# ATOMIC ABSORPTION METHOD FOR DETERMINATION OF ANTIMONY IN AQUEOUS SOLUTIONS

Georgiana VASILE,[*] Andreea MOISE and Elena MIHAILA

National Research and Development Institute for Industrial Ecology – ECOIND
90-92 Panduri Road, sector 5, 050663 Bucharest, Roumania
phone: +40/21/4100377; fax: +40/21/4100575; e-mail: ecoind@incdecoind.ro

Due to the very different sources of polluted water, the estimation of a great number of constituents which are present in a large concentration range implies the development of suitable analysis methods, adapted to every type of matrix. In the present paper we worked out and validated in house an analytical method for the quantitative analysis of antimony in aqueous solutions, using on atomic absorption spectrometry – hydride technique. The described method is based on atomic absorption spectrometry of antimony resulted from the breakdown of antimony hydride. In the conditions used, only Sb (III) reacts with sodium borohydride to form antimony hydride. Due to this fact, prior to hydride treatment, antimony solutions are reduced to Sb (III). The reaction of Sb (III) with $NaBH_4$ takes place in HCl solutions. Antimony is quantitatively estimated at $\lambda = 217.6$ nm, with a linearity range between 1 µg/L and 5 µg/L. The developed method's accuracy is 103.3 %, the precision 2.49% and the repeatability 0.22 µg/L. The determined LoD is 0.127 µg/L and the limit of quantitation (LoQ) 0.425 µg/L.

## INTRODUCTION

Antimony could arise in environment from natural weathering, industrial production, municipal waste disposal, and manufacturing of flame-retardants, ceramics, glass, batteries, fireworks, and explosives. Undoubtedly, antimony compounds, especially those of trivalent antimony, have definite toxic effects and that makes necessary monitoring their concentration in water, sediments, sludge, etc.

The legal provisions concerning maximum accepted levels of antimony [1-4] implies the development of suitable analysis methods for this element, adapted to every type of matrix.

## EXPERIMENTAL

### Method's principle

The trivalent antimony compounds react with sodium borohydride in an acidic medium generating antimony hydride, a gaseous compound which is drawn off under inert atmosphere (argon) into a heated quartz cell where is decomposed by collision processes, forming free Sb atoms.

Only trivalent antimony compounds form hydride in these conditions making it necessary to reduce pentavalent antimony compounds if total content of this element is to be analyzed.

The atomized antimony is quantitatively determined in an optical system, the absorbance being measured at $\lambda = 217.6$ nm.

### Reagents

All reagents, analytical grade, have been purchased from MERCK.

Antimony standard solution (Merck) of 1000 mg/L was diluted to 1-5 µg/L to obtain the calibration solutions.

### Instrument

For the analysis of antimony the Atomic Absorption Spectrophotometer (AAS NOVA 300 Analytik Jena AG), Hydride System HS5 (Analytik Jena AG), and Argon Carrier Gas with 99.99% purity were used.

### Procedure of Analysis

The sample solution (10-50 mL), containing Antimony (III) compounds is acidulated with 4 mL concentrated (37%) hydrochloric acid and is diluted to 200 mL with water. 10 mL of this solution is taken into reaction cell of the hydride system. The peristaltic pump of the system feeds in this cell the borohydride solution (3% $NaBH_4$), which reduces antimony (III) compounds to $SbH_3$.

The optimal working parameters, recommended by instrument's producer, are presented in Table 1.

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[*] Coresponding author: georgianavasile2004@yahoo.com

*Table 1*

Working parameters for AAS with Hydride System

| Hydride System | |
|---|---|
| NaBH$_4$ conc. | 3%, stabilized with 1% NaOH |
| Carrier | Argon (99.99%) – 18 l/h |
| Sample volume | 10ml/25ml |
| Pump time | 7 sec. |
| Reaction time | 8 sec. |
| Wash time | 20 sec |
| **Atomic Absorption Spectrometer** | |
| Measuring wavelength | 217.6 nm |
| Slit width | 0.8 nm / 1.2 nm |
| Lamp current | 3 mA |

In this study we tried to optimize some of the analysis and instrument variables, in order to obtain best performance. We have investigated the following factors: the reaction time, the wavelength for maximum absorbance, the integration time, slit width, the concentration of the reducing reagent (NaBH$_4$), the impact of reagents purity upon reaction. Finally the most important performance parameters of the method have been calculated.

## RESULTS AND DISCUSSION

The calibration curve was established, observing all the recommendations in SR ISO 8466:98.[5]

The concentration linear range was determined by repeatedly assessing the lowest and highest concentrations for the calibration, calculating the corresponding dispersion values for these concentrations. The ratio between these two dispersions, PG, was compared to the value of F distribution for $\alpha = 1\%$ (P = 99 %), the number of the degrees of freedom being the number of repeated analysis for each of the concentrations (9.8).

$$PG = \frac{s_9^2}{s_1^2} = \frac{0.00004764}{0.00001342} = 3.55$$

F (9.8; 99 %) = 5.47 ; PG < F

According to the SR ISO 8466:98 standard, if PG is less than the value of F distribution (5.47, in our case), the difference between the two dispersions, $s_1^2$ and $s_9^2$ is not a significant one and accordingly the concentration range examined matches all the criteria to be used for calibration.

