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NUCLEAR AND RELATED ANALYTICAL METHOD APPLIED IN ENVIRONMENT: PIXE

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Abstract. *Nuclear Analytical Methods (NAM) can be used for research activities on environmental studies like water quality assessment, pesticide residues, global climatic change (transboundary), pollution and remediation. Prominent features of NAMs are sensitivity, selectivity, multielement determination and linearity of the calibration function. In this article we present one analytical PIXE and her applications in trace elements analysis on fountain water, aerosol, and mosses samples.*

Keywords: environment, method PIXE, pollution, *Mnium undulatum* Dambovita

1. Introduction

With a particular NAM we can made research activities on environmental studies like water quality assessment, pesticide residues, global climatic change (transboundary), pollution and remediation. Prominent features of NAMs are sensitivity, selectivity, multielement determination and linearity of the calibration function covering a concentration range of several orders of magnitude. Moreover, ion beam techniques allow depth profiling with nm-resolution in several cases while the ion microprobe additionally offers a lateral resolution in the wm-scale. As NAMs require expensive apparatus (nuclear reactor, accelerator in radioactive control areas) their availability is restricted to a small number of suitably equipped institutes. However, they are able to solve complex analytical tasks, take part in key comparisons and play an essential role in the certification of reference materials. Many fields like the biology and environment, use for solving different problems, the results of researches obtained by a series of methods of analysis and techniques of high and ultra-high sensibility, including profile methods.

2. Experimental method

The type of spectroscopy depends on the physical quantity measured. Normally, the quantity that is measured is an intensity, either of energy absorbed or produced. Electromagnetic spectroscopy involves interactions of matter with electromagnetic radiation, such as light. Electron spectroscopy involves interactions with electron beams. Auger spectroscopy involves inducing the Auger

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effect with an electron beam. In this case the measurement typically involves the kinetic energy of the electron as variable. Most spectroscopic methods are differentiated as either atomic or molecular based on whether or not they apply to atoms or molecules. Along with that distinction, they can be classified on the nature of their interaction. Absorption spectroscopy uses the range of the electromagnetic spectra in which a substance absorbs. This includes atomic absorption spectroscopy and various molecular techniques, such as infrared spectroscopy in that region and nuclear magnetic resonance (NMR) spectroscopy in the radio region. Emission spectroscopy uses the range of electromagnetic spectra in which a substance radiates (emits). The substance first must absorb energy. This energy can be from a variety of sources, which determines the name of the subsequent emission, like luminescence. Molecular luminescence techniques include spectrofluorimetry.

3. Particle Induced X-ray Emission (PIXE)

Particle induced x-ray emission (PIXE) [1], is a powerful yet non-destructive elemental analysis technique now used routinely by geologists, archaeologists, art conservators and others to help answer questions of provenience, dating and authenticity. Quantum theory states that orbiting electrons of an atom must occupy discrete energy levels in order to be stable. Bombardment with ions of sufficient energy (usually MeV protons) produced by an ion accelerator, will cause inner shell ionization of atoms in a specimen. Outer shell electrons drop down to replace inner shell vacancies, however only certain transitions are allowed. X-rays of a characteristic energy of the element are emitted. An energy dispersive detector is used to record and measure these x-rays and the intensities are then converted to elemental concentrations. The target samples for PIXE are doped with standard solution (1:1) of Yttrium (standard for spectrum normalisation and systematical error elimination) consisting of 130 mg/l of Yttrium (prepared from Y_2O_3) in deionised water. Measurements of target elements are made using a 3.0 MeV proton beam extracted from the TANDEM Van der Graaff accelerator and passes through a collimator (3×4 mm) before reaching the target.

X-ray spectra were measured with a spectrometric chain having a Ge hyperpure detector (100 mm2×7mm) with a 160 eV resolution at 6.4 KeV of Ka line of iron. The detection limit is in the range (10-100 ppm).

