

## Atmospheric Aerosol Characterization by Means of Impactor Samples Analyzed by PIXE

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Continuous size-distribution functions are generally considered as the dominant physical properties of the atmospheric aerosol (AA). The complexity of this physico-chemical system is manifest in the large number of investigative methods, the results of which are often difficult to compare. The cascade impactor and PIXE method, among these, supplies the mass concentrations  $m_{K,Z}$  of elements, with  $Z > 13$ , detected in the  $K$ -stage of the impactor. In this paper we examine the AA characteristics which can be directly inferred from the data set  $\{m_{K,Z}\}$  and elaborate a scheme that, under approximate conditions, allows for the interrelation of  $\{m_{K,Z}\}$  and the size-distributions more commonly used in the mathematical treatment of aerosols, e.g.,  $n(D)$  and  $n_v(D)$  of Friedlander.

As funções contínuas de distribuição de tamanho são geralmente consideradas as propriedades físicas dominantes dos aerossóis atmosféricos (AA). A complexidade desse sistema físico-químico traduz-se no grande número de métodos de investigações usados, o que torna muitas vezes difícil a comparação entre os seus resultados. O método Impactador em Cascata-PIXE, entre estes, fornece as concentrações de massa  $m_{K,Z}$  dos elementos, com  $Z > 13$ , detectados no  $K^{\text{ésimo}}$  estágio do impactador. Neste trabalho examinamos as características de AA que podem ser diretamente inferidas do conjunto de dados  $\{m_{K,Z}\}$  e elaboramos um esquema que, sob condições aproximadas, permite a inter-relação de  $\{m_{K,Z}\}$  com as distribuições de tamanho mais comumente utilizadas no tratamento matemático de aerossóis, tais como  $n(D)$  e  $n_v(D)$  de Friedlander.

## 1. INTRODUCTION

The atmospheric aerosol (which we denote by AA), i.e., particles of solids or liquids suspended in the earth's atmosphere, is an extremely complex physico-chemical system. One needs only to recall the diversity of aspects that it can present: fog, smoke, dust, etc. Furthermore, the sizes of its particulates vary from slightly above molecular diameters ( $10^{-3}$   $\mu\text{m}$ ) to a few hundred microns, thus spanning five orders of magnitude. The mass range is still larger, showing a variation on the order of  $10^{15}$ . Moreover, this situation is complicated by the high heterogeneity of both shape and chemical composition of the particulates in the AA.

One immediate consequence of this complexity is the availability of several methods for the investigation of the AA, none of which covers more than two or three orders of magnitude in size. The variability of methods is still greater if we consider that the observations of the AA include generally field sampling and the analysis of the collected samples. These aspects constitute separate and independent processes for the most part. This is true in the case of our studies in the PIXE-SP Project which aims primarily at the São Paulo AA characterization. This paper deals with the use of cascade impactors (CI) for particulate samplings and the PIXE method for elemental chemical analyses for that project.

More specifically, for the aerosol samplings we use single-orifice Battelle type impactors with five impaction stages and one back-up filter, and for PIXE we use 8.0 MeV alpha particles from the IFUSP Pelletron Accelerator. Our PIXE system has been described elsewhere<sup>1</sup>.

The CI-PIXE method usually supplies the mass concentrations of the elements,  $m_{K,Z}$ , with  $Z > 13$ , detected in the  $K$ -stage of the CI (in our case  $K = 1, \dots, 6$ ). Due to the variety of methods for AA investigations it is often difficult to compare the results of authors using different methods. In this paper we examine the AA characteristics which can be directly inferred from the results obtained with the CI-PIXE method and elaborate a scheme that makes it possible, under approximate conditions, to obtain relations between the results of this method and

the size-distributions more commonly used in the mathematical treatment of aerosols<sup>2</sup>.

## 2. ATMOSPHERIC AEROSOL CHARACTERIZATION

The continuous size-distributions functions are generally considered as the dominant physical properties of the AA. Thus, it may be assumed that the knowledge of these functions should suffice for the aerosol characterization.

