream. This can be the result, among other causes, of new production coming on-stream and being commingled with existing production or field maintenance. The analyst or refiner can use the so-called "Flash Assay Tool" [97] to update an existing comprehensive assay on the stream in question with a minimum of data. The tool uses HTSD and various whole crude properties such as American Petroleum Institute (API) gravity or density and total sulfur content to adjust the older assay. The "new" assay, together with a refinery LP model, can then be used to make quick decisions such as purchasing and running an opportunity (challenging) crude oil. The flash assay can also be used to indicate when another full assay should be run. With the proliferation of new streams and with new production frequently being added into existing streams, a flash assay can result in considerable cost and time savings. With the relatively limited data incorporated into flash assay updates, it must be kept in mind that precision and accuracy are not optimum.

Moreover, today's trend is toward automated, real-time analysis using on-line detectors to the extent permitted by available instrumentation. Some of this instrumentation has the capability to provide data suitable for custody transfer determination of crude oil properties, but this is currently quite limited. However, it seems likely that significant advances in this area will be accomplished in the near future, further removing the laboratory analyst from routine characterization of crude oil feedstocks.

SUMMARY

Crude oils, unlike refined products, do not have specifications. As such, it is fundamentally important that assays provide sufficient and accurate data so that the producers, traders, refiners, and other users of the data can achieve several objectives. Moreover, the analytical test methods and procedures used must be defined so that different laboratories can be reasonably expected to obtain comparable data on replicate samples.

From the time a crude oil stream is produced until it reaches a refinery and is processed, several factors can affect its quality. Depressurization and cooling at the wellhead can result in flocculation of asphaltenes and crystallization of waxes. Production making up a defined stream varies over time because of several factors, including well maintenance and workovers, reservoir aging, and commingling of new production. During subsequent marine transportation, two or more crude oils of somewhat different quality may be commingled on the same vessel.

In common carrier pipeline systems, crude oils of different quality are commonly batched. Interfacial mixing will take place between the head and tail of sequential batches until they reach a breakout terminal. At the terminal, the crude oil may be stored in a tank containing a "heel" of different quality.

Assays provide assurance that the crude oil received is what is expected and help to define the changes that have taken place during transportation and storage. Refinery operation personnel use assays to assess handling and processing characteristics of a new stream or one that has changed in quality. Assays provide important information on the presence and concentration of impurities and contaminants that may affect refinery process systems. Moreover, they are important to the producer because they provide the data needed to demonstrate acceptability of a stream in a common carrier pipeline system. Furthermore, assays are used in various ways in ascertaining compatibility of different streams.

Assay data are input to refinery LP models to optimize crude oil blends and predict product yields. These data are directionally correct, but they do not replicate refinery conditions. Assays do not indicate how the fraction material will behave in process units such as reformers, catalytic crackers, or cokers or how the process streams will interact with the many and complex catalysts used today. Moreover, they do not provide data on the storage stability of refined products. However, the data available are seldom from recent shipments or cargoes.

Finally, detailed assays are costly and can take weeks to complete. The data they provide may not be representative of the shipment recently received, especially if it is an opportunity crude oil. Assays do not account for variations between cargoes and may not be representative of current production quality. Furthermore, and perhaps most important of all, assays are fundamentally dependent on the care and attention paid to sampling and handling.

5

Quality Assurance

Petroleum laboratories, large and small, should have a quality assurance program that helps provide confidence to all interested parties that the analytical data it provides fall within the limits of precision and accuracy defined in the ASTM test methods used. These data are important in the following respects, and inaccurate data can have severe financial and operational consequences:

- Conformity to what is expected, that is, "Is the crude oil I am receiving what I am expecting and what I am paying for?"
- If I am a shipper, does the crude oil meet common stream pipeline specifications? If not, it may be necessary for me to batch my crude oil at additional cost.
- Are the data I am providing accurate for payment of customs duty?
- Are the concentrations of impurities and contaminants I have determined correct for planning refinery operations and making deductions from the cost of the crude oil?
- Are my data accurate for regulatory and environmental, safety, and health reporting requirements?

ASTM International's Crude Oil Interlaboratory Crosscheck Program (ILCP) is a statistical quality assurance program that enables facilities to assess their performance in conducting test methods within their own laboratories when their data are compared against those of other participating laboratories. In early 2010, over 140 laboratories worldwide participated in the crude oil ILCP program. Table 1 lists the properties and test methods used in the program at that time.

Three times yearly, program participants receive samples. The laboratory performs the tests that they normally conduct within their own facility using the specified ASTM methods cited in the program. Single determinations by each laboratory are required because the program does not allow the reporting of averages of replicate determinations.

Final summary reports provided to participants contain

- Each participating laboratory's test results (coded for confidentiality)
- Statistical analyses of test data
- Charts plotting test results versus laboratory code
- Other pertinent information

These final statistical summary reports will help laboratories

- Monitor strengths and weaknesses of their laboratory's performance.
- Compare test results and calculated statistical parameters with other laboratories worldwide.
- Demonstrate proficiency in the specific analysis to meet laboratory accreditation requirements.
- Monitor process performance over time as part of each laboratories quality control (QC) program and prompt the respective laboratory to investigate their process if the quality changes–particularly if precision degrades over time.
- In some cases the retained ILCP sample may be used by the laboratory for future check standards of some tests in which no standards are commercially available.

An example of the statistical data summary provided in a crude oil ILCP test report is shown in Table 2.

TABLE 1—ASTM crude oil interlaboratory crosscheck program test methods[a]

Test No.[b]	Test Property	Test Method(s)	Test No.	Test Property	Test Method(s)
1	Vapor pressure	D323, D5191	9	Metals (Ni, V, Fe)	D5708, D5863
2	HTSD	D7169	10	Carbon residue	D4530
3	API gravity	D287, D1298	11	Acid number	D664
4	Density	D1298, D5002	12	Pour point	D97, D5853
5	Salts	D3230, D6470	13	Nitrogen (total)	D4629, D5762
6	Water	D4006, D4377, D4928	14	Viscosity	D445
7	Sediment	D473, D4807	15	Asphaltenes	D6560
8	Sediment and water	D4007	16	Sulfur (total)	D2622, D4294

[a] Current as of November 2009.

[b] Listed in order in which tests should be performed. By definition, vapor pressure must be the first test on a sample withdrawn from container. Sulfur should be the last.

TABLE 2—Typical statistical data summary from a crude oil ILCP test

Parameter	Results
Number of valid results	86
Robust mean	0.4237
Robust standard deviation	0.0132
Reproducibility ASTM standard	0.0418
Reproducibility these test data	0.0366
Anderson-Darling[a]	0.36
TPI[b]	1.14

[a] Anderson-Darling test is used to test if a sample of data came from a population with a specific distribution; namely, it performs a "goodness of fit" test to determine if the data are from a normal distribution.

[b] TPI = test performance index (Industry) provides an index similar to that defined in ASTM D6792-06 and is calculated as test method reproducibility/these test data reproducibility. This definition of the TPI for use in the ASTM-ILCP reports differs from the definition in D6792, which uses the ratio of "test method reproducibility/site precision". A note is being added to D6792 to reference the TPI (Industry) used in this report. It is suggested that the TPI interpretation guide mentioned in D6792 section 10 can also be applied to the interpretation of TPI (Industry).

$$TPI\ (Industry) = R_{\mathrm{ASTM}}/Robust\ R_{\text{These Data}}$$

It must be kept in mind that in accordance with the way in which the test program is set up

- Samples are not analyzed in duplicate–in contrast to good analytical practice.
- Material provided does not necessarily fall within range in test method's Scope.
- There is no assurance that participating laboratories followed test methods as written, and the data in the final report for some laboratories may be suspect.
- The ILCP is not a substitute for an assay.

Participation in an interlaboratory proficiency program in which multiple laboratories test samples using a specific method should be an integral part of a laboratory's QC program. The laboratory can participate in the tests and use the results as appropriate to demonstrate testing proficiency relative to other laboratories. ASTM D6792: Practice for Quality Systems in Petroleum Products and Lubricants Testing Laboratories covers the establishment and maintenance of the essentials of a quality system in laboratories engaged in the analysis of petroleum products and lubricants–including crude oils. The practice is best used in conjunction with ASTM Practice D6299: Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance.

6

Crude Oil Compatibility and Stability

The blending of compositionally different crude oils and condensate with crude oil can result in significant problems in transportation, storage, and refining. This is usually manifested by agglomeration or flocculation of waxes and/or asphaltenes. These can accumulate and clog tubular components such as pipelines and heat exchangers or contribute to sludge buildup in tanks, requiring costly and time-consuming cleanup and equipment downtime.

The problem has been recognized for many years, but no standard method has been developed that reliably predicts whether particular blends will be incompatible, quantify the extent to which waxes and asphaltenes will accumulate, nor when onset of incompatibility will begin once components are mixed. This latter is complicated by the fact that considerable empirical evidence indicates there can be an induction period of three or more days before onset.

ASPHALTENES

Historically, two test methods used for testing compatibility of residual fuel oil mixtures have been applied to crude oil blends. ASTM D4740: Test Method for Stability and Compatibility of Residual Fuels by Spot Test and a modified version of ASTM D4870: Test Method for Determination of Total Sediment in Residual Fuels. ASTM D4740 is a simple test to perform, but the results are subjective and not quantitative. In determining compatibility of crude oils, two oils are mixed in a predetermined ratio and the blend tested and rated for compatibility against ASTM D4740 Adjunct Reference Spots (Fig. 1). Crude oil blends may exhibit an induction period and evidence of incompatibility may not become evident for several days. If, on initial testing, a blend seems compatible, it may be advisable to retest the mixture several days later to determine if a change in rating has occurred. ASTM D4870, as modified, provides a quantitative measure of the amount of inorganic and insoluble organic material in a blend of crude oils of interest. In the modified version of the test method, a 10-g sample of the blend is mixed at 60°C then filtered at 60°C through the apparatus described in the test method. The test does not differentiate inorganic from organic sediment, and the former must be determined by a method such as ASTM D473 and subtracted from the total to obtain the organic sediment content.

Other test methods, which range from simple to complex, include "modified Shell Spot test" [98], "Asphaltene Stability Index" [99], "Oil Compatibility Model" [100], and "Automated Flocculation Titrimetry" [101]. The latter method was developed for determining compatibility of heavy oils and asphalts but has been applied to blending of crude oils.

Two automated instrumental test methods seem promising for determining stability and compatibility of crude oils. ASTM D7112: Test Method for Determining Stability and Compatibility of Heavy Fuel Oils and Crude Oils by Heavy Fuel Oil Stability Analyzer (Optical Detection) is a procedure involving titration and optical detection of precipitated asphaltenes for determining the stability and compatibility of crude oils. Stability in this context is the ability to maintain asphaltenes in a peptized or dissolved state and not undergo flocculation or precipitation. Similarly, compatibility relates to the property of mixing two or more crude oils without precipitation or flocculation of asphaltenes occurring. In the test, different mixtures of the crude oil of interest plus xylene are titrated with *n*-heptane to cause precipitation of asphaltenes. The titrated mixture is continuously circulated through an optical system that detects precipitated asphaltenes by back-scattering of visible light. Stability and compatibility parameters as defined in the method are then calculated.

ASTM D7157: Test Method for Determination of Intrinsic Stability of Asphaltene-Containing Residues, Heavy Fuel Oils, and Crude Oils (*n*-Heptane Phase Separation; Optical Detection) is a procedure for quantifying the intrinsic stability of the asphaltenes in an oil. The method uses an integrated automated analytical measurement system with an optical probe for the detection of asphaltene precipitation from a toluene solution of the sample. Three test specimens are dissolved in three different quantities of toluene. The three solutions are automatically and simultaneously titrated with *n*-heptane to cause precipitation of the asphaltenes. A computer program calculates stability parameters and subsequently the intrinsic stability of the oil in terms defined in the method.

WAXES

As discussed earlier, waxes are a complex mixture of mostly normal- and iso-alkanes having chain lengths of greater than approximately 30 carbon atoms that contribute to several problems in crude oil production, transportation, storage, and handling. Among these, they congeal in pipelines and other production equipment restricting flow [102], and they agglomerate and contribute to sludge buildup in tanks. As offshore production moves into deeper and colder waters, concern about wax deposition in subsea pipelines becomes increasingly relevant. Moreover, precipitation of waxes during marine transportation can result in relatively significant "remain-on-board" (ROB) losses when the vessel discharges. This is an especially important consideration for cargoes that undergo considerable cooling from the time they are loaded until discharge. For example, a cargo may be loaded at an Arabian Sea port at a temperature of approximately 38°C and then discharged at a transshipment terminal in Canada at a temperature of 20°C after a voyage through frigid ocean waters.

Cloud point or wax appearance temperature (WAT) is probably the single most important measure of the potential for a crude oil to deposit waxes as it cools. Cloud point is

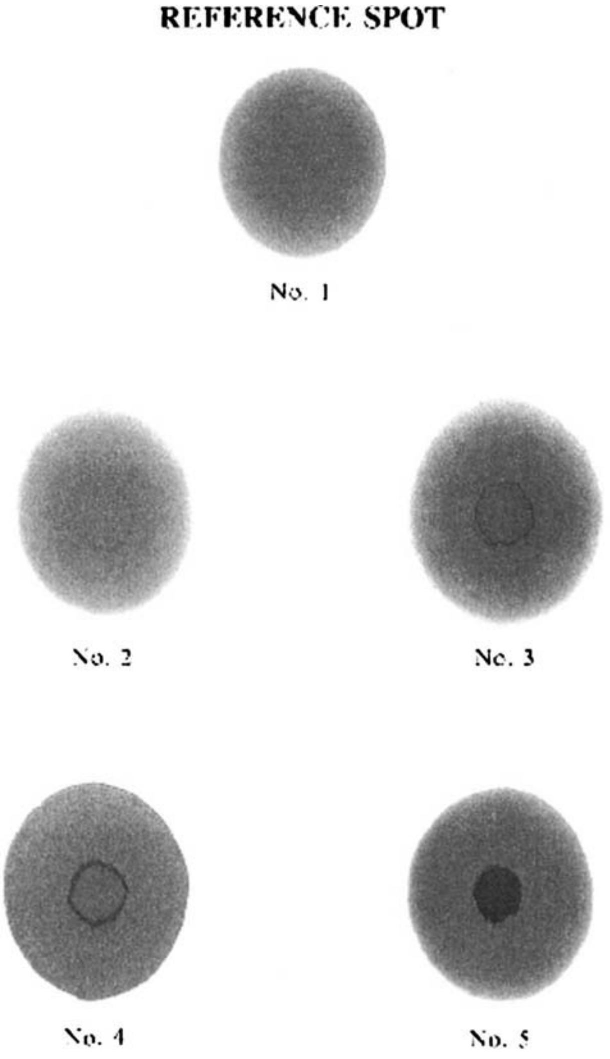


Fig. 1—ASTM D4740 Reference Spots.

defined as the temperature at which wax crystals begin to form in an oil as it is cooled. Traditional methods for determining cloud point involve visual inspection of an oil as it is cooled. Because most crude oils are very dark, cloud point per se is very difficult or impossible to measure by these methods, and several alternative methods for measuring WAT have been proposed. These include near-infrared light attenuation, dynamic filtration cloud point, low-resolution pulsed nuclear magnetic resonance, viscosity measurements, differential scanning calorimetry (DSC), and crossed polar microscopy (CPM) [103–105]. Of these, only the latter two are generally considered to be reliable and to provide a "realistic" measure [106]. As noted earlier in the section on methanol, the measured WAT can be lowered by methanol that has partitioned into the crude oil phase, complicating its accurate determination.

DSC is the simplest of these, is rapid, and may be appropriate to routine assays. Moreover, DSC is the only one of the several techniques that has been standardized [(IP389 Determination of Wax Appearance Temperature (WAT) of Middle Distillate Fuels by Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC)]. However, because it is a dynamic method, the rate of temperature scanning may be too fast for equilibrium to be achieved in the sample under study. Although the test method's Scope restricts its application to distillate fuels, several laboratories are routinely using DSC for determining WAT of crude oils.

CPM is probably the most widely used technique for measuring WAT. The method uses an optical polarizing microscope with heating stage for the determination. To minimize operator subjectivity, time-lapse photography is commonly used to monitor appearance of wax crystals. Given the very small volume used, the sample may not be representative. Moreover, the small field of view may not reveal the first crystals that appear. Utmost care must be taken in obtaining a representative sample and in its subsequent handling to avoid loss of waxes or alteration. Further, the

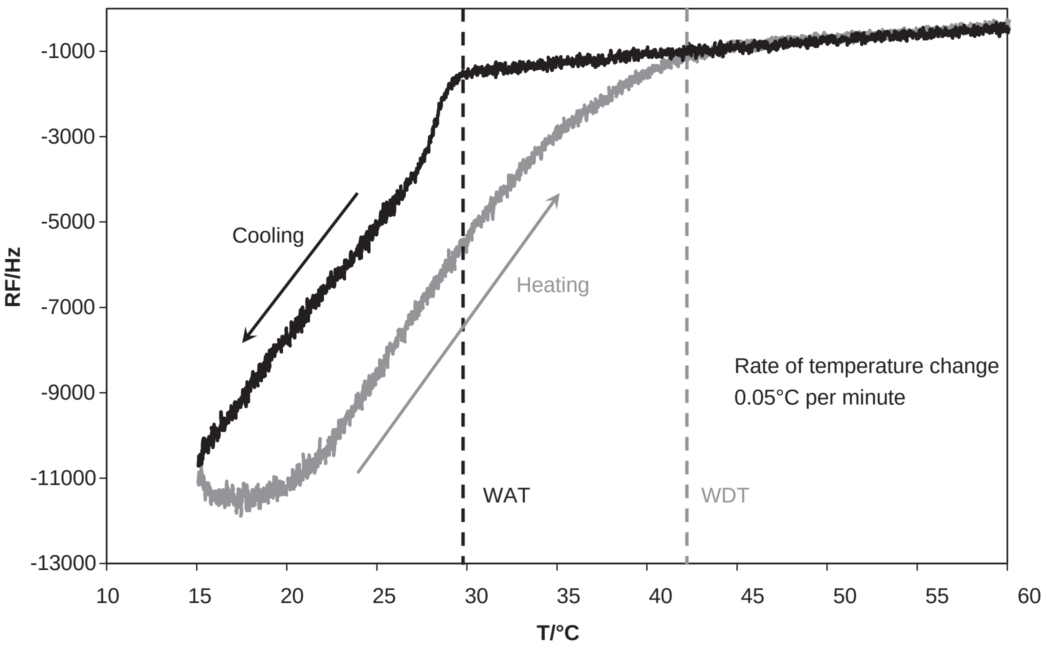


Fig. 2—Measurement of wax appearance and disappearance temperatures using changes in the resonant frequency of a quartz crystal microbalance (Courtesy of Professor B. Tohidi).

presence of pour point depressants will drastically affect the sample's WAT.

Contrasting with WAT is the wax disappearance temperature (WDT), the temperature at which the last wax crystal is in equilibrium with the liquid phase. This latter is measured while heating the sample rather than cooling the sample as is done for WAT. WAT and WDT can conveniently be measured on the same sample using DSC. A newer technique for determining WAT and WDT involves measuring changes in resonant frequency (RF) of a sample with a quartz crystal microbalance as illustrated in Fig. 2 [107]. Although WAT and WDT should thermodynamically be the same, the WAT is invariably 3–20°C lower than the WDT [103]. These differences result from subcooling and superheating of the sample [108].

7

Crude Oil as Fuel

Crude oil has been used directly as a fuel for power generation in several applications for more than 100 years. Among the earliest documented uses was as fuel for the Cleveland City Cable Railway power plant in Cleveland, Ohio, in 1891 [109]. In 1892, it was reported "there are some such progressive brick manufacturers in Chicago, who use neither coal nor wood in the drying or burning of their clay products. Crude oil is the fuel which they employ…." [110]. In 1893, "a very extensive trial of crude petroleum fuel was made in Chicago … in connection with the World's Fair" [111]. The article went on to caution "the main things to bear in mind in burning crude oil are, (1) the liability to fires and explosions from the ignition of vapor given off by the oil…." Crude oil was used to power a railroad locomotive in a trial run in Corsicana, Texas, in 1895.

