

Reference Materials for Trade and Development: Quality and Comparability

A. Introduction

Scientific measurements are a basic input to decisions made in many areas of human activity. In particular, physical and chemical measurements are used for estimating the quality and fitness for purpose of traded goods such as food, pharmaceutical products, ores, and chemical products. Measurement results also play an important role in the areas of human health (diagnostics and treatment), environmental protection, and exploitation of water, mineral and energy resources. In all of these areas the quality of associated measurement results needs to be assured and demonstrated in order for them to be accepted as part of the decision making process. Laboratories are experiencing increased demand in the area of quality assurance for traded goods, in particular, due to the growth in international trade (Fig. III-1).

This is where metrology, standardization and conformity assessment play important roles. They are the pillars of knowledge for developing a technical infrastructure, and thereby enabling sustainable development and full participation in international trade. To this end there is an international measurement infrastructure that works closely together in order to promote a world-wide metrology system (Fig. III-2), supported by international standardisation and harmonization activities, by national metrological infrastructure, certification and accreditation bodies and at the laboratory level by appropriate quality management, including quality assurance and quality control.

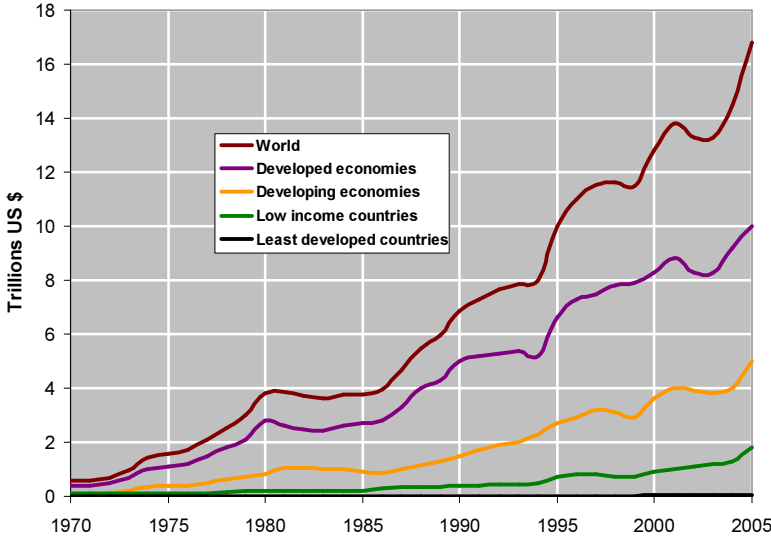


FIG. III-1. World Trade Development in trillions of US\$ (Source UNCTAD)

In many areas comparability is the main quality component of measurement results. This term describes the property of measurement results which enables them to be compared independent of the time, place, analyst and procedure used. It involves the assurance of metrological traceability. Other quality characteristics of importance are accuracy, reproducibility and measurement uncertainty, which give an indication of whether or not the measurement results are actually fit for their intended use. These quality characteristics underpin confidence in analytical measurement results and help avoid unnecessary duplicate measurements, which are still often present in the export and import of goods.

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FIG. III-2. Schematic presentation of the current international and regional measurement and standardization infrastructure. (Note: This Figure is not exhaustive and does not cover the national level.)

B. Tools for assuring and checking measurement results

Basic tools which are used by laboratories to assure and demonstrate the quality of their measurement results include the following:

- use of standardized methods for sampling and analysis,
- proper calibration of measuring instruments,
- routine quality control practices, and
- regular participation in interlaboratory comparisons and proficiency tests.

B.1. Standardized methods for sampling and analysis

Sampling is an integral part of the measurement process, and can strongly influence the comparability of the final measurement results based on the use of agreed sampling procedures. Sampling should result in a representative sample, which often will be composed of spot samples selected according to the specific sampling strategy.

