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Kinetic Determination of Arsenic(III) as Inhibitor of Victoria Blue 4R Oxidation in Strong Acid Solution

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A new selective, sensitive and simple kinetic method was developed for the determination of As^{3+} traces in solution on the basis of their inhibiting effect on Victoria blue 4R (VB) oxidation by $KBrO_3$ in the presence of HCl. The reaction was followed spectrophotometrically at 596.3 nm. The detection limit was 50.00 ng cm^{-3}. The relative error vas 4.2 % to 1.5 % for As^{3+} in the concentration range from 80.00 to 350.00 ng cm^{-3}. Also, appropriate kinetic equations were formulated and the influence of different ions upon the reaction rate was studied. The developed procedure was successfully applied to the determination of As^{3+} in various model and real samples.

Keywords
As^{3+} determination
kinetic determination
Victoria blue 4R

INTRODUCTION

Arsenic is the twentieth most abundant element in the earth's crust. Many arsenic compounds are present in the environment and in biological systems. Arsenic is naturally present in all environmental compartments in various forms, depending on the nature of the sample. The toxicological behavior and biochemical activity of arsenic depend on its chemical form.[1–5] Inorganic arsenic species, (arsenite and arsenate) are more toxic than the simple methylated arsenicals (methylarsenic acid (MA) and dimethylarsenic acid (DMA)) followed by the more complex organic arsenicals (arsenobetaine, arsenocholine, tetramethylarsonium ion, arsenoribosides), which are considered non-toxic to living organisms. Arsenic occurs in the earth's crust at an average level of 2–5 ppm. Arsenic is a toxic element. Its biochemical effects include protein coagulation, enzyme inhibition, and uncoupling of phosphorylation. Acute poisoning results from ingestion of *ca*. 100 mg of the element, and much lower levels cause chronic poisoning. There is some evidence that arsenic is also carcinogenic.[6]

Therefore, simple, rapid, highly sensitive, and accurate methods are required for the determination of trace amounts of arsenic in samples. Different methods have been used for arsenic determination. These include polarography,[7] chemiluminescence,[8,9] titrimetry,[10,11] hydride generation atomic absorption spectrometry,[12,13] high performance liquid chromatography (HPLC) coupled with hydride generation and atomic fluorescence spectrometry (AFS) or hydride generation and inductively coupled plasma mass spectrometry (ICP-MS),[14] microwave-assisted extraction with HPLC–ICP-MS,[15] ICP-MS,[16] HPLC with hydride generation AFS,[17] elevated temperature

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HPLC with ICP-MS,[18] and spectrophotometry.[19–23] Some of these methods are either not sensitive enough or require complicated and expensive instruments or only allow direct determination of the total amount of arsenic, that is, the distinction between As^{3+} and As^{5+} requires ancillary manipulation.

