Soil Environ. 37(2): 109-115, 2018
DOI:10.25252/SE/18/61588
Online ISSN: 2075-1141
Print ISSN: 2074-9546

Identification and investigation of halite in suspended particulate matter by X-ray diffraction & scanning electron microscope-energy dispersive spectrum in the environment of an industrial city Faisalabad (Pakistan)

Syed Kamran Ajmal*[*1], Sonia Bukhtawar[2] and Tahir Bashir[3]
[1,2]Department of Physics, University of Central Punjab (UCP), Faisalabad Campus, Faisalabad, Pakistan
[3]Department of Physics, Baha Uddin Zakariya University, Multan-60800, Pakistan

Abstract

Air pollution has numerous distinct and hazardous influences upon living organisms. Faisalabad one of the most polluted and big industrial city with huge air quality problems. The lack of enough knowledge with poor characterization of suspended particulate matter (SPM) showed the inorganic clay minerals present in the atmosphere of Faisalabad city. The characterization of soil compounds and elements were carried out using X-ray diffraction (XRD) and scanning electron microscope (SEM) with energy dispersive spectrum (EDS) technique. The XRD analysis was carried out using Hanawalt method of phase identification. The sources of quartz, calcite, gypsum, clinoclore, talc, halite, albite and illite are showing local and remote. Morphology were observed in three micrographs obtained by SEM found particle size 10μm and the composition (% age) of various elements measured by EDS. It has been observed the analysis of silicon (Si), calcium (Ca), iron (Fe) and aluminum (Al) are present in the atmosphere of Faisalabad. Sodium (Na), Potassium (K) and chloride (Cl) are present in little amount showed the presence of halite in the SPM samples.

Keywords: Suspended particulate matter (SPM), qualitative phase analysis, air pollution, hanawalt method, energy dispersive spectrum (EDS)

Introduction

Atmospheric aerosols are of two types: coarse particles and fine particles diameter < 2.5 μm, and the diameter of coarse particles > 2.5 μm (Wolff *et al*., 1985) these particles were the tiny particles dispersed. The nuclei mode of fine particles 0.005-0.1 μm diameter and its accumulation mode is 0.1-2.5 μm (Hussain *et al*., 1990, 1997). The SPM in air is generally marked into two groups, namely suspended (particle size may be >2.5 μm diameter) and settle-able matter (Boix *et al*., 2001). The result of suspended matter on human health is strongly dependent on their capability to penetrate the respiratory track (Ferron *et al*., 1988).

In general, smaller particles go through into the respiratory system more deeply; the coarse particles may be deposited into the pharynx and larynx, causing dryness of the nose and throat, but no effect in the mucociliary clearance (Ata *et al*., 2013). A relationship between increases in particulate awareness and respiratory infections, Cardiac diseases, Bronchitis, Asthma, Pneumonia, Skin diseases, Emphysema and Lung diseases (Wark & Warner *et al*., 1981) statistical analysis indicated rises in the number of clinic and hospitals. Particulates of size ≥15 μm were filtered out in the upper respiratory system and approximately 30% of the particles from 3-5 μm were deposited in the lower respiratory system, while about 70% of the particles from 0.02-0.2 μm were deposited in the pulmonary system (Ferron *et al*., 1988). Emphasis of environmental protection agency (EPA) was aimed at the specific size fraction of particles (Ata *et al*., 2013) which can reach the trachea (Davis *et al*., 1990). XRD quantitative analysis by means of the reference intensity method was demonstrated in the study which measured reference intensity constants have been obtained by the aerosol suspension technique (Davis *et al*., 1982).

The upper cut-off limit for inhalable particles of size 10-15μm diameter has been proposed by Chow (1973) & (Wolf *et al*., 1985). The choice of the 15μm cut off point is based on the worst case situation of mouth breathers, because in case of nose breather's particles larger than 10μm are rejected (Hussain *et al*., 1990). The dividing line between suspended and deposit-able matter diameter of 10 μm was considered (Farthing *et al*., 1982)**.** SPM may have a variety of sources most of the particulates come from earth's surface as wind-blown dust (Smith *et al*., 1996). While some of them is generated from the combustion of fuels such as coal and fuel oil in furnace and from diesel fuel in automobiles. SPM consists of solid particles present in air in the form of dust suspended for a long period of time

*Email: kamranajmalcn@gmail.com

© 2018, Soil Science Society of Pakistan (http://www.sss-pakistan.org)

becomes the main source of haze which reduces visibility (Hussain *et al*., 1990), the approximate size of dust particle was about 1 μm. Davis *et al*., (2000) studied the airborne particulate in five cities of china and found some calcium sulfate dust components, chemical and atmospheric reactions directly can take part in the atmosphere.

