Designation: D 3561 – 02

An American National Standard

Standard Test Method for Lithium, Potassium, and Sodium Ions in Brackish Water, Seawater, and Brines by Atomic Absorption Spectrophotometry[1]

1. Scope

1.1 This test method[2] covers the determination of soluble lithium, potassium, and sodium ions in brackish water, seawater, and brines by atomic absorption spectrophotometry.

1.2 Samples containing from 0.1 to 70 000 mg/L of lithium, potassium, and sodium may be analyzed by this test method.

1.3 This test method has been used successfully with artificial brine samples. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[3]

D 1193 Specification for Reagent Water[3]

D 2777 Practice for the Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water[3]

D 3370 Practices for Sampling Water from Closed Conduits[3]

D 5810 Guide for Spiking into Aqueous Samples[3]

D 5847 Standard Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

4. Summary of Test Method

4.1 This test method is dependent on the fact that metallic elements, in the ground state, will absorb light of the same wavelength they emit when excited. When radiation from a given excited element is passed through a flame containing ground state atoms of that element, the intensity of the transmitted radiation will decrease in proportion to the amount of ground state element in the flame. A hollow cathode lamp whose cathode is made of the element to be determined provides the radiation. The metal atoms to be measured[5] are placed in the beam of radiation by aspirating the specimen into an oxidant fuel flame. A monochromator isolates the characteristic radiation from the hollow cathode lamp, and a photosensitive device measures the attenuated transmitted radiation, which may be read as absorbance units or directly as concentration on some instruments.

4.2 Since the variable and sometimes high concentrations of matrix materials in the waters and brines affect absorption differently, it is difficult to prepare standards sufficiently similar to the waters and brines. To overcome this difficulty, the method of additions is used in which three identical samples are prepared and varying amounts of a standard added to two of them. The three samples are then aspirated, the concentration readings recorded, and the original sample concentration calculated.

5. Significance and Use

5.1 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

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] Fletcher, G. F. and Collins, A. G., *Atomic Absorption Methods of Analysis of Oilfield Brines: Barium, Calcium, Copper, Iron, Lead, Lithium, Magnesium, Manganese, Potassium, Sodium, Strontium, and Zinc,* U.S. Bureau of Mines, Report of Investigations 7861, 1974, 14 pp. Collins, A. G. Geochemistry of Oilfield Waters, Elsevier, New York, NY 1975.

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

[4] *Annual Book of ASTM Standards,* Vol. 11.02.

[5] Angino, E. E., and Billings, G. K., *Atomic Absorption Spectrophotometry in Geology,* Elsevier Publishing Co., New York, NY 1967. Dean, J. A., and Rains, T. C., Editors, *Flame Emission and Atomic Absorption Spectrometry,* Vol 1, Theory, Marcel Dekker, New York, NY 1969.

water as a possible pollutant, or as a commercial source of a valuable constituent such as lithium.

6. Interferences

6.1 Ionization interference is controlled by adding large excesses of an easily ionized element. Sodium ion is added in the potassium and lithium determinations, and potassium ion is added in the sodium determinations.

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*—The instrument shall consist of an atomizer and burner, suitable pressure-regulating devices capable of maintaining constant oxidant and fuel pressure for the duration of the test, a hollow cathode lamp for each metal to be tested, an optical system capable of isolating the desired line of radiation, an adjustable slit, a photomultiplier tube or other photosensitive device as a light measuring and amplifying device, and a readout mechanism for indicating the amount of absorbed radiation.

7.1.1 *Multielement Hollow-Cathode Lamps*.

7.2 *Pressure-Reducing Valves*—The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

8. Reagents and Materials

8.1 *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 on Analytical Reagents of the American Chemical Society, [6] 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.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D 1193, 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.

8.3 *Lithium Solution, Standard* (1 mL = 1 mg Li)—Dissolve 5.324 g of lithium carbonate (Li_2CO_3) in a minimum volume of HCl (1 + 1). Dilute to 1 L with water. One millilitre of this solution contains 1 mg of lithium. A purchased stock solution of adequate purity is also acceptable.

8.4 *Potassium Solution, Stock* (1 mL = 100 mg K)—Dissolve 190.7 g of potassium chloride (KCl) in water and dilute to 1 L with water. A purchased stock solution of adequate purity is also acceptable.

