

Evaluation of Chlorine Isotope Blank in Cl-37/Cl-35 Isotopic Measurements Using Total Evaporation Thermal Ionization Mass Spectrometry (TE-TIMS)

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Abstract We report the analytical method for chlorine isotope ($^{37}\text{Cl}/^{35}\text{Cl}$) by total evaporation thermal ionization mass spectrometry (TE-TIMS). Replicate analyses of CsCl standard solution and seawater chloride yielded an analytical reproducibility for $^{37}\text{Cl}/^{35}\text{Cl}$ better than 0.2‰ for 2 μg -Cl. Reproducibility seems to be strongly controlled by counting statistics of total amounts of $\text{Cs}_2^{35}\text{Cl}^+$ ($m/e=301$) and $\text{Cs}_2^{37}\text{Cl}^+$ ($m/e=303$) ion beam intensities integrated by Faraday cups. Blank loading runs using CsNO_3 without chlorine yielded chlorine blanks derived from mass interferences from filament and activator with a little higher $^{37}\text{Cl}/^{35}\text{Cl}$ ratio than the median of the CsCl standard isotopic ratio. The signal of chlorine blank, (less than 3×10^{-15} A), however, was too low to be detected by Faraday cups. Thus, it is unlikely that the blank signal influences the measured value of chlorine isotope ratio for the sample with more than several hundred nano-g of chlorine.

Key words: Chlorine blank, total evaporation, Chlorine isotopic ratio, TE-TIMS

1. Introduction

Chlorine is composed of two stable isotopes, ^{35}Cl and ^{37}Cl , which can be measured by two completely different methods, gas source dual inlet isotope ratio mass spectrometry (IRMS) and by TIMS (Godon *et al.*, 2004). The former is better for the large samples ($>300 \mu\text{g}$ of Cl) with a reproducibility of $<0.1\%$ (2σ) and the latter, which is sensitively and stably detected in the form of Cs_2Cl^+ in TIMS (Xiao & Zhang, 1992, Xiao *et al.*, 1995), is better for the small samples (1–50 μg of Cl) with a reproducibility of 0.2‰ (2σ) (Xiao *et al.*, 2002). In this study, we adapt TIMS for the measurement of chlorine isotopes, because of its high sensitivity. This Cs_2Cl^+ method uses a high mass ($m/e=301, 303$) and the mass dependent isotope fractionation (mass discrimination effect) is relatively small and reproducible, which results in precise isotopic measurement. As this element has only two isotopes, however, the mass discrimination effect cannot

be corrected by internal correction utilizing the isotope ratio of two of the stable isotopes, combined with conventional TIMS. In such cases, the total evaporation method, which has been used for precise and accurate analysis of isotopes of U, Pu, Ra, Re (Callis & Abernathy, 1991; Fiedler *et al.*, 1994; Hara *et al.*, 1997; Aggarwal *et al.*, 2000; Yokoyama and Nakamura, 2004; Suzuki *et al.*, 2004) could be also adapted for chlorine isotopic ratio determinations (Miyata *et al.*, in prep.)

For more precise, accurate and sensitive chlorine isotope determinations in TE-TIMS, it is important to evaluate the influence of chlorine blank, derived from the filament, activator and the ion source chamber of TIMS. However, previous studies seem to have not paid enough attention on it. In this work, we report the influence of the chlorine isotope blank in TIMS using TE-TIMS (Miyata *et al.*, in prep.)

2. Experiments

2.1. Sample solutions and materials

Commercial grade CsCl (>99%, Nacalai tesque) was used for chlorine standard, which was stored as 9.5 g/L (2 g-Cl/L) solutions. Seawater samples used in this study were collected during the KH-04-3 cruise by research vessel Hakuho-maru of Ocean Research Institute, The University of Tokyo. We use flat undegassed Ta filaments (99.95%; 0.025×0.75 mm, Nilaco) with a high purity graphite (JMC) as activator to enhance Cs₂Cl⁺ beam. Water was deionized with a mixed-bed resin using a Milli-Q water system (Millipore Co.)

2.2. Instrumentation

Isotopic measurements of chlorine in this study were performed a solid-source thermal ionization mass spectrometer, VG Sector 54-30 at the National Science Museum. The mass spectrometer is equipped with seven Faraday cup collectors at the end of the magnet and a Daly detector system, which is placed at the end of the electrostatic filter (ESF).

