ORIGINAL PAPER

AEROSOL SAMPLES ELEMENTAL ANALYSIS FROM SOME ROMANIAN URBAN REGIONS BY PIXE TECHNIQUE

ION V. POPESCU[1,2,3,4], AGATA OLARIU[2], CLAUDIA STIHI[1], GABRIEL DIMA[1], IOANA DANIELA DULAMA[4,5], CARMELIA PETRE[5], RALUCA STIRBESCU[5]

[1] *Valahia University of Targoviste, Faculty of Science and Arts, 130082, Targoviste, Romania*
[2] *National Institute for Physics and Nuclear Engineering, 077125, Magurele, Romania*
[3] *Academy of Romanian Scientists, 050094, Bucharest, Romania*
[4] *Valahia University of Targoviste, Multidisciplinary Research Institute for Sciences and Technologies, 130082, Targoviste, Romania*
[5] *University of Bucharest, Faculty of Physics, Doctoral School, 050107, Bucharest, Romania*

Abstract. *Aerosols deposits on filters from ten Romanian towns with different kinds and levels of industrial development were studied in this work. The elemental composition of samples was established by performing Particle-Induced X-ray Emission (PIXE) measurements. The concentrations of the following elements: S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As and Pb were determined.*

Keywords: *aerosols, pollutants, PIXE.*

1. INTRODUCTION

The pollution of some industrialized regions of Romania is a crucial problem for their inhabitants and also for the future development of these areas.

Using Particle-induced X-ray emission (PIXE) method were analyzed aerosols deposits on filters from ten Romanian towns: Pitesti, Giurgiu, Resita, Ramnicu-Valcea, Baia-Mare, Craiova, Timisoara, Calarasi, Braila and Arad, cities with different levels of industrial development.

Particle Induced X-ray Emission is a high sensitivity method, partially nondestructive which can be use simultaneously with other ion-beam techniques and microprobes.

This method is based on the fact that the sample bombardment with charged particles causes the ionization of the atomic inner shells of different elements followed by a subsequent of the characteristic X-rays. When the X-rays spectrum is detected by a high resolution detector, the well- known Z-dependence of the X-rays energies, as well as the intensities of the individual X-rays line, allow a straightforward determination of the elements present in the target.

The use of protons or alpha particles for the production of inner-shell vacancies combines a high ionization cross section with low X-ray background

The background in the region of low-Z elements is determined by the bremsstrahlung from secondary electrons while at higher X-ray energies from the background is normally determined by γ-rays produced in the target and the Compton electrons scattered in the detector crystal. The selection of various X-rays absorbers improves the sensitivity over the whole elemental range.

Corresponding authors: ivpopes@yahoo.com

The absolute detection limits in thick samples of low Z-elements are normally in the interval 0.1 – 10 μg/g. The advantages and disadvantages of the PIXE method are well known and documented in several reviews, articles and textbooks [1].

2. EXPERIMENTAL

For analysis was used a proton beam with a 3 MeV energy supplied by the FN tandem accelerator from the Institute of Physics and Nuclear Engineering - Bucharest.

The irradiation chamber has a 0.2 mm Be window for X-rays. The target was oriented at the 45° angle by respecting the specifications regarding the beam and detector direction. The beam passes through a collimator (Φ=2mm) before reaching the target. The beam current was kept below 10 nA to maintain a count rate of about 250 counts/s, which implies negligible dead-time and pile-up corrections. X-rays were detected with an HPGe (100 mm^2 x 10 mm) detector with 160 eV energy resolution at 5.9 keV. The experimental set-up was described also, in a previously articles [2,3].

The aerosol samples were collected by the Institute of Hydrology and Waters of Bucharest and prepared in the following manner: aerosol particles were collected using cellulose fiber filter (Whatman 41). The flow rate was 15÷20 l/min. The air volumes were measured with calibrated gasmeters with a precision of about 5%.

The concentrations of observed elements in aerosol samples were determined by using the internal standard method [3], using Yttrium as internal standard. Yttrium was chose because this element is very rare element in the environment items. The intense peaks of Yttrium in the X-spectrum could obscure the peaks of some elements possible existing in the samples. For that reason, the samples were analyzed also without Yttrium and any new elements were not detected. A sample of Yttrium on Whatman 41 filter was measured also. Weak impurities like Ca, Fe and Zn were found. The concentrations of the elements in the aerosol samples were corrected relative to these impurities on the filter.

3. RESULTS AND DISCUSSION

In the present work, the results obtained by PIXE analysis of atmospheric aerosols deposits filters from Romanian towns with different kinds and levels of industrialization are reported.

The concentration of: S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As and Pb ($\mu g/m^3$) in air filters, in five Romanian towns aerosol probes, with known processed air volumes, obtained by PIXE method are given in table 1. The experimental errors were less then 6%.

