The instruments, operated for measuring the various physical and optical properties of aerosols are Sunphotometer, Microtops, Quartz Crystal Microbalance Cascade Impactor, Aethalometer, Nephelometer and Aerosol Size Spectrometer for the present study at different locations. The working principle, methodology and the measurement uncertainties are briefly discussed in this chapter.

### 2.1 Sunphotometer

Aerosol Optical Depth (AOD) was measured by hand-held Sunphotometer by measuring the direct solar radiation intensity at the ground. This instrument is built in-house at the Physical Research Laboratory, Ahmedabad. The Sunphotometer consists of an interference filter, photodiode and necessary electronics (Acharya and Jayaraman, 1995). Direct solar intensity was measured at seven wavelength bands using optical interference filters, centered around 0.400, 0.500, 0.670, 0.750, 0.875 and 1.050 μm. The total field of view of the sunphotometer is 8° and was achieved using a baffle attached in front of the photometer. The measurement was...
Measurement Techniques

taken only on cloud-free days form 0830 to 1630 local hours. Beer-Lambert law is used to calculate AOD and shown below:

\[
I(\lambda) = I_0(\lambda) \left( \frac{r_0}{r} \right)^{-2} \exp[-m\tau]
\]  

(2.1)

where \(I(\lambda)\) and \(I_0(\lambda)\) are the instantaneous intensity of the monocromatic solar radiation at wavelength \(\lambda\), at the ground and top of the atmosphere (TOA), respectively, \(m\) is relative air mass (ratio of actual path to the vertical path), \(\tau\) is the total optical depth and \(r\) is the Sun Earth instantaneous distance and \(r_0\) is the Sun Earth mean distance. The solar intensity \(I\) at the ground was measured by the Sunphotometer in volt. \(I_0\) is derived from the Langley plot technique in which the logarithm of \(I\) is plotted against the relative airmass and \(I_0\) is the value of \(I\), extrapolated to relative airmass of zero. The relative airmass can be derived from the relation (Young, 1994),

\[
m = \frac{1.002432 \cos^2 \chi + 0.148386 \cos \chi + 0.0086467}{\cos^3 \chi + 0.149864 \cos^2 \chi + 0.0102963 \cos \chi + 0.000303978}
\]  

(2.2)

where \(\chi\) is the solar zenith angle which can be derived from the relation,

\[
\cos \chi = \cos \delta \cos \phi \cos h + \sin \delta \sin \phi
\]  

(2.3)

where \(\delta\) is the sun’s declination, \(\phi\) is the longitude of the location and \(h\) is the local hour angle. Eq. 2.2 provides a better accuracy for Earth’s curvature and the atmospheric refraction of the solar radiation and for smaller solar zenith angles (<60°) Eq. 2.2 becomes \(m = \sec \chi\). The atmospheric molecules and aerosols contribute to the total optical depth \(\tau(\lambda) = \tau_a(\lambda) + \tau_{ray}(\lambda) + \tau_{ma}(\lambda)\), where \(\tau_a\) is the aerosol optical depth, \(\tau_{ray}\) is the Rayleigh scattering by the air molecule and \(\tau_{ma}\) is the molecular absorption. The direct solar radiation received at the Earth’s surface depends on the composition of the atmosphere and amount of each species. To calculate the AOD, the transmittance \((T_i)\) of the different components in the atmosphere in the optical band from 0.300 \(\mu\text{m}\) to 1.200 \(\mu\text{m}\) was obtained from the
Santa Barbara DISORT Atmospheric Radiative Transfer (SBDART) Model (Ricchiazzi et al., 1998). The optical depth of a particular atmospheric component \( c \) was obtained using the relation,

\[
\delta_c(\lambda) = \frac{\int_{\lambda_1}^{\lambda_2} T_c(\lambda) FT(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} FT(\lambda) d\lambda}
\]  

(2.4)

where \( FT(\lambda) \) is the filter transmission for the wavelength from \( \lambda_1 \) to \( \lambda_2 \). The filter transmission was observed in the laboratory with the help of a double-beam spectrometer. The Rayleigh Optical Depth (ROD) was obtained by calculating the effective Rayleigh scattering cross section \( \sigma_{\text{eff}} \) by the relation,

\[
\sigma_{\text{eff}}(\lambda) = \frac{\int_{\lambda_1}^{\lambda_2} \sigma_{\text{ray}}(\lambda) FT(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} FT(\lambda) d\lambda}
\]  

