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Journal of Aerosol Science (ISSN: 0021-8502)

Citation for the published paper:
Shaltout, A. ; Boman, J. ; Shehadeh, Z. (2015) "Spectroscopic investigation of PM2.5 collected at industrial, residential and traffic sites in Taif, Saudi Arabia". Journal of Aerosol Science, vol. 79 pp. 97-108.

http://dx.doi.org/10.1016/j.jaerosci.2014.09.004

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PII: S0021-8502(14)00149-9
DOI: http://dx.doi.org/10.1016/j.jaerosci.2014.09.004
Reference: AS4825

To appear in: *Journal of Aerosol Science*

Received date: 9 August 2014
Revised date: 25 September 2014
Accepted date: 29 September 2014

Cite this article as: Abdallah A. Shaltout, Johan Boman, Zuhair F. Shehadeh, Dhaif-allah R. Al-Malawi, O.M. Hemeda, Mohamed Morsy, Spectroscopic investigation of $PM_{2.5}$ collected at industrial, residential and traffic sites in Taif, Saudi Arabia, *Journal of Aerosol Science,* http://dx.doi.org/10.1016/j.jaerosci.2014.09.004

Spectroscopic investigation of $PM_{2.5}$ collected at industrial, residential and traffic sites in Taif, Saudi Arabia

Abdallah A. Shaltout[a,b,*], Johan Boman[c], Zuhair F. Shehadeh[a], Dhaif-allah R. Al-Malawi[a], O. M. Hemeda[d], Mohamed Morsy[e]

[a] *Physics Department, Faculty of Science, Taif University, 21974 Taif, P.O. Box 888, Saudi Arabia*

[b] *Spectroscopy Department, Physics Division, National Research Center, El Behooth Str., 12622 Dokki, Cairo, Egypt*

[c] *Department of Chemistry and molecular biology, Atmospheric Science, University of Gothenburg, SE-412 96 Göteborg, Sweden*

[d] *Physics Department, Faculty of Science, Tanta University, Tanta, Egypt*

[e] *Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*

* Corresponding author; E-mail address: Abdallah A. Shaltout (shaltout_a@hotmail.com)

Telefax: +202 3337 0931

Telephone: +202 3366 9974-2101

Abstract

The present work aims at detecting and characterizing the semiquione free radicals and inorganic composition of atmospheric aerosols particles, $PM_{2.5}$, collected at three different sites (industrial, residential, and traffic dominated) in Taif city, Saudi Arabia, during 2011/2012. $PM_{2.5}$ particles have been collected on polycarbonate filters in a collection cartridge in a cyclone. The duration of the collection was 24 h at an air flow of 3 L min^{-1}. The average $PM_{2.5}$ mass concentration was 37 ± 22 μg/m^3, 57 ± 22 μg/m^3 and 50 ± 31 μg/m^3 at the residential, industrial and traffic sites, respectively. These values are higher than the target value for air quality standards of European Union (25 μg/m^3). Energy Dispersive X-ray Fluorescence (EDXRF) and Electron Paramagnetic Resonance (EPR) spectroscopic techniques were chosen for sample analysis. Fourteen elements were quantified by EDXRF; Si, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Rb, Sr and Pb. The measured concentrations of the potentially hazardous trace elements As, Cu, Sb, Cr, Mn, Ni and Pb were either below the detection limit or below the limits defined by international guidelines and national standards of ambient air quality. Furthermore, electron paramagnetic resonance (EPR) technique was used for testing and identifying paramagnetic species in the $PM_{2.5}$ particles.The EPR spectra of $PM_{2.5}$ from the three sites have a g-value in the range from 2.0033 to 2.235 which is characteristic for semiquinone radicals. The $PM_{2.5}$ samples showed three EPR signals indicate to the presence of semiquinone radical anion.

Keywords: Atmospheric aerosols $PM_{2.5}$; Energy Dispersive X-ray fluorescence; Electron paramagnetic resonance.

1. Introduction

Among the environmental problems, air pollution, especially particulate matter (PM), attracts the attention of many researchers. Particulate matter represents the particles found in the air including dust, dirt, soot, smoke and liquid droplets coming in a wide range of sizes (Stephanou 2012). Particles with an aerodynamic diameter ≤2.5 μm ($PM_{2.5}$) have received attention over the years as they, compared to particles >2.5 μm, have an higher probability of deposition in the respiratory system, from the tracheobronchial tract and deeper in the lung (Chaloulakou et al. 2003; Englert 2004; Gilmour et al. 2004, Stephanou 2012). Once inside the lungs they can aggravate respiratory conditions which might lead to respiratory diseases. During the last decades, many epidemiological studies have focused on the connection between concentrations of ambient particles and daily mortality (Goldberg et al. 2013; Green& Armstrong 2003). $PM_{2.5}$ occurs in the atmosphere from natural sources like volcanoes, dust storms, forest and grassland fires, living vegetation and sea spray. In addition, anthropogenic sources such as the burning of fossil fuels in vehicles, power plants, and various industrial processes contribute to $PM_{2.5}$.

Many spectroscopic methods are utilized for characterization of atmospheric particles. X-ray fluorescence (XRF) spectroscopy, mainly energy dispersive X-ray fluorescence (EDXRF), is one of the most common one (Boman et al. 2013; Shaltout et al. 2013; Boman et al. 2010). It is a powerful technique in discovering many of the elements in air particulate samples without any sample preparation. Unfortunately, knowing the elements alone may not be enough to solve all environmental problems associated with particulate air pollution. In fact, many recent studies have proved that certain environmental problems are associated with species in the air particles that contain unpaired electrons, (free radicals, paramagnetic molecules, organic ion-radicals, etc.). Electron Paramagnetic Resonance (EPR) spectroscopy is a technique for studying materials with unpaired electrons. It is highly selective, non-destructive, simple and inexpensive. Furthermore, the analysis of radical species with EPR may reveal the conditions of the generation and chemical

changes of the PM in the atmosphere. Studies of electron paramagnetic resonance (EPR) have been reported in coals, chars, and soot (Yamanaka et al. 2005; Van Maanen et al. 1999), however, EPR studies of atmospheric $PM_{2.5}$ have been insufficient (Dellinger et al. 2001; Gehling et al. 2014). A previous EPR study reported that the fractions of elemental carbon in PM were in the range of 31–84%, and averaged 63% (Zielinska et al. 1998). EPR of carbon-centered radicals in charcoal is used for oximetry especially in vivo biological measurements (Jordan et al. 1998). Recently, the carbonaceous PM (particulate matter or soot) and the suspended particulate matters (SPM) from automobile exhaust was investigated by EPR dosimetric technique (Yamanaka et al. 2005). The existence of hydroxyl radicals (HO) in the total suspended particulates, diesel and gasoline exhaust particles and urban streets dust from Athens, Greece was confirmed by EPR (Valavanidis et al. 2000). Results showed that oxidant generating activity is related with soluble iron ions and the urban particulate matter can release large amounts of Fe^{3+} and lesser amounts of Fe^{2+}. Additional epidemiologic studies (Valavanidis et al. 2008) showed statistical associations between particulate air pollution in urban areas and increased morbidity and mortality. As the size of particulate matters decreases, the toxicity through mechanisms of oxidative stress and inflammation increases. An EPR study of particles in tobacco smoke (Valavanidis et al., 2009) showed that there was synergistic effect between identified radicals and $PM_{2.5}$ particles illustrating the benefit of studying both radicals and $PM_{2.5}$ simultaneously. Several reports on the biological effects of combustion emissions are indicative of free-radical-mediated damage of the type that can be initiated by semiquinone-type radicals (Samet et al. 1995; Sagai et al. 2000; Oettinger et al. 1999). Recently, it has become evident that fine particulate matter has the ability to generate reactive oxygen species (ROS) (Pryor 1997; Hellack et al., 2014). Furthermore, iron and other contents of the particulate matters play a major role in ROS generation (Donaldson et al. 1997; Van Maanen et al. 1999). Diesel exhaust particulates, a major constituent of $PM_{2.5}$, have a remarkable role for the involvement of oxygen radicals in lung carcinogenesis (Sagai et al. 2000).

