CHAPTER III
Chapter III

METHODOLOGY

When a high explosive is detonated to cause explosion, it produces a large quantity of gas and heat in a very short time resulting in development of a very high pressure. There is sustained shock wave and sufficiently effective blast pressure. During the explosion, the temperature developed may be as high as 5000°C. There is absorption and adsorption of volatile and nonvolatile constituents of explosive substances and their combustion products in different layers of soil. Thus, the soil at the site of explosion is likely to undergo significant physical, chemical and mineralogical changes. Depending upon the type and quantity of explosives there would be variation in the resultant changes. More is the explosive charge; deeper will be the crater. The explosion will accordingly effect even the deeper layers (B Horizon) of the soil resulting in scattering of the affected soil to a larger area keeping the crater as center. Therefore, the debris collected from the site of explosion is usually available in large quantities. The first priority of examination of soil samples so collected from the site of
explosion is to detect and identify the explosive used. A wide range of methods has been used by workers in the field for analysis of post explosion residues (Yinon and Zitrin, 1981, 1993; Washington and Midkiff, 1986, Beveridge, 1992). The widely used techniques are chemical spot tests, thin layer chromatography, infrared spectroscopy and spectrometric techniques like ICP, AAS, etc. In addition to TLC and IR approaches, other instrumental techniques are also used for detection of explosive. X-ray diffraction technique identifies crystalline explosives, other materials and soil mineralogy. Extracts from debris can be identified, with proper database, by using GC, HPLC, ion chromatography etc.

It may not be possible to identify explosive materials if proper soil sample from the debris is not available due to scanty amount of explosive substances admixed with the soil. The explosive may not be identified from the available small quantity of soil carried by the suspect from the site of explosion in apparel, shoes and other belongings. It is still more difficult after considerable time lapse. A foolproof methodology is therefore warranted for the examination of soil samples to arrive at some significant forensic conclusions.
Since minerals provide greatest diversity in soil, the specific mineral identification of the constituent grains of the soil sample and allied chemical study of the inter grain space is very significant. Physical, chemical and mineralogical changes in soils that are subjected to explosion provide necessary distinguishing parameter even if explosive is not detected and identified.

In view of the aforesaid discussion, a detailed study of soil samples has been undertaken in the present work. They are:-

1. Detection of explosives.
2. Study of post blast geochemical changes in soil samples.

1. Detection of explosives:

The following methods of examinations were employed for the detection of explosives.

a) Chemical spot tests
b) Chemical Confirmatory tests
c) Thin Layer Chromatography (TLC)
d) Fourier Transform Infra-red (FTIR) spectrometry
a) CHEMICAL SPOT TESTS

The investigation of the explosive residues present in the debris necessitates adoption of a quick screening method, which may help in narrowing down the elimination of certain class of explosives. Chemical spot tests have been found very useful for screening and they are extensively used in forensic laboratories (Amas and Yallop, 1966a). Various authors have suggested qualitative chemical tests both for cations and anions and they are well documented. (Azzam, 1937; Stevens, 1966; Amas and Yallop, 1966b; Pristera, 1971; Sanger, 1973; Menke, 1974; Midkiff and Washington, 1974, and Parker et al, 1975a). Three reagents are widely used for initial screening purposes and they are Griess reagents (Griess, 1864, 1879; Feigl and Anger, 1966) and reagents for tests with Diphenylamine (Feigl and Anger, 1966) and alcoholic KOH. (Reese, 1966). These reagents have been used in the present work for qualitative chemical spot tests.

