

**ANALYTICAL METHOD FOR BISMUTH DETERMINATION FROM
STATIONARY SOURCES BY ATOMIC ABSORPTION SPECTROMETRY**

Mihaela Petrescu; Elena Bucur; Ileana Nicolescu; Liviu Ionita

National Research and Development Institute for Industrial Ecology –**ECOIND**,
90-92 Panduri St., sector 5, Bucharest, Romania, e-mail:
ecoind@incdecoind.ro, poluare.aer@incdecoind.ro

Abstract:

This paper reports determination of bismuth from stationary emission sources using atomic absorption spectrometry with atomisation in a graphite tube (GFAAS) and with generation of hydrides (HGAA).

In the last years hydride generation technique (HGAA) became more and more popular in laboratories for estimating trace metals in materials with changeable composition, while the graphite furnace method is often not reliable due to the strong and variable matrix effect and signal splitting.

The metals sampling train is used to determine the bismuth in stationary source emissions. The stack gas is withdrawn isokinetically from the source with the particulate emissions collected in a probe and on heated filters and the gaseous emissions collected in a series of chilled impingers with absorption

solutions. The filter, absorptions solution and rinsing solutions are recovered for analysis.

This paper presents the results obtained by optimizing the method for bismuth determination, respectively the characteristic parameters by atomic absorption spectrometry, with atomisation in a graphite tube (GFAAS) and with hydrides generation technique (HGAA).

The limit of detection values obtained were between 1.84 µg/l for method GFAAS and 0.06 µg/l for HGAA.

Both methods can be used to determine the concentration of bismuth in fixed emissions sources but with a better accuracy and recovery for HGAAS.

Keywords: Bismuth, AAS, GFAAS, HGAA

INTRODUCTION

Bismuth finds its main uses in pharmaceuticals, glass, ceramics, alloys and also as a catalyst in rubber production.

Bismuth is a recognized toxic element, (and is not a recognized carcinogen) however some of its compounds need to be handled with care due to their corrosiveness (e.g. bismuth chloride). Overexposure to bismuth can lead to the formation of a black deposit on the gingival (this is known as a bismuth line).

Bismuth and its salts can lead to kidney damage, albeit usually to a mild degree. However large doses can be fatal, although industrially it is considered one of the less toxic heavy metals. Inhalation of bismuth may affect both the liver and kidneys. Direct contact with bismuth may cause irritation to the eyes and skin [1].

EXPERIMENTAL

Determination of bismuth from the stationary emission sources involves an isokinetic air sampling by a process in which the waste gas is contacted with an absorbing solution whereby bismuth compounds are absorbed. The treated waste gas is then passed through a glass fiber filter which collects the remaining amounts of bismuth from the waste gas.

In order to make a quantitative recovery of the bismuth, the traces from the sampling system are taken with an acid solution of nitric acid, and analyzed [2].

For the filter digestion it was used concentrated nitric acid in a closed system as MARS 5 microwave digester with pressure and temperature sensor.

In this paper are presented two methods for bismuth determination by using atomic absorption spectrometry and two different techniques:

- 1.- AAS, with hydride generation (HGAAS).
- 2.- AAS, with graphite furnace (GFAAS).

An atomic absorption spectrometer SpectraAA-280FS VARIAN with deuterium background correction equipped with a graphite tube atomizer GTA 120 and a PSD 120 programmable sample dispenser and VGA-77 vapor generation unit, was used for the experiments [3,4,].

For both methods was used a reference material consisting in a solution of 1000mg/l Bismuth - MERCK.

All reagents were of analytical grade.

The best results were obtained in the following operating conditions[5,6,7]:

1. Operating conditions for vapor generation

Flame Air acetylene
Instrument mode Absorbance
Calibration mode Concentration
Measurement Mode Integration
Lamp current 10 mA
Slit Width 0.5 nm
Wavelength 223.1 nm
Measurement Time 10 s
Pre-Read Delay 70 s
Background Corection BC On

Flow rates:

HCl (5 M HCl)solution 1 mL/min
NaBH₄(NaBH₄ 0.6% in NaOH 0.5%) 1 mL/min
Sample 6.5 mL/min

2. Operating conditions for graphite furnace AA

Instrument mode Absorbance
Calibration mode Concentration
Measurement mode Peak height
Slit width 0.2 nm
Wavelength 223.1 nm
Lamp current 10 mA
Background Corection BC On
Sample volume 20 µl
Bulk Conc. 50 µg/l
Modifier(1000 µg/MI Palladium) Co Inject
Modifier volume 10 µl

The temperature program used s for graphite furnace is presented in table 1.

