

IFUSP/P 417
B.I.F. - USP

UNIVERSIDADE DE SÃO PAULO

INSTITUTO DE FÍSICA
CAIXA POSTAL 20516
01000 - SÃO PAULO - SP
BRASIL

publicações

08 AGO 1993



2 IFUSP/P-417

THE SÃO PAULO - PIXE SYSTEM AND ITS USE ON A
NATIONAL MONITORING AIR QUALITY PROGRAM

by

Celso Q. Orsini, Paulo A. Netto, and Manfredo
H. Tabacniks

Instituto de Física, Universidade de São Paulo

Julho/1983

THE SÃO PAULO - PIXE SYSTEM AND ITS USE ON A NATIONAL (*)
MONITORING AIR QUALITY PROGRAM

CELSO Q. ORSINI, PAULO A. NETTO, AND MANFREDO H. TABACNIKIS
 INSTITUTO DE FÍSICA DA UNIVERSIDADE DE SÃO PAULO
 CAIXA POSTAL 20516
 01498 - SÃO PAULO, SP, BRASIL

ABSTRACT

The SP-PIXE has been installed on the 8 MV Pelletron accelerator of the IFUSP. Its characteristics and calibration procedure are presented below. The SP-PIXE is being used as the reference analytical method on a national monitoring air quality program performed by the Group for Air Pollution Studies (GEPA) of the IFUSP. As part of the program eight sites around Brazil, seven having critical air pollution problems and one with natural atmosphere, have been selected for sampling. Each aerosol is sampled continuously for one year using stacked filter units and, for period of 3 to 5 days, by 10-stage cascade impactors. Partial results from the two first sites investigated are presented here by figures of element size distribution curves and histograms of relative concentrations.

(*) Presented in the Third International PIXE Conference (Heidelberg, Germany, July/83). To be published in Nuclear Instruments and Methods.

1. CHARACTERISTICS AND CALIBRATION

PIXE is the main analytical method used by the GEPA of the Institute of Physics of the University of São Paulo - IFUSP. It is installed at the IFUSP 8 MV Pelletron accelerator and its main characteristics are:

Beam - 8 MeV alpha particles beam with a maximum 200 nA before the diffusion foil, reduced to 10 nA on the target. It is collimated by a circular carbon collimator $\phi = 3.7$ mm;

Diffusion foil - Nickel, $200 \mu\text{g}/\text{cm}^2$ thick, located 2.1 m from the target;

Detector - Si(Li), 4 mm diameter, 8 μm berilium window in vacuum, forming a 120° angle relative to the beam;

X-Ray Absorber - 103 μm Mylar foil with a 0.8 mm coaxial hole fixed immediately in front of the detector Be window;

Targets - Thin, held in sets of 8 on a target changer placed at 45° to the beam. Samples are collected on Kinfol and Nuclepore. Calibration standards evaporated on 3 μm Mylar foil as well as commercially available (from Micromatter) standards have been used.

In the figure 1 we can see a horizontal cross section of the SP-PIXE irradiation chamber.

The quantitative calibration has been achieved by irradiating thin standards of Al, Si, BaCl_2 , K_2CrO_4 , Ti, Cr, Mn, Fe, Cu, Ge, Ag, Sn, and Au evaporated on Mylar and weighted on a micro-balance. A theoretical sensitivity curve calculated according to the following equation:

$$R = \frac{\Omega}{4\pi} \epsilon \frac{\sigma_x}{A} \frac{T}{S}$$

where σ_x is the X-Ray production cross-section calculated by PWBA, T is the X-Ray transmission of the absorber with hole, S is the beam cross section, Ω , ϵ and A are, respectively, the solid angle, detector efficiency and the atomic mass.

The detection limit has been estimated by means of irradiation of blank kinfol and Nuclepore targets by using the relation $3\sqrt{N_b}$, where N_b is the background counts under a considered peak. They ranged approximately from 0,1 to 1 ng for the $k\alpha$ lines and 1 to 10 ng for $L\alpha$ lines, within the beam area.

The overall precision is estimated to be 30% for elements with $11 < Z < 16$ and $Z > 30$, and improving to 10% for $16 < Z < 30$. Further details may be found in reference 1.

2. THE NATIONAL MONITORING AIR QUALITY PROGRAM BASED ON THE SP-PIXE

2.1 - OBJECTIVES AND METHODOLOGY

Does it make sense to base a national monitoring air quality program on PIXE methodology?

