CHAPTER 3

Description of Study Area and Experimental Details

This chapter provides a brief introduction of the study area. It also presents the methodologies adopted for sampling and pre–treatment of collected samples on filter papers and instrumental procedures for the analysis of elements in particulate matter. This chapter also describes the outlines the collection of primary and secondary data during the field work. The details of sampling methods and analyses of different air pollutants followed by air quality index and national ambient air quality standards constitute an integral part of this chapter for the fulfillment of the objectives of the research. The summary of the statistical methods employed in this study area is depicted in this chapter also.

3.1 General

Particulate Matter, which consisted of particles less than 10 microns and inhalable suspended particulate matter (ISPM), which includes particles of less than 2.5 microns, has emerged as the most critical among all the criteria for air pollutants. These particulate matters are originating from many natural and anthropogenic activities. The major contributors of particulate matters to air pollution are industrial activities, mining activities, vehicular movement, wind dust, household fuel used for cooking and heating, burning of waste, resuspended road dust, construction activities, agricultural activity, naturally occurring dust and trans–boundary migration of dust from other regions. It is necessary to

monitor the air particulate periodically to determine the extent of pollutants and identify emission sources to control air pollution.

The sampling of particulate matter in the ambient atmospheric aerosol was a plan and executed systematically at the Singrauli Coalfield complex in Singrauli and Sonbhadra Districts of Madhya Pradesh and Uttar Pradesh. The collected particulate matter analysis in the ambient atmospheric aerosol was a plan and executed consistently at Health Physics Division, Bhabha Atomic Research Centre, Mumbai. The whole process includes the criteria for selecting sampling locations, methods of sampling, sample dissolution, analysis for metals, and the techniques used for the analyses.

3.2 Description of the study area

The selected study area consisted of highly mechanized opencast coal mines and coal–based thermal power plants located in the Singrauli Coalfield industrial complex. This area is one of the largest individual clusters, mainly having coal mining and thermal power plants.

The Singrauli Coalfield is divided into two basins, namely the Main basin and Moher sub–basin. Moher sub–basin having an area of 312 Km^2. Out of which 80 Km^2 on the Eastern side lies in Sonebhadra District of Uttar Pradesh and rests in the Singrauli district of Madhya Pradesh. The Main basin has located west of Waidhan. The Moher sub–basin is the center of mining activities. The Singrauli Coalfield area's industrial activities were started in the seventies and during the first decade of the current century. This area has grown gradually and now is an important industrial hub of India.

The Singrauli coalfield is located between latitudes 23˚47' and 24˚12'N and longitudes 81˚48' and 82˚52' E and extends over an area of 2200 square kilometers. The only moher sub–basin area is selected for detailed study. For this study, the sampling stations are

installed in Singrauli Coalfield and nearby areas. The site location map is shown in **Fig. 3.1.** Besides mining within the study area, other activities, such as coal transportation from surrounding opencast mining areas, power generation commercial businesses, and domestic use of coal. All these activities damage the air quality of the region. Accordingly, it was deemed essential to emphasize air quality monitoring measures that could minimize ecological damage to the area.

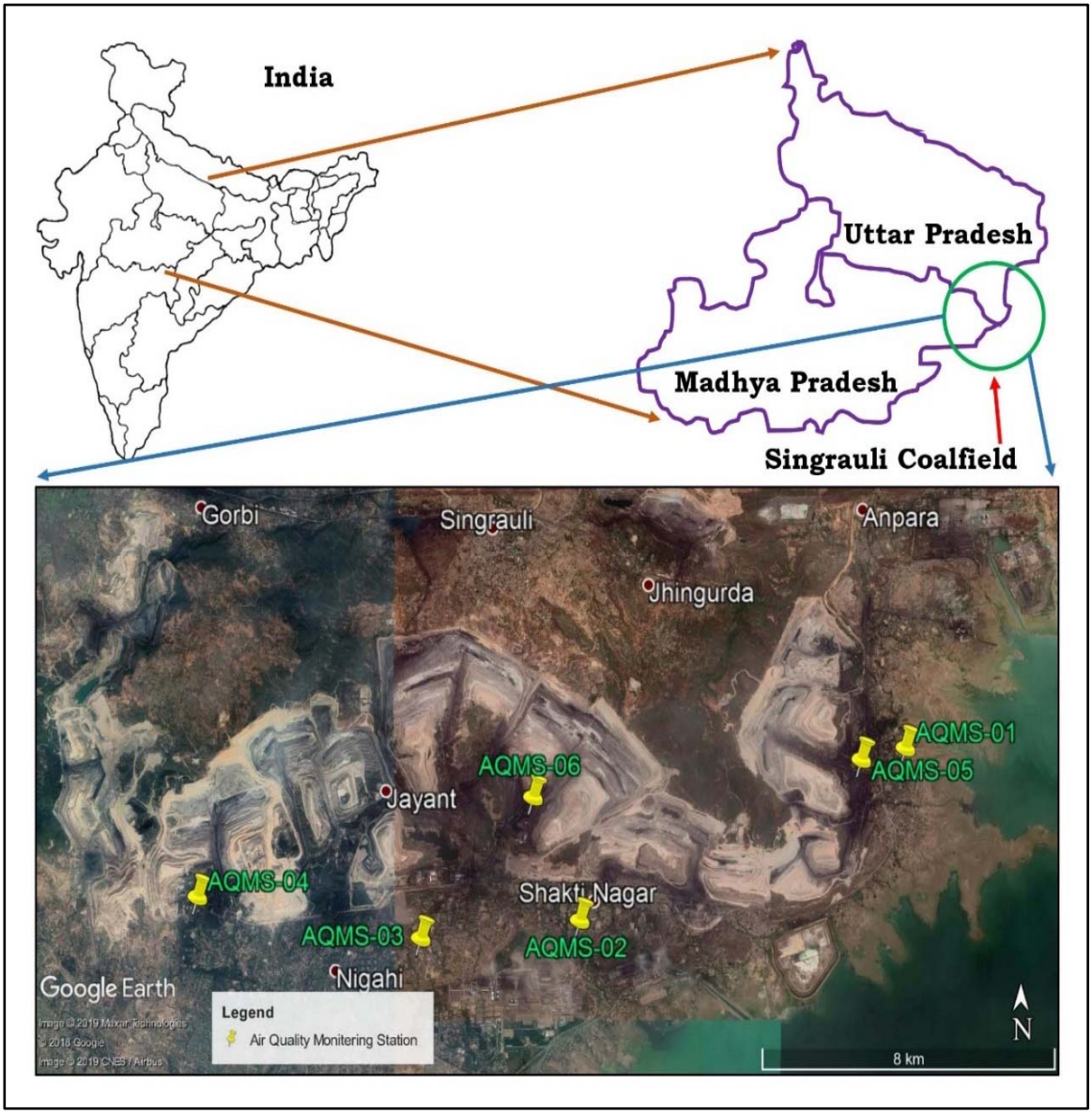


Fig. 3.1: Location map of air quality monitoring station at Singrauli coalfield (Image © 2019 CNES/Airbus, Image © 2019 Maxar Technologies, © 2018 Google)

3.3 Selection of air quality monitoring station

The primary criteria for selecting sampling sites are that each sampling location should represent the study area. The selection of sampling stations mainly depends on sampling, particulate matter sampling, instruments, sources of particulate matter, and resources available. During the selection of sampling stations, care has been taken and the samplers were located at places where there was no interferences and it was away from the primary pollution sources.

The distance between the sampling station and sampler depends on the sources, the height of emission. The sampling sites were also away from the dust absorbing bodies. As the sampling is meant for a long time, the location should be selected so that it should be exposed to remain a representative site over a long time, and there is no land–use changes and construction in nearby future. The instrument has been located in such a place where free airflow was available.

The sampling intake was at 1 m above the ground to prevent re-entrainment of particulate matter from any obstacles. The sampler was kept at a distance of 200 m from the unpaved road. The number of sampling stations generally depends on the area's size, the variability of pollutant concentration over the study area, the objective of monitoring, pollutant type to be monitored, and the area's population. In this study, six sampling stations were selected for the selected highly mechanized opencast and thermal power plants in the Singrauli coalfield. All the chosen stations were chosen to cover up the total industrial and residential area of Singrauli coalfield. The particular consideration was taken on the wind direction, wind speed, electricity supply, and instruments' security during the monitoring stations' selection. Stations were selected by considering meteorology of the area and source of particulate matter generation. Generally, the sampler was kept at the height of above 1 to 15 m (depending on the suitability at the sampling is location) from the ground level and

sufficiently away from the disturbance or direct obstacle from the source under consideration.

Hence, the following points were considered while selecting the sampling locations:

1) The location of the area should be representative of the region of interest
2) Different types of sources should potentially impact the site
3) It should not be located very near to the source, and
4) Easy accessibility and safety of the instrument.

The present research focused on the distribution of $PM_{2.5}$, PM_{10}, SPM, NO_2, and SO_2 and their temporal and seasonal variation, and ions and radioactive content in particulate matter of the respective area.

3.4 Methodology used for particulate matters along with NO_2 and SO_2 sampling

The human respiratory system is capable of arresting particle sizes of more than 10μm. So in recent times, the importance of monitoring a particular matter shifted to the range of PM_{10} and $PM_{2.5}$ as per NAAQS **[101]**. In this study area, particulate matters (SPM, PM_{10}, and $PM_{2.5}$) along with NO_2 and SO_2 are affecting the health of mining and associated professionals and adjoining population. Particulate matters (PMs) decrease the performance of mine professionals, a life of machinery. The suspended particulate matter decreases the visibility and nuisance in mine and affects vegetation's growth & its effect on the mining operations.

The analysis of trace metal concentration in particulate matter requires either an ultra–sensitive technique of measurement or collection of a very large volume of the sample so

that some processes may concentrate them before the actual measurement. Several factors like total mass, size distribution, and chemical composition influence selecting a sampling method. The overall objectives require a balance between sampling and analytical methods. Atmospheric elements like lead, cadmium, zinc, and copper are mostly present in particulate matter, covering various particle sizes. Due to these metals' lower atmospheric concentrations, an efficient filter paper is needed to collect particulate matter. The selection of filters for air particulates collection must consider the collection efficiency and interferences from metals present in the filter medium and its non–hygroscopic nature.

Different types of filter papers such as cellulose acetate, glass fiber, polystyrene, membrane, and polytetrafluoroethylene (PTFE) are commercially available. Cellulose filters like Whatman41 have been frequently used due to their lower collection efficiency. Glass fiber filters have been widely used, but the limitations of this filter paper are higher metallic content and toxic components, which introduce higher blank values the analysis. However, the glass fiber filter paper is used for PM_{10}, and SPM sampling and, PTFE filter paper is used for $PM_{2.5}$ sampling as its collection efficiencies are high. Ambient Fine Dust Sampler (Instrumex IPM–FDS 2.5µ/10µ; respirable dust sampler (APM 460 NL) and fine particulate sampler (APM550)) for PM_{10} and $PM_{2.5}$ (Instrumex, Mumbai, India; Envirotech Instruments Private Limited, New Delhi, India) and high volume sampler (ENVIROTECH APM 43–411) for suspended particulate matter (Envirotech Instruments Private Limited, New Delhi, India), and the flow rates of which are 16.67×10^{-3} for Instrumex IPM–FDS 2.5µ/10µ and fine particulate sampler and 1 $m^3\ min^{-1}$ for APM 460 NL and APM 43–411, respectively. The NO_2 and SO_2 were collected through ENVIROTRACK (Instrumex, Mumbai, India) with a flow rate of 0.012 $m^3\ h^{-1}$ for twenty–four hours. However, there is a temporary air sampling monitoring station for regular air sampling during the study period also.

The sampling was carried out for 24 hours, simultaneously for SPM, PM_{10}, and $PM_{2.5}$ along with NO_2 and SO_2 of two consecutive years (January 2016 to December 2017). The whole year has been divided into three seasons, i.e., winter, summer, and rainy seasons to study the seasonal variation of the particular matter concentration, if any, different study area locations. The details of the monitoring station with geographical location and characters are present in **Table 3.1**.

The sampling substrate used was 25.4×20.3 cm^{-2} glass fiber filters (Whatman EPM2000, Sigma–Aldrich, Bangalore, India), and circle diameter 47 mm glass microfiber filter (Whatman GF/A, Sigma–Aldrich, Bangalore, India) due to its high efficiency for SPM and PM_{10}, respectively. The circle diameter of 47 mm of polytetrafluoroethylene filter paper was used (Whatman PTFE, Sigma–Aldrich, Bangalore, India) due to its high efficiency for $PM_{2.5}$. The weighed filter papers were desiccated for moisture removal at controlled temperatures (20 ± 1°C) for at least 24 h, and it was taken away to the field for sampling in closed envelopes to avoid contamination. After sampling, the filter papers were again desiccated, then weighed with Sartorius CP225D microbalance (Sartorius CP225D microbalance, Data Weighting Systems, Inc. Elk Grove, IL) with a resolution of 10^{-5} g for SPM and MYA 5.3Y microbalance (MYA 5.3Y microbalance, LCGC–RADWAG Weighing Solutions Private Limited, Hyderabad) with a resolution of 10^{-6} g for PM_{10}.

Concentrations of SPM and PM_{10} have calculated using the mass of particulates collected on the filter paper and the volume of air sampled in glass impingers filled with high volume air sampler. After weighing, the filter papers were stored in desiccators for further chemical analysis. All the samples were then brought back to the Radiological Analytical Laboratory, Health Physic Division, Bhabha Atomic Centre, Mumbai, for further processing and analysis.

