

ORIGINAL ARTICLE

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa



Speciative determination of total V and dissolved inorganic vanadium species in environmental waters by catalytic-kinetic spectrophotometric method



Ramazan Gürkan*, Aysel Tamay, Halil İbrahim Ulusoy

University of Cumhuriyet, Faculty of Science, Department of Chemistry, TR-58140 Sivas, Turkey

Received 24 September 2011; accepted 12 June 2012 Available online 21 June 2012

KEYWORDS

Kinetic spectrophotometry; Gallamine blue; Catalytic effect; Fixed-time method; Vanadium speciation **Abstract** A kinetic determination of V(V) as a catalyst was spectrophotometrically performed by using the indicator reaction of Gallamine blue (GB⁺) and bromate at pH 2.0. The reaction was followed by measuring absorbance change for a fixed-time of 3 min at 537 nm. The variables such as reagent concentration, pH, buffer concentration, ionic strength and temperature were optimized to improve the selectivity and sensitivity. Under the optimized conditions, the determination of V(V) was performed in the range 1–100 µg L⁻¹ with limits of detection and quantification of 0.31 and 0.94 µg L⁻¹. The developed kinetic method is sufficiently sensitive, selective and simple. It was successfully applied to the speciative determination of total V and inorganic dissolved vanadium species, V(V) and V(IV) in environmental water samples. The oxidizing property of permanganate is used to differentiate between V(IV) and V(V) species. The V(IV) content was found by subtracting the V(V) content from those of total V. The recovery is above 95% for V(V) spiked samples. Additionally, the accuracy was validated by analysis of a certified water sample, CRM TMDA-53.3, and the results were in good agreement with the certified value.

© 2012 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

1. Introduction

Vanadium is an essential trace element due to its significant role in environment and physiological systems, involving par-

Peer review under responsibility of King Saud University.



ticipation in different enzymatic reactions as an inhibitor and cofactor (Crans et al., 1990), catalysis of the oxidation of various amines and normalization of sugar levels (Thompson et al., 1999). Vanadium is used widely in industrial processes including the production of special steel, temperatureresistant alloys, glass, pigments and paints, and for lining arc welding electrodes and as a catalyst. Vanadium compounds released in large quantities, mainly by burning fossil fuels and also from various industrial processes, are precipitated on the soil drained by rain and groundwater and can be directly adsorbed by plants (Pyrzynska and Wierzbicki, 2004). Dissolved vanadium generally exists in natural waters in two oxidation states, as vanadium(IV) and vanadium(V) (Wang and Wilhelmy, 2008), while vanadium(V) is more toxic

http://dx.doi.org/10.1016/j.arabjc.2012.06.006

1878-5352 © 2012 Production and hosting by Elsevier B.V. on behalf of King Saud University.

This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

^{*} Corresponding author. Tel.: +90 346 2191010/2136, mobile: +90 537 7910122.

E-mail addresses: rgurkan@cumhuriyet.edu.tr, rgurkan95@gmail. com (R. Gürkan).

than vanadium(IV) (Taylor and Staden, 1994). Therefore, it is important to monitor the concentration of individual oxidation form and total vanadium in the environment for evaluating both the potential risk and benefits. The concentration of vanadium in water is largely dependent on geographical location and ranges from 0.2 to >100 µg L⁻¹ in freshwater (Committee on Biologic Effects of Atmospheric Pollutants, 1974), from 0.2 to 29 µg L⁻¹ in seawater (Waters, 1977), and from about 0.2 to >100 µg L⁻¹ in drinking water (Vouk, 1979), typical values being between 1 and 6 µg L⁻¹ (Davies and Bennett, 1983).

Various analytical methods have been reported for the speciation and quantification at trace levels of vanadium in diverse samples. These techniques include: spectrophotometry (Kumar et al., 2007; Filik et al., 2004), flow injection spectrophotometry (Wei et al., 2008; Nakano et al., 2003), and spectrofluorimetry (Rama et al., 2005), air-segmented continuous flow analysis (Okamura et al., 2001), potentiometry (Umetsu et al., 1991), cathodic stripping voltammetry (Vega and Berg, 1994), thermometry (Mateu et al., 1994), flame and electrothermal atomic absorption spectrometry (Filik et al., 2008; Thomaidis and Piperaki, 1996), X-ray spectrofluorimetry (Civici, 1995), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Abbasse et al., 2002a,b), inductively coupled plasma mass spectrometry (ICP-MS) (Yang et al., 1996), capillary zone electrophoresis with UV detection (Jen et al., 1997), and liquid chromatography (Shijio et al., 1996). Some of these methods are sensitive and accurate but are expensive and time-consuming and require skillful operators. Various comprehensive reviews have also been reported in the literature addressing recent trends in the speciation and determination of vanadium in environmental and biological sample matrices, including important analytical aspects such as sample clean-up, preconcentration and method development (Pyrzynska and Wierzbicki, 2004; Amorim et al., 2007; Chen and Owens, 2008). Additionally, 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 (Chakrabarti, 1995; Sharma, 1982; Agnihotri et al., 2000; Melwanki and Seetharamappa, 2000). These methods are based on vanadium catalytic properties concerning the oxidation of certain organic compounds.

There are the recently published other reports (Leon-Camacho et al., 1991; Wang and Zhang, 1997; Pyrzynska, 2005; Safavi et al., 2000; Absalan and Alipour, 2003; Pouretedal and Keshavarz, 2006; Ensafi et al., 1999; Balaji et al., 1998; Sikalos et al., 2000; Liu et al., 2004; Zhou et al., 2007; Mastoi and Khuhawar, 2007; Abbaspour et al., 2007; Zhai et al., 2008; Ulusoy and Gürkan, 2009; Ji et al., 2010; Keyvanfard and Abedi, 2010; Shishehbore and Jokar, 2011; Gürkan and Gürkan, 2011) on the kinetic catalytic determination of vanadium, V(V) or V(IV) as catalyst using spectrophotometric and phosphorimetric methods based on the oxidation of various organic dyes with bromate, iodate and hydrogen peroxide in the presence or absence of activators. 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, accurate and reproducible kinetic spectrophotometric method with good selectivity and sensitivity for the determination of V(V) using its catalytic effect on the oxidation of Gallamine blue by bromate at pH 2.0 and 537 nm.

