CHARACTERIZATION OF MINERALS IN AIR DUST PARTICLES IN THE STATE OF TAMILNADU, INDIA THROUGH FTIR SPECTROSCOPY

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ABSTRACT.

The abstract of this paper explains the presence of minerals in air which causes great concern regarding public health issues. The spectroscopic investigation of air dust particles of several samples in various locations in the state of Tamilnadu, India is reported. Qualitative analyses were carried out to determine the major and minor constituent minerals present in the samples based on the FTIR absorption peaks. This study also identified the minerals like quartz, asbestos, kaolinite, calcite, hematite, montmorillonite, nacrite and several other trace minerals in the air dust particles. The presents of quartz is mainly found in all the samples invariably. Hence the percentage of quartz and its crystalline nature were determined with the help of extinction co-efficient and crystallinity index respectively.

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Keywords: Air pollution, FTIR, Air Suspended Particles, Minerals, Relative distribution.

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1 Introduction

All over the world, air pollution is becoming a major concern. Governments in many countries are developing variety of technologies to reduce harmful minerals in air. Both gaseous and particulates are emitted as pollutants from the various pollution sources. Suspended Particulates Matter (SPM) is constituted of aerosol dust or other particulates of size <<1 to 200 microns suspended in air (Chandrasekaran et al., 1997). Depending on the conditions, the fine and ultra-fine particulates may persist in the atmosphere for days or weeks and travel hundreds or thousands of miles from their source (Tyagi, 2009). Primary particles are those emitted directly from a source eg. Windblown soil, or soot from vehicle exhaust. Secondary particulates are those formed from the interaction of other compounds; for eg. Nitrate formation from the photo-oxidation of NO_x, or the condensation and agglomeration of terpenes from a forest stand (Street et al., 1996).

It has been estimated that about 3 million people were die and many more suffered from serious health effects by every year because of air pollution as reported by WHO (WHO, 2003). The epidemiological literature has more than 100 published papers, which for the most Part, support association of PM with increases in morbidity and/or mortality (WHO, 2000). The Air pollution may cause serious health implications including high blood pressure, digestive problems, nerve and kidney disorders, memory and concentration problems, muscle and joint pain and also it affect the immune systems and may even lead to cancer. An estimate made by Central Pollution Control Board (CPCB) during the year 1995 showed that 2000 metric tons of air pollutants (Total Suspended Particulate Matter)

are pumped into the atmosphere every day in Delhi, India (Tyagi, 2009). It is implied that maternal exposure to industrial metal dust or fumes during pregnancy may reduce fetal growth (Siew lai et al., 2010).

Particulate pollution is a serious health problem throughout the world, exacerbating a wide range of respiratory and vascular illness in urban areas (Wang Lie et al., 2006). Populations at risk from inhaled particles are those most susceptible to pulmonary and heart diseases, infants and elderly people. A joint study of the World Health Organization (WHO), World Resource Institute (WRI) and the US Environmental Protection Agency (EPA) estimated that nearly 700,000 deaths worldwide are related to air pollution and that this number can escalate to 8 million deaths by 2020 (Working Group, 1997). Occurrence of respiratory diseases in South Asia resulting from air pollution both indoors and outdoors is estimated to be quite substantial. In each of the 23 cities with a million plus population in India, air pollution level exceed WHO standards (Sagareswar et al., 2011). Recent acknowledgement of the sensitivity of an air quality to changes in climate has initiated a closer examination of the relationships between meteorology and air quality (John et al., 2011). The swift pace of industrial and economic activity in many developing countries contributed significantly to an increased level of air borne particulate matter, enriched in many toxic heavy metals (Sagareswar et al., 2011). Several studies have demonstrated the negative effect of particulate matter on human health and have confirmed an association between the elevated level of particulate air pollution and decline in lung function or increase in various respiratory diseases (Raimonnda et al., 2012).

Plants in urban areas may improve air quality by removal of gaseous pollutant and of particles (Wang Lie et al., 2006). Many scientist recommends growing green vegetation in and around the industrial/urban areas (Ghose and Majee, 2001; Shannigrahi et al., 2003). Heavy metals and other toxic particles have been shown to accumulate, causing damage and death of some species (Alfani et al., 1996). It also exerts aggravating effect on agricultural production and the green house effect (Ndukwe and Jenmi, 2008). In this paper, an attempt has been made to overlook on mineralogical compositions existing in air dust particles in various districts of Tamilnadu, India.

2 Methods

A large variety of field techniques for assessing settled dust have been described in the literature (Adams and Fordio, 2001; Beaman and Kingsbury, 1984). Keeping the above problem in view, the suspended particulate matter (SPM) has been under taken in Tamilnadu. The air suspended particles which are deposited on tissue papers at the height of 20 feet in road side and land area were collected (Ramasamy and Ponnusamy, 2009). These tissue papers were washed in distilled water. The settled dust particles at the bottom of container are then dried at 110°C in oven and are used for analysis. The samples collected from 38 towns and cities of Tamilnadu, which are labeled as 1 to 111. The samples were mainly collected from Vehicular area (say Bus stand), Industrial area and Residential area which cover almost all major districts of Tamilnadu. The sample collected areas are visualized (Fig. 1) and are listed out with their latitude and longitude in table 1.

The major and minor minerals are qualitatively determined by using FTIR technique. The Nicolet avatar 360 series available in Centralized Instrumentation and Service Laboratory (CISL), Annamalai University, Chidambaram, Tamilnadu, India is made use of this in all the present work for recording the FTIR spectra of all the samples at room temperature. The samples are usually subjected to various pre-treatments in order to remove organic matter and certain other materials to improve the quality of the spectrum. The samples are mixed with Potassium Bromide (KBr) at various ratios like 1:10, 1:20, 1:30, 1:40 and 1:50. The pellets were prepared and the spectra were taken. The maximum absorption and large number of peaks were observed for the samples in the ratio of 1:20 (sample-KBr). The spectra were taken in the region of 4000-400 cm^{-1}. The instrument scans the spectra 16 times in 1 minute. The resolution is ± 4 cm^{-1} and its accuracy is ± 1 cm^{-1}.

