Sensitive Kinetic-Spectrophotometric Determination of Sb^{III} Based on Its Inhibitory Effect on the Decolorization Reaction of Methyl Orange

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A method for rapid and accurate determination of trace quantities of Sb^{III} was developed based on its inhibitory effect on the decolorizing reaction of methyl orange in the presence of bromate and bromide ions in acidic media. Decolorization of methyl orange by the reaction products was used to monitor the reaction spectrophotometrically at 525 nm. The method allows determination of antimony in the range 10–5000 μg dm^{-3}. The relative standard deviation for ten determinations of 500 μg dm^{-3} antimony is 1.21 % and the detection limit of the method is 8.0 μg dm^{-3}. The method is applied to the determination of antimony in natural water samples.

INTRODUCTION

Antimony is a relatively toxic element and its toxicity depends on the oxidation state. Elemental antimony is more toxic than its salts and generally trivalent Sb compounds are more toxic than the pentavalent ones.[1–3] The International Agency for Research on Cancer (IARC) has assigned antimony trioxide to the group of substances that are suspected of being carcinogenic in humans.[4] Therefore, the determination of antimony is of significant importance from the environmental and health viewpoints. Analytical procedures used to determine antimony in environmental samples need to be highly sensitive, and should also be capable of distinguishing between Sb^{III} and Sb^{V} species.

Several methods, including graphite furnace atomic absorption spectrometry,[5] hydride generation inductively coupled plasma atomic emission spectrometry (HG-ICP--AES),[6] differential pulse anodic stripping voltammetry,[7] potentiometry,[8] flow analysis–hydride generation–Fourier transform infrared spectrometry[9] and flow injection hydride generation atomic absorption spectrometry[10] have been used for antimony determination. Therefore, the need for a sensitive, simple and reliable method for the determination of antimony is obvious.

Kinetic methods of chemical analysis are attractive methods for rapid determination of trace amounts of inorganic species.[11,12] These methods have some advantages, including high sensitivity, extremely low detection limit, good selectivity, rapid analysis and inexpensive instruments such as a spectrophotometer or spectrofluorimeter. There are only few reports on the determination of antimony by kinetic methods. Sicilia *et al.*[13] determined Sb^{III} in the range 100–1800 μg dm^{-3} based on its accelerating effect on the reduction of 12-phosphomolybdate by ascorbic acid in a micellar media. Wang and He[14] reported a stopped-flow FIA method for simultaneous determination of Fe^{II} and Sb^{III} based on their mutal catalytic effect on the Cr^{VI}-iodide kinetic reactions. They determined Fe^{II} and Sb^{III} in the range 0.0–3500 and 0.0–3700 μg dm^{-3}, respectively.

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Burgess and Ottaway reported a method for the determination of Sb^{III} based on its effect on the redox reaction of bromate with bromide ion in sulfuric acid media.[15] Decolorization of methyl orange with liberated bromine was used to measure the reaction time. They used different experimental conditions for the determination of different concentrations of Sb^{III}. No calibration equation or other analytical parameters were reported.

In this work, we describe a kinetic spectrophotometric method for Sb^{III} determination based on its inhibitory effect on the decolorizing reaction of methyl orange in acidic media. The method is rapid, simple, sensitive, precise and accurate. As little as 10.0 µg dm^{-3} antimony could be determined by the method.

EXPERIMENTAL

Reagents

Triply distilled water and analytical-reagent grade chemicals were used.

Antimony(III) stock solution (1000 mg dm^{-3}) was prepared by dissolving 0.6855 g of $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$ (Merck) in water and diluting it to the mark in a 250 cm^3 volumetric flask. A 0.10 mol dm^{-3} potassium bromate solution was prepared by dissolving 1.770 g of $KBrO_3$ (Merck) in water and diluting it to 100 cm^3 in a volumetric flask. A solution of 100 mg dm^{-3} methyl orange was prepared by dissolving 0.01 g of methyl orange (Merck) in water and diluting it to 100 cm^3 with water. Chloride and bromide solutions were prepared from NaCl and KBr (both from Merck). Hydrochloric acid and sulfuric acid solutions were prepared by appropriate dilution of their concentrated solutions (Merck).

