Designation: D3869 – 15

Standard Test Methods for Iodide and Bromide Ions in Brackish Water, Seawater, and Brines[1]

This standard is issued under the fixed designation D3869; 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 These test methods[2] cover the determination of soluble iodide and bromide ions, or both, in brackish water, seawater, and brines. Four test methods are given as follows:

1.1.1 *Test Method A for both Iodide and Bromide Ions*—Volumetric, for concentrations from 0.2 to 2000 mg/L iodide and from 5 to 6500 mg/L bromide (Sections 7 – 15).

1.1.2 *Test Method B for Iodide Ion*—Colorimetric, for concentrations from 0.2 to 2000 mg/L iodide (Sections 16 – 25).

1.1.3 *Test Method C for Iodide Ion*—Selective electrode, for concentrations from 1 to 2000 mg/L iodide (Sections 26 – 34).

1.1.4 *Test Method D for Bromide Ion*—Colorimetric, for concentrations from 40 to 6500 mg/L bromide (Sections 35 – 44).

1.2 Test Method A is intended for use on all brackish waters, seawaters, and brines that contain appreciable amounts of iodide or bromide ions or both. Test Methods B, C, and D, because of their rapidity and sensitivity, are recommended for the analysis of brackish waters, seawaters, and brines in the field and in the laboratory.

1.3 Samples containing from 0.2 to 2000 mg/L of iodide or 5 to 6500 mg/L of bromide may be analyzed by these methods.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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.* For specific precautionary statements, see 20.2 and 39.2.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology D1129.

4. Significance and Use

4.1 Identification of a brackish water, seawater, or brine is determined by comparison of the concentrations of their dissolved constituents. The results are used to evaluate the origin of the water, determine if it is a possible pollutant or determine if it is a commercial source of a valuable constituent such as iodine or bromine.

5. Reagents

5.1 *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 specification of the Committee

[1] These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] Additional information is contained in the following references: Collins, A. G., *Geochemistry of Oilfield Waters,* Elsevier, New York, N.Y., 1975, 496 pp.American Petroleum Institute, API *Recommended Practice for Analysis of Oilfield Waters*, Subcommittee on Analysis of Oilfield Waters, API RP, 45 2nd ed, 1968, 49 pp.Hoke, S. H, Fletcher, G. E., and Collins, A. G., "Fluoride and Iodide Selective Electrodes Applied to Oilfield Brine Analysis," US Department of Energy, Report of Investigations, BETC/RI-78/7, 1978.

[3] 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**

on Analytical Reagents of the American Chemical Society,[4] where such specifications are available. 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.

5.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D1193, Type I. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the precision and bias of the test method. Type III water was specified at the time of round robin testing of this test method.

6. Sampling

6.1 Collect the sample in accordance with Practices D3370.

TEST METHOD A—VOLUMETRIC FOR IODIDE AND BROMIDE

7. Scope

7.1 This test method is applicable to brackish waters, seawaters, and brines, and is recommended for such waters containing appreciable amounts of iodide or bromide, or both. The test method can be used for concentrations as high as 2000 mg/L iodide and 6500 mg/L bromide.

8. Summary of Test Method

8.1 Iodide in the sample is oxidized with bromine to iodate in a buffered solution, the excess bromine is decomposed with sodium formate, and the iodate reacts with added iodide to form iodine which is titrated with sodium thiosulfate.

8.2 Iodide and bromide are oxidized to iodate and bromate, respectively, with hypochlorite. The excess hypochlorite is destroyed with sodium formate, leaving iodate and bromate to react with added iodide to liberate iodine which is titrated with sodium thiosulfate.

8.3 The bromide concentration is calculated by difference between the iodide and combined iodide and bromide determinations.

9. Interferences

9.1 Iron, manganese, and organic matter can interfere (Note 1). They are removed by precipitation and filtration. Remaining traces of iron are masked with fluoride.

NOTE 1—Brines containing surfactants can cause emulsion problems, in which case a suitable emulsion breaker can be used.

10. Apparatus

10.1 *Mechanical Bottle Shaker.*

10.2 *Bottles,* 200-mL, for use on mechanical shaker.

10.3 *Pipets.*

10.4 *Hot-Water Bath,* thermostatically controlled to ±1°C.

10.5 *Erlenmeyer Flasks,* 250-mL.

11. Reagents and Materials

11.1 *Acetic Acid,* glacial.

11.2 *Ammonium Molybdate Solution*—Dissolve 2 g of ammonium molybdate in water and dilute to 100 mL.

