The use of information theory in atomic spectrochemistry III.* Optimization of the analytical process

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Optimization of the analytical chemistry procedures can be realized in two ways: experimental and chemometric. Among the chemometric methods, the information theory is the one enabling to express the total performance of the analytical method by one digital result only, *i.e.* by the information contents or measure of information contents in case of multielemental analysis. The general efficiency of the individual optimization steps is studied by mathematical simulation changing the basic performance parameters of the analytical methods.

Information theory parameters [1, 2], determined on the basis of preliminary defined sequence of computation [3] are suitable for control of optimization processes of the analytical methods. The information content values $I(p, p_0)$ and measure of information content values $\mathrm{MI}(p, p_0)$ derived from the former by addition, represent initial values of elements of the optimization degree. The second stage of optimization already requires the knowledge of information efficiency values $E(p, p_0)$, as well as of the measure of information efficiency values $\mathrm{ME}(p, p_0)$.

Optimization of analytical chemistry processes is based on two statistical evaluating parameters: the relative precision value of concentration determination $s(c_{\mathrm{X,r}})$ and the detectability expressed by the limit of guarantee $c(\mathrm{X_G})$ or by the detection limit $c(\mathrm{X_L})$. In the optimization process the changes of the above given parameters are observed. At their determination three factors play the leading role: the number N of individual measurings used in analytical calibration, the applied concentration range $\langle c(\mathrm{X_1}), c(\mathrm{X_2})\rangle$ and finally the achieved precision of concentration determination $s(\bar{c}_{\mathrm{X}})$, which is derived from the value $s(c_{\mathrm{X,r}})$.

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* For Part *II* see Ref. [8].

Theoretical*

For the calculation of information content values $I(p, p_0)$ the divergent criterion of *Kulback* [4] applied by *Eckschlager* [5] was defined, and in the given formulation (*1*) the standard deviation (*2*) is considered to be the centre of concentration range $\bar{c}(\mathrm{X})$.

$$I(p, p_0) = \ln \frac{c(\mathrm{X}_2) - c(\mathrm{X}_1)}{s(\bar{c}_\mathrm{X})} \frac{\sqrt{N}}{2t(F, \alpha)} \tag{1}$$

Values $s(\bar{c}_\mathrm{X})$ must be standardized by the relations (*2*) and (*3*).

$$s(\bar{c}_\mathrm{X}) = s(c_{\mathrm{X,r}}) \quad \bar{c}(\mathrm{X})/100 \tag{2}$$

$$\bar{c}(\mathrm{X}) = \frac{1}{2}(c(\mathrm{X}_1) + c(\mathrm{X}_2)) \tag{3}$$

Measure of information content value $\mathrm{MI}(p, p_0)$ is obtained by addition because the values $I(p, p_0)$ are in this case additive

$$\mathrm{MI}(p, p_0) = \sum_{i=1}^{Q} (I(p, p_0))_i \tag{4}$$

where $i = 1, \ldots, Q$ and Q represents the number of individual element specific values $(I(p, p_0))_i$. The measure of information efficiency value $\mathrm{ME}(p, p_0)$ is obtained by identical addition.

Theoretical solution of the influence of partial parameters on forming the $I(p, p_0)$ value is purposefully realized by mathematical simulation. Changing of simulation parameters must be defined preliminarily. For the study of the influence of changing the relative precision of concentration determination $s(c_{\mathrm{X,r}})$, this value is gradually increased from 3 % to 30 %. Of course, this simulation supposes order constant value $s(c_{\mathrm{X,r}})$ for all used concentration values $c(\mathrm{X}_i)$ of applied concentration range, *i. e.* homoscedastic dependence. This increasing of $s(c_{\mathrm{X,r}})$ value was applied for constant values N of the concentration range (Fig. 1). If the condition $s(c_{\mathrm{X,r}}) = f(c(\mathrm{X}))$ is valid, it would be treated as a heteroscedastic course [6] in which case the simulated function would have more complicated course. Graphical illustration of simulation results for $s(c_{\mathrm{X,r}}) = \mathrm{const}$ is given in Fig. 2.

