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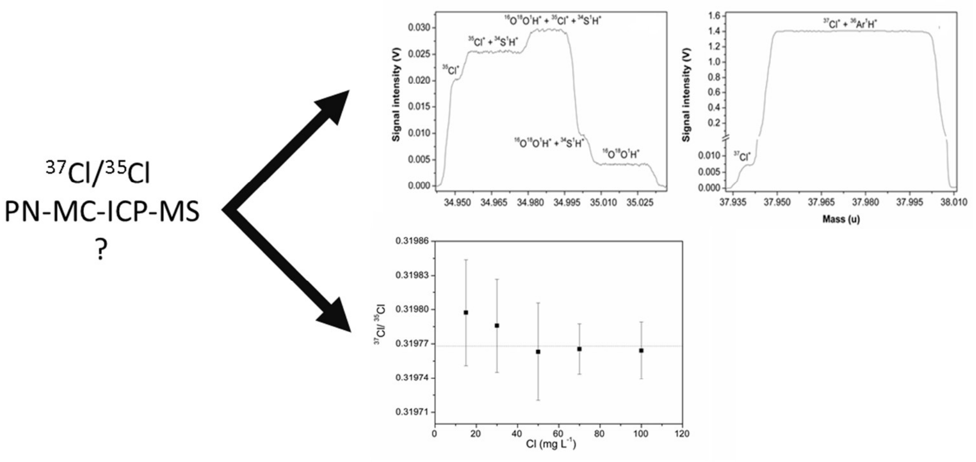

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A simple method for high-precision isotopic analysis of chlorine via pneumatic nebulization multi-collector inductively coupled plasma-mass spectrometry

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Chlorine isotope ratio measurement using multi-collector ICP-mass spectrometry (MC-ICP-MS) with sample introduction using traditional pneumatic nebulization suffers from spectral interference in addition to low sensitivity. Pronounced memory effects may jeopardize the accuracy of the results and/or the sample throughput. In this work, these limitations were overcome by using i) high mass resolution (mass resolving power of about 10,000) to resolve spectral interference, ii) 5 mmol L^{-1} NH_4OH as wash solution to avoid memory effects and iii) a Cl concentration of ≥ 70 mg L^{-1}. The major cation load of seawater and chloride salts (NaCl, KCl) sample solutions was efficiently removed without affecting the original isotopic composition of Cl via cation exchange chromatography with Dowex® 50WX8 resin. The method developed was demonstrated to be accurate and precise, as attested by the measurement result for the $^{37}Cl/^{35}Cl$ isotope ratio in NIST SRM 975a (experimental value of 0.319765 ± 0.000022, compared to a reference value of 0.319768 ± 0.000187 and a precision of ~0.007% RSD, n = 3), Additionally, the $\delta^{37}Cl$ value (vs. standard mean ocean chlorine, SMOC) was determined for five different standards; the values ranged from -0.54 to +0.89‰.

Introduction

The $^{37}Cl/^{35}Cl$ isotope ratio is considered a useful diagnostic parameter for geochemical processes in seawater, sea ice and the atmosphere.[1,2] However, high-precision isotopic analysis of Cl still is an analytical challenge.

Several techniques have been deployed for the measurement of the Cl isotope ratio, including electron impact ionization mass spectrometry (EIIMS),[3] negative chemical ionization mass spectrometry (NCIMS)[4-5] and, more recently, high-resolution continuum source atomic absorption spectrometry (HR CS AAS).[6] Unfortunately, these techniques are characterized by a number of drawbacks, such as the need for time-consuming sample preparation procedures, the occurrence of memory effects and/or a poor precision.

