Determination of niobium(V) and tantalum(V) as 4-(2-pyridylazo)resorcinol–citrate ternary complexes in geological materials by ion-interaction reversed-phase high-performance liquid chromatography

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Abstract

A method for the simultaneous separation and determination of Nb(V) and Ta(V) as ternary complexes formed with 4-(2-pyridylazo)resorcinol (PAR) and citrate was developed using ion-interaction reversed-phase high-performance liquid chromatography on a C_{18} column. Method parameters, such as pre-column complex formation conditions and composition of the complexes were investigated using spectrophotometry and HPLC. Under the optimum conditions, the Nb(V) and Ta(V) complexes were eluted within 12 min with a mobile phase of methanol–water (32:68, v/v) containing 5 mM acetate, 5 mM TBABr and 5 mM citrate buffer at pH 6.5, with detection at 540 nm. A typical separation efficiency was 33 000 and 20 000 theoretical plates per metre for Nb(V) and Ta(V), respectively. The relative standard deviation of retention times for the Nb(V) and Ta(V) complexes were 0.16% and 0.17% and for peak areas were 0.28% and 1.36%, respectively. The detection limits (signal-to-noise ratio=3) for Nb(V) and Ta(V) were 0.4 ppb and 1.4 ppb, respectively. Results obtained for standard reference rock samples agreed well with certified values and results obtained by inductively coupled plasma MS. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Geological samples; Niobium; Tantalum; Metal complexes; Pyridylazoresorcinol

1. Introduction

Niobium (Nb) and tantalum (Ta) have very similar chemical behaviour due to their similar ionic radii and their common occurrence in the same oxidation states [1]. Determination of Nb and Ta in various matrixes is important in both industrial and geological applications.

In industrial fields, Nb and Ta find important applications in the microelectronics industry, fabrication of semiconductor components and production of various types of catalysts and materials with special electro-physical characteristics [2].

In geochemistry, Nb and Ta are extremely important tracers to understand the evolution of Earth's major crustal and mantle reservoirs [3,4]. Continental crust is characterised by a selective depletion of Nb and Ta relative to other elements of otherwise similar geochemical behaviour (e.g., U, Th and La [3,5]). Precise determination of ratios such as Nb/U or

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Nb/Th therefore gives valuable insights into the processes taking place during generation of continental crust from the mantle. Furthermore, this depletion of Nb and Ta can be observed worldwide in subduction related volcanic rocks, thus allowing the use of these elements for identification of this rock type. Due to their similar ionic radii and valency states [4,6], Nb and Ta generally show extremely similar geochemical behaviour and were long thought to occur at a constant ratio (ca. 17.5) in most rocks [4,7]. However, recent work has showed Nb/Ta ratios in mafic igneous rocks to vary over the range of 8 to 25 [8–10], thus making a precise determination of both elements of high interest. The abundance of Nb in rocks usually varies between 0.1 and 200 ppm [3,4,8,9,11] whereas equivalent Ta abundances lie an order of magnitude lower. For geological materials, which are generally analysed at a dilution of 1/1000, detection limits for Nb and Ta must therefore be at the ppb level for Nb and even lower for Ta.

Several analytical methods have been used to determine trace amounts of Nb and Ta in geological and other materials. These include X-ray fluoresence (XRF) [12–21], inductively coupled plasma (ICP) mass spectrometry (MS) [11,22–25], ICP atomic emission spectrometry (AES) [26–31], atomic absorption spectrometry (AAS) [32,33], neutron activation analysis (NAA) [34] and reversed-phase high-performance liquid chromatography (RP-HPLC) [35–41]. The detection limits for these methods are summarised in Table 1. The main disadvantage of ICP-AES, ICP-MS and NAA methods are high costs, whilst for XRF and AAS, low sensitivity limits their utility for geological analyses.

There are several previous reports of the use of metallochromic reagents for pre-column formation of complexes with Nb(V) and Ta(V), with subsequent separation of these complexes by RP-HPLC. The metallochromic ligands used include 4-(2-pyridylazo)resorcinol (PAR) [35,41], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) [36,37], 2-(2-thiazolylazo)-5-diethylamino phenol (TADAP) [38], 2-(5-nitro-2-pyridylazo)-5-diethyl-aminophenol (5-NO$_2$-PADAP) [39] and 4-(5-nitro-2-pyridylazo)resorcinol (5-NO$_2$-PAR) [40]. However, all of the RP-HPLC methods [35,37,39] give a very broad peak for the Ta(V) complex (peak width of about 3 to 5 min) and/or incomplete separation of the Nb(V) and Ta(V) complexes. Split peaks were obtained under conditions reported in Ref. [36]. Because of the generally poor peak shapes for methods [36–40], the previously reported detection limits were not confirmed.

