

Application of the Ion Pair of 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol and Ammonium Tetrphenylborate for Pre-concentration of Trace Vanadium and Determination by Third Derivative Spectrophotometry

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Vanadium is quantitatively retained on 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP)-ammonium tetrphenylborate with microcrystalline naphthalene or by a column method in the pH range of 2.1—4.5 from a large volume of aqueous solutions of various samples. After filtration, the solid mass consisting of the vanadium complex and naphthalene was dissolved with 5 mL of dimethylformamide and the metal was determined by the third derivative spectrophotometry. Vanadium complex can alternatively be quantitatively adsorbed on ammonium tetrphenylborate-naphthalene adsorbent packed in a column and determined similarly. About 0.05 μg of vanadium can be concentrated in a column from 250 mL of aqueous sample, where its concentration is as low as 0.2 ng/mL. The interference of a large number of anions and cations has been studied and the optimized conditions developed were utilized for the determination of trace amount of vanadium in various samples.

Keywords trace vanadium determination, derivative spectrophotometry, 5-Br-PADAP-TPB-naphthalene

Introduction

Vanadium is one of the most important element which affects the physical properties of steel, alloys and high purity metals. It is widely distributed in the earth's crust, and its compounds can be highly toxic to man and animals and cause environmental diseases when released in the atmosphere.¹ It has also been noted that the environmental background levels of vanadium have been slowly rising as a result of the combustion of fossil fuels which

have high vanadium content.² Vanadium is therefore, important not only because of the toxicity at high levels but also because it is an environmental pollutant.³ Occupational exposure to vanadium has been observed in several industrial processes, for example, in iron and steel production, in the manufacture of pigments, printing inks and paints, in the glass industry and the cleaning and repairing of oil fired boilers, particularly in electricity power station.⁴⁻⁶ Very low concentrations of vanadium are present in various matrices such as plants, soils, sea-water, etc. Therefore, it is very important from the analytical point of view to develop sensitive, selective, rapid and economical methods for its quantitative determination even when present in trace amounts. Neutron activation analysis (NAA), atomic absorption spectrometry (AAS), graphite furnace-AAS, inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) may be used for the trace determination of metals in complex materials. But these instruments are highly expensive. Their maintenance cost is high and is not free from various types of inherent interferences.⁷⁻¹⁰ A survey of the literature reveals that vanadium may be determined spectrophotometrically using various complexing agents,^{11,12} but many of them have limited sensitivity, preconcentration factor and selectivity as compared to the present method.

Derivative spectrophotometry offers the advantages of increased selectivity and sensitivity compared with normal

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spectrophotometry.^{13,14} Spectrophotometers equipped with suitable derivative units enable the observation of the derivative spectra of the first and second orders, or even higher orders.

The increased selectivity in derivative spectrophotometry results from the fact that bands which overlap in normal absorption spectra appear as separated bands in the derivative spectra. Derivative spectrophotometry can increase the sensitivity owing to the amplification of derivative signals, and lowering of noise, improvements in selectivity and sensitivity are easier to obtain in instances where the bands in the normal absorption spectra are fairly sharp.¹⁵

Sodium tetraphenylborate (TPB) and its derivatives have been used in the estimation of alkali and univalent metal ions.¹⁶ It has also been used as a counter ion in the extraction and adsorption of some metal complexes into molten naphthalene¹⁷ and microcrystalline naphthalene respectively.¹⁸ A survey of the literature reveals that metal ions may be preconcentrated on various adsorbents such as thiol cotton,¹⁹ silanized glass beads,²⁰ silica gel,²¹ Amberlite XAD-4 resin,²² cellulose,²³ green tea leaves²⁴ and polythioether foams.²⁵ Some of these adsorbents may be fairly effective for preconcentration of metal ions, but their methods of preparation are lengthy and involve rigid control of conditions. The desorption of the metal is carried out by the slow process of elution (the metal complex is probably held by the interior surfaces of the adsorbent and thus the adsorbed complex is not eluted easily), hence the procedure is time consuming. Solvent extraction is a simple and convenient technique for separating and concentrating metal ions, but it can not be applied directly to metal ions which form stable complexes with the chelating agents only at elevated temperature. This difficulty can be overcome by using naphthalene as the extractant²⁶ for thermally stable metal chelates.²⁷ Solid-liquid separation after adsorption of metal chelates on microcrystalline naphthalene is more rapid and convenient and can be applied to many types of metal complexes.¹⁸ The preconcentration of vanadium ion is also possible by passing its aqueous solution over naphthalene-NH₄-TPB adsorbent packed in a column. The microcrystalline naphthalene method is rapid but the column method gives a better preconcentration factor.¹⁴