2. Experimental

2.1. Reagents and chemicals

Double-distilled water and analytical purity chemicals were used during experiments. 6.39×10^{-4} M of Gallamine Blue (GB^{+}) (Chroma) solution was prepared by dissolving 0.025 g of dye in water. 0.1 M of KBrO₃ (Merck) solution was prepared by dissolving it in water. Vanadium (IV) standard solution (1000 mg L^{-1}) was prepared from vanadyl sulphate, VOSO₄·5H₂O (Merck). Vanadium(V) standard solution (1000 mg L^{-1}) was prepared from ammonium metavanadate, NH₄VO₃ (Merck). Working solutions of V(V) and V(IV) were prepared by diluting stock solutions with water sequentially. Additionally, pH 2.0 phosphate buffer solution was prepared by using 0.2 M NaOH and 0.2 M H₃PO₄ solutions and monitoring the pH of the mixture with a pH meter. All stock solutions were stored in polyethylene containers. All labware used for handling solutions were cleaned with detergent solution, soaked in 1:1 (v/v) HCl, followed by vigorous shaking, rinsed thoroughly with deionized, distilled water.

2.2. Instrumentation

In this study, UV–Visible Spectrophotometer (Shimadzu UV1800-PC) equipped with the constant temperature cell holder. A water bath with a thermostat (Nüve NF 120) (operating in the range 20–100 °C) was used to control the temperature of reaction environment. A stopwatch was used to record the reaction time.

2.3. General procedure

Reaction rate was monitored at 537 nm by using the fixed-time method of 3 min with measuring spectrophotometrically the change in absorbance of reaction mixture. A portion of a sample solution containing V(V) was added to a volumetric flask of 10 mL. Then, 2 mL of pH 2.0 buffer solution and 1.0 mL of 6.39×10^{-4} M GB⁺ were added to flask. The solution was diluted to approximately 8 mL with water. Then 1 mL of 0.1 M KBrO₃ was added and the solution is diluted to 10 mL with water and thoroughly mixed. The absorbance change for catalyzed reaction ($\Delta A_{\rm C}$) was calculated by using absorbance difference at a fixed-time of 3 min. A reagent blank without V(V) for uncatalyzed reaction was prepared to obtain absorbance changes (ΔA_0). The net reaction rate or analytical signal, $(\Delta(\Delta A): \Delta A_{\rm C} - \Delta A_0)$ was calculated from the difference in absorbance changes at fixed-time of 3 min. A calibration graph was prepared by plotting the net analytical signal ($\Delta A_{\rm C}$ - $-\Delta A_0$ against V(V) concentration. All solutions were also pre-incubated in a water bath thermostated to 30 ± 0.1 °C prior to absorbance measurements.

2.3.1. Analysis of natural water samples

Before analysis, rainwater, stream water and lake water samples were filtered through 0.45 µm membrane filters after collecting them and stored in refrigerator at 4 °C. The pH of filtrates was acidified by using $6 \mod L^{-1}$ HNO₃. For tap water, the sample was collected after discharging tap water for about 30 min and boiled for 5 min to remove free chlorine. These sample solutions were acidified by adding nitric acid of 6 mol L^{-1} to pH about 1.0–1.5. In order to control the possible effect of interfering ions such as Fe(III), Hg(II), Cu(II), Cr(VI) and nitrite their interfering effects were removed by either adding a suitable complexing agent like EDTA, NaF and sulfamic acid to the reaction media or using a strongly cation-exchange resin after reduction of Cr(VI) to Cr(III) with ascorbic acid at the known concentration if necessary before detection of V(V)ions. In addition, the certified reference material, TMDA-53.3 was employed without any pretreatment process. Based on the kinetic method and FAAS analysis after preconcentration with evaporation of water samples into a known volume, they were comparatively analyzed by means of calibration curve and standard addition curve methods in order to control its accuracy and precision.

3. Results and discussion

Gallamine blue, a cationic oxazin group dye, which is known as phenoxazin-5-ium,1-(aminocarbonyl)-7-(dimethylamino)-3, 4-dihydroxy-, chloride (1:1), has the following structural formula in Scheme 1 and it shows an absorption maximum at 537 nm. A reason of dye being used as a substrate in indicator reaction, undergoes oxidation rapidly, selectively and quantitatively on treatment with bromate ion in the presence of trace levels of V(V) due to the participation of both redox sensitive and chelating agent functional groups such as cyclic hetero N-/ O-atoms and dihydroxy groups as well as chromophore and auxochrome groups.

The studies indicate that the oxidation rate of GB^+ by bromate is rather slow, in the absence of vanadium(V), whereas the indicator reaction is rather fast in the presence of vanadium(V) at trace levels. The absorption spectra for different vanadium concentrations were shown in Fig. 1.

3.1. Effect of pH

The pH effect on the catalyzed and uncatalyzed reaction rate for determination of V(V) at level of 25 μ g L⁻¹ was investigated in the range of 1.0–2.6 while the other variables are kept constant. As it can be seen in Fig. 2, pH 2.0 was found as an



Scheme 1 The open molecular structure of Gallamine blue (GB^+) .



Figure 1 The change of absorbance of GB⁺ with increasing V (V) concentration by using the fixed-time method of 3 min at 30 °C and 537 nm under the optimized conditions: (a) 2 mL pH 2.0 buffer solution, 1.0 mL of 6.90×10^{-4} M GB⁺. (b) 2 mL pH 2.0 buffer solution, 1.0 mL of 6.90×10^{-4} M GB⁺ and 1.0 mL of 0.1 M KBrO₃. (c) 2 mL pH 2.0 buffer solution, 1.0 mL of 6.90×10^{-4} M GB⁺ and 1.0 mL of 6.90×10^{-4} M GB⁺, 25 µg L⁻¹ V(V) and 1.0 mL of 0.1 M KBrO₃. (d) 2 mL of pH 2.0 buffer solution, 1.0 mL of 6.90×10^{-4} M GB⁺, 50 µg L⁻¹ V(V) and 1.0 mL of 0.1 M KBrO₃. (e) 2 mL of pH 2.0 buffer solution, 1.0 mL of 0.1 M KBrO₃. (e) 2 mL of pH 2.0 buffer solution, 1.0 mL of 6.90×10^{-4} M GB⁺, 75 µg L⁻¹ V(V) and 1.0 mL of 0.1 M KBrO₃. (e) 2 mL of pH 2.0 buffer solution, 1.0 mL of 6.90×10^{-4} M GB⁺, 75 µg L⁻¹ V(V) and 1.0 mL of 0.1 M KBrO₃. (h) 2 mL of 0.1 M KBrO₃ in final volume of 10.0 mL.



