

XRF Analysis of Powder Microsamples of Multielement Mono- and Polycrystals. Determination of Cr, Mn, Ni, Cu, Zn, Ga, As, Se, Sb, Yb

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A quick method has been worked out for preparation of powder samples in the sub-microanalytical area for XRF analysis. Investigations were carried out using as an example three- and four-component mono- and polycrystals: CuZnCrSe, ZnGaCrSe, CuNiCrSe, ZnNiCrSe, YbZnSb, YbMnAs, ZnMnAs. The concentrations of elements being determined were in the range: Cu 12–40%, Zn 2.7–28%, Cr 0.8–24%, Se 53–67%, Ni 0.5–13%, Yb 24–49%, Mn 23–37%, As 28–43%, Sb ~48%, Ga ~0.4%. Powdered and weighed material (0.5 mg) is transferred onto the substrate (a Millipore filter) and a few drops of carbon tetrachloride are dropped. After drying a sample with uniformly distributed material is formed. Then acetone is dropped and after drying at room temperature a Millipore filter forms a smooth thin film with “embedded” grains of the analyzed material. Minimization of matrix effects due to application of thin layer method allows to prepare calibration curves common for various materials. The obtained limits of detection for 0.5 mg samples are, in μg : Cr – 0.34, Mn – 0.22, Ni – 0.20, Cu – 0.29, Zn – 0.32, Ga – 0.27, As – 0.37, Se – 0.40, Sb – 1.82, Yb – 1.27.

Opracowano szybką metodę przygotowywania próbek proszkowych w obszarze sub-mikroanalitycznym do analizy XRF. Badania prowadzono na przykładzie trój- i czterokładnikowych mono- i polikryształów: CuZnCrSe, ZnGaCrSe, CuNiCrSe, ZnNiCrSe, YbZnSb, YbMnAs, ZnMnAs. Oznaczane pierwiastki występowały w zakresie stężeń: Cu 12–40%, Zn 2.7–28%, Cr 0.8–24%, Se 53–67%, Ni 0.5–13%, Yb 24–49%, Mn 23–37%, As 28–43%, Sb ~48%, Ga ~0.4%. Rozdrobniony i odważony materiał (0.5 mg) przenosi się na podłoże (sączek Millipore) i nakrapla kilka kropeł tetrachlorku węgla. Po wyschnięciu z utworzonej zawiesiny tworzy się próbka z równomiernie

rozprowadzonym materiałem. Następnie nakrapla się aceton, po wysuszeniu w temperaturze pokojowej sączek Millipore tworzy cienki, gładki film z „wtopionymi” ziarnami analizowanego materiału. Minimalizacja efektów matrycy dzięki zastosowaniu techniki cienkiej warstwy pozwoliła na sporządzenie wykresów kalibracyjnych wspólnych dla różnych materiałów. Uzyskane granice wykrywalności dla próbek o masie 0.5 mg wynoszą w mg: Cr – 0.34, Mn – 0.22, Ni – 0.20, Cu – 0.29, Zn – 0.32, Ga – 0.27, As – 0.37, Se – 0.40, Sb – 1.82, Yb – 1.27.

A interelement influences are one of the main sources of errors in the X-ray fluorescence analysis. There are lots of methods, consisting both in mathematical correction and in special preparation of samples, that allow minimizing the matrix effects. The thin layer method belongs to this second category [1,2]. At a sufficiently small thickness (mass per unit area) decreasing of both absorption effects [3] and secondary amplification [4] allows to obtain a linear relationship between the intensity of fluorescent radiation and the concentration of the element being determined. A few methods of thin samples' preparation are used. In the case of powder samples the methods are used, in which the material is deposited on the substrate, *e.g.* a Mylar film, in various ways [5]. Filtration methods employing suspension of the analyzed material in water [6,7] or in an organic solvent, *e.g.* acetone [8], are used. In this way the material deposited on a filter, frequently protected with, *e.g.* an acrylic resin is ready for analysis. Authors of paper [9] have presented the method of thin powder samples' preparation by filtering the powder of the analyzed sample suspended in a stream of air. Other methods of preparation of powder samples of rocks or ceramic materials include also the method of pressing into pellets [10]; however, relatively frequently large values of mass per unit area require then taking into account absorption effects. Effects of secondary excitation are often minimized in these methods by press moulding the analyzed material with a “thinner”, *e.g.* cellulose.

The thin layer method creates a possibility of its application to analyze materials, a synthesis of which is complicated and leads to obtaining small amounts of the product. In previous papers [11,12] the authors have analysed multielement mono- and polycrystals. Multielement synthetic samples were used as the calibration material. A direct digestion of the analyzed material on the substrate was the basis of natural samples preparation for analysis. A similar preparation was previously also used to determine trace amounts of metals in minerals and silicate rocks [12,13]. In the present paper the authors describe a simple method of preparation of thin powder samples using three- and four-component mono- and polycrystals [14]: CuZnCrSe, ZnGaCrSe, CuNiCrSe, YbZnSb, ZnNiCrSe, YbMnAs, ZnMnAs as an example. The determined elements were in the range: Cu 14–40%, Zn 2.8–28%, Cr 0.8–24%, Se 53–67%, Ni 0.5–7%, Yb 24–49%, Mn 23–37%, As 28–43%, Sb 48%, Ga 0.4%. A material of known chemical composition and samples of diversified masses from about 0.1 to 1.2mg have been used for calibration.

