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## OPTIMAL METHOD FOR PREPARATION OF SILICATE ROCK SAMPLES FOR ANALYTICAL PURPOSES

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**Ključne riječi:** otapanje silikatne stijene, mikroelementi, FAAS

### Abstract

The purpose of this study was to determine an optimal dissolution method for silicate rock samples for further analytical purposes. Analytical FAAS method of determining cobalt, chromium, copper, nickel, lead and zinc content in gabbro sample and geochemical standard AGV-1 has been applied for verification. Dissolution in mixtures of various inorganic acids has been tested, as well as  $\text{Na}_2\text{CO}_3$  fusion technique. The results obtained by different methods have been compared and dissolution in the mixture of  $\text{HNO}_3 + \text{HF}$  has been recommended as optimal.

### Sažetak

Svrha rada bila je utvrđivanje optimalnog postupka otapanja uzoraka silikatne stijene za dalje analitičke svrhe. Za verifikaciju je primijenjena analitička metoda FAAS određivanja udjela kobalta, kroma, bakra, nikla, olova i cinka u uzorku gabra i u geokemijskom standardu AGV-1. Istraženo je otapanje u smjesama različitih anorganskih kiselina kao i taljenje s  $\text{Na}_2\text{CO}_3$ . Uspoređeni su rezultati dobiveni različitim postupcima te se kao optimalni postupak preporuča otapanje u smjesi  $\text{HNO}_3 + \text{HF}$ .

### Introduction

Determination of chemical composition, of both major and trace elements is very important in the study of different geological materials. For most of the analytical methods, the sample should be dissolved, which is a difficult part of the procedure especially in the case of hardly soluble silicate rocks, as well as of insoluble residues of carbonate rocks, bauxites and soils.

Trace elements occupy corresponding sites in crystal lattices of silicate minerals. Their analyses are particularly useful in petrogenetic studies of igneous rocks providing constrains for different magma types and their tectonic settings.

The flame atomic absorption spectrophotometry (FAAS) is a relatively quick method for determining the trace elements content in rocks. Dissolution of rock sample destroys crystal lattices, extracting trace elements from them and makes their content accessible for determination.

Based on numerous measurements of cobalt, chromium, copper, nickel, lead and zinc content in several differently prepared solutions of the same silicate rock – gabbro, this study suggests the optimal dissolution method.

### Previous investigations

In a few published papers, that considered the problems of silicate rocks dissolution, the two essentially different procedures were suggested (Doležal et al., 1968). One is fusion with different salts,  $\text{Na}_2\text{CO}_3$ ,  $\text{LiBO}_2$ , as well as with  $\text{KHSO}_4$ ,  $\text{Na}_2\text{O}_2$  and  $\text{KHF}_2$  (Srivastava et al., 2003), and the other is dissolution in one of the inorganic acids ( $\text{HF}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$ ,  $\text{HCl}$ ), or in their mixtures using numerous combinations (Kalembkiewicz & Sitarz-Palczak, 2001). Both methods are equal in terms of their advantages and disadvantages (Castillo et al., 1988). Various composition of geological samples and refractory nature of their numerous parts make their analysis difficult and time-consuming (Satyanarayana & Nayeem, 1993). In the case when the analytical method FAAS is not used for determination of silica content in a rock sample, it is preferable to apply dissolution in the mixture of inorganic acids (Belt, 1964; Trent & Slavin, 1964; Billings & Adams, 1964; Langmyhr & Paus, 1968; Beccaluva & Venturelli, 1971; Rantala & Loring, 1975; Roy & Roychowdhury, 2002; Satyanarayana & Nayeem, 2002) because the solution obtained by fusion has a dense matrix, i.e. high concentration of salts which causes disturbances during measurement. If there is a small amount of insoluble residue left after dissolution in the

inorganic acids, it can be transformed into solution using small amount of flux, mostly  $\text{Na}_2\text{CO}_3$ . That solution has no high salt content.

