EVALUATION OF IRRADIATED ENVIRONMENTAL SAMPLES IN THE TRIGA REACTOR USING THE NEUTRON ACTIVATION ANALYSIS METHOD

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Abstract

The purpose of this paper is to determine the chemical elements concentrations which affect both the population health and environment, such as toxic agents which are contained in air and are retained by precipitation inside the biomonitors like soil and mosses. Neutron Activation Analysis is an analytic technique based on measuring the numbers and the energy of gamma radiation emitted by the radioactive isotopes produced in the sample matrix by irradiation with thermal neutrons in a nuclear reactor. Usually, the samples are irradiated together with specific neutron flux monitors, duplicates and interest elements standards for a prior selected period of time inside the core of nuclear reactor. After the irradiation and the specific radioactive decaying, it can proceed measuring the gamma energies spectrum by using a high-resolution detection system (HPGe – High Purity Germanium crystal) for gamma spectrometry. The impact of the traced elements on population and environment can be then assessed.

Keywords: *Neutron Activation Analysis, Biomonitor, HPGe*

Introduction

In urban areas, air quality is strongly influenced by many human activities. High population density, heavy traffic, domestic heating in winter and other industrial activities, are influencing concentrations of trace chemical dangerous elements in the atmosphere. Consequently, the population is exposed to potential adverse effects arising from changes in the composition of urban air. Thus, monitoring air quality has become one of the standard quality control procedures for assessing urban environment.

The environment must be protected from pollutants to avoid its destruction and hence affecting the population in terms of health. What must be kept under control, especially nowadays, are massive heavy metal pollution from various industrial activity and beyond. For this reason, we must have a fair and accurate assessment of these quantities of metals (how much is allowed to exist in the environment without affecting our health) and also a qualitative assessment of these pollutants (what contains the air we breathe every day).

There are many studies about atmospheric contamination but most of these have been limited because of the financial problems, i.e., high costs and the difficulty of carrying out extensive studies in terms of both time and space. To determine these dangerous chemical elements that adversely affect human health, an indicator namely *moss plant* is used, as explained in [1, 2]. This plant has the ability to retain in the vegetative tissues precipitated chemical elements from the atmosphere because it lacks the cuticle that would stop entry of elements within cells.

Mosses were sampled and processed and the final form of dry residue obtained was inserted into polypropylene cartridges; they were then irradiated in TRIGA SSR rabbit. After the samples were activated in thermal neutron flux for a certain period of time, they were measured using a high-resolution gamma-ray detection system with crystal detector and an electronic system (preamplifier, pulsating unit, polarization module, amplifier) and a multichannel analyser provided with a genuine specific software. These devices have led to the highest achievement of qualitative analysis of the sample (which chemical elements are contained in the sample) and quantitative analysis (the traced elements concentration) using Neutron Activation Analysis K0 standardization method [3].

The results can be used to achieve graphical representation of areas with a high degree of pollution, and based on it important decisions can be made to reduce the pollution.

Experimental part of the work

Analytical steps of Neutron Activation Analysis (NAA) are, as follows:

- ✓ *Phase I*: sample preparation means in most cases just grinding (pulverization), homogenization, mass determination, roasting, packaging and selecting the best analytical process and preparation standards, if any.
- ✓ *Phase II*: irradiating the samples. For irradiating the samples, TRIGA SSR facility was used, which is a high efficiency neutron source for applying NAA (neutron flux in the range from 10^{12} to 10^{14} neutron·cm^{-2}·s^{-1}).

- ✓ *Phase III*: measurement, evaluation and calculation considering gamma spectrum and the trace elements concentrations level. The most widely used γ spectrometer consist of Ge based semiconductor detectors connected to a computer using as a multi-channel analyser for assessing and calculating the spectrum.

Phase I of analysis

For the experimental part of the research work we have taken a number of 8 samples (4 soils and 4 of ground mosses) from different locations in Pitesti city, Argeş County. These locations were chosen based on the assumption of a high pollution level due to the traffic, heavy industry, chemical factory, as shown in Table 1.

