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First application of Actinide Resin in the preparation of water samples for multi-actinide analysis with accelerator mass spectrometry

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A novel sample preparation procedure for highly sensitive concurrent analysis of ^{236}U, ^{237}Np, ^{239}Pu and ^{240}Pu from river and sea water samples with Accelerator Mass Spectrometry (AMS) was developed. A selective extraction chromatography resin, instead of $Fe(OH)_3$ co-precipitation, is used to separate the actinides as a group from most of the matrix elements for "multi-actinide analysis" with AMS, as previously published [Quinto *et al.*, Analytical Chemistry, 2015, 253, 451–458]. The new extraction method has been tested on two environmental water systems, which differ substantially in terms of salinity, namely, 2 L Rhine river water samples collected in the vicinity of the Fessenheim Nuclear Power Plant (NPP) and 250 mL surface sea water samples from the vicinity of the La Hague nuclear reprocessing plant (NRP). In addition, aliquots from the CRM IAEA-443 (Irish Sea water) are analysed for method validation. It is observed that extraction chromatography yields results that are consistent with the use of $Fe(OH)_3$ co-precipitation for multi-actinide analysis and can increase the signal count rates of the AMS detector for sample systems where co-precipitation would concurrently precipitate significant amounts of sample matrix, diluting the analytes in the final AMS target material. The novel method can be applied to ultra-trace analysis of low-volume samples, such as environmental samples contaminated by global fallout and nuclear installations.

1 Introduction

With its outstanding abundance sensitivity and effective suppression of molecular interferences, Accelerator Mass Spectrometry (AMS) is one of the most sensitive mass spectrometric techniques. Depending on the analysed nuclide, detection limits (DLs) can be orders of magnitude lower than for other mass spectrometric techniques like Inductively Coupled Plasma Mass Spectrometry (ICP-MS).[1] For heavy, long-lived radionuclides such as the actinides, DLs of 10^4 at/sample (*ca.* 5 ag/sample) can be achieved, *e.g.* at the Vienna Environmental Research Accelerator (VERA) at the University of Vienna.[2] AMS offers the capability to analyse environmental samples for ultra-trace concentrations of actinides, *e.g.* fallout from atmospheric weapon tests or releases of nuclear reprocessing plants (NRPs) and determine their origin.[3,4]

For accurate determination of radionuclide concentrations with AMS (as well as with other mass spectrometric techniques), it is necessary to spike the sample with yield tracers. Optimal yield tracers are isotopes of the element to be analysed that are not contained in the sample or present at negligible levels. High purity of an isotopic tracer is required for an ultra-trace analysis technique like AMS. If no suitable isotopic tracer is available, use of a non-isotopic tracer is an option when both elements show similar chemical behaviour during the chosen sample preparation process, *e.g.* the use of a Pu isotope for determination of ^{237}Np after adjustment of their oxidation state to Pu(IV) and Np(IV).[5]

Sample preparation for AMS analysis of actinides necessitates, in most cases, the separation of the actinides from most of the sample matrix. In general, this is achieved *via* column separation using extraction chromatographic resins such as TEVA®, UTEVA® and TRU® (TrisChem International).[6] This process may also allow for the separation of the target actinide elements from other actinide elements with similar nuclide masses as the nuclides of interest (*e.g.* ^{241}Pu and ^{241}Am), which would otherwise interfere with the AMS measurement. Subsequently, the actinides are removed from solution, *e.g.* by co-precipitation with $Fe(OH)_3$ and conversion to an iron oxide AMS target material.

AMS analysis is, in general, carried out with a solid material that is filled into a small Al sample holder (max. sample mass, *ca.* 10 mg), serving as the cathode during the ionisation process in the Cs-sputtering ion source. Iron oxide is known empirically to be a suitable sample matrix for ionisation of actinide

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elements in a Cs-sputtering ion source. Co-precipitation of significant amounts of sample matrix may increase the sample mass so that it may not entirely fit into the sample holder, resulting in a dilution of the analytes, and may also reduce the ionisation yield and, hence, the overall detection efficiency. For sample systems that do not show relevant matrix content, a simplified sample preparation procedure that allows for separation of the actinide group *via* a single $Fe(OH)_3$ co-precipitation and their concurrent AMS determination ("multi-actinide analysis") can be carried out. In this way, the determination of ^{236}U, ^{237}Np, several Pu isotopes and ^{243}Am in low-volume ground water and sea water samples (using a Pu isotope and ^{248}Cm as non-isotopic tracers for ^{237}Np and ^{243}Am, respectively) was achieved.[7]

An alternative method for actinide group separation is the use of Actinide Resin, an extraction chromatographic resin by Eichrom Technologies and developed by Horwitz *et al.*[8] It is composed of an extractant called DIPEX® adsorbed on a polymer substrate. DIPEX® exhibits a high affinity for the actinide group and has found use for preconcentration of actinides from solution, *e.g.* for determination of the gross alpha radioactivity of water samples with Liquid Scintillation Counting (LSC).[9] However, this high affinity for the actinides makes their recovery by stripping them from the extractant impractical. For measurement with LSC, the resin can be added directly to the scintillation cocktail, where the solvent of the cocktail will dissolve the extractant from the substrate. For other purposes, such as Alpha Spectroscopy[10] or ICP-MS,[11] the extractant–actinide complex can be stripped from the substrate with an alcohol (*e.g.* isopropanol).[8] Subsequently, the complex dissolved in the alcohol can be decomposed by *e.g.* microwave digestion[12] or fusion processes.[10] Simple ashing of the extractant and subsequent leaching is reported not to be quantitative.[10]

The present study aimed to test and develop a method for multi-actinide analysis with AMS by using Actinide Resin for chemical separation of the actinide group from the sample matrix. For this purpose, two sample systems were considered: (1) Rhine river water samples collected in the vicinity of the Fessenheim Nuclear Power Plant (NPP) and (2) surface sea water collected from the vicinity of the La Hague NRP, as well as the certified reference material (CRM) IAEA-443. The hypothesis is that extraction of the actinides with Actinide Resin may be superior to the use of $Fe(OH)_3$ co-precipitation for sample systems for which also a considerable amount of the sample matrix itself might be co-precipitated. This can be the case for highly saline samples, like sea water, but also for fresh water like river water, when these samples are submitted to total digestion of their mineral particulate matter. Significant matrix co-precipitation may result in a dilution of the analyte in the combined matrix and $Fe(OH)_3$ precipitate and, thus, in a loss of sensitivity of the AMS analysis.

The choice of these sample systems allows for the testing of Actinide Resin separation for ultra-trace AMS analysis of environmental samples, possibly affected by different sources of nuclear contamination, namely, global fallout and the Fessenheim NPP for the Rhine river water, as well as the NRPs La Hague and Sellafield for the sea water.

AMS analysis of the anthropogenic actinides ^{236}U, ^{237}Np, ^{239}Pu and ^{240}Pu was complemented with ICP-MS and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis of the naturally occurring actinides ^{238}U and ^{232}Th and major matrix elements, respectively, to evaluate the efficiency of the separation procedures. To determine the AMS target material composition, the material was analysed with Scanning Electron Microscopy Energy Dispersive Spectroscopy (SEM-EDS) after the AMS measurement.

2 Experimental

2.1 Reagents and materials

Nitric acid (HNO_3, 69% ROTIPURAN® Ultra), hydrochloric acid (HCl, 34% ROTIPURAN® Ultra) and isopropanol (C_3H_8O, 99.95% ROTISOLV® Ultra LC-MS) were purchased from Carl Roth GmbH + Co. KG (Karlsruhe, Germany). L-(+)-ascorbic acid ($C_6H_8O_6$, 99+ %) and iron powder (−22 mesh, metal basis, 99.998%) were supplied by Alfa Aesar (Massachusetts, USA). Ammonium hydroxide (NH_4OH, 25% SUPRAPUR®), hydrofluoric acid (HF, 48% ULTRAPUR®), boric acid (H_3BO_3, 99.9999% SUPRAPUR®) and hydrogen peroxide (H_2O_2, 30% SUPRAPUR®) was provided by Merck KGaA (Darmstadt, Germany).

High-purity deionized water (18.2 MΩ cm^{-1}) was produced with a Milli-Q water purification system (Merck KGaA). Actinide Resin (100–150 μm) was bought from Eichrom Technologies, LLC (Lisle, USA). Empty chromatographic columns (2 mL, glass frit) were purchased from TrisKem International (Bruz, France). "Sea salt" ASTM D1141-98 was provided by Lake Products Company LLC (Florissant, USA).

