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Flotation–Spectrophotometric Determination of Vanadium with 3,5-Dinitrocatechol and Rhodamine B

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A new method of flotation separation and preconcentration of vanadium traces is described. The ion-associate formed by the anionic vanadium(V)-3,5-dinitrocatechol complex and Rhodamine B is floated with cyclohexane. The separated and washed compound readily dissolves in acetone, giving an intensely coloured solution which forms the basis for a sensitive spectrophotometric determination of vanadium. The molar absorptivity is $2.1 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 555 nm and the detection limit is 3 ng/ml. Beer's law is obeyed up to a vanadium concentration of 0.3 $\mu\text{g/ml}$. The composition of the floated compound was established. Its proposed formula is $[(\text{RB})_2\text{-VO}(\text{OH})(\text{DNC})_2]$. EDTA, oxalate and some metals interfere. The method becomes specific for vanadium after a preliminary extraction of the metal as its *N*-benzoyl-*N*-phenylhydroxylamine (BPHA) chelate from a HCl–HF medium. The method was applied to the vanadium determination (0.2–9 ppm) in some vegetables.

Keywords Vanadium, flotation separation, spectrophotometric determination, 3,5-dinitrocatechol, Rhodamine B, vegetable analysis

Recently, interest has been growing in flotation separation and preconcentration of trace amounts of metals.^{1–3} The floated compounds often used are ion-associates of multivalent anionic complexes of metals with basic dyes as cationic partners. Owing to the presence of aromatic rings, they form particles hydrophobic enough to be separated by flotation without the participation of surfactants which is necessary in other systems.^{1,3} The separated precipitate readily dissolves in polar organic solvents and the analyte element can be determined in the solution by any instrumental technique. However, in view of the intense colour of the solution, resulting from the presence of several dye cations corresponding to one atom of the metal in the multivalent anion, it is of great advantage to combine flotation separation with spectrophotometry.

The anionic complexes able to associate with basic dyes include the bromide and/or iodide complexes of bismuth, tellurium, cadmium, gold and mercury, thiocyanate complexes of molybdenum and tungsten^{4–8} as well as trichlorostannate(II), halogenide and thiocyanate complexes of all platinum metals.³

There is a lack of sensitive spectrophotometric methods for the determination of vanadium. In this work, a flotation–spectrophotometric method of the determination of this element is developed. As vanadium does not form complexes able to form ion-associates with basic dyes either with halogenide or with thiocyanate, a suitable organic ligand forming a multivalent complex

with vanadium should be found. In this study, catechol and some of its derivatives were tested for this purpose.

Experimental

Reagents and solutions

Vanadium(V) standard stock solution (1 mg/ml) was prepared by dissolving 1.786 g of vanadium pentoxide (Aldrich), ignited previously at 500°C, in 0.01 M NaOH solution, acidifying with H₂SO₄ and diluting with water in a calibrated flask to 1 l. The solution was standardized by titration with permanganate after reduction of V(V) with iron(II). Working solutions were prepared by appropriate dilution of the stock solution with water.

3,5-Dinitrocatechol (DNC) solution, 5×10^{-4} M (ca. 0.01%) in 25% ethanol. DNC was synthesized from catechol (Aldrich) as described elsewhere⁹ and purified by double recrystallization from ethanol. The purity of the reagent was confirmed by the m.p. measurement and elemental analysis as well as IR and NMR spectroscopy.

Rhodamine B (RB) solution, 5×10^{-4} M (ca. 0.025%) in water. A commercial preparation (POCH Gliwice, Poland) was purified by adding 10 volumes of anhydrous diethyl ether to 1 volume of ethanol saturated with the dye and washing the crystals with water.¹

N-Benzoyl-*N*-phenylhydroxylamine (BPHA) solution,

0.1% w/v in chloroform.

Twice distilled water was used throughout. All other chemicals used were of analytical-reagent-grade.

Apparatus

The absorbance was measured using a VSU2-P spectrophotometer (Zeiss Jena). The absorption spectra were recorded using a Specord UV-VIS spectrophotometer (Zeiss Jena) with 10 mm glass cells. An ELPO Model 1572 pH meter was used for pH measurements.

