METHODS FOR EVALUATING THE UNCERTAINTY OF THE RESULTS OF DIRECT AND INDIRECT MEASUREMENTS OF ANALYTICAL VALUES

[1]Masharipov Shodlik Masharipovich, [2]Rakhmatullaev Sarvar Anvarovich,
[3]Fattoev Firuz Farkhod ogli
[1]PhD in technical sciences
[1,2]senior lecturer Tashkent State Technical University
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Abstract. *Methods of estimating uncertainty of results of direct and indirect measurements of analytical values have been analysed. Analytical expressions for numerical calculation of main sources of physical and chemical values are given. Significant sources of measurement uncertainty have been simulated. The apparatus effects may include, for example, mistake limits of the analytical weights; The presence of a temperature regulator that can maintain an average temperature that differs (within specified limits) from the temperature recorded; Automatic analyzer, which can be subject to overload effects. Taking into account these specifics of analytical measurements, calculations of standardized standard uncertainties of measurement results according to GOST 1770 have been performed.*

Keywords: *Coverage factor, coverage probability, coverage interval, type A uncertainty, type B uncertainty, extended uncertainty, measurements, measured value, analytical values, direct measurements, indirect measurements, correlated value, uncorrelated value.*

Introduction

Many important decisions are based on the results of chemical quantitative analysis; results are used, for example, to estimate yields, to check materials against specifications or statutory limits, or to estimate monetary value. Whenever decisions are based on analytical results, it is important to have some indication of the quality of the results, that is, the extent to which they can be used to achieve the stated goal. Users of chemical analysis results, especially in those areas related to international trade, are facing increasing pressure to eliminate duplication of effort often expended in obtaining them [1-3]. Confidence in data from outside the user's own organization is a prerequisite for achieving the above goal.

Main part

In some analytical chemistry sectors, it is now a formal (often legal) requirement for the laboratory to introduce quality assurance measures to ensure the ability and provide data of the required quality. Such measures include: use of proven methods of analysis; использование определенных процедур внутреннего контроля качества; participation in proficiency testing programs; accreditation based on ISO / IEC 17025: 2017 and establishing traceability of measurement results. Depending on the type of information available about the quantity and on the possible variability of the quantity value (statistical or non-statistical), it is known that the uncertainties of the input quantities are estimated by type A or type B.

If the information about a quantity is statistical, that is, it is obtained experimentally by repeated measurements or tests, then its standard uncertainty due to random effects is estimated by type A (1) [4,5]:

$$u_A(\bar{x}) = s(\bar{x}) = \sqrt{\frac{1}{n(n-1)} \cdot \sum_{i=1}^{n} \left(x_i - \bar{x}\right)^2} \quad (1)$$

where $\bar{x}$ is the estimate (arithmetic mean) of the input X quantity; x_i – result of the i-th observation of the input quantity; n – number of observations.

In this case, the experimental variance of observations is estimated by (2):

$$s^2(x) = \frac{1}{n-1} \cdot \sum_{i=1}^{n} \left(x_i - \bar{x}\right)^2 \quad (2)$$

Before measuring, first of all, we compile a list of influencing factors on the expanded measurement uncertainty.

When measuring the density of ethanol (C_2H_5OH) using a volumetric flask (according to GOST 1770), the density is found by the equation.

$$\rho(C_2H_5OH) = \frac{m_2 - m_1}{V} \quad (3)$$

where m_1 - is the mass of the flask, m_2 – weight of the flask with ethanol.

This mathematical model reflects the main sources of uncertainty (Fig. 1).

Fig. 1. it can be seen that the main sources of measurement uncertainty are directly related to the total mass of the flask and volume. In addition, the standardized mistake limit of the flask is regulated at t=20 ºC [6].

The total standard uncertainty is calculated by the formula (4):

$$u_c(y) = \sqrt{\sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i)} \quad (4)$$

