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A NOVEL SOLID-PHASE EXTRACTION SCHEME FOR THE GROUP SEPARATION OF HIGH FIELD STRENGTH ELEMENTS (Nb, Ta, Zr, Hf) FROM Al-, Ti-, AND Fe-RICH GEOLOGICAL MATERIALS

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ABSTRACT

This paper reports a novel solid-phase extraction scheme for the group separation of high field strength elements (HFSE) Nb, Ta, Zr, and Hf from Ti-, Fe-, and Al-rich geological materials. The solid-phase extraction resin was prepared by impregnating hydrophobic microporous polymer beads with *N*-benzoyl-*N*-phenylhydroxylamine (BPHA) dissolved in chloroform followed by evaporating the solvent. Geological samples were attacked with concentrated hydrofluoric acid and treated with perchloric acid fuming to remove silica. The rock sample was then made up with 4 M HCl solution and loaded onto an extraction column packed with the solid-phase extraction resin. All the major rock constituents (Ca, Mg, K, Na, Al, Fe, Mn, and Ti) were eluted with 4 M hydrochloric acid followed by 2 M sulfuric acid containing 1% v/v H_2O_2. The HFSE were retained on the extraction column and subsequently eluted with 0.5 M oxalic-0.2 M hydrofluoric acid or 5 M hydrofluoric acid. The potentialities of the separation scheme are highlighted by the easy separation of HFSE from the rock matrix and Ti. The solid-phase extraction is superior to liquid-liquid extraction in analytical separations with respect to selectivity and manipulation.

Key Words: High field strength element; Solid-phase extraction; Geological materials.

INTRODUCTION

The elements Zr, Hf, Nb, and Ta occur as small highly charged cations, known as "high field strength elements" (HFSE), and are of great interest in geo- and cosmo-chemistry. The HFSE belong to the so-called incompatible trace elements, that is, they strongly partition in the melt phase during either fusion of silicate source rocks or fractional crystallization of silicate liquid, as do the rare earth elements (REE), Th, U, Ba, K, and Rb. Interestingly, incompatible elements do not behave as a coherent group during igneous processes, but display systematic fractionation patterns that have proved to be highly informative in studies of magmatic rocks petrogenesis and in fingerprinting lavas from different tectonic settings. In addition, the HFSE are relatively immobile during hydrothermal alteration and metamorphism. For this reason, they play a major role in discrimination schemes aiming to determine the tectonic environment of ancient magmatic suites and provide an important contribution to paleogeographic studies (1). Therefore, accurate measurements of HFSE contents in geological materials are needed. However, their determination has always presented a challenge to the analyst. The major difficulties concerning geological samples come from their low concentrations, their instability in solutions, and the high salt matrix leading to serious physical and spectral interference and matrix effects in inductively coupled plasma mass spectrometry (ICP-MS) analyses (2–6). Although the HFSE can be measured by direct analysis of bulk rock solutions using ICP-MS (7), effective and simple chemical methods for their isolation from the matrix constituents (Si, Al, Fe, Ca, Mg, K, Na, Mn, and Ti) are useful to reduce spectral interferences and matrix effects in ICP-MS measurement, particularly in the case of very low content.

However, no straightforward chemical methods for the separation of HFSE as one group from geological materials have been reported. Anion-exchange methods in the HCl-HF system were used for the separation of Nb and Ta (8) or Ta and Hf (9) from geological samples; however, the solution employed to elute Nb and Ta was a mixture of ammonium chloride-hydrofluoric acid or ammonium chloride-ammonium fluoride, which are not recommended in ICP-MS measurements. Anion-exchange chromatography in sulfuric acid medium was also used for the separation of Zr and Hf from geological samples (10), but the precipitation of insoluble sulfates of alkaline earth elements (Ca, Sr, Ba) can be troublesome. Cation exchange in HCl-HF medium was used for the separation of Zr and Hf (11) (along with Nb and Ta), but two major elements, Al and Ti, accompany the HFSE as fluoride complexes, together with P as anionic phosphate. Hall et al. (12) developed a precipitation method using cupferron (ammonium salt of nitrosophenylhydroxylamine) for the separation of Nb, Ta, Zr, and Hf prior to ICP-MS measurements. The shortcomings of this method include the coprecipitation of Fe and Ti (two major elements in geological materials) with the HFSE and the instability and toxicity of cupferron. Goguel (13) employed a liquid-liquid extraction method using N-benzoyl-N-phenylhydroxylamine (BPHA) for the separation of Nb, Ta, Mo, and W before ICP-MS measurements. The disadvantages of this method are also the coextraction of Ti with the analytes and the failure to separate Zr and Hf as a group with Nb and Ta. Fedotov et al. (14) proposed an extraction system based on tetraoctylethylenediamine (TOEDA) for preconcentrating Zr, Hf, Nb, and Ta by countercurrent partition chromatography, but Ti was not separated with their method.

