

Determination of low level of actinium 227 in seawater and freshwater by isotope dilution and mass spectrometry

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Abstract :

By diffusing from the sediments into the ocean, ²²⁷Ac (half-life = 21.7 y) is a powerful tracer of vertical mixing in the deep ocean on decadal time scales. However, its use is limited by its very low concentration resulting in large volumes (hundreds of L) of water required for its analysis. We have developed a new method of ²²⁷Ac analysis by isotope dilution and MC-ICPMS that significantly improves the measurement accuracy and reduces the sample size (10–30L). After spiking water samples with ²²⁵Ac milked from a ²²⁹Th solution, actinium isotopes are preconcentrated by manganese co-precipitation, purified by chromatographic methods and then measured by MC-ICPMS. The performance of the analytical method (accuracy, precision) was estimated with a homemade actinium standard solution. An internal quality control was carried out to validate the method by repeated measurements of 2 L of surface seawater doped with ²²⁷Ac (1000 ag/kg) and duplicates of the Vienne river water (6.1 ± 1.7 ag/kg and 4.1 ± 1.3 ag/kg). ²³¹Pa was also co-precipitated, purified during the chromatography and analysed by MC-ICPMS. The combined measurement of ²²⁷Ac and ²³¹Pa from the same sample allows discriminating ²²⁷Ac supported by ²³¹Pa decay from the ²²⁷Ac released by remobilization from the sediments. The ²²⁷Ac concentrations measured on the first seawater samples of 29 L from the South China Sea water range from below the detection limit in surface water (~ 0.5 ag/kg for 30 L) to 3.4 ± 0.5 ag/kg at 2760 m depth (uncertainties are given in 2σ). The ²²⁷Ac measured in the deep South China Sea waters entering through the Luzon strait are consistent with previous data obtained in the same water mass in the Pacific Ocean (PDW). Seawater from the southernmost station of Bonus GoodHope, in the Weddell Gyre, were also analysed, with ²²⁷Ac concentration ranging from 4.2 ± 0.4 ag/kg to 10.9 ± 1.0 ag/kg in good agreement with previous measurement in the Weddell Gyre by Geibert et al. (2002, 2008).

Highlights

- ▶ Analytical protocol for very low concentration of ²²⁷Ac and ²³¹Pa in 10-30 L water samples. ▶
- Improvement of ²²⁷Ac measurement by mass spectrometry compared to nuclear spectrometry. ▶
- Consistent measurement of ²²⁷Ac concentration with previous studies in Weddell Sea.

Keywords : Actinium, Environmental water, Anion exchange chromatography, Multi-collection mass spectrometry

1. Introduction

Natural radioelements of the uranium decay and thorium chains are recognized chronometers of ocean processes. ^{227}Ac (half-life = 21.8 y) is produced by radioactive decay of ^{231}Pa (half-life = 32400 y), its precursor in the ^{235}U decay chain. In the ocean, highly insoluble ^{231}Pa is scavenged by marine particles and transported to the seafloor where it decays to ^{227}Ac . Then soluble ^{227}Ac is released to the bottom water where it becomes a chronometer of the vertical eddy diffusion (Nozaki, 1993, 1984). The ^{231}Pa of seawater must be determined to calculate the excess of ^{227}Ac ($^{227}\text{Ac}_{\text{ex}}$) compared to the ^{227}Ac expected at the equilibrium with ^{231}Pa (also called supported ^{227}Ac). However, ^{227}Ac measurement is rarely used in oceanographic studies due to its very low concentration in seawater: from 0.5 ag/kg to 30 ag/kg (1 ag/kg = 10^{-18} g/L; 1 dpm/m³ = 6.23 ag/kg) and the need for large seawater volumes that are needed to perform each measurement, limiting the use of this tracer. Initially, ^{227}Ac measurements were made by alpha-spectrometry after processing of several hundred litres of seawater (Geibert et al., 2002; Nozaki, 1984). Subsequent developments on alpha spectrometry allowed (1) reducing sample size below 100 litres and (2) using ^{225}Ac as yield tracer (Bojanowski et al., 1987; Geibert and Vöge, 2008). Recently, ^{227}Ac analysis by Radium Delay Coincidence Counting (RaDeCC) was introduced, with actinium being concentrated on cartridges with *in situ* pump, requiring thousands litres of seawater (Le Roy et al., 2019; Shaw and Moore, 2002, Kipp et al, 2015). Since then, RaDeCC has become the only method used to analyse ^{227}Ac in seawater within the GEOTRACES international program (Geibert, 2015). However, aside from the large volume requirements, RaDeCC brings also large analytical uncertainties due to poor counting statistics and to uncertainty of the preconcentration yield. Also, RaDeCC does not allow determination of the ^{231}Pa concentration.

Recently, the analysis of ^{227}Ac by isotope dilution (ID) and MultiCollector Induced Coupled Plasma mass spectrometry (MC-ICPMS) was developed for nuclear forensic applications (Kayzar and Williams, 2015). This method was applied to ^{227}Ac -rich samples (uranium oxide, geological samples) typically allowing the analysis of around 100000 ag of ^{227}Ac , which is a factor 200 to 5000 more than what we can expect in ~10-30 L of seawater. Recent developments made at LSCE allow us to measure quantities as low as 0.1 fg (100 ag) of ^{231}Pa by MC-ICPMS (Gdaniec et al., 2020; Roy-Barman et al., 2020), a level comparable to the ^{227}Ac content of a few tens of litres of deep seawater. In the present work, we build on Kayzar and Williams (2015) to propose a new protocol to pre-concentrate and purify ^{227}Ac from 10-30 L of seawater or continental water and analyse it by isotopic dilution and MC-ICPMS, with a precision at least equivalent to the alpha counting or RaDeCC.

2. Methods

1. Standards, spike and samples

All reagents were prepared with NormatomTM trace element analytical grade acids and 18.2 M Ω MilliQTM water.

Several uranium and thorium solutions and an uraninite powder were used as sources of actinium isotopes and references for concentration calibration during the course of this work.

^{229}Th and ^{225}Ac spikes: a ^{229}Th spike solution from Eckert and Ziegler (^{229}Th concentration ≈ 1 ng/g) was used as source of ^{225}Ac spike. At secular equilibrium, 1.0 ng of ^{229}Th (half-life = 7917 y, Varga et al., 2014) is at equilibrium with 3370 ag of ^{225}Ac (half-life = 9.92 d, Pommé et al., 2012). This ^{229}Th spike was calibrated against a ^{232}Th standard described below.

²³²Th standard: a ²³²Th (+ ²³⁰Th) in-house standard solution was used to calibrate the ²²⁹Th spike. The concentration of this ²³²Th standard is relatively well known. It is used at LSCE as reference to calibrate new ²²⁹Th spikes solutions for seawater analysis, in particular during the GEOTRACES intercalibration process (Anderson et al., 2012, Gdaniec et al., in prep.). Therefore, we consider that we know its concentration with an expanded uncertainty within 1 or 2%.

Harwell Uraninite: We used the Harwell Uraninite (HU1) that is known to be at secular equilibrium for the ²³⁵U decay chain (Komura et al., 1990) to prepare a purified ²²⁷Ac solution.

Moreover, different samples artificially enriched in ²²⁷Ac were prepared to test the method:

- *Artificial seawaters enriched in ²²⁷Ac* (hereafter referred to as “Artificial seawaters”) were prepared by dissolving 8.75 g of NaCl in 250 mL of water, and adding 200 ng of Re (equivalent Re in 10~30 L of seawater). These artificial seawaters were then enriched by adding 2000 ag of ²²⁷Ac (grossly the ²²⁷Ac amount expected in 30 L of deep water) from our stock solution.

