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Determination of antimony in environment samples by gas phase chemiluminescence detection following flow injection hydride generation and cryotrapping

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ABSTRACT

A novel method for the determination of antimony in environmental samples was developed with gas phase chemiluminescence detection following flow injection hydride generation and cryotrapping. The stibine, generated from samples by borohydride reduction of antimony using flow injection technique, was separated by using a new gas–liquid separator, dried with an ice-salt cryogenic bath and concentrated in a glass U-tube immersed in liquid nitrogen. Re-vaporization of stibine based on its boiling point was achieved by allowing the tube to warm at room temperature. A gas phase chemiluminescence signal was produced during the ozonation of the hydride in a reflective chamber. Under optimal conditions, the proposed method was characterized by a wide linear calibration range from 1.0 $\mu g\,L^{-1}$ to 10.0 $mg\,L^{-1}$ with a detection limit of 0.18 $\mu g\,L^{-1}$ ($n = 11$). The relative standard deviation for 10.0 $\mu g\,L^{-1}$ antimony was 3.56% ($n = 11$) and the sampling rate was 15 samples h^{-1}. Blank signal was reduced by the purification of reagents and the interference from transition metal ions was eliminated by the addition of L-cysteine into samples. The method was applied to the determination of antimony in environmental samples with satisfactory results.

1. Introduction

Antimony is a potentially toxic element and known to cause adverse health effects on humans and animals due to environmental and occupational exposure [1]. The United States Environmental Protection Agency drinking water standards for maximum contaminant level goal and maximum contaminant level are both 6 $\mu g\,L^{-1}$ [2], and the European Union admissible level for this element in drinking water is 5 $\mu g\,L^{-1}$ [3]. So it is significant to monitor Sb in environment because of its implications in health.

Of all the methods for the determination of Sb, the technique of hydride generation coupling with atomic detection is most widely reported. Hydride generation enables the highly efficient formation of stibine and effective separation of the analyte from the matrix, which ensures these methods' high sensitivity and prominent freedom from interference [4,5]. Coupled with hydride generation, atomic detection techniques, such as atomic absorption spectrometry (AAS) [6,7], atomic fluorescence spectrometry [8,9], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [10,11], and inductively coupled plasma-mass spectrometry [12,13] have been reported and used for the determination of Sb in a variety of samples. However, these techniques require expensive and bulky spectrometric equipments and expensive consumables.

Chemiluminescence is an attractive detection technique for analytical applications because of its very low detection limit, rapidity and wide linear working range that can be achieved while using relatively simple instrumentation [14]. Studies have been conducted on the gas phase chemiluminescence (GPCL) with ozone oxidation for the determination of As [15–26], Sb [15,18,20], Sn [15] and Se [15]. The hydride forming elements were first reduced to their hydrides by borohydride with mild reaction conditions at room temperature. Luminescence occurred when the formed hydrides reacted with ozone in gas phase. The GPCL with ozone oxidation exhibited fairly good sensitivity with low-cost construction of instrumental system. Among the hydride forming elements, arsine produces the most intensive luminescence when reacted with ozone. The sensitivity for As was dozens of times higher than those of other hydride forming elements [15,21]. Therefore, the studies of GPLC were reported mainly on the analysis of arsenic [15–17,19–26]. Yet, mutual interferences could not be avoided if these elements were not separated because their hydrides could be oxidized by ozone to yield luminescence and their luminescence spectra overlapped. Recently GPCL was used successfully as the

