Spectrochemical Determination of Minor and Trace Elements in Polymetallic Ores – Development of Method and Determination of Information Characteristics

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The present work is concerned with solving the problems of development of methods for determination of some minor and trace elements in polymetallic ores. Optimization of the method was directed towards investigation of the evaporation properties of the elements determined and towards matrix effects. Experimental determination of the basic information characteristics of the method developed enabled to evaluate the method on the basis of information theory.

A complex chemical investigation should be carried out on perspective mining fields already in the stage of exploration. The analytical method applied has to be developed as maximum complex but its information characteristics should not be ignored, either. First of all, an exact definition of the analytical order is required. The choice of elements was influenced by geochemico-mineralogical factors [1]. The elements Cu, Pb, Sn, and Zn had to be observed in the concentration range from 0.03 to 10 %. The ores composition consisted mainly of pyrite and chalcopyrite, sphalerite, galenite, and tetraedrite were also present [2]. The following set of minor and trace elements is characteristic of the given mineralization: Ag, Ba, Bi, Cd, Co, Cr, Cu, Mo, Ni, Sn. The elements Cu and Sn were investigated in the trace analysis range from 1000 to 5 ppm. The requirement for the relative precision of the concentration determination was defined on the basis of the social order as follows: 10 % for minor and 15 % for trace elements.

EXPERIMENTAL

The emission atomic spectrography method used is characterized in Table 1. The chosen spectral lines of the analytical (X) and reference (R) elements and their basic characteristics [3] are shown in Table 2. Densitometric treatment of the analytical signal – spectral line density – was based on l-transformation [4] and on the corresponding calculation programs [5—7].

During the excitation of powder samples in D.C. arc, fraction distillation of elements occurs as a consequence of their different volatility. The evaporation of

Table 1. Spectrochemical Experimental Conditions

Spectrograph	PGS-2 grating spectrograph, $m = 2$
Dispersion	0.363 nm mm^{-1}
Focussing	Zeiss-type 3-lens system
Aperture of intermediate diaphragm	3.2 mm
Slit width	0.03 mm
Electrodes	graphite, Elektrokarbon, Topoľčany
carrier electrode	SU-304
counter electrode	SU-202
electrode gap	4 mm
Emulsion	ORWO, WU-3
Development	10 min at 20 °C in developer type ORWO F-43
Excitation	D.C. arc
Current intensity	10 A
Exposure time	70 s (without pre-burning)
Microdensitometer	4 D densitometer, MFKI Budapest

matrix may not be complete if the silicides content is high. Therefore, the first step of optimization was the investigation of the evaporation processes according to the *Ahrens* [8] theory using the integral correlation curves method [9, 10], *i.e.* the relationship

$$\sum I_X = f\left[\sum I_R\right] \qquad (1)$$

The medium- and high-volatile elements were combined with Pd whereas the low-volatile ones with In as reference elements. The method development continued by matrix effects control [11, 12] on the basis of calibration line courses [13—15] of the investigated elements in five different matrices: SiO$_2$, Fe$_2$O$_3$, galen-

Table 2. Spectral Lines Used

Element		Wavelength nm	Relative intensity in Cu-arc
Analytical spectral lines			
Ag	I	328.068	55000
Ag	I	338.289	28000
Ba	I	307.158	180
Bi	I	289.798	4000
Bi	I	306.772	36000
Cd	I	326.106	320
Co	I	344.364	8800
Co	I	345.350	21000
Cr	I	302.156	2800
Cu	I	282.437	500
Cu	I	324.754	50000
Cu	I	327.396	25000
Mo	I	315.816	6000
Mo	I	317.035	8700
Ni	I	300.249	4000
Ni	I	341.476	8200
Pb	I	280.199	10000
Pb	I	283.306	9500
Pb	I	287.332	2800
Sb	I	287.792	1400
Sn	I	283.999	14000
Sn	I	317.505	5500
W	I	294.699	2400
Zn	I	334.502	1400
Reference spectral lines			
In	I	293.263	1100
In	I	325.609	13000
Pd	I	302.791	1500
Pd	I	325.878	3500

