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Aerosol composition from Tlaxcoapan, Hidalgo in central Mexico

M.A. Martínez-Carrillo, C. Solís, and E. Andrade
Instituto de Física, Universidad Nacional Autónoma de México,
Apartado Postal 20-364 México D.F., 01000, México.

K. Isaac-Olivé
Facultad de Medicina, Universidad Autónoma del Estado de México,
Paseo Tollocán s/n, esq. Jesús Carranza, Toluca, Estado de México, 50120, México

R.I. Beltrán-Hernández
Universidad Autónoma del Estado de Hidalgo, Centro de Investigaciones Químicas,
Carretera Pachuca-Tulancingo km. 4.5. 42174. Pachuca, Hgo., México.

S.A. Medina Moreno, G. Martínez-Resendiz, A. Ramírez Reyes, and C.A. Lucho-Constantino
Universidad Politécnica de Pachuca, programa de Ingeniería en Biotecnología,
Carretera Pachuca-Cd. Sahagún Km. 20. Hidalgo, México.

L.M. Del Razo
Sección Externa de Toxicología, Centro de Investigación y de Estudios Avanzados
del Instituto Politécnico Nacional, México.

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Air quality mexican regulations about atmospheric aerosols refer to particle sizes and to the total suspended particle. None of these norms establishes the allowed values based on the particulate chemical composition. Mexican environmental legislation also considers as critical zones those with high concentration of contaminants in the atmosphere. One of these zones is the Tula-Vito-Apasco corridor where no chemical composition characterization in terms of trace metal associated to the air particulate matter has been made. Along this corridor near Tlaxcoapan there are important contaminant sources as petrochemical and electric power plants, metal-mechanical industry, limestone quarry and contaminated soils. In this work PIXE and SEM-EDS were applied to the PM_{10} fraction collected on filters. The trace element values thus determined were compared with those of a similar critical zone. It was found that most of the coarse particles come from limestone quarry as fugitive dusts while V, Ni, Cr and Pb values are moderately high and seems to be associated to industrial activities and contaminated soil as well.

Keywords: PIXE; atmospheric aerosols; trace metals; Mexico.

En México, las leyes que regulan la calidad del aire solo están referidas al tamaño de partícula y al número total de partículas suspendidas. Ninguna de estas normas ha establecido los valores permitidos para el caso de la composición química de estas partículas. Además, la legislación ambiental mexicana, considera como zona crítica aquellas zonas con altas concentraciones de contaminantes en la atmósfera. El corredor Tula-Vito-Apasco, es una de estas zonas, y hasta el momento no hay una caracterización de la composición química en términos de metales trazas asociados al material particulado. Tlaxcoapan, perteneciente a este corredor, es un pueblo que tiene cerca importantes fuentes de contaminación como: una planta petroquímica y de producción eléctrica; una industria metal mecánica, extracción de cal y suelos contaminados. En este trabajo, PIXE y SEM-EDS se utilizaron en el estudio y caracterización de la fracción PM_{10} colectada en filtros. Los valores de elementos traza se compararon con los de zonas críticas similares. Como resultado, se encontró que las partículas cercanas a 10 μm, son polvos fugitivos provenientes de las minas de cal. Los valores de V, Ni, Cr y Pb son moderadamente altos y están asociados a la actividad industrial y probablemente a los suelos contaminados.

Descriptores: PIXE; aerosoles atmosféricos; metales traza; México.

PACS: 78.70; 34.50; 79.20.Rf; 32.30; 07.88.+y

1. Introduction

The presence of particulate matter in air is one of the major issues concerning public and environmental health in the world since they can be deeply inhaled into the lungs, causing several health problems. Metals contained in these particles may increase the risk [1]. Population health-protection norms, in terms of air quality, are NOM-025-SSA1-1993 and NOM-024-SSA1-1993 [2,3]. The first evaluates air quality referred specifically to particle sizes. The two following criteria are: size particles equal to or smaller than 10 microns (PM_{10}) and size equal to or smaller than 2.5 microns ($PM_{2.5}$). The last norm mentioned does not regulate particle size; instead it considers the total suspended particles allowed in air as a whole. None of these norms has established the allowed values based on the particle's chemical composition. This means, that norms do not take into account that suspended particles in the air may or may not contain heavy and/or toxic metals. One reason could be the lack of studies on the ratio between human health effect and the particle's chemical composition, with the exception of those achieved for Pb. [4,5].

