Elemental and Chemical Analysis of PM_{10} and $PM_{2.5}$ Indoor and Outdoor Pollutants in the UAE

Nasser M. Hamdan, Hussain Alawadhi, and Najeh Jisrawi

Abstract—**Knowledge of both the size distribution and elemental composition of different size fractions of aerosol particles is useful not only in providing information about the chemical composition and source apportionment of pollutants, but also in understanding the transformation chemistry of pollutants during transport in the atmosphere. We have used a low pressure-multistage inertial impactor and a double stage low volume sampler for particulate matter with aerodynamic diameter between 10 μm, and 2.5 μm respectively (PM_{10} and $PM_{2.5}$) to collect both indoor and outdoor samples. We have integrated various spectroscopic techniques to obtain complementary information about the composition of various size fractions of pollutants, their transformation and their possible sources. Our results show that the coarse fraction of PM is mainly due to natural sources such as dust storms crustal matter and seas salts, while the fine and ultrafine fractions of PM matter contains compounds created through reactions of the natural coarse pollutants with anthropogenic emissions such as sulfur dioxide (SO_2) and nitrogen oxides (NO_x), during transport in the atmosphere. The major phase of such new compounds was ammonium sulfate.**

Index Terms—**Aerosol pollution, particulate matter, source apportionment, XRF, XRD.**

I. INTRODUCTION

Air pollution in the United Arab Emirates (UAE) and in the Gulf region in general is of great concern due to its adverse public health effects. Outdoor and indoor air pollution have been identified by a national strategic plan [1], [2], to be the top two among fourteen environmental health hazards.

The number of studies dealing with aerosol air pollutants in the UAE (mainly PM_{10} and $PM_{2.5}$) has been limited. [3]-[11] $PM_{2.5}$ is potentially of greater concern for human health because the smaller particle size allows them to penetrate deeper into lungs and cause extensive damage. The existing studies lack a systematic identification of the size distribution, elemental and chemical compositions of particulate matter (PM) pollutants. In the present study, we have collected both indoor and outdoor samples of air pollutants from an urban region in Sharjah and applied spectroscopic techniques in an attempt to identify major pollutants and their possible sources.

PM pollutants are made up of different chemical species. There are two major sources of air pollutants in the UAE: natural (such as sea salts, crustal materials, soil and ash), and anthropogenic (such as industrial and traffic emissions). Natural pollutants are usually the main source of coarse particles with aerodynamic diameter between 10 μm, and 2.5 μm, (PM_{10}) while anthropogenic emissions are the main source of fine particle with aerodynamic diameter of less than 2.5 μm ($PM_{2.5}$) and ultrafine particle pollutants, with aerodynamic diameter of less than 0.5 μm. Natural emissions such as dust storms, that are common in the Gulf region, also contribute to the fine fraction of air pollution [12]-[15].

Information on elemental and chemical composition of aerosol size fractions provides insight into PM chemistry and its impact on the environment and on human health. For example, the interaction of natural and anthropogenic emissions could lead to the modification of toxicity of coarse aerosol constituents. Another example is the possibility of the reaction of nitric acid (formed from NO_x emissions) or sulfur dioxide (emitted from fossil fuel burning for energy generation and traffic) with desert dust. This can contribute to increased deposition of nutrients and acidifying agents into coastal waters.

II. EXPERIMENTAL

A. Sampling and Sampling Sites

Samples were collected from the University City, an urban area in Sharjah, United Arab Emirates. The indoor samples were collected from teaching and research laboratories at the physics department of the American University of Sharjah, during a break period in July-August 2014. The outdoor samples were collected from a backyard of a villa that is located within the University campus, away from the main road or highway, representing an urban background site.

Two different sampling methods and devices were used in the present study. Of which the first was performed utilizing a double stage ISAP 1050e sampler for PM_{10} and $PM_{2.5}$, with a constant flow rate of 2.3 m^3/h. Indoor sampling was performed over a 24 hour period with an air volume of about 55 m^3, whereas the outdoor samples were collected over a period of 12 hours with an air volume of about 27 m^3. No gravimetric measurements were performed in this study. Coarse particulates (PM_{10}) were collected on ring shaped Kapton films coated with a thin layer of Apiezone M grease to prevent bouncing, while fine particles ($PM_{2.5}$) were

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collected on 47 mm diameter Teflon filters with a 2 μm pore size and 30 μm thickness.