The ^{233}U standard material (CBNM-IRM-040/1) and the ^{244}Pu standard material (CBNM IRM-042a) used as spike solutions were provided by the Central Bureau for Nuclear Measurements (Joint Research Centre, Geel, Belgium). The ^{237}Np standard material used as spike solution was provided by Eckert & Ziegler (Berlin, Germany). The certified reference material IAEA-443 (Irish sea water) was provided by the International Atomic Energy Agency (Vienna, Austria). For the isotopic composition of the standard and reference materials, see Table S1 to S6 in the SI.

2.2 Instrumentation

AMS measurements were conducted at the AMS facility VERA of the Faculty of Physics, University of Vienna, Austria, using a 3-MV tandem accelerator. The measurement parameters were set according to the optimised procedure for AMS analysis of the actinides in an iron oxide matrix at the VERA facility, as recently reported.[13] The actinides were analysed in the 3+ charge state by using He as a stripper gas and a terminal accelerator voltage of 1.65 MV. With known or suspected sample concentrations of the actinide analytes, a preliminary schedule of the measurement duration for each nuclide was created and constantly adjusted throughout the measurement. The goal was to achieve a similar level of relative uncertainty for each nuclide by improving the counting statistics for nuclides at lower concentrations with a prolonged measurement duration. The detailed AMS setup and measurement procedure for the actinides at VERA can be found in the publication by Steier *et al.*[13]

ICP-MS measurements were performed with an Element XR sector field ICP-MS (Thermo Fisher Scientific Inc., Waltham, USA). ICP-OES measurements were performed with an Optima 8300 (PerkinElmer, Inc., Waltham, USA). SEM-EDS measurements were achieved with a Zeiss Crossbeam 350 KMAT FIB-SEM (Carl Zeiss AG, Oberkochen, Germany).

2.3 Sample systems

Six Rhine river water samples (further called "RRW samples") – collected as surface water (8 L sample volume each) at different locations of the Rhine River in the vicinity of the French NPP in Fessenheim – were prepared for multi-actinide AMS analysis to determine the status quo of the actinide content of the Rhine river water before the shutdown and subsequent decommissioning of the Fessenheim NPP in 2020.[14] The six sampling locations were chosen in such a way as to allow the investigation of a possible influence of the NPP on the actinide content of the Rhine river water. The Fessenheim NPP is located at the Grand Canal of Alsace, an artificial canal built for easy navigation by boat that flows parallel to the Old Rhine River. Samples were collected upstream, at height and downstream of the NPP from both the river and the Grand Canal, totalling six samples (for sampling coordinates see Table S1).

A first set of six river water samples (2 L sample volume each) was digested with a mixture of HF and HNO_3 to dissolve all present mineral particulate matter together with any organic components, resulting in total digestion. However, application of $Fe(OH)_3$ co-precipitation for separation of the actinides from this solution resulted in precipitation of large amounts of CaF_2 before reaching the necessary pH for $Fe(OH)_3$ to precipitate and was, thus, unsuitable for AMS sample preparation, as will be described in Section 2.4.1. A second identical set of river water samples was prepared and digested without HF, leaving present silicate particles undigested. Because no fluoride was added to the samples, it was now possible to use $Fe(OH)_3$ co-precipitation without significant precipitation of CaF_2 and to successfully prepare AMS target materials.

The first set of completely digested river water samples, for which $Fe(OH)_3$ co-precipitation was no longer feasible, was instead used to test a new procedure employing Actinide Resin as an alternative to $Fe(OH)_3$ co-precipitation. As such, the precipitated CaF_2 was redissolved, and Actinide Resin was used in a batch sorption reaction to separate the actinides from solution.

To investigate the performance of Actinide Resin – for samples with higher matrix content than river water – the CRM IAEA-443 (radionuclides in Irish Sea water)[15] was used to prepare two sample sets consisting of two replicates each (100 mL sample volume; further called "CRM" samples). One sample set was prepared for multi-actinide AMS analysis *via* $Fe(OH)_3$ co-precipitation, while the second sample set was prepared for multi-actinide AMS analysis using Actinide Resin. Because of the high ^{237}Np content in the CRM, leading to too-high count rates and pile-up events in the AMS detector (see Section 3.2) the ^{237}Np concentration of the CRM samples could not be accurately determined in a 1st AMS analysis. Consequently, two additional sets – prepared by $Fe(OH)_3$ co-precipitation and Actinide Resin, respectively – of three replicates of diluted CRM (10 mL sample volume diluted to 100 mL) were measured in a 2nd AMS analysis. Artificial sea water prepared with certified "Sea Salt" ASTM D1141-98 (further called "artificial sea water") was used for dilution to match the matrix to that of the sample as closely as possible.

Finally, the sample preparation procedure with Actinide Resin was applied to sea water samples from the English Channel – collected from the sea surface at a beach *ca.* 8 km to the south of the La Hague NRP (N 49° 36′ 33 E −1° 50′ 39) in 2022 – as two sets of two replicates of an environmental sample (100 mL and 250 mL sample volume; further called "LH samples"). The 2nd AMS analysis also included two additional 100 mL replicates of the LH sample. Table 1 gives an overview of all samples analysed in the three AMS analyses throughout this work.

Table 1 Number of samples, procedure blanks and calibration samples and their respective volume for the three AMS analyses of this work

		Sea water			
	River water	1st AMS analysis		2nd AMS analysis	
	RRW	CRM	LH	CRM	LH
Samples					
Actinide Resin	6 × 2 L	2 × 100 mL	2 × 100 mL; 2 × 250 mL	3 × 10 mL	2 × 100 mL
$Fe(OH)_3$ co-precipitation	6 × 2 L	2 × 100 mL	—	3 × 10 mL	—
Blanks					
Actinide Resin	2×	1 × 100 mL	1 × 100 mL, 1 × 250 mL	3 × 100 mL	1 × 100 mL
$Fe(OH)_3$ co-precipitation	2×	1 × 100 mL	—	3 × 100 mL	—
Calibration samples					
Actinide Resin	2 × 2 L	2 × 100 mL, 2 × 250 mL		3 × 100 mL	
$Fe(OH)_3$ co-precipitation	2 × 2 L	—		3 × 100 mL	

For each sample system, procedure blanks and calibration samples were included in the AMS analysis (Table 1). For the RRW system, the calibration samples were prepared with a matrix of 2 L deionised water, while the blank did not include additional matrix. All procedure blanks and calibration samples for the sea water system were prepared with artificial sea water as matrix.

The calibration samples, spiked with both ^{237}Np and ^{244}Pu, were used to determine the chemical and ionisation yield (CIY) of both elements, which was needed in normalisation calculations for non-isotopic analysis of ^{237}Np with ^{244}Pu.[7,16]

2.4 Sample preparation procedure

2.4.1 Rhine river water (RRW) samples. Prior to any sample preparation, the six river water samples were acidified in their containers to pH < 1 with HNO_3 to prevent/reverse potential sorption of actinides to the container wall.

Two sets of six aliquots, each 2 L volume, were prepared from the individual acidified river water samples. Additionally, for each set, two procedure blanks containing all chemicals added throughout the sample preparation process and two calibration samples of 2 L acidified deionised water were prepared. All samples, blanks and calibration samples were spiked with ^{233}U and ^{244}Pu. In addition, ^{237}Np was added to the calibration samples. Subsequently, the solutions were evaporated to dryness and redissolved in 4 mL 69% HNO_3.

The first sample set was completely digested, submitted to an unsuccessful $Fe(OH)_3$ co-precipitation and subsequently used to test a sample preparation procedure employing Actinide Resin (Section 2.4.1.2), while $Fe(OH)_3$ co-precipitation was employed successfully for the second, only partially digested, sample set (Section 2.4.1.1).

2.4.1.1 Multi-actinide analysis with $Fe(OH)_3$ co-precipitation. The sample solutions, redissolved in 4 mL 69% HNO_3, were transferred to microwave digestion vessels and a HNO_3 microwave digestion (START-1500, Mikrowellen-Laborsysteme GmbH, Germany) was carried out at 230 °C for 10 minutes. Digestion without using HF left silicates in the sample undissolved, which remained throughout the sample preparation process as fine particulate and became part of the final AMS target material. The solutions were evaporated to dryness and (partially) redissolved in 20 mL 1 M HNO_3. Fe solution (Fe powder dissolved in 1 M HCl and oxidised to Fe(III) by addition of one drop of 30% H_2O_2 solution) was added to all samples to arrive at a total iron content of 2 mg per sample, suited to the employed AMS sample holders.

