

A Method for the Determination of Mass Per Unit Area Inhomogeneity of Thin Samples in XRF Analysis

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The authors have presented a simple method for the determination of possible inhomogeneity of thin samples in a wadedispersive XRF analysis after previous examination of intensity distribution of exciting radiation on sample's surface. Investigations were carried out using as an example microsamples of mono- and polycrystals. Samples were prepared by digesting an analyzed material directly on the substrate. The obtained results have been presented in a graphical way.

Autorzy przedstawili prosty sposób wyznaczania ewentualnej niejednorodności cienkich próbek w falowodyspersyjnej analizie XRF po uprzednim przebadaniu rozkładu natężenia promieniowania wzbudzającego na powierzchni próbki. Badania przeprowadzono na przykładzie mikropróbek mono- i polikryształów. Próbki przygotowano poprzez roztworzenie badanego materiału bezpośrednio na podłożu. Uzyskane wyniki przedstawiono graficznie.

Application of thin layer method in XRF analysis allows to minimize to a large extent the inter-element influences; effects connected with the morphology of sample, such as granulation, mineralogical effect or inhomogeneity of the mass per unit area remain and their elimination is possible by appropriate preparation of the sample. The first two sources of error are frequently eliminated by a wet method through digestion of the investigated material and dropping the obtained solution onto the substrate. However, a granularity effect may occur then as a result of recrystallization [1]. Minimization of the aforementioned effects in the case of powder samples consists in homogenization and disintegration of material to achieve appropriate grain

size, ensuring sample's representativeness with respect to the entire population studied [2]. An inhomogeneity effect connected with uneven distribution of a material on the substrate may remain. There are numerous techniques used that require application of appropriate apparatus to filter or precipitate a disintegrated material on the substrate, *e.g.* under pressure [3]. In the case of dropping standard solutions there is, among other things, a problem of selecting conditions of drying [4]. Apart from a traditional method of dropping solutions authors of paper [5] present a method of depositing standard solutions in the form of an aerosol using a specially constructed apparatus. Paper [6] presents a simple method of determination of intensity distribution of exciting radiation in EDXRS analysis and a method of analysis of thin inhomogeneous samples precipitated and deposited on a Millipore filter. Having in mind an inhomogeneity of exciting radiation distribution on sample's surface one can expect varied intensities of fluorescent radiation from various places of dropping the standard solution onto the sample [7], *e.g.* at investigating the chemical composition of environmental samples. Preparation of microsamples for XRF analysis by the thin layer method, both in the case of mineralogical materials [8,9] and multielement mono- and polycrystals [9,10], by digesting the material directly on the substrate not always leads to obtaining samples of homogeneous thickness and the control of the analyzed material distribution on the substrate is especially difficult, hence the attempt presented in this paper to study the inhomogeneity of samples' mass per unit area.

EXPERIMENTAL

Apparatus and conditions of measurement

PW 1410 and PW 1450 wadedispersive sequential spectrometers with Mo and W X-ray tubes, respectively; 45° angle of primary radiation incidence on the sample, angle of reflection depending on the determined element; LiF 200 analyzing crystal; 150 μm fine collimator; measurements in vacuum with rotation of sample; detection time $t = 100$ s; analytical lines: K_{α} Cu (0.1542 nm, flow counter), K_{α} Se (0.1106 nm, flow and scintillation counter).

PROCEDURES AND DISCUSSION OF RESULTS

Authors of papers [9,10] have presented a quick method for the preparation of microsamples (weighing fractions of milligram) of multielement mono- and polycrystals of M/N/Cr/Se compositions, where M,N – Cu, Zn, Ga, Co, Ni and Yb/Zn/Sb. Material disintegrated and weighed on a microbalance (~0.5 mg with accuracy of 0.001 mg) was digested directly on the substrate used by dosing portions of concentrated nitric and hydrochloric acids. The choice of a digesting agent depended on the studied material and conditions of the reaction carried out. A Millipore filter was the

substrate (AA type, Bedford, Mass., USA; Ø25 mm) glued onto a glass plate by means of a two-sided adhesive tape.

During digestion of disintegrated natural samples of the aforementioned mono- and polycrystals a convection of still not digested material to the edges of a filter by added acids and a chromatographic effect were observed. These processes may result in concentration of the digested materials on filter edges or in various places of its surface. The observation of the described phenomenon was possible due to a green color of chromium (Cr^{3+}) cations originating in digestion of spinels containing this element. The described phenomenon occurring also in the case of other materials was studied having in mind its likely consequences inter alia in deterioration of the precision of obtained results as an effect of inhomogeneity of sample's mass per unit area. The other effect considered was the possible intensification of inter-element influences in various parts of the filter as a result of concentration of elements and a local increase of samples' thickness in this area.

