Scanning and transmission electron microscope of suspended lead-rich particles in the air of San Luis Potosi, Mexico

A. Aragón Piña[a,*], G. Torres Villaseñor[b], P. Santiago Jacinto[c], M. Monroy Fernández[a]

[a] *Instituto de Metalurgia, U.A.S.L.P., Sierra Leona No. 550 Lomas 2a Secc., San Luis Potosí, S.L.P. 78210, Mexico*
[b] *Instituto de Investigaciones en Materiales, U.N.A.M., Ciudad Universitaria, México, D.F. 04510, Mexico*
[c] *Instituto Nacional de Investigaciones Nucleares, Carretera Mexico-Toluca Km. 36.5, Mpo. Ocoyoacac, Edo. de Mexico, C.P. 52045, Mexico*

Abstract

In the city of San Luis Potosi exists an important metallurgical plant and is known that in the adjacent urban zone, there is a high concentration of lead in the air, it is also supposed that most of the particles with lead have an anthropogenic origin because these particles show morphological characteristics and chemical composition very different in comparison with common lead minerals. In this work it was proved that most of the airborne particles with lead present in this urban zone, effectively came from the copper smelter. The airborne particles with lead were compared with particles with lead obtained starting from samples of slag and lead calcine of the copper smelter. To perform the comparative study, these particles were studied with energy dispersive X-ray microanalysis (EDS) in conjunction with scanning electron microscope to obtain chemical composition and associated morphological characteristics. Results suggest that these particles, composed of only one phase, are chemically distinct from any crustal lead mineral. Because of the complexity of the chemical composition of these particles (Pb, S, Cu, As, Fe, Zn, Cd, Sb, O), some of the airborne particles were analyzed by transmission microscopy in order to associate crystalline structure with any particular chemical phase.

1. Introduction

The city of San Luis Potosi, Mexico has a long tradition of metallurgical activities. At the beginning of the 20th century what was to become the nation's most important copper smelter was installed in the area. Sulfide mineral concentrates from the rest of the country were sent to this smelter. In 1982 a zinc smelter was established in this city, and is currently the most productive of its type in the country and one of the most important in Latin America.

Anthropogenic emissions of particulate matter coming from the copper and zinc smelters contribute to air pollution in the city. Slag produced by the copper smelter is deposited inside the confinement zone of the plant and is exposed to the environment. The high level of lead and other heavy metals in the air seems to be related with these smelters (Aragón et al., 2000).

The air quality was evaluated in San Luis Potosi City and the annual mean concentration for lead was $Pb = 0.68 \, \mu g \, m^{-3}$. Levels for other heavy metals were also determined (Luszczewski et al., 1988; Medellín and Hernández, 1988; Monsivais and Flores, 1995). These

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*Corresponding author. Fax: +52-444-8254584.

E-mail addresses: aragon@uaslp.mx (A.A. Piña), gtorres@servidor.unam.mx (G.T. Villaseñor), psj@nuclear.inin.mx (P.S. Jacinto).

values exceeded World Health Organization (WHO) recommendations for lead ($Pb = 0.2 \, \mu g \, m^{-3}$) and the other heavy metals too. Public health studies carried out in the city revealed a higher number of respiratory diseases, dermal problems and arterial hypertension cases, and could be associated with heavy metal particulate air pollution (Batres et al., 1993).

In previous work carried out in San Luis Potosi (Monsivais and Flores, 1995; Aragón et al., 1996), 300 samples of airborne particles were collected in 1994 using High-Vol samplers. The samplers were placed in five urban locations situated within 10–15 km of the zinc and copper smelters (Fig. 1). Each sampler consisted of a heavy-duty rotary pump and a fiberglass filter with a collection efficiency of 99% for particles of diameter $> 0.3 \, \mu m$ (most of the mass in the PM10 range). These samplers filtered approximately $1.4 \, m^3 \, min^{-1}$ of air and ran continuously for 24 hours for each sample. This involved a 24-hour acclimatization period for the