Table 3.1: Detail description of sampling locations

Sl. No.	Station Code	Location	Geographic Location	Domination Activity
1	AQMS–01	Bina industrial cum–residential area	24º09′00.20″N 82º46′30.45″E	This location is mainly exposed by traffic–related emissions, coal, and biomass burning.
2	AQMS–02	NTPC Shaktinagar industrial cum–residential area	24º06′45.56″N 82º41′16.81″E	
3	AQMS–03	Dudhichua industrial cum–residential areas	24º06′31.65″N 82º38′43.76″E	
4	AQMS–04	Amlohri Residential area	24º07′03.90″N 82º35′08.73″E	
5	AQMS–05	Bina opencast mining area	24º08′51.15″N 82º45′47.99″E	This location is mainly exposed by mining activity and vehicular movement
6	AQMS–06	Dudhichua opencast mining area	24º08′21.87″N 82º40′31.95″E	

3.4.1 Monitoring and collection of air pollutants

The particulate matters ($PM_{2.5}$, PM_{10}, and SPM) were monitored and collected on filter paper using Instrumex IPM–FDS, APM550, APM 460NL, and APM 43–411, respectively, (**Figs. 3.2a–d)**. The glass fiber filter paper (EPM 2000) with very low elements blanks and size 20 x 25 cm was used for particulate matter collection **(Fig. 3.3)**. The PTFE (polytetrafluoroethylene) filter paper, of size 47 mm diameter used for $PM_{2.5}$ collection **(Fig. 3.4)**. The particulate matters of different size samples were collected (~800 samples for $PM_{2.5}$, PM_{10}, SPM each) on the PTFE (polytetrafluoroethylene) and glass fiber filter papers. The flow rate of samplers was 16.67 l min^{-1} and 1000 l min^{-1}, and it's operating continuously for twenty–four hours during the period of two consecutive years (January 2016 – December 2017). The collected particulate matter samples were desiccating for twenty–four hours before weighing the samples **(Fig 3.5)**. The gaseous pollutants (NO_2 and SO_2) samples are collected through ENVIROTRACK (Instrumex, Mumbai, India). The total volume of air filtered was calculated using the airflow rate and the time of sampling. The nitrogen dioxide from ambient air was absorbed in a sodium hydroxide solution and sodium arsenite in one of the impingers attached to the air sampler by drawing the ambient

air at a fluctuating flow rate predetermined time. The NO_2 reacts with sodium hydroxide to form $NaNO_2$ in the presence of sodium arsenite. This compound is resistant to oxidation by atmospheric oxygen or Ozone. Hence, the sampled solution in which $NaNO_2$ can be stored for some time (15–20 minutes) before analysis. This step is necessary for the removal of the Ozone absorbed in the solution during the sampling.

After this period, the impinger solution is made to react with the following two chemicals:

1) Sulphanilamide
2) NEDA (N–(1–naphthyl)–ethylenediamine dihydrochloride)

With this addition, intensely colored complexes formed. The absorbance of these colored complexes is measured by the spectrophotometer viz. ENVIROTRACK and related to the concentration of NO_2 in ambient air.

Sulphur dioxide from ambient air is also absorbed in a solution of sodium tetrachloromercurate (STM) in one of the impingers attached with the air sampler by drawing the ambient air at a fluctuating flow rate and for a predetermined time. The SO_2 reacts with STM to form a dichlorosulphitomercurate complex. This complex is resistant to oxidation by atmospheric oxygen or Ozone. Hence, the sampled solution with the above sulphur complex has been stored for some time (15–20 minutes) before analysis. After this period, the impinger solution was allowed to react with pararosaniline and formaldehyde to form an intensely colored pararosaniline methyl sulphonic acid. The absorbance of this colored complex, thus formed, is measured by the spectrophotometer and related to the concentration SO_2 in ambient air. Calibrate the equipment and draw standard graphs for knowing the concentration of SO_2 in the sample.

The $PM_{2.5}$ air sampler comprises an Omni–directional air inlet, impactor for particles larger than 10 µm and a $PM_{2.5}$ impactor by a tube's length. The air inlet has a circular symmetry

so that air entry is unaffected by wind direction and is designated to keep out rain, insects, and very–large particles. The inlet section immediately leads to an impactor stage designed to trap particles with an aerodynamic diameter larger than 10 microns. Thus the airstream in the down tube consists of only medium and fine particulates. The down tube's streamlined airflow is accelerated through the nozzle of the well-shaped impactor designed to trap medium-sized particulates with an aerodynamic diameter between 2.5 and 10 microns. To avoid sampling errors due to small particles' tendency to bounce off the impaction surface, a 37mm diameter GF/A paper immersed in silicone oil is used as an impaction surface.

The air stream leaving the WINS impactor consists of only fine particulates with an aerodynamic diameter smaller than 2.5 microns. These fine particles are collected on a PTFE membrane filter of 47mm diameter. The air inlet section and impactor stages used in the Envirotech APM550 Fine Particle sampler and Instrumex IPM–FDS 2.5µ/10µ carefully follow US EPA specifications. The impactor system is designed to operate at an air–flow rate of 1 $m^3\ hr^{-1}$ or 16.7 LPM. The EPA has recommended that this sampling rate be held constant within +/– 5% by using a suitable flow control device. The APM 550 and IPM–FDS 2.5µ/10µ system uses an oil–less rotary pump to produce the suction pressure and a critical flow control orifice for maintaining a constant sampling rate. Therefore, the flow control objective is achieved in the APM 550 and IPM–FDS 2.5µ/10µ with minimum moving parts, and as such, the system requires very little field maintenance. The pump is driven by a brushless induction motor capable of withstanding large voltage fluctuations prevalent in the mains power supply at many places.

a) Respirable dust sampler (APM 460NL)

b) Fine particulate sampler (APM 550)

c) Respirable dust sampler APM 460–411 NL dust samplers

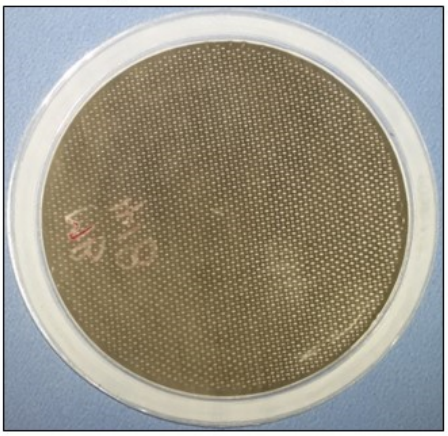
d) Ambient fine dust sampler (Model Instrument IPM–FDS 2.5/10µ)

Fig. 3.2: Samplers used for collecting particulate matter

a) Before sampling b) After sampling

Fig. 3.3: EPM 2000 filter paper before and after collection of particulate matter

a) Before sampling



b) After sampling

Fig. 3.4: PTFE filter paper of $PM_{2.5}$

Fig. 3.5: Desiccator

A thermal cut–out has also been incorporated to protect the motor from burnout. As some of the $PM_{2.5}$ particles are known to be volatile, it has been stipulated that the filter temperature will not exceed the surrounding temperature by more than 5ºC. Envirotech has ensured this requirement by placing all heat–dissipating components such as the pump assembly in a separate cabinet. The main instrument cabinet has also been painted white to minimize the absorption of heat from incoming insolation. A dry gas–meter has been provided to measure and totalize the air volume sampled by the system at actual ambient temperature and pressure.

The mass concentration of fine particles ($PM_{2.5}$) in ambient air is computed as the total mass of collected particles (after the WINS impactor) divided by fine the volume of air sampled and is expressed in micrograms per cubic meter of air. The air sampler comprises an air inlet subsystem, cyclone separator for particles larger than 10µm, suction subsystem, a filter assembly, and the associated instrumentation and control subsystem.

The air inlet has a circular symmetry so that air entry is unaffected by wind direction and is designated to keep out rain, insects, and very–large particles The inlet section immediately leads to a cyclone separator designed to trap particles with an aerodynamic diameter larger than 10 microns. The particles smaller than 10µm are passed through the glass microfiber filter paper.

The suction subsystem acts as the prime mover of the air to be sampled. The sampled air is sucked through a filter paper, which does not permit particles above a given size to pass through. These particles get collected on the filter paper. The suction system and allied instrumentation control the flow rate and the period of sampling.

The APM 460NL is designed to operate at an airflow speed of 1 $m^3\ min^{-1}$ with a maximum sampling time of 28 hours. The EPA has recommended that this sampling rate be held constant within +/– 5% by using a suitable flow control device. This uses an imported

brushless, continuous rated induction motor driven blower to significantly reduce equipment downtime, maintenance efforts, and inconvenience to the community. This instrument has substantially lower noise as compared to almost all other dust monitoring samplers. The blower of APM 460 NL has an inbuilt thermal cut off. Hence there is no need for an external voltage stabilizer to compensate for voltage fluctuations.

The high–volume sampler (APM 430–411) is a primary instrument used primarily for measuring the concentration of suspended particulate matter in atmospheric air. By definition, suspended particulates are too small to have a considerable falling velocity and are likely to remain in the atmosphere for significant periods. These particulates usually range from 1 micron to approximately 100 microns in size and may be caused by various processes such as incomplete combustion of solid, liquid, or gaseous fuels, wastes from metallurgical, chemical and refining operations, incineration, etc. Moreover, natural sources also contribute to suspended materials like spores, saltwater spray, and pollens.

High Volume Sampling is an internationally accepted standard technique for monitoring the concentration of suspended particulates. A large volume (1500 cubic meters) of atmospheric air is passed through a suitable filter medium over up to 24 hours in these systems. Thus, they will yield measurable dust samples in areas with dust levels as low as one microgram per cubic meter of air. However, where dust concentrations are high, shorter sampling times may suffice.

3.5 Calculation of major air pollutant concentration

The gravimetric measurement of filter paper was performed with a microbalance in humidity and temperature–controlled environment. The sensitivity and reliability of the electro–balance was about 1 µg. The weight difference of the filter paper before and after sampling was used to calculate particulate matter concentration. The calculation of particulate matters and gaseous pollutants were monitored and collected samples through different samplers with a gravimetric method as done by the equation as given below:

a) Sample collected by fine particulate matter sampler (APM–550 and IPM–FDS 2.5µ/10µ)
b) Sample collected by RDS (APM–460NL)
c) Sample collected by ENVIROTECH APM 460–411
d) Calculation of NO_2 concentration in air by ENVIROTRACK
e) Calculation of SO_2 concentration in air by ENVIROTRACK

a) Sample collected by fine particulate matter sample (APM–550 and IPM–FDS 2.5µ/10µ)

$$PM_{2.5} = \frac{W_{2.5}}{V_{2.5}} \qquad ------ 3.1$$

where,

$PM_{2.5}$ = mass concentration of $PM_{2.5}$ particulates (µg m^{-3})

$W_{2.5}$ = total mass of the $PM_{2.5}$ collected (µg)

$V_{2.5}$ = Total volume of air sampled for $PM_{2.5}$ sampling (m^3)

The total mass of $PM_{2.5}$ is the difference between the initial and final weight of filter paper.

b) Sample collected by RDS (APM–460NL)

$$W_{10}\ (\mu g)\ = (W_f - W_i)\ mg \times 10^3\ \mu g \qquad ------3.2$$

where,

W_{10} = total mass of the PM_{10} collected (µg)

W_f = Final mass of the conditioned EPM2000 filter after sample collection (mg)

W_i = Initial mass of the conditioned EPM2000 filter before sample collection (mg)

10^3 = unit conversion factor for milligrams (mg) to micrograms (µg)

After the calculation of the total mass of PM_{10}, the calculation of the total volume of air sampled as follows:

$$V_{10} = Q_{avg} \times t \times 10^{-3}\ m^3 \qquad ------3.3$$

where,

V_{10} = Total volume of air sampled for PM_{10} sampling

Q_{avg} = Average flow rate over the entire duration of the sampling period (l min^{-1})

t = duration of the sampling period (min)

10^3 = unit conversion factor for liters (l) into cubic meters (m^3)

The concentration of PM_{10} in the air –

$$PM_{10} = \frac{W_{10}}{V_{10}} \qquad ------3.4$$

where,

PM_{10} = Mass concentration of PM_{10} (µg m^{-3})

W_{10} = Total mass of the PM_{10} collected (µg)

V_{10} = Total volume of air sampled for PM_{10} sampling (m^{-3})

c) Sample collected by ENVIROTECH APM 460–411

$$W_{SPM}\ (\mu g)\ = (W_f - W_i)\ mg \times 10^3\ \mu g \qquad ------ 3.5$$

where,

W_{SPM} = total mass of the suspended particulate matter collected (µg)

W_f = Final mass of the conditioned EPM2000 filter after sample collection (mg)

W_i = Initial mass of the conditioned EPM2000 filter before sample collection (mg)

10^3 = unit conversion factor for milligrams (mg) to micrograms (µg)

After the calculation of the total mass of SPM, the calculation of the total volume of air sampled as follows:

$$V_{SPM} = Q_{avg} \times t \times 10^{-3}\ m^3 \qquad ------ 3.6$$

where,

V_{SPM} = Total volume of air sampled for SPM sampling

Q_{avg} = Average flow rate over the entire duration of the sampling period (l min^{-1})

t = duration of the sampling period (min)

10^3 = unit conversion factor for liters (l) into cubic meters (m^3)

The concentration of SPM in the air –

$$SPM = \frac{W_{SPM}}{V_{SPM}} \qquad ------ 3.7$$

where,

SPM = Mass concentration of SPM (µg m^{-3})

W_{SPM} = Total mass of the SPM collected (µg)

V_{SPM} = Total volume of air sampled for SPM sampling

d) Calculation of NO_2 concentration in air by ENVIROTRACK

The concentration of NO_2 was calculated using the given below equation

$$C\ (NO_2, \mu g\ m^{-3}) = (A_s - A_b) \times CF \times \frac{V_s}{V_a} \times V_t \times 0.82 \qquad ------3.8$$

where,

C (NO_2, µg m^{-3}) = Concentration of nitrogen dioxide (µg m^{-3})

A_s = Absorbance of sample

A_b = Absorbance of reagent blank

CF = Calibration factor

V_s = Volume of air sampled (m^3)

V_a = Volume of the sample (ml)

V_t = Volume of aliquot taken for analysis (ml)

0.82 = Sampling efficiency

e) Calculation of SO_2 concentration in air by ENVIROTRACK

The concentration of SO_2 was calculated using the given below equation

$$C = \frac{(V_1 - V_2) \times N \times K}{V} \qquad ------3.9$$

where,

C = SO_2 concentration (µg ml^{-1})

V_1 = Volume of thiosulfate for blank (ml)

V_2 = Volume of thiosulfate for sample (ml)

N = Normality of thiosulfate

K = 32000 (Milliequivalent weight SO_2/µg)

V = Volume of standard sulphite solution (ml)

$$C\,(SO_2, \mu g\, m^{-3}) = (A_s - A_b) \times CF \times \frac{V_s}{V_a} \times V_t \qquad ------3.10$$

where,

C (SO_2, µg m^{-3}) = Concentration of sulphur dioxide (µg m^{-3})

A_s = Absorbance of sample

A_b = Absorbance of reagent blank

CF = Calibration factor

V_a = Volume of the sample (ml)

V_s = Volume of air sampled (m^3)

V_t = Volume of aliquot taken for analysis (ml)

After calculating the different sizes of particulate matter and gaseous ($PM_{2.5}$ PM_{10}, SPM, NO_2, and SO_2), the observed concentration levels under consideration were compared with the National Ambient Air Quality Standard, 2009 1994 **[101, 102]**. The national ambient air quality standard is given in **Table 3.2**.