11.3 *Bromine Water (Saturated)*—Add to 250 mL of water slightly more liquid bromine (8 to 10 mL) than will dissolve on shaking. Store in a glass-stoppered amber bottle.

11.4 *Calcium Carbonate* ($CaCO_3$), powdered.

11.5 *Calcium Oxide* (CaO), anhydrous powdered.

11.6 *Hydrochloric Acid* (1 + 1)—Add 1 volume of HCl (sp gr 1.19) to 1 volume of water.

11.7 *Hydrochloric Acid* (1 + 3)—Add 1 volume of HCl (sp gr 1.19) to 3 volumes of water.

11.8 *Hydrochloric Acid* (1 + 199)—Add 1 volume of HCl (sp gr 1.19) to 199 volumes of water.

11.9 *Methyl Red Indicator Solution* (0.1 g/L)—Dissolve 0.01 g of water-soluble methyl red in water and dilute to 100 mL.

11.10 *Potassium Fluoride* ($KF{\cdot}2H_2O$)—crystalline.

11.11 *Potassium Iodide* (KI), crystals, free of iodates when tested in accordance with American Chemical Society (ACS) specifications.

11.12 *Sodium Acetate Solution* (275 g/L)—Dissolve 275 g of sodium acetate trihydrate ($NaC_2H_3O_2{\cdot}3H_2O$) in water, to dilute to 1 L, and filter.

11.13 *Sodium Chloride* (NaCl), crystals, which, in addition to satisfying ACS specifications, must be free of iodide, iodate, bromide, and bromate.

11.14 *Sodium Formate Solution* (500 g/L)—Dissolve 50 g of sodium formate ($NaCHO_2$) in hot water and dilute to 100 mL. This solution must be freshly prepared.

11.15 *Sodium Hypochlorite Solution*—Use a fresh commercial sodium hypochlorite or bleach solution containing approximately 5 % NaClO.

11.16 *Sodium Thiosulfate Solution* (0.1 *N*)—Prepare and standardize as directed in Practice E200.

11.17 *Sodium Thiosulfate Solution* (0.01 *N*)—With a calibrated pipet transfer 25 mL of the 0.1 *N* $Na_2S_2O_3$ solution (11.16) into a 250-mL volumetric flask. Dilute to the mark with water that has been freshly boiled and cooled then mix well. This solution shall be prepared not more than 2 days before it is to be used.

11.18 *Starch Indicator Solution*—Make a paste of 6 g of arrowroot or soluble iodometric starch with cold water. Pour the paste into 1 L of boiling water. Add 20 g of KOH, mix thoroughly, and allow to stand for 2 h. Add 6 mL of glacial acetic acid. Mix again and add sufficient HCl (sp gr 1.19) to

[4] *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.

adjust the pH to 4.0. Store in a glass-stoppered bottle. Starch solution prepared in this manner will remain chemically stable for at least 1 year.

11.18.1 If a proprietary starch indicator powder is used, it shall be so indicated in reporting the results of the analysis.

11.19 *Filter Paper*—Purchase suitable filter paper. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

12. Procedure

12.1 To remove iron, manganese, and organic matter from the sample, add exactly 100 mL of sample to a bottle. Add 1 g of calcium oxide (11.5), stopper, and place the mixture in a shaker for 1 h. Allow the mixture to stand overnight and filter on a dry folded filter (11.19), discarding the first 20 mL that come through. Brines with specific gravities less than 1.009 may be filtered without standing overnight. Prepare a blank in the same manner.

12.2 Transfer an aliquot of the filtrate containing 1 to 2 mg of iodide to a 250-mL Erlenmeyer flask. Add sufficient water to provide a total volume of 75 mL.

12.3 Add 3 drops of methyl red indicator (11.9). Add HCl (1 + 199) (11.8) dropwise until the mixture is just slightly acid.

12.4 Add 10 mL of sodium acetate solution (11.12), 1 mL of glacial acetic acid (11.1), 4 mL of bromine water (11.3), and allow to stand for 5 min.

12.5 Add 2 mL of sodium formate solution (11.14), blow out any bromine vapor from the neck of the flask, and wash down the sides with water.

12.6 When the solution is completely colorless, add 0.2 g of KF (11.10) and 0.5 g of KI (11.11). Mix until dissolved and add 15 mL of HCl (1 + 1) (11.6).

12.7 For final treatment and titration of the sample, proceed as directed in (12.13).

12.8 To determine the combined iodide and bromide, transfer an aliquot of the filtrate (12.1) containing 1 to 2 mg of bromide to a 250-mL Erlenmeyer flask. Add sufficient water to make the total volume 75 mL.