Among the different kinetic methods for trace determination in solution, As^{3+} was mentioned for the first time by Sandell and Kolthoff. They used the reaction between As^{3+} and Ce^{4+}, which is catalyzed by I^- ions, for the determination of I^-.[24,25] Other authors used different laboratory techniques[26,27] to study the influence of various factors on the reaction rate: concentration of the reactants, the type of acid (HNO_3 and H_2SO_4) and the presence of Cl^- ions in the solution. The As^{3+}-Ce^{4+} reaction system was also studied by Worthington and Pardue.[28] Garcia *et al.*[29] determined As^{3+} in the range of 6.2–62.6 μg dm^{-3} as an inhibitor of the reaction between pyronine G and hypophosphyte ions, which is catalyzed by Pd^{2+}. Koukli and Calokerinos used the variable-time method for the determination of As^{3+} by monitoring the iodide produced in the reaction of As^{3+} with iodate using an iodide-selective electrode.[30] Alekseeva and Kurtova determined As^{3+} in the range of 0.03–0.15 μg cm^{-3} based on its effect on the induction period of the oxidation reaction of Br^- by periodate.[31] Burgess and Ottaway reported a method for the determination of As^{3+} based on its effect on the redox reaction of bromate with bromide ion in sulfuric acid media.[32] Mitic *et al.* developed two methods for the kinetic determination of As^{3+} in solution. The first was based on the catalytic effect of As^{3+} ions on the oxidation of sodium pyrogallol-5-sulphonate by dichromate in acidic media[33] while the other on the same effect on the oxidation of pyrogallol by dissolved oxygen.[34] The reaction between $Fe(phen)_3^{2+}$ and Cr^{6+} was photometrically monitored at 513 nm[35] and the method was applied for determination of As^{3+} in wastewater. Stoytcheva *et al.* determined As^{3+} based on its inhibition action on the enzyme acethylcholinesterase.[36] Sicilia *et al.* determined As^{3+} in the range of 7–320 μg dm^{-3} on the basis of its accelerating effect on the Os^{8+}-catalyzed reaction between iodide and bromate in micellar media.[37] Spectrophotometric determination of As^{3+} in the presence of As^{5+} based on its inhibition effect on the redox reaction between bromate and hydrochloric acid was reported by Abbas Afkhami *et al.*[38] The method allowed determination of arsenic in the range of 6–1000 μg dm^{-3}. The proposed method was applied for the determination of As^{3+} in water samples.

Here, we present a new simple, selective and sensitive method for determination of As^{3+} in solution based on its inhibiting effect on Victoria blue 4R (VB) oxidation by $KBrO_3$ in the presence of HCl. The method was applied for determination of As^{3+} in samples of $FeSO_4$ and mineral-vitamin premixtures for animal food.

EXPERIMENTAL

Apparatus

A UV-VIS Perkin-Elmer-Lambda 15 spectrophotometer with 10 cm cylindrical cells connected to the thermocirculating bath was used for the absorbance measurements. The pH-values of solutions were determined by a Radiometer PHM 29 b pH-meter. Sigma buffers, pH = 7±0.01 and pH = 4±0.01, were used for the pH meter calibration. All measurements were done at a wavelength of 596.3 nm.

Reagents and Chemicals

All chemicals were of analytical–reagent grade, and they were provided by Merck unless indicated otherwise. The stock solution of As^{3+}(1×10^{-3} g cm^{-3}) was prepared by dissolving 0.1320 g As_2O_3 in 2.50 cm^3 of 20 % (*v*/*v*) KOH solution, neutralized with 20 % (*v*/*v*) H_2SO_4 to a phenolphthalein endpoint and diluted to 100.00 cm^3 with 1 % (*v*/*v*) H_2SO_4. The 1×10^{-4} mol dm^{-3} stock solution of VB (Fluka AG, Buchs SG c.i. number 42563, c.i. name Basic Blue 8, Figure 1) was prepared by dissolving 0.0130 g VB in an adequate volume of absolute ethanol. Concentration of the solution was checked spectrophotometrically. The stock solution was further diluted with absolute ethanol as required by the experiment. The 1×10^{-2} mol dm^{-3} solution of $KBrO_3$ was prepared by dissolving 0.1670 g of dry substance in 100.00 cm^3 deionized water. The 2 mol dm^{-3} stock solution of KCl was prepared by dissolving 14.9120 g KCl in an adequate volume of deionized water and was used to keep the ionic strength constant ($\mu = 0.1$ mol dm^{-3}). All stock solutions were stored in polyethylene containers. All polyethylene containers and the glassware were washed with the solution of potassium hydroxide in ethanol, hydrochloric acid diluted with deionized water in 1:1 ratio and then repeatedly rinsed with tap water, distilled water and finally with deionized water.

Treatment of $FeSO_4$ Samples

Arsenic can be separated from most other elements by suitable distillation procedures.[39] As^{3+} can be quantitatively removed as the chloride from an aqueous solution containing HCl. Distillation at a temperature of 110 °C was required. A sample of $FeSO_4$ (10.0000 g) was dissolved in 10 cm^3 of conc. HCl, distilled and the distillate was diluted to 50.00 cm^3 volume with deionized water.

