Eclética Química
ISSN: 0100-4670
atadorno@iq.unesp.br
Universidade Estadual Paulista Júlio de
Mesquita Filho
Brasil

Ibrahim Ulusoy, Halil; Gürkan, Ramazan
A novel indicator reaction for the catalytic determination of V(V) at ppb levels by the kinetic spectrophotometric method
Eclética Química, vol. 34, núm. 4, diciembre, 2009, pp. 49-64
Universidade Estadual Paulista Júlio de Mesquita Filho
Araraquara, Brasil

ECLÉTICA química
www.scielo.br/eq
Volume 34, número 4, 2009
Artigo/Article

A Novel Indicator Reaction for the Catalytic Determination of V(V) at ppb Levels by the Kinetic Spectrophotometric Method

Halil İbrahim Ulusoy[1] *& Ramazan Gürkan*[1,*]
[1]*University of Cumhuriyet, Faculty of Science & Arts, Department of Chemistry, TR–58140, Sivas, TURKEY*
*(*Corresponing author: E-mail: rgurkan@cumhuriyet.edu.tr)*

Abstract: A novel sensitive and relatively selective kinetic method is presented for the determination of V(V), based on its catalytic effect on the oxidation reaction of Ponceau Xylydine by potassium bromate in presence of 5-sulfosalicylic acid (SSA) as activator. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of Ponceau Xylydine at 640 nm between 0.5 to 7 min (the fixed time method) in H_3PO_4 medium at 25°C. The effect of various parameters such as concentrations of H_3PO_4, SSA, bromate and Ponceau Xylydine, temperature and ionic strength on the rate of net reaction were studied. The method is free from most interferences, especially from large amounts of V(IV). The decrease in absorbance is proportional to the concentration of V(V) over the entire concentration range tested (1–15 ng mL^{-1}) with a detection limit of 0.46 ng mL^{-1} (according to statistical $3S_{blank}/k$ criterion) and a coefficient of variation (CV) of 1.8% (for ten replicate measurement at 95% confidence level). The proposed method suffers few interferences such as Cr(VI) and Hg(II) ions. The method was successfully applied to the determination of V(V) in tap water, drinking water, bottled mineral water samples and a certified standard reference material such as SRM-1640 with satisfactory results. The vanadium contents of water samples were also determined by FAAS for a comparison. The recovery of spiked vanadium(V) was found to be quantitative and the reproducibility was satisfactory. It was observed that the results of the SRM 1640 were in good agreement with the certified value.

Keywords: Catalytic effect; V(V); Kinetic-spectrophotometric method; fixed-time method; Bromate; Ponceau Xylydine and 5-Sulphosalycilic acid

---

1. Introduction

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

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

In another work [22] researchers proposed a kinetic-catalytic spectrophotometric method for the determination of trace amounts of V(IV) and V(V) ions. The vanadium (IV) as VO^{2+} ion and vanadium(V) as VO_3^- ion showed a catalytic effect on the kinetic reactions between methylthymol blue (MTB) and bromate in acidic media. The linear ranges for the determination of vanadium were obtained in the range of 1.0-150 and 5.0-100.0 µg L^{-1} by the fixed-time and slope methods, respectively. Using the fixed-time method, the limit of detection was found to be 0.5 µg L^{-1} of vanadium. The detection limit of vanadium by the slope method was found to be 3.5 µg L^{-1} of vanadium. Many of this and similar kinetic methods lack either sensitivity or satisfactory selectivity or they have a limited dynamic calibration range. Hence, the development of more sensitive and selective catalytic methods for the kinetic determination of vanadium (V(V) or V(IV)) is still sought.

In the present study, we describe a simple, rapid, precise, relatively selective and sensitive analytical method for the kinetic determination of V(V) at ppb levels using its catalytic effect on the oxidation of Ponceau Xyldine by BrO_3^- ion in 0.16 mol L^{-1} H_3PO_4 medium in the presence of 5-sulfosalycylic acid as an activator.

2. Experimental

2.1. Apparatus

In the present study, a Shimadzu Model UV-Visible 1601 PC spectrophotometer equipped with a 1 cm quartz cell was used for absorbance measurements. This spectrophotometer has a wavelength accuracy of ±0.2 nm and a bandwidth of 2 nm in the wavelength range of 190–1100 nm. A TCC-140A mark temperature-controlled cell holder to this instrument was attached for absorbance measurements at a fixed wavelength. A Shimadzu AAS–6300 atomic absorption spectrophotometer with a deuterium background correction was used for the determination of vanadium in the following conditions: wavelength: 318.4 nm, lamp current: 10 mA, slit width: 0.7 nm, burner height: 11 mm, C_2H_2 flow: 7.5 L min^{-1}, N_2O flow: 11.0 L min^{-1}. In order to control the temperature of reaction medium with an accuracy of ±0.1°C a Grant LTG-6G model thermostatic water bath regulated at the desired temperature was used (operating in the temperature range of -20 and 100°C). A stopwatch was used for recording the reaction time. All solutions were preheated to a temperature of 25±0.1°C shortly before the initiation of indicator reaction with and without catalyst. All absorbance measurements were made at a working wavelength of 640 nm.

2.2. Reagents and solutions

All chemicals were of analytical reagent grade from Merck or Fluka. Triply distilled, deionized water was used in preparation of all solutions.

Vanadium(V) stock standard solution (1.000 mg mL^{-1}) was prepared by dissolving 0.2296 g of ammonium metavanadate (NH_4VO_3, Merck) in 100 ml water. Working solutions were subsequently prepared before use by appropriate dilution of the stock solution. Indicator reagent dye (1×10^{-3} mol l^{-1}) solution was made by dissolving a suitable amount of Ponceau Xylydine (Fluka) in 100 ml water. A stock solution of $KBrO_3$ (0.10 mol L^{-1}) solution was prepared by dissolving 1.670 g potassium bromate (Merck) in 100 ml water; 5-sulfosalycilic acid solution (0.02 mol L^{-1}) was prepared by dissolving 2.000 g 5-sulfosalycilic acid (Merck) in 100 ml water; H_3PO_4 (2.00 mol L^{-1}) solution was made by mixing appropriate volumes of concentrated H_3PO_4 in 100 ml water. Stock solutions of interfering ions (1 mg mL^{-1}) were prepared by dissolving suitable salts in water, hydrochloric acid or a sodium hydroxide solution. More dilute solutions were prepared daily from the appropriate stock solution.

