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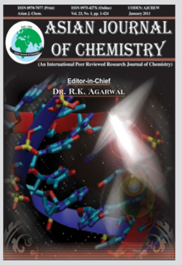

Kinetic-Spectrophotometric Determination of Trace Amounts of Vanadium(V) Based on its Catalytic Effect on the Reaction of *o*-Anisidine and Potassium Bromate

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A simple and sensitive first order kinetic-spectrophotometric method is proposed for the determination of vanadium(V) in nanogram amounts. This method is based on the catalytic effect of vanadium(V) on the oxidation of *o*-anisidine by potassium bromate in acidic medium (HCl). The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of *o*-anisidine solution at 420 nm by fixed time method (20 min). The proposed method allows determination of vanadium in the range of 0.128-7.213 ng/mL with good precision and accuracy. The optimization of the operating conditions regarding concentrations of the reagents, temperature and interferences are also investigated. The reaction was found to be first order in *o*-anisidine, vanadium(V) and bromate. The rate of the reaction is found to have an inverse dependence on H^+ concentration. The pseudo-first order rate constants are determined at different temperatures and thermodynamic parameters were evaluated. A possible mechanism has been proposed. The method was applied to the determination of vanadium(V) in meat sample, ground nut oil, seafood, black pepper and jack fruit. The results obtained were in excellent agreement with the standard methods such as atomic absorption spectrometry. The coefficient of variance and % error were in the range of 1.87- 3.26, 0.78-1.57 % respectively.

Key Words: Vanadium(V), *o*-Anisidine, Potassium bromate, Oxidation, Kinetic method.

INTRODUCTION

Kinetic methods of analysis have been frequently used in trace analysis to obtain high sensitivity combined with relatively simple procedure[1]. Many kinetic catalytic methods have been developed for determination of traces of vanadium because of its sensitive and selective oxidation catalysis of the oxidation reaction with potassium bromate[2]. Fuller and Ottaway[3-5] carried out a detailed study of unanalyzed and catalyzed oxidation of bourdeaux by bromate and proposed a method for determination of micro amounts of vanadium in several methods. Processes for determination of vanadium oxidation by catalytic reaction of gallic acid[6], chromotropic acid[7] and orothopehelene diamine[8] by potassium bromate are very useful. The reaction between chromotopic acid and bromate, catalyzed by vanadium has been studied by Takeshi Yamene *et al.*[7] for the determination of vanadium in microgram amounts. The catalyzed oxidation of gallic acid by bromate was investigated by Fukaseva *et al.*[9] to ascertain the kinetics of flow injection method spectrophotometrically. The suitability of the PDO system for the development of a kinetic method to determine small amounts of vanadium has been demonstrated by Comocha *et al.*[10]. Bazsa and Fabial[11] studied the vanadium(V) catalysis of the clock reaction involving bromate iodide-ascorbic acid and elucidated the mechanism of the reaction. Sasu and Constache[12] reported that vanadium(V) catalyzed reaction between BrO_3^- and Bourdeux R dye enabled to determine vanadium(V) in range of $4.5\text{-}27.2 \times 10^{-9}$ g/mL. These authors stated that the rate of the reaction is $2.3\text{-}10.6 \times 10^{-2}$ mol dm^{-1}. A method has been described for kinetic determination of vanadium by making use of its catalytic action for the oxidation reaction of eriochrome black T with bromate and it is reported[13] that this method enables to determine vanadium in the range of $1.14 \text{-}9.12 \times 10^{-10}$ g/mL. Trace amounts of vanadium were determined from study of kinetics of the system consisting of bromo-phenol blue, potassium bromate, vanadium(V) and citric acid[14]. Similarly another indicator reaction reported, basing on the catalytic effect of vanadium(V) on the oxidation of catechol violet by potassium bromate and α,α^- bipyridyl was also used as an activator in the reaction[15]. Kattschmer[16] developed kinetic method for the determination of vanadium, based on the kinetic action on the oxidation of mordent blue dye-9 with bromate at pH 2 in acetic acid medium. The vanadium content in urine and mineral waters was determined by above catalytic methods in perchloric acid medium[17]. Vanadium content has been determined by Xue *et al.*[18] for the determination of vanadium(V) in the mineral waters and human hair. Recently gallocyanine and gallamine blue were used in the indicator reaction with bromate for catalytic determination of vanadium(V) in nanogram amounts[19,20]. Kinetic spectrophotometric determination of vanadium(V) based on its catalytic effect on the reaction of chromotropic acid-bromate[21], 1,4-dihydroxyphthalimidedioxime[6], gallocyanine-bromate[7], 1-naphthyl red[22,23], DBM-arsenazo[24], indigo carmine[25] and potassium bromate had been reported. The authors in the present investigation have initiated work on the kinetic method of determination of vanadium(V) in nanogram amounts, utilizing its catalytic effect on the oxidation of *o*-anisidine with potassium bromate in acetic acid medium using fixed time method.