We believe so. In fact this is the main project now being carried out by the GEPA^(*). However, it should be emphasized that the

(*) The project is supported by FINEP (Financiadora de Estudos e Projetos), from the Brazilian federal government and is co-assisted by the SEMA (Secretaria Especial do Meio Ambiente), the Brazilian agency for the protection of the environment.

project does not intend to replace the daily routine works of the air pollution control services.

Actually, the main goals may be described as follows:

1. To perform a preliminary characterization of one natural and 7 critical atmospheric aerosols, selected around the country (see map in figure 2), for their properties of the trace-element constituents of the fine and coarse components of the inhalable particles, and, when ever possible, relate them to their natural or anthropogenic sources.

2. To promote the transfer of technology and education on air pollution problems by involving local people in intensive training courses and in the field experiments.

2.2 - EXPERIMENTAL METHODOLOGY

Summarily, the experimental methodology adopted by the project can be described as follows: the selected atmospheric aerosols should be sampled, during one year, by means of one SFU (Stacked Filter Unity) sampler⁽²⁾. After 3 to 5 days of sampling the SFU containing the exposed filter is air mailed to our laboratory and is changed for an unexposed one. Beside these long term samplings an intensive short term (one week) sampling is also performed by means of two sampling-stations, each one operating with one 10-stage CI (Cascade Impactor), Battelle model, plus one SFU⁽²⁾.

All the SFU samples are analyzed gravimetrically to determine the total fine, coarse and inhalable air particle concentrations of the investigated aerosols. As much as possible of the collected samples, from both SFU and CI, are analyzed by

PIXE to determine their trace-element concentrations.

Sampling commenced last September, in the remote sea-shore aerosol of Juréia, SP, according to the plans of the Project. Followed the ones in Porto Alegre, RS, (November) and Salvador, Ba, (March). Details may be found elsewhere in the published periodic reports of the project⁽³⁾.

3. RESULTS

To facilitate the interpretations and discussions of the results obtained, they are presented here in the following figures: (1) the element size-distribution curves ESDC; (2) the element relative histograms, ERH.

The most significant element size-distribution curves obtained for the first two sampled aerosols (Juréia and Porto Alegre) are shown in figure 3. For comparative purposes, curves from the urban aerosol of São Paulo City (from 1976 to 1981) and the remote aerosols of Goiás (central plateau) and Amazonas (tropical forest)^(4,5,6) are also presented.

Next, in figure 4, we present relative histograms, separately for the fine and coarse components of the inhalable particles. These histograms were obtained by dividing each trace-element concentration by the corresponding fine or coarse total particle concentrations.

The averaged concentrations (in $\mu\text{g}/\text{m}^3$) obtained up to May/83 by the gravimetric measurements of the filters of SPU, are:

	Fine Particles	Coarse Particles	Inhalable Particles
Juréia	7,6	14,6	24,2
Porto Alegre	11,7	49,0	60,7

4. DISCUSSIONS AND CONCLUSIONS

A qualitative examination of the ESDC in figure 3 reveals the main difference between the natural (Ju,Go, Am) and the anthropogenic (SP,PA) aerosols investigated: the anthropogenic concentrations (the fine component of S, Cl, K, Fe and Zn - and possibly Ti - and part of the coarse component of Si, Ca, K and Fe) are at least one order of magnitude above those observed at the remote locations (fine S and K, and coarse Si, S, Cl, Ca, K, Ti and Fe). The good reproducibility and low detection limit of the PIXE, favoring the determination of the element size-distribution curve with high precision make it possible to observe the constancy of the size-distribution curves of São Paulo aerosol during the period 1976-1981 in spite of a slight decrease of the absolute values. In the last two years this decrease may well be consequence of meteorological variations, or be due to the industrial recession, beginning by the end of 1979.

The influence of changing atmospheric conditions on the trace-element concentrations can be minimized by the use of a histogram of these concentrations normalized to the total fine or coarse (depending on each case) particulate concentrations. These relations should remove a good part of the concentration variations because the element structure of the atmospheric aerosols are not sensitive to moderate change in pressure and temperature. So, we expect that these relations (and the whole histogram) are kept approximately constant during the period. Unfortunately we still do not have a data set over a sufficiently large time period to observe this effect. However, the ERH presented in figure 4 emphasizes the differences between both, the fine-coarse and the Juréia-Porto Alegre distributions.

Among the many others conclusions which can be drawn from figures 3 and 4 we note the dominant presence of S (about 13%) among the trace-element (N, C and O not included) constituents of the fine particulate matter of Jurêia, a fact which is consistent with the well-known exudation of sulfur by plants.