Fig. 1. Integral evaporation curves presenting the $\sum I_X = f[\sum I_R]$ plot. X = Ag (■), Co (□), Mo (▲), and Ni (○); R = Pd.

ite, sphalerite-tetraedrite concentrate. Synthetic matrix of the composition 45 % SiO_2, 25 % CaO, 16 % MgO, 6 % Al_2O_3, 2 % MnO, 6 % Fe_2O_3 was used as a basic matrix. Such composition reflected most really the main components of the actual ore samples. The single mineral galenite and the sphalerite-tetraedrite concentrate originated from Banská Štiavnica and Slovinky, respectively [2]. The last step following the arrangement of experimental conditions according to the above described steps was the analytical calibration [14, 15]. The values $s(w_{X,r})$ and the element specific value of the limit of detection [16] $w(X_L)$ were also determined.

RESULTS AND DISCUSSION

Fig. 1 shows the dependence $\sum I_X = f[\sum I_{Pd}]$. For most of the investigated spectral line pairs, the proportionality of evaporation is confirmed in the time period 60 to 100 s. The proportionality is disturbed in the case of Ag after 90 s. The evaporation of easily volatile elements in combination with the reference element In is preceded by a remarkable evaporation of In (Fig. 2) and the evaporation of the analytical el-
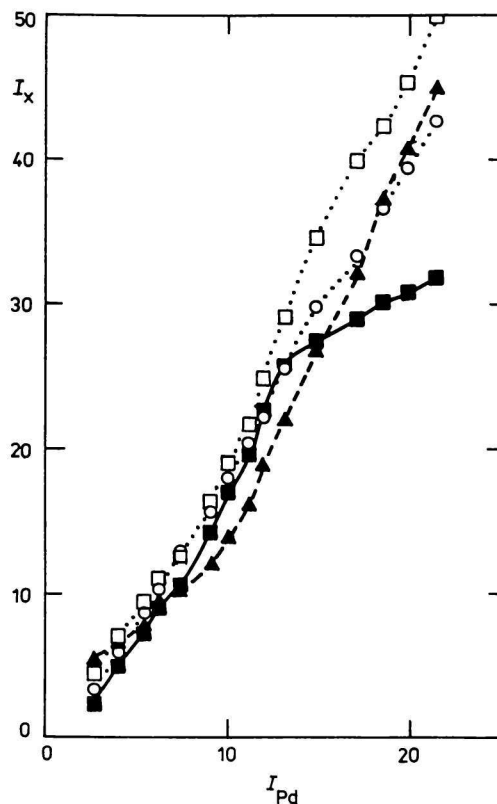
ements themselves follows approximately after 30 s. The optimum exposition time was then determined as a compromise taking into account the spectral line intensities to the background ratio as the main factor of detectability.

The comprehensive evaluation of matrix effects leads to the conclusion that practically identical courses of the calibration lines of the studied elements are reached in both model and actual matrices providing the defined limiting value of the relative precision of concentration determination is kept and the chosen experimental conditions are used in both cases. The results for Mo presented in Fig. 3 may serve as an example. The analytical calibration itself completed by calculation of the correlation-regression characteristics [14, 15] was the last step of the experimental optimization. The evaluation with regard to the information content and information efficiency followed. In Table 3 are listed the calculation results of the adequacy test of the linear model used as well as the limit of detection values $w(X_L)$ for all combinations of both analytical (X) and reference (R) spectral lines of the minor and trace elements studied.