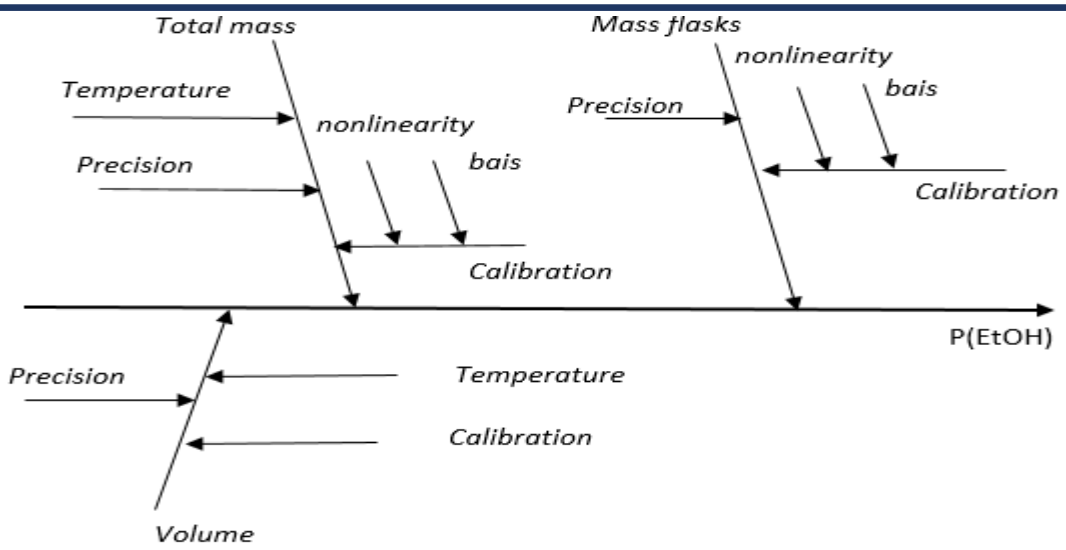
if the input quantities are uncorrelated. Otherwise, i.e. for correlated input quantities, it is calculated by the formula (5):

$$u_c(y) = \sqrt{\sum_{i=1}^{n}\sum_{j=1}^{n} \frac{\partial f}{\partial x_i}\frac{\partial f}{\partial x_j} u(x_i, x_j)} = \sqrt{\sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n} \frac{\partial f}{\partial x_i}\frac{\partial f}{\partial x_j} u(x_i, x_j)} \quad (5)$$

where are the partial derivatives $\partial f / \partial x_i$ – sensitivity coefficients; $u(x_i,x_j)$ – covariance of input quantities.

Fig. 1.

The main groups and subgroups of sources of uncertainty when measuring the density of ethanol



Sensitivity coefficients [7.8]

$$c_i = \frac{\partial f}{\partial x_i} \quad (6)$$

show how the output estimate y changes with the change in the values of the input estimates $x_1, x_2, ..., x_n$.

Taking into account (6), formulas (4) and (5) are transformed into the following expressions

$$u_c(y) = \sqrt{\sum_{i=1}^{n} \left(\frac{\partial y}{\partial x_i}\right)^2 \cdot u^2(x_i)} = \sqrt{\sum_{i=1}^{n} u_i^2(y)} \quad (7)$$

$$u_c(y) = \sqrt{\sum_{i=1}^{n} \left(\frac{\partial y}{\partial x_i}\right)^2 \cdot u^2(x_i) + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \left(\frac{\partial y}{\partial x_i}\right) \cdot \left(\frac{\partial y}{\partial x_j}\right) \cdot u(x_i) \cdot u(x_j) \cdot r(x_i, x_j)} \quad (8)$$

$$u_i(y) = \frac{\partial y}{\partial x_i} \cdot u(x_i) \quad (9)$$

For the special case, when all input estimates are correlated with the correlation coefficients r (xi, xj) = +1, equation (8) is reduced to

$$u_c(y) = \sum_{i=1}^{n} u_i(y) \quad (10)$$

For the sum or difference of two correlated quantities (Y = X1 ± X), the total standard uncertainty (in accordance with (8)) will be equal to:

$$u^2(y) = u^2(x_1) + u^2(x_2) \pm 2 \cdot u(x_1) \cdot u(x_2) \cdot r(x_1, x_2) \quad (11)$$

If two input quantities Xi and Xj are correlated to a certain extent, that is, they are dependent on each other in one way or another, then when evaluating the total standard uncertainty among the contributions of the uncertainties of the input quantities, their covariance should be taken into account, which is estimated by the following formula [9, 10]:

$$u(\bar{x}_i, \bar{x}_j) = u(\bar{x}_i) \cdot u(\bar{x}_j) \cdot r(\bar{x}_i, \bar{x}_j), \quad i \neq j \quad (12)$$

The degree of correlation is determined using the correlation coefficient. The estimated correlation coefficient is obtained from equation (1.12).

$$r(\bar{x}_i, \bar{x}_j) = u(\bar{x}_i, \bar{x}_j) / u(\bar{x}_i) \cdot u(\bar{x}_j) \cdot, \quad i \neq j, \quad \left| r(\bar{x}_i, \bar{x}_j) \right| \leq 1 \quad (13)$$

Figures 2 and 3 show the permissible mistakes from the nominal capacity of glass volumetric glassware and the permissible mistake limits for the volume of pipettes with one mark. If the certificate or other technical documentation gives the limits of permissible mistake without specifying the confidence level, or the estimate is given in the form of a maximum range (± a), and the shape of the distribution is unknown, a uniform distribution law should be used (Fig. 4.)

