CATALYTIC SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM (IV) BASED ON THE OXIDATION OF ALKALI BLUE BY POTASSIUM BROMATE[*]

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Abstract – A simple, rapid and sensitive spectrophotometric method has been proposed for the determination of Vanadium (IV). The method is based on the catalytic effect of V (IV) on the oxidation of Alkali Blue by potassium bromate at pH 4. The rate of decrease in the absorbance of Alkali Blue (at 572 nm) was proportional to the concentration of V (IV) in the range of 100-6000 ng ml^{-1}. The detection limit was 40 ng ml^{-1}. The proposed method shows a good selectivity for V (IV) over a wide variety of interference species. It is also valuable in that the presence of a 400 fold excess of V (V) can be tolerable, contrary to many methods for the determination of V (IV) which suffer from severe interference of V (V). This method was successfully applied to the determination of V (IV) in river water, alloy samples and several synthetic samples.

Keywords – Catalytic, vanadium (IV), Alkali Blue, spectrophotometric

1. INTRODUCTION

Determination of vanadium is important, particularly from a biological and industrial point of view. Vanadium is a metallic element that occurs in six oxidation states in numerous inorganic compounds. It is used primarily as an alloying agent in steels and non-ferrous alloys. Vanadium compounds are also used as catalysts and in chemical, ceramic or specialty applications. Also, in-vitro studies have shown that vanadium is essential for cell growth at μg dm^{-3} levels, but can be toxic at higher concentrations. The toxicity of vanadium depends on its physico-chemical state; particularly on its valance state and solubility [1-2]. In body, vanadium can undergo changes in oxidation state (V (V) and V (IV) forms) and it can also bind with blood protein. V (IV) is less toxic than V (V) in environmental systems and can be produced by various industrial redox processes. It was observed that V (IV) in aqueous solutions forms complexes, most easily with reagents containing oxygen or sulfur donor ligands [3-5]. This point testifies to the interest in the determination of V (IV) and the presentation of simple, selective, precise and inexpensive methods for the determination of this metal ion. Different methods such as ICP-MS, ICO-AES, NSAA, AAS, and spectrophotometry [6-12] are most frequently used for the determination of vanadium compounds. However, the relatively high instrumental cost and need for preconcentration, chromatographic separation, extraction or coprecipitation are common disadvantages. Kinetic methods of analysis based on catalyzed or uncatalyzed reactions have been applied to trace analyses for vanadium determination because of their extremely high sensitivity. On the other hand, among the most important kinetic methods, catalytic methods are very well known because of their simplicity, sensitivity, selectivity and low cost of instrumentation [13-16]. These methods are based on vanadium catalytic properties concerning the oxidation of certain organic compounds.

Several researchers have reported the use of catalytic reaction for the determination of V (IV), since

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V (IV) is a very good catalyst for the oxidation of various organic dyes in the presence or absence of activators [17-18]. Bromates have been extensively used as the principal oxidant agent, although iodate and hydrogen peroxide have also been investigated [19]. According to Safavi et al. [20], a method based on the oxidation of Aniline Blue by bromate is very selective for the determination of V (IV), even in the presence of a large excess (250 mg L^{-1}) of vanadium (V). Kinetic-catalytic determination of V (IV) using a Methyl Orange-bromate redox reaction was proposed by Absalan and Alipour [21], the measured kinetic parameter was net absorbance-vs-time by measuring the decrease in absorbance of Methyl Orange at 507 nm after a fixed time. It was found that the determination of vanadium (IV), based on its catalytic effect on the reaction between Methyl Orange and bromate, was seriously affected by the presence of V (V). This method was successfully applied to the determination of V (IV) in water samples with good sensitivity.

In another work [22] researchers proposed a kinetic-catalytic spectrophotometric method for the determination of trace amounts of vanadium (IV) and V (V) ions. The vanadium (IV) as VO^{2+} ion and vanadium (V) as VO_3^- ion showed a catalytic effect on the kinetic reactions between methylthymol blue (MTB) and bromate in acidic media. The linear ranges for the determination of vanadium were obtained in the range of 1.0-150 and 5.0-100.0 µg/L by the fixed-time and slope methods, respectively. Using the fixed-time method, the limit of detection was found to be 0.5 µg/L of vanadium. The detection limit of vanadium by the slope method was found to be 3.5 µg/L of vanadium.

