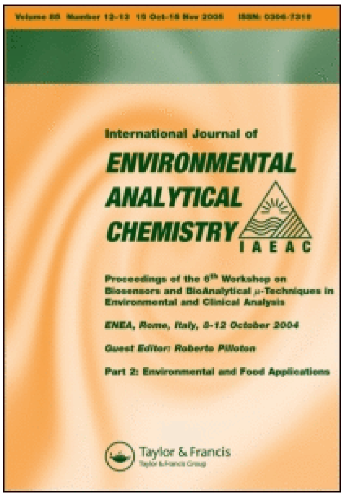

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Extraction of Vanadium(V) with Hydroxyamidine in the Presence of Adductants and its Spectrophotometric Determination with Diphenylcarbazide

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To cite this Article Deb, M. K. , Patel, K. S. and Mishra, R. K.(1991) 'Extraction of Vanadium(V) with Hydroxyamidine in the Presence of Adductants and its Spectrophotometric Determination with Diphenylcarbazide', International Journal of Environmental Analytical Chemistry, 43: 4, 209 — 217

To link to this Article: DOI: 10.1080/03067319108027525

URL: http://dx.doi.org/10.1080/03067319108027525

Intern. J. Environ. Anal. Chem., Vol. 43, pp. 209–217
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EXTRACTION OF VANADIUM(V) WITH HYDROXYAMIDINE IN THE PRESENCE OF ADDUCTANTS AND ITS SPECTROPHOTOMETRIC DETERMINATION WITH DIPHENYLCARBAZIDE

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(Received 31 May 1989; in final form 6 June 1990)

The extraction of V(V) with N-hydroxy-N,N'-diphenylbenzamidine(HOA) in the presence of 100 adduct-forming substances, e.g. inorganic acids, carboxylic acids, phenols, aldehydes and amides from weakly acidic solution into chloroform has been studied. The molar absorptivities of the resultant adducts lie in the range of $(1.5–7.8) \times 10^3 \, l \, mol^{-1} \, cm^{-1}$ at λ_{max} 575–635 nm. The most sensitive adductant, 4-nitro-phenol(NPhOH) has been chosen for detailed studies. The colour can be intensified at least 3-fold by the oxidation of diphenyl-carbazide to diphenylcarbazone with the extract in strong hydrochloric acid. The molar absorptivity of the resulting diphenylcarbazone in chloroform in terms of vanadium is $2.45 \times 10^4 \, l \, mol^{-1} \, cm^{-1}$ at λ_{max} 540 nm. The method is simple, rapid and reproducible and can be used for the detection of V(V) in water samples with a detection limit of 6 μg/l.

KEY WORDS: Vanadium(V), adductants, N-hydroxy-N,N'-diphenylbenzamidine, spectrophotometry, coal ash, cement dust, industrial waste water.

INTRODUCTION

Vanadium is a toxic micro-element present in environmental samples like coal dust, coal ash, cement dust, fuel oil, stack gas and industrial waste water. Therefore, the development of a new spectrophotometric method for the selective extraction and determination of vanadium is of great importance. Several spectrophotometric methods for the determination of vanadium have been reported.[1–10] Of these, the PBHA method is well known and commonly employed for the determination of the metal.[1] However, it suffers from interferences by many metal ions, e.g. Mn, Cr, Ti, Zr, Mo and W.[2] The results then obtained are too low and erratic.[3] Sulphochlorophenol-N,2,2-(3,5-dibromopyridyl)azo-5-dimethylaminobenzoic acid and PAR in the presence of xylometazoline hydrochloride are recommended for the sensitive spectrophotometric determination of vanadium, but they suffer from interferences by many metal ions, the pH range is also critical in these methods.[4–6] Other established methods lack selectivity and are prone to the interferences of Fe and one or more base metals.[7–10] In this paper, we use N-hydroxy-N,N'-diphenylbenzamidine (HOA) as extractant for the spectrophotometric determination of vanadium(V) in the presence of various adduct-forming substances containing —COOH, —OH (phenolic), —CHO, —COOH(—OH), —CHO(—OH), —SH, —COOH(−CONH$_2$) or H_nX (X=Cl, Br, I, ClO$_4$, BO$_3$) groups. From among the various adductants, 4-nitrophenol has been chosen for detailed studies.

EXPERIMENTAL

Apparatus

A Carl Zeiss Spekol equipped with 1-cm quartz cuvettes was used for the absorbance measurements. A Systronic type-322 pH meter was used to measure pH values.

