



Designation: D4929 – 19a

Standard Test Method for Determination of Organic Chloride Content in Crude Oil¹

This standard is issued under the fixed designation D4929; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope*

1.1 The procedures in this test method cover the determination of organic chloride (above 1 $\mu\text{g/g}$ organically-bound chlorine) in crude oils, using either distillation and sodium biphenyl reduction, distillation and microcoulometry, or distillation and X-ray fluorescence (XRF) spectrometry.

1.2 The procedures in this test method involve the distillation of crude oil test specimens to obtain a naphtha fraction prior to chloride determination. The chloride content of the naphtha fraction of the whole crude oil can thereby be obtained. See Section 5 regarding potential interferences.

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

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

1.5 Procedure C covers the determination of organic chloride in the washed naphtha fraction of crude oil by X-ray fluorescence spectrometry.

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

1.6.1 The preferred concentration units are micrograms of chloride per gram of sample, though milligrams of chloride per kilogram of sample is commonly used for Procedure C.

1.7 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recom-*

mendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:²

D86 Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure

D1193 Specification for Reagent Water

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

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

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants

D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

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

3. Summary of Test Method

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

3.2 There are three alternative procedures for determination of the organic chloride in the washed naphtha fraction, as follows.

¹ This test method is under the jurisdiction of ASTM Committee **D02** on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee **D02.03** on Elemental Analysis.

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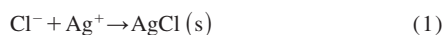
² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

*A Summary of Changes section appears at the end of this standard

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

3.2.2 Procedure B, Combustion and Microcoulometry—The washed naphtha fraction of a crude oil specimen is injected into a flowing stream of gas containing about 80 % oxygen and 20 % inert gas, such as argon, helium, or nitrogen. The gas and sample flow through a combustion tube maintained at about 800 °C. The chlorine is converted to chloride and oxychlorides, which then flow into a titration cell where they react with the silver ions in the titration cell. The silver ions thus consumed are coulometrically replaced. The total current required to replace the silver ions is a measure of the chlorine present in the injected samples.

3.2.3 The reaction occurring in the titration cell as chloride enters is as follows:



3.2.4 The silver ion consumed in the above reaction is generated coulometrically thus:



3.2.5 These microequivalents of silver are equal to the number of microequivalents of titratable sample ion entering the titration cell.

3.2.6 Procedure C, X-ray Fluorescence Spectrometry—The washed naphtha fraction of a crude oil specimen is placed in the X-ray beam, and the peak intensity of the chlorine K α line is measured by monochromatic wavelength dispersive X-ray fluorescence (MWDXRF), monochromatic energy dispersive X-ray fluorescence (MEDXRF), or energy dispersive X-ray fluorescence (EDXRF) spectrometry. The resulting net counting rate is then compared to a previously prepared calibration curve or equation to obtain the concentration of chlorine in mg/kg.

4. Significance and Use

4.1 Organic chlorides do not occur naturally in crude oil. When present, they result from contamination in some manner, such as disposal of chlorinated solvent used in many dewaxing pipeline or other equipment operations.

4.1.1 Uncontaminated crude oil will contain no detectable organic chloride, and most refineries can handle very small amounts without deleterious effects.

4.1.1.1 Most trade contracts specify that no organic chloride is present in the crude oil.

4.1.2 Several pipelines have set specification limits at <1 mg/kg organic chlorides in the whole crude, and <5 mg/kg in the light naphtha, on the basis of the naphtha fraction being 20 % of the original sample.

4.1.2.1 To ensure <1 mg/kg organic chloride in the crude oil, the amount measured in the naphtha fraction shall be <1/f (where f is the naphtha fraction calculated with Eq 3).

4.1.3 Organic chloride present in the crude oil (for example, methylene chloride, perchloroethylene, etc.) is usually distilled into the naphtha fraction. Some compounds break down during fractionation and produce hydrochloric acid, which has a corrosive effect. Some compounds survive fractionation and are destroyed during hydro-treating (desulfurization of the naphtha).

4.2 Other halides can also be used for dewaxing crude oil; in such cases, any organic halides will have similar impact on the refining operations as the organic chlorides.

4.3 Organic chloride species are potentially damaging to refinery processes. Hydrochloric acid can be produced in hydrotreating or reforming reactors and the acid accumulates in condensing regions of the refinery. Unexpected concentrations of organic chlorides cannot be effectively neutralized and damage can result. Organic chlorides are not known to be naturally present in crude oils and usually result from cleaning operations at producing sites, pipelines, or tanks. It is important for the oil industry to have common methods available for the determination of organic chlorides in crude oil, particularly when transfer of custody is involved.

5. Interferences

5.1 Procedure A—Other titratable halides will also give a positive response. These titratable halides include HBr and HI.

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

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

5.3 Procedure C—X-ray fluorescence spectrometry techniques may have interferences due to high sulfur content and matrix effects due to differences in the carbon-hydrogen ratio.

5.3.1 Matrix effects result when the elemental composition (excluding chlorine) of samples differs significantly from the standards, and significant errors in the chlorine determination can result. For example, differences in the carbon-hydrogen ratio of sample and calibration standards introduce errors in the determination.

5.3.2 In general, naphthas with compositions that vary from white oils as specified in 27.1 can be analyzed with standards made from base materials that are of the same or similar composition. A base material for naphtha may be simulated by mixing *isooctane* and toluene in a ratio that approximates the expected aromatic content of the samples to be analyzed.

5.3.3 Naphtha samples may contain high amounts (≥ 0.5 mass %) of sulfur leading to significant absorption of chlorine K α radiation and low chlorine results. Such samples can, however, be analyzed using this test method provided either that the calibration standards are prepared to match the matrix of the sample or correction factors are applied to the results. In some cases, dilution of samples with sulfur-free and

chlorine-free oil can be used to reduce the effect. The main disadvantage is, however, that dilution also lowers the amount of chlorine in the specimen. Make sure that in the diluted specimen, the chlorine content is higher than 1 mg/kg before resorting to dilution.

5.3.4 Matrix matching requires the knowledge of typical sulfur concentration in the naphtha sample and preparing calibration standards, which contain a similar sulfur concentration. This technique is not applicable for naphtha samples with an unknown or differing sulfur content than the calibration samples.

5.3.5 Sulfur correction factors are typically applied by using the software and algorithms supplied by the equipment vendor and typically uses one of the following forms: manual input of sulfur concentration followed by automatic correction, direct measurement of sulfur followed by automatic correction, correction by use of Compton scattering, and correction by applying fundamental parameters. Follow manufacturer's instructions for application of sulfur correction factors and when to apply those factors.

6. Purity of Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type III of Specification **D1193**.

DISTILLATION AND CLEANUP PROCEDURE

7. Apparatus

7.1 *Round-Bottom Boiling Flask*, borosilicate, 1 L, single short neck with 24/40 outer ground-glass joint.

7.2 *Tee Adapter*, borosilicate, 75° angle side-arm, 24/40 ground-glass joints.

7.3 *Thermometer*, ASTM thermometer 2C (−5 °C to 300 °C) or 2F, (20 °F to 580 °F).

7.3.1 Other temperature measuring devices, such as thermocouples or resistance thermometers, may be used when the temperature reading obtained by these devices is determined to produce the same naphtha fraction that is obtained when mercury-in-glass thermometers are used.

7.4 *Thermometer Adapter*, borosilicate, 24/40 inner ground-glass joint.

7.5 *Liebig Condenser*, borosilicate, 300 mm length, 24/40 ground-glass joints.

7.6 *Vacuum Take-Off Adapter*, borosilicate, 105° angle bend, 24/40 ground-glass joints.

7.7 *Receiving Cylinder*, borosilicate, 250 mL capacity, 24/40 outer ground-glass joint.

7.8 *Wire Clamps*, for No. 24 ground-glass joints, stainless steel.

7.9 *Receiver Flask*, for ice bath, 4 L.

7.10 *Copper Tubing*, for heat exchanger to cool condenser water, 6.4 mm outside diameter, 3 m length.

7.11 *Electric Heating Mantle*, Glas-Col Series 0, 1 L size, 140 W upper heating element, 380 W lower heating element.

7.12 *Variacs*, 2, for temperature control of upper and lower heating elements, 120 V, 10 amps.

8. Reagents and Materials

8.1 *Acetone*, chloride-free. (**Warning**—Extremely flammable, can cause flash fires. Health hazard.)

8.2 *Caustic Solution*, 1 M potassium hydroxide (**Warning**—Can cause severe burns to skin.) prepared in distilled/deionized water.

8.3 *Distilled/Deionized Water*.

