



Designation: D8150 – 22

# Standard Test Method for Determination of Organic Chloride Content in Crude Oil by Distillation Followed by Detection Using Combustion Ion Chromatography<sup>1</sup>

This standard is issued under the fixed designation D8150; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope\*

1.1 This test method covers the determination of organic chloride (above 1  $\mu\text{g/g}$  organically-bound chlorine) in crude oils, using distillation and combustion ion chromatography.

1.2 This test method involves 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 6 regarding potential interferences.

1.3 The test procedure covers the determination of organic chloride in the washed naphtha fraction of crude oil by combustion ion chromatography. Other halides can be determined but are not included in the precision statement of the test method.

1.4 The values stated in SI units are to be regarded as standard. The preferred concentration units are micrograms of chloride per gram of sample.

1.4.1 *Exception*—The values given in parentheses are for information only.

1.5 **Warning**—Mercury has been designated by many regulatory agencies as a hazardous substance that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Use caution when handling mercury and mercury-containing products. See the applicable product Safety Data Sheet (SDS) for additional information. The potential exists that selling mercury or mercury-containing products, or both, is prohibited by local or national law. Users must determine legality of sales in their location.

1.6 *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*

*safe practices and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *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 Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- D86 Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure
- D1193 Specification for Reagent Water
- D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
- D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
- D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
- D4929 Test Method for Determination of Organic Chloride Content in Crude Oil
- 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, Liquid Fuels, 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

<sup>1</sup> 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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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto: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

E288 Specification for Laboratory Glass Volumetric Flasks  
E969 Specification for Glass Volumetric (Transfer) Pipets

### 3. Terminology

#### 3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology [D4175](#).

### 4. Summary of Test Method

4.1 *Distillation*—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 as well as Test Method [D4929](#) for determination of organic chloride content in crude oil. 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).

4.2 *Detection Using Combustion Ion Chromatography*—A sample of known weight or volume is placed into a sample boat and introduced at a controlled rate into a high temperature combustion tube. There, the sample is combusted in an oxygen rich pyrohydrolytic environment. The gaseous by-products of the combusted sample are trapped in an absorption medium where the hydrogen halides (HX) formed during combustion disassociate into their respective ions, X<sup>-</sup> while the sulfur oxides (SO<sub>x</sub>) formed are further oxidized to SO<sub>4</sub><sup>2-</sup> in the presence of an oxidizing agent. An aliquot of known volume of the absorbing solution is then automatically injected into an ion chromatograph (IC) by means of a sample injection valve. The halide and sulfate anions are separated on the anion separation column of the IC. The conductivity of the eluent is reduced with an anion suppression device prior to the ion chromatograph's conductivity detector, where the anions of interest are measured. Quantification of the chlorine in the original combusted sample is achieved by first calibrating the system with a series of standards containing known amounts of chlorine and then analyzing unknown samples under the same conditions as the standards. The combined system of pyrohydrolytic combustion followed by ion chromatographic detection is referred to as Combustion Ion Chromatography (CIC).

### 5. Significance and Use

5.1 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.

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

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

5.1.2 Several pipelines have set specification limits less than 1 µg/g organic chlorides in the whole crude, and less than 5 µg/g in the light naphtha, based on the yield of naphtha being 20 % of the original sample.

5.1.2.1 To ensure less than 1 µg/g organic chloride in the crude oil, the amount measured in the naphtha fraction shall be

less than  $1/f$  (where  $f$  is the naphtha fraction calculated with Eq 1). For example, a crude oil sample with 1 µg/g of organic chloride but a 10 % yield of naphtha would create a naphtha containing 10 µg/g organic chloride. Further, a crude containing 1 µg/g of organic chloride but a 40 % yield of naphtha would create a naphtha containing 2.5 µg/g organic chloride. Due to the difference in naphtha yields, the impact on refining operations can be significantly different.

5.1.2.2 Since crude oil deposits worldwide exhibit different yields of naphtha, the working range of detection for this method shall cover a broad range, possibly as high as 50 µg/g in a naphtha fraction.

5.1.3 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).

5.2 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.

5.3 Organic chloride species are potentially damaging to refinery processes. Hydrochloric acid can be produced in hydro-treating 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.