- *surface Mediterranean water enriched in ²²⁷Ac* (hereafter referred to as “enriched Mediterranean seawater”) were also prepared by adding 2000 ag of ²²⁷Ac to 2 L of surface seawater (depth = 60 m) collected in the Sicily Strait. Due to very low ²³¹Pa content of this water (Gdaniec et al., 2018), the contribution of ²²⁷Ac initially present in the sample was less than 0.2% of the added ²²⁷Ac (²²⁷Ac in this surface water = 2 ag/kg).

Different water samples were collected to test the analytical procedure:

- freshwater from the Vienne river (46°24.25'N, 0°42.12'E), a river draining a strongly granitic watershed;
- freshwater from the “mare du Rusquec”, a small pond in Brittany (France, 48°19.68'N, 3°48.63'W), where very high ^{227}Ac concentrations in the pond sediments have been observed previously;
- seawater from a vertical profile in the South China Sea (21°26.49'N, 120°12.57'E) collected during the HYDROSED cruise in June 2018. All the samples were filtered on board using AcroPak 500 capsule filter (porosity: 0.8-0.45 μm) before being acidified to $\text{pH} < 2$ with ultra-pure 6M hydrochloric acid. HYDROSED seawater samples were sub-sampled to measure Pa and Th independently with 4 L.
- Seawater samples from the Atlantic sector of the southern Ocean (57°55'S, 00°03'W) were collected during the Bonus GoodHope cruise in 2008 (Roy-Barman et al., 2019). They were filtered (Nuclepore, 90mm diameter, 0.4 μm pore size) and acidified on board ($\text{pH} = 2$).

2. Chemical protocols

We developed several protocols:

- (1) to prepare a ^{227}Ac standard from an uraninite powder,
- (2) to calibrate the ^{227}Ac with a ^{229}Th spike at secular equilibrium with ^{225}Ac ,
- (3) to extract ^{225}Ac by “milking” of a ^{229}Th source to avoid using large quantities of ^{229}Th for sample analysis (both for saving spike and for safety purpose),
- (4) finally, to preconcentrate and purify Ac from natural water samples.

a. ^{227}Ac standard preparation

We prepared a ^{227}Ac stock solution by extracting and purifying ^{227}Ac from the HU1 uraninite. 200 mg of HU1 powder were dissolved in 8M HNO_3 . ^{227}Ac was then separated by chromatographic methods. The first column (Triskem, 0.67 cm, h = 6 cm) was filled with 2 mL of anion exchange resin Dowex AG1x8 200-400 mesh (Gdaniec et al., 2020, 2018). To prevent the resin saturation by U, we split the dissolved uraninite into four columns eluted simultaneously in parallel. We extracted three fractions: first, thorium (Th), radium (Ra) and actinium (Ac) were eluted with 10 mL 9M HCl, then protactinium (Pa) was eluted with 10mL 9M HCl + 0.1M HF and finally, uranium (U) was recovered eluted with 6 mL of MilliQ water. The Ac-Th-Ra fraction was evaporated on a hotplate and then dissolved in 4M HNO_3 . A second column was used to separate Ac from Ra and Rare Earth Elements (REE) which could produce isobaric interferences during the measurement by MC-ICPMS (see measurement section). This second column was filled with 1 mL ($\varnothing = 0.67$ cm, h=3cm) of an extraction resin: the Triskem TODGA 200-400 mesh resin (Kayzar and Williams, 2015; Marinov et al., 2016; Radchenko et al., 2015). First, Ra was eluted with 15 mL 4M HNO_3 . Then, purified Ac was recovered with 30mL of 10M HNO_3 . The ^{227}Ac stock was diluted to a concentration close to 10 fg/g.

b. Calibration of the ^{227}Ac standard

The ^{227}Ac stock solution concentration needed to be calibrated because the yield of the procedure described in the previous section may not be 100%. Around 2000 ag of ^{227}Ac were used to calibrate the concentration of the stock solution. The calibration was made by isotopic dilution by adding 1 ng of ^{229}Th at equilibrium with ^{225}Ac . We separated actinium from the thorium with a 1 mL TODGA column. The ^{225}Ra was eluted with 15 mL of 4M HNO_3 and then actinium isotopes were eluted with 30 mL 10M HNO_3 . The actinium fraction was

evaporated and dissolved in 1M HNO₃ + 0.013M HF. The solution was filtered at 0.4 μm to remove any resin grain before analysis by MC-ICPMS.

c. Milking ²²⁵Ac

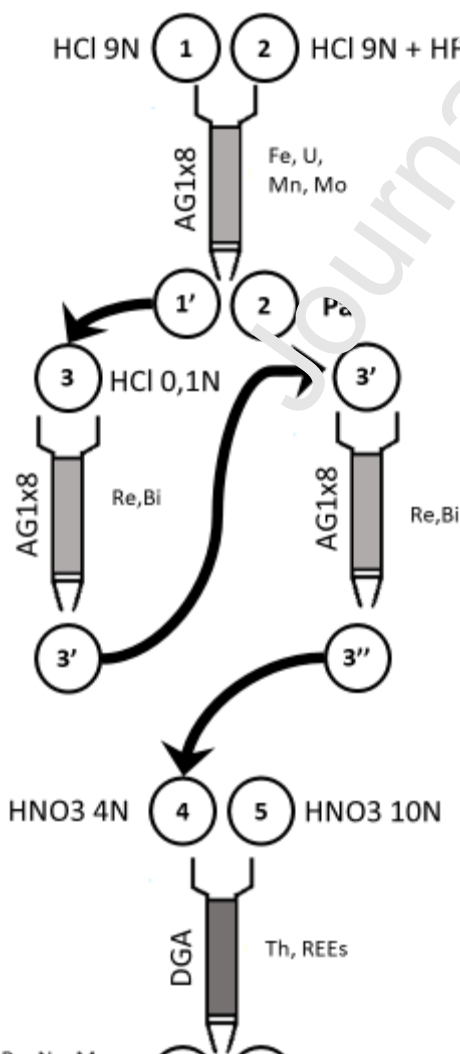
A purified ²²⁵Ac spike was used for the actinium analysis in seawater samples by isotopic dilution. The spike was produced by milking ²²⁵Ac from 8 ng of a ²²⁹Th solution. The separation of ²²⁵Ac from ²²⁹Th and ²²⁵Ra was done through a chromatographic column (Triskem TODGA 1 mL). Radium was eluted with 15 mL of 4M HNO₃ (no Ra sorption in nitric acid on TODGA, while Ac K_d is 1000), the actinium was eluted with 30 mL of 10M HNO₃ (Radchenko et al., 2015). Thorium has a very strong affinity for the TODGA resin (K_d > 10⁴, Pourmand and Dauphas, 2010), so the ²²⁹Th was stored directly on the column until the next milking. For this purpose, the column was filled with 4M HNO₃ and tightly closed to avoid the drying of the resin.

d. Artificial and natural water processing

Analysing 10-30L seawater samples required to pre-concentrate ²²⁷Ac through an iron or manganese coprecipitation step. The different iron solutions used for our initial tests of coprecipitation brought around 250 cps of isobaric interferences on the masses 225 and 227. Coprecipitation tests made with manganese revealed no obvious interferences. Therefore, manganese was selected. We tested every other reagent of the chemistry to estimate their contribution to interferences.

