

Characterization of inorganic atmospheric particles in air quality program with SEM, TEM and XAS

R. Ramírez Leal, H. Esparza Ponce, and A. Duarte Moller

Physical and chemical characterization of inorganic atmospheric particle samples collected on TSP and PM10 filters from January 2003 through December 2005 from three zones within the city of Hermosillo, Sonora; using Transmission Electron Microscopy, Scanning combined with EDS and Stanford University's Synchrotron X-Ray. The sample preparation for electron microscopy was deposited as an alcohol suspension using a sample holder. The different elements found amongst individual particles were Al, Ba, Bi, Br, Ca, Ce, Cl, Cr, Cu, Fe, K, La, Mn, Mg, Na, P, Pb, S, Si, Ti, U, V, W, Zn and Zr. These particles' morphology and chemical composition, illustrate an abundance of natural elements within the zone. However some of the elements present are directly related with human activities, and are of much interest from the public health and environmental perspectives.

Keywords: SEM; TEM; XAS.

El trabajo se enfoca a la caracterización física y química de las partículas atmosféricas inorgánicas presentes en los filtros de los muestreadores de alto volumen de las Partículas Suspendidas Totales (PST) y Partículas Menores a 10 micras (PM10), ubicadas en tres zonas de la ciudad de Hermosillo, Sonora, durante el período de enero 2003 a diciembre del 2005; a través del empleo de las técnicas de Microscopia Electrónica de Transmisión, de Barrido, equipados con EDS, y del Sincrotrón de la Universidad de Stanford; se adecuó la metodología para la preparación de las muestras a analizar por medio de la microscopia electrónica, permitiéndonos el análisis de una

mayor cantidad de muestras en un menor tiempo; en donde los elementos encontrados en las partículas individuales han sido el Al, Ba, Bi, Br, Ca, Ce, Cl, Cr, Cu, Fe, K, La, Mn, Mg, Na, P, Pb S, Si, Ti, U, V, W, Y, Zn y Zr; cuya morfología y composición química de las partículas, nos señalan una importante aportación de los elementos naturales ubicados en la zona, pero con una incidencia de los elementos de origen antropogénico que son de interés desde el punto de vista ambiental, como de salud pública.

Descriptores: SET; TEM; aire.

Introduction

The atmosphere is a thin layer of gases that surrounds to the Earth and presents a complex and dynamic mixture of natural and anthropogenic compounds, constituted mainly by oxygen, nitrogen and small amounts of other gases, like the water vapor, carbon dioxide, noble gases, as well as by particles (2,3,8,14,22,33,65). These particles have diameters that go from a few nanometers to 100 microns. Among these are particles generated by combustion processes, such as those in automobiles and some energy generation plants, which can be very small and as long as one micron. Dust dragged by the wind, pollen, fragments of plants and the marine salt is generally greater to one micron. In addition, the atmosphere also contains materials produced by photochemical processes can be found in form of particles smaller than one micron. (3.6,12,31,42,48.52,57)

The size of particles and their concentrations are the basic characteristics of the atmospheric aerosols, allowing us to classify them, by its multimodal nature, in coarse particles, which have sizes larger than 10 microns, in fine particles, with sizes smaller than 10 microns and larger than 1 micron, and ultrafine particles, that have diameters

smaller than 0,1 microns; all of these can be emitted so much by natural sources as by anthropogenic sources. (14, 12, 28, 30, 32, 39, 44, 49) These characteristics are important because they have influence on a particle's dwell time within the atmosphere and on its physical and chemical properties; these properties also have influence on global climate, the environment and on people's health. (11, 17, 19, 29, 33, 46, 54, 59, 66, 68, 70) Their influence on global climate is due to their ability to intensify or moderate the effects of the meteorological phenomena, by means of absorbing or to turning aside solar radiation, where the specific size of particles is comparable with the wavelengths of light. (2,7,11,17,18,21,27,29,30,33,39,48,55,59,63)

