

The New Measurement Concept Explained by Using an Introductory Example

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“Edgar Davids has been suspended by FIFA¹ after failing drug tests and will not be able to play for his national side, Holland, in the forthcoming World Cup qualifiers”. This news was filed by *Telegraph.co.uk* in May 2001. What had happened? Davids, a Dutch soccer star, had failed the test for nandrolone twice. Nandrolone is an anabolic steroid (a muscle-building substance) that occurs naturally in the human body, but only in trace quantities (1). The analysis of Davids’ urine sample had yielded 2.3 and 2.6 ng/mL. The limit of the International Olympic Committee was 2.0 ng/mL and, therefore, Davids was banned for two years.

Was Davids justifiably accused and banned? In dubio pro reo—it is common practice in national and international law that measurement uncertainty is used to the benefit of an accused who has been tested positive by any measurement method. Therefore, the measurement uncertainty should have been subtracted from Davids’ measured nandrolone concentration first and only then the resulting value should have been compared with the given limit (2) (Figure 1). Was the measurement uncertainty of the results in fact so small that the arbitral tribunal of FIFA could account for the penalty? As the test laboratories involved only calculated the standard deviation from three measurements but not the combined standard uncertainty, which is a measure of the reliability of the result, it will never be sure whether the accusation was justifiable or not.

It is not surprising that the test laboratories did not know the measurement uncertainty of their results. Although the basic principles for the evaluation of the overall measurement uncertainty in analytical chemistry are available (3, 4), they have not been implemented in most laboratories yet. Therefore, individual results are often misinterpreted and many re-

sults that are produced in various laboratories still cannot be compared directly. This situation might lead to false conclusions, thus, creating considerable commercial damage.

The current state-of-the-art concept was launched in 1980 based on recommendations issued by the Comité International des Poids et Mesures (CIPM), one of the highest international authorities for metrology. During the following fifteen years a modern measurement concept was developed on an international level and has resulted in the *Guide to the Expression of Uncertainty in Measurement* (GUM) (4). The GUM has been published in the name of seven important scientific organizations.² A summary is given online by the National Institute for Standards and Technology, the former National Bureau of Standards (5).

This article presents a basic example for the implementation of measurement uncertainty for lectures on analytical chemistry and compares the main features of the previous measurement concept to the one described in the GUM. More complex examples can be found in ref 3. Transparencies for a two-hour lecture on the current measurement concept are shown in ref 6.

Example of Measurement Uncertainty

The evaluation of measurement uncertainty is illustrated by an example that can easily be followed: an analyst prepares a zinc standard solution. She or he quantitatively pours a Titrisol solution containing 1.000 g Zn(II) into a volumetric flask, $V = 500$ mL, and fills the flask to the mark with water. As the standard solution will not be used for several days, the flask is closed and stored at room temperature. We are interested in the concentration of zinc and its uncertainty just before the first aliquot is taken from the standard solution.

Specification of the Measurand

The concentration of zinc, c_{Zn} , in the standard solution is calculated according to

$$\begin{aligned}
 c_{\text{Zn}} &= \frac{m_{\text{Zn}}}{M_{\text{Zn}}V} \\
 &= \frac{1.000 \text{ g}}{65.409 \frac{\text{g}}{\text{mol}} \times 500 \text{ mL}} \times 10^6 \frac{(\text{mmol/L})}{(\text{mol/mL})} \\
 &= 30.58 \frac{\text{mmol}}{\text{L}}
 \end{aligned}
 \tag{1}$$

where m_{Zn} (g) is the mass of zinc in the Titrisol solution, M_{Zn} (g/mol) is the atomic weight of zinc, V (mL) is the volume of the volumetric flask, and 10^6 is the factor to convert

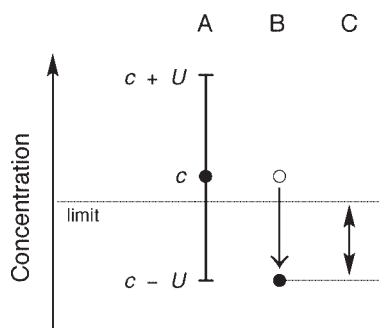


Figure 1. Comparison of a measurement result with a limit that must not be exceeded. The comparison is based on the principle “in dubio pro reo”: (A) Measurement value c with its uncertainty U . (B) The uncertainty U is subtracted from the measurement value. (C) The resulting value is compared with the limit. In this case the resulting value clearly lies below the limit, while the measured value lies above.

the unit from mol/mL to mmol/L. As c_{Zn} is the measurand, eq 1 is called “equation of the measurand”. It describes the model of the measurement, that is, *what* is to be measured and *how* it is measured.