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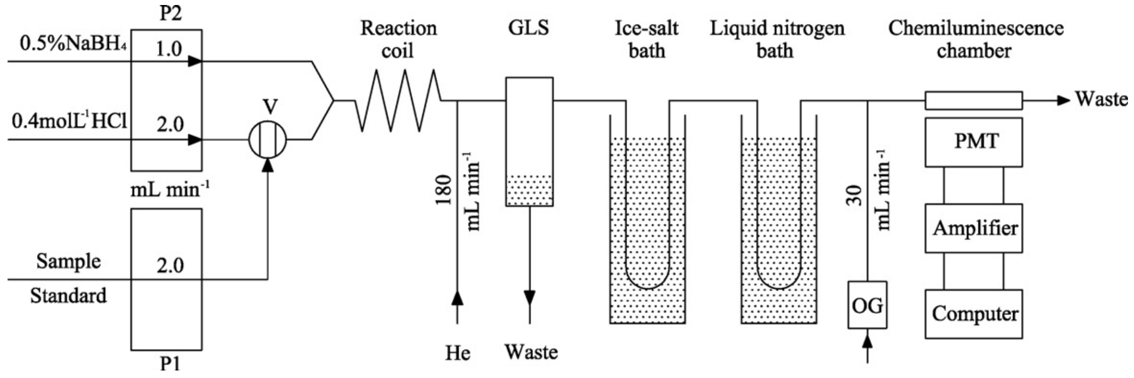

Fig. 1. The manifold for the determination of Sb with gas phase chemiluminescence detection. P_1, P_2, peristaltic pumps; V, injector valve; GLS, gas–liquid separator; OG, ozone generator.

detector of liquid chromatography for arsenic speciation [22,24,25]. With the chromatographic separation, interferences from other hydride forming elements could be eliminated effectively while speciation of arsenic was achieved.

In this study, a system for the determination of Sb in environmental samples was proposed with GPCL detection. To our best knowledge, the application of such a system on the determination of Sb in environmental samples has not yet been reported. Following hydride generation, cryotrapping was used with the aim of enhancing the sensitivity so that the system could meet the requirement of sensitivity for the analysis of environmental samples. Meanwhile, re-vaporization of cryotrapped hydrides could alleviate the interference from other hydride forming elements so as to improve the system's selectivity. Flow injection technique was used to generate stibine by controlling the timing of merging and reaction of the reductant and sample reproducibly and precisely [27].

2. Experimental

2.1. Apparatus

The scheme of the system is shown in Fig. 1. A FIAS-400 (Perkin-Elmer) flow injection system with one six-port injection valve and two peristaltic pumps was used to deliver all aqueous streams. Poly(tetrafluoroethylene) (PTFE) tubes were used as connection and reaction lines in the flow system with 1.00 mm i.d. except 0.5 mm i.d. for the inlet lines.

An 800 mm long, 2.5 mm i.d. Pyrex glass U-tube, about 3/4 of which was immersed in a Dewar flask filled with liquid nitrogen, was used to collect the generated SbH_3 cryogenically. To eliminate moisture in the hydride after gas–liquid separation, another same apparatus was used except that was immersed in an ice-salt bath (approximately −15 °C). The ozone generator (Ican, China) was offered by Hangzhou Rongxin Electronic Equipment Co., Ltd.

A home-made flat rectangular flow-through colorless glass cell (25 mm length, 9 mm width, and 5 mm height) was used as the GPCL reaction chamber, which was mounted closely to the window of an R105UH photomultiplier tube (PMT) (Hamamatsu, Japan). The reaction chamber was wrapped by aluminum foil to reflect the chemiluminescence. The GPCL signals measured by the PMT were amplified with an RFL-1 chemiluminescence analyzer (Xi'an Remex Analysis Instrument Co., Ltd., China) and recorded through an NI USB-6008 (National Instruments) by the same computer which controlled flow injection system. A Varian AA240FS atomic absorption spectrometer with hydride generation accessory was used for the verification tests.

2.2. Chemicals

All chemicals used were of ultra-pure grade and offered by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) except the noted. All solutions were prepared with deionized water (18 MΩ cm), which was produced by a Milli-Q system (Millipore, USA).

The stock solution of Sb(V) was purchased from National Analysis Center for Iron and Steel (Beijing, China). Working standard solutions needed were prepared by serial dilution of the stock solution immediately before use. HCl and $NaBH_4$ were purified according to the procedure described later. 0.5% (w/v) $NaBH_4$ (98%, Alfa Aesar) was prepared in 0.1% (w/v) NaOH fresh daily. A 0.5% (w/v) L-cysteine stock solution was obtained by initial dissolution of 0.5 g L-cysteine and diluting to 100 mL with deionized water.