In this paper, a highly selective and sensitive preconcentration method which, in addition to the (NH₄⁺) (TPB⁻) ion pair supported on naphthalene, uses 2-(5-

bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) as the complexing reagent, has been developed. The 5-Br-PADAP and its derivatives are highly selective for vanadium. The 5-Br-PADAP reacts with vanadium to form a water-soluble complex cation, but in the presence of the TPB anion it forms a water-insoluble complex (V-5-Br-PADAP-TPB). Preliminary observations revealed that the V-5-Br-PADAP complex cation could be quantitatively retained on an ammonium tetraphenylborate adsorbent supported on naphthalene. The solid mass, consisting of the metal ion associated complex and naphthalene, can easily be dissolved with a suitable organic solvent such as dimethylformamide (DMF) and the vanadium is determined by the third derivative spectrophotometry. The interference of a number of metal ions and anions on the estimation of vanadium has been studied in detail and the developed method is found to be highly sensitive and selective and has been employed for the estimation of vanadium in complex materials.

Experimental

Apparatus

A Shimadzu UV 160 spectrophotometer with a 1.0-cm quartz cell was used. A Beckman pH meter was employed for pH measurements. A funnel-tipped glass tube (60 mm × 6 mm) was used as a column for preconcentration. It was plugged with polypropylene fibbers and then filled with the adsorbent to a height of 1.0–1.2 cm after being pressed lightly with a flat glass rod. All atomic absorption measurements were made with an atomic absorption spectrometer (Shimadzu AA 670). All glassware were treated with a mixture of concentrated sulfuric and nitric acids (H₂SO₄:HNO₃ = 1:1, V:V) before use.

Reagents

All the reagents were of analytical grade. The vanadium (V) solution was prepared by dissolving 2.3000 g of NH₄VO₃ in a few mL of 1 mol/L NaOH, acidified with dilute HCl, diluted to 1000 mL in a standard flask and standardized by known methods.²⁸ A 1.0 ppm solution was prepared by appropriate dilution of the standard solution. A 0.01% solution of 5-Br-PADAP was prepared in ethanol. Buffer solutions of pH 3–6, 6–8 and 8–11 were prepared by mixing appropriate ratios of a 0.5 mol/L

acetic acid and 0.5 mol/L sodium acetate solution, 0.1 mol/L sodium dihydrogen phosphate solution and 0.1 mol/L dipotassium hydrogen phosphate solution, and 0.5 mol/L ammonia solution and 0.5 mol/L ammonium acetate solution, respectively. A 1% solution of TPB was prepared in distilled water. A 20% solution of naphthalene was prepared in acetone. Solutions of alkali metal salts (1%) and other metal salts (0.1%) were used for studying the interference of anions and cations respectively.

Preparation of naphthalene-NH₄-TPB adsorbent

A solution of naphthalene was prepared by dissolving 20 g of naphthalene in 40 mL of acetone on a hot-plate stirrer at 30–35 °C. This solution was transferred into 1500 mL of distilled water containing 25 mL of 1 mol/L ammonium acetate and 75 mL of 1 mol/L ammonia solution (pH 9.5), in a fast stream continuous flow with continuous stirring at room temperature. Then, to this solution, 500 mL of an aqueous solution containing 1.7 g of TPB was added. The naphthalene coprecipitated with NH₄⁺ and TPB⁻. The solution was stirred for about 2 h and then allowed to stand for 2 h. The supernatant solution was decanted off and the remaining solid mass was washed twice with distilled water. The adsorbent in the form of a slurry was stored in a bottle for subsequent use.

