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Selective speciation of inorganic antimony on tetraethylenepentamine bonded silica gel column and its determination by graphite furnace atomic absorption spectrometry

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ABSTRACT

A speciation system for antimony (III) and antimony (V) ions that based on solid phase extraction on tetraethylenepentamine bonded silica gel has been established. Antimony was determined by graphite furnace atomic absorption spectrometry (GF-AAS). Analytical conditions including pH, sample volume, etc., were studied for the quantitative recoveries of Sb (III) and Sb (V). Matrix effects on the recovery were also investigated. The recovery values and detection limit for antimony (III) at optimal conditions were found as $>95\%$ and 0.020 $\mu g\,L^{-1}$, respectively. Preconcentration factor was calculated as 50. The capacity of adsorption for the tetraethylenepentamine bonded silica gel was 7.9 $mg\,g^{-1}$. The validation was checked by analysis of NIST SRM 1573a Tomato laves and GBW 07605 Tea certified reference materials. The procedure was successfully applied to speciation of antimony in tap water, mineral water and spring water samples. Total antimony was determined in refined salt, unrefined salt, black tea, rice, tuna fish and soil samples after microwave digestion and presented enrichment method combination.

1. Introduction

Antimony is ubiquitous elements in the environment originating from natural sources as well as human activities. Antimony compounds are used in various industrial processes like glassware, ceramics and textile industry [1,2]. Antimony is known to be one of the most toxic elements and has serious effects on plants, animals and human health [3,4]. Inorganic compounds of antimony are more toxic than the organic compounds [5–8]. The toxicity of Sb (III) ions is 10 times higher than Sb (V) ions [9–11]. Antimony can accumulate in living organisms and exert high-toxic potential on human being and animals over a lifetime and its toxicity may cause lung cancer [12,13]. Antimony in drinking water should be lower than 5 $\mu g\,L^{-1}$ [14,15]. Therefore, a highly sensitive and simple method is necessary for the determination of antimony concentration in environment [8].

Several analytical techniques such as hydride generation atomic absorption spectrometry, inductively coupled plasma optical emission spectrometry, electrothermal atomic absorption spectrometry etc. have been used for the determination of antimony levels in environmental samples. To obtain reliable results, an efficient separation and enrichment step is necessary prior to analysis of antimony species. Several separation-enrichment procedures including coprecipitation, cloud point extraction, membrane filtration, liquid–liquid extraction, solid phase extraction, etc. have been used for antimony species analysis [6,13–21].

In this present study, a simple, low cost, safety, sensitive and selective speciation method was developed for determination of Sb (III) and Sb (V) ions by using modified silica gel with GFAAS. Tetraethylenepentamine bonded silica gel were used as an adsorbent to solid phase extraction procedure for speciation of antimony (III) and antimony (V) in tap water, spring water and mineral water samples. Antimony was determined in refined salt, unrefined salt, black tea, rice, tuna fish and soil samples after microwave digestion and presented method combination.

2. Experimental

2.1. Instrumental

Antimony was determined by A Perkin Elmer AAnalyst 700 model (Norwalk, CT, USA) atomic absorption spectrometry equipped with HGA graphite furnace and with deuterium background corrector. The operating parameters for antimony are given in

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Table 1. Pyrolytic-coated graphite tubes (Perkin Elmer part no.: B3 001264) with a platform were used. Samples of 20 μl plus 10 μl of mixture of 0.015 mg Pd + 0.010 mg $Mg(NO_3)_2$ as matrix modifier during the study were injected into the furnace using Perkin Elmer AS-800 autosampler. The signals were measured as peak areas. Jasco FT/IR-430 was used for IR spectra of modified and unmodified silica gel and Leco (TruSpec MICRO Series) model elemental analyzer was used for elemental analysis of modified and unmodified silica gel. pH values in the aqueous phase were measured with Sartorius pp-15 Model glass-electrode pH meter.

