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Talanta 68 (2006) 535–541

Talanta

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Liquid chromatographic determination of vanadium in petroleum oils and mineral ore samples using 2-acetylpyridne-4-phenyl-3-thiosemicarbazone as derivatizing reagent

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Received 12 January 2005; received in revised form 24 March 2005; accepted 20 April 2005
Available online 20 June 2005

Abstract

Liquid chromatographic method has been developed, based on precolumn derivatization of vanadium(V) with 2-acetylpyridine-4-phenyl-3-thiosemicarbazone (APPT). The complex is extracted in chloroform together with palladium(II), tin(II) and iron(III) and eluted and separated completely from Kromasil 100 C-18, 10 μm (25 cm × 4.6 mm i.d.) column with methanol:water:acetonitrile (60:30:10, v/v/v) with a flow rate of 1 ml/min. UV detection was at 260 nm. Linear calibration curve was obtained with 1–12.5 μg/ml vanadium(V) with detection limit of 8 ng/injection (20 μl). A number of metal ions tested did not affect the determination of vanadium. The test mixtures were analyzed for vanadium(IV) and vanadium(V) contents and relative% error was obtained ±1–8%. The method was applied for the determination of vanadium in petroleum oils and mineral ore samples with vanadium contents of 0.32–2.3 and 121.7–717.3 μg/g with R.S.D. of 1.5–4.5 and 0.38–4.7%, respectively. The results correlated with reported values and by atomic absorption spectrophotometry.

Keywords: Liquid chromatography; 2-Acetylpyridne-4-phenyl-3-thiosemicarbazone; Vanadium

1. Introduction

Vanadium is a transition metal widely distributed in the environment and in biological samples [1]. Vanadium is used widely in industrial process including the production of special steels, temperature resistant alloys, in glass industry, in the manufacture of pigments and paints, for lining arc welding electrodes and catalysts. The determination of vanadium species in the environmental samples has been reviewed [2]. The analytical procedures for the analysis of geological materials are commonly based on atomic absorption [3], inductively coupled plasma atomic emission [4,5], and inductively coupled plasma-mass spectrometry [6,7], radioisotope X-ray fluorescence spectroscopy [8] and neutron activation analysis [9]. The analytical procedures based on spectrophotometry [10,11], electrochemical [12], gas [13,14] and liquid chromatography [15,16] are also available. LC separation followed by air segmented flow analysis, based on catalytic reaction with green leuco base has been used for the determination of vanadium(IV) and vanadium(V) [17]. High performance liquid chromatography (HPLC) coupled with UV detection is interesting because of the ease of the separation and the capability for the simultaneous determination of a number of a number of metal ions, using a suitable complexing reagent.

A number of complexing reagents have been used for the HPLC separation of vanadium from cobalt, iron, chromium, nickel, copper, palladium, aluminum and zinc [18–23]. Some of the complexing reagents used are 8-hydroxyquinoline [24,25], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol [20–26], 2,2-dihydroxyazobenzene [21–27], 2-(8-quinolylazo)-5-*N*,*N*-diethylaminophenol [22], 4-(2′-pyridylazo)resorcinol [28,29] and bis(salicylaldehyde) tetramethylethylendiimine [15]. Normal phase [24], reversed

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doi:10.1016/j.talanta.2005.04.065

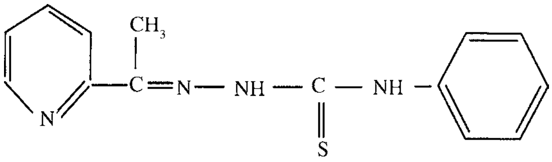

Fig. 1. Structural diagram of the reagent APPT.

phase [22–25] and ion pair reversed phase [19,21,26] modes have been used. Vanadium has been determined in rain, seawater, air borne particles and crude petroleum oils [15,22,23,25].

Thiosemicarbazones and phenyl thiosemicarbazones are interesting complexing reagents, because they form highly stable and intensely colored complexes immediately by binding through sulphur and hydrazine nitrogen atoms, which are ideally suited for spectrophotometric detection [30,31].

The reagent 2-acetylpyridine-4-phenyl-3-thiosemicarbazone (APPT) (Fig. 1) has been used for HPLC determination of cobalt(II), iron(II) and copper(II) from pharmaceutical preparations [32] and cisplatin from drugs and blood serum of cancer patients [33]. The present work examines the reagent APPT for HPLC determination of vanadium together with iron(III) from geological materials using simple isocratic elution with UV detection and determination of vanadium(IV) and vanadium(V) in a mixture.

