

Characterization of
minerals in air dust
particles

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P. Rajkumar

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Characterization of minerals in air dust particles in the state of Tamilnadu, India through ftir spectroscopy

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Received: 25 April 2013 – Accepted: 30 July 2013 – Published: 26 August 2013

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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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.

5 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
10 and its crystalline nature were determined with the help of extinction co-efficient and crystallinity index respectively.

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.
15 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 $\ll 1$ 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
20 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).

25 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

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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 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 (Pearce 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 (Totoni et al., 2012).

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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). 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 ft in road side and land area were collected (Ramasaamy 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 the geogenic and anthropogenic polluted areas, i.e. vehicular area (say bus stand), industrial area and residential area which cover almost all major districts of Tamilnadu. Here residential area may come under the geogenic polluted area and the other two may comes under the anthropogenic. 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

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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 min. The resolution is $\pm 4 \text{ cm}^{-1}$ and its accuracy is $\pm 1 \text{ cm}^{-1}$.

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 °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.

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.

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 (CaCO₃). Calcite crystals are trigonal-rhombohedral, though the actual calcite rhombohedra are rare as natural crystals. The frequencies of CaCO₃ correspond, according to assignments reported by Herzberg (1945), to a symmetric stretching, ν_1 , an out-of plane bending, ν_2 , a doubly degenerate asymmetric stretching, ν_3 and a doubly degenerate planar bending ν_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; Chester and Green, 1968; Farmer, 1974; Chester and Elderfield, 1967; Senthil Kumar 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 (CO₃)⁻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, ν_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 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

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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 ν_3 but the peak at 1422 cm^{-1} and 1431 cm^{-1} is present within the range $1400\text{--}1450\text{ cm}^{-1}$. 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 Kaolinit

A typical dioctahedral species is kaolinit, with an ideal structural formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Kaolinite is electrostatically neutral and has triclini 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 et al. (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 Madejova and Komadel (2011), Russell (1987), Ramaswamy and Venkatachalapathy (1992) and Hlavay et al. (1978). The

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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 kaolinosis. It is characterized by the presence of rounded opacities in the lung (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 but distinct crystals are not known. In the ideal case, the structural formula is expressed by $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ 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 $(\text{Mg}, \text{Fe}^{2+}, \text{Al})_3(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$ 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 Symmetrical bending mode vibration. The frequency at 811 cm^{-1} is due to O–H out of plane bending mode (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 (Madejova and Komadel, 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 (Madejova and Komadel, 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 (Madejova and Komadel, 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}

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is assigned for imogolite mineral and it is due to O–H deformation mode (Madejova and Komadel, 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 (Baranska 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

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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, 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 $1200\text{--}900\text{ cm}^{-1}$ 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 $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$ (US 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 $\text{CaMg}(\text{CO}_3)_2$. 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 $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ 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 $\text{Al}(\text{OH})_3$. 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 (Jubb and Allen, 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 $(\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20}\cdot n\text{H}_2\text{O}$. The montmorillonite minerals are composed of hydrous aluminum 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 (Pluske et al., 2013) 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 $(\text{KAlSi}_3\text{O}_8)$ 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

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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 CaAl₂Si₂O₈. 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}Si₄O₁₀(OH)₂) is observed at the frequencies of 656 cm⁻¹ is due to Si–O stretching mode vibration (Ali et al., 2009).

Dickite (Al₂Si₂O₅(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.

Nowadays *Beidellite* ($\text{Na}_{0.7}\text{Al}_4(\text{Si}_{7.3}\text{Al}_{0.7})\text{O}_{20}(\text{OH})_4 \cdot x\text{H}_2\text{O}$) 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.

Glaucosite is ferric-iron silicate mineral with micaceous structure $((\text{K}, \text{Na})(\text{Fe}^{3+}, \text{Al}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2)$. Glaucosite 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 (Palmer and Frost, 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 $\text{K}(\text{Mg}, \text{Fe}^{2+})(\text{Fe}^{3+}, \text{Al})(\text{Si}_4\text{O}_{10})(\text{OH})_2$. 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 ($\text{Pb}(\text{CO}_3)$) 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 (Palmer and Frost, 2006; Lascola and Andrews, 1987). *Ankerite* ($\text{CaFe}_{0.6}^{2+}\text{Mg}_{0.3}\text{Mn}_{0.1}^{2+}(\text{CO}_3)_2$) mineral is identified by the frequency at 1448 cm^{-1} is due to C-H bending mode vibration (Rebenstorf, 1988; Jubb and Allen, 2010). *Aliettite* ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2\text{Ca}_{0.1}\text{Na}_{0.2}\text{AlFe}_{0.7}^{2+}\text{Mg}_{0.5}\text{Al}_3\text{SiO}_{10}(\text{OH})_2 \cdot 3(\text{H}_2\text{O})$) 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

