Designation: D 4929 – 99

An American National Standard

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM

Standard Test Methods for Determination of Organic Chloride Content in Crude Oil[1]

This standard is issued under the fixed designation D 4929; 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 reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

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

1.2 These test methods involve the distillation of crude oil test specimens to obtain a naphtha fraction 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 Test Method A covers the determination of organic chloride in the washed naphtha fraction of crude oil by sodium biphenyl reduction followed by potentiometric titration.

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

1.5 *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.*

1.6 Values expressed in acceptable SI units are to regarded as the standard. The preferred concentration units are micrograms of chloride per gram of sample.

2. Referenced Documents

2.1 *ASTM Standards:*

D 86 Test Method for Distillation of Petroleum Products[2]

D 1193 Specification for Reagent Water[3]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[4]

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[4]

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance[5]

3. Summary of Test Methods

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 D 86 for the distillation of petroleum products. The naphtha cut is washed with caustic, repeatedly when necessary, until all hydrogen sulfide is removed. The naphtha cut, free of hydrogen sulfide, is then washed with water, repeatedly when necessary, to remove inorganic halides (chlorides).

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

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

3.2.2 *Test Method B, Combustion and Microcoulometry*—The washed naphtha fraction of a crude oil specimen is injected into a flowing stream of gas containing 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:

$$Cl^- + Ag^+ \rightarrow AgCl\ (s) \quad (1)$$

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

$$Ag° \rightarrow Ag^+ + e^- \quad (2)$$

3.2.5 These microequivalents of silver are equal to the

[1] These test methods are under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

Current edition approved Jan. 10, 1999. Published March 1999. Originally published as D 4929 – 89. Last edition D 4929 – 94.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 05.02.

[5] *Annual Book of ASTM Standards*, Vol 05.03.

number of microequivalents of titratable sample ion entering the titration cell.

4. Significance and Use

4.1 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 *Test Method A*—Other titratable halides will also give a positive response. These titratable halides include HBr and HI.

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

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

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.[6] 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 D 1193.

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 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:** See Note 1.)

NOTE 1—**Warning:** Extremely flammable, can cause flash fires. Health hazard.

8.2 *Caustic Solution*, 1 *M* potassium hydroxide (**Warning:** See Note 2.) prepared in distilled/deionized water.

NOTE 2—**Warning:** Can cause severe burns to skin.

8.3 *Distilled/Deionized Water*.

8.4 *Filter Paper*,[7] Whatman No. 41 or equivalent.

8.5 *Stopcock Grease*.[8]

8.6 *Toluene*, chloride-free. (**Warning:** See Note 3.)

NOTE 3—**Warning:** Flammable. Health hazard.

9. Sampling

9.1 Obtain a test unit in accordance with Practice D 4057 or D 4177. 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.

NOTE 4—**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.

NOTE 5—**Precaution:** When heating is required, care should be taken so that no organic chloride containing hydrocarbons are lost.

10. Preparation of Apparatus

10.1 Clean all glassware by rinsing successively with toluene and acetone. After completing the rinse, dry the glassware

[6] *Reagent Chemicals, American Chemical Society Specifications*, 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.

[7] Whatman No. 41 has been found satisfactory. An equivalent may be used.

[8] Dow Corning silicone has been found satisfactory.

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 6—A diagram illustrating the appropriate positioning of the thermometer can be found in Test Method D 86.

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 free-standing water. Store the naphtha fraction in a clean glass bottle. This naphtha fraction can now be analyzed for organic chlorides by either sodium biphenyl or combustion/microcoulometric techniques.

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.

TEST METHOD 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.[9]

NOTE 7—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 *Titrator*, potentiometric. The titrator is equipped with a 5-mL or smaller buret and a magnetic stirring motor.

14. Reagents and Materials

14.1 *Acetone*, chloride-free. (**Warning:** See Note 1.)

14.2 *Congo Red Paper*.

14.3 *2,2,4, trimethyl pentane (isooctane)*, reagent grade. (**Warning:** See Note 3.)

14.4 *Nitric Acid* (**Warning:** See Note 8.), approximately 5 *M*. Add 160 mL of concentrated nitric acid to about 200 mL of water and dilute to 500 mL.

NOTE 8—**Warning:** Corrosive, causes severe burns.

14.5 *2-Propanol*, chloride-free. (**Warning:** See Note 3.)

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

14.7 *Sodium Biphenyl Reagent*[10]—This is packed in 0.5-oz French square bottles (hereafter referred to as vials). The entire contents of one vial are used for each analysis. One vial contains 13 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:** See Note 3.)

15. Preparation of Apparatus

15.1 *Recoating Silver-Silver Chloride Electrodes*—Clean

[9] Beckman No. 41262 has been found satisfactory. An equivalent may be used.
[10] Available from Southwestern Analytical Chemicals, P.O. Box 485, Austin, TX.

