Use of PIXE analysis to study urban atmospheric aerosols from downtown Havana City

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Abstract

The present work shows the results of a first study aimed at determining the elemental composition in airborne particulate matter (in fine and coarse particle size fractions). It was collected at the Atmospheric Monitoring Station in the Municipality of Centro Habana, using the Particle-Induced X-ray Emission (PIXE) technique. At present, there is no information available about elemental contents in airborne particulate matter from this region. For this study, we carried out a sampling campaign during five months (November 14, 2006 to April 19, 2007). The samples were collected every second day during 24 h under an air flux of 20 l/min. The air sampler used was a Gent Sampler equipped with a Stacked Filter Unit (SFU) system which allows the aerosol collection in both size fractions simultaneously. A total of 144 aerosol samples were collected (72 correspond to the fine mass particle and 72 to the coarse mass particle). For PIXE analysis, the samples were irradiated by 2.0 MeV energy protons from the 2 MV Tandetron Accelerator from the Laboratory of PIXE analysis at ININ, Mexico. A total of 14 elements (S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br and Pb) were consistently detected in both of particle size fractions with minimum detection limits in the range of 1-10 ng/m^3. The quantitative results obtained from PIXE elemental analysis for mass of particles in both fractions have revealed important information that has been used in a first attempt to understand and characterize the atmospheric pollution in this area. A general discussion about these results is presented in this paper.

Aplicación del análisis PIXE al estudio de aerosoles atmosféricos urbanos en el centro de Ciudad de La Habana

Resumen

El presente trabajo reporta los resultados de un primer estudio realizado para determinar la composición elemental en material particulado atmosférico (en tamaños de partícula fina y gruesa) colectado en la Estación de Monitoreo Ambiental del Instituto Nacional de Higiene y Epidemiología, del Municipio de Centro Habana, utilizando la técnica PIXE (emisión de rayos X inducida por partículas). Para este estudio se realizó una campaña de muestreo durante cinco meses, entre los meses de noviembre, 2006 y abril, 2007, con un período de colección de una toma cada segundo día y 24 horas de duración. Se utilizó un muestreador de aire del tipo Gent con posibilidades de colectar de forma simultánea el material particulado fino y grueso. Un total de 144 muestras de MPA se colectaron para este estudio (72 de fracción fina y 72 de fracción gruesa). Las muestras se irradiaron tras la incidencia de un haz de protones de 2,5 MeV. Un total de 14 elementos (S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br y Pb) fueron consistentemente detectados en la mayoría de las muestras, con límites mínimos de detección entre 1-10 ng de partículas/m^3 de aire. Los resultados del análisis PIXE para ambos tamaños de partícula revelaron una importante información que se ha utilizado en una primera intención para entender y caracterizar la contaminación atmosférica del área muestreada. Se presenta una discusión general de estos resultados en este trabajo.

Key words: *particulates, air pollution monitoring, pixe analysis, urban areas*

Introduction

Atmospheric pollution studies in more populated cities of the world have been an important issue to diverse authors in recent years, because of the relevant impact that pollution has on the health of the population [1-6]. One of the most important factors of air pollution problem in Havana City is the presence of airborne particles, which are responsible for effects on public health, especially when their dimensions are below 10 μm, as they can penetrate deeply into the human respiratory tract, reason for which studying the properties of these kind of pollutants and its elemental characterization have become an important task to achieve.

In the frame of an ARCAL Regional Project promoted by the IAEA, a first study of multielemental contents in airborne particulate matter (in fine and coarse particle size fractions) from an urban area heavily populated of the Havana City was performed using the Particle-Induced X-ray Emission (PIXE) technique [7, 8].

