Accurate Determination of High Field Strength Elements (HFSE) in Geological Samples by ICP-MS Using an Improved Closed Digestion With Tartaric Acid as Matrix Modifier

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ABSTRACT

An accurate determination of high field strength elements (HFSE) in geological samples provides information on the diagenetic evolution of rocks and is also of great significance for revealing the formation and evolution process of the continental crust and mantle. However, currently the concentration of HFSE in rocks is usually obtained using a conventional acid closed digestion process and its corresponding analytical result is relatively poor because of irreversible hydrolysis and polymerization. Fortunately, HFSE can be stable in solution when they complex with α -hydroxy acids due to their strong coordination abilities. After comprehensive consideration of the reagent blank and

the complexing ability of the three α -hydroxy acids, it was found that when the tartaric acid concentration was 20% (v/v) together with the ratio of tartaric acid to nitric acid at 1:1, the tested values of HFSE for six rock standard reference materials agreed well with the certified values. Meanwhile, the structure of the complex products for HFSE with tartaric acid were resolved using a Q Exactive mass spectrometer. The detection limits of Nb, Ta, Zr, and Hf were obtained at 0.042, 0.018, 0.011, and 0.036 $\mu\text{g g}^{-1}$ for this method, respectively. In this study, 35 geological SRMs were analyzed using this proposed method, and their accurate results for HFSE confirmed that it has great potential for the analysis of most types of geological samples.

ical methods for HFSE (10, 15-19). Due to the strong tendency to hydrolyze and to occur as polymerized species in acid solution chemistry (20, 21), the concentrations of HFSE, particularly Nb and Ta with extremely low levels in mantle rocks (22), are still virtually difficult to measure precisely with conventional ICP-MS methods.

Previous studies have shown that HFSE can be stabilized in solution by adding HF to form soluble HFSE fluoro-complexes (22-25). However, some authors reported that F^- can easily form fluoride precipitates with matrix elements such as Al, Mg, and Ca, which may adsorb some trace elements (HFSE included) from the HF solution and result in the loss of trace elements (26-32). In early analytical studies, tartaric acid (TA) was generally used as one of the auxiliary complexing agents for spectrophotometric determination of niobium and tantalum (33). It has been proven that due to the strong coordination of HFSE, they easily form complexes which can be stable in the solution with TA, citric acid, oxalic acid, malic acid, or other organic compounds of α -hydroxy acids (34-36). It was also found that only a proper amount of TA can stabilize the complex in a wide range of pH (33). In subsequent studies, Li et al. (37) effectively overcame the hydrolysis of Nb and Ta using potassium sodium tartrate complexing, and the detection limits of Nb and Ta based on

INTRODUCTION

High field strength elements (HFSE), mainly Nb, Ta, Zr, and Hf, are tracers of considerable importance for large-scale mass and energy transfer in the Earth's interior for their relatively stable geochemical properties (1-4). Interpretive studies of the diagenetic evolution of magmatic rocks in the continental crust and mantle

require precise and accurate data for these elements at their abundance levels in geological materials. Although instrumental neutron activation analysis (INAA) and X-ray fluorescence spectrometry (XRF) could be used for the determination of HFSE (5-9), these two methods are inappropriate for these four elements together and lack adequate sensitivity at trace levels (10). As a sensitive and immensely powerful multi-element analytical technique (11-14), the inductively coupled plasma source mass spectrometer (ICP-MS) is equipped to develop precise analyt-

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ICP-MS were obtained at 1.05 ng mL⁻¹ and 0.13 ng mL⁻¹, respectively (38). Undoubtedly, the use of TA is effective in stabilizing HFSE in solutions. However, due to the limitation of the analytical techniques, there are few reports on the mechanism of the complexation reaction between HFSE and TA, which directly affects the combined forms and the stability conditions of HFSE in TA solution. Researchers have speculated that TA and tantalum form polynucleic acid complexes (33, 34), but their specific polymer needs to be further discussed.

In this work, a validated method was developed for the simultaneous and accurate determination of HFSE in geological samples using an improved closed digestion ICP-MS method with TA as the matrix modifier, aiming to prevent the hydrolysis and polymerization of HFSE in acid medium. On the basis of optimizing the dosage and concentration of TA, the types of complex products of high field strength elements with TA were preliminarily resolved by HPLC-MS. A series of 35 geological standard reference materials (SRMs) of different properties were evaluated by the method under study. It was found that this method works well for analyzing HFSE in various geological samples.

