

Advances in Chemical and Environmental Metrology

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Need for metrology in chemistry and its applications in environmental measurements

The globalization of trade and industry requires reliable and comparable measurements. Calibration, measurement and testing results with stated measurement uncertainty should not be doubted and refused. International recognition and acceptance of reliable results should become guaranteed. It is a general policy to strive towards taking away at least the non-tariff barriers to trade in the world, which is an important if not essential issue on the agenda of the WTO Technical Barriers to Trade committee.

However, metrology in chemistry is not only addressing industry, export and trade issues. Health care, food safety, forensics and many other areas also require reliable measurements traceable to globally agreed and recognized long term stable references. Similarly environmental and pollution control measurements, aiming to improve the environment in which we live and to monitor possible climate change, require accurate comparable measurements, traceable to long-term stable references as defined and agreed internationally under the Inter-Governmental Treaty of the Metre Convention, being the International System of Units SI. Faulty measurements and wrong measurement results lead to wrong decisions with considerable damage for our environment and /or enormous financial, economic and social losses.

The international metrological infrastructure as organised under the Inter-Governmental Treaty of the Metre Convention

The Inter-Governmental Treaty of the Metre Convention created in 1875 and signed by the governments of the Member States aims at the establishment of a globally harmonized and coherent system of units and measurement standards and methods, traceable to long term stable references, nowadays mainly the fundamental constants of nature. The Metre Convention has so far been signed by 51 Member States, covering about 95% of global trade. Apart of Member States now also some 30 other states and economies cooperate as Associates of the General Conference of Weights and Measures (CGPM) under the Metre Convention. Taking into account the importance of having own measurement results internationally accepted there is a rapidly growing interest of countries, not yet cooperating and having their national measurement and testing system recognized and accepted, to sign up as an Associate of the CGPM and through that to become a participant in the CIPM Mutual Recognition Arrangement.

The International Committee of Weights and Measures (CIPM), acting on behalf of the Member States, is responsible for the execution of the decisions by the Member States and acts as the governing board of the International Bureau of Weights and Measures (BIPM). The CIPM is assisted by 10 technical/scientific Consultative Committees covering all fields of metrology.

The BIPM is the executive office of the Metre Convention. It has a number of metrological laboratories in charge with the realization and maintenance of global measurement standards and rather unique transfer standards. The BIPM also organizes international comparisons of

the national measurement standards as realized and maintained by the NMI's of the different countries. Offices and laboratories of the BIPM are located in Sèvres (Paris), France.

The Consultative Committee for Metrology in Chemistry – CCQM

The CIPM established in 1993 the Consultative Committee for Amount of Substance – Metrology in Chemistry (CCQM), addressing all issues on metrology in chemistry. The CCQM has developed very quickly, now being the biggest Consultative Committee under the CIPM. The CCQM has about 50 member and observer organizations, being NMI's and other designated institutes and several inter-governmental and other international organizations, like the World Meteorological Organization (WMO), World Health Organization (WHO), International Federation of Clinical Chemistry and Laboratory Medicine (IFCC), Joint Committee on Traceability in Laboratory Medicine (JCTLM), International Atomic Energy Agency (IAEA), International Union of Pure and Applied Chemistry (IUPAC), ISO Reference Materials Committee (ISO REMCO), Cooperation on International Traceability in Analytical Chemistry (CITAC), International Laboratory Accreditation Cooperation (ILAC), World Anti Doping Agency (WADA), pharmacopoeia, forensics and security. In a number of cases the CIPM has signed formal Memoranda of Understanding and Cooperation with these Inter-Governmental and international organizations.

The CCQM meets yearly in April while five of its seven working groups meet twice a year. The aim of the CCQM is to establish worldwide comparability through traceability to the SI and if not (yet) feasible to other internationally agreed references, for example like the WHO International Units for biological activity. The development and understanding of primary methods is fostered, while also considerable attention is paid to primary pure reference materials and the validation of traceable methods.

Other activities under the CCQM include the calculation of the measurement uncertainty, the vocabulary and the final discussion on the quality and validity of the calibration and measurement capabilities (CMC's) and CRM's claimed by the NMI's and other designated institutes as credible and reliable services and means of delivering traceability to their customers.