A widely used metallochromic ligand available in good purity and at a low price is PAR [42]. However, a previously reported method using pre-column formation of ternary complexes of Nb(V) and Ta(V)

Table 1
Previous analytical methods used for trace determinations of Nb and Ta

Methods	Detection limit (in solid sample, ppb)		Ref.	Application
	Nb	Ta		
XRF	60–10 000	245–20 000	[12–21]	Rock
ICP-MS	19–100	0.8–200	[11,22–25]	Rock
ICP-AES	3–2000	6–10 000	[26–31]	Rock
AAS	3100–8800	600–13 700	[32,33]	Rock
NAA	–	–	[34]	Rock
RP-HPLC with:				
(1) PAR and tartaric acid	10[a]	60[a]	[35]	Alloy
(2) Br-PADAP and H$_2$O$_2$	0.5[a]	2[a]	[36]	Human hair
(3) Br-PADAP and tartaric acid	0.22[a]	1.79[a]	[37]	Mineral GSD-2
(4) TADAP and tartaric acid	0.32[a]	1.77[a]	[38]	Mineral GSD-2
(5) NO$_2$-PADAP and tartaric acid	0.13[a]	1.41[a]	[39]	Mineral GSD-2
(6) NO$_2$-PAR	0.65[a]	–	[40]	Rain water
(7) PAR and tartaric acid	5[a]	–	[41]	Rock

[a] In injected solution.

with PAR and tartrate and their separation on a C_{18} column [35] offered only relatively poor detection limits. Therefore there is a demonstrable need for a better method for separation and determination of Nb(V) and Ta(V) by HPLC. As the retention mechanism for charged amphiphilic metal complexes with metallochromic ligands in ion-pair RP-HPLC separation can be quite complex, a thorough investigation and optimisation of separation parameters may also be necessary to provide a workable method.

The aims of the present research were to develop a method for the determination of traces of Nb and Ta in geological materials. For such a method to be successful, it must give high separation selectivity to permit separation of the Nb(V) and Ta(V) complexes, as well as a higher level of detection sensitivity than has been achieved to date using RP-HPLC methods. We have based the new method on the formation of a ternary complex (to provide selectivity) using a metallochromic ligand (to provide detection sensitivity) and an auxiliary complexing agent.

2. Experimental

2.1. Reagents and solutions

Throughout this study all water used was distilled and then deionised using a Milli-Q system (Millipore, Bedford, MA, USA), after which it was filtered through a 0.45-μm membrane filter (type HA, Millipore) before use. HPLC-grade methanol was obtained from BDH (Poole, UK).

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). The PAR was 98% purity (Aldrich) and solutions of the dye were prepared freshly in 0.1 M ammonium hydroxide before use. Analytical-reagent grade tetrabutylammonium bromide (TBABr, Sigma, St. Louis, MO, USA), anaytical-reagent grade 1-octanesulfonic acid sodium salt (OSA, Sigma), analytical-reagent grade citric acid (BDH) and analytical-reagent grade ammonium hydroxide (NH$_4$OH, Ajax Chemicals, Sydney, Australia) were used. Reagents used in the preparation of the geological samples were as fol-

lows: analytical-reagent grade perchloric acid (BDH), 99.99+% purity hydrofluoric acid (HF, Aldrich), analytical-reagent grade hydrochloric acid (BDH), analytical-reagent grade sulfuric acid (Ajax Chemicals), analytical-reagent grade nitric acid (HNO$_3$, BDH). Concentrated HF and HNO$_3$ were doubly distilled before used.

Reference geological materials (ACE, AGV-1, BHVO-1 and GSR-1) were obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA).

Mobile phases were prepared by dissolving TBABr, acetic acid and citric acid in water, adding the required volume to the desired amount of methanol, adjusting the pH with ammonium hydroxide and then diluting with water in order to adjust the final methanol concentration to the desired level. The optimal mobile phase composition was methanol–water (32:68, v/v), pH 6.5 containing 5 mM each of TBABr, acetic acid and acetic acid.

2.2. Instrumentation

A PicoTrace apparatus (Göttingen, Germany) was used for pressure-digestion of rock samples. Spectrophotometric studies were carried out using a Cary 5E UV–Vis–near IR spectrophotometer (Varian, Mulgrave, Australia).

The chromatographic system consisted of a Waters (Milford, MA, USA) Model 510 pump, a Rheodyne (Cotati, CA, USA) Model 7125 stainless steel injector (100 μl loop), a SPD-6AU UV–Vis spectrophotometric detector (Shimadzu, Tokyo, Japan) operated at 540 nm, and a Maxima 820 Chromatography Data Station (Waters). A NovaPak C_{18} reversed-phase column (150 mm×3.9 mm I.D, particle size 4 μm, Waters) was used as the analytical column, and was fitted with a C_{18} (particle size 10 μm) guard column housed in a Guard-Pak pre-column module (Waters). The flow-rate of the mobile phase was maintained at 1.0 ml min^{-1} and the column temperature was kept at 30°C. Detection was accomplished by absorbance measurements at 540 nm.

