**A Simplified Method Using a Single N,N,N',N'-Tetraoctyl Diglycolamide Resin Column for the Purification of Sr, Nd and Hf in Geological Materials and the Determination of Their Isotopic Ratios by Multi-collector Inductively Coupled Plasma-Mass Spectrometry**

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A simplified method using a single column of N,N,N',N'-tetraoctyl diglycolamide (TODGA) resin is developed for the separation of Sr, Nd and Hf with matrix and interference elements from geological samples, and for subsequent determination of their isotopic ratios by multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS). The analytes of Sr, Nd and Hf are absorbed by the TODGA resin and eluted with 6 mol/L HNO₃, 1.2 mol/L HCl and 1 mol/L HNO₃·1.6 mol/L HF, respectively. The separation procedure is validated by the certified reference materials (CRMs) of BHVO-2, BCR-2 and AGV-2 with analyte recovery greater than 97%. The ratios are measured for ⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd and ¹⁷⁶Hf/¹⁷⁷Hf and the mean values (2σ) are 0.703455 (16), 0.512977 (12) and 0.283108 (8) for BHVO-2, 0.705008 (18), 0.512633 (10) and 0.282878 (4) for BCR-2, and 0.703989 (20), 0.512791 (8) and 0.282982 (8) for AGV-2, which are consistent with the certified values.

**Keywords** Sr-Nd-Hf isotopes, TODGA resin, single column separation, MC-ICP-MS, geological samples

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**Introduction**

The Rb-Sr, Sm-Nd and Lu-Hf isotopic systems are important geochemical tools for understanding Earth’s evolution and magmatic activity.¹⁻⁴ Therefore, precise determination of Sr, Nd and Hf isotopic compositions in geological samples is required. Due to isobaric interferences, Sr, Nd and Hf must be chemically separated and purified before isotopic measurement. Effective removal of the isobaric interference is of significance for the accurate measurement of isotopes by multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS).

For the determination of Sr isotopes, the isobaric interferences of ⁸⁴Kr, ⁸⁶Kr and ⁹⁰Rb should be removed. Similarly, the isobaric interferences of ⁴⁴Ce, ⁴⁺⁴Sm, ¹⁴⁴Sm and ¹⁴⁶Sm on the isotopes of ¹⁴²Nd, ¹⁴⁴Nd, ⁴⁺⁴Nd and ¹⁴⁸Nd, respectively should be separated. For the determination of Hf isotopes, there are isobaric interferences of ¹⁷⁶Hf with ¹⁷⁶Yb, ¹⁷⁸Hf with ¹⁷⁸Yb and ¹⁷⁶Lu, and ¹⁸⁰Hf with ¹⁸⁰Ta and ¹⁸⁰W. In general, Sr, Nd and Hf are chemically separated by using ion-exchange resins,⁴⁻⁶ and more recently by specific extraction chromatographic resins.⁷⁻⁹ The latter has been widely applied in the determination of Sr, Nd and Hf isotope ratios.⁷⁻¹⁰,¹¹ However, the individual separation of Sr, Nd and Hf for isotopic analysis is time-consuming and tedious, and one sample preparation generally requires more than two kinds of resins, such as the combination of cation and LN resins⁷⁻¹¹ and the combination of SR and TODGA resins.⁸⁻¹⁰ Among specific extraction resins, the TODGA resin is a relatively new separation material, which strongly absorbs actinides and lanthanides by the extractant tetraoctyl diglycolamide.⁷⁻¹⁰,¹⁵ So far, the TODGA resin has been applied to geological samples for analysis of Sr, Nd, Hf and Ca isotopes.⁷⁻¹⁰,¹⁵⁻¹⁶ However, the separation of Sr, Nd and Hf with a single TODGA resin column has not been systematically investigated.

In a previous study, it was reported that the separation of Hf can be eluted from the TODGA resin at the temperature of 90°C.¹⁰ However, this high temperature condition will hinder its application. The Ca element, as a major element in geological materials, can be absorbed strongly by the TODGA resin in HNO₃,¹⁰,¹⁵,¹⁷ but the effect of Ca on the absorption of Sr, which has a lower distribution coefficient than Ca,¹⁰ has not been systematically investigated when the amount of Ca exceeds the capacity of the resin column.¹⁰

In this study, one-stage separation of Sr, Nd and Hf using a single TODGA resin column is investigated based on the elemental distribution coefficients on the resin,¹⁰,¹⁵ and the aim is to develop a practical method for the determination of Sr, Nd and Hf isotopic ratios by MC-ICP-MS.
Experimental

