Designation: D 3561 – 96

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]

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[4] 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 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

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[1] This test method is under the jurisdiction of ASTM Committee D-19 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] 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.

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, [5] 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 roundrobin 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.

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.

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.

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.

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.

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 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,

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[5] *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.

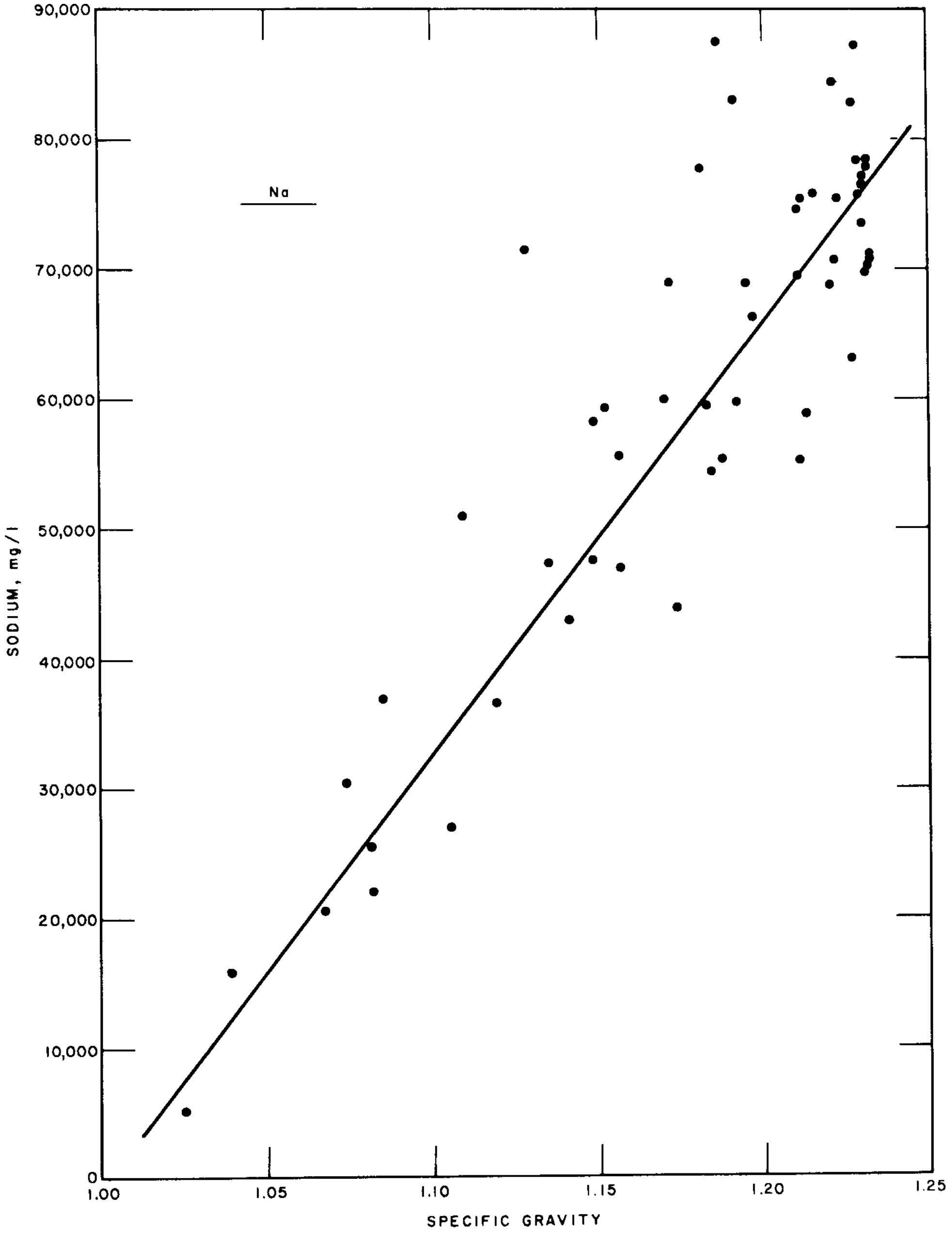

FIG. 1 Relationship of the Concentration of Sodium in Some Oilfield Brines to Specific Gravity

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

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

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_{std}^{2} in mg/L.

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

12. Precision and Bias [6]

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

Lithium,

$$S_t = 0.0677X + 3.127$$

$$S_o = 0.0486X + 1.936$$

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

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.

13. Keywords

13.1 brackish; brine; lithium; potassium; seawater; sodium

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.