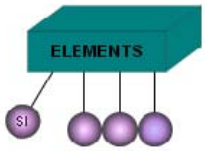


# FINAL PUBLISHABLE JRP REPORT

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| JRP short name | ELEMENTS |
| JRP full title | Primary standards for challenging elements |
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| (Home organisation Short name, country) | UGent, Belgium | Duration: 24 months (30 months FTE) |
| Researcher name, title | Volker Hoffmann | Start date: 01 January 2013 |
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## 1. Executive Summary

### 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.

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 the lack of primary standards for element determination in Europe and worldwide. 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 and 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 the 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 allow 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.

## 2. Project context, rationale and objectives

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 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.

Prior to the SIB09 project there were hardly any demonstrated primary standards in this field and although primary solutions and solutions declared as secondary were omnipresent, in practice primary materials characterised for total purity to underpin these declarations rarely existed. As a consequence, elemental determination in field laboratories and NMIs were 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; Mg and Al are of great importance for industry for use as lightweight construction materials in car and plane construction. 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. Rh is an important noble metal widely used in chemical catalysis and in car catalysts. 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 and EU Directives or customer needs this directly affects the quality of life, in particular 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. Therefore there is an urgent need to realise and to disseminate primary standards to underpin these measurements.

The SIB09 project aimed to provide the technical basis for resolving this lack of primary standards for element determination, within the scope of a activity by NMIs running in parallel to the project. Efficient procedures, which improved the methodology for realising fit for purpose primary standards for most of the challenging elements frequently used in elemental analysis, were developed and applied for the selected guide elements: Mg, Zn, Al, Mo and Rh.

Practical work was split into three main parts. First there was the development of procedures for purity analysis with respect to metallic and non-metallic impurities of high purity materials with a focus on efficient methods and challenges in non-metal determination. The second was 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 was the dissemination of the primary standards through loss free decomposition, the linking of two solutions of similar composition and the direct linkage of a solution to a solid material with small uncertainty.

The three objectives for the SIB09 project 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

# 3. Research results

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

### Introduction

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 difficult to dissolve elements Mo and Rh. To achieve a purity statement with very small uncertainties of < 0.05% indirect determination of the impurities and subtracting them from the ideal purity of 100 % were developed.

### Results

*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) were carried out to evaluate the potential of this solid sampling technique for a fast analysis of the matrices without excessive sample preparation for investigations of the homogeneity of materials and the sensitive determination of traces in high purity materials. All parameters affecting the calibration strategies were studied thoroughly.

Homogeneity concerning metallic impurities of high purity Al, Mg and Zn materials was established experimentally. The (unusual) behaviour of Mg matrix in GDMS analysis was investigated and the results were published in a special issue of *Analytical and Bioanalytical Chemistry* on “Emerging Concepts and Strategies with Analytical Glow Discharges”. In close collaboration with several labs including those from industry the ability to perform non-metal determination using GDMS was evaluated. For the first time, synthetic doped pressed powder and sintered samples for non-metal determination were prepared.

For the calibration of GDMS, compacted liquid doped powder samples were prepared and applied for Mg, Al and Zn matrix.

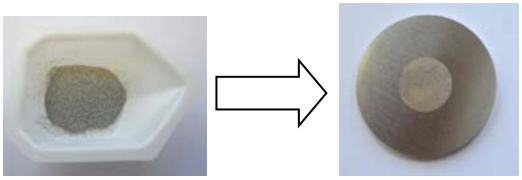

**Figure 1: Pressed powder Mg sample**

The results of the use of matrix-specific calibrations for oxygen in analytical glow discharge spectrometry were published in Analytical and Bioanalytical Chemistry (ABC). Instrumental neutron activation analysis (INAA) procedures were developed for homogeneity studies on Mg, Al, Rh and Mo. The methods have been applied on Rh, Mo, and Mg samples. This allowed the homogeneity determination of Rh subsamples by measuring the impurities mass fraction. The findings and methodology have been published in *Metrologia*. A good practice guide on the strategy to access homogeneity of high purity materials was also compiled.