Table 3.2: Ambient air quality standard

Parameter	**Conc. in ambient air**		**Methods of measurement**	**Reference**
	24h	**Annual**		
	µg m^{-3}			
$PM_{2.5}$	60	40	Gravimetric	NAAQS, 2009 **[101]**
PM_{10}	100	60		
SPM	500	360		NAAQS, 1994 **[102]**
NO_2	80	40	Chemiluminescence	NAAQS, 2009 **[101]**
SO_2	80	50	Ultraviolet fluorescence	
As	6.0	6.0	AAS/ICP method after sampling on EPM 2000 or equivalent filter paper	
Pb	1.0	0.5		
Ni	20.0	20.0		

** Annual Arithmetic mean of minimum 104 measurements in a year at a particular site taken twice a week 24 hourly at the uniform interval.*

*** 24 hourly 08 hourly or 01 hourly monitored values, as applicable, shall comply with 98% of the time in a year. 2% of the time, they may exceed the limits but not on two consecutive monitoring days.*

NOTE: Whenever monitoring results on two consecutive days of monitoring exceed the limits specified above for the respective category, it shall be considered an adequate reason to institute regular or continuous monitoring and further investigation.

3.6 Characterization of particulate matter

The characterization study of the different sizes of particulate matter was performed by the use of various advanced analytical techniques:

1) DBAAS (Double Beam Atomic Absorption Spectrophotometer),
2) DPSV (Differential Pulse Stripping Voltammetry),
3) DMA (Direct Mercury Analyser),
4) ICP–AES (Inductively coupled plasma atomic emission spectroscopy),
5) Dual-Channel Alpha Beta Counter Model PNC–αβ,
6) 8K PC–based multichannel analyzer of p–type High–Purity Germanium (HPGe) detector of carbon fibre window,
7) Metrohm 850 Professional Ion–Chromatography,
8) CHNS Analyser (Elementar vario MICRO cube),
9) X–ray Powder Diffraction (XRD), and
10) Scanning electron microscope (SEM).

The details of the methodology of various advanced analytical techniques for characterization are described, and sample preparation procedures for characterization are also summarized below.

3.6.1 Sample treatment and analysis of particulate matters

Sample treatment and analysis as following steps –

a) Pre–treatment and storage of air particulate samples
b) Decomposition of particulate matter air particulate samples

a) Pre–treatment and storage of air particulate samples

Mass measurements were carried using microbalance for weighing the filters before and after sampling. Filters were desiccated in a chamber with constant air humidity (50% relative humidity) and temperature between 20–23ºC before weighing. Before and after sampling, the filter papers have desiccated for 24 hours before weighing **(Fig. 3.5)** previously.

b) Decomposition of particulate matter air particulate samples

Sample decomposition is an essential step for the analysis of the metals. It is necessary to destroy the organic matter before analysis as natural constituents usually interferes with the separation and measurement of trace metals. The decomposition of samples comprises ashing and digestion. Ashing is of two types –

1) Dry ashing
2) Wet ashing.

In our case, wet ashing has been done.

i) Wet ashing

For metal analysis of the samples, wet ashing with a mixture of inorganic acids is most suitable. The advantage is that it includes speed and more efficient removal of the organic residue and the comparatively lower temperature, resulting in smaller trace metals losses. In this method, the organic matrix is decomposed by treating the sample with strong acids such as HNO_3 (≥99.5, Sigma–Aldrich, Bangalore, India), HCl (≥38.0, Sigma–Aldrich, Bangalore, India), H_2SO_4 (≥97.0, Sigma–Aldrich, Bangalore, India), Hydrofluoric acid (HF) (≥48.0, Sigma–Aldrich, Bangalore, India), and $HClO_4$ (≥99.9, Sigma–Aldrich, Bangalore, India) or a combination of these for glass fiber and PTFE filter paper. Since this

method is conducted at a comparatively lower temperature (less than 180ºC), evaporation loss of trace metal is minimum. Among various wet ashing methods, the combination of oxidizing agent i.e., $HNO_3 + H_2SO_4$, $HNO_3 + HClO_4$, HNO_3, $+ H_2SO_4 + HClO_4$, and $HNO_3 + HCl + H_2SO_4 + HF + HClO_4$ were considered.

The oxidizing mixture selection depends on the sample's characteristics to be decomposed and the elements to be analyzed. The use of H_2SO_4 is more effective. Besides the higher oxidation power at elevated temperature, the main advantage of H_2SO_4 is that it helps raise the boiling point and does not allow the reaction mixture to go dry.

However, one of the disadvantages is its non–volatility, for which the evaporation time will be more, and the trace metals will evaporate earlier than the acid. The metallic impurity in H_2SO_4 is more than other acids, and it forms insoluble sulphates with certain metals such as calcium, barium, etc., which are present in the sample.

In the present study, a mixture of HNO_3, HCl, H_2SO_4, HF, and $HClO_4$ was used to digest air particulate matters. In the case of anion, the filter paper dissolved in double distilled water type–1, resistively 18.1 MΩ.

ii) Air particulate sample processing

The filter papers on which the sample was collected were kept in desiccators to remove the moisture absorbed. The particulate matter's weight is evaluated by subtracting the filter paper's weight before sampling the weight of the filter paper. The filter paper was then cut into pieces and put into beakers containing an acid mixture meant for digestion. They were covered by decontaminated watch glasses and kept for heating on the hot plate. Here, it must be mentioned that proper digestion needs an optimum temperature. At shallow temperatures, the absorption is prolonged and inappropriate, and at high temperatures, the acid evaporates completely without digesting the sample. The samples were digested until

the black filter paper turns white, and the remaining is evaporated to near dryness. These were then made up to 25 ml by adding 0.25% nitric acid. These prepared samples were then used for the trace metal content determination.

iii) Air particulate digestion

The first step in digestion is to prepare the containers ready for use. For this purpose, the beakers were initially appropriately washed and then kept immersed in 0.25% HNO_3 for one day. Before the digestion, the beakers were taken out, washed again with tap water, and then rinsed with ultrapure water to make the beakers free of contaminants and ready for further use. The picture of the acid digestion chamber is shown in **Fig. 3.6**.

Secondly, the standardization of the required amount digestion mixture was done, i.e., few trial digestions of filter papers were carried out to determine the amount of digestion mixture required to digest the given amount of filter paper containing the particulate matter.

Fig. 3.6: Acid digestion chamber for filter paper

It was found that a combination of 15 ml of an electronic grade of HNO_3 and 10 ml of $HClO_4$ was sufficient for half of each filter paper containing particulate matter (Processed for digestion as described before). It took 7–8 hours for the absorption of each sample. The samples were digested till the black filter paper turned white, and 1–2 ml of the acid mixture was left in the beaker **(Fig. 3.7)**.

The sample was not digested till complete evaporation to avoid the loss of volatile trace metals. Finally, the digested sample was extracted by filtration (Whatman 542 filter paper) with ultrapure water. After filtration, it was kept in decontaminated acid cleaned volumetric flasks of 25 ml. The samples were made up to 25 ml by adding 0.25% HNO_3. Filter paper blanks and acid blanks were also taken simultaneously. This is done to store the samples at pH 2, where the adsorption on the container walls was minimum.

Fig. 3.7: Digestion of filter papers

iv) Precautions during air particulate sample processing

Sampling, sample decomposition, and storage are essential steps affecting the accuracy of the analysis. However, the data quality is lost if sufficient care is not taken during the sampling, pre–treatment, and storage, even if the analytical technique is very reliable and sensitive. Problems of contamination and loss of elements are present at every stage of trace metal analysis. This problem is especially relevant for a lower concentration of analyte and smaller sample size **[103]**. Airborne particulate can contribute significantly to trace element contamination from the environment **[104]**. Therefore, attention was paid to containers, reagents, ashes and wet methods, laboratory conditions, and good laboratory practices (GLP) of the analysis.

There is a tendency for metals to get adsorbed on the containers' walls if they are not pre–treated. On the other hand, the acid–treated samples may leach some of the metals from the containers themselves. Quartz, Teflon, and high purity polyethylene containers are generally suitable for storing the solutions. Several investigators have studied the interactions between trace elements in dilute solutions and container materials for various elements. Many authors reported the adsorption characteristic of Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, and Zn on borosilicate glass, polyethylene and polypropylene container surfaces **[105,106]**.

The adsorption losses can be prevented by using the containers of non–wettable walls (Teflon, Polyethylene, etc.). The surface conditioning of quartz and glass containers can be carried out by mineral acids, such as nitric acid (HNO_3) and hydrochloric acid (HCl), followed by thorough rinsing with ultrapure water.

In the present study, all laboratory glassware used in sample collection, ashing, analysis, and storage were soaked in 10% HNO_3 for several days and then rinsed thoroughly with ultrapure water (Type–1, Resistively 18.1 MΩ) before use. Since inorganic acids are

required for decomposing the samples, the purity of these acids was taken into consideration. When samples are subjected to concentration procedures, the inorganic acids' metal impurities are also similarly concentrated.

Therefore, the minimum amount of good quality acids such as analytical and electronic grades are used in the present study for digesting the samples. Acid blanks were taken along with each batch of sample processing, and the metal content in these blanks was estimated and subtracted from the same batch of samples.

All processed samples for elemental analysis were stored approximately at pH 2, where the adsorption on the walls of the container was found to be minimum.

3.6.2 Analytical technique used

The determinations of trace metals in environmental samples were quite difficult due to the lower concentrations, unknown constituents, and interferences due to the ambiguous nature of chemical species present. The concentration of some of the trace metals in environmental samples is very–low, normally ppb to sub ppb range, which is near the detection limits of most conventional techniques. Therefore analytical methods suitable for trace metal determination have to be selected by using the following criteria:

1) High sensitivity at low concentrations
2) Good precision and accuracy
3) Large sample throughput
4) Simple to operate
5) Minimum contamination problem
6) Independent of matrix effects and chemical interference
7) Simultaneous multi–elemental capability
8) High linear dynamic range

Besides the above criteria, the method's speed, the number of the samples to be analyzed, the nature of the samples, availability of the instruments, and the methodology are also considered.

a) DBAAS (Double beam atomic absorption spectrophotometer)
b) DPSV (Differential pulse stripping voltammetry)
c) DMA (Direct mercury analyser)
d) ICP–OES (Inductively coupled plasma–optical emission spectroscopy)
e) Dual–channel alpha beta counter
f) 8K PC–based multichannel analyzer of p–type high–purity germanium (HPGe) detector of carbon fibre window
g) Ion–chromatography
h) CHNS analyser
i) X–ray diffraction
j) Scanning electron microscope

All these instruments were used during the present study.

In the present study, the DBAAS (Double beam atomic absorption spectrophotometer), DPSV (Differential pulse stripping voltammetry), DMA (Direct mercury analyser), ICP–OES (Inductively coupled plasma–optical emission spectroscopy), and IC (Metrohm 850 professional ion–chromatography) techniques were used for heavy and trace element analysis. Ion–chromatography is used for the anion in the particulate matter. CHNS analyser is used for the C, H, N, and S. XRD and SEM are used for the mineralogical analysis in the particulate matter. Dual–channel alpha beta counter (Model PNC–αβ),

HPGe (8K PC–based multichannel analyzer of p–type High–Purity Germanium) detector of carbon fibre window is used for the radioactivity elements. The techniques' basic principles, general interferences that occurred, and methods adopted to overcome the interventions are discussed briefly.

a) Double beam atomic absorption spectrophotometer

A double beam atomic absorption spectrophotometer (DBAAS) is commonly used in most laboratories for routine trace metal analysis in environmental and biological materials due to their high sensitivity, ease of sample preparation, and reduction of interferences from other elements. The working principle schematic diagram of double beam atomic absorption spectrophotometer is shown in **Fig. 3.8**.

