



Standard Guide for Elemental Analysis of Crude Oil¹

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1. Scope

1.1 This guide summarizes the current information about the test methods for elemental and associated analyses used in the analysis of crude oils. This information can be helpful in trade between the buyers and sellers of crude oil. Elemental analyses tests form an important part of quantifying the crude oil quality.

1.2 The values stated in SI units are to be regarded as the standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

- D129 Test Method for Sulfur in Petroleum Products (General High Pressure Decomposition Device Method)
- D482 Test Method for Ash from Petroleum Products
- D1548 Test Method for Vanadium in Heavy Fuel Oil¹ (Withdrawn 1997)³
- D1552 Test Method for Sulfur in Petroleum Products by High Temperature Combustion and IR Detection
- D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry
- D3227 Test Method for (Thiol Mercaptan) Sulfur in Gasoline, Kerosine, Aviation Turbine, and Distillate Fuels (Potentiometric Method)
- D3228 Test Method for Total Nitrogen in Lubricating Oils and Fuel Oils by Modified Kjeldahl Method

- D3230 Test Method for Salts in Crude Oil (Electrometric Method)
- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
- D4294 Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry
- D4629 Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection
- D4929 Test Methods for Determination of Organic Chloride Content in Crude Oil
- D5185 Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
- D5291 Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants
- D5708 Test Methods for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry
- D5762 Test Method for Nitrogen in Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence
- D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
- D5863 Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry
- D6259 Practice for Determination of a Pooled Limit of Quantitation for a Test Method
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- D6470 Test Method for Salt in Crude Oils (Potentiometric Method)
- D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories
- D7260 Practice for Optimization, Calibration, and Validation of Inductively Coupled Plasma-Atomic Emission

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

Spectrometry (ICP-AES) for Elemental Analysis of Petroleum Products and Lubricants

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

D7372 Guide for Analysis and Interpretation of Proficiency Test Program Results

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

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

D7578 Guide for Calibration Requirements for Elemental Analysis of Petroleum Products and Lubricants

D7621 Test Method for Determination of Hydrogen Sulfide in Fuel Oils by Rapid Liquid Phase Extraction

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

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

D7691 Test Method for Multielement Analysis of Crude Oils Using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

D7740 Practice for Optimization, Calibration, and Validation of Atomic Absorption Spectrometry for Metal Analysis of Petroleum Products and Lubricants

2.2 Other Standards:

IP 570 Hydrogen Sulfide in Fuel Oils—Rapid Liquid Phase Extraction Method⁴

ISO 8754 Petroleum Products, Determination of Sulfur Content, Energy Dispersive X-ray Fluorescence Spectrometry⁵

ISO 14596 Petroleum Products, Determination of Sulfur Content, Wavelength Dispersive X-ray Fluorescence Spectrometry⁵

UOP 163 Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration²

UOP 938 Total Mercury and Mercury Species in Liquid Hydrocarbons²

3. Significance and Use

3.1 This guide summarizes the test methods used in the elemental analysis of crude oils. Additional information on the significance and use of the test methods quoted in this guide can be found under discussion of individual test methods in Sections 8 through 15.

3.2 Crude oils are highly complex hydrocarbons also containing some organometallic compounds, inorganic sediment, and water. Nearly 600 individual hydrocarbons, over 200 separate sulfur compounds, and about 40 trace elements have

been found in crude oils (1).⁶ Generally, sulfur and nitrogen are the two most abundant elements found in crude oils except for carbon and hydrogen. Most other inorganic elements are present at trace levels (mg/kg). Sulfur, nitrogen, vanadium, nickel, and iron are the most frequently determined elements in the crude oils. Ratios such as vanadium to vanadium + nickel, and iron to vanadium are suggested as being useful for oil type characterizations. Since organometallic compounds are concentrated in the heavy ends of petroleum, transition element concentrations and ratios can serve as excellent oil-oil correlation parameters. Generally, vanadium and nickel content increases with asphaltic content of crude oil (API gravity is an indicator). Lighter crude oils contain lesser amounts of metals (2, 3).

3.3 Metal complexes called porphyrins are a major component of metallic compounds in crude oils. The principal porphyrin complexes are Ni⁺² and VO⁺² compounds. There are also other non-porphyrin complexes and other metallic compounds present in crude oils (4, 5).

3.4 Some typical literature citations in this area are included in the reference section at the end of this guide.

4. Sampling

4.1 Collection of a meaningful and representative sample is often the most critical step in an analytical procedure. In trace element analysis, in particular, extreme care must be taken to avoid contamination of the sample during the sampling step and all subsequent analysis steps. By its very nature, crude oil is typically non-homogenous, containing some percentages of sediment and water. It also typically contains volatile light ends, and finally, crude oil will often exhibit high pour point and high viscosity properties, due to its asphaltenes and paraffin wax content.

4.1.1 The water and sediment component of the crude oil will tend to naturally separate and stratify in tanks, marine vessel compartments, and in flowing pipelines.

4.1.2 There are various types of containers that can be used for storage of liquid hydrocarbon products. Not all of them are suitable for crude oil storage. According to Practice **D5854** for tests of interest in elemental analysis area (salts, sulfur, and trace metals) in crude oil, the containers employed may be made of hard borosilicate glass, stainless steel, or epoxy-lined steel and are considered satisfactory for immediate use, storage up to six months or reuse. Less satisfactory are tin-plated soldered steel, polytetrafluoroethylene propylene (PTFE), and high-density linear polyethylene containers. See **Table 1**.

4.2 Three principal protocols are available for sampling of a representative aliquot from a bulk sample: Practice **D4057** for manual sampling, Practice **D4177** for automatic sampling, and Practice **D5854** for mixing and handling of liquid samples.

4.3 Crude oil to be sampled may be in static storage in a tank, a marine vessel, or a pipeline. Stabilized crude oils typically contain multiple phases, particulates, and volatiles.

⁴ Available from Energy Institute, 61 New Cavendish St., London, W1G 7AR, U.K., <http://www.energyinst.org>.

⁵ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

⁶ The bold numbers in parentheses refer to the list of references at the end of this standard.

TABLE 1 Recommended Sample Containers for Crude Oil Storage^A

Container Material	For Immediate Use	For Storage for 6 months	For Reuse
Hard Borosilicate Glass	Preferred	Preferred	Suitable
Stainless Steel	Suitable	Suitable	Suitable
Epoxy-lined Steel	Suitable	Suitable	Suitable
Tin-plated Soldered Steel	Not recommended	Not recommended	Not recommended
Polytetrafluoroethylene Propylene (PTFE)	Preferred	Not recommended	Suitable
High-density Linear Polyethylene (HDPE)	Preferred	Not recommended	Not recommended

^A Excerpted from Practice [D5854](#).

Decisions whether to separate the phases and analyze them separately, or homogenize the whole sample need to be made prior to analysis.

4.4 If the sample does not readily flow at room temperature, heat it to a sufficiently high and safe temperature to ensure adequate fluidity. Great care needs to be taken in heating the viscous sample prior to analysis. Changes in chemical composition, loss of volatile elements, and so forth are causes for concern.