The following statements could be made on the basis of the evaluation of the individual criteria of the so-called analytical order. The required upper limit of the calibration (10 %) was not reached for most of the
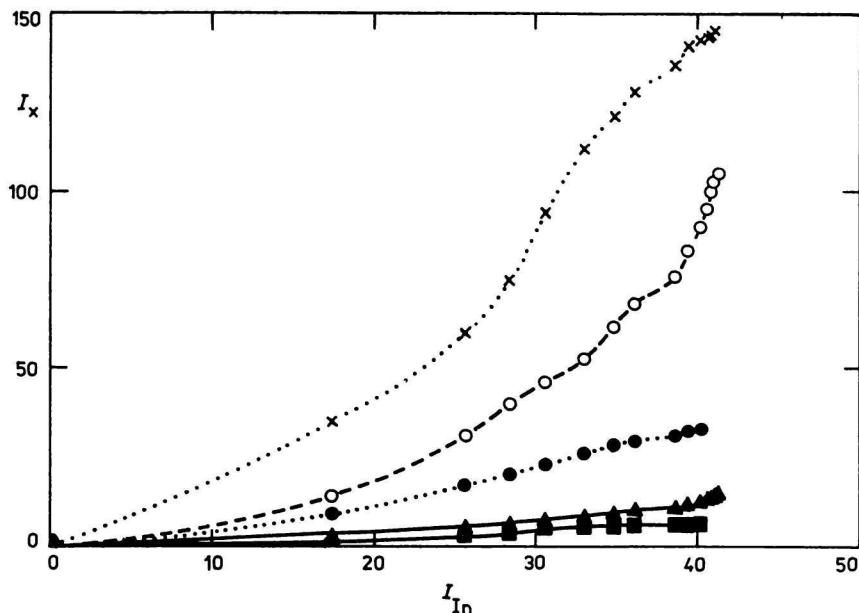
Fig. 2. Integral evaporation curves presenting the $\sum I_X = f[\sum I_R]$ plot. X = Ba (■), Bi (●), Cu (○), Pb (×), and Sb (▲); R = In.
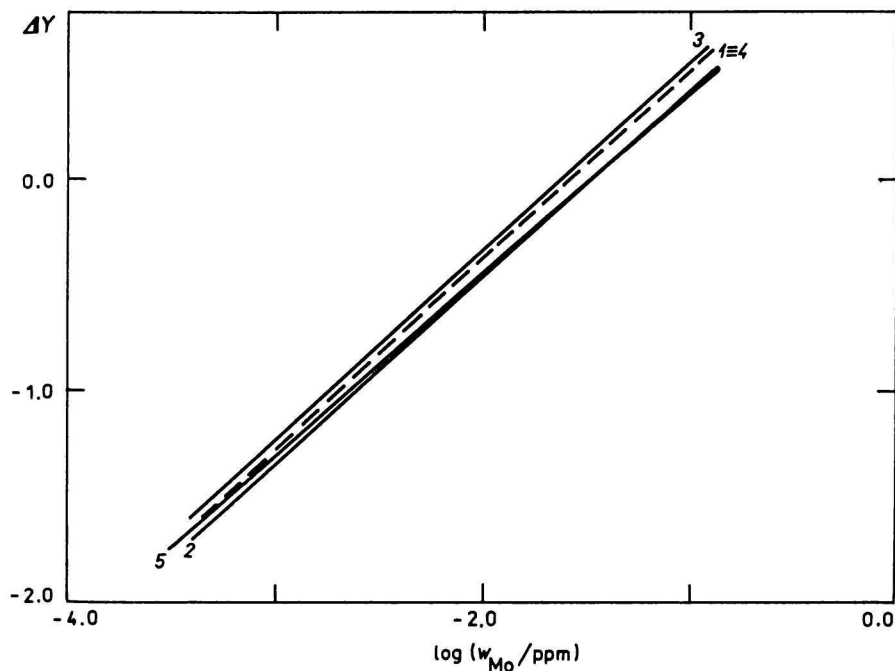

Fig. 3. Calibration lines of the spectral line pair Mo 317/Pd 325 in five matrices: *1.* model matrix for the final calibration, *2.* SiO_2 matrix, *3.* Fe_2O_3 matrix, *4.* galenite matrix, *5.* sphalerite-tetraedrite matrix.

minor elements, which is understandable with respect to exceeding the upper limit by 5 % for these elements [17]. In the case of trace elements, the required lower calibration limit (5 %) was reached only occasionally although the determined limit of detection values is mostly lower or close to this value. This is evidenced also by the fact that the efficiency coefficient values $\hat{E}(X)$ are in most cases equal or at least very close

to one. The precision of the method is within the defined limits with some exceptions as Cd, W and some combinations of spectral line pairs X/R with elements where several pairs were tested. The adequacy of linear model was confirmed. The calculated sensitivity values, the B_X slopes, are also favourable; for six cases (Ba, Bi, Cu, Ni, Sb, Sn) even an ideal value of $B_X = 1$ was confirmed by testing.

