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A New Sample Processing Protocol for Separation and Purification Enabling Precise Analysis of Various Non-Traditional Isotopes in Geological Samples with Low Concentrations

Jianye Gui * and Wei Zou

Fujian Provincial Key Laboratory of Water Cycling and Eco-Geological Processes, Key Laboratory of Groundwater Science and Engineering of Nature Resources, Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences (CAGS), Zhengding 050803, China

* Correspondence: agui_mail@163.com; Tel.: +86-13315157801

Abstract: Many non-traditional isotopes, such as chlorine, magnesium, calcium, etc., are widely used as groundwater tracers. A new sample processing protocol of purification and concentration for isotopic analysis is presented to overcome many of the major drawbacks of existing methods. Contemporary sample preparation often requires several laborious off-line procedures in a ultra clean laboratory prior to instrumental determination; additionally, interference ions in real samples are difficult to completely remove, especially when the concentration of those ions is equal to that of the target ions. The new protocol includes the following steps: (i) one-step purification using a newly developed isotopic preparative chromatograph (IPC) with a background suppressed mode to obtain extremely pure components that only have target ions and H₂O; (ii) enrichment of the collected pure solution from the previous step using a newly developed ultra clean concentrator filled with high purity nitrogen; (iii) transforming the enriched target ion into suitable speciation inside the ultra clean concentrator; (iv) finally, sending the enriched solutions to a multi-collector inductively coupled-plasma mass-spectrometer (MC-ICP-MS) or thermal ionization mass spectrometer (TIMS). The present method was validated using certified reference materials and real samples for both chlorine and magnesium; the precision of chlorine ratio value was generally below 0.22‰ and that of Mg was below 0.12‰. This processing protocol provides a potential method for isotope sample preparation and analysis in a small number of geological samples with low concentrations of many other elements or compounds such as nitrate, sulfate, lithium, calcium, strontium, etc.

Keywords: matrix interference; stable isotopes; tracer; isotopic preparative chromatography (IPC); thermal ionization mass spectrometry (TIMS)



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1. Introduction

The geochemical cycling of metals and nonmetals in natural systems is often accompanied by stable isotope fractionation, which can now be determined thanks to recent analytical advances [1]. In consequence, a new research field has emerged over the last several decades, complementing the traditional stable isotope systems (C, H, O, N, S) with many more nontraditional elements across the periodic table (Cl, Br, Li, Mg, Ca, Sr, Si, Fe, Ni, Zn, Cu et al.) which are being developed and are potentially applicable as new geochemical tracers [2].

Stable isotope ratios of different elements in geological samples contain valuable information on sources and processes which have defined the behavior and fate of the samples [3]. Stable isotope analysis of light elements (C, H, O, S, N) has been successfully applied for many decades to study their geological cycling in many different settings and to address a variety of basic and knotty problems in the field of geochemistry or environmental

geology [4,5]. These so-called “traditional” stable isotopes include only chemical elements which can be conveniently transformed into a gaseous form and analyzed with gas isotope mass spectrometers, usually equipped with an electron impact ion source (EI). A lack of suitable protocols to resolve natural variations in the stable isotope ratio of heavier elements prevented further progress for a long time, mainly because the pure target elements are not easily obtained owing to the concomitant interference ions in real samples, especially when the concentration levels of those ions are equal to or higher than that of the target ions. Analytical improvements and equipment developments over the last two decades have now improved the feasibility of high-precision stable isotope analyses, making them applicable to plenty of elements in the periodic table, and thereby triggered the growing development of many new scientific fields.

Generally, the sample preparation of heavier elements is based on ion exchange resin, which is an off-line process, and this process need be performed in a ultra clean laboratory [6,7]. The requirements of the preparation process are very strict; incomplete adsorption, insufficient elution, and careless introduction of ambient impurities will lead to the failure of the process [2]. Ultra clean operating environments and purified acids are routinely analyzed for ultra-trace element compositions to ensure high purity and to exclude blank additions [8].

Preparative liquid chromatography has been used in many fields for many years. Ion chromatography, as a branch of liquid chromatography, was difficult to update to preparative ion chromatography because of the ion chromatographic column and suppressor. The higher sample volumes in preparative ion exchange column can lead to non-linear, broad, or overlapping elution peaks, and higher elution concentrations will be difficult to suppress in a normal suppressor volume.