Co-precipitation was achieved by addition of 25% NH_4OH solution until a pH > 5 was reached. After waiting for 5 d for the precipitation reaction to conclude, the precipitate was centrifuged and the supernatant was removed by decantation, followed by two washing steps with dilute NH_4OH solution and repeated centrifugation and decantation. The washing solutions were combined with the supernatant and collected for further analysis with ICP-MS and ICP-OES, together with a small aliquot (1 mL) of the sample solution before co-precipitation. Finally, the $Fe(OH)_3$ precipitate (together with the silicate particulate) was dried and converted to iron oxide at 800 °C[7] in a quartz glass crucible. The solid sample was ground and mixed. The additional silicate matrix resulted in a final target material volume up to three times larger than the free sample volume of the AMS sample holders. Hence, only a fraction of the silicate/iron oxide blend could be pressed into a sample holder and analysed (also see SEM-EDS analysis of RRW target materials in Fig. S3 and S4).

2.4.1.2 Multi-actinide analysis with Actinide Resin. The sample solutions, redissolved in 4 mL 69% HNO_3, were transferred to microwave digestion vessels, 1 mL 48% HF was added to each vessel and a HF/HNO_3 microwave digestion was carried out at 230 °C for 10 minutes. To dissolve precipitated insoluble fluorides and mask remaining HF, 5 mL of a 3.5% H_3BO_3 solution was added and a second microwave digestion was carried out at 160 °C for 10 minutes.[17] Precipitated fluorides were still present after the second digestion, but after 14 h, all precipitate had dissolved. The samples were evaporated to dryness and redissolved in 20 mL 1 M HNO_3, yielding a clear solution.

To achieve the (ultimately unsuccessful) $Fe(OH)_3$ co-precipitation for separation of the actinides from solution, Fe solution was added to all samples for a total iron content of 2 mg per sample. For $Fe(OH)_3$ co-precipitation, a 25% NH_4OH solution was added dropwise to increase the pH of the sample solution. Before reaching the necessary pH for precipitation of $Fe(OH)_3$, precipitation of a large amount of sample matrix was observed, which was later identified as CaF_2 (see Fig. S9 and S10), indicating that the masking of the residual HF with H_3BO_3 was not, or only partially successful. This matrix precipitate accounted for many times the free volume of an AMS sample holder, preventing the use of the $Fe(OH)_3$ co-precipitation procedure for this set of completely digested samples.

As an alternative procedure, Actinide Resin was used for sample preparation. The matrix precipitate was redissolved by acidification with HNO_3 and the solution was evaporated to dryness. Significant Fe(III) content of the sample is a strong interference in the uptake of actinides on Actinide Resin since Fe(III) shows high affinity to the DIPEX® extractant.[8] As such, the Fe added to the samples had to be reduced to Fe(II) by dissolution of the sample residue in 0.1 M HCl[8] and addition of ascorbic acid (in excess of four times the stoichiometric amount). The success of the reduction reaction was confirmed by addition of ammonium thiocyanate to a small aliquot of the sample solution (the Fe(III) thiocyanate complex shows a vivid red colour).

Separation of the actinides from solution was achieved by direct addition of 5 mg Actinide Resin to the sample (20 mL volume) in a batch reaction while stirring continuously. After a contact time of 1 h, the resin was separated from the solution by filtration through an empty chromatographic column (2 mL volume) provided with a glass frit filter, followed by three washing steps with 2 mL 0.1 M HCl. The washing solutions were combined with the eluant and collected for further analysis with ICP-MS and ICP-OES, together with a small aliquot (1 mL) of the sample solution before resin extraction.

To separate the DIPEX® extractant from the resin substrate, 10 mL isopropanol[8] was added to the column and collected by filtration. The resin substrate still left on the column was discarded. Fe solution equivalent to 2 mg of total Fe was added to the isopropanol solution containing the extractant-actinide complexes. The solution was evaporated to dryness, and the small amount of yellow-orange-coloured sticky residue was dissolved with a few drops of isopropanol, transferred to a quartz glass crucible and again evaporated to dryness. Finally, the residue was combusted at 800 °C[7] and the resulting resin ash/iron oxide blend was collected from the crucible, mixed and pressed into an AMS sample holder.

2.4.2 Certified reference material (CRM) samples. Fig. 1 shows a flow chart of the sample preparation procedure for the novel method with Actinide Resin and for the standard method of co-precipitation with $Fe(OH)_3$ of the sea water samples (CRM and LH).

The CRM IAEA-443 was acidified throughout its fabrication process[15] and the pH, measured before the actual use, was *ca.* 1.5. Two sets of two replicates were prepared with 100 mL of the CRM. Further two sets of three replicate samples were prepared with 10 mL of the CRM and diluted to 100 mL with artificial sea water (83.9 mg certified "Sea Salt" ASTM D1141-98, added to 2 L deionised water and acidified to pH 1.5 with HCl) to retain a sea water matrix. The respective procedure blanks and calibration samples (see Table 1) were prepared with 100 mL artificial sea water. All samples and blanks were spiked with ^{233}U and ^{244}Pu and, in addition, ^{237}Np was added to the calibration samples. Subsequently, the solutions were evaporated to one-third of their original volume, lowering the volume but preventing precipitation of $CaSO_4$ from the sea water matrix by further evaporation.

2.4.2.1 Multi-actinide analysis with $Fe(OH)_3$ co-precipitation. Only 1 mg of Fe from the previously prepared Fe solution was added to the CRM samples, since a surprisingly high iron content of *ca.* 1 mg per 100 mL was found in the batch of CRM used in this work (see Section 3.4). Co-precipitation was achieved by addition of 25% NH_4OH solution until a pH > 5 was reached. After a waiting time of 1 h, the resulting precipitate was centrifuged and the supernatant was removed by decantation, followed by two washing steps with dilute NH_4OH solution and repeated centrifugation and decantation. The washing solutions were combined with the supernatant and collected for further analysis with ICP-MS and ICP-OES, together with a small aliquot (1 mL) of the sample solution before co-precipitation. Finally, the $Fe(OH)_3$ precipitate was dried and converted to iron oxide at 800 °C[7] in a quartz glass crucible. The solid sample was ground, mixed and pressed into an AMS sample holder.

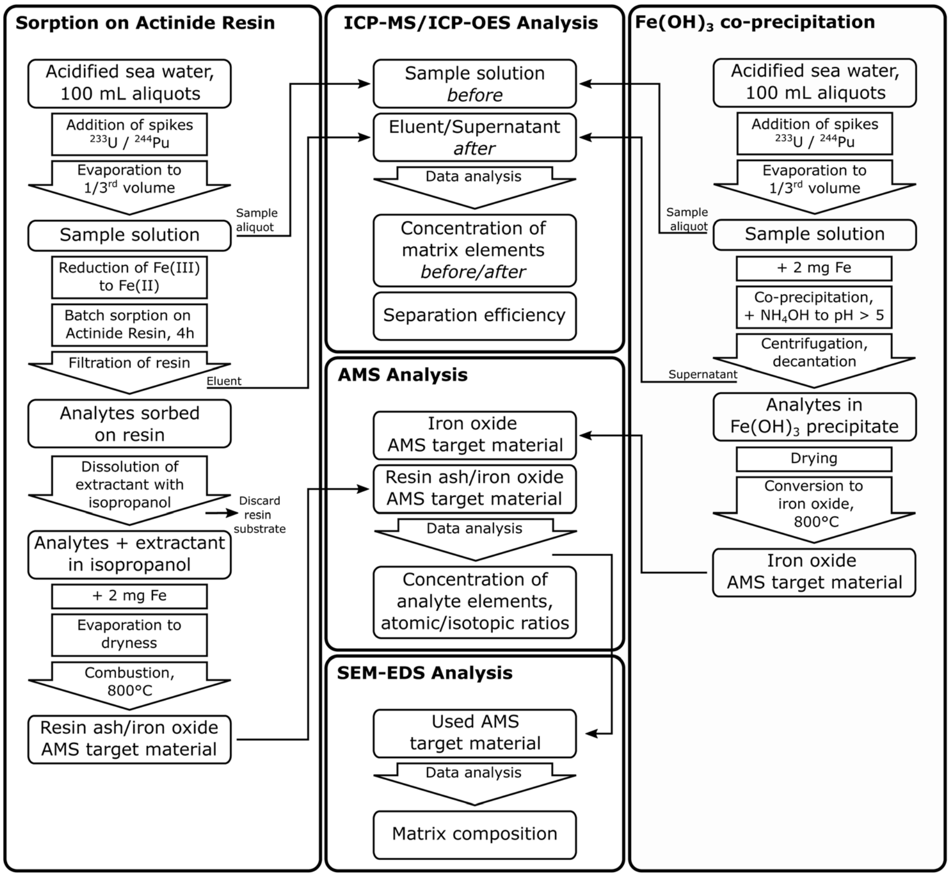

Fig. 1 Schematic of the sample preparation for multi-actinide analysis with the novel method using Actinide Resin (left) and the common method of co-precipitation with $Fe(OH)_3$ (right) for the sea water samples (LH and CRM). The schematic depicts an optimised version of the original procedure, applied to the RRW samples. As such, the scheme is not representative for the RRW sample system.

