THE INFORMATION-THEORETICAL AND SYSTEM BASIS OF QUANTITATIVE ANALYSIS*

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Dedicated to late Academician Eduard Hála.

It is shown that the individual subsystems of a stochastic analytical system affect the a posteriori uncertainty and thereby, the information gain of the analytical result. The effects of sampling, separation procedures and calibration on the information gain of quantitative analysis, expressed in terms of the extended divergence measure, are discussed, and rules that can be utilized in the optimization of analytical procedures are given.

The information and system background of chemical analysis was first drawn attention to by Malissa[1] in the early 1970s. More recently, a complex treatment of the practical use of information theory[2,3] and system theory[4,5] in chemical analysis was presented. A unified concept of analytical working procedures in information theory terms has been put forth by Doerffel[6].

The present work is an attempt at a unification of the information-theoretical viewpoint with the system approach and with the physico-chemical discussion of the error aspect of the individual operations. The following facts have to be taken into account.

Analysis, as a process of gaining information about the chemical composition and its changes, takes place in a stochastic system. Although requisite for the function of the analytical system as a whole, its subsystems contribute each more or less to the uncertainty of the output data. This uncertainty is given by the variance and bias of the results.

The analytical operations occurring in the subsystems of the analytical system, such as sampling, component separation, etc., have their own error aspects, affecting the overall uncertainty of the output. This error aspect, which is largely associated with the "nonideal" course of the operation in question (establishing equilibria, slow reactions) can be discussed in terms of the underlying physico-chemical laws and

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principles. Hence, an analytical method cannot be looked upon as a black box (see also ref.[1], Paragraph 2.2.3.).

Information on the chemical composition is not gained directly but by measuring some property that is related to the kind and amount of analyte. This information is encoded in the analytical signal whose position (z) carries information about the kind of analyte while its intensity (y) carries information about its amount. Information on the quantitative chemical composition is derived from the signal intensity at a position either by means of a stoichiometric equivalent or empirically, e.g. by calibration of the stochastic dependence observed.

Therefore, we distinguish between the information content of the signal and the information gain obtained by carrying out the analysis (including the signal decoding); what we wish is that the information gain be no lower than the signal information content, i.e. that no loss of infomation occur during the signal processing.

The effect of the analytical procedure on the information gain of results of quantitative analysis has been dealt with in refs[2,3,7], although at a rather qualitative level. The divergence measure[3,8-10] did not enable this effect to be addressed in its whole complexity because it did not make allowance for bias, the reference material quality and other factors of this kind having a marked effect in practice.

In this work we present a more detailed and more generally valid treatment of the effect of the function of the various subsystems, using the extended divergence measure concept[8] for determining the information gain.

THEORETICAL

The information content of the signal intensity y, for the case of the a priori $p_0(y)$ uniform $U(y_{\min}, y_{\max})$ distribution and the a posteriori $p(y)$ normal $N(\mu_y, \sigma_y^2)$ distribution, $y_{\min} + 3\sigma_y \leqq \mu_y \leqq y_{\max} - 3\sigma_y$, $\sigma_y > 0$, has been determined to be[11]

$$I(p, p_0) = \int_{y_{\min}}^{y_{\max}} p(y) \ln [p(y)/p_0(y)] \, dy = \ln \frac{y_{\max} - y_{\min}}{\sigma_y \sqrt{2\pi e}}, \qquad (1)$$

where $y_{\min}$ and $y_{\max}$ are the lowest and highest values, respectively, of the signal intensity recorded by the apparatus.

The information gain attainable by quantitative analysis (including the signal processing), for the true $r(x)$ normal $N(X^*, \sigma_r^2)$ distribution; $\sigma_r \geqq 0$, a posteriori $p(x)$ normal $N(\mu, \sigma^2)$, $\sigma \geqq 0$, and for the a posteriori $p_0(x)$ uniform $U(x_1, x_2)$ distribution, $x_1 + 3\sigma \leqq \mu \leqq x_2 - 3\sigma$, is given by the relation[8]

$$I(r; p, p_0) = \int_{x_1}^{x_2} r(x) \ln [p(x)/p_0(x)] \, dx = \ln \frac{x_1 - x_2}{\sigma \sqrt{2\pi e^k}} - \frac{1}{2} \left(\frac{\delta}{\sigma}\right)^2. \qquad (2)$$