EXPERIMENTAL

Preparation of reagents: All reagents used were of analytical reagent grade quality. The triply distilled water was used for preparation of all the solution.

***o*-Anisidine:** 1 % or 0.0812 M solution of o-anisidine in 2 % methanol is prepared from Aldrich USA. The solution is diluted with triply distilled water and stored in the amber colour bottle. *o*-Anisidine was standardized by spectrophotometric, chromatography or TLC methods[26,27].

Potassium bromate: A 0.1 mol dm^{-3} potassium bromate (BDH, AR) solution was prepared by dissolving the requisite amount in triple distilled water and standardized[16].

Ammonium metavanadate solution: A 0.1 mol dm^{-3} ammonium metavanadate (BDH, Anala R) is prepared and standardized[28]. The solution was appropriately diluted whenever necessary.

A Shimadzu double beam spectrophotmeter (model No.UV140) with 10 nm matched quartz cells equipped with thermostat for kinetic measurement was used in this investigation.

Method: The course of the reaction is followed spectrophotometrically by measuring optical density of unreacted *o*-anisidine at 420 nm (Fig. 1), which is in good agreement with reported values[29]. At this wavelength Beer's law is obeyed in concentration range of substrate and hydrogen ion. All other materials concerned have negligible absorbtion at this wavelength. In all the kinetic runs the ionic strength is maintained constant by the addition of sodium chloride 5.0 mL of 1.62×10^{-4} mol dm^{-3} of *o*-anisidine was taken in a clean dry 50 mL volumetric flask 2.5 mL of 2.0×10^{-4} mol dm^{-3} HCl and 0.1 mL of 1.0×10^{-2} mol dm^{-3}. Vanadium(V) were added and the total volume is made upto 50 mL with 2.5-5.0 mL of 1.0×10^{-2} mol dm^{-3} potassium bromate solution with triply distilled water. A portion of this is transferred into a spectrophotometric cell and absorbance measurements were made at different time intervals.

RESULTS AND DISCUSSION

Dependence of rate of reaction on the concentration of *o*-anisidine: Several kinetic runs have been carried out for different concentrations of *o*-anisidine keeping the concentration of all the other reagents constant. The plots of log of optical density *versus* time for different initial concentration of *o*-anisidine were found to be linear, thus this showed that the reaction obeys first order kinetics with respect to concentration of *o*-anisidine. These straight lines were parallel, further confirming the first order behaviour (Fig. 2). The values of pseudo first order rate constants for different initial concentrations of *o*-anisidine are tabulated in Table-1 for the catalyst vanadium(V).