2.3. Chemical separation

Seawater separation technique used at this study basically followed that described in Numata *et al.* (2001). The seawater sample was passed through Ba-form cation exchange resin (AG 50 W×8) to remove sulphates, and then through Cs-form cation exchange resin (AG 50 W×8) to produce a solution of CsCl. This solution was loaded on a Ta filament together with graphite solution and dried up.

2.4. Total Evaporation-TIMS (TE-TIMS)

Chlorine isotope measurements by total evaporation technique (TE-TIMS) were carried out in the following way, the detail description will be reported elsewhere (Miyata *et al.*, in prep.):

One isotope measurement run consisted of many cycles, one cycle was made of 5 seconds-integration. During each cycle, all of the ions which reached to the Faraday cups, Axial

(Cs₂³⁵Cl, m/e=301) and High 1 (Cs₂³⁷Cl, m/e=303) were integrated. The filament current was raised by 0.005 A/cycle until 1.8 V and 0.003 A/cycle from 1.8 V to 2.4 V and then 0.001 A/cycle until 3.0 V. When the intensity increased beyond the preset value (3.0 V), the filament current was kept constant or reduced in order to keep the Cs₂Cl⁺ ion beam intensity nearly constant. An isotope measurement run is stopped when the ion signal decays away. The number of cycles in an isotope measurements run depend on the amount of chlorine loaded on filaments. The signals of four hundred nano-gram and two microgram loadings typically last 300 and 2000 cycles, respectively. An example of chlorine isotope ratio measurements by TE-TIMS could be schematized in Fig. 1. Fig. 1 shows the Cs₂³⁵Cl ion beam (m/e=301) profiles and behavior of the individual Cs₂³⁷Cl/Cs₂³⁵Cl ratio and integrated ratio. Fluctuations in the individual ratio are observed, the integrated ratio increased almost monotonously with time.

3. Results and Discussion

3.1. Replicate analyses of CsCl standard (Nacalai tesque) and seawater

The results of chlorine isotopic measurements of CsCl solution are shown in Table 1. The total integrated Cs₂³⁵Cl voltages (V) are positively correlated with the loading amounts of the CsCl solution. The ³⁷Cl/³⁵Cl ratio is obtained with a high reproducibility (0.320355±0.000056 (1σ), R.S.D.=0.17%) for 2 μg-Cl of a CsCl standard solution using TE-TIMS. This reproducibility is similar to the analytical uncertainty of the previous studies (0.1~0.2%) with conventional-TIMS measurement (Xiao & Zhang, 1992; Xiao *et al.*, 1995).

The results of chlorine isotopic measurements of seawater chloride are shown in Table 2. In the case of chlorine separated from seawater, the integrated Cs₂³⁵Cl voltages of seawater chlorine are much lower than that of the CsCl standard at the same loading amounts of chlorine because of the sample matrix effects. However, the ³⁷Cl/³⁵Cl

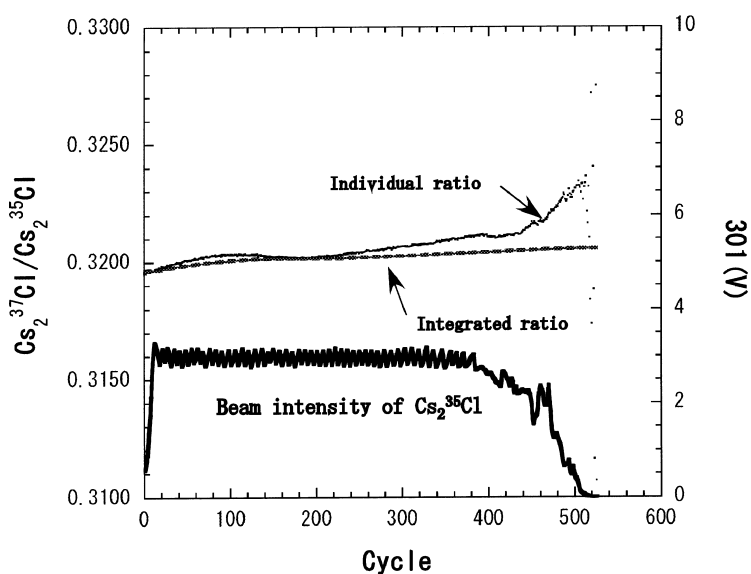


Fig. 1. $\text{Cs}_2^{37}\text{Cl}/\text{Cs}_2^{35}\text{Cl}$ ion beam profiles and the variation of individual $\text{Cs}_2^{37}\text{Cl}/\text{Cs}_2^{35}\text{Cl}$ ratio and integrated ratio.