Here x_1 and x_2 are the lowest and highest amounts of analyte, respectively, assumed prior to the analysis. It will be clear that the $\langle x_1, x_2 \rangle$ interval in Eq. (2) has a meaning different[11] from that of $\langle y_{min}, y_{max} \rangle$ in Eq. (1). If x and y are interrelated by a calibration dependence

$$y = f_C(x) \tag{3a}$$

or by an analytical dependence

$$x = f_A(y)\,, \tag{3b}$$

then generally the relations $x_1 = f_A(y_{min})$ or $y_{max} = f_K(x_2)$ do not hold true. It is convenient, though, if $x_1 \geqq f_A(y_{min})$ and, at the same time, $x_2 \leqq f_A(y_{max})$, because if this is not the case then several analytical methods have to be combined, i.e. a preliminary screening must precede the precise analytical determination[12]. The determination of the σ and $\delta = |X^* - \mu|$ values has been discussed[8]. The mean error δ can be established by analyzing a reference material with the analyte content X^*, known with a precision characterized by variance σ_r^2; then in Eq. (2), $k = (\sigma_r/\sigma)^2$ (ref.[8]). The mean error is inserted in Eq. (2) for any $\delta > 0$ although it is considered systematic only if it is statistically significant at a preselected $(1 - \alpha)$ level.

The information gain attained by performing repeated higher precision analysis[12,13], for the a priori $p_0(x)$ normal $N(\mu_0, \sigma_0^2)$ distribution, the a posteriori $p(x)$ distribution and the true $r(x)$ distribution is given, similarly as above, by the relation

$$I(r;\, p,\, p_0) = \int_{-\infty}^{\infty} r(x) \ln [p(x)/p_0(x)]\, \mathrm{d}x =$$
$$= \ln (\sigma_0/\sigma) + \tfrac{1}{2}\{(\delta_0/\sigma_0)^2 - (\delta/\sigma)^2 + k[(\sigma^2 - \sigma_0^2)/\sigma_0^2]\}\,. \tag{4}$$

The difference $\delta_0 = |X^* - \mu_0|$, which is no metrological quantity, can be regarded as a measure of accuracy of the pre-information about the result. The dependences of $I(r;\, p,\, p_0)$ in Eq. (2) on σ and of $I\,(r;\, p,\, p_0)$ in Eq. (4) on the σ_0/σ ratio for various values of $k \in \langle 0, 1 \rangle$ are shown in Figs 1*a*, 1*b*, respectively (left-hand side).

Any analytical system is stochastic, i.e., a whole probability distribution of output data, hence, an a posteriori distribution $p(x)$, which is regarded as normal $N(\mu, \sigma^2)$ in this treatment, is obtained for a given input on repetition. The functions of the individual subsystems of the analytical system, i.e. the course of the operations of the analytical procedure, affect the μ and σ^2 values of the a posteriori distribution. For the expected value $\mathbf{E}[x] = \mu$ and variance $\mathbf{V}[x] = \sigma^2$ in combination with an additive constant we have

$$\mathbf{E}[x \pm d] = \mathbf{E}[x] \pm d = \mu \pm d \tag{5a}$$

$$\mathbf{V}[x \pm d] = \mathbf{V}[x] = \sigma^2\,, \tag{5b}$$

and in combination with a multiplicative constant,

$$\mathbf{E}[xc] = c\,\mathbf{E}[x] = c\mu \tag{6a}$$

$$\mathbf{V}[xc] = c^2\,\mathbf{V}[x] = c^2\sigma^2\,. \tag{6b}$$

If two independent random quantities x_A and x_B combine, then

$$\mathbf{E}[x_A \pm x_B] = \mathbf{E}[x_A] \pm \mathbf{E}[x_B] = \mu_A \pm \mu_B \tag{7a}$$

$$\mathbf{V}[x_A \pm x_B] = \mathbf{V}[x_A] + \mathbf{V}[x_B] = \sigma_A^2 + \sigma_B^2\,, \tag{7b}$$

i.e., the variances are added even in case that the quantities themselves are subtracted.

In other cases the result is derived by calculation from partial values $x_A, x_B, \ldots, x_Z$ obtained by measurement; the error can be then determined by using the linearized Taylor series as shown in ref.[2] (Appendix B5) or in the metrologically oriented paper[10].

