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Separation/preconcentration of antimony(III) by nickel/nickel boride nanoparticles prior to hydride generation atomic absorption spectrometric determination

Miray Kavas[1], Nur Aksuner[1,2], Raif Ilktac*[2], Emur Henden[1]

[1]University of Ege, Faculty of Science, Department of Chemistry, Izmir, Turkey.

[2]University of Ege, Central Research Testing and Analysis Laboratory Research and Application Center, Izmir, Turkey.

Abstract

A new, simple, fast and inexpensive method has been developed for the preconcentration of trace amounts of antimony(III) ions using nickel/nickel boride nanoparticles prior to their determination by hydride generation atomic absorption spectrometry. Optimization of the analytical parameters including initial pH, sorbent amount, contact time, sample volume, eluent type, and interference effects have been performed. Under the optimized conditions, the enrichment factor was 25 and the limit of detection was 0.02 µg/L. Calibration graph was obtained in the range of 0.08-0.80 µg/L with a correlation coefficient of 0.9924. The sorption capacity of the nickel/nickel boride nanoparticles was found to be as high as 2500 mg/g. The proposed method was applied to tap water and bottled drinking water. The quantitative recovery values were obtained in the range of 95-104 %. Langmuir and Freundlich adsorption models were evaluated and the results showed that the sorption process fitted the Langmuir isotherm and monolayer adsorption process occurred. The proposed method was validated with a certified reference material. With the high capacity of the novel nickel/nickel boride nanosorbent, dynamic calibration range with suitable limit of detection and quantification, suitable enrichment factor, rapidity and cost-effectiveness, the proposed method is ideal for the preconcentration and determination of antimony(III).

Keywords

Antimony, hydride generation atomic absorption spectrometry, nickel/nickel boride nanoparticles, preconcentration.

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***Corresponding author:** Raif Ilktac, **e-mail:** raifilktac@gmail.com

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INTRODUCTION

Antimony exists in the environment due to human facilities and natural sources. Soil run-off and rock weathering are the main natural sources, whereas the traffic is the primary source of the human activitiessince numerous antimony-containing addditivesare used in car brake lines, flame retardants and tire vulcanization processes (Filella *et al.*, 2002; Benzce*et al.*, 1994; Berman, 1980). Antimony is potentially toxic at very low concentrations and inhalation of antimony compounds may lead to pneumonitis, fibrosis and bone marrow disease (Fowler and Goering, 1991). Antimony and its compounds are included in the priority pollutant list of Environmental Protection Agency of the United States (USEPA) and European Union (USEPA, 1976; Council of European Communities, 1976). The USEPA drinking water standards for maximum contaminant level goal (MCLG) and maximum contaminant level (MCL) for antimony are both stated as 6 µg/L (USEPA, 2003). The European Union established the maximum admissible concentration of antimony in drinking water as 5 µg/L (Council of European Communities, 1998).

Due to its toxicity, the development of sensitive and selective methods for the determination of trace levels of antimony in various samples is very important. The commonly used analytical methods for the determination of antimony include flame atomic absorption spectrometry (FAAS) (Titretir *et al.*, 2012), electrothermal atomic absorption spectrometry (ET-AAS) (López-García *et al.*, 2017; Rojas *et al.*, 2007), inductively coupled plasma emission spectrometry (ICP-OES) (Ilander and Vaisanen, 2011; Biata *et al.*, 2017), inductively coupled plasma-mass spectrometry (ICP-MS) (Lin *et al.*, 2017), spectrophotometry (Frizzarin *et al.*, 2016) and voltammetry (Renedo and Martinez, 2007). Hydride generation technique combined with atomic absorption spectrometry (HGAAS) is a simple and well established technique for the determination of antimony (Dedina and Tsalev, 1995). It is often difficult to determine the extremely low concentrations of antimony directly by most of the analytical techniques due their insufficient sensitivity or interference effects. Thus, preconcentration and separation of trace levels of antimony prior to the determination step are usually necessary. Various kinds of separation and preconcentration methods such as co-precipitation (Zhang *et al.*, 2007), liquid–liquid extraction (Fan, 2007; Li *et al.*, 2008), high-performance liquid chromatography (Fontanella *et al*., 2016; Müller *et al*., 2009) and solid-phase extractionhave been proposed (Yu *et al*., 2002; Erdem *et al*., 2005; Pacheco *et al*., 2007; Zih-Perenyi *et al*., 2008; Souza and Tarley, 2008). Different types of sorbents have been successfully used for the preconcentration of antimony(III) (Zheng *et al*., 2006; Nomngongo *et al*., 2013; Huang *et al*., 2007).