2.2. Reagents and solutions

Analytical reagent-grades were used during the study. Silica gel 60 (Merck), mesh size of 0.063–0.200 mm, was used. A 1000 μg mL^{-1} Sb (III) stock solutions was prepared by $SbCl_3$ (Sigma-Aldrich). 1000 μg mL^{-1} Sb (V) stock solution was prepared by dissolving $SbCl_5$ (Sigma-Aldrich). The pH of the model solutions was adjusted to pH 2–4 with $H_2PO_4^-/H_3PO_4$ buffers, pH 4–6 with CH_3COO^-/CH_3COOH buffers and pH 8–9 with NH_4^+/NH_3 buffer solutions. Deionised water (Milli-Q Millipore 18.2 MΩ cm^{-1} resistivity) was used for all dilutions.

2.3. Synthesis of the tetraethylenepentamine bonded silica gel (TPA-SG)

Silica gel (20 g) was purified and activated with concentrated HCl for 6 h, then filtered and washed several times with deionized water and dried at 150 °C for 24 h. For synthesis of 3-chloropropyltrimethoxysilane bonded silica gel (Cl-SG), dry activated silica gel (10 g) were mixed with 10 mL of 3-chloropropyltrimethoxysilane in 100 mL anhydrous toluene and refluxed 24 h under nitrogen atmosphere. The mixture was filtered and washed with toluene, ethanol and diethyl ether and dried 60 °C for 6 h. The reaction is given below in Scheme 1.

For synthesis of tetraethylenepentamine bonded silica gel (TPA-SG), 3-chloropropyltrimethoxy-silane bonded silica gel (10 g) were reacted with triethylamine (12 mL) and tetraethylenepentamine (10 mL) in 100 mL of dry toluene and refluxed at 24 h under nitrogen atmosphere. The product, TPA-SG was filtered and washed with toluene, ethanol and diethyl ether and dried 60 °C for 6 h [22,23]. The reaction is shown in Scheme 2.

Table 1
Instrument settings for GFAAS determination of antimony.

Wavelength (nm)	217.6
Slit width (nm)	0.71
Lamp current (mA)	18
Argon flow (mL min^{-1})	250
Atomization site	Pyrolitic/platform
Reading time	5 s
Heating program temperature	
	°C (ramp time (s), hold time (s))
Drying 1	100 (5, 20)
Drying 2	140 (15, 15)
Ashing	1100 (10, 20)
Atomization	2000 (0, 5)
Cleaning	2600 (1, 3)

2.4. Preparation of tetraethylenepentamine bonded silica gel column

500 mg of TPA-SG was loaded into a $10 \times 100\ mm^2$ glass column (resin bed: 2 cm) equipped with porous disc. The TPA-SG column was preconditioned by passing a buffer solution prior to use. After each the elution, the TPA-SG column was washed with 10 mL of water.

2.5. Analytical procedure for antimony species

Model solutions (50 mL) containing 1.0 μg of antimony (III) and 1.0 μg antimony (V) were buffered to pH 6 using buffer solution. Then, the solutions were passed through the glass column filled with TPA-SG at a flow rate of 4 mL min^{-1}. Adsorbed Sb (III) was eluted with 5 mL of 2 mol L^{-1} HNO_3. Antimony (III) concentration was determined by GF-AAS.

2.6. Reduction of Sb (V) to Sb (III) and determination of total antimony

For the determination of total antimony, 0.5% (m/v) L-cysteine at pH 6 was added to 50 mL of model solution containing 1 μg of Sb (III) and 1 μg of Sb (V) and heated for 25 min in boiling water bath [2,13]. After the reduction, the solutions were passed through the column filled with TPA-SG at a flow rate of 4 mL min^{-1}. Adsorbed antimony ions on the TPA-SG were eluted with 5 mL of 2 mol L^{-1} HNO_3. Antimony concentration was determined by GF-AAS. The Sb (V) ion concentration was calculated by subtracting the Sb (III) concentration from the total antimony concentration.

