



Designation: D6470 – 99 (Reapproved 2004)

Standard Test Method for Salt in Crude Oils (Potentiometric Method)¹

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1. Scope

1.1 This test method covers the determination of salt in crude oils. For the purpose of this test method, salt is expressed as % (m/m) NaCl (sodium chloride) and covers the range from 0.0005 to 0.15 % (m/m).

1.2 The limit of detection is 0.0002 % (m/m) for salt (as NaCl).

1.3 The test method is applicable to nearly all of the heavier petroleum products, such as crude oils, residues, and fuel oils. It may also be applied to used turbine oil and marine diesel fuel to estimate seawater contamination. Water extractable salts, originating from additives present in oils, are codetermined.

1.4 The values stated in SI units are to be regarded as the standard.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D329 Specification for Acetone

D770 Specification for Isopropyl Alcohol

D843 Specification for Nitration Grade Xylene

D1193 Specification for Reagent Water

D4006 Test Method for Water in Crude Oil by Distillation

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D4377 Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration

D4928 Test Methods for Water in Crude Oils by Coulometric Karl Fischer Titration

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

3. Summary of Test Method

3.1 After homogenizing the crude oil with a mixer, a weighed aliquot is dissolved in xylene at 65°C and extracted with specified volumes of alcohol, acetone, and water in an electrically heated extraction apparatus. A portion of the aqueous extract is analyzed for total halides by potentiometric titration.

4. Significance and Use

4.1 A knowledge of water extractable inorganic halides in oil is important when deciding whether or not the oils need desalting. Excessive halide, especially in crude oil, frequently results in higher corrosion rates in refining units.

5. Apparatus

5.1 *Extraction Apparatus*, made of borosilicate glass, conforming to the dimensions given in Fig. 1, and consisting of the following component parts:

5.1.1 *Boiling Flask*, 500 mL capacity.

5.1.2 *Hopkins Reflux Condenser*, having a vapor outlet connected by a rubber tube to an outside vent or to a suction hood.

5.1.3 *Thistle Tube*, approximately 70 mL capacity, with a line to indicate approximately the 50 mL level.

5.1.4 *Heating Tube*, containing a chimney for increasing convection in the liquid.

5.1.5 *Heating Coil*, 250 W, consisting of a suitable gage of Nichrome wire.

5.1.6 *Rheostat*, of suitable resistance and capacity, for regulating the heater.

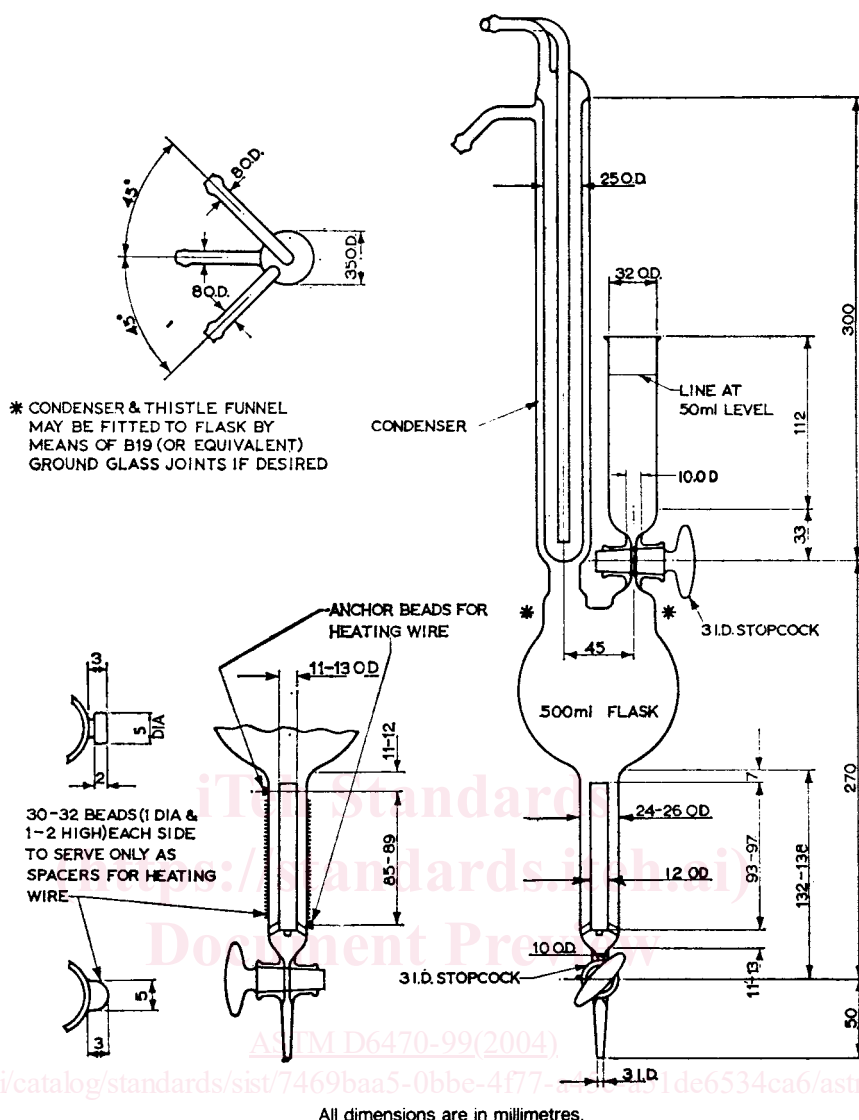
5.2 *Safety Shield*, colorless safety glass, or equivalent, to be mounted in front of the extraction apparatus (see 5.1).

