Asian Journal of Chemistry Vol. 19, No. 5 (2007), 3851-3861

Determination of Vanadium, Niobium and Tantalum by HPLC using 2-(2-Quinolinylazo)-Resorcin as Pre-column Derivatization Reagent

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A new method for analysis of vanadium, niobium and tantalum as metal chelates of 2-(2-quinolinylazo)-resorcin (QAR) was developed using high performance liquid chromatography. The vanadium, niobium and tantalum ions were pre-column derivatized with QAR to form coloured chelates. The V-QAR, Nb-QAR, Ta-QAR were enriched by solid phase extraction with C_{18} cartridge. The enrichment factor of 100 was achieved by eluted the retained chelates from the cartridge with tetrahydrofuran (THF). The chelates were separated on a ZORBAX Stable Bound, 4.6 × 50 mm, 1.8 μm rapid analytical column with acetonitrile-water (42:58, v/v) containing 0.01 mol L^{-1} pH 4.5 phosphatic buffer and 0.01 mol L^{-1} of citrate as mobile phase. The vanadium, niobium and tantalum chelates were separated completely within 2.5 min. The detection limits (S/N=3) of vanadium, niobium and tantalum are 3.2, 3.2 and 3.8 ng L^{-1}, respectively. This method was applied to the determination of vanadium, niobium and tantalum in alloy steel, water and geologic samples with good results.

Key Words: Vanadium, Niobium, Tantalum, 2-(2-Quinolinylazo)-Resorcin, HPLC.

INTRODUCTION

Vanadium, niobium and tantalum are important elements in alloy steel, geologic samples and environmental samples[1-3]. Therefore, the determination of trace vanadium, niobium and tantalum in these samples with high accuracy, sensitivity and rapidity is of great importance. The separation and determination of vanadium, niobium and tantalum are extremely difficult because of their approximate atomic radii and similar chemical properties. Therefore, how to eliminate the interference between them is the key point to be solved. At present, there are several analytical methods for the determination of vanadium, niobium and tantalum including

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spectrophotometry, atomic absorption spectrometry, fluorescence and mass spectrometry (MS)[4-15]. However, the traditional spectrophotometry usually need a tedious and complicate chemical separation processes. AAS and AES have low sensitivity because of spectral interference or high background. XRF and MS have high sensitivity in the determination of V, Nb and Ta, but they have the disadvantage of high costs. Therefore, a requirement exists for a more affordable alternative method.

The RP-HPLC technique with pre-column derivatization has been proved to be a favourable and reliable technique for the separation and determination of trace amount of vanadium, niobium and tantalum[16-27]. However, the routine chromatographic methods have some disadvantages. On the one hand, these methods need a long separation time (more then 10 min is needed). On the other hand, the used derivatization reagents have low sensitivity, or need long time heating for a complete reaction[16-27]. To development a more sensitive and rapid method for the simultaneous determination of vanadium, niobium and tantalum, in this work, a new pre-column derivatization regents, 2-(2-quinolinylazo)-4-methyl-1,3-dihydroxybenzene (QAR) for vanadium, niobium and tantalum was studied and a ZORBAX Stable Bound rapid analysis column (4.6 × 50 mm, 1.8 μm) was used for the separation of metal-QAR chelates. The three chelates were separated to baseline within 2.5 min. The separation time was greatly shortened compared to the routine chromatographic methods. This method can be applied to the determination of vanadium, niobium and tantalum in alloy steel, geologic samples and water with good results.

EXPERIMENTAL

Synthesis of QAR: The QAR was synthesized according to reported method[28]. 2-Aminoquinoline (7.2 g) was dissolved in 500 mL anhydrous ethanol, to which, sodamide (2.0 g) was added and the mixture was refluxed in boiling water bath for 5 h, followed by the addition of isoamyl nitrite (7.4 mL). The solution was refluxed for 0.5 h with boiling water bath. The solution was cooled and placed over night under 0ºC. The diazo salt was obtained by filtering this solution with an isolation yield of 95 %. Thereafter, the diazo salt was dissolved in 200 mL anhydrous ethanol, followed by the addition of resorcinol (5.5 g). The carbon dioxide was flushed into the solution with stirring until the pH reaches *ca.* 8.0. The solution kept for 2 d and then diluted the solution with 400 mL water and extracted with chloroform. The solvent was evaporated and the residue was re-crystallized with 30 % ethanol. QAR was obtained with 45 % yield.