Table 3. The Parameters of the Analytical Calibration

Spectral line pair	$\dfrac{w(X_{max})}{ppm}$	$\dfrac{w(X_{min})}{ppm}$	t_{LIN} $\alpha = 0.05$	$B(X)$	$\dfrac{s(w_{X,r})}{\%}$	$\dfrac{w(X_L)}{ppm}$
Ag 328/Pd 325	160	1.6	+	0.85	25.0	0.31
Ag 338/Pd 325	320	1.6	+	0.82	15.8	0.10
Ba 307/In 293	5000	500.0	+	0.98*	11.4	236.00
Bi 289/In 293	1000	100.0		0.80	12.7	18.00
Bi 306/In 293	1000	32.0	+	0.94*	9.5	7.50
Cd 326/In 325	5000	158.0	+	0.71	17.3	9.30
Co 344/Pd 325	1000	100.0	−	0.86	13.5	17.00
Co 345/Pd 325	320	3.2	+	1.03	7.0	8.00
Cr 302/Pd 302	1000	100.0	+	0.69	11.6	
Cr 302/Pd 325	1000	10.0	+	0.83	10.8	7.60
Cu 282/In 293	10000	1000.0	+	1.07*	11.9	200.00
Cu 324/In 325	100	3.2	−	0.96*	9.8	0.32
Cu 327/In 325	100	3.2	+	0.87	18.7	0.27
Mo 315/Pd 325	1000	32.0	+	0.90	7.7	36.20
Mo 317/Pd 325	1000	10.0	+	0.90	9.1	3.20
Ni 300/Pd 302	320	32.0	+	0.89	8.4	11.60
Ni 341/Pd 325	1000	10.0	+	0.86	7.2	1.40
Ni 341/Pd 325	1000	32.0	+	0.96*	6.3	7.30
Pb 280/In 293	10^5	320.0	+	0.56	17.1	2.20
Pb 283/In 293	3200	32.0	+	0.49	17.5	0.46
Pb 287/In 293	10^5	3200.0	+	0.74	9.1	28.70
Sb 287/In 293	1000	320.0	+	0.97*	8.7	200.00
Sn 283/In 293	1000	32.0	+	0.94*	5.7	15.60
Sn 317/In 293	1000	3.2	+	0.93*	11.7	2.80
W 294/Pd 302	1000	320.0	+	0.78	16.0	90.00
Zn 334/In 325	5×10^5	1500.0	+	1.12	13.0	57.00

* Spectral line pairs with statistical significance of $B(X) = 1$.
$w(X_{max})$ – the highest calibration concentration, $w(X_{min})$ – the lowest calibration concentration, t_{LIN} – test of linearity, $B(X)$ – sensitivity (the slope of the calibration straight line), $s(w_{X,r})$ – relative precision, $w(X_L)$ – detection limit.
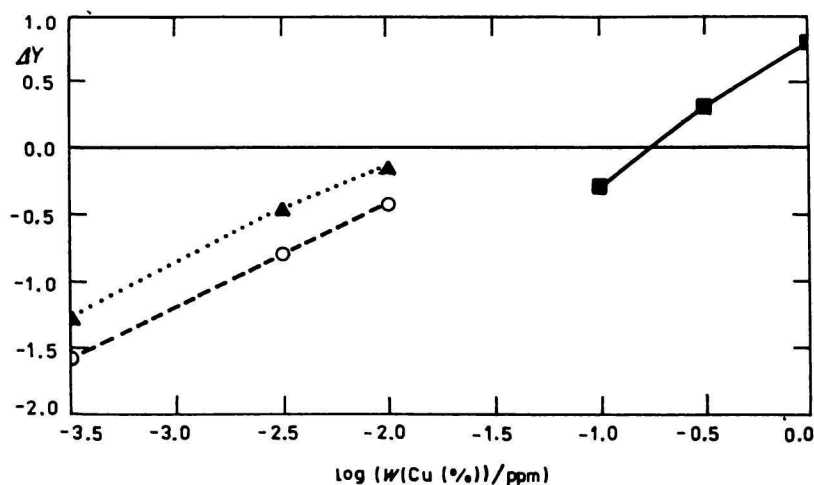

Fig. 4. Calibration lines for Cu in the model matrix for three various pairs of spectral lines Cu/In. ■ Cu 282/In 293, ▲ Cu 324/In 325, ○ Cu 327/In 325.