2.3. Procedure

A peristaltic pump was employed to propel the carrier and reductant streams. Samples or stock solutions were introduced into the system for 180 s and merged with sodium borohydride solution. As the result of the reduction of Sb(V) with $NaBH_4$, hydrides were generated and separated from liquid by the gas–liquid separator. The separated hydrides were carried by helium to two U-tubes sequentially, which were immersed in the ice-salt bath and the liquid nitrogen bath, respectively. Water moisture was removed in the ice-salt bath and hydrides were collected and concentrated in the liquid nitrogen bath. The preconcentration was conducted while the sample was continuously introduced for 180 s. The collected hydrides were re-vaporized by taking the U-tube out of the liquid nitrogen bath and allowed it to warm at room temperature for 60 s. The vaporized hydrides were delivered to the GPCL reaction chamber by helium. Meanwhile, ozone was produced by the ozone generator while pure oxygen was fed continuously at 30 mL min^{-1}. The oxidation of hydrides by ozone took place in the reaction chamber mounted very closely on the optical window of the PMT and the luminescence was produced. The signal received by the PMT was amplified by the chemiluminescence analyzer and then recorded by the computer.

2.4. Reagent purification and sample preparation

The method for the purification of HCl and $NaBH_4$ was described previously [28]. The concentration of $NaBH_4$ was about 0.5% after purification.

Six environmental samples were collected in the local industrial area. Three water samples were filtered through Whatman filter paper no. 42; other soil samples were prepared as described in detail elsewhere [29]. All samples were acidified with the purified HCl to a final concentration of 0.4 mol L^{-1}.

3. Results and discussion

3.1. Cryotrapping concentration and separation of stibine from other hydrides

Hydride forming elements, such as As, Sn and Se, could also produce GPCL signals during the oxidation of their hydrides by ozone and their luminescence spectra overlapped in the range of 195–700 nm [18]. Previous studies indicated that the GPCL spectrum of Sb was characterized in the visible range between 360 and 680 nm with a maximum at 470 nm [18], which made GPCL signal of Sb easily be interfered by other hydride forming elements if they were not separated prior to the gas phase reaction. And particularly, arsenic could interfere most seriously because the GPCL intensity of As was 67 times higher than that of Sb and was the strongest among the hydride forming elements [15,21]. Other hydride forming elements could also interfere the measurement but less interference was expected since their GPCL intensity was less than that of Sb. On the other hand, experimental results indicated that it was difficult to determine Sb in environmental samples by the GPCL system reported previously due to its relatively poor sensitivity.

In order for the GPCL system to be used for the determination of Sb in environmental samples, the interference from other hydride forming elements must be minimized and the sensitivity of the system should be improved. In the present work, cryotrapping technique was used to concentrate stibine after gas–liquid separation following hydride generation. The hydrides were collected and concentrated in the cryotrapping tube immersed in the liquid nitrogen bath. A cryotrapping time of 180 s was used in this study and the sensitivity was hence improved about 100 times compared with the direct GPCL system without cryotrapping.

After the cryotrapping, the re-vaporization of hydrides was conducted simply by taking the cryotrapping tube out of the liquid nitrogen bath and allowed it to room temperature. Because the boiling points of AsH_3, SnH_4 and SbH_3, are −55, −52, and −17 °C, respectively, AsH_3, SnH_4 and SbH_3 were vaporized in sequence and thus SbH_3 was separated from other hydrides. As shown in Fig. 2, SbH_3 was separated effectively from AsH_3 and SnH_4 while the latter two hydrides were vaporized and yielded chemiluminescence almost simultaneously. The separation of other hydrides besides AsH_3 and SnH_4 was also investigated (figure not shown). The results shown later in the interference study indicated that they were also separated from stibine effectively.