Positive thermal ionization mass spectrometry (PTIMS), relying on the monitoring of the polyatomic Cs_2Cl^+ ion, and dual inlet gas source stable isotope ratio mass spectrometry (SIRMS) are normally employed for Cl isotopic analysis and they have been applied to the measurement of the Cl isotope ratio in different samples.[1,7-10] Also these techniques are not free from problems; it has, e.g., been shown that instrumental fractionation in TIMS is strongly dependent on the amount of Cl.[10]

Multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) is a powerful technique dedicated to high-precision isotopic analysis of metals and metalloids. Its application to Cl isotopic analysis is far from trivial, mainly due to i) the low sensitivity, resulting from the high ionization potential of Cl (12.967 V), ii) the occurrence of spectral interference, mainly due to the formation of polyatomic ions containing elements, such as H, O, S and/or Ar – e.g., $^{16}O^{18}O^{1}H^+$ and $^{34}S^{1}H^+$, the signals of which overlap with that of $^{35}Cl^+$, and $^{36}Ar^{1}H^+$, the signal of which overlaps with that of $^{37}Cl^+$, iii) memory effects and iv) potential contamination from samples in HCl medium, routinely analyzed with this instrumentation.[11-13]

The introduction of the target element Cl as a dry vapor was shown to be an efficient strategy to avoid or at least strongly reduce the level of spectral interference in Cl determination and

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isotopic analysis by ICP-MS, as it allows the separation of Cl from the matrix of the sample. In addition, the introduction of a dry aerosol using vapor generation (VG), laser ablation (LA), electrothermal vaporization (ETV), gas chromatography (GC) or a dessolvator system may improve the sensitivity due to the enhancement of the sample introduction efficiency.[9-16]

Despite the fact that VG has improved the capabilities for Cl determination and isotopic analysis via ICP-MS, the overall procedure is laborious and requires specific equipment and reagents, which on occasions prevents the use of an autosampler. The use of a wet plasma and sample introduction via conventional pneumatic nebulization (PN) allows a simpler measurement protocol, use of the standard autosampler and an increased sample throughput with the standard MC-ICP-MS configuration.[17]

The feasibility of high-precision Br isotopic analysis by MC-ICP-MS using wet plasma conditions, which presents approximately the same problems as those reported for Cl, has been reported recently.[17,18] The problems originally jeopardizing successful Br isotopic analysis were addressed by careful optimization of the instrument settings, the use of “pseudo” high mass resolution to avoid spectral interference, the selection of an appropriate analyte element concentration and rinsing of the sample introduction system with an appropriate wash solution.[17-19]

Most of the current literature on isotopic standards for Cl presents the data as the δ^{37}Cl value, calculated relative to Standard Mean Ocean Chloride (SMOC). However, it was reported that δ^{37}Cl in seawater may range from -0.07‰ (Miyajima, Japan) to +0.08‰ (Woods Hole, US), depending on the geographical provenance of the sample.[1] In igneous rocks, a variation in δ^{37}Cl (always relative to SMOC) from -0.85 to +0.25 was reported.[12] For different commercially available inorganic standards, δ^{37}Cl values from -2.24 ‰ (for KCl) to 0.92 ‰ (for HCl) were reported and for organic solvents δ^{37}Cl varied from -5.01 ‰ (for 1,1,1-Trichloroethane) to +2.85 ‰ (for 1,1-dichloroethene).[7]

The NaCl isotopic standards SRM 975 and SRM 975a, both from the National Institute of Standards and Technology (NIST, USA), and ISL-354, from the International Atomic Energy Agency (IAEA, Austria) were used for evaluating the accuracy of the measurements. Those standards were accurately characterized in terms of their Cl isotopic composition by Wei, *et al.*,[8] who reported ^{37}Cl/^{35}Cl isotope ratios of 0.319876 ± 0.000067 for NIST SRM 975, of 0.319768 ± 0.000187 for NIST SRM 975a, and of 0.319549 ± 0.000044 for ISL-354. The δ^{37}Cl values (expressed relative to SMOC) compiled by Brand *et al.* in a IUPAC Technical Report were +0.43 ‰ for NIST SRM 975, +0.2 ‰ for NIST SRM 975a and +0.05 ‰ for ISL-354.[20]

The aim of the present work was to assess the feasibility of traditional MC-ICP-MS (wet plasma conditions & use of PN for sample introduction) for high-precision isotopic analysis of Cl by adequately addressing the problems of spectral interference, low sensitivity and memory effects. After method optimization δ^{37}Cl was determined for a number of commercially available standards.

