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PIXE ANALYTICAL METHODS APPLIED IN ENVIRONMENTAL

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Abstract: *Nuclear Analytical Methods 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 the analytical methods PIXE Particle Induced X-rays Excitation) with applications in trace elements analysis on aerosol and antarctic samples.*

Keywords: *PIXE, pollution, heavy metal*

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 intensity, either of energy absorbed or produced. Electromagnetic spectroscopy involves interactions of matter with electromagnetic radiation, such as light. PIXE spectroscopy involves interactions with atoms. Particle induced x-ray emission (PIXE), 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).

3. Results and discussions

3.1. Aerosols samples

We have analyzed aerosols deposits on filters from ten Romanian towns: Pitesti, Giurgiu, Resita, Ramnicu-Valcea, Baia-Mare, Craiova, Timisoara, Calarasi, Braila 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 table 1.

Table 1. The elemental concentrations with respect to the concentration of the Ca for all analyzed samples.

City/ Element	Pitesti	Giurgiu	Resita	Rm. Valcea	Baia Mare	Craiova	Timi soara	Calarasi	Braila	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						.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(fig.): 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. Calarasi has the highest ratio of Mn/Ca and the filter from Braila is put in evidence by the Hg/Ca. Certainly the level of pullution of a region can not be determined by a single filter and is need of a good statistic to draw conclusions.

3.2. Antarctic samples.

Antarctica is supported to suffer minimally from anthropogenic pollution. The recent interest in Antarctica atmosphere, due to the "Antarctic ozone Hole" had resulted in recognition of the need for long term background environmental characterization studies.

We have analyzed samples of ice from different depths of a glacier from Antarctic zone. The samples heave been collected during a Bulgarian Antarctic Expedition, by dr. V. Gourev. We have applied Proton Induced X-Ray (PIXE) method in order to determine polluting elements. The samples of 200 ml of molten ice have been passed through Nucleopore filters.

The glaciers at the Livingston Island, Antarctica are of the warm type, whose zero-degree isoterm is at a relatively high altitude (~ 300 m nowadays). This results in an intensive process of melting of the glacier surface below this altitude during the astral summer, which results in washing out of the glacier structure in its lower part [1]. The dome of Perunika glacier, which flows above the South Bay of the Livingston Island is at an altitude of about 350 – 400 m and is above the zero-degree isoterm, which was measured in the late 1990's to be at 280 m [2].

This result is in a relatively narrow accumulation zone of the glacier. Obviously, small variations of the average annual temperature influence strongly the accumulation of the glacier at its present regime, which is reflected by the overall fluctuation of the glacier boundaries. All this is related to the more general problem of global change of the Earth's climate. Thus, the glaciers in Sub-Antarctica, where the Livingston Island belongs, turn out to be a very sensitive tool to detect the global change effect on top of the background of temperature fluctuations. Out primary motivation to study trace-element concentrations was to understand the accumulation and ablasion pattern of Perunika glacier. Another goal of this research was to determine the average values of aerosol inclusions for different elements over the last decades, to study the correlations between them and find possible trends in the data.

It should be noted that the glacier dynamics is much more complicated due to the existence of pyroclastic layers in the glacier, which result from the periodic eruptions of the Deception volcano (situated at the neighboring Deception Island), the last one been in 1967-1969. These layers appear on its surface in the lower part of the glaciers at the South Shetlands, which changes their albedo and influences their dynamics and mass balance for long periods of time. Several dark layers, which correspond to volcanic eruptions are observed at the glacier front of Perunika glacier. These provide a time scale, which can be used for chronolization of the lowest part of the glacier. At the dome of Perunika glacier at present these layers lie deep below its surface. For example, for one drill site the first pyroclastic layer was found at a depth of 13 m (see also the trace-element depth profiles in Fig. 5). This allows a time scale at the dome of the glacier to be fixed, too.