Reagents

N-Hydroxy-N,N′-diphenylbenzamidine (HOA) was synthesized according to Satyanarayana.[11] The solution of HOA in chloroform (0.1 %, W/V; 0.003 M), solutions of the adductants in water $(1.2-50.0)\times 10^{-3}$ g mol or chloroform $(1.2-20.0)\times 10^{-3}$ g mol and 0.5 % diphenylcarbazide in acetone were used for the extraction work. The stock solution of V(V) (0.5 mg/l) was prepared by dissolving 1.1482 g ammonium metavanadate in deionised water and diluting to 1 litre. All chemicals used were of analytical reagent quality grade (BDH/E. Merck).

Extraction of V(V) with HOA in the presence of adductant

10 ml or less of a solution containing 50–150 μg of V(V) are taken into a 100-ml separatory funnel. The nature of the adductants affects the method of extraction, as is explained below.

Extraction with water-soluble adductants. The aqueous solution is treated with the appropriate amount of adductant (0.0075 gmol formic acid; 0.05 gmol acetic acid; 0.005 gmol chloroacetic acid or formaldehyde; 0.0025 gmol boric acid, perchloric acid, bromic acid, iodic acid, iminoacetic acid, 2,4-dichlorophenyl acetic acid, salicylacetic acid, lactic acid, maleic acid, malonic acid, citric acid, tartaric acid, fumeric acid, stearic acid, thioglycolic acid or glycine; 0.002 gmol chlorobenzoic acid; 0.00125 gmol dichlorophenol, mono-, di-, or trinitrophenol) and the pH of the solution is adjusted to 2.0 ± 0.2 in a 25-ml aqueous solution. The solution is extracted with 10 ml chloroform solution of HOA for 2 min. The extract is transferred to a 25 ml beaker. The aqueous phase is washed with 3 × 2 ml chloroform. The combined $CHCl_3$ extracts are dried over 2 g sodium sulphate, filtered and transferred to a 25-ml volumetric flask and adjusted to 25 ml with chloroform. The absorbance of the adduct is measured at λ_{max} using chloroform as a reference.

Extraction with chloroform-soluble adductants. The aqueous solution is diluted to 25 ml with distilled water and the pH is adjusted to 2.0 ± 0.2. The aqueous solution is equilibrated as above with 10 ml chloroform solution of HOA containing the appropriate amount of adductant (0.0025 gmol aliphatic carboxylic acid; 0.02 gmol aromatic carboxylic acid or aldehyde; 0.00125 gmol phenol). The aqueous phase is washed with 3 × 2 ml chloroform. The combined extracts are dried, filtered, diluted and the absorbance is measured at λ_{max} of the complex as above.

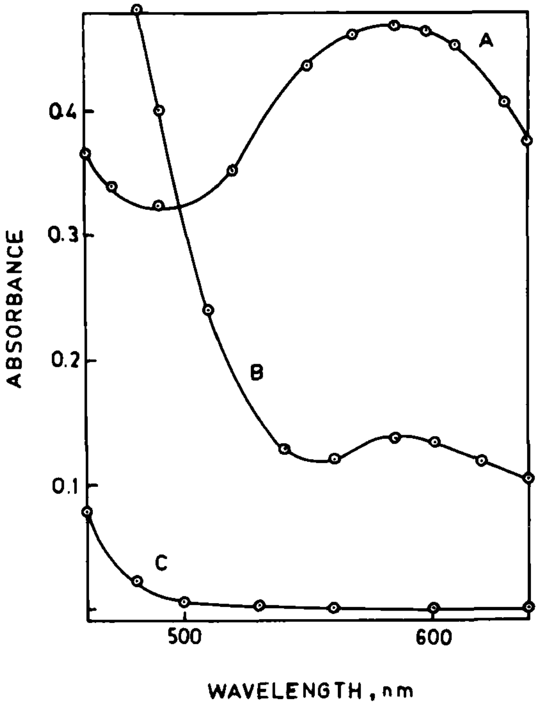

Figure 1 Absorption spectra of the reagent blank and [$VO(OA)_2OH$] complex in the presence and absence of NPhOH in chloroform. pH = 2 ± 0.2, [V^{5+}] = 5.88×10^{-5} M, [HOA] = 3×10^{-3} M, [NPhOH] = 1×10^{-2} M. (A), V(V)-HOA-NPhOH adduct; (B), V(V)-HOA-HCl adduct; (C), Reagent blank.

