

Trace Amounts Determination of Vanadium (V) Using a New Kinetic-Catalytic Reaction System

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ABSTRACT

This study describes a new simple, sensitive and selective catalytic kinetic spectrophotometric method for the determination of vanadium (V). The method is based upon the catalytic effect of vanadium (V) on the oxidation of Carminic acid by bromate in sulfuric acid media. The reaction was followed spectrophotometrically by measuring the decrease in absorbance at 490 nm and the dependence of sensitivity on the effective reaction variables was studied. Under optimum experimental conditions, the fixed time procedure was used to obtain a calibration curve over the range of 0.05–10.8 $\mu\text{g mL}^{-1}$ of vanadium (V). The calculated detection limit was 0.015 $\mu\text{g mL}^{-1}$ for twelve replicate measurement of blank signal. The relative standard deviations ($n = 6$) were 1.12, 0.98% for 2.0, 8.0 $\mu\text{g mL}^{-1}$ of vanadium (V), respectively. The effect of various species commonly associated with vanadium (V) in real samples was also investigated. The proposed method was successfully applied for the determination of vanadium (V) in water and standard alloy samples.

Keywords: Carminic acid; Kinetic; Spectrophotometry; Vanadium (V)

INTRODUCTION

Vanadium which is extensively distributed in nature is not in metallic form. However, vanadium does occur in over 65 known, naturally occurring minerals and is a major trace metal in fossil fuels. Although foods generally contain low concentrations of vanadium, food is the major source of exposure to vanadium. Daily intake of vanadium is in order of 10 - 30 μg and may vary widely [1]. The discovery of vanadium-activated enzymes in lower forms of life suggests that it may have a similar role in higher animals. It has been hypothesised that vanadium may function to regulate the sodium potassium-adenosine triphosphatase ([Na, K] - ATPase) enzyme and thus, the sodium pump [2]. Most ingested vanadium

is apparently unabsorbed (95%) and is excreted via the feces. Absorbed vanadium is mainly bound to transfer in and transported in the plasma, with 40 – 60% of the assimilated vanadium being excreted in the urine within 24 hours [3]. As a general rule, along with the increase of valency, the toxicity of vanadium increases. Therefore, vanadium (V) being the most toxic. In humans, toxicity causes diverse effects on the respiratory system, central nervous system, digestive system, kidneys and skin. There are very few reported cases of vanadium toxicity in humans where exposure has not been by inhalation [4]. A number of analytical techniques have been reported for vanadium (V) determination.

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Some of the most recently used methods are high performance liquid chromatography (HPLC) [5, 6], electrothermal atomic absorption spectrometry (ETAAS) [7], inductively coupled plasma mass spectrometry (ICP-MS) [8], colorimetric solid phase extraction (C-SPE) [9], catalytic adsorptive stripping voltammetry (CASV) [10, 11], high performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS) [12-14], liquid chromatography (LC) [15], inductively coupled plasma atomic emission spectrometry (ICP-AES) [16], inductively coupled plasma optical emission spectrometry (ICP-OES) [17, 18].

Kinetic-spectrophotometric method is an attractive alternative method for vanadium (V) determination, because they have advantages such as high sensitivity, sufficient accuracy, simple procedures and the necessity of less expensive apparatus that used for the determination of different species such as iodide [19], bromide [20], and morphine [21]. Some kinetic methods have been reported for vanadium (V) determination. The most of the methods are based on the catalytic effect of vanadium (V) on oxidation of organic compounds by bromate such as p-methyldibromoarsenazo [22], gallocyanine [23], perphenazine [24], 1-naphthyl red [25], metol [26], N, N-diphenylhydrazine [27], Nile blue [28], n-(3-sulfopropyl)-3,3',5,5'-tetramethyl benzidine [29], thionin [30], indigo carmine [31], 1,8-diaminonaphthalen [32], anyline blue [33], n, n'-bis (2-hydroxyl-3-sulfopropyl)-tolidin [34], ponceau xyldine [35], gallic acid [36], 3,5-diaminobenzoic acid [37].