Experimental section

Instrumentation

All isotope ratio measurements were carried out using a Thermo Scientific (Germany) Neptune MC-ICP-MS instrument, with a sample introduction system consisting of a 100 µL min^{-1} PFA nebulizer mounted onto a dual spray chamber, consisting of a cyclonic and a Scott-type sub-unit.

The measurements were performed using static collection with Faraday cups connected to 10^{12} Ω amplifiers. Gain calibration and baseline correction were performed before each measurement session. The instrument settings and data acquisition parameters are summarized in Table 1.

Quantification of Cl and Na were carried out using a quadrupole-based Elan DRC*Plus* ICP-MS unit (Perkin Elmer, CT, USA). The nuclides monitored were ^{35}Cl, ^{23}Na and ^{103}Rh (as internal standard).

Reagents, standards and samples

All reagents used were of analytical grade or higher purity. Ultrapure water (resistivity ≥ 18.2 MΩ cm) was obtained from a Milli-Q Element water purification system (Millipore, France).

Table 1 Instrument settings, Faraday cup configuration and data acquisition parameters for Cl isotopic analysis via MC-ICP-MS.

Instrumental parameters	
	RF power: 1350W Plasma gas flow rate: 15 L min^{-1} Auxiliary gas flow rate: 0.8 L min^{-1} Nebulizer gas flow rate: 0.95 L min^{-1} Focus Quad: -4.0 V Dispersion Quad: 0 V Focus: -772.0 V X-Deflection: 2.07 V Y-Deflection: 1.26 V Shape: 195.00 V Rotation quad: 0.00 V Source offset: 10.00V
Cones	Standard geometry
	Ni Sampler (1.1 mm orifice diameter) H-Type Ni Skimmer (0.8 mm orifice diameter)
Data acquisition parameters	
	Mode: Static Resolution: High (resolving power of approx. 10,000) Integration time: 4 s Blocks: 6 Cycles/Block: 6
Cup configuration	
	C: ^{35}Cl and H2: ^{37}Cl

Pro-analysis purity grade 14 mol L^{-1} HNO_3 (ProLabo, Belgium) was further purified by sub-boiling distillation in PFA equipment. *TraceSELECT*® NH_4OH was obtained from Sigma-Aldrich (USA).

Polypropylene chromatographic columns (Eichrom, USA) filled with 1 mL of Dowex® 50WX8 (200-400 mesh) cation exchange resin were used for matrix removal. Chlorine isotope measurements were carried out for NIST SRM 975a NaCl isotopic reference material (MD, USA), BCR CRM 579 reference material (mercury in coastal sea water) from the Institute for Reference Materials and Measurements of the European Commission (IRMM, Belgium) and in commercially available extra pure NaCl (batch # K04243400), pro analysis KCl (batch # K36308936641) and Suprapur NH_4Cl (batch # B363143), all of which supplied by Merck (Germany). $(NH4)_2SO_4$ was obtained from Merck (Suprapur purity). Individual 1,000 mg L^{-1} standard solutions of Cl, Na and Rh (Inorganic Ventures, the Netherlands) were used in the context of elemental assay via quadrupole-based ICP-MS.

Procedures

Each sample or standard was prepared by loading a polypropylene chromatographic column filled with 1 mL of Dowex® 50WX8 cation exchange resin (previously washed with ultrapure water to remove soluble organic compounds) with 1 mL of sample solution containing 1,000 mg L^{-1} of Cl. The Cl-fraction (Cl^- shows no affinity towards the resin) was eluted with 2 mL of milli-Q water and this fraction was diluted to a final volume of 10 mL. The Cl concentration, as well as the residual (post-column) Na concentration were determined using quadrupole-based ICP-MS after addition of Rh (final concentration of 1 µg L^{-1}) as an internal standard. Chlorine quantification was carried out via external calibration (calibration curve). Standard, blank and sample solutions were prepared in 5 mmol L^{-1} NH_4OH in order to decrease memory effects. Sodium determination was carried out using solutions prepared in 0.07 mol L^{-1} HNO_3.

