

Application Note

Radioactive pollution monitoring: trace and ultratrace level uranium isotopes in seawater by ICP-MS and the MassNeb nebulizer

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1. Introduction

Uranium is a trace element with a quite conservative behavior in aqueous oxidizing media. Average uranium concentrations in the ocean are in the range of $\sim 3 \mu\text{g/L}$ with some deviations that follow the water salinity (Henderson, 2002). The abundance of its three natural isotopes is relatively homogeneous in the open ocean, being in the range of 99.3% (^{238}U), 0.72% (^{235}U) and 0.006% (^{234}U). Certain deviations from these reference values can appear because of natural processes and the effect of NORM (Naturally Occurring Radioactive Material) industries, mainly affecting the $^{238}\text{U}/^{234}\text{U}$ isotope ratio, and pollution from nuclear facilities, mainly affecting the $^{238}\text{U}/^{235}\text{U}$ isotope ratio. These are the reasons why monitoring these isotopes in seawater samples is of great interest for researchers and pollution control authorities.

ICP-MS proved to be a reliable, sensitive and precise instrument for the analysis of long-lived radionuclides such as uranium isotopes, providing better limits of detection than conventional radiometric detection and high sample throughput. However,

according to the above-mentioned abundances, a sample containing ~ 3 µg/L of ²³⁸U contains < 22 ng/L of ²³⁵U and < 0.2 ng/L of ²³⁴U. Seawater's high salinity precludes its direct insertion into an ICP-MS unless certain dilution is applied, leading to isotope concentrations that can fall below the limit of detection of the technique. Therefore, the analysis of uranium isotopes in seawater samples requires the application of a radiochemical method able to remove matrix elements and compounds and increase their concentration regarding the starting sample. Then, the resulting solutions can be analyzed by ICP-MS once provided the instrument offers 1) good sensitivity and low background levels, 2) good signal stability bearing in mind that isotope ratios can vary through several orders of magnitude (~ 20-20000) and 3) good wash-out performances to avoid memory effects. Achieving requirements 1-3 depends in a high proportion of the quality of the nebulizer used in the analytical running.

This note presents the analysis of uranium isotopes in seawater samples coupling an ICP-MS to the new MassNeb® nebulizer using two alternative configurations, as described below.

2. Experimental

Instrumentation

The measurements were performed with an Agilent 8800 ICP-MS/MS instrument (Servicio de Radioisótopos, CITIUS, Univ. of Seville, Spain). The general operating conditions are provided in Table 1. Nebulization was carried out using the new MassNeb® inert nebulizer (Ingeniatrics, Camas, Seville, Spain), which is specifically designed for its use in ICP-MS instruments. This nebulizer allows high TDS levels (100 g/L) and being built with a combination of inert materials (PFA/ETFE/PTFE/PEEK/LCP) it can be used with aqueous solutions, HF and organic solvents. The instrument was tested using two configurations: direct sample introduction from MassNeb® to the plasma (configuration C1) and connecting MassNeb® to a desolvating system CETAC Aridus II (C2).

The nebulizer's external diameter allows its direct and immediate connection both with conventional endcaps and the Aridus II system, as it doesn't require additional gas or liquid adaptors.

Parameter	Conditions
Carrier gas flow rate	0.71 mL/min
Make up gas	0.37 mL/min
Aridus II	
Desolvation chamber	160°C
Spray Chamber	110°C
Ar (Sweep gas)	6,2 L/min
N ₂ gas	4 mL/min
ORS	Off (no gas)
Measurement mode	SingleQuad
Detection	1 peak per mass, 4 replicates, 1000 sweeps
Counting times:	233, 234: 4.5 ms 235: 0.5 ms 238: 0.21 ms 108, 118, 195, 197, 202, 204, 208, 232: On demand, ranging 0.12-0.26 s

Table 1. Operating conditions for the Agilent 8800 ICP-MS/MS coupled to MassNeb® nebulizer. The operating conditions for the desolvating chamber CETAC Aridus II (Configuration C2) are also included.

The instrument was first tuned for the actinide mass range using a Savillex C400® nebulizer, as the default setup at this laboratory. A second tune comprising just the plasma variables (RF power, sampling depth, carrier gas flow, makeup gas, etc.) was performed using the new MassNeb® nebulizer, first using C1 configuration, then with the C2 configuration. In this way we can test that the new nebulizer performances are high enough as to perform isotopic analysis under the requested conditions.

