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Analysis of organic functional groups and some trace heavy metals in the settleable dust particles (dustfall) of Sulaimani City/ KURDISTAN REGION-IRAQ

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Abstract

Ambient settleable (dustfall) dust particles samples were collected during August 2009 to March 2010 from 18 locations in Sulaimani City/KRI for qualitative analyzing by Fourier Transform Infrared (FTIR) spectroscopy instrument to characterize the common functional groups that existed in the samples. Furthermore, the samples were quantitatively analyzed for the heavy metals contents of; V, Co and As by Inductively Coupled Plasma-Optical Emission Spectroscopy ICP-OES. The collected samples involved samples of settleable dust particles from local source of the city (location 1 to 15) and settleable dust particles from dust storm event of 22 February, 2010 (location 16 to18). The FTIR analysis identified the following functional groups; Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group in all the samples of (1 to 15) for the local source of dust particles except sample location number 6 which was free from sulfoxide, p. amine (bend.), carbonyl and p. amine (str.) as compared to the samples of other locations and it was also the only sampling location that had a silicate group. Moreover, sample location number 13 was the only location that had an extra functional group of isocyanide or alkynes HC functional group. For the dust storm samples of location numbers 16, 17 and 18 had also all the above mentioned 9 functional groups except the alkanes HC functional group. On the other hand, the concentration ranges of the studied heavy metals were (0.20 – 3.20), (2.02 – 5.45) and (2.89 – 45.50) mg dust kg^{-1} dust for As, Co and V respectively in all the studied locations.

Introduction

Airborne dust particles, also called particulate matters (PM) play a major part in the overall atmospheric pollution and they are also most of the key components of the atmosphere. Therefore, atmospheric dust particles are considered to be one of the most important criteria for air quality standards worldwide. Airborne dust particles in the atmosphere originate either from direct emission of anthropogenic and biogenic sources or from secondary reactions between pollutants. These particles are referred to as primary and secondary particles respectively. The researchers **[1]** described particulate matters as a complex mixture of small and large particles of varying origin and chemical compositions. Variation in particle properties is dependent on several conditions including emissions source and regional atmospheric composition. Anthropogenic dust comes from particulate matter which has been disturbed by wind or human activities such a earth moving vehicles, traffic on paved and unpaved surface **[2].** According to **[3]** the values of dust concentrations in this study area during a study period from 31.9.2009 to 13.7.2010 were ranged from 13.1 to

170.0, 18.7-181.7 and 40.4 to 374.0 µg m^{-3} for PM1.0, PM2.5 and PM10.0 respectively, moreover, in most of those locations the limits of the different aerodynamic size of the dust particles have exceeded the legislative limits of air quality standards set by the Environmental Protection Agency (EPA) and European Commission (EC).

Environmentally persistent free radicals (EPFRs) have been shown to form on the surfaces of particles containing transition metal oxides and they are known to cause adverse health impacts **[4 and 5]**. A free radical can be defined as any molecular species capable of independent existence that contains an unpaired electron in an atomic orbital. The presence of an unpaired electron results in certain common properties that are shared by most radicals. Many radicals are unstable and highly reactive **[6].**

On the other hand, air pollution due to heavy metals, is a product of urbanization and other factors related to population density, industrialization, and mechanization, which are providing human beings requirements. Emissions of heavy metals to the environment occur via a wide range of processes and pathways, including to the air (e.g. during combustion, extraction and processing), to surface waters (via runoff and releases from storage and transport) and to the soil (and hence into ground waters and crops) **[7].** Chemical composition of particulate matters (PM) especially in terms of heavy metals content is a matter of concern due to the both acute and chronic adverse health effects linked with heavy metals. Long-time exposure to toxic trace metals such as arsenic, cadmium, chromium, nickel even at low concentrations can causes cancer **[8]**.

Heavy metals present in the atmosphere in trace amounts may pose a serious risk to human health in urban populations. The potential hazard of several toxic elements such as As, Cd, Cr, Hg and Pb is well known **[9]**. Therefore, WHO gives guidelines for some trace metals which can be present in urban air well above natural background levels as the result of anthropogenic processes **[10]**.

So far, there have been no published researches on functional groups and some heavy metal pollution for the airborne dust particles in Sulaimani city. Therefore, this study aimed to qualitatively investigate the functional groups in settleable dust particles and dust storm source collected from different location of Sulaimani city. The other objective of this study was to carry out a quantitative analysis for the heavy metals vanadium (V), cobalt (Co) and arsenic (As) in settleable dust samples. These might in turn provides information about the chemical composition of atmospheric particulate matter and associated risks.

MATERIALS AND METHODS

A. General description of Sulaimani city

Sulaimani is a governorate in Iraqi Kurdistan region and it is located far north east of Iraq and southeast of the Iraqi Kurdistan Region. Sulaimani city is in the center of Sulaimani Governorate, its center coordination are (35° 33′ 14.99″ N) and (45° 26′ 58.68″ E) and has an elevation of 864 m above sea level. Sulaimani city is surrounded by the mountains: Azmar, Goizja and the Qaiwan Ranges in the north east (with the peak of 1709 m above sea level), Baranan and Glazarda Mountains in the south (with the highest peak of 1373 m above sea level) and the Tasluje Hills in the west (with the highest peak of 1118 m above sea level) **[11]**.

B. Settleable dust (Dustfall) sampling

For collecting the settleable dust, a sheet of black plastics in dimension of 1.5 x 2.5 m were placed and fixed at a height of 4 to 8 m on the roof of private building houses in (15) fifteen locations from 22nd August 2009 till March 2010. The roofs were firstly cleaned and made free from all materials. Sampling locations had covered the different quarter of Sulaimani city, some locations were selected directly on the main street of a high densified urban and traffic volume, while others were far away from direct effect of traffic volume and had low densified urban. Sampling locations were defined according to GPS coordination (Table 1 and Figure1) and the accumulated dust particles were collected on a weekly basis by using plastic brushes and a plastic collector then were kept in a plastic container of 100 ml. The amount of collected dust particles varied from 0.1 to about 1.0 g per a week according to the predominant condition of the locations. Collection of settleable dust was carried out only in dry days (not rainy) and when no dust storm was associated.

