THEORY OF INFORMATION AS APPLIED TO ANALYTICAL CHEMISTRY. III.* EFFECTIVENESS OF INFORMATION

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Received June 25th, 1970

The determination of effectiveness of information, *i.e.* of the amount of information, obtained from an analytical method in a time unit, has been applied to compare several possible alternatives of an analytical procedure.

Modern development of analytical chemistry is characterized by intensification of analytical procedures, *i.e.* by the effort to gain information on composition of the analyzed sample most effectively. In papers[1,2], fundamental relations for the determination of the amount of information from the results of analyses have been defined, some examples of the loss of information due to unsuitable experimental arrangement as well as certain principles that are necessary to maintain during analyses to gain as large amount of information as possible, have been presented. Sometimes, of course, the conditions under which a large amount of information is achieved are of such a nature, that the whole procedure is complicated or requires an expensive instrumental equipment.

In order to be able to judge, whether complexicity of the procedure or time and financial costs are proportional to the increase in the amount of information gained, we introduce the effectiveness defined previously[1]

$$E_0 = k \ln \frac{(c_2 - c_1)\sqrt{n}}{2st} . \qquad (1)$$

Here, we substitute for $k = 1/\tau$, where τ is the time or costs that must be expanded to carry out the analysis. Expression $(c_2 - c_1)$ indicates uncertainty before analysis, *i.e.* the concentration range known by the content of the component to be determined, lying within it, n is the number of parallel determinations and s is the estimation of standard deviation, made from n_s determinations, and t the critical value of the Student characteristics for $\nu = n_s - 1$ and significance level $\alpha = 0{\cdot}039$. Values t for $\nu \leq 10$ and $\alpha = 0{\cdot}039$ are tabulated in paper[1], where likewise instructions for calculating them for $\nu > 10$ have been presented. The E_0 value is given in nit. time^{-1} or nit. (unit of currency)$^{-1}$. In case that we would like also other aspects to be included

* Part II: This Journal *32*, 137 (1972).

in the effectiveness value, as for example the resolution sensitivity of analytical methods[3] *etc.*, we can include them in a suitable manner into constant k from relationship (*1*). For purposes followed in this paper, however, time-information effectiveness, *i.e.* $k = \tau^{-1}$, is sufficient, since such alternatives of the analytical procedure will be compared, which differ only in the amount of information gained and time of duration, in some cases also in the redundance, too. Since time-information effectiveness can sometimes quite unsuitably prefer rapid but less precise methods by that measure of precision is here in a logarithmic relation to the linear reciprocal value of time, τ^{-1}, yet another limiting condition is often laid down, concerning, for example, the minimum precision required or the amount of information; furthermore, in the trace analysis, the requirement that a positive result, if possible, must be achieved, should be taken into account.

As example for a practical utilization of calculations of the time-information effectiveness in analytical chemistry, the effectiveness of two alternatives involving determination of Ag, Ca, Cu, and Ni in pure salts by absorption spectrometry[4] is presented. The enrichment by dithizone extraction is applied in case of Cu, Ag, and Ni (for Ni also diacetyldioxime is used). For Ca, the extraction with glyoxal-bis-2-hydroxyanil into chloroform, chloroform + n-butanol or into n-hexanol was made use of. As the chloroform solution cannot be used for the determination itself, reextraction with dilute acid is made. This way of enrichment, it is true, decreases the detection limit approx. by two orders of magnitude, but it extends the time needed to carry out the analyses, from $\tau = 20$ to $\tau = 140$ min, *i.e.* by two hours that are necessary for the extraction and reextraction to be carried out. This, of course, will affect the time-information effectiveness very much. For the event of positive or negative results, the amount of information can be calculated on the basis of relationships presented in paper[1]. In Table I, values of the detection limit for a procedure without enrichment and on enrichment by extraction and reextraction are given, whereas Table II presents calculated values of the amount of information for a positive or negative result and for the procedure without and with the enrichment. If we insist on the requirement that a positive result, if possible, is wanted, we can consider three procedure alternatives altogether: *1*. The result is always positive also without the enrichment, the latter procedure must not be therefore carried out. *2*. The result is always positive only after the enrichment, extraction and reextraction must always be made. *3*. The result is sometimes positive also without the enrichment, some other time not before extraction and reextraction have been made. If the result is negative even on enrichment, we have no possibility to meet our requirement with use of the method given. The time-information effectiveness for all three possible cases is listed in Table III. Using the results of this Table we can make a decision, for the case when the result is sometimes positive even without the enrichment and sometimes on extraction and reextraction, whether it is more advantageous to include always the extraction and reextraction into the common procedure (variant A), or to carry

