

## **Semimicroanalysis of Silicate Minerals by Means of XRF Thin Layer Method. Determination of Selected Chromatic Elements – V, Cr, Mn, Fe, Co**

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**Key words:** minerals, X-ray fluorescence analysis, thin layer method

50 mg of a powdered silicate mineral is spread on a substrate (filter paper glued on to glass or teflon by means of two-sided adhesive tape), dissolved in a concentrated hydrofluoric acid and dried under an infrared heater; a sample is then protected with a Mylar film.

Apparatus parameters: a sequence wadedispersive X-ray spectrometer; an X-ray tube with a Mo anode; 50 kV; 40 mA;  $K_{\alpha}$  lines; LiF 200; flow counter; vacuum measurements; rotation of the sample; 100 s counting time for V, Cr, Mn, Co and 40 s or 100 s for Fe, according to the concentration; synthetic standards for calibration.

Statistical parameters: detection limits for 50 mg samples: V (3–6 ppm), Cr (3–6 ppm), Mn (25 ppm), Fe (4–5 ppm), Co (2–7 ppm).

50 mg rozdrobnionego minerału krzemianowego nanosi się na podłoże (bibuła przyklejona na szkło lub teflon za pomocą taśmy obustronnie przyklepnej), roztwarza w stężonym kwasie fluorowodorowym i suszy pod promiennikiem IR, próbkę zabezpiecza folią mylarową.

Parametry instrumentalne: spektrometr sekwencyjny falowodispersyjny, lampa rentgenowska z anodą Mo, 50 kV, 40 mA, linie analityczne  $K_{\alpha}$ , LiF 200, licznik przepływowy, pomiar w próżni, rotacja próbki, czas zliczania impulsów 100 s dla V, Cr, Mn, Co i 40 s lub 100 s dla Fe w zależności od stężenia, wykorzystanie syntetycznych wzorców do kalibracji.

Parametry statystyczne: granice wykrywalności dla próbek o masie 50 mg: V (3–6 ppm), Cr (3–6 ppm), Mn (2–5 ppm), Fe (4–5 ppm), Co (2–7 ppm).

The chemical composition of minerals is most often analyzed by classical methods. These methods are time-consuming (multielement analysis), difficult from

practical point of view, most often they require dissolution of the sample by melting. To determine small or trace amounts of elements preconcentration of traces or their preliminary separation, is necessary depending on the method used for quantitative determination [1–7]. The use of XRF methods [3,5] creates difficulties in determination of small and trace concentrations of elements (in the ppm range) as the need of melting the sample (so-called borax bead) results in additional dilution of the sample (e.g. 1:10), while powder samples, pressed into a tablet with or without binder, generally give poor reproducibility of the analytical cycle. In both technologies usually minimum 1 g of a sample is used per the analysis.

As a possibility of obtaining precious stones, among others based on  $\text{SiO}_2$  is of increasing interest, a necessity has appeared [8] of determination, of chromatic elements that decide on the colour of the product, these elements include, among others, V, Cr, Mn, Fe, and Co.

The authors of this paper suggest that a significant improvement of a quick, multielement analysis of minerals on a  $\text{SiO}_2$  base can be achieved by the application of a thin layer method in an XRF wavedispersive semimicroanalysis, that minimizes the interelement influence (the effect of intensification and attenuation). With respect to difficulties in creation of permanent and reproducible “thin layers” for powder materials we have decided to examine a possibility of a “thin sample” preparation by a direct dissolution of the investigated material (decomposition) on a appropriate selected substrate; a sample of 50 mg was used for multielement analysis.

The investigations were carried out using in the analysis the following minerals:

spodumenes	$\text{LiAl}[\text{Si}_2\text{O}_6]$ – kunzite and two hiddenites,
diopside	$\text{CaMg}[\text{Si}_2\text{O}_6]$ ,
grossularite (garnet)	$\text{Ca}_3\text{Al}_2[\text{SiO}_4]_2$ ,
apophyllites	$\text{KCa}_4(\text{F,OH})(\text{Si}_4\text{O}_{10})_2 \cdot 8\text{H}_2\text{O}$ – colourless, greenish and pink varieties.