Table (1): GPS coordinates for the locations of settleable dust samples collection

No.	Locations	GPS Coordinates	Elevation (m)
1-	Raparin/ Near to Sulaimani International Airport	N 35º 34′ 22.74″ E 45º 20′ 21.48″	765
2-	Maleek Mhmood Circle/ Lovan Hotel	N 35º 33′ 22.56″ E 45º 24′ 22.02″	775
3-	Tanjaro / Tanjaro Mosque	N 35º 29′ 00.36″ E 45º 25′ 34.50″	668
4-	Nawgrdan Village/ Osman Gas Fact.	N 35º 28′ 02.46″ E 45º 25′ 59.40″	688
5-	Charakhan Quarter	N 35º 31′ 21.18″ E 45º 26′ 32.70″	789
6-	Kaziewa Quarter/ Near to Goizha Apartments	N 35º 33′ 32.52″ E 45º 28′ 24.90″	999
7-	Kurdsat/ Quarter 1	N 35º 35′ 18.30″ E 45º 25′ 55.68″	916
8-	Kurdsat Quarter 2	N 35º 35′ 43.80″ E 45º 26′ 18.36″	948
9-	Maleek Mhmood Circle/ Beside Zargata Underpass	N 35º 34′ 50.22″ E 45º 24′ 35.46″	830
10	Farmanbaran Quarter	N 35º 35′ 03.18″ E 45º 24′ 04.92″	809
11-	Salim Street/ Beside Khsrawkhal Bridge.	N 35º 33′ 45.00″ E 45º 24′ 25.32″	787
12-	Chawrbakh Quarter / Near to Sulaimani Stadium	N 35º 33′ 01.32″ E 45º 25′ 50.64″	815
13-	Sarkarez/ Dastaraka Crossing	N 35º 32′ 57.30″ E 45º 26′ 25.68″	826
14-	Kanat Street	N 35º 33′ 43.38″ E 45º 26′ 46.56″	868
15-	Main Internal Buses Transportations Center	N 35º 33′ 41.04″ E 45º 26′ 20.40″	854
16-	German Village (sampling location of dust storm event which occurred on 22 Feb., 2010).	N 35º 34′ 57.12″ E 45º 27′ 14.41″	975
17-	Mamostain Quarter (sampling location of dust storm event which occurred on 22 Feb., 2010).	N 35º 33′ 54.42″ E 45º 26′ 22.08″	864
18-	Kurdsat Quarter (sampling location of dust storm event which occurred on 22 Feb., 2010).	N 35º 35′ 43.80″ E 45º 26′ 18.36″	948

In addition to that, extra samples from the massive dust storm event of 22 February, 2010 were taken out separately from three locations of 16, 17, and 18. Dust storm sampling locations were far away from high densified urban and traffic volume location and the collection process took 12 hours in order to enable the collection of an acceptable amount of the deposited dust storm particles for the intended analysis purposes (Figure 1)**.**

The dry dust deposits for all samples were sieved through a 140 mesh stainless-steel (106 micrometer), since tiny airborne particles or aerosols that are less than 100 micrometers are collectively referred to as total suspended particulate matter (TSPM) **[12]**, and then sealed in plastic container for subsequent analyses.

C. Dust samples analysis

Hygroscopic moisture was measured gravimetrically at 105 °C for 1.0 g air-dried dust samples by using a moisture meter (Model Mettler Toledo). The pH of the 1:10 dust: water suspension ratio was prepared by mixing 1.0 g dust sample with10 ml distilled water and allowing the mixture to equilibrate for 30 minutes with occasional shaking, then the pH-values were measured in the supernatant using a portable pH-meter (model WTW 330i/ Germany) according to soil survey standard test method **[13]**. Organic carbon (OM) content in dust samples were determined by Walkley-Black method (wet oxidation by potassium dichromate $K_2Cr_2O_7$ and concentrated H_2SO_4) as it is described by **[14]**.

Total carbonates ($CaCO_3$ equivalent) in dust samples were determined by the acetic acid method **[15]** which was approved for the local soils by **[16]**.The active calcium carbonate equivalents was determined according to the methods described by **[17]**.