2.3. Procedures

2.3.1. Sample preparation
Geological samples were prepared using a pres-

sure digestion method adapted from a previously described procedure [9]. Duplicate 0.1000 g powdered rock samples were dissolved in 3 ml of concentrated HF and 3 ml of concentrated $HClO_4$ in a polytetrafluoroethylene (PTFE) crucible. The sample was digested at 180°C for about 15 h under high pressure. For granite samples (GSR-1 and ACE), H_2SO_4 was used instead of $HClO_4$ because granite contains minerals of low solubility in $HClO_4$, such as zircon and monazite. The mixture was then evaporated to dryness at 180 °C for 16 h (for $HClO_4$) or 100 h (for H_2SO_4). The precipitate was dissolved in 2 ml of concentrated HNO_3 followed by 1 ml of concentrated HCl by warming at 60°C for a short period before the temperature was increased to 180 °C for 4–5 h in order to dissolve all the residues. The solution was transferred to a plastic container and made up to 10 ml with water. Each solution was divided into two portions. The first portion was used for HPLC experiments and it was found that it was stable about four days. The second portion was diluted to give a final concentration of 2% HNO_3 and 1% HCl and used for ICP-MS measurements. The solutions prepared for ICP-MS were analysed within 24 h to limit the risk of precipitation of Nb and Ta on standing and the adsorption of the precipitate on the wall of the container [9].

2.3.2. Pre-column complex formation

The following techniques were used for pre-column formation of the ternary complex for standard solutions and for samples:

In the case of standard solutions, citric acid (1.70 ml, $1.5 \cdot 10^{-2}$ *M*) was placed in a 25-ml plastic container and then a standard solution of Nb(V) and Ta(V) was added, followed by a 0.50 ml of freshly prepared PAR solution ($1 \cdot 10^{-2}$ *M*), and the pH was adjusted to 6.0 with dilute ammonia solution. The solution was transferred to a 25-ml plastic volumetric flask and made up to the mark with water. After 50 min, a 100-μl aliquot of the solution was injected onto the HPLC column. The concentration of the metal ion(s) was determined by measuring the peak area.

In the case of a geological sample, the sample digest (1.00 ml) was added to 1.70 ml of citric acid solution ($1.5 \cdot 10^{-2}$ *M*) in a plastic container, to which 3.00 ml of freshly prepared PAR solution

($1 \cdot 10^{-2}$ *M*) was added. The pH of the solution was then adjusted to 6.0 with dilute ammonia solution, the solution transferred into a 25-ml plastic volumetric flask and made up to the mark with water. After 50 min, the sample solution was filtered through a 0.45-μm filter before a 100-μl aliquot was injected onto the HPLC column.

For quantitative analysis, the analyte concentrations were determined using external standard and/or standard addition methods.

2.3.3. ICP-MS

Analyses were performed using a Finnigan Element high-resolution ICP-MS system (Bremen, Germany). Nb and Ta were analysed at masses 93 and 181, respectively, and were calibrated using freshly prepared standard solutions. Instrument detection limits for Nb and Ta were approx. 10 ppt and 0.1–3 ppt, respectively. Indium (In) was used as an internal standard for both elements. All results were corrected for drift by analysing standard solutions throughout each analytical sequence. Instrument sensitivity was typically 100 000 counts per second per ppb of [115]In (i.e., 100 MHz/ppm). Analyses of the real samples were performed on the same solutions, which were used for HPLC.

2.3.4. Evaluation of separation efficiency, baseline noise and limit of detection (LOD)

As the peaks were symmetrical, the separation efficiency (number of theoretical plates, *N*) was evaluated from the peak width at the half height. The baseline noise was evaluated graphically using two segments of baseline (approx. 0.5 min each) situated at the sides of the analyte peaks. The LOD was calculated for a signal-to-noise ratio of 3.

3. Results and discussion

3.1. Pre-column complex formation

As a first step in the development of the desired HPLC method, several literature methods were evaluated with slight modifications. The approach using PAR–tartrate ternary complexes [35] gave low sensitivity and very broad peak shapes for both Nb(V) and Ta(V), whereas the methods using Br-
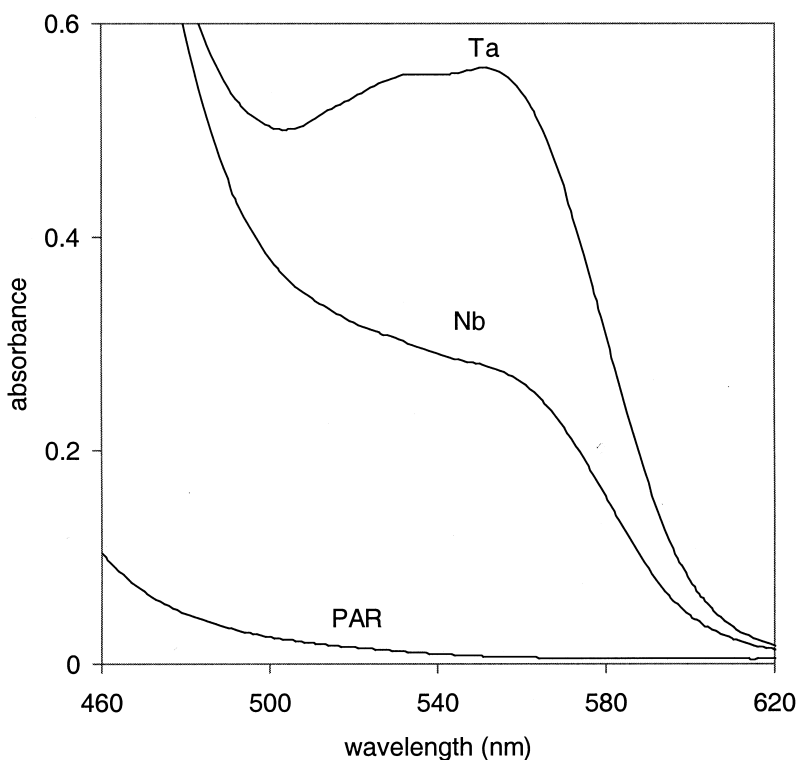
Fig. 1. Absorption spectra of PAR–citrate, Nb–PAR–citrate (0.5 ppm) and Ta–PAR–citrate (2 ppm) at pH 6. Conditions [PAR]=0.2 m*M*, [citrate]=10 m*M*.

