



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:

D 329 Specification for Acetone²

D 770 Specification for Isopropyl Alcohol²

D 843 Specification for Nitration Grade Xylene³

D 1193 Specification for Reagent Water³

D 4006 Test Method for Water in Crude Oil by Distillation⁴

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products⁴

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products⁴

D 4377 Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration⁴

D 4928 Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration⁵

E 200 Practice for Preparation, Standardization, and Stor-

age of Standard and Reagent Solutions for Chemical Analysis⁶

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.

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

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 *Annual Book of ASTM Standards*, Vol 06.04.

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.

⁶ *Annual Book of ASTM Standards*, Vol 15.05.

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 E 200 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 ten-fold 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 D 843. (**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 D 4057 and D 4177 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 D 4177 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 the extraction apparatus, rinsing the beaker with two separate

portions of 15 ± 1 mL of hot xylene and adding these rinsings also to the extraction apparatus.

9.1.2 While the solution is still hot, add 25 ± 1 mL of ethanol or isopropyl alcohol and 15 ± 1 mL of acetone, using these portions for further rinsing of the beaker. Switch on the heating element of the extraction apparatus to full heat until boiling begins, then adjust the rheostat to regulate the heat to maintain boiling at a vigorous rate, but not at such a rate to cause bumping in the flask or to cause the condenser to flood. Allow to reflux for 2 min after the liquid starts boiling (see 8.1). Switch off the heater. When boiling ceases, add 125 ± 1 mL of water and again bring the liquid to the boil and reflux for a further 15 min.

9.1.3 Switch off the heater, and allow the two phases to separate for 5 to 10 min. Draw off the aqueous phase, filtering through a filter paper into a conical flask of suitable capacity, stopper the flask, and retain the contents for the total halide determination as described in 9.2 and 9.3.

9.2 *Removal of Sulfur-Containing Compounds*—Pipet 50.0 mL of the aqueous extract (see 9.1.3) into a beaker, and add 5 mL of 5 mol/L nitric acid (see 6.7). Cover the beaker with a watch-glass, and bring the contents to the boil. Test the vapors periodically for hydrogen sulphide with lead acetate paper and continue boiling for a further 5 min after a negative result has been obtained. Allow the contents of the beaker to cool and quantitatively transfer to a 250-mL titration vessel, rinsing the beaker with water. (**Warning**—Hydrogen sulfide presents a health risk if incorrectly handled. Avoid inhalation. Extract escaping gas by working in a fume cupboard.)

9.3 Salt Determination:

9.3.1 Pipet 10.0 mL of the 1 mmol/L sodium chloride solution (see 6.10; see Note 2) in the titration vessel (see 9.2). Adjust the volume of the sample solution in the vessel to 150 mL with acetone (see Note 3). Add approx. 0.5 g of barium nitrate crystals. Stir to dissolve the barium nitrate.

NOTE 2—To obtain a titration end point even for small amounts of chloride, a fixed amount of sodium chloride is added to the blank and sample solution.

NOTE 3—Acetone is added to lower the solubility of the silver chloride precipitate.

9.3.2 Fill the burette with 0.01 mol/L silver nitrate solution, place the beaker on a magnetic stirrer, and immerse the electrodes in the sample solution. Immerse the tip of the burette approximately 25 mm below the liquid surface, and adjust the magnetic stirrer to produce vigorous stirring without spattering.

9.3.3 Titrate as follows:

9.3.3.1 When applying manual titration, record the initial burette reading and the pH/millivolt meter reading. Titrate with standard silver nitrate solution, adding the titrant in small portions. After each addition, wait until a constant potential has been established and record the burette and meter readings (see Note 4). In regions between inflections where the potential change is small for each increment of silver nitrate used, add volumes as large as 0.5 mL. When the rate of change of potential becomes greater than 5 mV per 0.1 mL, use 0.1 mL increments of silver nitrate solution. Construct a graph by plotting the meter readings versus the volumes of standard

silver nitrate solution used in the titration.