The HPLC system is consisted of a Waters 2690 Alliance separation model and a 996 photodiode array detector (Waters Corporation, USA). The pH values were determined with a Beckman Φ-200 pH meter. The

spectrophotometric studies were carried out using UV-160 A spectrophotometer (Shimadzu, Japan). The separation column used is a ZORBAX Stable Bound rapid column (4.6 × 50 mm, 1.8 μm) (Agilent Corporation, USA). The cartridge used is Zorbax C_{18} solid phase extraction cartridge (1 cc/50 mg, 30 μm) (Agilent Corporation, USA). The extraction was performed on Waters Solid Phase Extraction (SPE) Device (The device can prepare 20 samples simultaneously).

Chemicals: All of the solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). Standard metal (V, Nb and Ta) solutions (1.0 mg mL^{-1}) were obtained from Chinese standards center and appropriately dilutions were made to prepared working solutions. A 2.0×10^{-3} mol L^{-1} QAR solution was prepared by dissolving QAR with acetonitrile. The acetonitrile used is HPLC grade (Fisher Corporation, USA). A 0.5 mol L^{-1} phosphatic buffer solution (pH = 4.5) and a citrate solution (1.0×10^{-2} mol L^{-1}) were used. The mobile phase used is acetonitrile-water (42:58, v/v) (containing 0.01 mol L^{-1} phosphatic buffer (pH 4.5) and 0.01 mol L^{-1} of citrate).

Sample preparation: The alloy steel samples and Geologic samples analysized are Certified Chinese Standard Materail. The standard values were determined by Atomic Absorption Spectrum (AAS), Atomic Fluorescence Spectrum (AFS), Neutron Activation Analysis (NAA), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-IES) and Ion Chromatography (IC) method. The water samples were collected form Panlong River, Kunming, P.R.China.

For alloy steel, a 0.1000-0.200 g of sample was weighted accurately into the Teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China). To which, 5 mL of diluted nitric acid (1:2, v/v) and 2-3 drops of hydrofluoric acid were added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full power for 6.0 min. The digest was evaporated to near dryness. 10 mL of sulfuric acid (10 % v/v) was added to dissolve the residue, then 20 mL of tartaric acid (5 %, m/v) was added. The solution was heated until it was completely clear. After cooling to room temperature, the solution was transferred into a 100 mL Teflon volumetric flask and diluted to the mark with water.

For geologic samples, a 0.1000-0.200 g of powdered rock was digested by 2 mL of concentrated hydrofluoric acid and 1 mL of concentrated nitric acid with microwave acid-digestion for 0.5 h. The digest was evaporated to incipient dryness at low temperature, after which, 1 mL concentrated nitric acid was added and the samples were evaporated again to incipient

dryness. 10 mL of 5 % hydrochloric acid was added to the solid residues, then 20 mL of tartaric acid (5 %, m/v) was added. The solution continued heated until it was completely clear. After cooled to room temperature, the solution was transferred into a 50 mL teflon volumetric flask and diluted to the mark with water.

For water samples, 50 mL of sample were took into a 200 mL flask and 2.0 mL of concentrated nitric acid was added. The sample was concentrated to about 5 mL by heating on a hot plate and was digested by 2.0 mL concentrated nitric acid with microwave acid-digestion for 6.0 min. The digest was evaporated to near dryness. The residue was dissolved with 5 mL 5% HCl and transferred into a 50 mL of calibrated flask quantitatively, then diluted the solution to volume with water.