The theoretical basis of preparative ion chromatography was proposed by Neville G, Pinto [9] and G.V. Samsonov [10]. Linear separation conditions of proteins were developed by Gallant, S. R. [11] and Gerberding [12], and many other preparative conditions for organic compounds were developed because no suppressor was required [13–16]. For the pure sample preparation of chlorine, magnesium, potassium, calcium etc., preparative ion chromatography was not invented until now. In order to achieve the goals of high precision analysis, a larger net content was required if we wish to use analytical ion chromatographic coupled with isotope mass spectrometry [17–19]. It is a challenge to attain 10 µg chlorine for TIMS or 0.7 µmol of chlorine for MC-ICP-MS, and only brine sample can meet the requirement [20].

The evolution process of liquid chromatography from analytical style to preparative style was reviewed by Jack Silver [21]. The preparation process of the ion exchange chromatographic column was furtherly optimized by Christopher A. Pohl [22], and commercial preparative ion chromatography was developed by Gui in 2020 [23], but it is a pity that only large concentration samples (>50 mg/L) can be prepared to satisfy the requirements of TIMS [24].

From the overview above, we can draw the conclusion that there are at least three problems to be solved: (1) precise analysis of isotopes in geological samples with low concentrations is still a challenge; (2) the preparative cost is still high because of the ultra clean requirement; (3) automatic preparative instruments which can satisfy TIMS and MC-ICP-MS urgently need to be developed.

The main purpose of this study was to develop an automatic effective processing protocol for isotope analysis in geological samples with low concentrations using isotopic preparative chromatograph coupled with a newly designed ultra clean concentrator. The major objectives included the following: (1) to present an alternative protocol for chlorine and magnesium isotope ratios analysis using a new sample preparation (2) to provide a new processing protocol for purification and enrichment in geological samples with low concentrations.

2. Materials and Instrumentation

2.1. Reagents and Chemicals

All chemicals and reagents used were GR (guaranteed reagent) grade. HCl, NaOH, HF, HNO₃, Na₂CO₃, NaHCO₃, Na₂SO₄, NaNO₃, and CsNO₃ were obtained from Sinopharm Chemical Reagent Co., Ltd. China, Shanghai, China. All dilutions to prepare calibration and working samples were performed in ultrapure water (18.2 MΩcm⁻¹) from a reverse osmosis system (Merk Milli-Q). Dowex 50 W × 8 H-resin (200–400 mesh) were purchased from DuPont company; tantalum filament (99.995%), ultra superior purity graphite powder (99.9999%, <200 mesh) were obtained from Alfa Aesar Supplier; ethanol and teflon resin column (about 100 μL) were from Merck (Darmstadt, Germany). Ground water standard material (GNM-M040352-2013), a second isotopic reference material of chlorine (ISL 354), were collected from seawater (located at 4°18' N, 161°08' E, and made by Qinghai Institute of Salt Lakes, Chinese Academy of Sciences (ISL 354); the ³⁷Cl/³⁵Cl values are 0.319025 ± 0.000038 and 0.319090 ± 0.00009 [25]. CDFN-SRM980 Mg standard were purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) and used as the bracketing standard during Mg isotope analysis; δ²⁶Mg value are −3.405‰, δ²⁵Mg value are −1.744‰.

2.2. Samples Preparation

A total of 9 sets of samples were used: sample ISL 354 was prepared by diluting standard material of chlorine with ultrapure water. Mixed solution M354 was prepared using chemical reagents and chlorine isotope standard material (with concentrations of Cl⁻, NO₃⁻ and SO₄²⁻ all are 20 mg/L for each), N-6 and N-8 were collected from a canal, and N-7,9,12,14,105 were groundwater near the canal. The compositions of Cl⁻, NO₃⁻ and SO₄²⁻ of those samples were measured using a Dionex ICS-1500 ion chromatograph equipped with an AS14 chromatographic column. Compositions of K⁺, Na⁺, Mg²⁺, and Ca²⁺ ions of those samples were measured with a Thermo iCAP6300 Inductively coupled plasma emission spectrometer. The detailed samples information are shown in Tables 1 and 2.

Table 1. The water-type and concentrations (average ± standard deviation, *n* = 3) of Cl⁻, NO₃⁻, and SO₄²⁻ ions in studied samples.