In the present work, atmospheric $PM_{2.5}$ from Taif city, Saudi Arabia, were characterized by energy dispersive X-ray fluorescence (EDXRF) spectrometer equipped with a secondary target of Mo. Since one of the main sources of airborne fine particles is combustion and combustion sources generate stabilized free radicals (Stone et al. 1995), we suspected that $PM_{2.5}$ may contain radicals. For this reason the samples of $PM_{2.5}$ were examined using electron paramagnetic resonance (EPR).

2. Experimental Setup

2.1. Sampling

The atmospheric aerosol particle samples, $PM_{2.5}$, were collected from three different sites, namely; industrial (Industrial district), residential (Television Street) and a traffic dominated site (Abobakr Street), in Taif city, Saudi Arabia, during the period from October 2011 to June 2012. The industrial site is situated in the industrial district, 8 km northwest from the center of the city, while the residential site is located at the highly populated area of Taif city, Television street, southeast from the city center. The third site represents a traffic dominated site and it is located at the center of the city which is the most crowded street, Abobakr Street. Four PM samples were collected every month from each site (1 sample/week/site). The samples were collected on polycarbonate filters loaded inside a collection cartridge in a cyclone (CASELLA Company, UK). It was operated with a flow rate of 3 L min^{-1}. The flow rate was maintained by a critical orifice placed between the pump and the cyclone. The polycarbonate filters have a diameter of 25 mm and a pore size of 0.4 μm. These filters were used in previous studies and have high particle collection efficiency (Boman et al. 2013; Shaltout et al. 2013; Boman et al. 2010). The duration of the collection of each sample was 24 h with filters being exchanged at 11 am. In order to avoid the influence of traffic as a single source, the equipment (cyclone, flow meter, and the pump) was mounted on 20 m height, and more than 50 m from the nearest main road.

2.2. Energy Dispersive X-Ray Fluorescence

The Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer used for the analysis of the atmospheric aerosols samples is built in a three-axial arrangement around a silver fine focus X-ray tube and utilizes a molybdenum secondary target that makes the beam almost monochromatic before it reaches the sample (Boman 1999; Chimidza 2001). The spectra from the EDXRF are further processed by the PyMca software package (Solé et al. 2007) before converting the results into airborne concentrations (ng/m^3). The EDXRF method of analyzing samples is multi-elemental, easy to use and inexpensive compared to many other analysis techniques for determination of the elemental content of samples. For most of the elements from Ca to Y, it gives elemental concentrations within an error margin of 10%, primarily due to instrument specific uncertainty. From S to K, the error margin is between 20 to 25 % mainly because the X-ray intensity is lower for these light elements. The error margins are specific to the present EDXRF setup. The detection limits for the EDXRF were calculated in accordance with the procedure and guidelines given by the International Union of Pure and Applied Chemistry (IUPAC 1976). The detection limits given as absolute amounts and as minimum airborne concentrations are shown in Table 1. The validity of the obtained results was confirmed at a level of confidence equal p=0.05 (Boman et al. 2013; Shaltout et al. 2013).

Table 1. The detection limits (DL) for the elements determined by EDXRF. The detection limits are given in ng for the absolute mass per filter, as well as in ng/m^3 for the lowest detectable atmospheric mass given the flow of 3 L min^{-1} and a collection time of 24 hours.

Element	Detection Limits	
	ng	ng/m^3
S	1000	230
Cl	500	120
K	110	25
Ca	77	18
Ti	31	7.1
V	20	4.6
Cr	10	2.3
Mn	9.2	2.2
Fe	8.5	2.0
Ni	6.0	1.4
Cu	4.5	1.0
Zn	4.8	1.1
Br	4.8	1.1
Rb	4.7	1.1
Sr	4.8	1.1
Pb	5.6	1.3

2.3. Electron Paramagnetic Resonance (EPR)

It is well known that EPR is the only technique for studying paramagnetic chemical species that have one or more unpaired electrons, such as organic and inorganic free radicals or inorganic complexes possessing a transition metal ion (Dellinger et al. 2001; Jordan et al. 1998). The effective g-value has a great importance and it has been determined by comparison with 2,2-

diphenyl-1-picrylhydrazyl (DPPH) as a standard. The effective g-value can be calculated using the relation $g_{sample} \times B_{sample} = g_{std} \times B_{std}$ where g_{std} is the effective g-value of DPPH which is very close to the value of unpaired electron = 2.0026 and B_{std} is the value of the magnetic field of this standard and it is equal 3.375 kG (Dellinger et al. 2001). The EPR spectra of all atmospheric $PM_{2.5}$ samples were measured at room temperature using MiniScope MS300 spectrometer, Magnettech GmbH, Germany, equipped with rectangular TE102 X-band resonator. The tissue cell consists of a flat part (sample holder) with the dimensions 65x7x2 mm and the cover slide was used as sample holder in this study. The polycarbonate filters with and without samples were carefully folded and sandwiched between the two quartz plates of the electron paramagnetic resonance (EPR) tissue sample holder. The typical EPR parameters are 100 kHz X-band; microwave frequency 9.395 GHz; attenuation 15 dB; modulation amplitude 4 G; time constant 1 s; receiver gain 2500; scan time 2 min and scan range 100 G. At the maximum magnetic field in the cavity, EPR spectra of the atmospheric $PM_{2.5}$ particles were recorded as first derivative spectra.

2.4. Carbon Reflectometer

The present EDXRF setup cannot be used for carbon determination due to the limitation of the present Silicon Drift Detector (SDD), and that the analysis is made in ambient air instead of under vacuum condition. Therefore, a black smoke detector model FH621-N (ESM Emberline, Erlangen, Germany) was used to determine the Black Smoke (BC) concentrations in the samples. It is a reflectometer that has light emitting diodes (LEDs) and photo sensors enclosed in a completely black casing (Reid et al. 2005; Heintzenberg & Bussemer 2000).

