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SOURCES OF UNCERTAINTY IN MEASUREMENTS OF PHYSICOCHEMICAL QUANTITIES

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Abstract

The article discusses the main sources of uncertainty in measurements of physicochemical quantities, which are an integral part of any experimental research in physics and chemistry. Various factors affecting the accuracy and reliability of measurement results are analyzed, including errors in instrumental systems, the influence of external conditions, and the human factor. Particular attention is paid to methods for estimating and minimizing uncertainty, such as the use of standards, instrument calibration, and statistical data processing. The work also provides examples of practical measurements in chemical analytics and materials physics, where uncertainty is critical to the results obtained. Recommendations for uncertainty management can be useful for both researchers and specialists working in the field of quality control and product certification.

Keywords

Measurement uncertainty, physicochemical quantities, experimental research, instrumental errors, external conditions, human factor, standards, instrument calibration, statistical data processing, chemical analytics.

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Introduction

Estimation x_i of the input value X_i may be the reading of a measuring device in the case of a single measurement, the arithmetic mean value in the case of multiple measurements, or taken from regulatory documents, a certificate, testimonials, reference book, manufacturer's labels, etc.

Before attempting to estimate measurement uncertainty, a first step is to list the possible sources of uncertainty. At this stage, there is no need to consider quantitative aspects; the aim is only to ensure that there is complete clarity as to what exactly needs to be considered.

When compiling a list of uncertainty sources, it is usually convenient to start with the main expression used to calculate the result from intermediate quantities, i.e. the mathematical model of the measurement. All parameters in this expression may have their own uncertainties and are therefore potential sources of uncertainty. In addition, there may be other parameters that are not explicitly included in the expression used to find the value of the measure and but which nevertheless influence the result (e.g. extraction time or temperature). There may also be hidden sources of uncertainty. All these sources should be included in the list. The main sources of uncertainty are the specification, modelling, method, measuring instrument, environment, operator and measured object.

The types of uncertainty components are divided according to the sources of their occurrence into uncertainties of the specification of the measured quantity, modeling, method, measuring instruments (instrumental), environment, operator (person) and the measured object.

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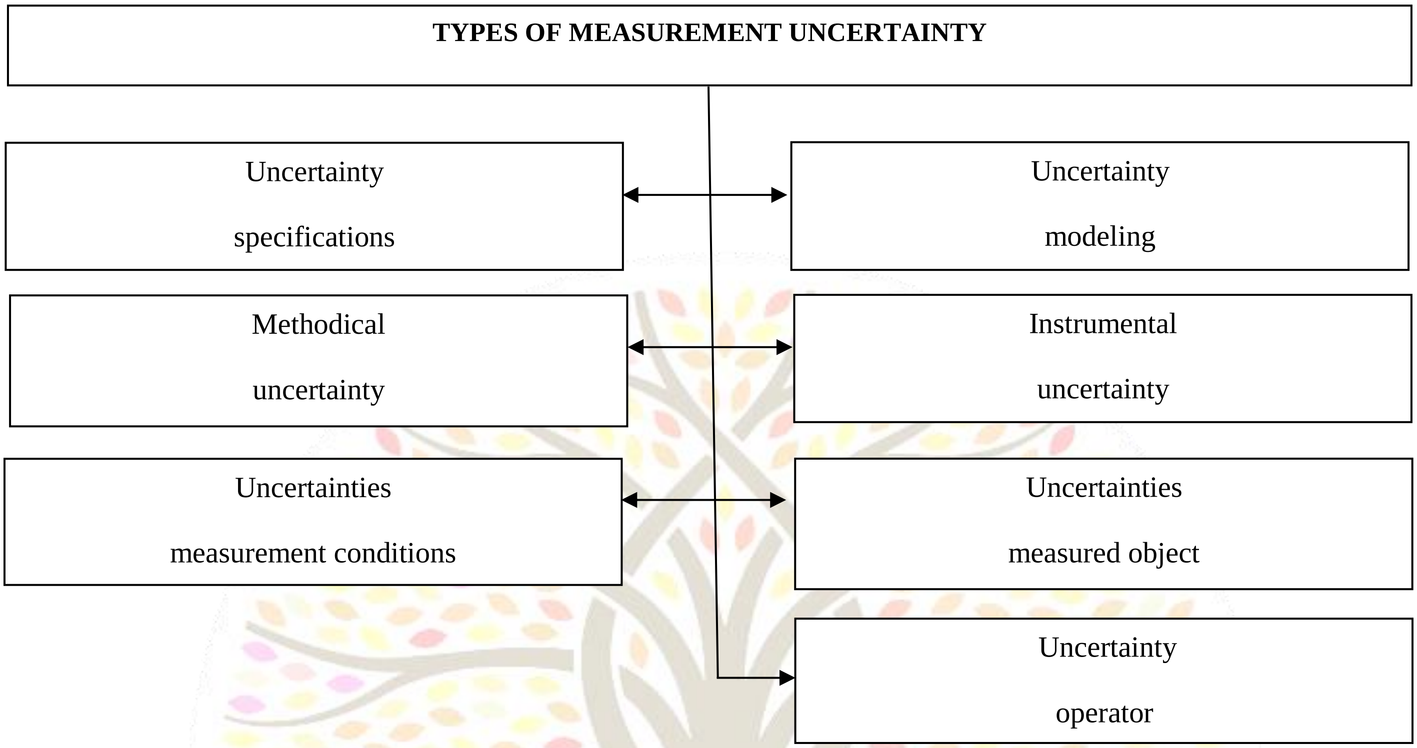

