

A simple distillation method to extract bromine from natural water and salt samples for isotope analysis by multi collector inductively coupled plasma mass spectrometry

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Rationale: In natural samples bromine is present in trace amounts, and measurement of Br stable isotopes necessitates its separation from the matrix. Most methods described previously need large samples or samples with high Br/Cl ratios. The use of metals as reagent, proposed in previous Br distillation methods, must be precluded for MC-ICP-MS analyses, because of risk of cross contamination, since the instrument is also used to measure stable isotopes of metals.

Methods: Dedicated to water and evaporite samples with low Br/Cl ratios, the method is a simple distillation that separates bromide from chloride for isotopic analyses by MC-ICP-MS. It is based on the difference in oxidation potential between chloride and bromide in the presence of nitric acid. The sample is mixed with dilute (1:5) nitric acid in a distillation flask and heated over a candle flame for 10 minutes. The distillate (bromine) is trapped in an ammonia solution and reduced to bromide. Chloride is only distilled for a very small part. The obtained solution can be measured directly by MC-ICP-MS for stable bromine isotopes.

Results: The method was tested for a variety of volumes, ammonia concentrations, pH and distillation times and compared to the classic ion-exchange chromatography method. The method more efficiently separates Br from Cl, so that samples with lower Br/Cl ratios can be analysed, with Br isotope data in agreement with previous methods.

Conclusions: Unlike other Br extraction methods based on oxidation, the distillation method presented here does not use any metallic ion for redox reactions that could contaminate the mass spectrometer. It is efficient in

separating Br from samples with low Br/Cl ratios. The method assures reproducible recovery yields and a long-term reproducibility of $\pm 0.11\%$ (1SD). The distillation method was successfully applied to samples with low Br/Cl ratios and low Br amounts (down to 20 μg).

1/ INTRODUCTION

In recent years the interest in bromine (Br) stable isotope ratios is steadily growing. Although Br shows geochemical characteristics that are comparable to chlorine (Cl) recent studies determined significant and currently unexplainable differences in their isotopic behaviour^{1,2}. Initial techniques to measure Br stable isotope ratios were based on earlier developed techniques to measure Cl stable isotopes using dual-inlet isotope ratio mass spectrometry (IRMS)^{3,4} later adapted to introduce the gas through a continuous flow interface⁵. These techniques required fairly large amounts of Br which are often not available in geological samples. In order to be able to measure Br stable isotope ratios in smaller samples various multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) methods have been developed in recent years to measure Br isotopes in natural water samples⁶⁻¹⁰. However due to the high first ionisation energy of Br and to the interference of Ar_2H^+ on $^{81}\text{Br}^+$ in ICP-MS, still a fairly high minimum concentration of bromide (Br^-) needs to be present in the sample solution that is fed into the mass spectrometer. Although high-resolution (HR) techniques have been developed⁸, the intrinsic instrumental mass drift of MC-ICP-MS can generate inaccurate measurements, due to the reduced width of the Br^+ plateau in HR mode, making low-resolution measurements a more robust method⁹. This Ar_2H^+ interference is avoided when bromine isotopes are measured by thermal ionisation mass spectrometry (TIMS) in the form of Cs_2Br^+ ions¹⁰. However Cs is a very good ion emitter in TIMS, resulting in a high and persistent Cs^+ memory effect in the source. Experience at the Institut de Physique de Globe de Paris (IPGP) is that Cs^+ can stay in the source for more than 1 year and either induce parasitic ion beams in the mass range of other elements or reduce the ionisation/emission efficiency of other elements. For this reason it was decided not to apply TIMS for the measurement of Br (and for the same reason Cl) stable isotope ratios at IPGP (J.L. Birck, pers. comm.).

The main problem that arises if one needs to extract bromide (Br^-) from natural waters for isotope analysis is that it is generally a trace ion whereas chloride (Cl^-) is a major element, present in solutions with concentrations that are 100 to 10000 times as high as the Br^- concentrations. Most commonly Br^- is separated from Cl^- by ion-chromatographic⁷ or ion-exchange techniques⁹. The problem with both techniques is that in samples with very low Br/Cl ratios, such as in halite salt deposits, the Cl to Br separation is not sufficient enough due to supersaturation of the chromatographic column or ion-exchange resin with Cl^- , resulting in a significant level of Cl^- remaining in the Br^- fraction recovered. A summary of the various methods for the analysis of Br stable isotopes is given by Louvat et al.⁹.

