

Multielement XRF Analysis of Mono- and Polycrystal Microsamples by the Thin Layer Method. Determination of Ni, Cu, Zn, Ga, Cd, Cr, Se

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0.5mg of the investigated disintegrated mono- or polycrystals of M/N/Cr/Se, where M, N-Cu, Zn, Ni, Ga, Cd, Co, In and others are spread on the substrate (a Millipore filter glued on a glass plate by means of two-sided adhesive tape), digested by spreading concentrated nitric and hydrochloric acid and dried under an IR heater. A standard graph is performed on the basis of synthetic standard samples with the same chemical composition but varied weights: 0.1–1.2 mg, prepared by transferring a multielement solution on the substrate by means of a micropipette.

Instrumental conditions: a sequential wavedispersive spectrometer, X-ray tube with a W anode, 50 kV, 40 mA, K_{α} lines; LiF 200 crystal, flow or scintillation counter or their combination depending on the element, vacuum measurements, rotation of the sample, 40 s counting time.

Statistical parameters: detection limits for 0.5 mg samples: Cu 0.041–0.048% (0.21–0.24 μg), Zn 0.024–0.034% (0.12–0.17 μg), Ga 0.079–0.102% (0.40–0.51 μg), Ni 0.016% (0.08 μg), Cd 1.9% (9.5 μg), Cr 0.018–0.030% (0.09–0.15 μg), Se 0.108–0.151% (0.54–0.76 μg), linear correlation coefficients $R > 0.99$.

0.5mg rozdrobnionego badanego mono- lub polikryształu M/N/Cr/Se, gdzie M, N- Cu, Zn, Ni, Ga, Cd, Co, In i inne, nanosi się na podłoże (sącdek Millipore przyklejony na płytke szklaną za pomocą taśmy obustronnie przylepnej), roztwarza się przez nakładanie stężonego kwasu azotowego i solnego i suszy pod promiennikiem IR. Wykres wzorcowy sporządza się na podstawie syntetycznych próbek wzorcowych o jednakowym składzie chemicznym lecz zróżnicowanych masach: 0.1–1.2 mg, przygotowanych poprzez dawkowanie roztworu wielopierwiastkowego na podłoże za pomocą mikropipety.

Parametry instrumentalne: spektrometr sekwencyjny falowodyspersyjny, lampa rentgenowska z anodą W, 50 kV, 40 mA, linie analityczne K_{α} , kryształ LiF 200, licznik przepływowy, scyntylacyjny lub ich kombinacja w zależności od pierwiastka, pomiar w próżni, rotacja próbki, czas zliczania impulsów 40 s.

Parametry statystyczne: granice wykrywalności dla próbek o masie 0.5 mg: Cu 0.041–0.048% (0.21–0.24 μg), Zn 0.024–0.034% (0.12–0.17 μg), Ga 0.079–0.102% (0.40–0.51 μg), Ni 0.016% (0.08 μg), Cd 1.9% (9.5 μg), Cr 0.018–0.030% (0.09–0.15 μg), Se 0.108–0.151% (0.54–0.76 μg), współczynniki korelacji liniowej $R > 0.99$.

Development of semiconductor technology, learning their properties by appropriate physical and chemical investigations [1,2], set high requirements both in synthesis of such materials as well as in analytical chemistry, to determine the quantitative composition of a product, to assign chemical formula and to control the process of synthesis itself. Interesting, multielement materials include mono- and polycrystals, characterized often by interesting electrical and magnetic properties (insulators, conductors, superconductors, p and n type semiconductors, ferromagnetic, ferrimagnetic, antiferromagnetic materials, *etc.*). Assigning a strict chemical formula and hence including the crystal to the appropriate type of structure requires a precise determination of elements contents at possibly small weighed amount of the sample taken for analysis. A usually limited amount of material available for analysis, dictated among other things by difficulties in synthesis of discussed compounds, creates a necessity of analyzing samples of weights of fractions of a milligram, and capable of determining simultaneously 3–5 and more components (multielement analysis). Performing such a task by classical methods seems to be difficult [3–6]. Suggested ICP–AES methods [7,8] require weighed amounts from a few to 100 mg. Also methods of X-ray fluorescence (XRF), using various techniques (solutions, fused samples), require weighed amounts of samples usually above 10 mg [9–12]. Interpretation of results of quantitative multielement analysis of mono- and polycrystals, using an X-ray microanalyser (MAR) might be difficult due to a very small area subjected to investigation. The precision is usually not satisfactory [13]. Investigations on the example of Bi/Pb/Sr/Ca/Cu/O and Tl/Ba/Ca/Cu/O type compounds have shown differences in a quantitative point X-ray microanalysis from 400 (for Ca: 7.03–27.69%) to 1250 (for Pb: 0.22–2.77%) relative percent [14].

