

## ANALYTICAL APPLICATION OF ACIDIC VICTORIA BLUE 4R MIXTURE WITH $\text{KBrO}_3$ FOR THE KINETIC DETERMINATION OF TRACES OF ANTIMONY(III) BY SPECTROPHOTOMETRY

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The present paper describes a simple, selective and sensitive kinetic method for the determination of trace amounts of Sb(III) in the presence of Sb(V) based on its inhibition effect on the redox reaction between bromate and Victoria blue 4R (V.B. 4-R) in hydrochloric acid media. The reaction was followed spectrophotometrically by measuring the decrease in the absorbance of V.B. 4-R at 596.3 nm. Optimum operating conditions regarding reagent concentrations were established. The optimized conditions yielded a theoretical detection limit of  $1.30 \cdot 10^{-8} \text{ g cm}^{-3}$  Sb(III) based on the  $3S_0$  criterion. The method allows the determination of Sb(III) in the range of  $5 \cdot 10^{-8} - 1.1 \cdot 10^{-6} \text{ g cm}^{-3}$ . The effects of certain foreign ions the reaction rate were determined for an assessment of the selectivity of the method. The kinetic parameters of the reaction were reported, and the rate equations were suggested. The results were validated statistically and through recovery studies. The proposed method has been successfully applied to the determination of Sb(III) in various model and real samples.

**Keywords:** Sb(III) determination; kinetic determination; bromate; Victoria blue 4-R

## АНАЛИТИЧКА ПРИМЕНА НА КИСЕЛА СМЕСА НА ВИКТОРИЈА СИНО 4R СО $\text{KBrO}_3$ ЗА КИНЕТИЧКО ОПРЕДЕЛУВАЊЕ ТРАГИ НА АНТИМОН(III) СО СПЕКТРОФОТОМЕТРИЈА

Во оваа статија е опишан едноставен, селективен и осетлив кинетички метод за определување на траги на Sb(III) во присуство на Sb(V) врз основа на нивниот инхибиторен ефект врз редокс-реакцијата помеѓу броматот и викторија сино 4R (V.B. 4-R) во средина на хлороводородна киселина. Реакцијата била следена спектрофотометриски со мерење на намалувањето на апсорбанцата на V.B. 4-R на 596,3 nm, при што биле определени оптимални услови за работа. Врз основа на критериумот  $3S_0$ , при овие оптимизирани услови теоретската граница на детекција е  $1,30 \cdot 10^{-8} \text{ g cm}^{-3}$  Sb(III). Методот овозможува определување на Sb(III) во областа од  $5 \cdot 10^{-8} - 1,1 \cdot 10^{-6} \text{ g cm}^{-3}$ . Било определувано влијанието на некои други јони врз процената на селективноста на методот. За методот се дадени кинетички параметри и биле предложени соодветни кинетички равенки. Резултатите се валидирани со статистички методи, како и со методот на стандардни додатоци. Предложениот метод бил успешно применет за определување на Sb(III) во различни моделни и реални примероци.

**Клучни зборови:** определување на Sb(III); кинетичко определување; бромат; викторија сино 4-R

## 1. INTRODUCTION

Antimony is present in the aquatic environment as a result of rock weathering, soil runoff, atmospheric deposition and human activities. It is a cumulative element with similar chemical and toxicological properties to arsenic [1]. Due to its many industrial uses, it is one of those elements that show anthropogenic mobilization into the environment [2]. In the last decades the global fluxes of Sb have increased at least 10-fold. The determination of antimony species is fundamental for environmental studies because its toxicity and biological behaviour depend on the oxidation state. Elemental antimony is more toxic than its salts. Toxicity of Sb(III) has shown to be 10 times higher than that of Sb(V) [2]. The toxicity and physiological behaviour of antimony not only depend on its oxidation state but also on organic substituents, which are bonded to this metal [3]. The toxic effects of antimony are the result of the irreversible binding to thiol-containing enzymes [4]. Sb(III) shows affinity for red cells and sulfhydryl groups of cell constituents, while red cells are almost impermeable to pentavalent antimony. Due to the presence of low concentrations of antimony in environment, high toxicity of the element and considerably different toxicity level of Sb(III) and Sb(V), several techniques for determination and speciation of antimony are required [5].