Identification of the Influence Quantities

Influence quantities are quantities that affect the result of a measurement (7); that is, they are sources of uncertainty. They are identified by listing all quantities that are relevant for an analytical procedure. In practice, a cause-and-effect diagram (sometimes known as an Ishikawa or fishbone diagram) is helpful to structure the quantities in such a way that all the relevant random and systematic effects are identified and no effects are counted double. The principles of building the diagram are described explicitly in refs 3 and 8.

When constructing the cause-and-effect diagram, we draw a horizontal arrow first (Figure 2). This arrow is dedicated to the measurand, in our case, c_{Zn} . The main sources of uncertainty are identical to the variables on the right-hand side of eq 1; they form the main branches of the diagram (M_{Zn} , m_{Zn} , and V). Contrary to the volume, the branches of m_{Zn} and M_{Zn} have no lateral arrows, because the all-embracing reliability of their values is specified by the manufacturer or published in the literature, respectively (see below). The volume is influenced by three uncertainty sources represented by the corresponding lateral arrows: the tolerance of the specified internal volume of the flask (cal), the variation in filling the flask to the mark (rep), and the temperature (T) influencing the initially measured volume.

Quantification of the Influence Quantities

Quantitative information about uncertainties is often given as a maximal deviation from the specified value (lower and upper limit of tolerance) without any specification of confidence. The uncertainty source “calibration of the volumetric flask” (cal) is such an example; the real volume of the flask lies between 500.0 ± 0.25 mL according to the declaration³ of the manufacturer. Tolerances must be converted into standard uncertainties to calculate the combined standard uncertainty using the uncertainty propagation law (4). But how are such conversions done? The distribution of the single values within the lower and the upper limit is usually assumed to be symmetrically rectangular or symmetrically triangular. If only little information is available about the uncertainty source, the rectangular probability distribution should be chosen (Figure 3). In this distribution, a_- and a_+ correspond to the lower and the upper limit, respectively. The best estimate for the influence quantity μ (parameter that affects c_{Zn} , see Figure 2) lies in the middle of a_- and a_+ and has a standard uncertainty of $u(\mu) = a/\sqrt{3}$. This equation tells us that the half of the overall range of variation, a , is converted into a standard uncertainty u by dividing with $\sqrt{3}$.

If values close to μ are more likely than values near the limits, a triangular distribution is assumed (Figure 4). The best estimate for μ also lies in the middle of both limits and its standard uncertainty amounts to $u(\mu) = a/\sqrt{6}$. Thus, the half of the overall range of variation, a , is converted into the standard uncertainty u by dividing with $\sqrt{6}$. The mathematical fundamentals of these two a priori distributions are described in several statistical textbooks (e.g., ref 9).

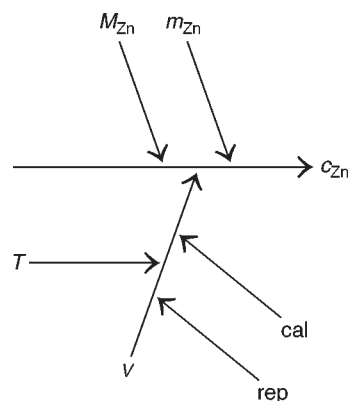


Figure 2. Cause-and-effect diagram for the concentration of Zn in a standard solution prepared volumetrically.

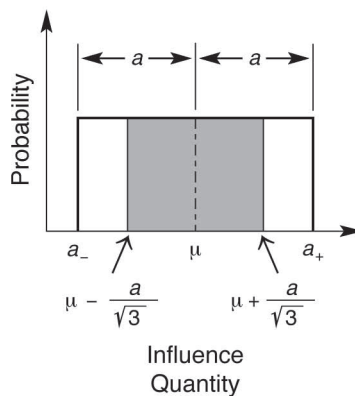


Figure 3. Symmetric rectangular probability distribution.

