ISSN : 0974 - 7451 Volume 7 Issue 6

Trade Science Inc.

Environmental Science

An Indian Journal

Current Research Paper

ESAIJ, 7(6), 2012 [210-217]

Elemental composition of $PM_{2.5}$ particles sampled in industrial and residential areas of Taif, Saudi Arabia, using energy dispersive x-ray fluorescence

Abdallah A.Shaltout*[1,2], Daifullah R.Almallway[1], Zuhair F.Shehadeh[1], Johan Boman[3]

[1]Physics Department, Faculty of Science, Taif University, 21974 Taif, P.O. Box 888, (SAUDI ARABIA)

[2]Spectroscopy Department, Physics Division, National Research Center, El Behooth Str., 12622 Dokki, Cairo, (EGYPT)

[3]Department of Chemistry, Atmospheric Science, Göteborg University, SE-412 96 Göteborg, (SWEDEN)

Received: 11th March, 2012 ; Accepted: 11th April, 2012

ABSTRACT

The present work is the first part of an initiative to evaluate the trace element composition of atmospheric aerosols $PM_{2.5}$ in two different areas of Taif city, Saudi Arabia. The influence of different inorganic matter on regional air quality has been demonstrated. Atmospheric aerosols of $PM_{2.5}$ from two different sites (industrial and residential) of Taif were collected and analyzed during June and July 2011. The industrial site was situated at the famous industrial areas in Taif whereas the residential site was situated at the most crowded street in Taif, namely Television Street. Atmospheric aerosols have been collected on polycarbonate filters loaded inside a collection cartridge in a cyclone of $PM_{2.5}$. The duration of the collection was 24 hours at air flow of 3 L min^{-1}. Energy Dispersive X-ray Fluorescence (EDXRF) with Mo secondary target has been chosen for direct solid sampling analysis because of the relative simplicity and the availability of the technique in many routine laboratories. The use of Mo secondary target has a lot of advantages for decreasing the continuum radiation coming form the x-ray tube. Quantitative X-ray Analysis Software (QXAS/AXIL) has been used for the quantitative analysis of the atmospheric aerosols $PM_{2.5}$. A certified reference material (#2783, Air Particulate on filter media, NIST, USA) has been used in order to verify the validity of the obtained results. Direct solid sampling analyses were carried out for fifteen elements using EDXRF namely; S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Pb, and C. The measured concentrations of the potentially hazardous trace elements As, Cu, Sb, Cr, Mn, Ni and Pb were below the limits defined by international guidelines and national standards of ambient air quality. Further long-term research is required to validate the quantification of trace elements collected on polycarbonate filters.

KEYWORDS

EDXRF;
Aerosol particle $PM_{2.5}$;
Trace element determination.

INTRODUCTION

The knowledge of the chemical composition of air particulate matter is very important because it has an essential relation to health problems[1] and climate change[2,3]. In addition, it gives important information

on their origin and also reveals whether they were emitted as primary or secondary particles. The smaller the particle, the more harm it may cause, as it penetrates deep into the lungs[4]. In addition, fine air particulate matters have an effect on the radiation balance of the earth[5] because they scatter and absorb most of the radiation in the visible region and it is therefore of great interest to measure their concentration in the ambient air. Furthermore, fine air particle matters have a long atmospheric residence time, which facilitates their transportation over long distances covering many thousands of kilometers. The bulk of these particles originates from anthropogenic emissions[6,7], both directly and as secondary formation in the atmosphere from gases like SO_2, NO_x and volatile organic compounds. The local emission of fine particles can become an issue of regional and even global concern, since these particles are able to affect air quality in other countries through transnational and even transcontinental transport. Black carbon (BC) represents also one of the main air pollution whereas it is produced by incomplete combustion and always mixed with other atmospheric constituents[8]. Generally, there are two aspects to the importance of knowing the elemental content in air particulate matters. First there are heavy elements such as Cd, Pb, As, and Sb, that are in themselves toxic to human health. It is of interest to follow the ecocycles of these metals as environmental hazards, once they are released into the atmosphere, biosphere and technosphere. The second aspect is that single elements or ratios between elements can be used as a fingerprint of a special source emitting other hazardous species that are less stable and more difficult to measure. According to the legislation in the USA and European Union, there are recommended limits on the concentration of inhalable particles[9].