EXPERIMENTAL

Analytical Instrumentation

The experiments for elemental analysis were carried out using a quadrupole ICP-MS instrument, NexION® 350D (PerkinElmer, Inc., Shelton, CT, USA) (39-42). The performance of the instrument was checked daily with a NexION Setup Solution (Be, Ce, Fe, In, Li, Mg, Pb, and U, 10 µg L⁻¹, 1% HNO₃) to obtain maximum signal intensities, while keeping the minimum oxide formation rate and doubly charged ratio. The typical instrumental operating conditions and measurement parameters are listed in Table I.

Structural elucidation of the organic complexes was performed using a Q Exactive Hybrid Quadrupole-Orbitrap mass spectrometry (Thermo Scientific, Bremen, Germany) (43). The instrument control and mass spectra processing were carried out by using the Xcalibur 3.0 software package (Thermo Scientific). A 10 µL sample solution was injected into doubly distilled water containing 0.1% formic acid at a flow rate of 0.3 mL min⁻¹. The identification experiments were processed in a negative ionization full-scan mode with a mass range of 120–600. The system was operated with a sheath gas flow rate of 30 L min⁻¹, auxiliary gas flow rate of 5 L min⁻¹, spray voltage of –3.2 kV, capillary temperature of 320 °C, S-lens RF level of 50%, and mass resolution of 70,000. All other instrumental parameters were set at the default values.

Reagents and Standards

Solutions used in this study were prepared with 18.2 MΩ cm ultra-pure water produced by a water purification system (90005-02, Labconco WaterPro PS, USA). All chemicals used were of at least guaranteed reagent grade and most of them were purchased from

Sinopharm Chemical Reagent Co., Ltd (Shanghai, P.R. China), except tartaric acid and citric acid which were obtained from Sigma-Aldrich, USA. To reduce the blank testing value, commercially available nitric acid and hydrofluoric acid were purified by subboiling in a two-bottle Teflon® still (Saville Corporation, USA). External calibrators and internal standard solutions were respectively prepared by gravimetric serial dilution from 10 µg mL⁻¹ multi-element standard solutions (SPEX CertiPrep, USA) and a single-element standard solution of rhodium at 1000 µg mL⁻¹ (National Center for Analysis and Testing of Steel Materials, Beijing, P.R. China). The single element standard solutions of HFSE at 100 µg mL⁻¹ used in the mass spectrometric analysis were purchased from the National Center for Analysis and Testing of Steel Materials, Beijing, P.R. China.

Geological Reference Materials

Thirty-five geological SRMs were used to evaluate the accuracy of the established method. Three rock standard reference materials (SRMs) including AGV-2 (andesite), BCR-2 (basalt) and BHVO-2 (basalt) were purchased from the U.S. Geological Survey (USGS, USA), three SRMs (ORTO-1 rhyolite, OU-7 gabbro, GSM-1 gabbro) were obtained from the International Association of Geoanalysts (IAG, UK), and 29 geological SRMs (GBW07103 granite, GBW07105 basalt, GBW07106 quartz sandstone, GBW07107 shale, GBW07108 carbonate, GBW07110 trachyte, GBW07111 diorite, GBW07112 gabbro, GBW07114 dolomite, GBW07120 limestone, GBW07121 granite-gneiss, GBW07403 yellow-brown earth, GBW07404 soil, GBW07405 yellow-red earth, GBW07407 latosol, GBW07423 Hongze lake deposit, GBW07426 soil from Xinjiang, GBW07428 soil from Sichuan basin, and stream sediments GBW07302-GBW07306, GBW07307a,

TABLE I
Instrumental
Operating Parameters

NexION 350D ICP-MS	
RF plasma power	1500 W
Plasma gas flow	18 L min ⁻¹
Nebulizer gas flow	0.90 L min ⁻¹
Auxiliary gas flow	1.2 L min ⁻¹
Peak pattern	3 points/peak
Sampling depth	8 mm
Dwell time	50 ms
Integration time	1250
Sweeps per reading	25
Reading per replicate	3
¹⁵⁶ CeO/ ¹⁴⁰ Ce ratio	< 2.0%
Ce ²⁺ /Ce ⁺ ratio	< 2.0%

GBW07309-GBW07313) were from the Institute of Geophysical and Geochemical Exploration (IGGE, P.R. China).