5. Sample Preparation

5.1 Often different test methods for specific determination of elements require different sample preparation steps. Guide [D7455](#) reviews alternative techniques for sample preparation for elemental analysis. The means of sample preparation vary from no sample preparation to simple sample dilution to extensive detailed procedures such as sample decomposition depending on the measurement technique to be used for the final determination.

5.2 Among the test methods used for the elemental analysis of crude oil, test methods such as XRF – Test Methods [D2622](#) or [D4294](#) for sulfur need no special preparation. However, they may need dilution with a solvent if the sulfur levels are above the scope of the test methods. Other non-XRF test methods that do not need special sample treatment include Test Method [D3230](#) for salt by titration, and Test Methods [D5291](#) for carbon-hydrogen-nitrogen by combustion.

5.3 Some methods require sample dilution such as in atomic absorption spectrometry (AAS) Test Method [D5863 B](#) for nickel, vanadium, iron, and sodium; inductively coupled plasma-atomic emission spectrometry (ICP-AES) Test Method [D5708](#) for nickel, vanadium, and iron; and ICP-AES Test Method [D7691](#) for multi-element analysis of crude oils.

5.4 Decomposition agents are employed to bring the desired parameter in aqueous solution for final measurement. Examples of these are Kjeldahl method for nitrogen: Test Method [D3228](#), acid decomposition of crude oil for vanadium: Test Method [D1548](#), and AAS method for nickel, vanadium, iron, and sodium: Test Method [D5863 A](#).

5.5 For volatile elements such as nitrogen or sulfur, combustion trains using adsorbants have been used in Test Method [D1552](#) for sulfur, and Test Methods [D4629](#) and [D5762](#) for nitrogen.

5.6 Organic chloride in crude oil is determined by Test Methods [D4929](#) after elaborate pre-treatment of samples to separate organic chloride fraction from crude oil.

5.7 Determination of mercury in crude oil poses special problems both in sample collection and in measurement. These are discussed elsewhere in detail in Practice [D7482](#), Test Method [D7622](#), and Test Method [D7623](#).

6. Calibration

6.1 Depending upon the analysis being done, different calibration practices may have to be followed. A review of calibration practices used in elemental analysis is given in Guide [D7578](#).

7. Analysis of Crude Oils

7.1 A number of elemental analysis techniques have been used in the analysis of crude oils. These include instrumental techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), isotope dilution mass spectrometry (IDMS), neutron activation analysis (NAA), energy-dispersive X-ray fluorescence (ED-XRF), and wavelength-dispersive X-ray fluorescence (WD-XRF). The highlights of these techniques and the examples of their utilization to elemental analysis of petroleum products and lubricants, and particularly to crude oils have been discussed in detail elsewhere ([2](#), [6](#), [7](#)).

7.2 Parameters that are usually determined for elemental analysis are listed in [Table 2](#) along with their scope and the applicability of the test methods to crude oil assay. Several of the tests methods are not specifically designated for crude oil analysis but conventionally they are widely used for such analyses in the industry.

7.2.1 Some of the ASTM tests listed in [Table 2](#) have their international counterparts listed in [Table 3 \(8\)](#).

7.3 When performing several tests on a crude oil sample, it is very important to ensure that the sequence of testing is evaluated to minimize altering the properties of the remaining sample to be tested or retained. For crude oil samples, the vapor pressure, H₂S, or any other test in which retention of light ends is critical need to be analyzed first from the original sample container. For elemental analysis parameters, the sequence of testing should be mercaptan sulfur, metals by AAS or ICP-AES, nitrogen, salts, and sulfur by XRF, in that order.

7.4 For several elemental tests, special precautions need to be taken in handling the crude oil samples during analysis. Some of these are listed below in [Table 4](#) excerpted from Practice [D4057](#).

TABLE 2 Scope and Applicability of Test Methods Used for Analysis in Crude Oils

NOTE 1—ICP-AES: Inductively Coupled Plasma Atomic Emission Spectrometry
 CVAAS: Cold Vapor Atomic Absorption Spectrometry

ASTM Standard	Analysis	Measurement Technique	Scope
D129 ^A	Sulfur	Combustion – Gravimetry	0.09 % to 5.5 % by mass
D482 ^A	Ash	Combustion	0.001 % to 0.180 % by mass
D1552 ^A	Sulfur	Combustion – IR Detection	>0.06 % by mass
D2622	Sulfur	Wavelength Dispersive X-ray Fluorescence	3 mg/kg to 4.6 % by mass
D3227 ^A	Mercaptan Sulfur	Potentiometric Titration	0.0003 % to 0.01 % by mass
D3228 ^A	Nitrogen	Digestion – Titration	0.015 % to 2.0 % by mass
D3230	Salts	Conductivity	0 mg/kg to 500 mg/kg
D4294	Sulfur	Energy Dispersive X-Ray Fluorescence	17 mg/kg to 4.6 % by mass
D4629 ^A	Nitrogen	Oxidative Combustion and Chemiluminescence Detection	0.3 mg/kg to 100 mg/kg
D4929	Organic Chloride	Sodium Biphenyl Reduction and Potentiometry; or Combustion and Microcoulometry	>1 mg/kg
D5291 ^A	Carbon – Hydrogen-Nitrogen	Combustion and Instrumental Detection	<0.1 % to 2 % by mass Nitrogen
D5708	Nickel, Vanadium, Iron	Acid Decomposition or Solvent Dilution + ICP-AES Measurement	V: 50 mg/kg to 100 mg/kg; Ni: 10 mg/kg to 100 mg/kg; and Fe: 1 mg/kg to 10 mg/kg
D5762 ^A	Nitrogen	Boat Inlet Combustion and Chemiluminescence Detection	40 mg/kg to 10 000 mg/kg
D5863	Nickel, Vanadium, Iron, Sodium	Acid Decomposition or Solvent Dilution + AAS Measurement	V: 50 mg/kg to 500 mg/kg; Ni: 10 mg/kg to 100 mg/kg; Fe: 3 mg/kg to 10 mg/kg; and Na: 1 mg/kg to 20 mg/kg
D6470	Salts	Solvent Extraction and Potentiometric Measurement	0.0005 % to 0.15 % mass/mass
D7621	Hydrogen Sulfide	Dilution with base oil, extraction of H ₂ S with air, and detection with H ₂ S specific electrochemical detector.	0 mg/kg to 150 mg/kg
D7622	Mercury	Combustion + CVAAS	5 ng/mL to 350 ng/mL
D7623	Mercury	Combustion Gold Amalgamation + CVAAS	5 ng/mL to 400 ng/mL
D7691	Iron, Sulfur, Nickel, Vanadium	Solvent Dilution + ICP-AES Measurement	Fe: 1 mg/kg to 40 mg/kg; Ni: 1 mg/kg to 100 mg/kg; S: 400 mg/kg to 50 000 mg/kg; and V: 1 mg/kg to 1000 mg/kg

^A Method scope does not include crude oils.

TABLE 3 International Equivalent Test Methods for Crude Oil Analysis^A

Analysis	ASTM	Institute of Petroleum/ Energy Institute (IP)	International Standards Organization (ISO)	German Institute for Standardization (DIN)	Japanese Industrial Standards (JIS)
Sulfur by Bomb Method	D129	61		51-577	
Ash	D482	4	6245		K 2272
Sulfur by WD-XRF	D2622		14596	51-400T6	K 2541
Mercaptans	D3227	342	3012		K 2276
Sulfur by ED-XRF	D4294	336	8754		
Nitrogen-Chemiluminescence	D4629	379			
Metals by AAS	D5863	441			
Hydrogen Sulfide	D7621	570			

^A From reference (8).

