# Determination of Trace Elements in Aerosol Samples by Instrumental Neutron Activation Analysis

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## ABSTRACT

Two nuclear techniques, Energy-Dispersive X-Ray Fluorescence Analysis (EDXRF) and Instrumental Neutron Activation Analysis (INAA), were used to analyze aerosol samples collected in the city of São Paulo, Brazil. Na, Cl, Mn, V, Al, Sm, Mo, W, La, As, Br, Sb, K, Ba, Se, Th, Cr, Rb, Ca, Fe, Ce, and Sc were determined by INAA, and Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Hg, and Pb were determined by EDXRF. A preliminary identification of the main source of the atmospheric aerosol was performed based on enrichment factor and correlation coefficient calculations.

**Index Entries:** Aerosol; EDXRF; INAA; enrichment factor; correlation coefficient; source identification.

## INTRODUCTION

In recent years, air pollution has become a critical problem, with effects on atmospheric properties, human health, soil, water, vegetation,

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animals, and ecosystems. The aerosols in urban and industrialized areas are clearly mutagenic and, most probably, traffic and certain industrial sources contribute to this occurrence (*1*).

São Paulo, the largest industrialized city in Latin America, has approximately 12 million people within the city and 14 million if we consider the surrounding zones. There are approximately 150,000 industries of all types and sizes and 4 million vehicles, of which 80% use only gasoline blended with 24% ethanol and the other 20% use pure alcohol fuel.

To protect the environment against pollution, it is necessary to have techniques that not only monitor the air pollution, but also clarify its origin. Nuclear techniques, in particular Instrumental Neutron Activation Analysis (INAA) (*2–4*) and Energy-Dispersive X-Ray Fluorescence Analysis (EDXRF) (*5,6*) are useful and have been widely used to nondestructively analyze the elemental composition of aerosols.

This work is part of the "Co-ordinated Research Programme on Use of Nuclear and Nuclear-Related Techniques in the Study of Environmental Pollution Associated with Solid Wastes" initiated by the IAEA in December 1987, and it is being carried out in cooperation with the CETESB—Companhia de Tecnologia de Saneamento Ambiental-Governmental Institution responsible for environmental control in the state city of São Paulo.

This investigation has the purpose of obtaining more information about the aerosols of the city of São Paulo and to perform, by means of the trace element results obtained by EDXRF and INAA, a preliminary identification of the main sources of the atmospheric aerosol based on enrichment factor (EF) and correlation coefficient ($r$) results.

## EXPERIMENTAL

### *Air Sampling*

The collection of the aerosols was made by CETESB using a Sierra Instruments model 244 Dichotomous Sampler (Virtual Impactor) that fractionates suspended particles into two size fractions, 2.5–15 μm (coarse, noninhalable particles) and less than 2.5 μm (fine, inhalable particles). The two particle fractions were collected uniformly on two 37 mm Teflon membrane filters. The virtual impactor head has a single stage design with a cut point of 2.5 μm and a flow rate of 1 $m^3$/h. The sampling site was on the western periphery of the city, 2 m above ground level. The time of collection was 24 h.

### *Analytical Procedures*

The filters were analyzed first at CETESB by EDXRF and after that at IPEN-CNEN/SP by INAA.

### *EDXRF*

The sample was analyzed on a TEFA system that has a dual anode Mo/W-X-ray tube. Mo and Cu primary X-ray filters can be used to obtain monochromatic excitation.

The X-ray spectrometer consists of a Si(Li) X-ray detector, amplifier, and pulse-height analyzer that measures the energy and intensity of characteristic X-rays generated in the excitation procedure.

### *INAA*

A nondestructive neutron activation analytical procedure has been established. Samples and standards were irradiated for 5 min using a pneumatic rabbit station of the swimming pool type research reactor, whose flux is about $10^{12}$/n/cm$^2$s, for the analysis of elements that give rise to short-lived radionuclides. For the analysis of long-lived radionuclides, samples were irradiated for 24 h on a neutron flux of $10^{13}$/n/cm$^2$s.

Standards were prepared by pipeting suitable aliquots of standard solutions, obtained by dissolution of high degree of purity metal or oxide, of elements on pieces of Whatman no. 41 filter paper and drying under an infrared lamp. The measurements were carried out after suitable cooling times with Ge(Li) detector Ortec model 8001-1022V, resolution of 2.6 keV at the 1332 keV gamma peak of $^{60}$Co, coupled to a 4096 channel gamma spectrometer Ortec model 6240B.