Here we propose a different technique to produce Cl⁻ poor solutions that can directly be fed to the MC-ICP-MS, with the same Br isotope measurement protocol as in Louvat et al.⁹. Our method is based on the difference in redox behaviour of the two ions chloride and bromide, and is applicable to samples with very low Br/Cl ratios.

The biggest challenge when measuring the Br isotope ratio of a sample is the removal of Cl. When the first method to measure Br isotopes by IRMS was developed it was essential to remove Cl from the samples as thoroughly as possible due to the fact that Cl and Br react similarly in the formation of CH₃Br, the gas used for IRMS measurements⁴. This problem was solved by applying a method developed during the 19th century that was based on the difference in redox potential between the two ions Cl⁻ and Br⁻. Its principle is that Br⁻ in solution is oxidised to Br₂, that is distilled into a KOH solution and subsequently the produced BrO⁻ is reduced back to Br⁻ by boiling it with metallic Zn¹¹. The result is a solution containing quantitatively all Br from the original solution and containing less than 1% of the original Cl, which was sufficient for most Br isotope measurements by IRMS.

At IPGP the method developed by Louvat et al.⁹ is successfully in use for Br isotope measurements of saline solutions, but unfortunately this method is not applicable to samples with very low Br/Cl ratios as it works with 1 mL of the AG 1-X4 resin (Bio-Rad, Hercules, CA, USA), which has a maximum total ion-exchange capacity of 1 mmole/mL. At low Br/Cl ratios (≤0.002) the big Cl⁻ elution peak overlaps the very small Br⁻ elution peak, resulting in solutions with Br/Cl concentration ratios ≤0.01 hampering precise MC-ICP-MS measurement of the Br isotope ratios for solutions with low Br concentrations. To solve this problem the idea of oxidative distillation was reconsidered. But, due to the fact that isotope ratios of most transition metals are also measured at the IPGP on the same instrument as Br, the new method should not use any metallic reagent. Even the smallest amount of metals transferred will cause unacceptable memory effects, since these metallic elements are measured at very low concentrations.

As it was long known that a dilute HNO₃ solution will oxidise Br⁻, but not Cl⁻^{12,13}, Murphy et al.¹⁴ developed a method to quantitatively separate Br from Cl. During oxidation of Br⁻ Br₂ is formed and in alkaline solutions Br₂ is disproportionated into Br⁻ and BrO⁻, which subsequently disproportionates to Br⁻ and BrO₃⁻ following:



The final solution thus contains Br⁻ and BrO₃⁻ in a 5:1 ratio. As the Br is trapped in an ammonia solution, which is a strongly reducing agent, the BrO₃⁻ that is formed is reduced to Br⁻ so that this solution could directly be introduced into the inlet system of an MC-ICP-MS.

The method that we developed for the analysis of Br isotopes follows this procedure¹⁴ with several modifications:

1/ At IPGP Br isotopes are routinely measured in a 0.2 M NH_4NO_3 solution, that result from ion exchange chromatography for Br extraction as described by Louvat et al.⁹. We found it appropriate to keep this medium (0.2M NH_4NO_3) for the new method as it has proven to produce reproducible measurements of Br isotope ratios and fast washouts. The use of the same medium for both analytical procedures (distillation and ion exchange) also allows for immediate comparison between the two methods to extract Br from geologic samples. For that reason the distilled Br_2 was trapped in an ammonia solution.

2/ While Murphy et al.¹⁴ used a distillation flask with a size of 300 mL, as the size of our samples is mostly between 1 and 25 mL, such a large flask would be very inconvenient, especially because the volume of the distilled solution should be as small as possible (roughly about 2 mL) to obtain a good signal level during analyses.

3/ The main objective of this new method is the analysis of natural water and salt samples. In order to facilitate this and to ensure that results are compatible with those obtained by the methodology developed by Louvat et al.⁹ a series of tests were conducted in order to assess the distillation time, ammonia concentration and final pH.