Apparatus

Absorption-time graphs at a fixed wavelength were recorded on a Shimadzu model UV-265-UV-Visible recording spectrophotometer.
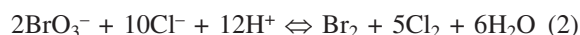
Procedure

Inhibited reaction was followed spectrophotometrically by monitoring the change in absorbance at 525 nm. A suitable aliquot of sample solution containing 0.10–40 µg Sb^{III} was transferred into a 10 cm^3 volumetric flask, then 1.0 cm^3 of 1.8×10^{-2} mol dm^{-3} KBr solution and 1 cm^3 of 1.2 mol dm^{-3} H_2SO_4 solution were added, followed by 1.0 cm^3 of 100 mg dm^{-3} methyl orange solution. The solution was diluted to *cca.* 8 cm^3 with water, then 1.0 cm^3 of 1.0×10^{-3} mol dm^{-3} bromate solution was added and the solution was diluted to the mark with water and a portion was transferred into a glass cell within 20 s to measure absorbance variation with time. If higher concentrations of Sb^{III} have to be tested, the amount of added bromate should be increased. For example, 1 cm^3 of 4.0×10^{-3} mol dm^{-3} bromate solution is needed for determination of Sb^{III} up to 50 µg.
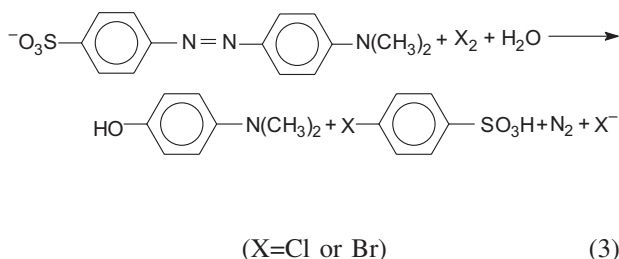
RESULTS AND DISCUSSION

Inhibitory Effect of Sb^{III}

Reduction of bromate with bromide and chloride proceeds rapidly in acidic media according to the following reactions:

$$BrO_3^- + 5Br^- + 6H^+ \Leftrightarrow Br_2 + 3H_2O \qquad (1)$$

$$2BrO_3^- + 10Cl^- + 12H^+ \Leftrightarrow Br_2 + 5Cl_2 + 6H_2O \quad (2)$$

The liberated Br_2 and Cl_2 react with methyl orange to decolorize it.[16]

$$(X = Cl \text{ or } Br) \qquad (3)$$

The decolorizing reaction of methyl orange can be monitored spectrophotometrically by measuring the decrease in absorbance *versus* time at 525 nm.

The presence of reducing agents that react very slowly with bromate but rapidly with bromine and chlorine inhibits the decolorizing reaction. The amount of inhibition depends on the quantity of the reducing agent. Sb^{III} reacts with Br_2 and Cl_2 according to the following reaction and causes an inhibitory effect on the decolorization of methyl orange by bromine and chlorine.[15]

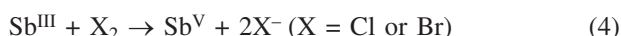$$Sb^{III} + X_2 \rightarrow Sb^V + 2X^- \ (X = Cl \text{ or } Br) \qquad (4)$$

Figure 1 shows the graph of the absorbance change of a mixture of BrO_3^-, Br^- and methyl orange in acidic media *versus* time in the presence of different amounts of Sb^{III}. As Figure 1 shows, the graphs contain two different linear regions. The first linear region has a smaller slope than the second linear region. This is due to the competition of Sb^{III} with methyl orange in the reaction with Br_2. The slope then increases dramatically when all of Sb^{III} is consumed by the reaction with Br_2. An increase in the Sb^{III} concentration causes an increase in the induction period of the reaction. The graph of the induction period of the reaction versus Sb^{III} concentration is linear over a certain concentration range. Therefore, this system is suitable for simple and rapid determination of Sb^{III}.