Traditionally, researchers in this field use the following kinds of size-distribution functions indiscriminately:

(i) by volume  $v$  of the particulates, defined as

$$n_v(v, \vec{x}, t) = \frac{dN}{dv}$$

where  $\frac{dN}{dv}$  is the number of particles per unit volume of air at a given position  $\vec{x}$  in the space and at a given time  $t$  in the particle size volume range  $v$  to  $v + dv$ ;

(ii) by particle size  $D$  of the particulates, defined as

$$n(D, \vec{x}, t) = \frac{dN}{dD}$$

where  $\frac{dN}{dD}$  is particle density in the size range from  $D$  to  $D + dD$ . Other types of size distribution functions can be deduced from these two basic ones, with some additional hypotheses, e.g.:

$$\frac{dN}{d \log D} \quad \text{or} \quad \frac{dS}{d \log D} \quad \text{or} \quad \frac{dV}{d \log D} \quad \text{or} \quad \frac{dm}{d \log D}$$

where  $S$ ,  $V$  and  $m$  are respectively the total surface, volume and mass of the particles in the size range considered ( $D$  to  $D + dD$ ) per unit volume of air.

In general all physical phenomena concerning the AA can thus be related to these size distributions. For instance, if we take the moments

$$M_v(\vec{r}, t) = \int_0^{\infty} n(D, \vec{r}, t) D^v dD$$

it is possible to show the mass flux of the particles undergoing sedimentation is proportional to  $M_5$  while the total light scattering by particles much smaller than the incident light wavelength is proportional to  $M_6$ , that is,  $M_6 \propto \bar{b}_{\text{scatt}}$  ( $\bar{b}_{\text{scatt}}$  is the Rayleigh Light Scattering coefficient by small particles).

Of course, the possibility of AA characterization by size-distribution continuous functions is a consequence of the fact that these are affected by the intern (gas-to-particle conversion and coagulation) and extern (diffusion and sedimentation) processes which are permanently intervening in the AA. More specifically, a general dynamic equation for  $n(v, \vec{r}, t)$  including all of these processes can be derived. Anthropogenic effects can also be included in this general equation allowing for the modeling of air pollution situations.

A still more general description of the AA could be obtained if we introduce the generalized size-composition distribution function, where all the chemical species components of the AA particles are also considered<sup>2</sup>. However, the use of such a general function is not yet warranted by the existing experimental data, besides being still in an incipient stage of mathematical formalism. Perhaps in the future we can benefit from such an extreme generalization.

### 3. THE AA SAMPLING BY MEANS OF CASCADE IMPACTORS

When sampling with cascade impactors the fraction of the aerosol collected in a given  $K$ -stage will depend on the relative collection efficiencies,  $\epsilon_1(D)$ , of all previous stages plus the  $K$ -stage efficiency (i.e.,  $i = 1, 2, \dots, K$ ), as is shown below.

If an AA, described by the size distribution function  $n(D)$ , is sampled by an  $\ell$ -stage CI, the number of particles retained in each of its stage (by unit volume sampled) will be given by:

$$\begin{aligned}
 N_1 &= \int_0^{\infty} n(D) \varepsilon_1(D) dD \\
 N_2 &= \int_0^{\infty} n(D) [1 - \varepsilon_1(D)] \varepsilon_2(D) dD \\
 \hline
 N_\ell &= \int_0^{\infty} n(D) \prod_{i=1}^{\ell-1} [1 - \varepsilon_i(D)] \varepsilon_\ell(D) dD
 \end{aligned}$$

or, in general for the  $K$ -stage we have:

$$N_K = \int_0^{\infty} n(D) \prod_{i=1}^{K-1} [1 - \varepsilon_i(D)] \varepsilon_K(D) dD \quad (1)$$

Thus, if we measure the amounts  $N_k$ , the  $\ell$  integral equations (1), subjected to the normalization condition:

$$\sum_{i=1}^{\ell} N_i = N \text{ (total aerosol concentration)} \quad (2)$$

can be solved for the distribution function  $n(D)$ , at least formally. In practice we can adopt one of the two approaches:

(i) describe  $n(D)$  by means of suitable continuous functions, e.g., log-normal size distributions, and evaluate the corresponding parameters using computer fitting procedures<sup>3,4</sup>;

(ii) describe  $n(D)$  by means of average values  $n_K$  for each impactor stage and solve the set of linear equations which we can derive from equations (1). In this case no prior knowledge about the specific analytical form of  $n(D)$  is necessary, which can then be investigated using the resulting set of  $n_K$  values.

