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, 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 cross border trade, laboratory medicine, and 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 (NMIs) and Designated Institutes (DIs) as well as to demonstrate the uptake of the improved capabilities through the application of case studies.
Training will be provided to less experienced NMIs/DIs, so they can acquire the necessary level of measurements capacities, the analytical methods implemented will be used to provide reference values in proficiency testing schemes, certified reference materials (CRMs) and training to the end user community.

Need

As limit values set by legislation decrease, the need for traceability in chemical sectors is significantly increased. Trace analysis is essential in almost all chemical sectors, especially when monitoring waste and environmental pollutants (such as organic, inorganic and macroscopic contaminants) in air, water and soil and when measuring impurities in industrial products as well as residues in food.
Field laboratories for routine chemical analysis need reliable tools such as 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) which are 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) 2000/60/EC 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.

pH measurements are among the most common routine analysis providing quick information about pollution and potential contamination risk. pH levels are 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 > 0.01 pH are needed. Primary methods such as isotope dilution mass spectrometry (IDMS) and secondary pH measurements need to be developed further in order to be able to provide well-characterised reference materials and reference measurements however, at present not all European NMIs/DIs have 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 this project, in terms of measurement procedures, will help to establish direct traceability to SI units and in terms of metrology in chemistry will support sustainable approaches for the provision of reliable tools such as certified reference materials (CRMs) and proficiency testing (PT) schemes to enhance confidence in chemical analysis results. For example, in the field of environmental monitoring, EU Member States are required to implement the Water Framework Directive (WFD) 2000/60/EC,w ith a strong emphasis on Europe's waters achieving good ecological and chemical status to protect human health, water supply, natural ecosystems and biodiversity. In this respect, transnational research collaboration is a priority, particularly for members with shared interests. A typical case is the Black Sea area, which requires coordinated action at the regional level, in accordance with the Black Sea Convention. In order to implement EU Policies such as the WFD, partners in this project from countries in the Black Sea Region (Bulgaria, Romania, Turkey and Greece) will need to improve the quality of the routine analysis performed by field laboratories. These countries also need to reinforce their synergies which 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 will need to dispose of reliable and acceptable data in compliance with the EU import requirements in order to improve the exchanges with the EU Countries. This will be addressed by objectives 4 and 5.

Objectives

The overall aim of the project is to improve the measurement capabilities of less experienced NMIs/DIs in the field of metrology in chemistry.

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 inter-laboratory 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

One of the most common analytical techniques for elemental trace analysis is Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Different calibration approaches such as external calibration and standard addition are possible for ICP-MS. Calibration based on the Isotope Dilution (IDMS) approach is a primary reference measurement procedure owing the highest metrological standing, with measurement uncertainties lower than 10 percent. However, the IDMS approach requires experienced operators due the complexity of the technical aspects that have to be carefully evaluated and taken into account in order to obtain accurate results. This project will improve the capabilities of the emerging NMIs/DIs in elemental quantification by using the IDMS approach in matrices representative of both environmental and food safety issues with uncertainties lower than 10 %.

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 functional than the Harned cell. Unfortunately, very few NMIs/DIs are equipped with secondary cells for pH measurements, therefore this project aim to implement a secondary method for pH measurements for the characterisation of buffers with a target uncertainty of 0.008 pH, which can be used by field laboratories.

Prior to the start of this project, less experienced NMIs/DIs were not able to apply IDMS to different matrices, including the more complex ones. This project will develop strategies to provide methods to cover a wide range of analytes in the 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 and 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 complexity.

When a measurement procedure has been developed, NMIs/DIs will be invited to participate in peer-to-peer inter-laboratory comparisons in order to demonstrate their measurement capabilities in a specific field. The NMI/DI will then publish their Calibration and Measurement Capabilities (CMCs) in the Key Comparison Data Base (KCDB)

At present, less experienced NMIs/DIs don't have CMCs in the field of inorganic analysis for the IDMS approach and were able to provide very few services in their own countries. The project will lead to improved research capabilities for emerging NMIs/DIs, such as the capability to develop reference methods for new pollutants/contaminants, By the end of the project it is expected that new CMCs (at least one per NMI/DI) will be published In the KCDB and services (such as provision of reference values, reference materials and calibration facilities) which are not currently available in the countries of the emerging NMIs/DIs involved in the project will become available.

Results

To develop traceable measurement capabilities for the analysis of heavy metals (Objective 1).

LNE provided training on ID-ICPMS to scientists from BIM, BRML and IAPR. The scientists studied the main concepts of the technique and practice in the laboratory and work was conducted on the following points: matrix digestion of 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 standards (including the evaluation of its purity if not certified); evaluation of the blanks; and the application of the ID equations and estimation of the uncertainty budget following the *Guide to the Expression of Uncertainty in Measurement* (GUM) approach.

Based on the training provided by LNE, the ID-ICPMS method has been implemented by BIM in their own laboratory. Experiments on the determination of Zn and Cu in estuarine water and fish CRMs were performed.

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 (Objective 2)

A secondary cell has been produced incorporated into a measuring system at BIM. This secondary cell was tested with respect to the parameters which affect measurement accuracy such as: the stability of the signal in time and the potential difference when both half-cells contain the same solution. The measured difference potential value was higher than 3 µV so it will be used as an off-set to correct the potential difference measured for the subsequent analysis. Further to this, the software used to measure and process the results was developed and tested prior to completion.

