CHAPTER - I

GENERAL INTRODUCTION
INTRODUCTION

Coal essentially consists of some organic and inorganic matter as major constituents. It also contains a variable amount of elements in traces. Some of these are more concentrated in the less dense fraction of the coal, i.e. appear to be incorporated mainly with the organic components. Others are concentrated in the dense mineral-rich materials and appear to have a dominant inorganic affinity (Gluskoter 1977, Ward 1980). They may represent either metallo-organic compounds in the coal structure; minor amounts of a mineral with an abundance of the particular elements (e.g. Zinc in Sphalerite) or major amounts of a mineral in which the element itself occurs in trace proportions (e.g. manganese in Ankerite).

In some areas, the trace elements may be useful as aids to seam correlation or as indicators of the coal's depositional environments. Boron, for example, appears to be more abundant in coals influenced by marine environment (Swaine 1962, Bohor and Gluskoter 1973).

In coal conversion process, a number of trace elements may get transferred to liquid hydrocarbons, coke and other products. They may act as catalysts or inhibitors in some of the complex coal conversion processes too. (Ward, 1984)

Some of the trace elements are released to the environment during combustion of coal or its products and by weathering of coal ash and colliery waste materials. The elements involved include many that are essential to biosphere processes as well as those are
toxic to plants, animals and human being. High concentrations of critical elements such as lead, arsenic, cadmium, mercury may limit the suitability of a coal from the standpoint of sensitive situation. In other areas, the trace elements may represent potentially valuable byproduct from the materials concerned. e.g. germanium, indium, gallium etc.

Most significant characteristics of coal is it's extremely high concentration of carbon compared to other sedimentary rocks. It is also enriched in hydrogen, nitrogen and sulphur along with oxygen as more common element. Enrichment of these elements however does not reflect their biogenic history and therefore further geochemical evidences need to be collected from the study of other elements. Coal beds contain all the elements formed in rocks from which the sediment was derived in varying proportions. Over and above, additional elements can be incorporated into the coal by percolating ground water; either through precipitation as minerals or through ion-exchange in the clays or organic matter. (Volkovic, 1983)

Zubovic (1966) considered the ability of any particular element to form from chemical emplacement processes in the coal forming swamp is controlled by several geological processes in the source area. Rapid and extensive uplift of the source areas would tend to reduce the length of time necessary for chemical weathering and result in the greater influx of clastic materials and a smaller amount of soluble inorganic matter into the depositional basin. Under these conditions, a large amount of trace element would be associated with the non-authigenic but
mostly detrital mineral matter of coal and as lesser amount with the organic fraction.

Tectonic and climatic activity in the depositional basin also play an important role in the accumulation of organic matter. With very rapid subsidence, little or no vegetation will be able to grow and clastic materials will dominate sedimentation. If little or no subsidence takes place, the biochemical cycle will be completed with oxidation of most of the vegetal matter and as a result, no biomass will be accumulated. Therefore, there must be an optimum balance of tectono-climatic condition for accumulation and preservation of organic matter in sizable quantities.

Rate of accumulation of organic matter is important in determining the concentration of trace element in the resulting coal. If availability of trace element from the source area remains constant, then concentration in the organic matter will be inversely proportional to the rate of accumulation of the inorganic matter. (Volkovic, 1983)

Again, low concentration of trace elements usually occurs when the areal extend of the site of organic deposition is large. As a result, generally thick widespread coal beds have low trace element concentration while thin bedded coal have high concentration of trace elements.

During the early phase of organic accumulation in a basin, the trace element may be obtained by the plants from underlying soil profile. When forest starts growing on accumulated peat surface,
surrounding border land renders elemental influx through erosion of soil.

Type of vegetation also determines preferential affinity to different elements and this again has a direct bearing on evolutionary trends of the plants which again reflects age of a coal seam.

It is interesting to note that numerous and varied elements are enriched in coal ashes relative to their average contents in the earth crust (Nicholls 1968), Swaine (1962) noted except, occasionally, elements like arsenic, boron, lithium, molybdenum and lead in total coal samples, exceeds their average contents in shale but their is a definite and relative impoverishment of coal in minor and trace elements when compared with shale.