PIXE is a nuclear analytical technique that has long been applied to the study of atmospheric aerosols and it continues as one of the most important areas of application [9-15]. The technique has certainly contributed to the understanding of source-receptor relationship for aerosol particles as well as to aerosol physics and chemistry. It is a method based on charged particle accelerators, that allows fast simultaneous analysis of all elements with atomic number larger than 13 (> Al), with a high sensitivity (around 1 ng of an element per 1 m^3 of air), non-destructive and extremely small targets can be effectively analyzed because of the well defined dimension of the incident proton beam on the samples. PIXE does not offer information on chemical states of elements and it is not applicable for lighter elements, such as C, N, H and O, which generally occupy more than 80% of the atmospheric aerosols, but as in this type of analysis the sample is not destroyed, PIXE aerosol analysis can be complemented with other techniques. Examples of theme are PESA (proton elastic scattering analysis) for measurement of hydrogen, PIGE (proton induced gamma ray emission) for detection of light elements, like B, Li, Na, Mg, Al, Si and P and RBS (rutherford backscattering) for measurement of C, N and O, allowing to obtain a complete reconstruction of the aerosol mass and to achieve a more comprehensive view of the characteristic elements of the aerosol.

Due to all these advantages in order to determine elemental concentrations of a variety of airborne pollution samples, the use of PIXE technique is recommended over other ones that can be used too for aerosol analyses.

In the present work, the quantitative results obtained from PIXE elemental analysis for fine and coarse particles mass collected at the Municipality of Centro Habana, Cuba, are presented.

Experimental measurements

Sampling. The sampling site (latitude 23.1N, longitude 82.4W) is located at the Air Pollutant Monitoring Station of INHEM, in the central part of the urban area of Havana City. This place is a heavily populated area with a great variety of industries (factories of detergents, soft drinks, tobaccos, biological products) and a high-traffic of vehicles. The site counts also with several sites of high humans activity to its around, as for example: Christina's Trains Station (1.2 km), Central Bus Station (0.81 km) visited every day by thousands commuters, Pediatric Hospital (a few meters from it), and Unique Market (1 km). All this together makes that this places must be observed and studied carefully for what is a part of Havana City's conurbation that contributes significantly to its atmospheric pollution.

The aerosol samples were collected during five months (from November 14, 2006 to April 19, 2007), every second day, during 24 h (00:00 h-24:00 h) each one at an average flow rate of 20 l/min. The sampler used in this study was a Gent Sampler with a Stacked Filter Unit (SFU-PM10\PM2,5) system [9, 16]. This sampling device allowed the particulate collection into two size fractions simultaneously: particles PM2,5 smaller than 2.5 μm (fine fraction) and particles PM2,5-10 with aerodynamic diameter between 2.5 μm and 10 μm (coarse fraction). The particles were collected on a 47 mm diameter Nucleopore polycarbonates filters; coarse mode on filters with 8.0 μm pore size and fine particles on filters with 0.4 μm pore size. A total de 144 aerosol samples were collected (72 correspond to the PM2,5 fine mass particle and 72 to the PM2,5-10 coarse mass particle).

The total amount of mass deposited of fine and coarse particles on the samples were obtained by gravimetric analysis. The filters were weighed before and after sampling in a Cahn 33 electronic microbalance with 0.1 μg sensitivity. Before weighing, all filters were stabilized during 48 h under constant relative humidity and temperature conditions (45% and 22 °C). An alpha source of ^{210}Po was used to eliminate static charge on the samples during weighing. Measured fine particulate