Three buffer solutions were prepared by BIM as CRMs and successfully measured by the secondary cell. All of the results are in good agreement with the certified values and the uncertainty is lower than the target of 0.008 pH. This secondary system is now fully operational and has been used to test the stability and homogeneity of a certified reference material.

To apply the methods developed (ID ICPMS) to environmental and food samples to determine the heavy metals content in representative matrices (Objective 3)

A training was given by TUBITAK to INRAP on the production and characterisation of CRMs. As a result of the training, two reference materials were produced by TUBITAK and distributed to other project partners. The less experienced NMIs/DIs have applied the procedures and techniques acquired during the training at LNE to test the improvement of their measurement capabilities on both reference materials.

The results have shown that most NMIs have improved their measurement capabilities due to the training provided, particularly in analysing the element concentration ranges suitable for addressing the WFD Directive 2000/60/EC. During this exercise, there has been a knowledge transfer between the most experienced NMIs and the emerging NMIs/DIs. Difficulties encountered by the less experienced NMIs/DIs have been addressed by providing a better understanding on the source of their discrepancies and how best to overcome the most critical steps of analysis.

To validate the developed methods by participation in suitable international comparisons and hence to underpin the development of appropriate CMCs for submission to the BIPM Key Comparison Database. (Objective 4)

The project partners have discussed how best to identify the suitable international comparisons (which will be organised at Consultative Committee for Amount of Substance (CCQM) level or at the EURAMET Technical Committee of Metrology in Chemistry (TC-MC) level, in which they will be able to validate their improved measurement capabilities. For pH, BIM will participate in CCQM-K19.2018 key comparison which focuses on pH determination of borate buffer solution, in order to validate the secondary cell which was developed during the project.

Impact

The project has produced 2 peer-reviewed publications, 5 internal training workshops, 7 oral presentations, and 3 posters which were presented at International and European conferences. In addition, the results of the project have been presented to two subcommittees of the EURAMET TC-MC

BIM has planned meetings with their main stakeholders (i.e. the Bulgarian Institute for Standardization and the Executive Environment Agency) to discuss the priorities for metrology in chemistry. Furthermore, INRAP has launched a national survey in Tunisia to identify the national needs in metrology in chemistry (organic and inorganic fields).

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 field laboratories. The production of reference samples with assigned reference values by a primary method of measurement along with pH secondary reference materials in the participating countries will help reduce the cost of purchasing imported reference materials for calibration as well as; the costs of participation in PT) schemes for competence demonstration abroad.

With this in mind, an initial PT scheme was organised by BIM for the Bulgarian field laboratories on the determination of elements. The measurement skills developed in objective 1 are being used by BIM to provide a reference value. Furthermore, a new PT scheme is also being organised by IAPR, the materials and the samples are being prepared and will be dispatched mid-October 2019 to the participating laboratories for analysis. The partners of the project will assign independent reference values obtained by IDMS methodology, as developed during the project.

Accreditation bodies will benefit from the strategies that the NMIs/DIs will developed for the implementation of national metrological infrastructures, which will be another important output of the project. The less experienced NMIs/DIs are aiming to develop individual roadmaps for national strategies for long term uptake of the developed capacities. To achieve this aim, the project partners are planning meetings with their main stakeholders and launching surveys to collate and prioritise national needs.

Impact on the metrology and scientific communities

The main expected impact on the metrological community after the end of the project 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.

Based on the measurement methods developed and validated during the project, the less experience NMIs/DIs have elaborated specific procedures within their internal quality system. This will ensure that the capabilities acquired will be more easily transferred to other operators within the NIMs/DIs.

BIM has also planned to participate in a CCQM comparison on pH measurement to validate the secondary system developed within the project.

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 is encouraging 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.

The partners who are members of technical committees regularly inform them about the results of this project and will endeavour to ensure they are incorporated in any updates to the standards or guidelines. For instance, a presentation has been given at the EURAMET TCMC meeting in February 2018 on the elemental analysis activities and a second one has been given in February 2019 on the secondary pH activities.

Longer-term economic, social and environmental impacts

Each emerging NMI/DI has started to develop a strategy for the implementation of the acquired capabilities in national traceability infrastructures. These national traceability infrastructures will include relevant national representatives 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. Less experienced NMIs/DIs have launched discussions in their countries to collect and prioritize the needs of their internal stakeholders and end-users.

The example 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) has been illustrated with the aim of adapting the approach to the specific needs of each participant's country. These networks gather expert national laboratories in a way that each of them brings its complementary expertise within the consortia. One of the aims is 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.

List of publications

1. "*Recent progress in chemical measuring capabilities in INM as a result of EMRP/EMPIR Programme*", Mirella Buzoianu, Mihail Radu, George Victor Ionescu, published in *19th International Congress of Metrology, 20004 (2019)*, https://doi.org/10.1051/metrology/201920004

Project start date and duration:	1 June 2017, 36 months	
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Internal Funded Partners: 1 LNE, France 2 BIM, Bulgaria 3 BRML, Romania 4 TUBITAK, Turkey	External Funded Partners: 5 IAPR, Greece 6 INRAP, Tunisia	Unfunded Partners:
RMG1: - BIM, Bulgaria (Employing organisation); LNE, France (Guestworking organisation)		