

## Flow analysis for determination of inorganic arsenic and antimony in seawater with on-line liquid nitrogen trap and hydride generation

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**Abstract**—An automatic flow analysis system with on-line liquid nitrogen trap, hydride generation and flame-less atomic absorption spectrophotometry was presented for the determination of inorganic arsenic and antimony in seawater. The experimental conditions such as acidity of reduction reaction, the amount of sodium borohydride, the flow rate of carry gas (high purity of nitrogen) were tested and selected optimally. The limit detection of the method presented was 0.15 µg/L for arsenic and 0.24 µg/L for antimony. During the determination of seawater samples with levels microgram arsenic and antimony per litre the variation coefficient would be  $\pm 4\%$  for arsenic and  $\pm 10\%$  for antimony. The volume needed for one measurement was 9 mL for arsenic and 12 mL for antimony. The frequency of sample determination reached 20 times per hour for arsenic and 15 times per hour for antimony.

### INTRODUCTION

Arsenic and antimony occur generally in a level of microgram or submicrogram per litre in seawater. In the early 1970's the determination of As and Sb in seawater with hydride generation, cold trap and AAS was presented (Andreae, 1983a; Braman *et al.*, 1972) and its use has been extended to marine sample measurement by many laboratories in the world (Andreae *et al.*, 1981; Andreae, 1983b). The advantages of this method lie in the high sensitivity so that the background value of As and Sb in seawater can be measured directly, the separation of the volatile hydrides of interest elements from the matrix of salt interfering general AAS measurement, and the speciation of inorganic and methyl compounds of those elements with a chromatographic column. The development of flow analysis especially FIA makes it possible for many manual methods used previously to be automated and miniaturized. Meanwhile, the general analysis rate can be accelerated to a great extent, the contamination minimized due to the isolated system and the precision enhanced due to the exact timing in the manifold (Ruzicka and Hansen, 1981). All these merits involved in the flow analysis would fit quite well to the trace element analysis of seawater. It is the idea that the combination of hydride generation-cold trap-AAS with the flow analysis can improve the manual method in the determination of inorganic arsenic and antimony in seawater. Therefore, the experimental conditions were investigated

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and optimized.

## EXPERIMENTATION

### Reagents

Hydrochloric acid; G. R. grade.

Sodium borohydride; (SIGMA Chem. Co., USA). According to the experimental requirement a solution was made up with a certain concentration (W/V). The solution was stabilized with a content of 0.02 mol/L NaOH and put to use after filtration.

Standard solution of arsenic; 0.132 g of  $As_2O_3$  (G. R.) was weighed and dissolved in 6 mL of 6 mol/L KOH solution which was then diluted with 2 mol/L HCL to the mark of 100 mL volumetric flask to make up the storage standard of 1 000 mg/L As.

The operating standard of 100  $\mu\text{g/L}$  As was made up by successive dilution with 2 mol/L HCl solution.

Standard solution of antimony; 1.371 0 g of potassium antimonyl tartrate ( $KSbOC_4H_4O_6 \cdot \frac{1}{2}H_2O$ ) was weighed and dissolved with distilled water to make up 500 mL volume in a volumetric flask. The storage standard contained 100 mg/L Sb.

The operating standard of 1 000  $\mu\text{g/L}$  Sb was made up by a successive dilution with distilled water.

### Manifold

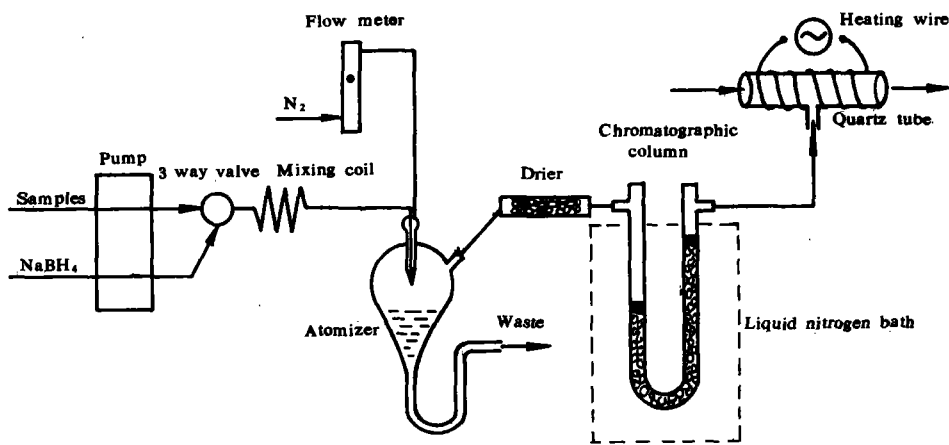


Fig. 1. Schematic layout of the manifold for flow analysis of As and Sb in seawater.