Mexico City, Monterrey and Guadalajara metropolitan areas have been considered as Critical Zones (CZ) by Mexican environmental legislation according to NOM-043-ECOL-1993 and NOM-085-SEMARNAT-1994 norms [6, 7]. A zone with high concentration of contaminants in the atmosphere is considered a CZ. Other places considered as CZ, although smaller than those previously mentioned, are: Coatzacoalcos-Minatitlán, Veracruz; Irapuato-Celaya-Salamanca, Guanajuato; Tula-Vito-Apasco, in Hidalgo and Estado de México states; Tampico-Madero-Altamira, Tamaulipas Industrial Corridor; and Tijuana, Baja California and Ciudad Juárez municipalities in Chihuahua.

From the previous CZ, studies of the negative effects in human health due to the atmospheric contamination have been carried out only in highly dense populated and industrial areas such as Mexico City [8,9], Monterrey and Guadalajara metropolitan zone. From the rest, chemical characterization of particulate matter has been published for Irapuato-Celaya-Salamanca [10], and Tampico-Madero-Altamira [11] zones.

Another CZ, is the Tula-Vito-Apasco corridor with several towns with population not exceeding 20 000 inh. Industrial activities in this corridor include petrochemical industry, lime and cement production, electricity generation, food processing, transformation industries and assembly plants among others. Large amounts of pollutants present in the atmosphere, such as suspended particulate matter (SPM), SO_2, CO_2, NOx, are routinely monitored in Tula and other nearby towns by a network of air quality stations (COEDE 2000, 2002, 2006). However scarce data are available about elements present in atmospheric aerosols.

It is important to have a complete study that includes not only the criterion polluting agents monitored by the State Council of Ecology, Hidalgo (COEDE), but also a characterization of the trace elements present in the particulate matter emitted in this region as resulting from the industrial activity, the possible re-suspension of dust with heavy metals from cropland irrigated with residual water [12] and fugitive dust coming from the operation of lime mines to open sky, the cement production activity present in the region and the circulation of vehicles.

Although major and trace elements in aerosols can be determined by conventional techniques such as Atomic Emission Spectrometry (AES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), graphite furnace atomic absorption (GFAA or dispersive X-ray fluorescence (EDXRF), etc., high sensitivity and non destructiveness of nuclear techniques make them very suitable to study air particulate matter trace element content. Particle induced X-ray emission (PIXE) in particular, does not require any chemical agent that could interfere in the analysis and no harmful or radioactive residues are generated in the process, which makes this technique environmentally friendly. PM_{10} multielemental composition can be employed as a fingerprint from a particular location because of its short residence time and travel distance. Therefore in order to characterize a zone, a morphological and chemical composition of single particulate in the coarse fraction should be included.

The aim of this work was to determine trace metals composition and levels as well as the morphology and internal composition of particulate matter present in Tlaxcoapan, Hidalgo, a small agricultural town (20,000 inh) surrounded by multiple polluting sources, located along the Tula-Vito-Apasco corridor, a CZ not studied yet. Coarse PM_{10} aerosols were collected in polycarbonate filters and exposed every third day for 24 hours, from June to December 2007 (rainy season and beginning of dry season. PIXE was applied to detect trace elements in airborne particulate matter. Electron microscopy was performed to characterize particulate matter morphology as well as internal composition.

2. Material and methods

2.1. Sampling site

Tlaxcoapan, (N 20° 05.509', WO 99° 13. 671') (Fig. 1), is a small agricultural town (20,000 inh) located in the CZ of the Tula Vito Apasco corridor. In a radius less than 10 Km, industrial activities such as petrochemistry, limestone extraction and cement production, electricity generation, food processing, metal mechanics among others, take place. Large amounts of pollutants present in the atmosphere, such as suspended particulate matter (SPM), SO_2, CO_2, NO_X, are routinely monitored in Tula and other nearby towns by a network of air quality stations (COEDE 2000, 2002, 2006). Tlaxcoapan also belongs to the Mezquital Valley, an area that has been a matter of intense research because of the presence of toxic metals and other contaminants introduced by irrigation with wastewater from Mexico City.