> An experiment was made in using the crude oil from the oil wells at Corsicana, Texas for fuel for the locomotive in hauling passenger trains between Corsicana and Hillsboro, which proved satisfactory and arrangements have been made to continue use oil in that locomotive, and also in the switch locomotive at Corsicana [112].

A history of Anheuser-Busch, the American brewing giant, mentions that Adolphus Busch obtained the American rights to build diesel engines in 1897 and that the company's first engine was installed in the Anheuser Busch power plant in 1898. Although not stating explicitly that crude oil was used to fuel this engine, the history states "as now is well known, the Diesel engine operates very economically, using crude oil as fuel" [113].

In 1915, *The New International Encyclopedia* stated "nearly all crude oil can be used by fuel (for ships). If it contains very little sulphur or asphalt, it is suitable for heavy oil engines of the Diesel type." The article went on to state that "crude oil is not, however, much used for either of these purposes and the reasons are … the presence of the more volatile oils renders storage dangerous…." [114].

In 1975, crude oils with a wide range of properties were investigated for direct use as fuel in U.S. Army high-speed diesel engines [115]. Results of this study indicated that, with proper selection and pretreatment, crude oils are feasible for emergency use.

In recent years, crude oil has been used as fuel under boilers, in gas turbines used for standby power generation, and in diesel engines worldwide. Since 1990, crude oil has replaced other sources of energy to fire cement kilns in Cuba [116]. During the 1990s, thermoelectric power stations in the Republic of Macedonia were fueled by some 1 million tons of crude oil every year [117]. In 2004, China purchased three diesel engines from a Finnish company for installation on one of its offshore production platforms specifically to generate electricity using crude oil from the oilfield's production as fuel [118]. In 2006, Japan used on the order of 90–100 thousand barrels per day of crude oil to fire some of its thermal power plants [119]. And, contrary to the admonitions in the report on the 1893 World's Fair and in the 1915 encyclopedia article about crude oil's dangers, several tanker operators have, at times, surreptitiously and unlawfully diverted some of their cargo to power their ships. These incidents have not been without disastrous consequences, and fires and explosions have occurred.

Cost and availability–especially in remote operational areas–are certainly factors influencing the selection of crude oil over conventional burner, diesel, and gas turbine fuels. Other factors must also be considered, among them safety, environmental emissions, and the effect that use of crude oil will have on the performance and maintenance of engines, turbines, and boilers.

No specifications have been established for crude oil to be used in these applications, but certain properties critical to the operation of burners, engines, and turbines must be taken into consideration. Among these are flash point, sulfur, ash content, pour point, viscosity, wax content, carbon residue, and metals content–especially vanadium, nickel, and sodium. Because crude oils usually have relatively low flash points, their use as a fuel has an associated fire hazard and inherent risk of explosion necessitating that storage facilities be appropriately configured. Furthermore, crude oils selected for use as burner fuels must have suitable fluidity properties to ensure they are pumpable and can be aspirated in the burner or turbine. Moreover, the crude oil should have low ash and sulfur contents. These are important environmental considerations from the standpoints of fly ash (particulates) and sulfur dioxide emissions. The asphaltic residuum from burning of crude oils can build up on heat transfer surfaces, reducing their efficiency, and can clog burners. Crude oils to be used for gas turbines must also have low concentrations of trace metals to ensure that turbine blades are not adversely affected.

The standard test methods described elsewhere in this manual for characterizing crude oils as refinery feedstocks are equally applicable to determining its use as a fuel.

8

Future Needs in Crude Oil Characterization

The average quality of crude oil being processed in refineries is becoming higher in sulfur and heavier [120]; that is, a greater content of heavy ends or residuum. With the growing demand for transportation fuels, the refiner is faced with mounting pressure to make better use of the "bottom of the barrel"—the residuum that formerly went into low-quality products such as No. 6 and bunker fuel oils. Diminishing worldwide demand for these latter fuels is exacerbating the need to use this material to produce other products, especially lighter fuels [121]. Moreover, as environmental restrictions increasingly limit sulfur and aromatics in transportation and burner fuel oils, refiners are facing new challenges to economically producing a marketable slate of products from heavier, higher sulfur feedstocks. These challenges generally require new or expanded processing and treatment technology at the refinery. This, in turn, translates into the need for new analytical test methods in the laboratory to adequately evaluate feedstocks and monitor product quality (Table 1).

However, existing analytical methods may not be suitable for characterizing many of today's crude oil streams. The scope of these methods may not be sufficiently broad to cover the range in quality of some of the heavier and higher sulfur crude oils, nonconventional streams such as bitumen, and "synthetic crude oil" derived from Canadian oil sands and Venezuelan heavy oils. Table 2 summarizes some of the improvements needed to existing test methods to make them more applicable to these streams. In making revisions to test methodology, it may be necessary to conduct new interlaboratory round-robin studies to validate the precision statements. With the consolidations within the industry and the growing demands being placed on the analyst, this may not be practical.

The Canadian Crude Quality Technical Association has used the extensive experience of its members to compile a manual, *Heavy Oil and Bitumen Analytical Methods* [122]. This manual provides a review of existing test methods for eight parameters commonly used in assessing quality of heavy oils and bitumen and discusses their capabilities and limitations. When available, precision data obtained from round-robin studies on heavy oils and bitumen are included. The analytical sections in this manual are not a substitute for standardized test methods specific to heavy oils and bitumen, but they do help users to make informed decisions on method selection, sample preparation, test modifications, and interpretation of resultant data.

Sulfur reduction processes are sensitive to amount and structure of the sulfur compounds being removed. Tests that can provide information about both are becoming increasingly important. Several laboratories have combined gas chromatography with sulfur-selective detectors to provide data on the boiling range distribution of the sulfur compounds and probable molecular types. In addition, gas chromatography detectors that provide selectivity for other constituents of interest (e.g., nitrogen and organometallics) are also commercially available and being increasingly used for characterizations.

The supply of high-acid crude oils (i.e., those with a total acid number >1.0) is increasing substantially on a global basis. To adequately assess and plan the effective refinery processing of these, it is important to know the acid species present. Naphthenic acids in particular can be especially detrimental throughout a refinery. Several crude oils today contain high concentrations of calcium that will contribute to formation of egregious naphthenic acid soaps. These soaps can cause formation of highly stable emulsions that can be carried through to wastewater treatment plants. Naphthenic acids can be very corrosive, but it is important to know their species because they behave differently depending on the varying conditions of temperature, flow velocity, and metallurgy existing within a refinery. ASTM D664, which is used almost universally for determining the acid content of a crude oil, provides no information on the acid species present or their relative strength. A rapid and reliable method for characterizing the components contributing to the acidity of a crude oil and their relative strength is needed.

Upgrading the "bottom of the barrel" involves converting more—ideally all—of the residuum into a more salable, higher-valued product (i.e., 100% residuum conversion). Whatever the means to this end, improved characterization methods are necessary for process design, crude oil evaluation, and operational control. Characterization methods that define the boiling range and the hydrocarbon type distribution of heavy residuum are of growing importance. High-temperature gas chromatography simulated distillation (HTSD) has been used to obtain cutpoint data up to an atmospheric equivalent boiling point temperature of 740°C [123].

The distributions of hydrocarbon types in gas oil and heavier materials are important in evaluating them as feedstocks for further processing. Some older mass spectrometric methods for determining hydrocarbon types are being updated for use with modern quadrupole mass spectrometers, either with batch inlets or with gas chromatographic inlets (GC/MS). Another technique that has been successfully applied for determining hydrocarbon types in these materials involves the use of high-performance liquid chromatography (HPLC), which can provide information comparable to the mass spectrometric methods. Standardized HPLC techniques are now being used to determine aromatic hydrocarbon types in middle distillate and aviation fuels.

With the large volumes of crude oil being moved in today's markets and with the growing availability of opportunity or challenged crude oils comes increasing pressure to determine key properties in less time and with a high degree

TABLE 1—New analytical methods needed
Quantitative determination of organic silicon
Methanol in real time and in presence of water
Cracked stocks (olefins) content of blended and synthetic crude oils to <0.1 % vol
Naphthenic acid speciation, relative strength, and distribution

of confidence in the results [124]. Although opportunity crudes may be financially attractive to the crude oil buyer, they can be a problem to the refiner. Opportunity crudes may be high-acid oils or contain excessive levels of certain contaminants. Their product yields and qualities may be unknown or undesirable. For example, excessive residuum yields can overload a coker, and the coke produced may not be of the quality needed to satisfy the existing market. With the need for rapid turnaround of stocks and the relatively limited storage available in most refineries, these streams may be processed before conventional analyses are complete.

Rapid, automated, instrumental methods of analysis continue to be the option of choice in responding to these demands. Laboratories are constantly seeking to reduce analysis time, improve the quality of test results, and eliminate dependency on time-consuming manual methods of analysis. Advances in technology are helping to meet the analytical challenges of the industry.

TABLE 2—Needed improvements in analytical methods
Trace metals (Hg, Se, As) at ng/kg levels and below
Sulfur speciation
Hydrocarbon types in heavy ends and bitumen
Compatibility of commingled stocks
Stability of waxes and asphaltenes
Rapid and reliable method for WAT
Basic nitrogen species and distribution
Characterization of heavy and synthetic crude oils and bitumen

Predictive methods that can rapidly provide accurate physiochemical and boiling range data are the “Holy Grail” of the crude oil analyst. Several systems have been proposed, but all have limitations that constrain their usefulness. Molecular modeling can be used to provide the degree of characterizations necessary, but it involves tedious sample preparation, lengthy component separation, use of advanced analytical instrumentation, and development of a large database containing reference material [15].

Perhaps the most advanced and complicated version of molecular modeling is what is termed “petroleomics” [125]. This entails use of multihyphenated analytical techniques such as Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). This particular technique is purported to have the ability to identify thousands of elemental constituents in a crude oil. The requisite instrumentation to conduct this analysis is available in few laboratories, interpretation of the resultant data requires a highly trained and experienced analyst, and accuracy or the results are directly dependent on how representative the analyte is of the bulk sample from which it was collected. The old adage “garbage in–garbage out” is highly applicable here and must be kept in mind when relying on molecular modeling techniques for characterization of a crude oil. Moreover, because crude oil quality can change significantly over a short period of time, even the most accurate of analyses by one of these techniques can be outdated before results are available.

In the absence of these predictive methods, refiners and analysts are fortunate to have at their disposal linear programming (LP) programs with their built-in correlations and ability to recut data to their specific needs. However, they still must ultimately rely on a comprehensive assay together with operational experience in crude oil similar in quality to those of interest to validate output from computer models.

Appendix 1: Procedures for Collection of Samples for Hydrogen Sulfide Determination [37]

These procedures have been found suitable for collection of samples for determination of hydrogen sulfide (H_2S) in crude oil. Before collecting high-density polyethylene (HDPE) or floating piston cylinder samples, thoroughly flush the sampling point and all connections.

NARROW-MOUTH HDPE BOTTLES—1-L CAPACITY

Prepare the bottles by placing approximately 10 g of dry ice into each. Place the cap on the bottle and tighten loosely. Shake the bottle vigorously, and periodically loosen–but do not remove the cap–to relieve excess pressure. Continue this process until the dry ice has evaporated. Once the dry ice has evaporated, tighten the cap and set aside until the bottle is needed for sampling. Do not overpressure the bottles. If the bottles are not relieved of pressure buildup, they may explode.

Bottles may be prepared up to 2 days in advance of when they will be needed. It is advisable to prepare at least one extra bottle in case one leaks.

When ready to collect the sample, remove the bottle cap. There must be an audible hiss indicating the presence of carbon dioxide (CO_2) overpressure. If not, use another bottle. Slowly fill the bottle using a Teflon™ tube extending to the bottom. When the bottle is full to the top of the shoulder (i.e., just below the threads) squeeze the bottle at the center just enough to cause a small amount (a few drops) of oil to spill over the lip of the bottle. Screw the cap tightly onto the bottle and seal with plastic tape. Keep the bottle refrigerated or on ice. If shipping is necessary, package samples with dry ice and in accordance with applicable U.S. Department of Transportation and International Air Transport Association (IATA) regulations.

Samples collected in this manner, when kept cold, may be used for determination of H_2S for up to 10 days after their collection.

FLOATING PISTON CYLINDERS (SULFINERT® TREATED)

Before use, cylinders should have a back pressure at least 100 psi greater than that of the pipeline from which samples are to be collected. Argon (not nitrogen or helium) should be used as back pressure gas. No further preparation is necessary. Make connections to the pipeline with Sulfinert-treated stainless steel or high pressure Teflon tubing. Slowly open the valve nearest the pipeline and check for leaks. Next, slowly open the bleed valve on the cylinder and bleed at least 250 mL to waste to purge the system and displace air. Then, slowly open the third valve and gradually reduce the back pressure until it approaches that of the pipeline. Once the indicator rod begins to move, continue to slowly bleed the back pressure until the tip of the indicator rod is within approximately 1 cm of the red end cap. Several minutes should be allowed for this process to maintain a single phase in the cylinder. Tighten all valves, and then disconnect from the pipeline. Replace all plugs using Teflon tape.

Floating piston cylinders do not need to be refrigerated. Samples collected in this manner may be used for determination of H_2S for up to 30 days after their collection. This presumes the Sulfinert coating is not damaged and that sufficient pressure is maintained within the cylinder to preclude air from leaking in.

Appendix 2: Referenced ASTM and Other Standards

ASTM	Title
D5	Penetration of Bituminous Materials
D36	Softening Point of Bitumen (Ring-and-Ball Apparatus)
D56	Flash Point by Tag Closed Cup Tester
D93	Flash Point by Pensky-Martens Closed Cup Tester
D96	Water and Sediment in Crude Oil by Centrifuge Method (Field Procedure) (withdrawn 2000)
D97	Pour Point of Petroleum Products
D129	Sulfur in Petroleum Products (General Bomb Method)
D189	Conradson Carbon Residue of Petroleum Products
D287	API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)
D323	Vapor Pressure of Petroleum Products (Reid Method)
D341	Viscosity-Temperature Charts for Liquid Petroleum Products
D445	Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)
D473	Sediment in Crude Oils and Fuel Oils by the Extraction Method
D482	Ash from Petroleum Products
D524	Ramsbottom Carbon Residue of Petroleum Products
D664	Acid Number of Petroleum Products by Potentiometric Method
D1160	Distillation of Petroleum Products at Reduced Pressure
D1250	Petroleum Measurement Tables
D1298	Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
D1480	Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer
D1552	Sulfur in Petroleum Products (High-Temperature Method)
D2161	Conversion of Kinematic Viscosity to Saybolt Universal Viscosity or to Saybolt Furol Viscosity
D2622	Sulfur in Petroleum Products by X-Ray Spectrometry
D2887	Boiling Range Distribution of Petroleum Fractions by Gas Chromatography
D2892	Distillation of Crude Petroleum (15-Theoretical Plate Column)
D3228	Total Nitrogen in Lubricating Oils and Fuel Oils by Modified Kjeldahl Method
D3230	Salts in Crude Oil (Electrometric Method)
D3279	*n*-Heptane Insolubles
D4006	Water in Crude Oil by Distillation
D4007	Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure)
D4052	Density and Relative Density of Liquids by Digital Density Meter
D4057	Manual Sampling of Petroleum and Petroleum Products
D4177	Automatic Sampling of Petroleum and Petroleum Products
D4294	Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectrometry

ASTM	Title
D4377	Water in Crude Oil by Potentiometric Karl Fischer Titration
D4530	Determination of Carbon Residue (Micro Method)
D4629	Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence
D4740	Cleanliness and Compatibility of Residual Fuels by Spot Test
D4807	Sediment in Crude Oil by Membrane Filtration
D4840	Sampling Chain-of-Custody Procedures
D4870	Determination of Total Sediment in Residual Fuels
D4928	Water in Crude Oil by Coulometric Karl Fischer Titration
D4929	Determination of Organic Chloride Content in Crude Oil
D5002	Density and Relative Density of Crude Oils by Digital Density Analyzer
D5134	Detailed Analysis of Petroleum Naphthas through *n*-Nonane by Capillary Gas Chromatography
D5185	Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively-Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
D5191	Vapor Pressure of Petroleum Products (Mini Method)
D5236	Distillation of Heavy Hydrocarbon Mixtures (Vacuum Potstill Method)
D5291	Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants
D5307	Determination of the Boiling Range Distribution of Crude Petroleum by Gas Chromatography
D5708	Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively-Coupled Plasma (ICP) Atomic Emission Spectrometry
D5762	Nitrogen in Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence
D5842	Sampling and Handling of Fuels for Volatility Measurement
D5853	Pour Point of Crude Oils
D5854	Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
D5863	Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry
D6299	Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance
D6377	Determination of Vapor Pressure of Crude Oil: $VPCR_X$ (Expansion Method)
D6470	Salt in Crude Oils (Potentiometric Method)
D6560	Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products
D6792	Quality Systems in Petroleum Products and Lubricants Testing Laboratories
D6822	Density, Relative Density, and API Gravity of Crude Petroleum and Liquid Petroleum Products by Thermohydrometer Method
D7059	Determination of Methanol in Crude Oils by Multidimensional Gas Chromatography
D7112	Determining Stability and Compatibility of Heavy Fuel Oils and Crude Oils by Heavy Fuel Oil Stability Analyzer (Optical Detection)
D7157	Determination of Intrinsic Stability of Asphaltene-Containing Residues, Heavy Fuel Oils, and Crude Oils (*n*-Heptane Phase Separation; Optical Detection)
D7169	Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High-Temperature Gas Chromatography
D7279	Kinematic Viscosity of Transparent and Opaque Liquids by Automated Houillon Viscometer
D7343	Optimization, Sample Handling, Calibration, and Validation of X-Ray Fluorescence Spectrometry Methods for Elemental Analysis of Petroleum Products and Lubricants

(*Continued*)

ASTM	Title
D7455	Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis
D7482	Sampling, Storage, and Handling of Hydrocarbons for Mercury Analysis
D7622	Total Mercury in Crude Oil Using Combustion and Direct Cold Vapor Atomic Absorption Method with Zeeman Background Correction
D7623	Total Mercury in Crude Oil Using Combustion-Gold Amalgamation and Cold Vapor Atomic Absorption Method
IP	**Title**
389	Determination of Wax Appearance Temperature (WAT) of Middle Distillate Fuels by Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC)
570	Determination of Hydrogen Sulfide in Fuel Oils—Rapid Liquid-Phase Extraction Method
UOP	**Title**
46	Paraffin Wax Content of Petroleum Oils and Asphalts
163	Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration
375	Calculation of UOP Characterization Factor and Estimation of Molecular Weight of Petroleum Oil
938	Total Mercury and Mercury Species in Liquid Hydrocarbons

Appendix 3: Excerpts from Standards Used for Sampling, Handling, and Analysis

This appendix includes excerpts from the Scope and certain other sections of the ASTM test methods and practices most commonly used in the sampling and handling, and analysis of crude oils. All of the test methods used in the ASTM Crude Oil Interlaboratory Crosscheck Program are included here. This is intended as a quick reference guide to familiarize the reader with the standards that may be applicable to particular needs. It is not a substitute for a thorough reading and understanding of the standard. This appendix is divided into sampling and handling practices and test methods, with the standards given in numerical order in each section.

SAMPLING AND HANDLING PRACTICES

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

1. SCOPE

1.1 This practice covers procedures for manually obtaining representative samples of petroleum products of a liquid, semiliquid, or solid state for which the vapor pressure at ambient conditions is below 101 kPa (14.7 psia). If sampling is for the precise determination of volatility, use Practice D5842 in conjunction with this practice.