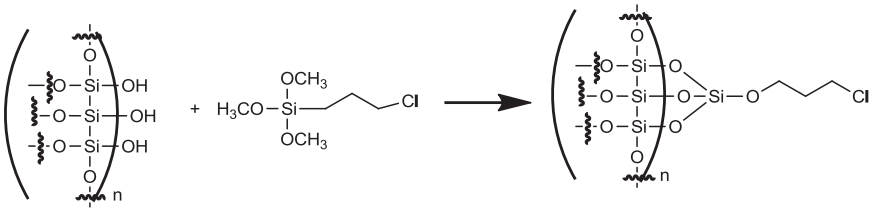
2.7. Analysis of the real samples

2.7.1. Application to microwave digested samples

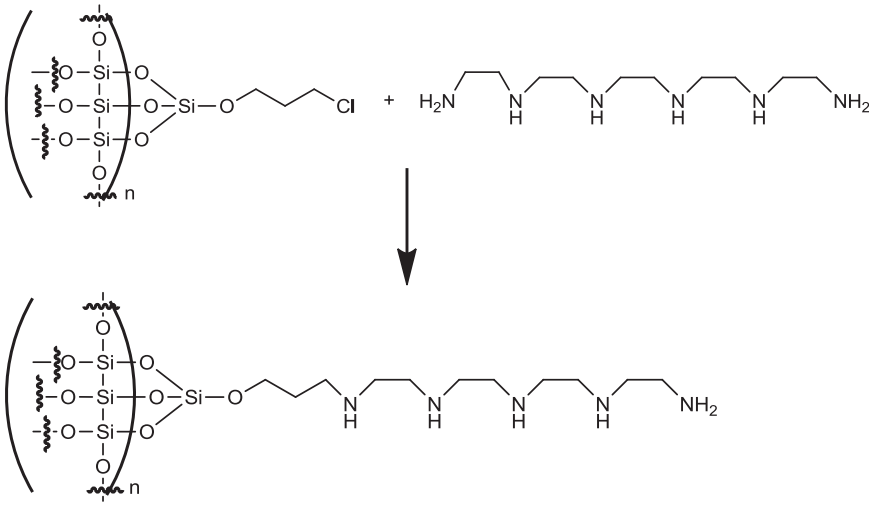
Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used for digestion of the solid samples. Digestion conditions for microwave system for the samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min [3]. NIST SRM 1573a Tomato laves, GBW 07605 Tea standard reference materials (250 mg), refined salt, unrefined salt, black tea, rice, tuna fish and soil (1.0 g) were digested with 6 mL of HNO_3 (65%) and 2 mL of H_2O_2 (30%) in closed microwave digestion system and diluted to 50.0 ml with deionized water. A blank digest was carried out in the same way. Then the procedure given above was applied to the final solutions.

2.7.2. Application to natural water samples

The water samples (tap water, mineral water and spring water) were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. The pH of the samples was adjusted to 6.0 with buffer solution. Then the speciation procedure given



Scheme 1. Synthesis of 3-chloropropyltrimethoxysilane bonded silica gel (Cl-SG).



Scheme 2. Synthesis of tetraethylenepentamine bonded silica gel (TPA-SG).

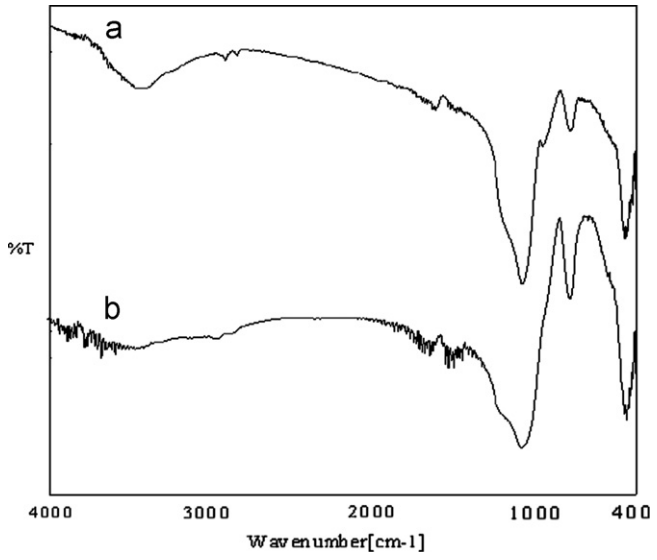


Fig. 1. FT-IR spectra of silica gel; (a) activated silica gel and (b) tetraethylenepentamine bonded silica gel.

