The Use of Information Theory in Atomic Spectrochemistry IV*. Extension of the Number of Partial Efficiency Coefficients of the Information Theory

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To enable the complex valuation of analytical methods footing in the information theory the expansion of the number of partial efficiency coefficients is suggested in accordance with the criterion of ISO validation procedures. For the validation procedure, a novel conversion process for the determination of the efficiency of analytical method was defined. The partial efficiency coefficients in this calculation were defined as the ratio of tolerance and experimentally determined figures of merit.

From the point of view of the information theory, the efficiency of analytical methods is qualified by the values of partial efficiency coefficients. The determination of the values of partial efficiency coefficients is determined by the analytical order (request), especially by the defined tolerance value parameters, and also by the experimentally obtained validation parameters. It is dependent on the fundamental power parameters, which define mainly the precision of the concentration determination, detectability, actual analytical range, the range of the linear part of the analytical straight line, the trueness and the recovery of the analytical determination.

Until now, only three efficiency coefficients [1, 2] have been used in the information theory. The first coefficient e_1 is qualified by the precision of concentration determination. Reaching of the requested detectability connects the second coefficient e_2, and the rarely used third coefficient e_3 is conditioned by the time factor of analysis. Based on the previous definitions it is evident that the values of the efficiency coefficient $E(X)$ and the partial efficiency coefficients e_i exist in the interval $\Delta \in \langle 1, 0 \rangle$. Using the above definition and logical consideration, the values of the efficiency coefficients and the partial efficiency coefficients are either equal to unity or smaller, but never reach zero. At present, the very complicated ISO complex validation system [3] is used. Therefore it is advantageous to expand the number i of partial efficiency coefficients, by including such parameters which are fundamental from the standpoint of the ISO validation.

THEORETICAL

Before calculation of the information efficiency value $E(p, p_o)$ it is necessary to calculate the information content value $I(p, p_o)$. For this calculation, eqn (1) may be used only if three fundamental figures of merit [4] are known: the minimum concentration value $c(X)_{min}$, the maximum concentration value $c(X)_{max}$, and the standard deviation of the concentration determination $s(c)_X$, the so-called absolute precision value. Eqn (1) is derived from the Kulback's divergence criterion [5]. The final form of eqn (1a) was related by *Eckschlager* and *Štepánek* [6].

$$I(p, p_o)_X = \ln \frac{c(X)_{max} - c(X)_{min}}{s(c)_X} \cdot \frac{\sqrt{N}}{2t(\alpha, F)} \quad (1a)$$

$$\Delta c(X) = c(X)_{max} - c(X)_{min} \quad (1b)$$

In eqn (1) N represents the number of individual independent measurements used for determination of $s(c)_X$, X represents the actual analytical element being determined. The value $t(\alpha, F)$ is received from Ref. [5], where α is the value of the significance level $\alpha = 0.03874 \div 0.04$ and F is the value of the degrees of freedom $F = N - 1$. The information efficiency is given by

$$E(p, p_o)_X = E(X) \cdot I(p, p_o)_X \quad (2)$$

where $E(X)$, the actual efficiency coefficient, is given by the following point product

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*For Part III see Ref. [2].

$$E(X) = \prod_{i=1}^{p} e_i \qquad (3)$$

Definition of the Analytical Order

In eqn (3) the value $E(X)$ represents the total efficiency coefficient, which is the subject of this paper. The partial efficiency coefficients should be defined by means of the analytical order. For this procedure it is necessary to define a set of the tolerance values specified below.

First, it is necessary to define the value of the required absolute precision of the concentration determination $s(c)_{X,T}$, and the relative precision of the concentration determination $c(X)_{X,r,T}$ referred to the centre $\overline{c}(X)_T$ of the requested concentration range. But the calculation of the value $\overline{c}(X)_T$ claims the limiting tolerance concentration values $c(X)_{max,T}$ and $c(X)_{min,T}$.

$$\overline{c}(X)_T = \frac{1}{2}\left(c(X)_{max} - c(X)_{min}\right) \qquad (4)$$

Secondly, it is necessary to define the required limit of detection (LOD) of the analytical elements $c(X)_{L,T}$, determined in accordance with the IUPAC canonical Kaiser's 3σ criterion. The following tolerance value is required: the analytical range $\Delta c(X)_T$ for the analytical determination, and this range is given by the difference (5) of the suggested maximum and minimum tolerance concentrations of the analytical determination.

