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Dependence of Determination Quality on Performance Capacity of Researching Technique, Exemplified by the Electron Probe X-Ray Microanalysis

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1. Introduction

The quality of results obtained by any analytical method depends on every stage of data acquisition: representativeness of study object; appropriate sample preparation; optimum conditions for analytical signal excitation and registration; availability of reference materials for comparison; procedure to process acquired values referred to the content to be determined. These characteristics vary in different analytical methods. In some cases, the sample preparation represents the major source for analytical errors, in some others, the complexities arise from the incorrect selection of calibrating plot, and thus availability of reference materials for comparison is essential. The technique specifications pose the requirements to every stage of analysis.

The problem of quality has ever been critical in analytical work, and every time it depends on the level of progress in the theory and application of selected technique.

Quality has emerged and remained the dominant theme in management thinking since the mid-twentieth century (Beckford, 2010).

2. Quality of the electron probe X-ray microanalysis at each stage

The electron probe X-ray microanalysis is a fairly young technique. The first papers describing the basics of electron probe microanalysis (EPMA) (Castaing, 1951; Borovskii, 1953) and original designs and constructions of microanalyzers (Castaing & Guinier, 1953; Borovskii & Il'in, 1956) were published in 1951-1956 in France and the USSR. The technique was rapidly progressing. In 1973 Borovskii (Borovskii, 1973), the founder of EPMA in Russia, admitted that one could hardly identify the fields of science and engineering, where the EPMA had not been successfully used. The instruments and theory were developing simultaneously.

At present it is difficult to overestimate the significance and application of the method. It is one of the leading methods in mineralogy, and similarly in metallurgy and biology. The investigations of the micro-level are required at approbation of technological processes in all fields of science and engineering.

The quality of results is of prime importance for researchers in all fields of science. The specifics of the method related to obtaining information suggest it to be the research technique, thus intensifying the problem of determination quality, rather than the analytical method. The studies on developing the theoretical foundation of the method and upgrading the instruments, reported in numerous publications, and partly mentioned in the articles reviewed by authors of articles (Szaloki et al., 2004; Pavlova et al., 2000), allow the way of improving quality of the electron probe X-ray microanalysis to be observed. The topical studies undertaken by the author are included into this chapter.

2.1 Representativeness of materials

The representativeness of the sample substance is initially defined when posing problem, and it depends on the requirements of particular analytical technique. These requirements imply the subsample weight, homogeneity of components, and particle size in the subsample, solubility and miscibility of subsample substance with a binding substance or a solvent, and others.

In case of EPMA the representativeness of determinant, namely the quantity of samples and size of the surface, prepared for examination, depend on the frequency of component occurrence in material, probability of their occurrence on the prepared surface and their phase distribution over the investigated surface. In electron probe microanalysis, when we study the inclusions rarely occurring in the groundmass, it is essential to have a sufficient amount of the geological substance to be examined.

In EPMA a correct solution of the problem posed is dependent on the frequency of determinant occurrence within the observation zone. With EPMA, an absence on the studied surface of the element to be defined is not suggestive of its complete lack in the sample. It might be assumed, that the sought element has skipped from the study zone.

It can be exemplified by searching for the invisible gold in lithochemical stream sediments of the Dukat gold-silver deposit in northeastern Russia. Initially, the studies of rock in thin and polished sections did not provide wanted results - fine gold inclusions have not been detected. The probability of gold inclusion occurrence on the studied surface was negligibly small. Only having extracted the heavy fraction and prepared the briquette thin sections and after locating grains on the surface and polishing thin sections and thoroughly studied numerous grains in the thin section we managed to obtain positive results.

If the sought inclusion had not been found on the surface, a thin layer of substance was removed, and researched through entire sample. The process was being repeated until the sought inclusion was found (Fig. 1). If the grains of heavy fraction were completely polished down a new briquette thin section of the same sample was prepared and searching was continued. Figure 1 presents the gold inclusion found in the mineral only after the third try of surface polishing. The size of the inclusions is 10 μm, while the area of thin section is about 25mm². In such cases the quality of investigations and conclusion correctness result from both correctly selected and prepared material and thorough search.

2.2 Sample preparation

In any technique sample preparation is truly important, that is decisive for analytical procedures. In different analytical methods the laboriousness of sample preparation varies. Because the EPMA, in effect, is the analysis of a surface, the sample surface is required to be flat, well polished, smooth and clean and to have a good conductivity. Sample preparation
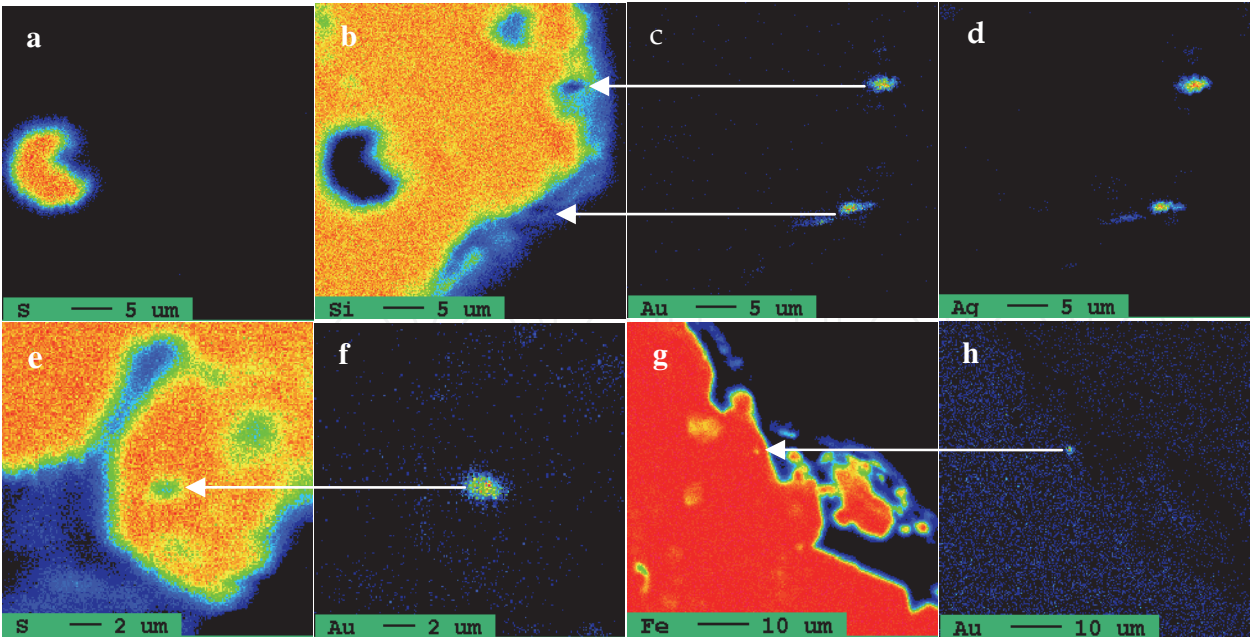
Fig. 1. The gold inclusion found in the mineral only after the third try of surface polishing.

for the electron probe microanalysis is in many ways still as much of an art as a science (Goldstein et al., 1992). Different procedures are applied in EPMA for sample preparation. The solid samples for EPMA may be thin sections, thick micro sections, briquette sections and isolated particles. The preparation of polished thin sections and thick micro sections consists in selecting sized solid material, its cutting, polishing selected surface with diamond pastes.

2.2.1 Particle preparation

When examining the grinded substance the particles should be fixed so that they are not scattered in air and retain the representativity of material when investigated in the vacuum microanalyzer. Various preparation procedures are used to analyse different solid particles (Pavlova et al., 2001): (1) fixing particles on substrate with colloid; (2) pasting particles on the carbon double-faced adhesive tape; (3) preparing briquette sections. In the first case particles are fixed on the polished surface of the substrate with collodion. The particles are distributed as a thin layer on the surface of the substrate, which is preliminarily covered by a thin layer of the liquid collodion. While drying the collodion fixes the particles on the surface. Gluing particles on the carbonic adhesive tape is commonly applied when studying conductive materials. In this case the glued particles cannot be covered by the conductive layer.

Two techniques to prepare briquette thin sections: 1) Particles of any solid material are mixed with epoxy resin, and after the surface is hardened it is polished. 2) Grains of any solid material are glued on the adhesive tape and coated with epoxy resin. After the resin is hardened, the sample is removed from the adhesive tape and the surface with particles is polished to make it mirror-smooth. Due to this procedure plenty of grains are included in the same puck. The briquette thin sections with particles are often used for quantitative determinations of particle composition using the wave spectrometers applied for studying horizontal well polished surfaces. Table 1 presents the data on the comparison of two garnet particles composition processed by different methods of sample preparation.

Preparation			Non-polished particles				Polished particles			
Analytical method			EDS		WDS		EDS		WDS	
Sample	Oxide	Certified concent- ration, wt. %	Concentrat ion, wt. %	Relative error, %	Concentrat ion, wt. %	Relative error, %	Concentrat ion, wt. %	Relative error, %	Concentrat ion, wt. %	Relative error, %
Garnet O-145	MgO	20	20,59	2,95	21,325	6,63	20,91	4,55	19,93	-0,35
	Al_2O_3	23,4	23,62	0,94	21,286	-9,03	23,19	-0,90	23,36	-0,17
	SiO_2	42,3	42,55	0,59	43,527	2,9	42,07	-0,54	42,56	0,61
	CaO	4,03	4,14	2,73	3,06	-24,02	4,34	7,69	4,03	0,00
	MnO	0,17	0,07	-58,82	0,12	-29,41	0,16	-5,88	0,16	-5,88
	FeO	10,1	9,3	-7,92	9,63	-4,65	9,36	-7,33	10,04	-0,59
Garnet C-153	MgO	21,09	22,61	7,21	23,46	11,24	21,25	0,76	20,93	-0,76
	Al_2O_3	18,09	17,73	-1,99	19,97	10,39	18,86	4,26	17,84	-1,38
	SiO_2	41,52	42,24	1,73	42,98	3,52	42,27	1,81	41,94	1,01
	CaO	3,4	3,7	8,82	3,94	15,88	3,62	6,47	3,38	-0,59
	Cr_2O_3	7,41	6,59	-11,07	6,89	-7,02	7,09	-4,32	7,3	-1,48
	MnO	0,32	0,21	-34,38	0,27	-15,63	0,534	66,88	0,34	6,25
	FeO	7,59	6,85	-9,75	6,57	-13,44	6,163	-18,8	7,41	-2,37

Table 1. Compared compositions of two garnet particles processed by different methods of sample preparation. Relative error=100*(C-Ccer)/Ccer; C- is concentration; Ccer – is certified concentration.

The composition of non-polished particles is not determined with wave spectrometers splitting the X-ray spectrum by the wave length. The quality of determinations is low and the error can reach as high as tens percent. When the particles are glued on the substratum and adhesive tape it is feasible to study the shape and size of particles; when using the energy-dispersive spectrometer it is possible to identify (i) what elements compose grains, (ii) how elements are distributed over the surface, (iii) element contents.

2.2.2 Preparation of biological samples

The surface suitable for the analysis is hard to receive in examining porous samples, which are often biological samples. Preparation of biological materials is differently approached. For example, sponges are first rinsed in distilled water, then dehydrated in alcohol, freed from alcohol with acetone and impregnated with epoxy resin (Pavlova et al., 2004). The samples obtained are fit in one or some briquette sections. The briquette sections with specimens are polished with diamond paste to get the surface flat and mirror-smooth. The Figure 1 displays the sponge image. The solid part of the sponge, its skeleton consists of spicules. This kind of preparation of fragile biological specimens ensures intact solid part of sponge. It avoids distortions due to destructions when polishing. With this procedure we determine silicon concentration in the center of spicule cross-section and on its margins: they are higher in the center than in the margins.