A significant fraction of atmospheric particulate mass is composed of inorganic species such as sulfate, nitrate, chloride, sodium, and ammonium ions (Queralt *et al*., 2001). For instance, on average sulfate and its associated ammonium (NH_4) ions account for 50% or more of the fine (≤ 2.5 μm diameter) particle mass (Davis *et al*., 1984), while it accounts for 25-45%. Davis (1987) quantitatively determined the mineral content of geological samples by XRD.

Hussain *et al*., (1997**)** studied the SPM, one of major source of pollution in an environment, has different physical and chemical characteristics with different concentrations at various locations and at different levels in atmosphere. No doubt, advancement of science and technology has added to the human relief in the form of automobiles, electrical appliances, better medicines, and chemicals to control diseases (Hussain *et al*., 1990). But these things have created the problems of environmental pollution**.**

In this article, the results obtained from an investigation of SPM in the metropolitan city and the Manchester of Pakistan, the biggest industrial city Faisalabad. The XRD analysis was carried out using Hanawalt method of phase identification. The aim of the present study was qualitative phase analysis of the unknown phases. SPM is an active field of research in other countries but in Pakistan, research work on SPM is at initial stages. Unfortunately, the comprehensive research of the SPM has been not conducted as yet. A preliminary study was carried out by a few researchers, this critical situation also motivated to work on SPM. Identification of SPM was done by XRD & SEM-EDS in the environment of an industrial city Faisalabad.

Materials and Methods

An easy way was adopted for the collection of SPM; each sample was strained in order to remove fibrous material. Sample preparation is the most careful and important requirement in the analysis of powder XRD. The powder contains finely divided particles recommended size range is around 10 μm and then purified with the help of a thin and fine clothe. The powder samples were stored carefully in separate packs and marked. The collected samples were ground to powder form using mortar and pestle until homogenous consistency achieved. Before further grinding, the mortar and pestle were washed with acetone and dried in air. The SPM samples were dried and heated in an oven/furnace at 150 $^{\circ}$C in order to remove humidity.

The XRD experiments were performed with Pak Diff-1000 (PINSTECH Lab, Islamabad). The angular range from stop angle 6° (2θ) to start angle 36° (2θ), step scan mode using Cu-Kα (Ni-filtered); divergence slit 1° with receiving slit size 0.16 mm and solid state detector. The working conditions of X-ray tube voltage and current were 50 kV with 30 mA, scan speed 0.02°/sec, a counting time of 10 sec per step with preset time 0.6 sec. Contribution from Kα_2 was eliminated /stripped off with the help of diffraction software. The final XRD patterns were due to only Kα_1 radiation (Cu-Kα radiation) with λ=1.5406Å. There were different methods such as Chemical Analysis, X-ray Fluorescence (XRF), Atomic absorption spectrometry and XRD to determine the phases in the SPM samples. Out of these techniques, XRD is an important analytical method and play a vital role in research. This technique is being used by industries for the purpose of quality control and it is an important tool of solid state Physics. XRD is the most accurate, quick, cheap, useful and frequently used. Sample analysis method is a powerful and readily available method for determining the atomic arrangements in crystals to identify compounds present in the atmospheric samples. Before loading sample into aluminum rectangular sample holder of diffractometer, it was thoroughly washed with acetone then the sample was pressed gently onto the XRD goniometer.

For the investigation of atmospheric pollution, the samples were examined in SEM and elemental analysis by EDS was carried out using electron probe microanalysis (EPMA). The three micrographs were taken from SEM at various magnifications show the particle size 10 μm and show the shape and surface of even large particles, EDS was also for the conformation of the elements. Elemental analysis of some SPM samples from different environments analyzed by EDS showed the composition (wt. % age) of various elements present in SPM samples.