Treatment of Samples of Mineral-vitamin Premixtures for Animal Food

After grinding in the agate mortar, the samples were dried at 105 °C to constant mass and then destroyed by wet digestion.[40] The sample (10.0000 g) was placed in a Kjeldahl flask, 100.00 cm^3 HNO_3 (65 %) was added and heated for 45 minutes at 100 °C. After cooling, 20.00 cm^3 $HClO_4$ (70 %) was slowly added and the mixture was very gently heated until the solution became nearly colorless. It was then concentrated to a small volume. The solution was diluted with

1.5 % HCl, filtrated over Whatman 44 filter paper (pre-rinsed with 1.5 % HCl) and quantitatively transferred to a calibration flask of 100.00 cm^3. Arsenic was separated from most other elements in the samples by a suitable distillation procedure, and the distillate was diluted to 50.00 cm^3 with deionized water.

Spectrophotometric Measurements

The vessels were washed with the solution of potassium hydroxide in ethanol, hydrochloric acid diluted with deionized water in 1:1 ratio and then repeatedly with tap water, distilled water and finally with deonized water. Aliquots of VB, $KBrO_3$, and As^{3+} solutions were separately measured in a Budarin vessel,[41] until solutions of KCl, HCl and deionized water (total volume 10 cm^3) were measured into one compartment of the vessel. The vessel was thermostated for ten minutes at 22±0.1 °C, then the solution was stirred and the chronometer was simultaneously turned on. The spectrophotometer cell was rinsed well and filled with the appropriate solution. Absorbance, *A*, was measured, starting from the 30th second, every 15 s within the first four minutes of the reaction.

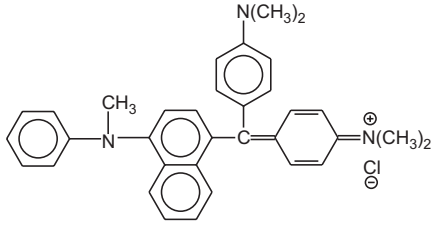

Figure 1. Chemical structure of Victoria Blue 4R. c.i. number 42563, c.i. name Basic Blue 8. (4-{(4-Dimethylamino-phenyl)-[4-(methyl-phenyl-amino)-naphtalene-1-yl]-methylene}-cyclohexa-2,5-dienylidene)-dimethyl-ammonium chloride.

RESULTS AND DISCUSSION

Absorption Spectrum

Victoria blue 4R (VB) (Figure 1) was oxidized by $KBrO_3$ in strong acid media. In the presence of traces of As^{3+}, the reaction was strongly inhibited and this change could be monitored spectrophotometrically. The absorption spectrum of VB and the spectrum of the indicating reaction mixture taken 0.5 min after the reaction started exhibit an absorption maximum at λ_{max} = 596.3 nm (Figure 2). As the reaction proceeded, the absorption maxima decreased with a bathochromic shift. In this range there was no absorption at all by the other reagents used in the study.

Kinetic Studies

With the progress of oxidation, the initial blue color of solution disappeared and a colorless reaction product was formed. The differential variant of the tangent[42] method was used for processing the kinetic data. The reaction rate was followed by the change in the values of the tangent of the angle (tg α) of the slope of the linear part of the kinetic curve to the abscissa in the coordinates *A*-*t* (as tg $\alpha = dA/dt$).

Effect of Reaction Parameters

To find the lowest possible concentration of As^{3+} that could be determined, the experimental conditions should be optimized. Therefore, the dependencies of the rates of both the indicating (VB, HCl, $KBrO_3$, KCl) and inhibiting (VB, HCl, $KBrO_3$, KCl, As^{3+}) reactions on the concentration of each of the reactants were determined.