The spectrum for each site was considered as a representative spectrum of the site. Sample of 2 mg is mixed with 40 mg of spectroscopic KBr in the ratio 1:20 using an agate mortar and pestle. Before mixing, necessary amount of KBr powder is dried at 120^0 C for six hours in an oven. Otherwise the broad spectral peak due to free OH will seriously affect the interpretation on the bound hydroxyls associated with any of the minerals. The major and minor minerals are qualitatively determined by FT-IR technique.
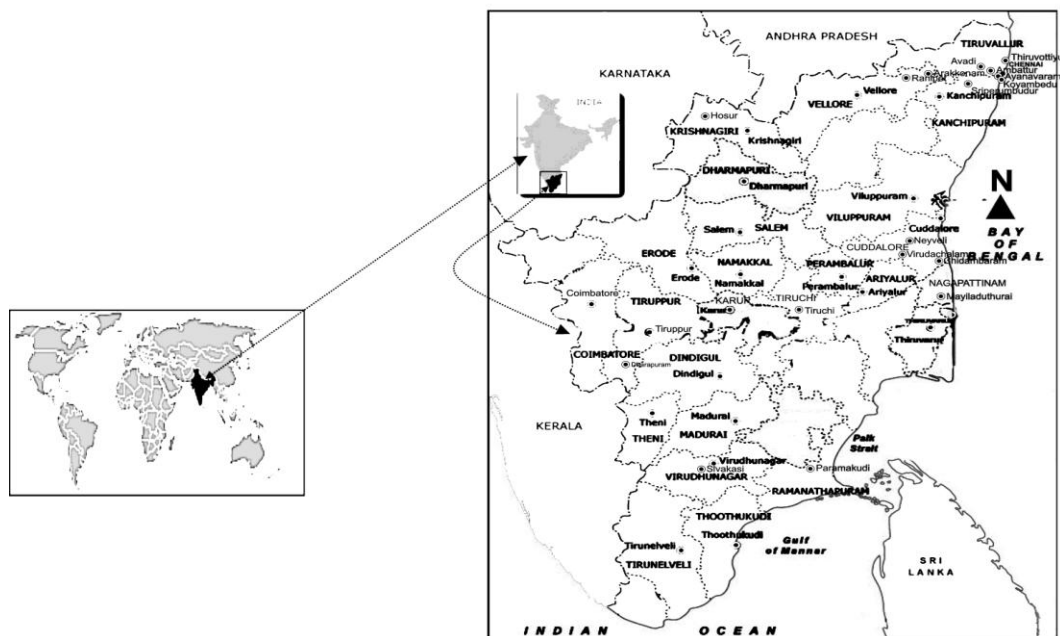

Fig. 1. Location of sample collected areas in various places of Tamilnadu, India

Table 1. Latitude and Longitude of sampling sites

City/ Town	Latitude	Longitude	District	Sample Numbers		
				Vehicular Area	Residential Area	Industrial Area
Kanchipuram	N 12° 50' 3"	E 79° 42' 13"	Kanchipuram	1	2	3
Arakkonam	N 13° 4' 57"	E 79° 40' 142"	Vellore		4,5,6	
Villupuram	N 11° 56' 22"	E 79° 29' 51"	Villupuram	7	8	9
Cuddalore	N 11° 45' 0"	E 79° 45' 0"	Cuddalore	10	11,12	13
Ranipet	N 12° 55' 42"	E 79° 19' 56"	Vellore	14	15,16	17
Krishnagiri	N 12° 31' 7"	E 78° 12' 49"	Krishnagiri	18	19	20
Vellore	N 12° 54' 59"	E 79° 7' 56"	Vellore		21	22
Hosur	N 12° 43' 58"	E 77° 49' 48"	Krishnagiri	23	24,25	26
Dharmapuri	N 12° 7' 38"	E 78° 9' 28"	Dharmapuri	27	28	29
Salem	N 11° 39' 51"	E 78° 8' 45"	Salem	30	31	32
Namakkal	N 11° 13' 10"	E 78° 10' 4"	Namakkal	33	34	35
Erode	N 11° 20' 32"	E 77° 43' 38"	Erode	36	37	38

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Tiruppur	N 11° 6' 43"	E 77° 21' 15"	Tiruppur	39	40,41	42
Coimbatore	N 11° 1' 0"	E 76° 57' 20"	Coimbatore	43	44	45
Dharapuram	N 10° 44' 12"	E 77° 31' 56"	Tiruppur	46	47	48
Karur	N 10° 57' 26"	E 78° 4' 51"	Karur	49	50	51
Tiruchirappalli	N 10° 47' 25"	E 78° 42' 16"	Tiruchirappalli (Trichy)	52	53	
Ariyalur	N 11° 8' 13"	E 79° 4' 32"	Ariyalur	54	55	56
Neyveli	N 10° 58' 0"	E 78° 32' 50"	Cuddalore	57	58,59	60
Perambalur	N 11° 13' 59"	E 78° 52' 59"	Perambalur	61	62,63	64
Dindigul	N 10° 22' 2"	E 77° 58' 49"	Dindigul	65	66	67
Theni	N 10° 0' 37"	E 77° 28' 36"	Theni	68	69	
Madurai	N 9° 55' 30"	E 78° 7' 11"	Madurai	70,71	72	73
Virudhunagar	N 9° 35' 1"	E 77° 57' 30"	Virudhunagar	74	75	76
Paramakudi	N 9° 32' 42"	E 78° 35' 27"	Ramanathapuram	77		78
Sivakasi	N 9° 26' 54"	E 77° 47' 53"	Virudhunagar	79	80,81	103
Tuticorin	N 8° 45' 50"	E 78° 8' 5"	Tuticorin	82	83,84	85
Tirunelveli	N 8° 43' 58"	E 77° 42' 0"	Tirunelveli	86	87,88	89
Chidambaram	N 11° 23' 53"	E 79° 41' 43"	Cuddalore	90	91	92
Virudhachalam	N 11° 30' 50"	E 79° 19' 40"	Cuddalore	93		94
Tiruvarur	N 10° 46' 16"	E 79° 38' 13"	Thiruvarur	95		96
Mayiladuthurai	N 11° 6' 6"	E 79° 39' 7"	Nagapattinam	97		98
Thiruvottiyur	N 13° 9' 36"	E 80° 17' 60"	Thiruvallur	99	100	101
Avadi	N 13° 7' 12"	E 80° 5' 60"	Thiruvallur	102		104
Sriperumbudur	N 12° 58' 2"	E 79° 56' 30"	Kanchipuram		105,106	
Ambattur	N 13° 5' 60"	E 80° 9' 36"	Thiruvallur			107
Ayanavaram	N 13° 6' 1"	E 80° 13' 45"	Chennai	108	110	109
Koyambedu	N 13° 4' 8"	E 80° 11' 28"	Chennai	111		

3 Results and Discussion

The FTIR spectra of all samples are analyzed and the minerals are assigned using available literatures. The observed wave numbers from all the spectra are given in table 2 along with their corresponding minerals name.

