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Annex 5

**APPLICATION OF NEUTRON ACTIVATION ANALYSIS TO TRACE ELEMENT  
IN ENVIRONMENTAL AEROSOL SAMPLES IN SAO PAULO - BRAZIL**

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**SUMMARY**

*Fine and coarse particles in suspension in the atmosphere were collected on two teflon filters using a dichotomous sampler. The concentration of Al, Br, Ca, Ce, Cl, Co, Cr, Fe, K, La, Mn, Na, P, Pb, S, Sb, Sc, Se, Si, Sm, Th, V, and Zn was determined by ED-XRF and INAA. The elemental concentration was analyzed using linear correlation coefficients, enrichment factors and principal factor analysis, in order to identify the aerosol sources. The main sources of the aerosol particles were the marine one, re-suspended soil, fuel oil combustion, phosphatic rocks, refuse incineration and residual high temperature processes.*

**INTRODUCTION**

Atmospheric pollution is a world-wide problem which importance has grown, mainly in urban areas like Sao Paulo, owing to the increasing effects of pollutants on human health.

Approximately 15 million people live in the Sao Paulo Metropolitan area, which is located on the Atlantic Plateau, 700 to 900 m above sea level, on the Tropic of Capricorn, 80 km from the Atlantic coastline. The general topography is rather complex and the air flow is strongly influenced by local conditions.

Besides, Sao Paulo has a wide urban industrial area, with 150,000 industries such as cement, sulphuric acid, fertilizer and petrochemical plants, iron and steel works,

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refineries, chemical manufacturing, etc and an automobile fleet greater than 4.5 million vehicles.

One of the most important problems in the atmospheric aerosol studies, is to determine the relation between values measured in the environment and those emitted by sources.

Now a days, special emphasis is being given to the application of models which go from the elemental concentrations [1-6] obtained in a receptor to the sources.

In this paper, correlation coefficients, enrichment factors and principal factor analysis on elemental concentration data obtained by Energy Dispersive X-Ray Fluorescence (ED-XRF) and Instrumental Neutron Activation Analysis (INAA), were used to characterize the aerosol profile of the city of Sao Paulo.

#### ***ANALYTICAL QUALITY CONTROL***

For the quality control of the analytical procedure for aerosol samples, two intercomparison sample series and two reference materials were analyzed. The values presented for these materials were results of only one determination and the standard deviations were calculated from statistical counting error.

##### *1. Samples provided by Dr. Sadasivan (India)*

These samples were distributed during the second RCM, Jakarta, November 20-24, 1989, and were collected in Bombay, India, on Whatman 41 filters using a high volume sampler. The collection data and results obtained for two samples are presented in Table 1.

##### *2. Samples provided by Dr. Landsberger (USA)*

These samples were prepared from the Japan NIES Vehicle Exhaust Reference Material. Four teflon filters: two blanks, one loaded with fine fraction ( $< 2.5 \mu\text{m}$ ), and one with coarse fraction ( $2.5$  to  $10 \mu\text{m}$ ) were analyzed.

These filters were reweighed on a microbalance in a room with about 50%

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humidity. The filter rings were cut using a stainless steel scissors which left approximately an one millimetre border on each filter ring.

The results in  $\mu\text{g/g}$  of filter, without subtraction of blank values and based on filter weight, are presented in Table 2.

### 3. Reference materials

About 30 mg of two reference materials: Urban Particulate Matter (NIST-SRM-1648) and Vehicle Exhaust (NIES-CRM-08) were also analyzed. The results are presented in Table 3.

## EXPERIMENTAL

### *Aerosol sample collection and analysis*

The sample collection was made using a Sierra Instruments model 244 Dichotomous Sampler (virtual impactor) which fractionated suspended particles into two size fractions, 2.5 to 10  $\mu\text{m}$  (coarse particles) and less than 2.5  $\mu\text{m}$  (fine particles). These two fractions were collected uniformly on two teflon membrane filters with a flow rate of 1  $\text{m}^3/\text{h}$ . Samples were collected at the western periphery of the city, 1.5 m above ground level. The collection time was 24 h.

