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MEASUREMENT UNCERTAINTY IN ANALYTICAL CHEMISTRY: THEORETICAL FOUNDATIONS AND CALCULATION METHODS

Abstract. This paper examines the theoretical foundations and methods for evaluating measurement uncertainty in analytical chemistry. The main sources of uncertainty, approaches to its quantitative evaluation, and its relationship with measurement error and accuracy are discussed. The role of metrological approaches in ensuring the reliability of analytical results and establishing the limits of justified conclusions is analyzed. The importance of comprehensive uncertainty evaluation for the validation of analytical methods, the interpretation of experimental data, and the advancement of scientific knowledge is substantiated.
Keywords: analytical chemistry; measurement uncertainty; uncertainty evaluation; metrology; measurement error; accuracy of analytical results; validation of analytical methods.

Introduction

Analytical chemistry combines the functions of an instrumental basis for research with those of an independent scientific discipline aimed at establishing закономірності, developing new research methods, and generating knowledge about chemical systems. The results of chemical analysis provide a quantitative and qualitative basis for decision-making in various fields and require critical consideration of their reliability and validity [1].

No measurement provides an absolutely accurate representation of the value of a measurand. The result is influenced by the properties of the object under study, sampling and sample preparation conditions, the characteristics of the analytical procedure and measuring instruments, and data processing methods. Therefore, measurement uncertainty must be evaluated, as it characterizes the justified limits within which values can be attributed to the measurand.

An analytical result is part of the process of knowledge acquisition, within which hypotheses are formulated and tested, закономірності are established, and transformation mechanisms are explained [2]. Therefore, uncertainty concerns not only the numerical characteristics of a result but also the validity of its interpretation and its use in supporting scientific statements.

The aim of this work is to elucidate the theoretical foundations of measurement uncertainty in analytical chemistry and determine its methodological significance for evaluating analytical results and generating new scientific knowledge.

Metrological and epistemological approaches to the analysis of measurement uncertainty

Measurement uncertainty is one of the fundamental concepts of modern analytical chemistry, as it enables a measurement result to be characterized not in isolation, but in the context of the information on which it is based. Any chemical analysis result arises from the interaction between the object under investigation, the analytical method, the measuring instrument, and the adopted data-processing procedure [3]. Each of these elements may affect the final result and must therefore be appropriately taken into account when evaluating measurement quality.

In metrological terms, measurement uncertainty characterizes the dispersion of values that can reasonably be attributed to the measurand. It is not synonymous with measurement error, which is defined as the difference between a measured value and a reference value, whereas uncertainty reflects the limitations of knowledge about the value of the measurand. Similarly, uncertainty should not be equated with accuracy, as accuracy is a qualitative concept describing the closeness of agreement between a measured value and a true or reference value, whereas uncertainty can be quantitatively evaluated.

Sources of uncertainty in analytical chemistry vary in nature. They include variations in the results of repeated measurements, calibration uncertainty, limitations in instrument performance, sample preparation procedures, sample heterogeneity, matrix effects, and characteristics of the analytical procedure employed. The adequacy of the measurement model linking the observed analytical signal to the quantity of interest is also an important factor. Failure to account adequately for significant uncertainty contributions may lead to a misleading assessment of the quality of the result obtained [4].

Understanding uncertainty in analytical chemistry requires distinguishing between two interrelated approaches: metrological and epistemological. The former focuses on the quantitative characterization of measurement results, whereas the latter addresses the formation, justification, and interpretation of scientific knowledge. The distinction between these approaches lies not so much in opposing objectives as in the different levels at which the research problem is examined (Figure).

The metrological approach aims to establish how well-founded a numerical result is and to what extent it can be used for further calculations, comparisons, or decision-making [5]. Its object is the measurement result for a specific quantity, such as the concentration of a chemical compound, the mass fraction of an element, or particle size. Statistical methods, repeated measurement results, calibration data, measuring instrument performance characteristics, and other relevant information are used to evaluate the uncertainty contributions.