Mason (1958) suggested several possibilities for the enrichment of elements in ash which may be related to (1) primary plant growth and subsequent selective decay of the material, (2) accumulation of element from ground water by absorption of chemicals during calification process, (3) concentration of element in the mineral deposited along with plant material. Intra-basinal and Inter-basinal variability in content possibly suggest that no single process can account for the accumulation of all minor or trace element in coal and later in ash. A number of different processes must be involved and their relative importance are being determined by local conditions. This implies that attention should be focussed on samples collected from one seam at one geographical location, rather than on a widespread survey of all
available data without reference to its source (Nicholls 1968). The author selected a very small area and investigated only two successive thick coal seams to focus the problem with several restrictions on the extraction and handling of data.

Geochemistry of trace elements in coal and associated sediments need attention since the knowledge in the subject is still in a formative state and lot of information is yet to arrive. The nature and mode of occurrence together with variation in distribution of trace elements in organic sediments in time and space can reveal geochemical history of a coal deposit which in turn can help in reconstructing the palaeegeographic panorama of an area.

The trace element study of coal is gaining importance due to its several practical applications. The most important are (a) understanding the coal genesis particularly depositional environment, (b) the correlation of coal seams and also (c) in the contamination hazards abatement which has already been mentioned.
BRIEF DESCRIPTION OF THE AREA

The area of investigation (Plate - 1) lies in Orissa state, between latitudes 21° 40' and 22° 05' East, and longitudes 83° 40' and 83° 50' North and comprising south eastern sector of IB-River Coalfield which in turn forms part of upper Mahanadi Valley basin belt. The area forms an undulating plane along the course of IB-River with a mean altitude of about 250 m above mean sea level (MSL). IB-River, the main drainage of the area is a tributary of Mahanadi which flows in a general southerly direction. Nearest railway station is Belpahar.

Barakar Formation is only encountered and described in the area occurring as a NW - SW trending patch and comprises a series of low and parallel ridges of sandstone bodies with inter-spaced valleys occupied by shale and coal seams.

The estimated thickness of the Barakar Formation is around 600m, (Pande and Chakraborty, 1964). But the maximum thickness has so far been recorded is 350m in a borehole drilled south of Belpahar. The Barakar sequence commences with a 15m to 20m thick Sandstone unit which grades upward into a thick pile of sediments represented by greyish white to pink, medium to coarse-grained, micaceous sub-arrowsic sandstones with calcareous and ferruginous cement, grey micaceous shale, carbonaceous shale, alternating fine bands of shale and sandstone, fireclay and thick carbonaceous horizons containing coal seams. The Barakar Sandstones are generally current bedded with tabular sets having individual foreset ranging between 30 cm. and 2 metres in thickness. Flaser bedding and penecontemporaneous deformation
structures like slump balls, load casts, sand dykes, minor folds, and faults are observed. The Barakar Formation has yielded a plant fossil assemblage, which includes Glossopteris indica, Schizoneura gondwanensis, Vertebraria indica and Sphenopteris polymorphs, etc.

The monoclinal beds of Barakar Formation strikes NW and SE with a dip at an angle 2 - 8 towards SW (Plate - 1).

The Barakar Formation in the area contains more than twenty carbonaceous horizons varying in thickness from less than a metre to over 50 metres.

Sequences of Coal horizons as reported by G.S.I. (1982) follows:

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Parting</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belpahar</td>
<td>Parting</td>
<td>21.65 to 27.88 m</td>
</tr>
<tr>
<td>Parkhani</td>
<td>Parting</td>
<td>112 m (approx)</td>
</tr>
<tr>
<td>Lajkura</td>
<td>Parting</td>
<td>0.5 to 10.45 m</td>
</tr>
<tr>
<td>Rampur</td>
<td>Parting</td>
<td>92 to 119 m.</td>
</tr>
<tr>
<td>IB - Seam</td>
<td>Parting</td>
<td>2.29 to 10.3 m</td>
</tr>
</tbody>
</table>

With two minor Coal Seams.

