Traceability And Practice In Metrology In Chemistry

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Abstract

Traceability in chemical metrology has been discussed and given scientific bases for the understanding of primary methods since the formation of CCQM-CIPM. In spite of the importance at this level, NMI has still a serious task in each country to establish traceable chain for support of so diversified field measurements, which should cover all principles of chemical analysis and be applicable for all kinds of material and substances.
Description is made on an important effort done in the development of reference materials, and consequently in the comparison exercises with other NMIs, since it is a first step for CENAM to establish comparable measurement and calibration capability. An additional program is presented to invite reference materials users to convert into producers of reference materials under the program of MRTC. This program has a similar philosophy of NTRM of NIST, and looks for the efficient production and certification of CRM for the most demanded fields, by putting into practice traceability.
Additional considerations on the strategy for establishing traceability is discussed in order to achieve harmonization of traceability systems among countries, with particular considerations to the accreditation of analytical laboratories based on the competence.

Introduction

Since the signing of the CIPM MRA in 1999, the demonstration of the capability of measurement and calibration (CMC) of NMI has become one of the principal responsibilities for the establishment of a comparable and internationally recognized national measurement capability. This urgent task implies to a young NMI like CENAM a significant challenge and at the same time strong pressure.
The fact is that each NMI has a responsibility to implement the CIPM MRA according to certain guidelines, and each claim of CMC must be underpinned by evidences such as;

- a track record for delivering services in the area of the CMC
- results from relevant international comparisons
- a functional quality system that will assure the consistency of the service delivered and assure that the results obtained in RMO and CCQM comparisons are reflective of the services being delivered.

The claims of NMIs are reviewed and evaluated in RMO and JCRB after being evaluated by other RMOs, and finally accepted in the CIPM Key Comparison Data Base (KCDB), if there is no objection among RMOs. The review process in SIM has been carried out twice; on March in

2001 and 2002. The results of the first round have been now accepted in CIPM KCDB with the equivalence statement.

In 2000 NCSL meeting CENAM concluded that it is necessary that the metrology program in chemistry should have to:

1. Enhance substantially the research capability at CENAM in chemistry and materials science as well as measurement technology in collaboration with other NMIs, whereby human resource development will be an urgent task.
2. Develop institutional programs to conduct research works oriented to support primary metrology in chemistry.
3. Develop collaboration programs with reference laboratories, to ensure the national dissemination capability and traceability in chemical measurements.
4. Involve actively with standardization activities to support reasonably practicable decision-making by reliable chemical measurements.
5. Develop collaboration programs with private entities to increase the efficiency and coverage of the metrological services at CENAM.

In this paper some experiences obtained of these actions in the last two years will be discussed for establishing traceability in chemical measurements in Mexico.

Traceability in chemical measurements and the role of NMI

The principal elements of the traceability in chemical measurements are: primary analytical methods, reference materials and valid analytical methods suitable to some available instruments for a group of materials, according to their nature, intervals of measurements in a specific matrix. These elements should serve to establish an uninterrupted chain of comparisons in chemical measurements.

Based on the CCQM proposals on potential primary methods CENAM has been working with primary pH measurement system, electrolytic conductivity measurement system and coulometry [2], which turned out to be major supports for the satisfaction of the principal needs of the industry. In the same direction effort has been maid in establishing primary methods in gravimetry and isotopic dilution with mass spectrometry and CENAM is now participating some Key comparisons (KC) and Pilot Comparisons of CCQM and of SIM by using these primary methods for the CMC claims. Now it is considered essential to establish our capability in measurement for purity assessment of high purity chemicals, on which largely depends the capability of NMI for calibration and certification of reference materials.

Dissemination structure

In order to offer traceable metrological services to field laboratories, it is necessary to provide them with some tools for evaluating the measurement methods as well as for providing reference values for quantification. Consequently, the role of NMI is not only to develop primary and transfer methods and instruments, but also to make certified reference materials (CRMs) available to them.

In most field analysis in which separation techniques are principal difficulties, the traceability chain could not be accomplished easily by the use of calibration standards of simple matrix. Consequently, either the validation of analytical methods or calibration by complex matrix reference materials is required. However, unless the process is clearly described with corresponding uncertainty, the validation process becomes a bottleneck for establishing a traceable measurement. Then, in most applications, the role of CRMs of similar matrix becomes crucial in the quality of measurements.