EXPERIMENTAL

Apparatus and instrument setting

A wadedispersive sequential X-ray spectrometer PW 1410 Philips; excitation: an X-ray tube with a Mo anode, 50 kV, 40 mA; LiF200 crystal, fine collimator (150 μ m), vacuum, rotation of sample; detection time: 40 s

		analytical lines	counter
Cr	K $_{\alpha}$	0.2291 nm	fl
Mn	K $_{\alpha}$	0.2103 nm	fl
Ni	K $_{\alpha}$	0.1659 nm	fl
Cu	K $_{\alpha}$	0.1542 nm	fl
Zn	K $_{\alpha}$	0.1437 nm	fl + sc
Ga	K $_{\alpha}$	0.1341 nm	fl + sc
As	K $_{\alpha}$	0.1177 nm	fl + sc
Se	K $_{\alpha}$	0.1106 nm	fl + sc
Sb	L $_{\alpha 1}$	0.3439 nm	fl
Yb	L $_{\alpha 1}$	0.1672 nm	fl

fl – flow counter, sc – scintillation counter.

Substrate for samples

A Millipore filter (AA Type, Bedford, Mass., USA) of 25 mm diameter (4.9 cm² surface) mounted onto a 45 \times 25 \times 2 mm glass plate (adapted to the dimensions of the spectrometer cassette) by means of a two-sided adhesive tape.

Preparation of samples for analysis

The studied material, disintegrated as much as possible to grains below 5 μ m, is weighed on a microbalance (0.5 mg). After transferring onto the substrate a few drops of carbon tetrachloride are dropped on, attempting to distribute particles of created suspension on the filter in a uniform way. After evaporation of the solvent another its portion is added and the described actions are repeated until obtaining a relatively uniform distribution of the material on the filter. Then about 10 drops of acetone are dropped and dried at room temperature. Under the action of acetone the Millipore filter creates a smooth, thin, transparent film with “embedded” grains of the analyzed material. In this way durable samples are prepared, they do not need protection and may be analyzed many times.

Calibration

A series of standard samples is prepared in an identical way as the studied samples using a material of the known chemical composition, e.g. CRM. Materials used in the presented paper had the chemical composition determined on the basis of synthetic standards [11, 12]. A series of standard samples was prepared by weighing diversified amounts of the material. The range of standard samples masses and their chemical composition are given in Table 1. Ten samples were prepared for calibration each time.

Table 1. Chemical composition of materials used for calibration

Material	Range of reference samples' mass, mg	Concentration of element, %			
		Cu - 13.53	Zn - 2.75	Cr - 22.47	Se - 61.25
Cu-Zn-Cr-Se	0.139-1.170	Zn - 9.32	Ga - 0.38	Cr - 23.71	Se - 66.59
Zn-Ga-Cr-Se	0.137-1.157	Cu - 40.08	Ni - 6.50	Cr - 0.77	Se - 52.65
Cu-Ni-Cr-Se	0.111-1.099	Zn - 13.09	Ni - 2.22	Cr - 20.61	Se - 64.09
Zn-Ni-Cr-Se	0.107-1.112	Yb - 23.70	Zn - 28.14	Sb - 48.16	-
Yb-Zn-Sb	0.117-1.039	Yb - 49.33	Mn - 22.91	As - 27.76	-
Yb-Mn-As	0.127-1.044	Zn - 19.41	Mn - 37.36	As - 43.23	-
Zn-Mn-As	0.098-1.057				

DISCUSSION OF RESULTS

The assumption of a linear relationship between the intensity of radiation and the concentration of the determined element is based on mathematical approximation:

$$\exp(-\bar{\mu} \cdot w) \approx 1 - (\bar{\mu} \cdot w)$$

where w is the mass per unit area of the sample, $\bar{\mu} = (\bar{\mu}_\lambda/\sin\varphi) + (\bar{\mu}_{\lambda i}/\sin\psi)$ is the average mass absorption coefficient of the exciting λ and fluorescent radiation λi taking into account the angles φ and ψ of exciting and characteristic radiation, $\bar{\mu}_\lambda$ and $\bar{\mu}_{\lambda i}$ are calculated according to formulae:

$$\bar{\mu}_\lambda = \sum_{k=1}^n c_k \cdot \mu_{k,\lambda} \quad \bar{\mu}_{\lambda i} = \sum_{k=1}^n c_k \cdot \mu_{k,\lambda i} \quad \sum_{k=1}^n c_k = 1$$

where $\bar{\mu}_\lambda$ is the average mass absorption coefficient of the exciting radiation λ , $\bar{\mu}_{\lambda i}$ is the average mass absorption coefficient of the fluorescent radiation λi , c_k is the mass fraction of k -element in the sample, $\mu_{k,\lambda}$ is the mass absorption coefficient of the exciting radiation λ for k -element, $\mu_{k,\lambda i}$ is the mass absorption coefficient of the fluorescent radiation λi for k -element.