2. Experimental

The reagent APPT was prepared as reported [32,34] by heating together equimolar (0.01 M) solution of 2-acetylpyridine and 4-phenyl-3-thiosemicarbazide in methanol. The spectrophotometric studies were carried out on Hitachi 220 (Hitachi (Pvt.) Ltd., Tokyo) spectrophotometer. IR spectrum of the reagent APPT was recorded in KBr on Perkin-Elmer 1360 IR spectrophotometer. A Hitachi 655A Liquid Chromatograph connected with variable wave length UV monitor and Rheodyne 7125 injector was used. UV monitor was connected with computer with CSW-32 (Data Apex Ltd.© 2001 www.dataapex.com) software. A Kromasil 100 C-18, 10 μm (250 mm × 4.6 mm i.d.) (Teknokroma, S. Coop. C. Ltd. (Barcelone)) column was used throughout the study. Varian spectr AA 20 atomic absorption spectrophotometer with air–acetylene or nitrous oxide–acetylene flame was used for the determination of iron and vanadium contents at 248.3 and 318.5 nm, respectively. The analysis was carried out in quadruplet with delay time 3 s and integration time 3 s. The analysis was carried out at the conditions recommended by the manufacturer.

The petroleum oil samples were obtained through Pakistan State Oil, Karachi from Hydrocarbon Development Institute of Karachi, Pakistan. Eight samples were received (1) Badin crude oil, (2) Qatter marine crude oil, (3) Badin blended crude oil, (4) Tando Aalam, (5) Kunner crude oil, (6) Mari gas field, (7) Boby condensate and (8) Mazarani condensate. All the oil fields except Qatter marine are located in South Indus Basin, near Hyderabad, Sindh, Pakistan. The vanadium ore samples were obtained from Atomic Energy Mineral Centre, Lahore, Pakistan.

GR grade chemicals: sodium acetate, acetic acid, sodium bicarbonate, sodium carbonate, boric acid, borax, ammonium chloride, ammonia (23%), chloroform, acetonitrile, hydrochloric acid (37%), perchloric acid (70%), sulphuric acid (95–98%) and nitric acid (65%) (E-Merck, Germany) were used. Freshly prepared doubly distilled (d.d.) water from all glass was used for HPLC studies. The buffer solutions in the pH range 1–10 at unit interval were prepared from the following: hydrochoric acid (0.1 M)–potassium chloride (1 M), pH 1–2; sodium acetate (1 M)–acetic acid (1 M), pH 3–6; ammonium acetate (1 M)–ammonia, pH 7; boric acid (1 M)–borax (1 M), pH 8–9; ammonium chloride (1 M)–ammonia (1 M) pH 10.

2.1. Analytical procedures

2.1.1. Spectrophotometric procedure

An aliquot of solution (1–3 ml) containing vanadium(V) (50–400 μg), palladium(II) (10–50 μg), tin(II) (50–250 μg) or iron(III) (2.5–12.5 μg) was transferred to 10 ml volumetric flask separately. Vanadium(V), tin(II) and iron(III) solution was added sodium acetate–acetic acid buffer pH 3 (2 ml), but palladium(II) solution was added borate buffer pH 9 (2 ml). The reagent APPT solution 2 ml (0.02%, w/v, in methanol) was then added. The final volume was adjusted with methanol and absorption spectra were recorded against reagent blank within 600–250 nm.

2.1.2. HPLC procedure

Solution (1–3 ml) containing vanadium(V) (1–12 μg), palladium(II) (1–8 μg), tin(II) (1–5 μg) and iron(III) (1–5 μg) was transferred to separating funnel and were added sodium acetate buffer pH 3 (2 ml), APPT solution (2 ml) (0.02%, w/v in methanol) and chloroform (2 ml). The contents were mixed well and layers were allowed to separate. The organic layer was collected and aqueous layer was added borate buffer pH 9 (2 ml). The extraction was repeated with chloroform (2 ml). The solvent from combined extract was evaporated under nitrogen atmosphere and the residue was dissolved in methanol (1 ml). The solution (20 μl) was injected on Kromasil 100, C-18, 10 μm (250 mm × 4.6 mm i.d.) column and eluted with methanol:water:acetonitrile (60:30:10, v/v/v) with a flow rate 1 ml/min. The detection UV was at 260 nm.

