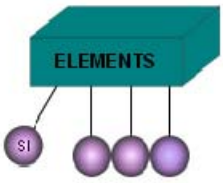

Final Publishable JRP Summary for SIB09 ELEMENTS
Primary Standards for Challenging Elements

Overview

Millions of chemical analysis measurements of different elements are performed in Europe each year to support healthcare, diagnostic tests, environmental monitoring, material assay, product development and safety; but few standards are available to enable chemical analysis traceability to the SI. This project looked at accurately determining the purity of primary standard materials, concentrating on the elements: Magnesium (Mg), Aluminium (Al), Zinc (Zn), Rhodium (Rh) and Molybdenum (Mo). Different measurement techniques are suited to particular elements, so this project examined and compared a range of measurement techniques. The elements were characterised with different analytical methods based on directly measuring the purity of the sample, and indirect measurement via the amount of impurities. Some techniques required a solution of the element and new methods were developed for producing accurate solutions of Mo and Rh. The project also enabled the purity of the materials to be defined with an uncertainty of 0.05%. It will be possible to use the techniques and measurements developed in this project for other elements.

Need for the project

The results of chemical analysis measurements must be the same everywhere and every time they are made. In order to achieve this analysis results need to be comparable. Our modern society relies on this comparability, and it has a direct impact on the quality of our life; such as measurements to ensure compliance with legal limits for environmental pollutants, measurements in clinical diagnostics or for specifying technical products. A comparison of measurement results needs reference standards which in turn rely on primary standards.

Due to the complexity of elemental characterisation, there are hardly any validated primary standards in this field. Although solutions declared as secondary are common, in practice validated primary materials characterised for total purity to underpin these declarations rarely exist. As a consequence, elemental determination in field laboratories and NMIs are usually undertaken using materials which do not meet the basic metrological requirements of primary standards and are therefore insufficient to establish SI traceability.

The lack of comparability of chemical analysis measurements affects a wide range of elements, and virtually all industrial sectors base important decisions on these measurements. The project identified five elements which are important for industry to have accurate references for. Mg and Al are important for in the automotive and aeronautical industry as they seek to make structures lighter; Rh is widely used in chemical analyses and catalysts to reduce exhaust pollution and Mo is important in producing hardened steel alloys for the aerospace and micro-electronics industries. These elements are also representative of a wider range of other elements, so any techniques established during the project can be used for other elements.

Harmonised data produced from standardised chemical analysis techniques with traceability to the SI will support legally binding EU Directives, such as the *in vitro* diagnostic (IVD) devices for laboratory medicine, European Pharmacopoeia and the EU Water Framework Directive (WFD) for environmental protection. There is also an urgent need to realise and to disseminate primary standards to improve chemical analysis traceability and to establish comparability of analytical measurement results around the world.

EMRP
European Metrology Research Programme
Programme of EURAMET

The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Scientific and technical objectives

The first objective for the project focused on providing an efficient methodology for accurately determining the purity of primary standards for Mg, Zn and Al, as well as the more challenging elements Mo and Rh. Measurements were both direct, measuring the amount of the main component, and indirect, measuring the impurities and subtracting them from 100 %. The elements have a combination of isotopes, and therefore the second objective looked at how to use the proportion of different isotopes to determine purity. Dissolving samples and comparing the resulting solution with standards can be used to determine purity. Objective three looked at how to completely dissolve materials in order to compare and link solutions. Different sample preparation techniques were investigated and the results from the different techniques were compared.

The three objectives were:

1. To develop measurement methods for measuring the total purity of high purity materials of selected elements (at the mg/kg level)
2. 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
3. To develop methods and to establish loss free and complete decomposition of materials and to realise the linking of standards to the embodied SI unit (primary standard) by methods of comparing elemental solutions or solutions and solid materials directly

Results

Development of methods for measuring the total purity of high purity materials of selected elements

A significant improvement in the efficiency of the metrological traceable characterisation of primary standards was realised. Technical progress was also achieved in impurity analysis; in particular elemental and isotope characterisation to evaluate the potential of solid sampling for a fast analysis of the pure elements without excessive sample preparation Glow Discharge Mass Spectrometry (GDMS) was used for this and several research institutes and industrial partners evaluated GDMS for non-metal determination, i.e. the impurities in the material. For the first time, synthetic doped pressed powder and sintered samples were prepared and used for non-metal determination. For the challenging task of determining the amount of non-metals in gas a Carrier Gas Hot Extraction (CGHE) method was constructed and characterised.