Design of novel nanomaterials has become of great importance since the last decade, due to awide range of applications that they have. Their novel optical, electronic, magnetic, and chemical properties that are ascribed to the extremely small dimensions and special surface nature have attracted the interest of analytical chemists on metallic nanoparticles (Starowicz *et al*., 2006; Welch and Compton, 2006; Lu *et al*., 2000). Nickel nanoparticles have important applications in catalytic reactions (Yoon *et al*., 2005). According to our knowledge, nickel containing nanoparticles have not been used for the preconcentration of antimony so far.

According to our previous observation on the determination of arsenic and antimony by HGAAS, the signal suppression of nickel(II) is due to the sorption of arsenic(III), arsenic(V) and antimony(III) ions by the black nickel/nickel boride nanoparticles generated via the reduction of sodium tetrahydroborate(III) (Henden *et al*., 2011). Therefore, in the present study, a novel procedure for the preconcentration and determination of antimony(III) at low concentration by HGAAS using nickel/nickel boride nanoparticles as sorbent has been proposed. For this purpose, nickel/nickel boride nanoparticles were prepared by the reduction of nickel(II) with sodium tetrahydroborate(III). The synthesized nanoparticles were utilized for the selective and sensitive preconcentration and determination of antimony. In order to determine the accuracy of the proposed method, certified reference material (CRM) was analysed and satisfactory results were obtained. The proposed method was also applied toreal water samples for the determination of trace antimony and quantitative recovery values were obtained. Because of the high capacity of the novel nickel/nickel boride nanosorbent, dynamic calibration range with suitable limit of detection (LOD) and limit of quantification (LOQ), rapidity and cost-effectiveness, the proposed method is thought to be an ideal method for the preconcentration and determination of antimony.

MATERIALS AND METHODS

Reagents

1000 mg/L stock solutions of antimony(III) were prepared by dissolving potassium antimony tartrate (Merck) in 2 M hydrochloric acid (HCl) (Merck). Lower concentration standards were prepared daily from the stock standards.

$NaBH_4$ solutions were prepared daily by dissolving sodium tetrahydroborate(III) pellets (Merck) in 0.15 M and 0.01 M NaOH, respectively. HCl and nitric acid (HNO_3) were purchased from Merck. 25 % Ni(II) solution was prepared by dissolving $Ni(NO_3)_2.6H_2O$ (Merck) in water and adjusting the final acidity to 0.004 M with HCl.

Apparatus

GBC 904 PBT model atomic absorption spectrometer (Illinois, USA) equipped with GBC HG3000 continuous-flow hydride generation system was used for antimony determination. Antimony hollow cathode lamp was operated with a maximum current of 10 mA at 217.6 nm and Deuterium (D_2) background correction was performed in all measurements. Air-acetylene flame was used for heating the quartz tube externally. Nüve water bath shaker (Ankara, Turkey) equipped with a thermostat was used for sorption studies. pH measurements were performed by using an Orion 4 Star pH meter (Beverly, USA). pH meter was calibrated before every measurement. For centrifugation, Nüve NF 800 (Ankara, Turkey) was used at 3000 rpm. All weight measurements were performed by using a Precisa XB220A balance (Dietikon, Switzerland). The morphologies of the nanoparticles were analyzed by scanning electron microscopy (SEM) (Thermo Fisher Scientific, Oregon, USA). X-ray photoelectron spectra (XPS) were recorded on a ThermoScientific K-alpha X-ray photoelectron spectrometer (Thermo Fisher Scientific, UK). Kα radiation was employed as the excitation source.

Procedure for the determination of antimony(III)

Unadsorbed antimony(III) remained in the solution was determined by using continuous flow HGAAS. In this system, sample, sodium tetrahydroborate(III) and acid solutions were introduced to the spectrometer with the aid of peristaltic pump after passing through the reaction loop and gas/liquid separator, respectively. Operating and working conditions of the system used for the determination of antimony are shown in Table 1.

