

APPLICATION OF X-RAY FLUORESCENCE SPECTROMETRY FOR ANALYSIS OF SLUDGE FROM MINE WATER TREATMENT

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A method for simultaneous analysis of Fe, Mn, Al, Ca, Mg, Cd, Cr, Cu, Hg, Ni, Pb, Zn and As from mine water treatment sludge was developed using an NEX CG - Energy Dispersive X-ray Fluorescence Spectrometer.

The XRF analysis results were verified with other consecrated method such AAS and ICP-MS using standardized methodologies, including pretreatment of samples.

Good correlation of results between methods was achieved (usually 0.93-0.98).

Minimum sample preparation (drying, sieving and prolene cup preparation) is needed, and up to 4 samples can be analyzed per hour.

Usual limit of detection for analyzed elements was between 3 and 30 mg/Kg dw, with higher limits for light elements as Mg (384 mg/Kg dw) Al(162 mg/Kg dw).

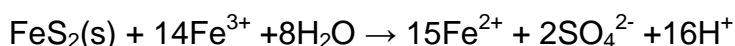
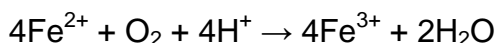
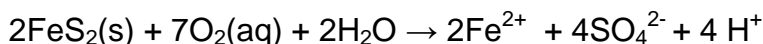
XRF analysis method was successfully used for analysis of some precipitates obtained from mine waters using various precipitation methods. Mine water was sourced from some closed Romanian mines.

Keywords: Energy Dispersive X-ray Fluorescence, mine water treatment, heavy metals.

Introduction

One major challenge in the field of environmental protection is represented by acidic mine drainage (AMD). The primary cause of AMD is the biochemical oxidation of sulphide minerals (e.g. *pyrites* FeS₂, *chalcopyrite* CuFeS₂, *sphalerite* ZnS) in the presence of water and oxygen [1, 2].

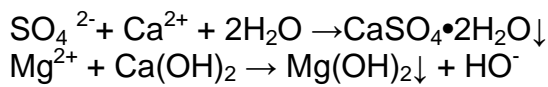
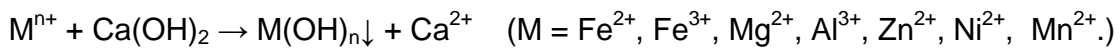
The reactions involving the oxidation of pyrite are expressed as follows [3]:



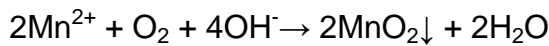
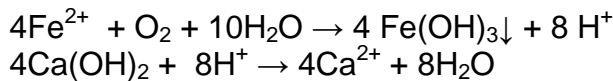
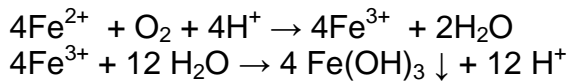
This autocatalytic process will proceed in a similar way for the other metal sulphides, the result being the acidic mine water loaded with heavy metal ions and the associated sulphate ion. As the acidic water is percolating the rock, other compounds will be dissolved (such as calcium and magnesium sulphates or carbonates, aluminosilicates by acid attack). The environmental impact of the AMD is due to heavy metals and acidity.

One of the most common treatment method for the heavily polluted mine waters is the lime neutralization and oxidation of Fe²⁺ and Mn²⁺ with air oxygen[4]. The final stage of the liming process will produce a sludge containing species with low solubility as the heavy metals will precipitate as hydroxide, oxyhydroxides or oxides. The sludge will also include carbonates and calcium sulphate (if the sulphate concentration for the mine water is over 1,5 mg/l). Magnesium will precipitate as hydrotalcite Mg₆Al₂(CO₃)(OH)₁₆·4H₂O or magnesium hydroxide, depending on the reactor pH (usually 8.5, but up to 10.0).