The mass of particulate matter was determined gravimetrically with a precision of 1  $\mu\text{g}$  using a microbalance and a  $^{210}\text{Po}$  radioactive source to eliminate electrostatic effects, in a room with humidity controlled between 40 to 60%.

The filters were analyzed first by ED-XRF using a TEFA system which had a dual anode Mo/W - X-Ray tube. Mo and Cu primary X-ray filters were used to obtain monochromatic excitation. The X-ray spectrometer consists of a Si(Li) X-ray detector, amplifier and pulse height analyser which measures the energy and intensity of characteristic X-rays generated in excitation procedure.

After that, filters were submitted to an INAA. Samples and standards were irradiated for 5 minutes under a neutron flux of about  $10^{12} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ , for the analysis of

elements that give rise to short-lived radionuclides. For long lived radionuclide analysis, samples were irradiated for 24 h under a neutron flux of  $10^{13} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ .

Standards were prepared by pipetting suitable aliquots of standard solutions obtained by dissolution of high degree of purity metal or oxide of elements on pieces of 41 Whatman 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, with resolution of 2.6 keV at the 1332 keV gamma peak of  $^{60}\text{Co}$  coupled to a 4096 channel gamma spectrometer Ortec model 6240B.

## **RESULTS AND DISCUSSION**

### *Aerosol sample results*

The above procedure allowed the determination of the following elements: Al, Br, Ca, Ce, Cl, Co, Cr, Fe, K, La, Mn, Na, P, Pb, S, Sb, Sc, Se, Si, Sm, Th, V, and Zn in 52 aerosol samples. Range, geometric means, and detection limits, calculated using criterion of IUPAC [7], are presented in Table 4.

The elemental concentration data were analyzed by means of correlation coefficients, enrichment factors, and principal factor analysis in order to obtain information about aerosol sources.

### *Correlation coefficients and enrichment factors*

The usual correlation coefficients were calculated. It was observed that the number of significant correlations was higher in the coarse particulate matter than in the fine ones. Elements Al, Ce, Fe, La, Sc, Si, Sm, and Th were clearly associated in the coarse particles, while in the fine fraction elements most frequently associated were Br, P, S, Sb, and V.

In order to evaluate the contribution of anthropogenic aerosol sources, the enrichment factors (EF) were calculated using Fe and Na as reference elements to Earth crust and seawater, respectively and the average composition of them reported by the [9,10] literature. The results are presented in Table 5.

The investigation of sources using the criterion established by RAHN [11], where elements with EF less than 7 have got their origin in the investigated source, while those with EF greater than 10 are enriched in relation to that source, allowed to observe that elements Br, Cl, Cr, Pb, S, Sb, Se and Zn were enriched in relation to Earth crust while the probable source of Al, Ca, Ce, Co, K, La, Mn, Na, Sc, Si, and Th was re-suspended soil, once they presented EF values less than 7 in both fine and coarse particles. Only the element V presented a different behaviour, with EF greater than 10 in fine and less than 7 in coarse particulate matter. On the other hand, all elements were enriched in relation to seawater except Br and Cl, which probably are of marine origin, since their EF values were less than 7, for both fine and coarse particles.

#### *Principal factor analysis*

The PFA was carried out using the Statgraphics, software of the Statistical Graphics Co, on the elemental concentration data. After extraction of the principal factors, an orthogonal rotation (VARIMAX) was carried out to make the interpretation of the factors easier. Coarse and fine particulate matter were treated separately.

#### *Results for coarse particles*

The result of PFA for coarse particles are presented in Table 6. Six factors explained 88.7% of the data variance. All elements presented high communality, indicating a good data fitting. Although the sixth factor presented unrotated eigenvalue less than 1.0, it was considered in the analysis because it presented eigenvalue greater than 1.0 after rotation.

The first factor was responsible for 43.4% of the variance and had high loadings for Al, Fe, Sc, Th and rare earths.