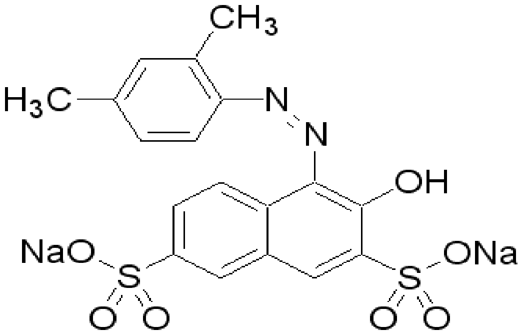
2.3. Experimental procedure

All solutions were thermally equilibrated at 25°C in a thermostatic water bath before addition of reagents. A suitable portion of vanadium (V) solution in the range of 1-15 ng mL^{-1} was placed into a 10-ml calibrated flask, then 0.80 ml of 2 mol L^{-1} H_3PO_4 solution, 0.6 mL $1x10^{-3}$ mol L^{-1} Ponceau Xylydine, 0.3 mL 0.02 mol L^{-1} SSA were added and the solution was diluted to about 7 ml. To this solution 1.3 ml 0.1 mol L^{-1} BrO_3^- solution were added and he mixture was diluted to 10 ml with water. It should be noted that the order of the addition of the reagents is very important. Time was measured just after the addition of the last drop of bromate solution. The solution was mixed and a portion of that was transferred within 30 s into a 1 cm spectrophotometric cell to record the absorbance change (ΔA_C) against water at 640 nm over the period 0.5–7.0 min after the initiation of the reaction by using fixed-time method. Similarly, the measurement in the absence of vanadium as catalyst was repeated to obtain the values ΔA_0 for the uncatalyzed reaction. By the use of a serial of standard vanadium solution, a calibration graph of net change of absorbance, $\Delta(\Delta A)$ at a fixed time versus vanadium concentration was constructed.

3. Results and Discussion

3.1. Preliminary investigations

Ponceau Xylidine, a textile azo-group indicator dye, which is known as Acid Red 26, Ponceau 2 R and Xylidine ponceau 2R has the following structural formula;



Due to having a large number of Π electrons and a chromopher azo-group, the indicator substance shows an absorption maximum in the visible region. Because of very large absorption coefficient (ε_{max} : 9275.50 L mol^{-1} cm^{-1} in the range of $1x10^{-6}$-$1x10^{-4}$ mol L^{-1}) it may be observed too small even concentrations. Ponceau Xyldine is an azo dye that can be oxidized by oxidizing agents such as bromate, chlorate, iodate, periodate, H_2O_2 and $K_2S_2O_8$ in acidic media at high temperatures. The rate of the reaction of Ponceau Xyldine and bromate at low temperatures (lower than 40°C) is very low. However, in the presence of low concentrations of V(V) as a catalyst and SSA as activator the reaction proceeds quickly. This causes a rapid decrease in the absorbance of Ponceau Xylidine in the visible region. This reaction can be monitored spectrophotometrically by measuring the decrease in absorbance (at 640 nm) against duration of the first 7.0 min from the initiation of the reaction. In order to give the best analytical results of the present kinetic method, all of the reaction variables must be optimized. From literature scannings, it was concluded that the similar indicator reactions were carried out in strong acidic environment and therefore, to the experimental studies were begun in the environment found strong mineral acids such as H_3PO_4, H_2SO_4, HCl and HNO_3. In result of experimental studies made, it was observed that the best result or the highest sensitivity obtained in media containing H_3PO_4. Therefore, the experiment was continued with phosphoric acid. Another important study for the catalytic reaction was performed to determine the most appropriate activator. With this purpose, in environments containing oxalic acid, citric acid, tartaric acid, salycilic acid and the sulfosalycilic acid at same concentrations the experiments were repeated and the best analytical signal was obtained in the presence of sulfosalycilic acid.

3.2. Effect of the indicator reaction variables

For the optimization of indicator reaction, the impact of reaction variables such as $KBrO_3$, Ponceau Xyldine, H_3PO_4 and SSA concentration, ionic strength and temperature of environment on analytical sensitivity, $\Delta(\Delta A)$ was investigated. Also the time to measure changes in absorbance was optimized. It was found that the maximum change in absorbance as analytical signal ($\Delta(\Delta A)$: ΔA_C-ΔA_0)) was occurred within the first 7 minutes passing after the initiation of the catalytic reaction. The best correlation coefficient between analytical sensitivity and the vanadium concentration as catalyst have been obtained for fixed-time of 7-minute. For this reason, 7-minute fixed-time measurement was chosen as the most suitable reaction time.

3.2.1. Effect of H_3PO_4 concentration

The influence of acid concentration on analytical sensitivity as a result of the rate differences of the catalyzed and uncatalyzed reactions was studied in the range of 0.05-0.30 M (Fig. 1). The rate of the net catalyzed reaction increased with increasing H_3PO_4 concentration up to 0.15 M while decreasing at higher acid concentrations. However, the largest difference between the rate of the blank and that of the sample reaction was obtained in the H_3PO_4 concentration of 0.15 M. Thus, 0.15 M was selected as the optimum acid concentration for further studies.

