Designation: D 3230 – 99

An American National Standard

Standard Test Method for Salts in Crude Oil (Electrometric Method)[1]

This standard is issued under the fixed designation D 3230; 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 the approximate chloride (salts) concentration in crude oil. The range of concentration covered is 0 to 500 mg/kg or 0 to 150 lbs/1000 bbl as chloride concentration/volume of crude oil.

1.2 This test method measures conductivity in the crude oil due to the presence of common chlorides, such as sodium, calcium, and magnesium. Other conductive materials may also be present in the crude oil.

1.3 The values stated in SI units are regarded as standard. Acceptable concentration units are g/m^3 or PTB (lbs/1000 bbl).

1.4 *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.* For specific precautionary statements, see 7.3, 7.4, and 7.11.

2. Referenced Documents

2.1 *ASTM Standards:*

D 91 Test Method for Precipitation Number of Lubricating Oils[2]

D 381 Test Method for Existent Gum in Fuels by Jet Evaporation[2]

D 1193 Specification for Reagent Water[3]

D 4928 Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration[4]

D 5002 Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer[4]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *salts in crude oil*—commonly, chlorides of sodium, calcium, and magnesium dissolved in crude oil. Other inorganic chlorides may also be present.

3.1.2 *PTB*—lbs/1000 bbl

4. Summary of Test Method

4.1 This test method measures the conductivity of a solution of crude oil in a mixed alcohol solvent when subjected to an electrical stress. This test method measures conductivity due to the presence of inorganic chlorides, and other conductive material, in the crude oil. A homogenized test specimen is dissolved in a mixed alcohol solvent and placed in a test cell consisting of a beaker and a set of electrodes. A voltage is impressed on the electrodes, and the resulting current flow is measured. The chloride (salt) content is obtained by reference to a calibration curve of current versus chloride concentration of known mixtures. Calibration curves are based on standards prepared to approximate the type and concentration of chlorides in the crude oils being tested.

5. Significance and Use

5.1 This test method is used to determine the approximate chloride content of crude oils, a knowledge of which is important in deciding whether or not the crude oil needs desalting. The efficiency of the process desalter can also be evaluated.

5.2 Excessive chloride left in the crude oil frequently results in higher corrosion rates in refining units and also has detrimental effects on catalysts used in these units.

5.3 This test method provides a rapid and convenient means of determining the approximate content of chlorides in crude oil and is useful to crude oil processors.

6. Apparatus

6.1 The apparatus (see Annex A1) shall consist of a control unit capable of producing and displaying several voltage levels for applying stress to a set of electrodes suspended in a test beaker containing a test solution. The apparatus shall be capable of measuring and displaying the current (mA) conducted through the test solution between the electrodes at each voltage level.

NOTE 1—Some apparatus are capable of measuring voltage and current internally and, after comparison to internal calibration curves, of displaying the resultant concentration.

6.2 *Test Beaker*—See Annex A1.

6.3 *Pipet, 10 mL (total delivery)*—The type of pipet that is rinsed to ensure the entire volume of the material is contained in the intended volume.

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricantsand is the direct responsibility of Subcommittee D02.03on Elemental Analysis.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 05.03.

6.4 *Cylinders, 100 mL*, stoppered.

6.5 *Other volumetric and graduated pipets and volumetric flasks.*

7. Reagents and Materials

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 American Chemical Society, where such specifications are available.[5] Other grades may 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II in Specification D 1193.

7.3 *Mixed Alcohol Solvent*—Mix 63 volumes of 1-butanol and 37 volumes of absolute methyl alcohol (anhydrous). To each litre of this mixture, add 3 mL of water. (**Warning**—Flammable. Liquid causes eye burns. Vapor harmful. May be fatal or cause blindness if swallowed or inhaled.)

NOTE 2—The mixed alcohol solvent is suitable for use if its conductivity is less than 0.25 mA at 125 V ac. High conductivity can be due to excess water in the solvent and can indicate that the methyl alcohol used is not anhydrous.