## RESULTS AND DISCUSSION

In order to test the accuracy of the INAA method, about 50 mg of two USGS rock standards (W-1 and AGV-1) and 2 filters of the IAEA reference material (AIR 3/1) were analyzed. Table 1 gives a comparison between the results obtained and the certified values (*8,9*). The relative standard deviations obtained for most elements were smaller than 10%, which is generally considered as a good result in trace analysis. For the elements V in W-1 and As in AIR 3/1, the reproducibility was not so good owing to their low activities for Ge(Li) counting.

The described analytical procedures were applied to the analysis of aerosols collected on 24 filters (fine and coarse particulate). Twenty-two elements could be determined by INAA: Na, Cl, Mn, V, Al, Sm, Mo, W, La, As, Br, Sb, K, Ba, Se, Th, Cr, Rb, Co, Fe, Ce, and Sc, whereas by means of EDXRF, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Hg, and Pb could be determined. The distribution of the results obtained was considered log-normal (*4*).

Geometric means, geometric standard deviation, and median of elemental concentration obtained by EDXRF and INAA and the number of data used for calculation of the means ($n$) are given in Tables 2 and 3, respectively. In the calculation of the means only the number of samples

Table 1
Results Obtained by INAA for Some Certified Reference Materials
in ppm, Unless Indicated

| ELEMENT | W - 1 | | AGV - 1 | | AIR 3/1 (µg/filter) | | |
|---|---|---|---|---|---|---|---|
| | This Work mean ± SD[a] | Certificate[8] mean ± SD | This Work mean ± SD[a] | Certificate[8] mean ± SD | This Work mean ± SD[a] | Certificate Content | Confidence limit(0.05)[9] |
| Na (%) | 1.55 ± 0.16[4] | 1.58 ± 0.08 | 3.10 ± 0.04[3] | 3.15 ± 0.09 | 104 ± 8[2] | (b) | (b) |
| Al | 7.80 ± 0.53[4] | 7.93 ± 0.14 | 8.50 ± 0.09[2] | 9.07 ± 0.18 | 92.0 ± 3.7[2] | (b) | (b) |
| Sc | 36.2 ± 0.5[5] | 35 ± 2 | 11.8 ± 0.09[3] | 12.1 ± 0.9 | (c) | (b) | (b) |
| V | 282 ± 43[4] | 260 ± 25 | 140 ± 6[2] | 123 ± 12 | 8.42 ± 0.24[2] | 7.8 | 5.8 ÷ 8.3 |
| Cr | 119 ± 2[4] | 120 ± 14 | (c) | 12 ± 3 | 5.04 ± 0.01[2] | 5.0 | 4.5 ÷ 5.1 |
| Mn | 1314 ± 38[4] | 1300 ± 125 | 733 ± 28[4] | 740 ± 60 | 31.76 ± 0.20[2] | 30 | 28 ÷ 32 |
| Fe (%) | 8.27 ± 0.52[5] | 7.79 ± 0.16 | 4.93 ± 0.08[4] | 4.73 ± 0.13 | 226 ± 3[2] | 204 | 196 ÷ 210 |
| Co | 46 ± 2[4] | 46 ± 4 | 14.8 ± 0.7[3] | 15.1 ± 1.2 | 1.18 ± 0.03[2] | 1.1 | 0.8 ÷ 1.4 |
| As | (c) | 2.2 ± 0.3 | (c) | 0.84 ± 0.27 | 4.98 ± 0.58[2] | 5.0 | 4.6 ÷ 5.8 |
| Se (ppb) | (c) | 113 ± 7 | (c) | (b) | 0.93 ± 0.02[2] | 1.0 | 0.8 ÷ 1.2 |
| Ba | 162 ± 10[2] | 162 ± 5 | (c) | (b) | (c) | (b) | (b) |
| La | 11.9 ± 0.7[3] | 10.9 ± 1.3 | 40.7 ± 0.8[3] | 38 ± 3 | (c) | (b) | (b) |
| Sm | 3.3 ± 0.2[3] | 3.5 ± 0.3 | 5.5 ± 0.3[3] | 5.9 ± 0.5 | (c) | (b) | (b) |
| Th | 2.8 ± 0.1[3] | 2.4 ± 0.4 | 7.4 ± 0.2[3] | 6.50 ± 0.37 | (c) | (b) | (b) |

[a]Number of determination used in the mean calculation.
[b]Certified value not presented.
[c]Element not determined in this work.