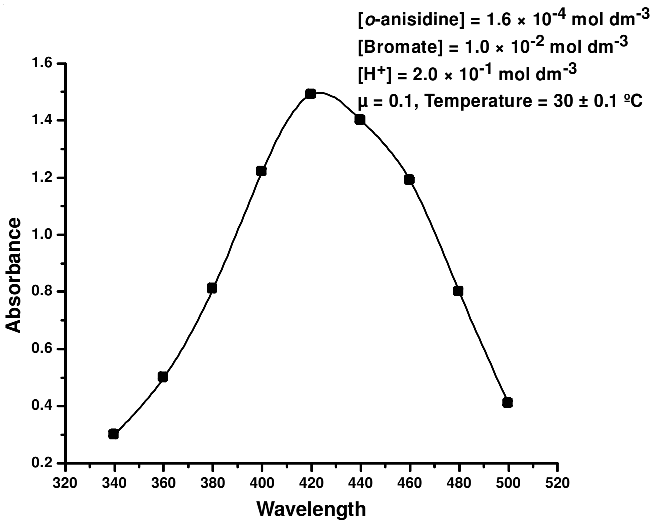

Fig. 1. Plot of absorbance against wavelength

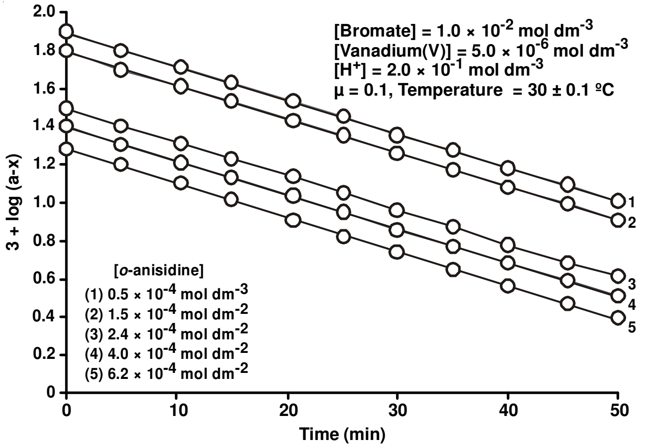

Fig. 2. First order plots for vanadium(V) catalyzed bromate-*O*-anisidine reaction, variation of [*o*-anisidine].

TABLE-1
DEPENDENCE OF RATE OF REACTION ON THE CONCENTRATION OF *o*-ANISIDINE

S. No.	*o*-Anisidine × 10^4 mol^{-1} dm^{-3}	$K_1 \times 10^3$ min^{-1} [vanadium(V)]
1	0.5	9.2
2	1.5	9.1
3	2.4	9.2
4	4.0	9.2
5	6.2	9.2

$[BrO_3^-] = 1.0 \times 10^{-2}$ mol dm^{-3}, Vanadium(V) = 5.0×10^{-6} mol dm^{-3}
$[H^+] = 2.0 \times 10^{-1}$ mol dm^{-3}, $\mu = 0.1$, Temperature = 30 ± 0.1 ºC

Dependence of rate of reaction on concentration of bromate ion: Several kinetic runs were carried out for different concentration of BrO_3^- keeping the concentration of all other reagents constant. The plot of logarithm of optical density *versus* time are found to be straight lines. The pseudo first order rate constants calculated for each concentration of BrO_3^- are tabulated in Table-2. The plots of pseudo first order rate constant *versus* BrO_3^- concentration for vanadium(V) were found to be straight line passing through origin (Fig. 3). This indicates first order dependence of rate on the concentration of BrO_3^-.

TABLE-2
DEPENDENCE OF RATE OF REACTION ON CONCENTRATION OF BrO_3^-

S. No	$[BrO_3^-] \times 10^2$	$K_1 \times 10^3$ min^{-1}
1	1.0	3.2
2	2.0	9.4
3	2.7	12.4
4	3.2	14.5
5	4.5	20.9
6	5.0	23.0

[*o*-anisidine]= 1.62×10^{-4} mol dm^{-3}, [Vanadium] = 5.0×10^{-6} mol dm^{-3}
$[H^+] = 2.0 \times 10^{-1}$ mol dm^{-3}, $\mu = 0.1$, Temperature = 30 ± 0.1 °C

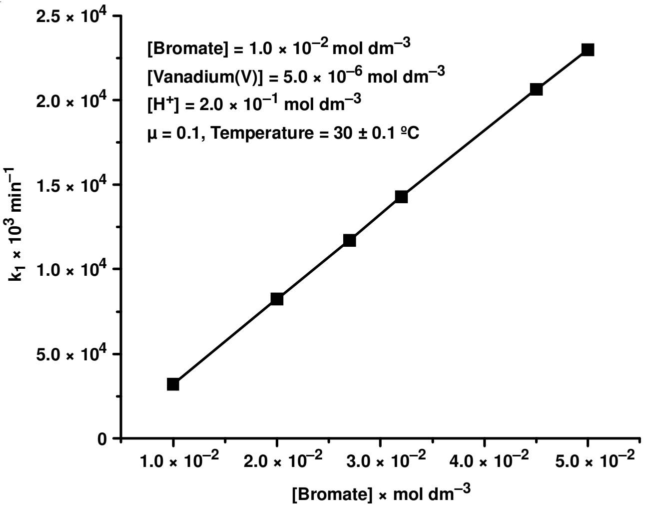

Fig. 3. Plot of first order rate constant against [bromate].