In addition two rock reference materials issued by the State Geological Institute, Warsaw, *i.e.* GM\* granite, and KH\* limestone – that differs in composition from other materials (small  $\text{SiO}_2$  content) were also analysed.

Table 1 gives the chemical composition of the matrix of analyzed minerals and reference materials.

**Table 1.** The chemical composition of the matrix of the examined minerals and reference materials (RM)

Minerals	$\text{SiO}_2$	CaO	$\text{Al}_2\text{O}_3$	MgO	$\text{Li}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	FeO	$\text{Fe}_2\text{O}_3$	$\text{TiO}_2$
Spodumenes	65%		27%		8%					
Granite (RM)	73.4%	1.07%	13.5%	0.37%		3.78%	4.76%		2.01%	0.212%
Diopside	55%	26%		19%						
Grossularite (garnet)	41%	35%	17%						7%	
Limestone (RM)	8.60%	47.8%	2.39%	0.74%			0.41%		0.92%	0.130%
Apophyllites	25%	53%					5%			

## EXPERIMENTAL

### Apparatus and instrument setting

Wavedispersive sequential spectrometer. Excitation: an X-ray tube with a Mo anode, 50 kV, 40 mA. LiF 200 analyzing crystal; fine collimator; flow counter; vacuum; rotation of the sample.

Detection time: for V, Cr, Mn, Co – 100 s  
for Fe – 40 or 100 s, depending on the concentration.

Analytical lines  $K_{\alpha}$ :

V 0.2505 nm

Cr 0.2291 nm

Mn 0.2103 nm

Fe 0.1937 nm

Co 0.1791 nm

### Substrate for the samples

An analytical filter paper ( $\varnothing$  25 mm) glued onto a plastic disc ( $\varnothing$  50 mm) or on a glass plate (45×26×3 mm) using a two-sided adhesive tape.

### Preparation of samples

**Real samples:** 50 mg of powdered silicate mineral (the grain size below 0.06 mm) is deposited on prepared substrate, decomposed by repeated addition of concentrated hydrofluoric acid and heating under an infrared lamp; the sample is then protected with a Mylar film.

**Synthetic samples:** Matrix elements (see Table 1) are deposited on the substrate (except of  $\text{SiO}_2$ ), in the form of chlorides by means of a 0.100 ml pipette and dried under the infrared lamp. Then, on the substrate prepared in this way, solutions of the metals being determined (V, Cr, Mn, Fe, Co) are deposited by means of a pipette or micropipette and dried under an infrared lamp. Finally  $\text{SiO}_2$  is deposited, dissolved in the hydrofluoric acid, dried and protected with a Mylar film. The flow sheet the analytical procedure is presented in Fig. 1.

## RESULTS AND DISCUSSIONS

In the technique of thin samples the secondary radiation originates from the whole mass of the sample and the measured intensity of fluorescence radiation for the given element is proportional to its absolute mass. To be within the range of the thin layer method the thickness of the examined material must be smaller than the effective thickness  $d_{\max}$  (the sample thickness participating in 99.9% of fluorescent radiation emission that can be roughly determined on the basis of the formula:  $d_{\max} = 4.6/\mu_1$  [5]). This condition had to be met in the present paper. To calculate the thickness of the analytical layer it was necessary to determine the composition of minerals after the process of digesting with the hydrofluoric acid. The results of appropriate calculations are given in Table 2. Calculations were performed on the basis of the composition of the analyzed material (Table 1) assuming that the total amount of silicon is removed from the sample in the form of silicon tetrafluoride. Mean attenuation coefficients calculated for individual minerals and analytical lines are given in Table 3 [9]. Densities of the investigated materials (Table 4), calculated as weighted averages of fluorides densities, were used to calculate mean linear attenu-

