

# Determination of Arsenic and Antimony in High-Purity Phosphoric Acid by Atomic Absorption Spectrometry with Electrothermal Atomization

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An atomic absorption spectrometric method with electrothermal atomization (AAS-ETA) for the determination of arsenic and antimony in high-purity phosphoric acid is described. The determination is based on the rapid generation of arsine and stibine based on reduction with a solution of sodium tetrahydroborate, their absorption in a solution of nickel salt, nitric acid, and bromine, and is suitable for  $\text{ng g}^{-1}$  levels of As and Sb in  $\text{H}_3\text{PO}_4$  and other mineral acids.

Hydride generation was introduced around 1970 [1–3] to overcome problems associated with flame AAS determinations of volatile hydride-forming elements such as arsenic and antimony, especially in complex matrices. From a number of various up-to-date designs of techniques of generation of volatile hydrides the most popular is the reduction by sodium borohydride [1, 4–6].

The generated hydrides are diluted with co-generated hydrogen and transport gas. The direct atomization of hydrides in the argon-hydrogen diffusion flame does not attain the necessary low detection limits. For the preconcentration of hydrides from carrier gas their freezing is used [1, 7, 8]. The procedures using freezing of hydrides or their trapping on a heated wall of measuring cell are not suitable for all types of atomic absorption spectrometers and elements because this is dependent on configuration of measurement devices and stability of hydrides [4].

At the electrothermal atomization both the decomposition of hydrides on the wall of graphite measuring cell [9, 10] and the other atomizer [11] and absorption of the hydrides in the solutions containing different atomization modifiers (most often silver salts), when the resulting solution was aspirated directly into an argon-hydrogen flame, were used in works [12–14].

Graphite furnaces have been used for hydride atomization almost since introduction of hydride techniques [15]. There are three approaches to using graphite furnaces: *in situ* trapping of hydrides in the furnace [11, 16], on-line atomization [17–20], and

atomization from absorption solution obtained after trapping of hydrides.

*Shaikh* and *Tallman* [21] have described the determination of organically bound arsenic species. They used a  $50 \text{ cm}^3$  sample volume and sodium tetrahydroborate to reduce the arsenic to arsine, which was then trapped in a small volume of chloroform—ephedrine solution of silver diethyldithiocarbamate. The arsenic content was then determined by graphite furnace atomic absorption spectrometry.

The hydride generation methods commonly used are summarized in Fig. 1 [15].

The presented method is based on trapping the arsenic and antimony hydrides in an absorption solution containing nickel salt, nitric acid, bromine, and in case of antimony also tartaric acid. If it does not come to the precipitation of solid reaction products in this solution and the absorption of hydrides is full, both good reproducibility and accuracy of the results are obtained.

## EXPERIMENTAL

All acids were Suprapur grade (Merck, Germany). Working standards were prepared daily from the  $1 \text{ mg cm}^{-3}$  stock As or Sb solutions. The stock As solution was prepared by dissolving  $\text{As}_2\text{O}_3$  in isothermally distilled  $\text{NH}_4\text{OH}$ . The stock Sb solution was prepared by dissolving metallic Sb in a mixture of concentrated  $\text{HCl}$ ,  $\text{HNO}_3$ , and tartaric acid was added on final concentration 0.1 %. A 1 %  $\text{NaBH}_4$  solution was prepared

