Pergamon

0039-9140(94)00125-1

Talanta, Vol. 41, No. 11, pp. 1841–1844, 1994

0039-9140/94 $7.00 + 0.00

DETERMINATION OF TRACE AMOUNTS OF VANADIUM WITH A NEW REAGENT [1-(3-METHOXYSALICYLIDENE-AMINO)-8-HYDROXY-3,6-NAPHTHALENE DISULFONIC ACID, DISODIUM SALT] BY FLUORESCENCE QUENCHING METHOD

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(*Received* 8 *September* 1993. *Revised* 12 *April* 1994. *Accepted* 19 *April* 1994)

Summary—A fluorescence quenching method is described for the determination of trace amounts of vanadium(V) based on the formation of a complex in acidic medium with a new reagent [1(3-methoxysalicylideneamino)-8-hydroxy-3,6-naphthalene disulfonic acid, disodium salt]. The fluorescence emission is measured at 415 nm (wavelength of excitation 360 nm), and the experimental variables and interferences in this determination have been studied. The detection limit is 12.5 ng/ml and linear range is between 50 and 600 ng/ml. The method has been applied to determine trace vanadium(V) in steel and cast iron.

Only a few methods for the fluorimetric determination of vanadium are described in the literature.[1–4] Most of these are based on kinetic measurement.[1–3] One important kind of fluorescence substance is a Schiff base[5] and aromatic Schiff base compounds have been studied as useful fluorimetric reagents for aluminum, magnesium and other metal ions[6] which can form fluorescence complexes. In this paper a vanadium(V) complex with a new reagent [1-(3-methoxysalicylideneamino)-8-hydroxy-3,6-naphthalene disulfonic acid, disodium salt] (MSHND) is discussed and fluorescently measured to find a method for determination of trace amounts of vanadium(V). MSHND is a typical Schiff base compound containing the group =C=N—. Compared with other Schiff base compounds, it is stable and easily dissolved in water. It can emit a strong fluorescence (415 nm) at E_x wavelength 360 nm in acidic medium. The fluorescence intensity was decreased by forming the V (V)–MSHND complex. In acidic solution (pH 4) the fluorescence quenching of MSHND was proportional to the amount of vanadium(V) in the test solution. The linear range covered 50–600 ng/ml with RSD 1.25% for 10 determinations of 100 ng/ml. The detection limit reached 12.5 ng/ml. Many ions did not affect the determination except for Cr(VI), Mo(VI), Co(II) and Mg(II). The metals vanadium, chromium and molybdenum may be separated from the other constituents of steel and cast iron by passing an acetate buffered solution of the steel and cast iron through a strongly basic anion exchanger and selectively eluting the vanadium from the resin column with aqueous solutions of 0.6*M* sodium hydroxide. The proposed method is then used for the determination of vanadium.

EXPERIMENTAL

Apparatus

All fluorimetric measurements were performed on a Hitachi-850–fluorescence spectrophotometer, equipped with an Ushio xenon lamp and 1-cm quartz cells. The width of the excitation and emission slits was 5.0 nm. A standard solution of Rhodamine B was used weekly to adjust the spectrofluorimeter to compensate for changes in source intensity. No correction was made for the instrumental response.

Chemicals

Standard vanadium(V) solution 0.1 *mg/ml.* Pure ammonium vanadate (0.23 g) was dissolved with 10 ml 4.5*M* sulfuric acid solution in

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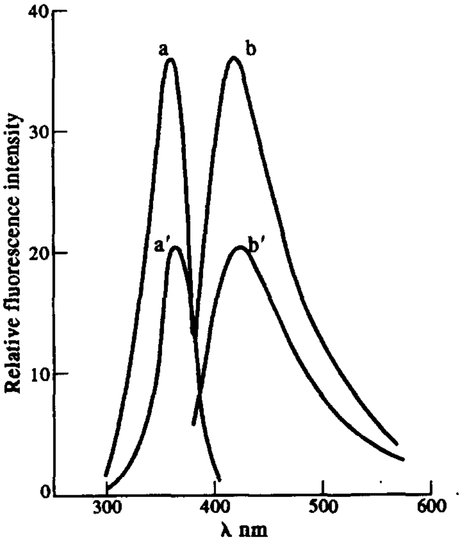
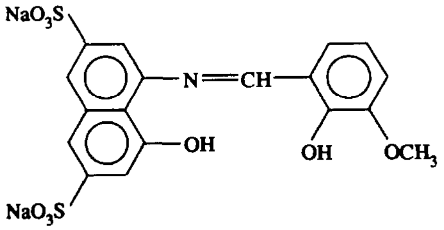


Fig. 1. Fluorescence excitation (a) and emission (b) spectra. a, b, MSHND; a', b', MSHND + V(V). V(V): 250 ng/ml, MSHND: 0.01%.

a 100-ml volumetric flask and diluted to the mark with redistilled water. Working solutions were prepared by appropriate dilution of the standard solution.