The precipitation process can be represented by the general equations:



Oxidation and precipitation of Fe²⁺ and Mn²⁺ (pH ≥ 9.0)



The basic flow-sheet for the lime treatment of mine water is as shown in Fig. 1

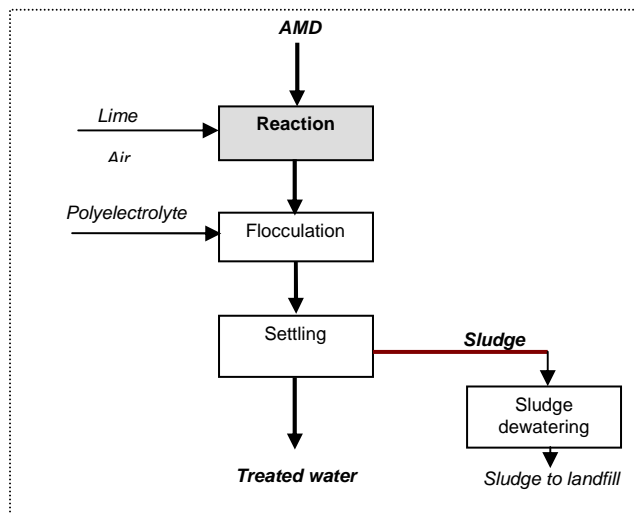


Figure 2 AMD treatment flow sheet

The composition of the obtained sludge is an important parameter required by environmental legislation, but also useful for the treatment evolution (e.g. for step neutralization).

Usual analysis of the sludge include total digestion determine the concentrations of components, even when the primary research is based on partial chemical extractions. Although there are many total digestion procedures, all are relatively time consuming and involve the use of highly hazardous chemicals. The ideal solution to this problem is a rapid, non-destructive technique for total elemental analysis of the sample, which can be used in conjunction with other analytical procedures. Energy dispersive X-ray fluorescence (XRF) analysis meets all of these requirements the major drawbacks being relatively low sensitivity and some matrix interference with obtained values.

The basis of any XRF technique is the photoelectric fluorescence x-ray generated, that produce characteristic secondary X-rays in a sample [5]. Energies of the secondary X-rays generated within the sample are characteristic for the source elements, and the rate of emission is largely a function of the concentration and absorption of the outgoing X-rays by the sample, as can be seen in figure 1.

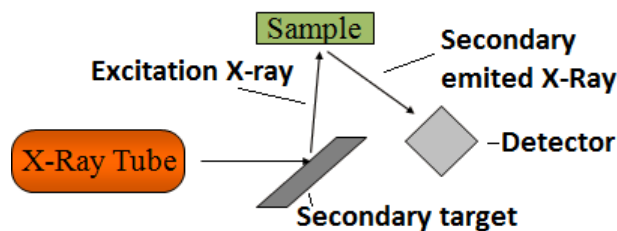


Figure 3 Principle of XRF

For analysis of the sludge obtained after treatment, an EDXRF method was developed. The advantages of XRF analysis method are fast, non-destructive analysis, easy sample preparation protocol, good accuracy and repeatability and high range of concentrations that can be determined, from mg/Kg to 100% of sample mass [6-9].

Experimental procedure

AAS and ICP-MS

The soil samples were digested [10] using *aqua regia* digestion method. 3 g of soil was placed in a 100mL round bottom flask with 21mL of concentrated HCl (35%) and 7mL concentrated HNO₃ (65%). The solution was heated until total volume drop to ~5mL. Dissolved samples were then diluted with approx. 20 mL of deionised water and filtered using a Whatman No. 42 filter. The filtered residue was rinsed three times with 5mL of water and the solution was made up to 50 mL. All solutions were prepared with deionised water. The above procedure was also used to obtain a blank and control samples and all samples

were blank-corrected. Concentrations of Fe, Mn, Al, Ca, Mg, Cd, Cr, Cu, Ni, Pb, and Zn in the digested samples were determined using AAS, using a Novaa300 atomic absorption spectrometer produced by Analytik Jena AG, Germany. Concentrations of Ba, Hg, and As in the digested samples were determined using an ICP-MS Aurora 90, produced by Brucker, USA.

Calibration was carried out using multi-element standard solutions. Digested samples which exceed calibration range were correspondingly diluted

EDXRF analyses were performed using a Rigaku CG instrument [11] obtained from Rigaku, Japan. X-ray tube has 50W power and has a single target (anode), made by Pd. The Pd tube has high excitation efficiency for heavy and light elements with its characteristic X-rays of the K- and L-series. An SDD (silicon drift detector) with Peltier cooling system is used to collect electrons produced when X-rays irradiate the sample. The secondary target is selected automatically according to components contained in a sample and elements to be analyzed, in following conditions:

Secondary target	Tube voltage (kV)	Tube current (mA)	Measurement time (sec)	Element analyzed
Al	50	auto	200	Mo, Cd, Sb, Se, Ba
Mo	50	auto	100	Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Hg, Pb
Cu	50	auto	100	Ca, Cr, Mn, Fe, Ni, Cd, Ba
RX9	25	auto	100	Mg, Al, Ca, Zn, Mo, Pb.