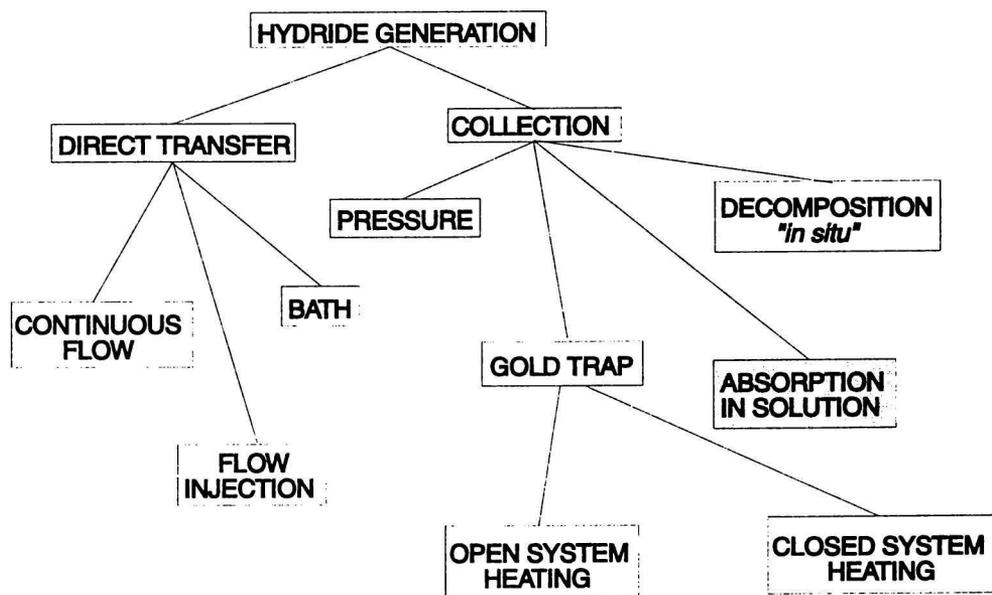
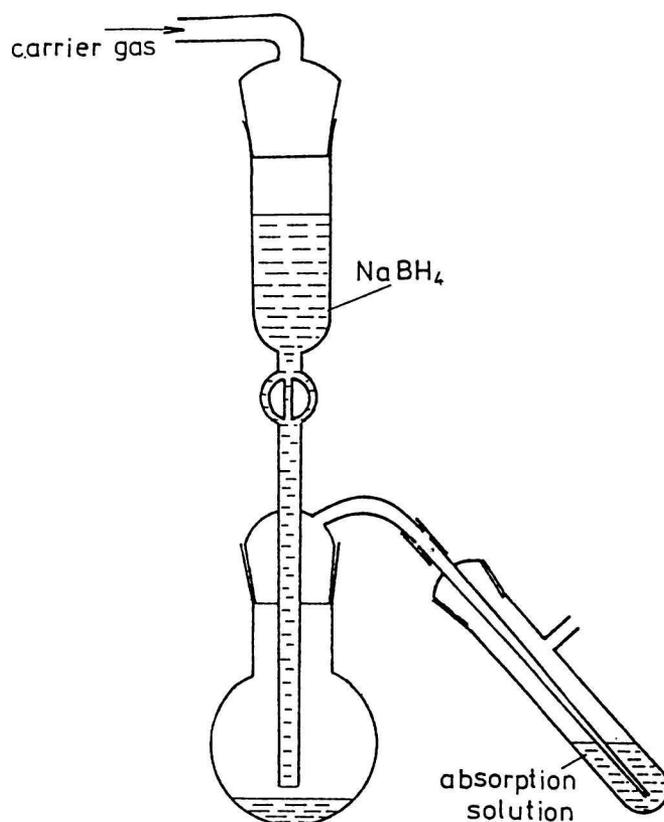


Fig. 1. Methods of hydride generation.

Table 1. Conditions for the Determination of As and Sb

Parameter	As	Sb
Wavelength/nm	193.7	217.6
Bandpass/nm	0.5	0.5
HCL current/mA	8.0	13.5
Ashing temperature/°C (time/s)	110 (20)	110 (20)
Drying temperature/°C (time/s)	800 (20)	800 (20)
Atomization temperature/°C (time/s)	2600 (5)	2300 (5)
Cleaning temperature/°C (time/s)	2900 (3)	2900 (3)

Fig. 2. Apparatus for generation of AsH<sub>3</sub> and SbH<sub>3</sub>.

by dissolving the reagent in 1 % Suprapur NaOH. The absorption solution was composed of 0.1 % nickel salt in 0.1 % HNO<sub>3</sub> saturated with bromine. The excess of bromine was eliminated with 30 % H<sub>2</sub>O<sub>2</sub> after absorption.

Arsenic and antimony were determined by using a Pye Unicam SP 9 spectrometer equipped with a deuterium background corrector, an SP 9 graphite furnace, a PU 9095 video furnace programmer, a PU 9090 data graphics system, and an SP 9 autosampler. The cuvettes were made from totally pyrolytic graphite. The conditions for As and Sb determination are given in Table 1. The hydrides of arsenic and antimony were generated and absorbed in the apparatus system represented in Fig. 2. It consists of a 100 cm<sup>3</sup> generation vessel closed with separating funnel with outlet introducing the carrier gas containing hydrides into the absorption solution.

### Procedure

Into the generating vessel containing 3 M-HCl (10 cm<sup>3</sup>) and KI (0.1 g) is introduced phosphoric acid

(about 1 g) and the absorber with 4 cm<sup>3</sup> of the absorption solution is joined. Then 2 cm<sup>3</sup> of 1 % sodium borohydride solution (in 1 % of NaOH) are slowly added into the generating vessel, and bubbled by argon stream (max. 100 cm<sup>3</sup> min<sup>-1</sup>). After 5 min the

same volume of  $\text{NaBH}_4$  solution is added again and argon is introduced for further 10 min. When absorption is complete, the excess of bromine is removed by the addition of  $100 \text{ mm}^3$  of 30 %  $\text{H}_2\text{O}_2$ . The obtained solution is filled up to the volume of  $5 \text{ cm}^3$  and then 10–40  $\text{mm}^3$  of this solution are sampled into the graphite furnace.