However, most of the activities by the CCQM can be distinguished in studies (research, try outs, etc.) and key comparisons. For further details see the BIPM webpage www.bipm.org

Areas defined in the overall framework

The very broad field of metrology in chemistry has been defined in a number of fields, namely:

- health (clinical diagnostic markers, steroids, hormones, electrolyte elements)
- food (pesticides, toxins, drinking water)
- environment (air, global warming, water, soil, contaminants in sediments and tissues)
- advanced materials (semiconductors, alloys, polymers, plastics, catalysts)
- commodities (oil, cement, precious metals, alcohol content, moisture)
- forensics (drugs, explosives, breath analysis, DNA)
- pharmaceuticals
- bio-technology (GMO's, DNA profiling, proteins, diagnostics)
- general analytical applications (purity, pH, isotopic standards, calibration solutions)
- surface analysis

The examples between brackets are not at all a full list of all what is going on.

Traceability and comparability

The aim of the global measurement system and thus of the BIPM, being the global organization coordinating and promoting this, is to realize comparability of measurement results in time and place. **Comparability** is the possibility to compare a measurement result obtained in country A with the result of the same type of measurement in country B. This does not mean that it is necessary that all measurement and test results must have the same accuracy, but within the statement of uncertainty the results should be comparable. Of course, one should measure the same quantity/measurand and express it in the same units.

Comparability can only be reached through making measurement and test results **traceable** to the same long term stable global reference system, which is the SI. In general results of chemical measurements are expressed in terms of the mol, kg, liter or any combination (multiple and sub-multiple). At the highest level of accuracy primary methods are applied and reference is made to well characterized primary pure reference materials. Among others, potential primary methods are gravimetry, coulometry, titrimetry, calorimetry, IDMS, INAA and cavity ring down spectroscopy, assuming these methods are fully understood and applied properly. In the practical situation many other methods are used. This is fully acceptable as long as these methods are calibrated and have been validated and have an uncertainty fit-for-purpose. In particular much attention has to be paid to a careful and complete understanding and definition of the measurand, and to sample preparation and treatment, as these phases of the measurement process often generate the largest contributions to the overall measurement uncertainty.

Pure reference materials play an essential role in building up the traceability chain for chemical measurements as, according to the nowadays definition of the mole, one has to identify the entities concerned. This means that high accuracy purity analysis is very important.

Primary Reference Materials are CRM's of which the composition, stability, homogeneity and life time have been characterized completely. The value assignment has to be done on the basis of the application of several different, preferably primary, methods. Further a complete measurement uncertainty budget has to be given. The whole certification process should take into account the guidance given in the ISO Guides 34 and 35.

Matrix materials are used for validation and the determination of recovery factors. As such matrix CRM's can be part of the calibration chain and are thus also considered by the CCQM.

CCQM Working Groups and results of activities

The work under the CCQM is carried out by 7 working groups:

- Key Comparisons and CMC Quality, chaired by Dr. L. Mackay, NMIA, Australia
- Organic Analysis, chaired by Dr. W. May, NIST, USA
- Inorganic Analysis, chaired by Dr. M. Sargent, LGC, UK
- Gas Analysis, chaired by Dr. E. de Leer, NMi-VSL, The Netherlands
- Electro-chemical Analysis, chaired by Dr. M. Mariassy, SMU, Slovakia
- Surface Analysis, chaired by Dr. W. Unger, BAM, Germany
- Bio-Analysis, chaired by Dr. H. Parkes, LGC, UK

All the working groups have an extensive programme of studies (research, technical/scientific/methodology development work, try out comparisons, etc.) and of Key Comparisons.

The Key Comparisons are used to assess the capabilities and the competences of the participating NMI's and other designated institutes. The results of the Key Comparisons also

form the basis for determining the amount of equivalence between the participating NMI's, which gives us the answer to the question how well comparable we are.

The Key Comparison Reference Value (KCRV) is often based on a measurement value obtained by the application of a primary method, for example gravimetry, or on a (weighted) mean/median value calculated from all the measurement results. The final choice is determined case by case, on scientific considerations and depending on the conditions under which the Key Comparison has been carried out.