On the basis of experience obtained earlier in the paper by Jurczyk, Buhl *et al.* [12] and using four-component $M_xN_{1-x}Cr_2Se_4$ type spinels (M, N–Zn, Cu, Ga, Ni, Cd and others) synthesized by I. Kozłowska-Okońska [15,16], it has been decided to investigate a possibility of application of the thin layer method in the XRF analysis using, unlike other authors [17,18], direct digesting of samples on the substrate (carrier of the sample) and using a simplified but effective method of calibration. Advantages of the thin layer method are known (among other things including all the weight of sample in the analysis, a linear relation between the measured intensity of fluorescent radiation and the absolute content in the sample of the determined element); 0.5 mg samples were predicted for analysis.

EXPERIMENTAL

Apparatus and Conditions

Wavedispersive sequential spectrometer. Excitation – an X-ray tube with a W anode (for Se a tube with a Mo anode is recommended), 50 kV, 40 mA. LiF 200 analysing crystal, fine collimator, amplitude discriminator, gross pulse measurement, vacuum; rotation of the sample. Detection time (t) – 40 s.

analytical lines:			detector:
Cr	K α	0.2291 nm	flow counter
Ni	K α	0.1659 nm	flow counter
Cu	K α	0.1542 nm	flow counter
Zn	K α	0.1436 nm	flow + scintillation counter
Ga	K α	0.1341 nm	flow + scintillation counter
Se	K α	0.1106 nm	flow + scintillation counter
Cd	K α	0.0536 nm	scintillation counter

Samples substrate

A two-sided adhesive tape, on which a filter of diameter ~2 cm is centrally situated, is glued on a prepared 45×25×2 mm glass plate (or other fitted to dimensions of the spectrometer cassette). It is recommended to use a Millipore filter for this purpose because, as the experience has shown, it is relatively resistant to action of acids and does not change during drying (does not get folded and bubbles are not created).

Preparation of natural samples for analysis

The studied material, disintegrated and then weighed on a microbalance (~0.5 mg, d = 0.001 mg), is spread on a prepared substrate, digested by spreading the digesting agent a few times at the amount necessary for total dissolution of the sample (in case of studied mono- and polycrystals in about 5 portions of the digesting agent two drops of concentrated nitric acid and 5 drops of concentrated hydrochloric acid, *i.e.* total about 0.5 ml HNO₃ and about 1.2 ml HCl). The sample is heated, dried under an IR heater at the temperature of 50°C what allows for direct observation of the process of digesting the studied material. It is possible to use a drier for this purpose, however, in such a case one might expect hindrances during dispensing acids and during observation of the process of digesting, strict control of which is necessary because of a possibility of substrate damage, *e.g.* by filter carbonization. After drying the sample is durable and basically does not require protection.

Preparation of synthetic samples for calibration

Elements of the investigated mono- or polycrystal in the form of appropriate solutions containing the metals being determined: M, N (M, N-Cu, Ni, Zn, Ga, Cd and others), chromium and selenium are spread on the prepared substrate by means of a micropipette. The quantitative ratio of elements in the solution shall refer to the average composition of the analyzed material, in the described work M:N:Cr:Se 10:10:20:60%, that is 1:1:2:6. The volumes of the dropped solution correspond to the assumed weights of standard samples – in the described work 0.1, 0.3, 0.4, 0.5, 0.7, 1.0, 1.2 mg and shall include the range of concentrations of the determined metals in the investigated material, at preselected weighed amount of the sample (0.5 mg). After drying samples under an IR heater, concentrated nitric and hydrochloric acids are spread in an identical way as for studied samples and then heated and dried under an IR heater at 50°C. After drying the samples are durable and basically do not require protection.

Preparation of a blank sample

Concentrated nitric and hydrochloric acids are spread on the substrate in the identical way as for studied and standard samples, heated and dried under an IR heater at the temperature of 50°C.

Satisfactory results were obtained in the work using tungsten tube as an excitation source. Application of molybdenum tube provides a possibility of improvement of the signal to background ratio for selenium (avoiding coincidence of K α Se and L γ_1 W). These ratios amount for tungsten and molybdenum tubes about 5.8 and 12.4, respectively (0.5 mg sample, 60% Se). Also in the case of gallium, because of proximity of tungsten L β_4 line, slightly better results may be achieved using a tube with molybdenum anode (0.5 mg sample, 10% Ga: signal/background – 3.8 for the Mo tube, while for the W

tube signal/background – 2.6). For the remaining elements better results were obtained for the tungsten tube, for instance the discussed ratios amount to 20 for Cr (11 for molybdenum tube), 14.5 for Ni (7.8 for Mo tube), 6.5 for Zn (3.6 for Mo tube). Results refer to 0.5 mg samples at 10% contents of determined metals and the same parameters of tubes operation, *i.e.* 50 kV, 40 mA. Figure 1 presents the spectrum for a blank sample and for a typical sample. The diagram of the analytical procedure is presented in Figure 2.

