The use of reference materials in environmental measurements; Case study - Hg analysis and speciation

Milena Horvat

Department of Environmental Sciences, "Jožef Stefan" Institute, Ljubljana, Slovenia;
milena.horvat@ijs.si

Abstract: Reference materials are widely used in nearly every measurement process in nearly every field of analysis. Some critical assessments of their use and possible missuese is demonstrated in the present presentation using mercury analysis and speciation in environmental studies.

Key words: Reference materials, artifacts, mercury, methylmercury

Introduction

Quality assurance refers to those procedures that ensure that analytical results are valid, traceable, reproducible, representative, complete and accurate, i.e. close to "true value". It also includes measures developed to assess performance. In order to properly understand the role of reference materials (RMs) it is first necessary to understand the measurement process itself. Although the RMs are almost a MUST in the analytical laboratory, their role in the whole measurement process is important in a few steps only to make sure that the results produced in a laboratory are reliable and fit for its intended use. In case of measurements in environmental samples the use of RMs is limited to the production of the results in the laboratory, while their role in the field sampling is rather limited.

Many guides and books are available on "use of reference materials". An ISO guide on the use of "certified reference materials" is also available. However, practitioners claim that it does not respond adequately to their needs and it is somewhat outdated. There are also many producers of reference materials. Reference materials of different quality levels are available on the market (i.e. certified reference materials that are fully traceable to S.I. units and non-certified reference materials).

The following questions are raised by practitioners in every day work practice:

- when and how to use reference materials? Should their application be generalized or only limited to a number of specific situations? If yes, which ones?
- what are the criteria to choose a specific reference material (quality needed) according to specific demands?

Numerous literature is available on the use and misuse of reference materials. However, the most practical access to information of RMs is available through a 'Virtual Institute for Reference Materials' (VIRM) *http://www.virm.org/* has been set up to create a knowledge network and to communicate and

Short scientific paper

disseminate information, advice and training on reference materials for producers, distributors, users, service providers, and research organisations.

Information is also available from the Reference Materials Advisory Service (REMAS) *http://www.vam.org.uk/advice/advice_services_reference.asp*, which "provides advice and information on reference materials such as: (i) Availability of reference materials in a particular field of application; (b) How to select and use an appropriate reference material; (c) Detailed information on the appropriate reference materials such as certified/ reference values, name of producer, form of the material, etc; (d) Information available from the international reference

The presentation will address these questions and provide some useful examples from practical work.

DISCUSSION

It is generally accepted that mercury analysis and speciation must be done by well trained staff that, in principle, should be involved in the measurement process from sampling to the production of final results, particularly if speciation of mercury is intended. The use of reference materials certified for mercury and its compounds play an important role in methods validation and demonstration of traceability. At present there are many reference materials certified for total mercury concentrations in various matrices (sediment, soil, ash, water, plants, and tissues) from different origins. Unfortunately, only a few reference materials are certified for methylmercury compounds.

It is understood that these materials are not sufficient to satisfy the quality assurance requirements in many laboratories performing methylmercury compounds analyses. Therefore, apart from the analyses of CRMs, the accuracy of analytical procedures for determination of methylmercury were tested by several intercomparison exercises on biological, soil, sediment and water samples. A review of these exercises has shown that the total methylmercury compounds determination in samples such as soil, sediment and water is difficult and is also method dependent.

It is generally accepted that the use of CRMs represents only one aspect of the QA/QC programme and can only cover a limited number of environmental samples. For example, concentration levels of mercury in air and water are extremely low and even highly sophisticated equipment can not guarantee accurate measurements. The reliability of the results depends on the overall procedure including sampling, storage, and laboratory handling. One way to check the accuracy of the results is to participate in field intercomparison exercises or by comparison of the results obtained by various methods. Such exercises are now regularly organized by different international agencies, RM producers, and programmes. The results obtained are encouraging, demonstrating the comparability of the data sets being generated by diverse groups around the world.

An example to demonstrate the importance of overall procedure was presented by HORVAT ET ALL. (2004) in which the effect of sampling on monomethylmercury (MeHg) concentration in coastal marine sediments was investigated. It was shown that samples taken under nitrogen atmosphere provided

significantly higher results compared to those processed under open atmospheric conditions. This study confirms that the sampling is the most important factor influencing the accuracy and uncertainty of MeHg in sediments, which can not be controlled by the CRMs. A practical consequence of this observations is that the results reported for MeHg in the literature obtained under uncontrolled sampling conditions should, therefore, be treated with great caution. This also suggests that further development and optimization is needed for mercury analyses and speciation/fractionation in soils and sediments and "Dynamic" measurements (transformation and transport measurements). It is suggested that "method specific" techniques should be avoided unless they provide information which is biogeochemically important.

Conclusions

In conclusions, chemical metrology in mercury analysis and speciation needs to further develop in order to achieve comparability of the results. Currently available matrix CRMs are not sufficient to establish comparability of chemical measurements due to poor coverage of concentration and matrix match. In order to demonstrate traceability to an international standard calibration standards for Hg speciation with small uncertainties are urgently needed. The question related to operationally defined parameters (RGM, reactive Hg in water etc.) needs to be addressed from the metrology point of view in order to demonstrate comparability of the results.

Acknowledgements

This work was supported by the Slovenian Ministry of Higher Education Science and Technology through a programs P-0143 and partially through the 5.FP of the EU, projects METROPOLIS and VIRM.

References

Horvat, M., Logar, M., Ogrinc, N., Fajon, V., Lojen S., Akagi, H., Tomyasu,T., Matsuyama, A., (2004). The effect of sampling and sample pretreatment on MeHg concentration in coastal marine sediments : presented at 7th International Conference on Mercury as a Global Pollutant. *RMZ-mater. geoenviron.*, 51 (2), 1939-1943.