$$\Delta c(X)_T = c(X)_{max,T} - c(X)_{min,T} \qquad (5)$$

The next very similar tolerance values are the higher $c(X)_{max,T,lin}$ and lower $c(X)_{min,T,lin}$ limiting tolerance concentrations of the linear part of the analytical straight line. From these limiting values it is possible to derive the range $\Delta c(X)_{T,lin}$ of the linear part of the analytical straight line

$$\Delta c(X)_{T,lin} = c(X)_{max,T,lin} - c(X)_{min,T,lin} \qquad (6)$$

The definition of this value has its significance only in the case of combined, linear and nonlinear analytical line. Otherwise, the equality $\Delta c(X)_{T,lin} = \Delta c(X)_T$ is valid. The next tolerance value is similar to the tolerance value $c(X)_{st}$ of the analytical element (X) that presents the concentration of noncertified but well-known reference powder standard or solution.

Finally, it is necessary to define two additional tolerance time limits: the necessary time t_1 of the analysis, and the last usable time t_2 of the analysis, as well as the number of requested analytical elements Q_{max}.

The tolerance values of the partial efficiency coefficients e_i, and the tolerance efficiency coefficient $E(X)$ are principally equal to unity, contrary to the values of the partial efficiency coefficients $\hat{e}_i$, derived from the experimentally confirmed figures of merit which range within the interval $\Delta \in \langle 1, 0 \rangle$. It means that their maximum values are equal to one, and the maximum values never reach zero. In addition to the above given tolerance values for the calculation of the individual partial efficiency coefficients $\hat{e}_i$ it is necessary to establish novel experimental values, which are determined on the basis of actual experimental measurements. They are represented by the following figures of merit [7] and constants: $\hat{c}(X)_{max}$, $\hat{c}(X)_{min}$, $s(\hat{c})_X$, $\hat{c}(X)_{max,lin}$, $\hat{c}(X)_{min,lin}$, $s(\hat{c})_{X,lin}$, $\hat{c}(X)_L$, $\hat{c}(X)_{st}$, t, and Q. These constants and figures of merit [7] are necessary to be determined on the basis of analytical calibration [8], and on the basis of calculation of limit of detection [9]. On the basis of obtained figures of merit and constants it is possible to express the procedure of determination and calculation of values of partial efficiency coefficients. The values of the given partial efficiency coefficient $\hat{e}_i$ are in the interval $\Delta \in \langle 1, 0 \rangle$ like those of the efficiency coefficient $\hat{E}(X)$.

The determination of the first partial efficiency coefficient $\hat{e}_1$ dependent on the precision of the concentration determination $s(\hat{c})_X$ of the element (X) is given by following equations. If the inequality $\hat{s}(c)_X \leq s(c)_X$ is valid, the partial efficiency coefficient is conventionally regarded as equal to unity, $\hat{e}_1 = 1$. If the inequality $\hat{s}(c)_X > s(c)_X$ is valid, the value of the partial efficiency coefficient is less than unity, $\hat{e} < 1$, and is calculated by the equation

$$\hat{e}_1 = s(c)_{X,T}/\hat{s}(c)_X \qquad (7)$$

Determination of the second partial efficiency coefficient $\hat{e}_2$ dependent on the detectability of the analytical determination of the element (X) is given in the following eqn (8). If the inequality $\hat{c}(X)_L \leq c(X)_{L,T}$ is valid, then the value of the partial efficiency coefficient $\hat{e}_2$ is conventionally equal to unity, $\hat{e}_2 = 1$. If the inequality $\hat{c}(X)_L > c(X)_{L,T}$ is valid, then the value of the partial efficiency coefficient $\hat{e}_2$ is less than unity, $\hat{e}_2 < 1$, and is calculated by the equation

$$\hat{e}_2 = c(X)_{L,T}/\hat{c}(X)_L \qquad (8)$$

The determination of the third partial efficiency coefficient $\hat{e}_3$ is dependent on the experimentally determined actual concentration range $\Delta \hat{c}(X) = \hat{c}(X)_{max} - \hat{c}(X)_{min}$, as well as the required concentration range $\Delta c(X)_T = c(X)_{max,T} - c(X)_{min,T}$ of the analytical determination of the element (X). If the inequality $\Delta \hat{c}(X) \leq \Delta c(X)_T$ is valid, then the value of the partial efficiency coefficient $\hat{e}_3$ is conventionally equal to unity, $\hat{e}_3 = 1$. If the inequality $\Delta \hat{c}(X) < \Delta c(X)_T$ is valid, then the partial efficiency coefficient $\hat{e}_3$ is less than unity, $\hat{e}_3 < 1$, and is calculated by the equation

