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SEM/EDS as Complementary Techniques to XRD and XRF for Structural Determination of Particulate Matter Pollution

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Airborne Particulate Matter (PM) pollution are of major concern because of its adverse health and environmental effects. Fine particulates with diameters less than 2.5 μm ($PM_{2.5}$) are of greater concern because they can penetrate deep into the lung, irritate and corrode the alveolar wall, and consequently impair lung function and cause damage to the respiratory system. Because of their large surface area, fine particles are more capable of carrying various toxic materials that can reach the end of the respiratory tract and even get into the bloodstream, causing extensive damage and increasing the risk of cancer, respiratory, cardiovascular, and ischemic heart diseases[1-5]. Anthropogenic sources such as traffic emissions will potentially be more harmful, not only because of their size, but also because of their chemical compositions. Therefore, determination of the PM chemical composition is necessary in order to identify their structure and sources. X–ray fluorescence (XRF) is a commonly used technique for the identification of the PM elemental composition, while X-ray diffraction (XRD) is used to determine crystallographic phases present in the airborne PM. The later cannot detect trace, amorphous or organic phases. Therefore, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) combined with elemental mapping can complement results obtained by both XRF and XRD. In this work, we present some examples of how SEM/EDS measurements complement XRD and XRF results.

We have carried out two simultaneous sampling campaigns for $PM_{2.5}$ and PM_{10} at a traffic site following international protocols. PM samples were collected on 47 mm diameter Teflon filters using a low volume sampler twice weekly. Mass concentrations of $PM_{2.5}$ and PM_{10} were determined from gravimetric measurements. Elemental composition was determined from XRF measurements and analysis using comparable thickness Micromatter film standards and a NIST Standard Aerosol Reference Material 2783. XRD measurements were performed using a Bruker D8 ADVANCE system with a Cu tube and a linear detector (LYNXEYE XE) [2, 6]. Imaging and elemental maps were performed for selected filters of $PM_{2.5}$ on a TESCAN environmental scanning electron microscope (VEGA3 XMU).

XRF results revealed the elemental concentrations of 22 elements in $\mu g/m^3$. For $PM_{2.5}$, most of the samples analyzed by XRD revealed the presence of two major sulfates: ammonium sulfate (Mascagnite) and calcium ammonium sulfate (Koktaite). Only a few samples showed the presence of other mineral phases. Nevertheless, XRF data revealed the presence of many other elements including Ca, Si, Fe, Al, Na, Cl and other trace elements. The two methods do not indicate any information about the chemical states of these elements. SEM and EDS elemental maps provided useful information in identifying several compounds and species that were not observed in the XRD pattern. Several minerals that could not be seen in XRD measurements were identified by integrating the elemental maps together with the XRF results. Among these minerals and compounds: Quartz [SiO_2], Calcite [$CaCO_3$], Palygorskite [$(Mg, Al)_2Si_4O_{10}(OH)\bullet_4(H_2O)$], Chlorite-serpentine [$(Mg,Fe)_6AlSi_3O_{10}(OH)_8$], sodium nitrates [$NaNO_3$] and Gypsum *[$CaSO_4 \cdot 2H_2O$]*.

We present here one example to demonstrate the use of microscopy in identifying several pollutants, both primary and secondary, that were not detected in the XRD, or helped us index low intensity peaks for nitrate and other mineral phases. Figure 1 shows the XRD pattern for sample #21 collected on February 10, 2018, a dusty day with $PM_{2.5}$ mass concentration of 42 $\mu g/m^3$. The figure shows the presence of Calcite, Quartz and Gypsum. There are no lines corresponding to Halite (NaCl) or sodium nitrate ($NaNO_3$) in this sample. Figure 2 shows the elemental maps (Si, S, Ca, O, Cl, Na and N) for the same sample. This figure shows clear correlations among the maps for Na and Cl (for Halite), Na, N and O (for $NaNo_3$), Si and O (for Quartz, S), and Ca, S and O (for Gypsum). Al, Mg and Fe (Mg and Fe are not shown) maps are also observed in the sample representing Chlorite-serpentine and/or Palygorskite. Elemental maps together with XRF data enabled us to identify all the compounds in the aerosol PM, even the compounds that were not detected by XRD. This example shows that electron microscopy and elemental mapping are very powerful tools that complement XRF and XRD in the investigation of the PM chemical composition. We will present more examples, where the XRD results show clearly the presence of only two phases (Mascagnite and Koktaite) in most $PM_{2.5}$ samples, while microscopy and elemental maps show the presence of other phases. We will also show how microscopy helped us identify low intensity peaks of sulfate and nitrate phases in the XRD patterns.

