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On-line preconcentration of niobium(V) and tantalum(V) as 4-(2-pyridylazo) resorcinol–citrate ternary complexes in geological samples by ion interaction high-performance liquid chromatography

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Abstract

4-(2-Pyridylazo) resorcinol (PAR) and citrate were used as pre-column complexing agents for the determination of Nb(V) and Ta(V) as ternary complexes in geological samples. Aliquots of 2 ml of the standard and sample solutions containing the Nb(V) and Ta(V) complexes were loaded onto a concentrator column (C_{18} , 0.4 cm \times 4.6 mm) with a carrier mobile phase comprising 20% (v/v) methanol and containing 5 mM acetic acid, 5 mM citric acid and 10 mM tetrabutylammonium bromide (TBABr), pH 6.5 at 2 ml/min for 2 min, with the effluent being directed to waste. An automatic switching valve was then switched to flush both complexes from the concentrator column onto a C_{18} analytical column using a mobile phase comprising 32% (v/v) methanol and containing 5 mM acetic acid, 5 mM citric acid and 3 mM TBABr, pH 6.5 for 2.5 min. The switching valve was then switched back to the original position, and cleaned with methanol for 7 min to eliminate unwanted species still adsorbed to the concentrator column. This procedure prevented later eluting compounds from reaching the analytical column, which reduced the overall run time. The detection limits of Nb(V) and Ta(V) (determined at a signal-to-noise ratio of 3, detection wavelength of 540 nm and a 2-ml sample volume) were 0.012 and 0.039 ppb for Nb(V) and Ta(V), respectively. Recoveries of Nb(V) and Ta(V) were 99.4 and 96.2%, respectively. The HPLC results obtained from the reference granite and basalt samples agreed well with inductively coupled plasma MS and certified values, but the HPLC method yielded slightly low values of the Nb/Ta ratio. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Geological samples; Sample preparation; Complexation; Niobium; Tantalum; Inorganic cations; Metal complexes

1. Introduction

In geological materials, the Nb/Ta ratio demonstrates fractionation of these two elements during crustal evolution and suggests that Nb/Ta variation may be indicative of a particular chemical process within the crust–mantle system [1]. In most rock

samples, the background levels of Nb are at low ppm levels and Ta at sub-ppm levels. Therefore, the determination of Nb and Ta in various types of rocks requires precise and accurate data at low detection limits, and inductively coupled plasma (ICP)-atomic emission spectrometry (AES) [2] and ICP-MS [3] have been applied successfully. The major disadvantage of these methods is the high cost of the instrumentation. Reversed-phase high-performance liquid chromatography (RP-HPLC) offers a relatively simple and low cost alternative for the determination of Nb(V) and Ta(V) and also enables the

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Nb/Ta ratio to be determined from a single analysis rather than from using two analytical methods.

Recently, we have presented three RP-HPLC methods for the determination of Nb(V) and Ta(V) in geological samples by the separation of ternary complexes of the metal ions with 4-(2-pyridylazo) resorcinol (PAR) and citrate [4], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) and citrate [5] and 2-(5-bromo-2-pyridylazo)-5-[*N*-propyl-*N*-(3-sulfopropyl)amino] phenol (Br-PAPS) and citrate [6]. These methods provided good separation of Nb(V) and Ta(V) from other elements and also gave high sensitivity, and proved suitable for the determination of Nb(V) in all of the representative rock samples studied. However, these methods did not provide sufficient sensitivity and/or separation selectivity for the trace determination of Ta(V) for those geological samples in which its concentration was below 1 ppm in the untreated rock (or 1 ppb in the digested rock solution). Analyses performed using the Br-PADAP–citrate or PAPS–citrate ternary complexes gave detection limits for Ta(V) which were approximately three times lower than for the PAR–citrate complexes but there was an interfering peak at the retention time of Ta(V) in andesite and basalt samples. Therefore, a means to improve the detection limits and selectivity for the determination of Ta(V) is required.