Chlorine isotope ratio measurements were performed in diluted samples with a Cl concentration of 100 mg L^{-1} (samples and standards were all prepared in 5 mmol L^{-1} NH_4OH). In-between every two solutions, the sample introduction system was rinsed with 5 mmol L^{-1} NH_4OH solution during 3 min. The mass bias was corrected for using external correction in a sample-standard bracketing approach (SSB) using NIST SRM 975a NaCl isotopic reference material as an external standard. The approach was demonstrated to provide reliable results, but it may add one additional source of uncertainty to the expanded uncertainty, due to the uncertainty on the certified value. In this work, however, only the standard deviation and relative standard deviation (RSD) of the measurements are reported.

Results and discussion

Spectral interference

Chlorine isotope ratio measurements with MC-ICP-MS may suffer from severe spectral interference, depending on the composition of the sample, the analyte element concentration, the sample introduction system selected and the mass resolution used.

After proper optimization of the instrument settings, a mass resolving power 10,000 (defined as R = m/Δm, with Δm the difference between the masses where the analyte intensity amounts to 95% and 5% of the maximum signal intensity, respectively) was achieved. A resolving power corresponds to a mass resolution (R=m/Δm with Δm the full peak width at 5% of its maximum peak height) of approximately 5,000.[19] The theoretical resolution required to resolve the analyte signal from that of the polyatomic ion, interfering at low mass resolution, at an *m/z* ratio of 35 ($^{35}Cl^+$) is about 1,000 for $^{16}O^{18}O^{1}H^+$ and 5,100 for $^{34}S^{1}H^+$ (assuming equal intensities for analyte and interfering signal). At an *m/z* ratio of 37 ($^{37}Cl^+$), a resolution of about 3,900 is required for resolving the analyte signal from that of $^{36}Ar^{1}H^+$ (assuming equal intensities for analyte and interfering signal). The calculations of the resolutions required were done based on the atomic masses as provided by the Commission on Isotopic Abundances and Atomic Weights (CIAAW) from IUPAC.[21]

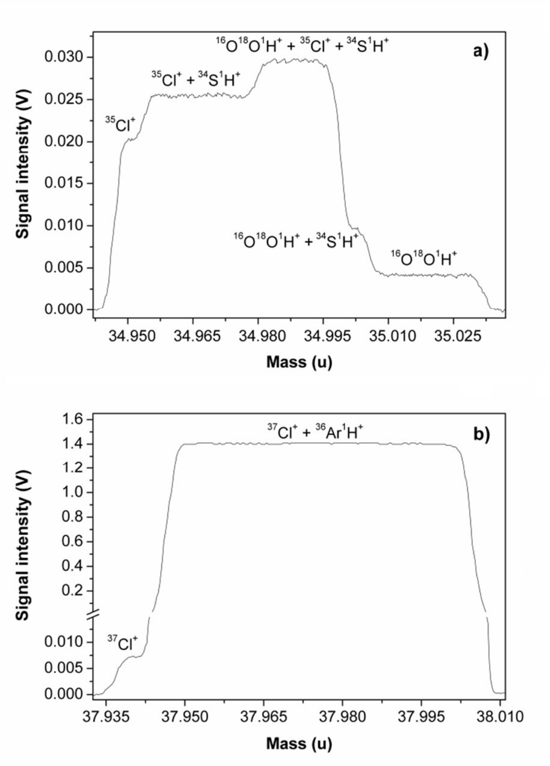

Fig. 1 Mass spectra recorded at an *m/z* ratio of 35 (a) and *of* 37 (b) using MC-ICP-MS with sample introduction via conventional pneumatic nebulization at pseudo high resolution (resolving power of approximately 10,000) for a standard solution containing 1 mg L^{-1} of Cl and 500 mg L^{-1} of S.