Sample No	Type	Cl ⁻ /mg/L	NO ₃ ⁻ /mg/L	SO ₄ ²⁻ /mg/L
ISL 354	Isotope standard	5000 ± 11	16.02 ± 0.65	3.31 ± 0.25
M 354	Mixed solution	20 ± 3.8	20 ± 5.3	20 ± 6.3
N-6	Surface water	5.59 ± 0.22	5.17 ± 0.26	25.69 ± 1.59
N-7	Groundwater	19.56 ± 1.97	6.03 ± 0.58	126.7 ± 2.99
N-8	Surface water	5.24 ± 0.19	4.44 ± 0.19	26.83 ± 1.1
N-9	Groundwater	16.42 ± 0.52	13.66 ± 0.31	58.41 ± 2.31
N-12	Groundwater	225.8 ± 6.22	66.95 ± 1.56	228.3 ± 5.91
N-14	Groundwater	85.78 ± 3.11	11.62 ± 0.18	84.13 ± 3.22
N-105	Groundwater	43.66 ± 2.64	7.94 ± 0.13	154.1 ± 3.92

Table 2. The water-type and concentrations (average ± standard deviation, *n* = 3) of K⁺, Na⁺, Mg²⁺, and Ca²⁺ ions in studied samples.

Sample No	Type	K ⁺ /mg/L	Na ⁺ /mg/L	Ca ²⁺ /mg/L	Mg ²⁺ /mg/L
STD-1	Isotope standard	0.05 ± 0.13	3.1 ± 0.3	1.02 ± 0.66	1000 ± 2.21
M 980	Mixed solution	20.00 ± 1.1	20.00 ± 2.2	20.00 ± 5.5	20.00 ± 1.27
NSBD-6	Surface water	2.02 ± 0.24	5.52 ± 0.26	39.85 ± 0.98	7.87 ± 0.28
NSBD-7	Groundwater	2.01 ± 0.15	14.99 ± 1.17	110.80 ± 2.99	18.29 ± 1.11
NSBD-8	Surface water	2.14 ± 0.22	5.75 ± 0.37	40.10 ± 1.18	7.90 ± 0.56
NSBD-9	Groundwater	1.34 ± 0.03	12.79 ± 0.87	70.91 ± 2.01	17.41 ± 1.06
NSBD-12	Groundwater	28.37 ± 2.12	113.80 ± 3.92	131.90 ± 4.28	4.23 ± 0.26
NSBD-14	Groundwater	1.58 ± 0.19	105.50 ± 5.01	56.47 ± 2.69	24.62 ± 1.29
NSBD-105	Groundwater	0.55 ± 0.22	40.78 ± 2.91	174.00 ± 5.98	21.49 ± 1.11

All the samples were filtrated using 200 mesh polyethylene film in order to remove solid particles. For Mg isotope analysis, the purified Mg portion was evaporated to dryness at 80 °C and redissolved in 2% HNO₃ (v/v). For Cl isotope analysis, 3 mol/L HNO₃ was used to transform the Dowex 50 W × 8 strong acid resin to H-type resin, then saturated CsNO₃ solution was used to transform the H-type resin into Cs-type resin. Both of them were washed to neutral with ultrapure water, after which spectroscopic-grade graphite powder was mixed with 80% ethanol—20% water (v/v) to form a slurry. The entire procedure was completed in the ultra clean concentrator [24].

2.3. Instrumental Setup, Tuning, and Data Acquisition

An isotopic preparative chromatograph (IPC Pre-Isotope I) (which was made in China by the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Shijiazhuang, China), coupled with a Dionex IonPac AS19 (4 × 250 mm) or Dionex IonPac CS12A (4 × 250 mm), was used to separate the Cl[−] from the NO₃[−] and SO₄^{2−} or to separate Mg²⁺ from K⁺, Na⁺, and Ca²⁺. Samples were injected with a syringe into a quantitative loop (about 100 μL). If the concentration of the samples was below 50 mg/L, the samples should be injected additional times in order to obtain 5 μg chloride or 5 μg Magnesium. The collected solutions (about 3 mL to 20 mL) were transferred to the ultra clean concentrator (which was made in China by the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences) filled with nitrogen (>0.9999) to evaporate to near-dryness.

2.4. Determination of Isotope Ratio

The measuring process was based on the method reported by Xiao [25]. The tantalum filaments were treated with 3 μL of a graphite slurry that consisted of about 100 μg graphite. A total of 5–10 μg chloride was added to the filament and evaporated nearly to dryness with 900 mA. Then, the sample was loaded into the mass spectrometer.