Procedure

Flotation of vanadium. A sample solution containing not more than 3 μg of vanadium(V) was placed in a separating funnel and 1.5 ml of the DNC solution and 1 ml of the RB solution were added. The solution was made up with water to about 20 ml and its pH was adjusted to 2.2 ± 0.2 using an H_2SO_4 or NaOH solution. Then a 5-ml portion of cyclohexane was added, and the funnel was shaken for 1 min. After separation of the phases, they were both removed, leaving the precipitate accumulated on the wall of the funnel.

Spectrophotometric determination of vanadium. The isolated precipitate was washed by shaking it with 5 ml of hexane and 2 ml of water for 30 s. Then both liquid phases were discarded and the precipitate off the wall was dissolved in acetone. The solution was transferred into a 10-ml calibrated flask, acidified with 0.1 ml of 0.1 M H_2SO_4 and diluted to the mark with acetone. The absorbance was measured at 555 nm against the blank prepared in the same way.

The calibration graph was obtained by applying the above procedure to solutions containing initially 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 μg vanadium.

Results and Discussion

Choice of the system

Preliminary investigations aimed at finding a system: vanadium(IV or V)-catechol derivative-basic dye-solvent, which would allow a quantitative flotation of vanadium. Catechol, tetrabromocatechol (TBC) and DNC were tested. It was found that both V(IV) and V(V) react with catechol and DNC but not with TBC. In an acidic (pH 1–3) medium, vanadium(V) forms a yellow complex ($\lambda_{\text{max}}=428 \text{ nm}$) with DNC. It proved to be more stable than the complex formed with catechol and therefore it was chosen for further investigations.

The following basic dyes were tested as cationic partners: Rhodamine B and Rhodamine 6G (xanthene dyes), Crystal Violet, Brilliant Green, Malachite Green and Methyl Violet (triphenylmethane dyes), Methylene Blue and Azur II (thiazine dyes), Nile Blue A, Capri Blue, Meldola Blue (oxazine dyes), Bindschedler's Green (indamine dye). A possibility of the flotation of V-DNC-basic dye ion-associates from various media ranging from pH 0 to pH 4 (HCl or H_2SO_4) by several weakly polar organic solvents was investigated.

It was found that only pentavalent vanadium-DNC complex forms ion-associates. They are formed with all the basic dyes examined (apart from Methylene Blue) and are either extracted into the organic phase (benzene, toluene, chloroform) or floated (cyclohexane, hexane, diisopropyl and petroleum ethers). Quantitative recoveries of vanadium were obtained only in two systems: V-DNC-Brilliant Green (extraction) and V-DNC-xanthene dye (flotation). The most promising (giving the highest sensitivity and the greatest preconcentration factor) was the system: V(V)-DNC-RB-cyclohexane; it was studied further in detail.

Flotation of vanadium compound

Choice of optimum parameters. The aim of the optimization was to find the conditions for a quantitative isolation of vanadium. The acidity range tested was pH 1–4. Both the DNC and the RB concentrations were varied from $1 \times 10^{-5} \text{ M}$ to $1 \times 10^{-4} \text{ M}$. The optimal parameter values obtained from the experiments were: pH 2–3, $[\text{DNC}]=(3-4) \times 10^{-5} \text{ M}$, $[\text{RB}]=(2-3) \times 10^{-5} \text{ M}$. Shaking 20 ml of the aqueous phase with 5 ml of cyclohexane for 45 s is sufficient to get a quantitative isolation of vanadium.

Effect of pH. The effect of the initial acidity of the aqueous phase on the percent of the vanadium compound flotation, assuming other parameters optimal, is shown in Fig. 1. The acidity of the test solution can be adjusted to pH 2–2.5 without the use of a buffer. To obtain the data in Figs. 1–3, vanadium was determined both in the precipitate after its mineralization and in the aqueous phase after flotation by the developed flotation-spectrophotometric method. The total of vanadium found was $100 \pm 3\%$.