Spectrophotometric determination of V(V) with diphenylcarbazide

20 ml or less of a solution containing less than 20 μg V(V) are extracted as above with 5 ml HOA solution in the presence of the appropriate adductants and washed with 2 ml of chloroform. The combined extracts are transferred into another 100-ml separatory funnel containing 0.5 ml diphenylcar-bazide in acetone and 0.4 ml concentrated HCl, and shaken for 2 min. The pink extract of diphenylcarbazone obtained is dried over anhydrous $CaCl_2$ (2 g), filtered and transferred to a 10-ml volumetric flask and adjusted to 10 ml with chloroform. After 15 min the absorbance of the extract is measured at λ_{max} 540 nm against chloroform as a blank.

RESULTS AND DISCUSSION

Extraction of Vanadium(V) with hydroxyamidine in presence of adductants

The absorption spectra of V(V)-HOA-NPhOH and V(V)-HOA-HCl adducts against the respective reagent blanks and that of the reagent blank in chloroform are shown in Figure 1. The position of the absorption maximum with the various adductants tested falls between 575 and 635 nm and the molar absorptivities of the complexes formed between V(V), HOA and the various adductants in chloroform lie in the range of $(1.5–7.8) \times 10^3 \, l \, mol^{-1} \, cm^{-1}$ (see Table 1). At these wavelengths, the reagent blank has practically negligible absorption. 4-Nitrophenol gives the highest molar absorptivity of $7.8 \times 10^3 \, l \, mol^{-1} \, cm^{-1}$ at λ_{max} 585 nm. The limit of detection with HOA and NPhOH is 20 μg V/l. The optimum concentration range on the basis of Beer's law is 1.0–16.0 mg V/l in the organic solution. The precision of the method for 10 replicate measurements at a level of 3.0 mg V/l in the organic solution was found to be ±0.8%.

Acids. The effect of various acids like HCl, HBr, H_2SO_4, H_3PO_4, HCOOH and CH_3COOH on the extraction of the metal with HOA and NPhOH was examined, and all of them were found to be adequate. In the present investigation, hydrochloric acid and dilute ammonia were employed for pH adjustment in all systems cited except the strong acids. The optimum pH range for extraction of V(V) with NPhOH is 1.5–5.8, while with other adductants the optimum range is between 1.0 and 6.0.

Organic solvents. The effect of various organic solvents like carbon tetrachloride, chloroform, benzene, toluene, xylene, 1-pentanol and methylisobutyl ketone on the extraction of V(V) with HOA and NPhOH was examined. All of them quantitatively extract the metal with different values for the absorption maximum and molar absorptivity: carbon tetrachloride (ε, 7800; λ_{max}, 585), chloroform (ε, 7800; λ_{max}, 585) benzene (ε, 8200; λ_{max}, 585), toluene (ε, 8300; λ_{max}, 580), xylene (ε, 8500; λ_{max}, 585), 1-pentanol (ε, 2500; λ_{max}, 430), methylisobutyl ketone (ε, 3800 $l \, mol^{-1} cm^{-1}$; λ_{max}, 580 nm). Of these, aromatic hydrocarbons give the most sensitive colour reaction but the reagents has relatively lower distribution than with chloroform. In the present investigation, chloroform was chosen as solvent because of the higher colour intensity of the extract, and the higher distribution ratio of the reagent.

Extraction. The effect of the amount of HOA and NPhOH on the extraction of the metal was examined. An at least 10-fold molar excess of HOA in chloroform and 0.005 M NPhOH in the aqueous solution were necessary for full colour development of the adduct in chloroform; the addition of more reagent (up to 0.01 M HOA and 0.03 M NPhOH) caused no adverse effect. The order in which the reagents were added is not critical. The extraction of the metal was not affected by changing the temperature from 15 to 45 °C. The extract was stable for at least 10 h at room temperature (27 ± 2 °C). An equilibrium period of 1 min was sufficient for full extraction of the metal and prolonged extraction up to 10 min was not critical. Electrolytes such as KCl, NH_4Cl or K_2SO_4 up to 2 M did not affect the extraction of the metal. The metal can be preconcentrated from very dilute solutions. Quantitative extraction has been observed when the volume ratio of the organic phase to the aqueous phase is from 1:0.5 to 1:20.