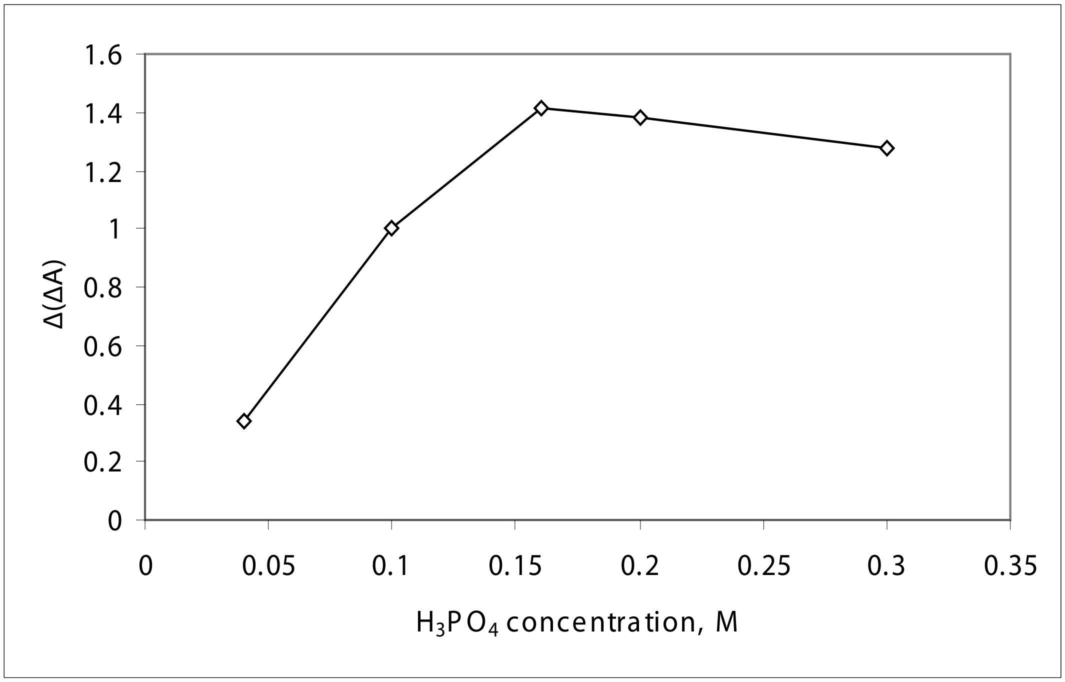


Fig.1. Effect of H_3PO_4 concentration on analytical sensitivity.[Optimum conditions: $1x10^{-4}$ mol L^{-1} Ponceau Xylidine, 9 ppb V(V), $2x10^{-4}$ mol L^{-1} SSA and $1x10^{-3}$ mol L^{-1} BrO_3^- at 640 nm and 25°C for the fixed-time method of 7 min]

3.2.2. Effect of BrO_3^- concentration

The effect of bromate concentration on the net reaction rate was studied in order to determine the best bromate concentration. As can be seen from Fig. 2, the net reaction rate for a sample solution increased with increasing bromate concentration and reached a maximum plateau at approximately 0.015M bromate. At higher bromate concentrations the analytical signal, Δ(ΔA) has gradually decreased. The reason of this decrease may be the increase in the uncatalyzed reaction rate in higher bromate concentrations. Therefore, 0.016 M bromate concentration was adopted as optimum value for further studies.

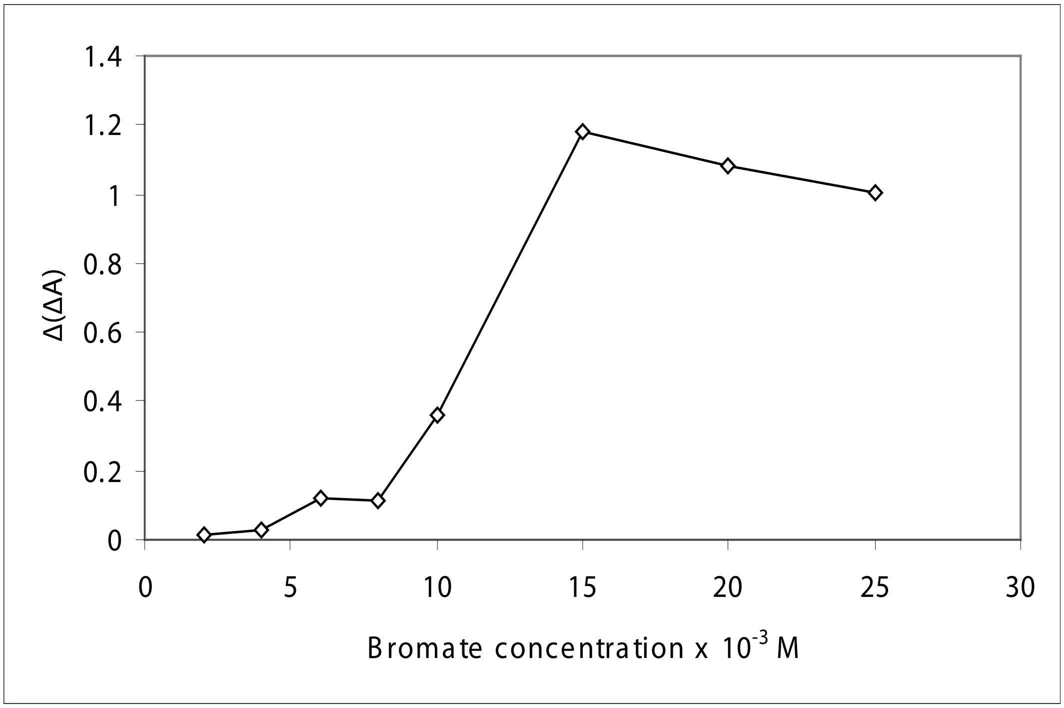


Fig.2. Effect of bromate concentration on analytical sensitivity.[Optimum conditions: 1x10^{-4} mol L^{-1} Ponceau Xylidine, 9 ppb V(V), 2x10^{-4} mol L^{-1} SSA and 0.16 mol L^{-1} H_3PO_4 at 640 nm and 25°C for the fixed-time method of 7 min]

3.2.3. Effect of Ponceau Xylidine concentration

Fig. 3 shows the change in the net reaction rate with Ponceau Xylidine concentration. In the presence of vanadium (V), the net reaction rate increases with increasing indicator dye concentration up to 6x10^{-5} mol L^{-1} and gives a peak at this concentration. The net reaction rate gradually decreases in the range of 6x10^{-5}-1x10^{-4} mol L^{-1} and reaches a plateau at 1x10^{-4} mol L^{-1}. This state can be explained by the fact that the rate of uncatalyzed reaction is independent of indicator dye concentration in higher concentrations. Thus, a dye concentration of 6x10^{-5} M was selected as the optimum Ponceau Xyldine concentration.

