Studies on Isotope Ratio Measurement of Cl by Inductively Coupled Plasma Triple-quad Mass Spectrometry

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Fundamental studies on isotope ratio measurement of Cl were carried out using inductively coupled plasma triple-quad mass spectrometry (ICP-MS/MS) and the analytical performance obtained was compared to that obtained by ICP sector field mass spectrometer (ICP-SFMS). Though the polyatomic ion interferences of $^{16}\text{O}^{18}\text{O}^+\text{H}$ and $^{36}\text{Ar}^+\text{H}$ with respect to ^{35}Cl and ^{37}Cl , respectively, made a negative effect on the accuracy and the precision for isotope ratio measurements of Cl, the ICP-SFMS could eliminate these interferences by medium mass resolution mode ($m/\Delta m = 4000$) and achieved the isotope ratio measurements with 0.2 – 0.5% of relative standard deviation (RSD) at the concentrations of Cl from 1 to 10 mg kg⁻¹. In the case of ICP-MS/MS, both the single-MS mode without collision reaction gas and the MS/MS mode with collision reaction gases such as oxygen (O₂) and hydrogen (H₂) were examined and compared their analytical sensitivities as well as the precisions of isotope ratio measurement of Cl. The precisions of Cl isotope ratio measurements were 3 – 14% of RSD at the concentrations of Cl from 5 to 100 mg kg⁻¹, when single-MS mode was carried out, even though the similar isotope ratios of $^{35}\text{Cl}/^{37}\text{Cl}$ could be obtained. In the case of O₂ gas for MS/MS mode with mass-shift method, precisions of 0.3 – 2% of RSD were obtained at the concentration range of 1 – 100 mg kg⁻¹. In the case of H₂ gas, similar sensitivities as those obtained by ICP-SFMS and the precisions of 0.2 – 0.5% of RSD at the concentration range of 1 – 10 mg kg⁻¹ were obtained. From these results, it was evaluated that the ICP-MS/MS in MS/MS mode with collision reaction gas could be used for Cl isotope ratio measurements for such studies as stable isotope tracers, isotope abundance measurements in nuclear chemistry and accurate determinations by isotope dilution mass spectrometry.

Keywords Isotope ratio measurement of Cl, ICP-SFMS, ICP-MS/MS, single-MS mode, MS/MS mode, collision reaction gas, oxygen, hydrogen

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Introduction

Isotope ratio measurement of elements is well recognized to be increasingly widespread use in disciplines such as bioavailability studies using stable isotope tracers,¹⁻⁶ isotope abundance measurements in nuclear chemistry,⁶⁻¹⁰ the determination of isotope variations in geological, environmental and cosmic samples including age determinations,^{3,4,11-19} food authenticity,^{3,4,20} or forensic science.^{3,4,21,22} Isotope ratio measurement is also important for the production of accurate analytical results in trace element determinations by isotope dilution mass spectrometry (IDMS).²³⁻²⁹ Isotope ratio measurements have traditionally been carried out by isotope ratio mass spectrometry (IRMS)^{3,12,13,20,22} and by thermal ionization mass spectrometry (TIMS).^{4,8,14,20} Disciplines of IRMS are the ability to accurately and precisely measure variations in the abundance of isotope ratios of light elements

such as H, C, N, O and S. On the other hand, TIMS can cover the whole range of elements from Li to U except for the gaseous elements measured by IRMS. An inductively coupled plasma mass spectrometry (ICPMS) has also been more and more involved in isotope ratio measurements, especially for heavy elements such as Fe, Cu, Mo, Cd, Cs, Nd, Hf, W, Tl, Pb, U, and so on.^{2,5-10,15-21,30-34} However, the subjects still remain with respect to the analysis of light elements such as H, C, N, and O as well as Si, S and Cl, that suffer from the huge background signals from H₂O, air entrainment (N₂, O₂, CO₂) and Ar plasma gas.