2/ EXPERIMENTAL

2.1/ The Br distillation method

The distillation equipment built for the Br distillation (see Figure 1) consists of a 25 or 50 mL two-neck (angled) round bottom flask (LENZ 3 2111 22 or 3 2111 28), a small distillation bridge (LENZ 5 0400 01) and a straight adapter (LENZ 5 0920 01). All glassware came from LENZ (Wertheim, Germany). To this adapter a plastic 1mL pipette tip is attached in order to direct the distilled liquid into a 5 mL vial containing 1 mL NH_3 solution. This tip needs to be installed such that the distilled liquid bubbles through the ammonia solution. The sample mixture is heated by a small candle on top of a laboratory jack, which allows regulating the boiling by increasing or decreasing the distance between the candle and the distillation flask. Following Murphy et al.¹⁴ a 1:5 diluted nitric acid solution would be the best compromise for a good distillation of Br and thus separation of Cl and Br. At more concentrated HNO_3 solutions Cl starts to distil and at more dilute concentrations the distillation is too slow. Following this procedure¹⁴ we propose the following method. The distillation equipment is assembled as visible in Figure 1. In the round-bottom flask a few anti-bumping granules (VWR 330093Y; VWR, Fontenay-sous-Bois, France) made of porous aluminium oxide are added to facilitate gentle boiling. This is essential because due to the small volume of the solution in the distillation flask and the high temperature of the candle flame, initial boiling will be vigorous and results in “bumping” a significant amount of the solution present to the distillation bridge and thus to the bromide trap.

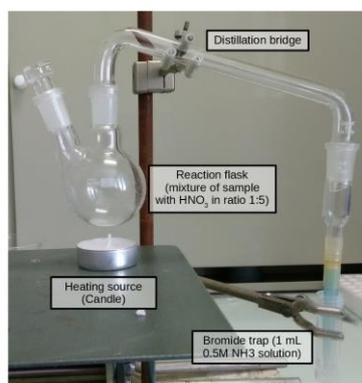


Figure 1: Photograph of the distillation set-up used in this study.

The volume of sample needed for Br isotope measurements is calculated for 20 μg of Br (for MC-ICP-MS measurement at 10 ppm, but the same performance is observed at 5ppm⁹). For small samples (less than 8 mL) the 25 mL flask was used. The acid mixture was prepared as follows for samples up to 4 mL: x mL sample, (4-x) mL of MilliQ H₂O (18.2 M Ω , Merck, Darmstadt, Germany) and 1 mL of HNO₃ (69% or 16N, VWR NORMAPUR 20422.297), resulting in a total volume of 5 mL. For sample sizes up to 8 mL, x (x = 5 to 8) mL sample (8-x) mL H₂O were mixed and 2 mL of HNO₃ were added. For sample volumes larger than 8 mL, the 50 mL round-bottom flask was used and samples were prepared following the same ratios, such that 1:5 of the final volume is concentrated HNO₃. If the required volume of the prepared sample solution increases above 25 mL (for samples with very low Br concentrations) it is suggested that larger round-bottom flasks are used, however we did not test these larger sample sizes here. At the receiver end a plastic 5 mL vial is filled with 1 mL of a 0.5 M NH₃ solution (prepared by dilution from our in house distilled 4 M NH₃ solution). In all cases HNO₃ is added at the last moment through the lateral neck that is immediately closed with a hollow stopper (LENZ 1 4003 14) to preclude any loss of Br₂. The sample solution is then heated to boiling and boiled for up to 10 minutes, until the recovered volume reaches approximately 1 mL, so that the total volume is close to 2 mL. Due to the nature of the distillation it is not possible to reach this volume exactly, and in reality the total volume in the receiving vial at the end of the distillation is 1.5 to 3 mL. When the volume has reached this point, the candle is blown, the distillation set-up disassembled and the sample vial removed, capped and stored until MC-ICP-MS measurement.

2.2/ MC-ICP-MS Br stable isotope ratio measurement

The samples are measured as described before⁹ on a Thermo Neptune multi collector inductively plasma mass spectrometer (ThermoFisher Scientific, Bremen, Germany, a double focusing high-resolution magnetic sector field mass spectrometer with Ar inductively coupled plasma and multi-collection on 9 mobile Faraday cups. The operating conditions are summarized in Table 1 (to be found at the end of the document). Samples are introduced to the mass spectrometer through a small 20 mL cyclonic spray chamber with a 50 $\mu\text{L}/\text{min}$ PFA nebulizer (ESI, USA). Measurements are done in low-resolution mode. The instrument is tuned such that the $^{40}\text{Ar}_2\text{H}^+ / ^{81}\text{Br}^+$ ratio is minimized while

