

# Precise measurement of chlorine isotopes by thermal ionization mass spectrometry

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**Abstract** A procedure for the determination of chlorine isotopic ratios by positive thermal ionization mass spectrometry of the  $\text{Cs}_2\text{Cl}^+$  ion has been investigated. The chlorine isotopic composition in  $\text{CsCl}$  spectroscopically pure has been measured with a precision of 0.034. The chlorine composition in sea water samples has also been determined.

**Key words** chlorine isotopes • mass spectrometry • thermal ionization

## Introduction

Chlorine has the two naturally occurring isotopes,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , with relative abundances of about 0.7553 and 0.2547, respectively [1]. The first measurement of the isotopic abundance of chlorine has been reported by Aston 1941, and recently the interest for chlorine isotopes arose. Subsequently, electron impact ionization has been used in several experimental determinations of chlorine isotopic abundance. Owen and Schaeffer [5] as well as Kaufman *et al.* [3] determined  $^{37}\text{Cl}/^{35}\text{Cl}$  ratios based on the measurement of  $\text{CH}_3\text{Cl}^+$  produced by ionization of methyl chloride. Variations in  $^{37}\text{Cl}/^{35}\text{Cl}$  and D/H ratios were minimized by using the same batch of methyl chloride. The experimental error for isotopic ratios were 0.2%. Kaufmann *et al.* [3] increased the precision of the measurement to 0.024% and reported significant isotopic variation in natural chloride. Hoering and Parker [2] used an HCl gas to measure chlorine isotopic ratios in 81 samples of natural materials and they found no significant variations beyond their stated limit of 0.1%. HCl was chosen as the source material because it could be prepared quantitatively from a small sample and because it had a sampler cracking pattern as distinct from methyl chloride in the mass spectrometer. However, HCl has disadvantages of being corrosive and possessing a long-term mass spectrometric memory effect [4].

A procedure for determination of the absolute isotopic abundance ratio of natural chlorine was reported by Shields *et al.* [6] based on negative thermal ionization mass spectrometry of  $\text{Cl}^-$ . The  $^{37}\text{Cl}/^{35}\text{Cl}$  ratio of 3.1272 was reported with an uncertainty of 0.2‰, resulting in a calculated atomic weight of Cl of 35.45273. Recently, Vengosh *et al.* [7] studied the isotopic composition of Cl in geological materials using negative thermal ionization and showed that the  $^{37}\text{Cl}$  isotope is incorporated preferentially into the solid phase of the halite-brine and carnallite-brine systems with fractionation factors of 0.2‰ and 0.4‰, respectively.

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However, control of the mass spectrometric determination factor in negative thermal ionization of  $\text{Cl}^-$  may be a problem because of the relatively light masses of the chlorine isotopes.

In this study, a positive thermal ionization mass spectrometric method for chlorine measurement based on the ion  $\text{Cs}_2\text{Cl}^+$  has been developed.  $\text{Cs}_2\text{Cl}^+$  has a high mass (301 and 303) and the mass spectrometric discrimination effect is small and reproducible, resulting in precise isotopic ratio measurement. The aim of this work was the application of this high measurement precision to study the possible variation in chlorine isotopic abundances in sea water samples.

## Materials and methods

We investigated in detail the characteristics of graphite in the thermal emission of  $\text{Cs}_2\text{Cl}^+$  ions. We indicated that the  $\text{Cs}_2\text{Cl}^+$  ion was more suitable than  $\text{Rb}_2\text{Cl}^+$  for determination of chlorine isotopes because Cs is monoisotopic and no corrections are required to chlorine ratios which are determined directly. Xiao *et al.* [8] reported previously that strong  $\text{Cs}_2\text{Cl}^+$  ion peaks were observed during measurement of boron isotopes using  $\text{Cs}_2\text{BO}_2^+$  species. The amount of CsCl that was loaded in these experiments corresponded to a level of 5  $\mu\text{g}$  of chlorine. The  $\text{Cs}_2\text{Cl}^+$  ion is monitored and used to focus the instrument. This ion intensity is adjusted to  $6 \times 10^{-12}$  A by controlling the filament current. The data are collected on spiraltron by switching magnetically between the masses 301 and 303.