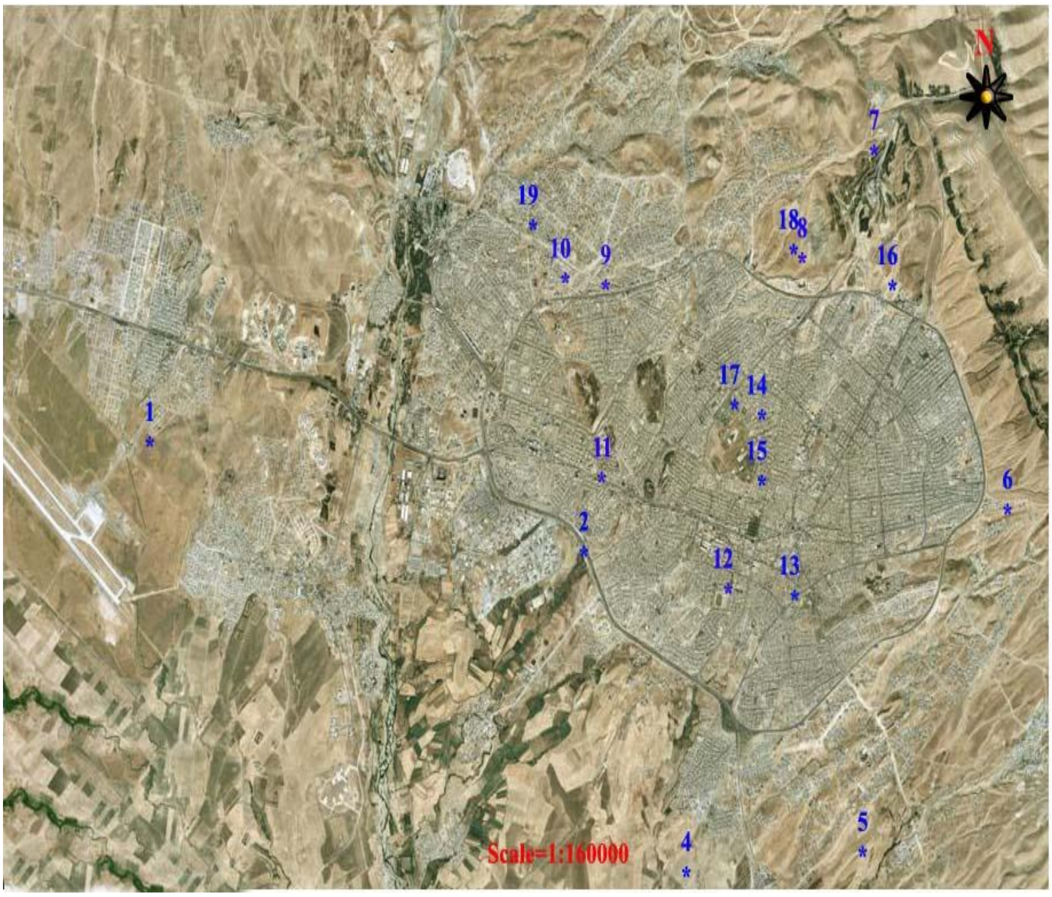


Figure (1): Dust sampling path. (Google Earth)

D. Functional groups analysis: Functional groups in dust samples were analyzed by Fourier transform infrared (FTIR) spectroscopy (Model PerkinElmer precisely Spectrum one /USA), Plate (3-2H and I). The KBr-dust pellets were prepared by mixing (0.6) mg dried sample with (99.4) mg of oven dried KBr and ground to a fine powder in an agate mortar then pressed at 6000 to 6500 psi (11 to 12 tons on ram) using hydraulic lab press (Model ICL's new patented E-Z Press/ USA) within a wavenumber range of 450 to 4000 cm^{-1} following the method described by **[18].**

E. Heavy metals analysis: The total heavy metal content of V, Co and As in settleable dust sample were determined by digestion with aqua regia extraction solution, following the procedure recommended by **[19]**. A 1.0-g dust of each sample was digested with 20 ml aqua regia (HCl of 37% and HNO_3 of 70% in a ratio of 3:1) at room temperature for 16 hours. Thereafter, the mixtures were digested at 130 C^o for 2 hours using the automated kjeldahl digester (model Tecator Digestion System Unit 2540 Auto/ Denmark-Sweden, Plate 3-2 J and K). The final suspensions were then filtered through an ashless Whatman 41 filter, diluted to 100 ml with 0.5 M HNO_3, and stored in polyethylene bottles at 4 C^o for element analysis. All glass- and plastic-wares used were previously soaked in 10% HNO_3 and rinsed thoroughly with deionized water. The metals were analyzed or determined using both inductively coupled plasma-optical emission spectroscopy ICP-OES (model PerkinElmer, precisely Optima 2100/USA. All the used chemicals were Analar grade.

RESULTS AND DISCUSSIONS

The results of chemical properties of settleable dust (dustfall) were shown in Table (2). pH values of the 1:10 dust: water suspension had an alkaline reaction and generally were in the range of 9.07 to 10.48. The highest value was 10.48 and found in location number 3 (Tanjaro), while, the lowest value of pH was recorded by location 17 of the dust storm sample. The alkalinity of the dust samples might be due to the presence of high calcium carbonates minerals content and/or cement dust particles, since there are many cement planets in the vicinity of Sulaimani city.

Table (2): Some chemical properties of the collected settleable dust samples for the studied locations

Sample locations numbers	pH at 25 ºC of the suspension	g kg $^{-1}$ dust			%
		Organic matter	Total $CaCO_3$ equivalents	Active $CaCO_3$	Active to total $CaCO_3$
1	10.28	80.10	287.5	241.7	84.1
2	10.38	51.20	268.0	240.2	89.6
3	10.48	80.20	296.7	249.6	84.1
4	10.20	60.40	275.1	241.8	87.9
5	9.94	6.190	263.2	235.8	89.6
6	9.91	29.10	270.2	258.9	95.8
7	9.94	97.90	260.3	231.7	89.0
8	9.91	76.69	284.5	244.8	86.1
9	9.88	65.55	290.0	255.5	88.1
10	9.76	48.60	256.8	239.4	93.2
11	9.42	99.10	234.5	219.6	93.6
12	9.82	94.00	218.4	188.9	86.5
13	9.13	90.90	285.1	245.8	86.2
14	9.72	66.00	247.1	218.8	88.6
15	9.62	103.31	253.3	229.1	90.4
16	9.08	16.40	200.0	189.6	94.8
17	9.07	16.90	199.2	189.1	94.9
18	9.09	15.70	200.18	189.9	94.8

The carbonate minerals content were relatively high and the values were ranged between 199.2 to 296.7 g kg $^{-1}$. On the other hand, the results showed that most of the carbonate minerals were predominantly in active forms. As it is also presented in Table (2), the active carbonate minerals content ranged from 188.9 to 258.9 g kg $^{-1}$ and these values accounted for 86.5 to 95.8% of the total carbonates minerals. This was to be expected simply because the local soils are calcareous and rich in carbonate minerals and the active carbonate minerals were predominately present in fine particles. This result was in very close agreement with **[20]**, who reported that in countries with Mediterranean, arid and desert climates, soils containing calcium carbonate in one or several of their horizons are frequent.

The organic matter content was relatively high and the values ranged from 15.70 to 103.31 g kg $^{-1}$ Table 2). The associated organic matter constituents with fine particles (100 µm) might be present as discrete particles, adsorbed or associated as complexes and/ or chelated with different soil particles such as carbonates, free oxides and clay minerals. Organic matter constitutes is an important fraction of aerosol mass, both in remote and urban locations **[21].** The presence of organic compounds in aerosol particles is due to primary emissions and secondary organic aerosol (SOA) formation. SOA can be formed by condensation of species produced by gas phase oxidation of volatile compounds. The chemical composition of the organic fraction affects the hygroscopicity of aerosol particles which in turn affects the aerosol size distribution, residence time in the atmosphere and optical properties **[22 and 23].**

The functional groups that were identified in the settleable dust samples along with their corresponding wavenumbers are shown in (Tables 3 and Figures 2, 3, 4, 5 and 6). The results of this study revealed that most functional groups that were present in all the studied samples were; sulfinate ester, sulfate ion, thiol and bounded free hydroxyl group. Also the following functional groups of sulfoxide, p. amine (bend.), carbonyl and amine (bend.) were also present in all the studied samples except the sample of location number 6 (Kaziewa Quarter), and it was the only sampling location that had a silicate group. This might be due to the fact that this location was not highly implicated with a heavy traffic volume and also the effects of urban densification. In a FTIR study **[24]** for investigation the functional groups in an episodic appearance of Saharan dust incursion over Istanbul, Turkey. It has been found that the observed IR peaks for silicate ions was at 1,030 and 800 cm^{-1}, this result was in agreement with our finding for the silicate ion.

