MASTER

EMISSION SPECTROGRAPHIC ANALYSIS
OF PURIFIED CALCIUM METAL

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

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ABSTRACT

A successful method for determining fifteen trace impurities in pure calcium has been developed. The average limit of error at the 95 percent confidence level for the fifteen elements determined was ± 16.3 percent at the lowest level and ± 14.9 percent at the highest level. The simplicity of sample preparation and utilization of direct-current arc excitation provide improved accuracy at a lower cost when compared to the emission spectrographic analysis of calcium oxide previously used.

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SUMMARY

The emission spectrographic determination of fifteen trace impurities in purified calcium metal combines the ease of preparation of the porous-cup technique and the sensitivity of direct-current arc excitation.

A Jarrell-Ash 21-foot grating spectrograph was used in conjunction with a Bausch and Lomb prism spectrograph to simultaneously determine and record a spectral range from 2200 to 8000 angstroms.

The impurity spectra are recorded photographically and compared visually with standards exposed under identical excitation conditions. The average limit of error at the 95 percent confidence level for fifteen elements determined was ± 16.3 percent at the lowest level and ± 14.9 percent at the highest level.

INTRODUCTION

The purity of calcium metal used in many experiments must be carefully controlled to ensure final products of high purity. While chemical methods for the determination of impurities in calcium have been reported, ⁽¹⁾ they are very time consuming. Emission spectroscopy affords a more sensitive, rapid, and economical method for determining the impurity level in highly purified calcium metal.

Although other spectrographic methods for a few selected elements in calcium have been reported, ^(2 - 5) this method combines the better features of the porous-cup preparation with the sensitive detection limits of direct-current arc excitation. Other advantages of this method are:

1. Sample preparation is simple. The metal is reacted with distilled water, dissolved in hydrochloric acid, and pipetted into the waxed electrode crater. The method of sample preparation previously used involved reaction with water, drying the hydroxide, igniting to the oxide, grinding the oxide, weighing the sample charge, loading the electrode, tamping, and center venting.
2. Emulsion calibration and microphotometry are not required since the impurity standards are photographed on the spectrographic plates with the unknown samples. These standards are then compared visually with the unknown samples to obtain the concentration of the impurity elements.
3. The detection limit of most impurity elements is approximately a factor of two lower than that obtained using the previous method.
4. No special electrode or equipment is required.

ANALYTICAL METHOD

EQUIPMENT AND REAGENTS

The principal items of equipment and the reagents needed in the analysis are as follows:

Equipment

Grating Spectrograph - Jarrell-Ash with a 21-foot Wadsworth mount and a dispersion of 2.56 Å/mm in the second order (see Figure 1).

Figure 1. PRINCIPAL COMPONENTS OF THE JARRELL-ASH - LITTROW SPECTROGRAPH.

Prism Spectrograph - Bausch and Lomb, large Littrow.

Power Source - DC, 15 amperes.

Balance - Analytical.

Comparator - Visual.

Crucible - Platinum, 75 milliliters.

Electrode - 6-mm diameter, 3-mm deep; in 7-mm graphite stock.

Electrode - Counter, 3-mm diameter, 75-mm long.

Pipette - 100 lambda.

Spatula - Platinum.

Vial - Plastic, 20 mls; with cap.

Photographic Plates - Eastman Kodak, Type SA-I, I-N.

Tray - Developing.

Reagents

Hydrochloric Acid - Reagent grade.

Carbon Block - Electrode, 40 holes.

Chloroform - Reagent grade.

Paraffin - Reagent grade.

Developer - Eastman Kodak, D-19.

Fixer - Rapid Fixer with hardener, Eastman Kodak.

PROCEDURE

Sample Preparation

The following steps were observed in preparing the sample:

1. Weigh a 2.000-gram sample of calcium metal and transfer it to a 75-milliliter platinum crucible.
2. Place the crucible in an enameled developing tray partly filled with crushed dry ice.
3. React the metal by slow addition of distilled water.
4. Dissolve the reacted sample with 10 milliliters of concentrated hydrochloric acid; stir slowly with a platinum spatula.
5. Allow the solution to cool, then transfer it to a 20-milliliter plastic vial and dilute to volume.
6. Cap the vial and mix thoroughly.