After sampling, the mosses were stored in polyethylene bags at room temperature for 10 days after which they were weighed and then placed in an oven at a temperature of 40 °C. Measurements were performed regularly after which the mass was further dried in an oven until the weight of the mosses remained constant.

The samples were then burned out in CTD 2-type oven at the temperature of 450 °C until a white ash was obtained. The burning is performed to remove the water content from the vegetative tissue and to have a homogenous composition of elements in the sample during irradiation experiment. For measuring the value of thermal neutron flux inside the irradiation location a gold thin foil was used (Aluminium diluted gold 0.1%). This monitor foil was washed with alcohol and then dried at 40 °C.

Table 1. Samples identification for irradiation experiment conducted in TRIGA SSR Reactor

Sample ID	Sampling location	Type	Sample Mass [g]
P1	ŞTRAND Park	Ground moss	25815 E-5
P2	TRIVALE Stadium	Ground moss	32927 E-5
P3	DAVILA Theatre (Downtown)	Soil	66560 E-5
P4	PITESTI SOUTH South Railway Station	Soil	55316 E-5
P5	VIILOR Bridge	Ground moss	32669 E-5
P6	ARPECHIM Petrochemical Factory	Soil	57639 E-5
P7	Găvana District (ROLAST S.A. area)	Soil	65454 E-5
P8	Craiovei District (C.A. Rosetti area)	Ground moss	28975 E-5

Phase II of analysis

The samples were inserted in polyethylene cartridges after being weighted and then they were placed inside the TRIGA SSR rabbit together with the gold foil monitor.

Table 2 shows the values for the reaction rates of the flux monitor reaction, [^{197}Au (n, γ) ^{198}Au] and thermal neutron flux values indicated by the monitor (obtained from the calculations).

Table 2. Thermal neutron flux measurements indicated by gold monitor inside the TRIGA SSR rabbit

Neutron thermal flux measurements - TRIGA Steady State Reactor - K11 irradiation location from Beryllium reflector

Irradiation date:	01.10.2020		Indicator	M1	
Start:	11:49:25				
Stop:	12:19:25	Tirr [s]	1800		
Power [MW]:	10 MW				
Monitor:	Au 0.1%-Al	Φmonitor	4mm		
m [g]:	6.07E-03				
σ0 [cm^2]:	9.88E-23				

Measurement no.	Cooling time [h]	Rate [s^{-1}]	Rcd	Thermal flux [cm^{-2}·s^{-1}]	R (average) [s^{-1}]	Std dev (rate)	Av. flux [cm^{-2}·s^{-1}]	Std dev (thermal flux)
1	38.56	1.26E-09	3.61	9.29E+12	1.26E-09	8.37E-12	9.30E+12	2.17E+10
2	63.06	1.27E-09	3.61	9.32E+12				
3	111.36	1.25E-09	3.61	9.27E+12				
4	138.21	1.27E-09	3.61	9.32E+12				
5	186.05	1.26E-09	3.61	9.29E+12				

Calculations resulting from irradiation showed an average thermal neutron flux of $9.30 \cdot 10^{12}$ neutrons·cm^{-2}·s^{-1}.

Fig. 1 presents the evolution of the neutron thermal flux for the five measurements.