(2.5)

where \( \sigma_{\text{ray}}(\lambda) \) is the Rayleigh scattering cross section using Nicolet's equation (Nicolet, 1984). ROD was calculated by using the column integrated air number density \( N = 2.16E + 25 \text{cm}^{-2} \) for the tropical model atmosphere, multiplied by the average Rayleigh scattering cross section in the optical band from \( \lambda_1 \) to \( \lambda_2 \). For the AOD calculation the maximum error is less than \( \pm 15\% \) due to instrumental error (due to bias and precision). Ignoring the contribution from “forward” scattering to the measured solar radiation intensity (Jayaraman et al., 1998) also contributes to the error.

### 2.2 Microtops

Aerosol Optical Depth (AOD) was measured using a hand-held Microtops II (Solar Light Co., Inc., USA) (Morys et al., 2001; Ichoku et al., 2002) on cloud-free days. This instrument can measure AOD at five different wavelengths centered at 0.380, 0.440, 0.500, 0.675, 0.870 \( \mu \text{m} \) simultaneously. To measure the AOD at 1.020 \( \mu \text{m} \) wavelength associated with ozone and columnar water vapor another Microtops II was used. Both the Microtops were regularly calibrated once in a month and all
the calibrated constants were obtained from Langley’s plot analysis carried out at Mount Abu (26.6°N, 72.7°E, 1.7 km asl), less affected by anthropogenic activity. To obtain the calibration constant observations have been made on cloud-free days.

![Figure 2.1](image)

**Figure 2.1:** Langley plots are shown for 0.5 μm wavelengths for four months. The blue circles and magenta triangles represent the forenoon and afternoon observed solar radiance at the surface. The best fitted linear lines, obtained from the Beer-Lambert’s relation are drawn for forenoon and afternoon separately and the intercept of the y-axis gives the solar radiance at the top of atmosphere \( I_0(\lambda) \) and the difference slope is due to slightly change of AOD during forenoon and afternoon observation.

In Fig. 2.1 Langley plots have been shown for four months at 0.5 μm wavelength. The best fitted linear line, obtained from the Beer-Lambert’s relation (Eq. 2.1) during the observational period gives the solar radiance \( I_0(\lambda) \) at the top of atmosphere. \( I_0(\lambda) \) values are given in Table 2.1 for 6 different channels of Microtops during the period 2006-2007. During the observations three consecutive measurements were taken at a time to reduce the manual error. The absolute uncertainty
Table 2.1: The Calibration Constants \( I_0(\lambda) \) for six different channels of Microtps readings during Feb'06 to Dec'07 at Mt. Abu. These constants are obtained from Langley Plot method.

<table>
<thead>
<tr>
<th>Month and Year</th>
<th>Calibration Constants ( I_0(\lambda) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.380 ( \mu m )</td>
</tr>
<tr>
<td>Jun 2006</td>
<td>6.80</td>
</tr>
<tr>
<td>Sep 2006</td>
<td>6.78</td>
</tr>
<tr>
<td>Dec 2006</td>
<td>6.98</td>
</tr>
<tr>
<td>Jan 2007</td>
<td>6.92</td>
</tr>
<tr>
<td>Feb 2007</td>
<td>6.89</td>
</tr>
<tr>
<td>Jun 2007</td>
<td>6.46</td>
</tr>
<tr>
<td>Oct 2007</td>
<td>6.84</td>
</tr>
<tr>
<td>Dec 2007</td>
<td>6.84</td>
</tr>
</tbody>
</table>

of measured AOD is not more than 0.03 at every wavelength (Morys et al., 2001; Ichoku et al., 2002).