All characteristic lines of analyzed elements were automatically assigned by software. Diaphragm opening was set at 20 mm.

Samples were analyzed in semi-quantitative mode under vacuum.

Sludge was filtered under vacuum, then dried at 105 °C. Dried samples were then homogenized using a mortar. No sieving was needed. Approximately 3 g of dried material was added to XRF polypropylene cup (32 mm diameter) equipped with Prolene transparent film, then added to sample carousel and analyzed.

Experimental results

For method testing, 5 different sludge types produced by treatment of different acid mine water sources were sampled. Samples were collected over time in our laboratory. Samples were prepared as was described previously and then analyzed. The comparison of obtained values is presented in tables no.1-3. Every sample was analyzed using the XRF method 3 times and in parallel, samples were analyzed by AAS.

Tables 4, 5 and 6 - Comparison between XRF and other analysis methods for selected elements, expressed as mg/Kg dry weight.

Element		Fe		Mn		Al		Ca		Mg	
Method		XRF	AAS	XRF	AAS	XRF	AAS	XRF	AAS	XRF	AAS
Sample	A1	4300 0 ±70.6	4180 0	2500 0 ±80.2	2300 0	11700 0 ±332	10800	24700 0 ±476	22300 0	1690 0 ±371	1730 0
	A2	6180 0 ±65.5	6260 0	5980 ±41.4	5730	88800 ±267	93000	20100 0 ±421	18900 0	6280 0 ±459	6110 0
	A3	3370 0 ±70.3	3320 0	8150 ±55.6	7800	11000 0 ±336	11800 0	29400 0 ±501	27300 0	1360 0 ±381	1410 0
	A4	3600 0 ±74.3	3410 0	1270 0 ±66.1	1210 0	12700 0 ±328	13020 0	23800 0 ±426	24000 0	2830 0 ±390	2550 0
	A5	4220 0 ±71.2	3950 0	5720 ±24.6	6300	12300 0 ±311	11800 0	21800 0 ±404	21300 0	2620 0 ±365	2180 0

Element		Zn		Ni		Pb		Cd		Cr	
Method		XRF	AAS	XRF	AAS	XRF	AAS	XRF	AAS	XRF	AAS
Sample	A1	2590 ±16.1	2320	99.6 ±4.62	102	18.3 ±1.66	19	9.26 ±1.72	11.2	153 ±8.8	161
	A2	5110 ±21.9	4830	40.9 ±3.38	38	51.5 ±3.02	53	ND	1.6	76.4 ±7.29	83
	A3	2990 ±17.5	2320	39.7 ±3.58	36	14.3 ±1.55	12	4.47 ±1.51	4.1	198 ±8.25	184
	A4	13200 ±36.1	14800	73.4 ±4.23	76	20.2 ±1.68	23	12.9 ±1.87	10.8	159 ±7.72	131
	A5	20100 ±44.4	23000	61.4 ±3.83	64	64.2 ±2.61	60	14.8 ±1.99	16.2	158 ±6.92	142

Element		Cu		As		Hg	
Method		XRF	AAS	XRF	AAS	XRF	AAS
Sample	A1	150±4.61	127	46.3±1.67	42.3	ND	<1
	A2	2990±19.6	2300	153±2.76	143	ND	<1
	A3	70.7±3.39	75	20.1±1.17	18.2	ND	<1
	A4	112±4.26	121	25.5±1.34	22	ND	<1
	A5	107±5.14	114	13.8±1.47	14.1	13.6±2.17	12.3

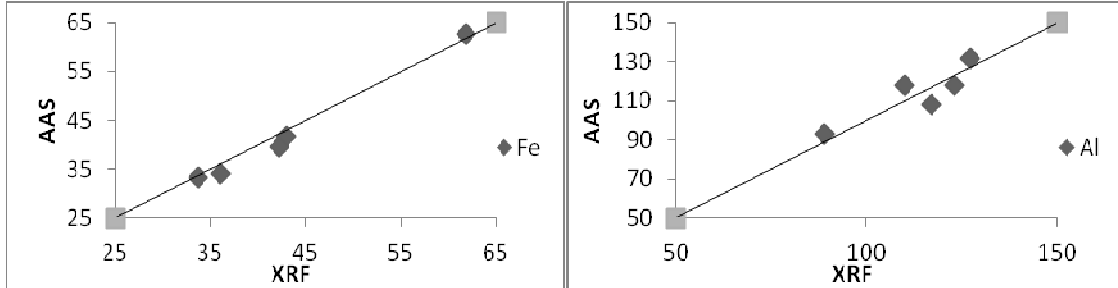


Figure 4 XRF vs. AAS for Fe and Al (g/Kg dw) from 5 samples comparatively analyzed

Mo, Se, and Sb were also searched using XRF, but they were not detected in any of analyzed materials because of low concentration of those elements in analyzed matrix. Mercury was found only in one sample.