### 6. Interferences

6.1 *Detection Using Combustion Ion Chromatography*—Substances that co-elute with the anions of interest will interfere. A high concentration of one anion can interfere with other constituents if their retention times are close enough to affect the resolution of their peak.

### 7. Purity of Reagents

7.1 *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.<sup>3</sup> Other grades can 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.

<sup>3</sup> *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.

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

## DISTILLATION AND CLEANUP PROCEDURE

### 8. Apparatus

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

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

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

8.3.1 Other temperature measuring devices, such as thermocouples or resistance thermometers, can 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.

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

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

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

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

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

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

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

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

8.12 *Variable Transformer*, 2, for temperature control of upper and lower heating elements, 120 V, 10 amps.

### 9. Reagents and Materials

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

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

9.3 *Deionized Water*.

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

9.5 *Stopcock Grease*.<sup>4</sup>

<sup>4</sup> 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. 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,<sup>1</sup> which you may attend.

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

### 10. Sampling

10.1 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 can 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.)

10.2 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 ensure sample homogenization. (**Warning**—When heating is required, care should be taken so that no organic chloride containing hydrocarbons are lost.)

### 11. Preparation of Distillation Apparatus

11.1 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**.

11.2 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.

### 12. Procedure

12.1 Add a 500 mL crude oil test specimen to a 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.

NOTE 2—Appendix X2 describes a caution regarding crude oil sample preparation using water washing prior to distillation. While this method permits water washing of the distilled naphtha, as described in Section 12.2, it does not include neat sample preparation by water washing of the crude oil sample prior to testing. The information provided in Appendix X2 should not be interpreted as support for this preparation practice.

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

12.2 Transfer the naphtha fraction from the receiving cylinder to a 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 combustion ion chromatography.

12.3 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.

NOTE 3—Alternatively, the density of the crude oil specimen and the naphtha fraction can be determined using a digital density meter as specified in Test Method D4052.

### 13. Calculation

13.1 Calculate the naphtha fraction,  $f$ , using Eq 1 as follows:

$$f = \frac{M_n}{M_c} \quad (1)$$

where:

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

13.2 Calculate the density of the naphtha fraction using Eq 2 as follows:

$$\text{Density, g/mL} = \frac{m}{v} \quad (2)$$

where:

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

## DETECTION USING COMBUSTION ION CHROMATOGRAPHY

### 14. Apparatus

14.1 *Autosampler*, capable of accurately delivering a known volume of sample, typically in the range of 10  $\mu\text{L}$  to 100  $\mu\text{L}$ , into the sample boat.

NOTE 4—The sample syringe should be rinsed with clean solvent followed by a rinse with the next sample when changing from one vial to another. Follow the manufacturer's recommendation to minimize carry-over.

14.2 *Balance*, analytical, with sensitivity to 0.0001 g.

14.3 *Boat Inlet System*, The system provides a sampling port for the introduction of liquid samples into the sample boat and is connected to the inlet of the combustion tube. The system is swept by a humidified inert carrier gas and shall be capable of allowing the quantitative delivery of the material to be analyzed into the oxidation zone at a controlled rate.

14.4 *Boat Inlet Cooler*—Sample volatility requires an apparatus capable of cooling the sample boat prior to sample injection into the boat.

14.5 *Gas Flow Control*—The apparatus shall be equipped with flow controllers capable of maintaining a constant flow of oxygen and argon or helium carrier gas.

14.5.1 *Gas Regulators*, two-stage, gas regulators capable of regulating the pressures to 40 psi to 60 psi shall be used for the carrier and combustion gases. Follow instrument manufacturer's recommendations for pressure regulation.

14.6 *Furnace*—An electric furnace which can maintain a minimum temperature of 900 °C.

14.7 *Gas Absorption Unit*, having an absorption tube with sufficient capacity to hold a minimum of 5 mL which is automatically filled with a known volume of absorption solution by a built-in burette or other similar device. The gas absorption unit is interfaced to the IC and injects an aliquot of the absorption solution into the IC after the sample is combusted and the by-products of combustion are absorbed. The gas absorption unit rinses the absorption tube and the transfer lines from the combustion tube to the gas absorption unit with Type I reagent water ( 9.3) or other appropriate absorption solution prior to sample combustion and after the absorption solution is injected into the IC to minimize cross contamination.