Sample Pretreatment

A 50 mg homogenized sample powder (<200 mesh) was weighed into a 10 mL homemade PTFE-lined stainless steel bomb and soaked with several drops of ultrapure water. Then 1 mL of purified HNO₃ and HF were successively added, and the sample was digested under high pressure at 190 °C in an electric oven for 48 hours. After cooling, the bomb was opened, and the digestion solution evaporated to incipient dryness at 120 °C on a heater. This was followed by adding 1 mL HNO₃ and evaporating it for a second round of dryness in order to remove HF thoroughly. The resultant salt was redissolved while it was hot by adding 1.5 mL of 30% (v/v) HNO₃ and 1.5 mL of 20% (m/v) TA. The final solution was diluted to ~100 g with 2% (m/v) HNO₃ for ICP-MS analysis. A reagent blank solution was prepared using the same procedure.

RESULTS AND DISCUSSION

Effect of Different Complexant

Niobium and tantalum reacting with organic carboxylic acid can be stabilized in the form of complex anions in acid medium. It has been reported that the stability of complexes formed by niobium and different compounds is in the following order: oxalic acid > hydrogen peroxide > citric acid > TA (34). Therefore, in order to investigate the overall complexation ability between HFSE and three organic complexants (including TA, oxalic acid, and citric acid), the relative errors (REs) of detection results for HFSE coupled with these reagents in six rock SRMs were compared (Figure 1). The data showed that the REs of HFSE results using TA were less than those with the other

two organic complexants, which may be due to the effect of the nature of the HFSE and the difference in concentration of the matrix elements. The reagent blanks of these three complexing agents at a uniform concentration (0.2% m/v) were inspected at the same time. The levels of Nb, Ta, Zr, and Hf in TA and citric acid were both less than in oxalic acid, which are listed in Table II. Based on comprehensive consideration of the experimental results, TA was selected as the desired organic complexing agent for the present work.

Optimization of Concentration and Dosage for TA

The stability and reactivity of HFSE in the organic complex both depend on the concentration and dosage of the organic complexing reagent. Previous studies indicated that stable anionic complexes formed by TA and tantalum usually required 18 times the concentra-

tion of TA than that of Ta (34). Otherwise, uncomplexed HFSE will produce insoluble oxide precipitates in the dilute acid medium due to hydrolysis and polymerization. In our research, TA was added in the extraction stage to prevent hydrolysis of HFSE. It was found that 20% TA was sufficient to complex HFSE in rock samples, as shown in Figure 2a.

On the other hand, when the amount of TA is excessive, high levels of Total Dissolved Solids (TDS) in sample solution will not only cause blockage of the atomizer or sampling cone, but also will lead to significant matrix effects and potential spectral interferences during the analysis process, which affects accuracy of the analytical results. We optimized the proportion of 20% TA and high purity nitric acid. Figure 2b shows that when the ratio of TA to nitric acid is 1:1 (v/v), the tested values of HFSE for the six rock SRMs agreed well with the

Fig. 1. Relative errors (REs) of detection results for HFSE coupled with (a) oxalic acid, (b) citric acid, and (c) TA in six rock SRMs.

TABLE II
Concentrations of Zr, Nb, Hf, and Ta
in 0.2% (m/v) TA, Citric Acid, and Oxalic Acid, Respectively (ng mL⁻¹)

Reagent Blank	Zr	Nb	Hf	Ta
Oxalic acid (H ₂ C ₂ O ₄)	1.7	0.077	0.043	0.080
Citric acid (C ₆ H ₈ O ₇)	0.036	0.0036	0.0011	0.0075
TA (C ₄ H ₆ O ₆)	0.051	0.011	0.0038	0.011

Fig. 2 Effects of concentration (a) and volume (b) of TA on accuracy of HFSE in six rock SRMs.

certified values, and at this point TA did not cause significant matrix effects in the testing process by ICP-MS.