The aim of the present study was to develop a method for the group separation of HFSE from all major elements of geological materials, with special emphasis on the separation of Ti, Al, and Fe.

EXPERIMENTAL

Materials and Reagents

Stock standard solutions containing 1000 μg/mL each of Nb, Ta, Zr, Hf, Mo, Hf, Ti, Al, Fe, Ca, Mg, and chloroform (99.8%, A.C.S. reagent) were obtained from Aldrich Chemical Co., Inc., USA. N-benzoyl-N-phenylhydroxylamine (BPHA, analytical grade) was obtained from Beijing Tongxian Chemicals, China. The support for preparation of the solid-phase extraction resin was Amberchrom CG-71md, a highly cross-linked methacrylate copolymer resin, obtained from Supelco, Inc., USA. All other chemicals were of analytical grade and were used as received. 18 MΩ·cm water, purified using a Milli-Q system (Millipore, France) was used throughout. The rock samples used for the method setup were two in-house standards of basaltic (LAG) and trachy-andesitic (VOL) composition (rich in HFSE and Ti, Al, and Fe). A USGS geological standard

Table 1. Composition of the Two In-House Rock Standards Used in This Work Obtained by Inductively Couple Plasma Atomic Emission Spectrometry (ICP-AES), X-Ray Fluorescence-Wavelength Dispersive Spectrometry (XRF), and Instrumental Neutron Activation Analysis (INAA) Methods and an International Rock Standard (BHVO-1)

Sample	LAG	VOL	BHVO-1 [25]
Major elements (wt%)			
SiO_2	45.4	57.4	49.94
Al_2O_3	14.8	18.0	13.80
$Fe_2O_{3(T)}$	13.1	6.74	12.23
MgO	7.37	1.95	7.23
CaO	9.95	4.52	11.40
Na_2O	3.12	5.59	2.26
K_2O	1.60	3.42	0.52
TiO_2	3.09	1.11	2.71
MnO	0.21	0.20	0.168
Trace elements (μg/g)			
Nb	75	125	19
Ta	4	7.4	1.23
Zr	256	490	179
Hf	6	11	4.38

material (BHVO-1) was used for testing the validity of the proposed method. The compositions of these materials are listed in Table 1.

Apparatus and Instrumentation

Polypropylene columns (Ø8 × 40 mm), prepared from pipette tips (Varitips L, Eppendorf, Germany) fitted with a 30 μm porous polyethylene frit, were used for separation work. The measurements necessary for developing the separation procedure were made by ICP-AES, with a combined simultaneous/sequential instrument (Jobin-Yvon 70 II, France), using the polychromator for major elements and a high-resolution monochromator for HFSE determinations.

Liquid-Liquid Extraction

An aqueous phase containing 10 μg/mL of each HFSE, Al, Fe, and Ti was brought into contact with an equal volume of a 0.2 M BPHA-chloroform for 10 min at 25°C. The concentrations of metals in the aqueous phase were determined by ICP-AES, and those in the organic phase were calculated on the basis of mass balance.

Preparation of Solid-Phase Extraction Resin

The solid-phase extraction (SPE) resin was prepared by impregnating 10 g of Amberchrom CG-71 md resin (50–100 μm size) in 50–100 mL chloroform solution containing 5 g BPHA, stirring the mixture slightly and evaporating to dryness at room temperature (25°C). This took about 4 h. We hereafter refer to the resulting material as HFSE resin.