RESULTS AND DISCUSSION

We will show how the standard deviation of the a posteriori distribution σ and the mean error δ are affected by the individual operations of the analytical procedure, i.e., by the function of the subsystems of the analytical system, and how, in turn, the σ and δ values affect the information gains, expressed by Eqs (*2*) and (*4*).

Sampling. In the case of an inhomogeneous material, the sampling procedure is of crucial importance for the determination of the average chemical composition. The variance of the result of signal measurement then is given, according to Eq. (*7b*), by the sum

$$\sigma_y^2 = \sigma_M^2 + \sigma_A^2 \tag{8}$$

where σ_M^2 is the variance of the signal intensity measurement and σ_A^2 is the variance due to the sample inhomogeneity. If σ_A^2 is statistically significantly higher than σ_M^2, which can be verified by variance analysis, then we usually attempt to ascertain whether the heterogeneity is random or the analyte amounts follow some trend, because this is of importance when choosing the sampling strategy. A treatment of the effect of sampling on the information content is presented in ref.[3], Paragraph 4.6. Sampling, particularly from an inhomogeneous material, can increase the σ_y value considerably and, if performed in an inappropriate manner, can even give rise to a systematic error δ.

Separation. If some separating operation such as precipitation and filtration, extraction, ion exchange, etc., has to be included, the variance will increase by a contribution σ_B^2; it is even possible that an error δ will arise, largely as a consequence of establishing equilibrium ("nonquantitative course of reaction") (see ref.[14], Chapter 2). In some cases this error can be roughly assessed from the corresponding physico-chemical relations, equilibrium constants, etc. (ref.[15], Chapter 3, and in more detail, refs[16,17]). Hence, the mean error arising as a consequence of imperfectness of the analytical procedure has a cause different from that giving rise to the error of calibration[17] (see ref.[13]), their impact on the information gain, however, is alike. Calculations of errors performed using the corresponding physico-chemical relations are not only of practical importance but they also enable us to gain a better insight into the function of some subsystems of the analytical system in question and demonstrate that even in the system approach, it is inappropriate to look upon the analytical method as a black box (see also ref.[1], Paragraph 2.2.3).

Analytical signal decoding. In "classical" chemical analysis the relation between the analyte concentration or amount and the signal intensity, $y = b \,.\, x_A$, is functional, b being an equivalent known in advance (a stoichiometric equivalent for instance), hence, a constant. According to Eq. (*6b*), the standard deviation then is $\sigma = \sigma_y/b$ (see also Table I).

If, however, the x_A value is determined from y by means of the dependence (*3b*) obtained by calibration according to Eq. (*3a*), then the σ value depends on the

TABLE I
Effect of calibration dependence on the σ value

Calibration dependence	Coefficients	Dependence of σ on σ_y
$y = bx$	b = stoichiometric constant	$\sigma = \sigma_y/b$
$y = \beta x$	β' calibration straight line	$\sigma = \frac{\sigma_y}{b}\left[\frac{1}{m} + \frac{1}{n} + \left(\frac{\sigma_b}{b\sigma_y}\right)^2 y^2\right]^{1/2}$
	standard addition	$\sigma = \frac{\sigma_y}{b}\frac{(q^2+1)^{1/2}}{q}[2(1-\varrho)]^{1/2}$
$y = \alpha + \beta x$	α' calibration β' straight line	$\sigma = \frac{\sigma_y}{b}\left[\frac{1}{m} + \frac{1}{n} + \left(\frac{\sigma_b}{b\sigma_y}\right)^2 (y - \langle y\rangle)^2\right]^{1/2}$

calibration procedure and conditions[2,3,7,17]. The dependences of σ on σ_y for typical calibration approaches are given in Table I (for some other calibrations see ref.[17]). In other cases the dependences can be estimated by approximation using the Taylor series (ref.[2], Appendix B5).