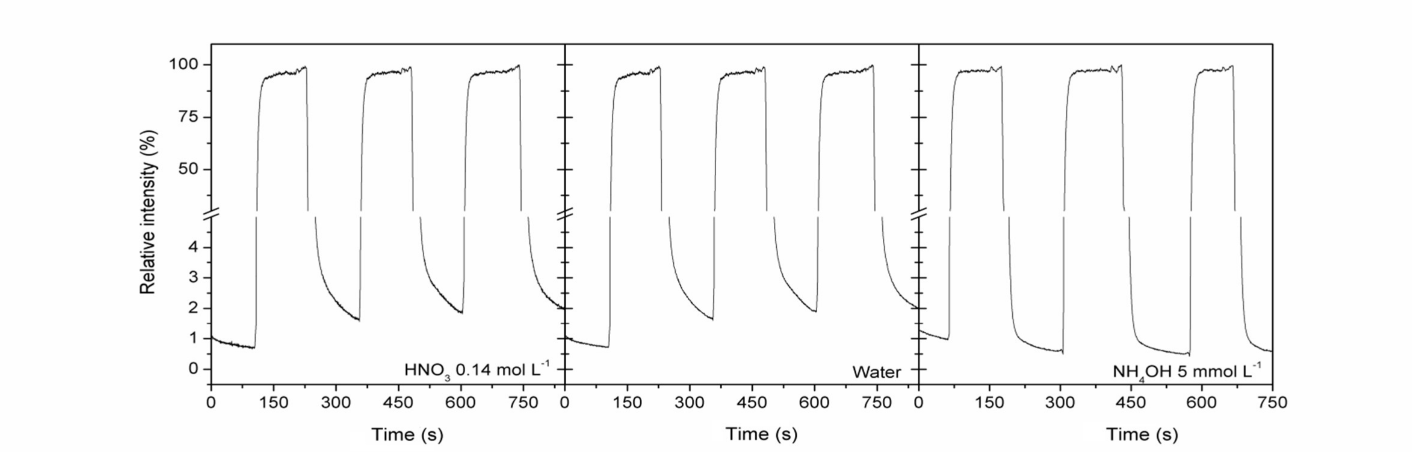

Fig. 1 Transient signals recorded for ^{35}Cl using conventional nebulization and MC-ICP-MS with aspiration of different wash solutions between successive injections of a 100 mg L^{-1} Cl standard. The standard solutions were prepared in the same medium.

The major cation load of seawater can be removed easily via the use of a cation exchange resin.[14] However, anions containing S (such as $S0_4^{2-}$) are self-evidently not expected to be removed using this approach, leading to the formation of $^{34}S^1H^+$ in the plasma. Cl can be isolated from other matrix compounds via alternative or additional approaches, such as precipitation using Ag$^+$,[6] vapor generation (VG) and the use of high performance liquid chromatography (HPLC) or gas chromatography (CG).[11] However, these approaches add complexity to the procedure; therefore, it was decided to rely on the pseudo-high resolution mode to resolve this interference.

Although sulfur is present in seawater, no signal for the $^{34}S^1H^+$ polyatomic ion was observed for a seawater sample after submitting it to cation exchange chromatography, which is due to the low concentration of S compared to Cl in seawater, for which the $[S0_4^{2-}]/[Cl^-]$ ratio is, on average, 0.14.[22]

In order to promote the formation of $^{34}S^1H^+$ and thus, to identify the exact positions of the signals of the analyte and interfering ions, the spectral peaks at *m/z* ratios of 35 and 37 (Fig. 1) were recorded for a standard solution containing 1 mg L^{-1} of Cl and 500 mg L^{-1} of S. As can be seen in Fig. 1, it is possible to identify a narrow mass window in the lower mass range (left side) of the signal in both figures in which the signal derives solely from Cl. Hence, the final measurements (static mode) were performed in these narrow mass windows with regular monitoring for mass shift. Additionally, due to the use of wet plasma conditions, it is possible to observe a significant contribution of polyatomic ions containing O and H to the signal measured at an *m/z* ratio of 35 and containing Ar and H at an *m/z* ratio of 37.