8.4 *Filter Paper*, Whatman No. 41 or equivalent.

8.5 *Stopcock Grease*.^{4,5}

8.6 *Toluene*, chloride-free. (**Warning**—Flammable. Health hazard.)

9. Sampling

9.1 Obtain a test unit in accordance with Practice **D4057** or **D4177**. To preserve volatile components, which are in some samples, do not uncover samples any longer than necessary. Samples should be analyzed as soon as possible, after taking from bulk supplies, to prevent loss of organic chloride or contamination due to exposure or contact with sample container. (**Warning**—Samples that are collected at temperatures below room temperature may undergo expansion and rupture the container. For such samples, do not fill the container to the top; leave sufficient air space above the sample to allow room for expansion.)

9.2 If the test unit is not used immediately, then thoroughly mix in its container prior to taking a test specimen. Some test units can require heating to thoroughly homogenize. (**Warning**—When heating is required, care should be taken so that no organic chloride containing hydrocarbons are lost.)

³ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

⁴ The sole source of supply of the stop-cock grease known to the committee at this time is Dow Corning silicone, available from Dow Corning Corporation, Corporate Center, PO Box 994, Midland, MI.

⁵ If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, ¹ which you may attend.

10. Preparation of Apparatus

10.1 Clean all glassware by rinsing successively with toluene and acetone. After completing the rinse, dry the glassware using a stream of dry nitrogen gas. Obtain and record the masses of the round-bottom flask and receiving cylinder. Assemble the glass distillation apparatus using stopcock grease to seal all joints and wire clamps to prevent loosening of the joints. Adjust the thermometer position within the adapter tee such that the lower end of the capillary is level with the highest point on the bottom of the inner wall of the adapter tee section that connects to the condenser.

NOTE 1—A diagram illustrating the appropriate positioning of the thermometer can be found in Test Method **D86**.

10.2 Form the copper tubing into a coil to fit inside the receiver flask, leaving room in the center of the flask for the receiving cylinder. With the PVC tubing, connect one end of the copper coil to the water source, and connect the other end of the coil to the lower fitting of the Liebig condenser cooling jacket. Connect the upper condenser fitting to the water drain. Fill the receiver flask with an ice/water mixture, and turn on the water. Maintain the temperature of the condenser below 10 °C.

11. Procedure

11.1 Add a 500 mL crude oil test specimen to tared round bottom flask. Obtain and record the mass of the crude oil-filled flask to the nearest 0.1 g. Connect the flask to the distillation apparatus. Place the heating mantle around the flask, and support the heating mantle/flask from the bottom. Connect the heating mantle to the variacs. Turn on the variacs and start the distillation. During the distillation, adjust the variac settings to give a distillation rate of approximately 5 mL/min. Continue the distillation until a thermometer reading of 204 °C (400 °F) is attained. When the temperature reaches 204 °C (400 °F), end the distillation by first disconnecting and removing the receiving cylinder. After the receiving cylinder has been removed, turn off the variacs and remove the heating mantle from the flask. Obtain and record the mass of the receiving cylinder and distillate.

11.1.1 The precision and bias statements were determined using mercury-in-glass thermometers only. Therefore, when alternate temperature measuring devices are used, the cut-off temperature so obtained shall be that which will produce a naphtha cut similar to what would be yielded when mercury-in-glass thermometers are used. Such alternate temperature measuring devices shall not be expected to exhibit the same temperature lag characteristics as mercury-in-glass thermometers.

11.2 Transfer the naphtha fraction from the receiving cylinder to the separatory funnel. Using the separatory funnel, wash the naphtha fraction three times with equal volumes of the caustic solution (1 M KOH). Follow the caustic wash with a water wash, again washing three times with equal volumes. The caustic wash removes hydrogen sulfide, while the water wash removes traces of inorganic chlorides either originally present in the crude or from impurities in the caustic solution. After the washings are complete, filter the naphtha fraction to remove residual freestanding water. Store the naphtha fraction

in a clean glass bottle. This naphtha fraction can now be analyzed for organic chlorides by either sodium biphenyl, combustion/microcoulometric techniques, or X-ray fluorescence spectrometry.

11.3 Measure the density of the crude oil specimen and the naphtha fraction by obtaining the mass of 10.0 mL (using a 10 mL volumetric flask) of each to the nearest 0.1 g.

12. Calculation

12.1 Calculate naphtha fraction as follows:

$$f = M_n/M_c \quad (3)$$

where:

f = mass fraction of naphtha collected,
 M_n = mass of naphtha collected, and
 M_c = mass of crude oil specimen.

12.2 Calculate the density as follows:

$$\text{Density, g/mL} = m/v \quad (4)$$

where:

m = mass of sample specimen, g, and
 v = volume of sample specimen, mL.

PROCEDURE A—SODIUM BIPHENYL REDUCTION AND POTENTIOMETRY

13. Apparatus

13.1 *Electrodes*—The cleaning and proper care of electrodes are critical to the accuracy of this test. Manufacturer's instructions for the care of electrodes shall be followed.

13.1.1 *Glass*, general purpose. When glass electrodes are in continuous use, weekly cleaning with chrome-sulfuric acid (**Warning**—Strong oxidizer; can cause severe burns; recognized carcinogen), or other strongly oxidizing cleaning solution, is recommended.

13.1.2 *Silver-Silver Chloride*, billet-type.

13.2 *Titration*, potentiometric. The titration is equipped with a 5 mL or smaller buret and a magnetic stirring motor.

14. Reagents and Materials

14.1 *Acetone*, chloride-free. (**Warning**—Extremely flammable, can cause flash fires. Health hazard.)

14.2 *Congo Red Paper*.

14.3 *2,2,4, trimethyl pentane (isooctane)*, reagent grade. (**Warning**—Flammable. Health hazard.)

14.4 *Nitric Acid*, approximately 5 M. (**Warning**—Corrosive, causes severe burns.) Add 160 mL of concentrated nitric acid to about 200 mL of water and dilute to 500 mL.

14.5 *2-Propanol*, chloride-free. (**Warning**—Flammable. Health hazard.)

14.6 *Silver Nitrate*, 0.01 M, standard aqueous solution.

14.7 *Sodium Biphenyl Reagent*^{5,6}—This is packed in 0.5 oz French square bottles (hereafter referred to as vials). The entire

⁶ The sole source of supply of the sodium biphenyl reagent known to the committee at this time is Southwestern Analytical Chemicals, P.O. Box 485, Austin, TX.

contents of one vial are used for each analysis. One vial contains 13 meq to 15 meq of active sodium. Store the sodium biphenyl reagent in a cool storage area, but do not refrigerate. Prior to using, warm the reagent to approximately 50 °C and shake thoroughly to ensure a homogeneous liquid.

14.8 *Toluene*, chloride-free. (**Warning**—Flammable. Health hazard.)

15. Preparation of Apparatus

15.1 *Recoating Silver-Silver Chloride Electrodes*—Clean the metal surfaces of a pair of silver-silver chloride electrodes with mild detergent and scouring powder. Rinse the electrodes in distilled water. Immerse the metallic tips in saturated potassium chloride solution. Connect one electrode to the positive pole of a 1.6 V battery and the other to the negative pole. Reverse the polarity for several intervals of a few seconds each to alternately clean and recoat the receptor electrode (connected to the positive pole). When adequately coated, the receptor electrode tip will turn violet in color. This results from the action of light on the fresh silver chloride.

16. Procedure

16.1 Use extreme care to prevent contamination. Reserve all glassware for the chloride determination. Rinse glassware with distilled water followed by acetone just prior to use. Avoid using chlorine-containing stopcock greases such as chlorotrifluoroethylene polymer grease.

16.2 Place 50 mL of toluene in a 250 mL separatory funnel and add the contents of one vial of sodium biphenyl reagent. Swirl to mix and add about 30 g, obtaining the mass to the nearest 0.1 g of the washed naphtha fraction of crude oil sample. Obtain the mass of the sample bottle to determine the exact amount taken. Stopper the separatory funnel and swirl to mix the contents thoroughly. The solution or suspension that results should be blue-green in color. When it is not, add more sodium biphenyl reagent (one vial at a time) until the solution or suspension is blue-green.

16.3 Allow 10 min after mixing for the reaction to be completed, then add 2 mL of 2-propanol and swirl gently with the funnel unstoppered for a time until the blue-green color changes to white, indicating that no free sodium remains. Stopper the funnel and rock it gently, venting pressure frequently through the stopcock. Then add 20 mL of water and 10 mL of 5 M nitric acid. Shake gently, releasing the pressure frequently through the stopcock. Test the aqueous phase with Congo red paper. If the paper does not turn blue, add additional 5 M nitric acid in 5 mL portions until the blue color is obtained.