It was necessary to direct the simulation of the influence of the used concentration range with change in two directions. First, the concentration range

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* The symbols used in this text are partially listed on page 754, and are identical with the symbols in paper [8].

from the basic values $c(X_2) = 10^{-1}$ % and $c(X_1) = 10^{-2}$ %, was gradually widened to the value $c(X_1) = 10^{-5}$ % (Fig. 3). Second, from the concentration range $c(X_1) = 10^{-3}$ % and $c(X_2) = 10^{-2}$ %, this range was gradually increased

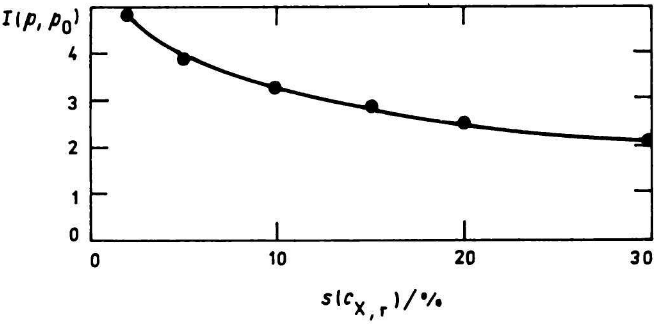

Fig. 1. Graphical illustration of the values $I(p, p_0)$ in dependence on stepwise changed values of the relative precision of concentration determination $s(c_{X,r})$. The value N is considered to be constant ($N = 30$) for the total actual concentration span.

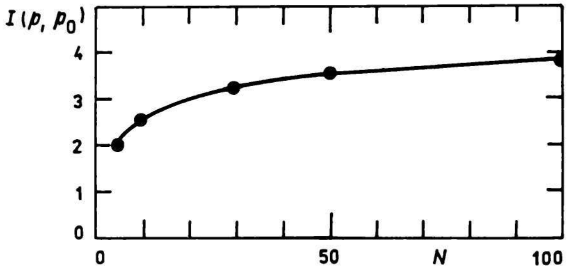

Fig. 2. Graphical illustration of the values $I(p, p_0)$ in dependence on stepwise changed values of the individual measurings number N. The value $s(c_{X,r})$ is then constant for the calibration range; $s(c_{X,r}) = 10$ %.

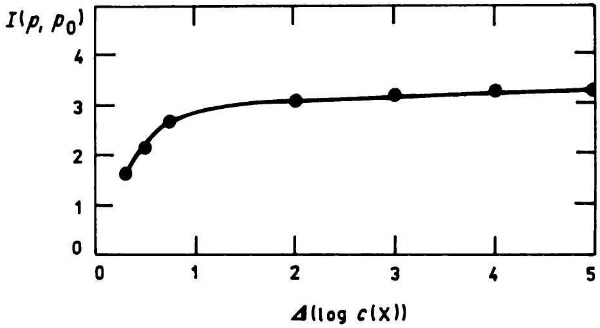

Fig. 3. Graphical illustration of the values $I(p, p_0)$ in dependence on stepwise applied concentration ranges expressed by the value $\Delta(\log c(X))$; $N = 30$; $s(c_{X,r}) = 10$ %.

to the value $c(X_2) = 10$ % (Fig. 4). At this simulation, the values N and $s(c_{X,r})$ were kept constant. Invariability of the value N is substantiated by the fact that at lower concentration spans it is necessary to use more individual measurings for a given concentration value $c(X_i)$. By first variation the trace analysis was simulated (Fig. 3). By the second one, the analysis of minor and partially of major elements (Fig. 4) was simulated. The extending of concentration range is very often linked with gradual worsening of the value of the relative precision of the concentration determination. By next simulation this fact was also taken into consideration (Fig. 5). In the concentration range $\Delta(\log c(X)) = 2$ it was worked with the value $s(c_{X,r}) = 5$ %, but in the range of three orders with the value 7 % and, finally, in the range of four orders with the value 15 %. The value N was also in these cases left constant ($N = 30$).