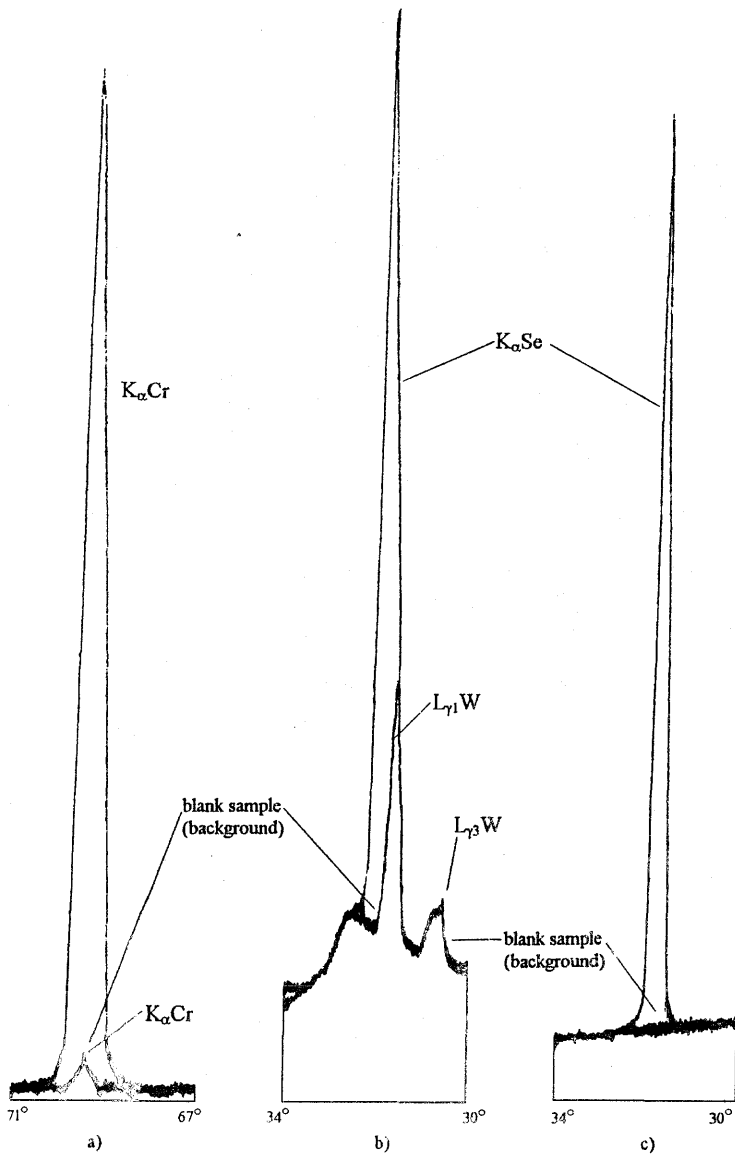


Figure 1. The spectrum for a blank sample and for a typical sample

- a) $K_{\alpha}Cr$ – 0.5 mg Cu/Zn/Cr/Se (10:10:20:60%), PW 1450 spectrometer, tungsten tube
- b) $K_{\alpha}Se$ – 0.5 mg Cu/Zn/Cr/Se (10:10:20:60%), PW 1450 spectrometer, tungsten tube
- c) $K_{\alpha}Se$ – 0.5 mg Cu/Zn/Cr/Se (10:10:20:60%), PW 1410 spectrometer, molybdenum tube