### Experimental part

A sample of gabbro was used for the study, pretreated in such a manner that the parts with signs of weathering and macroscopically visible accretions of secondary minerals in the veins, amygdules or nests were removed.

As trace elements are heterogeneously distributed in the rock, due to their incorporation in the specific minerals, homogenization was a necessary method to obtain a representative sample. The sample was crushed and, after quartering, pulverized in the amount approximately fiftyfold greater than required for the analysis. Pulverizing was done in agate mill in order to prevent contamination of the samples with the same elements contained in iron mills as were the analyzed ones.

Pulverized gabbro sample and geochemical standard AGV-1 sample were dissolved by  $\text{Na}_2\text{CO}_3$  fusion technique and by dissolution in following mixtures of inorganic acids:  $\text{HNO}_3 + \text{HF}$ ,  $\text{H}_2\text{SO}_4 + \text{HF}$  and  $\text{HClO}_4 + \text{HF}$ .

The measurements of cobalt, chromium, copper, nickel, lead and zinc content were performed using flame atomic absorption spectrophotometer, Pye Unicam SP 9.

#### *$\text{Na}_2\text{CO}_3$ fusion technique*

$\text{Na}_2\text{CO}_3$  fusion technique was modified after Trent & Slavín (1964). Sample powder was mixed with sixfold amount of  $\text{Na}_2\text{CO}_3$  in the platinum crucible, with the addition of few grains of  $\text{KClO}_3$ . Melt obtained by ignition in a muffle furnace was dissolved in diluted HCl. Obtained solution had high salt concentration which caused disturbances in measurement. After bringing the solution into flame, salt crystallized on the burner slot, which resulted in high background and irregular peaks. Achieving zero after injection of distilled water into flame required longer time, due to memory effect. The work had to be interrupted more frequently due to the cleaning of the burner slot. In addition, impurities of the used chemical,  $\text{Na}_2\text{CO}_3$ , containing 12 ppm of cobalt, 8 ppm of copper and 13 ppm of nickel, made the obtained trace element contents unreliable. Due to the unreliable measurement results, contents of elements in the solution obtained by fusion are not listed in this paper.

#### *Dissolution in the mixtures of inorganic acids*

***Dissolution in the mixture of  $\text{HNO}_3 + \text{HF}$***  was modified after Billings & Adams (1964). To a wetted sample (2 g) in the platinum dish 20 ml of concentrated (40%) HF was added. After digestion for approximately 30 minutes the content was evaporated to dryness on the water-bath. Then it was re-evaporated to dryness after the addition of 5 ml of HF. 20 ml of concentrated (65%)

$\text{HNO}_3$  was added to the mixture. After evaporation to dryness on the water-bath, additional 10 ml of  $\text{HNO}_3$  was added and re-evaporated to dryness. 20 ml of 8%  $\text{HNO}_3$  was added to the residue. After approximately 30 minutes of digestion the mixture was filtered off (blue ribbon) into the 50 ml flask and filled up to the mark with 8%  $\text{HNO}_3$ .

***Dissolution in the mixture of  $\text{H}_2\text{SO}_4 + \text{HF}$***  was modified after Trent & Slavín (1964). To the wetted sample (2 g) in the platinum dish few drops of concentrated (96%)  $\text{H}_2\text{SO}_4$  and 20 ml concentrated (40%) HF were added. After approximately 30 minutes digestion the content was evaporated almost to dryness using water-bath. Additional 10 ml of HF was added and the mixture re-evaporated to dryness on the water-bath and fumed on the burner. 10 ml of 18% HCl was added to the residue, the mixture was digested and filtered off (blue ribbon) into the 50 ml flask and filled up to the mark with 8%  $\text{HNO}_3$  solution.