3. Results and Discussion

3.1. $PM_{2.5}$ mass concentrations

In order to calculate the mass concentration, the filters were weighed before and after sampling using a microbalance with μg-range. The average concentrations of each month as well as the average of the whole period of study were calculated. The average $PM_{2.5}$ mass concentration was 37 ± 22 μg/m^3, 57 ± 22 μg/m^3 and 50 ± 31 μg/m^3 at the residential, industrial and traffic dominated sites, respectively. Compared to the European commission's target value of the yearly mean of air quality standard (25 μg/m^3) for ambient air (European Commission, (2012), the average concentrations of $PM_{2.5}$ at the three sites range from one and half time at the residential site to two times higher at the industrial and traffic sites. A seasonal variation can be noticed when these concentrations are compared to the $PM_{2.5}$ concentrations obtained in the summer period of 2011, 46 ± 31 μg/m^3 and 47 ± 15 μg/m^3, at the same residential and industrial sites, respectively (Shaltout et al., 2013). The $PM_{2.5}$ averages in this study are also higher than the average $PM_{2.5}$ mass concentration in Jeddah city in 2011, 28.4 ± 25.4 μg/m^3 (Khodeir et al., 2012). Moreover, the mass concentrations of $PM_{2.5}$ collected in the end of March 2012 were remarkably high compared to the average concentrations. Especially the samples from the traffic site had four times higher PM concentration in the end of March 2010, compared to the average of the whole measurement period, Figure 1. This is correlated with the variations of the local climate and the strong north westerly winds blowing over Iraq and Saudi Arabia that creats remarkable sandstorm during that month. Fine and ultrafine particulates of dust and suspended particulate matter are also resuspended by the traffic, contributing to the higher concentrations at the industrial site. Additional high mass concentrations of $PM_{2.5}$ collected from the industrial site were seen in May 2012. The possible explanations for the variation are different industrial activities at the industrial location such as

metallurgical activities, blacksmithing and construction, and waste burning. The mass concentrations of $PM_{2.5}$ collected during other months do not show the same dramatic variation.

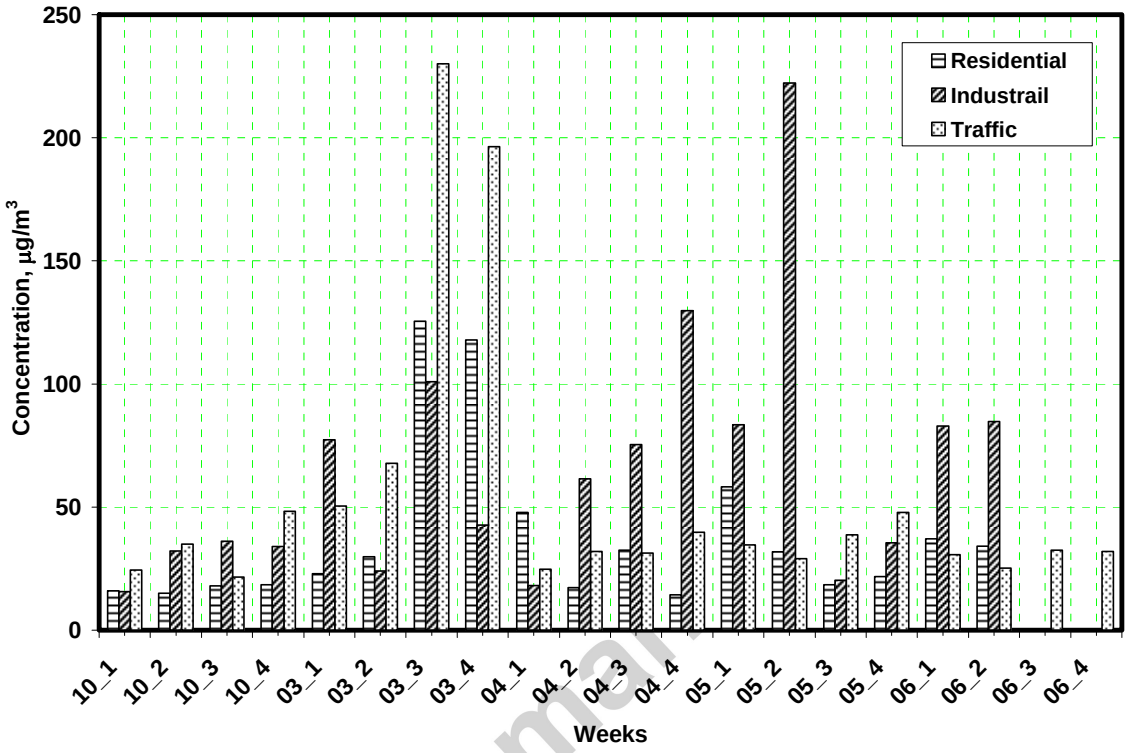


Figure 1, The mass concentration of $PM_{2.5}$ collected from residential, industrial and traffic areas of Taif city, Saudi Arabia. XX_Y denotes month and week number in 2011 and 2012 when the samples were collected.

3.2. Trace element concentrations

The final concentration of the elements in the atmospheric aerosol samples were given in ng/m^3. Figure 2 illustrates the measured characteristic fluorescent radiation as well as the fitting of each line for one of the present atmospheric aerosol samples collected from the industrial site. The scattering radiation of Mo secondary target was located above 16 keV and it was removed from the figure. As illustrated in Figure 2, fourteen elements could be determined in most of the samples.

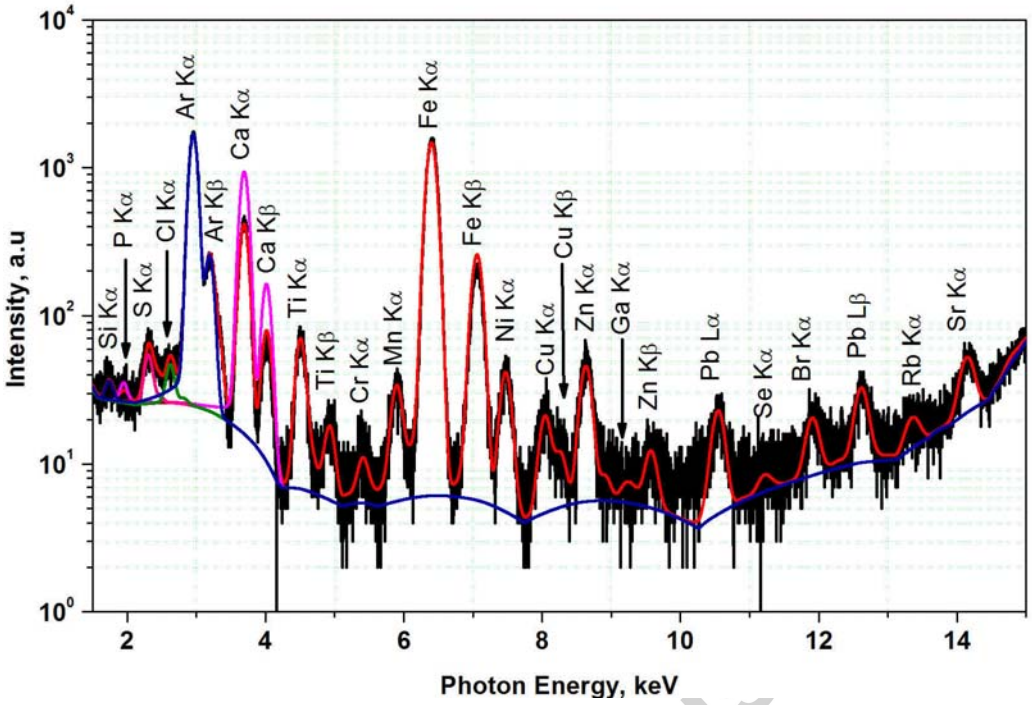


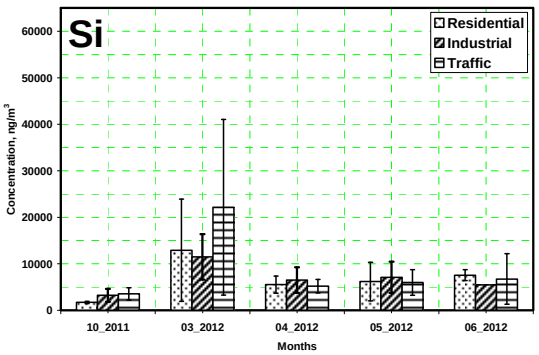
Figure 2, EDXRF spectra showing the identified trace elements in $PM_{2.5}$ collected at industrial site of Taif, Saudi Arabia.