The present work represents the first study of the constituents of air particulate matter ($PM_{2.5}$) in Taif region. Taif city is located in the Mecca province, in the western part of Saudi Arabia. The town is about 100 km and 190 km southeast of Mecca and Jeddah cities respectively and it represents one of the largest cities in Saudi Arabia. It stands 1879 meters above sea-level on the eastern slopes of the famous Al-Sarawat Mountains. Therefore, the main characteristic of Taif city is the high altitude and the low humidity. The population of Taif has been growing up and it has a population more than 0.8 Million. The climate of Taif represents the most convenient not only during summer months but also during the other seasons whereas the temperature is ranging from 29 ^oC to 35 ^oC. Therefore, its climate marked the city out from its dry and barren neighbors closer to the Read Sea. Its elevation gives it a climate far cooler and pleasanter than either Jeddah or Mecca and without the uncomfortable humidity. Taif city would be considered as an attractive location for Saudi inhabitants during summer, and it is one of the most popular holiday resorts as an escape from the uncomfortable summers in other Saudi cities. In additions, thousands of vacationers from other Arab Gulf states spend the summer season in Taif resort to enjoy its green scenery and beautiful parks. Furthermore, it has become the official summer seat of the Saudi government. The city's infrastructure has been expanded and modernized over the decades in order to keep up with growth and to support the blooming tourist industry. The intensification of human activity (tourism, transport, industry) associated with the population growth represent the main reason of air pollution in the city. During summer, the high population density in Taif would be expected as a secondary source of air pollution. In addition, there is a strong relationship between Taif and Makkah cities. Taif supplied the residents and pilgrims in Makkah with fresh produce from its fertile fields. Strategically located, Taif was also a gateway to Makkah for pilgrims coming from the east across the peninsula, as well as being the summer residence of the wealthy merchant families of Makkah. This was mentioned in the Holy Qur'an, (Sura 63, 31) refers to Makkah and Taif as "al-Qariyyatain" or the two cities. Therefore, the expected sources of air pollution in Taif would be; the poor dispersion factor due to the lack of rain, the vehicle emission, and urban industrial operations. Fumes from vehicles, combined with suspended particulate matter (including lead) and sand blown into urban areas from the surrounding desert, create the haze. In addition, there is no ideal collection and management for the waste which represents a huge health hazard. Previous studies on air particulate matters as well as the volatile organic compounds have been conducted in different cities in Saudi Arabia[10-15]. There are not investigations of air particulate matters in Taif city. A characterization of airborne bacteria in the atmospheric

of El-Taif was only found in the literature[16].

In the present work, atmospheric aerosols from two sites (Industrial and residential) in Taif city were sampled using polycarbonate filters. The sampling collection was carried out weekly for 24 h/sample during June and July 2011. At each location a sampler was installed consisting of a cyclone loaded with polycarbonate filters. The collected air particulate filters were quantitatively analyzed for trace elements by Energy Dispersive X-ray Fluorescence (EDXRF) with secondary target of Mo. Mo secondary target used in order to obtaining quasimonochromatic excitation, allows the reduction of the background and to improve the detection limits. The usage of Mo secondary target provides better sensitivity and selectivity. Closed-coupled setup with Mo secondary target allows greater flux and superior sensitivity. The aim of the study was to evaluate trace elemental concentrations in fine particles ($PM_{2.5}$) and to investigate its influence on regional air quality. Fifteen trace elements including carbon were analyzed namely; S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Pb, and C their concentrations evaluated.

EXPERIMENTAL

Sampling sites

Atmospheric aerosols of $PM_{2.5}$ from two different sites (industrial and residential) of Taif, Saudi Arabia, were collected and analyzed from June and July 2011. The industrial site was situated at industrial street, 20 km away from the center of the city whereas the residential site was situated at the high populated area at Television Street in the northeast of the city. Figure 1 illustrates the map of the two locations.