Rock Sample Dissolution

0.1 g rock powder was placed in a 15-mL PFA (perfluoroalkoxy) Teflon vial followed by addition of 1 mL 5 M HNO_3, 1 mL 29 M HF, and 0.5 mL 11.8 M $HClO_4$. The vial was closed and heated at *ca.* 80°C on a hot plate for 4 h. Then the vial was opened and the solution was evaporated to remove volatile SiF_4 and the excess of HF. The solution was heated to near dryness, then 1 mL $HClO_4$ was added and transferred to a 25-mL quartz beaker. The beaker was heated on a hot plate and under an IR quartz lamp for 2–3 h until near dryness. The walls of beaker were washed with 1–2 mL water and 0.5 ml $HClO_4$ was added and heated again to near dryness. Then the walls of the beaker were washed with 1 mL 4 M HCl, and the solution was heated as before to near dryness. This step was repeated until no crystal of $KClO_4$ was observed. The residue was dissolved in 2 mL 4 M HCl for the column separation step.

Solid-Phase Extraction

0.8 g HFSE resin suspended in water was slurry-transferred into a polypropylene column, and the resin bed was pressed slightly with a glass rod to eliminate air bubbles. The height of the resin bed was about 40 mm. A 30-μm polyethylene frit was placed on top of the column bed to prevent disturbance of the resin during the elution steps. The column was preconditioned with 4 mL of 4 M hydrochloric acid. The rock solution was then loaded onto the column. The elution separation was carried out with 10 mL of 4 M HCl, 60–180 mL (depending on the expected Ti content) of 2 M H_2SO_4-1% H_2O_2 and 30 mL of 0.5 M oxalic-0.2 M HF, successively, under gravity flow (0.2–0.3 mL/min). Finally, the column was washed with 20–30 mL of water for the next use. The concentrations of the HFSE in the fractions of effluents were determined by ICP-AES, and the elution curves were drawn by plotting the concentration versus the effluent volumes.

RESULTS AND DISCUSSION

Liquid-Liquid Extraction

Effect of HCl Concentration on Extraction in the Presence of HF Acid

It has been demonstrated that BPHA is superior to cupferron both in stability and analytical applications (15–17). BPHA can quantitatively extract many high-valency elements within a wide range of HCl concentration (1–11 mol/l) whereas the elements of Groups IA, IIA, IIB, IIIA, and IIIB are not extracted (17). As the rock sample was decomposed by HF-HNO_3, and even though the sample was thoroughly treated with $HClO_4$, trace amount of fluorides might still remain in the sample solution. Therefore, the effect of the presence of HF acid on the extraction should be examined. Lyle and Shendrikar (18) found that in 0.05 M HF-1 M HCl solution, BPHA in chloroform could quantitatively extract Nb (tracer quantities) leaving a microgram amount of Zr in the solution. Later, these authors reported on the solvent extraction separation of protactinium (Pa) from Nb and Ta with BPHA-chloroform (19). They demonstrated that the extraction efficiency of Nb and Ta decreased rapidly with increasing fluoride ion concentration (19), but HF did not impede the extraction of Nb below 0.05 M and that of Ta below 0.4 M.

Goguel (13) reported BPHA solvent extraction for the separation of HFSE for ICP-MS by employing boric acid to buffer fluoride activity. At low fluoride activities ($[F^-] < 3.2 \times 10^{-4}$) Nb, Ta, Mo, and W were extracted equally with over 96% of extraction; however, the extraction of Zr and Hf under these conditions was only 30–40%. As a result, Zr and Hf were not included in Goguel's method. It is obvious that the extraction of Zr and Hf is considerably more sensitive to fluoride ions than that of Nb, Ta, Mo, and W. Hala (20) investigated the solvent extraction of hafnium (IV) and zirconium (IV) by BPHA from strongly acidic solutions ($HClO_4$ and HCl) and found that Zr and Hf were extracted as Zr (IV)$X_4 \cdot 2$BPHA and Hf (IV)$X_4 \cdot 2$BPHA ($X = Cl^-$ or ClO_4^-). It was also shown that the distribution ratios of Zr (IV) and Hf (IV) increased with increasing HCl concentration from 4 to 10 M. Cristallini et al. (21) reported that the distribution coefficient of Nb increased nearly linearly with increasing HCl concentration (4–10 M) in the presence of 0.5 M HF. Therefore, it should be expected that the extraction of Zr and Hf would increase with an increase in HCl concentration even in the presence of very low HF concentration (a trace amount of HF in the solutions of HFSE is preferable to stabilize the solutions).

