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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- D1548 Test Method for Vanadium in Heavy Fuel Oil¹ (Withdrawn 1997)³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.