Emphasizing that the magnitudes of the effects that aerosol conforming particles have on solar radiation depends on its composition, measurement and size of distribution, abundance, hygroscopic and surface properties, densities and index of refraction. These parameters are interdependent and vary accordingly to each locality, the sources of emission and to environmental variables, like solar light intensity and relative humidity. Aerosols can also act like condensation nuclei and therefore can modify the radioactive properties of clouds.(7,10,13,17,24,26,28,38,45,49,59,66,68)

Observing that during the last few decades, human activities have increased the amount, kind and distribution of aerosols inputs to the atmosphere, plus the fact that anthropogenic particles are especially abundant within the submicron fraction of aerosols, there is great uncertainty about the estimation of its effects on climate.

Previous studies on aerosols have been focused on their classification based on size, concentration and on chemical composition of whole particle masses; with

relatively few details on the size, shape and chemical composition of their individual components. (1,13,15,17,19,20,22,25,28,31,35,38,43,46,48,52,57,59,60,61,66,69,70)

Knowledge of the kinds of particles, especially those which are of wide spatial and chronological distribution, such as particles derived from industrial activities and from geological sources such as volcanoes and deserts, is necessary to build a specific assemble of each particle, being that the chemical composition of atmospheric aerosols varies according to its size, its geographic position and the season of the year.

Thanks to this, there has been a constant development and improvement of necessary instruments used for better and more precise characterization of atmospheric aerosols. Presently, the Scanning Electron Microscope, Transmission Electron Microscope and X-Ray Synchrotron are considered the most reliable equipment for studying of inorganic particles that can be found in our atmosphere, thus, in direct contact with population. (2,3,5,8,9,13,15,19,22,25,27,29,35,37,41,47,56,59,61,64,68,70)

The use of electrons for the study of particles has had an enormous impact, allowing us to obtain an immense amount of information about the nature, origin, and chemical composition of a research's subject. Plus, these sorts of technologies are specific enough for the analysis of small sized particles bellow the range of nanometers and provide information which is essential for aerosol observation, because through them, we are able to individually identify and completely characterize each particle present among a group of numerous particles.

Experimental Details

This work is based on samplings collected in three atmospheric monitoring stations property of the Air Quality Improvement Municipal Program for the City of

Hermosillo (Fig. 1). Each monitoring station consist of proper equipment for collecting Total Suspended Particles (TSP) and of Particles Smaller than 10 microns (PM10), and are established in three different zones within the city. The first station is located in the northwestern area of the city, the second station in the downtown area, and the last station in the northeast area.

The northeastern station is surrounded by residential and roadside areas; the downtown station, by office commercial buildings and by high traffic areas, and finally, the northwestern station is also surrounded by high traffic zones and commercial buildings plus areas of industrial activity.

The characterization of individual particles was completed by using Scanning Electron Microscopy combined with EDS (JEOL JSM-5800LV), Philips CM200 Transmission Electron microscopy and XAS.

Specimens were initially processed by separating the collected particles from the filters by means of submersing a 2 cm² section of each filter into isopropilic alcohol within a test tube for 5 minutes. Then, an aliquot of the suspension was placed over a sample holder and into the TEM. The same was done with each filter sample. For the particles analyzed through the SEM, a section of the filter was placed over a sample holder and then covered with gold, then placed in position for its viewing (Fig. 2).

Later on, we made a variation of this sample preparation method by applying ultrasonic waves to the submerged filter sections inside the test tubes for 10 seconds at the beginning of the 5 minute separation period, we then carried on with the rest of the microscopic method for the TEM.

