EVALUATION OF INDIRECT MEASURUMENT UNCERTAINTY IN ANALYTICAL CHEMISTRY

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The objective of the chemical analysis is to extract information about the material using various measuring equipment. Thus, the chemical analysis is a complex, multistage measurement process. Evaluation of results uncertainty of the chemical analysis is the most important task of the Chemical Metrology. An indirect measurement is finding the measured value by calculation from other measurement results. All the results of the chemical analysis, i.e. experimentally determined values of the component contents are also indirectly measured.

Measurements are key element in most areas of practical activities. More over the reliability of decisions made on the basis of the measurement results depends on the accuracy of the latter. In addition, the measurement accuracy often determines the level of material costs in manufacturing and non-manufacturing spheres. That is exactly why improving the accuracy of measurements is one of the most important issues of modern metrology [1].

Any measurement process is influenced by many factors that distort the measurement result. The difference of measurement results from the true value of the measured quantity is called - an error. Due to the fact that any measurement result generally contains error, the true value of measurement quantity, respectively, the extent of error of the specific result can never be established. The reliability of accuracy estimation is also important in cases where the errors of measurement results are input data while analyzing the errors of other measurements and, transforming by measurement equation, affect the error of the result. However it is possible to evaluate a certain range of values within which the true value can present with some degree of reliance, i.e., to specify the range of possible values of the error. This range is called the uncertainty of the measurement result.

Measurement uncertainty – is generally acknowledged quantitative characteristic of the measurement result quality [2] (GUM). Any laboratory that makes measurement should evaluate the uncertainty and, if necessary, provide its value with the measured value to the customer. [3] The measured value with the uncertainty forms the measurement result.

The objective of the chemical analysis is to extract information about the material using various measuring equipment. Thus, the chemical analysis is a complex, multistage measurement process. The study of general issues related to the measurement, processing and interpretation of the results of chemical analysis is carried out by a special section of the analytical chemistry, called Chemical Metrology.

Evaluation of results uncertainty of the chemical analysis is the most important task of the Chemical Metrology. An indirect measurement is finding the measured value by calculation from other measurement results. An example of indirectly measured value may be the average value of x in a series of measurements. All the results of the chemical analysis, i.e. experimentally determined values of the component contents are also indirectly measured. [7] In general, the indirectly measured value of y can be represented as a function of its arguments of experimentally measured values of $x_1, x_2, \ldots x_n$:

$$y = f(x_1, x_2, \ldots x_n). \quad (1)$$

If the value uncertainty of argument of $s2\ (x_1)$, $s2(x_2)$, ... $s2\ (x_n)$ are known, and all arguments are independent from each other, the uncertainty value of y can be calculated as follows

$$s^2(y)=\left(\frac{\partial f}{\partial x_1}\right)^2 s^2(x_1)+\left(\frac{\partial f}{\partial x_2}\right) s^2(x_2)+\ldots.+\left(\frac{\partial f}{\partial xn}\right)^2 s^2(x_n). \qquad (2)$$

Expression (4) is called the Law of uncertainty propagation. It is an essential relation, which allows evaluating the uncertainty of the indirectly measured value when carrying out its repeated measurements is impossible or unpractical. There are some important special cases of expression (2) with respect to the simple functional relationship. The true values are indicated as a, b and c symbols.

$$y= ax_1 \pm bx_2+c \qquad s^2(y)=a^2s^2(x_1)+ b^2s^2(x_2); \qquad (3)$$

$$y= ax_1x_2 \text{ or } y=\frac{ax_1}{x_2} \qquad \left(\frac{s(y)}{y}\right)^2 = \left(\frac{s(x_1)}{x_1}\right)^2 +\left(\frac{s(x_2)}{x_2}\right)^2. \qquad (4)$$

Put it otherwise, when adding and deducting the absolute uncertainties (variance, standard deviation squares) are combined, when multiplying and dividing the relative uncertainties (the squares of the relative standard deviations) are combined.

As an example, let's consider the uncertainty evaluation of values of the standard solution concentrations of Na2CO3 prepared by dissolving Na2CO3 sample in measuring flask of volume of V=200.0 ml. The weight of cup with sample is m1 = 10.1324 g, the weight of the empty cup is m0 = 9.1152 g. To take the uncertainty of weight value caused by the weighing error equal to 0.0002 g, and the uncertainty of the value of the flask volume - 0.1 ml. The molar mass of Na, C and O are equal to 22.990, 12.011 and 15.999, respectively. The uncertainty of the molar mass of elements consider to be equal to the unity in the last decimal digit.