Standards and sample preparation

Instrument was tuned with a solution containing 0.5-1.0 ng/mL of ⁷Li, ⁸⁹Y, ¹⁴⁰Ce and ²⁰⁵Tl (Spex Certiprep, NJ, USA). Uranium isotope ratios were corrected for mass bias effects by using the IRMM-056 standard solution at different uranium concentration levels ranging 0.2-1.0 ng/mL.

The element concentration was calculated by the isotope dilution technique after spiking to each sample ~ 16 pg of ^{233}U (ETH, Zurich, Switzerland) at the beginning of the sample preparation.

Four replicates of a seawater sample collected in the Irish Sea was used to test this experimental setup. The samples were prepared using a radiochemical scheme that has been summarized in Fig.1; details can be found in (López-Lora et al., 2019). In brief, actinides are preconcentrated through $\text{Fe}(\text{OH})_2$ precipitation; after adapting the sample matrix, uranium isotopes are extracted, purified and concentrated by using a tandem combination of extraction chromatography columns TEVA and UTEVA (Triskem, Bruz, France).

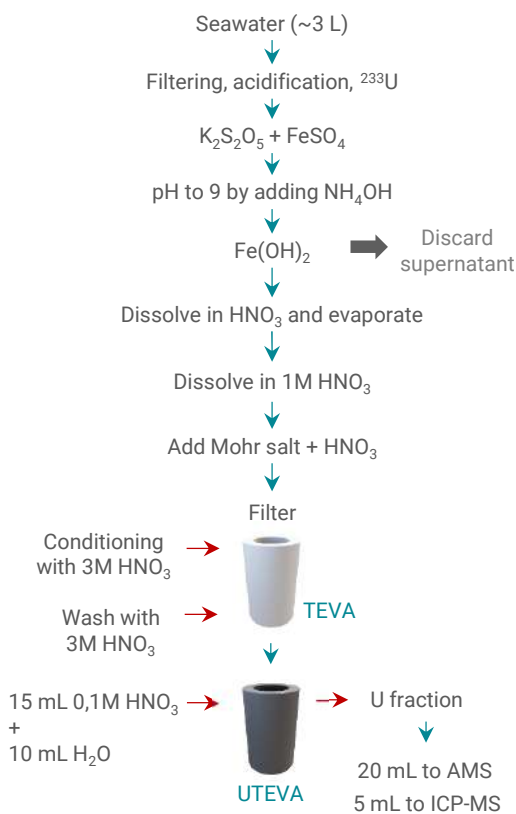


Fig. 1. Summary of radiochemical procedure applied to seawater samples

This procedure has been optimized for the separation, concentration and Accelerator Mass Spectrometry (AMS) measurement of ^{237}Np , $^{239,240}\text{Pu}$ and uranium isotopes, including sub-ppq level ^{236}U .

To this end, ~ 3 L of seawater per sample were used. The procedure allows the concentration of uranium isotopes in about 25 mL of solution and ~ 5 mL were sent for analysis by ICP-MS.

The final eluate solution can contain very high concentrations of ^{238}U and ^{235}U but very small concentrations of ^{234}U and ^{233}U . Uranium chemical yields can reach ~ 90%, leading to isotope concentrations in the uranium extract in the range of 330 ppb (^{238}U), 2.3 ppb (^{235}U), 19 ppt (^{234}U) and 0.58 ppt (^{233}U).

Under these conditions the first two isotopes could be concentrated enough as to force the detector to operate in the analog mode, which offers far less precision than pulse counting mode. To prevent this effect, a small aliquot of each sample was diluted, ~ 1:300 m/m. Therefore, ^{233}U and ^{234}U were measured in the provided solutions, and ^{234}U (again), ^{235}U and ^{238}U were analyzed in the diluted aliquots.

The potential interfering elements were monitored as shown in Table 1 in order to test that the application of the radiochemical method allowed their removal from the analyzed uranium extracts. All the potential interfering element concentrations were several orders of magnitude less than those of uranium.

3. Results and discussion

Fig. 2. summarizes the performances found with the MassNeb® nebulizer during tuning with configurations C1 and C2. For C1, sensitivity in high mass range increases by a factor > ×2 (regarding C400) reaching more than 2 Mcps/ppb while the Ce oxides level remain within the range 1-3%.