Figure 1 shows the manifold schematically. The sample with a certain acidity and the sodium borohydride are pumped at the rate of 3 mL/min and 1 mL/min respectively by a peristaltic pump. After mixing through three way valve and the mixing coil (polyethylene tube 0.9 mm in inside diameter and

1.5 m in length) the mixture is led to a separator consisting of a glass atomizer with concentric spraying gun. The small beads of water carried by nitrogen are removed by a drier packed with calcium chloride and the hydrides of interest elements are trapped in a chromatographic column cooled with liquid nitrogen bath. The U tube of the chromatographic column is filled with silanized glass beads (60~80 mesh). After being cooled 2~3 min in the trap the U tube is put into a water bath at a certain temperature. As the temperature rising the condensed hydrides will be volatilized and transported by carrying gas into a quartz furnace, a tube with 6 mm in inner diameter and 6.5 cm in length which is wound by electric wire and heated to about 900°C with electric power supplied by a transformer. The absorbance of the related elements is measured with an atomic absorption spectrophotometer (model WXF-4D made by Beijing Second Optical Instrumentation Co.). The resonance lines used in measurement are 193.7 nm for As and 217.6 nm for Sb.

#### RESULTS AND DISCUSSION

##### *Optimization of experimental conditions*

Reaction acidity of hydride generation: As Andreae stated (1983 a), As (III) could react with borohydride in pH 6~7 and Sb (III) in pH 6, but for As (V) and Sb (V), pH value of the reaction had to be reduced to about 1 or less. In flow system like that designed here, however, a strong acidic medium would be essential to accelerate the rate of the hydride generation and enhance the sensitivity because the time is very short (about 20 s) for the flow to take in the coil where the sample mixes with the borohydride before reaching the separator. Figure 2 exhibits the reaction of hydride generation in different acidities. For arsenic, when the acidity is down to less 0.4 mol/L HCl, the absorbance will drop quickly implying the rapid decrease in the rate of hydride generation. However, at higher acidity such as the above 1.0 mol/L HCl the efficiency of the reduction reaction also tends to decline as shown in Fig. 2. That decline would be caused by the fast decomposition of borohydride in a strong acidity medium. The optimum range of acidity for hydride generation of arsenic, therefore, is from 0.5 to 1.0 mol/L HCl. For antimony the efficiency of the reduction reaction also has a trend of slow increase with the solution acidity. Sequentially, 0.5 mol/L HCl is selected as the medium of hydride generation for As and Sb, and obviously As and Sb determined in such acidity would be the total inorganic species.

Concentration of sodium borohydride: The amount of sodium borohydride used in hydride generation is different significantly one from the other in literature. The differences would be mainly relevant to the respective acidity, size of samples, flow rate of carry gas, purity and pH of the sodium borohydride in the employed methods. Figure 3 is the results associated with the experiment of reagent amount. While the concentration of sodium borohydride is less than 2% the sensitivity would drop considerably and the incompleteness of the reduction reaction would appear. Meanwhile, when the concentration of reagent is larger than 3%, a great deal of gas bubble could be produced in the flow mixture and so the separation of volatile hydride from solution would be disturbed significantly resulting in a poor reproducibility. Therefore, we choose 3% of sodium borohydride in the manifold and it is shown

experimentally that this concentration of sodium borohydride can be suitable for measuring a wider concentration range of the interest elements.

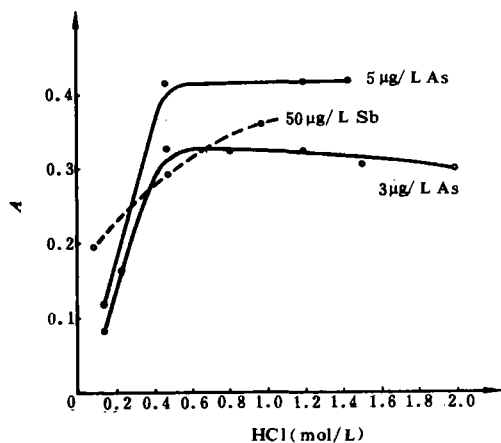


Fig. 2. The effect of acidity on the reaction of hydride generation.