12.9 If necessary add sufficient NaCl (11.13) to produce a 3-g chloride content. Add, in order, 10 mL of sodium hypochlorite solution (11.15) and approximately 0.4 g of $CaCO_3$ (11.4) (or enough so that approximately 0.1 g will remain after the next step).

12.10 Adjust the pH of the solution with HCl (1 + 3) (11.7) to a pH between 5.5 and 6.0. Heat at 90°C for 10 min. (A small amount of undissolved $CaCO_3$ should remain at this point.)

12.11 Remove the flask and cautiously add 10 mL of sodium formate solution (11.14), return the flask to the water bath, and keep the contents hot for 5 min more. Observe the timing closely. Rinse down the inside of the flask with a few millilitres of water and allow the solution to cool to room temperature. Do not use a water bath.

TABLE 1 Determination of Precision and Bias of Iodide Ions, Volumetric Methods

Amount Added, mg/L	Amount Found, mg/L	S_O	S_T	±Bias	Statistically Significant (95 % Confidence Level)
12.1	11.4	1	1	–5.78	yes
116.3	112.5	2	3	–3.27	yes
771	743	12	15	+2.63	no
1375	1282	40	73	–6.76	yes

12.12 Add 3 drops of ammonium molybdate solution (11.2), 0.5 g of KF (11.10) (if iron is present), 0.5 g of KI (11.11), mix until dissolved, and acidify with 15 mL of HCl (1 + 1) (11.6).

12.13 Titrate the sample (12.7) for iodide or the sample (12.12) for combined iodide and bromide with 0.01 *N* sodium thiosulfate solution (11.17) using starch indicator (11.18). Disregard any return of blue color after the endpoint.

13. Calculation

13.1 Calculate the concentration of iodide and bromide ions in milligrams per litre as follows:

13.2 *Iodide:*

$$C = E - D$$

where:

C = corrected millilitres of $Na_2S_2O_3$ solution,
E = millilitres of $Na_2S_2O_3$, sample solution, and
D = millilitres of $Na_2S_2O_3$ blank solution.

$$I^-, \text{ mg/L} = \frac{CN}{S} \times 21150$$

where:

N = normality of $Na_2S_2O_3$ solution, and
S = millilitres of sample.

13.3 *Bromide:*

$$C = E - D$$

$$Br^-, \text{ mg/L} = \frac{CN}{S} \times 13320 - X$$

where:

X = concentration of I^- as determined above.

14. Precision and Bias[5]

14.1 The overall precision (S_T) and single-operator precision (S_o) of this test method within their designated ranges vary with the quantity being tested in accordance with Table 1 and Table 2.

14.2 The bias of the test method determined from recoveries of known amounts of iodide and bromide in a series of prepared standards are given in Table 1 and Table 2.

NOTE 2—The precision and bias estimates are based on the interlaboratory study on four artificial brine samples containing various amounts of iodide, bromide, and interfering ions as shown in Table 3. Two analysts in

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1061. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Determination of Precision and Bias of Bromide Ions, Volumetric Method

Amount Added, mg/L	Amount Found, mg/L	S_O	S_T	±Bias	Statistically Significant (95 % Confidence Level)
30.3	31.7	1	5	+4.62	yes
534	531	15	25	−0.56	no
1286	1249	23	182	−2.88	no
5734	5688	65	227	−0.80	no

TABLE 3 Composition of Artificial Brine Samples

Sample No.	mg/L			
	1	2	3	4
I	12.1	116.3	771	1 375
Br	30.3	534	1 286	5 734
Na	9 500	65 000	31 000	75 000
K	300	1 400	2 000	5 000
Ca	550	1 000	700	2 000
Mg	1 200	1 200	500	250
Ba	30	650	300	300
Cl	19 000	107 000	52 000	121 000

each of three laboratories performed duplicate determinations on each of 2 days. Practice D2777 was used in developing these precision and bias estimates.

14.3 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

15. Quality Control

15.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing iodide and bromide.

15.2 *Calibration and Calibration Verification:*

15.2.1 Verify the sodium thiosulfate solution (11.17) according to Practice E200.

15.2.2 Verify solution by analyzing a sample at the concentration of a mid-range standard should fall within ±15 % of the known concentration.

15.2.3 If calibration cannot be verified, remake the sodium thiosulfate solution.

15.2.4 It is recommended to analyze a blank and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

15.3 *Initial Demonstration of Laboratory Capability:*

15.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

15.3.2 Analyze seven replicates of a known solution prepared from an Independent Reference Material containing a mid-range concentration of iodide and bromide. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

15.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 1 and Table 2. This study should be repeated until the recoveries are within the limits given in Table 1 and Table 2. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

15.4 *Laboratory Control Sample (LCS):*

15.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a mid-range concentration of iodide and bromide with each batch (laboratory-defined or 20 samples). the laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within ±15 % of the known concentration.