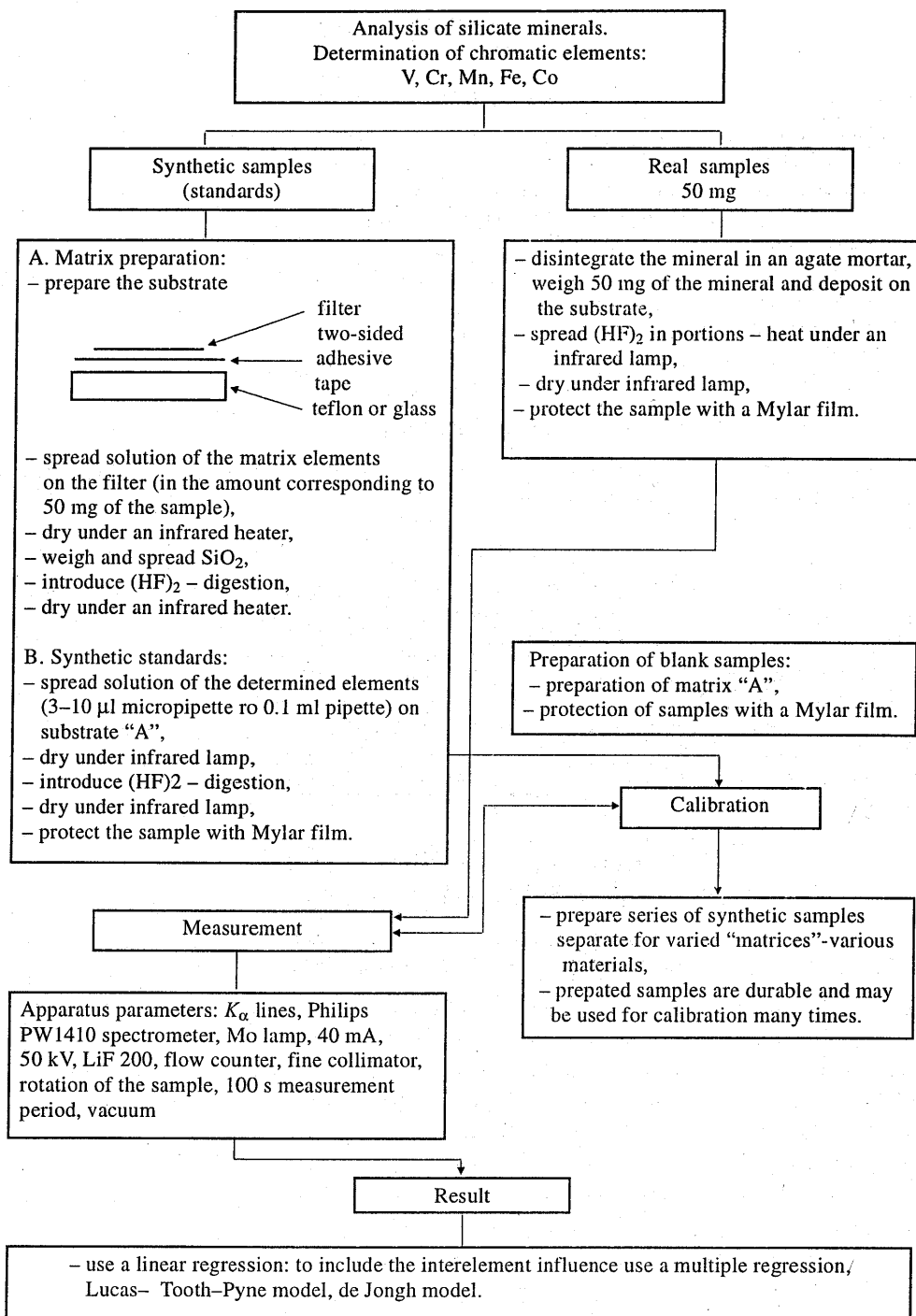


Figure 1. The flow shat of the analytical procedure

ation coefficients (Table 5). To check whether all the mass of the sample is included in the analysis the thickness of samples was calculated after digestion with the hydrofluoric acid. In all the performed determinations the mass of the sample taken for analysis was constant and amounted to 50 mg. The analytical thickness of the sample was calculated according to the formula:

$$d_{\text{sample}} = m_{\text{sample}} / \rho \pi r^2$$

where  $m_{\text{sample}}$  denotes the mass of the sample after the process of digestion with  $(\text{HF})_2$  (Table 4),  $\rho$  is the density of the sample (Table 4), and  $r$  – the radius of the sample ( $\approx 1$  cm).