## Reagents

High purity reagents were used in this study. The HCl standard solution was prepared from seawater using cation exchange chromatography with resin in the  $\text{Ba}^{2+}$  form. The reference solution of chlorine for isotopic measurement was prepared by diluting the HCl solution with water to a concentration of 2 mg per ml. Spectroscopic grade graphite was mixed with ethanol and water to form a graphite slurry. The  $\text{Cs}_2\text{CO}_3$  reagent was used directly.

## Mass spectrometry measurements

Flat undegassed Re filaments ( $7.5 \times 0.76 \times 0.025$  mm) were used. At first the filaments were treated with 3  $\mu\text{l}$  of the graphite slurry or about 10  $\mu\text{g}$  of graphite to coat the whole filament. The slurry was allowed to go nearly to dryness before addition of the sample solution, which was prepared by neutralizing HCl with  $\text{Cs}_2\text{CO}_3$  solution. The sample solution was dried for 2 min with a current of 1.1 A passing through the filament. The filaments were loaded into the source of the mass spectrometer and the isotopic analysis is begun when the base pressure in the instrument was  $10^{-7}$  torr. The data were collected by switching magnetically between the masses 301 ( $^{133}\text{Cs}_2^{35}\text{Cl}^+$ ) and 303 ( $^{133}\text{Cs}_2^{37}\text{Cl}^+$ ). Data were acquired for a period of 1.5 h with a high precision of 0.034.

The analyses were carried out on a 12-in radius,  $90^\circ$  sector, magnetic instrument of local design. Isotopic composition of seawater sample is reported as per mil deviation of the  $^{37}\text{Cl}/^{35}\text{Cl}$  ratio, where  $\delta^{37}\text{Cl}/^{35}\text{Cl} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 10^3$ , and R is the measured  $^{37}\text{Cl}/^{35}\text{Cl}$ .

## Interferences

Impurities in the sample can cause interferences, poisoning the ionization process that will result in changes of natural isotopic fractionation. The presence of nitrate and sulphate anions was examined and no peak were observed in the mass spectrum from  $m/z$  290–305 under normal operating conditions. Ba and Ca are the major ingredients of sea waters and their presence did not significantly effect the ionization process.

## Results

A method for separating chloride from the sulfate,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  was developed in preparation for mass spectrometric measurements using  $\text{Cs}_2\text{Cl}^+$  [7]. A chloride separation based on anion exchange and AgCl precipitation is effective, but suffers from complexity and a high blank for chlorine. We applied a method based on cation exchange with resin in the  $\text{Ba}^{2+}$  form followed by cation exchange with resin in the  $\text{H}^+$  form which removes the remaining cations. Since there is no ion exchange between the resin and chloride which is directly eluted, there is no possibility of isotopic fractionation due to the separation.

The validity of the method was checked on the seawater sample collected in Constanca (Romania). The commercial NaCl was used as the working standard that was determined in respect to the Arizona laboratory seawater standard ( $\delta^{37}\text{Cl}/^{35}\text{Cl} = 0.00\text{‰}$ ). The three measurements gave the mean value of  $0.39 \pm 0.03$  for  $\delta^{37}\text{Cl}$ .

The NaCl laboratory standard samples were dissolved in water and the above separation was applied to all the solution samples. The chlorine is eluted as HCl in this separation. The HCl is neutralized as described above by the addition of  $\text{Cs}_2\text{CO}_3$  to pH 3 for mass spectrometric loading.

The result from triplicate samples of seawater was  $8.8 \pm 1.2$  for  $\delta^{37}\text{Cl}$ . Since the chlorine isotopic composition of seawater is uniform [8], a high obtained value probably resulted from chemical preparation and mass spectrometry equipment. This method is in progress and we expect the improvement of applicability.

## Conclusions

The positive thermal ionization mass spectrometric procedure based on measurement of  $\text{Cs}_2\text{Cl}^+$  reported here is accurate, precise and simple to implement. The addition of graphite in filament loading significantly enhances  $\text{Cs}_2\text{Cl}^+$  emission from CsCl, thus increasing the sensitivity. This increased sensitivity and the demonstrated ratio measurement precision are significant improvements over other mass spectrometric methods. The combined separation – mass spectrometry procedure is simple to apply when compared with the high precision gas mass spectrometric method for chlorine measurement. The method is ideally suited to studying the variation of chlorine isotopic composition in nature.

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