In this study, we propose a simple and sensitive kinetic spectrophotometric method for the determination of vanadium (V) based on its catalytic effect on the oxidation of Carminic acid (CA) with bromate in acidic media. The absorbance change of CA at 490 nm is proportional to the vanadium (V) concentration. The reaction was followed

spectrophotometrically by monitoring the decrease in absorbance at 490 nm with a fixed time of 0.5 - 3.5 minutes. Thus, we developed a simple, sensitive and selective method for the kinetic determination of vanadium (V). The resulting method which has a detection limit 0.015 ng mL^{-1} , has been successfully applied to the determination of vanadium (V) in real samples with different matrices.

EXPERIMENTAL

Materials and method

Analytical-grade chemicals and redistilled water were used. At first, 100 mL of a vanadium (V) solution of $60.0 \text{ } \mu\text{g mL}^{-1}$ (as vanadium (V) stock solution) was prepared by dissolving 0.0138 g of NH_4VO_3 (Merck) in water and diluting to 100 mL in a volumetric flask. Working solutions were prepared by appropriate dilution with water daily. A solution of Carminic acid ($1.2 \times 10^{-3} \text{ mol L}^{-1}$) was prepared by dissolving 0.0591 g of it in water and then diluting to 100 mL in a volumetric flask. A sulfuric acid solution (2.0 mol L^{-1}) was prepared by diluting appropriate amount of sulfuric acid ($a = 98\%$, $d = 1.84 \text{ kg L}^{-1}$) to 100 mL; a 0.06 mol L^{-1} of potassium bromate stock solution was subsequently prepared by dissolving 1.0020 g of KBrO_3 in water and diluting to 100 mL in a volumetric flask.

Apparatus

A Shimadzu UV-Vis spectrophotometer (160-A, Japan) with 1-cm glass cell was used to measure the absorbance. A thermostated water bath (Heidolph, Germany) was used to keep the temperature of all solutions at the working temperature ($25.0 \pm 0.1^\circ\text{C}$). A stop-watch was used to record the reaction time.

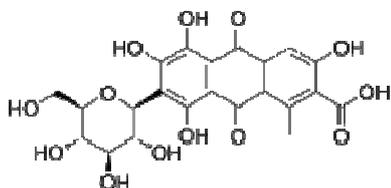
General procedure

After initial kinetic spectrophotometric studies of the reaction, the reagent concentrations (except the catalyst) were

judiciously chosen for the analytical procedure. To a series of 10 mL calibrated flasks, 1.0 mL of 2.0 mol L⁻¹ sulfuric acid solution, 0.75 mL of a 1.2 × 10⁻³ mol L⁻¹ CA solution and 1.0 mL of 0.06 μg mL⁻¹ of vanadium (V) solution were added. Then, 0.5 mL of 6.0 × 10⁻² mol L⁻¹ bromate solution was added and diluted to the mark with redistilled water. The time measurement started just after adding the last drop of the oxidant solution. After thorough mixing, a portion of this solution was transferred to a glass cell, and the absorbance was measured against water at 490 nm and 25 °C for fixed times of 0.5 and 3.5 min. The measurements were repeated in the absence of vanadium (V) to obtain the value for the uncatalyzed reaction as the absorbance of blank. The absorbance changes of the catalyzed and uncatalyzed reactions were labeled ΔA_c and ΔA_u respectively. The difference in the absorbance (ΔA = ΔA_c - ΔA_u) was considered as the response.

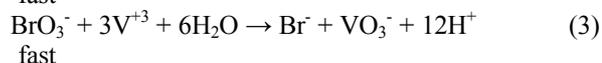
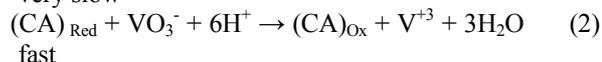
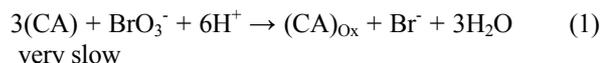
RESULTS AND DISCUSSION

CA (see Scheme 1 as molecular structure) is a basic dye that can be oxidized by oxidizing agents, such as bromate in acidic media as a slow reaction to produce a colorless oxidized form. It was used as an indicator for the catalytic determination of cobalt [38], iron [39], nitrite [40], gallium [41], osmium [42].

