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Thematic course: Software in Analytical Chemistry. Part I.

ALGORITHM OF EXPERT SYSTEM MEASUREMENT ESTIMATIONS FOR ANALYTICAL METHODS.

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Abstract

The fundamental notions of analytical chemistry have been defined with unambiguous optimality in terms of mathematics. The expert systems worked out on this basis are proposed to provide for the calculations to be estimated so that the specific analytical problems are solved; as well as to evaluate the analytical techniques and methods of analysis which can serve as a basis for the creation of electronic tutorial. The algorithms of estimations and measurement procedures based on mathematical, technological criteria and those used in training have been put to consideration. Some estimations of the analysis results have also been presented.

Introduction

The information technology is based on processing and expert programs for sorting out and estimation of the results of analysis [1,2]. These programs, unambiguous and optimal calculation algorithms are expected to be successfully applied for the solution of actual analytical problems, in particular, for training the students and for routine computer analytical control in manufacture and ecology [2-9]. The modern manuals of analytical chemistry [10-12] involve the extensive factual, theoretical and reference data necessary for carrying-out the analysis, however their volume is limited. A problem of intensive application of all-round information needed to carry out the analysis can be effectively solved by means of expert systems. At present, however, many criteria and parameters for examining the analysis data are not sufficiently developed and still disputed by mathematicians, chemists and teachers in works [12]. This problem is getting more acute with the development of processing programs acting on the scheme: analytical experiment - data input - examination and estimation of the results of analysis. Considering the object of analysis and the component of the object (substance) which is the aim of the analysis, it is possible to distinguish determinative concepts including the consept of substance quantity and those defined by it - concentration and content. Further in the order of importance comes the concept of accuracy. This one has recently been varying from defining the characteristic errors and estimation of their combined action, to the technological assessment criteria.

Results and Discussion

Many unified expert opinions on the quantity of the substance should be defined only by the number of gram-molecules represent a serious obstacle to the development of expert programs. These experts refer to the International System of Units [13], where the concept of substance quantity is given only as kilomole in the section of molecular physics and thermodynamics. Defining units of physical magnitudes such as weight and meter are given as fundamental ones. They allow to calculate such derived units as volume and the object's area, which are presented in the section devoted to mechanical units. However, the analytical practice and the facts we encountered at the creation of expert system on Analytical Chemistry showed that there are three ways of measurement of the quantity of a substance which could be equally accepted :

1. Piece measurement of identical elementary components making up the substances and the measurement object at the atomic and molecular level (unit of measure - kilomole).
2. Measurement of the substance and the weight of the object - kg.
3. Measurement of space dimensions of the objec - litre (cubic meter). Accepting the fact that the above-stated ways of quantitative measurements of a substance are equivalent, it becomes possible to define the concentration of a substance as the quantity of a substance in standardized quantity of an object. Thus, three basic (and other) dimensions of concentration: mol/l, g/ml, % (mole and volume fractions, as well as the fraction of the total mass) should be considered as equivalent and calculated by appropriate formulas on an equal basis. Otherwise, we should accept the statement that the concentration expressed in mole fractions is the only rightful one. Equating the concepts of concentration and content that can be often observed in the literary sources is erroneous. At the same time, the content of a substance in an object should be defined as the substance quantity of the entire object which is accepted as a single whole.

By solving the tasks on estimation and examination of analysis results and measurement procedures it is necessary to define the concept of accuracy as insignificancy of all types of measurement errors (gross errors, accidental and permanent errors). The term "gross error" makes sense only when the confidence interval of the permissible error calculated by a standard way and considered as a technological assessment criterion is exceeded. An accidental error can be determined in consequence of a standard calculation of confidence interval after preliminary estimation of gross error significance. The presence of permanent error shows that the module of difference of reliable and expectated values of permissible error is exceeded. Along with the criteria included in the sections of mathematical statistics, it is necessary to use the technological criteria such as product quality loss, economic effectiveness and safety. The technological criteria are more important for estimation of analysis results than mathematical ones, as they allow to come to solution of qualitative tasks.

The criteria given in tables 1, 2, 3 have been taken as a principle of ST5 program on experimental data processing for subsequent calculation of the results of direct and indirect measurements taking into account the gross errors, systematic and accident errors, as well as the estimation of results by five-mark or other scales. The experimental data are processed in the following sequence:

1. standard calculation of confidence interval;
2. check of accidental ($\Delta X \leq \Delta X_з$) and systematic ($|a - X| \leq \Delta X_з$) errors (where a - valid value of measurable quantity; $\Delta X_з$ - permissible error);
3. if only one of these requirements is not fulfilled, the removal of gross errors with the selection of compact group of the results for estimating their asymmetry and masking effect will be performed.

Table 1. Parameters and criteria of the estimation of measurements used in ST5 program.