Table (3): Detected functional groups content in the collected airborne dust samples for the study locations.

Sampling locations numbers	Detected functional groups content in the wave number ranges of 700 to 3800 cm^{--1}
1	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
2	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
3	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
4	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
5	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
6	Sulfinate ester; Silicate; Sulfate ion; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
7	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.);Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
8	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
9	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
10	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
11	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
12	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
13	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Isocyanide or Alkynes HC; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
14	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
15	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; Alkanes HC; P. Amine (str.); Bonded and free hydroxyl group.
16	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; P. Amine (str.); Bonded and free hydroxyl group.
17	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; P. Amine (str.); Bonded and free hydroxyl group.
18	Sulfinate ester; Sulfoxide; Sulfate ion; P. Amine (bend.); Carbonyl; Thiol; P. Amine (str.); Bonded and free hydroxyl group.

Where, HC: Hydrocarbon; P.: Primary; bend.: bending vibration; str.: stretching vibration.

On the other hand, the dust storm samples of the locations 16, 17 and 18 were the only samples which were free of the functional group of alkanes as compared to the other samples of local source dust. Alkanes are hydrocarbons that contain only single bonds of carbon and hydrogen atoms, they can be subdivided into the following three groups: the linear straight-chain alkanes, branched alkanes, and cycloalkanes. Alkanes are also saturated hydrocarbons and the simplest alkanes are methane and ethane **[25]**. This can be due to the fact that the dust particles that carry the alkanes group are transported over long distances and might undergo several important reactions, despite their relative inertness, since alkanes are probably the least chemically reactive class of organic compounds.

Additionally, the sample of location number 13 (Sarkarez/ Dastaraka crossing) was the only location that had a functional group of isocyanide or alkynes hydrocarbons. The variability of functional groups within this sample of number 13 could be attributed to the changes in air composition due to a heavy traffic volume and congestion in this location, which consequently led to the so-called hot-spot location.

From the previous findings of the functional groups in this study it has been observed that oxygenated functional groups carbonyl C=O and organic hydroxyl C-OH were observed in most of the studied samples.

In a FTIR spectroscopy analysis study **[36]** for aerosol particle samples collected at four different locations in eastern North America during the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) 2004 campaign the following functional groups of; Saturated aliphatic C-C-H groups, unsaturated aliphatic C=C-H groups, organic hydroxyl C-OH groups from alcohols and carboxylic acids, carbonyl C=O groups from carbonyl in ketones, aldehydes, and carboxylic acids, organosulfur C-O-S groups, ammonium, sulfate, and nitrate were detected during most of the ICARTT 2004 study on all sampling platforms, these findings were somewhat in agreement with the results of current study.

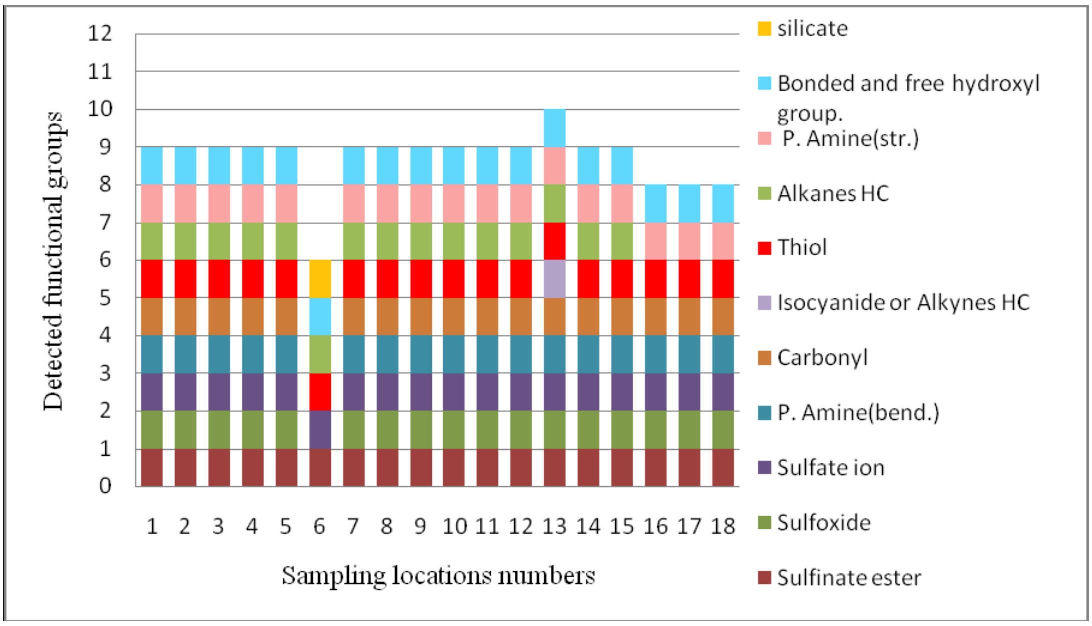
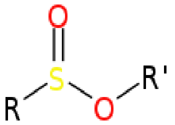
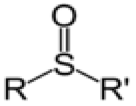
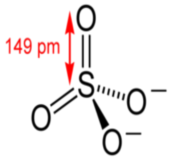
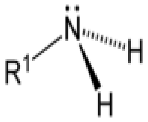
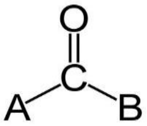
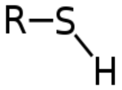
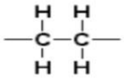
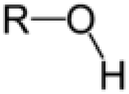
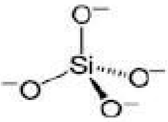


Figure (2): Detected functional groups content in the collected airborne dust samples for the study locations.

