INORGANIC AEROSOL ANALYSIS

Concepts, Analytical Techniques and Indian Perspectives

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Dedicated

To

Parents & Faimly

Preface

The authors take pleasure in presenting this book entitled "**Inorganic Aerosol Analysis**''. Since inorganic aerosols are comprised of water-soluble ions, trace metals, mineral dust, and other elemental species, are of particular scientific interest due to their diverse natural and anthropogenic origins and their involvement in atmospheric chemical processes.Besides this, India presents a unique and complex aerosol environment owing to its vast geographical diversity, rapid urbanization, industrial development, agricultural activities, biomass burning, desert dust transport, and varied climatic conditions. Consequently, aerosol studies conducted across different regions of the country have generated a wealth of scientific information over the past several decades. However, these valuable findings remain scattered across journals, reports, and institutional publications, making it difficult for students, researchers, and policymakers to access a consolidated source of information.

In present work, selected Reports from India, has been prepared with the objective of bringing together important concepts, analytical methodologies, and selected Indian studies related to inorganic aerosols.

The entire book has been divided into six units according to the various aspects of inorganic aerosol analysis. Itbegins with an introduction to aerosols, including basic terminology, the need for aerosol analysis, and the scope of inorganic aerosol research. It then discusses the inorganic aerosol complosition, emphasizing major inorganic constituents and their environmental significance. Subsequent chapters describe aerosol sampling techniques, filter media selection.

A major portion of the book is devoted to analytical techniques used for inorganic aerosol characterization. Various elemental

and ionic analytical methods—including X-ray fluorescence spectroscopy, proton-induced X-ray emission, atomic absorption spectroscopy, inductively coupled plasma spectrometry, ion chromatography, capillary electrophoresis, potentiometry, and Fourier transform infrared spectroscopy—are explained with emphasis on their principles, applications, strengths, and limitations. These techniques constitute the backbone of modern aerosol chemistry and are widely employed in environmental monitoring laboratories worldwide.

The book further summarizes selected reports from different regions of India, highlighting the spatial variability of aerosol composition, dominant ionic and elemental species, source characteristics, and regional environmental conditions.

This book concludes with recommendations intended to encourage the adoption of advanced analytical techniques for future inorganic aerosol investigations.At the end book, selected and some specific references have also been mentioned therein.

It is hoped that this volume will serve as a useful reference for undergraduate and postgraduate students, research scholars, environmental scientists, chemists, atmospheric researchers, and professionals engaged in air quality monitoring and environmental management. The authors also hope that this compilation will stimulate further research on inorganic aerosols and contribute to improved understanding of atmospheric chemistry in India.

We take this opportunity to express our sincere thanks to all the administration, colleagues and scholars who took pains to send us their valuable suggestions and support for the betterment and improvement of the book.

The authors sincerely hope that the present book will be warmly received by the research scholars and academicians who have keen interest in the field and the growing environmental problems. Authors strongly request the reader’s suggestions and valuable inputs for further improvement of this work.

Contents

UNIT 1
Introduction

An aerosol is a complex mixture of liquid and solid particles suspended in air. Aerosols originate from both biogenic (natural) and anthropogenic (man-made) sources and are emitted either directly into the air (primary particles) or formed through chemical reactions between pre-cursors in the atmosphere (secondary particles). Primary particles are created for most part through mechanical processes such as weathering or other grinding processes, and are therefore typically observed in particles larger than 2.5 micrometers (μm) in aerodynamic diameter (Mattias and Johan, 2004). In general the major components of primary particles are soil-related material (e.g., Fe, Si, Ca, and Mg) and organic material (e.g., pieces of pollens and spores). Precursors to secondary anthropogenic particles include nitrogen oxides, sulphur oxides and organic compounds emitted mostly from combustion process (Sitaram and Ravin, 2007). Reaction products of these compounds include a wide variety of species, many of which exist in gas phase and secondary condensed phase under normal atmospheric conditions (e.g., gas phase HNO_3 and NH_3 with solid NH_4NO_3 particles). Secondary particles are typically smaller than 2.5 μm in aerodynamic diameter and mostly composed of nitrates, sulphates, organic carbon, and elemental carbon (Soot) (Kirchnera et al., 2003).

1.1 Terminology

Aerosol is a system of fine solid or liquid particles in gaseous suspension, collectively referred to as 'particulate matter'. Dust refers to a relatively coarse range of solid particles (diameter, d > 1 μm), produced by disintegration of minerals or from resuspension by wind when sand-blasting of soil particles may often cause comminution. Fine particles formed from the gas

phase by condensation are termed as ‘smoke’ and ‘fume’. In the case of fume the particles are generally from 0.01-1 μm diameter, and are often observed as agglomerates of smaller particles. Suspended particulate matter < 15 μm diameter is usually defined as smoke. Liquid droplets are often referred to as mists *(*d > 40 μm) and fogs *(*d = 5-4 μm). Small hygroscopic particles, or condensation nuclei, are classified into Aitken nuclei (d < 0.2 μm), large (d = 0.2-2 μm), and giant (d > 2 μm) types. The term ‘haze aerosol’ is frequently encountered in optical studies and includes any air born particles that affect visibility.

1.2 Need for aerosol analysis

Aerosol analysis has seen tremendous interest and growth in the past decade. The ever-increasing demand for maintaining a healthy environment requires sophisticated ambient monitoring technologies for the determination of low contaminant concentration levels in a diversity of environmental samples. Identification and quantification of chemical components in aerosols provides important information for investigation of air pollution sources and sinks, transport, effects on human health, visibility degradation, acid deposition, material and crop damage, global climate change, and general soiling of property (U.S. Environmental Protection Agency (EPA), 2011. Increasing epidemiological studies have shown that trace metallic species in ambient fine particulate matter, are associated with cardiopulmonary morbidity and mortality. Two cohort studies estimated that a 10 μgm^{-3} increase in yearly $PM_{2.5}$ were associated with a 6% to 10.9% increase in all-causes mortality (Sorina et al., 2008; Pope et al., 2002). Also, other studies have indicated that $PM_{2.5}$ is strongly linked with hospitalization for cardiopulmonary disease (WHO 2006). Many of the adverse health effects are believed to derive from oxidative stress initiated by the formation of reactive oxygen species (ROS) within cells (Gonzalez-Flecha, 2004; Baulig et al., 2003). Numerous authors have described the induction of genotoxicity, cytotoxicity by metallic species (Florea

et al., 2005c; Florea et al., 2005a; Florea & Busselberg, 2005b) and neurotoxicity of metals, associated with their ability to penetrate the blood-brain barrier (Clarkson, 1997).Inorganic ions, especially nitrate and sulphate, contribute significantly to particulate mass and are often major important contributors to regional haze.

The chemical components of atmospheric particulate matter provides clues to identify source particles, as different sources can produce particles of different chemical composition. Source identification is then performed by advanced statistical techniques (e.g., receptor modelling, an advanced statistical analysis method for linking pollution observed at an ambient location back to its source) or by the use of mathematical simulation models (e.g., grid based) that integrate source emissions, atmospheric chemistry, and meteorology to trace the fate of source emissions through the atmosphere. Research on particulates in the atmosphere, their transfer pathways and effects has now become more inter-disciplinary, demanding the efforts of meteorologists, oceanographers, agriculturists, and medical and veterinary specialists, in addition to atmospheric chemists and physicists.

1.3 Goals and Scope of This Review

The area of aerosol analysis attracts tremendous research attention as indicated by the number of publications in the 'Atmospheric Environment' and related Journals. The number of papers submitted to 'Atmospheric Environment' and other journals, has shown major emphasis on aerosol (physico-chemical) research, covering both particulate and gaseous forms. In fact the total number of articles has increased exponentially since 1960. Although there are several excellent reviews on different analytical techniques and several books describing aerosol measurements, no comprehensive review is available regarding the bulk aerosol analysis of inorganic analytes either directly on filters or after leaching processes.

This review has three broad goals to stimulate research in this rapidly expanding multidisciplinary area. The first goal is to link requirements of known and emerging analytical systems with the principles, methodologies, and requirements for aerosol analysis. The second goal is to critically analyze the current non satisfactory performance of some analytical systems for the analysis of interest and to facilitate potential solutions to this important problem. The third goal is to demonstrate the breadth of possible applications, highlight success stories of a given analytical methodology used extensively by analysts all over the globe.

In this review, emphasis is placed on the analysis in bulk aerosol samples. Although the individual character of the particles is lost in this way, even their size distribution can be measured by bulk methods by applying sampling devices (e.g., cascade impactors and minivolume samplers) which collect the particles according to their size. Airborne samples collected on filters must be dissolved first in a solvent before analysis. Frequently, water is used as an appropriate extraction solvent. The objective is to summarize and briefly discuss the methods employed for ion and elemental analysis in bulk aerosol samples. Some of these methods show close similarity in analytical procedure and will be discussed together, but summary of different papers and articles regarding different analytical procedures for aerosol analysis has been organized in the end, according to the extensive popularity of the technique, because in this way it is easier to find the approach more similar to one concrete problem. The choice of focus and detail on techniques discussed in this review was provided by their current and future potential applicability to aerosol analysis.

UNIT 2
Inorganic composition of aerosols

The inorganic fraction comprises a major proportion of the particulate matter (PM) in the atmosphere; of the remainder benzene-soluble organic compounds and biological debris, including bacterial and fungal spores. Of the major sources, soil accounts for the largest identifiable component of the coarse fraction ($PM_{2.5-10}$), whereas SO_4^{-2}, NO_3^- and NH_4^+ dominate the identifiable components within the fine fraction ($PM_{2.5}$) (Brook et al., 1997; Chan et al., 1997). In general, these components account for about 20-45% of the $PM_{2.5}$ (Scott, 2000).

Sulfate, nitrate, and ammonium are formed in the atmosphere from direct emissions of sulphur dioxides (SO_2), oxides of nitrogen (NO_x), and ammonia (NH_3) gases, respectively. Equilibrium between gas and particle species has been clearly described using models (Bassett and Seinfeld, 1983, 1984; Wexler and Seinfeld, 1991).Larson and Cass, 1989; Larson et al., 1988, also provided a scheme for the speciation of ionic material for ambient aerosols (Amundson et al., 2006). The degree of oxidation of gas species to particle species could be utilized as an index of occurrence as well as level of secondary aerosol formation (Colbeck and Harrison, 1984; Ohta and Okita, 1990).

UNIT 3
Filter media for aerosol sampling

Gravity is not fast enough to separate respirable dust and aerosol particles from air samples. Inertia, thermal and electrostatic forces must be applied to speed particle deposition, or an efficient filtration method must be used. All these methods are suitable for sampling aerosols to estimate chemical composition, particle numbers or mass concentrations.There are several instruments available for sampling of aerosol particulates in ambient air, like Konimeters, Cascade impactors, High volume Samplers, Impingers, Precipitators, etc., Samples collected on different filter media may be extracted by either hot acid procedure or by microwave extraction, with microwave extraction as a preferred method.

Several air sampling filter types are available, and the specific filter used depends upon the desired physical and chemical characteristics of the filter and the analytical methods used (Table. 3). Single filter medium is inappropriate for all desired analysis (Walter et al., 1986). Particle sampling filters consist of a tightly woven fiber mat or plastic membrane penetrated by microscopic pores. Several characteristics are important in selecting a filter media; these characteristics include (1) Particle sampling efficiency, (2) Mechanical stability, (3) Chemical stability, (4) Temperature stability, (5) Blank concentrations, (6) Flow resistance and loading capacity, and (7) Cost and availability.