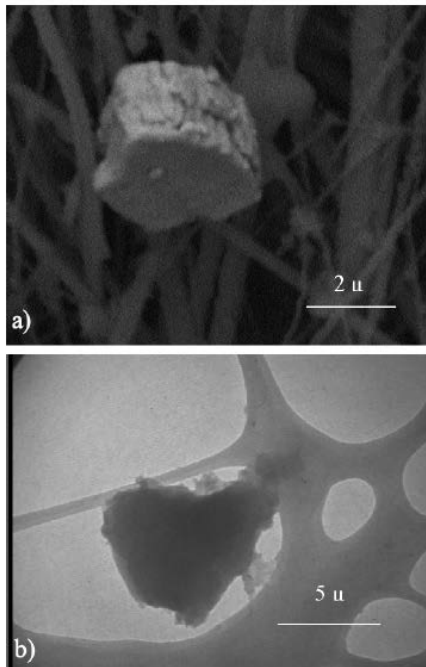


FIGURE 1. SEM (a) and TEM (b) particles from PM10 filters.

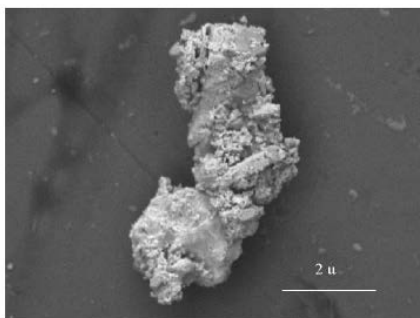


FIGURE 2. SEM image of a PM10 particle containing S.

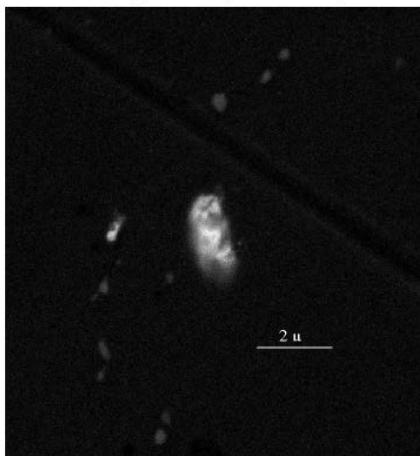


FIGURE 3. SEM image of the particle containing Pb.

Another variation was made to the previously mentioned method of sample preparation for SEM of the samples. Instead of using a gold covered section of the filters, we took several aliquots from the same alcohol suspensions made for TEM, and placed each one over individual aluminum sample holders. These individual holders were then placed on a holder grid and into the SEM for the viewings (Figs. 3 and 4).

The experiments of the XAS were made in the Stanford Synchrotron Radiation Laboratory in Stanford, CA.; using the Lytle detector, the adjustments of the $F(r)$ were made using FEFF 8.0.

Meteorological factor

The annual average temperature in the city of Hermosillo is 25°C; with an annual precipitation of 315 mm. This agrees to a dry-warm climate classification with extreme thermal oscillation, mostly of 14°C. Precipitation is mainly restricted to a summer rain regime. During July, August and September, there is a season of strong winds whose velocities range between 60 to 80 km/hr and average relative humidity is 55%; while on the rest of the year, mostly weak and dry winds occur. However, there are approximately 129 days of wind calm per year.

Results and discussion

The change developed in the sample preparation for its analysis in the scanning and transmission microscope, was an important factor to make agile the study in the mentioned microscopes, because it allowed to the saving of the time search and analysis of the interest particle; then in the scanning microscope the time to analyze of one to two samples, with the initial form, took us from 1,5 hr to 2 hr, and with the

done adjustment, the number of samples was extended, because with the same time that has been mentioned we analyzed between six to seven samples of filters.

The studies by EDS to TSP showed in all monitoring stations, that elements are Al, Ba, Br, Ca, Ce, Cl, Cr, Cu, Fe, K, Mg, Si, Ti, Zr, in two stations, northeast and northwest, the principal elements were Mo, S, V, Zn y W; in downtown the principal element was Pb and northwest with Br, La and Na (Table I).

With respect to PM10 in the three stations we found Al, Ca, Cr, Fe, K, Mg, Na, S, Si and Ti; in the northwest and northwest the Zn was the more abundant; in the downtown and northwest only Pb and minor proportion Ce, Cl, Ni, U, V y Zr (Table II).