The epistemological approach broadens the scope of analysis by addressing not only the reliability of a measured value but also what that value enables us to learn about the object under investigation. Analytical data do not always lend themselves to an unambiguous interpretation. The same signal may arise from different sample components, interactions between substances, or characteristics of the analytical method. Even when the uncertainty of a result has been appropriately evaluated, its interpretation may remain ambiguous owing to limitations in the experimental data or deficiencies in the theoretical model.

Methodological challenges in uncertainty evaluation and its role in the generation of new knowledge.

The central methodological challenge associated with uncertainty in analytical chemistry lies in the transition from experimental data to scientific claims. A measurement result acquires epistemic significance not only through its quantitative determination but also through its interpretation in the context of the research question. It is at this stage that it becomes necessary to distinguish between what is directly supported by the data and what remains an assumption or requires further substantiation.

One source of uncertainty in scientific conclusions is the limited availability of experimental information. An insufficient number of measurements, sample heterogeneity, limited method sensitivity, or interference from extraneous components may complicate the identification of underlying relationships. Another source is the inadequacy of the theoretical model in representing the actual properties of the system under investigation [6]. A model may adequately describe certain aspects of a phenomenon while failing to account for factors that become significant under different conditions. In such cases, uncertainty concerns not only the quantitative result but also the explanatory capacity of the approach employed.

Another important methodological task is to prevent premature conclusions. Detecting a statistically significant difference between results does not necessarily establish the cause of that difference. Similarly, the absence of a clear difference does not necessarily demonstrate the equivalence of the objects under investigation, since the capabilities of the analytical method may be limited by its sensitivity or the level of measurement uncertainty. Therefore, the interpretation of analytical data requires consideration of both the quantitative characteristics of the measurement and the nature of the research hypothesis, the experimental conditions, and possible alternative explanations.

However, uncertainty should not be regarded solely as an obstacle to scientific inquiry. When recognized and properly analyzed, it can serve as a source of new research questions. Identifying insufficient method sensitivity encourages the refinement of the analytical procedure; establishing matrix effects motivates the search for ways to eliminate or account for them; and ambiguity in signal interpretation may prompt the use of an independent analytical method. If the available results are

inconsistent with the theoretical model, this may provide grounds for revising the model or developing an alternative explanation.

In this context, the constructive role of uncertainty is realized through a systematic research process. First, the limitations must be identified and their nature established. Next, the specific data or explanations that are lacking must be determined. Additional hypotheses are then formulated, appropriate verification methods are selected, and further experiments are conducted. The resulting findings make it possible to refine our understanding of the system under investigation, assess the explanatory capacity of existing models, or generate new scientific knowledge [7]. Thus, a conscious and systematic approach to uncertainty can guide research activities and shape future directions in analytical chemistry.

Evaluation of Measurement Uncertainty in Analytical Chemistry

The evaluation of measurement uncertainty in analytical chemistry, both as a practical tool and as a scientific discipline aimed at generating new knowledge, relies on common metrological principles and fundamental mathematical relationships. In particular, standard uncertainty, combined standard uncertainty, expanded uncertainty, and relative uncertainty are used. However, the use of a common computational framework does not imply that the underlying methodological objectives are identical. In applied chemical analysis, uncertainty evaluation is primarily intended to establish whether a result is fit for practical decision-making and for assessing compliance with specified requirements. In fundamental research, it also plays an important role in determining the validity of experimental data interpretation, testing scientific hypotheses, and establishing the limits of the conclusions that can be drawn from the results obtained. Thus, although the equations used to evaluate uncertainty remain the same, the selection of uncertainty components, experimental design requirements, and interpretation of results depend on the objectives of the study.

The evaluation of uncertainty begins not with substituting numerical values into an equation, but with clearly defining the measurand and analyzing the entire procedure by which the result is obtained. The factors that may affect the result must be identified, their significance assessed, and their respective contributions quantified wherever possible. This assessment draws on experimental data, method validation results, reference material data, calibration information, interlaboratory comparison results, and other relevant information. This approach makes it possible to link uncertainty calculations to actual measurement conditions rather than treating them as an isolated mathematical operation.

