Publishable Summary for 16RPT01 ChemMet-Cap
Development of scientific and technical capabilities in the field of chemical analysis

Overview

Metrology in chemistry is a rapidly growing field of metrology, strongly driven by societal needs for reliable chemical measurements as well as legislation and international agreements. Metrological comparability of measurement results is a key requirement in many situations, such as in cross border trade, in laboratory medicine, and in transnational implementation of environmental regulations. Therefore, this project aims to improve the research capabilities in the field of metrology in chemistry, such as the capability to develop analytical procedures, for emerging National Metrology Institutes and Designated Institutes as well as to demonstrate the uptake of the improved capabilities through the application to case studies.

This will be addressed providing training to the less experienced NMIs/DIs. When these have acquired the necessary level of measurements capacities, the analytical methods implemented will be used to provide reference values in proficiency testing schemes, certify reference materials and providing trainings to the end users community.

Need

In almost all chemical sectors, trace analyses are essential. This may be environmental monitoring of pollutants (such as organic, inorganic and macroscopic contaminants) in air, water and soil but also for waste monitoring, measuring impurities in industrial products and as residues in food. Trace analyses are particularly important as limit values set by legislation decrease. Clearly, small concentration levels of those chemicals must be measured with small uncertainties, typically better than 10 %. Moreover, establishing metrological traceability of measurement results is a prerequisite to obtain the spatio-temporal comparability of measurement results.

Field laboratories for routine chemical analyses need reliable tools such reference materials and reference measurements in order to establish metrological traceability and to demonstrate their capabilities to meet the environmental EU Directives and food safety requirements in terms of low limit of quantification (LOQ) often close to, or even lower than, few nanograms per kilogram (ng/kg). Heavy metals such as cadmium (Cd), lead (Pb), mercury (Hg) and nickel (Ni), are among the inorganic pollutants regulated by the Water Framework Directive (WFD) with set Environmental Quality Standards (EQS) of 0.2 µg/l for Cd, 7.2 µg/l for Pb, 0.05 µg/l for Hg, and 20 µg/l for Ni.

Moreover, pH is one of the most common routine analyses providing quick information about pollution and/or contamination risk. The pH is typically measured by field laboratories with an uncertainty of 0.01 pH but in order to assess their performances and to calibrate the routine instruments, buffer solutions characterised with an uncertainty better than 0.01 pH are needed.

Primary methods such isotope dilution mass spectrometry (IDMS) and secondary pH measurements need to be developed in order to be able to provide well-characterised reference materials and reference measurements but not all the NMIs/DIs have today the analytical capabilities to provide field laboratories with the necessary metrological tools. These needs will be addressed by objectives 1, 2 and 3. The capabilities developed in the frame of this project in terms of measurement procedures will able to establish the direct traceability to SI units and for research in metrology in chemistry will support sustainable approaches for the provision of reliable tools such as certified reference materials and proficiency testing schemes to enhance the confidence in the chemical analysis results.

As an example in the field of environmental monitoring, since the beginning of 2015 EU Member States have to implement the European Water Framework Directive (WFD Directive 2000/60/EC) with the engagement that waters must achieve good ecological and chemical status, to protect human health, water supply, natural ecosystems and biodiversity. In this respect, transnational research collaboration is a priority and particularly in region having common interests. A typical case is the Black Sea region, which is an area that requires coordinated action at the regional level, according to the Black Sea Convention. In order to implement EU Policies such as the WFD, the Countries of the Black Sea Region partners in this project (Bulgaria, Romania, Turkey and Greece) need to improve the quality of the routine analyses performed by field laboratories, in order to be able to assess the actual state of the national water bodies. These Countries also need to reinforce their synergies. This will lead to a sharing of the analytical competencies and the services for end-users such as field laboratories and accreditation bodies.

Through its European Neighbourhood Policy (ENP), the EU works with its southern and eastern neighbours to achieve the closest possible political association and the greatest possible degree of economic integration. Tunisia needs to dispose of reliable and acceptable data in compliance with the EU import requirements in order to improve the exchanges with the EU Countries. These needs will be addressed by objectives 4 and 5.