Kinetic methods of analysis are attractive methods for rapid determination of trace amounts of antimony. Such methods have the general advantage of combining high sensitivity, good selectivity with relatively simple, rapid procedures and inexpensive instruments, such as a spectrophotometer or spectrofluorimeter. Sensitive and reproducible extraction-spectrophotometric methods for differential determination of antimony(III) and antimony(V) were proposed by Sato [6]. It was found that antimony(III) reacts easily with mandelic acid to form a complex anion extractable into chlorobenzene with malachite green from weakly acidic media at room temperature, whereas antimony(V) reacts

only slowly, and heating. The significant difference between the rates of reaction of mandelic acid with antimony(III) and antimony(V) was applied to the differential determination of these two species. The calibration graph was linear over the range 0.15–6.0  $\mu\text{g}$  for antimony(III), and 0.20–10  $\mu\text{g}$  for antimony(V). Yamada and co-workers [7] proposed the kinetic determination of Sb(III) and Sb(V) based on the difference in their rates of complexation with 3-hydroxy-7-methoxyflavone. The detection limits were 7  $\text{nmol dm}^{-3}$  and 20  $\text{nmol dm}^{-3}$  for Sb(III) and Sb(V), respectively. Sicilia *et al.* [8] reported the kinetic determination of Sb(III) based on its accelerating effect on the reduction of 12-phosphomolybdate by ascorbic acid in a micellar medium. The lowest detectable concentration was 70  $\text{ng cm}^{-3}$ , seven times lower than that of the method in aqueous solution. Stopped-flow (define) FIA method for simultaneous determination of Fe(II) and antimony(III) employing their mutual catalytic effect on Cr(VI)-iodide kinetic reactions was proposed by Wang *et al.* [9]. Fe(II) and antimony were determined in the range 0.0–3.5 and 0.0–3.7  $\mu\text{g cm}^{-3}$ , respectively. R. Igov and co-workers [10] proposed the kinetic determination of Sb(III) on the basis of their inhibiting effect on crystal violet oxidation by  $\text{H}_2\text{O}_2$ . The method's sensitivity is 0.08  $\mu\text{g cm}^{-3}$ . The probable relative error was 6.7–12.8 % for Sb(III) concentration intervals of 0.5 to 0.1  $\mu\text{g cm}^{-3}$ . The method was applied for the determination of Sb(III) in the sample of microalloy. The H-point standard addition method (HPSAM) was applied [11] to kinetic data for simultaneous determination of Sb(V) and Sb(III) and also selectively determines Sb(V) in the presence of Sb(III). The method is based on the differences between rate of complexation of pyrogallol red with Sb(V) and Sb(III) at pH=2. Sb(V) can be determined in the range of 0.3–2.0  $\mu\text{g cm}^{-3}$ . Afkhami and co-workers [12] reported kinetic-spectrophotometric method for determination of Sb(III) based on its inhibitory effect on the discoloration reaction of methyl orange. The method allows determination of antimony in the range 10–5000

$\mu\text{g cm}^{-3}$ . The detection limit of the method was  $8.0 \mu\text{g dm}^{-3}$ . The method was applied to the determination of antimony in natural water samples.

The present work describes a simple, sensitive, selective and inexpensive kinetic method for the determination of trace amounts of Sb(III) ions in solution based on its inhibiting effect on Victoria blue 4R oxidation by  $\text{KBrO}_3$  in the presence of HCl. The method was applied for determination of Sb(III) ions in synthetic samples and mineral-vitamin pre-mixtures for animal food.

## 2. EXPERIMENTAL

### 2.1. Apparatus

The reaction rates were monitored spectrophotometrically. The readings were done on a high performance UV/VIS double beam spectrophotometer with double monochromator, Perkin-Elmer Lambda 15 UV/VIS, with wavelength range: 187 to 900 nm, spectral band pass from 0.1 nm to 5 nm large and scan speed  $120 \text{ nm min}^{-1}$  with thermostated cylindrical cells (length of 10 cm), connected to a thermo-circulating bath. A Hanna Instruments pH-meter was used to measure the pH values of the solution.

