Trace elements analysis of aerosol samples from some Romanian urban zones

I. V. Popescu, T. Badica, Agata Olariu

*National Institute for Physics and Nuclear Engineering*

*76900 P. O. Box MG-6, Magurele Bucharest, Romania*

September 1, 2018

**Abstract**

Aerosols deposits on filters from ten Romanian towns with different kinds and levels of industrial development have been studied. The concentration of elements with Z ≥ 16 have been measured by particle-induced X-ray emission (PIXE) analysis. It has been determined 15 elements: S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Hg and Pb.

Keywords: aerosols, pollutants, PIXE

1 **Introduction**

In this paper 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 method of particle-induced X-ray emission (PIXE). This method is based on the fact that the bombardment
of the sample charged particles causes the ionisation of the atomic inner shells 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 elements present in the target. The properties of PIXE can be summarized as: high sensitivity in small samples, high speed, surface analysis, genuinely multielemental and quantitative, partially nondestructive, possible to combine simultaneously with other ion-beam techniques and microprobes.

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 the background is normally determined by γ-rays produced in the target and the Compton electrons scattered in the crystal of the detector. The selection of various X-rays absorbers can improve the sensitivity over the whole elemental range. Although the ionization cross sections also increase for high elements with increasing particle energy up to rather high energies, the variation in the background radiation leads to the lowest general detection limits being obtained for 1.5-3.5 MeV protons. While the absolute detection limits in thick samples of low Z-elements are normally in the interval from 0.1 to 10 µg/g. The advantages and disadvantages of the method as long in use as the PIXE analysis are well known and documented in several reviews, articles and textbooks [1].

In the present work we report the first PIXE analysis of atmospheric aerosols deposits filters from ten Romanian towns with different kinds and levels of industrialization.
2 Experimental method

The experimental set-up was described previously [2]. The irradiation chamber has a 0.2 mm Be window for X-rays. The target was oriented at the 45° angle with respect to both the beam and detector direction. The beam passes through a collimator (Φ=2mm) before reaching the target. For analysis we used proton beams of 3 MeV energy supplied by the FN tandem accelerator from the Institute for Physics and Nuclear Engineering - Bucharest. 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 a HPGe (100 mm$^2$mm) detector with 160 eV energy resolution at 5.9 keV. Sample targets to be annualized 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 (Whatman 41). The flow rate was 15 to 20 liters per minute. Air volumes were measured with calibrated gasmeters with a precision of about 5% (to our regret half of samples have an unknown air volumes). The absolute concentrations of observed elements in aerosol samples were determined by advantage of the internal standard [3]. This calibration method implies doping the sample with a known amount of the standard element and relating the unknown concentrations to those of the standard element. We choose Yttrium as the calibration standard because it 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: L and K lines of Yttrium overlap SK$_\alpha$ and (Rb and Sr)K lines respectively. Therefore we have analyzed targets without Yttrium too and we have not observed any new elements. A sample of Yttrium on Whatman 41 filter was measured too. Weak impurities of Ca, Fe and Zn were found. Concentrations of elements present in the aerosol samples were corrected for these impurities of the filter.
3 Results and discussions

A typical PIXE spectrum of an air filter sample is shown in Fig. 1. We have identified 15 elements: S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Hg and Pb. The measured elemental concentrations are given in µg per m$^3$ air in Table 1 for five samples with the known processed air volumes, and with respect to the concentration of the Ca for all analyzed samples in Table 2.

The great number of identified elements in the samples is similar to these of big cities as Livermore (USA) and Munich (Germany). It is worth to mention the absence of the Cadmium element in our studied samples.

One could remark from the Table 1 the air filters from the town Pitesti, for the highest concentrations of the following elements: Ti: $9.63 \mu g/m^3$, V: $1.20 \mu g/m^3$, Ni: $0.59 \mu g/m^3$, S: $7.6 \mu g/m^3$, the town Resita for: Cr: $1.24 \mu g/m^3$, Mn: $10.04 \mu g/m^3$, Fe:253 $\mu g/m^3$, Baia-Mare for Cu: 36 $\mu g/m^3$, Zn: 13.5 $\mu g/m^3$, As: 5.09 $\mu g/m^3$, Pb:12.1 $\mu g/m^3$.

From the ratios of concentrations shown in the Table 2 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: 0.505, Cr/Ca: 0.035, Fe/Ca: 5.38, Co: 0.015, Zn/Ca: 0.036, As: 0.005 and Pb: 0.043. Calarasi has the highest ratio of Mn/Ca: 0.078 and the filter from Braila is put in evidence by the presence of Mercury, Hg/Ca: 0.003. Certainly the level of pollution of a region can not be determined by a single filter and it is need of a good statistics to draw conclusions. This work want rather to demonstrate that the PIXE method is a suitable tool in the analysis of air filters in the pollution studies and and also the results of this analysis draw the attention on the presence of the pollutants elements from the atmosphere of towns discussed in this paper.
References

[1] PIXE- a Novel Technique for Elemental Analysis, Wiely, New-York, 1988.

[2] T. Badica, C. Ciortea, A. Petrovici, I. Popescu, Revue Roumaine de Physique 26 (1981) 653.

[3] T. Badica, C. Ciortea, V. Cojocaru, M. Ivascu, A. Petrovici, A. Popa, I. Popescu, S. Spiridon, Nucl. Instr. Meth. 231(1984)288.

[4] A. I. Antolak and G. S. Bench, Nucl. Instr. Meth. B90 (1994) 956.

[5] B. Sansoni, R. K. Iyer, R. Kurth, Fresenius Z., Anal. Chem. 306 (1981) 212.
Table 1. Concentrations in air filters, $\mu g/m^3$, towns in Romania, by PIXE, with known processed air volumes

| Element | Pitesti | Giurgiu | Resita | Ramnicu-Valcea | Baia-Mare |
|---------|---------|---------|--------|----------------|-----------|
| S       | 7.58    | -       | -      | -              | -         |
| K       | 38.2    | 28.7    | 58.3   | -              | 21.29     |
| Ca      | 67.500  | 105.6   | 475    | 63.9           | 406.2     |
| Ti      | 9.63    | 5.33    | 9.096  | 3.98           | -         |
| V       | 1.200   | -       | -      | 0.784          | -         |
| Cr      | 0.157   | 0.733   | 1.243  | 0.432          | -         |
| Mn      | 1.8     | 1.49    | 10.04  | 11.084         | 2.44      |
| Fe      | 73.5    | 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. Ratios of concentrations with respect to the concentration of the Ca, air filters from industrialized towns in Romania, by PIXE

| Element | Pitesti | Giurgiu | Resita | Ramnicu-Valcea | Baia-Mare | Craiova | Timisoara | 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  | 0.046|
| V       | 0.018  | -       | -      | 0.012         | -         | 0.05    | 0.05      | 0.073    | 0.024  | 0.017|
| Cr      | 0.002  | 0.007   | 0.003  | 0.007         | -         | 0.035   | -         | 0.12     | 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  | 0.03 |
| 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|


Fig. 1 Pixe spectrum. 3 MeV protons, air filter from Pitesti