

Accuracy in Analytical Measurements

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Abstract. The paper presents some essential differences between analytical measurements and measurements of physical quantities. The rules of accuracy presentation are also not the same. Additionally they are incoherent. It creates a great confusion which ought to be overcome by close cooperation of NMI's, accreditation institutions and international organisations.

Keywords: Analytical Measurements, Accuracy Terms, International Documents

1. Introduction

The theory of measurements in a very wide scope, as a method of empirical cognition of the nature, should have a common understanding. In practice however, both laboratory and industrial practice, one has to distinguish between measurements of physical quantities and analytical measurements. The term analytical measurements include biological, chemical and medical measurements. Both categories of measurements mentioned above have been developed separately one to another by use of different methods, procedures and presentation of the results. There are several reasons for it, namely:

1. The amount of analyte in the matrix (probe) is often very small. The measuring procedure must be extremely sensitive and of great resolution.
2. The matrix has unpredictable and unrepeatable contents and forms. The methods of analyte recognition must be sufficiently selective with respect to the variety of matrix.
3. Accessibility of etalons is sometimes limited. The measurements even with the use of Reference Certificated Materials give different results in case of different matrix composition.
4. The results of the analytical measurements are often important juristically and from the moral point of view.

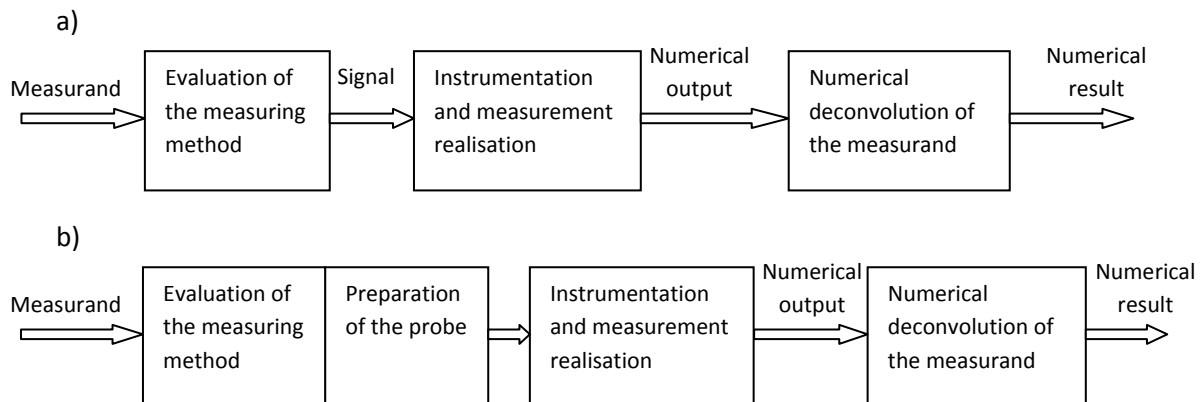


Fig.1. Fundamental parts of measuring chains (a) in physical measurements (b) in analytical measurements (b)

The chain of physical quantities measurement has three main parts presented in Fig.1a. Analytical measurements include an additional part involving preparation of the probe, that depends on the matrix, and often is the most important and most complicated part of the measuring procedure (Fig 1 b).

The methods of the measurement result calculation and presentation specified in GUM [1] are known and commonly respected in practical measurements of physical quantities. They serve as an essential material in laboratory accreditation procedure. In analytical laboratories GUM is treated with dislike or even with aversion. The reason is evident. The specific problems of analytical measurements are in GUM completely neglected. Analytical laboratories have created their own elaborate systems of the proper work including validation and confirmation of the results obtained. The methods of calculating and presenting the results are based on the existing literature and other documents. Unfortunately these documents are incoherent in presentation the metrological terms and their meanings. It leads to numerous problems.

2. Documents Study

Accuracy is an essential term in metrology. According to VIM [2] accuracy is a qualitative term. In many publications and documents however, accuracy is presented as a quantitative measure. The meaning of that measure is not unified and depends on the author. For example in old document [3] accuracy is described as “*A quantity referring to the differences between the mean of a set of results or an individual result and the value which is accepted as true or correct value for the quantity measured*”. But also in a new document [4] we find a definition like “*Closeness of agreement between a quantity value obtained by measurement and the true value of the measurand*”. The quantitative definition of accuracy can be found also in ASTM standards (American Society for Testing and Material). Nowadays qualitative meaning of accuracy is becoming more popular. So, in [5] accuracy is defined as “*Ability of a measuring instrument to give responses close to a true value. Note: In this context accuracy is a qualitative concept*” The idea of “true value” belongs to the past. It exists still in VIM but with a notice underlining its restricted application. Some documents like [6] and [7] don't use the term at all. In [8] True value is replaced by “*target or reference value*”.

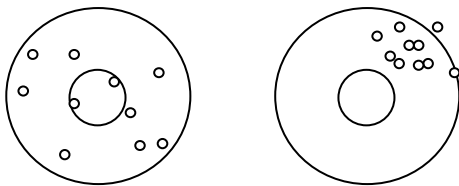


Fig. 2 Presentation of precision and trueness incoherent with GUM codification

Documents published by Eurachem seem to be very important for chemical laboratories. The definition presented in [9] “*The closeness of agreement between a test result and the accepted reference value. Note: The term accuracy, when applied to a set of test results, involves a combination of random components and a common systematic error or bias component*” is hard to understand and different from the one given in GUM.