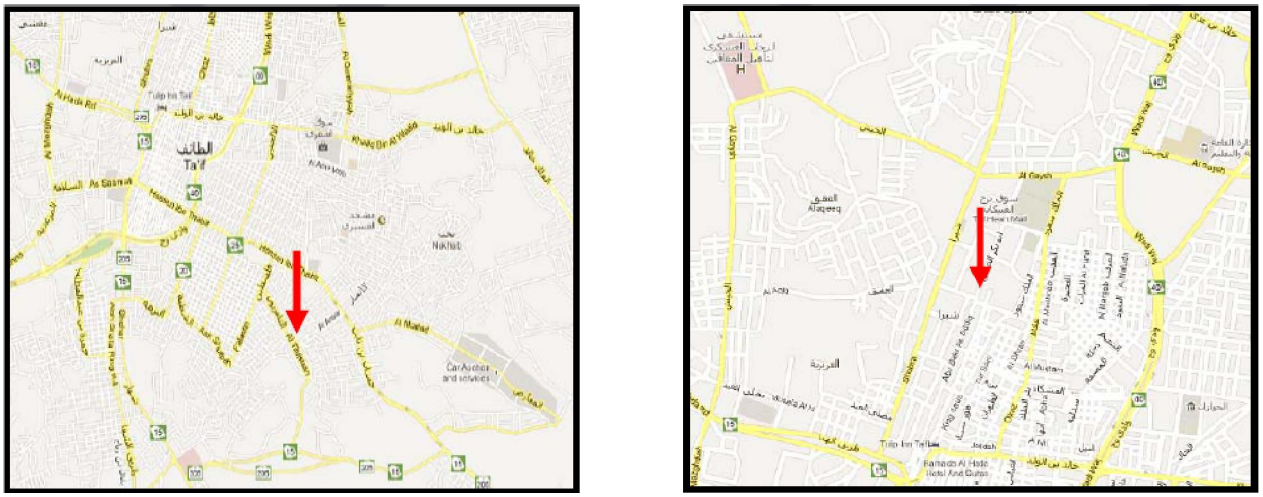

Figure 1 : Locations of the collected air particulate matters from industrial and residential areas of Taif, Saudi Arabia.

Sampling equipment

Atmospheric aerosols have been collected on polycarbonate filters loaded inside a collection cartridge in a cyclone of $PM_{2.5}$. The present cyclone is from CASELLA company, UK which is used for the atmospheric aerosols collection. The cyclone makes an airstream move in a cyclonic orbit where larger particles are separated from the fine particles because their higher inertia prevents them from following the air flow. It operates with a flow rate comparable to the breath of an adult person. The polycarbonate filters have a diameter 25 mm and a pore size of 4.0 µm. These filters have been used in previous studies and have a high particle collection efficiency and high purity[17]. The duration of the collection was 24 h at an air flow of 3 L min^{-1}. The filters were exchanged at 11 a.m, giving 24 h period. In order to avoid the influence of the traffic as a single source, the equipment (cyclone, flow meter, and the air atmospheric pump) was mounted on 20 m height, and more than 50 m from the main nearest road. A critical orifice was placed between pump and cyclone to restrict the air flow to 3 L min^{-1}. In order to have parallel measurements, two individual equipments with the same type of cyclones were used at the two sites simultaneously. A standard reference Materials of air particulate on filter media was used (SRM #2783, National Institute of standard and technology) in order to confirm the validity of the obtained results.

EDXRF setup

The Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer used for the analysis of the particle samples is built in a three-axial arrangement around a tungsten X-ray tube and utilizes a molybdenum secondary target that makes the beam nearly monochromatic before it reaches the sample[18,19]. The spectra from the EDXRF are further processed by the QXAS/AXIL software package[20] and the results are converted into airborne concentrations (ng m^{-3}). The EDXRF method of analyzing samples is multi-elemental, easy to use and inexpensive. It gives elemental concentrations within an error margin of 10% including statistical counting errors of X-rays fluoresced from each detected element in the sample. 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[21] and are published elsewhere, both in ng cm^{-2} and as minimum airborne concentrations[22].

Black carbon detector

The present EDXRF setup can not be used for black carbon determination due to the limitation of present Si(Li) detector, Therefore, a black smoke detector model FH621-N (ESM Emberline, Erlangen, Germany) was used to determine the BC concentrations in the samples. It is a reflectmeter that has light emitting diodes (LEDs) and photosenesors enclosed in a completely black casing. The LEDs illuminate the sample with optimized light that is tuned at a wavelength of 0.6 μm. The reflected light intensity is sensed by the photosensors that transduce the light intensity to electrical current. This instrument was calibrated with an empty filter and a filter loaded with BC powder. The instrument electrical voltage reading is related to the level of sample blackness and subsequently the equivalent concentration of atmospheric BC was calculated using the mathematical model this is described in the instrument manual. Despite the variable specific absorption of BC[23,24] that causes higher errors when compared to a thermal analytical technique, this method is simple, cheap and nondestructive. The concentration of black carbon; C_R was determined in μg/m^3 using the following equation;

$$C_R = -\frac{RM_1}{V}.\ln\left(1-\frac{RZ-RZ_0}{k*RZ_{max}}\right);$$
$$RZ = RZ_{max} * \frac{U_{RZ_0}-U_{RZ}}{U_{RZ_0}-U_{RZ\,max}} \quad (1)$$

