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Scanning electron microscope and statistical analysis of suspended heavy metal particles in San Luis Potosi, Mexico

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Abstract

Three hundred samples of urban aerosol were collected in high-volume samplers from five urban locations situated near an important metallurgical plant in the city of San Luis Potosi, Mexico. Whole samples were analyzed by atomic absorption (AA) for Pb, Cd, As, Cu, Ni, Fe and Cr. One hundred eighty of these samples were subjected to X-ray microanalysis (EDS) coupled with a scanning electron microscope to classify individual particles according to their chemical or mineralogical composition.

The principal component analysis (PCA) obtained from the bulk sample analysis, and X-ray microanalysis from individual particles, confirmed chemical associations among elements directly and indirectly. PCA from bulk assays made the most effective use of X-ray microanalysis to characterize major particle types. Some chemical associations would be difficult to detect using microanalysis, alone, for example, in anthropogenic complex phases. In this work, the combined use of microanalysis and statistical methods permitted identification of associations among elements. We observed an association of Pb–As–Cd and Fe–Mn among the samples. In a second order, Pb–Fe, Pb–Mn, Fe–As, Fe–Cd, Cd–Mn and As–Mn showed a lower association. Only Ni and Cu appeared unassociated with any other element analyzed by AA. We characterized the mineral phases by size range, morphology and chemical composition using SEM-EDS to obtain a compositional approach of anthropogenic phases and peculiar morphology and size. A high percentage of heavy metal particles smaller than 2 μm were detected. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Atmospheric aerosol; Single-particle analysis; Electron microprobe; Principal component analysis; Size distributions; Metallurgy

1. Introduction

The city of San Luis Potosi, Mexico has a long tradition of metallurgic activity. At the beginning of the 20th century what was to become the nation's most important copper refinery was installed in the area. Sulfide mineral concentrates from the rest of the country were sent to this

refinery. In 1982 a zinc refinery, currently the most productive in the country and one of the most important in Latin America, was established in this city. San Luis Potosí also has significant steelworks industry and manufacturing activity.

Anthropogenic emissions of particulate matter seems to contribute to air pollution in the city. Air quality studies from different areas of the city carried out between 1984 and 1994, revealed that the atmospheric air contained a high level of suspended particulate matter (Luszczewski et al., 1988; Medellín and Hernández, 1988; Aragón et al., 1996). In a previous work, the annual mean concentrations were determined for $\text{TPS} = 167.7 \mu\text{g m}^{-3}$,

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Cu = $1.81 \mu\text{g m}^{-3}$, As = $0.88 \mu\text{g m}^{-3}$, Pb = $0.68 \mu\text{g m}^{-3}$, Cd = $0.03 \mu\text{g m}^{-3}$ (Monsivais and Flores, 1995). These values exceeded World Health Organization (WHO) recommendations (TPS = $90 \mu\text{g m}^{-3}$, Cu = $0.6 \mu\text{g m}^{-3}$, As = $0.01 \mu\text{g m}^{-3}$, Pb = $0.2 \mu\text{g m}^{-3}$, Cd = $0.01 \mu\text{g m}^{-3}$). Public health studies carried out in the city revealed a high number of respiratory diseases, dermal problems and arterial hypertension cases that could be associated with the heavy metal particulate air pollution (Batres et al., 1993).

The main aim of this work was to characterize the heavy metal particles suspended in the air of San Luis Potosi city in order to propose a classification based on their chemical composition, morphology and size. A further work on air pollution sources could then differentiate the contribution of each source on the air pollution of San Luis Potosi.

To develop this work, we analyzed the composition of heavy metal particles in the city's urban aerosol from samples collected in 1994. These samples were available from a previous research work carried out to identify the pollution levels in San Luis Potosi city (Monsivais and Flores, 1995).

2. Methods

Three hundred samples of airborne particles, were collected in 1994 using high-vol samplers. Each sampler consisted of a heavy-duty rotary pump and a fiberglass filter with a collection efficiency of 99% for particles of diameter $> 0.3 \mu\text{m}$ (most of them in the PM10 range). These samplers filtered approximately $1.4 \text{ m}^3 \text{ min}^{-1}$ of air and ran continuously for 24 h for each sample. This involved a 24-h acclimatization period for the fiberglass filter for each sample, before and after sampling (25°C and $< 50\%$ relative humidity). The samplers were placed in five urban locations situated within 10–15 km from the zinc and copper refineries (Fig. 1). One hundred eighty samples were then obtained for the microscopic study.

In a previous work, elemental analyses (Pb, As, Cu, Fe, Ni and Cd) of airborne samples were obtained by atomic absorption spectroscopy (Monsivais and Flores, 1995). The analyses were performed with a Varian AA spectrophotometer, model Spectro AA-20 (Melbourne, Australia). The AA analysis involved a previous sample acid dissolution step with a mixture of nitric (85%) and perchloric (15%) acid prior to analysis. Blanks were also prepared with this mixture. The limit detection for AA analyses is $0.1 \mu\text{g g}^{-1}$.