In the present study, the isotope ratio measurement of Cl by ICP triple-quad mass spectrometry (ICP-MS/MS) was examined because Cl is one of the subject elements for ICPMS measurement. Though the present study is out of scope for the isotope ratio measurements with high precision (0.005 – 0.0001% of relative standard deviation, RSD) which is expected by IRMS^{35,36} and TIMS,^{37,38} it is expected to be applicable to the studies for stable isotope tracers,^{2,5,6} isotope abundance measurements in nuclear chemistry^{7,8,10} and the accurate determination by IDMS,²³⁻²⁹ which require the precision of *ca.*

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Table 1 Operating conditions of ICP-SFMS (Element XR)

ICP torch	Fassel type quartz torch
Torch injector	Quartz injector with inner diameter of 1.7 mm
RF power	1300 W
Plasma gas (Ar)	15.0 L min ⁻¹
Aux. gas (Ar)	0.95 L min ⁻¹
Carrier gas (Ar)	0.96 L min ⁻¹
Spray chamber	Quartz double pass spray chamber
Nebulizer	Isomist (uptake rate: <i>ca.</i> 180 µL min ⁻¹)
Mass spectrometer	Sector field mass spectrometer
Mass resolution ($m/\Delta m$)	4000 (medium mass resolution mode)
Detector dead time	18 ns
Measured mass (m/z)	35 and 37
Number of peaks for mass	5 points/peak
Number of accumulation	600 times
Dwell time	2 ms
Repetition	10 times

0.5% RSD or less. In order to improve the analytical performance on the isotope ratio measurement of Cl by ICPMS, polyatomic ion interferences such as $^{16}\text{O}^{18}\text{O}^+\text{H}$ and $^{36}\text{Ar}^+\text{H}$ with respect to ^{35}Cl and ^{37}Cl , respectively, should be reduced. From these points of view, the fundamental studies on isotope ratio measurement of Cl were carried out by ICP-MS/MS using Cl standard solutions in the present study. The ICP-MS/MS and the ICP sector field mass spectrometer (ICP-SFMS), which were expected to reduce or eliminate the polyatomic ion interferences by the MS/MS with collision reaction technology and the high mass resolution analysis, respectively, were used for the isotope ratio measurements of Cl and basic analytical performances observed between ICP-MS/MS and ICP-SFMS were compared in the present study.

Experimental

Instruments

Tables 1 and 2 show the operating conditions of ICP-sector field mass spectrometer (ICP-SFMS, Element XR, Thermo Fisher Scientific) and ICP triple-quad MS (ICP-MS/MS, Agilent 8800, Agilent Technologies Inc.), respectively. The medium mass resolution mode ($m/\Delta m = 4000$) was applied for ICP-SFMS to eliminate polyatomic ion interferences of $^{16}\text{O}^{18}\text{O}^+\text{H}$ and $^{36}\text{Ar}^+\text{H}$ with respect to ^{35}Cl and ^{37}Cl , respectively. The detector dead time of 18 ns was set for ICP-SFMS, as also listed in Table 1. On the other hand, ICP-MS/MS consists of two quadrupole mass filters along with an octopole collision reaction cell (ORC). The ORC is set between first (Q1) and second quadrupole mass filters (Q2) and each mass filter can pass any selected mass (m/z) with unit mass resolution as MS/MS mode. The on-mass or the mass-shift methods can be selected in MS/MS mode whether or not Q1 and Q2 pass the same mass, respectively. The ICP-MS/MS can be also operated as single-MS mode if Q1 is operated as an ion guide. In the present study, both single-MS and MS/MS modes were examined for Cl isotope ratio measurements by ICP-MS/MS. The detector dead time of 30 ns was set in the present study, as shown in Table 2. In the case of single-MS mode, the collision reaction gas was not used, which demonstrated the isotope ratio measurement of Cl by conventional ICP quadrupole mass spectrometer (ICP-QMS) without collision reaction cell. Either oxygen (O_2) or hydrogen (H_2) gas was examined as collision reaction gas by

Table 2 Operating conditions of ICP-MS/MS (Agilent 8800)

ICP torch	Fassel type quartz torch
Torch injector	Quartz injector with inner diameter of 2.5 mm
RF power	1300 W
Plasma gas (Ar)	15 L min ⁻¹
Aux. gas (Ar)	0.95 L min ⁻¹
Carrier gas (Ar)	0.85 L min ⁻¹
Sweep gas (Ar)	0.30 L min ⁻¹
Spray chamber	Scott type double pass spray chamber
Nebulizer	PFA-100 (uptake rate: <i>ca.</i> 180 µL min ⁻¹)
Mass spectrometer (MS)	Quadrupole mass spectrometer
MS mode	MS/MS or single-MS
Measured mass (m/z)	35 and 37 in single-MS mode without collision reaction gas 35 (Q1) → 37 (Q2) and 37 (Q1) → 39 (Q2) in MS/MS mode with H_2 gas 35 (Q1) → 51 (Q2) and 37 (Q1) → 53 (Q2) in MS/MS mode with O_2 gas
Number of peaks for mass	3 points/peak
Number of sweeps	1000 times
Dwell time	1 ms
Repetition	10 times
Collision reaction gas	O_2 gas or H_2 gas or non gas

