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PHOTONEUTRON ACTIVATION ANALYSIS APPLIED FOR ENVIRONMENTAL RESEARCHES*

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Abstract. An instrumental highly sensitive photon activation method based on the (γ, n) reactions and following gamma-ray spectrometry analysis for the multielement determination from several environmental media is developed. The environmental samples and standards were irradiated simultaneously for 4 hours with 24 MeV bremsstrahlung produced by the MT-25 linear electron accelerator of the Flerov Laboratory for Nuclear Reactions of the Joint Institute for Nuclear Researches. The analytical results for up to 32 elements in the analyzed samples are presented.

Key words: photoneutron activation analysis, gamma-ray spectrometry analysis, multielement analysis, environmental samples.

1. INTRODUCTION

In the last decades several authors employed different analytical techniques to study the elemental distribution in biological materials which can be particularly useful for assessing the contamination status of environment and population [1,2].

Because it is a nondestructive method and allows a wide range of spatial resolutions, activation analysis is a suitable procedure which follows the variations in the content of an element in the same type of distinct samples. It has been demonstrated that activation analysis by high energy photons is a precise and reliable method for determining heavy metal content in soil, air filters, sediments, plants and other environmental materials, without any chemical treatment [3,4]. The photoneutron activation method of the analysis is based on the measurement of neutron radiation arising as a result of the (γ, n) nuclear reactions.

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In order to investigate the possibilities of photoneutron activation analysis for effective environmental applications, highly accurate and precise multielement determinations in four environmental materials, such as soil, epiphytic mosses, vascular plants and alluvial sediments, were accomplished.

This paper describes the analytical method and its application to following environmental monitoring of a region surrounding a medium industrialized town.

2. EXPERIMENTAL

2.1. SAMPLE COLLECTION AND PREPARATION

The environmental materials used in the present study were collected in the area of the medium industrialized town of Oradea, in a similar manner with the work [5].

Previously the assessment of environmental situation for some spots has already been carried out in the monitored area. Unfortunately no clear distinction between different local sources of chemical element releases was possible. The hot spots located in the area surrounding the town were chosen since the expected significant deposition of trace metals in their soil and plants [6].

Prior to analytical measurements, the environmental samples were carefully cleaned from all impurities, grounded (soil and sediment samples); respectively, divided in small pieces (mosses and leaves), then were let to dry at room temperature on a filter paper for a month [5]. Later were kept at 40°C for 48 hours in thermostat until constant weight and then were finely powdered in an agate mortar. The average weight losses of these samples were 2.5 for soil, 2.1 for alluvial river sediments and about 6.2–8.7 for plant material.

A total of 147 teeth were collected from several human subjects of the same geographical region. The sampled teeth were not treated stomatologically in the past and present only the original tooth material. Part of work dealing with the teeth collection and preparation had already been published. Some features are presented shortly here, but the detailed evaluation constitutes the subject of the other reports [7-9].

The experimental material was subjected to photoneutron activation analysis.

2.2. PHOTONEUTRON ACTIVATION ANALYSIS

The all samples were activated by the photoneutron activation method at the electron linear accelerator MT-25 of the Flerov Laboratory for Nuclear Reactions in the Joint Institute for Nuclear Research (Fig. 1). The linac was operated using photons of maximum energy of 25 MeV with a beam pulse width of 2.2×10^{-6} μs

and a γ-quanta flux of 10^{14} s^{-1} [10]. Typical irradiations were carried out for 4 hours with an average beam current of about 20 μA at the position of beam exit window. Samples of 2 g were placed in polyethylene cassettes. Then a vial consisting of 10 cassettes with samples, Cu monitors and etalons (СП-3 and РЖИ standard materials [11]) was activated each time next to the beam axis. The vial was turned at an angle of 180^0 during irradiation (*i.e.* at the half of the irradiation time) in order to avoid the difference in the activity of the samples.