Studying the inhomogeneity of prepared thin samples in XRF analysis the authors have initially determined the distribution of primary radiation incident on the surface of the sample. A simple and quick procedure was used. The substrate was prepared – a polystyrene disk with a glued on two-sided adhesive tape on which a millimetre scale was superimposed. A disk of 5 cm diameter was fitted to dimensions of the spectrometer cassette. Measurements were carried out as follows: a copper element of dimensions about 0.7×3 mm was glued on the substrate according to the superimposed scale starting from the centre of the disk (radius = 0), two measurements were carried out, the aforementioned element was detached, glued on the same place and two measurements were carried out again. This procedure allowed to reduce errors resulting from inaccuracy of the place of gluing the copper element. The subsequent points of measurements were obtained in an analogous way moving the copper sheet by one millimetre (radius = 1, 2, 3, ... 20 mm). Measurements were carried out during rotation of the spectrometer cassette, hence in the range from -20 to 20 mm at location of the copper element for $r = 0 \dots 20$ mm. The obtained results, for both spectrometers, averaged for four measurements (K_{α} Cu line) are presented in a graphical way in Figure 1 after normalization. The substrate itself without copper was a blank sample. For PW 1410 spectrometer with a molybdenum tube a slightly larger area covered by the exciting radiation was found. The obtained results provide not only the information on the geometry of radiation incidence on the sample but also on its detection.

Having the information on the distribution of radiation incident on the sample and on its detection the authors have investigated the inhomogeneity of a typical sample prepared for previous analyzes by digesting the analysed material – Cu/Zn/Cr/Se spinel (about 14% Cu, 3% Zn, 22% Cr and 61% Se) directly on the substrate. Measurements of intensity of fluorescent radiation originating from various points of the sample were carried out. A copper masking frame with a sliding aperture of 2 mm diameter was used for that and the measured sample was placed behind it. The location of measuring points is shown in Figure 2. Measurements were carried out for sele-

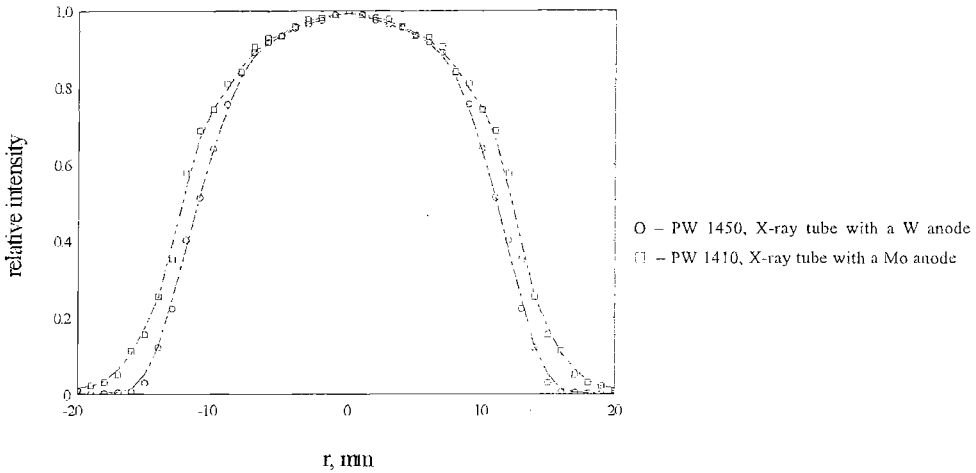


Figure 1. Distribution of X-ray tube radiation distribution on the surface of the sample

nium, concentration of which in the analyzed material was the largest (about 61%). In the case of remaining elements, *i.e.* copper, zinc and chromium, that occur at smaller concentrations, the obtained intensities of fluorescent radiation were insufficient due to a very small area covered with analysis ($\varnothing 2$ mm) at a small mass of the analyzed sample, *i.e.* 0.13 mg cm^{-2} (weight of sample about 0.6 mg on a filter of 4.52 cm^2 area). The masking frame made of copper was thicker than the critical thickness for K_{α} Se line for which measurements were carried out (PW 1410 spectrometer with an Mo tube). The obtained average results for individual points of radial $r = 0, 2, 4, 6, 8$ and 10 mm and angular $\alpha = 0^{\circ}, 45^{\circ}, 90^{\circ}, 135^{\circ}, 180^{\circ}, 225^{\circ}, 270^{\circ}$ and 315° coordinates are