Identification of Organic Complexes of HFSE with TA

The properties of Nb and Ta in TA solution directly affect their reactivities, reaction characteristics, and reaction rules. But there were few data on the complexes of HFSE with TA. Some researchers have speculated that the composition of the complexes of niobium, tantalum, and TA might be complex salts, such as $\text{H}[\text{NbO}(\text{C}_4\text{H}_4\text{O}_6)_2]$, $\text{H}_5[\text{NbO}_4(\text{C}_4\text{H}_4\text{O}_6)] \cdot 2.5\text{H}_2\text{O}$, $\text{Me}_2\text{ONb}_2\text{O}_5(\text{C}_4\text{H}_4\text{O}_6)_2 \cdot n\text{H}_2\text{O}$, $\text{MeH}[\text{TaO}(\text{C}_4\text{H}_4\text{O}_6)]$, and so on (34). In the present study, mass spectra of possible organic complexes of HFSE with TA were analyzed using the Q Exactive mass spectrometer, and chemical formulas for these were calculated using the Xcalibur software which allowed for the calculation of the basic elements C, H, O, and HFSE atom within a 5 ppm mass tolerance.

The single element standard solutions of Nb, Ta, Zr, and Hf ($100 \mu\text{g mL}^{-1}$ each) were mixed with 20% tartaric acid and 30% nitric acid, respectively, and then diluted to $1 \mu\text{g mL}^{-1}$ with deionized water to simulate the complex products of HFSE with tartaric acid in dilute nitric acid matrix. In these complexing solutions, the obtained mass spectrum was characterized by the base peak at m/z 149.0097, which is attributed to the excess deprotonated tartaric acid. Firstly, we studied the complexes of Zr and Hf, which are easy to be analyzed by mass spectrometry because both of them have multi-natural isotopes. As shown in Figure 3, five isotopic mass spectra peaks of Zr (relative abundances are 51.46, 11.23, 17.11, 17.40, and 2.80) were found at m/z 384.9001 (Figure 3a), 404.9066 (Figure 3b), and 534.9168 (Figure 3c), and the

proposed molecular formulas were $[\text{C}_8\text{H}_7\text{O}_{12}\text{Zr}]^-$, $[\text{C}_8\text{H}_{17}\text{O}_7\text{Zr}_2]^-$, $[\text{C}_{13}\text{H}_{29}\text{O}_5\text{Zr}_3]^-$ or $[\text{C}_{30}\text{H}_5\text{O}_5\text{Zr}]^-$, respectively. We checked every

chemical formula according to the basic chemical criteria and finally selected its valid chemical formula of $[\text{C}_8\text{H}_7\text{O}_{12}\text{Zr}]^-$, whose structure

Fig. 3. Mass spectra of Zr/tartaric complex in negative mode: (a) m/z values of 384.9001; (b) m/z values of 404.9066; (c) m/z values of 534.9168.

should be $(\text{C}_4\text{H}_4\text{O}_6)_2\text{Zr}$. Unfortunately, no effective complex of Hf with tartaric acid has been found in our experiments.

Nb has only one natural isotope, which makes it difficult to analyze the possible complexes by mass spectrometry. Although Ta has two natural isotopes (^{180}Ta and ^{181}Ta), the relative abundance of ^{180}Ta is only 0.012, which is often annihilated in the process of mass spectrum elucidation. Therefore, for Nb and Ta, we used mass spectrometry to validate the possible complexes, which were boldly speculated based on previous work (34). On the basic chemical criteria, namely, that there may be five products in the complexation reaction of Ta with tartaric acid. The corresponding mass numbers of the five products were calculated by software Xcalibur. The results showed that the effective ionic currents and corresponding mass spectra peak of $\text{H}_5[\text{NbO}_4(\text{C}_4\text{H}_4\text{O}_6)]$, $\text{Me}_2\text{ONb}_2\text{O}_5(\text{C}_4\text{H}_4\text{O}_6)_2$ and $\text{MeH}[\text{NbO}(\text{C}_4\text{H}_4\text{O}_6)]$ did not appear, which confirms that these are not valid chemical formulas. Nevertheless, two effective mass spectra peaks have been found for Nb at m/z 272.8986 (Figure 4a) and 404.9051 (Figure 4b), the chemical formulas $[\text{C}_8\text{H}_8\text{O}_{13}\text{Nb}]^-$ and $[\text{C}_4\text{H}_4\text{O}_8\text{Nb}]^-$ resolved by software are in accordance with our expectations. Therefore, the complex product of Nb with tartaric acid might be $\text{H}[\text{NbO}(\text{C}_4\text{H}_4\text{O}_6)_2]$ and $\text{H}[\text{NbO}_2(\text{C}_4\text{H}_4\text{O}_6)]$. A similar procedure was used for Ta. The peak of $[\text{C}_8\text{H}_{10}\text{O}_{14}\text{Ta}]^-$ obtained at m/z 510.9556 is in agreement with what we expected (Figure 5), which confirms that the complex product of Ta might be $\text{HTa}(\text{OH})_2(\text{C}_4\text{H}_4\text{O}_6)_2$.