Memory effects

Cl isotope ratio measurement via PN-MC-ICP-MS is hindered by pronounced memory effects, which may also significantly affect isotope ratio measurements. Several wash solutions were studied in terms of washout behavior. Rapid reduction of the Cl signal intensity back to background levels is especially desirable when using external correction in a sample-standard bracketing correction for mass bias correction.[12,17,23] Three different wash solutions were evaluated: 0.14 mol L^{-1} HNO$_3$, ultrapure water (as obtained from a *Mili-Q* system) and 5 mmol L^{-1} NH$_4$OH. The standards were also prepared in the corresponding medium.

Fig. 2 presents the effect of these three different wash solutions on the remaining signal after measuring a standard containing 100 mg L^{-1} of Cl and made up in the same medium. Under acidic conditions, the formation of HCl is favorable,[11] which is not easily washed out due to vapor formation and retention of the vapor formed inside the spray chamber.

Chlorine concentration and mass bias correction

Due to its high ionization potential, the sensitivity demonstrated by ICP-MS for Cl is low when compared to other elements, an effect that is more pronounced using pneumatic nebulization due its low sample introduction efficiency when compared to vapor generation.[14,15] Therefore, establishing the minimum concentration required for Cl isotope measurement is a critical factor. Fig. 3 presents the difference in accuracy and precision observed at different Cl concentrations.

Under the conditions adopted in this work, the Cl isotope ratio could be measured with good accuracy and precision ($^{37}Cl/^{35}Cl = 0.319765 \pm 0.000022$ for NIST SRM 975a, RSD ~ 0.007% for n = 3) at a Cl concentration of ≥ 70 mg L^{-1}.

A high concentration of Cl is required due its low Ionization efficiency, which is estimated according to the *Saha* equation to be approximately 0.9%, while for the majority of the elements commonly determined by ICP-MS, this value is higher than 90%,[24] such that a Cl concentration approximately 100-fold higher than typical for other elements is required.

The relatively high concentration of Cl required for high-quality isotope ratio measurements via PN-MC-ICP-MS, is not

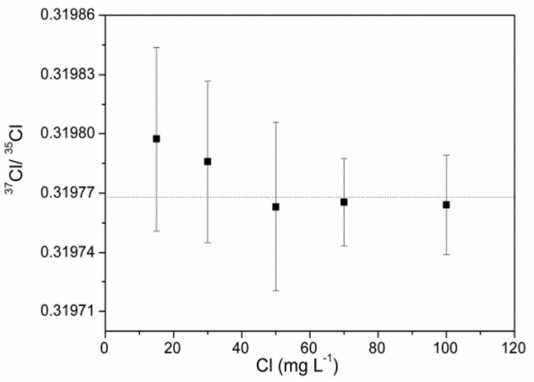

Fig. 3 Effect of Cl concentration on the Cl isotope ratio as measured using MC-ICP-MS (wet plasma conditions) in a solution of NIST SRM 975a NaCl (mass bias corrected for by external correction in a sample-standard bracketing approach, n=3).

problematic as the concentration of Cl in the natural sources of interest, such as seawater, is normally >> 100 mg L^{-1}.[18]

Mass bias correction was accomplished via external correction using an SSB approach. To obtain the best performance using this correction method, it is important that both, standard and sample solutions are matrix- and concentration-matched and the time interval between the measurement of two successive solutions (standard and sample or sample and standard) should not be too long. In this work, the major cation load of the samples was removed via cation exchange chromatography and pronounced Cl memory effects were avoided by using 5 mmol L^{-1} NH_4OH as wash solution. Under these conditions, the time interval between the analyses of two solutions was limited to 3 min and external correction was proven feasible.