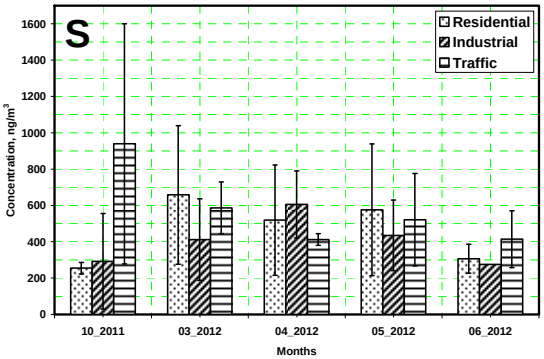
Figure 3 illustrates the average concentrations of some of the trace elements during the months of collection for the period of study. A high concentration of crustal elements (Si, Ca, Fe, K, Ti, Sr) was observed during March 2012, which could be related to the natural source of air pollution during that month, namely windy dust in the city, as already seen by the high PM concentration of March 2012. There are two possible reasons for the increased Sr concentration during March; firstly, Sr is formed by radioactive decays of ^{87}Rb that may arrive with the north westerly winds; secondly, by using LED television, there is a great number of useless cathode ray tubes in the wastes where Sr compounds are one of the main compounds. On the other hand, the concentrations of S, C, Cu, Zn and Pb didn't increase during March 2012 that confirms that these elements come from anthropogenic source of air pollution.

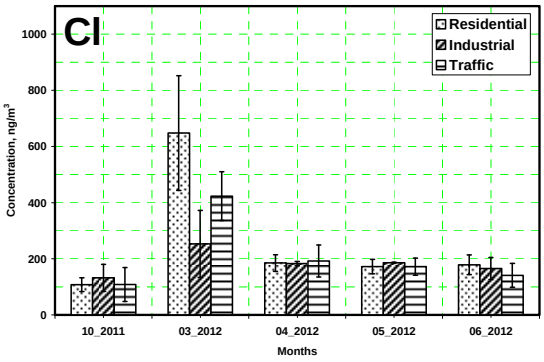
The ratios of the concentrations of the measured elements including Black Carbon (BC) to the mass concentrations of the collected samples equal 36 %, 24 % and 34 % for traffic, industrial and residential sites, respectively. Most of the elements were present at comparable levels in the industrial, residential and traffic dominated sites. In the case of Ni and Pb the average monthly concentrations indicated that the concentrations are below the European air quality standard level, 20 ng/m^3 and 500 ng/m^3, respectively, Table 2. During March 2012, the highest concentrations of Ni were found; 8.5 ng/m^3, 5.6 ng/m^3 and 9.7 ng/m^3 in the residential, industrial and traffic sites, respectively, Figure 3. This indicates that Ni is related to the natural sources such as the windblown dust as well as to anthropogenic sources like the motor vehicle emission and the different industrial activities (Shaltout et al. 2014). There is no clear seasonal trend in the Pb concentrations, Figure 3. It was found that the highest Pb concentrations in the residential, industrial, and traffic dominated sites were found during October 2011, March 2012 and May 2012. The relatively low Pb concentration in $PM_{2.5}$ particles in Taif city would refer to the banning of leaded gasoline in Saudi cities (Abulfaraj et al. 1999, Aburas et al., 2011). Based on Köppen-Geiger climate classification system (Peel et al. 2007), Taif city has arid or hot desert climate (Bwh), giving Taif a hot and dry summer and warm and dry winter. Figure 4 shows the minimum, maximum and average temperatures during the period of study. The temperature rise up from March 2012 and reaches to the maximum values during June 2012, Figure 4. The concentration of Black Carbon (BC) is generally small compared to the total $PM_{2.5}$ mass as indicated in Table 2. BC constitute 1.6%, 2.5% and 3.8% of the $PM_{2.5}$ mass at the residential, industrial, and traffic sites, respectively. It is recognized that the traffic site has the highest value of BC, which is probably correlated to the vehicle-related emissions (both exhaust and non-exhaust). During last years, the fast increase in vehicles population in Taif city and the increasing traffic congestions could be reasons for the observed BC concentrations (Oanh et al. 2010). The present BC content seem to be lower than the one found in Ouagadougou, Burkina Faso where it was 5.5% (Boman et al. 2009) and in Cairo, Egypt where it was 7.3% (Boman et al. 2013), indicating a better vehicle standard in Taif city.

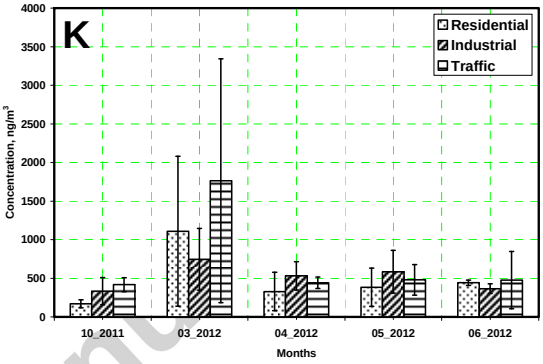
Table 2. Average concentrations and standard deviations (SD) in ng/m^3. QL refers to European yearly air quality limits valid from 1 January 2013 for Ni, already in force for Pb and $PM_{2.5}$. BC = Black Carbon.