2.1.3. HPLC determination of vanadium(IV) and vanadium(V)

Two portions of aqueous solutions (1–3 ml) containing vanadium(IV) and vanadium(V) (10–50 μg each) were taken and (a) portion was transferred to 10 ml volumetric flask and (b) to small beaker. The beaker was added nitric acid (65%, 0.5 ml) and heated to about 0.5 ml. The residue was dissolved in water (2 ml), the pH adjusted to 3 and was transferred to 10 ml-volumetric flask. Each of the flask was added sodium acetate buffer pH 3 (1 ml) and APPT solution (2 ml) (0.02%, w/v, in methanol). The volume was adjusted to the mark with methanol and solution (20 μl) was injected and elution was carried out as Section 2.1.2. The amounts of vanadium(V) in the solutions (a) and (b) was evaluated from external calibration curve. The solution (a) corresponded for vanadium(V) and solution (b) total vanadium (vanadium(V) and vanadium(IV)). A difference between total vanadium and vanadium(V) provided a data for vanadium(IV) contents.

2.1.4. Determination of vanadium in mineral ore samples

Mineral ore (1.0 g) from each of the samples Nos.: 40948, 40229, 40577, 40946 and 40936 was added aqua regia (HNO_3:HCl 1:3, v/v) (5 ml) and heated gently to near dryness. The process was repeated with aqua regia (5 ml) and then twice with hydrochloric acid (5 ml). The residue was dissolved in water and filtered. The final volume was adjusted to 50 ml with d.d. water. The solution (2 ml) from samples 40577, 40936 and 40946, 3 ml from 40948 and 5 ml from sample 40948 was adjusted to pH 3 and were added sodium acetate–acetic acid buffer pH 3 (2 ml), APPT solution (2 ml, 0.02%, w/v, in methanol) and chloroform (2 ml). The organic layer was collected and the extract was evaporated under nitrogen atmosphere. The residue was dissolved in methanol (1 ml) and the elution was carried out as Section 2.1.2. The blank determination was also carried out simultaneously. The quantitation was carried using external calibration curve.

2.1.5. Determination of vanadium from mineral ore samples by standard addition technique

Two portions of 2 ml each from sample 40577 and 4 ml each from sample 40229 were taken from the solutions prepared as Section 2.1.4. A portion from both the samples was added vanadium 10 μg and all the solutions were processed as Section 2.1.3. The amount of vanadium in mineral ore samples was evaluated from the average increase in the response with vanadium added.

2.1.6. Determination of vanadium and iron from petroleum oils

To petroleum oils (10 g) from each of the eight samples collected was added sulphuric acid (95–98%) (10 ml), nitric acid (65%) (20 ml) and perchloric acid (70%) (4 ml) in tall beaker. The contents were heated gently and more nitric acid was added until solution became clear. The solution was concentrated to 2–4 ml and pH of the solution was adjusted to 2. The final volume was made to 10 ml. The solution 1–5 ml was taken and procedure was followed as Section 2.1.4. A blank was also prepared simultaneously. The quantitation of vanadium and iron was made by external calibration.

2.1.7. Determination of vanadium and iron in petroleum oils by standard addition technique

Aqueous solutions (2 ml) portion in duplicate were taken from Qatter marine, Kunner crude, Boby condensate and Badin blended crude oil prepared as Section 2.1.6. A (2 ml) portion of Qatter marine and Kunner crude was added vanadium (10 μg), solution (2 ml) from Boby condensate was added vanadium (5 μg) and iron (5 μg) and solution (2 ml) of Badin blended was added iron (5 μg) only. All the solutions were processed as Section 2.1.6. The amounts of vanadium and iron in petroleum oils were calculated from the increase in the peak height due to amount added.

3. Results and discussion

The reagent APPT reacts immediately with vanadium(V), palladium(II), tin(II) and iron(III) to form colored complexes in water–methanolic solution. The complexes are also extractable in chloroform or 1,2-dicholoroethane. The effect of pH on the formation of the complex was examined within pH 1–10 and the condition which gave maximum color was considered as optimum. Maximum color development for vanadium(V), tin(II) and iron(III) was observed at pH 3, but palladium(III) indicated at pH 9 (Fig. 2). The colors of the complexes were highly stable both in aqueous–methanolic solution and chloroform and no change in absorbance was observed up to 24 h.