PAR–citrate ternary complexes of Nb(V) and Ta(V) had proved to be the most selective, but gave the poorest detection sensitivity, so a method to improve the sensitivity of this method was sought. In the present study, we have developed an on-line preconcentration method utilising a concentrator pre-column and an automatic switching valve in order to improve the detection limits for the separation of Nb(V) and Ta(V) as PAR–citrate ternary complexes. This method was then applied to the determination of Nb(V) and Ta(V) in geological samples.

2. Experimental

2.1. Reagents and solutions

Atomic absorption standard solutions of Nb(V) (1.005 mg ml⁻¹) and Ta(V) (0.990 mg ml⁻¹) were obtained from Aldrich (Milwaukee, WI, USA) and QCD ANALYSTS [Standard mixture contains: 100 ppm: Nb(V), Ta(V), Hf(IV), Zr(IV), Mo(VI), Ge(IV), Si(IV), Ti(IV) and W(VI) in water with trace HF, from NJ, USA]. The PAR was 98% purity (Aldrich) and solutions of the dye were prepared freshly in 0.1 M ammonium hydroxide before use. Details of other chemicals were as described in Ref. [4], Section 2.1. Several reference geological materials were used: GSR-1 (granite, obtained from the institute of Rock and Mineral Analysis, Beijing, China); ACE (granite, provided by Geostandards B.P.20, 54501 Vandoeuvre Cedex, France); BHVO-1 (basalt, obtained from the National Institute of Standards and Technology, Gaithersburg, MD, USA); GSR-4 (granite, obtained from the Institute of Rock and Mineral Analysis, Ministry of Geology and Mineral Resources, Beijing, China); and G1485 (basalt, from Macquarie Island, Antarctic, Australia and supplied by T. Crawford).

The composition of the mobile phase for loading the Ta(V) and Nb(V) complexes onto the concentrator column and the analytical mobile phase are shown in Table 1.

2.2. Instrumentation

Screw-top Savillex PTFE beakers (Savillex, Minnesota, USA) were used for digestion of the rock samples. Spectrophotometric studies were carried out using a Cary 5E UV–Vis–NIR spectrophotometer (Varian, Mulgrave, VIC, Australia).

The chromatographic system for the preconcent-

Table 1
Composition of the mobile phases

Mobile phase	Methanol (% v/v)	[Acetic acid] (mM)	[TBABr] (mM)	[Citric acid] (mM)	Eluent pH
Eluent 1	20	5	10	5	6.5
Eluent 2	32	5	3	5	6.5

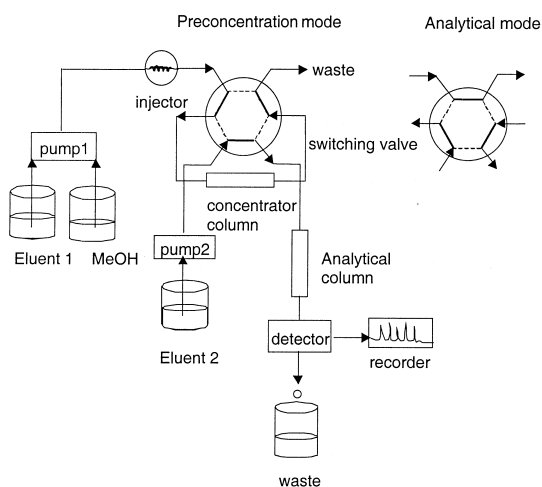


Fig. 1. Schematic diagram of on-line pre-concentration using RP-HPLC.

tration of Ta(V)–PAR–citrate and Nb(V)–PAR–citrate complexes is shown in Fig. 1. The pre-concentration flow-path consisted of a Waters (Milford, MA, USA) Model 600E gradient pump, a Rheodyne (Cotati, CA, USA) model 7125 stainless steel injector (2-ml loop) and a concentrator column packed with Resolve C₁₈ silica gel, 4 mm in length (Waters).