Table 2. Observed frequencies with their corresponding minerals, total number samples of dust collected areas and Tentative Assignment of frequencies. How is the frequncy resolution???

Sl. No	Minerals	Wave No. cm^{-1}	Total Number of Samples	Tentative Assignment
1.	Quartz	468, 693, 777, 800, 1077, 1090, 1144, 1861, 1872.	101,90,104,45,55, 13,9,1,7.	Si-O symmetric bending, Si-O symmetric stretching.
2.	Calcite	876,1422,1431,1636, 1786,1792,1798, 2516,2570,2873, 2982.	95,65,41,79,2,14, 1,2,5,4,2.	doubly degenerate asymmetric Stretching, CO_3 stretching, C=O stretching, combinational mode, O-H stretching.
3.	Kaolinite	433,938,1623,3623, 3695,3735.	63,3,29,8,68,8.	Si-O deformation, O-H deformation, O-H stretching.
4.	Disordered Kaolinite	478.	5.	Si-O-Si deformation.
5.	Pyrophyllite	737.	4.	O-H out of plane bending.
6.	Vermiculite	670,811.	89,1.	Si-O symmetrical bending, O-H out of plane bending.
7.	Smectite	522	3.	Al-O-Si deformation.
8.	Palygorskite	414,512,567,1647, 1681,3611.	18,2,7,20,2,1.	Si-O deformation, Si-O stretching, O-H deformation.
9.	Sepiolite	422,1657,3246,3619.	29,20,6,17.	O-H stretching.
10.	Imogolite	602 .	50.	O-H deformation.
11.	Proto Imogolite	680,854.	3,2.	Si-O bending.
12.	Hematite	536.	110.	Fe-O.
13.	Asbestos	1033.	101.	Si-O stretching.
14.	Chrysotile	405,453.	11,4.	Si-O stretching.
15.	Dolomite	582,2628.	52,1.	C-O stretching.
16.	Nacrite	905,915,1005,3648.	8,47,21,14.	Si-O stretching, Al-Al-OH deformation, O-H stretching.
17.	Magnetite	577,717.	4,56.	Fe-O bending.
18.	Gibbsite	3300,3529.	2,14.	O-H stretching.
19.	Aragonite	1457,2520.	21,82.	C-O bending, O-H stretching.
20.	Mont-	3405.	106.	H-O-H stretching.

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	morllionite		
21.	Organic Carbon	2853,2921.	106,108.	C-H stretching.
22.	Feldspar group	635,645,1772,727, 1113,440,591,1019, 3417.	5,47,9,34,29,9,4,6, 1.	Al-O coordination, Si-O stretching, O-H bending, O-H stretching, O-H deformation.
23.	Goethite	495,894.	4,1.	Fe(III)-O-Si bending, O-H bending.
24.	Hectorite	656.	2.	Si-O stretching.
25.	Biotite	3712.	28.	O-H stretching.
26.	Dickite	755.	5.	Al-O-Si Perpendicular.
27.	Beidellite	886.	3.	Al-Fe^{3+}-OH deformation.
28.	Glauconite	984,3588.	1,6.	Si- O stretching, O-H stretching.
29.	Celadonite	1099.	13.	Si-O stretching.
30.	Anorthite	1159.	10.	Si-O stretching.
31.	Baryte	1182.	5.	Si-O-Si stretching.
32.	Cerussite	1385,1399.	50,3.	C-O bending.
33.	Ankerite	1448.	5.	C-H bending.
34.	Aliettile	788,3675.	1,50.	O-H stretching.
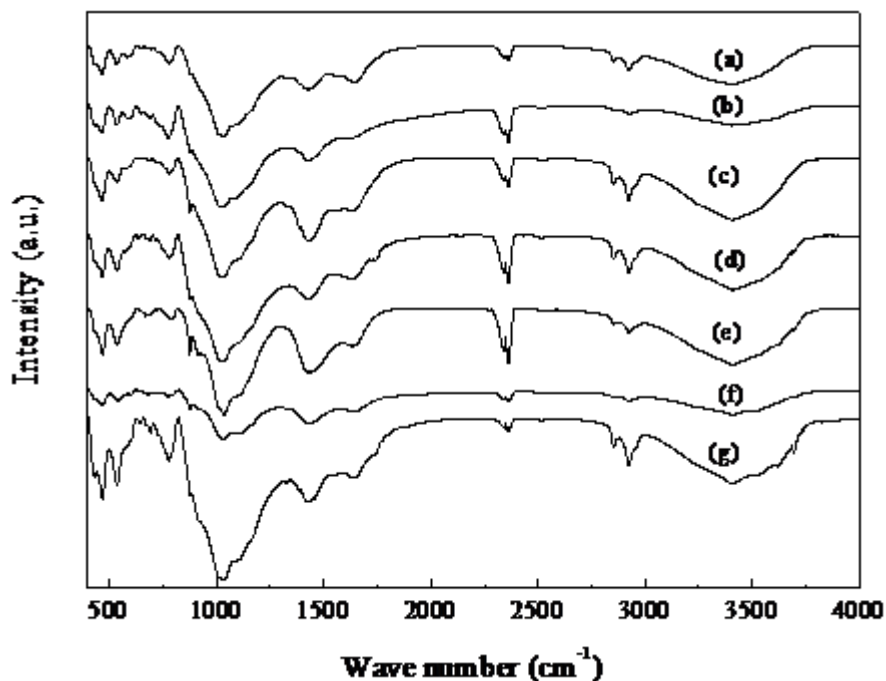
In the region between 800 and 1200 is a big broad negative peak, resulting from several minerals with high concentrations. To separate in this peak 5% Asbestos, using a single line is impossible. Therfore Asbestos has to be considered as an ARTEFACT!

Fig. 2. Representative FTIR spectra: sample no:1 (a), sample no:21 (b), sample no:41 (c), sample no:61 (d), sample no:81 (e), sample no:101 (f) and sample no:111 (g).