The second sampling method involved utilizing a PIXE cascade multi-stage, size-resolved inertial impactor which separates PM into nine different sizes. The cutoff aerodynamic diameters of PM for various stages are: 16, 8, 4, 2, 1.0, 0.5, 0.25, 0.125, 0.06 μm and less than 0.06 μm. The PM from each impactor stage was collected on Kapton coated films.

B. Elemental and Chemical Analysis

Elemental analysis was performed using an energy dispersive X-ray fluorescence technique utilizing a Horiba XGT 7200 micro XRF system with a beam size 1.2 mm. Scanning electron microscopy and energy dispersive analysis was done using a TESCAN SEM with an Oxford 50 mm^2 low vacuum detector.

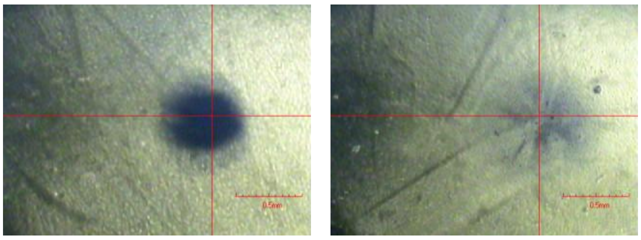
X-ray Diffraction measurements were performed using a Bruker D8 ADVANCE diffractometer.

III. RESULTS

A. Indoor Sample Results

1) Size distribution

Optical images for various size stages collected using the multistage PIXE impactor show that most indoor pollutants are of the fine size fraction (less than 0.5 μm). Very few particulates were present in the coarse fraction. Therefore, XRF measurements for the PIXE stages were performed only for the fine and ultrafine fractions (only samples with cutoff aerodynamic diameters of 0.5 and 0.25 μm). This is because this sampler utilizes a very low flow rate (1 l/min) and samples were collected for 24 h; whereas complete analysis was performed on both coarse and fine samples collected with the ISAP sampler. Fig. 1 shows optical images with the fine PM fraction.

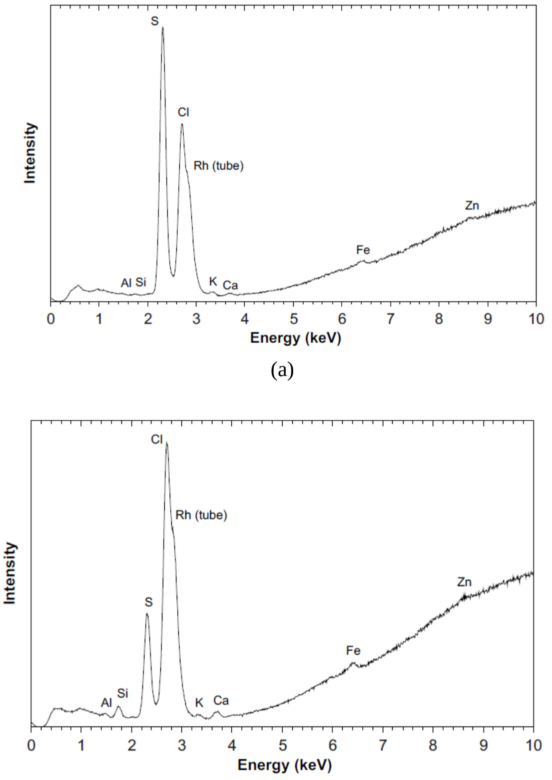


(a) (b)

Fig. 1. Optical images for samples with (a) cutoff diameter 0.25 μm and (b) 0.5 μm showing more particles density for the fine part.

2) Elemental analysis

XRF spectra of samples with aerodynamic cutoff diameters of 0.5 and 0.25 μm are shown in Fig. 2. The results show that the main constituent of the sample with 0.25μm cutoff diameter is S with about 80% mass weight, Cl about 10%, K, Ca and Al about 2%, Si about 1%, and smaller amounts of Fe and Zn. As the particle size increases, the amount of sulfur decreases. For the sample with a cutoff diameter of 0.5 μm, the amount of sulfur is about 60%, with a considerable increase of the amount of Si reaching 16% weight ratio, Al with about 8%, Ca about 6%, K and Fe about 2% and Zn about 0.3%.



(a)

(b)

Fig. 2. XRF spectra for samples with cutoff aerodynamic diameters of (a) 0.5 and (b) 0.25 μm.

Fig. 3 shows the XRF spectrum for the coarse particles with a cutoff diameter of 10 μm collected on the ring filter using the ISAP multistage sampler. Table I shows the weight percentages of various elements on the ring filter. The percentage of Si is now 37%, Ca is about 18%, whereas S is reduced to about 10%. The presence of 9% of both Mg and Al and 8% of Cl is also observed. P and Fe content are about 2% each with traces of Cu and Zn.