$$\hat{e}_3 = \Delta \hat{c}(X)/\Delta c(X)_T \qquad (9)$$

Determination of the fourth partial efficiency coefficient $\hat{e}_4$ represents a specific problem. It is dependent on the linear range $\Delta\hat{c}(X)$ of the analytical straight line and the required concentration range $\Delta c(X)_T$ of the analytical determination of the element (X). If the inequality $\Delta\hat{c}(X)_{lin} \geq \Delta c(X)_T$ is valid, then the value of the partial efficiency coefficient $\hat{e}_4$ is conventionally equal to unity, $\hat{e}_4 = 1$. But if the inequality $\Delta\hat{c}(X)_{lin} < \Delta c(X)_T$ is valid, then the value of the partial efficiency coefficient $\hat{e}_4$ is calculated by the equation

$$\hat{e}_4 = \Delta\hat{c}(X)_{lin}/\Delta c(X)_{T,lin} \qquad (10)$$

The determination of the value of the fifth partial efficiency coefficient $\hat{e}_5$ depends on the measure of the so-called trueness (previously denoted as the accuracy) of the analytical determination. This calculation procedure is conditioned by the fact whether an official certified, or similarly confirmed standard with declared concentration values $c(X)_{st}$ of the given analytical elements (X) is available.

If the equality $\hat{c}(X)_{st} = c(X)_{st}$ is valid, the value of the fifth partial efficiency coefficient $\hat{e}_5$ is equal to unity, $\hat{e} = 1$. However, this case is very rare. For the condition $\hat{c}(X)_{st} \neq c(X)_{st}$ therefore the following calculation of the partial efficiency coefficient $\hat{e}_5$ is necessary. For the inequality $\hat{c}(X)_{st} > c(X)_{st,}$ the precision of the measurement defined by the inequality $\Delta\hat{c}(X) = (\hat{c}(X)_{st} - c(X)_{st}) \leq 0.1 \cdot c(X)_{st}$ can be accepted as the suitable efficiency. In this case the value of partial efficiency coefficient $\hat{e}_5$ is equal to unity, $\hat{e}_5 = 1$. If the inequality $\Delta c(X) = (\hat{c}(X)_{st} - c(X)_{st}) > 0.1 \cdot c(X)_{st}$ is valid, then the value of partial efficiency coefficient $\hat{e}_5$ is less than unity, and it is calculated by the equation

$$\hat{e}_5 = c(X)_{st}/\hat{c}(X)_{st} \qquad (11)$$

For the inequality $\hat{c}(X)_{st} < c(X)_{st}$, the case defined by the inequality $\Delta c(X) = (c(X)_{st} - \hat{c}(X)_{st}) \leq 0.1 \cdot c(X)_{st}$ can be accepted as the suitable efficiency and the partial efficiency coefficient $\hat{e}_5$ is again equal to unity, $\hat{e} = 1$. If the opposite difference $(c(X)_{st} - \hat{c}(X)_{st}) > 0.1 \cdot c(X)_{st}$ is valid, then it is necessary to use the equation

$$\hat{e}_5 = \hat{c}(X)_{st}/c(X)_{st} \qquad (12)$$

The computation procedure (logic) of the sixth partial efficiency coefficient $\hat{e}_6$, which is conditioned by the recovery of the analytical determination of the element (X), is very similar to the above given procedure. It is necessary here to substitute the value $\hat{c}(X)_{st}$ in eqn (11) by the experimentally obtained value $\hat{c}(X)_{rec}$, and the value $c(X)_{st}$ by the tolerance value $c(X)_{T,rec}$. The last value does not represent the certified value of the standard $c(X)_{st}$ but the concentration value of the tested reference materials $c(X)_{rec}$.

Beside the described element-specific efficiency coefficients $\hat{e}_i$ it is also necessary to consider two efficiency coefficients ε_i, which are not element-specific, but are conditioned by the whole set of analyzed elements (X), and therefore possess a multielement character. The coefficients ε_i are conditioned by the efficiency of the multielement determination by means of the time limits t_i and the limiting number of determined elements Q_{max}.