It appeared to represent the contribution from the re-suspended soil. The high correlation of V with this factor indicated a contribution of another source. This source appeared to be emission from fuel oil combustion which was enriched in V and some rare earths.

The second factor presented a high correlation with Ca, K, P, S and Si, whose presence was attributed to a fertilizer plant located 4 km away from the sampling site. Phosphatic rocks are typical raw material of this kind of plant.

Only elements Cl and Na were separated in the third factor, which was clearly associated to marine aerosol.

The fourth factor was highly associated with Br and Sb, and seemed to represent emissions from high temperature processes.

Refuse incineration, a source known to be enriched in Zn [12], appeared to be represented in the fifth factor. This approach seemed to be reasonable since there was a municipal incinerator in operation near the sampling site during sample collection.

The sixth factor had high loadings for Cr and Pb and was attributed to emissions from industrial processes.

#### *Results for fine particles*

The Varimax rotated factor matrix for fine particulate matter is presented in Table 7. Five factors were responsible for 83.4% of the total variance. All elements were well explained by this fitting, except the element Br, whose communality was 0.59.

In general the interpretation of many of these factors was similar to that of the coarse particles.

The influence of phosphatic rocks (high loadings for K, Na, P, S and Si) and refuse incineration (high loading for Zn) appeared in the first factor, while in the second one a contribution of fuel oil combustion was identified (high correlation with V and rare earths).

The third factor had high loadings for Cl and Sb and was associated to high temperature processes.

A little contribution of soil appeared in the fifth factor. This seems reasonable once the majority of soil went to the coarse particles fraction.

The source associated with the fourth factor, with high loading for Ca and an intermediary one for Cr, was not clearly identified.

The element Pb was distributed between first and second factors. In the factor 2,

Pb was associated with Br, and this [13,14] emission is frequently associated with leaded automobiles. A CETESB report [15] has shown a Pb concentration decreasing in Sao Paulo during period from 1978 to 1983, due to the "Alcohol Programme" that stimulated the utilization of pure alcohol and gasoline blended with 20% alcohol, as vehicle fuel.

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TABLE 1

RESULTS OBTAINED FOR SAMPLES PROVIDED

BY Dr. SADASIVAN, in  $\text{ng. m}^{-3}$ 

ELEMENT	SAMPLE A	SAMPLE B
Al	4259 +- 117	8989 +- 388
As	67 +- 5	169 +- 13
Br	35 +- 2	77 +- 5
Ce	2.0 +- 0.3	4.8 +- 0.5
Cl	2219 +- 87	6581 +- 205
Co	2.96 +- 0.09	7.73 +- 0.08
Cr	134 +- 2	494 +- 5
Fe	4031 +- 46	8985 +- 60
K	1037 +- 40	2243 +- 179
La	1.53 +- 0.05	4.00 +- 0.05
Mn	271 +- 2	405 +- 3
Na	1170 +- 28	4396 +- 72
Sb	15.6 +- 0.9	50 +- 2
Sc	1.16 +- 0.01	2.68 +- 0.02
Th	0.41 +- 0.03	1.08 +- 0.07
V	17.6 +- 0.7	42 +- 1
COLLECTION PERIOD	FROM 17:45H 28/03/89 TO 9:45H 29/03/89	FROM 17:55H 29/03/89 TO 9:45H 30/03/89
AV. FLOW RATE	1298 l/min	623 l/min
TOTAL VOLUME	1246 $\text{m}^3$	592 $\text{m}^3$
VOL/DISC. SENT	15.31 $\text{m}^3$	7.37 $\text{m}^3$