Table 2
Geometric Means, Geometric Standard Deviation, and Median from EDXRF Analysis In ng/m³

| Element | Fine Particles | | | Coarse Particles | | |
|---|---|---|---|---|---|---|
| | n | GEOMETRIC MEANS ± SD | MEDIAN | n | GEOMETRIC MEANS ± SD | MEDIAN |
| Al | 12 | 256,4 ± 1,7 | 260,5 | 12 | 2307,4 ± 1,6 | 2391,0 |
| Si | 12 | 401,6 ± 1,8 | 399,5 | 12 | 3629,6 ± 1,5 | 3747,5 |
| P | 12 | 134,2 ± 1,6 | 142,0 | 12 | 162,1 ± 1,4 | 172,5 |
| S | 12 | 2693,3 ± 1,6 | 3195,5 | 12 | 1220,5 ± 2,0 | 1383,0 |
| Cl | 11 | 72,1 ± 3,1 | 78,0 | 12 | 535,3 ± 1,7 | 521,0 |
| K | 12 | 311,9 ± 2,1 | 355,5 | 12 | 342,6 ± 1,6 | 338,0 |
| Ca | 12 | 115,2 ± 2,5 | 161,0 | 12 | 1617,9 ± 1,8 | 1537,0 |
| Ti | 6 | 14,7 ± 1,6 | 12,9 | 9 | 161,3 ± 2,1 | 203,4 |
| V | 7 | 13,3 ± 1,6 | 14,8 | 8 | 27,0 ± 1,8 | 35,1 |
| Cr | 11 | 7,4 ± 2,3 | 6,3 | 12 | 25,3 ± 1,4 | 23,5 |
| Mn | 12 | 28,9 ± 3,8 | 21,6 | 12 | 59,8 ± 2,1 | 53,8 |
| Fe | 12 | 196,6 ± 1,7 | 191,0 | 12 | 1583,8 ± 1,5 | 1560,5 |
| Ni | 10 | 6,4 ± 2,1 | 8,1 | 10 | 7,6 ± 2,4 | 9,6 |
| Cu | 12 | 9,7 ± 2,7 | 13,0 | 12 | 29,7 ± 1,7 | 30,5 |
| Zn | 12 | 94,4 ± 2,0 | 79,5 | 12 | 69,6 ± 1,6 | 71,5 |
| Ga | 11 | 3,9 ± 2,4 | 4,9 | 12 | 3,8 ± 1,9 | 4,5 |
| As | 4 | 13,4 ± 1,2 | 13,4 | 4 | 7,6 ± 1,1 | 7,9 |
| Se | 11 | 2,8 ± 2,9 | 3,5 | 10 | 2,2 ± 2,5 | 2,6 |
| Br | 12 | 14,2 ± 2,0 | 15,8 | 12 | 3,2 ± 3,4 | 4,2 |
| Rb | 10 | 5,1 ± 2,9 | 6,0 | 12 | 3,2 ± 4,8 | 5,3 |
| Sr | 10 | 6,0 ± 4,0 | 8,6 | 12 | 11,8 ± 2,0 | 12,1 |
| Hg | 3 | 4,5 ± 1,6 | 5,6 | 4 | 4,3 ± 1,9 | 3,6 |
| Pb | 12 | 88,6 ± 1,8 | 88,5 | 12 | 58,3 ± 2,0 | 73,0 |

($n$) where the determination of the considered element was possible were used.

In order to obtain information about aerosol sources, the enrichment factor (EF) and correlation coefficients ($r$) were calculated:

$$EF = \frac{(E/R)\ \text{aerosol}}{(E/R)\ \text{reference}}$$

where $E$ and $R$ are geometric mean concentrations of any element $E$ normalized to a selected element $R$, and $r$ is the usual linear correlation coefficient.