***Dissolution in the mixture of  $\text{HClO}_4 + \text{HF}$***  was modified after Belt (1964). To the wetted sample (2 g) in the platinum dish 20 ml of concentrated (40%) HF was added. After approximately 30 minutes digestion 2 ml of concentrated (60%)  $\text{HClO}_4$  was added and the content was evaporated almost to dryness. The procedure was repeated with 10 ml of HF and 2 ml  $\text{HClO}_4$ . To the wet residue 10 ml of saturated solution of  $\text{H}_3\text{BO}_3$  and 2 ml  $\text{HClO}_4$  was added and the mixture was evaporated to dryness. The residue was dissolved in 2% HCl, transferred into a 50 ml flask and filled up to the mark.

#### *Measurement of trace element contents by FAAS method*

For cobalt and nickel determination Merck standards were used. For chromium, i.e. copper determination standards were prepared dissolving dried  $\text{K}_2\text{CrO}_4$  salt, i.e.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in water. Standards for lead, i.e. zinc determination were prepared dissolving lead metal in 2M  $\text{HNO}_3$ , i.e. zinc metal in 5N HCl.

For samples treated with all three solution preparation methods the content of aforementioned trace elements was determined and the differences of the results were discussed.

Precision of the results has been verified by means of USGS geochemical standard AGV-1 (Flanagan, 1969). It is a pulverized andesite whose composition was determined in numerous laboratories by different analytical methods providing a recommended value for each element.

For the purposes of accuracy of measurements, solutions of gabbro sample were prepared for each method twice, and AGV-1 standard once. Content of each trace element in each solution was measured five times.

Blanks were prepared and results accordingly corrected.

## Results and discussion

### Accuracy of determination

Table 1 shows mean value obtained by measuring contents of each trace element and variation coefficient for every dissolution method separately.

Accuracy of measurement was acceptable. For all the analysed trace elements in gabbro sample variation coefficient was mostly under 10%. In the solution prepared by  $H_2SO_4 + HF$  mixture chromium and nickel contents were lower compared to other methods thus indicating a lower extraction of chromium and nickel. For trace elements in AGV-1 geochemical standard variation coefficients were mostly under 10%, except for chromium, due to its low content close to detection limit. Therefore, chromium data are not accurate.

### Precision of determination

Deviation from recommended value of trace element content in AGV-1 geochemical standard (Govindaraju, 1989) was calculated for all the methods of dissolution and shown in table 2.

Precision of cobalt, copper, nickel and lead content determination was acceptable. Their content values obtained in this paper fit into the mentioned ranges. Great deviation from recommended content value for chromium might be caused by its low content in the solution.

Content values for zinc are lower than recommended. Recommended value for zinc content is chosen within a very wide range of content values, and deviation obtained in this work is approximately 15% of lower range limit.

### Efficiency of sample dissolution in mixtures of various inorganic acids

The lowest deviation of cobalt, copper and nickel content in the AGV-1 geochemical standard compared to the recommended values was obtained by using mixture of  $HNO_3 + HF$  (table 2). Deviations were larger using other two methods of sample dissolution, particularly for cobalt and nickel, but due to their low content in standard, all values obtained were acceptable. Deviation for lead was the largest for sample dissolved in the mixture of  $HNO_3 + HF$ . However, considering the fact that lead contents for all three methods of sample preparation were approximately equal, results obtained could have been considered as satisfactory. Results for zinc were uniform.

Table 3 shows variation coefficients for all three methods of dissolution taken together for trace element content in gabbro (30 measurements in total) and in AGV-1 geochemical standard (15 measurements in total).

Variation coefficients, except for chromium in AGV-1 geochemical standard, were acceptable, which means that, considered trace element contents, quantitative data do not significantly differ for silicate sample dissolution in mixtures of various inorganic acids.