3.1 Quartz

The silicate minerals are primary concern because of their relative abundance and importance. Quartz (SiO_2) is common and invariably present in all the samples. The Si-O bonds are the strongest bonds in the silicate structure and can be readily recognized in the infrared spectra of such minerals by very strong bands in the region 900 to 1100 cm^{-1} is due to stretching as well as less intense bands in the 400 to 800 cm^{-1} region is due to bending. The quartz mineral in the sample were detected with bands at 468 cm^{-1}, 693 cm^{-1}, 777 cm^{-1}, 800 cm^{-1}, 1077 cm^{-1}, 1090 cm^{-1}, 1144 cm^{-1}, 1861 cm^{-1} and 1872 cm^{-1} and the IR absorption peaks were reported by many authors (Chester and Green, 1968; Farmer, 1974; Coates, 1977; Hlavay et al., 1978; Russell, 1987; Ko and Chu, 2005). The quartz is present in almost all samples. These assignments are in good agreement with the observation on the quartz mineral (Hlavay et al., 1978).

3.2 Calcite

Calcite is the most stable polymorph of calcium carbonate ($CaCO_3$). Calcite crystals are trigonal-rhombohedral, though the actual calcite rhombohedra are rare as natural crystals. The frequencies of $CaCO_3$ correspond, according to assignments reported by Herzberg (1945), to a symmetric stretching, v_1, an out-of plane bending, v_2, a doubly degenerate asymmetric stretching, v_3 and a doubly degenerate planar bending v_4. The presence of IR absorption peaks at different frequencies like 876 cm^{-1}, 1422 cm^{-1}, 1431 cm^{-1}, 1636 cm^{-1}, 1786 cm^{-1}, 1792 cm^{-1}, 1798 cm^{-1}, 2516 cm^{-1}, 2570 cm^{-1}, 2873 cm^{-1} and 2982 cm^{-1} which are identified for calcite in the samples (Ndukwe and Jenmi, 2008; Adams and Fordio, 2001; Beaman and Kingsbury, 1984; Chester and Green, 1968; Farmer, 1974; Chester and Elderfield, 1967; SenthilKumar et al., 2001). Among various frequencies 876 cm^{-1} is due to the C=O stretching mode vibration. The frequency at 1422 cm^{-1} is due to doubly degenerate asymmetric stretching mode vibration. The frequency at 1431 cm^{-1} is due to $(CO_3)^{2-}$ stretching mode vibration. The frequencies of 1636 cm^{-1}, 1786 cm^{-1}, 1792 cm^{-1} are due to C=O stretching mode vibration. The frequency at 1798 cm^{-1}

is due to combinational mode of vibration. The frequencies of 2516 cm^{-1}, 2570 cm^{-1}, 2873 cm^{-1} and 2982 cm^{-1} are due to O-H stretching mode vibration. The symmetric stretching vibrations, v_3 lying between 1400-1450 cm^{-1} are interesting, as these vibrations are particularly sensitive to the side symmetry for the carbonate group. According to W.B. White (1971) if the peak is in between this range, the mineral prevailing low pressure during the formation or this peak increases in splitting of this vibration mode in calcite one can infer that the carbonate group becomes increasingly distorted in this phase with high compression. In the present case there is no splitting in this mode v_3 but the peak at 1422 cm^{-1} and 1431 cm^{-1} is present within the range 1400-1450 cm^{-1}. This indicates prevailing low pressure during the formation (Ramasamy et al., 2003).

3.3 Clay minerals

The term clay is generally applied to very fine mineral of fragments or particles which composed mostly of hydrous-layer silicates of aluminum, though occasionally it containing magnesium and iron. The SiO_2 ratio is a formula in the key factor of determining the clay mineral types.

3.3.1 Kaolinite

A typical dioctahedral species is kaolinite, with an ideal structural formula of $Al_2Si_2O_5(OH)_4$. Kaolinite is electrostatically neutral and has triclinic symmetry. Oxygen atoms and hydroxyl ions between the layers are paired with hydrogen bonding. The kaolinite clays are common soil minerals which often occur in atmospheric particulate matter. Infrared analysis of dust samples by Sakabe (1965), indicate that kaolinite type clays may make up a significant fraction of the mineral content of the atmospheric aerosol. The observed absorption frequencies of 433 cm^{-1}, 938 cm^{-1}, 1623 cm^{-1}, 3623 cm^{-1}, 3695 cm^{-1} and 3735 cm^{-1} are the characteristic peaks of clay mineral kaolinite. The frequencies at 3623 cm^{-1}, 3695 cm^{-1} and 3735 cm^{-1} are due to OH stretching of inner-surface hydroxyl groups (Russell, 1987). The frequencies at 938 cm^{-1} and 1623 cm^{-1} are due to OH deformation of inner-surface hydroxyl group and at 433 cm^{-1} is due to Si-O deformation. The obtained peak values of this mineral matches very well with the results obtained by Jana and peter (2011), Russell (1987), Ramaswamy and Venkatachalapathy (1992) and Hlavay et al. (1978). The intensity of the bands varies from sample to sample at different places, which means the amount of the kaolinite varies from sample to sample. It is also one of the most common mineral in ceramic industry (Jun Ojima, 2003). Almost all the samples in the present study are having kaolinite mineral. The inhalation of this dust mineral may develop a pneumoconiosis which often referred as kaoliniosis. It is characterized by the presence of rounded opacities in the lung (Malcolm Ross et al., 1993). The disordered kaolinite observed at the frequency at 478 cm^{-1} due to the presence of Si-O-Si deformation vibration.

3.3.2 Pyrophyllite

Pyrophyllite is a phyllosilicate mineral composed of aluminium silicate hydroxide. It occurs in two more or less distinct varieties, namely, crystalline folia and which compact masses. In the ideal case, the structural formula is expressed by $Al_2Si_4O_{10}(OH)_2$ for pyrophyllite. Therefore, the 2:1 layers of these minerals are electro statically neutral and are held together with Van der Waals bonding. One-layer triclinic forms are known for as polytypes of pyrophyllite. The frequency at 737 cm^{-1} is due to O-H out of plane bending mode vibration, which is identified by Pyrophyllite minerals (Durig et al., 1971).

3.3.3 Vermiculite

The vermiculite $(Mg, Fe^{2+}, Al)_3 (Al, Si)_4O_{10}(OH)_2 \cdot 4(H_2O)$ unit structure consists of the sheets of trioctahedral mica or talc which separated by the layers of water molecules and these layers occupy a space about two water molecules thick. Vermiculite is present nearly 90 samples out of 111. The observed frequencies of vermiculite are 670 cm^{-1} and 811 cm^{-1}. 670 cm^{-1} is due to Si-O Symmertrical

bending mode vibration. The frequency at 811 cm^{-1} is due to O-H out of plane bending mode (Audrius Misiunas et al., 2005).