Table 3
Geometric Means, Geometric Standard Deviation, and Median, from INAA Analysis in pg/m³, Unless Indicated

| Element | Fine Particles | | | Coarse Particles | | |
|---|---|---|---|---|---|---|
| | n | GEOMETRIC MEANS ± SD | MEDIAN | n | GEOMETRIC MEANS ± SD | MEDIAN |
| Na ($ng/m^3$) | 12 | 305,7 ± 1,9 | 296,5 | 12 | 245,0 ± 2,4 | 237,0 |
| Al ($ng/m^3$) | 11 | 154,6 ± 1,8 | 179,0 | 12 | 1480,0 ± 1,8 | 1642,0 |
| Cl ($ng/m^3$) | 10 | 74,5 ± 9,6 | 90,5 | 11 | 351,4 ± 1,8 | 314,0 |
| K ($ng/m^3$) | 9 | 476,6 ± 2,7 | 593,0 | 9 | 340,4 ± 2,7 | 475,0 |
| Sc | 8 | 12 ± 2 | 12 | 9 | 183 ± 2 | 252 |
| V ($ng/m^3$) | 12 | 15,0 ± 1,6 | 17,3 | 12 | 6,4 ± 1,6 | 6,4 |
| Cr ($ng/m^3$) | 9 | 5,3 ± 3,8 | 12,3 | 9 | 9,1 ± 2,1 | 11,8 |
| Mn ($ng/m^3$) | 12 | 36,5 ± 3,6 | 23,3 | 12 | 38,1 ± 2,4 | 29,6 |
| Fe ($ng/m^3$) | 9 | 171,5 ± 2,6 | 251,0 | 9 | 947,2 ± 2,3 | 1211,0 |
| Co | 3 | 265 ± 3 | 221 | 9 | 207 ± 4 | 220 |
| As | 8 | 2480 ± 2 | 1975 | 4 | 388 ± 2 | 367 |
| Se | 8 | 1718 ± 3 | 1482 | 8 | 357 ± 2 | 391 |
| Br | 8 | 8852 ± 2 | 9147 | 7 | 1010 ± 3 | 1289 |
| Rb | 6 | 3779 ± 2 | 4209 | 6 | 2236 ± 2 | 2300 |
| Mo | 7 | 1033 ± 2 | 952 | 6 | 1332 ± 2 | 1200 |
| Sb | 9 | 4018 ± 2 | 4872 | 9 | 1848 ± 2 | 1600 |
| Ba ($ng/m^3$) | 7 | 13,2 ± 1,3 | 12,6 | 7 | 42,0 ± 1,8 | 42,3 |
| La | 9 | 259 ± 2 | 279 | 9 | 1021 ± 2 | 1300 |
| Ce | 8 | 255 ± 4 | 342 | 9 | 2429 ± 2 | 3175 |
| Sm | 9 | 51 ± 2 | 48 | 9 | 157 ± 2 | 172 |
| W | 9 | 493 ± 2 | 409 | 9 | 755 ± 3 | 840 |
| Th | 8 | 60 ± 2 | 54 | 9 | 200 ± 2 | 246 |

The EF were calculated using soil dust and sea salt as reference composition (7), owing to the fact that they are well known. Si and Cl were used for normalization of the results obtained by EDXRF (Tables 4 and 5), whereas for INAA results, Fe and Na were used (Tables 6 and 7).

Although a small difference has been verified for EF results obtained by both techniques (EDXRF and INAA), the final conclusions are practically the same. The differences in EF values were probably owing to different elements being chosen as reference. For one to suggest that the

Table 4
Enrichment Factor (EF), Relative to Soil Dust, and the Correlation with Reference Element, *r*, Calculated from EDXRF Results

| | | Reference Element | Al | K | Ca | Ti | Mn | Fe |
|---|---|---|---|---|---|---|---|---|
| Fine | EF | Si | 1.6 | 17 | 3.3 | 1.5 | 16 | 2.2 |
| | r (a) | | 0.94 (1) | 0.92 (2) | 0.60 (3) | 0.20 (4) | 0.84 (2) | 0.73 (3) |
| Coarse | EF | Si | 1.5 | 2.1 | 4.9 | 1.8 | 3.7 | 2.0 |
| | r (a) | | 0.99 (1) | 0.92 (2) | 0.55 (3) | 0.91 (2) | 0.84 (2) | 0.96 (1) |
| Soil dust weight ratio element/Si . | | | 0.411 | 0.0444 | 0.0911 | 0.0249 | 0.0045 | 0.222 |

(a)Significance level: (1) $p < 0.001$; (2) $0.001 < p < 0.01$; (3) $0.01 < p < 0.1$; and (4) $p > 0.1$.