General procedure for the column method

To the sample solution (up to 250 mL) containing 0.20–40 µg of vanadium in a beaker was added 2.0 mL of 0.01% alcoholic solution of 5-Br-PADAP and 2.0 mL of acetate buffer of pH 3. The column loaded with the adsorbent NH₄-TPB-naphthalene was conditioned to pH 3 by passing 2–5 mL of the acetate buffer solution at a flow rate of 1 mL/min. The vanadium sample solution prepared above was then passed at a flow rate of 1 mL/min. The packing in the column was washed with a few milliliters of distilled water and then aspirated strongly for 2–3 min, pushing down the solid mass in the column with a glass rod in order to eliminate the excess water attached to the adsorbent. The metal complex was dissolved out of the column along with naphthalene with 5 mL of DMF. The third derivative absorption spectra in the range of 550–700 nm were recorded against a blank solution prepared in the same way. The signal was measured be-

tween $\lambda_1 = 664$ nm and $\lambda_2 = 630$ nm. A calibration curve was prepared by taking various known amounts of vanadium under the conditions given above.

General procedure for microcrystalline naphthalene

A sample solution (up to 100 mL) containing 0.20–40 µg of vanadium solution was placed in an Erlenmeyer flask with tightly fitting stopper. Then 2 mL of 0.01% of the reagent (5-Br-PADAP) was added. The pH was adjusted to 3 with 2 mL of the buffer, and then 2 mL of 1% TPB solution was added. The solution was mixed well and allowed to stand for a few seconds. Then, a 2 mL of 20% solution of naphthalene in acetone was added to it with continuous shaking. The solid mass so formed consisting of naphthalene and metal complex was separated by filtration on a Whatman filter paper (No. 1041). The residue was dried in the folds of a filter paper and transferred to the Erlenmeyer flask. The solid mass consisting of the metal complex along with naphthalene was dissolved with 5 mL of dimethylformamide (DMF). Finally, the third derivative absorption spectrum was recorded in the range of 550–700 nm against a blank solution prepared in the same way.

Results and discussion

Spectrophotometric measurements

The zero order (normal spectrophotometric) and the third order derivative spectra of the complex are shown in Fig. 1. As can be seen, the higher wavelength peaks of the third derivative spectra are more significant. The sensitivity of the third order derivative is much higher than these of the zero (normal), the first and the second orders. The third derivatization leads to sharper zero order bands (normal spectrophotometric bands) and gives stronger signals on the resulting spectra. The characteristics of derivative spectra, such as peak height and noise level, depend on the choice of parameters such as order of derivative, scan speed and integration time during recording of the spectra. The optimum parameters were chosen from preliminary experiments. The best results were obtained from the third derivative spectra due to high signals at $\lambda_1 = 664$ nm, $\lambda_2 = 630$ nm, with a length interval of 9 nm. Vanadium could be determined by measuring the signal between the baseline and the corresponding peaks. It

could also be determined from the signal between λ_1 and λ_2 . In the present work, a peak-to-peak method between λ_1 and λ_2 was applied.

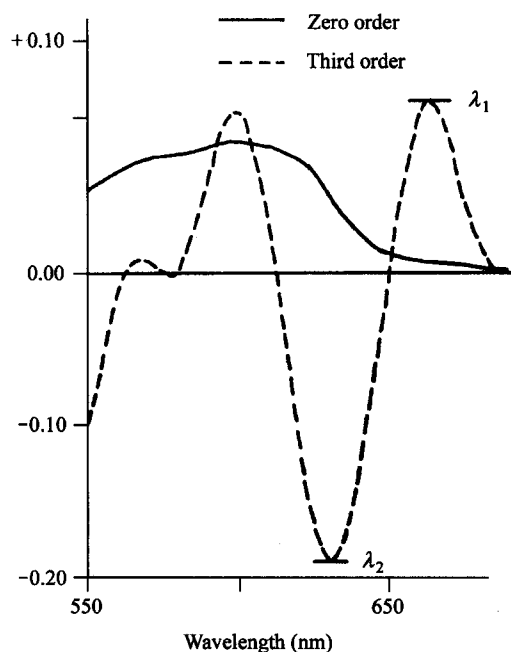
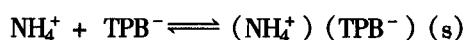


Fig. 1 Zero and the third order spectrum of the naphthalene-V-(5-Br-PADAP)-TPB complex. V, 4 μg ; buffer, 2 mL; pH, 3; 5-Br-PADAP, 2.0 mL (0.01%); solvent, 5 mL of DMF; reference, reagent blank.