TABLE 4 Sample Handling for Elemental Analysis Tests for Crude Oils

Analysis	Sample Volume, mL	Precautions to be Taken
Mercaptan Sulfur (UOP 163); D3227	200	Minimize sample exposure to air.
Metals (D5863 B)	25	Prior to weighing stir the sample and then shake in its container. Employ adequate mixing and sampling procedures for crude and heavy oils. Use paint mixer for mixing of crude oils. If the sample does not readily flow at room temperature, heat the sample to a sufficiently high and safe temperature to ensure adequate fluidity.
Nitrogen (D4629 ; D5762)	3	Test samples as soon as possible after taking from bulk supplies to prevent loss of nitrogen or contamination due to exposure or contact with the sample container. If the test sample is not used immediately, then thoroughly mix it in its container prior to taking a test specimen. Some test samples require heating in order to thoroughly homogenize.
Salts (D3230)	10	The presence of water and sediment will influence the conductivity of the sample. The utmost care shall be taken in obtaining homogenized representative samples. Samples of very viscous materials may be warmed until they are reasonably fluid before they are sampled. However, no sample shall be heated more than is necessary to lower the viscosity to a manageable level.
Salts (D6470)	50	Homogenize the sample within 15 min of drawing the test sample. Mix the sample at room temperature (15 °C to 20 °C), or less in the laboratory sample container. Heat waxy samples, solid at room temperature, to 3 °C above their pour point in order to facilitate sample withdrawal. See Annex A1 of D6470 for mixer requirements and containers to be used.
Sulfur (D2622 ; D4294)	25	Be sure the sample is homogenous, and that there is no sediment or water present in the sample aliquot taken.

8. Ash

8.1 *Significance*—Ash present in the crude oil results from the presence of non-combustible extraneous solids such as sediment, pipeline scales, rust and salt contamination from sea water. If the crude oil is used as a fuel, it is important to know its ash content because this could be related directly to particulate emission.

8.2 *Analysis*—Ash in petroleum products is determined using the Test Method **D482**. In this test, the sample contained in a suitable vessel is ignited and allowed to burn until only the ash and carbon remain. The carbonaceous residue is reduced to an ash by heating in a muffle furnace at 775 °C, cooled, and weighed.

8.3 *Test Precision*—Although crude oils were not specifically analyzed by this test method to estimate precision, in general, for petroleum products, the following precision is expected.

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

9. Mercaptans

9.1 *Significance*—Hydrogen sulfide and mercaptans are highly toxic and corrosive compounds that occur naturally in some crude oils. Thiols or mercaptans are considerably more prevalent in crude oil than H₂S. They are the least stable sulfur compounds and many decompose on heating to form H₂S (**3**).

9.2 *Analysis*—These compounds can be determined by non-aqueous potentiometric titration with silver nitrate (Test Method **D3227** and UOP 163). Although both methods are similar, the ASTM method did not include crude oils in its scope. IP method 570 and its equivalent Test Method **D7621** can determine amount of hydrogen sulfide in crude oils.

9.2.1 Test Method **D3227** is applicable to various fuels containing from 0.0003 % to 0.01 % by mass mercaptan sulfur. Organic sulfur compounds such as sulfides, disulfides, and thiophene do not interfere. Elemental sulfur in amounts less than 0.0005 % by mass does not interfere. Hydrogen sulfide will interfere if not removed as described in the test method. In this test method, the hydrogen sulfide-free sample is dissolved in an alcoholic sodium acetate titration solvent and titrated potentiometrically with silver nitrate solution, using as an indicator the potential between a glass reference electrode and a silver/silver-sulfide indicating electrode. Under these conditions, the mercaptan sulfur is precipitated as silver mercaptide and the end point of the titration is shown by a large change in cell potential.

9.2.2 Test Method **D7621** and its equivalent test method IP 570 are automatic methods suitable for laboratory testing or field use, and provides results in about 15 min. They can quantify hydrogen sulfide at a range from 0 mg/kg to 150 mg/kg hydrogen sulfide in the liquid phase in a wide variety of crude oils with an API ranging from 11.8 to 57.3, and sulfur levels from 0.1 % to 6.7 %. In this test method, a sample is introduced into a heated test vessel containing a diluent base oil. Air is bubbled through the oil to extract the H₂S gas. The air with the extracted H₂S is passed via a vapor phase processor to an H₂S specific electrochemical detector enabling the H₂S content of the air to be quantitated.

9.2.2.1 The alternative procedure for crude oil is given in Appendix X1 of Test Method **D7621**. The vapor phase processor (Procedure A) is required for this analysis as vapor present in the crude oil can damage the detector and chemical interferences can be present.

9.3 *Test Precision*—Following precision was obtained from interlaboratory studies.

9.3.1 Precision of Test Method **D3227** has been found to be as follows. This study did not include crude oils in the matrix.

Repeatability	0.00007 + 0.027 X
Reproducibility	0.0031 + 0.042 X

Where X is the average mercaptan sulfur, percent by mass.

9.3.2 Only repeatability estimate of Test Method **D7621** is available. In one study a single laboratory analyzed 21 samples of crude oil ranging in their H₂S levels from 0 mg/kg to 150 mg/kg and found a repeatability of 12 mg/kg. A similar analysis of 12 lowest H₂S level samples ranging in the concentration from 0 mg/kg to 50 mg/kg found a repeatability of 5 mg/kg.

10. Mercury

10.1 *Significance*—Mercury has been designated by Environmental Protection Agency (EPA) and many state agencies as a hazardous material that can cause central nervous system, kidney, and liver damage. Mercury or its vapors may be hazardous to health and corrosive to material. Mercury can occur in crude oil as volatile, dissolved, and particulate (suspended) species—all of which differ considerably in their chemical structure and chemical behavior. Elemental mercury has been found in condensed in cooled regions in refinery distillation towers and in cryogenic heat exchangers that liquefy petroleum gases. Mercury can be present in various distillation fractions across a broad boiling range (**1, 3**).

10.1.1 Mercury is present at low ppm to ppb levels in crude oils. Giles et al have reported mercury in the range from 0.02 ng/g to 10 ng/g (**1, 3**). Others also have reported mercury in the less than a ppb level in crude oil (**9, 10**). Mercury speciation is predominantly Hg(0) present as a mixture of dissolved Hg(0) atoms, adsorbed Hg(0) on particulates and suspended droplets of metallic mercury (**11**). Practice **D7482** should be used for guidance for sampling, storage, and handling of hydrocarbons for mercury analysis.

10.2 *Analysis*—Given the ultra-trace levels of mercury present in crude oil, there are only limited analytical techniques available for such analysis. Basically the methods available are a variation on the basic cold vapor atomic absorption spectrometry technique.

