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. The project enhanced the research capabilities in the field of metrology in chemistry by developing analytical procedures, for emerging National Metrology Institutes (NMIs) and Designated Institutes (DIs). Furthermore, it demonstrated the uptake of the improved capabilities through the application of case studies. With support from the project, four NMIs /DIs also prepared roadmaps and defined their long-term strategies, for the implementation of national metrological infrastructure and effective collaboration with neighbouring countries.

Need

When performing routine chemical analysis, field laboratories 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. Moreover, pH is one of the most common routine analyses providing quick information about pollution and/or 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. The metrological approach to calibration in chemistry is based upon Isotope Dilution Mass Spectrometry (IDMS). This method has the highest metrological standing and the potential of being a primary reference measurement procedure. Major advantages of the technique with respect to external calibration approaches is that, it can ensure direct traceability to SI units and that the analyte recovery does not need to be quantitative, providing that a good equilibration of the calibrant/sample blend has been achieved. In addition, the ratios can be reproducible and, thus, concentrations can be determined in a highly accurate way. Despite the relatively simple principle, the IDMS approach requires experienced operators, since many aspects (e.g. the selection of the proper isotopes, optimisation of the calibrant/sample blend equilibration), have to be carefully evaluated and considered for optimal results. Prior to the start of the project, few NMIs/DIs were sufficiently experienced in applying this methodology. The project addressed these needs by fulfilling Objectives 1, 2 and 3.'

In the field of environmental monitoring, EU Member States are required to implement the Water Framework Directive (WFD) 2000/60/EC, with 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 has been 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, project partners that were from countries in the Black Sea Region (Bulgaria, Romania, Turkey and Greece) needed to improve the quality of the routine analysis performed by field laboratories. These countries also needed to reinforce their synergies to enable a sharing of the analytical competencies and the services for end-users such as field laboratories and accreditation bodies. The capabilities developed in this project; in terms of measurement procedures, have aided direct traceability to SI units; and in terms of metrology in chemistry, have promoted sustainable approaches for the provision of reliable tools such as certified reference materials (CRMs) and proficiency

testing (PT) schemes thus strengthening confidence in chemical analysis results. Furthermore, 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. It indicated a need for Tunisia to dispose of reliable and acceptable data in compliance with the EU import requirements in order to improve the exchanges with the EU Countries. The project addressed these needs by addressing Objectives 4 and 5.

Objectives

The overall aim of the project was to improve the measurement capabilities of less experienced NMIs/DIs in the field of metrology in chemistry. This project focussed on 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 must be carefully evaluated and taken into account in order to obtain accurate results. This project has improved 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 require 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 has implemented a secondary method for pH measurements for the characterisation of buffers with a target uncertainty of 0.008 pH.

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 has established strategies to provide methods to cover a wide range of analytes in representative matrices. Furthermore, the project partners have developed matrices relevant for both environmental and food safety studies where the analytical challenges are 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.

Since, less experienced NMIs/DIs do not 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 contributed towards improved research capabilities of emerging NMIs/DIs, such as the capability to develop reference methods for new

pollutants/contaminants. Such efforts are expected; to result in new CMCs that will be published in the KCDB, in the near future; which will enable emerging NMIs/DIs involved in the project, to provide measurement services that were not available before the project started.

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.

TUBITAK provided two training courses to INRAP, one on ID-ICPMS and the second on the production of certified reference materials. The training course on ID-ICPMS was applied to the determination of the amount of Cu and Cd in seawater samples using High Resolution ICPMS and Quadrupole-ICP-MS/MS. Likewise, another training course; which focused on the production of the reference materials; was conducted on the characterisation of a fish sample and the determination of the amount of Hg.

This objective was fully met, since the less experienced NMIs/DIs, which had never performed ID-ICPMS analysis before the project, were able to conduct this measurement approach to exemplar elements in representative food and environmental matrices, with an uncertainty of about 10%.

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 was incorporated into a measuring system at BIM. This secondary cell was tested with respect to the parameters that 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 offset to correct the potential difference measured for the subsequent analysis. At the same time, the software used to measure and process the results was developed and tested prior to completion. Furthermore, 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 objective was fully met since this secondary system is now 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)

TUBITAK distributed two reference materials (RMs) to be used for the implementation of the methods which included samples of river water and fish. The less experienced NMIs/DIs have applied the procedures and techniques acquired during the training at LNE and TUBITAK 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 were addressed by providing a better insight t the source of their discrepancies and how best to overcome the most critical steps of analysis.

The project focused on demonstrating measurement services that NMIs/DIs could provide to disseminate metrological traceability. This was achieved through the organisation of a Proficiency Testing (PT) for field laboratories, using the material prepared by IAPR, (i.e. a tuna fish enriched with the elements relevant for the project). An invitation was circulated to the routine laboratories in their respective countries, around 45 laboratories (mainly from Bulgaria, Romania, Serbia, Tunisia and Greece) participated in the PT scheme and the project partners provided their results applying the ID-ICPMS procedure. Overall, this objective was fully met.