The results of the Key Comparisons are published in Appendix B (Key Comparison Data Base – KCDB) of the CIPM Mutual Recognition Arrangement on the BIPM web-page (www.bipm.org)

Results are also published in Metrologia or other scientific journals.

Also, important results of Studies are published in Metrologia or other journals.

In general one can observe that the results of the Studies and Key Comparisons are very promising. The uncertainty is often better than 1% and in some cases even one or two orders of magnitude better than 1%, while in many cases also the comparability for experienced laboratories is within the limits of uncertainty.

Environmental metrology

The need for accurate environmental measurements at ambient levels with a small to very small measurement uncertainty is evident. Decisions made on the basis of environmental and pollution measurements can have dramatic consequences, like the closure of factories, ending certain agricultural activities, prohibition of new building activities, etc. As a result, for example, the electronics industry has developed systems of very careful production of chips controlling all the possible pollution aspects.

The determination of the type of pollution and its isotopic composition may lead to the source of pollution like stack emissions, car exhaust gases and industrial and agricultural activity spoiling our water.

In the scope of the Kyoto Treaty states can trade CO₂ shares. As large amounts of money may be involved, accurate measurements are very desirable. The same applies in cases of waste disposal trading.

Conclusions with respect to possible climate change have to be based on very accurate measurements which, over long periods of time, are traceable to long term stable references. This requires traceability to the International system of Units – SI. The activities carried out under the World Meteorological Organization (WMO) by the Global Atmospheric Watch (GAW) programme require accurate measurements of the air composition (ozone and other green house gases) with very small uncertainties approaching 1×10^{-4} , globally comparable and traceable to very long term stable references. This requires primary gas mixtures and the application of primary methods.

Environmental measurements include measurements of air, water, soil, and living organisms. Water includes surface, river, ocean, drinking and waste water.

As most of the pollution, created by industrial and agricultural activities as well as a result of washing, personal care and the use of medicines finally ends up in the coastal waters the status of the living organisms in the coastal waters, like shrimp, oysters, fish and dolphins are very good indicators for the measure of pollution and the changes in pollution over time. In particular NIST's Hollings Marine laboratory in Charleston, SC is focussing on these issues.

Activities by the BIPM and the CCQM Working Groups in support of environmental measurements

As already indicated above, the CCQM is in charge with establishing global comparability and traceability in all fields of chemical measurements. So, its studies and comparisons cover a much wider field than the environmental area. Nevertheless many activities are addressing important environmental issues. A number of these are reported below.

The world primary standards for ozone measurements are realized and maintained by NIST (USA) and the BIPM. The BIPM nowadays organizes regular comparisons of primary ozone standards owned and used by different laboratories in the world including laboratories operating in the scope of the WMO GAW programme.

The CCQM WG on Gas Analysis organises regular comparisons of all types of green house gases (CO₂, CH₄, NO, SO₂, CFCs, SF₆, etc.). By the activities of the WG on Gas Analysis the comparability of the measurements and the measurement uncertainty has been improved considerably.

The studies and comparisons organised by the CCQM WG on Inorganic Analysis include among others Cd and Pb and other trace metals in water and in sediments and sewage sludge, TriButylTin in sediment As in fish and shellfish, methyl-mercury in salmon, As, Se, Hg, Pb and methyl-Hg in tuna fish.

The CCQM WG on Organic Analysis has studies and comparisons, among others with respect to p,p'-DDE in fish oil, p,p'-DDT in fish oil, Gamma-HCH in fish oil, malachite green in fish, organic contaminants in mussel tissue, PAHs in soils and sediments, PCBs congeners in soils and sediments and VOCs.

The CCQM WG on Electrochemical Analysis is in charge with improving the quality of pH and electrolytic conductivity measurements. Accurate electrolytic conductivity measurements are very important for the salinity measurements of the oceans. And the salinity is also an indicator for climate change.

As it is impossible to carry out comparisons for all types of measurands and matrix combinations and methods and procedures, the CCQM focuses on those types that are key for judging the competences and capabilities, including the different techniques used, of the NMI's and other participating designated laboratories in delivering reliable traceability to the calibration, measurement and testing laboratories.