3.3.4 Smectite

Smectite is structural formula of the dioctahedral aluminous species may be represented by $(Al_{2-y}Mg^{2+}/_y)$ $(Si_{4-x}Al_x)O_{10}(OH)_2M^+/_{x+y}$ nH_2O, where M^+ is the interlayer exchangeable cation expressed as a monovalent cation and where *x* and *y* are the amounts of tetrahedral and octahedral substitutions, respectively. The frequency at 522 cm^{-1} for smectite is due to Al-O-Si deformation (Jana and peter, 2011).

3.3.5 Palygorskite

Palygorskite are papyrus-like or fibrous hydrated magnesium silicate minerals and are included in the phyllosilicate group because they contain a continuous two-dimensional tetrahedral sheet of composition Si_2O_5. Palygorskite is present in all this samples which have frequencies of 414 cm^{-1}, 512 cm^{-1}, 567 cm^{-1}, 1647 cm^{-1}, 1681 cm^{-1} and 3611 cm^{-1}. The vibration assignment for 414 cm^{-1} and 512 cm^{-1} are due to Si-O deformation. The frequency at 567 cm^{-1} is due to Si-O stretching mode vibration. The frequencies at 1647 cm^{-1}, 1681 cm^{-1} and 3611 cm^{-1} are due to O-H deformation (Jana and peter, 2011).

3.3.6 Sepiolite

Sepiolite is a clay mineral, a complex magnesium silicate, a typical formula for which is $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$. It can be present in fibrous, fine-particulate, and solid forms. Sepiolite is present in all this samples which have frequencies of 422 cm^{-1}, 1657 cm^{-1}, 3246 cm^{-1} and 3619 cm^{-1}. The frequencies at 422 cm^{-1}, 1657 cm^{-1}, 3246 cm^{-1} and 3619 cm^{-1} are due to O-H stretching of hydroxyl group (Jana and peter, 2011).

3.3.7 Imogolite

Imogolite is frequently found together in main clay component. Imogolite is an aluminium silicate clay mineral with formula $Al_2SiO_3(OH)_4$. The frequency at 602 cm^{-1} is assigned for imogolite mineral and it is due to O- H deformation mode (Jana and peter, 2011). Imogolite is present nearly 50 samples. The spectrum of Proto-imogolite has substantially the same pattern as imogolite but is more diffuse. Proto-imogolite (Malgorzatabaranska et al., 2005) sols can be considered as highly dispersed forms of proto-imogolite allophone. The frequencies at 680 cm^{-1} and 854 cm^{-1} are observed for Proto-imogolite. The frequencies at 680 cm-1, 854 cm-1 are due to Si-O bending mode.

3.4 Hematite

Hematite is the mineral form of iron (III) oxide (Fe_2O_3). Hematite crystallizes in the rhombohedral system and it has the same crystal structure as limonite and corundum. According to Russell (1987) and Ramaswamy and Venkatachalapathy (1992) were observed the absorption frequencies of Hematite is explained well. It observed almost in the entire samples which shows peak at 536 cm^{-1} which is the characteristic peak of hematite. The peak of hematite is due to Fe-O stretching mode vibration. In all these samples, the intensities of the hematite peaks are weak to medium. Hence this mineral can be considered as trace mineral, thus the inhalation of such small grain sized iron bearing mineral (hematite) along with other minerals will also create lung disease, because the particles are coated in the surface of lungs.

3.5 Asbestos

Asbestos is a naturally-occurring silicate mineral. The prolonged inhalation of asbestos fibers can cause serious illnesses, including malignant lung cancer, mesothelioma (a formerly-rare cancer strongly associated with exposure to amphibole asbestos) and asbestosis (a type of pneumoconiosis). Asbestos can be found naturally in the air outdoors and in some drinkable water including water from natural sources (Centre for disease, 2010). Studies have shown that members of the general (non-occupationally exposed) population have tens of thousands to hundreds of thousands of asbestos fibers in each gram of dry lung tissue, which translates into millions of fibers and tens of thousands of asbestos bodies in every person's lungs (Medscape article, 2010). The particle size and shape plays an important role in the inhalation and long penetration mechanisms, especially with amphibole fibrous (Coates, 1997). Generally Asbestos is exhibit intense absorptions in the region 1200-900 cm^{-1} of the infrared spectra. The spectrum of Asbestos is shown by the observed frequency at 1033 cm^{-1} which is due to Si-O stretching mode vibration.

3.6 Chrysotile

Chrysotile or white asbestos is the most commonly disordered form of asbestos. It is a soft, fibrous silicate mineral in the serpentine group of phyllosilicates. As such it is distinct from other asbestiform minerals in the amphibole group. The idealized chemical formula is $Mg_3(Si_2O_5)(OH)_4$ (U.S. Department, 2005). On the lines of Coates (1997) the presence of the band at 605 cm^{-1} is due to chrysotile asbestos. The frequencies at 405 cm^{-1} and 453 cm^{-1} show the Chrysotile mineral, which are due to Si-O stretching mode vibration (Rector and Fayer, 1998).

3.7 Dolomite

Dolomite is a carbonate mineral composed of calcium magnesium carbonate $CaMg(CO_3)_2$. The mineral dolomite crystallizes in the trigonal-rhombohedral system. The IR absorption bands at 582 cm^{-1} and 2628 cm^{-1} show the presence of dolomite in the samples (Dolomite, 2001-2005). This Dolomite mineral is present nearly in 53 Samples. The frequencies assignment for 582 cm^{-1} and 2628 cm^{-1} are due to C-O symmetric stretching mode vibration (Russell, 1987).

3.8 Nacrite

Nacrite $Al_2Si_2O_5(OH)_4$ is a clay mineral that is a polymorph or polytype of kaolinite. It crystallizes in the monoclinic system. Nacrite is present in nearly 90 samples. The observed frequencies of nacrite are 905 cm^{-1}, 915 cm^{-1}, 1005 cm^{-1} and 3648 cm^{-1}. The frequencies at 915 cm^{-1} is due to Al-Al-OH deformation of inner hydroxyl group. The frequencies at 905 cm^{-1} and 1005 cm^{-1} are due to Si-O stretching and at 3648 cm^{-1} is due to O-H stretching of inner hydroxyl group (Russell, 1987).