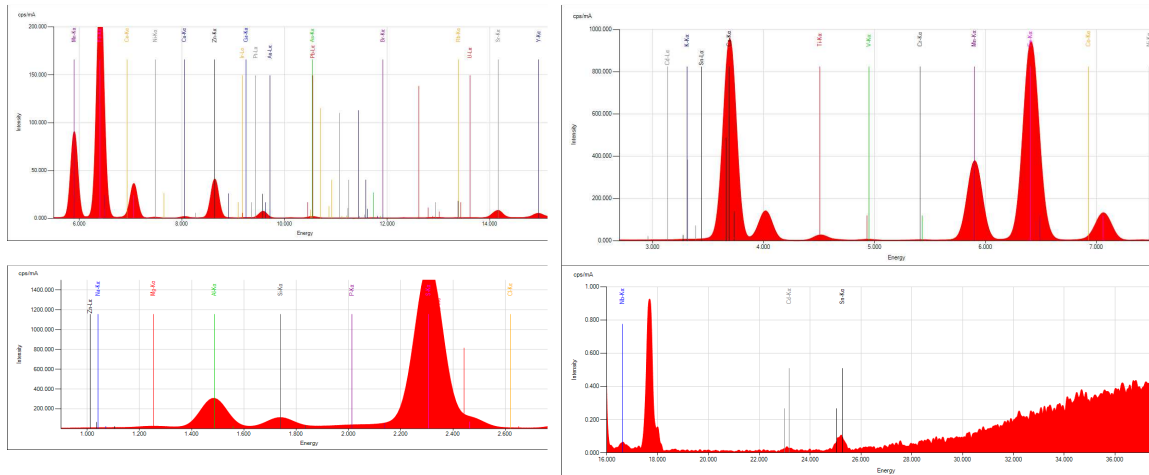
Limit of detection

The usual practice in analytical chemistry is to define the detection limit in terms of uncertainty in the blank. A value of two or three times the standard deviation of the blank value is arbitrarily accepted as the detection limit. This approach can seldom be used directly for XRF because appropriate blanks rarely exist. However, an analogous approach is possible, using samples with low but known concentrations. Instead of using the standard deviation, the standard error of regression for samples with low known concentrations is substituted. Detection limits for the reference materials were determined using this approach.

Table 7 LOD for analyzed elements from AMD sludge using the XRF method

Element	Fe	Mn	Al	Ca	Mg	Zn	Ni
LOD (mg/Kg dw)	39,55	24,72	162,4	31,18	384	4,128	6,61
Element	Pb	Cd	Cr	Cu	As	Hg	
LOD (mg/Kg dw)	4,12	3,65	16,98	6	2,74	5,7	

Table 8 Typical XRF spectrums obtained with different secondary targets 1) Mo, 2) Cu, 3) RX9, 4)Al for sludge obtained after AMD treatment.



Conclusion

XRF analysis proved to be a useful tool for analysis of the sludge obtained after treatment of acidic mine drainage, with a good correlation with values obtained with standardized methods employing AAS and ICP-MS.

In the way of improving a pilot AMD treatment station efficiency, present method will be used to analyze various sludge samples.

Good sensitivity was gained, with detection limits varying between 3 and 30 mg/ kg dw for most of elements and some higher values for lighter elements (Mg, Al) or for those in high amount (ex: Fe).

Analyzed matrices were characterized by high amount of Fe, Mn, Zn and Mg, Al, Ca precipitated during treatment, as well as Ca is introduced with the lime.

