

## CHAPTER SEVEN

### CONCLUSIONS

- Among the studied coal fields of Sindh (i.e., Thar, Sonda and Meting-Jhimpir), the Thar coal field occurs in the Bara Formation of the Paleocene-Eocene age, Sonda coal field occurs in both Bara Formation and Laki Formation (Eocene) while the Meting-Jhimpir coal field is found in the Sonhari Member of early Eocene age of the Laki Formation.
- The heavy and trace element chemistry of these coal fields indicate that these coals have variable concentration of heavy and trace elements with decreasing trend from Fe to Cd as Fe>Ni>Zn>Pb>Cr>Cu>Co>Mn>Cd in the Thar coals; as Fe>Zn>Ni>Cu>Pb>Cr>Co>Mn>Cd in Sonda coals and as Fe>Zn>Pb>Ni>Cu>Cr>Co>Mn>Cd in the Meting-Jhimpir coals.
- These coals, especially of Sonda and Meting-Jhimpir, have relatively high amount of total sulfur and hence may have higher SO<sub>2</sub> emission as flue gases to the environment. However, the studied coals have no environmental impact as far as the NO<sub>x</sub> emission is concerned.
- The mineralogy of the Sindh coals suggests that these coals have quartz and kaolinite as the dominant phases with minor amount of calcite, dolomite, pyrite, illite and muscovite.

- The sequential leaching of the Sindh coals indicates that most of the heavy and trace elements (i.e., Pb, Zn, Cu, Cd and Mn) in these coals are present in the HCl-soluble compounds while some (i.e., Cr, Ni) occur as insoluble organically shielded matters. Fe is generally present as mono-sulfide (i.e., pyrite, marcasite) in the studied coals.
- The presence of pyrite and marcasite further suggest that the studied coals may cause sever problems in mining of these coals because of oxidation and formation of soluble toxic organic compounds of heavy and trace elements and hence contamination of underground water.
- The relative high concentration of sulfur and the various heavy and trace elements in the Sindh coal may have environmental problems during the coal combustion in the future power generation plants. Wherefrom there are chances of liberation of the toxic elements as fly ash particulates which may cause severe heath hazards in the region.
- To overcome this problem the special measures should be taken to reduce the particulate emission level by following the guide-lines proposed by the World Bank Group.

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# **APPENDIX-1**

## **METHODOLOGY**

### **A. FIELD METHODS**

#### **Collection of samples**

Representative coal samples ( $\cong$  2-4 kg) were hammered through the coal seam in the Meting-Jhimpir coalfield and for Thar and Sonda coalfield drill core samples were collected from the core library of Geological Survey of Pakistan's Sindh regional office located in Karachi. Both samples were collected in different sample bags, these samples were properly numbered in the field and brought to the Geochemistry Laboratory of the National Centre of Excellence in Geology, University of Peshawar for further experimentation.

### **B. LABORATORY METHODS**

#### **CRUSHING AND PULVERIZING OF COAL SAMPLES**

Representative coal samples collected during field were air-dried and crushed by the jaw-crusher. The crushed coal samples were then pulverized in a tungsten carbide ball mill to - 75 micron (200 mesh size) with a quartz flush between the samples. A portion of

individual sample was collected after proper quartering and coning. During this whole process greater care was practiced to avoid contamination. The powdered samples were stored in the airtight glass bottles. These bottles, after removing the lids, were kept in the oven at 110 °C for two hours in order to remove the moisture.

## **PREPARATION OF STOCK SOLUTION-A FOR COAL SAMPLES**

For the decomposition of the coal samples, a method of Jeffery and Hutcheson (1986) was adopted as follows. About 1.0 g of finely powdered coal sample was taken in a 100 ml teflon beaker. 10ml of hydrofluoric acid (HF) was added to it and was kept on hot plate at low temperature. After half an hour, about 4 ml perchloric acid ( $\text{HClO}_3$ ) was added and let the acid to evaporate until paste was obtained. Then 15 ml of concentrated  $\text{HNO}_3$  was added and the heating was continued until complete dryness. Then 20 ml 3N HCl was added to the residue and was heated until the maximum dissolution of residue. The solution was filtered through a fine filter paper with thorough washing with de-ionized water. The final volume was made to 50 ml with 3N HCl and was stored in polythene bottle. This solution was then used for the determination of heavy, trace and light elements by using atomic absorption spectrophotometer (AA).

