21GRD09 MetroPOEM

D3: Report describing the development of measurement methods for isotope ratios that are traceable to the SI and summarising the advantages/disadvantages of applying them to more commonly available techniques by providing suitable operation procedures focusing on stable polluting elements

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Glossary

CRC	collision/reaction cell
ICP-MS	inductively coupled plasma mass spectrometer
ICP-MS/MS	inductively coupled plasma tandem mass spectrometer
ICP-TOF-MS	inductively coupled plasma time-of-flight mass spectrometer
KED	kinetic energy discrimination
MC-ICP-MS	multicollector inductively coupled plasma mass spectrometer
TIMS	thermal ionisation mass spectrometer
IIF	instrumental isotopic fractionation
iRM	isotopic reference material
SI	International System of Units

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1 Summary

The objective of WP2 – Advancing stable and long-lived radiogenic isotope ratio measurements of environmental pollutants was to develop robust and broadly applicable methods for the determination of isotope ratios of stable and long-lived radionuclides by mass spectrometry. The target performance was to achieve measurement uncertainties sufficiently low to resolve natural mass-dependent isotope fractionation. For the development and optimisation of these methods, the environmentally relevant elements Li, B, Cr, Cd, Ni, Sb, Pb, and U were selected as key indicators.

This report presents the state of the art and the methodological improvements achieved within the MetroPOEM project. The work focused on isotope ratio determination using a range of mass spectrometric techniques and includes i) a systematic comparison of accuracy and precision across different instrument platforms; ii) the development and optimisation of both manual and automated chemical separation procedures; and iii) the implementation of collision/reaction cell technologies to resolve spectral interferences.

2 Introduction

The scope of any measurement is to collect accurate data, according to the context in which the obtained results are intended to be used [1]. Measurements of chemical properties involve assigning numbers reflecting dimensions of the measured properties, which can be compared to well-characterized standards [1,2]. Acquiring accurate results is essential for many applications. Therefore, a significant effort should be taken to make chemical measurements as accurate as possible. This is only possible when all the relevant processes involved in the signal detection and quantification are understood and taken into account. The commonly used instrumental methods require calibration using appropriate standards. Such calibration must be based on the most suitable chemical standards, which are selected specifically for the given purpose. It is also essential to perform an analytical risk assessment and to verify the analytical correctness of the conversion of the recorded values into meaningful quantitative results [1]. The indicator of analytical correctness is the measurement uncertainty, a numerical value necessary to compare measurement results among themselves, with reference values or other laboratory results[3].

Determining accurate and precise isotope ratios has remained a strong interest for researchers from various areas. It is because isotope ratios have many important applications such as accurate determination of trace elements and elemental speciation by isotope dilution mass spectrometry [4], the study of natural isotope variations and the biogeochemical cycles of metals [5], geochronology in earth sciences [6, 7], archaeology [8], metal bioavailability [9], provenance studies of environmental and food samples [10], investigations of the migration of animals and humans [11,12], and a multitude of other applications.

Among the plethora of mass spectrometers developed, the thermal ionisation mass spectrometer (TIMS) was once regarded as the most appropriate and reliable for isotope ratio determination due to its precision. In the late 1990s, multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) became available as an alternative to TIMS [13]. Nowadays, MC-ICP-MS allows determining isotope ratios with measurement precision comparable to those of TIMS (down to 0.001%) [14,15]. As MC-ICP-MS instruments present high expenses for the laboratories, and with the development and optimisation of single collectors ICP-MSs, they are becoming another useful tools. The precision of isotope ratios of quadrupole-based ICP-MS instruments is lower than the MC-ICP-MS as a result of the combination of the ICP being a noisy ion source and the presence of a single detector only, allowing monitoring of only one signal at any given time [14]. To overcome this limitation, the scanning or peak hopping rate is usually chosen as high as possible to compensate for signal drift and/or instability to the largest possible extent [14]. For many isotope ratio applications, high measurement precision is required as very small variations in the isotopic composition of a target element need to be measured.

For obtaining a good precision, analyte isotopes must be fully separated from the matrix [13] to overcome systematic errors derived from matrix-induced interferences as well as changes in instrumental isotopic fractionation (IIF) (or the mass bias). Over the last few decades, several different IIF correction methods have been successfully used for the determination of isotope ratios such as internal standardisation [13,14], external standard–sample–standard bracketing technique [13,14], and double or triple spike techniques [16]. Although the IIF corrections are used for years, there is still ongoing discussion as to which correction method provides the most accurate measurements. This is an issue of increasing importance as a result of the continuously improving isotope ratio precision attainable [14].

Work Package 2 (WP2) of the MetroPOEM project focused on advancing measurement capabilities for stable and long-lived radiogenic isotope ratios in environmental pollutants. The central aim was the development and optimisation of generic, high-accuracy mass spectrometry-based methods for key environmentally relevant elements: lithium (Li), boron (B), chromium (Cr), cadmium (Cd), nickel (Ni), antimony (Sb), lead (Pb), and uranium (U). These elements have been selected due to their environmental significance, regulatory relevance, or potential as markers of geochemical pathways and anthropogenic processes. Central to WP2 was the requirement to ensure that measurement results are traceable to the International System of Units (SI), with uncertainties low enough to detect natural, mass-dependent isotope fractionation.

This deliverable summarises the progress made in developing SI-traceable isotope ratio measurement methods (Task 2.1) and supporting analyte-matrix separation procedures (Task 2.2). Emphasis is placed on methods applicable to both advanced (e.g. MC-ICP-MS) and more broadly accessible instruments (e.g. single collector ICP-MS, ICP-MS/MS).

The methods developed utilise a range of instrumental platforms including multi-collector ICP-MS (MC-ICP-MS), single collector ICP-MS, sector field ICP-MS, ICP-MS/MS, and TIMS.

2.1 Development of SI traceable methods for the determination of isotope ratios of Li, B, Cr, Cd, Ni, Sb, Pb, and U by MC-ICP-MS and single collector ICP-MS

In the past, the generation of reproducible isotope ratio data was largely confined to specialists with extensive expertise in mass spectrometry. However, the advent and widespread adoption of ICP-MS have significantly broadened access to isotope analysis. Today, many laboratories with limited or no prior experience in mass spectrometry are routinely producing isotope data using ICP-MS systems. For such users, the availability and use of well-characterized isotopic reference materials (iRMs) are essential. iRMs play a critical role in ensuring the reliability and comparability of results by supporting robust method validation, quality control, and instrument calibration. As isotope ratio analysis expands into new application areas and user communities, the demand for accessible, traceable, and matrix-matched reference materials becomes increasingly important to uphold analytical accuracy and confidence [4].

2.1.1 Isotopic Reference Materials

Fast, sensitive, and inexpensive analytical methods are essential for detecting radioactive isotopes, stable pollutants, and their isotopic ratios in the environment. Mass spectrometry techniques have great potential to meet this need. Although the use of single collector ICP-MS is increasing, this potential cannot be fully realized unless techniques are validated with traceable reference materials.

Best-measurement results are obtained when a sample and a reference material are similar in their chemical and physical properties, including their isotopic compositions. However, multi-element iRMs are generally unavailable, and even single-element iRMs are limited to only a few elements. These reference materials are urgently needed to calibrate mass spectrometric measurements because of IIF effects that occur during measurements in mass spectrometers [17, 18, 19].

In the first stages of the project, extensive literature and market research were done on the availability of iRMs. They are listed in Table 1.

Table 1: Compilation of iRMs for Li, B, Cr, Cd, Ni, Sb, Pb, and U

Element	Reference material	Isotope ratio values with expanded uncertainty, k=2	Availability
Li	LSVEC	$n(^{6}Li)/n(^{7}Li)$ = 0.08215(23)	*Available; Under recertification*
B	BAM-AE123 NIST SRM 951a	$n(^{11}B)/n(^{10}B)$ = 4.042(6) $n(^{11}B)/n(^{10}B)$ = 4.0437(33)	*Available* *Out of Stock*
Cr	NIST SRM 979	$n(^{53}Cr)/n(^{52}Cr)$ = 0.11339(15)	*Available*
Cd	BAM-I012	$n(^{114}Cd)/n(^{111}Cd)$ = 2.2437(7)	*Available*
Ni	NIST SRM 986 NIST SRM 3136 NRCC HINI-1	$n(^{58}Ni)/n(^{58}Ni)$ = 2.596061(728) $n(^{58}Ni)/n(^{60}Ni)$ = 0.3854(30) $n(^{58}Ni)/ n(^{60}Ni)$ = 2.75740(375)	*Out of Stock* *Available* *Available*
Sb	BAM inhouse standard NRC candidate material	$n(^{123}Sb)/n(^{121}Sb)$ = 0.7479(11)	*Not available* *Data not yet avaiable*
Pb	NIST SRM 981	$n(^{204}Pb)/n(^{206}Pb)$ = 0.059042(37) $n(^{207}Pb)/n(^{206}Pb)$ = 0.91464(33) $n(^{208}Pb)/n(^{206}Pb)$ = 2.1681(8)	*Available*
	NIST SRM 983	$n(^{204}Pb)/n(^{206}Pb)$ = 0.000371(20) $n(^{207}Pb)/n(^{206}Pb)$ = 0.071201(40); $n(^{208}Pb)/n(^{206}Pb)$ = 0.013619(24)	*Available*
U	IRMM 184	$n(^{234}U)/n(^{238}U)$ = 0.000053196(16) $n(^{235}U)/n(^{238}U)$ = 0.0072631(11) $n(^{236}U)/n(^{238}U)$ = 0.00000012410(96)	*Available*
	NBL CRM 145	$n(^{234}U)/n(^{238}U)$ = 0.000052841(82) $n(^{235}U)/n(^{238}U)$ = 0.0072543(40)	*Available*

As shown in Table 1, some of the CRMs used for many years are no longer available. As a result, there will be a lack of comparability between previously published studies and those upcoming. For example, for Ni, there was a certified iRM, namely the NIST SRM 986, which is no longer available. In the literature, a single standard NIST SRM 3136 (Ni standard solution) is used, but the CRM does not have a certified value for the Ni isotopic composition. Recently, an iRM from the National Research Council of Canada (NIHI) has become available. On the other hand, no iRM is available for Sb. Currently, IUPAC tabulated values have to be used for the isotope ratio.