Figure 2 Effect of pH on analytical signal under the optimized conditions: pH 2.0, 1.0 mL of 6.39×10^{-4} M GB⁺, 1.0 mL of 0.1 M KBrO₃ and 25 µg L⁻¹ V(V) for fixed-time of 3 min at room temperature and 537 nm.

optimal value. The relation between analytical signal and pH for the net catalytic reaction was shown in Fig. 2.

Moreover, the effect of buffer concentration on analytical signal was also studied in the range of 0.03–0.170 M. It was found that the highest concentration was 0.11 M as a concentration giving a maximum signal. The effect of the buffer concentration on the analytical signal was also shown in Fig. 3.

3.2. Effect of reagent's concentration

Effect of indicator concentration has been examined by changing the concentration of indicator (GB^+) in the range



Figure 3 Effect of buffer concentration on analytical signal under the optimized conditions: pH 2.0, 1.0 mL of 6.39×10^{-4} M GB⁺, 1.0 mL of 0.1 M KBrO₃ and 25 µg L⁻¹ V(V) for fixed-time of 3 min at room temperature and 537 nm.

of $(1.3-13) \times 10^{-5}$ M while other variables are held constant. The results were shown in Fig. 4. A concentration of 6.39×10^{-5} M was chosen as the optimum concentration to give a maximum sensitivity.

The effect of bromate concentration on the net catalyzedreaction rate has been examined by increasing in the range of 0.002–0.018 M while other variables are held constant. The results were shown in Fig. 5. A bromate concentration of 0.01 M giving maximum sensitivity was chosen as optimum concentration.

3.3. Effect of temperature, time and ionic strength of environment

The effect of temperature on the rate of catalyzed and uncatalyzed reaction was examined in the range of 5–50 °C with the intervals of 5 °C while the other variables are held constant.



Figure 4 Effect of GB⁺ concentration on analytical signal under the optimized conditions: 2 mL of pH 2.0 buffer solution, 1.0 mL of 0.1 M KBrO₃ and 25 μ g L⁻¹ V(V) for fixed-time of 3 min at room temperature and 537 nm.



Figure 5 Effect of bromate concentration on analytical signal under the optimized conditions: 2 mL of pH 2.0 buffer solution, 1.0 mL of 6.39×10^{-4} M GB⁺ and 25 µg L⁻¹ V(V) for fixed-time of 3 min at room temperature and 537 nm.

The results were shown in Fig. 6. A value of 30 °C was selected as optimum temperature. Results showed that the reaction rate increases with temperature rising up 30 °C. The cause of this case is the fact that the speed of catalyzed-reaction is progressing faster than the speed of uncatalyzed-reaction. After this temperature, the analytical signal decreases slowly because of decomposition of the dye. Therefore, a reaction temperature of 30 °C was considered as an optimal value to keep analytical sensitivity stable.

Optimized time was found by measuring the absorbance and its variations changing during 0.5-7 min after the initiation of catalyzed- and uncatalyzed-reactions. The reaction rate for V(V)-catalyzed reaction increases up to 3 min. At higher times, the rates as a measure of sensitivity are almost constant while the uncatalyzed-reaction continues up to 5 min with a low slope. So, a fixed time of 3 min as the optimum reaction time was adopted in the proposed procedure in order to provide a high sensitivity and low reagent blank.



Figure 6 Effect of temperature on the net reaction rate under the optimized conditions: 2 mL of pH 2.0 buffer solution, 1.0 mL of 6.39×10^{-4} M GB⁺, 1.0 mL of 0.1 M KBrO₃ and 25 µg L⁻¹ V(V) for fixed-time of 3 min at 537 nm.

Under the selected optimal conditions, the effect of ionic strength of environment onto the analytical sensitivity, Δ (ΔA) was examined in the concentration range of 0.005–0.35 M KNO₃. It was observed that the reaction rate changed very little with increasing concentration approximately up to 0.075 M, after this concentration exhibited a negative change with increasing inclination. This case predicated that the catalyzed-indicator reaction would give accurate analytical signals for catalyst in real samples with a low matrix such as environmental surface waters. It can be expressed that inert salt effect should be checked at matrix systems with the high salt content such as sea water and wastewaters. Standard addition method can be suggested for analyzing inorganic vanadium in real water samples having a high salt content.

3.4. Analytical parameters

The calibration graph was obtained under the selected optimum conditions. Analytical signal was obtained to follow the change in absorbance immediately after the start of the indicator of reaction by fixed-time method at λ_{max} : 537 nm. Under optimized conditions: [GB⁺]: 6.39 × 10⁻⁵ M, [BrO₃⁻]: 5.0×10^{-4} M, 0.11 M of pH: 2.0 phosphate buffer at 30 °C, the following regression equation was obtained in the linear range of 1–100 µg L⁻¹ V(V).