fiberglass filter for each sample, before and after sampling ($25^{\circ}C$ and $< 50\%$ relative humidity). A representative portion of each sample was dried in an oven and stored in alcohol to avoid chemical changes over time. Heavy metal concentrations obtained from these samples exceeded permissible levels for airborne particles. The same samples preserved were analyzed by scanning electron microscopy and statistical analysis (Aragón et al., 2000). In that work the heavy metals particles were characterized and classified in mineral and anthropogenic phases by size range, morphology and chemical composition. In the case of rich lead particles, the most abundant kind showed a complex chemical composition (Pb, S, Cu, Zn, Fe, As, Sb, Cd) very different to common lead minerals. It was concluded that these complex lead phases did not correspond to crustal origin and could only be classified as possible anthopogenic phases. It was also determined that these complex lead phases were the most abundant of the
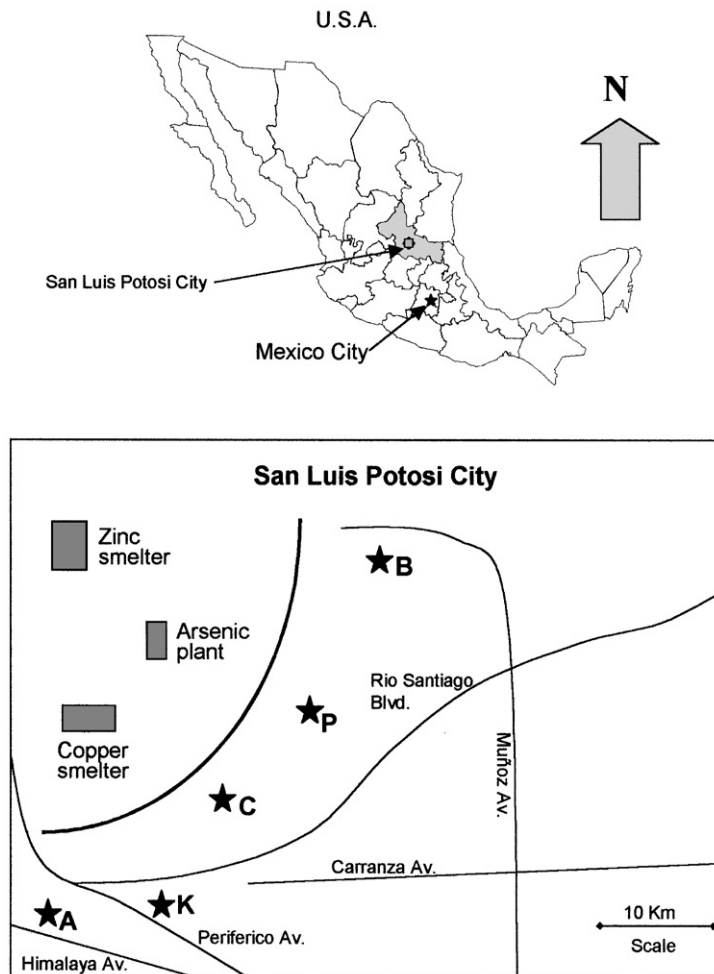

Fig. 1. Location of sampling stations.

heavy metal particles suspended in the air of the city, accounting for 17.5% of all particles containing heavy metals (Aragón-Piña, 1999).

The main aim of this work was to characterize the lead-rich phases that constitute the most of the particles with heavy metals suspended in the air of the urban zone of San Luis Potosi. The characterization consisted of obtaining the crystalline structure of the complex lead phase by TEM and associating it with the chemical composition obtained from individual particle analyses by SEM-EDS. Another aim was to compare the morphologic characteristics and chemical composition of these particles suspended in the air, with samples coming from the copper smelter. This smelter is considered as the main pollutant source of San Luis Potosi City, so, two samples were collected in 1999 coming from this copper smelter: lead calcine and slag. Slag sample was collected from deposits on the ground of the copper smelter, and lead calcine was collected from arsenic furnace.

It is considered that the high concentration of lead in the airborne dust and residues from the copper smelter are associated to the treatment of Cu–Au concentrates containing Pb, Zn, Cd and other heavy metals. This metal association results from the particular Cu–Pb–Zn ore deposits characteristic of Mexico (skarn type ores).

2. Methods

Particle composition, morphology and crystalline structure of lead-rich phases were obtained by combining SEM-EDS (Linton et al., 1980; Noll et al., 1987; Post and Buseck, 1985; Bernard and Van Grieken, 1986; Van Born and Adams, 1989) and TEM. Only few airborne dust samples were selected from the initial samples because all the anthropogenic lead-rich particles showed the same morphological characteristics and similar chemical composition (Aragón et al., 2000). The samples selected were representative of all the sampling sites. Ten of these preserved samples were dried in an electric oven at $30^{\circ}C$ to eliminate alcohol and then were prepared to be analyzed.

