



Designation: D 3352 – 03<sup>ε1</sup>

## Standard Test Method for Strontium Ion in Brackish Water, Seawater, and Brines<sup>1</sup>

This standard is issued under the fixed designation D 3352; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

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<sup>ε1</sup> NOTE—Editorial corrections were made throughout in August 2003.

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### 1. Scope\*

1.1 This test method covers the determination of soluble strontium ion in brackish water, seawater, and brines by atomic absorption spectrophotometry.

1.2 Samples containing from 5 to 2100 mg/L of strontium may be analyzed by this test method.

1.3 *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:*

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<sup>1</sup> 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. Current edition approved June 10, 2003. Published July 2003. Originally approved in 1974. Last previous edition approved in 1999 as D 3352 – 94 (1999).

\*A Summary of Changes section appears at the end of this standard.

- D 1129 Terminology Relating to Water<sup>2</sup>  
 D 1193 Specification for Reagent Water<sup>2</sup>  
 D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water<sup>2</sup>  
 D 3370 Practices for Sampling Water from Closed Conduits<sup>2</sup>  
 D 5810 Guide for Spiking into Aqueous Samples<sup>2</sup>  
 D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods in Water Analysis<sup>3</sup>

### 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 the 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<sup>4</sup> to be measured 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.

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 This test method<sup>5</sup> can be used to determine strontium ions in brackish water, seawater, and brines.

### 6. Interferences

6.1 The chemical suppression caused by silicon, aluminum, and phosphate is controlled by adding lanthanum. The lanthanum also controls ionization interference.

### 7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*—The instrument shall consist of 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 read-out mechanism for indicating the amount of absorbed radiation.

7.1.1 *Multi-Element Hollow Cathode Lamps* are available and have been found satisfactory.

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.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.02.

<sup>4</sup> For additional information on atomic absorption, see the following references: Angino, E. E., and Billings, G. K., *Atomic Absorption Spectrophotometry in Geology*, Elsevier Publishing Co., New York, N.Y., 1967. Dean, J. A., and Rains, T. C., Editors, *Flame Emission and Atomic Absorption Spectrometry Vol 1 – Theory*, Marcel Dekker, New York, NY, 1969.

<sup>5</sup> Additional information is contained in the following references: 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 Publishing Co., Amsterdam. The Netherlands, 1975.

**TABLE 1 Compositions of Artificial Brine Samples**

Sample No.	g/L			
	1	2	3	4
Sr	0.060	0.100	1.600	2.100
NaCl	24.0	170.0	80.0	200.0
KCl	0.5	2.0	1.5	3.0
KBr	1.0	2.0	2.0	2.0
KI	0.1	0.5	0.5	1.0
CaCl <sub>2</sub>	1.5	3.0	2.0	5.0
MgCl <sub>2</sub>	4.5	5.0	2.0	1.0
BaCl <sub>2</sub>	0.05	1.0	0.5	0.5

## 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 specifications of the Committee on Analytical Reagents of the American Chemical Society,<sup>6</sup> 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<sub>2</sub> water was specified at the time of round robin testing of this test method.

8.3 *Lanthanum Solution (5 % La)*—Wet 58.65 g of lanthanum oxide (La<sub>2</sub>O<sub>3</sub>) with water. Add 250 mL of concentrated hydrochloric acid (sp gr 1.19) very slowly until the material is dissolved. Dilute solution to 1 litre with water.

8.4 *Strontium Solution, Standard (1 mL = 1 mg Sr)*—Dissolve 2.415 g of strontium nitrate [Sr(NO<sub>3</sub>)<sub>2</sub>] in 10 mL of concentrated hydrochloric acid (sp gr 1.19) and about 700 mL of water. Dilute solution to 1 L with water. One millilitre of this solution contains 1 mg of strontium.

8.5 *Oxidant, for Atomic Absorption Spectrophotometer:*

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

8.5.2 *Nitrous Oxide* may be required as an oxidant for refractory-type metals.