Charging the Electrode Crater

The electrode crater was charged as follows:

1. Place duplicate 6-mm by 3-mm electrodes for each sample to be analyzed into an electrode block, fill the electrodes with a saturated paraffin-chloroform solution, then place the electrode block under infrared lights to dry.
2. Pipette 100 lambda (10 milligrams of calcium) of each sample solution into duplicate electrodes. Avoid air-bubble entrapment during pipetting.
3. Place the loaded electrode block approximately 50 centimeters below the infrared lights and leave it in position until near dryness (~ 30 minutes).
4. Lower the infrared lights to approximately seven centimeters above the electrode block to complete the drying.

Arcing the Samples

Sample arcing was accomplished by the following procedure:

1. Carefully remove the hot electrode block and place it on a preheated hot plate (90° C) at the spectrograph.
2. Arc the samples and the standards using the parameters shown in Table 1; use a fresh counter electrode for each crater electrode.

Table 1
SOURCE AND OPERATING PARAMETERS

Jarrell-Ash	Littrow
Exposure Timer (110 seconds)	Exposure Timer (30 seconds)
Diaphragm 20	Diaphragm 20
Plates (two Type SA-I)	Plate (Type I-N)
Camera (centered at 5800 Å)	Camera (centered at 6000 Å)
Power Source (15 amperes, DC)	Electrode Gap (5 mm)

Plate Processing

Plate processing was performed as follows:

1. Process the plates in Type D-19 Developer at 20° C for three minutes.
2. Wash the plates with water, fix for three minutes, rinse with distilled water, and dry.

STANDARDS PREPARATION

Stock Solution

1. Weigh the spectrographically pure compounds listed in Table 2 to prepare a standard stock solution. Dissolve the silicon dioxide in a platinum crucible using 10 milliliters of concentrated sulfuric acid and a minimum amount of hydrofluoric acid. Dissolve the other compounds in a 250-milliliter plastic beaker, using 50 milliliters of 6-normal hydrochloric acid.

Table 2
CALCIUM STOCK STANDARD

Element	Compound	Compound Factor	Calcium (ppm at 1X)	Compound Weight (gms)	Impurity Weight (gms)
Al	Al (metal)	1.000	5	0.0500	0.05
B	H ₃ BO ₃	5.715	1	0.0572	0.01
Be	BeO	2.774	0.5	0.0139	0.005
Cd	CdO	1.142	5	0.0571	0.05
Co	Co ₂ O ₃	1.407	5	0.0704	0.05
Cr	Cr (metal)	1.000	5	0.0500	0.05
Cu	CuO	1.252	5	0.0626	0.05
Fe	Fe ₂ O ₃	1.430	5	0.0715	0.05
Li	Li ₂ CO ₃	5.324	5	0.2662	0.05
Mg	Mg (metal)	1.000	500	5.0000	5.00
Mn	MnO ₂	1.583	5	0.0792	0.05
Na	NaCl	2.542	5	0.0271	0.05
Ni	Ni ₂ O ₃	1.409	5	0.0705	0.05
Si	SiO ₂	2.140	5	0.1070	0.05
V	V ₂ O ₅	1.785	5	0.0893	0.05

2. Transfer both solutions to a 500-milliliter volumetric flask, dilute to volume with distilled water, and mix thoroughly. Transfer the standard solution to a 500-milliliter plastic bottle for storage.

Working Solution

Weigh a 2.000-gram aliquant of pure calcium metal into each of six 75-milliliter platinum crucibles. Place the crucible in a tray of crushed dry ice and react the metal slowly with distilled water. Pipette 10 milliliters of concentrated hydrochloric acid into each crucible, while stirring with a platinum spatula. Pipette 0.10, 0.20, 0.5, 1.0, and 2.0 milliliters of the stock standard solution into five crucibles. The last crucible is used as the "blank" standard. Transfer the standards into appropriately marked 1 by 2-inch plastic vials, dilute to volume, cap, and mix thoroughly.