Retention characteristics of NH_4 -TPB

TPB^- , soluble in water, forms water-insoluble precipitates with some alkali metal ions such as K^+ , Rb^+ , Cs^+ (but not Li^+ , Na^+), and univalent metal ions such as Ag^+ , Tl^+ and Cu^+ , but no precipitates are formed with multivalent metal ions. It has been used as a gravimetric and volumetric reagent. Furthermore, it also reacts with ammonium salts to form water-insoluble precipitates. The TPB^- forms a weakly bonded ion-pair with NH_4^+ in aqueous solution and coprecipitates with microcrystalline naphthalene as follows:



From the experimental observation, the NH_4 -TPB ion-pair, produced from TPB^- and ammonium acetate in aqueous solution, when supported on naphthalene was unstable and partly desorbed from the surface of the naphthalene in the column on passage of the buffer of pH 3.

However, the NH_4 -TPB ion-pair prepared in acetate buffer of pH 9.5 is highly stable and TPB^- is not desorbed even on washing with water or the buffer of pH 3 in the present work. The adsorbent shows excellent absorption characteristics for various cationic metal complexes such as $\text{Fe}(1,10\text{-Phen})_3^{2+}$. In this work, TPB^- has been selected as the counter-ion because of its purity at moderate price.

Reaction conditions

These were established with the use of 4 μg of vanadium. The adsorption of vanadium on the NH_4 -TPB-naphthalene adsorbent was found to be a maximum in the pH range of 2.1–4.5. In subsequent studies, the pH was maintained approximately at 3. Addition of 0.5–5 mL of the buffer did not affect the retention of vanadium and the use of 2 mL was recommended. Various amounts of 0.01% alcoholic solution of 5-Br-PADAP were tried. Vanadium was quantitatively adsorbed on the adsorbent over the range of 0.6–3.0 mL of the reagent. Therefore, 2.0 mL of the reagent was recommended in the present study.

Various amounts of naphthalene (20% solution of naphthalene in acetone) were added to the sample solutions keeping other variables constant. It was observed that the signal height remained constant with the addition of 1.0–4.0 mL of 20% naphthalene solution. Therefore, 2.0 mL of 20% naphthalene solution was used in the subsequent studies. The effect of shaking time on the adsorption indicated that the signal height remained constant over a range of 0.5–5.0 min. Therefore, 1.0 min of shaking time was applied in the present work.

In the case of column method, the flow rate was varied from 0.2 to 8 mL/min. It was found that a flow rate of 0.2–5.0 mL/min did not affect adsorption. A flow rate of 1 mL/min was recommended in all experiments.

The volume of the aqueous phase was varied in the range of 10–700 mL under the optimum conditions keeping other variables constant. It was observed that the signal height was almost constant up to 100 mL (preconcentration factor of 20). However, for convenience, all the experiments were carried out with 40 mL of the aqueous phase. Whereas, in the case of column method, signal height was almost constant up to an aqueous phase volume of 250 mL. Therefore, a preconcentration factor of 50 could be achieved by the column.

Choice of solvent

A number of solvents were tried to dissolve the metal complex along with naphthalene. Since the solid mass is dissolved in a small volume (5 mL) of solvent, it is essential to select a solvent in which the chelate is highly soluble and also sensitive for UV-vis spectrophotometric measurements. The solid material is insoluble in ordinary organic solvents such as toluene, 1,2-dichloroethane, *n*-hexane, nitrobenzene, isoamyl alcohol, *n*-amyl alcohol, ethyl acetate, methyl isobutyl ketone, chloroform and dioxane, but soluble in DMF and propylene carbonate. DMF was preferred because of the high solubility and stability of metal complex on naphthalene. It was found that 5 mL of DMF was sufficient to dissolve the entire mixture, thus further enhancing the sensitivity of the method. Since only a small volume (5 mL) of the solvent is required to dissolve the solid mass, it was essential to study the effect of the surplus water attached to the absorbent. It was found that the surplus water caused the absorbance to decrease by 10%—12% and led to an error in the determination. Thus, it was necessary to eliminate the water attached to naphthalene in the column completely by aspirating the column for 2—3 min.