Almost all the samples are having the minerals like hematite, feldspar, quartz, asbestos, calcite, montmorillonite and kaolinite minerals. The relative distribution of major miner-

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als such as hematite, feldspar, quartz, asbestos, calcite, montmorillonite, and kaolin-
ite are explained through the determination of extinction co-efficient of the character-
istic 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.

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

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 min-
eral 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 overview,
the amount of all the samples are visually indicated in Fig. 3a–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 Ve-
hicular 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.

5 Crystallinity index of quartz

The crystallinity is defined as the fraction of crystalline materials in a mixture of crys-
talline 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

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vermiculite, smectite, palygorskite, sepiolite and some more minerals. In general the minerals quartz, calcium carbonate, kaolinite, nacrite, chrysotile, goethite, pyrophyllite, smectite, sepiolite, hematite, montmorillonite and feldspar may be considered under the category of geogenic minerals and the other minerals like total organic carbon, asbestos, calcium carbonate, cerussite, vermiculite, aragonite, dolomite, magnetite and gibbsite may be considered under the category of anthropogenic 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 anthropogenic areas > geogenic areas, i.e. Vehicular Area > Industrial Area > Residential Area. Moreover, from the crystallinity index value, the average value is higher at geogenic areas i.e., residential area implies that the crystalline nature of quartz is poor and it is lower at anthropogenic areas i.e., vehicular area shows the existence of well ordered quartz. As the minerals quartz and 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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Table 1. Latitude and Longitude of sites where the samples collected in Tamilnadu, India.

City/Town	Latitude	Longitude	District	Vehicula Area	Sample numbers	
					Residential Area	Industrial Area
Kanchipuram	12°50'3" N	79°42'13" E	Kanchipuram	1	2	3
Arakkona	13°4'57" N	79°40'142" E	Vellore		4,5,6	
Villupuram	11°56'22" N	79°29'51" E	Villupuram	7	8	9
Cuddalore	11°45'0" N	79°45'0" E	Cuddalore	10	11,12	13
Ranipet	12°55'42" N	79°19'56" E	Vellore	14	15,16	17
Krishnagiri	12°31'7" N	78°12'49" E	Krishnagiri	18	19	20
Vellore	12°54'59" N	79°7'56" E	Vellore		21	22
Hosur	12°43'58" N	77°49'48" E	Krishnagiri	23	24,25	26
Dharmapuri	12°7'38" N	78°9'28" E	Dharmapuri	27	28	29
Salem	11°39'51" N	78°8'45" E	Salem	30	31	32
Namakkal	11°13'10" N	78°10'4" E	Namakkal	33	34	35
Erode	11°20'32" N	77°43'38" E	Erode	36	37	38
Tiruppur	11°6'43" N	77°21'15" E	Tiruppur	39	40,41	42
Coimbatore	11°1'0" N	76°57'20" E	Coimbatore	43	44	45
Dharapuram	10°44'12" N	77°31'56" E	Tiruppur	46	47	48
Karur	10°57'26" N	78°4'51" E	Karur	49	50	51
Tiruchirappalli	10°47'25" N	78°42'16" E	Tiruchirappalli (Trichy)	52	53	
Ariyalur	11°8'13" N	79°4'32" E	Ariyalur	54	55	56
Neyveli	10°58'0" N	78°32'50" E	Cuddalore	57	58,59	60
Perambalur	11°13'59" N	78°52'59" E	Perambalur	61	62,60	64
Dindigul	10°22'2" N	77°58'49" E	Dindigul	65	66	67
Theni	10°0'37" N	77°28'36" E	Theni	68	69	
Madurai	9°55'30" N	78°7'11" E	Madurai	70,71	72	73
Virudhunagar	9°35'1" N	77°57'30" E	Virudhunagar	74	75	76
Paramakudi	9°32'42" N	78°35'27" E	Ramanathapuram	77		78
Sivakasi	9°26'54" N	77°47'53" E	Virudhunagar	79	80,81	103
Tuticorin	8°45'50" N	78°8'5" E	Tuticorin	82	83,84	85
Tirunelveli	8°43'58" N	77°42'0" E	Tirunelveli	86	87,88	89
Chidambaram	11°23'53" N	79°41'43" E	Cuddalore	90	91	92
Virudhachalam	11°30'50" N	79°19'40" E	Cuddalore	93		94
Tiruvavarur	10°46'16" N	79°38'13" E	Thiruvavarur	95		96
Mayiladuthurai	11°6'6" N	79°39'7" E	Nagapattinam	97		98
Thiruvottiyur	13°9'36" N	80°17'60" E	Thiruvallur	99	100	101
Avadi	13°7'12" N	80°5'60" E	Thiruvallur	102		104
Sriperumbudur	12°58'2" N	79°56'30" E	Kanchipuram		105,106	
Ambattur	13°5'60" N	80°9'36" E	Thiruvallur			107
Ayanavaram	13°6'1" N	80°13'45" E	Chennai	108	110	109
Koyambedu	13°4'8" N	80°11'28" E	Chennai	111		