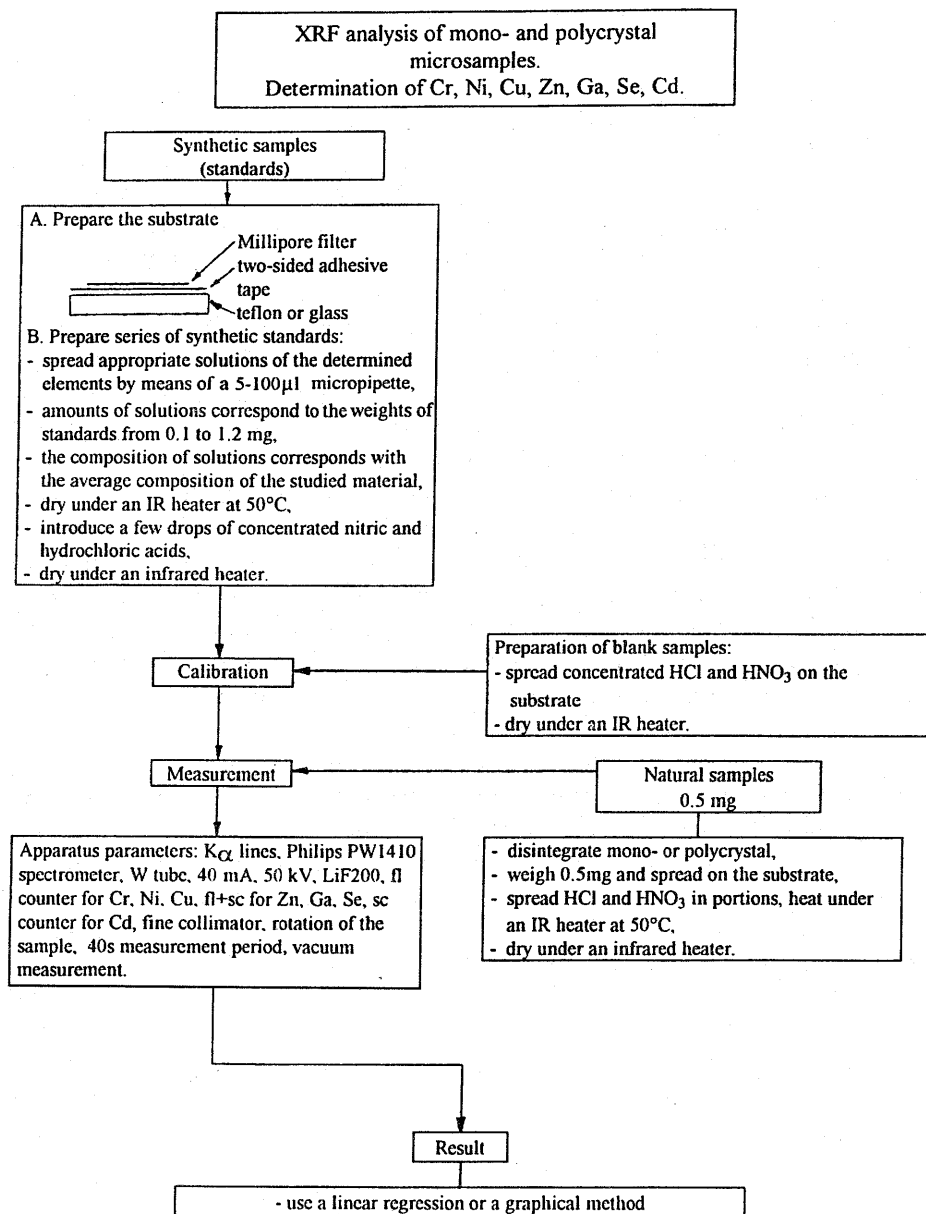


Figure 2. The diagram of analytical procedure

RESULTS AND DISCUSSION

A quick method of preparation of multicomponent mono- and polycrystal micro-samples (weights equal to fractions of a milligram) was worked out. Material disintegrated and weighed on a microbalance was digested directly on the substrate used, by addition of portions of concentrated nitric and hydrochloric acids. The choice of the digesting agent depends on the studied material and conditions of the conducted reaction. For instance YBaCuO, TlBaCaCuO, LaSrCuO, YBaCuFeO type superconductors [19–21] were digested in hydrochloric acid, other in nitric acid or in mixtures with hydrogen peroxide; combinations of the composition: Bi(Pb)SrCaCuO, Bi(Pb,Sb)SrCaCuO, Bi(Pb,Y)SrCaCuO [22], similarly like the described spinels, were digested in a mixture of nitric and hydrochloric acids. In the case of application of hydrofluoric acid in mixtures with other acids it is necessary to protect a glass substrate or use another one. The established digesting temperature (50°C) was a compromise between the rate of digesting and protection the filter against damage, possible folding or creation of bubbles. After drying, the cellulose of which the filter is made formed a thin, smooth film saturated with metals of the analyzed material. Samples prepared in this way are durable and can be used for measurement many times. To safeguard the surface of the sample against possible atmospheric action a possibility of protecting it with a Mylar foil has been predicted, using two-sided adhesive tape, on which the filter was previously glued.

The choice of the mono- or polycrystals weight taken for analysis (about 0.5 mg) was dictated by a limited amount of material assigned for analysis, its homogeneity and primarily, what was the assumption of this work, to be in the area of the "thin samples" method. Thanks to minimization of mutual interelement influences (effects of intensification and absorption) by using the mentioned method, it was possible to obtain a linear relationship between the concentration of the determined element and the intensity of fluorescent radiation in the interesting concentration range, or between the weight (thickness) of the sample and the radiation intensity what had a decisive meaning at performing calibration on the basis of standards of identical chemical composition but of varied weights.