Fig. 4 shows the XRF spectrum of the fine fraction of the PM particles ($PM_{2.5}$) that were collected on a 47 mm Teflon filter. As expected, the major element present in the spectra is sulfur with about 90% weight ratio of the measured elements (excluding organic and inorganic carbon that are considered the major part of pollutants and can’t be detected by XRF technique). Other elements present in the spectrum are Si, Al, K, Ca and Fe and traces of Vanadium.

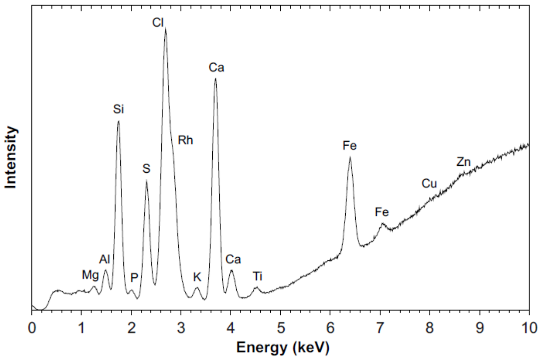


Fig. 3. XRF spectrum for the coarse particles with cutoff diameter of 10 μm that was collected on the ring filter with the ISAP sampler.

TABLE I: WEIGHT PERCENTAGES OF ELEMENTS ON THE RING FILTER

Elem.	Mass[%]
Mg	9.29
Al	9.25
Si	37.32
P	2.46
S	11.5
Cl	8.07
K	1.42
Ca	17.85
Ti	0.55
Fe	2.23
Cu	0.02
Zn	0.05

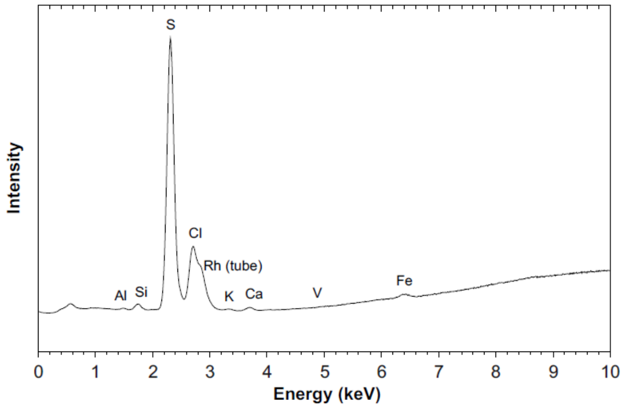


Fig. 4. XRF spectrum of the fine fraction of the PM particles ($PM_{2.5}$) that were collected on a 47 mm Teflon filter.

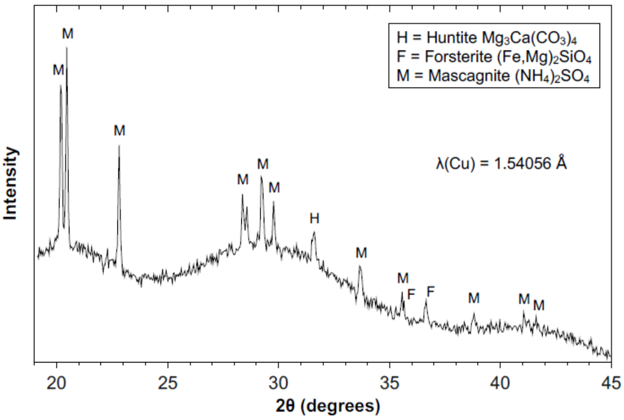


Fig. 5. X-ray diffraction pattern for $PM_{2.5}$ samples on Teflon filter.

The X-ray diffraction pattern (XRD) of $PM_{2.5}$ particulates collected on the Teflon filter is shown in Fig. 5. The Fig. 5 clearly shows that ammonium sulfate ($(NH_4)_2SO_4$) is the majority phase in the fine particles portion of air pollution and exists as a Mascagnite phase. The main peaks of this phase are labeled with (*M*) on the diffraction pattern. The pattern also shows the existence of small amounts of Huntite phase ($CaMg(CO)_3$) and even smaller amounts of Forsterite ($(Fe, Mg)_2SiO_4$).

B. Outdoor Samples Results

The optical images of all the stages of the PIXE impactor (not shown here) show that there are much more pollutants in the fine size range than the coarse one, despite having considerably more particles at all size ranges compared to the indoor samples.