What's most important in this study is underlining the detection of chemical elements that are highly relevant due to their potential impact on public health. Such found elements include Bi, Cr, Pb, S and U, that due to the size of the particles found, PM10, posses the capacity to penetrate deeper into the respiratory system and subsequently be relocated and settled within other body tissues and systems.

XAS results illustrate a distinct difference between those elements that were found to be abundant as Cr, Cd and Pb, these elements tend to be associated with natural and human sources (Figs. 5 to 8).

The results obtained from the characterization of the particles captured by TSP and PM10 filters, showed that elements such as Al, Si, Ca, Fe, K, and Mg are largely abundant, and are usually related with lithophilic sources, such as agricultural activities, areas of soil free of anthropogenic impact, paved streets and construction sites. While elements such as Cl are more frequently associated with incineration and combustion activities as well as derived from marine aerosols.

Other chemical elements such as Ba, Bi, Br, Cu, Cr, Mn, Na, Ni, P, Pb, Ti, and Zn are more commonly related various human and industrial activities. Elements such as V and S are indicators of the level of carburant combustion as well as of the regional sulfate supply.

TABLE I. The elements found in the filters (TSP) from each station At(%)

Northwest	At(%)	Downtown	At(%)	Northeast	At(%)
Al	14.402	Al	5.39	Al	10.02
Ba	4.035	Ba	0.475	Ba	.495
		Bi	0.324		
Br	0.75				
Ca	0.733	Ca	0.571	Ca	0.81
Ce		Ce	0.65	Ce	
Cl	0.91	Cl	0.60	Cl	0.216
Cr	2.64	Cr		Cr	2.62
Cu	2.56	Cu	0.15	Cu	4.303
Fe	6.17	Fe	12.27	Fe	10.555
K	1.148	K	0.984	K	0.74
Mg	0.945	Mg	7.56	Mg	7.73
Mo	0.958				
Ni	5.05	Ni	2.0		
				Na	4.622
		Pb	1.9		
S	14.34	S	0.75	S	0.125
Si	5.02	Si	5.96	Si	10.871
Ti	2.45	Ti	0.873		
Zn	4.19	Zn	1.35	Zn	0.685
		Zr	2.65		
W	12.53				

TABLE II. The elements found in the filters (PM10) from each station At(%)

Northwest	At(%)	Downtown	At(%)	Northeast	At(%)
Al	14.676	Al	3.055	Al	33.82
Ba	11.4	Ba	0.396		
Ca	2.503	Ca	0.737	Ca	0.745
		Cl	0.20		
Cr	5.23			Cr	0.21
Cu	1.05	Cu	4.72	Cu	0.7
Fe	9.15	Fe	3.054	Fe	4.157
K	0.521	K	1.566	K	0.603
Mg	1.787	Mg	1.051	Mg	1.38
		Mn	1.22	Mn	0.11
Na	1.482	Na	2.562	Na	0.893
		Pb	3.52		
S	1.575	S	0.40		
Si	3.55	Si	12.53	Si	14.43
Ti	3.041	Ti	0.36	Ti	2.225
		U	2.32		

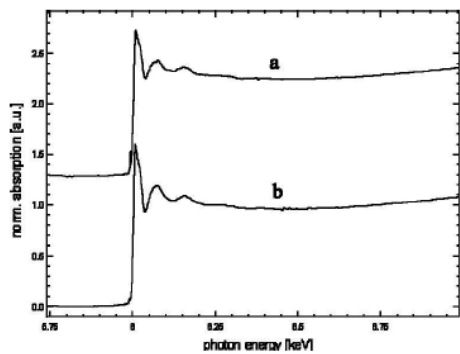


FIGURE 4. XAS spectrum of CrIII (a) and CrVI (b) present in the TSP samples.