Table 1: Instrumental operating parameters for the continuous-flow HGAAS in antimony determination**.**

Parameters	**Continuous flow HGAAS**
System type	Flame
Lamp current (mA)	10.0
Wavelength (nm)	217.6
Slit width	0.2
Sampling mode	Automated sampling
Flame type	Air-Acetylene
Acetylene flow rate (L/min)	2.10
Air flow rate (L/min)	13.50
Read time (s)	30
Measurement mode	Peak Area
Carrier gas	Nitrogen
N_2 flow rate (mL/min)	50
HCl (mol/L)	2.0
$NaBH_4$ (%)	0.6
HCl flow rate (mL/min)	2.0
$NaBH_4$ flow rate (mL/min)	2.0
Sample flow rate (mL/min)	8.0

Synthesis of nickel/nickel boride nanoparticles

Two mL 4 % $NaBH_4$ was added onto 10 mL of 1 g/L Ni(II) in 0.004 M HCl in a 50 mL beaker while stirring the solution with a magnetic stirrer. Black particles were formed immediately in the beaker and the particles were separated by centrifugation. The particles were washed with distilled water at least three times. The nanoparticles prepared with this procedure are called as oxic particles.

Preparation of the black nanoparticles was also performed under nitrogen atmosphere with the similar way. The nanoparticles prepared with this procedure are called as non-oxic particles.

Sorption and isotherm models

The sorption capacity and the percentage of antimony sorption were calculated respectively by the following equations:

$$Q = \frac{(C_i - C_e) \times V}{W} \qquad (3)$$

and

$$Sorption\ (\%) = \frac{(C_i - C_e)}{C_e} \times 100 \qquad (4)$$

Where Q represents the adsorption capacity (mg/g), C_i and C_e are the initial and equilibrium concentrations of antimony(III) ions (mg/L), respectively. W is the mass of sorbent (g) and V is the volume of the solution (L).

Freundlich and Langmuir models are the simplest and the most commonly used isotherms to simulate adsorption of components from a liquid phase onto a solid phase. The Langmuir model is a valid monolayer sorption on a surface containing a finite number of binding sites. It assumes uniform energies of sorption on the surface and no transmigration sorbate in the plane of the surface. The Freundlich equation is an empirical adsorption model. Langmuir and Freundlich isotherm models were applied by using the equations:

$$\frac{C_e}{C_s} = \frac{1}{Q_m L} + \frac{C_e}{Q_m} \quad (5)$$

and

$$\ln C_s = lnK_f + n_f lnC_e \quad (6)$$

where Q_m (mg/g) and L (L/mg) are Langmuir constants, Q_m is the amount of antimony ion sorption corresponding to monolayer coverage, L is the affinity of antimony for the sorbent, C_e (mg/L) is the amount of antimony in liquid phase at equilibrium and C_s (mg/g) is the amount of antimony adsorbed on the surface of the sorbent at equilibrium. K_f (mg/g) and n_f are the Freundlich constants (Limousin *et al*., 2007; Umpleby *et al*., 2001).

RESULTS AND DISCUSSION

Choise of sorbent for sorption of antimony(III)

In this study, sorption efficiencies of both oxic and non-oxic nickel/nickel boride nanoparticles were investigated for the sorption of antimony(III). 25 mL of 1000 µg/L antimony(III) solution at pH 6.0 was added onto 10 mg nickel/nickel boride nanosorbent and the mixture was shaken for 30 minutes at 25 °C. After sorption, the sorbent and the supernatant solution were separated by centrifugation. Then, the unadsorbed antimony(III) remained in the supernatant was determined by using continuous flow HGAAS. For the determination of the sorbed antimony, the sorbent was dissolved in 3 mL of concentrated HCl and the procedure explained above was applied for the determination of sorbed antimony. The sorption efficiencies of oxic and non-oxic nickel/nickel boride nanoparticles were found to be 99.2±1.7 % and 100.0±1.8 % (n=5), respectively. Since the sorption efficiencies were quantitative and comparable, non-oxic nickel/nickel boride nanoparticles were chosen to be used as sorbent for the determination and preconcentration of antimony(III).

Characterization of the sorbent

Characterization of the non-oxic nickel/nickel boride nanoparticles was performed by using SEM and XPS. The morphologies of the synthesized nanoparticles are shown in SEM images in Figure 1. According to the XPS results, the structure of the sorbent was suggested to be the mixture of Ni_xB, Ni(0) and $Ni(OH)_2$ (Figure 2) (Henden *et al*., 2011).