Factor analysis was then performed from the results of these chemical analyses using a Statview SE + Graphics TM software (Abacus Concepts, Inc., USA). A VARIMAX rotation was used in the factor analysis calculation. Previous works had reported a similar

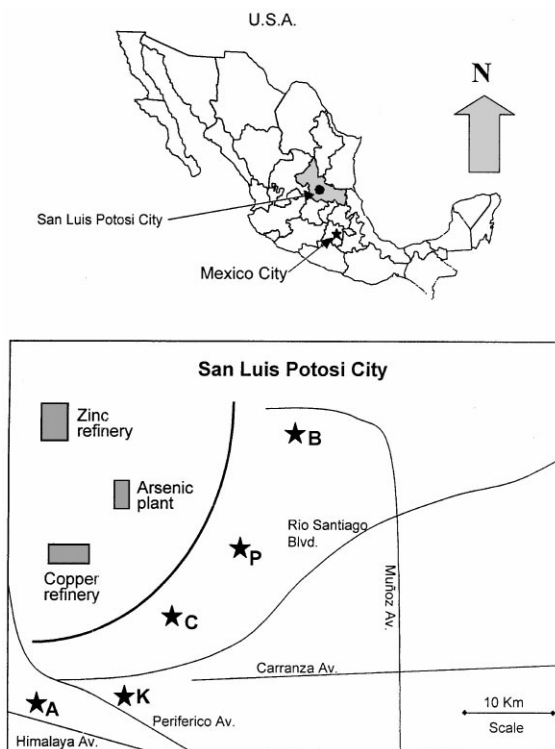


Fig. 1. Location of sampling stations.

methodology to analyze this kind of data (Rojas et al., 1990; Karue et al., 1992).

Particle composition and morphology were determined by combining scanning electron microscopy and electron probe microanalysis (EDS) (Linton et al., 1980; Noll et al., 1987; Post and Buseck, 1985; Bernard and Van Grieken, 1986; Van Born et al., 1987). For that, the particles were resuspended from the filters and the samples were washed with alcohol and dried in an electric oven at 30°C . Then, the particles were redeposited on a carbon tape stuck on the SEM sampler to analyze them by SEM-EDS. Each sample was coated with carbon before SEM observations.

A Leica S420 scanning electron microscope (Cambridge, UK), with 20 keV electron energy, and a 3–5 nA beam current was employed for the analysis. The microscope was equipped with a 30 mm^2 energy dispersive Si(Li) detector Link Oxford Pentafet (Buckinghamshire, UK) for analyses, and secondary and backscattered electron detectors for imaging. An energy dispersive X-ray spectrum (EDS) was collected from each heavy metal particle for a preset time of 100 s. The total X-ray count rate was between 1000 and 2000 counts s^{-1} . Conventional standard ZAF correction was carried out automatically for each particle microanalysis (atomic number, mass absorption and fluorescence). Some confirmatory-

microanalyses were carried out on specific particles using an EDAX DX4 energy dispersive detector coupled to a Philips XL-30 SEM, in order to detect the presence of oxygen in the airborne particles.

Approximately 150 000 particles from the 180 samples were observed by backscattered electron images to identify the heavy metal particles. Chemical compositions of at least 800 particles per sample were obtained from the microanalyses (clay minerals and silica particles at the most). We selected only airborne heavy metal particles using this technique, carrying out a total of 1217 chemical microanalyses. Chemical microanalyses were carried out for each heavy metal particle where the following elements were identified: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Sr, Y, Zr, Ag, Cd, Sn, Sb, Te, Ba, La, Ce, W, Au, Hg, Pb, Bi, Th. The SEM granulometric analysis has taken into account heavy metal particles within seven particle range sizes: < 0.5, 0.5–1, 1–2, 2–5, 5–10, 10–15 and > 15 μm .

3. Results and discussion

3.1. Principal component analysis

The results for the correlation matrix for bulk Pb, As, Cd, Cu, Fe, Ni and Mn analysis in the urban aerosol is shown in Table 1. These results correspond to 2030 bulk chemical analyses performed by means of AA

Table 1
Correlation matrix for elements

	As	Cd	Cu	Fe	Mn	Ni	Pb
As	1						
Cd	0.736	1					
Cu	0.075	0.054	1				
Fe	0.512	0.542	0.043	1			
Mn	0.430	0.504	0.049	0.773	1		
Ni	0.037	0.028	–0.006	0.043	0.042	1	
Pb	0.747	0.740	0.070	0.69	0.577	0.041	1

Table 2
Eigenvalues and explained variance percent distribution

	Before rotation			Variance after rotation %
	Magnitude	Variance %	Cumulative %	
Value 1	3.517	50.2	50.2	63.7
Value 2	1.007	14.4	64.6	18.2
Value 3	0.985	14.1	78.7	18.2
Value 4	0.786	11.3	90.0	0.0

spectroscopy (290 sample analyses for each element obtained during 1994). The correlation matrix shows that Pb–As–Cd and Fe–Mn are associated. At second order, Pb–Fe, Pb–Mn, Fe–As, Fe–Cd, Cd–Mn and As–Mn showed a lower association. We consider that a correlation coefficient greater than 0.70 is significant within 95% of confidence interval. Only Ni and Cu appeared unassociated with any other element, however, this apparent non-association is because of the very small number of elements analyzed by AA. These elementary associations were confirmed by a factor analysis.