5.3 *Sampling Tube*, glass, length approximately 600 mm, I.D. approximately 5 mm, with a bulb having a volume of 100 mL, or more, and drawn out at one end to an opening of inside diameter (I.D.) 2 to 3 mm. A pipette with cut-off tip makes a suitable sample tube.

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products 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.



All dimensions are in millimetres.

NOTE 1—Hopkins-type condenser is used.

FIG. 1 Extraction Apparatus

5.4 *Potentiometric Titration Equipment*, with a measuring accuracy of ± 2 mV, or better, provided with a silver indicating and a glass reference electrode and 10 mL burette, preferably piston type. If an automatic titrator is used, this shall be capable of adding fixed increments of titrant (see 9.3.3.2).

5.5 *Magnetic Stirrer*, with polytetrafluoroethylene (PTFE)-coated stirring bar.

5.6 *Homogenizer*. A mixer with counter-rotating blades operating at approximately 3000 r/min (50/s) is usually suitable for homogenization of samples up to 500 mL. Other designs can also be used provided the performance conforms to the requirements described in Annex A1.

5.7 *Oven*, explosion-proof, temperature $65 \pm 5^\circ\text{C}$.

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

5.9 *Stopwatch*.

6. Reagents and Materials

6.1 *Purity of Reagents*—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

6.2 *Purity of Water*—For all purposes where water is mentioned, reagent water of a suitable purity shall be used. Various types of reagent water are described in Specification D1193.

6.3 *Acetone (2-propanone)*, conforming to Specification D329. (**Warning**—Extremely flammable. Vapors may cause flashfire.)

6.4 *Alcohol*, for example, 95 % (V/V) ethanol, or propan-2-ol (isopropyl alcohol), conforming to Specification D770. (**Warning**—Flammable.)

³ *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 *Annual 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.

6.5 *Barium Nitrate*, A.R., crystals. (**Warning**—Barium compounds and their solutions present a health risk if incorrectly handled. Prevent all contact.)

6.6 *Hydrochloric Acid*, 0.1 mol/L, aqueous. Add 9 mL of A.R. concentrated hydrochloric acid (density 1.19 g/mL) to 1 L with water. (**Warning**—Corrosive. Causes skin burns.)

6.7 *Nitric Acid*, 5 mol/L, aqueous. Cautiously add 325 mL of A.R. concentrated nitric acid (density 1.42 g/mL) to 1 L water, while stirring. (**Warning**—Corrosive. Causes skin burns.)

6.8 *Silver Nitrate Solution*, standard, $c(\text{AgNO}_3) = 0.1$ mol/L, aqueous. Prepare, standardize and store as described in Practice E200 for 0.1 N aqueous solution, reading concentrations in mol/L in place of normality. Restandardize regularly, but in any case before preparation of the standard 0.01 mol/L solution (see 6.9)

NOTE 1—Alternatively, ampoules containing concentrated solutions for preparation of standard volumetric solutions are available from various suppliers. (**Warning**—Silver compounds and their solutions present a health risk if incorrectly handled. Prevent all contact.)

6.9 *Silver Nitrate Solution*, standard, $c(\text{AgNO}_3) = 0.01$ mol/L, aqueous. Prepare shortly before use by accurately diluting one volume of the recently restandardized 0.1 mol/L silver nitrate solution (**Warning**—see 6.8) to a tenfold volume with water.

