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The Spectrophotometric Determination of Trace Vanadium with 3,4,5,6-Tetrachlorogallein

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Synopsis. As a solution of 3,4,5,6-tetrachlorogallein (T.Cl.gall) in a weakly acidic medium was easily decomposed by vanadium(V), a simple and sensitive spectrophotometric determination of vanadium by using the difference in absorbance at 385 nm between T.Cl.gall and T.Cl.gall-vanadium(V) solutions in the presence of hexadecylpyridinium chloride (HPC) and poly (*N*-vinylpyrrolidone) (PVP) was established. Under optimum conditions, vanadium could be determined in the range of 0—0.8 μg/10 cm^3. The apparent molar absorptivity was calculated to be 7.0×10^5 dm^3 mol^{-1} cm^{-1}, with a Sandell sensitivity of 0.00006 μg cm^{-2}, by the use of a decomposed T. Cl. gall solution in the presence of vanadium(V) at 385 nm. The recovery tests of vanadium added to prepared artificial water were examined; the results were a good agreement with the certified values (98.6—102.8%).

We have already reported[1)] the spectrophotometric determination of vanadium by using the color reaction system between vanadium and Gallein (gall) in the presence of sodium sulfite and sodium dodecyl sulfate.

On the other hand, Cabeza et al.[2,3)] have reported the methods of the determination of vanadium utilizing the oxidation reaction of pyrogallolsulfophthalein=Pyrogallol Red (PR) by vanadium(V) or bromate ions. Also, we ourselves have recognized that 3,4,5,6-tetrachlorogallein (T.Cl.gall),[4)] in the presence of hexadecylpyridinium chloride (HPC) and poly (*N*-vinylpyrrolidone) (PVP) as surfactants in a weakly acidic medium, was readily decomposed by the coexistence of vanadium(V) (=oxidation of T.Cl.gall), and that the difference in absorbance between the T.Cl.gall solution (Solution A) and the T.Cl.gall-vanadium(V) solution (Solution B) was proportional to the concentration of vanadium.

This paper describes a simple and sensitive spectrophotometric determination of micro amounts of vanadium using the oxidation and decomposition of a T. Cl. gall solution by the catalytic reaction of trace amounts of vanadium(V) in the presence of HPC and PVP.

Experimental

Apparatus and Reagents. The absorption spectra and absorbance were measured by the use of Shimadzu model UV-200 and Hitachi model 150-20 recording spectrophotometers, with 1.0-cm silica cells. Hitachi-Horiba model M-5 and F-7AD glass electrode pH meters were employed for the pH measurements.

A 1.0×10^{-3} mol dm^{-3} T. Cl. gall solution was prepared by dissolving T.Cl.gall[4)] in methanol according to the method of a previous report.[5)] 1.0×10^{-2} mol dm^{-3} HPC and 1.0% PVP (K-90) solutions were prepared by dissolving HPC and PVP respectively in water. A 5.0×10^{-4} mol dm^{-3} vanadium(V) solution was prepared according to the method of a previous report.[1)] A 2.0×10^{-1} mol dm^{-3} sodium acetate-acetic acid buffer solution (Walpole buffer, pH 4.5) was used for the pH adjustments. The other reagents were of an analytical reagent grade, and twice-distilled or deionized water was used.

Standard Procedure. A solution containing up to 0.8 μg of vanadium(V) was placed in a 10-cm^3 volumetric flask. To this solution, 2.0 cm^3 of the buffer solution (pH 4.5), 1.5 cm^3 of a 1.0×10^{-2} mol dm^{-3} HPC solution, 1.0 cm^3 of a 1.0% PVP solution, and 1.4 cm^3 of a 1.0×10^{-3} mol dm^{-3} T.Cl.gall solution were added. This mixture was diluted to the mark with water and then heated at 60 °C for 30 min (Solution B). After the solution had then been cooled in water for 10 min, the absorbance of Solution B at 385 nm was measured against Solution A. The concentration of vanadium was determined by using a calibration curve.