### 2.2. Reagents and chemicals

Analytical-grade reagents, provided by Merck unless indicated otherwise, deionized water (Micro Med high purity water system, TKA Wasseraufbereitungssysteme GmbH) were utilized for all solution preparations. The stock solution of Sb(III) ( $1 \cdot 10^{-3} \text{ g cm}^{-3}$ ) was prepared from  $\text{K}(\text{SbO})\text{H}_4\text{C}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$  and standardized volumetrically. The  $1 \cdot 10^{-4} \text{ mol dm}^{-3}$  stock solution of Victoria blue (Fluka AG, Buchs SG colour index (CI) number 42563, c.i. name Basic Blue 8, structure published [13]) was prepared by dissolving 0.0130 g VB in adequate volume of absolute ethanol. The concentration

of solution was checked spectrophotometrically.  $\text{KBrO}_3$  ( $1 \cdot 10^{-2} \text{ mol dm}^{-3}$ ) solutions were prepared by dissolving the dry substance in deionized water. Hydrochloric acid solution was prepared by appropriate dilution of concentrated hydrochloric acid. The stock solution of KCl ( $2 \text{ mol dm}^{-3}$ ) was prepared by dissolving dried KCl in deionized water, and it was used to maintain a constant ionic strength ( $\mu = 0.1 \text{ mol dm}^{-3}$ ). All the 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. Working solutions with lower concentrations were prepared by appropriate dilution of their respective stock solutions. All concentrations described here are the initial concentrations in the reaction mixture at time zero after mixing. Each kinetic result is the average of three determinations.

### 2.3. Procedure

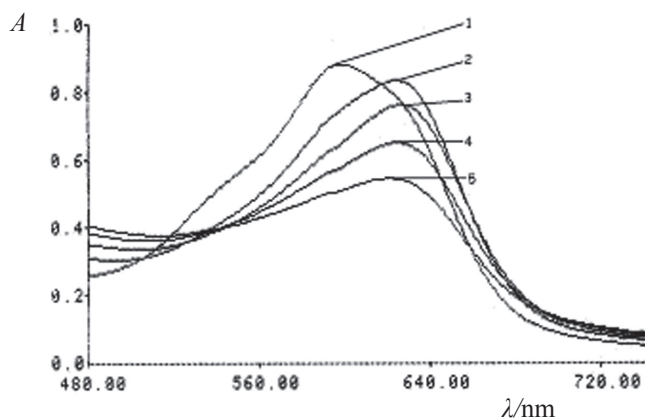
The initial concentration of each of the reactants was in turn systematically varied, while the initial concentrations of the reactants were kept constant. In order to obtain good mechanical and thermal stability, the instruments were run for 10 min before the first measurement. The reaction was carried out in the following way: In the reaction mixture vessel with four compartments, the solution of VB was placed in one compartment,  $\text{KBrO}_3$  in the second, Sb(III) the third, until solutions of HCl, KCl (electrolyte for the ionic strength) and deionized water (total volume  $10 \text{ cm}^3$ ) in the fourth compartment. The vessel was thermostated at  $24 \pm 0.1 \text{ }^\circ\text{C}$  and the reaction was initiated by mixing. The reaction solution was put into a spectrophotometer cell with a path-length of 10 cm, and the absorbance at 596.3 nm was measured every 30 s over a period of 2 – 7 min after mixing.

#### 2.4. Treatment of samples of mineral-vitamin pre-mixtures for animal food

After grinding in the agate mortar, the samples were dried at 105 °C until the constant mass and then destroyed by wet digestion [14].

### 3. RESULTS AND DISCUSSION

While the Victoria blue 4-R oxidation goes on, the initial blue colour of the reaction mixture disappears because the colourless reaction product is forming (Figure 1). The presence of Sb(III) inhibited the discolouration of the solution (Figure 2).



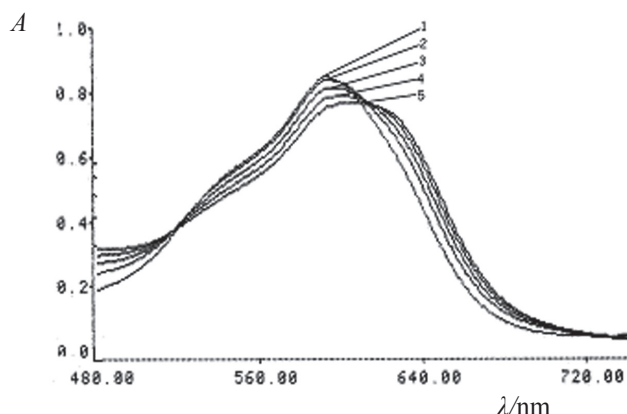
**Fig. 1.** Absorption spectra of indicating reaction mixture of VB and  $\text{KBrO}_3$  (1–6) in acidic medium: effect of reaction time.

Initial conditions:  $c(\text{VB})=1.8 \cdot 10^{-6} \text{ mol dm}^{-3}$ ,  $c(\text{HCl})=2.0 \cdot 10^{-2} \text{ mol dm}^{-3}$ ,  $c(\text{KBrO}_3)=1.5 \cdot 10^{-4} \text{ mol dm}^{-3}$ ,  $c(\text{KCl})=0.1 \text{ mol dm}^{-3}$ .

