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THE DETERMINATION OF CALCIUM IN PHOSPHATE, CARBONATE, AND SILICATE ROCKS BY FLAME PHOTOMETER

By Henry Kramer

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CONTENTS

Page

Abstract 4

Introduction 5

Experimental data 6

Apparatus 8

Reagents 10

Procedure 11

Flame photometric procedure 12

References 12

ILLUSTRATION

Page

Figure 1. Standard curves for calcium at 554 mμ 7

TABLE

Page

Table 1. Analytical data 9

THE DETERMINATION OF CALCIUM IN PHOSPHATE, CARBONATE, AND SILICATE ROCKS BY FLAME PHOTOMETER

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ABSTRACT

A method has been developed for the determination of calcium in phosphate, carbonate, and silicate rocks using the Beckman flame photometer, with photomultiplier attachment.

The sample is dissolved in hydrofluoric, nitric, and perchloric acids, the hydrofluoric and nitric acids are expelled, a radiation buffer consisting of aluminum, magnesium, iron, sodium, potassium, phosphoric acid, and nitric acid is added, and the solution is atomized in an oxy-hydrogen flame with an instrument setting of 554 mμ. Measurements are made by comparison against calcium standards, prepared in the same manner, in the 0 to 50 ppm range.

The suppression of calcium emission by aluminum and phosphate was overcome by the addition of a large excess of magnesium. This addition almost completely restores the standard curve obtained from a solution of calcium nitrate. Interference was noted when the iron concentration in the aspirated solution (including the iron from the buffer) exceeded 100 ppm iron. Other common rock-forming elements did not interfere.

The results obtained by this procedure are within ± 2 percent of the calcium oxide values obtained by other methods in the range 1 to 95 percent calcium oxide. In the 0 to 1 percent calcium oxide range the method compares favorably with standard methods.

INTRODUCTION

Investigations of the flame photometric determination of calcium have been made on glasses (5), minerals (2), biological materials (1), metallurgical products (3), and water samples (7). Techniques usually involve either the preliminary separation of calcium from interfering elements, the addition of a saturated solution of a radiation buffer to provide uniform radiation characteristics and minimize the interfering effects of diverse ions, or the comparison of the unknown solution with a standard which incorporates some or all of the interferences present in the unknown solution. In the latter procedure, for accurate quantitative analysis the qualitative make-up and approximate quantities of the components present in a given substance must be known.

Our problem was to determine calcium in phosphate, carbonate, and silicate rocks containing various concentrations of the usual rock-forming elements. The method was to be applicable to routine work, and the utmost in accuracy was not required.

Although most elements either enhance or suppress calcium emission to some extent, aluminum and phosphorus cause series suppression. This effect has been noted by many investigators; Mosher and coworkers partially overcame the effect of aluminum by the addition of a relatively large amount of magnesium (4). In the procedure described here the interference was almost entirely overcome by the addition of a large excess of magnesium. Separations are not required and the results are better than $\pm$ 2 percent of the calcium oxide found by gravimetric methods in the 1 to 95 percent range. The method compares favorably with standard methods in the 0 to 1 percent range, and the lower limit of sensitivity is 0.01 percent.

This study is part of a program conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

EXPERIMENTAL DATA

The most sensitive calcium band is at a wavelength of 554 mμ using the blue sensitive phototube. The oxy-hydrogen flame was selected because of the favorable emission-to-background ratio.

Interference studies were made by adding various amounts of nitric acid to 30 ppm calcium until no further radiation suppression occurred. Next, the effect of perchloric acid increments were tested on 30 ppm calcium plus the plateau quantity of nitric acid determined in the preceding experiment until another plateau was reached. Succeeding elements were studied in this order: aluminum, phosphoric acid, magnesium, iron, sodium, potassium, and manganese to establish plateau quantities. These experiments determined a radiation buffer containing all the elements which affect calcium emission in such concentrations that suppressing or enhancing effects were overcome. In the procedure developed, the radiation buffer is added to both samples and standards so that the concentration variations within the samples themselves are without effect on the sample emission. The radiation buffer also provides increased flame stability and minimizes drift so common to flame methods. Burner clogging was not experienced. The radiation buffer almost completely restores the standard curve obtained from an aqueous solution of calcium nitrate as shown in figure 1. Calibration curves for the ranges 0 to 50 ppm and 0 to 5 ppm calcium are presented.

