

THE ROLE OF ALUMINUM IN THE SYMPTOMATOLOGY OF ATTENTION DEFICIT HYPERACTIVITY DISORDER CHILDREN

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ABSTRACT

ALUMINUM IS A CHEMICAL ELEMENT ATOMIC NUMBER 13. IT IS WHITE-SILVER, INSOLUBLE IN WATER UNDER NORMAL CONDITIONS. DESPITE ITS NATURAL ABUNDANCE, ALUMINUM HAS NO KNOWN BIOLOGY FUNCTION. IT IS A TOXIC RESIDUE, ALUMINUM SULPHATE HAVING AN LD50 OF 6207 MG/KG BODY, CORRESPONDING TO 500 GRAMS PER 80 KG PERSON. EXTREMELY ACUTE TOXICITY WITHOUT HARM TO HEALTH IS OF INTEREST IN VIEW OF THE WIDESPREAD OCCURRENCE OF THE ELEMENT IN THE ENVIRONMENT AND IN TRADE⁷. TOXICITY CAN BE TRACKED AFTER DEPOSITION INTO THE BONES AND THE CENTRAL NERVOUS SYSTEM AND IS PARTICULARLY HIGH IN PATIENTS WITH RENAL INSUFFICIENCY. BECAUSE ALUMINUM COMPETES WITH CALCIUM FOR ABSORPTION, INCREASED ALUMINA CAN CONTRIBUTE TO OSTEOPENIA, PRETERM AND GROWTH RETARDATION. IN VERY HIGH DOSES, ALUMINUM CAN CAUSE NEURO TOXICITY ASSOCIATED WITH ALTERED FUNCTION OF THE BLOOD-BRAIN BARRIER⁸.

OBJECTIVES

THE STUDY PROPOSES A COMPARISON OF THE CONCENTRATION OF URINE ALUMINUM HARVESTED FROM A GROUP OF CHILDREN DIAGNOSED WITH ADHD VERSUS THE NORMAL "CHILDREN'S HOMES SOS CHILDREN'S VILLAGES" AND THE ANALYSIS OF THE INFLUENCE OF THE SEX OF THE CHILDREN ON URINE CONCENTRATIONS OF ALUMINUM.

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⁷ Helmboldt O. Aluminum Compounds, Inorganic. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, 2007

⁸ Banks W.A., Kastin A.J. Aluminum-induced neurotoxicity: alterations in membrane function at the blood-brain barrier. Neurosci Biobehav Rev, 1989, 13 (1): 47-53

DETERMINATION OF THE URINARY CONCENTRATION OF ALUMINUM, PERFORMED BY THE ATOMIC ABSORPTION SPECTROMETER WITH ATOMIZATION IN GRAPHITE FURNACE TECHNIQUE (GF-AAS)⁹. WAS USED TO DETERMINE THE ALUMINUM CONCENTRATION IN THE INJECTION MATRIX.

CONCLUSIONS

THERE IS NO SIGNIFICANT DIFFERENCE BETWEEN THE AVERAGE URINE CONCENTRATIONS OF THE TWO GROUPS OF NORMAL CHILDREN AND THE SYMPTOMS OF ADHD.

IT CAN BE ARGUED THAT THE OCCURRENCE OF SYMPTOMATIC SYMPTOMS CHARACTERISTIC OF ADHD CAN NOT BE CORRELATED WITH THE PRESENCE OF ABNORMAL VALUES OF ALUMINUM IN SUBJECTS WITH ADHD.

THE ANALYSIS OF ALUMINUM URINE CONCENTRATIONS IN CHILDREN WITH ADHD RELATIVE TO THE URINARY CONCENTRATION OF THESE ELEMENTS IN CHILDREN WITHOUT ADHD DID NOT REVEAL ANY STATISTICALLY SIGNIFICANT DIFFERENCE. THESE RESULTS SHOW THAT ALUMINUM CAN NOT BE RESPONSIBLE FOR THE PRESENCE OF ADHD SYMPTOMS.

THE DEVELOPED OPTOELECTRONIC METHOD IS RELATIVELY SIMPLE, REPRODUCIBLE AND HAS A SENSITIVITY THAT ALLOWS ANALYSIS OF THE COBALT CONCENTRATION IN THE URINE SAMPLES.