Reaction time: (1) 1 min, (2) 2 min, (3) 3 min, (4) 4 min, (5) 5 min, (6) 6 min

The wavelength of maximum absorbance attributed to Victoria blue 4-R was found to be  $\lambda = 596.3 \text{ nm}$ . Preliminary experiments showed that the position of the Victoria blue 4-R characteristic band does not change with the varying acidity and reagent concentrations.

According to data reported earlier [15], the possible reaction mechanism was suggested as follows:

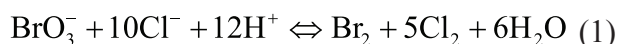


**Fig. 2.** Absorption spectra of indicating reaction mixture of VB,  $\text{KBrO}_3$  and  $\text{Sb(III)}$  (1–6) in acidic medium: effect of reaction time.

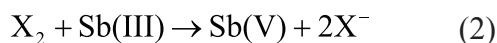
Initial conditions:  $c(\text{VB})=1.8 \cdot 10^{-6} \text{ mol dm}^{-3}$ ,  $c(\text{HCl})=2.0 \cdot 10^{-2} \text{ mol dm}^{-3}$ ,  $c(\text{KBrO}_3)=1.5 \cdot 10^{-4} \text{ mol dm}^{-3}$ ,  $c(\text{KCl})=0.1 \text{ mol dm}^{-3}$ ,  $c(\text{Sb(III)})=5 \cdot 10^{-7} \text{ g cm}^{-3}$ .

Reaction time: (1) 1 min, (2) 2 min; (3) 3 min, (4) 4 min, (5) 5 min, (6) 6 min

Bromate is reduced by chloride ion in acidic media:



The rate of the reaction between the bromate and HCl, increased by the increase in the concentration of HCl and/or the bromate, and this affects the rate of the discoloration of Victoria blue 4R. The decolorizing reaction of Victoria blue 4R could be monitored spectrophotometrically by measuring the decrease in absorbance versus time at 596.3 nm. The presence of reducing agents that react very slowly with bromate but rapidly with bromine and chlorine inhibit the decolorizing reaction. The amount of inhibition depends on the quantity of the reducing agent. The presence of Sb(III) in the reaction mixture significantly reduces the reaction progress. It can be assumed that this is the result of an oxidation of Sb(III) by the formed elementary bromine and/or chlorine:





On the basis of experimental results, the molar absorptivity  $\epsilon$  for the colour system was found to be  $4.9 \cdot 10^3 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ . The plot of the reaction as a function of the Sb(III) concentration is a straight line which can be used as a calibration graph.

The differential variant of the tangent method was used for processing the obtained kinetic data. The reaction rate was followed by the change in the values of the tangent of the angle ( $\text{tg } \alpha$ ) of the slope of the linear part of the kinetic curve to the abscissa in the coordinates A-t (as  $\text{tg } \alpha = dA/dt$ ). In this paper, for all parameters investigated, the rates of indicating (VB, HCl,  $\text{KBrO}_3$ , KCl) reaction and the inhibiting (VB, HCl,  $\text{KBrO}_3$ , KCl, Sb(III)) reaction were simultaneously measured. The rate of inhibiting reaction was expressed against the rate of indicating reaction.

### 3.1. Effect of reaction parameters

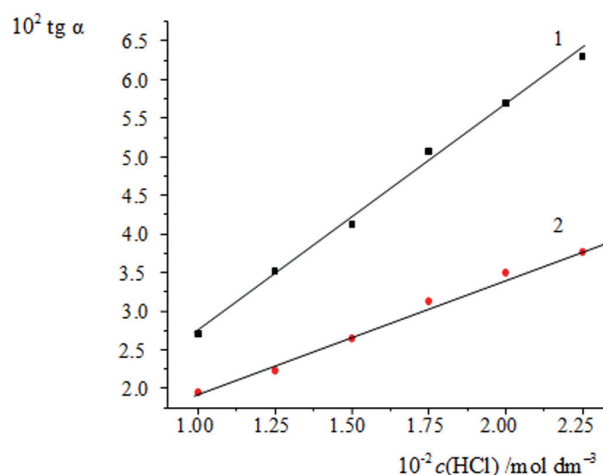
Main parameters influencing the performance of the proposed method were studied to determine the optimum working configuration. These parameters were optimized by the invariant method; i.e., each parameter was optimized by setting the other parameters to be constant.

