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 the latest years the air pollution has become a critical problem with effects on atmospheric properties, human health, soil, water, vegetation, animals and ecosystems.

The aerosols in urban and industrialized areas are clearly mutagenic and most probably traffic and certain industrial sources contribute to this occurence[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 the 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 analyze nondestructively 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 out in cooperation with the CETESB - Companhia de Tecnologia de Saneamento Ambiental Governmental Institution responsible for environmental control in the State of São Paulo.

This investigation has the purpose of obtaining more information about the aerosol 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 to 15 microns (coarse, non-inhalable particles) and less than 2.5 microns (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 microns 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 hours.

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 TEFA system which 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 analyser which measures the energy and intensity of characteristic X-rays generated in the excitation procedure.

INAA

A non-destructive neutron activation analytical procedure has been established. Samples and standards were irradiated for 5 minutes using a pneumatic rabbit station of the swimming pool type research reactor whose flux is about 10^{12} n.cm^{-2} s.$^{-1}$, for the analysis of elements that give rise to short-lived radionuclides. For the analysis of long lived radionuclides samples were irradiated for 24 hours on a neutron flux of 10^{13} n.cm^{-2} 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 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, two USGS rock standards (W-1 and AGV-1) and an IAEA reference material (AIR 3/1) were analyzed. A satisfactory agreement was obtained. Table 1 gives a comparison between the results obtained and the certified values.

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 while 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.

Arithmetic and geometric means, median of elemental concentrations obtained by EDXRF and INAA and the number of data used for calculation of the means are given in tables 2 and 3, respectively.

In order to obtain information about aerosol sources, enrichment factor (EF)

and correlation coefficients (r) were calculated:

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

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.

The EF were calculated using soil dust and sea salt as reference composition[7], due 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), while 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 pratically the same. The differences in EF values were probably due to differents elements being chosen as reference.

For one to suggest that the 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 to 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 element considered, except for Cl that is depleted. This can denote a complete desappearence of any marine contribution.

Also it is observed a high correlation between Fe and the elements Al, Mn, Se, Rb, La and Ce (> 0.80) 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, S could not be determined by INAA, it has been more interesting to combine the results obtained by both techniques.

Considering that the aerosol 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 and also considering the small number of samples, obtained from a single point of sampling which 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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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) Certificate		
	This Work	Certificate[8]	This Work	Certificate[8]	This Work	Content	Confidence limit (0.05)[9]
Al	7.80	7.93 ± 0.14	8.50	9.07 ± 0.18	92.0	-	-
Ba	162	162 ± 5	-	-	-	-	-
Cr	119	120 ± 14	-	12 ± 3	5.04	5.0	4.5 ÷ 5.1
As	-	2.2 ± 0.3	-	0.84 ± 0.27	4.98	5.0	4.6 ÷ 5.8
Co	46	46 ± 4	14.8	15.1 ± 1.2	1.18	1.1	0.8 ÷ 1.4
Fe (%)	8.27	7.79 ± 0.16	4.93	4.73 ± 0.13	226.56	204	196 ÷ 210
La	11.9	10.9 ± 1.3	40	38 ± 3	0.015	-	-
Mn	1314	1300 ± 125	733	740 ± 60	31.76	30	28 ÷ 32
Na (%)	1.55	1.58 ± 0.08	3.10	3.15 ± 0.09	104.35	-	-
Se (ppb)	-	113 ± 7	-	-	0.93	1.0	0.8 ÷ 1.2
Sc	36.2	35 ± 2	11.8	12.1 ± 0.9	-	-	-
Sm	3.3	3.5 ± 0.3	5.5	5.9 ± 0.5	0.16	-	-
Th	2.8	2.4 ± 0.4	7.4	6.50 ± 0.37	-	-	-
V	282	260 ± 25	140	123 ± 12	8.42	7.8	5.8 ÷ 8.3

TABLE 2 - ARITHMETIC AND GEOMETRIC MEANS AND MEDIAN, FROM EDXRF ANALYSIS, IN ng/m^3 UNLESS INDICATED.