Retention capacity of the adsorbent

The retention capacity of adsorbent was determined by a batch method. The experiment was performed by adding 500 μg of vanadium, 2 mL of the buffer (pH 3), a suitable amount of reagent 5-Br-PADAP and 40 mL of water in a beaker. This solution was transferred into a separatory funnel and then a suitable amount of the adsorbent naphthalene-NH₄-TPB was added. The separatory funnel was vigorously shaken on a mechanical shaker for 5 min. The solid mass was separated by filtration and vanadium was determined from the filtrate by atomic absorption spectrometry. The solid mass on the filter paper was dried in an oven, kept in a desiccator, and then weighed to determine the mass of the adsorbent. The maximum amount of vanadium retained was 4.1 mg/g of the adsorbent.

Calibration, sensitivity, precision, recovery and stability

Considering that it is possible to retain 0.05 μg of vanadium from 250 mL of solution passing through the column, the dissolution with 5.0 mL of DMF gives a de-

tection limit of 0.2 ng/mL for vanadium at the minimum instrumental settings. The linearity was maintained in the concentration range of 0.8 ng/mL to 4 μg /mL vanadium in an aqueous solution or 0.04 μg /mL to 8 μg /mL vanadium in the final DMF solution with a correlation factor of 0.9997. Eight replicate determinations of 4 μg of vanadium in 5 mL of DMF solution gave a mean intensity in the third derivative spectrum, measured from the peak-to-peak signal between λ_1 and λ_2 , of 0.297 with a relative standard deviation of $\pm 0.95\%$. The sensitivity was 0.376 ($d^3A/d\lambda^3$) mL/ μg from the slope of the calibration curve (A was absorbance, λ was wavelength, $d^3A/d\lambda^3$ was third derivative of absorbance to wavelength). The recovery of vanadium in the process of elution with DMF was more than 97%. The solution was stable over 9 d.

Interference of foreign ions

Various salts and metal ions were added individually to a solution containing 4 μg of vanadium and the general procedure was applied. The tolerance limit was set as the ion concentration required to cause a $\pm 3\%$ error in the determination of vanadium. The results obtained are given in Table 1. Among the anions examined none interfered. It is interesting to note that neither oxalate, tartrate, citrate, iodide, fluoride, nor EDTA interfered in the present

Table 1 Effect of foreign salts and metal ions

Salt or ion	Tolerance limit
CH ₃ COONa·3H ₂ O, KNO ₃	1 g
NH ₄ Cl, NH ₄ Br, Na ₂ SO ₄	200 mg
KI, NaF, K ₂ CO ₃ , thiourea	100 mg
Sodium potassium tartrate	50 mg
Sodium oxalate	15 mg
Trisodium citrate	10 mg
Na ₂ EDTA	0.5 mg
Al(III), Mg(II)	10 mg
Ga(III), U(VI), Te(IV)	0.8 mg
Se(VI), Sn(II), Sb(III), Nb(III)	0.6 mg
Pb(II), Mn(II), Ni(II), Cd(II)	80 μg , 0.5 mg ^a
Fe(III), Hg(II), Cu(II)	40 μg , 0.3 mg ^a
Ir(III)	90 μg , 0.4 mg ^a
Rh(III), Co(II)	300 μg ^a
Bi(III), Ru(III), Zr(IV), Ta(III)	200 μg

^a After being masked with 0.5 mg of Na₂EDTA.

determination while they do interfere mostly in the extraction spectrophotometric determination of several metal ions. Among the metal ions studied, Cu(II), Ni(II), Co(II), Pb(II), Mn(II), Fe(III), Hg(II), Cd(II), Rh(III) and Ir(III) interfered. Since Na₂EDTA has no influence, these metal ions were masked with the addition of 0.5 mg of Na₂EDTA. Thus the method is highly selective and may safely be applied to the determination of vanadium in various complex materials.

