CHAPTER II

INSTRUMENTATION

&

DATA ANALYSIS
2.1. Introduction

Near surface aerosols are those components of atmosphere aerosol system that reside within the Earth’s boundary layer or the so-called well mixed layer. Characteristics of near-surface aerosols are very important from the Geosphere and Biosphere perspective due to a variety of reasons. It is in this region that the aerosol abundance is the highest and most strongly related to the sources. They produce direct effect on human health, visibility, air quality, and environment and also lead to formation of dew, mist and fog. Thus, they have the most direct bearing on terrestrial life. Being strongly related to source processes, the near-surface aerosols exhibit a very high degree of variability at short scales; both spatially and temporally. They are highly susceptible to changes in the ambient conditions and on a larger scale to the boundary layer dynamics (Choularton et al., 1982, Parameswaran et al., 1998, Vakeva et al., 2000).

The variety of aerosol sources (natural and anthropogenic); the wide size spectrum and their short lifetimes result in a spatially and temporally heterogeneous aerosol field, making aerosol characterization a real challenge. As such, no single technique or group of techniques is adequate for entirely characterizing aerosol properties over the extremely wide range of particle size, shape, altitude profile and chemical composition found in the atmosphere. The devices employed range from simple instruments measuring light transmission and porous filters to collect material for determining the mass concentration, to very sophisticated sensors or collectors to characterize the particle size distribution and chemistry. In the case of atmospheric aerosols, the size distribution and mass concentration are important in order to understand their source strength, environmental impact; optical properties; radiative effects and climatic implications. Both, the size distribution and mass concentration
can be determined by a variety of methods whose operating principles are based on different properties of the particles.

In general, measurements of particles or particle collections in the ambient are done by: (a) in situ, (b) by remote sensing. Both techniques can be applied from different types of observations platforms like ground based, airborne and space borne. In situ measurements make direct measurements on the parameters at their location, while in remote sensing the parameters are deduced by measuring the impact on an electromagnetic radiation, interacting with the particle but without physical contact.

The present study relies most on in situ techniques for the measurement of the ambient aerosol mass and size distributions using Quartz Crystal Microbalance (QCM) Impactor. These measurements are used to characterize the near-surface aerosols.

2.2. QUARTZ CRYSTAL MICROBALANCE (QCM) IMPACTOR

Quartz Crystal Microbalance (QCM) is a cascade Impactor that has the potential to provide near real-time measurements of total as well as size segregated mass concentration of aerosols. It is designed based on the principle of inertial impaction.

2.2.1. Principle of inertial impaction:

When air-containing aerosols (particles) is sucked by means of a pump and directed towards a collecting surface or substrate, particles in the stream having inertia large enough will impact on the substrate while those with lesser inertia will follow the airflow on this principle are called inertial impactors.

There are two classes of inertial impactors; single stage impactors and multiple stage impactors (also called cascade impactors). In the case of single stage Impactor particles over a wide range of sizes are sampled (e.g., high volume sampler).
A cascade inertial Impactor is designed so that at each stage a discrete range of particle size is collected. Larger particles with much higher inertia, will deposit upon the immediate impaction surface; smaller particles will remain entrained in the airstream, flow around entrained particles will be deposited upon impaction surface within the series, or "cascade", of jet stages and impaction surfaces. At each stage, an aerosol stream passes through the jets and around the impaction surfaces. Higher jet velocities enable smaller particles to be characterized efficiently. By cascading a number of such stages, the particle mass size spectrum can be deduced. There are different types of cascade impactors that size particles over a wide size range, primarily in environmental particulate studies.

2.2.2. The Sensing Stack Subassembly

It consists of ten Impactor stages, which are held in place by a set of frames and each stage can be removed individually. A two-way ball valve (called sample valve) is on top of the stack at the inlet. The Impactor stages (ten in number) are cascaded with jets that segregate the larger aerosol particles on top. The jet diameters of the Impactor stages become progressively smaller in the lower stages. Quartz Crystal sensors are used in each stage as mass monitors to provide real-time mass collection data.