Sampling of the environment is especially complex due to its non-homogeneous nature, the number of environmental compartments needing to be sampled (soil, water, biota, atmosphere, etc.) and the large number of characteristics which may need to be measured on the samples. The effect of a lack of harmonized approaches to sampling was evident after the Chernobyl accident, as the different sampling strategies used at the time made a geographic comparison of results difficult. As a result, the International Commission on Radiation Units and Measurements and the International Union of Pure and Applied Chemistry have recently published guides on sampling in the environment to help address this issue (ICRU, 2006; de Zorzi et al. 2005). A well characterized and geostatistically stable sampling site, such as the one presented in Figure III-3, can be used for assessing sampling strategies and uncertainties associated with different sampling techniques. Such sites will be needed in the future and proficiency testing in sampling has become an important activity in recent years (Barbizzi et al. 2004). The need for standardized methods for sampling and analysis for radioactivity in the environment was one of the reasons for creation of the ALMERA (Analytical Laboratories for the Measurement of Environmental Radioactivity) laboratory network, which is coordinated by the IAEA, and makes available to Member States a world-wide network of analytical laboratories capable of providing reliable and timely analysis of environmental samples in the event of an accidental or intentional release of radioactivity. The network is a technical collaboration of existing institutions, and provides an operational framework to link expertise and resources, in particular when transboundary contamination is expected or when an event is of international significance.

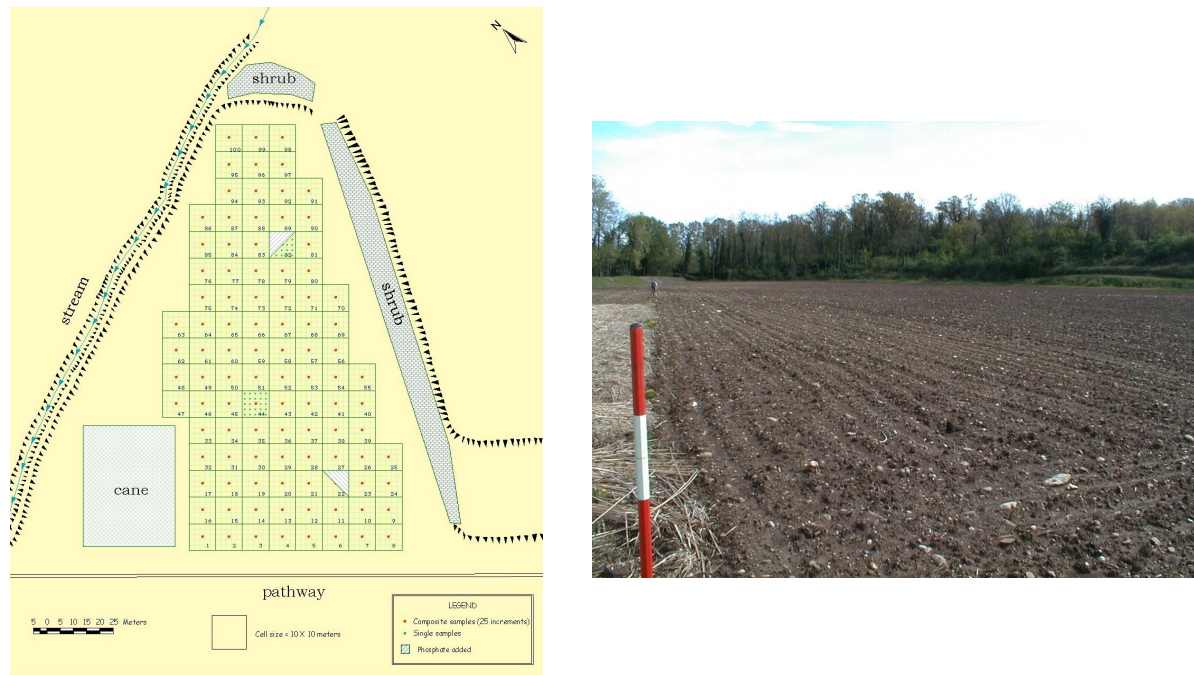


FIG. III-3. A reference sampling site for soil at Friuli, Italy. The schematic presentation shows a sampling grid used in the site characterization process.

B.2. Reference materials

Reference materials are materials for which one or more properties are well established. They are used for calibration of an apparatus; for the assessment of a measurement method; for establishing traceability of measurement results and for determining the uncertainty of these results (ISO 2000). Their application provides direct information on the quality of the measurement results in a laboratory. The final responsibility for selection and correct application of appropriate reference material will always rest with the users. They therefore need to be properly informed and aware of the characteristics and limitations of the selected reference material.