Principle: In this technique, the sample containing the metal is made to vaporize atomically in the radiation source path. The ground state atoms absorb a specific wavelength of light transmitted through the atomic vapors. The extent of radiation absorption is directly proportional to the number of atoms and is measured quantitatively by photomultiplier use. Beer–Lambert's law mathematically describes it.

$$A = \frac{\mathrm{Log} I_o}{I_t} \qquad ------ 3.11$$

where,

A= Absorbance

Io= Initial Intensity of radiation

It= Intensity of radiation after passing through the sample.

In AAS, the atom cloud is produced by supplying Thermal Energy to the sample to dissociate the chemical compound into free atoms by aspirating the solution into the flame

aligned in the light beam. The absorption by the ground state atoms from a source lamp is measured.

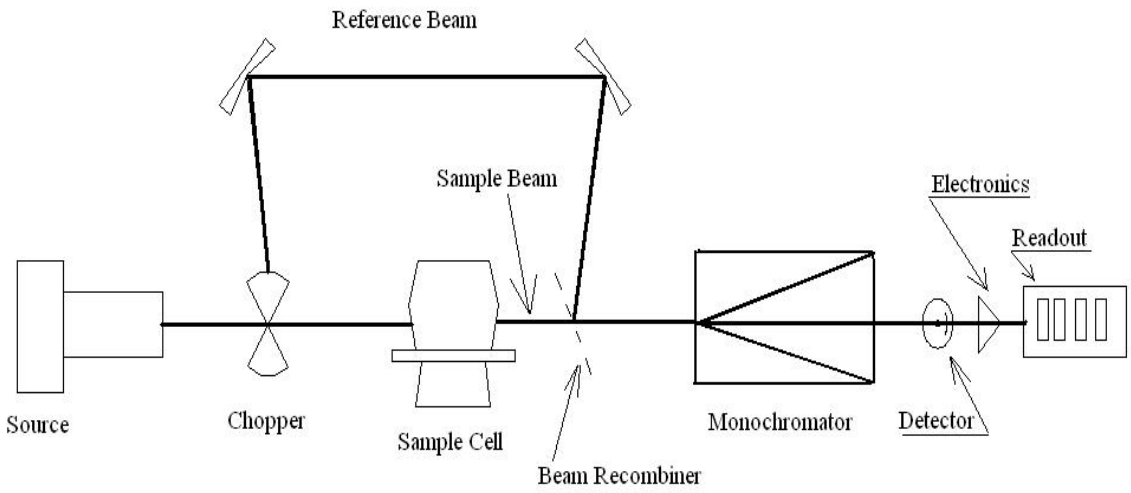


Fig. 3.8: Schematic diagram of double beam atomic absorption spectrometer

Knowing the absorption of light, the concentration of a particular element is determined with calibration standards. Matrix, chemical, and ionization are the main interferences encountered in the AAS, which can be compensated by taking special precautions in sample preparation, analyzing the samples using standard addition. Atomic absorption spectrometry is one of the most versatile analytical techniques commonly used in most laboratories for routine trace metal analysis in environmental and biological materials due to its high sensitivity, ease of sample preparation, well–established well-established throughput and, less interference from other elements.

According to Beer–Lambert law, the absorption of light is proportional to the concentration of metal in the solution in this analytical technique. The quantity of interest in atomic absorption measurements is the amount of light at the resonant wavelength, which is absorbed as the light passes through a cloud of atoms. As the number of atoms in the light path increases, the amount of light absorbed increases. Thus by measuring the amount of

light consumed, a quantitative determination of the amount of analyte element present can be made.

b) Differential pulse stripping voltammetry

Differential pulse stripping voltammetry an electroanalytical technique in which the current at an electrode is measured as a function of potential applied to the electrode. It's techniques such as anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), and adsorption voltammetry (AV) have been adopted widely for trace metal analysis. Their relatively inexpensive instrumentation determined elements accurately at trace to ultra–trace levels and multi–elemental determination capabilities. Out of these methods, particularly ASV, has become more widely accepted for the determination of trace elements in various matrices. From precision and accuracy. The electroanalytical methods, particularly differential pulse anodic stripping voltammetry (DPASV), are more suitable for routine trace analysis in environmental and biological samples than other methods.

This technique has high accuracy and detection, sensitivity, excellent precision, and the ability to determine several heavy metals over an extensive concentration range simultaneously. These features have made DPASV an important trace analytical method for analyzing toxic metals in various environmental matrices.

This study used this technique to estimate Pb, Cd, Ni, Co, Th, U, and Cu in particulate matter samples. The schematic diagram of DPASV is presented in **Fig 3.9,** and the calibration curve for Pb, Cd, Ni, Co, Th, U, and Cu have shown in **Figs. 3.10a–b,** respectively.

c) Direct mercury analyzer

Direct mercury analyzer (DMA) is a compact and sensitive analytical instrument for the precise and accurate determination of total mercury in nanogram levels in any solid or liquid without any sample processing matrices. It determines total mercury in any sample medium, may be solid, liquid or colloidal, and digested solutions without any sample wet chemistry or pre–treatment in both the laboratory and field environments. The determination of mercury in DMA–80 is a straightforward and quick method based on inbuilt sample decomposition, catalyst conversion, gold amalgamation followed by Atomic Absorption Spectrophotometry, a destructive sample analysis. All the above steps are carried out inside the instrument itself. The photo and flow sheet of sample processing in DMA–80 is given in **Fig. 3.11**. The integration of the thermal decomposition technique of sample preparation and atomic absorption detection reduces most samples' total analysis time to less than five minutes in either the laboratory or field setting. Total mercury (organic and inorganic) in soils, sediments, and sludge type materials as well as in aqueous wastes and ground waters can be determined without sample chemical pre–treatment using this method, except for unique circumstances when mercury could be bound in silicates or other matrices that may not thermally decompose.

Controlled heating in an oxygenated decomposition furnace is used to liberate mercury from solid and aqueous samples in the instrument. The sample is dried and then thermally and chemically decomposed within the decomposition furnace. Once the sample is manually or automatically dispensed into the sample boat, the boat is mechanically introduced into a quartz decomposition tube. The decomposition tube is heated by two independently programmable ovens, the decomposition and catalyst furnaces; each furnace can maintain a temperature of at least 7500C. The sample is dried and thermally decomposed in an oxygen environment, releasing mercury vapor. The decomposition

products are carried by flowing oxygen to the catalytic section of the furnace. Here oxidation is completed, and halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are then carried to a gold amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any residual gases or decomposition products, and once the sample is completely decomposed, then the amalgamator is rapidly heated, releasing mercury vapor. Flowing oxygen carries the mercury vapor through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance (peak height or peak area) is measured at 253.7nm as a mercury concentration function **[107]**. The mercury vapor passes through two absorbance cuvettes, separated by a collection flask outside the optical axis. The flow path through the spectrometer and cuvettes is maintained at approximately 1200C by a heating unit to prevent condensation and minimize carry–over effects. A mercury–vapor lamp is used as the light source. The detector is connected to a computer for data acquisition and analysis.

The typical working range for this method is 0.05–600ng. The mercury vapor is first carried through a long path length absorbance cell and a short path length absorbance cell. (The lengths of the first cell and the second cell are in a ratio of 10:1) The same quantity of mercury is measured twice, using two different sensitivities resulting in a dynamic range that spans at least four orders of magnitude. The two individual peaks correspond to the two absorbance cells of different sensitivities. The maximum intensity of the long path length cuvette (low range cell) occurs at ~8 seconds, and the maximum intensity of the short path length cuvette (high range cell) occurs at ~20 seconds. The instrument detection limit (IDL) for this method is 0.01ng total mercury. Filter paper samples of size (2×2cm) in duplicate or 2 ml of liquid sample was analyzed directly without any sample processing.

d) Inductively coupled plasma–optical emission spectroscopy

The Inductively coupled plasma–optical emission spectroscopy (ICP–OES) is a partially ionized gas (typically Ar, which is less than 1% ionized in the plasma) produced in a quartz torch using a 1–2.5–kW radio frequency power supply and detail of basic description **[108]**. Samples are usually introduced into the center of the plasma as aerosols. Commercial ICP–OES equipment has been available since 1974. The light emitted from a 3 mm to 5 mm high area of plasma is focused on the entrance slit of a monochromator or polychromator to monitor either sequential or simultaneous emission from various elements. The spectral lines produced from most charged ions are the most intense for most elements, and the atomic lines are the most intense for elements with high ionization potential and alkali metals. The detected signal depends on the number of ions (or atoms) analyzed in the plasma and the fraction of those ions (or atoms) excited.

A two–stage or three–stage, differentially pumped interface is used to extract ions from the atmospheric pressure plasma into the low–pressure (typically 10–5–10–6 Torr) mass spectrometer **(Fig. 3.12a)**. Ions pass through water–cooled sampling cone (often made of Ni or Cu) with a 0.5–1.0 mm orifice placed in the plasma. The atoms are then placed in the plasma. A small portion of the expansion gas passes through each other, a more acutely angled cone known as a skimmer. The pressure in the area between the sample cone and the skimmer is typically about 1 Torr. Ion optics, typically cylinders held at suitable voltages, are used to concentrate ions in a large–scale spectrometer, usually a quadruple system. The analysis signal depends on the number of analyzed ions in the plasma (independent of their state of excitation) and the possible extensive transport of ions to the mass spectrometer.

There are two significant differences in the generation of ICP–OES. First, the sample ions must be physically transported from the plasma to the mass spectrometer, while the collection of photons in the ICP–OES is irresponsible. Second, the emission intensity strongly depends on the fraction of ions (atoms) excited, whereas the mass spectrometric signals are dependent on ionization, but not excitation, conditions within the plasma **[109]**. The photo and flow sheet of sample processing in ICP–OES are given in **Figs. 3.12a–b**.

e) Dual–channel alpha beta counter

Dual–channel alpha beta counter model PNC–αβ (Electronic Enterprises (I) Pvt. Ltd., Mumbai, India) is a micro–controller based, economical, stand–alone, mains operated instrument for dual channel nuclear counting application for alpha-beta radiations. It is a versatile instrument designed to meet counting application requirements. It uses a composite detector (plastic Scintillator and ZnS (Ag) Scintillator) to detect and measure alpha/beta radiation. The high voltage required for the detector is generated in the instrument. Load resistors for photomultiplier tubes (PMTs) and pulse processing circuits for the detector are placed in the front–end electronics unit. The dual–channel alpha beta counter model PNC–α stores 1000 counts (500 alpha + 500 beta) data in non–volatile memory. It generates formatted USB 2.0 outputs to transfer data to the PC. A USB male connector is provided on the front panel to transfer data to the PC. Support for data transfer in a windows environment has supplied with the software system.

A drawer assembly is supplied as a standard accessory for holding 1 "dia or 2" dia filter paper. The detector turns upside down on the drawer assembly such that the detector's miler face sample is just 2 mm above the filter paper. A 40 mm thick lead shield for the detector can be supplied at an additional cost **(Fig. 3.13)**.

f) 8K PC–based multichannel analyzer of p–type high–purity germanium (HPGe) detector of carbon fibre window

Air filter samples were analyzed by using a high-resolution gamma spectrometry system consisting of a coaxial p–type high purity germanium detector (HPGe) having 40% relative efficiency (Ortec Gem40) to 7.6 × 7.6 cm NaI(Tl) detector for the 1332 keV gamma radiation of 60Co and a source–detectors distance of 25 cm, coupled with a 8K MCA and computer. The resolution of the detector was 1.69 keV for the 1332 keV gamma radiation of 60Co. The detector is housed in 7.5 cm thick bricks of lead shield to reduce the surrounding background. Spectrums were acquired for 200,000 seconds to 250,000 seconds for the air filter samples to obtain statistically significant Pb–210 peaks. Spectrum analysis was done by GammaVision software (Ortec). NIST Certified Reference Materials for Ra–226 in aqueous medium was spiked in Whatman EPM 2000 filter papers were used efficiency calibration for the sample geometry. The characteristic gamma line of 46.54 keV (4.25 % emission probability) of Pb–210 was used to determine the same radioactive concentration. The quality control of the analysis was carried out by spiking IAEA standard reference materials in filter paper media, and the precision of the investigations was within 10% of the certified values.

g) Ion–chromatography

An ion chromatographic (Metrohm 850 professional ion–chromatography), metal–free system (IC–850 professional model, Metrohm AG, Switzerland) controlled by Metrodata MagIC Net™ software and equipped with 858 professional sample processor, sample filtration system with a 0.2 µm regenerated cellulose membrane, six–channel injection valve, low pulsation high–pressure pump, chemical suppression and CO_2 suppression, eluent degasser and conductivity detector was used. The separation was performed on a

metrosep a supp 7–250 column (250 x 4 mm, polyvinyl alcohol with quaternary ammonium groups, 5 µm particle size), Metrosep RP 2 guard/3.5 (polymer with pore size 0.2 µm). To keep the baseline signal as low as 0.99 µS/cm, 0.1 M sulphuric acid solution was used for regenerated chemical suppression. The chromatogram of IC is shown in **Fig. 3.14**.