7.4 *ASTM Precipitation Naphtha*, conforming to the requirements of Test Method D 91. (**Warning**—Extremely Flammable. Harmful if inhaled. Vapors may cause flash fire.)

7.5 *Calcium Chloride ($CaCl_2$) Solution* (10 g/L)—Transfer 1.00± 0.01 g of $CaCl_2$, or the equivalent weight of a hydrated salt, into a 100-mL volumetric flask and dissolve in 25 mL of water. Dilute to the mark with mixed alcohol solvent.

7.6 *Magnesium Chloride ($MgCl_2$) Solution (10 g/L)*—Transfer 1.00 ± 0.01 g of $MgCl_2$, or the equivalent weight of a hydrated salt, into 100-mL volumetric flask and dissolve in 25 mL of water. Dilute to the mark with mixed alcohol solvent.

7.7 *Sodium Chloride (NaCl) Solution (10 g/L)*—Transfer 1.00 ± 0.01 g of NaCl into a 100-mL volumetric flask and dissolve in 25 mL of water. Dilute to the mark with mixed alcohol solvent.

7.8 *Oil, Refined Neutral*—Any refined chloride-free oil of approximately 20 mm^2/sec (cSt) viscosity at 40°C and free of additive.

7.9 *Salts, Mixed Solution (Concentrated Solution)*—Combine 10.0 mL of the $CaCl_2$ solution, 20.0 mL of the $MgCl_2$ solution, and 70.0 mL of the NaCl solution, and mix thoroughly.

NOTE 3—The 10:20:70 proportions are representative of the chlorides present in a number of common crude oils. When the relative proportions of calcium, magnesium, and sodium chlorides are known for a given crude oil, such proportions should be used for most the accurate results.

7.10 *Salts, Mixed Solution (Dilute Solution)*—Transfer 10 mL of the concentrated mixed chlorides solution into a 1000-mL volumetric flask, and dilute to the mark with mixed alcohol solvent.

7.11 *Xylene*, reagent grade, minimum purity. (**Warning**—Flammable. Vapor harmful.)

8. Sampling

8.1 Obtain a sample and test specimen in accordance with Test Method D 4928. Ensure that the sample is completely homogenized with a suitable mixer. See Annex A1 of Test Method D 4928 for suitable apparatus and proving.

8.2 Samples of very viscous materials may be warmed until they are reasonably fluid before they are sampled; however, no sample shall be heated more than is necessary to lower the viscosity to a manageable level.

8.3 Samples of crude oil contain water and sediment and are inhomogeneous by nature. The presence of water and sediment will influence the conductivity of the sample. The utmost care shall be taken in obtaining homogenized representative samples.

9. Preparation of Apparatus

9.1 Support the apparatus on a level, steady surface, such as a table.

9.2 Prepare the apparatus for operation in accordance with the manufacturer's instructions for calibrating, checking, and operating the equipment. (**Warning**—The voltage applied to the electrodes can be as great as 250 V ac, and hazardous.)

9.3 Thoroughly clean and dry all parts of the test beaker, the electrodes, and its accessories before starting the test, being sure to remove any solvent that had been used to clean the apparatus.

10. Calibration

10.1 The conductivity of solutions is affected by the temperature of the specimen when measurements are made. The temperature of the test specimen at the time of measurement shall be within 3°C of the temperature at which the calibration curves were made.

10.2 Establish a blank measurement by following the procedure in 10.3 and 10.4, omitting the mixed salts solution. When the indicated electrode current is greater than 0.25 mA at 125 V ac, water or another conductive impurity is present and its source must be found and eliminated before calibration can be completed. Determine a blank measurement each time fresh xylene or mixed solvent is used.