 $\Delta(\Delta A) = 0.0173 + 8.51 \times 10^{-3} C_{\rm V(V)}$

(with a correlation coefficient of 0.9938, n: 12)

Here, $C_{V(V)}$ symbolizes vanadium concentration, (V(V)) µg L⁻¹ used as catalyst. $\Delta(\Delta A)$ is the difference between sam-

Table 1The actbased on catalytic	curacy and precis effect of vanadiu	ion of the kinet m(V).	ic method
Added V(V)	Found V(V)	RSDs%	RE%
$(\mu g L^{-1})$	$(\mu g L^{-1})$	(<i>n</i> : 5)	(<i>n</i> : 5)
4	$4.1~\pm~0.09$	2.2	+2.5
16	16.4 ± 0.26	1.6	+2.5
40	40.2 ± 0.60	1.5	+0.5
80	$80.4~\pm~1.05$	1.3	+0.5

ple and blank analytical signals with and without V(V) as catalyst. The limits of detection and quantification of the developed kinetic method, LOD and LOQ were found to be 0.31 and 0.94 μ g L⁻¹, which were obtained by dividing the slope of calibration curve with 3.3 and 10 multiples of standard deviation (SD_{blank}: 0.0008) of 12 replicate measurements for blank solution without catalyst. Table 1 shows the accuracy and precision of the developed kinetic–catalytic method under optimum experimental conditions.

3.5. Interference study

The effect of anionic and cationic interfering species on indicator reaction was investigated in detail. An absorbance value giving a signal deviation of $\pm 5.0\%$ from analytical signal expect for vanadium, as a criterion for interference study is taken into account as net analytical signal, $\Delta(\Delta A)$. Under optimal conditions the interference effects on the catalytic determination of 50 µg L⁻¹ V(V) were studied. The results are shown Table 2 in detail.

3.6. Analytical applications

3.6.1. Determination of V(V) as catalytic active species in artificially prepared matrices

Several artificial samples containing V(V) as catalytic species and interfering ions at known concentrations were determined by the proposed kinetic method. The analysis results were also given in Table 3 in detail. Especially the reason for using citrate in mixtures is to include it in the analytical system as a matrix component, and to suppress the effect of interfering metal cations through complex formation and balance their effects on recovery of V(V). From results, it could be concluded that citric acid stabilized the catalytic effect of the components present in matrix system and protected analytical signal in the presence of certain interferences (see Tables 4 and 5).

3.6.2. Effect of V(V)/V(IV) ratio

It is accepted that V(V) prevails in contact with atmospheric oxygen and V(IV) might be present in reducing environments,

Table 2 The effect of some interfering species on the catalytic spectrophotometric determination of 50 μ g L⁻¹ V(V) under optimum conditions.

Interfering species	Tolerance limits ([Interfering species]/[V(V)])
K ⁺ , Na ⁺ , NH ₄ ⁺ , Mg(II), Sr(II), Ba(II), Ca(II), Cd(II), Ni(II)	3500-5000
F ⁻ , Cl ⁻ , CN ⁻ , EDTA, CH ₃ COO ⁻ , ClO ₃ ⁻ , H ₂ O ₂ , SO ₄ ²⁻ , SO ₃ ²⁻ , ClO ₄ ⁻ , NO ₃ ⁻ , HPO ₄ ²⁻	1000-2000
Phthalate, oxalate, tartrate, urea	750–1000
Mo(VI), W(VI), Al(III) ^a , Ni(II) ^b , Zn(II) ^b , Fe(III) ^a , Mn(II) ^b	500-750
Cr(III) ^b , Br ⁻ , Ag(I)	300-350
I ⁻ , Hg(II) ^b , Bi(III) ^b , Cd(II) ^b , Citrate	200-300
Cr(III) ^b , Al(III), Mn(VII) ^d , V(IV), Ce(III), Pb(II)	35–50
Ce(IV)	20
Fe(II) ^c and Cr(VI) ^c	5
^d NO ₂ ⁻	2.5
Ascorbic acid	1.25

^a Tolerance ratios observed when 1.0 mL of 1.0% (w/v) NaF solution is added to solution environment.

 $^{\rm b}$ Tolerance ratios observed when 1.0 mL of 0.1% (w/v) EDTA solution is added to solution environment.

^c Tolerance ratios observed when 1.0 mL of 1 mg L^{-1} urea solution is added to solution environment.

^d Tolerance ratios observed when 1.0 mL of 0.05 M H₂O₂ solution is added to solution environment.

Samples	Composition of mixture ($\mu g L^{-1}$)	Vanadium,	$V(V)\;(\mu g\;L^{-1})$	
		Added	Found ^a	Recovery \pm SD ^b (%)
1	V(V)	50	49	98.0 ± 0.2
		80	80	100.0 ± 0.1
2	V(V) + Zn (250) + Cd (250) + Ca (250) + Citrate (1000)	50	51	102.0 ± 0.3
		80	82	102.5 ± 0.4
3	V(V) + Zn (250) + Cd (250) + Ca (250) + Citrate (1000)	50	52	104.0 ± 0.5
	$+ Mn (250) - NO_3^- (500)$	80	83	103.8 ± 0.4
4	V(V) + Zn (250) + Cd (250) + Ca (250) + Citrate (1000)	50	52	104.0 ± 0.7
	+ Mn (250) + NO ₃ ⁻ (500) + NH ₄ ⁺ (250) + Cr (250))	80	84	105.0 ± 0.5
5	V(V) + Zn (250) + Cd (250) + Ca (250) + Citrate (1000)	50	53	106.0 ± 1.1
	+ Mn (250) + NO ₃ ⁻ (500) + NH ₄ ⁺ (1000)	80	85	106.3 ± 1.2

Table 3 Determination of vanadium(V) in artificially prepared mixtures by using the developed kinetic spectrophotometric method.

^a The average values of three repeated analysis for each sample mixture.

^b The average results and recoveries of three repeated analysis found by means of calibration curve.

Table 4 Recovery values of V(V) and total vanadium determined at different concentration ratios of V(V) and V(IV) as well as the calculated V(IV) concentrations (*n*: 3).

V(V)/V(IV)		V(V)			Total V			V(IV)
ratio	Added ($\mu g L^{-1}$)	*Found ($\mu g L^{-1}$)	**RSD%	Recovery%	Found ($\mu g L^{-1}$)	RSD%	Recovery%	Calculated ($\mu g L^{-1}$)
0.5	10	9.7 ± 0.15	1.55	97.0	29.2 ± 0.34	1.16	97.3	19.5
1	20	19.7 ± 0.28	1.42	98.5	39.1 ± 0.61	2.22	97.8	19.4
5	40	40.3 ± 0.65	1.61	100.8	48.6 ± 0.71	1.46	101.3	8.3
10	50	49.2 ± 0.80	1.63	98.4	54.4 ± 0.87	1.60	98.9	5.2
15	75	74.8 ± 1.24	1.66	99.7	80.05 ± 1.35	1.69	100.1	5.3

* The mean value and its standard deviation of three replicate measurements.