CHEMICAL TESTS AND REAGENTS:

All the chemicals used for the preparation of reagents were of analytical grade and are detailed in sequel.
Chemicals:
1. Acetone
2. Diphenylamine
3. Alpha-naphthylamine
4. Sulphanilic acid
5. KOH
6. Absolute alcohol
7. Glacial acetic acid

REAGENTS FOR SPOT TESTS:

A) Griess reagent:
Several formulations of Griess reagent are there (Zeichner and Glattstein, 1986).
In the present work the below written formulation was used.
Solution No: 1:
1 gm of sulphanilic acid was dissolved in 100 ml of 30 % acetic acid.
Solution No: 2:
1 gm of alpha-naphthylamine was dissolved in 230 ml of boiling distilled water and cooled. The decanted cool liquid was mixed with 100 ml of glacial acetic acid.
Freshly mixed solution in the ratio of 1:1 of solution Nos: 1 and 2 was used as Griess reagent for spot tests.

B) Reagent for tests with Diphenylamine:

1 gm of Diphenylamine was dissolved in 100 ml of concentrated sulphuric acid.

C) Reagent for tests with Alcoholic KOH:

10 gms of KOH was dissolved in 100 ml of absolute alcohol.

PREPARATION OF SOIL SAMPLES FOR SPOT TESTS:

All the explosives TNT, RDX, PETN and their combinations, undertaken for the present study are soluble in acetone to a sufficient degree. The least soluble is RDX, which requires 25ml of acetone to dissolve one gm of RDX. Therefore, explosive residues in soil samples were extracted in acetone for spot tests. The acetone extracts were filtered and used for chemical spot tests.

CHEMICAL SPOT TESTS:

One or two drops of the extracted and filtered solution of each of the pre- and post-blast soil samples were placed on a marble spot plate. The concentrated filtrate evaporated quickly to dryness. One drop of each of
the reagent (Griess, diphenylamine and alcoholic KOH) was then added to each of the soil samples separately and the results were noted. The results of spot tests are presented in Table No.10 to 13 and discussed in the Chapter on presentation of data Chapter No: IV.

b) CHEMICAL CONFIRMATORY TEST:
Confirmatory tests are detailed in Chapter no: IV.

c) THIN LAYER CHROMATOGRAPHY

The value of chemical colour reactions is greatly improved if they are combined with the separating power of thin layer chromatography. (Bohm, 1967; Jenkins and Yellop, 1970; Hoffman and Byall,1974; Midkiff and Washington, 1974; Parker et al, 1975; Midkiff and Washington,1976; Calmet, Helie and Forestie, 325, 1979; Calmet and Foresties, 326,1979; Douse,1982;, Twibell,et al, 1,1982; Twibell,et.al,4,1982; Dorones and Malotky,1983; Yinon and Zitrin,1993; and Stahl, 1969).

Though the sensitivity compared to many instrumental methods is far less, yet thin layer chromatographic method has superiority over spot tests and is accepted as an extremely valuable method for explosive identification. Therefore, colour reaction spot tests, in
the present study, have been confirmed by utilizing thin
layer chromatography.

Thin layer chromatography is a technique by which a mixture can be separated into its individual components. Separation is achieved by passage through a system of two phases, the moving and the stationary phase which have a relation to each other. The mixture dissolved in a solvent is transported by a moving medium i.e. a liquid, over a stationary thin uniform surface of an absorbent. A thin layer plate is prepared by coating a thin film of a granular material on a glass plate. Silica gel or Aluminum oxide is commonly used. Solid dissolved in suitable solvent or a liquid sample is spotted in micro quantity with the help of a capillary on thin layer plate near the lower edge. The plate is then put in a closed chamber, pre saturated with a selected solvent. Special care is taken so that the solvent does not touch the sample spot. The solvent slowly rises up the plate with capillary action, called as the moving phase. As it moves, the components of the sample spot get distributed between stationary and mobile phase. Separation occurs due to the difference in the distribution of constituents between moving and stationary phase. Components having greatest affinity for the moving phase travel up at a faster speed compared to
those having greater affinity for stationary phase. When the liquid front moves a distance of about 10 cms, the plate is removed from the chamber and dried. As most of the compounds are colourless, separation may not be visible. Various methods of visualisation are adopted such as examination under UV (Beveridge, 1998), spraying with a variety of eluents, iodine fumes, etc. The components of the sample are identified by a parameter called Rf. (ratio of fronts) or retention factor which is mathematically expressed as:

\[
Rf = \frac{\text{Distance travelled by a substance from the center of the spot}}{\text{Distance travelled by the solvent from the point of application to the solvent front}}
\]

This value is always less than 1 and remains same under identical conditions. A control is always run side by side along with the sample for comparison.