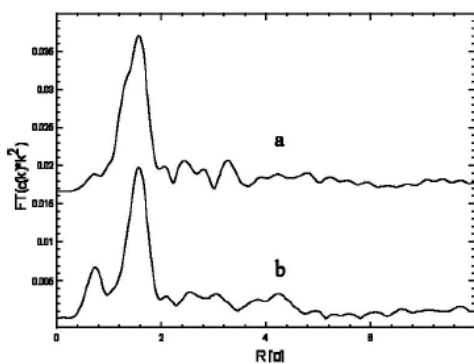


FIGURE 5. Radial distribution function of the CrIII (a) and CrVI (b) samples.

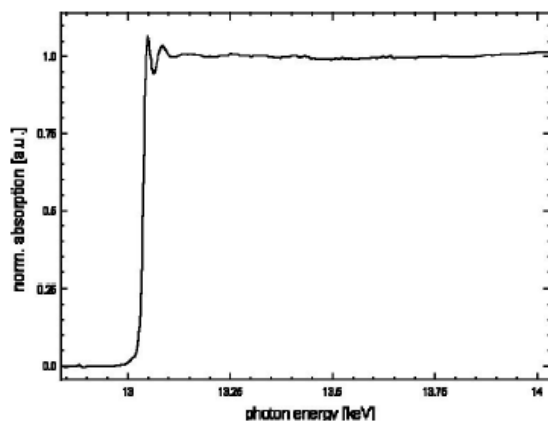


FIGURE 6. XAS spectrum of the trace element Pb.

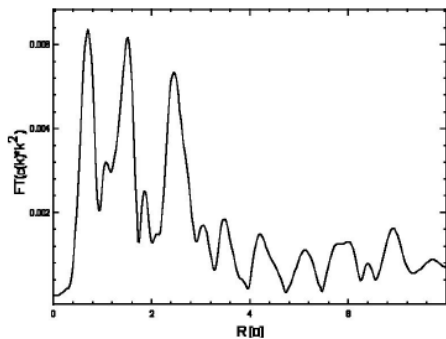


FIGURE 7. Radial distribution function of Pb.

The rare earth elements how Ce and La showed associated with P suggesting are common accessory mineral in plutonic and sedimentary rocks.

Zr is intensely associated to particles containing Fe and Ti as well as to particles with Ca and Al silicates.

Conclusion

Given that there is relatively little knowledge on speciation and size of atmospheric particles, the elements found among the atmospheric particles caught on the TSP and PM10 filters highlight the importance of individual characterization of atmospheric aerosol. This knowledge is valuable additional information about the possible actions and potential effects that air pollutants, of natural or anthropogenic origins, have within the studied area.

The chemical analyses performed on the aerosol forming conglomerates allow us to determine air quality on each city. However, these might ignore the chemical elements that occur in smaller amounts because these are not considered or detected during the elaboration the laws established according to normal determinations.

Among the particles studied, S was found in form of sulfates, both for TSP and PM10 samples. This is of particular interest because sulfates were found within every

particle analyzed. Sulfates are very important climate influents given that these particles deflect solar radiation, thus participating in global cooling. However, sulfates can also absorb this radiation and modify certain optical features of the atmosphere thanks to their hygroscopic properties, thus allowing global warming (Fig. 3).

This is the first time that the presence of U is reported within the results of a scientific research about an air quality monitoring program that is not part of a study on nuclear plants located near human population. Although the origin of the U present in the city's air suspended particles is considered to be natural, these uranium containing particles were found in all of the city's studied areas. Hence, the need of deeper, more specific studies on its possible significance for public health.

This highlights the necessity of carrying out more researches and specific studies that allow us to better know the urban aerosols to which a city's inhabitants are exposed and the need for the development of models that indicate their regional movements and their possible impact on global climate change.

Finally, results given by the XAS provide us information about the presence and concentration of trace elements, such as CrIII, CrVI and Pb, which are impossible to detect through SEM and TEM analyses.