For non-metal determination systematic studies were carried out for the unproven recovery for oxygen determination in $Al_2O_3$ and Al as well as MgO and Mg and in Zn matrix.

For the challenging determination of non-metals a gas dose system for calibration of the method of Carrier Gas Hot Extraction (CGHE) was designed, constructed and characterised.

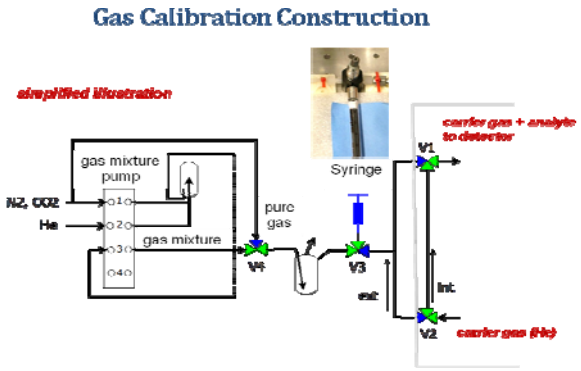


**Figure 2: Gas calibration of Carrier Gas Hot Extraction technique (CGHE)**

The system allows for a calibration with gases instead of very small amounts of solids and therefore with an improved uncertainty of factor 10. The results were presented at international conferences and meetings with industrial boards and published in *Analytical Methods*.

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

Through the combined effort of project partners, the materials Mg, Zn and Al were characterised with different analytical methods leading to materials with a well-defined content of their matrix element with an uncertainty of 0.01 %. The homogeneity of the materials were checked by Glow Discharge Mass Spectrometry (GDMS) and INAA and impurities in the materials were determined using a variety of methods such as ICP-MS, GDMS, INAA and Atomic Absorption Spectroscopy (AAS). The wide variety of method was necessary, since there is not one method able to deliver results for all possible impurities in a matrix material with sufficiently small uncertainty. A good practice guide on dealing with interferences in ICP-MS for investigations of high purity materials was produced and it outlines the specific challenges. In Figure 3 are shown the results for the determination of impurities of Cr in Mg shown, determined by 6 partners with 3 different techniques. The materials are available at the NMIs.

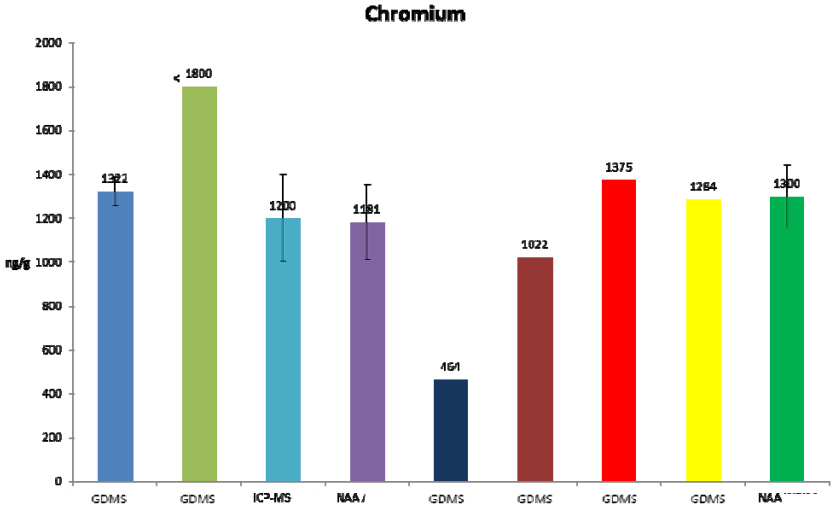


**Figure 3: Comparison of Cr content in Mg by three different techniques and six different partners**

The results of extensive measurements with different techniques were evaluated and as a result a guide on the strategy to assess homogeneity of high purity materials was produced and published on the project website. Further results of GDMS measurements compared with ICP were presented at the European Winter Conference on Plasma Spectrochemistry, Münster Germany in February 2015.