Results and Discussion

Absorption Spectra and Analytical Wavelength. The T.Cl.gall solution, including vanadium as vanadium(V) in a weakly acidic medium (pH 4.5) (Solution B), was unstable and was gradually decomposed in proportion to the concentration of vanadium(V). Moreover, the use of T.Cl.gall was superior to the use of gall in terms of sensitivity and reproducibility. As is shown in Fig. 1, a large differences in absorbance between Solutions A and B were found at around 555 nm and 385 nm. The absorbance at 555 nm was unsa-

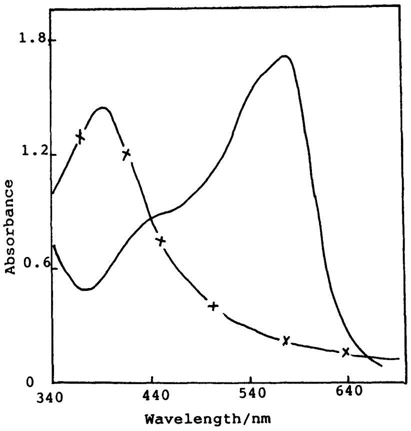

Fig. 1 Absorption spectra of T.Cl.gall and T.Cl.gall-vanadium(V) solutions in the presence of HPC and PVP at pH 4.5.

T.Cl.gall: 1.4×10^{-4} mol dm^{-3}; Vanadium(V): 1.0×10^{-6} mol dm^{-3}; HPC: 1.5×10^{-3} mol dm^{-3}; PVP: 1.0 cm^3 of 1.0% PVP solution/10 cm^3; Reference: Water.

—: T.Cl.gall solution; —×—: T.Cl.gall-vandium(V) solution.

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tisfactory in terms of reproducibility and the effect of foreign ions. On the other hand, the use of the difference in absorbance at 385 nm between Solutions A and B was satisfactory in reproducibility and the influence of foreign ions.

Consequently, the later measurements were carried out by measuring the absorbance of Solution B at 385 nm against Solution A.

Effect of pH. The maximum and constant absorbance was obtained in the pH range from 3.7 to 4.8 by using 2.0 cm^3 of a 2.0×10^{-1} $mol\,dm^{-3}$ sodium acetate-acetic acid buffer solution (Walpole buffer) for the pH adjustments. Subsequent measurements were carried out at pH 4.5 for the determination of vanadium.

Effects of Surfactants. Among the various surfactants tested (HPC, hexadecyltrimethylammonium chloride (HTAC), and Zephiramine (Zp) as cationic surfactants, and PVP and poly (vinyl alcohol) (PVA) as nonionic surfactants), the combination of HPC and PVP had the effect of remarkably increasing the stabilization, reproducibility, and sensitivity. The effects of the concentrations of HPC and PVP were also studied. A maximum and almost constant absorbance was observed upon the addition of 0.5—2.0 cm^3 of a 1.0×10^{-2} $mol\,dm^{-3}$ HPC solution, together with 1.0 cm^3 of a 1.0% PVP solution, to the final volume of 10 cm^3. Thus, all further measurements were made with 1.5×10^{-3} $mol\,dm^{-3}$ HPC and 0.1% PVP as the final concentrations.

Effect of T.Cl.gall Concentration. The effect of the T.Cl.gall concentration on the standard procedure was examined by measuring the absorbance at 385 nm for 5.0×10^{-6} $mol\,dm^{-3}$ vanadium(V). The absorbance at 385 nm was constant when the volume of the 1.0×10^{-3} $mol\,dm^{-3}$ T.Cl.gall solution was varied between 1.25—1.5 cm^3 in the final 10 cm^3. Hence, 1.4 cm^3 of the 1.0×10^{-3} $mol\,dm^{-3}$ T.Cl.gall solution was chosen for the determination of vanadium.

Effects of Temperature and Time. The absorbance at 385 nm of Solution B against Solution A was instantaneously unconstant at room temperature (15—25 °C) and was gradually decomposed. The effect of the temperature was examined by heating Solutions A and B at various temperatures (10, 20, 40, 60, and 80 °C). The most favorable results were obtained by heating Solutions A and B at 60 °C for 20—30 min and by then cooling these solutions to room temperature (15—25 °C) in water for 10 min. The solution B decomposed by the standard procedure was relatively stable, but further standing (for more than 60 min) caused a gradual and slight decrease in the absorbance.

Calibration Curve, Sensitivity, and Reproducibility. A good linear relationship was observed over the range of 0—0.8 μg of vanadium in the final volume of 10 cm^3 at 385 nm against a reagent blank (Solution A). The sensitivity on Sandell's scale and the apparent molar absorptivity were calculated for vanadium to be 0.00006 $\mu g\,cm^{-2}$, and 7.0×10^5 $dm^3\,mol^{-1}\,cm^{-1}$ at 385 nm, using a T.Cl.gall solution decompsed by the presence of vanadium(V) in the presence of HPC and PVP. Although a further investigation of the mechanism and the produced species of this reaction is necessary, this reason for the high sensitivity was assumed to be that the oxidation and decomposition of the T.Cl.gall solution in the presence of HPC and PVP was catalyzed by trace amounts of vanadium(V). The relative standard deviation was 1.7% at the concentration of 0.5 μg/10 cm^3 vanadium (n=5).