Preparation of samples with a smaller thickness than the critical thickness, calculated for our needs roughly according to formula: $d_{\max} = 4.9/\mu_1$ [23], where μ_1 is an average linear absorption coefficient, was the basic condition for analyzing the whole mass of the sample. Average mass absorption coefficients of studied spinels after the process of digestion, necessary to calculate critical thicknesses, are presented in Table 1. Table 2 presents critical thicknesses and thicknesses of samples after the process of digestion in the described conditions: $d_{\text{sample}} = m_{\text{sample}}/\rho\pi r^2$, where m_{sample} is the mass of the sample after digestion, ρ is the density of the sample calculated as the weighted average of chlorides density, r is the radius of the sample ≈ 1 cm. Comparing the obtained results it can be seen that thicknesses of samples are many times smaller than the critical thickness. For cadmium that among the determined elements emits the most penetrating radiation the thickness of the sample is almost 900 times smaller than the critical thickness while for chromium this ratio amounts to around 40 times. The results obtained ensure not only analyzing the whole

mass of the sample but also a linear relationship between the intensity of the fluorescent radiation and the concentration of an element. This is confirmed by results of calculated surface densities according to thin sample criteria [24,25]. Calculations performed for a tungsten tube as the excitation source and chromium emitting radiation of the lowest energy among the elements being determined indicate that surface densities of the studied samples shall be roughly smaller than about 0.25 mg cm^2 , *i.e.* at the substrate surface of about 5 cm^2 the mass of the sample shall be smaller than 1.3 mg, so that the aforementioned criteria are met.

Table 1. Mean attenuation coefficients $\mu_m \text{ cm}^2 \text{ g}^{-1}$ for spinels of average composition 10:10:20:60% after the process of digestion (K_α lines)

Cu/Zn/Cr/Se	Cu 107.9	Zn 88.9	Cr 274.4	Se 54.4
Cu/Ni/Cr/Se	Cu 107.5	Ni 131.7	Cr 273.4	Se 53.3
Zn/Ga/Cr/Se	Zn 89.2	Ga 74.0	Cr 276.2	Se 55.3
Cd/Ga/Cr/Se	Cd 13.2	Ga 78.3	Cr 293.9	Se 52.3

Table 2. Critical thicknesses of samples d_{max} mm and analytical thicknesses after the process of digestion d_{sample} mm

Cu/Zn/Cr/Se	d_{max} Cu 0.156	d_{max} Zn 0.190	d_{max} Cr 0.062	d_{max} Se 0.311	d_{sample} 0.0015
Cu/Ni/Cr/Se	d_{max} Cu 0.147	d_{max} Ni 0.120	d_{max} Cr 0.058	d_{max} Se 0.300	d_{sample} 0.0014
Zn/Ga/Cr/Se	d_{max} Zn 0.196	d_{max} Ga 0.236	d_{max} Cr 0.063	d_{max} Se 0.316	d_{sample} 0.0016
Cd/Ga/Cr/Se	d_{max} Cd 1.236	d_{max} Ga 0.209	d_{max} Cr 0.056	d_{max} Se 0.312	d_{sample} 0.0014

Calibration graphs were prepared on the basis of standards of the same chemical composition but varied weights (0.1, 0.3, 0.4, 0.5, 0.7, 1.0, 1.2 mg) what substantially simplifies the onerous calibration stage. Synthetic standards of $M_xN_{1-x}Cr_2Se_4$ spinels (M, N-Cu, Zn, Ga, Ni) had the following quantitative composition: 10:10:20:60%. Its choice was dictated by the average composition of analyzed natural spinels, *i.e.* with about 20% of chromium content, 60% of selenium and varying contents of metals M and N built-in in the crystal lattice. The obtained values of coefficients of linear correlation R and of absolute standard deviations STD and relative standard deviations STD_{rel} , characterising residual errors of linear functions, are given in Table 3. In all cases the coefficients of linear correlation are larger than 0.99 what well confirms a linear relationship between radiation and the mass of the sample. Only for chromium in the Cd/Ga/Cr/Se spinel the correlation coefficient is slightly

smaller and amounts to 0.98. Equations of calibration straight-lines (linear regression) are given below:

Cu/Zn/Cr/Se	Cu	$m = 3.774 \cdot 10^{-7} \times I - 0.0023$
	Zn	$m = 2.825 \cdot 10^{-7} \times I - 0.0005$
	Cr	$m = 3.548 \cdot 10^{-7} \times I - 0.0050$
	Se	$m = 9.085 \cdot 10^{-7} \times I - 0.0015$
Zn/Ga/Cr/Se	Zn	$m = 2.292 \cdot 10^{-7} \times I - 0.0018$
	Ga	$m = 5.730 \cdot 10^{-7} \times I - 0.0027$
	Cr	$m = 2.864 \cdot 10^{-7} \times I - 0.0099$
	Se	$m = 7.614 \cdot 10^{-7} \times I - 0.0137$
Cu/Ni/Cr/Se	Cu	$m = 3.419 \cdot 10^{-7} \times I - 0.0012$
	Ni	$m = 1.850 \cdot 10^{-7} \times I - 0.0023$
	Cr	$m = 3.211 \cdot 10^{-7} \times I - 0.0001$
	Se	$m = 8.355 \cdot 10^{-7} \times I - 0.0076$
Cd/Ga/Cr/Se	Cd	$m = 9.235 \cdot 10^{-6} \times I - 0.0063$
	Ga	$m = 6.665 \cdot 10^{-7} \times I - 0.0028$
	Cr	$m = 4.022 \cdot 10^{-7} \times I - 0.0201$
	Se	$m = 9.069 \cdot 10^{-7} \times I - 0.0204$