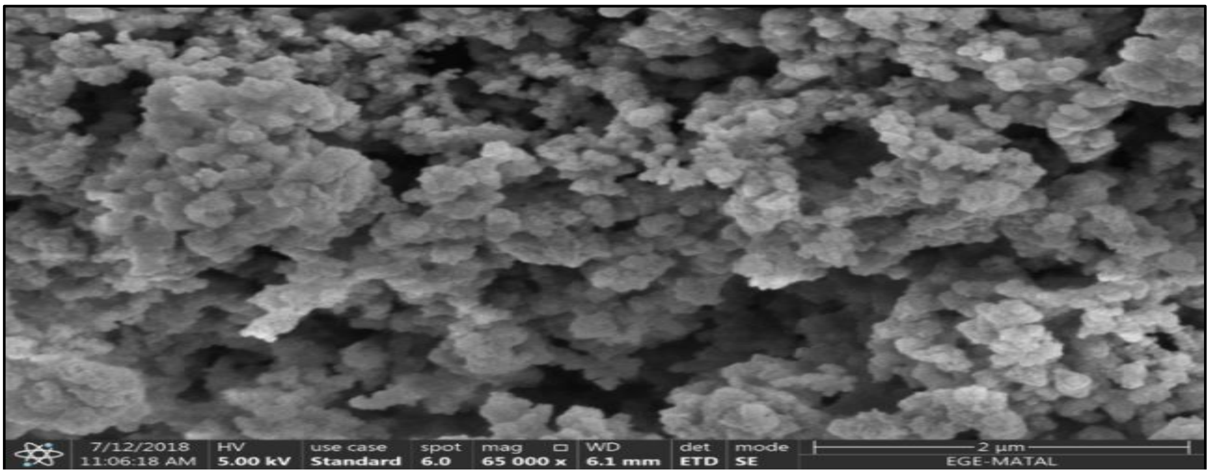

Figure 1: SEM image of nickel based nanoparticles.

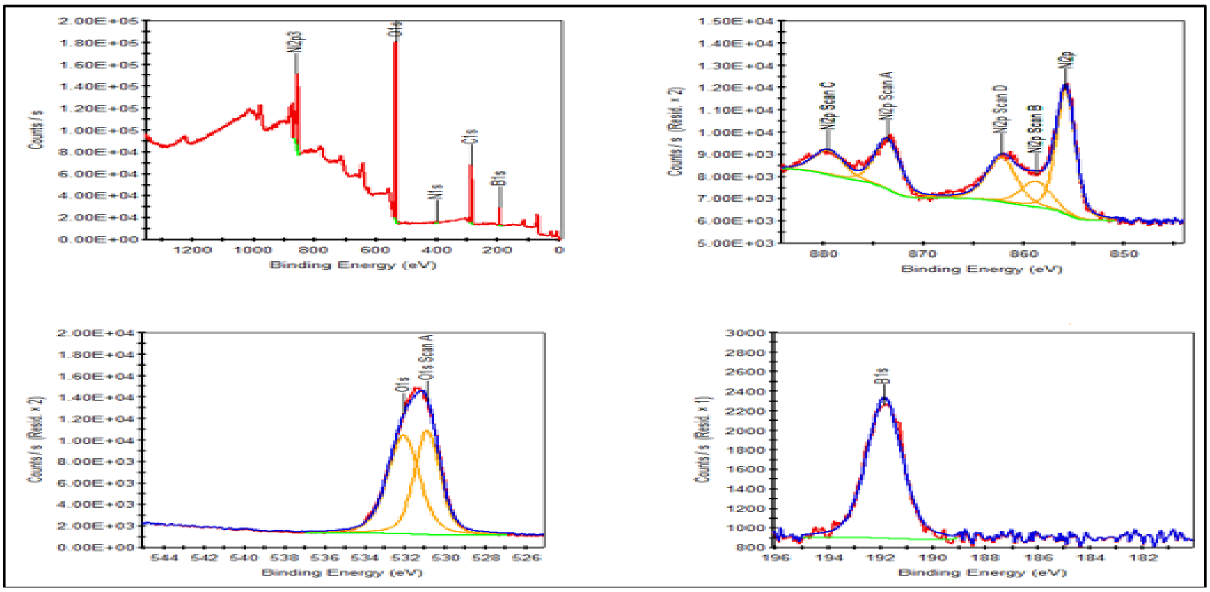

Figure 2: XPS results of the non-oxic nickel/nickel boride nanoparticles.