GUM codification deliberately does not refer the concepts of systematic errors and random errors. Instead of them we can find precision and trueness. The difference between those terms is sometimes explained in the form presented in Fig. 2 as a result of shooting to the

target. It is completely wrong explanation. The hunter sees the target and knows where is the centre but he doesn't succeed. A person executing the measuring procedure don't know the "true value". Only ones knowledge and skills allows to obtain the result near to that value. A better interpretation of Fig. 2 would be, that Fig. 2a presents a situation when uncertainty type A is greater than type B and Fig. 2b, the opposite case.

In order to avoid terms "systematic error" and "random error" unacceptable by GUM, the term "bias" is often used. The definition given by NIST [8] seems to be a good one "In particular, for a measurement laboratory, bias is a difference between a laboratory's average value (over time) for a test item and the average that would be achieved by the reference laboratory if it undertook the same measurements on the same test item". Other definitions are less precise and sometimes false. They are also based on the systematic error as in [4] and [10] after ISO 3534-1.

It is worth to notice that in analytical laboratories the word "precision" is used in a form "intermediate precision" with a different meaning, i.e. interlaboratory or externlaboratory reproducibility. In contrast to the procedures used for measurement of physical quantities, chemical laboratories attach a great importance to interlaboratory measurements and to the hierarchy of laboratories. They elaborated some specific kind of evaluation of the measuring results, not used in physical measurements, named recovery. The procedure depends on the adding of the precisely known small amount of analyte to the probe and then measuring the increase of the result. It is a specific method of calibration where the influence of matrix composition is reduced. In [11] recovery is identified with accuracy and a specific relative standard deviation RSD, namely variability coefficient CV is calculated according to the Horvitz equation $CV = 2^{1-0.196c}$ where c is an analyte concentration. That CV (possibly with coefficient equal to 0,67) is used to validate the measuring procedure.

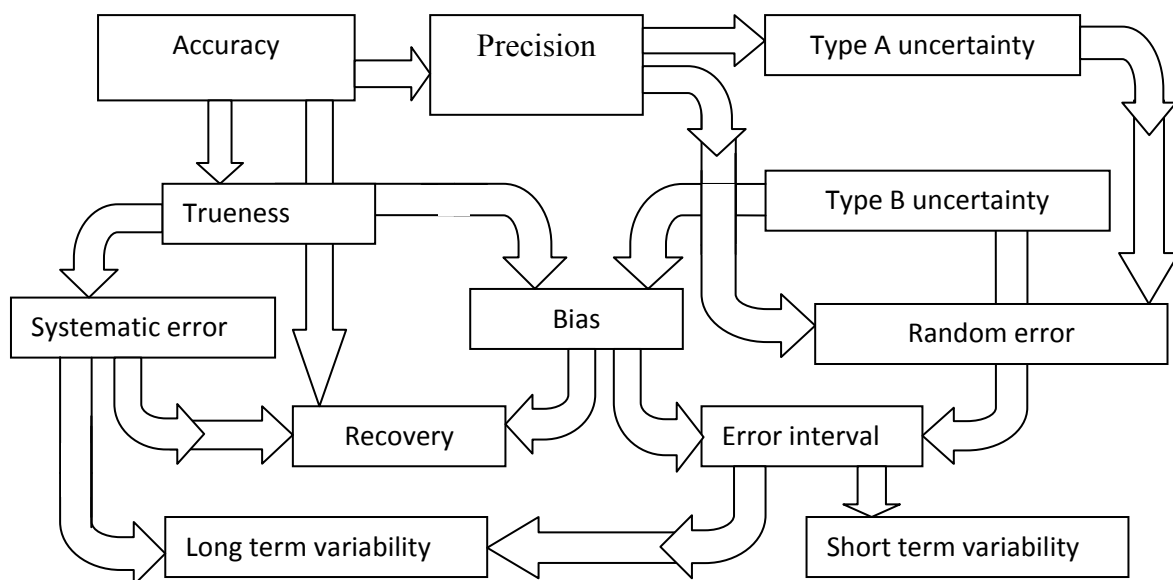


Fig. 3. Relations between essential metrological terms presented in various documents (sic!)

Fig. 3 presents the relations between mentioned above terms according to the documents cited in references and to many others. The lack of coherence is evident, in spite of the fact that majority of documents are the relatively new ones. That situation is highly uncomfortable especially for laboratories striving for accreditation. Even excellent performed validation procedure is not sufficient for accreditation when the results are not calculated and presented in the form required by auditors. The question “which form ought to be used as the obligatory one” is still open.

3. Conclusion

Majority of analytical laboratories; chemical, medical, biological, environmental, etc. work perfectly but the methods they use for presentation their results are not unified. At present, the unification is impossible because of disorder and incoherence of normative documents. There is an urgent need to indicate a set of not contradictory documents and rules dealing with the measurement results presentation and accepted by analytical laboratories with respect to the specific procedures implemented there. It is a challenge for National Measuring Institutes cooperating with Accreditation Centres. The expectation the problem to be solved by international organisations is not realistic. It must be done at the level of national organisations. Globalisation of those directives may be expecting eventually as the next step.

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