

Chemical and Morphological Study of PM₁₀ Analysed by SEM-EDS

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Abstract

Single particle characterization can provide information on the evolution of size distribution and chemical composition of pollution aerosol. The work described the use of Scanning Electron Microscopy (SEM) combined with X-ray Dispersive Energy Spectrometry (EDS) to characterize inorganic atmospheric particles samples collected on PM₁₀ filters from January 2013 to October 2013 from three zones within the city of Hermosillo, Sonora. 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 SEM. The different elements found amongst individual particles were Al, Ba, Ca, Cl, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, S, Si, Ti and U. The predominant elements are Al (17.10 At%), Si (10.17 At%), Ba (5.90 At%), Fe (5.45 At%) and U (2.32 At%). The particles were classified into groups based on morphology and elemental composition: particles of aluminosilicate, salts of sodium chloride, sulfates, metal particles, barium and uranium. These particles morphology and chemical composition, illustrate an abundance of natural elements within the zone. However, some of the elements presented are directly related with human activities, and are of much interest from the public health and environmental perspectives.

Keywords

PM₁₀, Air Quality, SEM, EDS, Morphology

1. Introduction

The particulate air pollution is a growing problem in cities with emissions generating activities; these activities

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are mainly industrial and vehicular widely developed in large cities in different countries. Particulate also called aerosols air pollution is caused due to very small liquid and solid particles suspended in the air. They originate from a variety of stationary and mobile sources and may be directly emitted (primary emission) or formed in the atmosphere (secondary emission) by transformation of gaseous emissions [1] [2].

The use of Scanning Electron Microscope (SEM) has found application in the field of particulate air pollution for several years, its use has helped the study of particle morphology and single particles chemical composition. In fact, the simultaneous characterization of both physical-chemical and morphological parameters of a complex mixture of organic and inorganic particulate matter is one of the major aspects for the characterization and identification of emission sources that contribute to particulate concentrations in the atmosphere [2].

Size and chemical composition of ambient particulates strongly influence on human health, visibility and ecosystem etc. thus it is crucial to investigate the physicochemical characteristics of atmospheric particles and also to evaluate their potential toxicity. A large number of health-related studies recognized that fine particles particularly submicron sizes, penetrate deep into lung and exacerbate chronic respiratory and pulmonary diseases [3] [4]. Such diseases also induce morphological and functional alterations in human pulmonary epithelial cells [5]. Apart from this, elemental composition of particulate plays an important role in the chemical characteristics of particulate matters (PM) and provides interesting data, not only for the evaluation of its impact on human health [6] [7], ecology and environment [7] [8] but also for the identification of specific emission sources [9] [10].

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 [2]-[11].

The size of the particles is then the characteristic most studied in terms of classification and health damage. However, if other features such as the chemical composition of the particle are considered the risk of health damage would probably be higher [12] [13].

Particulate matter with aerodynamic diameters less than 10 μm (PM10) has been found to cause health problems. It can trigger or exacerbate conditions, such as asthma, emphysema, bronchitis, silicosis and lung cancer [13] [14]. PM10 has also been related to problems such as reduced visibility and unpleasant odour.

The chemical composition of inhalable particulate matter (PM10) suspended in the atmosphere is geographically variable and dependent on the type of local activity [14]. A typical mixture of PM contains sulfates (ammonium and calcium), nitrates (mainly ammonium), chlorides (mainly sodium), organic and elemental carbon (particularly related to vehicular traffic), biological materials and other organic compounds, iron compounds, trace metals and minerals derived from rocks, soil and construction, among other organic and inorganic compounds [14]-[16].

In this context, it is of fundamental importance to understand the origin, *i.e.* natural or anthropogenic, of the particles in the atmosphere. 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 [8]-[17].

Characterization of aerosol samples at the level of individual particles, using micro-analytical techniques, generally permits to obtain more unambiguous and detailed information than bulk analysis, and so it simplifies recognition of the sources of pollution and their processes [18] [19].

As the development of tools for more precise characterization of atmospheric aerosols has been steady, as is the case for the use of electron microscope as the impact it has had the use of electrons, the study of particles, has been enormous, since it has allowed to obtain a vast information on the nature, origin and chemical composition of our object of investigation [8] [10] [18].

