Fresenius J Anal Chem (1998) 360 :366–369 

CONFERENCE CONTRIBUTION

**Peter J. Jenks · A. Henk Boekholt**
**John F. N. Maaskant · Robert D. Rucinski**

# Are certified reference materials a victim of quality systems? The need for working matrix-certified reference materials

Received: 23 May 1997 / Revised: 19 August 1997 / Accepted: 26 August 1997

**Abstract** The use of natural matrix-certified reference materials by commercial environmental laboratories is increasing rapidly. These materials are now an essential component of the quality systems of most commercial environmental laboratories. The use is increasing faster than existing producers, principally government agencies, can meet. The use of data from well established laboratory proficiency schemes is shown to be one alternative way of producing natural matrix-certified reference materials designed for use as day-to-day within-batch control materials.

## Introduction

Agreement between analyst and customer is essential, especially when monitoring the environmental consequences of chemical discharges. Industry, including commercial environmental laboratories, uses accreditation to ISO 9000 Series and related quality systems including EN 45000 and Total Quality Management (TQM) to demonstrate the quality of their product. It has become generally accepted that the perceived quality of a product or service can be significantly improved by eliminating disagreements over measurement. In analytical chemistry this belief has created a need for results from similar determinations carried out in different laboratories to be truly comparable, also accurate and precise, and with a known and believable uncertainty.

P. J. Jenks (✉)
Promochem GmbH, P.O. Box 100 955,
D-46469 Wesel, Germany

A. H. Boekholt · J. F. N. Maaskant
RIZA, P.O. Box 17, NL-8200 AA Lelystad, The Netherlands

R. D. Rucinski
Resource Technology Corporation (RTC),
P.O. Box 1346, Laramie, WY 82070, USA

## Development of demand

Agencies such as the International Organization for Standardization (ISO), and various national bodies such as the British Standards Institution (BSI), the Netherlands Standard Institute (NNI), Deutsche Industrie Norm (DIN) and the US Environmental Protection Agency (EPA), have compiled many thousands of standards governing the way procedures should be carried out and measurements be made. In many countries laboratories analyzing natural samples (e.g. soils, sediments and waters) for environmentally sensitive materials use mandated, standardized procedures in order to try and achieve comparability.

The USA was the first nation to establish a comprehensive program for the analysis of such samples when, in the late 1970's, the Environmental Protection Agency (EPA) assumed responsibility for method development and overall assurance of quality in this area. The EPA programme was unique as some reference materials were distributed without charge. Even so the program was mainly made up of single substance reference materials, with few natural matrix-certified reference materials.

When the first BERM [1] meeting took place in 1983 it attracted a handful of scientists interested in chemical metrology. At that time most scientists working in this field were either involved in academic research or staff in government agencies. There was little commercial usage of chemical reference materials outside instrument calibration and the analysis of metals and alloys; so these new matrix reference materials were made available to other researchers at a nominal cost. Since then two factors have worked together to create a commercial analytical chemistry market that is both highly competitive and heavily regulated. An ever increasing control on the discharge of chemicals into the environment increased the need for chemical analysis and the economic revolution of the late 1980's pushed many analytical functions previously carried out by government into the marketplace. To demonstrate competence and stay in business most analytical chemistry laboratories working in the environmental market must achieve and maintain accreditation. The basis for accreditation, and therefore economic survival, is a so-called "quality system". In developing their quality systems laboratory managers have begun to appreciate that the use of procedural standards will help, but does not go all the way to achieving acceptable results. Through such meetings as the BERM series and publications by AOAC [2] and others there is a growing realization that the only real way to fully control an analytical system, from sample to result, is by using an external matrix reference material. So most quality systems now require or encourage both the use of certified reference materials for within and between batch assessment of the complete analytical process and participation in interlaboratory studies. Although the desirability of linking commercial analysis to the SI system has been demonstrated [3], most such quality systems show little practical concern for the finer aspects of traceability to the mole!

Commercial labs quickly realized that suitable reference materials and certified matrix reference materials were available at a low cost from BCR, NIST and others; so certified matrix reference materials were used as routine quality control or as working standards. By the late 1980's the EPA could no longer finance the growing demand for its certified reference materials, so in 1990 contracts were let with specialist companies to make the reference materials and distribute them on a commercial basis. The EPA remained responsible for certification. Three years later the EPA withdrew from the contracts amidst much acrimony and legal disputes. The commercial companies who had been partners of the EPA took over the production of the simple pure materials and mixtures. The demand for naturally accrued certified matrix reference materials continues to increase rapidly. It has reached a level that the traditional suppliers, such as the EU SM&T (BCR) Program, NIST and others, now admit that they can no longer meet. The scale of the problem was recently highlighted when NIST admitted that the overall availability of some groups of NIST SRMs® was not acceptable [4]. Their answer was to propose the widening of the "NIST Traceable Reference Materials" program (NTRM), first introduced for gas mixtures in 1994 and intended to help increase the availability of "working" certified reference materials that can be accepted as traceable to a NIST SRM®. There is no reason to doubt that many of the existing commercial producers of reference materials will be able to successfully develop the NTRM concept to produce pure substance reference materials for instrument calibration and other applications, but little was said about how the NTRM concept could be applied to matrix reference materials. This was not surprising as there are only one or two commercial producers of natural matrix reference materials.