Effect of pH

pH values of antimony(III) solutions were adjusted using dilute HCl or sodium hydroxide solutions. The effect of initial pH on the sorption of antimony(III) was investigated within the range of 3-10. 25 mL 1000 µg/L antimony(III) solutions with different pH values were added onto 10 mg sorbent. After centrifugation, unadsorbed antimony was determined. As shown in Figure 3, the quantitative sorption efficiencies for antimony(III) were obtained in the range of pH 3-10. The pH did not have a significant effect on the sorption efficiency and the initial pH of the solutions was adjusted to pH 6.0 for the further analyses.

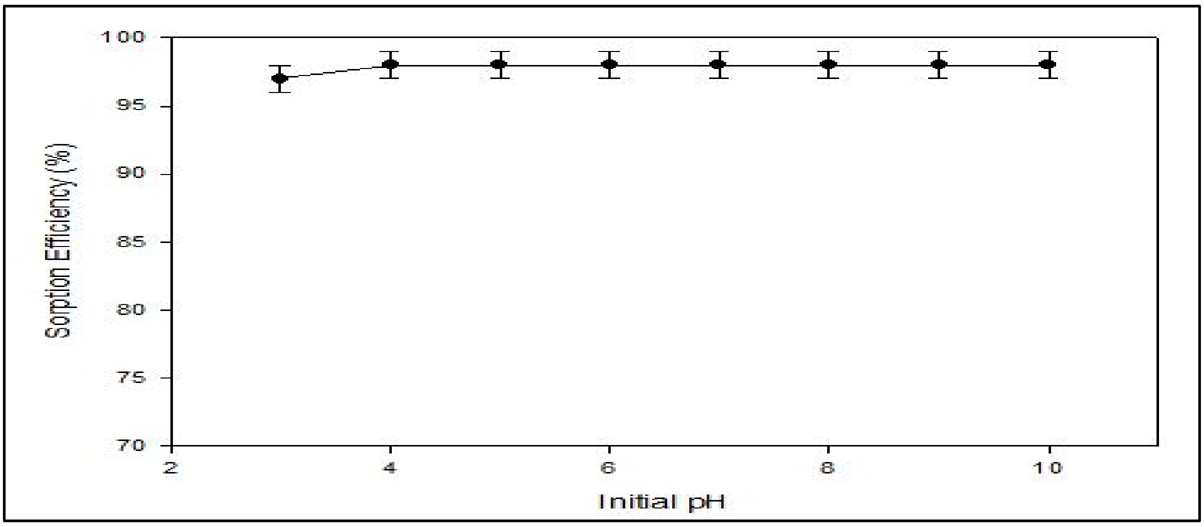

Figure 3: The effect of initial pH on antimony sorption efficiency (Sorbent amount: 10 mg, 25 mL 1000 µg/L antimony(III) solution).

Effect of the sorbent amount

In order to determine the effect of the amount of the sorbent on the preconcentration of antimony, 25 mL of 1000 µg/L antimony(III) solution was shaken with different amounts (10 to 60 mg) of non-oxic nickel/nickel boride nanoparticles and unadsorbed antimony(III) remained in the solution was measured.

Quantitative recoveries (>96 %) of antimony(III) were attained in all of the dosages used. Therefore, further studies were performed with 10 mg of the sorbent.

Effect of contact time

In order to determine the optimumcontact time on antimony sorption efficiency, 25 mL of 1000 µg/L antimony(III) solutions at pH 6.0 were shaken with 10 mg of the sorbent with different contact times (10-120 minutes) at 25 ^{o}C. After centrifugation, the unadsorbed antimony(III) concentration in solution was determined. As shown in Figure 4, optimum contact time for antimony sorption was chosen as 30 minutes that was used in the futher analyses.