All field operations were conducted at Perunika glacier. Ice-core samples were collected during the Third (1994/95), Forth (1995/96) and Sixth (1997/98) Bulgarian Antarctic campaigns. The logistic support of St. Kliment Ohridsky base (62°38′29″ S and 60°21′53″ N), which is operated by the Bulgarian Antarctic Program, was utilized. The base is situated at the beach of the South Bay at the Livingston Island. Usually 5-6 researchers work there during the astral summer season and they are supported by 4-5 technical assistants and base personnel. The base can accept maximum 15 people and no wintering is done there. It is equipped with a field laboratory, a room 2.5 x 4 m, which is heated through the central heating system of the base and provided with running water and a stable source of electric power for operation of scientific equipment and computers. There the primary manipulation of the samples took place.

All drill sites were 5 – 7 km away from the base on Perunika glacier, whose lowest part is as far as 50 m from St. Kliment Ohridsky base. Transport to and from the drill sites was accomplished by means of a Nansen sled. Owing to the severe weather conditions and the numerous crevasses, which open in the glacier during the summer season, it was necessary to flag the track between the drill sites and the base, so that the transport could be accomplished safely under the frequent whiteout or foggy conditions that were encountered in most of the cases. Motor ski-doe transport was avoided in order not to contaminate the drill sites. Three sample sites were chosen: below, at and above the zero isoterm of the glacier. Each drilling reached a depth of 15 - 30 m. Different techniques were used for sample collection: vertical ice-core drilling or horizontal drilling in crevasses. In the latter case ice-climbing techniques were used to enter the crevasses. The surface layers of the crevasse were removed with a Teflon-covered spade before sampling. In all cases special measures were taken to avoid contact of the field assistant and the equipment with the cleaned surface of the crevasse or with the ice core. Different procedures were developed in order to reduce as much as possible the degree of contamination, which is introduced in the process of sample collection. In addition different control samples were taken in order to eliminate systematic errors.

Drill site no. 1 was chosen in the vicinity of Burdick peak at an altitude of about 370 m, which is definitely above the zero isoterm of the glacier. Close to the glacier surface (the top 3 m) samples were taken at every 10 cm in order to study the accumulation process. Deeper in the glacier the step was 50 cm and the profile reached a depth of 15.5 m.

Drill site no. 2 was situated in the vicinity of Nunatak del Castillo at an altitude of about 280 m. From each sample a volume of 100 ml and was sealed in a clean polyethylene bottle and transported back to Bulgaria for laboratory analysis.

Drill site no. 3 was situated in the vicinity of Burdick peak at an altitude of about 260 m. A mechanical Ti drill was constructed and horizontal ice drilling was performed. Each sample had a volume of 100 ml and was sealed in a clean polyethylene bottle and transported back to Bulgaria for laboratory analysis.

The samples were analyzed by different methods: the ICP-AES/USN technique (ICP-AES is short for optical emission spectrometry with inductively coupled plasma in combination with an ultrasonic nebulizer) [3,4], the proton induced X-ray emission spectrometry (PIXE) [5,6], as well as neutron-activation analysis and measurements of the electric conductivity of the samples. The samples from drill sites no. 2 and 3 were analyzed with the ICP-AES/USN technique. A Liberty 110 Varian spectrometer in combination with a ultrasonic nebulizer (USN) of CETAC-5000 AT+ with Peltie cooler and the Varian ET-AAS with a Zeeman corrector Spectra 880 Z and an automatic sample holder were used for these measurements. The limits of detection (LOD) are usually in the ppb range (1 ÷ 10 μg/l) for most of the elements [4]. The limits of detection are improved 10 ÷ 50 times by using an USN. It was possible to carry out fast elemental analysis using 2 ml/min of the sample. A quality control (accuracy and reproducibility) of the analysis was carried out [3]. Solutions, diluted from the certified solutions of Breit-Lauder GmbH with concentrations five times higher than the LOD, were used. A set of 10% of the samples was repeated with secret names. The results of these studies were published recently [7, 8]. The samples from drill sites no. 1 and 2 were analyzed with the PIXE technique. The PIXE analysis was carried out at IFIN-HH, in Bucharest. The samples, as well as a blank filter have been irradiated by a 3 MeV proton beam, which was supplied by the FN-tandem accelerator.