2.2.3 The influence of surface on the quality of results

The distortion of horizontal position of surface (effect of absence of flat horizontal surface) is the cause of false conclusions and considerable deterioration of analytical results. If the surface is either not flat or not horizontal the analytical signal is distorted.

Figure 3 presents the pattern of x-ray radiation distribution of manganese in Mn-pure (a) and gold in Au-pure (b). Samples of pure Mn and Au have flat polished, even if not horizontal surfaces, displaying the x-ray intensity distortion. Manganese shows decrease in intensity to the right and to the left of center (Fig. 3a), because the sample surface is tilted relative to the center: the right part is higher, and the left one is lower. In Fig. 3b the gold particle bottom is in focus, but the top part is elevated toward horizon, therefore AuL_α – intensity is deformed in the top markedly lower, though the sample is homogeneous, but some inclusions. The gold image in backscattered electrons does not exhibit the surface inclination (Fig. 3c). Both gold images in Fig. 3b and Fig. 3c were simultaneously produced.

Because the grains of majority of natural samples are dielectrics, a layer of carbon (20-30 nm thick) is vacuum-sprayed onto the polished surface of all tablets to make it conductive and to remove the accumulative charge.
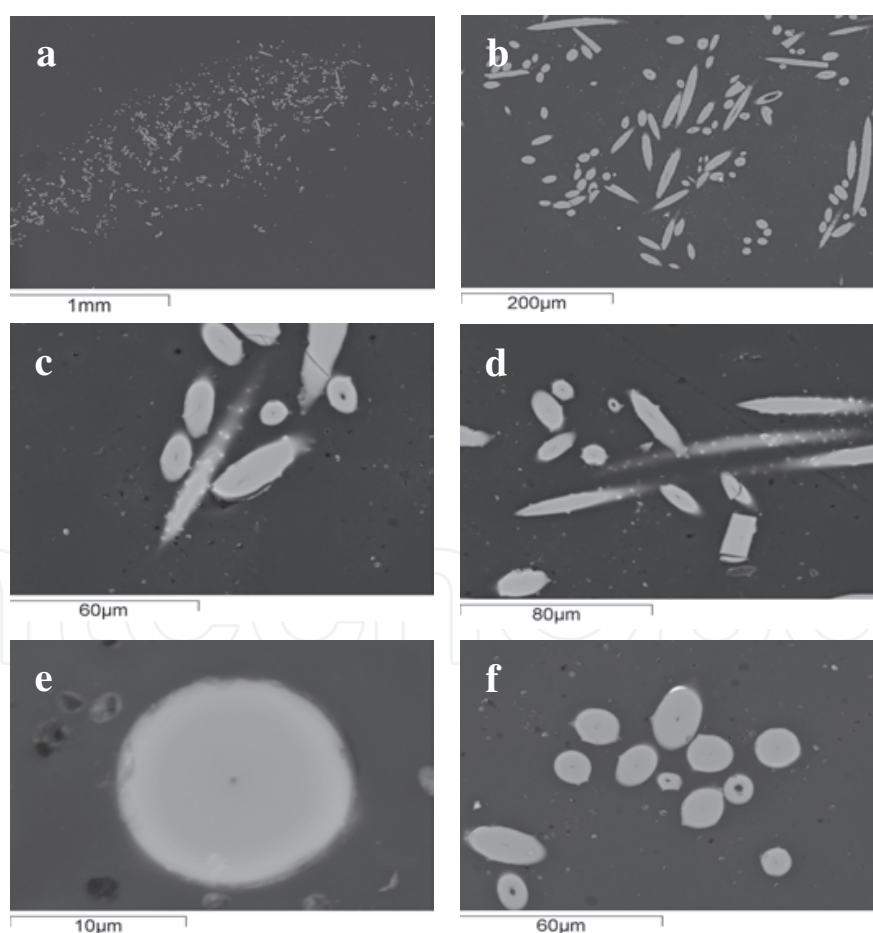

Fig. 2. The sponge surface prepared for EPMA studies. The image is given in back- scattered electrons. Section of whole sponge in epoxy resin (a). Section of sponge part (b). Sections several separate sponge spicules (c, d). Cross-sections of sponge spicules (e, f).
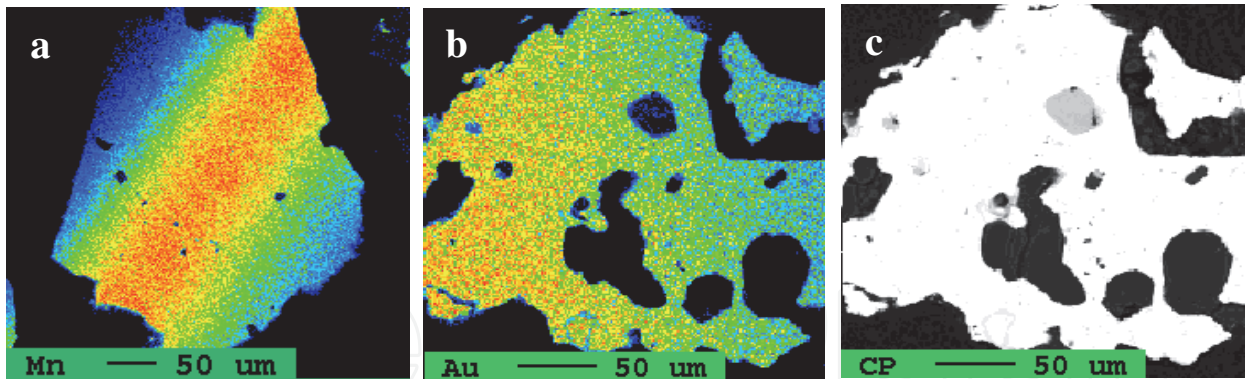
Fig. 3. Patterns of x-ray radiation distribution of manganese (a) and gold (b) in Mn- and Au-pure samples. The samples have flat polished but not horizontal surfaces.

The mass absorption coefficients are basic quantities used in calculations of the penetration and the energy deposition by photons of x-ray in biological, shielding and other materials. The different authors offer special absorption coefficients of x-ray radiation in the same element, specifically in carbon. Varying mass absorption coefficients defined in about twenty articles are discussed in the work (Hubbell et al., 2011). In Table 2 the x-ray absorption cross sections, determined by different authors for energy 0,277 keV in carbon have been compared with the experimental data contained in the National Bureau of Standards collection of measured x-ray attenuation data (Saloman et al., 1988)

The x-ray attenuation coefficients have been approximated by Finkelshtein and Farkov (Finkelshtein & Farkov, 2002). The article by Farkov with co-autors (Farkov et al., 2005) reports the data on compared absorption coefficients of nitrogen and oxygen radiation in carbon from different literature sources (Table 2). Table 3 presents the absorption coefficients of carbon, nitrogen and oxygen radiation in carbon, as well as relative deviations in the data of different authors.

Authors (Reference from the article of Saloman et al., 1988)	Fomichev V.A. & Zhukova I.I. (68FO1)	Henke et al. (67HE1)	Denne D.R. (70DE2)	Denne D.R. (70DE1)	Weiswe-iler W. (68WE1)	Messner R.H. (33ME1)	Duncumb P. & Melford D.A. (65DU1)	Kurtz H. (28KU1)	Dershem, E. & Schein, M. (31DE1)
XACS, barns/atom $*10^4$	5,600	4,569	3,850	4,09	5,056	3,43	4,587	4,200	4,400
Relative error, %	3,7	-17	-40	-31,8	-6,6	-57,2	-17,5	-28,4	-22,5

Table 2. X-ray absorption cross sections, determinated by different authors (Saloman et al., 1988). XACS - is X-ray absorption cross sections of authors; Relative error= -EXPS - XACS)/ EXPS)*100; EXPS - is experimental data contained in the National Bureau of Standards collection of measured x-ray attenuation data.

Emitter	CK_{α}			NK_{α}			OK_{α}		
Authors	(Heinrich, 1986)	Henke*, 1967	(Henke, 1993)	(Heinrich, 1986)	Henke*, 1967	(Henke, 1993)	(Heinrich, 1986)	Henke*, 1967	(Henke, 1993)
Carbon absorber	2147	2292	1960	23585	21784	25000	11575	9079	12100
Athor-Heinrich, 1986	-	6,3	-9,5	-	-8,3	5,7	-	-27,5	4,3
Athor – Henke*, 1967	-6,7	-	-16,9	7,6	-	12,9	21,6	-	25,0
Athor – Henke, 1993	8,7	14,5	-	-6,0	-14,8	-	-4,5	-33,3	-

(Leftmost rotated label for the last three rows: Relative deviation, %)

Table 3. X-ray absorption coefficients (centimeter²/g) in the carbon and relative deviations in the data of different authors. *Henke's data from work of Saloman (Saloman et al., 1988). Relative deviation=(Author-Comp)/Author*100%. Author - is data of author; Comp – is comparison data.

It might be assumed how the quality light elements (carbon, nitrogen and oxigen) determination depends on choice of absorption coefficients.
The thickness of carbonic film on the studied surface and on the sample for comparison should be the same not to deteriorate the quality of results.

2.3 Optimum conditions to excite and register analytical signals

Ensuring a high quality of results depends on uniformity of analytical signal through the time of observation. The conditions of exciting and registering analytical signal are to provide such uniformity. Selection of optimum conditions to excite and register analytical signals is the major condition to obtain correct information on a sample. It is one of the main conditions for any method of analytical chemistry.

With EPMA applied the surface of different samples: glassy materials, sponges, bones, argentiferous samples and others can be destroyed during excitation with x-radiation, when electron probe falls on the sample surface, and as this takes place, the analytical signals become heavily contorted. Selection of optimum conditions of measurement can be based on the criteria of (a) minimum detection limit of sought elements, (b) uniformity of analytical signal during measurement, (c) variations of element intensity depending on the electron beam density or (d) sample stability while performing measurements (Buseck @ Goldstein, 1969).

2.3.1 The criterion of minimum detection limit

The detection limit variations depending on measurement conditions were identified for scandium, strontium and barium in basalt glasses. Figure 4 illustrates the plotted variations of detection limits for scandium, strontium and barium in basalt glasses depending on measurement conditions (Paradina @ Pavlova, 1999).
Radiation of SrL_{α} -, BaL_{β} - and ScK_{α} - lines is measured with the PET crystal for different accelerating voltages, counting times and probe currents. The curves show that the optimum conditions for electron probe microanalysis with wavelength spectrometers (WD EPMA) of

Ba , *Sc* and *Sr* are accelerating voltage 25 kV, sample current 80-100 nA and counting time 20 s. With the other measurement conditions the detection limits of above-indicated elements are higher, thus the determination quality of these elements in glasses is worse.
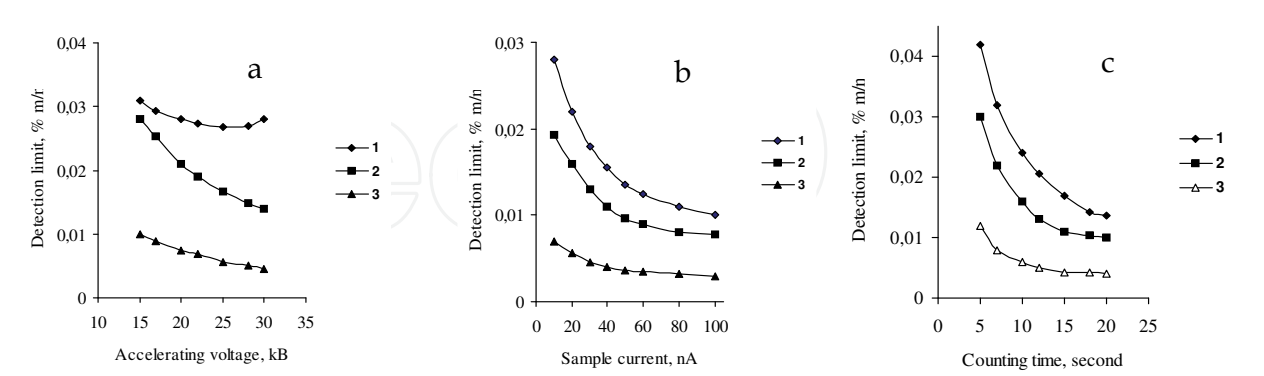

Fig. 4. Detection limits for SrL_α - (1), BaL_β - (2), and ScK_α - (3) as the functions of: (a) accelerating voltage (sample current 15 nA, counting time 10 s); (b) sample current (accelerating voltage 25 kV, counting time 10 s); (c) counting time (probe current 15 nA, accelerating voltage 25 kV). Measurements were made by Camebax-micro and Camebax SX-50 microprobes (Paradina @ Pavlova, 1999).

