

AN OVERVIEW OF DEVELOPMENTS IN ENVIRONMENTAL CERTIFIED REFERENCE MATERIAL FROM THE BRAZILIAN NMI

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Abstract: This paper aims to present the developments performed by the Chemical Metrology Division of the Brazilian NMI – Inmetro, considering the environmental demand. Inmetro addresses great part of its activities to the study of the traceability transference based on production and dissemination of certified reference material (CRM) of different areas in chemistry. So, the achievements made are the growth in developing CRM, in order to support the needs of the national industry and to disseminate traceability among the society.

Keywords: certified reference material, metrology, traceability, environment.

1. INTRODUCTION

The results from chemical measurements form the main basis for decision-making in economic, political, environmental, medical or legal fields. The ongoing economic globalization requires that these results are reliable, comparable and traceable. The Metrology is defined as "the science of measurement and its applications" and metrological traceability is a concept associated with the quality of a measurement. In the year 2000, the Brazilian NMI, Inmetro, started its activities in the field of Metrology in Chemistry, mainly responsible for keeping the national metrological standards of reference, as well as for carrying or reproducing and spread (spread is the process of providing the traceability to a large number of users via a metrological chain) of the SI units of measurement, and its harmonization on a global level, which is the essence of a NMI in each country. The performance of these tasks requires high scientific and technological knowledge, as well as, international recognition, which implies ongoing activity of scientific and technological research in the frontier of knowledge. The Chemical Metrology Division from Inmetro (Dquim) has five (05) laboratories: Organic, Inorganic, Electrochemistry, Gases and Motor Laboratories. All these branches from Dquim act in the development of certified reference material (CRM), focusing the necessity concerning trustworthy and accurate chemical analysis.

The chemical metrology plays an indispensable role mainly towards the development of reference materials, geared for many different analytical techniques in various industrial sectors. The reference materials are the pillars of standardization and metrology in chemistry ensure greater

security in the calibration of measuring instruments. Another important observation is environmental legislation, that has significantly increased, and which requires international standards of comparison. These standards (or CRM) are performed by primary methods, that are essential to the realization of the SI units and, therefore, are indispensable for establishing traceability of measurements.

2. IMPORTANCE OF CHEMICAL METROLOGY

- Reliability of measurements;
- Transpose technical barriers to trade;
- Ensuring fair terms of trade;
- Supply confidence in health, forensic and environment sectors of society;
- Quality, innovation and competitiveness.

3. THE ROLE OF A NATIONAL METROLOGY INSTITUTE (NMI)

- Locus of knowledge and credibility, based on excellence in S&T, rather than just a "deposit of standards";
- "National Reference" and its limited number
- Commitment to support the national competitiveness and defend national interests (instrument for the national industrial policy);
- Generation and diffusion of knowledge in metrology;
- International articulation and representation of the country.

4. METROLOGICAL TRACEABILITY CHAIN

A hierarchy system is represented by the metrological traceability chain, which is defined as a "sequence of standards and calibration used to relate a measurement result to a reference". A metrological traceability chain has a great importance since it shows where a measurement result is derived, that means, presents that the result of a reference measurement is metrologically traceable.

Traceability can refer to the documentation, i.e., sampling procedure, laboratory, analyst, method, etc; but as in ISO/IEC 17025 we are dealing with traceability of measurement results. That is, measurement results have to

be traceable to the metrological references used. To be specific we here use the wording metrological traceability. The current VIM [5] definition of metrological traceability is:

“Property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations each contributing to the measurement uncertainty.”

Inmetro, along with 38 other countries, is a signatory to the Mutual Recognition Agreement (MRA) of the International Committee on Weights and Measures (CIPM). The objectives of the CIPM is the establishment and maintenance of an open, transparent and inclusive of quantitative information on the comparability of services provided by National Metrology Institutes (NMI), providing technical basis for agreements involving international trade and regulatory activities. This eliminates the need to repeat analysis conducted in other countries that signed the MRA. To meet the requirements of this agreement, the NMI constantly promotes comparisons between themselves and undergoes assessments of their quality system. It is this complex and robust structure that CRM developed by Dquim are grounded, considering that the main goal always is to provide tools to Brazilian society to quality assurance and greater competitiveness of their products and services.

5. CERTIFIED REFERENCE MATERIAL

The use of reference material is an important tool in the implementation of various aspects of measuring quality. Considering that most of measuring techniques in use are based on relative measurements, it has to be recognized that calibration is a very important step in proper analytical procedures, and appropriate reference materials (RMs) are necessary to accomplish it. Besides equipment calibration and validation of analytical procedures, RM is a useful tool for periodic control of laboratory performance (proficiency estimate) and also for determining the repeatability and the uncertainty of measurements.

According to the ISO definition [1], a RM is a substance that has one or more features that are homogenous and well described, so that they can be used for calibrating a measuring device, validating a measuring method or determining chosen parameters of the materials. A RM can be either a pure substance or a mixture of components, and it may be solid, liquid or gaseous. A certified reference material (CRM) is a material that carries a certificate. One or more parameters of a CRM has been determined and confirmed according to the procedure that ensures proper referencing to the measuring unit used for the determination of a given parameter. To each certified parameter an uncertainty should be assigned at a given confidence level. The applicability of a procedure for a precise determination of the material parameters has to be confirmed several times and each time accepted independently. Certificates are issued by recognized bodies.

The use of certified reference materials (CRM) ensures that the results obtained by different laboratories are comparable and traceable. In this context, CRM are essential in maintaining a system of universal and consistent measurements make it possible to compare the measured values from one laboratory to another.