Out of major five horizons, only Lajkura and Rampur Seams were met with in the following explotary boreholes as described (Table - 1b)
The Geological succession encountered in the IB-River is enumerated in the table (Table - 1a) as suggested by Raja Rao, 1983:

<table>
<thead>
<tr>
<th>Age</th>
<th>Group</th>
<th>Formation</th>
<th>Lithology and (thickness) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recent</td>
<td>Holocene</td>
<td>Alluvium</td>
<td>sand, silt and clay laterite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Laterite</td>
<td>Gravel horizon gravel and conglomerate beds.</td>
</tr>
<tr>
<td>Up. Permian to</td>
<td>Kamthi</td>
<td>L</td>
<td>Conglomerates, ferruginous sandstone and red shales(300m)</td>
</tr>
<tr>
<td>Lr. Triassic</td>
<td></td>
<td>G</td>
<td>Feldspathic sandstones with conglomerate bands and lenses, white, grey and carbonaceous shales, fireclay and coal Seams (600m).</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>E</td>
<td>Mostly Coarse-grained sandstones with one thin coal Seam (90-125 m).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R</td>
<td>Diamictite, greenish sandstones, olive and chocolate coloured needle shales and rhythmites (130m +)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>G</td>
<td>Unconformity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N</td>
<td>Precambrian</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N</td>
<td>Metamorphics Granite gneisses, amphibolites, migmatites etc.</td>
</tr>
</tbody>
</table>

* Thickness values are approximate.
### Table _1b

**Details of the Boreholes**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Name of the Borehole</th>
<th>Latitudes and Longitudes</th>
<th>Name of the Seam Drilled with thickness</th>
<th>Total No. of Sample Collected</th>
<th>Description of the Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HGK - 15</td>
<td>21° 58' 55&quot; Lajkura (75.20 m)</td>
<td></td>
<td>50</td>
<td>Kulda - Monohorpur Block</td>
</tr>
<tr>
<td></td>
<td></td>
<td>83° 45' 30&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>HGM - 6</td>
<td>21° 44' 18&quot; Lajkura (22.65 m)</td>
<td></td>
<td>23</td>
<td>Kulda - Monohorpur Block</td>
</tr>
<tr>
<td></td>
<td></td>
<td>83° 44' 04&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CMHG - 68</td>
<td>22° 03' 00&quot; Lajkura(60.45m) and Rampur(47.40m)</td>
<td></td>
<td>49</td>
<td>Gopalpur Block Village - Ratanpur.</td>
</tr>
<tr>
<td></td>
<td>(newly name given by CMPDI)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
SCOPE OF THE WORK AND OBJECTIVE

Objective of the work is to understand the latent informations stored in the contents of minor and trace elements in the system as well as their mutual relationship. It is found that synthesis of informations from varied source could serve as a tool in reconstructing the genetic history of an area or a deposit. The present study is to identify geochemical indicators for recognition of depositional environment of coal in the area. Severe restrictions on the handling of data are necessary, otherwise a deviation from focussing the main problem may arise which in turn could be a mere reporting.

Vertical and lateral distribution pattern of various trace elements, of a single thick seam, and also its comparison with immediately underlying another thick seam has been attempted. Various statistical tests were employed to establish relationship between the elements necessary to interpret their behavioural pattern.

"Rare Earths in coal" in India has not so far been attempted which is also included in the work.

Behavioural pattern of trace elements in understanding the genetic history of coal has been the main area of emphasis. The account of previous works reveals that systematic study as well as interpretation of trace elements in coal in India is migre and needs attention and of which IB-River coalfield is least attended. Therefore, the present investigation is a partial fulfillment of the long felt need of research on "Trace elements in Coal".
PRESENT APPROACH

The data produced through different analytical techniques are systematically organised and processed through computer and subsequently compared and interpreted under the following heads.

Statistical Processing

(IIA) Analysis of variance (ANOVA) -
To examine reliability of data and find out ideally suited analytical method.

(IIB) Factor analysis - To understand mode of formation, concentration and association of trace elements which so far remained narrative.

Geochemical Interpretation

(IIIA) Source of trace element
To find out Organic/inorganic association and to establish geochemical Indicators.

(IIIB) Analysis of Rare earth elements
To interpret of paleoenvironment and evaluate nature of source material.