KEY WORDS: ADHD, URINE, ALUMINIUM, GF-AAS

INTRODUCTION

Aluminum is a chemical element atomic number 13. It is white-silver, insoluble in water under normal conditions. It is a common chemical element, occupying the third position, after oxygen and silicon, SD a terrestrial spread of 7.4%. Aluminum compounds make up 8.13% of the earth's crust, being found in mineral substances SD well SD in the plant and animal world. It is naturally occurring in the form of minerals, silico aluminates (feldspar, small clays), cryolite (sodium fluoaluminate), bauxite, and corindone. After iron, it became the most widely used metal. Aluminum was noted for being a lightweight metal with a density of 2.7 g/cm³. This quality makes it used in large quantities in the naval and aeronautical industries. High reflectivity is used in the construction of metal mirrors¹⁰. Aluminum is remarkable for its low metal density and its ability to withstand corrosion. Despite its prevalence in the environment, aluminum salts are not known to be used by any form of life. According to its omnipresence, aluminum is well tolerated by plants and animals¹¹.

Aluminum is durable, ductile and malleable, with looks ranging from silver to gray matte, depending on the surface roughness. It is non-magnetic and does not light easily. Aluminum alloys have yield strength ranges ranging from 200 MPa to 600 MPa¹². Aluminum

⁹ Ionică M. Dispozitive optoelectronice pentru măsurarea radiației electromagnetice ultraviolete, vizibile sau infraroșii. Curs anul II masterat Optoelectronică 2017/2018, Departamentul Tehnologie Electronică și Fiabilitate, Facultatea de Electronică Telecomunicații și Tehnologia Informației, Universitatea „Politehnica” din București; Davițoiu A.M. Bărcănescu Ș., Negulescu V.Al., Avram O., Voicu V.A., Macovei R., Tudosie M., Caragea G., Forje M., Mladin C., Fragkos A., Ardelean L., Bumbea V. Selenium removal study in patients with chronicrenal disease. Therapeutics pharmacology and clinical toxicology, December 2013, Vol. XVII: 167-177

¹⁰ Shakhashiri B.Z. Chemical of the Week: Aluminum. *SciFun.org*. University of Wisconsin, 17 March 2008

¹¹ Helmboldt O. Aluminum Compounds, Inorganic. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, 2007

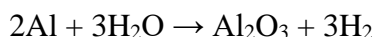
¹² Polmear I.J. Light Alloys: Metallurgy of the Light Metals (3rd ed.). Butterworth-Heinemann, 1995

has about one-third of the density and stiffness of the steel. It is easy to process, cast, draw and extrude.

Aluminum atoms are arranged in a cubic-centered structure. Aluminum has a stacking energy of approximately 200 MJ/m^2 ¹³. Aluminum is a good thermal and electric conductor, having 59% of the conductivity of copper both thermally and electrically, with only 30% of the copper density. Aluminum is capable of being a superconductor with a critical superconductor temperature of 1.2 Kelvin and a critical magnetic field of about 100 Gauss (10 mT)¹⁴.

CHEMICAL PROPERTIES

Corrosion resistance can be excellent due to a thin layer of aluminum oxide that forms when the metal is exposed to air, effectively preventing oxidation. The strongest aluminum alloys are resistant to corrosion due to galvanic copper alloy reactions¹⁵. Due to the corrosion resistance, aluminum is one of the few metals that retain silver reflection in the form of fine dust. Aluminum is oxidized by water to produce hydrogen and heat:



This conversion is of interest to hydrogen production. The formed oxide layer inhibits the storage of the energy of the regeneration of metals¹⁶.

ALUMINUM ISOTOPES

Aluminum has many known isotopes, only ²⁷Al (stable isotope) and ²⁶Al (radioactive isotope, $t_{1/2} = 7.2 \times 10^5$ years) occur naturally. ²⁷Al has a natural abundance of over 99.9%. ²⁶Al is produced from argon. The ratio between ²⁶Al and ¹⁰Be was used to study the role of transport, deposition, sediment storage and erosion over time¹⁷. Meteorite research has shown that ²⁶Al was relatively abundant when it was planetary. Most scientists believe that the energy released by meteorites through ²⁶Al disintegration was responsible for melting and differentiating asteroids 4.5 billion years ago¹⁸.