Analysis of standard alloys

The proposed method has been applied to determination of vanadium in Nippon Keikinzo Kogyo (NKK) CRM 916 Aluminum Alloy, NKK No. 920 Aluminum Alloy and NKK No. 1021 Al, Si, Cu, Zn Alloy. A sample (0.1 g) of the standard alloy was completely dissolved in 4–5 mL of concentrated hydrochloric acid by heating on a water-bath and then 1 mL of 30% hydrogen peroxide was added. The excess peroxide was decomposed by heating the solution on a water-bath. The solution was cooled and filtered if needed and the filtrate was diluted to 100 mL with doubly distilled water in a calibrated flask. An aliquot (1–2 mL) of this solution was taken and vanadium was determined by the general procedure. The results obtained are given in Table 2.

Analysis of synthetic samples

A synthetic sample containing vanadium was prepared in 10 mL of concentrated hydrochloric acid. The solution was filtered if needed, and the volume was made to 100 mL in a standard flask. An aliquot of the sample (40–100 mL) solution was analyzed by the general procedure and the results are given in Table 3.

Conclusion

A solid ion-pair compound produced from NH₄⁺ and TPB⁻ naphthalene provides a simple and economical method for the preconcentration of vanadium from large volumes of alloys and synthetic samples using 5-Br-PADAP as the complexing agent. This reagent is fairly sensitive and selective for vanadium, but with the precon-

Table 2 Analysis of vanadium in standard alloys

Sample	Composition (%)	Concentration (%)	
		Certified value	Found ^a
NKK 916 aluminum alloy	Si, 0.41; Mg, 0.10;	0.02	0.019 ± 0.002 ^b
	Cr, 0.05; Ni, 0.06;		
	Zn, 0.30; Tl, 0.01;		
	Sn, 0.05; Pb, 0.04;		
	Zr, 0.05; Bi, 0.03;		
	Co, 0.03; Sb, 0.01;		
	B, 0.0006; Fe, 0.54;		
Cu, 0.27; Mn, 0.11;			
NKK No. 1021 Al, Si, Cu, Zn alloy	Pb, 0.18; Ni, 0.14;	0.007	0.0068 ± 0.0004 ^b
	Zn, 1.76; Sn, 0.10;		
	Mg, 0.29; Cr, 0.03;		
	Ti, 0.04; Si, 5.56;		
	Zr, 0.01; Bi, 0.01;		
	Sb, 0.01; Ca, 0.004;		
	Fe, 0.99; Cu, 2.72;		
Mn, 0.20			
NKK No. 920 aluminum alloy	Co, 0.10; Ni, 0.29;	0.15	0.147 ± 0.005 ^c
	Cr, 0.27; Si, 0.78;		
	Ti, 0.15; Sn, 0.20;		
	Pb, 0.10; Bi, 0.06;		
	Ga, 0.05; Zn, 0.80;		
	Sb, 0.10; Ca, 0.03;		
	Mg, 0.46; Fe, 0.72;		
Cu, 0.71; Mn, 0.20;			

^a Average of five determinations ± standard deviation. Standard addition method was applied and after being masked with 0.5 mg of Na₂EDTA. ^b Column method was applied. ^c Microcrystalline naphthalene was applied.

centration step and the use of derivative spectrophotometry the sensitivity and selectivity have been further improved. Thus the developed method can be used safely for the estimation of vanadium in a number of complex materials. Since the adsorbent provides TBP⁻ as the counter anion, the adsorbent may therefore be used for the preconcentration of various types of cationic metal complexes. As a whole the method described is highly sensitive, selective, simple and highly economical (it requires simple glassware, and a small volume of the organic solvent to dissolve the solid mass from the column) for the estimation of vanadium.

Table 3 Analysis of vanadium in synthetic samples

Composition of synthetic sample ($\mu\text{g/g}$)	Concentration of vanadium ($\mu\text{g/g}$)	
	Certified value	Found ^a
As, 4.0; Cd, 3.0; Cu, 0.60; Ca, 150; Fe, 6.0; Ni, 6.5; Mn, 10.0; Hg, 8.0; Mg, 100; Pb, 25; Zn, 3.5; Tl, 1.5; Pd, 7.5; Rh, 0.85; Ir, 5.5	6.5	6.3 ± 0.3^b
Mn, 3.5; Pb, 2.0; Sb, 1.5; Ni, 6.0; Mo, 4.5; Mg, 75; Ca, 74; Cd, 7.5; Hg, 2.5; Bi, 8.0; Zn, 12; Al, 2.5; Pd, 7.5; Rh, 18.0; Ir, 15.0	25.0	24.7 ± 0.5^c
Ni, 15; Fe, 3.5; Zn, 6.5; Ca, 120; Mg, 65; Mn, 25; As, 3.5; Bi, 16; Mo, 6.5; Sb, 7.5; Hg, 15.0; Pd, 3.5; Rh, 17.5; Ir, 25.5	48.0	48.3 ± 0.7^c

