CHAPTER 2

CHARACTERIZATION TECHNIQUES INSTRUMENTATION AND MATERIALS

Air Particulate Matter is characterized by using different experimental techniques namely; Fourier Transform Infrared (FTIR) spectroscopy, X-ray Diffraction (XRD), elemental analysis, magnetic study and Field Emission Scanning Electron Microscopy (FESEM). Details of these characterization techniques are discussed in this chapter. The details of sampling methods and sampling area are also discussed in this chapter.

2.1 FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

The major and minor minerals are qualitatively determined by using FTIR technique (Russell 1987). 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 120º 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.

2.1.1 Working Principle

Infrared spectroscopy is non-destructive technique for materials analysis and used in the laboratory for over seventy years. Infrared absorption spectroscopy is the study of interaction of infrared radiation with matter as a function of photon frequency. Fourier Transform Infrared Spectroscopy (FTIR) provides specific information about the vibration and rotation of the chemical bonding and molecular structures, making it useful for analyzing organic materials and certain inorganic materials. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material.

Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis. The IR region is commonly divided into three smaller areas: near to IR (400 to 10 cm\(^{-1}\)), mid to IR (4000 to 400 cm\(^{-1}\)) and far to IR (14000 – 4000 cm\(^{-1}\)).
Infrared photons have enough energy to cause groups of atoms to vibrate with respect to the bonds that connect them. Like electronic transitions, these vibrational transitions correspond to distinct energies and molecules absorb infrared radiation only at certain wavelengths and frequencies. Chemical bonds vibrate at characteristic frequencies and when exposed to infrared radiation, they absorb the radiation at frequencies that match their vibration modes. Measuring the radiation frequency produces a spectrum that can be used to identify functional groups and compounds. Some impurities produce their own characteristic bands in infrared region. Spectral measurements of these bands are used to determine concentration of the impurities and their bonding with the host materials.

Figure 2.1 The basic instrument design of an FTIR spectrometer
2.1.2 Sample Analysis Process

(i) Instrumentation

There are three basic spectrometer components in an FT source, an interferometer and detector. Interferometer divides radiant beams, generates an optical path difference between the beams and then recombines them in order to produce repetitive interference signals measured as a function of optical path difference by a detector. As its name implies, the interferometer produces interference signals, which contain infrared spectral information generated after passing through a sample. The most commonly used interferometer is a Michelson interferometer. It consists of three active components: a moving mirror, a fixed mirror and a beam splitter (Figure 2.1). The two mirrors are perpendicular to each other. The beam splitter is a semi-reflecting device and is often made by depositing a thin film of germanium onto a flat KBr substrate. Radiation from the broadband IR source is collimated and directed into the interferometer and impinges on the beam splitter.

(ii) Sample preparation

IR spectra can be measured using liquid, solid, or gaseous samples that are placed in the beam of infrared light. A drop of a liquid can be placed as a thin film between two salt plates made of NaCl or KBr, which are transparent to infrared light at most important frequencies. A solid can be ground with KBr and pressed into a disk that is placed in the light beam. Alternatively, a solid sample can be ground into a pasty mull with paraffin oil. As with a liquid, mull is placed between two salt plates. Solids can also be dissolved in common solvents such as CH₂Cl₂, CCl₄, or CS₂ that do not have absorption in the areas of interest. Gases are placed in a longer cell with
polished salt windows. These gas cells often contain mirrors that reflect the beam through the cell several times for stronger absorption.

2.1.3 Analytical information of FTIR

FTIR can be analysed by two techniques namely: Qualitative and Quantitative.

(i) Qualitative analysis

The combination of the fundamental vibrations or rotations of various functional groups and the subtle interactions of these functional groups with other atoms of the molecule results in the unique, generally complex IR spectrum for each individual compound. IR spectroscopy is mainly used in two ways: (a) structural elucidation and (b) compound identification.

a. Structural Elucidation

Because of complex interactions of atoms within the molecule, IR absorption of the functional groups may vary over a wide range. However, it has been found that many functional groups give characteristic IR absorption at specific, narrow frequency ranges regardless of their relationship with the rest of the molecule. Generalized tables of the positions and relative intensities of absorption bands have been established and used to determine the functional groups present or absent in a molecule. Correlation charts are available in many data books (Lide 1994, Silverstein et al. 1981).
b. Compound Identification

Since the IR spectrum of every molecule is unique, one of the most positive identification methods of an organic compound is to find a reference IR spectrum that matches that of the unknown compound. Transmittance (T) is the ratio of radiant power (I) transmitted by the sample to the radiant power (I0) incident on the sample. Absorbance (A) is the logarithm to the base 10 of the reciprocal of the transmittance.

\[ A = \log_{10} \left( \frac{1}{T} \right) = -10 \log_{10} T \]

The transmittance spectra provide better contrast between intensities of strong and weak bands because transmittance ranges from 0 to 100 % T whereas absorbance ranges from infinity to zero.

