

Improvement of a Batch Hydride Generation - Atomic Absorption Spectrometry

Nobuhisa WATANABE, Saburo INOUE and Hisao ITO

Osaka City Institute of Public Health and Environmental Sciences
(8-34 Tojoh-cho, Tennohji-ku, Osaka 543-0026)

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Summary

Batch hydride generation - electrically heated quartz furnace- atomic absorption spectrometry for the analysis of arsenic, selenium and antimony is presented. Pre-reduction of arsenic was verified by the secondary injection of sodium tetrahydroborate solution. "Memory" was considered to be caused by deposition of low volatile elements or oxides onto the quartz surface, which was intensive for antimony. This problem was solved by modifying the quartz furnace structure. Humidity control was needed for selenium analysis and was achieved by employing a large hydride generator, ice cooling of the sample and a silicon gas transfer tube. The present method was applied to sea water.

Key words: hydride generation, arsenic, selenium, antimony, pre-reduction, memory

INTRODUCTION

Hydride generation technique is widely used for analysis of arsenic, selenium and antimony. Most of commercially available apparatus for hydride generation are of continuous or flow injection systems connected to AAS or ICP-AES. However, the detection limits of those apparatus are in the region of $1 \mu\text{g}/\ell$, which is sometimes not satisfactory. For example, Japanese water criteria demands the concentration of 10, 10 and $2 \mu\text{g}/\ell$ for arsenic, selenium and antimony, respectively, which needs sub-ppb analysis.

Batch hydride generation system is an old technique¹⁻³⁾, however its advantage over the continuous or flow injection systems is now remarkable. Although the absolute sensitivity of a batch system is comparable with continuous or flow injection systems, the quantifiable limit in concentration of a batch system is much lower than those of continuous or flow injection sys-

tems, because a batch system allows 10 times or more amount of sample in one analysis.

We reported a batch hydride generation - flame heated quartz tube - atomic absorption spectrometry⁴⁾. However, it showed disadvantage of consuming fair amount of reagents for the analysis (for example, 10ml of 12 M hydrochloric acid per one sample). Therefore, we have developed a small size system with an electrically heated quartz tube and have applied it to antimony analysis in natural river waters⁵⁾, waste samples and ashes from city waste incineration⁶⁾. We describe here the method for not only antimony but also arsenic and selenium, followed by discussion about checking of pre-reduction in arsenic analysis, the memory effect in a quartz tube and the humidity control to preserve hydrogen selenide. These issues have not been fully discussed yet, although some workers may be annoyed with these problems.

EXPERIMENTAL

Apparatus

The set of the batch hydride generation and the electrically heated quartz tube are shown in Fig. 1. The hydride generator was made of a test tube and a cap equipped with a carrier gas frit, an injection port and a gas outlet. A T-quartz tube was placed on the burner head of the atomic absorption spectrometer (AA-670, Shimadzu, Japan) equipped with hollow cathode lamps (Hamamatsu, Japan). Signal from the spectrometer was processed by A/D converter (E-1, Nippon Filcon, Japan) and transferred to a computer (PC9801, NEC, Japan). The T-quartz tube was wrapped with a nichrome wire (0.4mm in diameter; ca. 600 mm long and 8 ohm resistance), which was insulated with a quartz wool and a couple of ceramic boards. The temperature of the inner quartz surface was ca. 900°C with a power supply of 25 V.

In the analysis of selenium, for the sake of humidity control, a larger test tube was employed as a hydride generator, and the material of transfer tube was silicon. The discussion is given later.

Condition and procedure

Sodium tetrahydroborate of AAS grade was purchased from Wako (Japan) and its solution (0.1% (m/v) for antimony, 0.5% (m/v) for arsenic and selenium) was prepared just before the use and spent within a few hours. Hydrochloric acid (12M), potas-

sium iodide and thiourea were of analytical grade. The solution of 1M potassium iodide was prepared by dissolving 17g of potassium iodide in 100ml of water in an amber bottle, which was spent within a few days. The solution of 0.1M thiourea was prepared by dissolving 3.8g of thiourea in 500ml of water, which was stable for a month at least in an amber bottle. The analytical conditions are listed in Table 1. All the sample preparation were conducted in test tubes.

Pre-reduction of arsenic was carried out by adding appropriate amount of hydrochloric acid and pre-reductant to the sample and keeping it at the room temperature for 1 hour. Antimony analysis was carried out immediately after the preparation. Selenium pre-reduction was conducted in heated hydrochloric acid (4M) at 90°C for 30min in a water bath. Until the sample was brought to hydride generation, it was cooled in an ice bath.