4. Experimental results

With a particular NAM we can made research activities on environmental studies like water quality assessment, pesticide residues, global climatic change (transboundary), pollution and remediation.

4.1. Fountain water

We have analyzed samples collected from underground waters (potable or non-potable) for establish if they are good for consumption. The target samples were prepared by evaporation of 2 l of water. The obtained dust was mixed with a known amount of Yttrium (internal standard) and depicted on 3μm mylar support. Using a 3MeV proton beam we obtain characteristic X rays spectrums. We have identified 8 elements: S, Cl, K, Ca, Fe, Zn, Br and Sr and their concentrations are shown in the table below:

Table 1. The elemental concentrations of analyzed underground waters

Element	*Sample(mg/l)*					*Ceiling admittance*	
	Ruda-Moreni fountain	*Salcâmi-Moreni fountain*	*Viforata 1 fountain*	*Viforata 2 fountain*	*Paltinu-Moreni fountain*	*Germany*	*U.S.A.*
S	42.5					80	83.5
Cl	51.3		45.3	9.3		250	250
K	8.6	7.0			0.08	12	
Ca	138	140	280	265	3.05	400	
Fe		0.21		1.1	1.4	0.02	0.3
Zn		1.38		0.12			5
Br	0.51		0.08				
Sr	3.29		1.8	0.05			8

Comparing with the ceiling admittance in Germany (S. Eberle, IAEA-Viena 1995) and U.S.A. (Public Law 93-523) we can observe that in two samples (Viforata 2 fountain and Paltinu-Moreni fountain) the concentration of Fe exceeds the maximal admittance levels.

4.2. Aerosols samples

We have analyzed aerosols deposits on filters from ten Romanian towns: Pitesti, Giurgiu, Resita, Râmnicu-Vâlcea, Baia-Mare, Craiova, Timişoara, Călăraşi, Brăila and Arad with different kinds and levels of industrial development by PIXE method.

Sample targets to be analyzed were collected by the Institute of Hydrology and Waters of Bucharest and prepared in the following manner: aerosol particles were collected on cellulose fiber filter.

The flow rate was 15 to 20 liters per minute. Air volume was measured with calibrated gasmeters with a precision of about 5%. We use PIXE in internal standard variant. We use Yttrium like an internal standard because it is a very rare element in the environment items.

There are identified 15 elements: S, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Hg and Pb. The measured elemental concentration are given with respect to the concentration of the Ca for all analyzed samples in the following table:

Table 2. The elemental concentrations with respect to the concentration of the Ca for all analyzed samples

City / *Elem.*	*Piteşti*	*Giurgiu*	*Reşiţa*	*Rm. Vâlcea*	*Baia Mare*	*Craiova*	*Timi-şoara*	*Călăraşi*	*Brăila*	*Arad*
S	0.112						0.02		0.012	0.047
K	0.57	0.272	0.122		0.052	2.51	0.2	0.26	0.174	0.36
Ca	1	1	1	1	1	1	1	1	1	1
Ti	0.14	0.05	0.019	0.063		0.505	0.15	0.66	0.017	0.04
V	0.018			0.012						
Cr	0.002	0.007	0.003	0.007		0.035		0.012	0.006	0.001
Mn	0.027	0.014	0.021	0.017	0.006	0.05	0.007	0.078	0.024	0.017
Fe	1.09	0.49	0.532	0.647	0.075	5.38	0.52	4.32	0.28	0.58
Co						0.015				
Ni	0.009			0.006						
Cu	0.004		0.001	0.021	0.089		0.001	0.008	0.002	0.003
Zn	0.012		0.019	0.023	0.033	0.036	0.002	0.015	0.004	0.011
As				0.004	0.004	0.005				0.001
Hg							0.001		0.003	0.001
Pb				0.006	0.03	0.043		0.005	0.002	0.0003

For the ratio concentrations shown before we could make a comparison between the analyzed filters from all the towns considered here, from the point of view of the pollutant elements: the town Craiova is put in evidence by its high ratios of concentrations Ti/Ca, Cr/Ca, Fe/Ca, Co/Ca, Zn/Ca As/Ca, Pb/Ca. Călăraşi has the highest ratio of Mn/Ca and the filter from Brăila is put in evidence by the Hg/Ca. Certainly the level of pollution of a region can not be determined by a single filter and is need of a good statistic to draw conclusions.