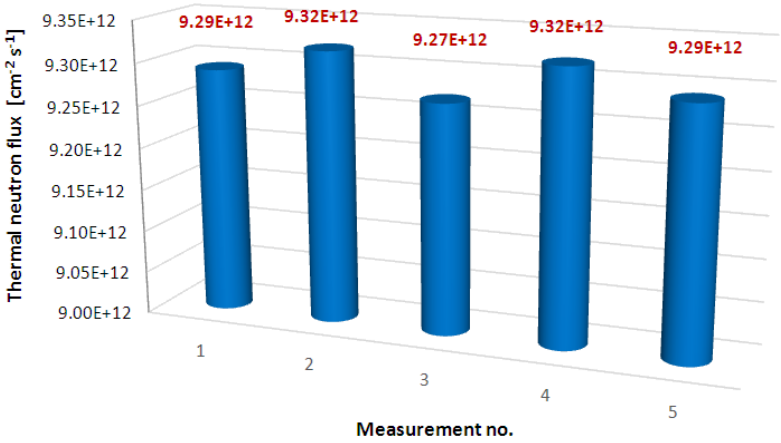


Fig.1. Thermal neutron flux for the considered measurements

Phase III of analysis

It should be noted that the irradiation time was too short and so it did not permit to activate any of heavy metal elements. In 1800 seconds of irradiation were successfully activated isotopes with short lifetime like: ^{55}Mn, ^{41}K, ^{45}Sc, ^{121}Sb, ^{139}La, ^{151}Eu, ^{75}As, ^{81}Br, and ^{58}Fe. For every irradiated sample a set of 8 measurements for each was conducted.

Qualitative - quantitative measurements of the elements retained in the moss were done by using k_0 standardization method of NAA. According to NAA k_0-standardization method, one trace element concentration in a sample is given by following equation detailed explained in [4, 5]:

$$\rho_a(\mu g/g) = \frac{\left(\frac{N_p/t_c}{SDC \cdot w}\right)_a}{A_{sp,m}} \cdot \frac{1}{k_{0,m}(a)} \cdot \frac{G_{th,m} \cdot f + G_{e,m} \cdot Q_{0,m}(\alpha)}{G_{th,a} \cdot f + G_{e,a} \cdot Q_{0,a}(\alpha)} \cdot \frac{\varepsilon_{p,m}}{\varepsilon_{p,a}} \cdot 10^6$$

where:

ρ_a - concentration of the traced element "a" (μg/g);

m - co-irradiated monitor for neutron fluency monitoring;

N_p - net peak area measured and corrected by pulse losses (dead time, real coincidence);

t_c - measuring time [s];

S - Saturation factor; $= 1 - \exp\left(-\lambda_{t_{irr}}\right)$, t_{irr} is irradiation time and $\lambda = (\ln 2)/T_{1/2}$ with $T_{1/2}$ – halftime;

D - Decay factor; $= 1 - \exp\left(-\lambda_{t_d}\right)$, where t_d is decay time (from the end of irradiation to start of measurement);

C - Counting factor; $= \left[1 - \exp\left(-\lambda_{t_c}\right)\right] / \lambda_{t_c}$ correction for decay during measurement;

W - Sample mass [g];

A_{sp} - $= (N_p/t_c)/SDC \cdot w$, specific counting rate, with w – monitor element mass [g];

$k_{0,m}(a)$ - k_0 experimental factor calculated of the traced element "a" relative to "m" monitor, defined as:

$$k_{0,m}(a) = (M_m \theta_a \sigma_{0,a} \gamma_a) / (M_a \theta_m \sigma_{0,m} \gamma_m)$$

with M - molar mass, θ - isotopic abundance, σ_0 – cross-section of (n,γ) reaction at 2200 m·s^{-1} and γ – absolute γ-ray intensity;

G_{th} - thermal neutron self-shielding correction factor;

G_e - epithermal neutron self-shielding correction factor;

f - Φ_{th}/Φ_e, thermal to epithermal neutron ratio; (for SSR reactor, f factor value at the experiment time was 17.12);

$Q_0(\alpha) = \left\{(Q_0 - 0.429)\bar{E}_r^{-\alpha} + 0.429 / [(0.55)^{\alpha}(2\alpha + 1)]\right\}(1eV)^{\alpha}$,

where $Q_0 = I_0/\sigma_0$, and I_0 represents the resonance integral defined as:

$$I_0 = \int_{0.55eV}^{\infty} \sigma(E)\, dE/E$$

$\bar{E}_r$ - effective energy of the resonance expressed in eV;

α - value for distribution deviation of the epithermal neutron compared with the ideal shape 1/E, approximated by a $1/E^{1+\alpha}$ dependency; (for SSR reactor, f factor value at the experiment time was 0.01159);

ε_p - detection efficiency for full energy peak.

Results

Results of Neutron Activation Analysis k_0-standardization obtained after measuring all the samples on HPGe detector are presented in Figs. 2 - 10.

Bromine

Long-term use of potassium bromide (or any of the salts of bromine) may lead to bromism. This state of central nervous system depression is caused by bromide moderate doses on the order of several grams to humans or other mammals. Ingesting bromine can also cause a rash on the skin similar to acne.