16.4 Drain the aqueous phase into another separatory funnel containing 50 mL of *isooctane* and shake well. Drain the aqueous phase into a 250 mL titration beaker. Make a second extraction of the *isooctane* phase with 25 mL of water that has been acidified with a few drops of 5 M nitric acid. Add this second extract to the 250 mL titration beaker. Evaporate the solution on a hot plate kept just below the boiling point of the liquid until 25 mL to 30 mL remains. Do not boil or evaporate to less than 25 mL as loss of chloride may occur.

16.5 Cool the solution and add 100 mL of acetone. Titrate the solution potentiometrically with standard 0.01 M silver nitrate, using glass versus silver-silver chloride electrodes. If an automatic titrator, such as a Metrohm, is available, use the semi-micro 5 mL piston buret. If the titration is carried out with a manually-operated pH meter, use a 5 mL semi-micro buret that can be estimated to three decimal places in millilitres.

16.6 Determine the endpoint for the manual titration by plotting the data showing emf versus volume of silver nitrate solution used. Determine the endpoint for the automatic titrator from the midpoint of the inflection of the titration curve.

16.7 Determine a blank for each group of test specimens by using all of the reagents, including the sodium biphenyl, and following all the operations of the analysis except that the sample itself is omitted.

17. Calculation

17.1 Calculate chloride concentration in the naphtha fraction as follows:

$$\text{Chloride, } \mu\text{g/g} = \frac{(A - B) (M) (35\,460)}{W} \quad (5)$$

where:

A = volume of titrant for the sample specimen, mL,
B = volume of titrant for the blank, mL,
M = molarity of silver nitrate, and
W = mass of sample specimen, g.

17.2 The concentration of organic chloride in the original crude oil sample specimen can be obtained by multiplying the chloride concentration in the naphtha fraction (see 17.1) by the naphtha fraction (see 12.1).

PROCEDURE B—COMBUSTION AND MICROCOULOMETRY

18. Apparatus

18.1 *Combustion Furnace*—The sample specimen is to be oxidized in an electric furnace capable of maintaining a temperature of 800 °C to oxidize the organic matrix.

18.2 *Combustion Tube*—Fabricated from quartz and constructed so a sample, which is vaporized completely in the inlet section, is swept into the oxidation zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube shall hold a septum for syringe entry of the sample and side arms for the introduction of oxygen and inert gases. The center section is to be of sufficient volume to ensure complete oxidation of the sample.

18.3 *Titration Cell*—Containing a sensor-reference pair of electrodes to detect changes in silver ion concentration and a generator anode-cathode pair of electrodes to maintain constant silver ion concentration and an inlet for a gaseous sample from the pyrolysis tube. The sensor, reference, and anode electrodes shall be silver electrodes. The cathode electrode shall be a platinum wire. The reference electrode resides in a saturated silver acetate half-cell. The electrolyte contains 70 % acetic acid in water.

18.4 *Microcoulometer*, having variable gain and bias control, and capable of measuring the potential of the sensing-reference electrode pair, and of comparing this potential with a bias potential, and of applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. The microcoulometer output signal shall be proportional to the generating current. The microcoulometer may have a digital meter and circuitry to convert this output signal directly to nanograms or micrograms of chloride.

18.5 *Sampling Syringe*—A microlitre syringe of 50 μL capacity capable of accurately delivering 5 μL to 50 μL of sample into the pyrolysis tube. A 3 in. or 6 in. (76.2 mm or 152.4 mm) needle is recommended to reach the inlet zone of approximately 500 $^{\circ}\text{C}$ in the combustion zone.

18.6 A constant rate syringe pump or manual dispensing adaptor may be used to facilitate slow injection of the sample into the combustion tube. It is recommended that the injection rate not exceed 0.5 $\mu\text{L/s}$.

19. Reagents and Materials

19.1 *Acetic Acid*, glacial acetic acid. (**Warning**—Corrosive, causes severe burns.)

19.2 *Argon, Helium, Nitrogen, or Carbon Dioxide*, high purity grade (HP) used as the carrier gas. (**Warning**—These gases are normally stored in cylinders under high pressure. These gases also dilute the oxygen content of the surrounding air when they leak.)

19.3 *Cell Electrolyte Solution*, 70 % acetic acid, combine 300 mL reagent water (see 6.2) with 700 mL acetic acid (see 19.1) and mix well.

19.4 *Chloride, Standard Stock Solution*, 1000 mg chloride per litre. Accurately dispense 1.587 g of chlorobenzene into a 500 mL volumetric flask and dilute to volume with 2,2,4, trimethyl pentane (*isooctane*).

NOTE 2—The exact concentration of chloride may be determined by multiplying the mass of chlorobenzene by the product of the atomic mass of chlorine divided by the molecular mass of chlorobenzene and then multiplying that result by 2000.

$$\text{Cl (mg/L)} = \frac{w \times m_1 \times 2000}{m_2} \quad (6)$$

where:

w = mass of chlorobenzene weighed,
 m_1 = atomic mass of chlorine, and
 m_2 = molecular mass of chlorobenzene.

19.5 *Chlorine, Standard Solution*, 10 mg chloride per litre. Pipet 1.0 mL of chloride stock solution (see 19.4) into a 100 mL volumetric flask and dilute to volume with 2,2,4, trimethyl pentane (*isooctane*).

19.6 *Chlorobenzene*, reagent grade.

19.7 *Gas Regulators*, two-stage gas regulator must be used on the reactant and carrier gas.

19.8 *Isooctane*, 2,2,4-trimethylpentane, reagent grade.

19.9 *Oxygen*, high purity grade, used as the reactant gas.

19.10 *Silver Acetate*, powder purified for saturated reference electrode.

20. Preparation of Apparatus

20.1 Set up the analyzer in accordance with the equipment manufacturer instructions.

20.2 The typical operational conditions are as follows:

Reactant gas flow, O_2	160 mL/min
Carrier gas flow	40 mL/min
Furnace temperature:	
Inlet zone	700 $^{\circ}\text{C}$
Center and outlet zones	800 $^{\circ}\text{C}$
Coulometer:	
Bias voltage, mV	240 to 265
Gain	ca. 1200

20.3 Optimize the bias voltage setting for the titration cell null-point by injecting 30 μL of chloride-free water directly into the titration cell using a 6 in. needle. Adjust bias up or down to minimize the total integrated value due to this dilution effect.

21. Procedure

21.1 Fill a 50 μL syringe with about 30 μL to 40 μL of the sample of washed naphtha fraction of crude oil, being careful to eliminate bubbles. Then retract the plunger so that the lower liquid meniscus falls on the 5 μL mark, and record the volume of liquid in the syringe. After the sample has been injected, again retract the plunger so that the lower liquid meniscus falls on the 5 μL mark, and record the volume of liquid in the syringe. The difference in the two volume readings is the volume of sample injected.

21.2 Alternately, obtain the sample injection device mass before and after injection to determine the amount of sample injected. This method provides greater precision than the volume delivery method, provided a balance with a precision of ± 0.01 mg is used and the syringe is carefully handled to obtain repeatable weighings.

21.3 Inject the sample into the pyrolysis tube at a rate not to exceed 0.5 $\mu\text{L/s}$.

21.4 Below 5 $\mu\text{g/g}$, the needle-septum blank will become increasingly more obvious. To improve precision, insert the syringe needle into the hot inlet and then wait until the needle-septum blank is titrated before injecting the sample or standard.

21.5 For specimens containing more than 25 $\mu\text{g/g}$ Cl only 5.0 μL of sample need be injected.

21.6 Verify the system recovery, the fraction of chlorine in the standard that is titrated, every 4 h by using the standard solution (see 19.5). System recovery is typically 85 % or better.

21.7 Repeat the measurement of the calibration standard at least three times.

21.8 Check the system blank daily with reagent grade *isooctane* (see 19.8). Subtract the system blank from both sample and standard data. The system blank is typically less than 0.2 $\mu\text{g/g}$ chloride once the needle-septum blank has been titrated (see 21.4).