15.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

15.5 *Method Blank:*

15.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of iodide and bromide found in the blank should be less than 0.5 times the reporting level. If the concentration of iodide and bromide is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

15.6 *Matrix Spike (MS):*

15.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each laboratory-defined batch by spiking an aliquot of the sample with a known concentration of iodide and bromide and taking it through the analytical method.

15.6.2 The spike concentration plus the background concentration of iodide and bromide must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

15.6.3 Calculate the percent recovery of the spike (P) using the following calculation:

$$P = 100\,[A\,(V_s + V) - BV_s]/CV$$

where:

A = analyte concentration (mg/L) in spiked sample;
B = analyte concentration (mg/L) in unspiked sample;

C = concentration (mg/L) of analyte in spiking solution;
V_s = volume (mL) of sample used; and
V = volume (mL) of spiking solution added.

15.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 3—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

15.7 *Duplicate:*

15.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

15.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

15.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

15.8 *Independent Reference Material:*

15.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

TEST METHOD B—COLORIMETRIC FOR IODIDE

16. Scope

16.1 This test method [2] covers the colorimetric determination of iodide in brackish water, seawater, and brines where concentrations range from 0.2 to 2000 mg/L.

17. Summary of Test Method

17.1 Iodide in the sample is oxidized with nitrous acid and extracted into carbon tetrachloride. The concentration is proportional to the intensity of the purple color measured at 517 nm.

18. Interference

18.1 Hydrocarbons that might interfere with the spectrophotometric measurement can be removed from the sample by a carbon tetrachloride extraction.

18.2 Hydrogen sulfide can interfere and is removed by boiling an acidified sample.

19. Apparatus

19.1 Spectrophotometer or filter photometer having a light path of approximately 10 mm for use at 517 nm. Filters, when required, shall be green, have a narrow-band pass, and a maximum transmittance at or about this wavelength. Photometers and photometric practices prescribed in this method shall conform to Practice E60. Spectrophotometers shall conform to Practice E275.

19.2 *Chemical (Filters) Funnel,* approximate inside diameter of top of funnel 45 mm.

19.3 *Separatory Funnel,* 125-mL capacity, borosilicate glass with a TFE-fluorocarbon stopcock and a linear high-density polyethylene stopper.

19.4 *Volumetric Flask,* 50-mL capacity, borosilicate glass, with a linear high-density polyethylene stopper.

19.5 *Filter Paper,* rapid qualitative, 70-mm diameter. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

19.6 *Buret,* precision-bore, micro, 10-mL capacity with a TFE-fluorocarbon stopcock.

20. Reagents

20.1 *Bromphenol Blue Indicator Solution* (1 g/L)—Dissolve 0.1 g of water-soluble bromphenol blue in water and dilute to 100 mL.

20.2 *Carbon Tetrachloride* (CCl_4). (**Warning—**Avoid inhalation and conduct all manipulation in a well-ventilated hood.)

20.3 *Hydrochloric Acid* (1 + 1)—Add 1 volume of HCl (sp gr 1.19) to 1 volume of water.

20.4 *Iodide Solution, Standard* (1 mL = 0.25 mg I^-)—Dry about 3 g of potassium iodide (KI) crystals for 6 h at 105°C. Any large crystals should be crushed before drying, but not ground in a mortar for a long time. Dissolve 0.3270 g of the KI in water and dilute to exactly 1 L in a volumetric flask. Alternatively, certified iodide stock solutions are commercially available through chemical supply vendors and may be used.

20.5 *Potassium Nitrite Solution* (100 g KNO_2/L)—Dissolve 10 g of KNO_2 in water and dilute to 100 mL.

21. Calibration

21.1 Using a microburet, to five 125-mL separatory funnels add respectively 0.0 (blank), 2.0, 4.0, 6.0, and 8.0-mL aliquots of standard iodide solution (20.4). Add sufficient water to bring the volume in each funnel to about 50 mL.

21.2 Follow 22.2 – 22.7.

21.3 Prepare a calibration curve by plotting absorbance against milligrams of iodide.

22. Procedure

22.1 From the sample that is free of hydrocarbons and hydrogen sulfide, pipet an aliquot containing less than 2.5 mg of iodide into a separatory funnel and adjust the volume with water to 50 mL.