Standard procedure: A proper volume of standard or sample solution was transfered into a 100 mL of Teflon volumetric flask. To which, 3.0 mL of 2.0×10^{-3} mol L^{-1} QAR solution, 5.0 mL of phosphatic buffer solution with pH 4.5 and 3 mL of 1.0×10^{-2} mol L^{-1} citrate were added. The solution was diluted to required volume with water and mixed well. After 15 min, the solution was passed through the C_{18} cartridge at a flow rate of 10 mL min^{-1}. When the enrichment had finished, the retained chelates were eluted from the cartridge with 1.0 mL of THF at a flow rate of 5 mL min^{-1} in an opposite direction. The solution was filtered with 0.45 μm of filters and adjusted to the volume of 1.0 mL. 5.0 μL of sample was injected for HPLC analysis. A tridimensional (X axis: retention time, Y axis: wavelength, Z axis: absorbance) chromatogram was recorded from 450~650 nm with photodiode array detector and the chromatogram of 580 nm was shown in Fig. 1.

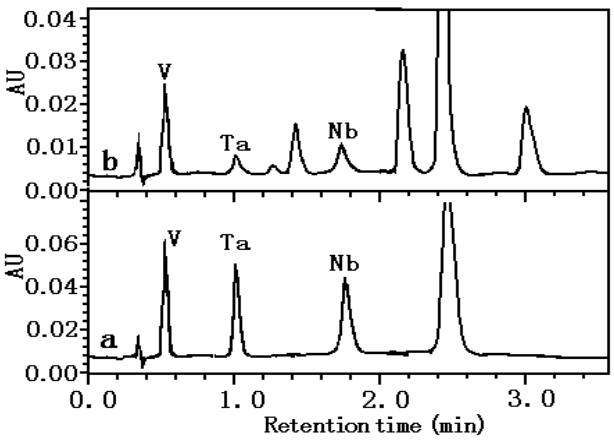

Fig. 1. Chromatogram of standard sample (a) and the water sample (b). The concentration of V(V), Nb(V) and Ta(V) is 0.5 μg L^{-1} in standard sample. The sample injected is 5.0 μL

RESULTS AND DISCUSSION

Formation of the chelates and their absorption spectra: According to the literature[29], the V(V), Nb(V) and Ta(V) can form ternary chelates with heterocyclic azodye in citrate medium. Therefore, in this work, the formation of the chelates of QAR with V(V), Nb(V) and Ta(V) was studied. The results shown that in a citric acid medium, a violet ternary aqueous soluble chelates of V(V), Nb(V) and Ta(V) with QAR and citrate are formed over the pH range 2.1~5.5. Absorption spectra of V(V), Nb(V) and Ta(V) chelates measured at various pH values were similar (except for differing absorptivities) with both showing strong absorbance at pH 4.5. The wave length of maximum absorbance was 576, 586 and 580 nm for V(V), Nb(V) and Ta(V) chelates, respectively. Therefore, 580 nm was selected as detecting wavelength. Fig. 2 shows a comparison of spectra of the V(V), Nb(V) and Ta(V) chelates at the optimal pH of 4.5. The corresponding molar absorptivities were 1.06×10^5, 1.04×10^5 and 0.96×10^5 L mol^{-1} cm^{-1} for V(V), Nb(V) and Ta(V) chelates, respectively. In order to determine the conditions under which a single, stable chelate for each analyte could be obtained, studies on the composition of the chelates were undertaken and in particular on the mole ratios of V(V)-QAR-citrate, Nb(V)-QAR-citrate and Ta(V)-QAR-citrate. Using the method of continuous variations[29], the mole ratio were determined to be 1:2:1 for V(V)-QAR-citrate, Nb(V)-QAR-citrate and Ta(V)-QAR-citrate chelate. The HPLC studies showed that use of a two-fold excess QAR resulted in the appearance of only one chromatographic peak for V(V), Nb(V) and Ta(V). If the V(V), Nb(V) and Ta(V)-citrate molar ratio were less than 1:2, a split peaks or multiple peaks were observed, indicating the presence of at least two chelates. Therefore a six-fold molar excess of citrate over V(V), Nb(V) and Ta(V) was necessary to ensure that only a single peak was produced in the HPLC analysis.