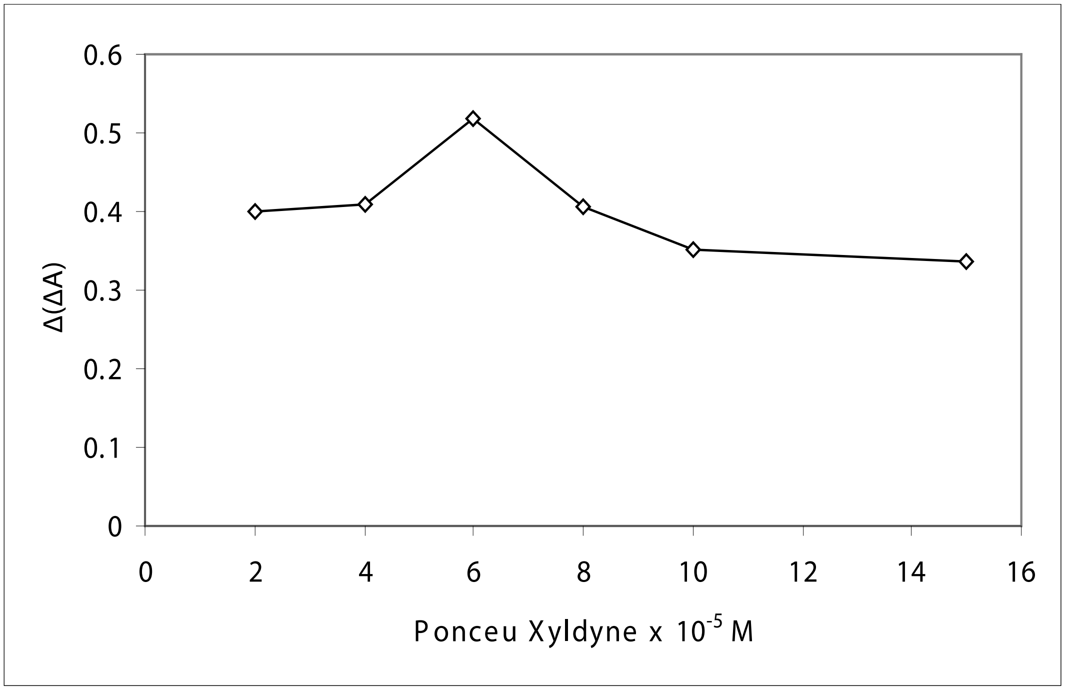


Fig.3. Effect of Ponceau Xylidine concentration on analytical sensitivity.[Optimum conditions: 0.015 mol L^{-1} BrO_3^-, 9 ppb V(V), $2x10^{-4}$ mol L^{-1} SSA and 0.16 mol L^{-1} H_3PO_4 at 640 nm and 25^oC for the fixed-time method of 7 min]

3.2.4. Effect of SSA concentration

The use of properly selected activators for catalytic reactions offers an improvement in both the sensitivity and the selectivity [23]. There have been numerous reports on vanadium-catalyzed indicator reactions in which some ligands acted as activators: oxine [24], oxalic, citric [25] and sulfosalicylic acids [26,25], Tiron [27-29], tartrate [30], gallic acid [31] and hydrogen carbonate [32]. The possibility for further increase in the sensitivity of catalytic method is the application of a suitable activator into the catalytic system. The various activators examined were oxalate, tartrate, citrate, sulfosalycilic acid (SSA), and salicylic acid. Among them, it was found that SSA has the greatest activating effect on this reaction. In the present study we employed sulfosalycilic acid (SSA) as the best suitable activator for the catalytic oxidation of Ponceau Xylidine. The effect of SSA concentration on the net reaction rate, Δ(ΔA) was shown in Fig. 4. In the concentration range of $2x10^{-4}$-$6x10^{-4}$ mol L^{-1}, the pronounced increase in the net reaction rate has been observed. However, the rate of catalytic net reaction remained almost constant at SSA concentrations higher than $6x10^{-4}$ mol l^{-1}. Thus, a SSA concentration of $6x10^{-4}$ mol L^{-1} was selected as the optimum activator concentration.

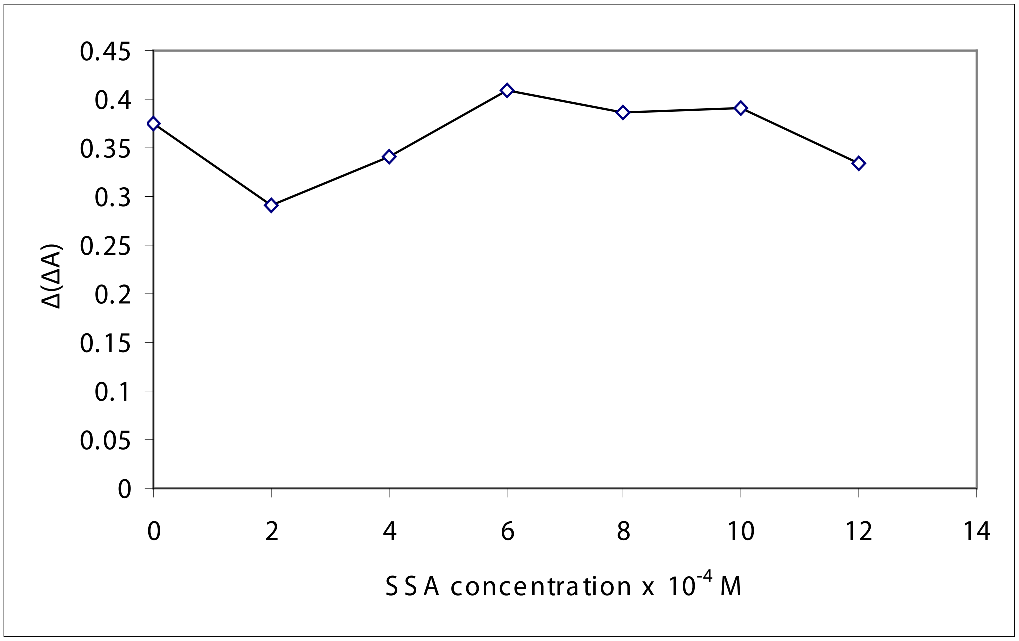


Fig.4. Effect of SSA concentration on analytical sensitivity.[Optimum conditions: $6x10^{-5}$ mol L^{-1} Ponceau Xylidine, 0.015 mol L^{-1} BrO_3^-, 9 ppb V(V) and 0.16 mol L^{-1} H_3PO_4 at 640 nm and 25^oC for the fixed-time method of 7 min]

3.2.5. Effect of ionic strength

The effect of ionic strength on the rate of the net reaction was studied by the addition of different concentrations of Na_2SO_4 into the solution in the range of 0.001–0.500 mol L^{-1}. Based on the results, increasing the electrolyte concentration up to 0.200 mol L^{-1} cause a decrease in the sensitivity and then reach a plateau. The change in ionic strength with increasing electrolyte concentration in the range of 0.200–0.050 mol L^{-1} did not have any effect on the reaction rate. Therefore, a concentration of 0.200 mol L^{-1} was considered as optimum value for further study. However, it may be recommended that a better signal could be taken at lower ionic strength ($\mu \leq 0.1$ mol L^{-1}); therefore, no salt addition to the test solution was used for further studies. Standard addition method is suggested for analyzing vanadium(V) in real samples having high salt content.

