

CALCIUM and compounds, as Ca

7020

Ca

MW: Table 1

CAS: Table 1

RTECS: Table 1

METHOD: 7020, Issue 2

EVALUATION: FULL

Issue 1: 15 February 1984

Issue 2: 15 August 1994

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: soft, reactive metal; valence 2;
 MP 848 °C; VP not significant

SYNONYMS: Quicklime (CaO); limestone (CaCO₃); marble (CaCO₃); hydrated lime (Ca(OH)₂)

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (0.8-µm cellulose ester membrane)	TECHNIQUE:	ATOMIC ABSORPTION, FLAME
FLOW RATE:	1 to 3 L/min	ANALYTE:	calcium
VOL-MIN:	20 L @ 5 mg/m ³	ASHING:	conc. HNO ₃ , 6 mL; 140 °C 60% (w/v) HClO ₄ , 2 mL; 400 °C
-MAX:	400 L	FINAL SOLUTION:	5% HCl; 100 mL 1000 µg/mL Cs; 1000 µg/mL La
SHIPMENT:	routine	FLAME:	air-acetylene, reducing
SAMPLE STABILITY:	stable	WAVELENGTH:	422.7 nm
BLANKS:	2 to 10 field blanks per set	BACKGROUND CORRECTION:	none used
ACCURACY		CALIBRATION:	Ca ²⁺ in 5% HCl
RANGE STUDIED:	2.6 to 10.2 mg/m ³ [1] (85-L samples)	RANGE:	0.08 to 1.7 mg per sample [2]
BIAS:	- 0.39%	ESTIMATED LOD:	0.001 mg per sample [3]
OVERALL PRECISION (S_{r,T}):	0.063 [1]	PRECISION (S_r):	0.02 [1,3]
ACCURACY:	± 11.5%		

APPLICABILITY: The working range is 1 to 20 mg/m³ for an 85-L air sample. This is an elemental analysis, not compound specific. Verify that the compounds in the samples are soluble with the ashing procedure. Aliquots of the samples can be analyzed separately for many additional metals.

INTERFERENCES: The use of 1000 µg/mL Cs controls ionization in the flame caused by metals such as Na, K, Li, and Mg. The presence of Si, Al, or H₃PO₄ require the use of 1% (w/w) La as a releasing agent.

OTHER METHODS: This method combines and replaces P&CAM 173 [4] and S205 [2]. Method 7300 (ICP-AES) is an alternate analytical method.

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Hydrochloric acid, 5% (v/v). Add 50 mL conc. HCl to 500 mL water; dilute to 1 L.
4. Calibration stock solution, 1000 µg Ca/mL. Commercially available or add 50 mL deionized water and minimum volume of HCl (20 mL) to dissolve 2.498 g CaCO₃. Dilute to 1 L with deionized water.
5. Cs solution, 50 mg/mL. Dissolve 73.40 g CsNO₃ in water to make 1 L solution.
6. La solution, 50 mg/mL. Dissolve 156 g La(NO₃)₃·6H₂O in water to make 1 L solution.
7. Distilled or deionized water.
8. Air, filtered.
9. Acetylene.
10. Perchloric acid, 60% w/v.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with an air-acetylene burner head and calcium hollow cathode lamp.
4. Regulators, 2-stage, for air and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 25- and 100-mL.*
7. Micropipets, 5 to 500 µL.*
8. Hotplate, surface temperature 140 and 400 °C.

* Clean with conc. HNO₃ and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all perchloric acid digestions in a perchloric acid fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 20 to 400 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD). Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassette filter holders and transfer the samples and blanks to separate clean beakers.
4. Add 5 mL conc. HNO₃ and cover with a watchglass. Start reagent blanks at this point.
5. Heat on hotplate (140 °C) until most of the acid has evaporated.
6. Add 2 mL conc. HNO₃ and 1 mL 60% HClO₄.
7. Heat on 400 °C hotplate until dense fumes of perchloric acid appear.
8. Remove watchglass and rinse into the beaker with distilled water.
9. Place the beakers on the 400 °C hotplate and allow to go to dryness.
10. Cool each beaker and dissolve the residues in 5 mL 5% HCl.
11. Transfer the solution quantitatively to a 100-mL volumetric flask containing 2 mL of 50 mg/mL Cs solution and 2 mL of 50 mg/mL La solution.
NOTE: Dilute to a smaller volume (e.g., 10 mL) with proportionally less Cs and La if required for sensitivity of analysis for other metals in the sample.
12. Dilute to volume with 5% HCl.

CALIBRATION AND QUALITY CONTROL:

13. Add known amounts, covering the range 0 to 500 µg Ca per sample, of calibration stock solution to 100-mL volumetric flasks containing 2 mL each of the 50 mg/mL Cs and La solutions and dilute to volume with 5% HCl.
14. Analyze the working standards along with the samples and blanks (steps 19 and 20).
15. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
16. Aspirate a standard for every 10 samples to check instrument drift.
17. Check recoveries with at least one spiked media blank per 10 samples.
18. Use method of additions occasionally to check for interferences.

MEASUREMENT:

19. Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7020-1.
20. Aspirate standards and samples. Record absorbance readings.
NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 5% HCl and an appropriate amount of the 50 mg/mL Cs and La solutions, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

21. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of calcium in the sample, C_s , and average media blank, C_b , from the calibration graph.
22. Using the solution volumes (mL) of the sample, V_s , and media blanks, V_b , calculate the concentration, C (mg/m³), of calcium in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S205 [2] was issued on September 26, 1975, and validated over the range 2.6 to 10.2 mg/m³ using an 85-L air sample by lab testing with spiked filters and generated atmospheres of CaO, verified by EDTA titration [1]. Collection efficiency of 1.00 was determined for the sampling device. Precision and accuracy data are given on page 7020-1. An additional check showed an estimated LOD of 1 µg Ca per sample [3].

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, S205, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
- [2] V. 3, S205, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1979).
- [3] User check, UBTL, NIOSH Seq. #3990-Q (unpublished, November 29, 1983).
- [4] Ibid, NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).

METHOD REVISED BY:

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TABLE 1: General Information

FORMULA	M.W.	CAS #	RTECS #	EXPOSURE LIMITS (mg/m ³)		
				OSHA	NIOSH	ACGIH
Ca	40.08	7440-70-2	EV8040000	--	--	--
CaO	56.08	1305-78-8	EW3100000	5	2	2
Ca(OH) ₂	74.10	1305-62-0	EW2800000	None	5	5
Ca(CO ₃) ₂ total dust	100.09	471-34-1	EV9580000	15 (total); 5 (resp.)	10 (total); 5 (resp.)	10