Furthermore, Table (4) show the wave number in cm^{-1}, structural formula and compounds examples for the detected functional groups in the studied dust samples, while Figure 3, 4,5 and 6 show the spectrums of the detected functional groups along with the wavenumbers of some sample for the FTIR-spectroscopy.

Despite that organonitrate (ON) groups are thought to be important substituents in secondary organic aerosols, but much lower quantities are observed in the atmosphere **[26].** This might explain our results also since organonitrate groups had not been detected.

Table (4): Wave number (cm^{-1}), structural formula and compounds examples for the detected functional groups in the studied dust samples.

No.	Functional group	Wave number (cm^{-1})	Chemical formula	Structural formula	Compounds examples
1-	Sulfinate esters	710 to 880	R-SO_2R' esters (stretching)		Ethyl methanesulfonate Mesylate
2-	Sulfoxide (Sulfinyl)	1025 to 1035	RSOR' (stretching)		Diphenyl sulfoxide Dimethyl sulfoxide
3-	sulphate ion	1420 to 1445	SO_4^{-2} (stretching)		calcium sulfate ($CaSO_4$) lead sulfate ($PbSO_4$) barium sulfate ($BaSO_4$)
4-	Primary amine	1610 to 1625 3400 to 3410	RNH_2 (bending) or RNH_2 (stretching)		Methylamine 2-aminopentane
5-	Carbonyl	1725 to 1775	RCOR' (stretching)		Aldehyde Ketone Carboxylic acid Ester
6-	Thiol	2514 to 2516	RSH (stretching)		Ethanethiol - C_2H_5SH (Ethyl mercaptan) Thiophenol
7-	Alkyne	2370 to 2380	RC≡CR' (stretching)		Acetylene
8-	Isocyanide	2370 to 2380	RNC (stretching)		Benzonitrile (Phenyl cyanide)
9-	Alkane	2925 to 2935	C-H or C-C (stretching)		$CH_3CH_2CH_3$ (propane) CH_3CH_3 (ethane)
10-	Hydroxyl group	3615 to 3620 (bonded) 3695 to 3705 (free)	–OH (stretching)		Methanol
11-	Silicate group	at ~1000	SiO_4		minerals, as quartz, olivine, mica, clay, pyroxene, amphibole

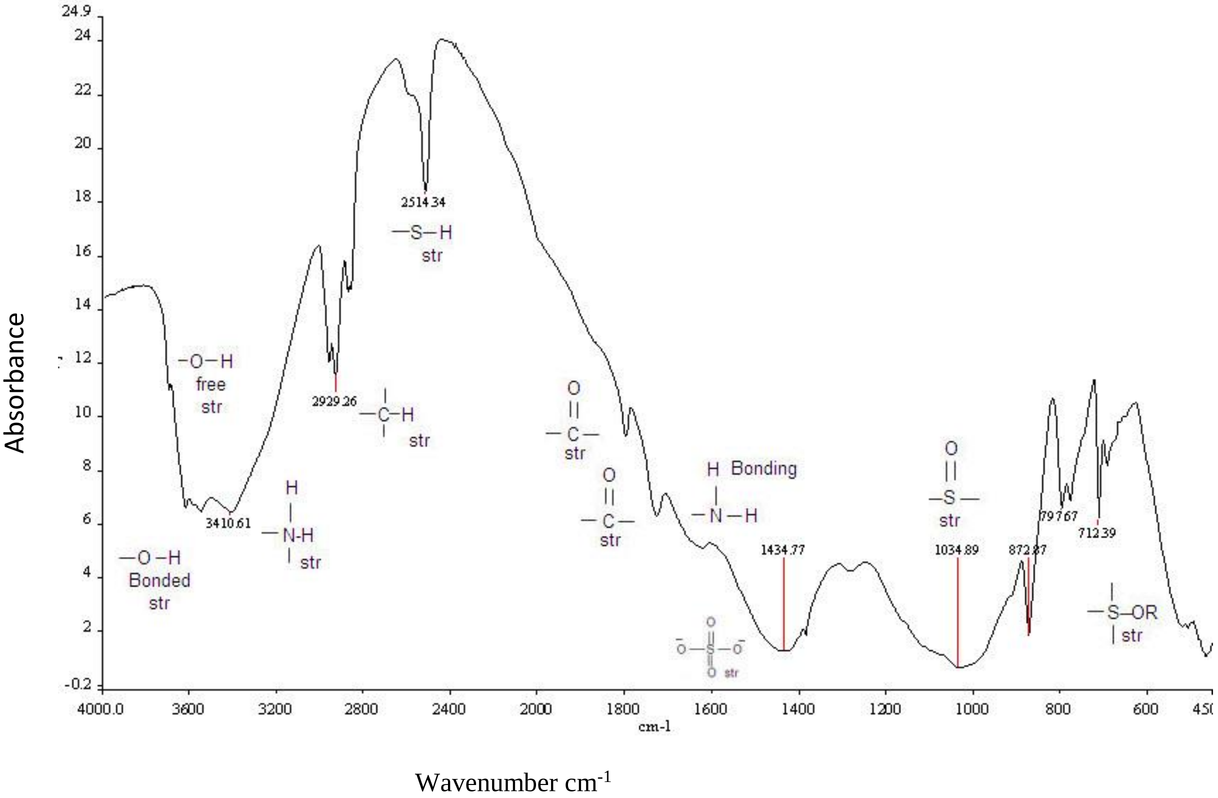


Figure (3): FTIR-Spectrum Analysis for sample location number (1)