**EXPERIMENT:**

Fine spots of concentrated acetone extract of studied soil samples were applied on pre-coated silica
gel of 0.25 mm thickness. These pre-coated TLC plates (20x20 cm) with UV indicator were activated before use for an hour at 110°C. Spots of pure explosive samples of RDX, TNT and PETN dissolved in acetone were also applied on these plates side by side. Plates were air dried for 10 minutes. Toluene, an eluent, was taken in a jar and the jar was saturated for half an hour. The plates were then put in the jar in erect position. The jar was covered with lid. Toluene was allowed to attain a height of 10 cm on the plates using ascending technique. Plates were taken out and spots were visualised by spraying N sodium hydroxide. Thereafter, the plates were dried in an oven at 100°C for 10 minutes, cooled and sprayed with Griess reagent (Yinon and Zitrin, 1981). Rf values of all the samples were determined. The Rf values of the soil samples were compared with those of control pure explosives and tabulated in Table no.14 to 20. (Yinon and Zitrin, 1993). and the details of retention factor of soil and control explosive samples are detailed in Chapter no. IV on presentation of data.
d) FTIR ANALYSIS FOR Detection OF EXPLOSIVES

Infra Red Spectroscopy is one of the most powerful analytical technique which offers the possibility of identifying explosives, narcotic drugs, poisons and paints etc. This has become a very useful tool in the field of forensic science and its applications is becoming increasingly extensive in forensic work every year (Pinchas, 1951; Brown, 1955; Carol, 1960; Jones and Tippet, 1962; Tippet, 1963; Urbanski, 1963; Leclercq, 1963; Kind et al., 1965; Alha et al., 1965; Cleverty, 1967) as well in forensic explosives (Miller and Wilkins, 1952; Nyquist and Kagel, 1971; Chasan and Norwitz, 1972). IR spectrometry is very important for identification of organic ions mainly in unexploded mixtures in post explosive residues (Beveridge et al., 1975; 1983; Washington et al. 1977; Kaplan and Zitrin, 1977). IR spectra of solids are usually recorded by using KBr pellet technique (Chasan 1972, Alm et al., 1978). Leclercq, (1963), used infrared for the identification of residues of explosives, which has been burnt or detonated in laboratory controlled experiments. Glattstein et. al., (1978) used Infra Red Spectroscopy to detect PETN and RDX used in letter bombs. Extensive special information is available on a wide variety of explosives and explosive ingredients.
Infrared spectroscopy is one of the powerful tool for the confirmation of the explosive materials in the explosive residues. The major strength lies in its capability of determining both qualitative and quantitative chemical substance. Infrared spectroscopy is used as a technique for identifying both organic and in-organic materials present in the exploded samples. Thus IR spectra is unique and serves as fingerprint to identify the whole molecule (explosive) from the residue by matching against known reference spectra. Inorganic ions which appear in explosive mixture (nitrate, chlorate etc.) have strong characteristic absorption in the IR region.

With the advent of Fourier Transformer IR technology, the sample required for IR analysis may be as low as 0.5 microgram. FTIR has the advantage of increased optical output, a modulated IR beam at the sample and the capacity to fast signal averaging resulting in quickly analysing nanogram size of samples with simple sample preparation and simple beam condenser. In FTIR, the IR beam is not separated to discrete wavelength before its detection. An interferometer is used for simultaneously sending the transmitted wavelengths to the detector. The interference pattern so obtained is transformed by computer
software into an IR Spectrum. Thus FTIR instruments have higher sensitivity and better resolution.