2.3.2 Variations of x-ray intensity versus counting time

Intensity variations of the elements present in the bones versus counting time are examined by microprobe Superprobe-733 (Pavlova et al., 2001). Intensity variations of elements present in bone tissue are shown in the fig. 5.
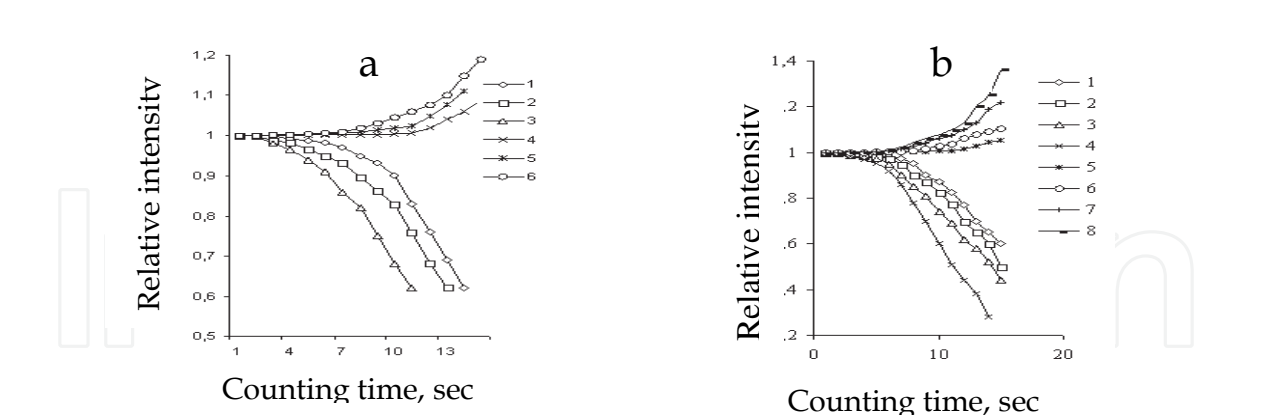

Fig. 5. Intensity variations of elements present in bone tissue versus counting time: (a) NaK_α (curves 1–3 correspond to accelerating voltage 10, 15 and 20 kV, respectively, and probe current 15 nA) and MgK_α (curves 4–6 correspond to accelerating voltage 10, 15 and 20 kV, respectively, and probe current 15 nA); (b) NaK_α (curves 1–4 correspond to sample current 10, 15, 20 and 25 nA, respectively, and accelerating voltage 15 kV) and MgK_α (curves 5–8 correspond to sample current 10, 15, 20 and 25 nA, respectively, and accelerating voltage 15 kV). Measurements were made by Superprobe-733 microprobe (Pavlova et al., 2001).
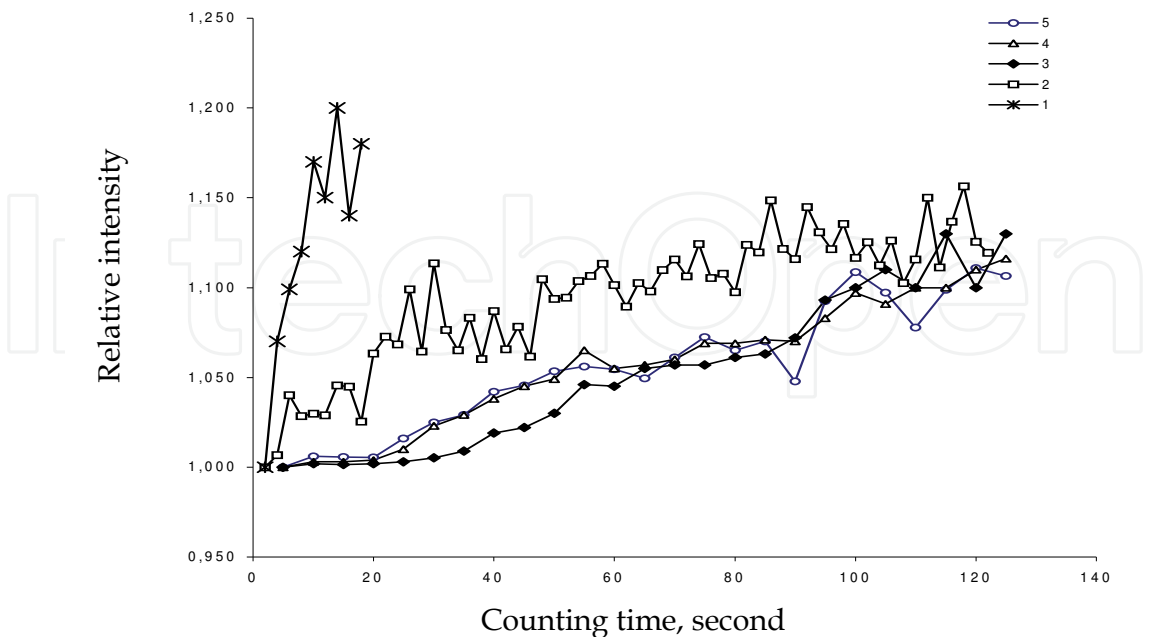
Fig. 6. The change of CaK_α - line intensity in accordance with the electron beam power densities ($\mu W / \mu m^2$): 1 – 191,00; 2 – 3,82; 3 – 2,54; 4 – 2,86; 5 – 3,06.

The X-ray intensity of calcium versus counting time (Fig. 6) with varying electron beam power density assessed for omul fish otoliths (Pavlova et al., 2003). This change of CaK_α - line intensity versus the electron beam power densities has been chosen as the criterion for selecting optimum conditions for analyzing the elements in omul fish otoliths. As seen on the plot the CaK_α intensity of otoliths remains constant during twenty seconds, if the beam power density is below 2.8 $\mu W / \mu m^2$. The increase of measuring time causes signal distortion and deterioration of result quality.

2.3.3 Criterion of sample stability while performing measurements

The stability of argentiferous samples can be studied quantitatively by Buseck's technique (Buseck @ Goldstein, 1969), and it can also be used as the criterion for selecting optimum conditions for EPMA and thereby refinement of substance test (Pavlova @ Kravtsova, 2006). According to the recommendations (Buseck and Goldstein, 1969) the sample is stable (analytical signal is constant for counting time), if it obeys the relationship

$$S_c < \sigma_c \qquad (1)$$

where the repeatability of standard deviation of the measured x-ray counts for the major elements Sc is given by:

$$S_c = \sqrt{\sum_{i+1}^{n} (N_i - \overline{N})^2 / (n-1)} \qquad (2)$$

where N_i is the number of x-ray counts in each measurement i and n is the number of individual measurements, and average number of x-ray counts is

$$\overline{N} = \sum_{i+1}^{n} (N_i / n) \tag{3}$$

the population standard deviation stipulated by the Poisson counting statistics σ_c is:

$$\sigma_c = \sqrt{\overline{N}} . \tag{4}$$

The stability characteristics of argentiferous sample were determined according to the recommendations (Buseck and Goldstein, 1969). Table 4 provides stability characteristics of argentiferous samples.

It was found that the response from argentiferous sample was stable through period from 1 to 1.5 min depending on the beam power densities.

The beam power density <2.55 $\mu W / \mu m^2$ is admissible for the analysis of argentiferous samples. The best compromise conditions for exciting the x-ray radiation and recording analytical signal for WD EPMA of argentiferous samples are: accelerating voltage of 15-20 kV, beam current of 10 nA, probe diameter of 10 µm and counting time of 10 s. Hence, so as to obtain the correct results of analysis it is necessary to select optimum conditions for exciting and registering analytical signals.

Counting time, second				10		20		30		40		50		60	
Conditions of measurements															
E_0 kV	i nA	d_b µm	P µW /	S_c	σ_c	S_c	σ_c	S_c	σ_c	S_c	σ_c	S_c	σ_c	S_c	σ_c
2	1	2	0,64	15	33,	16,	33,	15,	34,	16,	33,	16,	34,	15,	33,
2	1	2	0,96	16	35,	15,	35,	16,	35,	16,	35,	16,	35,	16,	34,
2	2	2	1,27	15	37,	16,	37,	16,	37,	15,	37,	15,	37,	42,	38,
2	5	1	1,27	16	37,	16,	37,	16,	37,	16,	37,	16,	37,	42,	38,
2	8	1	2,04	15	39,	16,	39,	16,	38,	18,	39,	50,	39,	49,	39,
2	1	1	2,55	16	40,	16,	40,	16,	39,	49,	41,	52,	41,	62,	42,
2	1	1	3,06	16	41,	48,	41,	51,	42,	53,	42,	59,	43,	63,	43,
2	1	1	3,82	47	45,	69,	44,	69,	43,	59,	44,	63,	44,	65,	44,
2	5	1	127,	49	48,	96,	48,	98,	49,	97,	50,	98,	56,	99,	49,

Table 4. The stability characteristics of argentiferous sample. d_b – beam diameter; E_0 – accelerating voltage; i – probe current; P – beam power densities; S_c is repeatability standard deviation of the measured X-ray counts; σ_c is population standard deviation, stipulated by Poisson counting statistics.

2.4 Reference samples and standard materials for electron probe microanalysis

The accuracy of results of any analytical technique depends on the application of a sufficient number of required reference and control samples of top quality. An important condition to acquire appropriate analytical results of required quality is the application of a sufficient number of required reference samples meeting all requirements of analytical method employed. It is desirable to use certified standards as control and reference samples.

A specific feature of electron probe X-ray microanalysis is its locality, which is 10^{-13} g of the substance, causing toughening the requirements for standard and reference materials claimed for EPMA. In the case of EPMA, reference and connrol samples should correspond with the following requirements simultaneously: (1) have known chemical composition; (2) be uniform at macro and micro levels of spatial resolution; (3) remain stable under action of electron probe; (4) do not decay in vacuum (up to 10^{-16} mm Hg); (5) must be well polished. Evidently, only the samples being standard samples of structure and properties at the same time may become standard and reference samples for EPMA. The standard samples widely utilized in the other analytical techniques are often inapplicable in the case of EPMA, because they are not homogeneous both at macro and micro levels.

2.4.1 Homogeneity and stability of samples

The homogeneity (at macro- and micro-level) of space resolution and substance stability resulting from the effect of electron beam is of particular interest for the EPMA. There are different approaches to assess the substance homogeneity (Borkhodoev, 2010; Buseck @ Goldstein, 1969; MI, 1988). Two methods to test the homogeneity of elements distribution at macro and micro levels (Buseck @ Goldstein, 1969; MI, 1988) are described for the copper-rich alloys and basaltic glass.

According to the recommendations of Buseck and Goldstein (Buseck @ Goldstein, 1969) the sample is homogeneous on micrometer- to millimeter scale if

$$S_c / 2\sigma_c < 1 \tag{5}$$

the homogeneity is doubtful if

$$1 < S_c / 2\sigma_c < 2 , \tag{6}$$

the sample is inhomogeneous if

$$2 < S_c / 2\sigma_c , \tag{7}$$

S_c and σ_c values are determined from (2)-(4) formulae.

The macro homogeneity at the micrometer to millimeter scale was evaluated by recording EPMA profiles across a few different profile lines of sample.