Results and Discussion

Total 60 samples were collected from different environments (zones) in the atmosphere of Faisalabad city and 11 SPM samples were selected randomly. The Sample Codes, Locations, Zones and Colors are described in Table 1. The diffraction patterns of all the samples were obtained along with printout of the diffraction data and pattern of identified compounds shown in Figure 1.

The comparison of the observed "d-values" (from XRD data) and calculated d-values (from JCPDS cards) mineral phases were identified by applying Hanawalt method (Cullity, 1978). XRD give complete information of major

Table 1: **Selected locations (environments) and colors of samples**

Sample Code	Locations and Environments (zones)	Color of Sample
KA-09	Madina Town (House)	Light Brown
KA-14	Jhang Bazar, Clock Tower (Grain Market)	Dark Brown
KA-27	University of Agriculture (Institute)	Light Brown
KA-32	Rex City Market, Sitana Road (Interior Shop)	Brown
KA-33	Akbar Market, Railway Road (Interior Shop)	Black
KA-36	Kashmir Banaspati Industry Nashtabad (Industry)	Dark Grey
KA-37	New Abadi Samundri Road(Road)	Black
KA-40	10-Jail Road(Road)	Black
KA-42	Near General Bus Stand (House)	Dark Brown
KA-45	Civil Hospital (Inside Hospital)	Light Grey
KA-50	Allied Hospital (Inside Hospital)	Light Grey

Table 2: Minerals/compounds with their formula, crystal system and mineral identified in the SPM samples (Hussain, 1990; Tazaki 1996 & Shahid 2012)

Mineral	Chemical Formula	Crystal System	Bragg Reflection (hkl)
Albite	$NaAlSi_3O_8$	Triclinic	002
Calcite	$CaCO_3$	Hexagonal	014
Clinochlore(chlorite)	$(MgAl)_6(Si,Al)_4O_{10}(OH)_8$	Monoclinic	002
Gypsum	$CaSO_4.2H_2O$	Monoclinic	001
Halite	NaCl	FCC	110
Illite	$K_{0.7}Al_2(Si,Al)_4O_{10}.H_2O$	Monoclinic	001
α-Quartz	α-SiO_2	Hexagonal	101
Talc	$Mg_3Si_4O_{10}(OH)_2$	Monoclinic	001

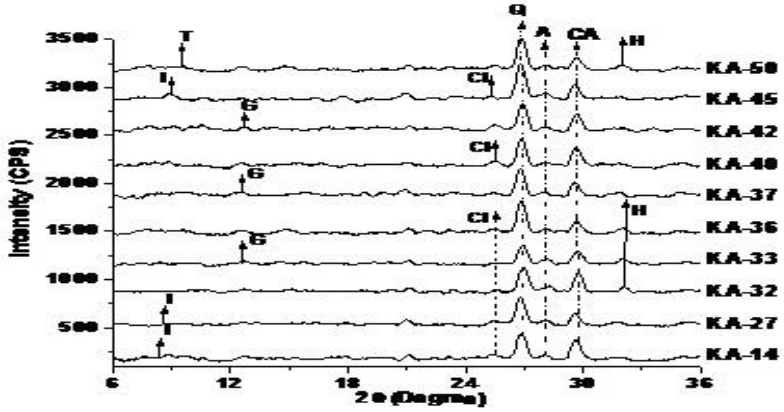


Figure 1: XRD pattern of SPM samples

compounds present and is a useful tool for examining the atmospheric aerosols (Davies *et al*., 1984, 1980).

Every crystalline substance gives a unique XRD pattern, which is a characteristic of the substance. The XRD pattern contains two parameters, scattering (diffraction) angle ($2\theta^{\circ}$) and integrated intensities of the diffraction peaks. Shahid *et al*., (2012) carried out Hanawalt method (Cullity, 1978) the qualitative phase analysis of all the SPM samples. By the comparison of observed d-values with calculated d-values (provided by ICDD in the form of JCPDS cards) different phases in the samples were identified. The identified phases were quartz, illite, albite, calcite, clinochlore, halite, talc and gypsum given in Table 2.

Hussain *et al.,* (2008) investigated indoor SPM as source of air pollution in commercial, industrial and residential areas of Faisalabad city found the pollution level is same and can act similar towards the health of local resident. Shahid *et al*., (2011) also verified by comparing all the relative intensities with the values on the identifying cards. When the unknown sample is a single crystalline material and enlisted in the file, then identifications completed within few minutes. But if the unknown sample is a mixture of two or more components, the procedure is

not simple. For such a case, three strongest lines are taken which are checked in the index book (Hussain *et al*., 2008).