A review on vanadium determination has recently been published by Pyrzynska [19]. This review shows recent developments in the spectrophotometric determination of vanadium. Table 1 shows more reports on the kinetic catalytic determination of vanadium using spectrophotometric methods. However, among the several analytical techniques for the determination of vanadium, spectrophotometric methods are quite popular due to their simplicity and low-cost instrumentation. Various attempts have been made to modify these methods in order to improve their sensitivity and selectivity. The present work describes a simple, precise kinetic spectrophotometric method with good selectivity and sensitivity for the determination of Vanadium (IV) using its catalytic effect on the oxidation of Alkali Blue by potassium bromate at pH 4 and 572 nm.

Table 1. Some reports on kinetic catalytic determination of
vanadium using spectrophotometric methods

Indicator reaction	D.R ^{a} (µg L^{-1})	D.L^b (µg L^{-1})	RSD (%)	Interferences	Ref.
Aniline Blue+BrO$_3^-$	5-1200	0.002	3.0	Nitrite, Iodide	[20]
Methyl Orange+BrO$_3^-$	2.5–300	0.8	2.0	Fe, As, Hg, V(V)	[21]
Nile Blue+BrO$_3^-$	4–520	3.0	3.0	-	[23]
Gallic Acid+S$_2$O$_8$$^{2-}$	4.1–33.3	1.0	4.0-8.0	Chloride	[24]
Diphenylamine+H$_2$O$_2$	400–4000	4.0	0.5	Fe	[25]
Diaminonaphthalene+BrO$_3^-$	0.05–50	0.0088	-	Cu, Fe	[26]
Present work	100-6000	40.0	3.47	I$^-$, SCN$^-$ Cr (III)	-

a: Dyanamic range   b: Detection limit

2. EXPERIMENTAL

a) Reagents

All chemicals were of analytical reagent grade and were used directly without further purification (from Merck or Fluka). Triply distilled water was used to prepare buffer and all reagent solutions.

A stock solution of Alkali Blue (3.66×10^{-4} M) was prepared by dissolving 0.0210 g of Alkali Blue in water and diluting to 100 ml. A vanadium stock solution (1000 µg.ml^{-1}) was prepared daily by dissolving 0.1952 g of vanadyl sulfate ($VOSO_4.2H_2O$) in water and adding 2.0 ml of 0.5 M sulfuric acid (as the V (IV) solution is unstable in nonacidic solution) and diluting to 50 ml in a volumetric flask. A stock solution of BrO_3^- (0.35 M) was prepared by dissolving 5.8457 g $KBrO_3$ in water and diluting to 100 ml in a volumetric flask.

Stock solutions of interfering ions (1000 µg ml^{-1}) were prepared by dissolving their suitable salts in water. More dilute solutions were prepared daily from the appropriate stock solution. Titrosol buffers (pH=1.0-9.0) were used for adjusting the pH.

b) Apparatus

A Philips UV- Visible single beam spectrophotometer (model PU 8675) with a 1.0 cm glass cell was used for absorbance measurements. To adjust the temperature of the cell compartment a thermostated water bath (model COLORA type NB) regulated at the desired temperature was used.

c) Procedure

All solutions were thermally equilibrated at 28°C in a thermostatic water bath before the addition of reagents. To a series of 10 ml volumetric flasks, 2.0 ml of Alkali Blue (3.66×10^{-4}M), 1000-60000 ng of V (IV), and 2 ml of buffer (pH 4.0) were added and the solution was diluted to about 7 ml with distilled water. This solution was shaken and 3.0 ml of $KBrO_3$ (0.35 M) was added; the solution was then diluted to 10 ml with distilled water.

The zero time was taken as the moment at which the last drop of bromate was added. The decrease in the absorbance was measured for the first 300s at 572 nm and 28°C.