The factor analysis was carried out by the principal component analysis (PCA), beginning this by means of calculating magnitude and percentage of variance of eigenvalues attributed to each factor. It was considered to take into account the first three factors considering a percent of variance equal to 78.7%. If we consider the Kaiser–Guttman rule, only the first two factors should be equal to the number of factors having an eigenvalue greater than 1.0. So, it was obtained the matrix corresponding to these factors before any rotation. Then, a VARIMAX orthogonal rotation was carried out, the variance contribution for the first two factors was increased to 81.9% and for the first three factors to 100% (Table 2). The coordinates corresponding to the variables in these three factors were obtained and their representation after rotation is shown in Fig. 2. Fig. 2a shows a clear statistical association among Pb, As, Cd, Fe and Mn, considering factors 1 and 2. The correlation of factors 1 and 3 show a similar statistical association among these elements (Fig. 2b). In both cases, Ni and Cu are independent and did not correlate with any element considered in this analysis.

3.2. Scanning electron microscopy and X-ray microanalysis (SEM-EDS)

Heavy metal particles were classified on the basis of their chemical composition and morphology (Van Born and Adams, 1989; Miggon and Caccia, 1990). Particles rich in lead, copper, iron, arsenic, zinc, tin, barium–strontium, silver, rare earths, titanium, zirconium, manganese,

gold and vanadium–sulfur–nickel were identified within these groups of heavy metal particles. The main chemical associations of these individual particles are shown in Table 3. The morphology of the particles is also described in Table 3, where common mineral shapes were easily distinguished from particular morphologies associated to anthropogenic particles (Fig. 3). The most abundant heavy metal particles are those rich in lead, iron, copper, arsenic and zinc. Their mean compositions are shown in Table 4. It is necessary to note that the chemical compositions reported in Table 4 does not consider the

oxygen concentrations as it was reported in Table 3, because the EDS used in most of the microanalyses did not detect this element. The presence of oxygen was detected in the confirmatory analyses. It is very remarkable that the high standard deviation for most of the elements corresponding to the different phases could be identified in this work, because many of them must correspond to complex phases where the chemical composition is highly variable.

Two types of Pb-rich particles were identified based on their chemical composition and morphology. The most

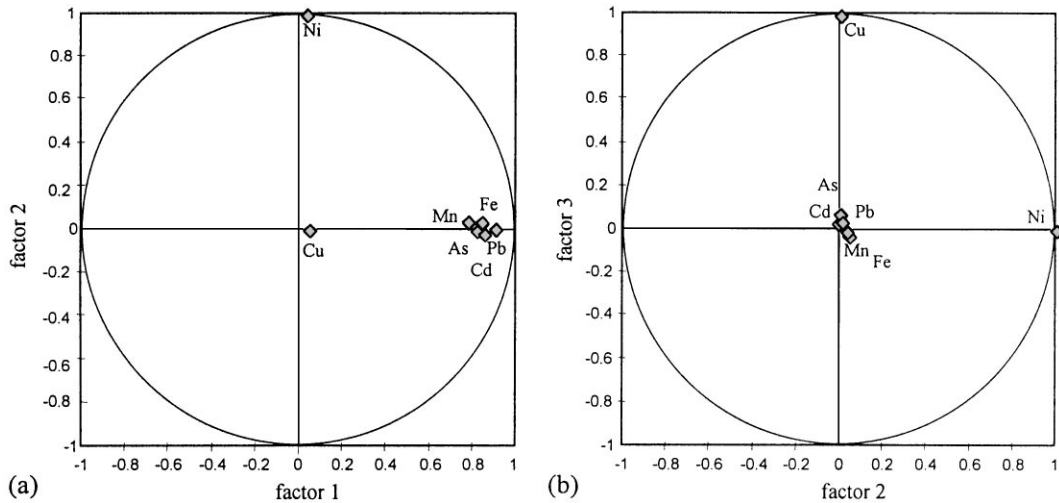


Fig. 2. Graphs for 1 vs. 2 (a) and 2 vs. 3 factors (b) after orthogonal rotation VARIMAX.

Table 3
Classification of heavy metal particles according its composition

Heavy metal association	(%) ^a	Morphology	Attributed phase
Pb, As, Cd, Fe, Zn, Cu, S, O	24.08	Cluster particles	Lead complex phases
Fe, O	15.28	Spherical	Iron oxides
Pb, S	11.67	Common mineral shape	Galena (PbS)
Cu	9.53	Spherical	Metallic copper
As, O	9.45	Octahedral crystals	Arsenite (As ₂ O ₃)
Cu, Fe, S	9.20	Common mineral shape	Chalcopyrite (CuFeS ₂), Bornite (Cu ₅ FeS ₄), Chalcocite (Cu ₂ S), Covellite (CuS)
Zn, S, C, O	6.74	Common mineral shape	Sphalerite (ZnS) Smithsonite (ZnCO ₃)
Fe, S	3.20	Common mineral shape	Pyrrhotite (Fe _{1-x} S), Pyrite (FeS ₂)
Sn, O	2.88	Common mineral shape	Cassiterite (SnO ₂)
Ba, Sr, S, O	2.71	Common mineral shape	Barite (BaSO ₄)
Ti, Fe, O	1.31	Common mineral shape	Ilmenite (FeTiO ₃), Rutile (TiO ₂)
Ni, V, S	0.49	Porous particles	Fossil oil combustion particles
Others associations	3.46	Common mineral shape, rounded particles, irregular forms	Silver, Monazite, Metallic bismuth, gold and antimony, Zircon, Manganese oxides

^aThe percentage was determined by the number of particles.