Relative intensity of a mineral was calculated by the ratio of intensity of that mineral to the intensity of KCl (Ahmad *et al*., 2013).

$$K_i = \left[\frac{I_i}{I_S}\right]_{1:1} \quad (1)$$

In Eqn. (1), 'I_i' is the integrated intensity and 'K_i' is the relative intensity ratio given by $K_i=I_i/I_{KCl}$ calculated by mixing the component 'I_i' with standard material KCl. The ratio calculated by Shahid *et al*., (2012) mixing the component "*i*" with standard material "*s*" in a ratio of 1:1 by weight. The particle size of NaCl & KCl must be same, grounding the material to fine powders and then passing through the sieve of same size. This gives the percentage composition of a component '*i*' in a mixture of component. The K_i value of halite was determined using Eqn. (2).

$$K_i = \left[\frac{I_{NaCl}}{I_{KCl}}\right]_{1:1} \quad (2)$$

Table 3: The d(Å) and 2θ values of SPM

Mineral	2θ (degree)	d(Å) values	
		This study	References (Hussain, Boix)
Halite	32.15	2.79	2.82
Calcite	29.45	3.02	3.03
Albite	27.76	3.18	3.24
Quartz	26.65	3.32	3.34
Clinochlore	25.13	3.52	3.54
Gypsum	12.50	7.16	7.60
Talc	9.49	9.31	9.35
Illite	8.89	9.92	9.98

Powders of NaCl and KCl 99.5% pure were purchased from Faisalabad chemical company. Grounding the material to fine powders and then passing through a sieve of same size, then NaCl mixed with KCl in ratio 50:50. The K_i-value was determined by mixing NaCl with KCl in equal ratio by weight as written in Equ. (2). The K_i-value found for halite is 0.61 as mentioned in Table 4. Figure 2 shows the X-ray reflections from NaCl and KCl powders both have FCC structure (C. Kittel 7th edition, pp-46). The three lines were selected and checked from index book and compared with JCPDS card data for identification of the substance. This procedure goes on and all the samples were identified. The already determined K_i-values of quartz, albite, calcite, illite, clinochlore, gypsum and talc (Hussain, 1990; Shahid, 2000; Hussain, 2008) except halite (Fukasawa 1980, Boix 2001) have been given in Table 3. For an investigation, SEM with EDS has been carried out for morphology and elemental analysis of SMP samples. The three micrographs were taken from SEM at various magnifications to show the particle size was 10 μm as clear in the Figure 3 also showed the shape and surface of even large particles in sample # KA-09, KA-37 & KA-40. The study of EDS is for the confirmation of the elements present in the SPM samples.