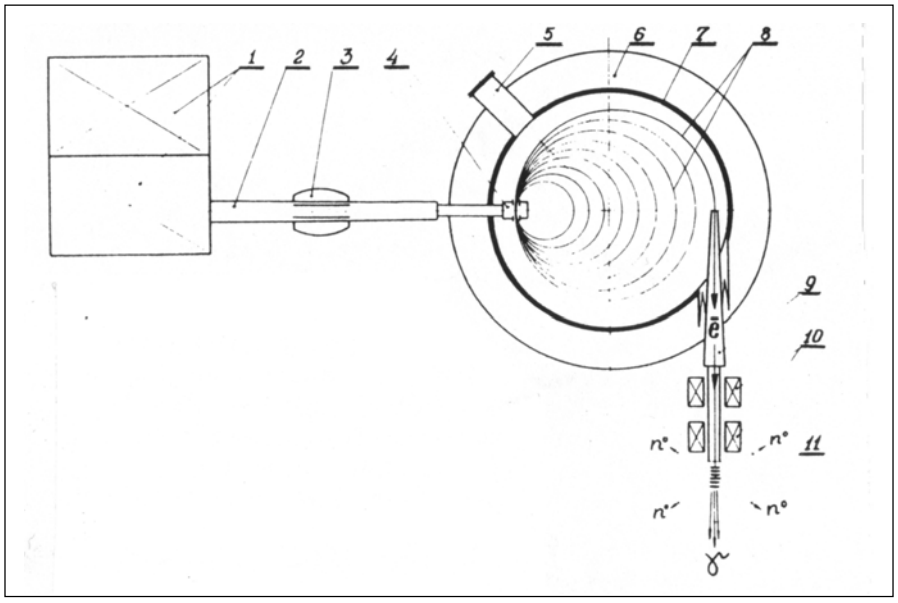

Fig. 1 – Scheme of the microtron MT – 25 [10]: 1 – system of high frequency; 2 – wave channel; 3 – ferrite isolator; 4 – resonator; 5 - vacuum system; 6 – magnet; 7 – vacuum camera, 8 – orbits of accelerated electrons; 9 – exit of electron beam; 10 – magnet, focusing electron beam; 11 – brake target).

The radioactivity measurements of the induced activity were carried out by using an automatic γ-ray spectrometer equipped with a HPGe detector of a 2.0 keV resolution at the line of 1333 keV. In the all measurements, the dead time of the detection system was kept below 10%. The distribution of photon beam intensity over the samples was determined by measuring the activity of Cu monitors.

Short lived isotopes were recorded by 5 min measurements after 2 h cooling, and the medium and long-life isotopes were determined by 1h measurements after 1, 5 and 10 days of cooling, respectively.

Identification of the radionuclides produced was done by measuring the γ-ray energies and half-lives. The peak areas from the γ spectrum (Fig. 2) by the SPM software developed in FLNR were calculated [12]. Then the amounts of elements in measured samples were accounted by using the relative method, applied to

multielement determination in environmental materials by using the comparative standard containing accurately known amount of each element to be determined.

The detection limits of the photoneutron activation method range from $3 \cdot 10^{-2}$ mg/kg (for potassium) to 10^{-5} mg/kg (for tantalum). The accuracy of the obtained results for the most elements was below than 10%.

3. RESULTS AND DISCUSSION

3.1. MULTIELEMENT DETERMINATION OF FOUR ENVIRONMENTAL MATERIALS

The characteristics of photoneutron reactions giving an opportunity to identify those or other elements, is the existence of the certain power threshold of reactions for each isotope. At energy of γ-quanta below the threshold section of reactions is equal to zero, *i.e.* reaction does not occur. Starting with the threshold, with the energy increasing the section grows and reaches a maximum (area of a resonance) then falls practically up to zero.

As an example, the γ-ray spectra obtained from the soil sample after 20 days after the end of irradiation is shown in Fig. 2. A number of radionuclides shown in Fig. 2 were identified.