(ii) Quantitative analysis

The basis for quantitative analysis of absorption spectrometry is the Bouguer–Beer–Lambert law, commonly called Beer’s law (IUPAC 1997). For a single compound in a homogeneous medium, the absorbance at any frequency is expressed as,

\[ A = abc \]

Where A is the measured sample absorbance at the given frequency, a is the molecular absorptivity at the frequency, b is the path length of source beam in the sample and c is the concentration of the sample. This law basically states that the intensities of absorption bands are linearly proportional to the concentration of each component in a homogeneous mixture or solution.
2.2 X-RAY DIFFRACTION (XRD)

The selected samples were analyzed through XRD in Department of Nuclear Physics, Madras University, Chennai, Tamilnadu. The X-ray diffraction powder pattern was recorded at room temperature using Seifert 3003 TT(Germany) and which is shown in the Figure 2.2. X-ray diffractometer having a curved graphite crystal diffracted monochromator, with a source of CuKα (λ=1.5420 Å) radiation and NaI (Tl) scintillation counter detector. This software has the capability of least square fitting and other routine refinements and directly outputs the lattice parameters data. The experimental set-up, its calibration, measurements on standard materials and initial studies using the system were reported by Cullity (Cullity 1959). The diffraction patterns were obtained over the 2θ values in the region of 20 to 80°. The estimated error in the lattice parameter is of the order of 0.005 Å. The experimental pattern was compared with patterns obtained from the JCPDS (Berry 1974) database.

The structural phases of Particulate Matter were identified by the X-ray diffraction (XRD) pattern obtained using an X-ray diffractometer manufactured by Siefert Inc., Germany. The grain size calculations were done using the full width at half maximum (FWHM) of the XRD peak in the modified Scherrer formula (Cullity 1997), which takes care of instrumental resolution and widening of the peaks due to residual stress.
In a crystalline solid, the constituent particles (atoms, ions or molecules) are arranged in a regular order. An interaction of a particular crystalline solid with X-rays helps in investigating its actual structure. Crystals are found to act as diffraction gratings for X-rays and this indicates that the constituent particles in the crystals are arranged in planes at close distances in repeating patterns. The phenomenon of diffraction of X-rays by crystals was studied by Bragg and his father Bragg (1913). They used crystals of zinc sulphide (ZnS) for this purpose.

**Figure 2.2 XRD Diffractometer System (3003 TT)**

![XRD Diffractometer System (3003 TT)](https://tp.dresden-concept.de/userdata/b8bd767ab48f10f6d9ba58e39278b086_thumb.png)
2.2.1 Basic Theory

Bragg gave a mathematical equation to establish a relationship between wavelengths of the incident X-ray, the distance between the layers and the angle of diffraction.

\[ n\lambda = 2d \sin \theta \]

Here, \( \lambda \) = wavelength of X-ray used, \( \theta \) = Angle between incident X-rays and plane of the crystal. The diffracted beam makes an angle 2\( \theta \), \( d \) = Distance between planes of the constituent particles in a crystal, \( n \) = integers (1, 2, 3, 4 etc.) which represents the serial order of diffracted beams.

Bragg’s equation can be used to calculate the distances between repeating planes of the particles in a crystal. Similarly, if inter planar distances are given, the corresponding wavelengths of the incident beam of X-ray can be calculated. In case of fine particles, with reduction in the size of the particles, the XRD lines get broadened, which indicates clearly that particle size has been reduced. Information of the particle size is obtained from the full width at half maximum (FWHMs) of the diffraction peaks. The FWHMs (\( \beta \)) can be expressed as a linear combination of the contributions from the strain (\( \varepsilon \)) and particle size (\( L \)) through the following relation:

\[
\frac{\beta \cos \theta}{\lambda} = \frac{1}{l} + \frac{\varepsilon \sin \theta}{\lambda}
\]

2.2.2 XRD Instrumentation

A typical powder XRD instrument consist of four main components such as X-ray source, specimen stage, receiving optics and X-ray detector as shown in Figure 2.3.
Figure 2.3 A schematic representation of X-ray diffraction by crystal

The source and detector with its associated optics lie on the circumference of focusing circle and the sample stage at the centre of the circle. The angle between the plane of the specimen and the X-ray source is \( \theta \) (Bragg’s angle) and the angle between the projection of X-ray and the detector is \( 2 \theta \). For the XRD analysis, fine powder samples can be mounted on the sample holder and the powder was assumed to consist of randomly oriented crystallites (Maslen et al. 2004). When a beam of X-ray is incident on the sample, X-rays are scattered by each atom in the sample. If the scattered beams are in phase, these interfere constructively and one gets the intensity maximum at that particular angle. The atomic planes from where the X-rays are scattered are referred to as reflecting planes.

2.2.3 XRD Data Analysis

After recording the X-ray diffraction pattern, first step involves the indexing of XRD peaks. The indexing means assigning the correct Miller indices to each peak of the diffraction pattern (Harper 1999). There are three main methods for indexing of X-ray diffraction pattern (i) Comparing the
measured XRD pattern with the standard data base (JCPDS-cards), (ii) Analytical methods and (iii) Graphical methods.

X-ray diffraction (XRD) is used to check the monophasic nature of the samples. XRD is the most essential technique to investigate the structural aspects of the material. It helps to identify the presence of different phases, including the impurities and unreacted components in a given material. Such information provides a very useful guideline towards modification of synthesis procedures (Harper 1999). Analysis of XRD data gives the unit cell parameters of the system. In the present study, X-ray diffraction was extensively used to investigate the course of the reaction during the synthesis of the samples and to change the heat treatment procedures accordingly.