## PREPARATION OF STOCK SOLUTION- B FOR CERTIFIED ROCK STANDARDS

The stock solution-b for the certified rock standards AGV-1 and W-2 was also prepared by the same method as described above and was used for the verification of the analysis accuracy.

## ANALYSIS OF HEAVY AND TRACE ELEMENTS

### Determination of Copper (Cu)

**Instrument:** Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

### Instrument conditions

Mode	Absorption
Wave length	325.8nm
Slit width	0.4nm
Fuel flow	1 l/min
Air flow	5 l/min
Burner height	10 mm

**1. Standard stock solution of 1000 ppm:** 1 g of copper metal was dissolved in 30 ml of (1:1)  $\text{HNO}_3$  and was made to the volume of one liter with de-ionized water.

**2. Standard stock solution of 100 ppm:** 10 ml of 1000 ppm standard stock solution was taken in 100 ml volumetric flask and was made to the mark with de-ionized water.

**3. Working standards:** 0.5, 1, 2, 4 and 8 ppm of working standards were prepared by taking 0.5, 1, 2, 4, and 8 ml from 100 ppm standard stock solution into a series of 100 ml volumetric flasks and made to the volume with de-ionized water.

**Procedure:** The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Cu cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspirated into the flame and the Cu concentration of each sample was noted. The Cu contents in ppm were calculated.

## Determination of Lead (Pb)

**Instrument:** Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

### Instrument conditions

Mode	Absorption
Wavelength	217 nm
Slit width	0.4 nm
Fuel flow	1 l/min
Air flow	5 l/min
Burner height	10 mm

**1. Standard stock solution of 1000 ppm:** 1.598 g of lead nitrate  $\text{Pb}(\text{NO}_3)_2$  was dissolved in 1%  $\text{HNO}_3$  and was diluted to 1 liter with de-ionized water.

**2. Standard stock solution of 100 ppm:** 10 ml of 1000 ppm standard stock solution was taken in 100 ml volumetric flask and was made to the volume with de-ionized water.

**3. Working standard solutions:** 0.5, 1, 2, 4 and 8 ppm of working standards were prepared by taking 0.5, 1, 2, 4 and 8 ml of 100 ppm stock solution in a series of 100 ml volumetric flask and volume was made to the mark with de-ionized water.

**Procedure:** The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Pb cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspirated into the flame and the Pb concentration of each sample was noted. The Pb contents in ppm were calculated.

### **Determination of Zinc (Zn)**

**Instrument:** Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

#### **Instrument conditions**

Mode	Absorption
Wavelength	213.9 nm
Slit width	0.7 nm

Fuel flow	1 l/min
Air flow	5 l/min
Burner height	10 mm

**1. Standard stock solution of 1000 ppm:** 1g of zinc metal was dissolved in (1:1) HCl and was diluted to 1 liter with de-ionized water.

**2. Standard stock solution of 100 ppm:** 10 ml of 1000 ppm standard stock solution was taken in 100 ml volumetric flask and was made to the volume with de-ionized water.

**3. Working standard solutions:** 0.5, 1, 2, 4 and 8 ppm of working standards were prepared by taking 0.5, 1, 2, 4 and 8 ml of 100 ppm stock solution in a series of 100 ml volumetric flask and volume was made to the mark with de-ionized water.

**Procedure:** The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Zn cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspirated into the flame

and the Zn concentration of each sample was noted. The Zn contents in ppm were calculated.

### **Determination of Nickel (Ni)**

**Instrument:** Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

#### **Instrument conditions:**

Mode	Absorption
Wavelength	232nm
Slit width	0.2nm
Fuel flow	1 l/min
Air flow	5 l/min
Burner height	10 mm

**1: Standard stock solution of 1000 ppm:** 1g of Ni metal was dissolved in a minimum volume of(1:1) HNO<sub>3</sub> and was diluted to 1 liter with de-ionized water.