**Table 2.** Theoretical compositions of minerals after the process of digestion with the hydrofluoric acid  $(\text{HF})_2$

Minerals	CaF <sub>2</sub>	AlF <sub>3</sub>	MgF <sub>2</sub>	LiF	NaF	KF	FeF <sub>2</sub>	FeF <sub>3</sub>
Spodumenes		76%		24%				
Granite (RM)	4%	59%			11%	16%		8%
Diopside	56%		44%					
Grossularite (garnet)	59%	33%						7%
Limestone (RM)	94%	5%						
Apophyllites	92%					8%		

**Table 3.** Mean attenuation coefficients  $\mu_m$  [ $\text{cm}^2 \text{g}^{-1}$ ] for the analyzed materials after the process of digestion with  $(\text{HF})_2$

Minerals	$K_{\alpha V}$	$K_{\alpha Cr}$	$K_{\alpha Mn}$	$K_{\alpha Fe}$	$K_{\alpha Co}$
Spodumenes	94	73	58	45	36
Granite (RM)	156	122	96	77	61
Diopside	231	181	144	115	93
Grossularite (garnet)	242	190	150	121	97
Limestone (RM)	321	252	201	161	130
Apophyllites	336	265	210	169	137

**Table 4.** Calculated densities, masses and thicknesses of samples (50 mg) after the process of digestion with  $(\text{HF})_2$

Minerals	$\rho$ , $\text{g/cm}^3$	$m_{\text{sample}}$ , g	$d_{\text{sample}} = m_{\text{sample}} / \rho \pi r^2$ cm
Spodumenes	2.9	0.029	0.003
Granite (RM)	2.9	0.019	0.002
Diopside	3.1	0.033	0.003
Grossularite (garnet)	3.1	0.043	0.004
Limestone (RM)	3.1	0.037	0.004
Apophyllites	3.1	0.040	0.004

**Table 5.** Mean linear X-ray attenuation coefficient  $\mu_1 = \mu_m \rho$  [ $\text{cm}^{-1}$ ]

Minerals	$K_{\alpha}\text{V}$	$K_{\alpha}\text{Cr}$	$K_{\alpha}\text{Mn}$	$K_{\alpha}\text{Fe}$	$K_{\alpha}\text{Co}$
Spodumenes	271	210	167	130	104
Granite (RM)	452	354	278	223	177
Diopside	716	561	446	357	288
Grossularite (garnet)	753	591	467	376	302
Limestone (RM)	1008	791	631	506	408
Apophyllites	1048	827	655	527	427

The effective thicknesses characteristic for each investigated material and determined element are shown in Table 6. From Tables 4 and 6 it results that the analytical thicknesses of samples are smaller than or equal to the effective thickness. However, it should be noted that the surface of the sample is practically more developed, hence "sample thicknesses" are smaller. In practice there is a possibility of using a substrate providing a larger surface of the sample, but provided that it will be covered by the X-ray beam. In this paper the size of the filter (25 mm) was a compromise between the area covered by the X-rays and the distribution of 50 mg of the sample.

**Table 6.** The effective thickness  $d_{\text{max}} = 4.6/\mu_1$  [cm]

Minerals	$K_{\alpha}\text{V}$	$K_{\alpha}\text{Cr}$	$K_{\alpha}\text{Mn}$	$K_{\alpha}\text{Fe}$	$K_{\alpha}\text{Co}$
Spodumenes	0.017	0.022	0.028	0.035	0.044
Granite (RM)	0.010	0.013	0.017	0.021	0.026
Diopside	0.006	0.008	0.010	0.013	0.016
Grossularite (garnet)	0.006	0.008	0.010	0.012	0.015
Limestone (RM)	0.005	0.006	0.007	0.009	0.011
Apophyllites	0.004	0.006	0.007	0.009	0.011

To determine the characteristic parameter for each method, that is the detection limit, the Kaiser criterion has been used, *i.e.* for the detection limit the signal must be greater than the background by three standard deviations of the background intensity [10].