The analytical flow-path consisted of a Waters Model 510 pump, a SPD-6AU UV–Vis spectrophotometric detector (Shimadzu, Tokyo, Japan) operated at 540 nm and a Maxima 820 Chromatography Data Station (Waters). A NovaPak C₁₈ reversed-phase column (150×3.9 mm I.D., particle size 4 μm, Waters) was used as the analytical column. The Ta(V) and Nb(V) complexes were switched from the pre-concentration flow-path to the analytical flow path by means of an automated Rheodyne six port switching valve.

The flow-rate of the mobile phase for pre-concentration of Nb(V) and Ta(V) complexes on the concentrator column was 2 ml/min and the flow-rate of the mobile phase used to elute both complexes from the concentrator column and onto the analytical column was maintained at 1.0 ml/min. The column temperature was maintained at 30°C.

2.3. Procedures

2.3.1. Sample preparation

Duplicate 0.1000 g powdered rock samples were

prepared in Screw-top Savillex PTFE beakers using a previously described procedure [3], modified for use in HPLC separations [4]. This procedure involved pressurised digestion of the sample in concentrated HF and HNO₃, evaporation to incipient dryness and dissolution of the residue in HCl and HNO₃ to give a final volume of 20 ml. Each solution was then transferred to a plastic container and made up to 20 ml with water, before being divided into two portions. The first portion was used for HPLC experiments and this analysis was performed as quickly as possible in order to prevent loss of Nb(V) and Ta(V) from the solution. The second portion was prepared for ICP-MS measurements by taking 4 ml of the original solution and it diluting to 20 ml using 2 mM diethylenetriaminepentaacetic acid (DTPA). The solutions prepared for ICP-MS were analysed within 24 h to limit the risk of insufficient stabilisation of Nb(V) and Ta(V) and to prevent adsorption on the wall of the container.

2.3.2. Pre-column complex formation

The optimised conditions for the pre-column formation of the ternary complexes of Ta(V) and Nb(V) for the standard solutions and for the rock samples were obtained from earlier studies [4]. The standard solutions were prepared as follows: Citric acid (2.50 ml, 0.10 M) was added to a 25-ml plastic volumetric flask and then a standard solution of Nb(V) and Ta(V) was added, followed by a 1.00 ml of freshly prepared PAR solution (5·10⁻³ M), the pH was adjusted to 6.0 with dilute ammonia solution, and the solution was made up to the mark with water. After 50 min, a 2-ml aliquot of the solution was injected onto the concentrator column. (Fig. 1, pre-concentration mode). The concentration of the metal ions was determined by measuring the peak area.

The geological samples were treated as follows: The digested sample (2.00 ml) was added to 2.50 ml of citric acid solution (0.1 M) in a 25-ml plastic volumetric flask, to which 6.00 ml of freshly prepared PAR solution (5·10⁻³ M) was added. The pH of the solution was then adjusted to 6.0 with dilute ammonia solution, and the solution made up to the mark with water. After 50 min, the sample solution was filtered through a 0.45-μm filter before a 2-ml aliquot was injected onto the concentrator column (Fig. 1, pre-concentration mode). For quantitative

analysis, the analyte concentrations were determined using standard addition methods.

2.3.3. On-line preconcentration

The following techniques were used for preconcentration of the ternary complexes of Nb(V) and Ta(V) on-line using a two-way switching valve for standard solutions and for samples. The standard or rock samples containing Nb(V) and Ta(V) complexes were concentrated onto the concentrator column with eluent 1 (Table 1) for 2 min at a flow-rate of 2 ml/min. The switching valve was then switched to the analytical flow-path and the complexes were eluted from the concentrator column with eluent 2 (Table 1) at a flow-rate of 1.0 ml/min. After 2.5 min, the concentrator column was switched back to its original position and washed with pure methanol for 7 min to eliminate unwanted species still adsorbed to the concentrator column. The concentrator column was then re-equilibrated with eluent 1 for about 5 min before the next injection.

