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Kinetic Spectrophotometric Determination of Vanadium (V) Using Ponceau S

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Abstract

A sensitive and selective kinetic method is proposed for the determination of nanogram amounts of vanadium (V). The method is based on the catalytic effect of vanadium (V) on the oxidation of Ponceau S by hydrogen peroxide in acidic media. The rate of the reaction is monitored spectrophotometrically at 520 nm. The method allows determination of vanadium (V) concentrations in the range 2-400 ng mL^{-1} with a relative standard deviation of ± 2%. The proposed method has been applied successfully for the determination of vanadium (V) in tap water and wastewater samples.

***Keywords*:** Vanadium (V); Ponceau S, Catalytic effect; Kinetics

1. Introduction

Vanadium is present in abundance in the earth's crust [1]. It is also present in relatively higher concentrations in crude oils and coal [1-2] and their combustion gives rise to the higher concentrations of vanadium in the atomphere [1]. Indsutrial effluent from titanium and uranium processing plants as well as steel indusrties contain higher concentrations of vanadium [1,3].

Vanadium is one of the essential trace elements for animals and plants; however, vanadium essentiality for humans has not been established [2]. Nevertheless, Vanadium in higher concentrations is toxic to humans [4] and its toxicity includes respiratory illness [5] and a number of disorders including interference with a number of essential enzyme systems [6]. The toxicity of vanadium is determined by its oxidation state [7], which ranges from -1 to +5 [2], amongst which oxidation states 2 to 5 are the most stable in solution, V(V) followed by V(IV). However, vanadium with an oxidation state V(V) is more toixc than other states [7]. Various instrumental techniques, such as inductively coupled plasma atomic emission spectrometry (ICP-AES) [8], mass spectrometry (ICP-MS) [9] and atomic absorption spectrometry (AAS) [10] have been used for the determination of total vanadium, but for the nanogram (ng) or lower

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amounts, these methods can be applied only after preliminary isolation and preconcentration, and costly instruments are required [11]. This problem has been partly overcome by kinetic methods for the catalytic determination of vanadium [12,13,14]. The kinetic method has progressed recently because of its extremely high sensitivity and selectivity for detection at low limits.

Numerous catalytic methods (with spectrophotometric detection) have been reported for the determination of vanadium. Most of these are based on the catalytic effect of vanadium on the oxidation of organic compounds such as rhodamine B [15], indigo carmine [16], 1-naphthyl red [17], *o*-phenylenediamine [18,19], or chromotropic acid [20] by an inorganic oxidant. Many of these kinetic methods lack either sensitivity or satisfactory selectivity or they have a limited dynamic range. Hence, the development of more sensitive and selective catalytic methods for the kinetic determination of vanadium is still sought.

The aim of the present work is to determine selectively traces of vanadium (V) based on its catalytic effect on the oxidation of Ponceau S (2,7-Naphthalenedisulfonicacid, 3-hydroxy-4-[[2-sulfo- 4[(4sulfophenyl)_azo]phenyl]azo]-,tetra sodium salt) with hydrogen peroxide in an acidic medium. The method is based on the measurement of absorbance at the wavelength of maximum absorption of Ponceau S in an acidic media by applying a fixed time method. The proposed method permits the determination of vanadium (V) at ng mL^{-1} levels.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade. A standard vanadium (V) solution (1000 mg mL^{-1}) was prepared by dissolving the appropriate amount of vanadyl sulphate and diluting to 1000 mL. A stock solution of hydrogen peroxide (0.04 M) was prepared daily by diluting 1.05 mL of H_2O_2 (E.Merck) in water and diluting to 100 mL. This solution was standardized by potassium permanganate titration. Poncaeu S solution (0.004 M) was prepared by dissolving 0.306 g Poncaeu S in water and diluting to 100 mL. The solution was further diluted 10 times with double distilled water before kinetic spectrophotometric studies. All laboratory ware used for handling solutions was cleaned with detergent solution, soaked in 1:1(v:v) nitric acid, followed by vigorous shaking and thorough rinsing with deionised distilled water.

2.2. Apparatus

Absorbance measurements were recorded on a Hitachi 220 UV/V spectrophotometer equipped with a 150 W deuterium lamp and 1.0 cm quartz cells. All pH measurements were made with an Orion 420A digital pH meter with a combined glass-calomel electrode. The laboratory temperature was 30^0C (±1). And all solutions were previously brought to this temperature.