22. Calculation

22.1 Calculate chloride concentration in the naphtha fraction as follows:

22.1.1 For microcoulometers, which read directly in nanograms of chloride, the following equations apply:

$$\text{Chloride, } \mu\text{g/g} = \frac{\text{Sample Readout}}{(V)(D)(RF)} - \frac{\text{Blank Readout}}{(V)(D)(RF)} \quad (7)$$

or

$$\text{Chloride, } \mu\text{g/g} = \frac{\text{Sample Readout}}{(M)(RF)} - \frac{\text{Blank Readout}}{(M)(RF)} \quad (8)$$

where:

Readout = displayed integrated value (sample/standard/blank),

V = volume injected μL ,

D = density, g/mL (11.3),

RF = recovery factor, ratio of chloride determined in standard divided by known standard content minus the system blank.

$$RF = \frac{\text{Standard Readout}}{(V)(D)(C_s)} - \frac{\text{Blank Readout}}{(V)(D)(C_s)}$$

M = mass of sample specimen, mg , and

C_s = concentration of standard, mg/L

22.1.2 For microcoulometers with only analog signal output to a recorder the following equation applies:

$$\text{Chloride, } \mu\text{g/g} = \frac{(A)(X)(0.367)}{(R)(Y)(M)(RF)} - B \quad (9)$$

where:

A = area in appropriate units,

X = recorder sensitivity for full-scale response, mV ,

$0.367 = \frac{(35.45 \text{ gCl/eq})(10^{-3} \text{ V/mV})(10^6 \mu\text{g/g})}{(96\,500 \text{ coulombs/eq})}$

R = resistance, Ω ,

Y = area equivalence for a full-scale response on the recorder per second-area units per second,

M = mass of sample, g ,

RF = recovery factor, and

B = system blank, $\mu\text{g/g Cl}$.

22.2 The concentration of organic chloride in the original crude oil sample specimen can be obtained by multiplying the chloride concentration in the naphtha fraction (see 22.1) by the naphtha fraction (see 12.1).

PROCEDURE C—X-RAY FLUORESCENCE SPECTROMETRY

23. Apparatus

23.1 Any spectrometer of the following type: *Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF) Spectrometer*, *Monochromatic Energy Dispersive X-ray Fluorescence (MEDXRF) Spectrometer*, or *Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometer* can be used if it includes the following features for its type described in this section and the precision and bias of the test results are in accordance with

the values for its type described in Section 32. (**Warning**—Exposure to excessive quantities of high energy radiation such as those produced by X-ray spectrometers is injurious to health. The operator needs to take appropriate actions to avoid exposing any part of their body, not only to primary X-rays, but also to secondary or scattered radiation that might be present. The X-ray spectrometer should be operated in accordance with the regulations governing the use of ionizing radiation.)

23.2 *Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF) Spectrometer*, equipped for X-ray detection at 0.473 nm (4.73 Å) which also includes the following:

23.2.1 *X-ray Source*, capable of producing X-rays to excite chlorine. X-ray tubes with a power of >20 W capable of producing Pd La, Ag La, Ti Ka, Sc Ka, or Cr Ka radiation are recommended for this purpose.

23.2.2 *Optical Path*, designed to minimize the absorption along the path of the excitation and fluorescent beams using a vacuum or a helium (see 24.6) atmosphere. If vacuum is used, a level of lower than 2.7 kPa (<20 Torr) is recommended. The calibration and test measurements must be done with identical optical paths, including vacuum or helium pressure.

23.2.3 *Incident-beam Monochromator*, capable of focusing and selecting a single wavelength of characteristic X-rays from the source onto the specimen.

23.2.4 *Fixed-channel Monochromator*, suitable for dispersing chlorine Ka X-rays.

23.2.5 *Detector*, designed for efficient detection of chlorine Ka X-rays.

23.2.6 *Single-channel Analyzer*, an energy discriminator to monitor only chlorine radiation.

23.3 *Monochromatic Energy Dispersive X-ray Fluorescence (MEDXRF) Spectrometer*, including the following:

23.3.1 *Source of X-ray Excitation*, X-ray tube with Ag or Pd anode, in combination with HOPG Bragg monochromating X-ray optics. The monochromator must produce monochromatic Ag or Pd L radiation. Other anode materials and monochromators may be utilized, however stated precision and bias may not apply.

23.3.2 *Optical Path*, the system must allow flushing of the optical path with helium (see 24.6). Alternatively, a vacuum of $\leq 4.0 \text{ kPa}$ ($\leq 30.4 \text{ Torr}$) can be applied to the optical path. When the air in the optical path is relatively small, then vacuum or helium may be optional. Follow manufacturer's recommendations.

23.3.3 *X-ray Detector*, with a resolution value not to exceed 175 eV at 5.9 keV (10 000 cps). A Si drift chamber detector (SDD) has been found suitable for use. Using a detection system with this minimum spectral resolution has been shown to eliminate the potential effect of spectral interference from sulfur or other elements in the naphtha sample.

23.3.4 *Signal Conditioning and Data Handling Electronics*, including the functions of X-ray intensity counting, spectra handling by background subtraction and deconvolution, calculation of overlap corrections and conversion of chlorine X-ray intensity into mg/kg chlorine concentration.

23.4 *Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometer*, required design features include:

23.4.1 *Source of X-ray Excitation*, X-ray tube with excitation energy above 2.9 keV.

23.4.2 *X-ray Detector*, with high sensitivity and a resolution value (Full Width at Half Maximum, FWHM) not to exceed 175 eV at 5.9 keV (10 000 cps). A Si drift chamber detector (SDD) has been found suitable for use.

23.4.3 *Filters*, or other means of discriminating between chlorine K α radiation and other X-rays of different energy. The other means include software solutions.

23.4.4 *Optical Path*, the system must allow flushing of the optical path with helium (see 24.6). Alternatively, a vacuum of ≤ 4.0 kPa (≤ 30.4 Torr) can be applied to the optical path.

23.4.5 *Signal Conditioning and Data Handling Electronics*, that include the functions of X-ray intensity counting, a minimum of two energy regions, spectral overlap corrections, background corrections, and conversion of chlorine X-ray intensity into mass percent chlorine concentration.

23.5 Additionally, the following apparatus is needed when using all x-ray spectrometers within the scope of this method:

23.5.1 *Display or Printer*, that reads out in mg/kg chlorine.

23.5.2 *Removable Sample Cell*, compatible with the sample and the geometry of the XRF spectrometer. A disposable cell is recommended. The sample cell should not leak when fitted with X-ray transparent film (see 23.5.3).

23.5.3 *X-ray Transparent Film*, for containing and supporting the test specimen in the sample cell (see 23.5.2) while providing a low-absorption window for X-rays to pass to and from the sample. Any film resistant to chemical attack by the sample, free of chlorine, and X-ray transparent can be used, for example, polyester, polypropylene, polycarbonate, and polyimide. However, samples of high aromatic content can dissolve polyester and polycarbonate films.

23.5.4 *Analytical Balance*, for preparing calibration standards, capable of weighing to the nearest 0.1 mg and up to 100 g.

24. Reagents and Materials

24.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁷ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

24.2 *Calibration Check Samples*, portions of one or more liquid petroleum or product standards of known or certified chlorine content and not used in the generation of the calibration curve. The check samples shall be used to determine the precision and accuracy of the initial calibration (see 27.6).

24.3 *Chlorine Dopant (CD)*, a high-purity standard with a certified chlorine content. Trichloroethylene and 1,2,4-

trichlorobenzene have been found to be acceptable chlorine dopants. Use the certified chlorine concentration when calculating the exact concentrations of chlorine in calibration standards. (**Warning**—Breathing trichloroethylene vapors may cause drowsiness and dizziness. Causes eye and skin irritation. Aspiration hazard if swallowed. Can enter lungs and cause damage. May cause cancer based on animal studies. May cause liver damage.) (**Warning**—1,2,4-trichlorobenzene may cause respiratory tract irritation. Harmful if swallowed. Causes eye and skin irritation.)

24.4 *Counting Gas*, for instruments equipped with flow proportional counters. The purity of the counting gas should be in agreement with the specification provided by the instrument manufacturer.

24.5 *Drift Correction Monitor(s) (Optional)*—Several different materials have been found to be suitable for use as drift correction monitors. Appropriate drift monitor samples should be permanent materials that are stable with respect to repeated exposure to X-rays. Stable liquids, glass or metallic specimens are recommended. Liquids, pressed powders, and solid materials that degrade with repeated exposure to X-rays should not be used. Examples of chlorine containing materials that have been found to be suitable include a renewable liquid petroleum material, a metal alloy, or a fused glass disk. The monitor's counting rate, in combination with count time, shall be sufficient to give a relative counting error of less than 1 %. The counting rate for the monitor sample is determined during calibration (see 27.4) and again at the time of analysis (see 28.1). These counting rates are used to calculate a drift correction factor (see 29.1).

NOTE 3—Calibration standards may be used as drift-monitor samples. Because it is desirable to discard test specimens after each determination, a lower cost material is suggested for daily use. Any stable material can be used for daily monitoring of drift.

NOTE 4—The effect of drift correction on the precision and bias of this test method has not been studied.

