S68 Measurement procedure: from detailed description to technology

G R Nezhikhovskiy

D.I. Mendeleyev Institute for Metrology, St. Petersburg, Russia | E-mail: grn30@mail.ru

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Measurement procedures are developed as documents that allow operators to obtain results with uncertainty that does not exceed the target uncertainty. In accordance with the International Vocabulary of Metrology a description of measurement in the document should be detailed ("sufficiently detailed"). In practice, the degree of this detalization of measurement procedure is different. If we imagine a decreasing scale (see figure 1), then at its beginning there will be measurement procedure-prescription, implemented on specific instruments and punctually regulating the actions of operator. At the end of the scale there will be procedures that are easily adaptable to the equipment (reagents) and provide operators with a wide range of actions within the assigned limit values. (Such procedures are often considered as measuring technologies.) Measurement procedures-prescriptions border with measuring instruments, measurement procedures-technologies with measurement methods. In recent years, there has been a tendency for reducing the share of measurement procedures-prescriptions and increasing the share of measurement procedures with a lower degree of detalization.

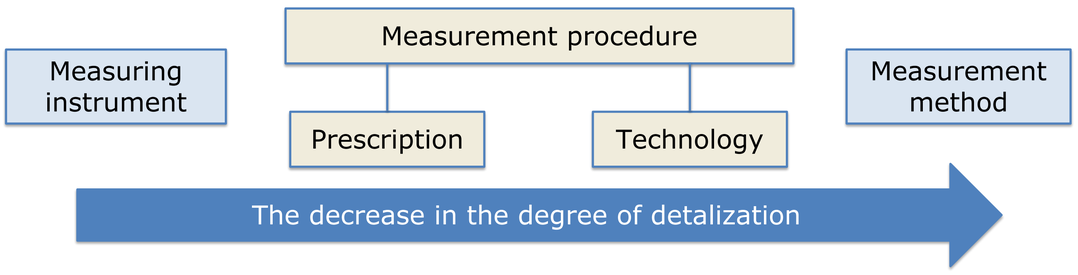

Figure 1. The degree of measurement procedure detalization.

There are several reasons for this trend. While in the past measurement procedures were usually developed for own use, now they are often developed by specialized organizations, including firms that supply universal measuring equipment. They are interested in the dissemination of typical solutions. The second reason is the availability for the user of a variety of auxiliary equipment, reagents and software, to which the measurement procedure can be adapted. The third reason is dissemination of a universal approach to expression and evaluation of measurement uncertainty. When a user purchases a measurement procedure with an uncertainty budget, he has the opportunity to assess the influence of certain changes on the combined standard uncertainty and expanded uncertainty of measurements himself. Another reason is the desire of many laboratories to apply a modern quality management system, one of the elements of which is the monitoring of the validity of the results. The availability of information on the stability of the results for each of the implemented measurement procedures allows to choose the optimal frequency of regulating and control operations.

For example, consider the procedure of measuring the mass fraction of an analyte in a sample of a solid object (W, %), which involves dissolving the sample of the object and subsequent measurement of the mass concentration of the analyte (C, mg/dm³) using a universal atomic emission spectrometer with microwave plasma. Every day, before starting work, the user builds a calibration function as the dependence of the analytical signal (Y in conventional units) on C. In order to construct the calibration function he uses five (m = 5) calibration standards with different mass concentrations of the analyte (C_i, where i is the solution number). And the C_5/C_1 ratio does not exceed 50. To prepare calibration standards, a reagent (pure substance) is used, in which the mass fraction of the main component is not less than W^m (%). The procedure provides for the operations of checking the acceptability of the calibration function and periodic checks of its stability using the solution with a mass concentration of analyte C_4. To obtain the measurement result, all operations are carried out with two weighing, while the final result is calculated as the arithmetic average of two values of the mass fraction of the analyte, unless their difference does not exceed the established norm – the limit of repeatability of the results of single measurements.

The procedure developer has recorded the range of measurements of the mass fraction of the analyte (from 0.050 % to 2.5 %), the weight of the sample ($M \approx 200$ mg), established the requirements for weighing instruments, volumetric vessels and solvents, set the values of the mass concentration of the analyte in the calibration solutions (from 1,00 to 50 mg/dm³) and confirmed the linearity of the calibration function $Y = a + bC$. At the same time, the user is given the opportunity to: a) select reagents available on the market with W^m from 97% to 99.5%; b) use spectrometers of various manufacturers; c) establish the time between stability checks of the calibration function. The mathematical model of measurement is represented by the expressions:

$$W = \frac{W^* + W^{**}}{2}, \quad (1) \qquad W^* = \frac{C^* V^*}{M^*} 100, \quad (2) \qquad C^* = \frac{Y^* - a}{b}, \quad (3)$$

where superscripts * and ** correspond to the first and second single measurements. For the second single measurement, expressions (2) and (3) are valid with the superscript replaced by **.

The relative total standard measurement uncertainty

$$u_c^0 = \sqrt{(u_r^0)^2 + (u_C^0)^2 + (u_V^0)^2 + (u_M^0)^2}, \quad (4)$$

where u_r^0 is the relative standard uncertainty due to the variation of measurement results under repeatability conditions, %;
u_C^0 – the relative standard uncertainty of measurements of the mass concentration of the analyte in solution, %;
u_V^0 – the relative standard uncertainty associated with the volume of the solution, %;
u_M^0 – the relative standard uncertainty associated with the mass of the weight, %.