The composition of metal chelates was investigated by changing the metal:ligand mole ratio spectrophotometrically. The absorbancies of vanadium(V), tin(II), iron(III) and palladium(II) were measured at 435, 372, 386 and 385 nm, respectively, in aqueous–methanolic solution at optimized pH. It was observed that vanadlium(V) and tin(II) formed metal chelates with 1:3, but palladium(II) and iron(III) with 1:2 metal ligand ratio (Fig. 3). The complexes at the wavelengths of maximum absorbance indicated molar absorptivity 8.4×10^2, 3.3×10^4, 3.3×10^3 and 3.3×10^4 l (mole cm)$^{-1}$ for vanadium(V), palladium(II), tin(II) and iron(II), respectively.

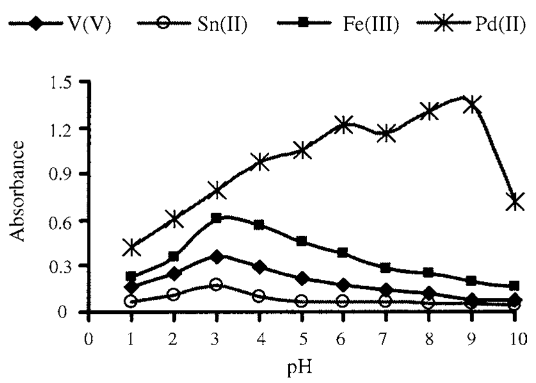

Fig. 2. Effect of pH on vanadium(V), palladium(II), tin(II) and iron(III) as APPT chelates.

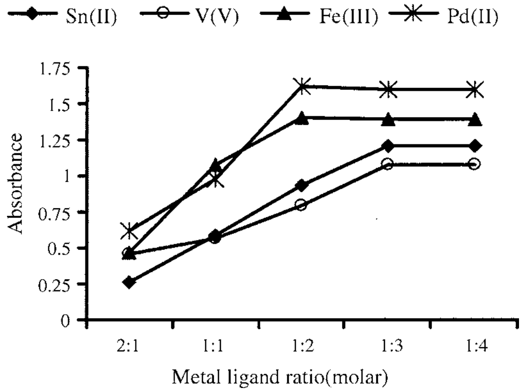

Fig. 3. Variation in metal:ligand ratio of vanadium(V), palladium(II), tin(II) and iron(III) as APPT chelates.

Vanadium(V), tin(II), iron(III) and palladium(II) as chelates of APPT eluted from Kromasil C-18 column with binary mixtures of methanol–water and separated from excess of derivatizing reagent. However complete separation between vanadium(V), tin(II), palladium(II) and iron(III) was obtained when eluted from Kromasil 100, C-18, 10 μm (250 mm × 4.6 mm i.d.) column with methanol:water:acetonitrile (60:30:10, v/v/v) with a flowrate 1 ml/min and UV detection at 260 nm (Fig. 4). The resolution factor (R_s) between two adjacent peaks was obtained > 2.0. The capacity factor (K') for palladium(II) 0.6 increased to 3.6 for iron(III).

The reagent APPT reacts only with vanadium(V) and did not show any reaction with vanadium(IV). It was, therefore, an attempt was made to determine vanadium(IV) and vanadium(V)in a mixture. The reagent APPT reacted to give a response corresponding to vanadium(V) in the solution. However after oxidation with nitric acid, total vanadium in the solution was detected. The results provided the data to calculate the concentrations of vanadium(IV) and vanadium(V) in test mixtures (Table 1) and indicated a good correlation with expected values with relative% error within ±1–8% and relative standard deviation (R.S.D.) within 1.67–4.87%.

Vanadium(V) did not indicate high values of molar absorptivity in the visible region at 435 nm for spectrophotometric detection, but when examined in UV region at 260 nm, the chelate indicated high sensitivity due to π–π* transition within the ligand molecule and was selected. Linear calibration curves for vanadium(V), palladium(II), tin(II) and iron(III) measured as average peak height ($n = 3$) versus concentration were observed with 2–12 μg/ml vanadium(V), 1–8 μg/ml palladium(II), 1–5 μg/ml tin(II) and 1–5 μg/ml iron(III) with coefficient of determination r^2, 0.9993, 0.9916, 0.9955 and 0.9961, respectively. The detection limits measured as three times the background noise were 400 ng/ml vanadium(V), 200 ng/ml palladium(II), 100 ng/ml tin(II) and 100 ng/ml iron(III), corresponding to 8, 4, 2 and 2 ng/injection (20 μl), respectively.