Fig.2 reveals that the highest content level of bromine was obtained at ARPECHIM Petrochemical Factory, with a concentration of 145 mg/kg bromine. Second and third positions is held by PITESTI SOUTH Railway Station and DAVILA Theatre, which is actually a normal trend due to the fact that these two locations are characterized by high level of pollution due to trains and car traffic.

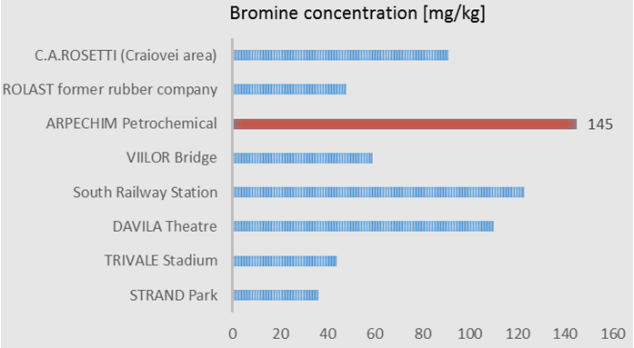


Fig.2. Bromine concentration in collected samples

Antimony

Antimony and many of its compounds are toxic; the effects of antimony poisoning are similar to arsenic poisoning. Inhalation of antimony dust is very harmful and in some cases can be even fatal. In small doses, antimony causes headache, dizziness and depression. Higher doses and prolonged skin contact may cause dermatitis. It can also cause liver and kidney damage, leading to violent vomiting and to death within few days. The highest level of antimony content (see Fig. 3) was obtained again for the ARPECHIM sample due to its industrial-based purpose (8.21 mg/kg).

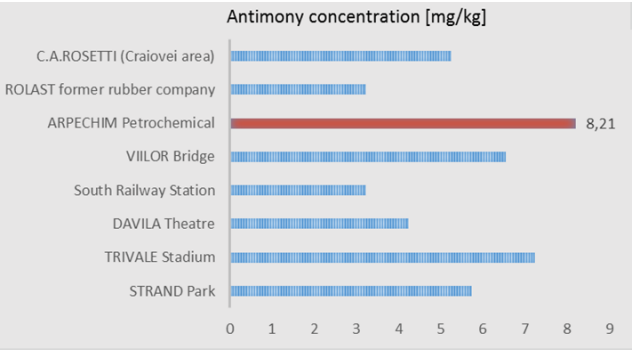


Fig.3. Antimony concentration in collected samples

Arsenic

Arsenic and many of its compounds are generally very strong poisons. Many water sources near mines are contaminated with these poisons. European Union under Directive 67/548/EEC of International Agency for Research on Cancer recognizes arsenic and its compounds as being in the first group of carcinogens. Arsenic is responsible for the most cases of poisoning from all heavy metals.

Arsenic is released into the environment through the process of smelting copper, zinc and lead, as well as by producing chemicals or bottles. ″Arsine″ gas is a by-product that occurs following the occurrence of pesticides that contain arsenic. Arsenic can be found in water sources all over the world, involving crustaceans and fishes' exposure. Other sources are paints, poisons for rats, fungicides and inhibitory substances of wood aging. Target organs are the blood, kidneys, central nervous system, digestive tract and skin. The sample take from ARPECHIM area has the highest content of arsenic followed by the VIILOR Bridge (caused by heavy traffic) and PITEŞTI SOUTH Railway Station (heavy train traffic), as shown in Fig.4.

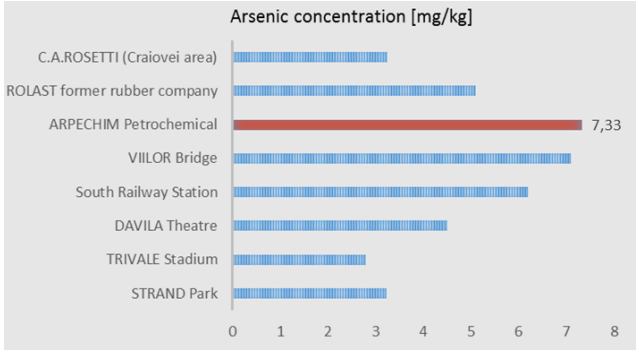


Fig.4. Arsenic concentration in collected samples

Europium

There are clear indications that Europium is particularly less toxic compared to other heavy metals. Europium dust presents the risks of fire (flammable) and explosion. The highest level of Eu content was determined for PITESTI SOUTH Railway Station caused, of course, by the heavy train traffic (see Fig.5).