References

1. BLOWES D., PTACEK C., JAMBOR J., WEISNER C., Treatise on geochemistry, **9**, nr., 2003, p. 149.
2. JOHNSON D. B., HALLBERG K. B., Research in Microbiology, **154**, nr. 7, 2003, p. 466.
3. SINGH G., RAWAT N. S., International journal of mine water, **4**, nr. 1, 1985, p. 17.
4. JOHNSON D. B., HALLBERG K. B., Science of the total environment, **338**, nr. 1, 2005, p. 3.
5. DANET A., *Analiza instrumentala*, Editura Universitatii din Bucuresti, 2010.
6. KALNICKY D. J., SINGHVI R., Journal of hazardous materials, **83**, nr. 1, 2001, p. 93.
7. BOYLE J. F., Journal of Paleolimnology, **23**, nr. 2, 2000, p. 213.
8. KIDO Y., KOSHIKAWA T., TADA R., Marine geology, **229**, nr. 3, 2006, p. 209.
9. KOT B., BARANOWSKI R., RYBAK A., Polish Journal of Environmental Studies, **9**, nr. 5, 2000, p. 429.
10. RADU T., DIAMOND D., Journal of hazardous materials, **171**, nr. 1, 2009, p. 1168.
11. RIGAKU, <http://www.rigaku.com/products/xrf/nexcg>.

DETERMINATION OF BERYLLIUM IN STATIONARY SOURCES EMISSIONS

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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^3 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 $0.0018 \text{ } \mu\text{g/m}^3$, the linearity range under optimized condition was $0.05 - 2 \text{ } \mu\text{g/L}$ and the limit of quantification (LOQ) was $0.0027 \text{ } \mu\text{g/m}^3$.

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

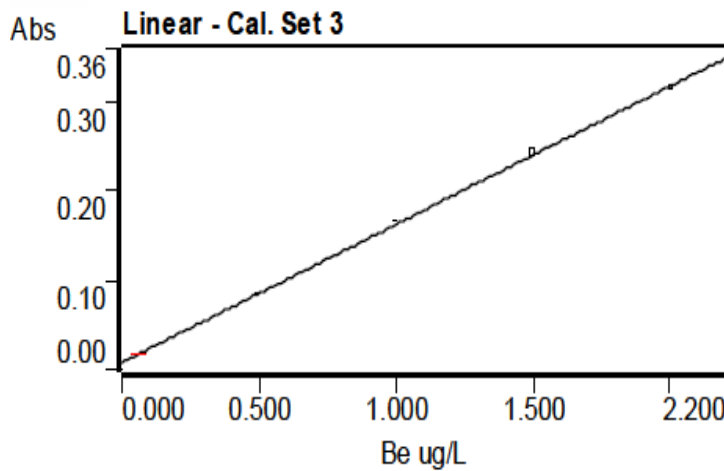
Step	Temp (C)	Time (s)	Flow (L/min)	Gas Type	Read	Signal Storage
1	85	5.0	0.3	Normal	No	No
2	95	40.0	0.3	Normal	No	No
3	120	10.0	0.3	Normal	No	No
4	1000	5.0	0.3	Normal	No	No
5	1000	1.0	0.3	Normal	No	Yes
6	1000	2.0	0.0	Normal	No	Yes
7	2300	0.7	0.0	Normal	Yes	Yes
8	2300	2.0	0.0	Normal	Yes	Yes
9	2300	0.1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

PARAMETRU	CRITERIA VALUE	RESULTS
Limit of detection (LOD)	0.1-2µg/L	0.036
Limit of quantification (LOQ)	≤ 0.250 µg/L	0.054
Relative repeatability	± 6-40%	2.72%
Correlation coefficient	r ≥ 0.995	0.9998
Recovery	85 – 125%	95.9%
Expanded uncertainty	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/m³ and the limit of quantification (LOQ) was 0.0027 µg/m³. 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.

REFERENCES

1. TAYLOR T.P., DING M., EHLER D.S., FOREMAN T.M., KASUBA J.P. AND SAUER N.N., Environ. Sci. Health J., Part A, nr. 38,2003, p.439–469.
2. MARK S., RICHARD K B., GARY RR, Sci Total Environ, vol.437, 2012, p.373-383.
3. I. HAGAROVÁ, L. MACHÁČKOVÁ, M. ŽEMBERYOVÁ, V. NÁVOJOVÁ-Global NEST J., Vol 14, No 1, 2012, p. 40-47.
4. SR EN 14385:2004 - „ Stationary source emissions. Determination of the total emission of As, Cd, Cr,Co,Cu, Mn,Ni, Pb, Sb, Tl, V.
5. MDHS 29/2- Beryllium and beryllium compounds in air. Methods for the Determination of Hazardous Substances.
6. PROFUMO A., SPINI G., CUCCA L., PESAVENTO M. Talanta vol 57,2002, p. 929-934.