The fundamental example of FTIR over dispersive instruments is that all frequencies are simultaneously measured instead of individual. The phenomena enables FTIR spectrometer to scan faster with greater sensitivity. IR absorption technique Usually cannot be considered conclusive in the identification of geological and soil samples but they can be considered reliable methods for comparison of sample. (Murray and Tedrow, 1991).

EXPERIMENT:

SAMPLE:

Concentrated samples prepared by preparative TLC were used.

Preparative TLC:

After confirming the identification of different explosive substances by thin layer chromatography as mentioned above. It is necessary to further purify the
explosives traces in more quantity by preparative TLC as mentioned below for instrumental analysis.

The pre-quoted TLC plates with silica gel and thickness of 0.25mm with UV indicator were taken. The plates were then activated for half an hour in an oven at 100°C. The concentrated extract from the debris of each sample taken in acetone as referred already (TLC) is shifted in a line at the base of each of these plates with the help of a capillary. The beaker may be washed with small amount of acetone for shifting the concentrated material on the plates. The plates are then again dried in the oven for fifteen minutes. TLC jars containing Toluene were saturated by covering with a lid for half an hour. The dried plates were then put in different jars and allowed the eluent to run up to 10 cm. in each case. The plates are then taken out and visualised under UV light. The silica gel line from these plates was removed with the help of a spatula in a separate beaker. It is then separated by dissolving in acetone and filter with whatman paper no:41, and then concentrated by keeping on a water bath at 100°C. The concentrated material is ready for instrumental analysis.
EXPERIMENT:

All the concentrated soil samples prepared by preparative TLC were subjected to FTIR spectrometer (for the presence of explosives) by using PRKIN ELMER-SPECTRUM RXI- FTIR SYSTEM. Spectras were obtained using KBr pellets. The results are detailed in Chapter no: IV on presentation of data.

2) Study of post blast geochemical changes in soil samples.

The following examinations were carried to identify the geochemical changes between pre- and post blast soil samples.

e) pH of the soil.
f) Colour of the soil.
g) Density distribution.
h) Ignition percentage
i) Mineralogical analysis by X-ray diffraction (XRD) technique. (Mineralogy of studied soil)
j) Mineralogical analysis by Fourier Transformation Infrared spectroscopy. (Mineralogy of studied soil)
k) Chemical analysis by ICP-AES "Inductively Coupled Plasma Atomic Emission Spectrometry" (Geochemistry of studied soil)

e) pH OF THE SOIL

A soil solution contains variety of elements in ionized condition. Some of the ions are negatively charged and they are acidic in reaction while the others are positively charged and are basic in reaction. The soil solution is neutral if it contains equal proportion of acidic and basic ions. Depending upon the domination of the positive or negative ions, the soil is classified as acidic or basic. The acidic and basic reactions are measured in terms of pH values. The pH value below 7 indicates acidic and above 7 indicates basic. Neutral reaction is indicated by pH = 7. Depending upon the nature of soil, the reaction usually varies between 4 pH and 9 pH. The pH of soil differs sample-wise and so also location-wise. Thus, pH provides clue for screening of soil samples, especially in criminal cases, even if they are from the same site (Dudley, 1976). However, acid soils can be limed to bring the pH nearer to 7. So also alkaline soils can be brought nearer to pH 7 by the addition of sulphur.
Soils, undertaken for explosion experiments in the present study, were clay soils of the city Chandigarh and those of Manesar area. The soils at the site of explosions were fine-grained (2 μ m or less) clay soil. They exhibit colloidal properties. Clay particles are negatively charged. As such positive ions in the soil such as calcium, potassium, magnesium and ammonium ions are attached to the negatively charged clay particles. The pH of the “control soil samples” of the site before explosion was ascertained. The soil samples (nos. 1-48), collected from the site after series of explosions were also subjected to the pH tests and the results compared.