** The relative standard deviation of three replicate measurements.

and different factors such as dissolved oxygen, pH and presence of natural organic matters affect the distribution of vanadium between these two oxidation states. It is expressed that V(IV) is also stable in the presence of oxygen at low pH (< 2.4), this oxidation state changes above this pH. So, control of the valence of vanadium in aqueous solutions is a major problem (Abbasse et al., 2002a,b). To oxidize V(IV) to V(V) in binary mixtures prepared synthetically, permanganate was initially studied in acidic medium. In order to provide a complete reduction and prevent back-reduction of V(V) to V(IV) in acidic media, a slightly more oxidizing reagent was preferentially used. In order to suppress the possible interfering effect of excess permanganate, 3-4 drops of freshly prepared sodium azide solution $(2.5\% \text{ w/v NaN}_3)$ were added and gently heated with a further addition of 2-3mL of water if necessary for 5 min to drive off the azide, cooled to room temperature. With this aim, prior optimization studies were conducted for binary mixtures. Under the optimized reagent conditions at 537 nm, firstly by keeping constant the other variables the effect of acidity on oxidation of V(IV) to V (V) was studied by using H_3PO_4 or H_2SO_4 in the pH range of 1.0-3.0, and a maximum sensitivity was obtained near to pH 2.0. Secondly, the effect of oxidant on the sensitivity as a measure of completeness of oxidizing procedure was studied in the range of 0.2-3.0 mL at fixed concentration of 1.0% (w/v) KMnO₄ solution, and a volume of 2.0 mL was found to be sufficient as optimum value for further studies. In order to study the effect of V(V)/V(IV) ratio, the binary mixtures prepared at different V(IV)/V(V) concentration ratios after oxidizing with permanganate at acidic media were analyzed by the present kinetic method, and the results obtained are given in Table 4. As could be seen, two species of vanadium are completely separated and recovered quantitatively with V(V)/V(IV) ratio varying from 0.5 to 15.

3.6.3. Speciative determination of total V and dissolved inorganic vanadium species in environmental water samples

The proposed method was applied to the determination of vanadium present in tap water, lake water, rain water and stream water samples in order to evaluate its analytical applicability. The inorganic V(IV) and V(V) contents of samples were detected with fixed-time method of 3.0 min in phosphate buffer media, pH 2.0 at 537 nm, and determined by using calibration curve and standard addition curve methods in order to control its systematic method error when necessary. Also, in order to control the accuracy of the kinetic method, an independent analytical method such as FAAS was used and their total vanadium contents were determined by the analysis of standard vanadium solutions spiked to the water samples after oxidation and evaporation of samples of 2-2.5 L to a volume of 10-15 mL with alkaline NaHCO₃-H₂O₂ mixture at known concentrations, respectively. The calibration curve obtained by means of FAAS was highly linear in the range of 1- 50 mg L^{-1} with the detection and quantification limits of 0.4 and 1.4 mg L^{-1} . The regression equation was Abs: 0.0126 [V (V), mg L^{-1}]-0.0020 with a correlation coefficient of 0.9998 (n: 5). 0.1% (w/v) KCl solution was added to restrain possible

Sample(s)	Added V(V) (µg L ⁻¹)	Found V(V) $(\mu g L^{-1})$	RSD% (<i>n</i> : 5)	Recovery%	Total V,V(V) + V(IV) $(\mu g L^{-1})$	RSD% (<i>n</i> : 5)	Added V(IV) (µg L ⁻¹)	Found V(IV) (µg L ⁻¹)	Recovery%	Total V found by FAAS (μg L ⁻¹)	RSD%	**The calculated Student's <i>t</i> - and <i>F</i> -values
Tap water ^a	_	5.84 ± 0.14	2.40	_	7.16 ± 0.16	2.23	_	1.32	_	7.21 ± 0.12	1.66	0.395, 1.78
1	10	16.05 ± 0.45	2.80	102.1	57.21 ± 0.85	1.49	40	41.16	103.0			,
	40	46.15 ± 0.54	1.17	100.8	56.08 ± 0.82	1.46	10	9.93	99.3			
Rain water ^b	_	5.89 ± 0.13	2.21	_	8.93 ± 0.24	3.8	_	3.04	_	9.05 ± 0.25	3.5	0.548, 1.09
	15	21.12 ± 0.48	2.27	101.5	59.07 ± 0.84	1.42	35	34.91	99.7			
	35	40.94 ± 0.56	1.34	100.1	59.12 ± 0.85	1.44	15	15.14	100.9			
Lake water ^c	-	13.88 ± 0.42	3.03	-	19.58 ± 0.46	2.35	-	5.70	-	19.45 ± 0.49	2.52	0.306, 1.14
	15	28.91 ± 0.52	1.80	100.1	69.65 ± 0.90	1.16	35	35.04	100.1			
	35	48.92 ± 0.56	1.14	100.0	69.70 ± 0.92	1.17	15	15.08	100.5			
Stream water ^d	_	24.12 ± 0.50	2.07		38.44 ± 0.53	1.38	-	14.32	-	38.48 ± 0.55	1.43	0.083, 1.08
	15	39.18 ± 0.54	1.38	100.4	88.46 ± 1.48	1.67	35	34.96	99.9			
	35	59.15 ± 0.90	1.52	100.1	88.48 ± 1.46	1.65	15	15.01	100.1			
CRM TMDA-53.3*	-				70.20 ± 2.35	3.35			-	$68.90~\pm~2.25$	3.27	0.208, 3.75 (0.615, 4.09)**
	10	80.15 ± 2.45	3.06	99.5	100.39 ± 2.75	2.74	20	20.24	101.2	-		
	20	90.35 ± 2.60	2.88	100.8	100.60 ± 2.78	2.76	10	10.25	102.5	-		

Table 5 Determination and speciation of total V and dissolved inorganic vanadium species V(IV) V(V) present in the environmental water samples

^a Collected at University of Cumhuriyet.