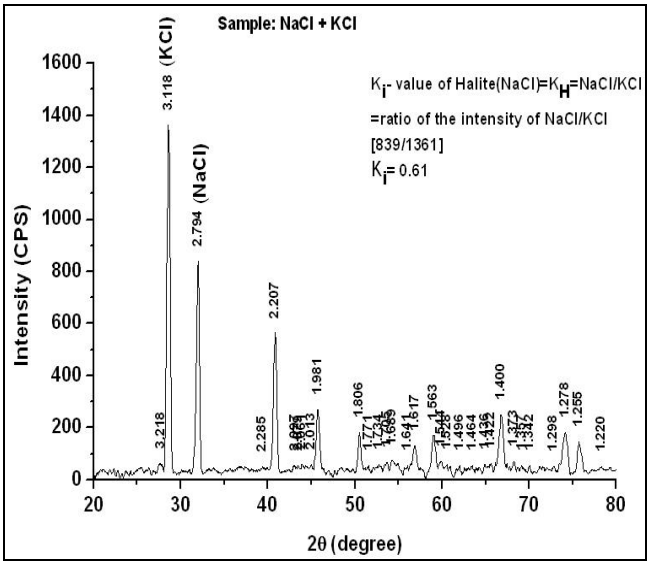
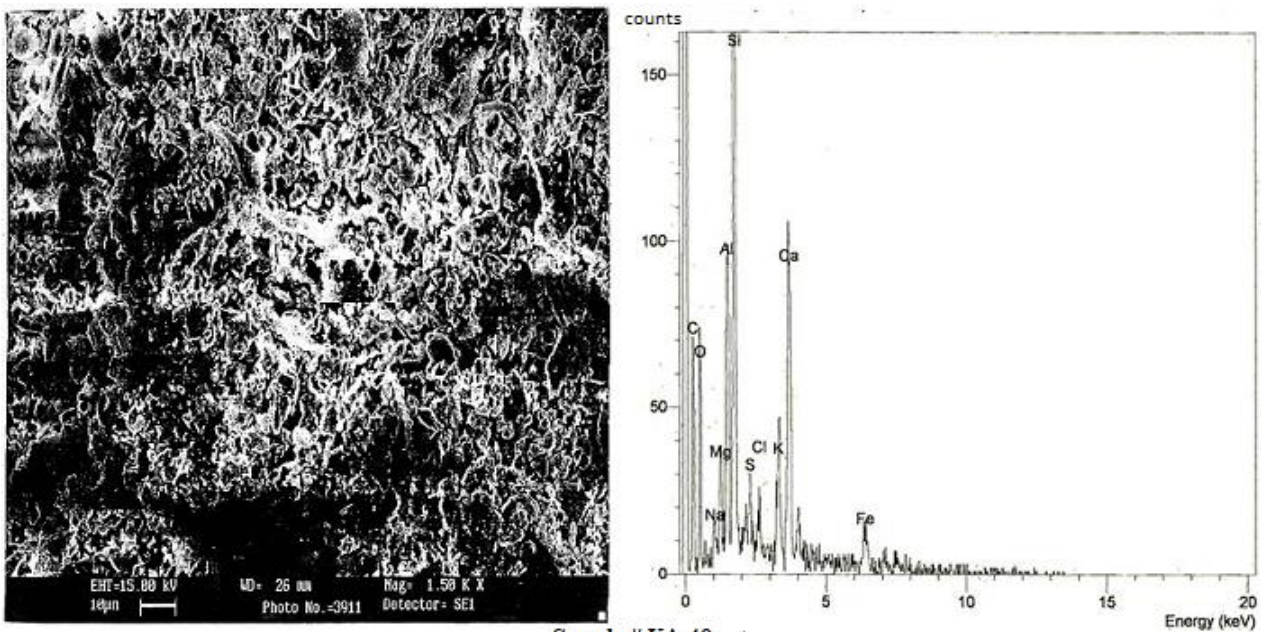