In this work, the effect of HCl concentration on liquid-liquid extraction in the presence of 0.05 M HF acid was examined, and the results are given in Fig. 1. The extraction of Nb, Ta, Mo, W, and Ti was more than 99% within the range of 2–10 M HCl-0.05 M HF, and that of Zr and Hf increased with increasing HCl

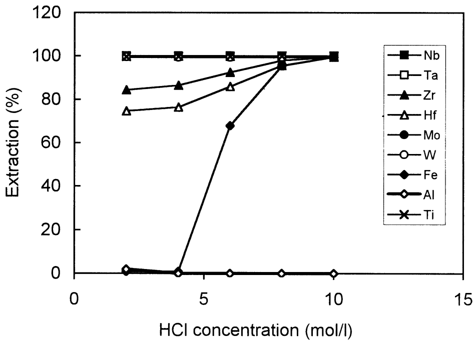

Figure 1. Effect of HCl concentration on the extraction of Al, Fe, Ti, Nb, Ta, Zr, Hf, Mo, and W (0.2 M BPHA-chloroform; 10 μg/ml HFSE in various HCl concentration- 0.05 M HF acid; organic:aqeuous phase ratio = 1:1; contact time 10 min). The symbols of Nb, Ta, Mo, and W are overlapped.

concentrations. At high HCl concentrations (>8 M), chloride displacement of fluoride was probably responsible in some way for the improved extraction, that is, Cl^- competes with F^- to complex with Zr (IV) and Hf (IV) forming the species to be extracted by BPHA. The extraction of iron (III) did not take place below 4 M HCl and increased rapidly with increasing HCl concentration above 4 M HCl. Al was not extracted over the whole range of 2–10 M HCl concentrations. Summarizing our liquid-liquid extraction experiments as well as literature data, it appears that BPHA could be exploited to separate Nb, Ta, Zr, Hf, Mo, and W as a group from geological materials. The difficulties lie in the separation of Ti from the HFSE as well as the extraction of Zr and Hf in the presence of hydrofluoric acid, as has been reported by Goguel (13).

Back-Extraction of Loaded BPHA-Chloroform

The elements Nb, Ta, Ti, Zr, Hf, Mo, and W can be extracted by BPHA from a wide range of concentrations of various mineral acid solutions, such as hydrochloric acid, sulfuric acid, and perchloric acid (17–22). Hence, their back-extraction using these acid solutions is difficult. Lyle and Shendrikar (18) reported that *aqua regia*, 6 M ammonia, and 7 M hydrogen peroxide were effective for the back-extraction of niobium and tantalum. In this work, the back-extraction from the BPHA-chloroform loaded with HFSE was investigated, using nitric and sulfuric acids containing hydrogen peroxide. As shown in Table 2, the back-extraction of the HFSE was effective only using concentrated nitric acid (15 M). Shijo et al. (23) also found that molybdenum in the organic phase (BPHA-xylene)

Table 2. Back-Extraction of HFSE as a Function of Nitric Acid Concentration

HNO_3 Concentration* (M)	Back-Extraction (%)			
	Nb	Zr	Mo	Ti
1	0.22	<0.01	0.40	10.0
4	0.33	0.22	0.29	14.3
12	4.44	2.22	4.40	4.84
15	100	100	106	100

* The nitric acid solution contained 2% H_2O_2.

could be back-extracted with concentrated nitric acid (98%). However, rapid decomposition of the organic phase was observed when the concentration of HNO_3 was greater than 4 M. In the case of 15 M HNO_3, some gas bubbles were immediately produced when the organic phase was mixed with nitric acid (>4 M), and after that the organic phase turned into brown from colorless. Therefore, the use of nitric acid is not recommended for the solid-phase extraction system, as this will adversely affect the performance of the solid-extraction resin. Figure 2 shows the back-extraction of Ti using 2 M H_2SO_4 solution containing varied H_2O_2 concentrations (0–6% v/v). About 40% of Ti was back-extracted with sulfuric acid containing <6% H_2O_2, whereas no back-extraction of Nb occurred by one-stage back-extraction (Fig. 2). Therefore, it is expected that the separation of Ti could be performed with a number of back-extractions using H_2O_2-containing sulfuric acid. However, the manipulation inherent to liquid-liquid extraction is not convenient for processing large batches of samples. It has been demonstrated that a huge number of separation stages is easily achieved in a column filled with solid-phase extraction resin by use of elution technique (24). Therefore, the solid-phase extraction technique was investigated for the separation of trace amounts of HFSE from geological samples.