2.1.2 Comparison of ICP-MS performances

For isotope ratio determination, multi-collector ICP-MS (MC-ICP-MS) offers superior precision and accuracy compared to quadrupole (ICP-QMS) or time-of-flight (ICP-TOF-MS) systems, making it the preferred choice for challenging applications. While ICP-QMS is simpler and more affordable, it lacks the precision needed for many isotopic studies, whereas MC-ICP-MS, utilizing multiple Faraday detectors, provides the high performance required for accurate isotope ratio measurements, even surpassing traditional techniques like TIMS in some aspects.

In Table 2, a general comparison of different ICP-MS systems is presented.

Table 2: General overview of the ICP-MS instruments used for isotope ratio determination.

Platform	Typical precision for isotope ratios	Accuracy potential (with proper normalization/corrections)	Ease of use	Best for
MC-ICP-MS (magnetic sector, multi-collector) e.g., Thermo Neptune/Neoma, Nu Plasma II, 3	0.01 ‰ - 0.05 ‰	**State-of-the-art**; routinely matches certified reference values across elements when using appropriate corrections for IIF	**Challenging**; magnet/ESA tuning, collector mapping, cup calibrations, mass-bias models; once set up, very stable. Newer systems (Neoma) streamline setup	Highest-precision for isotope ratios; radiogenic and stable systems;
High-resolution sector-field ICP-MS (SF-ICP-MS, single collector) e.g., Thermo Element 2/XR, Nu AttoM	0.1‰ - 1‰	**High;** when spectral interferences are resolved; limited by sequential (not simultaneous) collection	**Moderate**; simpler than MC, but HR slit/peak centering & abundance sensitivity management add complexity	Elements with stubborn overlaps where HR separation beats cell chemistry; moderate-precision isotope ratios
Triple-quadrupole ICP-MS (ICP-QQQ / MS/MS) e.g., Agilent 8900, Thermo iCAP TQ, NexION 5000	0.05 ‰ - 1%	**Good;** when MS/MS chemistry removes isobars (e.g., Rb/Sr, Hg/Pb, Lu/Hf) and with rapid SSB; not MC-level	**Easier;** guided methods, robust collision/reaction cell; day-to-day operation is approachable	Routine isotope ratios where interferences dominate and sub-per-mil precision isn't required; high-throughput labs
Quadrupole ICP-MS (single quad, with collision/reaction cell)	0.05‰ - 1%	**Fair;** adequate for natural-abundance screening/ratio flags; interference control is key	**Easiest;** overall; quickest to learn and maintain	Screening, process control, tracer spikes where ultra-high precision isn't mandatory
ICP-TOF-MS e.g., TOFWERK icpTOF, Nu Vitesse	0.5‰ - 5‰	**Moderate**; great for multi-isotope/event-based work (LA, SP-ICP-MS) but not a replacement for MC precision	**Moderate;** simpler tuning; powerful for discovery mapping; less mature IR workflows than MC/QQQ	Single-particle & LA imaging where capturing all nuclides at once matters more than ppm-level precision

In order to achieve the objectives of the MetroPOEM project, a range of instrumental techniques were used for measurements, including MC-ICP-MS, quadrupole ICP-MS, and ICP-MS/MS. The performance of these techniques and existing calibration approaches was assessed and compared in terms of accuracy and precision of measurement results to demonstrate the potential of recent advances in ICP-MS technology. In Figure 1, a comparison of the performances of different instruments from the participating laboratories on selected isotopic systems is presented.

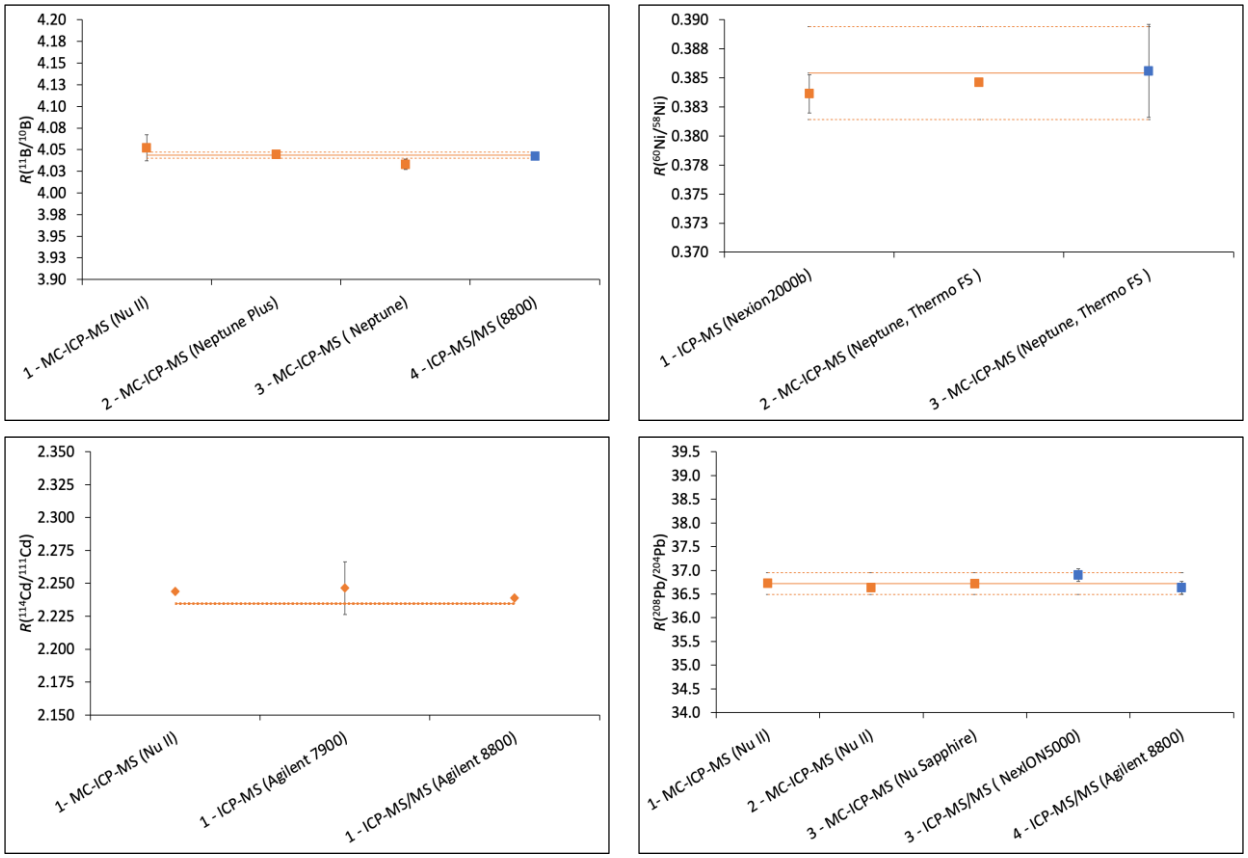

Figure 1: Comparison of isotope ratios for selected elements obtained with different mass spectrometers.

In the presented results, instrumental isotope fractionation was corrected applying: i) exponential law, ii) standard-sample bracketing method (SSB), iii) regression model, and iv) combination of SSB and Russell's law. The most frequently used was the SSB method. The application of the SSB method, exponential and Russell's laws was possible for isotopic systems with certified iRMs.

From Figure 1, it can be observed that, depending on the element, there is a good agreement of certified values regardless of the instrument used. As expected, the measurement uncertainties were bigger for single collector ICP-MS systems and for Ni isotopic data, as different reference materials were used. One was the iRM NIST SRM 986 (with certified isotopic ratio values) and the single element standard NIST SRM 3136 (not certified, reference value obtained from the GeoREM database and literature).

2.2 Development of analyte separation methods for high precision analysis

To obtain accurate and precise isotope ratios in environmental samples, proper preparation is essential. Several steps are typically involved before measuring isotope ratios. Depending on the sample type, a pre-treatment step may be necessary. For solid samples, this involves digestion or extraction, while for liquids, preconcentration and/or matrix removal are usually required. The next step is separation, which isolates the element of interest from the sample matrix that can cause signal suppression, as well as from isobaric and polyatomic interferences that may reduce precision and cause shifts in the measured values.

Currently, several separation methods are used in analytical chemistry to address interferences, each with its own strengths and limitations. These approaches range from simple mathematical corrections to chromatographic separations and advanced chemical resolution technologies.

One of the simplest approaches is mathematical correction, which is suitable when the interfering species are well characterized and occur only at low concentrations. By applying correction factors or algorithms, the contribution of the interfering signal can be subtracted from the overall measurement. This approach is cost-effective, quick, and can be easily automated within analytical software. However, its accuracy depends heavily on prior knowledge of the interference, and it becomes less reliable when interferences are complex, unexpected, or present in significant concentrations.

Another widely applied strategy is chromatographic separation, such as ion chromatography (IC) or extraction chromatography. These techniques make use of element-selective resins to physically separate the analyte from interfering species. Chromatographic methods are versatile and highly effective for handling complex mixtures, and they can be used in both manual and automated setups. Nevertheless, they are more time-consuming than mathematical corrections, require consumables such as resins and columns, and may lead to sample loss or dilution during processing.

A more advanced approach involves chemical resolution through cell technologies, most commonly applied in modern mass spectrometers. Collision or reaction cells use reactive gases or controlled conditions to neutralize or remove isobaric and polyatomic interferences, thereby isolating the target analyte. This method has the advantage of being integrated directly into the instrument, requiring minimal additional sample preparation. It is especially powerful for removing isobaric interferences that cannot be corrected mathematically. On the downside, the effectiveness of this approach depends on the suitability of the chosen reaction gas, and in some cases, new interferences may be formed. Moreover, the measurement uncertainty can be higher that the one obtained with classical chromatographic approaches.

Each separation method offers unique advantages depending on the type and level of interference. Mathematical corrections are most effective in simple cases, chromatographic separations are robust for complex mixtures, and cell technologies provide a powerful in-instrument solution for advanced analytical applications.