^a Average of five determinations \pm standard deviation, and after being masked with 0.5 mg of Na_2EDTA . ^b Column method was applied. ^c Microcrystalline naphthalene was applied.

References

- Lee, D. H. K. *Metallic Contaminants and Human Health*, Academic Press, New York, 1972.
- Nelson, W. L. *Oil Gas J.* 1973, 71, 54.
- Vouk, V. W.; Piver, W. T. *EHP, Environ. Health Perspect.* 1983, 47, 201.
- Kiviluoto, M. P. L.; Pakarinen, A. *Int. Arch. Occup. Environ. Health* 1981, 48, 51.
- Gylseth, B.; Leira, H.; Steinnes, E.; Thomassen, Y. *Scan. J. Work Environ. Health* 1979, 5, 188.
- Sabbioni, E.; Maroni, M. *A Study on Vanadium in Workers from Oil Fired Power Plants*, Commission of the European Communities, Publication No. EUR. 9005, Luxembourg, 1983.
- Jackson, K. W.; Oiao, H. *Anal. Chem.* 1992, 64, 50R.
- Jackson, K. W.; Mahmood, T. M. *Anal. Chem.* 1994, 66, 252R.
- Kantipuly, C. J.; Westland, A. D. *Talanta* 1988, 35, 1.
- Ramesh, A.; Krishnamacharyulu, J.; Ravindranath, L. K.; Rao, S. B. *Analyst* 1992, 117, 1037.
- Jain, S. K.; Puri, B. K.; Singla, A. L.; Rao, A. L. J. *Chim. Acta Turcia* 1998, 16, 327.
- Taher, M. A.; Puri, S.; Bhalotra, A.; Puri, B. K. *Quim. Anal.* 1999, 18, 181.
- Griffiths, T. R.; King, K.; Hubbard, H. V.; Schwing-Weill, M. J.; Meullemeestre, J. *Anal. Chim. Acta* 1982, 143, 163.
- Taher, M. A.; Puri, B. K. *Analyst* 1995, 120, 1589.
- Ishii, H.; Singh, R. B.; Odashima, T. *Mikrochim. Acta* 1983, III, 149.
- Reilly, C. N. *Advances in Analytical Chemistry*, Vol. 1, Interscience, New York, 1960.
- Chang, L. F.; Satake, M.; Kuwamoto, T.; Puri, B. K. *Microchem. J.* 1986, 33, 46.
- Taher, M. A. *Anal. Chim. Acta* 1999, 382, 339.
- Quig, Y. M.; Quin, L. G. *Talanta* 1983, 30, 265.
- Taguchi, S.; Yal, T.; Shimada, Y.; Goto, K. *Talanta* 1983, 30, 169.
- Kubota, M.; Matseemoto, K.; Terada, K. *Anal. Sci.* 1987, 3, 45.
- Sakai, Y.; Mori, N. *Talanta* 1986, 33, 161.
- Burba, P.; Willmer, P. G. *Talanta* 1983, 30, 381.
- Kimura, M.; Yamashita, H.; Komada, J. *Bunseki Kagaku* 1986, 35, 400.
- Khan, A. S.; Chow, A. *Talanta* 1986, 33, 182.
- Wasey, A.; Bansal, R. K.; Puri, B. K.; Rao, A. L. J. *Talanta* 1984, 31, 205.
- Satake, M.; Kano, G.; Usami, S.; Puri, B. K. *Indian J. Chem.* 1988, 27A, 265.
- Vogel, A. I. *A Text Book of Quantitative Inorganic Analysis*, 5th ed., Longmans, London, 1989.

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