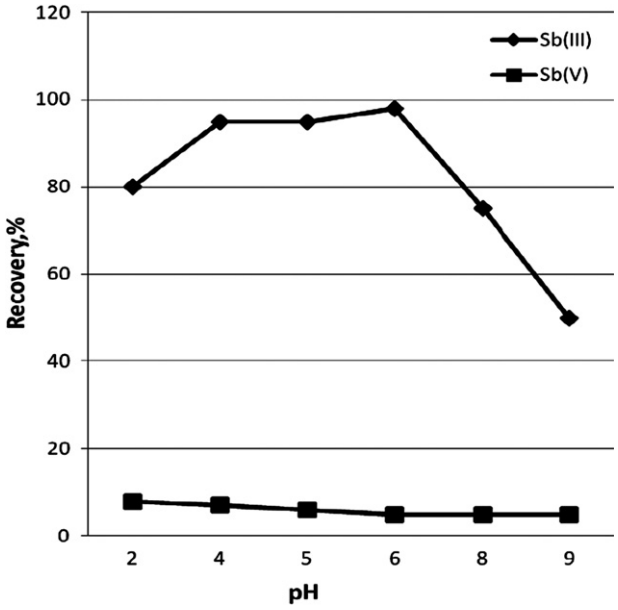


Fig. 2. The influences of pH on the recoveries of antimony species (1 μg Sb (III) and 1 μg Sb (V)) ($N=3$).

above was applied to the samples. Antimony in the samples was determined by GF-AAS.

3. Results and discussion

3.1. Characterizations of tetraethylenepentamine bonded silica gel (TPA-SG)

Elemental analysis and IR (FT-IR) spectrometric analysis were used for characterization of TPA-SG. Elemental analyses results are 3.82% N, 7.14% C and 1.65% H. The quantity of tetraethylenepentamine group attached to the silica gel surface calculated from the elemental analyses and was found 0.60 mmol g^{-1}. FT-IR spectra of silica gel (unmodified and modified silica gel) are shown in Fig. 1. Characteristic N–H and C–H bands are observed 1580–1650 cm^{-1} and 2800–3000 cm^{-1} in FT-IR spectrum of TPA-SG. The surface area of TPA-SG was found to be 243 m^2 g^{-1} by BET method [24].

3.2. Influences of pH

The pH is one of the critical parameter on the adsorption of metal ions [25–28]. To investigate influence of pH on involvement of antimony ions, model solutions containing Sb (III) and Sb (V) ions were used. The influences of pH on the recoveries of antimony (III) and antimony (V) were examined in the pH range of 2.0–9.0. The results are given in Fig. 2. Sb (III) was quantitatively recovered in the pH range of 4.0–6.0, but the recoveries of Sb (V) was not quantitative in this pH range. pH 6 was selected for the quantitative separation of Sb (III) and Sb (V) in further studies.

3.3. Eluent type and its volume

Different eluents and concentrations such as 1 mol L^{-1} HCl, 2 mol L^{-1} HCl, 1 mol L^{-1} HNO_3 and 2 mol L^{-1} HNO_3 were used for the eluent of antimony ions from column. Quantitative recoveries ($>95\%$) were obtained by using only 2 mol L^{-1} HNO_3

for Sb (III). The recoveries of antimony (III) were quantitative in the eluent volume range of 5–10 mL. The smallest eluent volume was used to obtain high enrichment factor. The quantitative elution volume was found to be as 5 mL.

3.4. Flow rates

Effects of flow rates of sample and eluent solutions on the recoveries of analyte ions on tetraethylenepentamine bonded silica gel column were investigated under the optimized conditions. The flow rate range of 1–10 mL min^{-1} was examined. Antimony (III) was quantitatively recovered in the sample and eluent flow rate range of 1–4 mL min^{-1}. In the all further works, 4 mL min^{-1} was selected as sample and eluent flow rate.

3.5. Effect of sample volume

The effect of sample volume on recovery of Sb (III) was examined for obtaining maximum applicable volume. The solutions containing Sb (III) ions from 25 mL to 500 mL were prepared and then operated according to the general procedure. The quantitative recoveries were obtained up to 250 mL. After 250 mL of sample volume, recovery values are not quantitative.

Table 2
Matrix effects on the recoveries of antimony (III) ($N=3$).