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Table 2. The observed frequencies with corresponding minerals in all samples and tentative assignment of frequencies.

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 ₂ 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	52	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.	Montmorillonite	3405	106	H-O-H stretching
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.	Hectorit	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.	Cerussit	1385, 1399	50, 3	C-O bending
33.	Ankerite	1448	5	C-H bending
34.	Aliettile	788, 3675	1, 50	O-H stretching

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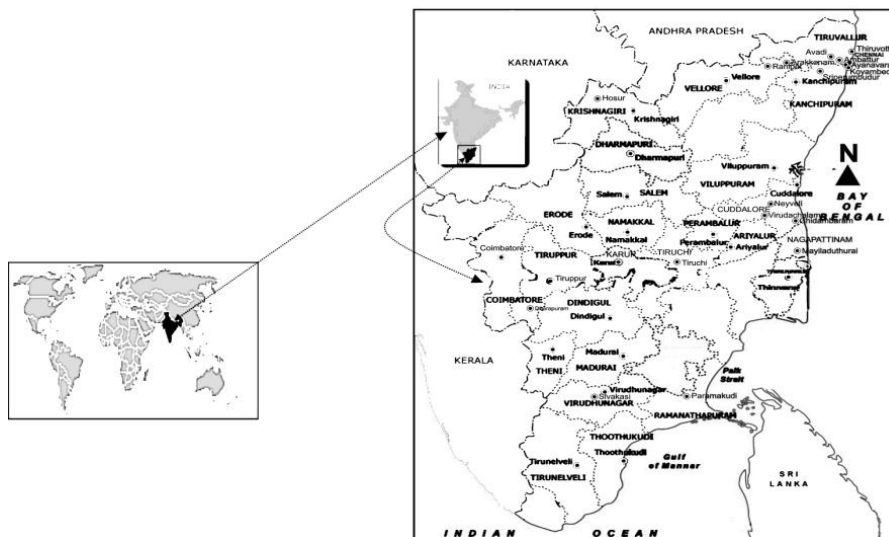


Fig. 1. The map showing the districts covered for the sample collection in Tamilnadu, India.