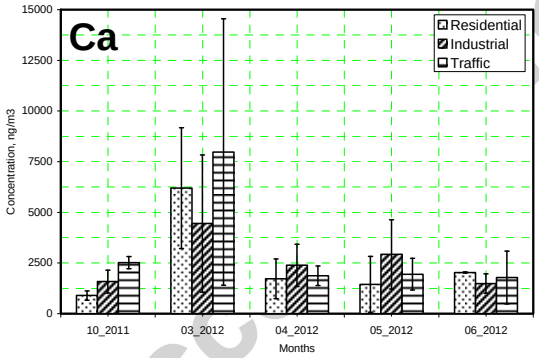
	Traffic		Industrial		Residential		QL
Element	Average Concentration	SD	Average Concentration	SD	Average Concentration	SD	
Si	8700	7600	6800	3000	6800	4000	
S	570	220	400	130	460	170	
Cl	210	120	180	44	260	220	
K	720	590	510	170	490	360	
Ca	3200	2700	2600	1200	2500	2100	
Ti	230	170	210	46	140	88	
Mn	52	42	40	11	34	19	
Fe	2500	1800	1800	520	1500	910	
Ni	4.0	3.4	3.5	1.6	3.9	3.1	20
Cu	12	3.5	11	2.9	4.9	1.6	
Zn	24	7.3	29	13	16	4.4	
Rb	2.7	2.0	2.0	0.5	3.1	3.2	
Sr	17	15	12	5.8	13	13	
Pb	8.5	2.2	6.9	1.9	6.3	2.6	500
BC	1900	410	1500	530	610	220	
$PM_{2.5}$	50000	31000	57000	22000	37000	22000	

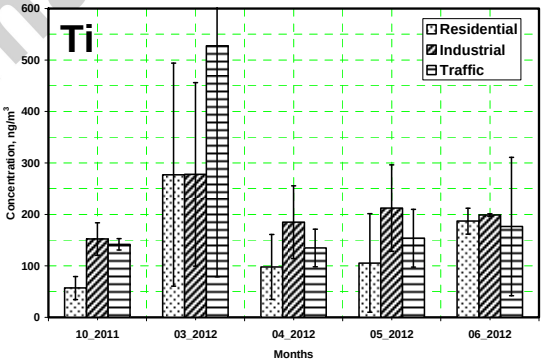


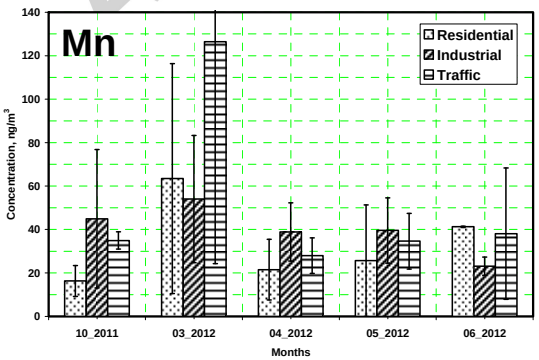


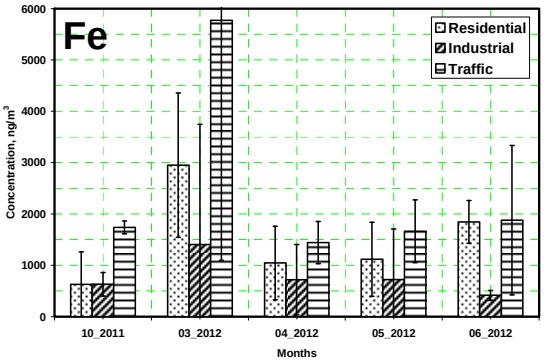












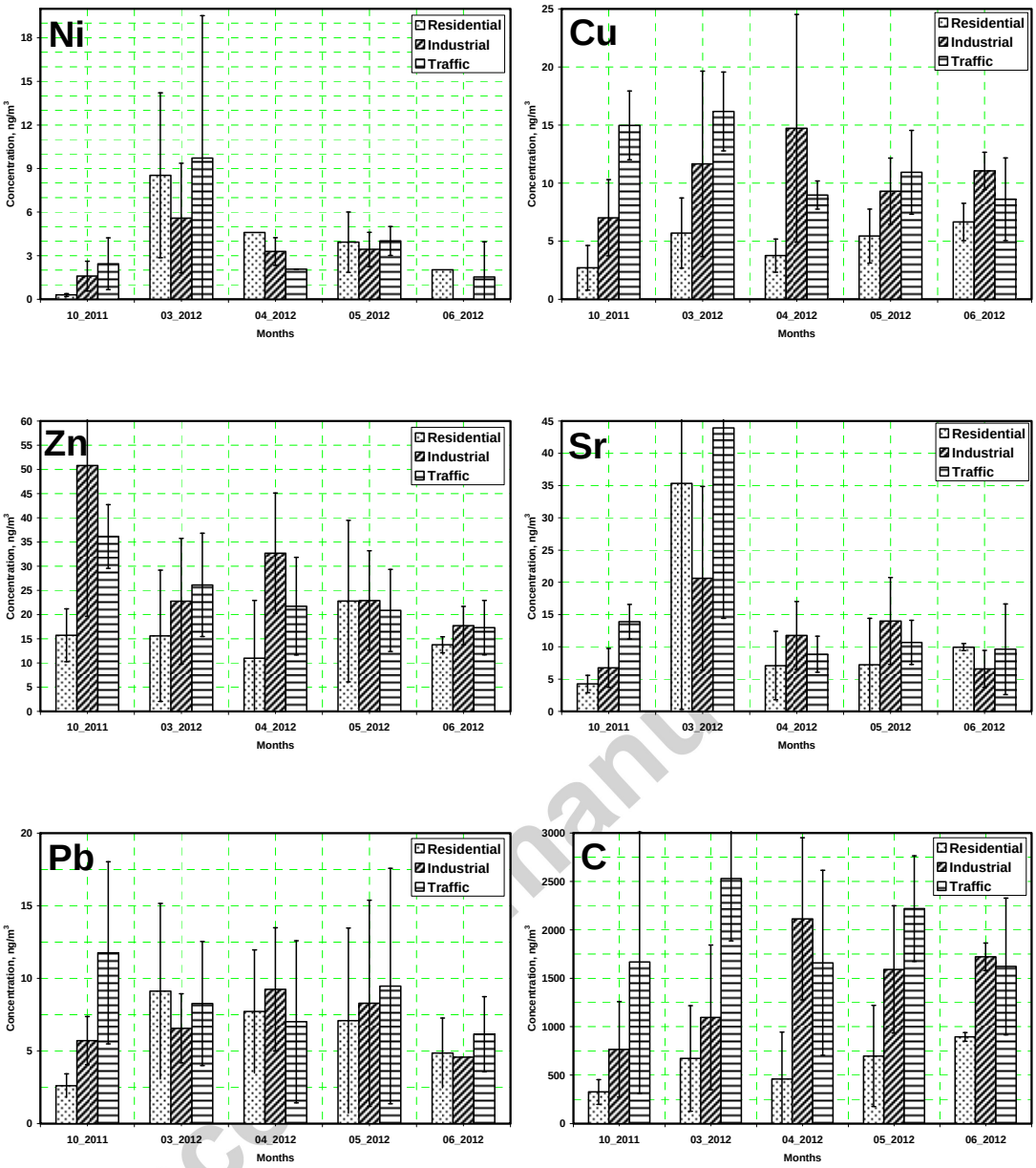


Figure 3: Concentrations of the detected elements during the collection months. The error bars represents one standard deviation.