2.2.1 Manual separation methods

For the isolation of elements from the seawater matrix, as applied in the MetroPOEM project, a variety of resins and techniques were tested depending on the target analyte. For lithium (Li), 50W-X12 resin was used. For boron (B), approaches included sublimation, AG 50W-X8, Amberlite IRA 743, and microsublimation. Chromium (Cr) was isolated using BioRad AG 1-X8, while nickel (Ni) was treated with Chelex 100 chelating resin, Ni-Spec, and other methods. Cadmium (Cd) was separated with AG 50W-X8 and BioRad MP-1M, whereas lead (Pb) required a broader range of resins, including Sr-Spec, DGA resin, Pb Resin (Triskem), and BioRad AG 1-X8 for anion exchange. Uranium (U) was also isolated by anion exchange using UTEVA (Triskem) resin.

In addition to manual methods, automated isolation procedures were developed with the seaFAST and prepFAST systems (ESI), offering higher efficiency and reproducibility in sample preparation.

In Table 3, a summary of manual separation methods developed and/or used isolating selected elements from seawater by participating laboratories is presented. The full descriptions of the procedures can be found in the Appendix.

Table 3: List of methods used for the separation of selected elements from the matrix for accurate isotope ratio determination.

Element	Separation procedure	Instrument	Laboratory
Li	Exchange chromatography using AG 50W-X8 (BioRad)	Neptune Plus, Thermo Fiscer Scinetific	IFE
	Two step cation exchange chromatography using AG 50W-X12 (BioRad)	Neptune Plus, Thermo Fiscer Scinetific	BAM
	Cation exchange chromatography using Dowex 50WX8-200	Neptune XT, Thermo Fisher Scientific	PTB
B	Microdistillation	Neptune Plus, Thermo Fiscer Scinetific	BAM
	Three step separation using Bio-Rad AG 1-X8 two times and IRA 743 resin with positive pressure SPE mainhold (CEREX 48)	Finnigan Element 2, Thermo	TUBITAK
Ni	Isolation of Ni from the seawater matrix with $Mg(OH)_2$ co-precipitation followed by two stage ion-exchange chromatography, first anion exchange followed by Cation-exchange on Chelex-100 resin	Neoma, Thermo Fishcer Scientific	LGC
	2 stage ion-exchange chromatography: Step 1: Fe isolation Bio-Rad AG MP-1M Step 2: Ni isolation Bio-Rad AG 1-X8	Nu Sapphire, Nu Instruments	MUL
Cd	Preconcentration of Cd by co-precipitation with $Mg(OH)_2$, separation of Cd by anion-exchange resin AG MP-1M (BioRad)	Nu II, Nu Instruments	JSI
Pb	Two stage extraction chromatograpy with Sr spec resin (Triskem)	Nu Sapphire, Nu Instruments	MUL
	Preconcentration of Pb by co-precipitation with $Mg(OH)_2$, separation of Pb by anion-exchange resin AG 1-X8 (BioRad)	Nu II, Nu Instruments	AU/UGOT
U	Separation of U from seawater by UTEVA (Triskem) resin	Neptune Plus, Thermo Fishcer Scientific	PTB

After the isolation of elements by the developed and optimised methods, the isotope ratios can be measured on any ICP-MS systems (single or multicollector). The main contribution to the measurement uncertainty

comes from the precision of the mass spectrometer used. The comparability data of the separation methods and the measurement system will be evident from the report on the reference material characterisation in deliverable D7.

2.2.2 Automated separation methods

In recent years, automated separation systems have been increasingly adopted for preparing samples before isotope ratio determination, particularly in fields such as geochemistry, oceanography, and environmental science. Traditional manual column chromatography, although reliable, is labor-intensive, prone to variability, and limits sample throughput. To address these limitations, platforms such as seaFAST and prepFAST (Elemental Scientific Inc., ESI) have been developed and extensively tested for a variety of elements. These platforms rely on programmable valve switching and resin-based columns to isolate specific elements while effectively removing matrix components that can interfere with isotope ratio measurements. By minimizing manual handling, they reduce the risk of contamination, improve consistency between samples, and enable the processing of larger sample sets with less labor. In addition, their flexibility allows the use of different resin chemistries tailored to particular analytes.

Published studies demonstrate that seaFAST is highly effective for isolating trace metals from complex, high-salt matrices such as seawater. By combining online preconcentration with matrix removal on resin columns, the system minimizes contamination risks and achieves low procedural blanks, which is essential for high-precision isotopic measurements. Applications include Cu, Ni, and Ga isotope determinations in marine samples, where automated methods have enabled reliable large-scale studies that would not have been practical using manual separations [21, 22].

The prepFAST MC system, specifically designed for isotope ratio studies, has been applied to elements such as Sr, Pb, Nd, U, and B, where accurate separation from matrix and isobaric interferences is critical. Studies report yields of 98 to 100 % with excellent reproducibility, allowing precise determination of isotope ratios such as $R(^{87}Sr/^{86}Sr)$, $R(^{206}Pb/^{204}Pb)$, and $R(^{235}U/^{238}U)$. The automation of sample loading, resin conditioning, elution, and fraction collection significantly reduces operator time and variability, while also improving cross-laboratory comparability [20].

Comparative assessments show that isotope ratio precision obtained with automated separations is comparable to, and in some cases indistinguishable from, that achieved with manual methods, while the reproducibility and efficiency are markedly improved. Importantly, the scalability of automated systems allows processing of tens to hundreds of samples per sequence, supporting studies that require large datasets, such as oceanographic transects, provenance tracing, and environmental monitoring.

In the frame of the MetroPOEM project, WP2, Task 2.2, the following was done (Table 4). More details can be found in the appendix.

Table 4: Development of automated separation methods.

Element	Separation procedure	Instrument	Laboratory
Li	Separation of Li using AG 50W-X8 or X-12 resins on the prepFAST MC (ESI)	Neptune Plus, Thermo Fiscer Scinetific	IFE
B	separation of B on Amberlite IRA 743 resin on the prepFAST MC (ESI)	Neptune Plus, Thermo Fiscer Scinetific	IFE
Pb	purification of Pb from the salt by seaFAST (ESI) and isolation using DGA resin on a prepFAST system (ESI)	Nu Sapphire, Nu Instruments	MUL

2.2.3 Resolution of isobaric interferences using collision/reaction cell ICP-MS instruments

Modern quadrupole ICP-MS instruments mitigate isobaric and polyatomic overlaps primarily via two complementary strategies inside a collision/reaction cell (CRC): (i) collision mode with kinetic energy discrimination (KED), most commonly using helium, and (ii) reaction mode using selective ion–molecule chemistry (e.g., H_2, O_2, NH_3, CH_3F).

In He-KED, polyatomic species undergo more frequent momentum-transfer collisions than atomic analyte ions of the same nominal m/z, so a downstream energy barrier preferentially attenuates interfering clusters while transmitting analyte ions; this “generic” approach is robust across complex matrices and underpins multi-element screening methods. Its principles, benefits, and limitations (e.g., partial analyte signal loss, reduced efficacy on some mono-isobaric overlaps) are well established.

Reaction mode introduces a reactive gas to remove the overlap, either on-mass (the interferent reacts away while the analyte remains) or via a mass-shift pathway (the analyte is converted to a product ion at a new m/z free of interferences). Controlling secondary chemistry in the cell is critical: reaction conditions must suppress the formation of new cluster/product ions and maintain analyte transmission. Dynamic bandpass control (e.g., DRC bandpass/RPq) and careful gas-flow/voltage tuning are used to stabilize reaction pathways and minimize side-products.

The strategy of chemical resolution using collision/reaction cell technologies has been successfully applied to eliminate isobaric interferences such as $^{87}Rb^+$ on $^{87}Sr^+$ and $^{204}Hg^+$ on $^{204}Pb^+$. This is achieved through the use of specific reaction gases tailored to each system, for example, a CH_3F/He mixture for Sr and NH_3/He for Pb. In the case of Sr, the reaction leads to a mass shift of +19, whereas for Pb, the interference from $^{204}Hg^+$ is removed via a charge transfer process. These highly selective and efficient reactions make it possible to determine the $R(^{87}Sr/^{86}Sr)$ and $R(^{206}Pb/^{204}Pb)$ isotope ratios free from spectral overlaps, achieving external precisions of ≤0.05% RSD [23, 24]. Nevertheless, the overall measurement uncertainty achievable with these cell-based approaches remains significantly higher compared to that obtained with multi-collector mass spectrometers.

In Activity 2.2.2, the collision/reaction cell technologies were applied to Cr, Pb and Cd isotopic systems. In the first step, the performances of different mass spectrometers were compared and result are presented in Figure 2.

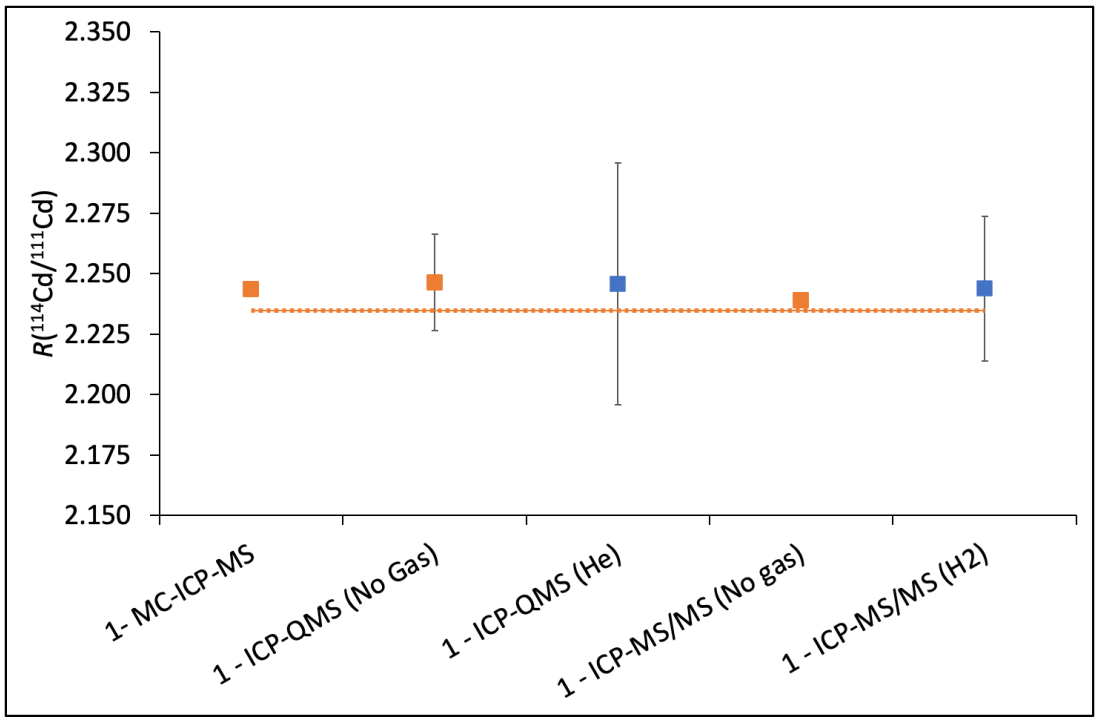

Figure 2: Comparison of Cd isotope ratios obtained in different modes of measurement.