2.2. Sampling

The particulate matter (PM_{10}) was collected from June to December 2007. Suspended particulate matter was collected by passing air through weighted Nucleopore membrane filters (47 mm in diameter, 0.4 μm pore size). The collection was performed during 24-hr periods using a low-volume air sampler (Minivol, Airmetrics) at flow rate of 5 L min^{-1}, according to the IO-2.1 and IO-3.1 methods (modified by USEPA, 1999). The equipment was calibrated with a temporizer Airmetric at 5 $Lmin^{-1}$ before each sampling. A total of 41 filters were collected. The sampler was mounted 8 m above the ground so that only local airborne particulates would be collected. PM_{10} was determined by gravimetry using a microbalance Ohaus-GA 2000. Filters were stabilized for 48 hrs. A ^{210}Po alpha source ("Staticmaster" model IC200R), was used to suppress the electrostatic charge of the filters.

2.3. PIXE analysis

The elements contained in the sample as well as their concentrations can be determined from X-Ray spectrum produced by the deexcitation of atoms in the sample. Elements present in the filters PM_{10}fraction were analyzed by PIXE. This analysis was carried out using the Pelletron NEC 9SDH accelerator from the Instituto de Física at the Universidad Nacional Autonóma de México, (UNAM). Samples were irradiated in a vacuum chamber using a 2.4 MeV proton beam of 0.3 cm^2 under a current of 5 nA,. Spectra were collected until an accumulative charge of 4 μC. The X-rays emitted by the sample were collected with a LEGe germanium Canberra detector. The detector was placed at 5 cm from the sample and 45° from the proton beam as it has been previously described [13]. An Al filter of 38 μm thick was placed in front of the detector to reduce light elements signal. The detection system was calibrated using Micromatter films (Deer Harbor, WA, the USA) for thin targets. PIXE spectra fit and concentration calculations were carried out using the GUPIX software package [14,15].

2.3.1. PIXE analysis external quality assurance

Assessment of the accuracy and precision of the PIXE method was carried out using the certified reference material NIST-SRM 2783 “Air particulate on filter media”. Reference material was analyzed under identical conditions as the samples. The result of this analysis reveals the accuracy and precision of the PIXE method employed.

2.4. SEM-EDS

Scanning Electron Microscopy coupled to Energy Dispersion Spectroscopy (SEM-EDS) is one of the techniques that can be employed in order to study the morphology of the collected dust. This analysis, among others, allows establishing the particulate matter sources. It was performed using the Jeol scanning microscope JSM 5600 LV (Jeol-USA. Inc, Peabody, MA) and a energy dispersive Si(Li) detector (resolution of 144 eV in 20 ms). An acceleration voltage of 20 keV was applied and the sample was located at 15 mm working distance. X-ray data for each filter were corrected by taking into account the analysis of a blank filter. A sample of 1 cm^2 portion from each filter was cut and mounted with a graphite tape on a glass sample holder. SEM-EDS was carried out on single particles of the largest sizes (close to 10 μm) randomly chosen in each filter.

TABLE I. Analysis by PIXE of a thin film containing certified aerosols (NIST-SRM 2783). PIXE values are the average of 3 samples (SD).

Element	**Certified Value** (ng/cm^2)	**PIXE value** (ng/cm^2)
Si	5883 (161)	6158 (360)
S	105 (26)	121 (22)
K	530 (52)	535 (23)
Ca	1325 (171)	1350 (170)
Ti	150 (24)	146 (34)
V	5 (0.6)	7.1 (2)
Cr	13.6 (2.5)	12.3 (3)
Mn	32 (1.2)	29.2 (4)
Fe	2660 (161)	2649 (53)
Ni	6.8 (1.2)	7.4 (1.9)
Cu	41 (4.2)	41.2 (7.8)
Zn	180 (13.1)	186.7 (24.5)
Pb	31.7 (5.4)	46.3 (11)

TABLE II. Atmospheric concentrations (ng/m^3) in Tlaxcoapan, Hidalgo and those reported for Altamira and Tampico Tamaulipas, for the coarse fraction (PM_{10}). In parenthesis: (SD/n $^{1/2}$).

Element	Tlaxcoapan	Tampico	Altamira	Maximum limit
n	36	na	na	na
μg/m^3				
Mass	45 (6)	23.4	52.4	120^a
Si	3.04 (0.2)			
S	2.1 (0.2)			
K	0.4 (0.04)			
Ca	4.93 (0.94)			
ng/ m^3			na	
Ti	50 (4)	15	100	
V	42 (12)	10	30	
Cr	12 (2)	1.5	4.5	
Mn	15 (2)	100	75	1000^a
Fe	511 (35)	288	700	32000^a
Ni	13 (1)	2.5	1.0	25^a
Cu	12 (1)	20	40	600^a
Zn	17 (2)	40	200	
Pb	25 (2)	1.8	4	200^a

^{a}NOM-025 ^{c}OMS

3. Results

3.1. PIXE analysis

Figure 1 shows a typical PIXE spectrum of an analyzed filter. As expected, heavy metals are very well detected; their X-ray peaks are well resolved allowing the simultaneous quantification of the elements. In general the sensitivity is quite good, for some elements excellent. Nuclear techniques, such as PIXE, can improve the sensitivity value of the analysis in various ways; one of them is increasing the irradiation time. This fact also helps to lower the detection limit of the analyzed elements. This is one of the many advantages that PIXE has in the analysis of particulate matter.