The reaction proceeds in acidic media. Keeping all other experimental parameters constant, we studied the dependence of hydrochloric acid concentration on the system in the range  $1.0 \cdot 10^{-2} - 2.25 \cdot 10^{-2} \text{ mol dm}^{-3}$  (Figure 3).

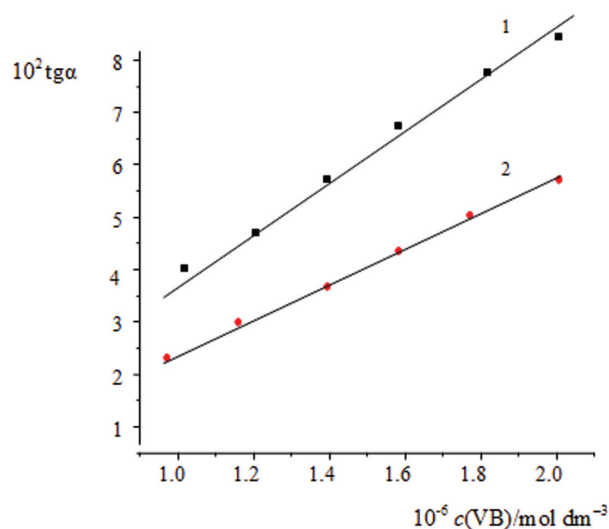
From Figure 3 it appears that there is a linear relationship between the pH and the indicating (1) and inhibiting reaction (2) rate in the range of concentrations studied, so both reactions were first order with respect in the all investigate interval of HCl concentrations. Thus, the hydrochloric acid concentration of  $2.0 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$  in the final solution was used throughout the experiment.

The correlation between  $\text{tg } \alpha$  and Victoria blue 4R concentration is shown in Figure 4.

The indicating (1) and the inhibiting (2) reaction were first order with respect to the VB concentration. Figure 4 shows that, with increas-



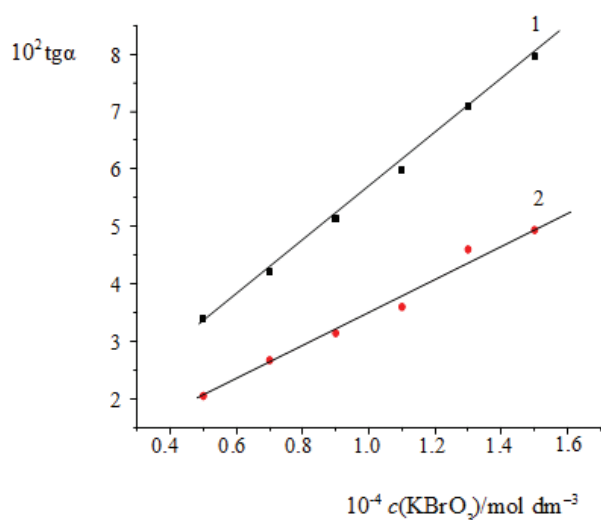
**Fig. 3.** Dependence of the reaction rate of VB and  $\text{KBrO}_3$  on HCl concentration  
1 – indicating reaction (without Sb(III)),  
2 – inhibiting reaction (with Sb(III)).  
Initial conditions:  $c(\text{VB}) = 1 \cdot 10^{-6} \text{ mol dm}^{-3}$ ,  
 $c(\text{KBrO}_3) = 1 \cdot 10^{-4} \text{ mol dm}^{-3}$ ,  $c(\text{KCl}) = 0.1 \text{ mol dm}^{-3}$ ,  
 $c(\text{Sb(III)}) = 5 \cdot 10^{-7} \text{ g cm}^{-3}$ ,  $t = 24 \pm 0.1^\circ \text{C}$



**Fig. 4.** Dependence of the reaction rate of VB and  $\text{KBrO}_3$  on VB concentration  
1 – indicating reaction (without Sb(III)),  
2 – inhibiting reaction (with Sb(III)).  
Initial conditions:  $c(\text{HCl}) = 2 \cdot 10^{-2} \text{ mol dm}^{-3}$ ,  
 $c(\text{KCl}) = 0.1 \text{ mol dm}^{-3}$ ,  $c(\text{KBrO}_3) = 1.0 \cdot 10^{-4} \text{ mol dm}^{-3}$ ,  
 $c(\text{Sb(III)}) = 5 \cdot 10^{-7} \text{ g cm}^{-3}$ ,  $t = 24 \pm 0.1^\circ \text{C}$

ing VB concentrations, the difference between the rates of the indicating (1) and inhibiting (2) reactions increases too. For further work, a VB concentration of  $1.5 \cdot 10^{-6} \text{ mol dm}^{-3}$  was selected.