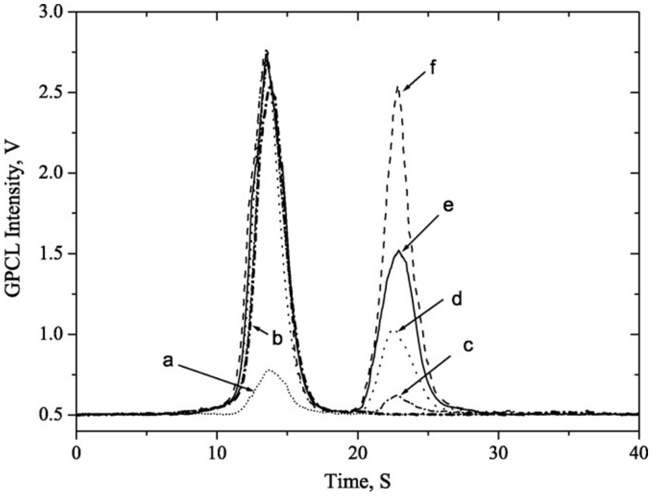

Fig. 2. The separative signals for Sb, Sn and As at the indicated concentrations with the proposed method.

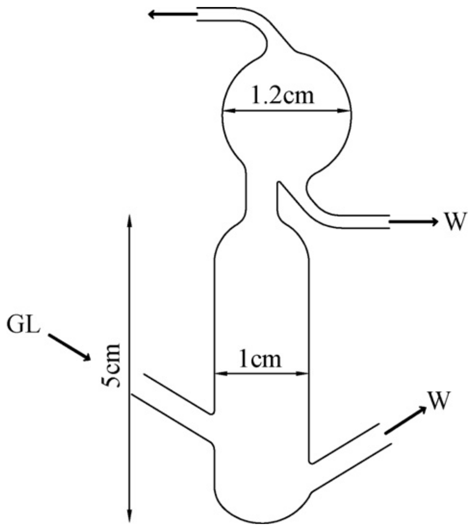

Fig. 3. Schematic diagram of the gas–liquid separator. GL, entrance for gas and liquid mixture; G, gas; W, waste.

The length of cryotrapping tube on the trapping and separation efficiency was studied. No significant difference was found within the range from 60 to 150 cm. The tube length longer than 150 cm caused substantial dispersion of analyte while shorter than 60 cm produced a poor trapping efficiency. Therefore a trapping tube length of 60 cm was chosen in this study.

3.2. Elimination of water moisture

After the gas–liquid separation followed by hydride generation, water moisture was produced. It must be removed prior to the cryotrapping of hydrides in liquid nitrogen bath to avoid both the suppression of hydride re-vaporization and the transfer of water into the GPCL reaction chamber. In order to separate gas and liquid as completely as possible, a new gas–liquid separator (GLS) was designed as shown in Fig. 3. The GLS had an additional glass bulb which could prevent efficiently the water moisture mixed in gas from entering the water trapping tube immersed in the ice-salt bath and thus very little moisture could get to the water trapping tube.

In order to further eliminate water moisture, an ice-salt bath (approximately −15 °C) was used. In the earlier development of the method, an attempt was made to use anhydrous calcium chloride as the drying agent. However, it yielded acceptable results but partial retention of the hydride was observed. The ice-salt bath used in the present system showed adequate removal of water moisture while allowing the hydrides to pass through to the liquid nitrogen cryotrapping tube.

3.3. Optimization of the operating conditions

Other operating conditions of the proposed system were optimized with the object of achieving maximum sensitivity and better reproducibility. During the optimization, 10 $\mu g\,L^{-1}$ of Sb(V) standard solution was used. The optimal operating conditions of system used for further work are listed in Table 1.

The effect of negative high voltage of PMT on GPCL intensity was examined between −600 and −1000 V. The best ratio of signal to noise was obtained when it was set at −800 V. Therefore,

Table 1
Optimal operating conditions of the proposed system.

Water trapping tube length	600 mm
Hydride trapping tube length	600 mm
Hydride trapping time	180 s
PMT potential	−800 V
Length of reaction coil	1000 mm
Helium flow-rate	180 mL min^{-1}
Oxygen flow-rate	30 mL min^{-1}
HCl concentration	0.4 mol L^{-1}
HCl flow-rate	2.0 mL min^{-1}
Sample flow-rate	2.0 mL min^{-1}
$NaBH_4$ concentration	0.5%
$NaBH_4$ flow-rate	1.0 mL min^{-1}

−800 V was selected as the optimal PMT potential in the following experiments.