Detection limits given in Table 7 have been calculated on the basis of measurements for synthetic samples, each time for three blank samples and three samples containing 0.1% of the determined metals. The obtained values of detection limits allow for determination of elements already at the trace level, *i.e.* the order of a few or a dozen or so ppm (at the original sample weight equal to 50 mg). This has a significant importance for the determination of chromatic elements that occur most often at a trace or impurity level.

Table 8 shows sensitivities corresponding to concentrations *ca.* 0.1% (1000 ppm), determined on the basis of measurements for three blank samples and three samples containing 0.1% of the determined metals. The change of the concentration corresponding to the value of one standard deviation of the number of counts ( $S = \sqrt{N_{\text{imp}}}$ ) was assumed as sensitivity – a real, measurable value, because the sensitivity defined in this way means the capability of differentiation of two close concentrations of the given element.

**Table 7.** Detection limits  $C_0$  [ppm] of determined metals in the analyzed minerals and rocks – 50 mg weighed samples ( $3S_{\text{background}}$  criterion)

Minerals	V	Cr	Mn	Fe	Co
Spodumenes	4	3	2	4	2
Granite (RM)	3	*	4	5	*
Diopside	*	5	3	5	*
Grossularite (garnet)	6	6	5	5	7
Limestone (RM)	3	*	5	*	*
Apophyllites	4	*	4	*	*

\*Detection limits have been calculated only for those elements that were found as a result of qualitative XRF analysis.

**Table 8.** The sensitivity of the method as the change of the concentration corresponding to one standard deviation of the peak intensity for the concentration of 0.1% of the metal (1000 ppm)

Minerals	V, ppm	Cr, ppm	Mn, ppm	Fe, ppm	Co, ppm
Spodumenes	*	*	2.8	4.2	*
Granite (RM)	3.7	*	3.0	5.7	*
Diopside	*	5.0	3.3	7.2	*
Grossularite (garnet)	5.7	4.5	4.1	8.4	3.3
Limestone (RM)	5.3	*	3.6	*	*
Apophyllites	5.3	*	3.6	*	*

\*The sensitivity of the method has been calculated only for those elements that were found as a result of qualitative XRF analysis.

Two series of synthetic samples (standards) were used in the investigations, a separate one for each material, with a close composition of the matrix. During preparation the addition of  $\text{SiO}_2$  was taken into account, despite the fact that later on it is removed in the form of silicon tetrafluoride during the process of digestion in the hydrofluoric acid. In a series each standard was prepared twice and for each of them three measurements were performed. Results after averaging were used to determine regression relationships. During preparation of synthetic samples only those elements were taken into account that were identified during qualitative XRF analysis. The numbers and concentration ranges of respective standards were follows: spodumenes – 2×4 standards Mn(0.005–0.050%), Fe(0.005–0.050%); granite – 2×5 standards V(0.005–0.100%), Mn(0.005–0.100%), Fe(0.100–2.000%); diopside – 2×8 standards Cr(0.050–1.000%), Mn(0.050–0.100%), Fe(0.050–2.000%); grossular – 2×6 standards V(0.005–0.100%), Cr(0.001–0.050%), Mn(0.005–0.200%), Fe(0.100–0.500%), Co(0.001–0.050%); apophyllites – 2×5 standards V(0.005–0.100%), Mn(0.005–0.100%).

To elaborate the results, except for a linear regression, mathematical models were used that take into account interelement influence, *i.e.* a multiple regression (M.R.), Lucas-Tooth–Pyne model (L.T.P.) – a model of intensities correction and de Jongh model (d.J.) – a model of concentration correction. For the multiple regression the exponential terms of the equation have not been taken into account [5]:

$$C_i = a_0 + a_i I_i + \sum \alpha_{ij} I_j$$

where  $C_i$  denotes the concentration of the determined element,  $a_i$  is the constant in the equation, involving the determined element,  $I_i$  – the intensity of radiation of the determined element radiation,  $\alpha_{ij}$  – the influence coefficient of the  $j$ -th element of the matrix on the determined element,  $I_j$  – the intensity of radiation of the disturbing element.