MSHND reagent. Hacid-mono sodium salt (1.8 g) was dissolved in about 100 ml warm water. The pH value was adjusted to 7 with 10% potassium hydroxide solution, then adjusted to 5 with concentrated hydrochloric acid solution. 3-Methoxy-salicy aldehyde (2.1 g in 10 ml ethanol) was added, stirred for 30 min and kept still overnight. The mixture was filtered and washed thoroughly with ethanol, yielding a yellow silky matter. The structure is shown below.



Element analysis: C, 41.04%; H, 3.45%; N, 2.56%. MSHND requires C, 40.83%; H, 3.87%; N, 2.65%.

MSHND solution 0.1%. MSHND (0.10 g) was dissolved with 1 g ascorbic acid and 5 ml of $0.1M$ sodium hydroxide in a 100-ml volumetric flask and diluted to the mark with redistilled water.

Potassium biphthalate buffer solution. Sodium hydroxide (0.4 ml of $0.1M$) was added to 25 ml of $0.2M$ potassium biphthalate solution, then diluted to 100 ml.

Procedure

Taking 1 ml of test solution in a 10-ml volumetric flask, 2 ml of pH 4.0 buffer solution of potassium biphthalate and 1 ml of 0.1% MSHND solution were added. The flask was shaken to mix well and then diluted to the mark with redistilled water. After 30 min, the fluorescence intensity at 415 nm (wavelength of excitation 360 nm) was measured and the fluorescence intensity difference ΔF against a reagent blank, prepared in same way but without vanadium(V), was obtained.

RESULT AND DISCUSSION

Spectral characteristics

The excitation and emission fluorescence spectra of the complex in the presence of vanadium(V) and of the reagent alone were obtained with a pH 4 buffer solution of potassium biphthalate and are shown in Fig. 1. A decrease of the fluorescence intensity in the maximum emission peak (415 nm) can be observed in the presence of vanadium(V). All results show that the fluorescence intensity difference ΔF was at a maximum at E_x 360 nm and E_m 415 nm; therefore, E_x 360 nm and E_m 415 nm were selected as operating parameters during all laboratory work.

Effect of pH

The acidity of the test solution had a significant effect on the determination of vanadium(V). Several buffer solutions were tested: potassium biphthalate (pH 3–5), ammonium acetate–acetic acid (pH 5.7), sodium acetate–acetic acid (pH 4). The results show that in a buffer solution of potassium biphthalate there was a satisfactory linear relationship between fluorescence intensity difference (ΔF) and

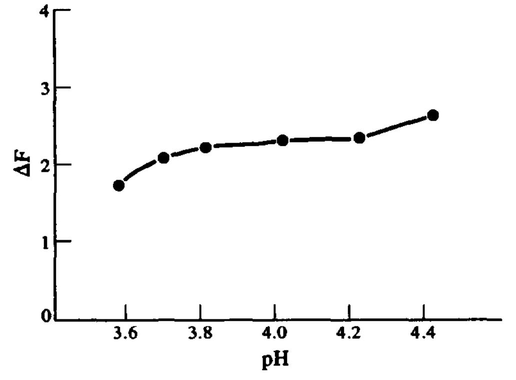


Fig. 2. The effect of pH. V(V): 200 ng/ml, MSHND: 0.01%. Potassium biphthalate solution.

Table 1. Effect of various ions on the determination of 100 ng/ml of V(V)

Foreign ion	Added (μg)	Found V(V) (μg)	Error (%)	Foreign ion	Added (μg)	Found V(V) (μg)	Error (%)
NO_3^-	500	1.02	+2.0	Fe^{3+}	20	0.99	−2.0
HPO_4^{2-}	500	1.04	+4.0	Ni^{2+}	50	0.98	−2.0
HCO_3^-	500	1.04	+4.0	Cu^{2+}	10	1.01	+1.0
Ca^{2+}	500	0.97	−3.0	Pb^{2+}	10	0.98	−2.0
Ba^{2+}	100	1.00	0	Zn^{2+}	10	0.97	−3.0
Sr^{2+}	100	0.95	−5.0	Cd^{2+}	500	0.98	−0.2
Cr^{3+}	100	0.97	−3.0	Mn^{2+}	20	0.97	−3.0
ClO^-	100	1.03	+3.0	SO_4^{2-}	500	0.98	−2.0
$Cr_2O_7^{2-}$	10	4.05	+305	Co^{2+}	10	3.87	+287
Mg^{2+}	10	4.54	+354	Mo^{6+}	10	4.75	+375

vanadium(V) concentration. When the pH of the buffer solution of potassium biphthalate varied from 3.7 to 4.2 the fluorescence difference (ΔF) was constant for the same solution (Fig. 2). Thus pH 4 buffer solution of potassium biphthalate was chosen.