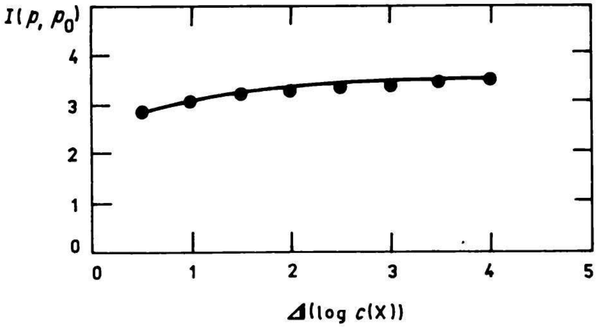

Fig. 4. Graphical illustration of the values $I(p, p_0)$ in dependence on the applied concentration ranges expressed by the value $\Delta(\log c(X))$; $N = 30$; $s(c_{X,r}) = 10$ %.

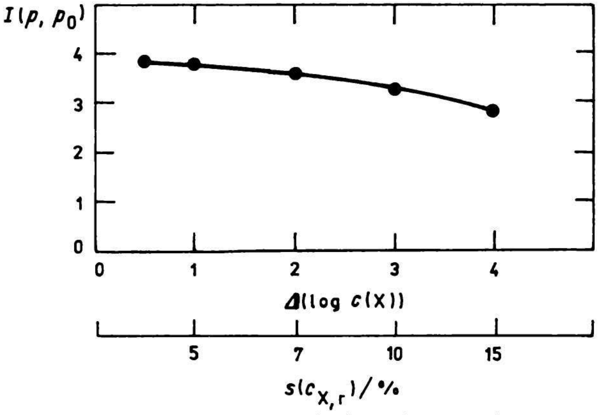

Fig. 5. Graphical illustration of the values $I(p, p_0)$ in dependence on simultaneously changed values $s(c_{X,r})$ and $\Delta(\log c(X))$; $N = 30$.

Discussion

Gradual worsening of the value of relative precision of concentration determination $s(c_{X,r})$ results in monotonic decreasing of information content values $I(p, p_0)$. From Fig. 1 it is evident that increasing of the information content value can be brought about only by effective improving of the relative precision. This increasing is evident mainly in the region of relative precision values from 10 % to 3 %.

On the contrary, gradual increase of the N value, *i.e.* of the number of individual measuring values of analytical calibration is not markedly improving the $I(p, p_0)$ value after achieving the value $N \geq 30$. It must be stated that in the analytical calibration for one concentration order, three to four calibration standards are used. In case that the calibration is related to the range of three concentration orders, which is maximum in the majority of analytical methods, it is purposeful to use maximum eight to ten calibration samples with gradually changing concentration values. If every calibration reference sample undergoes minimum three and maximum five measurings, a total data matrix with minimum 24 and maximum 50 elements can be obtained. As it is evident from Fig. 2, increasing of the value $N > 50$ does not lead to remarkable increase of the information contents. This value can thus be considered as limiting from the point of view of the optimization.

Extension of the concentration interval towards trace concentrations (Fig. 3) shows remarkable improvement of the information content values, approx. to $\Delta(\log c(\mathrm{X})) = 1.5$. Even by exceeding the value $\Delta(\log c(\mathrm{X})) > 2$, increments of the value $I(p, p_0)$ are monotonic and therefore negligible. Of course, from the point of view of the "analytical order" fulfilment in the sphere of detectability such extending is not only useful, but necessary.

This necessity is motived mainly by the fact that both the information efficiency value $E(p, p_0)$ and the efficiency coefficient $E(\mathrm{X})$ value are markedly influenced by fulfilment of the requirement that $c(\mathrm{X_G}) \leqslant c(\mathrm{X_{min}})$. On the contrary, extending of the concentration span towards higher concentration values (Fig. 4) is accompanied only by monotonic increase in the value $I(p, p_0)$. This change of information content values is narrowed to just one order. That means however that optimization of the method by its extension to higher values is purposeful only if "analytical order" is fulfilled, namely the inequality $c(\mathrm{X_2}) > c(\mathrm{X_{max}})$ must be reached.

Finally, the effect of simultaneous extension of the concentration interval and gradual adjoining of still worse value of the relative precision of concentration determination was tested. This dependence (Fig. 5) confirmed that extending of the concentration range with simultaneous worsening of relative precision of the concentration determination results in monotonic decrease of the values $I(p, p_0)$, which means that the information content value falls down. This case is, unfortunately quite typical of trace analysis and often causes simultaneous decrease in the information efficiency values.