Table 1. Furnace Parameters

Step No	Temperature (°C)	Time (sec)	Gas Flow (L/min)	Read	Signal Storage
0	1	2	3	4	5
1	85	0.1	0.3	No	No
2	85	5	0.3	No	No
2	95	40.0	0.3	No	No
3	120	10.0	0.3	No	No

0	1	2	3	4	5
4	300	5.0	0.3	No	No
5	300	1.0	0.3	No	No
6	400	2.0	0.0	Yes	Yes
7	1800	0.8	0.0	Yes	Yes
8	2000	2.0	0.0	Yes	Yes
9	2400	0.2	0.3	No	Yes
10	400	9.3	0.3	No	Yes

RESULTS AND DISCUSSIONS

Experiments were conducted to determine the calibration curve and performance parameters for atomic absorption spectrometry methods (working range, detection limit, limit of quantification, trueness and precision).

Blanks quartz filters and additional solutions of concentration 5 µg/L Bi for HGAAS technique and 20 µg/L Bi for technical GTAAS were used for the experiments.

Calibration curves were generated using linear regression analysis and working standard solutions with concentrations in the range 10 - 50 µg/l Bi for GTAAS and 2-10 µg/l Bi for HGAAS, with correlation coefficients (r) higher that 0.9997 and 0.9995.

Figure 1 Calibration curves for Bismuth – GTAAS

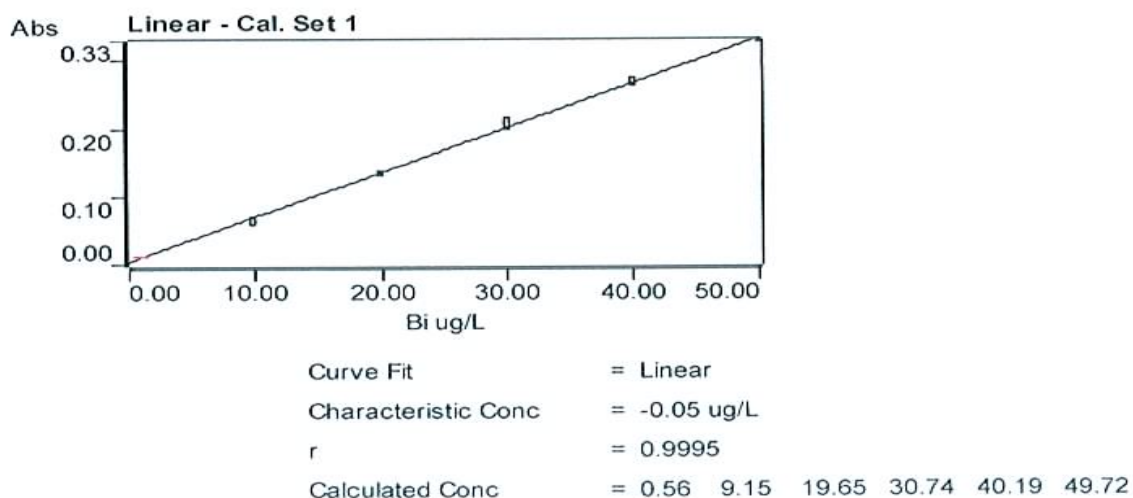
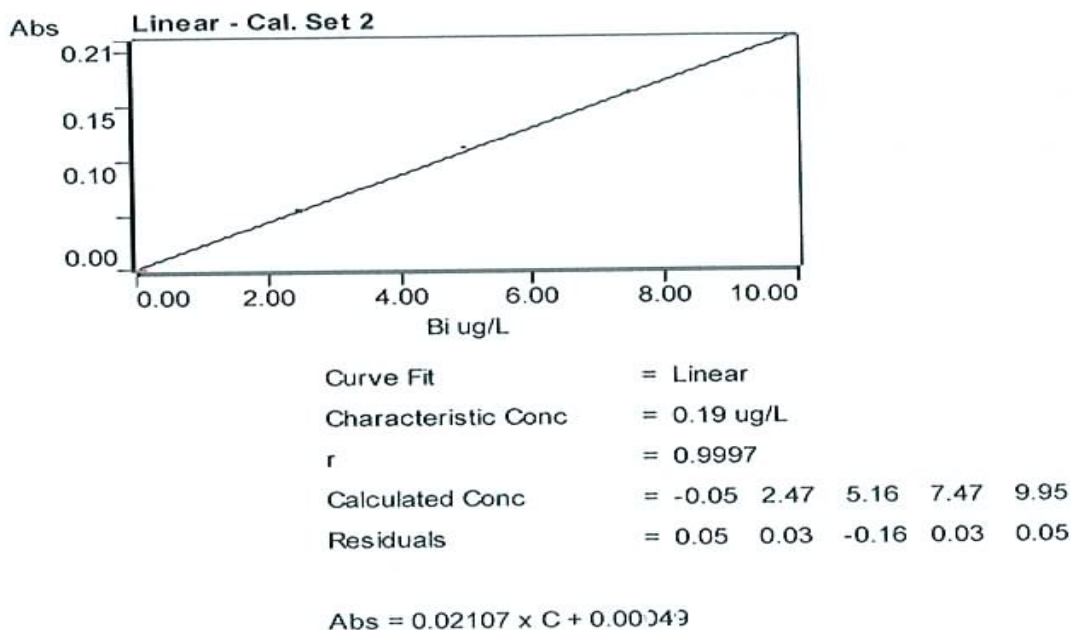