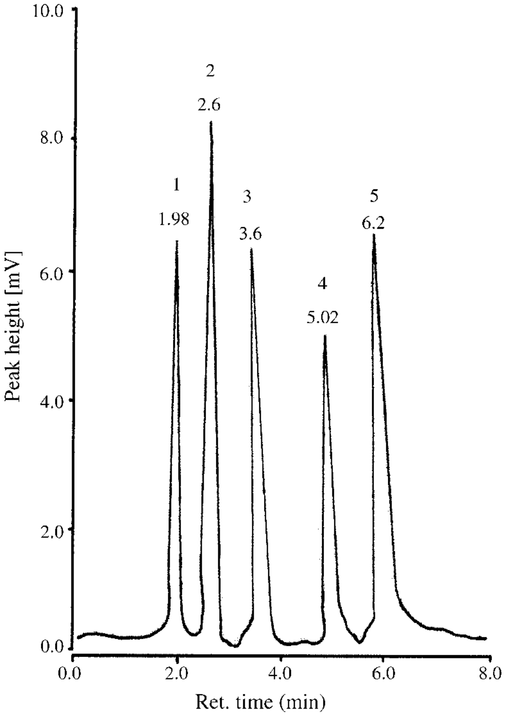

Fig. 4. HPLC separation of (1) palladium(II), (2) APPT, (3) vanadium(V), (4) tin(II) and (5) iron(III) complexes of APPT. Column Kromasil 100, C-18 (250 mm × 4.6 mm i.d.). Elution with methanol:water:acetonitrile (60:30:10, v/v/v), with flow rate 1 ml/min and UV detection at 260 nm.

In order to ascertain lower limit of detection of vanadium(V) in original solution, 10 ml of water was added vanadium(V) and the solvent extraction procedure was followed. The extract was evaporated and redissolved in methanol (0.2 ml). Based on preconcentration factor of 50, the detection limit which gave signal:noise (3:1) was observed 9 ng/ml. However, when percentage of water in eluent was decreased and acetonitrile was increased by 10% to give sharp peak, the detection limit improved to 5 ng/ml.

Reproducibility of the elution of 10 μg/ml of vanadium(V) and 5 μg/ml iron(III) was measured in terms of average peak height and retention time ($n = 5$) and relative

Table 1
Quantitative analysis of vanadium(IV) and vanadium(V) in a mixture

S. no.	V(IV) present (μg/ml)	V(V) present (μg/ml)	V(IV) found (μg/ml) (R.S.D.%) ($n = 3$)	V(V) found (μg/ml) (R.S.D.%) ($n = 3$)
1	1.0	1.0	0.99 (2.3)	0.97 (1.9)
2	2.0	2.0	1.99 (4.1)	1.98 (3.7)
3	1.0	2.0	1.08 (3.8)	1.92 (2.8)
4	5.0	1.0	5.01 (4.8)	0.99 (1.3)
5	3.0	2.0	2.93 (1.6)	2.09 (4.5)

Table 2
HPLC determination of vanadium from vanadium ores

S. no	Sample no.	Amount reported by A.E.M.C (μg/g)	Amount found by HPLC (μg/g) (R.S.D.%) ($n = 4$)	%R.D. (μg/g)	Amount found by AAS (μg/g) (R.S.D.%) ($n = 4$)
1	40948	110	121.7 (2.1)	10.6	114.4 (48)
2	40229	160	150.5 (4.7)	5.9	147 (53)
3	40577	735	717.3 (038)	2.4	728.5 (3.1)
4	40946	150	165.2 (1.6)	10.1	141.3 (5:5)
5	40936	395	423.5 (2.9)	7.2	401.8 (3.9)
By standard addition					
2	40229	160	162.5 (1.8)	4.4	
4	40946	150	151.2 (2.4)	0.8	

standard deviations (R.S.D.) were obtained within 1.8–2.4 and 1.5–3.5%, respectively. Copper (II), cobalt(II), platinum(II), selenium(IV), ruthenium(IV), lead(II), arsenic(III), tellurium(VI) and bismuth(III) also react with APPT to form color complexes. Their interfering effects on the determination of vanadium 5 μg/ml and iron 2.5 μg/ml were examined. These cations eluted separately and their concentrations similar to vanadium(V) and iron(III) did not affect their determinations.