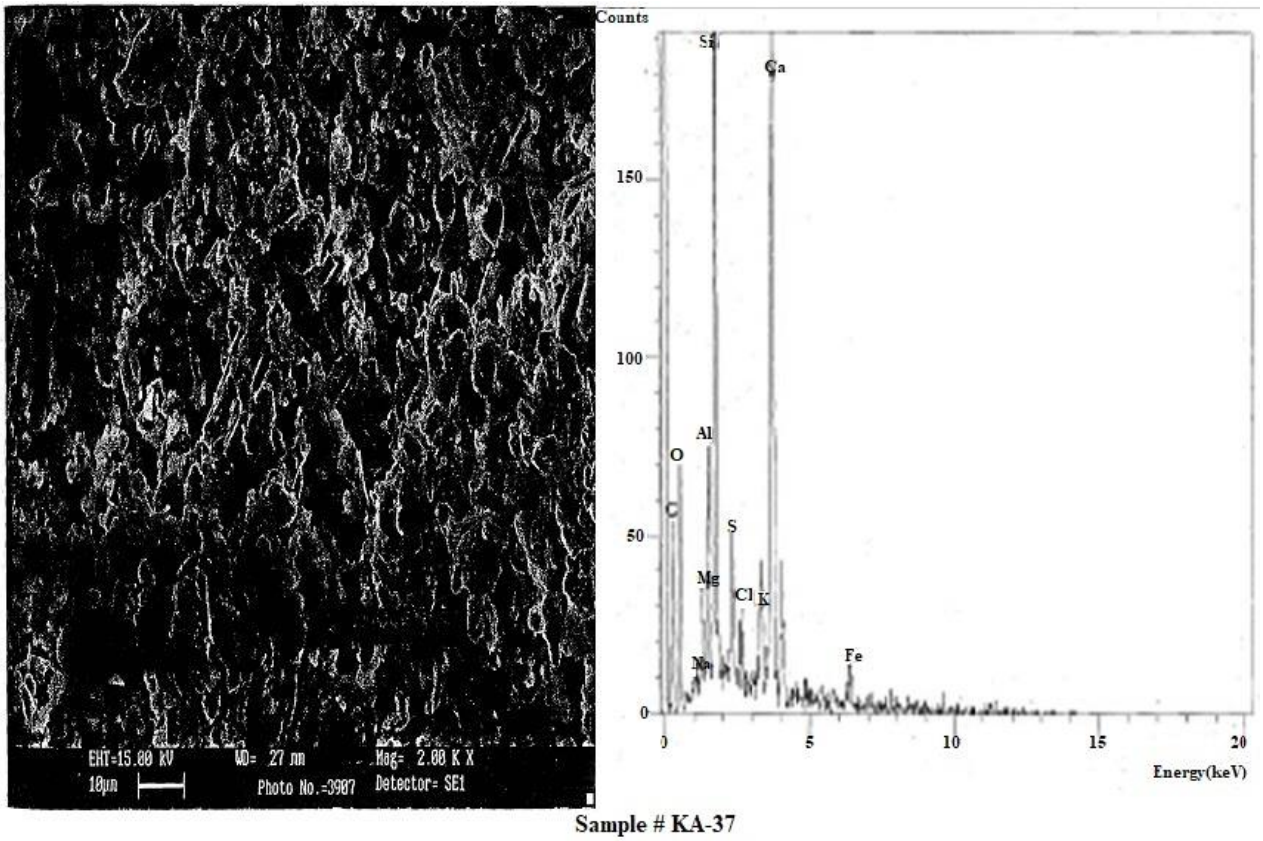
Figure 2: XRD pattern of Sodium Chloride (NaCl) and Potassium Chloride (KCl)

Table 4: The K_i -values for identified minerals

Mineral	Relative Intensity $K_i = \left[\frac{I_i}{I_{KCl}}\right]_{1:1}$
Quartz	0.85
Gypsum	0.83
Calcite	0.74
Halite	0.61
Albite	0.36
Talc	0.32
Clinochlore	0.23
Illite	0.20