ICP-MS/MS in MS/MS mode with mass-shift method. In the case of O_2 gas, $^{35}\text{Cl}^{16}\text{O}$ ($m/z = 51$) and $^{37}\text{Cl}^{16}\text{O}$ ($m/z = 53$) transmitted sequentially by Q2, which could be obtained by the reaction between the O_2 gas and either ^{35}Cl or ^{37}Cl transmitted sequentially from Q1, were measured for the isotope ratio measurement of Cl. On the other hand, $^{35}\text{Cl}^+\text{H}_2$ ($m/z = 37$) and $^{37}\text{Cl}^+\text{H}_2$ ($m/z = 39$) transmitted by Q2 were measured after the reaction between the H_2 gas and either ^{35}Cl or ^{37}Cl transmitted sequentially from Q1. The optimum flow rate of collision reaction gas was also examined in the present study.

Samples

A 1000 mg kg⁻¹ of Cl standard solution with Milli-Q purified water (Millipore, USA) was prepared at National Metrology Institute of Japan (NMI) from high purity sodium chloride (NaCl) powder whose purity was characterized well by NMIJ. The concentrations of 1 – 100 mg kg⁻¹ of Cl standard solutions for isotope ratio measurements were prepared by further dilution of the 1000 mg kg⁻¹ of Cl standard solution with Milli-Q purified water. The Milli-Q purified water was also used as a blank solution (0 mg kg⁻¹) for the Cl standard solutions.

Cl isotope ratio measured

The Cl isotope ratio measured was calculated by Cl related isotope signals of ^{35}Cl , ^{37}Cl , $^{35}\text{Cl}^{16}\text{O}$, $^{37}\text{Cl}^{16}\text{O}$, $^{35}\text{Cl}^+\text{H}_2$ and $^{37}\text{Cl}^+\text{H}_2$. All signals measured were blank subtracted ones and the net signals were used for the calculation of Cl isotope ratios. Though the Cl isotope ratio calculated should be considered as Cl signal intensity ratio since mass bias was not corrected, the description of Cl isotope ratio was used in the text because the signal intensity ratio was strongly related to the isotope ratio.

Results and Discussion

Isotope ratio measurements carried out by ICP-SFMS

In the isotope ratio measurement of Cl, we had concerns that the polyatomic ions such as $^{16}\text{O}^{18}\text{O}^+\text{H}$ and $^{36}\text{Ar}^+\text{H}$ that interfered

Fig. 1 $^{35}\text{Cl}/^{37}\text{Cl}$ intensity ratios obtained by ICP-SFMS with medium mass resolution mode ($m/\Delta m = 4000$) as a function of concentrations of Cl. The bar indicates standard deviation obtained from 10 replicated measurements.

with ^{35}Cl and ^{37}Cl , respectively, would have a negative influence on the accuracy and the precision of measurements. Therefore, ICP-SFMS was applied since the mass spectra between Cl isotopes and polyatomic ion interferences could be separated by medium mass resolution mode ($m/\Delta m = 4000$). Figure 1 shows the obtained results for the isotope ratio measurements of Cl as a function of the concentrations of Cl standard solution in a range of 1 – 10 mg kg^{-1} . Though a linear correlation between the signals and the concentrations of Cl from 1 to 100 mg kg^{-1} for both Cl isotopes could be obtained, Cl isotope ratios observed for more than 30 mg kg^{-1} showed larger deviations, which were attributed to their analogue signals, compared to those obtained by pulse signals for 1 – 10 mg kg^{-1} . As can be seen in Fig. 1, similar Cl isotope ratios were observed for 1 – 10 mg kg^{-1} Cl standard solution and their relative standard deviations (%RSDs) obtained were 0.2 – 0.5% which provided enough precisions for such studies as stable isotope tracers,^{2,5,6} nuclear chemistry^{7,8,10} and quantitative analysis of elements by IDMS.^{23–29} The observed isotope ratios of *ca.* 2.83 revealed –9.6% deviation from the theoretical value of 3.13.³⁹ The deviation, called as mass bias, was attributed to the mass discrimination effect depending on the different type of mass spectrometers such as ICP-SFMS and ICP-QMS as well as their operating conditions. The similar isotope ratios (*ca.* 2.83) obtained at a certain concentration range (*e.g.* 1 – 10 mg kg^{-1}) are important for accurate isotope ratio measurements, since the mass bias obtained by the isotope ratio measurement of the standard solution is corrected by the theoretical value (3.13).³⁹ From these results, the isotope ratio measurements of Cl by ICP-SFMS with medium mass resolution mode was expected to be applicable to the studies for stable isotope tracers, nuclear chemistry and ID-ICPMS, even though the appropriate concentration range giving pulse signals should be considered in advance.