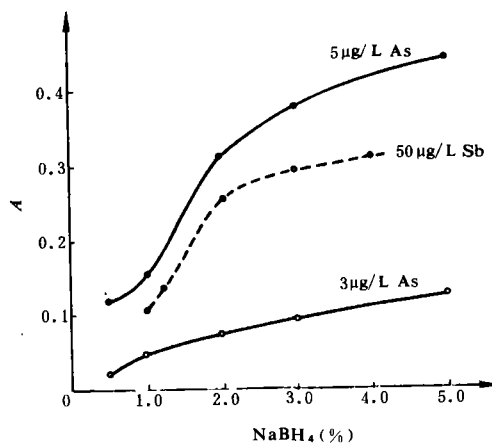


Fig. 3. The effect of sodium borohydride concentration of the reaction of hydride generation.

**Flow rate of carrier gas;** The effect of nitrogen flow rate on the determination of As and Sb is also very substantial (see Fig. 4). With plotting the flow rate of carrier gas vs. the absorbance a peak would appear in the curve showing the maximum of the absorbance of arsenic at about 100 mL/min of flow rate of carrier gas. And the higher the concentration of determined element is, the sharper the peak appears in the curve, suggesting that it is essential to control the rate strictly due to its effect on the efficiency of gas-liquid separation, cold trapping and atomization at furnace. If too low the flow rate would reduce the efficiency of gas-liquid separation to a great extent, but if too high the flow rate would reduce the efficiency of cold trapping and atomization at furnace rapidly. The optimum range of flow rate of nitrogen for arsenic is different from that for antimony on account of the different boiling point of the two hydrides. For arsenic it is at 100~150 mL/min of nitrogen and for antimony it is about 300 mL/min.

**Release temperature of the trapped hydride;** The experiment of release temperature is conducted in a water bath with adjustable temperature. The results are plotted in Fig. 5. For arsenic, when the temperature is lower than 20°C, a lower result could occur, but the release of the hydride is not affected very much at a temperature range of 20~70°C. Therefore, 20~30°C water bath is selected in the procedure of arsenic release, especially in winter. The effect of release temperature for stibine is more sensitive which would require strict temperature control of water bath. In the experiment 30°C water bath is adopted for stibine release. The higher temperature for release is avoided due to the difficulty in temperature control although the sensitivity could be enhanced.

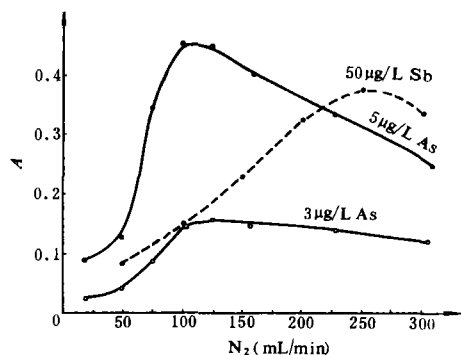


Fig. 4. The effect of flow rate of nitrogen on the absorbance of arsenic and antimony.

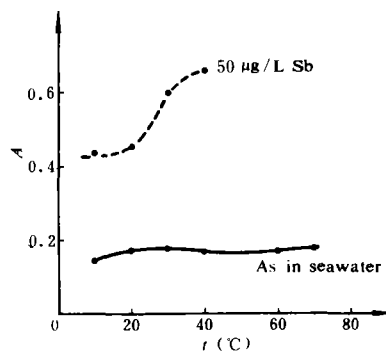


Fig. 5. The effect of the temperature in water bath on the absorbance of arsenic and antimony.

### Calibration

The calibration curves of distilled water and seawater as media are tested respectively with standard addition of As and Sb. For arsenic the experimental conditions are selected as follows;

acidity	0.5 mol/L HCl;	flow rate of N <sub>2</sub>	125 ml/min;
sodium borohydride	3%;	time of trapping	2 min.

Linear correlation between concentration and absorbance in a range of 0~3µg/L As is obtained in both media of distilled water and seawater. There are similar slopes (0.097 3 A (µg/L) in distilled water and 0.096 5 A (µg/L) in seawater) with good correlation coefficients ( $r = 0.990 9$  and  $0.999 3$  respectively and  $n = 6$ ). The results show no significant salt error so that the distilled water medium can be used to calibrate arsenic in seawater. For antimony the experimental conditions are as follows;

acidity	0.5 mol/L HCl;	flow rate of N <sub>2</sub>	314 ml/min;
sodium borohydride	3%;	time of trapping	3 min.