From the point of view of forming the information efficiency $E(p, p_0)$, or measure of information efficiency values $\mathrm{ME}(p, p_0)$, the values of two partial efficiency coefficients, namely e_1 and e_3 are decisive [1]. Consideration of influence of the partial efficiency coefficient e_2 is necessary only in specific cases [1], if short time limits $t < 2$ h are given for the analysis. For this reason, it is not necessary to consider the influence of this coefficient in general cases.

The former coefficient e_1 is conditioned by the relation

$$e_1 = s(c_{\mathrm{X,T}})/s(c_{\mathrm{X}}) \tag{5}$$

It means that from the point of view of optimization it is necessary to improve the value $s(c_{\mathrm{X,r}})$ and also the standard deviation value $s(c_{\mathrm{X}})$ by which the value e_1 is increased up to the value of unity. In case of the third partial efficiency coefficient e_3 it holds that

$$e_3 = c(\mathrm{X_{T,min}})/c(\mathrm{X_L}) \tag{6}$$

This means that optimizing extension of the concentration range is useful only if $c(\mathrm{X_{T,min}}) \gg c(\mathrm{X_L})$. If the inequality $c(\mathrm{X_{T,min}}) \leq c(\mathrm{X_G})$ is reached, further optimizing by extending the concentration interval mainly as regards individual elements of multicomponent determination is not desirable. A nondesirable effect could appear, namely by optimization of the elements concerned, the detectability would although improve but simultaneously the relative precision of concentration determination would deteriorate. There is no guarantee that in such a case by experimental optimization the advantageous evaluating parameters of further elements, not needing optimization, would not deteriorate.

Changes of the information theory parameters in the optimization process of the detectability and precision of concentration determination of individual elements, are given in Table 1. In case of Cr only the detectability optimization takes place. In case of Bi simultaneous optimization of precision (example *A*) took also place. This optimization was achieved by changing the choice of the spectral lines of the elements Cr and Bi. According to the data in Table 1, it is evident that optimization in case of Cr is most remarkably observed in calculation of the information efficiency values $E(p, p_0)$. In case of Bi, where by change of experimental parameters also precision optimization was achieved, the value of information content $I(p, p_0)$ was markedly improved by optimization.

In case of exclusive optimization of the precision of concentration determination (example *B*) as in cases of Cu and Mn, the values $I(p, p_0)$ were instantly improved. Proportionally to that also unitary values of partial efficiency coefficients were achieved and the values $E(p, p_0)$ were also markedly improved.

Table 1

Information theory parameters in the optimization process of detectability and precision

A. Observing of the detectability optimization process

Element	Step	Experimental values				$I(p, p_0)$	Partial efficiency coefficient		$E(\mathrm{X})$	$E(p, p_0)$
		$c(\mathrm{X}_2)$ ppm	$c(\mathrm{X}_1)$ ppm	$s(c_{\mathrm{X,r}})$	$s(c_\mathrm{X})$ ppm		e_1	e_3		
Cr	1	1000	12.0	5.8	29.4	3.75	1.00	0.42	0.42	1.58
	2	1000	4.8	5.8	29.1	3.77	1.00	1.00	1.00	3.77
Bi	1	1000	13.0	12.0	60.8	3.03	0.62	0.39	0.24	0.72
	2	1000	5.0	6.0	30.2	3.74	1.00	1.00	1.00	3.74

$\mathrm{MI}(p, p_0)_1 = 6.78$ $\mathrm{ME}(p, p_0)_1 = 2.30$

$\mathrm{MI}(p, p_0)_2 = 7.51$ $\mathrm{ME}(p, p_0)_2 = 7.51$

Tolerance values $c(\mathrm{X}_{\mathrm{T,min}}) = 5.0$ ppm, $s(c_{\mathrm{X,T}}) = 37.7$ ppm. 1 — Initial state of optimization, 2 — after-optimization state.