Analyses of systematically collected samples from the field have been meticulously done by the author himself and this part of the work was extremely laborious and most time consuming.
PREVIOUS WORK

Geology

The report on coal deposits of the IB River field was first brought to light in the later parts of the nineteenth century when the construction of the railway line was taken up. The credit for preparing the first ever Geological map of the area goes to V. Ball (1875) while W. King (1884-86) carried out boring operation in the area. The results of the later investigation, however, were not considered to be very encouraging. The area was subsequently remapped by G.F. Reader (1901). G.C. Chatterjee (1943) investigated the leasehold of the orient colliery of M/s. Birla Brothers ltd. V. S. Krishnaswamy (1946) investigated the part of the field falling within the submergence area of the Hirakud reservoir. E.R. Gee. (1947) also surveyed the area in connection with the possible use of coal from the area in a cement factory at Hirakud. A resurvey of the coalfield was carried out by D.R.S. Mehta and M.A. Anandlwar in 1954-55. Large scale mapping with the aid of aerial photographs on 1 : 42,240 scale, was carried out by B. C. Pande and S. N. Chakraborthy during 1961-63. Regional drilling in this coalfield was carried out in the Belpahar area by P. S. Paul in 1964-65 while the areas on the dip side of the working Collieries and the Jurabagan Darlipalli - Ubra area have been taken up for regional exploration by G. S. I. since 1974. The Directorate of Mines, Orissa on behalf of Coal India Limited, is engaged in detailed exploration in the orient and Rampur Collieries and their extension areas since 1975-76. Detailed exploration in the
Belpahar block was taken up by CMPDI Ltd. during 1978-79 and still being continued.

**Geochemistry of Coal (General)**


**Geochemistry of Coal (Indian)**

In India the trace element study in coal and coal ashes began in 1950 when Mukherjee and Dutta analysed some Indian coals spectrographically. The earlier studies were confined to few of the elements only. The presence and modes of accumulation of Ge and Co in some of the Gondwana and Tertiary coals and Lignites have been discussed by Iyer and Sundaram (1955), Rao and Rao (1965), Das (1958), Banerjee et al. (1972) and Dasgupta and Kathing (1979). Rishi (1970) reported concentrations of a number
of trace elements in coals from the Umaria Coalfield, M.P. Mukherjee and Ghosh (1976) carried out a detailed study of the occurrence and source of the trace elements in the North Karanpura coals. Mallick and Ahmed (1979) reported abnormally high values of Zr, Mo and Pb in coals from the Jharia and Raniganj coalfields. Dey (1980) examined coals from the Extra Peninsula India and reported high concentrations of B, Mn and Co. Chandra et al. (1981) carried out trace elements study of Korba coals in the light of the pollution problem. Mukherjee et. al. (1982) made a systematic approach to study the occurrence and concentration of a number of trace element in the major Gondwana and Tertiary coalfields of India. Singh et al. (1983, 1985) discussed the occurrence, distribution and probable source of the trace elements in coals from the Ghugus coalfield, Wardha valley. They also indicated the possibilities of contamination hazards due to the higher levels of Pb, Cu, and Cr. in these coals. Recently Pareek and Bardhan (1985) determined a number of elements in coal from the East Bokaro coalfield and discussed their distribution, behaviour and source.
EXPERIMENTAL METHODS

SAMPLING:

A total number of 122 samples of coal and associated sediments were collected at specified depths from three different borehole cores around the area of Belpahar. During the course of work, samples were analysed systematically from different boreholes at regular interval of two very thick coal seams i.e. Lajkura and Rampur Seam.

CHEMICAL ANALYSIS:

The coal samples were powdered and passed through -100 mesh sieve. Sample preparation techniques are specific to the method of analysis which were rigidly followed. The preferences for a particular technique are generally used according to the analyst's experiences, equipment availability and many other subjective factors.

Analytical Procedure:

1) Proximate analysis (Ash, Moisture, Volatile matter, Fixed Carbon).