2.3.4. ICP-MS

Details of the ICP-MS instrument employed in this work have been described in Ref. [4], Section 2.3.3.

3. Results and discussion

3.1. Determination of mole ratios of the Nb(V) and Ta(V) PAR–citrate complexes

The conditions used for the preparation of Nb(V) and Ta(V) as PAR–citrate ternary complexes and the detection wavelength (540 nm) were the same as for the previous study [4]. The mole ratios of [Nb(V)]:[PAR]:[citrate] and [Ta(V)]:[PAR]:[citrate] complexes were investigated using continuous variations of the mole fraction of the metal ion, the PAR reagent and citric acid at pH 6, with the absorbance at each mole ratio being measured at 540 nm. For each measurement the total mole sum of the components was $2.27 \cdot 10^{-6}$ mol in 25 ml. The requirement for large molar excesses of PAR and citrate to ensure quantitative complex formation with Nb(V) and Ta(V) introduces some uncertainty into the determination of the actual mole ratio in the complex by using the mole ratio method [4], but this study suggested that the most likely mole ratio for the

[Nb(V)]:[PAR]:[citrate] and [Ta(V)]:[PAR]:[citrate] ternary complexes was 1:2:1.

3.2. Preconcentration and separation parameters

The mobile phase used to load the ternary complexes onto the preconcentrator column was modified from the optimal mobile phase conditions identified in our previous studies of the separation and determination of Ta(V) and Nb(V) [4]. Four mobile phase parameters affected separation, namely [MeOH], [TBABr], [citrate] and [acetate]. Of these, the first two were shown to exert the greatest influence on retention. Therefore, the composition of the loading mobile phase was investigated over the range of 0–20% MeOH and 5–15 mM TBABr, with the concentration of citrate and acetate being maintained at 5 mM each. A loading mobile phase comprising 20% (v/v) methanol, 10 mM TBABr, 5 mM acetic acid and 5 mM citrate buffer at pH 6.5 provided the maximum peak height for the Ta(V) complex and gave quantitative binding of the complexes to the concentrator column. This composition was therefore selected as the optimum loading mobile phase.

The analytical mobile phase was also modified from our earlier studies [4]. A mobile phase comprising 32% (v/v) methanol, 3 mM TBABr, 5 mM acetic acid and 5 mM citrate buffer at pH 6.5 was found to provide a good separation of Nb(V) and Ta(V) complexes without any interference from the matrix metal ions [V(V), V(IV), Co(II) and Fe(III)]. Other matrix metal ions that could form complexes with PAR [Cu(II), Ni(II), Cr(III), Mn(II), Zn(II) and Cd(II)] were not eluted from the analytical column. Fig. 2 shows the separation of Ta(V) and Nb(V) from the matrix metal ions using the above mobile phase composition.

The chromatogram of Nb(V) and Ta(V) as PAR–citrate complexes contained an unidentified impurity peak present in the PAR reagent at a retention time of about 50 min (not shown), which considerably added to the total analysis time. Therefore, the preconcentration column was also used as a means to reduce the total analysis time. A chromatogram of the standard and blank solution was obtained using eluent 2 and the pre-column alone and is shown in Fig. 3. It is clear from this chromatogram that Ta(V) and Nb(V) were eluted from the pre-column within