3. RESULT AND DISCUSSION

3.1. Optimization of procedure

A solution of Alkali Blue in the presence of $KBrO_3$ (0.105 M) was relatively stable at room temperature but underwent a rapid decomposition when V (IV) at ng ml^{-1} level was added. In order to find the optimum conditions, the influence of the concentration of all reagents, temperature, ionic strength, and pH on the reaction rate was studied.

3.1.1. Effect of pH

The influence of pH on the rate of both the catalyzed and uncatalyzed reaction was studied over the pH range of 1.0-9.0, using an appropriate Titrosol buffer solution for pH adjustment. For this purpose, an appropriate volume of buffer was added to a series of solutions containing 4 µg.ml^{-1} of vanadium (IV) and 1.5 ml 3.6×10^{-4} Alkali Blue and the solution diluted to about 7 ml. To this solution 3 ml of $KBrO_3$ (0.35 M) was added and the solution diluted to 10 ml with distilled water. For the uncatalysed reaction, a series of solutions was prepared in the same way except that the vanadium solution was not present. Figure 1 shows the influence of pH on the rate of both the catalyzed and uncatalyzed reactions. According to the results, the rate of both the catalyzed and uncatalyzed reactions were increased rapidly at pH values larger

than 6. Before this region, no significant change was observed in the rate of an uncatalyzed reaction. However, in this study it is found that better sensitivity can be achieved at about pH 4.0, so this pH was selected as the optimum pH for the determination of vanadium (IV).
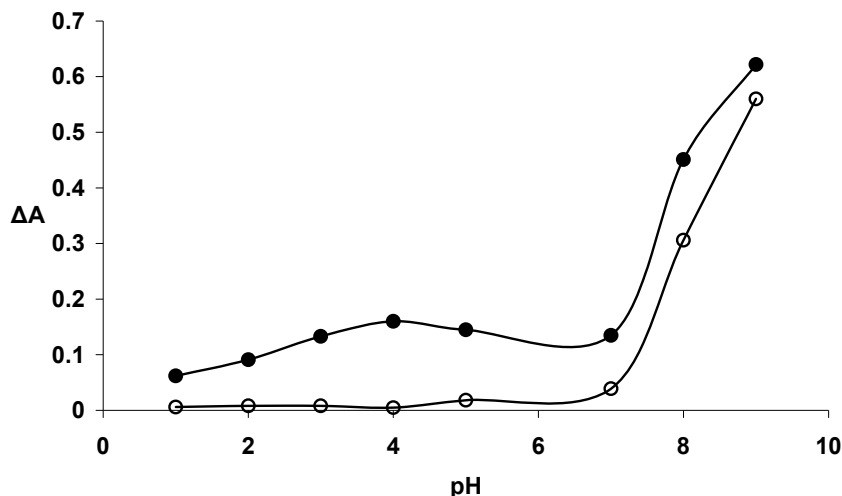

Fig. 1. Effect of pH on the rate of catalyzed (■) and uncatalyzed (●) reactions. Experimental
Conditions: Alkali Blue 5.4×10^{-5} M; bromate 0.105 M; V (IV) 4 ppm; temperature, 28°C

3.1.2. Effect of reagents' concentration

The effect of the concentration of each reagent on the rate of both the catalyzed and uncatalyzed reactions was studied. The rate of the catalyzed reaction increased with the bromate concentration (Fig. 2) at 0.01-0.14 M of bromate, but there is no significant change in the rate of the uncatalyzed reaction. Thus, 0.105 M of $KBrO_3$ was adopted for further studies.

The influence of the Alkali Blue concentration on the reaction rate was also studied (Fig. 3). The results show a good increase in the rate of the catalyzed reaction with an increase in the Alkali Blue concentration up to 1.3×10^{-4} M of reagent, while the rate of the uncatalyzed reaction is almost constant. Thus, an Alkali Blue concentration of 1.28×10^{-4} M was used for further work.

3.1.3. Effect of ionic strength

The effect of ionic strength on the reaction rate for both the catalyzed and uncatalyzed reactions was investigated; salt concentration was varied from 0.1 to 0.6 M using 2.0 M KNO_3 solution. According to the obtained results this parameter had no significant effect on the reactions rate.