5. Mosses as bioindicators of air quality

The main polluting regional industries are: stainless steel works (Târgovişte), cement and related materials production (Fieni), glass and lighting sources production (Târgovişte, Fieni), chemicals materials production (Târgovişte, Doiceşti), coal mining and thermal power station (Doiceşti), oil exploration (Târgovişte, Moreni, Găieşti). The most affected towns are Fieni, Doiceşti, Moreni, Găiesti and Târgovişte in decreasing order regarding pollution with sedimentable powder.

The cement factory in the town of Fieni is responsible for the third place in the list of the most polluted localities of Romania (Romanian Statistical Yearbook–2001: National Institute of Statistics).

Mosses are particularly effective biomonitors [4, 9] of atmospheric heavy metal contamination because of their bioaccumulative properties. These plant groups are amenable to biomonitoring because they are widespread, easy to handle and they lack a cuticle and root system thus reflecting directly atmospheric heavy metal deposition. The elemental composition of mosses can be determined using a sensitive analytical method like Particle Induced X-ray Emission (PIXE) [2,3]. Sampling of mosses *(Mnium undulatum)* was carried out in the investigated area – the transect from north to south of the Dâmbovița county (Figure 1.) in summer-autumn 2004. Sample preparation: generally the solid samples are chemically digested followed by internal standard addition. In the case of mosses a few tens of milligrams were weighted and put into 50 mL HDPE vials. Depending on the mosses density, for each sample an equal volume of 2–4 mL HNO_3 (Merck, 65%, suprapur) and a few hundred microliters H_2O_2 and HF (Merck, p.a.) were added. In order to assure complete digestion the samples were heated for 4 hours at 75°C. After digestion each sample was diluted with a convenient volume of deionized water followed by addition of internal standard (200 µL solution of Y_2O_3 in HNO_3 medium, containing 160.8 µg Y/mL).

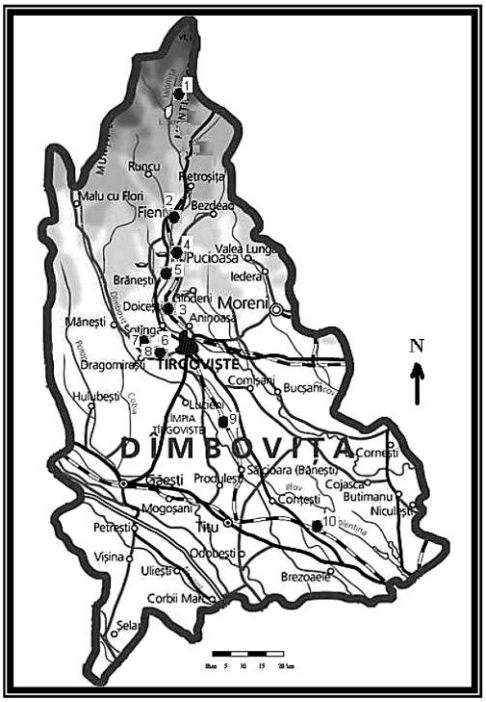


Fig. 1. Map of the Dâmbovița county with samples localization.

Volumes of 150 µL (exception for sample P-8 of 50 µL) were deposited and evaporated on mylar foil (2.5 µm thickness) fixed on aluminium frames. The moss amounts corresponding to evaporated samples on mylar are given in Table 3.

Table 1. Sample characterization.