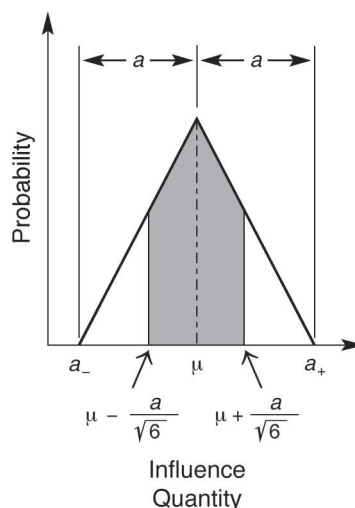


Figure 4. Symmetric triangular probability distribution.

Coming back to our example, first we quantify the influence quantities that affect the volume. The quantities are listed in Table 1, along with the values a , the factors to convert the values a into the standard uncertainties, CF, as well as the standard uncertainties, u . When studying the influence of the temperature on the volume, we should remember that the mass of a solution does not depend on the temperature if there is no loss of material. Therefore, we can state

$$m_s = \rho_f V_f = \rho_a V_a \quad (2)$$

where m_s is the mass of the solution, ρ_f is the density of the solution when the flask is filled to the mark, V_f is the initially measured volume of the solution (500.0 mL), ρ_a is the density of the solution just before the first aliquot is taken, and V_a is the volume of the solution just before the first aliquot is taken. It follows from eq 2:

$$V_a = V_f \frac{\rho_f}{\rho_a} \quad (3)$$

We want to know the uncertainty of V_a due to the temperature variation between the preparation of the standard solution and its first use. Contrary to the densities, the initially measured volume V_f does not depend on the temperature and is taken as constant. According to the principles of uncertainty propagation in products and quotients (10, 11), the relative variance of V_a is given by the sum of the relative variances of the densities,

$$\left[\frac{u(V_a)}{V_a} \right]^2 = \left[\frac{u(\rho_f)}{\rho_f} \right]^2 + \left[\frac{u(\rho_a)}{\rho_a} \right]^2 \quad (4)$$

where u is the uncertainty of the variables in parentheses. The absolute uncertainty of V_a is

$$u(V_a) = V_a \sqrt{\left[\frac{u(\rho_f)}{\rho_f} \right]^2 + \left[\frac{u(\rho_a)}{\rho_a} \right]^2} \quad (5)$$

In order to calculate the uncertainty of V_a according to eq 5, the temperature variation of the standard solution must be estimated. Assuming that the solution is usually kept and used at room temperature, the variation of the room temperature can be applied. If a temperature change occurred owing to enthalpy of solution, the corresponding influence on the initial density would have to be taken into account. The room temperature might vary between 295 and 303 K in our example. The corresponding density limits are estimated using the density table for air-saturated water (12): $\rho(295 \text{ K}) = 0.99777 \text{ g/mL}$ and $\rho(303 \text{ K}) = 0.99564 \text{ g/mL}$. The half of the difference of these two values corresponds to the value a and is 0.00107 g/mL (Table 1). Assuming that any value of the temperature of the standard solution and, therefore, any value of ρ_f and ρ_a has approximately the same probability within the tolerance limits, the frequency of the values is described by a rectangular distribution. Thus the value a is multiplied by $1/\sqrt{3}$ resulting in the corresponding standard uncertainty of 0.00062 g/mL. We obtain from eq 5:

$$\begin{aligned} u(V_a) &= 500.0 \sqrt{\left(\frac{0.00062}{1} \right)^2 + \left(\frac{0.00062}{1} \right)^2} \text{ mL} \\ &= 0.44 \text{ mL} \end{aligned} \quad (6)$$

Table 1. Quantification of the Quantities that Influence the Volume

Quantity	a	CF ^a	u
ρ_f /[g/mL]	0.00107	$1/\sqrt{3}$	0.00062
ρ_a /[g/mL]	0.00107	$1/\sqrt{3}$	0.00062
V_a /mL	—	—	0.44
cal/mL	0.25	$1/\sqrt{6}$	0.10
rep/mL	—	—	0.13
$u(V)$ /mL	—	—	0.47

^aThe values for the conversion factors (CF) are dimensionless.

