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

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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 a 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 ten stage cascade impactors. Partial results from the two first sites investigated are presented here by element size distribution curves and histograms of relative concentrations.

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 with a maximum current of 200 nA before the diffusion foil, reduced to 10 nA on the target. It is collimated by a circular carbon collimator of 3.7 mm diameter.

Diffusion foil – nickel, 200 $\mu g/cm^2$ thick, located 2.1 m from the target.

Detector – Si(Li), 4 mm diameter, 8 μm beryllium window in vacuum, placed at 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 eight on a target changer placed at 45° to the beam. Samples are collected on kimfol and nuclepore. Calibration standards evaporated on 3 μm mylar foil as well as commercially available (from Micromatter) standards have been used.

The quantitative calibration was 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 weighed on a microbalance. A theoretical sensitivity curve was established 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 limits were estimated by means of irradiation of blank kimfol and nuclepore targets and using the relation $3\,(N_b)^{1/2}$ where N_b is the background count under a considered peak. They ranged approximately from 0.1 to 1 ng for the Kα lines and 1 to 10 ng for Lα lines, within the beam area.

The overall precision was 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 ref. 1.

2. The national monitoring air quality program based on the SP-PIXE

2.1. Objectives and methodology

We believe it makes sense to base a national monitoring air quality program on PIXE methodology. In fact this is the main project now being carried out by the GEPA *. However, it should be emphasized that the project does not intend to replace the daily routine work 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 seven critical atmospheric aerosols, selected

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around the country (see map in fig. 1), of the properties of the trace-element constituents of the fine and coarse components of the inhalable particles, and, whenever possible, to 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

The experimental methodology adopted by the project can be summarized as follows: the selected atmospheric aerosols should be sampled during 1 year by means of one SFU (stacked filter unit) 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. Besides these long term sampling an intensive short term (1 week) sampling is also performed by means of two sampling stations, each one operating with one ten-stage CI (cascade impactor), Battelle model, plus one SFU [2].

Fig. 1. The geographic location of the one natural and seven 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.)

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

Sampling commenced last September in the remote sea-shore site of Juréia, SP, according to the plans of the project. The ones in Porto Alegre, RS (November), and Salvador, Ba (March) followed. 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: (i) the element size-distribution curves ESDC; (ii) 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 fig. 2. 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) [4–6] are also presented.

Next, in fig. 3, 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 of coarse total particle concentrations.

The averaged concentrations (in $\mu g/m^3$) obtained up to May 1983 by the gravimetric measurements of the filters of SFU are given in table 1.

4. Discussions and conclusions

A qualitative examination of the ESDC in fig. 2 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 PIXE, favoring the determination of

Table 1

	Fine particles	Coarse particles	Inhalable particles
Juréia	7.6	14.6	24.2
Porto Alegre	11.7	49.0	60.7