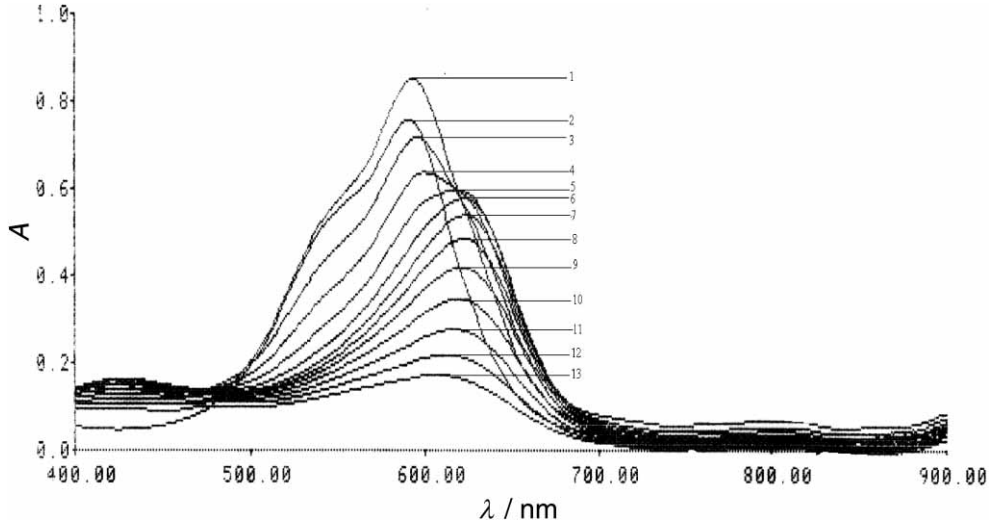

Figure 2. Absorption spectra of VB (1) and the indicating reaction mixture of VB and $KBrO_3$ (2–13) in acidic medium: effect of reaction time. Initial conditions: (1) $c(VB) = 1.6 \times 10^{-6}$ mol dm^{-3}, $c(HCl) = 2.25 \times 10^{-2}$ mol dm^{-3}, $\varphi(C_2H_5OH)$ = 13 %; (2)–(13) $c(VB) = 1.6 \times 10^{-6}$ mol dm^{-3}, $c(HCl) = 2.25 \times 10^{-2}$ mol dm^{-3}, $\varphi(C_2H_5OH)$ = 13 %, $c(KBrO_3) = 0.5 \times 10^{-3}$ mol dm^{-3}, c(KCl) = 0.1 mol dm^{-3}. Reaction time: (1) and (2) 0.5 min; (3) 1.0 min, (4) 1.5 min, (5) 2.0 min, (6) 2.5 min, (7) 3.0 min, (8) 3.5 min, (9) 4.0 min, (10) 4.5 min, (11) 5.0 min, (12) 5.5 min, (13) 6.0 min.

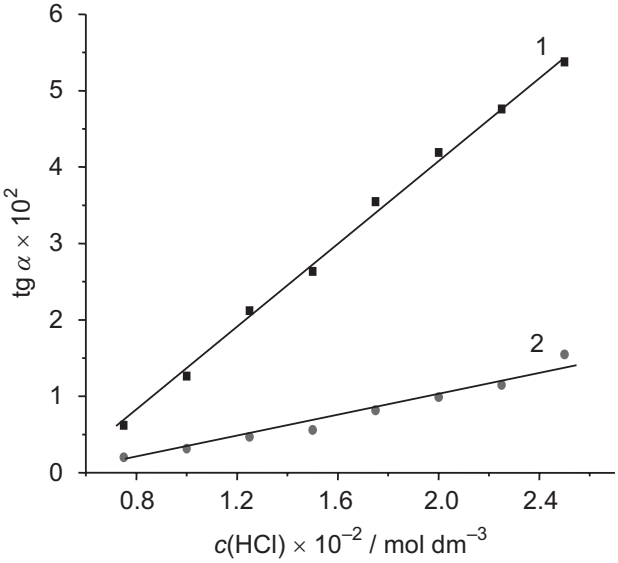

Figure 3. Dependence of the reaction rate of VB and $KBrO_3$ on HCl concentration. 1 – indicating reaction (without As^{3+}), 2 – inhibiting reaction (with As^{3+}). Initial conditions: c(VB) = 2.0×10^{-6} mol dm^{-3}, c($KBrO_3$) = 5×10^{-4} mol dm^{-3}, c(KCl) = 0.1 mol dm^{-3}, γ(As^{3+}) = 5×10^{-7}g cm^{-3}, t = 22±0.1 °C.