It is important to distinguish between standard uncertainty, combined standard uncertainty, expanded uncertainty, and relative uncertainty. These are distinct measures, each serving a specific purpose in the evaluation and reporting of measurement results [2, 8].

1. Standard Uncertainty from Repeated Measurements

When measurements are performed repeatedly under the same conditions, the Type A component of uncertainty can be evaluated statistically. The standard uncertainty of the mean is given by:

$$u_A(\bar{x}) = \frac{s}{\sqrt{n}} \quad (1)$$

де:

– $u_A(\bar{x})$- standard uncertainty of the mean measurement result;

– s - sample standard deviation of the measurement results;

– n - number of replicate measurements.

The standard deviation is calculated using the following equatio:

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

де (x_i) — individual measurement result, а ($\bar{x}$) - arithmetic mean of all measurement results.

These equations are used to evaluate the uncertainty of the mean based on repeated observations. They do not automatically account for all other sources of uncertainty, such as calibration, sampling, or systematic effects that are not reflected in repeatability.

2. Combined Standard Uncertainty

In the simplified case where the result depends on several independent components that are already expressed in the same units and directly characterize their contributions to the result, the equation takes the following form:

$$u_c = \sqrt{u_1^2 + u_2^2 + \cdots + u_N^2} \quad (3)$$

For example, if the standard uncertainty associated with repeatability is 0,10 mg/L, standard uncertainty associated with calibration — 0,08 mg/L, assuming these two components are independent:

$$u_c = \sqrt{0.10^2 + 0.08^2} \approx 0.13 \text{ mg/L} \quad (4)$$

Therefore, the combined standard uncertainty is approximately 0.13 mg/L. This is an illustrative example demonstrating the principle of combining two independent uncertainty contributions.

3. Expanded Measurement Uncertainty

Expanded uncertainty is commonly used for reporting measurement results:

$$U = k \cdot u_c(y) \quad (5)$$

де:

– U - expanded uncertainty;

– (uc(y)) - combined standard uncertainty;

– k - coverage factor.

When (k = 2), the expanded uncertainty often corresponds approximately to a 95% coverage level, provided that the relevant statistical assumptions are satisfied. However, this coverage level is not guaranteed by the choice of (k = 2) alone; it depends on the distribution of the measurement result, the effective degrees of freedom, and the method used for evaluation. The coverage factor should therefore be selected and justified according to the specific measurement context.

4. Relative Uncertainty

Relative standard uncertainty is used to compare measurement results expressed on different scales or in different units:

$$u_r(y) = \frac{u_c(y)}{|y|} \tag{6}$$

Expressed as a percentage (%):

$$u_r(y)(\%) = \frac{u_c(y)}{|y|} \times 100\% \tag{7}$$

Relative uncertainty characterizes the combined standard uncertainty in relation to the estimated value of the measurand and is useful for comparing concentration determination results that differ by several orders of magnitude. Near zero, absolute uncertainty is preferable.

Mathematical evaluation is an important but not self-sufficient component of uncertainty analysis, as it depends on the completeness of identified uncertainty sources, the quality of input data, the validity of assumptions, and the appropriateness of the measurement model. Systematic uncertainty analysis contributes to the improvement of analytical procedures, hypothesis testing, the planning of further experiments, and the soundness of scientific results.

Conclusions

Measurement uncertainty in analytical chemistry is a multidimensional problem that combines the metrological principles of result evaluation with methodological issues related to the formation and substantiation of scientific knowledge. It is an essential characteristic of analytical results that determines both their quantitative reliability and the limits of their interpretation. The metrological approach provides a basis for quantitative uncertainty evaluation, while the epistemological approach addresses the validity of data interpretation and the justification of scientific conclusions. Their integration enables a comprehensive assessment of analytical results, supports the critical evaluation of hypotheses, and guides the improvement of analytical methods and the design of further experiments. Thus, systematic uncertainty evaluation is fundamental to ensuring the reliability of analytical findings and advancing scientific knowledge.

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