THE BIOLOGICAL ROLE OF ALUMINUM

Despite its natural abundance, aluminum has no known biology function. It is a remarkable toxic, aluminum sulfate having an LD50 of 6207 mg/kg (oral dose) corresponding to 500 grams per 80 kg person. Extremely acute toxicity without harm to health is of interest in view of the widespread occurrence of the element in the environment and in trade¹⁹. Toxicity can be tracked after deposition into the bones and the central nervous system and is particularly

¹³ Dieter G.E. Mechanical Metallurgy. McGraw-Hill, 1988

¹⁴ Cochran J.F., Mapother D.E. Superconducting Transition in Aluminum. Physical Review 111 (1): 132–142. Bibcode 1958 PhRv: 111-132C

¹⁵ Cochran J.F., Reaction of Aluminum with Water to Produce Hydrogen. U.S. Department of Energy. January 1, 2008

¹⁶ Dickin A.P. In situ Cosmogenic Isotopes. Radiogenic Isotope Geology. Cambridge University Press. 2005

¹⁷ Dickin A.P. In situ Cosmogenic Isotopes. Radiogenic Isotope Geology. Cambridge University Press. 2005

¹⁸ Dodd R.T. Thunderstones and Shooting Stars. Harvard University Press. 1986: 89–90

¹⁹ Shakhshiri B.Z. Chemical of the Week: Aluminum. *SciFun.org*. University of Wisconsin, 17 March 2008

high in patients with renal insufficiency. Because aluminum competes with calcium for absorption, increased amounts of aluminum can contribute to osteopenia in preterm and growth retarded children. In very high doses, aluminum can cause neuro toxicity associated with altered function of the blood-brain barrier²⁰. A small percentage of people are allergic to aluminum. Other issues are related to contact dermatitis, digestive disorders, vomiting, or other symptoms when contacting or ingesting products containing aluminum, such as deodorants or antacids. Seafaring personnel, who come into direct contact with aluminum through the nature of the profession, have not been found to have any higher values than the average population²¹. In non-allergic patients, aluminum is not as toxic as other metals, but there is some evidence of toxicity if consumed in excessive amounts²². In patients with chronic renal disease, due to modification of dialysis technology, aluminum contamination of the dialyzer was significantly reduced²³. Although the use of aluminum cans has not been shown to be harmful, in general, excessive use of antacids with aluminum compounds offers several significant levels of exposure.

Studies have shown that the consumption of acidic foods or fluids in aluminum vessels increases significantly the absorption of aluminum²⁴. Furthermore, aluminum increases estrogen secretion associated with gene expression in neoplastic breast cells²⁵. These effects have led to their classification as metalloestrogens.

The effects of aluminum in antiperspirants have been examined for decades, with little evidence of skin irritation²⁶. There is little evidence that normal exposure to aluminum poses a risk to healthy adults²⁷. There are also studies on the risks associated with increased exposure to metal²⁸. Aluminum in food can be absorbed more from water²⁹. The role of aluminum as a

²⁰ Helmboldt O. Aluminum Compounds, Inorganic. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, 2007

²¹ Ionică M., Macovei R., Caragea G., Dănescu I. Aluminium levels determination by GF-AAS for aircraft employees. 45th Congress of the European Societies of Toxicology, 05-08 octombrie 2008, Rhodes, Greece. TOXICOLOGY LETTERS, vol. 180, Supplement 1: S128-S129; Ionică M., Voicu V., Rusea D., Macovei R., Caragea G., Forje M. Urine aluminium levels in airport technical involved employees. Balkan Military Medical Committee 10th Anniversary Congress, 2-6 octombrie 2005, Varna, Bulgaria

²² Abreo V. The Dangers of Aluminum Toxicity. Archived from the original on 18 April 2009

²³ Păun S.C., Tudose M.S., Macovei R., Ardelean Luminița, Bumbea Viorica, Caragea Genica, Ionică M., Mircioiu C., Piperea-Sianu A., Mladin C. Evaluation and modeling of kinetics of aluminium in plasma and dialysis fluid. Therapeutics, Pharmacology and Clinical Toxicology Vol XVI, Number 4, December 2012: 269 – 273

²⁴ Slanina P., French W., Ekström L.G., Löf L., Slorach S., Cedergren A. Dietary citric acid enhances absorption of aluminum in antacids. Clinical Chemistry (American Association for Clinical Chemistry), 1986, 32 (3): 539–541; Van Ginkel M.F., Van Der Voet G.B., D'haese P.C., De Broe M.E., De Wolff F.A. Effect of citric acid and maltol on the accumulation of aluminum in rat brain and bone. The Journal of laboratory and clinical medicine, 1993, 121 (3): 453–60

²⁵ Darbre P.D. Metalloestrogens: an emerging class of inorganic xenoestrogens with potential to add to the oestrogenic burden of the human breast. Journal of Applied Toxicology, 2006. 26 (3): 191–7