where m is the absolute mass of the element [mg], I is the radiation intensity (counts/40 s).

To determine a detection limit the criterion: $C_0 = 3S_b/m$ [26] has been assumed, where $S_b = \sqrt{N_b}$ is the standard deviation of background counts number, m is the slope of a straight line characterizing the sensitivity of the method. Results for 0.5 mg samples are presented in Table 4. Slopes of straight lines of calibration equations presented above characterize the sensitivity of the method. For additional presentation of a possibility of differentiation of two close concentrations of the given element (sensitivity of the method) the change of concentration corresponding to the value of one standard deviation of counts number ($s = \sqrt{N_{imp}}$) is also presented in Table 5.

Table 3. Linear correlation coefficients, absolute and relative residual errors of linear functions

spinel	Cu			Zn			Cr			Se		
	<i>R</i>	STD	STD _{rel}	<i>R</i>	STD	STD _{rel}	<i>R</i>	STD	STD _{rel}	<i>R</i>	STD	STD _{rel}
		[mg]			[mg]			[mg]			[mg]	
Cu/Zn/Cr/Se	0.9987	0.0023	4.58%	0.9985	0.0025	4.98%	0.9984	0.0052	5.16%	0.9990	0.0124	4.12%
Cu/Ni/Ce/Se	Cu			Ni			Cr			Se		
	<i>R</i>	STD	STD _{rel}	<i>R</i>	STD	STD _{rel}	<i>R</i>	STD	STD _{rel}	<i>R</i>	STD	STD _{rel}
		[mg]			[mg]			[mg]			[mg]	
	0.9968	0.0036	7.20%	0.9954	0.0044	8.70%	0.9972	0.0068	6.83%	0.9991	0.0117	3.90%
Zn/Ga/Cr/Se	Zn			Ga			Cr			Se		
	<i>R</i>	STD	STD _{rel}	<i>R</i>	STD	STD _{rel}	<i>R</i>	STD	STD _{rel}	<i>R</i>	STD	STD _{rel}
		[mg]			[mg]			[mg]			[mg]	
	0.9982	0.0028	5.52%	0.9963	0.0039	7.78%	0.9963	0.0078	7.84%	0.9967	0.0221	7.37%
Cd/Ga/Cr/Se	Cd			Ga			Cr			Se		
	<i>R</i>	STD	STD _{rel}	<i>R</i>	STD	STD _{rel}	<i>R</i>	STD	STD _{rel}	<i>R</i>	STD	STD _{rel}
		[mg]			[mg]			[mg]			[mg]	
	0.9947	0.0047	9.36%	0.9983	0.0027	5.38%	0.9791	0.0185	18.46%	0.9975	0.0192	6.40%

Table 4. Detection limits of determined elements in 0.5 mg samples (criterion $C_0 = 3S_0/m$) expressed in relative % and absolute μg units

Cu/Zn/Cr/Se	Cu		Zn		Cr		Se	
	%	μg	%	μg	%	μg	%	μg
	0.048	0.240	0.034	0.170	0.026	0.130	0.151	0.755
Cu/Ni/Cr/Se	Cu		Ni		Cr		Se	
	%	μg	%	μg	%	μg	%	μg
	0.041	0.206	0.016	0.078	0.020	0.104	0.124	0.622
Zn/Ga/Cr/Se	Zn		Ga		Cr		Se	
	%	μg	%	μg	%	μg	%	μg
	0.024	0.120	0.079	0.395	0.018	0.090	0.108	0.540
Cd/Ga/Cr/Se	Cd		Ga		Cr		Se	
	%	μg	%	μg	%	μg	%	μg
	1.90	9.5	0.102	0.508	0.030	0.148	0.139	0.695

Table 5. Change of concentration corresponding to one standard deviation of counts for 0.5 mg samples