Isotope ratio measurements carried out by ICP-MS/MS in single-MS mode without collision reaction gas

The isotope ratio measurement of Cl by ICP-MS/MS in single-MS mode without collision reaction gas was carried out in the present study. The results observed are representative for those obtained by ICPMS with single quadrupole MS without collision reaction gas. Though the linear correlations between the signals for both Cl isotopes and their concentrations of 5 – 100 mg kg^{-1} could be obtained, the high background signal of ^{37}Cl attributed to the $^{36}\text{Ar}^1\text{H}$ polyatomic ion interference was

Fig. 2 $^{35}\text{Cl}/^{37}\text{Cl}$ intensity ratios obtained by ICP-MS/MS in single-MS mode without collision reaction gas as a function of concentrations of Cl. The bar indicates standard deviation obtained from 10 replicated measurements.

observed which resulted in poorer precision of isotope ratio measurements of Cl. Figure 2 shows the results of the Cl isotope ratios obtained by ICP-MS/MS in single-MS without collision reaction gas. The RSDs of 2 – 14% observed were larger than those obtained by ICP-SFMS, even though similar isotope ratios of *ca.* 2.2 attributed to polyatomic ion interferences were observed for the concentrations of 5 – 100 mg kg^{-1} . From these results, it was concluded that signals from the polyatomic ion interferences, especially $^{36}\text{Ar}^1\text{H}$, should be reduced to improve accuracy and precision for isotope ratio measurements of Cl by ICP-MS/MS.

Isotope ratio measurements carried out by ICP-MS/MS in MS/MS mode with collision reaction gas of oxygen (O_2)

In order to reduce the polyatomic ion interferences with respect to Cl isotopes and improve accuracy as well as the precision for isotope ratio measurements of Cl, MS/MS mode with oxygen (O_2) gas as collision reaction gas was examined by ICP-MS/MS. Figures 3(a) and 3(b) show the changes of both ClO signals and signal to background (S/B) ratios obtained as a function of O_2 gas flow rate as collision reaction gas in MS/MS mode with mass-shift method. The different masses were set for both Q1 and Q2 in mass-shift method as listed in Table 2. As can be seen in Figs. 3(a) and 3(b), the maximum ClO signals was observed at 0.2 mL min^{-1} of O_2 gas flow rate and obtained S/B ratios of ClO were larger than that obtained at 0 mL min^{-1} O_2 gas. From these results, the mass-shift method was expected to improve accuracy and precision for isotope ratio measurements of Cl. Figure 4 shows the results of the isotope ratio measurements of Cl as a function of Cl concentrations. The correlations observed between the signals for both Cl isotopes and their concentrations showed linear and the high background signal of ^{37}Cl attributed to the $^{36}\text{Ar}^1\text{H}$ polyatomic ion interference was significantly reduced by the observation of $^{37}\text{Cl}^{16}\text{O}$ in mass-shift method. The RSDs of 0.3 – 2% observed were smaller than those obtained by ICP-MS/MS in single-MS mode, and the similar isotope ratios of *ca.* 3.04, corresponding to –2.9% mass bias from the theoretical value of 3.13,³⁹ were observed within their standard deviations at the concentration range of 5 – 100 mg kg^{-1} . The mass bias observed (–2.9%) was smaller than that obtained by ICP-SFMS (–9.6%) and this was attributed to the different types of mass spectrometers as well as whether or not the use of collision reaction gas. The ICP-MS/MS in single-MS mode with O_2 gas, which could be corresponding to ICPMS with single quadrupole MS with O_2 gas, was also

Fig. 3 Signal intensities and signal to background (S/B) ratios observed for (a) $^{35}\text{Cl}^{16}\text{O}$ and (b) $^{37}\text{Cl}^{16}\text{O}$ obtained by ICP-MS/MS in MS/MS mode with mass-shift method as a function of O_2 gas flow rate as collision reaction gas.