2.3 ELEMENTAL ANALYSES

Different techniques are used to find the trace minerals. The concentration of elements is measured in the Chemical Institute of Research and Training (Chemical analysis and consultancy services) 239/131, s.e.e.d colony, alagapuram, Salem – 636 016, Tamilnadu. The elements Si, Al, Ca, Mg, Fe, Mn, Pb, Na and K were measured by using instruments Spectrophotometer (Systronics, 2203, Japan) and Flame photometer (Systronics). All reagents used in this study were of analytical reagent grade and distilled water was used for the preparation of solutions.

Initially 2 grams of sodium hydroxide were taken in a nickel crucible. The electric Bunsen furnace at 90 divisions was set and waited for half an hour. Samples of 50 milligrams were added after the complete melting of sodium hydroxide and covered the crucible. The sample was kept in dull red hot condition for 5 minutes. The crucible were taken out and kept it on porcelain tile and cooled it at room temperature. Crucible has filled with a
$\frac{3}{4}$th of distilled water and kept it covered for overnight. The contents were washed in a 250 ml beaker and added 10 ml of HCl (Conc.). This solution was taken in a 250 ml standard flask after cooling it in a room temperature; it was transferred into a plastic bottle. This solution was named as ‘A’ solution.

Silica and Alumina have estimated by the Ammonium molybdate method and Alizarin red s method.

Silica is the most abundant element after oxygen. It is commonly found in crystalline form such as quartz or combination of other oxides and metals in a variety of silicates. Silica is slightly soluble in water, resulting from the gradual degradation of silica-containing minerals. 5 ml of solution ‘A’ were taken in a 50 ml standard flask. 2.5 ml of 7.5% Ammonium molybdate solution was added and waited for 10 minutes. This was measured at 410 nm by using a spectrophotometer.

10 ml of Acetate, Acetic acid buffer were added and Thioglycolic acid were mixed and waited for 10 minutes. 0.1% of Alizarin Red S solution (5ml) was added and makes up to 50 ml. The absorption was measured at 475 nm by using spectrophotometry after 90 minutes.

500 mg sample was placed in a Teflon hanker. 20 ml of HF and 2 ml of HClO$_4$ was added and digested it on the hot plate maintained at 30 div. The sample was digested till all the substances dissolved and the volume reduced to 4 ml. The contents were washed carefully into a beaker and added. The sample digested on heating till a clear solution is obtained. This solution was made up to 250 standard flasks after cooling. This solution named as ‘B’ solution.

The titration method involving EDTA was used for the element Calcium. 20 ml of Solution ‘B’ was taken in a conical flask.
Triethanolamine was added. 25-50 mg of calcium indicator and 100 ml of water were added. 10 ml of 30% KOH added and shacked well. This solution was titrated within EDTA, till the color changes from Bluish green to purple color. The titration method involving EDTA was used for the element Magnesium. 20 ml of Solution ‘B’ was taken in a conical flask. 5 ml of 50% Triethanolamine was added and shacked well. Sufficient quantities of NH₄Cl-NH₄OH Buffer solution were added. Few drops of Eriochrome Black-T indicator (freshly prepared) were added. This solution was titrated with EDTA (0.04) till color changes from wine red to steel blue.

The trace elements of Fe has estimated by 1,10 Phenonthoroline Method. 5ml of Solution ‘B’ was taken into 50 ml standard flask. 5ml of 10% Hydroxyl ammonium chloride was added and waited for 10 minutes. 2.5 ml of 1,10 Phenonthoroline solution was added (100 mg in 100 ml water). 5 ml of Buffer solution was added (CH₃COONa + CH₃COOH). 68 gms Sodium Acetate + 120 ml CH₃COOH + 380 ml H₂O were added. This solution mixed thoroughly and diluted with distilled water up to the mark and waited for 10 minutes. This solution was measured at 525 nm by the Spectrophotometer (ISI 1997).

The mineral Mn has estimated by Periodate oxidation method. 5ml of Solution ‘B’ was taken in a 100 ml beaker. 10 ml of mixed acid (10 ml H₂SO₄ + 10 ml H₃PO₄) was added. 0.2 gm of Potassium periodate was added. This solution was boiled for 5 minutes and then cooled. This solution was diluted to 100 ml in standard flask. Solution was measured at 525 nm by the spectrophotometer (Figure 2.4).
The following reagents were used to measure the mineral Lead. Ammonia-Ammonium Chloride Buffer, Lead stock solution 1.599 gm of anhydro Lead nitrate was dissolved in water and diluted to 1000 ml (1000 mg/l). The appropriate volume of stock solution was diluted with water to obtain a concentration of 5 mg/l. This solution was prepared freshly on the day of used (Standard solution), 0.01 gm of PAR was dissolved in 100 ml of water and preserved in a refrigerator (4-(2-pyridylazo) resorcinol) (0.01 %). The sample was transferred to 25 ml flasks. 10 ml of buffer solution was added to provide the pH 10 followed by 1 ml of 0.01 % PAR. The solution was diluted up to the marks with water. The absorbance was measured at 520 nm by using Spectrophotometer.

Flame photometry is an atomic emission method for the routine detection of metal salts, especially Na, K. Quantitative analysis of the sample was performed by measuring the flame emission of solutions containing the metal salts. Solutions were aspirated into the flame. The hot flame evaporates the solvent, atomizes the sample and excites a valence electron to an upper state. Light is emitted at characteristic wavelengths for each metal as the electron returns to the ground state. Comparison of emission intensities of unknowns standard solutions, allows
quantitative analysis of the analyte metal in the sample solution. Sodium chloride and potassium standard solutions were prepared by volumetric dilution of the stock solution. The following approximate concentrations were made 5, 10, 25, 50, 75 and 100 µg/ml for Na and K. These standards were prepared in scrupulously clean volumetric glassware and transferred the solutions to plastic bottles. Extremely high or low pH solutions were allowed to stand in glass could alter the Na, K concentrations in solution. The flame photometer is shown in Figure 2.5.