UNIT 4
Techniques for inorganic aerosol analysis

In aerosol research, particulate matter ($PM_{2.5-10}$) has typically been studied using conventional analysis methods; however, a move toward on-line analysis with mass spectrometry (MS) has taken place, which will not be discussed in this review, rather emphasis has been laid on conventional sampling of PM on different filter media for an allotted amount of time followed by off-line chemical analysis by numerous techniques.There are severaltechniques utilized by analysts all over the globe for inorganic analysis of ambient PM. Some of theextensively used techniques, for inorganic component analysis, have been described here.

4.1 Elemental Analysis

Elemental analysis is a process where a sample of some material (soil, waste, particulate matter, body fluids, water, chemical compounds) is analyzed for its elemental and sometimes for its isotopic composition. It involves both qualitative and quantitative aspect of analysis. It falls with the ambit of analytical chemistry, the set of instruments involved in deciphering the chemical nature of our world. As far as chemical analysis of aerosols ($PM_{2.5-10}$) is concerned, so many techniques, including both destructive and non destructive are being used by analysts all over globe.The Chemical Speciation Network uses XRF analysis for determing elemental composition of ambient aerosols collected on teflon filters. The IMPROVE visibility network uses proton induced X-ray emission (PIXE). Neutron activation analysis is a sensitive multielemental method that complements XRF and PIXE. Here

emphasis are being laid to describe some of the widely used techniques for PM analysis.

4.1.1 X-ray spectrometry.

X-ray spectrometric methods have been used widely for trace analysis of environmental samples and continues to be a fertile area for research (Bos, 1984). They have found wide spread application in the atmospheric analysis such as airborne particulate matter, because of very low limit of detection (LOD) and besides they also provide matrix insensitivity. X-ray spectrometric methods are attractive for aerosol analysis, because in principle, the determinations may be performed by using the specimen on the filter. Their application for analysis of aerosol particles in various forms has been summed up here in this review and their extensive use by analysts, has also been summerised at the end. The various X-ray spectrometric methods are mainly categorised as;

4.1.1.1X-ray fluorescence (XRF)

The analysis of aerosols is one of the major applications of X-ray fluorescence and it has been in extensive use for two decades, also for official monitoring programs like in the USA. There are hundreds of publications on this topic; every year approximately 50 or so still appear in the literature and several extensive reviews have also been published (Steven et al., 2003). XRF measurements of aerosols are usually done in the context of monitoring of toxic heavy metals. The determination of the content of heavy metals in airborne particulate matter does, of course, involve different steps: first the particles are sampled by filters or impactor collection plates, and then the collected particles are preferably measured directly. The fact that loaded aerosol filters can be presented directly to an XRF instrument, often as an ideal thin target, constitutes a major advantage of XRF over nearly all other trace analysis techniques like AAS, ICP-AES, ICP-MS, etc.

XRF iscommonly used as a non-destructive technique involved in quantification of broad range of minor and trace elements in ambient aerosols collected on filters. It is generally applicable to elements with atomic number (Z) > 12 due to the some instrumental limitations and low X-ray yields for lighter elements. The ability of this method to detect and quantify key elements of an aerosol deposit depends in part on the type of filter, aerial density of filter, filter impurities relative to the expected concentration in the PM deposit, and the variability of these impurities between filters as both the deposit and filter are analysed simultaneously (Adams and Van Grieken,1975). X-ray fluorescence analysis can be quantitative by comparing sample X-ray spectra to a library of known element spectra or quantitative by calculating spectral peak areas and relating them to calibration standards, with corrections for X-ray attenuation. Elemental concentration can be obtained by dividing the mass of element calculated per filter by the volume of the air sampled through filter.

In X-ray fluorescence, the filter deposit is irradiated by high energy X-rays that eject inner shell electrons from the atoms of each element in the sample. When a higher energy electron drops into the vacant lower energy orbital, a fluorescent X-ray photon is released. The energy of this photon is unique to each element, and the number of photons is proportional to the concentration of the element (Dennis and RaJ,2001).

XRF instruments using polarised optics are now being used for routine air monitoring applications. The sensitivity of XRF methods depends upon, energy of the incident radiation, the geometry of the instrument used and the efficiency of the detector. The LOD achieved depends upon sensitivity of instrument and the background level of sample matrix. The overall precision of XRF measurements is promising.

XRF methods can be broadly divided into two categories: wavelength dispersive X-ray fluorescence (WDXRF), which

utilizes crystal diffraction for observation of fluorescent X-raysand energy dispersive X-ray fluorescence (EDXRF), which uses a silicon semiconductor detector. The WDXRF method is characterized by high spectral resolution, which minimizes peak overlaps. It requires high power excitation to overcome low sensitivity, resulting in excessive sample heating and potential degradation (Haupt, 1997). Conversely, EDXRF features high sensitivity but less spectral resolution, requiring complex spectral deconvolution procedures. The spectrum obtained is automatically analysed at the end of the accumulation period by a microcomputer system which uses a spectrum stripping program and the stored spectra of the elements to be analysed.

The bulk chemical characterization of the aerosol samples has been performed by EDXRF. This method was successfully applied earlier by Camuffo et al. (1997) to analyse aerosol samples collected in the Correr Museum, Venice, Italy. Injuk et al. (2002) used EDXRF to determine the chemical composition of the aerosol samples taken in the Miyagi Museum of Art, Sendai, Japan. Japanese researchers, undertaking measurements in Osaka, report calculated detection limits of 3.6, 3.5 and 1.0 $ngcm^{-3}$for S, Pb and Zn respectively (Owen et al., 2011).

XRF methods can be further categorized as direct/filtered excitation, where the X-ray beam from the tube is optionally filtered and then focused directly on the sample, or secondary target excitation, where the beam is focused on a target of material selected to produce X-rays of the desired energy (Holynska et al., 1997). The secondary fluorescent radiation is then used to excite the samples. The direct/filtered approach has the advantage of delivering higher incident radiation flux to the sample for a given X-ray tube power, since about 99% of the incident energy is lost in a secondary fluorescence. However, the secondary fluorescence approach produces a more nearly monochromatic excitation that reduces unwanted scatter from the filter, there by yielding better detection limits. By using secondary target, high sensitivities have been achieved for wide

range of elements like Titanium, Molybdenum and Samarium (Fittschen et al., 2006; Robert and Thomas, 1978).

Although XRF is a fast and inexpensive technique; however, it cannot be used for the analysis of elements lighter than AI, nor routinely to observe some trace elements important for atmospheric pollution such as Se, As, Sb, Cd, and Sn. Another potential problem is the interference of spectral lines with heavy elements; for example, the K-lines of sulphur suffer interference from one of the M-lines of lead (Alfoldy, 2001). In this case, the uncertainty in the result for sulphur is estimated to be about 5 percent of the lead concentration. XRF analysis results in precession values of 5-10% for atmospheric samples. XRF is an excellent method for the analysis of atmospheric samples. Except for e.g., Neutron Activation Analysis (NAA) (which measures a very different suit of elements), hardly any other analysis method can measure directly on loaded filter; nearly always a tedious digestion step is required in which refractory elements may not be dissolved. Therefore the use of XRF should be encouraged in this field, even if other analysis methods are available.

4.1.1.2 Particle Induced X-Ray Emission Analysis (PIXE)

PIXE is a powerful method for multi-elemental (including heavy metals) analysis of solid samples.It was invented in the early 70's when the need for trace element analyses of environmental samples coincided with available capacity on low energy accelerators, originally designed for nuclear physics studies, and the development of high resolution semiconductor detectors, which enabled separation of the characteristic X-rays from elements with $Z \geq 13$ (Ryan, et al., 2008). Used routinely for simple bulk analysis, PIXE is fast, reliable as compared to other techniques and cost efficient. Solid samples can be analysed without any pre-treatment. Detection limits below 1 ppm can be achieved for many elements (Van Malderen et al., 2001).

PIXE is a highly sensitive and efficient means of analyzing the elemental composition of bulk samples of atmospheric aerosols (Staskal et al., 2008). It offers an attractive alternative to the tube excited technique (XRF). PIXE can be used for routine quantitative analysis of 10 to 15 elements simultaneously in atmospheric aerosol samples (Thomasin et al., 2005).PIXE has been applied where light elements are of main concern e.g.,from F to S, and reduces problems of attenuation of soft X-ray. This technique is a non-destructive, multi-elemental procedure in which protons excite the atoms of a sample; the characteristic emitted X-rays are used to identify and quantify of each element. The analysis is carried out by 5 MeV proton irradiation in a Van de Graf accelerator, measurement of the characteristic X-rays by Si-Li detector and X-ray spectrum resolution by small computer. Complementary information may be collected by proton elastic scattering analysis (PESA), which provides hydrogen mass concentrations through measurements of forward proton scattering and uses higher energy photons than PIXE (Bench et al., 2002). Both methods are commonly used for the analysis of aerosol samples collected by a Davis Rotating-drum Uniform-size-cut Monitoring (DRUM) impactor onto continuously moving substrates capable of following chemical changes in aerosol composition in a time-resolved manner (Johnson et al., 2008).

Several limitations of the PIXE analyses must be considered, namely, the loss of semi volatile compounds under a vacuum during analysis and the inability to determine the molecular form of individual elements. Although in principle XRF and PIXE are used to analyse the same group of elements, PIXE is capable of measuring smaller quantities of particulate matter. In addition, PIXE allows the analysis of more than 250 samples per 24-hour accelerator day, providing 5000 or more elemental determinations. Some of the studies conducted using PIXE for aerosol analysis (Winchester et al., 1981a; Lannefors et al., 1983; Aldape et al., 1996; Makra et al., 2002 and Treiger et al., 1994).

4.1.1.3 Micro X-ray fluorescence (MXRF)

Micro X-ray fluorescence is used to study both homogeneous and heterogeneous particle systems. MXRF is a method that shows promise for both bulk and single particle analysis (Tianxi et al., 2010). MXRF employs polycapillary optics that are used in conjunction with the X-ray source to focus incident X-rays (Thomasin et al., 2005). This results in smaller beam diameters (i.e., 10-50 μm) and higher X-ray fluxes (107 photons/s) at the sample surface, increasing detection sensitivity and enhancing performance over conventional X-ray fluorescence instruments. The smaller X-ray focal spot allows for much smaller sample features to be observed and characterized than larger spot techniques such as XRF, TXRF, and PIXE. Unlike PIXE and other techniques which require specialized instrumentation rarely accessible to the average user, such as a synchrotron source, MXRF is readily available as a simple bench-top instrument (Nicolas et al., 2008).

It is a non-destructive technique, leaving the sample intact for other analyses to be performed on it. In addition to bulk and single particle analysis,elemental imaging can be performed by MXRF with the ability to scan over large areas to map the distribution and elemental characteristics of particles deposited on or impregnated into a given substrate. Some of the reports using MXRF for aerosol analysis (Thompsin et al. 2005); Van Malderen et al., 2001; Lachlan et al., 2011; Silvia et al., 2005; Tianxi Sun et al., 2010).

4.1.1.4 Total reflection X-ray fluorescence (TXRF)

Total reflection X-ray fluorescence analysishas shown successful applications for the analysis of total element contents of atmospheric particulate matter (Nobert et al., 2009). In total reflection X-ray fluorescence (TXRF); incoming radiation is incidented on the sample at less than critical angle and is totally

reflected. Using synchrotron radiation sources, with very high photon fluxes, limit of detection (LODs) upto 0.03pg is possible.