References

1. B. Appel, Environ. SCI. Tech. 12 (1978) 418.
2. R. Alley, Manual de la Calidad del Aire, (MacGraw-Hill, México, D.F 2001).
3. ARB/SSD/SES, Toxic Air Contaminant Identification, List Summaries (1997).
4. J.D. Brain, Am. Rev. Respir. Dis. 128 (1983) S87.
5. V.L. Castranova, J Toxicol. Environ. Health 13 (1984) 845.



6. CEPA/FPAC, National Ambient Air Quality Objectives for Particulate Matter, Minister, Public Works and Government Services, (Canada 1998).
7. D.O.F. NOM-025-SSA1-1993, "Salud Ambiental. Criterio Para Evaluar la Calidad del Aire Ambiente, con Respecto a la Partículas Menores de 10 Micras (PM10). Valor Permisible para la Concentración de Partículas Menores de 10 Micras (PM10) en el Aire Ambiente, Como Medida de Protección a la Salud de la Población" (México, D.F. 1994).
8. E. Enkerlin, Ciencias ambientales y desarrollo sostenible, International Thomson Editores (1997).
9. G.D.F. Términos de Referencia para los estudios sobre el tema: Contaminación Atmosférica, CONSERVA, (México, D.F. 2002).
10. W. Hinds, Particulate Air Pollution, "Departament of Environmental Healt Sciences", (UCLA 2002).
11. P.H. Howard, Environ. Sci. Tech. 12 (1978) 398.
12. D.H.K. Lee, Environ. Res. 6 (1973) 121.
13. L. Morris Brown, Environ. Res. 34 (1984): 250.
14. I. Romieu et al., "Monitoreo de la calidad del aire" OPS, (México, D.F. 1998).
15. Secretaría de Desarrollo Urbano y Ecología. Curso sobre evaluación de la calidad del aire (técnicas manuales) (México 1985).
16. J.H. Seinfeld, Contaminación Atmosférica (Fundamentos físicos y químicos), Instituto de Estudios de Administración Local, (Madrid 1978).
17. J.H. Seinfeld, Atmospheric chemistry and Physics, John Wiley & Sons, Inc. (USA 1998).

18. A.C. Stern, Fundamentals of air pollution, Academic Press, Inc., (New York 1973).
19. K. Wark, Contaminación del Aire, 4a. Ed., Editorial Limusa, (México 1997).
20. WHO, Guidelines for Air Quality, World Health Organization, (Geneva 2002).
21. WHO, Guidelines for concentrations and exposure-response measurement of fine and ultrafine particulate matter for use in epidemiological studies, European Commission, World Health Organization (2002).
22. S. Wilson, Particles in Our Air, Concentrations and Health Effects, Harvard University Press (1996).
23. E. Drab et al., Atmospheric Environment 36 (2002) 5365.
24. A. Skogstad, M. Lene, and E. Wijnard, J. Environ. Monit. I (1999) 379.
25. L. Paoletti et al., Atmospheric Environment 37 (2003) 4869.
26. K. He et al., Atmospheric Environment 35 (2001) 4959.
27. T.A. Pakkanen et al., Atmospheric Environment 35 2001 5537.
28. X. Song, A.V. Polissar, and P.K. Hopke, Atmospheric Environment 35 (2001) 5277.
29. H. Naoe and O. Kikuo, Atmospheric Environment 35 (2001) 5765.
30. A. Aragón Piña et al., Atmospheric Environment 34 (2000) 4103.
31. L.Y. Chan and W.S. Kwok, Atmospheric Environment 34 (2000) 4403.
32. X. Querol et al., Atmospheric Environment 35 (2001) 6407.
33. F. Aldape et al., International Journal of PIXIE 1 (1991) 373.
34. A. Robache et al., Analyst 125 (2000) 1855.
35. P. Buseck and M. Pósfai, PNAS 96 (1999) 3372.