NOTE 4—If silver halides are precipitated on the silver electrode, tap the electrode gently to dislodge the clinging precipitate and ensure that an equilibrium has been reached before taking a meter reading.

9.3.3.2 When using an automatic recording titrator, titrate with standard silver nitrate solution, adding fixed increments.

NOTE 5—It is essential that incremental titration is applied, as described in 9.3.3, to ensure that complete precipitation occurs between additions.

9.3.3.3 After each titration, clean the electrodes with water (see also 8.2)

9.4 Curve Interpretation:

9.4.1 The end-point of the titration is found as the most positive value of the steepest portion of the observed inflection of the titration curve.

9.4.2 The exact location of the inflection point is dependent on the chloride concentration, the electrodes used, the nature of the titration medium, and the concentration of the silver nitrate solution applied. To establish the value of the cell potential at the inflection point, prepare a typical solution containing 0.001 to 1 mol of chloride, titrate this solution as described in 9.3, and determine the inflection point.

9.5 *Blank Determination*—Prepare a blank solution by pipetting 10.0 mL of 1 mmol/L sodium chloride solution (see 6.10) in a titration vessel. Add 50 mL demineralized water, 5 mL of 5 mol/L nitric acid (see 6.7) and approximately 0.5 g of barium nitrate crystals (see 6.5). Adjust the volume of the sample solution in the vessel to 150 to 175 mL with acetone. Stir to dissolve the barium nitrate. Titrate the solution as described in 9.3.

10. Calculation

10.1 Calculate the amount of chloride present in the aqueous solution, in μmol , by means of the following equation:

$$\text{Amount of chloride, } \mu\text{mol} = (V - V_b) \times C \times 10^3 \quad (1)$$

where:

V = volume of standard silver nitrate solution used to endpoint, mL,

V_b = volume of standard silver nitrate solution used for blank titration, mL, and

C = concentration of standard silver nitrate solution, mol/L.

10.2 Calculate the salt content of the sample, expressed as % (m/m) sodium chloride, by means of the following equation:

$$\text{Salt, as sodium chloride, \% (m/m)} = \frac{A \times 58.44}{m \times P \times 10^6} \times 100 \quad (2)$$

where:

A = amount of chloride found in the aliquot of the aqueous extract (see 10.1), μmol ,

P = proportional part of extract used in analysis; P = 50/158 for ethanol and 50/152 for isopropyl alcohol (see Note 6), and

m = mass of the sample, g.

NOTE 6—If the water content of the sample (for example, in accordance with Test Method D 4006) is less than 5 % (m/m), the volume of the extract from a single extraction may be assumed to be 158 mL when using ethanol or 152 mL when using isopropyl alcohol. Hence P will be 50/158

or 50/152. If, however, the water content of the sample exceeds 5 % (m/m), the appropriate amount of water should be added in calculating *P*.

$$R = 0.0477 X^{0.612} \quad (4)$$

11. Report

11.1 Report the result calculated in 10.2 as salt (as NaCl), mass %, rounding to two significant digits. State that the result was obtained in accordance with Test Method D 6470.

12. Precision and Bias ⁸

12.1 *Precision*—The precision of this test method as determined by a statistical examination of interlaboratory test results is as follows:

12.1.1 *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 the correct operation of the test method, exceed the following values in only one case in twenty.

$$r = 0.0243 X^{0.612} \quad (3)$$

where:

X = the salt concentration in mass % (as NaCl).

12.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test materials, would, in the long run, and in the normal and the correct operation of the test method, exceed the following values in only one case in twenty.

where:

X = the salt concentration in mass % (as NaCl).

NOTE 7—The precision data from the interlaboratory program were obtained on three different crude oils ranging in density between 825 and 950 kg/m³, spiked with varying amounts of (artificial) sea water and formation water where the salt content (as NaCl) varied from 0.0005 to 0.15 mass %. Statistical evaluation could not detect any dependency of precision on crude oil density or water type, except for reproducibility. The reproducibility variance (power transform) proved to be inversely related to crude oil density and varied from 0.49 for the heavy crude to 1.35 for the light crude. The above quoted reproducibility represents the overall variance of 0.99.