However, the aim of the project was to come up with a total purity statements for the high purity materials. To achieve this with an uncertainty on the mass fraction of the matrix element below 0.01 % all possible

impurities in the material need to be detected and subtracted from 100 %. In Figure 4 the purity statement for Zn is shown.

| | matrix in % | impurity in mg/kg | sum 'above' in mg/kg | um/2 'below' in mg/kg | not relevant (estimate) | under nvestigation |
|---|---|---|---|---|---|---|
| mass fraction | 99,9874 | 126,00 | 74,07 | 51,94 | | |
| abs. uncertainty | 0,0025 | 25,15 | 11,27 | 22,49 | | |

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H < 30 | | | | | | | | | | | | | | | | | He < 0,001 |
| Li < 0,015 | Be < 0,0233 | | | | | | | | | | | B < 0,045 | C < 8,8 | N < 21 | O < 23 | F < 5 | Ne < 0,001 |
| Na < 0,6137 | Mg < 0,06 | | | | | | | | | | | Al < 0,768 | Si < 1,5 | P < 0,15 | S < 6 | Cl < 1 | Ar < 0,001 |
| K < 0,15 | Ca < 2,693 | Sc < 0,005 | Ti < 0,0728 | V 0,0173 | Cr 4,4044 | Mn 0,6091 | Fe 23,431 | Co 0,0801 | Ni 2,8611 | Cu 7,9354 | Zn matrix | Ga < 0,01 | Ge < 0,0193 | As < 0,0330 | Se < 0,75 | Br < 1 | Kr < 0,001 |
| Rb < 0,0120 | Sr < 0,003 | Y < 0,002 | Zr < 0,0021 | Nb < 0,015 | Mo 0,1164 | Tc < 0,001 | Ru < 0,001 | Rh < 0,0021 | Pd < 0,0061 | Ag 1,535 | Cd 1,1604 | In < 0,005 | Sn 1,8080 | Sb 0,1872 | Te < 0,003 | I < 1 | Xe < 0,001 |
| Cs < 0,0017 | Ba < 0,015 | La < 0,0013 | Hf < 0,0013 | Ta < 0,001 | W < 0,0143 | Re < 0,001 | Os < 0,03 | Ir < 0,001 | Pt < 0,001 | Au < 0,001 | Hg < 0,0145 | Tl 0,8429 | Pb 27,59 | Bi 1,4876 | Po < 0,001 | At < 0,001 | Rn < 0,001 |
| Fr < 0,001 | Ra < 0,001 | Ac < 0,001 | | | | | | | | | | | | | | | |
| | | | Ce < 0,001 | Pr < 0,0011 | Nd < 0,001 | Pm < 0,001 | Sm < 0,001 | Eu < 0,0008 | Gd < 0,001 | Tb < 0,001 | Dy < 0,001 | Ho < 0,001 | Er < 0,001 | Tm < 0,001 | Yb < 0,001 | Lu < 0,0012 | |
| | | | Th < 0,0014 | Pa < 0,001 | U < 0,001 | | | | | | | | | | | | |

**Figure 4: Purity statement for the investigated Zn material**

## Conclusions:

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 characterisation to evaluate the potential of solid sampling techniques for a fast analysis of the pure materials 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 by CGHE a direct gas calibration unit was constructed and characterised.

Homogeneity testing of the material was needed to ensure that 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 a very sensitive measurement principle 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.

### *3.2 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.*

**Introduction**

Direct measurements determining the amount of the main component were carried out to validate elemental calibration standards. As most elements are a mixture of isotopes, this objective looked at the determination of isotopic composition.

**Results**

A procedure for the purification of natural Mg was developed. All three highly enriched Mg isotopes were purified by two sublimation cycles, 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 for isotopic mixing.