Cu/Zn/Cr/Se	Cu		Zn		Cr		Se	
	%	μg	%	μg	%	μg	%	μg
	0.028	0.140	0.023	0.115	0.038	0.188	0.100	0.502
Cu/Ni/Cr/Se	Cu		Ni		Cr		Se	
	%	μg	%	μg	%	μg	%	μg
	0.027	0.137	0.020	0.099	0.038	0.191	0.102	0.508
Zn/Ga/Cr/Se	Zn		Ga		Cr		Se	
	%	μg	%	μg	%	μg	%	μg
	0.022	0.111	0.036	0.178	0.037	0.186	0.100	0.498
Cd/Ga/Cr/Se	Cd		Ga		Cr		Se	
	%	μg	%	μg	%	μg	%	μg
	0.152	0.758	0.039	0.195	0.048	0.242	0.113	0.564

The elaborated method of thin layer sample preparation was examined by the authors on the example of the synthesized [15,16] mono- and polycrystals spinels with a theoretical composition: $\text{Cu}_{0.02}\text{Zn}_{0.98}\text{Cr}_2\text{Se}_4$, $\text{Cu}_{0.1}\text{Zn}_{0.9}\text{Cr}_2\text{Se}_4$, $\text{Cu}_{0.2}\text{Zn}_{0.8}\text{Cr}_2\text{Se}_4$, $\text{Cu}_{0.25}\text{Zn}_{0.75}\text{Cr}_2\text{Se}_4$, $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Cr}_2\text{Se}_4$. To assess the repeatability of natural samples preparation each sample was analyzed three times and three measurements were carried out for each element. The obtained results of quantitative XRF analysis are presented in Table 6. Differences in results between samples a, b, c for the same spinel might result from the sample preparation, the material inhomogeneity and to a smaller extent from the precision of the experiment itself, that alone does not justify such differences. Absolute and relative standard deviations were used to assess these three parameters (Table 7):

$$S = \sqrt{\frac{\sum_{i=1}^m \sum_{j=1}^n (c^- - c_{ij})^2}{m(n-1)}}$$

$$S_{\text{rel}} = \frac{S}{c} 100\%$$

where: $m = 3$ is the number of samples, $n = 3$ is the number of measurements for each sample, c_{ij} is the result of the measurement, \bar{c} is the average concentration of the element.

Table 6. Results of XRF analysis of spinel mono- and polycrystals

Spinel $\text{Cu}_x\text{Zn}_{1-x}\text{Cr}_2\text{Se}_4$	sample	Cu, %	Zn, %	Cr, %	Se, %	sum, %
$\text{Cu}_{0.02}\text{Zn}_{0.98}\text{Cr}_2\text{Se}_4$	a	0.31	14.87	26.02	57.74	98.94
	b	0.19	13.85	25.96	59.58	99.58
	c	0.66	14.44	26.06	59.66	100.82
	mean	0.39	14.39	26.01	58.99	99.78
$\text{Cu}_{0.1}\text{Zn}_{0.9}\text{Cr}_2\text{Se}_4$	a	10.00	4.76	25.58	58.66	99.00
	b	10.38	5.11	25.88	58.64	100.01
	c	10.45	5.11	25.88	58.82	100.26
	mean	10.28	4.99	25.78	58.71	99.76
$\text{Cu}_{0.2}\text{Zn}_{0.8}\text{Cr}_2\text{Se}_4$	a	14.16	2.57	24.24	57.26	98.23
	b	13.36	2.75	25.31	57.05	98.47
	c	12.62	2.86	25.91	57.62	99.01
	mean	13.38	2.73	25.15	57.31	98.57
$\text{Cu}_{0.25}\text{Zn}_{0.75}\text{Cr}_2\text{Se}_4$	a	18.55	1.13	21.89	56.65	98.22
	b	19.33	1.54	21.69	56.89	99.45
	c	18.69	0.93	22.38	57.02	99.02
	mean	18.86	1.20	21.99	56.85	98.90
$\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Cr}_2\text{Se}_4$	a	15.17	0.20	26.17	57.99	99.53
	b	14.90	0.19	25.99	58.66	99.74
	c	14.67	0.25	26.54	58.69	100.15
	mean	14.91	0.21	26.23	58.45	99.80

a,b,c – see in text.

Table 7. Relative and absolute standard deviations characterizing reproducibility of natural samples preparation

spinel	Cu		Zn		Cr		Se	
	S, %	S _{rel.} , %	S, %	S _{rel.} , %	S, %	S _{rel.} , %	S, %	S _{rel.} , %
$\text{Cu}_{0.02}\text{Zn}_{0.98}\text{Cr}_2\text{Se}_4$	0.243	62.31	0.512	3.56	0.051	0.20	1.084	1.84
$\text{Cu}_{0.1}\text{Zn}_{0.9}\text{Cr}_2\text{Se}_4$	0.242	2.35	0.200	4.01	0.173	0.67	0.099	0.17
$\text{Cu}_{0.2}\text{Zn}_{0.8}\text{Cr}_2\text{Se}_4$	0.769	5.75	0.146	5.35	0.845	3.36	0.288	0.50
$\text{Cu}_{0.25}\text{Zn}_{0.75}\text{Cr}_2\text{Se}_4$	0.416	2.21	0.311	25.92	0.355	1.61	0.188	0.33
$\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Cr}_2\text{Se}_4$	0.250	1.68	0.032	15.24	0.280	1.07	0.395	0.68

Conclusion

1. Multielement XRF analysis of mono- and polycrystals with spinel structures was carried out using samples weighing fractions of milligram what has a decisive meaning when the amount of material assigned for investigations is limited.