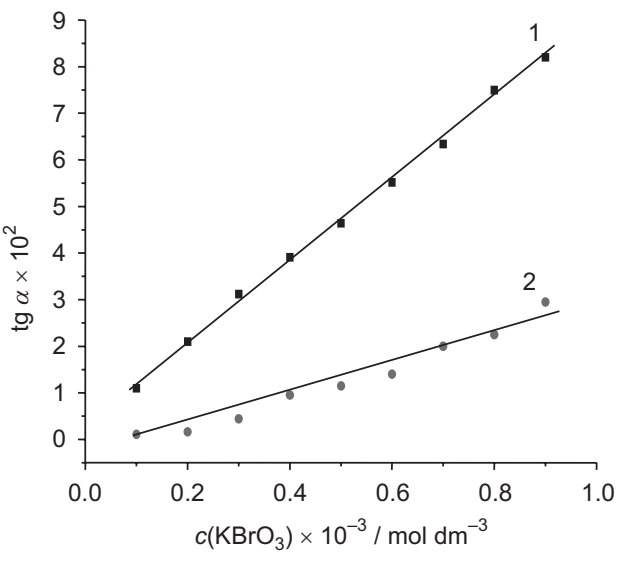

Figure 4. Dependence of the reaction rate of VB and $KBrO_3$ on $KBrO_3$ concentration. 1 – indicating reaction (without As^{3+}), 2 – inhibiting reaction (with As^{3+}). Initial conditions: c(VB) = 2.0×10^{-6} mol dm^{-3}, c(HCl) = 2.25×10^{-2} mol dm^{-3}, c(KCl) = 0.1 mol dm^{-3}, γ(As^{3+}) = 5×10^{-7} g cm^{-3}, t = 22±0.1 °C.

Keeping the other experimental parameters constant, the influence of the HCl concentration was studied. It can be seen (Figure 3) that in the investigated interval (0.75×10^{-2} – 2.75×10^{-2} mol dm^{-3}), both the indicating and inhibiting reactions were first order with respect to the HCl concentration. As the value with the best reproducibility, the HCl concentration of 2.25×10^{-2} mol dm^{-3} was selected and kept constant in further experiments.

Study of the dependence of reaction rates on the $KBrO_3$ concentration (in a range from 1.0×10^{-4} to 9.0×10^{-4} mol dm^{-3}) showed that with an increase in $KBrO_3$ concentration, the difference between the rates of the indicating and inhibiting reactions also increased (Figure 4). Both reactions were first order with respect to the $KBrO_3$ concentration. For further experiments, the $KBrO_3$ concentration of 5×10^{-4} mol dm^{-3} was selected as optimal.

The correlation between tg α and Victoria blue 4R concentration (Figure 5) showed that the indicating reaction was negative first order with respect to the VB concentration, whereas the inhibiting reaction was first order with respect to the VB concentration. In the presence of VB in a concentration of 1.6×10^{-6} mol dm^{-3}, all measured values of the absorbance were in an interval of the highest accuracy for spectrophotometric determinations and lay in the range of 0.2 to 0.8.[43] This value was selected as optimal.