Mineral ore samples obtained from Atomic Energy Mineral Centre, Lahore were analyzed for vanadium contents. The samples after acid dissolution were examined following HPLC procedure. The results are summarized in (Table 2) and are in the range 121.7–717.3 μg/g with R.S.D. of 0.382–4.7%. The samples 40229 and 40946 were also analyzed by standard addition technique (Fig. 5). The amounts were found 162.5 and 151.2 μg/g with R.S.D. 1.8 and 2.4%, respectively. HPLC results obtained were compared with the reported values by Atomic Energy Mineral Centre, Lahore, and relative% deviations (%R.D.) were observed within 2.4–10.6%. The samples were also analyzed by nitrous oxide–acetylene flame atomic absorption spectrophotometry and a reasonable correlation was obtained with HPLC analysis (Table 2).

The petroleum oils were also analyzed for the contents of vanadium. A stable HPLC response at the retention time of

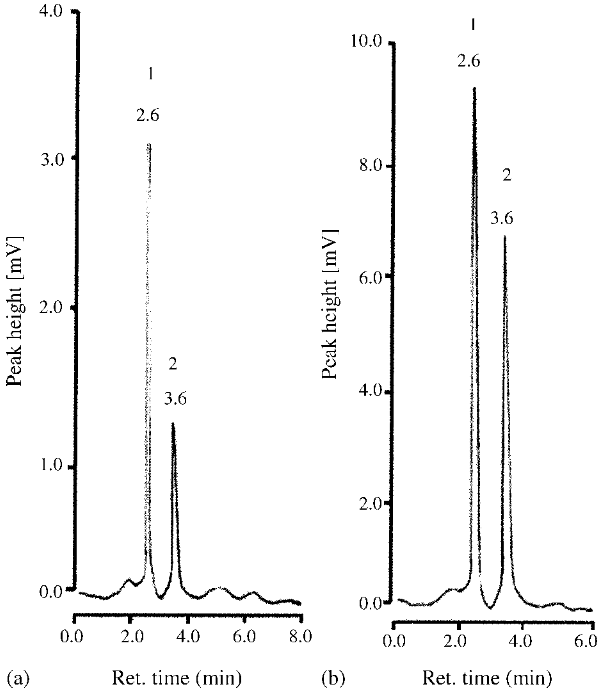

Fig. 5. (a) HPLC response of mineral ore sample, (b) after spiking with 10 μg vanadium. Conditions as Fig. 4.

Table 3
Simultaneously HPLC determination of vanadium and iron from crude petroleum oils

Sample no.	Product	Vanadium found by HPLC (μg/g) (%R.S.D.) ($n = 4$)	Vanadium found by AAS (μg/g) (%R.S.D.) ($n = 4$)	Fe found by HPLC (μg/g) (%R.S.D.) ($n = 4$)	Fe found by AAS (μg/g) (%R.S.D.) ($n = 4$)
1	Badin crude oil	1.6 (4.5)	1.5 (3.1)	4.1 (2.6)	3.8 (1.1)
2	Qatter marine crude oil	2.3 (4.2)	2.5 (6.1)	4.9 (2.5)	4.8 (2.7)
3	Badin Mended crude oil	1.7 (2.1)	1.6 (4.0)	2.7 (3.8)	2.7 (3.5)
4	Tando Aalam crude oil	0.73 (3.7)	0.82 (4.9)	2.3 (4.5)	2.4 (1.2)
5	Kunner crude oil	1.1 (3.7)	1.2 (3.4)	1.99 (2.2)	2.0 (53)
6	Mari gas	0.8 (1.5)	0.67 (5.8)	1.7 (3.7)	1.6 (3.9)
7	Boby condensate	0.32 (4.4)	0.39 (2.6)	0.59 (1.9)	0.63 (7.2)
8	Mazarani condensate	–		0.38 (3.6)	0.36 (5.4)
By standard addition					
2	Qatter marine	2.29 (0.18)		–	
5	Kunner crude	1.18 (038)		–	
7	Boby condensate	0.32 (1.4)		0.6 (2.2)	
3	Badin blended	–		2.6 (0.5)	