14.8 *Gas-Tight Sampling Syringe*, of 10  $\mu\text{L}$ , 25  $\mu\text{L}$ , 50  $\mu\text{L}$ , 100  $\mu\text{L}$ , or 250  $\mu\text{L}$  capacity and capable of accurately delivering microliter quantities.

14.9 *Pyrohydrolytic Combustion Tube*, made of quartz and capable of withstanding temperatures up to 1100 °C. The combustion tube shall be of ample volume and can include quartz wool or other suitable medium to provide sufficient mixing and surface area to ensure complete combustion of the sample.

14.10 *Humidifier Delivery System*, capable of delivering Type 1 reagent water (Section 9.3) to the combustion tube at a controlled rate sufficient to provide a pyrohydrolytic environment.

14.11 *Ion Chromatograph (IC)*, (see Note 5) an analytical system with all required accessories including columns, suppressor and detector.

NOTE 5—Many different companies manufacture automatic ion chromatographs. Consult the specific manufacturer instruction manuals for details regarding setup and operation.

14.11.1 *Injection System*, capable of delivering 20  $\mu\text{L}$  to 500  $\mu\text{L}$  with a precision better than 1 % or as recommended for this determination by the manufacturer. Larger volumes can be used as long as the performance criteria of the method are not degraded.

14.11.2 *Pumping System*, capable of delivering mobile phase flows between 0.2 mL/min and 2.5 mL/min with a precision better than 2 %, or as recommended for this determination by the manufacturer.

14.11.3 *Continuous Eluent Generation (optional)*, to automatically prepare and purify the eluent used in the ion chromatography. Electrolytic eluent generation and auto-buret preparation of eluent by means of in-line dilution of a stock solution have been found satisfactory for this method. Other continuous eluent generation devices can be used if the precision and accuracy of the method are not degraded.

14.11.4 *Anion Pre-concentration Column (optional)*, used for anion pre-concentration and matrix elimination. Pre-concentration enables larger volumes of absorbing solution (1 mL to 3 mL) to be analyzed without the associated water dip. Matrix elimination refers to the elimination of any unreacted hydrogen peroxide in the absorbing solution prior to injection onto the guard and anion separator columns and potentially interfere with the fluoride peak resolution.

14.11.5 *Guard Column*, for protection of the analytical column from strongly retained constituents. Improved separation is obtained with additional theoretical plates.

14.11.6 *Anion Separator Column*, capable of producing satisfactory baseline separation of the anion peak of interest as shown in Fig. 1.

14.11.7 *Anion Suppressor Device*, reduces the background conductivity of the eluent after separation by the anion separator column. Both chemical and continuous electrolytic suppressors have been found satisfactory for this method. Other anion suppressor devices can be used as long as the precision and accuracy of the method are not degraded.

14.11.8 *Conductivity Detector*, temperature controlled to 0.01  $^{\circ}\text{C}$ , capable of at least 0  $\mu\text{S}/\text{cm}$  to 15 000  $\mu\text{S}/\text{cm}$  on a linear scale.

14.11.9 *Data Acquisition System*, an integrator or computer data handling system capable of integrating the peak areas of the ion chromatograph.

14.12 *Quartz or Ceramic Sample Boats*, of sufficient size to hold 10  $\mu\text{L}$  to 100  $\mu\text{L}$ . The boat is filled with quartz wool or other suitable material (9.4) to wick any remaining drops of the sample from the tip of the syringe needle prior to introduction of the sample into the furnace.

14.13 *Volumetric Flasks—Type Class A*, in accordance with Specification E288 at the volume required for the preparation of standards, reagents, and solutions.

14.14 *Volumetric Pipets—Type Class A*, in accordance with Specification E969 at the volume required for preparation of standards, reagents, and solutions.

## 15. Reagents and Materials

15.1 *Purity of Reagents*—Reagent grade or higher purity chemicals shall be used for the preparation of all samples, standards, eluent, and regenerator solutions. Unless otherwise indicated, it is intended that all reagents shall conform to the specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>3</sup> Other grades can be used, provided that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

NOTE 6—Purity of reagents are of particular importance when performing trace analysis (samples containing 1 mg/kg or less in analyte concentration). A system reagent blank should provide a chromatographic area response no greater than 50 % ( $1/2$ ) of the lowest calibration standard.