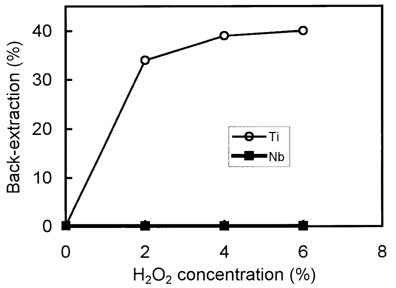

Figure 2. Back-extraction of Nb and Ti from loaded BPHA-chloroform using 2 M H_2SO_4-containing variable concentration of H_2O_2.

Solid-Phase Extraction Separation

Separation from Synthetic Solutions

A synthetic solution (2 mL) consisting of 50 μg Nb, Ta, Zr, Hf, and Ti each, 500 μg Al, and 550 μg Fe in 10 M HCl-0.05 M HF was loaded onto a HFSE resin column (8 mm i.d. × 65 mm high). Then the column was eluted in 2-mL fractions with 10 mL 10 M HCl, 14 mL 4 M HCl, and 30 mL 0.5 M oxalic acid-0.2 M HF, consecutively. The elution behavior of microamounts of HFSE, Al, Fe, and Ti on this column is shown in Fig. 3. Al was eluted with 10 M HCl from the column, while Fe, Ti, and HFSE were retained on the column. Then Fe was eluted when the mobile phase was changed to 4 M HCl. This is in agreement with the liquid-liquid extraction data described previously. However, Ti was not separated from HFSE in this scheme. It should be noted that although the loading solution contained trace amounts of HF acid, no HFSE was detected in the fractions (24 mL in total) of 10 M and 4 M HCl used to elute Al and Fe, respectively. It was found that the transparent polystyrene vials collecting the effluents of 10 M HCl mobile phase turned into opaque, suggesting that considerable losses of chloroform solvent from the resin occurred during the elution of 10 M HCl. Although the solvent chloroform was evaporated during the preparation of the resin, it is believed that a small amount of solvent still resided within the macropores of the supporting material (Amberchrom CG-71m). It has been reported that the solubility of BPHA-chloroform in aqueous phases increases significantly when the concentration of hydrochloric acid in the aqueous phase is greater than 5 M (17). Therefore, in the subsequent work, 4 M HCl will be adopted as the mobile phase for separating Al and Fe.

Based on the fact that part of the Ti can be stripped from the HFSE-loaded BPHA-chloroform solution using sulfuric acid containing H_2O_2 while the HFSE

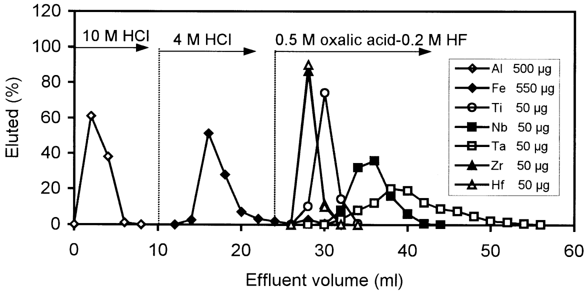

Figure 3. Separation of Al, Fe, Ti, Nb, Ta, Zr, and Hf from a synthetic solution, achieved on a column of HFSE resin. Column: 8 mm i.d. × 65 mm, flow rate 0.13 ml/min.

were not back-extracted (Fig. 2), Ti separation was investigated by using 2 M H_2SO_4 containing 1% (v/v) H_2O_2 as a mobile phase. Figure 4 shows the elution profile of 0.5 mg of Al, Fe, and Ti and 0.1 mg of Zr and Hf (loaded in 0.5 ml of 4 M HCl-0.02 M HF) using 4 M HCl for eluting Al + Fe, 2 M H_2SO_4-1% (v/v) H_2O_2 for eluting Ti and 0.5 M oxalic acid-0.2 M HF for eluting Zr + Hf. Although the Ti elution peak was quite broad, Ti can be effectively eluted from the column using 2 M H_2SO_4-1% H_2O_2. No Zr and Hf were detected in the Ti fractions.