N	Criteria	Unit of measure	Notes and parameters (a star (*) symbolizes a criterion introduced by the authors)
1	ΔX_3, $\Delta X_3\%$ - absolute and relative metering errors	Dimension of measurable parameter	Presently, the parameter is specified along with certification of a measurement procedure and is included in state standards
2	P - reliability of measurements	Probability	is specified along with certification of a measurement procedure
3	a, X - true value and expected parameter	Dimension of measurable parameter	a- is determined by higher skilled specialists by means of more sensitive instruments and using standard samples
4	$t_{n,P}$ - Student criterion	there isn't	is automatically chosen depending on n and P, where n - a number of repetitive measurements
5*	α_n - a fraction of gross errors not influencing on estimation (a condition of insignificancy of gross errors)	there isn't	CT5 eliminates the multiple gross errors, whereas significance and homogeneity tests meet the requirements of state branch standard № 8504 (GOST- 8504). Under production conditions this criterion corresponds to reject allowance
6*	K_1, K_2, K_3, K_4 - factors of estimation of the measurements	there isn't	K_1 и K_2 increase α_n, and change a mark for good or satisfactory. Similarly, K_3 и K_4 increase $\Delta X_3\%$.
7*	K_5, K_6. - factors of calculation of skill level of the specialists and seasonality	there isn't	Change $\Delta X_3\%$ depending on a skill level of the specialists and seasonality (are used in training)
8	$\Delta X\% \le \Delta X_3\%$	Dimension of measurable parameter	A condition of insignificancy of an accidental metering error
9	$\mid a - X \mid \le \Delta X_з$	Dimension of a parameter	A condition of insignificancy of permanent error

Table 2. Criteria of estimation of measurement procedures.

N	Criteria and Parameters	Unit of measure	Notes
1	*Metrological* 1.1 (p. 8 tab.1). 1.2 (p. 9 tab.1) 1.3 B -sensitivity. 1.4 X_{min} - X_{max}. 1.5 M_{min}, V_{min}	$\Delta Y/\Delta X$ Dimension of parameter g, l Dimension of measurable parameter	Δ - addition , Y - analytical signal, X - measurable parameter Calculation of B value in ST5 is carried out over the range of X_{min} (lower definition limit) and X_{max} (upper definition limit), as well as subject to P and ΔX_3 values. $M_{min}=X_{min}* V_{min}* M$, where M_{min} - minimal weight of analyzable substance and V_{min} - minimal volume of analysis object (is defined by a measurement procedure, X_{min} - concentration of analyzable substance in mol/l), M - molar mass of a substance
	1.6 S - selectivity		is defined by limiting concentration or by a mixing ratio in an object with violation of conditions 1.1 and 1.2.
	1.7 I - informativeness		is defined by a number of analytical signals achieved at single realization of a technique without additional sample preparation.
	1.8 i		Calculation of mutual influence of components and matrix.
2	*Economical* 2.1. Effectivity 2.2 Expressiveness 2.3. Serializability 2.4. Automation 2.5. Operation safety 2.6. Organization.	rouble/measurement sec/measurement	Calculations are carried out at each stage of a procedure and completed by summation of obtained results. The time expended for getting one result of analysis. 2.1 and 2.2. items are heavily influenced by 2.3 - 2.6. items. The calculation is carried out within the limits of concrete way of control..
3	Unique		For example, indestructibility of an object at the analysis

Estimation principles presuppose the decrease of a mark whenever error significance tests are violated. However, it should be noted that a mark decrease does not occur at combined violations, and, furthermore, a principle of independence of results from an order in which data are entered and a principle of single-valuedness of results are fulfilled. For example, the metrological characteristics of the data entered without earlier rejected data and those of all input data should coincide, whereas their qualitative estimations are at variance.

Presently, ST5 program works in WINDOWS 95 environment. ST5 includes the following sections:

1) Direct experiment.
2) Linear regression analysis.
3) Nonlinear regression analysis.
4) Approximation and function smoothing.
5) Balance computation.
6) Resolution of compound functions into components (for example, resolution of spectra into gauss components).
7) Numerical solution of equations by the method of maximal likelihood.
8) Application program package (calculations of titration curves (including calculations with the use of Grane method [10]), mutual influence of substances and object's matrix, kinetic and thermodynamic parameters, ionic force, viscosity etc.).
9) Standard programs of data processing.

The differences of ST5 program from the standard processing programs come from using a wide range of metrological characteristics at calculations and qualitative estimations involving oral conclusions. In table 2 the parameters and assessment criteria of the methods and techniques of analysis used in ST5 program package are given. In section 3 of table 2 the criteria of unique characteristics of a technique or a method of analysis influencing the parameters given in tables 1 and 2 are included. These are, for example, the criteria of overlapping or reduction of analysis stages, indestructibility of analysis object, analysis of small concentrations and quantities of substance, composite analysis, cumulative properties of sorbents at sample preparation, registration of the special technological parameters such as sewage discharge hydrodynamic regimes, emergency state detection, absence of junctions and power supply in samplers etc.