XRF spectrum of the coarse fraction of particles collected on the Kapton ring filter is shown in Fig. 6. Table II shows the weight percentages of various elements on the ring filter. As it is the case for the indoor results above, the content of S is less than 10% and the major pollutants of the coarse size are Si, Ca, Al, Mg, Cl, K, Fe and Ti with traces of Cr, Mn, Ni, V, Cu, Zn and Sr, as shown in Table II.

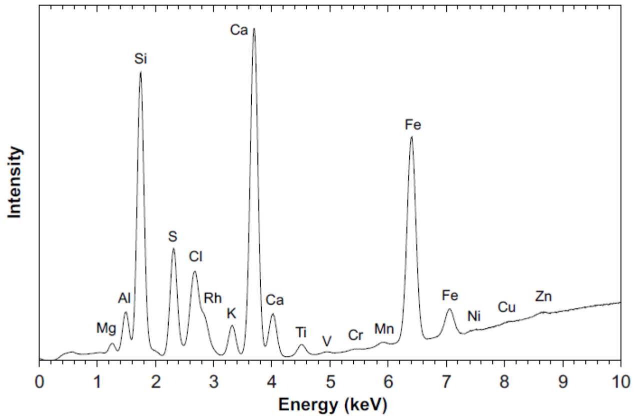


Fig. 6. XRF spectrum of the spot of the coarse fraction of particles collected on the Kapton ring filter.

TABLE II: WEIGHT PERCENTAGES OF VARIOUS ELEMENTS ON THE RING FILTER (PM_{10})

Elem.	Mass[%]
Mg	9.5
Al	10.96
Si	42.11
S	8.76
Cl	3.27
K	2.42
Ca	18.5
Ti	0.58
V	0.02
Cr	0.03
Mn	0.09
Fe	3.69
Ni	0.02
Cu	0.01
Zn	0.03
Sr	0.01

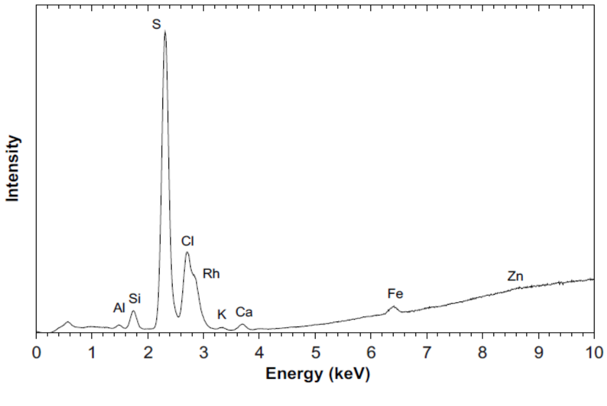


Fig. 7. A representative XRF spectrum for the fine fraction of the PM particles ($PM_{2.5}$) that were collected on a 47 mm Teflon filter.

Fig. 7 shows a representative XRF spectrum for the fine fraction of the PM ($PM_{2.5}$) which were collected on a 47 mm Teflon filter. It is obvious that the S is now the major element appearing in the XRF results with a weight ratio of about 75% and Si is now about 10%, whereas Mg, Al, Ca, Cl, Fe and Ti exist in smaller amounts and traces of Zn, Sn, Ni, Mn and V.

Fig. 8 shows the SEM-EDS elemental maps for outdoor particles on the Kapton coated foil with cutoff aerodynamic diameter less than 0.25 μm. The images show a strong correlation between S, N and O for the same particle aggregates, indicating the existence of ammonium sulfate phase as a major phase rather than ammonium nitrates.

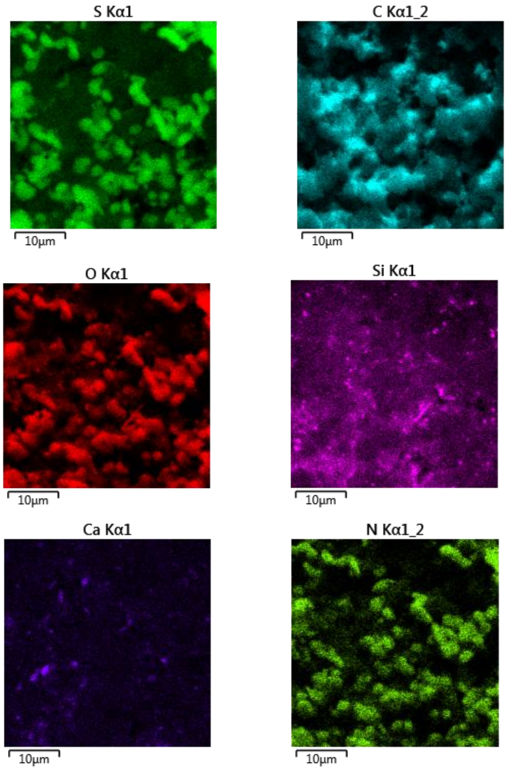


Fig. 8. SEM-EDS elemental maps for particles on the Kapton coated foil with cutoff aerodynamic diameter less than 0.25 μm.