The Impactor is provided with a small pump (diaphragm vacuum pump) to aspirate the ambient air into the stack, and a flow meter to monitor the flow rate. The instrument operates at a flow rate of 240 ml min\(^{-1}\) and segregates aerosol samples into ten size bins between 25 and 0.05μm. The low flow rate is used as only a very small amount of aerosol mass is required to produce a measurable frequency drift or because the QCM is a highly sensitive balance.
2.2.3. Pump and Airflow System

By means of the pump, air is sucked into the sampler through the sample inlet. Air enters the stack at the valve assembly, either through the standby port or through the sample port on top. During standby, ambient air is drawn into a filter and passes through the flow meter before entering the valve block and stack. The flow rate is monitored only during standby and not during actual sampling. The metering valve is connected between the 10th stage and the pump and controls the flow through the system. A flow controller combines a pressure regulator with the metering (needle) valve to maintain a constant flow rate under varying conditions. The regulator maintains a constant pressure drop across the metering valve. The variable -area meter varies the orifice area with the flow rate to maintain a nearly constant pressure drop. The most common type of variable area meter is the rotameter consisting of a float, free to move up and down in a vertical column. The float rises in the tapered tube until its weight balances the upward drag force due to the fluid flowing up through the tube. The area between the float and the tube wall increases as the float rises, reducing the velocity and drag force of the fluid. Float position is calibrated by marks on the tube in terms of volumetric flow rate at standard pressure.

2.2.4. The crystal mass sensor

There are two crystals in each of the Impactor stages, one for collecting aerosols and another as a reference. It has a pair of AT cut crystals (having a very low frequency drift with temperature). The quartz plate is approximately 0.5" in diameter. The crystals form part of a pair of identical crystal oscillators, (each one associated with one of the oscillator), reference or sensing. Both crystals have a resonant frequency of ≈10 MHz, but the frequency of the reference oscillator is purposely set
higher than that of the sensing crystal oscillator by about 3 KHz. Signals from each stage of the stack enters the control and data logger assembly through a set of cables.

2.2.5. Control Unit Subassembly

The data from the QCM sensing stack are processed in a microprocessor based control unit, which then provides printouts of the mass concentration in each stage and a histogram of the relative mass concentrations of each size range. When the valve is in the sampling position a micro switch mounted on the back of the valve (in the sensing stack) senses the valve position and triggers an elapsed time meter in the control unit. The duration for which the valve remains open is displayed on the control unit in seconds. Ten frequency signals, one from each stage emanate from the sensing stack and are fed to the control unit where they are stored and processed by a microprocessor. By monitoring and recording the frequency from each stage before and after aerosol sampling, change in frequency in each stage caused by mass loading is calculated by the microprocessor automatically. The sampling time is also fed to the microprocessor through the setting of the thumbwheel switch on the control unit’s from panel.
Fig. 2.1. Quartz Crystal Microbalance Cascade Impactor along with Control Unit
2.2.6. Principle of operation

By means of the pump, the aerosol stream is accelerated through a nozzle with a small high-speed jet and impinges on a quartz crystal plate mounted close to the jet's exit and normal to direction of flow. The aerosol stream entering the instrument encounters the largest nozzle first, and the nozzle becomes progressively smaller in subsequent stages. The jet of air is forced to turn sharply to flow around the crystal, and the aerosol particles carried in the air stream, because of their inertia, continue to travel forward and impact against it. Particles which are too small and do not have sufficient inertia to move forward and impact against the sensing crystal are carried by the air stream to the following stage which is similar to the preceding stage, except that the nozzle is smaller.

The smaller nozzle accelerates air to a higher speed than in the preceding stage and hence smaller particles are captured. A thin coating of silicon grease on the crystal ensures capture of the impacted particles and prevents bounce off of solid hard particles. As the particles impact, the mass of the sensing crystal increases, and its oscillating frequency decreases. Immediately behind the sensing crystal, is an identical reference crystal whose frequency does not change because no particles are impacted against it.

The two frequencies are mixed so that the beat frequency emanating from the mixer is a lower frequency in the 2 to 4 KHz range. This beat frequency changes in accordance with the frequency change of the sensing crystal caused by mass collection and increases as particles continue to impact on the crystal. The output beat frequency is therefore the signal whose changes are proportional only to the mass loading on the sensing crystal. Although the resonant frequency of the sensing crystal decreases as mass is added to it, the signal output from the QCM, the beat frequency,
will go up because of the dual crystal arrangement where the reference oscillator frequency is kept higher. The frequency signals, emanated from each of the sensing stack, are fed to the control unit where they are stored and processed by the microprocessor. The ratio of frequency change over time is used by the microprocessor, which is programmed to calculate the mass concentration, in units of $\mu g \, m^{-3}$.