As can be seen from Figure 2, when collision gases are applied, measurement uncertainties are much higher compared to the No-gas mode in ICP-MS and especially compared to the MC-ICP-MS data. This can be due to the instability of the system when a gas is introduced in the collision-reaction cell. It was also noted in the literature that mass discrimination effects become more pronounced and variable in ICP-QMS when the collision/reaction cell is pressurized with a gas, as a result of slight differences in the collisional and/or chemical behavior of the isotopes as a function of their mass [25, 26].

The collision/reaction cell technology in the frame of the WP2 was tested on a real sample of seawater with measurable amounts of Pb, Cd and Cr. The selected elements in seawater matrix may suffer from interferences of ^{204}Hg, $^{95,98}Mo^{16}O^{+}$, and $^{54}Fe^{+}$ and $^{40}Ar^{12}C^{+}$, respectively. An overview of the performed checks is summarised in Table 5.

Table 5: Summary of the work done on the collision/reaction removal of interferences.

Isotopic systems	Available Cell gases	Available Instruments	Comments
Pb	H2, He, NH3, N2O	Agilent 8800 and 8900	Spiking experiments were conducted with a special focus on ^{204}Hg interfering ^{204}Pb with concentration ratios (Pb:Hg) of 1:1, 1:10 and 1:100
Cd	O2, N2O, H2	Agilent 8800	Spiking experiments were conducted with a special focus on MoO+ interference on Cd
Cr	He, HEHe	Agilent 7700/7900	Spiking experiments were conducted with a special focus on FeC+ interference on Cr

The results showed promising results. The proper selection of the collision-reaction gas successfully diminished the influence of the interfering ions. Further work is needed in order to understand the effect of added gases on the mass bias and measurement uncertainty.

3 Conclusions

Work Package 2 of the MetroPOEM project has advanced the development of high-accuracy methods for isotope ratio determination of environmentally relevant elements (Li, B, Cr, Cd, Ni, Sb, Pb, and U). The work demonstrated that both multi-collector and single-collector ICP-MS instruments can provide reliable results when supported by appropriate calibration strategies and isotopic reference materials, though the highest levels of precision and lowest uncertainties remain achievable with MC-ICP-MS. The comparison of different platforms confirmed that accuracy is highly dependent on the availability of well-characterised iRMs, highlighting a critical need for the continued development and certification of such materials to ensure comparability across laboratories.

In parallel, the development and optimisation of manual and automated analyte separation procedures have significantly improved the robustness and efficiency of sample preparation. Automated platforms such as prepFAST and seaFAST demonstrated strong potential for increasing throughput, reducing contamination risks, and improving reproducibility, thereby supporting large-scale studies and wider adoption of isotope ratio methods. Manual separation methods remain indispensable, particularly for specialised applications requiring tailored chemistries or higher precision.

The evaluation of collision/reaction cell technologies confirmed their utility in mitigating spectral interferences for selected isotope systems, particularly in complex matrices such as seawater. While these approaches broaden the applicability of quadrupole- and sector-field-based ICP-MS instruments, their precision and accuracy remain limited compared to multi-collector systems. Further optimisation of reaction gas conditions and a deeper understanding of their influence on mass bias are needed to reduce uncertainties to levels suitable for demanding applications.

Overall, WP2 has substantially improved isotope ratio measurements for key pollutant elements by combining advanced mass spectrometric techniques with optimised separation procedures and interference mitigation strategies. These developments provide a stronger analytical basis for environmental monitoring, source tracing, and regulatory applications. At the same time, the work underscores the importance of accessible isotopic reference materials, continued interlaboratory comparisons, and further refinement of instrumental approaches.

4 References

[1] E. Bulska, B. Wagner, Quantitative aspects of inductively coupled plasma mass spectrometry, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences. 374 (2016).
[2] A. Virgilio, J.A. Nóbrega, G.L. Donati, Multi-isotope calibration for inductively coupled plasma mass spectrometry, Analytical and Bioanalytical Chemistry. 410 (2018) 1157–1162.
[3] „Guide to the expression of uncertainty in measurement". International Organization for Standardization, 1995, ISBN 92-67-10188-9.
[4] J. Vogl, W. Pritzkow, Isotope Dilution Mass Spectrometry-A Primary Method of Measurement and Its Role for RM Certification. Mapan 25 (3) (2010) 135-164.
[5] J.G. Wiederhold, Metal stable isotope signatures as tracers in environmental geochemistry, Environmental Science and Technology. 49 (2015) 2606–2624.
[6] M.B. Andersen, C.H. Stirling, S. Weyer, Uranium isotope fractionation, in: Non-Traditional Stable Isotopes, Walter de Gruyter GmbH, 2017: pp. 799–850.
[7] J.M. Cottle, M.S.A. Horstwood, R.R. Parrish, A new approach to single shot laser ablation analysis and its application to in situ Pb/U geochronology, Journal of Analytical Atomic Spectrometry. 24 (2009) 1355–1363.
[8] J. Baker, S. Stos, T. Waight, Lead isotope analysis of archaeological metals by multiple-collector inductively coupled plasma mass spectrometry. Archaeometry. 48 (2006) 45–56.

[9] K. Schilling, A. Basu, A. Kaplan, W.T. Perkins, Metal distribution, bioavailability and isotope variations in polluted soils from Lower Swansea Valley, UK, Environmental Geochemistry and Health. 43 (2021) 2899–2912.
[10] S. Kelly, K. Heaton, J. Hoogewerff, Tracing the geographical origin of food: The application of multi-element and multi-isotope analysis, Trends in Food Science and Technology. 16 (2005) 555–567.
[11] E. Thomsen, R. Andreasen, Agricultural lime disturbs natural strontium isotope variations: Implications for provenance and migration studies, (2019). https://www.science.org.
[12] M. Willmes, C.P. Bataille, H.F. James, I. Moffat, L. McMorrow, L. Kinsley, R.A. Armstrong, S. Eggins, R. Grün, Mapping of bioavailable strontium isotope ratios in France for archaeological provenance studies, Applied Geochemistry. 90 (2018) 75–86.
[13] L. Yang, Accurate and precise determination of isotopic ratios by mc-icp-ms: A review, Mass Spectrometry Reviews. 28 (2009) 990–1011.
[14] F. Vanhaecke, L. Balcaen, D. Malinovsky, Use of single-collector and multi-collector ICP-mass spectrometry for isotopic analysis, Journal of Analytical Atomic Spectrometry. 24 (2009) 863–886.
[15] J. Irrgeher, T. Prohaska, Application of non-traditional stable isotopes in analytical ecogeochemistry assessed by MC ICPMS - A critical review, Analytical and Bioanalytical Chemistry. 408 (2016) 369–385.
[16] J. Vogl, The triple-isotope calibration approach: a universal and standard-free calibration approach for obtaining absolute isotope ratios of multi-isotopic elements, Analytical and Bioanalytical Chemistry (2021) 413:821–826.
[17] W.A. Brand, T.B. Coplen, J. Vogl, M. Rosner, T. Prohaska, Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report). Pure and Applied Chemistry. 86(3) (2014), 425-467.
[18] Inn, K.G.W., LaMont, S., Jerome, S.M., Essex, R., Johnson, C.M., Morrison, J., Frechou, C., Branger, T., and Dion, H., Roadmap for Radioanalytical Reference and Performance Evaluation Materials for Current and Emerging Issues, Journal of Radioanalytical and Nuclear Chemistry, 307(3) (2016) 2529-2538.
[19] J. Vogl, M. Rosner and W. Pritzkow, The need for new isotope reference materials. Analytical and Bioanalytical Chemistry. 405 (2013) 2763–2770.
[20] A. Retzmann, T. Zimmermann, D. Pröfrock, T. Prohaska, J. Irrgeher, A fully automated simultaneous single-stage separation of Sr, Pb, and Nd using DGA Resin for the isotopic analysis of marine sediments. Analytical and Bioanalytical Chemistry, 409(23) (2017) 5521–5531.
[21] X. Bian, S.C. Yang, R.J. Raad, N.J. Hawco, J. Sakowski, K.F. Huang, K.P. Kong, T.M. Conway, S.G. John, A rapid procedure for isotopic purification of copper and nickel from seawater using an automated chromatography system. Analytica Chimica Acta, 1312 (2024) 342753.
[22] M. Gilbert, P. Ho, L. Whitmore, A. Shiller, Automated determination of gallium in seawater using seaFAST pre-concentration and high-resolution inductively coupled plasma mass spectrometry. Analytica Chimica Acta. 1241 (2023) 340799.
[23] E. Bolea-Fernandez., L.I.L. Balcaen, M. Resano, F. Vanhaecke, Tandem ICP-mass spectrometry for Sr isotopic analysis without prior Rb/Sr separation. Journal of Analytical Atomic Spectrometry. 31 (2016) 303-310.
[24] Agilent Application Handbook / Agilent 8800 ICP-QQQ Application Handbook. Lead isotope analysis: Removal of 204Hg isobaric interference on 204Pb using ICP-QQQ in MS/MS mode (2015). Agilent Technologies.
[25] D. R. Bandura, V. I. Baranov, S. D. Tanner, Effect of collisional damping and reactions in a dynamic reaction cell on the precision of isotope ratio measurements. Journal of Analytical Atomic Spectrometry. 15 (2000) 921 - 928.
[26] C. P. Ingle, B. L. Sharp, M. S. A. Horstwood, R. R. Parrish, D. J. Lewis, Instrument response functions, mass bias and matrix effects in isotope ratio measurements and semi-quantitative analysis by single and multi-collector ICP-MS. Journal of Analytical Atomic Spectrometry. 18 (2003) 219 - 229.