The influence of the  $\text{KBrO}_3$  was presented in Figure 5, from which it can be seen that both the reactions (indicating (1) and inhibiting (2)) are first order with respect to the  $\text{KBrO}_3$  concentration. It was found that the greatest difference between the rates of both the reactions, occurs at  $1.5 \cdot 10^{-4} \text{ mol dm}^{-3}$ , when  $\text{Sb(III)}$  maximally decrease the reaction rate, so for further work, a  $\text{KBrO}_3$  concentration of  $1.5 \cdot 10^{-4} \text{ mol dm}^{-3}$  was selected.



**Fig. 5.** Dependence of the reaction rate of VB and  $\text{KBrO}_3$  on  $\text{KBrO}_3$  concentration.

1 – indicating reaction (without  $\text{Sb(III)}$ ),  
2 – inhibiting reaction (with  $\text{Sb(III)}$ ).

Initial conditions:  $c(\text{HCl}) = 2.0 \cdot 10^{-2} \text{ mol dm}^{-3}$ ,  
 $c(\text{VB}) = 1.5 \cdot 10^{-6} \text{ mol dm}^{-3}$ ,  $c(\text{KCl}) = 0.1 \text{ mol dm}^{-3}$ ,  
 $c(\text{Sb(III)}) = 5 \cdot 10^{-7} \text{ g cm}^{-3}$ ,  $t = 24 \pm 0.1^\circ\text{C}$

The linear dependencies were established between the slopes of the absorbance-time curves and  $\text{Sb(III)}$  concentration. The calibration graphs (Figures 6, 7) were constructed under the established optimal conditions for kinetic determination of  $\text{Sb(III)}$ :  $c(\text{HCl}) = 2.0 \cdot 10^{-2} \text{ mol dm}^{-3}$ ,  $c(\text{KBrO}_3) = 1.5 \cdot 10^{-4} \text{ mol dm}^{-3}$ ,  $c(\text{VB}) = 1.5 \cdot 10^{-6} \text{ mol dm}^{-3}$ ,  $c(\text{KCl}) = 0.1 \text{ mol dm}^{-3}$ .

The analytical and statistical data of the calibration graphs for the determination of  $\text{Sb(III)}$  estimated by the linear-regression method with standard deviation of the fit and the correlation coefficient  $r$  are given in Table 1.

**Table 1**

*Analytical and statistical analysis of the calibration graph for the determination of  $\text{Sb(III)}$*

Analytical data	Dynamic range / $10^{-7} \text{ g cm}^{-3}$	
	0.5 to 3.0	3.0. to 11
Number of points	12	5
Limit of detection	$1.30 \cdot 10^{-8} \text{ g cm}^{-3}$	
Limit of quantification	$4.33 \cdot 10^{-8} \text{ g cm}^{-3}$	
Slope	-0.73709	-0.3050
Intercept	7.43809	6.0990
Correlation coefficient	0.9993	0.9990
S – Standard deviation of the slope	0.00714	0.00802
St – Standard deviation of the intercept	0.01371	0.06056

The following kinetic equations for the investigated process were deduced on the basis of the graphic correlations obtained.

For the indicating reaction:

$$-dc(\text{VB})/dt = kc(\text{HCl})c(\text{KBrO}_3)c(\text{VB}) \quad (3)$$

For the inhibiting reaction:

$$-dc(\text{VB})/dt = k_1c(\text{HCl})c(\text{KBrO}_3)c(\text{VB})c(\text{Sb(III)})^{-1} \quad (4)$$

where  $k$  is a constant of the indicating reaction and  $k_1$  is a constant of the inhibiting reaction.

### 3.2. Accuracy and precision

The precision and accuracy of the above system were studied by performing the experiment 5 times for different concentrations of  $\text{Sb(III)}$  concentrations in the range of calibration curve. The relative error ranges from 4 % to 0.7 %, while the relative standard deviation is 5.5 % to 1.1 % for  $\text{Sb(III)}$  in the concentration range from  $8.0 \cdot 10^{-8} \text{ g cm}^{-3}$  to  $1.0 \cdot 10^{-6} \text{ g cm}^{-3}$ .