![Fig.2.2. Schematic diagram of the QCM stage.](image)

2.3. Instrumentation and Data Analysis

Measurements of mass-size distribution of aerosols made regularly using a Quartz Crystal Microbalance (QCM) Impactor (model PC-2 of California Measurements Inc.) at Anantapur. The instrument sucks in the ambient air and segregates the aerosols in accordance with the aerodynamic diameter into one of its
ten size bins. For spherical particles with a density \( \rho \), the aerodynamic diameter \( (D_a) \) and particle diameter \( (D_p) \) are related through

\[
D_p - D_a \sqrt[3]{\rho}
\]

QCM provides mass concentration of the particles collected in each stage \( (m_c) \) as a function of particle diameter assuming a value of 2\( \text{g/cm}^3 \) for \( \rho \). Accordingly, it yields mass concentration in ten size bins; the 50% cut-off diameter and the mean diameter \( (d_i) \) of these bins is given in the below Table 2.1. Stage 1 collects all the particles with diameter >25\( \mu \)m, and hence no mean diameter is assigned to that stage.

### Table 2.1. Stage and cut points of QCM Impactor

<table>
<thead>
<tr>
<th>Stage No.</th>
<th>Particle diameter ( (d_{pi}) )</th>
<th>Geometric mean diameter ( (d_{gi}) )</th>
<th>Aerodynamic Diameter ( (d_{ai}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.0</td>
<td>--</td>
<td>35.37</td>
</tr>
<tr>
<td>2</td>
<td>12.5</td>
<td>17.58</td>
<td>17.68</td>
</tr>
<tr>
<td>3</td>
<td>6.4</td>
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</tr>
<tr>
<td>4</td>
<td>3.2</td>
<td>4.53</td>
<td>4.53</td>
</tr>
<tr>
<td>5</td>
<td>1.6</td>
<td>2.26</td>
<td>2.26</td>
</tr>
<tr>
<td>6</td>
<td>0.8</td>
<td>1.13</td>
<td>1.13</td>
</tr>
<tr>
<td>7</td>
<td>0.4</td>
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</tr>
<tr>
<td>8</td>
<td>0.2</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>9</td>
<td>0.1</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>10</td>
<td>0.05</td>
<td>0.17</td>
<td>0.07</td>
</tr>
</tbody>
</table>
QCM makes estimates of the mass concentration \( (m_{ci}) \) in each size bin by measuring the change \( (\Delta f) \) in frequency difference \( (F_R - F_S) \) between the reference crystal \( (F_R) \) and sensing crystal \( (F_S) \); the former being higher. This \( \Delta f \) is proportional to mass of aerosols deposited on the sensing crystal. As \( m_c \) is directly related to \( \Delta f \), the short-term stability of the crystal oscillator (during the sampling time, which varies from 3 to 5 min) is of more important than the long-term drifts. Random checks are made 3-4 times on the days of observation by making \( \Delta f \) measurements with the ambient air bypassed from the sampler stages by using the inlet valve so that no aerosol enters the QCM during this measurement. The value of \( \Delta f \) was mostly 1 Hz, very rarely reaching 2 Hz. The sampling period is taken such that a minimum frequency shift of 5 Hz is registered by the stage having the lowest mass concentration and this leads to a 20% error in the estimated mass concentration in that stage. However, at other stages which register higher values of \( \Delta f \), (going to as high as 30-40 Hz in the stage with highest mass concentration), the error reduces proportionally to as low as 2 or 3%. Converting these into actual mass concentrations, it works out that \( m_{ci} \) estimates below \(~10 \mu g m^{-3}\) are generally more uncertain (by ~15-20%, which in absolute terms work out to be \( \approx 1 \mu g m^{-3} \)), while the errors are quite small at higher values of the mass concentrations. Ambient RH and its variation are important due to the affinity of the quartz substance to moisture. QCM measurements require rather stable RH levels during the sampling period, if the RH exceeds 65-70%. However at lower RH, and also when the changes in RH are considerably slower the instrument is quite stable. The QCM has yielded reliable information on mass concentration and size distribution even on cruises (for e.g., during the INDOEX cruises of 1998 and 1999) and coastal station (Jayaraman, 1999; Pillai and Moorthy, 2001).
Raw data from QCM provided the total mass concentration ($M_t$) as well as the size segregated mass concentration ($m_{ci}$ for the $i^{th}$ size bin) for each size bin, for each measurement. Besides yielding characteristic information by themselves, they can also be used to derive physically meaningful parameters describing the aerosols. From direct considerations,

$$M_t = \sum_{i=1}^{10} m_{ci}$$  \hspace{1cm} 2.2

The volume concentration of aerosols in the $i^{th}$ size bin is estimated as

$$V_{ci} = \frac{m_{ci}}{\rho}$$  \hspace{1cm} 2.3

where $\rho$ is taken as $2\text{g cm}^{-3}$, dividing $V_{ci}$ by the mean particle radius ($r_i$) of the $i^{th}$ size bin, we get an estimate of the area of the aerosols ($a_{ci}$) in the $i^{th}$ size bin,

$$a_{ci} = \frac{V_{ci}}{r_i}; r_i = \frac{d_i}{2}$$  \hspace{1cm} 2.4

The volume and area estimates are used to estimate the effective radius of aerosols $R_{\text{eff}}$

$$R_{\text{eff}} = \frac{\sum_{i=2}^{10} V_{ci}}{\sum_{i=2}^{10} a_{ci}}$$  \hspace{1cm} 2.5

In estimating $R_{\text{eff}}$, Eq (2.5), the summation is made only over stages 2-10. Stage 1 is not considered because it collects all particles with size exceeding 25$\mu$m and hence that stage cannot be assigned a meaningful mean radius.

