National Measurement Conference 99

AT

BRIGHTON METROPOLE
2-4th November 1999

organised by

NMP
NATIONAL
MEASUREMENT
PARTNERSHIP

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ISBN 0 946754 34 9

National Measurement Standards and Systems for Chemistry

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Industrialised countries require an infrastructure for providing traceable measurements (usually known as the National Measurement System) that maintains the long-term stability and international comparability of measurements. Recent international initiatives have stimulated debate about how a NMS can be developed to include chemical as well as physical measurements. We discuss how the approach used to develop a NMS for physical measurements can be extended to cover various measurements of chemical quantities. In both cases such a system must include: National standards, a capability to measure them and an infrastructure for the dissemination of measurements. The combination of these three elements are the essential components required to provide traceable measurements and for international comparability to be achieved.

Background

The economic strength of the chemical industry and its use of advanced technologies to develop new products and to reduce costs suggests, that there may be a significant requirement for any National Measurement System (NMS) to cover chemical as well as physical measurements. The DTI's Valid Analytical Measurement (VAM) Programme has pioneered an approach to meeting the requirements for valid chemical measurements within the UK. In this paper, we discuss how the provision of standards and traceable measurements for chemistry fit within the model of a NMS that was originally developed to cover physical measurements [1].

The formation of the Consultative Committee for Amount of Substance (CCQM) in 1995 with a remit covering "traceability to the SI base units of quantitative chemical measurement" has stimulated discussions amongst participating countries about suitable approaches to providing chemical measurements. Such discussion is timely since policy at national and European level [2,3] is being developed rapidly to meet needs that have been identified. This paper explains some of the background to the NMS that has been developed in the UK and takes account of international developments in discussing the potential for extending it to cover chemical measurements.

National Measurement Systems

The UK White Paper "Measuring up to the Competition" [4] provides a useful definition of a "National Measurement System" as:

> *"the technical and administrative infrastructure which ensures a consistent and internationally recognised basis for measurements in a nation."*

This definition provokes the question - what is the "technical and administrative infrastructure" that is required ? In this section, we describe three elements that form the major components of the technical and administrative infrastructure required for an effective NMS:

> *The availability of (national) measurement standards* - These are usually considered to be the central component of an NMS and cannot be considered in isolation from the certificates establishing their values. They are the basis for providing traceability since they are accepted as the final point of reference nationally. Holding such standards is often considered to be the defining role of a National Metrology Institute (NMI).
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> *A measurement (or analysis) capability* - An NMI must have the capability to carry out comparisons of national standards both with other standards that are disseminated more widely on a national basis and with those from other countries. These comparisons must be carried out with methods that give traceable results with uncertainties that are comparable with those of the national standards. Such a measurement capability is essential for participation in "key comparisons" [5] with NMI's from other countries.
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> *An infrastructure for the dissemination of traceable standards and measurements.* The work carried out by the NMI to develop standards and measurement capabilities can only be effective as a national system, if it can be accessed and exploited by interested users throughout the country concerned. The impact of an NMS is dependant on the effectiveness and thoroughness with which its results and services are disseminated. The operation of a dissemination infrastructure may involve the use of several different mechanisms such as:
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> - the direct transfer of measurement standards to users,
> - the measurement (or calibration) of artefacts supplied by users to the NMI,
> - the validation of widely-used or specialised measurement techniques.
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> As the requirements for measurement standards have grown, many countries have increased the leverage of their dissemination activities by linking working standards to the NMI through chains of direct measurement comparisons. As these mechanisms have become more complex, quality and accreditation systems have been developed to ensure that they deliver the required levels of accuracy and traceability.

Although the realisation of the above three elements of an NMS will have to meet the different requirements of different fields of measurement, an NMS cannot be complete for any particular type of measurement without some mechanism to fulfil each of these functions. These elements naturally define a hierarchy in which national measurement standards are linked by a measurement capability to the dissemination infrastructure and hence to users. In some cases, the scope of these functions and activities is sufficiently extensive to require the co-ordinated work of many organisations.

Rationale for Including Chemical Measurement in an NMS

The absence of a comprehensive infrastructure providing traceable chemical measurements is often used as a major justification for establishing one. A much stronger rationale could be developed by reference to the general rationale used by Governments for funding a National Measurement System. This rationale may be based on some of the following [6]:

the cost of providing a NMS is far too great for one company,

measurement standards and services must be made available on an equitable basis to all interested users in a country,

the requirement to demonstrate comparability between different nations can not be funded on a commercial basis.

When expressed in this way, it is apparent that all aspects of the work required to provide improved measurements (of physical or chemical quantities) may not fall within these criteria. In the following section we discuss some aspects of the field of chemical measurements and propose how some elements can be identified that are analogous to physical measurements covered by the NMS, while others are not.

Calibration Standards for Chemical Measurement

At a fundamental level, there is no significant difference between the measurements of physical quantities (such as mass and length) and chemical quantities (such as concentration, purity or reaction rate), since the fundamental elements of the measurement process are present in both. Nevertheless, the provision of a cost-effective NMS for chemical measurement presents different challenges to those presented by physical measurement.

Research in analytical chemistry has traditionally concentrated on the quantitation and quantification of complex samples that may include large numbers of "unknown" components. Attempts to develop a flexible approach to dealing with the complexity of such samples have concentrated on the development of methods that are accurate and resistant to "matrix" or cross-interference effects These often make use of "matrix" reference materials to demonstrate the repeatability and reproducibility of the methods. Since very few of these matrix reference materials have values for their contents that are traceable to the international system of units (SI), their use can only provide traceability to the SI for a limited range of analyses. The relatively limited scope for this approach providing widespread traceability for analytical measurements has led to the view that a hierarchical approach to the dissemination of measurement standards is not applicable to chemical measurements.

When this approach is compared with the description of the components of a National Measurement System given in this paper, it becomes apparent that matrix reference materials do not play the same role in chemical measurement that measurement standards do in physical measurement. This is because they are largely used to deal with the problems of sampling and matrix dependence. They are not specifically used to disseminate traceable calibrations. There is a much better correspondence between calibration standards with known or very well characterised composition in chemistry and physical measurement standards.

This can be illustrated by three examples:

routine measurements of elements in various matrices are made by different types of emission or absorption spectrometer. These can be calibrated using elemental calibration solutions which are prepared by gravimetric addition of pure elements into a simple solution, laboratory and field measurements of pH are measured using non-ideal glass electrode systems that are calibrated using buffer solutions. The buffer solutions are well-understood systems of low ionic strength that may not be typical of the actual matrix being measured.

automatic monitors measuring ambient air quality are calibrated using secondary standards of gas composition. These are traceable to primary gas standards which consist of gravimetric mixtures of pure gases.

In each of these examples, traceability is achieved by the use of a calibration standard which does not have the same characteristics as the system being measured. In each case the calibration standard has a chemical property (elemental concentration, pH or gas concentration) that can be traced to a recognised reference.

Conclusion

A discussion of the role of a National Measurement System and its component parts, shows how some of the requirements for improving chemical measurements could be met. Examples of requirements that can be met in this way include calibration standards which have chemical properties that are traceable to recognised references. The requirement for a very wide range of specialised matrix reference materials that do not have traceable values does not fit so readily within the well-established model for a National Measurement System.

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