### 3.3. Interference studies

In order to test the applicability of the method the effect of foreign ions on the determination of fixed concentration of antimony  $5.0 \cdot 10^{-7} \text{ g cm}^{-3}$  was investigated. The results are summarized in Table 2. The tolerance limit for foreign substances was estimated as the concentration of the substance that gives up to a 3 % relative error in the determination of antimony.

Regarding the selectivity, as determined by this criterion for a Sb(III) concentrations of  $5.0 \cdot 10^{-7} \text{ g cm}^{-3}$  up to a molar ratio of 100 : 1, most cations and anions have practically no influence

on the Sb(III) determination by this method. Inhibitory effects for As(III),  $I^-$ , hydrazine and phenyl hydrazine were observed because they could also inhibit the indicating reaction, when present in 0.5 : 1 ratio to Sb(III). The results in Table 2 reveal that this method has a good selectivity. As the results show, Sb(V) did not interfere even when present in a 100-fold excess over Sb(III) species. This shows that the method is suitable for distinction between Sb(III) and Sb(V) species. The substances that interfere the determination of Sb (III) by proposed kinetic method can be easily removed – As(III), hydrazine and phenylhydrazine by distillation, and iodide ions by masking with the addition of  $Cu^{2+}$ .

Table 2

*Interference studies:  
Effect of foreign ions on the determination of Sb(III)*

Ion added*	Tolerated ratio of foreign species to Sb(III)
$Li^+$ , $K^+$ , $Na^+$ , $NH_4^+$ , $Ca^{2+}$ , $Ba^{2+}$ , $Sr^{2+}$ $C_2O_4^{2-}$ , $CH_3COO^-$ , $HCO_3^-$ , $CO_3^{2-}$	1000
$SO_4^{2-}$ , $NO_3^-$ , Sb(V), As(V), $Pb^{2+}$ , $Cd^{2+}$ , $F^-$ , Mo(VI)	100
$Hg^{2+}$ , $Co^{2+}$ , $Zn^{2+}$ , $Mn^{2+}$ , $PO_4^{3-}$ , Se(IV), $HPO_4^{2-}$	10
$Fe^{3+}$ , $Cu^{2+}$ , $Ni^{2+}$ , $Cr_2O_7^{2-}$	1
As(III), $I^-$ , hydrazine, phenylhydrazine	0.5
	Inhibited

$c(\text{Sb(III)}) = 5.0 \cdot 10^{-7} \text{ g cm}^{-3}$

\*Cations added as chlorides or nitrates, anions as sodium or potassium salts

### 3.4. Determination of Sb(III) in samples

In order to check the validity of the proposed method, the technique described in Procedure was applied to the determination of Sb(III) using the direct calibration curve, in different synthetic samples, synthetic water samples and samples of mineral-vitamin pre-mixtures for animal food. The synthetic samples were prepared by mixing common cations at various concentrations higher (about 10 times and more) than the Sb(III) concentration. Also, synthetic water samples were prepared by adding known amounts of Sb(III) to the water samples. The results for Sb(III) determination in the

synthetic samples, synthetic water samples and samples of mineral-vitamin pre-mixtures for animal food using the calibration curve method are shown in Tables 3, 4, 5.

The obtained results by using simple calibration curve method, indicating the accuracy of this method, and its viability for the analysis of antimony in this type of samples. The obtained recoveries (98.1–102.1 %) demonstrated the general reliability of the proposed method. The concentrations of antimony determined in all samples of mineral-vitamin pre-mixtures for animal food by the proposed method were in close agreement with the values obtained by control method (HG-AAS) (Table 5). The assessment by Student's  $t$  test

Table 3

*Sb(III) determination in model samples*

Model sample SS	Composition of model sample $\gamma(\text{Ion}) / \text{ng cm}^{-3}$	Sb(III) found* $\gamma / \text{ng cm}^{-3}$	Recovery %
SS1	150.0 Sb(III), 1500.0 Sb(V)	149.3	99.5
SS2	150.0 Sb(III), 1500.0 Sb(V), 1500.0 Pb(II)	152.3	101.5
SS3	150.0 Sb(III), 1500.0 Sb(V), 150.0 Cu(II), 150.0 Mn(II)	153.1	102.1

\* From the calibration graph

All data are average of three replicate determinations

Table 4

*Determination of Sb(III) in synthetic water samples*

Sample	Sb(III) added $\text{ng cm}^{-3}$	Sb(III) found* $\text{ng cm}^{-3}$	Recovery %
Spring water	80.0	81.2	101.5
	500.0	503.4	100.7
	900.0	896.4	99.6
Rainwater	90.0	91.4	101.6
	600.0	591.9	98.6
	850.0	842.1	99.1