APPENDIX 1 – PARTICIPANTS PROCEDURES FOR ISOLATION OF ELEMENTS

In this part of the document, the descriptions of methods used by the participants are presented element by element.

A1. Lithium

Partner: IFE

Work on automated separation of Lithium using a PrepFAST MC system (ESI) has been done in collaboration with ESI, and tests performed at ESI at the end of 2024 show Li quantitatively separated and recovered from Na in a solution with a 1/1 Li/Na ratio in a 3 mL bed volume column. At the end of the MetroPOEM project (September 2025) tests are still ongoing with larger column sizes. Despite some success with high-Lithium samples, the separation of Lithium from seawater has still not been performed successfully due to insufficient separation between the Li and Na peaks.

Work was performed on improving measurements on the MC-ICP-MS by adjusting the blank measurement method and washing times with the aim of achieving a low stable blank with highest possible signal-to-noise ratio. Blank correction due to buildup on the sample and skimmer cones is one of the largest source of uncertainty for these measurements, particularly towards the end of long sequences. Implementation of a NaF (0.2 mg/mL) wash (180 s) before each sample using a cyclonic/Scott spray chamber showed good effect in suppressing Li buildup on the sample (Ni jet sample) and skimmer (Ni X skimmer) cones throughout long (approx. 7 hour) sequences (figure hereunder).

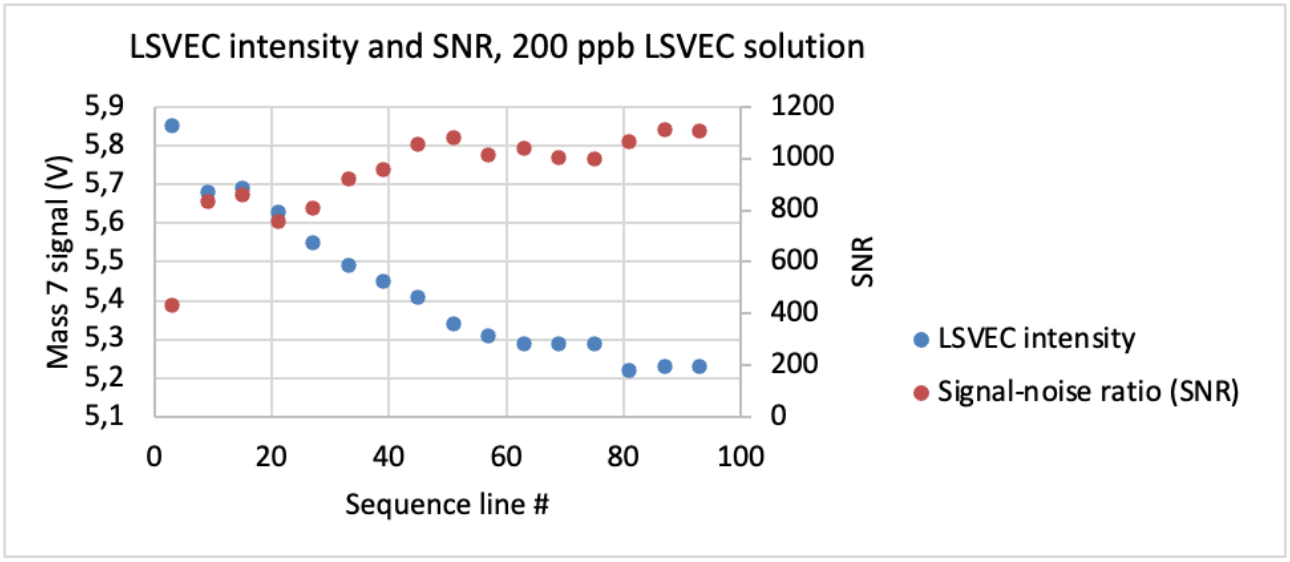

Figure A1: signal-to-noise ratio and analyte intensity throughout the course of a 7 hour analytical sequence (LSVEC analyzed every 6th sample)

A typical analytical sequence using a NaF wash is as follows, presented in Table A1.

Table A1: Example sequence using NaF wash for blank reduction. All samples/blanks/wash are in 2 % v/v HNO3 (except NaF solution)

Sample #	Sample Name	Wash time (s)	Takeup time (s)	Analysis time
1	NaF 0.2 mg/mL wash	0	180	30 s
2	2 % HNO3 blank	150	55	30s
3	LSVEC	0	55	5 min (5x10, 4.1s)
4	NaF 0.2 mg/mL wash	0	180	30 s
5	2 % HNO3 blank	150	55	30s
6	Sample 1	0	55	5 min (5x10, 4.1s)
7	NaF 0.2 mg/mL wash	0	180	30 s
8	2 % HNO3 blank	150	55	30s
9	LSVEC	0	55	5 min (5x10, 4.1s)
10	NaF 0.2 mg/mL wash	0	180	30 s
11	2 % HNO3 blank	150	55	30s
12	Sample 2	0	55	5 min (5x10, 4.1s)
13	NaF 0.2 mg/mL wash	0	180	30 s
14	2 % HNO3 blank	150	55	30s
15	LSVEC	0	55	5 min (5x10, 4.1s)
16	NaF 0.2 mg/mL wash	0	180	30 s
17	2 % HNO3 blank	150	55	30s
18	Sample 3	0	55	5 min (5x10, 4.1s)
19	NaF 0.2 mg/mL wash	0	180	30 s
20	2 % HNO3 blank	150	55	30s
21	LSVEC	0	55	5 min (5x10, 4.1s)

Partner: BAM

The chromatographic separation of lithium isotopes was performed using a two-step cation exchange column system. Both columns were packed with Bio-Rad AG50W-X12 resin with a mesh size of 200-400mm and a capacity of 2.1meq/mL. The columns were calibrated using IAPSO seawater and IRMM-016 standard. The first column, made of polypropylene with an inner diameter of 6.4mm and filled with 3 mL of resin. The columns were cleaned with 6 mol/L HCl and sample loading and elution were carried out with 0.2 mol/L HCl. The details of the elution procedures are given in Table 1.

Table A2. Lithium elution protocol for the first column

Procedure	Eluent	Volume
Cleaning	6 mol/L HCl	18
Backwash	H_2O	
Cleaning	6 mol/L HCl	18
Conditioning	0.2 mol/L HCl	18
Sample loading	0.2 mol/L HCl	0.5
Fixing	0.2 mol/L HCl	1
Pre elution	0.2 mol/L HCl	21
Pre Li fraction	0.2 mol/L HCl	1
Li elution	0.2 mol/L HCl	26
Post Li fraction	0.2 mol/L HCl	1

Lithium fractions were collected in pre-cleaned 30 mL Teflon beakers and evaporated to dryness at 100^{0}C on a hotplate. Dried samples were redissolved in 0.15 mol/L HCl and loaded onto the second columns, Teflon mini columns with resin volume of 0.5mL. The details of the elution procedures for the second column are given in Table 2. Li elution fraction was collected in 10mL pre-cleaned Teflon vials and evaporated to dryness at 100 ºC on a hotplate. After evaporation, the vials were refluxed with a mixture of HNO_3 and H_2O_2 to remove organics and redissolved in 2 % HNO_3 in a concentration same as of the bracketing standard.

Table A3. Lithium elution protocol for the second column

Procedure	Eluent	Volume
Cleaning	6 mol/L HCl	3
Conditioning	0.15 mol/L HCl	3
Sample loading	0.2 mol/L HCl	0.1
Fixing	0.2 mol/L HCl	0.3
Pre elution	0.2 mol/L HCl	3.3
Pre Li fraction	0.2 mol/L HCl	0.5
Li elution	0.2 mol/L HCl	7.5
Post Li fraction	0.2 mol/L HCl	0.5

The pre- and post-fractions collected are diluted in 2% HNO_3 and analyzed with ELEMENT2 HRICPMS to confirm the absence of sodium and lithium and ensure quantitative lithium recovery.

Mass spectrometry

Lithium isotope ratio measurements were conducted with a MC-ICP-MS(Neptune Plus, Thermo Fischer Scientific) with a stable introduction system, spray chamber and aluminum sampler and skimmer cones. The measurements were performed at low resolution. The samples and standards were diluted to a mass fraction

of 60 ng/g and yielded an intensity of 6 V on ^{7}Li. All samples and standards were tested for intensity matching and under a 5 % matching limit. The blank solution(2 % HNO_3) was measured before and after every sample and standard and the average blank intensity was reduced from the sample and standard intensities. The wash time was set as 180 s and the blank contribution was approximately 1 % to the intensity provided by the samples. All samples were measured with SSB method to correct for the instrumental fractionation. The absolute isotope ratios were determined by calculating the K factor obtained from the average ratio of the bracketing standards and certified value.

Results

The recovery of lithium after dual column separation is 104 % ± 6 %, determined from the analysis of known concentrations of samples. The mean of the $\delta^{7/6}Li$ of IAPSO seawater standards separated with the dual column method is 31.01 ‰ ± 0.72 ‰(2SD, N=10), which comes within the reported $\delta^{7/6}Li$ value(31 ± 0.5 ‰).