TXRF is a very sensitive method for element determinations which has been successfully used for size-resolved aerosol analysis e.g, direct analysis of airborne dust collected with an impactor on glassy carbon and Si-wafer carriers using conventional X-ray tube excitation (Ebert et al., 1997; Stahlschmidt et al., 1997).Even more sensitive is the excitation with synchrotron radiation. Its combination with size-resolved aerosol sampling is promising using synchrotron radiation in conventional XRF geometry (incident beam 45°) (Theisen et al., 1999). However in elemental determinations of aerosol samples collected with the aid of impactors and analyzed with synchrotron radiation X-ray fluorescence (SR-TXRF), an accurate and reliable calibration up to now, however, is often problematic. The addition of standard solution with micropipettes for aerosol analyses with TXRF may suffer from the sample spots or line destruction as a result of the relatively high amount of liquid (Fittschen et al., 2006). However calibration with nano-droplets of 10 to 50 nano litre (nL) was found to give excellent results in the determination of trace impurities with TXRF in semiconductor material (Miller et al., 2004).Therefore, it was decided to investigate the suitability of a calibration in aerosol sample analysis by SR-TXRF under the use of pico-droplets, generated by inkjet printers and having a volume ranging from 5 to 130 picolitre (pl). Other multielemental methods like PIXE, Inductively coupled plasma optical emission spectroscopy (ICP-OES), Inductively coupled plasma mass spectrometry (ICP-MS), Atomic absorption spectrometry (AAS) require large (milligram) amounts of sample for analysis, and a separation step of the sample from the collection substrate, which is time-consuming and subject to risks of contamination and loss of analyte (Gerhard et al., 2007). This offers microanalysis (requiring less than a few micrograms) and analysis of the particles directly on the collection substrate, but requires an accelerator facility for sample

excitation. Due to its high sensitivity, TXRF is suitable for size segregated aerosol analysis when spatially focused and applied for homogeneous samples (Schmeling et al., 1997).

TXRF was used to determine S, Ca, Cl and K in atmospheric aerosol samples with LOD's 325pg for S and 60pg for Ca (Esaka et al., 2003). Italian researchers[113] described preliminary work using TXRF for the direct analysis of aerosol particles (Margaret et al., 2011). Some more reports about TXRF application in aerosol analysis include (Fittschen et al., 2005; Borgese et al., 2012; Fittschen et al., 2008; Bontempi et al., 2010).

4.1.1.5 X-ray absorption near edge spectroscopy (XANES)

Synchrotron based X-ray absorption fine structure (XAFS) spectroscopy is a powerful technique used to investigate chemical speciation in environmental samples (Higashi and Takahashi, 2009). XFAS near absorption edge is called X-ray absorption near edge structure XANES, provides information about electronic structure of absorbing atom, reflecting oxidation stateand coordination environment of an element (Yoshio et al., 2004). Different elements have different absorption energies, which minimizes interference from other elements in sample synchrotron-based XAFS spectroscopy has, in recent years, emerged as an important tool for trace metal speciation in PM (Thoresten et al., 2000). Being non-destructive, it preserves the chemical integrity of the sample and thus eliminates the need for sequential extraction method where sample loss and undesirable chemical reaction are concerns.

Fluorescence yield XANES (FY-XANES) and conversion electron yield XANES (CEY-XANES) can be applied effectively in chemical speciation of aerosols (Takahashi et al., 2006).The former method may be regarded as bulk analysis considering size of aerosolparticles while as later is surface sensitive, because of shallow escape depth of Auger electrons from atoms irradiated by

X-rays. Coupling these two modes enables to distinguish S^{2-} species formed at the surface and in bulk of aerosol particles (Takahashi et al., 2008).Also absorption edge shows shift towards higher energies with increase in oxidation state. Apart from this the electro negativity of atoms bound to sulphur, influences the energy of absorption edge. Further S (IV) species are not very stable in ambient air, S (IV) not detectable by IC, but could be detected by XANES. For this method LOD was found to be 10% and range of quantification (RQ) 2.9%.

To the best of our knowledge, XANES proved to be successful for sulphur speciation in aerosols, although, very few works have focused on sulphur (S) XANES speciation. Takahashi et al. (2006) reported speciative S analyses from size-fractionated aerosols from a single site, collected in Japan during an episode of heavy dust transport from China and in absence of such transport.Matsumoto et al. (2006) reported some S speciative analyses on diesel vehicular emissions. Tanabe et al. (2004) have reported the valence state of sulphur on Kosa particles collected in Chinese industrial cities using XANES spectroscopy method. However Elzingaet al. (2002) applied sulphur K-edge XANES to sulphate species in carbonates, capable of distinguishing various sulphate species, depending on the counteraction in the sulphate salt. Takahashi et al. (2006) used Sulphur K edge XANES, capable of distinguishing various types of sulphates,[121] showing that main sulphate was $CaSO_4.2H_2O$ (gypsum) in coarse aerosol particles and $(NH_4)_2SO_4$ in finer particles in aerosol samples from Tsukuba city of japan. Apart, some of the reports describing speciation studies for aerosols using the XANES method include (Matrajt etal., 2008) and Speciation of Fe, Mn and Zn from aerosols collected in China and Japan during dust events by Atsuyuki et al. (2006). Huggins et al. (2002) involved the combination of XAFS spectroscopy and a simple leaching protocol involving aqueous and acidic reagents provides significant speciation information about sulphur and key metals in PM derived from combustion of fossil fuels. Moreover,

information was also obtained on readily soluble metal species that are of major interest to health effect studies of both source PM and also fine ambient PM. Sidhartha et al. (2007) used XANES for speciation of Ni and Sulphur in residual oil fly ash.

Some of the advantages of XANES include (i) its applicability to the small amount of size-fractionated samples. (ii) measurement of spectra under ambient conditions, even in the presence of a variety of other minerals and elements in aerosols, (iii) extraction of mixing ratio of several sulphur species can be through the simulation of the spectra, and (iv) by coupling fluorescence XANES and CEY-XANES, sulphur species in the bulk and at the surface of the particles can be distinguished. It is expected that the coupling of bulk chemical analysis using ion chromatography and sulphur speciation using XANES for more samples will provide information on the precise characterization of sulphate aerosols. This non-destructive method requires no pre-treatment and measurements in a fluorescence mode are extremely sensitive.

4.1.1.6X-ray-induced photoelectron spectroscopy (XPS or ESCA).

ESCA is one of the multielemental offline techniques for the identification and characterization of surface-enriched material in aerosol particles. This technique employs soft X-rays usually Mg K_α or Al K_α radiation at photon energies of hw = 1254 and 1487 eV, respectively to excite photoemission of core level electrons. Their measured kinetic energy (E_{kin}) is uniquely related to the core level binding energy (E_B)via the equation;

$$E_{kin} = hw - E_B - ø$$

Where ø is the work function of the sample. The binding energy is not only characteristic for the emitting element (via Mosely's law) but in many cases also specific for the chemical state and

environment, i.e. the oxidation state of the emitting atom(Borai et al., 2002).

ESCA is surface sensitive because only electrons excited from atoms within outer 5 nm or less (depending on $E_B$and the material) can escape from the sample without attenuation by inelastic collisions. Therefore, the ESCA technique is very promising for detailed studies of surface phenomena on aerosol particles (Gerrard et al., 1988). For example; surface chemical reactions with the carrier gas or with other aerosols, surface condensation, and surface segregation processes could be investigated. Surface concentrations differing from the bulk composition of an aerosol particle are in particular accessible to photoelectron-spectroscopical techniques. Also thin film (< 10-nm) coating procedures of aerosol particles (microencapsulation) could be monitored reliably.

ESCA measurements are generally performed "off-line" and quantitative (absolute) interpretation of signals is difficult. Despite these challenging aspects, only a few authors report the application of ESCA to aerosol samples (Gardella and Hercules, 1979; Campbell et al., 1979; Muller et al., 1987; Zhu et al., 2001).

4.1.2. Atomic Spectrometry

Atomic spectrometry encompasses a multitude of techniques of elemental analysis that are based on the decomposition of samples into the state of free atoms followed by spectroscopic determination of their concentrations. (Aleksandr et al., 2006). Atomic spectrometry is usually used to complement XRF and PIXE analysis. It can be used to analyse concentration of over 62 different metals in solution.

As far as chemical analysis of aerosols is concerned; different scientists have used different atomic spectrometric techniques for analysis (Bings et al., 2006). The main techniques include ICP-MS, ICP-AES, ICP-AAS, FAAS and GF-AAS. The nature of these techniques means that, unless technique is coupled with a

chromatographic process, there is no speciation or production of chemical data, only total elemental content. However techniques, especially ICP MS, provide accesses to the lowest LODs currently available in routine analytical chemistry (Nicolas et al., 2002). They are useful, since they provide analysis of total element content present in sample, regardless of the matrix or the environment of target element. Here we have given overview of techniques in atomic spectrometry and provide the information necessary to help analysts or beginners in the analytical field to select the one thatbest suits the specific needs and applications in aerosol analysis.

4.1.2.1 Flame atomic absorption spectroscopy (FAAS).

FAAS involves the introduction of sample into a flame where it is dissociated into its constituent atoms. Electromagnetic radiation in the UV/Visible part of the spectrum is directed through the flame and is partially absorbed in a manner characteristic of the atoms present (Deniz et al., 2002).

FAAS is relatively inexpensive and simple to operate. FAAS can be used for the analysis of liquid samples only and relatively large sample volumes are required. FAAS is also a relatively slow technique and is best used when only single elements or a few elements are to be determined within a sample. When a large number of elements require measurement, other techniques may be substantially quicker (Veselin et al., 2003). Compounds of the alkali metals and many of the heavy metals such as lead or cadmium and transition metals like manganese or nickel are all atomized with good efficiency, with typical FAAS detection limits in the sub-ppm range. However, some refractory elements cannot be determined with good sensitivity because flame temperatures are often not hot enough to induce complete atomization. At its worst, this problem means that trace levels of B, W, Ta, Zr, As and Sn may not be determined by FAAS (Hywel et al., 2001).

A number of studies conducted worldwide have used FAAS for elemental analysis in aerosols. One of the analysis conducted by Voutsa et al. (2002) employed FAAS, after sonication of loaded filters with a mixture of HNO_3 and HCl acid for the determination of Cd, Cu, Mn, Ni, Pb and V. Hofmann et al. (1998) and Shah et al. (2006) include some more reports about application of FAAS for aerosol analysis.

4.1.2.2 Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS).

GF-AAS uses much higher atomization temperatures (up to 3000K), compared to FAAS. It exhibits LODs 10-100 times better than those of FAAS. It is a single elemental technique. However, relatively small quantities of both solid and liquid samples may be analyzed and many of the interferences from which GF-AAS used to suffer, mostly associated with the sample matrix, can be overcome with a combination of background modification. However because of temperature limitation, refractory elemental performance is still somewhat limited. LODs for many elements by GFAAS exceed those of ICP-AES and in fact rival those of ICP-MS for a fraction of the cost (Steven et al., 1996; Joseph et al., 1990).