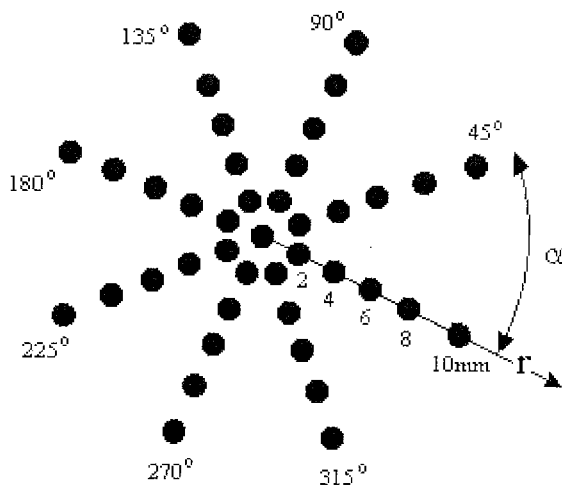


Figure 2. Location of measuring points

given in Table 1. Table 2 presents a relative selenium concentration in various points of the sample. Calculation were carried out taking into account the proportionality of fluorescent radiation to the intensity of exciting radiation:

$$I \sim C \cdot I_0$$

The relative intensity of the primary radiation for individual areas of radiation measurement was determined by calculating the area under the curve of radiation distribution (Fig. 1) for PW 1410 spectrometer.

Table 1. Results of selenium (K_{α}) radiation intensity measurements performed in various places of the sample

α	I_s counts/100 s (net)					
	$r = 0$ mm	$r = 2$ mm	$r = 4$ mm	$r = 6$ mm	$r = 8$ mm	$r = 10$ mm
0	7 417	8 033	8 170	7 993	9 023	10 783
45	—	7 050	9 700	8 328	9 778	10 723
90	—	9 573	9 140	9 610	10 300	13 560
135	—	8 148	9 893	10 363	14 805	16 405
180	—	7 543	9 510	10 415	13 943	13 720
225	—	8 373	8 445	9 818	10 550	14 068
270	—	8 583	8 808	9 433	11 840	12 433
315	—	7 695	8 185	8 818	9 803	11 983

Table 2. Relative concentration of selenium in individual areas of the sample

α	$r = 0$ mm	$r = 2$ mm	$r = 4$ mm	$r = 6$ mm	$r = 8$ mm	$r = 10$ mm
	$\int_{-1}^1 I_0(r) dr = 1$	$\int_1^3 I_0(r) dr = 0.991$	$\int_3^5 I_0(r) dr = 0.965$	$\int_5^7 I_0(r) dr = 0.928$	$\int_7^9 I_0(r) dr = 0.856$	$\int_9^{11} I_0(r) dr = 0.746$
0	0.337	0.369	0.385	0.391	0.479	0.657
45	—	0.324	0.457	0.408	0.519	0.654
90	—	0.440	0.431	0.471	0.547	0.827
135	—	0.374	0.466	0.508	0.786	1.000
180	—	0.346	0.448	0.510	0.741	0.837
225	—	0.384	0.398	0.481	0.560	0.858
270	—	0.394	0.415	0.462	0.629	0.758
315	—	0.353	0.386	0.432	0.521	0.730

Relative values of individual integrals are also given in Table 2. The selenium concentration was calculated with respect to the area of the highest concentration of this element:

$$C_{rel,\alpha,r} = \frac{1}{C_{max,\alpha,r}} \cdot \frac{I_{\alpha,r}}{\int_{r-1}^{r+1} I_0(r) dr} = \frac{\int_{r'-1}^{r'+1} I_0(r') dr'}{I_{\alpha,r'}} \cdot \frac{I_{\alpha,r}}{\int_{r-1}^{r+1} I_0(r) dr}$$

In the case of the studied sample it was the area of coordinates $\alpha = 135^\circ$, $r = 10$ mm:

$$C_{rel,\alpha,r} = \frac{\int_9^{11} I_0(r) dr}{I_{135,10}} \cdot \frac{I_{\alpha,r}}{\int_{r-1}^{r+1} I_0(r) dr} = \frac{0.746}{16405} \cdot \frac{I_{\alpha,r}}{\int_{r-1}^{r+1} I_0(r) dr} = 4.547 \cdot 10^{-5} \cdot \frac{I_{\alpha,r}}{\int_{r-1}^{r+1} I_0(r) dr}$$

where: α, r – coordinates of the measuring point; $C_{rel,\alpha,r}$ – concentration of the element in the place of coordinates α and r ; $I_{\alpha,r}$ – intensity of fluorescent radiation; α' and r' – coordinates of the measuring point corresponding to the highest concentration of the element $C_{max,\alpha',r'}$; $\langle r-1, r+1 \rangle$ – integration range (2 mm diameter of the measurement area).

Taking into account the intensity distribution of the primary radiation allows to obtain a real distribution of the studied material concentration after its direct digestion on the filter. As predicted, the obtained results indicate that there is a pre-concentration of the sample on edges of the filter. The described phenomenon is presented in a graphical way in Figure 3.

