Publishable JRP Summary Report for JRP SIB09 ELEMENTS
Primary Standards for Challenging Elements

Background

Millions of elemental measurements are performed in Europe each year for chemical analysis to support healthcare, diagnostic tests, environmental monitoring, material assay, product development and safety. Calibration is based on solutions which are available from commercial producers or solutions prepared from ‘high purity’ materials. Primary standards are materials known for their total purity and therefore appropriate to realise the link with the International System of Units (SI). The realisation and dissemination of primary standards is of fundamental importance for comparability of measurement results through traceability in all fields of chemical analysis.

Due to the complexity and effort involved, the characterisation of such materials is usually driven more by what is easy to achieve rather than what is really needed and therefore most of the currently available materials are only partially characterised. Since adequate theoretical modelling is very difficult, measurement devices require calibration with samples of known composition (which are preferably linked to the SI). Because modelling of the measurement process is incomplete, calibration for one element is usually not transferable to other elements. Therefore it is necessary to provide primary standards for all elements of the periodic table.

Need for the project

Due to the complexity and effort involved/necessary for their characterisation, there are hardly any demonstrated primary standards in this field and although primary solutions and solutions declared as secondary are omnipresent, in practice validated primary materials characterised for total purity to underpin these declarations rarely exist. As a consequence elemental determination in field laboratories and NMs are usually undertaken using materials which do not meet the basic metrological requirements of primary standards and which are consequently insufficient to establish SI traceability.

The lack of comparability of measurement results affects almost all elements and virtually all sectors that base important decisions on elemental measurements. For example; magnesium (Mg) and aluminium (Al) are of great importance for industry for use as lightweight construction materials in car and plane construction. Zinc (Zn) is an element with interesting prospects for energy production via the reduction of water or the use of ZnBr$_2$ for high density energy storage. Additionally Mg and Al are relevant in clinical chemistry, especially with respect to Alzheimer’s disease. Rhodium (Rh) is an important noble metal widely used in chemical catalysis and in car catalysts. Molybdenum (Mo) has a huge variety of technical applications, its use ranges from an alloying element for the hardening of steel, an important constituent in alloys for space and aeronautic applications, to a contact material in microelectronics and thin film solar cells.

Through legal regulations (EU Directives) or customer needs this directly affects the quality of life of EU and world citizens whenever measurement results are compared with other data, via e.g. clinical diagnostics and therapies, consumer protection, sustainability of resources and other measurement results, legal limit values or product specifications. Without primary standards European directives such as In vitro diagnostic (IVD) devices for laboratory medicine and the EU Water Framework Directive (WFD) for environmental protection cannot be implemented as required. There is an urgent need to realise and to disseminate primary standards to underpin these measurements.
Scientific and technical objectives

The JRP aims to provide the technical basis for resolving this lack of primary standards for element determination in a sustainable way within the scope of a worldwide activity by National Metrology Institutes running parallel to the project. Efficient procedures, which improve the methodology for realising fit for purpose primary standards for most of the challenging elements frequently used in elemental analysis, will be developed and applied for selected guide elements. These guide elements are Mg, Zn, Mo and Rh.

Practical work is based on three pillars. First there will be the development of procedures for purity analysis with respect to metallic and non-metallic impurities of high purity materials with focus on efficient methods and challenges in non-metal determination. The second pillar will be matrix investigations involving direct determination of the main components as a universal approach, purification to establish blank materials, measurement of the isotopic composition and development of efficient methods for dealing with isotopic composition. In the third pillar work will be on the dissemination of the primary standards through loss free decomposition, linking two solutions of similar composition and to directly link a solution to a solid material with small uncertainty.

Scientists and technical objectives

The specific objectives of this project are summarised as following:

1. To develop methods for measuring the total purity of high purity materials of selected elements including determination of metallic and non-metallic impurities and the development of a Neutron Activation Analysis Procedure (INAA) as a reference for homogeneity measurements for metallic impurities

2. The production and availability of well characterised materials for Mg, Zn and Mo for the metrological community.

3. To develop measurement methods for directly measuring the main component of a high purity metal and also its isotopic composition, as needed to convert from mass to amount of substance.

4. To develop purification techniques and the ability to directly determine the content of the main component of a high purity material.

5. To prepare synthetic isotope mixtures for calibration of isotope ratio measurements and test efficient approaches for the calibration of isotopic ratio measurements.

6. To develop methods and to establish loss free and complete decomposition of materials, including:

   ▪ Development of new measurement methods for comparing two elemental solutions of similar composition with small uncertainty (0.05 %) based on a Multicollector Inductive Coupled Plasma Spectrometry (MC-ICP-MS.) This is necessary to realise the unbroken traceability chain from the primary standard solution to the secondary one with a small uncertainty – comparable with the linking of national primary kilograms to the primary kilogram in Sèvres.

   ▪ Development of a new measurement method for comparing the content of a liquid directly to the content of a solid material by INAA. This approach is to link a solution directly to the solid primary standard.

   ▪ Development of new methods for the complete and loss-free digestion of refractory elements (such as Mo and Rh) for the preparation of primary elemental solutions. This is necessary to ensure that 100% of a solid and very difficult to dissolve material is transferred into solution.

These objectives focus on providing an efficient methodology for the realisation of demonstrated primary standards for element determination of challenging elements which up to now has been lacking. As a by-product it will provide primary standards for Mg, Zn and Mo.

Objectives 1-3 concentrate on the characterization of the investigated materials as primary standards for elemental determination.