10.3 Into a dry, 100-mL graduated, glass-stoppered mixing cylinder, add 15 mL of xylene. From a pipet (total delivery), add 10 mL of neutral oil. Rinse the pipet with xylene until free of oil. Make up to 50 mL with xylene. Stopper and shake the cylinder vigorously for approximately 60 s to effect solution. Add a quantity of dilute mixed salts solution, in accordance with Table 1, that is appropriate to the range of salt contents to be measured. Dilute to 100 mL with mixed alcohol solvent. Again shake the cylinder vigorously for approximately 30 s to effect solution, and allow the solution to stand approximately 5 min. Pour the solution into a dry test beaker.

[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D.C. 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.

TABLE 1 Standard Samples

Salt g/m^3 of Crude Oil	Salt lbs/1000 bbl of Crude Oil	Mixed Salts Solution (dilute), mL
3	1.0	0.3
9	3.0	1.0
15	5.0	1.5
30	10.0	3.0
45	16.0	4.5
60	21.0	6.0
75	26.0	8.0
90	31.0	9.5
115	40.0	12.0
145	51.0	15.0
190	66.0	20.0
215	75.0	22.5
245	86.00	25.5
290	101.0	30.5
430	151.0	45.0

10.4 Immediately place the electrodes into the solution in the beaker, making sure that the upper edge of the electrode plates are below the surface of the solution. Adjust the indicated electrode voltage to a series of values, for example 25, 50, 125, 200, and 250 V ac. At each voltage, note the current reading and record the voltage displayed and the current to the nearest 0.01 mA. Remove the electrodes from the solution, rinse with xylene followed by naphtha, and allow them to dry.

NOTE 4—With some apparatus, the detailed settings will not be required since the electronics are built-in for auto-ranging. Determination of the blank and the calibration standard responses are the same.

10.5 Repeat the procedure in 10.3, using other volumes of mixed salts solution (dilute solution) as needed to cover the range of chloride contents of interest.

10.6 Subtract the value obtained for the blank measurement from the indicated current readings of each standard sample, and plot the chloride content (ordinate) against net current (mA) readings (abscissa) for each voltage on 3 by 3 cycle log-log paper, or other suitable format.

NOTE 5—Some apparatus are capable of internally recording the current readings, standard concentration, and blank, and they provide an output in direct concentration units.

NOTE 6—The apparatus are calibrated against standard solutions of neutral oil and mixed chloride solutions in xylene because of the extreme difficulties in keeping crude oil-brine mixtures homogeneous. The calibration may be confirmed, if desired, by careful replicate analysis of crude-oil samples by exhaustive extraction of salts with hot water, followed by titration of the chlorides in the extract.

NOTE 7—In calibrating over a wide range of chloride concentrations, it may be necessary to apply several voltages to obtain current readings within the limit of the apparatus current level display (0 to 10 mA). Higher voltages are applied for low concentrations and lower voltages are applied for high concentrations.

11. Procedure

11.1 To a dry, 100-mL graduated, glass-stoppered cylinder, add 15 mL of xylene and pipet (total delivery) in 10 mL of the crude oil sample. Rinse the pipet with xylene until free of oil. Make up to 50 mL with xylene. Stopper and shake the cylinder vigorously for approximately 60 s. Dilute to 100 mL with mixed alcohol solvent, and again shake vigorously for approximately 30 s. After allowing the solution to stand for approximately 5 min, pour it into the dry test beaker.

11.2 Follow the procedure in 10.4 to obtain voltage and current readings. Record the indicated electrode current to the nearest 0.01 mA and the nearest voltage.

11.3 Remove the electrodes from the sample solution, and clean the apparatus.

12. Calculation

12.1 Subtract the value obtained for the blank measurement from the value obtained from the specimen measurement to obtain the net current reading. From the calibration graph, read the indicated salt concentration corresponding to the net current (mA) reading of the sample.

