Method for determination of Ba and Sr in natural zeolites by inductively coupled plasma optical emission spectrometry

ICIA
INCDO - INOE 2000
Subsidiary Research Institute for Analytical Instrumentation Cluj-Napoca

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Introduction

Ba and Sr may occur in relatively high content in natural zeolites that can contribute to the zeolites ion-exchange properties. In addition, some soluble compounds of Ba and Sr can be toxic.

Inductively coupled plasma atomic emission spectrometry (ICP-OES) is widely accepted technique for metals determination due to the speed of analysis, multi-elemental capability and wide dynamic range.

The present work was initiated with the aim to develop a simple and reliable microwave-assisted extraction method in combination with ICP-OES technique for the determination of Ba and Sr in zeolite samples. The digestion step involves closed microwave extraction using a mixture of concentrated HNO3, HCl, and HF.

The optimum composition of acid mixture for the best recovery of Ba and Sr was established by using a Certified Reference Material (CRM) BCS-CRM 357/1 soda feldspar with known amounts of Ba and Sr. The figures of merit, such as limit of detection, limit of quantitation and precision of ICP-OES were also estimated. Finally, the proposed method was applied to measure Ba and Sr content in five natural zeolites samples.

Material and methods

An amount of 0.500 g of sample, with particulate size <100 μm, was digested with a mixture of 3 mL HNO3 65%, 9 mL HCl 37%, and 1 - 5 mL HF 40%, for method optimization, in a closed-vessel MWS-3+ microwave system.

Fig. 1. Microwave digestion system, SpeedWave Berghof

Standard solutions for external calibration of ICP-OES were prepared by stepwise **dilution** of a Merck Millipore CertiPur ICP multi-elemental standard solution IV 1000 mg L^{-1}. HNO3 65%, HCl 37%, and HF 40%, purchased from Merck (Darmstadt, Germany) were used for digestion of samples.

For the optimization of digestion procedure and for recovery study a Certified Reference Material CRM BCS-CRM 375/1 soda feldspar from Bureau of Analysed Samples Ltd (United Kingdom) was used. Five natural zeolites samples (Z1–Z5) were collected from a quarry located in Chilioara, Salaj County, Romania. The samples were crushed and further grounded to a fine powder in a tungsten-carbide swing mill.

Analyses were carried out using a dual viewing inductively coupled plasma optical emission spectrometer Optima 5300DV (Perkin Elmer, USA). 7-point linear calibration curves over the range 0 – 2 mg L^{-1} element were plotted.

RESULTS and DISCUSSION

Optimization of microwave-assisted acid digestion procedure

The ratio of mineral acids used for digestion may influence the recovery rate. In order to evaluate this factor for the digestion HCl and HF were used. The ratio between HNO3 and HCl was kept at 1:3 (v/v), as in aqua regia mixture, but the volume of concentrated HF was varied, in order to have the following HNO3:HCl:HF ratios: 3:9:1 (v/v/v), 3:9:2 (v/v/v), 3:9:3 (v/v/v), 3:9:4 (v/v/v), 3:9:5 (v/v/v). The applied digestion program was similar for all the experiments. The CRM BCS-CRM 375/1 soda feldspar with known amounts of Ba and Sr was used to evaluate the recovery.

At the end of each microwave extraction process, the sample digest was diluted to required volume with ultrapure water for subsequent determination of Ba and Sr by ICP-OES. The extraction efficiency was evaluated by recovery of each analyte. Three replicates were carried-out for this assay, with an average standard deviation of repeatability of 5%. The results are illustrated in Figure 2.