**pH Test Experiment:**

Solutions of 10 gm of “control soil samples” (pre-explosion) and each of the post-explosion soil samples (nos. 1-48) were prepared in distilled water. All the soil solutions were filtered separately with the help of Whatman paper no. 41. The filtered solution of each sample was subjected to pH analysis with pH papers and the pH value was noted. Results of pH tests are tabulated in table No: 22 in Chapter No: IV on presentation of data.
f) COLOUR OF THE SOIL:

One of the identifying characteristics of soils and minerals is the colour. It is usually the first examination undertaken in the laboratory for identification of soils (Dudley, 1975, Saferstein, 1982). The colour is due to the geological materials and mineral assemblage. Colours of various soil horizons are different. O- and A-horizons tend to be dark in colour due to abundance of organic matter. The E-horizon may be almost white due to leaching of iron and aluminium oxides from the horizon. The B-horizon often shows significant changes in colour, varying from yellow / brown to light red / brown to dark red depending upon the presence of clay minerals and iron oxides. Carbonate-containing horizon (Bk) may have lighter colour, almost white, because of abundance of calcium carbonate. Though the colour depends upon the organic matter content and metallic compounds present in the soil, it also depends upon its stage of decomposition. (Arakeri, Chalam, Satyanarayana and Donahue, 1967). The colour may be dark, despite a very low percentage of organic matter if it contains metallic compounds that also give dark colour shades such as titanium compound. Iron compounds are responsible for yellow to red colour shades; hematite for red colour and limonite to yellow colour. The draining
conditions also influence the soil colour. Well-drained soils are well-aerated, suitable for oxidizing conditions and, therefore, the soil may be red in colour due to iron oxides. Poorly drained soils are wet, and iron is reduced imparting yellow colour to the soil. Besides moisture contents, the light intensity also affects the colour of the soil (Saferstein, 1982). Thus, if soils are different in colour, their properties are evidently different. Depending upon the proportion of different minerals, their compounds and organic constituents, the colour of the soil vary from one place to the other and so also from the ground level to varying depths in the soil profile.

The soil, in the case of an explosion, is subjected to a very high temperature of about 3000°C to 5000°C. Such a high temperature may destroy the organic matter to a considerable extent and the minerals may undergo chemical changes resulting in the change in the colour of the soil. Besides, solid and gaseous explosive residues admixed with the soil may also contribute to the colour change. Thus, the colour change would depend upon the type and quantity of explosives used and the heat produced. The colour of the soil, therefore, may provide a distinguishing physical parameter in cases involving explosives.
A comparative study of soil samples collected before and after explosion was undertaken in the present work. The colour of the solid soil samples after sieving through -100+200 mesh was viewed under natural light and under the microscope.

The colour of the pre- and post explosion soil samples as observed by the naked eye (Blatt, Middleton and Murray 1979) and under microscope is tabulated in Table No:23 to 26. The results of the comparative study of colours are detailed in Chapter NO: IV on presentation of data.

g) DENSITY DISTRIBUTION OF PARTICLES

The soil, when viewed under microscope, may indicate dust of minerals, rocks or other solid particles, oxides of iron, particles of vegetation such as grass, leaves, seeds, wood, fungi and other micro organisms including fragments of bones etc. The organic particles have higher density than those of the mineral particles. Depending upon the chemical composition of the particles, the minerals present and the porous space between the mineral grains and the moisture content, the density (weight per unit volume) of the soil varies (Dudely, 1975). Density, as a physical parameter is thus helpful in the
study of soil samples. Density distribution of particles (constituents) in soil samples indicates whether two soil samples are similar or not. This phenomenon is widely used in the forensic field. It helps in establishing the linkage of the questioned sample with that of the crime scene. (Thornton, and Fitzpatrick 1975) as no two soil samples are similar (in all respects) unless taken from the same spot / horizon / soil profile. The density distribution of soil samples is routinely used in various types of criminal cases such as rape, murder, theft of vehicles, automobile accidents etc. (Saferstein, 1982). However, its significance in cases involving explosives has not been explored.