Two time limits have to be chosen in advance. The time t_1 represents the time limit when the analysis is already necessary and the time t_2 is the time limit when the analysis, from the standpoint of technological or scientifical aspects, is not actual. The value of the partial efficiency coefficient ε_1 is for the time interval $\Delta t_1 \in (0, t_1\rangle$ conventionally regarded as equal to unity, $\varepsilon_1 = 1$. For the time interval $\Delta t_2 \in (t_1, t_2\rangle$ the value ε_1 is always less than unity, $\varepsilon_1 < 1$, and the partial efficiency coefficient is calculated by the equation

$$\varepsilon_1 = t_1/t \qquad (13)$$

The time t represents the real time of the complex analysis duration. For the undesirable case when $t > t_2$, the partial efficiency coefficient ε_1 is equal to zero, $\varepsilon_1 = 0$.

In the multielement analysis, it may occur that it is not possible to determine all requested elements (X) by the given complex analytical procedure with successful figures of merit. The maximum number of the analytical elements is marked as Q_{max} and the number of successfully determinable elements as Q. The partial efficiency coefficient ε_2 is either equal to unity, $\varepsilon_2 = 1$, or is less than one, $\varepsilon_2 < 1$, but never reaches the zero value.

The calculation of the partial efficiency coefficient ε_2 is given by the equation

$$\varepsilon_2 = Q/Q_{max} \qquad (14)$$

The calculation of the coefficient of information efficiency $\hat{E}(X)$ is based on the multiplication principle of the partial efficiency coefficients $\hat{e}_i$ and is given by the equation

$$\hat{E}(X) = \hat{e}_1 \cdot \hat{e}_2 \cdot \hat{e}_3 \cdot \hat{e}_4 \cdot \hat{e}_5 \cdot \hat{e}_6 \qquad (15)$$

In a special case, the individual partial efficiency coefficients $\hat{e}_i$ may have different importance; it is necessary to use different statistical "weights" k_i which multiply the individual partial efficiency coefficients. The k_i are between one and zero, $k_i \in \langle 1, 0)$, but never reached the zero value.

The fundamental calculation of the value of information efficiency $\hat{E}(p, p_o)_X$ is given by the equation

$$\hat{E}(p, p_o)_X = \hat{E}(X) \cdot \hat{I}(p, p_o)_X \qquad (16)$$

The final calculation of the measure of information efficiency is given by the equation

$$\hat{ME}(p, p_o) = \sum_{1}^{Q} \hat{E}(p, p_o)_{X,i} \qquad (17)$$

In multielement determinations, when the value ε_1 is different from zero, it is unambiguous to express this fact by the formation of the measure of information efficiency

$$\hat{ME}(p, p_o)_{corr} = \hat{ME}(p, p_o) \cdot \varepsilon_1 \cdot \varepsilon_2 \qquad (18)$$

In the specific case, when the element nonspecific efficiency coefficient is equal to zero, $\varepsilon_1 = 0$, the value of the corrected measure of information efficiency is logically equal to zero.
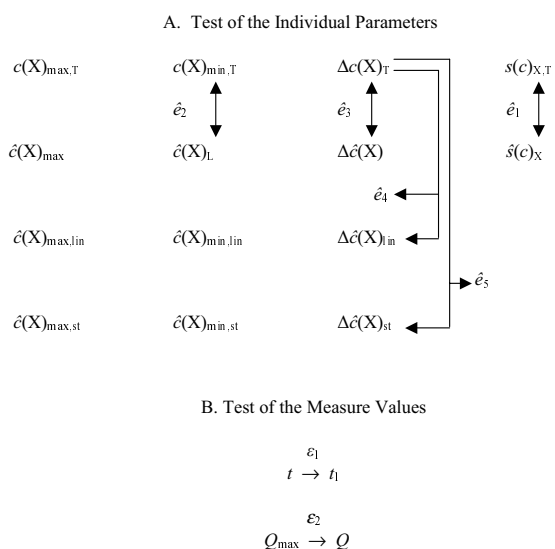
In the evaluation of the information efficiency of an analytical method, it is necessary to distinguish between the theoretical so-called tolerance values $E(p, p_o)_X$, $ME(p, p_o)$ and the experimental values $\hat{E}(p, p_o)_X$, $\hat{ME}(p, p_o)$. The differences in eqns (19) and (20) express the success of the experimental optimization procedure and are decisive for the optimization.

$$\Delta E = E(p, p_o)_{X,T} - \hat{E}(p, p_o)_X \qquad (19)$$

$$\Delta ME = ME(p, p_o)_T - \hat{ME}(p, p_o) \qquad (20)$$

The scheme of the testing procedure of the above-mentioned parameter values of the information theory is shown in Table 1.