![Figure 2.5 Flame Photography](http://ping.tradeindia.com/00287353/b/2/Micro-Controller-Based-Flame-photometer-128.jpg)

**Figure 2.5 Flame Photography**

### 2.4 MAGNETIC STUDY

Each sample was subsampled for magnetic studies using plastic containers (2.3 cm³). Dry samples were packed, weighted (about 1 gram) and labeled. After that, all samples were fixed using sodium silicate to prevent unwanted movements in studies of remanence magnetization. Each sample was impregnated and saturated with a sodium silicate (diluted at 5% weight) solution and dried at room temperature until its consolidation.
Magnetic measurements were carried out in the laboratory of the CIFICEN, Universidad Nacional del Centro de Le provincial de Buenos Aires, Pinto, 399, 7000 Tandil, Argentina. Magnetic susceptibility measurements were performed using a magnetic susceptibility meter MS2, Bartington Instruments Ltd., linked to MS2B dual frequency sensor (0.47 and 4.7 KHz). The volumetric susceptibility ($\kappa$), $\kappa_{FD}$% frequencydependence ($\kappa_{FD}$% = 100 * $(\kappa_{0.47}-\kappa_{4.7})/\kappa_{0.47}$) and mass-specific magnetic susceptibility (\(\chi=\kappa/\rho\), where $\rho$ is the density) were computed.

The Anhysteretic Remanent Magnetization (ARM) was imparted using a partial ARM (pARM) device attached to a shielded demagnetizer Molspin Ltd., superimposing a DC bias field of 50 and 90 $\mu$T to an alternating field (AF) of 100 mT and an AF decay rate of 17 $\mu$T per cycle. Remanent magnetization was measured by a spinner fluxgate magnetometer Minispin, Molspin Ltd. Anhysteretic susceptibility ($\kappa_{ARM}$) was estimated using linear regression for ARM acquired at different DC bias fields. Related parameters, such as $\chi_{ARM}$, King's plot ($\chi_{ARM}$ versus $\chi$, King et al. 1982) and the $\kappa_{ARM}/\kappa$ ratio were also calculated.

The isothermal remanent magnetization acquisition (IRM) studies were carried out by using a pulse magnetizer model IM-10-30 ASC Scientific. Each sample was magnetized by exposing it to growing stepwise DC fields, 27 forward steps from 1.7 mT to 2470 mT. The remanent magnetization after each step was measured using the abovementioned magnetometer Minispin. In these measurements, IRM acquisition curves and SIRM (IRM@2470mT) were found using forward DC fields. Remanent acquisition coercivity (H1/2, the field required to reach the SIRM/2), remanent coercivity (HCR, the backfield required to remove the SIRM, or IRM= 0) and S-ratio (=IRM-
300/SIRM, where IRM-300 is the acquired IRM@-300 mT) were also calculated from IRM measurement.

An electronically operated constant temperature bath was used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is ± 0.01K.

### 2.4.1 Instrumentation

The MS2 Magnetic Susceptibility System comprises a portable measuring instrument, the MS2 meter and a variety of sensors. Each sensor is designed for a specific application and sample type and is connected to the MS2 meter via a simple coaxial cable. The meter displays the magnetic susceptibility value of materials when these are brought within the influence of the sensor. The range of sensors allow measurements of individual laboratory soil or rock samples, sediment cores, soil surfaces, rock outcrops or down auger holes.

![Figure 2.6 The MS2 Magnetic susceptibility meter](http://www.gmw.com/magnetic_properties/images/bart026.jpg)
2.4.2 **Principles of Operation**

The magnetic state of a specimen is generally described by the following equation:

\[ B = \mu_0 (H + M) \]

Where, \( B \) is the flux density of the specimen in T (Tesla), \( \mu_0 \) is the permeability of free space in \( \text{N} \cdot \text{A}^{-2} \), \( H \) is the applied field strength in \( \text{A} \cdot \text{m}^{-1} \), \( M \) is the magnetisation of the specimen in \( \text{A} \cdot \text{m}^{-1} \). Dividing through by \( H \) we get:

\[ \mu = \mu_0 + \mu_0 k \]

where: \( \mu \) is the permeability of the specimen (in \( \text{N} \cdot \text{A}^{-2} \)), \( k \) is the volume magnetic susceptibility of the specimen (dimensionless). Rewriting, we get:

\[ \mu_0 k = \mu - \mu_0 \]

The MS2 instrument measures the magnetic susceptibility in the following way. The sensor consists of a very high thermal stability oscillator for which a wound inductor is the principle frequency-determining component. The inductor contains only air the value of \( \mu_0 \) determines the frequency of oscillation. When the inductor is placed within the influence of the specimen to be measured, the value of \( \mu \) determines the frequency of oscillation. The meter to which the sensor is connected digitizes the \( \mu_0 \) and \( \mu \) dependant frequency values with a resolution of better than one part in a million and computes the value of magnetic susceptibility. The value of \( \mu_0 \) is constant but the variable of interest is relatively small. Therefore any thermally induced sensor drift needs to be eliminated by occasionally obtaining a new "air" value (to re-establish the \( \mu_0 \) reference) by depressing the "zero" the MS2 meter. The \( \mu \) value is obtained by pressing the "measure"
button. The magnetic susceptibility value is displayed digitally and output via a serial interface.