Effect of reagent concentration

The fluorescence intensity of higher concentrate solution of reagent MSHND was unstable. The fluorescence intensity was stable and the difference (ΔF) had a linear relationship with the concentration of vanadium(V) when 0.75–1.25 ml of 0.1% MSHND solution was added. Hence 1 ml of 0.1% MSHND was chosen as optimum.

Effect of temperature

The influence of temperature on the measurement was studied from 20 to 60°C using a thermostat. The temperature did not affect the fluorescence intensity in this temperature range and ΔF was nearly constant for same solution. Therefore, all experiments were at room temperature (Fig. 3). For 30–90 min after pouring MSHND into the test solution the fluorescence intensity of the test solution remained almost constant.

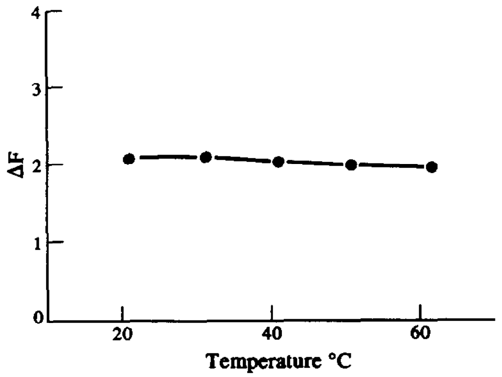


Fig. 3. The effect of temperature. V(V): 200 ng/ml, MSHND: 0.01%.

Composition of the complex

The complex formed between V(V) and MSHND, as determined by the mole ratio method, was in a 1:1 ratio.

Analytical parameters

Under the above operating conditions, there was a satisfactory linear relationship between ΔF and vanadium(V) concentration in the range 50–600 ng/ml. The detection limit was 12.5 ng/ml and the relative standard deviation ($n = 10$) was 1.25% for determinations of 100 ng/ml vanadium(V).

Effect of foreign ions

The effect of foreign ions on the determination of 100 ng/ml of vanadium(V) was studied and the results obtained are summarized in Table 1. Only Cr(VI), Mo(VI), Co(II) and Mg(II) were found to interfere with the determination.

Determination of vanadium(V) in samples

The contents of vanadium in steel and cast iron were determined. Pre-treatments of samples referred to the literature.[7] Samples (0.4 g) were dissolved in 8 ml of mixed acid (nitric acid: hydrochloric acid, 1:3) by heating. After cooling, 6 ml of H_2O_2 (30%) was slowly added. After filtering the solution and discarding the insoluble matter, the filtrate was diluted to

Table 2. Analysis of results of V(V) in samples

Sample	Weight (g)	V(V) found (%)*	Certified (%)
Steel BH1007-1	0.4462	0.024	0.022
Cast iron BH2009-1	0.3914	0.034	0.032

*Average of five separate determinations.

Table 3. Addition recoveries

Sample	Found V(V) (*ng/ml*)	Added V(V) (*ng/ml*)	Found V(V) (*ng/ml*)	Average recovery (%)
Steel	106	100	207	
BH1007-1	106	100	208	101.5
Cast iron	131	100	232	
BH2009-1	131	100	234	102

nearly 50 ml. Ammonium acetate (1 g) and mannitol (0.5 g) were added and the pH adjusted by dropwise additions of concentrated ammonia solution to 2.5–3. The solution was added to a column (1 × 50 cm) with basic anion exchanger, approximately 25 ml of the resin having been lightly packed and converted to the nitrate form with sodium nitrate. The flow rate during adsorption and the subsequent water wash was equal to 15 drops per min. Adsorbed vanadium(V) was eluted with about 50 ml of 0.6*M* sodium hydroxide at a flow rate of 10 drops per min to give a final volume of approximately 50 ml. The pH was adjusted to 2 with sulfuric acid and the solution diluted to a mark of 50 ml. One millilitre of the treated solution was placed in a 10-ml volumetric flask and determined by the proposed method. The results are given in Tables 2 and 3.

Acknowledgement—We thank Miss Wang Fang for supplying the reagent MSHND.

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