Optimization of the pre-column chelate formation: The parameters used for the pre-column formation of the ternary chelate were investigated in order to identify conditions leading to reproducible formation of the chelate. A pH of 4.5 had been selected previously on the basis of pH effects on the absorption spectrum of the chelate. The optimal concentration range of QAR was then determined to be 1.0×10^{-5}–3.0×10^{-4} mol L^{-1} for a standard mixture of V(V) (3.0 μg mL^{-1}), Nb(V) (3.0 μg mL^{-1}) and Ta(V) (3.0 μg mL^{-1}) in 1.2×10^{-3} mol L^{-1} citrate medium and 2.4×10^{-4} mol L^{-1} of QAR was therefore used for preparation of the chelate for standard solutions. Since some of the metal ions present in the sample matrix can also form chelates with the QAR, the optimum concentration of QAR was also studied for real samples (standard reference samples of rocks). Peak areas

of V(V), Nb(V) and Ta(V) chelates in several real samples were measured using 2.0×10^{-4}–5.0×10^{-4} mol L^{-1} QAR for the sample preparation and showed that 2.4×10^{-4} mol L^{-1} QAR gave optimal performance and this concentration was therefore used for all samples. Since the kinetics of chelate formation is critical to method development, the time required for complete chelate formation and the stability over time of the resultant metal-QAR-citrate chelates were investigated using four different citrate concentrations. These studies showed that 6.0×10^{-4}-3.0×10^{-3} mol L^{-1} citrate gave optimal results for the formation and stability of the chelate in both standard and sample solutions and under these conditions. Therefore 1.2×10^{-3} mol L^{-1} was selected as citrate concentration. The results show that at least 10 min was required to form the chelate and the chelate remained stable for at least 6 h after preparation.

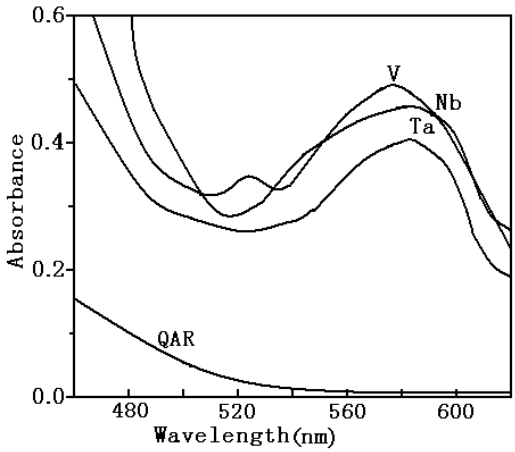

Fig. 2. Absorption spectra of QAR and its metal chelates. The concentration of V, Nb, Ta is 5.0×10^{-6} mol L^{-1}; pH is 4.5; QAR concentration is 1.0×10^{-4} mol L^{-1}; citrate concentration is 1.0×10^{-3} mol L^{-1}

Solid phase extraction: Both the enrichment and the elution were carried out on Waters SPE device, which can prepare 20 samples simultaneously. The flow rate was set to 10 mL min^{-1} when enrichment and 5 mL min^{-1} when elution.

Some experiments were carried out in order to investigate the retention of metal-QAR chelate on the cartridge. It was found that the V-QAR, Nb-QAR, Ta-QAR chelates could be retained on cartridge quantitatively when they pass the cartridge as aqueous solution. The capacity of the cartridge for QAR was determined to 30 mg and for its metal-QAR chelate was determined to 25 mg. In this experiment, the cartridge has adequate capacity to enrichment the metal-QAR chelate because the V(V), Nb(V) and Ta(V) concentration is only μg L^{-1} in the samples.