Synthetic solutions were also used for measuring recovery of HFSE and assessing the stability of the resin to test the viability of the separation procedure. The synthetic solution (2 mL in 10 M HCl), containing 5000 μg Al, 5000 μg Fe, 6000 μg Ca, 1000 μg Ti, 10 μg of each HFSE element, and 0.1 mmol of HF, was loaded onto the column, then 10 mL of 4 M HCl, 50 mL of 2 M H_2SO_4-0.5% H_2O_2, 30 mL of 0.5 M oxalic-0.2 M HF, and 20 mL of water were passed through the column successively. The concentrations of HFSE in the oxalic-HF acid solution fractions were determined by ICP-AES. Quantitative recovery of Nb, Ta, Zr, and Hf was obtained (Table 3). For the third use of the column, the recovery was still satisfactory. Therefore, the resin was, at the least, stable within three runs. However, the recovery of Mo and W was incomplete. Even 50 mL of 0.5 M oxalic acid-0.2 M hydrofluoric acid or 30 mL of 0.25 M oxalic acid-0.2 M tartaric acid-1% H_2O_2 did not achieve efficient stripping of Mo and W from the column. Therefore, high concentration of HF acid was examined to elute Mo and W. The elution profile of HFSE from the HFSE resin column using 5 M hydrofluoric acid is shown in Fig. 5. Although the peaks of Nb, Zr, Hf, and W are sharp, that of Ta shows significant tailing, and the Mo peak is very broad. Even so, 5 M HF is effective for eluting all the elements of interest.

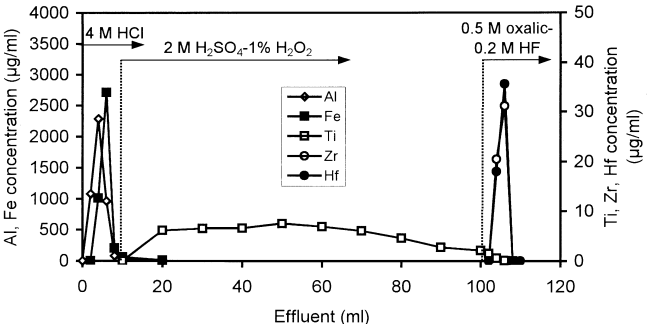

Figure 4. Separation of 0.5 mg Al, Fe, Ti, and 0.1 mg Zr and Hf (loaded in 0.5 ml of 4 M HCl-0.02 M HF); Flow rate = 0.36 ml/min. Column 8 mm i.d. × 40 mm.

Table 3. Chemical Recovery of HFSE from the Synthetic Solution

Element	Nb	Ta	Zr	Hf	Mo	W
Taken (µg)	10.2	9.9	9.9	10.0	9.9	10.1
First run:[a]						
Found (µg)	10.2	11.0	10.3	10.8	<0.1	3.0
Recovery (%)	100	111	104	108	<1	29.7
Second run:[a]						
Found (µg)	10.1	10.8	9.91	10.4	0.66	6.19
Recovery (%)	99.0	109	100	99.4	6.7	61.3
Third run:[a]						
Found (µg)	11.2	8.75	9.54	9.31	1.1	10.1
Recovery (%)	110	88.4	96.4	93.1	11.1	100
Taken (µg)	20.4	19.8	19.8	20.0	19.8	20.2
Found (µg)[b]	20.0	19.5	20.4	21.5	5.37	5.67
Recovery (%)	98.0	98.5	103	108	27.1	28.1

[a] HSFE eluted with 30 ml of 0.5 M oxalic acid-0.2 M hydrofluoric acid.

[b] HSFE collected with 30 ml of 0.25 M oxalic acid-0.2 M tartaric acid-1% H_2O_2.