To process samples, we added around 1000 ag of milked ²²⁵Ac and around 3 fg of ²³³Pa to each sample. The relatively large amount of ²²⁵Ac used here took into account its decay during the 2-3 week's duration of the protocol. We carried out a manganese oxide

coprecipitation by adjusting the pH to 8-9 and adding 9 mg of KMnO_4 (300 μL of 30 g/L KMnO_4 solution) and 24 mg of MnCl_2 (240 μL of 100 g/L MnCl_2 solution). We let the reaction occur for at least 8 hours (Ghaleb et al., 2004; Rutgers van der Loeff and Moore, 1999). When the water processed had a high dissolved silica content (eg; deep Pacific waters), MnO_2 precipitation also produced silica gel formation (Gdaniec et al., 2017). The Mn oxides (and silica gel) were recovered by filtration on a NucleporeTM filter (diameter: 142 mm, pore size: 0.45 μm , nitrocellulose). The precipitate was rinsed on the filter with at least 2L of MQ to leach out major elements as Na and Ca from the precipitate. We dissolved the Mn oxide from the filter in a bath of 75mL of 6 M HCl with 100 μL of H_2O_2 and 100 μL of 27M HF during 30 min. After manganese oxides dissolution, the filter was rinsed with 6M HCl. The dissolution bath was evaporated to dryness and the residue dissolved in 10 mL of HCl, 6M. This silica gel was separated from the solution by centrifugation (5 min at 4000 rpm). After



removal of the supernatant, the silica gel “sink” was washed with 6M HCl and separated again by centrifugation before dissolution with 100 μL of 27M HF. The solution was dried and dissolved with 80 μL of 12M HCl saturated with boric acid. The resulting solution was added to the supernatants to be dried and dissolved in 9M HCl.

Figure 1 : column sequence of actinium purification with element separation during the protocol. The column 2 is repeated to improve the rhenium removal

To purify actinium from the Mn precipitate and potential interfering element, we used several chromatographic columns, summed up in figure 1 and Tab. ES1. The first column was filled with 2 mL of AG1x8 200-400 mesh and preconditioned with 9M HCl. After sample loading, Th, Ra and Ac were eluted with 10mL HCl 9M, then Pa was eluted with 10 mL 9M HCl + 0.1M HF, while most Mn stayed adsorbed on the resin. The Th-Ra-Ac fraction was dried and dissolved in 0.1M HCl. The second column was added to remove Re, Bi, Pb, Mo ..., some of the most troublesome element that could interfere during mass spectrometry analysis. It was filled with 2 mL of AG1X8, but preconditioned with 0.1M HCl. Th, Ac and Ra were eluted directly in 0.1 M HCl while Re and Bi were kept on the resin. This step was performed twice as preliminary tests had shown that a single column was not sufficient to remove all the seawater Re. The resulting Ac-Th-Ra fraction was dried and dissolved in 4M HNO₃. The last column was filled with 1 mL of TODGA resin 200-400 mesh, preconditioned with 30 mL of 0.1M HCl and 20 mL of 4M HNO₃. After loading the sample, the radium fraction was eluted with 15 mL of 4M HNO₃, together with Ba, Ca and Sr and the leftover of Mn. Ac was eluted with 30 mL of 10M HNO₃. The last fraction, containing Th and REEs, was eluted with 15 mL of 0.1M HCl. The Ac fraction was converted in 1mL of 1M HNO₃ + 0.013M HF and filtered at 0.4 µm to remove any resin grain before analysis by MC-ICPMS.

For seawater samples from the South China Sea (HYDROSED) samples, 4L of seawater were subsampled to analyse ²³¹Pa and Th isotopes independently. The preparation protocol used was the same as Gdaniec and al. (2018), except that co-precipitation was carried out with Mn oxides like the Ac preparation protocol presented above. For the Southern Ocean seawater samples (Bonus GoodHope), ²³¹Pa was extracted directly from the 9 L samples using the full protocol (Fig. 1).

3. Mass spectrometry

The analyses were done on a ThermoScientific Neptune^{plus} Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) equipped with a Jet interface, hosted at LSCE. An Aridus II and an Apex Omega HF were used as desolvating systems for Pa analysis (Gdaniec et al., 2018) and for Ac, respectively. Comparison of these two desolvating systems showed that they lead to the same sensitivity improvement (around 10^8 cps/ppb, corresponding to an ion yield of 2%), but the signal was more stable with the Apex Ω HF system due to a better gas flow control which allows reducing uncertainties for samples analysis and the instrumental blank. The nebulizer had an uptake flow of 100 μ L/min. To improve the stability of low level signals, we used the ion counters with the lowest dark noises. To reduce potential interferences and keep the background as low as possible, we used a sample introduction system (cones, probe, nebulizer, Apex Omega HF) specifically dedicated to Ac analyses. This introduction system was rinsed for at least 12h with 1M HNO₃ + 0.01 M HF before the first analysis. The measurements were made in static mode, one ion counter by isotope, by counting 30 runs of 8.4s integration time. The mass calibration of the instrument and peak positioning were made with a solution prepared by diluting some ²²⁷Ac stock solution and adding ²²⁵Ra recovered from the milking (mass deviation between ²²⁵Ra and ²²⁵Ac = 0.0004 amu).

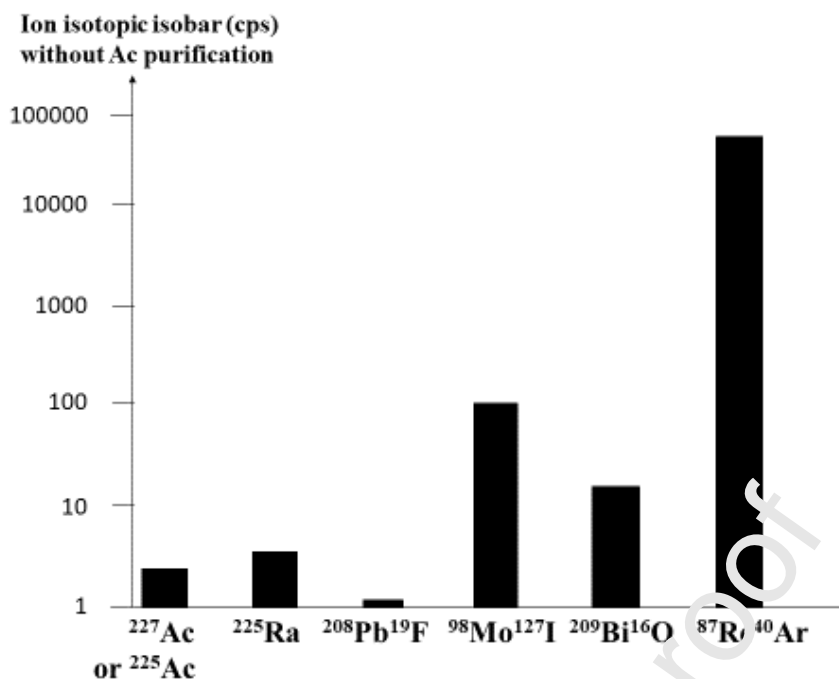


Figure 2 : Expected signal on MC-ICPMS at mass 227 or mass 225 asuming a ratio 1:1 from actinium isotopes and the different interfering recombination from main elements brought by seawater matrix and by the reagents

When measuring very low ion signals, it is necessary to consider possible interferences with polyatomic ions (Foster et al., 2004). Mass to charge ratios of ^{225}Ac and ^{227}Ac might potentially be interfered by isobaric interference made of mono or polyatomic ions (Fig. 2). The most obvious one was ^{225}Ra from the spike. Several elements producing significant isobaric interferences if they are concentrated from the seawater samples were specifically removed during the chemical purification (Fig. 2): Bi ($^{209}\text{Bi}^{16}\text{O}$), Re ($^{185}\text{Re}^{40}\text{Ar}$ and $^{187}\text{Re}^{40}\text{Ar}$), Pb ($^{208}\text{Pb}^{19}\text{F}$), Mo ($^{98}\text{Mo}^{127}\text{I}$), REE (although the precise nature of the ions was not determined, REE standard solution analysed at ppb level yielded peaks at mass 225 and 227). In spite of the cautions taken (use of a desolvator system, a nebulizer, tubing and cones dedicated to Ac isotopes only), some parasitic peaks were still observed close to mass 225 and 227 with count rates of 2 to 10 cps. These interferences were often observed even while the introduction system was rinsed with 1M HNO_3 + 0.01M HF. These peaks were lighter by ~ 0.17 amu compared to the actinium isotope

masses (Fig. 3). This is why, during Ac analysis, we did not carry out the measurement on the true ^{225}Ac and ^{227}Ac masses (225.0232 and 227.0278 amu), but we shifted to higher masses (around 225.12 and 227.12) to collect ions over the non-interfered part of the Ac peaks. It reduced the background level to ~ 0.2 counts per second, without Ac signal loss compared to the analysis at the peak centre.