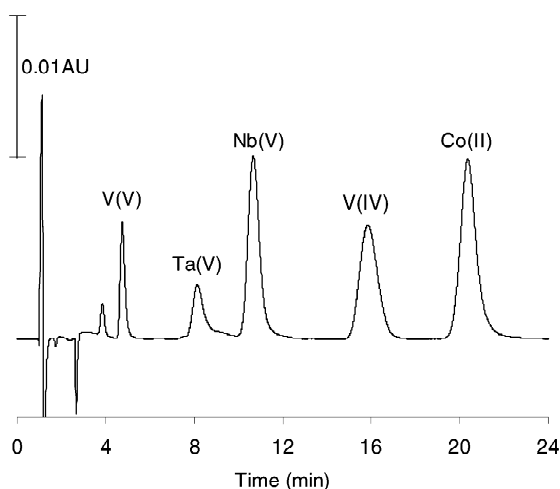


Fig. 2. Preconcentration chromatogram of Nb(V)–PAR–citrate (10 ppb), Ta(V)–PAR–citrate (10 ppb), V–PAR (40 ppb) and Co(II)–PAR (40 ppb). Mobile phase for the concentration step was eluent 1 (see Table 1) and for the analytical separation was eluent 2 (see Table 1). Time for elution of complexes from the concentrator column to analytical column: 3 min. Concentrator column: Resolve C_{18} ; length: 4 mm; flow-rate: 2 ml/min. Analytical column: 150×3.9 mm I.D., $4 \mu\text{m}$, NovaPak C_{18} ; flow-rate: 1 ml/min. Injection loop: 2 ml; temperature 30°C ; detection: 540 nm.

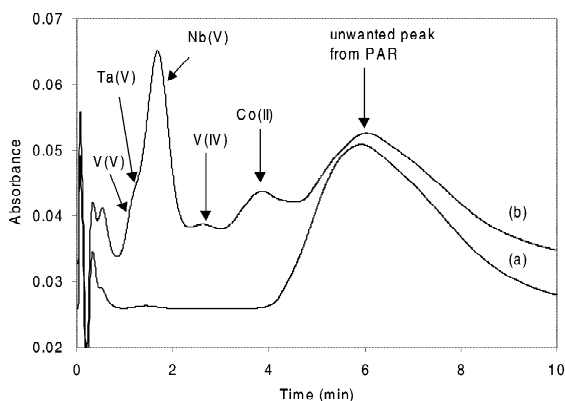


Fig. 3. Chromatogram of (a) blank and (b) standard Nb(V), Ta(V), V(IV), V(V) and Co(II) mixture obtained using the concentrator column only. Mobile phase for preconcentration complexes at concentrator column (Resolve C_{18} , 4 mm in length) was eluent 1 with a flow-rate of 2 ml/min for 2 min. Mobile phase for elution of complexes from the concentrator column direct to detector was eluent 2 with a flow-rate of 1 ml/min. Injection loop: 2 ml; temperature 30°C ; detection: 540 nm.

approximately 2 min. The Co(II) and unwanted impurity PAR peak were eluted at around 3 and 4 min, respectively, and could be prevented from entering the analytical column by moving the switching valve back to its original position after 2.5 min. Under these conditions all of the Ta(V) and Nb(V) complexes were eluted from the concentrator and onto the analytical column, whilst Co(II), other strongly bound matrix metal complexes and the unwanted impurity were still retained on the concentrator column, and could be washed off by changing the loading mobile phase to 100% MeOH for 7 min. The concentrator column was then re-equilibrated for 5 min with the loading mobile phase (eluent 1) prior to the next injection.

3.3. Analytical performance parameters

The detection limits (determined at a signal-to-noise ratio of 3) were 0.012 and 0.039 ppb for Nb(V) and Ta(V), respectively, for a 2-ml portion of the standard solution. Percentage recoveries of Nb(V) and Ta(V) from the concentrator column were investigated by comparison of the slope of the calibration curves obtained from direct injection and preconcentration. A $100\text{-}\mu\text{l}$ loop and the concentration range of 5, 10, 20, 40, 80 and 160 ppb of both Nb(V) and Ta(V) were used for the direct injection calibration curve, and a 2-ml loop and the concentration range of 0.25, 0.50, 1, 2, 4 and 8 ppb of both Nb(V) and Ta(V) was used for the preconcentration calibration curve. This arrangement resulted in exactly the same amounts of Ta(V) and Nb(V) injected for each of the calibration curves. The direct injection calibration curve exhibited good linearity [$r^2=0.9994$ and $r^2=0.9996$ for Nb(V) and Ta(V), respectively] and the preconcentration injection calibration curve also showed good linearity [$r^2=0.9998$ and $r^2=0.9987$ for Nb(V) and Ta(V), respectively]. The percentage recoveries, obtained from the ratio of the slopes of the two calibration curves, were 99.4 and 96.2% for Nb(V) and Ta(V), respectively.