Dependence of rate of reaction on the concentration of vanadium(V): Several kinetic runs were carried out for different concentrations of vanadium(V) keeping the concentration of all other reagent constant. The log of absorbance was plotted against time. These are straight lines (Fig. 4), indicating the first order dependence of rate of the reaction for the concentration of vanadium(V). The pseudo first order rate constants are calculated and tabulated in Table-3.

TABLE-3
DEPENDENCE OF RATE OF REACTION ON THE CONCENTRATION OF VANADIUM(V)

S. No.	[Vanadium(V)] × 10^6	$K_1 \times 10^3$ min^{-1}
1	2.5	4.8
2	5.0	9.2
3	7.5	14.1
4	8.7	15.2
5	10.0	19.4

[*o*-anisidine] = 1.62×10^{-4} mol dm^{-3}, $[BrO_3^-] = 1.0 \times 10^{-2}$ mol dm^{-3}
$[H^+] = 2.0 \times 10^{-1}$ mol dm^{-3}, $\mu = 0.1$, Temperature = 30 ± 0.1 °C

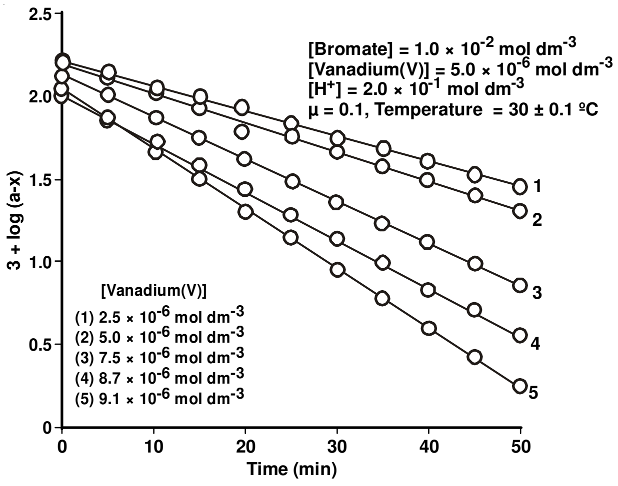

Fig. 4. First order plots for vanadium(V) catalyzed bromate-*o*-anisidine reaction, variation of [vanadium(V)].

Dependence of rate on H^+ concentration: To understand the nature of dependence of the rate of the reaction on H^+ concentration, several kinetic runs were carried out at different concentrations of HCl in the range 1.0 - 3.0 × 10^{-1} mol dm^{-3}. The plots of log of absorbance *versus* time are found to be straight lines. The pseudo first order constants are plotted against reciprocal of H^+ concentration. A straight line passing through origin is obtained for vanadium(V) indicating the inverse dependence of rate of the reaction on the H^+ concentration and results are present in Table-4 (Fig. 5).

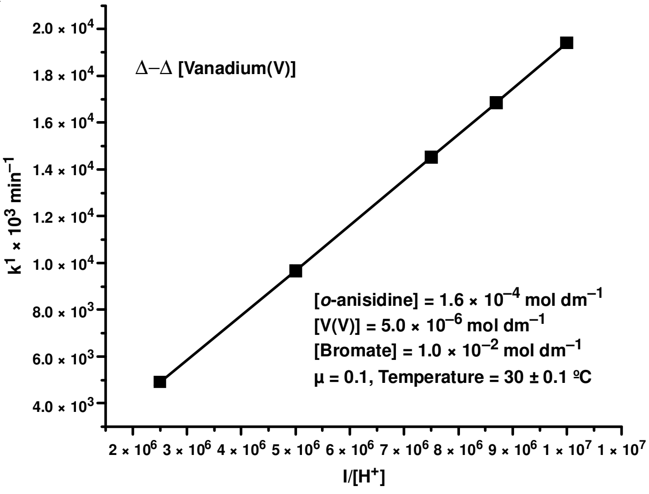

Fig. 5. Plot of first order rate constant against 1/[H$^+$]