The analysis was done in the low resolution of the Neptune (the mass resolution was $m/\Delta m \approx 500$ where Δm is the peak width and the resolving power was $m/\Delta m \approx 1800$ where Δm is the width of the peak side; Ireland, 2013), because at medium or high resolution, due to the ion transmission reduction, the sensitivity was too low to obtain sufficient counting statistics.

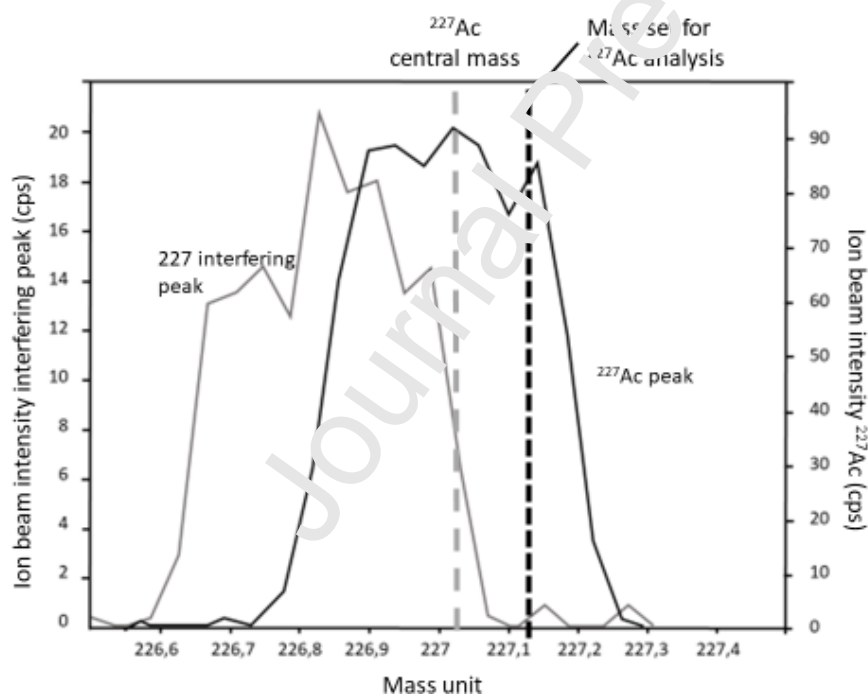


Figure 3: ^{227}Ac peak and its interfering peak close to $m/z = 227$. Composite figure showing the partial overlap between ^{227}Ac (black) and the isobaric interfering peak (grey). The black dotted line at $m/z = 227.12$ is located where the ^{227}Ac peak was measured while the grey dotted line is at $m/z = 227.02$, where is the ^{227}Ac centre peak.

3. Results

3.1. Standard analyses and calibration

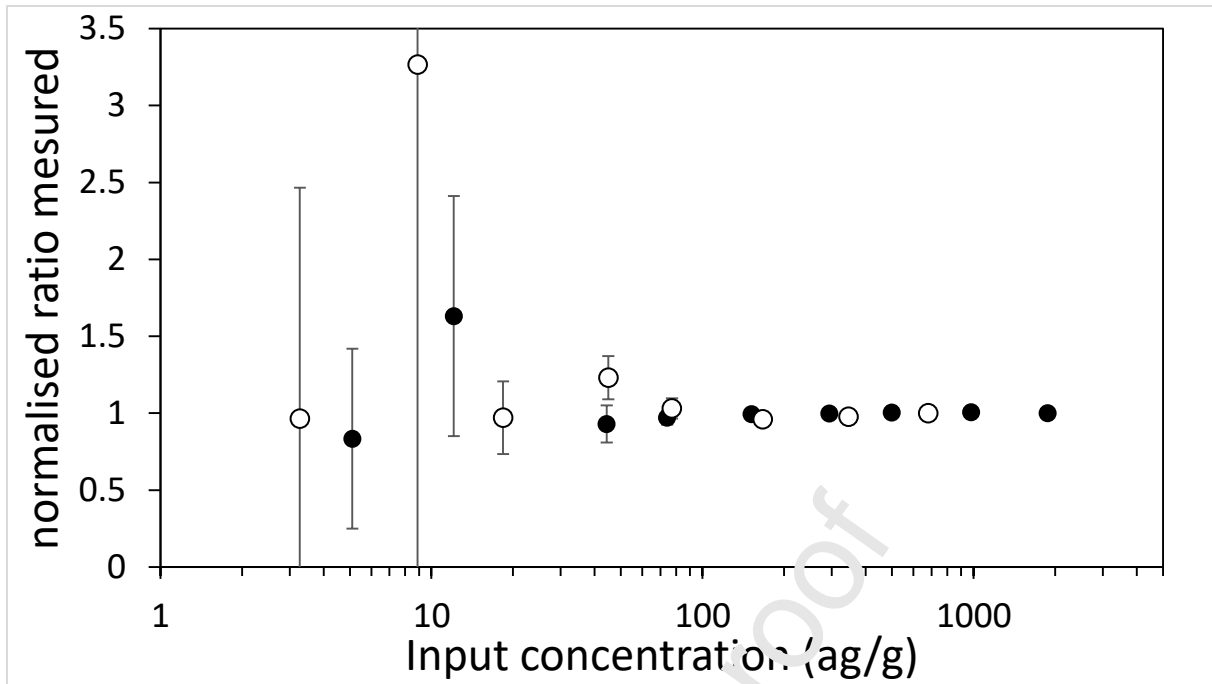


Figure 4: Normalised ($^{225}\text{Ac}/^{227}\text{Ac}$) ratio measured by MC-ICPMS versus the Ac content for two series of successive dilutions of a spiked actinium solution (uncertainties $2\sigma_n$)

A sensitivity test was made with successive dilutions of an Ac solution, with ^{225}Ac and ^{227}Ac at a ratio 1:1, from 2000 ag/g to 5 ag/g (Fig. 4). We used the ratio measured with the highest concentration input as a reference to normalisation of the measured ratios. When the concentration introduced in the instrument decreased, the measured ratio remained constant while the uncertainties grew significantly. For instance, the relative expanded uncertainty (confidence interval = 95%) is 30% with a concentration of 20 ag/g introduced into the instrument. These lowest concentrations correspond to a signal of ~ 1 cps for each Ac isotopes, whereas a noise of 0.2 cps is typically measured for the acid blanks. The uncertainties of the most diluted solutions were dominated by the noise from the very low signal acquired by MC-ICPMS, while the uncertainties for the least diluted solution were dominated by the uncertainties on the ^{225}Ac spike concentration. The uncertainties were estimated through 20 runs of measurement and propagated by Monte Carlo through all the signal treatment and isotopic dilution calculation.

