ANNEX 5

APPLICATION OF NEUTRON ACTIVATION ANALYSIS TO TRACE ELEMENTS IN ENVIRONMENTAL AEROSOLS SAMPLES IN SAO PAULO, BRAZIL

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INTRODUCTION

In the lasted years air pollution has became a critical problem with effects on atmospheric properties, human health, soil, water, vegetation, animals and ecosystem.

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. INAA is useful for this purpose because of its high sensitivity and its ability to make in a single measurement, qualitative and quantitative analyses of numerous elements in a sample [1-3].

The aerosols in urban and industrialized areas are clearly mutagenic. Most probably traffic and certain industrial sources contribute to this occurrence [4].

The purpose of this investigation is to obtain information about the aerosol in the city of Sao Paulo and perform, by mean of the trace element results obtained by INAA, a preliminary identification of the main sources of the atmospheric aerosol based on enrichment factor (Ef) and correlation coefficient (r) results.

Quantitative analyses of fly ash candidate reference material, CTA-FFA-1, were also made.

EXPERIMENTAL

Air sampling

All the air particulate samples used in this study were collected using a Sierra Instrument model 244 Dichotomous Sampler (Virtual Impactor) that fractionates suspended particles into two sized fractions, 2.5 to 10 microns and less than 2.5 microns. 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 flow rate of 1 m^3/h. The sampling site was on the western periphery of the city. The time of collection was 24 h.

Analytical procedure

A non-destructive neutron activation analytical procedure was established. For the analyses of elements that give rise to short-lived radionuclides, samples and standards were irradiated for 5 minutes using a pneumatic rabbit station with swimming pool type research reactor whose flux is about 10^{12} $n.cm^{-2}.s^{-1}$. For the analyses of long-lived radionuclides, samples were irradiated for 24 h on a neutron flux of 10^{13} $n.cm^{-2}.s^{-1}$. Some experimental conditions and the elements analyzed are summarized in Table 1.

Standards were prepared by pipeting suitable aliquots of standard solutions obtained by dissolution of high degree purity

elemental metals or oxides on pieces of Whatman No. 41 filter paper and dried under an infrared lamp.

The measurements were carried out after suitable cooling times with a 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

Analysis of fly ash

Quantitative analyses of fly ash candidate reference material, CTA-FFA-1, were made. The analytical procedure adopted was the same that was used for the filters and is indicated in Table 1.

In all, 19 elements were determined and the results are presented in Table 2, together with their relative standard deviations, SD(rel)%, and estimated lower limits of detection.

As can be seen from Table 2, 14 elements could be determined with precision less than 5%. For the other elements, the precision was around 10%.

The detection limit achieved was considered equal three times the standard deviation of the background counts for a given interval of time [5].

$$lim = 3x(N_{backg})^{1/2}$$

Analysis of aerosols

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, Al, Cl, K, Sc, V, Cr, Mn, Fe, Co, As, Se, Br, Rb, Mo, Sb, Ba, La, Ce, Sm, W and Th.

Geometric means, geometric standard deviation and median of elemental concentration obtained and the number of data used for calculation of the means (n) are given in Table 3.

In order to obtain information about aerosol sources, correlation coefficient and enrichment factor were calculated.

The number of significant correlations is higher in the coarse particle fractions as compared to the fine fractions. For the coarse fraction elements Al, Sc, Fe, Rb, La and Ce are clearly associated. In the fine particle fraction the elements most frequently associated are Br, Co, As and Cl.

To evaluate the contribution of anthropogenic aerosol sources for each element identified, the enrichment factor, Ef, was evaluated using

[EQUATION]

where C_{ax}, C_{xt} are the concentrations of element X in the atmosphere and the earth's dust, respectively.

The reference element utilized in this study was Fe, since it is considered to be the most significant indicator of the earth's crust [6].

The elemental concentrations in the earth's crust according to data given by Mason and Moore [7] were used as a basis for calculating the respective enrichment factors as shown in Table 4.

Following the criterion established by Rahn [6], elements with Ef < 7 are of natural origin and those elements with Ef > 10 are anthropogenic.

Sodium, Al, K, Sc, Fe, Co, La, Ce, Sm and Th are typical elements of natural origin. Bromine, arsenic and chlorine are representative of anthropogenic combustion sources with the expected predominance of small particles.

Vanadium and Mn are typical elements produced from both physical (large particle) and combustion/condensation (fine particle) processes. Both have anthropogenic sources.

Considering that the aerosol of Sao Paulo is one of the most complex of the world because it includes about 150,000 industries of all types and sizes, 14 million people if we consider the surrounding zones, and 4.5 million vehicles 80% of which use gasoline blended with 20% ethanol and the other 20% pure alcohol fuel. For these reasons characterizing Sao Paulo's aerosol is very difficult.