It can be seen a high concentration of Ti (9.63 $\mu g/m^3$), V (1.20 $\mu g/m^3$), Ni (0.59 $\mu g/m^3$) and S (7.6 $\mu g/m^3$) respectively in the air filters samples collected in Pitesti town; a high concentration of Cr (1.24 $\mu g/m^3$), Mn (10.04 $\mu g/m^3$) and Fe (253 $\mu g/m^3$) respectively in air filters samples collected in Resita town and a high concentration of Cu (36 $\mu g/m^3$), Zn (13.5 $\mu g/m^3$), As (5.09 $\mu g/m^3$) and Pb (1.2.1 $\mu g/m^3$) respectively in air filters samples collected in Baia-Mare town.

In table 2 are presented the concentrations ratios between Ca, as impurity, and the other elements detected in the air filters samples from ten Romanian towns.

It can be seen some high ratios of Ti/Ca: 0.505, Cr/Ca: 0.035, Fe/Ca: 5.38, Zn/Ca: 0.036, As/Ca: 0.005 and Pb: 0.043 respectively for air filters samples collected in Craiova town. Also, a high ratio of Mn/Ca: 0.078 can be seen for the air filters samples collected in Calarasi town.

Table 1. Concentrations in air filters, μg/m^3, in some Romanian towns aerosol probes, with known processed air volumes.

Element	Pitesti	Giurgiu	Resita	Ramnicu-Valcea	Baia-Mare
S	7.58	-	-	-	-
K	38.20	28.7	58.3	-	21.29
Ca	67.50	105.6	475	63.9	406.2
Ti	9.63	5.33	9 096	3.98	-
V	1.20	-	6	0.784	-
Cr	0 157	0.733	1.243	0.432	-
Mn	1.80	1.49	10.04	11.084	2.44
Fe	73.50	51.60	253	41.1	30.41
Ni	0.599	-	-	0.410	-
Cu	0.238	-	0.344	1.31	36.03
Zn	0.802	-	9.14	1.45	13.45
As	-	-	-	0.284	5.097
Pb	-	-	-	0.369	12.06

Table 2. The concentrations ratios between Ca and the others considered elements from different Romanian town air filters samples.

Element	Pitesti	Giurgiu	Resita	Ramnicu-Valcea	Baia-Mare	Craiova	Timisoara	Calarasi	Braila	Arad
S	0.112	-	-	-	-	-	0.02	-	0.012	0.017
K	0.57	0.272	0.122	-	0.052	2.51	0.2	0.26	0.171	0.36
Ca	1	1	1	1	1	1	1	1	1	1
Ti	0.11	0.05	0.019	0.063	-	0.505	0.15	0.66	0.017	0.016
V	0.018	-	-	0.012	-	-	-	-	-	-
Cr	0.002	0.007	0.003	0.007	-	0.035	-	0.12	0.006	0.001
Mn	0.027	0.011	0.021	0.017	0.006	0.05	0.007	0.078	0.021	0.017
Fe	1.09	0.19	0.532	0.617	0.075	5.38	0.52	1.32	0.28	0.58
Ni	0.009	-	-	0.006	-	-	-	-	-	-
Cu	0.001	-	0.001	0.021	0.089	-	0.001	0.008	0.002	0.03
Zn	0.012	-	0.019	0.023	0.033	0.036	0.002	0.015	0.001	0.011
As	-	-	-	0.001	0.001	0.005	-	-		0.001
Pb	-	-	-	0.006	0.03	0.013	-	0.005	0.002	0.0003

4. CONCLUSIONS

In this work were identified 13 elements: S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As and Pb in the air filters samples collected in different Romanian towns. The great number of identified elements in the samples analyzed in this work is similar with the number of elements identified in air filters from two big cities: Livermore (USA) [4] and Munich (Germany) [5].

Certainly the level of pollution of a region can not be determined by a single filter and good statistics are necessary to draw conclusions.

This work demonstrated that PIXE method is a suitable tool in the analysis of air filters, in the pollution studies. Also, the results of this work draw the attention on the presence of the pollutants elements from the atmosphere in Romanian towns monitorized in this study.

REFERENCES

[1] Johansson, S., Campbell, J.L., *PIXE – A Nowel Technique for Elemental Analysis*, Wiely, New-York, 1988.
[2] Badica, T., Ciortea, C., Petrovici, A., Popescu, I., *Revue Roumaine de Physique*, **26** 653, 1981.
[3] Badica, T., Ciortea, C., Cojocaru, V., Ivascu, M., Petrovici, A., Popa, A., Popescu, I., Spiridon, S., *Nucl. Instr. Meth*, **231**, 288, 1984.
[4] Antolak, A.I., Bench, G. S., *Nucl. Instr. Meth. B*, **90**, 956, 1984.
[5] Sansoni, B., Iyer, R.K., Kurth, R., Fresenius, Z., *Anal. Chem*, **306,** 212, 1981.

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