## RESULTS AND DISCUSSION

Direct determination of arsenic and antimony in concentrated mineral acids is not favourable due to the cuvette and furnace corrosion even after the additions of atomizing stabilizers. Matrices containing increased concentration of phosphates except the corrosion cause difficulties at the determination of As and Sb by the spectral interferences of molecular bands and the creation of the so-called "phosphate glass" (interstitial compounds phosphates and graphite) has also influence on the accuracy and reproducibility of results.

For this reason we separated arsenic and antimony from the matrix in the form of hydrides. Trapping was checked on the samples spiked with 200 ng of arsenic or antimony before generation. When the generation was finished the residual content from the original solutions and the amount of elements in the absorption solution was determined as a recovery.

Residual content of As and Sb in original solution and amount before generation was determined after extraction by chloroform as a solution of diethyldithiocarbamate complex. For example, from the sample spiked with 200 ng of As there was determined 197.12 ng by extraction before the generation, *i.e.* 98.6 % and in the absorption solution after the generation 194.20 ng, *i.e.* 97.1 %, in the residue after the generation it was only 1.23 ng of arsenic. Similarly for Sb there was determined 198.73 ng by extraction before the generation (99.4 %), in the absorption solution after the generation 197.32 ng (98.7 %) and in the residue after the generation it was only 0.86 ng of Sb. The results of the efficiency of generation of  $\text{AsH}_3$  and  $\text{SbH}_3$  from spiked samples are summarized in Table 2 (given as the average from five measurements).

The calibration graphs were made for the concentration ranges 5–45  $\text{ng cm}^{-3}$  Sb and 5–65  $\text{ng cm}^{-3}$

**Table 2.** Efficiency of Generation of  $\text{AsH}_3$  and  $\text{SbH}_3$  (Samples Spiked with 200 ng of As and Sb)

Determination	$m(\text{As})$ found ng	RSD %	Recovery %
Before generation			
$\text{AsH}_3$ (extr. tech.)	197.12	3.4	98.6
$\text{SbH}_3$ (extr. tech.)	198.73	2.9	99.4
Absorption solution			
(after gen. $\text{AsH}_3$ )	194.20	5.7	97.1
(after gen. $\text{SbH}_3$ )	197.32	2.4	98.7
Residual As and Sb			
(after gen. $\text{AsH}_3$ , extr. tech.)	1.23	12.9	0.6
(after gen. $\text{SbH}_3$ , extr. tech.)	0.86	8.6	0.4

As by the above described procedure. Table 3 gives the results of analyses of samples from other producers of  $\text{H}_3\text{PO}_4$  obtained by calibration curve and by standard addition techniques (results as the average from three measurements).

## CONCLUSION

Great attention has been paid to the determination of arsenic and antimony by different methods and in different matrices. Rapid determination in the diffuse argon-hydrogen flame by using hydride kits [22] is suitable for the contents higher than  $0.05 \text{ mg dm}^{-3}$ .

At the direct determination of As and Sb in the electrothermal atomization it was found that interferences from the phosphoric acid matrix [23] could not be overcome by variations of the furnace program or by background correction. Therefore we decided to separate the arsenic and antimony as hydrides. Cryogenic or thermal decomposition preconcentration of hydride before atomization step is complicated and not suitable for all types of atomic absorption spectrometers (construction, program or safety blocks). The advantages of methods based on absorbing the hydrides prior to determination are in lower dependence on hydride generation step which is critical in direct flame or electrothermal methods, and in the possibility of preconcentration given by the ratio of the sample volume to the volume of absorption solution.

**Table 3.** Content of Arsenic and Antimony in High-Purity Phosphoric Acid (for Metal Oxide Semiconductor Technology (MOS) and for Analysis (PA))

Method	Producer I (MOS)	Producer II (MOS)	Producer III (PA)
$w_{\text{cal. c.}}(\text{As})/\%$	$(1.5 \pm 0.1) \times 10^{-6}$	$(2.6 \pm 0.1) \times 10^{-6}$	$(8.3 \pm 0.4) \times 10^{-6}$
$w_{\text{st. add.}}(\text{As})/\%$	$(1.3 \pm 0.1) \times 10^{-6}$	$(2.3 \pm 0.1) \times 10^{-6}$	$(8.2 \pm 0.7) \times 10^{-6}$
$w_{\text{cal. c.}}(\text{Sb})/\%$	$< 3 \times 10^{-7}$	$< 3 \times 10^{-7}$	$(0.9 \pm 0.1) \times 10^{-6}$
$w_{\text{st. add.}}(\text{Sb})/\%$	$< 3 \times 10^{-7}$	$< 3 \times 10^{-7}$	$(1.2 \pm 0.1) \times 10^{-6}$

Note: cal. c. — method of calibration curve, st. add. — method of standard addition.

The presented method has shown to be suitable for the determination of arsenic and antimony in high-purity phosphoric acid. The procedure may be applied also for other matrices with high contents of phosphorus (for example solid and liquid fertilizers).

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