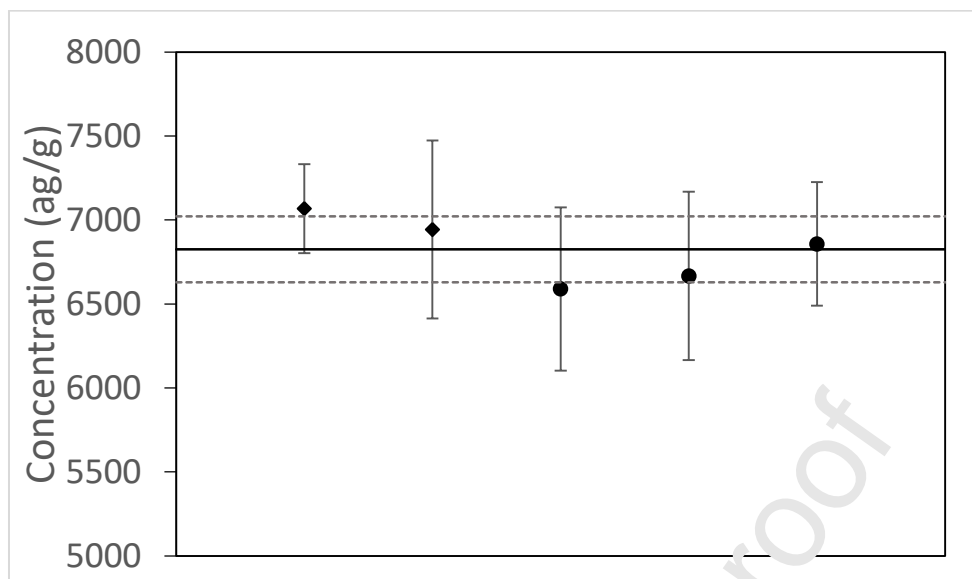


Figure 5: Repeated measurements of the standard calibration solution carried out in February 2019 (diamonds) and in October 2019 (circles). The concentration measured in February 2019 were corrected from the ^{227}Ac decay to be compared with the October data. The solid line represents the average value of all the measurements and the dotted lines the 95% confidence interval.

The standard calibration was done twice in February 2019 and three times in October 2019.

The concentrations measured in October 2019 were corrected from the ^{227}Ac decay to be compared with the February data. The average concentration was at 6800 ± 200 ag/g ($2\sigma_n$) (Fig. 5).

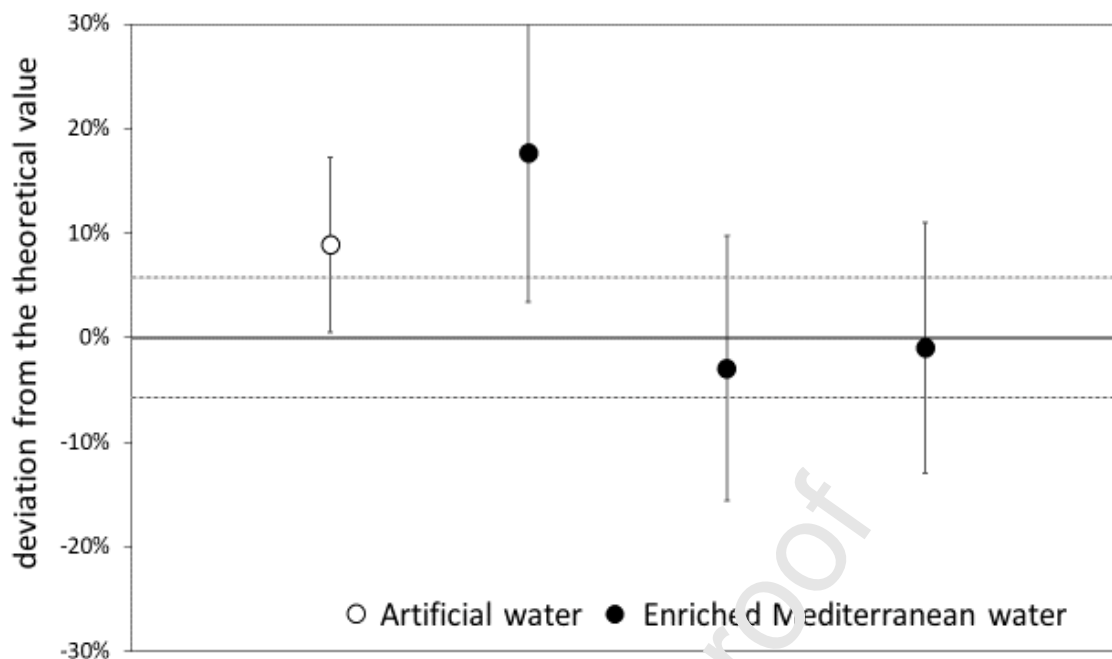


Figure 6 : Deviation of the concentration measured against the concentration calculated from the dilution of our standard in artificial water (blank) and in Mediterranean seawater (black). The solid line represents the concentration of the home standard and the dotted lines the 95% confidence interval over the concentration of the home standard.

The ^{227}Ac concentrations in artificial seawaters and Mediterranean seawaters enriched in ^{227}Ac from the stock solution were measured and compared to the calculated concentration. There is a good agreement between the theoretical concentration and the concentrations measured directly by MC-ICPMS (Fig. 6).

Table 1: Actinium recovery yield for column chemistry and total protocol estimated from the signal intensity acquired on MC-ICPMS for different preparations

	Standard solution without	Column chemistry	Mn precipitation + Column	Mn precipitation

	chemistry	only	chemistry	
Signal intensity 29 L (cps)	5.80	5.11	2.8	
Yield 29 L		88%	48 %	55 %
Signal intensity 10 L (cps)	16.2	14.7	12.86	
Yield 10L		91%	79 %	87%

The chemical yield was estimated for the different steps of the purification process based on the intensity of the ^{225}Ac signal measured by MC-ICPMS after different processing (Table 1) during the seawater sample HS6 analyse batch (20 kg of seawater). The yield of the ion exchange protocol was 88%. The full procedure yield was estimated to be ~ 48%. Comparing the yield of the column chemistry (88%) and the full protocol suggests that the precipitation yield on 30 L was $\sim 0.48/0.88 = 55\%$. We also determined the Mn preconcentration yield from 10 L of seawater sample and using the same amount of Mn as for 29 L of seawater. This yield was estimated to 87% by the ion counting comparison. The improvement compared to the precipitation with 29 L is certainly due to the threefold increase of the Mn/sample ratio. The Mn preconcentration yield was also performed by isotope dilution on 10 L of artificial water and the same amount of Mn, the yield measured were 92% and 98% that is in good agreement with the ion counting estimation.

Chemical blanks were triplicated for each analysis batch and the detection limit was defined from these measurements. The blanks ranged from 4.8 ag to 8.5 ag with a standard deviation of 2.5 ag. The detection limit of ^{227}Ac was estimated at 7.5 ag of ^{227}Ac (3 times the blank standard deviation) introduced in the MC-ICPMS. For the HS6 samples, the detection limit (LD) was 0.3 ag/kg for 30 L of seawater. For the “Bonus GoodHope” sample, the LD was 0.8 ag/kg for 10L of seawater.