(a) Ash:

Trace elements are usually determined from coal ash made at low temperature. However, temperature and time of ashing are important factors in order to prevent the loss of volatile trace elements. Coal samples were ashed at 450 C and later, trace elements were determined from these ash samples. Otherwise, 1 gm
coal sample was weighed in a dry clean empty Silica dish and the sample was spread on the dish uniformly. The sample was then heated to 500 °C in 30 minutes and from 500 °C - 800 °C for a further 30-60 minutes. This temperature has maintained for at least one hour. The dish with ash was then removed from furnace and allowed to cool first on a metal slab and finally in a desicator. The dish with ash was then weighed and again the weight was taken for the clean empty dish. From the difference of weight, percentage of ash was calculated.

(b) Moisture:
One gm of coal sample was weighted in a dry clean dish. The sample was spread on the dish uniformly. It is heated in an air-oven at 105 ± 5 °C for 1 hour. Then it was cooled in a desicator and weighted. From the loss in weight, total moisture could be calculated and the percentage of moisture was then computed.

(c) Volatile Matter:
One gm coal sample was weighed accurately into a standard volatile matter determination crucible and the crucible was put on an appropriate stand and charged into the muffle furnace heated 900 ± 25 °C and left for exactly 7 minutes. The crucible was then removed and cooled and finally weighed. Percentage of volatile matter content was computed in coal after correcting it for moisture content in the coal.

(d) Fixed Carbon:
Fixed carbon was calculated from the following formula:

\[ F.C = 100 - (\text{Moisture \%} + \text{Ash \%} + \text{Volatile matter \%}) \]
(2) **Ultimate Analysis**

(a) Sulphur : Sulphur occurs in coal in three forms.

(i) as Sulphates : Generally as gypsum (CaSO$_4$, 2 H$_2$O)

(ii) as Sulphide of Iron (Pyrite or marcanrite FeS)

(iii) Combined with organic matter.

One gm coal sample was mixed with Escha's mixture (about 5 times of the sample) and was taken in a procelien crucible. It was heated to a high temperature (900$^\circ$C) in an oxidising atmosphere to remove combustible matter and to convert the sulphur to sulphate. The fused mass was extracted with dil HCl solution and sulphate was determined by gravimetric method by precipitation as Barium Sulphate with 10% Barium chloride solution. The precipitate was ignited at high temperature (900$^\circ$C), cooled in a dessicator and weighed. The weight of the residue is BaSO$_4$.

$$S(\%) = \frac{\text{weight of the residue} \times 0.1374 \times 100}{\text{weight of the sample taken}}$$

(b) Phosphorus (as P$_2$O$_5$):

One gm of coal sample was first ashed at a temperature of 450$^\circ$C, then the whole ash was transferred into a Teflon Beaker. About 10 ml of Nitric acid and 5 ml of HF were added to it. The mixture was slowly evaporated over a hot plate, then it was dried and dehydrated. A few ml of Conc HNO$_3$ and 50 ml of distilled water was added to the mass, boiled and filtered. The filtrate was collected in a 100 ml volumetric flask. 10 ml of ammonium molybdate and ammonium vanadate solution was then added to it.
The volume of the flask was made up with distilled water and mixed thoroughly. After 30 minutes, the absorbance was measured at 415 nm. Another reagent blank was also taken. The percentage of $P_2O_5$ was computed with respect to the calibration graph prepared by using standard solutions of phosphorus exactly in the manner stated above.

**Wet chemical analysis**

Determination of $SiO_2$, $Al_2O_3$, $Fe_2O_3$, $TiO_2$, $CaO$, $MgO$, $Na_2O$ and $K_2O$.

**Sample decomposition**

One gm of sample (ash) was taken in a platinum crucible. About 5 gm of sodium carbonate was then added and mixed thoroughly by means of a glass rod. The mixture was fused in an electric muffle furnace at 900°C temp. The melt was allowed to swirl. The crucible was removed when fusion was complete. The crucible was rotated so that the melt solidified on the side of the crucible. It was allowed to cool. The melt was extracted in a beaker by boiling with 10 ml of Conc HCl and 100 ml of distilled water. The platinum crucible was washed with hot dil HCl several times and the washings were transferred to the beaker. It was evaporated slowly over a low heat and then the residue was baked at 110°C for half an hour and cooled. Then 5 ml of Conc HCl and 100 ml of water was added, boiled and filtered through No. 42 whatman filter paper. The residue was washed three to four times with hot 1% HCl and finally five to six times with hot water. The filtrate was reserved for the determination of other radicals. The residue
was ignited in a platinum crucible and weighed. Three to four drops of dilute sulphuric acid and about 10 to 15 ml. of hydrofluoric acid was added and evaporated slowly. The dry mass after complete evaporation was ignited and weighed. The difference in the weights would give the silica content (as SiO₂).