Element	Fine Particles				Coarse Particles			
	n	ARITHMETIC MEANS	GEOMETRIC MEANS	MEDIAN	n	ARITHMETIC MEANS	GEOMETRIC MEANS	MEDIAN
Al ($\mu g/m^3$)	12	0.290	0.260	0.260	12	2.560	2.300	2.390
Si ($\mu g/m^3$)	12	0.500	0.400	0.400	12	3.950	3.620	3.740
P ($\mu g/m^3$)	12	0.150	0.130	0.140	12	0.171	0.162	0.172
S ($\mu g/m^3$)	12	3.000	2.700	3.200	12	1.520	1.220	1.380
Cl ($\mu g/m^3$)	11	0.130	0.070	0.080	12	0.603	0.533	0.521
K ($\mu g/m^3$)	12	0.390	0.310	0.350	12	0.379	0.338	0.343
Ca ($\mu g/m^3$)	12	0.150	0.120	0.160	12	1.930	1.620	1.540
Ti ($\mu g/m^3$)	6	0.016	0.015	0.013	9	0.200	0.161	0.203
V	7	14.6	13.3	14.8	8	31.1	27.0	35.1
Cr	11	9.8	7.4	6.3	12	27.0	25.3	23.5
Mn	12	81.9	28.9	21.6	12	82.9	59.6	53.8
Fe ($\mu g/m^3$)	12	0.230	0.200	0.190	12	1.730	1.580	1.560
Ni	10	7.9	6.4	8.1	10	9.8	7.6	9.6
Cu	12	14.3	9.7	13.0	12	34.3	29.7	30.5
Zn ($\mu g/m^3$)	12	0.120	0.094	0.080	12	0.076	0.070	0.071
Ga	11	5.2	3.9	4.9	12	4.2	3.3	4.5
As	4	13.6	13.4	13.4	4	7.6	7.6	7.9
Se	11	4.2	2.8	3.5	10	2.7	2.2	2.6
Br	12	17.4	14.2	15.8	12	4.6	3.2	4.2
Rb	10	7.7	5.1	6.0	12	6.6	3.2	5.3
Sr	10	11.0	6.0	8.6	12	14.8	11.8	12.1
Hg	3	4.8	4.5	5.6	4	5.1	4.3	3.6
Pb ($\mu g/m^3$)	12	0.103	0.089	0.088	12	0.071	0.058	0.073

TABLE 3 - ARITHMETIC AND GEOMETRIC MEANS AND MEDIAN, FROM INAA ANALYSIS, IN ng/m^3 UNLESS INDICATED.

Element	Fine Particles				Coarse Particles			
	n	ARITHMETIC MEANS	GEOMETRIC MEANS	MEDIAN	n	ARITHMETIC MEANS	GEOMETRIC MEANS	MEDIAN
Na ($\mu g/m^3$)	12	0.372	0.306	0.296	12	0.359	0.245	0.237
Cl ($\mu g/m^3$)	10	0.569	0.075	0.090	11	0.423	0.351	0.314
Al ($\mu g/m^3$)	11	0.179	0.155	0.179	12	1.730	1.480	1.642
Mn	12	96.6	36.5	23.3	12	59.3	38.1	29.6
Sm	9	0.07	0.05	0.05	9	0.2	0.2	0.2
Mo	7	1.2	1.0	1.0	6	1.5	1.3	1.2
W	9	0.6	0.5	0.4	9	1.1	0.8	0.8
La	9	0.3	0.3	0.3	9	1.3	1.0	1.3
As	8	3.2	2.5	2.0	4	0.5	0.4	0.4
Br	8	11.9	8.8	9.2	7	1.4	1.0	1.3
Sb	9	4.6	4.0	4.9	9	2.1	1.9	1.6
K ($\mu g/m^3$)	9	0.650	0.480	0.590	9	0.456	0.340	0.475
Ba	7	13.6	13.2	12.6	7	48.0	42.0	42.3
Se	8	3.0	1.7	1.5	8	0.4	0.4	0.4
Th	8	0.08	0.06	0.05	9	0.3	0.2	0.2
Cr	9	8.7	5.3	12.3	9	10.9	9.1	11.8
Rb	6	4.4	3.8	4.2	6	3.0	2.2	2.3
Co	3	0.4	0.3	0.2	9	0.4	0.2	0.2
Fe ($\mu g/m^3$)	9	0.230	0.170	0.250	9	1.214	0.947	1.211
Ce	8	0.4	0.2	0.3	9	3.1	2.4	3.2
Sc	8	0.02	0.01	0.01	9	0.2	0.2	0.2
V	12	16.6	15.0	17.3	12	7.0	6.4	6.4

TABLE 4 - ENRICHMENT FACTOR (EF), RELATIVE TO SOIL DUST, AND 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) $0.01 < P < 0.1$; (4) $P > 0.1$

TABLE 5 - ENRICHMENT FACTOR (EF), RELATIVE TO SEA SALT, AND 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) $0.01 < P < 0.1$; (4) $P > 0.1$

TABLE 6 - ENRICHMENT FACTOR (EF), RELATIVE TO SOIL DUST, AND 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) $0.01 < P < 0.1$; (4) $P > 0.$

TABLE 7 - ENRICHMENT FACTOR (EF), RELATIVE TO SEA SALT, AND 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) $0.01 < P < 0.1$; (4) $P > 0.$