Measurement of Induction Time

Induction period could be measured either by a graphical or mathematical method. The induction period was measured mathematically from the regression equations
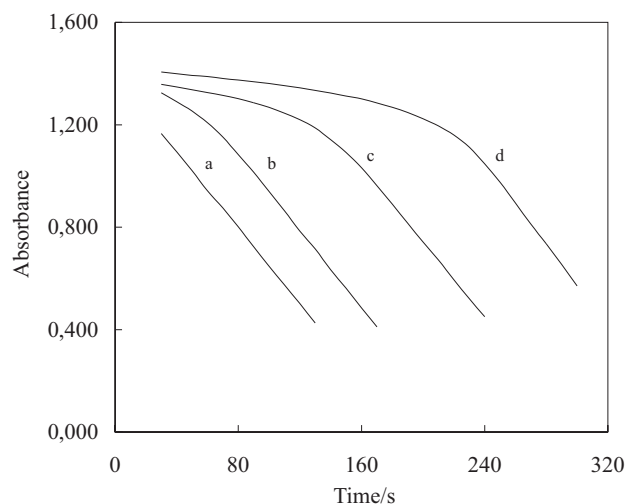
Figure 1. Change in absorbance of 10 mg dm^{-3} methyl orange with time in the presence of 0.12 mol dm^{-3} H$_2$SO$_4$, 1.8 ×10^{-3} mol dm^{-3} bromide, 6 × 10^{-4} mol dm^{-3} BrO$_3^-$, and (a) 0.00, (b) 80, (c) 400, and (d) 800 mg dm^{-3} Sb^{III}.
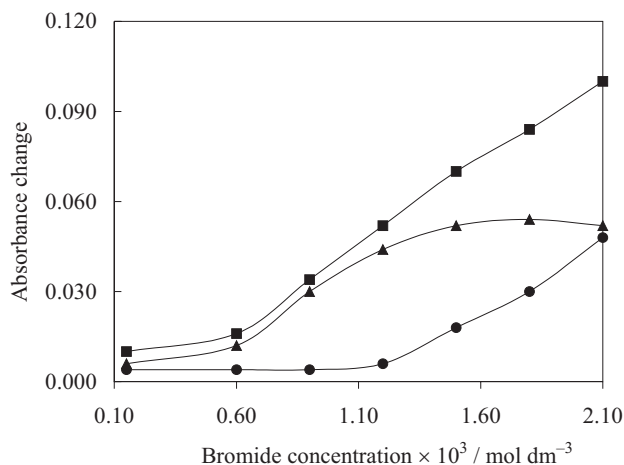

Figure 2. Absorbance change for uninhibited (■) and inhibited (●) reactions, and their difference (▲) as a function of bromide concentration. Conditions: methyl orange, 10 mg dm^{-3}; H$_2$SO$_4$, 0.12 mol dm^{-3}; BrO$_3^-$, 1.0 × 10^{-4} mol dm^{-3}; Sb^{III}, 1000 µg dm^{-3}; Δt = 70 s.

of the linear parts of absorption-time graph. The regression equation for the first linear part of the graph is:

$$A = a_1 + b_1 t$$

and for the second linear part:

$$A = a_2 + b_2 t$$

By equating these equations, the induction period is calculated as:

$$t_{ip} = (a_1 - a_2) \, / \, (b_2 - b_1)$$

Effect of Variables

To take full advantage of the procedure, the reagent concentrations and reaction conditions must be optimized. Various experimental parameters were studied in order to obtain an optimized system. These parameters were optimized by the invariant method, *i.e.,* each parameter was optimized by setting other parameters constant.

Bromide as Reducing Agent

The effect of bromide ion concentration was studied in the range 1.0×10^{-4} to 2.1×10^{-3} mol dm^{-3}. An increase in Br$^-$ concentration caused a decrease in the induction period and an increase in the slope of the absorbance change after reaction of the total amount of Sb^{III}. To find the optimum concentration of the bromide ion, the absorbance change for uninhibited reaction (reaction in the absence of Sb^{III}) and inhibited reaction (reaction in the presence of Sb^{III}) at a fixed time of 70 seconds as a function of Br$^-$ concentration was measured. The results are shown in Figure 2. As seen from Figure 2, the absorban-

ce change for both inhibited and uninhibited reactions increased with increasing the bromide concentration. But, the difference between the absorbance change for uninhibited and inhibited reactions increased with increasing the bromide concentration up to 1.5×10^{-3} mol dm^{-3} and remained nearly constant at higher concentrations. Therefore, the final concentration of 1.8×10^{-3} mol dm^{-3} bromide was selected as optimum.