The particles were redeposited on grids (Maxtaform Grids H15, 135 mesh) to make it easy for the location of lead-rich particles for analysis by SEM-EDS and then by TEM. A Philips XL-30 SEM scanning electron microscope with 20 keV electron energy and a 50 nA beam current was employed for the microanalysis. The microscope was equipped with a $30\,mm^2$ energy dispersive Si(Li) detector EDAX DX4 for analyses, secondary and backscattered electron detectors for imaging. The particles were observed by backscattered electron images to identify the anthropogenic lead-rich particles, and then by secondary electron images. An energy dispersive X-ray spectrum (EDS) was collected

from each lead-rich 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 micro-analyzed (atomic number, mass absorption and fluorescence). The analyses obtained by EDS and morphology of these lead-rich particles were compared to those obtained in previous work (Aragón-Piña, 1999) in order to find out if these particles were of the same kind.

Subsequently, the samples were observed by TEM localizing and analyzing exactly the same lead-rich particles analyzed by SEM-EDS. A Jeol-1200 EX transmission electron microscope was employed for the particle analyses. In this way, electron diffraction patterns were obtained of the lead-rich particles, using an acceleration voltage equal to 200 kV and a chamber length of 120 cm. The CaRine Crystallography 3.0 program was employed to identify the planes corresponding to the reciprocal lattice of the possible phases, according to the chemical composition obtained previously by SEM-EDS.

Two samples coming from the copper smelter, the main pollutant source, were analyzed by SEM-EDS. The first sample was a lead calcine. It contains lead, copper, gold and silver that are recovered by a pyrometallurgical process in the copper smelter. 2 kg of this sample was screened through 400 mesh (particles smaller than 35 μm). The powder obtained was deposited on a carbon tape stuck on the SEM sampler and coated with carbon to analyze the particles by SEM-EDS. The powder was analyzed by X-ray diffraction too with a Rigaku D MAX-2200 diffractometer using a copper K_α radiation, $6^{\circ}\,min^{-1}$ and $2\Theta = 5-120^{\circ}$. The other sample studied was a slag produced by the copper smelter. 5 kg of the sample was screened through 325 mesh (particles smaller than 44 μm), followed by heavy media separation with sodium polytungstate solution. The powder obtained was washed with demineralized water and dried in an electric oven at $30^{\circ}C$. Finally, particles of this powder were deposited on a carbon tape stuck on the SEM sampler and coated with carbon to analyze them by SEM-EDS. The powder was analyzed by X-ray diffraction too. The analysis condition for SEM-EDS and X-ray diffraction were similar to the previously reported.

3. Results and discussion

3.1. Airborne dust samples

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

Two types of Pb-rich particles were identified based on their chemical composition and morphology: a lead-rich phase with a complex chemical composition and a

lead sulfide phase. The lead sulfide phase showed the typical chemical composition and morphology of galena, the most common lead mineral, so, only the complex lead phase was studied. This interesting complex phase is most abundant and the particles consisted of agglomerates of small spherical sub-particles (monomers). In Fig. 2 are shown agglomerates of these lead-rich particles and although in these micrographs are shown big clusters (up to 20 μm), most of them were aggregates smaller than 2 μm, previously it was determined that 71% of these aggregates showed a cluster size smaller than 2 μm (Aragón et al., 2000). The sub-particles that constitute the clusters are no larger than 300 nm. A typical X-ray spectrum obtained by ESD of the clusters is shown in Fig. 2d.

This lead phase of clustered particles showed a complex chemical composition where lead is the major element and it is often associated with lower concentrations of S, O, As, Zn, Fe, Cu, Sb and Cd apparently in one phase (Table 1), backscattered electron images showed only one phase. This phase was initially attributed to a lead sulfate according to the main elements identified in the EDS microanalysis (Pb, S, O).

Due to the very small size particles (monomers <300 nm) that constituted the clusters, it was not possible to analyze individual particles with SEM-EDS, so we decided to study these small particles by TEM.