Consequently, applications of GFAAS for ambient aerosol monitoring have been more successful than ICP-AES. Chakrabarti et al. (1987) filtered ambient air through a porous graphite probe at 0.1L min^{-1} and then inserted the probe directly into the graphite furnace for analysis of Pb, Cd, Zn, Mn Cu, Cr, Ni, and V.However higher flow rates could not be used because of the high pressure drop across the graphite probe. Sneddon and co-workers (Sneddon 1985; Lee et al., 1996) have developed a system for collecting atmospheric particles directly or to the interior surface of the graphite furnace tube by inertial impaction. The small orifice size of a graphite furnace tube limits the system to a single nozzle which is incapable of collecting particles <0.3 μm in diameter, wherein lie primary emissions from high-

temperature combustion sources. Detection limits were generally 10 to 20 fold greater than needed for analysis of ambient air. Manuel et al. (1986) described analysis of Te and Se in atmospheric aerosols by ion exchange and atomic absorption using graphite furnace atomiser. Here ion exchange reduced negative errors from other samples that are concentrated in atmospheric aerosols to a level of <10%. This method takes advantage of high sensitivity of AA for Te after removing elements by cation exchange.

4.1.2.3 Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) or ICP-OES.

ICP-AES, often referred to simply as ICP, is a multi-element analysis technique that uses an inductively coupled plasma source to dissociate the sample into its constituent atoms or ions, exciting them to a level where they emit light of a characteristic wavelength (Wendt et al., 1965). A detector measures the intensity of the emitted light, and calculates the concentration of that particular element in the sample. When undergoing ICP analysis, the sample experiences temperatures as high as 10,000°C, where even the most refractory elements are atomized with high efficiency (Taketoshi et al., 2005). As a result, detection limits for these elements can be orders of magnitude lower with ICP compared to FAAS techniques, typically at the 1-10 ppb level.

ICP-AES is more expensive than the AAS techniques and can suffer from more interferences, meaning that positively biased results, particularly at low concentrations, are common. Simultaneous ICP instruments can screen for up to 60 elements in a single sample run of less than one minute, with no compromise of precision or detection limits. Sequential ICPs can provide analytical results for about five elements per minute.

ICP-AES has been used all over word for atmospheric analysis, some of examples include; Taku et al. (2007) carried out

multielement analysis of PM_{10} samples collected in ambient air of Nagoya City by ICP-AES and ICP-MS after sample decomposition. Upto 30 elements were analysed including Cs, Mn, Ba, Ca, Sr, Co, Fe, Ti Ca, Al, Mg, Ni, Rb, Ce, La, Co, etc, in the concentration range of sub-µg. Guvenius et al. (2003) resuspended of filter extracts with1 M HCl and analyzed by ICP-AES for preliminary evaluation of their elemental content in terms of six metals, using an analytical protocol closely following U.S. Environmental Protection Agency (U.S. EPA).Menzel et al. (2002) showed the comparative study of elemental analyses of aerosol material by PIXE and ICP-AES, results showed agreement upto 15% or better.

4.1.2.4 Inductively Coupled Plasma - Mass Spectrometry (ICP-MS).

ICP-MS remains at the forefront as a routine means of determining trace levels of metals captured on air filter samples. So this section of the review focuses on important applications of this technique. ICP-MS, as in mass spectrometry, ionizes the sample using same type of intense argon plasma used for ICP-AES, but detection of elemental species involves conventional MS techniques. This can employ either quadruple or a magnetic sector as the mass filter. The technique is expensive even after several years of development but offers the best characteristics of all the atomic spectrometries in terms of sensitivity, LODs, throughput and multi-element measurement (Karl et al., 2002).

IC P-MS has several attractive features compared with other analytical techniques, e.g., the spectra are simple to interpret and mainly free from inter-element interferences, isotopic information is inherent, the multi-elemental capability allows a high sample throughput, the detection limits are superior to those in most conventional techniques with a wide dynamic range and most of the elements in the Periodic table can be detected (Danadurai et al., 2011)

Since being a routine means of determing trace elements in aerosol samples all over the world, so some of the important examples of this analysis include; method developed by (Norbert Jakobowski, 1998), in which ion exchange chromatography has been coupled with (ICP-MS) for elemental speciation of chromium. Both Cr (III) and Cr (IV) were detected with detection limits just above 0.1µg.This approach proved to be a promising one for development of multielemental speciation procedures. Direct solidsampling, such as in laser ablation ICPMS (LA-ICP-MS), is also useful with these techniques as it avoids not only wet decomposition but also the risk of contamination during sample preparation, and it increases the power of detection. Naoki Furuta's research group in Japan has provided a progress report on the development of their ICP-MS based system for the determination of metals, particularly Pb, in single nanoparticles (Yoshinari et al., 2010). Ambient air particles are directly aspirated into the plasma following selective particle sampling using a differential mobility analyser and an aerosol particle mass analyser. Benjamin et al. (2009) used LA-ICP-MS to examine the spatial distribution of metals in airborne particulate matter collected on air filters. Jakob et al. (2010)studied the atmospheric stability of arsines and their oxidative products in PM_{10} airborne particles. They could measure the total As content of airborne particles below 1 ngm^{-3}. Arsenic species, namely methylarsonic acid (MA), dimethyl arsenic acid (DMA) and trimethyarsineoxide (TMAO) were determined using an HPLC-ICP-MS/ES-MS methodology and were detected in 90% of the air samples collected.

4.1.3. Voltametry

Voltametry is one of the techniques of electrochemical analysiswith metals as analytes of intrest (Buffle and Tercier-Waeber, 2005). There are various types of voltametric techniques used by different analysts for trace element detection applications in different analysis and environmental samples, including anode

stripping voltametry (ASV), cathode stripping voltametry (CSV), differential pulse stripping voltametry and square wave voltametry (SWV) (Eric and Charlotte, 1999; Robert and Miloslav, 1989; Kounaves et al., 1987; Van den berg, 1991; Andrew et al., 1999).

Among these trace metal analytical techniques, ASV offers the required sensitivity and capability for multielemental analysis. ASV involves a combination of a concentration and stripping step. During the concentration step the solution is stirred or the electrode rotated, followed by a controlled potential at the hanging mercury dropping electrode (HMDE) at a potential more negative than the half wave potential of the metal ion (Migon, 1997).This leads to the reduction of the metal ion, thus forming an amalgam. The reduced reaction is allowed to take place over a fixed time period and under identical conditions. The concentration step is followed by the stripping step, the stirring is stopped and the solution allowed to come to rest. The potential applied to the electrode is then reversed to potential more positive than the half wave potential of the metal ion. As the applied potential reaches the half wave potential of the metal ion, oxidation of the amalgam occurs and the metal ion is stripped from the amalgam back into solution. In case stripping step is performed using any polarographic technique (Differential Pulse Polarography) the technique is known as differential pulse anodic stripping voltametry (DPASV).This technique is highly sensitive due to the high ratio of Faradic to non-Faradic currents generated in the electrochemical cell.

ASV method can be applied to studies to access emission from specific sources such as Pb from fuel combustion (Macleod and Lee, 1973), can be applied to ambient particles in the vicinity of Smelters and Incinerators and research studies such as monitoring metal aerosols in animal exposure chambers. The low cost of instruments, high sensitivity of the technique and the capability of determining more than one metal in a single sample solution, prompted scientists to apply the ASV technique to many diverse

areas of analysis. Colovos and co-workers developed an anodic stripping voltametric technique for determining Cd, Cu, Pb and Zn in ambient aerosols. This procedure involved collecting the particulate matter by filtration onto a membrane filter and decomposing the sample by low-temperature ashing in a bomb. The results obtained were comparable to those obtained with AAS. Ochsenkuhn-Petropoulou et al. (2001) carried out comparative study of ICP-OES, ASV and INAA for the determination of Cd, Fe and Pb in airborne particulate matter, showed good correlation coefficient for results from ICP-OES and ASV. Harrison and Winchester successfully used ASV for air pollution control studies whilst other workers monitored air samples adjacent to highways where the suspended particulate matter comprised mainly of fuel combustion products. Faraghaly and Mohamed (2004) used of square-wave voltammetry (SWV) for the determination of eight elements viz. Cd (II), Pb (II), Cu (II), Zn (II), Co (II), Ni (II), Cr (VI), and Mo (VI) in soil and indoor-airborne particulate matter. The cathodic and anodic types of the SWV technique were examined for the detection of these metal ions and It was found that the square-wave anodic stripping voltammetry is the conventional technique for the determination of Zn (II), Cd (II), Pb (II), and Cu (II), but square-wave adsorptive cathodic stripping voltammetric method was used for the determination of Co (II), Ni (II), Mo (VI) and Cr (VI). The detection limits of these metal ions were 0.03, 0.4, 0.04, 0.1, 0.15, 0.05, 0.2, and 3.2 µg/kg for Cd(II), Pb(II), Cu(II), Zn(II), Co(II), Ni(II), Cr(VI), and Mo(VI), respectively, with very good accuracy (standard deviation below 2). A comparison of analytical data for analyzing real samples was also carried out between the SWV method and GFAAS method. By the standard addition method, the recoveries were 96.6-104% with standard deviation (SD) 0.75-2.5%. The great advantage of SWV is the simplicity, selectivity, sensitivity, and shortening analysis time over the GFAAS method. Annibaldi et al. (2007), for the first time, applied an ultrasensitive square wave anodic stripping voltammetric (SWASV) procedure set up to aerosol samples for

the determination of Cd, Pb and Cu in water soluble and acid soluble fractions. Similarly **Nimmo and Gray (1994)** carried out analysis of Cu, Cd, Ni and Co in acid digested atmospheric samples using Adsorptive Cathode Stripping Voltametry (ACSV). Apart from this several studies have demonstrated the potential of the portable ultrasonic extraction (UE-ASV) method for lead monitoring in samples of interest for environmental and occupational health purposes (Ashley, 1995; Ashley et al., 1999; Sussell and Ashley, 2002).

Stripping voltametry like potentometry presents the possibility of systematic bias due to poor definition of the measurand. SV assesses the concentration of free ions in solution and ions bound with labile complexes. But it will not be able to able to assess the concentration of elements bound with the compounds that are reduced (or oxidized) at lower (or higher) potentials than applied during pre-concentration. SV will therefore usually give larger values of elemental content than potentiometry but a lower value than atomic spectrometry. In addition, the range of accessible elements, especially for ASV, is not as wide as other trace analytical techniques (about 20 elements are measured using SV compared with more than 70 for atomic spectrometries). Many elements especially for absorptive stripping voltametry require sample-preparation steps that can introduce challenging matrices and possible inaccuracies. The mostly widely encountered interference in SV is the overlap of stripping peaks of different (interfering) elements in the sample. This interference is similar in nature to secondary ion interference in ISEs.

4.1.4 Activation Analysis

The term activation analysis refers to the identification and quantitative determination by the use of radio nuclides produced from the target element. It includes Neutron activation analysis (NAA), prompt gamma-ray neutron activation analysis (PGNAA), radiochemical neutron activation analysis (RNAA) and molecular activation analysis (MAA). As for as atmospheric

analysis is concerned, it is the NAA that has been used as non-destructive technique for elemental analysis. Other methods for atmospheric perspective are not so important, so their description has been omitted.

NAA is one of the major techniques for the determination of many minor and trace elements in a large variety of solid environmental and pollution samples, such as atmospheric aerosols, particulate emissions, fly ash, coal, incineration ash and sewage sludge, etc (Lei, 2002). NAA is a sensitive analytical technique useful for performing both qualitative and quantitative multielementanalysis of major, minor, and trace elements in samples from almost every conceivable field of scientific or technicalinterest. For many elements and applications, NAA offers sensitivities that are superior to those attainable by other methods, on theorder of parts per billion or better. In addition, because of its accuracy and reliability, NAA is generally recognized as the "refereemethod" of choice when new procedures are being developed or when other methods yield results that do not agree. Worldwideapplication of NAA is so widespread it is estimated that approximately 100,000 samples undergo analysis each year.