DENSITY DISTRIBUTION EXPERIMENTS:

In the present investigation, density gradient column technique has also been used to study the density distribution of particles of soil samples. Glass columns were prepared by mixing bromoform and nitrobenzene in varying proportions of 10:0; 8:2; 6:4; 4:6; 2:8; and 0:10. respectively. The columns were allowed to stabilize for twelve hours. Thereafter, homogeneous control and post-explosion soil samples were slowly poured in the glass
The columns (density gradient tubes). The columns were again allowed to settle overnight (Nicklos, 1962; Kirk, 1974). The particles, as expected, were distributed in the density gradient column according to their densities. The heavier particles settled at lower levels compared to the lighter ones. The distribution patterns of control and post-explosion soil samples were photographed. (Fig.G). The comparative distribution of soil particles (Fig G) is detailed in the chapter no. IV on presentation of data.

h) IGNITION PERCENTAGE

Percentage ignition or weight loss after heating at 100°C for an hour is an another important parameter studied for the identification of soil samples. At 100°C the weight loss is usually for loss of organic matter, humus, and absorbed moisture contents (Saferstein, 1982). The ignition of soil at elevated temperature of about 1000°C results in, dehydration of the minerals, dehydroxylation of the clay minerals and destruction of some minerals like calcite in addition to removal of organic material. The higher the temperature, greater is
the effect on the soil materials. The temperature developed during explosion by high explosives is far more than 1000°C (may be even 5000°C or more) and therefore these effects are almost always expected. Since the attained temperature varies with the type of the explosive used, the resultant effect may also vary. A comparative study of the ignition percentage of pre- and post soil samples was also undertaken in the present investigation. The soil samples collected before and after explosion were heated to 100° C to study the loss in weight and ignition percentage.

Experiment:

The soil samples and the control were studied by using the same grain-size. The soil samples were pulverized after cleaning the gritty mass and debris. They were sieved by using ASTM sieve set of 100-mesh size. (-100+200 ASTM mesh). Four sets of crucibles were used for heating soil samples. The empty crucibles were heated and weighed by using Metlar analytical balance. They were thereafter put in a dessicator. Each crucible was used for a specific set of soil samples. The weight of the empty crucibles for each set is tabulated below.
Sample number | Weight of empty crucible (mg)
--- | ---
Control | 13905
1 to 17 | 13319
18 to 35 | 13488
36 to 40 | 12359
41 to 48 | 13905

1000 mg of each of the control and studied soil samples was placed in the crucible and was heated in an oven at 100°C for one hour. They were kept in a dessicator for cooling. After cooling, the crucibles were taken out from the dessicator and weighed again. The loss of weight in each sample and ignition percentage was noted. Their details are mentioned in Table nos.27 to 31 in the chapter no.IV on presentation of data and Fig.(G')

1) MINERALOGICAL ANALYSIS BY X-RAY DIFFRACTION TECHNIQUE

(MINERALOGY OF STUDIED SOIL)

X-ray diffraction technique(XRD) is used to identify specific mineral phases. Diffraction patterns produce unique “finger prints.” It is a very valuable tool for identifying the mineralogy of sedimentary rocks, soil,
rocks and other materials. Apart from the identification of mineral species, in some cases, semi quantitative determination of minerals and other constituents can also be made. The x-rays diffracted by crystalline materials produce unique "finger prints" (diffraction pattern) that can analyse the structure present. Indeed it is the most important technique in evaluating the chemical composition. X-ray diffraction was recommended (Washington and Midkiff, 1972) for unique identification of crystalline solids.

A monochromatic beam of X-ray passing through a mineral grain is scattered by the atoms that compose the mineral. At specific angles of incidence, the scattered X-rays produce intensified secondary beam. This phenomenon is known as diffraction.