### 2.3 Quartz Crystal Microbalance Cascade Impactor

Aerosol mass concentration was measured using a 10-stage Quartz Crystal Microbalance (QCM) cascade impactor (model PC-2, California Measurements Inc., USA) and the aerosol size distribution at the ground level was determined. The aerosols were collected in 10 stages of the impactor with 50% efficiency cut-off radii at 12.5, 6.25, 3.2, 1.6, 0.8, 0.4, 0.2, 0.1, 0.05 and 0.025 \( \mu m \) from stage 1 to 10, respectively. The air flow rate through the impactor was kept at 240 \( ml/min \). The typical sampling period was 300 \( sec \) for each measurement. The QCM observations were made at every hour throughout the day. The air inlet was installed vertically to minimize the loss of aerosol particles within the inlet tube. Each stage of the impactor has two identical piezoelectric crystal sensors, as shown in Fig. 2.2 and
Figure 2.2: Schematic of one of the stages of a Quartz Crystal Microbalance Cascade Impactor

the ambient air passes through each of these stages. The aerosol stream accelerates through a nozzle with a small high-speed jet and impinges on the closer quartz crystal plate, known as sensing crystal. The heavier particles collide with the crystal plate due to their inertia and lighter particles are carried out by the air flow and continue to travel forward. A thin coating of grease on the crystal ensures the capture of the particles impinged and the frequency of the crystal changes instantaneously. The other identical crystal is immediately behind the sensing crystal and is known as reference crystal. As it is behind the sensing crystal, there is no particle impaction and hence its frequency is unchanged. Once the sampling is over, the difference between the sensing and reference crystal frequencies ($\Delta f$) gives the corresponding aerosol mass concentration, $\Delta m = -(1.4 \times 10^{-9}) \Delta f$. The main uncertainty comes into the aerosol mass concentration due to the bouncing of aerosols and their sliding from the crystal plate. A thin grease coating on the crystal reduces these effects. Another cause which contributes to the uncertainty, is the reduction of crystal frequency due to aging effect. The relative temperature change of the crystals during each sampling period of 5 minute is very small and uncertainty due to change of temperature can be neglected. The maximum uncertainty due to
all the above mentioned factors in the measured aerosol mass concentration of all the ten stages is within 25% (Jayaraman et al., 1998). The other major uncertainty which arises due to the swelling of aerosol during higher relative humidity (RH) conditions. This effect is also included in the aerosol mass calculation according to necessity (Ramachandran and Jayaraman, 2002; Ramachandran et al., 2006).

2.4 Aethalometer

Black Carbon (BC) mass concentration is derived from the measured real-time light attenuation using a multichannel Aethalometer (AE-47 of Magee Scientific, Berkeley, USA). Aethalometer is a time based light attenuation instrument which has seven wavelength narrow bandwidth light sources ranging from the near ultraviolet to the near infrared region with a reference and a broadband sensing detectors. This is a filter based technique used to measure the light attenuation due to the particle deposition onto a quartz fiber filter (Hansen et al., 1982, 1984). In the present study, BC concentration is determined by measuring the attenuation of a beam of light, at seven wavelengths, viz, 0.380, 0.470, 0.520, 0.590, 0.660, 0.880 and 0.950 μm, transmitted through the sample collected on the filter. With the help of a pump and inlet tube ambient air is sucked at a rate of 3 l.min⁻¹ and measurements are taken round the clock, and the data are averaged for every five minutes and stored.

The absorption coefficient (β_{abs}) is defined by Beer-Lambert’s law \( I = I_0e^{\beta_{abs}l} \), where \( I_0 \) is the intensity of the incident light and \( I \) is the intensity of the transmitted light passing through a medium of thickness \( l \). Aethalometer measures light attenuation (\( ATN = 100ln \frac{I}{I_0} \)) through an aerosol embedded quartz filter, where \( I \) and \( I_0 \) are the intensities of light transmitted through the sampled and a blank spot (unsampled) filter, respectively. The attenuation absorption coefficient (\( \beta_{ATN} \)) for a sampled time duration \( \Delta t \), is \( \beta_{ATN} = \frac{A}{100Q} \frac{ATN}{\Delta t} \) where \( A \) is the area of the spot of
sample over the filter and \( Q \) is the volumetric sampling flow rate. BC concentration (\( \mu g.m^{-3} \)) is calculated by the following relation

\[
BC = \frac{\beta_{\text{abs}}}{\sigma_{\text{abs}}} = \frac{\beta_{\text{ATN}}}{\sigma_{\text{ATN}}R(\text{ATN})}
\]