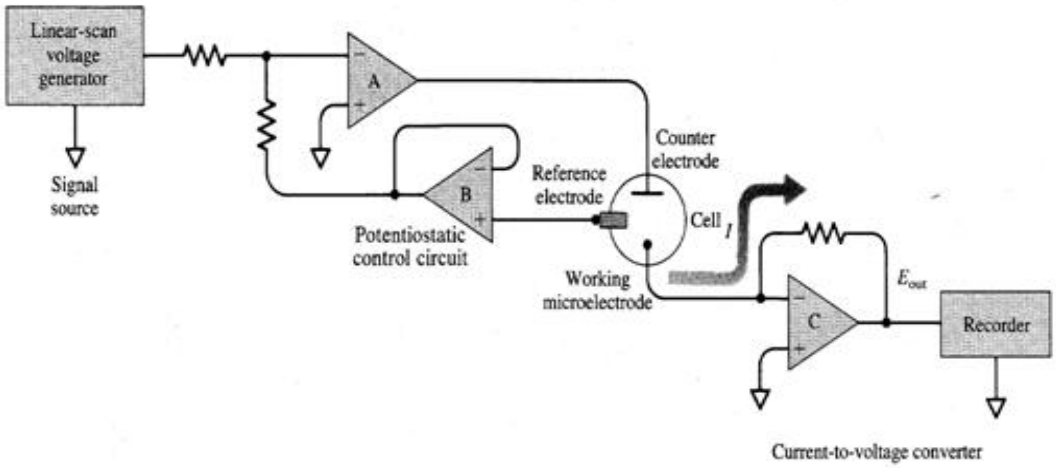


Fig. 3.9: Schematic diagram of differential pulse stripping voltammetry

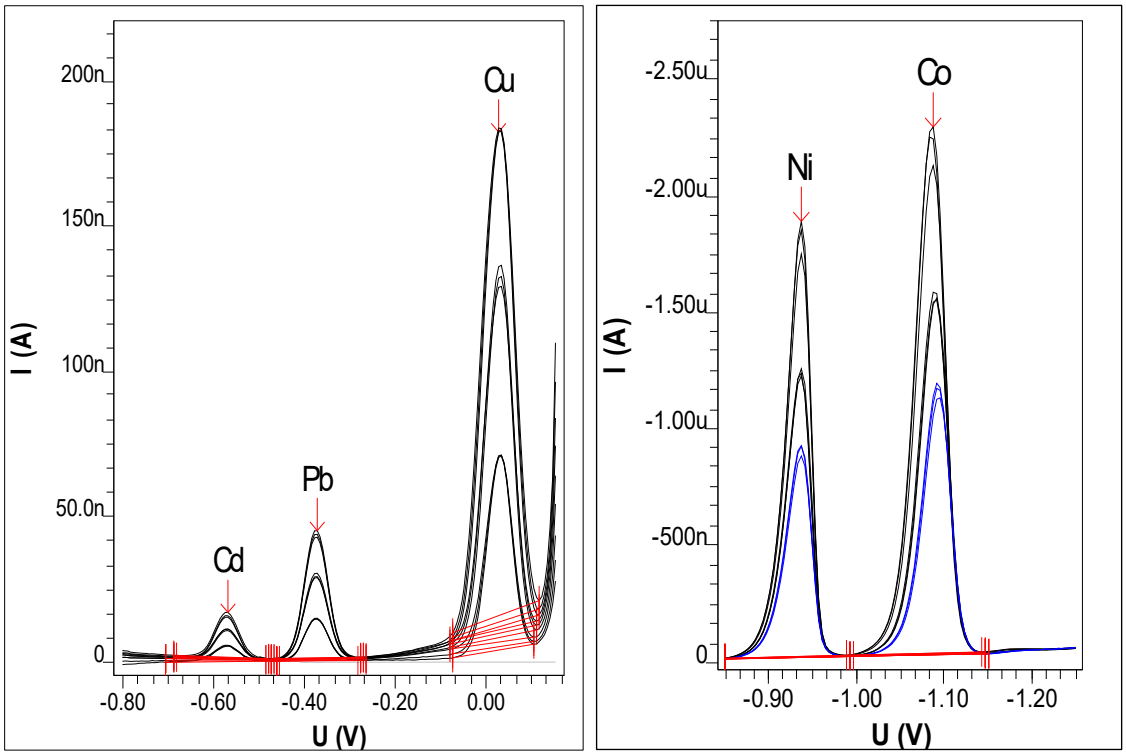


Fig. 3.10a: Calibration curve Cd, Pb, Cu, Ni, and Co by DPASV

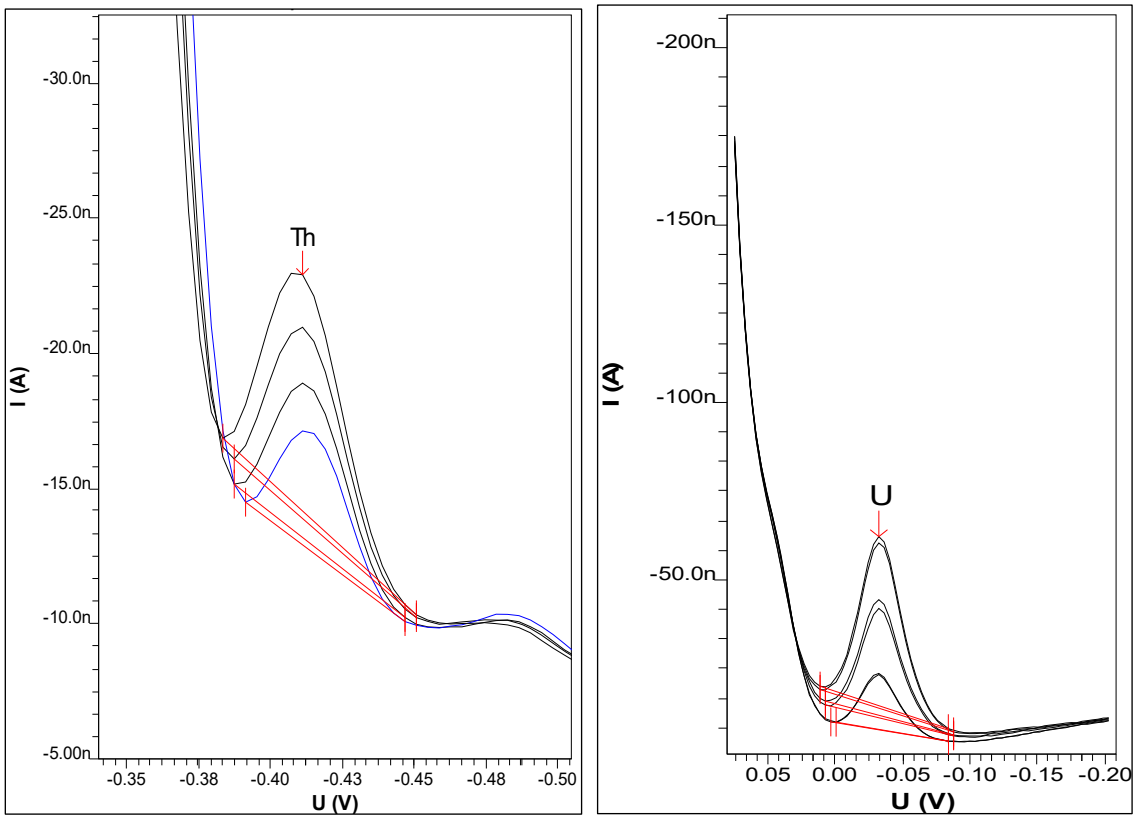


Fig. 3.10b: Calibration curve of Th and U by DPASV

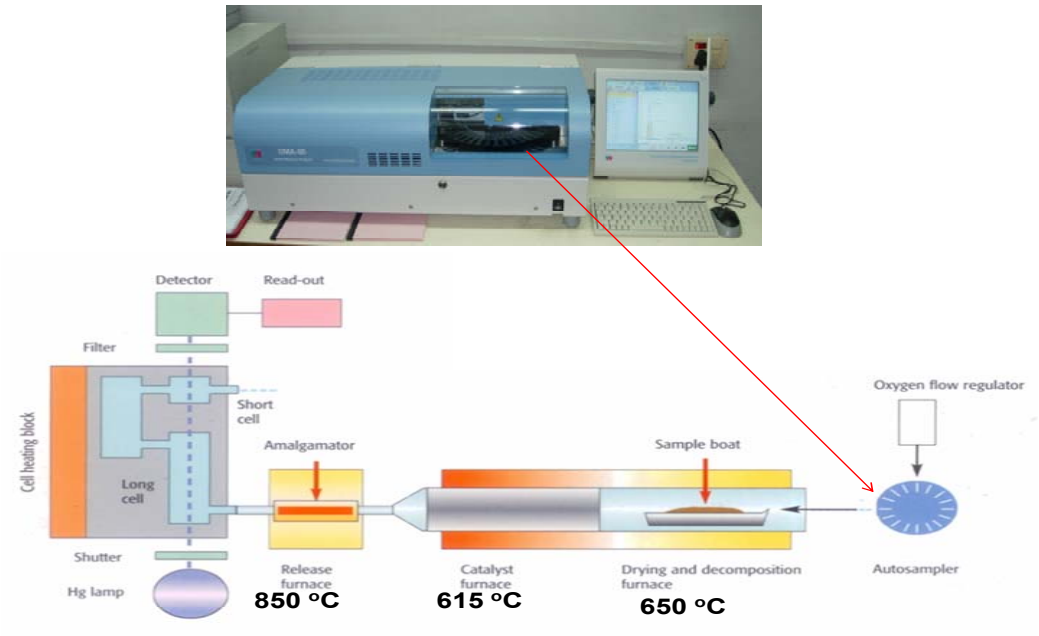


Fig. 3.11: Flowsheet of sample processing in direct mercury analyzer

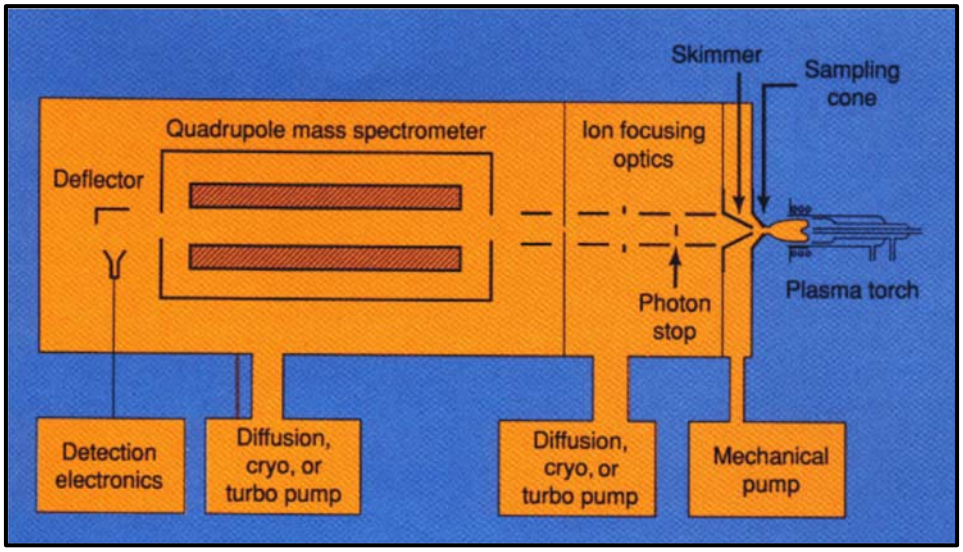


Fig. 3.12a: Flow chart of the working principle of ICP–OES instrument

Fig. 3.12b: Using the ICP–OES for element analysis

Fig. 3.13: Using the dual–channel alpha beta counter model PNC–αβ for αβ counting

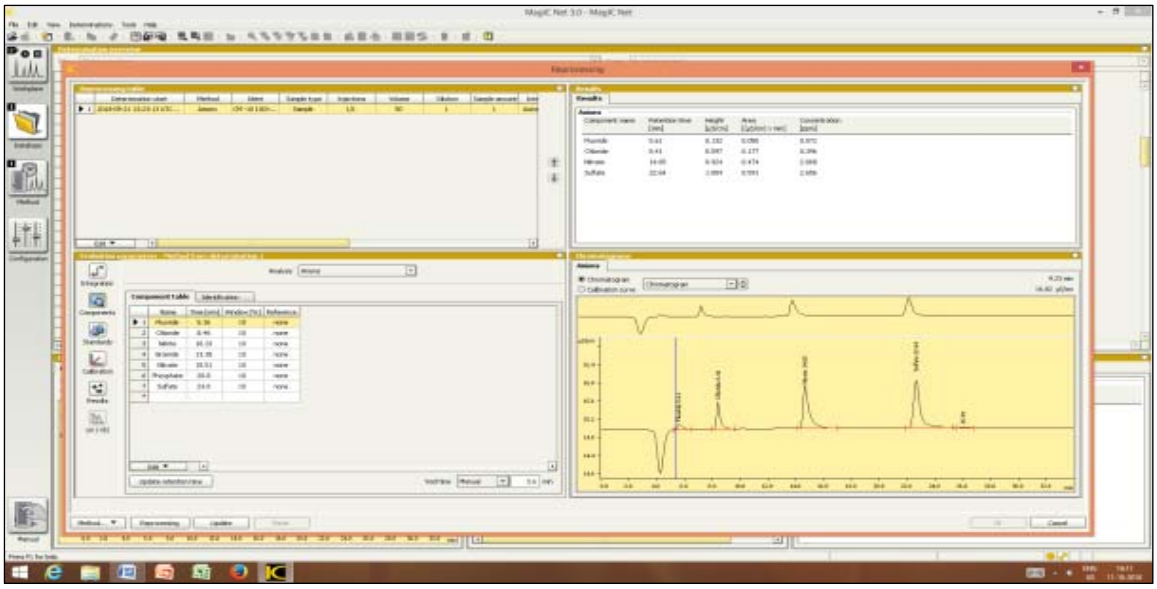


Fig. 3.14: Chromatogram of IC analysis of anions

h) CHNS analyzer

CHNS elemental analyzer (Elementar vario MICRO cube) provides a means for the rapid determination of carbon, hydrogen, nitrogen, and sulphur in organic matrices and other types of materials. They can handle a wide range of sample types, including solids, liquids, volatile and viscous samples in pharmaceuticals, polymers, chemicals, environment, food, and energy. The picture of the schematic diagram and working with the CHNS analyzer is showing in **Fig. 3.15**. In the combustion process (furnace at ca. 1000°C), carbon is converted into carbon dioxide; Hydrogen for water, nitrogen to nitrogen gas/oxides of nitrogen, and sulfur to sulfur dioxide. If other chlorine elements are present, they will also be converted into combustion products, such as hydrogen chloride. Various absorbers are used to remove these excess combustion products and some key elements, such as sulfur, if no determination of these additional elements is required. The combustion products are extracted from the combustion chamber with an inert carrier gas such as helium and passed overhead (about 600ºC) of high purity copper. It may be located at the base of the copper combustion chamber or in a separate furnace. This copper's function is not to remove any

oxygen consumed in the initial combustion and convert any nitrogen-to-nitrogen gas oxides. The gases are passed through absorbent traps to release only carbon dioxide, water, nitrogen, and sulfur dioxide.