3.2. Water samples

Pa data are corrected from the ingrowth of ^{231}Pa from the ^{235}U decay and from the ^{231}Pa decay as follows:

$$N_{Pa}^0 = e^{t\lambda_{Pa}} \times \left(N_{Pa}^t + \frac{\lambda_U}{\lambda_{Pa} - \lambda_U} \times N_U^0 \times (e^{-t\lambda_{Pa}} - e^{-t\lambda_U}) \right)$$

With N_{Pa} the atom concentration of ^{231}Pa , at the sampling time ($t = 0$) and analysis time (t), N_U the atom concentration of ^{235}U , estimated from the salinity of seawater (Owens et al., 2011). λ_{Pa} and λ_U are the decay constant respectively for ^{231}Pa and ^{235}U , respectively.

The ^{227}Ac concentration is corrected by considering the decay of ^{227}Ac and its ingrowth from ^{231}Pa decay and the radioactive decay of ^{231}Pa and its ingrowth from ^{235}U decay (that can be significant, especially in surface water) between the sampling time and the analysis time (Bateman, 1910):

$$N_{Ac}^0 = e^{t\lambda_{Ac}} \times \left(N_{Ac}^t - N_U^0 \times \lambda_{Pa} \lambda_U \times \left(\frac{e^{-t\lambda_U}}{(\lambda_{Ac} - \lambda_U)(\lambda_{Pa} - \lambda_U)} + \frac{e^{-t\lambda_{Pa}}}{(\lambda_{Ac} - \lambda_{Pa})(\lambda_U - \lambda_{Pa})} + \frac{e^{-t\lambda_{Ac}}}{(\lambda_{Pa} - \lambda_{Ac})(\lambda_U - \lambda_{Ac})} \right) - \frac{\lambda_{Pa}}{\lambda_{Ac} - \lambda_{Pa}} \times N_{Pa}^0 \times (e^{-t\lambda_{Pa}} - e^{-t\lambda_{Ac}}) \right)$$

With N_{Ac} the atom concentration of ^{227}Ac , at the sampling time ($t = 0$) and analysing time (t), and λ_{Ac} the constant decay of ^{227}Ac .

The Ac concentration supported by the Pa decay in ag/kg (Fig. 7.a) is calculated from Pa (conversion factor around 0.66), with M_{Ac} the molar mass of ^{227}Ac and M_{Pa} the molar mass of ^{231}Pa :

$$Ac_{supported} (ag/kg) = Pa (fg/kg) \times \frac{M_{Ac}}{M_{Pa}} \times \frac{\lambda_{Pa}}{\lambda_{Ac}} \times 10^3$$

For continental waters, ^{227}Ac concentrations of 4.1 ± 1.3 ag/kg and 6.1 ± 1.7 ag/kg were measured in 20 L and 35 L water samples from Vienne River, respectively (Table 2). By contrast, a ^{227}Ac concentration as high as 2640 ± 260 ag/kg was measured in a water sample from the Rusquec pond, in Britany (France), characterized by a high environmental Ac background level.

^{227}Ac concentrations measured for seawater samples from IS6 station ranged from below the detection limit (0.5 ag/kg) to 3.9 ± 1.0 ag/kg at 1200 m (Fig. 7.a), followed by a sharp decrease at 2400 m (2.0 ± 0.5 ag/kg) and then an increase at the seafloor (3.3 ± 0.7 ag/kg). The concentration of ^{231}Pa was also measured at this station, allowing to calculate the concentration of $^{227}\text{Ac}_{supported}$. The $^{227}\text{Ac}_{supported}$ was 0.23 ag/kg in surface waters, increased to 1.5 ag/kg at a depth of 2000 m and then decreased in deeper waters. This profile is similar to the ^{230}Th profile (Fig. 7.b), with an increase from 1 fg/kg in surface waters to 13 fg/kg at 1800 m and a lower and roughly constant concentration of 7 fg/kg in deeper water.

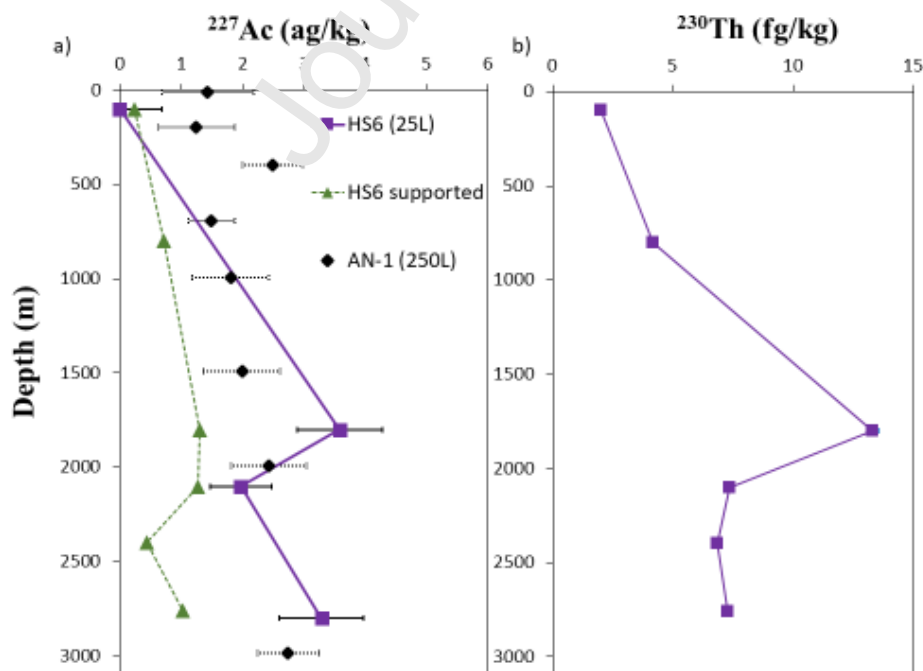


Figure 7 : (a) ^{227}Ac concentration profile in China Sea (purple square), with the actinium concentration supported by the Pa decay (green triangle), and the concentration measured in west Pacific (black diamond) by Nozaki (1990), (b) ^{230}Th profile at the station HS6 in the China Sea. All the uncertainties are expressed at $2\sigma_n$

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Table 2 : ^{227}Ac concentrations measured in environmental water. All the concentrations are corrected from the decay between sampling time and analysis time.

Sample	sample mass (kg)	^{227}Ac (ag/kg) ($2\sigma_n$ uncertainties)	^{231}Pa (fg/kg) ($2\sigma_n$ uncertainties)
<i>Seawater</i>			
Hydrosed			
HS6 100 m	29	0.1 ± 0.7 (<LD)	0.36 ± 0.03
HS6 800 m	4		1.08 ± 0.06
HS6 1800 m	29	3.9 ± 1.0	1.99 ± 0.09
HS6 2100 m	29	2.0 ± 0.5	1.93 ± 0.07
HS6 2400 m	4		0.67 ± 0.04
HS6 2760 m	29	3.3 ± 0.7	1.56 ± 0.05
Bonus GoodHope			
Super V 134 m	9.4	4.1 ± 1.1	0.42 ± 0.04
Super V 247 m	10.2	3.9 ± 1.8	0.98 ± 0.05
Super V 396 m	9.4	6.7 ± 1.1	1.84 ± 0.03
Super V 692 m	10.6	5.1 ± 1.6	1.90 ± 0.09
Super V 1185 m	8.8	5.2 ± 2.0	2.29 ± 0.11
Super V 1776 m	9.1	6.3 ± 1.2	2.39 ± 0.06
Super V 2462 m	9.0	7.3 ± 1.3	2.12 ± 0.08
Super V 3848 m	9.5	9.9 ± 1.6	3.45 ± 0.06
<i>Continental water</i>			
Vienne river	20	6.1 ± 1.7	
Vienne river	35	4.1 ± 1.3	
Rusquec pond	1	2640 ± 261	