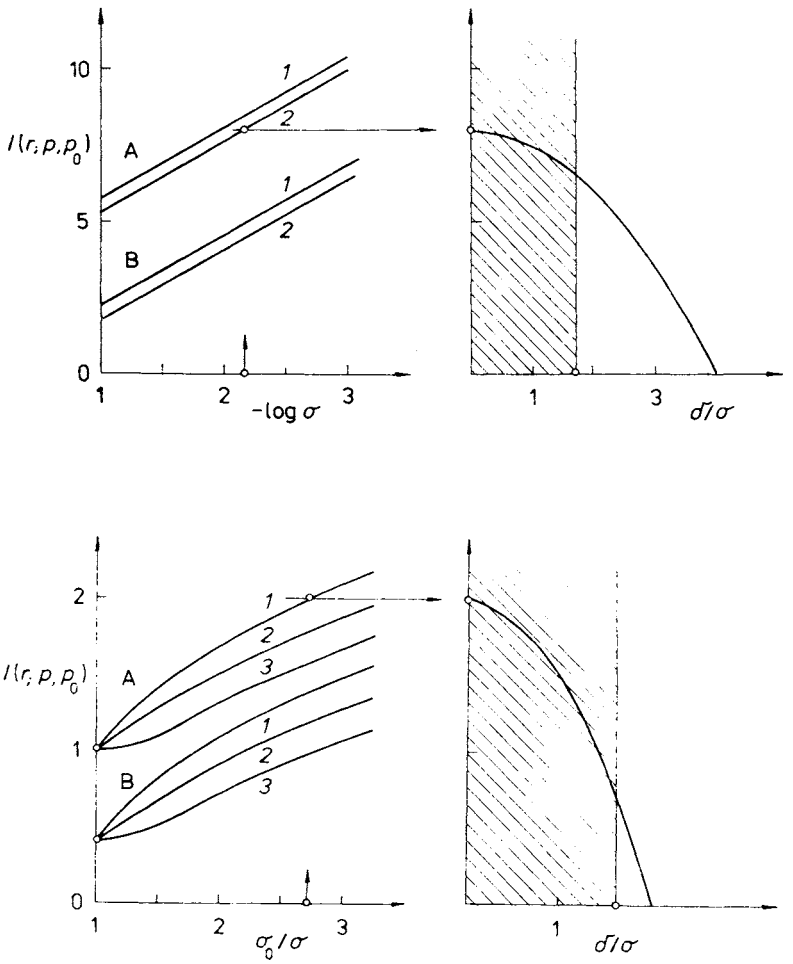

FIG. 1

Dependences of $I(r; p, p_0)$ according to Eq. (2) (*a*) and Eq. (4) (*b*) on variance and error. *a* Left: dependence on $-\log \sigma$; $x_2 - x_1 = 83{\cdot}05$ (A), $4{\cdot}13$ (B); k: *1* 0, *2* 1. Right: dependence on the δ/σ ratio; $x_2 - x_1 = 83{\cdot}05$, $k = 1$, $\sigma = 0{\cdot}7$. *b* Left: dependence on the σ_0/σ ratio; $\delta_0/\sigma_0 = 1{\cdot}415$ (A), $0{\cdot}895$ (B); k: *1* 0, *2* 0·5, *3* 1. Right: dependence on the δ/σ ratio; $\sigma_0/\sigma = 2{\cdot}70$, $\delta_0/\sigma_0 = 1{\cdot}415$, $k = 1$. Regions where δ is statistically insignificant at the $1 - \alpha = 0{\cdot}90$ level are hatched

Calibration, however, does not only affect the σ value; it can also give rise to a mean error δ. The calibration function (*3a*) can be written more precisely as

$$y = f_C(x_A)\{x_i\}\{p_j\}), \tag{9}$$

where x_A is the concentration of analyte, $\{x_i\}$, $i = 1, 2, \ldots, n$, $i \neq A$ are concentrations of other components present ("matrix"), and $\{p_j\}$, $j = 1, 2, \ldots, k$ are parameters, i.e.conditions under which the analysis is performed. The sensitivity then is

$$S = \mathrm{d}y/\mathrm{d}x_A = \mathrm{d}f_C(x_A)/\mathrm{d}x_A . \tag{10}$$

We can claim that calibration is no source of systematic error in the case if $\mathrm{d}y/\mathrm{d}x_i \ll S$ and $\mathrm{d}y/\mathrm{d}p_j \ll S$; otherwise the occurrence of an error $\delta > 0$ cannot be ruled out. Although the causes of the nonzero mean errors in the individual operations of the analytical procedure and in the calibration are different, their ultimate effect on the information gain is the same and is expressed by the δ/σ ratio (Figs 1*a*, 1*b*, right-hand side). In some instances the calibration can serve to compensate for error arising from some operations of the analytical procedure.