3.1.4. Effect of temperature

A study of the influence of the temperature on the rate of the oxidation of Alkali Blue (1.28×10^{-4} M) in the presence of $KBrO_3$ (0.105 M), and V (IV) (4 μg.ml^{-1}) was performed in the temperature range of 10-45 °C at pH 4.0. As the results show, the rate of the catalyzed reaction increases with increasing temperature much faster than the uncatalysed reaction. The increase in the reaction rate with increasing temperature for both reactions was shown in Fig. 4, but for simplicity of temperature control through the experiments, a temperature of 28 °C was chosen for routine work.
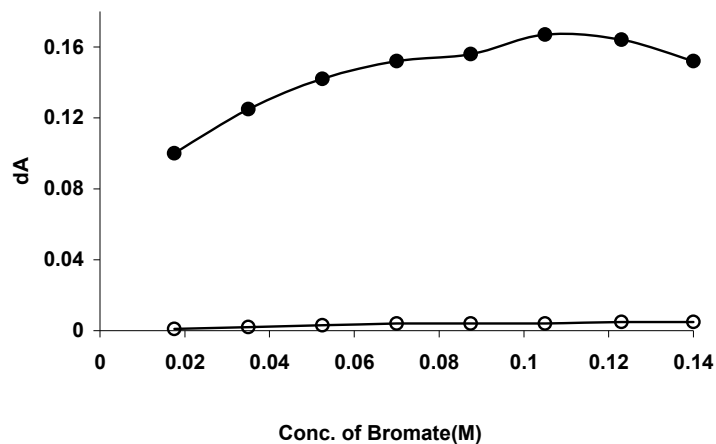
Fig. 2. Effect of bromate concentration on the rate of catalyzed (■) and uncatalyzed (●) reactions, Conditions: Alkali Blue concentration, 7.32×10^{-5} M; V (IV) concentration, 4 ppm; temperature, $28°$C
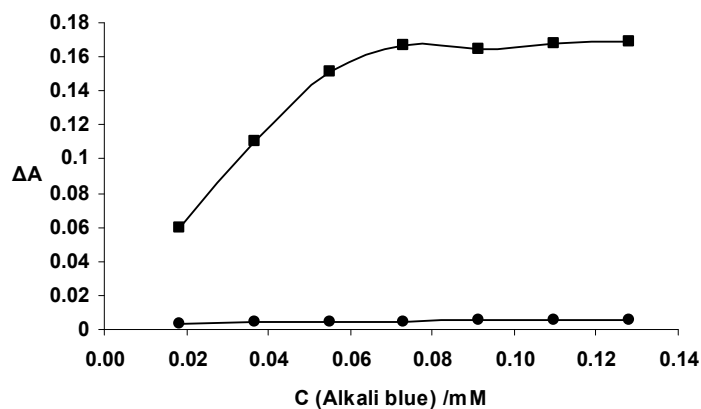

Fig. 3. Effect of Alkali Blue concentration on the rate of catalyzed (■) and uncatalyzed (●) reactions, Conditions: bromate concentration, 0.105 M; V (IV) concentration, 4 ppm; temperature, $28°$C
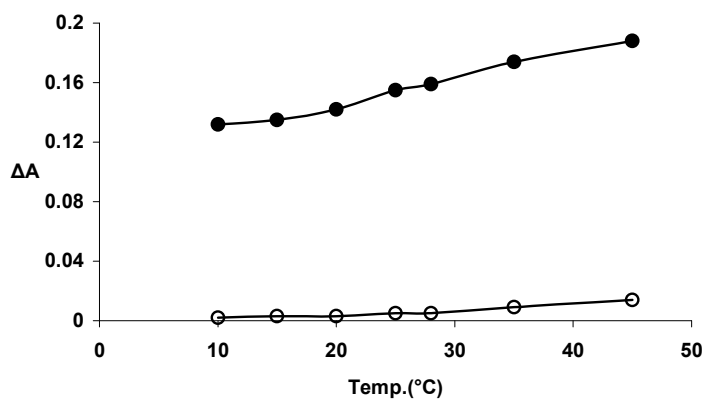