Effect of the DNC and RB concentration. Figure 2 shows that at least 10-fold molar excess of DNC (with respect to vanadium is necessary, so the optimum concentration of DNC is $3.5 \times 10^{-5} \text{ M}$. The excess of the dye required is slightly lower, its optimum concentra-

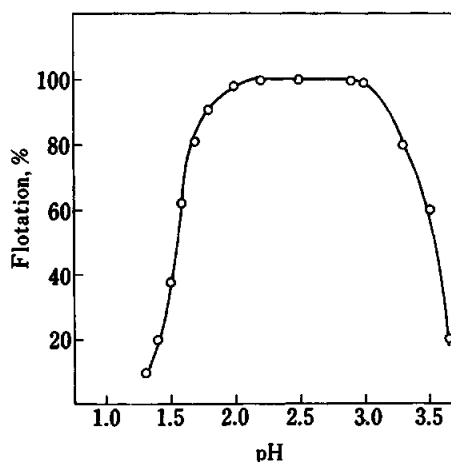


Fig. 1 Effect of pH on the percent of flotation of the vanadium compound. $[\text{DNC}]=3.5 \times 10^{-5}$, $[\text{RB}]=2.5 \times 10^{-5} \text{ M}$.

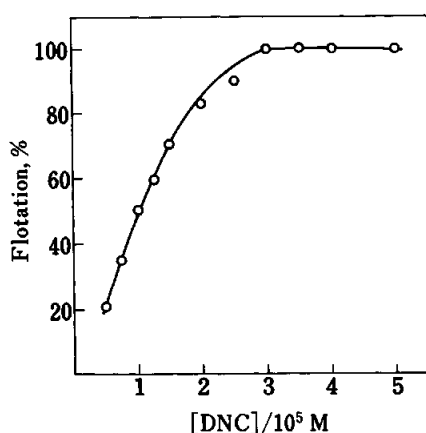


Fig. 2 Effect of the DNC concentration on the percent of flotation of the vanadium compound. pH=2.2, [RB]= 2.5×10^{-5} M.

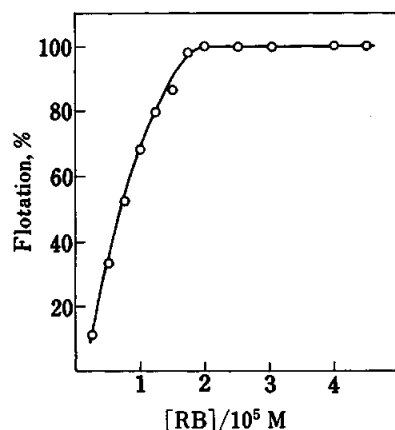


Fig. 3 Effect of the Rhodamine B concentration on the percent of flotation of the vanadium compound. pH=2.2, [DNC]= 3.5×10^{-5} M.

tion is 2.5×10^{-5} M (Fig. 3).

Effect of the ethanol concentration. The presence of ethanol results from the use of ethanolic or ethanol-aqueous solutions of DNC. Up to 3% of ethanol in the aqueous phase can be tolerated. A higher concentration of ethanol leads to a lower flotation yield.

The precipitate easily dissolves in polar solvents and vanadium can be determined in the obtained solution by any instrumental technique, e.g. electrothermal AAS or INAA. However, owing to the intense colour of the solution, the spectrophotometric determination of vanadium leads to an equally sensitive but much simpler method.

Conditions for the determination of vanadium

Although a direct spectrophotometric determination of vanadium (by measuring the absorbance of the coloured solution) is possible, it is hampered by a high blank value (about 0.20). This occurs because, under

the above conditions, the flotation of the vanadium compound is accompanied by the flotation of the salt of the dye with DNC. The latter, however, can easily be washed out.

Optimization of washing conditions. A good washing agent should completely dissolve the salt of the dye, while at the same time it should not decompose the vanadium compound. Washing with water fulfilled these requirements, but the precipitate lost its adherence to the wall of the separating funnel. To avoid this, washing in a two-phase system: water-nonpolar solvent (mentioned above) was attempted. The best results were obtained using the system: water-hexane. The optimum parameters found were: pH of the aqueous phase 5-7, shaking time 30 s, and the ratio of water to hexane 2.5:1.

The loss of vanadium from the compound during washing under the chosen conditions is small (about 5%) and the precipitate obtained is practically free of the salts of the dye both with DNC and with sulphate. The blank is low and equals to 0.05 ± 0.004 .