Hence in practice the results may be charged with an additional error resulting from this approximation. To avoid that, the maximum mass per unit area (thickness) of the sample is defined [15] that the sample should have to get the aforementioned errors consistent with the requirements set in respect to the accuracy of results. The authors of the paper have determined the maximum mass per unit area that shall not be exceeded by the samples to get the error resulting from absorption effects not higher than 1%. The calculations were carried out for a tube with a molybdenum anode, assuming simply that the excitation of the determined elements is carried out mainly by the K_α Mo line (so-called length of effective wave [16]). The next approximations consist in the assumption of homogeneity of the mass per unit area and in assuming

the following geometry of exciting and characteristic of X-rays: $\phi = 45^\circ$ and $\psi = 45^\circ$. The maximum mass per unit area was calculated for the lightest elements in the sample, radiation of which is subject to the highest absorption. Results of calculations, presented in Table 2, based on some approximations are only estimations, however they confirm a possibility to qualify the powder samples as thin ones. Greater absorption effects may be expected only in the case of antimony for samples of the mass higher than 0.7 mg. In further investigations masses of samples used for calibration were in the range from about 0.1 to 1.2 mg, while masses of studied samples amounted to about 0.5 mg. Thicknesses of 0.5 mg samples (surface of the filter $\sim 5 \text{ cm}^2$) are from 70 times smaller (for antimony in Yb-Zn-Sb material) to 260 times smaller (for manganese in Zn-Mn-As) than the critical thickness, corresponding with thick samples.

Table 2. Maximum mass per unit area w_{\max} that samples can have to ensure that errors resulting from absorption do not exceed 1%

Material	Line	w_{\max} , mg cm ⁻²	m_{sample}^* , mg
Cu-Zn-Cr-Se	Cr K $_{\alpha}$	≤ 0.36	≤ 1.8
Zn-Ga-Cr-Se	Cr K $_{\alpha}$	≤ 0.36	≤ 1.8
Cu-Ni-Cr-Se	Cr K $_{\alpha}$	≤ 0.36	≤ 1.8
Zn-Ni-Cr-Se	Cr K $_{\alpha}$	≤ 0.36	≤ 1.8
Yb-Zn-Sb	Sb L $_{\alpha 1}$	≤ 0.14	≤ 0.7
Yb-Mn-As	Mn K $_{\alpha}$	≤ 0.32	≤ 1.6
Zn-Mn-As	Mn K $_{\alpha}$	≤ 0.50	≤ 2.5

* m_{sample} – maximum samples' mass on the filter with 4.9 cm² surface.

Table 3. Calibration straight lines, relative std_{rel} and absolute standard deviations std (residual errors) and linear correlation coefficients r of calibration straight lines

Material	Element	Equation; I – intensity in counts/40 s m – mass of the element in μg	Range, μg	std , μg	std_{rel} , %	r
Cu-Zn-Cr-Se	Cu	$I = (1.24 \cdot 10^4 \pm 61) \cdot m + (2445 \pm 5459)$	19–158	3.26	3.7	0.9978
	Zn	$I = (2.12 \cdot 10^4 \pm 116) \cdot m + (705 \pm 2079)$	4–32	0.72	2.0	0.9974
	Cr	$I = (9.13 \cdot 10^3 \pm 70) \cdot m + (4821 \pm 10222)$	31–263	8.26	5.6	0.9945
	Se	$I = (1.68 \cdot 10^4 \pm 93) \cdot m + (33894 \pm 37366)$	85–717	16.41	4.1	0.9973
Zn-Ga-Cr-Se	Zn	$I = (1.99 \cdot 10^4 \pm 86) \cdot m - (534 \pm 4992)$	13–108	1.84	3.0	0.9984
	Ga	$I = (2.29 \cdot 10^4 \pm 193) \cdot m + (180 \pm 458)$	0.5–4.4	0.16	6.5	0.9939
	Cr	$I = (8.28 \cdot 10^3 \pm 39) \cdot m - (1197 \pm 5613)$	33–274	4.95	3.2	0.9982
Cu-Ni-Cr-Se	Se	$I = (1.59 \cdot 10^4 \pm 84) \cdot m + (26457 \pm 35024)$	91–771	16.15	3.7	0.9975
	Cu	$I = (1.42 \cdot 10^4 \pm 84) \cdot m + (4638 \pm 20340)$	44–441	10.42	4.3	0.9969
	Ni	$I = (1.65 \cdot 10^4 \pm 86) \cdot m + (597 \pm 3352)$	7–71	1.47	3.8	0.9976
	Cr	$I = (1.65 \cdot 10^4 \pm 95) \cdot m + (8 \pm 437)$	1–8	0.19	4.2	0.9971
	Se	$I = (1.77 \cdot 10^4 \pm 59) \cdot m + (14864 \pm 18668)$	58–579	7.68	2.4	0.9990