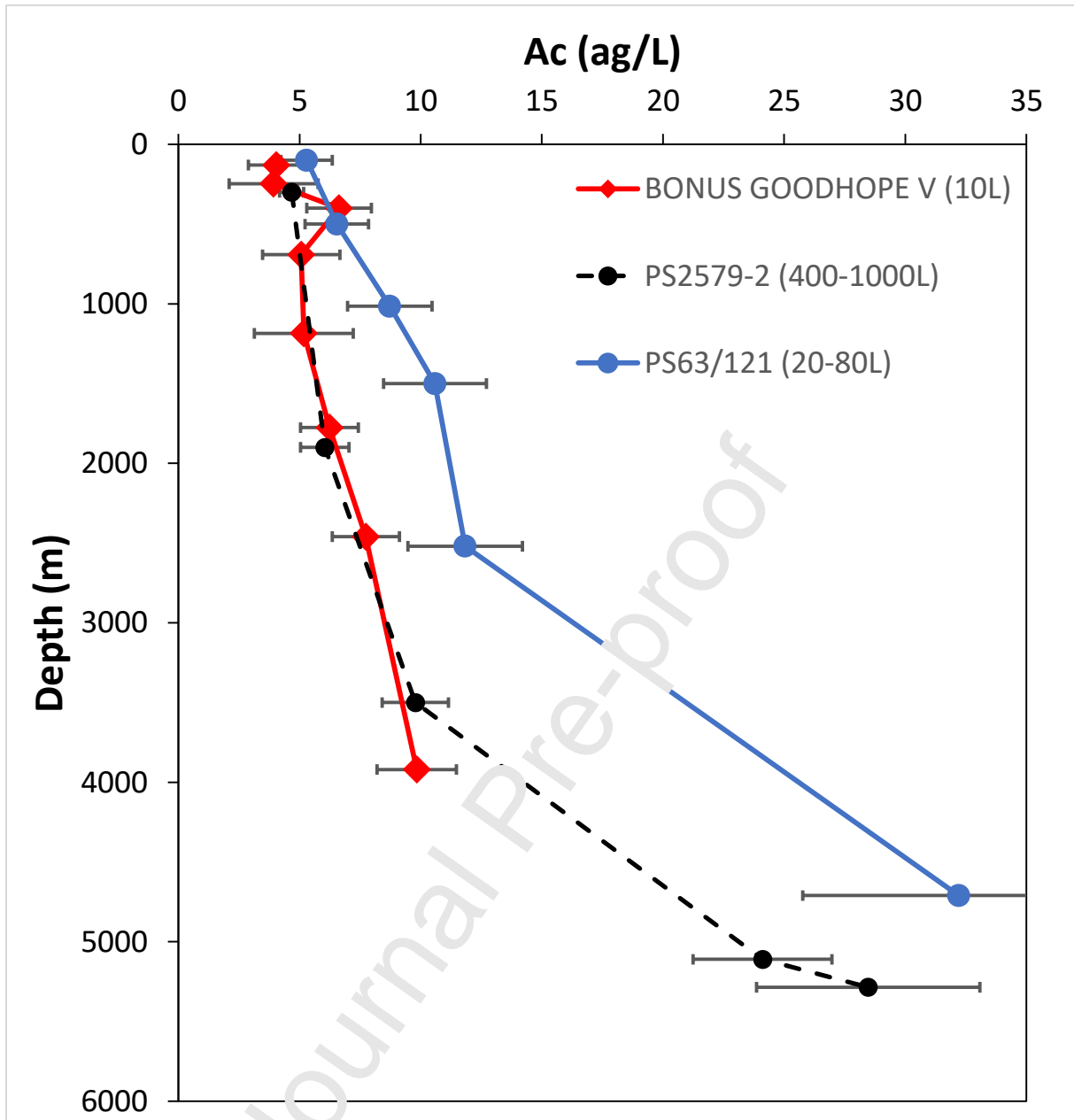


Figure 8 : Seawater ^{227}Ac profiles in Weddell Gyre, at station Super V from Bonus GoodHope cruise, measured by mass spectrometry (red diamonds) and at station PS2579-2 (Geibert, 2002) (black dot) and PS63-121 measured by alpha-spectrometry (Geibert and Vöge, 2008) (blue dots). All uncertainties are expressed at $2\sigma_n$

The ^{227}Ac concentrations measured in Bonus GoodHope samples from the Weddell gyre increase steadily with depth, from 4.1 ± 1.1 ag/kg at 136 m, to 9.9 ± 1.6 ag/kg at 3848 m (Fig. 8). The average uncertainty is around 20% (expressed as $2\sigma_n$). Samples at 247 m, 692 m and 1185 m have larger uncertainties because their analysis had to be delayed by more than 2

weeks due to a breakdown of the MC-ICPMS, leading to a loss of more 50% of the ^{225}Ac spike during this period. The ^{227}Ac profile is in good agreement with the data from the Weddell Gyre (Geibert et al., 2002; Geibert and Vöge, 2008). We did not have a sample from just above the seafloor at 3932 m to observe the expected large increase in ^{227}Ac concentration due to diffusion from the sediment.

4. Discussion

4.1. ID-MC-ICPMS method assessment

The main challenge of this protocol for ^{227}Ac analysis in natural waters is to remove every element which could produce isobaric interferences with ^{227}Ac or ^{225}Ac (Fig. 2). First, we identified likely interferences which consist of isobaric recombination between elements from the sample and from the matrix (^{40}Ar , ^{16}O , ^{14}N , ^{19}F , ^1H) in the plasma, in order to remove problematic elements during the chromatographic purification. Most of the interfering peaks were removed, but some remained. Then, we tried to identify the remaining interferences with two different methods. First, we compared mass scans from mass 215 to mass 231 with the isotopic abundance patterns of elements which may constitute the poly-atomic ions. This allowed us to identify, during a particular run, the MoI recombination that had not been considered before. The second method consisted in the precise determination of the masses of the interfering peaks. This was done by averaging the masses at half-maximum peak height of the interfering peaks. For mass 227, the ^{227}Ac atomic mass is 227.028, while the atomic mass of the interfering peak was around 226.83. Interestingly, the atomic mass of $^{187}\text{Re}^{40}\text{Ar}$ is 226.92 amu, which is significantly higher than the measured mass of the interference, discarding Re as the cause of the interference. Some atomic combination could have similar masses like $^{147}\text{Sm}^{40}\text{Ar}_2$ (226.840) but the mass scan around the 227 mass did not show the

pattern that would be expected with this element. Moreover, there was no signal at the masses around the 225 and 227 and only 200 cps were recorded at m/z of ^{187}Re , which is too low to expect a significant interference from ReAr . Therefore, as of now the nature of these interferences at masses 225 and 227 remains undetermined. Nevertheless, we took advantage of this mass offset to analyse ^{225}Ac and ^{227}Ac peaks on the high side of these peaks at masses where the interfering ions can be neglected (Fig. 3).

In addition, we performed different tests to assess the robustness of our new ^{227}Ac analysis method. First, we tested the reproducibility of the measurement by MC-ICPMS by the analyses of successive dilutions of a single solution (Fig. 2), carried out several times with a consistent result whatever the dilution and the dates of these experiments. This demonstrates that our settings for the MC-ICPMS is suitable to analyse low level signals of Ac isotopes and the statistical uncertainty estimated allow us to expect good reliability for the seawater concentrations. Most published ^{227}Ac measurements (RaDeCC and alpha spectrometry) in seawater are given with a $1\sigma_n$ relative standard uncertainties around 10-20%, so we choose a $2\sigma_n$ relative expanded uncertainty of 20% as suitable uncertainty for our measurements by MC-ICPMS. For smaller signals, uncertainties of the MC-ICPMS measurements increase significantly (Fig. 4). The required concentration of the solution injected into the plasma to have a measurement with a statistical relative expanded uncertainty of 20% was around 20 $\mu\text{g/g}$, corresponding to a count rate of around 1 cps for ^{225}Ac and ^{227}Ac (Fig. 4). These limits allow us to make reliable measurements with 10 L samples with ^{227}Ac concentrations of ~ 2 $\mu\text{g/kg}$ with a detection limit around 0.7 $\mu\text{g/kg}$ estimated from our chemical blank.