2.4.2.2 Multi-actinide analysis with Actinide Resin. Due to the significant Fe content (see Section 3.4) that would be present as Fe(III), ascorbic acid was added to these samples in excess of *ca.* four times the stoichiometric amount necessary for reduction to Fe(II). Separation of the actinides from solution was achieved by addition of 8 mg Actinide Resin to the sample (20 mL volume) in a batch reaction while stirring continuously. After a contact time of 4 h, the resin was separated from the solution by filtration through an empty chromatographic column provided with a glass frit filter, followed by three washing steps with 2 mL 0.1 M HCl. The washing solutions were combined with the eluant and collected for further analysis with ICP-MS and ICP-OES, together with a small aliquot (1 mL) of the sample solution before resin extraction. The subsequent steps of the sample preparation are identical to those carried out for the RRW samples as described at the end of Section 2.4.1.2.

2.4.3 La Hague (LH) samples. Prior to any sample preparation, the original LH sea water was acidified in its container to pH 1.5 with HCl to prevent/reverse potential sorption of actinides on the container wall.

Three sets of two replicates were prepared with 250 mL (1st AMS analysis) or 100 mL (1st and 2nd AMS analyses) acidified LH sea water. The corresponding procedure blanks (see Table 1) were prepared with 250 mL or 100 mL artificial sea water. Both samples and blanks were spiked with ^{233}U and ^{244}Pu. Subsequently, the solutions were evaporated to one-third of their original volume. The sample preparation of the LH samples with Actinide Resin was identical to the procedure used for the CRM samples. Even though no significant amount of Fe was found in the LH sea water, the samples were still treated with an amount of ascorbic acid identical to the RRW and CRM samples for consistency.

2.4.4 Additional information. Further information (valid for the three sample systems) on the chosen amounts of Fe and Actinide Resin for sample preparation, sample volume limitations and other practical considerations are given in Section 12 in the SI.

2.5 Determination of the chemical separation efficiency of matrix elements

Directly before and after the chemical separation of the actinides, small aliquots of the sample solution (before separation) and the supernatant solution of the $Fe(OH)_3$ co-precipitation (after separation), as well as the first eluting solution after separation with Actinide Resin, were collected and prepared for measurement with ICP-OES and ICP-MS (Fig. 1). The aliquots were diluted with 2% HNO_3 to adjust the solution salt content to a level that was appropriate for measurement with the respective analytical method.

With ICP-OES measurements before and after separation, the concentrations for common matrix elements found in environmental samples were analysed to characterise the samples and to investigate a possible effect of those elements on the separation of the actinides with Actinide Resin and $Fe(OH)_3$ co-precipitation.

With ICP-MS measurements before and after separation, the concentrations of a selection of lanthanide elements, as well as the naturally occurring ^{238}U and ^{232}Th as an analogue for anthropogenic ^{236}U and for Pu(IV), respectively, were obtained to determine an element-specific separation efficiency (*i.e.* the percentage of the elemental content that was separated from solution and is, therefore, part of the AMS target material) for use of actinides resin and $Fe(OH)_3$ co-precipitation.

2.6 SEM-EDS analysis of AMS target materials

To determine the composition of the sample matrix (apart from the bulk component Fe_2O_3) present in the AMS target materials prepared by either Actinide Resin or $Fe(OH)_3$ co-precipitation, and to further investigate a potential correlation between the output of the AMS Cs-sputtering ion source and the composition of the final sputter matrix, the target material of a select number of targets was analysed with SEM-EDS after measurement with AMS.

The Al sample holders were sputtered with Cs throughout the AMS measurement, resulting in visible degradation. The residual target material was scraped out of the sample holder, pressed onto In foil and coated with C to prevent a fast charge-up of the surface. As such, the EDS signal for Al, Cs, In or C in the target materials could not be assigned as original content of the materials and is assumed to have been introduced throughout the AMS measurement or the SEM-EDS sample preparation.

2.7 Determination of uncertainties

For both of the two series of the RRW sample system (six samples) all data (concentrations, atomic ratios, separation efficiencies) are presented as average values with a respective uncertainty calculated as a 95% confidence interval ($n = 6$, $k = 2.571$).

For the CRM and LH sample system with two and three replicates, an average value would be too imprecise. Consequently, all data related to the CRM and LH sample system (concentrations, atomic/isotopic ratios, separation efficiencies, target masses, detector signals) are presented individually for each replicate with a respective uncertainty calculated as the propagated error from sample preparation (*i.e.* mass and volume determination), instrumental analysis (measurement error) and further data analysis (*i.e.* blank corrections, normalisation with calibration samples, determination of the concentration from spike solutions). The sample replicates are always listed in the same order, *i.e.* the first replicate will always be listed as the first table entry. The respective uncertainty for the values of figures and tables are also stated in the figure and table captions.

3 Results and discussion

3.1 Rhine river water (RRW) samples

As stated in Section 2.3, the RRW sample system included six environmental river water samples that were collected at six different locations of the Rhine River and Grand Canal with varying proximity to the Fessenheim NPP. The results for the individual RRW samples obtained by AMS analysis show no significant difference in concentration for ^{236}U, ^{239}Pu or ^{237}Np based on their sampling location (Fig. S7). As such, no influence of the NPP on the actinide content of the river water could be identified and the samples were, from this point on, treated as replicates.

Fig. 2 shows the average actinide concentrations of the river water, comparing the sample set prepared with $Fe(OH)_3$ co-precipitation to the second set prepared with Actinide Resin. With $(6.9 \pm 1.3) \times 10^6$ at/L and $(5.8 \pm 1.0) \times 10^6$ at/L for ^{236}U and $(9.8 \pm 3.9) \times 10^6$ at/L and $(9.1 \pm 1.9) \times 10^6$ at/L for ^{237}Np, for the sample set prepared with co-precipitation and resin, respectively, the results for both methods are consistent. The consistent concentrations, determined in these two sets of six independent samples (Fig. S1), also show that both sample preparation methods yield reproducible results. The reported ^{239}Pu concentrations were similar to the concentrations found in the procedure blanks and are assumed to be purely background, which explains the high error on both values as they are based on an average of only 3 counts ($Fe(OH)_3$) and 2 counts (resin) over the whole measurement time of 30 min. Because of these low count rates for ^{239}Pu, no heavier Pu isotopes were analysed.

The atomic ratio $^{236}U/^{237}Np$ is estimated to be equal to 0.71 ± 0.31 for the sample set prepared by co-precipitation and 0.61 ± 0.17 for the sample set prepared by Actinide Resin. In a natural water sample collected from the peat bog 'Wildseemoor' (approx. 110 km northeast of the Fessenheim NPP), a $^{236}U/^{237}Np$ atomic ratio equal to 0.43 ± 0.05 was obtained.[7] This value is partially consistent with that determined for the RRW samples of this work, suggesting a similar origin and perhaps a similar geochemical behaviour of U and Np in the two surface water systems. The Wildseemoor water sample also contained a significant concentration of Pu. Based on its $^{240}Pu/^{239}Pu$ ratio, which was consistent with isotopic ratios of global fallout expected in the region the sample was located in, global fallout was recognised as the source of the anthropogenic actinides.[7] This result was additionally supported by the findings of global-fallout-derived Pu isotopes in a peat bog core collected at the Wildseemoor.[18] The different Pu concentrations of the RRW and the Wildseemoor water may be explained by their different sample matrix and geochemical conditions. In oxic surface river water, Np and U show a more conservative behaviour than Pu. *I.e.* Pu is less soluble than U and Np and more likely to be sorbed to suspended particles or sediment.[19,20] While the Wildseemoor surface water is acidic and reducing with a higher amount of organic matter (humic acids)[7,18] that could complex Pu and prevent its precipitation.

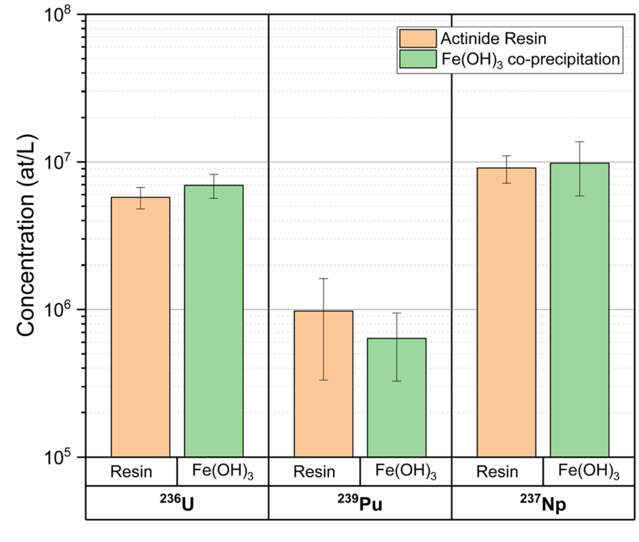

Fig. 2 Results of AMS analysis of Rhine river water (RRW) samples, comparing the two sample preparation methods. Use of Actinide Resin for AMS sample preparation produces results consistent with the standard method of $Fe(OH)_3$ co-precipitation. Reported concentrations are averages of six replicates. Error bars represent 95% confidence intervals ($n = 6$, $k = 2.571$).