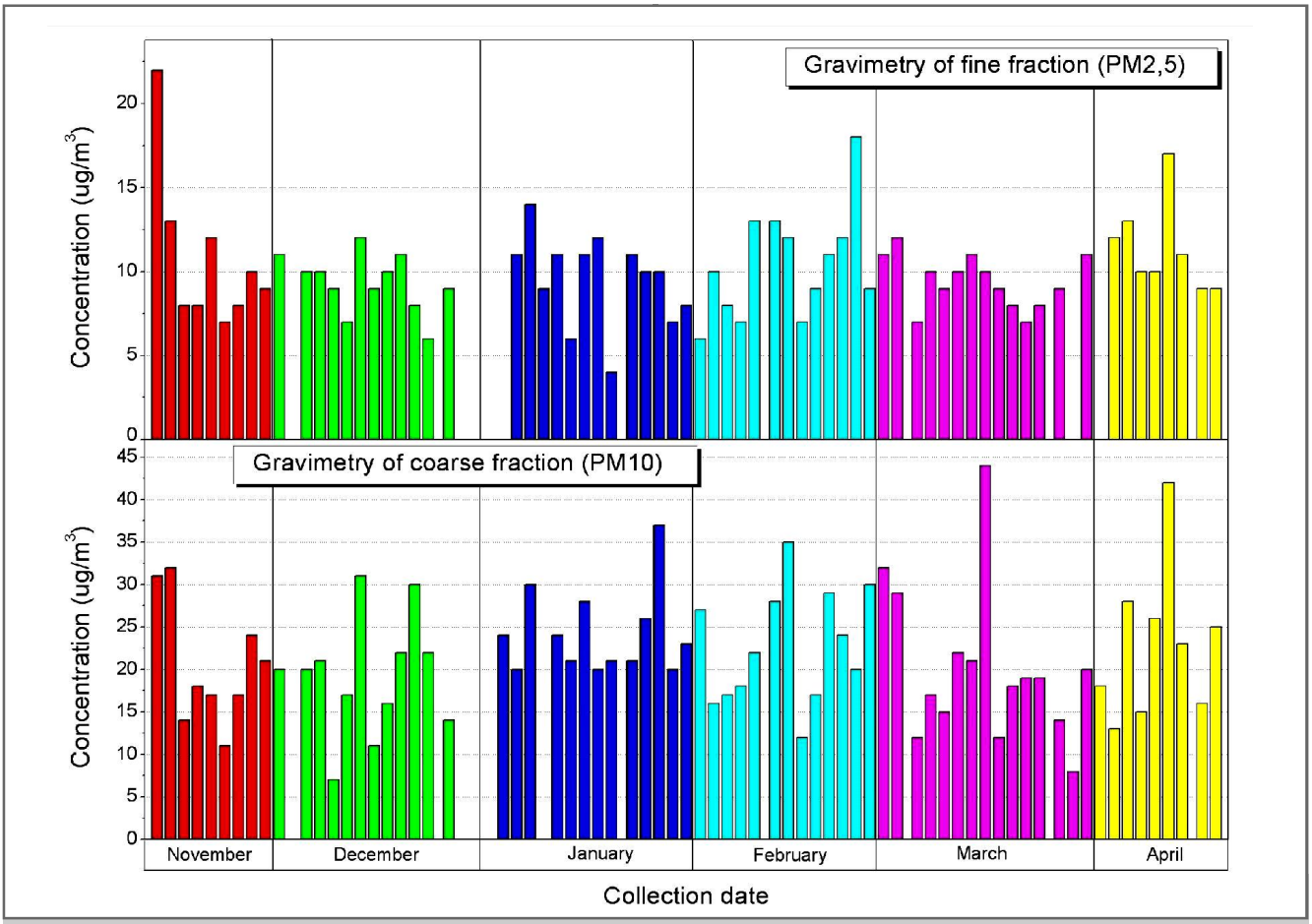

Figure 1. Fine and coarse aerosol mass concentrations for all individual measurements.

matter (FPM) and coarse particulate matter (CPM) mass concentrations ($\mu g/m^3$) are shown in figure 1. Levels of PM2,5-10 up to 44.2 $\mu g/m^3$ and PM2,5 values up to 22.4 $\mu g/m^3$ were obtained.

Other analytical equipments operating simultaneously at this station provided complementary data of several variables such as SO_2 and NO_2.

PIXE analysis. The experimental system of PIXE analysis consists of an accelerator, an ion beam, a vacuum irradiation chamber with a target holder included and a measurement system.

The aerosol samples, without any pre-treatment, were bombarded by 2.5 MeV protons from the 2 MV Van de Graff (Tandetron) accelerator, located at the Laboratory of PIXE Analysis of the ININ, Mexico. Ion beam currents in the system were 15 nA and total integrated charges were 6 μC. For the irradiation, the samples were placed in a sample holder with an angle of 45° with respect to the beam direction. The characteristics X-rays emitted from the samples were detected with an Ortec Si(Li) detector with an active area of 80 mm^2 and 200 eV resolution at 5.9 keV of the Mn K_α line, coming from an ^{55}Fe source. The detector in the experimental arrangement was located outside the irradiation chamber at 90° angle with respect to the ion beam direction and is coupled to standard electronics and PC based multichannel analyser. Spectra were obtained in this experimental line using EG&G Ortec Maestro II computer code [17]. The precision and reproducibility of the PIXE system were verified on a regular basis, using spectroscopically pure thin films of known area density, deposited on Nucleopore filters (MicroMatter Co., Deer Harbor, WA, USA). Details of the experimental setup, instrumentation and analytical procedures used to perform the PIXE analysis at the ININ PIXE Laboratory are better explained in reference [18].