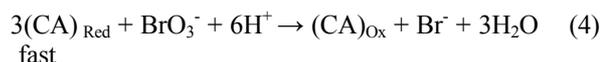


Scheme 1. Molecular structure of Carminic acid (7-α-D-Glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxoanthracenecarboxylic acid).

The reaction mechanism for CA-bromate system may be represented as follow:
Catalytic reaction carries out in a cyclic way by these reactions:



In the presence of vanadium (V):



The catalytic effect of vanadium (V) on the reaction system was shown in Fig. 1. As it can be seen, the change in absorbance on the mixture of sulfuric acid (0.32 mol L⁻¹) and CA (1.2 × 10⁻⁴ mol L⁻¹) (spectrum *b*) in comparison of initial spectrum that was recorded at the same conditions in absence of bromate (spectrum *a*) is negligible. Adding trace amounts of vanadium (V) to the mixture resulted to increasing the reaction rate. The spectra of *c* and *d* that recorded in presence of 6.0 and 8.0 ng of vanadium confirm the declare. Therefore, vanadium (V) has a good catalytic effect on the proposed reaction system and can result to develop a sensitive method with low detection limit for the determination of it.

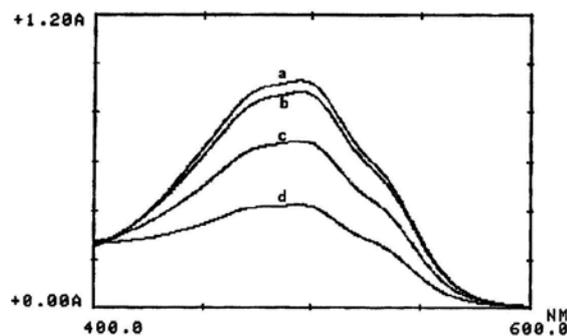


Fig. 1. Absorption spectra of the Carminic acid-bromate system at 25 °C and time 3.5 min.
(a) CA (1.2 × 10⁻⁴ mol L⁻¹); H₂SO₄ (0.32 mol L⁻¹).
(b) CA (1.2 × 10⁻⁴ mol L⁻¹); H₂SO₄ (0.32 mol L⁻¹); bromate (6 × 10⁻³ mol L⁻¹).
(c) CA (1.2 × 10⁻⁴ mol L⁻¹); H₂SO₄ (0.32 mol L⁻¹); Vanadium(V) (6.0 ng); bromate (6 × 10⁻³ mol L⁻¹).
(d) CA (1.2 × 10⁻⁴ mol L⁻¹); H₂SO₄ (0.32 mol L⁻¹); Vanadium (V) (8.0 ng); bromate (6 × 10⁻³ mol L⁻¹).

Optimization of reaction variables

In order to establish the experimental conditions under which the catalytic effect of vanadium (V) and therefore, the sensitivity in

its determination to be at maximum, the dependence of the reaction rate to temperature, time and reagents concentration were studied. The change in absorbance after fixed time as a measure of initial rate was used to plot the graph for each variable. Optimum conditions were taken from the graphs for the subsequent study of the variables. The reagent concentration optimization was carried out on the uncatalyzed and catalyzed reactions for a constant time of 3.5 minutes in the presence of 1.0 mL of $0.06 \mu\text{g mL}^{-1}$ of vanadium (V).

Effect of sulfuric acid concentration

The effect of sulfuric acid concentration on the uncatalyzed and catalyzed reactions was studied in the concentration range 0.12 to 0.45 mol L^{-1} . As shown in Fig. 2, the reaction rate increases with increasing concentration of sulfuric acid up to 0.32 mol L^{-1} . At higher concentrations, the reaction rate was decreased. This decrease at higher acidic conditions may be attributed to the protonation of CA which might stop oxidation or make oxidation quite difficult to occur. Thus, 0.32 mol L^{-1} of sulfuric acid was used for further study.