Because the scanning electron microscope has sufficient specificity for the analysis of small particles and below the range of nanometers, we provide the information that was essential for observation of aerosols, since we can identify and fully characterize and individually, what is in our interest, from among a large group of particles [1] [2] [18].

Scanning microscope combines a brilliant image of the particle morphology, *i.e.* shape, size, roughness, etc. as well as analytical information of the chemical elements that comprise the analysis of single atmospheric particles by Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM-EDS) is a powerful tool

of recognizance emissions in urban places because the SEM may examine particles which are too small to be studied in the conventional optical microscope and also inform on the nature and origin of the particles revealed after the morphology, size and chemical composition [8]-[16].

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.

The aim of this work is identification and characterization (morphology and chemical composition) of particles present in samples of PM₁₀ as part of an air quality study by SEM-EDS.

2. Materials and Method

2.1. Study Area

Figure 1 indicates that the City of Hermosillo is located between latitude 20°01'00" and 20°08'30" north latitude and between the meridian 110°54'30" and 111°01'00" west longitude at an altitude of 200 m above sea level; is the state's capital, located to the center-west of the coastal plain, in the northwest region of Mexico.

The annual average temperature in the city of Hermosillo is $\pm 25^{\circ}\text{C}$; with an annual precipitation of 315 mm. This agrees to a dry-warm climate classification with extreme thermal oscillation, mostly of $\pm 14^{\circ}\text{C}$. 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/h 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.

In this investigation, high volume samplers were used to collect PM₁₀ from three atmospheric monitoring stations property of the Air Quality Improvement Municipal Program for the City of Hermosillo. The map shown in **Figure 2** shows these locations. 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.

Table 1 describes the characteristics each zone; 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.

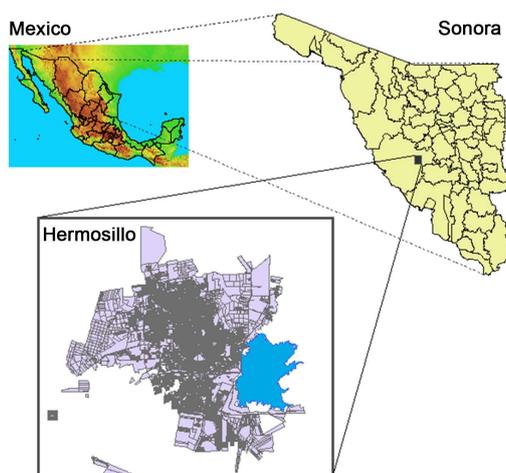


Figure 1. Geographic location.

Table 1. Atmospheric monitoring stations.

Area of the city	Characteristics of the zone
Northeast (1)	Residential and roadside
Downtown (2)	Office commercial buildings and by high traffic
Northwestern (3)	High traffic zones and commercial buildings plus areas of industrial activity

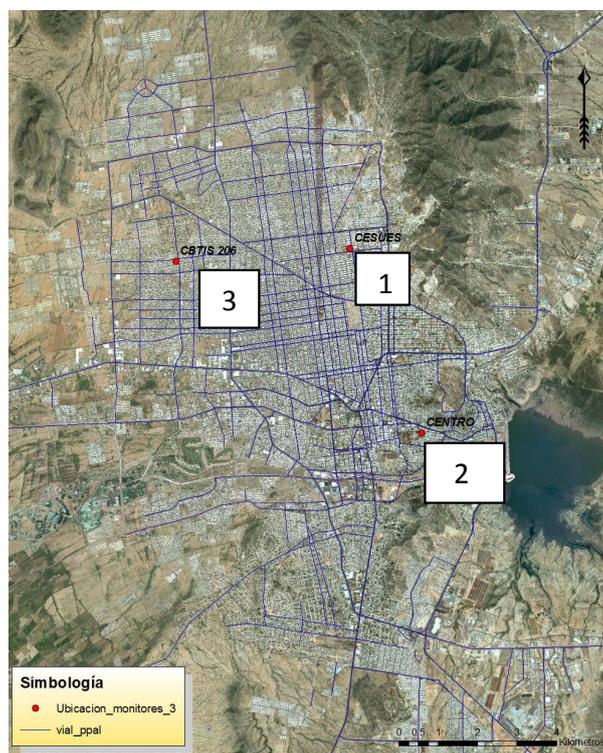


Figure 2. Hermosillo city. Station location.