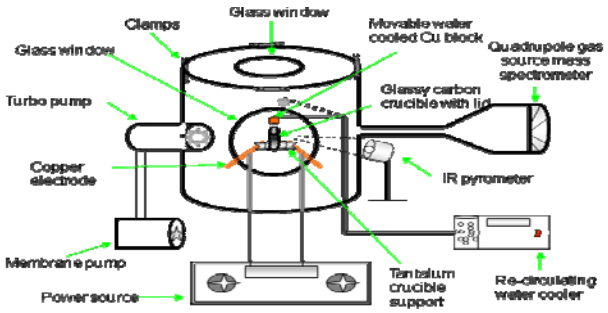


**Figure 5: Purification of Mg**

*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 a great improvement compared to the target value of uncertainty ($U$ < 0.02%). In Figure 6 the calculated uncertainty contributions on the direct determination of Zn are summarised.
Validated assay procedures for titrimetric methods were developed for direct assay of Mg, Zn and Al and were achieved with an expanded uncertainty below 0.1%. This is low enough to enable the key application of independent validation of elemental calibration solutions.

Based on these results a good practice guide on the technical application of the EDTA titration approach for certification of primary standards was produced and is available to the public.

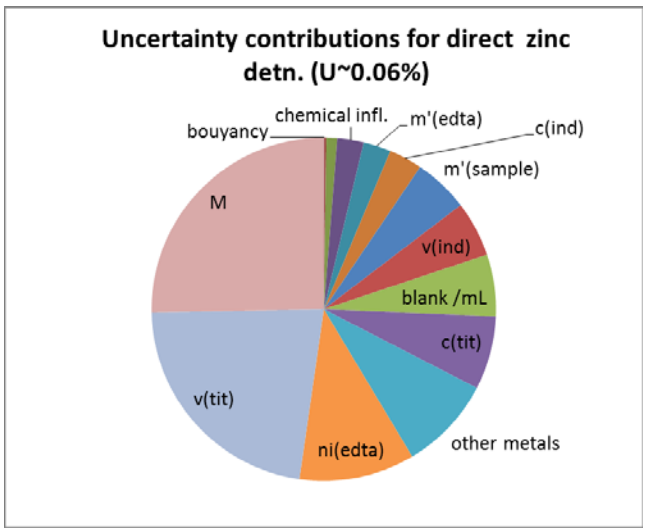


Figure 6: Uncertainty contributions for the direct determination of Zn

*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 multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) using calibration with synthetic isotope mixtures (SIMs) has been achieved and a paper published in *ABC*. For the first time, synthetic isotope mixtures prepared from seven commercially available isotopically enriched molybdenum 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 MC-ICP-MS is consistent with mass-dependent isotope distribution. This avoids any assumption on mass-dependent isotope fractionations in MC-ICP-MS, inherent to the method of double spike previously used for Mo isotope amount ratio measurements. The data obtained show experimentally for the first time that instrumental mass discrimination in MC-ICP-MS is consistent with mass-dependent Mo isotope fractionation.

Furthermore, cold vapour generation (CV) was combined with multi-collector ICP-mass spectrometry for Hg isotopic analysis. A 20-fold gain in signal intensity versus pneumatic nebulisation was achieved.

**Figure 7: Cold vapour generation MC-ICP-MS**

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

**Conclusions:**

Metal calibration solutions were produced and measured directly for the main component. 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 for independent validation of elemental calibration solutions by NMIs. 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 %).

A procedure for purification of natural Mg was developed. All three Mg isotopes were purified by two sublimation cycles, 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. 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.

### *3.3 To develop methods and to establish loss free and complete decomposition*

**Introduction**

The solubility of materials very strongly depends on the purity of the material. In general the higher the purity the harder it is to dissolve the material. Complete and loss free digestion is difficult to achieve especially for elements such as Mo and Rh. Thus dissolving samples and comparing the resulting solution with other standards/references can be used to determine purity. This objective looked at how to completely dissolve materials in order to compare and link different solutions. Different sample preparation techniques were investigated and the results from the different techniques were compared.

**Results**

The work on the development of methods and establishment of loss free and complete decomposition of materials, included:

- Development of new measurement methods for comparing two elemental solutions of similar composition with small uncertainty (0.05 %) based on a 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.
- Development of a new measurement method for comparing the content of a solution 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/or a very difficult to dissolve material is transferred into solution.