TABLE 4 Determination of Precision and Bias of Iodide Ions, Colorimetric Method

Amount Added, mg/L	Amount Found, mg/L	S_O	S_T	±Bias	Statistically Significant (95 % Confidence Level)
12.1	12.1	1	1	0.0	yes
116.3	119.2	10	15	+2.49	no
771	786	58	63	+1.94	no
1375	1488	160	225	+8.22	yes

TABLE 5 Composition of Artificial Brine Samples

Sample No.	mg/L			
	1	2	3	4
I	12.1	116.3	771	1 375
Na	9 500	65 000	31 000	75 000
K	300	1 400	2 000	5 000
Ca	550	1 000	700	2 000
Mg	1 200	1 200	500	250
Ba	30	650	300	300
Cl	19 000	107 000	52 000	121 000

22.2 Add 3 drops of bromphenol blue solution (20.1).

22.3 Swirl the mixture and add HCl (1 + 1) (20.3) dropwise until the indicator turns yellow (pH 5).

22.4 Add 10 mL of carbon tetrachloride (20.2), 1 mL of potassium nitrite solution (20.5), and mix by shaking the contents vigorously, relieving the pressure occasionally. (A violet color in the carbon tetrachloride phase indicates the presence of iodide in the sample).

22.5 After the phases have separated drain the carbon tetrachloride phase through a dry filter paper into a 50-mL volumetric flask.

22.6 Repeat the extraction with two more 10-mL portions of carbon tetrachloride (20.2) and drain through the same filter paper into the same volumetric flask (22.5).

22.7 Dilute the combined extracts to 50 mL with carbon tetrachloride (20.2). Measure the absorbance at 517 nm in a 10 nm transmittance cell using the blank extract as a reference (see 21.3). The iodine-CCl_4 solution is fairly stable. However, avoid undue delay unless precautions are taken to prevent evaporation of the CCl_4.

23. Calculation

23.1 From the analytical curve (see 21.3) determine the milligrams of iodide corresponding to the absorbance obtained for each sample.

23.2 Calculate the concentration of iodide ion in the sample, in milligrams per litre, as follows:

$$I^-, \text{mg/L} = \frac{M \times 1000}{S}$$

where:

1000 = 1000 mL / litre
M = milligrams of iodide from curve, and
S = millilitres of sample.

24. Precision and Bias[5]

24.1 The overall precision (S_T) and single-operator precision (S_o) of this test method within their designated ranges vary with the quantity being tested in accordance with Table 4.

24.2 The bias of the test method determined from recoveries of known amounts of iodide in a series of prepared standards are given in Table 4.

NOTE 4—The precision and bias estimates are based on an interlaboratory study on four artificial brine samples containing various amounts of iodide and interfering ions as shown in Table 5. Two analysts in each of four laboratories performed duplicate determinations on each of two days. Practice D2777 was used in developing these precision and bias estimates.

24.3 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777– 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

25. Quality Control

25.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing iodide.

25.2 *Calibration and Calibration Verification:*

25.2.1 Analyze at least four working standards containing concentrations of iodide that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument.

25.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The absorbance shall fall within 4 % of the absorbance from the calibration. Alternately, the concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a blank to verify cleanliness.

25.2.3 If calibration cannot be verified, recalibrate the instrument.

25.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

25.3 *Initial Demonstration of Laboratory Capability:*

25.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

25.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of iodide. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

25.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 4. This study should be repeated until the recoveries are

within the limits given in Table 4. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

25.4 *Laboratory Control Sample (LCS):*

25.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a mid-range concentration of iodide with each batch (laboratory-defined or 20 samples). the The laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within ±15 % of the known concentration.

25.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

25.5 *Method Blank:*

25.5.1 Analyze a reagent water test blank with each batch. The concentration of iodide found in the laboratory-defined blank should be less than 0.5 times the lowest calibration standard. If the concentration of iodide is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

25.6 *Matrix Spike (MS):*

25.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of iodide and taking it through the analytical method.

25.6.2 The spike concentration plus the background concentration of iodide must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

25.6.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = 100\left[A\left(V_s + V\right) - BV_s\right]/CV$$

where:

A = analyte concentration (mg/L) in spiked sample;
B = analyte concentration (mg/L) in unspiked sample;
C = concentration (mg/L) of analyte in spiking solution;
V_s = volume (mL) of sample used; and
V = volume (mL) of spiking solution added.