2.2. Sampling

The PM₁₀ particles were collected by high-volume sampler, using a sampling flow of 1.3 m³/min. Sampling was carried for 24-h one day a week. The filters used were quartz, with size of 8 × 10 inch that captured PM₁₀ particles.

Analysis of PM₁₀ were performed using electron scanning microscopy (SEM) JEOL Model JSM-5800LV coupled with energy dispersive spectrometer (EDS) EDAX DX prime brand, for determination of morphology and elemental composition of airborne particles. Specimens were processed by separating the collected particles from the quartz 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 is introduced into the chamber of SEM.

The images of the samples were taken at a magnification of 500×, 1500×, 2500×, 5000×, 7500×, 10,000× and 35,000×. These selected magnifications allow to analyse the chemical and morphological parameters of particles in the entire particle size range considered. Spectra of individual particles were obtained after scanning an electron beam with an accelerating voltage of 15 kV for determination of individual elemental chemical composition of the particles.

Will be identified with EDS spectra the main chemical groups that make up the particles in the study area.

3. Results and Discussion

We obtained 150 images of PM₁₀ particles where its morphology and chemical composition of each particle individually was analyzed by SEM-EDS. **Figure 3** indicates compositional data of elemental chemical constituents and atomic percentage (At%) from PM₁₀ particles which showed the following elements: Al, Ba, Ca, Cl, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, S, Si, Ti and U; and the predominant elements were Al (17.10 At%), Si (10.17 At%), Ba (5.90 At%), Fe (5.45 At%) and U (2.32 At%).

In **Table 2** images and spectra of individual particles were examined and classified into six groups as particles of alumino-silicate; salts of sodium chloride; sulfates; metal particles; barium and uranium.

The analysis of the data obtained from the images and their respective spectra show that the main characteristics

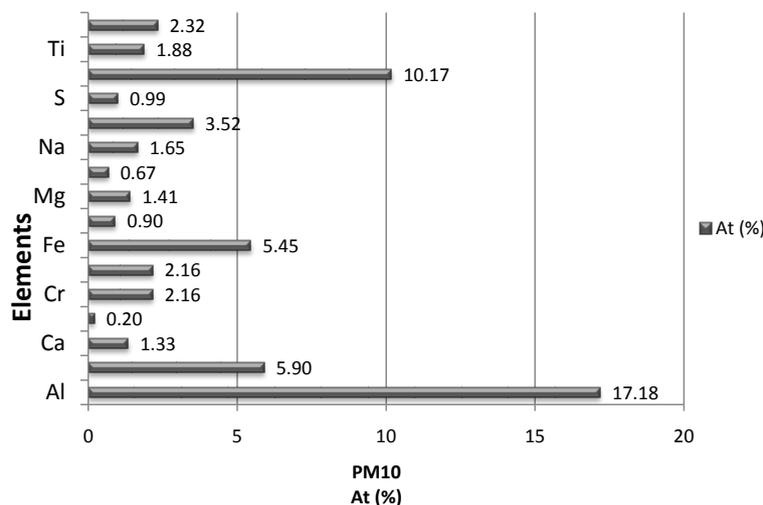


Figure 3. Majority of elemental constituents of PM10 samples in urban area (Averaged values of atomic percentage (At%) for all filter samples).

Table 2. Classification main SEM-EDS of PM10.

Groups	Subgroups	Morphology and texture of particles
1) Alumino-silicate	Oxide of silica-aluminium whit trace Na-Ca	Irregular
2) Cl-Na rich	Sodium chloride	Crystals tabular
3) Sulfates	Calcium sulfate	Simmetrical, elongated and irregular
4) Metals	Pb, Cu, Cr and Fe oxide and sulphate	Irregular and spheroidal
5) Ba-rich	barite (BaSO_4)	Edges defined
6) Uranium	Oxides and carbonates of uranium	Irregular outlying edges and fracture lines

and origin of the six groups are:

1) Alumino-silicate: these particles are composed primarily of feldspar (Al, Si, Ca or Al, Si, K) and clay (Al, Si or Al, Si, Fe), their origin is mainly crustal, but they can also come from erosion of building products and road dust. Other elements are present in minor concentration in the alumino-silicate particles and they are Na, Mg, Ti, Mn, Ni and Zn. Within the family of alumino-silicates some crustal particles rich in Si (principally quartz) as described in **Figure 4**, are included for the similar origin. These particles mainly present an angular shape, ranging from polyhedral to sharp one [2]-[10].