Instrumentation

Rates of $^{87}Sr/^{86}Sr$, $^{143}Nd/144Nd$ and $^{176}Hf/177Hf$ were determined by MC-ICP-MS a Nu Plasma II instrument (Nu Instruments, Wrexham, UK) at the Institute of Tibetan Plateau Research, Chinese Academy of Sciences. This instrument is a double-focusing magnetic sector field mass spectrometer equipped with 16 Faraday cups and 5 ion counting detectors. For the focusing magnetic sector field mass spectrometer equipped with French L’Aiguillon, 1300 w 13.0 L/min and 0.8 L/min 0.9 mm (nickel) and 0.6 mm (nickel) Routine solution system Sample uptake rate: 100 µL/min Andrus II desolvation system Sweep gas (Ar) flow rate: 4 L/min for Nd and 4.5 L/min for Hf Spray chamber and desolvator temperature: 110°C and 160°C Sample uptake rate: 100 µL/min (PFA nebulizer)

Reagents and resin column

Purified water with a resistivity of 18.2 MΩ cm was used in the experiments. Acids (hydrochloric acid, nitric acid and hydrofluoric acid) received from Electronic Industry Grade (Beijing Institute of Chemical Reagents) were further purified using a Savillex DST-1000 sub-boiling distillation system. Pure boric acid (H$_3$BO$_3$) was used after purification by TODGA resin in 3 mol/L HNO$_3$.

A polypropylene column was filled with about 4 mL of TODGA resin (50 – 100 µm particle size, TrisKem International, France) and the bed height was ~10 cm. Before use, the resin column was washed with 30 mL of 0.05 mol/L HNO$_3$, 20 mL of 0.05 mol/L HNO$_3$–1.5 mol/L HF and 20 mL of H$_2$O in sequence. Before loading, the column was conditioned with 15 mL of 3 mol/L HNO$_3$.

Samples and sample preparation

Certified reference materials of BCR-2 (basalt), AGV-2 (andesite) and BHVO-2 (basalt) were employed to validate the accuracy and precision of the method since the precise values of Sr, Nd and Hf isotope ratios are already known.

Each sample (~100 mg) was weighed into a 15-mL PFA beaker and wetted with water. After an addition of 1 mL of HNO$_3$ and 1 mL of HF, the beaker was tightly capped and heated on a hotplate at 150°C for 48 h. Then, the samples were evaporated to incipient dryness at 120°C. After adding 1 mL of HNO$_3$ and 1 mL of HF, it was capped again and heated on a hotplate at 150°C for 24 h in order to completely dissolve the samples. After the sample solution was concentrated at 120°C to incipient dryness, 1 mL of HNO$_3$ was added and the sample was evaporated to dryness. Then, 4 mL of 3 mol/L HNO$_3$–0.15 mol/L H$_2$BO$_3$ were added into the beaker to re-dissolve the residue at 120°C for 4 h.

An appropriate quantity of the sample solution with the amount of Ca ≤5 mg was loaded onto the pre-conditioned TODGA resin column and the column was rinsed with 9 mL of 3 mol/L HNO$_3$. The column was eluted using 8 mL of 6 mol/L HNO$_3$ for Sr, 14 mL of 1.8 mol/L HCl for Ce, 8 mL of 1.2 mol/L HCl for Nd and 12 mL of 1 mol/L HNO$_3$–1.6 mol/L HF for Hf.

Table 1: MC-ICP-MS instrumentation and operating conditions

| Nu Plasma II MC-ICP-MS | 1300 w | 13.0 L/min and 0.8 L/min | 0.9 mm (nickel) and 0.6 mm (nickel) | Routine solution system | Sample uptake rate: 100 µL/min | Andrus II desolvation system | Sweep gas (Ar) flow rate: 4 L/min for Nd and 4.5 L/min for Hf | Spray chamber and desolvator temperature: 110°C and 160°C | Sample uptake rate: 100 µL/min (PFA nebulizer) |
|------------------------|-------|--------------------------|-----------------------------------|--------------------------|-------------------------------|-----------------------------|-------------------------------------------------------------|-----------------------------------------------------------|-------------------------------------------------------------|

The analysis method for a sample was consisted of 2 blocks, with 20 cycles per block and an integration time of 15 s per cycle, and the total time was approximately 10 min. Between two sample analyses, the sample injection system was washed with 2% HNO$_3$ to decrease the interference of background. Under these conditions, the isotopic standard solutions of Sr, Nd and Hf were measured for 15 replicates, yielding a ratio (2σ) of 0.710256 (12) for $^{87}Sr/^{86}Sr$, 0.512116 (6) for $^{143}Nd/144Nd$, and 0.282166 (6) for $^{176}Hf/177Hf$, which were all consistent with the certified values of NBS-987 (0.710248 for $^{87}Sr/^{86}Sr$), JNd-1 (0.512116 for $^{143}Nd/144Nd$) and JMC-475 (0.282178 for $^{176}Hf/177Hf$).
The last fraction was evaporated to dryness, and dissolved with 2% HNO₃ for the determination of Hf isotope ratios by MC-ICP-MS. The eluate solutions of 6 mol/L HNO₃ and 1.2 mol/L HCl were diluted for the determination of Sr and Nd isotope ratios by MC-ICP-MS.