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)

Since no EURAMET or CCQM key comparison was organised for food or environmental matrices during the lifetime of project, it was not possible for the project partners to participate in a comparison able to underpin CMC submission. However, the comparison conducted on the TUBITAK reference materials showed that the emerging NMIs/DIs have acquired the necessary measurement capabilities.

Although the objective has been partially met, the project partners will continue to pursue this beyond the lifetime of the project. The project partners have already identified a suitable key comparison (the CCQM-K158 elements in rice) within the Inorganic Analysis Working Group of CCQM. Also, for pH measurements, BIM has registered to participate in CCQM-K19.2018 key comparison that focuses on pH determination of borate buffer solution, in order to validate the secondary cell that was developed during the project.

To develop individual strategies for the long-term operation of the capacity developed (Objective 5).

Overall, this objective was fully met. LNE shared its expertise from being a member of two national networks in France for both air and water quality monitoring (Central Laboratory for Air Quality monitoring – LCSQA and Reference National Laboratory for Aquatic Media Monitoring – AQUAREF). These networks gather expert national laboratories form 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 LNE plays the main role.

LNE also organised a workshop for the project partners in order to initiate brainstorming of national needs in the respective countries for the implementation infrastructures similar to the model adopted in France, as described above. BIM, BRLM, IAPR and INRAP also consulted their national stakeholders (such as environmental agencies, accreditation bodies, proficiency testing providers), to define a strategy that addressed the national needs. As a result of this stakeholder-need based stratification, INRAP are now preparing for ISO 17034:2016 accreditation. The training and knowledge acquired during this project has also enabled INRAP to develop improved methods and capabilities in the production of calibration solutions (Hg)

Impact

The project has produced 3 peer-reviewed publications, 8 training courses (6 internal, 2 external), 7 oral presentations and 3 posters; which were presented at International and European conferences. The project's results have been disseminated further through the organisation of a proficiency testing scheme, the contribution to the certification of 2 reference materials, the organisation of 2 stakeholder surveys. In addition, the results of the project have been presented to 2 sub-committees of the EURAMET TC-MC and another standardisation committee. During the lifetime of the project regular progress updates announced on the project website and circulated in newsletters on the NMIs websites.

Impact on industrial and other user communities

The reference values provisioned for proficiency testing schemes and reference materials were key project outputs which will directly benefit field laboratories. The production of reference samples with assigned reference values using 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. During the project, a case study on a PT scheme was organised by IAPR. The materials and the samples were prepared and dispatched to the participating laboratories for analysis. The partners of the project assigned independent reference values obtained by IDMS methodology, as developed during the project. This led to more precise and reliable evaluation since the accuracy of the individual results obtained by the laboratories was better than what could have been achieved when comparing with a consensus value.

Furthermore, the less experienced NMIs/DIs have developed individual roadmaps for national strategies to promote long-term uptake of the developed capacities, based on meetings with their main stakeholders and surveys; that were organised by the project partners; to collate and prioritise national needs. This was an important output of the project which will also benefitted accreditation bodies, since it provided them with the necessary metrology tools to establish national traceability chains, i.e. reference methods, reference materials and proficiency testing schemes.

Impact on the metrology and scientific communities

The project established reliable capabilities for traceable measurements in chemistry (in particular for elemental inorganic analysis and pH) which created significant impact within the metrology community. Based on the measurement methods developed and validated during the project, the less experienced NMIs/DIs have enhanced specific procedures within their internal quality system. Thus, ensuring easy and effective transfer of knowledge acquired during the project, to other operators within the NIMs/DIs. To further support these efforts after the project has ended, the NMIs/DIs involved have also identified relevant CCQM key comparisons which will be used to validate the ID-ICPMS procedures and the secondary pH system developed within the project.

It is anticipated that the project partners will be able to adapt the measurement procedures developed in the project, to different samples of a similar complexity. Overall, the project has supported emerging NMIs/DIs of the countries involved through the knowledge sharing activities undertaken, which has led to improved capabilities and exposure to delivering research projects (i.e. access to research funding, creation of research consortia, writing of scientific papers). This will enable emerging NMIs/DIs to participate in more future research programmes of EURAMET and other EU research initiatives.

Impact on relevant standards

The project has encouraged 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. A presentation was given at the EURAMET TCMC meetings on the elemental analysis activities and another presentation on the secondary pH activities. BIM also presented the project results to the Bulgarian standardisation committee TC 28/ Metrology. In addition, the project partners regularly informed technical committees about the results of this project and endeavour to ensure they are incorporated in any futures updates to the relevant standards and guidelines beyond the lifetime of the project.

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
2. "*Work at the INM to Develop Measurement Capabilities to Assign Reference Values in Proficiency Testing Schemes*", M.Buzoianu, published in Proceedings of *PT CONF 2019,* http://www.pt-conf.org/2019/wp-content/uploads/2019/09/Proceedings-PT-Conf-2019.pdf

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)		