Objectives 5 & 6 are dedicated to the transfer of the primary standard into standard calibration solutions in the field laboratory.
Expected results and potential impact

Two stakeholder workshops were planned to disseminate the JRP output to the target and end user community, which comprises industry, metrology organisations and the producers of calibration solutions. The first workshop took place at PTB in Berlin (22nd May 2013) for dissemination of information about the JRP to stakeholders and getting their feedback on current demands and problems.

Development of methods for measuring the total purity of high purity materials of selected elements including determination of metallic and non-metallic impurities and the development of INAA as a reference for homogeneity measurements for metallic impurities

Extensive measurements by Glow Discharge Mass Spectrometry (GDMS) – to evaluate the potential of this solid sampling technique for a fast analysis of the matrices without excessive sample preparation were completed. In close collaboration with REG(IFW) and the stakeholder AQUARA the ability for non-metal determination using GDMS was evaluated. For the first time, synthetic doped pressed powder and sintered samples were prepared and used for non-metal determination. The results for Mg matrix were summarized and published in *Analytical and Bioanalytical Chemistry*. For the challenging determination of non-metals gas dose system for calibration of the method of Carrier Gas Hot Extraction (CGHE) was designed, constructed and characterized. The results were presented at different international conferences and meetings with stakeholders and published in the Journal *Analytical Methods*.

INAA procedures have been developed for the homogeneity study on Mg, Al, Rh and Mo. The methods have been applied on Rh samples supplied by PTB. This allowed the homogeneity determination of Rh subsamples by measuring the impurities mass fraction. Results have been published in the Journal *Metrologia*.

Production and availability of well characterised materials for Mg, Zn and Mo for the metrological community.

By combined effort from project partners, the materials Mg, Zn and Mo were characterized with different analytical methods leading to materials with a well-defined content of the matrix element with an uncertainty of 0.01% The materials will be available to the NMIs at the end of the project.

Development of measurement methods for directly measuring the main component of a high purity metal and also its isotopic composition, as needed to convert from mass to amount of substance.

Coulometric measurement of EDTA was further studied and optimised, and the evaluation of titration curves was improved. The measurement uncertainty achieved (U=0.01%) is great improvement compared to the target value of uncertainty (U<0.02%).

Development of purification techniques and the ability to directly determine the content of the main component of a high purity material.

A procedure for purification of natural Magnesium was developed. All three Mg isotopes have been purified by two sublimation cycles to this point, reaching a chemical purity estimated to be better than 99.5 %. A final sublimation cycle was followed by digestion and conversion into the stock solutions.

Preparation of synthetic isotope mixtures for calibration of isotope ratio measurements and test efficient approaches for the calibration of isotopic ratio measurements.

Methodology for absolute Mo isotope amount ratio measurements by multicollector inductively coupled plasma-mass spectrometry (MC-ICP-MS) using calibration with synthetic isotope mixtures (SIMs) has been achieved an a paper published in ABC). For the first time, synthetic isotope mixtures prepared from seven commercially available isotopically enriched molybdenum metal powders (92Mo, 94Mo, 95Mo, 96Mo, 97Mo, 98Mo, and 100Mo) have been used to investigate whether instrumental mass discrimination of Mo isotopes in MC-ICP-MS is consistent with mass-dependent isotope distribution. This avoids any assumption on mass-dependent isotope fractions in MC-ICP-MS, inherent to the method of double spike previously used for Mo isotope amount ratio measurements. The data obtained in this work show experimentally for the first time
that instrumental mass discrimination in MC-ICP-MS is consistent with mass-dependent Mo isotope fractionation.

Furthermore REG(UGent) combines cold vapour generation (CVG) with multi-collector ICP-mass spectrometry for Hg isotopic analysis. Several approaches for correction of mass discrimination have so far been assessed. None of the experiments indicated occurrence of mass-independent mass fractionation in MC-ICP-MS.

To develop methods and to establish loss free and complete decomposition

New methods were developed and successfully applied for the complete and loss-free digestion of refractory elements Mo and Rh for the preparation of primary elemental solutions. A paper about Gravimetric preparation of reference solutions of rhodium and molybdenum was published in Analytical and Bioanalytical Chemistry.

Furthermore, the two REGs contributed to the JRP. REG(UGent) combines cold vapour generation (CVG) with multi-collector ICP-mass spectrometry for Hg isotopic analysis. Several approaches for correction of mass discrimination have so far been assessed. None of the experiments indicated occurrence of mass-independent mass fractionation in MC-ICP-MS. REG(IFW) successfully applied sintered calibration samples (for O in Al, Mg and Cu) for matrix specific calibration in GD-OES and -MS. In cooperation with the project partners progress was achieved especially at the GD-MS analysis of Mg.

A stakeholder group has been established, a workshop has been held and stakeholders are regularly updated on the technical progress of the JRP. Eleven papers have been published in peer reviewed journals and thirteen presentations were given at international conferences. The research results are of great value to the research community, for instance the joint publication of the project partners (D4.1.9) shows a high response (more than 150 views and more than 60 uploads from ResearchGate) in the scientific community. All scientific papers, presentations are available on the JRP webpage.

### JRP start date and duration:
01 September 2012, 36 months

### JRP-Coordinator:
Dr. Heinrich Kipphardt, BAM
Tel: +49 30 8104-1116
E-mail: heinrich.kipphardt@bam.de

JRP website address: [http://www.ptb.de/emrp/sib09.html](http://www.ptb.de/emrp/sib09.html)

### JRP-Partners:
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The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.