For the Cl isotope: The solutions were received from the conductivity cell and transformed into CsCl with the Cs-resin, then chlorine isotopic compositions were measured with the Thermo Scientific TRITON Mass Spectrometer. The Center Cup and H1 Cup were used to collect the ¹³³Cs₂³⁵Cl⁺ (*m/z* 301) and ¹³³Cs₂³⁷Cl⁺ (*m/z* 303), respectively, and 100 data were collected in 10 blocks in one analysis. All the parameters of instruments and measuring conditions are shown in Table 3.

Table 3. Optimum parameters of isotopic preparative chromatograph and thermal ionization mass spectrometer and their conditions.

Isotopic Preparative Chromatograph		Thermal Ionization Mass Spectrometer	
Type	Pre-Isotope I	Type	TRITON
Column	AS19	Accelerating field	10 kV
Eluent	30 mM NaOH	Magnetic field	81 cm
Flow rate	1 mL/min	Resolution ratio	451
Current	80 mA	Sensitivity	≥3 ion/100 μmol
Temperature	30 °C	Measuring ions	¹³³ Cs ₂ ³⁵ Cl ⁺ / ¹³³ Cs ₂ ³⁷ Cl ⁺
Inject volume	100 μL	<i>m/z</i>	303/301

For magnesium: The solutions were collected from the conductivity cell and diluted with 2% HNO₃, then magnesium isotopic compositions were measured with Multiple-collectors Inductively Coupled Plasma Mass Spectrometry (Nu-instruments NP II). All the parameters of instruments and measuring conditions are shown in Table 4.

Table 4. Optimum parameters of isotopic preparative chromatograph and MC-ICP-MS and their conditions.

Isotopic Preparative Chromatograph		MC-ICP-MS	
Type	Pre-Isotope I	Type	Nu-instruments NP II
Column	CS12A	RF powder	1300 W
Eluent	20 mM CH ₃ SO ₃ H	Cooling gas	13.0 L/min
Flow rate	1 mL/min	Auxiliary gas	0.8 L/min
Current	80 mA	Accelerating voltage	6000 V
Temperature	30 °C	Nebulizer	~37 psi
Inject volume	100 µL	Resolution	Low resolution (≥200)

3. Results and Discussion

3.1. Principle of Isotopic Preparative Chromatograph (IPC)

The isotopic preparative chromatograph (IPC) was modified on the basis of ion chromatography; the working principle of IPC is briefly introduced as follows: anion chromatography column AS19 was used to separate Cl[−] from the SO₄^{2−} and NO₃[−] according to the different retention times for those ions; the working mode of the suppressor was changed to external water supply with a higher suppressor current; the fraction collector was added to the outlet of the detector [23]. The eluted liquid from the column was injected into the suppressor to reduce the background of NaOH, and chromatographically pure chlorine was obtained in the form of HCl in pure water, which was extremely suitable for the following TIMS analysis.

The complex chemical reaction of the traditional purification process can hardly ensure high repeatability. The time, temperature, and chemistry reagents of the reaction, even personal skill, could cause differences in the analytical results. In this experiment, separation was completed with the automatic IPC instrument, so the above uncertain factors can be avoided.

3.2. Principle of Ultra Clean Concentrator

The ultra clean concentrator (UCC-Isotope-I) was developed on the basis of a nitrogen-blowing concentrator [26]; the working principle of UCC is briefly introduced as follows: a nitrogen-blowing concentrator was installed in a sealed glove box which was filled with high-purity nitrogen (>0.9999). The glove box consists of two chambers: a buffering chamber and an enclosed chamber. The samples were sent into the buffering chamber first and, after 2–3 replacements of the residual air, transferred into the enclosed chamber and placed on the heating module of the nitrogen-blowing concentrator. An automatic pressure sensor was internally installed in the enclosed stores to monitor the inside pressure; excess nitrogen will be released through the evacuation valve.

