Chem. Anal. (Warsaw), **51**, 221 (2006)

Extractive-Spectrophotometric Determination of Vanadium(IV/V) in Catalysts Using 4-(2-Pyridylazo)-resorcinol and Tetrazolium Violet

by Kiril Gavazov*[1], Vanya Lekova[1], Georgi Patronov[1] and Murat Tũrkyilmaz[2]

[1] *Faculty of Chemistry, University of Plovdiv, 24 Tsar Assen Str., 4000 Plovdiv – Bulgaria*
[2] *Faculty of Science, Chemistry Department, University of Trakya, 22030 Edirne – Turkey*

Keywords: Vanadium(IV/V); Speciation analysis; 4-(2-pyridylazo)-resorcinol; Tetrazol violet; Extraction-spectrophotometry; Catalysts

An extractive-spectrophotometric method for determination of V(V) and V(IV) has been developed. V(V) was converted to ternary ion-associate complex with 4-(2-pyridylazo)-resorcinol and tetrazolium violet. In the presence of diaminocyclohexanetetraacetic acid and NH_4F as the masking agents determination of V(V) was highly selective, and V(IV) was among the masked ions. Due to this fact V(IV) could be determined indirectly from the difference in the absorbance measured in the presence and absence of the oxidizing agent, which oxidised V(IV) to V(V). The factors influencing determination of V(V) in the presence of large excess of V(IV) have been investigated. The method was applied to the determination of V(IV/V) in catalysts used for oxidation of SO_2 to SO_3. The precision and accuracy were satisfactory (R.S.D $\leq$ 1.9%). Detection limit of V(V) was 3.3 ng mL^{-1}. Beer's law was obeyed up to V(V) concentration of 1.45 μg mL^{-1} in dichloroethane extract. The corresponding molar absorptivity coefficient was 3.05×10^4 L mol^{-1} cm^{-1}.

Opracowano ekstrakcyjną, spektrofotometryczną metodę oznaczania V(V) i V(IV). V(V) był przekształcony w trzeciorzędowy kompleks z 4-(2-pirydylazo)rezorcinolem i fioletem tetrazoliowym. W obecności kwasu diaminocykloheksanotetraoctowego i NH_4F jako czynnika maskującego oznaczanie V(V) okazało się wysoce selektywne. V(IV) był maskowany, w związku z tym mógł być oznaczany pośrednio z różnicy między absorbancją roztworów zawierających i niezawierających utleniacza. Badano czynniki wpływające na oznaczanie V(V) w obecności dużego nadmiaru V(IV). Opracowaną metodę zastosowano do oznaczania V(IV/V) w katalizatorach użytych do utleniania SO_2 do SO_3. Precyzja i dokładność były zadowalające (względne odchylenie standardowe < 1,9%). Granica wykrywalności wynosiła

---

[*] Corresponding author. E-mail: kgavazov@abv.bg

3,3 ng mL^{-1}. Prawo Beer'a było zachowane do stężenia 1,45 μg L^{-1} w ekstraktach dichloroetanowych. Molowy współczynnik absorpcji wynosił 3,05 × 10^4 L mol^{-1} cm^{-1}.

V_2O_5 immobilised on the silica support is the most popular catalyst used in some gas-phase processes, in particular in the oxidation of SO_2 to SO_3 during production of H_2SO_4. Although this catalyst is much more resistive to poisons than the platinum one, it slowly loses its activity and must be partially or fully replaced after a certain time. The reasons for the loss of catalytic activity are: conversion of V_2O_5 to inactive V(IV)-form, and decrease of vanadium content due to formation of volatile compounds with admixtures containing either arsenic or fluorine.