For the elemental analysis the filters with the aerosol were cut in two pieces: 1/4 of it was analysed by PIXE; the remaining 3/4 was kept for other possible measurements.

The PIXE analysis revealed the presence of 14 elements in both particle size fractions, ranging from sulphur (S) to lead (Pb). Irradiation time was in the interval 10-15 min. Elemental minimum detection limits (MDL) were in the range of 0.1-10 ng/m^3 for most of the detected elements. The precision of the elemental concentration measurements was typical in the range of 5-10%.

The evaluation of the PIXE spectra was performed with the softwares AXIL v3.0 and WinAxil v4.5.3 [19]. Two of the obtained PIXE spectra are shown in figure 2 for the airborne particulate matter PM2,5 and in figure 3 for PM2,5-10.

Results and Discussion

The basis of the present work is the elemental mass concentrations of 144 aerosol samples (fine and coarse) analysed by PIXE. The PIXE analysis permitted to identified and to quantify the elemental content of the airborne particulate matter (APM) deposited on the filter and revealed consistently the presence of the following 14 elements: S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br and Pb; in both particle size fractions. A summary of the elemental concentrations for the PM2,5 and PM2,5-10 particles is presented in table 1. The table allows an easy comparison of the results obtained for each particle size fraction. The information presented shows the MDL of the system for each element, the number of appearan-ces of each element above the MDL (n) and the mini-mum, maximum, mean and stan-dard deviation values reached by each element. As can be seen from the values showed in the table 1, remarkable differences are observed between fine and coarse components.

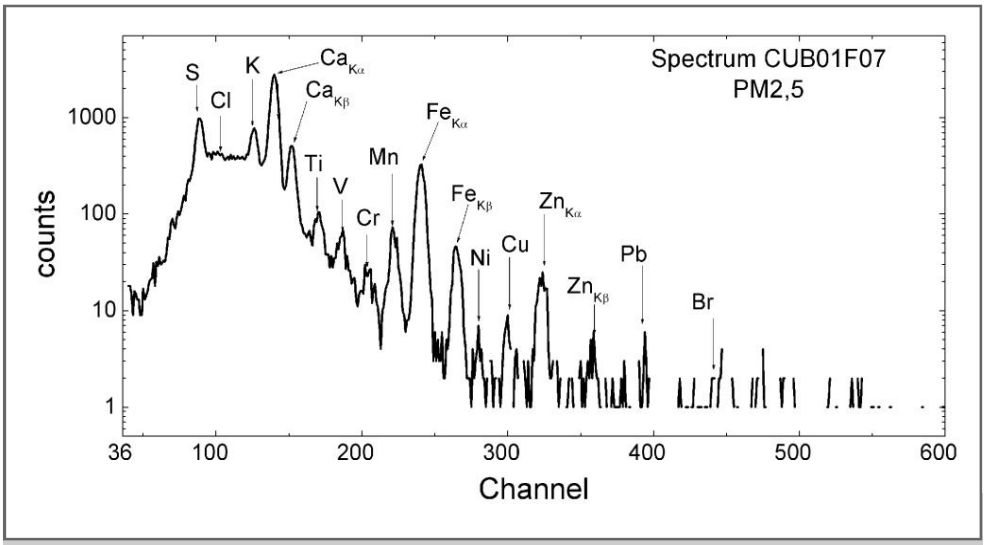

Figure 2. Representative PIXE spectra of the fine airborne particulate matter collected in the sampling site.