TABLE I

Detection Limits and Coefficients of Variation

Metal	Detection limit		Coefficient of Variation		Extraction
	without extr.	on extr.	without extr.	on extr.	
Ni	$1 . 10^{-3}$	$1 . 10^{-5}$	4·7	5·5	[a]
		$1 . 10^{-5}$	—	5·3	[b]
Cu	$5 . 10^{-4}$	$5 . 10^{-6}$	3·8	5·1	[a]
Ag	$5 . 10^{-4}$	$5 . 10^{-6}$	4·4	5·2	[a]
Ca	$7 . 10^{-3}$	$7·5 . 10^{-5}$	5·1	6·2	[c]
		$7·5 . 10^{-5}$	—	5·9	[d]

[a] Extraction with dithizone into chloroform, reextraction with dilute HNO_3. [b] Extraction with diacetyldioxime into chloroform, reextraction with dilute HCl. [c] Extraction with glyoxal-bis-2-hydroxyanil into chloroform and 1-butanol, reextraction with dilute HCl. [d] The same as for [c] but the extraction into chloroform and n-hexanol is involved.

TABLE II

Amount of Information in Natural Units

Metal	Without extraction		On extraction and reextraction	
	+	—	+	—
Ni	7·367	2·303	6·909	2·881
Cu	8·099	2·996	7·602	3·786
Ag	8·079	2·996	7·602	3·641
Ca	5·185	0·287	4·892	0·568

TABLE III

Time-Information Effectiveness

Metal	Without extraction +	On extraction +	Without extraction — on extraction +
Ni	0·386	0·0493	0·0431
Cu	0·405	0·0543	0·0475
Ag	0·404	0·0543	0·0475
Ca	0·259	0·0349	0·0306

out the determination without the extraction and to repeat the determination with extraction and reextraction (variant B), only if we obtain a negative result. In the events in which the content of the component lies always below or above the detection limit without the enrichment by extraction and reextraction, it is not difficult to decide for one of both possibilities. Where, however, the content of the component

TABLE IV
Effectiveness of Both Variants
For $q = 0$ or 1 is A more effective variant, for $q = 2$ or 3 is B more effective.

q	A				B			
	Ni	Cu	Ag	Ca	Ni	Cu	Ag	Ca
0	0·0493	0·0543	0·0543	0·0349	0·0431	0·0475	0·0475	0·0306
1	0·0493	0·0543	0·0543	0·0349	0·0463	0·0511	0·0511	0·0329
2	0·0493	0·0543	0·0543	0·0349	0·0496	0·0546	0·546	0·0354
3	0·0493	0·0543	0·0543	0·0349	0·0528	0·0582	0·0582	0·0377

determined is close to the detection limit of the atomic absorption spectrophotometry itself and has a greater variance for individual samples so that it will be for some examples higher and for the other ones lower than the limit of detection, the total effectiveness of variant B can be determined as dependent on the mean per cent of the results which are positive also without the extraction, if we use relationship

$$E_0 = \frac{q(I_0/\tau_0) + (100 - q)\, I_e(\tau_0 + \tau_e)^{-1}}{100}, \qquad (2)$$

where q is the per cent of the results which are positive also without the extraction. For different q values, the time-information effectiveness of both variants is summarized in Table IV. It follows from this Table that already when two or three events provide a positive result also without the extraction, it pays to attempt at a rapid and easy determination without the enrichment before the time-consuming and laborious extraction and reextraction are carried out.

From this paper as well as from the previous ones[1,2] then follows that use of the fundamental relationship of the theory of information allows useful modification of the analytical procedure so that the latter should result in obtaining as large an amount of information on the analyzed sample as possible[1]. In addition, with the dependent methods a loss of information can be easily involved, which can be often prevented by using a suitable way of comparison with the standard. In analytical practice, namely, not only gain of the largest amount of information is concerned, but also the fact of gaining the information in the most effective way must be taken into account. In this paper, the problem of the time-information effectiveness has been solved.

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Translated by J. Hejduk.