B. Observing of the optimization of the precision of concentration determination

Element	Step	Experimental values				$I(p, p_0)$	Partial efficiency coefficient		$E(\mathrm{X})$	$E(p, p_0)$
		$c(\mathrm{X}_2)$ ppm	$c(\mathrm{X}_1)$ ppm	$s(c_{\mathrm{X,r}})$	$s(c_\mathrm{X})$ ppm		e_1	e_3		
Cu	1	10	0.005	13.8	0.69	2.91	0.57	1.00	0.57	1.66
	2	10	0.005	6.5	0.33	3.65	1.00	1.00	1.00	3.65
Mn	1	200	2.0	16.6	16.77	2.71	0.46	1.00	0.46	1.25
	2	200	2.0	7.2	7.27	3.54	1.00	1.00	1.00	3.54

$\mathrm{MI}(p, p_0)_1 = 5.62$ $\mathrm{ME}(p, p_0)_1 = 2.91$

$\mathrm{MI}(p, p_0)_2 = 7.19$ $\mathrm{ME}(p, p_0)_2 = 7.19$

Tolerance values $c(\mathrm{Cu}_{\mathrm{T,min}}) = 0.01$ ppm, $s(c_{\mathrm{Cu,T}}) = 0.38$ ppm; $c(\mathrm{Mn}_{\mathrm{T,min}}) = 5.0$ ppm, $s(c_{\mathrm{Mn,T}}) = 7.69$ ppm.

Table 2

Information theory parameters in the process of optimization of the limestones and dolomites
A. Observing of the optimization process on the basis of changing the $I(p, p_0)$ values

		Tolerance values			Experimental values					
Element	Step	$c(X_{T,max})$	$c(X_{T,min})$	$s(c_{X,T})$	$c(X_2)$	$c(X_1)$	$s(c_X)$	$I(p, p_0)_T$	$I(p, p_0)$	$\Delta I = I(p, p_0) - I(p, p_0)_T$
		ppm	ppm	ppm	ppm	ppm	ppm			
Al		1200	10	121	1200	5	95.2	2.52	2.77	+0.25
Cu		1200	10	121	1200	7	71.2	2.52	3.06	+0.54
Mn		1200	10	121	1200	6	100.1	2.52	2.72	+0.20
Ni		1200	60	126	1200	60	87.6	2.44	2.81	+0.36
Fe	1	1200	60	126	1200	70	88.0	2.44	2.79	+0.35
	2	1200	60	126	1200	55	130.0		2.41	−0.03
V	1	1200	60	126	1200	72	131.5	2.44	2.39	−0.05
	2	1200	60	126	1200	40	140.0		2.35	−0.09
Cr	1	1200	60	126	1200	80	62.7	2.44	3.12	−0.02
	2	1200	60	126	1200	60	123.0		2.47	+0.03
W		1200	60	126	1200	300	198.8	2.44	1.75	−0.69

$\mathrm{MI}(p, p_0)_T = 19.76$

$\mathrm{MI}(p, p_0)_1 = 21.41$
$\mathrm{MI}(p, p_0)_2 = 20.34$

1 — Initial state, 2 — after-optimization state.

Table 2 (Continued)

B. Observing of the optimization process on the basis of changing the $E(p, p_0)$ values

Element	Step	Partial efficiency coefficient e_1	 e_3	E(X)	$I(p, p_0)$	$E(p, p_0)$	$\Delta I = I(p, p_0) - I(p, p_0)_T$
Al		1.00	1.00	1.00	2.77	2.77	—
Cu		1.00	1.00	1.00	3.06	3.06	—
Mn		1.00	1.00	1.00	2.72	2.72	—
Ni		1.00	1.00	1.00	2.81	2.81	—
Fe	1	1.00	0.86	0.86	2.79	2.40	−0.39
	2	0.97	1.00	0.97	2.41	2.34	−0.07
V	1	0.96	0.83	0.80	2.39	1.91	−0.18
	2	0.90	1.00	0.90	2.35	2.12	−0.24
Cr	1	1.00	0.75	0.75	3.12	2.34	−0.78
	2	1.00	1.00	1.00	2.47	2.47	—
W		0.20	0.63	0.13	1.75	0.56	−1.19

