

## DETERMINATION OF BERYLLIUM IN STATIONARY SOURCES EMISSIONS

M. Petrescu, E. Bucur, E. Barbu, V. Danciulescu

*National Research and Development Institute for Industrial Ecology – INCD  
ECOIND, 71-73 Drumul Podu Dambovitei street, sector 6, zip 060652,  
Bucharest, Romania, poluare.aer@incdecoind.ro*

### ABSTRACT

Systemic toxic pollutants such as heavy metals, exerts its actions on different organs and human body systems, the effect being specific to this substance.

Their spread in the environment is increasing and their accumulation in the environment and in the human body is important for the pathological changes that occur.

Beryllium is an important component of nuclear reactors as a neutron source with low neutron-absorbing capacity. Beryllium oxide is used in insulators, resistors, spark plugs and microwave tubes from the electronics industry.

Little information about atmospheric input of beryllium (Be) into ecosystems is known, despite its highly toxic behavior. Beryllium is a toxic material and an inhalation risk causing sensitization and chronic beryllium disease (CBD) to receptors.

Beryllium and its compounds are included in Class I carcinogens” according to Order 462/1993, and the emission limit value is 0.1 mg/m<sup>3</sup> at a mass flow greater that 0.5g/h.

Beryllium emissions are isokinetically sampled from the source. The particulated emissions are collected in a probe and on heated filters and the gaseous emissions are collected in a series of chilled absorbes with absorption solutions.

This paper presents the results obtained by optimizing the beryllium determination method from stationary sources emissions using electrothermal atomic absorption spectrometry (ETAAS) and at also presents the performance characteristics of the method. The limit of detection (LOD) was 0.0018 µg/m<sup>3</sup>, the linearity range under optimized condition was 0.05 -2 µg/L and the limit of quantification (LOQ) was 0.0027 µg/m<sup>3</sup>.

**Keywords:** stationary sources emissions, Be, ETAAS, isokinetically

### INTRODUCTION

Beryllium is one of the most toxic elements in the periodic table. It is responsible for the often-fatal lung disease, Chronic Beryllium Disease (CBD) or berylliosis, and is listed as a Class A EPA carcinogen. [1]

Although, acute and chronic beryllium poisoning occurs mainly by the inhalation of industrial gases and dust, the determination of trace amounts of beryllium in stationary emission sources is of interest as it can indicate

environmental pollution and could provide some information of the metal uptake through these sources.[2]

Beryllium and its compounds are included in the Class A-carcinogen by the Order 462/1993. The Emission Limit Value for beryllium is 0.1 micrograms per cubic meter at a flow mass higher than 0.5g/h.

Different methods have been used for the determination of beryllium in environmental samples. These include molecular spectrophotometer, spectrofluorimetry, inductively coupled plasma atomic emission spectrometry (ICP–AES), inductively coupled plasma mass spectrometry (ICP–MS), flame atomic absorption spectrometry (FAAS) or electro thermal atomic absorption spectrometry(ETAAS).[3]

Among these methods, ETAAS offers relatively low cost, simplicity, high selectivity and sensitivity. In ETAAS, the use of various chemical modifiers such as magnesium ammonium phosphomolybdate, lanthanum nitrate, calcium nitrate, aluminum nitrate, strontium nitrate, palladium nitrate, ammonium nitrate, and Zr have been reported for the determination of beryllium in environmental samples(3).

This paper reports determination of beryllium from stationary emission sources using atomic absorption spectrometry with atomization in a graphite tube.

The validation methodology, used in this study, includes many stages: method optimization, study of working range, linearity, accuracy and precision, and detection and quantification limits. [4, 5, 6]

## **EXPERIMENTS**

Determination of beryllium from the stationary emission sources involves an isokinetic air sampling by a process in which the waste gas is retained as particulate matters on quartz filter and the volatile forms in oxidizing absorbing solutions. Beryllium from the filter is solubilized through acid digestion and analyzed by atomic absorption spectrometry with atomization in a graphite tube spectrometry. The absorbing solutions as well as the cleaning solutions are analyzed using the same atomic absorption technique after a proper sample preparation.

### **The following materials and equipments were used:**

- Spectrometer absorption atomic Spectra AA type 280 FS, Varian with deuterium background correction, equipped with graphite tube Atomizer type GTA -120, Varian and programmable sample dispenser type PSD-12, Varian.
- Microwave digestion systems Mars 5, CEM Corporation with pressure and temperature sensor, and XP-1500Plus High Pressure Digestion Vessel accessory
- **Sampling equipment:** Isokinetic dust sampler Paul Gothe according with SR EN 14385:2004, for isokinetic sampling on filters and in absorbing solutions.
- Absorbers and filter of quartz fiber,
- Nitrogen 99.999% purity,

- Reagents: Merck solution for calibration (1000mgBe/L- AA Standard), nitric acid(65%, suprapure) for filter digestion, absorption solution, ultra pure water.