3.1.2. Transmission electron microscopy and X-ray microanalysis (SEM-EDS)

We analyzed by TEM the same clusters of lead-rich particles selected previously for SEM-EDS. The analyses performed by TEM corresponded to individual particles
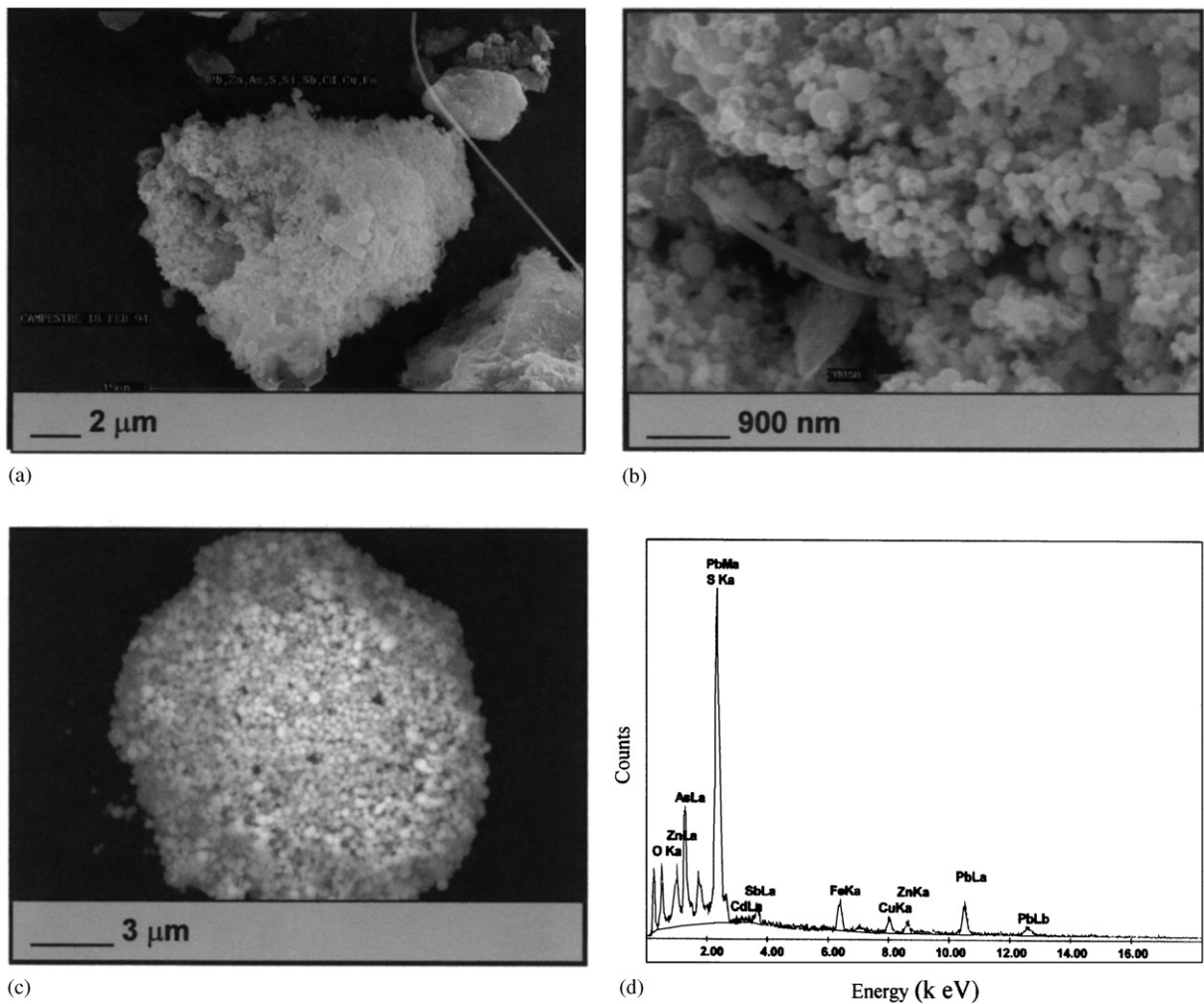

(a)

(b)

(c)

(d)

Fig. 2. (a–c) Complex lead phase particles found suspended in the air of San Luis Potosi. This type of heavy metal particle is the most abundant in the city's aerosol. (d) Typical X-ray spectrum corresponding to this kind of particle.

Table 1
Mean chemical composition of agglomerates of lead rich particles obtained by SEM-EDS (wt%)

	O	S	Fe	Cu	Zn	As	Cd	Sb	Pb	Total
(a) *Airborne dust samples* $n = 20$										
Average	15.18	9.70	3.00	3.50	3.48	7.46	0.54	2.21	54.94	100.00
SD	4.62	4.17	3.30	4.23	1.83	4.59	0.54	2.04	10.60	
(b) *Calcine sample* $n = 20$										
Average	14.08	9.21	4.58	2.83	7.55	6.08	0.27	2.63	52.76	100.00
SD	5.20	2.82	2.87	4.00	2.76	2.72	0.42	3.53	9.74	
(c) *Slag sample* $n = 8$										
Average	15.88	8.25	4.43	2.37	2.39	5.55	0.19	0.88	60.06	100.00
SD	4.46	3.45	3.59	2.06	2.71	4.93	0.36	0.85	9.95	