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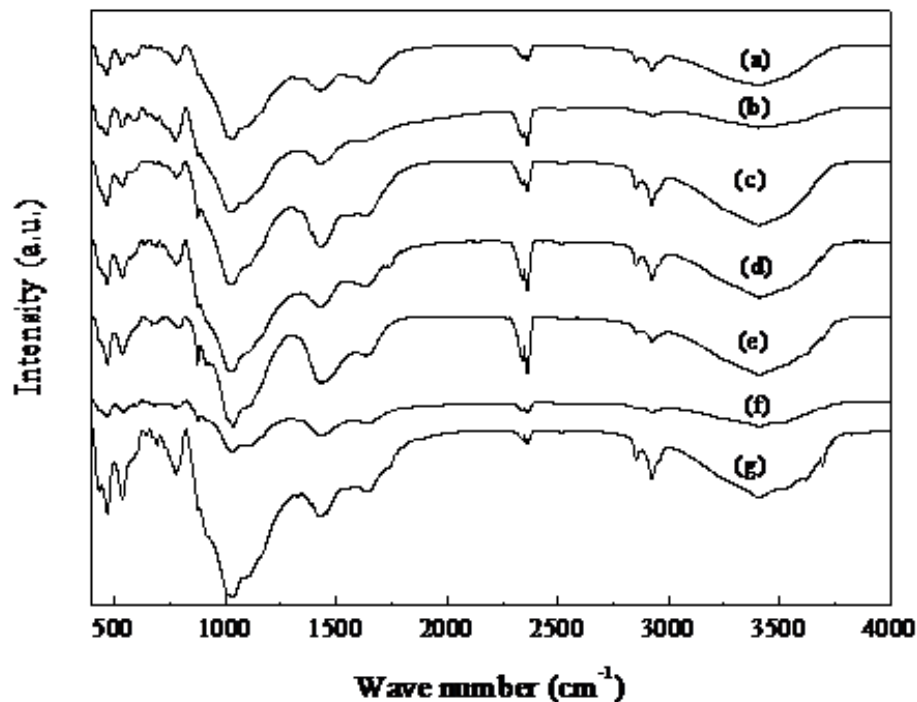
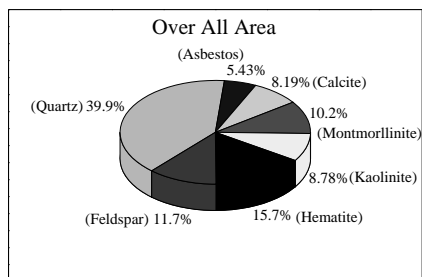
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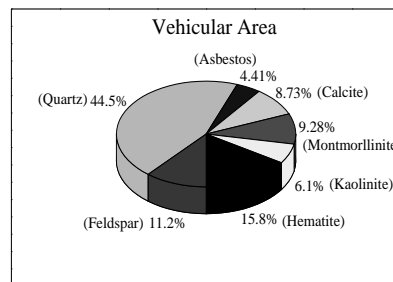
Fig. 2. The overlapped FTIR spectra of representative samples (a) sample no:1, (b) sample no:21, (c) sample no:41, (d) sample no:61, (e) sample no:81, (f) sample no:101 and (g) sample no:111.

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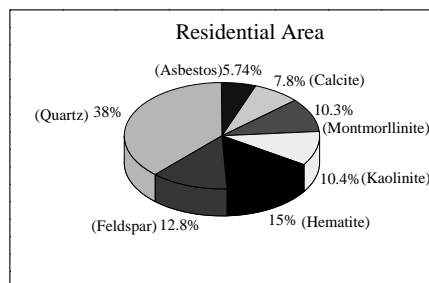
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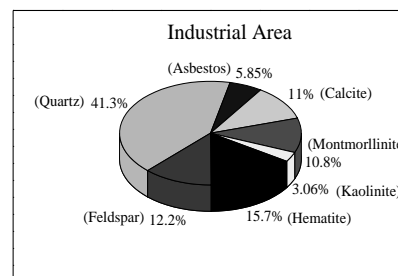
(a)



(b)

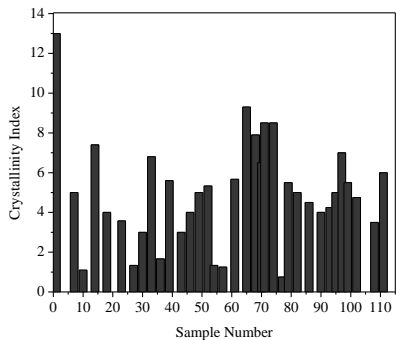


(c)

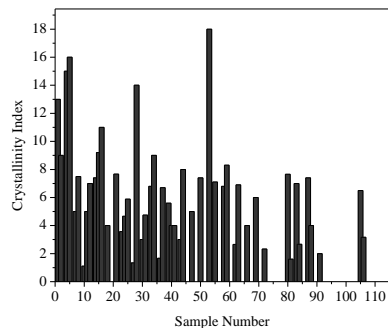


(d)

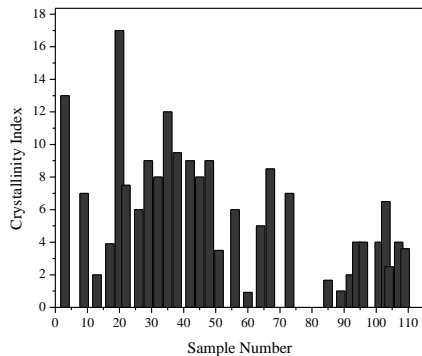
Fig. 3. The distribution of minerals in all sites, **(a)** Overall Area, **(b)** Vehicular Area, **(c)** Residential Area and **(d)** Industrial Area.



(a)



(b)



(c)

Fig. 4. The variation of Crystallinity Index of quartz **(a)** in Vehicular Area, **(b)** in Residential Area and **(c)** in Industrial Area.

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