When low amounts of analyte are determined, it is often necessary to subtract the value of the blank y_{bl}; Eqs (*7a*) and (*7b*) then give $y = y_M - y_{bl}$ and $\sigma_y^2 = \sigma_M^2 + \sigma_{bl}^2$, where σ_{bl}^2 is the variance of the blank determination. We often put $\sigma_M^2 = \sigma_{bl}^2$, where upon $\sigma_y = \sigma_M \sqrt{2}$. Problems of allowance for the blank have been treated; for the results see ref.[14], Paragraph 1.3.4.3.3. A suitable number of replicate determinations is usually chosen in a manner shown in ref.[2], Paragraph 6·3, and in refs[7,15,17], so as to attain the maximum information profitability possible.

The effect of the σ and δ values on the information gain of results of quantitative analysis has been mentioned before[8,18]. For the relations (*2*) and (*4*) it is demonstrated in Figs 1*a*, 1*b*. Interpretation of the information gain $I \leqq 0$, appearing at high δ/σ ratios as a case where incorrect results misinform us, has been presented in refs[7,8,13]. This interpreatation can be extended as follows: accurate results converge to the true value during refinement, whereas inaccurate results, containing an error δ, would converge to the value of μ, which differs from the true value by the error δ.

CONCLUSIONS

The linking of the information theory concept with the system approach where, however, the analytical system is not regarded as a black box, in conjunction with the extended divergence measure concept[8] enables several rules of practical value and some theoretically important facts to be derived. Starting from the situation outlined in the introduction, we can formulate them as follows.

The occurrence of a systematic error δ is a significant factor in the uncertainty of results of quantitative analysis and hence, in the information gain. Random errors, characterized by variance σ^2, are always present; they only should not be too high. If the δ/σ ratio is high, then the absolutely incorrect result represents no information gain; it can even misinform us. If the variance σ^2 is high, then the information gain from the result is low even in case that $\delta = 0$, and only a high δ value can be established as statistically significant and eliminated by appropriate calibration (for a discussion see ref.[19]).

The variance of the final result of determination of the analytical signal intensity is contributed to by the operations of the analytical procedure A, B, C, ..., so that

$$\sigma_y^2 = \sigma_M^2 + \sigma_A^2 + \sigma_B^2 + \sigma_C^2 + \ldots . \qquad (11)$$

The variance of results of analyses σ^2 then depends not only on σ_y^2 but also on the calibration procedure (Table I). This procedure can be a priori chosen with respect to the effect of the various calibration procedures on the information gain[7].

The mean error δ arises either during some of the operations of the analytical procedure or during calibration, mostly due to the matrix effect. Some errors arising, e.g., from the establishing of an equilibrium can be determined from the equilibrium constant values[15,16]. Occasionally the errors can be partly or completely eliminated by adapting the analytical procedure, or compensated for by a suitable calibration. A method for the determination of the confidence interval of results biassed by a systematic error δ has been reported by Grabe[20]; as to the randomization of systematic error, see ref.[10].

In the practice, it does not suffice to choose an analytical method and optimize it so that it be able to provide the maximum relevant information; actually, provisions must be made for the information to have always the same high information content. These provisions are usually metrological by nature[19,21] and differ somewhat according to whether the dependence by Eq. (*3a*), (*3b*) is homoskedastic or heteroskedastic[8]. What must be taken care of in the analysis are quality assurance[22,23] and good laboratory practice (GLP)[24] (see also ref.[19]). Well-elaborated theory is available for quality assurance and good laboratory practice, and it can be extended and generalized by applying the information and system approach.

The physico-chemical relations describing processes that occur in the course of the operations of the analytical procedure and which can account for the systematic error or the matrix effect in the method in question not only are of importance for the a priori estimate of the error δ, which is advantageous for the choice of the optimal analytical strategy[17], but they also link the theoretical physico-chemical basis of the methods to the general information-theoretical and system foundations of the whole methodologically differentiated analytical chemistry. We should never

look upon an analytical method as a black box, even if no mathematical description of the corresponding process is available; rather, we should attempt to find this description. The combination of the physico-chemical foundations of the various analytical methods with the system and information-theoretical approach to the understanding of the analytical process can form a basis of the theory of analytical chemistry[27].