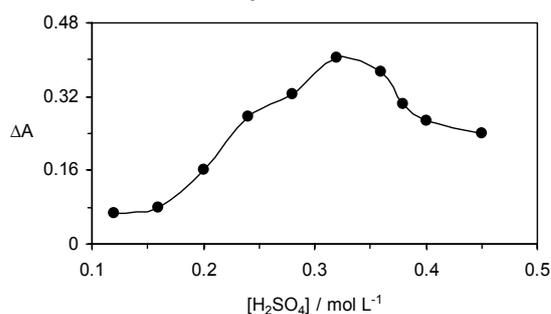


Fig. 2. Effect of sulfuric acid concentration on the rate of reaction: Carminic acid, $0.75 \text{ mL } (1.2 \times 10^{-3} \text{ mol L}^{-1})$; Vanadium (V), 6.0 ng ; bromate, $0.5 \text{ mL } (6.0 \times 10^{-2} \text{ mol L}^{-1})$; temperature, 25°C ; time, 3.5 min .

Effect of carminic acid concentration

The experimental results on the study of CA concentration effect in the range 75 to $170 \mu\text{mol L}^{-1}$ indicates that difference in absorbance increases with the concentration

of CA up to $120 \mu\text{mol L}^{-1}$ (Fig. 3). Therefore, $120 \mu\text{mol L}^{-1}$ of CA was selected as optimum value.

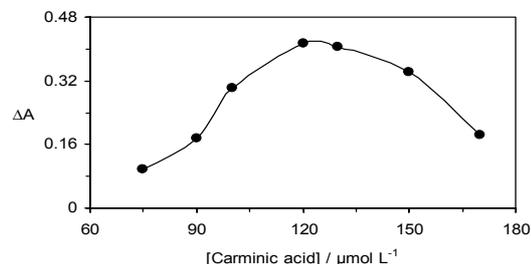


Fig. 3. Effect of Carminic acid concentration on the reaction rate: H_2SO_4 , $1.6 \text{ mL } (2.0 \text{ mol L}^{-1})$; Vanadium (V), 6.0 ng ; bromate, $0.5 \text{ mL } (6.0 \times 10^{-2} \text{ mol L}^{-1})$; temperature, 25°C ; time, 3.5 min .

Effect of bromate concentration

The dependence oxidation reaction rate to bromate concentration was studied in the range of 1.0 to 9.0 mmol L^{-1} . As shown in Fig. 4, under optimum concentrations of H_2SO_4 and CA, the reaction rate increased up to 6.0 mmol L^{-1} of bromate. Therefore, the optimum value of 6.0 mol L^{-1} of bromate was selected for following the procedure.

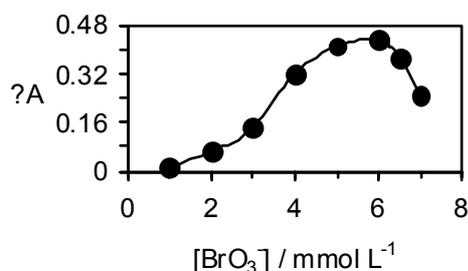


Fig. 4. Effect of bromate concentration on the reaction rate: H_2SO_4 , $1.6 \text{ mL } (2.0 \text{ mol L}^{-1})$; Carminic acid, $1.0 \text{ mL } (1.2 \times 10^{-3} \text{ mol L}^{-1})$; Vanadium (V), 6.0 ng ; temperature, 25°C ; time, 3.5 min .

Effect of temperature

Under optimum reagents concentration, temperature effect on the rate of reaction was studied in the range of 15 to 40°C . As shown in Fig. 5, increasing the temperature up to 30°C caused the change in absorbance was increased. Thus, 30°C was selected as optimum.