TABLE 2

RESULTS OBTAINED FOR SAMPLES PROVIDED BY Dr. LANDSBERGER,  
IN  $\mu\text{g/g}$  OF LOADED FILTER WEIGHT

ELEMENT	BLANKS		SAMPLES	
	16	17	25F	25C
Al	11.9+-0.4	8.6+-0.3	13.6+-0.4	32.3+-0.8
As	-	0.004+-0.001	0.009+-0.003	0.038+-0.003
Br	0.09+-0.01	0.069+-0.003	0.28+-0.03	0.54+-0.01
Ca	69+-31	114+-45	58+-12	96+-49
Cl	14+-1	-	78+-3	-
Co	0.07+-0.01	0.065+-0.004	0.088+-0.009	0.077+-0.006
Cr	0.32+-0.05	0.40+-0.06	0.28+-0.03	0.39+-0.04
Fe	12+-2	32+-5	19+-2	34+-3
Mn	0.09+-0.01	0.27+-0.01	0.25+-0.01	0.53+-0.02
Na	1.9+-0.2	2.1+-0.3	9.6+-0.5	18.6+-0.7
Sb	0.005+-0.001	0.005+-0.001	0.032+-0.002	0.045+-0.004
Sc	0.0010+-0.0002	0.0005+-0.0003	0.0021+-0.0002	0.0045+-0.0004
W	-	0.009+-0.002	0.016+-0.005	0.049+-0.005
Zn	9.34+-0.6	11.7+-0.5	14.7+-0.3	16.3+-0.3

TABLE 3

RESULTS OBTAINED FOR REFERENCE MATERIALS, in ug/g

ELEMENT	URBAN PARTICULATE MATTER NIST-SRM-1648		VEHICLE EXHAUST NIES-CRM-8	
	THIS WORK	RECOMMENDED VALUE <sup>b</sup>	THIS WORK	RECOMMENDED VALUE <sup>b</sup>
As	115 +- 12	115	a	2.6
Ba	644 +- 83	737	142 +- 19	b
Br	557 +- 16	500	60.1 +- 0.4	53
Ca	58000 +- 18000	b	5100 +- 1800	5300
Ce	44 +- 3	55	a	3.1
Co	18.7 +- 0.3	18	3.2 +- 0.1	3.3
Cr	395 +- 3	403	27.8 +- 0.8	25.5
Fe	33400 +- 600	39100	4000 +- 100	b
La	33 +- 3	42	1.23 +- 0.08	1.2
Rb	48 +- 5	62	a	4.6
Sb	44.6 +- 0.6	45	6.10 +- 0.08	6.0
Sc	6.56 +- 0.08	7	0.52 +- 0.05	0.55
Se	30 +- 5	27	a	1.3
Sm	3.03 +- 0.03	4.4	0.180 +- 0.001	0.20
Th	7.0 +- 0.2	7.4	0.32 +- 0.03	0.35
W	4 +- 1	4.8	6.0 +- 0.2	b
Zn	4802 +- 32	4750	996 +- 10	1040

a - Element not determined

b - There are no recommended value

TABLE 4

RANGE, GEOMETRIC MEANS AND DETECTION LIMITS FOR COARSE  
AND FINE PARTICULATE MATTER, IN  $\text{ng. m}^{-3}$

ELEMENT	COARSE		FINE		DETECTION LIMITS
	RANGE	GEOMETRIC MEAN	RANGE	GEOMETRIC MEAN	
Al	349-2396	1041	49-258	115	1.1
Br	0.82-3.07	1.78	3.04-27.74	8.21	0.03
Ca	100-4631	818	21-236	109	0.7
Ce	0.60-4.07	1.56	0.06-1.57	0.36	0.14
Cl	81-1128	356	17-558	71	34
Co	0.15-0.90	0.47	0.12-0.80	0.37	0.03
Cr	2.03-19.89	12.3	0.52-21.65	11.5	0.3
Fe	176-1564	706	79-408	216	17
K	66-533	214	74-639	297	17
La	0.31-1.56	0.74	0.06-0.40	0.19	0.01
Mn	5.5-126.5	27.5	5.4-161.8	26.5	0.2
Na	89-1077	215.8	134-894	254.8	12
P	49-260	104.4	57-216	120.7	0.8
Pb	9-118	30.7	31-160	72.2	0.8
S	174-3882	714	672-4051	2096	14
Sb	0.77-7.17	2.57	1.02-8.42	3.18	0.01
Sc	0.04-0.39	0.13	0.003-0.026	0.009	0.003
Se	0.08-1.84	0.35	0.33-5.84	1.31	0.2
Si	694-4387	2040	142-535	342	2
Sm	0.02-0.28	0.09	0.011-0.244	0.049	0.001
Th	0.05-0.39	0.16	0.004-0.271	0.03	0.01
V	1.78-11.52	4.7	4.16-27.15	10.8	0.2
Zn	13-125	53.8	32-326	95.3	0.2
MP	8000-33900	17198.6	12200-52500	26492.4	