3.9 Magnetite and Gibbsite

Magnetite is a ferrimagnetic mineral with chemical formula Fe_3O_4, and a member of the spinel group. Gibbsite is an aluminium hydroxide mineral of the oxides and hydroxides group, with structural formula $Al(OH)_3$. Gibbsite's structure is made up by the stacking of octahedral sheets of aluminium hydroxide. Each layer consists of octahedral six-fold coordinated Al^{3+} cations sandwiched between two close packed layers of OH (Aaron and Heather, 2010). Magnetite is present in 60 samples and Gibbsite is present in 16 samples among the collected samples. Magnetite is observed at the frequencies of 577 cm^{-1} and 717 cm^{-1} and Gibbsite is observed at the frequencies of 3300 cm^{-1} and 3529 cm^{-1}. The frequency at 577 cm^{-1} is due to Fe-O bending mode and at 717 cm^{-1} is due to Fe-O bending mode vibration. The frequencies at 3300 cm^{-1} and 3529 cm^{-1} is due to O-H stretching mode vibration.

3.10 Aragonite

Aragonite is a carbonate mineral and is formed by biological and physical processes including precipitation from marine and fresh water environments. The study of aragonite in the infrared wavelength region was prompted by differences in the data on aragonite reported by Hunt et al. (1950) and Huang and Kerr (1960). The IR absorption peaks at 1457 cm^{-1} and 2520 cm^{-1} shows the Aragonite mineral and it presents nearly in 103 samples. The assignment for 1457 cm^{-1} is due to C-O bending mode vibration and 2520 cm^{-1} is due to O-H stretching mode vibration.

3.11 Montmorillonite

Montmorillonite is a very soft phyllosilicate group of minerals that typically form in microscopic crystals. The theoretical formula for montmorillonite i.e., without structural substitutions is $(OH)_4 Si_8 Al_4 O_{20} nH_2O$. The montmorillonite minerals are composed of hydrous aluminuim silicates in the form of extremely small particles. The IR absorption peaks at 3405 cm^{-1} shows presence of montmorillonite (Russell, 1987). It is presents nearly in 106 samples. This is due to O-H stretching mode vibration of water molecule.

3.12 Organic carbon

Total organic carbon (TOC) is the amount of carbon bound in an organic compound. Organic carbon forms are derived from the decomposition of plants and animals. They are capable of decay or are the product of decay. They contain organic compounds whose molecules contain carbon, oxygen, nitrogen and hydrogen (Wayne Pluske et al.) Organic carbon is present in almost all the samples, which have frequencies at 2853 cm^{-1} and 2921 cm^{-1}. They are due to C-H symmetric stretching mode vibration.

3.13 Feldspar

The feldspar group of minerals are of several types having different compositions such as orthoclase, microcline, sanidine (K-feldspar), albite (Na-feldspar) and anorthite (Ca-feldspar). Though three feldspars (orthoclase, microcline and sanidine) are having the same chemical formula ($KAlSi_3O_8$) but differ in structure (orthoclase - monoclinic, microcline - triclinic and sanidine – tetrahedral). The observed frequency for Feldspar is at 645 cm^{-1} and 1772 cm^{-1}. The frequencies of Hydrous Feldspar are observed at 440 cm^{-1}, 591 cm^{-1}, 1019 cm^{-1} and 3417 cm^{-1}. The observed frequency at 635 cm^{-1} for Orthoclase is due to Al-O coordination vibration (Coates, 1997). The observed frequency at 645 cm^{-1} and 1772 cm^{-1} for Feldspar is due to Si-O stretching mode vibration (Russell, 1987). The frequency at 440 cm^{-1} is due to O-H bending mode vibration at 591 cm^{-1} and 3417 cm^{-1} is due to O-H symmetric stretching mode vibration. Hydrous Feldspar is observed at frequency 1019 cm^{-1}, which has O-H deformation. The frequency at 727 cm^{-1} is due to Si-O stretching mode vibration which is identified by the microcline Feldspar. The frequency at 1113 cm^{-1} is due to Si-O-Si stretching mode vibration which is identified by Microcline Feldspar. Anorthite is the calcium end member of plagioclase feldspar. Plagioclase is an abundant mineral in the Earth's crust. The formula of pure anorthite is $CaAl_2Si_2O_8$. The frequency at 1159 cm^{-1} is due to Si-O stretching mode vibrations, which is identified by Anorthite mineral.

3.14 Other minerals

Goethite (FeOH) is an iron bearing oxide mineral found in soil and other low-temperature environments. Goethite has had a reputation for making rather uninteresting, dull and dirty mineral specimens. Goethite is observed at the frequencies of 495 cm^{-1} and 894 cm^{-1} which are due to bending mode vibration. The frequency at 495 cm^{-1} is due to Fe(III)-O-Si bending mode vibration. The observed

frequency at 894 cm^{-1} is due to O-H bending mode vibration. **Hectorite** ($Na_{0.4}Mg_{2.7}Li_{0.3}Si_4O_{10}(OH)_2$) is observed at the frequencies of 656 cm^{-1} is due to Si-O stretching mode vibration (Ibraheem et al., 2009).

Dickite ($Al_2Si_2O_5(OH)_4$) is a phyllosilicate clay mineral which is chemically composed of aluminium, silicon, hydrogen and oxygen. Dickite has a monoclinic crystal system and its crystal class is domatic. Dickite is observed at the frequency of 755 cm^{-1} which has Al-O-Si of perpendicular vibration (Russell, 1987). **Botite** mineral shows the frequency at 3712 cm^{-1} is due to O-H Stretching mode vibration.

Now a days **Beidellite** ($Na_{0.7}Al_4(Si_{7.3}Al_{0.7})O_{20}(OH)_4.xH_2O$) has been defined as a dioctahedral Al-smectite with an average layer charge of 0.6 to 0.7. This charge is completely created by the substitution of Si^{4+} by Al^{3+} on the tetrahedral positions. Russell (1987) reported well-resolved OH-deformation bands at 886 cm^{-1} for Al-Fe$_3$-OH deformation in beidellite.

Glauconite is ferric-iron silicate mineral with micaceous structure ($(K, Na)(Fe^{3+},Al, Mg)_2(Si, Al)_4O_{10}(OH)_2$. Glauconite has frequencies of 984 cm^{-1} and 3588 cm^{-1} which are due to Si-O stretching mode and O-H stretching mode vibration respectively (Sara and Ray, 2006). **Baryte** is observed at the frequency of 1182 cm^{-1} is due to Si-O-Si stretching mode vibration.

Celadonite is a mica group mineral, a phyllosilicate of potassium, iron in both oxidation states, aluminium and hydroxide with formula $K(Mg,Fe^{2+})(Fe^{3+},Al)(Si_4O_{10})(OH)_2$. It crystallizes in the monoclinic system. Celadonite is observed at the frequency of 1099 cm^{-1} which is due to Si-O of stretching mode vibration.