^{79}Br intensity is maximized, and the $^{40}\text{Ar}_2\text{H}^+$ interference is corrected by blank subtraction. Instrumental mass bias is corrected by sample-standard bracketing, and $^{81}\text{Br}/^{79}\text{Br}$ is expressed as $\delta^{81}\text{Br}$ (in ‰ unit) following:

$$\delta^{81}\text{Br}_{\text{Std}} = \left\{ \left(\frac{^{81/79}\text{Br}_{\text{sample}}}{^{81/79}\text{Br}_{\text{Std}}} \right) - 1 \right\}$$

where the standard was either an in-house HBr solution ($\delta^{81}\text{Br}_{\text{HBr}}$) with a $\delta^{81}\text{Br}_{\text{SMOB}}$ value of -0.02 ± 0.09 ‰⁹ or the NIST SRM 977 ($\delta^{81}\text{Br}_{977}$) international standard with a $\delta^{81}\text{Br}_{\text{SMOB}}$ value of -0.64 ‰ relative to seawater^{4,5,15}. In order to reduce the memory effect of Br in the introduction system, and to compare with the previous method of Br extraction by ion exchange chromatography, all Br solutions were prepared with NH_4NO_3 at 0.2 mol/L. $\delta^{81}\text{Br}$ measurements are triplicated for each sample (Std-Smpl-Std-Smpl-Std-Smpl-Std). The bracketing standard solutions are prepared to the same Br and Cl concentrations as the analysed samples, in order to avoid linearity bias and matrix effects. Using this set-up an estimation of the internal reproducibility over five $\delta^{81}\text{Br}$ determinations for each sample can be calculated.

3/ RESULTS AND DISCUSSION

3.1/ Choice of HNO_3 and NH_4OH concentrations

Experiments applied by Murphy et al.¹⁴ have shown that nitric acid diluted at a 1:2 ratio with water will start to oxidise Cl^- and distil it, while nitric acid diluted at a 1:9 ratio will oxidise Br complete but at a very slow rate. The best concentration range was thus 1:3 to 1:6 HNO_3 and following Murphy et al.¹⁴ we applied a 1:5 diluted nitric acid solution as the best compromise for a good distillation of Br and thus separation of Cl and Br.

During the distillation process a small amount of HNO_3 is transferred to the ammonia trap. This HNO_3 is transferred due to boiling of the initial mixture and will be trapped in the NH_3 and form an NH_4NO_3 solution. This solution will be alkaline for as long as the transferred nitric acid is buffered by the presence of ammonia. The pH of the final solution in the ammonia trap was determined using pH-paper. It was observed that when the final volume was up to 2 mL the pH of the solution was alkaline, however when the volume is larger it was observed that this solution proofed to be acid. As a consequence tests were done to determine the influence of the pH on the final isotope ratio determination (see section 3.3). The change in the pH at about 2 mL volume indicated that it is important to keep the total volume close to 2 mL. It was decided that starting with 1 mL of a 0.5M ammonia solution the final solution would have a composition that is close to the composition of the solution produced in the ion-exchange chromatography method developed by Louvat et al.⁹. At this volume the Br is concentrated in the smallest possible volume to secure a high enough concentration in the mass spectrometer inlet for representative Br isotope measurements.

3.2/ Influence of NH_4NO_3 concentration on Br isotope ratio

Louvat et al.⁹ measured Br isotope ratios in 0.2 M NH_4NO_3 solution at pH 9 after ion exchange extraction of Br. At 0.2 M NH_4NO_3 is a low enough concentration to avoid blocking of the inlet system due to precipitation of NH_4NO_3 . However due to the nature of the present technique it is not possible to keep the final ammonium concentration in our distillate solution at such constant level. We start the distillation with 1 mL of a 0.5M NH_3 -solution. After the distillation the final volume is between 1.5 and 3 mL, although it would be ideally between 2 and 2.5 mL. This leads to a variability of the NH_4NO_3 concentration in the final solution of between 0.17 and 0.33 M, but even in ideal solutions it is between 0.2 and 0.25 M. We thus tested how changing the NH_4NO_3 concentration between 0.15 and 0.35 M would affect the Br isotope ratio of our HBr in-house standard solution ($\delta^{81}\text{Br}_{\text{HBr}}$ of 0 ‰) at a constant concentration of 10 ppm. We found no significant deviation from the original $\delta^{81}\text{Br}$ value ($+0.03 \pm 0.07$ ‰, 1σ , $n=5$), and even more importantly no variation with the concentration over this range (see figure 2).