A similar conclusion in a range of 0~10 µg/L Sb can be obtained by linear regression, i. e., similar slopes in both media of distilled water (0.017 3 A / (µg/L) and seawater (0.017 8 A / (µg/L)) showing no significant salt error. The correlation coefficients ( $r$ ) are 0.981 8 (distilled water) and 0.9880 (seawater), respectively.

### Limit of detection and precision

Nine duplicates of seawater samples assumed as the blank solution are made for the estimation of limit of detection (L. D.) according to three times of the standard deviation (S. D.) of the concentration results. All data are shown in Table 1. Limit detection 0.15 µg/L for arsenic and 0.24 µg/L for antimony are generally suitable for the routine determination of arsenic and antimony in seawater samples.

**Table 1.** Limit of detection for As and Sb in seawater obtained with on-line cold trapping, hydride generation and AAS

No of samples	As( $\mu\text{g/L}$ )				Sb( $\mu\text{g/L}$ )			
	measured	average	S. D.	L. D.	measured	average	S. D.	L. D.
1	1.30				0.947			
2	1.18				0.797			
3	1.20				0.797			
4	1.22				0.797			
5	1.20	1.19	0.048	0.145	0.697	0.797	0.079	0.24
6	1.15				0.747			
7	1.18				0.847			
8	1.18				0.847			
9	1.13				0.697			

The blank test suggests that the blank of sodium borohydride seems to be negligible for both As and Sb, and the main source of blank comes from the applied acid. The blank of antimony in available hydrochloric acid (G. R. grade) is about 0.2  $\mu\text{g/L}$  Sb which is in the same level of antimony in seawater. However, the blank of arsenic varies substantially with difference of the applied acid. Table 2 lists the blank of arsenic in different HCl. The distilled water and Milli-Q water have not significant blank of arsenic after the treatment with  $\text{Fe}(\text{OH})_3$  coprecipitation. The blank in HCl made in Laiyang (1.2  $\mu\text{g/L}$  As) having triple amount of the blank in other HCl is too high to determine arsenic in seawater with a level of submicrogram per litre of As. Therefore, selecting suitable reagents for the blank test is necessary for arsenic determination in seawater.

**Table 2.** Blanks of arsenic in applied hydrochloric acid

Medium	Treatment *	Blank( $\mu\text{g/L}$ As)		
		EMK **	GR1 **	GR2 **
Distilled water	no	0.36	0.43	1.15
Distilled water	yes			1.22
Milli-Q	no			1.18
Seawater	yes			1.19

\* Treatment with  $\text{Fe}(\text{OH})_3$  coprecipitation.

\*\* EMK: Made in Merck, Suprapur; GR1: made in Shanghai G. R. grade; GR2: made in Laiyang G. R. grade.

The standard deviations shown in Table 1 suggest that the variation coefficient of arsenic determination in seawater is about 4% and that of antimony 9.9% which can be regarded as satisfactory for trace element analysis.

#### *Determination of seawater samples*

Several samples of coastal water around Qingdao are tested with calibration curve. The result is

listed in Table 3. The concentration of inorganic arsenic ranges in 0.72~1.02  $\mu\text{g/L}$  As and that of inorganic antimony in 0.79~0.90  $\mu\text{g/L}$  Sb which is characterized as typically coastal seawater. The samples required in the method is 9 mL for each measurement of arsenic with 2 min of trapping and 1 min of washing so that the frequency of the flow analysis can be 20 times per hour. For antimony the sample requirement is 12 mL and frequency 15 times per hour. Compared with manual method the flow analysis is of a character of rapidity, simplification and small consumption of samples and reagents.

Table 3. Determination of inorganic arsenic and antimony in seawater

Sampling regions	Arsenic( $\mu\text{g/L}$ )	Antimony( $\mu\text{g/L}$ )
Qingdao Luxun Park (unfiltered)	1.08 $\pm$ 0.02	
Qingdao Luxun Park (filtered)	0.72 $\pm$ 0.05	0.896
East China Sea (filtered)	0.85 $\pm$ 0.02	
Qingdao loading stage (filtered)	0.96 $\pm$ 0.04	0.797

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