In table 3 the examples of particular application of ST5 program for processing and estimation of the experimental data obtained by the students in the course of their laboratory practical works on analytical chemistry are presented. In addition, ST5 provides for estimation and choice of techniques, methods and ways of control after preliminary mathematical formalization of analysis problems, for example, by the criteria of table 1. Thus, ST5 is on the higher level as compared to the programs solving individual analytical tasks such as the calculations of titration curves, equilibrium states, regression parameters etc. [4], and allows to solve the following tasks:

1) metrological (estimation of errors).
2) qualitative (rating estimation).
3) economic.
4) research planning.
5) pedagogical (stepwise and final control, correction of knowledge).

Table 3. Examples of application of ST5 program.

Basic data	Mark	Results and comments
Direct experiment(quantitative chemical titrimetric analysis) A test for the concentration of HCl solution by sodium carbonate: P = 0.95, $\Delta X_{3\%}$=1%, a= 0.1021 mol/l, α_n = 0.1, K1= 1.3, K2= 1.3, K3= 1.3, K4= 1.3, K5= 1.3, K6=1.3.		X Δ X % Δ X
Analysis results, mol/l (* - gross error): a) 0.1020, 0.1015, 0.1018, 0.1021, 0,1017	5 (excell.)	0.1020 0.38 0.0004
b) 0.1010, 0.1008, 0.1007, 0.1009, 0,1006*	3 (satisf.)	0.1021 0.20 0.0002 Δ X3% is extended to K1
c) 0.1013, 0.1009*, 0.1012, 0.1009, 0,1010	4 (good)	0.1011 0.29 0.0003
d) 0.1020, 0.1025, 0.1018, 0.1063*, 0.1019 0.1021, 0.1024, 0.1009, 0.1058, 0.1022	5 (excell.)	A fraction of gross errors is insignificant
e) 0.1020, 0.1025, 0.1018, 0.1063*, 0.1019 0.1021, 0.1024, 0.1009, 0.1072* 0.1022	4 (good)	A fraction of gross errors is significant (gross errors are non-central)
f) 0.1020, 0.1025, 0.1018, 0.1063*, 0.1019 0.1021, 0.1024, 0.1009, 0.0973*, 0.1022	4 (good.)	A fraction of gross errors is significant (masking effect)
Inderect experiment (physicochemical methods of analysis). Photocolorimetrical copper test. P = 0.95, Δ X3%= 3%, = 0.75 10^{-3} g/ml, Measuring data of standard solutions: CCu, g/ml 10^3 = 0.505, 0.631, 0.758, 1.01, 1.25 A = 0.113, 0.135, 0.164*, 0.204, 0.244. Optical density of observable solution: A_x = 0.158	4 (good)	0.76 2.6 0.02 There is a gross error at carrying out optical density measurement. Systematic and accidental errors are insignificant.
Kinetic method of molybdenum(VI) analysis. P = 0.95, Δ X3%= 10%, a = 2.4 10^{-7} g/ml, Measuring data of standard solutions: CMo, g/ml 10^7 = 1.00, 1.56, 2.43, 6.08, 9.73 tgα = 0.202, 0.310, 0.499, 1.25,. 1.96. tgα_x = 0.51	5 (excell.)	$2.5\cdot10^{-7}$ 6.3 $0.2\cdot10^{-7}$ $C_{eff.}$ = (1.5 - 10) $\cdot10^{-7}$, g/ml (effective range of definition)
Development of analysis techniques. Flame photometric test for potassium concentration in drinking water. To show a possibility of carrying out the analysis by external standard method. P = 0.95, ΔX3% = 5%, a = 0.99 10^{-5} g/ml. Measuring data of standard solutions: CK, g/ml 10^{-5} = 0.160, 0.320, 0.640, 0.960, 1.60 I = 7.0, 14, 31, 45, 77 Analytical signal of investigated water I_x=49. Analytical signal of investigated water with addition of standard (ΔCK = 0.85 10^{-5}g/ml) Δ Ix = 41		$1.02\cdot10^{-5}$ 3.6 $0.04\cdot10^{-5}$ Divergence of the data obtained by the additive method and by the method of external standard is insignificant. Systematic and accidental errors are also insignificant. The analyses can be further carried out by the method of external standard.

The fundamental feature of PC application from the modern point of view is its transition to a new level of analysis and training, when the calculation of additional important parameters of analytical process and improvement of reliability of analysis results and economic characteristics, as well as preservation of experts's knowledge and improvement of analysis quality become possible at last.

Conclusions

The fundamental notions of analytical chemistry such as quantity, concentration, content, accuracy etc, needed for realization of metrological estimation of analysis results, estimation and choice of techniques and methods of analysis have been determined and put for discussion.

ST5 application program package has been created with the aim of measurement assurance of programs, solving special analytical problems (calculation of direct and indirect measurement results taking into account gross, permanent and accidental errors and estimation of the results by five-mark or other scale, with three types of errors contributing to the general assumption).

The mathematical, technological criteria and the ones used in training process have been also considered. Algorithms of estimation of the analysis results, measurement routine and optimization of analytical measurements have been offered.

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