(2.6)

where \( \sigma_{\text{abs}} \) and \( \sigma_{\text{ATN}} \) are the mass specific absorption and attenuation cross-sections (in unit \( m^2.g^{-1} \)), respectively and \( \sigma_{\text{ATN}} \) is derived using the simple relation \( \sigma_{\text{ATN}} \equiv \sigma_{\text{abs}}C \). It is well known that attenuation absorption coefficient, \( \beta_{\text{ATN}} \) may differ from the actual aerosol absorption coefficient, \( \beta_{\text{abs}} \) of the deposited aerosol particles (Petzold et al., 1997; Weingartner et al., 2003; Schmid et al., 2006, etc.). This significant difference occurs due to enhancement of the optical path length by the multiple scattering of light beam at the filter fiber and also due to “shadowing effect”. For these reasons the calibration constants \( C \) and \( R(\text{ATN}) \) are introduced to correct for the attenuation absorption coefficient. \( C \) is the calibration constant due to the multiple scattering of the light at the filter fibers in the unloaded filter and is greater than unity. This multiple scattering of light leads to an enhancement of optical path (Lioussse et al., 1993). \( C \) generally depends on the nature of the filter. Other calibration constant, \( R(\text{ATN}) \) is introduced due to “shadowing effect”. This effect occurs due to the increase in filter loading which reduces the optical path length and hence decreases the absorption coefficient. \( R(\text{ATN}) \) varies with the amount of aerosol particles deposited on the filter and also on the optical properties of the deposited particle. For the unloaded filter \( R \) should be unity i.e., \( R(\text{ATN}=0)=1 \). \( R \) also depends on the single scattering albedo \( (\omega) \) of the sampled aerosol associated with the deepness of the aerosol embedded into the filter matrix which depends on the particle size, particle morphology and the flow rate. For Aethalometer (AE-47) the highest particle loading on the filter is appreciable for maximum change in ATN up to 0.78, 0.55 and 0.30 for 0.380, 0.520 and 0.880 \( \mu m \), respectively, and beyond which the filter tape is automatically forwarded to expose a new pristine filter spot (ATN\~0). In the Fig. 2.3 time series of three absorbance, ATN(380), ATN(520), ATN(880) are shown, represented by blue circles, green triangles and red squares, respectively.
The main uncertainty in the measurements comes from the variability in $\sigma_{ATN}$ in Eq. 2.6. The exact knowledge of $\sigma_{ATN}$ is necessary for the calculation of BC concentration from Aethalometer. $\sigma_{ATN}$ strongly depends on the aerosol type and age (Lioussse et al., 1993; Petzold and Niessner, 1995). The observed value of $\sigma_{ATN}$ (measured with the incandescent lamp instrument) varies from 5 m$^2$g$^{-1}$ (remote area) to 14 m$^2$g$^{-1}$ (urban region). At the remote continental site $\sigma_{ATN}$ is taken as 9.3 m$^2$g$^{-1}$ (Lavanchy et al., 1999) whereas for the most polluted site; near the street it is 20 m$^2$g$^{-1}$ (Lioussse et al., 1993). In the present study $\sigma_{ATN}$ is taken as 16.6 m$^2$g$^{-1}$ corresponding to 0.880 µm for the AE-47 Aethalometer. This value is comparable with that of the urban region but for the other regions this is either comparable or higher than the actual value. As a result the reported BC concentration represents the minimum values. The other uncertainties in the measured BC concentration come from the measurement of flow rate of ambient air, sampled spot area and the detector response. The flow rate was checked periodically with a bubble flow meter. Considering the combined effect of all these factors, the maximum uncertainty
in the measured BC concentration is about 10% (Ramachandran and Rajesh, 2007).