Lucas-Tooth–Pyne model (L.T.P.) [11]:

$$C_i = a_0 + I_i(a_i + \alpha_i I_i + \sum \alpha_{ij} I_j)$$

de Jongh model (d.J.) [12]:

$$C_i = (a_0 + a_i I_i)(1 + \sum \alpha_{ij} C_j)$$

The same notations were used as in the case of the multiple regression. Correlation coefficients and absolute standard deviations STD (residual errors of the function) obtained for individual mathematical models are given in Table 9.

**Table 9.** Correlation coefficients  $R$  and absolute standard deviations STD (residual errors of the function)

Minerals	L.R.		M.R.		L.T.P.		d.J.	
	$R$	STD, %	$R$	STD, %	$R$	STD, %	$R$	STD, %
Spodumenes								
Mn	0.99967	0.0006	0.99996	0.0002	0.99993	0.0004	0.99986	0.0004
Fe	0.99696	0.0019	0.99996	0.0002	0.99929	0.0009	0.99935	0.0009
Granite								
V	0.99592	0.0039	0.99986	0.0007	0.99990	0.0006	0.99970	0.0011
Mn	0.99918	0.0017	0.99986	0.0007	0.99981	0.0008	0.99978	0.0009
Fe	0.99700	0.0689	0.99957	0.0261	0.99957	0.0260	0.99766	0.0609
Diopside								
Cr	0.99406	0.0391	0.99948	0.0116	0.99915	0.0146	0.99929	0.0135
Mn	0.99984	0.0006	0.99989	0.0006	0.99987	0.0006	0.99986	0.0006
Fe	0.99921	0.0275	0.99955	0.0208	0.99939	0.0242	0.99942	0.0236
Grossularite								
V	0.99869	0.0020	0.99974	0.0009	0.99996	0.0003	0.99995	0.0004
Cr	0.99965	0.0005	0.99998	0.0001	0.99989	0.0003	0.99994	0.0002
Mn	0.99993	0.0009	0.99998	0.0005	0.99999	0.0004	0.99999	0.0004
Fe	0.99516	0.1882	0.99944	0.0643	0.99925	0.0563	0.99925	0.0742
Co	0.99707	0.0015	0.99997	0.0001	0.99982	0.0004	0.99991	0.0003
Apophyllites								
V	0.99792	0.0028	0.99998	0.0002	0.99998	0.0003	0.99998	0.0003
Mn	0.99996	0.0004	0.99998	0.0002	0.99999	0.0002	0.99999	0.0002

The obtained values of correlation coefficients for the linear regression are contained within the range 0.99406–0.99996 and are satisfactory. Taking into account the interelement influences (effects of intensification and attenuation) in multiple regression models, Lucas-Tooth–Pyne and de Jongh, results in improvement of precision and correlation between the intensity of the characteristic radiation and the



concentration of the determined element. However, this improvement is not as prominent as to justify their application in every day analytical practice. No regularity and no preferential mathematical model could be established.

Results of the quantitative analysis of the investigated minerals are presented in Table 10. Due to specific characteristics of sample preparation, *i.e.* their digestion (or deep etching) directly on an appropriate substrate the precision of results of analysis reproducibility was tested on natural samples. To assess the precision of the method reproducibility (*i.e.* the measurement precision and the sample preparation) standard deviation  $S$  has been used as well as relative standard deviation  $S_r$ . The obtained results are given in Table 11.

**Table 10.** the quantitative analysis of the examined minerals and rocks

Minerals	V, %	Cr, %	Mn, %	Fe, %	Co, %
Kunzite (spodumene)	*	*	0.40	*	*
Hiddenite I (spodumene)	*	*	0.028	0.031	*
Hiddenite II (spodumene)	*	*	0.020	0.023	*
Diopside	*	0.531	0.041	1.072	*
Grossularite (garnet)	0.020	0.011	0.090	4.112	56
Apofyllite, pink varieties	*	*	0.030	*	*
Apofyllite, greenish varieties	0.114	*	*	*	*
Apofyllite, colourless varieties	*	*	*	*	*

\*The element was not detected.

