



Designation: D8150 – 22

Standard Test Method for Determination of Organic Chloride Content in Crude Oil by Distillation Followed by Detection Using Combustion Ion Chromatography¹

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 (ε) 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 µg/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 appro-*

priate safety, health, 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:²

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

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

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^- while the sulfur oxides (SO_x) formed are further oxidized to SO_4^{2-} 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.³ 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.

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.