The beam diameter ranged from 1 to 10 µm, the profile length was about 1000 µm, the point spacing was 10 µm and the line spacing was 20 µm. $S_c / 2\sigma_c$ values in Table 5 demonstrate that at micron-mm level in alloys CA-2 and CA-6 all elements are distributed irregularly and the tin homogeneity in CA-4 alloy is doubtful.

According to the National Standard for homogeneity assessment (MI, 1988) the material is uniform on a micrometer scale, if

$$\sigma_i = \sqrt{\sigma_b^2 + \sigma_l^2} < RSD , \tag{8}$$

Sample		Element	C_{cer}, wt. %	Stability (for 2 min) σ_c / S_c	homogeneity $S_c / 2c$	σ_b	σ_l	σ_i	$\sigma / 8$
Coppery alloys	CA-1	Sn	1,62	1,38	0,77	0,03	0,71	0,71	0,71
		Ni	0,10	n.d	0,76	0,08	1,94	1,94	2,10
		Fe	0,05	n.d	0,88	0,09	2,05	2,05	2,50
	CA -2	Cu	68,74	1,48	2,96	n.d	n.d	n.d	n.d
		Sn	0,97	1,75	2,95	n.d	n.d	n.d	n.d
		Zn	30,00	1,13	2,27	n.d	n.d	n.d	n.d
	CA -3	Zn	0,71	n.d	0,80	0,12	1,12	1,12	0,26
		Cu	98,53	1,49	0,98	0,14	1,12	1,13	0,31
		Sn	0,19	n.d	0,79	0,00	1,55	1,55	1,56
		Ni	0,26	n.d	0,79	0,07	1,13	1,13	1,20
		Fe	0,30	n.d	0,76	0,06	1,16	1,16	0,81
	CA -4	Zn	1,56	1,36	0,73	0,04	0,68	0,68	0,85
		Sn	0,09	n.d	1,48	n.d	n.d	n.d	n.d
	CA -5	Zn	1,00	1,46	0,92	0,11	1,12	1,12	1,13
		Sn	0,12	n.d	0,83	0,00	1,55	1,55	1,56
		Ni	0,51	n.d	0,89	0,07	1,13	1,13	1,20
		Fe	3,63	1,45	0,87	0,14	0,79	0,80	0,81
	CA -6	Cu	63,00	1,23	2,46	n.d	n.d	n.d	0,31
		Zn	33,80	1,43	2,87	n.d	n.d	n.d	n.d
Basalt glass		Ba	2,30	1.94	0,47	0,00	1,73	1,73	3,80
		Sr	2,01	1.75	0,375	0,00	1,56	1,56	2,80
		Si	21,84	1.84	0,42	0,02	0,13	0,13	0,13
		Al	9,50	1.72	0,36	0,20	0,34	0,40	0,44
		Ca	7,34	1.68	0,34	0,13	0,38	0,40	0,40
		Mg	3,49	1.88	0,44	0,17	0,49	0,52	0,58
		Fe	8,94	1.66	0,33	0,12	0,32	0,35	0,35
		Na	2,02	1.58	0,29	0,02	0,96	0,96	1,00
		Ti	0,87	n.d	0,39	0,17	0,81	0,83	0,88

Table 5. Characteristics of stability and uniformity of copper alloys and basalt glass. n.d. means that the value was not determined. CA stands for coppery alloys; S_c is repeatability standard deviation of the measured X-ray counts; σ_c is population standard deviation, stipulated by Poisson counting statistics; σ_i is total root mean square deviation; σ_b is the root mean square deviation of random components of error for some parts of the specimen; σ_l is the root mean square deviation of random components of error for the analytical areas; *RSD* is the relative standard deviation (Thompson et al., 1997).

where σ_b is the root mean square deviation of random components of error for some parts of the specimen; σ_l is the root mean square deviation of random components of error for the analytical areas; RSD is the relative standard deviation used for certification (Thompson et al., 1997).

The total X-ray counts were recorded at each point of the sample by the static beam to detect possible micro heterogeneity at 1–10 μm scale. The X-ray intensities of analytical lines were measured from 20 to 30 points of a sample. The pattern of these points was chosen from the table of random numbers. At each point two measurements were made using the optimum conditions. The homogeneity of the material in the surface layers was estimated by repeating measurements after the repeated polishing. The results for each element were processed by a dispersion analysis with a three-step grouping of material. Evidently the samples are homogeneous on micrometer scale excepting alloys CA-2, CA-6 and CA-4.

At EPMA the stability of reference samples and standards under the microprobe is significant both during measuring the analytical signal and using the sample for studies. The data on stability of alloys and glasses, given in Table 5, are obtained by the following method (Pavlova et al., 2001). The X-ray radiation of the most intensive lines was excited by the electron beam at 5 arbitrary points of the selected sample. This was the x-ray radiation of copper Kα-line for alloys and calcium Kα-line for basalt glass recorded by the WD EPMA technique. The measurements were made 30 times and lasted for 5 minutes per point. Relationship (1) was applicable for some elements of all copper alloys and basalt glass. Table 5 indicates that all copper alloys and basalt glass are resistant to electron action during 2 minutes.

2.4.2 Valuation of laboratory reference samples

The necessity to have certified standard samples is obvious; they help to achieve the requisite quality of results. But in some cases the certified standard samples are absent and researchers are forced to apply laboratory reference materials after having the control study fulfilled and these materials assessed (Wilson & Taggart, 2000).

One of the techniques to assess quality of the EPMA results obtained using laboratory reference samples instead of standards is described below for the silicate mineral analysis (Pavlova et al., 2003). Measurements were performed on the Jeol Superprobe-733 electron microprobe using accelerating voltage of 15 kV and probe current of 20 nA with an electron beam diameter of 1 and 10 μm. Assessment was done by analyzing 26 control samples (glass K-412, garnet IGEM, Ti - glass, Mn-glass, Cr –glass, basalt glasses BHVO-2G, BCR-2G, BIR-1G, diopside, ilmenite, garnet O-145, olivine, spinel, garnet C-153, albite, garnet UD-92, orthoclase, chromite UV-126, oxides MgO, MnO, Fe_2O_3, Cr_2O_3, Al_2O_3, TiO_2, SiO_2 and $CaSiO_3$). The glass K-412 was supplied by the National Institute of Standards and Technology of the USA (NIST, 1990). Garnet IGEM, Ti - glass, Mn-glass and Cr -glass were prepared as laboratory reference samples at the Institute of Geology and Mineralogy, Moscow, Russia. Three basalt glasses BHVO-2G, BCR-2G andBIR-1G were produced by the US Geological Survey (Denver Federal Center) (Wilson & Taggart, 2000). The diopside, ilmenite, olivine, spinel, garnets C-153 and UD-92, albite and orthoclase were certified as the laboratory reference samples at the Institute of Geology and Geophysics, Novosibirsk,

Russia. The oxides MgO, MnO, Fe_2O_3, Cr_2O_3, Al_2O_3, TiO_2, SiO_2 and $CaSiO_3$ were supplied by JEOL Ltd., Tokyo, Japan. Each reference sample producer has reported that all samples meet the requirements needed for the samples for comparison at EPMA.

These control samples comprised the following. (I) Seven glasses, in which the contents of the elements analyzed varied over the following ranges (wt.%): SiO_2, 45.35–54.11; MgO, 3.48–19.33; Al_2O_3, 1.40–16.68; FeO, 8.46–12.04; CaO, 6.87–23.38; TiO_2, 0.81–9.11; MnO, 0.17–8.48; and Cr_2O_3, 10.20. (II) Eight oxides: MgO, SiO_2, Al_2O_3, TiO_2, Fe_2O_3, MnO, Cr_2O_3 and $CaSiO_3$. (III) Twelve minerals with concentrations varying as follows (wt.%): MgO, 1.02–49.20; Al_2O_3, 0.50–26.10; SiO_2, 0.30–55.50; CaO, 2.24–53.80; TiO_2, 0.33–50.00; Cr_2O_3, 0.08–44.80; MnO, 0.17–30.76; and FeO, 0.05–62.40.

All samples were at first used as control samples before being accepted as reference samples. The available reference samples were divided into three groups (Table 6). Group I comprised the basic components (Si, Al, Fe, Mg and Ca) which were defined using glass K-412, while Ti, Mn and Cr were defined from Ti-glass, Mn-glass and Cr-glass. The second complete set (II) consisted of simple minerals: diopside (for Si and Ca); ilmenite GF-55 (for Ti); olivine (for Mg); spinel $MnFe_2O_4$ (for Fe); garnets C-153 (for Al), UD-92 (for Cr) and IGEM (for Mn). Simple oxides MgO, MnO, Fe_2O_3, Cr_2O_3, Al_2O_3, TiO_2, SiO_2 and $CaSiO_3$ (Ca) represent the third complete set of reference samples (III). In all three cases the sodium content was determined from albite and that of potassium from the orthoclase standard sample. The analyzed values were corrected for matrix effects using the PAP method (Pouchou @ Pichoir, 1984) through the MARCHELL program (Kanakin @ Karmanov, 2006) adapted for the Superprobe-733 operating system. When applying three complete sets of calibration samples the three series of concentration data (C_I, C_{II} and C_{III}) have been received. Table 6 shows the analytical results for USGS TB-1 glass measured by EPMA. The same analytical results have been acquired for every control sample.

The results obtained in this study (Table 6) showed that deviations from the recommended/certified value varied in value and sign, however, they did not depend on the group of the reference samples selected for calibration. The largest deviations were observed in the elements with concentrations close to the detection limit. The relative standard deviations do not exceed the target precision (σ_r) in all cases. The values of z-scores for all elements determined lie within permissible limits (-2<z<2) for the elements ranging in concentration from 0.1 to 100%. The relative standard deviation for each element assessed in all control samples depends on the concentration and varies as (%): Na_2O, 0.30–2.89; MgO, 0.42–1.76; Al_2O_3, 0.29–2.4; SiO_2, 0.11–2.32; K_2O, 0.43–2.00; CaO, 0.37–1.91; TiO_2, 0.84–2.16; Cr_2O_3, 0.71–2.25; MnO, 0.72–2.59; and FeO, 0.45–2.80. The relative standard deviations for each element in all control samples were not higher than the admissible relative standard deviations (σ_r), defined for 'applied geochemistry' category of analysis (category 2) in the GeoPT proficiency testing program (Thompson et al., 1997). Fig. 7 shows the correlation of concentrations for MgO and Cr_2O_3 analyzed using the different sets of reference samples vs. their recommended or certified values.

Each trend of data plotted in Figure 7 is well described as a straight line. In all cases the correlation coefficients (R^2), describing the reliability of the linear dependence, is close or equal to 1 (Table 7). This confirms the absence of systematic differences and confirms the reliability of each set of reference samples in the calibration of the EPMA instrument.