24.5.1 Drift correction is usually implemented automatically in software, although the calculation can readily be done manually. For X-ray instruments that are highly stable, the magnitude of the drift correction factor may not differ significantly from unity.

24.6 *Helium Gas*, for instruments equipped with a helium optical path (optional for some analyzers). The minimum purity 99.9 %. If helium is used, it is recommended to limit variations in pressure and temperature to within 10 % relative. When connecting a new helium gas cylinder, always run a blank measurement to ensure the helium gas line is purged of air.

24.7 *Quality Control Samples*, stable petroleum or product samples or solids representative of the samples of interest that are run on a regular basis to verify that the system is in statistical control (see Section 31).

NOTE 5—Verification of system control through the use of QC samples and control charting is highly recommended. It is recognized that QC procedures are the province of the individual laboratory.

NOTE 6—Suitable QC samples can often be prepared by combining retains of typical samples if they are stable. QC samples must be stable over long periods.

⁷ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

24.8 *White Mineral Oil (WMO)*, ACS Reagent Grade containing less than 1 mg/kg chlorine or other suitable base material containing less than 1 mg/kg chlorine. The chlorine content, if any, of the base material needs to be included in the calculation of calibration standard concentration (see 27.1). When the chlorine content of the solvent or reagent is not certified, verify the absence of chlorine. Use the purest grades for the preparation of calibration standards. It is also important to measure and correct for the C/H ratio (see Section 29.7), if it differs significantly from the calibration standards when calculating the final results.

25. Sampling and Specimen Preparation

25.1 Samples shall be taken in accordance with the instructions in Practices D4057 or D4177 when applicable.

25.2 When reusable sample cells are used, clean and dry cells before each use. Disposable sample cells shall not be reused. For each sample, an unused piece of X-ray film is required for the sample cell. Avoid touching the inside of the sample cell, the portion of the window film in the cell, or the instrument window (if the instrument is so equipped) that is exposed to X-rays. Oil from fingerprints can affect the reading when analyzing for low levels of chlorine. Wrinkles in the film will affect the intensity of the chlorine X-rays transmitted. Therefore, it is essential that the film be taut and clean to ensure reliable results.

25.3 Use the appropriate film for the sample type. Samples of high aromatic content may dissolve polyester, polypropylene and polycarbonate films. In these cases, other materials besides these films may be used for X-ray windows, provided that they do not contain any elemental impurities. Follow instrument manufacturer's recommendations where possible.

25.4 Because impurities and thickness variations can occur in commercially available transparent films and vary from lot to lot, use calibration-check samples (see 24.2) to verify calibration integrity after starting each new batch of film. The analyzer may need recalibration if the type or thickness of the window film is changed.

25.5 Place the sample in the cell using techniques consistent with good practice for the particular instrument being used. Although chlorine radiation will emerge from only a small distance into the sample, scatter from the sample cell and the sample can vary. Laboratory personnel shall ensure that the sample cell is filled above a minimum depth, beyond which additional sample does not significantly affect the count rate. Generally, fill the sample cell to a minimum of one-half of the cell's capacity. After the sample cell is filled and film is attached, provide a vent above the sample to prevent bowing of the film by accumulating vapors.

25.6 Ensure the sample is not leaking after preparation, and perform the analysis of the specimen promptly after preparing the specimen. Do not let the specimen remain in the sample cell any longer than necessary before collecting the data.

25.7 If the instrument (see Section 23) is equipped with a replaceable secondary (also called safety) window, it should be checked periodically and changed if it is wrinkled, ripped,

dirty, or contaminated by a leaking sample cup. When changing the window, follow the precautions given in 25.2 and 25.3.

25.8 See Practice D7343 for more detailed sample handling and preparation information.

26. Preparation of Apparatus

26.1 Ensure that the XRF analyzer has been installed and put into operation according to manufacturer's instructions. Allow sufficient time for instrument electronics to stabilize. Perform any instrument checkout procedures required. When possible, the instrument should be run continuously to maintain optimum stability.

26.1.1 Use the count time (T) recommended by the instrument manufacturer for the lowest chlorine concentration expected.

27. Calibration

27.1 Prepare a set of calibration standards bracketing the expected concentration range in the samples by careful mass dilution of a chlorine dopant (CD, see 24.3) with a chlorine-free white mineral oil (WMO, see 24.8) or other suitable base material. Trichloroethylene and 1,2,4-trichlorobenzene have been found to be suitable chlorine dopants (see 24.3). The concentrations of the unknown samples must lie within the calibration range that is used. All standards used in the analysis must be from a reliable and consistent source, which can include commercially available standards. Recommended nominal chlorine concentration standards are listed as follows for the scope of this test method: 0 mg/kg (base material), 5 mg/kg, 10 mg/kg, 25 mg/kg, 50 mg/kg, and 100 mg/kg.

NOTE 7—It is recommended to calibrate the XRF analyzer higher than the expected organic chloride concentration in the crude oil, because distillation of the crude oil will concentrate organic chlorides in the naphtha fraction. Use the amount of naphtha collected (Eq 3) to optimize the calibration curve. For example, if the naphtha fraction is 0.5, the measured concentration of chloride in the naphtha fraction can be expected to be twice the amount of the crude.

27.1.1 Take into account any chlorine in the base materials when calculating the chlorine content (mg/kg) in each of the calibration standards as shown in Eq. 10:

$$Cl = [(CD \times Cl_{CD}) + (WMO \times Cl_{WMO})] / (CD + WMO) \quad (10)$$

where:

- Cl = mass fraction of the chlorine of the prepared standards, mg/kg,
- CD = actual mass of the chlorine dopant, g,
- Cl_{CD} = the mass fraction of chlorine in the chlorine dopant, mg/kg, typically 0.8095 mg/kg for trichloroethylene and 0.861 mg/kg for 1,2,4-trichlorobenzene,
- WMO = actual mass of white mineral oil, g, and
- Cl_{WMO} = mass fraction of chlorine in the white mineral oil, mg/kg.

27.1.2 Alternatively, commercially available standards can be used provided their chlorine concentrations are accurately known and they approximate the nominal recommended concentrations listed in 27.1.

27.1.3 Store all standards and QC samples in glass bottles in a cool, dark place until required. The glass bottles shall either be dark or wrapped in opaque material, and closed with glass stoppers, inert plastic lined screw caps, or impermeable enclosures. As soon as any sediment or change of concentration is observed, discard the sample.

27.2 Establish calibration curve data by carefully determining the net intensity of the emitted chlorine radiation from each of the standards by the procedures described in Sections 28 and 29.

27.3 Construct a calibration model by using the software and algorithms supplied by the equipment vendor. The calibration model typically takes one of the following linear forms (refer to the equipment vendor's software documentation to determine the exact form):

$$I = Cl * m + b \quad (11)$$

$$Cl = I * m + b \quad (12)$$

where:

I = net intensity for the chlorine radiation,
 Cl = chlorine concentration in mg/kg,
 m = slope, and
 b = intercept.

27.4 When using drift correction monitors, determine the intensity of the drift correction monitor sample(s) during the calibration procedure. The value determined corresponds to the factor A in Eq 13 in 29.1.

27.5 A sulfur calibration model may be required for spectrometers utilizing a direct sulfur measurement in the sulfur correction factor. If required, construct a calibration model by using the software and algorithms supplied by the equipment vendor. The calibration model may be empirical or make use of fundamental parameters (refer to the equipment vendor's software documentation to determine the exact form).

27.6 Immediately after completing the calibration, determine the chlorine concentration of one or more of the calibration check samples (24.2). The determined value shall be in the range defined by the certified concentration plus or minus the repeatability of this test method. When this is not the case, the calibration process and calibration standards are suspect and corrective measures should be taken. The degree of matrix mismatch between samples and standards should also be considered when evaluating a calibration. Statistical quality control charts may be prepared for these materials to establish if the method is in statistical control, as described in Section 31.

28. Procedure

28.1 When using drift correction monitors, before analyzing samples on a given day, analyze the drift correction monitor(s) and determine the counting rate, using the same material as used at the time of calibration. The value determined corresponds to the factor B in 29.1.

28.2 Analyze each sample of interest as follows:

28.3 Prepare a test specimen of the sample of interest according to Section 25. Quality control samples shall be prepared and run identically to any unknown sample.

28.4 Place the sample cell containing the test specimen in the X-ray beam, as directed in the instrument manufacturer's instructions. Allow the X-ray optical path to come to equilibrium.

28.5 Determine the net chlorine intensity for MWDXRF spectrometers by measuring the total counts of chlorine fluorescence, and then dividing the total counts by the measurement time in seconds to calculate I (see Eq 11). Calculate the concentration of chlorine in the test specimen as instructed in Section 29.