Sample code	*Sample localization*	*Mass of dry mosses (μg)*
P1	Saua Strunga	141.94
P2	Fieni	156.52
P3	Doiceşti	112.82
P4	Pucioasa	134.37
P5	Brăneşti	147.87
P6	Priseaca	117.54
P7	Ungureni	110.50
P8	Priseaca	43.87
P9	Mircea Vodă	119.56
P10	Tărtăşeşti	140.92

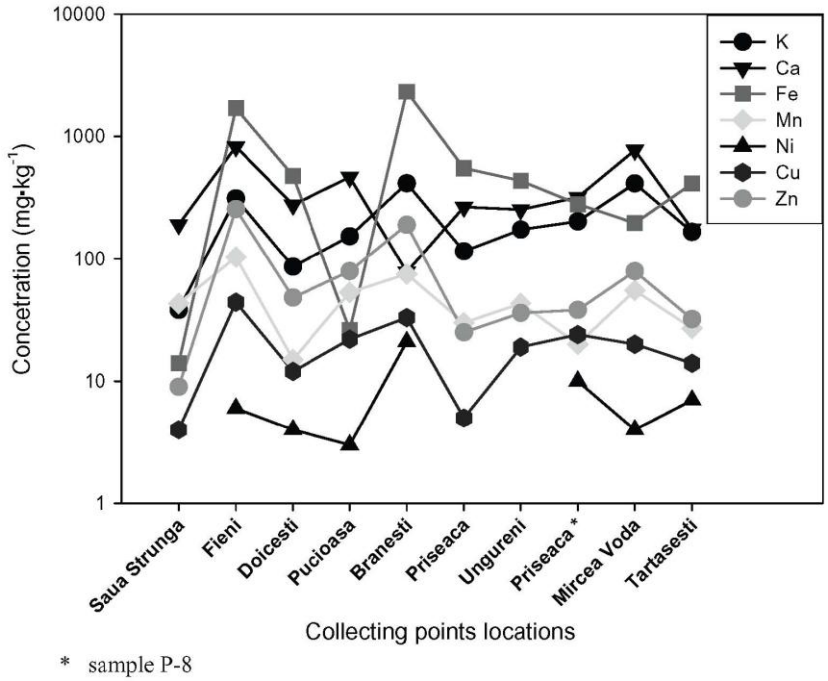
Analytical method: the samples were analyzed by the PIXE technique using 3 MeV protons delivered by the 9 MV Van de Graaff Tandem Accelerator of NIPNE. The analyses were carried out in vacuum. A collimated beam (3 mm diameter) bombarded the target oriented at an angle of 45° with respect to the beam direction. The emitted X-rays were detected by a Canberra Ge(HP) detector, having an energy resolution of 180 eV / 5.9 keV and placed at an angle of 90° to the incident beam direction. For the present measurements, the X-rays passed through the Be windows of the scattering chamber (0.25 mm thick) and detector (76 μm thick), and a 2 cm air gap. The signals from the detector preamplifier were processed with a Tennelec spectroscopic amplifier model TC244, enabling pile-up rejection, and then fed into a model 1520 Canberra ADC and mixer-router. Data manipulation and storage were performed with a Canberra S100 counting system, based on an IBM personal computer. The X-ray spectra were analyzed using the code LEONE, which models the X-ray peaks with Gaussian functions and subtracts a polynomial background (of degree 1-3). The peak area derived from the fitting routine, corrected for X-ray attenuation and detector efficiency, were then used to determine the elemental concentrations of Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Sr, Cd and Pb in samples. Table 4 summarizes data on elemental content in the moss samples collected from the Dâmboviţa county expressed in $mg \cdot kg^{-1}$. Uncertainties in the table (1σ) are statistical. It should be noted that heavy metal (Fe, Ni, Cu, Zn) concentration in samples is an important component of air quality and an excess of heavy metal concentration in the environment can modify negatively the quality of life. Figure 2 illustrates by the distribution of heavy metals in mosses – note should be taken of a high content of: Fe, Mn, Ca and Zn detected in Fieni and Brăneşti; Ni and Cu are detected in Fieni and Priseaca (Târgovişte neighborhood). The different concentrations of elements in sample are the results of the different industrial levels of the sampling regions.