Table 1

Permissible mistakes from the nominal capacity of glass volumetric glassware, см^3

Nominal Capacity	Permissible mistake				
	Cylinders		Beakers	Flasks	
	1st class	2nd class		1st class	2nd class
5	0,10	0,10	-	0,025	0,05
10	0,10	0,20	-	0,025	0,05
25	0,25	0,50	-	0,04	0,08
50	0,25	1,00	2,50	0,06	0,12
100	0,50	1,00	5,00	0,10	0,20
200	-	-	-	0,15	0,30
250	1,25	2,00	5,00	0,15	0,30
300	-	-	-	0,20	0,40
500	2,50	5,00	12,50	0,25	0,50
1000	5,00	10,00	25,00	0,40	0,80
2000	10,00	20,00	-	0,60	1,20

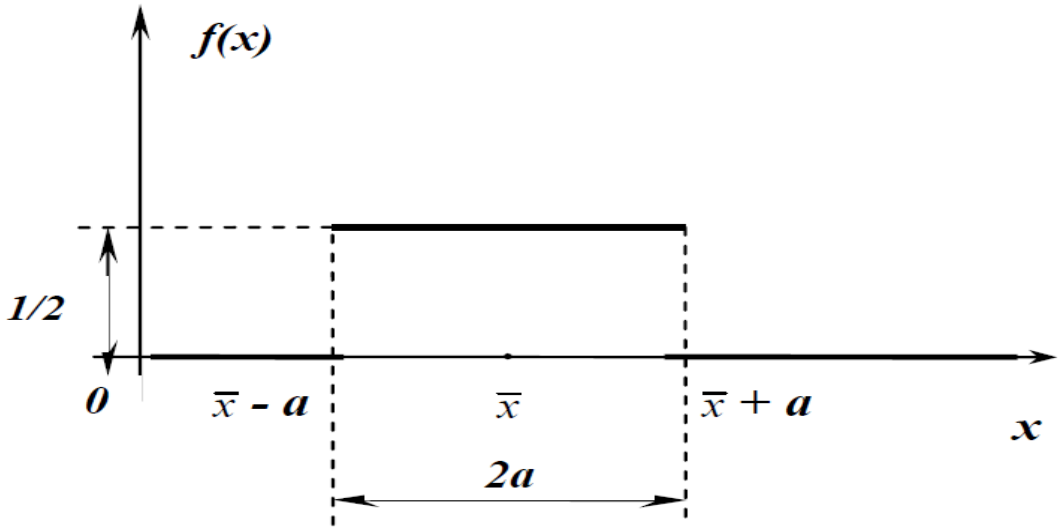
Table 2

Limits of permissible mistake for the volume of pipettes with one mark, см^3

Mistake of nominal	Limit of permissible mistake	
	1st class	2nd class
0,5	±0,005	±0,01
1	±0,008	±0,015
2	±0,01	±0,02
5	±0,015	±0,03
10	±0,02	±0,04
10,77	±0,02	±0,04
20	±0,03	±0,06
25	±0,03	±0,06
50	±0,05	±0,1
100	±0,08	±0,15
200	±0,1	±0,2

Fig 2.

Probability density function of uniform distribution



(a- is the half-width of the interval, x- is a random measurement result)

Fig. 3.

Normalized standard uncertainty (*Ust*) of the cylinder, K = 1 (accuracy class)