TABLE-4
DEPENDENCE OF RATE ON HYDROGEN ION CONCENTRATION

S. No	[HCl] × 10^2 mol dm^{-3}	$K_1 \times 10^3$ min^{-1}
1	1.0	9.2
2	2.0	5.5
3	3.0	5.2
4	4.0	4.3
5	8.0	2.1

[*o*-anisine] = 1.62×10^{-4} mol dm^{-3}, [vanadium(V)] = 5.0×10^{-6} mol dm^{-3}, $[BrO_3^-] = 1.0 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-1}$ mol dm^{-3}, $\mu = 0.1$, Temperature = 30 ± 0.1 °C

Effect of temperature: The pseudo-first order rate constants are determined at different temperatures and thermodynamic parameters evaluated from the study are

$$\Delta E = 13.67 \text{ Kcal mol}^{-1}$$

$$\Delta S = -66.67 \text{ Kcal deg}^{-1} \text{ mol}^{-1}$$

$$\Delta H = -21.28 \text{ Kcal mol}^{-1}$$

The salient kinetic features of kinetic investigation of vanadium(V) catalyzed oxidation of *o*-anisidine by BrO_3^- are:

(1) The reaction follows first order kinetics with respect to *o*-anisidine.

(2) The reaction obeys first order kinetics with respect to BrO_3^- and catalyst vanadium(V).

(3) The rate of the reaction shows inverse dependence on H^+ concentration.

Vanadium(V) is known to exist completely[30-33] in the form VO^{2+} at pH ≤ 2. The acid dissociation constant of $HBrO_3$ has a value of 5.0 [34] and hence an acid concentration employed $3.0\text{-}10.0 \times 10^{-2}$ mol dm^{-3}. Protonation of BrO_3^- giving $HBrO_3$ is negligibly small and all the Br exists in the form of BrO_3^-. The assumption that the unprotonated form being more nucleophilic, acts as a better reducing species than the protonated form and lack of appreciable ionic strength effects on the rate of the reaction suggests the participation of electrically neutral species in the rate determining step. The authors propose the following scheme which satisfactorily explains the observed kinetic results.

Scheme-I

$$VO_2^{2+} + BrO_3^- \xrightleftharpoons{K_1} VO_2BrO_3^+ \qquad (1)$$

$$OAH^+ \xrightleftharpoons{K_2} OA + H^+ \qquad (2)$$

$$VO_2BrO_3 + OA \xrightarrow{K} \text{Products} \qquad (3)$$

In this scheme OAH^+ and OA represent protonated and unprotonated *o*-anisidine respectively.

Derivation of rate law: The mass balance for the protonated and unprotonated forms of *o*-anisidine can be represented by equation.

$$[OA]_t = [OAH^+] + [OA] \qquad (4)$$

where, $[OA]_t$ represents total concentration of *o*-anisidine. But according to eqn. (2)

$$K_2 = [OA][H^+]/[OA\ H^+] \qquad (5)$$

from eqn. (4) and (5)

$$[OA]_t = (OA)(H^+)/K_2 + (OA)$$

$$= (OA)\ ([H^+]) + K_2)/K_2 \text{ (or)}$$

$$[OA] = [OA]_t + K_2/[H^+] + K_2 \qquad (6)$$

The pk_2 value for the protonation equilibrium of *o*-anisidine[35] was 1.9×10^{-10} mol dm^{-3} and kinetic investigation has been carried out in the range of $3.0\text{-}10.0 \times 10^{-2}$ mol dm^{-3}. in the equation (6) $K_2 << [H^+]$ and hence the equation (6) undergoes modification as:

$$[OA] = K_2\ [OA]_t\ /[H^+]$$

According to proposed mechanism:

$$\text{Rate} = -d/dt\ [OA]$$

$$= k\ [VO_2BrO_3]\ [OA]$$

$$= kK_1K_2[VO_2^+][BrO_3^-][OA]t/[H^+] \qquad (7)$$

The pseudo first order rate constants, K_1 under the conditions $[BrO_3^-] >> [OA]_t$

$$K_1 = kK_1K_2[VO_2^+][BrO_3^-]/[H^+] \qquad (8)$$

The equations (7) and (8) satisfactorily explain all the observed kinetic features of the reactions. In view of kinetic results obtained in the studies on the vanadium(V) catalyzed oxidation of *o*-anisidine by bromate, present authors made an attempt to exploit the profound catalytic behaviour of vanadium(V) for the determination of various metal ion in the nanogram amounts using fixed time method.