Separation from Rock Solutions

The removal efficiency of major elements and the recovery of Zr, Hf, and Nb from rock samples (in-house standards LAG and VOL) are summarized in Table 4. 10 mL of 4 M HCl were able to remove >95% of Al and Fe from the column. An excellent separation of Ti from HFSE was obtained using sulfuric acid containing 1% (v/v) H_2O_2. For sample VOL (containing 1.1% TiO_2), more than 99% of Ti was removed with 100 mL of 2 M H_2SO_{4-} 1% H_2O_2 (Table 4).

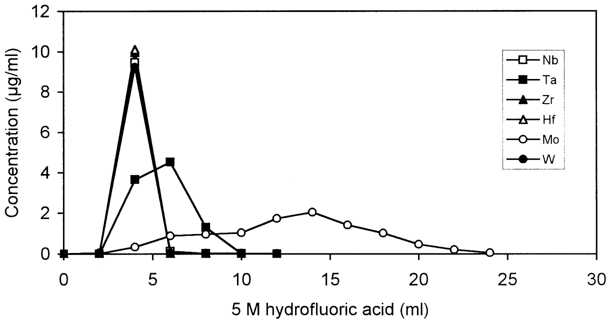

Figure 5. Elution behavior of HFSE (20 µg) loaded in 0.5 ml of 4M HCl-0.02M HF solution with 5 M HF acid as mobile phase; Column 8 i.d. × 40 mm; flow rate = 0.25 ml/min.

Table 4. Efficiency of the Solid-Phase Extraction Procedure in Removing the Major Elements (Al, Fe, Ti) and Recoveries of Nb, Zr, and Hf from LAG and VOL Rock Samples; Concentrations of Elements Were Determined by ICP-AES

	LAG				VOL		
Column No.	1	2	3	4	5	5[a]	6
Eluent Sequence and Volume							
(1) 4 M HCl (ml)	10	10	10	10	10	10	10
(2) 2 M H_2SO_4-1% H_2O_2 (ml)	0	20	80	180	0	30	100
(3) 0.5 M oxalic-0.2 M HF (ml)	30	30	30	30	30	30	30
Concentration in Eluate 3 3 (μg/ml)							
Al	0.51	0.30	0.17	0.06	0.14	0.09	0.047
Fe	14.4	0.24	0.14	0.075	5.49	0.33	0.045
Ti	65.1	33.5	15.1	0.29	28.02	8.04	0.18
Zr	0.916	0.916	0.950	0.913	1.653	1.636	1.655
Hf	0.021	0.019	0.020	0.021	0.039	0.039	0.041
Nb	0.243	0.248	0.250	0.258	0.397	0.403	0.388
Removal Efficiency (%)[b]							
Al	99.80	99.88	99.93	99.96	99.96	99.97	99.99
Fe	95.30	99.92	99.95	99.98	96.50	99.79	99.97
Ti	0	45.70	75.52	99.54	0	65.54	99.23
Recovery (%)[b]							
Zr	107	107	111	107	101	100	101
Hf	104	96.7	97.7	104	96.7	98.3	102
Nb	97.2	99.2	99.9	103	95.2	96.7	93.1

[a] Second use of the column 5.

[b] The removal efficiency of major elements and recovery of Zr, Hf, Nb were calculated based on the element contents listed in Table 1.

For sample LAG (containing 3.1% TiO_2), 180 mL of 2 M H_2SO_4-1% H_2O_2 were required to remove the Ti quantitatively. Even in this case, no loss of HFSE was detected in the 2 M H_2SO_4-1% H_2O_2 fractions (Table 4). In addition, this allowed a more effective removal of Fe to be achieved. With the elution of 10 ml of 4 M HCl only, about 95% of Fe was removed. When the 4 M HCl fraction was followed by 20 mL of 2 M H_2SO_4-1%H_2O_2, greater than 99.9% of Fe was removed. We have also tried to use 2 M H_2SO_4-1% H_2O_2 instead of 4 M HCl from the beginning of the separation, in an attempt to elute both Fe and the other major elements in a single step, but the precipitation of sulphates of alkaline earth elements (Ca, Sr, Ba) plugged the column. After separation, the concentrations of the major elements (Al, Fe, Ti) in the final HFSE solutions was reduced to the same trace level as the HFSE, thereby eliminating the possibility of significant interferences and matrix effects in ICP-AES/MS measurements. In contrast, the