Adduct composition. A solid adduct was prepared by taking an aliquot of V(V) and NPhOH (1:10 molar ratio) in a 400-ml beaker. A 2-fold molar excess of HOA in ethanol (20 ml) was added to it, and the solution was digested on a water bath

Table 1 Spectral data of $[VO(OA)_2OH]$ with various adductants in chloroform

Adductant	*ε(l mol^{-1} cm^{-1})^a*	*Adductant*	*ε(l mol^{-1} cm^{-1})^a*
Formic acid	4700	3-Nitrophthalic acid	5400
Acetic acid	4300	Sulphanilic acid	4600
Monochloroacetic acid	4000	1-Phenylanthranilic acid	3600
Dichloroacetic acid	4050	1-Acetylanthranilic acid	4100
Trichloroacetic acid	4100	Ethyl-4-aminobenzoic acid	3800
Iminoacetic acid	2100	Cinnamic acid	4300
Phenylacetic acid	4500	2-Furoic acid	4700
2,4-Diphenylacetic acid	4300	Pyruvic acid	2600
3,4,5-Triphenoxyacetic acid	5640	Valeric acid	3800
4-Nitrophenylacetic acid	4500	Nicotinic acid	4200
2,4-Dichlorophenylacetic acid	4450	Benzilic acid	3900
1-Naphthylacetic acid	4250	Hippuric acid	4850
1-Naphthoxyacetic acid	4700	Rubin-S	2400
Salicylacetic acid	3950	Boric acid	3800
Propionic acid	4300	Perchloric acid	5150
n-Butyric acid	3500	Bromic acid	3600
Iso-Butyric acid	4700	Iodic acid	4300
Bepanic acid	3200	Phenol	5300
Lactic acid	2150	4-Chlorophenol	7100
Maleic acid	4700	2,4-Dichlorophenol	5500
Malonic acid	4100	2-Methylphenol	4150
Citric acid	1550	3-Methylphenol	4450
Tartaric acid	1850	4-Methylphenol	4450
Fumeric acid	1600	2-Ethoxyphenol	4550
Myristic acid	2000	2-Aminophenol	4000
Mandelic acid	4300	3-Aminophenol	4350
Sebacic acid	4200	4-Aminophenol	4000
Stearic acid	3950	2-Nitrophenol	4300
Thioglycolic acid	3050	3-Nitrophenol	5000
Azalic acid	3400	4-Nitrophenol	7800
Glycine	3000	2,4-Dinitrophenol	5400
Aspartic acid	4000	2,4,6-Trinitrophenol	4900
Sarine	3600	1-Naphthol	4000
Arginine	2400	2-Naphthol	5200
Benzoic acid	3300	Sulphophenol	3300
2-Chlorobenzoic acid	4800	Thiophenol	2600
4-Chlorobenzoic acid	3000	Thymol blue	4450
2-Iodobenzoic acid	4500	Bromothymol blue	4000
2-Methylbenzoic acid	3400	Formaldehyde	3600
3-Methylbenzoic acid	3900	Benzaldehyde	4200
4-Methylbenzoic acid	3900	3-Nitrobenzaldehyde	4300
3-Nitrobenzoic acid	4650	4-Nitrobenzaldehyde	5000
4-Nitrobenzoic acid	3500	Anisaldehyde	4200
2-Aminobenzoic acid	3500	4-Methoxybenzaldehyde	4200
4-Aminobenzoic acid	3500	1-Naphthyldehyde	4300
4-Methoxy benzoic acid	4000	4-Hydroxybenzaldehyde	7000
5-Methyl-2-Nitrobenzoic acid	4400	Vanillin	5350
Salicylic acid	4900	Cinnamaldehyde	1700
Aspirin	5000	Furfuraldehyde	3900
Sulphosalicylic acid	3000	Sulphonal	4300
Phthalic acid	4650	Phthalamide	3100

[a] At λ_{max} 585 ± 10 nm except 1-naphthol, 635 nm and 2-naphthol, 615 nm.

for 15 min in order to precipitate the adduct. The adduct was filtered and washed with distilled water till a colourless filtrate was obtained. The melting point of the dried adduct is 78 °C. The adduct was analyzed by elemental analysis, and by destruction with acid, and the metal obtained was determined by the diphenylcarbazide method. The data obtained correspond with the empirical formula, $[VO(C_{19}H_{15}N_2O)_2OH]OH.C_6H_4.NO_2$. The solid complex dissolved in chloroform has the same spectral properties as the adduct obtained by the above extraction method.