Ion	Added as	Concentration (mg L^{-1})	Recovery (%)
Na^+	NaCl	10000	95 ± 3
K^+	KCl	2000	96 ± 3
Ca^{2+}	$CaCl_2$	3000	98 ± 3
Mg^{2+}	$MgCl_2$	2000	95 ± 2
Cl^-	NaCl	25000	95 ± 2
F^-	NaF	1000	95 ± 2
NO_3^-	KNO_3	1000	96 ± 2
SO_4^{2-}	Na_2SO_4	2000	97 ± 2
PO_4^{3-}	Na_3PO_4	2000	96 ± 3
Mn^{2+}	$MnSO_4$	50	95 ± 3
Fe^{3+}	$FeCl_3$	50	96 ± 3
Cu^{2+}	$CuSO_4$	50	95 ± 3
Pb^{2+}	$Pb(NO_3)_2$	50	96 ± 3
Zn^{2+}	$ZnSO_4$	50	95 ± 2
Cd^{2+}	$Cd(NO_3)_2$	50	95 ± 3
Al^{3+}	$Al(NO_3)_3$	50	95 ± 2
Sb^{5+}	$SbCl_5$	100	95 ± 3
Mixture of matrix components			95 ± 4

mean ± standard deviations.

The preconcentration factor is calculated by the ratio of the highest sample volume (250 mL) and the lowest eluent volume (5 mL). The preconcentration factor was calculated as 50.

3.6. Influences of matrix ions on the recoveries

The effects of matrix of the real samples are one of the important problems in the spectrometric determinations of metal ions [29–32]. The influences of matrix ions were investigated on the recoveries of the analyte ions at pH 6. Various maximum amounts of matrix ions were added to the sample solution containing 1.0 μg of Sb (III) and 1.0 μg Sb (V) ions and the present procedure was performed for investigation of matrix ions effects on the proposed preconcentration systems. Analyte ions were generally quantitatively recovered in some maximum matrix ions. The results are given in Table 2. The tolerance limit is defined as the ion concentration causing a relative error smaller than ± 5% related to the preconcentration and determination of antimony species. Quantitative recovery was found for antimony in the presence of all foreign elements together.

3.7. Analytical performance

The relative standard deviations for atomic absorption spectrometric measurements for analyte ions were found 7% in the model solutions. The capacity of new sorbent was determined by batch method [29]. The capacity of TPA-SG for antimony (III) was found 7.9 mg g^{-1}.

The limit of detection (LOD) of the presented study was calculated under optimal experimental conditions (pH: 6, sample volume: 250 mL, eluent volume: 5 mL) after application of procedure to blank solutions. LOD, defined as the concentration

Table 4
The level of total antimony in certified reference materials and food and soil samples after application of the presented procedure ($N=4$).

Samples	Certified value	Our value
GBW 07605 Tea (μg kg^{-1})	56	54 ± 3
NIST SRM 1573a Tomato laves (μg kg^{-1})	63	62 ± 4
Refined salt (μg kg^{-1})	–	17.5 ± 1.1
Unrefined salt (μg kg^{-1})	–	30.7 ± 2.1
Black tea (μg kg^{-1})	–	10.3 ± 0.9
Rice (μg kg^{-1})	–	25.4 ± 1.8
Tuna fish (μg kg^{-1})	–	20.3 ± 1.2
Soil (μg kg^{-1})	–	57.5 ± 2.7

Mean expressed as 95% tolerance limit.

Table 3
Tests of addition/recovery for the speciation of antimony (III) and antimony (V) in some water samples ($N=3$).