(a) Airborne dust samples, (b) calcine sample, (c) slag sample. Agglomerates are composed of very small globular particles (<300 nm).
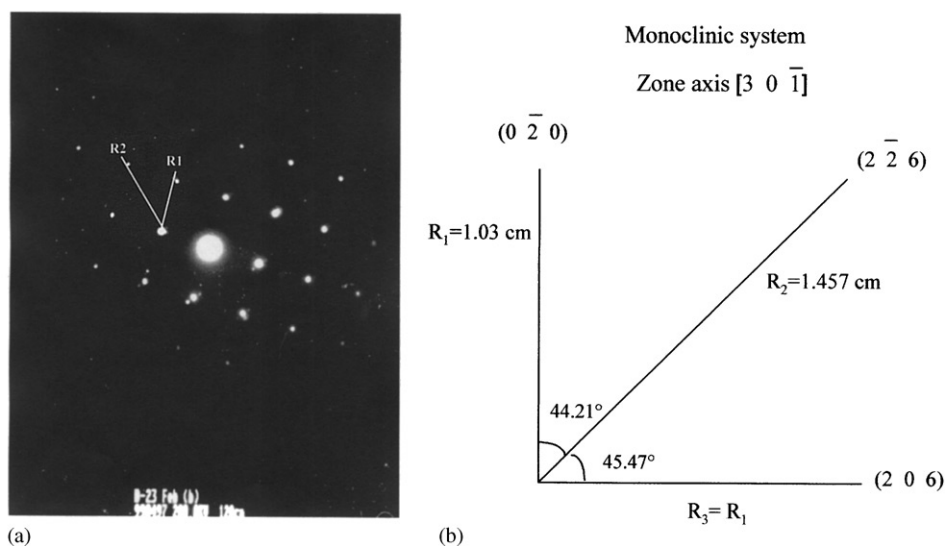

Fig. 3. (a) Electron diffraction pattern corresponding to one of the complex lead particles. (b) Representation of planes and angles corresponding to the reciprocal lattice for zone axis [3 0 $\bar{1}$].

of the clusters (<300 nm). As the particles always were clustered, it was very hard to find an individual particle in a suitable position for the electron beam to cross the particle in order to obtain the corresponding electron diffraction pattern. In spite of everything, we obtained the same electron diffraction pattern (reciprocal lattice) for several individual particles (Fig. 3a). The patterns could only be obtained for the same zone axis in spite of the fact that we tried to obtain other zone axes for the same particle: if we tilted the particle, its new position on the cluster obstructed the trajectory of the electron beam. Individual separate particles were not found.

The electron diffraction pattern was measured (Fig. 3b). The possible elements were considered to prove the lattice parameters corresponding to a particular phase. All these data were introduced in the CaRine Crystallography 3.0 program to identify the crystal planes corresponding to the reciprocal lattice. The zone axis was identified as [3 0 $\bar{1}$]. In this way, it was found that the crystalline structure corresponded with $PbCu_4(SO_4)(OH)_6 \cdot 3H_2O$ (JCPD 47-1810). This phase shows a monoclinic system with $a = 21.642$, $b = 6.040$, $c = 22.544$ and $\gamma = 108.2°$.

If we apply to this structure the elements obtained in the SEM-EDS study, it is obvious that an important quantity of arsenic is present, arsenic replacing sulfur in the crystal network. It was not possible to find a structure that corresponded to a lead–arsenic phase. The

other elements present in the lead sulfate structure, such as Zn, Fe, Cd and Sb, can replace either lead or copper, forming a solid solution in either case.

The structure obtained by TEM, the complicated chemical composition obtained by SEM-EDS and special morphological characteristics of the lead-rich phase, all indicate a phase which does not exist as a mineral in nature, so this compound must originate from an anthropogenic source.

3.2. Lead calcine sample

In the X-ray diffraction analysis of the prepared sample, crystalline compounds like galena (PbS), sphalerite (ZnS), pyrrotite ($Fe_{1-x}S$), pyrite (FeS_2), magnetite (Fe_3O_4), anglesite ($PbSO_4$), and probably elyite ($CuPb_4$

$(SO_4)(OH)_8$) (Fig. 4) were found. According to X-ray diffraction, the most abundant lead phases are galena and anglesite. The SEM-EDS study indeed was confirmed that the majority phases were galena and anglesite, with minor amounts of sphalerite, pyrrotite, pyrite and magnetite. Particles of the elyite phase were not detected by SEM-EDS, however, other lead sulfate phases of undetermined stoichiometry were detected.