Table 1. Replicate analyses of CsCl standard solution (nacalai tesque).

	Cl amounts	$\text{Cs}_2^{37}\text{Cl}/\text{Cs}_2^{35}\text{Cl}$ (mass 303/mass 301)	Total amounts of $\text{Cs}_2^{35}\text{Cl}$ voltage (V)
CsCl-1	200 ng	0.320754	72.3
CsCl-2	200 ng	0.321112	4.6
CsCl-3	400 ng	0.320462	862.4
CsCl-4	400 ng	0.320500	1251.0
CsCl-5	400 ng	0.320450	1070.0
CsCl-6	400 ng	0.320735	366.2
CsCl-7	400 ng	0.320674	447.4
CsCl-8	400 ng	0.320817	86.6
CsCl-9	400 ng	0.320708	763.6
CsCl-10	400 ng	0.320416	743.8
CsCl-11	400 ng	0.321062	447.7
CsCl-12	400 ng	0.320443	684.6
CsCl-13	400 ng	0.320493	1825.3
CsCl-14	400 ng	0.320370	1300.9
CsCl-15	400 ng	0.320694	1033.4
CsCl-16	2 μg	0.320298	4344.7
CsCl-17	2 μg	0.320355	7326.5
CsCl-18	2 μg	0.320337	4988.9
CsCl-19	2 μg	0.320430	7386.0
Average $\pm 1\sigma$ (n=19) (Cl amount upper 2 μg)		0.320585 ± 0.000237 (0.74%)	
Average $\pm 1\sigma$ (n=4)		0.320355 ± 0.000056 (0.17%)	

Table 2. Replicate analyses of seawater sample*.

	Cl amounts	$\text{Cs}_2^{37}\text{Cl}/\text{Cs}_2^{35}\text{Cl}$ (mass 303/mass 301)	Total amounts of $\text{Cs}_2^{35}\text{Cl}$ voltage (V)
Seawater-1	400 ng	0.320349	91.7
Seawater-2	400 ng	0.320453	207.3
Seawater-3	400 ng	0.320307	335.1
Seawater-4	400 ng	0.320265	506.4
Seawater-5	2 μg	0.320198	552.1
Seawater-6	2 μg	0.320437	1618.3
Seawater-7	2 μg	0.320374	1807.7
Seawater-8**	2 μg	0.320093	1275.9
Seawater-9	2 μg	0.320298	2315.5
Seawater-10	2 μg	0.320382	1863.5
Seawater-11	5 μg	0.320381	5018.4
Seawater-12	6 μg	0.320364	8358.8
Average $\pm 1\sigma$ (n=12) (upper 1000 V excluding No. 8**)		0.320325	± 0.000102 (0.32‰)
Average $\pm 1\sigma$ (n=6)		0.320373	± 0.000044 (0.14‰)

*seawater from KH-04-3 expedition

ratio derived from seawater is obtained with a high reproducibility (0.320373 ± 0.000044 (1σ), R.S.D.=0.14‰) for the measurements upper 1000 V excluding No. 8 sample. This reproducibility is also similar to the analytical uncertainty of the previous studies (0.1~0.2‰) with conventional-TIMS measurement (Xiao & Zhang, 1992; Xiao *et al.*, 1995).

3.2. The relationship between $\text{Cs}_2^{37}\text{Cl}/\text{Cs}_2^{35}\text{Cl}$ and total amounts of $\text{Cs}_2^{35}\text{Cl}$ actually integrated by Faraday cups

Fig. 2 shows the relationship between $\text{Cs}_2^{37}\text{Cl}/\text{Cs}_2^{35}\text{Cl}$ and total amounts of $\text{Cs}_2^{35}\text{Cl}$ actually integrated by Faraday cups. The samples of both CsCl standard and seawater with high integrated $\text{Cs}_2^{35}\text{Cl}$ signals have the chlorine isotopic ratios close to the median. This may imply that reproducibility depends on the counting statistics of the Faraday detectors. (Miyata *et al.*, in prep.)

