Designation: D4929 – 22

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

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 reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 The procedures in this test method cover the determination of organic chloride (above 1 µg/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 6 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 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

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

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

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

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *naphtha fraction, n*—the fraction of the crude oil collected from atmospheric distillation over a boiling range up to 204 °C.

3.2.2 *organic chloride compounds, n*—compounds containing carbon and at least one chlorine.

[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**

3.2.3 *total organic chloride compounds, n*—the sum of compounds containing carbon and at least one chlorine.

4. Summary of Test Method

4.1 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).

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

4.2.1 *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.

4.2.2 *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.

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

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

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

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

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

4.2.6 *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 Kα 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.

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 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.

5.1.2.1 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).

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 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.

6. Interferences

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

6.2 *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.

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

6.3 *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.

6.3.1 Matrix effects result when the elemental composition (excluding chlorine) of samples differs significantly from the standards, and significant errors in the chlorine determination