3.3. Confirming the Retention Time and Collection Time

Mixed solution (M354) was employed to confirm the retention time of Cl[−], NO₃[−] and SO₄^{2−} ions in AS19 chromatographic columns. As shown in Figure 1, the results indicate that the retention time of those ions in AS19 chromatographic columns had large intervals. It implied that those ions can be separated completely in the chromatographic column. The retention time for Cl[−], SO₄^{2−}, and NO₃[−] were 6.5–9.2 min, 12–14.8 min, and 23.5–30.0 min, respectively. As concentrations of Cl[−], SO₄^{2−}, and NO₃[−] increased, the retention time became enhanced, but the collection period was not influenced because of the adequate interval time for the separation of those ions. Due to the significant difference of retention time for Cl[−], SO₄^{2−}, and NO₃[−] in the chromatographic column, Cl[−] can be collected while the other ions are not eluted from the chromatographic column. According to the retention time of Cl[−], 6 to 10 min was regarded as the collecting time for AS19 chromatographic columns, and the recoveries are beyond 98%.

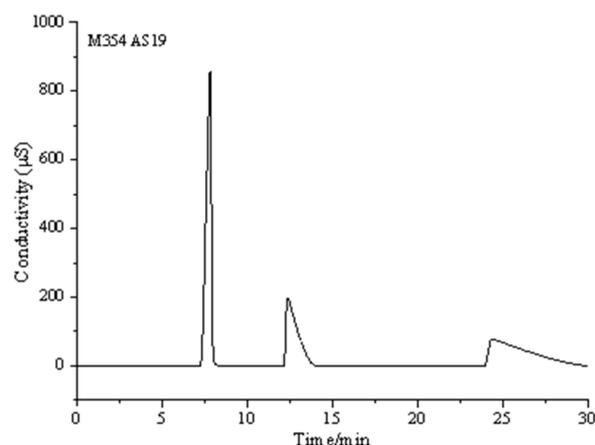


Figure 1. Confirm the retention time of Cl^- , SO_4^{2-} , and NO_3^- and collected time of Cl^- using M354 (a mixed solution with the concentrations of Cl^- , NO_3^- , and SO_4^{2-} all being 20 mg/L) in AS19 column.

Mixed solution (M 980) was used to confirm the retention time of K^+ , Na^+ , Mg^{2+} , and Ca^{2+} ions in CS12A chromatographic columns. As shown in Figure 2, the results indicated that the retention time of those ions in CS12A chromatographic columns had large intervals. This implies that those ions can be separated completely in the chromatographic column. Due to the significant difference of retention time for K^+ , Na^+ , Mg^{2+} , and Ca^{2+} in chromatographic column, Mg^{2+} can be collected while other ions are not eluted from the chromatographic column. According to the retention time of Mg^{2+} , 11.5 to 14.7 min was regarded as the collecting time for CS12A chromatographic columns, and the recoveries are beyond 96%.

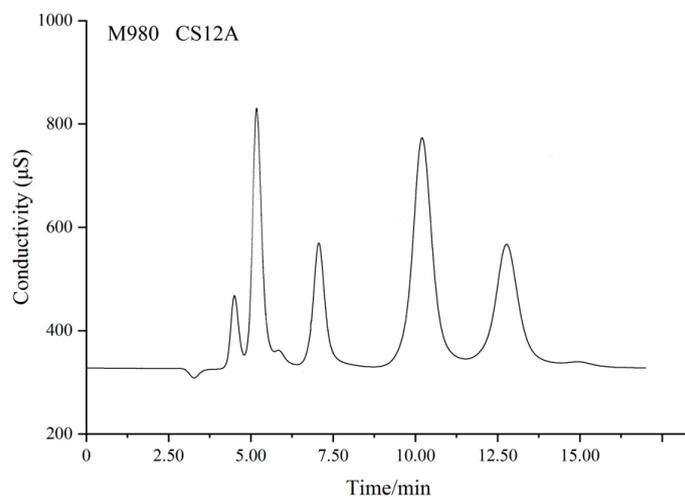


Figure 2. Confirm the retention time of K^+ , Na^+ , Mg^{2+} , and Ca^{2+} and collected time of Mg^{2+} using M354 (a mixed solution with the concentrations of K^+ , Na^+ , Mg^{2+} , and Ca^{2+} being 20 mg/L) in CS12A column.