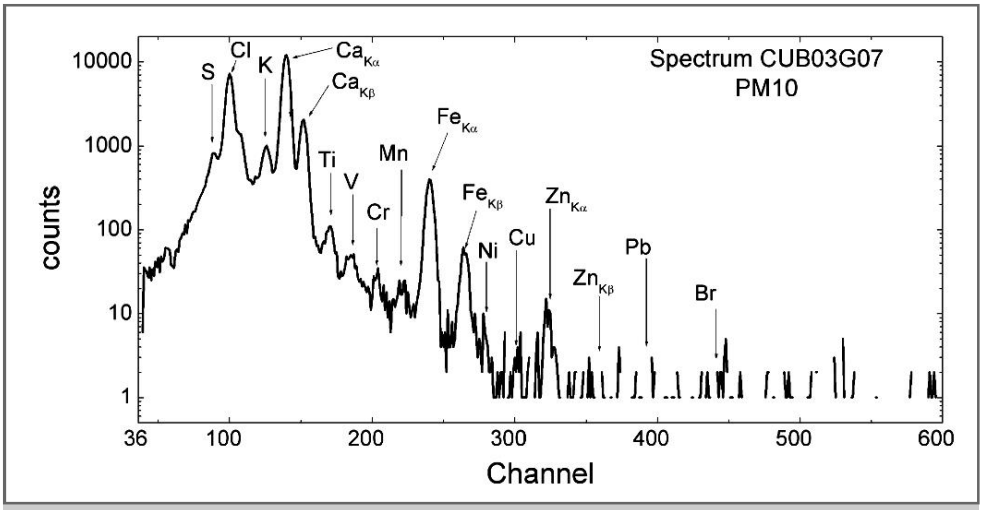

Figure 3. Representative PIXE spectra of the coarse airborne particulate matter collected in the sampling site.

The fine particle fraction shows significantly higher concentrations of S, than the coarse fraction and significantly lower values for K, Ca, Ti, while the coarse fraction has higher contents of Cl than the fine one and soil dust related elements, such as Ca, K, and Fe, dominate the elemental mass. Pb was found not in all samples above the MDL, but it was found in both the fine and coarse modes in significant quantities. Higher values of V, Cr, Ni, and Zn were observed too in the fine fraction, bromine concentration was found apparently uniform in both fractions.

Some elements (like S, V, Ni, Zn, Br and Pb) are

Table. Average, maximum and minimum concentrations and standard deviation σ for the detected elements. MDL is included. All data are referred to elements that were found above the MDL

Element (MDL)	Fine Particulate					Coarse Particulate				
	Mean (ng/m^3)	Max (ng/m^3)	Min (ng/m^3)	σ (ng/m^3)	n	Mean (ng/m^3)	Max (ng/m^3)	Min (ng/m^3)	σ (ng/m^3)	n
S (28.50)	658.83	1711.14	121.68	43.33	68	429.03	1178.91	91.46	28.92	71
Cl (11.60)	65.77	315.37	11.78	4.05	63	1835.54	4108.18	38.51	123.73	71
K (4.40)	42.98	209.80	5.82	2.89	68	117.36	252.72	31.40	7.91	71
Ca (2.80)	110.62	515.40	37.42	7.65	68	2029.86	4763.29	312.31	136.83	71
Ti (2.03)	5.02	26.32	2.08	0.20	32	22.08	115.08	3.03	1.49	71
V (1.88)	21.71	115.35	0.17	1.35	63	13.55	56.99	1.91	0.85	66
Cr (1.38)	3.05	12.15	1.47	0.18	55	2.89	7.08	1.39	0.18	62
Mn (0.87)	10.48	131.54	0.87	0.43	41	10.54	146.74	1.08	0.70	70
Fe (0.88)	60.75	655.98	15.52	3.96	67	235.49	852.97	27.39	15.65	70
Ni (0.95)	4.72	21.65	0.99	0.26	55	3.72	11.85	0.96	0.24	66
Cu (1.00)	2.43	10.49	1.01	0.14	53	3.78	11.64	1.02	0.25	70
Zn (1.20)	18.99	293.11	1.20	1.26	68	18.35	86.26	1.78	1.24	71
Br (5.30)	9.09	13.67	5.43	0.56	60	7.14	11.74	5.41	0.32	24
Pb (4.70)	10.59	55.63	4.77	0.43	35	10.45	39.79	4.82	0.53	48

considered element of anthropogenic origin and are present mainly in the fine fraction. Other elements (like K, Ca, Ti, Fe, and Cl) are considered element of natural origin and appeared mainly in the coarse fraction. These tendencies correspond to the chemical characteristics of atmospheric aerosols [20].