Several methods for determination of vanadium in catalyst have been employed, *e.g.* spectrophotometry [1–6], titrimetric analysis [1], amperometry [7], chromatography [8, 9], capillary zone electrophoresis [10], AAS [1, 11, 12], ESR [13], and NAA [14]. Spectrophotometric methods are simple and low-cost, but most of them are not enough selective [4, 6] and sensitive [3–5], or they are unsuitable for speciation analysis [6]. This paper aims at the development of a sensitive, selective, and rapid extractive-spectrophotometric method for determination of V(V) and V(IV). V(V) was converted to the ternary ion-associate complex with 4-(2-pyridylazo)-resorcinol (PAR) and tetrazolium violet (TV), which was described in a previous paper [15]. Similar complexes of V(V), PAR, and other tetrazolium salts have been applied for determination of vanadium in various environmental and industrial samples [16–18].

EXPERIMENTAL

Reagents and apparatus

NH_4VO_3 (Apolda, puriss), 1 × 10^{-4} mol L^{-1} aqueous solution. $VOSO_4.5H_2O$ (Fluka, purum), 5 × 10^{-2} mol L^{-1} aqueous solution. Concentration of V(IV) species was checked by titration with standard $KMnO_4$ solution. Working solutions of $VOSO_4$ were prepared by the appropriate dilution of 5 × 10^{-2} mol L^{-1} aqueous solution directly before use.

4-(2-Pyridylazo)-resorcinol disodium salt (PAR) (Sigma), 2 × 10^{-3} mol L^{-1} aqueous solution. Tetrazolium violet (TV) (Loba Chemie), 3.0 × 10^{-3} mol L^{-1} aqueous solution.

1,2-Diamino-cyclohexane-N,N,N',N'-tetraacetic acid (DCTA) (Fluka, purum), 0.125 mol L^{-1} solution was prepared as follows: 21.65 g of CDTA were added to the hot solution containing 7.5 g of KOH in *ca* 50 mL of water. The resulting solution was transferred to a 500 mL-in-volume calibrated flask, diluted to the mark with water, and left to equilibrate for two weeks.

NH_4F (Reachim, purum), 3.5 mol L^{-1} aqueous solution. $NaBrO_3$ (Carlo Erba), 0.15 mol L^{-1} aqueous solution. Acetate buffer solution, pH 5.8; it was prepared by mixing 0.1 mol L^{-1} solutions of CH_3COOH and CH_3COONa. 1,2-Dichloroethane, redistilled.

Specol spectrophotometer (Carl Zeiss, Germany) equipped with 1.0 cm-in-width cells.

Procedure

50–500 mg of the powdered catalyst sample was placed in a 100 mL-in-volume beaker. 25 mL of H_3PO_4 (1:1) were added and the contents were heated for about 30–40 min in inert CO_2 atmosphere. The resulting mixture was diluted to 100 mL and filtered through a filter paper at a medium speed. The precipitate of silicic acid was carefully washed. The filtrate and the liquid fraction obtained after washing were transferred into a 1000 mL volumetric flask and the contents were diluted with distilled water up to the mark.

Determination of V(V)

An aliquot of the obtained solution corresponding to 2.5–14.5 μg was transferred to a 125-mL separatory funnel. 2 mL of DCTA solution were added and the contents were stirred well. pH was adjusted to 4.5–5.5 by adding dropwise 5% ammonia solution. Then, 5 mL of acetate buffer solution, 1 mL of PAR solution, 5 mL of NH_4F solution, and 3 mL of TV solution were added. The volume was made up to 20 mL with distilled water, and after that 10 mL of 1,2-dichloroetane were added. The contents were shaken well for 2 min and a portion of organic layer was transferred through a filter paper into 1-cm-in-width cell. Absorbance of red extract was measured at 555 nm against a similarly prepared reagent blank. The content of V(V) was determined from the calibration plot.

Determination of total vanadium and V(IV)

For determination of total vanadium, 1 mL of $NaBrO_3$ solution was added to the aliquot of the catalyst sample (in order to oxidise V(IV) to V(V)) and the above procedure was applied. The content of V(IV) was determined from the difference between the total vanadium content and V(V) content.