25.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 5—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

25.7 *Duplicate:*

25.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

25.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

25.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

25.8 *Independent Reference Material (IRM):*

25.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

TEST METHOD C—SELECTIVE ELECTRODE FOR IODIDE

26. Scope

26.1 This test method is applicable to all brackish waters, seawaters, and brines containing from 1 to 2000 mg/L iodide.

27. Summary of Test Method

27.1 The iodide-selective electrode and the reference electrode are placed in the solution and the potential recorded. Additional potential readings are taken after each of two standard additions. The electrode slope is determined from potential measurements of two iodide solutions of known concentration. The iodide concentration of the unknown sample is then calculated.

28. Interferences

28.1 Ions commonly found in brines that interfere with the method are Cl^-, Br^-, and $S^=$. The maximum allowable ratio of interfering ion to iodide is as follows:[2] Cl^-, 10^6; Br^-, 5×10^3; $S^=$, $<10^{-6}$. Sulfide interference can be eliminated by buffering the sample at pH 6 or lower.

29. Apparatus

29.1 *Millivoltmeter (Accurate to ±0.1 mV) or Specific Ion Meter.*

29.2 *Iodide Selective Electrode,* reference electrode.

29.3 *Pipets,* microlitre, various sizes (100 to 1000 µL) with disposable polypropylene tips.

29.4 *Volumetric Flask,* 50-mL capacity, borosilicate glass.

30. Reagents

30.1 *Iodide Solution, Standard* (1 mL = 1 mg I^-)—Dissolve 1.308 g of KI in water and dilute to 1 L (see 20.4). Alternatively, certified iodide stock solutions are commercially available through chemical supply vendors and may be used.

30.2 *Ionic Strength Adjuster*—Dissolve 42.5 g of $NaNO_3$ in water and dilute to 100 mL.

31. Procedure

31.1 Pipet 500 µL of the sample and 1 mL of ionic strength adjuster 30.2 into a 50-mL volumetric flask. Dilute to the mark and transfer solution to a 100-mL beaker. Place electrodes in the solution to a depth of 30 mm. Stir the solution and record the potential across the two electrodes when the drift in potential is less than 0.1 mV/min. For high iodide levels this condition may be reached in less than 1 min; however, it may require several minutes for low levels. At this point, add iodide standard such that the change in potential is about 50 mV. After the potential has stabilized, record the mV reading. For the second addition, add the same volume of iodide standard and record the corresponding potential. For brines with low specific gravity smaller dilutions can be made to obtain greater sensitivity at low iodide levels.

31.2 In order to determine the slope of the electrode, it is necessary to measure the respective electrode potentials of two iodide solutions of known concentration.

32. Calculation

32.1 Calculate the slope of the electrode as follows:

$$\text{Slope} = \frac{E_B - E_A}{\log[B] - \log[A]}$$

where:

A *and* B = two iodide solutions of known concentration (mg/L),
E_A = electrode potential of Solution A, mV, and
E_B = electrode potential of Solution B, mV.

NOTE 6—The slope of the electrode should meet the manufacturer's specifications.

32.2 The concentration of iodide in the sample can be calculated as follows:[6]

$$A = \frac{Xf}{\text{antilog}\left(\frac{\Delta E}{\text{slope}}\right) - 1}$$

where:

X = change in concentration upon addition of standard (mg I^- added/50 mL of solution),
f = dilution factor (50 mL/mL of sample), and
ΔE = the change in potential resulting from addition of standard.

From the above procedure, two A values can be calculated and averaged for each sample.

TABLE 6 Determination of Precision and Bias of Iodide Ions, Selective Electrode

Amount Added, mg/L	Amount Found, mg/L	S_O	S_T	±Bias	Statistically Significant (95 % Confidence Level)
12.1	12.4	1	3	+ 2.48	yes
116.3	126.4	7	12	+ 8.68	yes
771	814	30	50	+ 5.57	yes
1375	1464	34	90	+ 6.47	yes

33. Precision and Bias[5]

33.1 The overall precision (S_T) and single-operator precision (S_o) of this test method within their designated ranges vary with the quantity being tested in accordance with Table 6.

33.2 The bias of the test method determined from recoveries of known amounts of iodide in a series of prepared standards are given in Table 6.

NOTE 7—The precision and bias estimates are based on an interlaboratory study on four artificial brine samples containing various amounts of iodide and interfering ions as shown in Table 7. Two analysts in each of four laboratories and one analyst in one laboratory performed duplicate determinations on each of two days. Also, one analyst in one laboratory performed duplicate determinations on one day. Practice D2777 was used in developing these precision and bias estimates.

33.3 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

34. Quality Control

34.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing iodide.

34.2 *Calibration and Calibration Verification:*

34.2.1 Determine the slope of the electrode. The slope should meet the manufacturer's specifications.

34.2.2 Verify the electrode by analyzing a sample at the concentration near the mid-range should fall within ±15 % of the known concentration.