A2. Boron

Partner: BAM

Boron was separated from the sample matrix by utilizing the micro distillation technique, which utilizes the volatility of the boric acid(HBO_3^-) at high temperatures to separate boron from complex matrices. Prior to the microdistillation process, the samples were acidified with HNO_3 to reduce the pH to ≤2 and a droplet(80 µL) of this sample is placed in the lid of a pre cleaned 5mL Savillex PFA fin legged vial with a conical interior. The lid is tightly closed in the upside-down position tightly to avoid any boron loss during micro-distillation. The vial is then wrapped with aluminum foil, except for the top of the beaker, where the distillate will condensate at the colder tip. The vials were heated to 95 ºC for 24 hours on the hotplate. The vials are then removed carefully to avoid disturbing the condensated droplet, it was inverted and replaced with fresh, clean lids. The vials are diluted with HNO_3 prior to the boron isotope measurement.
The quantitative recovery was determined using NIST SRM951 and ERM AE123

Mass spectrometry

Boron isotope ratios were determined using MC-ICPMS(Neptune Plus, Thermio Fischer Scientific) at BAM. The instrument is equipped with a quartz cyclonic spray chamber and normal Ni sample and skimmer cones. The measurements were performed at low resolution. The concentration of samples and standards were diluted to have a mass fraction of 200ng g^{-1}, yielding ^{11}B intensity of about 0.9V. The blank intensities for 11B varied between 2 to 3 mV, contributing less than 0.3 % to the intensity provided by samples. An extended wash time of 180s was chosen to reduce the blank at these levels. The samples were measured with the standard sample bracketing method, using NIST SRM 951 as the bracketing standard. Absolute isotope ratios of the samples were calculated from the observed ion intensity ratios by applying the correction factor K for mass bias. K is calculated from the average of the bracketing standards and the certified value of SRM 951

Results

The recovery of boron after micro sublimation was calculated to 100 %, determined from the known concentration of samples. The mean $\delta^{11/10}B$ of IAPSO seawater is calculated to be 38.91 ‰ ± 0.65 ‰ (2SD, *N*=3), which comes within the boron isotopic composition of seawater (39.61 ‰ ± 0.04 ‰).

Partner: IFE

Work on the automated separation and isotope ratio analysis on Boron has been primarily focused on adapting and implementing the method developed by de la Vega et al (2020) (https://doi.org/10.1002/rcm.8762) for automated analysis of boron from marine carbonates. This method is based on the use of Amberlite IRA 743 resin on the PrepFAST MC (ESI), which has an affinity for boron at pH 5.5. We adapted this method by using an ammonium acetate buffer instead of sodium acetate, which has the benefit of 1) not loading the column with unnecessary Na and eliminating the need for a reverse washout, and 2) requiring lower pumping pressure to pass the sample through the on-line separation column. This method was tested on a range of different matrices with variable salt load (seawater, groundwater, fresh water, landfill leachate) and showed good results for the seawater sample collected by Hereon (raw material for the proposed reference material). A mean $\delta^{11/10}B$ of 39.60 ‰ ± 0.45 ‰ (1sd) was obtained using the PrepFAST MC, compared to the accepted value of 39.61 ‰ ± 0.04 ‰ (1sd). The large uncertainty is due to a large blank contribution, and subsequent analyses were

performed using a NaF wash to reduce the washout time of boron from the spray chamber, following the sequence described in A1. Selection and characterization of the ammonium acetate buffer is critical for the preparation of samples, as both commercial solutions tested had boron concentrations in excess of 3 ng/mL.

A3. Chromium

Partner: JSI

To separate Cr (total) from the seawater matrix, a coprecipitation procedure with Mg(OH)2 and assisted by the addition of triethylamine, adapted from Arslan et al. (2018) was tested.

Procedure tested with model seawater, spiked with standards:

- Cr → conc. 15 ng/mL
- Fe, V, Ti → conc. 2 ng/mL
- Mg → conc. 500.000 ng/mL
- Ca → conc. 150.000 ng/mL

Cr recovery: 85.5 ± 5.9 %

The procedure was followed by a two-step Cr isolation method applying AG1-X8 and AG50W-X8 (BioRad) resins as described in Yamakawa et al. (2009).

1. The procedure tested was adapted from Yamakawa et al. (2009)[2]

- two step Cr separation:
  - 1 mL of **AG1-X8** resin
  - 1 mL of **AG50W-X8** resin
- three types of samples:
  - spiked model seawater after TEA-assisted $Mg(OH)_2$ coprecipitation
  - standards in MilliQ water/in acid for the column
  - spiked model seawater (only for the second step)

1 mL of **AG1-X8** resin		1 mL of **AG50W-X8** resin	
Rinsing	10 mL 3 M HNO_3 18 mL MilliQ 12 mL 6 M HCl	Rinsing	16 mL 6 M HCl 32 mL MilliQ
Conditioning	5 mL 6 M HCl	Sample loading	in 2.4 mL 1 M HCl
Sample loading	in 1 mL 6 M HCl	Cr elution	immediate + 3.6 mL 1 M HCl
Cr elution	immediate + 4 mL 6 M HCl		

Recovery after first step (**AG1-X8** resin)

- spiked model seawater after TEA-assisted $Mg(OH)_2$ coprecipitation
- Cr recovery = 95.4 ± 5.3 %
- sufficiently removed Mg, Ca
- insufficiently removed Fe (100 % remained), V (100 % remained), Ti (60 % remained)
  - standards in MilliQ water/in acid for the column
- Cr recovery = 85.9 ± 17.2 %
- sufficiently removed Fe
- insufficiently removed V (75 % remained), Ti (60 % remained)

Recovery after the second step (**AG50W-X8** resin)

- spiked model seawater
- Cr recovery = 16.8 ± 1.3 %
- sufficiently removed Fe
- insufficiently removed V (90 % remained), Ti (60 % remained), Mg (100 % remained), Ca (40 % remained)
  - spiked model seawater after TEA-assisted $Mg(OH)_2$ coprecipitation
- Cr recovery = 88.7 ± 22.3 %
- sufficiently removed Fe, Mg, Ca
- insufficiently removed V (10 % remained), Ti (100 % remained)
  - standards in MilliQ water/in acid for the column

- Cr recovery = 97.1 ± 5.1 %
- sufficiently removed Fe (already removed in the first step)
- insufficiently removed V (50 % remained), Ti (75 % remained)

2. The procedure tested was adapted from Liu et al. (2019)[3]
   - two step Cr separation:
     - 1 mL of **AG50W-X12** resin
     - 0.33 mL of **AG50W-X12** resin
   - two types of samples:
     - standards in MilliQ water/in acid for the column (Mg and Ca also added)
     - standards in MilliQ water/in acid for the column (without interferences)

1 mL of **AG50W-X12** resin		0.33 mL of **AG50W-X12** resin	
Rinsing	5 mL 6 M HCl 3 mL MilliQ	Rinsing	4 mL 6 M HCl 3 mL MilliQ
Conditioning	5 mL 1 M HCl	Conditioning	5 mL 0.16 M HNO_3
Sample loading	in 1.2 mL 1 M HCl	Sample loading	in 2 mL 0.16 M HNO_3
Cr elution	immediate + 3.5 mL 1 M HCl	Ti, Al elution	3 mL 0.5 M HF
		V, matrix elution	10 mL 1 M HCl
		Cr elution	5 mL 2 M HCl

Recovery after first step (**AG50W-X12** resin)

- standards in MilliQ water/in acid for the column

- Cr recovery = 9.97 ± 1.80 %
- sufficiently removed Mg, Ca, Ti
- insufficiently removed V (5 % remained), Fe (25 % remained)
  - standard in MilliQ water/in acid for the column (without interferences)
- Cr recovery = 11.8 %

Due to low Cr recoveries, we didn't proceed to the second step.

Arslan et al. (2018) Analytica Chimica Acta, 1008, 18–28, DOI:10.1016/j.aca.2018.01.017
Yamakawa et al. (2009) Analytical Chemistry, 81, 9787–9794, DOI: 10.1021/ac901762a

A4. Nickel

Partner: LGC

A new method for the determination of Ni isotope ratios in seawater with high accuracy and precision by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has been developed. It is based on a novel analyte purification procedure and an improved instrumental protocol. Prior to isotope ratio measurements, nickel was isolated from the seawater matrix using Mg(OH)2 co-precipitation, followed by two-stage ion-exchange chromatography. In the first stage, anion-exchange chromatography was used to purify the analyte from trace elements, forming negatively charged chloroanionic complexes, including V, Fe, Cu, and Zn, which can interfere with Ni isotopes during the measurements. In the second stage, nickel was separated from Mg through a cation-exchange on Chelex-100 chelating resin. Copper was employed as an admixed internal standard to correct for instrumental isotope fractionation. Copper was found effective in the determination of both relative nickel isotope ratios (delta values) and absolute nickel isotope ratios. The latter have been determined using the regression method for calibrating the mass spectrometer. The developed methodology has been demonstrated to be a promising tool for the characterisation of isotopic reference materials, with the characterisation of a seawater candidate reference material in WP4 is currently ongoing.

A5. Cadmium

Partner: JSI

Most frequently two different chemical purification protocols are in use; isolation of Cd on the AG1-X8 or AG-MP-1M BioRad resins. In the present project, Cd was pre-concentrated from the seawater matrix applying similar procedure as used for Ni. Namely, Cd was preconcentrated by triethylamine-assisted (TEA) $Mg(OH)_2$ coprecipitation by the procedure adopted from Arslan et al. (2018). The precipitate was then dissolved in 2M HCl and Cd was isolated from the interfering elements on the AG-MP-1M (BioRad) resin following the procedure described in Pallavicini et al. (2014).

Arslan et al. (2018) Analytica Chimica Acta, 1008, 18–28, DOI:10.1016/j.aca.2018.01.017
Pallavicini et al. (2014) J. Anal. At. Spectrom., 29, 1570–1584, DOI: 10.1039/c4ja00125g

A6. Lead

Partner: MUL

Approach 1: Pb from samples other than seawater; usually following the procedures developed in https://doi.org/10.1007/s00216-017-0468-6 and https://doi.org/10.1016/j.sab.2018.11.009; This procedure is based on Pb isolation using the DGA resin; for seawater, the sample requires prior purification from the salt matrix; this is currently done by ESI using the seaFAST-Primer system in Omaha, USA; this system is based on a double column approach for low metal quantification with a purification step using the HITACHI Nobias resin (discontinued); the seaFAST-Primer allows for a 1000 fold preconcentration of Pb whilst purifying from the salt matrix; first tests with seawater spiked with Pb sent to ESI and processed over there were successful. The samples were pre-concentrated by factors of 10, 20 and 100 resulting in full recoveries of Pb of around 100%. Currently, the seawater candidate CRM of WP4 is processed in Omaha and will be returned to MUL soon. The samples will then be further processed by the prepFAST-MC for Pb isolation.