**2. Standard stock solution of 100 ppm:** 10ml from 1000 ppm stock standard solution was transferred into a 100 ml volumetric flask and was made to the mark with de-ionized water.

**3: Working standards:** 0.5, 1, 2, 4, 8 ppm standard solution were prepared by taking 0.5, 1, 2 and 4, 8 ml from 100 ppm standard solution into a series of 100 ml volumetric flask and was made to the mark with de-ionized water.

**Procedure:** The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Ni cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspirated into the flame and the Ni concentration of each sample was noted. The Ni contents in ppm were calculated.

## Determination of Chromium (Cr)

### Atomic Absorption method

**Instrument:** Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

### Instrument conditions

Mode	Absorption
Wave length	357.9nm
Slit width	0.2nm
Fuel flow	4.5 l/min
Air flow	5.0 l/min
Burner height	10 mm

**1: Standard stock solution of 1000 ppm:** 3.735g of  $K_2CrO_4$  was dissolved in de-ionized water and diluted to one liter with de-ionized water.

**2. Standard stock solution of 100 ppm:** 10ml of 1000ppm standard stock solution was taken in 100 ml volumetric flask and was made to the mark with de-ionized water.

**3. Working standards:** 0.5, 1, 2, 4 and 8 ppm of working standards

were prepared by taking 0.5, 1, 2, 4 and 8 ml from the standard stock solution of 100 ppm in a 100ml volumetric flask and was made to the mark with de-ionized water.

**Procedure:** The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Cr cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspirated into the flame and the Cr concentration of each sample was noted. The Cr contents in ppm were calculated.

### **Determination of Cobalt (Co)**

**Instrument:** Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

#### **Instrument conditions:**

Mode	Absorption
Wave length	240.7 nm

Slit width	0.4 nm
Fuel flow	1.2 l/min
Air flow	5 l/min
Burner height	10 mm

**1: Standard stock solution of 1000 ppm:** 1.0 g of cobalt metal was dissolved in 30 ml of (1:1) HCl and was diluted to one liter with de-ionized water.

**2. Standard stock solution of 100 ppm:** 10ml of 1000 ppm stock solution was taken in 100 ml volumetric flask and was made to the mark with de-ionized water.

**3. Working standards:** 0.5, 1, 2, 4 and 8 ppm of working standards were prepared by taking 0.5, 1, 2, 4 and 8 ml from 100 ppm standard stock solution in a series of 100 ml volumetric flasks and made to the mark with de-ionized water.

**Procedure:** The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Co cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspirated into the flame

and the Co concentration of each sample was noted. The Co contents in ppm were calculated.

### **Determination of total iron (Fe)**

**Instrument:** Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

#### **Instrumental conditions**

Mode	Absorption
Wavelength	248.3 nm
Slit width	0.2 nm
Air flow	5litre/minute
Fuel flow	1litre/minute
Burner height	10 mm

**1. Stock solution of 1000 ppm for Fe:** 1 gram of pure iron metal was dissolved in minimum amount of HCl and was made to the volume with de-ionized water in one litre volumetric flask.

**2. Stock solution of 100 ppm:** 10 ml from 1000 ppm stock solution was taken in 100 ml volumetric flask and made to the mark with de-ionized water.

**3: Working standard solutions:** 1, 2, 4 and 8 ppm working standard solutions were prepared by taking 1, 2, 4 and 8 ml from the 100 ppm stock standard solution in a 100 ml volumetric flask and made to the volume with de-ionized water.

**Procedure:** The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Fe cathode lamp was turned ON and let it to warm up for 10

minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspirated into the flame and the Fe concentration of each sample was noted. The Fe contents in ppm were calculated.