DISCUSSION

When the porous-cup technique was first evaluated as a method for analyzing calcium, it was found that the reproducibility was poor and the limits of detection were not as low as desired. Sample preparation for the porous-cup method was so easy and simple, however, that it was retained for use when the direct-current arc method was evaluated. The direct-current arc is one of the most sensitive methods for determining trace impurities and this method was evaluated next. The optimum source and exposure parameters, listed in Table 1, were determined by the moving-plate technique. The impurity elements that were determined, the wavelengths used, and the lower reporting limits are given in Table 3.

The reproducibility of the method was determined by separate preparation and arcing of ten high-level and ten low-level standards on four separate days.

Statistical evaluation of the 80 analyses (Tables 4 and 5) showed that this method is satisfactory for determining trace impurities in calcium.

Table 3
WAVELENGTHS AND LOWER REPORTING LIMITS
OF IMPURITY ELEMENTS

Element	Wavelength (angstroms)	Lower Reporting Limit ($\mu\text{gs/gm Ca}$)
Al	3082.16	5
B	2496.78	1
Be	2348.61	0.5
Cd	2288.02	5
Co	2407.25	10
Cr	2835.63	5
Cu	3247.54	5
Fe	2483.27	25
Li	6707.84	5
Mg	3336.68	500 ⁽¹⁾
Mn	2605.69	25
Na	5889.95	5
Ni	3002.49	15
Si	2516.11	5
V	3183.98	10

(1) The calcium-base material used for the standard contained 500 micrograms of magnesium per gram of calcium metal.

Table 4
SPECTROGRAPHIC ANALYSIS OF LOW-LEVEL
CALCIUM STANDARDS

Element	Standard Value ($\mu\text{gs/gm Ca}$)	Mean ($\pm$ LE of the mean)	LE of a Single Result (relative %)
Al	5	5.2 $\pm$ 0.2	$\pm$ 21
B	1	1.0 (all results)	-
Be	0.5	0.52 $\pm$ 0.01	$\pm$ 17
Cd	5	5.0 $\pm$ 0.2	$\pm$ 20
Co	5	5.1 $\pm$ 0.1	$\pm$ 10
Cr	5	5.0 (all results)	-
Cu	5	5.0 $\pm$ 0.1	$\pm$ 16
Fe	5	5.6 $\pm$ 0.4	$\pm$ 43
Li	5	5.0 $\pm$ 0.2	$\pm$ 22
Mg	500	504 $\pm$ 8	$\pm$ 10
Mn	5	5.0 $\pm$ 0.1	$\pm$ 8
Na	5	5.2 $\pm$ 0.2	$\pm$ 23
Ni	5	5.5 $\pm$ 0.2	$\pm$ 18
Si	5	5.2 $\pm$ 0.3	$\pm$ 36
V	5	5.0 (all results)	-

Table 5
SPECTROGRAPHIC ANALYSIS OF HIGH-LEVEL
CALCIUM STANDARDS

Element	Standard Value ($\mu\text{gs/gm Ca}$)	Mean ($\pm$ LE of the Mean)	LE of a Single Result (relative %)
Al	50	49.4 $\pm$ 2.8	$\pm$ 36
B	10	9.6 $\pm$ 0.3	$\pm$ 17
Be	5	4.9 $\pm$ 0.1	$\pm$ 8
Cd	50	49.5 $\pm$ 0.9	$\pm$ 12
Co	50	48.4 $\pm$ 1.0	$\pm$ 13
Cr	50	49.4 $\pm$ 0.6	$\pm$ 8
Cu	50	49.4 $\pm$ 0.7	$\pm$ 9
Fe	50	48.9 $\pm$ 1.0	$\pm$ 13
Li	50	49.7 $\pm$ 0.8	$\pm$ 9
Mg	5,000	4,860 $\pm$ 73	$\pm$ 9
Mn	50	47.4 $\pm$ 0.9	$\pm$ 12
Na	50	50.5 $\pm$ 1.3	$\pm$ 16
Ni	50	48.4 $\pm$ 0.8	$\pm$ 11
Si	50	48.2 $\pm$ 2.5	$\pm$ 33
V	50	48.9 $\pm$ 1.4	$\pm$ 18

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