12.2 Calculate the concentration in mg/kg by using the appropriate equation given below:

$$\text{Salt, mg/kg} = X/d \quad (1)$$

$$\text{Salt, mg/kg} = 2.853\, Y/d \quad (2)$$

where:
X = measured salt concentration in mg/m^3,
Y = measured salt concentration in PTB, and
d = specimen density at 15 C in kg/m^3.

NOTE 8—The density of the specimen can be determined by various methods, such as Test Method D 5002 or other density measurement methods.

13. Report

13.1 Report the following information: The concentration in mg/kg as electrometric chloride in crude oil per Test Method D 3230. Alternately, report the concentration directly in mg/m^3 or lbs/1000 bbl, if so required.

NOTE 9—For reporting purposes, the values stated in PTB are the preferred units in the United States; in other countries, their common units can be used.

14. Precision and Bias

14.1 *Precision*—The precision of this test method as determined by the statistical examination of the 1997 interlaboratory test results[6] is as follows.

14.1.1 *Repeatability*—The difference between successive results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values in one case in twenty.

$$r\ (\text{mg/kg}) = 0.3401\, X^{0.75} \quad (3)$$

$$r\ (\text{lbs/1000 bbl}) = 0.2531\, Y^{0.75} \quad (4)$$

where:
X = the average of two test results in mg/kg, and
Y = the average of two test results in lbs/1000 bbl (PTB).

[6] Supporting data have been filed at ASTM Headquarters. Request RR:D02-1470.

14.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical material, would in the long run, exceed the following values in only one case in twenty.

$$R\ (\text{mg/kg}) = 2.7803\ X^{0.75} \quad (5)$$

$$R\ (\text{lbs/1000 bbl}) = 2.069\ Y^{0.75} \quad (6)$$

where:

X = the average of two test results in mg/kg, and

Y = the average of two test results in lbs/1000 bbl (PTB).

NOTE 10—Since all instruments in the 1997 interlaboratory cooperative test program were calibrated in PTB and results reported in PTB, the precision statement was directly obtained in PTB. The resulting precision data have been mathematically converted into precision in mg/kg, assuming an average density of the crude oil samples of 0.875 kg/L.

14.2 *Bias*—The procedure in Test Method D 3230 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 were 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 from 5 to 500 g/m^3(1.5 to 150 PTB) salt added, the recovery proved to be approximately constant and averaged 93 %.

14.3 The precision statements were derived from a 1997 interlaboratory cooperative test program. Participants analyzed eight sample sets comprised of crude oils with various concentrations of chlorides. Thirteen laboratories participated with the commercial available apparatus.[7]

15. Keywords

15.1 chlorides; crude oil; electrometric; halides; petroleum; salt in crude

[7] Supporting data concerning the apparatus used and the type of samples meeting the precision of this test method have been filed at ASTM Headquarters. Request RR:D02-1470.

ANNEX

(Mandatory Information)

A1. Apparatus

A1.1 Electrometric Chloride Apparatus (Custom Manufacture) (see Fig. A1.1 and Note A1.1)

A1.1.1 *Milliammeter*, 0 to 1 mA dc with 0 to 1 mA ac scale, 88 ohm internal resistance.

A1.1.2 *Bridge Rectifier*, full-wave, 0.75 A capacity at 60 Hz, ambient temperature; minimum of 400 PRV (Peak Reverse Voltage).

A1.1.3 *AC Voltmeter*, rectifier type, 2000 ohm/V, 0 to 300 V range.

A1.1.4 *Variable Voltage Autotransformer*, input 105 to 117 V, 50/60 Hz, output 0 to 132 V, 1.75 A capacity.

A1.1.5 *Transformer*, plate supply 240 V, center tap, 50/60 Hz, 250 mA dc capacity.

A1.1.6 *Potentiometer*, 25 ohm, ten turn.