After the test tube was set to the system and the line was purged by nitrogen gas (ca. 10 sec), the solution of sodium tetrahydroborate was gently injected taking ca. one second. Generated hydride was stripped and transferred by the nitrogen carrier gas to the T-quartz tube, where it was atomized and quantified by atomic absorption spectrometry.

For antimony analysis the wavelength of 231.2nm was selected instead of 217.6nm, which is the most popular line, because the analytical line of 231.2nm gave a smoother base line and a lower blank at the expense of sensitivity.

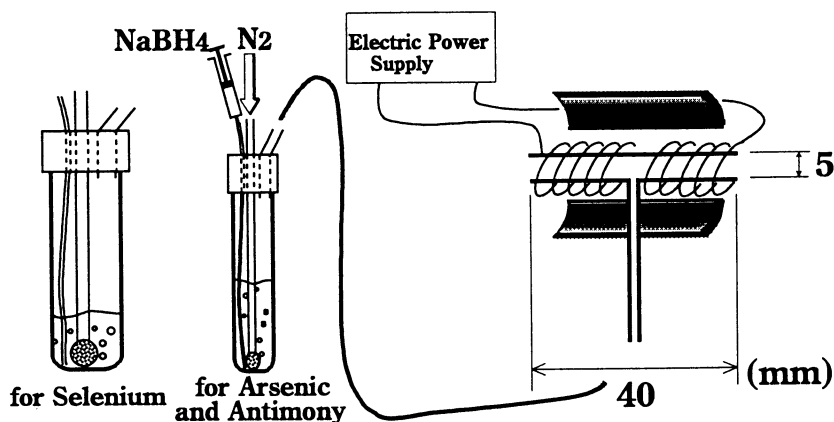


Fig. 1 Apparatus of batch hydride generation - electrical heated quartz tube

Table 1 Analytical Conditions

	Arsenic	Selenium	Antimony
Sample preparation			
Sample volume (maximum) (mL)	5	10	7
12M Hydrochloric acid (mL)	2	5	1
1M Potassium iodide solution (mL)	2-4	0	1
0.1M Thiourea solution (mL)	0-1	0	1
Total volume (mL)	5-12	15	10
Sodium tetrahydroborate solution			
Concentration (%)	0.5	0.5	0.1
Amount of injection (mL)	1	1	1
Nitrogen carrier gas			
Flow rate (mL/min.)	200	500	200
Hydride generation vessel			
Dimension (mm-i.d. × mm-height)	16×200	22×240	16×200
Transfer tube			
Material	PTFE	Silicon	PTFE
Dimension (i.d.×o.d.)(mm)	2×3	3×5	2×3
Atomic absorption spectrometer			
Lamp Current(mA)	5	10	5
Analytical line(nm)	193.7	196.0	231.2
Slit width(nm)	0.7	1.0	1.0

RESULTS AND DISCUSSION

Analytical chart

A typical analytical chart is presented in Fig. 2. The sensitivity was 1.3ng (for 0.00436 absorbance) for antimony, which was 150% of our former result⁴⁾ because of the low sensitive analytical line. The sensitivities of arsenic and selenium were nearly the same with formers⁴⁾. However, we achieved a smoother baseline by the electrical heated quartz tube for all elements compared with them by flame heated quartz tube. Since this system allowed to increase the sample volume up to 5 or 10ml for analysis, it was possible to conduct the analysis at sub-ppb levels.

For the quality control, periodical standard injections were desirable. Moreover, a blank injection after a large peak was effective to verify "memory" to be negligible.

Pre-reduction

Antimony pre-reduction is well known to be fast⁷⁾, while arsenic pre-reduction should be carefully treated. For this purpose, secondary injection of sodium tetrahydroborate solution is useful. If the pre-reduction of As(V) to As(III) was not completed, some peak would appear. In such a case, the amount of sample or pre-reductant should be reconsidered.

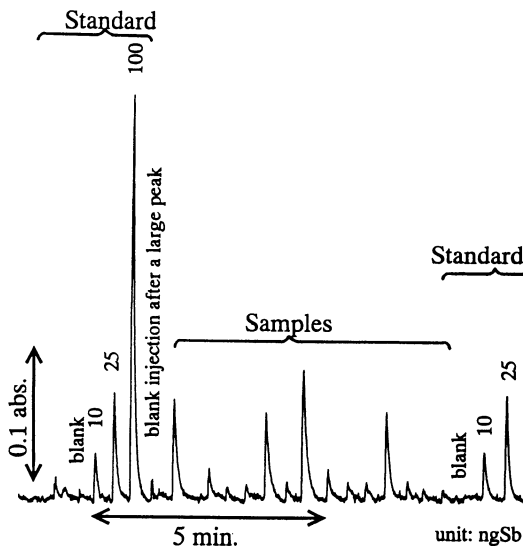


Fig. 2 Analytical chart of antimony

rahydroborate solution is useful. If the pre-reduction of As(V) to As(III) was not completed, some peak would appear. In such a case, the amount of sample or pre-reductant should be reconsidered.

