Calcium, atomic absorption spectrometric, direct

Parameters and Codes:
Calcium, dissolved, I-1152-85 (mg/L as Ca): 00915
Calcium, total recoverable, I-3152-85 (mg/L as Ca): none assigned
Calcium, suspended recoverable, I-7152-85 (mg/L as Ca): 81357
Calcium, recoverable-from-bottom-material, dry wt I-5152-85 (mg/kg as Ca): 00917

1. Application

1.1 This method maybe used to analyze atmospheric precipitation, water, brines, and water-suspended sediment.

1.2 Two analytical ranges for calcium are included: from 0.01 to 5.0 mg/L and from 1.0 to 60 mg/L. Sample solutions containing calcium concentrations greater than 60 mg/L need to be diluted.

1.3 Suspended recoverable calcium is calculated by subtracting dissolved calcium from total recoverable calcium.

1.4 This method may be used to analyze bottom material containing at least 10 mg/kg of calcium.

1.5 Total recoverable calcium in water-suspended sediment needs to undergo preliminary digestion-solubilization by method 1-3485, and recoverable calcium in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

2.1 Calcium is determined by atomic absorption spectrometry (Fishman and Downs, 1966). Lanthanum chloride is added to mask interferences.

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and a strip-chart recorder or printer or both (fig. 1).

3. Interferences

3.1 Phosphate, sulfate, and aluminum interfere but are masked by the addition of lanthanum. Silica also reportedly interferes. Because
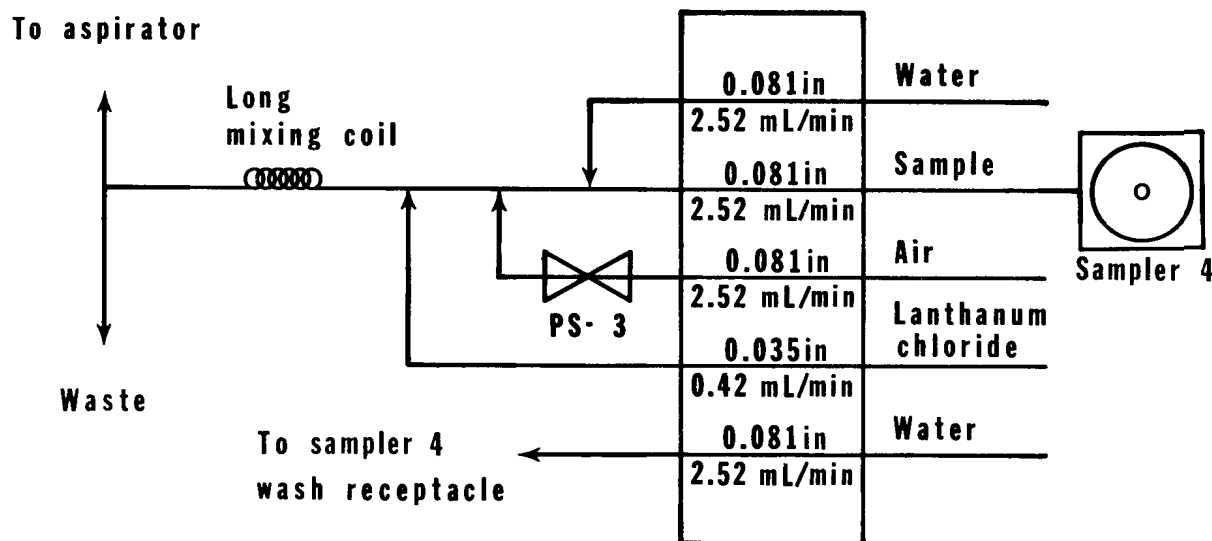

Figure 1. - Calcium manifold.

low calcium values result if the pH of the sample is above 7, standards are prepared in hydrochloric acid solution and samples are preserved in the field with use of nitric acid solution. Concentrations of magnesium greater than 1,000 mg/L also cause low calcium values.

3.2 Nitrate interferes, but in the presence of lanthanum chloride-hydrochloric acid solution at least 2,000 mg/L can be tolerated. The addition of nitric acid to the sample causes no problem in the following procedure.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout and automatic zero and concentration controls.

4.2 Refer to the manufacturer's manual to optimize instrument for the following:

Grating -------------------- Visible
Wavelength --------------- 422.7 nm
Source (hollow-cathode
     lamp) --------------- Calcium
Oxidant -------------------- Air
Fuel ------------------------ Acetylene
Type of flame ----------- Slightly
                  reducing

4.3 The 50-mm (2-in.), flathead burner allows a working range of 0.01 to 5.0 mg/L. This burner, rotated 90°, allows a working range of 1.0 to 60 mg/L.

4.4 Different burners may be used according to manufacturers' instructions. A nitrous oxide-acetylene flame will provide two to five times greater analytical sensitivity and freedom from chemical interferences; however, sodium or potassium chloride must be added to control ionization of calcium.

5. Reagents

5.1 *Calcium standard solution,* 1.00 mL = 0.500 mg Ca: Suspend 1.250 g $CaCO_3$, dried at 180°C for 1 h before weighing, in demineralized water and dissolve *cautiously* with a minimum of dilute HCl. Dilute to 1,000 mL with demineralized water.

5.2 *Calcium working standards:* Prepare at least six working standards containing either from 0.01 to 5.0 mg/L or from 1.0 to 60 mg/L of calcium by diluting the calcium standard solution. To each working standard add 1.0 mL of $LaCl_3$ solution for each 10 mL of standard.

Similarly, prepare a demineralized water blank.

5.3 *Lanthanum chloride solution,* 87 g/L: Mix 29 g of La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

6. Procedure

6.1 Add 1.0 mL of $LaCl_3$ solution per 10.0 mL of sample solution.

6.2 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the milligrams per liter of dissolved or total recoverable calcium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing calcium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine milligrams per liter of suspended recoverable calcium, subtract dissolved-calcium concentration from total-recoverable-calcium concentration.

7.3 To determine milligrams per kilogram of calcium in bottom-material samples, first determine the milligrams per liter of calcium in each sample as in paragraph 7.1; then

$$Ca\ (mg/kg) = \frac{mg/L\ Ca \times \dfrac{mL\ of\ original\ digest}{1000}}{wt\ of\ sample\ (kg)}$$

8. Report

8.1 Report calcium, dissolved (00915), total-recoverable (none assigned), and suspended-recoverable (81357), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 to 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

8.2 Report calcium, recoverable-from-bottom-material (00917), concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

9.1 Precision for dissolved calcium for 37 samples within the range of 0.84 to 184 mg/L may be expressed as follows:

$$S_T = 0.087X - 0.249$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of calcium, milligrams per liter.

The correlation coefficient is 0.8632.

9.2 Precision for dissolved calcium for five of the 37 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
20	0.84	24
14	10.7	6
45	50.1	8
23	110	8
36	184	10

9.3 Precision for dissolved calcium within the range of 0.05 to 5.0 mg/L in terms of the percent relative standard deviation by a single operator is as follows:

Number of replicates	Mean (µg/L)	Relative standard deviation (percent)
8	0.052	40.4
8	1.02	5.9
8	1.85	10.3
8	5.05	1.0

9.4 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable calcium and for recoverable calcium from bottom material will be greater than that reported for dissolved calcium.

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. C26-C28.