The calibration lines for Cu respect the requirement of a very wide concentration range (Fig. 4). The optimum parameters were not reached in the case of Pb with any of the spectral line pairs in spite of the linearity of the plot in a wide concentration range as it is shown in Fig. 5. The determination of both Zn and W determination by the given method is rather on a low level since neither the relative precision nor the detectability reach the desired values. This fact is, however, characteristic of multielemental methods and is one of the reasons to express the necessity of complex evaluation of these methods on the basis of information characteristics.

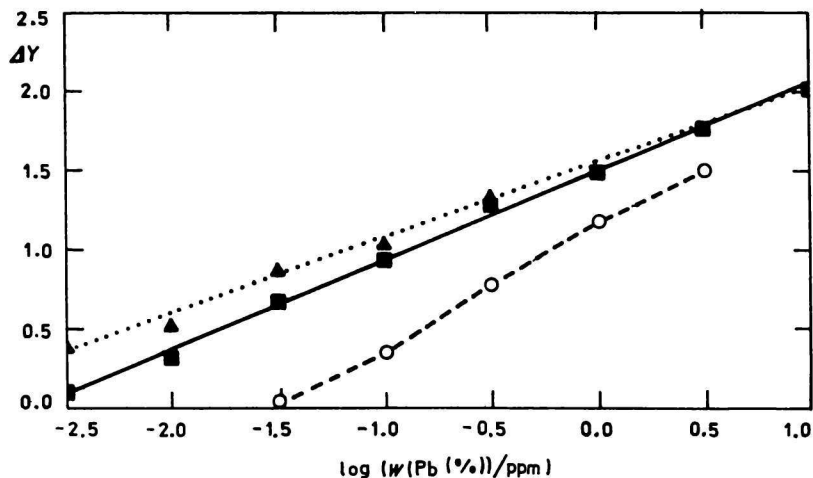The calibration line parameters enable to calcu-

Fig. 5. Calibration lines for Pb in the model matrix for three various pairs of spectral lines Pb/In. ■ Pb 280/In 293, ▲ Pb 283/In 293, ○ Pb 287/In 293.

Table 4. The Calculated Values of Information Content and Information Efficiency of the Analytical Elements

Spectral line pair	Parameter of the information theory							
	1	2	3	4	5	6	7	8
Ag 338/Pd	2.76	2.07	2.76	0.97	2.68	0.75	2.68	2.01
Ba 307/In	2.63	1.97	2.90	1.00	2.90	0.75	2.18	2.18
Bi 306/In	2.77	2.08	3.22	1.00	3.22	0.75	2.42	2.42
Cd 326/In	2.75	2.06	2.62	0.87	2.28	0.75	1.97	1.71
Co 345/Pd	2.80	2.10	3.39	0.60	2.03	0.75	2.54	1.52
Cr 302/Pd	2.81	2.11	3.14	1.00	3.14	0.75	2.36	2.36
Cu 282/In	3.21	3.21	2.86	0.71	2.03	1.00	2.86	2.03
Cu 324/In	2.77	2.08	3.18	1.00	3.18	0.75	2.39	2.39
Mo 317/Pd	2.77	2.08	3.31	1.00	3.31	0.75	2.48	2.48
Ni 341/Pd	2.81	2.11	3.54	1.00	3.54	0.75	2.68	2.68
Pb 280/In	3.15	3.15	3.26	1.00	3.26	1.00	3.26	3.26
Sb 287/In	3.15	3.15	3.31	1.00	3.31	1.00	3.31	3.31
Sn 283/In	3.14	3.14	3.65	1.00	3.65	1.00	3.65	3.65
Sn 317/In	2.85	2.14	3.11	1.00	3.11	0.75	2.33	2.33
W 294/Pd	2.21	1.10	2.10	0.92	1.93	0.50	1.05	0.97
Zn 334/In	2.93	2.20	2.91	1.00	2.91	1.00	2.91	2.91
	41.51	36.75	49.26		46.48		41.07	38.21
	9	10	11		12		13	14