4. SUMMARY OF PRACTICE

4.1 This practice provides procedures for manually obtaining samples of petroleum and petroleum products of a liquid, semiliquid, or solid state from tanks, pipelines, and other containers. It addresses, in detail, the various factors that need to be considered in obtaining a representative sample. These considerations include the analytical tests to be conducted on the sample, the types of sample containers to be used, and any special instructions required for special materials to be sampled. (Fig. 1 illustrates bottle assemblies typically used in sampling static tanks.)

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

1. SCOPE

1.1 This practice covers information for the design, installation, testing, and operation of automated equipment for the extraction of representative samples of petroleum and petroleum products from a flowing stream and storing them in a sample receiver. If sampling is for the precise determination of volatility, use Practice D5842 in conjunction with this practice. For sample mixing, refer to Practice D5854. Petroleum products covered in this practice are considered to be a single phase and exhibit Newtonian characteristics at the point of sampling.

1.2 *Applicable Fluids*—This practice is applicable to petroleum and petroleum products with vapor pressures at sampling and storage temperatures less than or equal to 101 kPa (14.7 psi). Refer to D5842 when sampling for Reid vapor pressure (RVP) determination.

6. AUTOMATIC SAMPLING SYSTEMS

6.1 An automatic sampling system consists of stream conditioning upstream of the sampling location, a device to physically extract a grab from the flowing stream, a flow measurement device for flow proportioning, a means to control the total volume of sample extracted, a sample receiver to collect and store the grabs, and, depending on the system, a sample receiver/mixing system. Unique properties of the petroleum being sampled may require that the individual components or the entire system be insulated, heated, or both.

6.2 Grabs must be taken in proportion to flow. However, if the flow rate during the total parcel delivery varies less than ±10 % from the average flow rate, a representative sample may be obtained by the time proportional control of the grabs.

6.3 There are two types of automatic sampling systems (see Fig. 2). Both systems can produce representative samples if properly designed and operated. One system locates the extracting device directly in the main line, whereas the other system locates the extracting device in a sample loop.

6.4 In a sample loop type system, a probe is located in the main pipeline and directs a portion of the fluid flow into the sample loop.

9. SPECIAL CONSIDERATIONS FOR MARINE APPLICATIONS

9.1 When pumping from a vessel, a significant amount of free water may be transferred during a short period of time (see Fig. 3). (Cargo is withdrawn from each vessel compartment through a downward-facing suction strum positioned just above the bottom. Accumulated water and sediment will be withdrawn within the first few minutes of unloading.)

D5842 Practice for Sampling and Handling of Fuels for Volatility Measurement

1. SCOPE

1.1 This practice covers procedures and equipment for obtaining, mixing, and handling representative samples of volatile fuels for the purpose of testing for compliance with the standards set forth for volatility-related measurements applicable to light fuels. The applicable dry vapor pressure equivalent range of this practice is 13–105 kPa (2–16 psia).

4. SUMMARY OF PRACTICE

4.1 It is necessary that the samples be representative of the fuel in question. The basic principle of each sampling procedure involves obtaining a sample in such a manner and from such locations in the tank or other container that the sample will be representative of the fuel. Each procedure is suitable for sampling a material under definite storage, transportation, or container conditions. The precautions required to ensure the representative character of the samples are numerous and depend on the tank, carrier,

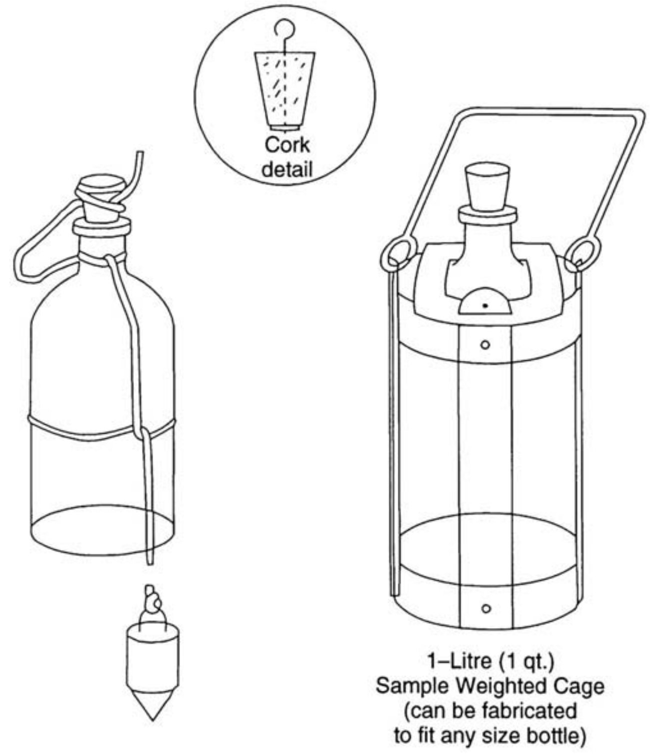


Fig. 1—Typical assemblies for bottle sampling of tanks.

container, or line from which the sample is being obtained; the type and cleanliness of the sample container; and the sampling procedure that is to be used.

D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products

1. SCOPE

1.1 This practice covers the handling, mixing, and conditioning procedures that are required to ensure that a representative sample of the liquid petroleum or petroleum product is delivered from the primary sample container/receiver into the analytical test apparatus or into intermediate containers.

1.2 Annexes cover acceptance test criteria for power mixer and sample container combinations and detail acceptance tests for mixing systems. An appendix provides a guide for selecting sample containers.

D7343 Practice for Optimization, Sample Handling, Calibration, and Validation of X-Ray Fluorescence Spectrometry Methods for Elemental Analysis of Petroleum Products and Lubricants

1. SCOPE

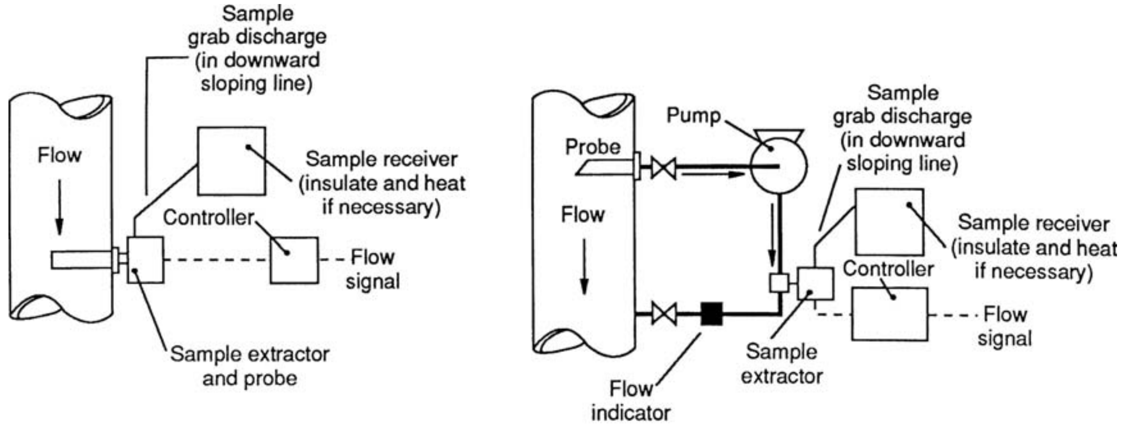
1.1 This practice covers information relating to sampling, calibration, and validation of X-ray fluorescence (XRF) instruments for elemental analysis, including all kinds of wavelength dispersive (WDXRF) and energy dispersive (EDXRF) techniques. This practice includes sampling issues such as the selection of storage vessels, transportation, and subsampling. Treatment, assembly, and handling of technique-specific sample holders and cups are also included. Technique-specific requirements during analytical measurement and validation of measurement for the determination of trace elements in samples of petroleum and petroleum products are described. For sample mixing, refer to Practice D5854. Petroleum products covered in this practice are considered to be a single phase and exhibit Newtonian characteristics at the point of sampling.

1.2 *Applicable Test Methods*—This practice is applicable to the XRF methods under the jurisdiction of ASTM Subcommittee D02.03 on Elemental Analysis: D2622, D4294, D5059, D6334, D6443, D6445, D6481, D7039, D7212, and D7220.

1.3 *Applicable Fluids*—This practice is applicable to petroleum and petroleum products with vapor pressures at sampling and storage temperatures less than or equal to 101 kPa (14.7 psi). Use Practice D4057 to sample these materials. Refer to Practice D5842 when sampling materials that also require RVP determination.

1.4 *Nonapplicable Fluids*—Petroleum products for which vapor pressure at sampling and sample storage conditions are above 101 kPa (14.7 psi) and liquefied gases (i.e., liquefied natural gas, liquefied petroleum gas, etc.) are not covered by this practice.

1.5 *Sampling Methods*—The physical sampling and methods of sampling from a primary source are not covered by this guide. It is assumed that samples covered by this practice are a representative sample of the primary source liquid. Refer to Practice D4057 for detailed sampling procedures.



Automatic Sampling-in-line **Automatic Sampling with a Fast Loop**

Fig. 2—Typical automatic sampling systems.

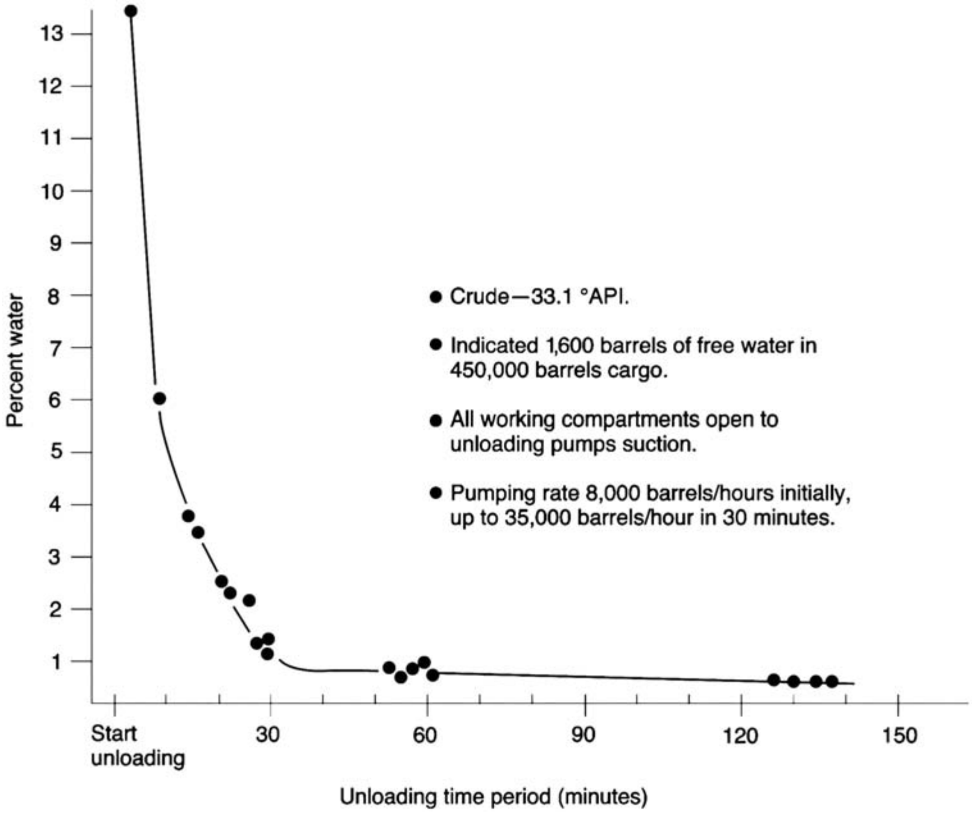


Fig. 3—Comparison of percent sediment and water versus unloading time period.

4. SAMPLE HANDLING

4.1 It is necessary to use precautions to minimize the possibility of contamination of trace elemental analysis samples. Good laboratory practices in this area include the following:

4.1.1 Samples received by the laboratory and required for trace element analysis should be stored in a designated specific location for storage while awaiting analysis. Whenever possible, this area should not contain samples that could contaminate those requiring trace element analysis.

4.1.2 All laboratory equipment used specifically for trace element analysis should be free of any source of contamination. This may require that specific equipment be used only for trace element analysis.

4.1.3 Analyses of blank samples are highly recommended.

4.1.4 Sample preparation should be carried out in a clean area. This area should use surfaces that can be decontaminated easily if a spillage occurs.

4.1.5 Operators should wear clean, fresh, protective gloves for sample preparation for trace element analysis. Tests should be run to confirm that the gloves do not contain interfering elements or elements of interest because they may cause contamination.

The development of clean area sample handling protocols is encouraged.

D7455 Practice for Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis

1. SCOPE

1.1 This practice covers different means by which petroleum product and lubricant samples may be prepared before the measurement of their elemental content using different analytical techniques.

1.2 This practice includes only the basic steps for generally encountered sample types. Anything out of the ordinary may require special procedures. See individual test methods for instructions to handle such situations.

1.3 This practice is not a substitute for a thorough understanding of the actual test method to be used, caveats the test method contains, and additional sample preparation that may be required.

1.4 The user should not expand the scope of the test methods to materials or concentrations outside of the scope of the test methods being used without thoroughly understanding the implications of such deviations.

3. SUMMARY OF PRACTICE

3.1 This practice covers alternate ways of preparing a petroleum product or lubricant sample for elemental analysis measurements. The means of preparation of samples may vary from no special steps to extensive detailed procedures dependent on the sample matrix and the measurement technique to be used.

D7482 Practice for Sampling, Storage, and Handling of Hydrocarbons for Mercury Analysis

1. SCOPE

1.1 This practice covers the types of and preparation of containers found most suitable for the handling of hydrocarbon samples for the determination of total mercury.

1.2 This practice was developed for sampling streams in which the mercury speciation is predominantly elemental mercury (Hg(0)) present as a mixture of dissolved Hg(0) atoms, adsorbed Hg(0) on particulates (e.g., carbonaceous or mineral fines and ferric oxide), and suspended droplets of metallic mercury.

1.3 The presence of suspended droplets of metallic mercury (often called "colloidal" mercury, because the droplet size can be very small) can make obtaining a representative sample very difficult for various reasons (e.g., nonisokinetic sampling of the liquid can result in over- or undercollection of suspended droplets and collection of mercury that has accumulated in dense larger drops and pools on the bottom of piping and in sample taps). Pay strict attention to the detailed procedure (Section 7) to ensure representative samples are collected.

1.4 When representative test portions are collected and analyzed in accordance with acceptable procedures, the total mercury is representative of concentrations in the sample.

4. SUMMARY OF PRACTICE

4.1 This practice describes the sampling, storage, transport, and handling of hydrocarbon samples used for determining mercury, and the precautions that need to be taken to prevent sample contamination and loss of analyte.

TEST METHODS

D97 Test Method for Pour Point of Petroleum Products

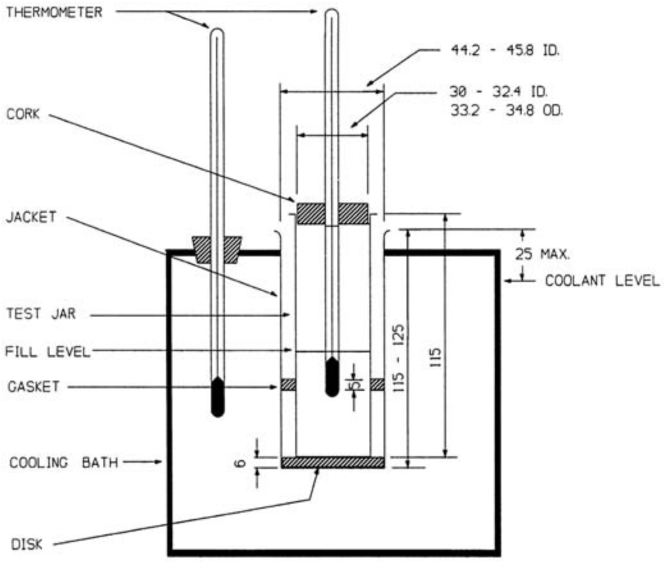
1. SCOPE

1.1 This test method is intended for use on any petroleum product. A procedure suitable for black specimens (such as crude oils) is described.

1.2 Currently there is no ASTM test method for automated Test Method D97 pour point measurements.

4. SUMMARY OF TEST METHOD

4.1 After preliminary heating, the sample is cooled at a specified rate and examined at intervals of 3°C for flow characteristics (Fig. 4). The lowest temperature at which movement of the specimen is observed is recorded as the pour point.



NOTE—Dimensions are in millimetres (not to scale).

Fig. 4—Apparatus for D97 pour point test.

D287 Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)

1. SCOPE

1.1 This test method covers the determination by means of a glass hydrometer of the American Petroleum Institute (API) gravity of crude petroleum and petroleum products normally handled as liquids and having a RVP (Test Method D323) of 180 kPa (26 psi) or less. Gravities are determined at 15.56°C (60°F) or converted to values at 60°F by means of standard tables.

Note 1—The international version of this test method is described in Practice D1298.

4. SUMMARY OF TEST METHOD

4.1 This test method is based on the principle that the gravity of a liquid varies directly with the depth of immersion of a body floating in it. The floating body, which is graduated by API gravity units in this method, is called an API hydrometer.

4.2 The API gravity is read by observing the freely floating API hydrometer and noting the graduation nearest to the apparent intersection of the horizontal plane surface of the liquid with the vertical scale of the hydrometer after temperature equilibrium has been reached. The temperature of the sample is read from a separate accurate ASTM thermometer in the sample or from the thermometer, which is an integral part of the hydrometer (thermohydrometer).

D323 Test Method for Vapor Pressure of Petroleum Products (Reid Method)

1. SCOPE

1.1 This test method covers procedures for the determination of vapor pressure (see Note 1) of gasoline, volatile crude oil, and other volatile petroleum products with a vapor pressure of less than 180 kPa (26 psi).

Note 1—Because the external atmospheric pressure is counteracted by the atmospheric pressure initially present in the vapor chamber, the RVP is an absolute pressure at 37.8°C (100°F) in kilopascals (pounds-force per square inch). RVP differs from the true vapor pressure of the sample because of some small sample vaporization and the presence of water vapor and air in the confined space.

3. SUMMARY OF TEST METHOD

3.1 The liquid chamber of the vapor pressure apparatus is filled with the chilled sample and connected to the vapor chamber that has been heated to 37.8°C (100°F) in a bath (Fig. 5). The assembled apparatus is immersed in a bath at 37.8°C (100°F) until a constant pressure is observed. The reading, suitably corrected, is reported as the RVP.

D445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)

1. SCOPE

1.1 This test method specifies a procedure for the determination of the kinematic viscosity, ν, of transparent and opaque liquid petroleum products by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity, η, can be obtained by multiplying the kinematic viscosity, ν, by the density, ρ, of the liquid.

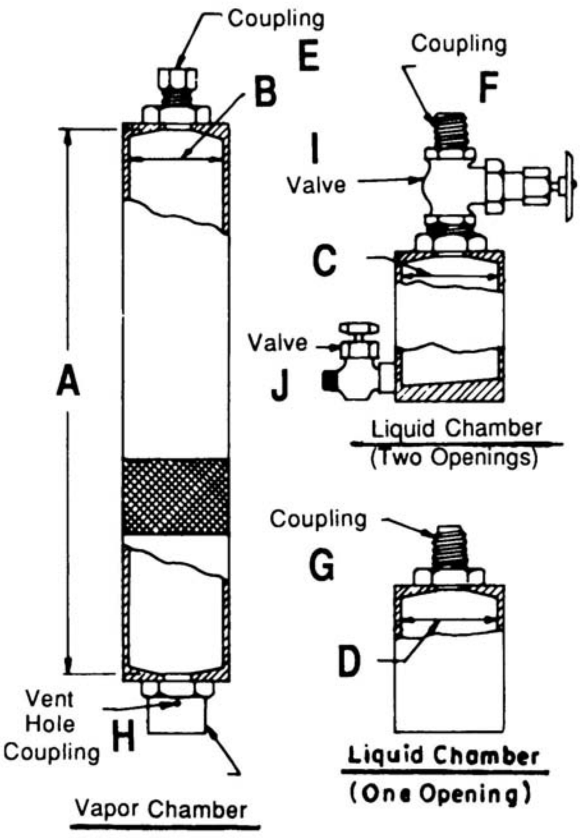


Fig. 5—D323 Vapor pressure apparatus.