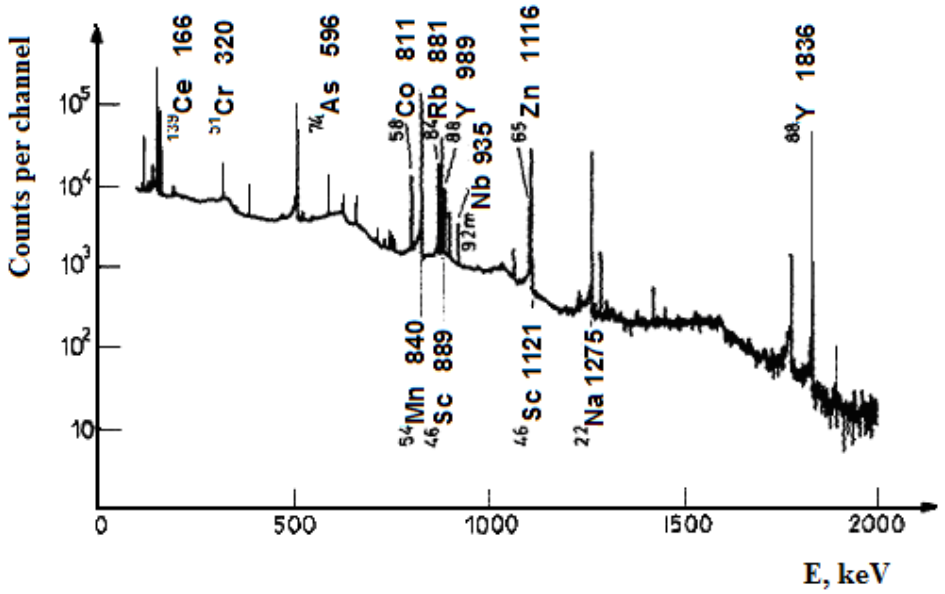

Fig. 2 – Gamma spectrum of a soil sample (t_i – 4h, t_d – 20d, t_m – 1h).

The γ-ray spectra obtained for the other samples showed similar patterns. Among them, the characteristic γ-rays due to radionuclides produced from Na, Mg, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sm, Ta, W, Re, Au, Tl, Pb, As, Se, Br, Rb, Sr, Y, Zr, Nb, Sb, Te, I, Cs, Ba and Ce were measured to determine the concentration of each element. The photonuclear reactions for some elements of interest are shown in Table 1 together with their nuclear characteristics.

Table 1

Usable photonuclear reactions for some elements to be determined

Element	Reaction	Eγ, keV	T1/2, d
Cr	$^{52}Cr(\gamma,n)^{51}Cr$	320	27.7
Co	$^{59}Co(\gamma,n)^{58}Co$	811	70.78
Ni	$^{58}Ni(\gamma,n)^{57}Ni$	1378	1.5
Cu	$^{68}Cu(\gamma,n)^{67}Cu$	185	2.58
Zn	$^{65}Zn(\gamma,p)^{64}Cu$	1116	243.8
As	$^{75}As(\gamma,n)^{74}As$	596 635	17.8
Se	$^{76}Se(\gamma,n)^{75}Se$	265	120
Sb	$^{123}Sb(\gamma,n)^{122}Sb$	565	2.7
Pb	$^{204}Pb(\gamma,n)^{203}Pb$	279	2.17

The results obtained on four environmental materials as surface soil, downstream river sediments, mosses *Hypnum cupressiforme* (HC) and poplar leaves were examined by basic statistics and the average contents relative to background are shown in Fig. 3. The values obtained for each sample were suitably, except V and Mn, and the relative standard deviations were not more than ±5%. The laboratory measurements with photoneutron activation method showed good correlation between As and Cu results.

However, the overloading tolerance limit concentration (TLC) value established in Romania for Ti in soil was observed. The concentrations of As in different soil samples varied between 5.4 and 17.2 ppm and of Pb varied between 20 and 200 ppm, respectively. The ratio between the concentrations of Pb and Zn in soil samples ranges from 5.3 to 1.4 exhibiting a median value of 2.85, suggesting for a moderate level of biodegradability. The registered comparative levels industry location/background are related with the contamination of soil released by industrial and urban emissions. The levels of toxic elements are even large in river sediments downstream the Oradea city than in soil reflecting the municipal waste discharges in the Crisul Repede river waters. The high levels of some elements such as Ca, Mn, Fe, Cu, Sm, Se, Cs and Ce are connected with the geologic structure of the bedrock and the geographical characteristics of the Crisul Repede river and of Oradea City (situated in a plane) and also could be explained by the mobility of ions in the alluvial sediments.

By univariate statistic analysis of vegetation samples, we determined that Ni and Pb content exceed more than 6 times the background value. Zn, Fe and As content exceed the background value by a factor greater than 3.5.

Previously it was established that the urban pollution is released mainly by power stations of CET 1 and CET 2, consideration supported also by the present research. It has a strict local character, approaching the background level at 15 - 20 km far from the plant [6,13].