Approach 2: The Sr spec resin (Triskem) was tested for its isolation capacity of Pb, known to have high affinity to Pb as well. In other samples, the approach has successfully worked (https://doi.org/10.1016/j.chemosphere.2020.127182) by eluting Pb in HCl solution whilst Sr is eluted in water. In presence of seawater with Sr levels of up to 7 µg/mL, first tests showed selectivity of the resin towards Sr whilst releasing Pb immediately upon sample load.
Therefore, a double column approach is being tested, with the first column to bind Sr and the second column to bind and purify Pb; first recoveries show good results; data is currently being processed; the procedure is promising and will be applied to the samples from characterization, stability and homogeneity of WP4.

Measurement
A single collector ICP-QMS instrument (NexION 2000 or NexION 5000, PerkinElmer, Ontario, Canada) equipped with a FAST introduction system and a multi collector ICP-MS (Nu Plasma HR or Nu Sapphire, Nu Instruments) equipped with a desolvation nebulization membrane unit (Aridus II, Cetac or Apex Omega, Elemental Scientific) in combination with a PFA nebulizer (Microflow ST Nebulizer, Elemental Scientific, Omaha, USA) as sample introduction system were used. The ICP-QMS instrument was operated using the quantitative method option by Syngystix software. Measurements of isotopes ^{202}Hg (20 ms), ^{204}Pb (75 ms), ^{206}Pb (20 ms), ^{207}Pb (20 ms), ^{208}Pb (20 ms) and ^{115}In (20 ms) were performed with dwell times given in parenthesis and a total measurement time of ca. 3 minutes (1 sweep, 1 reading, 900 replicates), allowing the simultaneous Pb quantification and Pb isotope ratio analysis. The number of replicates was chosen to optimize the precision for determining the ^{20x}Pb/^{20y}Pb isotope ratio.
The MC-ICP-MS was operated in low mass resolution and static mode allowing for the simultaneous measurement of all natural stable Pb isotopes, as well as of ^{202}Hg for monitoring the mercury background in the samples to correct a possible isobaric interference from ^{204}Hg to ^{204}Pb. Data collection was accomplished in 6 blocks of 10 measurements with an integration time of 10 s, resulting in a total of 60 measurements per sample. The samples and the isotopic standards NIST SRM 981 were introduced into the plasma in the following sequence: $standard_{SSB1\text{-}SRM981}$ - sample – $standard_{SSB2\text{-}SRM981}$, to enable correction for time-dependent instrumental isotopic fractionation (IIF) via classical sample standard bracketing (SSB).

Partner: AU/UGOT

1. Samples

Certified Reference Materials

TUBITAK provided two bottles each of 250 mL Certified Reference Materials as 250 mL: UME MetroPOEM CRM Unit No. 200 and UME MetroPOEM CRM Unit No.: 435.

Seawater sample collected from the North Sea in 2020

2. Lead pre-concentration by co-precipitation with magnesium hydroxide $Mg(OH)_2$

Seawater samples of 4, 8 and 12 mL and blanks of 12 mL of MQ water were added into acid-cleaned centrifuge tubes. Ammonium solution (25%, Merck) was added in a 1:40 volume ratio. The sample was left overnight to allow $Mg(OH)_2$ to precipitate. The sample was centrifuged, and the supernatant decanted. The precipitate was washed with 5 mL MQ water, shaken and centrifuged. The MQ water was decanted. A 2% HNO3 in-house distilled was added to the Mg(OH)2 precipitate. The samples were left to dissolve overnight. The sample was transferred to a Teflon beaker, dried, and redissolved in 1 mL of 0.5 M HBr (Fisher Optima) for column chromatography. A Pb yield of 95-100 % with the $Mg(OH)_2$ coprecipitation method was obtained. Most of Na and Ca were removed from the seawater matrix.

3. Pb purification by anion exchange chromatography

Pb was separated from the remaining seawater matrix by using BioRad anion exchange resin AG 1-X8, 200-400 mesh, and in-house Teflon columns, with a resin volume of 400 µL and a reservoir volume of 3 mL.

The resin was cleaned in batches 6 times with alternating 6.0 M HCl (in-house distilled) and MQ-water. The resin was loaded on the column and further cleaned with 2 x 3 mL of 6.0 M HCl and 2 x 3 mL of 0.5 M HBr. The sample was loaded onto the column in 1 mL 0.5 M HBr. The sample matrix was eluted with 4 x 1 mL of 0.5 M HBr. Pb was eluted and collected in a Teflon beaker with 4 x 0.5 mL of 6.0 M HCl. The samples were dried and redissolved overnight in 1 mL of 0.5 M HBr at 80 ºC, and the column procedure was repeated to achieve optimal separation of Pb from the matrix. After the second column separation, the samples were dried. The dried samples were dissolved in 1.5 mL of 2 % HNO3 at 80 °C overnight and analyzed by MC-ICP-MS.

4. Mass Spectrometric Analysis

The samples were analyzed using a Nu Instrument Plasma II Multi-Collector ICP-MS, configured with 16 Faraday cups and 5 ion counters. All Faraday cups are connected to 1011 Ω resistors. Given the uniform isotopic abundance distribution of the four Pb stable isotopes, from 1.4% ^{204}Pb to 52.4 % ^{208}Pb, the Pb isotope analysis was carried out using Faraday detectors and 1011 Ω resistors to minimize issues of detector calibration. A static cup configuration with 205 in the axial mass and a mass spacing of 1, with masses 201, 202, 203, and 204, in collectors L4, L3, L2, and L1, respectively, and masses 209, 208, 207, and 206, in collectors H4, H3, H2, and H1, respectively. The analysis was conducted in dry plasma mode with the samples introduced via a Nu Instruments DSN-100 desolvating nebulizer system connected to a Cetac ASX-112 FR auto-sampler.

To quantify Pb concentration in seawater, 20 µL sample was diluted with 1 mL of 2% HNO_3 and analyzed using a measurement protocol consisting of 12 integrations, each lasting 5 seconds and deflected baseline. Aliquots of NIST SRM 981 with a known concentration were run after every three samples and intensities were compared to calculate the Pb concentration in the samples. Based on the Pb concentration in the seawater samples, an optimal sample dilution factor was determined.

For mass bias correction, Tl was added to the seawater and standards samples to obtain a Pb/Tl ratio of around 4. The Tl standard from PlasmaCal, has been found to be isotopically indistinguishable from NIST Tl 997.

The seawater sample analysis was done with 80 integrations of 5 seconds each, for a total beam time of 400 seconds. Before the analysis, an on-peak baseline was recorded for 60 seconds. This combined with wash-out after analyses of 3.5 minutes and 1 minute uptake time for both blank and sample, gives a total analysis time of about 14 minutes.

The analysis sequence of the seawater samples included repeated measurements of the NIST SRM 981 standard at the beginning, at the end, and after every three samples. NIST SRM 981 was used as the primary standard. NIST SRM 981, as unknowns, were used as secondary standards, analyzed 4 times throughout the analysis sequence.

If Pb concentration in some seawater samples was high enough to allow for 4 analyses, these were also run throughout the sequence, together with the standards that have been run as unknown samples (these standards were not used in the polynomial curve), but are used to evaluate the external precision of the analytical session.

A polynomial fit was applied to the measured isotopic ratios of the primary standard. Deviations from the curve fit gave Δ values for standards run as unknown samples and seawater samples. The external precision was calculated as the average of the 2σ of all the secondary standards (standards run as unknown samples) and the seawater sample duplicates.

Partner: MUL

Isolation of Pb

Approach 1: Pb from samples other than seawater; usually following the procedures developed in https://doi.org/10.1007/s00216-017-0468-6 and https://doi.org/10.1016/j.sab.2018.11.009; This procedure is based on Pb isolation using the DGA resin; for seawater, the sample requires prior purification from the salt matrix; this is currently done by ESI using the seaFAST-Primer system in Omaha, USA; this system is based on a double column approach for low metal quantification with a purification step using the HITACHI Nobias resin (discontinued); the seaFAST-Primer allows for a 1000 fold preconcentration of Pb whilst purifying from the salt matrix; first tests with seawater spiked with Pb sent to ESI and processed over there were successful. The samples were pre-concentrated by factors of 10, 20 and 100 resulting in full recoveries of Pb of around 100%. Currently, the seawater candidate CRM of WP4 is processed in Omaha and will be returned to MUL soon. The samples will then be further processed by the prepFAST-MC for Pb isolation.

Approach 2: The Sr spec resin (Triskem) was tested for its isolation capacity of Pb, known to have high affinity to Pb as well. In other samples, the approach has successfully worked (https://doi.org/10.1016/j.chemosphere.2020.127182) by eluting Pb in HCl solution whilst Sr is eluted in water. In presence of seawater with Sr levels of up to 7 µg/mL, first tests showed selectivity of the resin towards Sr whilst releasing Pb immediately upon sample load.
Therefore, a double column approach is being tested, with the first column to bind Sr and the second column to bind and purify Pb; first recoveries show good results; data is currently being processed; the procedure is promising and will be applied to the samples from characterization, stability and homogeneity of WP4.

Measurement

A single collector ICP-QMS instrument (NexION 2000 or NexION 5000, PerkinElmer, Ontario, Canada) equipped with a FAST introduction system and a multi collector ICP-MS (Nu Plasma HR or Nu Sapphire, Nu Instruments) equipped with a desolvation nebulization membrane unit (Aridus II, Cetac or Apex Omega, Elemental Scientific) in combination with a PFA nebulizer (Microflow ST Nebulizer, Elemental Scientific, Omaha, USA) as sample introduction system were used. The ICP-QMS instrument was operated using the quantitative method option by Syngystix software. Measurements of isotopes ^{202}Hg (20 ms), ^{204}Pb (75 ms), ^{206}Pb (20 ms), ^{207}Pb (20 ms), ^{208}Pb (20 ms) and ^{115}In (20 ms) were performed with dwell times given in parenthesis and a total measurement time of ca. 3 minutes (1 sweep, 1 reading, 900 replicates), allowing the simultaneous Pb quantification and Pb isotope ratio analysis. The number of replicates was chosen to optimize the precision for determining the ^{20x}Pb/^{20y}Pb isotope ratio.
The MC ICP-MS was operated in low mass resolution and static mode allowing for the simultaneous measurement of all natural stable Pb isotopes, as well as of ^{202}Hg for monitoring the mercury background in the samples to correct a possible isobaric interference from ^{204}Hg to ^{204}Pb. Data collection was accomplished in 6 blocks of 10 measurements with an integration time of 10 s, resulting in a total of 60 measurements per sample. The samples and the isotopic standards NIST SRM 981 were introduced into the plasma in the following sequence: standard$_{SSB1\text{-}SRM981}$ - sample – standard$_{SSB2\text{-}SRM981}$, to enable correction for time-dependent instrumental isotopic fractionation (IIF) via classical sample standard bracketing (SSB).