Zn-Ni-Cr-Se	Zn	$I = (1.85 \cdot 10^4 \pm 95) \cdot m - (3609 \pm 7578)$	14–146	3.14	2.4	0.9977
	Ni	$I = (1.54 \cdot 10^4 \pm 104) \cdot m - (1565 \pm 1409)$	2–25	0.70	2.6	0.9960
	Cr	$I = (8.88 \cdot 10^3 \pm 39) \cdot m - (531 \pm 4732)$	22–229	4.07	3.2	0.9984
	Se	$I = (1.61 \cdot 10^4 \pm 59) \cdot m - (10038 \pm 22840)$	69–713	10.88	2.8	0.9988
Yb-Zn-Sb	Yb	$I = (2.49 \cdot 10^3 \pm 93) \cdot m + (714 \pm 1998)$	28–246	5.77	4.2	0.9970
	Zn	$I = (1.98 \cdot 10^4 \pm 36) \cdot m - (2762 \pm 6845)$	33–292	2.48	1.5	0.9996
	Sb	$I = (7.75 \cdot 10^2 \pm 11) \cdot m - (324 \pm 3155)$	56–500	29.29	10.5	0.9818
Yb-Mn-As	Yb	$I = (2.43 \cdot 10^3 \pm 20) \cdot m + (2100 \pm 6428)$	63–515	18.71	6.5	0.9935
	Mn	$I = (1.22 \cdot 10^4 \pm 39) \cdot m + (292 \pm 5320)$	29–239	3.07	2.3	0.9992
	As	$I = (1.66 \cdot 10^4 \pm 54) \cdot m + (3809 \pm 14657)$	35–290	2.89	1.8	0.9995
Zn-Mn-As	Zn	$I = (1.97 \cdot 10^4 \pm 77) \cdot m - (6879 \pm 9164)$	19–205	3.27	2.9	0.9987
	Mn	$I = (1.22 \cdot 10^4 \pm 48) \cdot m + (1844 \pm 10908)$	37–395	6.31	2.9	0.9987
	As	$I = (1.71 \cdot 10^4 \pm 41) \cdot m + (7733 \pm 7015)$	42–457	6.20	2.5	0.9991

Thanks to a possibility of neglecting interelement influences and in particular absorption effects it was possible to perform calibration using one material from a specified group of the known chemical composition. Preparation of standard samples that differ only in masses substantially simplifies and shortens the stage of calibration. The obtained coefficients of linear correlation presented in Table 3 fit within the range 0.9935–0.9996 and only for antimony this coefficient is smaller and amounts to 0.9818. This results from a smaller sensitivity of the method for this element – a relatively low intensity of $L_{\alpha 1}$ line and its strong absorption. Relative standard deviations std_{rel} given in Table 3 is calculated for the centre of the calibration line:

$$std_{rel} = \frac{std}{0.5 \cdot (m_{min} + m_{max})} \cdot 100\% \quad \text{where} \quad std = \sqrt{\frac{\sum (m'_i - m_i)^2}{N - 2}}$$

where std is absolute standard deviations (residual errors of the function), m_{min} and m_{max} are masses of the element in standards of smallest and the largest mass, m'_i is calculated mass of the element in standard, m_i is mass of the element in standard, N is the number of standards.

Relative standard deviations std_{rel} fit within the range 1.5–6.5% and on average amount to 3.7%. For antimony the relative standard deviation reaches a higher value of 10.5%. The obtained relative and absolute standard deviations (residual errors of the function) and the coefficients of linear correlation indicate a relatively good linear relationship between the intensity of fluorescent radiation and the mass of the element being determined.

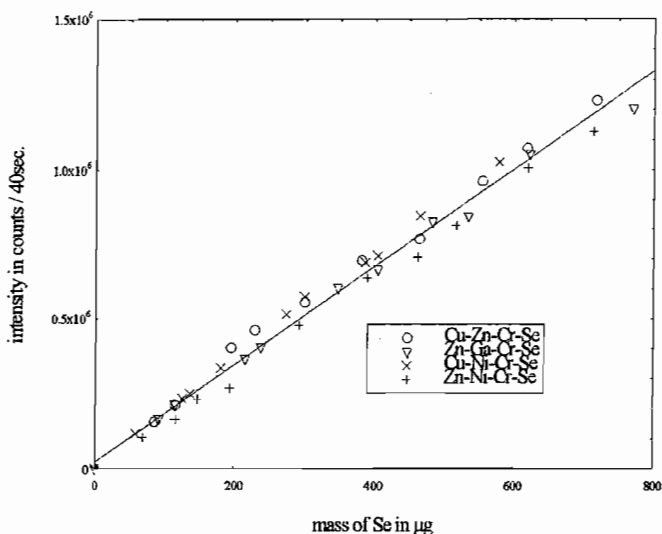


Figure 1. Calibration straight line for Se common for four materials: Cu-Zn-Cr-Se, Zn-Ga-Cr-Se, Cu-Ni-Cr-Se, and Zn-Ni-Cr-Se