For C2 configuration, sensitivity overpassed the 3.5 Mcps/ppb level (i.e. ~ 40% higher than the C400 + Aridus II setup). Additionally, the desolvating chamber allowed reducing the level of oxides to <0.1%. Therefore, MassNeb® nebulizer offers sensitivity high enough as to obtain a large response for ^{234}U (~ 34 kcp for C1 and 66.5 kcps for C2) and even ^{233}U (1.2 kcps and 2.0 kcps for configurations C1 and C2, respectively).

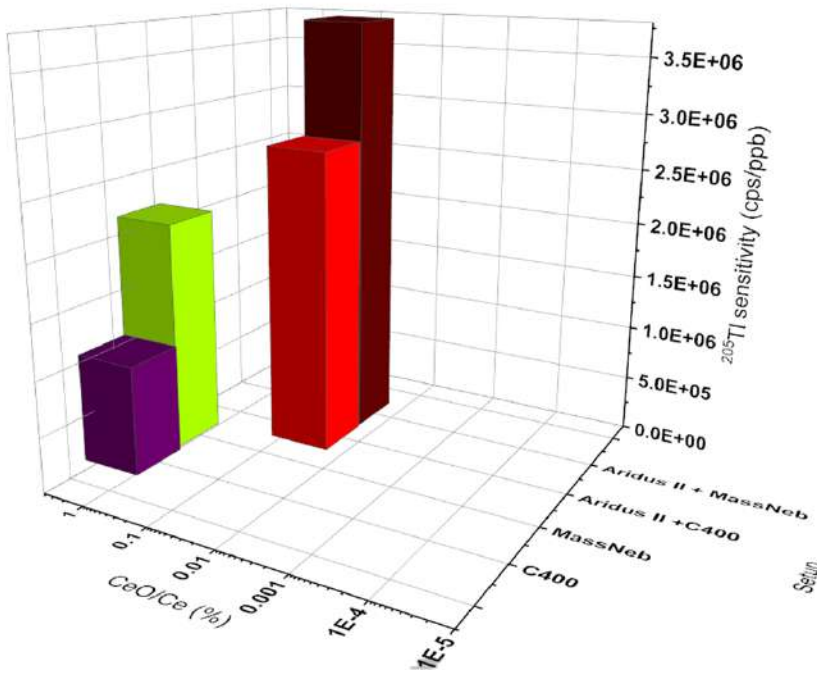


Fig. 2. Comparison of the performances of setups 1 and 2 between MassNeb® and Savillex C400®, alone and coupled to CETAC Aridus II desolvating chamber, respectively. Please note the logarithmic scale in the CeO/Ce axis.

- MassNeb + Aridus II
- C400 + Aridus II
- MassNeb
- C400

C1 configuration was tested for the analysis of uranium isotopes at 0.5 ppb-level for U concentration (²³⁵U: ~ 3.6 ppt; ²³⁴U: 0.025 ppt). The high sensitivity and the good stability of the signal can be deduced from Fig. 3a-Fig. 3b. The data are shown just after blank correction but without mass bias correction. It is easy to see that the measured isotope ratios are reproducible, stable and accurate, being RSD levels in the range of 0.5-3.5% (k = 2, 95% confidence level) for ²³⁸U/²³⁵U, without the need to use a desolvation chamber.

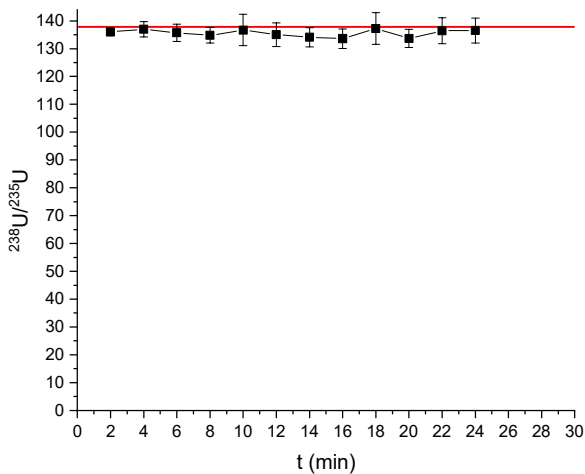


Fig. 3a. ²³⁸U/²³⁵U isotope ratios obtained in a 0.5 ppb-U level solution of the IRMM-056 standard using the C1 configuration (no desolvation chamber). Red lines show the expected values. No mass bias correction applied.