After the determination of silica, the small residue left in the platinum crucible was fused with potassium pyrosulphate. The fused mass was extracted with hydrochloric acid and mixed with mother liquor and the volume was made up to 250 ml. in a volumetric flask and mixed throughly. Suitable aliquot was taken for subsequent determination.

Determination of Aluminium

Fifty ml. of aliquot was taken and was brought near neutralization with 5% NaOH solution and slowly poured into another beaker containing 50 ml. of 10% NaOH and a pinch of sodium carbonate. The solution was boiled and filtered through No 40 whatman filter paper. The residue was washed for five to six times with hot 0.1% sodium hydroxide solution. The filtrate was taken and the pH was adjusted at 5 to 5.5. 50 ml. of acetic acid and ammonium acetate buffer was added and then 25 ml of EDTA solution was also added to it. The solution was boiled for about 15 minutes and cooled. The pH (5 to 5.5) was again adjusted and was titrated with standard zinc acetate solution, using Xylenol orange as indicator. From a blank, the amount of EDTA consumed by aluminium was determined and calculated as Al₂O₃ content in the sample.
Determination of Titanium

Twenty five ml of aliquot was taken in which 1 ml. dilute suphuric acid was added and evaporated on a hot plate. The dried mass was moistened with dilute sulphuric acid. Water is then added and the mass was dissolved by boiling. 5 ml. dilute H₂SO₄, 5 ml. phosphoric acid and then 10 ml (1 : 1) H₂O₂ were added. The volume was made up in a 100 ml. measuring flask and TiO₂ was determined Spectrophotometrically at a wavelength of 415 nm.

Determination of Fe₂O₃

Fifty ml. aliquot was taken and 50 ml of distilled water was added to it. About 0.5 gm of ammonium chloride was then added and R₂O₃ was precipitated with ammonium hydroxide using methyl red as indicator. It was boiled and filtered through No. 41 whatman filter paper. The residue was washed for five to six times with hot water containing ammonium chloride. The filtrate was reserved for the determination of CaO and MgO. The residue was dissolved in (1 : 1) HCl. Water was then added, boiled and reduced with SnCl₂ solution. It was cooled and 10 ml. HgCl₂ solution was added. 20 ml of H₂SO₄ and phosphoric acid mixture was added afterwards. It was titrated with N/20 standard K₂Cr₂O₇ solution using barium diphenylamine sulphonate as indicator till violet colour appeared. From the titration value, the Fe₂O₃ content was calculated.

Determination of CaO and MgO

The filtrate containing R₂O₃ was taken in a volumetric flask and then the volume was made up and CaO and MgO were determined by
EDTA method.

For CaO:

Twenty five ml aliquot of the sample was taken in a 250 ml conical flask. To this, 10 ml of 20% triethanolamine solution and 10 ml of 20% KOH solution were added. About 0.5 gm patton and Reader's reagent as indicator were added. The solution was titrated with standard M/50 EDTA solution till the colour changed from wine red to blue. The consumed EDTA was noted and the % of CaO present in the sample was calculated.

For Total (CaO + MgO):

Twenty five ml. aliquot was taken in a conical flask. To this, 10 - 15 ml. of ammonium chloride - ammonium hydroxide buffer and 5-6 drops of EBT as indicator were added. It was then mixed and titrated with standard M/50 EDTA till the red colour of the solution turned blue. This titre value corresponds to total of Ca + Mg values. From the titre value, if the titre value of CaO is subtracted then MgO could be available.