3. Recommended procedure

A suitable aliquot of sample solution containing 2-400 ng mL^{-1} of V (V) was transferred into a 10 mL volumetric flask. Then 1.4 mL of 0.0004 M Ponceau S and 2.0 mL of potassium chloride - hydrochloric acid buffer (pH 1) were added. The solution was diluted to approximately 9.5 mL and kept in a laboratory at 30°C for 10 min. A 0.2 mL of 0.04 M hydrogen peroxide previously brought to the same temperature was added to initiate the reaction. The stopwatch was started to record the time when the last drop of hydrogen peroxide was added to the solution. The solution was diluted to 10 mL and shaken. A portion of this solution was transferred to a quartz cell (1 cm) within 30 s and the absorbance at 520 nm was recorded for 2.0 min at 30 s intervals.

For the unutilized reaction, the same procedure was repeated but the addition of vanadium (V) solution was omitted.

4. Results and discussion

In the presence of traces of vanadium (V), Ponceau S is oxidized by hydrogen peroxide in acidic media. This reaction does not proceed in the absence of vanadium (V) as a catalyst. The decrease in the absorbance, i.e. decrease in the concentration of Ponceau S, was measured at 520 nm.

4.1. Influence of reaction variables

In order to find the optimum conditions, the influences of the concentration of all reagents, temperature and pH on the reaction rate were studied based on the fixed time method. The optimum conditions used for the final working procedure were chosen as a compromise in order to ensure low blank values, extended linearity and a short measuring time. Time is the fundamental factor in the chemical kinetics. The absorbance of the catalytic and un-catalytic reactions was measured at different times. The absorbance was recorded from 30 seconds up to 5.0 minutes at intervals of 30 seconds. It was observed that the absorbance remained constant between 2.0 minutes and 5 minutes. Hence, it may be suggested that the reaction is rapid, and indicated major conversion within 2.0 minutes, and was thus selected. The effect of pH between 1 and 10 was studied for catalytic and un-catalytic reactions of ponceau S using hydrogen peroxide as an oxidizing agent. At pH 10, the ponceau S changed its colour from red to blue. In the alkaline medium, attempts were made to catalyze the oxidation using various transition metals but there was no significant change in the absorbance of catalyzed and uncatalyzed solutions. When vanadium (V) was added to the reaction of Ponceau S and hydrogen peroxide in the acidic medium, a change in colour of catalyzed reaction was observed. The colour started decreasing from red to yellow. It was observed that at buffer (pH 1), a maximum decrease in colour was recorded and hence a buffer of potassium chloride–hydrochloric acid was selected for further study. The temperature of the solution mixture was varied over the range 10–60°C. An increase in temperature caused an increase in the rate of both catalyzed and uncatalyzed reactions. However, the rate of the blank reaction increased much faster with increases in temperature causing a net decrease in the signal-to-blank ratio. For the ease of operation, the room temperature of 30°C was selected as an optimum temperature for the determination of vanadium (V).

The rate of catalyzed reaction increased with increasing Ponceau S concentration (Fig.1), but because of high molar absorptivity of Ponceau S 32500 mol L^{-1} cm^{-1}, a limited range of concentration was tried and the optimum concentration of Ponceau S was 5.6 x 10^{-6} M in the final solution. The uncatalyzed reaction also showed dependence on the Ponceau S concentration but much less than the catalyzed reaction.