NAA induces nuclear reactions in samples by a flux of neutrons followed by measurement of the induced radioactivity to facilitate both qualitative and quantitative identification of the elements. The sequence of events occurring during the most common type of nuclear reaction used for NAA, namely the neutron capture or (n, Y) reaction. With the use of automated sample handling, gamma-ray measurement with solid-state detectors, and computerized data processing it is generally possible to simultaneously measure more than thirty elements in most sample types without chemical processing. The application of purely instrumental procedures is commonly called instrumental neutron activation analysis (INAA) and is one of NAA's most important advantages over other analytical techniques. It is being widely used and highly accepted multielemental analytical technique for

atmospheric particulate matter. It is highly sensitive with low detection limits for most metals, but does not quantify elements such as silicon, nickel, cobalt and lead.

Sitaram and Ravin (2007) calculated the elemental concentrations of cerium (Ce), cobalt (Co), chromium (Cr), europium (Eu), iron (Fe), hafnium (Hf), scandium (Sc), strontium (Sr), tantalum (Ta), thorium (Th), ytterbium (Yb) and zinc (Zn) by the neutron activation analysis (NAA) technique in the particulate matter. NAA was used to determine the total elemental content of lyophilized world trade centre (WTC) in $PM_{2.5}$ samples. Elements like, Al, Cl, Cu, Mg, Mn, Na, Ti, and V content, samples were irradiated for 30 sec at ≤ 900 kWth, decayed for 10-30 min, and counted for 5 min. For all other elements, samples were irradiated for 6 hr at ≤ 900 kWth. As, K, Mo and Sb content, samples were decayed for 1 week and counted for 15 min each. For Fe, Ni, Ba, Ca, Cr, Sr, and Zn content, samples were decayed for 2 weeks and counted for 30 min each. Y-ray spectra were counted and compared against calibration and quality control standards, and quantitative analyses were performed (Thomas, 2004). Similarly Voutsa et al. (2002) used INAA for the determination of As, Br, Co, Cr, Fe, K, La, Na, Sb, Sc and Zn in PM_{10}. Filters were enclosed in quartz containers and irradiated for 3h, with a neutron flux of 3×10^{13} $ncm^{-2}s^{-1}$. In short the publication in 1970 of the papers by Dams et al.(1970), literature now contains a large number of papers on the INAA of airborne particulates, referred to in review articles (Yli-Tuomi et al., 2003; Lei et al., 2002).

4.2 Ionic Analysis

Ionic species comprise the bulk of mass of secondary atmospheric particulate matter (Tolocka et al., 2001; Solomon et al., 1988; Chow and Watson, 1999). Furthermore, the ionic content of the aerosol can be used to estimate source attributions at a receptor (Chow et al., 1992; Watson et al., 2002; Magliano et al., 1999). Among some of mainly used techniques, IC is a method of choice for the chemical speciation. Concentrations of both simple and

polyatomic ions, including sulphate, nitrate and organic acids, can be determined. Since the requirement of sample extractioncreates possibility of some sample loss, so methods have been developedto measure a few species directely on filters. Some of the important methods which are being widely used for analysis of ions (both cations and anions) are described here.

4.2.1 Ion Chromatography

Ion chromatography (IC) is a subset of liquid chromatography applied to the determination of ionic solutes, such as inorganic anions, cations, transition metals, and low molecular- weight organic acids. The crux of this technique lies in the use of an ionic liquids (designated the eluent or mobile phase), which passes through a solid stationary phase (uniform small diameter inorganic or polymeric particles packed into a cylindrical column) before reaching a flow-through detector. The stationary phase particles contain fixed ions and exchangeable counter ions, which are displaced by eluent ions and sample ions as they traverse the column. Although significant developments are being made in instrumentation, column packings, modes of suppression detection, for the determination of metal pollutants in wide variety of complex analytically challenging systems but ion-exchange and chelating ion exchange substrates are suitable for complex sample analysis, the latter having the advantage of being able to remove matrix interferences and preconcentrate ions of interest using a single column, and suppressed conductivity remains the primary method of detection in IC (Shaw and Haddas, 2004; Rahmalan et al., 1996). IC can be considered as a well-established, mature technique for the analysis of ionic species and many organizations, such as, American Society for Testing and Materials (ASTM), Association of Official Analytical Chemists (AOAC) and United States Environmental Protection Agency (USEPA) have standard or regulatory methods of analysis based upon IC.

In terms of the solutes analyzed in aerosol applications by IC, inorganic anions are byfar the most important. The primary reason for this is thelack of alternative methods for anion analysis, which isnot the case for cations, where many other instrumental techniques are available. A variety of methods have been employed for the analysis of inorganic anions: traditional spectroscopic techniques such as colorimetry; wet chemical methods such as gravimetric analysis, turbidimetry, and titrimetry; and electrochemical techniques such the use of an ion selective electrode (ISE) and amperometric titrations (Andrew and Sergei, 2006). Many of these methods suffer from interferences and limited sensitivity; they can be labor intensive and are often difficult to automate. A detailed review of methods for predominantly anion analysis in environmental samples has been described by Meritxell et al. (2006). It is outside the scope of this review to provide an exhaustive account of the working principles and applications of IC for ionic analytes, and further information can be found in monographs (Haddad, 1990; Weiss, 2003 and Fritz, 2000).

Ion chromatography is being used extensively for determination of ion composition of aerosols by analysts all over globe. The main reasons for success of IC in aerosol analysisincludes high sensitivity, detection limits at ppb level, mult-ion analysis per sample, rapid and easy to perform, analysis takes place only in few minutes, simple sample preparation, separation of most interfering species that limits the accuracy of other analytical methods and ability to perform online analysis (Michalski and Kurzyca, 2006; Michele et al., 2003; Peter, 2000; Wilson et al., 2002).

IC has become a routine tool for sensitive determination of ion content in aerosol analysis. The value of IC for analysis of atmospheric aerosols was first demonstrated byMulik et al. (1976). Rahmalan et al. (1996) achived separation of heavy metal ions like Cu^{2+}, Ni^{+}, Zn^{2+}, Co^{+2}, Pb^{2+} and Fe^{2+} in particulate samples by the use of complexing eluent containing 20Mm oxalic

acid, 20Mm citric acid adjusted to pH 3.6 with LiOH in IC. Upon elution separated metals were reacted with 4-(2-pyridylazo) resorcinol to form colored complexes in a post column reactor and detected by using UV visible detector at 520nm. Yuan et al. (2003) reported eleven inorganic ions (SO_4^{-2}, NO_3^-, F^-, Cl^-, NO_2^-, PO_4^{-3}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+} and 4 organic acids (acetic, formic, oxalic, and methylsulfonic acid (MSA) by IC in Beijing. Similarly concentration of inorganic ions (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{-2}, NO_3^-, Cl^-, NO_2^-, PO_4^{-3})by IC in an aliquot of the water extract, with detection limits of 10 ppb (corresponding to an average air concentration of 3 ngm^{-3}) by Decesari et al. (2001), represent few examples describing the ion analysis and utility if IC for aerosols. Besides this, analysis of atmospheric particles by Ion chromatography based systems which couple filter collection of airborne particles with ion chromatographyare explored by researchers from past few years (Dean and Ring, 1991; Liu and Dasgupta, 1996; Yan et al., 2003; Lin et al., 2002; Dasgupta and Surowiec, 1996; Lee et al., 2003; Weber et al., 2003).

Dasguptaand Toda (2003) have reviewed methods for diffusion-based collection and analysis of atmospheric gasses, specially automated IC based systems for rapid determination of gaseous constituents using a wet denuder or a diffusion scruber. Simon and Dasgupta (1993) developed an aerosol monitoring system that mixed steam with a $101mLm^{-1}$ air. Analysis was performed with a concentrator column and IC providing sulphate with LOD of $2.2min^{-1}$ and 8min sampling time. Weber and co-Workers (2001) developed a particle into liquid sampler and coupled it to IC (PILS-IC). Both cations and anions could be analyzed when using separate chromatographs and a temporal resolution of 7min and LOD of $100ngm^{-1}$ was achived. However longer analysis times are required for monitoring oxalate, formate and acetate. Similarly Particle into Liquid Sampler coupled with organic carbon (PILS-TOC) and two IC's is being used to enable high time resolution measurements of water soluble ions and water soluble carbon content (Roldin et al., 2011).

However some of the limitations of using PILS are similar to those present in extraction of water soluble species from filters. PILS approach is also susceptible to artefacts created by combining external mixture of particles into a single liquid solution. Steam jet aerosol collector (SJAC) and Continuous soluble particle collector (CSPC) are also being coupled with IC for fast near real time aerosol ionic quantification (Slanina et al., 2001).

In summary, IC is shown to provide a quick, sensitive, and reliable method for the determination of the chemical composition of inorganic ions in the atmospheric aerosols in different monitoring programs. It is impossible to describe here the extensive usage of IC for ion analysis in aerosols all over world. We have tabulated IC analysis for aerosol research at major places all over globe with detection limits and corresponding references there in.

4.2.2. Capillary Electrophoresis

Capillary Electrophoresis (CE) is a separation technique based on the differential transportation velocities of charged species in an electric field through a conductive medium, with ions as primary candidates. The migration generally occurs under the combined action of electrophoretic and electro osmotic flows generated by an electric field across the capillary. Separation of ionic species is followed by quantitative detection with systems including UV/Visible detection, photometric, amperometric, conductivity detection, etc. UV/Visible detection is very attractive, in contrast to other techniques, because it doesn't interfere with electrophoretic separation process (Andrei et al., 1999).

Initially introduced as a technique for separation of biological macromolecules, CE has since attracted high interest in other application areas, including aerosol analysis. The prospects for CE in environmental analysis seem to be highly promising owing to the technique's merits such as the proven ability to separate

complex mixtures of ionic species in a fast and efficient manner, ease of operation, low running costs, and the possibility of automation. Additionally, the element speciation potential of CE is an important benefit related to the toxicity of inorganic species because the toxicity varies markedly with the particular chemical form. Also, capabilities to conduct analyses in a miniaturised format would interest analysts who analyse routinely samples containing hazardous chemicals (Dabek-Zlotorzynska et al., 1998). However, in view of the trace levels at which many toxic inorganics occur in environmental matrices, certain problems are encountered as a consequence of sometimes inadequate detection sensitivity. With the evolution of coupled methods combining CE separation with very sensitive detectors (e.g., ICP-MS), these problems appear to be solved in a majority of environmental applications. In this regard, the commercial availability of CE-ICP-MS and different detection systems designed for CE from many experienced, bona fide companies would enhance substantially the utility of CE.