2.4.3 General Description of the Meter Model MS2

The MS2 circuitry is housed in a sealed enclosure weighing 1.2kg with approximatedimensions of 260mm x 158mm x 50mm (10" x 6" x 2"). The operating switches, a TNC sensorcable connector and a 4-digit liquid crystal display are situated on the front panel (Figure 2.6). The RS232 serial interface connector and a battery charger input socket are located on the rearpanel of the instrument. Internal NiMH batteries provide 8 hours continuous use and can be recharged from either themains or a vehicle dashboard. An instrument stand is provided for laboratory use and a carryingbag is supplied for field portability.

2.4.4 Range of Sensorsand Operating Environment Considerations

Sensors available for use with the MS2 meter can be broadly defined as either field or laboratory sensors. The laboratory sensors are MS2B, MS2C, MS2E, MS2G, MS2W and field survey equipment are MS2D, MS2F, MS2H, MS2K.

The following environmental factors should be taken into account when using the MS2 system.

(i) Temperature induced drift-The MS2 sensors to operate on the principle of comparison between the permeability of free space and the relative permeability obtained with the added contribution of the sample magnetic susceptibility. The sensors are therefore required to measure the relative permeability to a resolution of a few ppm (parts per million). This is a very demanding requirement. Each of the sensors employs a unique technique.
for temperature compensation to minimise any temperature induced drift. Errors, which could arise from baseline drift, can be systematically eliminated through measurement procedures. A facility for automatic correction of temperature drift at the end of a measurement sequence is provided by the MULTISUS software package. Where the most sensitive measurements are to be performed on the weak material, the best precaution is to ensure that the operating temperature is constant and preferably cool and that sensor and samples have time to reach an equilibrium temperature. Clearly, this may not be an option when operating in the field.

(ii) Wet conditions to the instrument are protected against the ingress of moisture but operation in very wet conditions should be avoided.

(iii) Noise and interference check- This instrument should not be operated close to high power radio transmitters or heavy electrical machinery. Select the normal sensitivity, x1.0 range and with no sample present first press the Zero button and then select continuous measurements on the Measure toggle switch. If fluctuations of greater than 1 least significant digit per reading appear on the display, then external electrical noise should be suspected in which case the only solution is to re-site the equipment. Before using the laboratory sensors first, check the selected area for freedom from large ferrous objects by moving the sensor and watching for any changes on the display.

2.4.5 Software

The following software is available and is supplied with individual operation manuals. (i) MULTISUS to This Windows software runs on the user’s PC and provides data capture from the MS2 meter, via the RS232 serial port, when used with the MS2B, MS2C, MS2E, MS2G or MS2H sensor.
When used with the MS2B sensor the program allows volume or mass specific susceptibility measurements with corrections for sample volume or mass where appropriate and calculation of the coefficient of frequency dependant susceptibility. When used in conjunction with the MS2C, corrections for the ratio of core to sensor diameter can be automatically applied. The software offers baseline drift correction for all the above sensors. (ii) AMSWIN-BAR to This Windows program permits the measurement of the anisotropy of magnetic susceptibility. Sample adaptors are provided with the software. (iii) GEOLABSOFT for WINDOWS to This program is used in conjunction with the susceptibility/temperaturesystem to record the data in the selected temperature range.

2.4.6 SI and CGS Units

The instrument may be pre-set to display the susceptibility value directly in one or other of the dimensional systems thus producing a basic mass or volume specific unit of-Mass (χ) Volume (κ) are SI 10^{-8} (m^3/kg) and 10^{-5}, CGS 10-6 (cm^3/g) and 10^{-6} respectively Numerical conversion from SI to CGS units is accomplished by dividing the SI value by 4pi to i.e. \( \chi_{\text{CGS}} = \frac{\chi_{\text{SI}}}{4\pi} \) The meter model MS2 performs this function internally but by using the constant 0.4pi to keep the numbers in a similar range of magnitude.

2.5 SCANNING ELECTRON MICROSCOPE (SEM)

The samples have analyzed with Scanning Electron Microscope (JSM 6100, JEOL, Tokyo, Japan) in Nanotechnology research center, SRM University, Chennai, Tamilnadu, India. It has a large specimen chamber that allows observation of the entire surface of a specimen up to 150 mm and a tilt of -5 to 90°. The Scanning Electron Microscope (SEM) facilitates the observation of very fine details with high resolution (4.0 nm at 8mm working
distance) of powder materials and good focus over a wide range of specimen surface (large depth of field). It also produces clear image of specimen ranging from object visible to the naked eye to a structure spanning few nanometers. SEM is a type of electron microscope capable of producing high-resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for observing the surface structure of the sample. The microstructures of hexaferrites were examined using a scanning electron microscope.

2.5.1 Principle of SEM

Scanning electron microscope consists of an electron gun and electromagnetic lens system to study the surface structure and morphology of solids. A well defined electron beam impinges on the specimen and leads to the generation of secondary electrons, back scattered electrons, absorbed electrons, characteristic X-rays etc.. These electrons can be detected by suitable detectors and give information about the surface structure and morphology of the specimens. The characteristic X-rays generated are used for the identification and estimation of different elements present in the specimen by Energy Dispersive Spectrometer (EDS) and Wavelength Dispersive Spectrometer (WDS). The depth of focus is much larger than the optical microscope image even at lowest magnifications is one of the major advantages of SEM.