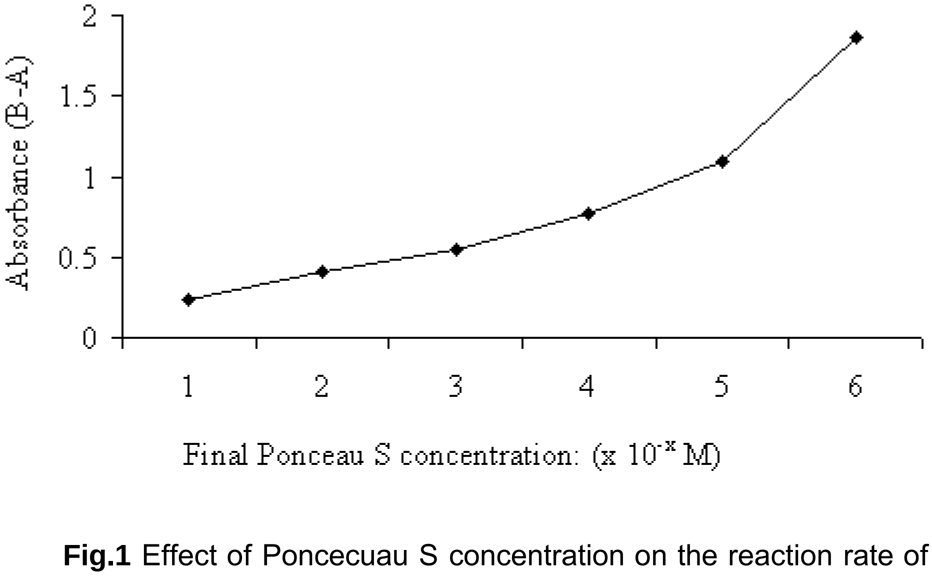

Fig.1 Effect of Poncecuau S concentration on the reaction rate of 200 ng mL^{-1} vanadium (V)
Conditions: Potassium chloride – hydrochloric acid buffer (pH 1) (2 mL); $[H_2O_2]$= $0.8x10^{-3}$ mol L^{-1}, measuring time 2.0 min; temperature 30 ^0C

The effect of the concentration of peroxide on the rate of the blank and the catalyzed reactions was investigated. As can be seen from Fig.2, the rate of catalyzed reaction increased with increasing reagent concentration up to 4x10^{-3} mol L^{-1}, but levelled off at higher concentrations and 0.8x10^{-3} mol L^{-1} hydrogen peroxide in the final solution was selected for the proposed study. For the uncatalyzed reaction, some dependence was also observed.

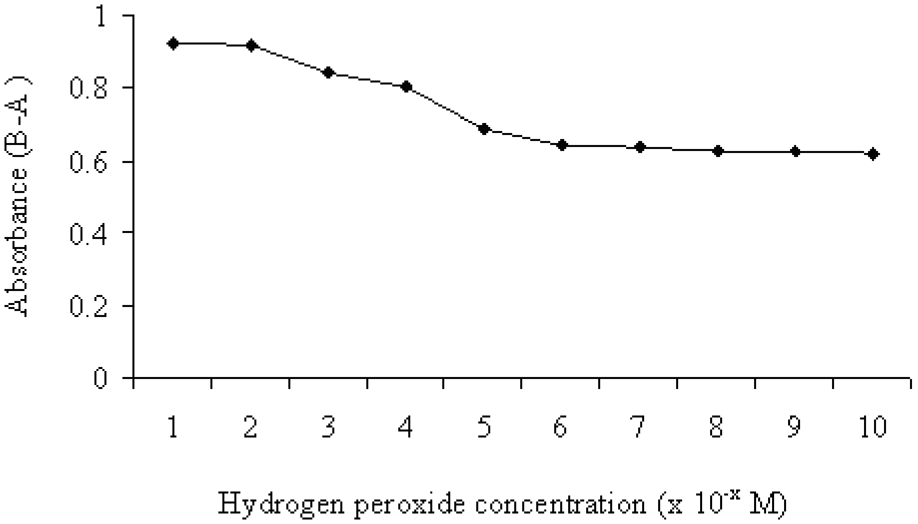

Fig.2 Effect of Hydrogen peroxide concentration on the reaction rate of 200 ng mL^{-1} vanadium (V)
Conditions: Potassium chloride – hydrochloric acid buffer (pH 1) (2 mL); Ponceau S$_{conc}$: 5.6x10^{-6} mol L^{-1}, measuring time 2.0 min; temperature 30 ^{0}C

The effect of ionic strength on the reaction rate was also investigated. The ionic strength was varied using KNO_3 solution. Variation in the ionic strength up to 0.18 M does not affect the performance of the catalytic method. Higher concentrations decrease the reaction rate slowly.

5. Analytical parameters

5.1. Calibration

Calibration graphs were obtained by applying the slope and fixed time method. The calibration graphs obtained by the fixed time method were linear in the range of 2–400 ng mL^{-1} and with the slope method in the range of 2–250 ng mL^{-1} of vanadium (V). The analytical figures of merit are illustrated in Table 1. The validity of the calibration model used was shown by using ANOVA. The sum of squares due to the regression as a percentage of the total sum of squares is 99.8%, showing that a reasonably large proportion of the variance is explained by the regression equation. It was found that the fixed time method offered a larger linear dynamic range as well as a higher precision. The calibration graph was obtained according to the recommended procedure. If higher concentrations of vanadium (V) have to be tested, the amount of added hydrogen peroxide should be decreased (Table 2).