Begin with let's calculate the mass of sodium carbonate weighment:
m = m1 – m0 = 10.1324-9.1152 = 1.0172 g;
the molar mass of the equivalent 1/2Na2CO3:
M = ½(2M(Na)+M(C)+3M(O)) = ½ (2.22.990 + 12.011 + 3.15.999) = 52.994
and the mole fraction value 1/2 Na2CO3:

$$c=\frac{m}{MV}=\frac{1.0172}{0.2000*52.996}=0.95969 \text{ M}.$$

To estimate the uncertainty value apply the formula (4):

$$\left(\frac{s(c)}{c}\right)^2 = \left(\frac{s(m)}{m}\right)^2 +\left(\frac{s(V)}{V}\right)^2 +\left(\frac{s(M)}{M}\right)^2.$$

Uncertainties of m and M, included in this expression, let's evaluate by the formula (3):

$s^2(m)=s^2(m_1)+ s^2(m_0)=0.0002^2+0.0002^2=8*10^{-8}$;
$s(m)=\sqrt{8*10^{-8}}= 2.8*10^{-}4$ (г)

$s^2(M)=1/4(4s^2(M(Na)+ s^2(M(C)) + 9s^2(M(O))=3.5*10^{-6}$
$s(M)= \sqrt{3.5*10^{-6}}=1.9*10^{-3}$

Therefore

$$\left(\frac{s(c)}{c}\right)^2 = \left(\frac{s(m)}{m}\right)^2 +\left(\frac{s(V)}{V}\right)^2 +\left(\frac{s(M)}{M}\right)^2 = \left(\frac{0{,}00028}{1{,}0231}\right)^2+\left(\frac{0{,}1}{200}\right)^2+\left(\frac{0{,}006}{52{,}994}\right)^2=7{,}5*10^{-8}+2{,}5*10^{-7}+1{,}3*10^{-9}=3{,}3*10^{-7}$$

$$\frac{s(c)}{c}=\sqrt{3.3*10^{-7}}=5.7*10^{-4}$$

$$s(c)=5.7*10^{-4}*0.95969=0.00009 \text{ M}$$

On the basis of the calculation it can be seen that the uncertainty due to the volume of the flask makes the main input to the overall uncertainty value of the concentration. The component of the uncertainty caused by the sample weight is comparable to it, but slightly smaller, and the uncertainty of the molar mass value is negligible. However, note that to calculate we use the molar masses of the elements accurate to 0.001 atomic mass units. It is easy to see that, if the value of M is rounded to 0.01 units, the corresponding input (s(M)/M)2 would be equal to 1.3.10-7, i.e. comparable with others. Rounding off to the 0.1 units is impossible: in this case, the uncertainty of the molar mass would be a basic component of uncertainty.

The concentration value uncertainty itself in this case would be 0.0004 M, i.e., would be increased to almost an order of magnitude.

The law of uncertainty propagation is valid not only for random, but for the systematic components, if they are unknown, but their maximum possible valuesб tolerance limits are known. For example, manufacturers of volumetric ware usually indicate the value of their products as V ± δ ml, where V - the nominal value of the volume, and δ-extreme deviation from it. For each separate flask the deviation of the actual volume from the nominal one is constant, and thus it is a systematic error. This systematic deviation should not be confused with the random error caused by incompletely accurate filling of the flask to the mark. It must be considered separately, and summarize with the random component under the law of uncertainty propagation.

When summing the systematic errors it should be remembered that in the uncertainty propagation law the dispersion, i.e., standard deviation squares s are occurred, while the value of δ is essentially a half-width of the confidence interval. Therefore, first you need to recalculate the value of δ in values of s. As we know, for a normal distribution, these values are directly proportional to each other, and the proportionality factor is Student's coefficient.

$$x \pm t(P, f)s(x) \ . \qquad (5)$$

However, for unknown systematic errors, not a normal but uniform distribution law is usually stated. For uniform distribution the half-width of the confidence interval is also proportional to the standard deviation, but the proportionality factor here is another, it is equal to $\sqrt{3}$:

$$\delta=\sqrt{3}s \qquad \text{and} \qquad s=\frac{\delta}{\sqrt{3}}$$

In conclusion, I would like to note that the above considered example is strong idealized. In fact, sources of uncertainty when performing this procedure is much more. These uncertainties due to the inevitable presence of contaminants in the reagents, temperature fluctuation and accordingly the volume, incongruence of pT indicator and pH equivalence point, etc. Each of them may seem negligible, but their cumulative effect may be significant. During the assay performance, requiring a graded dependence, it is critical to take into account the input made by this dependence. All such objectives are solved by the law of uncertainty propagation, thus is one of the basic mathematical tools of analytical chemistry.

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