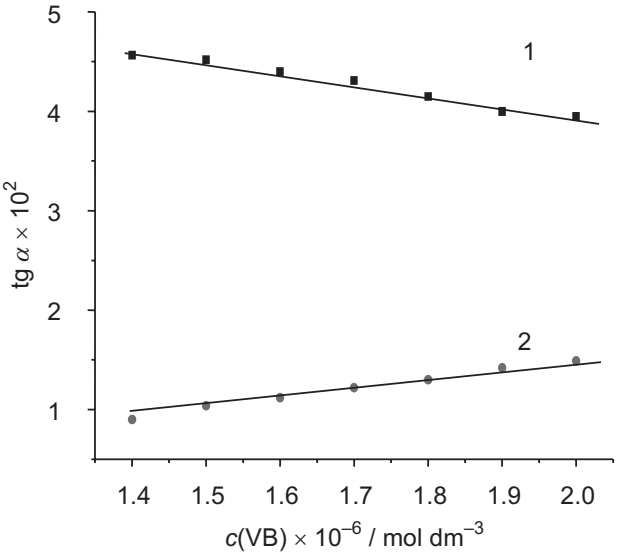

Figure 5. Dependence of the reaction rate of VB and $KBrO_3$ on VB concentration. 1 – indicating reaction (without As^{3+}), 2 – inhibiting reaction (with As^{3+}). Initial conditions: c(HCl) = 2.25×10^{-2} mol dm^{-3}, c($KBrO_3$) = 5×10^{-4} mol dm^{-3}, c(KCl) = 0.1 mol dm^{-3}, γ(As^{3+}) = 5×10^{-7} g cm^{-3}, t = 22±0.1 °C.

Calibration Graph

A calibration graph was prepared (Figure 6) under the optimal conditions chosen above. A linear relationship between tg α and As^{3+} concentration from 50.00 to 450.00 ng cm^{-3} was obtained and the fitted equation:

$$\text{tg}\,\alpha \times 10^2 = (4.11\pm0.01) - (0.00449\pm0.000039)\,\gamma$$
$$r = 99.92\ \%\qquad t = 22\pm0.1\ ^\circ\text{C}$$

where γ is the concentration of As^{3+} expressed in ng cm^{-3}.

Based on kinetic investigations, the kinetic equation for VB oxidation by $KBrO_3$ with As^{3+} as inhibitor was formulated.

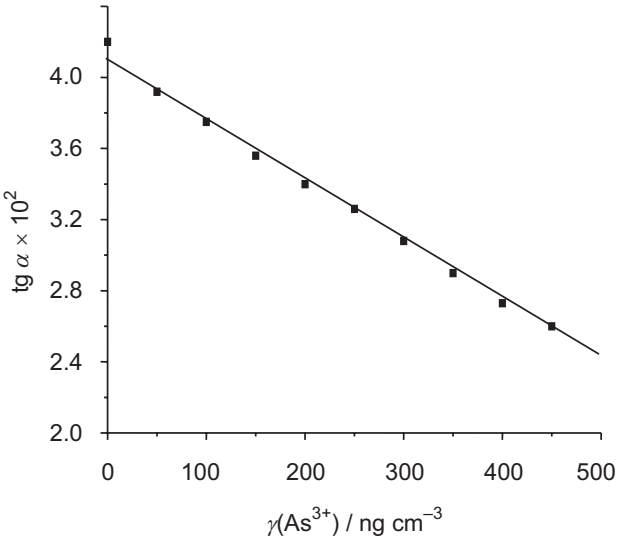

Figure 6. Calibration graph for As^{3+} determination. $c(HCl) = 2.25 \times 10^{-2}$ mol dm^{-3}, $c(KBrO_3) = 5 \times 10^{-4}$ mol dm^{-3}, $c(KCl) = 0.1$ mol dm^{-3}, $c(VB) = 2.0 \times 10^{-6}$ mol dm^{-3}, $t = 22 \pm 0.1$ °C.