Five replicate injections of the standard solution [20 ppb Ta(V) and 20 ppb Nb(V)] were carried out and the resulting %relative standard deviation (RSD) for retention time and peak area of Ta(V) was 0.12 and 1.8 and for Nb(V) was 0.12 and 0.52, respectively. Determination of the precision for the entire analytical procedure was not undertaken because of

the specialised apparatus needed and the lengthy time needed for sample preparation.

External standard calibration curves for the analysis of the digested samples were linear [$r^2=0.9997$ and 0.9999 for Ta(V) and Nb(V), respectively] up to at least 100 ppb of the metal ion and the standard addition calibration curves of the digested samples also showed acceptable linearity [$r^2=0.9767$ – 0.9994 for Ta(V) and $r^2=0.9881$ – 1.000 for Nb(V)].

3.4. Determination of Nb(V) and Ta(V) in rock samples

In this work, five representative reference geological materials containing Ta(V) at sub-ppb to ppb concentrations (in the digested solution) were used for analysis. Those were GSR-4 (granite), BHVO-1 (basalt), ACE (granite), GSR-1 (granite) and G1485 (unknown basalt sample) (Table 2). In order to distinguish error arising from the HPLC procedure, all sample solutions were analysed simultaneously by both HPLC and ICP-MS.

Fig. 4 shows a typical chromatogram obtained from the blank (a), BHVO-1 reference granite (b) and BHVO-1 spiked with 4 ppb of Ta(V) and 2 ppb of Nb(V) (c). Fig. 5 shows a typical chromatogram of (a) the blank, (b) the GSR-1 reference granite and

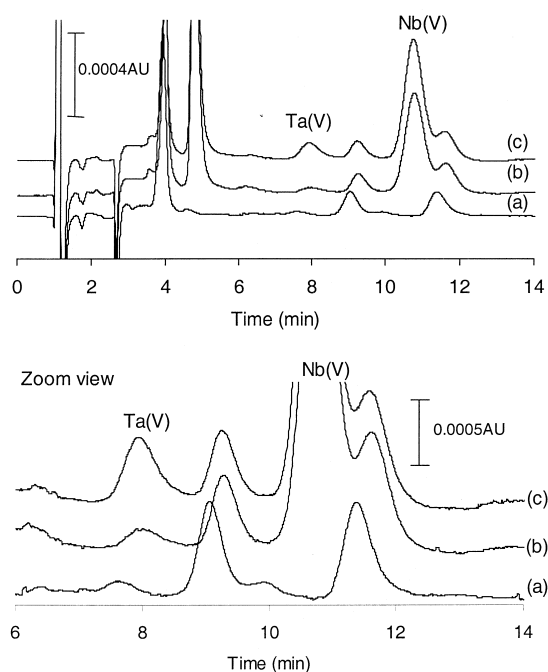


Fig. 4. Chromatogram of (a) blank, (b) reference basalt BHVO-1 and (c) reference basalt BHVO-1 spiked with 4 ppb of Ta(V) and 2 ppb of Nb(V). Top: complete view, bottom: zoom view. The samples contained [PAR]=1.2 mM; [citrate]=10 mM. Chromatographic conditions as in Fig. 2, except the time for elution of complexes was 2.5 min.