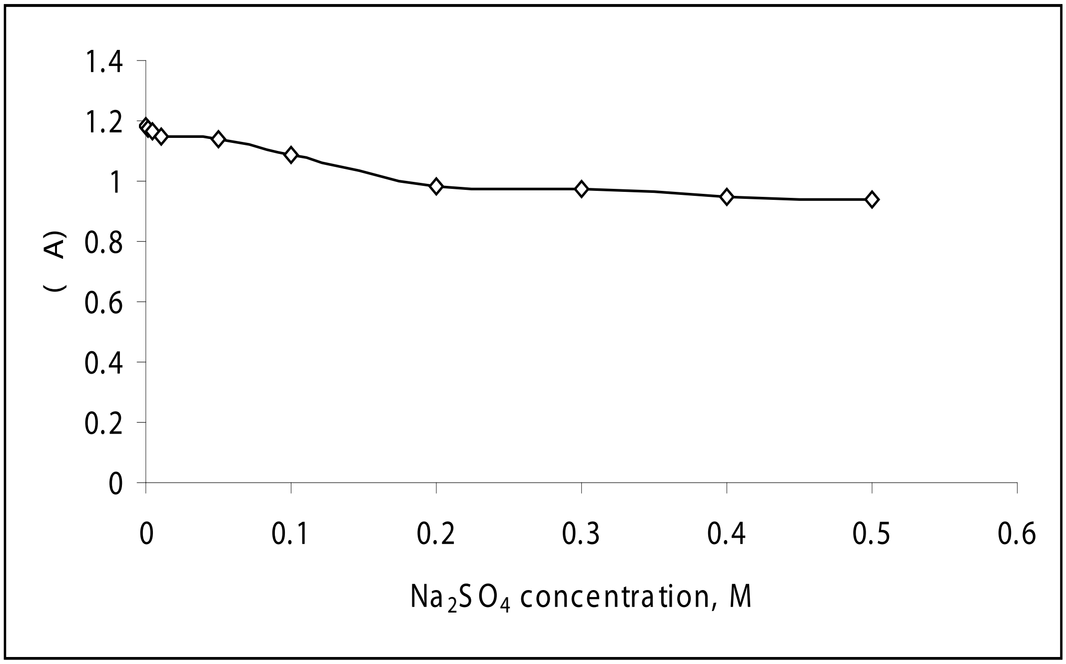


Fig.5. Effect of ionic strength on analytical sensitivity.[Optimum conditions: 6x10^{-4} mol L^{-1} Ponceau Xylidine, 0.015 mol L^{-1} BrO_3^-, 6x10^{-4} mol L^{-1} SSA, 9 ppb V(V) and 0.16 mol L^{-1} H_3PO_4 at 640 nm and 25^{o}C for the fixed-time method of 7 min]

3.2.6. Effect of temperature

The change of net reaction rate with temperature was studied between 20 and 50°C for the uncatalyzed and catalyzed reactions under optimum conditions. The reaction rate of the catalyzed reaction increases with increasing temperature and reaches a maximum value at 40°C. The reaction rate of the uncatalyzed reaction is constant and nearly zero, up to 40°C. At higher temperatures a small but meaningful change in the absorbance for uncatalyzed reaction was observed (Fig. 6). For this reason and also for simplicity of temperature control through the experiments, a temperature of 25°C was selected for further work.

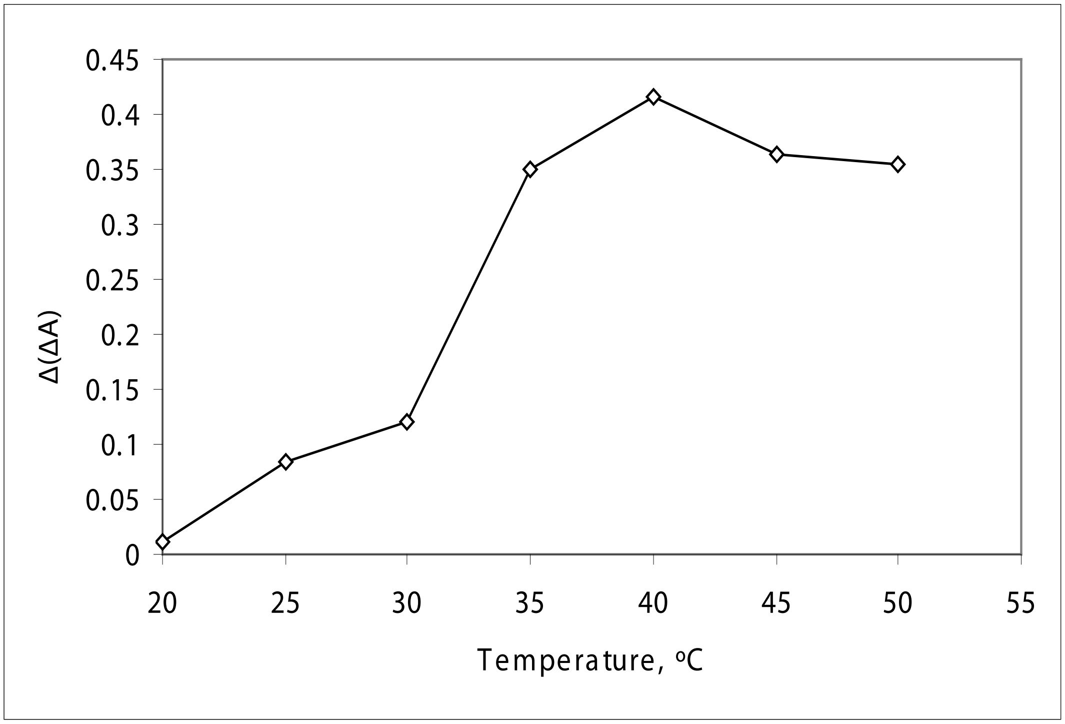


Fig.6. Effect of reaction temperature on analytical sensitivity.[Optimum conditions: 6x10^{-5} mol L^{-1} Ponceau Xylidine, 0.015 M BrO_3^-, 6x10^{-4} mol L^{-1} SSA, 9 ppb V(V) and 0.16 mol L^{-1} H_3PO_4 at 640 nm for the fixed-time method of 7 min]