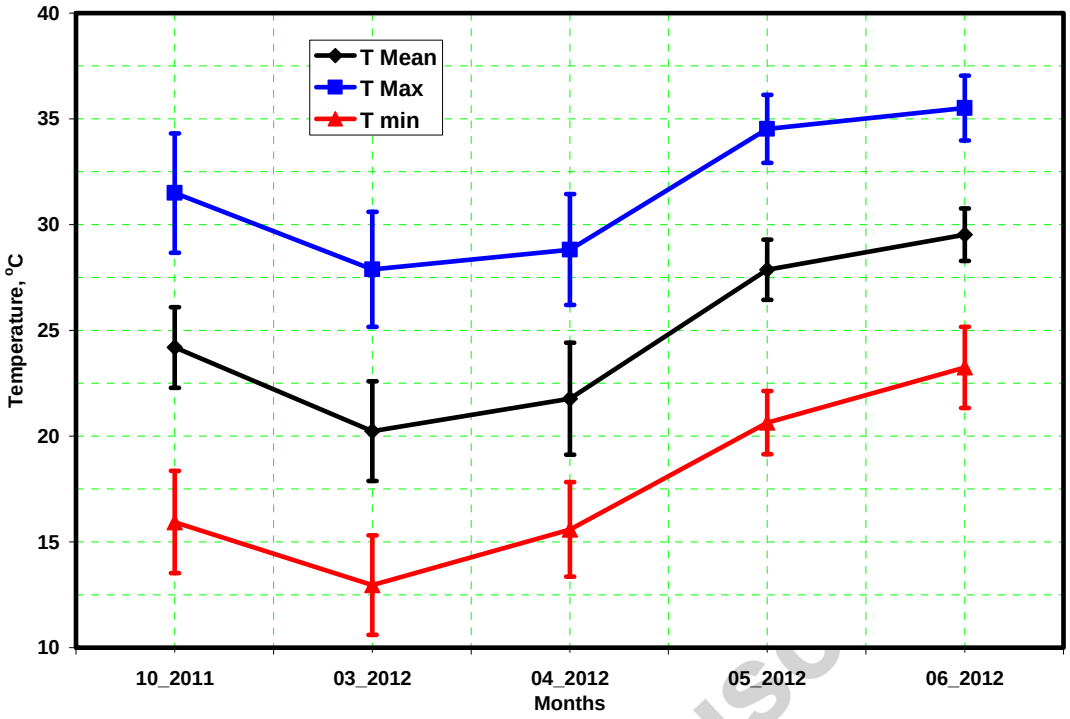


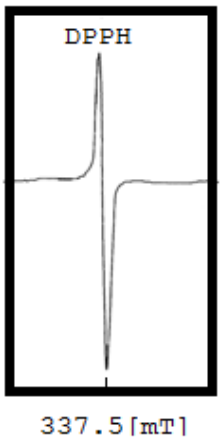
Figure 4. Temperature variations at Taif city, Saudi Arabia during the period of study.

3.3. Electron Paramagnetic Resonance

The collected atmospheric aerosol samples from the different sites were investigated by EPR spectroscopy to determine other sample parameters of relevance for environmental influence. Figure 5 illustrates the EPR measurements of the PM collected from residential, industrial and traffic dominated sites simultaneously in June 2012. The electron paramagnetic resonance (EPR) signal centered at 3000 Gauss with a narrow line width (ΔHp–p) of 9.5 to 14.3 Gauss. The $PM_{2.5}$ samples from the different sites have very similar EPR spectra with high intensity spectral line which indicates the stability of the contained free radicals although some broadness may be due to the inhomogeneity of the sample and to various degrees of interactions with metal ions The EPR spectra present a single broad unstructured peak with a g-value in the range from 2.0033 to 2.235 which corresponds to the g-value range, which is characteristic for semiquinone radicals (Hales 1975; Dellinger et al. 2001). The EPR spectra of the $PM_{2.5}$ samples are similar to the EPR spectra observed for the cigarette tar radicals which exhibits a g-value of 2.0030 and a peak-to-peak field

width of 4.9 Gauss. The concentrations of radicals in the $PM_{2.5}$ samples range from 1.6 to $5.8x10^{16}$ radicals/gram. This is comparable to the radical concentration in the cigarette tar sample ($2x10^{17}$ radicals/gram) (Valavanidis et al., 2009). Lyons et al. (Lyons et al. 1958) reported that radical concentrations in atmospheric soot might be 100-fold larger than in cigarette smoke. This cannot be seen in the present study, probably due to the low soot or BC content of the $PM_{2.5}$ particles. As an comparison, the pure, stable, low molecular weight crystals of 2,2-diphenyl-1-picrylhydrazyl (DPPH) contain about $2x10^{21}$ radicals/gram.

As shown in Figure 5, the presence of several lines indicates the hyperfine interaction between free radicals and the metal ions. The splitting constant *a,* in Gauss, is known as hyperfine structure (hfs). In general *n* equivalent protons give a spectrum of *n+1* hyperfine lines. The spacing between each two adjacent lines is the hfs constant (*a*) which range from 57 to 114 Gauss. The intensities are given by a binomial expansion.



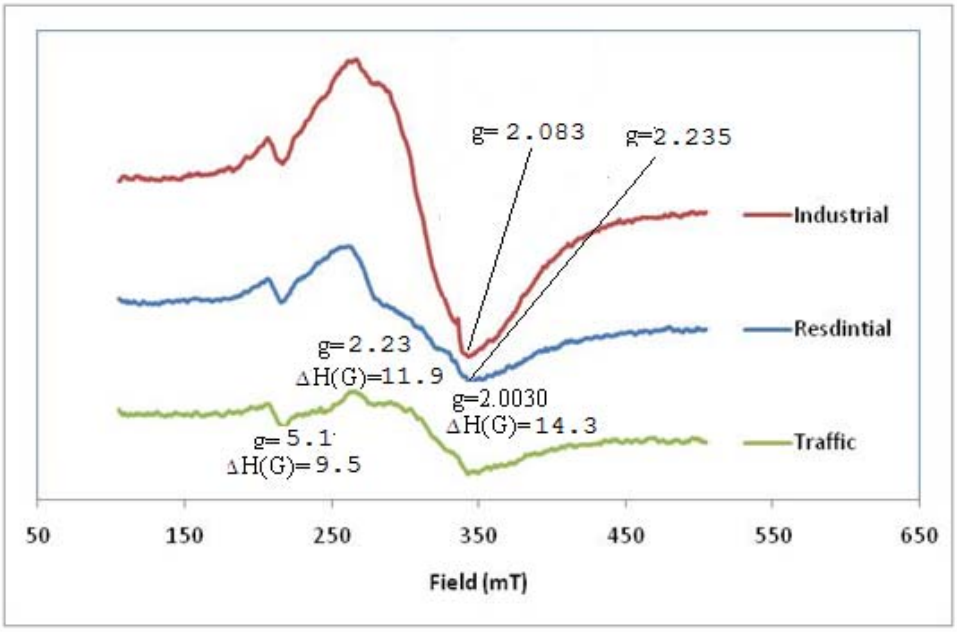


Figure 5, EPR Spectra of the PM collected from residential, industrial and traffic dominated sites during June 2012.