1.2 The result obtained from this test method is dependent on the behavior of the sample and is intended for application to liquids for which primarily the shear stress and shear rates are proportional (Newtonian flow behavior). However, if the viscosity varies significantly with the rate of shear, different results may be obtained from viscometers of different capillary diameters.

1.3 The range of kinematic viscosities covered by this test method is from 0.2 to 300,000 mm^2/s at all temperatures.

4. SUMMARY OF TEST METHOD

4.1 The time is measured 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 and known temperature. The kinematic viscosity (determined value) 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.

D473 Test Method for Sediment in Crude Oils and Fuel Oils by the Extraction Method

1. SCOPE

1.1 This test method covers the determination of sediment in crude oils by extraction with toluene. The precision applies to a range of sediment levels from 0.01 to 0.40 % mass, although higher levels may be determined.

3. SUMMARY OF TEST METHOD

3.1 Extract a test portion of a representative oil sample, contained in a refractory thimble, with hot toluene until the residue reaches constant mass (Fig. 6). The mass of residue, calculated as a percentage, is reported as "sediment by extraction."

D664 Test Method for Acid Number of Petroleum Products by Potentiometric Titration

1. SCOPE

1.1 This test method covers procedures for the determination of acidic constituents in petroleum products and lubricants soluble or nearly soluble in mixtures of toluene and propan-2-ol. It is applicable for the determination of acids for which the dissociation constants in water are greater than 10^{-9}; extremely weak acids for which the dissociation constants are less than 10^{-9} do not interfere. Salts react if their hydrolysis constants are greater than 10^{-9}. The range of acid numbers included in the precision statement is 0.1 mg/g potassium hydroxide (KOH) to 150 mg/g KOH.

4. SUMMARY OF TEST METHOD

4.1 The sample is dissolved in a mixture of toluene and propan-2-ol containing a small amount of water and titrated potentiometrically with alcoholic KOH using a glass indicating electrode and a reference electrode or a combination electrode. The meter readings are plotted manually or automatically against the respective volumes of titrating solution, and the endpoints are taken only at well-defined inflections in the resulting curve. When no definite inflections are obtained and for used oils, endpoints are taken at meter readings corresponding to those found for aqueous acidic and basic buffer solutions.

D1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

1. SCOPE

1.1 This test method covers the laboratory determination using a glass hydrometer of the density, relative density (specific gravity), or API gravity of crude petroleum normally handled as liquids and having a RVP of 101.325 kPa (14.696 psi) or less.

1.2 Values are measured on a hydrometer at the reference temperature or at another convenient temperature, and readings are corrected to the reference temperature by means of the Petroleum Measurement Tables (values obtained at other than the reference temperature being hydrometer readings and not density measurements).

1.3 Values determined as density, relative density, or API gravity can be converted to equivalent values in the other units at alternate reference temperatures by means of the Petroleum Measurement Tables.

4. SUMMARY OF TEST METHOD

4.1 The sample is brought to a specified temperature and a test portion is transferred to a hydrometer cylinder that has been brought to approximately the same temperature. The appropriate hydrometer, also at a similar temperature, is lowered into the test portion and allowed to settle. After temperature equilibrium has been reached, the

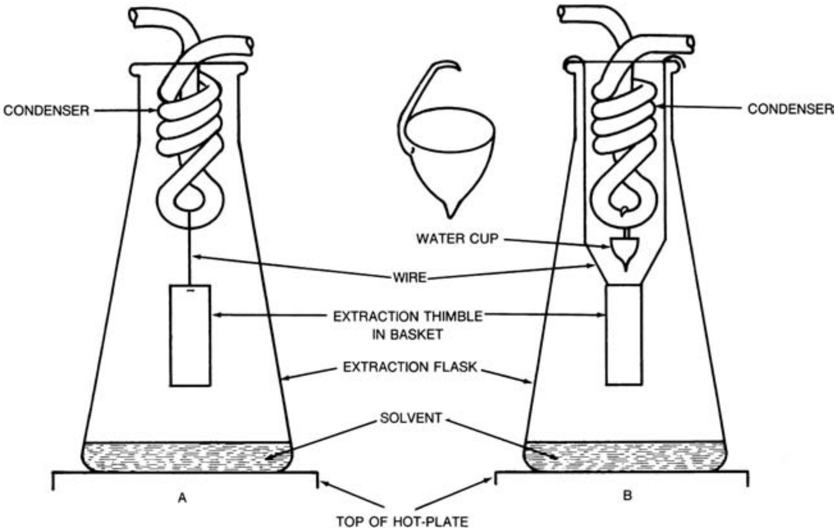


Fig. 6—Extraction apparatus for D473 determination of sediment.

hydrometer scale is read (Fig. 7), and the temperature of the test portion is taken. The observed hydrometer reading is reduced to the reference temperature by means of the Petroleum Measurement Tables. If necessary, the hydrometer cylinder and its contents are placed in a constant temperature bath to avoid excessive temperature variation during the test.

D1480 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer

1. SCOPE

1.1 This test method describes two procedures for the measurement of the density of materials that are fluid at the desired test temperature. Its application is restricted to liquids of vapor pressures below 600 mm Hg (80 kPa) and viscosities below 40,000 cSt (mm^2/s) at the test temperature. The method is designed for use at any temperature between 20°C and 100°C. It can be used at higher temperatures; however, in this case, the precision section does not apply.

1.2 This test method provides a calculation procedure for converting density to specific gravity.

4. SUMMARY OF TEST METHOD

4.1 The liquid sample is introduced into the pycnometer, equilibrated to the desired temperature, and weighed. The density or specific gravity is then calculated from this weight and the previously determined calibration factor, and a correction is applied for the buoyancy of air.

D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry

1. SCOPE

1.1 This test method covers the determination of total sulfur in 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 include crude oil among others.

1.2 Interlaboratory studies on precision covered various materials with sulfur concentrations ranging from approximately 3 mg/kg to 5.3 mass percent. For a subset of these samples, with sulfur concentrations below 60 mg/kg, the repeatability standard deviation (S_r) was 1.5 mg/kg. An estimate of the limit of detection is 3 × 3 S_r, and an estimate of the limit of quantitation is 10 × 3 S_r. However, because instrumentation 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.

1.3 Samples containing more than 5.0 mass percent sulfur can be diluted to bring the sulfur concentration of the diluted material within the scope of this test method.

1.4 Volatile samples may not meet the stated precision because of selective loss of light materials during the analysis.

1.5 A fundamental assumption in this test method is that the standard and sample matrix are well matched. Matrix mismatch can be caused by carbon-to-hydrogen ratio differences between samples and standards or by the presence of other heteroatoms.

D2892 Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)

1. SCOPE

1.1 This test method covers the procedure for the distillation of stabilized crude petroleum (see Note 1) to a final cut temperature of 400°C atmospheric equivalent temperature (AET). This test method uses a fractionating column having an efficiency of 14–18 theoretical plates operated at a reflux ratio of 5:1. Performance criteria for the necessary equipment are specified. This test method offers a compromise between efficiency and time to facilitate the comparison of distillation data between laboratories.

Note 1—Defined as having a RVP less than 82.7 kPa (12 psi).

1.2 This test method details procedures for the production of a liquefied gas, distillate fractions, and residuum of standardized quality on which analytical data can be obtained as well as the determination of yields of the above fractions by mass and volume. From the preceding information, a graph of temperature versus mass percent distilled can be produced. This distillation curve corresponds to a laboratory technique, which is defined at 15/5 (15-theoretical plate column, 5:1 reflux ratio) or true boiling point (TBP).

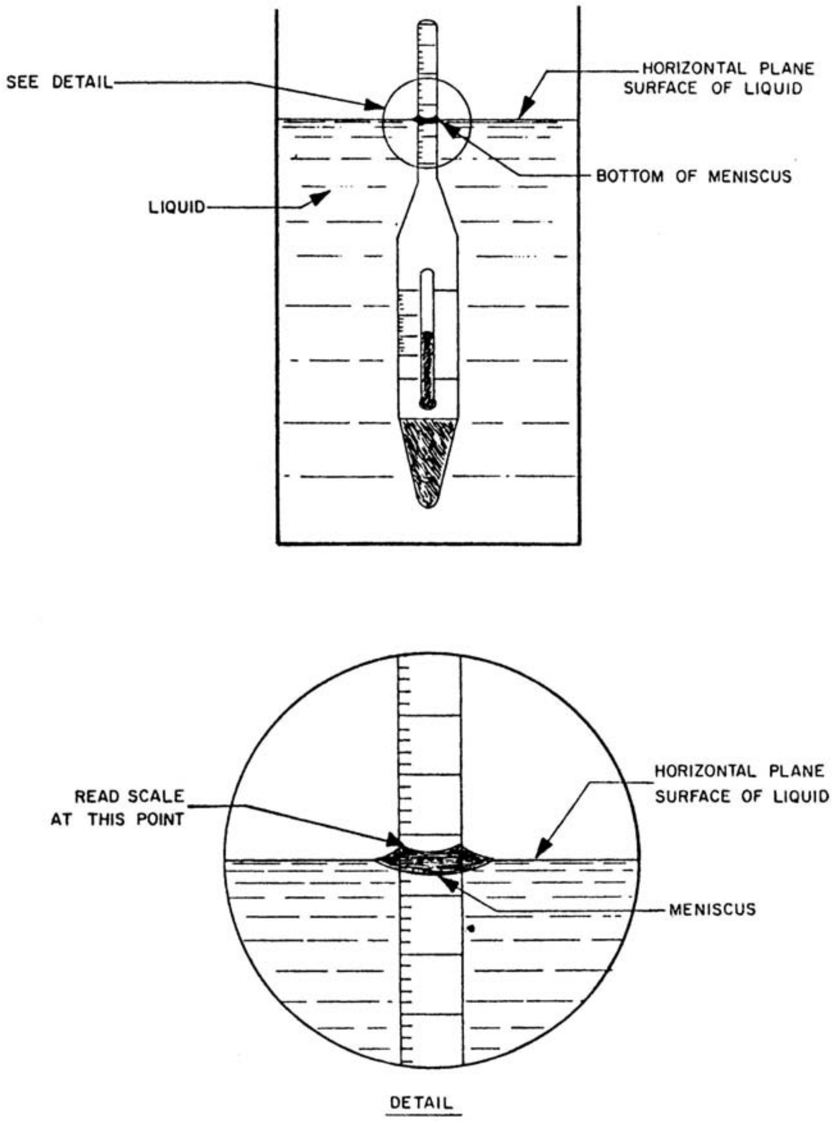


Fig. 7—Hydrometer scale reading for opaque fluids.

4. SUMMARY OF TEST METHOD

4.1 A weighed sample of 1–30 L of stabilized crude petroleum is distilled to a maximum temperature of 400°C AET in a fractionating column having an efficiency at total reflux of at least 14, but not greater than 18, theoretical plates (Fig. 8).

4.2 A reflux ratio of 5:1 is maintained at all operating pressures, except that at the lowest operating pressures between 0.674 and 0.27 kPa (5 and 2 mm Hg), a reflux ratio of 2:1 is optional. In cooperative testing or in cases of dispute, the interested parties must mutually agree on the stages of low pressure, the reflux ratios, and the temperatures of cutpoints before beginning the distillation.

4.3 Observations of temperature, pressure, and other variables are recorded at intervals and at the end of each cut or fraction.

4.4 The mass and density of each cut or fraction are obtained. Distillation yields by mass are calculated from the mass of all fractions, including liquefied gas cut and the residue. Distillation yields by volume of all fractions and the residue at 15°C are calculated from mass and density.

4.5 From these data, the TBP curves in mass percent, volume percent, or both versus AET are drawn.

D3230 Test Method for Salts in Crude Oil (Electrometric Method)

1. SCOPE

1.1 This test method covers the determination of the approximate chloride (salts) concentration in crude oil. The range of concentration covered is 0–500 mg/kg or 0–150 lb/1,000 bbl as chloride concentration/volume of crude oil.

1.2 This test method measures conductivity in the crude oil that is due to the presence of common chlorides such as sodium, calcium, and magnesium. Other conductive materials may also be present in the crude oil.

1.3 Acceptable concentration units are grams per cubic metre (g/m^3) or pounds per thousand barrels (PTB; lb/1,000 bbl).

4. SUMMARY OF TEST METHOD

4.1 This test method measures the conductivity of a solution of crude oil in a mixed alcohol solvent when subjected to an electrical stress. This test method measures conductivity

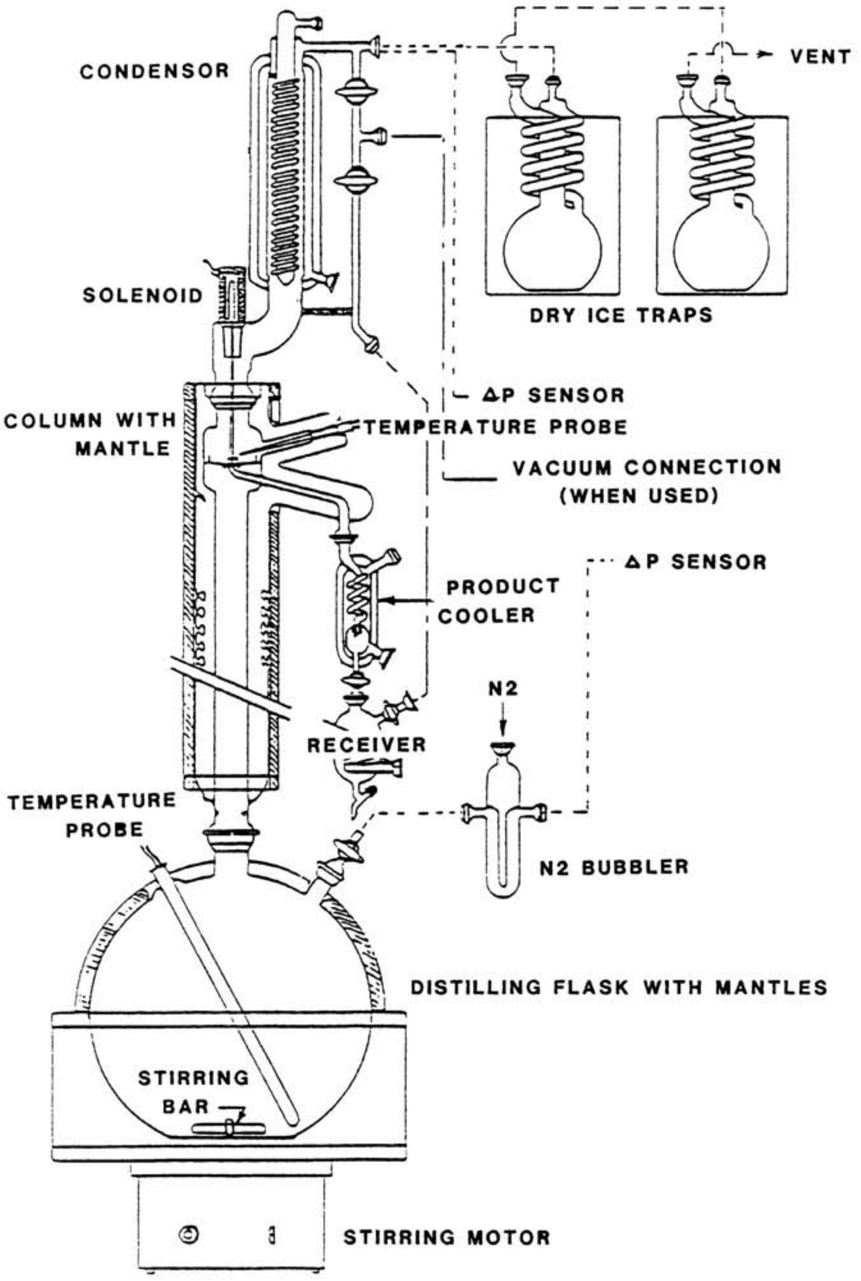


Fig. 8—Example of typical acceptable apparatus for D2892.

due to the presence of inorganic chlorides and other conductive material in the crude oil. A homogenized test specimen is dissolved in a mixed alcohol solvent and placed in a test cell consisting of a beaker and a set of electrodes. A voltage is impressed on the electrodes, and the resulting current flow is measured. The chloride (salt) content is obtained by reference to a calibration curve of current versus chloride concentration of known mixtures. Calibration curves are based on standards prepared to approximate the type and concentration of chlorides in the crude oils being tested.

D4006 Test Method for Water in Crude Oil by Distillation

1. SCOPE

1.1 This test method covers the determination of water in crude oil by distillation.

3. SUMMARY OF TEST METHOD

3.1 The sample is heated under reflux conditions with a water-immiscible solvent that codistills with the water in the sample. Condensed solvent and water are continuously separated in a trap–the water settles in the graduated section of the trap, and the solvent returns to the distillation flask (Fig. 9).

An appendix provides a summary of a round-robin testing program that showed that the distillation test method as practiced is somewhat more accurate than the centrifuge test method (D4007) for determining water in crude oils.

D4007 Test Method for Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure)

1. SCOPE

1.1 This test method describes the laboratory determination of water and sediment in crude oils by means of the

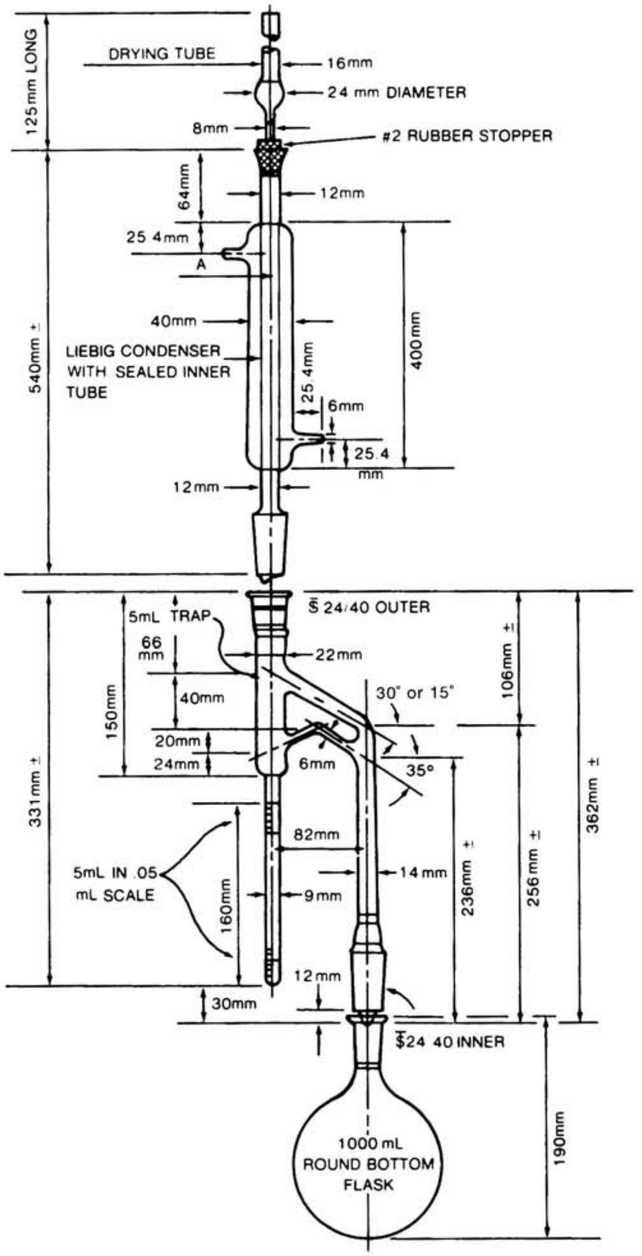


Fig. 9—Example of typical distillation apparatus for D4006.

centrifuge procedure. This centrifuge method for determining water and sediment in crude oils is not entirely satisfactory. The amount of water detected is almost always lower than the actual water content. When a highly accurate value is required, the revised procedures for water by distillation, Test Method D4006, and sediment by extraction, Test Method D473, shall be used.