8.6 *Fuel, for Atomic Absorption Spectrophotometer:*

8.6.1 *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 which only has 100 psig of acetylene remaining.

## 9. Sampling

9.1 Collect the sample in accordance with Practices D 3370.

## 10. Procedure

10.1 Strontium is determined at the 460.7-nm wavelength with an air-acetylene flame.

10.2 *Preliminary Calibration*—Using micropipets prepare standard strontium solutions containing 1 to 10 mg/L of strontium using the standard strontium solution and 50-mL volumetric flasks. Before making up to volume, add to each of these and to a blank, 5 mL of the lanthanum solution. Aspirate these standards and the 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- $\mu$ m filter) to a 50-mL volumetric flask. The specific gravity of the water or brine can be used to estimate the strontium content of the sample and, thereby, serve as a basis for selecting the aliquot size that will contain about 0.1 mg of strontium. Fig. 1 shows the relationship between strontium concentration and specific gravity for some oilfield brines from the Smackover formation. The concentrations of strontium in the Smackover brines will not necessarily correlate with the concentrations found in other formations. Therefore, the user of this test method may find it necessary to draw a similar curve for brine samples taken from other formations. Add 5 mL of the lanthanum stock solution, dilute to volume, and aspirate. Calculate the approximate sample concentration from the preliminary calibration readings, and determine the aliquot size that will contain about 0.1 mg of strontium.

10.4 Transfer equal aliquots containing about 0.1 mg of strontium to three 50-mL volumetric flasks. Add no strontium standard to the first flask. With a micropipet add 0.1 mg to the second and 0.2 mg to the third.

10.5 Add 5 mL of the lanthanum solution to each of the three flasks and dilute to volume. Aspirate and record the absorbance readings for each sample.

<sup>6</sup> *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 Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

**TABLE 2 Determination of Precision and Bias of Strontium Ion**

Amount Added, mg/L	Amount Found, mg/L	S <sub>O</sub>	S <sub>T</sub>	± Bias	Statistically Significant (95 % Confidence Level)
60	63.48	2.96	8.49	+ 5.8	yes
100	99.5	4.12	11.84	-0.5	no
1600	1665.6	54.87	157.3	+ 4.1	no
2100	2167.2	71.12	203.9	+ 3.2	no