34.2.3 If calibration cannot be verified, recalibrate the instrument.

34.2.4 It is recommended to analyze blank and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

34.3 *Initial Demonstration of Laboratory Capability:*

34.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for

[6] Rix, C. J., Bond, A. M., and Smith, J. D., "Direct Determination of Fluoride in Sea Water with a Fluoride Selective Ion Electrode by a Method of Standard Additions," *Analytical Chemistry,* ANCHA, Vol 48, 1976, p. 1236.

TABLE 7 Composition of Artificial Brine Samples

Sample No.	mg/L			
	1	2	3	4
I	12.1	116.3	771	1 375
Na	9 500	65 000	31 000	75 000
K	300	1 400	2 000	5 000
Ca	550	1 000	700	2 000
Mg	1 200	1 200	500	250
Ba	30	650	300	300
Cl	19 000	107 000	52 000	121 000

example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

34.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of iodide. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

34.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 6. This study should be repeated until the recoveries are within the limits given in Table 6. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

34.4 *Laboratory Control Sample (LCS):*

34.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a mid-range concentration of iodide with each batch (laboratory-defined or 20 samples). the laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within ±15 % of the known concentration.

34.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

34.5 *Method Blank:*

34.5.1 Analyze a reagent water test blank with each batch. The concentration of iodide found in the laboratory-defined blank should be less than 0.5 times the lowest calibration standard. If the concentration of iodide is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

34.6 *Matrix Spike (MS):*

34.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each laboratory-defined batch by spiking an aliquot of the sample with a known concentration of iodide and taking it through the analytical method.

34.6.2 The spike concentration plus the background concentration of iodide must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

34.6.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = 100\left[A(V_s+V) - BV_s\right]/CV$$

where:

A = analyte concentration (mg/L) in spiked sample;
B = analyte concentration (mg/L) in unspiked sample;
C = concentration (mg/L) of analyte in spiking solution;
Vs = volume (mL) of sample used; and
V = volume (mL) of spiking solution added.

34.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 8—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

34.7 *Duplicate:*

34.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

34.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

34.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

34.8 *Independent Reference Material (IRM):*

34.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

TEST METHOD D—COLORIMETRIC FOR BROMIDE

35. Scope

35.1 This test method is applicable to all brackish waters, seawaters, and brines with bromide concentrations ranging from 40 to 6500 mg/L.

36. Summary of Test Method

36.1 Bromides are oxidized to bromine in acid solution by chromium trioxide. The bromine is extracted into carbon tetrachloride and measured spectrophotometrically.

37. Interferences

37.1 This test method is free of interference from iodide and chloride. No other interferences are known in oilfield waters.

38. Apparatus

38.1 *Photometer*—Spectrophotometer or filter photometer having a light path of approximately 10 mm for use at 417 nm. Filters, when required, shall be blue, have a narrow-band pass, and a maximum transmittance at or about this wavelength. Photometers and photometric practices prescribed in this test method shall conform to Practice E60. Spectrophotometers shall conform to Practice E275.

38.2 *Separatory Funnel,* 250-mL capacity, borosilicate glass with a TFE fluorocarbon stopcock and stopper.

38.3 *Pipets,* various sizes, borosilicate glass.

38.4 *Filter Paper,* rapid. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

38.5 *Graduated Cylinder,* 25-mL capacity, borosilicate glass with a ground-glass stopper.

39. Reagents

39.1 *Bromide Solution, Standard* (1 mL = 1 mg Br^-)—Dissolve 1.4893 g of dry potassium bromide in water and dilute to 1 L in a volumetric flask. Alternatively, certified bromide stock solutions are commercially available through chemical supply vendors and may be used.

39.2 *Carbon Tetrachloride*(CCl_4)—**Warning—**Avoid inhalation and conduct all manipulation in a well-ventilated hood.

39.3 *Chromium Trioxide* (CrO_3).

39.4 *Sulfuric Acid* (1 + 1)—Slowly add 1 volume of H_2SO_4 (sp gr 1.84) to 1 volume of water while mixing and cooling the solution.

40. Calibration

40.1 Prepare a series of standards containing up to 400 mg/L of bromide (39.1).

40.2 Follow 41.1 – 41.6.

40.3 Prepare an analytical curve by plotting absorbance against milligrams of bromide. Read directly in concentration if this capability is provided with the instrument.