A clear hierarchy of measurement standards is already well established in the area of physical metrology, where the hierarchy must be traceable to national or international standards. However, unlike other fields of measurements, there is a demand for several chemistry standards for a very diverse range of species and these must cover a very wide range of matrix and concentrations. Moreover, often the development of a CRM is a pioneering work, namely, no previously available CRM for a particular parameter.

The problem areas for chemists are usually (chemical) method validation and calibration. Validation establishes that the method actually measures what it is intended to measure. Validation establishes that the measurement equation used to calculate the results is valid. Calibration is usually based on the use of gravimetrically prepared solutions of pure substance reference materials. The important issues here are identity and purity, the former being more of a problem in organic chemistry where much higher levels of structural detail are often required and confusion with similar components can readily occur. The uncertainty of a measurement will in part depend on the uncertainty of the purity of the chemical standard used. However, only in the case of some organic materials, where purity and stability problems can be acute, or where high accuracy assay of major components is required, will purity be a major problem. [6]

The production is directed by the CRM Guides series 30 to 35 of the International Organization for Standardization (ISO) and includes studies of homogeneity, stability and characterization as well as the estimation of measurement uncertainty at all stages. The evaluation of the homogeneity is particularly important in cases where the substance to be measured is present in a complex matrix. The stability study is divided into short and long duration. The first simulates the conditions of transport and should address the factors involved at this stage that can affect the CRM, such as temperature and time. The results of this study show that the form of transport and packaging are appropriate to the material. In the study of long term stability is developed to assess whether the material is stable during its period of validity conditions of storage. The variations observed during this period in the amount of the certified properties should be included in the determination of uncertainty, that this estimate may be considered by the user during the entire period of use of the CRM. Already at the stage of characterization may be used the following methods: a primary method for measuring, two or more independent methods on a same laboratory, measurements by an interlaboratorial comparison using one or more validated methods of accuracy. It is imperative that the values contained in the reference material certificate are traceable

the unit of measure. ISO Guide 34 [2] and an ILAC Guide [8] deal with criteria for the competence of reference material producers. These guides may provide the basis for future assessment of reference material producers.

What RM themselves should be traceable to, and how this traceability should be established, demonstrated, and reported on certificates is, therefore, a question of primary importance, mainly for RM producers. However, users of RM should also know what the endpoint of their traceability chain is, in particular for all purposes of cross-border acceptance of measurement results.

6. IMPORTANCE OF METROLOGY IN BRAZIL

- Metrology is the physical basis for quality, which is fundamental for the competitiveness of the productive sector;
- Metrology is an important factor for innovation;
- In the industrialized countries, metrological process represent about 5% of the GNP;
- Metrology is situated in the root of the productive chain in the industry.

7. METROLOGICAL TRACEABILITY AND THE ENVIRONMENT – A BRAZILIAN STUDY OF CASE

In Brazil, there are approximately eight thousand (8000) laboratories that perform metrological measurements. From all of these, only around two hundred (200) are concerning environmental analysis. Only eighty one (81) are accredited by ISO 17025 to perform these kind of analysis.

Concerning an overview in certified reference materials, from more than two thousand (2000) reference materials registered in database providers, the most part is not certified. Lots of them are not traceable to standards or primary methods.

When comparing, for instance, a national CRM of a gas mixture, such as automotive emission, and an international mixture developed at the same conditions, the price for the national CRM is two times cheaper than from a foreigner NMI.

One nice example of the activities of Dquim in order to supply the demand for CRM in society is the case of emission gases CRM. In the industrial and automotive sector, the growth and development of new technologies and the increasing number of cars on the roads, has derived a detrimental effect on the environment by changing the composition of the air and causing the warming of the earth's surface (a phenomenon known as the greenhouse effect). The greenhouse effect is due to certain gases that cause retention of infrared radiation in the atmosphere. These gases have always existed in most of Earth's history, but in recent years their concentration has increased

considerably. The identification of a source of air pollution depends, first of all, to set benchmarks of the pollutants and their effects on humans, animals, plants or other materials, as well as the criteria to measure the frequency of occurrence of pollutants and their effects.

Thus, people are exposed to pollutants at sufficient concentrations and so durable that can cause an increase in the probability of getting cancer or other serious effects of health. These health effects can bring damage to the immune system as well as neurological, reproductive (reduced fertility) and respiratory and other serious problems.

Nowadays, in cities, vehicle emissions play an important role in the level of air pollution, because they release gases such as volatile organic compounds (VOCs), carbon monoxide (CO), nitrogen oxides (NOx), sulfur oxides (SOx), and acid gases, among others. So, the analysis of air quality by the responsible agencies requires reliable and comparable analytical methods in order to reduce the emission of such gases.

Among the volatile organic compounds (VOC) it is highlighted the BTEX (benzene, toluene, ethylbenzene, o-xylene, m-xylene and p-xylene) which may be carcinogenic as mentioned above and furthermore may have neurotoxic effects and / or mutagenic. In this way, it is indispensable the strong actuation of Dquim in developing CRM destined to these areas.

These standards developed by Inmetro are produced not only to supply the internal demand, but also the international demand. There are several projects of cooperation with countries of South America, on which CRM are developed and used.

8. THE DEVELOPMENT OF CERTIFIED REFERENCE MATERIAL IN DQUIM/INMETRO RELATED TO ENVIRONMENTAL AREA

- Bioethanol and ethanol in water
- Emission gases, such as automotive and industrial emissions
- VOCs, such as BTEX in methanol (researches in developing new matrix as water and nitrogen)
- HPA in toluene (researches in developing a new matrix as soil)

9. REFERENCES

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