2.5.2 Working of SEM Instrument

Electrons from a thermionic or field emission cathode are accelerated by a voltage of 1-50 kV between cathode and anode. The smallest beam cross section at the gun (the crossover) with a diameter of the order of
10-50 μm for thermionic and 100-100nm for field-emission guns, is demagnified by two or three stage electromagnetic lens system, so that an electron probe of diameter 1-10 nm carrying current of $10^{-10}$ to $10^{-12}$ A is formed at the specimen surface. A deflection coil system in front of the last lens scans the electron probe in a raster across the specimen and in synchronism with the electron beam of a separate Cathode Ray Tube (CRT). The intensity of the CRT is modulated by one of the signals recorded to form an image. The magnification can be increased simply by decreasing the scan coil current and keeping image size on CRT constant.

An advantage of SEM is the wide variety of electron specimen interactions that can be used to form an image to give qualitative and quantitative information. The general schematic diagram of SEM is shown in Figure 2.7. The large depth of focus, excellent contrast and the straightforward preparation of solid specimen are advantages of SEM. Here an electron beam scans the object (the specimen) and because of synchronized scans of an electron beam and the CRT screen (nowadays, monitor), there is the one-to-one correspondence between the spot on the specimen and the spot on the screen.

![Figure 2.7 The general schematic diagram of SEM](https://www.purdue.edu/ehps/rem/rs/graphics/sem2.gif)
Unlike Optical microscopy, SEM requires the vacuum environment and specimen surface to be electrically conductive. The acceleration voltage of 5 to 50 kV can be applied between anode and cathode and hence we get the electron beam of such energy. This diverged electron beam passes through a pair of electro-magnetic lenses (coils) and finally passes through probe forming a lens, which makes the beam in a form of a fine probe (~10 nm diameter). This fine electron probe scans on the specimen area in a linear manner. Another electron beam is in synchronization with this beam which scans on the CRT (or monitor) with the help of same scan generator. In SEM, the formation of the image takes place because of electron beam-specimen interaction (Goldstein & Yakowitz 1977).

2.5.3 Sample Preparation

Specimen preparation is crucial for specimens to be examined under SEM as the specimen have to be occupied within the system vacuum and the incident beam is high voltage electron beam (of the order of thousands of Volts). The specimen (or its surface) must be electrically conductive and vacuum compatible. For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface and electrically grounded to prevent the accumulation of electrostatic charge at the surface.

Metallic samples and alloys can be examined as it is but for organic materials, insulators and non-conducting materials (like polycarbonates, rubber, plastics, concrete, ceramics, biological specimens such as bacteria and other biological specimens), objects tend to charge when scanned by the electron beam and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts. They are therefore usually coated with an ultra-thin (about 100-1000 Å) layer of
Electrically conducting material, like carbon, aluminium, gold, or Au-Pd alloy (Schatten & Pawley 2007). These coatings/depositions are applied to the specimen by high temperature evaporation or by plasma discharge techniques.

2.5.4 Electron Specimen Interaction

Electron beam specimen interaction gives various signals which can be used to form images and also can be used for other important information. In inelastic scattering, the trajectory of the incident electron is only slightly perturbed, but energy is lost through interactions with the orbital electrons of the atoms in the specimen. ‘Loss’ of kinetic energy (of the primary electron) is mainly caused by the interaction with the electrons of atoms of the specimen.

2.5.5 Magnification, Brightness and Contrast of the SEM Images

Electron images are obtained by rastering the electron beam across the specimen surface using the deflection coils inside the objective lens and synchronously rastering the output signal of the detector on a CRT.

The ratio of the area rastered on the specimen to that of the CRT gives the magnification. For example, a rastered area of 200 µm² (200 x 10⁻⁶ m²) displayed on CRT with an area of 20 cm (200,000 x 10⁻⁶ m²) yields a magnification of 1000x. This is a very different process than the production of an image by an optical microscope. Electronic images are sequentially constructed during the rastering of the beam, whereas in optical systems all parts of the sample are imaged simultaneously.

Working distance (WD), probe current and probe diameter, incorrect electron gun alignment, astigmatism, diffused scattering of electrons from the edges (edge effect), electrostatic charging of the sample, external
disturbances (magnetic fields, flooring, improper grounding) are factors affecting the quality of the image. The SEM image looks three dimensional because of SEM's ability to focus up to the certain depth and hence the images can be easily interpreted.

2.5.6 Detectors

There are number of detectors around the specimen in the specimen chamber which collects different signals for the required information. The most common imaging mode collects low energy (< 50 eV) secondary electrons that are ejected from the k-orbital of the specimen atoms by inelastic scattering interactions with beam electrons. Due to their low energy, these electrons originate within a few nanometers from the sample surface (Goldstein et al. 1981). The electrons are detected by a type of scintillator-photomultiplier system known as an Everhart Thornley detector. Image resolution less than 0.5 nm is possible using SEM technique.