PADAP–hydrogen peroxide ternary complexes with Nb(V) and Ta(V) [36] gave two peaks for Nb(V). In addition, Br-PADAP–tartrate ternary complexes were studied using the same conditions as in Ref. [37] but a very broad peak for Ta(V) was obtained. None of these methods was considered suitable for the desired analysis.

When using strongly coloured complexes of metallochromic ligands for the determination of metal ions by RP-HPLC, either pre-column or post column derivatisation can be employed for the formation of the metal complexes [43]. Post-column derivatisation can be used only when the kinetics of complexation is fast. Preliminary tests with the PAR–citrate system showed that this was not the case, so pre-column complexation was chosen for this work in a manner similar to previous RP-HPLC studies [35–41]. Optimal chromatography with pre-column derivatisation arises when only a single, stable product is formed by the derivatisation re-

action [43]. For this reason, initial studies were undertaken using spectrophotometry and RP-HPLC in order to optimise reaction conditions for the complex formation, and to maximise detection sensitivity.

3.1.1. Formation of the ternary complexes and their absorption spectra

PAR is well known to form coloured complexes with many metal ions [42]. In this work, it has been shown that in a citric acid medium, red ternary aqueous soluble complexes of Nb(V) and Ta(V) with PAR and citrate are formed over the pH range 5–6.5. Absorption spectra of Nb(V) and Ta(V) complexes measured at various pH values were similar (except for differing absorptivities) with both showing strong absorbance at pH 6.0. The wavelength of maximum absorbance was 550 nm for both Nb(V) and Ta(V) complexes but a detection wavelength of 540 nm was used for HPLC because

signal:noise was optimal at this wavelength. Fig. 1 shows a comparison of spectra of the Nb(V) and Ta(V) complexes at the optimal pH of 6; the corresponding molar absorptivities were $5.43 \cdot 10^4$ l mol^{-1} cm^{-1} and $5.01 \cdot 10^4$ l mol^{-1} cm^{-1} for Nb(V) and Ta(V) complexes, respectively.

In order to determine the conditions under which a single, stable complex for each analyte could be obtained, studies on the composition of the complexes were undertaken and in particular on the mole ratios of Nb(V)–PAR–citrate and Ta(V)–PAR–citrate. Using the method of continuous variations, the mole ratio of Nb(V)–PAR was determined to be 1:2. No accurate conclusion about the mole ratio of Ta(V)–PAR could be reached due to the inconclusive nature of the continuous variations plot, but HPLC studies showed that use of a two-fold excess of PAR resulted in the appearance of only one chromatographic peak for Ta(V). The mole ratio of Nb(V)–citrate was then investigated while the mole ratio of Nb(V)–PAR was kept constant at 1:2, with the results showing the mole ratio of Nb(V)–PAR–citrate in the complex was 1:2:2. If the Nb(V)–citrate molar ratio was less than 1:2, split peaks or multiple peaks were observed, indicating the presence of at least two complexes. In the case of Ta(V), a six-fold molar excess of citrate over Ta(V) was necessary to ensure that only a single peak was produced in the HPLC analysis.

The structure of the Nb–PAR–citrate ternary complex was not determined. However, the mole ratio of 1:2:2 and the facts that both PAR and citrate can act as bi- or tridentate ligands [42] and the coordination numbers for Nb(V) and Ta(V) generally lie between 4 and 9 [1], suggest that all available coordination sites at the central metal atom are likely be saturated by the PAR and citrate ligands.

3.1.2. Optimisation of the pre-column complex formation

The parameters used for the pre-column formation of the ternary complex were investigated in order to identify conditions leading to reproducible formation of the complex. A pH of 6.0 had been selected previously on the basis of pH effects on the absorption spectrum of the complex. The optimal concentration range of PAR was then determined to be 0.12–0.28 m*M* for a standard mixture of Nb(V) (40 ppb) and Ta(V) (80 ppb) in 10 m*M* citrate, and 0.20 m*M* PAR was therefore used for preparation of the complex for standard solutions. Since some of the metal ions present in the sample matrix can also form complexes with the PAR, the optimum concentration of PAR was also studied for real samples (standard reference samples of rocks). Peak areas of Nb(V) and Ta(V) complexes in several real samples were measured using 0.4–1.6 m*M* PAR for the sample preparation and showed that 1.20 m*M* PAR gave optimal performance and this concentration was therefore used for all samples.

