

Calcium, atomic absorption spectrometric, direct-EPA

Parameter and Code:

Calcium, total recoverable, I-3153-85 (mg/L as Ca): 00916

1. Application

1.1 This method may be used to analyze water-suspended sediment. Sample solutions containing from 0.1 to 60 mg/L of calcium may be analyzed without dilution; whereas, those containing more than 60 mg/L need to be diluted.

1.2 For ambient water, analysis may be made on a measured portion of the acidified water-suspended sediment sample.

1.3 For all other waters, including domestic and industrial effluent, the atomic absorption procedure must be preceded by a digestion-solubilization as specified below. In cases where the analyst is uncertain about the type of sample, the digestion-solubilization procedure must be used.

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 Effluent samples must undergo a preliminary nitric acid digestion followed by a hydrochloric acid solubilization.

3. Interferences

3.1 Phosphate, sulfate, and aluminum interfere but are masked by the addition of lanthanum. Silica reportedly also interferes. Because 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 as a preservative at the time of collection causes no problem in the following procedure. Samples should be evaporated just to dryness following nitric acid digestion to avoid any possible nitrate interference.

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 Different burners may be used according to manufacturers' instructions. A nitrous oxide-acetylene flame provides 2 to 5 times greater 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 a series of at least six working standards containing from 0.1 to 60 mg/L of calcium by dilution of calcium standard solution. To each working

standard add 1.0 mL of LaCl_3 solution for each 10 mL of standard.

5.3 *Hydrochloric acid, 6M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.4 *Hydrochloric acid, 0.3M*: Dilute 25 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.5 *Lanthanum chloride solution, 87 g/L*: Mix 29 g 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.

5.6 *Nitric acid, concentrated* (sp gr 1.41).

6. Procedure

6.1 Transfer the entire sample to a beaker.

6.2 Rinse the sample bottle with 3 mL concentrated HNO_3 for each 100 mL of sample and add to the beaker. Prepare a blank using 3 mL concentrated HNO_3 per 100 mL demineralized water.

6.3 Evaporate samples and blank to dryness on a hotplate, making sure the samples do not boil.

6.4 Cool and add an additional 3 mL concentrated HNO_3 to the beaker. Cover with a watchglass, return to the hotplate, and gently reflux the sample.

6.5 Continue heating, adding additional acid as necessary, until the digestion is complete (indicated by a light-colored residue). Evaporate just to dryness.

6.6 Add 6 mL 6M HCl solution per 100 mL of original sample and warm the beaker to dissolve the residue.

6.7 Wash the watchglass and beaker with demineralized water and filter the sample (Whatman No. 41 or equivalent), rinsing the

filter with hot, 0.3M HCl . Dilute to the original volume with demineralized water.

6.8 Add 1.0 mL lanthanum chloride solution per 10.0 mL of sample.

6.9 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

Determine the milligrams per liter of 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.

8. Report

Report calcium, total-recoverable (00916), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for total recoverable calcium over the range of the method will be greater than 8 percent.

References

- 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.
- U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 215.1-1.