RESULTS AND DISCUSSION

Beer's law was obeyed up to V(V) concentration of 1.45 μg mL^{-1} in dichloroethane extract. The obtained regression equation was: $A_{V(V)} = 0.5990 \times C + 0.0006$, $r = 0.999$, where C is V(V) concentration expressed in μg mL^{-1}. Detection limit was defined as $3s_B/b$ (where s_B is the standard deviation of ten measurements of the blank sample, and b is the slope of the calibration plot) and equaled 3.3 ng mL^{-1}. Relative standard deviation for 10 replicate measurements at a level of 0.50–1.00 μg mL^{-1} was in the range 1.7–1.9%. Apparent molar absorptivity ($\varepsilon = 3.05 \times 10^4$ L mol^{-1} cm^{-1}) was *ca* 24% lower than molar absorptivity measured in the absence of masking agents, and depended mainly on the PAR-to-DCTA ratio. This ratio was chosen as to provide optimum sensitivity and selectivity. It has been established that DCTA masks the most of foreign ions, while NH_4F is essential for eliminating the influence of V(IV) (Fig. 1). In the presence of a large amount of NH_4F, V(V)–PAR–TV complex was instantly formed, the phases were clearly separated, as well as repeatability of the measurements was satisfactory. The colour was developed immediately, so that the possibility of V(IV) oxidation by air oxygen at the applied pH was limited. It is known that at pH > 2 V(IV) is slowly transformed to V(V); at higher pH the oxidation process is even faster [19]. In PAR-DCTA methods used for determination of vanadium in the absence of fluoride, either 5–45 min are necessary for colour development, or pH should be above 7.0. In both cases V(IV)-to-V(V) tolerable ratio is not high and the possibilities of speciation analysis are limited.

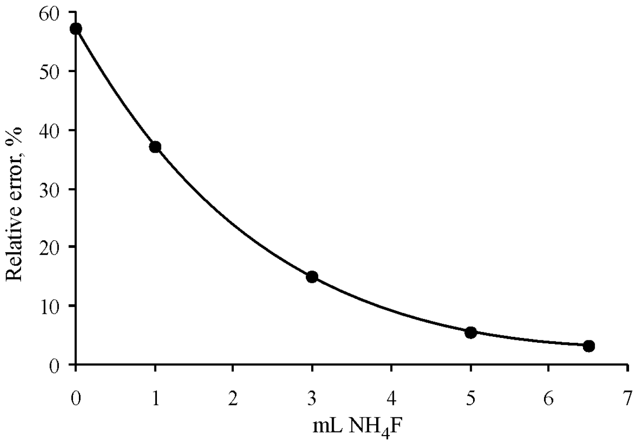

Figure 1. The relationship between the added volume of NH_4F solution (0.35 mol L^{-1}) and the relative error of determination of 10 μg of V(V) in the presence of 35-fold excess of V(IV)

The relationship between the V(IV)-to-V(V) ratio and recovery of V(V) in the proposed method is presented in Figure 2.

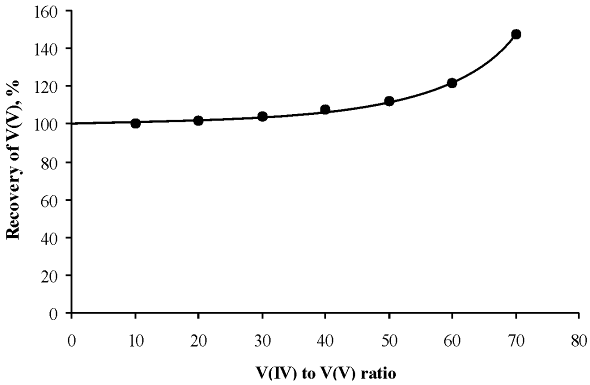

Figure 2. The relationship between the V(IV)-to-V(V) ratio and recovery of 6 μg of V(V)

It has been found that 30–40-fold excess of V(IV) does not interfere in the determination of V(V) at pH in the range 5.5–6.5. If the content of NH_4F exceeds the recommended level (5 mL), sensitivity of determination decreases.

The order of mixing of the reagents was very importance. NH_4F should not be introduced in strongly acidic medium. NH_4OH and buffer should be introduced after DCTA. The positive error caused by V(IV) was slightly smaller (up to 2%) when NH_4F was introduced after PAR.