Fig. 4 shows the effect of the reaction coil length for the hydride generation in the range of 50–200 cm. Better sensitivity and reproducibility were obtained when the length of 100 cm was chosen. It was observed that coils longer than 100 cm could increase the carry-over because of the dispersion of the analyte. Thus, a reaction coil length of 100 cm was used in the later study.

Helium was used in this study to carry the hydrides formed in hydride generation to the GPCL reaction chamber. Because a liquid nitrogen bath was employed in the cryotrapping step, it could be accumulated in the cryotrapping tube which could cause the blocking of the tube after a certain period of operation if nitrogen was used as the carrier gas. The flow-rate of helium was crucial since it affected not only the residence time of the analyte in the chamber but also the separation effectiveness. Fig. 5 shows how the flow-rate of helium affected on the sensitivity in the studied range of 40–240 mL min^{-1}. Increasing the flow-rate of helium favored the sensitivity because more hydrides was introduced into the GPCL reaction chamber in a certain period and the signal became sharper. Yet, the optimization experiments showed that the signals were reproducible with the range of 120–180 mL min^{-1} and the reproducibility was deteriorated if the flow-rate of helium was higher than 180 mL min^{-1}. Therefore, 180 mL min^{-1} was chosen as the optimal flow-rate of the carrier gas.

Chemiluminescence was produced when gaseous hydrides reacted with ozone and thus the concentration of ozone had a critical impact on the performance of the system. Because ozone was produced on-line by feeding pure oxygen into an ozone generator, the flow-rate of oxygen was optimized instead of the ozone concentration. As shown in Fig. 6, increasing the oxygen flow-rate resulted in a sharper signal peak but reducing the ozone concentration and a flow-rate of 30 mL min^{-1} oxygen provided optimal results. Redoximetric titration showed that the actual optimal ozone mass flow-rate was 1.97 mg min^{-1}.

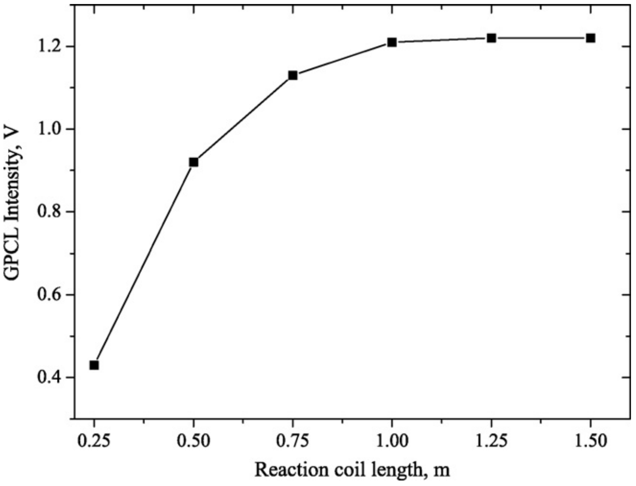

Fig. 4. The effect of the reaction coil length for hydride generation on chemiluminescence intensity. 10 μg L^{-1} Sb standard solution was used and other conditions as specified in Table 1.

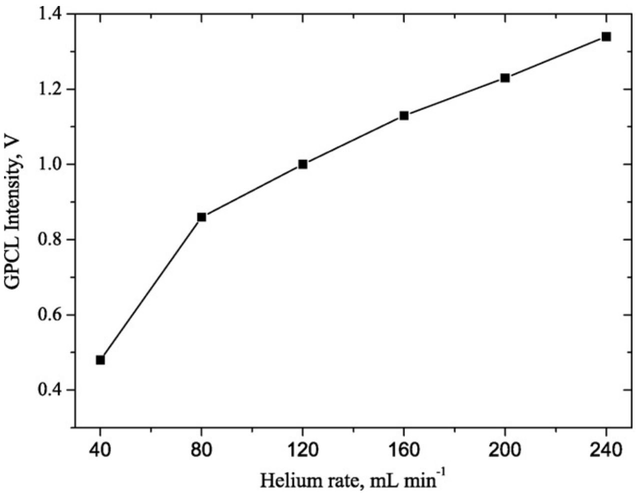

Fig. 5. The effect of helium flow-rate on chemiluminescence intensity. 10 μg L^{-1} Sb standard solution was used and other conditions as specified in Table 1.