Sample # KA-40



Sample # KA-37

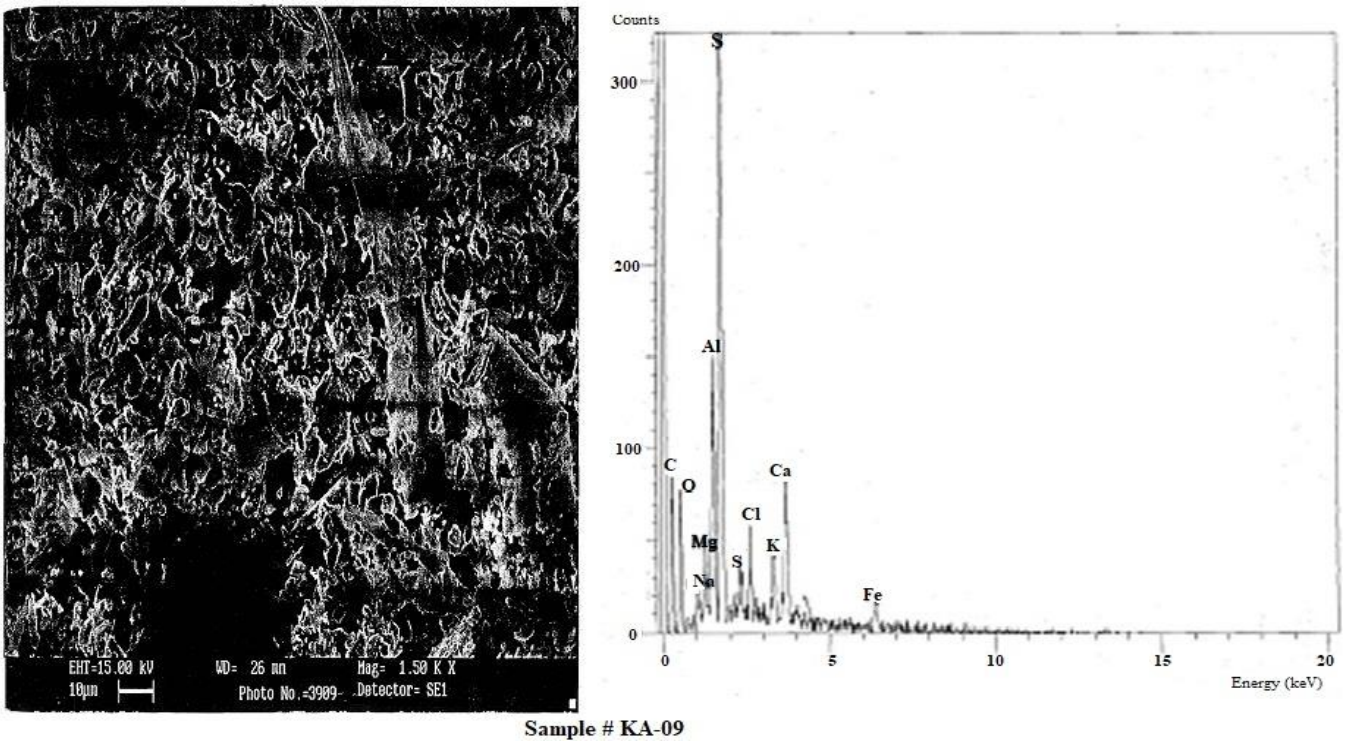


Figure 3: The SEM-EDS of SPM samples

Table 5: Composition (% age) of various elements measured by energy dispersive system (EDS) analysis

Elements	KA-09	KA-37	KA-40
	Concentration (%)		
Na	2.0	2.40	1.70
Mg	3.90	4.0	3.20
Al	9.30	11.2	6.20
Si	30.0	35.0	20.40
S	1.90	3.20	3.30
Cl	2.80	5.0	2.80
K	7.0	6.80	4.80
Ca	33.8	21.2	51.20
Fe	9.30	11.2	6.40
Average	100.0	100.0	100.0

Elemental analysis of some SPM samples described in Table 5 from different environments analyze by EDS to show the composition (wt. % age) of various elements present in SPM samples. Jamil *et al.*, (2008) studied the qualitative analysis of the SPM in the environment of an industrial and a non-industrial city of Pakistan.

Nakamura (1988) described the airborne pollutants in city have different sources ranging from wind migrated dust, anthropogenic activities such as stationary fuel combustion, industrial process, transport or solid waste disposal, power plants results in gas to particle conversion occurring in the atmosphere. Quartz, albite and calcite are present in all SPM samples. Halite, illite, gypsum and talc are present in only some of the SPM samples. The minerals such as quartz, albite, illite, calcite, clinochlore, talc, halite and gypsum were presented in the SPM samples collected from Faisalabad. X-ray diffraction technique was also recommended (Fukasawa *et al*., 1980) for the study of environmental pollution.

Presence of gypsum and talc in samples were due to crushing of marble rocks in building property. Quartz, albite and calcite would be major phases while clinochlore and halite were presented in considerable amounts (Fukasawa *et al*., 1980) however; talc and gypsum were the minor phases. Minerals such as quartz, albite, illite, calcite and clinochlore could be soil oriented. While halite, talc and gypsum were not soil oriented and having their sources away from Faisalabad.

Acknowledgement

The author Dr. S. K. A. Tirmizi would like to thank Dr. Shabir and Sardar Ahmad for their helpful discussions in manuscript and technical assistance in XRD & SEM-EDS, especially thanks to Ms. Irum Akram & Amer Mahmood.

References

Ahmad, N., K. Hussain and S. Naseem. 2013. Quantification of phases in Lahore (Pakistan) airborne particulates by Matrix-Flushing method. *Journal of minerals and materials characterization and engineering* 1: 168-183.

Ata, S., M.A. Qadir and A. Rasool. 2013. Tracer elements analysis of aerosols in the atmosphere of Lahore using radio analytical techniques. *Proceedings of the 16th International Conference on Heavy Metals in the Environment* 1: 20005-p.1-4.

Boix, A., M.M. Jordan, X. Querol and T. Sanfeliu. 2001. Characterization of total suspended particles around a power station in an urban coastal area in eastern Spain. *Environmental Geology* 40: 891-896.