Matrix reference materials are a type of reference material with a relatively complex matrix such as soil, fish flesh or milk powder (Fig. III-4). Differences in types of reference materials influence the possible methods for their characterization and certification, as well as their utilization in the analytical process.

A majority of matrix reference materials are characterized through interlaboratory comparisons, meaning that the assigned property values are established from the average of laboratory results. Therefore metrological traceability of these values can normally be claimed only to the respective laboratory intercomparison, and not to any other point of reference. Trends in the reference materials area depend in part on the development of new analytical techniques, of which two aspects should be mentioned. The first is the development of new, especially micro- and nano-, techniques. The second is the development of non-destructive analytical techniques involving solid sampling, such as neutron activation analysis (NAA), X-ray fluorescence (XRF) and gamma spectrometry. In both cases there is only a limited variety of appropriate reference materials presently available characterized for chemical element composition, radionuclide content, and stable isotopes ratios suitable for use with such techniques thus additional efforts are needed.

The role of nuclear and nuclear related analytical techniques in the development of new materials is significant. Among others, mass spectrometry techniques, neutron activation analysis (NAA), micro X

ray fluorescence, and alpha spectrometry, may be applied in the characterization process. An important step in this respect is the recent recognition of instrumental neutron activation analysis (INAA) as a potentially primary method of measurement by the Consultative Committee for Amount of Substance: Metrology in Chemistry (CCQM 2007)¹. Characterization by primary methods of measurement (for example by gravimetry, coulometry or isotope dilution mass spectrometry, etc.) may lead to the preparation of reference materials of highest metrological quality — materials that can be used as calibrants. Calibrants are usually pure materials (pure substance or element), transferred by the end user into the physical and chemical form appropriate for insertion into the measurement device. All such transformations, however, may influence the uncertainty of measurement results. Therefore another important field is the development of matrix reference materials that could be used as calibrants.



FIG. III-4. IAEA reference materials (fish flesh and soil) characterized for radionuclides.

In the case of non-destructive measurement techniques, the availability of matrix type calibrants would compensate for many uncertainty sources when test samples of similar composition and density as a calibrant are measured. It is expected that the trend towards preparation of such matrix materials useable as calibrants will grow. Preparation of such materials may be achieved using one of two broad approaches. The first is spiking of a base matrix with a standard which is metrologically traceable to SI units (Shkhashiro et al. 2007). The second approach is characterization of the original material through a characterization campaign involving a small number of expert laboratories, such as national metrology institutes.

One measurement area in which the first pilot studies have recently been initiated is the area of stable isotope ratio determination. A pilot study CCQM-P75, titled ‘Stable isotope delta values of ²H, ¹³C, ¹⁵N and ¹⁸O, ³⁴S in methionine’, coordinated by the Institute for Reference Materials and Measurements (JRC, EC), is the first that is tackling metrology issues for stable isotope measurements of light elements. Participation of laboratories from 18 countries demonstrates a strong interest and the need for this type of comparison.

Stable isotope ratio measurements are important in the study of water resources, agriculture and the environment. In this area the IAEA prepares and maintains a stock of relevant reference materials. The most known of these are the Vienna Standard Mean Ocean Water (VSMOW) and the Standard Light

¹ <http://www.bipm.org/en/committees/cc/ccqm/>

Antarctic Precipitation (SLAP), which fulfill the function of primary measurement standards for hydrogen and oxygen isotope ratios. For better understanding of the role of primary measurement standards, one can compare the role of VSMOW and SLAP with the function of the primary kilogram prototype stored at the Bureau International des Poids et Mesures (BIPM) in Paris, which defines the international mass scale. Both VSMOW and SLAP are materials established to define a certain unit, whether for mass or for a stable isotope ratio of elements. However, while the primary kilogram is an artifact kept under controlled conditions and only subsequently calibrated secondary standards are further used in the calibration process, VSMOW is an exhaustible material sent out in small portions to laboratories for their calibration.