For carbon centered organic free radicals, the g-factor is always close to the free electron value of 2.0036 (therefore diagnostically less important). For metal complexes, the g factor changes substantially and can be used to give information about the electronic structure of the metal ion. From Figures 6-8, it was found that, $PM_{2.5}$ particles contain abundant persistent free radicals, typically 10^{16} to 10^{17} unpaired spins/gram and these free radicals are stable for several months and contains semiquinone radicals. These semiquinone radicals undergo redox cycling, thereby reducing oxygen and generating reactive oxygen species. Shift in the EPR g-factor implied an increased presence of oxygen centered radicals. The reactivity of the radicals towards oxygen would be controlled by whether the unpaired electron which is located on a carbon or oxygen atom. If the electron were located on a carbon center, then reaction with oxygen would result in peroxide whereas reaction with an oxygen-centered site would result in a much less stable ozonide. Thus, carbon-centered radicals are expected be more reactive than oxygen-centered radicals. In principal,

the g-values of EPR spectra can be used to determine whether a radical is carbon-centered or oxygen-centered. As a general guide, the closer the unpaired electron is to an oxygen atom, the greater the g-value: for carbon- centered radicals g-values are <2.003 (i.e., for graphitic carbon, g = 2.0028 (Szent-Györgyi et al. 1960). Carbon-centered radicals with an adjacent oxygen atom typically have higher g-values in the range of 2.003–2.004) (Hales 1975), while for oxygen-centered radicals g-values are >2.004 (Graf et al. 1977). The values of g of the present $PM_{2.5}$ particles from the residential, industrial and traffic dominated sites are 2.003, 2.083 and 2.235 indicating that the radical are oxygen centered.The fine PM samples can cause oxidative DNA damage in A549 human lung epithelial cells (Shi et al. 2006). The DNA damaging depends on the sampling location, time and the hydroxyl-radical observed in the PM samples. Therefore, there is a strong relation between the DNA strand breakage and the hydroxyl-radical-generating capacities of the PM samples. The generation of reactive oxygen species (ROS) by particles is one current hypothesis for their toxic effects. The EPR spectra of the $PM_{2.5}$ from the three measurement sites at different sampling dates are shown in Figures 6-8. The intensity of EPR line spectra for $PM_{2.5}$ samples collected from the industrial site during different periods is shown in Figure 6. It was shown that the intensity increases clearly at March and June, due to the increase of the concentration of free radicals. This is due to the variations of the arid climate and the strong north westerly winds blowing over the city during March and June 2002. Additional industrial activities may also contribute such as metallurgical activities, blacksmithing and construction, and waste burning. Figure 7 and 8 show the EPR spectra from the traffic and residential sites, respectively. The spectra are the same for all time periods with a slight increase in intensity at May and June which referred to the increase of visitors to the Taif city in summer season. Due to the high altitude and low humidity of Taif, it is considered as an attractive location for Saudi inhabitants and tourists from other Arab Gulf states during summer in order to escape from the uncomfortable summers in the most of the cities of Arab Gulf. Consequently, the increasing of the number of vehicles was recognized during summer which could be one of the main anthropogenic sources.

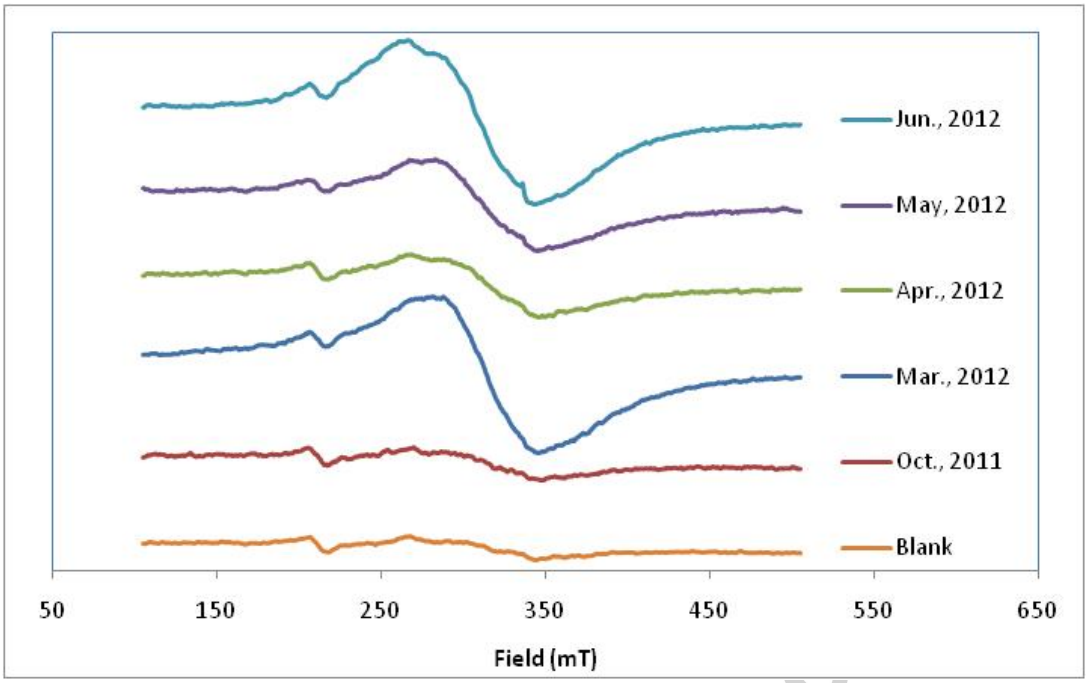


Figure 6, EPR Spectra of the PM collected from industrial site during the period of study.

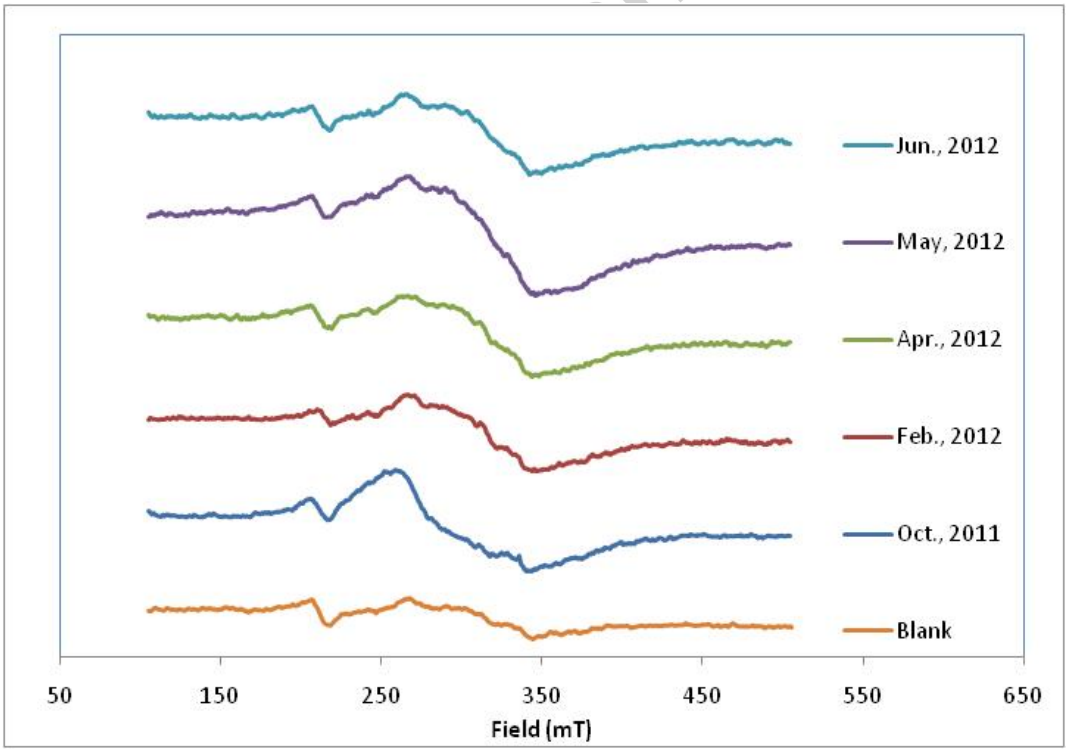


Figure 7, EPR Spectra of the PM collected from traffic dominated site during the period of study.