Figure 2 Calibration curves for Bismuth – HGAAS



Test results and from statistical treatment of data are presented in Tables 2 and 3.

Table 2. The performance parameters for bismuth measurement by using HGAAS.

Limit of detection (LOD)	0.06µg/L
Limit of quantification (LOQ)	0.110µg/L
Repeatability	0.02
Relative repetab.,%	0.30
Repeatability limit, µg/L	0.04
Just error, µg/L	0.07
Bias, %	1.47

Table 3. The performance parameters for bismuth measurement by using GTAAS

Limit of detection (LOD)	1.84 µg/L
Limit of quantification (LOQ)	2.98 µg/L
Repeatability	0.73
Relative repetab.,%	3.59
Repeatability limit, µg/l	2.00
Just error, µg/l	0.17
Bias, %	0.85

CONCLUSIONS

In this paper are presented two methods for bismuth determination by AAS and two separate techniques:

- AAS, with hydride generation (HGAAS).
- AAS, with graphite furnace (GFAAS).

AAS method using hydride generation (HGAAS) is more sensitive than the graphite furnace method (GFAAS), allowing an accurate determination of low concentrations of bismuth ($LOD_{HGAAS} = 0.06 \mu\text{g/L}$ and , $LOQ_{HGAAS} = 0.110 \mu\text{g/L}$, $LOD_{GFAAS} = 1.84 \mu\text{g/L}$ and , $LOQ_{GFAAS} = 2.98 \mu\text{g/L}$)

The obtained performance parameters as linearity, limit of detection [LOD], limit of quantification [LOQ], accuracy and precision, respect the theoretical values provided by specialty literature for these analytical methods permitting in this way their validation.

In order to determine bismuth from stationary emission sources the both methods can be used due to their performance parameters who are comparable.

REFERENCES

- [1] Serkan Sahan – An on-line preconcentration/separation system for the determination of bismuth in environmental samples by FAAS – *Talanta*, Volume 80, Issue 5, 15 March 2010, Pages 2127-2131;
- [2] SR EN 14385:2004 - Stationary source emissions. Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Ti, V.
- [3] Operation Manual VGA – 77 VARIAN – May 2004
- [4] L.Beach, K.Brodie, P.Doidge - *Analytical Methods for Graphite Tube Atomizers*, Varian Australia, Septembrie 1988.
- [5] Shaheb-ud Dea, Peter J. Tscheryonyi, and William J. Riley – Elimination of Matrix Effects IN Electrothermal Atomic Absorption Spectrophotometric Determination of Bismuth in Serum and Urine – *CLIN. CHEM.*38/1,119-122(1992)
- [6] Paul R.A.Froome, Abraham T. Wan, Paul M. Harrison, and Allan J. McLean- Improved Assay for Bismuth in Biological Samples by Atomic Absorption Spectrophotometry with Hydride Generation, *CLIN. CHEM.*34/2,382-384(1988)
- [7] C.G.Magalhaes, B.R. Nunes, M. B.O. Giacomelli and J. B. Borba de Silva – Direct determination of bismuth in urine samples by electrothermal atomic absorption spectrometry: study of chemical modifiers- *J. Anal. At. Spectrom.*2003,18,787-789.