3.3. Analytical figures of merit

3.3.1. Linear range, detection limit and reproducibility of the method

The linear range for vanadium determination was evaluated over a fixed time of 0.5–7.0 min from initiation of reaction under the optimum conditions. The rate of the net catalytic reaction increased linearly with V(V) concentration over the range 1–15 ng mL^{-1}. A detection limit (according to statistical $3S_{blank}/k$ criterion for ten replicate measurement) of 0.46 ng mL^{-1} of V(IV) was obtained. The statistical limit value was calculated by multiplying the standard deviation of eleven replicate measurements of absorbance for the reagent blank by three and dividing by the slope of the linear calibration curve. A study of the precision and accuracy of the method was made with five independent experiments and solutions of various concentrations of V(V) under the optimum conditions (Table 1). The vanadium(V) concentrations were evaluated from a calibration graph.

Table 1 Precision and accuracy of the the present kinetic method under optimum conditions

V(V) present (ng mL^{-1})	V(V) found (ng mL^{-1})	RSD (%)[a]
4.00	3.80	3.70
6.00	5.75	3.10
8.00	7.85	2.70
12.00	11.90	2.35

[a] Relative standard deviation for three replicate measurements

3.3.2. Interference study

The effect of interfering ionic species on the determination of V(V) was investigated. More than 20 ions were examined for their possible interferences in the determination of 10 ng mL^{-1} V(V) under the optimum conditions. The tolerance limit was defined as the concentration which gave an error of 5.0 % in the determination of 10 ng mL^{-1} V(V). The results are presented in Table 2.

Table.2 Interference of co-existing ions on the determination of V(V) (10 ng mL^{-1}) by the proposed kinetic method

Coexisting ion	Tolerance ratio, [Interfering species]/[V(V)]
K^+, NH_4^+, Cl^-, F-, CH_3COO^-, NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, Na^+ and Li^+	4000[a]
CN^-, Br^-, HSO_4^-, HCO_3^-, Ca^{2+}, Ba^{2+} and Sr^{2+}	2000
Al^{3+}, V(IV) and $S_2O_8^{2-}$	200
SeO_3^{2-}, $SO_3^{2-}$and SCN^-	120
Cd^{2+}, Mn^{2+}, Ce^{3+}, Zn^{2+} and Cr^{3+}	35-50
Cu^{2+}, NO_2^-, Ce^{4+}, Fe^{2+}, I-	15-35
Fe^{3+}	10[b]
Cu^{2+} and Hg^{2+}	5-10[c]
CrO_4^{2-}	2[d]

[a] The tolerance ratio was defined as that ratio causing a relative error of ≤ 5%.
[b] Added 0.1 ml of 0.1 % (w/v) EDTA solution.
[c] Added 0.5 ml of 1.0 % (w/v) NaF solution.
[d] Effectively eliminated with using masking agent such as EDTA or removing a strongly cation-exchange resin after pre-reduction of Cr(V) to Cr(III) with ascorbic acid.

From the results, it can be seen that a serious of various cations and anions can be tolerated in a satisfactory level of their limiting concentration ratio. The method has good selectivity. Only Fe^{3+}, Cu^{2+}, Hg^{2+} and CrO_4^{2-} have either increased or disturbed the rate of the catalytic reaction in the presence of vanadium(V) at weight ratio less than 100-fold. The masking agents examined for these ions, such as tartrate, EDTA and F^- at concentrations not affecting the determination of vanadium(V). The results indicate that F^- can effectively mask the Fe^{3+}, while EDTA can mask Cu^{2+} and Hg^{2+}, even more than

250-fold causing a relative error of less than or equal to 5%. However, higher concentrations of them must be separated and/or removed by using a strongly cation-exchange resin such as Amberlite IR120 prior to the determination of vanadium.

3.3.3. Analytical applications to different natural water samples and standard reference material

The proposed method was applied to the determination of vanadium in tap water, drinking water and bottled mineral water samples. 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 natural water samples were filtered through a Millipore membrane filter with a pore size of 0.45 μm. These sample solutions were acidified by adding concentrated hydrochloric acid to pH about 1. In addition, the standard reference material (SRM) 1640 (Trace Elements in Natural Water) issued by National Institute of Standard and Technology (NIST) was employed without any pretreatment process. These samples were directly analyzed by means of the proposed kinetic method. The certified reference sample was analyzed after dilution of 1/10. Also, the vanadium contents of samples were determined by FAAS for a comparison. All analytical results were obtained by using the linear calibration method. To examine the recovery of vanadium, the known amounts of vanadium(V) were added to the sample solution. The results are summarized in Table 3.

Table 3 Determination of vanadium(V) in different natural water samples

Sample(s)	V(V) added (ng mL^{-1})	V(V) found (ng mL^{-1})	RSD % (N:5)	Recovery %	Found by FAAS (V(V) (ng mL^{-1})
Tap water[a]	0	7.16	2.7	-	7.21
	1	8.14	2.5	98	
	3	10.23	2.4	102.3	
	5	12.18	2.1	100.4	
Drinking water[a]	0	3.12	3.2	-	3.16
	1	4.15	2.8	103	
	3	6.18	2.5	102	
	5	8.16	2.3	100.8	
Bottled mineral water[b]	0	5.35	2.8	-	5.38
	1	6.38		103	
	3	8.41		102	
	5	10.32		99.4	
SRM 1640[c]	0	1.36	1.9	-	1.39
	1	2.41		105	-
	3	4.36		100	-
	5	6.43		101.4	-
	10	11.45		100.9	-

[a] Collected at University of Cumhuriyet

[b] It was bought from a local market (Niksar water, Tokat)

[c] tandard reference material, SRM 1640 (Trace element in Natural Water) issued by National [c] Institute of Standard and Technology (NIST). The certified value of vanadium is 13.01±0.37 ng mL^{-1}

The recovery of spiked vanadium(V) was found to be quantitative and the reproducibility was satisfactory. It was observed that the results of the SRM 1640 were in good agreement with the certified value.