REFERENCES

1. M.H.Tabacniks, Master of Arts degree thesis (in Portuguese), IFUSP, 1983.
2. C.Q.Orsini, P.A.Netto, M.H.Tabacniks, V.L.Souares and T.Germano; Final Report on air quality evaluation in Cubatão (in Portuguese), IFUSP, 1982.
3. C.Q.Orsini, P.A. Netto, M.H.Tabacniks, V.L.Souares and A.S.Kerr; Report on the GEPA/SEMA Project (in Portuguese) to be published, IFUSP, 1983.
4. C.Q.Orsini, P.Artaxo and M. Tabacniks; Proc.(Posters) 6th World Congress on Air Quality, published by I.U.A.P.P.A. (1983) 69-71.
5. P.A.Netto, C.Q.Orsini, M.H.Tabacniks, L.C.Bouêres and A.Leslie, (in Portuguese) An.Acad. Brasil.Cienc. 54(2) (1982) 299-314.
6. C.Q.Orsini, P.A.Netto and M.H.Tabacniks; Atmospheric Environment 16(9) (1982) 2177-2181.

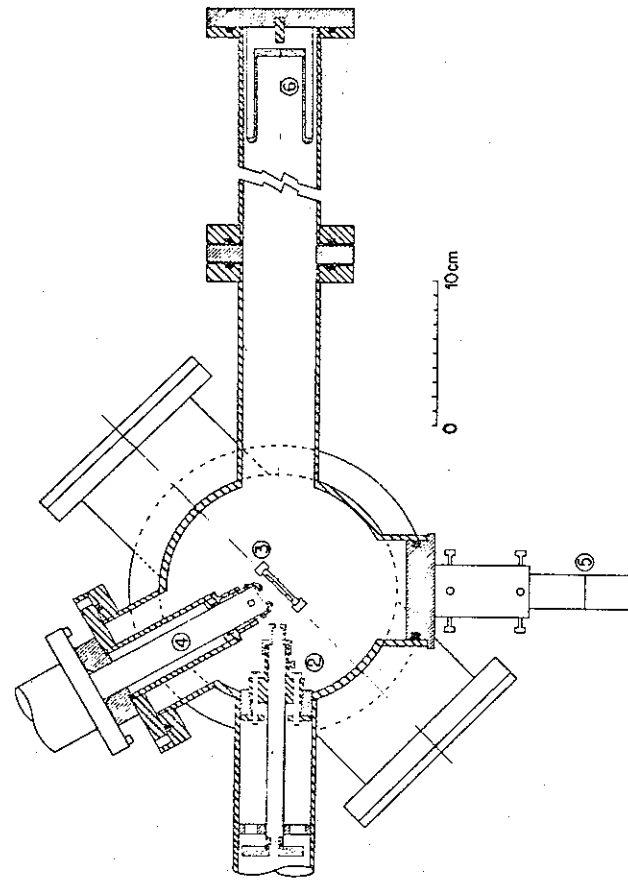


Figure 1: Horizontal cross section of the SP-PIXE irradiation chamber.
 (2) - Beam collimator; (3) - Sample; (4) - Si(Li) Detector;
 (6) - Faraday Cup; (7) - Optic System for Sample Centralization.



Figure 2: The geographic location of the 1 natural and 7 critical atmospheric aerosols selected to be sampled in the project (For comparison, results from São Paulo, Amazonas-Forest and Goiás - Central plateau are also presented).