The procedure blanks of Sr, Nd and Hf were assessed based on sample-free runs and 10 separate analyses by MC-ICP-MS and varied from 160 to 208 pg for Sr, 30 to 110 pg for Nd and 60 to 86 pg for Hf. These blank levels are negligible compared with their measured concentrations.

Results and Discussion

Separation of Sr from Rb and Ca

In this work, Sr was separated from both Ca and Rb. A mixture of 10 μg Sr and Rb with 1 mg of each Ca, Na, K, Mg, Fe and Al in 3 mL of 3 mol/L HNO₃ was loaded to a TODGA resin column. The column was rinsed using 3 mol/L HNO₃, and every 2 mL of eluate was collected in sequence until there was a total of 12 mL. After rinsing, the column was eluted with 0.5, 1, 2, 4, 5, 6, 7 and 8 mol/L HNO₃, respectively, and every 2 mL of eluate was collected until there was a total of 12 mL. These eluate solutions were analyzed for Na, K, Ca, Mg, Fe and Al by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Prodigy, Leeman, America), and for Sr and Rb by inductively coupled plasma mass spectrometry (ICP-MS) (X-Series II, Thermo Scientific, Germany).

The results show that Sr and Ca can be absorbed by the TODGA resin, while Rb, Na, K, Mg, Fe and Al can be rinsed in 3 mol/L HNO₃ solution (Fig. 1). Both of the absorbed Sr and Ca cannot be eluted by the 2 and 4 mol/L HNO₃ solutions, but the Sr can be eluted with the solutions of HNO₃ less than 1 mol/L and more than 5 mol/L. However, the absorbed Ca can be slightly eluted with the 1 mol/L HNO₃ solution (not shown) and partially eluted with the 0.5 and 8 mol/L HNO₃ solutions (Fig. 1). As a major element of geological samples, Ca deserves attention with respect to the eluate solutions of Sr in which the amount level of Ca could not produce a significant effect on the analysis of Sr isotope ratios by MC-ICP-MS. The effective separation of Sr with Ca can be achieved using the solutions of HNO₃ from 5 to 7 mol/L, and the 6 mol/L HNO₃ solution is used to elute Sr in this study.

In the 6 mol/L HNO₃ eluate, 98.8% of Sr is recovered while contents of Rb and Ca are lower than their detection (Fig. 1). The elution performance reveals that the TODGA resin has applicability to effectively separate Sr from Rb and Ca, and this can be attributed to the difference of their distribution coefficients on the resin in HNO₃ medium.

Effect of Ca absorbed by the TODGA resin on the absorption of Sr

As revealed above, the major elements of K, Na, Mg, Fe and Al are not retained on the TODGA resin in 3 mol/L HNO₃ whereas Ca is strongly absorbed. Therefore, the effect of Ca absorbed by the TODGA resin on the absorption of Sr was investigated in this study. A mixture of 10 μg Sr, 10 μg Rb and individual amounts of Ca in 3 mL of 3 mol/L HNO₃ was loaded to the column containing 4 mL of the TODGA resin, and the column was rinsed using 9 mL of 3 mol/L HNO₃. The total of eluate solution was analyzed for Sr, Rb and Ca, and the results show both Sr and Ca could not be detected when 5 mg Ca were loaded to the column. Besides Rb, however, ~43% of Sr but no Ca was found in the eluate solution when the amount of Ca to be loaded was up to 6 mg. This suggests that Ca is preferentially absorbed as compared to Sr, because the distribution coefficient of Ca is 10-fold higher than that of Sr. In this work, the quantity of Ca required in sample solutions is less than 5 mg for loading to the column containing 4 mL of the TODGA resin.

Separation of Nd with Ce and Sm

As the natural abundance of Nd in geological materials is generally at trace levels, Nd should be separated and preconcentrated before its isotopic determination. In this work, the separation of Nd with Ce and Sm was investigated. A mixture of 2 μg each of La, Ce, Pr, Nd and Sm in 3 mL of 3 mol/L HNO₃ was loaded to a TODGA resin column. After rinsing with 9 mL of 3 mol/L HNO₃, the column was eluted with 14 mL of 1.8 mol/L HCl and then 9 mL of 1.2 mol/L HCl. Every 1 mL of eluate was collected and analyzed by ICP-MS.