Three other matches of morphology to chemical composition were found, corresponding to anglesite (Fig. 5), lead arsenate (Fig. 6) and a complex lead-rich phase (Fig. 7). As can be seen in Fig. 7, the morphologic characteristics of the complex lead phase particles are very similar to the complex lead airborne particles (Fig. 2) and also are similar in chemical composition (Table 1). Fig. 5 (anglesite) and Fig. 6 (lead arsenate)
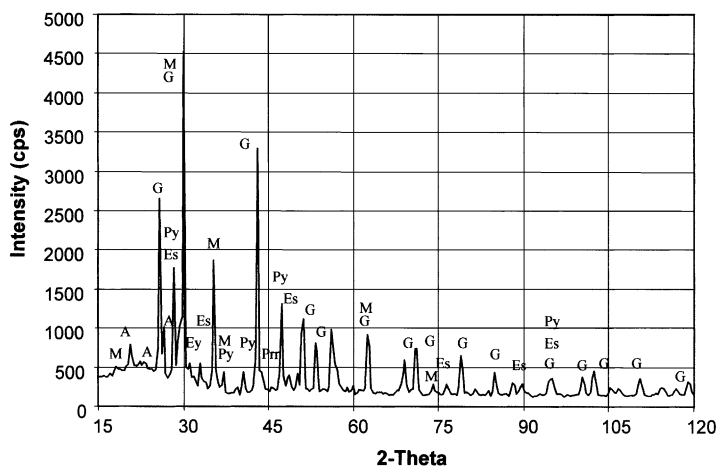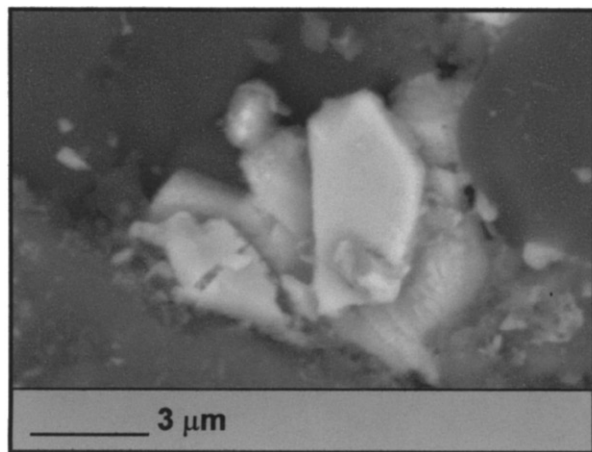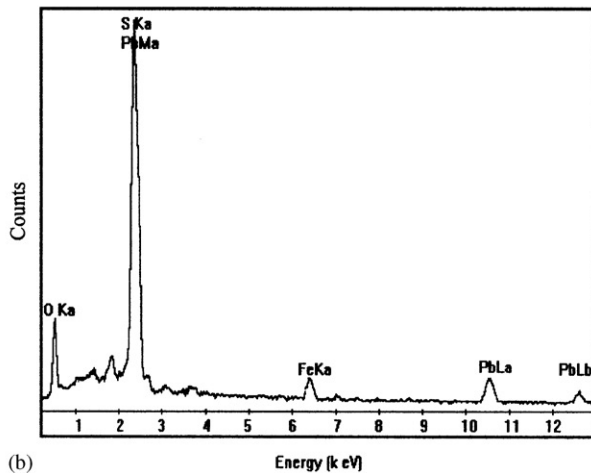

Fig. 4. X-ray diffraction pattern of lead calcine sample from copper smelter. Galena (G), magnetite (M), sphalerite (Es), pyrite (Py), pyrrotite (Prr), anglesite (A) and probably elyite (Ey).