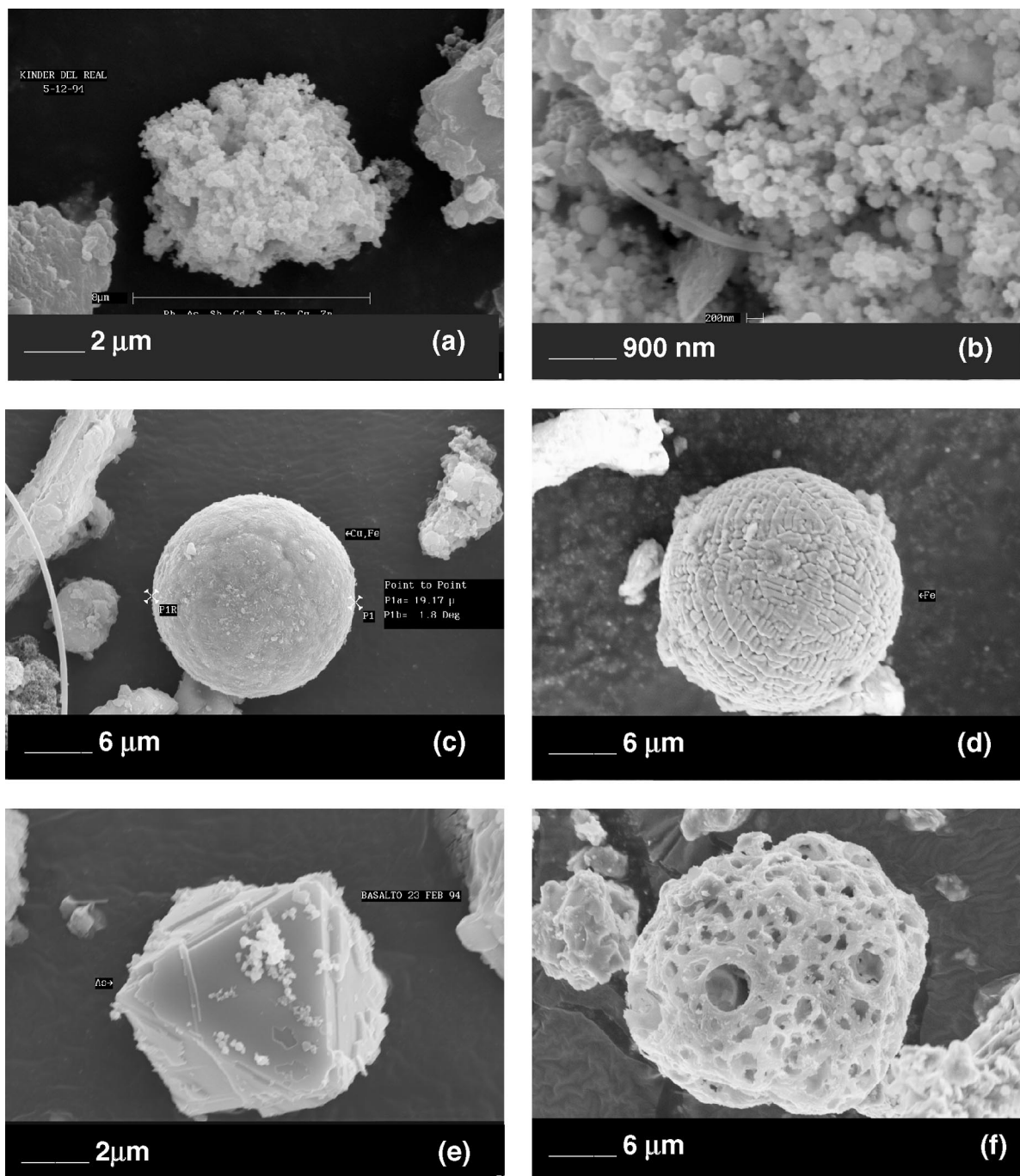


Fig. 3. (a) Pb-rich anthropogenic particle. This type of heavy metal particle is the most abundant in the city's aerosol; (b) details of the Pb-rich anthropogenic phase, that is compound of clusters of small spherical particles; (c) the most abundant types of Cu-rich phases are spherical particles which apparently emanate from a high-temperature furnace; (d) Fe-rich spherical particle apparently emanate from a high temperature furnace; (e) the main As-rich phase is arsenic trioxide (arsenite). Most of the particles are octahedral crystals; (f) nickel was found associated to sulphur and vanadium in porous particles that come from fuel oil combustion.