Using 14 mL of 1.8 mol/L HCl as the eluent, all of the La was eluted in the first 9 mL, 98.3% of the Ce was eluted from 6 to 13 mL, and 96.9% of the Pr was eluted from 8 to 14 mL, while no Nd was detected (Fig. 2). When 9 mL of 1.2 mol/L HCl were used as the eluent, the first eluate of 6 mL contained more than 98% of Nd whereas no Sm could be found (Fig. 2). The elution performance reveals that the TODGA resin has great potential for separation of Nd from Ce and Sm as reported previously. Such good separability of Nd from Ce and Sm can be attributed to the significant difference of their distribution coefficients on the TODGA resin in HCl medium.

![Fig. 1](image1.png)  
Elution curves obtained using the TODGA resin for major elements and Sr with different concentrations of HNO₃ solutions.

![Fig. 2](image2.png)  
Elution curves of La, Ce, Pr, Nd and Sm obtained using 1.8 mol/L HCl and 1.2 mol/L HCl for the TODGA resin.
separation of Sr with Ca. Besides La, Ce and Pr, major elements of Ca at 97% was found in the eluate of 1.8 mol/L HCl. In the eluate of 8 mL 1.2 mol/L HCl, Nd was found up to 98.9%, whereas no Ce and Sm were detected. Using the solution of 12 mL 1 mol/L HNO3–1.6 mol/L HF, up to 99% of Hf was eluted, while no Yb and Lu were found (Fig. 4). Such high recovery data indicate that one-stage separation of Sr, Nd and Hf from both major and interference elements can be achieved using a single TODGA resin column, and the TODGA resin has great potential for analysis of multi-elemental isotopes in geological materials.

**Determination of Sr, Nd and Hf isotopic ratios.** The analyte fractions of AGV-2, BCR-2 and BHVO-2 were analyzed for Sr, Nd and Hf isotopic ratios using TIMS, ICP-MS and MC-ICP-MS with a combination of ion-exchange and/or LN resin columns. The reported Sr isotopic ratios were further clarified that the effect of Ca could be considered insignificant using the TODGA resin for separation of Sr and Ca in geological samples. Values of 87Sr/86Sr ratios (σ) of 0.705008 (18) for BCR-2, 0.705008 (18) for AGV-2, and 0.703455 (16) for BHVO-2 are consistent with the reported values in the literature: 0.704950 (8)σ to 0.705023 (23)σ for BCR-2, 0.703971 (18)σ to 0.703995 for AGV-2 and 0.703435 (8)σ to 0.703487 (19)σ for BHVO-2. These reported 87Sr/86Sr ratios were generally determined by TIMS after the separation of Sr using cation-exchange or SR resins. These found 87Sr/86Sr ratios further clarified that the effect of Ca could be considered insignificant using the TODGA resin for separation of Sr and Ca in geological samples. Values of 143Nd/144Nd ratios (σ) of 0.512633(10) for BCR-2, 0.512791 (8)σ for AGV-2 and 0.512977 (12)σ for BHVO-2 are in good agreement with the reported values ranging from 0.512630 (10)σ to 0.512644 (12)σ for BCR-2, 0.512777 (10)σ to 0.512792 (4)σ for AGV-2 and 0.512976 (5)σ to 0.512998 (5)σ for BHVO-2. These reported 143Nd/144Nd ratios were obtained by TIMS or MC-ICP-MS combined with cation and/or LN resins commonly used for the separation of Nd. Average values of 176Hf/177Hf ratios (σ) of 0.282878 (4)σ for BCR-2, 0.282982 (8)σ for AGV-2 and 0.283108 (8)σ for BHVO-2 are consistent with the reported values within the range from 0.282871 (10)σ to 0.282885 (10)σ for BCR-2, 0.282967 (6)σ to 0.282984 (4)σ for AGV-2 and 0.283096 (20)σ to 0.283118(5)σ for BHVO-2. These values of 176Hf/177Hf ratios were measured by MC-ICP-MS with a combination of ion-exchange and/or LN resins generally used for the separation of Hf. Our proposed method is compared with the previous methods using different kinds of resins for the separation of Sr, Nd and Hf and subsequent isotope measurements and highlights its advantages for the determination of multi-elemental isotopes in geological samples.
Using a single column containing the TODGA resin, excellent separation of Sr, Nd and Hf with both the matrix and interference elements was achieved. As a result, isobaric and polyatomic interferences were also effectively eliminated. Their excellent separation was examined through measurements of \(^{87}\text{Sr}/^{86}\text{Sr}, ^{143}\text{Nd}/^{144}\text{Nd}\) and \(^{176}\text{Hf}/^{177}\text{Hf}\) ratios for the USGS CRMs. Using a single TODGA resin column to separate Sr, Nd, and Hf has great potential for effective removal of both matrix components and isobaric interference elements. As compared to currently used methods, this proposed method is simple and reliable to determine Sr, Nd and Hf isotopic ratios in geological materials.

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