2-Hydroxy-1-naphthaldehyde guanylhydrazone as analytical reagent for spectrophotometric estimation of vanadium

F SALINAS, J J BERZAS NEVADO* and A ESPINOSA

Department of Analytical Chemistry, Faculty of Science, University of Extremadura, 06071 Badajoz, Spain

Abstract. A spectrophotometric determination of V(V) with 2-hydroxy-1-naphthaldehyde guanylhydrazone can be performed in a concentration range varying from 0·70–8·70 ppm of vanadium; the molar absorptivity is $7·7 \times 10^3$ litres mol^{-1} cm^{-1} at 405 nm and the relative error is $\pm 0·60$. The stoichiometry (1 : 1) of the complex was established by different methods. This method of spectrophotometric determination has been applied satisfactorily to the determination of vanadium in steel.

Keywords. Vanadium(V); spectrophotometric determination; 2-hydroxy-1-naphthaldehyde guanylhydrazone.

1. Introduction

Guanylhydrazones are Schiff's bases that can be obtained by a condensation between aminoguanidine and an aldehyde or ketone. These compounds have been synthesized previously for use in pharmacological applications but a few have been studied as analytical reagents. We have initiated the utilization of these compounds in chemical analysis with pyridine-2-aldehyde guanylhydrazone (PAG) (Roman et al 1981) and we have studied its reactions with some cations. Salicylaldehyde guanylhydrazone (SAG) (Berzas et al 1984) has also been spectrophotometrically studied and a method of estimating iron using it has been described. 2-Hydroxy-1-naphthaldehyde guanylhydrazone (NAG) has also been synthesized and applied to spectrophotometric and extractive-spectrophotometric determination of iron (Salinas et al 1985).

In this work, the reaction between NAG and vanadium is studied and a new spectrophotometric method for the determination of vanadium in steel is described.

2. Experimental

2.1. Reagents and apparatus

All solvents and chemical reagents used were of analytical grade.

NAG solutions in dimethylformamide (DMF) were used at different concentrations. A standardized solution of V(V) (0·8510 g/l) was used. A buffer solution of

---

* To whom all correspondence should be addressed.

pH = 4·5 was prepared by dissolving 34·00 g of sodium acetate in 20·8 ml of acetic acid and diluting to 1 litre with demineralized water.

A Beckman 25 spectrophotometer with 1·0 cm glass or quartz cells as well as a Crison 501 digital pH-meter with a glass–AgCl electrode were used.

2.2. *Recommended procedure for the determination of vanadium*

To a vanadium solution, containing 0–217 μg of vanadium(V), in a 25 ml standard flask was added 5 ml of 0·08% (wt/wt) solution of NAG in DMF and 5 ml of a buffer solution of pH = 4·5. After dilution with water the absorbance at 405 nm was measured against a reagent blank prepared similarly.

Beer's law is obeyed between 0–8·7 ppm of vanadium. The optimum concentration range, evaluated by Ringbom's method, is 1·3–6·0 ppm of vanadium. The molar absorptivity at 405 nm is $7·70 \times 10^3$ litres mol^{-1} cm^{-1}. The relative error (95% confidence level) for 3·50 ppm of vanadium is $\pm 0·60\%$.

3. Results and discussion

3.1. *Spectral characteristics and effects of experimental variables*

NAG forms a yellow complex with V(V) in an acid medium which is slightly soluble in water and very soluble in a DMF-water mixture. The absorption spectra of the vanadium complex were recorded for samples containing 20% of DMF and the maximum absorption occurred at 405 nm.

3.1a *Influence of pH:* Samples were prepared in 25 ml volumetric flasks containing 3·50 ppm of V(V), 5 ml of 0·5 M KCl and 5 ml of 0·2% NAG solution in DMF and variable amounts of HCl and NaOH, to obtain the desired pH value. The formation of the yellow vanadium(V) complex is pH independent between 3–6·5 pH values (figure 1). A buffer acetate solution of pH = 4·5 is recommended.