In the previous work, mention was maid on three principal elements for establishing traceable dissemination structure in a country; namely producers of reference materials, reliable reference laboratories, which can provide secondary reference materials and validation of methods and reliable testing laboratories to provide with conformity assessments. In the present work some additional considerations are included to make a robust national traceability measurement system.

Strategy for implementing traceable chemical measurements.

In order to establish a sound nation-wide metrological dissemination process and to support reliable field measurements in chemical analysis or most generally in quantity of substances, CENAM has established the following strategy:

- Implementation of Primary Methods after CCQM
- Assessment of traceability to national standards of other countries
- Promotion of Sectorial Reference Laboratories
- Development and certification of Reference Materials by CRM program and MRTC program
- Promotion of Proficiency Testing (PT) scheme with certified value
- Recommendation of uncertainty budget in field analysis.

The second point has been requested and put into practice as a part of formal recognition process of accredited testing laboratories who have to demonstrate the traceability measurements through usage of standards traceable to national standards of foreign countries, instead of national standards. This is very common for chemical measurements, because only few CRMs of CENAM are yet available in the market, and analytical laboratories should look for other CRMs which have demonstrated traceability to national standards of foreign countries. Due to the historical reasons, there are many CRM providers who are not necessarily NMIs, but private companies or industrial associations who have been developing RMs as the tools for their quality management, and in the course of assessment, some difficulties were encountered in the traceability assessment process, because they normally declare very small uncertainties for chemical components of substances without any supporting evidences of traceability, but most analytical laboratories use them as references due to the lack of CRMs.

Consequently, one of the responsibilities of CENAM is to provide them with alternative to the simple assessment, by promoting national RM producers, according to their needs, and by assigning certified values traceable to the SI, in addition to its own CRM program. The idea is the promotion of SI traceable RM certification program which provides traceable reference materials starting with candidate materials provided by third party producers, and being certified by CENAM under the name of MRTC. This program is conceptually equivalent to the NTRM of NIST. This program is expected to meet the needs for CRMs in types and availability, and to reduce gradually the demands for CRMs traceable to national standards of foreign countries.

Sectorial Reference Laboratories

The availability of MRTC depends on the number of RM producers, which could be entities who have the responsibility in conformity assessment of regulations. From this stand point, more collaboration is expected with public sectorial laboratories, which are the technical authorities in the execution of mandatory standards and regulations. The idea is to give them a metrological responsibility in that sector called sectorial reference laboratories. The functions of them are expected to be as follows:

- Establish traceability of their measurements to CENAM in all the quantities required in their field of responsibility
- Disseminate the accuracy of the national standards to the field laboratories by participating in the program of MRTC
- Provide PT to field laboratories to establish comparability and reliability
- Develop and validate analytical methods in the field of responsibility
- Approve type of measurement instruments used by the field laboratories for the conformity evaluation to the specific regulations under their responsibility.

This task may deserve the highest priority of the government in the next few years, to extend collaboration programs to the fields of pharmaceuticals, health, advanced materials, commodities and forensics, and also to look for the modification of the actual law to incorporate explicitly into the national metrological infrastructure, by assigning a specific metrological responsibility to these reference laboratories.

One of the principal concerns in the accreditation of testing laboratories is how to evaluate their competence to demonstrate the traceability of their measurements to SI. For the analytical laboratories, the use of CRMs combined with MRTCs is one necessary condition, but may not be sufficient. In order to promote the establishment of reliable testing laboratories, CENAM has been organizing or collaborating in organization of inter-laboratory comparison exercises. The PT scheme adopted by CENAM for these exercise is the use of the reference value assigned by CENAM and the evaluation is proposed based on the comparison of the reported value of a laboratory to the assigned value, by defining a parameter called Mean Quadratic Error. This parameter is considered as the estimated uncertainty of the participating laboratory for the exercise and its measurement capability is expressed as the ratio to the measurement capability of CENAM by comparing their estimated uncertainty to that of CENAM. The effective improvement of the overall performance has been reported elsewhere[1].

These events will be organized in the future in coordination with CENAM by sectorial reference laboratories. These efforts should be in the highest priority of national metrology system to ensure and reinforce robust dissemination channels in each strategic field.