Fig. 4 presents raw measurement data and the corresponding mass bias corrected values. The bias between the raw data and the corresponding “true” isotope ratio is approximately 10% (5% per amu). The SBB approach for mass bias correction provided a accurate results.

Table 2 Experimentally determined δ^{37}Cl (vs. SMOC) values obtained via PN-MC-ICP-MS (n=3, mean ± standard deviation).

Sample	**Obtained value**	**Reference value**
[a]BCR CRM 579	0.00 ± 0.01	0.006 ± 0.038[1,*]
NIST SRM 975a	0.13 ± 0.08	0.2[15]
NH_4Cl (post-column)	0.89 ± 0.12	-
NH_4Cl	0.86 ± 0.10	-
KCl	-0.54 ± 0.08	-
NaCl	0.14 ± 0.07	-

*Average value calculated for several seawater samples, as reported by Brand, *et al.* [1]

[a] Number of replicates n=10 for this sample.

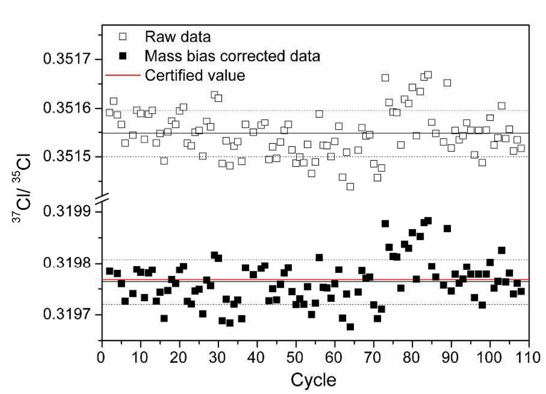

Fig. 4 Mass bias correction in PN-MC-ICP-MS using external correction in a sample-standard bracketing approach for NIST SRM 975a NaCl standard, at a Cl concentration of 100 mg L^{-1} and using a wash time of about 3 min with 5 mmol L^{-1} NH_4OH.

Sample preparation and method accuracy

The sample preparation approach described earlier allows efficient removal of the major cation load – as confirmed by the absence of Na (< LoD = 0.1 µg L^{-1}) in the post-column solution. Absence of Cl isotope fractionation was demonstrated by the results for δ^{37}Cl in NH_4Cl, analyzed before and after passage through the cation exchange column (Table 2) and recovery tests, which provided an average recovery of 99.4 ± 1.1 %. This comes as no surprise as Cl^- is not expected to show any affinity towards the chromatographic resin.

The results (Table 2) obtained for the seawater sample (BCR CRM 579) and for NIST SRM 975a were in good agreement with the values reported in the literature. A variation in δ^{37}Cl from -0.07 to +0.08‰ has been reported for seawater; the reference value reported in Table 2 is the average of the δ^{37}Cl values obtained for seawaters from different geographical locations.[1] δ^{37}Cl values were also reported for NaCl and KCl by Numata, *et al.*[6] However, the values found by these authors, +0.91 ± 0.15 for NaCl and -2.24 ± 0.07 for KCl, differ significantly from the values determined in the current work (Table 2). These differences may be attributed to differences in the production process of the reagents or in the source of the salts as products from a different brand were used in this work.

Conclusions

Despite the occurrence of spectral interference, memory effects and the characteristic low sensitivity, isotopic analysis of Cl in seawater can be successfully performed using PN-MC-ICP-MS (wet plasma conditions). High mass resolution, the use of 5 mmol L^{-1} NH_4OH as a wash solution and a minimum Cl concentration of 70 mg L^{-1} were required to achieve accurate and precise results. The method is applicable to seawater samples and to saline solutions, after a simple chromatographic cleanup step. The proposed procedure is simpler and faster than other methods typically deployed for Cl isotopic analysis.

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