The determination of inorganic ions in atmospheric aerosols using CE has received considerable attention (Fung et al., 1998; Stahl, 1994; Dabek-Zlotorzynska and Dlouhy, 1995; Brett and Marion, 2003; Van et al., 2006). The CE determination of alkali metal, alkaline-earth metal and ammonium cations in atmospheric aerosol extracts was achieved using various electrolytes and indirect UV detection. The results obtained by the CE method agreed well with those of IC. Optimisation of the composition of the carrier electrolytes for the characteristic matrix composition of atmospheric aerosols was reported by Krivacsy et al. (1997).By adding 3.8 $mmoll^{-1}$ 18-crown-6 ether and 13.1 $mmoll^{-1}$ hydroxyisobutryic acid (HIBA) to the 5 $mmoll^{-1}$ 4-methylbenzylamine electrolyte, ammonium and potassium could be well resolved up to a concentration of 16 mgl^{-1} and calcium, sodium and magnesium up to a concentration of 4 mgl^{-1}. Recently, Fung et al. (1998) reported a new analytical procedure for the determination of leachable and total metal and also

ammonium content in fine and coarse air particulate matter using a histidine-18-crown-6, ether-lactic acid electrolyte system. Satisfactory working ranges (μg^{-1} to mg^{-1}) and detection limits (μgl^{-1}) were reported for the cations investigated. In addition, the reliability of the procedure developed was established by parallel method comparison with the ICP-AES method. The results obtained showed a better precision of the CE procedure in comparison with the ICP-AES method with no statistical significant difference between the methods. Heintzenberge et al. (2002) and Heidi et al. (2003) used CE data for assessing the size distribution of the ions in aerosols and the composition of aerosols from different locations.

4.2.3. Potentiometry

Potentiometry is an electrochemical analytical method and makes use of Ion selective electrodes (ISEs) or potentiometric sensors (Hansen et al., 1997). ISEs are passive electrochemical devices in which changes in equilibrium voltage are monitored using zero current conditions and equilibrium potential is ideally described by Nernst Equation as;

For the general redox reaction (written as a reduction)

$$aA + ne \rightleftharpoons bB$$

The Nernst equation takes the form

$$E = E^0 - (RT/nF) \log [(A)^a / (B)^b]$$

Where Ris the gas constant (8.314 (VC)/ (K mol)), E the measured electrode potential and E^0 as the standard reduction potential,Tis temperature in K, nis the stoichiometric number of electrons involved in the process, Fis the Faraday constant (96,485 Columb) andA and B are the activities of the reduced and oxidised members of the redox pair, respectively.

ISEs are restricted only to sulphate, nitrate and ammonium ions in aqueous extracts of particulate matter (Smolyakov et al., 1996). These are membrane type electrodes that produce a response or potential once immersed in a solution of the appropriate ion present. The potentiometric response is obtained by selectively extracting the ion of interest into the membrane by an appropriate counter ion. Due to hydrophobicity of the organic matrix, counter ion is constrained. One can measure the potential with a pH meter.

ISEs are easy to deploy and are inexpensive, but are prone to interference by other ions in solution. The LOD of ISEs is calculated by a method different from that of most other analytical techniques. Whereas, it is common for LODs to be defined in terms of multiple of standard deviation of a blank response, effectively the repeatability of measurement. LOD for ISEs is defined as the activity at which the extrapolated Nernestian response, for target ion, intercepts with the extrapolated potentiometric response from an infinitely dilute solution. Most of the potentiometric devices had limit of detection in micro-molar range. For ammonium ions ISEs have an operating range from about 0.04 to 1700μgml^{-1} with precession values of 2-4% and with recoveries >90% from Teflon fibers. A unique feature of potentiometry is that it measures free ion concentration,rather than total ion concentration. This can be a hindrance as well as benefit because, unless the measurand is well defined, it can lead to some systematic bias between measurement results. There have been relatively few studies of comparability of measurement methods of trace elements using ISEs, due to their unique nature of measuring concentration of free ions in solution. Ceresa et al. (2001) undertook a comparative study between ISEs and inductively coupled plasma MS (ICP-MS) of lead content of an aqueous sample and got excellent agreement down to low ppb level.

4.2.4 Colorimetry

Colorimetry refers to the measuring of colour change of solution by absorption spectroscopy. In colorimetry Beer Lambert law describes the analyte concentration and is directly proportional to the amount of light absorbed. Here the transmission of light and its absorbance have very specific meanings. These are:

Transmittance (T) = Light transmitted (l) / Incident light (l_0)

$$\text{Absorbance} = \text{Log } (I/I_0) = abc$$

where: "a" is a constant --the ability of a given molecule to absorb a particular wavelength of light

"b" is the path length--the longer the path, the less light gets through.

"c" is the concentration--the more molecules in the solution, the more light is absorbed.

To get a straight line calibration curve, absorbance vs. concentration is to be plotted. The equation of

colorimetry used for the calibration curve is Beer's Law.

where: Beer's Law is the Transmitted light = Initial light x $10^{(-abc)}$

A number of automated colorimetric systems have been devised for the determination of variety of species like SO_4^{2-}, NO_3^-, NH_4^+ ion and NO_2^-. (Tymon and Agnieszka, 2007; Cerda et al., 1998; Santosh and Manas, 2007). A sensitive, selective and rapid automated method is often employed to measure ammonium ion based on Indophenol blue method (Felix and Cardoso, 2012; Qian, 2005).Measurement of sulphate is being done by Methyl thymol-blue method (Schafer, 1967; Purnendu et al., 1967).Likely Muller et al. (1979) made use of sulphonamide to react with nitrateforming a diazo compound and providing nitrate measurement.Photometric determination of Si in air born particulate matter was also described in a two step process,

involving digestion process with a mixture of acids followed by HF and finally addition of boric acid to remove HF and finally spectrophotometric determination of Molybdosilicate blue. Determination of atmospheric tellurium by colorimetric method has been done using Bithmuthiol-II, although it is a method of low sensitivity. Arsenic could be analyzed by the colorimetric silver Diethyldithiocarbamate method (Budesinsky, 1979).Likely standard analysis of atmospheric lead, based on dithiazone method, is also an important tool for lead analysis (Badiaka and Kenchaiah, 2009; Synder, 1947).

4.2.5. Fourier Transform Infrared Spectroscopy (FTIR)

The physical state and chemical composition of aerosols and condensed phases are frequently probed by passing an FT-IR beam through the suspended aerosol population or by using attenuated total reflectance (ATR) cells to selectively probe the surface composition of aerosol long passes (Kirchner et al., 2003; Yue and Zhongming, 2010).Even though FT-IR method is still under development for its application to aerosols, butis typically used to monitor phase transitions of aerosols as a function of composition and relative humidity. FT-IR is also used to measure the composition of ambient aerosols through remote sounding the instruments abroad orbiting satellites.

Although, the main method for analyzing major ions like, Nitrate, ammonium, sulphate, etc is IC, now a developed and mature method for studying the loading of inorganic salts in aerosols (Mehlmann and Warneck, 1995; Chow and Watson, 1999; Louie et al., 2005).One drawback of IC, however, is the time required for sample preparation (up to 1 week) and analysis (2-3 hours). Moreover, IC is a destructive method of analysis. Infrared spectroscopy serves as an alternative method for analyzing inorganic salts in aerosols. Because little or no sample preparation is required. The polyatomic ions found in aerosols absorb IR radiation. For example Nitrate shows strong vibration transitions at 1400cm^{-1}, while ammonium has medium strength vibrational

transitions in the same region. In case of particulate matter analysis, species are detected by passing the infra-red light through the filter substrateor on impaction into a crystal (Mc Clenny et al., 1967). Background subtraction is used to remove absorption features due to C-C stretching and bending modes found in Teflon fibers.

FT-IR can provide mass sensitivities in the high picogram and low monogram range (Allen and Palen, 1989). Determination of sulphate, nitrate and ammonium, and organic species by functional groups on low pressure impactor stages has resulted in unique aerosol size distribution information important for understanding aerosol chemistry (Allen et al., 1994). However this method is not directly quantitative and suffers from interferences. Qualitative and quantitative spectral identification of multi atomic inorganic ions and organic compounds mainly using attenuated total reflectance ATR-FTIR and diffuse reflectance Fourier transform infrared spectroscopy (DRS-FTIR) using zinc selenide substrate has been done to measure the concentration and chemical composition of aerosols (Ronit, 2011).SimilarlyTsai et al. (2006) used DRS-FTIR method to carry out quantitative analyses of sulfate, nitrate and ammonium content in aerosols (Yue and Zhongming, 2006; Santosh and Manas, 2007; Yong et al., 2007). The viability of DRS-FTIR technique for quantitative analysis of inorganic ions in atmospheric aerosols is assessed with low detection limit and relatively high sample throughput value.

UNIT 5
Inorganic aerosol analysis in India

5.1. Introduction

Systematic studies on atmospheric aerosols were virtually non-existent in India till 1980 (except a few isolated studies). During the Indian Middle Atmosphere Programme (IMAP), a series of experiments were conducted using ground-based, balloon-borne rockets and satellite techniques, to monitor the aerosol characteristics over the Indian region by setting up observatories at a few selected sites. IMAP has set the basis for conceptual networks for aerosols, radiation and trace gases, and some of these have evolved subsequently to grow into national endeavours under well focused programmes. These networks facilitate the long-term observations of aerosols over distinct geographical environments and to assess their impacts on the region (Moorthy et al., 2008).

Aerosol trends at different regions of India reflect the complex factors which control various sources. While an increasing trend in aerosols has been observed in many cities, some have shown a decreasing trend during the last few years. Studies by the Central Pollution Control Board (CPCB), which runs a network of 342 observing stations across India, have revealed that the Respirable Suspended Particulate Matter (RSPM) at several stations far exceeds the National Ambient Air Quality Standards (NAAQS). A decreasing trend in sulphur dioxide levels has been observed in many cities and this could be due to various measures taken, such as reduction of sulphur in diesel and use of LPG instead of coal as a domestic fuel. On the other hand, a decreasing trend has been observed in nitrogen dioxide levels probably due to various

measures taken for vehicular pollution control, such as stricter vehicular emission norms.

Based on the measurements made during the past 20 years, it is obvious that there has been a steady increase in the aerosol loading in the Indian region (Krishna et al., 1997). Theconcentration of aerosols in the Indian region has reached high values and may have adverse impacts on the regional climate, agricultural production and health.Some researchers have argued that aerosols cause air quality degradation in the Asian region during winter (Lelieveld et al., 2001; Nakajima et al., 2007). Others speculate that the presence of aerosols may have an impact on ozone production in this region.

5.2 Aerosol Study in the Indian region

There have been a number of studies on atmospheric aerosols in India. However we aim at highlighting some of the important aspects that have been addressed in studies regarding inorganic analysis in continental India. In this process, the attempt is to point out some critical gaps with reference to the study of techniques for inorganic components in the Indian context. In the inorganic (ions and trace metals) aerosol studies, some major sampling sites will be taken into consideration, including Cites, Oceans and high altitudes. Some of the major sampling sites include cities like Delhi, Kolkata, Mumbai, Allahabad, Kanpur, Agra, Raipur, and Ahmadabad. Apart studies conducted over Bay of Bengal, Arabian Sea, and Indian Ocean and at high altitudes like Himalayas, Darjeeling and Mount Abu, have also been highlighted here. Looking at the average inorganic component concentration in aerosols from activities sustained in different regions, represents a near-steady-state input to the lower atmosphere, where most of the human exposure occurs. The sources are usually a combination of vehicles, commercial, construction/demolition activities and natural sources like Oceans. Similarly transports of ionic components towards marine and other aqeous environment perturb the ecosystems in

communication with different process for aerosol generation from them. These studies are help full for the design of protection devices and also other transportation design aspects.