Fig. 4. Effect of temperature on the rate of catalyzed (■) and uncatalyzed (●) reactions, Conditions: bromate concentration, 0.105 M; Alkali Blue concentration 1.28×10^{-4} M; V (IV) concentration, 4 ppm

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3.2. Calibration graph and analytical figures of merit

A calibration graph was obtained by applying the fixed time method. The linear range was obtained under the following conditions: Alkali Blue concentration of 1.28×10^{-4} M, KBrO$_3$ 0.105 M, pH 4.0, a temperature of 28 °C and a V (IV) concentration of 100-6000 ng ml^{-1} ($\Delta A = 0.0322C + 0.0115$, R=0.9979 and C is the concentration of V (IV) in ng ml^{-1}); the detection limit [27] (defined as the concentration giving a signal equal to the average of the blank value plus three times its standard deviation) was also obtained. The experimental detection limit was 40 ng ml^{-1}. A study of precision was made with seven independent solutions containing 600 ng ml^{-1} V (IV). The relative standard error was obtained as 3.47%.

3.3. Interference study

The influence of various species was investigated on the determination of V (IV) 4 µg.ml^{-1} under optimum conditions. The tolerance limit was taken as the maximum concentration of the foreign ion causing a relative error of less than 3% .The results were shown in Table 2. As can be seen, the method is free from most interference. I$^-$, SCN$^-$, and Cr (III) showed serious interferences which can, however, be eliminated. I$^-$, SCN$^-$ inhibit the catalytic reaction rate. In order to eliminate their interferences, Hg^{2+} can be used as a masking agent [28]. Cr (III) showed a serious negative interference. However, this interference can be eliminated by the addition of fluoride (added NaF 1%) [28].

4. APPLICATION

In order to confirm the usefulness of the method, the proposed method (at optimum conditions) was applied for the determination of V (IV) in river water and some alloys and synthetic mixtures. The solutions were analyzed by the proposed method and AAS. The results indicate the successful applicability of the proposed method to real sample analysis, and are presented in Table 3.

Table 2. Interference of foreign ions on the determination of
V (IV) (4 µg ml^{-1}) by proposed method

Species	Tolerance limit/ µg ml^{-1}
Mo^{6+}, Sn^{2+}, Mn^{2+}, Ni^{2+}, Tl$^+$, Cu^{2+}, Zr^{4+}, Al^{3+} Mg^{2+}, Ca^{2+}, Na$^+$, NH$_4^+$, Ag$^+$, Hg^{2+}, K$^+$, Cl$^-$, Br$^-$, CH$_3$COO$^-$, F$^-$, EDTA, C$_2$O$_4^{2-}$, NO$_3^-$, Zn^{2+}	1000
Co^{2+}	700
Fe^{3+}, Ce^{3+}, Pb^{2+}, V^{5+}	400
I$^-$, SCN$^-$	50 [a]
Cr^{3+}	20 [a]

a: after removal interference

Table 3. Determination of V (IV) in some real and synthetic samples
using proposed method and atomic absorption spectroscopy

Sample	Amount of V(IV)/µg ml^{-1}		RE, %	RSD, %
		AAS Found		
alloy				
V–Al alloy[a]	3.50	3.45	1.4	1.65
V–Al alloy	2.20	2.11	4.09	2.23
River water 1	2.2	2.15	2.5	1.93
2	1.65	1.7	3	2.86
3	3	3.12	4	3.01
4	3.8	3.65	3.9	3.22
Synthetic solution 1	1	0.96	4	3.25
2	2	1.88	6	3.47
3	3.5	3.46	1.14	2.10
4	4.00	4.10	2.5	2.24

a: This alloy is also composed of 7.5 % Al, 0.4% Fe, (proposed method
can be applied after the removal of interferences).
RE; relative error; RSD; Relative standard deviation for n=5

5. CONCLUSIONS

The proposed kinetic catalytic method is simple, sensitive and relatively selective for the determination of V (IV) in a wide linear range with good accuracy and precision. The procedure provides a wide linear dynamic range, 100-6000 ng.ml^{-1}. The method is also valuable in that the presence of a 400 fold excess of V (V) can be tolerable, contrary to many methods for the determination of V (IV) which suffer from the severe interference of V (V).

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