The $^{37}\text{Cl}/^{35}\text{Cl}$ ratios of CsCl standard with low integrated $\text{Cs}_2^{35}\text{Cl}$ signals appear to be relatively higher than that of the median. On the contrary, the $^{37}\text{Cl}/^{35}\text{Cl}$ ratios of seawater with low integrated $\text{Cs}_2^{35}\text{Cl}$ signals seem to show opposite tendency. On the sufficient total amounts of $\text{Cs}_2^{35}\text{Cl}$ in-

tensity, the chlorine isotopic measurement by TE-TIMS has a high accurate and precision analysis.

3.3. Chlorine blank

The most of chlorine blank comes from mass interferences from activator and filament. Mass interferences on $m/z=301$ and 303 derived from the graphite and the Ta filament were checked by loading 1 μL CsNO_3 solution (11 g-Cl/L) onto a Ta filament instead of CsCl standard solution. No interference signal could be detected on Faraday cups. An acquisition with the ion counting Daly detector system gave 3×10^{-15} A signals on 301. The interference signal acquired on Daly detector seems to have relatively higher $^{37}\text{Cl}/^{35}\text{Cl}$ ratios, ranging from ~ 0.313 to ~ 0.321 . Considering the small intensity of the interference signal, however, seems to suggest that mass interferences from the activator and filament may be negligible to the chlorine isotope measurements using TE-TIMS. Fig. 2 shows anti-symmetric distribution of the measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios. Many samples with low integrated signal intensity seem to have high $^{37}\text{Cl}/^{35}\text{Cl}$ ratios. This anti-symmetric distribution may suggest the presence of interference with high $^{37}\text{Cl}/^{35}\text{Cl}$ ratio in ion source chamber.

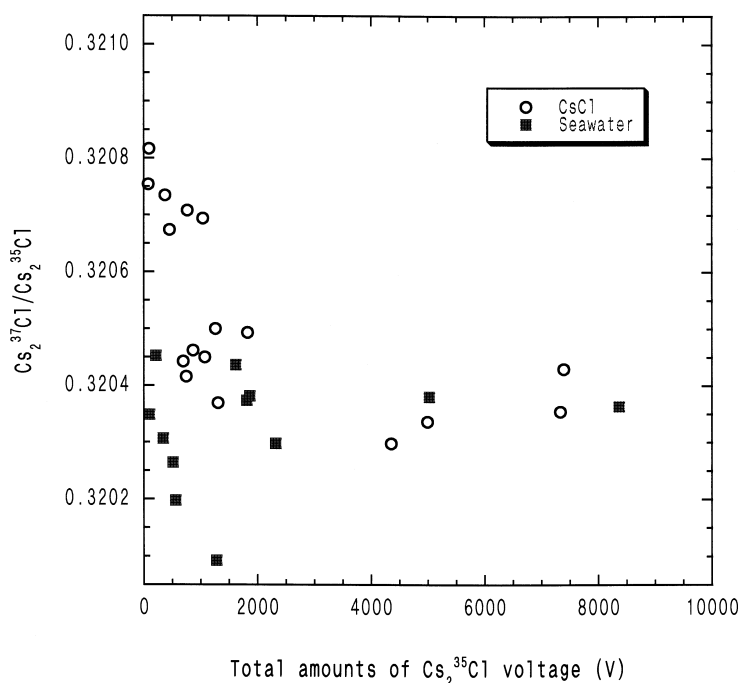


Fig. 2. Relationship between $Cs_2^{37}Cl/Cs_2^{35}Cl$ and total amounts of $Cs_2^{35}Cl$ actually integrated by Faraday cups.

In future, it is important to determine not only this chlorine isotopic blank ratio itself, but also blank values quantitatively using enriched isotope dilution TE-TIMS method, with or without chemical separation. As a result, we may be able to evaluate the possibility of the chlorine background of the ion source chamber and the ion lens system precisely.

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