Fig. 5. (a) Lead sulfate particles corresponding to anglesite found in calcine sample. (b) Typical X-ray spectrum obtained by EDS.
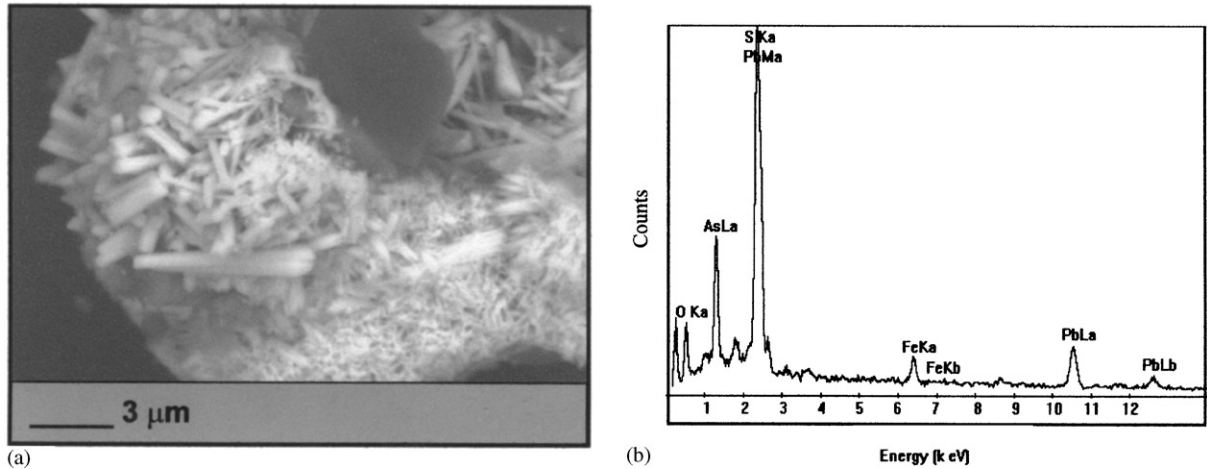
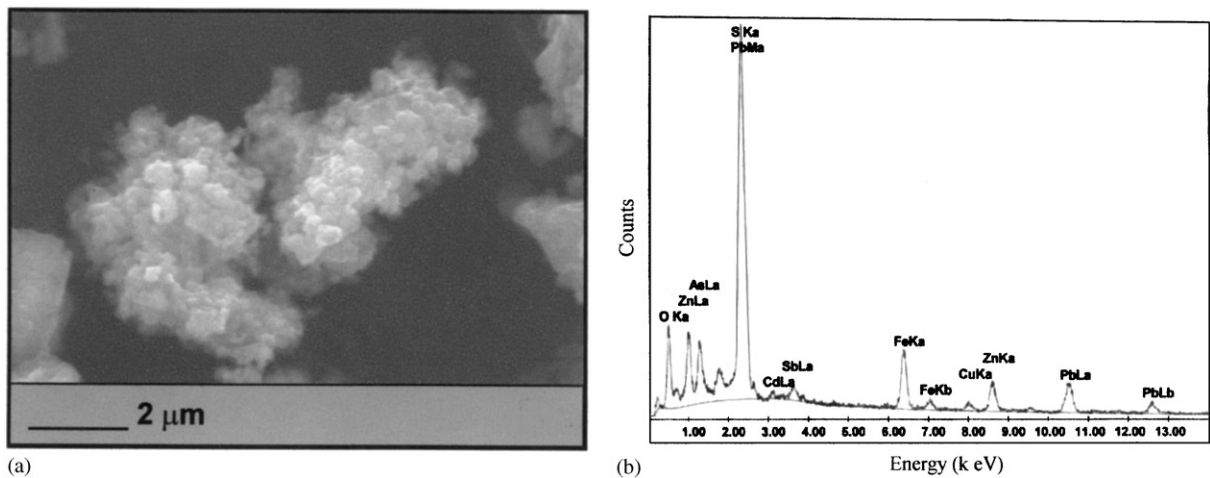Fig. 6. (a) Lead arsenate particles found in calcine sample. (b) Typical X-ray spectrum obtained by EDS.

Fig. 7. (a) Complex lead phase particles found in calcine sample. This type of heavy metal particle is very similar to the complex lead particles found in the city's aerosol. (b) Typical X-ray spectrum corresponding to this kind of particle.

show a bigger particle size than the complex lead sulfate particles as well as different crystal and particle morphology. These last two kinds of phases found in the calcine sample could be possibly present in the clusters of the complex lead phases of airborne particles.

3.3. Slag sample

In the X-ray diffraction analysis of the prepared sample, crystalline compounds like hedenbergite (CaFe-Si$_2$O$_6$), augite ((Ca,Na)(Mg,Fe,Al)(Si,Al)$_2$O$_6$), magne-tite (Fe$_3$O$_4$), almandine (Fe$_3$Al$_2$Si$_3$O$_{12}$) and monticellite (CaMgSiO$_4$) were found; lead phases were not found. In the SEM-EDS study the same phases were found in addition to particles of sphalerite (ZnS), bornite (Cu$_5$FeS$_4$), calcosine (Cu$_2$S) and smithsonite (ZnCO$_3$). Although it was difficult to find lead phases particles, a

complex lead phase in which particles showed similar morphologic characteristics (Fig. 8) was found and with the same kind of chemical composition (Table 1) as that of the lead rich airborne particles. A typical X-ray spectrum obtained by EDS is shown in Fig. 8b.