Since the kinetics of complex formation are critical to method development, the time required for complete complex formation and the stability over time of the resultant metal–PAR–citrate complexes were investigated using four different citrate concentrations. These studies showed that 10 m*M* citrate gave optimal results for the formation and stability of the complex in both standard and sample solutions, and under these conditions, at least 50 min was required to form the complex and the complex remained stable for at least 4 h after preparation.

3.2. Separation parameters

When using mobile phases containing only a citrate buffer in a methanol–water mixture, the Nb(V) and Ta(V) complexes are eluted unretained from a RP-HPLC C$_{18}$ column. The lack of appreciable hydrophobic interaction of the analytes suggests that the ternary complexes are quite polar or carry a charge. For charged species, retention on C$_{18}$ stationary phases can be increased by addition of amphiphilic ions of opposite charge to the mobile phase. The addition of the anionic octanesulphonate caused no increase in the retention of the complexes, but tetrabutylammonium ion (TBA$^+$) was found to cause increased retention of both complexes, indicating that these complexes are anionic.

The amount of methanol in the mobile phase was found to exert a very strong effect on retention, with retention times being excessively long for less than 32% methanol and resolution between the two complexes being poor above 38% methanol. On the other hand, peak areas increased marginally at higher methanol concentrations. After consideration of these

factors, the optimal concentration of methanol was selected to be 32%.

Citrate and acetate were investigated as buffers and were studied over a range of 5–15 mM citrate and 0–10 mM acetate. Minimal effects on detection sensitivity were noted, but the retention times of the Nb(V) and Ta(V) complexes decreased with increasing concentration of citrate or acetate, which can be explained in terms of the influence of ionic strength on the dynamic ion-exchange separation mechanism. The pH of the mobile phase had a significant effect on the peak area of both complexes, with increased pH giving increased peak area up to pH 7. The optimum for both Ta(V) and Nb(V) was pH 6.5 because of the possibility of hydrolysis of the metal ions at higher values of pH.

As expected for anionic analytes, the concentration of tetrabutylammonium ions in the mobile phase exerted a major influence on the retention of Nb(V) and Ta(V), as well as on the retention of the matrix metal ions (Fig. 2) A final concentration of 5 mM TBABr provided a good separation of both analytes and the matrix metal ions in a reasonable time. The separation of a standard mixture of several metal ions is illustrated in Fig. 3 and shows a baseline separation of Ta(V) and Nb(V) in 12 min

and elution of all the matrix metal ions in about 50 min.

3.3. Analytical method performance parameters

The detection limits (determined at signal-to-noise ratio=3) were 0.4 ppb and 1.4 ppb for Nb(V) and Ta(V), respectively, in the injected sample solution. For a sample dilution factor of 1/1000 this corresponds to a limit of detection in the solid rock sample of 0.4 ppm and 1.4 ppm for Nb(V) and Ta(V), respectively. A separation of Nb(V) and Ta(V) complexes at concentrations close to the detection limits is shown in Fig. 4. All external standard calibration curves were linear up to at least 40 ppb of the metal ion [r^2=0.9999 and r^2=0.9986 for Nb(V) and Ta(V), respectively]. The standard addition calibration curves also exhibited good linearity [r^2=0.995 to r^2=0.999 for both Nb(V) and Ta(V)]. Experiments on the reproducibility of retention times and peak areas for Nb(V) and Ta(V) were conducted using five replicates. The relative standard deviations (RSDs) of retention time of Nb(V) and Ta(V) were 0.16% and 0.17% while the RSDs of the peak area were 0.28% and 1.36%, respectively.
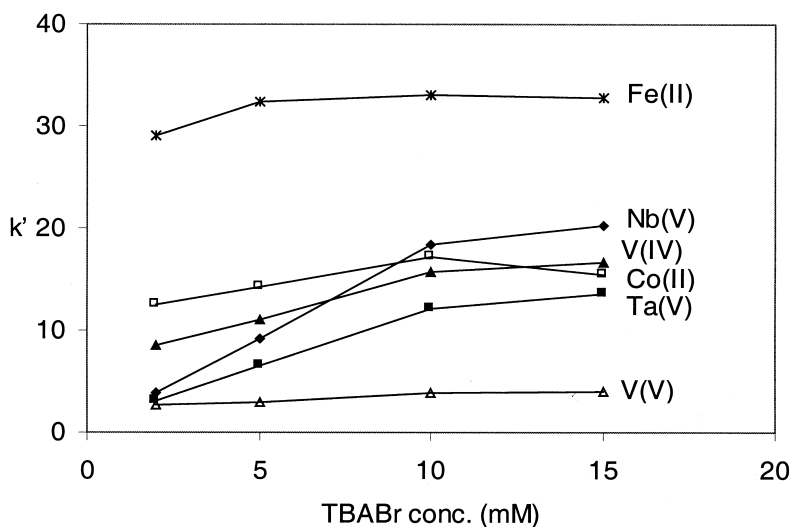