Dissolution of the vanadium compound. Various water-miscible polar solvents were tried for dissolving the vanadium compound: methanol, ethanol, acetone and dimethylformamide. Figure 4a shows that the shape of the absorption spectrum of the resulting solution strongly depends on the solvent used. This fact may be caused either by the presence of the dye in different forms or by only a partial decomposition of the compound in some solvents. In neutral solutions, Rhodamine B exists in two forms which remain in equilibrium:¹ the colourless lactone RB⁰ and the coloured zwitter-ion RB⁺. In order to attain the maximum sensitivity of the method it is necessary to shift the equilibrium towards the latter form; this can be achieved by acidifying the solution obtained. Absorption spectra of the solutions acidified with a few drops of 0.1 M H₂SO₄ are shown in Fig. 4b. It can be seen now that the shape of the spectra is practically independent of the solvent and each of the solvents tested can be used for the dissolution of the vanadium compound. Acetone was chosen for further use. The absorbances of the vanadium compound solutions in this solvent were constant at least for 24 h.

Composition of the vanadium compound

The molar ratio of vanadium to Rhodamine B in the separated and washed compound was established by comparing the absorbances of acetic solutions of the precipitates from a known amount of vanadium with those of the acetic solutions containing the dye in the same amount. The molar ratio V:RB found was 1:2. This result was confirmed by the Bent and French method¹⁰ (curve 2 in Fig. 5), and by the Job method.

The molar ratio of vanadium to DNC in the floated and washed compound was investigated by means of both the Bent and French logarithmic method and that of Job. Curve 1 in Fig. 5 clearly shows that the V:DNC molar ratio is 1:2.

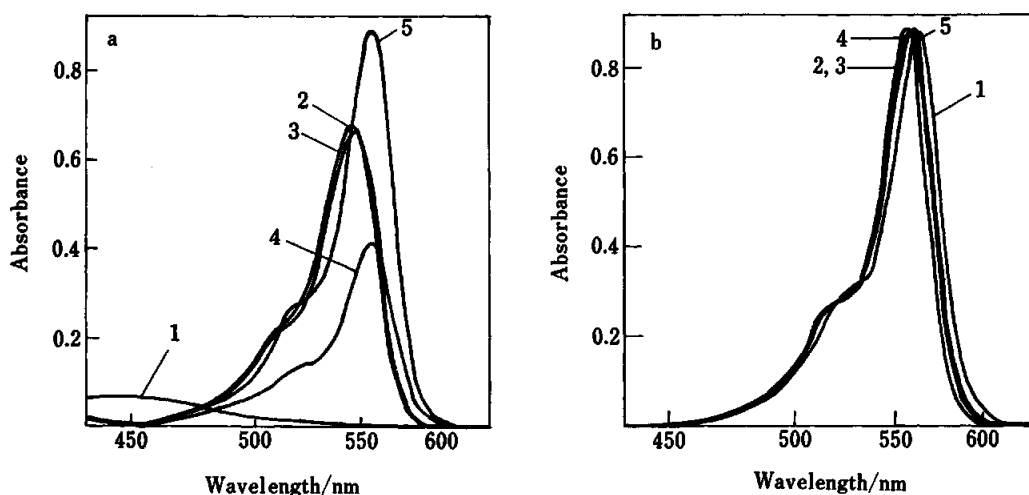


Fig. 4 Absorption spectra of the vanadium compound solutions in: (1) DMF, (2) methanol, (3) ethanol, (4) acetone. Curve (5) aqueous solution of Rhodamine B, $[V]=5 \times 10^{-6}$; $[DNC]=3.5 \times 10^{-5}$; $[RB]=2.5 \times 10^{-5}$ M; a) before acidifying; b) after acidifying.

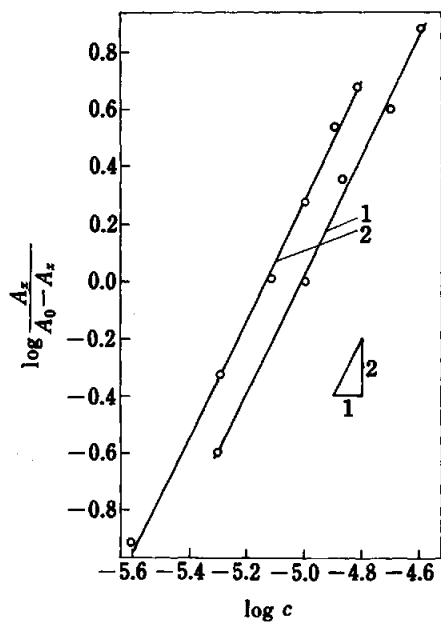


Fig. 5 Estimation of the molar ratios by the Bent and French's method. Curve (1) DNC:V; (2) RB:V. c , reagent (DNC or RB) concentration; A_x , absorbance corresponding to the reagent concentration c ; A_0 , maximal absorbance.