3.3.4. The possible catalytic reaction mechanism

It can be clearly known [33] that most indicator reactions used for kinetic-catalytic determination of trace of elements are based on oxidation-reduction reactions in which the catalyst that is usually a multi-charged ion such as V(V) changes its oxidation state during the reaction. Bontchev [34,35] reported that complexing and/or reducing agents for vanadium such as oxalate, tartrate, citrate and sulfosalycylic acid (SSA), gallic acid and Tiron act as activators on the catalytic oxidation of p-phenetidine by vanadium(V) in the presence of chlorate. Author also reported that such activators (A) are oxidized easily by vanadium(V) to radicals (A •), which then react with the co-existed *p*-phenetidine (S) to produce its radical (S•), followed by the recombination of (S•) radical. SSA has one hydroxyl group to be easily reduced. Hence the similar pathway as mentioned above can be thought to proceed in the present catalytic reaction. Thus, the activating effect of these complexing and/or reducing agents on the present indicator reaction was tested. Among these agents, SSA was found to have a stronger activating effect for vanadium(V). In fact, SSA can effectively activate the catalytic reaction, which can be explained according to Bontchev: multidentate activators such as sulfosalycylic acid, oxalate, tartrate and citrate capable of complexation with vanadium(IV) and/or reaction of vanadium(V) and at the same time forming hydrogen bonds with Ox could facilitate and accelerate the formation of charge-transfer complex necessary for the re-oxidation of vanadium(IV) and enhance the rate of the vanadium(V)-catalyzed reactions for the oxidation of Ponceau Xyldine by potassium bromate. The possible catalytic reaction mechanism for the chemical system in 0.16 mol L^{-1} H_3PO_4 media may be indicated by a serial of reactions as follows:

$$SSA_{ox} + VO_2^+ + H^+ \leftrightarrow SSA_{red} + VO^{2+} + CO_2 + H_2O \qquad (1)$$

$$6V^{4+} + BrO_3^- + 6H^+ \leftrightarrow 6V^{5+} + Br^- + 3H_2O \qquad (2)$$

$$BrO_3^- + 6SSA_{ox}^- + 6H^+ \leftrightarrow Br^- + 6SSA_{red} + 6CO_2 + 3H_2O \qquad (3)$$

$$5Br^- + BrO_3^- + 6H^+ \leftrightarrow 3Br_2 + 3H_2O \qquad (4)$$

$$Br_2 + HIn_{red}, indicator \leftrightarrow 2Br^- + HIn_{ox}, \deg radationproduct(s) \qquad (5)$$

The catalytic effect of vanadium(V) is to join reactions (1) and (2) repeatedly to produce Br^- and to catalyze reaction (4) The reaction of SSA is only as a buffering reduction reagent to provide sufficient Br^- in reactions (1), (2) and (3). Therefore, Br_2 is produced in reaction (4); then the indicator was oxidized by Br_2 its color was decreased. SSA doesn't show any effect on the uncatalytic reaction, and therefore it is a good reducing activator for the catalytic determination of vanadium (V).

4. Conclusions

A new catalytic-kinetic spectrophotometric method is proposed for the determination of ppb levels of vanadium(V). The method is based on the catalytic effect of vanadium(V) on the oxidation of Ponceau Xylydine with potassium bromate in 0.16 mol L^{-1} H_3PO_4 media. The sensitivity was enhanced by adding SSA as an effective activator, being determined as low as 0.46 ng mL^{-1} vanadium. The serious interference from Cr(VI) ion can be effectively eliminated with using masking agent such as EDTA or removing a strongly cation-exchange resin after prereduction of Cr(V) to Cr(III) with ascorbic acid. In comparison with most instrumental techniques that can usually be coupled with prior separation and preconcentration process, the present kinetic method is a new, simple, sensitive, selective and precise method for the vanadium determination in especially natural water samples down to 0.46 ng mL^{-1} using a simple spectrophotometer. On the other hand, among the numerous catalytic methods for vanadium determination only eleven methods [36-46] dealt with real samples, probably due to the limited sensitivity and/or selectivity of such methods.

Table.4 Comparison of the present kinetic method with similar catalytic spectrophotomeric methods for the determination of vanadium

Indicator reaction	Activator	Procedure	Dynamic range (ng mL^{-1})	Applications	Reference
AA+DMA+BrO$_3^-$	SSA	Fixed-time	0.05-1	River, lake, and sea water	[36,37]
Chlorpromazine+BrO$_3^-$	Tartaric acid	Initial rate	0.2-150	Rain and river water	[38]
Gallocyanine+BrO$_3^-$		Fixed-time	0.01-150	Food	[39]
Thionine+BrO$_3^-$		Fixed-time	0-0.5 µg mL^{-1}		[40]
Reduced Rhodamine B+BrO$_3^-$	Ascorbic acid	Fixed-time	0-100	Coal	[41]
Perphenazine+BrO$_3^-$	Citric acid	Tangent method	0.08-6.5	River water	[42]
Leucomethylene blue+BrO$_3^-$		Reaction rate	0.2-7	Salt	[43]
TMBZ-PS+BrO$_3^-$	SSA	FIA	0.05-8	River, pond and tap water	[44]
DNA+BrO$_3^-$	Tiron	Fixed-time	0.025-15	Rice and hair	[45]
Metol+THBA+BrO$_3^-$	Tartrate	Fixed-time	0.008-0.75	Natural and sea water	[46]
Ponceau Xyldine+BrO$_3^-$	SSA	Fixed-time	1-15	Three different natural water samples	The present method

DMA *N*,*N*-dimethylaniline, *AA* 4-aminoantipyrine, *TMBZ-PS* *N*-(3-sulfopropyl)-3,3′,5′,5′-tetramethylbenzidine, *DNA* 1,8-diaminonaphthalene, *THBA* 2,3,4-trihydroxybenzoic acid, *SSA* 5-sulfosalicylic acid, *Tiron* 1,2-dihydroxybenzene-3,5-disulfonate, *FIA* flow injection analysis

Table.4 shows the advantages and disadvantages of the present kinetic method. The method is successfully applied to the analysis of vanadium in natural water samples without preconcentration and separation. The accuracy and precision of the method was also controlled by means of the recoveries of V(V) spiked water samples and determination of vanadium in certified natural water reference material such as SRM 1640.