Fig. 2. Effect of TBA·Br concentration on k' of Nb–PAR–citrate, Ta–PAR–citrate, Co–PAR, V–PAR and Fe–PAR. Mobile phase was methanol–water (32:68, v/v) containing 5 mM acetate, various concentrations of TBABr and 5 mM citrate buffer at pH 6.5; analytical column: 150×3.9 mm I.D., 4 μm, NovaPak C$_{18}$; flow-rate: 1 ml/min; temperature: 32°C; detection at 540 nm.
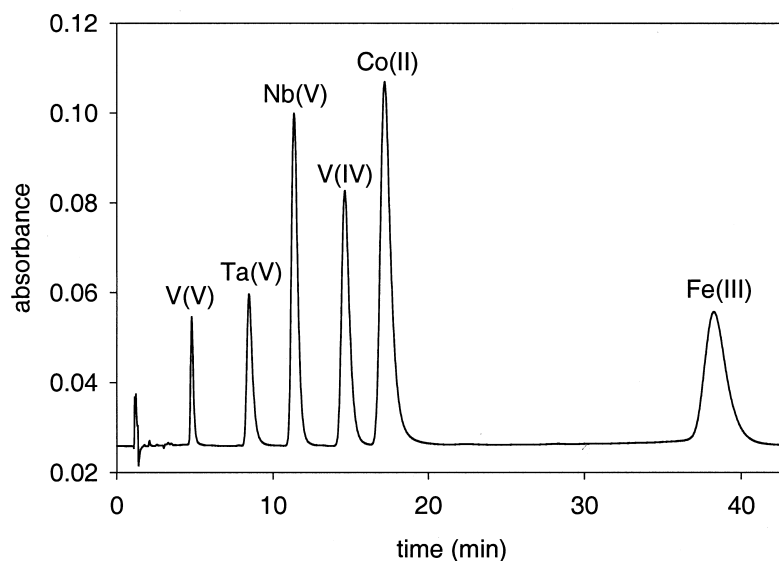
Fig. 3. Chromatogram of Nb–PAR–citrate (1 ppm), Ta–PAR–citrate (4 ppm), V–PAR (4 ppm), Co–PAR (1 ppm) and Fe–PAR (8 ppm). Mobile phase was methanol–water (32:68, v/v) containing 5 mM acetate, 5 mM TBA·Br and 5 mM citrate buffer at pH 6.5; analytical column: 150×3.9 mm I.D., 4 μm, NovaPak C_{18}; flow-rate: 1 ml/min; temperature: 32°C; detection at 540 nm.

The effect of potential interferences was also studied. It was found that although Cu(II), Ni(II), Cr(III), Mn(II), Zn(II) and Cd(II) formed red coloured complexes with PAR, no interferences were observed in the final chromatogram. Further, all reagents added during the sample preparation and complex formation were investigated as blank solutions and the RP-HPLC chromatogram showed no baseline disturbances over the entire retention time range 3–30 min.
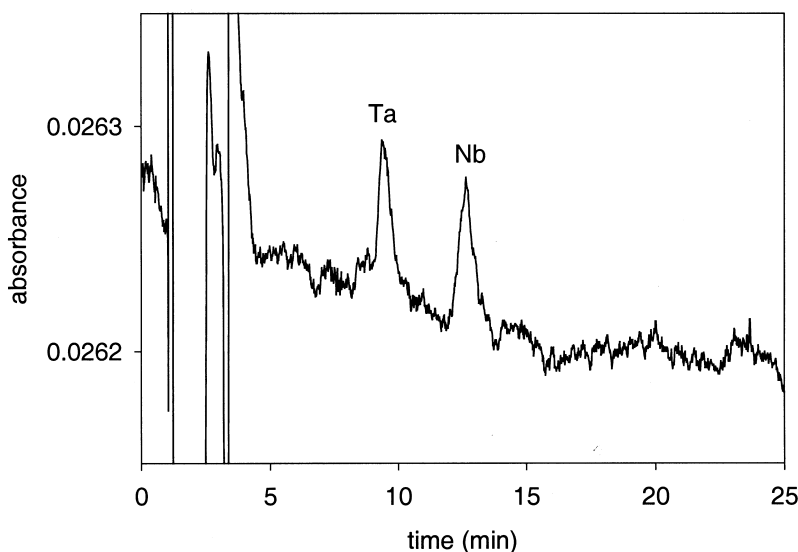

Fig. 4. Chromatogram of Nb–PAR–citrate (0.5 ppb) and Ta–PAR–citrate (2 ppb) containing [PAR]=0.20 mM; [citrate]=10 mM. Chromatographic conditions as in Fig. 3.