To describe quantitatively the individual components of uncertainty, some of the uncertainty sources almost always have to be considered separately. In some cases this is necessary only for a very small number of sources; in others, especially when there are few or no data on the performance of the method, each source may require separate consideration. There are several general techniques for identifying individual uncertainty components:

– experimental variation of input variables;

– use of information from technical documentation, such as measurement and calibration certificates;

– modeling based on theoretical principles;

– the use of judgments based on previous experience or simulation modeling.

The individual components of uncertainty are discussed below.

The size of the measured quantity initially depends on the parameters of external influences affecting the object of measurement. Therefore, a correct approach to measurement requires a complete preliminary description (specification) of the measured quantity. Incomplete specification of the measured quantity leads to the emergence of a corresponding uncertainty.

It is known that the purpose of measurement is to determine the (numerical) value of the measured quantity. The description (specification) of the

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measured quantity includes indications of the time of measurement and the conditions of their implementation. The conditions of measurement are specified as a set of influencing quantities, i.e. quantities that are not the subject of measurement, but affect their result, for example, the temperature of the measuring instruments.

The dependence of the measured physical quantity y on the parameters of external influences is described by means of the influence function. The influence function can be determined experimentally or exist only as an algorithm that must be implemented numerically.

Inadequate determination of influence quantities is a cause of specification uncertainty and can lead to inconsistency between measurements of the same quantity carried out in different laboratories.

In the example given, additional input quantities may be required to improve measurement accuracy, taking into account the known non-uniform temperature distribution across the resistor, the possible non-linear temperature coefficient of resistance, or the possible dependence of resistance on atmospheric pressure.

In practice, the specification of the measure and depends on the required accuracy of measurement. The measure and should be defined with sufficient completeness in relation to the required accuracy so that for all practical purposes related to the measurement its value is unique.

A person's idea of the object of measurement is reflected in his consciousness in the form of a certain model, described by a set of parameters. The measured quantities determined by models always differ from the properties of real objects, since a model can never be an absolute copy of the original. This difference is expressed by uncertainty, caused by the inadequacy of the model to the measured quantity.

In many cases, the developed physical theory allows us to construct fairly good models describing the influence of various factors on the measurement result. For example, the influence of temperature on volume and density is well studied. In such cases, the uncertainty can be calculated or estimated directly from the existing relationship using uncertainty propagation methods.

In other situations it may be necessary to use approximate theoretical models combined with experimental data. For example, if the result of an analytical measurement depends on some reaction to produce a derivative that takes some time to occur, then it may be necessary to estimate the uncertainty associated with the time. This can be done by simply varying the time taken for the reaction to occur.