Objectives

This project addresses the following scientific and technical objectives:

1. To develop traceable measurement capabilities for the analysis of heavy metals (for concentrations at ppt and ppb levels (depending on the matrices) with uncertainties less than 10 % by developing isotope dilution mass spectrometry (ID-ICPMS) methodology as a primary procedure for elemental determination.
2. To develop a secondary method for pH measurement and to apply the method for the production and characterisation of reference pH buffer solutions with a target uncertainty of 0.008 pH for the calibration of pH-meters and as reference samples for interlaboratory comparisons and proficiency testing.
3. To apply the methods developed (ID-ICPMS) to environmental and food samples to determine the heavy metals content in representative matrices, such as potable and natural waters, sediments, and different types of fish/biota samples.
4. To validate the developed methods (secondary pH procedures, ID-ICPMS) by participation in suitable international comparisons (organised by CCQM, EURAMET, another RMO, and/or bilateral – between the NMIs participating in the project) and hence to underpin the development of appropriate CMCs (Calibration and Measurement Capabilities) for submission to the BIPM Key Comparison Database.
5. To develop individual strategies for the long-term operation of the capacity developed, including regulatory support, research collaborations, quality schemes and accreditation. The involved NMIs/DIs will also develop strategies for offering calibration services from the established facilities to their own country and neighbouring countries.

Progress beyond the state of the art

To develop traceable measurement capabilities for thein inorganic analysis of heavy metals (for concentrations at ppt and ppb levels (depending on the matrices) with uncertainties less than 10 % by developing isotope dilution mass spectrometry (ID-ICPMS) methodology as a primary procedure for elemental determination. (Objective 1)

For chemical measurements, the formal establishment of calibration hierarchies is more recent than for physical metrology. The Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) has selected measurement approaches that have the potential for being primary reference measurement procedures, ensuring the direct traceability to International System of Units (SI) of the measurement results.

One of the common analytical techniques for elemental trace analysis is the Inductively Coupled Plasma Mass Spectrometry (ICP-MS). ICP-MS has many advantages over other elemental analysis techniques such as atomic absorption spectrometry (AAS) and ICP Atomic Emission Spectroscopy (ICP-AES), including detection limits for most elements equal to or better than those obtained by AAS, the ability to handle both simple and complex matrices with a minimum of matrix interferences due to the high-temperature of the ICP source, superior detection capability than ICP-AES with the same sample throughput, and the ability to obtain isotopic information.

Different calibration approaches such as external calibration and standard addition are possible for ICP-MS, but only the calibration approach based upon the Isotope Dilution (IDMS) is one of the primary reference measurement procedures owing the highest metrological standing, with measurement uncertainties of few percent.

However, the IDMS approach requires experienced operators, since many technical aspects have to be carefully evaluated and taken into account in order to obtain accurate results. This means that not all the NMIs/DIs are currently sufficiently experienced to apply this methodology.

The project will improve the capabilities of the emerging NMIs/DIs in elemental quantification by the IDMS approach in matrices representative of both environmental and food safety issues with uncertainties lower than 10 %.

So far, the three less experienced NMIs/DIs have started to acquire the skills necessary to perform isotope dilution autonomously.

To develop a secondary method for pH measurement and to apply the method for the production and characterisation of reference pH buffer solutions with a target uncertainty of 0.008 pH for the calibration of pH meters and as reference samples for interlaboratory comparisons and proficiency testing. (Objective 2)

For pH measurements, the primary method enabling metrological traceability to SI units is established by use of the Harned cell, a potentiometric cell without transference. Secondary methods involve cells that have greater uncertainties associated with the results but are more convenient practically than the Harned cell.

The project will allow the implementation of a secondary method for pH measurement for the characterisation of buffers used by field laboratories with a target uncertainty of 0.008 pH.

So far, a secondary cell has been designed and will be ready soon to start the work on the characterisation of the secondary buffers.

To apply the methods developed (ID-ICPMS) to environmental and food samples to determine the heavy metals content in representative matrices, such as potable and natural waters, sediments, and different types of fish/biota samples.(Objective 3)

Chemical analyses present difficulties in that almost specific measurement procedures would be needed for each of the millions of chemical compounds in different matrix chemical compositions. Therefore, the project will develop strategies to provide methods able to cover wide ranges of representative analytes in representative matrices. The partners will work on matrices relevant for both environmental and food safety studies where the analytical challenges will be representative of a large panel of difficulties that can be encountered, such as the risk of sample instability, the presence of interferences, difficulties in dissolving the material. By the end of the project it is expected that the partners will be able to adapt the measurement procedures developed in the project to different samples of a similar nature.