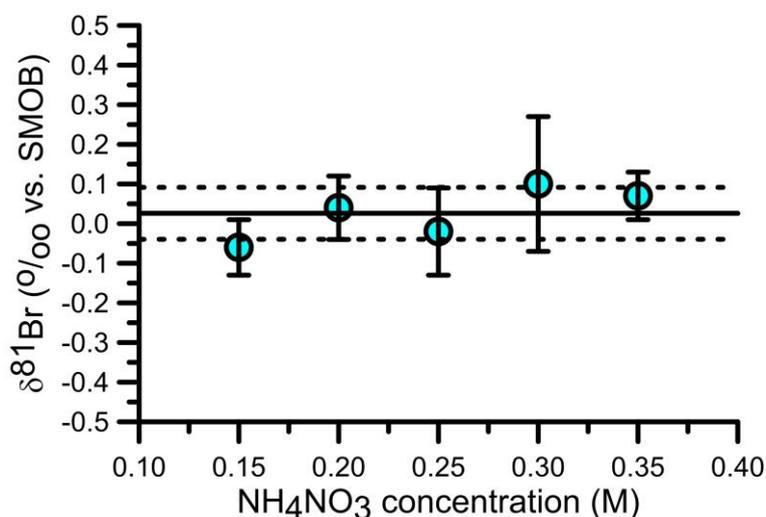


Figure 2: Effect of NH_4NO_3 concentration on the measured $\delta^{81}\text{Br}$ values of our in-house HBr standard solution. All samples were bracketed by a standard in 0.2 M NH_4NO_3 solution and all solutions contained 10 ppm Br. The solid and dashed lines represent the average and one standard deviation (1SD), respectively, of the five $\delta^{81}\text{Br}$ measurements at different NH_4NO_3 concentrations. The error bars represent 2SD values of the individual $\delta^{81}\text{Br}$ measurements ($n=5$ for each sample).

3.3/ Influence of pH on Br isotope ratio

After ion exchange chromatographic extraction of Br with 0.2 N NH_4NO_3 , measurements are done at pH 9⁹. Unfortunately with the distillation method it is not possible to keep the pH at this level. Although ammonia solutions are good pH buffers, addition of large HNO_3 amounts will finally decrease the pH. The pH of the Br solutions after the distillation process appeared to be still alkaline (pH 9-10) when the total recovered fluid volume was less than approximately 2 mL, but was acid when the volume was above 2 mL. At low pH values Br_2 is stable in solution, and unlike the anions Br^- and BrO_3^- it might theoretically escape from the solution. As the potential escape of Br_2 might be connected to isotope fractionation it is important to test if the pH of the samples solution has any influence on the measured isotope ratio. We

prepared samples containing 0.2 M NH_4NO_3 and 10 ppm of our in-house HBr standard solution at different pH values. The pH was adjusted by adding small amounts of HNO_3 (69%, 16N). At very small amounts of HNO_3 the pH is well buffered by the NH_3 solution, but at a certain point it decreases quickly. For that reason it was not possible to prepare an even distributed set of pH values, and finally we obtained samples with pH values of 9, 7, 3.5, 2.5 and 1. We did not find significant deviations from the original $\delta^{81}\text{Br}_{\text{HBr}}$ value (-0.02 ± 0.06 ‰, 1σ , $n=5$), and even more importantly no variation with the pH over this range (see Figure 3).