In order to choose a proper eluant for the retained QAR and its metal-chelate, various organic solvents were studied. It was found that the THF, acetone, acetonitrile, ethanol and methanol could elute the QAR and its metal-chelate from cartridge quantitatively. For eluting the metal-QAR chelates from cartridge, the volume of the solvent needed is THF 0.9 mL, isopentyl alcohol 1.4 mL, acetone 1.7 mL, acetonitrile 1.9 mL, ethanol 2.2 mL, methanol 2.4 mL. The maximal enrichment factor was achieved when THF was selected as eluant. Metal-QAR chelate has a good stability in weak acid medium. THF containing 0.1 % of acetic acid could increase the stability of the metal-QAR chelate in the course elution. So THF (containing 0.1 % of acetic acid) was selected as eluant. Experiment show it was easier to elute the retained QAR and its metal-chelate in reverse direction than in forward direction, so it is necessary to upturned the cartridge when elution. 1.0 mL of eluant was sufficient for elute the metal- QAR chelate from cartridge quantitatively at a flow rate of 5 mL min^{-1}. The volume of 1.0 mL was selected.

Chromatographic separation: The experiments showed that the V-QAR, Nb-QAR, Ta-QAR chelates have a good stability in the presence of pH 4.5 phosphatic buffer solution and citrate medium. The mobile phase containing a 0.01 mol L^{-1} pH 4.5 phosphatic buffer salt and 0.01 mol L^{-1} of citrate can avoid the metal-chelate decomposing in the course of separation and get a good peak shape. Therefore 0.01 mol L^{-1} pH 4.5 phosphatic buffer and 0.01 mol L^{-1} of citrate in mobile phase was selected.

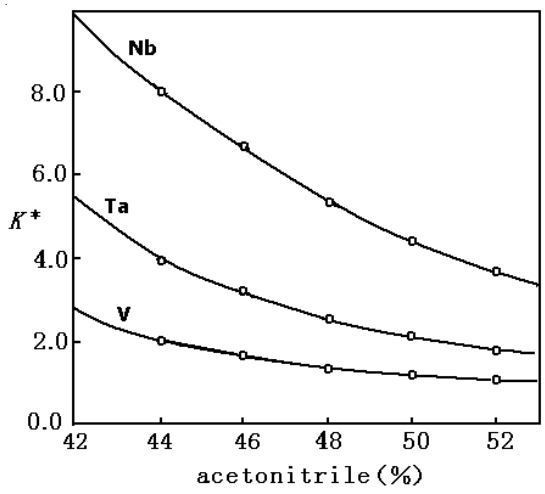

Fig. 3. Effect of acetonitrile concentration on k*.
The mobile phase containing a 0.01 mol L^{-1} pH 4.5 phosphatic buffer salt and 0.01 mol L^{-1} of citrate

The effects of the mixture of methanol, acetone and acetonitrile with water as mobile phase on the retention of the chelates were investigated. It was found that the most suitable system was acetonitrile-water system. The effects of the acetonitrile concentration on the capacity factors (k*) are shown in Fig. 3. When the composition of acetonitrile in the mobile phase was lower than 48 %, V, Nb and Ta can be separated on a baseline. If the composition of acetonitrile was higher, the peak of Ta chelate was sharper, however, that of Nb chelate overlapped with the injection peak gradually. When the composition of acetonitrile in the mobile phase was lower than 38 %, a long separation time was needed. Therefore, 42/58 was chosen as the optimum concentration of the aqueous acetonitrile.

To shorten the chromatographic separation time, a Zorbax Stable Bound rapid analysis column (50 × 4.6 mm, 1.8 μm) was selected in this experiment. With rapid analysis column, the V, Nb and Ta chelates were separated completely within 2.5 min. In comparison to the routine chromatographic method, more then 80 % of separation time was shortened.

Calibration graphs: Under the optimum conditions, regression equations of metal-QAR chelates were established based on the standard sample injected and its peak areas. The limits of detection were calculated by the ratio of signal to noise (S/N=3). The results were shown in Table-1. The reproducibility of this method was also examined for 0.5 μg L^{-1} of V(V), Nb(V) and Ta(V). The relative standard deviations (n=11) were also shown in Table-1.