Pre-reduction of arsenic in sea water sample by

potassium iodide was examined by secondary injection study. Two set of condition were examined: one is 5 ml of sea water, 1ml of 1M potassium iodide, 1ml of hydrochloric acid, which was volumed up to 9ml with distilled water, the other is 5ml of sea water, 2ml of 1M potassium iodide and 2ml of hydrochloric acid (9ml in total volume). Hydride generation was conducted at a few minutes, 10 minutes and 2 hours after the preparation.

The results are shown in Fig. 3. The sample prepared with 1ml of potassium iodide solution and 1ml of hydrochloric acid was not completely pre-reduced even after 2 hours, because the secondary peak was larger than a blank. On the other hand, the sample prepared with 2ml of potassium iodide solution and 2ml of hydrochloric acid was observed sufficiently pre-reduced in ten minutes.

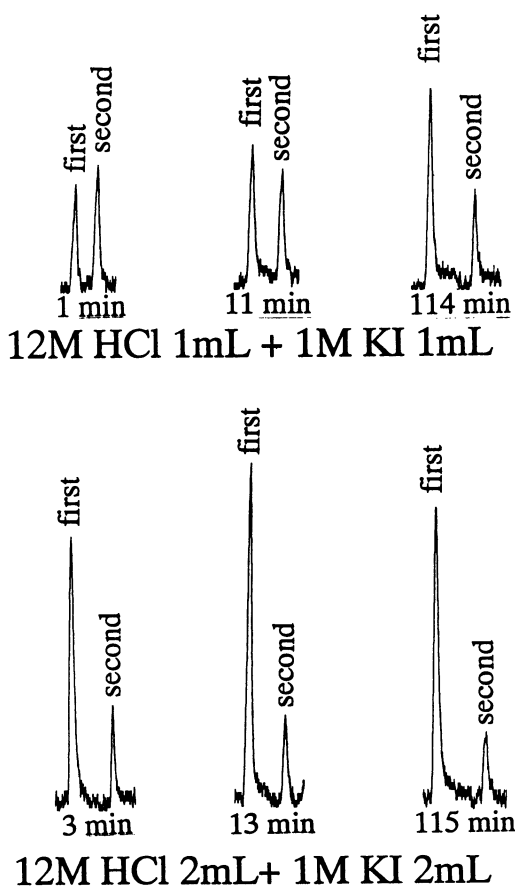


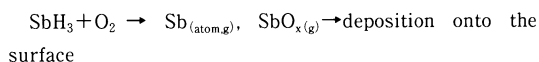
Fig. 3 Secondary injection study on arsenic pre-reduction

Consequently, 2ml of potassium iodide solution and 2ml of hydrochloric acid were indispensable. It could be presumed that the pre-reduction of arsenic in sea water finished within 10min, however, one hour waiting time should be recommended as mentioned by Dedina and Tsalev⁷⁾. Possible delay and interference may occur depending on sample matrices, which can be suspected by the secondary injection study. In such a case, the sample volume and the amount of pre-reductant should be reconsidered.

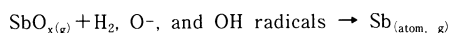
Memory in the quartz tube

Although few workers mentioned about the problem of "memory" in a quartz tube, we believe it occurs ordinarily, and we found "memory" was severe for antimony, even if D_2 background correction was conducted. The memory problem scarcely occurred for arsenic analysis, while selenium analysis did not suffer from it at all.

We propose the mechanism of memory as follows (Fig. 4). In the quartz tube, introduced antimony hydride would be atomized or oxidized, which would be deposited onto the surface of the quartz tube.



It would generate trace vapor, which would be atomized, when the hydrogen was supplied from the next analysis.



A similar discussion was already argued by Forsyth and Marshall⁸⁾ for lead analysis with GC-AAS.

Table 2 presents the boiling point and vapor pressure of arsenic, selenium, antimony, lead and their oxides⁹⁾. Lead, antimony and their oxides have high boiling point over 1000°C, which can cause the memory. On the other hand, arsenic, selenium and their oxides are comparatively volatile. Deposition of elemental arsenic onto the quartz tube might occur, however in a practical manner, "memory" in the arsenic analysis was trivial. Selenium made no problem, because of its volatility.