Table 4

Mean chemical compositions most of the abundant heavy metal particles suspended in the air obtained by SEM-EDS (wt%)

		S	Mn	Fe	Cu	Zn	As	Cd	Sb	Pb	Total
Lead (sulfates) ^a	Average	10.747	0.083	6.851	4.918	7.236	11.575	1.830	3.661	53.099	100
	SD	5.915	1.384	13.611	6.765	6.237	10.212	2.276	7.926	16.709	
Copper (metallic)	Average	0.880	0.003	0.748	93.266	4.558	0.223	0.038		0.285	100
	SD	1.582	0.033	3.418	16.615	11.524	2.259	0.491		1.841	
Iron (oxide) ^a	Average	1.632	1.428	90.121	1.378	3.698	0.506	0.005	0.286	0.946	100
	SD	4.179	4.334	19.746	3.440	7.832	2.956	0.051	1.607	3.324	
Arsenic trioxide ^a (Arsenite)	Average	1.194		0.600	1.791	0.176	68.043		27.352	0.844	100
	SD	2.300		1.142	1.547	0.734	27.576		23.887	2.780	
Zinc sulfide (Sphalerite)	Average	29.983	0.072	8.136	2.793	51.920	0.828	3.373	0.372	2.523	100
	SD	9.757	0.244	5.401	4.846	13.355	1.800	5.732	1.484	7.033	
Lead sulfide (galena)	Average	17.341		3.157	2.970	3.317	1.108	0.752	0.215	71.140	100
	SD	5.010		7.713	1.774	3.858	2.241	1.653	0.831	16.895	
Chalcopyrite	Average	29.007	0.009	29.631	34.273	1.932	2.571	0.145	0.226	2.206	100
	SD	7.986	0.082	8.328	8.762	3.265	4.226	0.563	0.791	7.295	
Bornite	Average	25.397	0.020	11.801	60.024	0.406	2.352				100
	SD	7.902	0.068	3.032	8.214	0.955	4.685				
Chalcocite	Average	20.762		1.386	76.569	0.587	0.082			0.614	100
	SD	4.339		2.128	9.242	2.560	0.357			2.675	
Covellite	Average	25.861		2.207	54.679	2.001	4.584	0.139	1.128	9.401	100
	SD	8.764		2.121	17.059	2.059	5.609	0.411	3.595	16.761	

^aElement oxygen is not included. The EDS spectrometer used did not detect oxygen concentration (see Figs. 8–10).

abundant lead phase were particles consisting of clusters of small spherical particles (Fig. 3a and b). The second type of Pb-rich particles was composed of the lead sulfide phase named galena (PbS).

Most of the Pb-rich particles showed a complex chemical composition where lead is the major element and is often associated with lower concentrations of As, Zn, Fe, Cu, Sb and Cd as a lead complex phase (Table 4). This lead complex phase was attributed to a lead complex sulfate as was identified in the EDS confirmatory microanalysis (Fig. 4a). Even if the lead sulfide was associated to the mineral galena, its composition includes lower concentrations of As, Zn, Cu, Sb and Cd, which is not common in the mineral.

Copper particles appear as metallic copper and copper sulfides meanwhile iron was detected as iron oxide and iron sulfides (Table 4). Metallic copper and iron oxide particles showed spherical shapes (Fig. 3c and d). Copper and iron sulfides showed common mineral shapes. The anthropogenic phases of As-rich particles, at the most, are constituted of arsenic trioxide particles, shaped in octahedral crystals (Fig. 3e). Antimony was observed as solid solution in this arsenic trioxide (Table 4). Iron and arsenic oxides were fully identified in the EDS confirmatory microanalyses (Fig. 4b and c).

It is important to note that zinc sulfide contains concentrations of cadmium higher than that reported for the mineral named sphalerite (ZnS).

3.3. Granulometric analyses of airborne particles

Heavy metal particles size distribution in the aerosol is presented in Fig. 5. 47.04% of the particles are less than or equal to 2 μm . As can be seen in this figure, the most abundant particles showed a size range between 1 and 2 μm (27.38%), this can be explained because the main phases as lead sulfates, iron oxides, metallic copper, galena, copper sulfides and zinc minerals showed a higher size distribution in this particle range size (Fig. 6). The particles bigger than 2 μm were mainly liberated from the other phases and did not agglomerate at the most, except for lead sulfate particles (Fig. 3a).

The particle size distribution (by number of particles) were obtained for the most abundant heavy metal particles suspended in the air as lead sulfates, metallic copper, copper sulfides, galena, zinc minerals (Fig. 6a), and iron oxides, arsenite and iron sulfides (Fig. 6b). In these figures it is observed that complex lead sulfates were more abundant than lead sulfides (galena). In the same way, the metallic copper particles were more abundant than copper sulfides, although many of these sulfide particles show complex compositions (Table 4). The dominant presence of iron and arsenic oxidized phases is much more important than sulfide particles as pyrite, pyrrhotite and arsenopyrite.

A granulometric study by SEM-EDS was performed for the most abundant phases focussed on particles