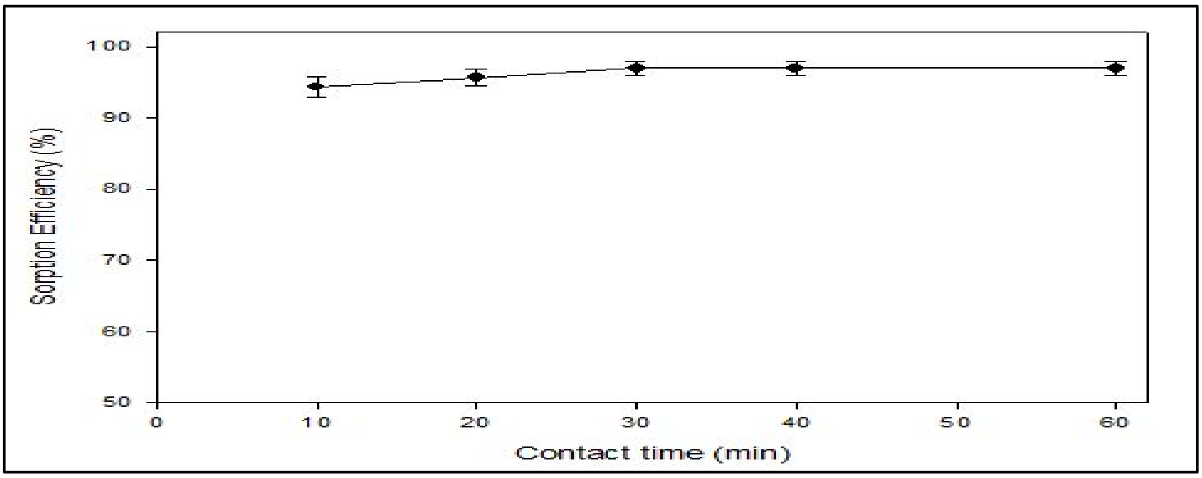

Figure 4: The effect of contact time on antimony sorption (Sorbent amount: 10 mg, 25 mL 1000 µg/L antimony(III) solution at pH 6.0).

Effect of sample volume

The effect of the sample solution volume on the antimony(III) sorption was investigated by shaking 25-250 mL of 1000 µg/L antimony(III) solution (pH 6.0) with 10 mg sorbent for 30 minutes at 25°C. After sorption, the unadsorbed antimony was determined. As shown in Figure 5, the sorption of the antimony(III) was quantitative and was not affected by the volume of the sample up to 250 mL.

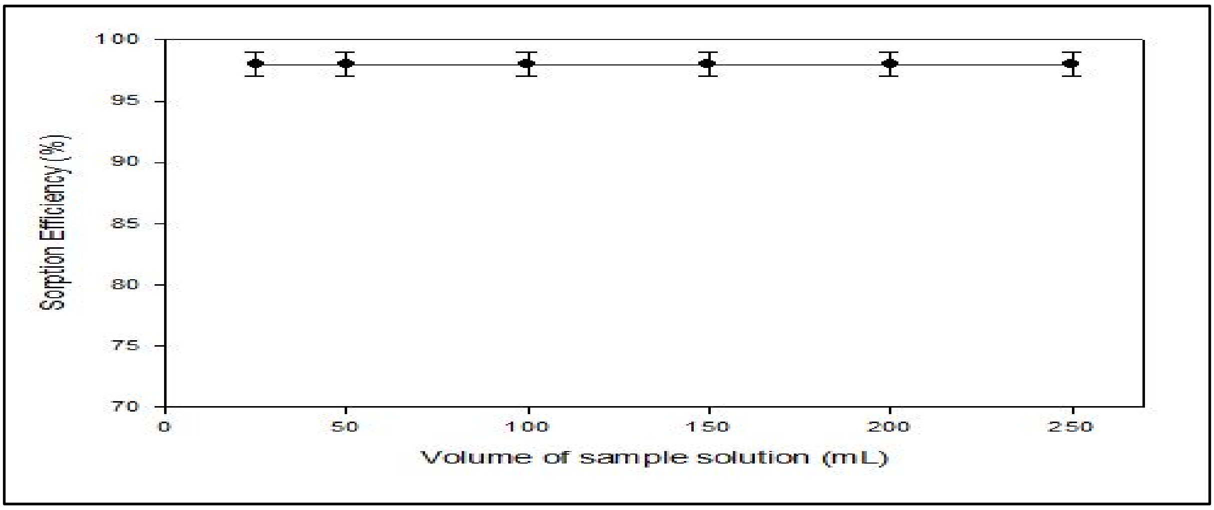

Figure 5: Effect of sample solution volume on the sorption efficiency (Sorbent amount: 10 mg, 1000 µg/L antimony(III) solution at pH 6.0).

