QUALITY ASSURANCE

Metrology for chemical measurements and the position of INAA

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Metrology systems are being established by various countries for the worldwide comparability of data related to trade, industrial products, health, and the environment. This has in turn led to an increased interest in methods that have the highest possible accuracy and precision. The relevance of instrumental neutron activation analysis (INAA) for metrological science has been evaluated. It is concluded that INAA is a suitable technique for method validation, proficiency testing, development of reference materials and reference methods. Moreover, it is concluded that INAA must comply with the CCQM definition of a definitive or primary ratio method provided that the uncertainty in the results is reduced to much lower levels compared to those currently encountered in most NAA laboratories.

Introduction

The internationally accepted metrology systems include requirements for comparability, traceability, accuracy, uncertainty, and long-term stability in measurements. The importance of such characteristics can be illustrated with the example of research involving modeling and observations of environmental trends. Environmental data are often used for national or global agreements on reductions in the quantity of emissions, which in turn often require expensive changes in power generation and manufacturing processes. Accurate assessments of trends in the global environmental quality require the comparability of the data obtained at various sites in the world over a long period of time. In addition, analytical measurements are made by a number of various laboratories located in different countries.

Comparability, accuracy, and to some extent traceability of chemical measurements are traditionally evaluated via analysis of (certified) reference materials and/or use of primary standards. However, most of the common analytical methods used to analyze solid samples are matrix sensitive, at least to some degree, and may suffer from dissolution losses, additive and multiplicative interferences, etc. Such methods would ideally require either a very large number of matrix-matched certified reference materials for calibration and quality assurance purposes, or confirmation by another analytical technique with totally different sources of error. It is also often difficult or impossible to make a full evaluation of the uncertainty for each individual measurement made by most common analytical techniques.

Another approach would be to use a primary method. The Comité Consultatif pour la Quantité de Matière (CCQM) has recently issued a revised definition of the primary method,\(^1,2\) and a distinction has now been made between a primary direct method (e.g., coulometry, gravimetry) by which the value of an unknown is measured without reference to a standard of the same quantity, and a primary ratio method (e.g., isotope dilution mass spectrometry) by which the value of an unknown is determined by means of the ratio of the unknown to a standard of the same quantity. The available references\(^3,4\) provide comments on the definition of a primary method with respect to other techniques including neutron activation analysis (NAA), plasma spectrometry, etc., and it is often stated, in a rather general way, that chemical matrix effects are absent in NAA, at least up to the level for which the chemical state of an element does not affect the final result for that element. However, many NAA laboratories are currently facing the problem of justifying their existence in view of the competition from other methods of elemental analysis. This factor is also affecting the continuation of funding for these labs. Although NAA is considered to be extremely valuable for the development of certain categories of reference materials, it is not a primary technique in most countries, even at national levels. However, its role within a national metrology system might be a strategic consideration for continued support and development of the associated NAA laboratory.

The potentials of NAA to contribute to a program for metrology in chemical measurements has therefore been evaluated, and particular attention has been given to the conformity of instrumental NAA (INAA) to the definition of the primary ratio method.
Metrology requirements and INAA

Metrology in chemical measurements include the following components, relevant for the assessment of the role of INAA.

Traceability

Requirements: The International Vocabulary of Basic and General Terms in Metrology (VIM) defines traceability as 'The property of a result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties'.

The CCQM adopted a statement on the meaning of traceability in measurements in chemistry: "...Strikingly, traceability to the SI in measurements of amount of substance...requires that the measurements be made using a primary method of measurement... with an evaluated uncertainty. There may be other, indirect ways of establishing traceability to the SI... and these are under study by the CCQM. These other methods may include combinations of methods that are not established as primary but have evaluated uncertainties...[linked] to national or international measurement standards of each SI unit... [and] comparison with reference materials of the same or similar substance or mixture...[linked] to the SI through... a measurement using a primary method". In the draft ISO/IEC FDIS 17025, the new International Standard that will replace the ISO/IEC Guide 25 and thus will be the future basis for accreditation of testing laboratories, it is stated that for testing laboratories "...where traceability to the SI units of measurement is not possible and/or not relevant...[laboratories]...shall provide confidence in measurements by establishing traceability to appropriate measurement standards such the use of certified reference materials provided by a competent supplier to give reliable physical or chemical characterization of a material...specified methods and/or consensus standards that are clearly specified and mutually agreed upon by all parties concerned...[will be used]".

Assessment of INAA: NAA is based on physical principles that are different from other methods used for elemental analysis. Moreover, the method can be carried out without chemical destruction of the sample and the chemical state of an element does not affect the measured concentration. The availability of well-type Ge detectors and Compton suppression systems, and in some cases higher neutron fluxes, has resulted in better sensitivities. The sources of uncertainty are understood and the uncertainty budget can be made complete, as will be demonstrated below. Finally, as has been explained above, NAA results can be made traceable.

Inferences: NAA has an important role in the development of reference materials for elemental analysis and in the certification thereof. The method can be of great value for the related homogeneity tests.

Reference methods

Requirements: Reference or standard methods may accommodate the growing need for demonstration of conformity to international regulations. Routine methods often are a compromise between ease-of-operation, economy and required levels of accuracy and precision. As such, they may be subject to various sources of errors and interferences. Reference methods are needed to monitor the performance of routine methods, and to verify the opportunities and performance of new equipment.