28.5.1 If the sulfur concentration of the sample is ≥ 0.5 mass %, it is recommended to sulfur correct the chlorine measurement results. This correction is performed automatically by the analyzer software either by manual input of the sulfur concentration or direct sulfur measurement of the sample. Refer to equipment vendor's software documentation to determine the exact form of the correction.

28.6 For MEDXRF spectrometers, determine the peak area of the chlorine $K\alpha$ radiation at 2.622 keV. The net count-rate will be calculated by subtracting the background. The background spectrum, measured with a chlorine-free white oil or other matrix matching blank sample (see 24.8) is adapted to the measured spectrum using adjustment regions (see Note 8) following the instrument manufacturer's instructions and then subtracted from the measured spectrum. Determine the corrected counting rate and calculate the concentration of the sample as described in Section 29.

NOTE 8—Background adjustment regions of 2.8 keV to 3.3 keV are suitable when using an Ag target X-ray tube. When using a Pd target X-ray tube, a region of about 2.7 keV to 3.2 keV can be used. Ensure that the region used is free from chlorine overlap.

28.6.1 *Sulfur Correction MEDXRF*—This correction is performed automatically by the analyzer software either by manual input of the sulfur concentration or direct sulfur measurement of the sample. Refer to equipment vendor's software documentation to determine the exact form of the correction.

28.7 For EDXRF spectrometers, the chlorine concentration is automatically calculated from the calibration, using the instrument software.

28.7.1 *Sulfur Correction EDXRF*—This correction is performed automatically by the analyzer software either by manual input of the sulfur concentration or direct sulfur measurement of the sample. Refer to equipment vendor's software documentation to determine the exact form of the correction.

28.8 If the measured intensity for a test specimen is greater than the highest count rate in the calibration curve, quantitatively dilute a fresh portion of the sample with the base material used to prepare the calibration standards. Dilute the sample so the resultant count rate is within the limits of the

calibration curve. Repeat the procedures described in 28.2-28.7 on a test specimen of the diluted sample.

29. Calculations

29.1 When using a drift monitor sample (optional), calculate a drift correction factor (F) for changes in daily instrument sensitivity according to Eq 13. If a drift monitor is not used, F is set equal to 1.

$$F = A/B \quad (13)$$

where:

F = drift correction factor,

A = counting rate of the drift correction monitor as determined at the time of the calibration (see 27.4), and

B = counting rate of the drift correction monitor as determined at the time of analysis.

29.2 For MWDXRF spectrometers, calculate the drift-corrected count rate, or intensity, (I_{cor}) for the test specimen as follows:

$$I_{cor} = F * I \quad (14)$$

where:

F = drift correction factor, calculated in Eq 13, and

I = net count rate (or intensity) for test specimen.

29.2.1 Calculate the chlorine content (Cl) of the test specimen by using the drift-corrected count rate (I_{cor}) in place of I in Eq 11 of 27.3. In many cases the instrument vendor will provide software or the required calculations. The use of the factor F to correct the counting rate of chlorine is optional.

29.3 For MEDXRF spectrometers, the net counting rate, or intensity, is given by the spectral deconvolution of the chlorine $K\alpha$ line after subtracting the background spectrum.

29.3.1 The use of the factor F to correct the counting rate of chlorine is optional.

29.3.2 Calculate the chlorine content (Cl) of the sample by inserting the corrected net counting rate in the calibration Eq 12 from 27.3. In many cases the instrument vendor will provide software for the required calculations.

29.4 For EDXRF spectrometers, the concentration of chlorine in the sample is automatically calculated from the calibration curve.

29.5 If the specimens have ≥ 0.5 % by mass sulfur, then it is recommended that matrix corrections for sulfur be made. In some systems, the sulfur lines might be interfering with the intensity of chlorine. In that case, line overlap corrections might be required. Manufacturer's software typically provides a method to correct for matrix effects and interferences. In some instances, both matrix correction and correction for interference may be required. In other specimens only one of these corrections must be applied, and in other specimens still no correction at all is required. Follow manufacturer recommendations for applying sulfur correction.

29.6 If the test specimen was prepared from a quantitatively diluted sample, correct the measured concentration for sample dilution. The chlorine concentration (Cl_o) in the original, undiluted sample is calculated as follows:

$$Cl_o = [Cl_d \times (M_o + M_b) / M_o] - [Cl_b \times (M_b / M_o)] \quad (15)$$

where:

Cl_d = concentration of chlorine in test specimen of the diluted sample (from 28.8), mg/kg,

M_o = mass of original sample, g,

M_b = mass of base material used to dilute sample, g, and

Cl_b = concentration of chlorine in diluent, mg/kg.

29.7 The carbon/hydrogen (C/H) ratio correction formula, which is applicable when the base material used for the calibration standards is white oil, is shown in Eq 16:

$$Cl_{CH} = \{[1.195 - 0.0164 (C/H)_{whiteoil}] / [1.195 - 0.0164 (C/H)]\} \times Cl_{whiteoil} \quad (16)$$

where:

Cl_{CH} = chlorine concentration corrected for C/H ratio matrix differences,

$(C/H)_{whiteoil}$ = mass ratio of carbon to hydrogen for white oil, typically 5.7,

(C/H) = mass ratio of carbon to hydrogen for the sample, and

$Cl_{whiteoil}$ = chlorine concentration as derived from the calibration graph.

29.7.1 The value for C/H mass ratio is input for each unknown sample. The $Cl_{whiteoil}$ will be corrected for the different C/H ratios. Accordingly, if standards are prepared with a different solvent, the C/H ratio for that solvent should be used in place of $(C/H)_{whiteoil}$. Differences between the C/H ratio between standards and samples will contribute to error in the measured result. It is the analyst's discretion as to when this error is large enough to be corrected by Eq 16. If unsure whether or not to apply correction, follow the analyzer manufacturer's instructions.

29.8 The concentration of the organic chloride in the original crude oil sample specimen can be obtained by multiplying the chlorine concentration in the naphtha fraction, Cl in Eq 11 and Eq 12 (see 27.3), by the naphtha fraction, f , in Eq 3 (see 12.1).

30. Report

30.1 Report the organic chloride content of the original crude oil sample specimen in $\mu\text{g/g}$ (or mg/kg) as calculated in accordance with 17.2 for Procedure A, 22.2 for Procedure B, and/or 29.8 for Procedure C.

30.1.1 The organic chloride content of the naphtha fraction is also expressed as $\mu\text{g/g}$ (or mg/kg) and is calculated in Eq 5 for Procedure A, Eq 7-9 for Procedure B, and/or Section 29 for Procedure C. These results are used to calculate the organic chloride content of the original crude oil sample specimen in 30.1.

30.2 Indicate that the organic chloride in crude oil results were determined by Test Method D4929, Procedure A; Test Method D4929, Procedure B; or Test Method D4929, Procedure C. For Procedure C, also report whether the result was obtained by MWDXRF, MEDXRF, or EDXRF. Denote if method modifications, such as described in Appendix X2, were used during the analysis.

31. Quality Assurance/Quality Control (QA/QC)

31.1 Confirm the performance of the instrument and the test procedure by analyzing a QC sample.

31.1.1 When QA/QC protocols are already established in the testing facility, these may be used when they confirm the reliability of test result.

31.1.2 When there is no QA/QC protocol established in the testing facility, [Appendix X1](#) may be used as the QA/QC system.

31.2 Users of this test method are advised that in contractual agreements, one or more of the contracting parties can and may make [Appendix X1](#) mandatory practice.

31.3 Additionally, the following QA/QC steps should be observed when using Procedure C:

31.3.1 In addition to running a quality control sample ([24.7](#)), it is strongly recommended that the calibration blank be analyzed on a daily basis.

31.3.1.1 The measured concentration for the blank should be less than 1 mg/kg chlorine. If the measured concentration for the blank is greater than 1 mg/kg, repeat the measurement of the blank (use a fresh sample and fresh cell). If the measured concentration of the blank is still greater than 1 mg/kg, restandardize the instrument and repeat the measurement of the blank (use a fresh sample and fresh cell). If the result falls outside the acceptable range, carry out a full calibration. If the sample loading port becomes contaminated, especially when analyzing <20 mg/kg chlorine level samples, it is necessary to open and clean it according to manufacturer's recommendations before further use.

31.3.2 It should be noted that in order to obtain a good fit for the calibration at low concentrations, it may be necessary to change the weighting factor in the regression. It may also be beneficial to change the weighting method used. Many software packages default to square root error weighting but have the possibility of using linear error weighting or no error weighting.