For diffraction to occur, the Bragg equation \( n\lambda = 2d \sin \theta \) must be satisfied and the conditions of the Bragg equation is eventually fulfilled if the sample is crystalline. Uniformly powdered sampler are preferred rather than irregular shaped solid blocks because the rotation of such a sample in the beam results in diffraction in all possible lattice planes. The diffraction pattern is thus dependent on the size and type of the crystal lattice which itself depends on the chemical compound present. The XRD technique, therefore, provides
information on the chemical compounds present. This gives XRD a unique role to play in the field of forensic analysis since other comparable techniques such as AAS, EPMA, XRF, ES etc., provide information only about the elements present and not about the compounds which comprise the elements. Also a very small quantity of the sample is required for obtaining diffraction patterns of a crystalline substance. After obtaining the diffraction pattern the compound is identified by measuring the lines and converting the same to d-values and comparing the results with the powder diffraction file (PDF) data.

In the past photographic film was the exclusive medium for recording X-ray diffraction patterns. Even today camera equipment is used because of moderate capital cost, easy to handle and reliability. In recent years, fast speed Polaroid film has become very popular because of very short exposure time and immediate development of the film without a darkroom. However, the camera technique for recording the diffraction pattern demands almost constant attention of the worker for loading and unloading of the film and its processing. In the present era of computerization, by incorporating appropriate software, a diffractometer can be programmed to operate round the clock unattended and, through the marvel
of modern-day electronics, one can record and store data from questioned samples, perform complicated mathematical calculations, search memory blanks to identify sample components, establish the percentage of each components and print out the final results.

The diffraction pattern of the soil samples was obtained by using PHILIPS X' Pert MPD System X-rays diffractometer.

**The operating conditions of XRD were as under:**

<table>
<thead>
<tr>
<th>Source:</th>
<th>Copper Kα-radiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage:</td>
<td>40 kVA</td>
</tr>
<tr>
<td>Current:</td>
<td>50m A</td>
</tr>
<tr>
<td>Bragg angle (2θ) :</td>
<td>10 – 50°</td>
</tr>
<tr>
<td>Diversion Slit:</td>
<td>1&quot;</td>
</tr>
<tr>
<td>Receiving Slit:</td>
<td>0.1 nanometer</td>
</tr>
<tr>
<td>Wavelength of source:</td>
<td>1.54060 Å</td>
</tr>
</tbody>
</table>

The computer prints of the diffraction pattern of all the control and post blast soil samples were carefully studied and d values were determined (Fang and Donald, 1966.) in each case to identify the compound present. The computer prints of the diffraction pattern of all soil sample are shown in Figs. S to Z and A', and their results are
j) Mineralogical analysis by FTIR

**EXPERIMENT:**

All the soil samples (control and post explosion) were subjected to FTIR spectrometer by using PERKIN ELMER-SPECTRUM RXI- FTIR SYSTEM. Spectras were obtained using KBr pellet (Mineralogical study). The computer prints of the diffraction pattern of all soil sample are shown in Figs. H to R, The results are Tabulated in table nos: 36 to 38 and 39 in Chapter no: IV on presentation of data.

k) CHEMICAL ANALYSIS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP-AES)

The ICP technique is widely accepted analytical technique for determining major and minor elements in various materials. This technique precisely determines the content of metals in ppm/ ppb (part per million / billion level in various media. ICP-AES has many advantages, including sample operation, rapid analysis

The underlying principle is that when atoms of an element are excited, their electrons change orbital by absorbing energy and emit light with a wavelength that is characteristic of each element on their return to their initial orbital. The energy required to make the electrons change their atomic orbital is supplied by introducing the elements to be analysed into an argon plasma. High frequency radiation via an induction coil is used to heat a stream of argon gas and to generate plasma. The samples added to the plasma are reduced to the state of individual atoms. When the plasma excites the electrons of these atoms, they re-emit the energy acquired in the form of electro-magnetic radiation. This energy is composed of wavelengths characteristic of the elements present. The discrimination of these wavelengths is performed by an optical system called a monochromator that is fed to a photo multiplier tube. The photo multiplier tube transforms
the radiation into electric signals, which are captured by the data processing system. The printouts are the results of the qualitative analysis of the examined samples. Along y-axis, intensity is plotted and along X-axis wavelength in nm is plotted. At the center of X-axis, the wavelength corresponding to the element being analysed is marked. Along y-axis depending on the concentration of the element in the sample, peaks of varying height are obtained. The y-axis values are numerical values showing the height of the element peak from X-axis. While comparing two or more peaks, the software arranges the peak intensity in an increasing order along Y-axis.