TABLE 5

ENRICHMENT FACTORS CALCULATED IN RELATION TO  
EARTH CRUST (EF<sub>soil</sub>) AND SEAWATER (EF<sub>sea</sub>)  
AVERAGE COMPOSITION<sup>9, 10</sup>

ELEMENT	COARSE		FINE	
	EF <sub>soil</sub>	EF <sub>sea</sub>	EF <sub>soil</sub>	EF <sub>sea</sub>
Al	0.91	>1000	0.33	>1000
Br	50.5	1.3	758	5.2
Ca	1.6	99.5	0.69	11.2
Ce	1.84	>1000	1.39	>1000
Cl	194	0.91	125	0.19
Co	1.34	>1000	3.46	>1000
Cr	8.73	>1000	26.5	26.5
Fe	1	>1000	1	>1000
K	0.58	27.4	2.65	32.2
La	1.74	>1003	1.43	>1000
Mn	2.05	>1000	6.44	>1000
Na	0.54	1	2.08	1
Pb	167	>1000	>1000	>1000
S	194	39.2	>1000	97.6
Sb	912	>1000	>1000	>1000
Sc	0.41	>1000	0.1	>1000
Se	491	>1000	>1000	>1000
Si	0.52	>1000	0.28	>1000
Sm	1.02	-	-	-
Th	1.58	>1000	0.1	>1000
V	2.47	>1000	18.4	>1000
Zn	54.5	>1000	314	>1000

TABLE 6

PRINCIPAL FACTOR ANALYSIS RESULTS FOR COARSE  
ELEMENTAL CONCENTRATION DATA

ELEMENT	FACTOR						COMMUNALITY
	1	2	3	4	5	6	
Al	0.89						0.93
Br				0.83			0.77
Ca		0.96					0.93
Ce	0.84						0.92
Cl			0.90				0.95
Co	0.69						0.77
Cr						0.75	0.74
Fe	0.83						0.86
K		0.93					0.97
La	0.89						0.95
Mn					0.89		0.87
Na			0.83				0.90
P		0.93					0.95
Pb		0.65				0.63	0.87
S		0.83					0.95
Sb				0.70			0.82
Sc	0.94						0.97
Si	0.58	0.77					0.96
Sm	0.76						0.92
Th	0.74						0.81
V	0.76						0.83
Zn					0.83		0.85
Eigenvalue	9.54	3.84	2.15	1.73	1.29	0.97	
Variance, %	43.4	17.5	9.8	7.9	5.8	4.4	

TABLE 7

PRINCIPAL FACTOR ANALYSIS RESULTS FOR FINE  
ELEMENTAL CONCENTRATION DATA

ELEMENT	FACTOR					COMMUNALITY
	1	2	3	4	5	
Al					0.79	0.90
Br		0.58				0.59
Ca				0.85		0.81
Ce		0.78				0.90
Cl			0.89			0.91
Cr				0.54	0.75	0.88
Fe		0.74				0.85
K	0.82					0.90
La		0.82				0.88
Na	0.87					0.89
P	0.67					0.81
Pb	0.51	0.67				0.83
S	0.63					0.82
Sb			0.73			0.82
Sc			0.59		0.52	0.79
Se			0.54			0.87
Si	0.72					0.87
V		0.59				0.72
Zn	0.87					0.80
Eigenvalue	8.31	2.58	1.97	1.71	1.28	
Variance, %	43.7	13.6	10.4	9.0	6.7	