

STUDYING ON THE CONTAMINATIVE DETERMINATION OF EXISTING FORMS OF As^{3+} , As^{5+} , Sb^{3+} AND Sb^{5+} IN GROUND WATER AT LAMDONG PROVINCE

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ABSTRACT: The project describes hydride generation atomic absorption spectrometry techniques for determination of arsenic (III), total arsenic, antimony (III) and total antimony concentration in water sample by investigating type and concentration of acide and sodium tetrahydroborate concentration.

The optimal conditions for determination of arsenic (III) were: 2% (m/v) citric acide and 2%(m/v) sodium tetrahydroborate. The same paramaters for determinaion of arsenic (V) were: 4N of HCl and 2%(m/v) of sodium tetrahydroborate in 10% (m/v) of KI.

The optimal conditions for determination of antimony (III) were: 2% (m/v) citric acide and 2%(m/v) sodium tetrahydroborate. The same paramaters for determination of antimony (V) were: 6 N of HCl and 2%(m/v) sodium tetrahydroborate in 10% (m/v) of KI.

Interference from ions on the analysis for arsenic (III), total arsenic, antimony (III) and total antimony were also investigated.

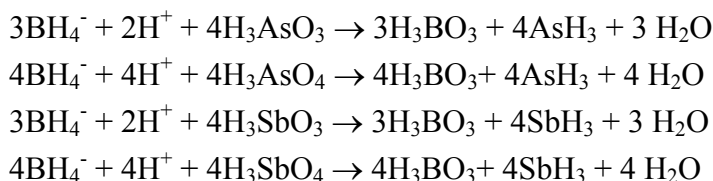
The sensitivity of this method was estimated to be 0.001ppm, 0.002ppm, 0.002ppm and 0.003ppm for As^{3+} , $As^{3+,5+}$, Sb^{3+} and $Sb^{3+,5+}$ respectively.

INTRODUCTION

In analytical chemistry, Atomic absorption Spectrophotometry method is a technique for determining the concentration of a particular metal element in a sample. Atomic absorption spectroscopy can be used to analyze the concentration of over 62 different metals in a solution and provides accurate quantitative analyses for metals in water, sediments, soils or rocks.

The atomic absorption spectrophotometry include: Flame - Atomic Absorption Spectrophotometry technique (F-AAS), hydride generator - Atomic Absorption Spectrophotometry technique (HG-AAS) graphic funace Atomic Absorption Spectrophotometry technique (GF-AAS), and Cold Vapor Atomic Absorption Spectrophotometry technique in which HG-AAS has been used extensively for determination of volatile element. It is base on hydride generation systems.

Arsenic and Antimony were formed hydridres (AsH_3 , SbH_3) in acidic solution with $NaBH_4$ for example the reaction of As^{3+} with $NaBH_4$ forms arsine AsH_3 and can be presented as follows:



Hydride generation involves several steps: the hydride is generated by chemical reaction, it is swept out of the solution into the atomizer by a carrier gas and they are determined by F-AAS and measured at 193.7nm and 231.2nm for As and Sb, respectively.

I. MATERIALS

I.1. Equipment

- An Atomic Absorption Spectrophotometer system (Chemito –AA230).
- Balance, micropipette, glassware, glass beakers. etc.

I.2. Reagents

- All chemicals used were of analytical grade. Deionized water was obtained by processing distilled water in an ion exchange unit.
- Hydrochloric acid (density 1.12 g/cc), citric acid: Acids must be analyzed to determine levels of impurities.
- Single-element solutions standards ($1000 \mu\text{g ml}^{-1}$) of As^{3+} , Sb^{3+} were obtained from Merck (Germany).
- Single-element solutions standards ($1000 \mu\text{g ml}^{-1}$) of As^{5+} , Sb^{5+} were prepared from SbCl_5 and NaAsO_3 (Germany).
- Intermediate antimony and arsenic solution: Pipet 1 mL stock antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.0 mL concentrated HCl/liter (1 mL = 10 μg each of Sb and As).
- Standard antimony and arsenic solution: Pipet 10 mL intermediate antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.0 mL concentrated HCl/liter (1 mL = 1 μg each of Sb and As).
- 10% Potassium iodide (KI): A 10% KI solution (10 g reagent-grade KI. Dissolved and brought to volume in 100 mL reagent water) must be prepared for reduction of antimony and arsenic to their +3 valence states.
- Sodium borohydride (NaBH_4).
- All equipments used for sampling and storing were washed with soap and water, treated with dilute nitric acid and then thoroughly rinsed with deionized water.