Detection of the gases can be carried out in a variety of ways, including

1. A GC separation followed by quantification using thermal conductivity detection
2. A partial separation by GC (frontal chromatography) followed by thermal conductivity detection (CHN but not S)
3. A series of separate infra–red and thermal conductivity cells for detection of individual compounds

Quantification of the elements requires calibration of each component using high purity micro–analytical standard compounds such as acetanilide and benzoic acid.

i) X–ray diffraction

The structure's determination using a diffractometer typically requires approximately 100 times more of the substance than the conventional Debye–Scherrer method. Compared to photographic techniques, diffractometry, in most cases, offers many advantages due to its high sensitivity, high resolving power, and accuracy of intensity measurements, and that too without the need for detailed work in dark rooms.

Above all, the diffractometric records can be obtained in a much shorter time than with photographic methods. The selected samples have been analyzed through the XRD technique used to determine the physical parameter.

The diffractogram pattern was recorded at room temperature, and 2θ value concerning intensity has recorded. The experimental set–up, calibration, measurements on standard materials, and initial studies using the system were reported by other researchers **[110,111]**. Here, the intensity had been taken as the arbitrary unit because instead of absolute intensity, XRD measures relative intensity (Rigaku Miniflex 600 Desktop X–Ray Diffraction System, RIGAKU Corporation, Tokyo, Japan).

j) Scanning electron microscope

Qualitative and visualization investigation of particulate matter aerosol particles impregnated on the glass fiber and PTFE filters of Singrauli Coalfield were analyzed using ZEISS EVO 18 (EVO – scanning electron microscope MA15/18, Carl Zeiss Microscopy Ltd., Cambridge CB23 6DW, United Kingdom) scanning electron microscope (SEM) equipped with energy dispersive X–ray spectrometer (EDS). The magnification of SEM varied from about 1000 to 10,000 times with an accelerating voltage of 20 kV and a working distance of 7 mm. This working condition enables us to visualize particulate matter from a few nanometers to a hundred nanometers. A pinch of moisture-free particulate matter samples was first mounted on a specially designed slide for coating. A fragile film of gold (Au) was deposited on each sample's surface using a vacuum coating unit. The fine coating of gold makes the samples electrically conductive. Then the samples were placed in the analysis chamber of the instrument. The working conditions were set at an accelerating voltage of 20 kV, a current of 40–50 μA, and placing a Si (Li) detector 10 mm away from the samples to be analyzed. SEM determined the information on particle characteristics in terms of particle shape. The analysis by SEM depends on image quality.

A relatively low magnification level was used in this study to visible more particles in a single frame. So, particles > 1 μm (longest visible dimension) were selected for analysis. For particle sizing, the long dimension and intermediate (i.e., perpendicular to the long) dimensions were reported. These were the same size parameters measured in the manual SEM–EDX dust characterization method. The manual method of the qualitative assessment of particle shape was done as rounded, angular, or transitional. The detection limit of X–ray was ~ 0.1%. The EDX analysis was carried out at each analysis point.

The electron beam from SEM fell on the particle's surface, and spectra are generated by the detection of X–ray emissions from the particle. Each element presents on the particle surface got excited by the impinging electrons and produced a characteristic X–ray. Each unique peak of a spectrum represents a specific element, and the peak heights provide some indication of the elemental composition (their atomic stoichiometry can identify, i.e., minerals).

The elements present on the surface of the particle were measured both qualitatively and quantitatively. The electrons may penetrate deep (about 1 μm) into the relatively small particles (respirable dust) and provide useful information on the overall composition.

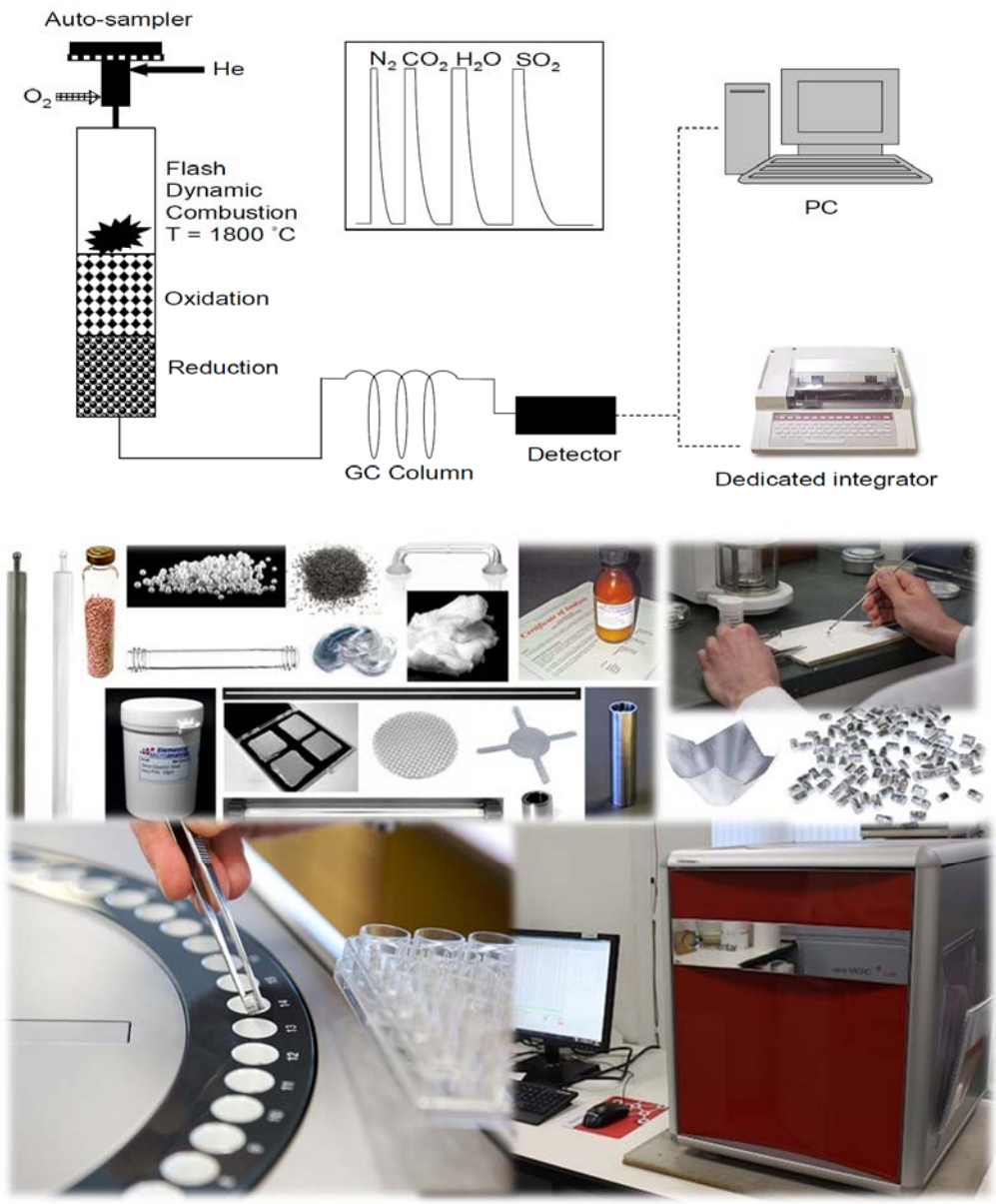


Fig. 3.15: Schematic diagram and working with CHNS analyzer

3.7 Quality control and assurance

The limits of detection for particulate matters have calculated as three times the average standard deviation of the day–to–day mass change of blank filters $\times \sqrt{n + {}^{1}/_{n}}$ Divided by the nominal sampling volume, as defined by Vaughan et al. **[112]**, and was 0.1 μg m^{-3}. The limits of detection for NO_2 and SO_2 passive diffusion tube measurements, defined as the field blank tubes' average plus three times the standard deviation of the blanks, were calculated to be equivalent to 6.4 μg m^{-3}. The NO_2 and SO_2 measurements were also field blank corrected with the corresponding blank for each week and site as similar to particulate matters

The product specifications have been set by national/international standards writing organizations to specify the quality of products and guidelines suitable for various uses. Their accurate characterization is necessary to ascertain the suitability of products. This is achieved by using certified reference materials to calibrate analytical instruments in quality control and verify test methods. It enhances measurement quality and provides traceability to national and international measurement systems.

The data quality is assured by following the protocols for sample collection, processing, and analysis prescribed by Central Pollution Control Board and the United States Environmental Agency. The data's quality control is carried out by analyzing the standard reference material obtained from the National Institute of Standards and Technology, USA. The results agreed very well with the certified values **(Tables 3.3a–b)**.

Quality control of elements in any matrix by any method, in general, is maintained by following the steps given below:

1) Analysis of standard reference materials
2) Replicate analysis

3) Spike recovery

4) Cross method checks

5) Low blanks (pure chemicals)

6) Use of internal standards

Table 3.3a: Comparison of element concentrations with certified values

Elements	Unit	Certified Value (NIST – 2710a soil)	Observed Value
Ag	µg g^{-1}	40	40.20±0.51
Al	%	5.95±0.05	5.88±0.08
As	µg g^{-1}	1540±10	1535±15
Br	———	———	———
Ca	%	0.964±0.045	0.92±0.06
Cd	µg g^{-1}	12.3±0.3	12.5±0.2
Co		5.99±0.14	5.8±0.4
Cr		23.0±6.0	18±4.2
Cu		3.4±0.05	3.5±0.08
Fe	%	4.32±0.08	4.26±0.06
Hg	µg g^{-1}	9.88 ± 0.21	9.75 ± 0.28
K	%	2.17±0.13	2.15±0.21
Li	———	———	———
Mg	%	0.73±0.03	0.69±0.05
Mn	µg g^{-1}	2.1±0.06	2.2±0.2
Na	%	0.89±0.02	0.86±0.1
Ni	µg g^{-1}	8.0±1.0	7.1±0.8
Pb	%	0.552±0.3	0.48±0.1
Se	µg g^{-1}	1	0.95±0.04
Si	%	31.1±0.4	30.3±0.74
Sr	µg g^{-1}	255±7	248±10
Th		18.1±0.3	17.0±0.5
U		9.11±0.3	8.35±0.6
V		82±9	78±12
Zn		4180±20	4165±28

± = Standard deviation

Table 3.3b: Comparison of mercury concentration with certified values

NIST SRM with code	Certified value	Observed value
Rice 1568a	5.8 ± 0.5	5.8± 0.4
Tomato leaves 1573a	34 ± 4	29.2±1.0
San Joaquin Soil 2709a	900 ± 200	828.96 ± 38.63

± = Standard deviation

3.8 Calculation of elements concentration

$$\text{Concentration of metals } \left(\frac{\mu g}{m^3} \text{ or } \frac{\eta g}{m^3}\right) \text{ analyzed by instruments } * = \frac{(\text{Sample concentration} - \text{Blank concentration}) \times 25\text{ml} \times \text{Dilution factor}}{\text{Volume of air filter } (m^3)} \quad ------ 3.12$$

Note:

1) * = AAS or ICP or DPSV or IC
2) Sample and blank concentrations are in μg ml^{-1} or ng ml^{-1}
3) The numerator is multiplied by 2 or 4 since half or one–fourth of the filter paper for each sample has been used for trace metal analysis

$$\text{Concentration of Hg in solid } \left(\frac{ng}{m^3}\right) \text{ analyzed by DMA } = \frac{\text{Total mercury (Sample } - \text{Blank) ng } \times (18 \times 23)\ cm}{\text{Volume of an air filter } (m^3) \times (2 \times 2)\ cm} \quad ------ 3.13$$

$$\text{Concentration of Hg in liquid } \left(\frac{ng}{m^3}\right) \text{ analyzed by DMA} = \frac{\text{Total mercury (Sample} - \text{Blank) ng} \times 25\text{ ml}}{\text{Volume of the air filter } (m^3) \times 0.5\text{ ml}} \quad ------- 3.14$$

3.9 Data analysis technique

a) Arithmetic mean

The arithmetic mean of the series is obtained by adding all observations' values and dividing the total by the number of observations.