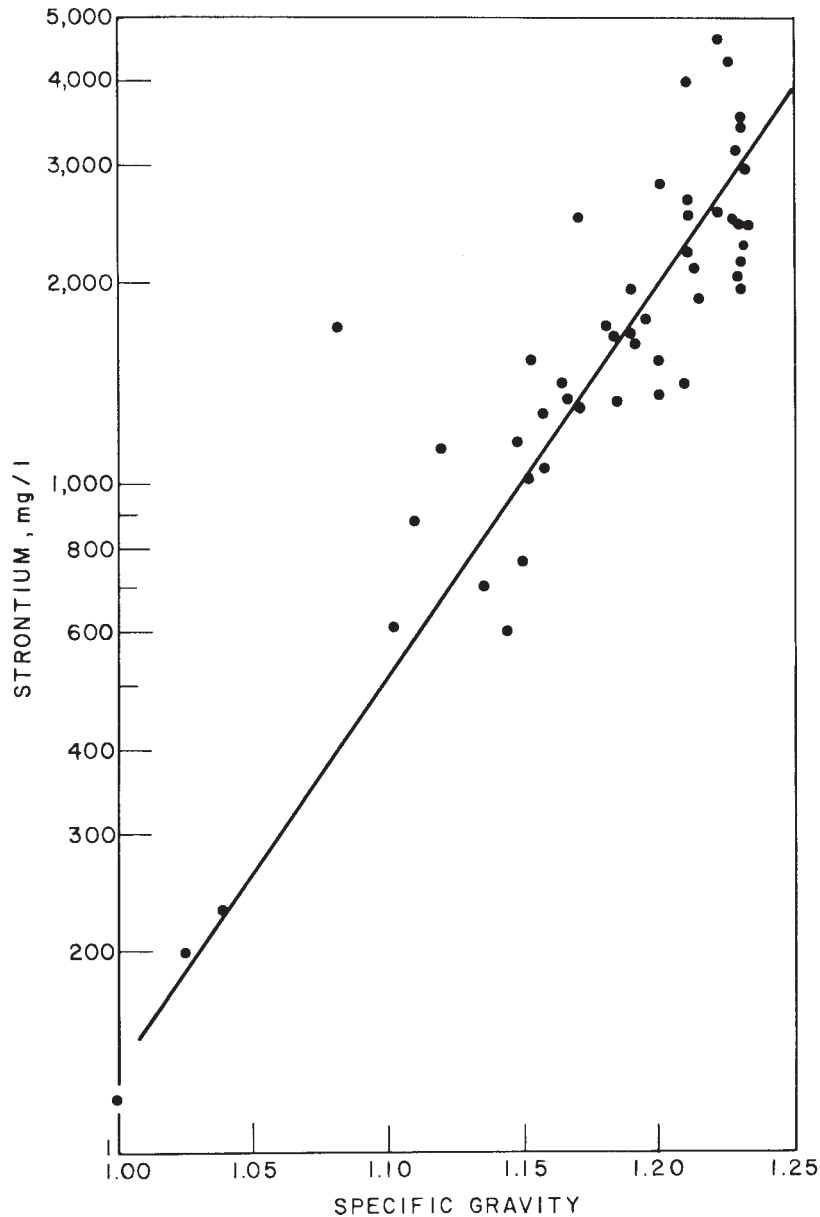


FIG. 1 Relationship of the Concentration of Strontium in Some Oilfield Brines to Specific Gravity

**11. Calculation**

11.1 Calculate the concentration of strontium ion in the original sample in milligrams per litre as follows:

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

where:

- $V_1$  = volume of the diluted samples, 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  $A_{std}$ , mg/L.

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

**12. Precision and Bias <sup>7</sup>**

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

<sup>7</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D19-1022.

$$S_t = 0.0929X + 2.596$$

$$S_o = 0.0324X + 0.901$$

where

$S_t$  = overall precision,

$S_o$  = single-operator precision, and

$X$  = concentration of strontium determined, mg/L.

12.2 The bias of the test method determined from recoveries of known amounts of strontium in a series of prepared standards are given in Table 2.

NOTE 1—The above precision and bias estimates are based on an interlaboratory study on four artificial brine samples containing various amounts of strontium and interfering ions as shown in Table 1. One analyst in each of three laboratories and two analysts in each of six laboratories performed duplicate determinations on each of two days. Practice D 2777 was used in developing these precision and bias estimates.

12.3 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 vanadium strontium.

#### 13.2 Calibration and Calibration Verification

13.2.1 Analyze at least three working standards containing concentrations of vanadium strontium that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. ~~The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.~~ 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, ~~and so forth, 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 midrange concentration of vanadium strontium. 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 ~~Table 1, 12.1~~. This study should be repeated until the recoveries are within the limits given in ~~Table 1, 12.1~~. 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.

#### 13.4 Laboratory Control Sample (LCS)

13.4.1 To ensure that the test method is in control, analyze a LCS containing a known mid-range concentration of vanadium strontium with each batch or ten samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every ten samples. ~~The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range~~ 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 vanadium strontium found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of vanadium strontium 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 vanadium strontium and taking it through the analytical method.

13.6.2 The spike concentration plus the background concentration of vanadium strontium 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:

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

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

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<sub>s</sub> = volume (mL) of sample used, and
- V = volume (mL) added with spike.

13.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Test Method D 5810, 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 2—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Test Method D 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 Practice 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; brines; seawater; strontium ion

## SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D 3352–94 (1999)) that may impact the use of this standard.

- (1) Section 8.2 was modified.
- (2) Section 12.3 was added.
- (3) The QC Section 13 was added to the test method.

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