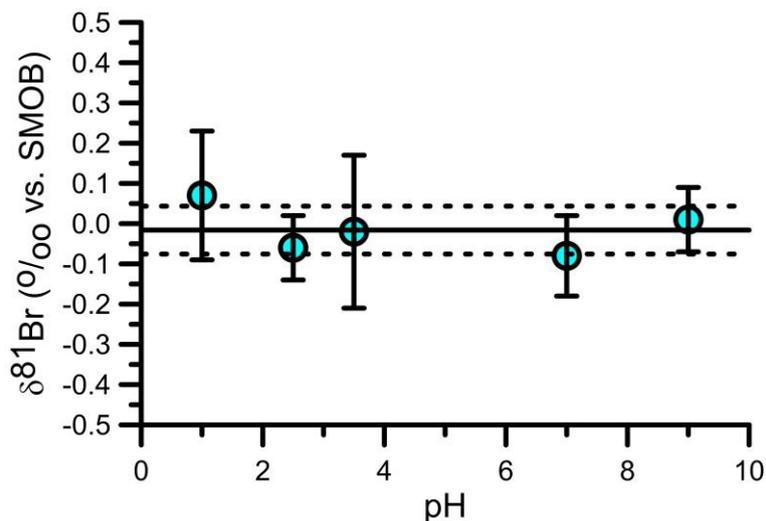


Figure 3: Effect of pH on the measured $\delta^{81}\text{Br}$ values of our in-house HBr standard solution. All samples were bracketed by a standard at pH 9. The solid and dashed lines represent the average and one standard deviation (1SD), respectively, of the five $\delta^{81}\text{Br}$ measurements at different pH values. The error bars represent 2SD values of the individual $\delta^{81}\text{Br}$ measurements ($n=5$ for each sample).

3.4/ Influence of distillation time on Br and Cl yield

The purpose of the distillation technique described here was twofold. First to extract Br from solutions with low Br concentrations, or perhaps better defined, from solutions with low Br/Cl ratios and concentrate this Br in a small (preferably 2 mL) amount of solution. Second to obtain a solution with as low as possible Cl content. We tested the amounts of Cl and Br that were extracted from 0.5 mL seawater when the distillation process lasted for 5, 10, 10 and 15 minutes, and whether this was time dependent. The results are shown in Figure 4. Visible from this figure is that the amount of Br extracted is nearly constant (18 to 24 μg) for all three distillation times. On the opposite the extracted Cl amount increases considerably with the distillation time from about 50 μg at 5 minutes to about 250 μg at 10 minutes and about 800 μg at 15 minutes. As the method is developed in order to separate Br from Cl as efficiently as possible it is chosen to use a distillation time of 10 minutes, which is a good compromise between an efficient distillation of Br from a mixture that contains a large surplus of Cl and a small but sufficient distilled volume of solution. Interestingly as is visible from figure 4 the absolute amount of Cl in the solution is still considerably higher than the absolute amount of Br. This indicates that Br isotope composition can still be measured very well when the Br/Cl ratio in the solution has a value of 0.08, 27 times higher than in seawater. It is however no indication of what would be the

lowest possible Br/Cl ratio for acceptable measurements. It might thus imply that when the distillation technique described here is applied to samples with extremely low Br/Cl ratios and Br concentrations it might become necessary to use the distillation method twice in order to get the Br/Cl ratio to a low enough level. This was however not tested during the current study.

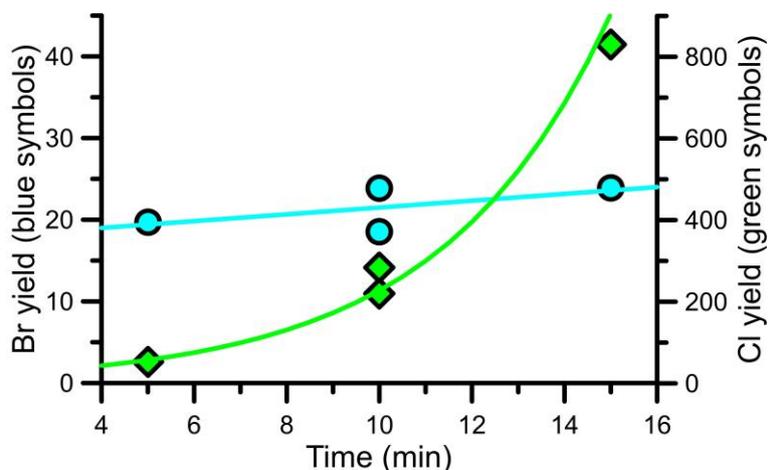


Figure 4: Amounts (in µg) of Br (blue circles) and Cl (green diamonds) recovered from the distillation process as function of the distillation time.

3.5/ Long-term reproducibility of the method

In order to test the reproducibility of the full analytical procedure (distillation plus the subsequent measurement of the sample) 15 aliquots of our standard seawater sample were distilled during the testing period (at least two aliquots were distilled each day) and they were also measured on different days during the period we analysed our samples. Figure 5 shows the $\delta^{81}\text{Br}$ variation of these samples relative to seawater ($\delta^{81}\text{Br}_{\text{SMOB}}$ value of 0 ‰). It is visible from this figure that the method is reproducible with an average value of +0.06‰ (compared to our long term Br seawater standard measurements⁹) and a standard deviation of 0.11‰ (1SD).