²⁶ Shakhshiri B.Z. Chemical of the Week: Aluminum. *SciFun.org*. University of Wisconsin, 17 March 2008

²⁷ Gitelman H.J. Physiology of Aluminum in Man, in Aluminum and Health, CRC Press, 1988

²⁸ Ferreira P.C., Piai Kde A., Takayanagui A.M., Segura-Muñoz Aluminum as a risk factor for Alzheimer's disease. Revista Latino-americana de enfermagem, 2008, 16 (1): 151–7

²⁹ Yokel R.A., Hicks C.L., Florence R.L. Aluminum bioavailability from basic sodium aluminum phosphate, an approved food additive emulsifying agent, incorporated in cheese. Food and chemical toxicology, 2008, 46 (6): 2261–6

factor in Alzheimer's disease is controversial³⁰. According to the Alzheimer Society, studies have not convincingly demonstrated a causal relationship between aluminum and Alzheimer's disease³¹. However, some studies such SD those on the PAQUID cohort cite exposure to aluminum SD a risk factor for Alzheimer's disease. Some brain plates have been found with high levels of aluminum³².

In any case, if there is no toxicity of aluminum, this aspect must be linked to a very specific mechanism, because the total human exposure of the clay-dust element to the natural soil is extremely high. There is no scientific consensus on the possibility that exposure to aluminum may directly increase the risk of Alzheimer's disease³³.

OBJECTIVES

The study aims to make a comparison between the concentrations of urine from the batch of children diagnosed with ADHD compared to those in the “*Children's House SOS Children's Villages*” and to analyze the influence of the sex of the children on the urinary concentrations of aluminum. Determination of the urinary concentration of aluminum was done by the atomic absorption spectrometer with atomization in graphite furnace, (GF-AAS)³⁴.

MATERIAL AND METHOD

The study was conducted between 2013 and 2014 at the “Children's home - SOS Children's Villages” on a 50-child group divided into two groups:

- A group, consisting of 25 children without ADHD, Sex repatriation was: 12 boys and 13 girls;
- B group of 25 children with ADHD, broken down by sex SD follows: 14 boys and 11 girls.

The criteria for inclusion of children in A group were:

- age between 7 and 15 years.

Criteria to exclude children in A group:

- the existence of psychiatric diagnosis (mental deficiency, autism, psychosis, etc.);
- the existence of chronic neurological diseases: paresis, infantile brain paralysis, etc.

Criteria for inclusion of children in B group:

- ages 7 to 15;
- ADHD diagnosis: hyperkinetic disorder accompanied by attention deficit, hyperkinetic disorder accompanied by impulsivity;

³⁰ Ferreira P.C., Piai Kde A., Takayanagui A.M., Segura-Muñoz Aluminum SD a risk factor for Alzheimer's disease. *Revista Latino-americana de enfermagem*, 2008, 16 (1): 151–7

³¹ Yokel R.A., Hicks C.L., Florence R.L. Aluminium and Alzheimer's disease, The Alzheimer's Society. Retrieved 30 January 2009.

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³⁴ Polmear I.J. *Light Alloys: Metallurgy of the Light Metals* (3rd ed.). Butterworth-Heinemann, 1995; Dieter G.E. *Mechanical Metallurgy*. McGraw-Hill, 1988

- duration of pharmacological treatment prior to inclusion in the group, less than or equal to 6 months;

- the possibility of following outpatient treatment.

Sex was not a selection criterion.

Criteria for exclusion of children in B group were:

- children with ADHD who also have other chronic conditions that may influence the quality of life (neurosis, anxiety, dissociation, organic diseases);

- the presence of mild, moderate or severe mental deficiency;

- the presence of neurological deficits of language reception;

- lack of compliance.

From all subjects enrolled in the study, urine was collected from the spot (10 mL).

To determine the concentration of cobalt in urine specimens, was used a Varian graphite atomizer coupled with atomic absorption spectrometer system.

Atomic Absorption Spectrometer - AAS 800.

Programmable sample dispenser, standards, modifiers and thinner – PSD.

Water Chiller Model Neslab CFT 33.

Domnick Hunter Nitrogen Generator.

Argon - gas cylinder under pressure purity 99.9999%.

Reagents and equipment specific to a laboratory of analytical toxicology.

To determine the incriminated cobalt in the occurrence of symptoms characteristic of ADHD syndrome, the following methods were used for the analytical toxicology laboratory.