Apart of chemical measurements also optical radiometry is used for measurements of environmental parameters. The Consultative Committee for Photometry and Radiometry (CCPR) in close cooperation with the WMO and the International Commission on Illumination (CIE) carries out studies and comparisons addressing these issues. And of course the Consultative Committee for Thermometry (CCT) addresses the issues of an accurate and long term stable temperature scale.

The CIPM Mutual Recognition Arrangement (CIPM MRA)

The CIPM Mutual Recognition Arrangement, operating under the Inter-Governmental Treaty of the Metre Convention has been created and signed for the first time in 1999 and has proven in the mean time to be very valuable to the users: NMIs, accreditors, regulators, measurement and test laboratories, traders, industry and other international and inter-governmental organizations, like the WMO. Participants in the CIPM MRA are the NMIs and other designated institutes of the Member States of the Metre Convention and of the Associate states and economies of the CGPM. Also other international and inter-governmental organizations with an interest in metrology can bring in their reference laboratories. So far, the CIPM MRA has also been signed by the International Atomic Energy Agency (IAEA) and

the European Commission, bringing in respectively their laboratories in Austria for ionizing radiation and chemistry (IAEA) and laboratories for chemical measurements and reference materials (EU JRC IRMM) and environmental measurements (EU JRC Ispra).

The WMO is now considering to sign up as well on behalf of the WMO GAW reference laboratories.

The CIPM MRA is based on globally recognized, peer reviewed capabilities and competences of the participating NMIs and other designated institutes, underpinned by the results of regular series of laboratory comparisons, while all participating institutes must have a quality system in place in compliance with ISO/IEC 17025 and ISO Guide 34 in the case the institutes claim Certified Reference Materials as the mechanism of delivering traceability to their clients. Regional and Inter-regional review of quality systems and claimed calibration and measurement capabilities takes place.

In the Key Comparison Data Base (KCDB) of the CIPM MRA (see the BIPM website www.bipm.org) the participating countries, economies and inter-governmental organizations can be found as well as the recognized NMIs and other designated institutes (in Appendix A). The reviewed and approved calibration and measurement capabilities and CRMs, delivered as a mechanism for disseminating traceability, in the field of chemistry are published in the Appendix C to the CIPM MRA. The results of comparisons demonstrating the validity of the MRA and indicating the degrees of equivalence between the participating institutes are published in the Appendix B to the CIPM MRA.

Establishing global comparability requires cooperation with several other national, regional and global organizations, like ILAC and ISO and sector specific organizations.

The CIPM MRA is an essential element in establishing confidence in other international arrangements, like the Arrangement of the International Laboratory Accreditation Cooperation (ILAC Arrangement). The CIPM MRA and the ILAC Arrangement are fully complementary and fully tuned to each other. The BIPM and ILAC have established a joint committee to discuss matters of importance and issues for further improvement and joint customer satisfaction.

Conclusions

Chemical and Environmental Metrology is well underway and has proven to be highly needed and valuable for those involved in environmental and pollution control. Over the last 15 years enormous progress has been made, demonstrating that much more accurate, traceable measurements in chemistry and its environmental applications can be realized.

The concept of measurement uncertainty has been introduced and is now becoming applied. Still much work has to be done. Cooperation with all the stakeholders will be broadened and training and know-how transfer will be fostered. It is essential that on the national and regional level also cooperation with the other stakeholders will become realized. It is highly recommended that where relevant the NMI's designate other competent institutes, for example in the field of environmental measurements, clinical chemistry and food testing, as a NMI for metrology in the area of environmental measurements, respectively clinical chemistry and in the area of food testing. These designated institutes join in the activities of the CCQM under the Metre Convention, while their CMC's may become published under the CIPM MRA. In this way a virtual NMI or a network of decentralized NMI's will be developed, serving the needs of a country in a quick and most efficient and effective way. There are still several points to pay attention to and to be solved. For example, much more attention has to be paid to the definition of the measurand, to method dependent measurands, measurement uncertainty budgets, matrix problems, which CRM's are really reliable and

traceable, which key comparisons are really key, etc. But national, regional and international cooperation will sort out all these issues during the coming years. It is therefore planned to organize in 2007 a joint symposium in Geneva by the CIPM/BIPM, WMO and the CIE addressing all the environmental measurement issues.

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