The composition of the adduct was verified by Job's method of continuous variation and the curve-fitting method (log molar concentration of HOA in the organic solution or log molar concentration of NPhOH in the aqueous solution versus log distribution ratio of the metal, D) which indicate the ratio metal: HOA:NPhOH to be 1:2:1 (see Figures 2–3). The overall extraction equilibrium can be expressed as:[12–13]

$$VO_2^+ + 2\,HOA_0 + NPhOH \rightleftharpoons [VO(OA)_2OH]NPhOH_0 + H^+ \quad (1)$$

where the subscript 0, HOA and NPhOH denote the organic phase, hydroxyamidine and 4-nitrophenol, respectively.

Spectrophotometric Determination of Vanadium(V) with Diphenylcarbazide

The extract $[VO.(OA)_2OH]L$ (L = adductant) is treated with diphenylcarbazide (DPCZI) in concentrated hydrochloric acid solution (0.2–0.6 ml) to oxidize that reagent to the red-violet diphenylcarbazone (DPCZO). The DPCZO so formed is extractable into chloroform and exhibits an absorption maximum at 540 nm against the reagent blank. The reagent blank obtained in chloroform has negligible absorption at this wavelength; therefore the chloroform blank (chloroform is shaken with DPCZI and concentrated HCl as in the procedure) is used as reference for all measurements.

At least 0.03 ml (0.5%) DPCZI is necessary for full colour development and has no adverse effect up to 1 ml. A waiting time of 15 min is required for maximum colour attainment and the colour of the extract is stable for at least 2 h at room temperature. The molar absorptivity of DPCZO formed in chloroform calculated in terms of vanadium is $2.45 \times 10^4\,l\,mol^{-1}\,cm^{-1}$ at λ_{max} 540 nm. The limit of detection is 6 μg/l. The system follows Beer's law up to 2 mg V/l. The relative standard deviation for the recovery of the metal was evaluated by making 10 replicate measurements at a level of 0.6 mg V(V)/l in chloroform, and found to be ±1.1%. Ther probable redox reaction mechanism was determined by plotting log D ($(A/(A_{max} - A)$; A_{max} = the colour of DPCZO when DPCZI is used in equilibrium) versus log concentration of DPCZI in acetone and can be written as:

$$DPCZI + 2[VO(OA)_2OH]_0 + H^+ \rightleftharpoons DPCZO_0 + VO^{2+} + 2\,HOA_0 + H_2O \quad (2)$$

where the subscript 0, HOA, DPCZI and DPCZO denote the organic phase, hydroxyamidine, diphenylcarbazide and diphenylcarbazone, respectively.

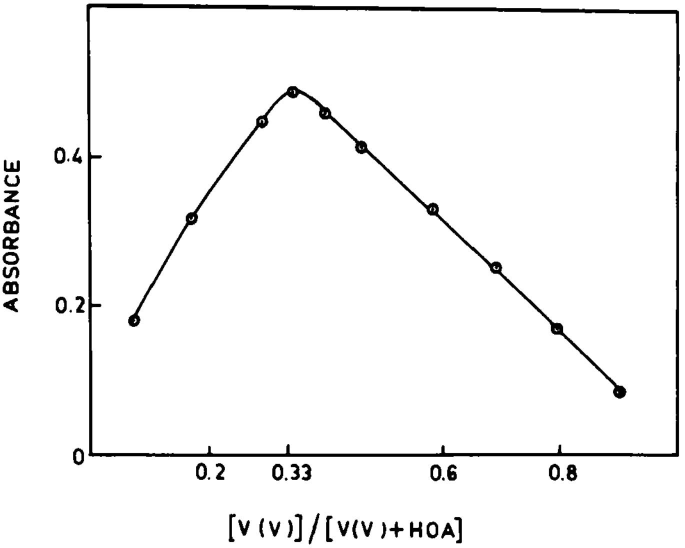

Figure 2 Determination of the ratio of V(V) to HOA in the extracted adduct by Job's method. pH = 2 ± 0.2; $[V^{5+}] = [HOA] = 7.85 \times 10^{-4}$ M; $[NPhOH] = 1 \times 10^{-2}$ M.