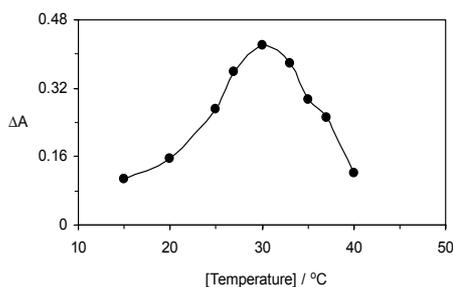


Fig. 5. Effect of temperature on the reaction rate: H_2SO_4 , 1.6 mL (2.0 mol L^{-1}); Carminic acid, 1.0 mL ($1.2 \times 10^{-3} \text{ mol L}^{-1}$); Vanadium (V), 6.0 ng; bromate, 1.0 mL ($6.0 \times 10^{-2} \text{ mol L}^{-1}$); time, 3.5 min.

Effect of reaction time

The optimum time was found by measuring the change in the absorbance during 30 to 360 s. The reaction rate was increased up to 210 s, and for longer times was almost constant. Therefore, 210 s was selected as optimum for further study.

Analytical parameters

Under optimum experimental conditions, calibration curve was obtained over the range of $0.05 - 10.8 \mu\text{g L}^{-1}$ of vanadium (V) using fixed time procedure. An analysis of the data gave the following regression equation: $\Delta A = 0.0755 [V^{+5}] + 0.0072$ ($R^2 = 0.9985$), where ΔA is the difference in absorbance between the blank and the sample, $[V^{+5}]$ is the vanadium concentration in $\mu\text{g L}^{-1}$ and R^2 is the correlation coefficient. Also, data analysis in concentration range $0.05 - 1.0 \mu\text{g L}^{-1}$ of vanadium (V) gave regression equation $\Delta A = 0.0451 [V^{+5}] + 0.0241$ ($R^2 = 0.9955$) and shows the good agreement between results in low concentrations. The detection limit ($3s_b/m$) was $0.015 \mu\text{g L}^{-1}$ of vanadium (V). The relative standard deviations ($n = 6$) were 1.12, 0.98% for 2.0, $8.0 \mu\text{g L}^{-1}$ of vanadium (V) respectively.

Interference studies

The interfering effect of foreign species in the determination of 10.0 ng mL^{-1} of vanadium (V) was investigated. The tolerance limit was defined as the concentration of the added

species causing an error (analytical signal) more than $\pm 5\%$. The results are given in Table 1. Interfering effect of nitrite was removed by adding 3.0 mL of 4% sulfamic acid solution to each sample. Also, the interfering effect of Fe^{+3} by adding 3.0 mL of 5% NaF was removed. Chloride interfering effect was removed by adding 3.0 mL of concentrated nitric acid and then boiling.

Real Sample Analysis

The accuracy and applicability of the proposed method has been confirmed by the determination of vanadium (V) water and standard alloy samples.

Analysis of Water Samples

The method has been employed for the determination of vanadium (V) in water samples with different matrices. The water samples from different sources were collected and filtered to remove suspended materials. The samples were spiked with different amounts of vanadium (V) and quantified using the recommended procedure. The results were given in Table 1. As it can be seen, the recovery varies in the range 98.8 to 101.8% that confirm the applicability of the developed method for the determination of vanadium (V) in water samples.

Analysis of Standard Alloy Samples

Also, the proposed method was applied for the determination of vanadium in Nippo Kcikinzoku Kogyo (NKK) No. 916 and No. 920 aluminum alloys. For this purpose, 0.1 g of the standard alloy sample was accurately weighed and dissolved in 10 mL of 1:1 nitric acid:water by heating and 1 mL of 30% (v/v) of hydrogen peroxide was added. After cooling and filtering, the solution was diluted to 100 mL in a volumetric flask. A suitable aliquot of the sample was used for the determination of vanadium by the proposed method. The results were given in Table 3. As it can be seen, the results are in good agreement with the certified value.