15.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type 1 having 18 M $\Omega$  cm resistance and conforming to Specification D1193.

15.3 *Quartz Wool*—(fine grade) or other suitable absorbent material can be used that is stable and capable of withstanding temperatures inside the furnace.

NOTE 7—Materials meeting the requirements in 9.4 provide a more uniform injection of the sample into the boat by wicking any remaining drops of the sample from the tip of the syringe needle prior to introduction of the sample into the furnace. Consult instrument manufacturer recommendations for further guidance.

15.4 *Argon or Helium*, carrier gas minimum 99.99 % purity.

NOTE 8—Purification scrubbers to ensure the removal of contaminants such as moisture (molecular sieve) and hydrocarbon trap filters (activated charcoal or equivalent) are recommended.

15.5 *Oxygen*, combustion gas minimum 99.75 % purity.

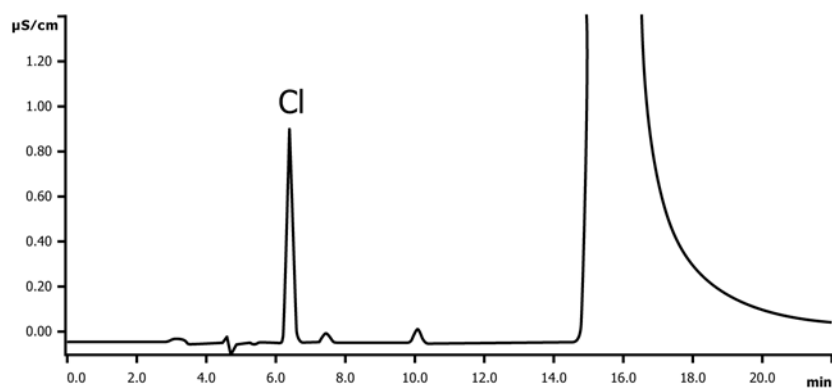


FIG. 1 Anion Peak of Interest (Chloride)

15.6 *Calibration Standards*, certified calibration standards from commercial sources or calibration standards prepared in the laboratory containing the elements or anions at the concentrations of interest.

15.6.1 *1-Chloropentane*, FW 106.59, 33.2% Cl.

15.6.2 *Organic Chloride Standard*, Chloropentane (FW 106.59, 33.2% Cl) diluted in isooctane has been used successfully for chloride calibration. Other sources of organic chloride can be used as long as performance, precision, and accuracy are not degraded.

NOTE 9—Calibration standards can have a useful shelf life of about three months if properly stored in a cool, dark place.

NOTE 10—A correction for chemical impurity can be used if deemed necessary.

15.7 *Eluent Solution*—Follow the specific guidelines for the preparation and use of the eluent solution from the manufacturer of the columns being used. Other concentrations can be used if precision and accuracy of the method is not degraded. The solutions recommended by the column manufacturer can be purchased from qualified vendors as long as the performance, precision, and accuracy are not degraded (see Section 16 regarding Hazards).

15.8 *Suppressor Solutions*:

15.8.1 *Chemical Suppressor Regenerant Solution*—Follow the specific manufacturer guidelines for the preparation and use of the suppressor solution. The manufacturer recommended solutions can be purchased from qualified vendors as long as the performance, precision, and accuracy are not degraded.

15.8.2 *Electrolytic Suppressor Current Setting*—Follow the specific guidelines for the current setting from the vendor of the suppressor being used based upon the flow rate and eluent concentration being used for the analysis.

15.9 *Solvent*—The solvent of choice should be capable of dissolving the standard or sample. The solvent should contain less than 0.05 mg/kg of the elements or anions of interest. The blank value shall be determined for each new bottle of solvent. Suggested solvents include, but are not limited to, iso-octane, xylene, toluene, and methanol.

15.10 *Stock Standard Solution(s) of approximately 1000 µg/mL*—Prepare a stock standard solution by accurately weighing to within 10 % of the target weight for the target standard compound listed in 15.6.1 into a 100 mL Type Class A volumetric flask. Dilute to volume with the selected solvent listed in 15.9. Calculate the actual concentration of the stock standard solution(s) for the element by using the formula in Eq 3 with the actual recorded weight of the target compound used for each element. This stock standard solution can be further diluted to other desired concentrations. Other suitable materials, weights and volumes can be substituted in preparing stock standard solution(s) as long as the performance of the method is not degraded.