According to the sampling site, the elements detected in these particles by the PIXE analysis can be associated to diverse emission sources, such are the cases of S, V and Pb, representing the fossil fuel combustion group from industrial and motor vehicles. The metal group formed by Cr, Mn, Ni, Cu and Zn can be associated to metallurgic industry and K, Ca, Ti and Fe are soil derived elements or road dust related elements. Our sampling site is located nearby important roads of the city. We assumed that the Cl found in coarse fraction is coming from the marine aerosol, but it should be careful treated, because the Na is an important component of that source and in our case it was not detected in the elemental composition of aerosol samples by this technique, due to specific limitations related with the used PIXE installation at ININ. The mean total seawater ratios for Cl/Na are well known [21], then, is our great interest to know the Na content in our samples, for what we need to analyze them by another technique that ensure the detection and quantiûcation of this element. Some work is in progress in this direction. In some articles in the literature Br is reported as a vehicular component [22] and in other studies appeared associated to the incineration of certain materials [23].

Sulphate particle is an important component of the aerosol in this area, mainly originating from gas to particle conversion from SO_2. S is considered an anthropogenic element, which is most likely present in the fine aerosol. Sulphur was present in all samples in concentrations ranging from 121 ng/m^3 to 1712 ng/m^3 of air sampled, however appeared significantly higher in the fine fraction of aerosol.

The elemental concentrations determined by the PIXE analysis were used to analyse the temporal variations of each element. The concentrations in the complete collection period are shown in figure 4 for S in fine mode and in figure 5 for Cl in coarse one.

In the temporal variation of the PM2,5 and PM2,5-10 mass concentrations showed in figure 1, the peaks of particulate concentrations coinciding with the periods of changes in the weather conditions, when dispersion of the contaminants is more difficult, i.e. entrance of a cold front with temperature decreasing and high pressure. High concentration for some elements, as the S in fine mode and Cl in coarse mode were also observed in these days (see figure 4 and figure 5).

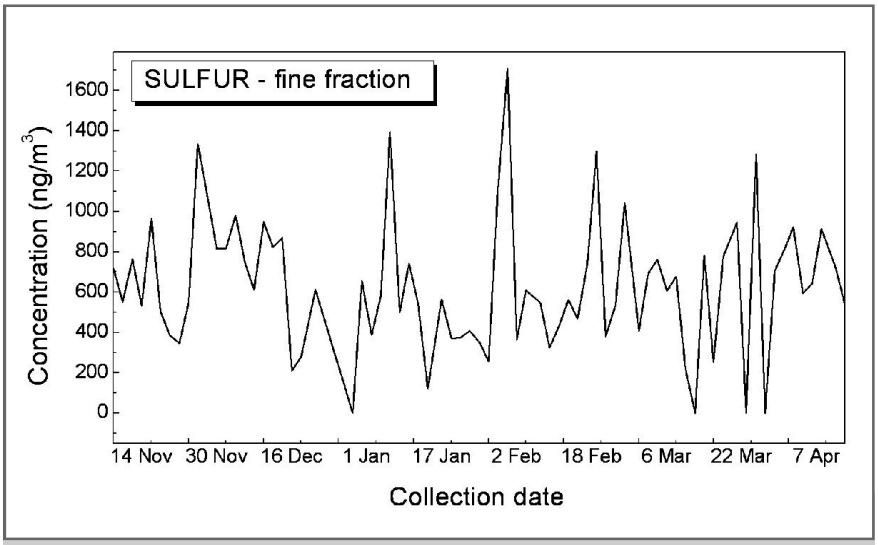

Figure 4. Temporal variations of S concentrations in fine atmospheric aerosol in the whole period of sampling.