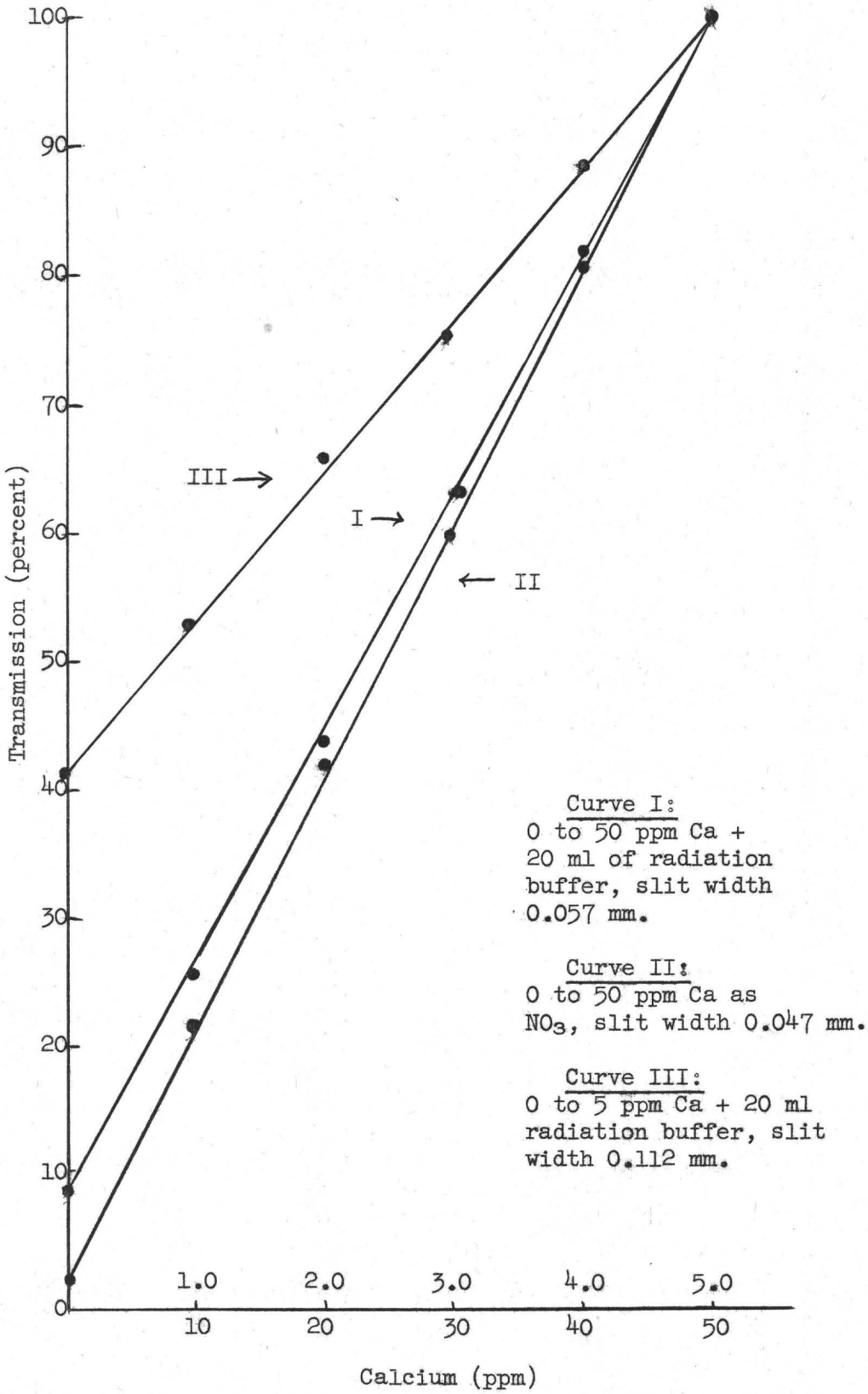

Figure 1.--Standard curves for calcium at 554 mμ.

Interference studies indicated the following concentration limits for the major rock-forming elements:

Constituent	mg/100 ml
Al_2O_3	100
MgO	100
P_2O_5	60
Fe_2O_3	15
Na_2O (no upper limit established)	15
K_2O (no upper limit established)	7
MnO	1.3

Nitric acid and perchloric acid tolerances are 6 percent v/v and 2.5 percent v/v respectively.

On the basis of 100 mg of sample made up to 100 ml as described below the sample can contain 60 percent P_2O_5, 15 percent Fe_2O_3, 15 percent Na_2O, 7 percent K_2O, and 1.3 percent MnO. These tolerances permit the analysis of most phosphate, carbonate, and silicate rocks without changing the procedure. Minor rock-forming elements such as chromium, titanium, vanadium, lithium, and barium, unless present as major constituents, do not interfere.

Table 1 compares the results obtained by the method with other methods on a variety of samples.

Apparatus

A Beckman model DU spectrophotometer with a model 9220 flame attachment and a model 4300 photomultiplier was used with an oxy-hydrogen flame.

Table 1.--Analytical data.