The effects of the concentration of HCl and $NaBH_4$ on the sensitivity were investigated. As observed in Fig. 7, the GPCL signal was found to be highly sensitive to the $NaBH_4$ concentration, reaching its maximal value at 0.5% $NaBH_4$. Meanwhile, the effect of HCl concentration was not significant because Sb(V) could form volatile hydride easily at pH less than 1 [4]. 0.4 mol L^{-1} HCl was thus chosen the optimal concentration.

3.4. Interference studies

The effects of potential interferons which likely existed in the environment samples were studied in order to assess the possible application of the present system on environmental analysis. The results shown in Table 2 indicated that transitional metal ions could somehow interfere the determination of Sb, but the interference could be alleviated by the addition of L-cysteine to the samples. Since the transitional metal ions mainly interfere the hydride generation process with the same mechanism as it did in HG-AAS [6,7]

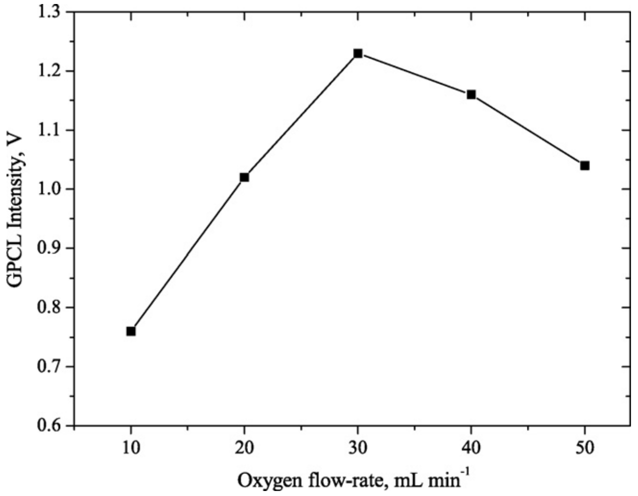

Fig. 6. The effect of oxygen feeding-rate on chemiluminescence intensity. 10 μg L^{-1} Sb standard solution was used and other conditions as specified in Table 1.

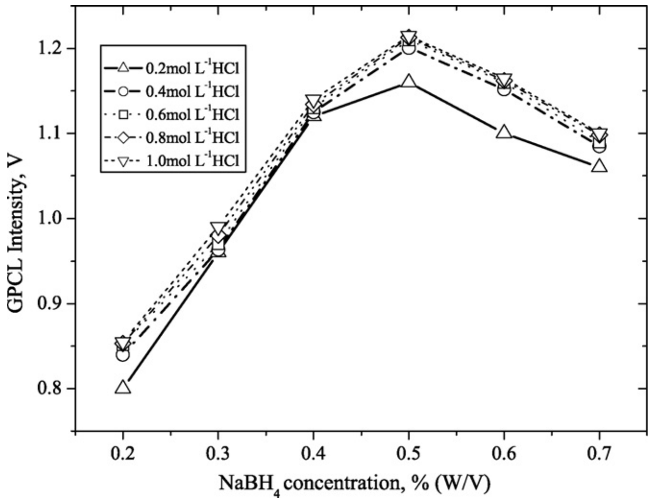

Fig. 7. The effects of HCl and $NaBH_4$ concentration on chemiluminescence intensity. 10 μg L^{-1} Sb standard solution was used and other conditions as specified in Table 1.

Table 2
Study of interferences from transitional metal ions on the recovery of the measurements of 10 μg L^{-1} Sb(V).

Ions	Concentrations (mg L^{-1})	Recovery (%)	
		L–Cysteine not added	L–Cysteine added
Ni(II)	0.2	78	105
	2.0	26	96
Cu(II)	0.2	86	108
	2.0	47	113
Fe(III)	0.2	93	106
	2.0	62	99
Co(III)	2.0	85	104
Mn(II)	2.0	95	103
Cr(V)	2.0	90	99

and HG-ICP-AES [10,11], the tolerance levels of these ions were more or less similar for these three techniques.