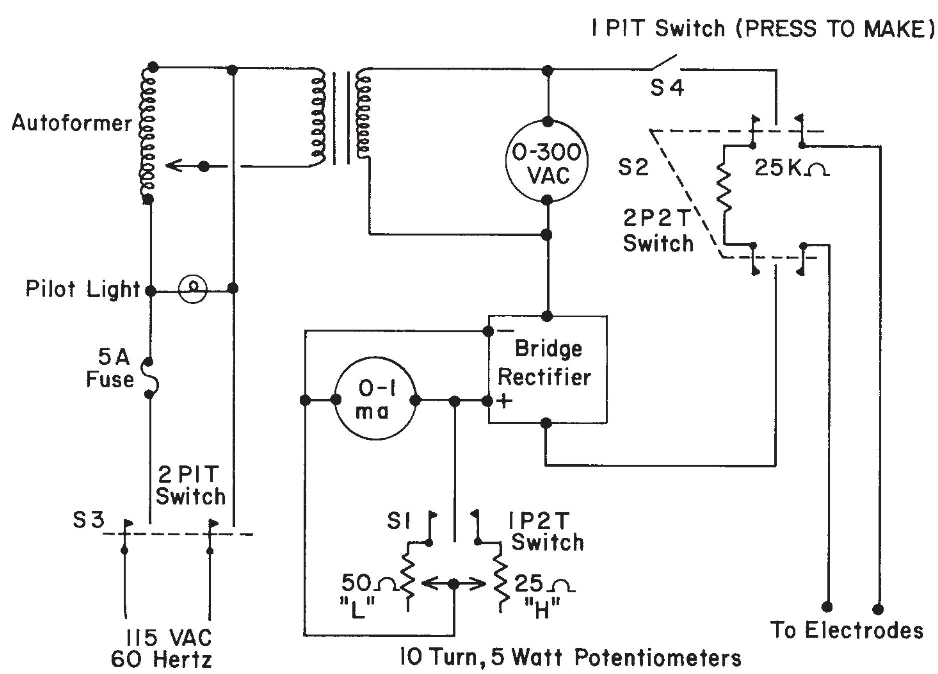

FIG. A1.1 250 or 540 Volt Transformer

A1.1.7 *Potentiometer*, 50 ohm, ten turn.

NOTE A1.1—An equivalent part can be substituted in each case, provided the electrical characteristics of the entire circuit remain unchanged and the inductive effects and stray currents are avoided.

A1.2 Test Cell Components (Custom Manufacture) (see Fig. A1.2)

A1.2.1 *Beaker*, 100-mL tall form without lip, as described for use in Test Method D 381.

A1.2.2 *Electrode Assembly*, as shown in Fig. A1.2 and Fig. A1.3. The electrodes mounted in parallel position, exactly opposed and 6.4 ± 0.1 mm apart, and electrically separated by a nylon or TFE-fluorocarbon spacer.

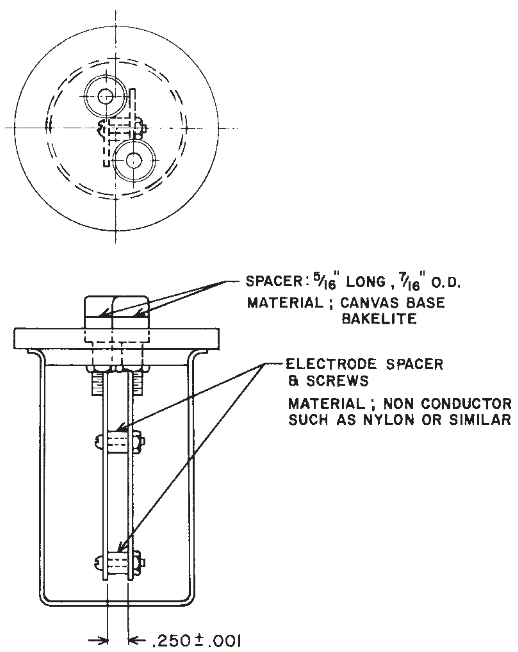

FIG. A1.2 Test Cell

A1.3 Electrometric Chloride Apparatus (Commercial Manufacture)[7]

A1.3.1 The apparatus shall consist of a control unit capable of producing and displaying several voltage levels for applying stress to a set of electrodes suspended in a test beaker containing a test solution. The apparatus shall be capable of measuring and displaying the current (mA) conducted through the test solution between the electrodes at each voltage level.