Two partners are working together to develop suitable reference materials (RMs), i.e. one fish RM and one water RM. These RMs will be ready in the next reporting period to be distributed to the partners to be characterised.

To validate the developed methods (secondary pH procedures, ID ICPMS) by participation in suitable international comparisons (organised by CCQM, EURAMET, another RMO, and/or bilateral – between the NMIs participating in the project) and hence to underpin the development of appropriate CMCs (Calibration and Measurement Capabilities) for submission to the BIPM Key Comparison Database. (Objective 4)

When a measurement procedure has been developed, NMIs/DIs will be invited to participate in peer-to-peer interlaboratory comparisons in order to demonstrate their measurement capabilities in a specific field. After the successful participation, the NMI/DI can publish on the Key Comparison Data Base (KCDB) their Calibration and Measurement Capabilities (CMCs), i.e. the services that they can provide on the basis of that measurement procedure. By the end of the project it is expected that new CMCs (at least one per NMI/DI) will be published on the KCDB.

To develop individual strategies for the long-term operation of the capacity developed, including regulatory support, research collaborations, quality schemes and accreditation. The involved NMIs/DIs will also develop strategies for offering calibration services from the established facilities to their own country and neighbouring countries. (Objective 5)

The project will lead to improved research capabilities for the less experienced NMIs/DIs, such as the capability to develop reference methods for new pollutants/contaminants, thanks to the participation in collaborative studies with more experienced Institutes in a way that they will be able to rapidly adapt their measurement capabilities towards new legal and standardisation requirements.

Moreover, services which are not currently available at the moment in the counties of the emerging NMIs/DIs involved in the project, such as calibration facilities, reference materials and provision of reference values, will become available by the end of the project. Finally, through the establishment of roadmaps for long term strategies, the emerging NMIs/DIs will create national networks with regulator bodies, such as standardisation and accreditation bodies.

Results

To develop traceable measurement capabilities for the analysis of heavy metals (for concentrations at ppt and ppb levels (depending on the matrices) with uncertainties less than 10 % by developing isotope dilution mass spectrometry (ID ICPMS) methodology as a primary procedure for elemental determination (Objective 1).

LNE has provided trainings on isotope dilution ICPMS to two Institutes (BIM and BRLM), according to the plans. The following points have been addressed:
Matrix digestion of a fish, rice and sediment samples, evaluation of the matrix composition, choice of suitable isotopes and characterisation of the natural isotopic composition of the analyte (in particular for elements with an high variability such as Pb), preparation of the standard (including the evaluation of its purity if not certified), evaluation of the blanks, application of the ID equations and estimation of the uncertainty budget following the GUM (Guide to the Expression of Uncertainty in Measurement) approach. Furthermore, two candidate reference materials have been agreed by the participants and two NMIs (TUBITAK and INRAP) are working to characterised them.

To develop a secondary method for pH measurement and to apply the method for the production and characterisation of reference pH buffer solutions with a target uncertainty of 0.008 pH for the calibration of pH meters and as reference samples for interlaboratory comparisons and proficiency testing. (Objective 2)

One scientist from BIM spent 2 weeks at LNE to design a secondary cell for pH measurements.
During the visit, the experts from LNE and BIM conducted a study by performing experiments to determine the cell structure, size, porosity of sintered-glass disk, etc., contacting experts NMIs on pH measurements using secondary cell to discuss further the cell parameters and selecting the equations to be used and determined the uncertainty budget. Based on this preliminary study, the cell has been ordered.

To apply the methods developed (ID ICPMS) to environmental and food samples to determine the heavy metals content in representative matrices, such as potable and natural waters, sediments, and different types of fish/biota samples. (Objective 3)

The partners will work on matrices relevant for both environmental and food safety studies where the analytical challenges will be representative of a large panel of difficulties that can be encountered, such as the risk of sample instability, the presence of interferences, difficulties in dissolving the material. By the end of the project it is expected that the partners will be able to adapt the measurement procedures developed in the project to different samples of a similar nature.

To validate the developed methods (secondary pH procedures, ID ICPMS) by participation in suitable international comparisons (organised by CCQM, EURAMET, another RMO, and/or bilateral – between the NMIs participating in the project) and hence to underpin the development of appropriate CMCs (Calibration and Measurement Capabilities) for submission to the BIPM Key Comparison Database. (Objective 4)

The project will lead to improved research capabilities for the less experienced NMIs/DIs, such as the capability to develop reference methods for new pollutants/contaminants, thanks to the participation in collaborative studies with more experienced Institutes in a way that they will be able to rapidly adapt their measurement capabilities towards new legal and standardisation requirements.