It is mathematically written as –

$$\overline{X} = \frac{X_1 + X_2 + X_3 + \ldots\ldots\ldots X_N}{N} \text{ or } \overline{X} = \frac{\sum X}{N} \quad ------ 3.15$$

where,

X_1, X_2, X_3, ..., X_N represent values of the X variable

N = Numbers of observations; Σ = means 'the sum of,'

b) Median

The middle observation if the number of observations N is odd. If N is even, then the median is the average of the two middle observations.

c) Geometric mean

It is N positive values is the Nth root of their product. It is mathematically defined as –

$$\mu_g = \sqrt[N]{X_1.X_2.X_3 \dots \dots \dots X_N} \qquad ------3.16$$

Here, N stands for the number of measures and X_1, X_2, X_3, ..., X_N are the various value.

d) Standard deviation

The most useful measure of dispersion is the Standard Deviation or root–man–square deviation. Symbolically,

$$\sigma = \sqrt{\frac{\sum_{i=0}^{n}(x_i - \bar{x})^2}{N-1}} \qquad ------3.17$$

Here, σ = Standard Deviation, x = Arithmetic Mean, N = Numbers of observations

e) Skewness

When the frequency distribution is not symmetrical, it is said to be asymmetrical or skewed. Skewness is a measure of symmetry, or more precisely, the lack of symmetry. The skewness for a normal distribution is zero, and any symmetric data should have skewness near zero. Negative values for the skewness indicate data that are skewed left, and positive values for the skewness indicate data that are skewed right. By skewed left, we mean that

the left tail is long relative to the right tail, and skewed right means that the right tail is long relative to the left tail. Some measurements have a lower bound and are skewed right.

f) Kurtosis: It is a measure of whether the data are peaked or flat relative to a normal distribution. Data sets with high kurtosis tend to have a distinct peak near the mean, decline rather rapidly, and have heavy tails. Data sets with low kurtosis tend to have a flat top near the mean rather than a sharp peak. A uniform distribution would be an extreme case. The kurtosis for a standard normal distribution is three, positive kurtosis indicates a peaked distribution, and negative kurtosis indicates a flat distribution.

g) Enrichment factor

The enrichment factors are the ratio of selected element concentrations with a reference element that is entirely crustal in origin. The crustal element concentration was extracted from previous studies that investigated a region. The typical reference elements include Al, Fe, Ti, and Mg, and there is still no well–established rule for the choice of a reference element **[71,92,113]**. Hence, this factor gauges the extent of anthropogenic influence. In the present study, enrichment factors were calculated using Fe as the reference element due to its abundance in the earth's crust and its stability to most anthropogenic contaminants **[114-116]**.

An enrichment factor of each metal (x) calculated by the given mathematical formula below:

$$\mathrm{EF_{(x)}} = \left[(\mathrm{X\,Fe^{-1}})_{\mathrm{sample}}\right]\left[(\mathrm{X\,Fe^{-1}})_{\mathrm{crust}}\right]^{-1} \qquad ------3.18$$

where,

($X\ Fe^{-1}$) sample and ($X\ Fe^{-1}$)crust refer to the average concentrations of the element and Fe in the atmospheric PM and continental crust, respectively. The average element concentrations in continental soil were taken from the CRC handbook **[117]**.

h) Correlation analysis

The correlation analysis study involving statistical calculation was devised by Pearson **[118]**. Based on the value of the correlation coefficient 'r', the correlation between two variable parameters shows in the matrix can be termed as positive or negative. Correlation analysis measures the closeness of the relationship between chosen independent and dependent variables **[61,93,119]**. If the correlation coefficient is nearer to +1 or –1, it shows the probability of a linear relationship between the variables. The parameters are strong, moderate, and weak based on correlation **[120,121]**.

The expression of the correction coefficient is described below.

Let (x_1, y_1), (x_2, y_2), ……, (x_n, y_n) be a given set of n pairs of observations on two variables x and y. The correlation coefficient or coefficient of correlation between x and y (denoted by the symbol R) is expressed in Equation:

$$R = \frac{\mathrm{cov}\,(x,y)}{\sigma_x \sigma_y} = \frac{\frac{\sum xy}{n} - (\frac{\sum x}{n})(\frac{\sum y}{n})}{\sigma_x \sigma_y} \qquad ------3.19$$

where,

σ_x and σ_y are the standard deviations of x and y, respectively, and cov (x, y) denotes the covariance of x and y. This expression is known as Pearson's product–moment formula or Pearson correlation coefficient.

3.10 Analytical methods for gross alpha and beta

Gross alpha and beta measurements are used in the air to test samples for relative levels of radioactivity. It is a measure of all the alpha and beta activity present, regardless of the specific radionuclide source. Alpha and beta emitter radionuclides are shown in **Table 3.4**. The samples were counted for gross alpha and gross beta radioactivity using a dual–channel alpha beta counter is a micro–controller based, economic, stand–alone, mains operated instrument for dual–channel nuclear counting application for alpha–beta radiations (Model PNC–αβ). It is a versatile instrument designed to cater to the counting application requirements. This counter uses a composite detector (Plastic Scintillator and ZnS(Ag) Scintillator) for the detection and measure alpha/beta radiation. The high voltage required for the detector is generated in an instrument. The load resistor for the photomultiplier tube and the front–end electronics for pulse processing circuits for the detector is housed in the unit. Lead shielding was used to attenuate external radiation. A drawer assembly to hold 1" or 2" dia filter paper is supplied as a standard accessory. The detector mounts upside down on the drawer assembly such that Myler face of the detector is just 2 mm above the sample filter paper. The detector's operating voltage was selected as +1200 V. The low–level planchet counter offers simultaneous, separate alpha and beta measurement of one planchet. The system was calibrated for α and β energies by preparing standard samples that contain equal concentrations. ^{241}Am (219 Bq) and ^{90}Sr (191 Bq) were used to calibrate the alpha and beta energies system, respectively. The counting efficiencies were detected as 25 % for alpha and beta based on the system's calculations.

All the alpha and beta activity calculations were corrected for the aerosol deposit's mass thickness collected in the filters. The detector's background was determined with measurements that routine samples were counted and measured using clean filters. This apparatus's average detection limit was approximately 0.3 ± 0.1 and 0.8 ± 0.4 mBq m^{-3}

background activity for alpha and beta. A background subtraction procedure was applied to each of the gross alpha and gross beta analyses. Due to the low concentration of alpha and beta emitters in the filters, long counting times of 10 h were used for each measurement.

Table 3.4: Natural and human–made alpha and beta emitters

Alpha–emitters	**Beta–emitters**
^{241}Am (Americium–241)	^{3}H (Tritium)
^{239}Pu (Plutonium–239)	^{40}K (Potassium–40)
^{238}U (Uranium–238)	^{90}Sr (Strontium–90)
^{232}Th (Thorium–232)	^{99}Tc (Technetium–99)
^{226}Ra (Radium–226)	^{129}I and ^{131}I (Iodine–129 and 131)
^{222}Rn (Radon–222)	^{137}Cs and ^{134}Cs (Cesium–137 and 134)
^{210}Po (Polonium–210)	^{14}C (Carbon–14)

The minimum detectable activity (MDA) was calculated by Currie equation as in **[122]**.

$$\text{MDA (Bq m}^{-3}) = \frac{L_d}{VT \in 60} \qquad ------3.20$$

with

$$L_d \text{ (Limit of detection)} = 3 \times SD \qquad ------3.21$$

where,

V (m^{-3}) is the volume of sample, T (min) the sample measurement time (which is the same as for the background), $\in$ the efficiency. In this study, SD (standard deviation) was calculated using a clean planchet and fresh filter measurement of ten times. Typical MDAs for counting time of 600 min was estimated to be 4.0×10^{-6} Bq m^{-3} for α and 3.0×10^{-6} Bq m^{-3} for β.

The following equation calculated the counting uncertainties:

$$Un = \sqrt{\frac{R}{t_R} + \frac{B}{t_B}} \qquad ------3.22$$

where,

Un count uncertainty for the sample, R count rate for the sample (cpm), B background count rate, t_R time for sample count (min), t_B time for background count (min).

The present measurements' average uncertainties are detected as 10–20 % for gross alpha and 8–15 % gross beta counts. These uncertainties are the sum of the errors caused by the preparation of standards alpha and beta sources and particle fractions.

a) Counting for gross alpha and beta

The following equation was used to calculate the alpha radioactivity:

$$A_{\alpha} = \frac{A \times 1000}{2.22 \times C \times V} \qquad ------3.23$$

where,

A is the net alpha count rate (gross alpha count rate minus the background count rate) at the alpha voltage plateau; C is the alpha efficiency factor read from the graph of efficiency versus mg of dust per cm² of filter area (cpm/dpm), V is the volume of sample aliquot (m³), and 2.22 is the conversion factor from dpm/pCi **[123]**.

Also, equations that were used to calculate beta radioactivity are given as Eqs. (3.24) and (3.25). In case of no significant alpha counts when the sample is counted at the alpha voltage plateau, the beta activity can be determined from the following equation:

$$A_{\beta} = \frac{B \times 1000}{2.22 \times V \times D} \qquad ------3.24$$

where,

B is the net beta count rate (gross count rate minus the background count rate at the beta voltage plateau), D is the beta efficiency factor read from the graph of efficiency versus mg of dust per cm² of filter area (cpm/dpm), V is the volume of sample aliquot (m³), and 2.22 is the conversion factor from dpm/pCi **[123]**.

When the counting beta radioactivity in the presence of alpha radioactivity by gas–flow proportional counting systems (at the beta plateau), alpha particles are counted; since alpha

particles are more readily absorbed by increasing sample thickness than beta particles, the alpha/beta count ratios vary with increasing sample thickness. Therefore, it is necessary to prepare a calibration curve by counting standards containing 241Am with increasing thickness of solids on the alpha plateau and then, on the beta plateau, plotting the two counts' ratios versus density thickness.

The alpha amplification factor (E) from that curve is used to correct the beta plateau's amplified alpha count. When the sample count indicates a significant alpha activity at the alpha voltage plateau, the sample's beta activity can be determined by counting the sample at the beta voltage plateau. Then the activity can be calculated by the following equation:

$$A_{\beta} = \frac{(B - AE) \times 1000}{2.22 \times V \times D} \qquad ------3.25$$

where,

B, D, A are as defined in Eqs. (3.23 and 3.24), E is the alpha amplification factor read from the graph of the ratio of alpha counted at the beta voltage/alpha counted at the alpha voltage versus sample density thickness, V is the volume of sample aliquot (m^3), and 2.22 is the conversion factor from dpm/pCi **[123]**. Finally, all results were converted from (pCi m^{-3}) to (Bq m^{-3}).

b) Calculation of total effective dose

Estimated effective dose due to the inhalation of natural radionuclide particles from the air as below:

$$D_{inh} = C_R \times I_F \times E_D \qquad ------3.26$$

where,

Dinh is the annual effective dose to an individual due to the inhalation of radionuclides (Sv/8 h), C_R is the activity concentration in the air (mBq m^{-3}), I_F represents the diary intake

of air (m^3 day^{-1}), and E_D is the inhalation dose conversion factor for radionuclide (Sv Bq^{-1}). The E_D values are taken from annals of the EPA reports **[124]**.

3.11 Analytical methods for natural radioactivity concentrations and risk assessment

a) Isotope activity concentration

An isotope of potassium (^{40}K), lead (^{210}Pb), thorium (^{232}Th), and uranium (^{234}, ^{235}, and ^{238}U) have measured in particulate matters ($PM_{2.5}$, PM_{10}, and SPM) aerosol by gamma spectrometry using p–type High–Purity Germanium (HPGe) detector with carbon fiber window. The radioactivity concentrations of the isotopes ^{40}K, ^{210}Pb, ^{232}Th, ^{234}, ^{235}, and ^{238}U in the collected $PM_{2.5}$, PM_{10}, and SPM samples were calculated using the following:

$$\text{Isotope activity concentration}\left(\frac{\mu Bq}{m^3}\right) = \frac{(S-B)\times 10^4}{A \times V \times \in} \qquad -----3.27$$

where,

S = Sample count per second

B = Background count per second

A = Abundance

V = Volume of air sampled (m^3)

$\in$ = Efficiency

b) Radium equivalent activity

Radium equivalent (Ra_{eq}) index in Bq kg^{-1} is a widely used radiological hazard index. It can be used to assess the real activity level of ^{40}K, ^{232}Th, and ^{238}U in soil (or accumulated $PM_{2.5}$, PM_{10}, and SPM).

It was calculated using the following equation **[125]**

$$Ra_{eq} = A_U + 1.429A_{Th} + 0.077A_K \quad ------3.28$$

where,

A_U, A_{Th} and A_K are the activity concentration (Bq kg^{-1}) of ^{238}U, ^{232}Th, and ^{40}K, respectively. The formula is based on the assumption the 10 Bq kg^{-1} of ^{238}U, 7 Bq kg^{-1} of ^{232}Th, and 130 Bq kg^{-1} of ^{40}K produce the same gamma dose rate.

c) Inhalation annual effective dose

The inhalation annual effective radiation dose $E_{h,i}$ due to $PM_{2.5}$, PM_{10} was calculated using the following equation adapted from **[126]**:

$$E_{h,i}\ (\mu Sv\ y^{-1}) = C_{a,i}\ (Bq\ m^3) \times B(m^3\ y^{-1}) \times d_{h,i}(Sv\ Bq^{-1}) \times \{(1 - F_0) + (F_0F_r)\} \quad ------3.29$$

where,

$C_{a,i}$ is the integrated activity concentration of radionuclide i associated with $PM_{2.5}$, PM_{10} in outdoor air (Bq m^{-3}), B is the breathing rate (m^3 y^{-1}), $d_{h,i}$ is the committed dose per unit intake from inhalation or effective dose coefficient (Sv Bq^{-1}), F_0 is the indoor occupancy factor and F_r is the ratio of indoor and outdoor air concentration.