Antimony recovery

Different concentrations of HCl, nitric acid, sulfamic acid and ascorbic acid were used to recover the adsorbed antimony. However, antimony(III) could not be desorbed quantitatively without decomposing the sorbent. Among the reagents used, concentratedhydrochloric acidprovided the highest recovery (99.3±1.2, n=3) and therefore concentrated hydrochloric acid was selected as recovery agent in the further studies. In recovery studies, to eliminate the nickel(II) interference on antimony(III) detection, 0.01 M EDTA was added to the solution.

Sorbent Capacity

In order to determine the sorption capacity of the sorbent, 10 mg non-oxic nickel/nickel boride nanoparticles wereshaken with 50 mL of 500 mg/L antimony(III) solution (pH ~6.0). After shaking for 30 minutes, the phases were separated by centrifugation, the sorbent was dissolved in 3 mL of concentrated HCl and the solution volume was adjusted to 25 mL. Then, antimony concentration in the solution was measured by continuous flow-HGAAS. The sorption capacity (Q, mg/g) was calculated by using the equation (3) and the results showed that the maximum amount of antimony(III) ions that can be adsorbed by the nickel/nickel boride nanoparticles was found to be 2500 mg/g. This value is unexpectedly high when compared to that in the literature (Table 2).

Table 2: Comparison of the proposed method with other reported methods for preconcentration of antimony(III).

Adsorbent	Linear range (µg/L)	Detection limit (µg/L)	Enrichment Factor	Adsorption capacity (mg/g)	Detection	Reference
Magnetic core-modified silver nanoparticles	0.05–2.5	0.03	325	10	ET-AAS	10
Isolute silica-based octyl (C8) sorbent	0–5.0	0.001	N.R.*	N.R.*	ICP-MS	23
–SH functional groups (Duolite GT-73)	0–80.0	0.06	N.R.*	N.R.*	HG-AAS	24
L-methionine	0.07–100	0.07	20	N.R.*	ICP-OES	25
Imino diacetic acid–ethyl cellulose	1–4	0.18	25	N.R.*	ET-AAS	26
Ammonium O,O- diethyl dithiophosphate	0.25-16	0.08	229	N.R.*	GF-AAS	27
Nanometer size titanium dioxide (rutile)	N.R.*	0.05	50	>29.6	HG-AAS	28
SPE-Dowex 1-x8	N.R.*	0.05	4	N.R.*	ICP-OES	29
Akaganeite	N.R.*	N.R.*	N.R.*	61.2	ICP-MS	38
Nano titania-chitosan beads	N.R.*	N.R.*	N.R.*	60.03	ICP-OES	39
Nickel/nickel boride nanoparticles	0.08–0.80	0.02	10	2500	HG-AAS	This study

*Not Reported.

Adsorption isotherms

The adsorption isotherm of the sorption of antimony(III) onto nickel/nickel boride nanoparticles was determined. In order to identify the adsorption type and determine the adsorption capacity, 10 mg non-oxic nickel/nickel boride nanoparticles were added to 10 mL of antimony(III) solution (20–3000 mg/L, pH~6) and the mixture was shaken for two hours at room temperature to reach the equilibrium. Then, unadsorbed antimony(III) concentration in the solution was measured by continuous flow-HGAAS. By using equations (5) and (6), the correlation coefficient (R^2) for Freundlich isotherm and Langmuir isotherm was found to be 0.7442 and 0.9986, respectively. Thus, it can be concluded that the adsorption processfitted to Langmuir isotherm and monolayer adsorption process occurred. Sorption capacity of the sorbent was found to be 2500 mg/g from the Langmuir equation andwasin accordance with the experimental value obtained from equation (3).

Analytical performance

Under the optimal conditions of the preconcentration, linear calibration graph was obtained within the concentration range of 0.08-0.80 µg/L by 25 times preconcentration. The calibration equation was $A=0.4238C_{Sb} + 0.1887$ ($R^2 = 0.9924$), where A is absorbance, and C_{Sb} is the concentration of antimony(III) in µg/L. The limit of detection (LOD) and the limit of quantification (LOQ) can bedefined as;

$$LOD = \frac{\sigma}{S} \times 3 \qquad (1)$$

and

$$LOQ = \frac{\sigma}{S} \times 10 \qquad (2)$$

where σ is the standard deviation of the responses of blank solution and S is the slope of the calibration curve. LOD and LOQ were found to be 0.020 µg/L and 0.066 µg/L, respectively. Precision of the proposed method was determined as 1.9 % for six replicated determination of 0.12 µg/L of antimony(III) for 50 mL solution.