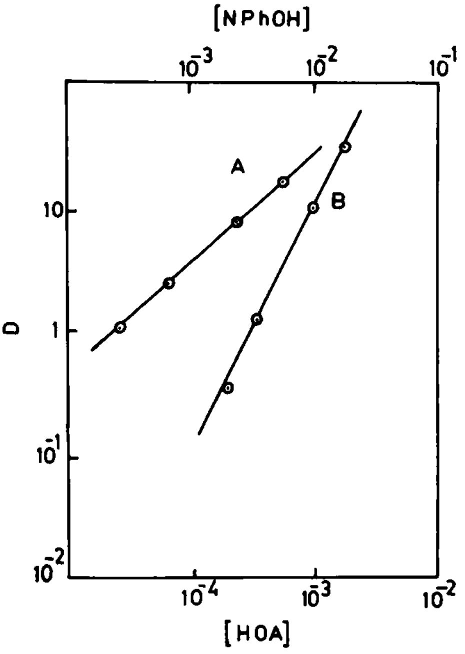

Figure 3 Determination of the ratio of V(V) to 4-nitrophenol and HOA by the curve-fitting method. pH = 2 ± 0.2; $[V^{5+}] = 1.96 \times 10^{-3}$ M. (A), Log D vs. log HOA; $[NPhOH] = 1 \times 10^{-2}$ M. (B), Log D vs. log NPhOH; $[HOA] = 3 \times 10^{-3}$ M.

Table 2 Tolerance limit[a] of diverse ions in the determination of 6 μg of V(V) at pH 2 ± 0.2

Ion	*Amount (mg/l)*	*Ion*	*Amount (mg/l)*
Fe^{3+},[b] U^{6+}	500	Mo^{6+}	200
Tl^{3+}, Zn^{2+}		W^{6+}	100
Cu^{2+}	300	Sb^{3+}	1200
Ni^{2+}, Cr^{3+}	500	Ag^{+}, Hg^{2+}	600
Mn^{7+}		Oxalate	1000
Cd^{2+}	1000	Nitrate	7000
Al^{3+}	1500	Thiourea	3000
Zr^{4+}	100		

[a] Error caused less than 2%.
[b] Masked with 2 g trisodium phosphate.

Effect of diverse ions

The effect of diverse ions on the extraction of 6 μg V(V) with HOA and NPhOH, and consequent colour development with DPCZI is examined as in the procedure. Only Fe(III) cause serious interference in the determination of the metal, which can be eliminated by masking with trisodium phosphate. The tolerance limits of various ions are summarized in Table 2.

Application of the method

This method has been applied to the determination of Vanadium(V) to industrial waste water, coal ash and cement dust. Vanadium the metal has been determined using a standard addition method. The recovery of the metal in the first step (extraction procedure) was determined by evaporating the extract, treatment with acid and determination with PAR.[6] It was found to be 99.2% after a single extraction.

An aliquot (1–5 ml) of a waste water sample is taken in a 100-ml separatory funnel and the metal content is determined as in the procedure. In the case of solid samples, a weighed amount of the sample (2 g) is digested by acid treatment (aqua regia, HCl and H_2SO_4), and the dry sample is dissolved in deionised water and determined as above. In Table 3, the data obtained by the present method are compared with that of HOA extraction of V(V) with acetic acid as in the literature;[11] the results are highly satisfactory.

CONCLUSION

Extraction of V(V) with a chloroform solution of HOA in the presence of various adductants proves to be a highly selective extraction-spectrophotometric method. Its sensitivity can be enhanced remarkably by reaction with diphenylcarbazide in strong hydrochloric acid, to allow the determination of the metal at microgram levels in environmental samples. The method has several advantages over other

Table 3 Determination of Vanadium(V) in various complex materials

Sample no.[a]	*Vanadium found by present method (mg/l)*	*Vanadium found by hydroxyamidine + CH_3COOH method (mg/l)*	*RSD*[b] (±%)
1	5	5.3	1.0
2	10	11.0	0.9
3	11	11.5	0.8
4	8	8.3	0.9
5	14	14.0	1.1

[a] Samples 1, 2 and 3 are total waste water obtained from Wagon Repair Shop (Raipur), Bhilai Wires (Bhilai) and Bhilai Steel Plant (Bhilai), M.P., India, respectively. Samples 4 and 5 are coal ash and cement dust obtained from Mandhar Cement Factory, Raipur, M.P., India, respectively.

[b] Average of five determinations.

well established methods. The degree of extraction of the metal as its adduct is very large, which allows considerable preconcentration (ca. 10-fold). The method is free from interference by elements such as Mn, Cr, Ti, Zr, Mo and W, which create difficulties in the PBHA method and other established methods.

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