When measuring the concentration of a solution by titration, sources of uncertainty may include errors in measuring the volume of the titrant, inaccuracies in the preparation of standard solutions, and the effect of temperature on the reaction rate.

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Temperature measurement in thermodynamic experiments: The use of thermocouples to measure temperature can be subject to uncertainty due to calibration errors, environmental influences (e.g. radiation from external sources), or faults in the measuring equipment.

Determination of the density of a substance: In density measurement experiments using a hydrometer, sources of uncertainty include errors in volume measurement (e.g. due to air bubbles in the liquid) and temperature variations affecting the volume of the liquid.

The inadequacy of the model to the real object gives rise to uncertainty even before measurements (a priori), called modeling (recognition) uncertainty.

The complexity of the model and the degree of its adequacy to the real object depends on the following factors:

a) the type and properties of the measurement object;

b) the purpose and required accuracy of the measurement;

c) the amount of a priori information about the object, the qualifications of the metrologist performing the measurements.

In the process of creating a model, a paradoxical situation arises. In order to measure the desired value, it is necessary to have a priori information about its properties, according to which the measurement model is established. And these properties can be determined (measured) only in the process of experimental study of the object.

It should be noted that the absence of differences in the measurement results does not always guarantee the correctness of the selected model [11]. Experimental verification of the selected model will be reliable only if a properly planned measurement methodology is used.

A measurement method is a logical sequence of operations described in general form and used when performing measurements [1, 10, 12]. Imperfections in a measurement method result in methodological errors. Their distinctive feature is that they can only be determined by creating a mathematical model or by simulating the measured object. After creating such a model and determining its parameters, it is possible to estimate the methodological error of measurement, which is systematic in nature. The estimate of the methodological error can be used as a correction to the measurement result. The corrected measurement result is burdened with an unexcluded residual systematic error (RESI), caused by errors in determining the model parameters. The standard deviation of the REI is an estimate of the methodological uncertainty. Let us consider some examples of methodological uncertainties.

Uncertainty in assessing the impact of a measuring instrument on the object of measurement. We will study this uncertainty using the example of a voltmeter connected to a voltage source with internal resistance R_i. The voltmeter itself has an input resistance R_{in}.

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Measurement results. The measurement method may include computational operations - determination of the mean, root mean square or mean absolute value of a series of observations of a changing parameter of the measured quantity, numerical integration or differentiation, calculation of the value of an elementary function by expansion into a series, etc. Depending on the selected processing algorithm, the measurement results may be burdened with corresponding errors. The standard deviation of these errors is an estimate of the uncertainty of the processing algorithm used.

Uncertainties arising from approximation and simplification. Such uncertainties include uncertainties of indirect measurements caused by the simplification of the relationship between the measured quantity and its arguments measured using direct measurements.

For example, the result of measuring the power P_n generator using a microwave absorption wattmeter, which is the load of the transmission line, depends on the parameters of their mismatch with the transmission line, expressed through the complex reflection coefficients of the generator and wattmeter [13].

Methodological uncertainty also includes uncertainties caused by the number of observations, duration of measurement, choice of methodology and measurement instruments, etc.

Conclusion

In the course of studying the sources of uncertainty in measurements of physical and chemical quantities, it was shown that the accuracy and reliability of measurements depend on many factors, including the characteristics of measuring instruments, their calibration methods, the influence of external conditions, and errors associated with the human factor. Analysis of these factors allows us to identify the main causes of errors and propose ways to minimize them, which is critically important for ensuring the reliability of experimental data.

Methods for assessing and accounting for uncertainty, such as statistical processing of results and the use of international standards, are essential tools for improving the accuracy of measurements. The practical implementation of these methods not only improves the quality of scientific research, but also increases the level of confidence in the data obtained in industry, analytical chemistry and other applied areas.

It is therefore important to continue improving uncertainty control methods to improve the quality of measurements and ensure the accuracy of scientific conclusions, as well as compliance with international standards and requirements for the results of product examination and certification.

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