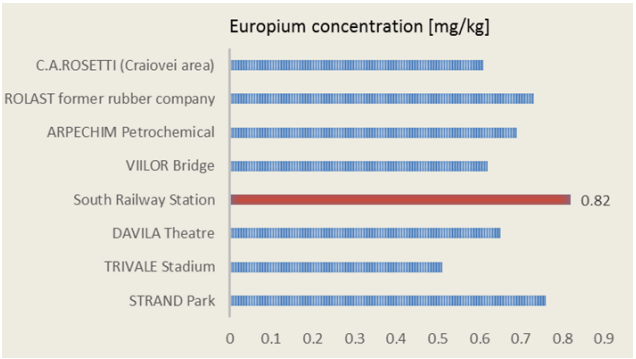


Fig.5. Europium concentration in collected samples

Scandium

Elemental Scandium is considered as non-toxic element. Average lethal dose for Sc chloride (III) for Guinea pigs was determined at a value of 4 mg/kg for the inter-stomach area and 755 mg/kg for oral administration. In the light of these results, Scandium compounds must be treated as having moderate toxicity. The highest level of Sc content was determined in the STRAND Park and PITEŞTI SOUTH Railway Station (heavy traffic), as Fig.6 shows.

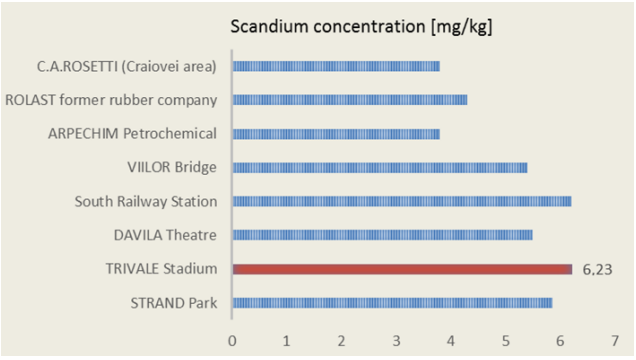


Fig.6. Scandium concentration in collected samples

Potassium

Considering the powerful reactive nature of Potassium, it must be handled with care, with skin and eye protection and preferably an explosion-resistant barrier between the user and the metal.

Ingesting large quantities of K can lead to hyperkalemia strongly influencing the cardiovascular system. The highest level of Potassium content was determined in the STRAND Park and PITEŞTI SOUTH Railway Station (heavy traffic), as shown in Fig.7.

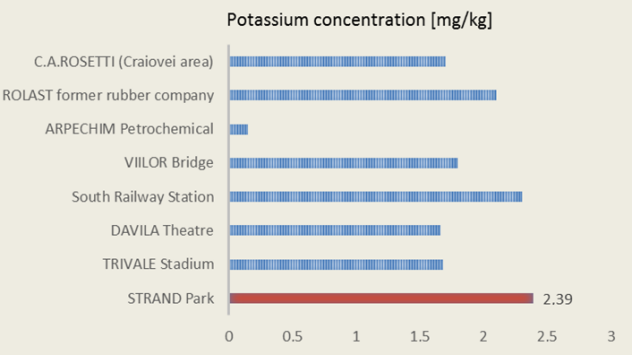


Fig.7. Potassium concentration in collected samples

Iron

This heavy metal has major importance, especially due to the iron-based supplements in the diet that can acutely poison young children. Ingestion is the main way iron enters the body exposing the toxic effects, taking into consideration that the iron is rapidly absorbed in the gastrointestinal tract. Corrosive nature seems to increase the absorption of iron.