Table 1. The Scheme of the Testing Procedure

A. Test of the Individual Parameters

B. Test of the Measure Values

$$\overset{\varepsilon_1}{t \to t_1}$$

$$\overset{\varepsilon_2}{Q_{max} \to Q}$$

Remark: $c(X)_{min,T} \equiv c(X)_{L,T}$

NUMERICAL EXAMPLES AND DISCUSSION

The fundamental performance parameters of any multielement determination of minor and trace elements [10—13] were chosen for the illustration of the suggested testing procedure (Table 1). The analysis time t_1 of the whole analysis of the analytical elements Q was always less than the required real time t, therefore the coefficient ε_1 is equal to unity, $\varepsilon_1 = 1$. The value of the coefficient ε_2 depends on the tested typical analytical methods. Evidently, the value of the total efficiency coefficient $\hat{E}(X)$ of the multielement determination follows the changes of this partial coefficient.

First, the testing procedure subordinated to the chosen parameter of the determination of minor and trace elements of the gravitation dust sediments [10, 11] was carried out. The required tolerance and experimentally obtained parameters defining the power of the tested method are presented in Table 2. The values $\hat{I}(p, p_o)_X$ are higher than the values $I(p, p_o)_{X,T}$. The case when $\hat{I}(p, p_o)_X < I(p, p_o)_{X,T}$ is the consequence either by impair of detectability $\hat{c}(X)_L$ or the precision $\hat{s}(c)_X$ of the concentration determination. The detailed results of the testing procedure are shown in Table 3. The valid inequality $\hat{MI}(p, p_o) > MI(p, p_o)$ confirmed that the method of optimization had reached the required measure of the information content. The increase of the value $\hat{MI}(p, p_o)$ by 12.84 % confirms the success in experimental optimization. Only for the elements Co and Ti, the experimentally obtained total efficiency coefficient $\hat{E}(X)$ was less than unity. Therefore the decrease of the measure of the information efficiency $\hat{ME}(p, p_o)$ was 18.03 %. Such a decrease is the tax for the impossibility of the full optimization of all required elements. In the case of multielement determination it is necessary to make a compromise between the improvement of the detectability and the precision of the determination.

In the tested AES method, for all determined elements in the given concentration range $\Delta\hat{w}(X)$, the convenient linearity was reached. Therefore the linearity testing was accomplished for the results of the AAS method [12] developed for the determination of the chemical quality of drinking water. In this case the values of the coefficients ε_1 and ε_2 were equal to unity. All $\hat{I}(p, p_o)_{X,lin}$ values of the linear straight lines were lower than the $\hat{I}(p, p_o)_X$ values of the nonlinear straight lines (Table 4). Evidently the $\hat{MI}(p, p_o)_{lin}$ value of the method was lower than the value $\hat{MI}(p, p_o)$. This decrease was about 10 %, and was caused by the decrease of the concentration ranges $\Delta\hat{w}(X)_{lin}$ in comparison to the value $\Delta\hat{w}(X)$. The increase of the precision value $\hat{s}(w)_{X,lin}$ cannot compensate for the decreasing influence of the values of concentration ranges $\Delta\hat{w}(X)_{lin}$. Consequently, the values of partial efficiency coefficients $\hat{e}_4$ for all

Table 2. Input Data of the Fundamental Parameters of Information Theory

Element	$\{w(X)_{\max,T}\}$	$\{w(X)_{\min,T}\}$	$\Delta\{w(X)_T\}$	$\{s(w)_{X,T}\}$	$I(p,p_o)_{X,T}$
Ag	100.0	3.2	96.8	7.7	2.77
Bi	1000.0	31.6	968.4	77.4	2.76
Co	3160.0	31.6	3128.4	239.4	2.81
Cr	1000.0	10.0	990.0	75.8	2.81
Fe	3160.0	316.0	2844.0	260.0	2.63
Mn	316.0	10.0	306.0	24.5	2.76
Mo	316.0	10.0	306.0	24.4	2.74
Ni	316.0	31.6	284.4	26.1	2.63
Pb	1000.0	10.0	990.0	75.8	2.81
Ti	3160.0	100.0	3060.0	244.5	2.77
V	1000.0	31.6	968.4	77.4	2.76
					$\mathrm{MI}(p,p_o)$
					40.98