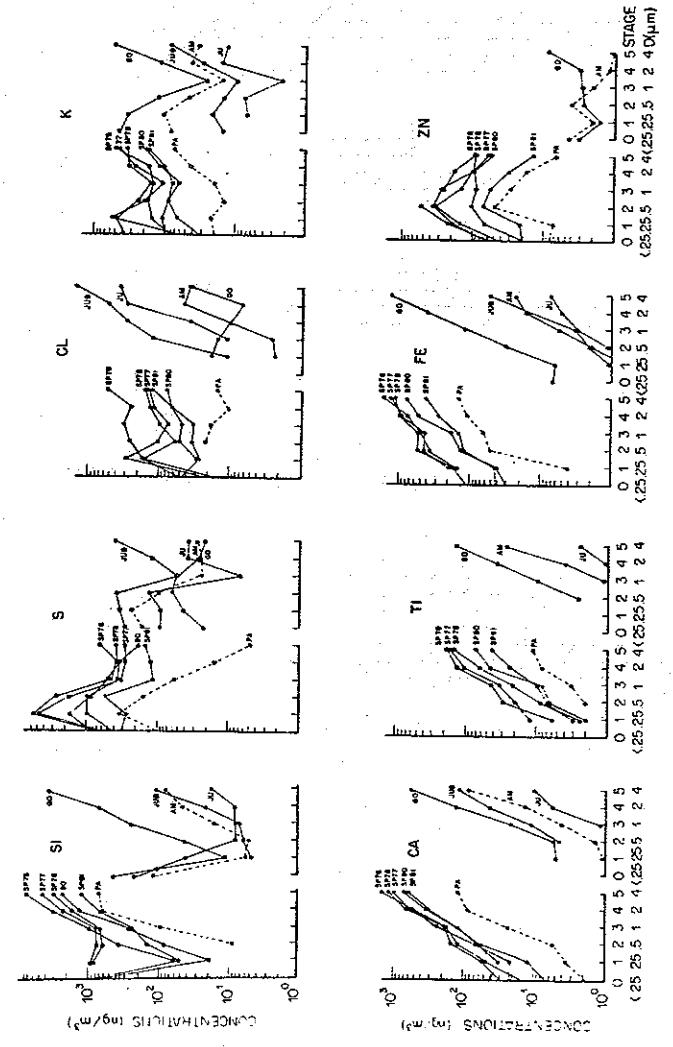


Figure 3: The element size-distribution curves of 8 trace-elements determined in São Paulo (SP 76 to SP 81), Porto Alegre (PA), Jureia sea-shore (JUB), Jureia-Forest (Ju). Amazon-Forest (AM) and Goiás-central plateau (Go). The urban aerosols are on the left and the natural ones on the right.

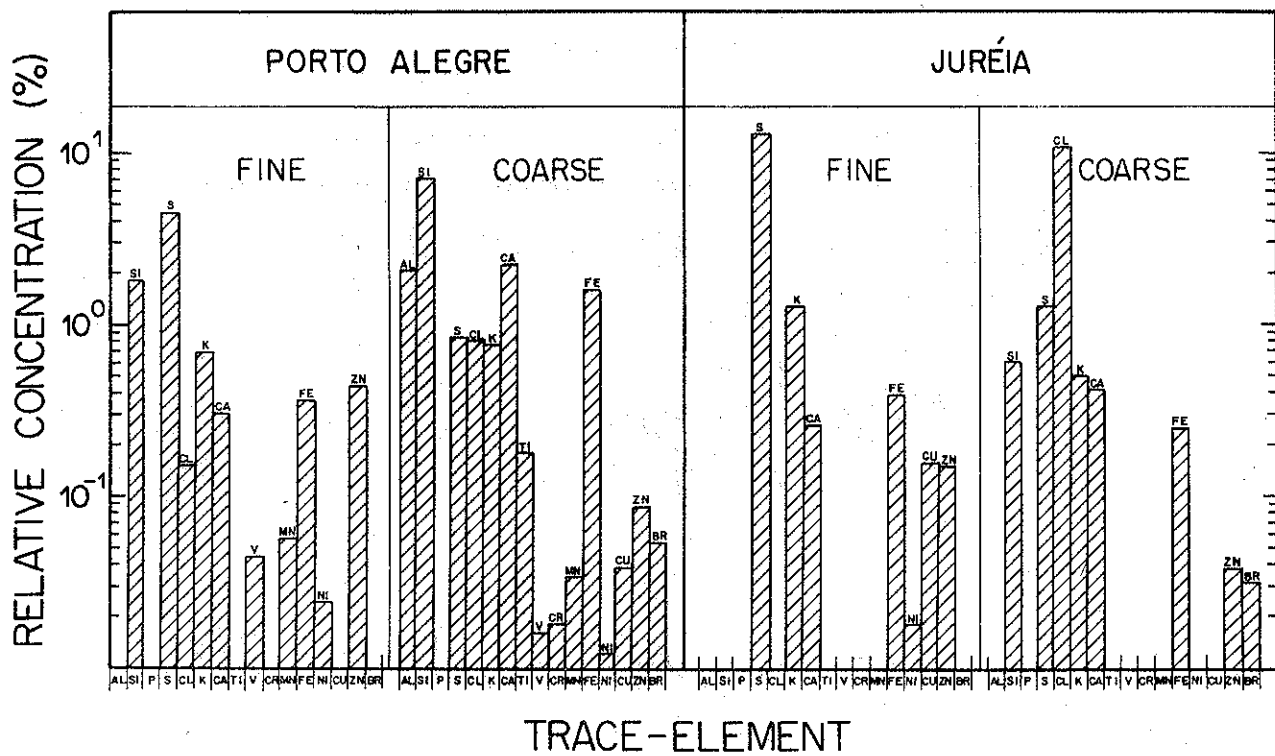


Figure 4: Histogram of the concentration of the trace-elements relative to the total fine and coarse particulate concentrations, respectively, obtained in Porto Alegre and Juréia.