López-Lora *et al.* suggested a $^{236}U/^{237}Np$ ratio of 0.56 ± 0.13 (calculated from their published $^{237}Np/^{236}U$ ratio of 1.77 ± 0.20) as a value characteristic for global fallout in sea water,[21] which is consistent with the ratios determined for the RRW in this work, for both of the sample preparation methods. They determined this ratio with AMS, as an average value from sea water samples collected at multiple offshore sampling stations at the south-western African coast. In a later publication, López-Lora *et al.* discussed the use of ^{237}Np and the $^{237}Np/^{236}U$ ratio as ocean tracers to investigate the potential influence of NRPs like Sellafield on water masses, based on the conservative behaviour of Np and U in sea water.[22] The consistent $^{236}U/^{237}Np$ ratios found in this work may point toward a similar conservative behaviour of Np and U in the Rhine river water.

3.2 IAEA-443 (CRM) samples

The CRM was prepared from sea water collected in September 1997 from the Irish Sea in the vicinity of the Sellafield NRP,[15,23] where low-level liquid effluents were regularly discharged from pipelines into the Irish Sea while the Sellafield site was in operation.[24]

For method validation, two sets of two (1st AMS analysis) and two sets of three replicates (2nd AMS analysis) of the CRM were prepared with both sample preparation procedures, respectively. As stated before in Section 2.3 and 2.4.2, the samples were measured in two different AMS analyses. The 100 mL volume samples of the 1st analysis yielded average count rates of 5 and 22 cps for ^{236}U, 4 and 38 cps for ^{239}Pu and 1 and 9 cps for ^{240}Pu for use of $Fe(OH)_3$ co-precipitation or Actinide Resin, respectively. However, the average count rates for ^{237}Np were up to 1000 cps, already causing considerable dead time in the AMS detection system and potential cross-talk in the ion source. To accurately determine the strongly elevated ^{237}Np concentration in the CRM, a second set of samples composed of 10 mL IAEA-443 and 90 mL artificial sea water was prepared and measured in a 2nd AMS analysis (see Section 2.4.2).

The results of the two AMS analyses are shown in Fig. 3 for the four analyte actinide nuclides ^{236}U, ^{239}Pu, ^{240}Pu (1st AMS analysis) and ^{237}Np (2nd AMS analysis). Blue solid lines represent the nominal nuclide concentrations, and blue dotted lines the respective uncertainty intervals, each reported as atoms/

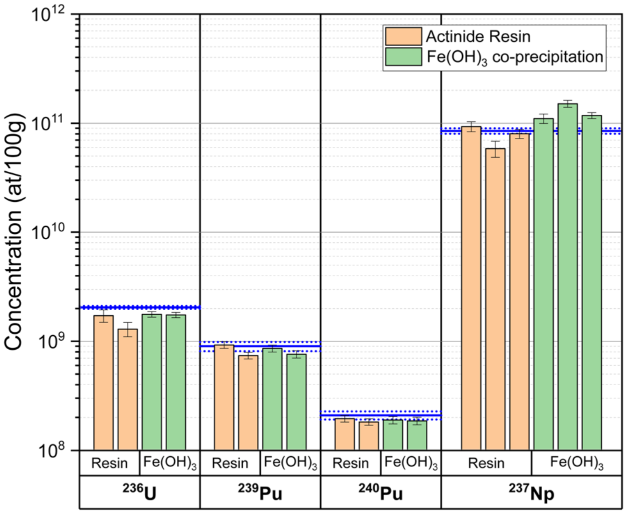

Fig. 3 Results of the 1st (^{236}U, ^{239}Pu, ^{240}Pu) and 2nd (^{237}Np) AMS analyses of the CRM, comparing the two sample preparation methods. Shown are the individual concentrations of two replicates (1st analysis) or three replicates (2nd analysis). Error bars represent the propagated error from sample preparation and AMS analysis. Blue lines represent the nominal values (solid line) and the error interval (dotted line) reported in the certificate of the CRM (^{238}U and ^{237}Np from IAEA-381;[23] ^{239}Pu and ^{240}Pu from IAEA-443 (ref. 15)).

100 g calculated from the massic activities of the CRM certificate. The nominal values of ^{236}U and ^{237}Np are based on the reported values of CRM IAEA-381 (^{236}U – information value; ^{237}Np – certified value),[23] as they were not reported in the reissued CRM IAEA-443. The nominal values of ^{239}Pu and ^{240}Pu are based on the reported information values of CRM IAEA-443.[15] Similar to the RRW samples, both sample preparation procedures seemingly produce consistent results, which indicates that Actinide Resin can be used as an alternative to $Fe(OH)_3$ co-precipitation for sea water samples.

Table 2 compares the results of both AMS analyses to the nominal values and literature values for the CRM. Eigl *et al.*[25] determined the ^{236}U concentration of the CRM *via* AMS and reported a lower concentration than the nominal value. They concluded that this discrepancy resulted from detector dead time issues and that their result was based on only a single short measurement of ^{236}U. Quinto *et al.*[7] also analysed the ^{236}U concentration *via* AMS and found a value consistent with the nominal concentration. The results of this work are higher than the concentration reported by Eigl *et al.*, partially consistent with the value reported by Quinto *et al.*, but slightly underestimate the nominal concentration.

Hain *et al.*[26] found concentrations for ^{237}Np that underestimated the nominal value by 22%, deeming such a precision typical when a non-isotopic tracer (^{242}Pu) is used for determination of ^{237}Np. Both Zhang *et al.*[27] and Quinto *et al.*[7] reported ^{237}Np concentrations that are consistent with the nominal value, which also seems to be the case for the concentrations determined in this work for the samples prepared by Actinide Resin. For the samples prepared by $Fe(OH)_3$ co-precipitation, concentrations were found that are seemingly consistent with the one reported by Quinto *et al.*, but slightly overestimate the nominal concentration.

There are multiple publications that validate the nominal concentrations of ^{239}Pu and ^{240}Pu of the CRM, determined by SF-ICP-MS[27,28] and AMS.[7,26] Wang *et al.*[29] reported a combined $^{239+240}$Pu activity of (0.0160 ± 0.0005) mBq g^{-1} that was higher than the certified range of (0.0143–0.0150) mBq g^{-1}.[15] They explained that this inconsistency was likely because of their use of ICP-MS for analysis, whereas the certified value was determined by alpha spectrometry. The analysis of this work found ^{239}Pu/^{240}Pu ratios, as well as individual ^{239}Pu and ^{240}Pu concentrations – for both resin and $Fe(OH)_3$ co-precipitation – that are consistent with the nominal values.

3.3 La Hague (LH) samples

The LH samples were considered for measurement with AMS as a further environmental sea water sample prepared by the novel AMS sample preparation procedure with Actinide Resin. Two replicates of 250 mL volume and two replicates of 100 mL volume were measured in a 1st AMS analysis, and further two replicates of 100 mL volume were measured in a 2nd analysis. Compared to the CRM samples, the ^{236}U, ^{239}Pu, ^{240}Pu and ^{237}Np content of the LH samples was multiple orders of magnitude lower, and no detector overload was observed. The count rates for all 100 mL sample volume replicates of the 1st, as well as the 2nd analysis, were low and acceptable count rates were achieved only for the 250 mL volume replicates of the 1st analysis. The results of the 1st AMS analysis of the 250 mL replicates of the LH sea water samples are listed in Table 3.