RM_1 is the mass of smoke in a single dust layer on the filter (17.5), V is the sample volume, RZ_0 is the black smoke number of empty filter (0.43), k is constant depending on the absorption coefficient of black smoke (0.95), RZ_{max} is the upper range of calibration scale (9), U_{RZ0}, U_{RZmax} is the voltage for empty (8 V) and black filters (0.41 V), and finally, U_{RZ} is the voltage measurement reading.

Micro balance

The polycarbonate filters were weighted on a microbalance with six digits () before and after sampling in order to determine mass concentrations. Prior to the initial and final weighting, the polycarbonate filters were conditioned in desiccators in order to stabilize the weight. The filter conditioning and weighting operation were performed in a room temperature and relative humidity was controlled within the ranges 17-23 ^oC and 45-55%, respectively.

RESULTS AND DISCUSSION

Sample weights of $PM_{2.5}$

Figure 2 illustrates the average mass concentrations of $PM_{2.5}$ collected from the two mentioned sites in Taif versus the sampling collection weeks of June (06-2011), July (07-2011) and August (08-2011). For each site, 2-5 samples were collected per month. The averages mass concentration of $PM_{2.5}$ measured in the period from June and August 2011 were 45.07±31.4 μg/m^3, 44.72±15.3 μg/m^3 for the residential (TV street) and industrial (Industrial area) sites respectively. The $PM_{2.5}$ concentrations in the residential site were in the range 22.99-67.72 μg/m^3 whereas the $PM_{2.5}$ concentrations in the industrial area were in the range 32.79-62.19 μg/m^3. According to the European commission environment for the ambient air quality standards[25], the concentrations of $PM_{2.5}$ collected from the two mentioned sites are higher than the mean of air quality standards (25 μg/m^3). As shown in Figure 1, the mass concentrations of $PM_{2.5}$ collected August 2011 represent the low-

est values for the industrial and residential areas. On the other hand, the mass concentrations of $PM_{2.5}$ collected during July 2011 represent the highest value. This would refer to the dust storm episode during July 2011, remarkable summer activity in the city during July 2011, as well as the seasonal variation. Generally, the concentrations of $PM_{2.5}$ in the industrial and residential areas are comparable as shown in Figure 2. This may be attributed to the fact that Taif city is small and the two areas are close to each other.

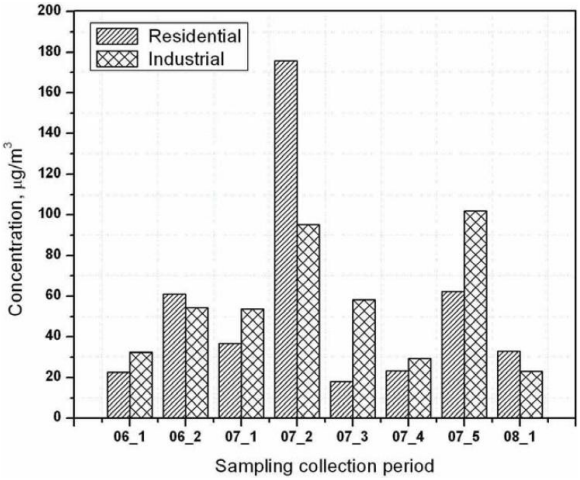

Figure 2 : Variation of mass concentration of $PM_{2.5}$ during the period from June 2011 to August 2011.

Elemental composition using secondary target EDXRF

Figure 3 depicts the characteristic fluorescent radiation of empty polycarbonate filter, air particulate filters collected from residential area, and air particulate filter of the certified reference material. Mo scattering radiation would be recognize at photon energy higher than 16 keV. The Kα and Kβ characteristic radiations seem to be predominant except in the case of Pb whereas Lα and Lβ lines were recognized. This would be compatible with QXAS/AXIL software whereas only characteristic radiation of Kα, Kβ and Lα of the different elements could be used. According to Figure 3, fourteen elements would be determined namely; S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Pb.