The spread of the measuring results was estimated in a series of experiments (12 pairs of measurements at five values of the mass fraction of the analyte). On the standard deviations found, the limits of repeatability of the results of single measurements of r (in %) were determined. The relative standard uncertainty was calculated using the expression:

$$u_r^0 = \frac{r}{2.8 \cdot \sqrt{2} \cdot W} 100, \quad (5)$$

For the lower limit of the measurement range (W = 0.050 %) r = 0.010 % is set. In this case, u_r^0 = 5 %.

u_C^0 was estimated on the assumption that the factor associated with the registration of analytical signals when measuring the mass concentration of an analyte is random and is covered by u_r^0.

Thus, u_C^0 includes only contributions related to the calibration function

$$u_C^0 = \sqrt{(u_S^0)^2 + (u_g^0)^2 + (u_d^0)^2}, \quad (6)$$

where u_S^0 is the contribution due to the calibration solutions, %;
u_g^0 – the contribution associated with the establishment of the calibration function, %;
u_d^0 – the contribution related to possible instability of the calibration function, %.

u_S^0 is formed on the basis of a mathematical description of the calibration standard preparation process from contributions related to the purity of the initial reagent, metrological characteristics of the weighing instrument and volumetric vessels used. The maximum value of u_S^0 will be 2.5 % (with W^m = 97 %), the minimum – 1.8 % (with W^m = 99.5 %).

The change in u_g^0 with the use of different spectrometers is most often due to the peculiarities of the algorithms for integrating analytical signals and determining regressions from experimental data. Spectrometers software rarely includes the calculation of u_g^0; usually, calibration results are accompanied by such parameters as correlation coefficient, residual standard deviation, absolute and relative deviations of the obtained analytical signals (or mass concentrations of the analyte) from the corresponding values on the calibration function. If we set the limit for the relative deviations of the analytical signals:

$$\frac{|Y_i - f(C_i)|}{f(C_i)} 100 \le g, \quad (7)$$

then for the linear dependence like $Y = a + bC$, the relationship between the norm and u_g^0 can be expressed by the formula (9)

$$u_S^0 \approx \frac{g}{2} \sqrt{\frac{1}{m} + \frac{(C_i - \bar{C})^2}{\sum_1^m (C_i - \bar{C})^2}}, \quad (8)$$

When m =5, (C_5/C_1) = 50 we have for i =1

$$u_S^0 \approx 0.4\, g \quad (9)$$

The calibration function is periodically checked for the stored solution with a mass concentration of analyte C_4. The calibration function is considered "stable", i.e. suitable for further use when the condition is met

$$\frac{|C_4^* - C_4|}{C_4} 100 \le d, \quad (10)$$

where C_4^* is the measured value of the mass concentration of the analyte in the fourth calibration standard, mg/dm³.

The relationship between u_d^0 and the limit d is given by expression (11):

$$u_d^0 = \frac{d}{2\sqrt{3}} \quad (11)$$

In this example, limits g = 10 % and d = 5 % were set. After substitution in (6), we obtain:

$$u_f^0 = \sqrt{(2.5)^2 + (0.4 \cdot 10)^2 + \left(5/2\sqrt{3}\right)^2} = 4.9\ \%. \quad (12)$$

Table 1. The uncertainty budget for the lower limit of the measurement range of the analyte mass fraction.

№	Uncertainty source		Contribution designation	Type of evaluation		
1	Measurement variability			A	5	
2	Measuring of mass concentration of analyte in solution	Preparation of calibration standard		B	2.5	4.9
3		Establishment of the calibration function		B	4.0	
4		Possible instability of the calibration function		B	1.4	
5	Solution volume measuring			B	0.1	
6	Weigh mass measuring			B	0.3	
Relative combined standard uncertainty, %					7	
The relative expanded measurement uncertainty					14	

$$U_c^0 = k \cdot u_c^0, \quad (13)$$

where k is the coverage factor (k = 2 at the level of confidence 0.95).

~~The calculated relative expanded uncertainty is 14 %, i.e. the target uncertainty was not~~ exceeded.

In practice, the use of expressions (1) - (13) solves one of the two problems. The first is to establish in the measurement procedure limits r, g and d, which provide the requirement for the value u_c^0. The second is to check the limits established by the developer of the procedure. In both cases, the ability to comply with the limits should be confirmed by experimental data available to the procedure developer. (Usually there are data of 4 or more experiments, including the construction and check of the stability of the calibration functions.) Of course, for individual users, the relative expanded uncertainty of measurements may be significantly lower. This circumstance does not reduce the effectiveness of the stated approach in the development of measurement procedures intended for broad application.

Conclusion

When determining the measurement uncertainty as a metrological characteristic of measurement procedures, in many cases it is necessary to ensure that the user can continuously monitor critical factors and at the same time give him some freedom to choose equipment, reagents, and frequency of checks. The solution to this problem is achieved by establishing norms and taking them into account when estimating uncertainty. Such a solution satisfies users of many analytical measurement procedures that have been attested by the D.I. Mendeleyev Institute for Metrology within the framework of the system of ensuring the uniformity of measurements adopted in Russia.