Homogeneity of the material was needed to ensure than the small test samples are representative of the whole. If material purity is determined through its impurities, homogeneity of their distribution in the material plays a crucial role. Spot contaminations can significantly distort the overall picture, therefore, homogeneity must be carefully checked right at the start. Neutron Activation Analysis (INAA) is very sensitive and works with very small subsamples. INAA procedures were developed for homogeneity studies on Mg, Al, Rh and Mo. The methods have also been applied on Rh samples which allowed the homogeneity determination of Rh subsamples by measuring the proportion of impurities.

Mg, Zn and Al were characterised with different analytical methods, which showed good agreement and precision. This means that materials can be produced with a well-defined content of the matrix element with an uncertainty of 0.03 %. These well characterised materials are now available to the metrological community, NMIs and industry as reference materials.

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.

Metal calibration solutions were produced and tested directly. Impurities only affecting the mass of the pure metallic element, such as surface oxygen, did not affect the final result, the mass or amount in the solution. However, all impurities affecting the direct quantification (e.g. coulometry, titrimetry) led to a bias in the final result, the mass or amount in the solution. Validated assay procedures for titrimetric methods developed for direct assay of Mg, Zn and Al were achieved with an expanded uncertainty below 0.1 %. Coulometric measurement was also studied and optimised, and the evaluation of titration curves was improved. These techniques will allow independent validation of elemental calibration solutions by NMIs. A procedure for purification of natural Mg was developed. All three Mg isotopes were purified by two sublimation cycles, reaching a chemical purity estimated of better than 99.5 %. A final sublimation cycle was followed by

digestion and conversion into the stock solutions. This will provide a high purity sample material for future use.

For the first time, synthetic isotope mixtures prepared from seven commercially available isotopically enriched Mo metal powders (^{92}Mo, ^{94}Mo, ^{95}Mo, ^{96}Mo, ^{97}Mo, ^{98}Mo, and ^{100}Mo) have been used to investigate whether instrumental mass discrimination of Mo isotopes in multicollector inductively coupled plasma-mass spectrometry (MC-ICP-MS) is consistent with mass-dependent isotope distribution. The data showed experimentally that instrumental mass discrimination in MC-ICP-MS is consistent with mass-dependent isotope distribution which means that the ratios between the isotopes could be used as an indication of the purity of the material.

Different methods were established to determine directly the purity of the material, and comparisons have been made between the different techniques at NMIs. The measurement uncertainty achieved with the optimised coulometric titration of (U=0.01 %) is a great improvement compared to the target value of uncertainty (U<0.02 %).

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 the refractory elements Mo and Rh in order to prepare primary elemental solutions. This was already possible for the other elements in the study. The results were compared between NMIs to validate the methods and it is now possible to put all of the elements in this study into a primary solution.

Actual and potential impact

The project compared different measurement techniques and sample preparation methods for five elements; Mg, Al, Zn, Rh and Mo. This includes the development, improvement and optimisation of sample preparation steps (e.g. complete digestion to assure the quantification of all impurities). Methods for the characterisation of the purity of the samples and standard materials were compared, and agreement between different methods and test laboratories (i.e. NMIs) was demonstrated. Primary standards in the form of well characterised reference samples were also developed.

The project developed an efficient methodology to overcome lack of primary standards for element determination in European and Internationally. The five elements addressed in this project are representative of a group of elements with similar behaviour and it is therefore anticipated that the methods and approaches developed in the project will be applicable to other elements. The project collaborated with the International Union of Pure and Applied Chemistry (IUPAC) and Eurachem (a European network with the goal of establishing a system for the international traceability of chemical measurements and the promotion of good quality practices), which will help to implement this long term goal of chemical analyses traceable to the SI.

Dissemination of results

The research results were published in high profile journals such as Analytical and Bioanalytical Chemistry, the Journal of Analytical Atomic Spectrometry and the Journal of Radioanalytical and Nuclear Chemistry. All scientific papers, presentations are available on the project webpage and the web of science. The project also held two open workshops for NMIs, industry and academia to give information about the project such as producing calibration standard solutions and the requirements of accreditation standards (such as ISO 17025) on traceable calibration.

The project coordinator was an invited speaker at the International Glow Discharge Spectroscopy Symposium in Liverpool 2016 to talk about the use of GDMS (as developed in objective 1) for high purity materials and as a way of determining primary standards. The topic was of great interest to Evonik Technology (a world-wide leading specialty chemicals company) and Mitsubishi Metals Corporation, Japan.