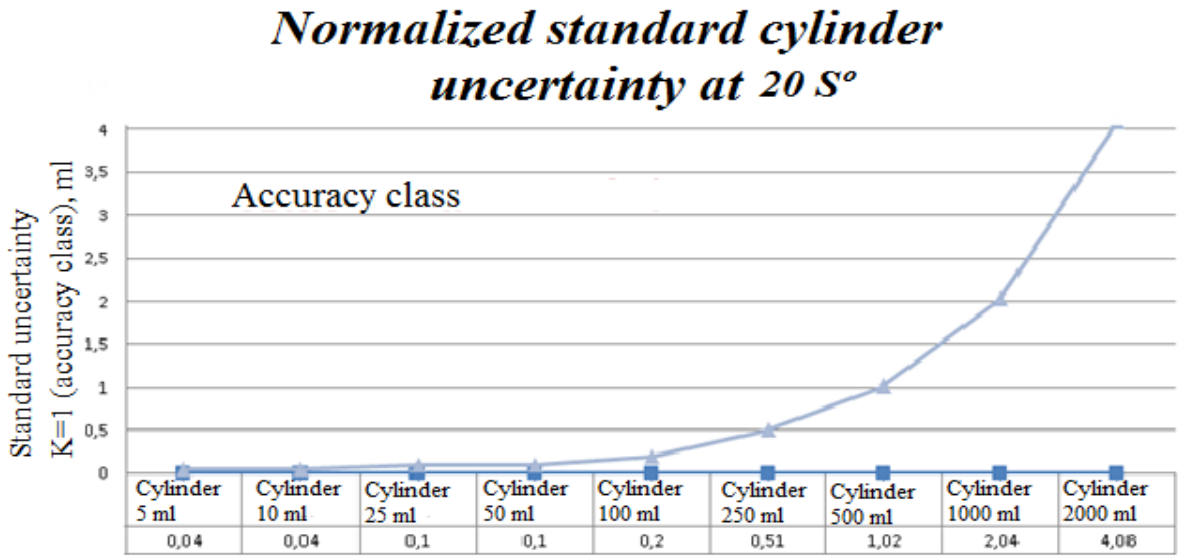
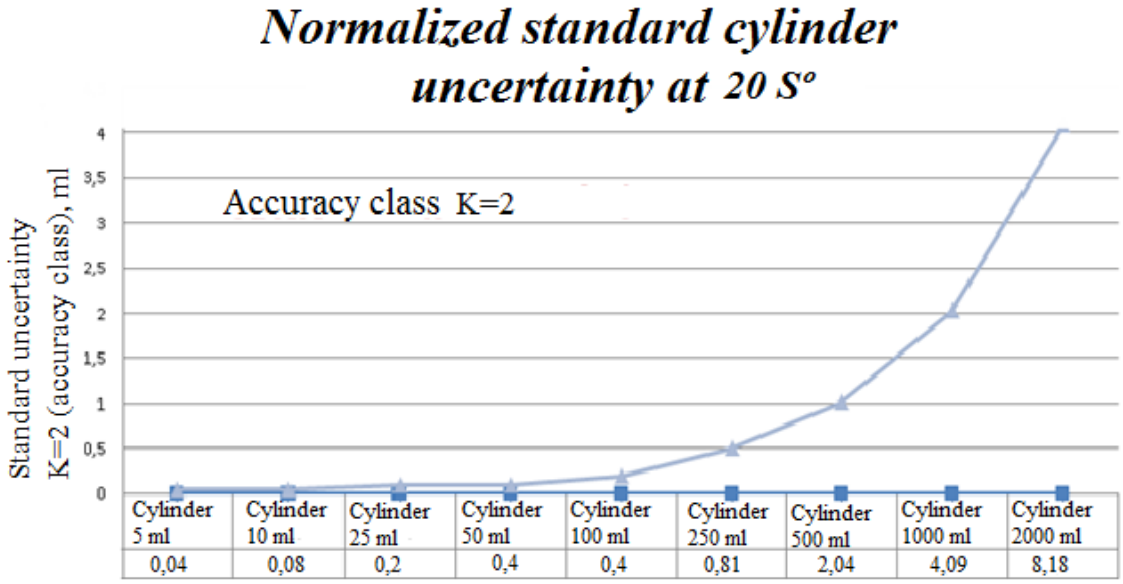


Table 1. 2 shows the permissible mistakes from the nominal capacity of glass volumetric glassware and the permissible mistake limits for the volume of pipettes with one mark. If the certificate or other technical documentation gives the limits of permissible mistake without indicating the confidence level or the estimate is given in the form of the maximum range (± a), and the shape of the distribution is unknown, then a uniform distribution law should be used (Fig. 2.). Fig. 3 shows the normalized standard uncertainty of the cylinder, K = 1 (accuracy class). Fig. it can be seen that the standard uncertainty decreases accordingly with an increase in the nominal volume of the cylinder. In addition, the value of uct depends on the accuracy class K (Fig. 4).

Fig. 4.

Normalized standard uncertainty (*Ust*) of the cylinder, K=2 (accuracy class)



Output: The main factors (not in all cases they are significant) affecting the total measurement uncertainty are discussed in the document of the International Organization for Cooperation in the Field of Laboratory Accreditation (ILAC), which also deals with the introduction of the concept of measurement uncertainty during testing, taking into account the application of the ISO / IEC 17025. According to ISO 10012, some components of uncertainty may be of little importance compared to other components, so their detailed determination may not be justified for economic or technical reasons. In this case, the decisions and justifications must be registered. In all situations, the effort to evaluate and record measurement uncertainty should be commensurate with the importance of the measurement results for product quality assurance.

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