## Shortage of certified matrix reference materials in the Netherlands

One example of the problems that can be caused by the shortage of suitable reference materials is the experience in the Netherlands in 1993 when mandatory accreditation was introduced for all environmental laboratories. Related to specific legislation, analytical methods, procedures for method validation and quality control criteria were contained in a so-called "Accreditation Program". To achieve and maintain accreditation, Dutch environmental laboratories needed to demonstrate that they could reliably produce good quality data. To demonstrate their competence to the accreditation body, the Dutch laboratories concerned were required to use standardized and validated methods where ever possible, belong to a recognized interlaboratory proficiency scheme and make regular use of relevant natural matrix reference materials.

Netherlands Institute for Inland Water Management and Waste Water Treatment (RIZA) was made responsible for the operation of an interlaboratory proficiency scheme. Working with their client laboratories, the RIZA scientists quickly realized that few suitable reference materials were available, especially for sludge and sediment analysis. Some use was made of BCR and other matrix materials, but it was found that many had values based on the total or complete destruction of the sample. This meant that when used for analysis by the mandated Dutch national standard methods, it was not always possible to reproduce the certified values. To make matters worse, the stocks of some suitable BCR certified reference materials, including CRM 140 to CRM 146, were insufficient for routine use. The RIZA scientists were reluctant to utilize synthetic or fortified matrix reference materials. Government funding for production was not available, and no commercial supplier could be found in Europe who could produce suitable natural matrix-certified reference materials at an acceptable cost.

## Production of a certified reference material

Most producers of certified matrix reference materials follow the guidelines produced by the REMCO committee of the International Standards Organisation (ISO), which describe in detail how the production and use of reference materials should be carried out [6]. Almost all certified reference materials and many reference materials presently available have been produced under some form of a subsidy. Examples are the US Department of Commerce's agency NIST, the UK Department of Trade and Industry funding the LGC through the VAM program, and the SM&T program of the EU which produces BCR reference materials. In another way cooperatives effectively provide subsidies by not charging for time and services provided by the participants. For example, the United States Pharmacopoeia relies on the good will of the pharmaceutical industry for much analytical work.

The real costs of producing and certifying matrix reference materials are enormous – the European SM&T program routinely publishes the cost of each approved project. Typically projects investigating new areas, for which no certified matrix reference material presently exists and which may require the development of new techniques, have budgets between ECU 250,000 and ECU 1, 250,000. The money is spent over a three- to five-year period. At the end of the action, between 300 and 1000 units of the certified matrix reference material and the report detailing the work behind it are released. For replacement batches the costs are lower, between ECU 50,000 and ECU 100,000, and the time taken is less, often not more than 12 months. This means that the cost of each certified reference material produced by SM&T projects range (at 1997 exchange rates) from US$50 for replacement materials to $2500 for new materials per unit. To commercially produce equivalent working certified matrix reference materials by copying known BCR procedures, would need a large initial investment in plant and equipment, financing of stock tied up during certification and the large stocks needed to ensure continuity of availability of a particular lot over a number of years. There is also a risk that a candidate material fails certification leading to a large cost write-off. Altogether, this would mean a selling price between $350 and $15,000 per unit needed to produce a real return on investment. Yet BCR, NIST and other certified reference materials are sold to users for between $150 and $300. This makes it impossible for a commercial company to compete.

## One solution

Commercial production of suitable natural matrix reference materials for use by Dutch environmental laboratories was shown to be impractical; so a number of possible solutions were investigated by RIZA, including "self-help". Their choice was to establish a cooperative research and development agreement (CRADA) between four parties to see if certified matrix reference materials could be produced quickly, and at an economic cost utilizing existing resources, which included:

- an existing interlaboratory scheme for proficiency testing organized by RIZA, membership of which was effectively mandatory for most of the laboratories needing certified matrix reference materials;
- a sufficient number of participant laboratories with demonstrated proficiency in the specific analysis undertaken, from which data from the interlaboratory scheme might be used to assign values to a certified reference material;
- experience in the production of candidate matrix certified reference materials meeting the requirements of ISO REMCO Guide 35, EPA and A2LA REFERENCE MATERIAL-03 and other appropriate quality standards;
- marketing, warehousing and distribution skills optimized to meet the particular needs of reference materials.