The highest level International metrology body in chemistry – the BIPM's Consultative Committee for Amount of Substance (CCQM) establishes global comparability of measurement results by promoting traceability to the SI, and where traceability to the SI is not yet feasible, to other internationally agreed references. It contributes to the establishment of a globally recognised system of national measurement standards, methods and facilities for chemical and biological measurements. The project results were disseminated at a workshop of the Inorganic Working Group of the CCQM on the approach to purity assessment of elemental

standards. The topic was raised as part of discussion linking SI traceability with NMIs who certify matrix materials using calibration standards prepared in-house. A large part of the workshop was dedicated to GDMS due to the applicability and speed of the technique but also the challenge of calibration and how to apply to purity assessments. The workshop included representatives from China and the US who provided insights into their approach to producing primary standard solutions.

Actual Impact
By developing the methodology to realise and disseminate primary standards for the ive elements; Mg, Al, Zn, Rh and Mo, the metrological community will be stimulated to solve the lack of primary standards for element determination. This in turn will enable reliable decision making and will provide enhanced information for research and development. The development and availability of primary standards for Mg, Zn and Mo will also provide an underpinning infrastructure for innovation beyond the metrological chain.

Improved measurements developed at NMIs in the project will impact on end-users and the first steps are already being taken:

- The detailed descriptions of digestion procedures for primary reference solutions for Rh and Mo were of particular interest. A EURAMET comparison (TC-MC 1377), for the validation of the developed methods for Al and Mo has been carried out.
- There is an initiative of the Inorganic Working Group of CCQM on purity assessment of elemental standards including a “roadmap” for purity assessment of inorganic calibrants based upon the experience of this project. They also plan to take forward the work of the project as a global activity to underpin traceability to the SI.
- The next step forward is for NMIs to compare copper calibration solutions. CCQM-P149 (the Consultative Committee for Amount of Substance and belongs to the BIPM) provides information on how NMIs characterise their national standards in practice. The results were discussed at the CCQM meeting in Tsukuba. NMIs are the milestones in establishing real traceability to SI in measurements, as they hold the national standards – contributed to the calibration labs – to the end users in the line of traceability of calibration solutions.
- Stakeholders from industry, Thermo Fisher Scientific and AQura GmbH, were interested in developing the project’s traceable calibration strategies using pressed powder calibration standards for GDMS Instrumentation (from objective 1).
- The project developed an improvement in the reliability of the measurements results and different ways of matrix depending calibration of typically solid sampling measurement techniques. The establishment of traceable calibration to the SI will allows them to fulfil the requirements of standards such as ISO 17025.
- CENAM, the NMI of Mexico, has been involved in the development of measurement methods for pure materials, and they are already being used in the certification of reference materials for CENAM customers with a clear traceability to the SI unit.
- A detailed description has been published about the preparation of an isotope reference material for Mg, which is available to the end-user by BAM.
- The project website has a database containing the available primary elemental materials held by BAM and the corresponding primary solutions prepared by PTB. End-users are able to search for primary elemental material and their corresponding solutions within this database. Therefore, it is now much easier to access those materials and the end-users are informed immediately, which materials are available to perform SI traceable measurements with traceable standards provided by their NMIs.

Potential impact
Examples of the practical application of this project include: (i) the work on the Mg will open the door to the study of the metabolism of Mg in the human body using isotopes and (ii) the accurate determination of non-metal content is crucial for ceramic materials and for example oxygen based supra conductors.

Providing traceable, and therefore reliable measurement, through primary standards and their dissemination will have an impact on a very broad range of fields in the thousands of European laboratories performing millions of chemical analysis measurements each year on the basis of elemental calibration solutions.

The project is expected to contribute in the longer term to a reduction in the costs arising from disputed and unnecessarily repeated measurements. In the field of healthcare, for example, estimations indicate that a significant fraction of all measurements could be avoided by an improvement of confidence in the measurement results which in Europe equates to billions of Euros each year.

List of publications

[1]. S. Richter, M. Sargent, D. Schiel, H. Kipphardt; *Known purity - the fundament of element determination by atomic spectrometry,* J. Anal. At. Spectrom., 2013, 28 (10), 1540 – 1543.

[2]. H. Kipphardt, D. Schiel, M. Sargent, H. Goenaga-Infante, P. Fisicaro, G. D'Agostino, L. Bergamasch, M. Máriássy, M. Buzoianu, S. Richter, J. Vogl; *Primary Standards for Challenging Elements - Joint Research Project EMRP-SIB09,* Revista Metrologie, 2012, 59 (3/4), 13ff.

[3]. T. Zhou, S. Richter, R. Matschat, H. Kipphardt; *Primary standard for element determination of silver,* Accred. Qual. Assur., 2013, 18, 341-349.