Note 1–Test Method D4006 has been determined to be the preferred and most accurate method for the determination of water.

3. SUMMARY OF TEST METHOD

3.1 Equal volumes of crude oil and water-saturated toluene are placed into a coneshaped centrifuge tube. After centrifugation, the volume of the higher density water and sediment layer at the bottom of the tube is read (Fig. 10).

D4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter

1. SCOPE

1.1 This test method 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°C and 35°C. Its application is restricted to liquids with vapor pressures below 600 mm Hg (80 kPa) and viscosities below approximately 15,000 cSt (mm^2/s) at the temperature of test.

1.2 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. For the determination of density in crude oil samples, use Test Method D5002.

4. SUMMARY OF TEST METHOD

4.1 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 of the sample.

D4294 Test Method for Sulfur in Petroleum and Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectrometry

1. SCOPE

1.1 This test method covers the measurement of sulfur in hydrocarbons such as crude oils. The applicable concentration range is 0.0150–5.00 mass percent sulfur.

3. SUMMARY OF TEST METHOD

3.1 The sample is placed in the beam emitted from an X-ray source. The resultant excited characteristic *X* radiation is measured, and the accumulated count is compared with counts from previously prepared calibration standards that bracket the sample concentration range of interest to obtain the sulfur concentration in mass percent.

5. INTERFERENCES

5.1 Spectral interferences result when some sample component element or elements emit X rays that the detector cannot resolve from sulfur X-ray emission. As a result, the lines produce spectral peaks that overlap with each other. Spectral interferences may arise from samples containing water, silicon, calcium, potassium, and halides if present at concentrations greater than one tenth of the measured concentration of sulfur or more than a few hundred milligrams/kilogram.

5.2 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. These types of interferences are always present in X-ray fluorescence analysis and are completely unrelated to spectral interferences.

5.3 Both types of interferences are compensated for in contemporary instruments with the use of built-in software. It is recommended that these interferences be checked from time to time and that the software corrections offered by the manufacturer not be accepted at face value.

Note 1–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

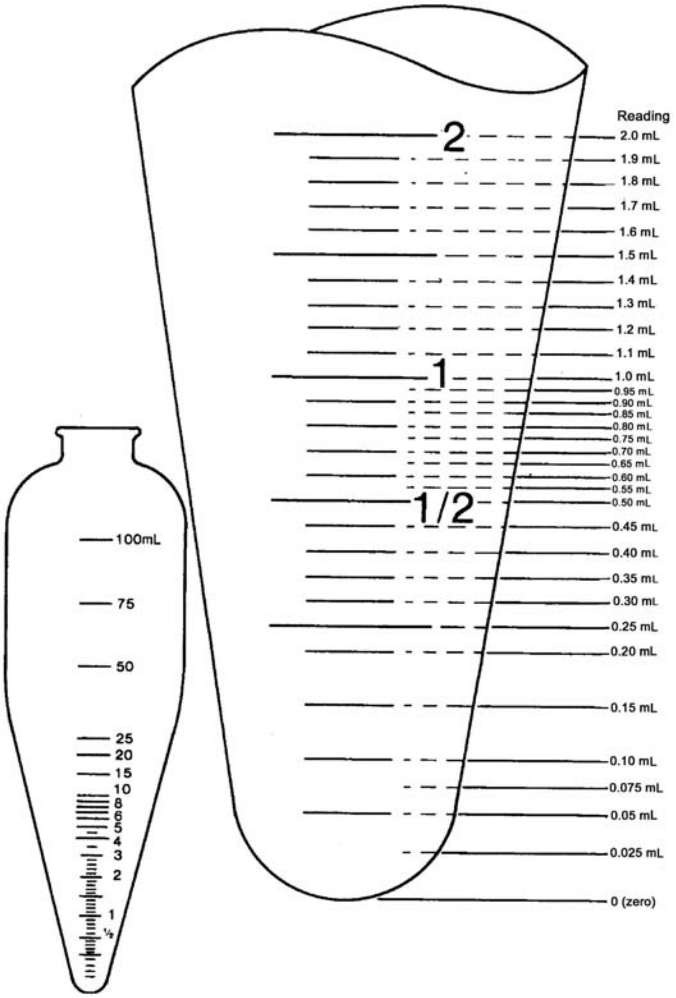


Fig. 10—Procedure for reading water and sediment when using an ASTM 100-mm cone-shaped centrifuge tube.

greatest if the water creates a layer over the transparent film because it will attenuate the X-ray intensity for sulfur. One such method 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.

D4377 Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration

1. SCOPE

1.1 This test method covers the determination of water in the range from 0.02 to 2 % in crude oils. Mercaptan and sulfide (S^- or H_2S) sulfur are known to interfere with this test method.

3. SUMMARY OF TEST METHOD

3.1 After homogenizing the crude oil with a mixer, an aliquot of the crude, in a mixed solvent, is titrated to an electrometric endpoint using Karl Fischer reagent. (Fig. 11).

5. INTERFERENCES

5.1 Several substances and classes of compounds associated with condensation or oxidation-reduction reactions interfere in the determination of water by Karl Fischer reagent. In crude oils, the most common interferences are mercaptans and sulfides. At levels of less than 500 µg/g (ppm) (as sulfur), the interference from these compounds is insignificant.

D4530 Test Method for Determination of Carbon Residue (Micro Method)

1. SCOPE

1.1 This test method covers the determination of the amount of carbon residue formed after evaporation and pyrolysis of petroleum materials under certain conditions and is intended to provide some indication of the relative coke-forming tendency of such materials.

1.2 The test results are equivalent to the Conradson Carbon Residue test (see Test Method D189).

1.3 This test method is applicable to petroleum products that partially decompose on distillation at atmospheric pressure and was tested for carbon residue values of 0.10–30 % (m/m). Samples expected to be below 0.10 weight % (m/m) residue should be distilled to remove 90 % (v/v) of the flask charge. The 10 % bottoms remaining is then tested for carbon residue by this test method.

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

4. SUMMARY OF TEST METHOD

4.1 A weighed quantity of sample is placed in a glass vial and heated to 500°C under an inert (nitrogen)

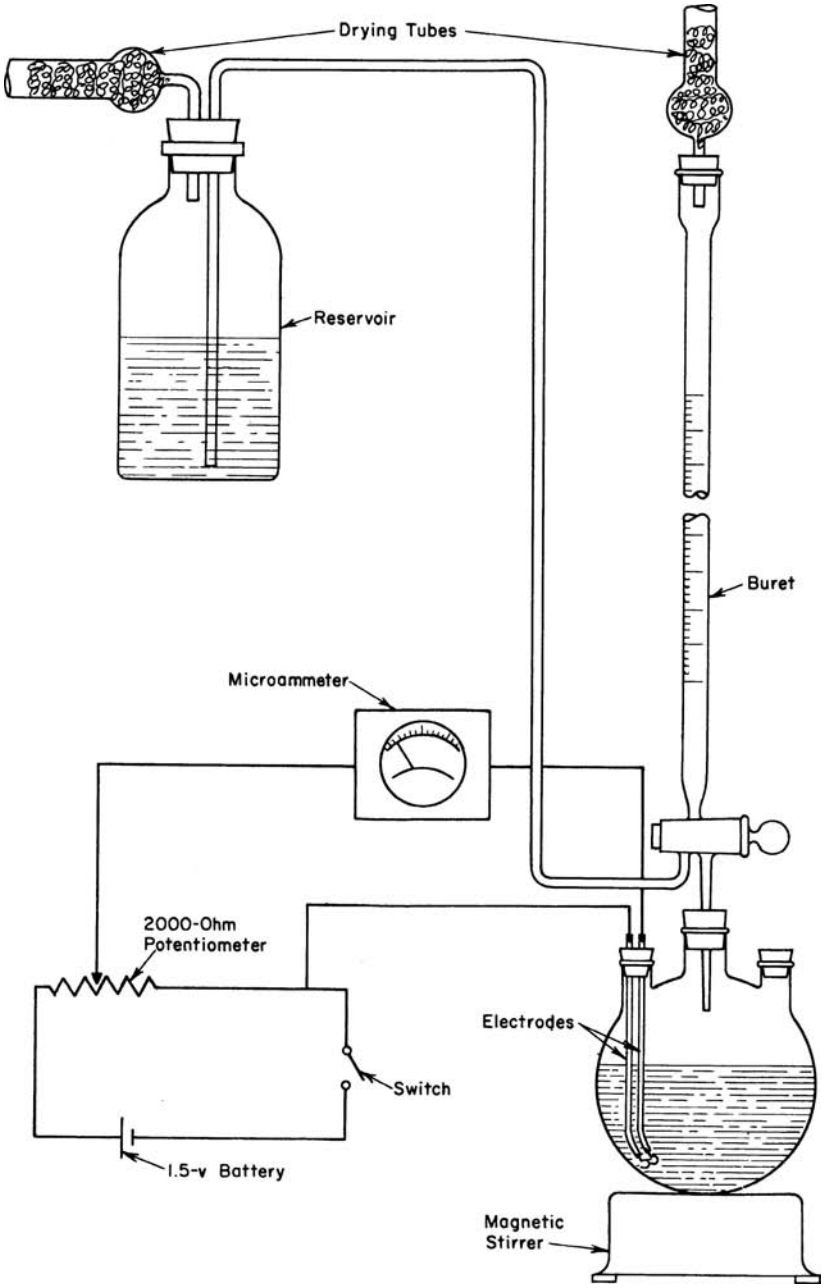


Fig. 11—Apparatus for determination of water by Karl Fischer reagent.

atmosphere in a controlled manner for a specific time. The sample undergoes coking reactions, and volatiles formed are swept away by the nitrogen. The carbonaceous-type residue remaining is reported as a percent of the original sample as "carbon residue (micro)."

4.1.1 When the test result is expected to be below 0.10 % (m/m), the sample can be distilled to produce a 10 % (v/v) bottoms, before performing the test.

D4629 Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection

1. SCOPE

1.1 This test method covers the determination of the trace total nitrogen naturally found in liquid hydrocarbons boiling in the range from approximately 50°C to 400°C with viscosities between approximately 0.2 and 10 cSt (mm^2/s) at room temperature. This test method is applicable to naphthas, distillates, and oils containing 0.3–100 mg/kg total nitrogen. For liquid hydrocarbons containing more than 100 mg/kg of total nitrogen, Test Method D5762 can be more appropriate. This test method has been successfully applied during interlaboratory studies to sample types outside of the range of the scope by dilution of the sample in an appropriate solvent to bring the total nitrogen concentration and viscosity to within the range covered by the test method. However, it is the responsibility of the analyst to verify the solubility of the sample in the solvent and that direct introduction of the diluted sample by syringe into the furnace does not cause low results because of pyrolysis of the sample or solvent in the syringe needle.

3. SUMMARY OF TEST METHOD

3.1 The sample of liquid petroleum hydrocarbon is introduced by syringe or boat inlet system 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 organically bound nitrogen is converted to nitric oxide (NO). The NO contacts ozone and is converted to excited nitrogen oxide (NO_2). A photomultiplier tube detects the light emitted as the excited NO_2 decays, and the resulting signal is a measure of the nitrogen contained in the sample.

D4807 Test Method for Sediment in Crude Oil by Membrane Filtration

1. SCOPE

1.1 This test method covers the determination of sediment in crude oils by membrane filtration. This test method has been validated for crude oils with sediments up to approximately 0.15 mass percent.

1.2 The accepted unit of measure for this test method is mass percent, but an equation to convert to volume percent is provided (see Note 1).

Note 1—Because water and sediment values are commonly reported as volume percent, calculate the volume of the sediment as a percentage of the original sample. Because a major portion of the sediment probably would be sand (silicon dioxide, which has a density of 2.32) and a small amount of other naturally occurring materials (with a relative density lower than that of sand), use an arbitrary density of 2.0 for the resulting sediment. Then, to obtain volume percent sediment, divide the mass percent sediment by 2.0 and multiply by the relative density of the crude oil. (Note that this calculation is provided only for convenience, and the precision and bias for this standard are based on mass percent sediment and not on volume percent of sediment.)

$$S_V = \frac{S}{2.0} \times \text{relative density of oil}$$

where:

S_V = the sediment content of the sample as a percentage by volume, and

S = the sediment content of the sample as a percentage by mass.

3. SUMMARY OF TEST METHOD

3.1 A portion of a representative crude oil sample is dissolved in hot toluene and filtered under vacuum through a 0.45-μm porosity membrane filter. The filter with residue is washed, dried, and weighed to give the final result.

D4928 Test Methods for Water in Crude Oils by Coulometric Karl Fischer Titration

1. SCOPE

1.1 This test method covers the determination of water in the range from 0.02 to 5 mass or volume percent in crude oils. Mercaptan (RSH) and sulfide (S^- or H_2S) as sulfur are known to interfere with this test method, but at levels of less than 500 μg/g (ppm), the interference from these compounds is insignificant (see Section 5).

1.2 This test method can be used to determine water in the 0.005 to 0.02 mass percent range, but the effects of the mercaptan and sulfide interference at these levels has not been determined.

3. SUMMARY OF TEST METHOD

3.1 After homogenizing the crude oil with a mixer, an aliquot is injected into the titration vessel of a Karl Fischer apparatus in which iodine for the Karl Fischer reaction is generated coulometrically at the anode. When all of the water has been titrated, an electrometric endpoint detector detects the excess iodine and the titration is terminated. On the basis of the stoichiometry of the reaction, one mole of iodine reacts with one mole of water, thus the quantity of water is proportional to the total integrated current according to Faraday's law.

3.2 The precision of this test method is critically dependent on the effectiveness of the homogenization step. The efficiency of the mixer used to achieve a homogeneous sample is determined by the procedure given in Practice D5854.

3.3 Two procedures are provided for the determination of water in crude oils. In one procedure, a weighed aliquot of sample is injected into the titration vessel and the mass percent of water is determined. The other procedure provides for the direct determination of the volume percent of water in the crude oil by measuring the volume of crude oil injected into the titration vessel.

5. INTERFERENCES

5.1 Several substances and classes of compounds associated with condensation or oxidation-reduction reactions interfere in the determination of water by Karl Fischer reagent. In crude oils, the most common interferences are mercaptans and sulfides (not total sulfur). At levels of less than 500 μg/g (ppm) (as sulfur), the interference from these compounds is insignificant. Most crude oils, including crude oils classified as "sour crude," have mercaptan and sulfide levels of less than 500 μg/g (ppm) as sulfur.

5.2 The significance of the mercaptan and sulfide interference on the Karl Fischer titration for water levels in the range of 0.005–0.02 mass percent has not been determined experimentally. However, at these low water levels, the interference may be significant for mercaptan and sulfide levels of less than 500 μg/g (ppm) (as sulfur).

D4929 Test Methods for Determination of Organic Chloride Content in Crude Oil

1. SCOPE

1.1 These test methods cover the determination of organic chloride (above 1 μg/g organically bound chlorine) in crude oils using distillation and sodium biphenyl reduction or distillation and microcoulometry.

1.2 These test methods involve the distillation of crude oil test specimens to obtain a naphtha fraction before chloride determination. The chloride content of the naphtha fraction of the whole crude oil can thereby be obtained. See Section 5 regarding potential interferences.

1.3 Test Method A covers the determination of organic chloride in the washed naphtha fraction of crude oil by sodium biphenyl reduction followed by potentiometric titration.

1.4 Test Method B covers the determination of organic chloride in the washed naphtha fraction of crude oil by oxidative combustion followed by microcoulometric titration.

3. SUMMARY OF TEST METHOD

3.1 A crude oil distillation is performed to obtain the naphtha cut at 204°C (400°F). The distillation method was adapted from Test Method D86 for the distillation of petroleum products. The naphtha cut is washed with caustic, repeatedly when necessary, until all hydrogen sulfide is removed. The naphtha cut, free of hydrogen sulfide, is then washed with water, repeatedly when necessary, to remove inorganic halides (chlorides).

3.2 There are two alternative test methods for determination of the organic chloride in the washed naphtha fraction, as follows.

3.2.1 *Test Method A, Sodium Biphenyl Reduction and Potentiometry*—The washed naphtha fraction of a crude oil specimen is weighed and transferred to a separatory funnel containing sodium biphenyl reagent in toluene. The reagent is an addition compound of sodium and biphenyl in ethylene glycol dimethyl ether. The free radical nature of this reagent promotes very rapid conversion of the organic halogen to inorganic halide. In effect, this reagent solubilizes metallic sodium in organic compounds. The excess reagent is decomposed, the mixture acidified, and the phases are separated. The aqueous phase is evaporated to 25–30 mL, acetone is added, and the solution is titrated potentiometrically.

3.2.2 *Test Method B, Combustion and Microcoulometry*—The washed naphtha fraction of a crude oil specimen is injected into a flowing stream of gas containing approximately 80 % oxygen and 20 % inert gas, such as argon, helium, or nitrogen. The gas and sample flow through a combustion tube maintained at approximately 800°C. The chlorine is converted to chloride and oxychlorides, which then flow into a titration cell where they react with the silver ions in the titration cell. 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 samples.

5. INTERFERENCES

5.1 *Test Method A*—Other titratable halides will also give a positive response. These titratable halides include hydrogen bromide (HBr) and hydrogen iodide (HI).

5.2 *Test Method B*—Other titratable halides will also give a positive response. These titratable halides include HBr and HI (HOBr and HOI do not precipitate silver). Because these oxyhalides do not react in the titration cell, approximately 50 % microequivalent response is detected.

5.2.1 This test method is applicable in the presence of total sulfur concentration of up to 10,000 times the chlorine level.

D5002 Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer

1. SCOPE

1.1 This test method covers the determination of the density or relative density of crude oils that can be handled in a normal fashion as liquids at test temperatures between 15°C and 35°C. This test method applies to crude oils with high vapor pressures provided appropriate precautions are taken to prevent vapor loss during transfer of the sample to the density analyzer.

1.2 This test method was evaluated in round-robin testing using crude oils in the 0.75- to 0.95-g/mL range. Lighter crude oil can require special handling to prevent vapor losses. Heavier crudes can require measurements at higher temperatures to eliminate air bubbles in the sample.

4. SUMMARY OF TEST METHOD

4.1 Approximately 0.7 mL of crude oil 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 of the sample.

D5191 Test Method for Vapor Pressure of Petroleum Products (Mini Method)

1. SCOPE

1.1 This test method covers the use of automated vapor pressure instruments to determine the total vapor pressure exerted in vacuum by volatile liquid petroleum products containing air. This test method is suitable for testing samples with boiling points above 0°C (32°F) that exert a vapor pressure between 7 and 130 kPa (1.0 and 18.6 psi) at 37.8°C (100°F) at a vapor-to-liquid ratio of 4:1. Measurements are made on liquid sample sizes in the range from 1 to 10 mL. No account is made for dissolved water in the sample.

Note 1—Samples can also be tested at other vapor-to-liquid ratios, temperatures, and pressures, but the precision and bias statements need not apply.

Note 2—The interlaboratory studies conducted in 1988 and 1991 to determine the precision statements in Test Method D5191 did not include any crude oil in the sample sets. (Nevertheless, the method is used by a considerable number of laboratories for determining vapor pressure of crude oils). Test Method D6377 has been shown to be suitable for vapor pressure measurements of crude oils.

4. SUMMARY OF TEST METHOD

4.1 A known volume of chilled, air-saturated sample is introduced into an evacuated, thermostatically controlled test chamber, the internal volume of which is five times that of the total test specimen introduced into the chamber. After injection 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 also measure the absolute pressure of the sample.

D5236 Test Method for Distillation of Heavy Hydrocarbon Mixtures (Vacuum Pot still Method)

1. SCOPE

1.1 This test method covers the procedure for distillation of heavy hydrocarbon mixtures having initial boiling points greater than 150°C (300°F), such as heavy crude oils, petroleum distillates, residues, and synthetic mixtures. It uses a pot still with a low-pressure-drop entrainment separator operated under total takeoff conditions (Fig. 12). Distillation conditions and equipment performance criteria are specified and a typical apparatus is illustrated.