Except for performing calibration separately for each analyzed material an attempt was made to draw calibration graphs common for various analyzed materials. Figure 1 presents exemplary relationships of the fluorescent radiation versus the mass of the selenium being determined in various materials. Calibration equations common for various materials are presented in Table 4. Confidence intervals for equation coefficients refer to the significance level equal to 0.95. The obtained coefficients of linear correlation fit within the range 0.9930–0.9998, the relative standard deviations within the range 2.4–6.9% while the values of absolute standard deviations are strongly dependent on the range of masses of the determined element, similarly as in Table 3. Despite relatively good linear relationships between the intensity of fluorescent radiation and the mass of the determined element in various materials there are small differences between equation coefficients obtained for individual materials (exemplary equations are given in Table 3). These differences are rather not justified by interelement influences. In the case of selenium existing in the Cu-Ni-Cr-Se the mass absorption coefficient reaches the highest value (Table 5) that would indicate a smallest value of slope of a straight line (defining the sensitivity of the method) compared to other materials. In fact, this coefficient reaches the highest value that rather cannot be explained by secondary excitation as the lines of the remaining elements are situated in the longer wave region than the K absorption edge for selenium (Fig. 2). In a similar way for chromium the discrepancies between slopes of straight lines for various materials do not result from absorption effects – the relative difference between absorption coefficients amount to only about 2.5%. The absorption edge for chromium is also not situated in the nearest vicinity of the lines of the remaining elements. A substantially larger value of slope of a straight line for chromium in

Cu-Ni-Cr-Se compared to the remaining materials results from a few times smaller content of this element in the calibration materials (0.77%). In the other materials the chromium content is of the order of 20%. In the discussed case large differences in values of slopes of straight lines indicate a necessity of using a calibration material with a composition close to the studied material. This seems to be especially necessary when the contents of the determined element is close to the detection limit (for chromium ~0.07%). For zinc also differences between values of slopes of straight lines are rather not justified by various absorption of radiation in various materials or by the secondary excitation. Another situation occurs in the case of manganese, for which the difference between calibration coefficients for Yb-Mn-As and Zn-Mn-As is very small while the difference between average mass absorption coefficients is very large, about 68%. The difference results from a strong absorption (case considered for thick samples) of K_{α} Mn radiation by Yb (M edges) existing at a relatively high content in Yb-Mn-As (Fig. 3). The absorption effect rather cannot be compensated with secondary excitation with less intensive ytterbium lines $L_{\beta 1}$ and $L_{\alpha 1}$. Also for arsenic the differences between slopes of straight lines are of the same order, like in the discussed cases of selenium, chromium or zinc, while the relative difference between mass absorption coefficients that amounts to 84% might indicate very substantial differences in K_{α} As radiation absorption in both materials (absorption of K_{α} As line by close absorption edges of ytterbium – in the case of thick samples). The nature of the above considerations is rather qualitative than quantitative. However, they indicate that discrepancies in slopes of straight lines are not caused by interelement influences, what is also confirmed by calculated mass per unit area. On the contrary, these differences may originate from likely granularity effects as well as from some errors of analysis of calibration material, that could be avoided to a large extent having a certified reference material – CRM (it isn't easy available for those materials). Granularity effect may be minimized ensuring appropriate grain diameter – below 5 μm .

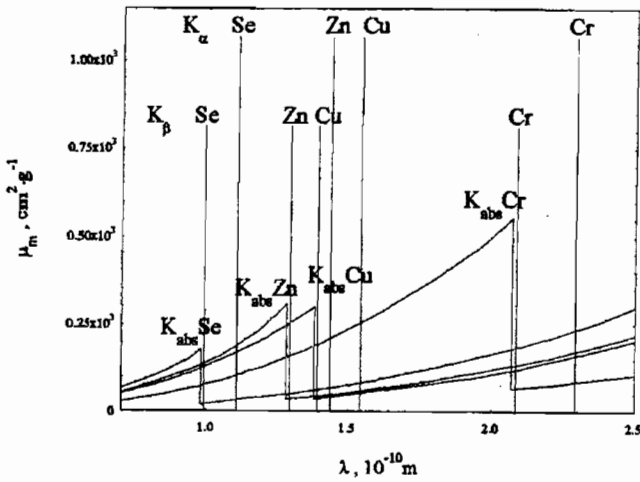
Table 4. Calibration straight lines common for various materials