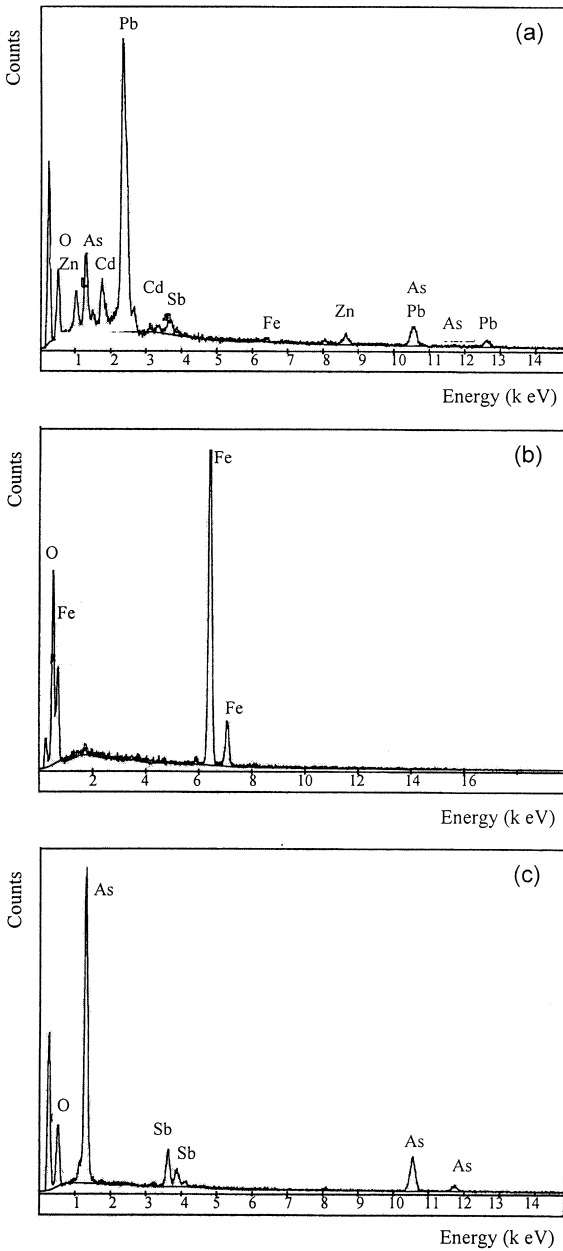


Fig. 4. X-ray spectra corresponding to (a) lead sulfates; (b) iron oxides; (c) arsenite.

smaller than 2 μm . In this way we obtained the size distribution calculated by the number of particles and the weight equivalence considering the particles as spheres and the mean density of the corresponding phase. In Fig. 7 it is showed that there exists a high percentage of particles less than or equal to 2 μm , for lead sulfates (71.4%), metallic copper (85.7%), copper sulfides (60.0%), arsenic trioxide (100%) and iron oxides (70.6%).

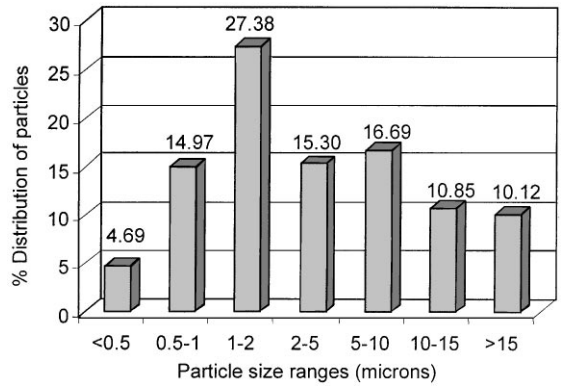
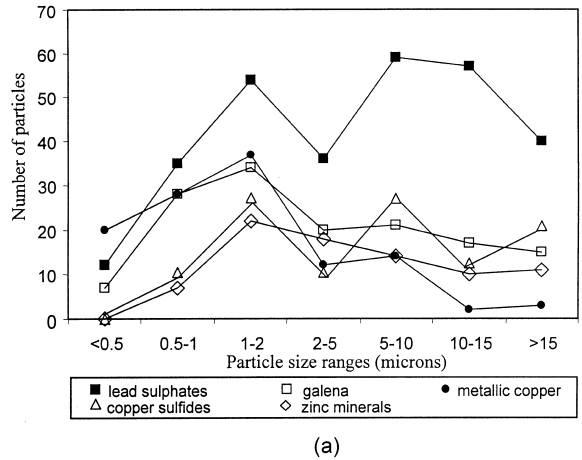
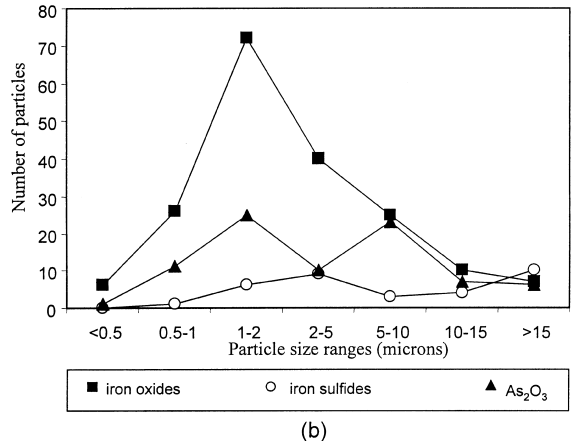


Fig. 5. Heavy metal particle size distribution for the airborne particles in San Luis Potosi.



(a)



(b)

Fig. 6. Particle size distributions (number of particles vs. range in μm). (a) lead sulfates, galena, metallic copper, copper and zinc sulfides; (b) arsenite, iron sulfides and iron oxides.