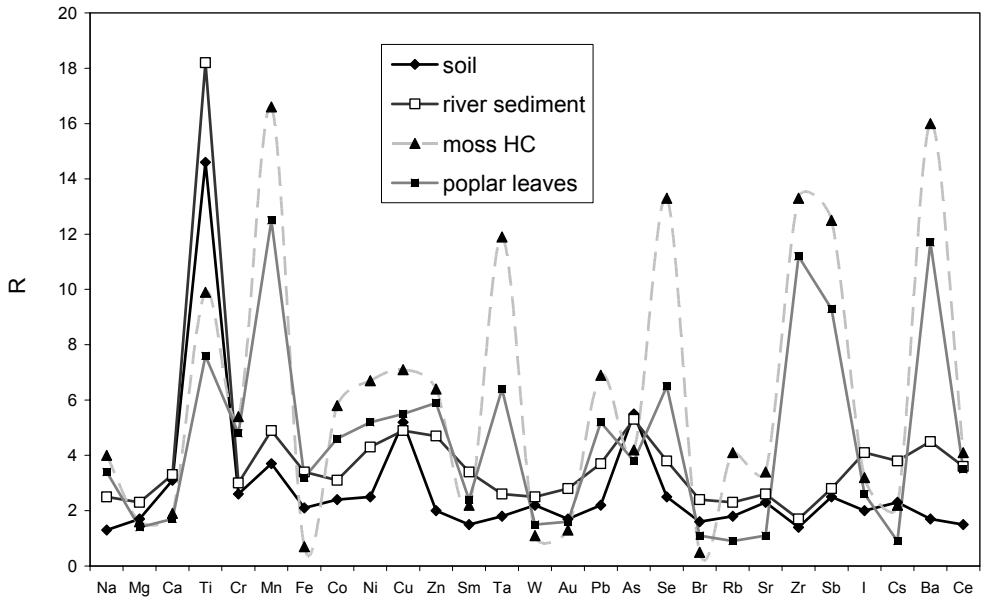

Fig. 3 – The relative average concentrations to background in the four environmental materials.

The metal concentrations in mosses and poplar leaves were compared and correlations between pairs of elements were examined in order to distinguish between various sources of sample content. The levels of the toxic elements in tree leaves were lower than those in moss leaves. This situation is explained by the morphological differences of plants in the rate uptakes of such inorganic compounds from the environment [14,15]. The Ni, Pb, Ti, As, Sb, Fe and Cr concentrations were consistently correlated, certifying for the urban emissions as source of those substances into the vegetation and atmosphere.

3.2. R-MODE FACTOR ANALYSIS RESULTS

The correlation matrixes of measured elemental concentrations in soil and human teeth were constructed and compared by multivariate statistical analysis procedures. The comparisons were undertaken by means of statistical methods

such as varimax method, Kaiser normalization and R-mode Factor Analysis [16]. The programs used in calculations were Microsoft Excel and SPSS for Windows.

R-mode factor analysis used to determine correlations among the measured elements, confirmed that elements Ni, Zn, As, Cu, Cr and Fe contribute to an urban pollution factor. The more significant factors extracted from soil data (F2) and teeth data (F1 and F2) are represented as factor fractions (Figs. 4 and 5).

The results for the all trace heavy metals, mainly for the three elements of major concern (Ni, As and Cu) show a similar large factor fraction in soil and in human teeth suggesting the population exposure at the local industry and urban activity. It includes important sources of toxic emissions as power plants stations of CET 1 and CET 2, metallurgical and chemical industry, traffic and other manufacture related emissions [17].

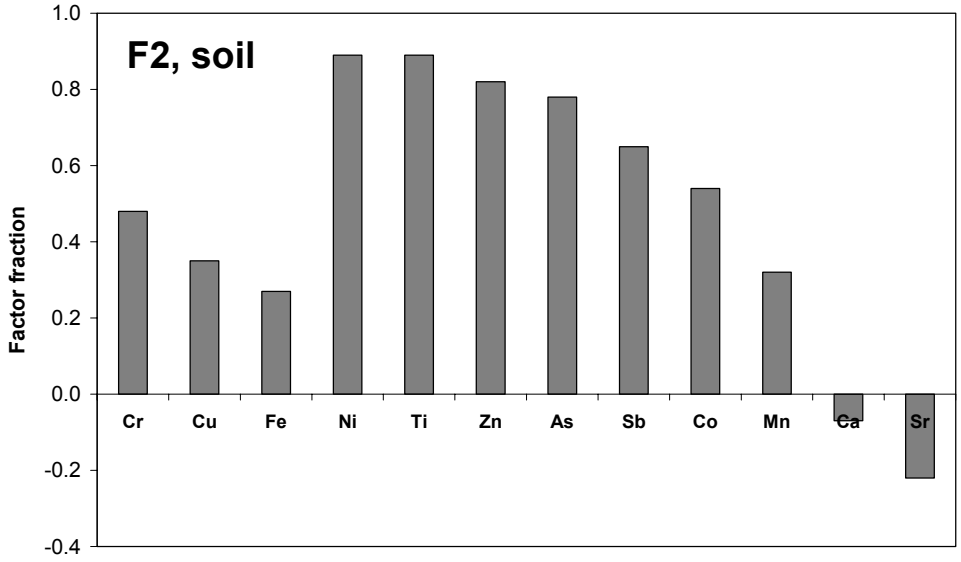

Fig. 4 – The second factor (F2) fractions results for soil data. It accounted for 35.8% from the total variance of the data set.