NOTE 11—Stock standard solutions from commercial sources can be used if the accuracy, precision, and performance criteria of the method are not degraded.

15.10.1 *1-Chloropentane, (Chlorine)*, 0.3007 g target weight.

15.10.2 Calculate the actual concentration of the stock standard solution(s) for chloride using Eq 3 with the actual recorded weight of the target compound.

$$\text{Stock standard solution, } \mu\text{g/mL} = \frac{A \times B \times P}{V \times K} \times 10^6 \quad (3)$$

where:

A = mass of the target compound in grams, g,

B = % concentration of the elements in the respective target compounds listed in 15.6.1,

V = final diluted volume, mL,

P = % purity of target standard compounds listed in 15.6.1, and

K =  $10^6$  (correction factor to convert g/mL to µg/mL).

15.11 *Absorption Solution*—Type I water conforming to Specification D1193.

15.12 *Working Standard Solution*—Calculate the correct concentrations obtained from the stock standard solution in 15.10 and prepare a working standard by diluting the stock standard solution with solvent (15.9).

15.12.1 Prepare a 50.0 µg/mL working standard by using a 5.0 mL Type Class A volumetric pipet (Specification E969) and pipet 5.0 mL of the 1000 µg/mL stock standard solution(s) (15.10) into a 100 mL Type Class A volumetric flask (Specification E288) and dilute to mark with solvent (15.9).

15.13 *Calibration Standards*—Prepare calibration standards by diluting the working standard solution (15.12) to create 0.5 µg/mL, 1.0 µg/mL, 5.0 µg/mL, 10 µg/mL, and 25 µg/mL calibration standards by pipetting 1.0 mL, 2.0 mL, 10.0 mL, 20.0 mL, and 50.0 mL of working standard solution with the appropriate Class A volumetric pipets into five separate 100 mL Class A volumetric flasks and dilute to the mark with solvent (15.9). The calibration standards used to calibrate the system will include the solvent (15.9) as zero, the working standard for the 50 µg/mL and encompass the following approximate concentrations of calibration standards: 0.0 µg/mL, 0.5 µg/mL, 1.0 µg/mL, 5.0 µg/mL, 10 µg/mL, 25 µg/mL, and 50 µg/mL. The volume of working standard, in mL, needed to prepare a calibration standard is determined using the formula in Eq 4.

$$Vol_{work}, \text{ mL} = \frac{Conc_{cal} \times Vol_{cal}}{Conc_{work}} \quad (4)$$

where:

$Vol_{work}$  = volume of working standard needed to prepare the desired calibration standard, mL,

$Conc_{cal}$  = concentration of calibration standard desired, µg/mL,

$Vol_{cal}$  = volume of calibration standard desired, mL, and

$Conc_{work}$  = concentration of working standard, µg/mL.

15.13.1 A summary outlining the preparation of the calibration standards is shown in Table 1.

15.13.2 Final dilution volumes can be calculated using the formula in Eq 4.

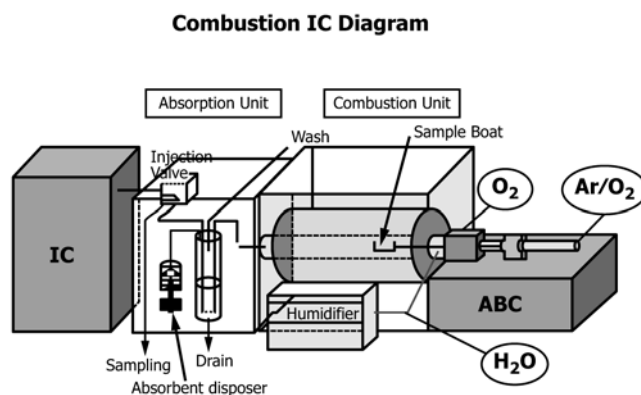
NOTE 12—Alternative volumes and concentrations of working and calibration standards can be prepared so long as the preparation meets the concentration range needed to properly bracket the response of the

**TABLE 1 Calibration Standards—Preparation from Working Standard Solution**

Calibration Standards Conc (µg/mL)	Working Standard Solution		Final Diluted Volume (mL) <sup>B</sup>
	Conc (µg/mL)	Volume (mL) <sup>A</sup>	
25	50.0	50	100
10	50.0	20	100
5.0	50.0	10	100
1.0	50.0	2.0	100
0.5	50.0	1.0	100

<sup>A</sup> Use Class A volumetric pipets or equivalent meeting Specification E969.