The proposed method was applied for determination of V(IV/V) in the used catalysts of SO_2 oxidation (Tab. 1). The results were in good agreement with those obtained by other methods.

Table 1. Results of determination of vanadium in the used catalysts (n = 8, P = 95%)

Sample		Vanadium found (%)			
		Proposed method	PAR-INT [18]	NC-NTC [20]	ICP-OES
Monsanto LP–110	V_{tot}	2.86±0.02	2.87±0.02	2.87±0.02	2.86±0.01
	V(V)	2.45±0.02	2.45±0.01	–	–
	V(IV)	0.41±0.04	0.42±0.03	–	–
Monsanto LP–120	V_{tot}	2.59±0.03	2.59±0.02	2.59±0.03	–
	V(V)	2.30±0.02	2.31±0.02	–	–
	V(IV)	0.29±0.04	0.28±0.04	–	–
Bitterfeld (sample 1)	V_{tot}	2.50±0.02	2.49±0.02	2.51±0.03	–
	V(V)	1.77±0.02	1.77±0.02	–	–
	V(IV)	0.73±0.03	0.72±0.03	–	–
Bitterfeld (sample 2)	V_{tot}	2.08±0.02	2.09±0.02	2.10±0.02	–
	V(V)	1.27±0.02	1.27±0.02	–	–
	V(IV)	0.81±0.04	0.82±0.03	–	–

Other components (%): SiO_2 (43.26–61.30), K (8.72–12.15), Na (0.48–2.78), S (7.61–8.85), Fe (0.27–2.31), Al (0.5–1.24), Ca (0.14–1.37), Mg (0.06–0.10), Cu (0.012–0.96), Zn (0.010–0.015), Pb (0.0075–0.31), Cd (0.0002–0.0034), Co (0.0007–0.0022), Ni (0.0046–0.048), Mn (0.007–0.13), Sb (up to 0.36), As (up to 0.0095), Cr (0.0048–0.028), Hg (up to 0.001), Se (up to 0.001); INT – iodonitrotetrazolium chloride, NC – 4-nitrocatechol, NTC – neotetrazolium chloride.

Some authors recommend to dissolve silica-based catalysts in a mixture of HF and other mineral acid [4, 7], as vanadium is not completely dissolved in the absence of HF. At the same time they point out at the risk of losses of vanadium [3, 7] due to its ability to form volatile fluoride compounds. In order to assess advantages of different sample preparation procedures, we have dissolved the Monsanto-LP110 catalyst in various acids: H_3PO_4 (1:1), H_2SO_4 (1:1), HF + HNO_3, and *aqua regia*. The samples dissolved in H_3PO_4 and H_2SO_4 were analyzed applying the proposed method, and the samples dissolved in HF + HNO_3 and *aqua regia* are analyzed applying ICP–OES. The differences in the determined total vanadium content were statistically negligible. The determined content of V(IV) dissolved in H_2SO_4 was *ca* 5% higher than that determined in H_3PO_4. This is in agreement with the result published in reference [21] and confirms that after heating with H_2SO_4 V(V) is partially reduced to V(IV). H_3PO_4 does not change the initial oxidation state of vanadium [21]. For this reason this is the best solvent for this kind of catalysts.

Selectivity of the proposed method was investigated by determination of 10 μg of V(V) in the presence of various ions. The results are shown in Table 2. It can be concluded that the proposed method is highly selective. The tolerable V(IV)-to-V(V) ratio is higher compared to the values reported on in tungstovanado(IV) phosphoric acid method [4], chromasol KS method [22], dibromhydroxyquinoline method [23], and PAR–DCTA methods of Lombard [2], Gavazov [17] and Filik [24].