The measured ^{240}Pu/^{239}Pu ratios of 0.22 ± 0.05 and 0.23 ± 0.05 are partially consistent but slightly higher than the ratio of 0.180 ± 0.007 typically found for global fallout in the northern hemisphere[31] and may point towards a contribution from nuclear reprocessing as a source. The LH sea water was collected approx. 8 km south of the La Hague NRP, as surface water directly at the beach. While most of the released discharge of the La Hague site is transported through the English Channel to the east, a fraction flows south and southwest towards the Channel Islands,[32] which includes the area where the LH sea water was collected. The ^{240}Pu/^{239}Pu ratios are similar to a ratio of 0.235 (no uncertainty stated) that was determined with multicollector ICP-MS by Cundy *et al.* in the highest layer of a salt marsh core from an estuary *ca.* 40 km south of the La Hague site.[33] Christl *et al.* analysed multiple sea water samples from the English Channel and the North Sea by AMS. For samples in the vicinity of La Hague they found ^{236}U concentrations of (50.3 ± 1.6) × 10^6 at/L (north of La Hague) and (45.1 ± 0.9) × 10^6 at/L (further north),[34] which are partially consistent with the concentrations of (4.5 ± 0.7) × 10^7 at/L and (6.1 ± 0.8) × 10^7 at/L found for the LH samples of this work. The determined ^{237}Np concentrations of (1.2 ± 0.3) × 10^7 at/L and (0.7 ± 0.2) × 10^7 at/L are, to the author's knowledge, the only analysis of ^{237}Np in sea water samples from the vicinity of La Hague.

A comparison of the LH sea water (Table 3) and the CRM sea water (Table 2), both affected by NRPs, shows very similar ^{240}Pu/^{239}Pu ratios. The ^{236}U/^{239}Pu ratios of the LH sea water are

Table 2 Comparison of the results of the 1st (^{236}U, ^{239}Pu, ^{240}Pu) and 2nd (^{237}Np) AMS analyses of the CRM (for both sample preparation methods) to the nominal values of IAEA-381, IAEA-443 and further literature values. Values listed from this work are reported for each replicate sample. The reported uncertainty is the propagated error from sample preparation and AMS analysis. The ^{236}U/^{237}Np and ^{237}Np/^{239}Pu ratios are calculated with the ^{236}U, ^{237}Np and ^{239}Pu concentrations of the three replicates of the 2nd AMS analysis. Values that were calculated from literature data are marked with ∇

	This work			
	Resin	$Fe(OH)_3$	Nominal value	Literature values
^{236}U (at/100 g)	$(1.7 \pm 0.2) \times 10^9$ $(1.3 \pm 0.2) \times 10^9$	$(1.8 \pm 0.1) \times 10^9$ $(1.7 \pm 0.1) \times 10^9$	$(2.05 \pm 0.06) \times 10^9$ (ref. 23)	$(1.4 \pm 0.1) \times 10^9$ (ref. 25); $(1.85 \pm 0.06) \times 10^9$ (ref. 7)
^{239}Pu (at/100 g)	$(9.2 \pm 0.6) \times 10^8$ $(7.4 \pm 0.5) \times 10^8$	$(8.6 \pm 0.6) \times 10^8$ $(7.6 \pm 0.6) \times 10^8$	$(9.44 \pm 1.10) \times 10^8$ (ref. 15)	$(8.8 \pm 0.3) \times 10^{8\,\nabla}$ (ref. 27); $(9.01 \pm 0.11) \times 10^{8\,\nabla}$ (ref. 28); $(9 \pm 3) \times 10^8$ (ref. 7); $(9.2 \pm 2.2) \times 10^6$ (ref. 26)
^{240}Pu (at/100 g)	$(1.9 \pm 0.1) \times 10^8$ $(1.8 \pm 0.1) \times 10^8$	$(1.9 \pm 0.1) \times 10^8$ $(1.9 \pm 0.2) \times 10^8$	$(2.18 \pm 0.21) \times 10^8$ (ref. 15)	$(2.03 \pm 0.06) \times 10^{8\,\nabla}$ (ref. 27); $(2.12 \pm 0.24) \times 10^{8\,\nabla}$ (ref. 28); $(1.98 \pm 0.54) \times 10^8$ (ref. 7); $(2.16 \pm 0.53) \times 10^6$ (ref. 26)
^{237}Np (at/100 g)	$(9.3 \pm 1.0) \times 10^{10}$ $(5.9 \pm 1.0) \times 10^{10}$ $(8.0 \pm 0.8) \times 10^{10}$	$(1.1 \pm 0.1) \times 10^{11}$ $(1.5 \pm 0.1) \times 10^{11}$ $(1.2 \pm 0.1) \times 10^{11}$	$(8.49 \pm 0.49) \times 10^{10}$ (ref. 23)	$(1.1 \pm 0.3) \times 10^{11}$ (ref. 7); $(8.4 \pm 0.3) \times 10^{10\,\nabla}$ (ref. 27); $(6.6 \pm 0.3) \times 10^8$ (ref. 26)
^{236}U/^{239}Pu ratio	1.9 ± 0.3 1.7 ± 0.3	2.1 ± 0.02 2.3 ± 0.02		2.0 ± 0.6 (ref. 7)
^{240}Pu/^{239}Pu ratio	0.21 ± 0.02 0.25 ± 0.03	0.22 ± 0.02 0.24 ± 0.03	0.229 ± 0.006 (ref. 15)	0.22 ± 0.06 (ref. 7); 0.2325 ± 0.0008 (ref. 30)
^{236}U/^{237}Np ratio	0.018 ± 0.003 0.022 ± 0.004 0.018 ± 0.003	0.012 ± 0.002 0.009 ± 0.001 0.011 ± 0.001		0.016 ± 0.004 (ref. 7)
^{237}Np/^{239}Pu ratio	56 ± 9 37 ± 7 53 ± 8	83 ± 9 117 ± 12 110 ± 9		124 ± 48 (ref. 7)

Table 3 Results of the 1st AMS analysis of the 250 mL LH sea water samples, measured with the novel AMS sample preparation procedure using Actinide Resin. Values are reported for each replicate sample. The reported uncertainty is the propagated error from sample preparation and AMS analysis

Concentration (at/100 g)		Atomic ratio	
^{236}U	$(4.5 \pm 0.7) \times 10^7$ $(6.1 \pm 0.8) \times 10^7$	^{236}U/^{239}Pu	3.2 ± 0.7 5.3 ± 1.0
^{239}Pu	$(1.4 \pm 0.2) \times 10^7$ $(1.2 \pm 0.2) \times 10^7$	^{240}Pu/^{239}Pu	0.22 ± 0.05 0.23 ± 0.05
^{240}Pu	$(3.1 \pm 0.5) \times 10^6$ $(2.7 \pm 0.4) \times 10^6$	^{236}U/^{237}Np	4 ± 1 8 ± 2
^{237}Np	$(1.2 \pm 0.3) \times 10^7$ $(0.7 \pm 0.2) \times 10^7$	^{237}Np/^{239}Pu	0.9 ± 0.2 0.6 ± 0.2

higher than the ratios the CRM sea water, while the ^{236}U/^{237}Np ratios of the LH sea water are *ca.* 2 orders of magnitude higher, indicating a significantly higher relative content of ^{237}Np in the CRM sea water. The overall concentration of the actinide analytes is *ca.* 2 orders of magnitude lower in the LH sea water, compared to the CRM sea water. While the CRM sea water was collected in proximity to the discharge pipe of the Sellafield site,[15,23] the LH sample was collected more than 8 km away. As such, the potential influence of the La Hague site on the LH sea water will be lower, due to dilution with sea water, and global fallout will constitute a larger and likely significant part of the overall actinide content.

3.4 ICP-MS and ICP-OES analysis of the sea water samples

ICP-OES analysis of the sample solutions for common matrix elements – before and after separation of the actinides – showed results in line with the expected concentrations of sea water for almost all analysed elements. A notable result is the very high Fe content that was found in the CRM samples – *ca.* 10 mg L^{-1} Fe (Tables S13 and S14) – that is orders of magnitude higher than the typical Fe concentration in sea water. This required the reduction of all contained Fe(III) to Fe(II) prior to separation of the actinides with Actinide Resin, since Fe(III) strongly interferes with the uptake of actinides on Actinide Resin (as described in section 2.4.2). The source of the high Fe content likely originates from the Sellafield site, where in 1994 the Enhanced Actinide Removal Plant (EARP) was opened, using $Fe(OH)_3$ co-precipitation to remove actinides and other contaminants from liquid waste before the supernatant was discharged into the Irish Sea.[24,35] The Irish Sea water used to produce the CRM IAEA-381 and IAEA-443 was collected in the vicinity of the Sellafield site in 1997.[15,23]

ICP-MS measurements of the sample solutions before and after separation of the actinides, for naturally occurring ^{238}U and ^{232}Th – as analogue for anthropogenic ^{236}U and Pu(IV), respectively – as well as a selection of lanthanide elements, were conducted for the samples of the 2nd AMS analysis to determine elemental concentrations. With concentrations before and after the actinide separation step (*via* sorption on Actinide Resin or $Fe(OH)_3$ co-precipitation, respectively), separation efficiencies for each element were estimated (see Table 4). The ^{232}Th concentrations were below the detection limit of the ICP-MS. As such, no separation efficiencies are listed. A separation efficiency of 100% would mean that all original sample content of the specific element was separated from the sample solution and would be found in the final AMS target material. Separation efficiencies of close to 100% for all detected elements were found for the LH samples.