### **Determination of Manganese (Mn)**

**Instrument:** Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

#### **Instrument conditions:**

Mode	Absorption
Wave length	279.5nm
Slit width	0.2nm
Fuel flow	1 l/min
Air flow	5 l/min
Burner height	10mm

**1:Stock solution of 1000 ppm for Mn:** 4.058g of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  was dissolved in 20 ml of 1N  $\text{H}_2\text{SO}_4$ . It was then transferred to 1000 ml volumetric flask and was made up to the mark with de-ionized water.

**2: Stock solution of 100 ppm:** 10 ml of 1000 ppm stock solution was taken in 100ml volumetric flask and was made up to the volume with de-ionized water.

**3: Working standards:** 1, 2, 4 and 8 ppm working standards of Mn were prepared by taking 1, 2, 4 and 8 ml of 100 ppm stock solution in a 100ml volumetric flask and was made to volume with de-ionized water.

**Procedure:** The atomic absorption spectrophotometer was set according to the above-mentioned conditions. Mn cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspirated into the flame and the Mn concentration of each sample was noted. The Mn contents in ppm were calculated.

### **Determination of Cadmium (Cd)**

**Instrument:** Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

### **Instrument conditions**

Mode	Absorption
Wavelength	228.8 nm
Slit width	0.7 nm

Tube/site	Pyro/Platform
Matrix modifier	0.2 mg $\text{NH}_4\text{H}_2\text{PO}_4$
Pretreatment T °C	700
Atomization T °C	1600

**1. Standard stock solution of 1000 ppm:** 1 g of copper metal was dissolved in 30 ml of (1:1) HCl and was made to the volume of one liter with de-ionized water.

**2. Stock solution of 1 ppm:** 0.1 ml from 1000 ppm stock solution was taken in 100 ml volumetric flask and made to the mark with de-ionized water.

**3. Working standard solutions:** 25, 50, 100 and 200 ppm working standard solutions were prepared by taking 2.5, 5, 10 and 20 from the 1 ppm stock standard solution in a 100 ml volumetric flask and made to the volume with de-ionized water.

**Procedure:** The graphite furnace was set according to the above-mentioned conditions. Cd cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp, the instrument was calibrated and standardized with working standards of 0.5-8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution-B of the certified standards was run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards are within the confidence limit, the sample stock solutions-B were then aspirated into graphite tube and the Cd concentration of each sample was noted. The Cd contents in ppm were calculated.

## ANALYSIS OF LIGHT ELEMENTS

### Determination of Calcium (Ca) and Magnesium (Mg)

**Instrument:** Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

#### Instrument conditions:

Element	Ca	Mg
Mode	Absorption	Absorption
Wavelength	422 nm	285.2nm
slit width	0.4nm	0.4nm
Air flow	5l/min	5 l/min
Fuel flow	5 l/min	To best flame
Burner height	10mm	10mm

**1. Stock solution of 1000 ppm for Ca & Mg:** 2.497g  $\text{CaCO}_3$  and 3.057g  $\text{MgCO}_3$  were dissolved in 1N HCl and was diluted to one liter with de-ionized water in a 1000 ml volumetric flask.

**2: Stock solution of 100 ppm for Ca & Mg:** 10 ml of 1000 PPM stock solution was taken in 100 ml volumetric flask and was made up to the mark with de-ionized water.

**3: Lanthanum 5% Solution:** 58.64g of  $\text{La}_2\text{O}_3$  was dissolved in 200 ml de-ionized water to which 150 ml 60 %  $\text{HClO}_4$  was added. It was heated until complete dissolution. The solution was then filtered through ordinary filter paper into 1000 ml volumetric flask and the volume was made up to the mark with de-ionized water.

**4. Working Standards:** 1, 2, 4 and 8 ppm of working standards for Ca and Mg were prepared by taking 0.5, 1, 2 and 4 ml of 100 ppm stock solution in a series of 50 ml volumetric flasks. To these flasks 10 ml lanthanum solution was added and the volume was made up to the mark with deionized water.

**5. Dilution of Samples:** 5 ml (depending upon the expected concentration of Ca & Mg) of the stock solution-A and B the studied coal samples and the certified rock standards respectively were taken in a series of 50 ml volumetric flasks. 10 ml of lanthanum solution was added to each flask and the volume was made to the mark.