10.2.1 *Test Method D7622*—The crude oil sample placed in a sample boat is inserted in the first chamber of an atomizer where the sample is heated at 300 °C to 500 °C. The mercury compounds are evaporated and partially dissociated forming elemental mercury vapor. Mercury and all decomposition products are carried to a second atomizer chamber heated to about 700 °C to 750 °C. 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 absorbance analytical cell heated up to 750 °C positioned in the light path of double-wave cold vapor Zeeman atomic absorption spectrometer. The mercury resonance line at 253.65 nm is split to several components, one of those falling within the mercury absorbance line profile and another one lying outside. Difference between the intensities of these two lines is proportional to the number of mercury atoms in the analytical cell.

10.2.2 *Test Method D7623 and UOP 938*—A crude oil sample is heated to dryness in an oxygen atmosphere in the instrument, and then thermally (at about 700 °C) and then chemically decomposed. The decomposition products are carried by flowing treated air to the catalytic section of the furnace (at about 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 about 600 °C, releasing mercury vapor. Flowing oxygen carries the mercury vapor through absorbance cells positioned in the light path of 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.

10.2.2.1 An Appendix to UOP 938 Test Method also contains a procedure that can be used to differentiate between elemental mercury, organic non-ionic mercury, and ionic (inorganic and organic) mercury species.

10.3 *Test Precision*—Based on an interlaboratory study (RR:D02-1692)⁷ following precision was obtained. Reproducibility limit is not yet available.

Test Method	Scope	Repeatability	Reproducibility
D7622	5 ng/mL to 350 ng/mL	0.7147 X ^{0.6}	NA
D7623	5 ng/mL to 400 ng/mL	0.4396 X ^{0.5864}	NA

Where X is the average mercury concentration in ng/mL.

11. Nitrogen

11.1 *Significance*—Nitrogen is an important element for determining in crude oil. Numerous nitrogenous compounds are present in crude oils. Many problems are caused by their presence in refining and product quality. As a group even their trace quantities present in feedstocks can contaminate refinery catalysts. Nitrogen compounds can also contribute to refined product instability, are responsible for formation and precipitation of gum, and contribute to environmental pollution when fuels are burned by emission of nitrogen oxides (NO_x) (**3**).

11.2 *Analysis*—There are four principle test methods for the determination of nitrogen in crude oils: Test Methods **D3228, D4629, D5291, and D5762**. None of them are specifically meant for analysis of crude oils. However, they are commonly used when necessary for crude oils.

11.2.1 *Kjeldahl Method*—Test Method **D3228** is not often used in analysis of crude oils, and uses sample digestion in a mixture of concentrated sulfuric acid, potassium sulfate, mercuric oxide, and copper sulfate to convert nitrogen species into inorganic nitrate compounds. After digestion, sodium sulfide is added to precipitate the mercury as mercuric sulfide, and the mixture is made alkaline with NaOH. Nitrogen, now in the form of ammonia, is distilled into a boric acid solution. The ammonia is titrated with standard sulfuric acid using methyl purple as an indicator. Kjeldahl method may not be applicable to certain materials containing N-O or N-N linkage.

⁷ Supporting data have been filed at ASTM International Headquarters and may be obtained by contacting ASTM Customer Service at service@astm.org.

11.2.2 *Syringe/inlet Oxidative Combustion and Chemiluminescence Detection Method*—Test Method **D4629** can analyze total nitrogen found in liquid hydrocarbons boiling in the range of approximately 50 to 400°C, with viscosities between approximately 0.2 and 10 cSt at room temperature. This method is applicable to naphthas, distillates, and oils containing 0.3 mg/kg to 100 mg/kg of total nitrogen. In this test method, a sample of liquid hydrocarbon is introduced either by syringe or boat inlet system, into a stream of inert gas such as helium or argon. The sample is vaporized and carried to a high temperature zone where oxygen is introduced and the organically bound nitrogen is converted to nitric oxide (NO). The NO contacts ozone, and is converted to excited nitrogen dioxide (NO₂). The light emitted as the excited NO₂ decays is detected by a photomultiplier tube and the resulting signal is a measure of the nitrogen contained in the sample.

11.2.3 *Instrumental Determination of Carbon-Hydrogen-Nitrogen*—Test Methods **D5291** consists of four separate procedures for simultaneous determination of carbon, hydrogen, and nitrogen in petroleum products including crude oil and lubricants. Each procedure is dedicated to a separate instrument type available. Basically, in each type of instrument, a sample is combusted at an elevated temperature in an atmosphere temporarily enriched in purified oxygen to convert the constituents to carbon dioxide, hydrogen halides, water vapor, elemental nitrogen and nitrogen oxides, and sulfur oxides. Different absorbers are used in each instrument to remove undesirable products and separate the desired constituents. Eventually, after the gaseous separation, the nitrogen species is measured using thermal conductivity cell or an IR detector.

11.2.4 *Boat-inlet Combustion and Chemiluminescence Detection Method*—Test Method **D5762** can be used for determining nitrogen in liquid hydrocarbons, including petroleum process streams and lubricating oils in the nitrogen concentration range from 40 µg/g to 10 000 µg/g. In this test method, a hydrocarbon sample is placed in a sample boat at room temperature. The sample boat is advanced into a high-temperature combustion tube where the nitrogen is oxidized to nitric oxide (NO) in an oxygen atmosphere. The NO contacts ozone and is converted to excited nitrogen dioxide (NO₂). The light emitted as the excited NO₂ decays is detected by a photomultiplier tube, and the resulting signal is a measure of the nitrogen contained in the sample.

11.3 *Test Precision*—Based on various interlaboratory studies following precisions were found for the above test methods for nitrogen (**Table 5**).

12. Organic Chloride

12.1 *Significance*—Organic chlorides do not occur naturally in crude oil. If present they result from contamination in some manner, such as disposal of chlorinated solvent in many dewaxing pipelines or other equipment operations. Uncontaminated crude oil will not contain any detectable organic chloride, and most refineries can handle very small amounts without deleterious effects. Most trade contracts specify that no organic chloride be present in the crude oil. Several pipeline organizations have set specification limits at <1 mg/kg organic chlorides in the whole crude oil, and <5 mg/kg in the light naphtha, on the basis of the naphtha fraction being 20 % of the original sample (**3**).

12.1.1 Organic chloride species are potentially damaging to refinery process. Hydrochloric acid can be produced in hydrotreating or reforming reactors, and the acid accumulates in the condensing regions of the refinery. Unexpected concentrations of organic chlorides can be effectively neutralized and damage can result (**3**).

12.2 *Analysis*—In Test Methods **D4929**, crude oil distillation is performed to obtain the naphtha cut at 204 °C. 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). This is followed by two alternative test methods for the determination of organic chloride in the washed naphtha fraction as follows.

12.2.1 *Procedure A*—The washed naphtha fraction is treated with sodium biphenyl reagent in toluene. The free radical nature of this reagent promotes very rapid conversion of the organic halogen to inorganic halide. The excess reagent is decomposed, the mixture acidified, and the phases separated. The aqueous phase is evaporated to a small volume, acetone is added and the solution is titrated potentiometrically.

12.2.2 *Procedure B*—The washed naphtha fraction is combusted in a flowing tube at about 800 °C in a flow of oxygen plus an inert gas. The chlorine is converted to chloride and oxychlorides which then flow into a titration cell where they are titrated with silver nitrate solution coulometrically.

TABLE 5 Precision of Test Methods for Determination of Nitrogen in Crude Oils

NOTE 1—Where X is the average of the two test results.