IV. DISCUSSIONS

A. Fine and Ultrafine Particles

The above results clearly show the existence of F as a major element detected by XRF in the fine and ultrafine fraction of particle pollutants. SEM-EDS maps shown in Fig. 8 also show an excellent correlation between S, N and O elemental maps for the majority of the particles in the mapping area of 10 μm. The micrographs also demonstrate evidence that the particles on this film are of the expected ultrafine size of 0.25 μm or less, as observed in the Si and Ca maps.

Ammonium sulfate ($(NH_4)_2SO_4$) is produced as a secondary pollutant through the reaction of sulfur dioxide (SO_2) emitted from power plants with ammonia(NH_3) and ammonium compounds associated with traffic emissions, fertilizer applications, agricultural operations and livestock. Ammonium sulfate is usually formed as a liquid or solid with particle size of less than 0.5 μm [16]-[21]. Unlike ammonium nitrates that require high humidity conditions in the atmosphere, ammonium sulfates form at all ranges of atmospheric humidity.

Considering all pollution sources, it is established [22] that organic carbon represents about 75% of the ultrafine particles (<0.1 μm in diameter), elemental carbon is about 10%-15% and the rest is due to metals and sulfates, whereas for the fine particles (< 2.5 μm) elemental and organic carbon form about 30%-40% % of the pollutants and the rest is due to nitrates, sulfates and metals. Contribution of sulfates and nitrates is about 60%-70% of the total elements detected by XRF according to a study done for Los Angles California [22].

Our results for fine and ultrafine particle show that elemental and chemical compositions are consistent with the findings in [16], where the sum of the metallic element percentages ranges from 10% for the ultrafine portion of particles, to about 25% for the fine fraction of pollutants measurable by XRF.

The XRD pattern shown in Fig. 5 indicates that natural pollutants such as Si, Ca, Fe, Mg, originating form dust storms (SiO_2), sea salts (MgCl and KCl) and crustal materials ($CaCO_3$), interact with anthropogenic emissions (SiO_2) and (NO_x) to form secondary pollutants in the fine and ultrafine size ranges of particles. These interactions have modified the particulate compositions and their toxicity by creating new compounds with fine and ultrafine particles, which may have serious public health impacts.

B. Coarse Particles

The main sources of coarse pollutants are dust storms, building and crustal materials and sea salts. The above results show that Si constitutes more than 40% in the weight ratio of the PM pollutants. The UAE experiences frequent desert dust storms that contribute to the large amount of Si seen in the coarse fraction. The amount of Si is reduced to 10% weight ratio for the fine particles ($PM_{2.5}$) and to only 1% for the ultrafine fraction ($PM_{0.25}$). The EPA report mentioned in [22] summarizes the compositions of PM pollutants for the coarse fraction (particles between 2.5 μm to 10 μm) for Los Angles, California. It shows that organic and elemental carbon represent only about 10% -15% of the pollutants (which are not measurable by XRF or XRD), while sulfates represent about 15%. Our results for the coarse particles above show that the percentage of S is about 12% indoors and about 8% outdoors. This is expected, as less coarse particles enter an air conditioned, sealed room, and therefore, a higher fraction of fine particles is expected indoors.

V. CONCLUSIONS

The above results and discussion show that the coarse fraction of PM pollutants is mainly due to direct natural sources, whereas the fine and ultrafine portion is due both to anthropogenic emissions and natural sources. The integration of XRF, SEM-EDS and XRD techniques was very useful in reaching the results obtained in this study, particularly determining the chemical composition of the fine and ultrafine fraction of PM pollutant and the formation of new compounds as a result of chemical interaction of natural and anthropogenic pollutants. Reduction of anthropogenic emissions (mainly SO_2 and NO_x) will lead to considerable reduction of the health impacts of these fine and ultrafine pollutants. In recent years, UAE has started building nuclear power plants, a project that will lead to a considerable reduction of these emissions.

The above results have also been observed on several other indoor and urban background outdoor samples collected from Sharjah [23]. We will extend this work using more samples collected from different sites (near highways, industrial and residential areas) by following a systematic sampling campaign, to include time dependent investigation to study weather effects (temperature and humidity), in addition to gravimetric measurements

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