2) Salts of sodium chloride: as seen in **Figure 5**, these particles consist essentially of Na and Cl, sometimes traces of Mg, K, Ca and S are detected. NaCl particles are mainly due to marine aerosols. The group of sodium chloride was observed in coarse particles which are originated from sea spray and other natural and anthropogenic activities. Moreover, chloride is also converted into sodium chloride and calcium chloride in the atmosphere which may be due to the secondary particles formation. The shape of these particles is crystals tabular [14].

3) Calcium sulfate: these particles are originated by acid-base neutralization reactions in atmosphere and by deterioration of building's surface, composed of CaCO_3 (marble and limestone), and it is due to reaction with sulfur compounds in the atmosphere. Calcium sulfate, described in **Figure 6**, is also used for the production of cement and it is a secondary product of desulphurisation of flue gas. The shape of these particles is typically simmetrical and elongated, even if there are irregular examples of particles, too [9]-[12].

4) Metal: these are particles with an high metal content such as Fe, Zn, Ti, Cu, Mn, Pb and Cr. Mineral particles with irregular shape were observed in coarse particle which may be mainly derived from natural sources such as soil dust, resuspension of dust from road, crust and some other anthropogenic activities such as construction and vehicles.; particles containing mainly Fe, present in **Figure 7**, and Pb, for example, can be of crustal

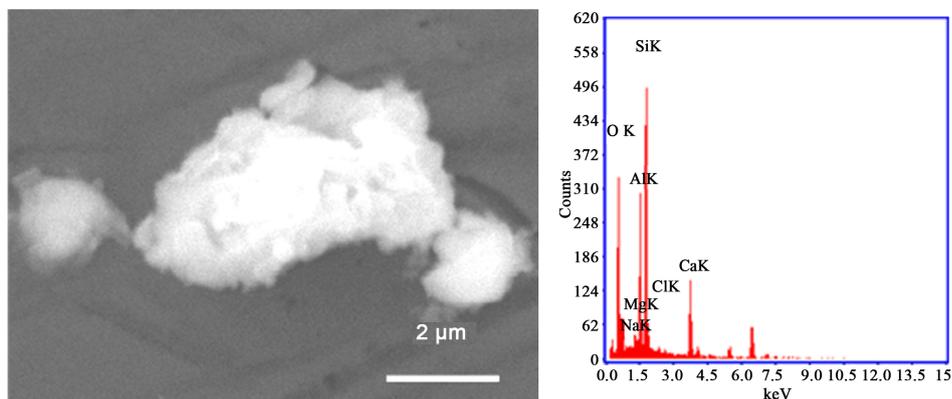


Figure 4. SEM image of quartz particle with characteristic EDS spectra.

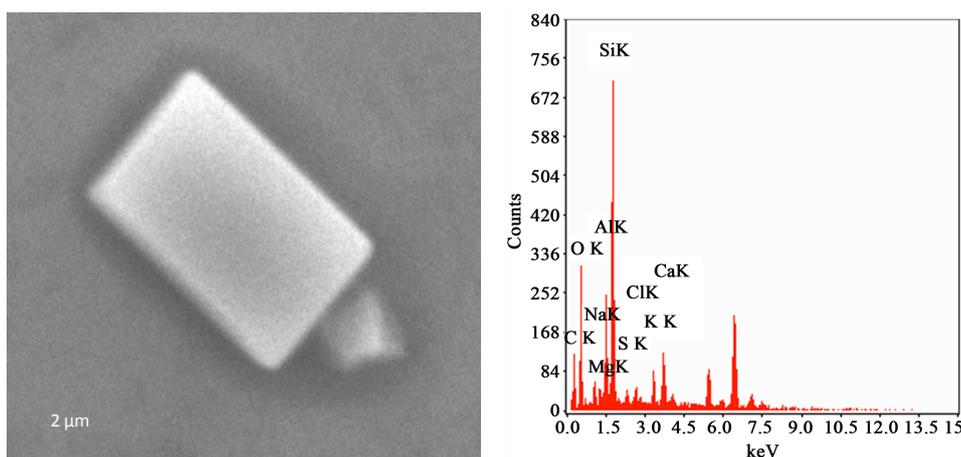


Figure 5. SEM image of sodium chloride particle with characteristic EDS spectra.

