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Review

Systematic errors in analytical measurement results

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Abstract

Definitions of the concepts of bias and recovery are discussed and approaches to dealing with them described. The Guide To Uncertainty in Measurement (GUM) recommends correction for all significant systematic effects, but it is also possible to expand measurement uncertainty to take account of uncorrected bias. Run, laboratory and method bias can be defined as components of the bias of a particular measurement result, and can be useful as concepts used in method validation. Estimation of run bias allows a simplification of the estimation of measurement uncertainty. Multivariate calibration brings its own biases that must be quantified and minimised.

Keywords: Bias; Recovery; Measurement uncertainty; Metrological traceability; Systematic errors

Contents

1. Introduction

The concepts of 'bias' (and 'recovery') are important aspects of the understanding of a measurement result in analytical chemistry. This paper will discuss the present definitions and will review different approaches to dealing with systematic effects. In addition to the metrological debate, field laboratories need to be able to estimate and, if necessary correct for, systematic effects. Example of present practice will be given.

The concept of bias of a measurement result is best understood in terms of a measurement model that recognises systematic and random components of error.

$$\hat{x} = x + \delta + \varepsilon \qquad (1)$$

The true value of a measurand, x, is estimated by $\hat{x}$ which differs from it by a systematic component, the bias δ and a random component ε. The random error is considered to be Normally distributed with expectation zero and standard deviation σ. Therefore, a large number of measurements will have a mean of $(x+\delta)$ as shown in Fig. 1. A single measurement result cannot distinguish between systematic and random error, but several

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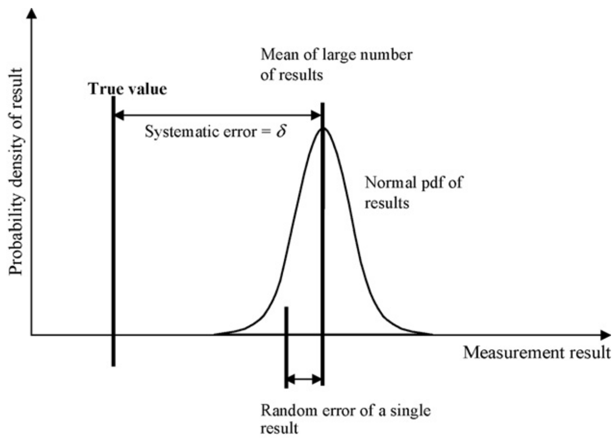

Fig. 1. Schematic representation showing the relationship between random and systematic error in a measurement result.

measurements combined with knowledge about the characteristics of the method can allow calculation of an interval about $\hat{x}$ that contains the true value with a certain level of confidence.

$$x = \hat{x} \pm U \tag{2}$$

U is known as the expanded uncertainty [1] and is obtained from considerations of all aspects of the uncertainty of the measurement result. The so-called GUM approach (after Guide to the Expression of Uncertainty in Measurement [1]) was first published in 1993 and has been the basis of the recommended methods for characterising a measurement result. A requirement of the international standard for testing laboratories (ISO/IEC 17025 [2]) is that an appropriate measurement uncertainty be estimated for the results. One reason that traditional concepts of systematic and random error have been subsumed into the uncertainty approach is that depending on the information used, one kind of error can be turned into another, and so there is no general definition of these terms and the measuring system must be described very carefully. This discussion will be expanded below.

2. Definitions

In measurement science there is a need to carefully define basic terms and concepts used on which the subject rests. Fundamental terms such as "measurement" must mean the same to a chemist as to an astronomer or psychologist. All major international bodies who have an interest in measurement, including the International Bureau of Weights and Measures, ISO, and IUPAC have come together to revise the International Vocabulary of Basic and General Terms in Metrology, in order to provide this sought after common basis. In the forthcoming third edition (VIM3, [3]) many of the changes have been made to accommodate chemical measurement. Measurement bias (synonym bias) will be defined as

2.19
measurement bias
bias
systematic measurement error or its estimate, with respect to a **reference quantity value**

where bold terms are also defined in the VIM. Systematic measurement error is defined as

2.18
systematic error of measurement
systematic error
component of **measurement error** that in replicate **measurements** remains constant or varies in a predictable manner
NOTES

(1) The **reference quantity value** for a systematic measurement error is a **true quantity value**, or a **measured quantity value** of a measurement standard of negligible **measurement uncertainty**, or a **conventional quantity value**.
(2) Systematic measurement error, and its causes, can be known or unknown. A **correction** can be applied to compensate for a known systematic measurement error.
(3) Systematic measurement error equals the difference of measurement error and **random measurement error**.

The earlier definition, and one used by ISO 5275 [4], is
3.8 bias: The difference between the expectation of the test results and an accepted reference value.
NOTE 5 Bias is the total systematic error as contrasted to random error. There may be one or more systematic error components contributing to the bias. A larger systematic difference from the accepted reference value is reflected by a larger bias value.

The depiction in Fig. 1 is consistent with these definitions. The definitions also imply that bias can be estimated by measurement of a reference quantity value, and then subsequently corrected for.

3. Components of the systematic error of a measurement result

In the definitions given above there is no distinction made among different sources of systematic error. However, identification of the source of systematic error can impact on its estimation and treatment. The headings below represent sources that have been proposed as worthy of individual attention. They may overlap, and it must be remembered that for a single measurement result there is but one, unknowable, 'measurement error'—the difference between x and $\hat{x}$ in Eq. (1).

3.1. Sampling bias

When the measurand is a quantity of a larger whole, sampling error can be a major systematic effect, and will not be treated in the same way as for effects in the laboratory procedures. A goal of a sampling protocol is often to randomise effects that can be then treated statistically [5]. Ramsey [6] has pointed out that the traditional, i.e. an assertion of random sampling does not guarantee the desired result. 'Analytical bias' (Ramsey's term for