Fig. 5 Signal intensities and signal to background (S/B) ratios observed for (a) $^{35}\text{Cl}^1\text{H}_2$ and (b) $^{37}\text{Cl}^1\text{H}_2$ obtained by ICP-MS/MS in MS/MS mode with mass-shift method as a function of H_2 gas flow rate as collision reaction gas.

Fig. 4 $^{35}\text{Cl}^{16}\text{O}/^{37}\text{Cl}^{16}\text{O}$ intensity ratios obtained by ICP-MS/MS in MS/MS mode of mass-shift method with 0.2 mL min^{-1} of O_2 gas as collision reaction gas as a function of concentrations of Cl. The bar indicates standard deviation obtained from 10 replicated measurements.

examined and observed RSDs and mass bias were 2 – 10% and *ca.* 2.45, respectively. The RSDs and the mass bias were similar to those observed by ICP-MS/MS in single-MS mode without collision reaction gas (2 – 14% and *ca.* 2.2, respectively). From these results, it was expected that the ICP-MS/MS in MS/MS mode with mass-shift method using collision reaction gas of O_2 could improve accuracy and precision for isotope ratio measurements of Cl.

Isotope ratio measurements carried out by ICP-MS/MS in MS/MS mode with collision reaction gas of hydrogen (H_2)

The use of hydrogen (H_2) gas as collision reaction gas was also examined by ICP-MS/MS in MS/MS mode to improve

Fig. 6 $^{35}\text{Cl}^1\text{H}_2/^{37}\text{Cl}^1\text{H}_2$ intensity ratios obtained by ICP-MS/MS in MS/MS mode of mass-shift method with 3 mL min^{-1} of H_2 gas as collision reaction gas as a function of Cl concentrations of (a) 1 – 100 mg kg^{-1} and (b) 1 – 10 mg kg^{-1} . The bar indicates standard deviation obtained from 10 replicated measurements.

Table 3 Comparison of detection capability on ^{35}Cl and ^{37}Cl

	^{35}Cl				^{37}Cl			
	ICP-SFMS with MR	MS/MS with O_2	MS/MS with H_2	Single MS without ORC gas	ICP-SFMS with MR	MS/MS with O_2	MS/MS with H_2	Single MS without ORC gas
Slope (cps/mg kg $^{-1}$)	400000	5400	640000	240000	150000	1800	220000	110000
Blank (cps)	58000	700	110000	48000	22000	250	38000	12000000
LOD (mg kg $^{-1}$)	0.05	0.02	0.01	0.01	0.05	0.03	0.01	0.8
BEC (mg kg $^{-1}$)	0.15	0.13	0.17	0.20	0.15	0.14	0.07	110