II. METHOD

II.1. HG-AAS method for determination of As^{3+}

25ml of water sample was filtered through with size $0.45\mu\text{m}$ membrane filter in order to remove suspending materials.

- A solution containing 2 percent (w/v) of citric acid was prepared.
- A solution containing 2 percent (w/v) of NaBH_4 was prepared.
- Prepare working standards from the standard solution of As^{3+} . Transfer 0, 0.1, 0.2, 0.5, 1.0, and 2.0 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 1, 2, 5, 10, and $20\mu\text{g As}^{3+}$ /liter.
- The HGAAS analysis was performed immediately.

II.2. HG-AAS method for determination of total arsenic

- 25ml of water sample was filtered through with size 0.45 μ m membrane filter in order to remove suspending materials.
- A solution containing 4N of hydrochloric acid was prepared.
- A solution containing 2 percent (w/v) of NaBH₄ in 10 percent (w/v) of KI was prepared.
- Prepare working standards from the standard solution of total arsenic. Transfer 0, 0.1, 0.2, 0.5, 1.0, and 2.0 mL of standard to 100-mL volumetric flasks and bring to volume with deionized water. These concentrations will be 0, 1, 2, 5, 10, and 20 μ g As (T)/liter.
- The HGAAS analysis was performed a minimum of 30 minutes after sample preparation.

Preconcentration of Sb³⁺ and Sb⁵⁺

500ml filtered samples, adjusting to approximately pH=3 then 0.05g of TiO₂ was added. After the solution was stirred for 15 minutes, the titanium dioxide was filtered out, washed twice with 5ml of 0.001N of HCl, Sb³⁺ and Sb⁵⁺ were eluted by 10ml of 5N of HCl.

II.3. HG-AAS method for determining of Sb³⁺

- A solution containing 2percent (w/v) of citric acid was prepared.
- A solution containing 2 percent (w/v) of NaBH₄ was prepared.
- Prepare working standards from the standard solution of Sb³⁺. Transfer 0, 0.1, 0.2, 0.5, 1.0, and 2.0 mL of standard to 100-mL volumetric flasks and bring to volume with deionized water.. These concentrations will be 0, 1, 2, 5, 10, and 20 μ g Sb³⁺/liter.
- The HGAAS analysis was performed immediately.

II.4. HG-AAS method for determining total antimony

- A solution containing 6 N of hydrochloric acid was prepared.
- A solution containing 2 percent (w/v) of NaBH₄ in 10 percent (w/v) of KI was prepared.
- Prepare working standards from the standard solution of total antimony . Transfer 0, 0.1, 0.2, 0.5, 1.0, and 2.0 mL of standard to 100-mL volumetric flasks and bring to volume with deionized water.. These concentrations will be 0, 1, 2, 5, 10, and 20 μ g Sb(T)/liter.
- The HGAAS analysis was performed a minimum of 30 minutes after sample preparation.

III. RESULTS AND DISCUSSION

Analytical quality control.

From analytical results of trace elements in multi – elements standard were determined by HG-AAS. The present results show that the implemented methods were reliable and have good accuracy and precision. Our results were usually within the quality control plan acceptance range 15 % of the certified value.

Table 1a: Comparison of the present results with certified values in multi-element standard.

As³⁺(ppb)		As⁵⁺(ppb)	
<i>Certified values</i>	<i>This work</i>	<i>Certified values</i>	<i>This work</i>
4	3.8 ± 0.4	4	4.2 ± 0.5
6	6.2 ± 0.6	6	6.3 ± 0.9
10	10.5 ± 0.9	10	9.6 ± 0.8

Table 1b: Comparison of the present results with certified values in multi-element standard.

Sb³⁺		Sb⁵⁺	
<i>Certified values</i>	<i>This work</i>	<i>Certified values</i>	<i>This work</i>
6	5.8 ± 0.6	6	6.3 ± 4.2
8	7.8 ± 0.7	8	7.5 ± 0.9
10	11.4 ± 0.14	10	9.7 ± 0.8

Table 2: Concentration of As³⁺, As⁵⁺, Sb³⁺ and Sb⁵⁺ in groundwater at Di Linh.