8.5 *Potassium Solution, Standard* (1 mL = 1 mg K)—Dissolve 1.907 g of potassium chloride (KCl) in water and dilute to 1 L with water. One millilitre of this solution contains 1 mg of potassium. A purchased stock solution of adequate purity is also acceptable.

8.6 *Sodium Solution, Stock* (1 mL = 100 mg Na)—Dissolve 254.2 g of sodium chloride (NaCl) in water and dilute to 1 L with water. A purchased stock solution of adequate purity is also acceptable.

8.7 *Sodium Solution, Standard* (1 mL = 10 mg Na)—Dissolve 25.42 g of sodium chloride (NaCl) in water and dilute to 1 L with water. One millilitre of this solution contains 1 mg of sodium. A purchased stock solution of adequate purity is also acceptable.

8.8 *Oxidant*:

8.8.1 Air that has been cleaned and dried through a suitable filter to remove oil, water, and other foreign substances, is the usual oxidant.

8.9 *Fuel*:

8.9.1 *Acetylene*—Standard, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder that has only 100 psig (690 kPa) of acetylene remaining.

9. Sampling

9.1 Collect the sample in accordance with the applicable ASTM standard (see Practices D 3370).

10. Procedure

10.1 Potassium is determined at the 766.5-nm wavelength, lithium at the 670.8-nm wavelength, and sodium at the 330.2 to 330.3-nm wavelength with an air-acetylene flame. For much greater sensitivity, sodium is determined at the 589.0 to 589.6-nm wavelength.

10.2 *Preliminary Calibration*—Using micropipets prepare lithium standards containing 1 to 5 mg/L of lithium, potassium standards containing 1 to 5 mg/L of potassium, and sodium standards containing 100 to 500 mg/L of sodium using the standard lithium, potassium, and sodium solutions and 50-mL volumetric flasks. Before making up to volume, add 0.5 mL of the sodium stock solution to the potassium and lithium standards, and to a blank and 0.5 mL of the potassium stock solution to the sodium standards and to a blank. Aspirate these standards and the appropriate blank (for background setting) and adjust the curvature controls, if necessary, to obtain a linear relationship between absorbance and the actual concentration of the standards.

10.3 Transfer an aliquot of water or brine (previously filtered through a 0.45-µm filter) to a 50-mL volumetric flask. The specific gravity of the water or brine can be used to estimate the lithium, potassium, or sodium content of the sample and, thereby, serve as a basis for selecting the aliquot sizes that will contain about 0.05 mg of lithium, 0.05 mg of potassium, or 5 mg of sodium. Fig. 1 shows the relationship between sodium concentration and specific gravity for some oilfield brines from the Smackover formation. The concentrations of sodium and also of lithium and potassium will not necessarily correlate with the concentrations found in other

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[6] *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K.," and the *United States Reagent Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