NA: Not available

Test Method	Matrix	Repeatability	Reproducibility	ASTM Research Report ^A
D3228	Lubricating Oils Fuel Oils	0.01 % by mass 0.066 x m ^{0.5}	0.02 % by mass 0.190 x m ^{0.5}	NA NA
D4629	Liquid Hydrocarbons	0.1825 X ^{0.5149}	0.8094 X ^{0.5149}	RR:D02-1199 and RR:D02-1527
D5291	Petroleum Products	0.1670 0.006897(X + 3)	0.4456 0.02967 (X + 3)	RR:D02-1289 and RR:D02-1679
D5762	Liquid Hydrocarbons	0.087 X	0.266 X	RR:D02-1370 and RR:D02-1507

^A Supporting data have been filed at ASTM International Headquarters and may be obtained by contacting ASTM Customer Service at service@astm.org.

12.3 *Test Precision*—Following precision of the two procedures in Test Methods D4929 was obtained based on an interlaboratory study (RR:D02-1293).⁷

Test Method	A	B
Repeatability	0.32 (X + 0.33) ^{0.644}	1.01 (X - 0.17) ^{0.467}
Reproducibility	0.7 (X + 0.33) ^{0.644}	1.32 (X - 0.17) ^{0.467}

13. Salts

13.1 *Significance*—A knowledge of the salt content of crude oil is important in deciding whether or not the crude oil needs desalting. The efficiency of the desalter process can also be evaluated. Excessive chloride left in the crude oil frequently results in high corrosion rates in refining units, and also has detrimental effects on catalysts used in these units. The salt content of crude oils can be highly variable, and results principally from the production practices used in the field and to a lesser extent from its handling by tankers abroad, which transport crude oil to the terminals. The bulk of the salt present will be dissolved in co-existing free water and can be removed in desalters. But small amounts of salt may be dissolved in the crude oil itself (3).

13.1.1 Salt in crude oil may be deleterious in several ways. Even in small concentrations, salts will accumulate in stills, heaters, and exchangers, leading to fouling that leads to extensive cleanup. During flash vaporization of crude oils, certain metallic salts can be hydrolyzed to hydrochloric acid according to the following equations:



13.1.2 The hydrochloric acid evolved is extremely corrosive, necessitating the injection of a basic compound such as ammonia into the overhead lines to minimize damage (3).

13.2 *Analysis*—There are two test methods available for this analysis: D3230 Salts in Crude Oil (Electrometric Method) and D6470 Salts in Crude Oil (Potentiometric Method). Samples of crude oil contain water and sediment and are inhomogenous by nature. Homogenization of crude oil is an important step in either of these two test procedures. Samples of very viscous crude oils may have to be warmed until they are reasonably fluid before they are sampled. However, no samples shall be heated more than necessary to lower the viscosity to a manageable level.

13.2.1 *Test Method D3230*—This test method measures conductivity in the crude oil due to the presence of common chlorides, such as sodium, calcium, and magnesium. Other conductivity materials may also be present in the crude oil. A homogenized test specimen of crude oil 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.

13.2.2 *Test Method D6470*—After homogenizing 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. A portion of the aqueous extract is analyzed for total halides by potentiometric titration.

13.2.3 Results by Test Method D3230 are expressed in units of mg/kg. Alternatively, they can also be reported in units of g/m³ or as lb/1000 bbl (a common industry reporting practice), if so required. Results by Test Method D6470 are reported as mass %. The result units can be converted by formula given below:

$$\text{Salt, mg/kg} = (1000 X) / d \quad \text{or} \quad (3)$$

$$\text{Salt, mg/kg} = 2.853 Y/d \quad (4)$$

where:

- X = measured salt concentration in g/m³,
- Y = measured salt concentration in PTB, and
- D = specimen density at 15 °C in kg/m³.

13.3 *Test Method Precision*—Based on interlaboratory studies following precisions have been obtained for the above two test methods (Table 6).

13.3.1 *Test Method Bias*—Since salt content of crude oil is defined only in terms of these tests, and since there are no standard reference materials available for such analysis, no statement regarding bias of these test methods can be made.

13.3.2 In one study (RR:D02-1470)⁷ the samples were near desalted crudes, spiked with known quantities of salt (as sea water and formation water), bias might be defined as percent recovery of added halides. Over the range from 5 g/m³ to 500 g/m³ (1.5 PTB to 150 PTB) salt added, the recovery proved to be approximately constant and averaged 93 % for D3230 test method. In a similar study (RR:D02-1458),⁷ over the range 0.0005 % to 0.0400 % by mass salt added, the recovery proved to be constant and averaged 97 % for D6470 test method. Over the range 0.0400 to 0.1500, the recovery proved to be a function of concentration and gradually decreased from 97 % at 0.04 % by mass to 88 % at the 0.15 % by mass level.

14. Sulfur

14.1 *Significance*—Perhaps the largest amount of data collected in the analysis of crude oils is for sulfur. This is

TABLE 6 Precision of Test Methods for Salt Content of Crude Oils

NOTE 1—Where:
 X = the average of two test results in mg/kg (for D3230) and in mass % (for D6470)
 Y = the average of two test results in lb/1000 bbl (PTB)

Parameter	D3230	D6470
Scope	0 mg/kg to 500 mg/kg or 0 lb/1000 bbl to 150 lb/1000 bbl	0.0005 % to 0.15 % m/m
Repeatability	0.3401 X ^{0.75} mg/kg or 0.2531 Y ^{0.75} lb/1000 bbl	0.0243 X ^{0.612} % by mass
Reproducibility	2.7803 X ^{0.75} mg/kg or 2.069 Y ^{0.75} lb/1000 bbl	0.0477 X ^{0.612} % by mass
ASTM Re- search Re- port ^a	RR:D02-1470	RR:D02-1458

^a Supporting data have been filed at ASTM International Headquarters and may be obtained by contacting ASTM Customer Service at service@astm.org.

appropriate given the importance of sulfur chemistry and its effect on utilizing crude oil in the industry. The sulfur content of crude oils can vary from less than 0.1 % by mass to over 5 % by mass. Chapter 23 in Ref (2), Chapter 7 in Ref (6), and Chapter 5 in Ref (7) have covered various aspects of occurrence and analysis of sulfur in petroleum products, fuels, and lubricants.

14.1.1 Sulfur compounds are some of the most egregious non-hydrocarbon materials present in crude oils. They contribute to corrosion of refinery equipment, poisoning of catalysts, cause corrosiveness in refined products, and contribute to environmental pollution through emission of sulfur oxides from combustion of fuel products (1, 3).

14.2 *Analysis*—As to be expected, a large number of test methods for sulfur determination in petroleum products and lubricants have been issued by ASTM (7, 8). Many of the earlier test methods such as D129 or D1552 have been superseded by modern instrumental test methods such as D2622, or D4294 based on X-ray fluorescence technology. Protocol for using XRF analyzers has been described in Guide D7343.

14.2.1 *Test Method D129*—This is a much older test method involving combustion of a sample in an oxidation bomb with subsequent gravimetric determination of sulfur as barium sulfate. This is not as accurate a method as Test Method D1552, partially because of interference from the sediment inherently present in crude oil.