1.2 This test method details the procedures for the production of distillate fractions of standardized quality in the gas oil and lubricating oil range as well as the production of standard residue. In addition, it provides for the determination of standard distillation curves to the highest AET possible by conventional distillation.

1.3 The maximum achievable AET is dependent upon the heat tolerance of the charge. For most samples, a temperature up to 565°C (1050°F) can be attained. This maximum will be significantly lower for heat-sensitive samples (e.g., heavy residues) and might be somewhat higher for non-heat-sensitive samples.

1.4 The recommended distillation method for crude oils up to a cutpoint of 400°C (752°F) AET is Test Method D2892. This test method can be used for heavy crude oils with initial boiling points greater than 150°C (302°F). However, distillation curves and fraction qualities obtained by these methods are not comparable.

1.5 This test method also contains an Annex for Dehydration of a Wet Sample of Oil.

4. SUMMARY OF TEST METHOD

4.1 A weighed volume of sample is distilled at absolute pressures between 6.6 and 0.013 kPa (50 and 0.1 mm Hg) at specified distillation rates. Cuts are taken at preselected temperatures. Records of vapor temperature, operating pressure, and other variables are made at intervals, including at each cutpoint.

4.2 The mass of each fraction is obtained. Distillation yields by mass are calculated from the mass of each fraction relative to the total mass recovery.

4.3 The density of each fraction is obtained. Distillation yields by volume are calculated from the volume computed for each fraction at 15°C (59°F) relative to the total recovery.

4.4 Distillation curves of temperature versus mass or volume percent or both are drawn using the data from 4.2 and 4.3.

D5708 Test Methods for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry

1. SCOPE

1.1 These test methods cover the determination of nickel, vanadium, and iron in crude oils and residual fuels by inductively coupled plasma (ICP) atomic emission spectrometry. Two different test methods are presented.

1.2 *Test Method A*–ICP is used to analyze a sample dissolved in an organic solvent. This test method uses oil-soluble metals for calibration and does not purport to quantitatively determine or detect insoluble particulates.

1.3 *Test Method B*–ICP is used to analyze a sample that is decomposed with acid.

1.4 The concentration ranges covered by these test methods are determined by the sensitivity of the instruments, the amount of sample taken for analysis, and the dilution volume. Typically, the low concentration limits are a few tenths of a milligram per kilogram.

3. SUMMARY OF TEST METHOD

3.1 *Test Method A*–Approximately 10 g of the sample are dissolved in an organic solvent to give a specimen solution containing 10 % (m/m) of sample. The solution is nebulized into the plasma, and the intensities of the emitted light at wavelengths characteristic of the analytes are measured sequentially or simultaneously. The intensities are related to concentrations by the appropriate use of calibration data.

3.2 *Test Method B*–One to 20 g of sample are weighed into a beaker and decomposed with concentrated sulfuric acid by heating to dryness. Great care must be used in this decomposition because the acid fumes are corrosive and the mixture is potentially flammable. The residual carbon is burned off by heating at 525°C in a muffle furnace. The inorganic residue is digested with nitric acid evaporated to incipient dryness, dissolved in dilute nitric acid, and made up to volume. The solution is nebulized into the plasma of an atomic emission spectrometer. The intensities of light emitted at characteristic wavelengths of the metals are measured sequentially or simultaneously. These intensities are related to concentrations by the appropriate use of calibration data.

D5762 Test Method for Nitrogen in Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence

1. SCOPE

1.1 This test method covers the determination of nitrogen in liquid hydrocarbons in the concentration range from 40 to 10,000 μg/g nitrogen. For light hydrocarbons containing less than 100 μg/g nitrogen, Test Method D4629 can be more appropriate.

3. SUMMARY OF TEST METHOD

3.1 A hydrocarbon sample is placed on a sample boat at room temperature. The sample and boat are advanced into a high-temperature combustion tube where the nitrogen is oxidized to NO in an oxygen atmosphere. The NO contacts ozone and is converted to excited 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.

D5853 Test Method for Pour Point of Crude Oils

1. SCOPE

1.1 This test method covers two procedures for the determination of the pour point temperatures of crude oils down to −36°C. One method provides a measure of the maximum (upper) pour point temperature; the other method provides a measure of the minimum (lower) pour point temperature. [In practice, few laboratories using this test method to determine the minimum (lower) pour point).]

3. TERMINOLOGY

3.1.2 *Maximum (Upper) Pour Point*, *n*–The pour point obtained after the test specimen has been subjected to a prescribed treatment designed to enhance gelation of wax crystals and solidification of the test specimen.

3.1.3 *Minimum (Lower) Pour Point*, *n*–The pour point obtained after the test specimen has been subjected to a prescribed treatment designed to delay gelation of wax crystals and solidification of the test specimen.

4. SUMMARY OF TEST METHOD

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

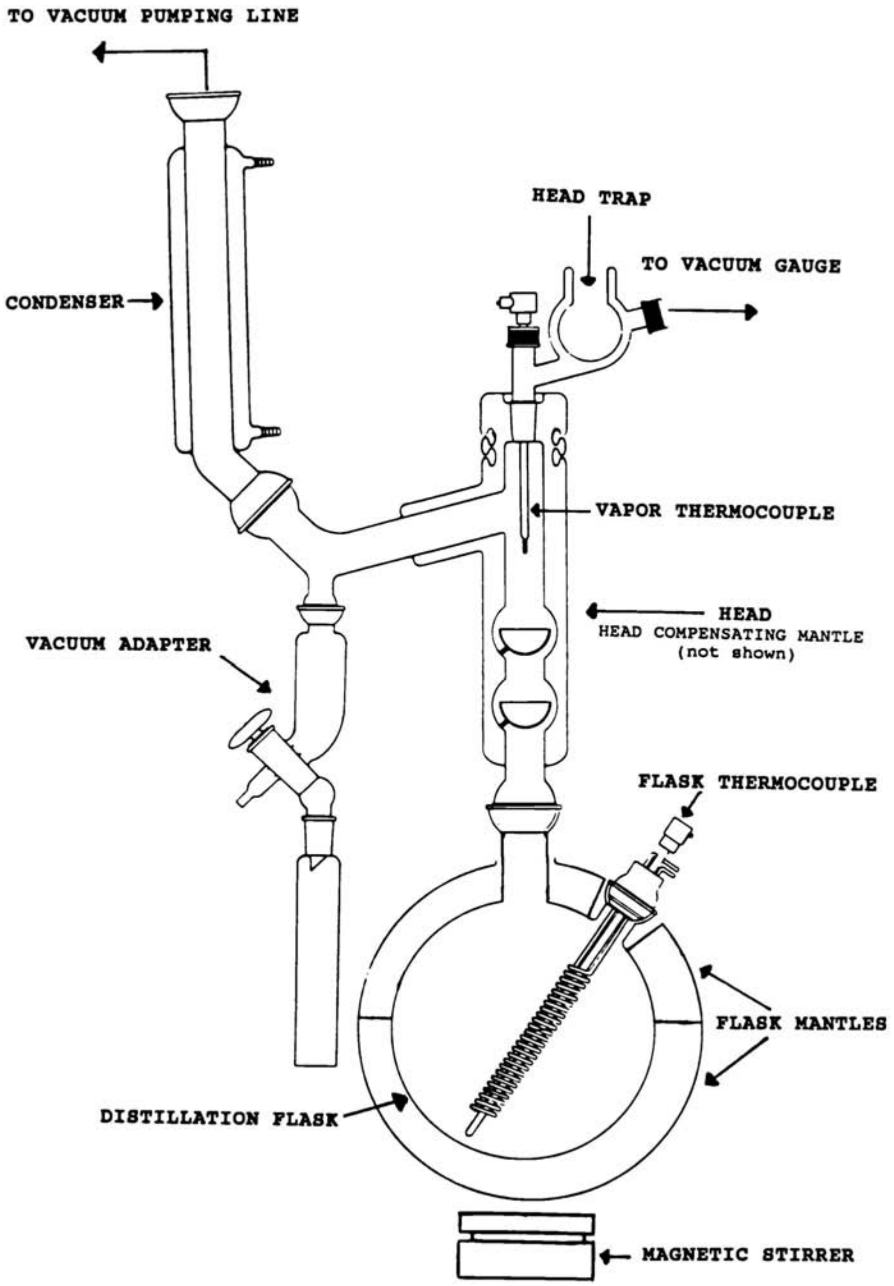


Fig. 12—Typical apparatus for D5236.

D5863 Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry

1. SCOPE

1.1 These test methods cover the determination of nickel, vanadium, iron, and sodium in crude oils and residual fuels by flame atomic absorption spectrometry (AAS). Two different test methods are presented.

1.2 *Test Method A*–Flame AAS is used to analyze a sample that is decomposed with acid for the determination of total nickel, vanadium, and iron.

1.3 *Test Method B*–Flame AAS is used to analyze a sample diluted with an organic solvent for the determination of nickel, vanadium, and sodium. This test method uses oil-soluble metals for calibration to determine dissolved metals and does not purport to quantitatively determine nor detect insoluble particulates. Hence, this test method may underestimate the metal content, especially sodium, present as inorganic sodium salts.

1.4 The concentration ranges covered by these test methods are determined by the sensitivity of the instruments, the amount of sample taken for analysis, and the dilution volume. A specific statement is given in Note 1.

Note 1–If it is desired to extend the lower concentration limits of the test method, it is recommended that the decomposition be done in 10-g increments up to a maximum of 100 g. It is not necessary to destroy all of the organic matter each time before adding additional amounts of the sample and acid. When it is desired to determine higher concentrations, reduce the sample size accordingly.

1.5 For each element, each test method has its own unique precision. The user can select the appropriate test method on the basis of the precision required for the specific analysis.

3. SUMMARY OF TEST METHOD

3.1 *Test Method A*—One to 20 g of sample are weighed into a beaker and decomposed with concentrated sulfuric acid by heating to dryness. The residual carbon is burned off by heating at 525°C in a muffle furnace. The inorganic residue is digested in dilute nitric acid, evaporated to incipient dryness, dissolved in dilute nitric acid, and made up to volume with dilute nitric acid. Interference suppressant is added to the dilute nitric acid solution. The solution is nebulized into the flame of an atomic absorption spectrometer. A nitrous oxide/acetylene flame is used for vanadium and an air/acetylene flame is used for nickel and iron. The instrument is calibrated with matrix-matched standard solutions. The measured absorption intensities are related to concentrations by the appropriate use of calibration data.

3.2 *Test Method B*—Sample is diluted with an organic solvent to give a test solution containing either 5 % (m/m) or 20 % (m/m) sample. The recommended sample concentration is dependent on the concentrations of the analytes in the sample. For the determination of vanadium, interference suppressant is added to the test solution. The test solution is nebulized into the flame of an atomic absorption spectrometer. A nitrous oxide/acetylene flame is used for vanadium and an air/acetylene flame is used for nickel and sodium. The measured absorption intensities are related to concentrations by the appropriate use of calibration data.

D6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance

1. SCOPE

1.1 This practice provides information for the design and operation of a program to monitor and control ongoing stability and precision and bias performance of selected analytical measurement systems using a collection of generally accepted statistical quality control (SQC) procedures and tools.

Note 1—A complete list of criteria for selecting measurement systems to which this practice should be applied and for determining the frequency at which it should be applied is beyond the scope of this practice. However, some factors to be considered include (*a*) frequency of use of the analytical measurement system; (*b*) criticality of the parameter being measured; (*c*) system stability and precision performance based on historical data; (*d*) business economics; and (*e*) regulatory, contractual, or test method requirements.

1.2 This practice is applicable to stable analytical measurement systems that produce results on a continuous numerical scale.

1.3 This practice is applicable to laboratory test methods.

1.4 This practice is applicable to validated process stream analyzers.

1.5 This practice assumes that the normal (Gaussian) model is adequate for the description and prediction of measurement system behavior when it is in a state of statistical control.

1.6 This practice does not address statistical techniques for comparing two or more analytical measurement systems applying different analytical techniques or equipment components that purport to measure the same property(s).

4. SUMMARY OF PRACTICE

4.1 Quality control (QC) samples and check standards are regularly analyzed by the measurement system. Control charts and other statistical techniques are presented to screen, plot, and interpret test results in accordance with industry-accepted practices to ascertain the in-statistical-control status of the measurement system.

4.2 Statistical estimates of the measurement system precision and bias are calculated and periodically updated using accrued data.

4.3 In addition, as part of a separate validation audit procedure, QC samples and check standards may be submitted blind or double-blind and randomly to the measurement system for routine testing to verify that the calculated precision and bias are representative of routine measurement system performance when there is no prior knowledge of the expected value or sample status.

D6377 Test Method for Determination of Vapor Pressure of Crude Oil: VPCR$_x$ (Expansion Method)

1. SCOPE

1.1 This test method covers the use of automated vapor pressure instruments to determine the vapor pressure exerted in a vacuum of crude oils. The test method is suitable for testing samples that exert a vapor pressure between 25 and 180 kPa at 37.8°C at vapor-to-liquid ratios (V/L) from 4:1 to 0.02:1 (X = 4 to 0.02).

Note 1—This test method is suitable for the determination of the vapor pressure of crude oils at temperatures from 0 to 100°C and pressures up to 500 kPa, but the precision and bias statements may not be applicable.

1.2 This test method allows the determination of vapor pressure for crude oil samples having pour points above 0°C.

4. SUMMARY OF TEST METHOD

4.1 Using a measuring chamber with a built-in piston, a sample of known volume is drawn from the sample container into the temperature-controlled chamber at 20°C or higher. After sealing the chamber, the volume is expanded by moving the piston until the final volume produces the desired V/L value. The temperature of the measuring chamber is then regulated to the measuring temperature.

4.2 After temperature and pressure equilibrium, the measured pressure is recorded as the VPCR$_x$ of the sample. The test specimen shall be mixed during the measuring procedure by shaking the measuring chamber to achieve pressure equilibrium in a reasonable time between 5 and 30 min.

4.3 For results related to Test Method D323, the final volume of the measuring chamber shall be five times the test specimen volume and the measuring temperature shall be 37.8°C. (The VPCR$_x$ at a V/L of 4:1 and a measuring temperature of determined by this test method can be related to the value determined by Test Method D323.)

D6470 Test Method for Salt in Crude Oils (Potentiometric Method)

1. SCOPE

1.1 This test method covers the determination of salt in crude oils. For the purpose of this test method, salt is expressed as percent (m/m) NaCl (sodium chloride) and covers the range from 0.0005 to 0.15 % (m/m).

1.2 The limit of detection is 0.0002 % (m/m) for salt [as sodium chloride (NaCl)].

3. SUMMARY OF TEST METHOD

3.1 After homogenizing the crude oil with a mixer, a weighed aliquot is dissolved in xylene at 65°C and extracted with specified volumes of alcohol, acetone, and water in an electrically heated extraction apparatus (Fig. 13). A portion of the aqueous extract is analyzed for total halides by potentiometric titration.

D6560 Test Method for Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products

1. SCOPE

1.1 This test method covers a procedure for the determination of the heptane-insoluble asphaltene content of crude petroleum that has been topped to an oil temperature of 260°C.

1.2 The precision is applicable to values between 0.50 and 30.0 % m/m. Values outside of this range may still be valid but may not give the same precision values.

1.3 Oils containing additives may give erroneous results.

4. SUMMARY OF TEST METHOD

4.1 A test portion of the sample is mixed with heptane; the mixture is heated under reflux; and the precipitated asphaltenes, waxy substances, and inorganic material are collected on a filter paper. The waxy substances are removed by washing with hot heptane in an extractor (Fig. 14).

4.2 After removal of the waxy substances, the asphaltenes are separated from the inorganic material by dissolution in hot toluene, the extraction solvent is evaporated, and the asphaltenes are weighed. (Unless it is known that the crude petroleum contains negligible quantities of material boiling below 80°C, the sample must be topped to an oil temperature of 260°C in accordance with procedures provided in an annex.)

D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories

1. SCOPE

1.1 This practice covers the establishment and maintenance of the essentials of a quality system in laboratories engaged in the analysis of petroleum products and lubricants. It is designed to be used in conjunction with Practice D6299.

5. GENERAL QUALITY REQUIREMENTS FOR THE LABORATORY

5.1 Establishment and maintenance of a quality system shall include stated objectives in a laboratory's adherence to test method requirements, calibration and maintenance practices, and its quality control program. Laboratory quality objectives should encompass the laboratory's continuous improvement goals as well as meeting customer requirements.

5.2 Management shall appoint a representative to implement and maintain the quality system in the laboratory.

5.3 Laboratory management shall review the adequacy of the quality system and the activities of the laboratory for consistency with the stated quality objectives at least annually.

5.4 The quality system shall have documented processes for the following:

  5.4.1 Sample management;
  5.4.2 Data and record management;
  5.4.3 Producing accurate, reliable, and properly represented test results;
  5.4.4 Audits and proficiency testing;
  5.4.5 Corrective and preventive action;
  5.4.6 Ensuring that procured services and materials meet the contracted requirements; and
  5.4.7 Ensuring that personnel are adequately trained to obtain quality results.

6. SAMPLE MANAGEMENT

6.1 The elements of sample management shall include, at a minimum, the following:

  6.1.1 Procedures for unique identification of samples submitted to the laboratory.
  6.1.2 Criteria for sample acceptance.
  6.1.3 Procedures for sample handling.
  6.1.4 Procedures for sample storage and retention. Items to consider when creating these procedures include the following:
    6.1.4.1 Applicable government–local, state, or national–regulatory requirements for shelf life and time-dependent tests that set product stability limits,
    6.1.4.2 Type of sample containers required to preserve the sample,
    6.1.4.3 Control of access to the retained samples to protect their validity and preserve their original integrity,
    6.1.4.4 Storage conditions,
    6.1.4.5 Required safety precautions, and
    6.1.4.6 Customer requirements.
  6.1.5 Procedures for sample disposal in accordance with applicable government regulatory requirements.

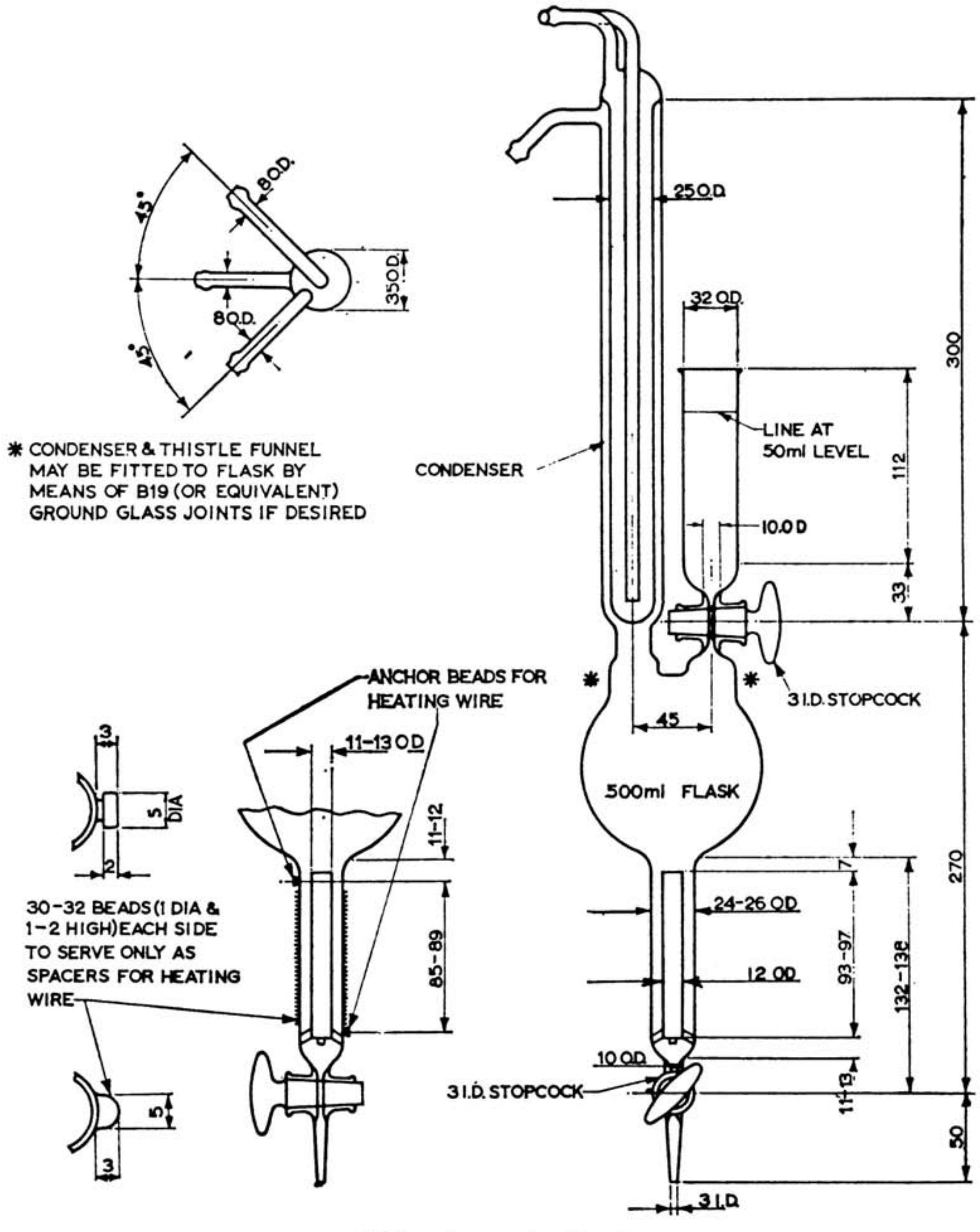
D7169 Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High-Temperature Gas Chromatography

1. SCOPE

1.1 This test method covers the determination of the boiling point distribution and cutpoint intervals of crude oils and residues by using high-temperature gas chromatography. The amount of residue (or sample recovery) is determined using an external standard.