Group of refe-rence samples	Metrological performance	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO
I	C_{cer} , wt. %	3,3	3,5	13,6	54,1	0,36	1,7	7	2,2	0,18	12
	n	17									
	C_{av} , wt.%	3,3	3,5	13,6	54	0,35	1,7	7	2,2	0,18	12
	s	0,1	0,1	0,17	0,6	0,01	0	0,1	0	0,01	0,2
	s_r , %	1,4	1,4	1,25	1,1	2,31	1,8	1,5	1,7	2,53	1,3
	σ_r , %	1,7	1,7	1,35	1,1	2,33	1,9	1,5	1,8	2,59	1,4
	ΔC , wt. %	0	0	0,08	0,3	0	0	0,1	0	0	0,1
	z	-0	0,4	-0,5	-0,2	-1,2	0,3	0,4	-1	-0,4	-0,1
II	n	8									
	C_{av} , wt.%	3,3	3,5	13,7	54	0,36	1,7	6,9	2,3	0,18	12
	s	0,1	0,1	0,16	0,6	0,01	0	0,1	0	0,01	0,2
	s_r , %	1,7	1,6	1,17	1	2,31	1,8	1,5	1,7	2,54	1,3
	σ_r , %	1,7	1,7	1,35	1,1	2,33	1,9	1,5	1,8	2,59	1,4
	ΔC , wt. %	0	0	0,11	0,4	0,01	0	0,1	0	0	0,1
	z	0,7	-0	0,38	0,2	-0,1	-1	-1	0,5	-0,7	-0,7
III	n	7									
	C_{av} , wt.%	3,3	3,6	13,7	54	0,37	1,7	7,1	2,2	0,18	12
	s	0,1	0	0,09	0,4	0,01	0	0,1	0	0,01	0,1
	s_r , %	1,5	1,1	0,64	0,7	2,27	1,8	1,4	1,7	2,5	1,2
	σ_r , %	1,7	1,7	1,35	1,1	2,33	1,9	1,5	1,8	2,59	1,4
	ΔC , wt. %	0,1	0,1	0,1	0,4	0,01	0	0,1	0	0,01	0,2
	z	1	1,8	0,46	0,4	1,19	-1	1,7	-1	0	1,2

Table 6. Analytical results for USGS TB-1 glass measured by EPMA with the calibrations obtained from three separate groups of reference materials for each of samples: C_{cer} is the certified concentration; n is number of measurements; $\Delta C = t * s / \sqrt{n}$ is confidence intervals; $s_r = s / C_{av}$ is standard deviations, where $s = \sqrt{\{[n\sum_{i=1}^{n}(C_i)^2 - (\sum_{i=1}^{n}C_i^2)] / [n(n-1)]\}}$; $C_{av} = \frac{1}{n}\sum_{i=1}^{n}C_i$ is average concentrations; $z = (C_{av} - C_{cer}) / \sigma_r$ is z-scores (Thompson et al., 1997); $\sigma_r = 100 * 0.02 * C^{0.8495} / C$ is acceptable standard deviation (Thompson et al., 1997), where C is the concentration expressed as fraction.
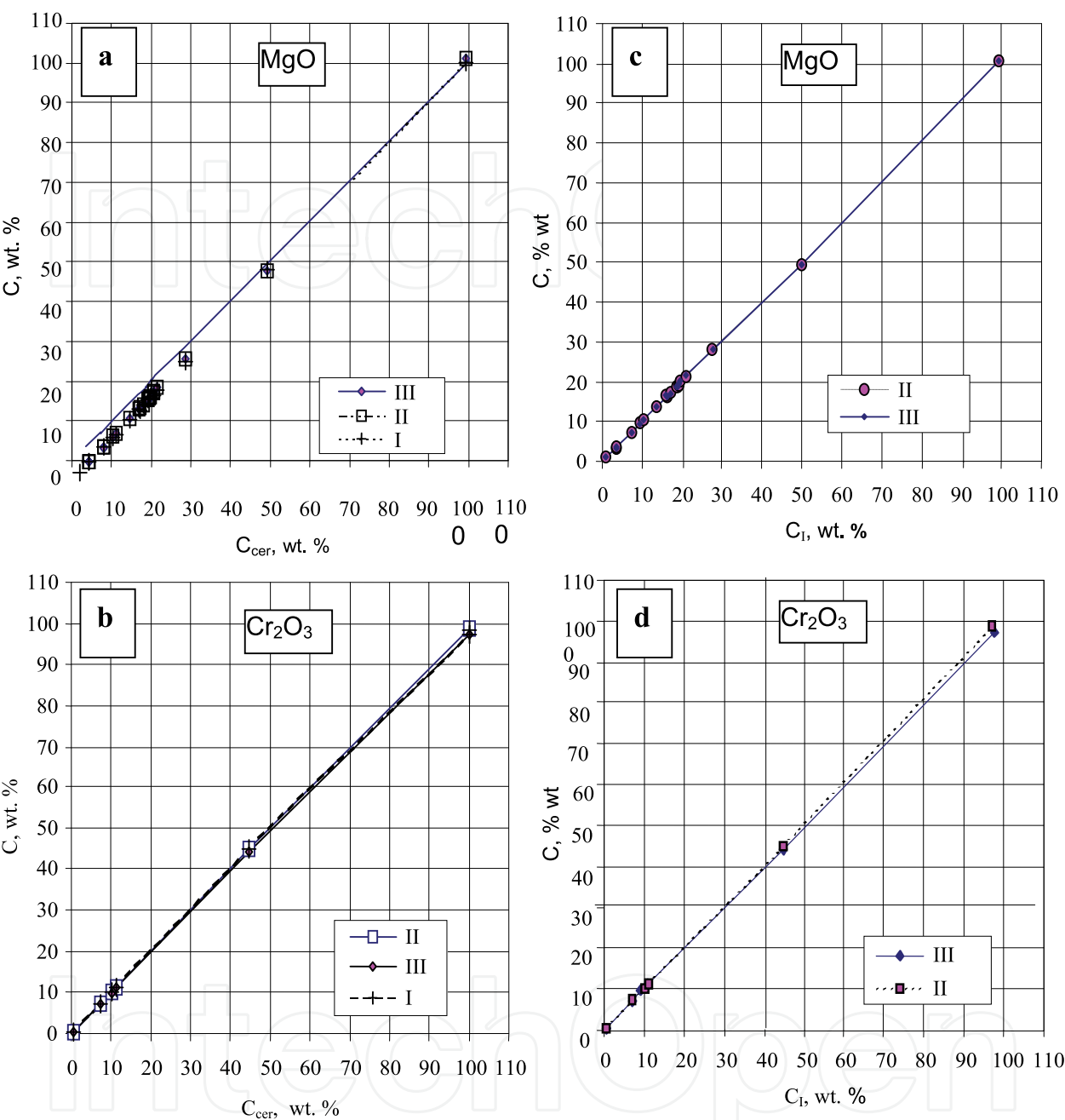
Fig. 7. The graphic correlation of concentrations for MgO and Cr_2O_3. a, b – the graphic correlation of concentrations (C) received according to three different reference sample sets (I, II, III), to their certified values (C_{cer}). Graphic representation of the ratio between the concentrations determined using laboratory reference samples II (C_{II}) and III (C_{III}) and C_I determined using standard sample glasses I. Graphs correspond to the concentrations, determined using: fist set of reference samples (I) – glass K-412, Ti-glass, Mn-glass, Cr-glass, albite and orthoclase; the second set (II) – diopside, ilmenite GF-55, olivine, spinel, garnets C-153, UD-92, IGEM albite and orthoclase; for the third set (III) – MgO, MnO, Fe_2O_3, Cr_2O_3, Al_2O_3, TiO_2, SiO_2, $CaSiO_3$, albite and orthoclase.

Oxides	C_{III} (C_{cer})	C_{II} (C_{cer})	C_I (C_{cer})	C_{III} (C_I)	C_{II} (C_I)
Al_2O_3	C_{III} = 1.003 C_{cer} - 0.0985; R^2 =0.9999	C_{II} = 1.0020 C_{cer} - 0.0782; R^2 = 0.9999	C_I = 1.0001 C_{cer} + 0.0674; R^2 = 0.9999	C_{III} = 1,0396 C_I - 0,0105; R^2 = 0,9998	C_{II} = 1,0414 C_I - 0,0104; R^2 = 0,9997
MgO	C_{III} = 1.0081 C_{cer} - 0.1342; R^2 =0.9999	C_{II} = 1.0068 C_{cer} - 0.0978; R^2 = 0.9999	C_I = 0.9977 C_{cer} - 0.1246; R^2 = 0.9998	C_{III} = 1,0101 C_I - 0,0048; R^2 = 0,9998	C_{II} = 1,0089 C_I + 0,0280; R^2 = 0,9998
SiO_2	C_{III} = 0.9943 C_{cer} + 0.234; R^2 =0.9997	C_{II} = 0.9966 C_{cer} + 0.1482; R^2 = 0.9997	C_I = 0.9964 C_{cer} + 0.0369; R^2 = 0.9991	C_{III} = 1,0044 C_I - 0,4210; R^2 = 0,9991	C_{II} = 1,0034 C_I - 0,3896; R^2 =0,9991;
Na_2O	C_{III} = 1.005 C_{cer} - 0.0361; R^2 =0.9987	C_{II} = 1.0001 C_{cer} + 0.0193; R^2 = 0.9997	C_I = 1.0042 C_{cer} - 0.0415; R^2 = 0.9996	C_{III} = 1,0016 C_I + 0,0838; R^2 = 0,9999	C_{II} = 0,9991 C_I + 0,2071; R^2 =0,9989;
K_2O	C_{III} =0.9974 C_{cer} + 0.0532; R^2 =0.9998	C_{II} = 0.9992 C_{cer} + 0.0359; м = 0.9990	C_I = 0.9821 C_{cer} + 0.0581; R^2 = 0.9999	C_{III} = 1,0148 C_I - 0,0107; R^2 = 0,9998	C_{II} = 1,0157 C_I - 0,0126; R^2 = 0,9990
CaO	C_{III} =0.9925 C_{cer} + 0.0026; R^2 = 0.9999	C_{II} = 0.9946 C_{cer} + 0.0351; R^2 = 0.9999	C_I = 1.0057 C_{cer} - 0.0203; R^2 = 0.9999	C_{III} = 0,9855 C_I + 0,0584; R^2 = 0,9998	C_{II} = 0,9889 C_I + 0,0720; R^2 = 0,9999
TiO_2	C_{III} = 1.0140 C_{cer} - 0.0105; R^2 = 1.0000	C_{II} = 1.0058 C_{cer} + 0.0202; R^2 = 0.9999	C_I = 1.0051 C_{cer} + 0.0339; R^2 = 1.0000	C_{III} = 1,0093 C_I - 0,0389; R^2 = 1,0000	C_{II} = 1,0005 C_I + 0,0036; R^2 = 1,0000
Cr_2O_3	C_{III} = 0.9747 C_{cer} + 0.0672; R^2 = 0.9999	C_{II} = 0.9872 C_{cer} + 0.1281; R^2 = 0.9999	C_I = 0.9780 C_{cer} + 0.2218; R^2 = 0.9998	C_{III} = 0,9950 C_I + 0,1126; R^2 = 0,9999	C_{II} = 1,0144 C_I - 0,1526; R^2 = 0,9999
MnO	C_{III} = 1.0130 C_{cer} - 0.0512; R^2 = 0.9999	C_{II} = 1.0075 C_{cer} + 0.0027; R^2 = 1.0000	C_I = 1.0140 C_{cer} - 0.0066; R^2 = 1.0000	C_{III} = 1,0013 C_I - 0,0551; R^2 = 0,9990	C_{II} = 0,9935 C_I + 0,0099; R^2 = 0,9999
FeO	C_{III} = 1.0031 C_{cer} - 0.0332; R^2 = 0.9999	C_{II} = 1.0013 C_{cer} - 0.0112; R^2 = 0.9999	C_I = 0.9880 C_{cer} + 0.1251; R^2 = 0.9999	C_{III} = 1,0107 C_I - 0,1443; R^2 = 0,9999	C_{II} = 1,0090 C_I - 0,1295; R^2 = 0,9999

Table 7. Evaluation of the linear function and correlation coefficients (R^2) between determinations made against the three sets of calibration samples (C_I, C_{II}, C_{III}) and the certified concentrations of control samples (C_{cer}) as well as between C_{II}, C_{III} and C_I. Concentrations C_I, C_{II}, C_{III} are determined using the respective sets of reference samples: (I) – glass K-412, Ti -glass, Mn-glass, Cr-glass, albite and orthoclase; (II) – diopside, ilmenite GF-55, olivine, spinel, garnets C-153, UD-92, IGEM, albite and orthoclase; (III) – MgO, MnO, Fe_2O_3, Cr_2O_3, Al_2O_3, TiO_2, SiO_2, $CaSiO_3$, albite and orthoclase.

Figure 7 includes the data for elements in which the maximum differences were observed between the results. It is evident that in all cases there are no essential systematic differences between the data sets. This confirms the absence of systematic differences and confirms the reliability of each set of reference samples in the calibration of the EPMA instrument.