Most overdoses are the result of wrong ferrous sulphate tablets ingestion by children as they are contained in red capsules, or by adults on basic multivitamin preparations. Other sources of iron include drinking water, iron pipes and cooking vessels. Target organs are the liver, kidneys and cardiovascular system.

Large amounts of ingested iron can cause excessive increase iron levels in the blood. High level of free iron in the blood reacts with peroxides and produces free radicals, which are highly reactive and can attack DNA, proteins, lipids and other cellular compounds. Iron usually affects heart cells, liver and is causing adverse effects including coma, metabolic acidosis, shock, impaired liver functions, coagulopathy, long-term organ damage and even death. A dose of 20 mg to 60 mg of iron per kg mass is considered to be lethal. The highest level of iron was recorded for the DAVILA Theatre sample (2.07 dg/kg) due to heavy traffic in the neighborhood, as Fig.8 presents.

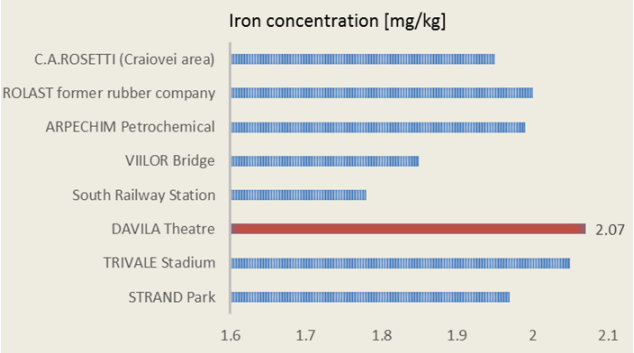


Fig.8. Iron concentration in collected samples

Manganese

Manganese compounds are less toxic than other metals such as Nickel and Copper. However, Mn dust exposure limit value should not exceed 5 mg/m^3 even for small periods of time because of its toxicity level. Manganese poisoning was coupled with disturbances in the body and locomotive function, and with cognitive disorders.

Manganese exposure among miners was associated with a form of neuro-degeneration similar to Parkinson's disease called ″manganism″. High levels of exposure to Mn in drinking water have been associated with impaired intellectual and reducing the coefficient of intelligence at school children.

″Manganism″ occurs to people engaged in the production or processing of Mn alloys, to workers exposed to Mn and fungicides. In general, concentrations of Mn in the environment higher than 5 mg/m^3 can cause specific symptoms. The highest level of Manganese was recorded for STRAND Park sample (the sample was taken from the vicinity of a high traffic road), as shown in Fig.9.

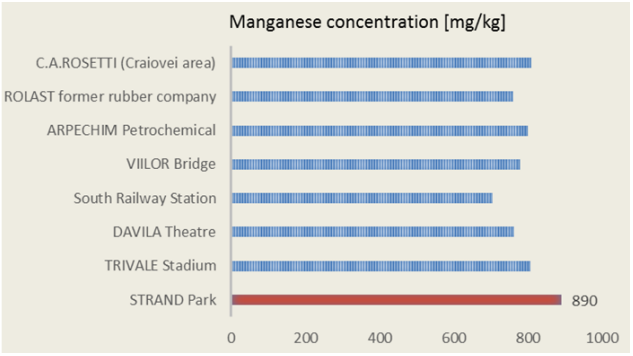


Fig.9. Manganese concentration in collected samples

Lanthanum

Lanthanum has a moderate level of toxicity and should be carefully handled. Lanthanum produces hyperglycemia, lower blood pressure, degeneration of the spleen and liver functions alteration. As presented in Fig.10, the highest Lanthanum content was determined for VIILOR Bridge sample (25.9 mg/kg), level caused by the heavy traffic.