The beam current varied between 5-10 nA, to provide a count rate below 300 counts/s. X-rays, emitted by the sample atoms, have been detected with a Si(Li) detector with a 160 eV resolution at 6.4 keV. The X-ray spectra were fitted off-line and after subtraction of the concentration given by the blank filter, the concentration data for a number of elements was obtained. First results of the PIXE analysis from drill site 2 were reported recently [9].

These studies were undertaken to meet the following objectives:

- to determine the mean snow accumulation at the dome of the glacier, *i.e.* above the zero isotherm;
- to determine the mean concentrations of different elements, eliminating as much as possible different systematic errors;
- to determine the origin of different inclusions in the glaciers: rock erosion, oceanic transport, volcanic activity, technogenic pollution, etc.;
- to perform stratigraphy of the glacier and determine the annual glacier layers.

The solution of each of these problems encounters different difficulties and in each case a complex approach is needed, *e.g.* the mean snow accumulation requires either continuous monitoring, or development of realistic models for the icefication of the snow, in combination with knowledge of the glacier stratigraphy, or both. The determination of the origin of the inclusions requires knowledge on the geochemistry of the Livingston Island, while the stratigraphy of the glacier is related to the knowledge of its flow. All these problems are in the scope of the Bulgarian Antarctic program, but answers are not straightforward and take time.

Table 1. Average concentrations of trace elements deposited at the dome of Perunica glacier at the Livingston Island, Antarctica. The concentrations are in μg/l. The uncertainties are of the order of 5 ÷ 10 %.

Element	Antarctica	Site no. 1	
	Average values [10]	PIXE Millipore	PIXE Micropore
K	3.1	3.1(1.0)	4.4(8)
Ca	2.2	4.9(8)	4.5(5)
Fe	2.9	12.0(2.8)	21(2)
Cu	-	1.3(2)	0.6(1)
Zn	-	1.4(4)	0.9(1)

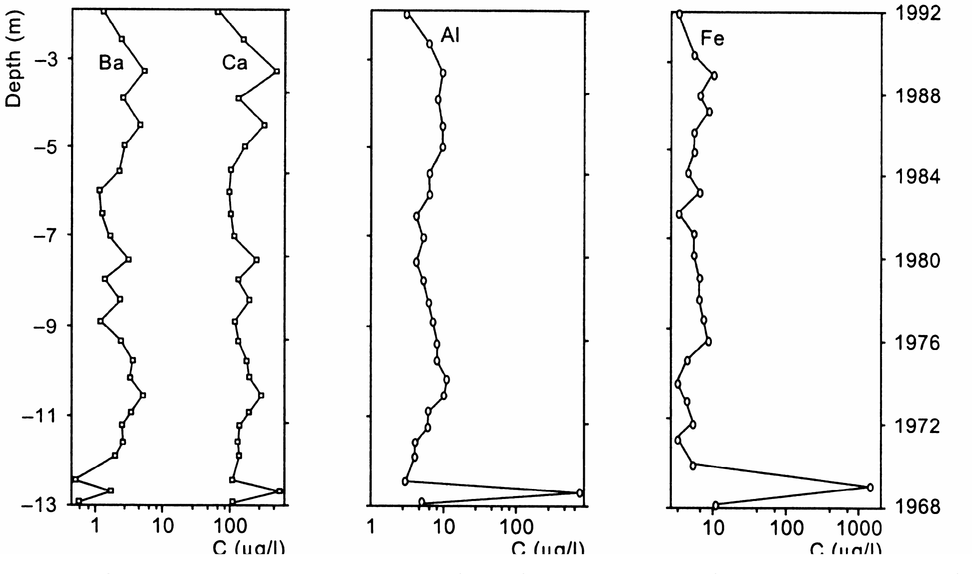

Fig. 1. Record of trace element concentrations in annual glacier layers at the Livingston Island, Antarctica. The uncertainties of the data points are of the order of 10%.

The analytical methods, which were utilized here shed light at two of the above defined problems: an estimate of the mean snow accumulation was done and the mean concentrations of different elements were determined.