^b Rain water was collected at a sampling site, situated in the Sivas city center in May 2011.

^c Surface lake water was collected from Hafik Lake, Sivas, Turkey (pH: 7.6).

^d Stream water, which is also known as Acı su by humans living in that environment, was collected from İmranlı, Sivas, Turkey (pH: 7.4).

* Standard reference material, CRM TMDA-53.3 (a trace element fortified calibration standard Trace element in Natural Water). The certified value of vanadium is $70.875 \pm 4.55 \,\mu g \, L^{-1}$. ** The tabulated values of Student's *t*- and *F*-tests at probability level of 0.05 (*n*: 5) are 2.31 and 6.39, respectively.

*** Values in parenthesis are the calculated values of Student's *t*-test and *F*-test at *P*: 0.05 for the results obtained by analysis of FAAS.

Table 6 Some spectrol	photometric methods reported in the lite	rature for the c	atalytic-kinetic de	etermination	of vanadium.	
Indicator reaction	Media with and without activator	Linear range $(\mu g L^{-1})$	Detection limit $(\mu g L^{-1})$	RSD%	Interferences (masking or removal)	References
Aniline blue-BrO ⁻ Methyl orange-BrO ⁻	Citric acid Citric acid	5-1200 2-5-300	2 0.8	3.0 2.0	NO ² and I (Ag ⁺) Fe (NaF) As Ho (FDTA)	Safavi et al. (2000) Absalan and Alinour (2003)
Nile blue-BrO ₃	H_2SO_4	4-520	3	3.0	Common metals in 1000-fold excess do not interfere	Ensafi et al. (1999)
Gallic acid- $S_2O_8^{2-}$	H_3PO_4	4.1 - 33.3	1	4-8	Chloride (preliminary fume-drying)	Balaji et al. (1998)
Diphenylamine-H2O2	Formic acid	400-4000	4.0	0.5	Fe (separation)	Sikalos et al. (2000)
Alkali blue-BrO ₃	pH 4.0 titrosol buffer	100 - 6000	40	3.47	I ⁻ and SCN ⁻ (Hg ²⁺), Cr(III) (NaF)	Abbaspour et al. (2007)
Ponceau Xylidine-BrO ₃	5-Sulfosalicylic acid	1-15	0.46	1.5	Cu^{2+} , Hg^{2+} (EDTA)	Ulusoy and Gürkan (2009)
Celestine blue- BrO_3^-	Citric acid in pH 2.0 phosphate buffer	25-1250	6.8	0.78–3.75	Fe^{3+} (NaF), CrO_4^{2-} (EDTA after reduction with ascorbic acid), Hg^{2+} , Cd^{2+} (EDTA)	Gürkan and Gürkan (2011)
Gallamine blue-BrO ⁷ ₃	pH 2.0 Phosphate buffer	1-100	0.31	1.16–3.8	$ \begin{array}{l} Fe^{3+}, \ Al^{3+} \ (NaF), \ NO_{2}^{-} \ (Urea), \ Fe^{2+}, \\ CrO_{4}^{2-} (H_{2}O_{2}), \ Hg^{2+}, \ Cd^{2+} \ (EDTA) \end{array} $	Present study

ionization at low concentrations if necessary. The confidence limits of the both methods at the confidence level of 95% (n: 5) are very clearly seen to be compatible in Table 6. Also, in order to test the validation of the present method a certified water sample, CRM TMDA-53.3 was analyzed by using both the kinetic method and standard AAS method. To examine the quantitative recovery of vanadium, the known amounts of standard V(IV) solution were added to the certified sample solution. The reliability of the kinetic method to analyze certified water sample was checked and verified by both recovery experiments, and comparing the results obtained with independent FAAS method. The results with recoveries changing in range of 99.3-103.0% with relative standard deviations of 1.16-3.8% and 1.43-3.5% for kinetic and FAAS methods, respectively are shown to be quantitative in Table. 6, indicating the high accuracy and precision of the method especially in higher concentrations than its detection limit. In the Student's t- and F-tests, no significant difference was not found between the calculated and theoretical values of both the proposed kinetic and the FAAS methods at 95% confidence level (n: 5). This indicated the similarities between the precision and accuracy of the present method and the reference method for the determination of vanadium in environmental water samples. As a result, it was observed that the mean values were quantitatively in good agreement with the certified value.

4. Conclusions

The catalytic kinetic method developed for speciative vanadium determination in environmental water samples is inexpensive and readily available and allows rapid determination at low operating costs and shows simplicity, adequate selectivity, low limit of detection and very good precision and accuracy, in relation to the other kinetic procedures. The validation of the method was achieved by determination of vanadium present in the certified water sample, CRM TMDA-53.3 by using the present kinetic and independent FAAS methods, and the results obtained by using both methods statistically showed a good agreement with its certified value in view of accuracy and precision. The kinetic method has a wide linear range of 100-fold with limits of detection and quantification of 0.31 and 0.94 μ g L⁻¹. Compared with the other catalytic kinetic methods given in Table 6, the proposed kinetic method shows many advantages such as shorter analysis time, low operational temperature, good reproducibility and low detection limit (Safavi et al., 2000; Absalan and Alipour, 2003; Ensafi et al., 1999; Balaji et al., 1998; Sikalos et al., 2000; Abbaspour et al., 2007; Ulusoy and Gürkan, 2009; Gürkan and Gürkan, 2011). Moreover, it can easily be adapted for a flow injection system analysis to improve the figures of merit for fast/in situ monitorization of inorganic vanadium species present in environmental waters.

Acknowledgments

This study has been partly supported by Cumhuriyet University Scientific Research Projects Commission as the research projects with the F-226 code.

The present study was also presented as a poster in the 5th Black Sea Basin Conference on Analytical Chemistry, which was taken place on September 23th–26th 2009, in Yalçın Hotel Fatsa, Ordu, Turkey.