Element	Materials	Equation of calibration I -intensity in counts/40s m -mass of the element in μg	std , μg	std_{rel} %	r
Zn	Cu-Zn-Cr-Se, Zn-Ga-Cr-Se, Zn-Ni-Cr-Se, Yb-Zn-Sb, Zn-Mn-As	$I = (1.95 \cdot 10^4 \pm 32) \cdot m + (2159 \pm 3427)$	4.01	2.7	0.9983
Cr	Cu-Zn-Cr-Se, Zn-Ga-Cr-Se, Zn-Ni-Cr-Se, Cu-Ni-Cr-Se	$I = (0.87 \cdot 10^4 \pm 32) \cdot m + (2382 \pm 4018)$	9.49	6.9	0.9937
Se	Cu-Zn-Cr-Se, Zn-Ga-Cr-Se, Zn-Ni-Cr-Se, Cu-Ni-Cr-Se	$I = (1.63 \cdot 10^4 \pm 62) \cdot m + (26853 \pm 24816)$	24.51	5.9	0.9930
Ni	Zn-Ni-Cr-Se, Cu-Ni-Cr-Se	$I = (1.70 \cdot 10^4 \pm 63) \cdot m + (2227 \pm 1890)$	1.49	4.0	0.9970
Yb	Yb-Zn-Sb, Yb-Mn-As	$I = (0.24 \cdot 10^4 \pm 12) \cdot m + (1552 \pm 2811)$	14.17	5.2	0.9952
Cu	Cu-Zn-Cr-Se, Cu-Ni-Cr-Se	$I = (1.44 \cdot 10^4 \pm 61) \cdot m + (6555 \pm 11306)$	10.32	4.5	0.9961
Mn	Yb-Mn-As, Zn-Mn-As	$I = (1.22 \cdot 10^4 \pm 28) \cdot m + (1283 \pm 5523)$	5.08	2.4	0.9988
As	Yb-Mn-As, Zn-Mn-As	$I = (1.66 \cdot 10^4 \pm 41) \cdot m + (11251 \pm 9347)$	6.25	2.5	0.9987

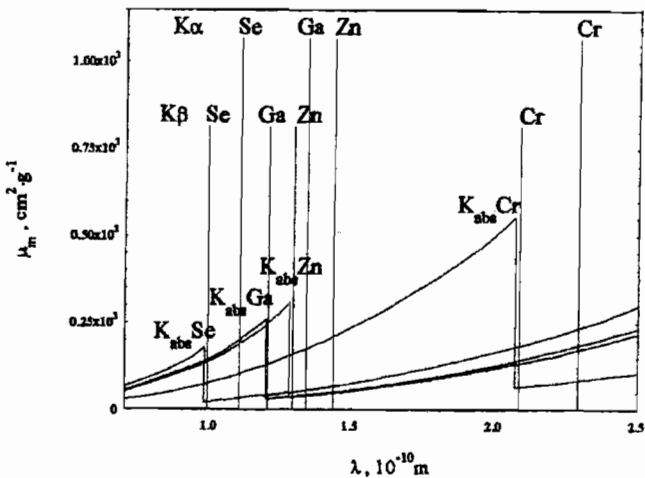
Table 5. Average mass absorption coefficients $\bar{\mu}_{\lambda,i}$ for lines of *i*-elements in different materials

Material	$\bar{\mu}_{\lambda,i}, \text{cm}^2 \text{g}^{-1}$							
Cu-Zn-Cr-Se	Cu K_{α}	118	Zn K_{α}	97	Cr K_{α}	198	Se K_{α}	72
Zn-Ga-Cr-Se	Zn K_{α}	101	Ga K_{α}	84	Cr K_{α}	203	Se K_{α}	66
Cu-Ni-Cr-Se	Cu K_{α}	71	Ni K_{α}	87	Cr K_{α}	203	Se K_{α}	96
Zn-Ni-Cr-Se	Zn K_{α}	101	Ni K_{α}	141	Cr K_{α}	203	Se K_{α}	71
Yb-Zn-Sb	Yb $L_{\alpha 1}$	228	Zn K_{α}	152	Sb $L_{\alpha 1}$	629	–	–
Yb-Mn-As	Yb $L_{\alpha 1}$	195	Mn K_{α}	227	As K_{α}	201	–	–
Zn-Mn-As	Zn K_{α}	124	Mn K_{α}	135	As K_{α}	109	–	–

a)



b)