5.3 Site description

Delhi, the capital city of India, situated in North India (28.37°N, 77.13°E) at an altitude between 213 and 305 m above sea level. It is surrounded by the Thar Desert of Rajasthan to the west and the hot plains of Central India to the south. The climate of Delhi is semi-arid and is mainly influenced by its inland position and prevalence of continental air during most of the year. Delhi, world's fourth most polluted city with respect to particulate matter (World Health Organisation., 1992) is one of the fastest developing cities of the world where about 13 million inhabitants are exposed to daily emission of pollutants from 3.6 million vehicles in addition to thousands of small-scale industries and natural sources like dust storm from the Thar desert during the pre-monsoon period. The average concentration of suspended particulate matter (SPM) remains well above the national standard throughout the year (360, 140 and 70 μg m^{-3} for industrial, residential and sensitive areas respectively (CPCB, 1999). It has been well recognised that in Delhi atmosphere, SPM is a major air pollutant originating mainly from vehicular and industrial emission besides numerous domestic coal burning units and three thermal power plants with the combined capacity of 1312 megawatt operating in different parts of the city. Coal with sulphur content of 0.5% is still used for domestic cooking in some parts of Delhi by people of low income groups. Increasing industries have been the major cause of concern for increasing air pollution problem in the city. Similarly rise of Motor vehicle population presently about 3.6 million vehicles are registered with the transport authorities.

Mumbai, commercial capital of India, highest density of population of all the Indian metropolitan cities, and is associated with with rapid industrial and commercial growth. It is situated

about midway on the western coast of India (19·23°N, 72.50°E) and is a peninsular city joined to the mainland at its northern end. Large petrochemical, fertiliser and power plants are located to the east and south-east of the city. Several thousand medium and small-scale industries, located in the city including chemical textile and dyeing, pharmaceutical, paint and pigment and metal-working industries are the sources of PM, along with oil burning and refuse burning.

Hyderabad (17.10°-17.50° N and 78.10°-78.50° E) one of the densely populated cities in India and is located on a granitic terrain and spreads over an area of 1,905sq km. The climate of the region is semiarid with a total rainfall of 700 mm with temperature variation going from 20-40°C. Because this city is fast expanding and is emerging as an important industrial and business centre, the number of vehicles has grown enormously, particularly during the last decade, results in enormous increase of aerosol particulate matter concentration in the atmosphere.

Ahmadabad (23.03°N and 72.06°E) a semi-arid climatic place with typical characteristics of an urban city (a population of about 5.5 million), highly polluted and hence a suitable choice for urban aerosol studies. It is located in the southeast of the great Thar Desert and northeast of the Arabian Sea. It a highly agriculture productive region of India and high level of pollution is observed from the burning of cow-dung, agricultural waste and wood-fuel used for residential heating purposes.

The city of Kanpur (26.46°N, 80.33°E) has a population of about 3.2 million and is situated in north-central part of in Gangetic Plane. The concentrations of particulate matter (PM_{10}) are quite high in city and the particulate matter is mostly alkaline in nature. The main sources of particulate matter emissions include industrial (200MW thermal power plants), rapidly growing vehicular transport and other combustion processes.

Kolkata (22.38°N, 88.26°E) is a highly urbanized region in eastern India with a subtropical climate. The annual mean

temperature is 26.8◦C, and humidity of 66% with maximum of 94% and minimum of 38% (Karar et al., 2006). Particulate air pollution represents a prominent environmental health concern for Kolkata city. The air quality of the city becomes worse during winter due to frequent thermal inversion and low wind speed (2-6 m/s) (Karar et al., 2006). The major contributor of particulates is mainly automobile exhaust and scattered industrial emission activities include the production of automobiles, ceramic, chemical, pharmaceuticals, food processing, heavy engineering, shipbuilding, etc. Several small-scale industries like rubber, plastic, printing, textile, metallurgical, and metal workshops are scattered mainly in the north and central part of the region.

Agra lies in a semi-arid tract of India (27.10ºN, 78.05ºE); two thirds of its peripheral boundaries are bounded by Thar Desert of Rajasthan. The main sources of aerosol production include industries, in operation in Agra city and its outskirts, are foundry and forging industry. Foundry emissions have a high concentration of particulate matter including some of the metals known to catalytically oxidize SO_2 and others gaseous pollutants. The foundries use cupolas as the melting units that use common fuels like hard coke, steam coal, wood and oil. The cupola emissions include both gases and particulates. Gaseous emissions include CO, CO_2, SO_2 and NO_xetc. The other industrial activities in Agra are rubber processing, lime oxidation and pulverization, chemicals, engineering and brick refractory kilns. Apart agricultural activity also contributes to the particulate pollution.

Raipur, the capital and the largest industrial city of a newly formed state Chhattisgarh. It lies between 21.14ºN and 81.38ºE at an elevation of 297 m above sea level with a total area of 160 km^2. Industrial and vehicular emissions, rapidly increasing constructions and fast growing population have led to a significant rise in PM levels in Raipur (Deshmukh et al., 2011). The rapid industrialization is due to the availability of ores and mineral resources in abundant including coal, limestone, granite, iron ore, bauxite, etc. Besides these, the alarming vehicular and

frequent traffic jams and overall a poor infrastructure has led to a significant rise in the PM level of the city. Bhilai Steel Plant (BSP) in Durg district happens to be largest integrated steel plant of the country. It is also a home to a number of large scale cement plants.

Oceans are the single largest sources of natural aerosols. Through the mechanism of bubble bursting at the surface of the ocean, large amounts of sea-salt particles are injected into the atmosphere (Fairall et al., 1983; Exton et al., 1985). Another important source contributing to the aerosol loading over oceans is the marine biogenic activity(Charlson et al., 1987). Oxidation of dimethyl-sulphide (DMS) emitted by marine phytoplankton is a major source of non-seasalt aerosols over remote oceanic areas (Savoie etal., 1989a;Kettle et al., 1999). In addition, a considerable amount of anthropogenic and crustal aerosols also get transported to the marine environments (Arimoto et al., 1996;Kulshrestha et al., 2001;Nair et al.,2004; Moorthy et al.,2005).The continentally derived aerosols from natural (mineral dust) and anthropogenic (SO_4^{2-} , NO_3^-) sources, when transported to the remote marine environment, can perturb the marine ecosystem in a changing climate scenario (Martin et al., 1988; Arimoto et al., 2001; Hoppel et al., 1986; Arimoto et al., 1996). So their chemical characterization helps in defining their influence on various atmospheric processes like visibility, cloud formation, dry/wet precipitation acidity, which ultimately affect the climate of a region.

The Arabian Sea, one of the most biologically productive oceanic regions and surrounded by the arid (Oman Desert on the west) and semi-arid (Thar Desert in western India) continental regions, provides an ideal marine environment to study the inflow of both natural and anthropogenic chemical constituents and their impact on the surface ocean biogeochemistry. With its unique geographical setting and well-known annual reversal in the windregimes, SW winds at the onset of SW monsoon (May onwards) and NE winds during winter months (December-

March), are expected to impart characteristic changes to the aerosol composition in the Arabian Sea-atmospheric boundary layer (AABL).Similarly, In case of BoB, the wind parcels mostly blow from the land mass (EES direction) showing the influence of anthropogenic pollutants on the marine aerosols. Most of the continental aerosols of both crustal and industrial origin are transported into the Bay of Bengal through prevailing winds in northeast monsoon season.

Increasing pollutant emissions associated with the fast-growing economies of south eastern Asian countries have led to the progressive increase of aerosol concentrations above the natural background(Gautam et al., 2009a).

Satellite observations have shown that the light absorbing aerosol hazes (which is about 3-5 mm thick) over India intensify over the Thar desert and the polluted Indo-Gangetic plain (IGP). The IGP has a sharp boundary to the north, where the Himalayas act as a barrier, extending thousands of miles southward and over the north Indian Ocean (Ramana and Ramanathan, 2007; Gautam et al., 2009c). Aerosol rich boundary layer air can be transported to higher altitudes by valley breezes on the Himalayan slopes. The transport of optically-active aerosol to the higher Himalayas is a matter of concern, since most of the glaciers in the region have been retreating since 1850 (Mayewski and Jeschke, 1979). With increasing melting rates, and are in danger of completely disappearing in the next decades The rising anthropogenic interferences from rapid urbanization and development in the Himalayas affect both the landscape and the atmospheric environments and are the causes of increasing concern (Safai et al., 1995;Sharma and Patil, 1992).

Darjeeling is one of the most popular tourist hill-stations in eastern India with a population of, 100,000. The overall areas of the Darjeeling district and Darjeeling Township are about 1200 and 11.44 square kilometres, respectively. Darjeeling Township is located at an average altitude of, 2000 meter above sea level

(masl) and surrounded by different types of topography of the lower-eastern-Himalayas. The southern region comprises the marshy low-lying area at an average height of, 100-300 masl. The apex is formed by the Phalut ridge (altitude of 3800 masl) at the border between Nepal and India. The eastern frontier lies along two rivers, locally called Tista and Rangeet.

5.4 Inorganic aerosol studies

5.4.1 Ionic analysis

Studies conducted regarding overall ionic composition in different regions are spread all over the country. Aerosol samples were collected from an industrialized part of Mumbai. These were analysed for 27 chemical species (Sharma and Patel, 1992). Size-segregated measurements of F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+ in aerosolswere made in Agra city. It was observed that the fine fraction was dominated by NH_4^+, K^+, NO_3^+ and SO_4^{2-}, whereas Na^+, Ca^{2+}, Mg^{2+}, F^- and Cl^- contributed to the coarse fraction (Kulshrestha et al., 1995). George et al. (2008) reported annual mean aerosol mass loading of 54 μg m^{-3} based on measurements of chemical composition at the tropical coastal location, Thiruvananthapuram. The chemical analysis of samples revealed the presence of Cl^-, SO_4^{2-} and NO_3^- as major anionic species, and Na^+, NH_4^+, Fe^{2+} and Ca^{2+} as the major cationic species. It was found that ions like Na^+, Cl^-, Mg^{2+} and K^+ are mainly of oceanic origin and showed a peak during monsoon season, and SO_4^{2-}, NH_4^+, PO_4^{3-}, Fe^{2+}, Al^{3+} and trace elements exhibited a peak in winter/summer. Safai et al. (2008) reported that concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ increased by 4, 2, and 3.5 times respectively, during foggy/hazy days based on measurements at Agra.Chakraborty and Gupta. (2010)analysed aerosol samples collected from Kanpur for ionic species (NH_4^+, SO_4^{2-}, NO_3^- and Cl^-) and elemental contents (Ca, Mg, Na, K, Al, Si, Fe, Ti, Mn, V, Cr, Ni, Zn, Cd, Pb, Cu, As and Se). Atmospheric aerosols were collected at a semi-urban site in Pune