Table 8 gives the results of calculations designed to check the hypothesis that there are no differences between sets of results obtained from any of these three sets of calibration samples.

The series of concentrations determined using calibrations established using three sets of reference samples have been compared with certified values using a two-tailed selective Student's *t*-test. Numerical values of probabilities for each pair of the series are significant, showing that the populations of results from all three series are statistically indistinguishable certified values.

The closeness in value of the significance data listed in Table 8 demonstrates the absence of systematic differences between the certified concentrations and the analyzed data for every series. Thus, the sets of reference samples tested in such a way can be successfully applied in EPMA for obtaining high-quality results.

Oxides	$C_{cer} - C_I$	$C_{cer} - C_{II}$	$C_{cer} - C_{III}$	$C_I - C_{II}$	$C_I - C_{III}$
MgO	0.312	0.355	0.299	0.359	0.268
AL_2O_3	0.244	0.237	0.215	0.251	0.267
SiO_2	0.310	0.363	0.328	0.265	0.368
CaO	0.455	0.444	-	0.292	-
MnO	-	0.503	0.490	-	-
FeO	0.359	0.390	0.346	0.374	0.328

Table 8. Results from checking the hypothesis that there is no significant difference between determinations made by any of the three sets of calibration and certified/recommended values using a 2-pair selective Students t-test. C_{cer} – certified concentrations of control samples; C_I, C_{II}, C_{III} – concentrations, determined using the following sets of reference samples: (I) – glass K-412, Ti-glass, Mn-glass, Cr-glass, albite and orthoclase; (II) – diopside, ilmenite GF-55, olivine, spinel, garnets C-153, UD-92, IGEM, albite and orthclase; (III) – MgO, MnO, Fe_2O_3, Cr_2O_3, Al_2O_3, TiO_2, SiO_2, $CaSiO_3$, albite and orthoclase.

2.5 The dependence of EPMA quality on homogeneity of reference samples

The influence of inhomogeneity of reference samples on the EPMA quality has been exemplified by copper-containing alloys (Pavlova, 2009). Ten copper-rich alloys, the standards for chemical, optical and x-ray fluorescence analysis have been quantitatively evaluated as the reference materials to be employed in the electron probe microanalysis.

The optimum conditions for measurements were selected considering the dependence of intensity and detection limit on conditions of the x-ray radiation excitation and analytical signal recording.

The reference samples were divided into the three groups: the control group 1 consisted of the certified glass (Fe), simple minerals (Zn, Sn), metals (Cu, Ni); two groups of samples for comparison included the assessed alloys: group 2 comprised the alloys MC76 (Fe), MC44 (Sn, Cu), MC104 (Ni), MC153 (Zn); and group 3 included MC71 (Zn), MC74 (Fe, Ni), MC42 (Sn) and metallic copper (Cu).

Three data sets (1, 2 and 3 - in agreement with the groups of reference samples) comprising the average concentrations, standard deviations, relative standard deviations, confidence interval and the z-score of data quality were calculated for 10 copper-rich alloys.

The average concentrations for all elements of every control sample were being defined from 8 to 18 times. The measured values were corrected for matrix effects using the PAP method (Pouchou and Pichoir, 1984) and applying the MARCHELL program (Kanakin & Karmanov, 2006) adapted for the microanalyzer Superprobe-733 operating system. Table 9 presents the data for one alloy.

The relative standard deviations obtained for each element were lower than the target values for all determinations in all cases except for set 2, where group 2 of reference samples was used. In two sets of data the z-score values for all elements determined lie within acceptable limits (-2<z<2) for concentrations ranging from 0.1 to 100%.

Figure 8 shows the graphic dependence of certified Ni, Fe, Sn, Zn concentrations and values obtained from different (1, 2 and 3) groups of reference samples. Obtained sets of concentrations were compared between each other and with the certificated/recommended values using 2-pair selective Student's t-test. The table 9 gives the results of calculations to

Group of reference samples	Metrological performance	Zn	Cu	Sn	Ni	Fe
1	C_{cer} , wt. %	1,96	88,8	4,89	1,09	2,46
	n	14				
	C_{av} , wt.%	1,94	88,5	4,85	1,11	2,48
	s	0,07	1,78	0,14	0,04	0,08
	s_r , %	3,56	2,01	2,98	3,89	3,41
	σ_r , %	3,61	2,04	3,15	3,95	3,49
	ΔC , wt. %	0,04	1,05	0,09	0,03	0,05
	z	-0,3	-0,2	-0,3	0,46	0,24
2	n	17				
	C_{av} , wt.%	1,75	85,7	4,56	1,34	2,95
	s	0,07	2,25	0,16	0,06	0,11
	s_r , %	3,78	2,63	3,45	4,22	3,76
	σ_r , %	3,61	2,04	3,15	3,95	3,49
	ΔC , wt. %	0,05	1,67	0,12	0,04	0,08
	z	-3,2	-1,4	-2,1	4,42	4,34
3	n	12				
	C_{av} , wt.%	1,98	89,3	4,92	1,08	2,45
	s	0,07	1,81	0,15	0,04	0,08
	s_r , %	3,54	2,03	3,12	3,92	3,46
	σ_r , %	3,61	2,04	3,15	3,95	3,49
	ΔC , wt. %	0,04	1,03	0,09	0,02	0,05
	z	0,29	0,26	0,2	-0,2	-0,1

Table 9. Analytical results for copper alloys measured by EPMA using calibrations obtained from three separate groups (1, 2 and 3) of reference materials for each of samples: C_{cer} is the certified concentration; n is number of measurements; $s_r = s / C_{av}$ is standard deviations, where $s = \sqrt{\{[n\sum_{i=1}^{n}(C_i)^2 - (\sum_{i=1}^{n}C_i^2)] / [n(n-1)]\}}$; $C_{av} = \frac{1}{n}\sum_{i=1}^{n}C_i$ is average concentrations;

$\Delta C = t * s / \sqrt{n}$ is confidence intervals; $z = (C_{av} - C_{cer}) / \sigma_r$ is z-scores (Thompson et al., 1997); $\sigma_r = 100 * 0.02 * C^{0.8495} / C$ is acceptable standard deviation (Thompson et al., 1997), where C is the concentration expressed as fraction.

check the hypothesis that there are no differences between the series of data obtained from any of the three groups of reference samples. We can see, the numerical values of probabilities in columns II, III and VI are not significant, thus indicating that the population of results from series C_2 is statistically different from the recommended values (column II),

and the values C_1 and C_3 obtained with groups 1 and 3 of reference samples (columns III and VI).

No systematic divergence was the case between the concentrations obtained from set 1 and set 2, when analyzed results were compared with the certified compositions. The set (2) of reference samples for copper-rich alloys yields erratic data because this set contained the inhomogeneous reference samples.

Lack of close values of probabilities (columns II, III and VI) demonstrates the presence of systematic differences between the concentration series C_2 and recommended concentrations (column II) as well as between the results of the second series C_2 and the data on the series C_1 and C_3 (columns III and VI). This confirms incorrectness of reference samples in group 2. It was previously shown that alloys CA-6 and CA-2 are not homogeneous (table 5).

The numerical values of probabilities are significant in columns I, IV, V and exhibit that the concentrations from selected sets are statistically indistinguishable. Similar values of probabilities listed in these columns for alloys demonstrate the absence of systematic differences of the first and third concentration series both between each other and the recommended concentrations.

Samples	Elements	Numerical values of probabilities for each pair of the series					
		I	II	III	IV	V	VI
		C_{cer} & C_1	C_{cer} & C_2	C_1 & C_2	C_{cer} & C_3	C_1 & C_3	C_2 & C_3
Alloys	Fe	0.341	0.031	0.013	0.421	0.296	0.021
	Ni	0.324	0.012	0.009	0.367	0.311	0.008
	Cu	0.336	0.003	0.026	0.383	0.382	0.017
	Sn	0.445	0.0154	0.0142	0.435	0.278	0.007
	Zn	0.425	0.009	0.001	0.398	0.318	0.011

Table 10. Comparison of concentrations using a coupled selective Student's t-test; C_{cer} is the certified concentration; C_1, C_2, C_3 are three series of concentration data obtained for each of copper-rich alloys using three groups of reference samples.

As a result, the systematic error is very small in the case when the compositions of control samples are calculated using groups 1 and 3 of reference samples. These experiments show that the quality of data obtained from alloy reference samples of group 3 is not inferior to that from the certified reference samples. The quality of results obtained from group 3 of reference samples corresponds to the 'applied geochemistry' type of analysis (category 2) as defined in the GeoPT proficiency testing program (Thompson et al., 1997)

2.6 Method to recalculate experimental values into concentrations
The choice of method of processing experimental values, when the concentration to be determined is concerned, influences determination of a true composition and thus the quality of analysis. Almost every analytical method of recalculating of experimental values into concentrations is developed for certain samples and conditions. Different methods of analytical chemistry have several ways of recalculating experimentally measured values in the concentration. Every way has its own advantages and disadvantages.
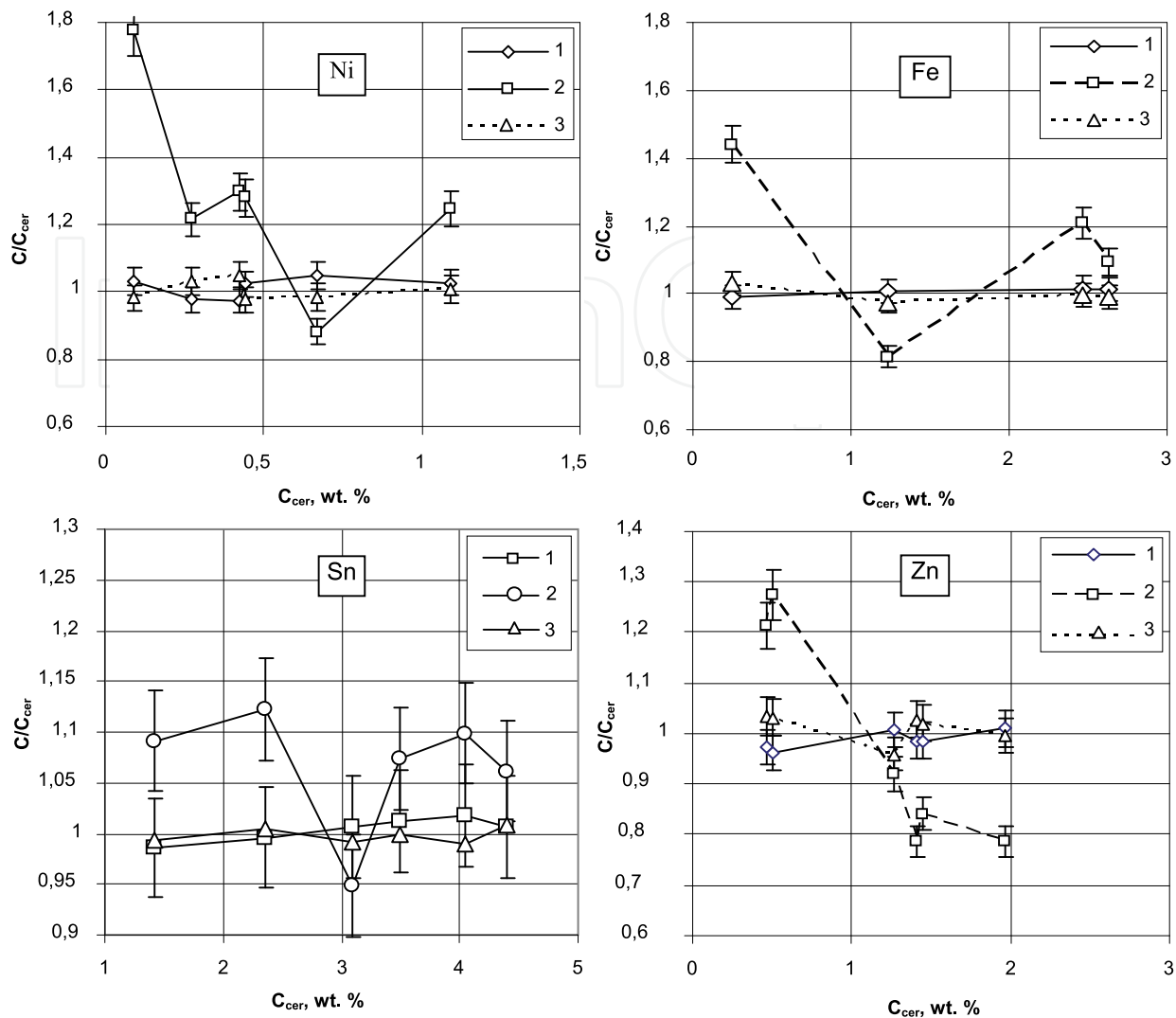
Fig. 8. Dependence of certified *Ni* , *Fe* , *Sn* , *Zn* concentrations and values obtained from different (1, 2 and 3) groups of reference samples.