Determination of vanadium(V) by the catalytic method: The authors in the present investigation have initiated work on the kinetic method of determination of vanadium(V) in the nanogram amounts utilizing its catalytic effect on the oxidation of *o*-anisidine with potassium bromate in the acetic acid medium using the fixed time method.

Recommended procedure: The authors recommend the following procedure for the determination of the Δx values to the measure the extent of reaction at the end of the twentieth minute.

Calculated quantities of *o*-anisidine and HCl to give an overall concentration of 5.0×10^{-6} mol dm^{-3} and 2.0×10^{-1} mol dm^{-3} respectively are mixed to known volume of vanadium(V) and total volume is made upto 50 mL using triply distilled water. Then calculated quantity of potassium bromate to give an overall concentration of 1.0×10^{-2} mol dm^{-3} was added to reaction mixture, simultaneously starting a stopwatch. Exactly after 20 min, optical density is measured. The initial optical density of a sample of the reaction mixture without adding potassium bromate is measured. The difference between the optical densities was taken as Δx.

Construction of calibration curve: The Δx value are determined at different known concentration of vanadium(V). The results obtained for typical study are given in Table-5. The plot of Δx *versus* vanadium(V) concentration is a straight line passing through the origin (Fig. 6), which serves as a calibration curve.

TABLE-5
DETERMINATION OF VANADIUM(V) BY THE CATALYTIC METHODS

S. No	Vanadium(V) (ng/mL)	Optical density at 20 min	ΔX
1	0.128	0.449	0.056
2	2.550	0.385	0.120
3	3.825	0.321	0.184
4	5.101	0.265	0.240
5	6.375	0.245	0.260
6	7.213	0.205	0.300

[*o*-anisidine] = 1.62×10^{-4} mol dm^{-3}, $[BrO_3^-] = 1.0 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-1}$ mol dm^{-3} $\mu = 0.1$, Temperature = 30 ± 0.1 ºC
Initial optical density = 0.505

Six Δx determination are made at different initial concentration of vanadium(V) keeping the concentration of all other reactants constant. Each of the Δx determinations is repeated six times in order to determine the standard deviation variance and percentage error from Δx values and by using calibration curve, the concentration of vanadium is determined in each case presented in Table-6. By using this data, authors calculated the standard deviation, coefficient of variance and percentage error. The results are presented in Table-7.

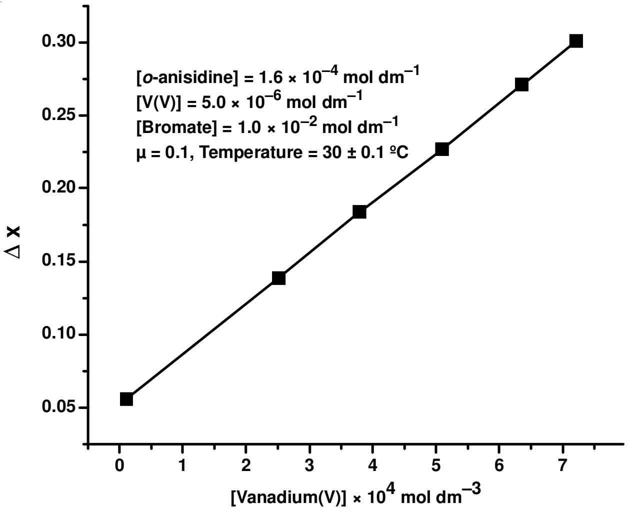

Fig. 6. Calibration graph for the kinetic catalyzed determination of vanadium(V).