Attempts were made to determine the cationic form of vanadium(V) in the floated compound. In the discussed pH range, VO^{3+} , $VO(OH)^{2+}$ and $VO(OH)_2^+$ can be present.¹¹ Thus, the unknown form of the vanadium(V) cation can be denoted by $VO(OH)_i^{(3-i)+}$; $i=0, 1$ or 2 .

Taking into account the molar ratios of the reagents in the floated compound, the reaction of its formation

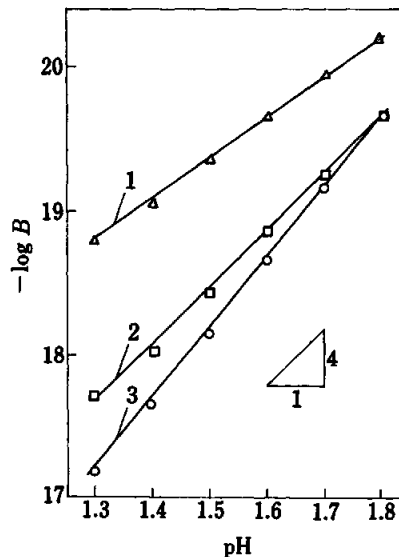
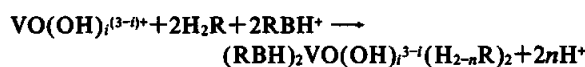


Fig. 6 Estimation of the form of the vanadium cation. Plot of $-\log B$ vs. pH calculated for: 1) VO^{3+} , $i=0$; 2) $VO(OH)^{2+}$, $i=1$; 3) $VO(OH)_2^+$, $i=2$. $[V]=5 \times 10^{-6}$; $[DNC]=3.5 \times 10^{-5}$; $[RB]=2.5 \times 10^{-5}$ M; B is defined by Eq. (3) in text.

can be written as follows:



where H_2R denotes DNC. The equilibrium constant equals:

$$K = \frac{c_k [H^+]^{2n}}{[VO(OH)_i^{(3-i)+}] [H_2R]^2 [RBH^+]^2} \quad (1)$$

where $c_k = [(\text{RBH})_2\text{VO}(\text{OH})_i]^{3-i}(\text{H}_2\text{-}n\text{R})_2]$

Hence:

$$-\log B = -pK + 2npH \quad (2)$$

where

$$B = \frac{[\text{VO}(\text{OH})_i]^{3-i}[\text{H}_2\text{R}]^2[\text{RBH}^+]^2}{c_k} \quad (3)$$

The dependence $-\log B = f(\text{pH})$ was investigated further for all possible vanadium(V) cation forms.

As the solutions studied obey Beer's law in the investigated range, the following expression holds for c_k :

$$c_k = c_v \frac{A}{A_{\text{max}}} \quad (4)$$

where c_v denotes total vanadium concentration and A the absorbance corresponding to the metal concentration c_k .

The concentration of vanadium not bound in the ion-associate- c_n equals:

$$c_n = c_v - c_k = [\text{VO}^{3+}] + [\text{VO}(\text{OH})^{2+}] + [\text{VO}(\text{OH})_2^+] + [\text{VO}(\text{OH})_3]$$

The concentration of each vanadium form can be expressed by c_n and the hydrolysis constants K_{1h} , K_{2h} and K_{3h} . Then:

$$[\text{VO}^{3+}] = \frac{c_v - c_k}{G([\text{H}^+])} \quad \text{when } i = 0 \quad (5a)$$

$$[\text{VO}(\text{OH})^{2+}] = \frac{c_v - c_k}{G([\text{H}^+])} \cdot \frac{K_{1h}}{[\text{H}^+]} \quad \text{when } i = 1 \quad (5b)$$

$$[\text{VO}(\text{OH})_2^+] = \frac{c_v - c_k}{G([\text{H}^+])} \cdot \frac{K_{1h}K_{2h}}{[\text{H}^+]^2} \quad \text{when } i = 2 \quad (5c)$$

where:

$$G([\text{H}^+]) = 1 + \frac{K_{1h}}{[\text{H}^+]} + \frac{K_{1h}K_{2h}}{[\text{H}^+]^2} + \frac{K_{1h}K_{2h}K_{3h}}{[\text{H}^+]^3}$$