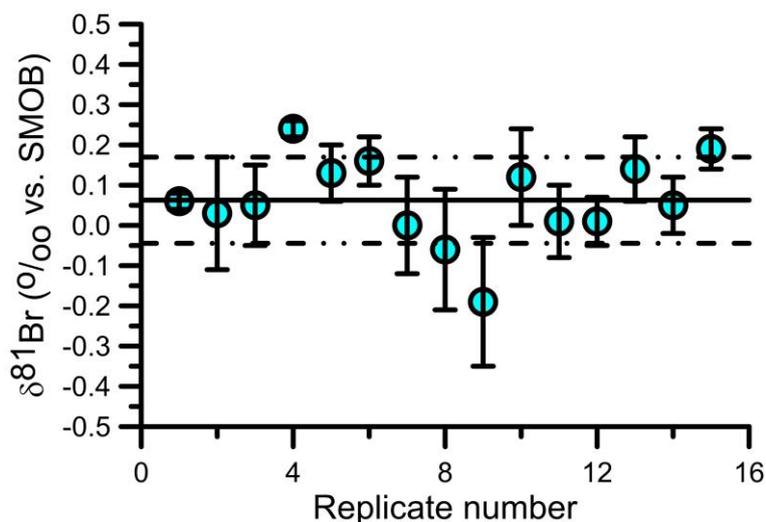


Figure 5: Long-term reproducibility of the $\delta^{81}\text{Br}$ of a standard seawater solution measured by MC-ICP-MS after Br extraction by the distillation method. The solid line represents the average, the dashed lines one SD from the average.

3.6/ Br yield of the distillation method

Although we have shown that the Br distillation technique leads to highly reproducible Br isotope measurements it is important to realise that the obtained Br yields are considerably smaller than 100%. The Br yields of the 15 standard seawater aliquots that were analysed (Fig. 5) were between 29 and 56%, a considerable range (with an average of 45.9% and a standard deviation of 8.5%, see Figure 6). These values are equivalent to Br concentrations in the measuring solution between 6.7 and 10.8 mg/L with an average value of 8.1 mg/L. As mentioned above these low yields did not lead to a bad reproducibility and did also not cause systematic variations in the $\delta^{81}\text{Br}$ measurements. The average $\delta^{81}\text{Br}$ value of the distilled seawater is indistinguishable from the $\delta^{81}\text{Br}$ value of our in-house HBr standard solution, as was also reported for the ion exchange chromatography + MC-ICP-MS and for IRMS measurements⁹. So, even with an extraction yield averaging only 50% no fractionation is observed during the distillation. This can be explained by the chemical reaction between nitric acid and bromide in the distilling flask. It is assumed that when the solution starts to boil the reaction from Br^- to Br_2 takes place almost immediately and not gradually and Br_2 is then distilled over quickly through the boiling water/nitric acid mixture. This conclusion follows also from the earlier discussed Br yield of the distillation as a function of time. In that test the Br yield was almost invariable with time, indicating that the oxidation reaction takes place immediately after the solutions starts boiling and that transfer of Br_2 is mostly during early boiling of the solution in the distillation flask.

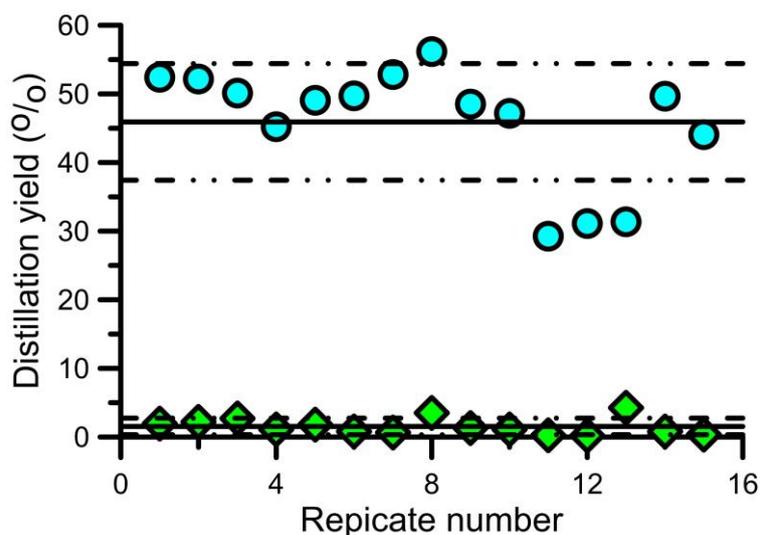


Figure 6: Cl (green diamonds) and Br (blue circles) extraction yields of the distillation method for the 15 replicates of seawater standard solution measurements. The continuous line represents the average, the dashed lines one SD from the average.