Table 2. Tolerance limits for the determination of 10 μg of V(V) (relative error: max. 3.3%)

Ion added	Tolerated amount, mg
Mg^{2+}, NH_4^+, Na^+, K^+, $H_2PO_4^-$, SO_4^{2-}, Cl^-	100
Ba^{2+}	50
Cd^{2+}	20
Zn^{2+}, Cu^{2+}, tartrate$^-$	10
Mo(VI)	7.5
Ni^{2+}, Ce(III), Br^-	5
Co^{2+}, Mn^{2+}, U(VI), NO_3^-	2.5
Cr^{3+}, Cr(VI)	1
Re(VII), Ca^{2+}	0.5
V(IV)	0.3
Fe^{3+}, Nb(V), Ti(IV)	0.2
W(VI)	0.01

Acknowledgements

The authors would like to express their gratitude to eng. Stefan Stoychev and to the Research Fund of the Plovdiv University for its financial support (Grant No 05-H-13).

REFERENCES

1. Muzgin V.N., Hamzina L.B., Zolotovin V.L. and Bezrukov I.Ya., *Analytical chemistry of vanadium*, Nauka, Moscow 1981, pp. 140, 160 (in Russian).
2. Taylor M.J.C. and Staden J.F., *Analyst*, **119**, 1263 (1994).
3. Sherbakova S.A., Mel'chakova N.V. and Peshkova V.M., *Zh. Anal. Khim*., **31**, 318 (1976).
4. Novoselova I.M. and Barkovskii V.F., *Zh. Anal. Khim.*, **32**, 1247 (1977).
5. Strautinya A.K. and Shimanskaya M.V., *Izv. AN Latv. SSR. Ser. Khim. Nauk*., **5**, 535 (1967).
6. Gavazov K. and Patronov G., *Scientific Researches of the Union of Scientists – Plovdine, Series C., Techniques and Technologies*, **5**, 290 (2005).
7. Elizarova G.L. and Kuznetsova A.S., *Zh. Anal. Khim*., **23**, 50 (1968).
8. Tsai S.J.J. and Hsu S.J., *Analyst*, **119**, 403 (1994).
9. Vicol O. and Berdan I., *Revista de Chimie*, **37**, 61 (1986).
10. Jen J.F., Wu M.H. and Yang T.C., *Anal. Chim. Acta*, **339**, 251 (1997).
11. Platteau O. and Casabiell D., *Analyst*, **119**, 1705 (1994).
12. Kowalewska Z. and Sikora Z., *Chem. Anal. (Warsaw)*, **41**, 821 (1996).
13. Stocker M., Tangstad E., Aas N. and Myrstad T., *Catalysis Letters*, **69**, 223 (2000).
14. Buenafama H.D. and Lubkowitz J.A., *Anal. Chim. Acta*, **96**, 285 (1978).
15. Gavazov K., Simeonova Zh. and Alexandrov A., *Journal of University of Chemical Technology and Metallurgy (Sofia)*, **38**, 909 (2003).
16. Morgen E.A. and Dimova L.M., *Zavod. Lab.*, **50**, 7 (1984).
17. Gavazov K., Simeonova Zh. and Alexandrov A., *Analytical Laboratory*, **7**, 127 (1998).
18. Gavazov K., Simeonova Zh., Alexandrov A., *Talanta*, **52**, 539 (2000).
19. Pyrzynska K., Wierzbiski T., *Talanta*, **64**, 823 (2004).
20. Gavazov K, Simeonova Zh. and Alexandrov A., *University of Plovdiv-Bulgaria, Scientific works-Chemistry*, **31**, 13 (2002).
21. Grigor'eva M.F. and Tsercovnictskaya I.A., *Vestnik Leningr. Univ. Ser. Fiz. Khim*., **4**, 117 (1975).
22. Gordeeva M.N., Fedorova L.N., Basargin N.N. and Yu.G. Rozovskij, *Vestnik Leningr. Univ. Ser. Fiz. Khim*., **16**, 98 (1978).
23. Tsercovnictskaya I.A., Grigor'eva M.F. and Kustova N.A., *Khimiya redkih elementov*, Leningr. Univ., Leningrad 1964, pp. 153–159 (in Russian).
24. Filik H., Berker K.I., Balkis N. and Apak R., *Anal. Chim. Acta*, **518**, 173 (2004).

Received December 2005
Accepted March 2006