However, we notice that both approaches preclude the knowledge of the efficiency curves  $\varepsilon_K(D)$  (usually known) and of the measured quantities  $N_K$ , which are not always available as is the case with the CI + PIXE method. With this method, as mentioned before, the mass concentration  $m_{K,Z}$  of the element with atomic number  $Z$  in stage- $K$  is obtained. Clearly, the  $m_{K,Z}$  are quite different quantities from the  $N_K$ .

Relative efficiency curves for our 6-stage Battelle impactors are given in Fig.1.

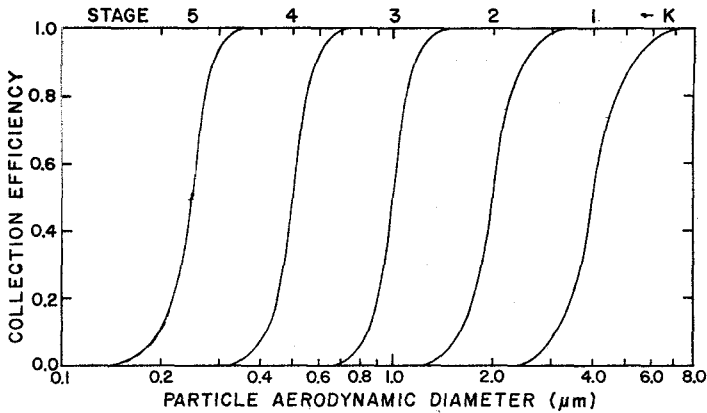


Fig.1 - Efficiency curves for the Battelle single orifice impactor stages 1-5.

#### 4. THE AA CHARACTERIZATION BY MEANS OF CI + PIXE DATA

There are two ways to use the CI + PIXE data in AA studies: first, to characterize the AA directly by the size distribution curves  $m_{K,Z}$  versus  $D$  (here  $D$  is the aerodynamic diameter, usually adopted in this case); second, to evaluate the size-distribution function  $n(D)$  from the measured set of values  $\{m_{K,Z}\}$ . Let us consider each of these procedures separately.

(a) In the *first case* we generally plot the  $m_{K,Z}$  values against the impactor stage number (in the inverse order) which, in our case, corresponds roughly to  $\log D$ . Examples of size-distributions plotted in this way are given in Fig.2, which we will briefly discuss below. Each one of the  $m_{K,Z}$  size distributions may give us information concerning the origin, permanence and fate of the particular element in the atmosphere. Thus, emphatically, we can say that the matrix  $m_{K,Z}$  can be used to characterize the AA under study.

We consider, for example, the case of some important elements in the AA of São Paulo. Hence Fig.2 shows the  $m_{K,Z}$  size-distributions of S, Ca, Fe, Zn, Br, and Pb, as measured by our group in the PIXE-SP Project. Actually in Fig.2 we present the geometric averages for each  $m_{K,Z}$  using data collected at different times and stations.