36. R.R. Chianelli, M.J. Y´acaman, and F. Aldape, Atmospheric nanoparticles in Photocatalytic and termal production of atmospheric pollutants. *Journal of Hazardous Substance Research* 1 (1998) 1.
37. J.M. Mäkelä et al., *Journal of Geophysical Research* 10 (2002) 14.
38. S. Utsunomiya and R.C. Ewing, *Environ. Sci. Technol.* 37 (2003) 786.
39. C. Xiong and S.K. Friedlander, *PNAS* 98 (2001) 11851.
40. D.B. Kittelson, W.F. Watts, and J.P. Johnson, *Atmospheric Environment* 38 (2004) 9.
41. J. Gulliver and D.J. Briggs, *Atmospheric Environment* 38 (2004) 1.
42. A.C. Lin and M.C. Goh, *Journal of Microscopy* 205 (2002) 205.
43. W. Chueinta, P.K. Hopke, and P. Paatero, *Atmospheric Environment* 34 (2000) 3319.
44. N. Mangelson et al., *J. Air & Waste Manage. Assoc.* 47 (1997) 167.
45. O. Kalashnikova and I.N. Sokolit, *Geophysical Research Leeters* 29 (2002) 38.
46. T. Rieker et al., *American Chemical Society* 15 (1999) 638.
47. K.H. Friedrichs and H. Behrendt, *Arch. Environ. Contam. Toxicol.* 32 (1997) 229.
48. W.A. Van Boro and F.C. Adams, *Atmospheric Environment* 23 (1989) 1139.
49. A. Chabas and R.A. Lef´evre, *Atmospheric Environment* 34 (2000) 225.
50. H. Ormstad, P.I. Gaarder, and B.V. Johansen, *The Science of the Total Environment* 193 (1997) 185.
51. B. Sitzmann, M. Kendall, J. Watt, and I. Williams, *The Science of the Total Environment* 241 (1999) 63.
52. B.L. Davis and Nam-Kun Cho, *Atmospheric Environment* 11 (1997) 73.

53. V. Esteve et al., *Atmospheric Environment* 31 (1997) 3963.
54. F.J.M. Rietmeijer and J. Janeczek, *Atmospheric Environment* 31 (1997) 1941.
55. B.J. Turpin, P. Saxena, and E. Andrews, *Atmospheric Environment* 34 (2000) 2983.
56. P.H. McMurry, *Atmospheric Environment* 34 (2000) 1959.
57. S. Utsunomiya et al., *Environmental Science & Technology* 36 4943.
58. T.L. Conner et al., *Atmospheric Environment* 35 (2001) 3935.
59. T.P. Jones et al., *Atmospheric Environment* 35 (2001) 3573.
60. Ch. Ro et al., *Atmospheric Environment* 35 (2001) 4995.
61. M. Wentzel et al., *Aerosol science* 34 (2003) 1347.
62. K. Okada and R.M. Hitzenberger, *Atmospheric Environment* 35 (2001) 5617.
63. L. Paoletti et al., *Atmospheric Environmental* 37 (2003) 4869.
64. S.J. Beck, *Electron Microscopy: A Handbook of techniques for the Biologist* Nassau Community College (1996) 58.
65. R.B. Husar, *Physics and Chemistry of Atmospheric Aerosol*. University of Stockholm (1976) 66.
66. EPA. 1999. *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air*. Center for Environmental Research Information Office of Research and Development U.S. Environmental Protection Agency, Cincinnati, OH
67. Department of the Environment and Heritage. 2002. *Technical Report No. 3: Review of Data on Heavy Metals in Ambient Air in Australia*. Australian Government.
68. A.T. Zimmer, A.D. Maynard, *Ann. Occup. Hyg.* 46 (2002) 663.
69. E.E. Silva-Filho et al., *J. Braz. Chem. Soc.* 9 (1998) 1.

<https://cimav.repositorioinstitucional.mx/jspui/>

70. R.F. Egerton, *Electron Energy-Loss Spectroscopy in the the Electron Microscope*,
Second Edition, (Plenum Press, New York 1996).