Acknowledgements

Authors wish to express their graduate to Professor Mehmet Akçay for all expertly discussions with him during his stay at University and were exchanged in a number of e-mails even after his departure, as all of his suggestions contributed enormously in the preparation of this manuscript. Authors would like to thank Professor Ferda Candan, Head of Chemistry Department, Faculty of Science & Arts, and University of Cumhuriyet for the technical support and facilities that was extended even after the normal time period.

References

[1]. M. B. Melwanki, J. Seetharamappa, S. P. Masti, Anal. Sci., 17 (2001) 979.
[2]. D. C. Crans, M. S. Gottlieb, J. Tawara, R. L Bunch, L. A. Theisen, Anal. Biochem., 188 (1990) 53.
[3]. A. Abbaspour, R. Mirzajani, Spectrochim. Acta Part A, 64 (2005) 646.

[4]. M. J. C Taylor, J. F. Vanstaden, Anal. Chim. Acta, 307 (1995) 1
[5]. A. Safavi, H. Abdollahi, F. Sedaghatpour, S. Zeinali, Anal. Chim. Acta, 409 (2000) 275.
[6]. R. R. Greenberg, H. M. Kingston Anal. Chem., 55 (1983) 1160.
[7]. T. Yamashige, M. Yamamoto, H. Sunahara, Analyst, 114 (1989) 1071.
[8]. A. Gaspar, J. Posta, Fresenius J Anal Chem., 360 (1998) 179
[9]. A. S. Mohamad, K. H. Fawy, Mikrochim. Acta, 134 (2000) 229.
[10]. A. Massoumi, H. Tavallali, Anal. Lett., 31 (1998) 193.
[11]. A. A. Ensafi, M. K. Amini, M. Mazloum, Anal. Lett., 32 (1999) 1927.
[12]. K. Gavazov, V. Lekova, G. Patronov, M. Turkyilmaz, Chem. Anal. (Warsaw), 51 (2006) 221.
[13]. A. K. Chakrabarti, Talanta, 42 (1995) 1279.
[14]. Y. Sharma, Analyst, 107 (1982) 582.
[15]. N. Agnihotri, R. Das, R. Mehta, J. Indian Chem. Soc., **77** (2000) 264.
[16]. M. B. Melwanki, J. Seetharamappa, Indian J. Chem.**,** 39A (2000) 465.
[17]. M. Leon-Camacho, M. Ternero-Rodriguez, M. Callejon-Mochon, A. Guiraum-Perez, Anal. Chim. Acta*,* 244(1) (1991) 89.
[18]. H. S Wang, A. M. Zhang, J. Microchem., 57 (1997) 218.
[19]. K. Pyrzynska, Microchim. Acta, 149 (2005) 159.
[20]. A. Safavi, M. R. Hormozi Nezhad, E. Shams, Anal. Chim. Acta, 409 (2000) 283.
[21]. G. Absalan, Y. Alipour, Anal. Sci., 19 (2003) 635.
[22]. H. R Pouretedal, M. H. Keshavarz, Chin. J. Chem., 24 (2006) 557.
[23]. P.R. Bontschev, Talanta, 19 (1972) 675.
[24]. P.R. Bontchev, B.G. Jeliazkowa, Inorg. Chim. Acta, 1 (1967) 249.
[25]. P.R. Bontchev, G.S. Nikolov, J. Inorg. Nucl. Chem.**,** 28 (1966) 2609.
[26]. T. Shiobara, N. Teshima, M. Kurihara, S. Nakano, T. Kawashima, Talanta**,** 49 (1999) 1083.
[27]. J. Gao, X. Zhang, W. Yang, B. Zhao, J. Hou, J. Kang, Talanta,51 (2000) 447.
[28]. S. Nakano, M. Tago, T. Kawashima, Anal. Sci., 5 (1989) 69.
[29]. S. Nakano, E. Tanaka, Y. Mizutani, Talanta**,** 61 (2003) 203.
[30]. A.A. Mohamed, K.F. Fawy, J. Trace Microprobe Tech., 20 (2002) 29.
[31]. S. Kawakubo, K. Kajihara, M. Iwatsuki, Anal. Sci., 12 (1996) 237.
[32]. S. Nakano, K. Sakamoto, A. Takenobu, T. Kawashima, Talanta**,** 58 (2002) 1263.
[33]. P.R. Bontchev, Talanta, 17 (1970) 499.
[34]. P.R.Bontchev, G.S. Nikolov, J. Inorg. Nucl. Chem., 28 (1966) 2609
[35]. P.R. Bontchev, Talanta, 19 (1972) 675
[36]. S. Nakano, C. Yamada, M. Sakai, T Kawashima, Anal Sci., 2 (1986) 61
[37]. S. Nakano, S. Kinoshita, M. Ikuta, T. Kawashima, Anal Sci., 6 (1990) 435.
[38]. S. Kawakubo, B. Liang, M. Iwatsuki, T. Fukasawa, Analyst, 119 (1994) 1391.
[39]. A.A. Ensafi, A. Kazemzadeh, Anal Chim Acta, 298 (1994) 27.
[40]. L. Bai, W. Zhang, X. Liu, L. Liang, Rare Metals, 26(1) (2007) 85.
[41]. Q. Shao Fuel and Energy Abstracts, 38(6) (1997) 447.
[42]. A.A. Mohamed, M. Iwatsuki, T. Fukasawa, M.F. El-Shahat, Analyst, 120 (1995) 2281
[43]. S. Kawakubo, K. Ogihara, M. Iwatuki, T. Fukasawa, J Trace Microprobe Tech., 15(1997) 189.
[44]. T. Shiobara, N. Teshima, M. Kurihara, S. Nakano, T. Kawashima, Talanta 49 (1999) 1083.
[45]. J. Gao, X. Zhang, W. Yang, B. Zhao, J. Hou, J. Kang, Talanta, 51 (2000) 447.
[46]. A.A. Mohamed, K.F. Fawy, Anal Sci. 17 (2001) 769.