Then, we tested the robustness of the chemical process by duplicating some experiments. The calibration of our ^{227}Ac standard against a ^{229}Th spike at secular equilibrium with ^{225}Ac was repeated for different periods, in different batches of samples giving consistent

results (Fig. 4). Similarly, the replication of the measurements of artificial and doped seawaters processed through the whole chemistry gave consistent results in good agreement with concentrations prepared by dilution of the ^{227}Ac stock solution (Fig. 6). The reproducibility of the results from the above experiments make us very confident in the successful application of our protocol for analysis of natural waters. This relies on the use of isotope dilution that removes uncertainties on the Mn coprecipitation and purification yields.

The first samples analysed were from South China Sea, near the Luzon strait. The surface concentration of ^{227}Ac was below our detection limit (10 ag from 30L of sample) for ^{227}Ac . Within analytical uncertainties, this result is not significantly different from the concentration of ^{227}Ac supported by the ^{231}Pa decay (IS6 100 m : $^{227}\text{Ac}_{\text{supported}} = 0.24 \text{ ag/kg}$) as expected for surface water. For the deep samples, ^{227}Ac concentrations are generally consistent with the signature of Pacific Deep Water (PDW) (Nozaki et al., 1990). However, the ^{227}Ac profile seems affected by scavenging below the Luzon strait (highlighted by the sharp decrease of the ^{230}Th concentrations below 1800 m) and diffusion from the seafloor (suggested by the increase between the concentration at 2400 m and 2700 m) (Fig. 7.b). We also analysed waters from the Weddell Gyre (Fig. 8). Our measurements are in good agreement with previously published data (Geibert et al., 2002, 2008), despite the use of only 10 L of seawater, collected 12 years before analysis. One of the unexpected results obtained by Geibert was the relatively high concentration ^{227}Ac in surface water in the Weddell Gyre, a feature that we confirm with ID-MC-ICPMS.

To our knowledge, there is no river data to compare the ^{227}Ac concentration measured in the Vienne River. Nevertheless, the 2 analyses of the same water sample agree within uncertainties. Despite concentrations similar to seawater, the uncertainties are still 20-25% ($2\sigma_n$), probably due to a lower precipitation yield because the filters needed to be changed several times during the coprecipitation step.

Overall, these different experiments strengthen our trust in the reliability of the ^{227}Ac concentration measurement by ID-MC-ICPMS for seawater and freshwater samples.

4.2. Comparison with other methods

The different tests that we have performed in this study give a ^{227}Ac detection limit of around 10 ag, with a $2\sigma_n$ uncertainty of $\sim 20\text{-}25\%$. This detection limit allows us to measure sample with around 10L, that size is comparable to the volume of the Niskin bottle generally used during oceanographic cruise. This is a very significant improvement compared to methods used until now. The method based on measurement by alpha-spectrometry used by Nozaki allowed to measurements of samples with ^{227}Ac concentrations of $\sim 1\text{ ag/kg}$ but required around 250 L (Nozaki, 1993). This method had a good reliability for the concentration measurement, thanks to the measurement of ^{227}Th which is at equilibrium with ^{227}Ac , after 100 days of equilibration, spiked with ^{230}Th . However, the yield of the preconcentration on Mn fibers for Ac was not well-known and is only assumed to be equal to the extraction efficiency of Ra.

Alpha spectrometry was also used for analysis of samples from the Weddell Gyre (Geibert et al., 2002; Geibert and Vöge, 2008). ^{227}Ac in the Weddell Gyre is more concentrated than in the Pacific Ocean, so only 20 to 80L of seawater were required. The implemented method was the same as the one of Nozaki, but spiking with ^{225}Ac was performed before the preconcentration step to have a better estimate of the yield and to decrease the total uncertainties on the measurement. The lowest volume (20 L) was used to analyse the most concentrated sample (32 ag/kg with a 2σ uncertainty of 18%). This must be compared with our results from the HYDROSED profile for which 29 L of seawater were used to analyse concentrations of the order of 3 ag/kg (with a $2\sigma_n$ uncertainty of 25%).

The RaDeCC method requires pumping over 1000L of seawater through a Mn-Cartridge to perform measurement at around 0.4 ag/kg with a 2σ uncertainty of $\pm 34\%$ (Le Roy et al., 2019) which is less precise and requires much larger volume than our method. This protocol is derived from the measurement of Ra isotopes with RaDeCC (scintillation cells) by measuring the activity of ^{223}Ra and ^{219}Rn at the equilibrium with ^{227}Ac after at least 3 months of equilibration (Shaw and Moore, 2002). With this method, the yield of Ac recovery on Mn-cartridge yield ranged from 31 to 78% with a mean value ($47 \pm 12\%$) that is arbitrarily used for all the low concentration samples for which the yield could not be directly determined. Keeping in mind that RaDeCC analysis requires 100 times more water than ID-MC-ICPMS, it has a lower detection limit (detection limit estimated around 400 ag or 0.1 ag/kg, if the yield on the Mn cartridge is taken into account).

At last, it is necessary to measure the dissolved ^{231}Pa to calculate the unsupported ^{227}Ac , which is the parameter for interpreting ^{227}Ac data in seawater. Our method by ID-MC-ICPMS allows to measure the two elements from the same water sample. ^{231}Pa is adsorbed on Mn oxide (Rutgers van der Loeff and Moore, 1999) and is purified during the first anion exchange chromatography (Gdaniec et al., 2018). Other tracers can be recovered during the chemical process, i.e. a Ra fraction with alkaline earth elements that could be used for ^{226}Ra and ^{228}Ra analyse, and a fraction with the Th and REEs that could be used for the measurement of the isotopic composition of Nd and relative abundance of the different REEs. Pa cannot be analysed with the RaDeCC protocol, but it can be measured by alpha spectrometry.

5. Conclusion

This study presented the first analytical protocol for measurement of the dissolved ^{227}Ac in natural waters by means of a thorough chemical purification-concentration procedure, MC-ICPMS and quantification of ^{227}Ac by isotopic dilution with ^{225}Ac . This method has an improved sensitivity and lower uncertainties than the methods based on nuclear counting. It allows significantly reducing the sample size to the volume of common sampling bottle (i.e. 10-30 L) and it will be particularly useful to analyse pore water or hydrothermal fluids (Geibert et al, 2008, Kipp et al, 2015). This method also provides purification-concentration of other oceanic tracers like ^{231}Pa , ^{226}Ra , REEs or ϵ_{Nd} . Some improvements are still needed to reduce the interferences on MC-ICPMS and to carry out inter-calibration of standards to strengthen the reliability of the Ac measurement. This new method paves the way for the analysis of ^{227}Ac by laboratories which are not equipped with nuclear counting systems, but which are already able to measure ^{231}Pa and ^{230}Th by MC-ICPMS. This will allow a rapid growth of the use of ^{227}Ac as an ocean tracer.

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Highlights:

- Analytical protocol for very low concentration of ^{227}Ac and ^{231}Pa in 10-30L water samples
- Improvement of ^{227}Ac measurement by mass spectrometry compared to nuclear spectrometry
- Consistent measurement of ^{227}Ac concentration with previous studies in Weddell Sea

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