Element	$I(p,p_o)_{X,T}$	$\{\hat{w}(X)_{\max}\}$	$\{\hat{w}(X)_L\}$	$\Delta\{\hat{w}(X)\}$	$\{\hat{s}(w)_X\}$	$I(p,p_o)_X$
Ag	2.77	100.0	0.3	96.8	7.2	2.86
Bi	2.76	1000.0	13.0	987.0	61.6	3.00
Co	2.81	3160.0	46.0	3114.0	229.3	2.79
Cr	2.81	1000.0	7.6	992.4	29.6	3.74
Fe	2.63	3160.0	2.0	3158.0	169.0	3.16
Mn	2.76	316.0	4.0	312.0	10.2	3.66
Mo	2.74	316.0	3.6	312.4	15.9	3.20
Ni	2.63	316.0	8.4	307.5	23.5	2.78
Pb	2.81	1000.0	5.4	994.6	69.2	2.90
Ti	2.77	3160.0	26.0	3134.0	265.4	2.70
V	2.76	1000.0	10.0	990.0	25.5	3.89
	$\mathrm{MI}(p,p_o)$					$\mathrm{M\hat{I}}(p,p_o)$
	40.98					46.24

Remarks: $w(X)_{\max,T} \equiv \hat{w}(X)_{\max}$; $w(X)_{\min,T} \equiv \hat{w}(X)_{L,T}$; $I(p,p_o)_X \equiv E(p,p_o)_X$; $\mathrm{MI}(p,p_o)_T \equiv \mathrm{ME}(p,p_o)$; $\hat{I}(p,p_o)_X \leq I(p,p_o)_X$. All concentration values w, $\hat{w}$, and s are given in ppm units. The linearity of straight lines was convenient.

Table 3. Results of the Testing of Fundamental Parameters

Element	$\hat{I}(p,p_o)_X$	$\hat{e}_1$	$\hat{E}_2$	$\hat{e}_3$	$\hat{E}(X)$	$\hat{E}(p,p_o)_X$
Ag	2.88	1.00	1.00	1.00	1.00	2.88
Bi	3.00	1.00	1.00	1.00	1.00	3.00
Co	2.79	1.00	0.69	0.99	0.68	1.90
Cr	3.74	1.00	1.00	1.00	1.00	3.74
Fe	3.16	1.00	1.00	1.00	1.00	3.16
Mn	3.66	1.00	1.00	1.00	1.00	3.66
Mo	3.20	1.00	1.00	1.00	1.00	3.20
Ni	2.78	1.00	1.00	1.00	1.00	2.78
Pb	2.90	1.00	1.00	1.00	1.00	2.90
Ti	2.70	0.92	1.00	1.00	0.92	2.48
V	3.89	1.00	1.00	1.00	1.00	3.89

$\mathrm{MI}(p,p_o)_T$	$\mathrm{M\hat{I}}(p,p_o)$	$\Delta M_{\hat{I}}$	$\Delta M_{\hat{I},r}/\%$
40.98	46.24	5.26	12.84
$\mathrm{ME}(p,p_o)_T$	$\mathrm{M\hat{E}}(p,p_o)$	$\Delta M_{\hat{E}}$	$\Delta M_{\hat{E},r}/\%$
40.98	33.50	−7.39	−18.03

Remarks: The linearity of all straight lines and the verification of the truest were fulfilled by all the elements. $\Delta M_{\hat{I}} = \mathrm{M\hat{I}}(p,p_o) - \mathrm{MI}(p,p_o)_T$; $\Delta M_{\hat{E}} = \mathrm{M\hat{E}}(p,p_o) - \mathrm{ME}(p,p_o)_T$.

tested elements were less than the unity, and the values $\hat{E}(p,p_o)_{X,\mathrm{lin}}$ decreased extremely, in average about 35 %. This final result means that the linear straight lines for the AAS determination have better precision and detectability but a narrower concentration range compared to the nonlinear straight-line case.