1.2 This test method extends the applicability of simulated distillation to samples that do not elute completely from the chromatographic system. This test method is used to determine the boiling point distribution through a temperature of 720°C. This temperature corresponds to the elution of n-C_{100}.

1.3 This test method is used for the determination of boiling point distribution of crude oils. This test method uses capillary columns with thin films, which results in the incomplete separation of C_4–C_8 in the presence of large amounts of carbon disulfide and thus yields an unreliable boiling point distribution corresponding to this elution interval. In addition, quenching of the response of the detector used to hydrocarbons eluting during carbon disulfide elution results in unreliable quantitative analysis of the boiling distribution in the C_4–C_8 region. Because the detector does not quantitatively measure the carbon disulfide, its subtraction from the sample using a solvent-only injection and corrections to this region via quenching factors results in an approximate determination of the net chromatographic area. A separate, higher



All dimensions are in millimetres.

Fig. 13—D6470 extraction apparatus.

resolution gas chromatograph (GC) analysis of the light-end portion of the sample may be necessary to obtain a more accurate description of the boiling point curve in the interval in question. (An appendix provides procedures for conducting a light-end analysis in the region C_4–C_8.)

4. SUMMARY OF TEST METHOD

4.1 This is a GC method utilizing an inlet and a capillary column, both of which are subject to a temperature program. A flame ionization detector is used as a transducer that converts mass to an electrical signal. A data acquisition system operating in the slice mode and chromatography software is used to accumulate the electronic signal. A retention time calibration mixture is used to develop a retention time versus boiling point curve. A solution of a reference oil that fully elutes from the column under the conditions of the test is used to determine the detector response factor. Solvent injections are made, and the resulting signal is subtracted from the response factor standard and the sample chromatogram. Finally, the sample solution is injected, and with the use of the response factor, the amount of sample recovered is calculated (Fig. 15). After converting the retention times of the sample slices to temperature, the boiling point distribution can be calculated up to the recovered amount.

D7279 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids by Automated Houillon Viscometer

1. SCOPE

1.1 This test method covers the measurement of the kinematic viscosity of transparent and opaque liquids such

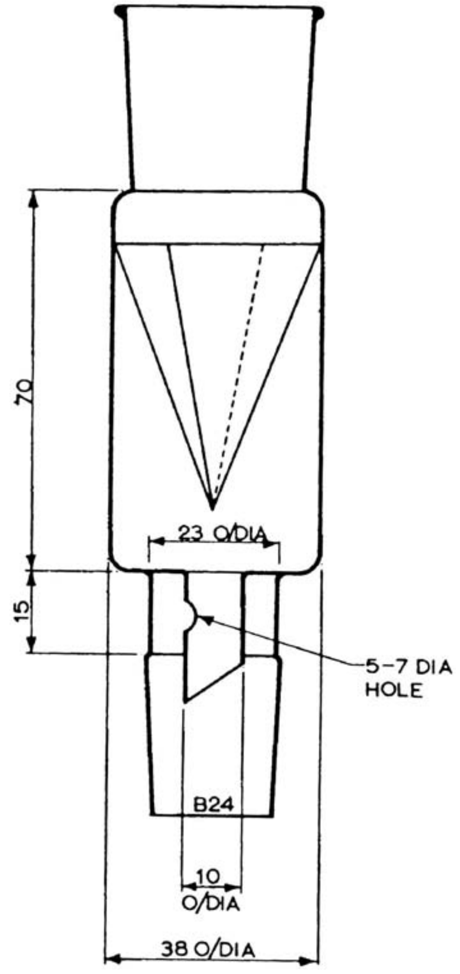


Fig. 14—Extractor.

as fresh and used lubricating oils using a Houillon viscometer in automated mode.

1.2 The range of kinematic viscosity capable of being measured by this test method is from 2 to 1500 mm^2/s. The range is dependent on the tube constant utilized. The temperature range that the apparatus is capable of achieving is between 20°C and 150°C, inclusive; however, the precision has only been determined for the viscosity range 25–150 mm^2/s at 40°C and 5–16 mm^2/s at 100°C for the materials listed in the precision section.

3. SUMMARY OF TEST METHOD

3.1 The kinematic viscosity is determined by measuring the time taken for a sample to fill a calibrated volume at a given temperature. The specimen is introduced into the apparatus and then flows into the viscometer tube, which is equipped with two detection cells. The specimen reaches the test temperature of the viscometer bath, and when the leading edge of the specimen passes in front of the first detection cell, the automated instrument starts the timing sequence. When the leading edge of the specimen passes in front of the second detection cell, the instrument stops timing the flow. The time interval thus measured allows for the calculation of the kinematic viscosity using a viscometer tube constant determined earlier by calibration with certified viscosity reference standards.

3.2 The kinematic viscosity is calculated using the formula

$$v = C \times t$$

where:
v = the kinematic viscosity in mm^2/s,
C = the viscometer tube constant in mm^2/s, and
t = the flow time in s measured during the test.

D7622 Total Mercury in Crude Oil Using Combustion and Direct Cold-Vapor Atomic Absorption Method with Zeeman Background Correction

1. SCOPE

1.1 This test method covers the procedure to determine the total mercury content in a sample of crude oil. This test method can be used for total mercury determination in natural and processed liquid and oil products.

1.2 This test method may be applied to samples containing between 5.0 and 350 ng/mL of mercury. The results may be converted to mass basis.

4. SUMMARY OF TEST METHOD

4.1 Controlled heating after thermal decomposition of the analysis sample in air is used to liberate mercury. The sample is placed into the sample boat, which is inserted in the first chamber of the atomizer, where the sample is heated at a controlled temperature of 300–500°C (depending on the selected operation mode). The mercury compounds are evaporated and partially dissociated forming elemental mercury vapor. Mercury and all decomposition products are carried to the second chamber of the atomizer heated to approximately 700–750°C (mercury reduction takes place on the surface of a heating NiCr coil, thus no catalyst is required). Mercury compounds are totally dissociated, and the organic matrix of the sample is burnt out. Continuously flowing air carries mercury and other combustion products through an absorbance analytical cell heated up to 750°C positioned in the light path of a double-wave cold-vapor Zeeman atomic absorption spectrophotometer. The mercury resonance line at 253.65 nm is split into several components, one of those falling within the mercury absorbance line (analytical line) profile and another one lying outside (reference line). The difference between the intensities of these compounds is proportional to the number of mercury atoms in the analytical cell. Absorbance peak area or peak height is a function of the mercury concentration.

Note 1—Mercury and mercury salts can be volatized at low temperatures.

Precautions against inadvertent mercury loss should be taken when using this test method.

D7623 Total Mercury in Crude Oil Using Combustion-Gold Amalgamation and Cold-Vapor Atomic Absorption Method

1. SCOPE

1.1 This test method covers the procedures to determine the total mercury content in a sample of crude oil.

1.2 The test method may be applied to crude oil samples containing between 5 and 400 ng/mL of mercury. The results may be converted to mass basis and reported as nanograms per gram of mercury.

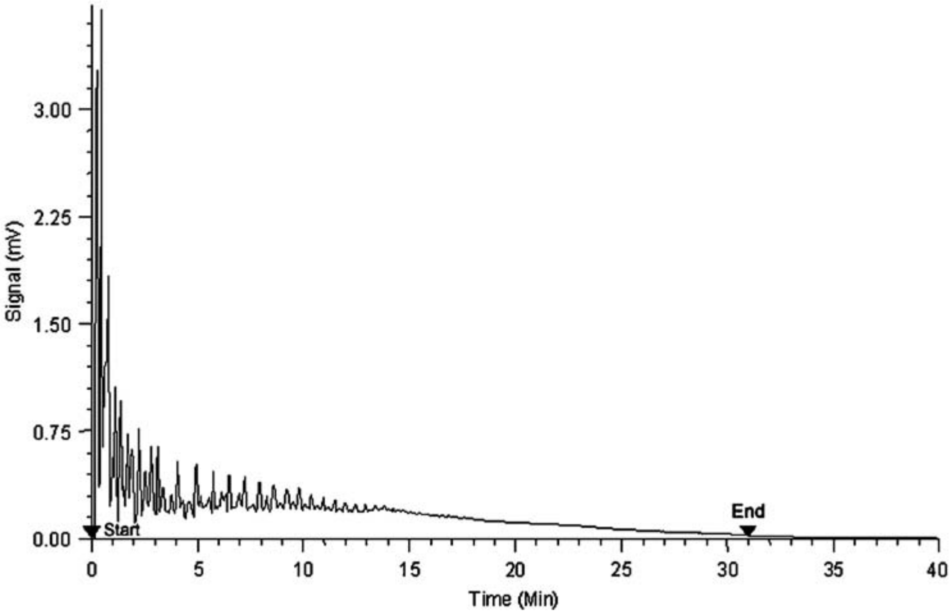


Fig. 15—Typical chromatogram (baseline corrected) of a crude oil (injected at −20°C) analyzed by D7169.

4. SUMMARY OF TEST METHOD

4.1 Controlled heating of the analysis sample in oxygen is used to liberate mercury. The sample is heated to dryness in the instrument and then thermally (at approximately 700°C) and chemically decomposed. The decomposition products are carried by flowing treated air into the catalytic section of the furnace (at approximately 850°C), where oxidation is completed. The decomposition products are carried to a gold amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any remaining decomposition products other than mercury, the amalgamator is rapidly heated to approximately 600°C, releasing mercury vapor. Flowing oxygen carries the mercury vapor through absorbance cells positioned in the light path of a single wavelength cold-vapor atomic absorption spectrophotometer. Absorbance peak height or peak area, as a function of mercury concentration, is measured at 253.65 nm.

Note 1—Mercury and mercury salts can be volatized at low temperatures. Precautions against inadvertent mercury loss should be taken when using this test method.

References

[1] Rossini, F. D., "Hydrocarbons in Petroleum," *J. Chem. Educ.*, Vol. 37, 1960 pp. 554–561.

[2] Mair, B. J., "Annual Report for the Year Ending, June 30, 1967," American Petroleum Institute Research Project 6, Carnegie Institute of Technology, Pittsburgh, PA,1967.

[3] Rall, H. T., Thompson, C. J., Coleman, H. J., and Hopkins, R. L., "Sulfur Compounds in Oil," Bulletin 659, U.S. Department of the Interior, Bureau of Mines, Washington, DC, 1972.

[4] Csoklich, C., Ebner, B., andSchenz, R., "Modern Crude Oil Practices–Austria's OEMV," *Oil Gas J.,* March 21, 1983, pp. 86–90.

[5] O'Donnell, R. J., "Modern Crude Oil Practices–Standard Oil of California Companies," *Oil Gas J.,* March 21, 1983, pp. 90–93.

[6] McNelis, F. B., "Modern Crude Oil Practices–Exxon Organizations," *Oil Gas J.,* March 21, 1983, pp. 94–97.

[7] Wampler, R. J. and Kirk, E. L., "Modern Crude Oil Practices–Gulf Companies," *Oil Gas J.,* March 21, 1983, pp. 98–104.

[8] Nelson, G. V., Schierberg, G. R., and Sequeira, A., "Modern Crude Oil Practices–The Texaco System," *Oil Gas J.,* March 21, 1983, pp. 108, 112, 116, 118–120.

[9] McCleskey, G. and Joffe, B. L., "Modern Crude Oil Practices–Phillips Petroleum Co.," *Oil Gas J.,* March 21, 1983, pp. 124, 126–127.

[10] Aalund, L. R., "Guide to Export Crudes for the '80s–1 to 13," *Oil Gas J.,* April 11, May 2, 23, June 6, 20, July 4, 25, Aug. 22, Sept. 5, Oct. 24, Nov. 7, 21, Dec. 12, 19, 1983.

[11] "Crude Oil Assay," In *Wikipedia, the Free Encyclopedia,* http://en.wikipedia.org/wiki/Crude_oil_assay, accessed Sept. 1, 2009.

[12] O'Donnell, J., "Crude Oils," *Criteria for Quality of Petroleum Products,* J. P. Allison, Ed., John Wiley, New York, 1973, pp. 10–21.

[13] Smith, N. A. C., Smith, H. M., Blade, O. C., and Garton, E. L., "The Bureau of Mines Routine Method for the Analysis of Crude Petroleum 1. The Analytical Method," Bulletin 490, U.S. Department of the Interior, Bureau of Mines, Washington, DC, 1951.

[14] Ali, M. A. "Full Range Crudes, Analytical Methodology of," *Encyclopedia of Analytical Chemistry,* R. A. Meyers, Ed., John Wiley, Chichester, United Kingdom, 2000, Vol. 8, pp. 6709–6726.

[15] Watts, M. R. and Roussis, S. G., "Crude Assay," *Practical Advances in Petroleum Processing,* C. S. Hsu and P. R., Robinson, Eds., Springer, New York, 2006, pp. 103–116.

[16] Herodotus, *The Histories,* G. Rawlinson, Trans., John Murray, London, 1862.

[17] Agricola, G., *De Natura Fossilium* (Textbook of Mineralogy), translated from the first Latin edition of 1546 by M. C. Bandy and J. A. Bandy for The Mineralogical Society of America. Geological Society of America Special Paper 63, New York, 1955.

[18] Mir-Babayev, M. Y., "Azerbaijan's Oil History. A Chronology Leading up to the Soviet Era," *Azerbaijan Intl.,* Issue 10.2, 2002, pp. 34–40.

[19] Totten, G. E., "A Timeline of Highlights from the Histories of ASTM Committee D02 and the Petroleum Industry," *ASTM Standardization News,* June, 2004.

[20] *Dictionary of Canadian Biography Online,* "Abraham Gesner," http://www.biographi.ca/009004-119.01-e.php?BioId=38570, accessed Aug. 31, 2009.

[21] "Ignacy Lukasiewicz," *Wikipedia, the Free Encyclopedia,* http://en.wikipedia.org/wiki/Ignacy_%C5%81ukasiewicz#Biography, accessed Aug. 31, 2009.

[22] Silliman, B., "Report on the Rock Oil, or Petroleum, from Venango Co., PA, with Special Emphasis to Its Use for Illumination and Other Purposes," J. H. Benham, New Haven, CT, 1855.

[23] Narimanov, A. A. and Palaz, I., "Oil History, Potential Converge in Azerbaijan," *Oil Gas J.,* May 22, 1995.

[24] Asbrink, B., "The Nobels in Baku. Swedes' Role in Baku's First Oil Boom," *Azerbaijan Intl.,* Issue 10.2, 2002, pp. 56–59.

[25] Bilkadi, Z., *Babylon to Baku,* Barrett Howe Group Ltd., Windsor, United Kingdom, 1996.

[26] Considine, T. J. and Dowd, K. M., "A Superfluous Petroleum Reserve? How Should the SPR Be Used, and What Benefits Does It Provide?" *Regulation,* The Cato Institute, Washington, DC, Summer 2005.

[27] "When Will the United States Navy Wake Up!" *Oil Gas J.,* March 5, 1907.

[28] Haudan, B. O., *Jahrbuch der Europäischen Erdölindustrie,* Otto Vieth Verlag, Hamburg, Germany, 1975.

[29] Yergin, D., *The Prize,* Simon & Schuster, New York, 1991.

[30] Eckes, A. E., Jr. and Zeiler, T. W., *Globalization and the American Century,* Cambridge University Press, Cambridge, United Kingdom, 2003.

[31] Giles, H. N., "Petroleum Stockpiling: Its History, and an Overview of Global Projects and Technologies," *Proceedings 8th International Conference on Stability and Handling of Liquid Fuels,* Steamboat Springs, CO, Sept. 16, 2003.

[32] De La Rue, W. and Müller, H., "Chemical Examination of Burmese Naphtha, or Rangoon Tar," *Proceedings of the Royal Society of London,* Taylor and Francis, London, 1857, Vol. 8, pp. 221–228.

[33] Forbes, R. J. and O'Breirne, D. R., *The Technical Development of the Royal Dutch/Shell 1890–1940,* Royal Dutch Petroleum Company, The Hague, Netherlands, 1957, p. 32.

[34] Smith, H. M., "Effects of Small Amounts of Extraneous Materials on Properties of Petroleum, Petroleum Products, and Related Liquids," STP304 *Symposium on Major Effects of Minor Constituents on the Properties of Materials,* ASTM International, West Conshohocken, PA, 1962.

[35] Oldenburg, T. B. P., Wilkes, H., Horsfield, B., van Duin, A. C. T., Stoddart, D., and Wilhelms, A., "Xanthones–Novel Aromatic Oxygen-Containing Compounds in Crude Oils," *Org. Geochem.,* 2002, Vol. 33, Issue 5, pp. 595–609.

[36] Nadkarni, R. A. K., Ed., STP1468 *Elemental Analysis of Fuels and Lubricants: Recent Advances and Future Prospects,* ASTM International, West Conshohocken, PA, 2005.

[37] *Strategic Petroleum Reserve Crude Assay Manual,* 3rd ed., U.S. Department of Energy, Washington, DC, 2008, Appendix B, p. 17, http://www.spr.doe.gov/reports/docs/CrudeOilAssayManual.pdf. Accessed May 5, 2009.

[38] Fish, D., "Isokinetic Crude Oil Sampling," *Pipe Line Industry,* April, 1992.

[39] "Protecting Crude Oil Quality," Report of the API Ad Hoc Crude Oil Quality Task Force, American Petroleum Institute, Washington, DC, 1993.

[40] "API Gravity," In *Wikipedia, the Free Encyclopedia,* http://en.wikipedia.org/wiki/API_gravity, accessed Sept. 1, 2009.

[41] Scott, P. J. B. and Davies, M., "Souring of New Irian Jaya Wells Traced to Indigenous Bacteria," *Oil Gas J.,* June 14, 1993.

[42] Vance, I. and Thrasher, D. R., "Reservoir Souring: Mechanisms and Prevention," Chapter 7 in *Petroleum Microbiology,* B. Ollivier and M. Magot, Eds., ASM Press, Washington, DC, 2005.