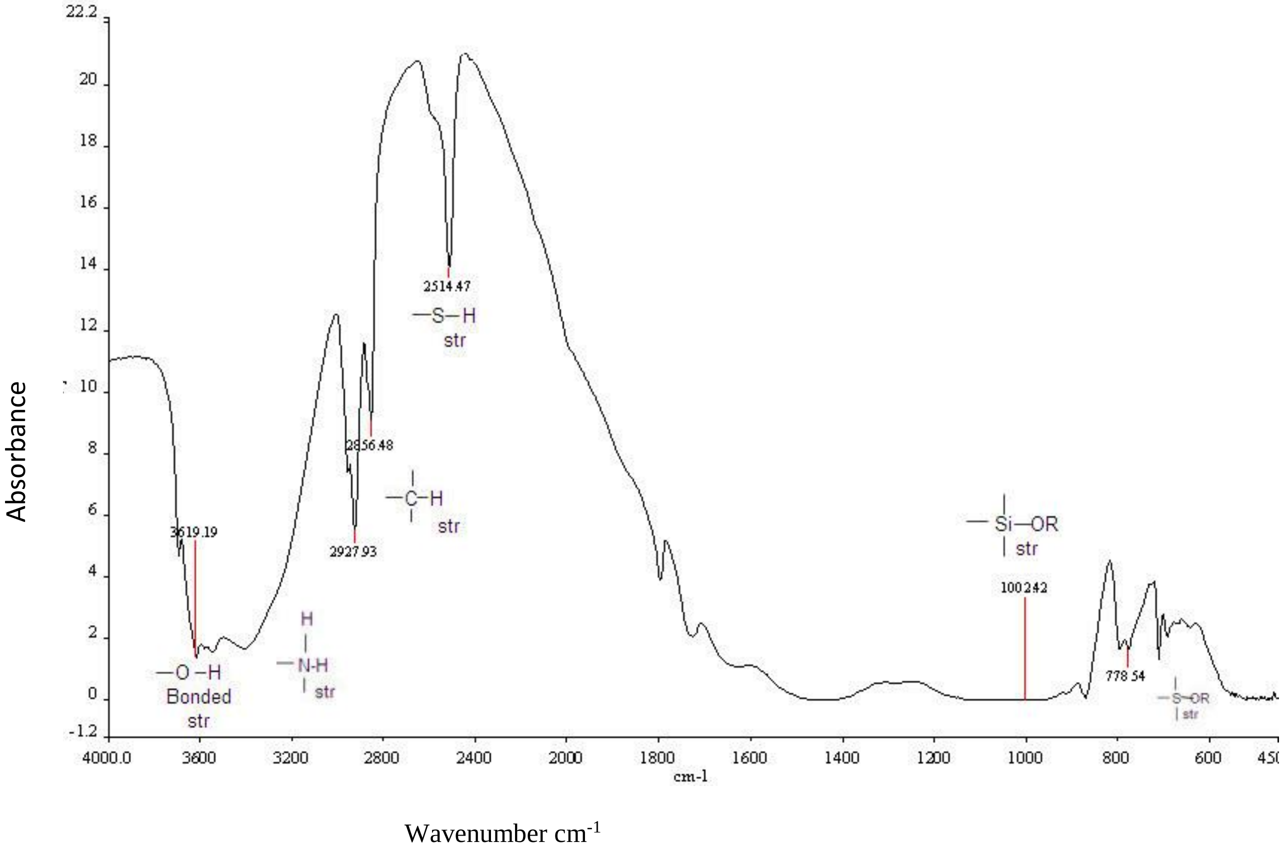


Figure (4): FTIR-Spectrum Analysis for sample location number (6)

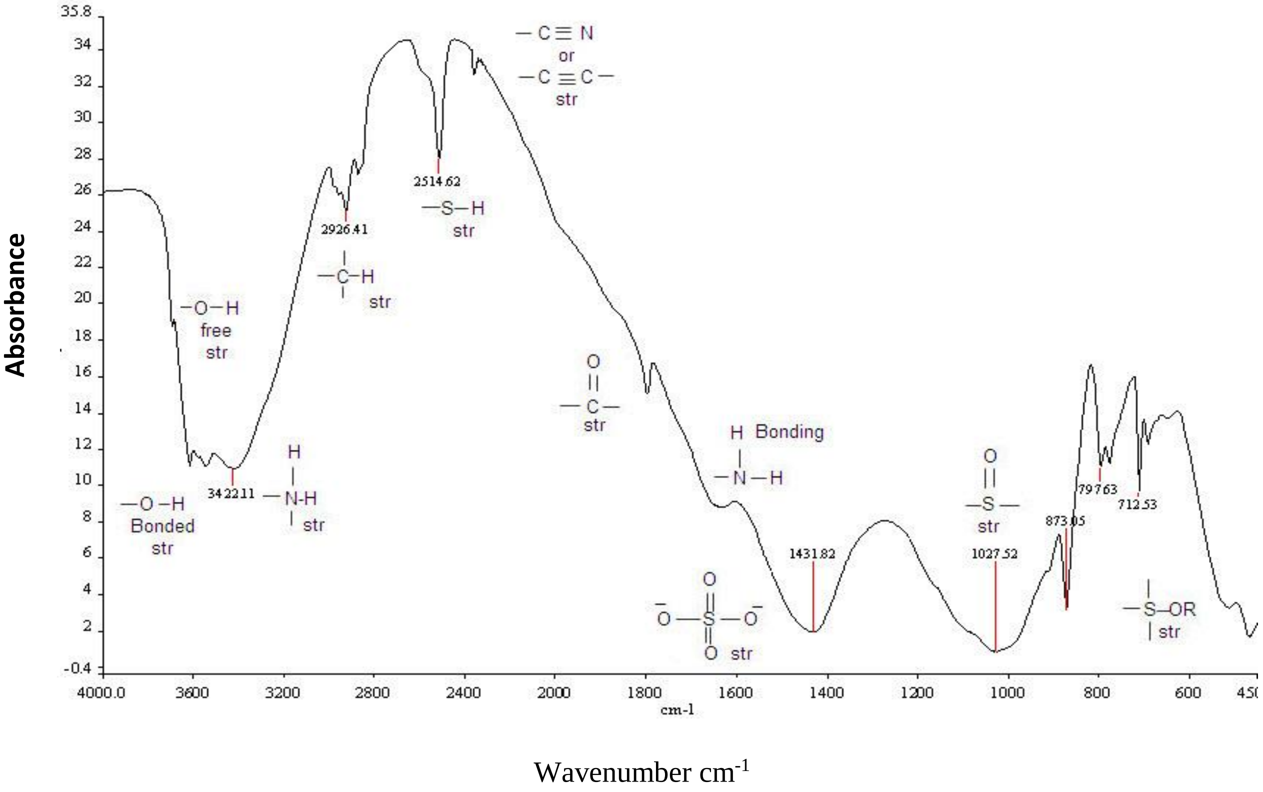


Figure (5): FTIR-Spectrum Analysis for sample location number (13)