Recently, in an international effort coordinated by the IAEA, the original and almost exhausted VSMOW was replaced by a successor material called VSMOW2. The isotopic composition of the original VSMOW was reproduced nearly perfectly. This was achieved by mixing three different water samples characterized by the world's leading stable isotope measurement laboratories (Fig. III-5). The uncertainty of the calibration is much smaller than the uncertainty of measurement that a field laboratory can normally achieve (indicated by the blue circle). In other words, VSMOW2 can be used as a direct replacement without any need for adjustment of measurement results due to the calibrant used. Hence comparability of measurement results is assured.

Several similar efforts were undertaken in the last few years to recalibrate existing reference materials for improved consistency of assigned values, coordinated by the U.S. National Institute for Standards and Technology (NIST), the International Union for Pure and Applied Chemistry, and the IAEA.

The importance of these activities is shown by a recently started project of the Commission of Isotopic Abundances and Atomic Weights², the international body for atomic weights data of all elements, to compile a list of available reference materials for all elements to improve the situation in areas and elements without proper internationally accepted reference materials. In this context also a project was launched recently at NIST to develop new reference materials for transition zone elements (copper, iron etc.) for new kind of mass spectrometers using ultra-low amounts of sample for analysis.

² <http://www.iupac.org/divisions/II/II.1/index.html>

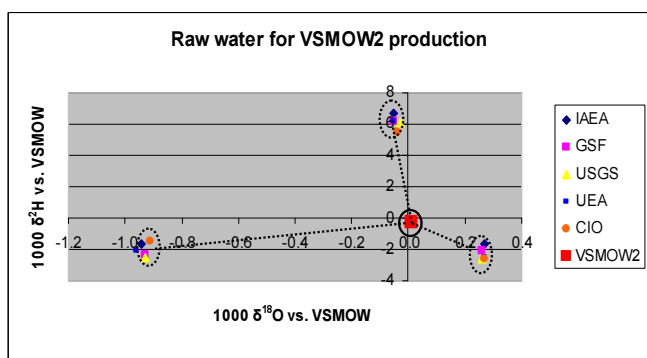


FIG. III-5. The measurement results for three water samples used in preparation of VSMOW2.

B.3. Interlaboratory comparisons — proficiency tests

Interlaboratory comparisons and proficiency testing are methods for regularly assessing the accuracy of the analytical data produced by laboratories. Proficiency testing schemes operate by providing participating laboratories with samples containing specified material but the actual quantity of the substance to be analysed in the material is known only to the organisers. The laboratory analyses the samples, preferably as part of their normal routine, and reports the results to the scheme organisers. The laboratory is then provided with a report showing how closely their results agree with the accepted value, and where necessary, can then take appropriate action to improve performance.

Regular participation in a proficiency-testing scheme provides independent verification of the analytical competence of a laboratory and shows a commitment to the maintenance and improvement of performance. It demonstrates to the public, customers, accreditation bodies, regulators, and management that analytical procedures are under control and gives analysts confidence that the service which they provide will withstand scrutiny.

The results generated in proficiency testing may be used for the purpose of a continuing assessment of the technical competence of the participating laboratories. With the advent of “mutual recognition” it is of importance that laboratories participate in proficiency testing schemes to provide an interpretation and assessment of results which is transparent to the participating laboratory and its “customer”.

C. Conclusions

The acceptance of information provided by analytical chemical laboratories strongly depends on quality measures implemented during the process of data generation. Increasing demands on laboratories to demonstrate the quality of their work leads in the direction of greater formalization in this field, including requirements that laboratories be accredited.

The importance of matrix reference materials has been recognized by international organisations such as WHO, WMO, FAO, OECD, UNEP, and WTO (TBT: Technical Barrier to Trade) as well as the EU. The producers of reference materials are increasingly requested to adopt ISO Guide 35 (Certification of Reference Materials) and receive ISO Laboratory accreditation (ISO Guide 43). They face new challenges due to the more complex nature of production, such as increased requirements due to new analytical methods, low levels of analytes (measurands), and newly required analyte

species. Nuclear analytical techniques are in many cases uniquely able to help address these challenges.

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