New methods were developed and successfully applied for the complete and loss-free digestion of the refractory elements Mo and Rh for the preparation of primary elemental solutions. A digestion procedure for 0.5 g of rhodium foil was established. In addition, a transformation of the matrix from rhodium bromide to rhodium nitrate was successfully accomplished. For the first time 2 g of molybdenum rods were successfully digested in a DURAN bottle, without the need to transfer the solution and risking any loss of the element of interest. A differential method was also developed linking two calibration solutions of similar composition for the measurement of the content of Rh by MC-ICP-MS. Bracketing measurements with MC-ICP-MS were applied. The stock solution contained 1 g/kg and the measurement solution 225 ng/g Rh and 185 ng/g indium as an internal standard. In addition, a differential method was developed linking two calibration solutions of similar composition for the measurement of the content of Mo by MC-ICP-MS. Again, bracketing measurements with MC-ICP-MS were applied. The stock solution contained 1 g/kg and the measurement solution 1250 ng/g Mo and 290 ng/g yttrium as an internal standard. The target measurement uncertainty of less than 0.1 % was reached in both cases. The project successfully developed differential methods linking two calibration solutions of similar composition ($w$(E) ≈ 1 g/kg) for the measurement of the content of Rh, Mo and Mg by ICP OES. Bracketing measurements with MC-ICP-MS were applied with yttrium as an internal standard. A method for the analysis of molybdenum solutions was developed, which demonstrates the possibility to compare the elemental mass content of two solutions. It was a differential method based on INAA, not exceeding the target uncertainty of 0.1 %.

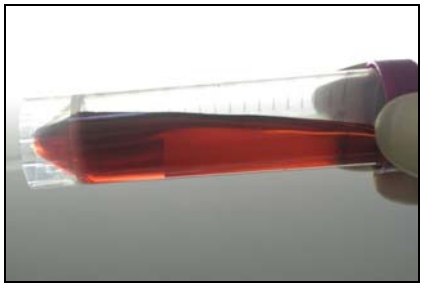

**Figure 8: Solution of completely digested Rh.**

The project produced a paper about the gravimetric preparation of reference solutions of rhodium and molybdenum which was published in *Analytical and Bioanalytical Chemistry.*

An inter-laboratory comparison was organised and used to evaluate for the validation of the MC-ICP-MS, ICP OES, and titrimetry. This included distribution of two solutions (about 1 g/L) for each element (4 solutions in total) to partners BRML, CENAM, INRIM, SMU, one industrial partner and PTB developed. This comparison measurement was approved as EURAMET comparison TC-MC 1377 and took place between March 2015 and August 2015. The results are shown in Figure 9.