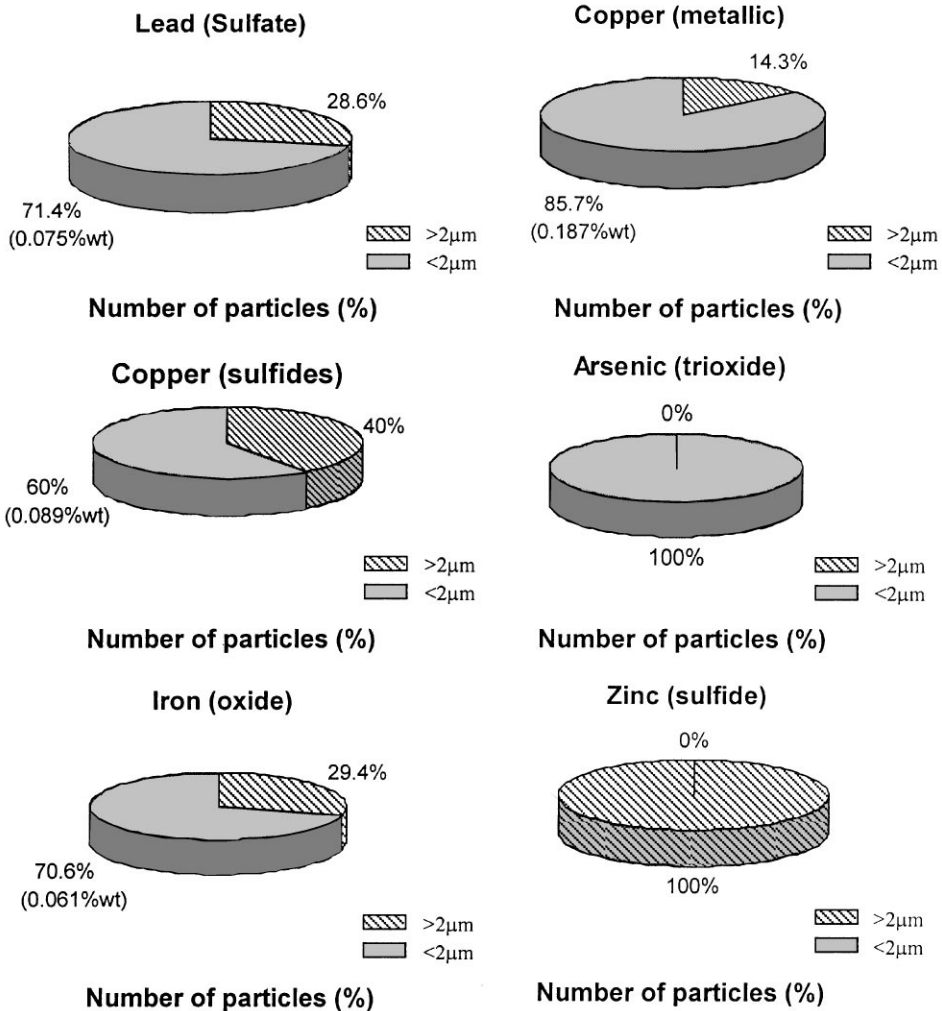


Fig. 7. Percentage of particles less than or equal to 2 μm and weight equivalence for lead sulfates, metallic copper, copper sulfides, arsenic trioxide and iron oxides.

Fig. 8 shows the distribution of particles for the main lead, copper, iron, arsenic and zinc phases to each air sampling station. A homogeneous distribution seems to be evident for the lead, iron, and arsenic-rich particles along the air sampling stations. Note that the air sampling stations are relatively near the copper and zinc refineries (Fig. 1). However, the higher concentration of metallic copper in the A and K stations could be associated with the nearness of the copper refinery. In the same way, the higher concentration of zinc-rich particles in the B station could be associated to the zinc refinery.

In this work, we have identified and classified airborne particles containing heavy metals. Initially, the PCA analysis reported an association of lead with As, Cd, Fe, and Mn but not with copper. This chemical association has been confirmed by the chemical composition of

particles reported by EDS microanalyses. A lead complex sulfate contains lower but highly variable concentrations of As, Fe, Zn, Cu, Sb and Cd. For example, SEM-EDS studies and PCA likewise indicated that cadmium was associated with lead, explaining its abundance in the aerosol. The lower statistical correlation of copper with the other elements could be explained by the presence of metallic copper and copper sulfides suspended particles in the air of San Luis Potosí. While manganese was found statistically associated to Pb, Cd, As and Fe, it was not detected by electron microprobe in the lead complex sulfate since its content was below the detection limit of this analysis (less than 0.1 wt%).

According to PCA analysis, nickel was the only element other than copper, that appeared independently. This finding was confirmed by the SEM-EDS analysis,