TABLE-6
REPLICATE DETERMINATION OF VANADIUM(V)

Vanadium Taken	Vanadium found					
	I	II	III	IV	V	VI
0.128	0.127	0.128	0.129	0.127	0.126	0.128
2.550	2.551	2.550	2.523	2.550	3.825	2.552
3.825	3.826	3.824	3.825	3.824	3.825	3.825
5.101	5.101	5.102	5.103	5.101	5.100	5.102
6.375	6.377	6.376	6.375	6.378	6.376	6.377
7.213	7.215	7.217	7.214	7.216	7.218	6.377

[o-anisidine] = 1.62×10^{-4} mol dm^{-3}, [BrO_3^-] = 1.0×10^{-2} mol dm^{-3}
[H^+] = 2.0×10^{-1} mol dm^{-3}, Temperature = 30 ± 0.1 ºC

TABLE-7
STATISTICAL TREATMENT OF RESULTS

Vanadium(V) taken (µg/mL)	Amount of vanadium found (µg/mL)	Number of analysis	Coefficient of variance	Error (%)
0.128	0.127	6	3.26	0.78
2.550	2.510	6	2.85	1.57
3.825	3.827	6	2.76	0.05
5.101	5.110	6	1.87	0.18
6.375	6.382	6	2.35	0.11
7.213	7.301	6	2.46	1.22

[o-anisidine] = 1.62×10^{-4} mol.dm^{-3}, [BrO_3^-] = 1.0×10^{-2} mol dm^{-3},
[H^+] = 2.0×10^{-1} mol dm^{-3}, Temperature = 30 ± 0.1 ºC

Interference of various Ions in the determination of vanadium(V): The interferences of various foreign ions were studied and the results are presented in the Table-8. Ions like Na^+, Mn^{2+}, Cl^- do not have any effect on the extraction of vanadium, *o*-anisidine and bromate complex, when present up to 6,000 µg. Ions like Tl^+, Zn^{2+}, Cu^{2+}, K^+, Cd^{2+}, Th^{4+}, Br^- and I^- can be tolerated up to 5,000 µg. Li^+, Hg^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+} and Se^{4+} do not interfere when present up to 4,000 µg. Fe^{2+}, Sr^{2+}, V(IV), EDTA and F^- do not have any effect in the determination when present up to 2500 µg.

Application of the developed method: The developed kinetic-spectrophotometric method was applied for the determination of vanadium(V) in meat sample, ground nut oil, seafood, black pepper and jack fruit. The dried sample (5 g of each sample) was weighed and brought into solution by dry ash and wet digestion methods. The results are shown in Table-9. The results showed that the concentration of vanadium(V) is 0.045 µg in meat sample, 0.032 µg in ground nut oil, 0.027 µg in seafood, 0.097µg in black pepper and 0.007 µg in jack fruit.The results are compared with atomic absorption spectrophotometry and they are found to be in good agreement.

TABLE-8
EFFECT OF VARIOUS IONS ON THE DETERMINATION OF V(V) USING THE OPTIMUM CONDITIONS REPORTED UNDER ANALYTICAL PROCEDURE

S. No	Ions added	Tolerance limit µg/mL
1	Na^+, Mn^{2+}, Cl^-	6,000
2	Tl^+, Zn^{2+}, Cu^{2+}, K^+, Cd^{2+}, Th^{4+}, Br^-,I^-	5,000
3	Li^+, Hg^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, Se^{4+}, Oxalate	4,000
4	Fe^{2+}, Sr^{2+}, V(IV), EDTA, F^-	2,500

[o-anisidine] = 1.62×10^{-4} mol dm^{-3}, [BrO_3^-] = 1.0×10^{-2} mol dm^{-3},
[H^+] = 2.0×10^{-1} mol dm^{-3}, Temperature = 30 ± 0.1 ºC

TABLE-9
DETERMINATION OF VANADIUM(V) IN FOOD SAMPLES

Name of the food sample (5.0 g of each sample)	Vanadium Found		Recovery % present method
	Present method* (µg)	AAS method (µg)	
Meat Sample	0.045	0.046	97.8
Ground nut oil	0.032	0.034	94.1
Seafood	0.027	0.028	96.4
Black pepper	0.097	0.099	97.9
Jack Fruit	0.007	0.007	100

*Average value of three determinations
[o-anisidine] = 1.62×10^{-4} mol dm^{-3}, [BrO_3^-] = 1.0×10^{-2} mol dm^{-3},
[H^+] = 2.0×10^{-1} mol dm^{-3}, Temperature = 30 ± 0.1 ºC

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