The integrated activity concentration $C_{a,i}$ ($Bq\ m^{-3}$) was calculated from the following equation:

$$C_{a,i}\ (Bq\ m^{-3}) = C_{PM_{2.5}}\ (\mu g\ m^{-3}) \times A_i\ (Bq\ kg^{-1}) \times 10^{-9} \qquad ------3.30$$

The annual effective radiation dose due to inhalation of $PM_{2.5}$, PM_{10} was calculated for the six age groups identified by the International Commission of Radiological Protection, namely 3 m, 1 y, 5 y, 10 y, 15 y, and adults. For each of the age groups, the corresponding breathing rate and indoor occupancy factor **[127]**, and the effective dose coefficient for inhalation **[128]** were used.

The default modes of absorption for the isotopes were used. For the last coefficient, the activity average aerodynamic diameter was assumed to be 1 mm. The ratio of indoor to outdoor air concentration (Fr) was assumed to be 0.3 [United Nations Scientific Committee on Effects of Atomic Radiation **[126]**].

Values used to calculate the annual inhalation effective radiation dose due to the inhalation of $PM_{2.5}$ and PM_{10} for various age groups are summarized in **Table 3.5 [128]**.

Table 3.5: Values used for calculating the inhalation annual effective radiation dose due to inhalation of $PM_{2.5}$ and PM_{10} for various age groups

Age group	3 months	1 year	5 year	10 year	15 year	Adult
Breathing rate, B ($m^3\ d^{-1}$)	2.86	5.16	8.72	15.30	20.10	22.2
Indoor occupancy factor, F_0	1.00	0.96	0.88	0.88	0.90	0.92
Effective dose coefficient, dh ($\mu Sv\ Bq^{-1}$)						
^{40}K (default mode F)	0.024	0.017	0.008	0.005	0.003	0.002
^{210}Pb (default mode S)	18.0	18.0	11.0	7.2	5.9	5.6
^{232}Th (default mode S)	54.0	50.0	37.0	26.0	25.0	25.0
^{234}U (default mode M)	15.0	11.0	7.0	4.8	4.2	3.5
^{235}U (default mode M)	13.0	10.0	6.3	4.3	3.7	3.1
^{238}U (default mode M)	12.0	9.4	5.9	4.0	3.4	2.9

d) Lifetime cancer risk

The equation calculated the lifetime cancer risk (LTCR):

$$\mathrm{LTCR} = \mathrm{AED} \times \mathrm{DL} \times \mathrm{RFSE} \qquad ------3.31$$

where,

AED is the annual effective radiation dose, DL is the duration of a lifetime, the average life 70 years consider for calculation of lifetime cancer risk in Singrauli Coalfield; the RFSE is the risk factor for stochastic effects of the common population, assigned by ICRP as 0.055 Sv^{-1} **[129]**.

3.12 Exposure inhalation dose and health risk assessment

Exposure is considered as an event during which a person comes in contact with pollutants **[130]**. It is a combination of two events, viz. the occurrence of a pollutant at a specific location and one person's presence at the same place. The duration of a person's contamination is defined as the contact at one or more boundaries (e.g., mouth and skin) between a human being and contaminant(s) at a specific concentration(s) over some time. There is a subtle difference between dose and exposure. Dosage occurs only when pollutants cross the physical envelope representing the person. Exposure is also done when the pollutant only comes in contact with the envelope.

For estimation of uptake of components through the inhalation breath introduction pathway, the breathing rate of 22.2 m^3 day^{-1} for adults (age > 17 years) as given by UNSCEAR **[131]** was considered. The following equation was used to calculate the uptake of elements through inhalation:

$$\text{Uptake of element } (\mu g\ d^{-1}) = 22.2\ (m^3\ d^{-1}) \times \text{average concentration of elements } (\mu g\ m^{-3}) \qquad --------3.32$$

Health risk assessment for the populace related with inhalation breath introduction of particulate matter depended on the assessed dosage rates and the lowest observed adverse effect levels (LOAELs), characterized as the most moderate tested doses of pollutants that have been accounting for to cause harmful (adverse) health effects on people **[132]**.

The present analysis is age–specific as it divides the total population under four age–specific categories: new-borns, children (1 year), children (8–10 years), and adults, have been considered **(Table 3.6) [132]** with different body weights and breathing rates. Representing the person's physical boundary as an envelope, the record of a person's exposure as a function of time throughout the day is represented in terms of occupancy factors. Subsequently, the dose rate for the present location has been estimated through the following expression over a day:

$$\text{Inhalation dose rate } (\mu g\ kg^{-1}) = \left(\frac{BR}{BW}\right)\int_0^{24} C(t)Of(t)dt \qquad ------3.33$$

where,

BR is age–specific breathing rate (L min^{-1}), C(t) is the concentration of pollutant (μg m^{-3}), BW is age–specific body weight (kg), and Of(t) is the occupancy factor. For occupancy factors in particulate matters and gaseous pollutants, the indoor and outdoor concentrations were assumed to be equal, i.e., Of(t) = 1.

The following mathematical equation calculates the health risk assessment **[132,133]**:

$$\text{Health risk assessment} = \frac{\text{Inhalation dose rate } (\mu g\ kg^{-1})}{\text{pollutants } (\mu g\ kg^{-1}) - \text{specific LOAEL } (\mu g\ kg^{-1})} \qquad -----3.34$$

If the inhalation dosage rate surpasses LOAEL, there might be a potential health danger of inhabitants' inhalation exposure of air pollutants.

Table 3.6: Breathing rates, body weights, and LOAEL values for morbidity

Age category	Inhalation volume (m^3 day^{-1})	Bodyweight (kg)	LOAEL (μg kg^{-1})
New born	0.8	3	14.7
Children (1 year)	3.8	10	20.9
Children (8–10 years)	10	30	27.5
Adult	20	70	15.7

3.13 Health risk assessment by the mathematical model

Evaluation of the risk to human health is calculated by estimating the probability of harmful factors on the human body's adverse effects after exposure to such factors. The health effects are then evaluated by linking levels of environmental pollution and human health events **[105,134]**. According to the EPA Integrated Risk Information Database (IRIS), National Toxicology Program, Department of Health and Human Services, and International Agency for Research on Cancer (IARC), the pollutants can be divided into carcinogens and non–carcinogens. In this study, these four metals, i.e., As, Cd, Cr(VI), and Ni are accepted as human carcinogens in one form or another or particular routes of exposure **[135-138]**, while Cu, Hg, Mn, Pb, and Zn are non–carcinogenic, and affect the human immune system through the respiratory system. The brief risk assessment of human health elements in carcinogenic and non–carcinogenic effects is discussed here.

a) Health risk

Normal average daily dose (ADD, in mg $(kg\ d)^{-1}$) is used for non–carcinogenic materials, and lifetime average daily dose (LADD, in mg $(kg\ d)^{-1}$) is used for carcinogenic materials. The exposure dose rate calculation by the following expression:

$$\text{ADD or LADD} = \frac{\text{C} \times \text{IR} \times \text{ED}}{\text{BW} \times \text{AT}} \qquad ------3.35$$

where,

C represents the concentration of pollutants (mg m^{-3}); IR is respiration rate (m^3 d^{-1}); ED is duration of exposure (d); BW is body weight (kg); and AT is the average exposure time (d) **(Table 3.7)**.

b) Assessment of carcinogenic risk

The following expression calculates an average annual excess risk of cancer for an individual:

$$R = \frac{1 - e^{-LADD/SF}}{70} \qquad ------3.36$$

where,

R is the average annual excess risk of cancer for an individual, dimensionless; SF is the level of intensity of carcinogenic chemicals [mg/(kg d)] **(Table 3.8)**; and 70 is the number of an individual's average lifetime in years.

c) Assessment of non–carcinogenic risk

The following expression calculates a dimensionless average annual excess risk for exposure to non–carcinogenic substances for an individual:

$$R = \frac{10^{-6}\ ADD}{70\ RfD} \qquad ------3.37$$

where,

RfD is the reference dose [(mg/(kg d)]; 70 is the number of an individual's average lifetime in years; 10^{-6} is the level of risk acceptance for the RfD **(Table 3.8)**.

Table 3.7: Exposure parameters for uptake through the respiratory system **[139, 140]**

Group	IR (m^3 d^{-1})	BW (kg)	ED (d)	AT for carcinogenic (d)	AT for non–carcinogenic (d)
Male	15.2	70	10950	25550	10950
Female	11.3	60	10950	25550	10950
Children	8.7	36	6570	25550	6570

Table 3.8: Reaction parameters for heavy metals entering the human body through the respiratory system **[139, 140]**

Element	Nature	SF (mg/kg d)	RfD (mg/kg d)
Cr	Carcinogenic	56	
Ni	Carcinogenic	1.19	
Cd	Carcinogenic	8.4	
As	Carcinogenic	20.7	
Cu	Non–carcinogenic		0.002
Zn	Non–carcinogenic		0.01
Pb	Non–carcinogenic		0.00043
Hg	Non–carcinogenic		0.0001
Mn	Non–carcinogenic		0.0003

3.14 Receptor modeling for source identification and apportionment

a) Mineralogical investigation for the particulate matter

A qualitative and quantitative study on particulate matter samples' mineralogy was carried out using XRD and SEM methods. Analysis work carried out at the Central Instrument Facility, Indian Institute of Technology (Banaras Hindu University), Varanasi, India. The method of measurement was based on direct sample analysis method. In this method, the specific amount of particulate matter sample was kept on a particular slide provided with the instrument, and then the slide along with simple inserted into the analysis chamber of XRD and SEM to get the impression pattern and images, respectively. Physical characterization of different particulate matter sizes was performed using electron scanning microscopy to determine the morphology of airborne particles. Approximately a piece of filter paper was cut and coated with gold (Au) to prepare the SEM analysis samples. Three images of one sample were taken at a magnification of ×3000, ×5000, and × 10,000. The

XRD patterns of particulate matter simple were made at room temperature in a wide range of Bragg angle 2θ ($20^{o} \leq 2\theta \leq 90$) with scanning speed of 1^{o} per minute using of CuKu radiation, and the operating condition was maintained at 34 kV, 24 mA, and Ni filter **[141,142]**. The raw output files are converted to .rd files by a converter software. After the conversion to .rd files, the XRD graphs were analyzed by specific software. XRD each peak corresponding d–spacing and 2^{o}theta values were compared with the reference pattern line to determine the corresponding compound or mineral present in the sample of different sizes of particulate matters. XRD pattern was recorded from each sample to find out different mineral present.

b) Principal component analysis

Among multivariate factor analysis, principal component analysis (PCA) is often used as an exploratory tool that combines FA with a multilinear regression to quantify particulate source contribution. The fundamental equation that governs the principal component analysis is the mass balance equation. Particulate, chemical speciation subject to principal component analysis forms a complementary set of components that need to be described as per source profile. The principal component analysis uses orthogonal decomposition to identify an individual group of elements (PCs) connected with variables through-loading factors. These PCs are used to share the datasets entire variability while the first PC shares the most. PCs with maximum variance are interpreted as the most influential source while each succeeding PC's, in turn, has the highest variation. A high correlation exists within every set of components, while among individual PCs, minimum or no correlation exists. In the principal component analysis, loading factors connect individual variables to different components through orthogonal rotations like varimax **[93,116]**.

The principal component analysis is the most common model for source apportionment studies, probably because of its simplistic analytic procedure. However, the physical significance of the PCA outcome is often subject to realization, and it is virtually dependent on the modeler on how to extrapolate the outcome **[143]**. The availability of specific tracers or usage of a single tracer for multiple sources again may critically limit its application. The principal component analysis is principally based on the statistical association of data rather than particulate, chemical nature, and, therefore, often used to generalize the datasets originally have **[92,144]**. Moreover, it is based upon the assumption that the dataset is distributed normally, which may not be valid for all the cases **[36,143]**.

Assuming a linear relationship between the total mass concentration and each species' contributions, Principal component analysis factors the data in several steps. First, the chemical composition data are transformed into a dimensionless standardized form:

$$Z_{ij} = \frac{C_{ij} - \overline{C_j}}{\sigma_j} \qquad ------3.38$$

where,

i = 1, …, n samples; j = 1, …, m elements; C_{ij} is the concentration of element j in sample i; and $\overline{C_j}$ and σ_j are the arithmetic mean concentration and the standard deviation for element j, respectively.

The principal component analysis model is expressed as

$$Z_{ij} = \sum_{k=1}^{p} g_{ik} h_{kj} \qquad ------3.39$$

where,

k = 1, …, p sources which is g_{ik} and h_{kj} as factor loading and factor score

This equation is solved by eigenvector decomposition. Varimax rotation is often used to redistribute the variance and provide a more interpretable structure to the factors.

c) Positive matrix factorization

Positive matrix factorization is a convenient and helpful factor analysis model that decomposes a matrix of sample data into two matrices: factor contribution matrix and factor profile matrix, in terms of observations at the sampling sites **[145,146]**.

The principle can be expressed as:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad ------3.40$$

where,

x_{ij} is the species concentration of j^{th} in the i^{th} sample,

g_{ik} is the contribution of the k^{th} factor to the i^{th} sample,

f_{kj} is the j^{th} species fraction from the k^{th} source,

e_{ij} is the residual related with the j^{th} species concentration measured in the i^{th} sample,

and p is the total number of independent sources.

The object function Q can be allowed to review the distribution of each species to evaluate the stability of the solution, which is defined as:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{\mu_{ij}}\right]^2 \qquad ------3.41$$

where,

μ_{ij} is the uncertainty of j^{th} species in the i^{th} sample, which is applied to weight the observations that contain sampling errors, detection limits, missing data, and outliers **[146-149]**. EPA PMF 5.0 was used to identify the potential sources of different sizes of particulate matter.