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Determination of calcium by atomic-absorption spectrometry in samples dissolved by acid mixtures

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Summary. The effect of lanthanum addition to the fluoboric-boric acid matrix for the determination of calcium by atomic absorption spectrometry has been studied. The samples were decomposed in a pressure vessel. The addition of hydrochloric acid before lanthanum addition in the dissolved samples allowed the use of the air-acetylene flame, which gives more accurate data than the acetylene-nitrous flame and is easier to handle.

Introduction

The dissolution of silicated materials with hydrofluoric acid in a pressure vessel [1–4] is a very practical method for their decomposition. The combination of this decomposition and the element determination by atomic absorption spectrometry is one of the more useful analytical methods. Boric acid is added to complex the hydrofluoric acid and the resulting matrix (fluoboric-boric acid) has been evaluated as a possibly favourable matrix. The medium is attractive because it does not introduce any cationic salts into the sample solution. The addition of lanthanum to enhance the calcium response in the determination of this element by atomic absorption spectrometry, causes a precipitation in the fluoboric-boric acid matrix and it is necessary to determine calcium by nitrous oxide-acetylene flame [3].

In this work a procedure is described to avoid the precipitation, allowing the determination of calcium in the air-acetylene flame after the sample dissolution in a pressure vessel.

Materials and methods

The materials used were two soils (P-1, P-2) and two silicate rocks (SE-3, SE-5) with different calcium content. Two geological standards were used as reference materials, Andesite AGV-1 from Oregon, USA, and granite G-2, from Sullivan Quarry, Bradford, Rhode Island, USA, supplied by the US Geological Survey.

The soil samples were crushed and sieved to 2 mm and subsequently all samples were finely powdered before carrying out the analysis. The method consists of the decomposition of the samples (0.2000 g) by 5 ml of 40% hydrofluoric acid, 0.25 ml of 65% HNO_3 and 0.75 ml of 37% HCl in a PTFE-lined Perkin-Elmer bomb, model "Autoclave 3". The bomb was heated to a temperature of 140°C for 1 h. After the decomposition, 5 g of boric acid was added and warmed at 60°C in a plastic beaker till the sample was dissolved; the solution was then diluted with water to a known volume.

The measurement of calcium was made by atomic absorption spectrometry with a Perkin-Elmer apparatus model 703. The determination was carried out in the decomposed samples without lanthanum oxide addition in the nitrous oxide-acetylene flame and with 1 ml of 37% HCl and 1 ml of 5% lanthanum oxide to 8 ml of sample in the air-acetylene flame.

Mineralogy. The mineralogical composition of the precipitates was determined by X-ray diffraction (XRD) using a Siemens diffractometer model D 500 with CuKα radiation.

Results and discussion

The normal procedure for the determination of calcium by atomic absorption spectrometry in the air-acetylene flame is the addition of lanthanum (as a buffer of ionization) to the decomposed samples. The fluoboric-boric acid matrix has been evaluated as a possibly favourable matrix for the atomic absorption measurements. However, when lanthanum (1 ml of 5% solution) was added to the decomposed samples (9 ml) a white precipitate appeared. The precipitates were isolated and studied by X-ray diffraction in order to determine their composition. The X-ray diffraction patterns corresponding to all white residues were similar and one of them is shown in Fig. 1. The XRD peaks at 3.659, 3.587, 3.229 A etc. indicate that the precipitate is lanthanum fluoride.

The precipitation of LaF_3 must have taken place according to the following processes: Tetrafluoboric acid is obtained by reaction between boric acid added and hydrofluoric acid present in the decomposed samples:

$$H_3BO_3 + 3\,HF \rightleftarrows HBF_3OH + 2\,H_2O \tag{1}$$

$$HBF_3OH + HF \rightleftarrows HBF_4 + H_2O\,. \tag{2}$$

Part of the tetrafluoboric acid is dissociated in solution, yielding F^- by hydrolysis of BF_4^-, which reacts with lanthanum:

$$BF_4^- + 3\,H_2O \rightleftarrows BO_3H_3 + 4\,F^- + 3\,H^+ \tag{3}$$

$$6\,F^- + 6\,H^+ + La_2O_3 \rightleftarrows 2\,F_3La\downarrow + 3\,H_2O\,. \tag{4}$$

