Evaluation of uncertainty in analytical measurement. From the ISO Guide to the EURACHEM/CITAC Guide

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The appearance of the EURACHEM document *Quantifying Uncertainty in Analytical Measurement* in 1995 became an event in realization of efforts undertaken internationally with the aim of comparability of analytical chemical results and adequate expression of their confidence. The main goal of the document was to demonstrate, on the basis of the general approach set forth in the *Guide to the Expression of Uncertainty in Measurement* (the ISO Guide), how to estimate uncertainties in such a specific field of measurement as chemical analysis. It is important that nowadays many national accreditation bodies require that analytical laboratories should provide information on uncertainty of the results produced. Just for this reason the problem of elaboration of unified rules for uncertainty estimation in chemical analysis has become urgent.

The EURACHEM document that is in essence a "chemical adaptation" of the ISO Guide provoked considerable debate among analytical chemists. First of all, the scheme of estimation of uncertainty implies a detailed analysis of possible sources, i.e. input quantities of a measurement equation. However, far being from it that every factor that affects the result of chemical analysis is known in advance and can be included in the measurement equation. Moreover, the evaluation of individual uncertainty sources in a complex multistage analytical procedure is a non-trivial task; what one obtains in practice are often summary uncertainty estimates that cannot be combined as independent contributions. Not taking this into account led to a number of mistakes in working examples in the EURACHEM Guide.

Furthermore, the principles of uncertainty estimation developed in the ISO Guide are significantly different from the methodology commonly used in analytical chemistry. The current practice in analytical procedure development and validation relies on establishing its performance characteristics with no requirement for an explicit mathematical model of the measurement process. The performance characteristics such as precision and trueness, detection limit, selectivity, sensitivity, etc. are obtained from experimental study of the procedure preferably through a collaborative trial in accordance with the accepted protocols, e.g. ISO 5725.

The noted problems were the subject of discussion at two EURACHEM workshops (Berlin, 1997; Helsinki, 1999) devoted to evaluation of measurement uncertainty in chemical analysis. These efforts resulted in the revised edition of the Guide (now as EURACEM/CITAC

Guide) with practical experience accumulated in chemical laboratories and suggestions put forward during the discussion in view.

The new edition is distinguished by the diversity of methods used for uncertainty estimation. It is recommended to draw on the data from the following sources:

- data on individual factors (sources of uncertainty) that affect the analytical results for a defined procedure;
- results from collaborative trials carried out to validate analytical procedure;
- results from internal quality control procedures established in a laboratory;
- results from proficiency testing schemes used to assess the competency of the laboratory.

Accordingly, the measurement uncertainty can be obtained by evaluating each individual source followed by combining the components in line with the ISO Guide as well as by the direct determination of the combined contribution to the uncertainty from some or all of these sources using the accuracy data available for the procedure in question.

The value of the EURACHEM Guide that was meant to be a special case of the general approach is evidently far beyond its intended scope. It should be recognized that the component-by-component method for evaluation of uncertainty originated in metrological studies is not the only one that is possible. Where the quantity measured cannot be rigorously described in terms of input parameters (such is indeed the case with the most of test methods), another approach is appropriate based on passive variation of influence factors in the course of a collaborative trial. We can say that the specific character of analytical measurement allowed one to look at the methods for uncertainty estimation in a broader perspective. The way from the general to the specific has resulted in a new generalization.