41. Procedure

41.1 Pipet up to 25 mL of sample into a 250-mL separatory funnel equipped with a TFE-fluorocarbon stopcock.

41.2 Cautiously add 1 volume of H_2SO_4 (1 + 1) (39.4) to 1 volume of sample to bring the H_2SO_4 concentration of the solution to 9 *N* and cool.

41.3 To the cooled solution add 15 mL of CCl_4 (39.2), 2 g of CrO_3 and shake well.

41.4 Drain the CCl_4 layer through a rapid filter paper into a graduated cylinder fitted with a ground-glass stopper, taking care that none of the aqueous layer is allowed to drain into the cylinder.

41.5 Repeat the extraction with 5-mL portions of CCl_4 (39.2) until that layer is no longer colored. Adjust the final volume of CCl_4 (39.2) to 25 mL, stopper, and mix well.

41.6 Measure the absorbance at 417 nm against CCl_4 (39.2) (measurements must be made immediately following extraction).

42. Calculation

42.1 From the analytical curve (see 41.3) determine the milligrams of bromide corresponding to the absorbance for each sample. Read directly in concentration if this capability is provided with the instrument.

42.2 Calculate the concentration of bromide in the sample, in milligrams per litre, as follows:

$$Br^-, \text{ mg/L} = \frac{B}{S} \times 1000$$

where:

1000 = 1000 mL / litre
B = milligrams of bromide from curve and
S = millilitres of sample.

43. Precision and Bias[5]

43.1 The precision of the test method within its designated range may be expressed as follows:

$$S_T = 0.092X - 2.47$$

$$S_o = 0.061X - 0.092$$

where:

S_T = overall precision,
S_o = single-operator precision, and
X = concentration of bromide determined, mg/L.

43.2 The bias of the test method determined from recoveries of known amounts of bromide in a series of prepared standards are given in Table 8.

NOTE 9—The above precision and bias estimates are based on an interlaboratory study of bromide and interfering ions as shown in Table 9. One analyst in each of two laboratories and two analysts in each of three laboratories performed duplicate determinations on each of two days. Practice D2777 was used in developing these precision and bias estimates.

43.3 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of

TABLE 8 Determination of Precision and Bias of Bromide Ions, Colorimetric Method

Amount Added, mg/L	Amount Found, mg/L	S_O	S_T	±Bias	Statistically Significant (95 % Confidence Level)
30.3	29.5	2	0	–2.64	yes
534	491	30	46	–8.05	yes
1286	1407	86	127	+9.41	yes
5734	6204	378	568	+8.20	yes

TABLE 9 Composition of Artificial Brine Samples

Sample No.	mg/L			
	1	2	3	4
Br	30.3	534	1 286	4 737
Na	9 500	65 000	31 000	75 000
K	300	1 400	2 000	5 000
Ca	550	1 000	700	2 000
Mg	30	650	300	300
Cl	19 000	107 000	52 000	121 000

Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

44. Quality Control

44.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing bromide.

44.2 *Calibration and Calibration Verification:*

44.2.1 Analyze at least three working standards containing concentrations of bromide that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument.

44.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The absorbance shall fall within 4 % of the absorbance from the calibration. Alternately, the concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify cleanliness.

44.2.3 If calibration cannot be verified, recalibrate the instrument.

44.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

44.3 *Initial Demonstration of Laboratory Capability:*

44.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

44.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of bromide. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

44.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 8. This study should be repeated until the recoveries are within the limits given in Table 8. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

44.4 *Laboratory Control Sample (LCS):*

44.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a mid-range concentration of bromide with each batch (laboratory-defined or 20 samples). The laboratory controls samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within ±15 % of the known concentration.

44.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

44.5 *Method Blank:*

44.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of bromide found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of bromide is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

44.6 *Matrix Spike (MS):*

44.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of bromide and taking it through the analytical method.

44.6.2 The spike concentration plus the background concentration of bromide must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

44.6.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = 100\left[A\left(V_s + V\right) - BV_s\right]/CV$$

where:

A = analyte concentration (mg/L) in spiked sample;
B = analyte concentration (mg/L) in unspiked sample;
C = concentration (mg/L) of analyte in spiking solution;

V_s = volume (mL) of sample used; and
V = volume (mL) of spiking solution added.

44.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 10—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

44.7 *Duplicate:*

44.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

44.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

44.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

44.8 *Independent Reference Material (IRM):*

44.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

45. Keywords

45.1 brackish; brine; bromide ion; colorimetric; iodide ion; selective electrode

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D3869 – 09) that may impact the use of this standard. (Approved March 15, 2015.)

(1) Revised Sections 11, 19, and 38 to add information on filter paper.

(2) Revised Sections 15, 25, 34, 40, 42, and 44.