As mentioned before, the reaction between bromate and bromide ion takes place in acidic media. The rate of this reaction is second order with respect to [H$^+$],[17,18] while the rate of the decolorizing reaction of methyl orange with Br$_2$ has an order of –1 with respect to [H$^+$].[15] The effect of sulfuric acid concentration was studied in the range 0.03–0.15 mol dm^{-3}. Again, like for Br$^-$, an increase in acid concentration caused a decrease in the induction period and an increase in the slope of the absorbance change after reaction of the total amount of Sb^{III}. In order to find the optimum concentration of sulfuric acid, the absorbance change for uninhibited and inhibited reactions at a fixed time of 70 seconds as a function of H$_2$SO$_4$ concentration was measured. The results are shown in Figure 3. The difference between absorbance change for uninhibited and inhibited reactions is maximum at 0.12 mol dm^{-3} H$_2$SO$_4$. Therefore, a final concentration of 0.12 mol dm^{-3} sulfuric acid was selected as optimum.

The effect of bromate concentration was also studied. As Figure 4 shows, an increase in bromate concentration caused a decrease in the induction period and an increase in the slope of the absorbance change after reaction of the total amount of Sb^{III}. It was also observed that the calibration range differed depending on the concentration of bromate and hence the concentration of bromate must be selected on this basis.
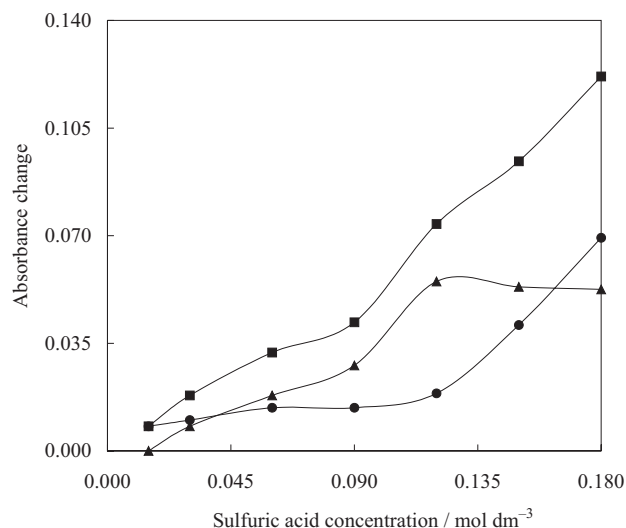
Figure 3. Absorbance change for uninhibited (■) and inhibited (●) reactions and their difference (▲) as a function of H_2SO_4 concentration. Conditions: methyl orange, 10 mg dm^{-3}; bromide, 1.5×10^{-3} mol dm^{-3}; BrO_3^-, 1.0×10^{-4} mol dm^{-3}; Sb^{III}, 1000 µg dm^{-3}; $\Delta t = 70$ s.

Figure 5. Absorbance change for uninhibited (■) and inhibited (●) reactions and their difference (▲) as a function of temperature. Conditions: methyl orange, 10 mg dm^{-3}; bromide, 1.8×10^{-3} mol dm^{-3}; H_2SO_4, 0.12 mol dm^{-3}; BrO_3^-, 1.6×10^{-4} mol dm^{-3}; Sb^{III}, 1000 µg dm^{-3}; $\Delta t = 70$ s.