Measurement capabilities of CENAM in metrology in chemistry

To support the national traceability scheme for chemical measurements, CENAM submitted over 150 claims to the first round SIM review process in 2001. These claims covered measurement capabilities basically in those fields where industrial and sectorial needs were detected, and CRMs were developed. Those evidences obtained in the participation in the SIM pilot studies before the CIPM-MRA (2 in 1997, 5 in 1998 and 13 in 1999), were not necessary be considered as supporting evidences, until CENAM participated for the first time in CCQM-K9 comparison of pH measurements in the end of 1999. As a consequence of the lack of sufficient evidences only 42 entries were sent to JCRB and approved in October 2001.

After the signing of CIPM-MRA the importance of the participation of CENAM in SIM pilot studies of comparisons has increased and participated successfully in most comparisons; namely, pH, trace elements in drinking water, trace elements in sediments and nutrition values in infant formula food, environmental gas analysis. In order to participate in the CCQM KCs, CENAM has asked to be included as a member in four Working Groups of the CCQM, as well as in CCQM.

At this moment CENAM holds an official observer status in CCQM since 2001, and member status in WGs in Gas Metrology, Electrochemistry, and Inorganic Analysis.

In the second cycle of the CMC claims of this year, CENAM has submitted only 30 claims, but 17 of them have been coded “under review”, because the supporting evidences derived by the results of comparisons of CCQM and SIM were not ready on the time of SIM review process.

The way how each NMI declares its measurement capabilities is to submit data to Appendix C of CIPM MRA, which is now available in the BIPM Web site, where every capability is referred to either the uncertainty declaration of the own CRMs or the calibration service. And the supporting evidences are in the Appendix B which stems from the results of KC´s

Future Plan

In the course of the evaluation process of the plan1999-2001, CENAM´s development plan 2002-2006 was also discussed and among many areas that CENAM have not developed its measurement capability, the following areas are considered important to develop economy and the quality of life: agrochemistry, bioscience and technology, macromolecular chemistry and medicinal chemistry.

While continuing development in the areas where real needs were detected, and our capabilities have been recognized such as; environmental chemistry, inorganic chemistry including geochemistry, effort should be made in establishing primary methods in organic chemistry, which should provide with metrological support to the most urgent needs in organic analytical chemistry, including clinical, and trace organic compounds in minerals.

One of the important tasks still under development in CENAM is the human resource development, which enables to lead research works in those fields where analytical chemistry

requires constant innovation, such as; electrochemical sciences, X-ray spectroscopy for evaluation of chemical composition, separation science, elemental mass spectrometry.
The role of CENAM as a key organization to construct a nationwide traceable system in chemical measurements has been recognized as a result of the effort of development in the decade. However it is required to make a big stride to guarantee the sound national metrology system in chemistry, by keeping-up with the constant progress in science and technology and by increasing its capacity to support the diversified needs for reliable measurements in chemistry. The most important mission of CENAM is to satisfy the metrological needs of the society, not only in the present but also in the future. That is why it is really important to make reasonable and realistic decisions in its development process, which satisfy the actual needs, but at the same time, which may give the positive impact in the future.
Within the region of North America, CENAM is playing a kind of complementary role with two giants, NIST and NRCC, since the local needs were very special and not have been satisfied timely fashion. The history of their development has an enormous pressure on the quality of the CENAM´s services. The CMC claims of NIST and NRCC recognized in the first cycle of CIPM-MRA are 733 and 102, respectively, and they are only partial capabilities of these Institutions. But CENAM is also contributing in a same manner to the development of infrastructure in other SIM member countries. CENAM is not only demonstrating one of the possible ways of development of metrological infrastructure in a small economy, which should be competitive against other big economies, but also the way how to collaborate in the development of RMO.

Concluding Remarks

Considering the necessity of a robust national traceable measurement system 6 strategic actions have been proposed based on the experience obtained in the construction of a modest infrastructure in metrology in chemistry in CENAM.
While CENAM´s primary task is to develop primary methods of measurements in quantity of substances, some complementary actions to enable easy access of the CRMs and traceable MRTCs to the final users, whereby the definition of sectorial reference laboratories should play crucial role in the success of the implementation through the modification of the legislation on the particular responsibilities for the sectorial reference laboratories.
It is considered important the role of CENAM in the development of metrological infrastructure in the Americas, according to the experience obtained and disseminated to the member countries.

References

[1] Arvizu-Torres R., et. al., Biological and environmental reference materials in CENAM, Fresenius´J. of Analytical Chemistry, vol. 370, No. 2-3, June 2001, pp156-159, Springer-Verlag

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