The proposed method was compared toother preconcentration procedures that are currently used for the determination of antimony and the results are summarized in the Table 2. LOD of the method was comparable to that obtained by other estalished methods and the capacity of the sorbent was much higher than other reported sorbents. Therefore, it was concluded that the proposed method is suitable for the preconcentration and determination of trace levels of antimony(III) and the novel sorbent with ultra-high-capacity is also suitable for antimony(III) removal.

Interferences study

In order to identify the potential interferences in the preconcentration of antimony using the proposed sorbent, the effects of some diverse ions, which may be present in real samples, were evaluated. In order to evaluate the interference effect, various excess amounts of diverse ions were added onto 25 mL of 50.0 µg/L of antimony(III) (pH~6) and the proposed procedure for determination of adsorbed antimony(III) was applied. An ion was considered as an interfering agent when its presence produced more than ±5.0 % change in the antimony signal. The results are summarized in Table 3. The results showed that excess amounts of common cations do not interfere the determination of trace quantities of antimony(III). Therefore, the proposed preconcentration procedure described not only preconcentrated the antimony but also eliminated such interferences.

Table 3: Tolerable concentration ratio of diverse ions to antimony(III).

Co-existing diverse ions	**Diverse ion to analyte concentration ratio**
copper(II), zinc(II), cobalt(II), nickel(II)	1000
iron(III), cadmium(II), aluminium(III)	500
tin(II), lead(II)	200
arsenic(III)	50

Accuracy of the method

For the evaluation of the accuracy of the proposed method, certified reference material (drinking water-LOW, EnviroMAT, EP-L-2) was analyzed for antimonyin three replicates after preconcentration procedure. The measured value (0.011 ± 0.004 mg/L) was in good agreement with the certified value (0.012 ± 0.005 mg/L).

Analytical application

The proposed method was applied to tap water, commercially bottled drinking water and mineral water to determine the amount ofantimony(III). The pH of the sample was adjusted to ~6.0 and shaken with 10 mg sorbent for two hours.

After sorption, the phases were separated and adsorbed antimony(III) was measured. Antimony(III) was not detected in any of the water samples and therefore, spike addition method was applied. The results shown in Table 4 indicated that the recoveries were quantitative for trace antimony analysis, ranging from 95 to 104 %.

As a conclusion, in the present study, nickel/nickel boride nanoparticles was successfully synthesized and used for the preconcentration and determination of antimony(III) by HGAAS. The proposed method was compared to the other preconcentration procedures that are currently used for the determination of antimony. LOD of the method was comparable to that obtained by other estalished methods. The sorption capacity was much higher than the other sorbents reported. Therefore, the sorbent was suggested for antimony removal. Furthermore, the preparation of the sorbent is simple and cost effective. The established preconcentration procedure is simple, rapid, economic and reliable. The method was validated with the analysis of a certified reference material. The proposed method was applied for the determination of antimony(III) in water samples and satisfactory results were obtained. The proposed preconcentration procedure was also shown to be successful for eliminating serious interferences of several ions at high concentration improving the applicability of hydride generation based atomic spectrometric techniques.

Table 4: Results of the determination of antimony(III) in different water samples.

Sample	**Added (µg/L)**	**Found[a] (µg/L)**	**Recovery (%)**
Tap water	-	BLD[b]	-
	10	10.3 ± 0.2	103.0±2.0
	20	19.4 ± 0.3	97.2±1.8
Drinking water 1	-	BLD[b]	-
	10	9.6 ± 0.1	96.0±1.0
	20	20.3 ± 0.4	101.6±1.9
Drinking water 2	-	BLD[b]	-
	10	9.8 ± 0.5	98.0±5.0
	20	19.0 ± 0.4	95.2±2.5
Mineral water 1	-	BLD[b]	-
	10	10.4 ± 0.6	104.0±6.0
	20	20.2 ± 0.3	101.0±2.6
Mineral water 2	-	BLD[b]	-
	10	9.5 ± 0.5	95.0±5.0
	20	20.4 ± 0.4	102.0±4.0

[a] Mean ± standard deviation, n=3.

[b] BLD= Below the limit of detection.

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