Only the separation efficiencies of ^{238}U and Ce could be determined for the CRM. ^{232}Th and all other lanthanide elements were below the detection limit. While the separation efficiencies of Ce for the CRM samples were found to be significantly lower than 100% for both methods, the separation efficiencies for ^{238}U were close to 100%. The near quantitative separation of ^{238}U for the LH and CRM samples is a further indication that ^{236}U was separated with high efficiency by use of both Actinide Resin and $Fe(OH)_3$ co-precipitation. The low separation efficiency of Ce for the CRM for both methods, however, may indicate that analysis of potential Am content for this system would also have resulted in only partial separation. This discrepancy of separation efficiencies between the LH and the CRM sample system – both sea water samples – will have to be further investigated.

Table 4 Separation efficiency (in per cent) of selected actinide and lanthanide elements for the LH samples (separation *via* Actinide Resin) and the CRM samples (separation *via* Actinide Resin or $Fe(OH)_3$ co-precipitation, respectively), determined by ICP-MS for the samples of the 2nd AMS analysis. Separation efficiencies are reported for each replicate sample. The reported uncertainty is the propagated error from sample preparation and ICP-MS analysis

	Separation efficiency (%)		
	LH [resin]	CRM [resin]	CRM [$Fe(OH)_3$]
^{238}U	100 ± 3	98 ± 1	96 ± 2
	100 ± 4	100 ± 1	96 ± 3
		100 ± 3	95 ± 3
Ce	96 ± 5	outlier	76 ± 11
	99 ± 4	52 ± 11	84 ± 11
		67 ± 13	79 ± 12
La	92 ± 6		
	93 ± 4		
Pr	95 ± 8		
	97 ± 9		
Tb	97 ± 17		
	97 ± 12		
Dy	94 ± 8		
	96 ± 8		
Ho	95 ± 15		
	97 ± 9		

Separation efficiencies have been determined with the same procedure for the RRW sample system and were found to be near quantitative for the $Fe(OH)_3$ co-precipitation. For Actinide Resin, separation efficiencies were above 80% but not quantitative for ^{232}Th and ^{238}U, and as low as 30% for Ce (Table S8). The improved separation efficiencies for the sea water samples may be related to longer batch sorption times with Actinide Resin, 4 h instead of the 1 h used for the RRW samples. An experiment conducted after the AMS measurement of the RRW showed that separation efficiencies could be improved with batch sorption times exceeding 1 h (Fig. S2). A sorption time of 4 h is consistent with the minimum time that is recommended in the Method "ACW11" used for "measurement of the total alpha radioactivity in water samples" with LSC by Eichrom Technologies.[9]

3.5 SEM-EDS analysis of CRM target materials

Fig. 4 shows a representative area of the phase EDS maps for four different target materials – two materials of the 1st and two of the 2nd AMS analysis, prepared by $Fe(OH)_3$ co-precipitation and Actinide Resin, respectively. The complete phase EDS maps, as well as further information, i.a. SEM images acquired

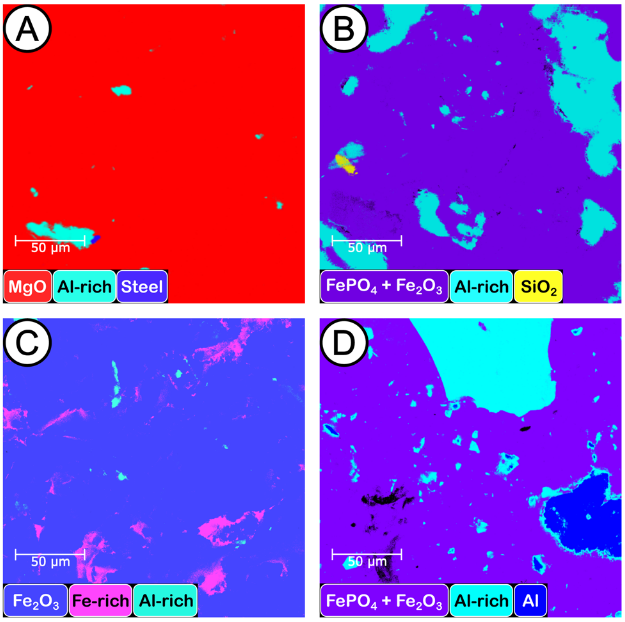

Fig. 4 Phase EDS maps, depicting regions of similar elemental composition by colour. (A) CRM target material, 1st AMS analysis, prepared by $Fe(OH)_3$ co-precipitation. (B) CRM target material, 1st AMS analysis, prepared by Actinide Resin. (C) CRM target material, 2nd AMS analysis, prepared by $Fe(OH)_3$ co-precipitation. (D) CRM target material, 2nd AMS analysis, prepared by Actinide Resin. The phase EDS maps shown here are representative sections of the full maps, which can be found in the SI.

using a backscattering electron detector and the composition of the major phases (in at%), can be found in the SI.

As stated in Section 2.6, Al found in the EDS analysis should be attributed to degradation of the Al sample holder. The major phase that is present in each sample is shown in Fig. 4. The target material prepared by $Fe(OH)_3$ co-precipitation for the 1st AMS analysis (A) is comprised of a significant amount of MgO with a comparatively small amount of Fe_2O_3, which was likely precipitated as $Mg(OH)_2$ concurrently with $Fe(OH)_3$, Mg being one of the most abundant components of sea water.

The target material prepared by $Fe(OH)_3$ co-precipitation for the 2nd AMS analysis (C), however, shows a major phase of Fe_2O_3 containing only a minor amount of MgO. The CRM samples for the 2nd analysis were prepared as replicates of the 1st analysis, only differing in the 1 : 10 dilution of the CRM with synthetic sea water. This dilution of the CRM, however, is unlikely to be the reason for this discrepancy in matrix composition between the 1st and 2nd analysis, as the synthetic sea water has a composition that is very similar to that of the CRM, with an even higher concentration of Mg (compare Tables S13–S15). Considering that $Mg(OH)_2$ should precipitate at a pH that is significantly higher than the pH of *ca.* 5, where $Fe(OH)_3$ should start to precipitate, the only explanation that was found for this case is that the pH was increased too much when carrying out the $Fe(OH)_3$ co-precipitation for the CRM samples of the 1st analysis. A more careful application of the $Fe(OH)_3$ co-precipitation seems to have prevented the co-precipitation of significant amounts of $Mg(OH)_2$ for the CRM samples of the 2nd analysis.

The CRM samples prepared by Actinide Resin for the 1st (B) and 2nd analysis (D) show a very similar composition. They are comprised of a major phase that seems to be a mixture of $Fe_3(PO_4)_2$ and Fe_2O_3. The functional group of the DIPEX® extractant of Actinide Resin, which is responsible for bonding with the actinide analytes, is a diphosphonic acid, which is presumably the source of the P content. A further component from the decomposition of the extractant may be C, but a quantitative analysis of carbon is challenging once samples are carbon-coated.

3.6 Comparison of Actinide Resin and $Fe(OH)_3$ co-precipitation

The composition of the four distinct target materials (shown in Fig. 4) did have a significant effect on the performance of the respective AMS analyses. The final mass of those target materials is displayed in the top part of Table 5. While three of the four distinct materials show similar masses of *ca.* 1.5 to 4 mg, the masses of the target materials of the 1st analysis that were prepared by $Fe(OH)_3$ co-precipitation are multiple times higher, due to the precipitation of $Mg(OH)_2$. Table 6 compares the AMS detector signal obtained for both sample preparation methods by displaying the ratio of the count rates in counts per second (cps), *i.e.* cps(resin)/cps($Fe(OH)_3$), for each investigated nuclide.

The detector signal ratios of the 1st AMS analysis show count rates for target materials prepared by Actinide Resin that are *ca.* 3 to 10 times higher. This is likely to be explained by the *ca.* 3 to 8 times higher masses of the target materials prepared by co-precipitation, resulting in a reduced concentration of the actinide nuclides.[16] Consequently, longer measurement times are required to produce the same number of actinide ions (*e.g.* $^{236}UO^-$) in the ion source when sputtering a larger mass of target material. *I.e.* in this case, the use of Actinide Resin for sample preparation resulted in higher count rates than use of $Fe(OH)_3$ co-precipitation because it compensated for a dilution effect originating from the relevant precipitation of matrix elements from the sea water. This indicates that use of the novel method could allow for shorter measurement times when applying multi-actinide AMS analysis to sample systems where analyte separation with co-precipitation is not possible without precipitation of large amounts of sample matrix.