3.1b *Influence of the concentration of NAG:* The effect of the chromogenic reagent was examined by measuring the absorbance of solution containing 3.50 ppm of
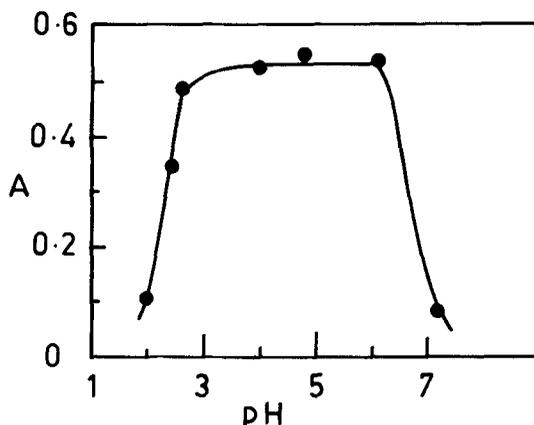

Figure 1. Influence of pH on complex formation.

vanadium and variable amounts of NAG. It was found that 2 ml of 0·2% (W/V) NAG solution sufficed to complex the amount of V(V) taken; with higher concentrations the absorbance was essentially constant. Five millilitres of 0·2% NAG solution are recommended as a suitable amount of reagent.

3.1c *Influence of amount of DMF:* The effect of the DMF content in the medium was examined. It was found that a 16% (v/v) of DMF is necessary for keeping the complex in solution. A 20% (v/v) of DMF is recommended for subsequent studies.

3.1d *Influence of the order of addition:* From experiments in which the order of addition of reagents was varied in all possible ways, it was deduced that the reaction between V(V) and NAG is independent of the order of addition.

3.1e *Stability of the vanadium(V) complex:* The stability of samples containing 1·00, 3·5 and 7·0 ppm of V(V) was studied. The absorbance at 405 nm is constant over a period of 14 hr.

3.1f *Stoichiometry and stability constant:* The metal–reagent ratio $(m : n)$ for the yellow vanadium(V) complex was determined by Job's method and was 1 : 1, metal : reagent. The stability constant calculated from these results following the method described by Meites and Thomas (1958) was log $K = 5·65$.

The stability constant was also determined by Gonzalez *et al* (1980) method. This method permits the differentiation between mononuclear and polynuclear complexes and it is based on the effect of dilution on the degree of dissociation of the complex. In this method the following general equation is used:

$$[(\beta A)^{1/m+n}]/[(b_0/\beta)^{m+n-1/m+n}] = (Km^m A_0(b_0)/n^{m-1})^{1/m+n}[1 - \beta A/A_0(b_0)]$$

where β is the dilution factor, b the metal concentration, and $A_{0(b_0)}$ the absorbance for complete complexation at metal concentration b_0. This equation must be a straight line when the correct values are given to m and n. The equation has been applied for $n = m = 1$ and $n = m = 2$. In figure 2 it can be observed that the vanadium(V) complex is a monomer of stoichiometry 1 : 1. The stability constant was log $K = 5·65$, in accordance with the value obtained when of Meites and Thomas' method (1958) was applied.

3.1g *Interferences:* The effect of diverse ions was studied for the determination of 3·5 ppm of vanadium. An error of 2% in the absorbance was considered as tolerable. The results obtained are presented in table 1.

3.2 *Applications*

The recommended procedure has been applied satisfactorily to the determination of vanadium(V) in steel.