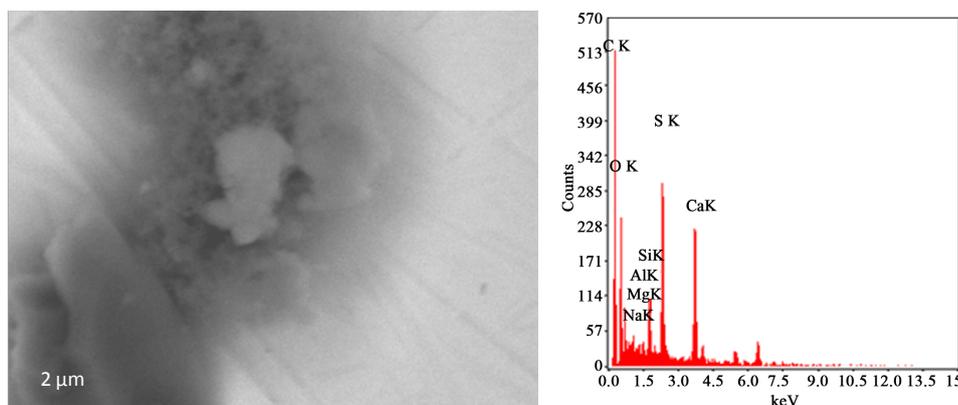


Figure 6. SEM image of calcium sulfate particle with characteristic EDS spectra.

origin, but may also come from human activities such as industrial processes, abrasion of metallic materials and traffic-related sources [15].

5) Barium: its occurrence can be explained partly as result of re-suspension processes, since high concentrations of Ba are found in soil, primarily as BaSO₄ as described in **Figure 8**, and partly due to contributions of road surface abrasion, road dust and soil resuspension, brake and tire wear [11].

6) Uranium: is a mixture of three types or isotopes called U-234/234U, U-235/235U and U-238/238U. All three are the same chemical, but they have different radioactive properties. The particles, as seen in **Figure 9**,

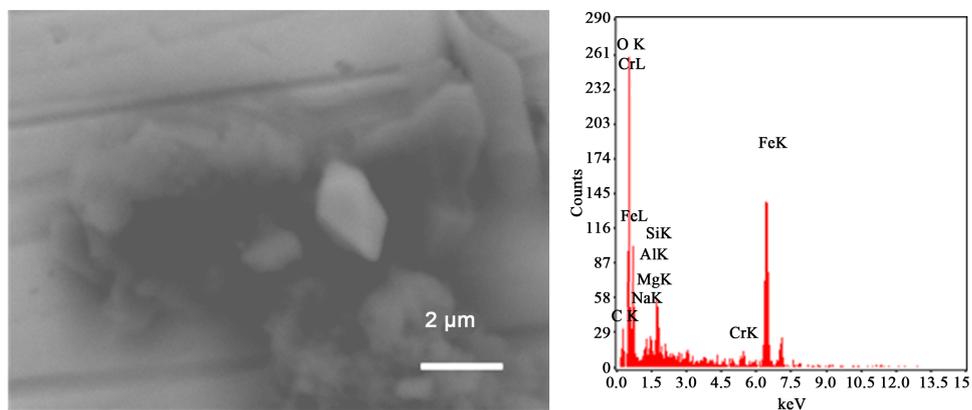


Figure 7. SEM image of iron oxide particle with characteristic EDS spectra.