Table 2
Comparison of the results (ppm) for Nb and Ta obtained from RP-HPLC, ICP-MS and the certified values

Sample	Metal ion	Concentration (ppm)			Nb/Ta ratio		
		Certified value [7]	ICP-MS ^a	HPLC	Certified value [7]	ICP-MS ^a	HPLC
GSR-4	Nb(V)	5.90	5.73	4.60	14.1	14.0	7.8
	Ta(V)	0.42	0.41	0.59			
BHVO-1	Nb(V)	19.00	19.50	21.60	15.5	16.3	13.5
	Ta(V)	1.23	1.20	1.60			
GSR-1	Nb(V)	40.00	43.90	38.80	5.6	6.5	4.7
	Ta(V)	7.20	6.80	8.10			
ACE	Nb(V)	110.00	126.80	113.00	17.2	18.4	15.9
	Ta(V)	6.40	6.90	7.10			
G1485	Nb(V)	157(XRF) ^b	166.00	156.00	–	20.2	17.0
	Ta(V)	–	8.20	9.20			

^a Results provided by Dr. Ashley Townsend, Central Science Laboratory, University of Tasmania.

^b Results provided by Mr. P. Robinson, School of Earth Sciences, University of Tasmania.

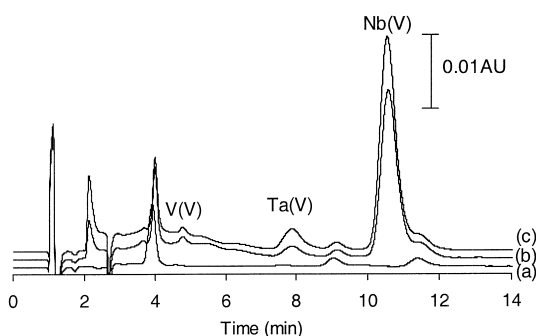


Fig. 5. Chromatogram of (a) blank, (b) reference granite GSR-1 and (c) reference granite GSR-1 spiked with 3 ppb of Ta(V) and 4 ppb of Nb(V). The samples contained [PAR]=1.2 mM; [citrate]=10 mM. Chromatographic conditions as in Fig. 2, except the time for elution of complexes was 2.5 min.

(c) the GSR-1 spiked with 3 ppb of Ta(V) and 4 ppb of Nb(V). Both Ta(V) and Nb(V) are well resolved from the other components present in each of the samples with the spike being used to confirm the peak identities. Analyses of ACE (granite), GSR-4 (granite), and G1485 (basalt) showed similar chromatograms.

Both external and standard addition calibration methods were used to quantify the amount of Ta(V) and Nb(V) in each of the rock samples. The results from the standard addition method provided good agreement with both the certified values and ICP-MS results, and are listed in Table 2. The external standard method generally returned low results (data not shown) with the exception of the granite samples. A possible reason was that a precipitate formed after complex formation for all of the samples, with the exception of the granites, and Nb(V) and Ta(V) complexes may have been adsorbed onto solid residues, leading to a reduced response. Nevertheless, the standard addition method overcame this problem and could be used for all type of rock samples.

Also shown in Table 2 are the results for the Nb/Ta ratio obtained by the ICP-MS and HPLC methods. These results show that the HPLC method gave a consistently low value in comparison to the certified value and the ICP-MS value. This effect arises predominantly from the fact that the HPLC results for Ta(V) were all slightly elevated. No explanation for this could be found. However, the

HPLC method provides sufficiently reliable values of the Nb/Ta ratio for meaningful geological interpretations to be made.

4. Conclusions

On-line preconcentration and simultaneous separation of anionic Nb(V) and Ta(V) PAR–citrate ternary complexes was achieved on a C_{18} reversed-phase column using tetrabutylammonium as an ion-interaction reagent in the mobile phase. On-line preconcentration provided adequate detection sensitivity for the determination of sub-ppm concentrations of Nb(V) and Ta(V) in the untreated rock samples. Based on a comparison with ICP–MS and certified values in the reference rock materials, accurate results were obtained for the determination of both Nb(V) and Ta(V) using a standard addition method. However, values for the Nb/Ta ratio showed that the HPLC method gave values which were slightly less than the certified values.

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