The study of the submicron accumulation mode aerosols is important because of their longer residence times and also because these aerosols contribute more to the scattering and indirect radiative forcing through clouds whereas the concentration and size spectrum of continental aerosols strongly depend on the wind speed. As such, we have separated $M_t$ into $M_a$ and $M_c$, where $M_a$ is the mass concentration in the accumulation size range and $M_c$ that in the coarse size range, such that,
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\[ M_i = M_a + M_c \]

2.6

For the configuration of the QCM, we took the cut-off diameter as 0.8\( \mu \)m to demarcate the two regimes and thus,

\[ M_c = \sum_{i=2}^{6} m_i \quad \text{and} \quad M_a = \sum_{i=7}^{10} m_i \]

2.7

where \( i \) is the stage number of the QCM and \( m_i \) is the measured mass concentration in that stage.

2.4. Estimation of PM, PM\(_{10}\) and PM\(_{2.5}\) from the QCM measurements:

In addition to optical effects and radiative interactions, which affect the Geosphere and Biosphere, atmospheric aerosols have a direct bearing on the Earth’s environment and thus to human health. The health hazards due to toxic aerosols and the environmental degradation is becoming increasingly important particularly in cities and large urban conglomeration where extensive anthropogenic activities thrive (Dockery and Pope, 1994; Schwartz et al., 1996; Abbey et al., 1999). Increases in ambient particle concentrations are associated with an array of adverse health outcomes, ranging from the least adverse, (increases in symptoms of respiratory irritation and small decreases in level of lung function), to the most adverse, mortality (Vedal, 1995). Because of the ability of particulate matter (aerosols) to enter the body via the respiratory tract, the size of it has important toxicological and regulatory relevance. Environmental regulators have chosen to divide particles up into various size factions (as measured by aerodynamic diameter) and measure them in units of particle mass per unit volume (\( \mu \)g m\(^{-3}\)). Mainly two size fractions PM\(_{10}\) (particulate matter whose aerodynamic diameter is less than 10\( \mu \)m) and PM\(_{2.5}\) (particulate matter whose aerodynamic diameter is less than 2.5\( \mu \)m) are of interest, especially in view of clean air regulations. PM\(_{10}\) may be emitted directly (primary particulate) or from

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Chemical or thermal reactions in the atmosphere (secondary particulate). It is commonly referred to as inhalable or thoracic particles as they can penetrate into the thoracic compartment of the human respiratory tract. Vedal (1995) reported that a 10 μg m⁻³ increment (an exposure increment) of inhalable particulate above a base level of 20 μg m⁻³ results in a linear increase in health impacts. With this view, the long-term data collected using the QCM have been examined for PM₁₀ and PM₂₅ concentrations; their seasonal dependence as well as compared these with standards set for safe environmental conditions by different countries.

Particulate matter (PM) is the mass of aerosols suspended in unit volume of air in the atmosphere which is similar to that of Mt. But it is introduced here because it is the index used in environmental terminology. Thus, PM is estimated as

\[ PM = \sum_{i=1}^{10} m_{ci} = M_i \]  \hspace{1cm} \text{(2.8)}

PM₁₀ are those particles whose aerodynamic diameter is less than 10 μm and PM₂₅ are those particles whose aerodynamic diameter is less than 2.5 μm. From the size segregated mass concentration provided by the QCM, PM, PM₁₀ and PM₂₅ are estimated based on the aerodynamic diameters. Referring to Table 2.1, it can be seen that most of the PM₁₀ is contributed by the QCM stages from 3 to 10 m while 5 to 10 contribute mostly to the PM₂₅ (Pillai and Moorthy 2001). Accordingly from the QCM data (mₙ as a function of I), PM₁₀, PM₂₅ are estimated as

\[ PM_{10} = \sum_{i=3}^{10} m_{ci} \quad PM_{25} = \sum_{i=5}^{10} m_{ci} \]  \hspace{1cm} \text{(2.9)}

The details of the results and discussion are given in the next chapter.