[43] Coleman, H. J., Thompson, C. J., Rall, H. T., and Smith, H. M., "Thermal Stability of High-Sulfur Crude Oils," *Ind. Engineer. Chem.,* 1953, Vol. 45, pp. 2706–2710.

[44] Neihof, R. A., Hydrogen Sulfide Analyzer with Protective Barrier. U.S. Patent No. 5,529,841, U.S. Patent and Trademark Office, Washington, DC, June 25, 1996.

[45] *ISGOTT (International Safety Guide for Oil Tankers and Terminals),* 5th ed., Witherbys Books, London, 2006, Chapter 2.3.6.

[46] "Guidelines for Identification of the Source of Free Waters Associated with Marine Petroleum Cargo Movements," *Manual of Petroleum Measurement Standards,* 1st ed., American Petroleum Institute, Washington, DC, 1992.

[47] *Impurities in Petroleum,* Petrolite Corporation, Houston, TX, 1958.

[48] Montemayor, R. G., Ed., MNL51. *Distillation and Vapor Pressure Measurement in Petroleum Products,* ASTM International, West Conshohocken, PA, 2008.

[49] Fuhr, B., Banjac, B., Blackmore, T., and Rahimi, P., "Applicability of Total Acid Number Analyses to Heavy Oils and Bitumens," *Energy & Fuels,* 2007, Vol. 21, pp. 1322–1324.

[50] Watson, K. M., Nelson, E. F., and Murphy, G. B., "Characterization of Petroleum Fractions," *Ind. Engineer. Chem.,* 1935, Vol. 27, pp. 1460–1464.

[51] Nelson, W. L., "Which Base of Crude Oil is Best?" *Oil Gas J.,* Jan. 8, 1979, pp. 112–113.

[52] Riazi, M. R., MNL50 *Characterization and Properties of Petroleum Fractions,* ASTM International, West Conshohocken, PA, 2005.

[53] Jones, M. C. K., and Hardy, R. L., *Petroleum Ash Components and Their Effect on Refractories, Ind. Engineer. Chem.,* 1952, Vol. 44, pp. 2615–2619.

[54] Woodle, R. A. and Chandler, W. B., Jr., "Mechanisms of Occurrence of Metals in Petroleum Distillates," *Ind. Engineer. Chem.,* 1952, Vol. 44, pp. 2591–2596.

[55] Dreyfus, S., "Origin and Nature of Trace Metals in Crude Oil," Crude Oil Quality Group, Meeting Archives, March 6, 2008, New Orleans, LA, http://www.coqa-inc.org. Accessed Sept. 16, 2009.

[56] Valkovic, V., *Trace Elements in Petroleum,* Petroleum Publishing, Tulsa, OK, 1978.

[57] Yen, T. F.,Ed., *The Role of Trace Metals in Petroleum,* Ann Arbor Science Publishers, Ann Arbor, MI, 1975.

[58] Jones, P. "Trace Elements and Other Elements in Crude Oil: A Literature Review," unpublished manuscript, The British Petroleum Co., Ltd., BP Research Center, Sunbury, United Kingdom, September 1975.

[59] Dekkers, C. and Daane, R., "Metal Contents in Crudes Much Lower than Expected," *Oil Gas J.,* March 1, 1999, pp. 44–51.

[60] Wilhelm, S. M., Kirchgessner, D. A., Liang, L., and Kariher, P. H. "Sampling and Analysis of Mercury in Crude Oil," STP1468 *Elemental Analysis of Fuels and Lubricants: Recent Advances and Future Prospects,* Nadkarni, R. A. K. Ed., ASTM International, West Conshohocken, PA, 2005.

[61] Long, S. E., Kelly, W. R., Mann, J. L., and Giles, H. N., "Determination of Mercury in Crude Oil Using a Novel Method," *Proceedings 10th International Conference on Stability, Handling, and Use of Liquid Fuels,* Tucson, AZ, Oct. 7–11, 2007.

[62] de Almeida, C. M. S., Ribeiro, A. S., Saint'Pierre, T. D., and Miekeley, N., "Studies on the Origin and Transformation of Selenium and Its Chemical Species along the Process of Petroleum Refining," *Spectrochim. Acta B,* 2009, Vol. 64, pp. 491–499.

[63] Duyck, C., Miekeley, N., da Silveira, C. L. P., Aucélio, R. Q., Campos, R. C., Grinberg, P., and Brandão, G. P., "The Determination of Trace Elements in Crude Oil and its Heavy Fractions by Atomic Spectrometry," *Spectrochim. Acta B,* 2007, Vol. 62, pp. 939–951.

[64] Speight, J. S., and Őzűm, B., *Petroleum Refining Processes,* Marcel Dekker, New York, 2002.

[65] Ball, J. S., VanderWerf, C. A., Waddington, G., and Lake, G. R., "Nitrogen Constituents in Petroleum," American Petroleum Institute, Washington, DC, 1954, API Research Project 52, Vol. 34, Section VI, pp. 152–165.

[66] Hannan, M. A., Oluwole, A. F., Kehinde, L. O., and Borisade, A. B., "Determination of Oxygen, Nitrogen, and Silicon in Nigerian Fossil Fuels by 14-MeV Neutron Activation Analysis," *J. Radioanal. Nucl. Chem.,* 2003, Vol. 256, pp. 61–65.

[67] Bauserman, J. W., Nguyen, K. M., and Mushrush, G. W., "Nitrogen Compound Determination and Distribution in Three Source Fuels by GC/MS," *Petrol. Sci. Technol.,* 2005, Vol. 22, pp. 1491–1505.

[68] Wilburn, G., "Contaminated Crude Poses Safety, Equipment Threat to U. S. Refiners," *The Oil Daily,* April 6, 1981.

[69] *Extent of Crude Oil Contamination is Uncertain,* U.S. General Accounting Office, Washington, DC, 1990, Report GAO/RCED-90-114BR.

[70] Gutzeit, J., "Effect of Organic Chloride Contamination of Crude Oil on Refinery Corrosion," *Corrosion/2000,* NACE International, Houston, TX, 2000.

[71] Craig, J. E., "Pipeline Program Combats Organic-Chloride Contamination," *Oil Gas J.,* Oct. 13, 1986, pp. 63–65.

[72] Bello, O. O., Ademodi, B. T., and Akinyemi, P. O., "Xylene-Based Inhibitor Solves Crude Oil Wax Problems in Niger Delta Pipeline," *Oil Gas J.,* March 14, 2005, pp. 56–59.

[73] "What Are Asphaltenes?"http://baervan.nmt.edu/Petrophysics/group/intro-2-asphaltenes.pdf. Accessed July 8, 2009.

[74] Haskett, C. T. and Tartera, M., "A Practical Solution to the Problem of Asphaltene Deposits–Hassi Messaoud Field, Algeria," *J. Petrol. Technol.,* 1965, April, pp. 387–391.

[75] Tuttle, R. N., "High-Pour-Point and Asphaltic Crude Oils and Condensates," *J. Petrol. Technol.,* 1983, June, pp. 1192–1196.

[76] Ellison, B. T., Gallagher, C. T., and Frostman, L. M., "The Physical Chemistry of Wax, Hydrates, and Asphaltene,"Offshore Technology Conference Houston, TX, May 1–4, 2000, OTC Paper 11963.

[77] Speight, J. G., "A Chemical and Physical Explanation of Incompatibility during Refining Operations," *Proceedings 4th International Conference on Stability and Handling of Liquid Fuels,* U.S. Department of Energy, Washington, DC, 1992, Vol. 1, pp. 169–185.

[78] Wang, J. X., Buckley, J. S., Burke, N. A., and Cheek, J. L., "Anticipating Asphaltene Problems Offshore–A Practical Approach," Offshore Technology Conference Houston, TX, May 5–8, 2003, OTC Paper 15254.

[79] Vazquez, D. and Mansoori, G. A., "Identification and Measurement of Petroleum Precipitates," *J. Petrol. Sci. Engineer.,* 2000, Vol. 42, pp. 49–56.

[80] Mousavi-Dehghani, S. A., Riazi, M. R., Vafaie-Sefti, M., and Mansoori, G. A., "An Analysis of Methods for Determination of Onsets of Asphaltene Phase Separations," *J. Petrol. Sci. Engineer.,* 2004, Vol. 42, pp. 145–156.

[81] Mansoori, G. A., "A Unified Perspective on the Phase Behaviour of Petroleum Fluids," *Intl. J. Oil Gas Coal Technol.,* 2009, Vol. 2, pp. 141–167.

[82] Stark, J. L., Nguyen, J., and Kremer, L. N., "New Method Prevents Desalter Upsets from Blending Incompatible Crudes," *Oil Gas J.,* March 18, 2002, pp. 89–91.

[83] Stark, J. L, and Asomaning, S., "Crude Oil Blending Effects on Asphaltene Stability in Refinery Fouling," *Petrol. Sci. Technol.,* 2003, Vol. 21, pp. 569–579.

[84] Villalanti, D. C., Raia, J. C., and Maynard, J. B., "High-Temperature Simulated Distillation Applications in Petroleum Characterization," *Encyclopedia of Analytical Chemistry,* R. A. Meyers, Ed., John Wiley, Chichester, United Kingdom, 2000, Vol. 8, pp. 6726–6741.

[85] Kelland, M. A., *Production Chemicals for the Oil and Gas Industry,* CRC Press, Boca Raton, FL, 2009.

[86] Clemens, J., "Methanol in Crude,"Crude Oil Quality Group Meeting Archives, Houston, TX, Oct. 5, 2000,http://www.coqa-inc.org. Accessed Aug. 4, 2009.

[87] Evans, J., "Methanol in Crude Using Near-Infrared Analysis,"-Crude Oil Quality Group Meeting Archives, New Orleans, LA, January 2005,http://www.coqa-inc.org. Accessed Aug. 4, 2009.

[88] Kők, M. V., Letoffe, J. M., and Claudy, P., "Comparative Methods in the Determination of Wax Content and Pour Points of Crude Oil," *J. Therm. Anal. Calorim.,* 2007, Vol. 90, pp. 827–831.

[89] Rand, S. J., Ed., MNL1 *Significance of Tests for Petroleum Products,* 8th ed., ASTM International, West Conshohocken, PA, 2010.

[90] Drews, A. W., Ed., MNL3 *Manual on Hydrocarbon Analysis,* 6th ed., ASTM International, West Conshohocken, PA.

[91] Totten, G. E., Ed., S. R. Westbrook and R. J. Shah,Section, Eds. MNL37 *Fuels and Lubes Handbook: Technology, Properties, Performance, and Testing,* ASTM International, West Conshohocken, PA, 2003.

[92] Nadkarni, R. A. K., MNL44 *Guide to ASTM Test Methods for the Analysis of Petroleum Products and Lubricants,* ASTM International, West Conshohocken, PA, 2000.

[93] Childs, W. V. and Vickery, E. H., "The Phillips Small Sample Octane Number Methods, Automation of a Knock-Test Engine," *Symposium on Laboratory and Pilot Plant Automation,* Washington, DC, Aug. 28–Sept. 2, 1983, American Chemical Society, Washington, DC, 1983, pp. 979–990.

[94] Richter, F. P., Caesar, P. D., Meisel, S. L., and Offenhauer, R. D., "Distribution of Nitrogen in Petroleum According to Basicity," *Indust. Engineer. Chem.*, 1952, Vol. 44, pp. 2601–2605.

[95] *Asphalt Binder Testing Manual,* Asphalt Institute, Lexington, KY, 2007, MS-25.

[96] Aalund, L. R., "Guide to Export Crudes for the '80s—1," *Oil Gas J.,* April 1, 1983, p. 71.

[97] Alexander, D., "How to Update an Old Assay," Crude Oil Quality Group Meeting Archives, New Orleans, LA, January 2003, http://www.coqa-inc.org. Accessed Sept. 15, 2009.

[98] Schermer, W. E. M., Melein, P. M. J., and van den Berg. F. G. A. "Simple Techniques for Evaluation of Crude Oil Compatibility," *Petrol. Sci. Technol.,* 2004, Vol. 22, pp. 1045–1054.

[99] Stark, J. and Falkler, T. J., "Index Correlates Asphaltene Stability to Coker Furnace Fouling," *Oil Gas J.,* Sept. 13, 2004, pp. 72–74.

[100] Wiehe, I. A. and Kennedy R. J., "The Oil Compatibility Model and Crude Oil Incompatibility," *Energy & Fuels,* 2000, Vol. 14, pp. 56–59.

[101] Pauli, A. T., "A Study of the Rates of Flocculation of Asphaltenes in Asphalt-Solvent Solutions Measured by Automated Flocculation Titrimetry," 227th American Chemical Society National Meeting, Anaheim, CA, March 28–April 1, 2004.

[102] Alboudwarej, H., Huo, Z., and Kempton, E., "Flow-Assurance Aspects of Subsea Systems Design for Production of Waxy Crude Oils," SPE Annual Technical Conference and Exhibition, San Antonio, TX, Sept. 24–27, 2006, SPE Paper No. 103242.

[103] Kruka, V. R., Cadena, E. R., and Long, T. E., "Cloud-Point Determination for Crude Oils," *J. Petrol. Technol.,*1995, August, pp. 681–687.

[104] Elsharkawy, A. M., Al-Sahfah, T. A., and Fahim, M. A., "Wax Deposition from Middle East Crudes," *Fuel,* 2000, Vol 79, pp. 1047–1055.

[105] Leontaritis, K. J. and Leontaritis, J. D., "Cloud Point and Wax Deposition Measurement Techniques," SPE International Symposium on Oilfield Chemistry, Houston, TX, Feb. 5–7, 2003, SPE Paper No. 80267.

[106] Coutinho, J. A. P. and Daridon, J. -L., "The Limitations of the Cloud Point Measurement Techniques and the Influence of the Oil Composition on Its Detection," *Petrol. Sci. Technol.,* 2005, Vol. 23, pp. 1113–1128.

[107] "Wax, Asphaltenes, Pour Points,"Hydrafact Ltd., Centre for Gas Hydrate Research, Heriot-Watt University, http://hydrafact.com/Wax_and_Asphaltenes.html. Accessed June 17, 2009.

[108] Hammami, A., Ratulowski, J., and Coutinho, J. A. P., "Cloud Points: Can We Measure or Model Them?" *Petrol. Sci. Technol.,* 2003, Vol. 21, pp. 345–358.

[109] "Cleveland City Cable Railway," *Manufacturer and Builder,* 1891 Vol. 23, Issue 11, November p. 242.

[110] "Burning Brick with Crude Oil Fuel," *Sci. American Suppl.,* 1892, Vol. XXXIII No. 841, Feb. 13.

[111] *The Locomotive,* Hartford Steam Boiler Inspection and Insurance Co., Hartford, CT, December 1898, Vol. XIX, no. 12, 181.

[112] *4th Annual Report to the Directors and Stockholders for the Fiscal Year Ended June 30, 1895,* St. Louis Southwestern Railway Co., Woodward & Tiernan Printing Co., St. Louis, MO, 1895, p. 65.

[113] Krebs, R., in collaboration with P. J. Orthwein, *Making Friends is Our Business: 100 years of Anheuser Busch,* Anheuser Busch, St. Louis, MO, 1953.

[114] "Fuel for Ships," *The New International Encyclopedia,* Dodd, Mead and Company, New York, 1915, Vol. IX, p. 329.

[115] Owens, E. C.and Frame, E. A., "Direct Utilization of Crude Oils as Fuels in U. S. Army Diesel Engines,"Southwest Research Institute, San Antonio, TX, 1975, Interim Report AFLRL No. 66.

[116] Babún, T. A., Jr., "Cuba's Cement Industry," *Cuba in Transition, Proceedings of the Annual Meeting of the Association for the Study of the Cuban Economy,* Washington, DC, 1997, Vol. 7, pp. 374–381.

[117] Alloway, J. L., "Macedonia Blockade,"American University, Washington, DC, 1996, Case 268, Trade and Environment Database Case Studies, Vol. 5, No. 1.

[118] "Crude-Oil-Burning Wärtsilä Engines for Offshore China," *Marine News,* 2004, Vol. 3, p. 27.

[119] "Japan Studies Effect of Possible Sudan Crude Oil Ban," *Sudan Tribune,* November 17 2007.

[120] Swain, E. "U.S. Refiners Continue to Process Crudes with Lower Gravity, Higher Sulfur," *Oil Gas J.,* Jan. 3, 2005, p. 51–55.

[121] Barrow, K., "Residual Fuel Market Issues," Crude Oil Quality Group Meeting Archives, Long Beach, CA, February 2009, http://www.coqa-inc.org. Accessed Aug. 25, 2009.

[122] *Heavy Oil and Bitumen Analytical Methods: Understanding Their Capabilities and Limitations,* Canadian Crude Quality Technical Association, Edmonton, Alberta, 2008.

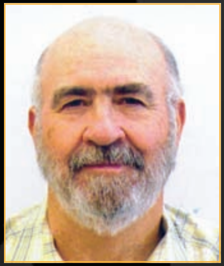
[123] Boduszynski, M. M., Grudoski, D. A., Rechsteiner, C. E., and Iwamoto, J. D., "Deep-Cut Assay Reveals Additional Yields of High-Value VGO," *Oil Gas J.,* Sept. 11, 1995, pp. 39–44.

[124] "Opportunity Crudes 2008:Challenges, Benefits, and Processing," *Conference Proceedings,* Houston, TX, April 30–May 2, 2008, Hydrocarbon Publishing, Southeastern, PA, 2008.

[125] Marshall, A. G. and Rodgers, R. P., "Petroleomics: Chemistry of the Underworld," *Proc. Natl. Acad. Sci.,* 2008, Vol. 105, pp. 18090–18095.

Index

Harry N. Giles is retired from the Department of Energy where he was manager of crude oil quality programs for the Strategic Petroleum Reserve. This included development and management of analytical programs for monitoring quality of stocks, and research related to the biological and geochemical aspects of petroleum stockpiling. He was employed by the Department of Energy for over 30 years, prior to which he held several positions with other U. S. Government agencies and at the University of Manchester (UK). He has authored or co-authored a number of articles on crude oil analysis, characterization, and storage, and on fuel stability and cleanliness. Mr. Giles has been involved with ASTM Committee D02 on Petroleum Products and Lubricants since the 1980s. He is past chairman of Subcommittee D02.14 on Fuel Stability and Cleanliness. He remains active in Subcommittees D02.02, D02.08, D02.14, and D02. EO., and is a technical advisor to ASTM for their Crude Oil Interlaboratory Crosscheck Program (ILCP). In 2005, he and Clifford Mills developed the ASTM training course on "Crude Oil: Sampling, Testing, and Evaluation." In 2009, he received the ASTM International George V. Dyroff Award of Honorary Committee D02 Membership. Other memberships include API Committee on Measurement Quality, and IASH, the International Association for Stability, Handling, and Use of Liquid Fuels. He is chairman emeritus of IASH, and was elected to honorary membership in 2009. Currently, he serves as Executive Director of the Crude Oil Quality Association.



Clifford O. Mills is retired from CONOCO where he served in numerous capacities. At retirement, after 35 years, he was a laboratory consultant with an emphasis on crude oil analysis. Mr. Mills has been involved with ASTM methods development since the early 1980s. Until recently, he was chairman of ASTM D02.05 on Properties of Fuels, Petroleum Coke and Carbon Material, and also chaired D02.H0 on LP-Gases for several years. He continues to be active in D02.03, D02.04, D02.05, D02.06 and D02.H0. Mr. Mills has been actively involved in development of numerous ASTM methods of analysis. Together with Mr. Giles, he serves as technical advisor to ASTM for their Crude Oil ILCP. For several years, Mr. Mills served as co-instructor for the crude oil training course and, together with Mr. Giles, presented this at numerous locations worldwide. He is a member of the Crude Oil Quality Association, and author of an authoritative paper on crude contaminants and analysis requirements presented at one of their meetings. This paper is now widely referenced and used as an instructional aid. In 2009, he received the ASTM International George V. Dyroff Award of Honorary Committee D02 Membership.

www.astm.org

ISBN: 978-0-8031-7014-8
Stock #: MNL68