2.5.7 Field Emission Scanning Electron Microscope with Energy Dispersive System (X-Ray Spectrometer) EDX

The Scanning Electron Microscope (SEM) has played an important role for many years in research and development. The samples have analyzed with Field Emission Scanning Electron Microscope with Energy Dispersive X-Ray (FESEM- Hitachi-japan - model no: su6600 & EDX to Horiba- japan, model no: 8121-H) in National center for Nano Science and Nano Technology, University of Madras, Tamilnadu, India. It utilizes advanced Variable Pressure Technology and an improved Schottky field emission electron source that provides exceptional imaging and high probe current with great stability. The Variable Pressure mode allows the operator to change vacuum conditions in the sample chamber from high vacuum (≤10-4Pa) to
low vacuum (10-300Pa). It is a new and versatile Field Emission SEM for a diversified range of applications including observations and analyses of advanced materials which have become increasingly important in modern science and engineering.

A basic knowledge of the principles of an EDX is useful for interpretation and evaluation of energy dispersive spectra. Field Emission Scanning Electron Microscope with Energy Dispersive X-Ray and its block diagram are shown in Figures 2.8 and 2.9. The energy dispersive system for photon detection has in general, a silicon semiconductor detector with a high impedance zone which is radiation-sensitive. Both the detector and the field-effect transistor of the first stage of preamplifier are cooled to get an optimum of energy resolution. Inside the detector, each absorbed X-ray quantum is converted into a cloud high consists of pairs of charge-carriers (electrons) and holes. A strict proportionality of the number of the charge carriers to the photon energy is given. Due to a high voltage, which is between both ends of the sensitive area of the detector, the charge carriers are moved and collected at the ends of the sensitive zone.

With a charge sensitive preamplifier the charge quantity is finally converted into a voltage-pulse. With a detector-capacity of approx. 2 pF, an X-ray quantum of 1 keV energy produces a voltage-pulse of approximately 20 microvolts. The pulse is amplified and shaped in a spectroscopic amplifier. Thus, the signal-to-noise ratio is increased. With an analog-digital converter, each pulse is measured individually.
Then the current channel contents of a pulse-height spectrum will be incremented at the concerned channel. Before the ADC is able to measure the value, the maximum of the intensified pulse must be detected or stretched for measurement (peak-detector or peak-stretcher PS). If the ADC is fast enough, the point of the maximum signal is determined only for analog-digital conversion (the PS is not needed).
Here the preamplifier signal is already digitized in the intensified condition and improved than by multiple scanning of the pulse amplitude the signal-to-noise ratio digitally (averaging). In the spectroscopic channel, the pulses are filtered with a long as possible shaping time. The noise is suppressed to reach a very good energy resolution. However, X-ray quanta are not differentiated if they arrive briefly one behind the other (in the shaping time). Additional mechanisms in the pulse-processing unit (the fast channel) permit the recognition and excluding those pulses, which arrive with a short delay time and are not visible in the spectroscopic amplifier due to bad time-resolution. Finally, a wrong pulse is avoided with a pulseheight composed of both pulses.

The time separation (resolution) is substantially better in the fast channel due to shorter pulse-shaping times (processing time for each X-ray quantum). But the energy resolution is worse. The signals, which arrive briefly one behind the other and cannot be differentiated by the spectroscopic amplifier, are recognized by the fast channel and then these pulses will be rejected over a gate (Pile-up discrimination). An additional dead time is produced, which rises with pulse density.

The Analog to Digital Converter and MCA (multi-channel analyser) pulses are digitized and stored as pulse height spectrum. The energy region which can be measured is divided into channels (typical number of 1024 or 2048). Energy width of a channel depends on the amplification gain and amounts to typically 20 or 10 eV/chnnel.

Both values results in the entire measured energy region of the spectrum. Each individual X-ray quantum is measured in the energy and sorted into the corresponding channel. Thus a pulse amplitude spectrum
develops, in which the stochastically measured discrete X-ray quanta are sorted according to the energy and are collected for different energy types.

The X-ray spectrum of the EDX is thereby a histogram (energy distribution of all collected X-ray quanta). The spectrum grows at the same time in all channels. Due to the statistic processes in the detector and in the field-effect transistor, it comes to a widening of the natural line width. The full width at half maximum (FWHM) depends on the energy of the X-ray quanta $E$ and corresponds to the following relationship:

$$\text{FWHM} = \sqrt{\left(\text{FWHM}_{el}^2 + 2.5 \, \text{eV} \times E\right)}$$

$\text{FWHM}_{el}$ is the electronic width, which is essentially determined by field-effect transistor, detector capacity, detector currents and pulse-shaping. The second part of the relationship (the detector portion) is computed for an ideal detector from Silicon material with an FANO-factor of approximately 0.12. All values are to be used in eV.

### 2.5.8 Spectra Artefacts

The energy dispersive measured spectra for monoenergetic radiation of 3.0 keV and to 4.0 keV (at Synchrotron, double crystal monochromator) are logarithmically represented in the illustration. Besides the main line, one can find in each case an additional line in the spectrum at a distance of approximately 1.75-kilo electron volt (keV) (within the low-energy spectrum range). These escape pulses result from charge-carrier collection-losses in the detector, exactly if an excited Si K-radiation quantum leaves out the detector during the ionization processes. Additional pulses are registered with double line energy. The height of these so-called 'pile-up' (Figure 2.10) pulses depends from on pulse density. The pile-up develops, if two or more X-ray quanta are registered within a so short time interval in the
detector that also the fast channel of the signal processing unit cannot differentiate between them any longer.