In order to determine possible Br blanks we ran one sample containing no added Br through the whole distillation procedure. The Br content of the yield solution was determined to be 0.06 ppm compared to an average value of 8 ppm in the seawater extractions indicating that a possible Br blank is less than 1% of the total Br recovery which will have, considering the analytical error in the Br measurements, no influence on the final Br isotope determination.

We also determined the Cl yields of the different extractions. This yield is always low with an average value of 1.5 % (and an associated standard deviation of 1.2 %). It still means however that the Cl concentrations in the solution that is fed into the mass spectrometer are higher than the Br concentration, but the Br/Cl ratio has increased considerable from 0.003 in seawater to an average value of 0.19 (with a standard deviation of 0.15) in the extractions. These Br/Cl ratios are comparable to or even higher than the Br/Cl ratios in the samples obtained from seawater using the ion-exchange method. Louvat et al.⁹ reported Br/Cl ratios between 0.02 and 0.1 in their final solution. This indicates that the distillation method can be used to obtain good quality Br isotope data of the samples it was developed for: 1) samples with very low original Br/Cl ratios such as halite samples and 2) samples that contain at least 20 µg Br. As the Br elution volume of the ion-exchange extraction method is 7 mL the Br concentration from low Br content samples might be too low to precisely measure the Br isotope ratio, while the same amount of Br is concentrated in the 2 mL produced during distillation of the sample and $\delta^{81}\text{Br}$ could be more precisely measured.

4/ CONCLUSIONS

We have applied the distillation method developed by Murphy et al.¹⁴ to separate Br from large amounts of Cl and have successfully adapted and applied it to the measurement of Br isotopes by MC-ICP-MS in natural samples. This methodology is especially useful for samples with very low Br/Cl ratios and/or low absolute Br content. Briefly, the sample solution is admixed with concentrated HNO_3 in order to achieve a HNO_3 dilution factor of 1:5 and the mixture is heated over a candle flame for 10 minutes in a distilling flask. The vapour is collected in a NH_3 solution at 0.5N. The final solution is ideally NH_4NO_3 0.2N at pH 8-9. The method has however been tested over a range of NH_4NO_3 concentrations (0.15 to 0.35N) and pH values (1 to 9) without any distinguishable effect on the $\delta^{81}\text{Br}$ values that were measured (within 1SD of 0.1‰). Despite the low distillation yield, as the oxidation reaction is instantaneous and occurs without isotope fractionation it is possible to use the proposed technique to extract Br while Cl is only poorly distilled in 10 min. We have shown that the distillation method produces consistent bromine isotope data that can be well compared to the ion-exchange chromatographic preparation of the samples⁹. Using this method it is now possible to analyse samples with low Br/Cl ratios or samples with a minimum total bromine content of 20 µg for reliable bromine isotope data.

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Instrument	MC-ICP-MS Neptune, Thermo Scientific
Cones	Nickel; Jet sampler and H skimmer
Introduction system	20 mL quartz spray chamber
Nebuliser	Teflon-PFA microconcentric 50 $\mu\text{L}\cdot\text{min}^{-1}$ (ESI)
RF Power	1200 W
Ar Sample gas flow rate	1.0 to 1.1 $\text{L}\cdot\text{min}^{-1}$
Argon Cooling Gas flow rate	15 $\text{L}\cdot\text{min}^{-1}$
Argon Auxiliary Gas flow rate	1.0 to 1.2 $\text{L}\cdot\text{min}^{-1}$
Cup configuration	^{81}Br in C, ^{79}Br in L2, 10^{11} ohm resistors
Resolution	$m/\Delta m = 400$ (low resolution mode)
Integration time	15 cycles of 8 s
Uptake time	1 to 2 min
Wash time	3 min
Sensitivity	1 $\text{V}\cdot\text{ppm}^{-1}$ on mass ^{79}Br (low resolution)

Table 1: Operating parameters for MC-ICP-MS measurements of Br isotope ratios