To overcome the "memory", it was effective to exclude the cold region from the quartz tube, where antimony deposition may occur. Therefore, the widen and un-heated sides of the former T-tube were cut off (Fig. 4). By this modification, blank and memory peak

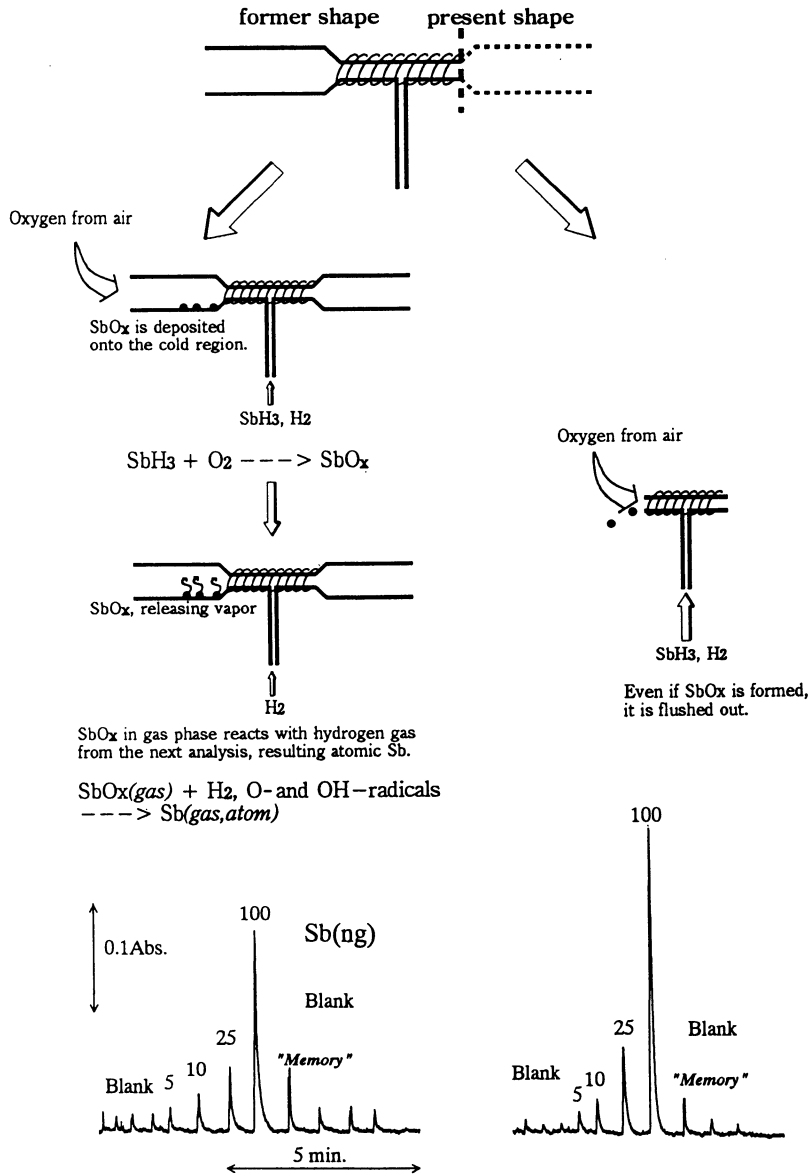


Fig. 4 Mechanism of memory in antimony analysis and the improvement of the quartz tube

Table 2 boiling points of arsenic, selenium, antimony, lead and their oxides

substrate	Temp(°C)	substrate	Temp(°C)	substrate	Temp(°C)	substrate	Temp(°C)
As	1800*	Se	685	Sb	1587	Pb	1746
As4O6	459	SeO2	300**	Sb4O6	1456	PbO	1700***

All the data are collected from MALT2(ref.9)

* at vapor pressure of 0.3 atm.(extrapolated data)

** at vapor pressure of 0.3 atm.

*** at vapor pressure of 0.9 atm.

were considerably suppressed. Nevertheless, an elevation of a blank peak was observed in the long run. Consequently, hydrofluoric acid treatment (20%, 10min.) of the quartz tube immediately before the analysis was indispensable for antimony quantification in the range of a few nanograms.

Humidity control in selenium analysis

Hydrogen selenide is very unstable with the presence of water vapor¹⁰⁾, therefore humidity control is needed. We achieved it in three manners. Ice-bath cooling after the pre-reduction was kept till the hydride generation. A relatively large test tube, which suppressed the mist entry to the transfer tube, was employed as a hydride generation vessel. Silicon tube was used as the gas transfer tube instead of PTFE tube.