Cerussite ($Pb(CO_3)$**)** is formed by the chemical action of carbonated water on the mineral galena. Cerussite mineral is identified by the frequencies of 1385 cm^{-1} and 1399 cm^{-1} are due to C-O bending mode vibrations (Sara and Ray 2006; Robert et al., 1987). **Ankerite (**$CaFe^{2+}_{0.6}Mg_{0.3}Mn^{2+}_{0.1}(CO_3)_2$**)** mineral is identified by the frequency at 1448 cm^{-1} is due to C-H bending mode vibration (Bernd rebenstorf, 1988; Aaron and Heather, 2010). **Aliettile (**$Mg_3Si_4O_{10}(OH)_2Ca_{0.1}Na_{0.2}AlFe^{2+}_{0.7}Mg_{0.5}Al_3SiO_{10}(OH)_2 \cdot 3(H_2O)$**)** mineral is identified by the frequencies of 788 cm^{-1} and 3675 cm^{-1} which is due to O-H stretching mode vibrations.

4 Relative distributions of hazardous minerals

The origin of the minerals should be discussed. These all are natural minerals from the geogenic background!!

Almost all the samples are having the minerals like <mark>hematite, feldspar, quartz</mark>, asbestos, <mark>calcite, montmorillonite and kaolinite minerals.</mark> The relative distribution of major minerals such as hematite, feldspar, quartz, asbestos, calcite, montmorillonite, and kaolinite are explained through the determination of extinction co-efficient of the characteristic peaks and frequencies (536 cm^{-1}, 645 cm^{-1}, 777 cm^{-1}, 1033 cm^{-1}, 1422 cm^{-1}, 3405 cm^{-1}, 3695 cm^{-1}) of respective minerals. The extinction co-efficient of above mentioned minerals have been calculated for all the air suspended samples under the investigation, by using the relation.

$$K = DA/m \qquad\qquad (1)$$

Where,
K- Extinction co-efficient, D- Optical density (D = log I_0/I), I_0- Intensity of incident radiation, I-Intensity of transmitted radiation, A- Area of the pellet, m- Mass of the sample.

The Extinction co-efficient values are calculated. The maximum value for the mineral hematite is 29.4785, feldspar is 35.55715, quartz is 59.8161, asbestos is 22.8922, calcite is 23.3484, montmorillonite is 21.0083 and kaolinite is 21.8317. In over view, the amount of all the samples are visually indicated in the Figures 2 (a, b, c and d). Almost the same trend is observed in all the three categories Vehicular Area, Residential Area and Industrial Area, since the quartz is distributed as a major constituent irrespective of the categories and hematite, feldspar etc. are in the next order. When it

is focused in depth, the order of amount of quartz, hematite and feldspar are determined as Vehicular Area > Industrial Area > Residential Area. The asbestos are more in industrial area which may be due to the polluted air, solid wastages from the industry which are dissolved in air etc.
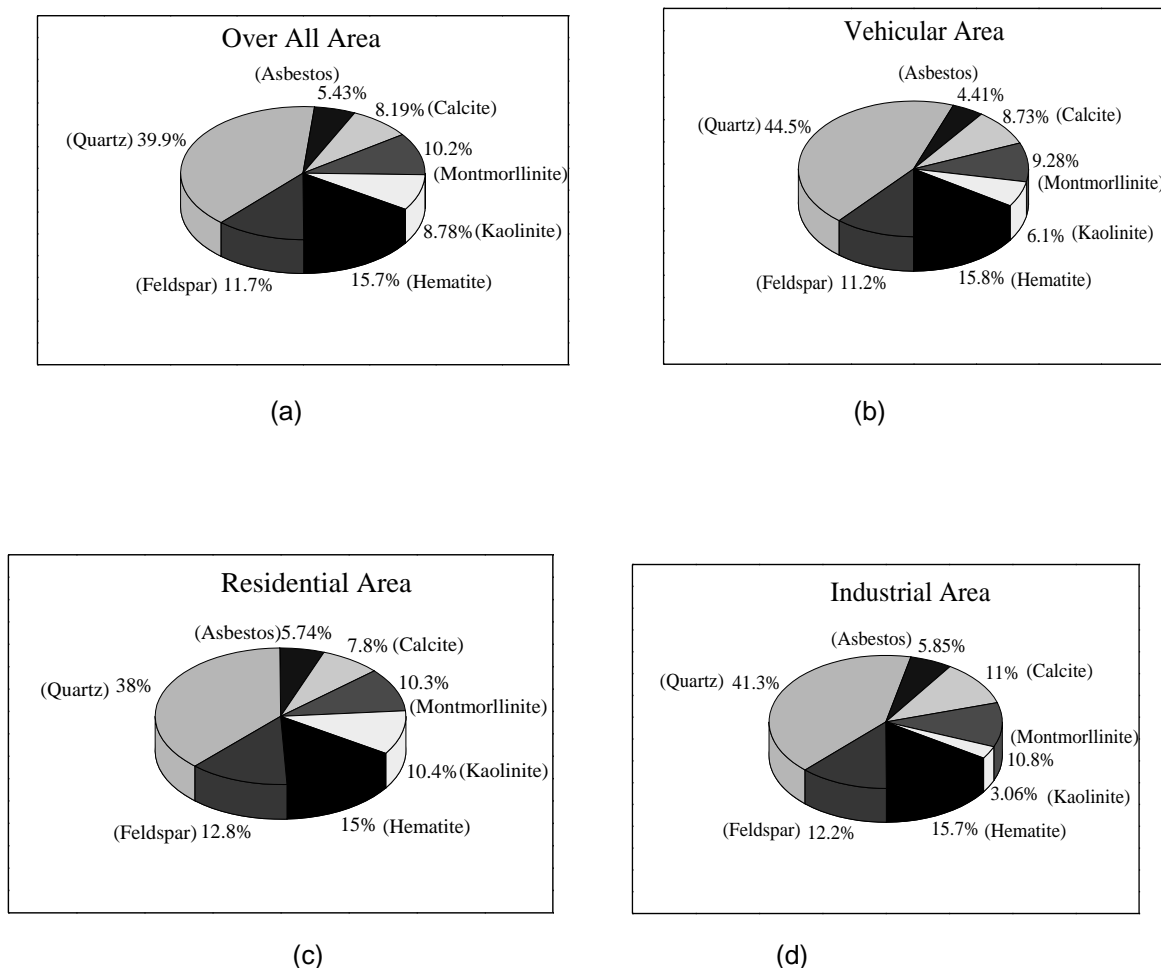

(a)

(b)

(c)

(d)

Fig. 3. Percentage of average value of extinction co-efficient in various sites of Overall Area (a), Vehicular Area (b), Residential Area (c) and Industrial Area (d).