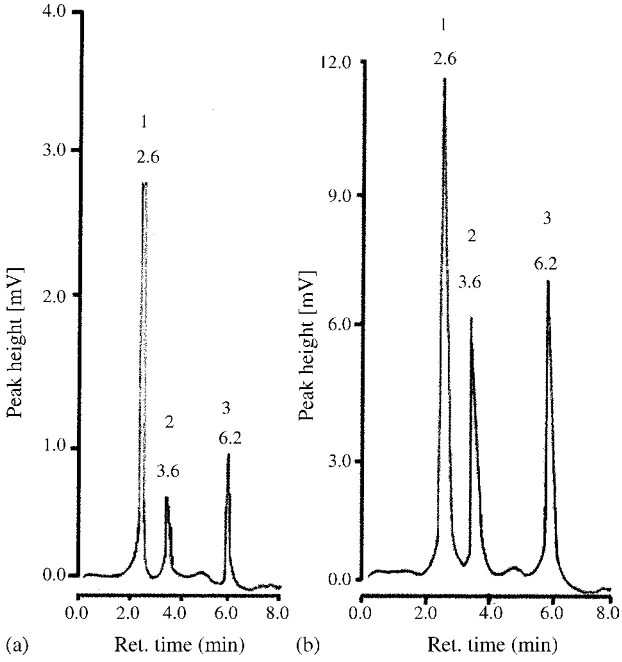

Fig. 6. (a) HPLC response of crude petroleum oil sample, (b) After spiking with 10 μg vanadium. Conditions as Fig. 4.

iron(III) was also observed. It was therefore vanadium and iron was determined simultaneously. The results of analyses are summarized in (Table 3). The amounts of vanadium and iron were found within the range 0.32–2.3 and 0.38–4.9 μg/g with R.S.D. 1.5–4.5 and 1.9–4.5%, respectively. Two samples were spiked with vanadium, one with vanadium and iron and one sample with iron only and the observed results correlated reasonably with the observed values by calibration method and indicated R.S.D. of 0.18–2.2 and 0.5–2.2%, respectively (Figs. 6 and 7) (Table 3). The samples were also analyzed by flame atomic absorption and results were within the limits observed by HPLC method.

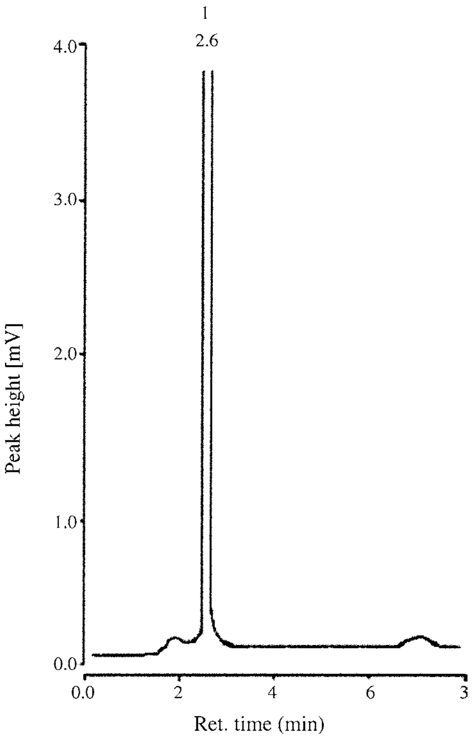

Fig. 7. HPLC response from blank. Conditions as Fig. 4.

4. Conclusion

Simple and sensitive reversed phase HPLC method has been developed for the determination of vanadium from geological materials. Isocratic elution was carried out with UV detection at 260 nm, with detection limit of 8 ng/injection (20 μl) for vanadium. Palladium(II), tin(II) and iron(III) separated completely and a number of cations tested did not interfere the determination of vanadium. Mineral ore samples were analyses with 121.7–717.3 μg/g vanadium, and petroleum oils with 0.32–2.3 μg/g of vanadium with R.S.D. within 4.5%. Vanadium(IV) and vanadium(V) contents in test mixtures were analyzed with R.S.D. within 1.67–4.87%.

Acknowledgement

Dr. Fazal-Ur-Rehman, CSO and the Director, Atomic Energy Mineral Centre, Lahore are acknowledged for providing us mineral ore samples for use in the development of HPLC method for vanadium. We also like to thank Dr. Altaf Hussain Soomro, Manager MQTU Network, Pakistan State Oil Corporation, Karachi for arranging petroleum oil samples for the analysis of vanadium and iron. The generous help of Dr. S.N. Lanjwani, Post Doctoral research fellow Department of Chemistry, University of Western Ontario, London, Ont., Canada, is acknowledged for up to date computer literature search.

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