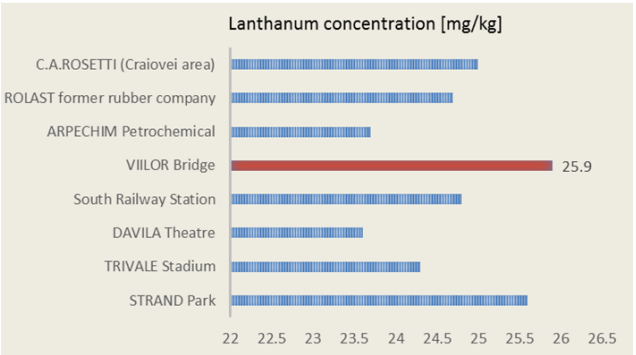


Fig.10. Lanthanum concentration in collected samples

A summary of the measurements carried out for the toxic pollutants of interest for Piteşti city air quality (Bromine, Manganese, Antimony, Arsenic, Europium, Scandium, Potassium, Iron and Lanthanum) is shown in Table 3; determinations' uncertainty is also given.

Table 3. Overall data for the irradiated moss samples

	Elemental concentration [mg/kg] / Uncertainty							
Chemical element	**STRAND Park**	**TRIVALE Stadium**	**DAVILA Theatre**	**PITESTI SOUTH Railway Station**	**VIILOR Bridge**	**ARPECHIM Petrochemical Factory**	**ROLAST area**	**C.A. Rosetti area**
Bromine	36±1.98	44±2.42	110±6.05	123±6.76	59±3.24	145±7.97	48±2.64	91±5.00
Manganese	890±48.95	807±44.38	762±41.91	705±38.77	780±42.9	800±44	760±41.8	810±44.55
Antimony	5.74±0.31	7.23±0.39	4.23±0.23	3.22±0.17	6.55±0.36	8.21±0.45	3.22±0.17	5.25±0.28
Arsenic	3.22±0.17	2.80±0.15	4.5±0.24	6.2±0.34	7.1±0.39	7.33±0.40	5.1±0.28	3.25±0.18
Europium	0.76±0.04	0.51±0.03	0.65±0.03	0.82±0.04	0.62±0.03	0.69±0.04	0.73±0.04	0.61±0.03
Scandium	5.86±0.32	6.23±0.34	5.5±0.30	6.2±0.34	5.3±0.29	3.8±0.20	4.3±0.23	3.8±0.20
Potassium	2.39±0.13	1.68±0.1	1.66±0.1	2.3±0.14	1.8±0.12	1.15±0.06	2.1±0.13	1.7±0.12
Iron	1.97±0.1	2.05±0.11	2.07±0.11	1.78±0.08	1.85±0.09	1.99±0.1	2.0±0.1	1.95±0.09
Lanthanum	25.6±1.4	24.3±1.33	23.6±1.29	24.8±1.36	25.9±1.42	23.7±1.30	24.7±1.35	25.0±1.37

Conclusions

The NAA-k_0 method allows tracing a wide range of chemical elements which can be activated in a nuclear reactor. Solid and liquid samples can be studied with it.

Characterization of the biomonitors samples performed in the paper represents a detailed work which can help to draw a map of the most polluted area from Piteşti city, Argeş County, the main purpose of this work targeting the improvement of the air quality monitoring system.

Air toxic agents' issue is a critical point in nowadays society and need to be treated with maximum care. Assessing theirs' impact on human health can support the decision making process regarding industrial activities carried out nearby living areas from Piteşti city. Precise measurements of the toxic pollutant from the environment are crucial for a fair assessment of the pollution level.

The concentration of the following toxic pollutants was recorded: Bromine, Manganese, Antimony, Arsenic, Europium, Scandium, Potassium, Iron and Lanthanum. Some discrepancies between the samples' elemental concentration were registered, due to differences between the pollution levels of the sampled areas.

Maximal values of the toxic pollutants concentration were obtained in the following sampling locations:
- STRAND Park – Manganese
- DAVILA Theatre (downtown) – Iron
- Piteşti South Railway Station – Bromine, Europium, Scandium, Potassium
- VIILOR Bridge – Lanthanum
- ARPECHIM Petrochemical Factory – Antimony, Arsenic

According to the toxic pollutants level recorded for the Piteşti city sampling locations, it can be concluded that ***Piteşti South Railway Station*** is the most polluted area.

Collaboration with the Environmental Protection Agency could be of benefit to compare the obtained results and to formulate some recommendations.

The data obtained allow the assessment of environmental pollution and, in the same time, can be used as a database for the authorities in taking the best decision to avoid pollution affecting human health.

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