5 Crystallinity index of Quatz

The crystallinity is defined as the fraction of crystalline materials in a mixture of crystalline and non-crystalline material. It is otherwise called as degree of disorder. When crystallinity is minimum, the minerals are said to be in disordered state and maximum then the minerals are considered to be in ordered state. Crystallinity is inversely proportional to the crystallinity index values.

Crystalline silica is one of the most abundant components in the dust samples both in natural and industrial environments. The crystalline nature of quartz may be confirmed through the presence of peak at around 695 cm^{-1}. According to Yariv and Mendelovici (1979), the absorption of band at 695 cm^{-1} is due to the vibration of octahedral site symmetry and at 777 cm^{-1} is due to the vibration in the tetrahedral site symmetry. The tetrahedral symmetry is stronger one than octahedral site symmetry. Hence, the present study indicates the presence of quartz is in disordered state which may be due to smaller particle size. According to Krivascy and Hlavay (1993), the inhalation of the disordered or crystalline silica can create the lung disease. The concentration of this quartz is proportional to the

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toxicity. Due to the presence of quartz in dust, the inhalation of the quartz particles in the size of 0.5- 0.7 µm may produce diseases such as chronic silicosis, acute silicosis, accelerated silicosis and silica tuberculosis (Malcolm Ross et al., 1993). The average values of crystallinity index of vehicular area, residential area and industrial area are 4.98, 6.15 and 5.608 respectively. From these values, it is observed that the residential area have disordered quartz and the vehicular area shows the existence of well ordered quartz. The industrial areas have in between nature.

(a)

(b)
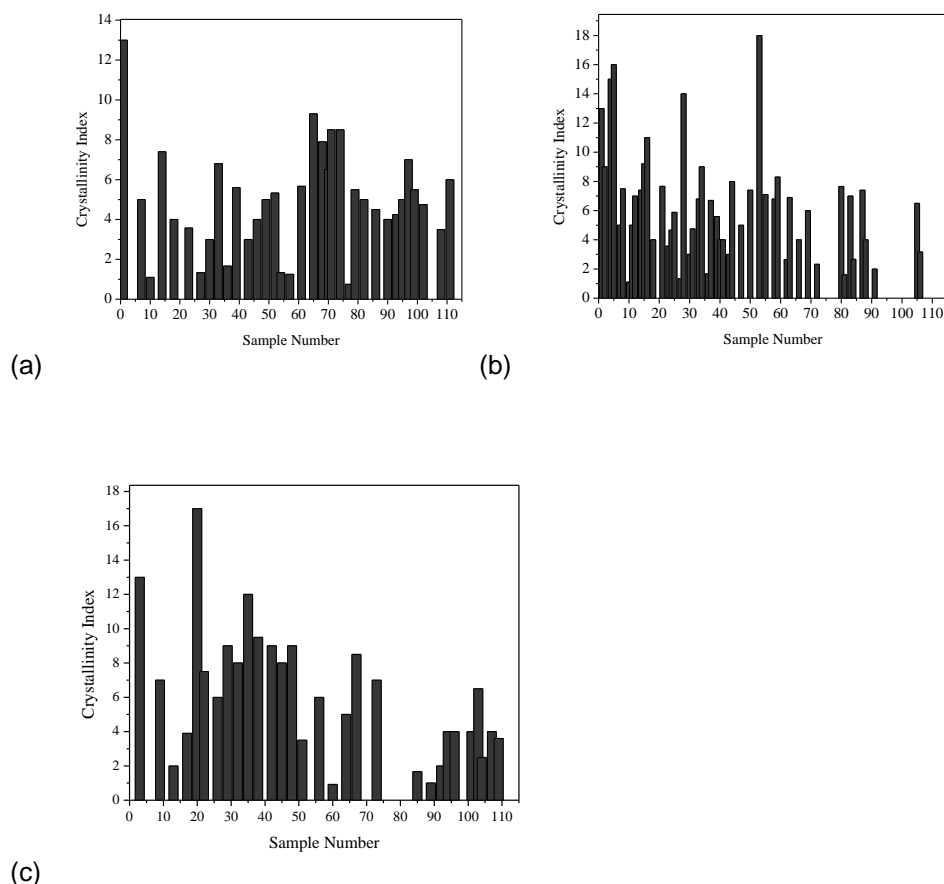
To evaluate the danger, the absolute amount (µg or mg/m³) has to be discussed.
All the other are just statements without a real meaning.

(c)

Fig. 4. Crystallinity Index of Quartz (a) Vehicular Area, (b) Residential Area and (c) Industrial Area.

no information about reproducibility and accuracy are given!!!!

6 Summary

The FTIR techniques have employed in the present paper which provides a rapid, reproducible and accurate method of determination of minerals in dust qualitatively and quantitatively. From the above studies it is concluded as follows.

The various dust samples have analyzed through infrared spectroscopic technique which was collected from different sites of Tamilnadu indicates the presence of Quartz, Calcite, Kaolinite, Pyrophyllite, Vermiculite, Smectite, Palygorskite, Sepiolite and some more minerals. Based on the references and the appearance of characteristic peaks shows the minerals like quartz, calcite, asbestos and kaolinite are considered as major constituent of the dust samples. The minerals such as montmorillonite and nacrite are considered as associate minerals which may be found in traces. The availability of hematite, feldspar, quartz, asbestos, calcite, montmorillonite and kaolinite in various sites were determined through extinction co-efficient of all these samples. In this study the major constituent is quartz in all samples. The order of amount of major minerals like quartz, hematite and feldspar are determined as Vehicular Area > Industrial Area > Residential Area. Moreover, from the crystallinity index value, the average value is higher at residential area implies that the crystalline nature of quartz is poor and it is lower at vehicular area shows the existence of well ordered quartz. As the minerals quartz and

to make such a statment on just one sample from each lacality is meaningless!!

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hematite are harmful to the human beings and the deciding factors for pollution, the Vehicular Area is considered as the most polluted Area. The inhalation of such minerals will lead to various respiratory diseases. The effect will be huge in the case of pregnant ladies. The toxicity is proportional to the concentration of these minerals. These forms of disease are progressive with a continuing decrease of lung function even in the absence of further dust exposure.

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