**Figure 2.** Interelement influences in: a) Cu-Zn-Cr-Se, b) Zn-Ga-Cr-Se, c) Cu-Ni-Cr-Se, d) Zn-Ni-Cr-Se

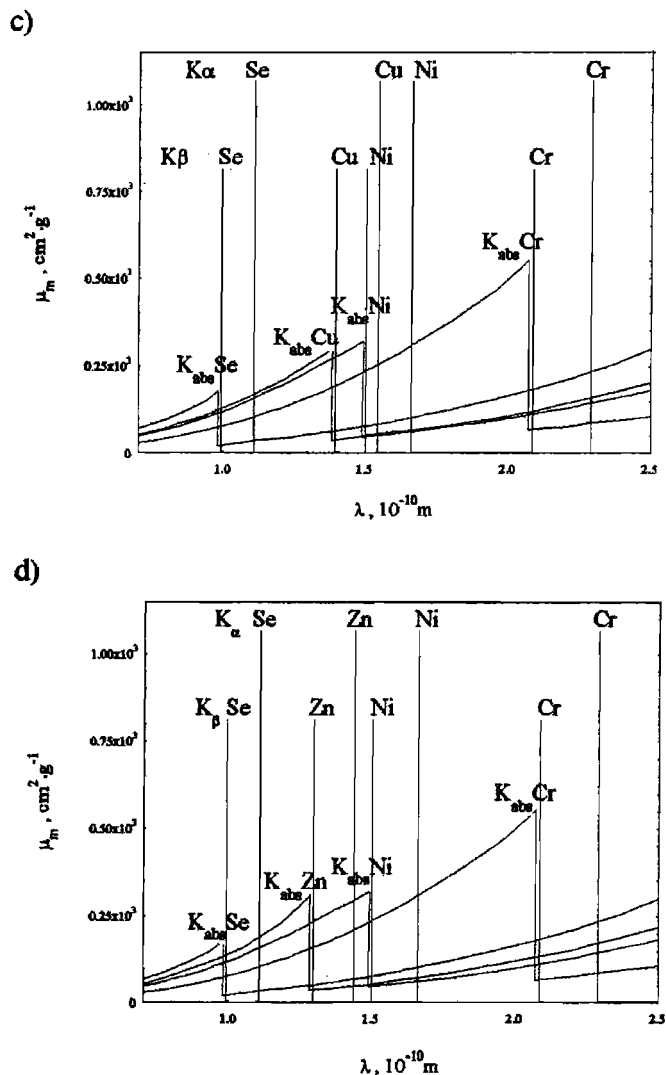


Figure 2. (Continuation)

To determine the detection limit the criterion was assumed: $C_o = 3S_b/k$ [17], where $S_b = \sqrt{N_b}$ is the standard deviation that characterises reproducibility of the background, k is the slope of a straight line that characterizes sensitivity of the method. The obtained values of detection limits for 0.5 mg samples are shown in Table 6. Both the fact that the entire mass of sample was included in the analysis and negligible absorption effects make that detection limits expressed in absolute units, e.g. μg , practically independent on the mass of material in the studied range [12]. Detection limits expressed in relative units are strongly improved with increasing mass of sample. This dependence is hyperbolic and may be one of criteria of sample mass selection

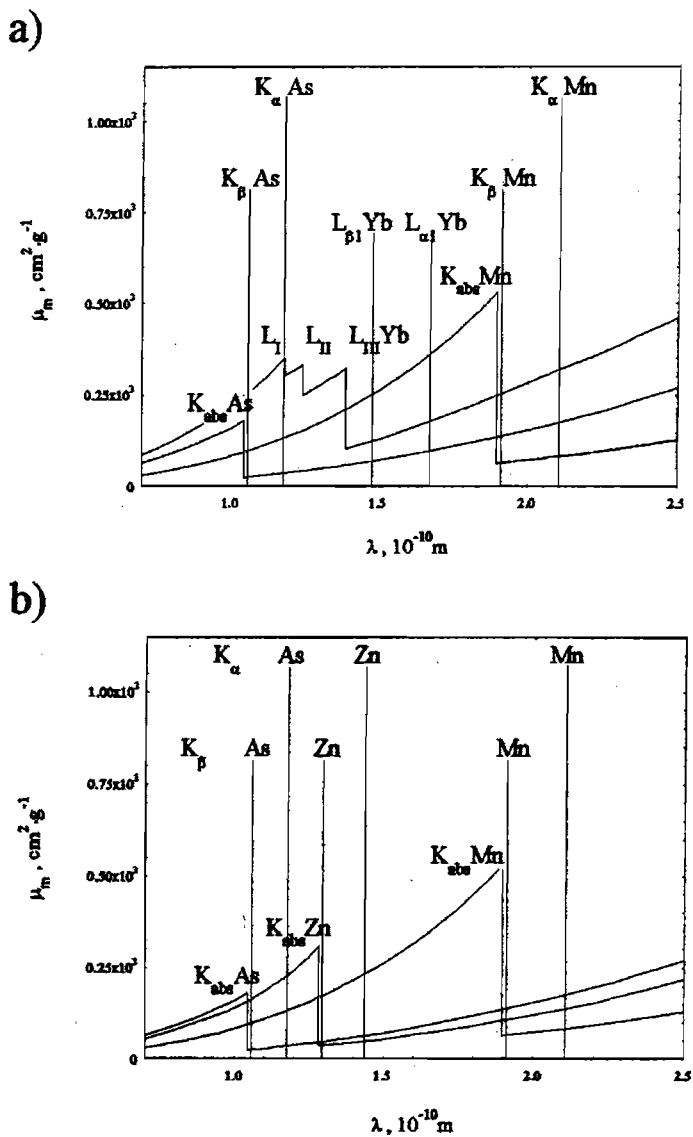


Figure 3. Interelement influences in: a) Yb-Mn-As, b) Zn-Mn-As

for analysis, especially where the concentration of determined elements are small. An example is presented in Figure 4. Detection limits expressed in relative units were calculated using formula $C_{o, \%} = (C_{o, \mu\text{g}}/m) \cdot 100\%$ where $C_{o, \mu\text{g}}$ is the detection limits expressed in absolute units (μg), m is the sample's mass in μg .