Table 1. Trace element content values x (ppm) and variation coefficient V (%) of gabbro and of AGV-1 geochemical standard

Tablica 1. Udio mikroelemenata x (ppm) i koeficijent varijacije V (%) u gabru i u geokemijskom standardu AGV-1

Element	Gabbro						AGV-1					
	$HNO_3+HF$		$H_2SO_4+HF$		$HClO_4+HF$		$HNO_3+HF$		$H_2SO_4+HF$		$HClO_4+HF$	
	x	V	x	V	x	V	x	V	x	V	x	V
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
Co	27	7	22	8	23	8	15	7	13	9	14	9
Cr	1229	1	868	2	1241	2	5	24	1	46	2	10
Cu	14	10	13	8	13	9	55	4	53	6	54	4
Ni	158	2	135	3	151	4	14	7	12	10	12	11
Pb	10	9	11	8	13	7	42	7	36	8	38	6
Zn	16	8	19	7	18	7	54	5	53	6	53	6

Table 2. Range of trace element contents in AGV-1 geochemical standard and deviation from recommended value of trace element content for three methods of dissolution (1\* – recommended value of the content after Govindaraju, 1989; 2\* – range of content values after Flanagan, 1969; 3\* – mean value of contents obtained by measurement; 4\* – deviation from recommended values)

Tablica 2. Raspon udjela mikroelemenata u geokemijskom standardu AGV-1 i odstupanje od preporučene vrijednosti za tri načina otapanja (1\* – preporučena vrijednost udjela prema Govindaraju, 1989; 2\* – raspon vrijednosti udjela prema Flanagan, 1969; 3\* – srednja vrijednost udjela dobivenih mjerenjem; 4\* – odstupanje od preporučene vrijednosti)

Element	1* ppm	2* ppm	HNO <sub>3</sub> + HF		H <sub>2</sub> SO <sub>4</sub> + HF		HClO <sub>4</sub> + HF	
			3*	4*	3*	4*	3*	4*
			ppm	%	ppm	%	ppm	%
Co	15,3	10 – 30	15	2	13	15	14	9
Cr	10,1	8 – 45	5	51	1	90	2	80
Cu	60	52 – 83	55	8	53	12	54	10
Ni	16	11 – 27	14	13	12	25	12	25
Pb	36	18 – 48	42	17	36	0	38	6
Zn	88	64 – 304	54	39	53	40	53	40

Table 3. Mean trace element content values  $\bar{x}$  (ppm) and variation coefficient  $V$  (%) in gabbro and AGV-1 geochemical standard for all three methods of dissolution taken together

Tablica 3. Srednja vrijednost udjela mikroelemenata  $\bar{x}$  (ppm) i koeficijent varijacije  $V$  (%) u gabru i u geokemijskom standardu AGV-1 za sva tri načina otapanja zajedno

Element	Gabbro		AGV-1	
	$\bar{x}$ ppm	$V$ %	$\bar{x}$ ppm	$V$ %
Co	24	12	14	10
Cr	1113	16	2,8	62
Cu	17,3	10	54	5
Ni	148	7	12,7	13
Pb	11,4	14	39	11
Zn	17,5	10	53,5	6

Although the ratios of solvent and sample, as well as dissolution time were equal for both gabbro sample and AGV-1 geochemical standard sample, variation coefficients were usually higher for trace element content determination in gabbro than in AGV-1. This is probably due to a higher content of refractory, hardly soluble ferromagnesian minerals in gabbro than in andesite.

Those minerals contain most of considered trace elements, hence incomplete disintegration of their crystal lattices might have caused the greater variation of the results. High chromium variation coefficient in the sample of AGV-1 geochemical standard is interpreted as the result of its aforementioned low content.

## Conclusion

From quantitative results obtained by measurement of trace element content using FAAS analytical method in the solutions of silicate rock samples, previously dissolved in a various mixtures of inorganic acids, it can be concluded that all three methods considered provide satisfactory precision. However, due to lower extraction efficiency of some trace elements by H<sub>2</sub>SO<sub>4</sub> + HF dissolution and time-consuming evaporation of H<sub>2</sub>SO<sub>4</sub> from one point of view, and explosive properties of concentrated HClO<sub>4</sub>, dissolution in the mixture of HNO<sub>3</sub> + HF is recommended. Fusion of the sample should be avoided due to high salt concentration in solution that causes disturbances in measurement like high background and irregular peaks making the obtained results unreliable.

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