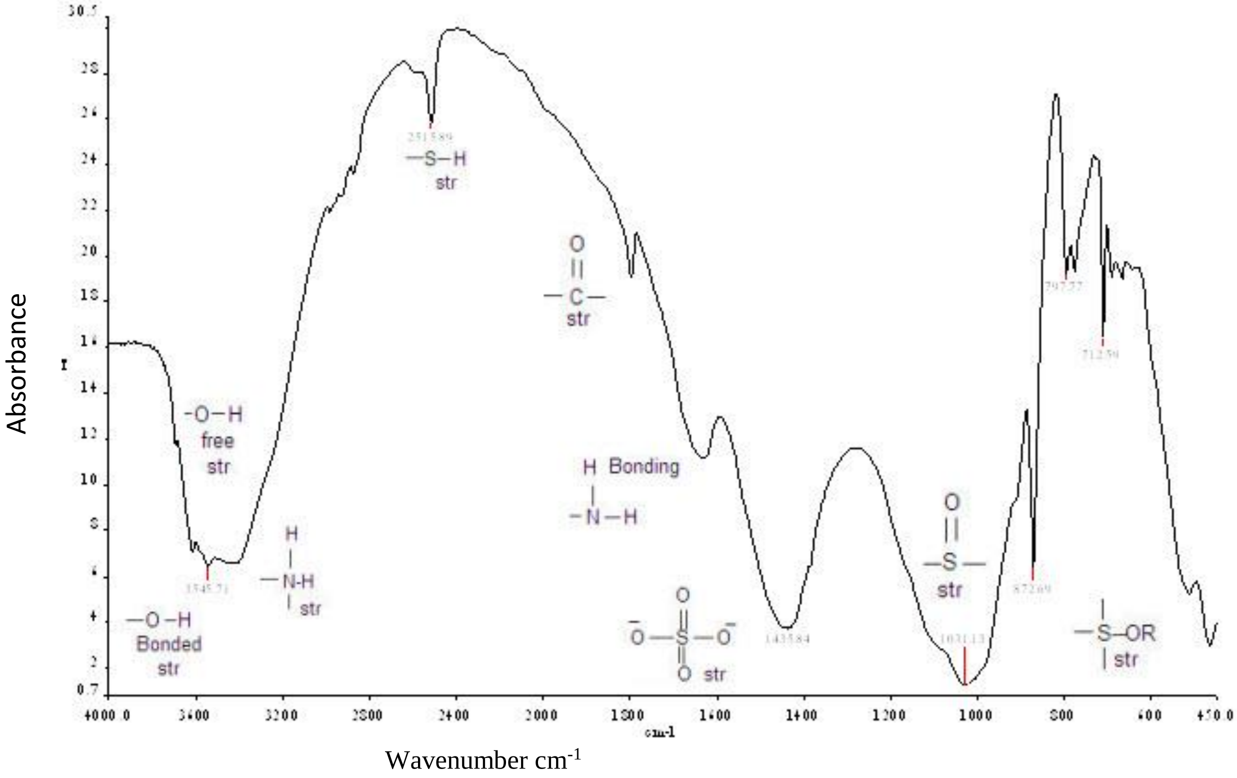


Figure (6): FTIR-Spectrum Analysis for sample location number (16).

Quantitative analysis of selected heavy metals (V, Co and As) was undertaken for the collected settleable dust samples of the 18 locations. As it is shown in Table (5), the concentration of the studied metals were ranged between (0.20 – 3.20), (2.02 – 5.45) and (2.89 – 45.50) mg kg^{-1} dust for As, Co and V respectively in all the studied locations. No distinct variation for the heavy metal content in dust storm samples was observed as compared with the heavy metal content for the sampling locations of the local settleable dust.

The concentration ranges showed a large variability among the locations and that was because each location had its specific condition from the point of view of urbanization, traffic volume, industrial activity, and sources of dust particle, climatic and geographical site. For example, the maximum concentration levels for both (Co and As) were found by location number 3 (Tanjaro). This might be due the fact that Tanjaro region is a landfill dumping place and is also an industrial region for many industrial that might lead to produce large amount of dust born heavy metals and fly ash into the atmosphere. Despite the fact that location number 6 (Kaziewa Quarter) was not highly influenced by industrial activity, heavy traffic volume and also urban densification, but the maximum level of (V) was measured in this location, this can be attributed to soil dust that can also contribute to the concentration of heavy metals in the air **[27].**

According to previous research studies, Vanadium is widely distributed in the earth's crust at an average concentration of 100 ppm (mg kg^{-1}), similar to that of zinc and nickel **[28]**. Vanadium is the 22nd most abundant element in the earth's crust **[29]** and there are about 65 different vanadium-containing minerals **[30 and 31]**. Vanadium is also found in phosphate rock and certain ores and is present in some crude oils as organic complexes **[31]**.

Cobalt compounds are released to the air from natural and anthropogenic sources, especially burning fossil fuels. Other sources of atmospheric cobalt emissions are vehicle exhaust and cigarette smoke **[32]**.

Cobalt has both beneficial and harmful effects on human health. Cobalt is beneficial for humans because it is part of vitamin B12, which is essential to maintain human health. The concentration of cobalt in soil varies widely, generally ranging from about 1 to 40 ppm, with an average level of 7 ppm. Soils containing less than about 3 ppm of cobalt are considered cobalt-deficient because plants growing in them do not have sufficient cobalt **[33].**

Table (5): Airborne heavy metal concentrations of the settleable dust samples (mg kg^{-1} dust).