Sample no.	Type of sample	Calcium oxide content (percent)	Calcium oxide found (percent)
NBS 1A	Limestone	41.32 1/	40.6
NBS 56B	Phosphate rock	44.06	43.9, 43.7
NBS 79	Fluorspar	94.83	96.6
NBS 80	Soda-lime glass	4.65	4.65
NBS 81	Glass sand	0.029	0.034
NBS 88	Dolomite	30.49	30.6
NBS 91	Opal glass	10.48	10.6, 10.7
NBS 98	Plastic clay	0.21	0.18
NBS 99	Feldspar	0.36	0.38, 0.38
NBS 102	Silica brick	2.29	2.36
NBS 104	Burned magnesite	3.35	3.42
NBS 120	Phosphate rock	49.62	49.4, 49.4
NBS 128	Soda-lime glass	4.76	4.72, 4.75
USGS W-1	Standard diabase	10.95 2/	11.0
USGS G-1	Standard granite	1.35 2/	1.36
1	Brecciated limestone	50.46 3/	50.0
2	Calcareous clay	4.58	4.65
3	Clayey sand	0.48	0.55
4	Conglomeratic limestone	1.80	1.74
5	Apatite	49.50	48.7, 48.5
6	Phosphate rock	1.96	2.02
7	do.	6.01	5.93
8	do.	1.40	1.45 (av. 8 det.)
9	do.	22.26	21.95 (av. 4 det.)
10	Phosphatic limestone	24.35	24.22
11	Phosphatic clay	0.22	0.23
12	Aluminum phosphate rock 4/	6.9	6.75
13	do.	1.41	1.70 (av. 2 det.)
14	do.	11.9	12.1
15	do.	8.6	8.60
16	do.	1.57	1.68

1/ Certificate values for National Bureau of Standards standard samples.
2/ Average reported value (6).
3/ Simple precipitation as oxalate and volumetric determination with potassium permanganate for samples 1-16.
4/ Samples 12-16 from the aluminum phosphate zone, Bone Valley formation of Pliocene age, Florida, usually containing wavellite, crandallite, quartz, and kaolinite.

Reagents

Hydrofluoric acid, 48 percent.

Nitric acid, (1+1).

Standard calcium solution (1 ml ≡ 1.00 mg Ca). Dissolve 2.498 g of reagent grade calcium carbonate dried at 105° C in 10 ml of (1+1) nitric acid, transfer to a 1-liter volumetric flask, and dilute to mark with water.

Radiation buffer. Weigh the following into a 400-ml beaker: aluminum metal, foil 0.005 inch, 4.000 g; magnesium ribbon, 9.000 g; iron wire, 0.500 g; sodium nitrate, 2.957 g; potassium nitrate, 0.776 g. Cover with a watch glass, add 100 ml of concentrated nitric acid (add additional nitric acid if necessary), and evaporate to dryness. Dissolve the residue in 1200 ml of (1+1) nitric acid and heat to effect solution. Filter through a fine paper if the solution is turbid.

Prepare a standard phosphate solution (1 ml ~ 50 mg phosphorus) by pipetting 22.0 ml of 85 percent phosphoric acid (sp. gr. 1.69) into a 200-ml volumetric flask and diluting to volume with water. Standardize.

The radiation buffer is prepared by adding a volume of the phosphoric acid solution equivalent to 2.50 g phosphorus to the entire mixed-salt solution and diluting to 2 liters in a volumetric flask.

When a 20-ml aliquot of the buffer is diluted to 100 ml it contains 400 ppm aluminum, 250 ppm phosphorus, 900 ppm magnesium, 50 ppm iron, 80 ppm sodium, 30 ppm potassium, and 6 ml of nitric acid.

Calcium standards equivalent to 50, 40, 30, 20, 10, 0 ppm are prepared by pipetting 5.00 ml, 4.00 ml, 3.00 ml, 2.00 ml, 1.00 ml of the standard calcium solution into 100-ml volumetric flasks, adding to each 2.5 ml of

75 percent perchloric acid, 20 ml of the radiation buffer by pipette, and diluting to volume with water.

Procedure

Weight 0.1000 g of sample into a platinum dish, add 5 ml of (1+1) nitric acid, 2.5 ml of 75 percent perchloric acid, and about 5 ml of 47 percent hydrofluoric acid. Evaporate on the steam bath until the first fumes of perchloric acid appear, wash down the sides of the dish with water, and again evaporate to the initial appearance of perchloric acid fumes. Repeat with additional nitric and hydrofluoric acid if necessary. Add about 20 ml of water and digest on the steam bath to effect complete solution. Transfer to a 100-ml volumetric flask, cool, add by pipette 20 ml of the radiation buffer, and dilute to volume with water.

If the sample is expected to contain over 7 percent calcium oxide, make an appropriate dilution before adding the radiation buffer so that the calcium concentration is less than 0.05 mg/ml.

If the sample is expected to be low in calcium, that is, less than 0.50 percent carry a reagent blank along with the sample.

Spectrophotometer settings:

Wavelength - 554 mμ

Sensitivity control - 5 turns from clockwise limit

Selector switch - 0.1

Phototube - blue with 22 megohm resistor

Slit - 0.057 mμ

Hydrogen - 5 psi

Oxygen - 10 psi

Photomultiplier - full sensitivity

Zero suppression - off

Flame photometric procedure

While the 50 ppm calcium solution is aspirating, adjust the wavelength dial to either side of 554 mμ to obtain maximum transmission with a minimum slit width. Adjust the 50-ppm calcium standard to read 100 percent transmission using the slit width knob. After this adjustment has been made, instrument drift is corrected by minor adjustment of the hydrogen gauge regulator. The sample is then analyzed by bracketing between the closest calcium standards. Calculations are based on the assumption that the curve is linear within each 10 ppm increment.

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