Cullity, B.D. 1978. Elements of X-ray diffraction, 2nd edition, assion-wesley publishing company, USA.

Chow, J.J. 1973. Chemistry in Britain, 9, 258.

Davis, B.L. and M.J. Walawender. 1982. Quantitative mineralogical analysis of granitoid rocks: a comparison of X-ray and optical techniques. *American Mineralogist* 67: 1135-1143.

Davis, B.L. 1984. X-ray diffraction analysis & source apportionment of Denver aerosol. *Atmospheric Environment* 18: 2197-2208.

Davis, B.L. 1987. Quantitative determination of mineral content of geological samples by X-ray diffraction: discussion. *American Mineralogist* 72: 438-440.

Davis, B.L. and G. Jixiang. 2000. Airborne particulate study in five cities of china. *Atmospheric Environment* 34: 2703-2711.

Fukasawa, T., M. Iwatsuki, S. Kawakubo and K. Miyazaki. 1980. Heavy-liquid separation & X-ray diffraction analysis of airborne particulates. *Analytical Chemistry* 52 (11): 1784-1787.

Ferron, G.A., B. Haider and W.G. Kreyling. 1988. Inhalation of salt aerosol particles. I. Estimation of the temperature and relative humidity of the air in the human upper airways. *Journal of Aerosol Science* 19: 343–363.

Hussain, K., R. Riffat and A. Shaukat. 1990. A study of suspended particulate matter in Lahore (Pakistan). *Advances in Atmospheric sciences* 7(2): 178-185.

Hussain, K., M.A.K. Shahid, M.K. Rahman and M.Y. Hussain, 1997. A preliminary comparative study of environmental airborne particulate pollution in Lahore & Faisalabad. *Science International* 9: 178-185.

Hussain, M.Y., M. Yousaf, I.D. Shahzad and M. Imran. 2008. Investigating indoor suspended particulate matter as source of air pollution in residential, commercial & industrial areas of Faisalabad city. *Pakistan Journal of Agriculture Science* 45(1): 112-115.

Hussain, M.Y., M. Yousaf, I.D. Shahzad and M. Imran. 2008. A pollutant of environment: qualification, quantification and characterization of airborne particulates. *Pakistan Journal of Agriculture Science* 45(1): 116-118.

Jamil, Y., N. Amin, M.R. Ahmad, Z. Haq and A. Hussain. 2008. Qualitative analysis of the suspended particulate matter in the environment of an industrial & a non-industrial city of Pakistan. *Soil & Environment* 27 (1): 84-87.

Nakamura, T. 1988. Quantitative determination by X-ray diffractometry of Calcium Sulfate and Calcium Carbonate in airborne dusts. *Powder Diffraction* 3(2): 86-90.

Queralt, I., T. Sanfeliu, E. Gomez and C. Alvarez. 2001. X-ray diffraction analysis of atmospheric dust using low-background supports. *Journal of Aerosol Science* 32: 453-459.

Shahid, M.K.A, K. Hussain and M.S. Awan. 2011. Morphological structure study & chemical composition of solid aerosols related to Faisalabad environment. CODEN JNSMAC 51: 01-11.

Smith, D.J.T., R.M. Harrison, L. Luhana, C.A. Pio, L.M. Castro, M.N. Tariq, S. Hayats and T. Quraishis. 1996. Concentrations of particulate airborne polycyclic aromatic hydrocarbons & metals collected in Lahore, Pakistan. *Journal of Atmospheric Environment* 30(23): 4031-4040.

Shahid, M.K.A, K. Hussain and M.S. Awan. 2012. Characterization of solid aerosols related to Faisalabad environment & their probable sources. CODEN JNSMAC 52: 09-29.

Wolff, G.T. and P.E. Korsog. 1985. Estimates of the contributions of sources to inhalable particulate concentrations in Detroit. *Atmospheric Environment* 19(9): 1399-1409.

Wark, K. and C.F. Warner. 1981. Air pollution its origin and control, Harper Collins, New York, NY.

Zhou, G. and K. Tazaki. 1996. Seasonal variation of Gypsum in aerosol & its effect on the acidity of wet precipitation on the Japan Sea side of Japan. *Atmospheric Environment* 30(19): 3301-3308.