Table 1. Effect of Foreign Ions

Foreign ions	Added as	Added μg/10 cm^3	Absorbance at 385 nm
—	—	—	0.460
Cu(II)	Nitrate	12.7	0.375
Zn(II)	Nitrate	26.2	0.380
Fe(III)	Sulfate	11.2	0.378
Al(III)	Sulfate	1.1	0.365
Sn(IV)	Sulfate	4.8	0.380
MoO_4^{2-}	Sodium	64.0	0.320
CN^-	Potassium	156.0	0.440
$S_2O_3^{2-}$	Sodium	11.2	0.420
SO_3^{2-}	Sodium	80.1	0.415
Citrate	Sodium	75.0	0.410

Vanadium taken: 0.3 μg/10 ml; T.Cl.gall: 1.4×10^{-4} $mol\,dm^{-3}$; HPC: 1.0×10^{-3} $mol\,dm^{-3}$; PVP: 1.0 cm^3 of 1.0% PVP solution/10 cm^3; pH: 4.5; Reference: Reagent blank (Solution A).

Table 2. Analytical Results for Vanadium(V) Added to Artificial Water

Molar ratio Total metal/ Vanadium[a)]	Masking agents	Absorbance at 385 nm	Recovery %[b)]
—	—	0.460	100.0
1:1	—	0.460	100.5
5:1	—	0.458	99.6
10:1	—	0.440	95.6
25:1	—	0.430	93.2
	NaF[c)]	0.425	92.3
	NaF+KCN[c)]	0.462	100.4

Vanadium(V) taken: 0.3 μg/10 cm^3; T.Cl.gall: 1.4×10^{-4} $mol\,dm^{-3}$; HPC: 1.5×10^{-3} $mol\,dm^{-3}$; PVP: 1.0 cm^3 of 1.0% PVP solution/10 cm^3; pH: 4.5; Reference: Reagent blank. a): Fe(II)+Co(II)+Al(III)+Zn(II)+Co(II), b): Mean of 5 determinations, c): NaF, 6.0×10^{-4} $mol\,dm^{-3}$; KCN, 6.0×10^{-4} $mol\,dm^{-3}$; notice that a potassium cyanide solution is used in an acidic medium.

Effect of Foreign Ions. The interfering effects of various foreign ions on the determination of vanadium were examined. As is shown in Table 1, the presence of copper(II), aluminum(III), and iron(III) interfered with the determination of vanadium in forming a colored complex in a weakly acidic media. The interference from aluminum(III), copper(II), or iron(III) could, however, be overcome by the addition of sodium fluoride or a nitrilotriacetic acid (NTA) or potassium cyanide (KCN) solution as masking agents respectively. (Needless to say, it must be kept in mind that a slight amount of HCN gas is produced by the addition of the KCN solution in a weakly acidic medium as a masking agent.)

Moreover, the presence of molybdate, tungstate, thiosulfate, citrate, and such oxidizing agents as permanganate, bromate and chlorate, seriously interfered. These interfering ions must be removed by a suitable procedure.

Application. The proposed methods were applicable for the recoveries of vanadium in prepared artificial water (involving various metal ions-iron(III), cobalt(II), aluminum(III), zinc(II), copper(II), etc.). The sample solution (as vanadium(V)) was treated with sodium carbonate solutions, and then filtered or centrifuged. The filtrated or centrifuged solution was adjusted to about pH 5 with hydrochloric acid and sodium hydroxide solutions. Also, sodium fluoride, potassium cyanide and NTA solutions were added to this sample solution as masking agents, and then the concentration of vanadium in the artificial water(molar ratio of total metal ions to vanadium=25 : 1) was determined by using the standard procedure, as is shown in Table 2. The experimental results were in a good agreement with the certified values (recovery test, 98.6—102.8%).

In conclusion, a rapid and sensitive spectrophotometric determination of trace amounts of vanadium (0—0.8 μg/10 cm^3 vanadium) was established by using the oxidation and decomposition of the T.Cl.gall solution by the catalytic reaction of vanadium(V) in the presence of HPC and PVP. The sensitivity of this proposed method was about 16 times greater than that of the method[6] using *N*-benzoyl-*N*-phenylhydroxylamine, and about 20—40 times greater than, that of the PR-oxidation method,[3] the 4-(2-pyridylazo) resorcinol (PAR) method,[7] or the gall-sodium sulfite method.[1] This proposed method should be useful for the determination of trace amounts of vanadium in air pollution, petroleum, steel, the sea, river and lake water, etc.

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