Oerenmark et al.¹⁰⁾ observed a latex tube better than a PTFE tube, and considered the air permeable property of latex would supply trace amount of oxygen to the gas transfer line, which enhanced the sensitivity. Although we obtained a similar result, we believe it was brought by the property of moisture absorption of silicon tube. Experimentally, if the silicon tube was replaced by a PTFE tube, the sensitivity did not change at the moment, however, it gave little peak after a blank purge for a few hours, on the other hand, a silicon tube presented a stable result. We considered it was due to the difference of the humidity in the tubes. The PTFE tube would keep the moisture on the inner surface,

while the silicon gum would absorb the moisture and keep the inside dry as a result. In addition, the oxygen supply at the detector from the open ends should be sufficient independently of the tube material.

DETERMINATION OF ARSENIC, SELENIUM AND ANTIMONY IN SEA WATER

Six samples of sea water were collected from Osaka Bay and analyzed. For arsenic, selenium and antimony determination, 5ml, 10ml and 7ml were brought to analysis, respectively. Triplicate analysis was carried out for arsenic, while five times for antimony. Selenium was determined with single analysis, however, in order to verify that no interference occurred, spiked-recovery experiment was also conducted (Fig. 5). Spiked 10ng of selenium from 10ml of sea water sample was sufficiently recovered.

The results are tabulated in Table 3. The concentration level of all sample were very similar, namely, 1.2 μg As/l, <0.2 μg Se/l and 0.5~0.6 μg Sb/l.

CONCLUSIONS

Batch hydride generation - electrically heated quartz tube - atomic absorption spectrometry for the analysis of arsenic, selenium and antimony was presented. It allowed up to 10ml of sample to one analysis with quantitative detection of a few ng. Pre-reduction of arsenic by potassium iodide was check-

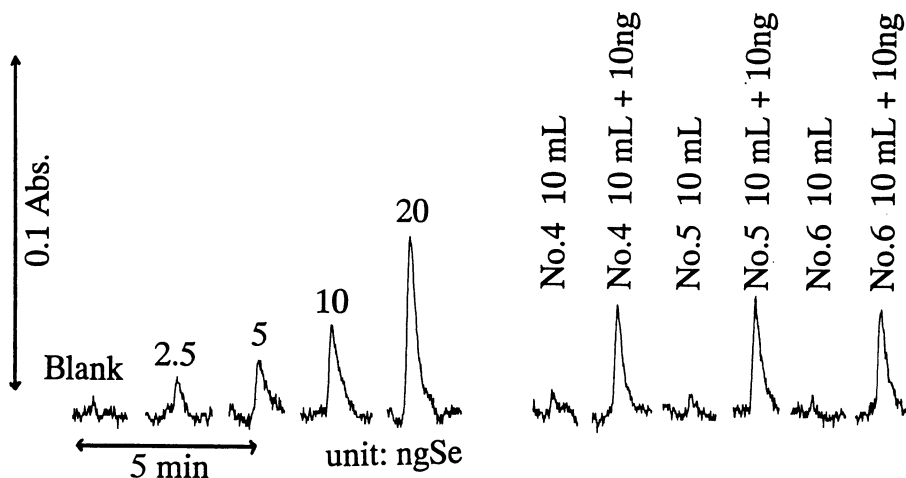


Fig. 5 Spiked - recovery experiment on selenium determination in sea water

Table 3 Concentration of Arsenic, Selenium and Antimony in the Sea Water from Osaka Bay

Collected Site	Arsenic (n=3)	Selenium (n=1)	Antimony (n=5)
No.1	1.16± 0.02	<0.2	0.64± 0.08
No.2	1.24± 0.02	<0.2	0.55± 0.02
No.3	1.18± 0.04	<0.2	0.62± 0.07
No.4	1.24± 0.02	<0.2	0.61± 0.12
No.5	1.24± 0.02	<0.2	0.51± 0.11
No.6	1.21± 0.06	<0.2	0.46± 0.03

unit: $\mu\text{g/L}$

ed by secondary injection of sodium tetrahydroborate solution, which should not generate further arsenic hydride. "Memory" was observed for antimony analysis. It was considered to be caused by deposition of antimony onto the quartz furnace. Changing the shape of the quartz furnace was highly effective. Hydrogen selenide is unstable under water vapor. For the humidity control, following three resolutions were effective: a large hydride generation test tube, an ice cooling of analytical solution, and silicon material as a gas transfer tube. Arsenic, selenium and antimony in sea water from Osaka Bay were determined. $1.2\mu\text{g As}/\ell$, $<0.2\mu\text{g Se}/\ell$, and $0.5\sim 0.6\mu\text{g Sb}/\ell$ were found.

Acknowledgement

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