Linearity checking was made by plotting the calibration data.

In Fig. 1 we give the calibration curve, which was obtained using the linear regression method, and the performance parameters resulted from the calibration data (the regression quotients a and b, linear range of the calibration curve $S_y$, $S_{xo}$, $CV_{xo}$).

The residual standard deviation $S_y$ estimates the dispersion of experimental data around the calculated regression line. This is a performance parameter, which estimates the accuracy of the calibration.

$S_y$ is calculated as follows:

$$s_y = \sqrt{\frac{\sum (y_i - \hat{y}_i)^2}{N-2}} = \sqrt{\frac{0.04862}{3}} = 0.0045$$

The standard deviation of the method $S_{x0}$ is the ratio between residual standard deviation and the method sensitivity, b:

$$S_{x0} = \frac{S_y}{b} = 0.02632$$

The coefficient of variance of the method $V_{x0}$ is the percent ratio between the standard deviation of the method, $S_{x0}$, and average x, which is the centre of the working range:

$$CV_{x0} = \frac{S_{x0}}{x}.100 = \frac{0.02632}{3.00} \times 100 = 0.88\%$$

The method for antimony analysis was 'in house' validated, according to IUPAC recommendations[6] and its performance parameters are presented in Table 2.
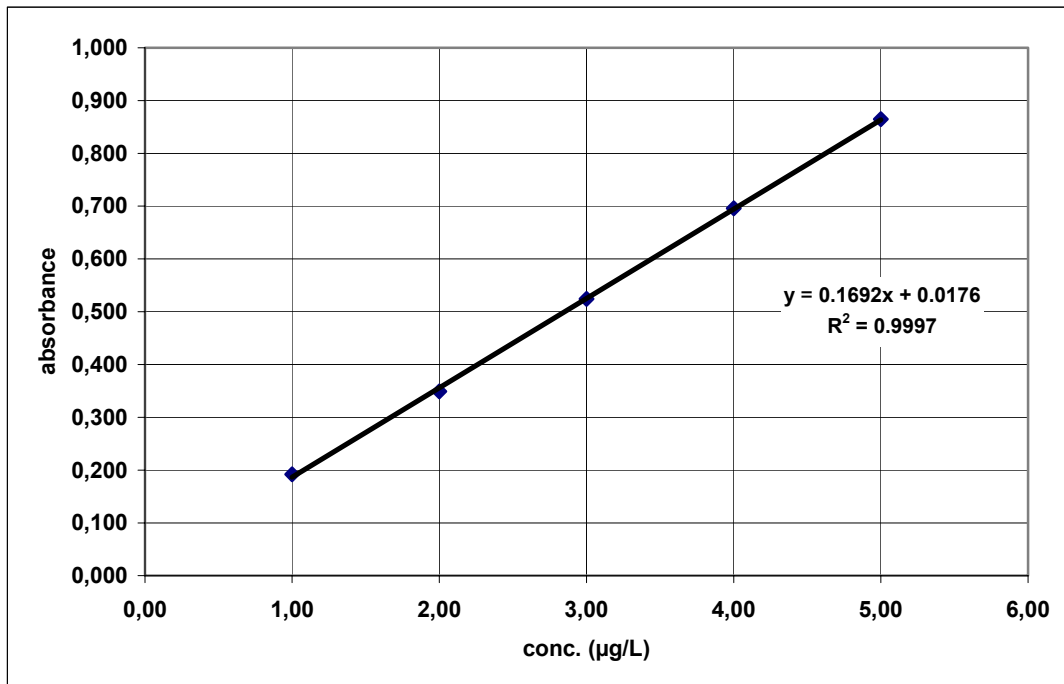
Fig. 1 – Calibration curve for antimony.

*Table 2*

The performance parameters of the 'in house' validated method for antimony determination

| Evaluated Parameter | Parameter's value |
|---|---|
| Accuracy | 103.6 %; |
| Repeatability | $r = 0.217$ μg/L |
| Intermediate precision | CV% = 2.49 %; |
| Reproducibility | $R_L = 0.32$ μg/L |
| Sensitivity | $b = 0.1692$ |
| Detection limit | LoD = 0.127 μg/L |
| Quantitation limit | LoQ = 0.4251 μg/L |
| Linear range | 1 μg/L - 5 μg/L |
| Uncertainty | ± 0.1 μg/L |

## CONCLUSIONS

The most relevant analytical parameters and instrument settings have been evaluated and optimized for the analysis of antimony by hydride technique: optimum reaction time for maximum absorbance, the wavelength for maximum absorbance, integration time for absorbance peaks, linear range of the calibration curve, slit width of the spectrometer, the concentration of reducing reagent ($NaBH_4$), the performance parameters of the analysis method. [7]

The method for antimony analysis has been validated 'in house' by evaluating the relevant method's performance parameters: accuracy, precision, repeatability, reproducibility, sensitivity, detection limit, quantitation limit, linear concentration range, uncertainty.

The proposed method is suitable to be used for the quantitative analysis of antimony in aqueous solution.

## REFERENCES

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