SAMPLE PREPARATION

In 10 ml of urine harvested from each subject in the study lot, 1 ml of 65% HNO₃ was added. The mixture was left in the tube for 20 min and subsequently centrifuged at 2500 rpm for 10 min.

The supernatant was the matrix for analysis on GF-AAS.

OPTOELECTRONIC AAS METHOD FOR ALUMINUM

To determine the concentration of aluminum in the injection matrix, the method used for the GF-AAS Varian system shown in Table 1 and Table 2.

RESULT AND DISCUSSIONS

The average of the urine concentrations of the aluminum was 10.54 µg/L with SD of 9.6 and ASD of 1.42. Sex analysis shows that the average urine concentration in boys was 12.12 µg/L with SD of 9.68 and ASD of 1.98 and in girls, the mean was 8.18 µg/L with SD of 9.26 and ASD of 1.89. The results are shown in Fig. 1. These results show a large distribution of urine concentrations of aluminum. The urinary concentration of aluminum allowance for children is in the range 5 - 30 µg/L³⁵. All children were within the permissible limits of urine concentrations of aluminum. Analysis by Sex shows that the value of urine concentrations of

³⁵ Helmboldt O. Aluminum Compounds, Inorganic. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, 2007

aluminum in girls is less than 3.92 $\mu\text{g/L}$ than that of boys. However, the odd Student test shows that the two urinary concentrations of aluminum do not differ significantly statistically for a probability $p > 0.2$. No value of urine concentrations of aluminum exceeds the maximum allowed, which shows that there can be no aluminum contamination of the children in the studied group.

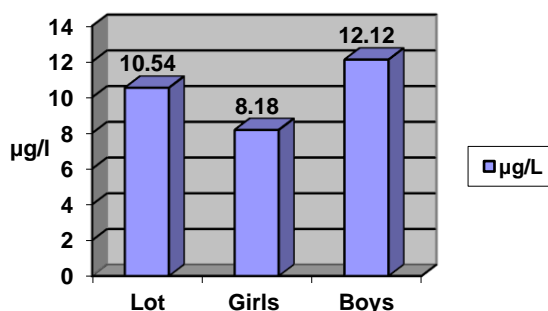


Fig. 1. Distribution of concentrations of aluminum in urine samples.

Within group A, the mean urine concentrations of aluminum were 10.2 $\mu\text{g/L}$ with an SD of 8.27 and an ASD of 1.76. Sex analysis shows that the average urine concentration in boys was 11.16 $\mu\text{g/L}$ with SD of 7.49 and ASD of 2.262 and in girls, the mean was 9.24 $\mu\text{g/L}$ with a SD of 9.25 and a 2.79 ASD. The results are shown in Fig. 2. These results show a large distribution of urine concentrations of aluminum.

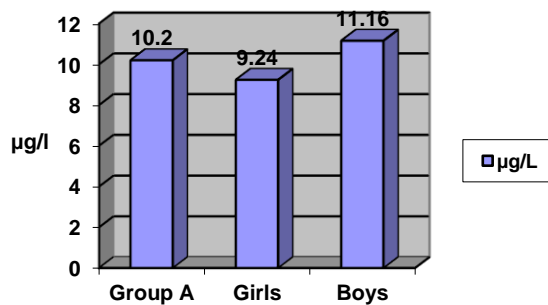


Fig. 2. Distribution of concentrations of aluminum in urine samples of group A.

Sex analysis shows that the value of urine concentrations of aluminum in girls is less than 1.82 $\mu\text{g/L}$ than that of boys. The odd Student Test shows that the two urinary concentrations of aluminum do not differ statistically significantly for a probability $p > 0.6$. Within group B, the mean urine concentrations of aluminum were 10.86 $\mu\text{g/L}$ with an SD of 10.84 and an ASD of 2.21. Sex analysis shows that the average urine concentration in boys was 12.94 $\mu\text{g/L}$ with SD of 11.46 and ASD of 3.18 and in girls, the mean was 8.4 $\mu\text{g/L}$ with SD of 10.02 and ASD of 3.02. The results are shown in Fig. 3. These results show a large distribution of aluminum in urine samples.

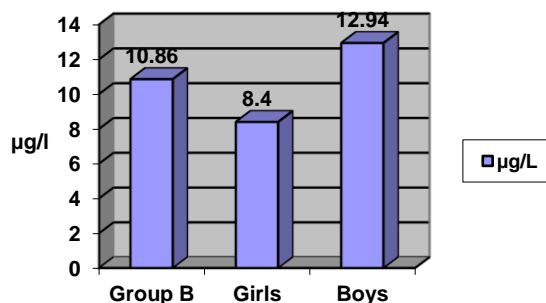


Fig. 3. Distribution of concentrations of aluminum in urine samples of group B.