12.2 *Bias*—The procedure in Test Method D 6470 has no bias since salt content is defined only in terms of this test method and certified reference materials are unavailable. However, since the samples from the interlaboratory study where neat desalted crudes, spiked with known quantities of salt (as sea water and formation water), bias might be defined as percent recovery of halide added. Over the range 0.0005 to 0.0400 mass % salt added, the recovery proved to be constant and averaged 97 %. Over the range 0.0400 to 0.1500, the recovery proved to be a function of concentration and gradually decreased from 97 % at 0.04 mass % to 88 % at the 0.15 mass % level.

13. Keywords

13.1 crude oil; extraction; potentiometric; salt

⁸ Supporting data have been filed at ASTM Headquarters. Request RR:D02-1458.

ANNEX

(Mandatory Information)

A1. HOMOGENIZATION EFFICIENCY OF UNKNOWN MIXER

A1.1 The homogenization efficiency of each unknown mixer must be evaluated before use. To evaluate the mixer, confirm that the expected water content can be obtained by the Karl Fischer titration, following the addition of a known amount of water to a nominally dry crude and the homogenization of this mixture. This procedure for checking the homogenization efficiency of a mixer is based upon the use of a 500-mL sample container; however, a similar procedure must be followed for the different sample sizes that may be received in a particular laboratory.

A1.2 Weigh the 500-mL sample container to the nearest 0.01 g. Fill the container to about 80 % with the dry crude (less than 0.1 mass % water). Insert the mixer shaft into the container so that the head is about 5 mm from the container bottom. Homogenize the contents of the container at 80 % power for 2 min, take test aliquot of the resulting emulsion, and determine its water content in duplicate, as described in Test Method D 4377 or D 4928. Obtain the average of the duplicate

results, and designate this as the inherent water content.

A1.3 Weigh the crude and container to the nearest 0.01 g. Record the temperature of the oil to the nearest 1°C. Immerse the mixer in the crude as in A1.2. Using a Grade A pipette, transfer 15 mL of water to the contents of the container. Homogenize the oil and water at 80 % power for 2 min. Record the temperature of the emulsion immediately after homogenization. The rise in temperature during homogenization should not exceed 10°C; otherwise, loss of water can occur and the emulsion can be destabilized. Determine the water content of the crude immediately after mixing. Sample the crude just below the liquid level.

A1.4 Without additionally mixing the crude, determine the water content (single determination) of the crude 15 and 30 min after the initial mixing in A1.3.

A1.5 The water contents (added plus inherent) of these

three portions (immediately, 15 and 30 min after homogenization) shall agree within 0.10 % absolute of each other and within 0.10 % of the calculated water content (that is, added plus inherent). If they do not agree, then the homogenization must be repeated on fresh portions of crude and water in a clean container while changing the power, mixing time, or the height of the mixer shaft, or a combination thereof, until the chosen conditions result in a mixture that yields the required agreement. These conditions of power, mixing time, and depth of immersion of the mixer shaft are then to be used for all subsequent mixings.

A1.6 The mixing conditions shall be evaluated for all new crudes and repeated periodically for known crudes spiked with water to 4 to 5 mass % to check that the conditions remain effective.

A1.7 This procedure need not be effective for crudes with abnormally low or high viscosity at room temperature. These crudes can require special treatment in order to obtain stable water-in-crude emulsions.

NOTE A1.1—Some crudes cannot hold a stable water emulsion for the 15 and 30 min described. In some cases, the crude oil can be cooled below room temperature to improve the stability of the emulsion. Alternatively, additional testing is needed to determine the time period over which the emulsion is stable for a given set of mixing conditions. The test specimen should be taken within the stability period established.

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