Other heavy elements such as Cd, Sb, Mo are less than the limit of detection and there is no possibility to measure it by the present EDXRF instrument. Further investigation will demonstrate by using High Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry (HR-CS-GF-AAS) in our future work[26]. For quantitative determination of trace elements in air particulate filters, a group of standard filters with well known concentrations of different elements were used in order to perform the calibration curve. The present calibration is performed by the calculation of the sensitivities of the elements in the standard filter group versus the atomic number. Once the intensity of the peak area and the concentration of each element were introduced to QXAS/AXIL software, the calculations of calibration curve was automatically performed via the "Perform calibration Menu" whereas the sensitivity "Sens" is given by;

$$\text{Sens} = \frac{\text{counts.abs.fac}}{\text{time.current.conc}} \quad (2)$$

Therefore, the unknown elements in the air particulate filters could be determined once the measured spectra were performed by the same manner. The final concentration of the elements in the polycarbonate filter was given in $\mu g/m^2$ and it was converted into ng/m^3. TABLES 1 and 2 show the elemental analysis results for the air particulate filters collected from the industrial and residential locations. The concentration was given

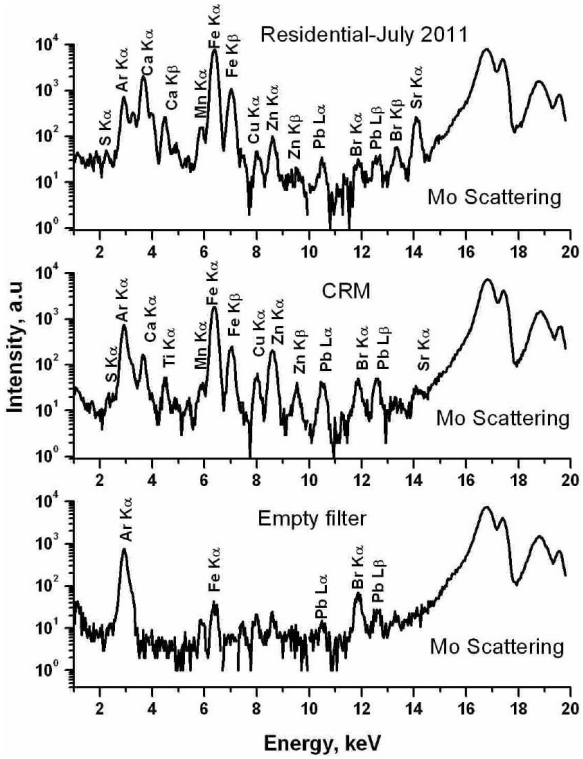

Figure 3 : EDXRF spectra of the present polycarbonate filter with without air particulates as well as the certified reference material.

in ng/m^3 and each value represents the average concentrations of the air particulate filters collected during each month. As shown in TABLES 1 and 2, the concentration of some trace elements was not performed successfully during some months whereas it was below the limit of detection. These elements are S, K, V, and Cr. In this case, the average concentration was calculated depending on the successful measured values. Fortunately, the concentration of heavy elements given in TABLE 1 and 2 are below the allowed standard level of European commission of air quality.

Remarkable high concentrations of S, K, Ca and Fe were generally recognized in the industrial location. On the other hand K, Ca and Fe were also high in the case of residential area. The concentration of K in the residential area is twice its concentration in the industrial area and this would refer to the human activities. The concentrations of Ca and Fe in industrial and residential areas were comparable. This would be due to the low of industrial activities in the industrial areas as well as the remarkable similarity of both sides. Other elements are relatively comparable in both industrial and residential locations. TABLE 3 illustrates the average concentrations of the measured elements during June 2011 and July 2011. For Black carbon determination, a black smoke detector was used as mentioned above. As shown from TABLES 1-3, the average concentration of black carbon in the industrial area is three times higher than its concentration in the residential area. This is due to the remarkable industrial activities such as blacksmith workshops, insecticides, construction activities and automobiles. Furthermore, the traffic seems to be more intensive in the industrial area whereas the number of motorized traffic is relatively greater than that in the residential area. Consequently, the expected soot concentrations in industrial area are much higher than that found in the residential.