31.3.3 *Results Validation*—Once a standard or sample has been measured, a procedure should be carried out to validate that measurement. This requires the operator to check for

obvious signs of damage to the sample such as leaking sample cells, crinkled sample cell window and inspection of any secondary film.

31.3.4 *Observation of the Resultant Analysis*—If a result is considered outside normal thresholds, a repeat of the analysis should be carried out to confirm anomalous results.

31.3.5 Regular checks should be carried out to ensure that purging gas performance is within the instrument manufacturer's specification.

31.3.6 Quality control standards shall be run on a regular basis. If drift monitors are used, they shall also be run on a regular basis. The tolerance levels of the checks made using these monitors should be such that a protocol of either drift correction or total recalibration is carried out if the results fall outside these levels. All measurements should be repeated between the last accepted monitor result and point of non-compliance should a current monitor measurement prove to be outside acceptable levels.

32. Precision and Bias⁸

32.1 *Precision*—The precision of these procedures as determined by the statistical examination of the interlaboratory test results is provided below. The precision statements were determined on samples analyzed by Procedures A, B, and C as written. When method modification is employed, such as that described in [Appendix X2](#), the published precision may not apply.

32.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation, exceed the following values only in one case in twenty.

32.1.1.1 *Procedure A*—Values can be obtained for organically-bound chlorine for any given concentration above 1 µg/g Cl (in the original crude oil specimen) as follows:

$$r = 0.32 (X + 0.33)^{0.644} \quad (17)$$

where:

X = µg/g chloride.

See [Table 2](#) for calculated values. See [Note 9](#) for details of the ILS.

32.1.1.2 *Procedure B*—Values can be obtained for organically-bound chlorine for any given concentration above 1 µg/g Cl (in the original crude oil specimen) as follows:

$$r = 1.01 (X - 0.17)^{0.467} \quad (18)$$

where:

X = µg/g chloride.

See [Table 2](#) for calculated values. See [Note 9](#) for details of the ILS.

32.1.1.3 *Procedure C*—Values can be obtained for organically-bound chlorine for any given concentration above

Recovery of Organic Chloride Spikes

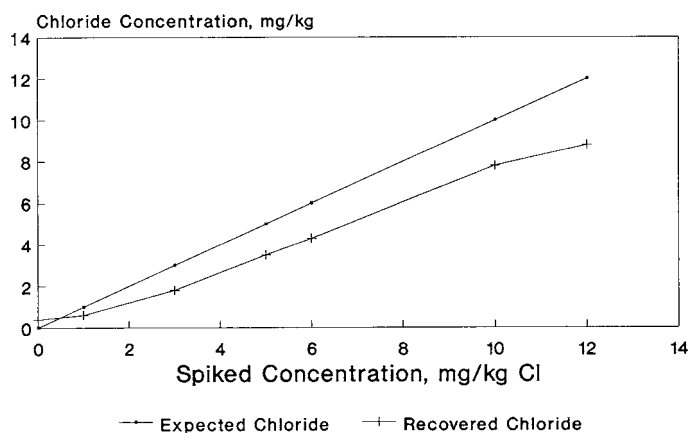


FIG. 1 Recovery of Organic Chloride Spikes

⁸ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1293 for Procedures A and B, and RR:D02-1875 for Procedure C. Contact ASTM Customer Service at service@astm.org.

TABLE 1 Precision Equations, Procedure C XRF

Repeatability r , mg/kg ^A		
MWDXRF	$r = 0.643 \cdot X^{0.44}$	(19)
MEDXRF	$r = 0.591 \cdot X^{0.44}$	(20)
EDXRF	$r = 0.934(X + 0.4)^{0.48}$	(21)
Reproducibility R , mg/kg ^A		
MWDXRF	$R = 1.235 \cdot X^{0.44}$	(22)
MEDXRF	$R = 1.500 \cdot X^{0.44}$	(23)
EDXRF ^B	$R = 2.000(X + 0.4)^{0.48}$	(24)

^A Where X = mg/kg chloride

^B The degrees of freedom associated with the reproducibility estimate from this round robin study are 29. Since the minimum requirement of 30 (in accordance with Practice D6300) is not met, users are cautioned that the actual reproducibility may be significantly different than these estimates.

TABLE 2 Calculated Repeatability r Values, All Procedures

Cl, mg/kg	Procedure A	Procedure B	Procedure C		
	r , $\mu\text{g/g}^A$	r , $\mu\text{g/g}^B$	MWDXRF	MEDXRF	EDXRF
1	0.4	0.9	0.6	0.6	1.1
2	0.6	1.3	0.9	0.8	1.4
3	0.7	1.6	1.0	1.0	1.7
4	0.8	1.9	1.2	1.1	1.9
5	0.9	2.1	1.3	1.2	2.1
6	1.1	2.3	1.4	1.3	2.3
8	1.3	2.6	1.6	1.5	2.6
10	1.4	2.9	1.8	1.6	2.9
12	1.6	3.2	1.9	1.8	3.1

^A Values calculated from Eq 17.

^B Values calculated from Eq 18.

^C Values calculated from Eq 19 for MWDXRF, Eq 20 for MEDXRF, and Eq 21 for EDXRF.

1 mg/kg Cl (in the original crude oil specimen) as specified in Table 1. See Table 2 for calculated values. See Note 10 for details of the ILS.

32.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical material would, in the long run, exceed the following values only in one case in twenty.

32.1.2.1 *Procedure A*—Values can be obtained for organically-bound chlorine for any given concentration above 1 $\mu\text{g/g}$ Cl (in the original crude oil specimen) as follows:

$$R = 0.7 (X + 0.33)^{0.644} \quad (25)$$

where:

X = $\mu\text{g/g}$ chloride.

See Table 3 for calculated values. See Note 9 for details of the ILS.

32.1.2.2 *Procedure B*—Values can be obtained for organically-bound chlorine for any given concentration above 1 $\mu\text{g/g}$ Cl (in the original crude oil specimen) as follows:

$$R = 1.32 (X - 0.17)^{0.467} \quad (26)$$

TABLE 3 Calculated Reproducibility R Values, All Procedures

Cl, mg/kg	Procedure A	Procedure B	Procedure C		
	R , $\mu\text{g/g}^A$	R , $\mu\text{g/g}^B$	MWDXRF	MEDXRF	EDXRF
1	0.8	1.2	1.2	1.5	2.4
2	1.2	1.8	1.7	2.0	3.0
3	1.5	2.1	2.0	2.4	3.6
4	1.8	2.5	2.3	2.8	4.1
5	2.1	2.8	2.5	3.0	4.5
6	2.3	3.0	2.7	3.3	4.9
8	2.7	3.5	3.1	3.7	5.6
10	3.1	3.8	3.4	4.1	6.2
12	3.5	4.2	3.7	4.5	6.7

^A Values calculated from Eq 25.

^B Values calculated from Eq 26.

^C Values calculated from Eq 22 for MWDXRF, Eq 23 for MEDXRF, and Eq 24 for EDXRF.

where:

X = $\mu\text{g/g}$ chloride.

See Table 3 for calculated values. See Note 9 for details of the ILS.

32.1.2.3 *Procedure C*—Values can be obtained for organically-bound chlorine for any given concentration above 1 mg/kg Cl (in the original crude oil specimen) as specified in Table 1. See Table 3 for calculated values. See Note 10 for details of the ILS.

32.1.3 *Procedure C*—Between-Method Relative Bias can be expressed as follows:

32.1.3.1 *Degree of Agreement between results by MEDXRF and MWDXRF*—Results on the same materials produced by MEDXRF and MWDXRF have been assessed in accordance with procedures outlined in Practice D6708. The findings are that the degree of agreement between results from MEDXRF and MWDXRF, can be further improved by applying Eq 27 listed in Table 4. No sample-specific bias, as defined in Practice D6708, was observed after the bias-correction for the materials in the scope of this method.

32.1.3.2 *Degree of Agreement between results by EDXRF and MEDXRF*—Results on the same materials produced by MEDXRF and MWDXRF have been assessed in accordance with procedures outlined in Practice D6708. The findings are that the degree of agreement between results from EDXRF and MEDXRF, can be further improved by applying Eq 28 listed in Table 4. No sample-specific bias, as defined in Practice D6708, was observed after the bias-correction for the materials in the scope of this method.