4. CONCLUSIONS

The photoneutron activation method in order to achieve the highly accurate and precise multielement determination of the four types of environmental samples has been applied. The specific pollutants emitted by urban activity showed similar profiles in the all analyzed environmental materials. High positive correlations were found between concentrations of trace heavy metals in the same type of samples as well as between different environmental materials. A low negative correlation was found between heavy metal concentrations and those of Ca, K and

Sr. The most significant feature of the environmental materials analysed by photoneutron activation analysis is the interaction of toxic heavy metals with mineral compounds of teeth as Ca and P, resulting by their partial replacing in the hydroxyapatite matrix in the contaminated habits.

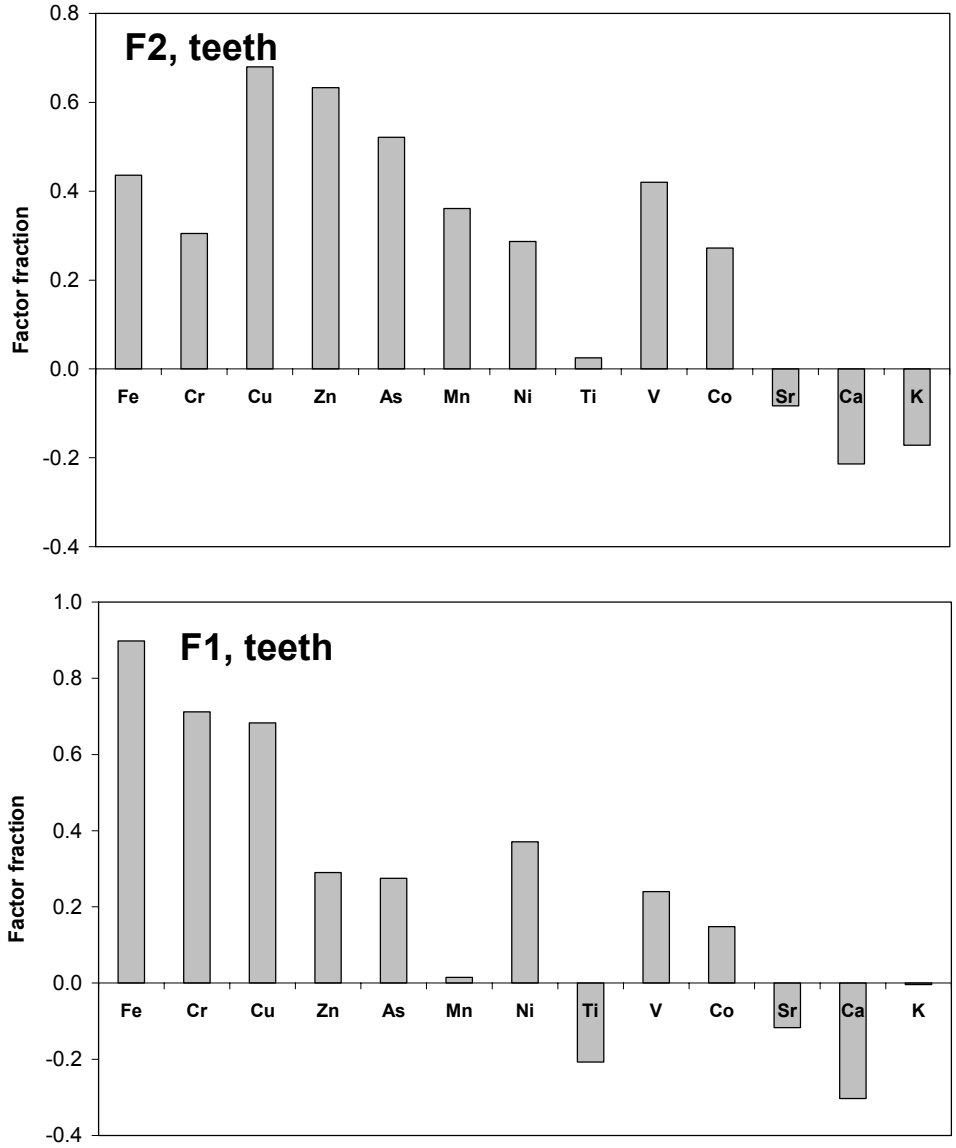

Fig. 5 – The fractions of the first two factors (F1 and F2) results for teeth data. They accounted for 42.9% and 26.4%, respectively, from the total variance of the data set.

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