Table 2. Quantification of the Main Contributions

Quantity	Value	a	CF ^a	u
m_{Zn} /g	1.000	0.002	$1/\sqrt{6}$	0.00082
M_{Zn} /[g/mol]	65.409	0.004	$1/\sqrt{3}$	0.0023
V /mL	500.0	—	—	0.47
c_{Zn} /[mmol/L]	30.58	—	—	0.038

^aThe values for the conversion factors (CF) are dimensionless.

The uncertainty only applies if both densities of eq 5, ρ_f and ρ_a , are independent of each other. When the standard solution is used just after its preparation, ρ_a cannot vary and therefore the temperature has no influence on V .

The tolerance limits of the specified volume (cal) are 500.0 mL \pm 0.25 mL. As the manufacturer usually tries to meet the specified volume as closely as possible, a triangular distribution of the single values is assumed. Therefore, we multiply the value a with $1/\sqrt{6}$ and obtain the corresponding standard uncertainty of 0.10 mL. The variation in filling the flask to the mark (rep) can be determined by repeated filling and weighing. The result is an estimation of the corresponding standard deviation (0.13 mL), which can be used directly for further calculation. The three components, V_a , cal, and rep, are independent of each other and influence the uncertainty of the volume additively. Thus, the uncertainty of the volume is given by the root of the sum of the variances:

$$\begin{aligned} u(V) &= \sqrt{u(V_a)^2 + u(\text{cal})^2 + u(\text{rep})^2} \\ &= \sqrt{0.44^2 + 0.10^2 + 0.13^2} \text{ mL} = 0.47 \text{ mL} \end{aligned} \quad (7)$$

The result is close to the uncertainty of the volume V_a , because the contributions are squared before summing them.

Table 2 shows the quantities that directly affect the concentration of Zn in the standard solution, together with the values a , their factors CF to convert the tolerance into the standard uncertainty as well as the standard uncertainties (u). The tolerance limits of the specified quantity of zinc specified by the manufacturer are 1.000 g \pm 0.002 g. A triangle distribution is assumed because the manufacturer usually tries to meet the specified value as closely as possible. The atomic weight of Zn and its tolerance have been redetermined (13). The uncertainty of the third variable, V , is taken from Table 1.

Calculation of the Combined Standard Uncertainty

As the components of Table 2 are independent of each other and operate multiplicatively (see eq 1), the relative uncertainty of the measurand is calculated by extracting the root of the relative variances:

$$\frac{u_c(c_{Zn})}{c_{Zn}} = \sqrt{\left[\frac{u(m_{Zn})}{m_{Zn}}\right]^2 + \left[\frac{u(M_{Zn})}{M_{Zn}}\right]^2 + \left[\frac{u(V)}{V}\right]^2} \quad (8)$$

The uncertainty of the measurand, $u_c(c_{Zn})$, also called combined standard uncertainty, is

$$u_c(c_{Zn}) = 30.58 \times \sqrt{\left(\frac{0.00082}{1.000}\right)^2 + \left(\frac{0.0023}{65.409}\right)^2 + \left(\frac{0.47}{500.0}\right)^2} \frac{\text{mmol}}{\text{L}} \quad (9)$$

$$= 0.038 \frac{\text{mmol}}{\text{L}}$$

The standard uncertainty is usually expanded by multiplying with a coverage factor $k = 2$,

$$U(c_{Zn}) = k u_c(c_{Zn})$$

$$= 2 \times 0.038 \frac{\text{mmol}}{\text{L}} = 0.076 \frac{\text{mmol}}{\text{L}} \quad (10)$$

where U is the expanded uncertainty. The result should always be expressed with a clear uncertainty statement, for example:

Concentration of zinc: $(30.58 \pm 0.08) \text{ mmol/L}^*$

*The reported uncertainty is an expanded uncertainty calculated using a coverage factor of 2, which gives a level of confidence of approximately 95%.

How Can the Combined Standard Uncertainty Be Reduced?