TABLE 1 : Quantitative analysis of $PM_{2.5}$ collected from residential area (TV Street, Taif) using Mo secondary target EDXRF

El	June 2011	July 2011
S		
K		1472.889
Ca	2794.723	8918.271
Ti	105.378	513.668
Cr		33.657
Mn	51.687	142.240
Fe	1659.604	6109.524
Ni	8.014	19.233
Cu	15.626	23.239
Zn	27.246	49.283
Br	4.407	8.815
Rb	4.007	18.431
Sr	14.424	40.468
Pb	7.613	11.219
C	0.3580	0.5439

TABLE 2 : Quantitative analysis of $PM_{2.5}$ collected from Industrial area (Taif) using Mo secondary target EDXRF

El	June 2011	July 2011
S	1317.43	748.46
K	612.64	855.45
Ca	3772.78	5485.27
Ti	409.49	386.25
Mn	65.71	100.57
Fe	2920.13	3800.42
Ni	8.41	11.22
Cu	26.44	31.65
Zn	68.52	79.33
Br	7.21	8.41
Rb	2.40	6.01
Sr	18.03	27.25
Pb	10.02	10.82
C	1.1521	1.3328

TABLE 3 : Average of concentration of elements including carbon in ng/m^3 in the Urban and industrial sites

El.	Residential, ng/m^3	Industrial, ng/m^3
S		1032.95
K	1472.889	734.04
Ca	5856.497	4629.02
Ti	309.523	397.87
Cr	33.657	
Mn	96.964	83.14
Fe	3884.564	3360.28
Ni	13.623	9.82
Cu	19.433	29.05
Zn	38.265	73.92
Br	6.611	7.81
Rb	11.219	4.21
Sr	27.446	22.64
Pb	9.416	10.42
C	0.451	1.24

Accuracy of the method

In order to check the effectiveness and the validity of the developed method for quantitative analysis of air particulates filter using Mo secondary target EDXRF, certified reference material (CRM) of air particulate on filter media was evaluated (Air particulate on filter medial #2783, National Institute of Standard and Technology (NIST), USA). The certified reference material was directly analyzed without any kind of preparation. The quantitative analysis of the CRM was calculated with the same procedure of the air particulate filter under investigation. TABLE 4 compares obtained values of the chosen reference standards and the certified values. As shown from the certificate of the CRM of air particulate on filter media #2783, the certified concentrations of Cl, Br, and Sr are not available and there is no opportunity to compare with the measured values. On the other hand, the concentration of S and V are below the limit of detection of the secondary target EDXRF, and it can not be detected. There is generally a good agreement for most but not all elements. The quantitative analysis results of the CRM for the measured and the certified values were analyzed statistically applying the student's '*t* ' test to see the significant difference between the measured and certified values at level of confidence equal p = 0.05. It was found that, the difference between the measured and the certified values was non-significant and this confirms the validity of the proposed method using for determination the elements in air particulate filters.

TABLE 4 : Quantitative analysis of certified reference material using Mo secondary target EDXRF setup

Elements	Measured Values, ng/m^3	Certified Values, ng/ m^3
S	Not detected	105.42
CL	848.00	
K	532.50	530.12
Ca	1409.50	1325.30
Ti	164.50	149.60
V	Not detected	4.87
Cr	17.00	13.55
Mn	58.50	32.13
Fe	3047.50	2660.65
Ni	8.50	6.83
Cu	59.00	40.56
Zn	210.00	179.72
Br	21.00	
Rb	6.00	2.41
Sr	8.00	
Pb	30.50	31.83

CONCLUSIONS

The present work represents the first part of an initiative to evaluate the trace element composition of atmospheric aerosols $PM_{2.5}$ in two different areas of Taif city, Saudi Arabia. Atmospheric aerosols of $PM_{2.5}$ from two different sites (industrial and residential) of Taif were collected and analyzed during June and July 2011. The residential site was situated at the high populated area at Television Street in the northeast of the city whereas the industrial site was situated at industrial street, 20 km away from the center of the city. Atmospheric aerosols have been collected on polycarbonate filters loaded inside a collection cartridge in a cyclone of $PM_{2.5}$ for 24 h at air flow of 3 L min^{-1}. Energy Dispersive X-ray Fluorescence (EDXRF) with Mo secondary target has been chosen for direct solid sampling analysis. Black smoke detector was used for black carbon determination. Quantitative analysis of fifteen elements including carbon was successfully determined. For the validation of the method, a certified reference material (CRM) of air particulate on filter media was evaluated and there is generally a good agreement for most but not all elements. Fortunately, the measured concentrations of the potentially hazardous trace elements were below the limits defined by international guidelines and national standards of ambient air quality.