FUTURE WORK

The next year we will continue the aerosol analysis initiated. We will concentrate our efforts on the characterization of the aerosol in Sao Paulo using factor analysis.

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TABLE 1

EXPERIMENTAL CONDITIONS FOR INAA OF AEROSOLS SAMPLES.

IRRADIATION TIME	COOLING TIME	COUNTING TIME	NUCLIDES MEASURED
5 min	2 min	3 min	^{28}Al ; ^{52}V
	10 min	10 min	^{24}Na ; ^{38}Cl
	90 min	20 min	^{56}Mn
24 h	3-5 days	12 h	^{153}Sm ; ^{99}Mo ; ^{187}W ; ^{76}As ; ^{140}La ; ^{82}Br ; ^{122}Sb ; ^{42}K
	25-30 days	12 h	^{131}Ba ; ^{75}Se ; ^{233}Pa ; ^{51}Cr ; ^{86}Rb ; ^{65}Zn ; ^{60}Co ; ^{141}Ce ; ^{59}Fe ; ^{46}Sc ; ^{152}Eu ; ^{124}Sb

Table 2. Results obtained for fly ash CTA-FFA-1

Elem	Results of individual determinations (ppm) 1	2	3	4	5	6	Mean ± SD (ppm)	SD(rel) %	Det. limit (ppm)
As	67.8	70.5	86.8	65.3	86.2		75.32 ± 10.37	13.8	10
Ba	845.7	880.7	853.0	941.1			880.13 ± 43.35	4.9	200
Ce	105.9	113.1	103.9	112.1	111.8	116.8	110.60 ± 4.80	4.3	1
Co	40.0	40.4	39.6	39.4	38.5	39.2	39.51 ± 0.65	1.6	0.5
Cr	137.4	143.0	136.6	145.0	142.4	148.3	142.12 ± 4.47	3.1	2.5
Eu	2.4	2.3	2.4	2.3	2.3	2.4	2.35 ± 0.055	2.3	0.1
Hf	5.9	5.7	5.5	6.0	5.5	5.9	5.75 ± 0.22	3.8	0.2
La	60.6	60.0	62.1	60.3	61.1		60.82 ± 0.82	1.3	10
Mn	1041.5	1061.6	1039.1	1112.9	1169.5	1112.9	1089.58 ± 51.22	4.7	20
Nd	57.2	59.6	50.9	52.2	51.0	56.8	54.62 ± 3.72	6.8	25
Rb	165.8	169.8	158.6	172.9	170.7	176.6	169.07 ± 6.24	3.7	20
Sb	16.7	17.9	16.3	18.6	18.3	18.5	17.72 ± 0.98	5.5	1.5
Sc	23.6	24.2	23.1	24.3	24.4	25.2	24.13 ± 0.72	3.0	0.1
Se	6.2	7.5	6.3	6.0			6.5 ± 0.68	10.5	1.5
Sm	11.3	12.5	12.0	13.4	11.0		12.04 ± 0.96	8.0	1
Ta	1.9	1.8	1.9	1.8	1.9	1.9	1.87 ± 0.052	2.8	0.3
Th	28.2	28.8	28.4	27.1	27.4	28.9	28.13 ± 0.74	2.6	0.3
V	262.8	225.4	275.6	287.6	274.0	235.0	260.07 ± 24.62	9.5	30
Yb	4.0	3.9	4.0				3.97 ± 0.0058	1.5	0.7

TABLE 3 - GEOMETRIC MEANS, GEOMETRIC STANDARD DEVIATION AND MEDIAN, FROM INAA ANALYSIS, IN pg/m^3, 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	47.2 ± 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

TABLE 4

ENRICHMENT FACTORS OF THE ELEMENTS IN FINE AND COARSE FRACTIONS

REFERENCE ELEMENT: Fe

Element	Ef	
	Fine	Coarse
Na	3.2	0.5
Al	0.6	1.0
Cl	105.9	142.7
K	5.4	0.7
Sc	0.2	0.4
V	32.4	2.5
Cr	15.5	4.8
Mn	11.2	2.1
Fe	1	1
Co	3.1	0.4
As	402.0	11.4
Se	10017.5	377.0
Br	1032.3	21.3
Rb	12.2	1.3
Mo	200.8	46.9
Sb	5857.0	488.0
Ba	9.1	5.2
La	2.5	1.8
Ce	1.2	2.1
Sm	2.5	1.4
W	96.0	26.6
Th	2.4	1.5