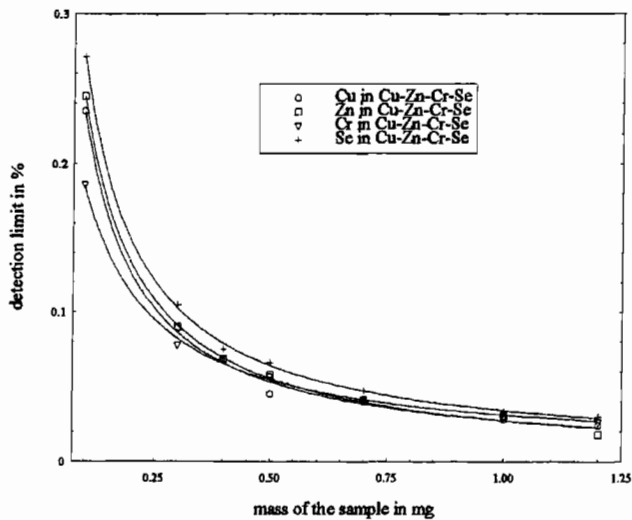


Figure 4. Dependence of detection limit in mass % of elements on mass of the sample for Cu-Zn-Cr-Se

Table 6. Detection limits C_0 in different units for 0.5 mg samples

Element	C_0		
	%	μg	$\mu\text{g cm}^{-2}$
Cr	0.068	0.34	0.07
Mn	0.044	0.22	0.04
Ni	0.040	0.20	0.04
Cu	0.058	0.29	0.06
Zn	0.064	0.32	0.06
Ga	0.054	0.27	0.05
As	0.074	0.37	0.07
Se	0.080	0.40	0.08
Sb	0.364	1.82	0.36
Yb	0.254	1.27	0.25

The elaborated method of the sample preparation was examined by the authors on the example of the polycrystals with a known chemical composition (synthesized by ceramic method). Each time the analysis was carried out on the basis of three samples, three measurements were performed for each of them. Average results \bar{C} of XRF analysis are presented in Table 7. Standard deviations s (Table 7) characterized sample preparation, precision of the measurements, inhomogeneity of the mass per unit area and also material inhomogeneity were calculated according to the following formula:

$$s = \sqrt{\frac{\sum_{i=1}^m \sum_{j=1}^n (\bar{C} - C_{ij})^2}{m \cdot (n-1)}}$$

where $m = 3$ is the number of samples, $n = 3$ is the number of measurements for each sample, \bar{C} is the average value of the element's concentration, C_{ij} – is the concentration calculated from one measurement. Values of the standard deviations are strongly dependent on the concentration of the determined element (Zn, Ni, Cu), for chromium with content 20–22% amount on average to 0.8% and for selenium to 1.1% (content 64–66%). Differences $\Delta = \bar{C} - C_{real}$ between results of XRF analysis \bar{C} and chemical composition C_{real} of the spinels $Zn_xNi_yCr_zSe_4$ and $Cu_xNi_yCr_zSe_4$ (where x, y, z are well-known) result rather from the accidental errors. The obtained results of accuracy and precision are satisfactory considering the simplicity of the sample preparation and the small amount of analyte.

Table 7. Results of powder samples analyses of Zn-Ni-Cr-Se and Cu-Ni-Cr-Se with well-known chemical composition C_{real}

Chemical composition of analyzed materials			XRF analysis		
Material	Element	$C_{real}, \%$	$\bar{C}, \%$	$s, \% *$	$\Delta, \%*$
$Zn_{0.9}Ni_{0.1}Cr_2Se_4$	Zn	12.14	11.85	0.47	-0.29
	Ni	1.21	1.32	0.09	0.11
	Cr	21.46	20.97	0.89	-0.49
	Se	65.18	66.04	0.92	0.86
$Zn_{0.2}Ni_{0.8}Cr_2Se_4$	Zn	2.72	2.65	0.08	-0.07
	Ni	9.79	8.97	0.79	-0.82
	Cr	21.67	22.53	0.95	0.86
	Se	65.82	65.11	1.21	-0.71
$CuNi_{0.1}Cr_{1.9}Se_4$	Cu	13.13	12.85	0.20	-0.28
	Ni	1.21	1.27	0.11	0.06
	Cr	20.41	20.03	0.79	-0.38
	Se	65.25	64.08	1.34	-1.17
$Cu_{0.9}Ni_{0.1}Cr_2Se_4$	Cu	11.84	12.74	0.88	0.90
	Ni	1.22	1.27	0.09	0.05
	Cr	21.53	20.76	0.59	-0.77
	Se	65.41	65.92	1.07	0.51

*see in text.

CONCLUSIONS

A quick and simple preparation allows preparing powder samples from a disintegrated material within about 15 min. The analysis of samples below 1 mg of weight allows to apply it there, where the amount of material assigned for analysis is limited, e.g. a synthesis of non-conventional materials. Application of one material for cali-

bration substantially simplifies the entire process of multielement analysis. Thanks to using the thin layer method a possibility of neglecting interelement influences creates a possibility of drawing calibration straight lines common for various materials. Using weighed amounts of the order of 0.1–0.2 mg there is a possibility to determine the inhomogeneity of the studied material, especially in the cases where the obtained product features a high inhomogeneity, for example in the case of heterogeneous synthesis carried out by thermal transport.

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