Instrument conditions and furnace programme for determination of beryllium are listed in table 1:

**Table 1**

Calibration Mode	Concentration
Measurement Mode	Peak Height
Wavelength:	234.9 nm
Slit Width:	1.0 nm
Lamp Current	5.0 mA
Background Correction	BC On
Workhead Height	13.2 mm
Total Volume	20 uL
Bulk Conc	2.000 µg/L

**Table 2.** Optimal furnace programme settings for measurements by graphite furnace

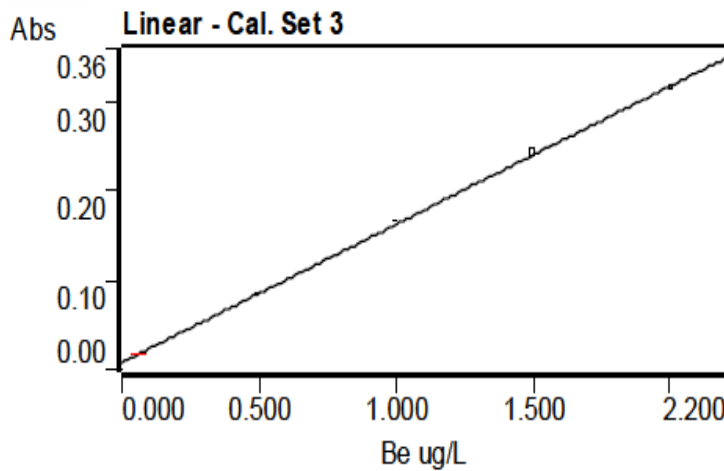
Step	Temp (C)	Time (s)	Flow (L/min)	Gas Type	Read	Signal Storage
1	85	5.0	0.3	Normal	No	No
2	95	40.0	0.3	Normal	No	No
3	120	10.0	0.3	Normal	No	No
4	1000	5.0	0.3	Normal	No	No
5	1000	1.0	0.3	Normal	No	Yes
6	1000	2.0	0.0	Normal	No	Yes
7	2300	0.7	0.0	Normal	Yes	Yes
8	2300	2.0	0.0	Normal	Yes	Yes
9	2300	0.1	0.3	Normal	Yes	Yes
10	2500	0.1	0.3	Normal	Yes	Yes
11	400	9.5	0.3	Normal	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).

For calibration curve were prepared 5 calibrating solution 0.250, 0.500, 1.000, 1.500, 2.000 µg/L Be which were measured in two replicates, with correlation coefficients (r) higher than 0.9998.

**Figure 1.** Calibration curves for Beryllium



Curve Fit	= Linear
Characteristic Conc	= -0.023 ug/L
r	= 0.9998
Calculated Conc	= 0.005 0.232 0.500 1.014 1.516 1.983
Residuals	= -0.005 0.018 0.000 -0.014 -0.016 0.017

$$\text{Abs} = 0.15387 \times C + 0.00787$$

Analytical characteristics of the methods, including:

- characteristic mass calculated as  $m_0 = 0.0044 \times 20/a$ , where **a** is the slope of the calibration curve and sample volume is 20 µL,
- the limit of detection (LOD) calculated as  $3SD/a$ , where **a** is the slope of the calibration curve and SD the standard deviation of 10 consecutive measurements of blank solutions,
- the limit of quantification (LOQ) calculated on the basis of  $10SD/a$  and
- precision (RSD, evaluated by ten replicate analyses of solutions containing 1 µg/L of beryllium) are summarized in Table 3.

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.

**Table 3.**

<b>PARAMETRU</b>	<b>CRITERIA VALUE</b>	<b>RESULTS</b>
<b>Limit of detection (LOD)</b>	0.1-2µg/L	0.036
<b>Limit of quantification (LOQ)</b>	≤ 0.250 µg/L	0.054
<b>Relative repeatability</b>	± 6-40%	2.72%
<b>Correlation coefficient</b>	r ≥ 0.995	0.9998
<b>Recovery</b>	85 – 125%	95.9%
<b>Expanded uncertainty</b>	25 -40%	16.2%

### **CONCLUSIONS**

This paper presents the results obtained by optimizing the beryllium determination method from stationary sources emissions using electrothermal atomic absorption spectrometry (ETAAS) and at also presents the performance characteristics of the method. At the optimal conditions, the technique shows good linearity with a correlation coefficient of more than 0.995 for the calibration curve.

The developed method is very sensitive with the limit of detection (LOD) was 0.0018 µg/m<sup>3</sup> and the limit of quantification (LOQ) was 0.0027 µg/m<sup>3</sup>. Also, the obtained recovery and RSDs met the specified acceptance criteria in the repeatability tests.

The presented analytical method is sufficient to determine and accurately quantify trace beryllium levels in stationary emission sources. This reveals that the proposed procedure has good accuracy and precision. This method provides substantial benefits to be simple to use, reliable and reproducible and requires instrumentation that is available in many laboratories.

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