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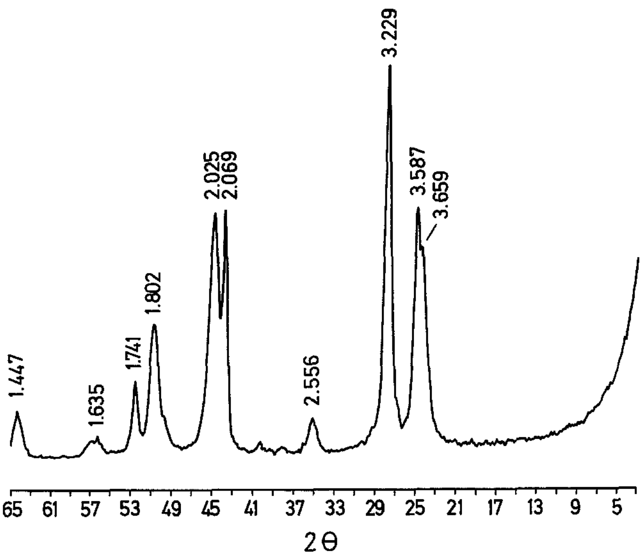

Fig. 1. X-Ray powder diffraction patterns of the precipitate after lanthanum addition to the fluoboric-boric acid matrix

We have determined calcium by the air-acetylene flame in this matrix in order to check the influence of the precipitation on the calcium determination. After removing the precipitate by centrifugation the calcium content was very low. This is in agreement with the disappearance of lanthanum from the medium, which is confirmed because the flame does not have the characteristic green colour when a solution containing this element is aspirated into the atomic absorption spectrometer.

The appearance of the precipitates was attributed at the beginning of the experiment to the low boric acid content. In order to check this assumption, different quantities of this substance were added to the samples before lanthanum addition, but the white precipitates always appeared.

Taking into account the chemical reaction (3), the hydrolysis of BF_4^- should be less favoured in the presence of a high quantity of protons, since the reaction would be shifted towards the left and no F^- ions would remain in the medium. For this reason, different quantities of 37% HCl were added to the samples before lanthanum oxide addition (1 ml) and it was observed that no precipitate appears when 1 ml of acid is added (to 8 ml of decomposed sample), and the calcium determination was possible by the normal method with the air-acetylene flame.

The calcium contents of the different samples determined by means of both kinds of flames are shown in Table 1.

Table 1. Calcium content of samples analysed with the nitrous oxide-acetylene flame and with the air-acetylene flame by the proposed method. The results are reported as w.t.% for the samples dried at 110°C

Sample	by nitrous oxide-acetylene flame			by air-acetylene flame		
	$\bar{X}$	S	C%	$\bar{X}$	S	C%
P-1	5.33	0.29	5.44	5.61	0.08	1.43
P-2	8.26	0.48	5.81	8.75	0.12	1.37
SE-3	1.95	0.12	6.15	2.02	0.03	1.48
SE-5	2.30	0.13	5.65	2.58	0.04	1.55
AGV-1	3.40	0.19	5.59	3.60	0.05	1.39
G-2	1.33	0.08	6.01	1.45	0.02	1.38

$\bar{X}$ = average of 4 analyses; S = standard deviation; C = relative standard deviation

The determinations of this element were carried out in the acetylene-nitrous oxide flame (without addition of lanthanum to the samples) and in the air-acetylene flame with hydrochloric acid plus lanthanum addition.

As the fluoboric-boric acid matrix does not completely eliminate the chemical interference of silicon and aluminium (Lee and Guven [3]), the standard solutions for the determination of calcium were prepared with silicon and aluminium concentration in the same proportions as the samples analysed. The results for the calcium content by lanthanum following hydrochloric acid addition were a little higher than in the other flame. According to the data set out above it is shown that the modification proposed in this paper (addition of HCl before lanthanum), gives more accurate results, allowing the use of the air-acetylene flame, which gives more constant data and is easier to handle.

The method has been checked with two geochemical reference samples, AGV-1 and G-2. The recommended values for these standards are 3.53 and 1.40%, respectively [5].

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