For the indicating reaction:

$$-dc(VB)/dt = k\, c(HCl)\, c(KBrO_3)\, c(VB)^{-1}$$

For the inhibiting reaction:

$$dc(VB)/dt = k_1\, c(HCl)\, c(KBrO_3)\, c(VB)\, \gamma(As^{3+})^{-1}$$

where k is a constant proportional to the rate constant of the indicating reaction and k_1 is a constant proportional to the rate constant of the inhibiting reaction. Formulated kinetic equations corresponded for the following reagent concentration ranges:

- HCl concentration from 0.75 to 2.75×10^{-2} mol dm^{-3}
- $KBrO_3$ concentration from 1.0×10^{-4} to 9.0×10^{-4} mol dm^{-3}
- VB concentration from 1.4×10^{-6} to 2.0×10^{-6} mol dm^{-3}
- φ (C_2H_5OH) = 13 %
- $\gamma(As^{3+})$ from 50.00 to 450.00 ng cm^{-3}

The linear relationship between the logarithm of the relative rate constant and the reciprocal of the absolute temperature was found for both reactions. The activation energies were found to be 57.04±0.19 kJ mol^{-1} for the indicating reaction and 86.84±0.23 kJ mol^{-1} for the inhibiting reaction.

Accuracy and Precision

To estimate the accuracy and precision of the method, reaction rates were determined in five replicate determinations[44] (Student's criteria) at each of three different As^{3+} concentrations in the range of the calibration curve (80.00, 200.00 and 350.00 ng cm^{-3}). The relative error was from 1.5 to 4.2 %, while the relative standard deviation was 1.03 to 3.45 % for As^{3+} in the concentration range from 350.00 to 80.00 ng cm^{-3}.

Interference Studies

Influence of several foreign ions on the determination of As^{3+} was tested by 2S (S-standard deviation) criteria[45] at a constant As^{3+} concentration of 300 ng cm^{-3}. The maximum tolerable concentrations of 29 foreign species are presented in Table I, where the tolerance level was defined as the ratio of mass concentrations of foreign ions and As^{3+} that produced a change in the inhibiting reaction rate of less than 5 %. Most cations and anions did not interfere with the As^{3+} determination, even at concentrations 1–1000 times higher than the mass concentration of As^{3+}. Negative interference of Ni^{2+} and Co^{2+}, and positive interference of $Cr_2O_7^{2-}$ was observed (in 1:1 ratio to As^{3+}) as they influenced the investigated reaction. Inhibitory effect for I^-, Sb^{3+} was observed as they could also inhibit the indicating reaction when present in 0.5:1 ratio to As^{3+}. The results in Table I demonstrate that this method provides good selectivity.

TABLE I. Effect of foreign ions on As^{3+} determination

Tolerance level $\gamma(Ion)/\gamma(As^{3+})$	Ion added
1000	Na^+, Li^+, K^+, NH_4^+, Ca^{2+}, Ba^{2+}, Sr^{2+}, CH_3COO^-, HCO_3^-, CO_3^{2-}, $C_4H_4O_6^{2-}$, Hg^{2+}
100	Pb^{2+}, SO_4^{2-}, NO_3^-, As^{5+}
10	WO_4^{2-}, Mo^{6+}, Cd^{2+}
1	Cu^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, HPO_4^{2-}
0.5	Ni^{2+}, Co^{2+}, $Cr_2O_7^{2-}$
Inhibited	I^-, Sb^{3+}

$\gamma(As^{3+}) = 300$ ng cm^{-3}

Determination of As^{3+} in Model and Real Samples

To check the validity of the proposed method, it was applied to the As^{3+} determination in model and real samples. Model samples were prepared from common cations at various concentrations, higher (about 10 times and more) and lower than the As^{3+} concentration, and recovery experiments were performed. The results for As^{3+} determination in the model samples using the calibration curve method are shown in Table II.

As^{3+} was determined in samples of $FeSO_4$ ("Zorka" Šabac, Serbia and Montenegro). The results obtained by interpolation on a calibration graph and by the standard addition method are given in Table III. The results obtained by the present method were compared with those obtained by atomic absorption spectrometry.