accuracy and precision for Cl isotope ratio measurements. Figures 5(a) and 5(b) show the changes of ClH_2 signals and their S/B ratios obtained as a function of the H_2 gas flow rate as collision reaction gas in MS/MS mode with mass-shift method, which set the different mass between Q1 and Q2 as listed in Table 2. As can be seen in Figs. 5(a) and 5(b), the maximum ClH_2 signals were observed at 3 mL min $^{-1}$ of H_2 gas flow rate and obtained S/B ratios of ClH_2 were *ca.* 2 fold larger than that obtained at 0 mL min $^{-1}$ H_2 gas. From these results, the mass-shift method was expected to improve accuracy and precision for isotope ratio measurements of Cl. Figures 6(a) and 6(b) show the results of the isotope ratio measurements of Cl as a function of Cl concentrations. The linear correlations between the signals and the concentrations of Cl for 1 – 100 mg kg $^{-1}$ could be obtained and the high background signal of ^{37}Cl attributed to the $^{36}\text{Ar}^1\text{H}$ polyatomic ion interference, was significantly reduced by the observation of $^{37}\text{Cl}^1\text{H}_2$ in mass-shift method. However, analogue signals were observed at the concentrations of more than 10 mg kg $^{-1}$ and 30 mg kg $^{-1}$ for ^{35}Cl and ^{37}Cl , respectively; which led to a larger deviation of the Cl isotope ratio compared to that obtained by pulse signal. As can be seen in Fig. 6(a), though similar RSDs to those obtained by ICP-SFMS were observed, different isotope ratios were observed in the concentration range of 30 – 100 mg kg $^{-1}$, which were due to the analogue signals obtained. The similar isotope ratios of *ca.* 2.96 with RSDs of 0.2 – 0.5% corresponding to –5.4% mass bias from the theoretical value were observed at Cl concentrations of 1 – 10 mg kg $^{-1}$ as shown in Fig. 6(b). The mass bias observed (–5.4%) was still smaller than that obtained by ICP-SFMS (–9.6%), but larger than that obtained by ICP-MS/MS in MS/MS mode with O_2 gas (–2.9%). The different mass biases obtained by ICP-MS/MS between H_2 and O_2 gases could be due to the different mass ranges measured between lighter (*m/z* 37 – 39) and middle (*m/z* 51 – 53) ones. The effects from polyatomic ion interferences that could not be removed completely were also considered. In the present study, ICP-MS/MS in single-MS mode with H_2 as collision reaction gas was not demonstrated because huge polyatomic ions of $^{36}\text{Ar}^1\text{H}$ and $^{38}\text{Ar}^1\text{H}$ were known to interfere with $^{35}\text{Cl}^1\text{H}_2$ and $^{37}\text{Cl}^1\text{H}_2$, respectively. From these results, it was expected that the ICP-MS/MS in MS/MS mode with mass-shift method using collision reaction gas of H_2 could improve accuracy and precision for isotope ratio measurements of Cl, even though the appropriate concentration range giving pulse signals should be considered in advance.

Comparison of the analytical sensitivity

Table 3 summarizes analytical sensitivities such as slope, blank, limits of detection (LODs, 3σ) and background equivalent concentration (BEC) observed for ICP-SFMS and ICP-MS/MS examined in the present study. The ICP-SFMS, ICP-MS/MS in MS/MS mode with H_2 gas and ICP-MS/MS in single-MS mode

without collision reaction gas showed similar values of slope and BEC for each Cl isotope, except for the BEC obtained by ICP-MS/MS in single-MS mode for ^{37}Cl which was attributed to the huge background signal from $^{36}\text{Ar}^1\text{H}$ polyatomic ion interference. The lower LODs could be obtained by the ICP-MS/MS with H_2 gas for both Cl isotopes as listed in Table 3. On the other hand, two orders of magnitude lower slope was observed for the ICP-MS/MS with O_2 gas, even though both BEC and LODs were similar to those obtained by other ICPMS. According to NASA's report,⁴⁰ the reaction rate coefficient of Cl^+ with respect to H_2 gas is 10^{-9} to 10^{-10} expecting *ca.* 100% reaction rate to form ClH_2 . On the other hand, the reaction rate coefficient of Cl^+ with respect to O_2 gas is not listed in the report, which lead us to expect very low reaction rate such as 1% or less to form ClO . The lower reaction rate might reflect lower slope observed for the ICP-MS/MS with O_2 gas, which allows similar isotope ratios of Cl with respect to the wider concentration range. From these results, since the suitable concentration ranges for Cl isotope ratio measurements were different between the ICP-MS/MS with O_2 gas (up to 100 mg kg $^{-1}$) and either ICP-SFMS or ICP-MS/MS with H_2 gas (up to 10 mg kg $^{-1}$), the operating conditions or the ICPMS instrument could be chosen with respect to the concentration of Cl in samples.

Conclusions

Fundamental studies on the isotope ratio measurements of Cl were carried out by ICP-MS/MS. The ICP-MS/MS in MS/MS mode with collision reaction gas showed better analytical results than that of the ICP-MS/MS in single-MS mode without collision reaction gas. The ICP-MS/MS in MS/MS mode with mass-shift method using collision reaction gas of H_2 showed similar analytical performance to that obtained by ICP-SFMS. The ICP-MS/MS in MS/MS mode with collision reaction gas of O_2 also showed sufficiently good analytical performance and it allowed for a wider Cl concentration range of 5 – 100 mg kg $^{-1}$ for similar isotope ratios of Cl. From these results, the ICP-MS/MS in MS/MS mode with mass-shift method using collision reaction gas could be useful for Cl isotope ratio measurements for the studies on stable isotope tracers, nuclear chemistry and accurate determinations by IDMS.

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