At the same time, we also scanned the blank solution of tartaric acid using the Q Exactive mass spectrometer. It was found that the

mass spectrum peak of the HFSE complex resolved in our work did not exist in the blank solution, which excluded the influence of background interference peak.

Analytical Performance

The analytical performance of the proposed method, including

Fig. 4. Mass spectra of Nb/tartaric complex in negative mode: (a) m/z values of 272.8986; (b) m/z values of 404.9051.

Fig. 5. Mass spectra of Ta/tartaric complex in negative mode.

TABLE III
Nb, Ta, Zr, Hf Levels in Six Geological SRMs by Present Method
(n=3, $\mu\text{g g}^{-1}$)

Nb				Ta			Zr			Hf		
Name	Ref. Value	This Work	RSD (%)	Ref. Value	This Work	RSD (%)	Ref. Value	This Work	RSD (%)	Ref. Value	This Work	RSD (%)
AGV-2	14.5	14.0	4.66	0.87	0.87	6.70	230	232	1.94	5.00	5.22	2.14
BHVO-2	18.1	18.6	2.66	1.14	1.19	3.11	172	170	2.96	4.36	4.41	4.07
BCR-2	12.6	12.1	3.35	0.78	0.79	3.35	184	184	0.61	4.90	4.83	2.54
OU-7	6.35	6.71	4.41	0.38	0.47	7.00	133	115	3.42	3.17	3.00	2.44
GSM-1	0.90	0.95	10.3	-	0.20	-	27.0	26.5	7.63	0.83	0.83	3.13
ORPT-1	11.6	11.6	5.19	0.99	0.88	14.7	245	251	3.93	7.53	7.36	3.16

precision, accuracy, and detection limits, was evaluated under the optimal conditions. Precision was studied by calculating the relative standard deviation (RSD) of three replicate measurements, and the accuracy was determined by comparing the obtained results with the certified or information values for AGV-2, BHVO-2, BCR-2, GSM-1, OU-7, and ORPT-1 (Table III). The detection limits of Nb, Ta, Zr, and Hf in this work, defined as the concentration equivalent to 10 times the standard deviation of 11 measurements for a blank solution, were 0.018, 0.036, 0.042, and 0.011 $\mu\text{g g}^{-1}$, respectively.

Analysis of Geological SRMs

Using the optimized procedure, a series of geological SRMs comprising seven soils, 17 rocks, and 11 sediments were chosen to validate the established analytical method in which these samples cover three basic rock types containing igneous (andesite, basalt, diorite, gabbro, trachyte), sedimentary (limestone, dolomite, sandstone, shale, carbonate), and metamorphic (gneiss) rocks. Due to the difference of the HFSE content in samples of distinct lithology and the test accuracy requirements of different concentration ranges are not the same, the results of 35 SRMs were evaluated according to the analytical accuracy

control rules in the specification of geochemical reconnaissance survey (1:50,000) (DZ/T 0011-2015) (44). The comparison for the logarithm values between the analytical results and the reference values for the HFSE in 35 reference materials is illustrated in Figure 6. Except for two sedimentary carbonate rocks (GBW07114 dolomite and GBW07120 limestone), whose contents of HFSE are at very low levels, the accuracy of the results in 33 geological reference materials was in good agreement with the requirements of the specification of the geochemical reconnaissance survey.

CONCLUSION

This work has demonstrated that the method of a modified closed digestion with TA as the matrix modifier based on ICP-MS analysis can precisely and accurately analyze HFSE in various geological samples at the same time. For HFSE, the irreversible hydrolysis and polymerization in acid medium and the loss due to adsorption of fluoride precipitation in HF medium were solved successfully by this proposed method. Furthermore, in order to clarify the mechanism for the stable existence of HFSE in TA, the complexing products of high field strength elements with TA were analyzed by

high resolution mass spectrometry. Except for Hf, the molecular formulas of complexing products for the other three HFSE (Nb, Ta, and Zr) were obtained. It can be stated that the proposed method is valid and was employed to measure 35 geological SRMs, and that the results of 33 materials were in good agreement with the certified or reference values.

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Fig. 6. Determination values of Nb, Ta, Zr, and Hf in this study vs. the reference values for 35 geological SRMs.

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