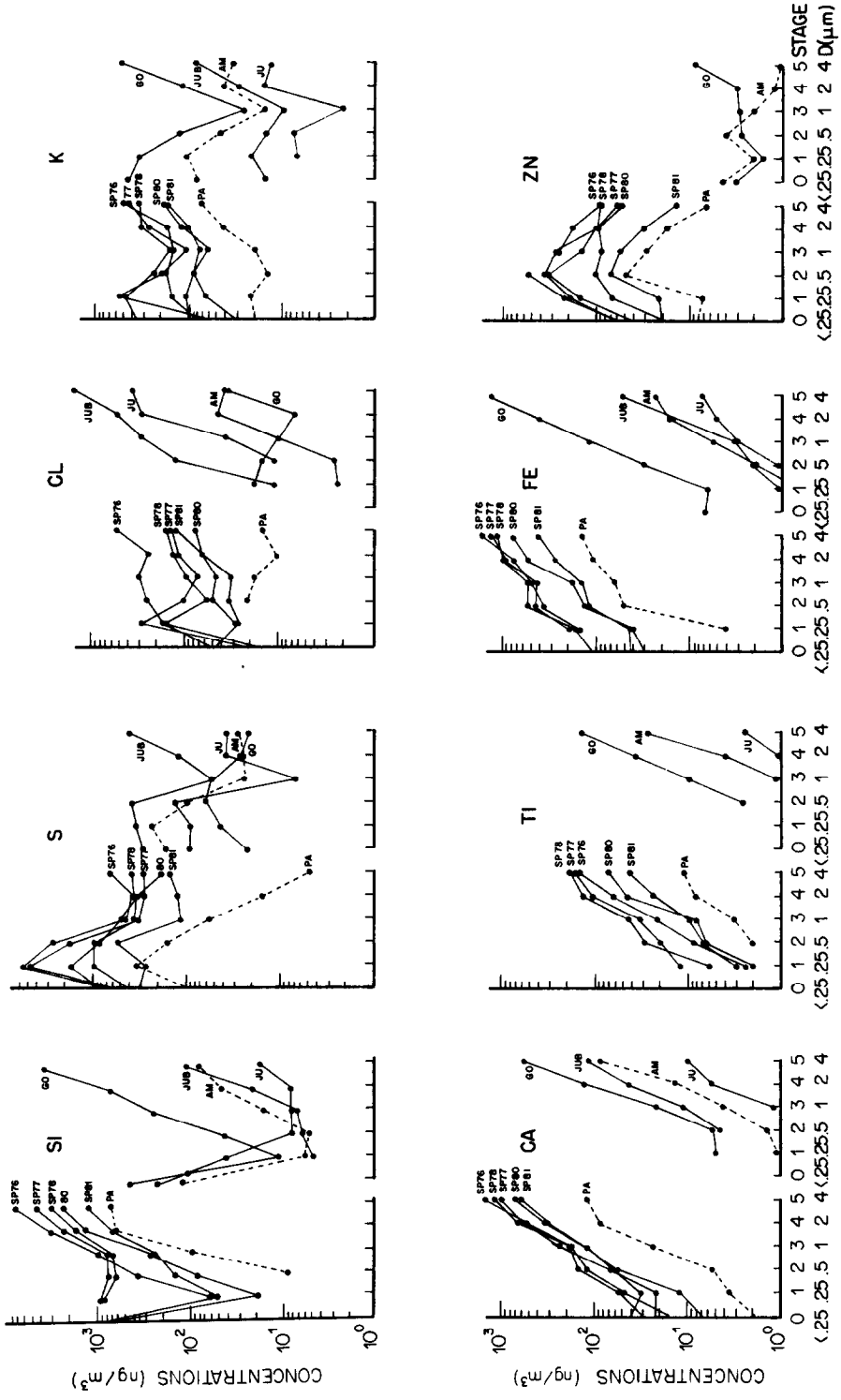

Fig. 2. The element size-distribution curves of eight trace elements determined in São Paulo (SP 76 to SP 81), Porto Alegre (PA), Juréia sea-shore (JuB), Juréia-Forest (Ju). Amazon-Forest (AM) and Goiás-central plateau (Go). The urban aerosols are on the left and the natural ones on the right.

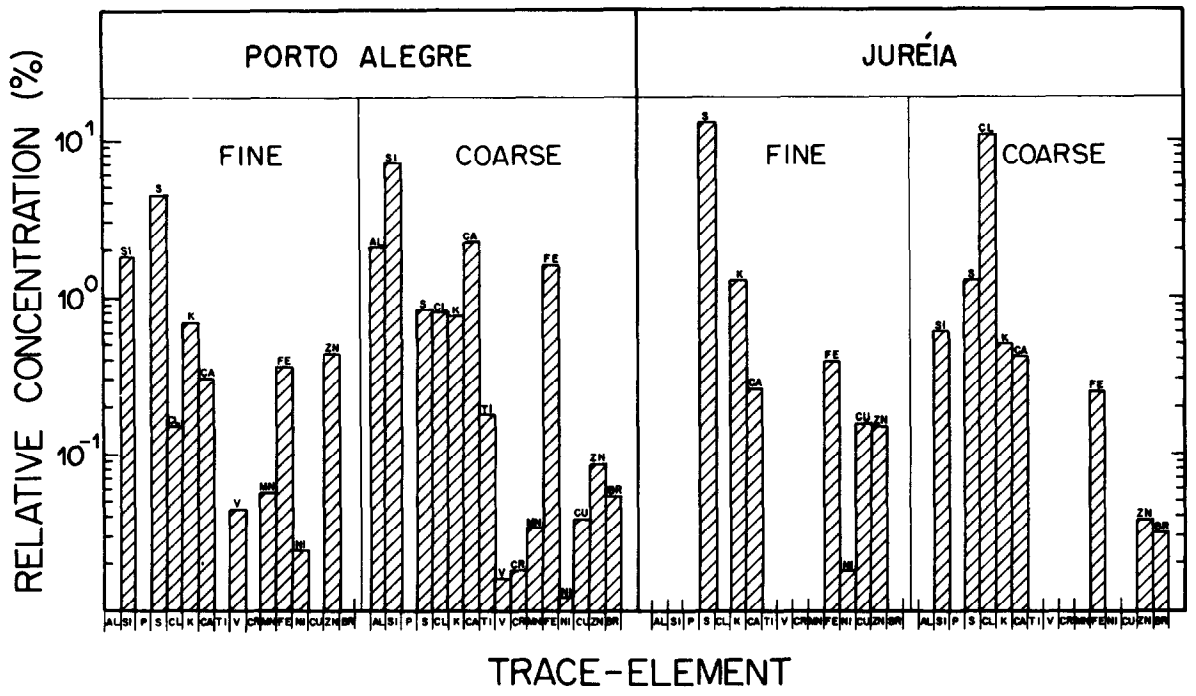

Fig. 3. Histogram of the concentration of the trace elements relative to the total fine and coarse particulate concentrations, respectively, obtained in Porto Alegre and Juréia.

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 2 years this decrease may well be the consequence of meteorological variations, or be due to the industrial recession, beginning at 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 is not sensitive to moderate changes 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 fig. 3 emphasizes the differences between both the fine-coarse and the Jureia-Porto Alegre distributions.

Among the many other conclusions which can be drawn from figs. 2 and 3 is the dominant presence of S (about 13%) among the trace-element (N, C and O not included) constituents of the fine particulate matter of Juréia, a fact which is consistent with the well-known exudation of sulfur by plants.

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