The inhomogeneity of the mass per unit area of prepared thin samples or intermediate samples may be the source of errors of the performed analysis due to local interelement influences in the areas, where the concentration of the sample increases and due to the inhomogeneity of intensity distribution of the exciting radiation – the element of diversified concentration in individual areas is excited to fluorescence with various intensity. In previous papers [9,10] the authors have analyzed Cu/Zn/Cr/Se, Zn/Ga/Cr/Se, Cu/Co/Cr/Se, Cu/Ni/Cr/Ce, Yb/Zn/Sb mono- and polycrystals of diversified chemical compositions. The calibration carried out using synthetic reference samples with a similar distribution of the analyzed material concentration allowed to avoid a likely systematic error. The precision of preparation a natural samples was determined. Thirteen materials were altogether analyzed, for each material three samples were prepared and three measurements were performed for each sample. The obtained values of standard deviations are determined not only by sample's preparation (inter alia inhomogeneity of mass per unit area) but also by inhomogeneity of the material itself (samples of 0.5 mg weight) and to a smaller extent by measurement's precision. For selenium existing in studied materials on average at the level of 62% the relative standard deviation (RSD) amounts on average to 0.87%, for chromium with average concentration of 19%, RSD on average is equal to 1.7%. The metals being determined Zn, Ga, Cu, Co, Ni, Yb, Sb existed in the studied

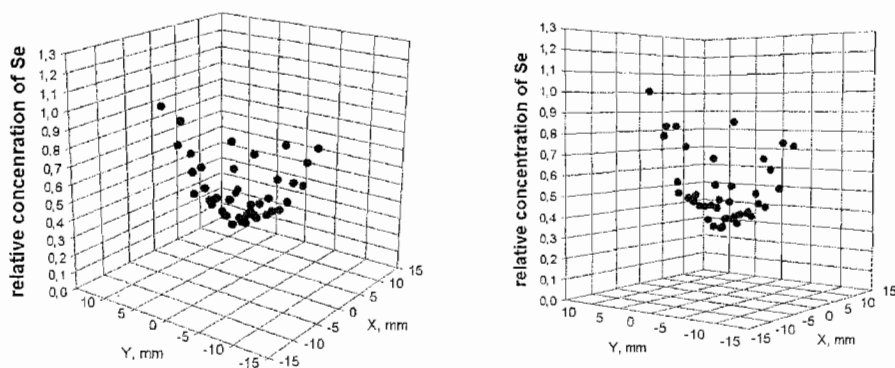


Figure 3. Distribution of concentration of the analyzed material digested directly on a filter; X, Y axes – situation of measuring points (Cartesian coordinates)

materials at very diversified levels from tenths of a percent to several dozens of percent. For metal contents of about a few or a dozen or so percent the RSD usually does not exceed the value of 3.5%. A relative standard deviation for small contents of elements, *i.e.* one percent and less, reaches very diversified values of a few or a dozen or so percent what may result from a large inhomogeneity of the material. The obtained results of precision of preparation of natural samples were considered as satisfactory taking into account its simplicity, small weights of the analyzed material (about 0.5 mg) and a large inhomogeneity of studied crystals resulting from the method of their synthesis.

CONCLUSIONS

The described method allows to determine a likely mass per unit area inhomogeneity of the samples in a quick and simple way, after previous determination of exciting radiation distribution on the sample's surface. The knowledge of inhomogeneity of sample distribution on the substrate is needed considering its effect on the reproducibility of results. A likely deterioration of precision and accuracy of results arises from various intensities of element's fluorescence in individual areas of the sample (inhomogeneity of the exciting radiation distribution). A similar distribution of the material on the substrate both in standard and in studied samples (as in the worked-out method [9,10]) causes compensation of the aforementioned errors. However, if the accuracy of the obtained results is unsatisfactory, *e.g.* as a result of various distribution of the material in standards and in the analyzed samples, the methods of preparation allowing to obtain samples of better homogeneity of samples' mass per unit area are looked for or there are attempts to use mathematical methods taking into

account the aforementioned inhomogeneity and the excitation radiation distribution on the sample's surface [6].

Classification of samples to the class of thin layer method according to frequently assumed criteria on the basis of knowledge of mass coefficients values and the geometry of measurements [11,12] may be erroneous for samples that are inhomogeneous with respect to mass per unit area. Local preconcentration of the analyzed material may be not only the cause for intensification of interelement influences but in an extreme case also a local excess of critical thickness of the sample (t_{\max}). These were the reasons that while classifying samples authors determined their relative thicknesses ($t_{\text{rel.}} = t_{\text{sample}}/t_{\max}$) measuring the element's radiation intensity in the studied sample and in the reference sample of much higher weight, situated outside the area of thin layer, but prepared in the identical way as the studied sample [9]. The obtained results indicated that the values of errors resulting from matrix effects were smaller than one percent. In places where the measurements were carried out the sample thicknesses were many times smaller than the critical thickness.

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