The concentration of DNC not bound to vanadium can be expressed as:

$$c_{\text{H}_2\text{R}} - 2c_k = [\text{H}_2\text{R}] \left[1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1K_2}{[\text{H}^+]^2} \right]$$

where K_1 and K_2 are the dissociation constants of DNC. Hence:

$$[\text{H}_2\text{R}] = \frac{c_{\text{H}_2\text{R}} - 2c_k}{1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1K_2}{[\text{H}^+]^2}} \quad (6)$$

The concentration of RB not bound in the compound equals:

$$c_{\text{RB}} - 2c_k = [\text{R}^+] + [\text{RH}^+] + [\text{RH}_2^{2+}] + [\text{RH}_3^{3+}]$$

The concentration of RBH_3^{3+} at $\text{pH} > 0$ and that of dimeric Rhodamine B species in such diluted solutions are negligible. Hence:

$$[\text{RH}^+] = \frac{c_{\text{RB}} - 2c_k}{1 + \frac{[\text{H}^+]}{K_{R1}} + \frac{K_{R2}}{[\text{H}^+]}} \quad (7)$$

where K_{R1} and K_{R2} are the protonation constants of R^+ .

On substituting (4)–(7) into (3), B values for each vanadium cation form are obtained. The constants K_{1h} , K_{2h} , K_{3h} ¹¹, K_1 , K_2 ¹², K_{R1} ¹, are known and the constant K_{R2} was determined spectrophotometrically and equals 1.31. The dependence $-\log B = f(\text{pH})$ is a straight line with a slope equal to an even number (n should be an integer) only for $i=1$, which corresponds to the cation $\text{VO}(\text{OH})^{2+}$ (Fig. 6).

Hence, it is reasonable to assume that the cation $\text{VO}(\text{OH})^{2+}$ forms with DNC a chelate capable of associating with two Rhodamine B cations. The vanadium compound may be postulated to have the formula shown in Fig. 7.

Characteristics of the method

The calibration graph obtained under the optimum conditions, as outlined above, obeys Beer's law in the range 0.003–0.3 $\mu\text{g}/\text{ml}$. The molar absorptivity is $2.1 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 555 nm and the specific absorptivity ($a = \epsilon / \text{atomic mass} \times 1000$) is 4.12. The vanadium detection limit (3 σ of the blank value) is 3 ng/ml. Thus, the proposed method is the most sensitive spectrophotometric method known for vanadium and is 40 times as sensitive as the commonly used BPHA and 8-hydroxyquinoline methods and 6 times more sensitive as the PAR method.¹³

The statistical evaluation of the results of the determination of vanadium in standard solutions (Table 1) shows the precision and the accuracy of the developed method.

The effects of many anions and cations were examined. Fluoride, chloride, bromide, iodide, nitrate, perchlorate, acetate, tartrate and citrate at up to 10000

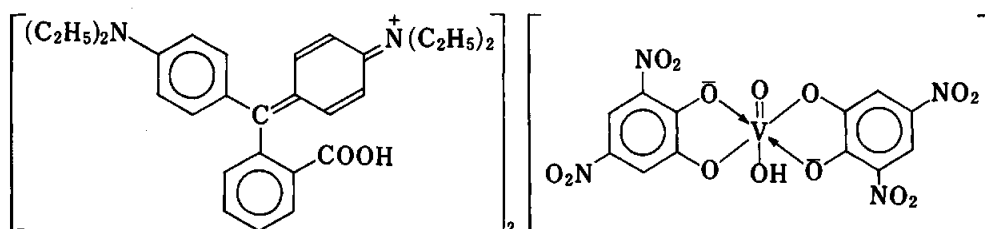


Fig. 7 The vanadium compounds postulated.

molar excess do not interfere (give an error of less than 5%). Thiocyanate up to 1000-fold and oxalate up to 10-fold molar excess can be tolerated. EDTA interferes by masking vanadium. The most interfering cations are Ti, Zr, Mo and W. An interference from Bi, Sb(III), Fe(III) or Ga present in equimolar amounts was also observed. Al and Cr(III) can be tolerated up to 5-fold molar excess. Mn, Ni, Zn, Cd, Cu as well as alkali and alkaline earth metals give an error of less than 5% even at 10000-fold molar excess.