REFERENCES

[1] L.C.Renwick, K.Donaldson, A.Clouter; Toxicol.Appl.Pharmacol., **172**, 119-127 **(2001)**.

[2] T.R.Karl, N.Nicholls, J.Gregory; Sci.Am., **276**, 54-59 **(1997)**.

[3] T.A.Cahill; Nucl.Instrum.Methods, **B109-110**, 402-406 **(1996)**.

[4] J.Schwartz, L.Neas; Epidemiology, **11(1)**, 6-10 **(2000)**.

[5] H.Horvath; In Atmospheric Particles, R.M.Harrison, R.E.Van Grieken, (Eds); Wiley: Chichester, 543-596 **(1998)**.

[6] F.Murray, G.Mc Granahan, J.Kuylenstierna; Water Air Soil Pollut, **130**, 1799-1804 **(2001)**.

[7] M.Ezzati, A.D.Lopez, A.Rodgers, S.V.Hoorn, C.J.L.Murray; Lancet, **360**, 1347-1360 **(2002)**.
[8] C.Liousse, H.Cachier, S.G.Jennings; Atmospheric Environment Part A-General Topics, **27**, 1203-1211 **(1993)**.
[9] D.Mark; In Atmospheric Particles, R.M.Harrison, R.E.Van Grieken, (Eds); Wiley: Chichester, 29-94 **(1998)**.
[10] W.H.Abulfaraj, M.Ahmed, K.M.Mousli, F.Erturk; Environment International, **16(1)**, 85-88 **(1990)**.
[11] K.O.Ahmed, H.M.Al-Swaidan; Science of the Total Environment, **136(1-2)**, 205-210 **(1993)**.
[12] K.O.Ahmed, H.M.Al-Swaidan, B.E.Davies; Science of the Total Environment, **138(1-3)**, 207-212 **(1993)**.
[13] H.M.Aburas, M.A.Zytoon, M.I.Abdulsalam; CLEAN-Soil, Air, Water, **39(8)**, 711-719 **(2011)**.
[14] A.O.Sabbak; Environment International, **16(3)**, 273-282 **(1990)**.
[15] H.A.Al-Jeelani; Environmental Monitoring and Assessment, **156(1-4)**, 211-222 **(2009)**.
[16] H.M.Mahdy, M.H.El-Sehrawi; Water, Air, and Soil Pollution, **98**, 317-324 **(1997)**.
[17] A.Wagner, J.Boman, M.J.Gatari; Spectrochimica Acta Part B, **63**, 1426-1431 **(2008)**.
[18] J.Boman; Detector Performance Measurement Techniques and Computer Software in an EDXRF-Spectrometer Applied to Environmental and Medical Studies. PhD Thesis, Göteborg University, Göteborg, Sweden, 31 **(1990)**.
[19] S.Chimidza; Characterization and Source Apportionment of Airborne Particles in Eastern Botswana. PhD Thesis, Göteborg University, Göteborg, Sweden, 62 **(2001)**.
[20] G.Bernasconi, A.Tajani, P.Kregsamer, (Eds); Manual for QXAS/AXIL. Version 3.5. Vienna: International Atomic Energy Agency, 200 **(2000)**.
[21] IUPAC; Pure Appl.Chem., **45**, 99-103 **(1976)**.
[22] M.J.Gatari, A.Wagner, J.Boman; Sci.Total Environ., **341**, 241-249 **(2005)**.
[23] J.S.Reid, R.Koppmann, T.F.Eck, D.P.Eleuterio; Atmospheric Chemistry and Physics, **5**, 799-825 **(2005)**.
[24] J.Heintzenberg, M.Bussemer; Journal of Aerosol Science, **31**, 801-812 **(2000)**.
[25] http://ec.europa.eu/environment/air/quality/standards.htm
[26] J.Boman, B.Welz, I.N.B.Castilho, A.M.Abouzied, S.K.Hassan, E.A.Alashkar, A.A.Shaltout; Elemental Determination of $PM_{2.5}$ Particles Sampled in Industrial and Urban Areas of Greater Cairo, Egypt using High Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry, Unpublished Work.