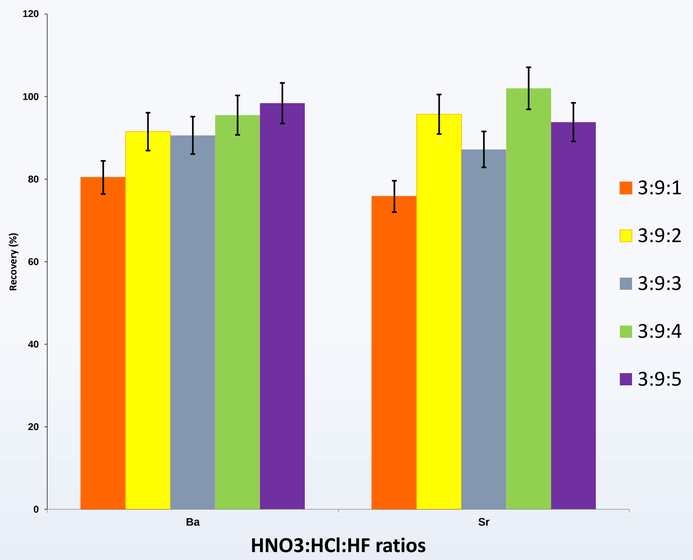

Fig. 2. Influence of HNO3:HCl:HF ratios on Ba and Sr recovery (%) from CRM BCS-CRM 357/1 soda feldspar following microwave-assisted digestion. Error bars with CI values are indicated

The recovery of Ba ranged between 80.4 – 98.4 %, with an increase from the ratio HNO3:HCl:HF of 3:9:1 (v/v/v) to the ratio of 3:9:5 (v/v/v). In case of Sr, for the ratio HNO3:HCl:HF of 3:9:1 (v/v/v), the recovery rate was of 75.8 %, below 80%, which is an unsatisfactory result, while for the increased HF content, the recovery was in all cases in the range of 80-120 %. Consequently, it was considered that for the quantitative extraction of Ba and Sr from 0.500 g of sample, the use 3 mL of HNO3 65% (w/w), 9 mL HCl 37 % (w/w) and 2 mL HF 40 % (w/w) is a suitable digestion method.

Figures of merit

The LODs for both elements were calculated using the 3sy/x/m criterion where sy/x is the residual standard deviation of the calibration curve and m the slope of the calibration curve. LoQs were calculated as three times the LoDs.

$$LoD = (3\ sy/x - y) / m$$

y is the intercept of the calibration curve

The obtained LoDs were of 0.008 mg L^{-1} for Ba and 0.006 mg L^{-1} for Sr. Considering the digestion procedure, the calculated LoQs in the solid sample are of 5.0 mg kg^{-1} for Ba and 3.8 mg kg^{-1} for Sr.

The characteristics of the calibration curves for the two elements obtained by ICP-OES are presented in Table 1.

Precision was assessed in term of repeatability for the 6 parallel measurements on a zeolite sample.

Table 1. Characteristics of calibration curves

Element	Intercept (a)	Slope (b)	PG	Correlation coefficient
Ba	235	18830	3.72	0.9999
Sr	230077	12069102	7.32	0.9999

The trueness was evaluated from the recovery study using a CRM (BCS-CRM 375/1 soda feldspar) with indicative values for Ba and Sr content. The calculated recoveries are showed in Table 2. The The measured concentrations of Ba and Sr in real zeolite samples are presented in Table 3.

Table 2. Recovery study using BCS-CRM 375/1 soda feldspar analysis

Components	Indicative Values μg g^{-1}	Average values ± CI μg g^{-1}	Recovery (%)
Ba	95	90.1 ± 11.1	95
Sr	101	92.5 ± 9.6	92

Table 3. Ba and Sr concentrations (mg kg-1) in zeolite samples

Sample	Ba mg kg^{-1}	Sr mg kg^{-1}
Z1	580 ± 88	170 ± 23
Z2	504 ± 77	115 ± 15
Z3	431 ± 66	134 ± 18
Z4	522 ± 79	167 ± 22
Z5	422 ± 64	183 ± 24

CONCLUSION

A ratio of HNO3:HCl:HF of 3:9:2 (v/v) with a total time of digestion of 40 min was found to give recoveries in the target values of 80-120%) for Ba and Sr from a CRM with silicate matrix. The digestion method based on microwave-assisted wet digestion is simple, faster, and it requires less chemicals than other digestion methods like that based on fusion with salts. The obtained LOQs in ICP-OES allowed the quantification of concentrations higher than 5.0 mg kg^{-1} for Ba and 3.8 mg kg^{-1} for Sr.

Acknoledgement

This paper was supported by the Ministry of Research and Innovation through the Competitiveness Operational Programme of the Ministry of European Funds through the Contract No. 7/01.09.2016, MY SMIS 105654.

"Agriculture and Food - current and future challenges, AGRIFA"
8rd of October 2021, Cluj-Napoca