**Procedure:** Atomic absorption spectrophotometer was set according to the above-mentioned conditions for Ca and Mg separately. The cathode lamp for both Ca and Mg were turn ON to warm up for at least 10 minutes. The instrument was then calibrated and standardized with the working standards of 1 to 4 ppm. All the working standards were run as unknown and their actual concentration was verified. For further accuracy the certified rock standards were run as unknown and the results were compared. After making sure that the results of the certified standards were within the confidence limit, the diluted stock solution containing lanthanum oxide were run on the atomic absorption and the concentrations of Ca and Mg in ppm were noted for each sample.

#### **Determination of Sodium (Na) and Potassium (K)**

**Instrument:** Perkin Elmer 3300 Atomic Absorption Spectrophotometer equipped with graphite furnace

#### **Instrument Conditions:**

Element	Na	K
Mode	Emission	Emission
Wavelength	589 nm	766 nm

Slit width	0.2 nm	0.4 nm
Air flow	5 l/min	5 l/min
Fuel flow	1 l/min	1 l/min
Burner height	20 mm	20 mm

**1. Stock solution of 1000 ppm for Na & K:** 3.087 g moisture free  $\text{Na}_2\text{SO}_4$  and 2.228g moisture free  $\text{K}_2\text{SO}_4$  were dissolved in de-ionized water and the volume was made to 1000 ml in a volumetric flask. The solution was stored in a polythene bottle.

**2. Stock solution of 100 ppm Na & K:** 10 ml of 1000 ppm stock solution was taken in a 100 ml flask and diluted to mark with de-ionized water.

**3. Working Standards:** 1, 2, 4 and 8 ppm working standards were prepared by taking 1, 2, 4, and 8 ml from 100 ppm stock solution in 100 ml volumetric flasks and was diluted up to the mark with de-ionized water.

**4. Diluted samples:** All the samples as well as certified rock standards were diluted to 20 times.

**Procedure:** The atomic absorption spectrophotometer was set according to the above-mentioned instrumental conditions in order to get the maximum absorbance. The instrument was set on emission mode and a conical burner head was used. In this case no cathode lamp was required. The instrument was calibrated and standardized by working standards of 1 to 8 ppm and then the working standards were also run as unknown in order to verify the standardization of the instrument. The diluted certified rock standards were then run and the results were compared to know the accuracy of the method. The diluted solutions of coal samples were sprayed one by one through the flame and the concentration of Na and K was noted in ppm each sample.

## PROXIMATE ANALYSIS OF COAL

The simultaneous determination of carbon, hydrogen, nitrogen and sulfur contents (in percent) in the samples of Sindh coalfields was made by the EurVector Elemental Analyzer in the Geochemistry Laboratory of the National Center of Excellence in Geology, University of Peshawar by the following procedure:

**Sample preparation:** The coal sample was ground to –60 mesh size and dried in the oven at 110°C for at least two hours. After cooling the sample in the desiccators, about 0.5-1.00 mg sample of coal was taken in the tin cap (provided with the machine) and wrap it in to a rounded capsule and then put it in the auto-sampler. This procedure was done for all the coal samples, a blank and a standard (L-Cystine) before running these samples on the machine.

**Instrumental conditions:** The instrument was turned ON and waited for the furnace to heat up to 1020°C. Then the required information of the samples and standards were entered through the software. The samples were run by the machine under the following standardizing conditions:

Carrier flow:	80 Kpa
Purge flow:	80 ml / min
Oxygen:	20 ml
PO <sub>2</sub> :	35 Kpa
Oxidation time:	8.7 Sec
Sampling delay time:	10 Sec

Run time:	500 Sec
Furnace T:	1020°C
GC-Oven T:	115°C

The machine started analyzing the samples simultaneously by taking these samples one by one from the auto-sampler. At the end, the simultaneous results of carbon, hydrogen, nitrogen and sulfur were obtained for the blank, standard and samples. The standards results were within 95% confidence limit of the certified values.