Figure 2.10 The escape pulses and 'pile-up' pulses of FESEM-EDX

A small temporal misalignment of the X-ray quanta is detected and rejected. An energy dispersive measured X-ray peak can be described in first approximation with a Gaussian form (due to the statistic causes of the line-broadening). Other incomplete charge carrier collecting-effects provide for additional energy-dependent asymmetry components (Tail). All these processes together can be described with the term ICC (incomplete charge collection).

2.5.9 Characteristics with Spectrometry below 1 keV

Shifts of peak positions toward smaller energies are possible with energies of less than 300 eV. Here the energy dispersive detector (EDX)
becomes non-linear. Ultra thin windows and already detectors with very thin beryllium window have a possibility for transmission of electrons with higher energies. An electron trap to protect the detector from high-energy scattered electrons from specimen inside the electron microscope is necessary. The electron traps are equipped with permanent magnets, which divert the electrons from their course. The electron trap works only up to a certain primary electron energy (typical to $E_o = 30$ keV). Model energy dispersive spectrum (EDX) is shown in Figure 2.11.

Backscattering electrons become apparent in the spectrum if the bremsstrahlung background within the high-energy range gets a not typically shape with turning points (heavy case), or simply, if the computed bremsstrahlung does not fit at the end of the spectrum. The analysis becomes incorrect for those elements, whose characteristic lines are affected by the electron continuum.

![Figure 2.11 The model energy dispersive spectrum (EDX)](http://microanalyst.mikroanalytik.de/Images/infos34.jpg)

### 2.6 TAMILNADU AT A GLANCE
- Area of 130,000 Sq.km (4% of India’s geographical area)
- 72 Million Population (50% Female population)
- 48.5% of the population live in urbanized locality
- 11% Contribution to India’s industrial output (Figure 2.12)
- 17% State’s share in number of factories, higher than any other State
- 48.5% India’s most urbanized State by geography and population.
- The road connectivity—nearly 200,000 km of road network and 60,000 km maintained by National and State highways department
- As of 2014-15, Tamilnadu has an installed capacity of over 20,000 MW. The State will be power surplus by 2016


**Figure 2.12 The industrial output of Tamilnadu**

- 21% Contribution to India’s Automobile exports
- 20% Contribution to the total installed of vehicle production
- 1st Tamilnadu is the largest contributor to the automobile sector in India in terms of Industrial Output
- 2nd Highest cumulative FDI inflow among the various sectors (attributing to 11% of the total FDI inflow) from 2000-2012 in Tamilnadu
- Tamilnadu houses more than 40% of total installed capacity of Spinning industry in India
- Tirupur is the biggest Knitting Cluster contributing 90% of Knitwear exports from India
- 35-40% contribution to total Yarn Production in India in last 5 years in Tirupur
- The State has 2614 Hand Processing Units (25% of total units in India) and 985 Power Processing units in Tirupur (40% of total units in India)
- 58% of total textile Mills in India are present at Tirupur in Tamilnadu (inclusive of SSI)
- Tamilnadu is the 3rd largest manufacturer of Electronic Hardware in India
- Tamilnadu’s contribution to the national electronic hardware output has increased from 10% in 2008-09 to 18% in 2012-13. Tamilnadu has over 23 Electronic Hardware Technological Parks located in major IT-centric Special Economic Zones (SEZs) of Sriperumbudur, Oragadam and Mahindra World City (Figure 2.13).

Figure 2.13 The industrial production of major subsectors and electronic Hardware export
• Leather sector in TN accounts for ~60% of India’s production

• TN accounts for 36% of total exports from the Country

• Central Leather Research Institute (CLRI), Chennai is the world’s largest Leather Research Institute

• TN accounts for 70% of the Tanning capacity of India and 6% of the Global leather requirement

• Provides direct employment to 2.5 million people

• Sivakasi – A fireworks manufacturing hub

• 90% India’s Firework production and 450 Firework Factories

0.5 Million direct employment in Sivakasi

• 0.2 Million indirect employment in Sivakasi

• 60% of Safety match production in Sivakasi

• 4500 Match Units in Sivakasi


2.7 METHODS OF SAMPLING

A large variety of field techniques for assessing settled dust have been described in the literature (Ramasamy & Ponnusamy 2009; Qian Zhang et al. 2014). The particulate matter has been undertaken in Tamilnadu, from the above problem in view. The air dust particles were collected at the height of 20 feet in roadside and land area (Ramasamy & Ponnusamy 2009; Qian Zhang et al. 2014). The deposition time of the collected samples is 20 days to
25 days and this work was carried out on summer season (February to May 2011) when the weather conditions were normal cloudy days. These samples were washed in distilled water. The settled dust particles at the bottom of the container are then dried at 110°C in an oven and are used for analysis. The samples collected from 38 towns and cities of Tamilnadu, which were labeled as 1 to 111. The samples were mainly collected from Vehicular area (i.e., Bus stand, more traffic and main junctions), Industrial area and the Residential area which cover almost all major districts of Tamilnadu. The sample collected areas are visualized (Figure 2.14) and are listed out with their latitude and longitude in Table 2.1.
Figure 2.14 Location of sample collected areas in various places of Tamilnadu, India
### Table 2.1 Latitude and Longitude of sampling sites

<table>
<thead>
<tr>
<th>City/ Town</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Population</th>
<th>District</th>
<th>Sample Numbers</th>
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