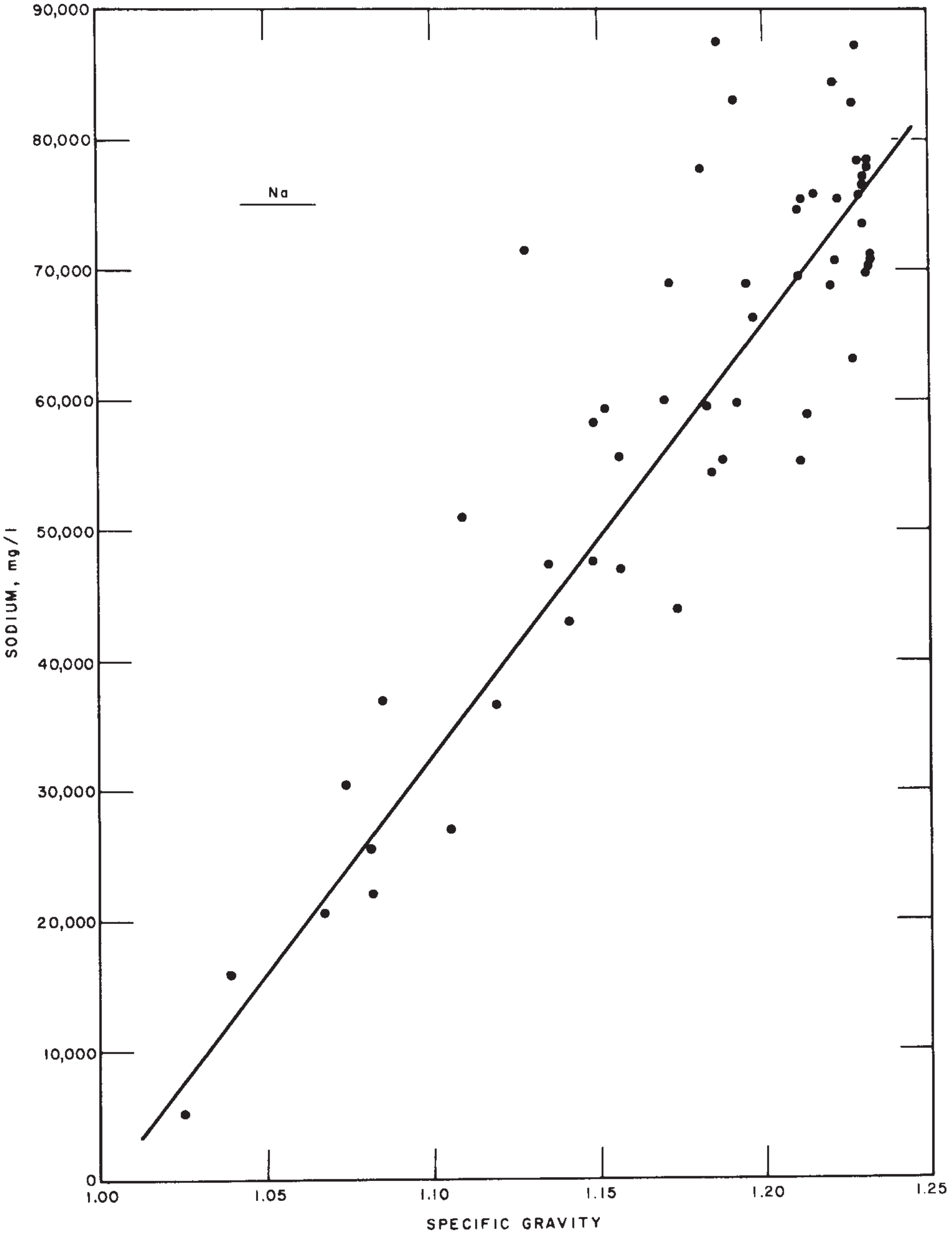

FIG. 1 Relationship of the Concentration of Sodium in Some Oilfield Brines to Specific Gravity

formations. Therefore, the user of this test method may find it necessary to draw similar curves for brine samples taken from other formations. Add 0.5 mL of the sodium stock solution to the lithium and potassium samples and 0.5 mL of the potassium stock solution to the sodium samples, dilute to volume, and aspirate. Calculate the approximate sample concentration from the preliminary calibration readings, and determine the aliquot sizes that will contain about 0.05 mg of lithium, 0.05 mg of potassium, or 5 mg of sodium.

10.4 Transfer equal aliquots containing about 0.05 mg of potassium or lithium, or 5 mg of sodium to three 50-mL volumetric flasks. Add no potassium or lithium standard to the first flask, using a micropipet add 0.05 mg to the second, and 0.1 mg to the third. For sodium, add no standard to the first flask, 5 mg to the second, and 10 mg to the third.

10.5 Add 0.5 mL of the sodium stock solution to the potassium and lithium samples and 0.5 mL of the potassium stock solution to the sodium samples, dilute to volume, aspirate, and record the absorbance readings for each sample.

11. Calculation

11.1 Calculate the concentration of potassium, lithium, or sodium ion in the original sample in milligrams per litre as follows:

11.2

$$\text{Concentration, mg/L} = \frac{V_1(A_s \times C_{std})}{V_2(A_{std} - A_s)} \quad (1)$$

where:

V_1 = volume of the dilute sample, mL,
V_2 = volume of the original sample, mL,
A_s = absorbance of dilute sample,
A_{std} = absorbance of one of the standard additions, and
C_{std} = concentration of the same standard addition as $A_{\text{std}}{}^2$ in mg/L.

Since there are two standard additions, calculate for each and average the two results.

12. Precision and Bias [7]

12.1 The precision of this test method within its designated range may be expressed as follows:

Lithium,

$$S_t = 0.0677X + 3.127$$

$$S_o = 0.0486X + 1.936$$

Potassium,

$$S_t = 0.1443X - 2.317$$

$$S_o = 0.0847X - 61.15$$

Sodium,

$$S_t = 0.08905X + 729$$

$$S_o = 0.0295X + 195$$

where:

S_t = overall precision,
S_o = single-operator precision, and
X = concentration of lithium, potassium, or sodium determined, mg/L.