[4]. G. D'Agostino, L. Bergamaschi, L. Giordani, M. Oddone, H. Kipphardt, S. Richter; *Use of Instrumental Neutron Activation Analysis to investigate the distribution of trace elements among subsamples of solid materials,* Metrologia, 2014, 51, 48-53.

[5]. N. Kivel, H.-D. Potthast, I. Günther-Leopold, F. Vanhaecke, D. Günther; *Modeling of the plasma extraction efficiency of an inductively coupled plasma-mass spectrometer interface using the direct simulation Monte Carlo method*, Spectrochimica Acta Part B 2014, 93, 34-40.

[6]. A. Plotnikov, J. Pfeifer, S. Richter, H. Kipphardt, V. Hoffmann; *Determination of Major Non-Metallic Impurities in Magnesium by Glow Discharge Mass Spectrometry with Fast Flow Source Using Sintered and Pressed Powder Samples,* Analytical and Bioanalytical Chemistry, 2014; 406 (29). *7463-7471*.

[7]. A. Kaltenbach, J. Noordmann, V. Görlitz, C. Pape, S. Richter, H. Kipphardt, G. Kopp, R. Jährling, O. Rienitz, B. Güttler; *Gravimetric preparation and characterization of primary reference solutions of molybdenum and rhodium;* Analytical and Bioanalytical Chemistry *2015. 407(11): p. 3093-3102*).

[8]. N. Kivel, H.-D. Potthast, I. Günther-Leopold, F. Vanhaecke, D. Günther; *Variable aperture extraction lens for ion beam investigation in inductively coupled plasma - mass spectrometry,* J. Anal. At. Spectrom., 2015, 30 (6), 1329-1335.

[9]. C. Gonzalez-Gago, P. Smid, C. Venzago, T. Hofmann, V. Hoffmann; *The use of matrix-specific calibrations for oxygen in analytical glow discharge spectrometry;* Analytical and Bioanalytical Chemistry, 2014, 406 (29), 7473-7482.

[10]. D. Malinovsky, P.J. H. Dunn, P. Petrov, H. Goenaga-Infante; *Investigation of mass dependence effects for the accurate determination of molybdenum isotope amount ratios by MC-ICP-MS using synthetic isotope mixtures;* Analytical and Bioanalytical Chemistry, 2015, 407 (3), 869-882.

[11]. H. Kipphardt, C. Kramer, P. Ried, S. Mahn, S. Richter, N. Langhammer; *Design and application of a versatile gas calibration for non-metal determination by carrier gas hot extraction;* Analytical methods, 2015, 7 (13), 5468-5475.

[12]. A. Rua-Ibarz, E. Bolea-Fernandez, F. Vanhaecke; *An in-depth evaluation of accuracy and precision in Hg isotopic analysis via pneumatic nebulization and cold vapour generation multi-collector ICP-mass spectrometry,* Analytical and Bioanalytical Chemistry, 2016, 408 (2), 417-429.

[13]. B. Brandt, J. Vogl, J. Noordmann, A. Kaltenbach, O. Rienitz; *Preparation and Characterization of Primary Magnesium Mixtures for the ab initio Calibration of Absolute Magnesium Isotope Ratio Measurements,* Journal of Analytical Atomic Spectrometry, 2016, 31 (1), 179-196.

[14]. G. D'Agostino, L. Bergamaschi, M. Di Luzio, J. Noordmann, M. Oddone, O. Rienitz; *The link-up of mono-elemental solutions to the SI using INAA: a measurement procedure and the achievable uncertainty;* Journal of Radioanalytical and Nuclear Chemistry, 2016, 309 (2), 777-786.

[15]. B. Brandt, J. Vogl, J. Noordmann, O. Rienitz, D. Malinovskiy; *Characterization of a New Absolute Isotope Reference Material for Magnesium: ab initio Calibration of the Mass Spectrometers and Determination of Isotopic Composition and Atomic Weight*; Journal of Analytical Atomic Spectrometry, 2016, 31 (7), 1440-1458.

JRP start date and duration:	1 Sept. 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	
JRP-Partners: JRP-Partner 1: BAM, Germany JRP-Partner 2: BRML, Romania JRP-Partner 3: INRIM, Italy JRP-Partner 4: LGC, United Kingdom JRP-Partner 5: LNE, France	 JRP-Partner 6: PTB, Germany JRP-Partner 7: SMU, Slovakia JRP-Partner 8: CENAM, Mexico JRP-Partner 9: HRMF, Greece
REG1-Researcher: (associated Home Organisation):	Frank Vanhaecke, Belgium UGent, Belgium
REG2-Researcher: (associated Home Organisation):	Volker Hoffmann, Germany IFW, Germany

The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union