Moreover, it is expected that services which are not currently available at the moment in the counties of the emerging NMIs/DIs involved in the project, such as calibration facilities, reference materials and provision of reference values, will become available by the end of the project.

Impact

The foremost impact of the project will be the establishment of reliable capabilities for traceable measurements in metrology in chemistry (in particular for elemental inorganic analysis and pH) at the level needed by each participating Country. Therefore, by the end of the project, it is expected that new Calibration and Measurement Capabilities (CMCs) will be developed by the project partners.

A stakeholder committee has been created to communicate on the activities of the project. 7 members from universities, accreditation and standardisation bodies have been included in the SC. The SC members have received information of the project via the publishable summary.

Impact on industrial and other user communities

It is expected that the outputs produced during the lifetime of the project, such as reference values for proficiency testing schemes and reference materials, will directly benefit to field laboratories: production of reference samples with assigned reference values by a primary method of measurement as well as pH secondary reference materials in the participating countries will lead to reduce the costs for laboratories for purchasing imported reference materials for calibration and participation in PT schemes for competence demonstration abroad.

Accreditation bodies will also benefit from the strategies that the NMIs/DIs will develop for the implementation of national metrological infrastructures, which will be another important output of the project by actions described in the case studies and roadmaps for individual strategies for long term uptake of the developed capacities.

Impact on the metrology and scientific communities

The main expected impact of this project on the metrological community is the establishment of reliable capabilities for traceable measurements in metrology in chemistry (in particular for elemental inorganic analysis and pH) in the participating country and the proposal of new Calibration and Measurement Capabilities (CMCs) of the involved partners for publication in the BIPM database.

Moreover, the findings of the project will support research and innovation in the scientific community of the countries involved by the acquisition by emerging NMIs/DIs of the required knowledge and practice in research projects (i.e. access to research funding, creation of research consortia, writing of scientific papers), allowing them to participate more in future research programmes of EURAMET and other EU research programmes.

Impact on relevant standards

The project will encourage active participation in key European chemistry related committees such as the EURAMET TC MC, as well as knowledge transfer and exchange with international metrology in chemistry community such as BIPM CCQM.

It is expected that the partners who are members of technical committees will inform them about the results of this project and will endeavour to ensure they are incorporated in any updates to the standards or guidelines.

Longer-term economic, social and environmental impacts

Each emerging NMI/DI will develop a strategy for the implementation of the acquired capabilities in national traceability infrastructures. These national traceability infrastructures will include relevant national actors in the field of chemical analyses for environmental monitoring and food safety. Collaborations will be established with the national accreditation bodies, environmental agencies and academic laboratories.

The examples of two French networks for air and water quality monitoring (Central Laboratory for Air Quality monitoring – LCSQA; and Reference National Laboratory for Aquatic Media Monitoring – AQUAREF) will be illustrated and adapted to the specific needs of each participant Country. These networks gather expert national laboratories in a way that each of them brings its complementary expertise within the consortia. Among the aims, ensuring the quality of the information produced by the national system via standardisation, technical guides, audits, as well as developing rules for measurement, sampling and analysis in order to foster the production of reliable data for monitoring programmes, are those where the NMI plays its main role.

The impact of such collaborations will therefore be the enhancement of the quality of measurements performed by field laboratories, though the provision of reference values for materials and Proficiency testing schemes, tools for method validation and uncertainty evaluation as well as support for accreditation plans.

The wider impact of the project will be the acquisition by emerging NMIs/DIs of the required knowledge and practice in research projects allowing them to rapidly adapt their measurement capabilities to emerging needs and new analyte/matrix combinations.

Moreover, the growing participation of the NMIs/DIs in future research programmes of EURAMET and other EU research programmes will contribute to strengthen the link with the scientific community, bringing to an improved awareness of the scientific community about the need for coherent and quality data.

Project start date and duration:	1st June 2017, 36 months	
Coordinator: Paola Fisicaro, LNE, France	Tel: +33 (0)1 40433759	E-mail: paola.fisicaro@lne.fr
Internal Funded Partners: 1 LNE, France 2 BIM, Bulgaria 3 BRML, Romania 4 TUBITAK, Turkey	External Funded Partners: 5 IAPR, Greece 6 INRAP, Tunisia	