Analysis by sex shows that the value of urine concentrations of aluminum in girls is less than 4.54 µg/L than that of boys. The odd Student test shows that the two media of urinary concentrations of aluminum do not differ statistically significantly for a probability $p > 0.3$. The difference between the average urinary concentrations of aluminum in the two groups is 0.66 µg/L. Sex analysis shows that the mean aluminum concentration in boys in group B is higher by 1.78 µg/L compared to the average of aluminum urine concentrations in group A boys. The average aluminum concentrations in the A group are higher than the aluminum urine concentrations in the B group with 0.84 µg/L. The results are shown in Fig. 4.

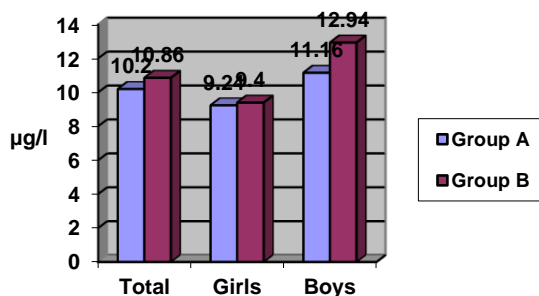


Fig. 4. Distribution of aluminum concentrations of urine samples by groups.

The average of urinary concentrations of aluminum in the two groups do not differ statistically significantly for a probability $p > 0.8$. The difference between the two media is 0.66 µg/L.

The average of urinary concentrations of aluminum in boys in the two groups do not differ statistically significantly for a probability $p > 0.6$. The difference between the two media is 0.78 µg/L.

The average of urinary concentrations of the aluminum of the girls in the two groups do not differ statistically significantly for a probability $p > 0.8$. The difference between the two media is 0.84 µg/L.

CONCLUSIONS

There is no statistically significant difference between the average urine concentrations of the two groups of normal children and the symptoms of ADHD.

It can be argued that the occurrence of symptomatic symptoms characteristic of ADHD can not be correlated with the presence of abnormal values of aluminum in subjects with ADHD.

Analysis of urinary aluminum concentrations in children with ADHD relative to the urinary concentration of these elements in children without ADHD did not reveal any statistically significant difference. These results show that aluminum can not be responsible for the presence of ADHD symptoms.

The developed optoelectronic method is relatively simple, reproducible and has a sensitivity that allows analysis of aluminum concentration in urine samples.

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Table 1. General parameters for AAS.

No.	Parameters	Programming
1.	Type of injection	Auto dilution
2.	Modul de calibrare	Concentrație
3.	Type of measurement	Height peak
4.	Standard replicates	2
5.	Sample replicates	2
6.	Smoothing	9
7.	Wavelength	309.3 nm
8.	Slit width	0.2 nm
9.	Lamp current	10 mA
10.	Background correction	Da
11.	Standard 1	20 µg/l
12.	Standard 2	50 µg/dl
13.	Standard 3	100 µg/dl
14.	Recalibration rate	10
15.	Reslope rate	1
16.	Concentration decimal places	2
17.	Calibration algorithm	New Rational
18.	Replicate % RSD limit	10%
19.	Correlation coefficient limit	0.998
20.	Required detection limit	1 µg/L
21.	Instrument detection limit	0.6 µg/l
22.	Injected volume	15 µl
23.	Sample volume	10 µl
24.	Dilution coefficient	2

Table 2. General parameters for graphite furnace.

PARAMETER	STEP 1	STEP 2	STEP 3	STEP 4	STEP 5	STEP 6	STEP 7	STEP 8
Temp. (°C)	40	85	85	95	120	120	1000	1000
Time (s)	2	5	5	40	40	4	6	2
Gases	N	N	N	N	N	Ar	Ar	Ar
Flow (mL/min)	3	3	3	3	3	3	3	0
Read	-	-	-	-	-	-	-	-
Store	-	-	-	-	-	-	-	YES

PARAMETER	STEP 9	STEP 10	STEP 11	STEP 12	STEP 13	STEP 14
Temp. (°C)	2700	2700	3000	3000	40	40
Time (s)	2	1	0.1	2	22.3	3
Gases	Ar	Ar	N	N	N	N
Flow (mL/min)	0	0	3.1	3.1	3	0
Read	YES	YES	-	-	-	-
Store	YES	YES	-	-	-	-