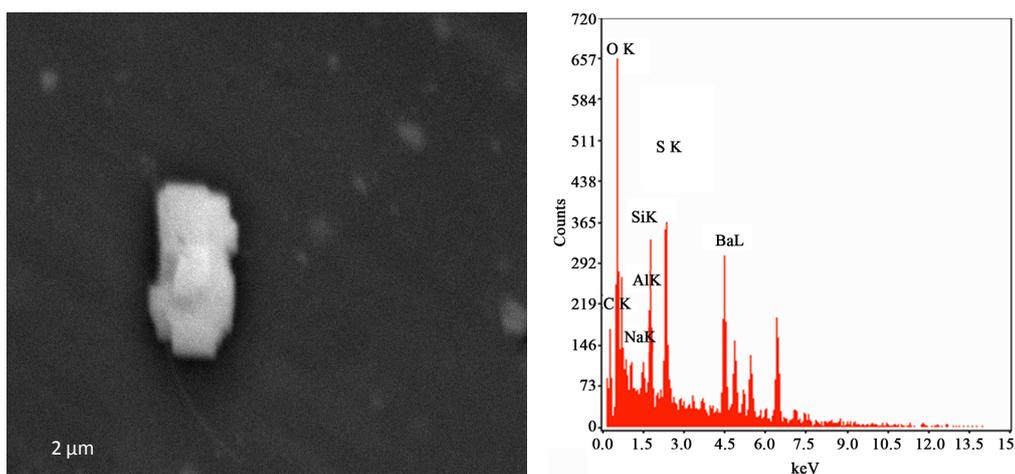


Figure 8. SEM image of barite particle with characteristic EDS spectra.

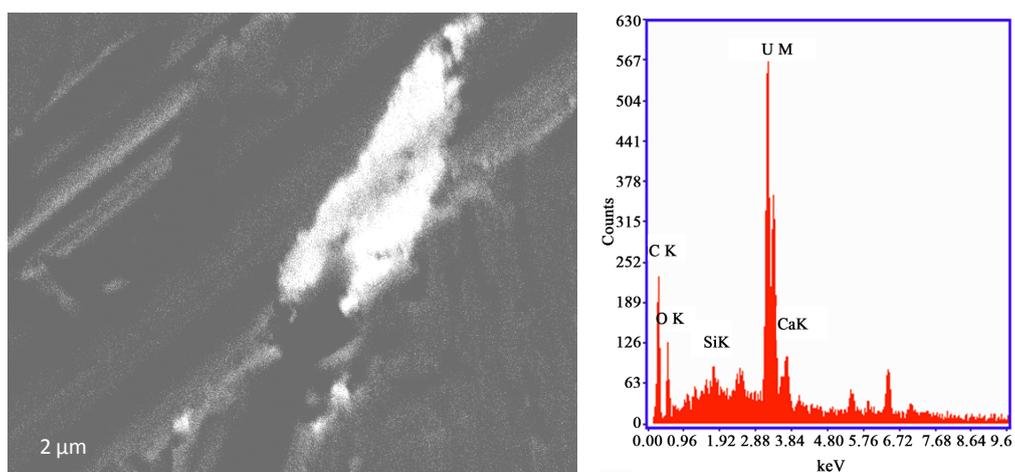


Figure 9. SEM image of uranium particle with characteristic EDS spectra.

have a matrix based on oxides and carbonates of silicon, calcium and uranium; the data indicates that the U is more than likely an intrinsic component of the mineral matrix. The structure of particles can be diverse and they usually present a two dimensional aspect. It is often found that such particles have outlying edges and fracture lines [19].

4. Conclusions

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 of the legislative standards.

The elements found in the filters of PM₁₀ indicate the importance of the individual characterization of atmospheric aerosols, because of the limited amount of information on the speciation and size of atmospheric particles, which allows us to have very valuable additional information on the potential action that these pollutants have. This knowledge is valuable additional information, within air quality program, about the possible actions and potential effects that air pollutants, of natural or anthropogenic origins, may have on the population in the study area.

The SEM-EDS technique is a valuable tool for the characterization of particles of less than 10 µm (PM₁₀). Additionally, the identification of the morphology and chemical composition of these particles provides valuable information for the determination of their origin. The results presented show the presence of a wide diversity of particles from natural and anthropogenic origin. The results from SEM-EDS microanalysis determined the main elements of the different particle groups and related them to their origin, whether natural (crustal, marine aerosol) or anthropogenic (agricultural fires, industry, fuel-oil combustion).

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