12.2 The bias of this test method determined from recoveries of known amounts of lithium, potassium, and sodium in a series of prepared standards were as follows:

Lithium, Amount Added, mg/L	Recovery, % Relative
21.0	102.0
52.3	101.1
74.1	100.5
164	95.0
Potassium, Amount Added, mg/L	Recovery, % Relative
591	111.0
1650	110.9
1670	113.2
1921	125.2
Sodium, Amount Added, mg/L	Recovery, % Relative
9 140	105.7
29 000	103.9
62 500	105.4
66 200	108.3

NOTE 1—The preceding precision and bias estimates are based on an interlaboratory study of lithium, potassium, and sodium and interfering ions as shown in Table 1. Two analysts in each of four laboratories and one analyst in each of two laboratories performed duplicate determinations on each of two days. Practice D 2777 was used in developing these precision and bias estimates.

12.3 It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

TABLE 1 Compositions of Artificial Brine Samples

	g/L			
Sample No.	1	2	3	4
Na [A]	9.14	62.5	29.0	66.2
K [B]	0.591	1.670	1.650	1.921
Li [C]	0.0210	0.0523	0.0741	0.164
$CaCl_2$	1.47	2.86	1.93	4.67
$MgCl_2 \cdot 6H_2O$	9.40	10.19	4.12	1.99
$BaCl_2$	0.05	0.95	0.48	0.47

[A] Added to the aqueous solution as NaCl.
[B] Added to the aqueous solution as KCl, KBr, and KI: Sample No. 1 contained 0.470 g/L of KCl, 0.979 g/L of KBr, and 0.098 g/L of KI; Sample No. 2 contained 1.774 g/L of KCl, 1.909 g/L of KBr, and 0.477 g/L of KI; Sample No. 3 contained 1.721 g/L of KCl, 1.928 g/L of KBr, and 0.482 g/L of KI; and Sample No. 4 contained 2.072 g/L of KCl, 1.870 g/L of KBr, and 0.934 g/L of KI.
[C] Added to the aqueous solution as LiCl.

12.4 Precision and bias for this test method conforms to Practice D 2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777-98, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

13. Quality Control

13.1 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 lithium, potassium, and sodium.

13.2 *Calibration and Calibration Verification*:

13.2.1 Analyze at least three working standards containing concentrations of lithium, potassium, and sodium that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument.

13.2.2 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.

13.2.3 If calibration cannot be verified, recalibrate the instrument.

13.3 *Initial Demonstration of Laboratory Capability*:

13.3.1 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, etc., a precision and bias study must be performed to demonstrate laboratory capability.

13.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of lithium, potassium, and sodium. 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. The replicates may be interspersed with samples.

13.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in 12.2. This study should be repeated until the recoveries are within the limits given in section 12.2. If a concentration other than the recommended concentration is used, refer to Test

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[7] Supporting data are available from ASTM Headquarters. Request RR: D19 - 1029.

Method D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

13.4 Laboratory Control Sample (LCS)

13.4.1 To ensure that the test method is in control, analyze a LCS containing a mid-range concentration of lithium, potassium, and sodium with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. 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.

13.4.2 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.

13.5 *Method Blank*:

13.5.1 Analyze a reagent water test blank with each batch. The concentration of lithium, potassium, and sodium found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of lithium, potassium, and sodium 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.

13.6 *Matrix Spike (MS)*:

13.6.1 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 lithium, potassium, and sodium and taking it through the analytical method.

13.6.2 The spike concentration plus the background concentration of lithium, potassium, and sodium 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.

13.6.3 Calculate the percent recovery of the spike (P) using the following formula: P = 100 [A(Vs + V) - B Vs] / C V 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 V = Volume (mL) added with Spike

13.6.4 The percent recovery of the spike shall fall within 80-120%. 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: acceptable spike recoveries are dependent on the concentration of the component of interest. See Test Method 5810 for additional information.

13.7 *Duplicate*:

13.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each 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.

13.7.2 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 Test Method D 5847 for information on applying the F test.

13.7.3 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.

13.8 *Independent Reference Material (IRM)*:

13.8.1 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.

14. Keywords

14.1 brackish; brine; lithium; potassium; seawater; sodium