14.2.2 *Test Method D1552*—This test method uses combustion of the sample in oxygen to convert the sulfur to sulfur dioxide, which is collected and subsequently detected by non-dispersive infrared (IR) spectroscopy.

14.2.3 *Test Method D2622*—This test method is widely used in the industry for analysis of a wide variety of petroleum and lubricant products including crude oils. A fundamental assumption of this test method is that the standard and sample matrices are well matched, or that the matrix differences are accounted for. Matrix mismatch can be caused by C/H ratio differences between samples and standards or by the presence of other interfering heteroatoms or species. However, as far as crude oils are concerned, none of the expected interfering elements are present in them. A typical analysis time is 1 min to 2 min per sample.

14.2.3.1 In this test method employing wavelength dispersive X-ray fluorescence (WD-XRF), a sample is placed in the X-ray beam, and the peak intensity of the sulfur K α line at 0.5373 nm is measured. The background intensity, measured at a recommended wavelength of 0.5190 nm for chromium or scandium target tubes (or 0.5437 nm for a rhodium target tube) is subtracted from the peak intensity. The resultant net counting rate is then compared to a previously prepared calibration curve or equation to obtain the concentration of sulfur in milligrams per kilogram or mass percent. Usually high-purity di-n-butyl sulfide of known sulfur content is used as a calibrant.

14.2.3.2 When this test method is applied to petroleum materials with matrices significantly different from the white oil calibration material specified in this test method, results should be interpreted with caution with regards to interferences.

In general, petroleum materials with compositions that vary from white oils can be analyzed with standards made from base materials that are of the same or similar composition.

14.2.4 *Test Method D4294*—This test method employing energy-dispersive X-ray fluorescence (ED-XRF) technique is also widely used in the oil industry for determination of sulfur. Reservations similar to those described in 14.2.3 and 14.2.3.2 regarding test interferences apply to this test method also. However, the D4294 instrumentation is far less expensive than the one required for Test Method D2622.

14.2.4.1 In this test method, a sample is placed in the beam emitted from an X-ray tube. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with counts from previously prepared calibration samples to obtain the sulfur concentration. A typical analysis time is 1 min to 5 min per sample. High-purity di-n-butyl sulfide of known sulfur content is used as the calibrant material. A minimum of three groups of calibration samples are required to span the concentration range of sulfur from 0.0 % to 5.0 % by mass. See Practice D7343 for protocol used for XRF analysis of petroleum products.

14.2.5 In both above XRF test methods, interferences from other inorganic elements present in crude oil need to be taken into consideration. Modern built-in software often can take care of required corrections. Sediment, water and waxes commonly present in crude oil samples can settle onto the Mylar™ film used for sealing the test cup and interfere in sulfur determination. Before analysis, water and particulates should be removed from the samples by centrifuging or settling, but care must be taken that the sample integrity is not compromised (1, 3).

14.3 *Test Method Precision*—Through a number of inter-laboratory studies following precisions have been established for the above four sulfur test methods (Tables 7 and 8).

14.3.1 Following precision is given for analysis of petroleum products by Test Methods D129 and D1552. It is not clear whether crude oils were included in this estimation (RR:D02-1278⁷ and RR:D02-1231,⁷ respectively).

14.3.2 The bias in using Test Methods D2622 and D4294 were studied using NIST crude oil standard reference materials (SRMs) and is shown in Table 9. No bias was evident for SRM 2721 for either of the two test methods as shown in Table 9. But a small bias was found for SRM 2722, perhaps because of the smaller amount of sulfur present in it.

TABLE 7 Precision of D129 and D1552 Test Methods for Sulfur

Sulfur, mass %	Repeatability		Reproducibility	
	D129 ^A	D1552	D129 ^A	D1552
0.1 to 0.5	0.04	0.04	0.05	0.13
0.5 to 1.0	0.06	0.07	0.09	0.21
1.0 to 1.5	0.08		0.15	
1.0 to 2.0		0.09		0.27
1.5 to 2.0	0.12		0.25	
2.0 to 3.0		0.12		0.38
3.0 to 4.0		0.13		0.44
2.0 to 5.0	0.18		0.27	
4.0 to 5.0		0.16		0.49

^A Equivalent IP method 61 gives a repeatability of 0.016 X + 0.06 and a reproducibility of 0.037 X + 0.13, where X is the mean of duplicate analysis, in percent mass.

TABLE 8 Precision of Sulfur Test Methods for Crude Oil Analysis by XRF

NOTE 1—Where X is the sulfur concentration in mg/kg.

Test Method	Concentration Range	PLOQ (per D6259)	Repeatability, mg/kg	Reproducibility, mg/kg	ASTM Research Report ^A
D2622	3 mg/kg – 4.6 mass %	3 mg/kg	0.1462 X ^{0.8015}	0.4273 X ^{0.8015}	RR:D02-1622
D4294	17 mg/kg – 4.6 mass %	16.0 mg/kg	0.4347 X ^{0.6446}	1.9182 X ^{0.6446}	RR:D02-1635

^A Supporting data have been filed at ASTM International Headquarters and may be obtained by contacting ASTM Customer Service at service@astm.org.

TABLE 9 Analysis of NIST Crude Oil SRMs for Sulfur

Parameter	NIST SRM 2721		NIST SRM 2722	
	D2622	D4294	D2622	D4294
NIST Sulfur Value, mg/kg	15 832	15 832	2104	2104
Average Measured, mg/kg	15 884	16 118	2054	2082
Measured Reproducibility, mg/kg	1170	988.4	181	264.2
Measured Bias, mg/kg	54	+288	-49	-21
Relative Measured Bias, %	0.34	1.82	-2.33	-1

15. Trace Metals

15.1 *Significance*—Besides sulfur and nitrogen, there are several inorganic elements present in crude oils at varying levels. As many as 45 elements have been reported to be present in crude oils. Their presence can have adverse effect on petroleum refining such as catalyst poisoning in the refinery, product quality and the environment. 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 (1, 3). Some organometallic compounds are volatile which can lead to the contamination of distillate fractions, and a reduction in their stability or malfunctions of equipment when they are combusted. It is widely accepted that trace elements are present in crude oil as porphyrins and non-porphyrin complexes.

15.2 *Analysis*—The most commonly analyzed trace elements in crude oils are nickel, vanadium, iron, sodium, and mercury. See Section 10 regarding discussion about mercury analysis. Two principal test methods used for multielement analysis of crude oil are Test Methods D5708, D5863, and D7691. While Test Method D5863 uses atomic absorption spectrometry (AAS) for measurements, the other two Test Methods D5708 and D7691 use inductively coupled plasma atomic emission spectrometry (ICP-AES). Both are widely used atomic spectrometric measurement techniques in the oil industry, and have been discussed in Practices D7260 (for ICP-AES) and D7740 (for AAS).

Test Method	Technique	Analytes	ASTM Research Report
D5708	ICP-AES	Ni, V, and Fe	RR:D02-1351
D5863	AAS	Ni, V, Fe, and Na	RR:D02-1351
D7691	ICP-AES	Ni, V, Fe, and S	RR:D02-1761

15.2.1 *Test Method D5708*—There are two procedures in this method. Method A analyzes a sample dissolved in an organic solvent and uses oil-soluble metals for calibration. In Method B the sample is decomposed with concentrated sulfuric acid before measurement in an aqueous solution. The measurement technique in both procedures is ICP-AES.