Finally, the testing of the trueness is illustrated by the results of the AES method [13] developed for the

Table 4. Input Data of the Specific Values of the Figures of Merit

A. Data for the Testing of the Linearity of Straight Lines

Element	$\{\hat{w}(X)_{max}\}$	$\{\hat{w}(X)_{min}\}$	$\Delta\{\hat{w}(X)\}$	$\{\hat{s}(w)_X\}$	$\hat{I}(p, p_o)_X$
Cd	10.0	0.5	9.5	0.03	6.00
Cr	15.0	1.0	14.0	0.07	6.09
Cu	10.0	0.1	9.9	0.04	5.68
Mo	10.0	0.5	9.5	0.04	5.71
$\hat{MI}(p, p_o)$	23.48				

Element	$\{\hat{w}(X)_{max,lin}\}$	$\{\hat{w}(X)_{min,lin}\}$	$\Delta\{\hat{w}(X)_{lin}\}$	$\{\hat{s}(w)_{X,lin}\}$	$\hat{I}(p, p_o)_{X,lin}$
Cd	5.0	0.5	4.5	0.02	5.66
Cr	12.0	0.5	11.5	0.05	5.62
Cu	8.0	0.1	7.9	0.03	5.67
Mo	3.5	0.1	3.4	0.01	5.38
$\hat{MI}(p, p_o)_{lin}$	21.13				

Element	$\hat{e}_4$	$\hat{E}(p, p_o)_{X,lin}$	$\Delta_{\hat{I},\hat{E}}$	$\Delta_{\hat{I},\hat{E},r}/\%$
Cd	0.47	2.66	−3.0	−53.0
Cr	0.82	4.61	−1.01	−18.0
Cu	0.80	4.54	−1.13	−19.9
Mo	0.36	1.94	−3.44	−63.9
$\hat{ME}(p, p_o)_{lin}$	13.75			

Remarks: The values of coefficients $\hat{e}_1$, $\hat{e}_2$, and $\hat{e}_3$ are equal to unity. The recovery was not tested. $\Delta_{\hat{I},\hat{E}} = \hat{E}(p, p_o)_{X,lin} - \hat{I}(p, p_o)_{X,lin}$; $\Delta_{\hat{I},\hat{E},r} = (\Delta\hat{I},\hat{E}/\hat{E}(p, p_o)_{lin}) \cdot 100$. All concentration values w and $\hat{w}$ are given in ppm units.

B. Results of the Testing of the Linearity of Straight Lines of AAS Determinations

Parameter	Cd	Cr	Cu	Mo
$\hat{I}(p, p_o)_X$	5.66	5.62	5.67	5.38
$\hat{e}_4 \equiv \hat{E}(X)$	0.47	0.82	0.80	0.36
$\hat{E}(p, p_o)_X$	2.66	4.61	4.54	1.94
$\Delta_{\hat{I},\hat{E}}$	−3.00	−1.01	−1.13	−3.44
$\Delta_{\hat{I},\hat{E},r}/\%$	−53.00	−17.97	−19.93	−63.94

$\hat{MI}(p, p_o)$	22.23	$\hat{ME}(p, p_o)$	13.75	$\Delta M_{\hat{I},\hat{E}}$	−8.48	$\Delta M_{\hat{I},\hat{E},r}/\%$	−38.15

Remarks: The verification of the trueness was for all elements fulfilled. The values of the partial efficiency coefficients $\hat{e}_1$, $\hat{e}_2$, and $\hat{e}_3$ are equal to unity and therefore $\hat{e}_4 \equiv \hat{E}(X)$. $\Delta M_{\hat{I},\hat{E}} = \hat{ME}(p, p_o) - \hat{MI}(p, p_o)$.

Table 5. Data for the Testing of the Trueness of Analytical Results

Element	$\{w(X)_{st}\}$	$\{\hat{w}(X)_{st}\}$	$|\Delta\{w(X)\}|$	$0.1 \times \{w(X)_{st}\}$	$\hat{e}_5$
Co	31.8	33.6	1.8	3.2	1.00
Cr	7.9	7.1	0.8	0.8	1.00
Mo	3.0	3.4	0.4	0.3	0.88
Ni	61.0	62.2	1.2	6.1	1.00
V	96.0	84.6	11.4	9.6	0.89

Element	$\hat{s}(w)_X$	$\hat{I}(p, p_o)_X$	$\hat{E}(p, p_o)_X$	$\Delta_{\hat{I},\hat{E}}$	$\Delta_{\hat{I},\hat{E},r}/\%$
Co	46.73	3.30	3.30	0	0
Cr	82.91	2.72	2.72	0	0
Mo	198.0	1.86	1.64	−0.22	−11.8
Ni	95.48	2.58	2.58	0	0
V	88.40	2.66	2.37	−0.29	−10.9