Table 1. Elemental concentration in the mosses samples from the Dâmbovița county, $mg \cdot kg^{-1}$ dry matter

Concentration							
Sample code	K	Ca	Fe	Mn	Ni	Cu	Zn
P1	380±7.2	191±12	14±1	43±7	ND	4±1	9±3
P2	311±143	824±2	1997±67	103±29	6±1	44±2	255±5
P3	86±1	176±1	477±4	15±1	4±1	12±1	48±2
P4	153±1	464±2	26±1	53±2	3±1	22±2	79±33
P5	414±2	78±3	2320±8	75±2	21±4	33±3	190±22
P6	115±1	262±2	550±4	30±1	ND	5±2	25±3
P7	173±1	252±2	434±4	43±2	ND	19±3	36±3
P8	202±10	318±2	280±3	20±1	10±1	24±2	38±3
P9	413±716	772±26	196±3	55±2	4±1	20±2	79±4
P10	166±2	175±3	411±3	27±1	7±2	14±2	32±3

ND - Not detected

The obtained elemental concentrations was compared with the Norway background level in mosses [9] and we can say that the Fe, As, Cd and Pb concentrations are greater at Fieni, Brăneşti and Mircea Vodă than at Şaua Strunga situated in the Bucegi, Carpathian Mountains.



* sample P-8

Fig. 2. Element concentrations in mosses (ppm) along the Dâmbovița county from north to south.

Conclusions

Mnium undulatum is a specific type of moss from the Muntenia region (including the Dâmboviţa county), so we can successfully use these for environmental biomonitoring. Experimental results of this work confirm that Fieni town is one of the most polluted towns from the Dâmboviţa county. The preliminary results are starting points for the future research project entitled *"Heavy metal pollution of the Dâmbovita county, Romania, studied by nuclear and related analytical techniques"*, between the Valahia University of Târgovişte and JINR Dubna.

R E F E R E N C E S

[1] S. A. E. Johanson, J.L. Campbell, PIXE – A Novel Technique for Elemental Analysis, (John Wiley and Sons, New York, 1988)

[2] Particle-Induced X-Ray Emission Spectrometry (PIXE), Eds. S.A.E. Johanson, J.L. Campbell, K.G. Malmqvist (J. Wiley and Sons, N.Y, 1995)

[3] T. Bădică et al., in Proc. Int. Conf. On Nuclear Data in Science and Techn., Trieste, 1997, Conf. Proceedings 59(2), 1389 (CIF, Bologna, 1997)

[4] M. A. S. Burton, Biological monitoring of environmental contaminants (plants). MARC Report Number 32. Monitoring and Assessment Research Centre, King's College London, University of London. 1986.

[5] E. Steinnes, E. M. Andersson, Atmospheric deposition of mercury in Norway: Temporal and spatial trends. Water, Air and Soil Pollution, 56, 1991, p. 391–404.

[6] E. Steinnes, J. P. Rambaek, J. E. Hanssen, Large scale multi-element survey of atmospheric deposition using naturally growing moss as a biomonitor. Chemosphere, 25, 1992, p. 735–752.

[7] E. Steinnes, O. Johansen, O. Royset, M. Odegard, Comparison of different multi-element techniques for analysis of mosses used as biomonitors. Environmental Monitoring and Assessment, 25, 2, 1993, p. 87–97.

[8] E. Steinnes, J. E. Hanssen, J. P. Rambaek, N. B. Vogt, Atmospheric deposition of trace elements in Norway: Temporal and spatial trends studied by moss analysis. Water, Air and Soil Pollution, 74, 1–2 1994, p. 121–140.

[9] M. V. Frontasyeva, V. M. Nazarov, E. Steinnes, Moss as a monitor of heavy-metal deposition – Comparison of different multi-element analytical techniques. Journal of Radioanalytical and Nuclear Chemistry-Articles, 181, 2, 1994, p. 363–371.