15.2.2 *Test Method D5863*—This test method also has two procedures. Method A uses flame AAS after a sample is decomposed with concentrated sulfuric acid for the determination of total nickel, vanadium, and iron. Method B uses a sample diluted in an organic solvent for measurement of nickel, vanadium, and sodium. The measurement technique in both procedures is flame AAS.

15.2.3 *Test Method D7691*—This test method utilizes ten-fold dilution of a thoroughly homogenized crude oil sample with mixed xylenes, kerosene, or other suitable solvent. An internal standard is added to the solutions to compensate for variations in test specimen introduction efficiency. The elements of interest are measured by ICP-AES. This work has been published in reference (12). Besides the four elements for which precision is given in Table 10 for this test method, a number of other trace elements were looked for in the analysis protocol. This included aluminum, boron, barium, calcium, chromium, copper, potassium, magnesium, manganese, molybdenum, sodium, phosphorus, lead, silicon, and zinc. Although ICP-AES technique is capable of detecting all of these elements, in the suite of crude oils analyzed in this study, none of them were detected.

15.2.3.1 *Test Methods D5708 and D5863* determine the elements either by straight organic solvent dilution or alternatively by first decomposing the matrix with concentrated sulfuric acid. It has been speculated that since organic solvent dilution may not dissolve particulates in the crude oil, this technique may give lower results and may not account for the total metal contents of elements. However, based on data obtained in ASTM Proficiency Testing Programs on crude oils, it is not clear that organic solvent dilution techniques would necessarily give lower results than those obtained using acid decomposition techniques (2, 12).

15.3 *Test Method Precision*—The precisions obtained for these three atomic spectroscopic test methods for metal analysis are given in Table 10.

16. Quality Control

16.1 It is recommended that each laboratory establish a program to ensure that the measurement system described in these test methods are in statistical control. One part of such a program might be the regular use of control charting of quality control samples. It is recommended that at least one type of quality control (QC) sample be analyzed that is representative of the typical laboratory samples. Further guidance on quality control charting and their interpretation can be found in Practices D6299 and D6792.

16.2 Stable petroleum product samples should be used as representative quality control samples. Suitable QC samples can be prepared by combining retains of typical samples of

TABLE 10 Precision of Atomic Spectroscopic Test Methods for Metal Analysis of Crude Oils

NOTE 1—Where X is the mean concentration in mg/kg.

Test Method	Element	Concentration Range, mg/kg	Repeatability	Reproducibility
D5708 A	Vanadium	50 – 500	0.07 X ^{0.88}	0.12 X ^{1.1}
D5708 B			0.02 X ^{1.1}	0.10 X ^{1.1}
D5708 A	Nickel	10 – 100	0.01 X ^{1.3}	0.41 X ^{0.78}
D5708 B			0.02 X ^{1.2}	0.05 X ^{1.3}
D5708 A	Iron	1 – 10	0.22 X ^{0.30}	0.68 X ^{0.35}
D5708 B			0.23 X ^{0.67}	0.91 X ^{0.51}
D5863 A	Vanadium	50 – 500	1.1 X ^{0.50}	0.33 X ^{0.90}
D5863 B			0.13 X ^{0.92}	1.2 X ^{0.80}
D5863 A	Nickel	10 – 100	0.20 X ^{0.65}	1.3 X ^{0.53}
D5863 B			0.005 X ^{1.4}	0.06 X ^{1.2}
D5863 A	Iron	3 – 10	0.98	1.45 X ^{0.45}
D5863 B	Sodium	1 – 20	0.12 X	0.69 X
D7691	Iron	1 – 40	0.1885 X ^{0.9145}	0.5649 X ^{0.9145}
	Nickel	1 – 100	0.1764 X ^{1.0168}	1.1389 X ^{0.7085}
	Sulfur	400 – 50 000	0.01971 X ^{1.1606}	0.06360 X ^{1.1606}
	Vanadium	1 – 1000	0.0392 (X+0.7485) ^{0.8668}	0.8628 (X+0.7485) ^{0.8668}

known sulfur concentration, if they are stable. Retains of D02.92 Proficiency Testing Programs of crude oil are available at a small cost from ASTM Proficiency Testing Program (PTP) office. They can be utilized in such a QC program in the laboratory.

16.3 Additionally, the QC program can also use Standard Reference Materials available from National Institute of Science and Technology (NIST). Some of the crude oil materials available from NIST are listed in Table 11. See the NIST website for detailed information about the analysis and availability of the SRMs.⁸

16.3.1 NIST certifies sulfur concentration in their SRMs using WD-XRF method ISO 14596 with zirconium as internal standard and isotope dilution—inductively coupled plasma mass spectrometry after microwave digestion of the sample.

17. Proficiency Testing Programs

17.1 For last several years, D02.92 has conducted a large number of proficiency testing programs (PTP) for a number of petroleum products and lubricants. Crude oil PTPs were initiated in 2000 and currently have 294 laboratories world-

wide participating in them. The crosschecks are conducted every March, July, and November. Among several analyses conducted in this program include elemental analysis Test Methods D5708 and D5863 for vanadium, nickel, and iron, Test Methods D4629 and D5762 for nitrogen, Test Methods D3230 and D6470 for salt, and Test Methods D2622 and D4294 for sulfur. Protocol for conducting PTP crosschecks is described elsewhere (13) and interpreting the PTP results is described in Guide D7372 and in Ref (14).

17.2 Examples of crude oil PTP results from 2015 cycle are given in Table 12. Generally, alternative test methods for the same parameter give equivalent results, for example, sulfur by Test Methods D2622 or D4294, nitrogen by Test Methods D4629 or D5762, iron, nickel, and vanadium by Test Methods D5798 A, D5708 B, D5863 A, or D5863 B. See Table 13 for a comparison of Test Performance Index (TPI_{Industry}) for these analyses. TPI is an approximate measure of a laboratory's testing capability defined by a calculated value of ratio of calculated ASTM test method reproducibility to site precision. TPI_{Industry} calculation is based on the ratio of the test method reproducibility to the robust reproducibility of the program data. These calculation routines are described in Guides D6792 and D7372. Usually TPI values less than 1 may be cause for concern regarding the performance of the laboratories involved

⁸ Available from National Institute of Standards and Technology (NIST), 100 Bureau Drive, Stop 1070, Gaithersburg, MD 20899-1070, <http://www.nist.gov>.

TABLE 11 Crude Oils Standard Reference Materials from NIST

SRM #	Description	Sulfur Concentration	Other Elements
2721	Light sour crude oil	1.5832 % ± 0.0044 % by mass	Mercury: 0.0417 µg/kg ± 0.0057 µg/kg Carbon: 84.6 % by mass Hydrogen : 11.8 % by mass
2722	Heavy sweet crude oil	0.21037 % ± 0.00084 % by mass	Mercury: 0.129 µg/kg ± 0.013 µg/kg Carbon: 85.9 % by mass Hydrogen: 11.9 % by mass
RM 8505	Crude Oil		Vanadium: 390 mg/kg ± 10 mg/kg

TABLE 12 Crude Oil Proficiency Testing Program Results for 2015

NOTE 1—Results are expressed as Robust Mean \pm Robust Standard Deviation (Valid Results).
 NA: Not available.