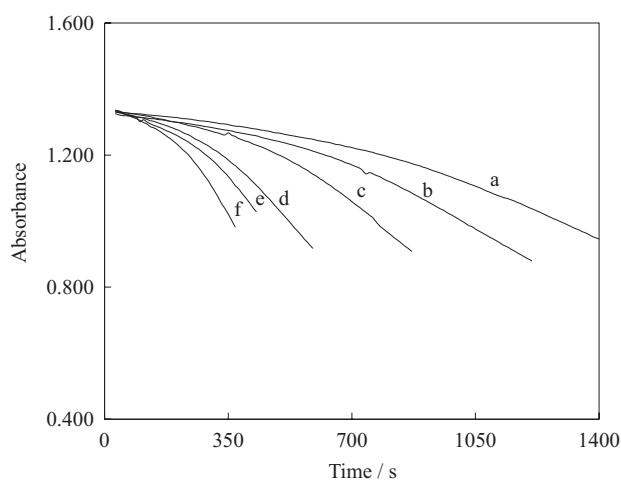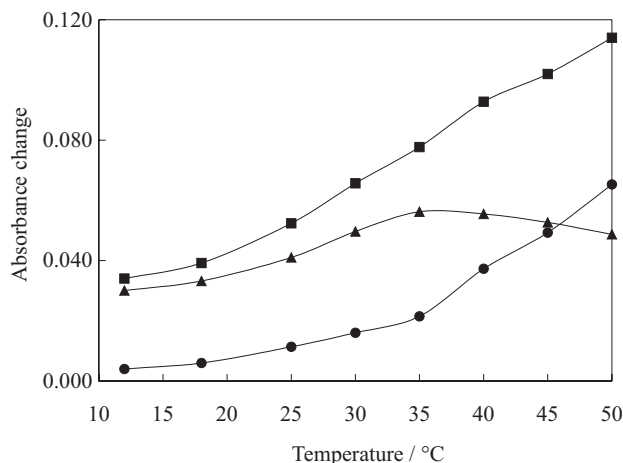

Figure 4. Change in absorbance of 10 mg dm^{-3} methyl orange with time in the presence of 1.8×10^{-3} mol dm^{-3} bromide, 0.12 mol dm^{-3} H_2SO_4, 1000 µg dm^{-3} Sb^{III}, and (a) 4.0×10^{-5}, (b) 5.0×10^{-5}, (c) 6.0×10^{-5}, (d) 1.0×10^{-4}, (e) 1.6×10^{-4}, and (f) 2.0×10^{-4} mol dm^{-3} BrO_3^-.

The effect of temperature on uninhibited and inhibited reaction rate in the range of 12–50 °C was investigated. The results are shown in Figure 5. As Figure 5 shows, the absorbance change for both the reactions increased by increasing temperature. The difference between the absorbance change for uninhibited and inhibited reactions was maximum at 35 °C. Therefore, 35 °C was selected as the optimum temperature.

Chloride as Reducing Agent

The effect of temperature, chloride, bromate and sulfuric acid concentrations on the decolorizing reaction of me-

thyl orange in the presence of bromate and chloride in sulfuric acid media was also investigated as described above. The results showed that the optimum temperature, acid concentration and chloride concentration are 30 °C, 0.25 mol dm^{-3} and 0.35 mol dm^{-3}, respectively. Bromate concentration must be selected based on the concentration range of Sb^{III}.

Analytical Parameters

Calibration graphs were constructed by measuring the induction period of the reaction as a function of Sb^{III} concentration. Induction period was measured mathematically by equating the equations of the linear parts of the absorbance-time graph as described before.

As mentioned before, the range of the calibration graphs was dependent on the bromate concentration. For each chloride or bromide as reducing agents, two different calibration graphs were obtained under the optimum conditions, described above using two different concentrations of bromate. Parameters of the linear regression of calibration data are given in Table I. As seen from Table I, by increasing the bromate concentration, the limit of detection increased and higher concentrations of Sb^{III} could be determined by the method.

The limit of detection, defined as $C_L = 3S_B/m$, where C_L, S_B and m are the limit of detection, standard deviation of the blank signal and slope of the calibration graph,[11] respectively, was also a function of bromate concentration (Table I). For a final concentration of 1.0×10^{-4} mol dm^{-3} bromate and bromide as reducing agents, the limit of detection was 8 µg dm^{-3}.