References

- Abbaspour, A., Moosavi, S.M.M., Mirzajani, R., 2007. Catalytic spectrophotometric determination of vanadium (IV) based on the oxidation of alkali blue by potassium bromate. Iranian J. Sci. Technol. Trans. A 31 (A3), 231–239.
- Abbasse, G., Ouddane, B., Fischer, J., 2002a. Determination of trace levels of dissolved vanadium in seawater by use of synthetic complexing agents and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Anal. Bioanal. Chem. 374, 873–878.
- Abbasse, G., Ouddane, B., Fischer, J., 2002b. Determination of trace levels of dissolved vanadium in seawater by use of synthetic complexing agents and inductively coupled plasma atomic emission spectroscopy. Anal. Bioanal. Chem. 374 (5), 873–878.
- Absalan, G., Alipour, Y., 2003. Kinetic-catalytic determination of vanadium (IV) using methyl orange bromate redox reaction. Anal. Sci. 19, 635–638.
- Agnihotri, N., Das, R., Mehta, J.R., 2000. Spectrophotometric determination of vanadium (v) as its 6-chloro-3-hydroxy-2-[2'-(5'methylfuryl)]-4H-chromen-4-one complex. J. Indian Chem. Soc. 77, 264–266.
- Amorim, F.A.C., Welz, B., Costa, A.C.S., Lepri, F.G., Vale, M.G.R., Ferreira, S.L.C., 2007. Determination of vanadium in petroleum and petroleum products using atomic spectrometric techniques. Talanta 72, 349–359.
- Balaji, B.K., Saravanakumur, G., Murugesan, P., Mishra, G., 1998. A modified catalytic-photometric method for the determination of vanadium in chloride rich hydro-geochemical samples. Talanta 46, 1299–1304.
- Chakrabarti, A.K., 1995. Selective extraction and photometric-determination of trace vanadium with cinnamohydroxamic acid in milk and its application to steel and rock ore analysis. Talanta 42, 1279– 1283.
- Chen, Z.L., Owens, G., 2008. Trends in speciation analysis of vanadium in environmental samples and biological fluids a review. Anal. Chim. Acta 607, 1–14.
- Civici, N., 1995. Determination of vanadium and nickel in oil, asphaltene and bitumen using thin-film energy-dispersive X-ray fluorescence spectrometry. X-ray Spectrom. 24, 163–166.
- Committee on Biologic Effects of Atmospheric Pollutants, 1974. Medical and Biologic Effects of Environmental Pollutants – Vanadium. National Academy of Sciences, Washington, DC.
- Crans, D.C., Gottlieb, M.S., Tawara, J., Bunch, R.L., Theisen, L.A., 1990. A kinetic method for determination of free vanadium(IV) and (V) at trace level concentrations. Anal. Biochem. 188, 53–64.
- Davies, D.J.A., Bennett, B.G., 1983. In: Exposure Commitment Assessments of Environmental Pollutants (MARC Report No. 30), vol. 3. University of London Monitoring Assessment and Research Centre, London.
- Ensafi, A.A., Amini, M.K., Mazeloum, M., 1999. Spectrophotometric reaction rate method for the determination of trace amounts of vanadium (V) by its catalytic effect on the oxidation of Nile blue with bromate. Anal. Lett. 32, 1927–1937.
- Filik, H., Berker, K.I., Balkis, N., Apak, R., 2004. Simultaneous preconcentration of vanadium(V/IV) species with palmitoyl quinolin-8-ol bonded to amberlite XAD 2 and their separate spectrophotometric determination with 4-(2-pyridylazo)-resorcinol using CDTA as masking agent. Anal. Chim. Acta 518 (1–2), 173–179.
- Filik, H., Yanaz, Z., Apak, R., 2008. Selective determination of total vanadium in water samples by cloud point extraction of its ternary complex. Anal. Chim. Acta 602, 27–33.
- Gürkan, R., Gürkan, O., 2011. Catalytic-kinetic spectrophotometric determination of vanadium (V) based on the Celestine bluebromate-vanadium (V)-citric acid reaction. Rare Metals 30 (4), 348–358.