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 1.5-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 *iso*octane and shake well. Drain the aqueous phase into a 250-mL titration beaker. Make a second extraction of the sample-and-*iso*octane mixture 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 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:

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

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).

TEST METHOD 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 microliter syringe of 50-µL capacity capable of accurately delivering 5 to 50 µL of sample into the pyrolysis tube. A 3- or 6-in. (76.2 or 152.4 mm) needle is recommended to reach the inlet zone of approximately 500°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 µL/s.

19. Reagents and Materials

19.1 *Acetic Acid* (**Warning:** See Note 8.), glacial acetic acid.

19.2 *Argon, Helium, Nitrogen, or Carbon Dioxide* (**Warning:** See Note 9.), high purity grade (HP) used as the carrier gas.

NOTE 9—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 (*iso*octane).

NOTE 10—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.

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

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 (*iso*octane).

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°C
Center and outlet zones	800°C
Coulometer:	
Bias voltage, mV	240–265
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-inch 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 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 µL/s.

21.4 Below 5 µg/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 µg/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 *iso*octane (see 19.8). Subtract the system blank from both sample and standard data. The system blank is typically less than 0.2 µg/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:

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

or

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

where:

Readout = displayed integrated value (sample/standard/blank),
V = volume injected µL,
D = density, g/mL (11.3),
RF = recovery factor, ration of chloride determined in standard divided by known standard content minus the system blank.

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

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:

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

where:
A = area in appropriate units,
X = recorder sensitivity for full-scale response, mV,
0.367 = 35.45 gCl/eq)/ (10−3 V/mV) (106µg/g);(96 500 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, µg/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).

23. Quality Assurance/Quality Control

23.1 Confirm the performance of the instrument and the test procedure by analyzing a control (QC) sample.

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

23.1.2 When there is no QA/QC protocol established in the testing facility, Appendix X1 may be used as the QA/QC system.

23.2 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.

24. Precision and Bias [11]

24.1 *Precision*—The precision of these test methods as determined by the statistical examination of the interlaboratory test results is as follows:

24.1.1 *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.

24.1.1.1 *Test Method 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:

$$r = 0.3\,[\text{Cl}]^{0.64} \quad (10)$$

24.1.1.2 *Test Method 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:

$$r = 0.7\,[\text{Cl}]^{0.6} \quad (11)$$

24.1.2 *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.

24.1.2.1 *Test Method 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:

$$R = 1.1\,[\text{Cl}]^{0.36} \quad (12)$$

24.1.2.2 *Test Method 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:

$$R = 1.0\,[\text{Cl}]^{0.71} \quad (13)$$

24.2 *Bias*—The bias for either Test Method 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.

25. Keywords

25.1 coulometry; crude oil; organic-chloride; organochlorine; sodium biphenyl

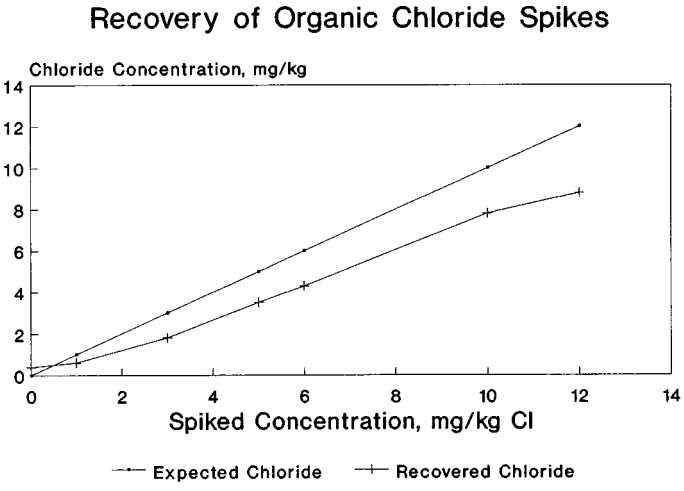

FIG. 1 Recovery of Organic Chloride Spikes

[11] Supporting data available from ASTM Headquarters Request RR:D02-1293.

APPENDIX

(Nonmandatory Information)

X1. GENERIC QUALITY CONTROL STATEMENT FOR D2 TEST METHODS

X1.1 Confirm the performance of the instrument and the test procedure by analyzing a quality control (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.[12,13]

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 process.[11,12] 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 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 Footnotes 12 and 13. for further guidance on QC and control charting techniques.

[12] Practice D 6299.

[13] ASTM MNL7: Manual of Presentation of Data Control Chart Analysis, 6th ed., Section 3: Control Chart for Individuals, available from ASTM Headquarters.