Analysis	Test Method	CO 1503	CO 1507	CO 1511
Sulfur, % by mass	D2622	0.969 \pm 0.031 (34)	3.715 \pm 0.118 (32)	0.579 \pm 0.028 (34)
	D4294	0.988 \pm 0.024 (167)	3.837 \pm 0.098 (168)	0.601 \pm 0.020(162)
Salts, mg/kg	D3230	6.98 \pm 2.14 (94)	20.971 \pm 9.166 (94)	82.99 \pm 48.8 (83)
	D6470	NA (4)	NA (4)	364.1 \pm 51.4 (7)
Nitrogen, mg/kg	D4629	1391.8 \pm 328.6 (34)	2542.1 \pm 953.0 (38)	1697.8 \pm 575.3 (42)
	D5762	1563.6 \pm 238.0 (54)	3053.0 \pm 576.2 (54)	1947.1 \pm 313.1 (58)
Chloride ,mg/kg	D4929 B	0.69 \pm 0.68 (8)	0.20 \pm 0.17 (11)	0.29 \pm 0.32 (12)
Iron, mg/kg	D5708 A	0.749 \pm 0.158 (39)	0.843 \pm 0.338 (37)	9.82 \pm 4.37 (51)
	D5708 B	1.166 \pm 0.474 (39)	1.672 \pm 0.427 (32)	16.83 \pm 6.40 (40)
	D5863 A	1.72 \pm 0.81 (21)	2.24 \pm 0.81 (17)	15.82 \pm 6.47 (19)
Nickel, mg/kg	D5708 A	11.29 \pm 1.56 (44)	56.46 \pm 5.22 (48)	9.84 \pm 1.30 (51)
	D5708 B	10.515 \pm 1.311 (42)	56.245 \pm 4.622 (39)	7.59 \pm 1.93 (40)
	D5863 A	11.23 \pm 1.43 (26)	57.75 \pm 7.03 (18)	7.87 \pm 1.21 (16)
	D5863 B	12.12 \pm 1.72 (20)	60.97 \pm (7.78) (17)	9.61 \pm 1.93 (20)
Vanadium,mg/kg	D5708 A	26.73 \pm 2.67 (47)	306.70 \pm 43.50 (50)	15.53 \pm 1.81 (51)
	D5708 B	24.692 \pm 2.235 (42)	301.005 \pm 19.281 (37)	13.94 \pm 1.43 (38)
	D5863 A	22.514 \pm 3.318 (24)	284.8 \pm 40.115 (19)	13.77 \pm 1.04 (13)
	D5863 B	26.92 \pm 3.64 (22)	295.94 \pm 21.39 (18)	16.72 \pm 4.10 (10)

TABLE 13 Test Performance Indices for 2015 Crude Oil PTP Analyses

NOTE 1—NA: Not Available.

Analysis	Test Method	CO 1503	CO 1507	CO 1511
Sulfur	D2622	0.78	0.60	0.56
	D4294	1.00	0.64	0.95
Salts	D3230	1.50	0.80	0.42
	D6470	NA	NA	0.44
Nitrogen	D4629	27.1 ^A	57.6 ^A	NA
	D5762	0.63	0.51	0.60
Chloride	D4929 B	0.53	0.55	0.55
Iron	D5708 A	0.72	1.46	0.12
	D5708 B	0.75	1.00	NA
	D5863 A	1.21	1.08	NA
Nickel	D5708 A	0.63	0.66	NA
	D5708 B	0.29	0.74	NA
	D5863 A	1.18	0.57	NA
	D5863 B	0.25	0.39	NA
Vanadium	D5708 A	1.66	0.54	NA
	D5708 B	1.82	1.00	NA
	D5863 A	1.69	0.48	NA
	D5863 B	0.60	1.92	NA

^A Results for nitrogen determination by D4629 needed a sample dilution and ASTM did not publish a TPI value.

in the cross check. Thus, the low TPIs in Table 13 would indicate laboratories determining sulfur (D2622 and D4294), nitrogen (D5762), organic chlorine (D4929), and metals by both test methods (D5708 and D5863) need improvement in their performance.

18. Future Directions

18.1 A number of areas remain of interest for further elemental characterization of crude oils. Some areas that have been suggested for future work in elemental analysis of crude

oils are described below. For several of these items, interlaboratory studies have already started (18.4 through 18.9).

18.2 *Mercury Speciation*—There is substantial evidence 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 (1, 3). It would be desirable to have specific test methods to differentiate these mercury species.

18.3 *Selenium Speciation*—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 (1, 3). 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(0)], and selenocyanate [SeCN⁻] have all been observed in wastewaters. In this study, analyzing 16 different crude oils total concentration of selenium was found to range from < 10 to 960 µg/kg (15). At present there are no ASTM test method(s) for the determination of selenium or its species in crude oil.

18.4 *Other Trace Elements*—A number of trace elements are now customarily included in the crude oil assay. Among these are calcium, copper, iron, mercury, nickel, selenium, sodium, and vanadium. The suite of elements will be dictated by refinery processes, product slate, regulations and environmental considerations (1). Analysis of some of these elements is mentioned above in this guide. Some alternative test methods desirable for a suite of elements could be extending ICP-AES Test Method D5185, which can determine a large number of trace elements but has not been applied to crude oils. X-ray fluorescence spectrometry is not usually used for analyzing metals in crude oils given that the matrix effects could be a problem due to the presence of water and sediment in the samples.

18.5 *Multiple Elements by XRF*—A study has been proposed to determine a suite of sulfur, chlorine, nickel, vanadium, iron, and calcium in crude oils and residual fuels using PBMS protocol. The samples will include sweet, sour, fracking, and residual crude oils.

18.6 *Chlorine*—An extension of Test Methods D4929 for this analysis is being pursued using WD-XRF, ED-XRF, and MWD-XRF as alternative measurement techniques. Using the sample preparation technique given in Test Methods D4929, the crude oil samples will be first distilled to separate organic chlorine, and then determine the analyte with different XRF techniques.

18.7 *Multi-element Analysis* using HD-XRF technique has been proposed. A ruggedness study has shown promising data for a number of samples for typical elements sulfur, chlorine, nickel, vanadium, iron, and calcium.

18.8 *Halide by Combustion Ion Chromatography*—An alternative measurement technique will be used after distillation of crude oil fractions by Test Methods D4929, and subsequently determine chloride, bromide, fluoride, and possibly sulfate by aqueous ion chromatography.

18.9 *Microwave Plasma for Atomic Emission Spectroscopy*—As an alternative to argon generated plasma, this technique uses nitrogen from air to generate the plasma. Axial magnetic and radial electrical fields sustain the nitrogen plasma into which an aerosol of a sample diluted in 0-xylene is introduced. Promising preliminary results have been obtained for the determination of iron, nickel, vanadium, calcium, sodium, and potassium in crude oils.

18.10 *Trace Elements using ICP-MS*—Several oil industry laboratories have been using this technique for many years for the determination of very low levels of trace elements in crude oils. A review of this area based on about 30 research papers has been published by Hwang (16). This work is being undertaken in the Subcommittee D02.03 on Elemental Analysis of Petroleum Products and Lubricants.

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