The ICP technique has been utilised in the present investigation for determining the inorganic elements present in the pre (control) and post explosion soil samples. There are different digestion or extraction methods for multi-element analysis of foliage and soil samples (Dalquist and Knoll, 1978., Jones, 1978., Heffernan, 1985., Havlin and Soltanpour, 1980., and Huang and Schulte, 1985.) the HCl and HNO₃ soil extraction method. In the present study, for sample preparation, the soil samples were extracted by HCl and HNO₃ method (Corre And France, 1998) AR grade HCl and HNO₃ were used.
EXPERIMENT

Two gms of each soil sample (-100 + 200 mesh) was digested with 15 ml HCl (50%) and 5 ml HNO₃ (Conc). The samples were kept over night for digestion using temperature up to 130°C and taken to dryness in Kjeldhol flask. The samples were re-dissolved in 5% HCl and filtered. The filtrate was then made to 50 ml with de-ionized water. Each digested soil sample was subjected to ICP-AES analysis for elemental study. The ICP equipment used in the present investigation was ICP-AES JY-24, Jobin-Yvon (France) Sequencial Type.

The operating conditions of the equipment ICP-AES JY 24 were as under:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Generator frequency</td>
</tr>
<tr>
<td>2.</td>
<td>Plasma gas flow rate</td>
</tr>
<tr>
<td>3.</td>
<td>Sheath gas flow rate</td>
</tr>
<tr>
<td>4.</td>
<td>Nebuliser gas flow rate</td>
</tr>
<tr>
<td>5.</td>
<td>Nebuliser pressure</td>
</tr>
<tr>
<td>6.</td>
<td>Sample uptake</td>
</tr>
<tr>
<td>7.</td>
<td>Argon humidifier</td>
</tr>
<tr>
<td>8.</td>
<td>Peristaltic pump speed</td>
</tr>
</tbody>
</table>
The wavelengths chosen for the elements are tabulate below:

<table>
<thead>
<tr>
<th>Sr/No:</th>
<th>ELEMENT</th>
<th>WAVELENGTH (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Aluminum</td>
<td>226.922</td>
</tr>
<tr>
<td>2.</td>
<td>Calcium</td>
<td>393.366</td>
</tr>
<tr>
<td>3.</td>
<td>Chromium</td>
<td>267.716</td>
</tr>
<tr>
<td>4.</td>
<td>Copper</td>
<td>224.700</td>
</tr>
<tr>
<td>5.</td>
<td>Iron (Fe 2+)</td>
<td>238.204</td>
</tr>
<tr>
<td>6.</td>
<td>Magnesium</td>
<td>279.553</td>
</tr>
<tr>
<td>7.</td>
<td>Manganese</td>
<td>293.930</td>
</tr>
<tr>
<td>8.</td>
<td>Sodium</td>
<td>588.995</td>
</tr>
<tr>
<td>9.</td>
<td>Nickel</td>
<td>221.647</td>
</tr>
<tr>
<td>10.</td>
<td>Zinc</td>
<td>213.856</td>
</tr>
</tbody>
</table>

The computer prints of the ICP-AES of all soil samples (Control and post-explosion) are shown in Figs. B'(1-10) to F'(1-10) and the results of qualitative elemental analysis of soil samples (Control and post-explosion) are tabulated in table No: 40 to 41 in the chapter no: IV on presentation of data.