To avoid such interferences, a separation step is necessary before determining vanadium in real samples. The method becomes specific for vanadium after its preliminary extraction with BPHA from a medium of 5 M HCl and 2 M HF.¹⁴

Determination of vanadium in vegetables

The described method was applied to the determination of vanadium in carrot, spinach, kale and parsley. The vegetables were rinsed carefully with tap water and then with distilled water. They were cut with a stainless steel knife into small pieces and dried at 110°C. The dried material was ground. Samples of 2 g of dry carrot, spinach, kale and 0.2 g of parsley were weighed

and ashed in quartz crucibles at 550°C during 24 h. The white residues were dissolved in 5 ml of hot 2 M HCl and the solution was transferred into a polypropylene separating funnel. Then, 4 ml of conc. HCl, 1 ml of conc. HF and 1 ml of 0.1% (NH₄)₂S₂O₈ solution were added and the funnel was shaken twice with 5-ml portions of the BPHA solution for 1 min each. The combined chloroform extracts were washed by shaking them with a 5 ml portion of 5 M HCl, then evaporated to dryness on the water bath and the residue was ashed at about 500°C for 15 min. The cooled residue was dissolved in 5 ml of 0.1 M NaOH solution and the determination of vanadium was continued as described in the Procedure section.

To check on the precision and accuracy, the proposed method was applied to the analysis of synthetic samples (I-III) containing vanadium at three concentration levels as well as Mo, W, Nb, Zr, Ti, Bi, Ga, In, Sb, Sn, Fe, Cu, Ni and Cd (100 µg of each element) and 500-fold mass excesses of Ba, Mg, Ca and Sr. The results of the determination of vanadium in three synthetic samples, as well as in the above enumerated vegetables, are shown in Table 2. The recoveries of the known amounts of vanadium added were 94-96% due to some losses during the preliminary separation step. Thus the results of the vanadium content in real samples should be corrected by increasing them by 5±1%.

The accuracy of the method was verified by the analysis of NBS SRM 1570 Spinach. The vanadium content found was 1.12±0.09 ppm (5 determinations). This result is well comparable with this (1.09 ppm) value obtained by NAA.¹⁵

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Table 1 Statistical evaluation of the results of the determination of vanadium in standard solutions

Vanadium Added/ µg	Found/ µg	Standard deviation ^a , µg	%	Confidence limits (α=0.95)
1.00	1.01	0.039	3.9	1.01±0.04
2.00	1.98	0.038	1.9	1.98±0.04
3.00	3.00	0.044	1.5	3.00±0.05

a. For seven determinations.

Table 2 Determination of vanadium in synthetic samples (I-III) (composition given in the text) and in some vegetables

Sample	Sample weight ^a g	Vanadium			Vanadium recovery, %	Standard deviation ^c		Confidence limits (α=0.95)
		added µg	found µg	ppm ^b		µg	%	
I		1.00	0.94	0.10	94.0	0.066	7.0	0.94±0.07
II		2.00	1.91	0.20	95.5	0.073	3.8	1.91±0.07
III		3.00	2.81	0.30	94.5	0.076	2.7	2.81±0.08
Carrot	2.0	—	0.54	0.28	—	0.051	9.5	0.57±0.05 ^b
		1.50	1.97		95.3	0.094	4.8	1.97±0.09
Kale	2.0	—	0.70	0.37	—	0.055	7.8	0.74±0.05 ^b
		1.50	2.12		94.6	0.106	5.0	2.12±0.11
Spinach	2.0	—	2.41	1.27	—	0.094	3.9	2.53±0.09 ^b
		0.50	2.89		96.0	0.101	3.5	2.89±0.10
Parsley	0.2	—	1.87	9.8	—	0.093	5.0	1.96±0.09 ^b
		0.50	2.34		94.0	0.096	4.1	2.34±0.10

a. Dried at 110°C; b. Corrected values (see in text); c. For seven determinations.

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