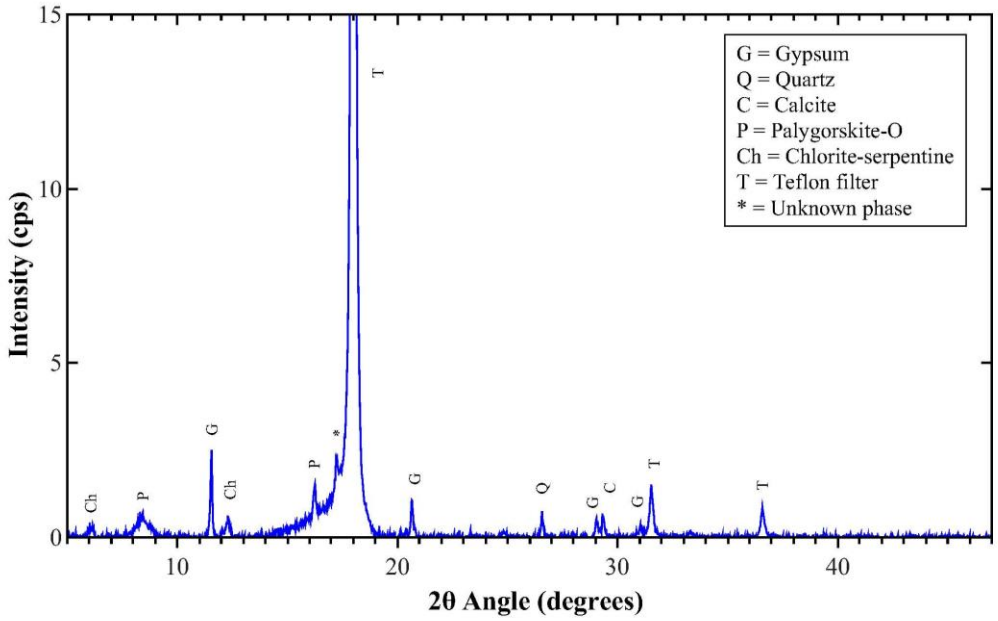

Figure 1. XRD pattern for sample # 21 collected on February 10, 2018.

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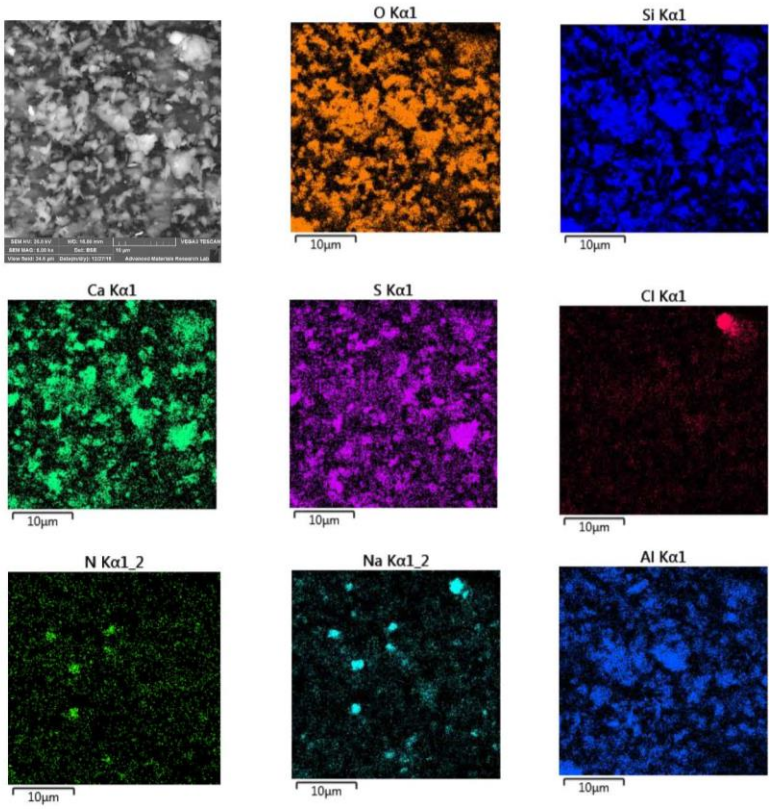

Figure 2. SEM micrograph and elemental maps of O, Si, CA, S, Cl, N, Na and Al

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