1 $I(p, p_0)_T = E(p, p_0)_T$
2 $I(p, p_0)_{T,REL} = E(p, p_0)_{T,REL}$
3 $\hat{I}(p, p_0)$
4 $\hat{E}(X)$
5 $\hat{E}(p, p_0)$
6 $k(REL)_X$
7 $\hat{I}(p, p_0)_{REL}$
8 $\hat{E}(p, p_0)_{REL}$

9 $MI(p, p_0)_T$
10 $\underline{MI}(p, p_0)_{T,REL}$
11 $\widehat{MI}(p, p_0)$
12 $\widehat{ME}(p, p_0)$
13 $\widehat{MI}(p, p_0)_{REL}$
14 $\widehat{ME}(p, p_0)_{REL}$

The valuation: $\widehat{MI}(p, p_0) - MI(p, p_0)_T = +3.75, +8.24 \%$
$\qquad\qquad\quad \widehat{ME}(p, p_0) - \underline{ME}(p, p_0)_T = +0.97, +2.13 \%$
$\qquad\qquad\quad \widehat{ME}(p, p_0) - \widehat{MI}(p, p_0) = -2.78, -5.6 \%$
The valuation with incorporating of relevance:
$\qquad\qquad\quad \widehat{MI}(p, p_0)_{REL} - MI(p, p_0)_{T,REL} = +4.32, +11.76 \%$
$\qquad\qquad\quad \widehat{ME}(p, p_0)_{REL} - \underline{ME}(p, p_0)_{T,REL} = +1.46, +3.97 \%$
$\qquad\qquad\quad \widehat{ME}(p, p_0)_{REL} - \widehat{MI}(p, p_0)_{REL} = -2.86, -6.96 \%$

The used symbols are identical with the symbols in Refs. [18—21].

late the whole set of evaluating parameters of the information theory [18, 21], namely the information content and efficiency values and corresponding measures of information content and efficiency values

listed in Table 4. These were calculated separately for the so-called tolerance (designed) and real (experimental) values. Comparison of these two groups of data, mainly those of the measures of information content and efficiency values enables to state more judgements on the efficiency of the suggested method. The difference $\widehat{MI}(p, p_0) - MI(p, p_0)_T$ is positive and thus the method tested achieves higher information content measure of 8.24 %. The measure of information efficiencies $\widehat{ME}(p, p_0) - ME(p, p_0)_T$ is positive and the achieved information efficiency measure is higher of 2.13 %. The evaluated method thus exceeds the required tolerance values. Since not all of the elements determined show equal information relevance [21], element specific *relevance coefficients* $\hat{k}(REL)$ were suggested for further evaluation. The difference $\widehat{MI}(p, p_0)_{REL} - MI(p, p_0)_{T,REL}$ is positive with an increase of 28.62 %. The difference $\widehat{MI}(p, p_0)_{REL} - ME(p, p_0)_{T,REL}$ is also positive with an increase of 26.44 %. Both these positive increases prove that the method on the whole reaches higher values of measures of information content and efficiency than are the required values. This means that the method disposes of sufficient reserves and is applicable for a whole geochemically and spectrochemically complicated set of elements and concentration regions.

CONCLUSION

Development of a multielement spectrochemical method represents always a compromise solution, mainly in the field of powder materials analysis by classical spectrographic procedures. Such is also the method presented here for determination of 14 minor and trace elements in ore matrices.

The choice of the most suitable experimental method and calibration model respecting wide variety of matrices considered was followed by the evaluation of the method. Following these introductory operations, collection of data took place enabling exact compromise evaluation of the method using advanced procedure based on the information characteristics.

The method and results of the presented evaluation demonstrate a suitable access to a comprehensively taken evaluation of multielement analytical methods. The mentioned procedure may be remarkably more efficient if the obtained analytical-information criteria were evaluated with required weight for individual elements and/or combination of elements on the basis of preliminary defined priorities [22].

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Translated by M. Gálová