3.4. Relation between airborne lead-rich particles and lead-rich particles from copper smelter

Although it is clear that most of the airborne lead-rich particles have a very similar morphology and chemical composition with some of the lead-rich particles coming from copper smelter, this similarity is focused mainly to the complex lead sulfates. These complex sulfates are always clusters or smaller aggregates ($<2\,\mu m$) constitut-ing very small monomers (300 nm at the most). According to the TEM study carried out on lead-rich
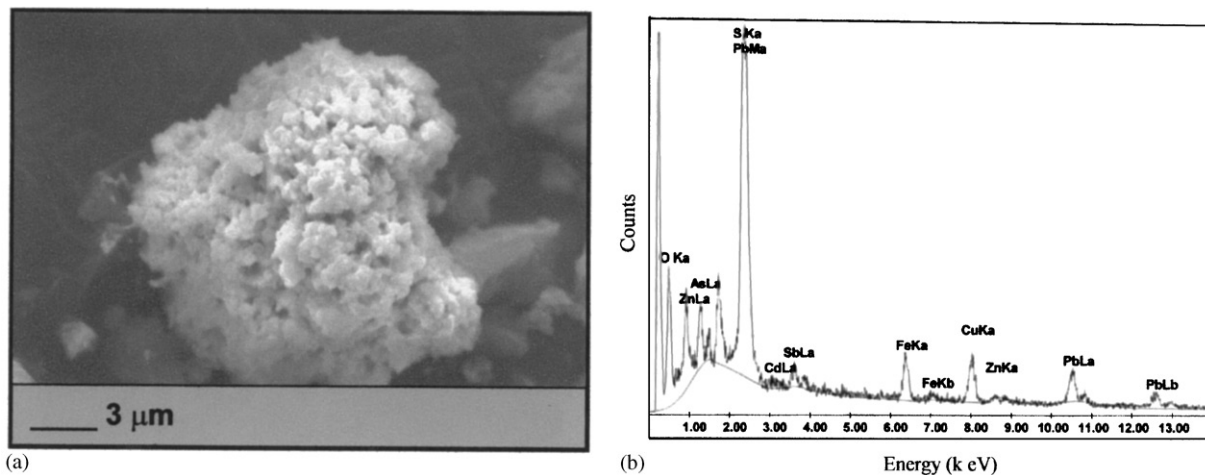
Fig. 8. (a) Complex lead phase particles found in slag sample. This type of heavy metal particle is very similar to the complex lead particles found in the city's aerosol. (b) Typical X-ray spectrum corresponding to this kind of particle.

airborne particles, it could be proved that the smallest particles were sulfates; however, it was not possible to analyze particles with a bigger size that could be lead arsenates, and this fact could also explain the presence of arsenic in the clusters of airborne lead-rich particles. It was also evident that only the smallest particles can remain suspended in the air for a long time.

Clusters of lead-rich particles were found in calcine sample. These particles showed a typical morphology and chemical composition similar to particles which were found in air. It was also observed that the crystals of lead arsenate were generally bigger than the lead sulfate complex particles. This could explain the fact that there were not lead arsenates identified in the smallest particles by TEM in these airborne particles.

The airborne lead-rich particles (complex sulfates) are clusters of very small particles and these clusters have a big surface area which could have an influence on chemical reactivity with humidity and SO_2 that exist in the air. This fact could explain that in TEM study the complex lead phase identified had H_2O in its structure.

In addition, these particles should be originated from the smelter and it is not probable that they could result from long range transport from other farther industrial sources. A couple of airborne samples coming from a mining zone situated not so far from the city were analyzed and were not found to contain lead-rich particles.

4. Conclusions

(a) The structure and chemical composition related to the most abundant heavy metal phase in fine particulates suspended in the air of San Luis Potosi City was determined.

(b) The SEM-EDS showed that a complex chemical composition was always associated to a special characteristic morphology. Furthermore SEM-EDS study showed that other elements, like Zn, Fe, Cd, As and Sb, were associated with the clusters.

(c) The electron diffraction patterns obtained by TEM from the smallest individual particles of the clusters showed that the corresponding crystalline structure was the specie $PbCu_4(SO_4)(OH)_6 \cdot 3H_2O$.

(d) The morphology and chemical composition of this complex lead phase suggested that these particles could have originated from anthropogenic sources such as copper and zinc smelters.

(e) Two samples coming from the main pollutant source of the city, the copper smelter, were analyzed and was proved that there existed the same complex lead phase in lead calcine and slag, similar to those complex lead particles that were found suspended in the air.

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