TABLE-1
REGRESSION EQUATION, COEFFICIENT AND DETECTION LIMIT

Components	Regression equation	Linearity range (ng L^{-1})	Coefficient	Detect limit (ng L^{-1})	RSD (%) (n = 11)
V-QAR	$A = 1.29 \times 10^6 C - 1581$	20~8500	r = 0.9996	3.2	3.0
Nb-QAR	$A = 1.72 \times 10^6 C + 2262$	20~ 8000	r = 0.9992	3.2	2.8
Ta-QAR	$A = 1.56 \times 10^6 C + 2108$	25~9000	r = 0.9994	3.6	3.1

Effect of foreign ions: The interference of some metal ions was studied in detail. Under the chosen derivative conditions, Hg(II), Mn(II), Bi(III), Cr(III), U(VI), Cr(VI), Ni(II), Fe(III) and Zn(II) could not react with QAR while In(III), Cu(II), Ti(IV), Zr(IV), Co(II) could, but no peak was observed or were separated completely with V(V), Nb(V), Ta(V) chelates under the chosen elution conditions. However, they would consume the precolumn reagent. The tolerance limit for the HPLC analysis was expressed as the maximum amount to be determined within an error of ± 5 %. When

3.0 mL of 2.0×10^{-3} mol L^{-1} was added and the amount of V, Nb and Ta was 10 μg L^{-1}, respectively, the tolerance limits were 6000 mg L^{-1} for Cu(II), Co(II) and 500 μg L^{-1} for Ti(IV), Zr(IV), In(III). If the amount of QAR increased, the metal ion tolerances would also increase. This method is high selectivity.

Application: This method was applied to determination of vanadium, niobium and tantalum in water, alloy, steel and geologic samples. The samples were prepared according to the sample preparation section and the vanadium, niobium and tantalum contents were analyzed by using a proper volume of this solution according to general procedure. The results (deducted the reagents blank) were also shown in Table-2 (alloy steel and geologic sample) and Table-3 (water samples). For water samples, an ICP-MS method was used as references method. The results were shown in Table-3.

TABLE-2
DETERMINATION RESULTS OF THE ALLOY STEEL AND GEOLOGIC SAMPLES

Samples	Standard value (GBW01602 and GBW01342 (%), GBW07103 (μg g^{-1}))	By this method	RSD(%) (n=5)
Stainless steel (GBW01602)	B(0.012±0.001), C(0.089±0.005), Cr(10.49±0.06), Co(6.20±0.06), Cu(0.084±0.03), Mn(0.92±0.02), Mo(0.79±0.01), Nb(0.35±0.01), Ni(0.538±0.007), P(0.023±0.001), S(0.015±0.002), Si(0.46±0.02), Ta(0.068±0.002), V(0.216±0.008)	Nb(0.342), Ta(0.0672, V(0.224)	3.2
Low alloy steel (GBW01342)	C(0.268±0.006), Cr(0.046±0.02), Cu(0.0.210±0.03), Mn(1.72±0.01), Nb(0.139±0.02), Ni(0.538±0.007), P(0.034±0.001), S(0.016±0.001), Si(0.904±0.009), Ta(0.042±0.001), V(0.258±0.005)	Nb(0.126), Ta(0.0436, V(0.265)	3.0
Geologic samples (GBW07103)	B(24±4), Ba(343±45), Ce(108±11), Co(3.3±1.0), Cu(3.2±1.3), Mn(463±27), Nb(47±5), Ni(2.3±1.2), P(405±10), Pb(31±4), Ta(7.2±0.7), Th(54±4), U(18.8±5), V(24±3), W (8.4±0.7), Zn(28±4), Al2O3(13.4±0.11%), CaO(1.55±0.07%), Fe2O3(2.14±0.08%), FeO(1.03±0.05%), K2O(5.01±0.10%), MgO(0.42±0.05%), Na2O(3.13±0.09%), SiO2 (72.83±0.15%)	Nb(48.2), Ta(7.08), V(25.9)	2.8