**Determination of Sodium and Potassium**

About 0.5 gm of sample (ash) was weighed in a teflon beaker. 10 ml HF and 5 ml perchloric acid were added to it. The beaker was placed on an asbestos covered hot plate and heated slowly until dense fumes of perchloric acid liberated. The beaker was removed from the hot plate, cooled and 5 ml of HF was added. The beaker was placed on the hot plate and heating continued until the mass was completely dried. The beaker was removed from the hot plate and cooled.
To this, 5 ml. of water and 5 ml of perchloric acid were added. It was heated again on hot plate until it was completely dried. 15 - 20 ml hydrochloric acid (1 : 1) was then added to the dried mass in the beaker and it was warmed to dissolve. The solution was transferred to a 100 ml volumetric flask and the volume was made up with water.

From this an aliquot of 10 ml was taken in a 100 ml volumetric flask. 10 ml lithium chloride solution (1%) was then added to it and the volume was made up with distilled water. The solution is used for AAS measurements.

Measurement are then made for each element by aspirating the calibration solutions (0, 1, 10, 100 μg/ml.), the process blank and the test solutions.

**Emission Spectrograph**

Trace Elements were determined by Jarrel - Ash Emission Spectrograph, using dispersion grating, Graphite anode 6 mm x 3 mm, anodic excitation 12 - 13 amp, 110 volts. First ash sample was mixed with Carbon in (1 : 1) ratio. Then the mixture was loaded (30 mg) in the carbon electrode and then arced. Spectral lines were identified by comparison with standard lines of the elements using the comparator and the standard plates.

**Atomic Absorption Spectroscopy**

Trace elements were also determined with the help of a Perkin Elmer A.A.S (model 303) using either air/acetylene or acetylene/nitrous oxide gas according to the nature of the element. An ash sample was decomposed in HF - HClO₄ mixture until the liberation of white fume was stopped. The pasty mass was
dissolved in water acidified with HCl. The total volume was made up with water to a suitable volume. It was aspirated in the flame of AAS. The ground state atoms of the determined element was measured by detector.

**X-Ray Fluorescence Spectrometry**

*(Destructive Process)*

This method has been used for determination of Cu, Cr, V and Mn in coal ash sample by Philips model PW 1410 X-ray fluorescence spectrometer. A PW 1130 X-ray generator was used, with a rhodium X-ray tube operated at 55 Kv and 30 mA and LiF crystal and Scintillation detector. The X-ray lines used (2). For all elements Kα lines are used.

About 0.5 gm sample (coal ash) was taken in a Pt - Au crucible and mixed with 5 gm sodium tetraborate (flux) and fused. The melt was poured in a Pt-Au mould. On cooling, a glassy disc was obtained. The X-ray intensity of the elements concerned was measured by detector. The instrumental parameters are given below:

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak angle (°2θ)</th>
<th>B.G. ±</th>
<th>Crystal</th>
<th>Counter</th>
<th>KV (Kv)</th>
<th>mA (mA)</th>
<th>Counting Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>76.93 ± 0.5</td>
<td>LiF 200</td>
<td>Flow</td>
<td>55 - 30</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>62.97 ± 0.5</td>
<td>LiF 200</td>
<td>Flow</td>
<td>55 - 30</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>45.03 ± 0.5</td>
<td>LiF 200</td>
<td>Flow</td>
<td>55 - 30</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>69.35 ± 0.5</td>
<td>LiF 200</td>
<td>Flow</td>
<td>55 - 30</td>
<td>40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**X-Ray Fluorescence Spectrometry**

*(Non Destructive Process for Selenium Only)*

It has been demonstrated that X-ray spectrometry is a suitable method for the non-destructive measurement of many elements.
selenium compounds present in coal being volatile at low temperature - can not be analysed by standard destructive test in coal ash. So it is determined by nondestructive method.

The sample was powdered to - 200 mesh in a Spexomill for 15 min in agate grinding cylinders. About 10g of powdered sample was taken in the sample holder fitted with mylar. The sample was slightly pressed with the help of a polythene lid. The instrumental parameters are given below:

<table>
<thead>
<tr>
<th>Element</th>
<th>Analyte</th>
<th>Peak angle</th>
<th>Detector</th>
<th>KV/mA</th>
<th>Time in Sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>Kα</td>
<td>31.89 ±0.50</td>
<td>LiF</td>
<td>40/20</td>
<td></td>
</tr>
</tbody>
</table>

The unknown concentration of Se in coal sample is determined by comparing its intensity with those of the calibration standards.