- Jen, J.F., Wu, M.H., Yang, T.C., 1997. Simultaneous determination of vanadium(IV) and vanadium(V) as EDTA complexes by capillary zone electrophoresis. Anal. Chim. Acta 339, 251–257.
- Ji, H., Sha, Y., Xin, H., Shuang Li, S., 2010. Determination of trace vanadium (V) in seawater and fresh water by the catalytic kinetic spectrophotometric method. J. Ocean Univers. China (English Ed.) 9 (4), 343–349.
- Keyvanfard, M., Abedi, N., 2010. The development of a new kinetic spectrophotometric method for the determination of vanadium(V) based on its catalytic effect on the oxidation of malachite green oxalate by bromate in acidic and micellar medium. Eur. J. Chem. 7 (4), 1612–1620.
- Kumar, K.S., Kamg, S.H., Suvardhan, H., Kiran, K., 2007. Facile and sensitive spectrophotometric determination of vanadium in various samples. Environ. Toxicol. Pharmacol. 24, 37–44.
- Leon-Camacho, M., Ternero-Rodriguez, M., Callejon-Mochon, M., Guiraum-Perez, A., 1991. Kinetic spectrophotometric determination of traces of vanadium (V) by its catalytic effect on the oxidation of 1,4-dihydroxyphtalimide dioxime with bromate. Anal. Chim. Acta 244 (1), 89–97.
- Liu, J.-M., Yang, T.-L., Wu, H.-B., Lu, Q.-M., Wu, A.-H., Li, L.-D., 2004. Determination of trace vanadium(V) by solid substrate room temperature phosphorimetry based on the catalyzed reaction of potassium bromate oxidizing safranine O activated by vitamin C. Anal. Lett. 37 (12), 2459–2467.
- Mastoi, G.M., Khuhawar, M.Y., 2007. Kinetic spectrophotometric determination of vanadium(V) using Ponceau S. Eurasian J. Anal. Chem. 2 (2), 69–77.
- Mateu, J., Forteze, R., Cerda, V., 1994. Kinetic thermometric determination of vanadium in atmospheric aerosols based on its catalytic effect on the oxidation of tannic acid by bromate ion. Thermochim. Acta 247, 457–464.
- Melwanki, M.B., Seetharamappa, J., 2000. Spectrophotometric determination of trace amounts of vanadium(V) with isothipendyl hydrochloride. Indian J. Chem. 39A, 465–467.
- Nakano, S., Tanaka, E., Mizutani, Y., 2003. Flow-injection spectrophotometry of vanadium by catalysis of the bromate oxidation of N,N'-bis(2-hydroxyl-3-sulfopropyl)-toluidine. Talanta 61, 203– 210.
- Okamura, K., Sugiyama, M., Obata, H., Maruo, M., Nakayama, E., Karatani, H., 2001. Automated determination of vanadium(IV) and (V) in natural waters based on chelating resin separation and catalytic detection with Bindschedler's green leuco base. Anal. Chim. Acta 443, 143–151.
- Pouretedal, H.R., Keshavarz, M.H., 2006. Determination of trace amounts of vanadium by kinetic-catalytic spectrophotometric methods. Chin. J. Chem. 24, 557–562.
- Pyrzynska, K., 2005. Recent developments in spectrophotometric methods for determination of vanadium. Microchim. Acta 149, 159–164.
- Pyrzynska, K., Wierzbicki, T., 2004. Determination of vanadium species in environmental samples. Talanta 64, 823–829.
- Rama, M.J.R., Medina, A.R., Diaz, A.M., 2005. A flow-injection renewable surface sensor for the fluorimetric determination of vanadium(V) with Alizarin Red S. Talanta 66, 1333–1339.
- Safavi, A., Hormozi Nezhad, M.R., Shams, E., 2000. Highly selective and sensitive kinetic spectrophotometric determination of vanadium (IV) in the presence of vanadium(V). Anal. Chim. Acta 409, 283–289.
- Sharma, Y., 1982. Spectrophotometric determination of microgram amount of vanadium with parasolphobenzeneazo-4-(2,3-dihydroxypyridine). Analyst 107, 582–585.
- Shijio, Y., Sato, H., Uehara, N., Aratake, S., 1996. Simultaneous determination of trace amounts of copper, nickel and vanadium in sea-water by high-performance liquid chromatography after extraction and back-extraction. Analyst 121, 325–328.

- Shishehbore, M.R., Jokar, R., 2011. A kinetic spectrophotometric method for vanadium(V) determination in food samples using a Janus Green-bromate system. Anal. Methods 3, 2815–2821.
- Sikalos, T.S., Arabatzis, Y.M., Prodromidis, M.I., Veltsistas, P.G., Karayannis, M.I., 2000. Spectrophotometric determination of trace amounts of vanadium based on its catalytic effect on the reaction of diphenylamine and hydrogen peroxide. Mikrochim. Acta 135, 197– 201.
- Taylor, M.J.C., Staden, J.F.V., 1994. Spectrophotometric determination of vanadium(IV) and vanadium(V) in each other's presence. Analyst 119, 1263–1276.
- Thomaidis, N.S., Piperaki, E.A., 1996. Comparison of chemical modifiers for the determination of vanadium in water and oil samples by electrothermal atomization atomic absorption spectrometry. Analyst 121, 111–117.
- Thompson, K.H., McNeill, J.H., Orvig, C., 1999. Vanadium compounds as insulin mimics. Chem. Rev. 99, 2561–2572.
- Ulusoy, H.I., Gürkan, R., 2009. A novel indicator reaction for the catalytic determination of V(V) at ppb levels by the kinetic spectrophotometric method. Eclet. Quím. 34 (4), 49–64.
- Umetsu, K., Itabashi, H., Satoh, K., Kawashima, T., 1991. Effect of ligands on the redox reaction of metal ions and the use of a ligand buffer for improving the end-point detection in the potentiometric titration of vanadium(V) with iron(II). Anal. Sci. 7, 115–118.
- Vega, M., Berg, C.M.B.V., 1994. Determination of vanadium in sea water by catalytic adsorptive cathodic stripping voltammetry. Anal. Chim. Acta 293, 19–28.

- Vouk, V., 1979. Vanadium. In: Friberg, L., Nordberg, G.R., Vouk, V. B. (Eds.), Handbook on the Toxicology of Metals. Elsevier-North Holland Biomedical Press, Amsterdam.
- Wang, D., Wilhelmy, S.A.S., 2008. Development of an analytical protocol for the determination of V(IV) and V(V) in seawater: application to coastal environments. Mar. Chem. 112, 72–80.
- Wang, H.S., Zhang, A.M., 1997. Microdetermination of vanadium (V) by its catalytic effect on the oxidation of 1-naphthyl red with potassium bromate. Microchem. J. 57, 218–223.
- Waters, M.D., 1977. Toxicology of vanadium. In: Goyer, R.A., Mehlma, M.A. (Eds.), Advances in Modern Toxicology, Toxicology of Trace Elements, vol. 2. Wiley, New York.
- Wei, J., Teshima, N., Sakai, T., 2008. Flow injection analysis for oxidation state speciation of vanadium(IV) and vanadium(V) in natural water. Anal. Sci. 24, 371–376.
- Yang, K.L., Jiang, S.J., Hwang, T.J., 1996. Determination of titanium and vanadium in water samples by inductively coupled plasma mass spectrometry with on-line preconcentration. J. Anal. At. Spectrom. 11, 139–143.
- Zhai, Q.Z., Zhang, X.X., Huang, C., 2008. Kinetic-spectrophotometric determination of trace amounts of vanadium(V) based on its catalytic effect on the reaction of DBM-arsenazo and potassium bromate. Spectrochim. Acta A Mol. Biomol. Spectrosc. 69 (3), 911–916.
- Zhou, Z.-R., Li, G.-Y., Luo, M.-B., 2007. Kinetic spectrophotometric determination of vanadium (V) based on its inhibitory effect on discoloring reaction of arsenazo I and sodium hypophosphite. Metallurgical Anal. 27 (4), 22–28.