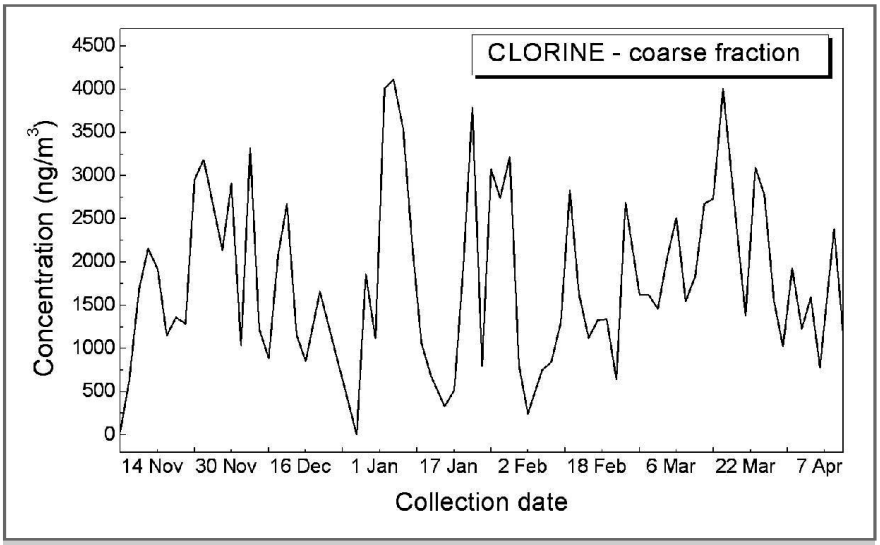

Figure 5. Temporal variations of Cl concentrations in coarse atmospheric aerosol in the whole period of sampling.

Conclusions

The results obtained in this work represent a first effort to evaluate the elemental composition in the airborne particulate matter (fine and coarse) in an urban area, heavily populated, of the Havana City with the use of nuclear analytical techniques.

A total of 144 aerosol samples were collected (72 correspond to the fine mass fraction and 72 to the coarse mass fraction). PIXE analysis revealed the detection of 14 elements (S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br and Pb) in both particle size fractions. Toxic elements (like S, V, Ni, Zn, Br and Pb) were observed with higher concentrations in the PM2,5 fine mode and are mainly considered element of anthropogenic origin, aspect that should be considered in the impact and health studies that are carried out in this place. Those elements that are considered from natural origin (like K, Ca, Ti, Fe, and Cl) appeared mainly in the coarse fraction.

PIXE has showed that is a suitable technique for the analysis of atmospheric aerosol and particularly for the fast and routine analysis of aerosol particulates collected on filters. It is a technique highly sensitive and multielemental, no sample preparations is required, analyses can be automated and carried out in few minutes, the low detection limits allow particle fractions to be observed and the sample is not destroyed, allowing further characterization using other techniques in the same filter. By means of PIXE, it is possible to measure a sample of few micrograms in a few minutes reaching MDL's in the order of ng/m^3 for most of the elements (Z>11).

These results obtained by the PIXE analysis have revealed important information about elemental composition of airborne particulate matter PM2,5 and PM2,5-10 from sampled area, and especially about the inhalable fine fraction, from which didn't exist any information. It is important to notice that with this technique was possible to measure significant elements in environmental and health related studies like S and Pb, which are difficult to detect and evaluate using other techniques.

Furthermore, the elemental database obtained from the PIXE analysis combined with gas measurements and statistical analysis will allow extracting a first idea of the pollution sources of the area under study, but much more work is required. It is necessary to get much more information, for example, if it is possible to sampling over a longer time (1 year), giving the possibility of study the elemental seasonal variations in a whole year, also to be able to correlate those profiles with meteorological varia-

bles and with larger amounts of samples get better statistically results.Furthermore, the analysis can be complemented on the same samples with other physics and chemical analytical techniques, as the ion beam analysis techniques for detection of light elements, ion chromatography for cation (Na^+, Mg^+, K^+, NH_4^+) and anion (Cl^-, SO_4^-, NO_3^-) species, reflectance technique for black carbon concentration, and gas chromatography – mass spectrometer for organic compound characterization.

All this will allow obtaining a complete scheme about atmospheric pollution in the area, allowing to understand how it is affecting life of people in the cities densely populated and in order to establish air pollution control and reduction programs.

Acknowledgements

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