3.4. Concentration of Samples and Times of Collections

Concentration dependence is necessary for isotope analysis. Samples with low concentrations is a problem that has long been pending a solution. An injection volume of 20–25 μL is usually used in analytical ion chromatography. In order to achieve a sufficient preparative quantity, 100 μL injection volume was employed in this preparative ion chromatography; using more than 100 μL will lead to non-linear elution, and broad, overlapping peaks will appear. In this condition, the analytical precision of samples with

lower than 50 mg/L will decline because of the low amount of Cl. More collection times is indispensable for different samples to achieve high precision data.

3.5. Analytical Results of Real Samples

A total of seven sets of real samples were collected in order to verify the new method. Both chlorine and magnesium isotopes were measured using this newly developed method. N-6 and N-8 were collected from a canal, and N-7,9,12,14,105 were from groundwater near the canal. The chlorine concentration of N-6 to 9 and N-105 ranged from 5.24–43.66 mg/L, so collection was repeated 12 times in order to obtain enough content. For magnesium, more than 12 repetitions were required for each sample because of the rather low concentration of magnesium. The details of collection times and recoveries are listed in Table 5, and the chlorine isotope and magnesium isotope results of determination in each sample are shown in Tables 6 and 7.

Table 5. Injection times and recoveries of different samples.

Sample No	Concentration of Cl ⁻ (mg/L)	Times of Preparation	Recovery (%)	Concentration of Mg ²⁺ (mg/L)	Times of Preparation	Recovery (%)
N-6	5.59	12	98.2	7.87	15	99.5
N-7	19.56	12	99.1	18.29	12	96.3
N-8	5.24	12	97.2	7.90	15	96.9
N-9	16.42	12	96.6	17.41	12	97.8
N-12	225.8	2	99.1	4.23	15	99.2
N-14	85.78	2	99.3	24.62	12	97.3
N-105	43.66	12	98.9	21.49	12	96.8

Table 6. Chlorine isotope results of determination in each sample.

Sample No	Results of 3 Times			Average Value	External Accuracy	δ ³⁷ Cl (‰)	SD (±)
	1	2	3				
N-6	0.319135	0.31903	0.319035	0.31907	0.00006	0.08	0.19
N-7	0.31901	0.319011	0.319031	0.31902	0.00001	-0.07	0.04
N-8	0.319044	0.319155	0.319172	0.31912	0.00007	0.26	0.22
N-9	0.318995	0.319017	0.319044	0.31902	0.00002	-0.07	0.08
N-12	0.318944	0.318932	0.318959	0.31895	0.00001	-0.30	0.04
N-14	0.319181	0.319285	0.319285	0.31925	0.00006	0.66	0.19
N-105	0.318962	0.318993	0.318977	0.31898	0.00002	-0.20	0.05

Table 7. Magnesium isotope results of determination in each sample.

Sample No	δ ²⁵ Mg _{DSM3} (‰)	SD (±)	Results of Determination		n
			δ ²⁶ Mg _{DSM3} (‰)	SD (±)	
N-3	-0.42	0.03	-0.56	0.05	3
N-4	-0.57	0.03	-0.91	0.09	3
N-5	-0.98	0.05	-1.46	0.12	2
N-6	-0.67	0.02	-1.10	0.05	3
N-7	-0.97	0.03	-1.59	0.06	3
N-8	-0.87	0.02	-1.37	0.04	3
N-9	-0.86	0.02	-1.45	0.07	2
N-12	-1.01	0.03	-1.70	0.01	2
N-14	-0.98	0.03	-1.75	0.05	3
N-105	-0.57	0.03	-0.89	0.06	3

4. Conclusions

Many isotope analyses of nontraditional elements are restricted by complex preparation because of the interfering ions having a serious effect on measuring with P-TIMS

or MC-ICP-MS, especially when the concentration of the element is low but that of the coexisting ion is high. In this study, A new sample processing protocol for purification and enrichment that enables precise analysis of various nontraditional isotopes in geological samples with low concentrations was developed. A novel method was developed to measure the chlorine and magnesium isotopic compositions for groundwater using isotopic preparative chromatography (IPC) coupled with a ultra clean concentrator (UCC) to prepare pure chlorine and magnesium based on the different retention times of these ions. The analytical results showed that the target ions can be separated completely, and the recovery reached 96%. Compared with traditional methods, purification via IPC greatly reduces the required amount and removes interference ions effectively; meanwhile, it is a more operational and eco-friendly method. This method may be a potential method applicable to other samples in more fields with low concentrations of chlorine or magnesium, such as rock, sediment, rainwater, snow, ice, aerosol, etc.

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