Samples	Added (μg L^{-1})		Found (μg L^{-1})			Recovery (%)		
	Sb (III)	Sb (V)	Sb (III)	Sb (V)	Total Sb	Sb (III)	Sb (V)	Total Sb
Tap water	0.0	0.0	ND	ND	ND	–	–	–
	1.0	1.0	0.97 ± 0.05	0.98 ± 0.06	1.95 ± 0.09	97 ± 2	98 ± 2	98 ± 2
	2.0	2.0	1.92 ± 0.11	1.89 ± 0.14	3.81 ± 0.17	96 ± 2	95 ± 2	95 ± 2
	5.0	5.0	4.89 ± 0.44	4.75 ± 0.45	9.64 ± 0.91	98 ± 3	95 ± 2	96 ± 2
Mineral water	0.0	0.0	ND	ND	ND	–	–	–
	1.0	1.0	0.98 ± 0.04	0.99 ± 0.05	1.97 ± 0.15	98 ± 2	99 ± 2	99 ± 2
	2.0	2.0	1.94 ± 0.12	1.91 ± 0.14	3.85 ± 0.16	97 ± 2	96 ± 2	96 ± 2
	5.0	5.0	4.92 ± 0.47	4.90 ± 0.49	9.82 ± 0.90	98 ± 2	98 ± 2	98 ± 2
Spring water	0.0	0.0	ND	ND	ND	–	–	–
	1.0	1.0	0.95 ± 0.07	0.96 ± 0.06	1.91 ± 0.13	95 ± 3	96 ± 2	96 ± 3
	2.0	2.0	1.95 ± 0.15	1.93 ± 0.16	3.88 ± 0.19	98 ± 2	97 ± 2	97 ± 2
	5.0	5.0	4.94 ± 0.41	4.91 ± 0.43	9.85 ± 0.93	99 ± 4	98 ± 3	99 ± 4

ND: not detected.

Table 5
Comparative data from some recent studies on speciation of antimony.

Media	Detection system	PF	DL	R.S.D (%)	Reference
Triton X-114 and APDC	ETAAS	–	0.02 ng L^{-1}	7.8	[2]
SWCNTs/ APDC	Fluorescence spectrometry	24.6	2.1 ng L^{-1}	4.8	[4]
Titanium dioxide	GF-AAS	20	0.14 μg L^{-1}	6.8	[8]
XAD-8 resin/APDC	FAAS	–	–	<10	[11]
Liquid membrane extraction	FAAS	160	0.8 ng L^{-1}	6.2	[13]
L-proline-controlled pore glass	ICP-OES	11	0.09 μg L^{-1} and 0.9 μg L^{-1}	<10	[14]
Triton X-114/iodide	Spectrophotometry	200	0.23 ng L^{-1}	3.32	[19]
APDC-xylene	GF-AAS	400	2 ng L^{-1}	<9	[20]
C_{16}-bonded silica gel/APDC	GF-AAS	–	0.007 μg L^{-1}	3.8	[33]
Dowex 1 × 4 resin	ICP-OES	–	32 and 42 μg L^{-1}	2.7	[34]
Tetraethylenepentamine bonded silica gel	GF-AAS	50	0.020 μg L^{-1}	7	Presented work

PF: Preconcentration Factor, DL: Detection Limit, R.S.D: Relative Standard Deviation, APDC: Ammonium pyrrolidine dithiocarbamate, SWCNT: Single walled carbon nano tube, GF-AAS: Graphite furnace atomic absorption spectrometry, FAAS: Flame atomic absorption spectrometry, ICP-OES: Inductively coupled plasma-atomic emission spectrometry.

equivalent to 3 times the standard deviation (n=20) of the reagent blank were found as: 0.020 μg L^{-1} for antimony (III) ions. The limit of quantification (LOQ) is defined as the concentration equivalent to 10 times the standard deviation (n=20) of the reagent blank were found as: 0.067 μg L^{-1} for antimony (III) ions.

In order to validate the accuracy of the presented preconcentration-separation procedure for analytes, different amounts of analyte ions were spiked to tap water, spring water and mineral water samples. The results were given in Table 3. Good agreement was obtained between the added and measured analytes.

3.8. Application of the method in real samples

The presented method was checked to certified reference materials (NIST SRM 1573a Tomato laves, GBW 07605 Tea) (Table 4). The results are in good agreement with the certified values. The procedure was successfully applied to the determination of total antimony in refined salt, unrefined salt, black tea, rice, tuna fish and soil samples. The results are given in Table 4.

4. Conclusion

The results show that TPA-SG column can be used for speciation of Sb (III) and Sb (V) ions in water samples by using GF-AAS. The presented speciation method ensures simple, accurate, rapid, inexpensive and efficient speciation of Sb (III) and Sb (V) ions. The results of antimony obtained by proposed method were compared with literature values. The results are given in Table 5. The detection limits, preconcentration factor and R.S.D values of antimony are superior to those of other preconcentration techniques.

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