TABLE II. Determination of As^{3+} in model samples

Model sample SS	Model sample composition, γ(Ion) / ng cm^{-3}	As^{3+} found ($\bar{x}$) γ / ng cm^{-3}	$\left(\frac{\bar{x}-\mu}{\mu}\right)$
SS_1	250 (As^{3+}), 2000 (As^{5+})	246±3	–1.6
SS_2	250 (As^{3+}), 2000 (As^{5+}), 200 (Pb^{2+})	255±2	2.2
SS_3	250 (As^{3+}), 200 (Cu^{2+}), 200 (Mn^{2+})	253±2	1.4

All data are an average of three replicate determinations.
μ – As^{3+} mass concentration added to SS.
$\bar{x}$ – As^{3+} mass concentration found in SS; mean value of three determinations.

TABLE III. Determination of As^{3+} in $FeSO_4$ samples

Sample	Sample volume of diluted distillate cm^3	As^{3+} added in diluted distillate µg cm^{-3}	As^{3+} found in diluted distillate µg cm^{-3}	$FeSO_4$ sample $w(As^{3+})$ / µg g^{-1}		$\left(\frac{\bar{x}-\mu}{\mu}\right)$
				VB method	AAS method	
$FeSO_4$	4.00	0.0	0.389	1.94±0.01	1.98±0.04	–2.02
$FeSO_4$	4.00	0.1	0.394	1.97±0.08	1.99±0.07	–1.00

All data are an average of three replicate determinations.
$\bar{x}$ – As^{3+} mass fraction determined by the VB method.
μ – As^{3+} mass fraction determined by the AAS method.

TABLE IV. Determination of As^{3+} in samples of mineral-vitamin premixtures for animal food

Sample S	Sample volume of diluted distillate cm^3	As^{3+} found in diluted distillate ng cm^{-3}	Food premixture sample, $w(As^{3+})$ / ng g^{-1}		$\left(\frac{\bar{x}-\mu}{\mu}\right)$
			VB method	AAS method	
S_1	3.00	66.4	332±8	347±8	–4.35
S_2	3.00	63.6	319±5	325±5	1.96
S_3	3.00	44.0	220±9	213±8	–3.58

All data are an average of three replicate determinations.
$\bar{x}$ – As^{3+} mass fraction determined by the VB method.
μ – As^{3+} mass fraction determined by the AAS method.

As^{3+} was also determined in samples of mineral-vitamin premixtures for animal food. The results obtained by interpolation on a calibration graph are given in Table IV. The results obtained by the present method were compared with those obtained by atomic absorption spectrometry.

Based on these results, the method seems to be applicable to the determination of As^{3+} in model and real samples.

CONCLUSIONS

Behavior of the VB-$KBrO_3$-HCl-KCl-As^{3+} system allowed the development of a simple kinetic method for the determination of trace amounts of As^{3+} ions. Simplicity, remarkable sensitivity and absence of most interference are the significant advantages of the method compared to the costly ICP-MS, AAS, ICP-AES techniques.

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SAŽETAK

Kinetičko određivanje arsena(III) kao inhibitora reakcije oksidacije Viktoria plavoga 4R u jako kiseloj sredini

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Razvijena je nova selektivna, osjetljiva i jednostavna kinetička metoda za određivanje tragova As^{3+} u otopini, koja se temelji na njegovom inhibicijskome utjecaju na oksidaciju Viktoria plavoga 4R (VB) pomoću $KBrO_3$ u prisutnosti HCl. Reakcija je praćena spektrofotometrijski pri 596.3 nm. Limit detekcije iznosio je 50.00 ng cm^{-3}. Relativna pogreška bila je 4.2 % do 1.5 % za As^{3+} u koncentracijskome opsegu od 80.00 do 350.00 ng cm^{-3}. Osim toga, formulirane su podesne kinetičke jednadžbe i ispitan je utjecaj različitih stranih iona na reakcijsku brzinu. Razvijena procedura uspješno je primjenjena na određivanje As^{3+} u različitim modelnim i realnim sustavima.