**Preparation of standards for XRF analysis**

The standards for XRF analysis were prepared by adding different known quantities of spectrochemically pure elements to similar matrices and pressing sequentially in the same mould. The procedure followed is mention above.

**Sequential Inductively - Coupled Plasma Emission Spectrometry:**

The method was used for the determination of rare-earth elements (REE) and Yttrium contents at trace levels in coal ash samples. The procedure is as follows:

The coal ash sample (1 gm) was decomposed by heating with a mixture of 10 ml. HF and 5 ml. of HClO₄ in a teflon beaker until fumes of perchloric acid appear. After cooling, the residue was treated with conc HF (5 ml) and conc HClO₄ (3 ml) and was again heated to dryness. The dried mass was dissolved by warming with
15 ml of HCl (1 : 1) in a 250 ml beaker and was diluted to 100 ml. Now 5 ml of the 10 mg/ml calcium solution was added and the solution was treated drop by drop with NH\(_4\)OH (1:3) until there was a partial precipitation of the mixed-oxide group element (pH 3.0 - 4.0). A few drops of conc. HCl were added to dissolve the precipitate. The solution was heated to boiling and 10 ml of 10% oxalic acid solution was added with vigorous stirring. The precipitate formed was allowed to stand for 2 hr at room temperature and was separated by filtration. The precipitate was washed twice with 0.1% oxalic acid solution. The paper along with the precipitate were transferred to a silica crucible, and it was ignited at 900°C in a muffle furnace. The residue, after cooling, was dissolved in 10 ml of HNO\(_3\) (1:1) and was diluted with water in a 25 ml volumetric flask. This solution was used for the ICP-AES measurements.

Each element was measured by aspirating the standard solutions, the process blank and the test solutions. All these operations were performed automatically by means of a computer program.

**Instrument and Working Conditions**

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP - AES instrument</td>
<td>Jobin Yvon JY 38, sequential, C-T scanning monochromator, holographic grating, 3600 grooves/mm, 1.0 m focal length.</td>
</tr>
<tr>
<td>RF Generator</td>
<td>56 MHz, 2 KW working power.</td>
</tr>
<tr>
<td>Plasma Torch</td>
<td>Quartz, 28 mm outer diameter.</td>
</tr>
<tr>
<td>Gas Flow</td>
<td>Plasma gas 20 l/min. Cooling gas 0.4 l./min.</td>
</tr>
</tbody>
</table>
Carrier gas 0.35 l./min
Nebulizer Pneumatic
Sample Uptake 1 ml/min.
Observation height 14 mm above load Coil.
Flush/integration time 10 Sec each.

**STATISTICAL ANALYSES OF DATA**

The present work involved handling of a large number of data obtained through chemical analysis. In order to reveal the nature of relationship existing amongst the different set of data, they were subjected to various statistical tests using PC-based statistical packages. A brief description of the different packages along with their applicability in the present problem is as follows:

1. **SYSTAT**

A versatile program used for general and special type of statistical analysis and is very convenient for handling a large volume of data set. (upto 200 variables and upto 32,000 cases). The commands are simple and less in number and complex operations can be performed with a few keystrokes only. The results obtained are highly accurate and the analyses are speedy. The package has been used exclusively to perform factor analysis tests that revealed the various interrelationships existing between the variables as well as the mode of origin of the individual variables.

2. **EPISTAT**

It is a collective program written in BASIC language and is aimed at statistical analyses of small to medium sized data samples. More than 40 common statistical tests can be performed with this
program. It can handle 28 samples at a time with the maximum number of records per sample being 2000/s. Options for data modification, printing, saving and loading of data files is also available.

In the present problem, the program has been used to perform the following statistical tests.

(a) Pearson's correlation coefficient to assess the linear relationships between 2 variables.

(b) To obtain the equation for least square linear regression line for paired samples, and to draw a scattered diagram of that line from that equation.

(c) Calculation of analysis of variance (ANOVA) to scrutinize the reliability of the data obtained and to find out the ideally suited analytical method.