3.4. Determination of Nb(V) and Ta(V) in standard reference materials

Complete dissolution of rock samples and subsequent stabilisation of Nb(V) and Ta(V) in solution is required for accurate measurements of Nb(V) and Ta(V) in such samples. Due to their high valency state, both Nb(V) and Ta(V) hydrolyse easily, resulting in a decrease in their concentration and the introduction of considerable errors. Therefore it was necessary to stabilise Nb(V) and Ta(V) after dissolution of the sample by dilution in a mixture of conc.
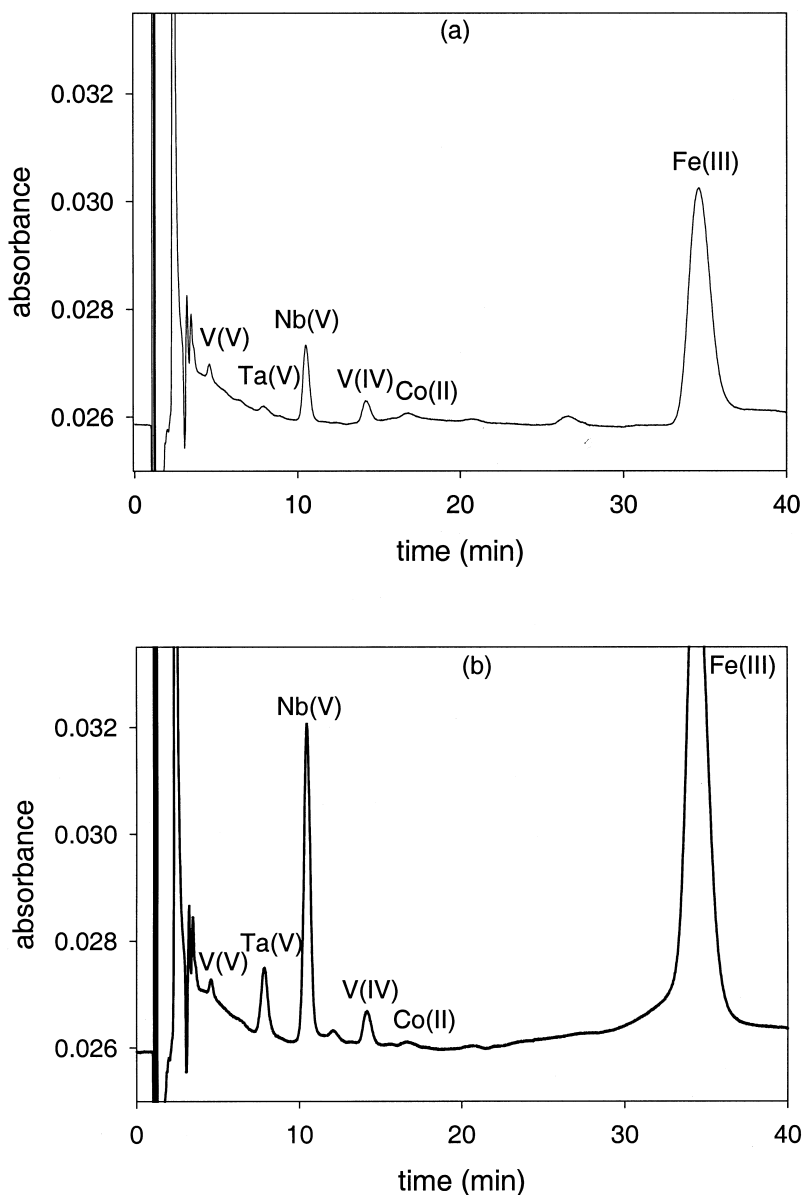

Fig. 5. Chromatogram of (a) reference granite rock GSR1 and (b) reference rock GSR1 spiked with 40 ppb Nb(V) and 40 ppb Ta(V). The samples contained [PAR]=1.20 mM; [citrate]=10 mM. Chromatographic conditions as in Fig. 3. Some precipitation of the Fe(III) complex has occurred in (a) causing reduced peak area.

HNO$_3$ and HCl, following the procedure of Münker [9]. In order to discriminate between errors arising from insufficient stabilisation Nb(V) and Ta(V) and errors arising from the HPLC procedure, all rock solutions were simultaneously analysed by both HPLC and ICP-MS.