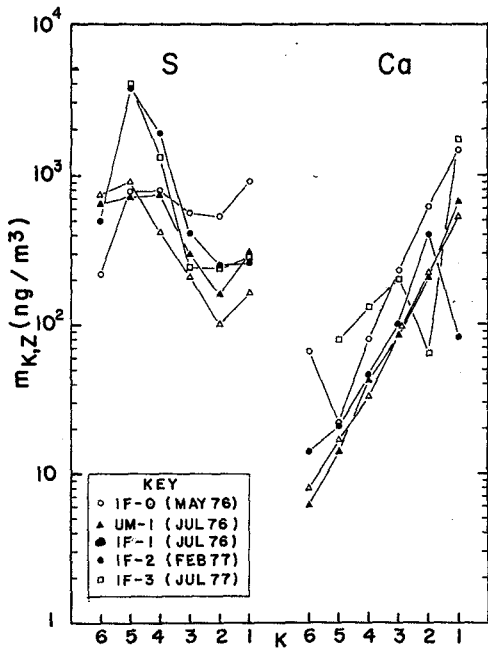


Fig.2a

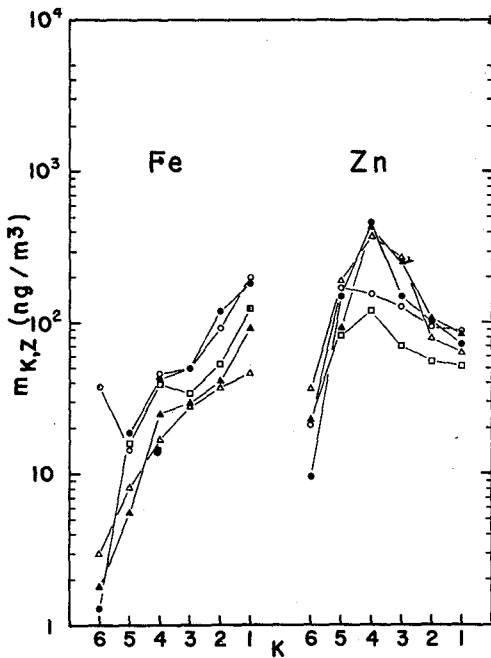


Fig.2b

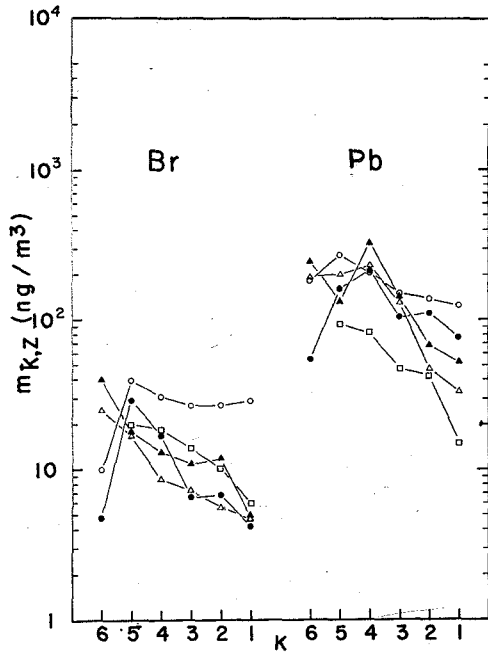


Fig.2 -  $m_{k,z}$  size-distributions of S, Ca, Fe, Zn, Br and Pb for the city of São Paulo. Most of these data refer to sites located inside the campus of the University of São Paulo. Each data point represents the geometric average of 3-14 impactor measurements of 4-12 hour intervals each.

It is not the specific purpose of this paper to discuss and interpret the  $m_{k,z}$  distributions of Fig.2. However, a simple visual examination of Fig.2 reveals that the S, Zn, Br and Pb distributions peak in the submicron size range, a fact that characterizes a combustion plus gas-to-particle conversion mechanism as responsible for these airborne particulates<sup>4,5</sup>.

On the contrary, the Ca and Fe distributions show a concentration of particles in the region of coarse particles ( $D > 2 \mu m$ ) which is compatible with mechanical processes of particle production (soil blown dust plus industrial sources)<sup>4,5</sup>.

Many other conclusions referring to the natural or anthropogenic origin of the particles can be obtained from statistical analysis of the data sets  $\{m_{k,z}\}$  (e.g. correlations among  $m_{k,z}$  elements for a given site and particular date, or else varying the time and space coordi-



nates).<sup>5</sup> Likewise, the comparison of the  $m_{k,Z}$  values with "standard aerosol" values may be used to separate the natural from the anthropogenic components of the aerosol. Furthermore, the use of meteorological parameters in these statistical analyses is essential when modeling air pollution situations.