After having calculated the combined standard uncertainty, the analysts check whether their analytical procedure is fit for the intended purpose. If the uncertainty is too large, the procedure should be optimized. In our example, there are two possibilities to reduce the combined standard uncertainty. The first one consists of correcting the result for systematic effects. If the temperature of the solution was measured just after filling the flask, and later when the solution is used, then exact values could be assigned to the corresponding densities ρ_f and ρ_a . The concentration c_{Zn} would then be corrected by supplementing eq 1 with the factor ρ_a/ρ_f . In this way, the uncertainty contribution of the densities (Table 1) would decrease except for the uncertainty of the correction. In laboratory routine, such corrections are usually not made, because the procedure is time consuming and therefore too expensive. Hence, the corresponding variations are estimated and the whole systematic effect is considered within the measurement uncertainty. The second way to reduce the combined standard uncertainty consists of carrying out the measurements in an air-conditioned environment. This would lead to a smaller temperature variation and, thus, to a decrease of the main contribution in our example (see Tables 1 and 2).

Repeatability versus Reproducibility

Validation data are a valuable source of information for measurement uncertainty. The most important parameter from validation may be the precision of the result. However, which components of the uncertainty affect the precision of the result? This depends on the experimental conditions and is demonstrated using the above example.

Again, we take a look at the cause-and-effect diagram (see Figure 2). When determining the variation in filling the flask to the mark (rep), a series of filling with water and subsequent weighing measurements is carried out by the same person within a short time using the same graduated flask. These conditions are called repeatability conditions and the resulting experimental standard deviation is called repeatability standard deviation (7). What would happen if the standard deviation was estimated by measurements uniformly distributed over twelve months using different graduated flasks? In addition to the repeatability (rep), the variation of the flask volume (cal) as well as that of the temperature (T), would automatically be considered. Moreover, cal as well as T lose their systematic character and become random influences. In this case, the experimental standard deviation would no longer be called repeatability standard deviation (rep), because it has been measured under reproducibility conditions. This is the case when an analysis is carried out under changed conditions, which may include: principle of measurement, laboratory, analyst, instrument, glassware, chemicals, reference materials, and time (7). A valid statement of reproducibility requires specification of the conditions changed. The resulting standard deviation (Rep) is usually considerably larger than the repeatability standard deviation (rep). Whether a random or a systematic character can be assigned to an effect obviously depends on the experimental conditions. This is the reason why precision is not well defined and it should always be mentioned which type of precision is meant (repeatability or reproducibility). The resulting cause-and-effect diagram for reproducibility conditions, with respect to our example, is shown in Figure 5. The subsidiary contributions, rep, cal, and T , are usually not drawn, as they are included in the reproducibility term Rep and, therefore, have not to be evaluated individually.

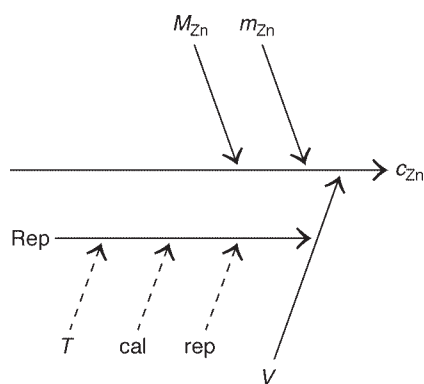


Figure 5. Cause-and-effect diagram for the concentration of Zn in a standard solution, volumetrically prepared under reproducibility conditions.

Regarding a complete analytical procedure, repeatability means the variation of the result when the whole procedure is carried out several times under repeatability conditions. Reproducibility is the analogous term if the corresponding variation is determined under reproducibility conditions. The analysis of an interlaboratory study delivers both the repeatability and the reproducibility standard deviation. The difference between repeatability and reproducibility is evident. Nevertheless, these terms are often confused during daily work in laboratories.

Evaluate the Measurement Uncertainty

After having introduced the calculation of uncertainty by means of a basic operation, let us look at the schedule when a complete analytical procedure is evaluated. Figure 6 shows a general scheme of how measurement uncertainty is evaluated for a given analytical procedure. Some of the steps are already known from our example. (In the following discussion of the Figure 6, we quote the respective relation to our example in parentheses.) Firstly, the validated measurement procedure must be entirely considered so that all observable influence quantities that have a relevant effect on the measurement are evaluated (Figure 2) and quantified (Tables 1 and 2). Every potentially relevant source of uncertainty is evaluated statistically (rep) or by other means (cal,