TABLE 4 Procedure C Between-Method Bias Outcome

Method X	Method Y	Suggested Bias Correction ^A
MEDXRF	MWDXRF	$\hat{Y} = X - 0.658$ (27)
EDXRF	MEDXRF	$\hat{Y} = X - 0.519$ (28)
EDXRF	MWDXRF	No bias correction

^A Where:

$\hat{Y}$ = predicted Y-method value

X = single X-method measured results

32.1.3.3 Degree of Agreement between results by EDXRF and MWDXRF—Results on the same materials produced by EDXRF and MWDXRF have been assessed in accordance with procedures outlined in Practice **D6708**. The findings are that no bias-correction considered in Practice **D6708** can further improve the agreement between results from EDXRF and MWDXRF for the materials studied. No sample-specific bias, as defined in Practice **D6708**, was observed for the materials in the scope of this method.

NOTE 9—Procedures A and B Interlaboratory Study—Ten crude samples were prepared from four crudes. Ten laboratories reported the distillation data. Eight laboratories reported data for Procedure A and six laboratories reported data for Procedure B. One laboratory's data was removed from the statistics for Procedure A. Separate precision statements were determined for each procedure. See RR:D02-1293 for details of this study.

NOTE 10—Procedure C Interlaboratory Study—Eight participants distilled ten crude samples in blind duplicate and performed washes on the twenty naphtha fractions. Six of the eight participants measured each washed naphtha fraction by monochromatic wavelength dispersive XRF (MWDXRF), monochromatic energy dispersive XRF (MEDXRF), and energy dispersive XRF (EDXRF) (three measurements per naphtha sample). One participant measured each washed naphtha fraction by MWDXRF and MEDXRF, and one participant measured each washed naphtha fraction once by MWDXRF and twice by MEDXRF using two MEDXRF analyzers manufactured by two vendors. The participant total

by technology was eight MWDXRF analyzers, nine MEDXRF analyzers, and six EDXRF analyzers. Practice **D6300** was followed for the analysis of data. The data would not support a pooled precision statement, so separate precisions were determined for each XRF technique. See RR:D02-1875 for details of this study.

32.2 Bias—The bias for either Procedure A or B has been demonstrated by performing analyses using known spiked concentrations of various organic chloride compounds in a variety of crude oils to be lower than the true value. This is because not all of the volatile components will distill from a complex crude oil under the conditions of this test method. The extent of this bias is shown in **Fig. 1**, where various recoveries are shown plotted against the known concentration of pure organic-chloride compound spikes.

32.2.1 See **Fig. 2** for a recovery plot of Procedure C.

33. Keywords

33.1 chlorine; coulometry; crude oil; EDXRF; Energy Dispersive X-ray Fluorescence; MEDXRF; Monochromatic Energy Dispersive X-ray Fluorescence; Monochromatic Wavelength Dispersive X-ray Fluorescence; Monochromatic X-ray; MWDXRF; naphtha; organic chloride; organo-chlorine; polarization; sodium biphenyl; spectrometry; X-ray; X-ray Fluorescence; XRF

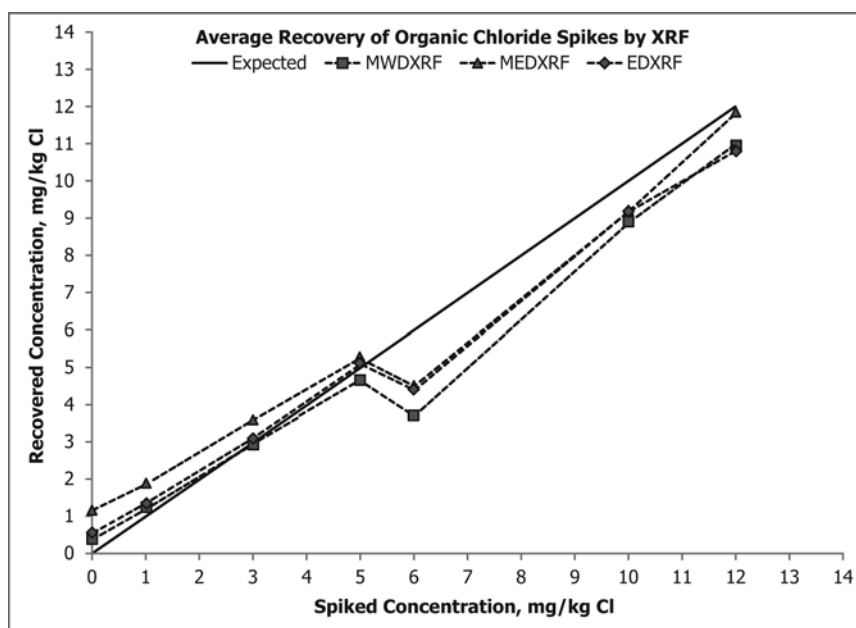


FIG. 2 Average Recovery of Organic Chloride Spikes by XRF

APPENDIXES

(Nonmandatory Information)

X1. GENERIC QUALITY CONTROL STATEMENT FOR D02 TEST METHODS

X1.1 Confirm the performance of the instrument and the test procedure by analyzing a QC sample.

X1.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample (see Practice D6299 and MNL7⁹).

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process⁸ (see Practice D6299 and MNL7⁹). Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the

criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed on each day of testing routine samples. The QC frequency should be increased when a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be periodically checked against the ASTM test method precision to ensure data quality.

X1.5 It is recommended that, when possible, the type of QC sample that is regularly tested be representative of the samples routinely analyzed. An ample supply of QC sample material should be available for the intended period of use and must be homogeneous and stable under the anticipated storage conditions.

X1.6 See Practice D6299 and MNL7⁹ for further guidance on QC and control charting techniques.

⁹ MNL7, *Manual of Presentation of Data Control Chart Analysis*, 6th ed., Section 3: Control Chart for Individuals, ASTM International, W. Conshohocken, PA.

X2. CAUTION REGARDING CRUDE OIL SAMPLE PREPARATION USING WATER WASHING

X2.1 Under certain conditions, salt (inorganic chlorides such as MgCl_2 and CaCl_2) contained within many crude oils can undergo hydrolysis during the Test Method **D86** distillation step used to isolate the $<204^\circ\text{C}$ fraction for analysis. The hydrolysis results in the formation of hydrochloric acid (HCl), which can subsequently react with available organic chloride precursors such as olefins, alcohols, and esters that are present in the naphtha fraction, and form organic chlorides. These formed organic chlorides remain in the naphtha fraction and are reported in the final test result. As a result, some users have adopted the practice of water washing neat crude samples prior to distillation, in order to remove what is often deemed a potential interference.

X2.2 This crude oil sample preparation practice has the potential to bias the final test results since the act of distillation simulates the conditions of an atmospheric crude distillation tower. Any organic chlorides that are present in the naphtha pose a risk to refinery operations. Therefore, their presence or absence in the Test Method D4929 test results are relevant.

Removal of inorganic salts prior to analysis can provide “false negative” results when considering refinery operations. The user of the method should consider how the data is to be used before choosing to implement a pre-distillation water wash. It is advised to conduct the method as written, without pre-distillation wash. Then, if deemed necessary, conduct the evaluation with the pre-distillation water wash in place, and report both results.

X2.3 In the event that a sample was prepared for Test Method D4929 testing by water washing the neat crude, the reported results shall include a statement indicating what sample preparation technique was employed, such as “D4929A-Modified with Crude Pre-Wash.”

X2.4 While Test Method D4929 permits water washing of the distilled naphtha, it does not include neat sample preparation by water washing of the crude oil sample prior to testing, and the information provided in this appendix shall not be interpreted as support for this preparation practice.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D4929 – 19) that may impact the use of this standard. (Approved Dec. 1, 2019.)

(1) Revised subsection **23.5.2**.

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D4929 – 17) that may impact the use of this standard. (Approved July 1, 2019.)

(1) Revised subsections **1.6.1**, **23.1**, **23.2.1**, **23.2.2**, **23.3.1**, **23.3.2**, **23.4.1**, **23.4.4**, **23.5.2**, **23.5.3**, **24.6**, **25.7**, **27.1**, **27.1.2**, **28.6**, **30.1**, **30.1.1**, **30.2**, **32.1.1.1**, **32.1.1.2**, **32.1.1.3**, **32.1.2.1**, **32.1.2.2**, and **32.1.2.3**.

(2) Deleted subsections **23.2.7**, **23.3.5**, and **23.4.6**.

(3) Added subsection **23.5.1** and renumbered rest of section.

(4) Added **Note 7** and **Note 9**, and renumbered subsequent notes.

(5) Revised **Note 8**.

(6) Removed Table 1 Recommended Chlorine (mg/kg) Standard Calibration Ranges and renumbered subsequent tables.

(7) Replaced Table 3 Calculated Precision Values, Procedure C XRF with **Table 2** and **Table 3** which contain calculated precision values for all procedures.

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