Site	As (µg/L)			Sb(µg/L)		
	<i>As³⁺</i>	<i>As⁵⁺</i>	<i>As³⁺/As⁵⁺</i>	<i>Sb³⁺</i>	<i>Sb⁵⁺</i>	<i>Sb³⁺/Sb⁵⁺</i>
DL-1	1.31±0.15	0.73±0.08	1.79	0.77±0.08	0.22±0.03	3.50
DL-2	1.15±0.12	1.94±0.14	0.59	0.61±0.07	0.36±0.03	1.69
DL-3	0.92±0.11	1.33±0.11	0.69	0.72±0.07	0.51±0.05	1.41
DL-4	1.52±0.18	1.16±0.12	1.31	0.45±0.05	0.62±0.07	0.73
DL-5	1.27±0.13	0.67±0.07	1.90	0.81±0.07	0.17±0.02	4.76

Table 3: Concentration of As³⁺, As⁵⁺, Sb³⁺ and Sb⁵⁺ in groundwater at BaoLam.

Site	As (µg/L)			Sb(µg/L)		
	<i>As³⁺</i>	<i>As⁵⁺</i>	<i>As³⁺/As⁵⁺</i>	<i>Sb³⁺</i>	<i>Sb⁵⁺</i>	<i>Sb³⁺/Sb⁵⁺</i>
BLA-1	0.84±0.09	1.11±0.13	0.76	0.33±0.04	0.11±0.01	3.00
BLA-2	1.17±0.09	1.00±0.12	1.17	0.41±0.05	0.14±0.02	2.93
BLA-3	2.75±0.22	3.67±0.28	0.75	0.52±0.05	0.17±0.02	3.06
BLA-4	1.60±0.11	0.93±0.10	1.72	0.37±0.04	0.21±0.03	1.76
BLA-5	1.35±0.14	1.80±0.15	0.75	0.28±0.03	0.13±0.02	2.15

Table 4: Concentration of As^{3+} , As^{5+} , Sb^{3+} and Sb^{5+} in groundwater at Baoloc.

Site	As ($\mu\text{g/L}$)			Sb($\mu\text{g/L}$)		
	As^{3+}	As^{5+}	As^{3+}/As^{5+}	Sb^{3+}	Sb^{5+}	Sb^{3+}/Sb^{5+}
BL-1	2.65±0.21	2.53±0.26	1.05	0.62±0.07	0.22±0.02	2.82
BL-2	1.31±0.14	1.47±0.12	0.88	0.91±0.09	0.10±0.02	9.10
BL-3	2.82±0.29	1.93±0.24	1.45	0.83±0.09	0.17±0.02	4.88
BL-4	1.23±0.15	1.61±0.18	0.75	0.94±0.11	0.27±0.03	3.48
BL-5	1.11±0.10	1.73±0.11	0.64	0.66±0.08	0.13±0.02	5.08

Table 5: Concentration of As^{3+} , As^{5+} , Sb^{3+} and Sb^{5+} in groundwater at Date.

Site	As ($\mu\text{g/L}$)			Sb($\mu\text{g/L}$)		
	As^{3+}	As^{5+}	As^{3+}/As^{5+}	Sb^{3+}	Sb^{5+}	Sb^{3+}/Sb^{5+}
DT-1	41.1±5.2	23.4±2.1	1.76	1.12±0.11	0.54±0.06	2.07
DT-2	17.7±2.4	18.5±2.0	0.96	0.78±0.09	0.52±0.06	1.50
DT-3	21.5±2.3	8.30±1.0	2.59	1.07±0.09	0.38±0.05	2.82
DT-4	3.12±0.41	4.40±0.51	0.71	0.55±0.06	0.27±0.03	2.04
DT-5	0.81±0.09	0.45±0.05	1.80	0.76±0.08	0.14±0.02	5.43

IV. CONCLUSION

Establish procedures for determination of As^{3+} , As^{5+} , Sb^{3+} và Sb^{5+} in groundwater by hydride generator - Atomic Absorption Spectrometry.

Determination of As^{3+} , As^{5+} , Sb^{3+} và Sb^{5+} in groundwater at Dilinh, Baolam, Baoloc and Date districts.

The concentration of As^{3+} , As^{5+} , Sb^{3+} và Sb^{5+} are presented in tables 2,3, 4 and 5. They are shown that concentration of As^{3+} , As^{5+} , Sb^{3+} và Sb^{5+} in groundwater which collected from Dilinh, Baolam and Baoloc district are lower respective permissible limits according to Vietnam standard. However, concentration of As^{3+} and As^{5+} in groundwater at Date are higher than recommended values by WHO and respective permissible limits according to Vietnam standard.

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