When applying EPMA, the recalculation of x-ray radiation intensity in the concentration of silver group elements depends on the correct choice of x-ray radiation absorption coefficients and ability to consider the matrix effects. The determination of the composition of silver-containing compounds can exemplify how the counting procedure influences the quality of composition determination. The results on the composition of silver minerals, differently obtained by calculating absorption coefficients, are compared in Table 10 (Pavlova @ Kravtsova, 2006). The measured intensities, acquired by microprobes JXA8200 and JCXA-733 (Japan), were corrected for matrix effects using programs of JXA8200 Unix platform and the PAP method (Pouchou & Pichoir, 1984) applying the original controlling computer program MARshell (Kanakin & Karmanov, 2006) adapted for JCXA-733 microprobe.

One can observe how available results differ in various methods of calculating matrix effects and how the quality of results depends on the correct calculation of absorption coefficients. It is evident, that the best results are gained by the PAP method (Pouchou & Pichoir, 1984), when the Marenkov's absorption coefficients are applied (Marenkov, 1982), as well as program of JXA8200 Unix platform by PPX method (Pouchou & Pichoir, 1991) from software of microprobe JXA8200 (Japan).

The change of the subject under study often requires the change in the method of recalculating of experimental intensities into concentrations. Thus, a correct determination of the composition of particles comparable in size with the area of generation of x-ray radiation is dependent on the particle size. The quality of obtained results for such particles depends on a correct consideration of size factor (Table 12). The dependence of quality of particle composition versus the method of calculation of their size is exemplified in the article (Belozerova, 2003). Here it is seen that the results obtained for particles with size 3–5 μm are closer to the stoichiometrical composition than those obtained for particles sized 1–2 μm size. One of the best commonly used methods of calculating element content in bulk samples (PAP-method) provides a relative error of determining the composition of one micron particles ranging from 0.5 to 45 %. Using the exponent model of particle composition calculation lowers this inaccuracy.

Method to calculate matrix effects	Authors of absorption coefficients	Sample 1		Sample 2		Sample 3	
		Concent-ration, wt. %	Relative error, %	Concent-ration, wt. %	Relative error, %	Concent-ration, wt. %	Relative error, %
(Pouchou & Pichoir, 1984)	(Marenkov, 1982)	65.56	-0.23	62.69	0.11	77.52	-0.51
	(Pouchou @ Pichoir, 1984)	67.16	-2.67	62.91	-0.24	79.51	-3.08
	(Heinrich, 1986)	66.03	-0.95	61.70	1.69	77.72	-0.77
(Lavrentiev et al., 1980)	(Marenkov, 1982)	73.20	-11.91	68.54	-9.20	86.65	-12.35
	(Pouchou @ Pichoir, 1984)	73.78	-12.79	68.95	-9.87	87.32	-13.21
	(Heinrich, 1986)	68.45	-4.64	62.49	0.42	78.82	-2.19
(Brizuela & Riveros,1990)	(Marenkov, 1982)	67.33	-2.94	63.36	-0.96	79.75	-3.40
	(Pouchou @ Pichoir, 1984)	67.93	-3.86	63.79	-1.63	80.45	-4.30
	(Heinrich, 1986)	66.39	-1.49	62.56	0.32	78.65	-1.97
(Sewell et al., 1985)	(Marenkov, 1982)	68.78	-5.15	64.26	-2.39	81.40	-5.53
	(Pouchou @ Pichoir, 1984)	69.35	-6.03	64.67	-3.04	82.06	-6.39
	(Heinrich, 1986)	67.85	-3.73	63.48	-1.14	80.32	-4.13
programs of JXA8200 (Philibert, 1963); (Reed, 1965); (Duncumb & Reed, 1968); (Berger & Zeltzer, 1964)	(Henke, 1966) (Henke, et al., 1982) (Heinrich, 1966) (Pouchou & Pichoir, 1991).	66,02	-0,93	63,18	-0,67	78,03	-1,16
(Pouchou & Pichoir, 1991)		65,94	-0,81	62,57	0,3	77,67	-0,71
Certified concentration, wt. %		65.41		62.76		77.13	

Table 11. Comparison of methods to compute matrix effects and coefficients of absorption to measure silver by EPMA.

Particle size. μm	Calculation technique	Sample	Albite			Quart	Calcit	Corun	Rutile	Pyrite	
		Element	Na	Al	Si	Si	Ca	Al	Ti	Fe	S
1	(Pouchou, & Pichoir, 1984)	C_i, wt. %	4.78	6.12	19.40	30.13	25.43	42.95	50.68	44.09	49.2
		R. er., %	45.50	40.50	39.62	35.54	36.49	18.89	15.46	5.28	7.82
	(Belozerova et al., 1998)	C_i, wt. %	5.54	8.06	25.04	35.58	36.87	47.23	57.48	46.56	52.8
		R. er., %	36.83	21.67	22.07	23.88	7.92	10.77	4.12	-0.02	1.08
	(Belozerova et al., 2003)	C_i, wt. %	6.82	9.93	30.86	44.15	42.28	51.40	58.42	46.67	52.9
		R. er., %	22.23	3.50	3.95	5.54	-5.59	2.89	2.55	-0.24	0.86
2	(Pouchou, & Pichoir, 1984)	C_i, wt. %	7.06	8.50	28.32	40.83	34.03	50.71	57.44	45.66	53.1
		R. er., %	19.50	17.39	11.86	12.64	15.00	4.19	4.19	1.91	0.56
	(Belozerova et al., 1998)	C_i, wt. %	7.12	8.87	29.59	43.62	36.86	50.85	58.05	45.67	53.3
		R. er., %	18.81	13.80	7.91	6.68	7.94	3.93	3.17	1.89	0.22
	(Belozerova et al., 2003)	C_i, wt. %	7.38	9.20	30.68	45.33	37.47	51.19	58.07	45.68	53.3
		R. er., %	15.85	10.59	4.51	3.02	6.42	3.28	3.14	1.86	0.22
3	(Pouchou, & Pichoir, 1984)	C_i, wt. %	8.28	9.93	31.54	45.50	38.80	52.26	59.15	46.09	52.9
		R. er., %	5.59	3.50	1.83	2.65	3.10	1.26	1.33	0.94	0.91
	(Belozerova et al., 1998)	C_i, wt. %	8.28	10.01	31.82	46.17	39.54	52.15	59.16	46.02	52.9
		R. er., %	5.59	2.72	0.96	1.22	1.25	1.47	1.32	1.14	1.01
	(Belozerova et al., 2003)	C_i, wt. %	8.33	10.08	32.04	46.52	39.62	52.18	59.16	46.02	52.9
		R. er., %	5.02	2.04	0.28	0.47	1.05	1.42	1.32	1.14	0.99
4	(Pouchou, & Pichoir, 1984)	C_i, wt. %	8.57	10.26	31.71	46.00	40.02	52.37	59.25	46.39	53.1
		R. er., %	2.28	0.29	1.31	1.58	0.05	1.06	1.17	0.34	0.60
	(Belozerova et al., 1998)	C_i, wt. %	8.56	10.27	31.72	46.19	40.19	52.25	59.19	46.34	53.0
		R. er., %	2.39	0.19	1.28	1.18	-0.37	1.28	1.27	0.45	0.71
	(Belozerova et al., 2003)	C_i, wt. %	8.57	10.28	31.76	46.25	40.20	52.25	59.19	46.34	53.0
		R.er., %	2.28	0.10	1.15	1.05	-0.40	1.28	1.27	0.45	0.71
Massive grain	(Pouchou, & Pichoir, 1984)	C_i, wt. %	8.71	10.27	32.06	46.69	40.57	53.00	59.60	46.59	53.4
		R. er., %	0.68	0.19	0.22	0.11	-1.32	-0.13	0.58	-0.09	0.07
	(Belozerova et al., 1998)	C_i, wt. %	8.71	10.27	32.07	46.76	40.62	52.97	59.63	46.55	53.3
		R. er., %	0.68	0.19	0.19	0.04	1.45	0.07	0.53	0.03	0.16
	(Belozerova et al., 2003)	C_i, wt..	8.71	10.27	32.07	46.76	40.62	52.97	59.63	46.55	53.3
		R. er., %	0.68	0.19	0.19	0.04	1.45	0.07	0.53	0.02	0.16
Stoichiometric composition		C_s, wt..	8.77	10.29	32.13	46.74	40.04	52.93	59.95	46.55	53.4

Table 12. Particle composition versus the method of calculation of their size. C_i is obtained concentration; $\mathrm{R.\,er.} = 100(C_s - C_i) / C_s$ %.

The EPMA technique (Belozerova, 2003) for calculating composition developed for approximately spherical particles, comparable in size to the X-ray generation volume, takes into account the particle-size factor. The size factor correction significantly improves the results in spite of a simple analytical function of average atomic number and particle size.

Taking into account the particle-size factor reduces the error of composition determination from 0.5–45 to 0.2–22% relative percent, for particles sized as 1–3 μm.

The relative error increases with decreasing the element concentration from 0.02% for bulk sample to 22.2% for 1 μm particle. The size-factor introduction markedly improves the quality of determinations of particles comparable in size with the area of x-ray radiation excitation.

3. Conclusion

This chapter shows the quality dependence of EPMA on every analysis stage, beginning from the representativeness of the material, sample preparation and conditions for analytical signal excitation and registration to the availability of reference samples and the calculation methods.

We have shown how important it is to correctly select the study area and to have properly prepared samples.

It has been found that the quality of study performance is dependent on the optimum conditions of measuring and processing analytical signal.

The comparison of different methods of taking into account the processes occurring in substance in the electron-excited x-ray radiation proves the necessity to correctly select the methods of their consideration in every study.

The method of assessing the selected set of reference samples and defining their appropriateness for EPMA is described.

The urgency to develop and certify new control samples is critical for the methods of analytical chemistry and especially EPMA.

We have shown the influence of inhomogeneity of samples for comparison on the quality of EPMA results.

Thus, the example of EPMA for the case study of determination content quality suggests, that every aspect of analytical technique is responsible for the quality of element tests.

4. Acknowledgment

5. References

Beckford, J. L. W. (2010). Quality: a Critical Introduction, Routledge, ISBN 978-0415996358, New York.

Belozerova, O.Y., Afonin, V.P. & Finkelshtein, A.L. (1998). Modified biexponential model and its application to the X-ray microanalysis of gold-containing alloys. *Russian Journal Analytical Chemistry*, Vol. 53, No. 10, pp.1060–1065, ISSN: 0044-4502.

Belozerova, O.Yu., Finkelshtein, A.L. & Pavlova, L.A. (2003). Electron-Probe X-Ray Microanalysis of Individual Particles of Solid Snow Sediment with Size Factor Correction. *Micron*, Vol. 34, No. 1, pp. 49-55, ISSN: 0968-4328.