As a starting point the following framework for cooperation was set up: One or two candidate materials would be added each year to the existing RIZA interlaboratory proficiency scheme. The candidate materials would be produced in large numbers by RTC, according to the procedures described in the relevant ISO Guides and the US EPA and A2LA RM-03 procedures. A portion of the resultant candidate material would be purchased by RIZA and distributed to the RIZA participants. Collating raw data and initial statistical review would be carried out by RIZA, as a part of their normal interlaboratory scheme. The raw data would also be sent to RTC to use the rigorous statistical program written by K. Kafadar [6] to see if the data could be used for certification. If good enough, the statistics would be reviewed by RIZA who would issue a certificate and instructions for use. The certified reference material would be distributed to RIZA members at a special low price, and sold to other users at a price below that of existing comparable certified reference materials from BCR.

## Results

The first material was a sewage sludge, prepared by RTC during 1993, circulated to the RIZA members the same year and the results compiled by the end of 1993. The finished certified matrix reference material was released for sale in 1994 and is described in the COMAR [7] database. So far over 350 units have been sold in the Netherlands and Western Europe, generating around $55,000 revenue.

The production of the candidate material and the results obtained from the Netherlands and other interlaboratory studies undertaken together with some of the lessons learnt have been reported at the BERM 7 meeting [8].

The successful conclusion of the first project resulted in a decision to plan further projects, including soils and sediments contaminated with mineral oil, BTEX (benzene, ethyl benzene, toluene and xylene), cyanide and heavy metals, a water contaminated with nutrients and lastly stabilized raw sewage. Work is proceeding with some of these candidate materials and it is expected that a further report will be presented in due course.

## Conclusions

Unless there is a radical change in the pricing policy of the institutional producers which results in prices of so-called "primary" certified reference materials increasing substantially, it is very unlikely that commercial production of working matrix certified reference materials will take place on a large scale. Therefore, the need for more and more matrix certified reference materials will have to be met in part by other routes. The establishment of the CRADA resulted in the cost-effective and speedy production of useful method-specific certified matrix reference materials that would not otherwise be available. It showed that data produced from routine interlaboratory studies can, with care, be used to produce certified matrix reference materials for routine use. A recent publication by the Institute for Interlaboratory Studies [9] shows how that organization has started to follow the same route.

Production of the candidate reference material involved some financial risk which was taken by the commercial members of the CRADA. The revenue generated just covered production costs and the time spent in project management, but with a larger membership of the interlaboratory study group and a larger potential customer base there would have been more sales which would have made the project quite attractive. This is an important point. The fragmented state of European environmental regulations means that there are many official methods in use for the determination of a specific analyte. The development of "Euronorm Standards" is a move in the right direction, but for now the demand for any one method specific matrix certified reference material is insufficient to justify investment.

The continued demand for matrix reference materials is based partly on actual need, and partly on a perceived need arising out of fear of loss of accreditation. A combination of many more "day-to-day" certified matrix reference materials produced from interlaboratory studies, together with better education of quality and laboratory managers, should mean that quality systems could then make the best possible use of the limited availability of so-called "primary" certified matrix reference materials. This has to be the way forward.

## References


1. BERM – Biological and Environmental Reference Materials series of Symposia. Details from AOAC International
2. AOAC International, 481 North Frederick Ave, Suite 500, Gaithersburg, MD ZD877-24/7, USA, Tel. +1-301-924-7077
3. de Bièvre P, Lamberty A (1995) Fresenius J Anal Chem 352: 255–260
4. Mays W (1997) Presentation at J.K. Taylor Memorial Symposium, PittConn 1997
5. ISO REMCO Guides 31 (under revision), 32, 33 (in preparation), 34 & 35. Available from ISO, Case Postal 56, CH-1211 Geneva 20, Switzerland
6. Kafadar K (1982) J Am Statistical Association, vol 77, 378: 416–424
7. COMAR Database for Certified Reference Materials, BAM, Sub Department 1.4, Unter den Eichen 87, D 12205 Berlin, Germany
8. Maaskant JFN, et al. Presentation at BERM 7 (8.13) An International Interlaboratory Study for the Production of a Sewage Sludge Certified Reference Material for Routine use in Inorganic Quality Control
9. Newsletter (1997) Institute for Interlaboratory Studies, PO Box 8204, 3301 CE Dordrecht, The Netherlands


---

"SRM" is a registered trademark of the US Department of Commerce