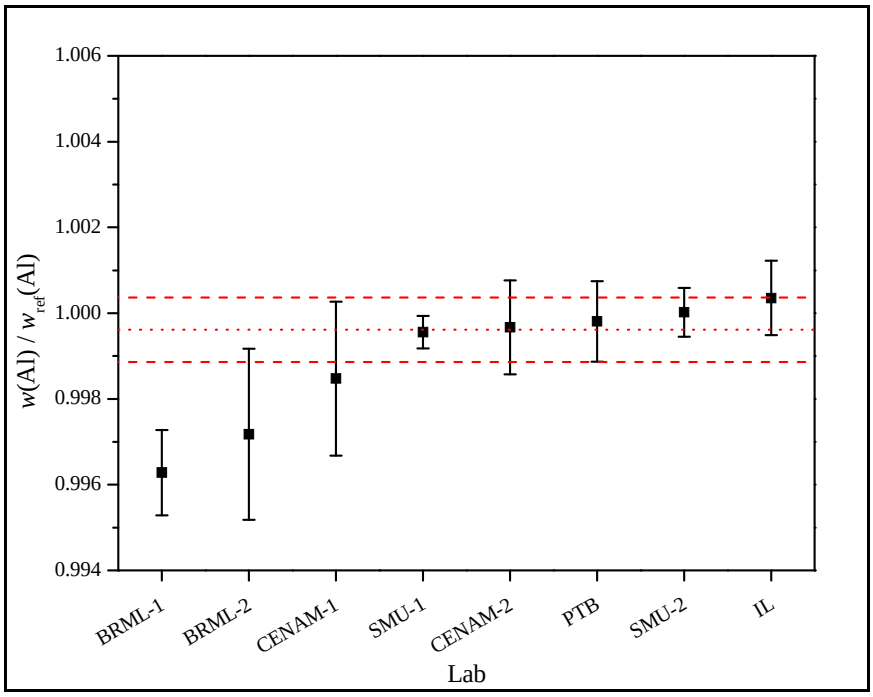


**Figure 9: Ratio of the aluminum mass fraction *w*(Al) as reported by the TC-MC 1377 participants relative to the gravimetric reference value. Error bars denote the expanded uncertainty *U*(*r*(Al)) for a coverage factor of *k* = 2 as reported. The dotted red line shows the median: $\bar{r}_{\mathrm{M}}(\mathrm{Al})$ = 0.99961. The dashed red lines indicate the range of the expanded uncertainty $U(\bar{r}_{\mathrm{M}}(\mathrm{Al}))$ associated with the M (median).**

## Conclusions:

New methods were developed and successfully applied for the complete and loss-free digestion of the difficult to decompose elements Mo and Rh in order to prepare primary elemental solutions. An interlaboratory comparison was conducted between the NMIs to validate the methodology for linking secondary calibration solutions to the prepared primary calibration solution.

## 4. 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 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 the lack of primary standards for element determination in Europe and worldwide. The five elements addressed in this project are representatives 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 metrological community (i.e. CCQM and EURAMET), 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 making inorganic chemical analysis results traceable to the SI.

*Dissemination of results*

The research results were published in high profile journals such as *Metrologia*, *Analytical and Bioanalytical Chemistry*, the *Journal of Analytical Atomic Spectrometry* and the *Journal of Radioanalytical and Nuclear Chemistry*. All scientific papers and 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 on producing calibration standard solutions and on the requirements for traceable calibration by accreditation standards (such as ISO 17025).

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 for 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 CIPM'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 reference 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 five elements; Mg, Al, Zn, Rh and Mo, the metrological community was 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.

- CCQM-P149 (the Consultative Committee for Amount of Substance) provides information on how NMIs characterise their national standards in practice. The results were discussed at the CCQM meeting in Tsukuba. NMIs are the fundament 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. The next step forward is for NMIs to compare copper 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.
- 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 and the corresponding primary solutions. End-users are able to search for primary elemental material and their corresponding solutions within this database.

*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.
In many documentary standards and directives, field laboratories are requested to use traceable measurement standards; however, traceability without demonstrated primary standards is not possible. The project is focused on filling the gap due to the current lack of demonstrated primary measurement standards, rather than the active contribution to standardisation bodies and documentary standards. Hence, by providing the methodology to realise primary standards for element determination, the project will provide the underpinning metrological basis for implementing the requirements within the huge variety of standards and Directives.
Specifically project SIB09 Elements is related through project partners and potential collaborators to standardisation via exchange of information and technical experience in the following bodies: DIN NA 062-02-21 AA "High purity reagents for use in semiconductor industry", CEN/TC230 "Water analysis". Following the regular reporting periods of the project, the chairs of these standardisation bodies are actively provided with slides and information on the technical progress in the project.

The research results are of great value to the research community. For instance the joint publication of the -partners shows a high response (more than 150 views and more than 60 uploads from Research Gate) in the scientific community. All scientific papers and presentations are available on the project webpage.
The end-users took advantage by this project through the provision of measurement or procedure protocols, which have been made public by the publication of papers. This project published detailed descriptions of digestion procedures for primary reference solutions for rhodium and molybdenum. Additionally, a detailed

description has been published about the preparation of an isotope reference material (IRM) for magnesium, which will soon be made available to the end-user by BAM.

## 5. Website address and contact details

Website: http://www.ptb.de/emrp/sib09.html

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