TABLE-3
DETERMINATION RESULTS OF THE WATER SAMPLES

Samples	Found ($\mu g\ L^{-1}$)			ICP-MS Method ($\mu g\ L^{-1}$)			RSD (%) (n=5)			Recovery (%) (n=5)		
	V	Nb	Ta	V	Nb	Ta	V	Nb	Ta	V	Nb	Ta
River water	0.212	0.0658	0.0458	0.226	0.0678	0.0415	3.2	3.5	3.4	91	85	86
Lake water	0.146	0.0825	0.0626	0.158	0.0868	0.0654	3.1	3.3	3.2	82	89	88

TABLE-4
THE COMPARISON HPLC METHOD FOR THE DETERMINATION OF VANADIUM, NIOBIUM AND TANTALUM

Ions analysized	Derivatization reagent	Column	Mobile phase	Separation time (min)	Detection limit ($ng\ mL^{-1}$)	Ref.
V, Nb, Ta	TADAP	C_{18} (150 × 4.6, 5 μm)	Methanol–water (55/45, v/v), pH 3.5	12	V (0.16), Nb (0.32), Ta (V1.77)	17
V, Mo	BPHA	Nitrile-bonded column	BPHA in chloroform	15	V (2.1), Mo (3.3)	18
Nb	5-Br-PADAP	C_{18} (150 × 4.6, 5 μm)	Methanol–water (56:44, pH 3.5	5	Nb (15)	19
V	H_2SA_2Ten	Si (200 × 4.6, 5 μm)	Chloroform - acetonitrile (95:5)	12	V (2.5)	20
Nb, Ta	PAR	C_{18} (150 × 3.9, 4 μm)	32% Methanol (v/v), pH 6.5	25	Nb (0.012), Ta (0.039)	21
Nb, Ta	PAPS	C_{18} (150 × 3.9, 4 μm)	Methanol–water (52%v/v), pH 7	25	Nb (0.03) and Ta (0.40)	25
Nb, Ta	PAR	C_{18} (150 × 3.9, 10 μm)	Methanol-water (32:68, v/v), pH 6.5	40	Nb (0.4), Ta (1.4)	27
V, Nb, Ta	QAR	C18 (4.6 × 50, 1.8 μm)	Acetonitrile–water (42:58), pH 4.5	3.5	V (0.0032), Nb (0.0032), Ta (0.0038)	This work

TADAP (2-(2-thiazolylazo)-5-diethylaminophenol); BPHA (*N*-benzoyl-*N*-phenylhydroxamate); PAR (4-(2-pyridylazo)resorcinol); 5-Br-PADAP (2-(5-Bromo-2-pyridylazo)-5- diethylamino phenol); H_2SA_2Ten (*bis*(salicylaldehyde)tetramethylenediimine); PAPS (2-(5-bromo-2-pyridylazo)-5-[N-propyl-N- (3-sulfopropyl)amino]phenol).

Conclusion

A comparison of the possibilities of the proposed method with those of other methods (Table-4) shows that the proposed method has the following characteristics: (1) QAR was synthesized and used as pre-column derivatization regents. Vanadium, niobium and tantalum ions can form stable colour chelates with QAR at room temperature rapidly. The molar absorptivity was calculated to be 1.06×10^5, 1.04×10^5 and 0.96×10^5 L mol^{-1} cm^{-1} for

V(V), Nb(V) and Ta(V) chelates, respectively. This is a sensitive and convenience pre-column derivatization regents for vanadium, niobium and tantalum. (2) The Zorbax rapid analysis column was used for the separation of V-QAR, Nb-QAR and Ta-QAR chelates and were separated completely within 2.5 min. In comparison to the routine chromatographic method, more then 80 % of separation time was shortened. (3) By solid phase extraction with C_{18} cartridge, a large volume of sample (10 mL) can be injected and the sensitivity of the method was greatly improved. The detection limits (S/N=3) of vanadium, niobium and tantalum reach 2.6, 2.6 and 3.0 ng L^{-1}, respectively. Thus, for the determination of vanadium, niobium and tantalum, this method is highly sensitive, selective and convenient.

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(*Received*: 3 July 2006; *Accepted*: 9 March 2007) AJC-5491