Details on Pb isotope ratio measurements by ICP-QMS is based on
https://doi.org/10.1007/s00216-022-04311-0
Details on Pb isotope ratio measurements by MC-ICP-MS is based on
https://doi.org/10.1021/acs.analchem.2c00546

A7. Uranium

Partner: PTB

This short report describes the separation of uranium from seawater using Triskem UTEVA resin columns. The described procedure may be adapted to the specific sample matrix. In the present case, the uranium mass fraction (w(U)) was approximately 3 ng/g. Therefore, the described procedure serves as an orientation. Initially, a subsample of approximately 60 g was transferred into 300 mL PFA vessels. The subsample was evaporated to dryness at roughly 120 °C using a hot plate. The residues were re-dissolved in 35 mL HNO_3 (w(HNO_3) = 0.65 g/g), 15 mL H_2O, evaporated to dryness again, and re-dissolved in 15 mL HNO_3 (c(HNO_3) = 3 mol/L). Afterwards, the uranium was radiochemically separated from the matrix using preconditioned Triskem UTEVA resin columns (UT-C50-A, Lot # FUTA240212, 2 mL pre-packed). The separation was carried out according to the modified Eichrom “Analytical Procedure Method No. ACS07” [1], for details see table below.

Table A4: Elution scheme used for uranium separation on Triskem UTEVA resin (2 mL pre-packed columns, Lot # FUTA240212).

fraction	**eluent**	***V*/mL**	
1	0.05 mol/L HCl	15	removal of uranium impurities
2	3 mol/L HNO_3	5	preconditioning
3	sample in HNO_3	15	loading of sample
4	3 mol/L HNO_3	16	removal of matrix
5	7.5 mol/L HCl	3	conditioning
6	0.05 mol/L oxalic acid & 5 mol/L HCl	5	removal of Th
7	7.5 mol/L HCl	5	waste
8	0.05 mol/L HCl	11	uranium fraction

The uranium fractions were collected in 15 mL PFA vessels, evaporated to dryness (hot plate at 120 °C) and the residue was re-dissolved in 1 mL HNO_3 (65 %) and 1 mL H_2O_2 (30 %). The samples were evaporated to dryness again on a hot plate at 80 °C (the temperature has been increased from 50 °C to 80 °C in 10 °C steps) . Finally, the residual was redissolved in 3.5 mL 2.5 % HNO_3 to prepare the measurement solutions with w(U) ≈ 50 ng/g. To validate that the separation procedure does not induce uranium isotopic fractionation, it was applied to four aliquots (each ~1.5 g) of a stock solution of IRMM-184. [2] This solution had a uranium mass fraction of roughly 50 ng/g. After separation, the isotope ratios (R($^{234}U/^{238}U$) and R($^{235}U/^{238}U$)) of the four aliquots were determined using MC-ICP-MS and IRMM-184 as certified reference material in a sample-reference bracketing scheme. Please note that reference IRMM-184 was an unprocessed aliquot of the aforementioned stock solution. Details of the MC-ICP-MS measurements are given in the next chapter. Figure and Figure show the determined isotope ratios R($^{234}U/^{238}U$) and R($^{235}U/^{238}U$), respectively. Additionally, to the single results for each aliquot, the certified value for IRMM-184 is shown as a horizontal red dashed line together with its error range of plus/minus the expanded uncertainty (k = 2). Since in all cases the isotope ratios of the four aliquots agree with each other and the certified value, it can be concluded that the presented procedure does not lead to measurable isotopic fractionation.

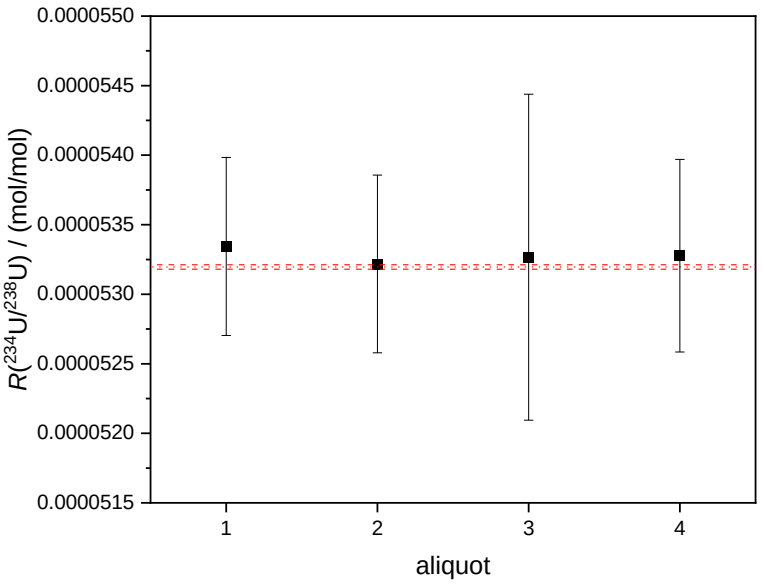

Figure A2: Absolute isotope ratio $R(^{234}U/^{238}U)$ of the four aliquots of IRMM-184 after being processed in the described way. Error bars indicate expanded uncertainties (k = 2). The red dashed line represents the certified value with its uncertainty range.

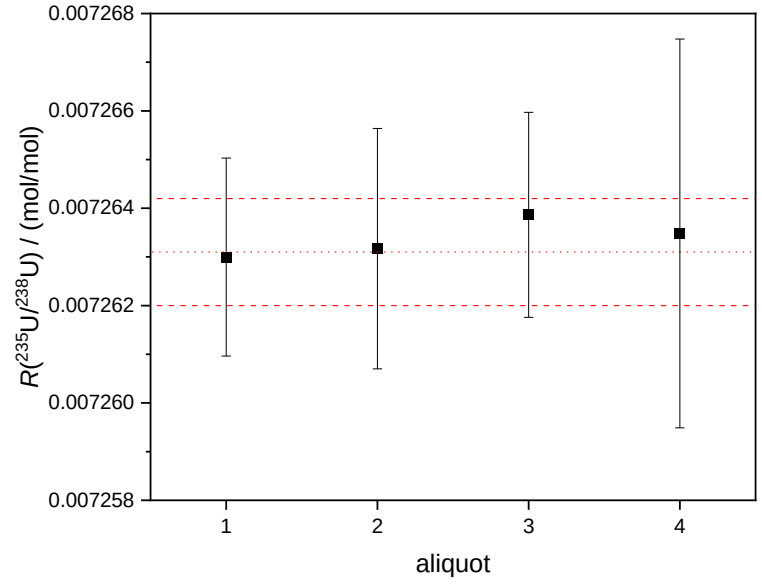

Figure A3: Absolute isotope ratio $R(^{235}U/^{238}U)$ of the four aliquots of IRMM-184 after being processed in the described way. Error bars indicate expanded uncertainties (k = 2). The red dashed line represents the certified value with its uncertainty range.

Uranium MC-ICP-MS Measurements

Principle: MC-ICP-MS using sample-reference bracketing
Instrument: MC-ICP-MS Neptune Plus, Thermo Fisher Scientific

- Ion source: inductively coupled argon plasma (ICP, Ar 5.0, Linde gases, Germany)

- Resolution: $M/\Delta M$ = 400 (low resolution)
- Detector: multi-collector, 5 Faraday cups were used, 4 of them were equipped with 10^{11} W resistors and one with a 10^{13} W resistor (see table below)
- Rotating amplifiers: Applied after each block
- Cones: Skimmer: Ni (X), Sampler: Ni jet cone
- Nebulizer: Savillex PFA, self-aspirating, 50 µL/min
- Desolvator: Cetac Aridus II with PFA spray chamber
- Autosampler: ASX-112FR, Cetac, USA

cup	L1	C	H1	H2	H3
Resistor / W	10^{11}	10^{13}	10^{11}	10^{11}	10^{11}
isotope	^{233}U	^{234}U	^{235}U	^{236}U	^{238}U

- 20 blocks with 1 cycle/block, 2 s integration time, 30 s baseline measurement, 3 s idle time
- Sequence (b = blank, x_i = i^{th} subsample of IRMM-184, r = reference material IRMM-184 untreated)
  2×b –(r-x_1) ×10–(r-x_2) ×10–(r-x_3) ×10–(r-x_4) ×10-r– 2×b, see following figure

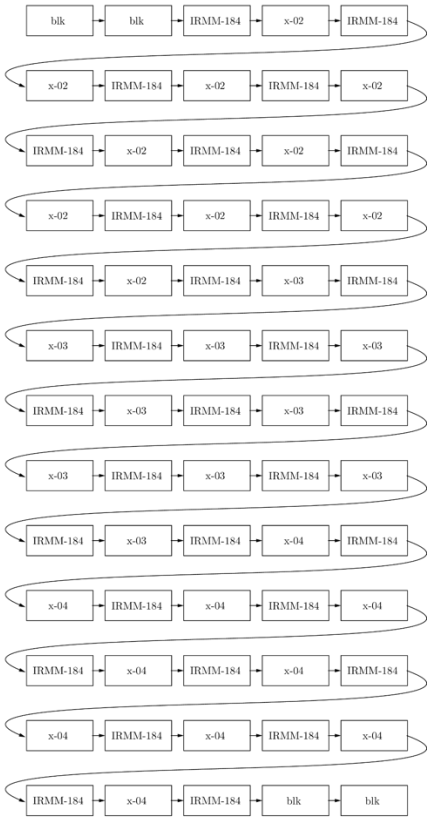

Figure 1: Schematic representation of the applied MC-ICP-MS measurements.

References

[1] Eichrom Technologies, LLC 2015. *Analytical Procedure "Uranium in Soil", Method No. ACS07*.

[2] Richter, S., Hennessy, C., Jakobsson, U., Aregbe, Y., Hexel, C. and others 2022. Re-Certification of the IRMM-183–187 series of uranium nitrate solution reference materials. *Publications Office of the European Union*. 10, (2022), 312568.