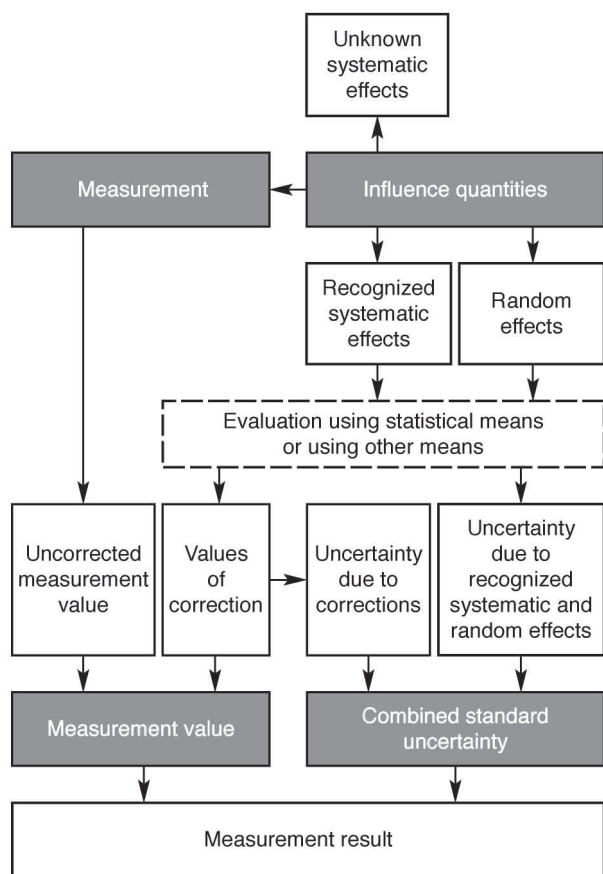


Figure 6. General scheme showing how to evaluate measurement uncertainty.

T , m_{Z_n} , M_{Z_n}). Both methods are equally able to quantify systematic as well as random effects. Whether an effect has a random or systematic character depends on the measurement conditions. Remember that cal and T lost their systematic character under reproducibility conditions. Therefore, it is not possible to classify the contributions according to their character. If appropriate, the result is corrected for relevant recognized systematic effects (not done in our example). This correction is obtained from separate measurements that have their own uncertainty. The uncertainty due to corrections is evaluated in the same way as all other uncertainty contributions and is also part of the overall measurement uncertainty. The procedure leads to a combined standard uncertainty of the corrected value. We assume that the combined standard uncertainty has an uncertainty of at least 20% relatively. The combined standard uncertainty is clearly larger than the standard deviation of the result that is obtained under repeatability conditions. For this reason, the reproducibility standard deviation, which results from a collaborative study of method performance and which might be smaller than the combined standard uncertainty (14), is typically 1.5–2.0 times greater than the repeatability standard deviation (15). This factor applies only to regular analytical procedures. After all, it has to be mentioned that there still might be undiscovered systematic effects. Thus, analysts in different laboratories may only be able to reproduce the same result within the stated uncertainty if they use exactly the same analytical procedure.

The benefit of uncertainty calculation is not limited to the knowledge of the total uncertainty and its use in a variety of situations, for example, in decision making. Uncertainty budgets also provide a basis for method optimization and development (16).

The New Measurement Concept Compared with the Old Concept

As listed in Table 3, the difference between the old and the current concept is considerable. To understand the new concept, it is important to realize that an error, as a term of the old concept, is always related to the true value. This applies also to random errors because a single measurement value arises from the addition of its random deviation from the mean with the systematic deviation of the mean from the true value. When the old concept was used, in order to achieve a valid result, great efforts were made to include the true value within the random error. This is a paradox in itself because the true value is not known and can only be determined with the aid of a perfect measurement. Additionally, there is not even a chance to determine the random error, because a scattering of single values around their mean would only represent the random error if the following conditions were fulfilled:

- The unknown systematic deviation of the mean from the true value remains constant during measurement.
- The deviation of each single value from the mean is completely free from systematic contributions.

As neither the first nor the second condition can be known, the random error can also not be known.