**Table 11.** The reproducibility of the preparation of real samples

Minerals	Concentration, %	Absolute standard deviation ( $S$ ), %	Relative standard deviation ( $S_r$ ), %
Kunzite (spodumene)			
Mn	0.040	0.0007	1.8
Hiddenite I (spodumene)			
Mn	0.028	0.0013	4.6
Fe	0.031	0.0008	2.6
Hiddenite II (spodumene)			
Mn	0.020	0.0004	2.0
Fe	0.023	0.00003	0.13
Granite			
V	0.0017	0.00006	3.4
Mn	0.033	0.0002	0.61
Fe	1.451	0.0039	0.27
Diopside			
Cr	0.531	0.0076	1.4
Mn	0.041	0.0003	0.73
Fe	1.072	0.0035	0.33
Grossularite			
V	0.020	0.0015	7.5
Cr	0.011	0.0004	3.7
Mn	0.090	0.0079	8.8

Fe	4.112	0.2804	6.8
Co	0.0056	0.0003	6.2
Limestone			
V	0.0022	0.0002	7.9
Mn	0.061	0.0008	1.2
Apophyllite, pink varieties			
Mn	0.030	0.0004	1.2
Apophyllite, greenish varieties			
V	0.114	0.0004	0.36

$$S = \sqrt{\frac{\sum \sum (c - c_{av})^2}{m(n-1)}}$$

$$S_r = (S/c_{av})100\%$$

where  $S$  is the absolute standard deviation [%],  $S_r$  – the relative standard deviation [%],  $c$  – the result (concentration) of a single determination [%],  $c_{av}$  – the average value of concentration [%],  $m$  – the number of natural samples ( $m = 2$ ),  $n$  – the number of measurements for each sample ( $n = 3$ ).

Because of the lack of natural samples with known contents of chromatic elements, the method has been tested on rock reference materials with certified contents of interesting elements, made available by the State Geological Institute (S.G.I.). Differences between certified and determined values allow for estimation of the accuracy of the elaborated method. The certified and determined contents of elements are given in Table 12.

**Table 12.** The analysis of rocks reference materials (S.G.I.)

Element	Granite		Limestone	
	analysis	analysis S.G.I.	analysis	analysis S.G.I.
V	17 ppm	11 ppm	22 ppm	22 ppm
Cr	*	11 ppm	**	15 ppm
Mn	0.033%	0.033%	0.061%	0.068%
Fe	1.45%	1.41%	**	0.64%
Co	*	3.7 ppm	**	5.3 ppm

\*The element were not found as a result of XRF analysis.

\*\*The element has not been determined.

## Conclusions

1. Multielement XRF analysis of minerals was carried out in the semimicroanalytical area ( $m = 50$  mg). Small weights of samples have a crucial meaning where the

amount of investigated material is limited, for example in the analysis of precious stones, semi-precious stones, synthetic ones, *etc.* The mass of the sample can be successfully reduced down to *e.g.* 20 mg, however, one can expect then a deterioration of detection and determination limits; the choice of the mass of the sample depends on the requirements set in practice.

2. The advantage of the elaborated method is its simplicity and a short time of natural samples preparation for multielement analysis – max. 1.5 h. A direct digestion of the examined material on the substrate used is a novelty in this work. This makes easier the control of manufacturing a thin layer of the sample below the effective thickness. A classical manufacturing of a “thin sample” by depositing the examined material on a substrate, *e.g.* by filtration, in practice creates a lot of problems. The applied conditions of digestion not always lead to a total destruction of the minerals structure and silicon removal. The method of minerals digestion in an appropriate mixture of acids or by melting (*e.g.* iron ores) and then dropping the obtained solution onto the substrate, often used in practice, gives proper effects for the macroanalysis [13].

3. An additional condensation of determined metals ( $\text{SiO}_2$  removal) is achieved by a direct digestion of silicate minerals by means of the hydrofluoric acid on the substrate, what positively affects the detection and determination limits.

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