<sup>B</sup> Use Class A volumetric flasks or equivalent meeting Specification E288.



**FIG. 2 Combustion IC Diagram**

samples and adhere to the scope of the method.

NOTE 13—Working standard solutions should be prepared on a regular basis depending upon the frequency of use and age. The working standard solution can be retained, if refrigerated, for up to three months. Do not refrigerate working standard solution if prepared in benzene as the benzene will freeze and cause erratic results.

NOTE 14—Alternatively, calibration standards can be prepared by gravimetric dilution provided the same solvents are used throughout. The solvent used for the stock standard solution, working standard and calibration standards shall all be the same. In this case, the final concentration unit for the calibration standards will remain µg/mL even though the dilutions were performed gravimetrically.

## 16. Hazards

16.1 Consult the current version of OSHA regulations, supplier’s Safety Data Sheets (SDS), and local regulations for all materials used in this test method.

16.2 High temperature and flammable hydrocarbons occur in the test method. Use materials that are rated for containing these hydrocarbons in all sample containers and sample transfer apparatus. Exercise extra care when using flammable materials near the oxidative furnace.

16.3 Potassium hydroxide is a caustic alkali, which in an anhydrous or strong solution forms, is a hazardous material. In contact with the skin, it produces burns that can be quite serious unless promptly treated. Its action is insidious since it produces no immediate stinging or burning sensation and damage to the skin can result before its presence is realized. Eyes are particularly vulnerable to severe damage from alkalis.

16.4 Use safety goggles or face shields and rubber gloves when handling alkalis and avoid spillage on clothing. These materials rapidly attack wool and leather.

16.5 Use all appropriate safety precautions to clean up and discard in accordance with all federal, state, and local health and environmental regulations.

## 17. Preparation of Apparatus

17.1 Set up the instrument in accordance with the manufacturer’s instructions. A typical diagram of a CIC system is shown in Fig. 2.

17.2 Set instrument parameters in accordance with the manufacturer’s instructions.

17.3 Adjust gas flows and pyrolysis temperatures to the operating conditions as recommended by the instrument manufacturer.

## 18. Calibration

18.1 Prior to the analysis of standards or samples, it is necessary to run a series of system blanks (18.1.1) and solvent blanks (18.1.2) to ensure cleanliness of the system. Follow the manufacturer’s recommendation for this process.

18.1.1 A system blank consists of a combustion ion chromatography (CIC) analysis with no solvent or sample injection in which the same combustion, chromatography and time protocols are used as for the sample analysis, but without the combustion of a sample or solvent blank. The system blank shall be equal to or less than 50 % (½) the area counts of the lowest calibration standard used for calibration.

18.1.2 A solvent blank consists of a combustion ion chromatography (CIC) analysis of the solvent used for preparation of the calibration standards in which the same combustion, chromatography, and time protocols are used for the sample analysis. The solvent blank area count shall be equal to or less than 50 % (½) the area counts of the lowest calibration standard used for calibration.

18.1.3 The series of system blanks should be analyzed repeatedly until a stable baseline response is achieved. Typically, 3 to 5 system blanks will be required following start-up of the instrument. A stable background is considered achieved when the analysis of a minimum of two consecutive system blanks have area counts equal to or less than 15 % relative difference for the anions of interest. If a stable baseline response is not obtained, follow the manufacturer’s recommendations to check for sources of contamination.

18.2 Prepare a series of calibration standards covering the range of samples to be analyzed by diluting the working standard (15.12) prepared from the stock standard solution (15.10) to the desired final concentrations.

NOTE 15—Commercially available standards can be used as long as the accuracy and precision of the method is not degraded.

18.3 Analyze the calibration standards covering the analytical range of the samples and determine the peak areas corresponding to the chloride ion. The use of an automated sampling device is required to ensure accurate and repeatable injection volumes and techniques.

18.4 An aliquot of absorbing solution following the combustion of each standard is introduced into the IC for separation