Table 5. Assessment of the Repeatability of the Proposed Separation Procedure for Nb, Zr, and Hf Based on Six Independent Analyses Throughout the Procedure Using ICP-AES Detection

	Nb		Zr		Hf	
Sample	ICP-AES (µg/g ± S.D.)	RV (µg/g)	ICP-AES (mg/g ± S.D.)	RV (µg/g)	ICP-AES (µg/g ± S.D.)	RV (µg/g)
LAG	73.8 ± 2.2	75 ± 5	281 ± 5	256 ± 5	6.19 ± 0.39	6 ± 0.6
VOL	119 ± 7	125 ± 7	498 ± 6	490 ± 10	11.7 ± 0.9	11 ± 1

Note: The 0.5 M oxalic acid-0.2 M HF acid fractions were directly analyzed with a dilution factor of 3. The results are compared with reference values (RV) obtained by purely instrumental methods: X-Ray Fluorescence-wavelength dispersive spectrometry (XRF) for Zr and Nb, Neutron Activation Analysis (NAA) for Hf (see Table 1).

separation of Fe was not possible with the cupferron precipitation method (12), and the separation of Ti was not achieved with the cupferron precipitation (12), the BPHA solvent extraction (13), and TOEDA countercurrent partition chromatography (14).

Table 5 shows the average analytical results of Nb, Zr, and Hf for six independent separations and analyses of the two in-house standards. The results are in

Table 6. Separation of Nb, Ta, Zr, and Hf from an International Geological Standard Material (BHVO-1, USGS); Separation Procedure: 10 ml 4 M HCl, 30 ml 2 M H_2SO_4-1% H_2O_2, 10 ml 5 M HF

		Element Mass in 0.1 g Sample (µg)		
Composition	Content [25] (%)	Before Separation[a]	After Separation[b]	Removal %
SiO_2	49.94	22310	<10	100
Al_2O_3	13.80	7310	12	99.8
$Fe_2O_{3\,(T)}$	12.23	8560	35	99.9
MgO	7.23	4340	0.04	100
CaO	11.40	8140	5.8	99.9
TiO_2	2.71	1630	59	96.6
Nb	19×10^{-4}	1.9	1.76	
Ta	1.23×10^{-4}	0.12	0.11	
Zr	179×10^{-4}	17.9	17.2	
Hf	4.38×10^{-4}	0.44	0.45	

[a] Calculated based on the reference values of the composition.

[b] Determined with ICP-AES and ICP-MS.

excellent agreement with the reference values, except a slightly higher Zr value for LAG. The precision expressed by the RSD of the six separate batches of separation is better than 8%, suggesting that repeatability of the proposed separation procedure is reliable. Because of its low abundance in the samples and its relatively low sensitivity by ICP-AES, Ta was not measurable. The validity of the method was also tested using ICP-mass spectrometry to analyze an international geological reference material (BHVO-1) and the results are shown in Table 6. With 10 mL 4 M HCl, 30 mL 2 M H_2SO_4-1% H_2O_2, greater than 99.9% of Al, Fe, etc. and 96% of Ti were removed. The recoveries of Nb, Ta, Zr, and Hf were satisfactory within 92–102%.

CONCLUSIONS

The group separation of Nb, Ta, Zr, and Hf from Al, Fe, and Ti-rich geological materials by means of solid-phase extraction separation using BPHA as extracting reagent was investigated in this work. Compared with the chemical precipitation (12), liquid-liquid extraction (13), and countercurrent partition chromatography (14), the proposed scheme provides a simple, rapid, and more effective separation from geological materials. The method was successfully applied to separate ppm levels of Nb, Zr, and Hf from basaltic and trachy-andesitic geological materials containing high levels of Al (15%), Fe (10%), and Ti (3%). Greater than 99% of the major elements (Al, Fe, Ca, Mg, Si, Na, K, Ti) were removed, and an HFSE solution of good purity was obtained with high recoveries. The method has been extended to other geological materials for determination of low levels of Nb, Ta, Zr, and Hf by ICP-MS.

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