As Table I shows, using bromide as the reducing agent results in lower detection limits and a wider linear dynamic range for the determination of Sb^{III} than those

TABLE I. Linear regression parameters of calibration data with chloride or bromide as reducing agents and for different bromate concentrations

Reducing agent	BrO3$^-$	Slope	Intercept	Correlation coefficient	Detection limit	Calibration range
	mol dm^{-3}	s dm^3 µg^{-1}	s		µg dm^{-3}	µg dm^{-3}
Br$^-$	1.0×10^{-4}	0.3305	28.8	0.9998	8	10–4000
	4.0×10^{-4}	0.1653	50.0	0.9999	175	200–5000
Cl$^-$	1.0×10^{-4}	0.0821	125.0	0.9993	44	50–3200
	4.0×10^{-4}	0.0523	85.0	0.9992	220	300–4000

TABLE II. Accuracy and precision of the proposed method (bromide as the reducing agent)

Sb^{III} taken / µg dm^{-3}	Relative error / %	RSD ($n = 8$) / %
30.0	2.30	2.19
60.0	−1.85	2.10
150.0	0.85	1.96
500.0	1.23	1.21
1000.0	−0.56	0.89

TABLE III. Tolerance limit for diverse ions in determination of 1000 µg dm^{-3} Sb^{III}

Ion	$W_{ion} / W_{Sb^{III}}$
Sb^V, CO$_3^{2-}$, PO$_4^{3-}$, ClO$_4^-$, As^V, ClO$_3^-$, SO$_4^{2-}$, CH$_3$COO$^-$, H$_2$PO$_4^-$, tartrate, NO$_3^-$, NH$_4^+$, C$_2$O$_4^{2-}$, Mo^{VI}, Cl$^-$, CN$^-$, citrate, Na$^+$, Ba^{2+}, Be^{2+}, Ca^{2+}, K$^+$, Mg^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, F$^-$, [b]NO$_2^-$, [b]SO$_3^-$	100[a]
Fe^{3+}, Cu^{2+}	20
I$^-$, AsO$_2^-$	1

[a] Maximum limit tested.
[b] After removal, as described in text.

obtained by chloride. Therefore, we used bromide as the reducing agent in the remaining part of our work.

To evaluate the accuracy and precision of the method, a series of independent standard samples was used. The results are given in Table II.

Selectivity

To study the selectivity of the proposed method, the effect of various cations and anions on the determination of 1000 µg dm^{-3} of Sb^{III} was studied. An error of ±3 % was considered tolerable. The results are given in Table III. As Table III shows, Sb^V and most of the investigated cations and anions did not interfere even when present in 100-fold excess over Sb^{III}. This shows that the method is suitable for distinguishing between Sb^{III} and Sb^V species. Among the investigated ions, NO$_2^-$, AsO$_2^-$, I$^-$ and SO$_3^-$ interfered with the determination of antimony due to their reaction with Br$_2$ and Cl$_2$. The interfering effect of sulfite and nitrite was completely eliminated by acidification of the solution followed by 10-min heating at 80 °C.

Application

To evaluate the analytical applicability of the method, it was applied to the determination of Sb^{III} in spring water and rainwater. The tested water was found to be free from Sb^{III} and so synthetic samples were prepared by adding known amounts of Sb^{III} to the water samples. The results are given in Table IV. The recoveries are close to 100 % and indicate that there is no serious interference in such water samples.

TABLE IV. Determination of Sb^{III} in natural water samples

Sample	Sb^{III} added / µg dm^{-3}	Sb^{III} found[a] / µg dm^{-3}	Recovery / %
Spring water	20.0	21.0	105.0
	50.0	51.3	102.6
	250.0	246.5	98.6
	500.0	500.0	100.0
Rainwater	30.0	30.6	102.0
	80.0	78.1	97.6
	200.0	202.0	101.0

[a] Average of five determinations.

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SAŽETAK

Osjetljivo kinetičko-spektrofotometrijsko određivanje Sb[III] temeljeno na njegovu inhibitornome djelovanju na reakciju dekoloriranja indikatora

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Razvijena je metoda za brzo i precizno određivanje tragova Sb[III] temeljena na inhibitornome djelovanju na reakciju dekoloriranja metil oranža uz bromate i bromidne ione u kiselom mediju. Upotrebljeno je dekoloriranje metil oranža s reakcijskim produktima za praćenje reakcije spektrofotometrijski kod 525 nm. Predložena metoda dopušta određivanje antimona u koncentracijama od 10 do 5000 µg dm^{-3}. Relativna standardna devijacija za deset određivanja uzoraka od 500 µg dm^{-3} bila je 1.21%, a granica osjetljivosti metode bila je 8.0 µg dm^{-3}. Metoda je uporabljena za određivanje antimona u uzorcima prirodnih voda.