This technique is also recognized by its accuracy. The results of the external quality assurance when the PIXE method is applied to the reference material (NIST-SRM 2783) are shown in Table I.

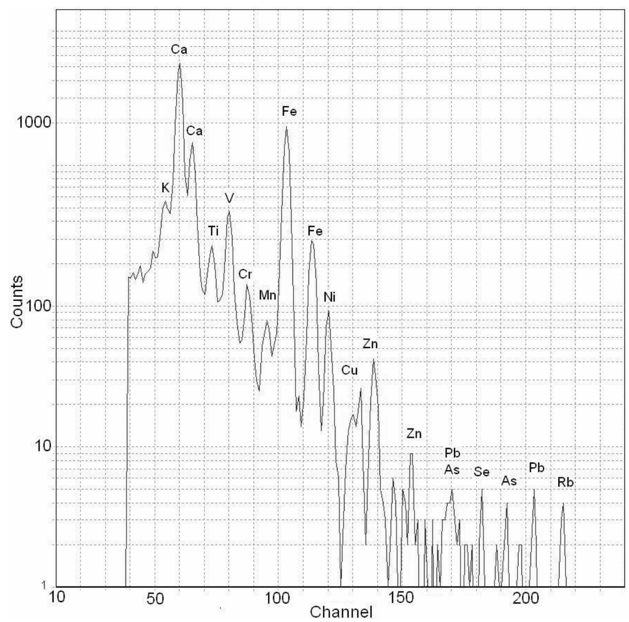

FIGURE 1. Typical PIXE spectrum of particulate matter from Tlaxcoapan.

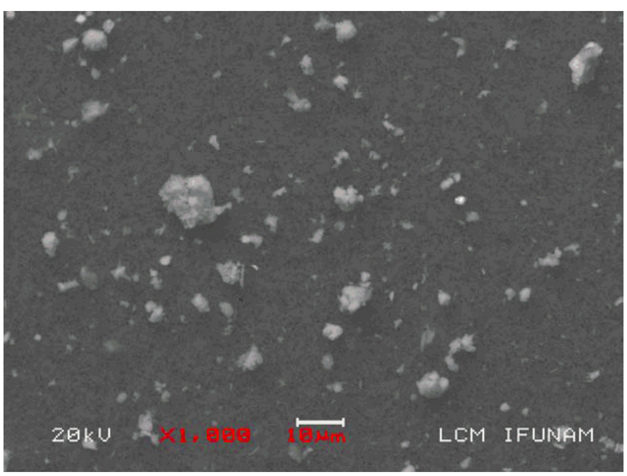

FIGURE 2. SEM microphotograph (magnification X1000) of particulate matter on a filter of Tlaxcoapan.

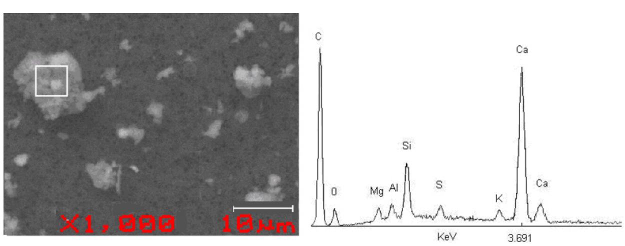

FIGURE 3. SEM microphotograph (magnification X1000) and corresponding EDS spectrum of a particle of mineral dust (in the square) composed by C, O, Mg, Al, Si, Ca. showing high content of Ca.

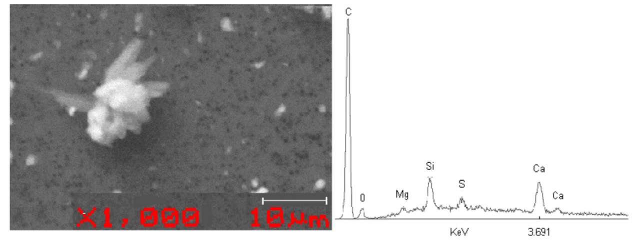

FIGURE 4. SEM microphotograph (magnification X100) and corresponding EDS spectrum of an irregular particle composed by C, O, Mg, Si, S and Ca.