The samples were dissolved according to the following procedure: Dissolve 2·5 g of steel in 20 ml of 1 : 1 sulphuric acid, add 5 ml of nitric acid and evaporate to fumes of sulphur trioxide. Take up in 50 ml of water. Cool, filter and wash the filter with hot dilute sulphuric acid and finally with hot water and dilute to 250 ml.
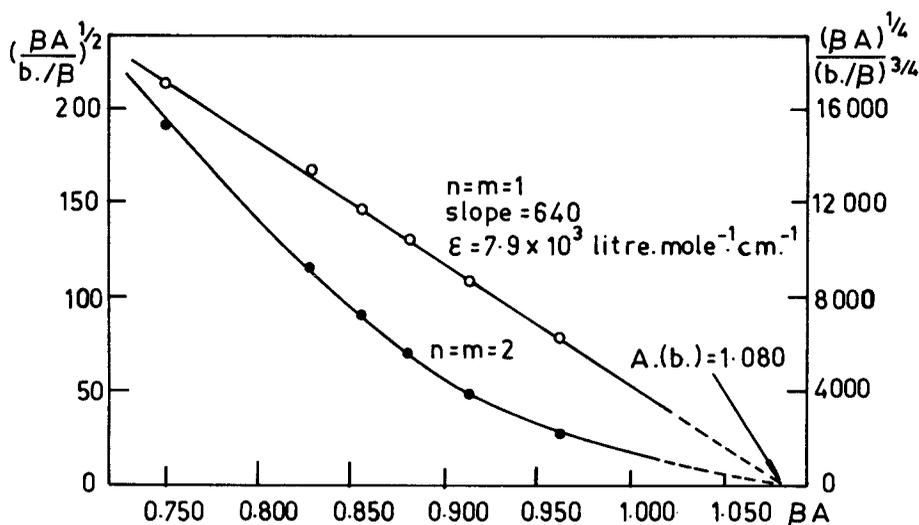
Figure 2. The method of Gonzalez *et al* (1980) applied to the V(V) complex.

Table 1. Effect of diverse ions in the spectrophotometric estimation of 3·50 ppm of vanadium(V).

Maximum tolerance diverse ion/V(V) ratio (wt/wt)	Ions
< 1	EDTA, $C_2O_4^{2-}$, Ti(IV).
1	W(VI), Ag(I).
2	Fe(III).
10	Cu(II)*, Mn(II), Pb(II), Bi(III)*
30	Citrate, Al(III)**, Zn(II), Cr(III)**, As(III), As(V)**, Mo(VI), Hg(II).
70	DCTA, thioglycollic acid.
200	Fluoride, tartrate.
1500	N,N-*bis*(2-hydroxy ethyl glycine, bicine), phosphate
7000	Triethanolamine.

* In the presence of 6·25 mg of 1,2-diaminocyclohexane-N,N,N′,N′-tetracetic acid (DCTA);
** In the presence of 0·61 g of triethanolamine.

A conventional ion exchange column 1·5 cm in diameter containing strong-acid cation exchanger (6 cm) are prepared and the column is purified according to Fritz and Abbink (1962).

Place on the column, 1 ml of the steel sample and elute the vanadium with 50 ml of 0·01 M H_2SO_4 containing 1% hydrogen peroxide. Evaporate the eluate to dryness, add 5 ml of 1 M NaOH and 2 ml of 0·3% bromide and again evaporate the sample to dryness to eliminate hydrogen peroxide. Dilute to 25 ml with

demineralized water. Aliquots of the above solutions were taken and a standard addition method was used to apply the proposed method.

The result obtained for the analysis of steel (Bureau of Analysed Samples, England, 64 b of composition: C 0·90%, Cr 4·55%, V 1·99%, Mo 4·95%, W 7·05%) is 1·95% (the average of three determinations).

Acknowledgements

References

Berzas J J, Espinosa A and Valiente P 1984 *Microchem. J.* **30** 380
Fritz J and Abbink J 1962 *Anal. Chem.* **34** II 1080
Gonzalez D V, Arrebola A and Roman M 1980 *Talanta* **28** 545
Meites L and Thomas H C 1958 *Advanced analytical chemistry* (New York: McGraw-Hill)
Roman M, Berzas J J and Espinosa A 1981 *Talanta* **28** 134
Salinas F, Berzas J J and Espinosa A 1985 *Bull. Soc. Chim. Belg.* **94** 719