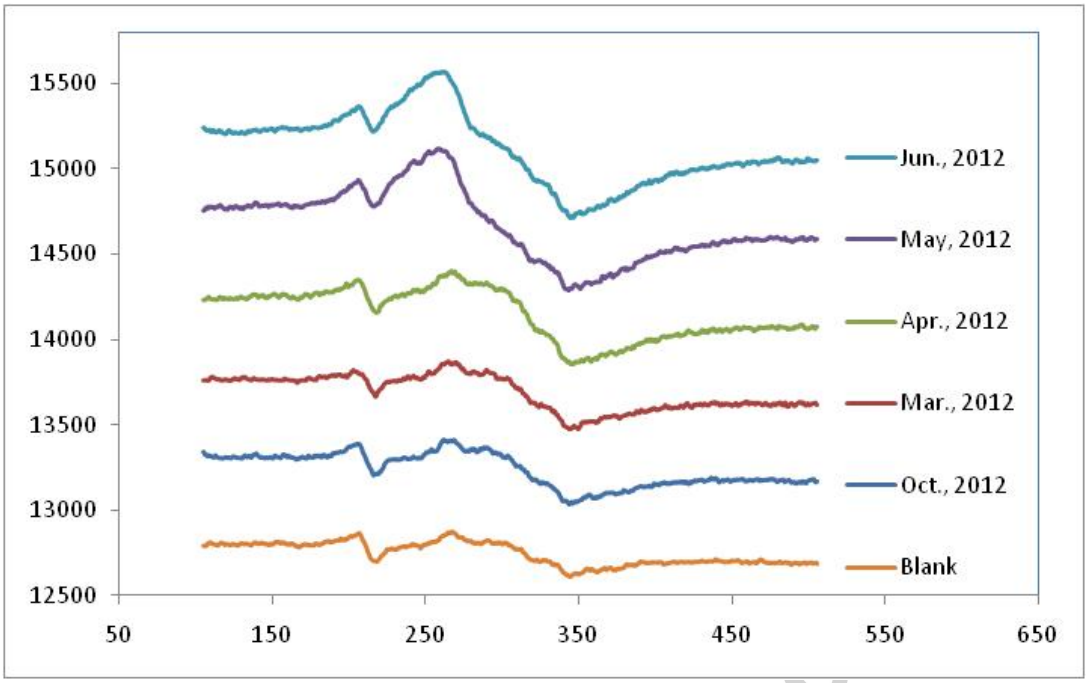


Figure 8, EPR Spectra of the PM collected from residential site during the period of study.

3.4. Statistical Analysis of data

As mentioned in our previous work, the statistical analysis is important in order to detect the hidden structure and association of elements in the data set in an attempt to explain the influence of latent factors on the data distribution and to obtain information about the dispersion and the similarity between the obtained results (Shaltout et al. 2011; Shaltout et al. 2012a; Shaltout et al. 2012b). Based on the mathematical background of Pearson's correlation analysis, the correlation coefficient between the detected concentrations of each location was calculated. The correlation coefficient values lie between −1 and +1. The maximum correlation coefficient corresponds to complete positive correlation when the data points lie on a perfect straight line with positive slope, whereas the minimum correlation coefficient corresponds to complete negative correlation with negative slope. Pearson's correlation coefficients were calculated to examine the relationship between the quantitative analysis results of the atmospheric aerosol samples at the different sites during the different months. It was found that there is a strong correlation between the different

months for each site ranging from 0.92 to 1. More verification of the strong correlation between the different sites was found (Table 3). Slightly lower correlation coefficients were recognized between the samples from the residential and the trafficdominated sites, especially during the spring 2012. Based on the mass concentrations of PM samples collected at the three different sites, the mass concentrations are comparable. In addition, the present calculations of Pearson's correlation are based on the average quantitative analysis results of each month which is also comparable even if the standard deviation of each month is little bit high. This was the main reasons of the high positive correlations.

Table 3, Correlation coefficients between the quantitative analysis at the different sites for the different months.

		Residential					Industrial				
		10_11	*03_12*	*04_12*	*05_12*	*06_12*	*10_11*	*03_12*	*04_12*	*05_12*	*06_12*
Industrial	10_11	0.993	0.976	0.965	0.955	0.971					
	03_12	0.981	0.995	0.995	0.986	0.993					
	04_12	0.977	0.957	0.970	0.971	0.978					
	05_12	0.989	0.983	0.983	0.977	0.987					
	06_12	0.953	0.942	0.970	0.977	0.981					
Traffic	10_11	0.966	0.907	0.882	0.867	0.884	0.966	0.904	0.948	0.944	0.909
	03_12	0.981	0.991	0.993	0.987	0.996	0.983	0.999	0.979	0.994	0.974
	04_12	0.975	0.957	0.971	0.972	0.979	0.984	0.975	1.000	0.994	0.996
	05_12	0.962	0.939	0.959	0.965	0.970	0.973	0.961	0.998	0.986	0.997
	06_12	0.966	0.959	0.982	0.987	0.992	0.977	0.980	0.993	0.990	0.996

4. Conclusion

This study establishes the necessity of using Electron Paramagnetic Resonance (EPR) along with Energy Dispersive X-ray Fluorescence (EDXRF) in studying the atmospheric aerosol particles ($PM_{2.5}$) collected from industrial, residential, and traffic sites of Taif city, Saudi Arabia. The integrity between these two spectroscopic techniques helps in finding correct solutions to evaluate the elemental analysis of as well as the different free radicals in the collected atmospheric aerosol samples. Although carbon-centered radicals have higher g-values than the oxygen-centered radicals, the fine PM samples can cause oxidative DNA damage in human lung epithelial cells whereas the DNA damaging is based on the observed hydroxyl-radical in the PM samples. Fourteen elements were quantitatively determined by using EDXRF using Mo secondary target. Based on EPR measurements, there are remarkable hyperfine interaction between the existed free radicals and metal ions and the measured g values refereed to the semiquinone radicals. Furthermore, an increase of the concentration of free radicals was recognized in industrial site especially during March and June. From a statistical point of view, strong correlation coefficients between the obtained results from the three different sites were found indicating a strong influence of both natural and anthropogenic sources of pollution at the three sites.

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Highlights

- Samples were collected from at three different sites industrial, residential, and traffic in Taif, Saudi Arabia.
- Energy Dispersive X-ray Fluorescence (EDXRF) was used for elemental quantification.
- Electron Paramagnetic Resonance (EPR) spectroscopic techniques were used to explain the interaction between free radicals and metal ions.
- The semiquinones free radicals were detected and characterized in $PM_{2.5}$.