An evidence of the reliability of the calibration performed on the PIXE detection system using GUPIX, as well as in the PIXE method employed, is the closeness of the experimental and certified values obtained and reported in the Table I. As expected, PIXE shows excellent accuracy and precision for analyzed metals. One more time, this accuracy and precision can be improved using longer irradiation times.

Table II shows the average chemical composition value found in Tlaxcoapan for those elements determined reliably. In the same table are also presented the reported value for a similar study carried out in Altamira and Tampico, Tamaulipas.

Altamira and Tampico are zones affected by the influence of a relatively close petrochemistry plant, where chemical composition of particulate matter has been studied. In Tula, a city placed 7 Km far from Tlaxcoapan, there is also a petrochemistry plant. The similarity among these places is the reason to compare chemical composition obtained in this work with that for Altamira and Tampico previously reported.

The PM_{10} mass values from Tlaxcoapan are similar to Altamira's and Tampico's average. The Mn and Zn values found in Tlaxcoapan are lower than those from the other places. The level of Fe is between the Altamira and Tampico's values, while Cu is at the level of Tampico's but lower than that from Altamira. Vanadium, Ni, Cr and Pb values are high in comparison to those from the other sites. This result is not surprising for V and Ni due to the closeness of the petrochemistry plant from Tula. Besides, Tula also has an electric power plant which is another source of both metals. In the case of Cr, its high level can also be attributed to the metal- mechanical industry that is also present near Tlaxcoapan. Regarding Pb, Tlaxcoapan belongs to the Mezquital Valley, an area well known by its high level of heavy metal in the soil due to the irrigation with waste water [16]. This may explain the high level of Pb, although it is still 10 times lower than the permissible value. More research is needed in order to find out what is the enrichment factor of this element in the filter before concluding that is coming from contaminated soil. Perhaps, there is another source of lead affecting Tlaxcoapan that it has not been taken into account yet. A more meticulous study of the area is necessary in order to detect all the contaminant sources.

3.2. SEM-EDS analysis

Particulate matter in the atmosphere is composed of highly soluble inorganic salts, insoluble mineral dust and carbonaceous material. The insoluble inorganic fraction, the less studied of them generally consist of metal oxides, silicates, aluminosilicate and clay minerals derived from soil dust. Figure 2 shows the SEM-EDS microphotograph at X1000 magnification of a representative filter of Tlaxcoapan. The microphotograph exhibits an abundant number of particles in the PM_{10} fraction. When individual particles close to 10 μm were analyzed (Fig. 3 and 4) it was found in the EDS spectrum the presence of C, O, Mg, Al, Si, and Ca. From this elemental composition and morphology it can be said that these particles are mineral dust. For some particles all these elements were present while for others just some of them; this indicates that some particles are in fact a mixture of substances.

A close analysis of the EDS spectra reveals a high concentration of Ca along with the presence of O, Mg and Si. This is very characteristic of fugitive dusts from limestone quarries [17]. In this particular case the composition may be associated to the fugitive dusts from a limestone quarry located approximately 10 km south of the monitoring site. Since Tlaxcoapan, as it has been explained before, is very close to a petrochemical and a power energy plants it is not surprising then, the presence of S in the EDS spectra of the particle of about 10 μm size. Sulphur is a typical tracer of the refinery and power energy plant emissions.

4. Conclusions

The application of the nuclear techniques, in this case PIXE in combination with SEM-EDS analysis allowed the determination of air particulate matter chemical composition in Tlaxcoapan, a town close to important air contaminant sources, placed in the Mezquital Valley and in the Tula-Vito-Apasco industrial corridor. This corridor is one of the CZ according to the Mexican environmental legislation and this work is the first attempt to characterize the trace element content associated to the PM_{10} fraction. According to EDS analysis and the microphotographs taken by SEM the particles close to 10 μm in the PM_{10} fraction are associated to fugitive dust coming from a near (10 km) limestone quarry. The region has high values of V, Ni, Cr and Pb in comparison with others similar CZ. It is known that V and Ni are associated to the refinery and electric power plant emissions. Cr is present probably due to the metal-mechanic industry activities and Pb may come from the contaminated soils of the Mezquital Valley, although more research is needed in order to determine all the contaminant sources.

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