\* From the calibration graph

All data are average of three replicate determinations

Table 5

*Determination of Sb(III) in samples of mineral-vitamin pre-mixtures for animal food*

Food pre-mixture sample, $\omega(\text{Sb(III)}) / \text{ng g}^{-1}$		
VB method*	HGAAS method**	Recovery %
293.8	297.8	98.7
309.4	303.5	101.9
278.7	284.1	98.1

\* From the calibration graph

\*\* Method described in reference [14]

All data are average of three replicate determinations



did not show a statistically significant difference between the methods used (95 %). Results shown in Tables 3, 4, 5 indicated that this proposed method is applicable for routine measurements.

#### 4. CONCLUSIONS

The system Victoria blue 4-R /  $KBrO_3$  / HCl / Sb(III) requires a short time to achieve kinetic equilibrium, has a good stability and repetition, and the reaction in the system can be controlled easily. Simplicity, reproducibility, satisfactory sensitivity and absence of most interference are significant advantages of this method. The newly developed method is inexpensive and efficient for use in the analyses of a large number of samples. Its analytical parameters, recommend the proposed method as an alternative to other reported kinetic-spectrophotometric methods for sensitive determination of Sb(III).

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#### REFERENCES

- [1] T. Gebel, Arsenic and antimony: comparative approach on mechanistic toxicology. *Biol. Interact.*, **107**, 131–144 (1997).
- [2] M. Filella, N. Belzile, Y. W. Chen, Antimony in the environment: A review focused on natural waters, I. Occurrence. *Earth Science Rev.* **57**, 125–176 (2002).
- [3] R. Iffland, *Handbook on Toxicity of Inorganic Compounds*, edited by H. Seiler, A. Sigel, Marcell Dekker, New York, 1998.
- [4] E. Berman, *Toxic Metals and Their Analysis*, Heyden, London, 1980.
- [5] P. Smichowski, Y. Madrid, C. Camara, Analytical methods for antimony speciation in waters at trace and ultratrace levels. A review. *Fresenius J. Anal. Chem.* **360**, 623–629 (1998).
- [6] S. Sato, Differential determination of antimony(III) and antimony(V) by solvent extraction-spectrophotometry with mandelic acid and Malachite green, based on the difference in reaction rates, *Talanta* **32**, 341–344 (1985).
- [7] S. Yamada, K. Maejima, A. Murata, Kinetic determination of antimony(III) and antimony(V) based on the difference in their rates of complexation with 3-hydroxy-7-methoxyflavone, *Bunseki Kagaku* **40**, 455–458 (1991).
- [8] D. Sicilia, S. Rubio, D. Pérez-Bendito, Kinetic determination of antimony(III) based on its accelerating effect on the reduction of 12-phosphomolybdate by ascorbic acid in a micellar medium, *Anal. Chem.* **64**, 1490–1495 (1992).
- [9] H. J. Wang, H. R. He, The mutual catalytic effect in kinetic reactions and its application to simultaneous determination of binary components, *Mikrochim. Acta* **117**, 23–28 (1994).
- [10] R. P. Igov, V. D. Mitić, T. G. Pecev, V. P. Stankov-Jovanovic, A new kinetic reaction for determination of ultramicro amounts of Sb(III), *J. Serb. Chem. Soc.* **63**, 817–821 (1998).
- [11] A. Abbaspour, M. Najafi, M. A. Kamyabi, Quantitative kinetic determination of Sb(V) and Sb(III) by spectrophotometric H-point standard addition method, *Anal. Chim. Acta* **505**, 301–305 (2004).
- [12] A. Afkhami, T. Madrakian, A. Abdolmaleki, Sensitive kinetic-spectrophotometric determination of Sb(III) based on its inhibitory effect on the decolorization reaction of methyl orange, *Croat. Chem. Acta* **78**, 569–574 (2005).
- [13] V. D. Mitić, S. D. Nikolić, V. P. Stankov-Jovanović, Kinetic-photometric determination of iodide based on its inhibitory effect on the bromate oxidation of Victoria blue 4-R., *Anal. Sci.* **20**, 931–934 (2004).
- [14] AY-6-Analysis of feeds: Wet Digestion, Analytical Methods for AAS, Perkin Elmer Instruments, 2000, Release E.
- [15] V. D. Mitić, S. D. Nikolić, V. P. Stankov-Jovanović, Kinetic spectrophotometric determination of hydrazine, *Cent. Eur. J. Chem.* **8**, 559–565 (2010).