2. The described method is used to control chemical composition of synthesized mono- and polycrystals [15,16].

3. The analysis of small weights of samples allows for using the thin layer method that enables minimization of the interelement effects.

4. Simplicity and short time of natural samples preparation for multielement analysis are the advantages of the elaborated method. Direct digestion of the studied material on the substrate used, that makes formation of a thin layer substantially easier, is the novelty in this work. Prepared samples are durable and can be analyzed many times.

5. Calibration on the basis of synthetic standards of the same chemical composition but varied weights makes performing the analysis much easier and shortens its time.

6. Contrary to the dissolution technique [12] the discussed method creates a possibility of performing measurements in vacuum and of improving the detection limits.

REFERENCES

1. McDevilt J.T., Riley D.R. and Haupt S.G., *Anal. Chem.*, **65**, 535 (1993).
2. Mroziewicz B., Bugajski M. and Nakwaski N., *Physics of Semiconductor Lasers*, PWN, Warszawa 1991.
3. Vasileva M.G., Lalukina V.M., Yermakova L.V., Obolestnik V.A., Asatyanin N.G. and Veschitkatschyan M.T., *Analiz Poluprovodnikovikh Splavov*, Metallurgisdat, 1975.
4. Sandell E., *Colorimetric determination of Traces of Metals*, Interscience, New York, 1959.
5. *Analyse der Metalle III/1. Betriebsanalyse I. Teil*, Springer Verlag, 1961.
6. Kazunobu Kodama, *Methods of Quantitative Inorganic Analysis*, Interscience, New York, 1963.
7. Kulkarni M.J., Argekar A.A., Thulasidas S.K., Page A.G. and Sastry M.D., *Fresenius J. Anal. Chem.*, **342**, 367 (1992).
8. Jianzhang Z., Vasileva J.G., Gibner J.I., Shilkina T.Y. and Boris Z.J., *J. Fresenius J. Anal. Chem.*, **342**, 363 (1992).
9. Doto K., *Japan Analyst*, **981**, 17 (1968).
10. Shevtsov N.I., Blank A.B., Nartova Z.M., Mirenskaya J.J., Eksperiandova L.P. and Sumarokov S.J., *Zav. Lab.*, **56**, 10 (1990).
11. Shevtsov N.I., Nartova Z.M., Kviczko L.A. and Blank A.B., *Zh. Anal. Chem.*, **46**, 591 (1991).
12. Jurczyk J., Buhl F. and Wilczek I., *Chem. Anal. (Warsaw)*, **38**, 519 (1993).
13. Newburg D.E., Swyt C.R. and Hyklebust R.L., *Anal. Chem.*, **67**, 1866 (1995).
14. Treiger B.A., Bondarenko I.I., Mazalov L.N. and Rezvickij W.W., *Zh. Anal. Chem.*, **49**, 389 (1994).
15. Okońska-Kozłowska I., *Z. Anorg. Chem.*, **558**, 225 (1989).
16. Okońska-Kozłowska I., Kopyczok I. and Jung M., *Z. Anorg. Chem.*, **571**, 157 (1989).
17. Kliment V., *J. Radional. Nucl. Chem.*, **155**, 91 (1991).
18. Hoffman P., Lieser K.H., Hein M. and Flakowski M., *Spectrochim. Acta*, **44B**, 471 (1989).
19. Nedeltcheva T., Simeonova P. and Lovchinov V., *Anal. Lab.*, **4**, 38 (1995).
20. Watanabe K., Demura K. and Fueki K., *Bull. Chem. Soc. Jpn.*, **67**, 1024 (1994).
21. Gautier E.A., Gettar R. and Servant R.E., *Anal. Chim. Acta*, **283**, 350 (1993).
22. Zhao Y.Z., *Fenxi-Shiyanshi*, **12**, 67 (1993).
23. Bertin E.P., *Principles and Practice of X-Ray Spectrometric Analysis*, Plenum Press, New York 1975.
24. Jenkins R., Gould R.W. and Gedke D., *Quantitative X-Ray Spectrometry*, Marcel Dekker, New York 1981.
25. *Handbook of X-Ray Spectrometry*, Eds. R. van Grieken, A. Markowicz, Marcel Dekker, 1993.
26. Hertroys P. de Vries J.L., *Counting Strategy*, Philips Scientific Reports, 16415/OL, (1967).

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