The interference from other hydride forming elements was also investigated and the results are shown in Table 3. It can be seen that without cryotrapping and re-vaporization, the hydride forming elements, particularly arsenic could cause serious interference in the determination of Sb. As discussed earlier, other hydrides could be separated from stibine owing to the re-vaporization process used in the present work, which acted as a similar gas chromatographic separation based on the difference of their boiling points. It should be pointed out that with cryotrapping and re-vaporization, the proposed system could tolerate more interference from other hydride forming elements than HG-AAS [6,7] and HG-ICP-AES [10,11]. This ensured a practical application of the system on the analysis of environmental samples.

Table 3
Effect of other hydride forming element ions on the recovery of 10 μg L^{-1} Sb measurements.

Ions	Concentrations (μg L^{-1})	Recovery (%)	
		Without cryotrapping and re-vaporization	Present method
As(V)	0.026	105	101
	2.6	606	105
	50	10,680	112
	100.0	19,880	118
Sn(IV)	4.8	105	102
	200.0	316	105
Se(IV)	22.6	105	100
	100.0	119	103
Bi(V)	100.0	102	101
Ge(IV)	500.0	103	102
Pb(II)	1000.0	102	102

Table 4
Analytical results of determination and recovery tests of Sb in environmental samples by the proposed method and HG-AAS[a].

No.	Sample	Measured concentration (μg L^{-1})		Recovery (%)
		Proposed method	HG-AAS	Proposed method
1	Water 1	4.25 ± 0.03	4.20 ± 0.04	93.4
2	Water 2	3.93 ± 0.02	3.98 ± 0.03	96.1
3	Water 3	3.86 ± 0.04	3.80 ± 0.03	104.2
4	Soil 1	708 ± 16	721 ± 21	102.4
5	Soil 2	1890 ± 32	1901 ± 30	95.6
6	Soil 3	4050 ± 50	4090 ± 60	92.8

[a] The results were obtained by three replicated measurements. For the recovery tests, 4.0 and 20.0 μg L^{-1} Sb(V) was spiked into water samples and diluted soil samples, respectively, after the samples were prepared appropriately.

3.5. Analytical characteristics

Under the optimal conditions described above, the relative GPCL intensity was correlated linearly with the concentration of Sb from 1.0 μg L^{-1} to 10.0 mg L^{-1}. The linear regression equation was $H = 0.0511 + 0.119 \times C_{Sb}$ with a correlation coefficient of 0.997, where H and C_{Sb} were expressed in volt and μg L^{-1}, respectively. The relative standard deviation of the signals at a level of 10.0 μg L^{-1} Sb was 3.56% ($n = 11$). The detection limit was 0.18 μg L^{-1}, based on 3σ of a blank solution ($n = 11$), which was as good as, or better than those of previously reported system by HG-ICP-AES [10,11] and HG-AAS [6,7]. The detection limit might be further improved if more sample or longer cryotrapping time was used. The sampling rate using the proposed method was 15 h^{-1}. It was lower than those of AAS and AES, which were generally 60 and 30 h^{-1}, respectively, because of the inherent merits of these techniques.

3.6. Analysis of environmental samples

The practical feasibility of the proposed method was tested on several environmental samples. The results are shown in Table 4 and recoveries of the spiked samples were generally satisfactory. The accuracy of the proposed method was evaluated by analyzing the samples with hydride generation-AAS. The results obtained by the proposed system were in good agreement with those by the hydride generation-AAS method.

4. Conclusions

In this paper, a new method was developed and applied successfully to the determination of antimony in environmental samples based on the chemiluminescence yielded during the oxidization of stibine by ozone in gas phase. The sensitivity of the system was improved significantly by the preconcentration of stibine with cryotrapping. Interference from other hydride forming elements was minimized by the separation during the re-vaporization of hydrides based on their different boiling points. Excellent detection limit was achieved with the simple instrumentation which allowed high efficiency of analyte introduction, ease of preconcentration and possibility of interference separation. The proposed system could be further developed for the on-line monitoring of antimony in environment and used for analysis of other hydride forming elements.

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