In Figure 1 we present results for trace-element abundances in an ice core from drill site no. 1 [7,8]. The samples were analyzed by different methods: the ICP-AES/USN technique (ICP-AES is short for optical emission spectrometry with inductively coupled plasma in combination with an ultrasonic nebulizer). Note the nice correlation between the concentrations of Ca and Ba, which are of oceanic origin and are deposited in the glacier through rainout and washout processes. Another feature, which is displayed in Fig. 1, is the peak in all profiles at a depth of 13 m. It corresponds to a sample close to the first pyroclastic layer in the glacier. This peak is much more pronounced for Al and Fe, and is hardly seen for Ba and Ca. This reflects the fact that the deposition of metals is connected to the vuclcano eruption. The small increase of the Ba and Ca concentrations is most probably due to the more intense evaporation processes in the period after the eruption, which are related to albedo changes.

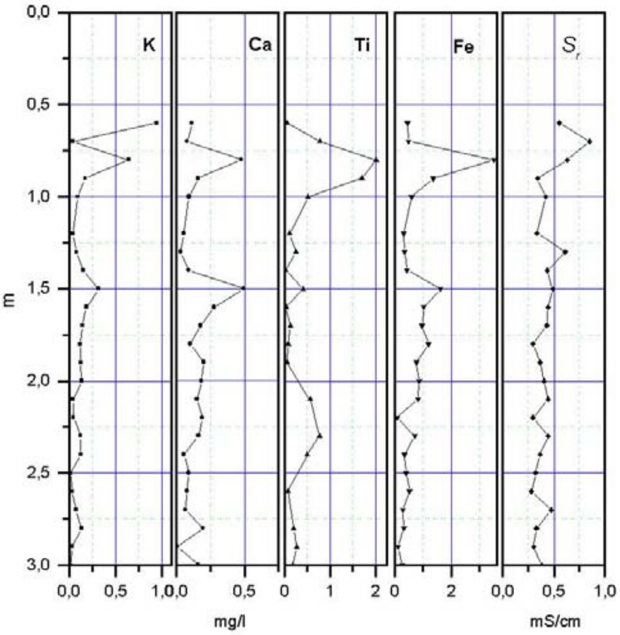

Fig. 2. Trace-element concentrations for several elemnts (K, Ca, Ti, and Fe) and electrical conductivity (*S_r*) record from the top 3 meters at the dome of Perunika glacier. The uncertainties of the data points are of the order of 10%

In Table 1 we present the data for the average concentrations for several elements from drill site 1. All control samples, which were used in the PIXE analysis (filtration of doubly de-ionized water or usage of blank filters), provide correct results. Note the difference in the average concentrations, which were measured e.g. for Zn and Cu with millipore and micropore filters for samples coming from drill site no. 1. This is due to the difference of the filter pore sizes: for the Millipore MAWP037A0 filter they are of the order of 0.8 mm, while for the micropore filter the average pore size is 0.5 μm. The large fraction in this case is clearly of terrestrial origin (rock erosion or transport of pyroclastides). There are no reported values for Cu and Zn in the Antarctica, which allow concluding that the observed increase is of a local origin. The increase of the Fe concentration, compared to the reported values elsewhere is due to the same reason.

The next problem, which has been tackled in these studies, was to determine the snow accumulation at the dome of the glacier (and in this way to shed light on its mass balance). For this purpose samples were taken at every 10 cm for the top 3 m at drill site no. 1. From general meteorological experience it should be expected that evaporation or sublimation at the snow or fern surface could modify considerably the concentration of the deposited aerosols in the glacier layers during longer periods without fresh snowfalls. This is the reason for the seasonal variations of the aerosol concentrations, which are observed in the Antarctic glaciers. The results from the PIXE analysis of these samples are presented in Fig. 2. They are compared with measurements of the electrical conductivity of the samples. Two peaks can be distinguished in the data. The first one corresponds to a depth of about 0.8 m and the second one to 1.5 m. The first peak, although somewhat shifted, is reproduced by the electrical conductivity analysis.

4. Conclusions

In summary, we have reported the results of the analysis of trace element deposition in Antarctic glaciers at the Livingston Island of the South Shetlands. The average concentrations were determined using the ICP-AES and PIXE techniques. These studies allowed the mass accumulation at the dome of Perunika glacier to be determined.

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