No.	Sample locations	Concentrations (mg kg^{-1} dust)		
		V	Co	As
1-	Raparin/ Near to Sulaimani International Airport	5.20	3.99	0.71
2-	Maleek Mhmood Circle/ Lovan Hotel	20.71	2.84	0.48
3-	Tanjaro / Tanjaro Mosque	3.23	5.45	3.20
4-	Nawgrdan Village/ Osman Gas Fact.	22.61	3.34	0.31
5-	Charakhan Quarter	44.14	2.02	0.20
6-	Kaziewa Quarter/ Near to Goizha Apartments	45.50	2.31	0.21
7-	Kurdsat/ Quarter 1	34.32	2.41	0.21
8-	Kurdsat Quarter 2	37.43	2.44	0.23
9-	Maleek Mhmood Circle/ Beside Zargata Underpass.	12.50	3.44	0.56
10-	Farmanbaran Quarter	8.42	5.12	0.89
11-	Salim Street/ Beside Khsrawkhal Bridge.	36.44	2.42	0.26
12-	Chawrbakh Quarter / Near to Sulaimani Stadium	6.82	5.71	1.50
13-	Sarkarez/ Dastaraka Crossing	25.24	2.14	0.25
14-	Kanat Street	18.62	3.36	0.42
15-	Main Internal Buses Transportations Center	11.43	3.29	0.34
16-	German Village	2.93	2.97	1.31
17-	Mamostain Quarter	3.23	3.31	1.34
18-	Kurdsat Quarter	2.89	2.98	1.32

Arsenic is a widely distributed metalloid, occurring in rock, soil, water and air **[34]**. Arsenic is classified chemically as a metalloid, having both properties of a metal and a nonmetal; however, it is frequently referred to as a metal. The concentration of arsenic in soil varies widely, generally ranging from about 1 to 40 ppm with an average level of 3- 4 ppm. Levels of arsenic in the air generally range from 1 to 2,000 ng m^{-3} **[35]**

.There is some evidence that exposure to arsenic in early life (including gestation and early childhood) may increase mortality in young adults. Arsenic (or metabolites) concentrations in blood, hair, nails and urine have been used as biomarkers of exposure. Arsenic in hair and nails can be useful indicators of past arsenic exposure, if care is taken to avoid external arsenic contamination of the samples **[7]**.

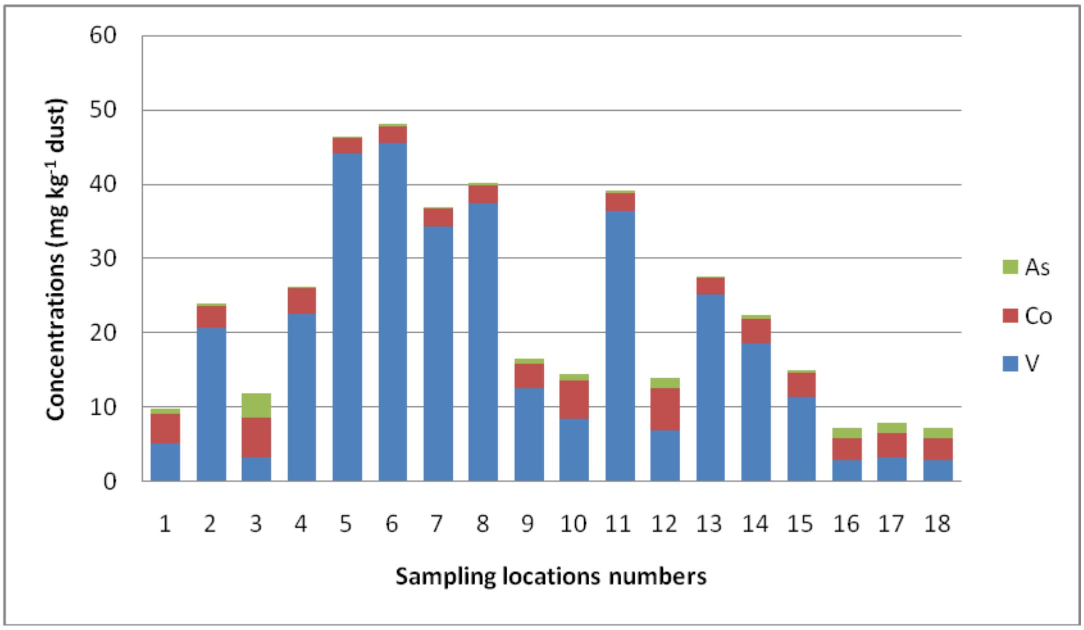


Figure (7): Concentration of **V, Co and As** in settleable dust particles for the study locations.

In a study of an environmental assessment of dust fall and the associated heavy metal contents in 8 dust fall stations around Assiut- Egypt **[36]** it has been demonstrated that As metal ranged between 0.41 to 3.46 µg g^{-1} and this result closely agrees with those obtained in current study. However, **[37]** found a range concentration between 0.4-18.2 µg g^{-1} for of arsenic (As) in road deposited dust at Ketu-South District, Ghana and it was clear that the uppers limit was inconsistent with the finding of this study.

Results of the researchers **[38]** indicated that heavier traffic density led to increase of many heavy metals content in dust samples, since traffic heavy metals such as zinc, barium, and copper, likely to originate from mechanical abrasion of brake pads and tires of motor vehicles. Moreover, the elements iron, chromium, cobalt, manganese, vanadium, and titanium, known to be associated with mechanical parts of motor vehicles and released as a result of mechanical friction. Other factor that contributes to heavy metals in dust samples is the fly ash that escaping from the fossil-fuel power plants for electricity generation. In Sulaimani city there were many power plants for electricity generation. Some of those are still in operation. The researchers **[39]** revealed that the heavy metal concentration of As, Co and V in fly ash in relevant ambient aerosol fraction of PM3 were 9.2-128.8 , 4.9-30.9 and 14.8-638.0 mg kg^{-1} , while for the fly ash in relevant ambient aerosol fraction of PM10 were 8.70 – 88.3, 6.1 – 30.4 and 11.5 -476.0 mg kg^{-1} respectively at three measuring sites.

Conclusions

This study showed that the FTIR spectroscopic method was fast and convenient method to identify these peaks of the functional groups which carried by particle dust incursion into the atmosphere. Therefore, this study contributes substantially to the understanding of ambient functional groups.

In brief, most of the detected functional groups were dominant in the samples of all the studied locations and there was no specific trend in the distribution of the studied heavy metals among the samples of the studied locations.

There are sufficient evidences that exposure to atmospheric functional groups and heavy metal is a health hazard in world wide. The importance of this study might provide insight into the chemical composition of atmospheric particulate matter and associated risks in Sulaimani city.

Future research is required to clarify the quantitative amount of the different functional groups and heavy metals that might be present in the total ambient dust by using air sampler instrument.

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