A range of representative reference rock samples

(GSR-1 AGV-1, ACE and BHVO-1) was chosen. Chromatograms obtained without and with a standard addition of Nb(V) and Ta(V) are shown in Fig. 5 for the GSR1 reference material, and in Fig. 6 for the BHVO-1 reference material. It can be seen that clear peaks were evident for both Nb(V) and Ta(V), but the background observed in chromatograms of
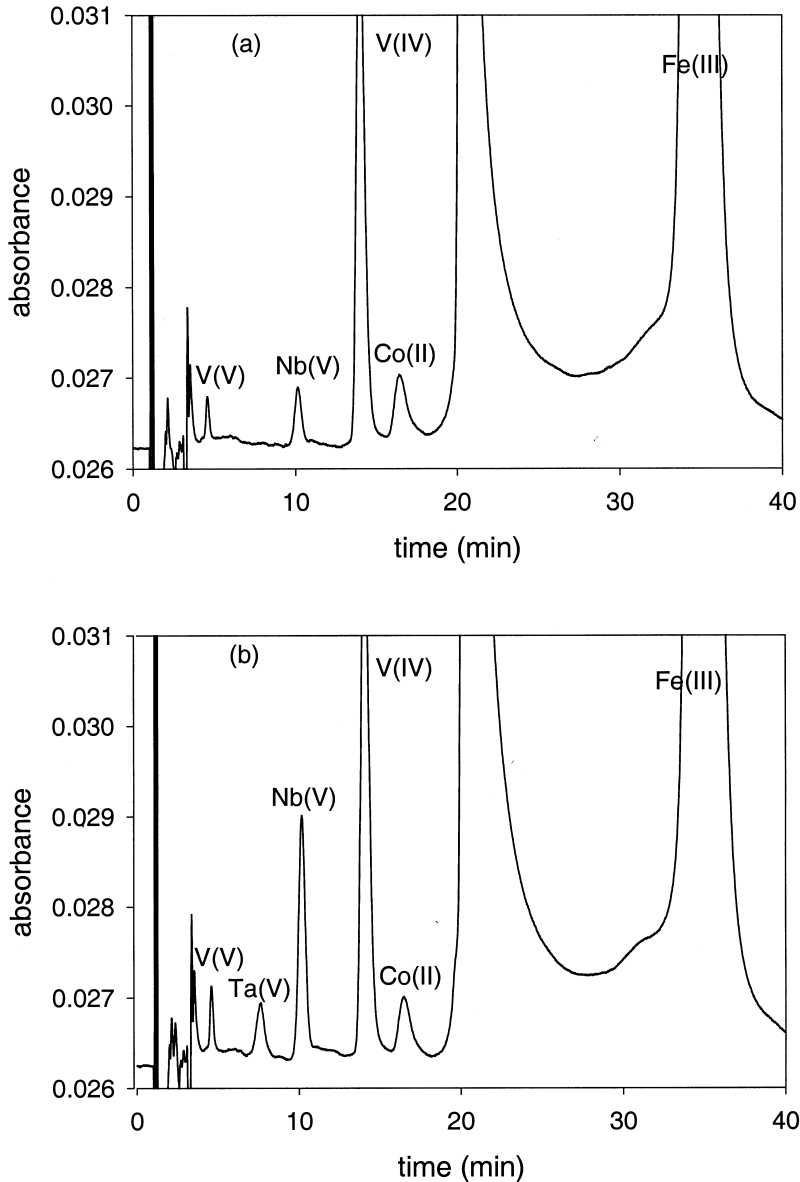

Fig. 6. Chromatogram of (a) reference basalt rock BHVO-1 and (b) reference basalt rock BHVO-1 spiked with 20 ppb Nb(V) and 20 ppb Ta(V). The samples contained [PAR]=1.20 m*M*; [citrate]=10 m*M*. Chromatographic conditions as in Fig. 3.

Table 2
Comparison of the results for Nb and Ta by RP-HPLC, ICP-MS and the certified values

Reference rocks	Metal	Certified value (ppb) [44]	ICP-MS (ppb)	RP-HPLC	
				External standard (ppb)	Standard addition (ppb)
ACE	Nb	110	127	98.8	103.5
AGV-1	Nb	15	13.1	13.2	15.3
BHVO-1	Nb	19	18.7	14.7	19.8
GSR-1	Nb	40	43.8	38.8	38.8
ACE	Ta	6.4	7.1	12.5	12.4
AGV-1	Ta	0.90	0.8	N.D.[a]	N.D.
BHVO-1	Ta	1.23	1.1	N.D.	N.D.
GSR-1	Ta	7.2	7.0	14.2	10.5

[a] N.D.=Not detected.

real samples is the main factor limiting the LOD. Increasing the analyte concentration by decreasing the dilution of the digested rock does not improve detectability because of the commensurate substantial increase of background signal. To determine the amount of Nb(V) and Ta(V) in reference materials, both external standard and standard addition methods were used and results are shown in Table 2. The RP-HPLC method showed consistent results between external standard and standard addition methods. The results for Nb(V) are in a good agreement with both certified values and ICP-MS results. For Ta(V), the concentration in AGV-1 and BHVO-1 was below the detection limit. Results for Ta(V) in ACE and GSR-1 (external standard and standard addition) were somewhat higher than certified values and ICP-MS results which can be explained by the high matrix background of these samples and the fact that the Ta(V) concentration in the final solutions was close to the detection limit. This illustrates the limitations of the method described here and the need for further developments.

4. Conclusions

Retention and separation of the anionic metal–PAR–citrate ternary complexes of Nb(V) and Ta(V) can be achieved on a C_{18} column using tetrabutylammonium as an ion-interaction reagent in the mobile phase. The separation selectivity is governed mainly by the concentrations of tetrabutylammonium, methanol and buffer in the mobile phase and also the mobile phase pH. The detection sensitivity depends on the conditions used for the pre-column complex formation, such as pH and reaction time, and sensitivity is also affected by the mobile phase composition. Based on a comparison with ICP-MS and certified values in reference materials, accurate results for the determination of Nb and Ta in geological materials. However, for Ta(V) determinations in a wider range of rock samples, a lower detection limit for Ta(V) than the presently obtained is required. Investigations using more sensitive metallochromic ligands, together with the use of sample preconcentration methods, are in progress.

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