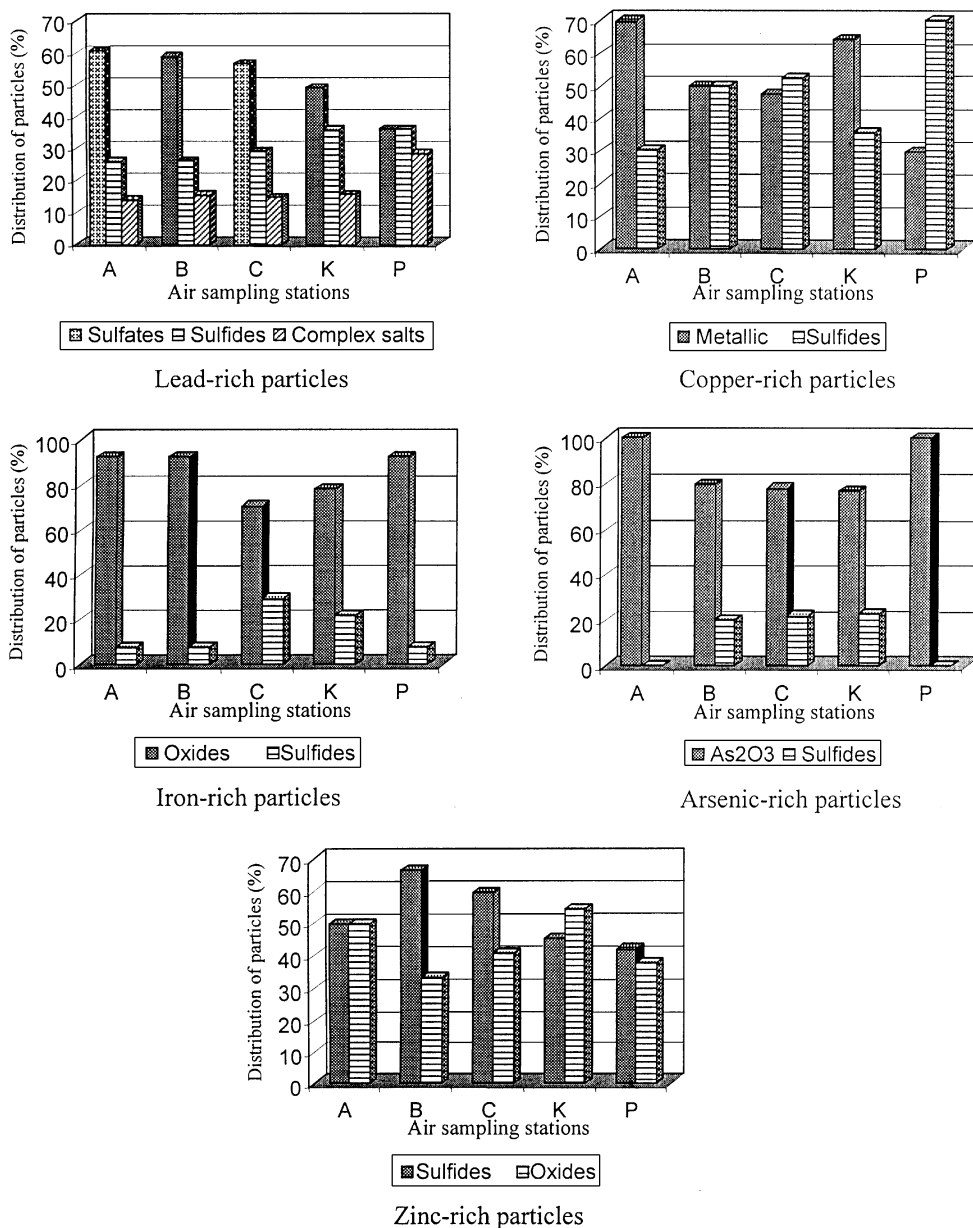


Fig. 8. Distribution of lead, copper, iron, arsenic and zinc-rich particles according to the air sampling stations.

where nickel was found associated to vanadium and sulfur in particles originating from fuel oil combustion (Lannefors et al., 1983; Van Borm et al., 1988).

The spherical shape and heterogeneous chemical composition of Cu and Fe-rich phases suggest that these kinds of particles originate from high-temperature furnace emissions. Even lead, copper, iron and zinc sulfides could originate from the metallurgical processes in the copper and zinc refineries. It must be marked that iron,

lead, arsenic, cadmium and antimony are common impurities contained in sulfide concentrates treated in these refineries.

4. Conclusions

The principal component analysis carried out after the orthogonal rotation VARIMAX, considering the

elements Pb, As, Cd, Cu, Fe, Ni and Mn, showed a clear statistical association among Pb, As, Cd, Fe and Mn. These elements were observed in the SEM-EDS analysis except Mn because of its low concentration in lead complex phases. In this case, the statistical analysis showed that it is an important tool that can be used to find associations of elements that cannot be detected by SEM-EDS because of its detection limit. Other elements such as copper and nickel were found unassociated because they were not considered in the PCA, however these associations were determined in the SEM-EDS study.

Airborne heavy metal particles were classified according to their composition and morphology in the SEM-EDS study. The most abundant heavy metal particles were lead sulfates, metallic copper, iron and arsenic oxides, lead, copper and zinc sulfides. Microanalysis of many of these particles showed a complex composition with high standard deviations for most of the elements corresponding to different phases. So, these complex compositions suggest that many of these phases would have originated from anthropogenic sources as copper and zinc refineries. Besides the complex compositions, many airborne heavy metal particles showed an uncharacteristic morphology. The abundance in the aerosol of other elements as cadmium, was due to the fact that cadmium was found associated with lead complex phases and in some particles of zinc sulfide.

In the granulometric study of airborne particles it was found that there exists a high percentage of particles less than or equal to 2 μm as lead sulfates, iron oxides, metallic copper, galena and copper sulfides. Lead complex sulfates are more abundant than lead sulfide, metallic copper particles are more abundant than copper sulfides, iron oxides and arsenic oxides are more abundant than the corresponding sulfides. These facts also suggest that most of these particles come from copper and zinc refineries.

It was hard to associate a clear concentration tendency according to the air sampling stations because these stations are relatively near the copper and zinc refineries. However, the higher concentrations of metallic copper and zinc-rich particles was found to be associated with copper and zinc refineries in accordance with the nearest air sample station.

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