NOTE A1.2—Some apparatus is capable of measuring voltage and current internally and after comparison to internal calibration curves, display the resultant concentration.

A1.3.2 The actual construction specifics of the apparatus, such as voltages utilized and means of displaying or recording the voltage, displaying or recording the current conduction, or calculating and displaying the calibration curves/specimen measurements, or combination thereof, are not critical to the application as long as each individual component remains specific to the given manufactured apparatus.

A1.3.3 The entire assembled apparatus, including the test cell components, shall have been qualified to meet the precisions of this test method in an interlaboratory program approved by the subcommittee with jurisdiction of this test method.

A1.4 Test Cell Components (Commercial Manufacture)

A1.4.1 *Beaker*, 100-ml tall form without lip, as described for use in Test Method D 381, is commonly used; however, minor variations on dimensions are acceptable to accommodate different manufacturing specifics. The beaker purpose is to provide for containment of the specimen.

A1.4.2 *Electrode Assembly*, shown by example in Fig. A1.2 and Fig. A1.3. The electrode assembly dimensional requirements and means of support in the beaker are not critical to the application as long as each individual component remains specific to the given manufactured apparatus.

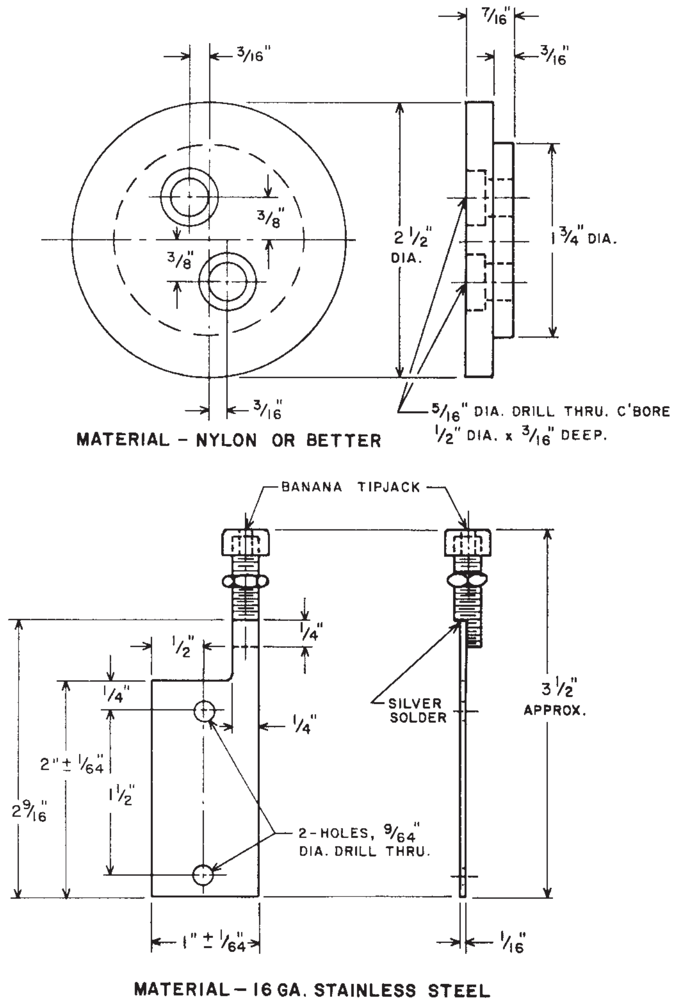

FIG. A1.3 Electrode Assembly