Chemical metrology, chemistry and the uncertainty of chemical measurements

Abstract  Chemical results normally involve traceability to two reference points, the specific chemical entity and the quantity of this entity. Results must also be traceable back to the original sample. As a consequence, any useful estimation of uncertainty in results must include components arising from any lack of specificity of the method, the variation between repeats of the measurement and the relationship of the result to the original sample. Chemical metrology does not yet incorporate uncertainty arising from any lack of specificity from the method selected or the traceability of the result to the original sample. These sources of uncertainty may however have much more impact on the reliability of the result than will any uncertainty associated with the repeatability of the measurement. Uncertainty associated with sampling may amount to 50–1000% of the reported result. Chemical metrology must be expanded to include estimations of uncertainty associated with lack of specificity and sampling.

Keywords  Metrology · Sampling · Chemical · Specificity · Uncertainty

Introduction

Dependable measurement is critical to both science and trade. Without a common understanding of the meaning of results of measurements, science would not function and systems of trade would become inefficient. Trade requires reliable measurements for quantity, quality and safety of goods and without these, delivery slows and disagreements as to their compliance with specifications proliferate. Reliable measurements in science and trade depend on having defined standards for analytes, demonstrable traceability of results to the defined standards and an understanding of the uncertainties of these processes.

International trade agreements under the World Trade Organization are now emphasizing the current, less satisfactory, state of chemical measurements. In trading relationships, both the buyer and seller usually repeat tests and often, regulatory agencies require their own independent check. This replication of effort is obviously inefficient [1] but reflects the current inability of chemical measurement to produce consistent results over distance and time.

The situation with respect to physical measurements is in complete contrast to results from different sources generally accepted as being comparable. Metrology, the science of measurement, has been developed from physical measurement and emphasizes results traceable to defined reference points, normally the International System of Units (SI), and fully analysed uncertainty budgets based on the processes set out in the Guide to the Expression of the Uncertainty of Measurement (GUM) [2]. This process involves identifying each component of the measurement that contributes to uncertainty, estimating the contribution of each component of uncertainty, then combining these estimations to calculate the total uncertainty. Much of the improvement in consistency of physical measurements has been achieved by use of the uncertainty budget to better define and control the test environment.
In the last ten years much effort has been applied to introduce these same concepts of physical measurement into chemical measurement. For example:

- The Bureau International des Poids et Mesures (BIPM) has put in place a consultative committee, the Consultative Committee on the Quality of Material (CCQM) [3], to strengthen the relationship of chemical measurements to its SI unit, the mole.
- ISO/IEC 17025:1999 [5] is replacing ISO Guide 25 [6] as the standard against which laboratories are accredited and supports these moves by having an increased emphasis on this metrological approach.

Incorporating traceability to the mole and uncertainty budgets into chemical analysis is more complex than is their application to physical measurement. Normally a chemical measurement depends on a combination of physical measurements, chemical separation of the compounds of interest and the selection of the test portion from the bulk material. An understanding of the chemistry involved in these separation processes is vital before reliable results can be achieved and chemical analysts have tended to concentrate on this area of analysis. It is however a part of the measurement that is tending to be ignored in moves to align chemical measurement with the traditional physical metrological process. The sampling process, both in the laboratory and outside in the field also contributes to the uncertainty of the measurement but has tended to be ignored by analysts. Understanding of the uncertainty of chemical measurements will not be achieved without an understanding of the whole process.

Discussion

Chemical measurement has a fundamental difference from physical measurement in that it does not take place under controlled and defined conditions. Almost always, the primary objective of a chemical measurement is to determine the amount of components of interest, not the total composition of the sample. Total composition will almost always remain unknown and therefore the total environment under which the measurement is taking place cannot be defined or controlled. Unknowns will always increase the uncertainty associated with any measurement.

Three components can be considered as contributing to uncertainty in chemical measurement. These are sources of uncertainty associated with the sampling process, the underlying chemistry of the chosen method, including its selectivity, and the more readily quantifiable aspects of uncertainty associated with the repeatability of the measurement. The cause and effect diagram in Fig 1 represents this situation. Each of these components is important. Get one wrong and the result is unlikely to be ‘fit for purpose’.

For many years, analytical chemists have used reference methods as a means of limiting the numbers of unknowns by removing those associated with traceability of the measurement to the defined chemical entity. Although reference methods remove uncertainty associated with traceability of the result to the named chemical entity and thereby eliminate most chemical unknowns as an issue, they always have the disadvantage that they redefine the analyte in terms of a method rather than as a chemical species. Amongst the best reference methods are those published by the Association of Official Analytical Chemists International (AOAC) [7]. These methods will have been validated within a number of laboratories from a collaborative study and will have associated estimations of uncertainty based on repeatability and reproducibility results from the study.

In reference methods, uncertainty in the result will directly relate to the measured repeatability. Defining the analyte as the method result eliminates any uncertainty related to the underlying chemistry. It may also define the procedure for taking the test portion in the laboratory and thereby include some of the uncertainty associated with sampling.

Modern methods of analytical chemistry are less conducive than traditional methods to the reference method approach. Instrument and equipment combinations are much more variable between laboratories and change over time as manufacturers add technical improvements. Reference methods also cause problems between countries unless they have international acceptance and they limit the adoption of new analytical methodology and equipment.

As a consequence of the problems associated with reference methods, there is now more emphasis on an absolute measure of analytes of interest where these are distinct chemical entities. For instance, the Codex Committee on Sampling and Analysis is presently debating whether analytical requirements for discrete chemical components in foods can be defined by method perfor-

![Fig. 1 Cause and effect diagram showing sources of uncertainty associated with chemical measurements](image)