Table 5
Enrichment Factor (EF), Relative to Sea Salt, and the Correlation with Reference Element, *r*, Calculated from EDXRF Results

| | | Reference Element | Al | S | K | Br |
|---|---|---|---|---|---|---|
| Fine | EF | Cl | 85 | 466 | 211 | 58 |
| | r (a) | | 0.23 (4) | - 0.15 (5) | 0.23 (4) | - 0.10 (4) |
| Coarse | EF | Cl | 99 | 28 | 30 | 1716 |
| | r (a) | | 0.59 (3) | - 0.32 (4) | 0.57 (3) | - 0.03 (4) |
| Sea salt weight ratio element/Cl | | | 0.0435 | 0.0827 | 0.0209 | 0.0352 |

(a) Significance level: (1) $p < 0.001$; (2) $0.001 < p < 0.01$; (3) $0.01 < p < 0.1$; and (4) $p > 0.1$.

Table 6
Enrichment Factor (EF), Relative to Soil Dust, and the Correlation with Reference Element, *r*, Calculated from INAA Results

| | | Reference Element | Na | Al | K | V | Cr | Mn |
|---|---|---|---|---|---|---|---|---|
| Fine | EF | Fe | 3.4 | 0.5 | 14 | 33 | 11 | 10 |
| | r (a) | | 0.61 (4) | 0.48 (4) | 0.64 (4) | 0.94 (3) | 0.41 (4) | 0.61 (4) |
| Coarse | EF | Fe | 0.5 | 0.8 | 1.8 | 2.5 | 3.6 | 2.0 |
| | r (a) | | 0.80 (3) | 0.97 (1) | 0.51 (4) | 0.70 (3) | 0.34 (4) | 0.39 (4) |
| Soil dust weight ratio element/Fe . | | | 0.528 | 1.850 | 0.200 | 0.0027 | 0.0027 | 0.0203 |

(a)Significance level: (1) $p < 0.001$; (2) $0.001 < p < 0.01$; (3) $0.01 < p < 0.1$; and (4) $p > 0.1$.

Table 7
Enrichment Factor (EF), Relative to Sea Salt, and the Correlation with Reference Element, *r*, Calculated from INAA Results

| | | Reference Element | Al | K | Fe | Cl | Br |
|---|---|---|---|---|---|---|---|
| Fine | EF | Na | 6.1 | 40 | 51 | 0.1 | 4.3 |
| | r (a) | | 0.46 (4) | 0.58 (4) | 0.61 (4) | 0.55 (4) | 0.04 (4) |
| Coarse | EF | Na | 73 | 35 | 355 | 0.75 | 16000 |
| | r (a) | | 0.75 (3) | 0.34 (4) | 0.80 (3) | 0.92 (2) | 0.82 (3) |
| Sea salt weight ratio element/Na . | | | 0.0825 | 0.0397 | 0.0109 | 1.90 | 0.0067 |

(a)Significance level: (1) $p < 0.001$; (2) $0.001 < p < 0.01$; (3) $0.01 < p < 0.1$; and (4) $p > 0.1$.

trace elements involved have a common origin, the EF must be close to unity, and it is also expected that $r$ values be close to unity too.

This is observed for fine and coarse particulates (Tables 4–7) relative to soil dust. Besides, high $r$ values are obtained for Al, K, Ti, Mn, and Fe, showing that soil dust is the dominant source of fine and coarse particulates. On the other hand, EF values show an enrichment relative to sea salt for all trace elements considered, except for Cl that is depleted. This can denote a complete disappearance of any marine contribution.

Also, a high correlation between Fe and the elements Al, Mn, Se, Rb, La, and Ce (>0.80) is observed in coarse particulate, which suggests a common source, perhaps soil dust or a new aerosol source, different from sea salt and soil dust.

## CONCLUSION

In this work, the results obtained by means of the two techniques applied, EDXRF and INAA were considered separately. But, since some important elements, such as Si, Ti, Cu, P, and S, could not be determined by INAA, it has been more interesting to combine the results obtained by both techniques.

Considering that the aerosols of São Paulo is one of the most complex of the world, because it includes a large urban-industrial area, and for this reason, its characterization is very difficult, also, considering the small number of samples, obtained from a single point of sampling that was analyzed and submitted to a simple mathematical treatment, it was possible to perform a preliminary investigation of the main sources of aerosol in the city of São Paulo.

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