city, located in the south western part of India, covering different seasons. Chemical analysis showed that anthropogenic aerosols (SO_4^{2-}, Cl^-, K^+, Ca^{2+} and Mg^{2+} together with NO_3^-, NH_4^+, Cu^{2+} and Zn^{2+}) contributed 73% of the total aerosol mass. Kulshrestha et al. (2009) studied the secondary aerosol formation at Allahabad in the Indo-Gangetic region. The average concentration of water soluble inorganic ions was 63.2μgm^{-3}. The NO_3^-, SO_4^{2-} (15.8 μgm^{-3}) and NH_4^+ concentrations contributed about 87% of the total mass of water-soluble aerosol species.Rengarajan et al. (2011) studied chemical composition of $PM_{2.5}$ over an urban site in a semi-arid region of western India during winter. The concentration of $PM_{2.5}$ ranged from 32 to 106 μg m^{-3}, in which water-soluble inorganic constituents contributed about 29% to the total aerosol mass. Das et al. (2011) measured suspended particulate matter over Bay of Bengal (BoB) and reported mass concentration of 39 μg m^{-3}. Na^+ and SO_4^{2-} were found to be the most dominant water-soluble constituents over BoB. During the ICARB field campaign, George et al. (2008) studied chemical composition of aerosols over the Arabian Sea. They found SO_4^{2-}, Cl^- and Na^+ as the major ionic species present. Apart from these, NO_3^- and Ca^{2+} were found to be dominant water soluble components. They concluded that non-sea-salt component dominates and accounts for 76% of the total aerosol mass.Nair et al. (2001) conducted studies on samples collected from the Arabian Sea and Indian Ocean. Cations such as Na^+, K^+, Mg^{2+}, Mn^{2+}, Zn^{2+}, Fe^{2+}, Cu^+ and Pb^{2+} and anions like Cl^-, SO_4^{2-} and NO_3^- were analysed. It was observed near the coastal regions only up to 40% of the total mass collected could be accounted by these ions, whereas over the open sea, 50-70% of the mass could be quantified. The first long-term measurements of aerosol chemical compositions were made by Ram et al. (2010) at Manora Peak (1950 m amsl), a high-altitude site in the central Himalayas. They reported the concentrations of Water soluble ionic species like NO_3^-, SO_4^{2-}, K^+, and Ca^{2+}. They reported that mass concentration of composite aerosols varied from 13 to 272 μg m^{-3} over this region. Measurements of chemical composition at Mount Abu

have been made at high-altitude site in western India and reported the presence of water soluble ionic species (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^-) in aerosols. They found that water-soluble ionic composition constitutes 50%, 39% and 31% of the aerosol $PM_{2.5}$ mass during winter, summer and monsoon respectively, with dominant contribution from SO_4^{2-}, NH_4^+ and HCO_3^-. Their studies indicate long-range transport of combustion products (biomass burning and fossil-fuel emissions) from northern India. They observed relatively high abundance of NO_3^- in the coarse mode during all seasons, indicating its association with mineral dust (Rastogi and Sarin, 2005; Kumar and Sarin, 2009).

5.4.2. Trace metal and elemental analysis

Apart from ionic measurements, there are a number of studies related to measurement of trace metal and different elemental concentrations in the ambient atmosphere. Pandey et al. (1998) reported concentrations of atmospheric particulate trace elements like F, As, Be, Cu, Zn, Mn, Ni, Pb, Ti, and V at Bhilai, an urban industrial location. Enrichment calculations show high enrichment of Zn, Pb, Cu, Cd, As, Be, and Cl in that area. Mahajan et al. (1996) also measured elemental composition of particulate matter and precipitation from a remote background site in India. A similar study has been carried out on trace elemental composition of atmospheric aerosols (PM_{10}) at a semi-urban site, Tirupati, southern peninsular India (Pandey et al., 1998). Sharma et al. (1992) used Energy Dispersive X-ray Fluorescence (EDXRF-Model Dewar and Cryostat with Si-Li detector) for analyzing Al, As, Br, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, S, Sb, Si, Ti, V and Zn during their study in an industrial belt in an Eastern suburban region of Bombay viz. Bhandup-Thane belt. Jyoti et al. (2007) carried out a study at Morinda, a non-industrial town of Punjab and using Proton Induced X-ray Emission (PIXE) techniqueanalysed thirteen elements namelyS, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Zn, As, Br and Pb. George et al. (2008) analysed the

metallic species like Al, Ca, Cu, Fe, Mg, Mn, Pb, Ti, Zn, etc using ICP-AES in Trivandrum, a tropical coastal location situated near the southern tip of peninsular India on its west coast. A study carried by Vankataraman et al., 2002 at the Indian Institute of Technology Bombay (IITB), a background urban site, about 10km inland from the coast and likely to receive both marine and continental aerosols. Trace elements were analysed by acid extraction and atomic emission spectroscopy (ICP-AES). Al, Si, Fe, Mn, Zn, Cu, Ca, Mg, Ni, Cr, V, As, Co, Sb, Cd and Pb. Detection limits for various elements ranged from $2x10^{-4}$ ppm. Sandeep et al. (2010) analysed aerosols for various elements like K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, and Pb using ED-XRF, from Kolkata. The concentration of different metallic elements were found in the order of Zn >Pb >Ni >Cu > Cr >Co. Chemical characterisations of atmospheric aerosols were carried out in the city of Delhi during different periods including Festival of Dewali by Perrino et al.(2011). Particulate matter collected on Teflon filters was analysed for the determination of major elements (Na, Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Sr, Ba, Pb), by using ED-XRF spectrometer mode. Cd, Sn and Sb were in principle detectable, but their atmospheric concentrations were generally below the instrumental detection limits (0.006, 0.052, 0.068 $\mu g\ m^{-3}$) respectively.

UNIT 6
Recommendations

The ionic analyses are usually done with the extraction of the ions from the filter media (Nylon or Teflon) with water or acids followed by analysis of the cations and anions separately using ion chromatography (IC). Apart from IC, there are few reports of alternative analytical methods such as the one using Raman spectroscopy, Colorimetry, Flame photometry, Flow injection analysis and few conventional ones. Although IC is a standard procedure established for aerosol analysis, has been fully discussed in this review, but other techniques like CE, XANES, Potentiometry, FTIR, e.t.c have proved attractive in terms ofease of operation, fast separation of mixture of ions, reasonable costs, Speciation analysis, reduction of time for sample preparation and prevention of sample destruction for other measurements. In India, except IC, other mentioned techniques seemed to be not in operation for required measurements and negligible reports are seen for the speciation analysis as the later is must as far as $PM_{2.5-10}$ analysis is concerned, since toxicity is directly related to the chemical form of the element of oxidation state. Convectional procedures like Photometry and Colorimetry are still been frequently used for required analysis even though procedures are costly, less efficient, time consuming and less informative for understanding different physical and chemical process going on in the atmosphere.

Elemental and trace metal analysis in comparison to ion analysis, mainly depends upon applicability of techniques like, including atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICPMS) with few reports utilizing X-ray fluorescence and scanning electron microscopy (SEM) using energy or wavelength dispersive spectra (EDS or

WDS). However there are hardly any reports from the continental India regarding aerosol analysis with techniques like, PIXE, ESCA, Voltametry including both (ASV and CSV) and Activation analysis like NAA. Study of identification and characterization of surface-enriched material in aerosol particles seems almost absent in theregion as the techniques like ESCA has not been in operation for the purpose of aerosol studies. There are paucity of reports regarding the study of toxic trace metals like Pb, Cd, Cr, Mo, Hg, e.t.c and hence study of environmental health is not fully presented. Apart from these, study of radio nuclides in the atmospheric particulate matter is almost absent. So in order to overcome these problems it is recommended that research community should look for the analytical instruments available for same.

UNIT 7
Summary and Perspective

This review focuses on the analytical methods and developments in inorganic aerosol analysis, involving the collection of aerosol material on a filter media, followed by analysis. Emphasis has been given mainly to methods with diverse practical application for routine measurements of inorganic and trace metals, with lower detection limits, shorter temporal resolution, and increased selectivity and hence reliable in terms of air quality assurance. Selected references are being mentioned which will provide the ground work for an individual to know quickly differently methods and hence their application for environmental needs. From this review one can establish that a successful decade of development in the field of inorganic aerosol determination, with advances more revolutionary than evolutionary taking place. The continuing efforts by many research groups have led to vast improvements in analytical ures of merit, expansions of the application areas and, in particular, to a better understanding of what the possible impact of inorganic environmental analysis are. The growing acceptance of these methods practised by analytical chemists, working in environmental control and regulatory laboratories, has underscored the need for a comprehensive treatise on the methodology and practices of this rapidly expanding area.

Trace levels at which inorganic pollutants occur in environmental matrices are often beyond the current detection capability of analytical techniques. On the other hand, even a range of commercially available, unsophisticated detectors adequately serve the needs of quantification of inorganic analytes, such as alkali and alkaline earth metals or common anions, which customarily attract acute interest in the local or global environment. The same is true about the separation methodology,

which appears to be well refined for a large proportion of inorganic analytes in essentially all major environmental samples and hence needs only small advances in terms of customising the separation procedures. Hence it is time to formulate what standard procedure for specific analytes and specific samples are. One of the major steps forward is likely to be made in the expansion of more sensitive detection systems, primarily ICPMS, which holds the most prominent position in the field of trace inorganic analysis.

This overview concludes with more than 300 references to applications which are mostly of real world use and which can keep the reader on top of the field. The future looks bright for analysts involved in developing new methods in environmental chemistry, even though there is still plenty of room for further advances, mostly in detection and sample preconcentration in method development. It is these facets that require the next stage of innovation. In this respect, it is important to remember that contaminants rather than components of natural origin tend to receive most attention in the environmental analyst's work. We hope this review inspires researchers with unique analytical and physical chemistry tools used for studying fundamental reaction dynamics in laboratory settings to delve into this existing area of research and to those who have something to do with or interest in the atmospheric aerosol analysis.

I. APENDIX.Abbreviations

AAS Atomic absorption spectrometry

AC Automated colorimetry

ASV Anode stripping voltametry

ACSV Adsorptive cathode stripping voltametry

ASTM American society for testing and materials

AOAC Association of official analytical chemists

ATR Attenuated total reflectance

CEY Conversion electron yield

CSV Cathode stripping voltametry

CSPC Continous soluble particle collector

CE Capillary electrophoresis

DMA Dimethyl arsenic acid

DPASV Differential pulse anode stripping volatmetry

DRS Diffuse reflectance

EDXRF Energy dispersive X-ray fluorescence

EPA Environmental protection agency

ESCA X-ray induced photoelectronic spectroscopy

EDTA Ethylenediamine tetra acetate

ES-MS Electron spary mass spectrometry

ET-AAS Electrothermal atomic absoption spectrometry

FY Fluorescence yield

FTIR Fourier transform infrared spectroscopy

GRAV Gravimetry

GF-AAS Graphite furnace atomic absorption spectrometry

HMDE Hanging mercury dropping electrode

HIBA Hydroxy isobutyric acid

HF Hydrofluoric acid

IC Ion chromatography

ICP-AES Inductively coupled plasma atomic emission spectrometry

ICP-MS Inductively coupled plasma spectrometry

INAA Instrumental neutron activation analysis

ICP-OES Inductively coupled plasma optical emission spectroscopy

ISE Ion selective electrode

INAA Instrumental neutron activation

LOD Limit of detection

LA-ICP Laser ablation inductively coupled plasma

MXRF Micro X-ray fluorescence

MAA Moleculat activation analysis

NAA Neutron activation analysis

OA Absorption or light transmission

OM Optical microscopy

PIXE Proton-induced X-ray emission

PESA Proton elestic scattering analysis

PM Particulate matter

ROS Reactive oxygen species

RQ Range of quantification

RNAA Radiochemical neutron activation analysis

SEM Scanning electron microscopy

SR Synchroton radiation

SWASV Square wave anode sripping voltametry

SJAC Steam jet aerosol collector

TMAO Trimethy arsenic oxide

PGNAA Prompt gamma ray neutron activation analysis

PILS-IC Particle into liqued sampler IC

PILS-TOC Particle into liqued sampler total organic carbon

TEM Transmission electron microscopy

TMOCA Thermal manganese oxidation carbon analysis

TOR Thermal-Optical reflectance carbon analysis

TOT Thermal-Optical transmission carbon analysis

TXRF Total reflection X-ray fluorescence

UE-ASV Ultrasonic extraction anode stripping voltametry

WDXRF Wave length dispersive X-ray fluorescence

WTC World trade centre

XRD X-ray diffraction

XRF X-ray fluorescence

XANES X- ray absoption near edge spectroscopy

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