Remarks: The linearity of straight lines for all elements was fulfilled. The recovery was not tested. The values of the partial efficiency coefficients $\hat{e}_1$, $\hat{e}_2$, and $\hat{e}_3$ are equal to unity and therefore $\hat{e}_5 \equiv \hat{E}(X)$. $\Delta_{\hat{I},\hat{E}} = \hat{E}(p, p_o)_X - \hat{I}(p, p_o)_X$.

determination of trace elements in silicate rocks. The input data for the testing of the trueness of analytical results and the final results are shown in Table 5. It is evident that the determinations of Mo and V exhibit poor trueness. The reduction of the trueness for the Cr determination is less than 5 %, which is an acceptable level. However, the reduction of the trueness of Mo and V is higher than 10 %, which is not acceptable level, and these determinations require further optimization.

The multielement method of the determination of minor and trace elements of gravitation dust sediments was tested also for total efficiency. The experimentally obtained value for measure of information content $\hat{MI}(p, p_o)$ is necessary to correct since it was not possible to determine all the required elements $Q_{max} = 15$ by the given optimized method but only eleven elements, $Q = 11$. In this case, the total efficiency coefficient $\hat{E}(X)$ of the multielement determination was only 0.74. The original uncorrected value of the measure of information efficiency (Table 3) was $\hat{ME}(p, p_o) = 33.50$, but the total efficiency coefficient reduced this value to 24.79, which means a reduction by 26.0 %. In this case, the reduction is conditioned by the optimization of all other elements.

SYMBOLS

$I(p, p_o)_X$	the information content of an element (X)
$I(p, p_o)_{X,T}$	the tolerance information content
$\hat{I}(p, p_o)_X$	the experimentally determined information content
$E(X)$	the efficiency coefficient of the element (X)
$E(X)_T$	the tolerance efficiency coefficient
$\hat{E}(X)$	the experimentally determined efficiency coefficient
$E(p, p_o)_X$	the information efficiency of the element (X)
$E(p, p_o)_{X,T}$	the tolerance information efficiency
$\hat{E}(p, p_o)_X$	the experimentally determined information efficiency
$MI(p, p_o)$	the measure of information content
$MI(p, p_o)_T$	the tolerance measure of information content
$\hat{MI}(p, p_o)$	the experimentally determined measure of information content
$ME(p, p_o)$	the measure of information efficiency
$ME(p, p_o)_T$	the tolerance measure of information efficiency
$\hat{ME}(p, p_o)$	the experimentally determined information efficiency
$\hat{ME}(p, p_o)_{corr}$	corrected value of the measure of information efficiency

$c(X)_{max}$	the maximal calibration concentration of the element (X)
$c(X)_{max,T}$	the maximal tolerance concentration
$\hat{c}(X)_{max}$	the experimentally confirmed maximal concentration
$c(X)_{min}$	the minimal calibration concentration of the element (X)
$c(X)_{min,T}$	the minimal tolerance concentration
$c(X)_{L,T}$	the required limit of detection
$\hat{c}(X)_{min}$	the experimentally confirmed minimal concentration
$\hat{c}(X)_L$	experimentally determined limit of detection
$c(X)_{st}$	the certificate concentration value
$\hat{c}(X)_{st}$	the determined concentration value of the standard st
$\Delta c(X)$	the concentration range of the element (X)
$\Delta c(X)_T$	the tolerance concentration range
$\Delta \hat{c}(X)$	the experimentally confirmed concentration range
$s(X)$	the standard deviation of the concentration determination
$s(c)_{X,T}$	the tolerance value of the standard deviation
$\hat{s}(c)_X$	the experimentally determined value of the standard deviation
Q	the number of real determined elements
Q_{max}	the number of maximal requested elements for the determination
t	the real time of the complex determination of all Q elements
N	the number of repeated concentration measurements by the determination of the standard deviation $\hat{s}(c)_X$
$t(\alpha, F)$	the critical value of the t-distribution (Student's test) $t(\alpha, F \equiv t_{1-\alpha/2}(N-1)$
α	the significance level
F	the number of degrees of freedom, $F = N - 1$

Remark: If the concentration values are given in the ppm unit, it is necessary to use the symbols w and $\hat{w}$ instead of c and $\hat{c}$ symbols.

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