Experiments are performed with a view to obtaining information that should as closely as possible approach the truth, which we assume is objectively existing. The results of accurate measurements and analyses converge to the true value with improving precision[25] whereas inaccurate results converge to a value that differs from the true value by the systematic error. If the δ/σ ratio is adopted as a measure of agreement between the observed and true values, then the results diverge from the true value as the variance decreases at a constant mean error.

The determination and elimination of the mean error δ by calibration meets with some problems. The δ value can be determined by analysis of a reference material having the analyte content X^* with a precision characterized by the variance σ_r^2. Knowing the mean error so established, we depend on this value being the same also in the analysis of sample. This, however, is only true if no matrix effect plays a significant part – which is only rarely the case – or if the reference and sample materials are identical in composition, which is difficult to accomplish in practice.

If the δ value is known and can be assumed to be the same for the reference and sample materials, it is necessary to test whether it is dependent on the analyte content $x_A \in \langle x_1, x_2 \rangle$ or not; but even if δ is constant, the δ/σ ratio can be concentration dependent if the calibration dependence is heteroskedastic[8].

For ensuring a good quality assurance of the results of analysis[21–23], the analysis must be backed up by sets of reference material certified based on round robin interlaboratory assays. It is important that the certificate involve precision of the reported analyte contents determination in terms of the σ_r value because a method can only be backed up by a reference material if $\sigma \gg \sigma_r$ (ref.[8]).

In this paper, the uniform distribution (Eq. (*2*)) or the normal a posteriori distribution (Eq. (*4*)) have been considered. Although Eqs (*2*) and (*4*) are mutually different, the effect of the δ and σ values on the information gain of the results is alike in the two cases (Figs 1*a*, 1*b*).

The information gain of the result of analysis should not be too small as compared to the information content of the analytical signal, i.e. the loss of information due to calibration should be as low as possible. Such loss can arise if the full span of signal intensities, from y_{min} to y_{max}, is not made use of as compared to the analyte content region, x_1 to x_2. The unfavourable situation can be improved by increasing sensitivity (Eq. (*10*)). It is necessary to choose a reference material with $k \ll 1$ and with its chemical composition identical with or at least closely approaching that of sample, and to verify that δ and σ are independent of x_A or make provisions for

the dependence[8]. The calibration procedure should reduce the error δ as much as possible while leaving the σ value very close to σ_y (Table I, ref.[7]).

When choosing a method for multicomponent analysis, we should consider how the information about the analytes, obtainable by the method in question, is relevant in the particular problem to be solved. This relevance can be treated in fuzzy set terms (ref.[3], p. 64; ref.[26]).

The application of the extended divergence measure[8] to the treatment of the information gain according to Eqs (*2*) and (*4*) and the distinguishing between the information content of the analytical signal and the information gain of the result, particularly in multicomponent analysis, can add considerably to the unified concept of analytical operations from the point of view of information theory, by Doerffel[6] the fundamentals of which have been extended; this may become a significant part of the theoretical basis of analytical chemistry[27-30].

LIST OF SYMBOLS

a	constant
b	stoichiometric constant, calibration straight line slope
k	variance ratio
m	number of points included in calibration straight line construction
n	number of replicate determinations
p, r	probability density
q	x_S/x, ratio of standard addition to analyte concentration
x	analyte content
y	signal intensity
z	signal position
$\mathbf{E}$	mean value operator
I	information content or gain
S	sensitivity
$\mathbf{V}$	variance operator
X	analyte content of reference material
α	significance level
α, β	regression dependence coefficients
δ	mean error
μ	mean value
ϱ	correlation coefficient
σ	standard deviation
σ^2	variance

Subscripts

b	slope (e.g. σ_b^2 is variance of determination of slope)
bl	blank (e.g. σ_{bl}^2 is variance of blank determination)
i	component (analyte)
j	signal

max	maximum
min	minimum
r	reference material
y	signal intensity (e.g. σ_y^2 is variance of signal intensity determination)
z	signal position
A, B, C	operations of analytical procedure
M	measurement (e.g. σ_M^2 is variance of results of measurement)

Special symbols

f_A, f_C	analytical and calibration dependences, respectively
$I(p, p_0)$	information content determined from a priori and a posteriori distributions
$I(r; p, p_0)$	information gain determined from true, a priori and a posteriori distributions
$\langle y \rangle$	estimate of the mean of y-values
α, β	coefficients of calibration dependence
α', β'	estimate of α, β

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