(b) In the *second case* we should consider the possibility of making the following transformation:

$$\{m_{K,Z}\} \rightarrow \{N_{K,Z}\} \rightarrow \{n_Z\} \rightarrow n \quad (3)$$

i.e., to evaluate the  $n$ -size distribution from the known matrix  $m_{K,Z}$

For this task, we need first a relation between the  $m_{K,Z}$  and  $N_{K,Z}$  values. This can be done only under very restrictive approximations as, for instance, to consider all particles of spherical size with diameter  $D$  and with constant density  $\rho_Z$  for each  $Z$ -element. Under this hypothesis we may write:

$$m_{K,Z} = \rho_Z \cdot \frac{1}{6} \pi D^3 \cdot N_{K,Z} \quad (4)$$

Since the CI selects particles by the aerodynamic diameter we have in the case of spherical particles to use the relation

$$D_a = \sqrt{\rho_p} \cdot D_p \quad (5)$$

where

$D_a$  is the aerodynamic diameter

$\rho_p$  is the density of the particle

$D_p$  is the diameter of the particle

By using equation (5), we get from (4)

$$m_{K,Z} = \rho_Z \frac{1}{6} \frac{D_a^3}{\rho_p^{3/2}} \cdot N_{K,Z}$$

which is the desired relation between  $m_{k,Z}$  and  $N_{K,Z}$ .

We now introduce  $n_Z$  distributions by making use of the equations (1) for the particular case of an element of atomic number  $Z$ , i.e.:

$$N_{K,Z} = \int_0^\infty n_Z \prod_{i=1}^{k-1} (1 - \varepsilon_i) \varepsilon_K dD \quad (6)$$

These equations allow the derivation of the  $\{n_Z\}$  set values from the  $\{N_{K,Z}\}$  ones.

By substituting equation (6) in (5), we get the direct relation between the  $m_{k,Z}$  and  $n_Z$  distributions:

$$m_{k,Z} = \frac{1}{6} \pi \rho_Z D^3 \int_0^\infty n_Z \prod_{i=1}^{k-1} (1 - \varepsilon_i) \varepsilon_K dD \quad (7)$$

Finally, to obtain the relation between the  $\{m_{k,Z}\}$  and the  $n$  distribution the simplest approximation can be introduced:

$$n = \sum_{i=1}^P a_i n_{Z_i} \quad (8)$$

Where the  $a_i$  are constant coefficients.

Equation (8) describes a stationary distribution of the  $P$  elements among the total  $N$  particles sampled in the unit volume of air. In this case, the  $a_i$  coefficients can be determined from the chemical specification of the elements if it is known. Actually, in the CI+PIXE method under discussion only part of the matrix  $\{n_{Z_i}\}$  is determined.

## 5. CONCLUSIONS

At present it seems to us more convenient to explore the data generated by CI + PIXE methods using the first approach [section 4 (a)] since the other one involves approximations not always justifiable and requires a better knowledge of the chemical composition of the aerosol.

The critical point of the second approach resides probably in the knowledge of the  $a_i$  coefficients of equation (8), i.e., more in-

formation about chemical composition is needed. However, another difficulty is the proper evaluation of the mass densities  $\rho_p$  and  $\rho_z$ , which also depend on the chemical speciation of the elements.

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## REFERENCES

1. C.Q. Orsini and L.C. Bouéres, Nucl. Instr. and Methods, 142, 27-32 (1977).
2. S.K. Friedlander, *Smoke, Dust and Haze, Fundamentals of Aerosol Behavior*, John Wiley and Sons (1977).
3. O.G. Raabe, Environ. Science & Technology, 12, 1162 (1978).
4. K.T. Whitby, Atm. Environ., 12, 135 (1978).
5. D. Lawson, Ph.D. Thesis, 1978, Florida State University, USA.