Table 1 Analytical figures of merit for determination of vanadium (V) using different kinetic methods

Linear range (ng mL^{-1})		correlation coefficient	detection limit (ng mL^{-1})	RSD%
Fixed time	2 – 400	0.999	0.4	2.24
Slope method	2 – 250	0.998	0.6	2.73

Table 2 Linear calibration range for vanadium (V) at different concentrations of hydrogen peroxide

$[H_2O_2]$ (mol L^{-1})	Linear range (ng mL^{-1})	Correlation coefficient	Detection limit (ng mL^{-1})	RSD (%)
0.0008	2–400	0.9991	0.4	2.24
0.001	200–2000	0.9986	200	1.9

5.2. Precision and limit of detection

The precision of the method was measured by the analysis of seven independent solutions of 200 ng mL^{-1} of vanadium (V). The relative standard deviation was 2.24% and the limit of detection for this study was 0.4 ng mL^{-1} using fixed time method.

5.3. Kinetic parameters

The partial orders in each variable were found based on the initial rate versus concentration plots. The order of the catalyzed reaction with respect to hydrogen peroxide, Ponceau S and vanadium (V) was calculated from the resulting log–log plots; that is, respectively 1.31, 0.83 and 0.66. The Arrhenius plot was used for the determination of activation energy for both catalyzed and uncatalyzed reactions. The activation energy of un- catalyzed reaction is 3.16 times of the catalyzed reaction. This indicates that vanadium (V) is an effective catalyst in this reaction.

5.4. Interference study

Under the same optimum conditions cited above and with 100 ng mL^{-1} of V (V), a systematic study of the effect of foreign ions was undertaken. The results are summarized in Table 3. The tolerance limit of ions was fixed, as the maximum amount causing an error not greater than 3% in the absorbance. As it is shown, the method is relatively specific for vanadium (V) and the determination of vanadium (V) can be easily and selectively performed in the presence of other ions and especially in the presence of cations that are usually interfering in vanadium (V) determination.

5.5. Application

To evaluate the analytical applicability of the method, the recommended procedure was applied to the determination of vanadium (V) in tap water and wastewater using standard addition method. The water samples were pre-concentrated in order to obtain reliable results by AAS [21], whereas this treatment is not required in the kinetic method. For comparing the results of this new kinetic method with those of an established procedure (AAS method), we applied the *t*-test to compare the two sample means $\bar{x}_{kin}$ and $\bar{x}_{AA}$. It can be concluded from Table 4 that there is no significant difference between the results obtained by the two methods. By using the *F*-test it has been shown (Table 4) that there is no significant difference in the precision of both methods. The results show that the method is suitable for the analysis of tap water and wastewater samples

Table 3 Tolerance ratios of various ions in the determination of 100 ng mL^{-1} V (V)

Ions	Tolerance ratio ions to V(V) (w:w)
NO_2^-, $H_2PO_4^-$, HPO_4^{2-}, MoO_4^{2-}, SCN^-, CN^-, ClO_4^- , $S_2O_5^{2-}$, $B_4O_7^{2-}$, SO_3^{2-}, SO_4^{2-}, CH_3COO^-, I^-, Br^-, Cl^-, HCO_3^-, CO_3^{2-}	2000[a]
Mg (II), UO_2^{2-}, Ca (II), Ba (II), NH_4^+, Mo (VII)	2000[a]
Cr (VI), Cr (III), Se (IV)	1000
In (III), Hg (II)	200
Hg (I), Co (II), Mn (II), Mn (VII), As(III)	100
Al (III), Pb (II), Ag (I), Zn (II), Fe(II), Cd(II), IO_3^-, IO_4^-Fe (III)	10

[a] Maximum concentration examined.

Table 4 Analysis of tap water and wastewater samples by the proposed method

Sample	$\bar{x}_{kin}$ [a]	$\bar{x}_{AA}$ [b]	s_{kin} [c]	s_{AA} [c]	t_{exp} [d]	F_{exp} [d]
Tap water	26	23	1.014	2.298	2.06	5.13
Wastewater	105.8	114.4	2.861	4.445	0.98	2.41

[a] Mean of three measurements by the proposed kinetic method.

[b] Mean of three measurements by atomic absorption method

[c] s_{kin} and s_{AA} are the standard deviations of measurements by the proposed kinetic method and atomic absorption method, respectively.

[d] t_{exp} and F_{exp} show the experimental student – t and F values, respectively ($t_{0.05}$ = 2.13) and $f_{0.05}$ (2.2) = 19.00.

6. Conclusion

This study successfully investigated vanadium (V) traces in the range 2–400 (± 2%) ng mL^{-1} based on vanadium's catalytic effect on the oxidation of Ponceau S (2,7-Naphthalenedisulfonicacid, 3-hydroxy-4-[[2-sulfo- 4[(4sulfophenyl)_azo]phenyl]azo]-,tetra sodium salt) with hydrogen peroxide in an acidic media. The method described in this study can have a useful application in the determination of vanadium especially in wastewater and tap water samples.

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