## ULTIMATE ANALYSIS OF COAL

The determination of Fixed carbon, Moisture, Volatile matter and Ash contents (in percent) in the samples of Sindh coalfields was made by the muffle furnace in the Geochemistry Laboratory of the National Center of Excellence in Geology, University of Peshawar by the following procedure:

**A) Moisture:** The coal sample was ground to –60 mesh size and a known weight (3g) of coal was taken in pre weighted crucible and placed in oven for one hour at 105°C. Moisture was calculated as follows:

Weight of moisture (X) = Wt. of crucible containing coal after heating – Wt. of crucible containing coal before heating .

X = Wt. of moisture

Y = Wt. of coal

3g coal contain moisture = x

$$100g = \frac{100x X}{3}$$

### B) Volatile matter:

The coal sample was ground to -60 mesh size and a 1 g of coal was taken in pre weighted crucible and the crucible was covered tightly. Then crucible was placed in furnace at 750°C for 5-7 minutes. It was cooled in desiccator, the lid of crucible was removed and weighed and calculated as follows:

$$\text{Volatile matter: } \frac{\text{Wt. of crucible containing coal before heating} - \text{Wt. of crucible containing coal after heating}}{\text{Weight of sample}}$$

% Volatile matter: 1gm coal contain = X Volatile matter

$$100\text{gm contain} = \frac{100 \times X}{1 \text{ gm}}$$

### C) Ash

The coal sample was ground to -60 mesh size and a 1 g of pulverized coal was taken in pre weighted crucible and placed in furnace at 750°C for 24 hours until the carbon contents completely diminishes. The crucible was cooled in desiccator, and calculated as follows:

$$\text{Ash: } \frac{\text{Wt. of crucible containing coal before heating} - \text{Wt. of crucible containing coal after heating}}{\text{Weight of sample}}$$

% Ash 1gm coal contain = X Ash

$$100\text{gm contain} = \frac{100 \times X}{1 \text{ gm}}$$

**Fixed Carbon** = 100 - (% of moisture + % of volatile matter + % of Ash)

## LEACHING OF COAL SAMPLES

The sequential leaching procedure as described by Finkelman et al. (1990) and Palmer et al. (2000) was used during this study. One representative coal sample of Sindh coal feed was prepared by mixing of 50 grams, pulverized – 60 mesh, each of the Thar coal, Soda coal and Meting –Jhampir coal. Duplicate 100 gram samples of this coal were combined with different solutions and agitated for 18 hours separately. The solutions were then centrifuged and the leachates were separated by filtration. The samples were first leached with 1N ammonium acetate ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ). The procedure was repeated in subsequent leaching steps using 3N Hydrochloric acid (HCl), concentrated hydrofluoric acid (HF) and 2N nitric acid ( $\text{HNO}_3$ ). These leachates were then used for the determination of heavy and trace elements by the Perkin Elmer Atomic Absorption Spectrometric technique under the standardizing conditions of each element as already discussed.

## ANALYSIS ON X-RAY DIFRACTOMETER

The X-ray diffractometer (XRD) analyses of few coal samples from Thar, Sonda and Meting Jhampir coalfields were carried out on the Rigaku XRD, calibrated with Cu (K-alpha) radiations generated at a tube voltage of 40Kv and tube current of 25mA. D spacing value was 2 $\theta$  count per second. The X-ray Diffraction patterns of the 2 $\theta$  verses intensity for an angular range of 2-37 $^\circ$  2 $\theta$  were obtained. The JCPDS Mineral Powder Diffraction File (1980) was used for interpreting the diffractograms by the Hanawalt methods of qualitative analysis.

## **ANALYSIS ON X-RAY FLUORESCENCE SPECTROMETER (XRF)**

To determine As, Sb and U in the coal samples, the S4- PIONEER X-ray spectrometer was used. This is a PC-based unit and controlled through a computer program, known as S4 tools. This is a standardless software and analyzes almost all the elements of the periodic table except some light elements, inert gases and some rare earth elements. The collected representative samples of the coal was analyzed for As, Sb and Uranium.