$\mathrm{ME}(p, p_0)_1 = 18.57$
$\mathrm{ME}(p, p_0)_2 = 18.85$

Changes of information theory parameters by the process of complex optimization of multielement analytical method are given in Table 2. Optimization in case of Fe, V, Cr elements was achieved by changing of spectral lines of the elements as well as by modification of the exposure time. In case of elements Al, Cu, Mn, and Ni, changes in exposure times do not cause significant change in operation parameters. Observation of $I(p, p_0)$ changes confirms that by optimization of the detectability (case *A*) significantly more advantageous values $I(p, p_0)$ were not achieved and the measure of information content $\mathrm{MI}(p, p_0)$ decreased insignificantly after optimization [2]. On the other hand, from the point of view of information efficiency (case *B*) the value of the efficiency coefficient E(X) always improved by optimization and thus it contributed to the fulfillment of the "analytical order"

In case of tungsten, optimization did not lead to desired success as it was not possible to use more intensive spectral line in the registered region of the wavelengths.

Conclusion

On the basis of given partial results, further final conclusions can be formulated. From the viewpoint of optimization of not only spectroscopic but also general analytical methods, it is purposeful to keep the total number of individual measurings of the whole calibration data set of the matrix between 30 to 50. Decreasing of N under 30 is not desirable, as it may cause significant decrease in the information contents as well as cast doubt on the reliability of the analytical calibration process. Increasing of N above 50 neither significantly improves the value $I(p, p_0)$ nor increases the relative precision of concentration determination.

Relative precision values obtained by experimental optimization should comply the inequality $s(c_{\mathrm{X,r}}) \leq 15\ \%$. The values from 10 % to 3 % are considered to be the optimum of the achievable range of relative precision of concentration determination when using the photographic registration. In case of photoelectric registration this range lies lower, from 5 % to 0.1 %. It means that in case of photoelectric registration more advantageous values $I(p, p_0)$ are achieved [7].

Extension of the valid concentration range $\langle c(\mathrm{X_{min}}), c(\mathrm{X_{max}})\rangle$ will increase the values $I(p, p_0)$ only if the value $s(c_{\mathrm{X,r}})$ is worsened only slightly by extending the concentration range. Such optimization is, as a rule, the aim of ultratrace analysis and positive results can be expected exclusively from the application of photoelectric registration [7].

The fact that only increase in the range to the first order of concentration interval influences significantly improvement of the value $I(p, p_0)$ is a very important information for the trace analysis optimization, and thus for concentration interval extending towards lower concentration values. That is also a limiting condition. On the other hand, by extending the concentration interval towards higher concentration values, the value $s(c_{\mathrm{X,r}})$ as a rule is not significantly changed, and that is why by this optimization the values $I(p, p_0)$ are increasing.

Finally it is necessary to state that every optimization of an analytical method represents special and unrepeatable problem. The problem is, as a rule, in different matrix effects and sometimes also in physical coincidences of a given measuring system. These preferentially influence the analytical signal to noise ratio and thus the detectability formation and only secondarily the relative precision of the concentration determination.

Symbols

N	number of individual analytical signal measurings or concentration determinations
$c(\mathrm{X_1})$	lower concentration value of the element X
$c(\mathrm{X_2})$	higher concentration value of the element X
$\Delta \log c(\mathrm{X}) = \log c(\mathrm{X_2}) - \log c(\mathrm{X_1})$	
$c(\mathrm{X_{min}})$	minimum concentration value or level

$c(\mathrm{X}_{\mathrm{max}})$	maximum concentration value or level
$s(c_{\mathrm{X}})$	standard deviation of the $c(\mathrm{X})$ value
$s(c_{\mathrm{X,r}})$	relative precision of the concentration determination of the $c(\mathrm{X})$ value
$c(\mathrm{X}_{\mathrm{T,min}})$	minimum tolerance concentration
$c(\mathrm{X}_{\mathrm{T,max}})$	maximum tolerance concentration
$s(c_{\mathrm{X,T}})$	standard deviation of the tolerance concentration
$E(\mathrm{X})$	efficiency coefficient of the element X
$c(\mathrm{X}_{\mathrm{L}})$	limit of detection

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