6.10 *Sodium Chloride Solution*, approximately 1 mmol/L, aqueous. Dissolve 59 ± 1 mg sodium chloride in 1 L water.

6.11 *Xylene*, conforming to Specification D843. (**Warning**—Xylene presents a health risk if incorrectly handled. Avoid inhalation. Extract vapor by working in a fume cupboard.)

6.12 *Lead Acetate Paper*.

6.13 *Polishing Paper*, 800 grit, or finer, to polish the silver electrode.

7. Sampling and Sample Preparation

7.1 Sampling is defined as all the steps required to obtain an aliquot representative of the contents of any pipe, tank, or other system, and to place the sample into the laboratory sample container. The laboratory sample container and sample volume shall be of sufficient dimensions and volume to allow mixing, as described in 7.4. (**Warning**—The results of the round robin have shown that for reliable results, strict adherence to the sampling and mixing procedure is of the utmost importance.)

7.2 *Laboratory Sample*—The sample of crude oil presented to the laboratory or test facility for analysis by this test method. Only representative samples obtained as specified in Practices D4057 and D4177 shall be used for this test method.

7.3 *Test Sample*—The sample aliquot obtained from the laboratory sample for analysis by this test method. Once drawn, the entire portion of the test sample will be used in the analysis. Mix the laboratory sample properly, as described in 7.4, prior to drawing the test sample.

7.4 Homogenize the laboratory sample of crude oil immediately (within 15 min) before drawing the test sample to ensure complete homogeneity. Mix the sample at room temperature (15 to 25°C), or less, in the laboratory sample container, and record the temperature of the sample in degrees

Celsius immediately before mixing. Heat waxy samples, solid at room temperature, to 3°C above their pour point in order to facilitate test sample withdrawal. Select the type of mixer related to the quantity of crude oil in the laboratory sample container. Before any unknown mixer is used, the specifications for the homogenization test (see Annex A1) shall be met. Reevaluate the mixer for any changes in the type of crude, the quantity of crude, the shape of the sample container, or the mixing conditions (such as mixing speed and time of mixing).

7.5 For small laboratory sample containers and volumes, 50 to 500 mL, a nonaerating, high speed (3000 r/min), shear mixer is required. Use the mixing time, mixing speed, and height above the bottom of the container found to be satisfactory to Annex A1. For larger containers and volumes, appropriate mixing conditions shall be defined by following a set of procedures similar to those outlined in Annex A1 and Practice D4177 but modified for application to the larger containers and volumes. Clean and dry the mixer between samples.

7.6 Record the temperature of the sample immediately after homogenization. The rise in temperature between this reading and the initial reading prior to mixing (see 7.4) shall not exceed 10°C, otherwise excessive loss of volatile vapors can occur or the dispersion can become unstable.

7.7 In order to ensure that crude oils with rapidly settling impurities are properly sampled, withdraw the test sample container immediately after homogenization by lowering the tip of the sample tube (see 5.3) almost to the bottom of the container, and withdrawing the test sample as quickly as possible. Clean and dry the sample tube before and after sampling.

8. Preparation of Apparatus

8.1 *Extraction Apparatus*—To reduce the risk of superheating and the resulting hazards, introduce a gentle stream of air into the bottom of the extraction apparatus. This can be done by passing a length of hypodermic tubing through the bore of the tap so that the lower end reaches the bottom of the heating tube, while the upper end of the tubing is passed through a rubber bung in the top of the thistle tube. Place the extraction apparatus behind a safety screen. Shield all electrical resistances and devices; alternatively, remove them from the immediate vicinity of the extraction apparatus.

8.2 *Potentiometric Titration Equipment*:

8.2.1 *Glass Electrode*—Before each titration (or each series of titrations), rinse the electrode with water and soak it for at least 10 min in 0.1 mol/L hydrochloric acid (see 6.6). Then rinse again with water. After titrations store the electrode immersed in reagent water.

8.2.2 *Silver Electrode*—Polish the silver electrode before each set of titrations with polishing paper (see 6.13) until a clean, polished metal surface is obtained.

9. Procedure

9.1 *Extraction*:

9.1.1 Weigh about 40 g of sample, to the nearest 0.1 g, into a 250 mL beaker and heat on a water bath or in an oven to $65 \pm 5^\circ\text{C}$. Heat 40 ± 1 mL of xylene to the same temperature and add slowly to the sample while stirring constantly until dissolution is complete. Transfer the solution quantitatively to