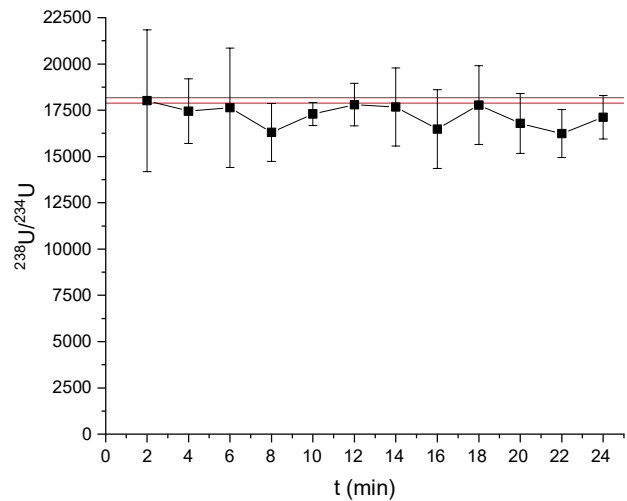


Fig. 3b. ²³⁸U/²³⁴U isotope ratios obtained in a 0.5 ppb-U level solution of the IRMM-056 standard using the C1 configuration (no desolvation chamber). Red lines show the expected values. No mass bias correction applied.

Under the same conditions, C400 offered RSD levels in the range 1.2-4.2%, showing that MassNeb® provides better sensitivity and better signal stability.

These performances, therefore, are convenient for the quantification of ultratrace-level analytes, and also for the application of the isotope dilution technique (ID-ICP-MS), which requires good signal stability in order to minimize the expanded uncertainties of the results.

Furthermore, the obtained values barely reproduce the expected values without the need to apply mass bias correction. It is worthy to note that the weighted average mass bias factor per mass unit was in the range of 0.968 ± 0.004 - 0.999 ± 0.010 . This means that sensitivity, background levels and general performance are good enough as to measure uranium isotope ratios at concentrations in the range of 0.5-1 ppb level.

Anyway, configuration C2 (desolvating) was used to improve the precision on isotope ratios involving low abundance isotopes (^{233}U , ^{234}U). The results obtained for the seawater samples are shown in Table 2. The same ^{238}U concentration was obtained for all the aliquots within the uncertainty intervals; these values are indeed in agreement to the expected values for this region. The $^{238}\text{U}/^{235}\text{U}$ isotope ratios agree, as expected, with the natural isotope ratio.

Finally, $^{238}\text{U}/^{234}\text{U}$ isotope ratios are shown in terms of the a_{234}/a_{238} activity ratios. The small relative uncertainties (1.5-4%) allows detecting a small deviation from the secular equilibrium condition (world ocean average ~ 1.16) as a consequence of the preferential leaching of the lighter isotope.

Sample	^{238}U (mg/kg)	$^{238}\text{U}/^{235}\text{U}$	a_{234}/a_{238}
1	2.90 ± 0.06	135.4 ± 1.2	1.16 ± 0.03
2	2.81 ± 0.08	136.1 ± 1.1	1.17 ± 0.04
3	2.74 ± 0.07	136.2 ± 0.9	1.18 ± 0.04
4	2.79 ± 0.07	136.5 ± 1.3	1.16 ± 0.04

Table 2. Results obtained in the four seawater samples for ^{238}U concentration, $^{238}\text{U}/^{235}\text{U}$ isotope ratios and $^{234}\text{U}/^{238}\text{U}$ activity ratios. Uncertainties are expressed as $k = 2$.

4. Conclusions

Uranium isotope ratios have been measured in seawater samples after applying a radiochemical procedure for their separation from the sample matrix and subsequent concentration.

The use of a high efficiency nebulizer specifically designed for its use in ICP-MS (MassNeb®) improves the quality of the results by providing high sensitivity and precision as required for the analysis of ultra-low concentration analytes and good signal stability and reproducibility as required for isotope analysis or, eventually, the application of the isotope dilution technique.

As expected, the performances improve after coupling this nebulizer to a membrane desolvator unit.

References

- Henderson, G. M. (2002). Seawater ($^{234}\text{U}/^{238}\text{U}$) during the last 800 thousand years. *Earth and Planetary Science Letters*, 199, 97–110.
- López-Lora, M. Levy, I., Chamizo, E. (2019). Simple and fast method for the analysis of ^{236}U , ^{237}Np , ^{239}Pu and ^{240}Pu from seawater samples by Accelerator Mass Spectrometry. *Talanta*, 200, 22-30.

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