Berger M.J. & Zeltzer S.M. (1964). *Tables of energy losses and ranges of electrons and positrons.* National Academy of Sciences – National Reseach Council. Publ. 1133, DC, pp. 205-267, Washington.

Borkhodoev, V. Ya. (2010). Assessment of reference samples homogeneity in electron microprobe analysis. *X-ray Spectrometry*, Vol. 39, No. 1, pp. 28–31, ISSN: 1097-4539.

Borovskii, I.B. (1953). To the 70th Anniversary of I.P. Bardin, In: *Problems of Metallurgy*, Borovskii, I.B. pp. 135-153, AN SSSR, Moscow.

Borovskii, I.B. & Il'in N.P., (1956). New method of chemical content investigation in micro volume. *Dokl. Akad. Nauk SSSR*, Vol. 106, No. 4, pp. 654-657, ISSN: 0869-5652.

Borovskii, I.B., Vodovatov, F. F., Zhukov, A.A. & Cherepin, V. T. (1973). *Lokal'ny Metody Analiza Mineralov*, Metallurgiya, Moscow.

Brizuela, H. & Riveros, J.A. (1990). Study of mean excitation energy and K-shell effect for electron probe microanalysis. *X-Ray Spectrometry*, Vol. 19, № 4, p. 173–176, ISSN: 1097-4539.

Buseck, P.R. & Goldstein, J.I. (1969). Olivine Compositions and Cooling Rates of Pallasitic Meteorites. *Geological Society of America Bulletin*, Vol. 80, No. 11, pp. 2141-2158, ISSN: 1943-2674.

Castaing, R. (1951). Application of electron probes to local chemical and crystallographic analysis (Thesis, Univ. of Paris), Translated by P. Duwez and D.B, wittry, CalTech, 1955 (*Special Technical Report* under U.S. Army).

Castaing, R. & Guinier, A. (1953). Point-by-point chemical analysis by X-ray spectroscopy: Electronic Microanalyzer, In: *Analytical Chemistry special issue "Symposium on X-rays as analytical chemical tool"*, Vol. 25, pp. 724-726.

Duncumb, P. & Reed S.J.B.(1968). The calculation of stopping power and backscatter effects in electron probe microanalysis. *Quantitative electron probe microanalysis : proceedings of a seminar held at the National Bureau of Standards*, pp. 133 -154, Gaithersburg, Maryland, June 12-13, 1967.

Farkov, P.M., Il'icheva, L.N., & Finkelshtein, A.L. (2005). X-ray Fluorescence Determination of Carbon, Nitrogen, and Oxigen in Fish Plant Samples. *Russian Journal Analytical Chemistry*, Vol. 60 , No. 5, pp. 485-489, ISSN: 0044-4502.

Finkelshtein, A.L. & Farkov, P.M., (2002). Approximation of X-ray Attenuation Coefficients in Energy Range 0,1 to 100 keV. *Analytic and control*, Vol. 6, No. 4, pp. 377-382, ISSN: 2073-1442 (Print), ISSN: 2073-1450 (Online).

Hubbell, J. H. & Seltzer, S. M. (April 2011). Tables of X-Ray Mass Attenuation Coefficients and Mass Energy-Absorption Coefficientsfrom 1 keV to 20 MeV for Elements Z=1 to 92 and 48 Additional Substances of Dosimetric Interest, In: *NIST X-ray Attenuation Datadases*, 05.04.2011, Available from: http:// NIST Home/PML/Physical Reference Data/X-Ray Mass Attenuation Coefficients (http://www.nist.gov/pml/data/xraycoef/index.cfm).

Heinrich, K.F.J. (1966). X-ray absorption uncertainty. *The electron microprobe; proceedings of the symposium sponsored by the Electrothermics and Metallurgy Division, the Electrochemical Society*, pp. 296-377, Washington, D.C., October, 1964.

Heinrich, K.F.J. (1986). Mass absorption coefficients for electron probe microanalysis. *11th International congress on X-ray optics and microanalysis. Proceedings of a conference held in London, Ontario, Canada*, pp. 67-119, 4–8 August 1986.

Henke, B.L. (1966). Application of multilayer analyzers to 15-150 angstrom fluorescence spectroscopy for chemical and valence band analysis. *Advance in X-ray Analysis*, Vol. 9, n.d., pp. 430-440, ISSN: 0376-0308

Henke, B.L., Lee, P., Tanaka, T.J., Shimabukuro, R.L. and Fujikawa, B.K. (1982). Low Energy X-ray Interaction Coefficients: Photoabsorption, Scattering and Reflection.E=10-2000 eV. Z=1-94. *Atomic Data and Nuclear Data Tables*, Vol. 27, pp. 1-144, ISSN: 0092-640X.

Henke, B.L., Gullikson, E.M., & Davis, J.C. (1993). X-ray interactions: photoabsorption, scattering, transmission, and reflection at E=50-30000 eV, Z=1-92. *Atomic Data and Nuclear Data Tables, Vol.* 54, No. 2, pp. 181-342.

Goldstein, J.I., Newbury, D.E., Echlin, P., Joy, D.C., Lyman, C.E., Fiori, C., Romig A.D. Jr. & Lifshin, E. (1992). *Scanning Electron Microscopy and X-Ray Microanalysis*, Plenum Press, NewYork.

Kanakin S.V. & Karmanov, N.S. (2006). ICA and main scope of the software package MARshell32, *Proceedings of the V All-Russian X-Ray analysis Conference*, Irkutsk, May–June, 2006.

Lavrentiev, Yu.G., Berdichevskiy, G.V., Chernyavsriy, L.I. & Kuznetsova, A.I. (1980). KARAT – is program for quantitative electron probe X-ray microanalysis, *Apparatus and Methods for X-Ray Analysis,* Mashinostroenie, Leningrad, Vol. 23, n.d., pp. 217–224.

Marenkov O.S. (1982). *Tables and Formulas X-ray analysis. Methodical recommendations.* Mashinostroenie, Leningrad.

MI. (1988). Standard sample homogeneity of monolithic materials for the spectral analysis. Technique of measurement. Standards Publish, Moscow.

NIST (1990) Standard Reference Materials Catalog 1990-1991, Ed: R.S. McKenzie, NIST Special Publication 260, U.S. Department of Commerce, National Institute of Standards and Technology.

Pavlova, L. A. Belozerova, O. Yu., Paradina, L. F. & Suvorova, L. F. (2000). *X-Ray Electron Probe Analysis of Environmental and Ecological Objects*, Nauka, ISBN 5-02-031533-8, Novosibirsk, Russia.

Pavlova, L. A., Paradina, L. F. & Belozerova, O. Yu. (2001) Electron Probe Microanalysis of Environmental Samples: Preparation of Reference Materials, Correction for Particle Size Effects and Representative Results on Sediments Recovered from Snow, Power Station Fly Ash and Bone Samples. *Geostandard Newsletter: the Journal of Geostandard and Geoanalysis*, Vol. 25, No 2-3, pp. 333-344, ISSN: 0150-5505.

Pavlova, L.A., Pavlov, S. M, Anoshko, P.N. & Tyagun, M.L. (2003). Determination of calcium and sodium in Baykal omul otoliths by Electron probe microanalysis, *Analytic and*

control, Vol. 7, No. 3, pp. 242-247, ISSN: 2073-1442 (Print), ISSN: 2073-1450 (Online).

Pavlova, L. A., Suvorova, L. F, Belozerova, O. Yu. & Pavlov, S.M. (2003). Quality of determinations obtained from laboratory reference samples used in the calibration of X-ray electron probe microanalysis of silicate minerals. *Spectrochimica Acta Part B*, Vol. 58, No. 2, pp. 289-296, ISSN: 0584-8547.

Pavlova, L.A., Pavlov, S. M, Paradina, L. Ph., Karmanov, N.S., Kanakin, S.V., Anoshko, P.N. & Levina, O.V. (2004). Investigation of Baykal flora and fauna representative using the techniques of electron probe microanalysis and electron microscopy. *Ecological chemistry*, Vol. 13, No. 4, pp. 249-256, ISSN: 0869-3498.

Pavlova, L.A. & Kravtsova, R.G. (2006). Studing modes of silver occurrence, discovered in the lithochemical stream sediments of Dukat gold-silver deposit by electron probe x-ray microanalysis. *Methods and objects of chemical analysis*, Vol. 1, No. 2, pp. 132–140, ISSN: 1991-0290.

Pavlova, L. A. (2009). Quality of electron probe X-ray microanalysis determinations obtained from laboratory reference materials of the coppery alloys and basaltic glasses. *Spectrochimica Acta Part B: Atomic Spectroscopy*, Vol. 64, No 8, pp. 782-787, ISSN: 0584-8547.

Paradina, L.F. & Pavlova, L.A. (1999). Definition of vanadium, rubidium and strontium impurities in a vitreous substance of Siberia. *Russian Journal Analytical Chemistry*, Vol. 54 , No. 1, pp. 78–82, ISSN: 0044-4502.

Philibert J.A. (1963). A method for calculation of the absorption correction in electron probe microanalysis. In: *X-Ray Optics and X-Ray Microanalysis*, V.E. Cosslet & A. Engstrom, pp. 379-392, Academic Press, ISSN: 0028-0836, N.Y.

Pouchou J.L. & Pichoir F. A. (1984). New model for quantitative X-ray microanalysis, Part 1. Applications to the analysis of homogeneous samples. *La Recherche Aerospatiale*, n.d., No. 3, pp. 13–38, ISSN: 0034-1223.

Pouchou J.L. & Pichoir F. A. (1991). Quantitative analysis of homogenous or stratified microvolumes applying the model "PAP". In: *Electron Probe Quantitation*, K.F.J. Heinrich and D.E. Newbury (Eds.), 31-75, Springer, ISBN: 0306438240, Plenum Press.

Reed S.J.B. (1965). Characteristic fluorescence correction in electron probe microanalysis. *British Journal of Applied Physics*, Vol. 16, No 7, pp. 913–926, ISSN: 0508-3443.

Saloman, E.B., Hubbell, J. H. & Scofield J.H. (1988) X-ray attenuation cross srctions for energies 100 eV to 100 keV and elements Z=1 to Z=92. *Atomic Data and Nuclear Data Tables*, Vol. 38, pp. 1-197, ISSN: 0092-640X/88.

Sewell, D.A., Love, G. & Scott, V.D. (1985). Universal correction procedure for electronprobe microanalysis. I. Measurement of X-ray depth distribution in solids. *Journal of Physics D: Applied Physics*, Vol. 18, No. 7, pp. 1233–1243, ISSN: 0022-3727.

Szaloki, I., Osan, J. & Van Grieken, R. E. *(2004).* X-ray Spectrometry. *Analytical Chemistry*, Vol. 76, No. 12, pp. 3445-3470, ISSN: 1097-4539.

Thompson, M., Potts, P.J. & Webb, P.C. (1997). GeoPT1. International proficiency test for analytical geochemistry laboratories — report on round 1 (July 1996). *Geostandard Newsletter: the Journal of Geostandard and Geoanalysis*, Vol. 21, No. 1, pp. 51–58, ISSN: 0150-5505.

Wilson, S.A. & Taggart, J.E. (2000). Development of USGS microbeam reference materials for geochemical analysis, *Proceedings of the 4th International Conference on the Analysis of Geological and Environmental Materials*, Pont a Mousson, France, 29th Aug.-1st Sep., 2000.
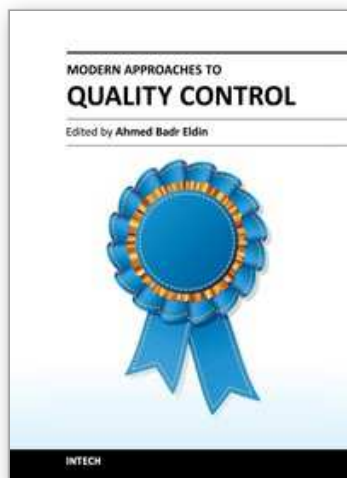
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