2.5 Nephelometer

Scattering coefficient of aerosol is obtained with the help of an Integrated Nephelometer (Model M903), manufactured by Radiance Research, California, USA. Nephelometer is used to measure the scattering coefficient of the aerosol in the ambient air which comes through a temperature controlled inlet and passes out from the measurement volume (Fig. 2.4). The measurement volume is illuminated by a flash lamp and the scattered light is measured at 0.530 µm by a photomultiplier tube kept perpendicular to air flow. The instrument is regularly calibrated in laboratory by the procedure as described by Charlson et al. (1968). The offset of the instrument is corrected by passing particle-free air and span calibration is done by passing gases of high scattering coefficient such as CO₂. In Fig. 2.4 the optical design of a typical Integrated Nephelometer is shown. The main body consists of a thin-walled aluminum tube. Optical receiver is kept at one end of the tube and a light trap at the other end to provide a dark background against which to view the light scattered by the aerosols and/or gases. Illumination is provided by a quartz-halogen lamp with a built-in elliptical reflector. The reflector focuses the light onto one end of the optical pipe, which serves to thermally isolate the lamp from the sensing volume. The output end of the optical pipe is an opal glass diffuser that provides a nearly Lambertian light source. A broadband-coated 400 mm focal length lens is used to collimate the diverging light defined by apertures in the body of the instrument. From the lens, the scattered light enters into the photomultiplier tube (PMT) passing through a 40 nm bandpass filter, centered at 0.530 µm, into a photomultiplier (Green channel). The reference chopper, which rotates at 23Hz, consists of three separate areas - signal, dark and calibrate - as shown in the inset. The signal section simply allows all light to pass through unaltered. The dark section blocks all light to provide a measurement of PMT background noise. The calibration section scattered by internal surfaces and gas portion of the aerosol.
Correction for changes in gas density is accomplished continuously by means of pressure and temperature sensors. In addition, the relative humidity (RH) of the sample volume is monitored and a second temperature sensor at the outlet keeps track of sample heating.

The major uncertainties in the scattering coefficient measurements arise during the calibration procedures, different environment conditions, photon counts etc. During the calibration procedure the uncertainties are introduced by changes in temperature (T) and pressure (P) of the standard gas and presence of water vapor. During the calibration period these sources of errors can be eliminated by using dry air (bottled standard air or dry ambient air) (Anderson et al., 1996). The total uncertainties in scattering coefficient are about 0.42% for air and 0.95% for CO₂ (Anderson et al., 1996). Other uncertainties come from photon counting and wavelength dependency. During measurement photon counts for three forms, i.e. raw, scale and normalized. Raw and scaled count rates (in Hz) are defined for three portions of the rotating shutter, i.e., calibrate, signal and dark. The normalized photon...
count represents the combination of the three scaled count to derive a signal that is corrected for dark counts and changes in lamp brightness. So the uncertainties of this normalized photon counts should be included into the total uncertainties of Nephelometer measurements. There is also a small correction for photomultiplier dead time but does not affect the uncertainties because it only comes into play at high photon count rates. For an ideal Nephelometer, the light source should be Lambertian point source, and scattered by volume elements that act as point sources of scattered light. Other uncertainties are related to the source of light and different particle sizes. The error in the Nephelometer measurement is less than 10% for accumulation-mode or smaller particles (Anderson et al., 1996).

2.6 Aerosol Size Spectrometer

Surface aerosol number concentrations were measured using Grimm Aerosol Technik (Ainring, Germany) Aerosol Spectrometers (model 1.108). The instrument is field portable, weighing 2.4 kg, with maximum operational period of up to 7 hours using an integral internal battery (or indefinite with an external 110/220V power supply). The ambient air is sucked by a small pump at air flow rate 1.2 $l\cdot min^{-1}$. The air passes though a detector cell which consists of a semiconductor laser source and a receptor diode. When particles are passing through the detector cell the laser light interacts with the particles and generates a scattered light signal proportional to the size of the aerosol particles. A receptor diode collects scattered light at 90° and the signal is processed in a multichannel size classifier. The optics are protected against contamination using a sheath air flow. According to the size the signal is counted in 15 different size bins of 0.3-0.4, 0.4-0.5, 0.5-0.65, 0.65-0.8, 0.8-1.0, 1.0-1.6, 1.6-2.0, 2.0-3.0, 3.0-4.0, 4.0-5.0, 5.0-7.5, 7.5-10.0, 10.0-15.0, 15.0-20.0, >20 $\mu$m diameter. This instrument is operated round the clock and data were collected continuously as 1 min averages, stored on a removable data card, and downloaded and processed using Grimm 1.174 software. Ambient temperature and humidity were measured continuously using a Grimm (Model 1.154)
accessory sensor probe, with data also stored as 1 minute averages. All particles are collected on an outlet filter for further chemical or other gravimetric analysis. This instrument is placed just beside the QCM instrument and it is made sure that both instruments are drawing the same air sample. The number distribution observed by Grimm is comparable with the number distribution calculated from aerosol mass concentration observed by QCM (Jayaraman et al., 2006).