Table 1. Interfering effect of foreign species on the determination of 10.0 $\mu\text{g L}^{-1}$ of vanadium (V)

Foreign species	Tolerance limit ($W_{\text{Species}}/W_{\text{Vanadium(V)}}$)
Li^+ , Na^+ , K^+ , Ca^{+2} , Mg^{+2} , Al^{+3} , NH_4^+	1000
Ca^{+2} , Zn^{+2} , Bi^{+3} , Zr^{+4} , Cu^{+2}	950
Co^{+2} , Ti^{+4} , Sn^{+4}	800
Pb^{+2} , Ni^{+2} , Sb^{+5} , Ni^{+2}	700
$\text{Fe}^{+3\text{a}}$, Mo^{+6} , Cr^{+3}	650
NO_3^- , SO_4^{-2} , CH_3CO_2^- , PO_4^{-3} , H_2PO_4^-	1000
$\text{Cl}^{-\text{b}}$, $\text{NO}_2^{-\text{c}}$	800
Ag^+	290
Hg^{+2}	250

^a After adding 3.0 mL of 5% NaF.^b After adding 3.0 mL of concentrated nitric acid and boiling.^c After adding 3.0 mL of 4% sulfamic acid.**Table 2.** Determination of vanadium (V) in water samples

Sample	Added ($\mu\text{g L}^{-1}$)	Found (ng mL^{-1}) ^a	RSD (%)	Recovery (%)
Well water 1	-	DL<	-	-
	4.0	3.96 ± 0.05	1.26	99.0
	8.0	8.11 ± 0.09	1.11	101.4
Well water 2	-	DL<	-	-
	4.0	4.07 ± 0.07	1.72	101.8
	8.0	7.92 ± 0.08	1.01	99.0
Tap water	-	DL<	-	-
	4.0	3.95 ± 0.06	1.52	98.8
	8.0	8.10 ± 0.10	1.23	101.2
Drinking water	-	DL<	-	-
	4.0	4.03 ± 0.04	0.99	100.8
	8.0	7.94 ± 0.07	0.88	99.2

^a Mean \pm standard deviation (n = 5).**Table 3.** Determination of vanadium (V) in standard alloys

Sample	Composition	Concentration (%)	
		Certified value	Found ^a
NKK No. 916 (aluminum alloy)	Si, 0.41; Fe, 0.54; Mg, 0.10, Cr, 0.05; Zn, 0.30; Ti, 0.10; Sn, 0.05; Pb, 0.04; Sb, 0.01; B, 0.0006; Zr, 0.05; Bi, 0.03; Co, 0.03; Co, 0.03; Mn, 0.11; Ni, 0.06; Cu, 0.27	0.02	0.019 ± 0.001
NKK No. 920 (aluminum alloy)	Si, 0.78; Fe, 0.72; Mg, 0.46; Cr, 0.27; Zn, 0.80; Ti, 0.15; Sn, 0.20; Sn, 0.20; Pb, 0.10; Sb, 0.10; B, 0.06; B, 0.06; Ga, 0.05; Ca, 0.03; Co, 0.10; Mn, 0.20; Ni, 0.29; Cu, 0.27	0.15	0.16 ± 0.003

^a Mean \pm standard deviation (n = 5).

CONCLUSIONS

The results presented clearly demonstrate the catalytic effect of vanadium (V) on the oxidation of CA by bromate in acidic media. The results were applied to develop a simple methodology for the determination of vanadium (V) at trace levels. The detection limit of the proposed method was $0.015 \mu\text{g L}^{-1}$, which is lower than the other reported kinetic procedures, metol [26], indigo carmine [31], anyline blue [33], ponceau

xyldine [35], gallic acid [36] and 3,5-diaminobenzoic acid [37].

The proposed method can be used for the determination of vanadium (V) in a wider concentration range $0.05 - 10.8 \mu\text{g L}^{-1}$, compared with the other kinetic procedures, 1-naphthyl red [25], nile blue [28], indigo carmine [31], anyline blue [33], ponceau xyldine [35], gallic acid [36] and 3,5-diaminobenzoic acid [37].

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