Table 3. Comparison between the Current and the Old Measurement Concept

	Old Concept	Current Concept
Main characteristic	Determination of the true value premises a perfect measurement	Due to unknown systematic effects, a measurement is never perfect and, therefore, the true value cannot be known. Hence, the concept is oriented exclusively by observable quantities
Goal	Comparability between labs by determining the true value	Comparability between labs based on observable quantities
Classification of the uncertainty contributions	According to the characteristic of the deviation of a measurement value: error type A: random deviation error type B: systematic deviation from the true value	According to the evaluation of the effects: by statistical means by non-statistical means
The way to comparability between labs	Determination of the true value (impossible!)	Proper validation, correction for recognized significant systematic effects, evaluation of the standard uncertainty, if necessary standardization
Result	Value (sometimes with repeatability) and unit	Value with combined standard uncertainty and unit

In contrast to the old concept, the new one is based exclusively on observable quantities. This is evident from the example shown above. When systematic influences were taken into account we have used the term “systematic effect”. A systematic effect is due to a deviation from the unknown true value but describes only the observable part of it. In other words, a systematic effect causes a measurable or assessable shift of the individual values together with their mean. The result can be corrected for the shift, or the whole shift can be regarded as a contribution to the measurement uncertainty. The latter was done in our example: a possible systematic deviation of the volume from the specified value, for example, was taken into account by estimating the maximum shift (tolerance limit) and its subsequent consideration in the measurement uncertainty. We do not need the true value for such operations.

The current concept accounts for the fact that random and systematic effects are not distinguishable in many cases. We again recall our example: the temperatures are randomized when the repeatability conditions changed to reproducibility conditions. For this reason, the current concept classifies the effects according to their experimental evaluation, namely effects evaluated by statistical means and effects evaluated by nonstatistical means. The evaluation of uncertainty contributions by statistical means is not restricted to random effects but applies to many recognized systematic effects, too. On the other hand, random effects, as well as recognized systematic effects, can be determined by estimates taken from minimum and maximum values. Sources of nonstatistically evaluated values can be any certificates, handbooks, experience, and so forth. The different orientation, that by the true value and that by observable quantities, is the most important difference between the old and the new concept.

To develop and validate a new procedure, the analysts should perform the following steps (17): They develop the procedure and appoint the necessary measurement conditions as far as an acceptable estimate of the measurand is obtained. They demonstrate that the equation of the measurand and the set of conditions are sufficiently complete for the intended purpose (validation). Once these conditions are met, the ana-

lysts only need to establish calibration or control for each value in the equation and for each of the specified conditions (traceability). The test as to whether an analytical procedure is fit for a particular purpose can be made by comparing the result with an appropriate reference value. “Appropriate” means that the property of the used reference (e.g., certified reference material) must meet the scope of the analysis procedure. The analysts correct for systematic effects, if necessary, and report the result as an interval (value and uncertainty). In addition, they report the description of the analytical procedure used, as unknown systematic effects can occur in spite of an exhaustive validation. In this way, the measurement is decoupled from the true value and comparability between laboratories can be achieved at least if the same analytical procedure is used and even in many cases if different procedures are used. The latter has been demonstrated several times in key comparisons by metrological laboratories, for example, for the determination of cholesterol in human serum (18), for the determination of Al, Cu, Mg, and Fe in mono-elemental calibration solutions (19), or for the determination of cadmium in rice (20). Sometimes, a closer standardization of the analytical procedure may be necessary to achieve comparability within a given measurement uncertainty.

Conclusion

Since 1995, a new but pragmatic and easy-to-use measurement concept has been available that allows a comparison between laboratories on a routine basis. The concept exclusively utilizes observable quantities. Universities should teach this concept to make sure that their students can join chemical laboratories with the newest knowledge in chemical measurement and quality assurance.

Notes

1. The FIFA is the Fédération Internationale de Football Association.
2. The Guide to the Expression of Uncertainty in Measurement has been published in the name of the following organiza-

tions: Bureau International des Poids et Mesures (BIPM), International Electrotechnical Commission (IEC), International Federation of Clinical Chemistry (IFCC), International Organization for Standardization (ISO), International Union of Pure and Applied Chemistry (IUPAC), International Union of Pure and Applied Physics (IUPAP), and International Organization of Legal Metrology (OIML).

3. Flask volumes are usually specified as integer values. We added a digit after the decimal point to agree with the tolerance quoted.

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