However, in the 2nd AMS analysis, for target materials prepared by resin with an average mass that is still *ca.* 50% below the average mass of the materials prepared by co-precipitation, detector signal ratios are nevertheless *ca.* 40 to

Table 5 (Top) mass of the CRM target materials, comparing both sample preparation methods for the 1st and 2nd AMS analysis. The mass is reported for each replicate sample. The reported uncertainty is the propagated error of the weight measurements. (Bottom) detector signal for the spiked nuclides ^{233}U and ^{244}Pu as a ratio cps(nuclide)/(number of spiked nuclide atoms). The reported uncertainty is the propagated error from the spike concentration and the AMS analysis

	1st AMS analysis		2nd AMS analysis	
	Resin	$Fe(OH)_3$	Resin	$Fe(OH)_3$
Mass of target material (mg)	2.9 ± 0.1	22.3 ± 0.1	1.4 ± 0.1	3.7 ± 0.1
	3.2 ± 0.1	10.9 ± 0.1	1.7 ± 0.1	3.5 ± 0.1
			1.5 ± 0.1	3.9 ± 0.1
Detector signal (cps/spiked atoms)				
^{233}U	$(2.02 \pm 0.07) \times 10^{-8}$	$(2.5 \pm 0.1) \times 10^{-9}$	$(1.5 \pm 0.1) \times 10^{-9}$	$(5.8 \pm 0.3) \times 10^{-9}$
	$(1.15 \pm 0.04) \times 10^{-8}$	$(3.2 \pm 0.1) \times 10^{-9}$	$(2.7 \pm 0.2) \times 10^{-9}$	$(3.7 \pm 0.2) \times 10^{-9}$
			$(1.6 \pm 0.1) \times 10^{-9}$	$(3.4 \pm 0.2) \times 10^{-9}$
^{244}Pu	$(4.5 \pm 0.3) \times 10^{-8}$	$(5.9 \pm 0.4) \times 10^{-9}$	$(1.2 \pm 0.1) \times 10^{-9}$	$(1.15 \pm 0.06) \times 10^{-8}$
	$(4.8 \pm 0.3) \times 10^{-8}$	$(4.7 \pm 0.3) \times 10^{-9}$	$(1.7 \pm 0.2) \times 10^{-9}$	$(5.4 \pm 0.3) \times 10^{-9}$
			$(1.6 \pm 0.1) \times 10^{-9}$	$(1.06 \pm 0.05) \times 10^{-8}$

Table 6 Comparison of AMS detector signal (cps) obtained for both methods, as a ratio cps(resin)/cps($Fe(OH)_3$). No ratio is reported for ^{237}Np for the first analysis because of detector overload. The ratio is reported for each replicate sample. The reported uncertainty is the propagated error from the AMS analysis

	1st AMS analysis	2nd AMS analysis
Detector signal (cps(resin)/cps($Fe(OH)_3$))		
^{233}U	8.2 ± 0.3	0.26 ± 0.02
	3.6 ± 0.1	0.73 ± 0.05
		0.32 ± 0.02
^{236}U	7.7 ± 0.1	0.29 ± 0.02
	3.1 ± 0.1	0.66 ± 0.04
		0.39 ± 0.02
^{237}Np	—	0.19 ± 0.01
	—	0.30 ± 0.01
		0.19 ± 0.01
^{239}Pu	8.2 ± 0.1	0.13 ± 0.01
	9.9 ± 0.2	0.40 ± 0.02
		0.21 ± 0.01
^{240}Pu	7.9 ± 0.2	0.14 ± 0.02
	9.9 ± 0.3	0.38 ± 0.04
		0.18 ± 0.02
^{244}Pu	7.7 ± 0.2	0.11 ± 0.01
	10.3 ± 0.3	0.32 ± 0.03
		0.15 ± 0.01

80% lower. *I.e.* use of Actinide Resin resulted in lower count rates for the AMS analysis. This may point towards a lower ionisation efficiency in the Cs-sputtering negative ion source for the iron oxide-resin ash mixture compared to an iron oxide matrix. While the ionisation processes that take place inside a Cs-sputtering negative ion source are still not well characterised, iron oxide is known empirically to be a good matrix for AMS analysis of actinides. In order to test our hypothesis that the presence of the resin ash may have reduced the ionisation efficiency, further experiments are required in which the cathodes prepared with both methods are sputtered until all of the respective target material is consumed, to determine the absolute ion yield.

The bottom part of Table 5 lists another indicator of the detector signal for the individual sample replicates, as a ratio of the count rate to the number of atoms of ^{233}U and ^{244}Pu spiked. The trend that is visible in the direct comparison of the detector signals for both methods in Table 6 is visible here as well: use of the resin, when compared to the $Fe(OH)_3$ co-precipitation, showed improved detector signals for the 1st AMS analysis but lower signals for the 2nd analysis.

Comparing the 1st and 2nd analyses for each individual method, the resin showed *ca.* one order of magnitude lower detector signals for the 2nd analysis. This may be explained by the overall performance of the AMS instrument. A uranium oxide target material, used at the VERA AMS facility as a standard material to test the performance of the instrument throughout the analysis, showed an average count rate that was also *ca.* one order of magnitude lower for the 2nd AMS analysis, indicating that the performance of the resin may have actually been similar for both analyses. The $Fe(OH)_3$ co-precipitation showed a detector signal that is higher for the 2nd analysis, which may again be explained by the aforementioned dilution effect that lowered the performance of the $Fe(OH)_3$ co-precipitation in the 1st analysis.

4 Conclusions

This work describes a novel method for concurrent AMS analysis of ^{236}U, ^{237}Np, ^{239}Pu and ^{240}Pu using Actinide Resin instead of $Fe(OH)_3$ co-precipitation for separation of the actinides from the sample solution for "multi-actinide analysis" with AMS as reported previously.[7] The use of Actinide Resin produced results consistent with $Fe(OH)_3$ co-precipitation, demonstrating that it can be successfully used as an alternative to $Fe(OH)_3$ co-precipitation for multi-actinide analysis.

Samples of 2 L of Rhine river water (RRW) as well as 250 mL of surface sea water collected in the vicinity of the La Hague NRP (LH) were successfully analysed, proving that the novel method can be used for highly sensitive analysis of samples with such low volume. Furthermore, the nuclear contamination source for three different sample systems could be identified. Namely, for the sea water samples IAEA-443 (CRM), contaminated by the Sellafield NRP, the sea water samples LH, contaminated by global fallout with a likely contribution of the La Hague NRP, as well as the river water samples RRW, where no influence of the Fessenheim NPP could be found, and global fallout was identified as the likely contamination source.

It was found that for samples where a significant amount of sample matrix would precipitate together with $Fe(OH)_3$, causing a dilution effect, use of Actinide Resin can improve the signal count rates of the AMS detector, enabling shorter measurement times. In particular, the novel method yielded improved AMS detector signals for the 1st AMS analysis of the CRM, where use of $Fe(OH)_3$ co-precipitation resulted in concurrent precipitation of $Mg(OH)_2$, but yielded worse detector signals for the 2nd analysis of the CRM with little precipitation of sample matrix. Further experiments will focus on the analysis of sample systems with significantly higher matrix content than sea water, such as soil and clay leachates, solid sample digestions and brine solutions, to investigate if use of Actinide Resin for these systems could indeed significantly increase analytical sensitivity, as the results of this work indicate.

The time and effort necessary to prepare a set of water samples for multi-actinide analysis with Actinide Resin is very similar to that when using $Fe(OH)_3$ co-precipitation, *ca.* 8 to 10 days of work for 25 samples, including blanks and calibration samples. Use of Actinide Resin will likely be more expensive, since it necessitates the upfront purchase of the expensive chromatographic resin. However, only a small amount of *ca.* 8 mg of resin is needed for a single sample, so the overall consumption will be relatively low.

For the first time, SEM-EDS analysis was used to determine the composition of AMS target materials. For this work, this information was primarily used to identify the sample matrix that was separated from solution with the respective sample preparation method. However, SEM-EDS may have further potential for use in conjunction with AMS. With systematic analysis of target materials directly after sample preparation, it may be possible to investigate the performance of distinct matrix compositions that will improve the ionisation yield in the AMS ion source and improve the sensitivity of the analysis.

Author contributions

Thomas Roth: conceptualisation, investigation, writing – original draft, visualisation. Francesca Quinto: supervision, conceptualisation, writing – review and editing. Markus Plaschke: supervision, writing – review and editing. Karin Hain: investigation, writing – review and editing. Peter Steier: investigation. Natalia Palina: investigation, writing – review and editing. Sylvia Moisei-Rabung: investigation. Horst Geckeis: supervision, writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d5ja00487j.

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