CHAPTER III

THEORIES AND MEASUREMENTS

In 1931 Götz found that the ratio of zenith sky radiances of two wavelengths in the ultraviolet where one has stronger absorption than the other can produce the Umkehr curve where the curve related to the vertical distribution of ozone. The maximum in the ozone profile is detected by inverting the relation between wavelength ratio measurement and solar zenith angle when the sun passes the 85 degree angle.

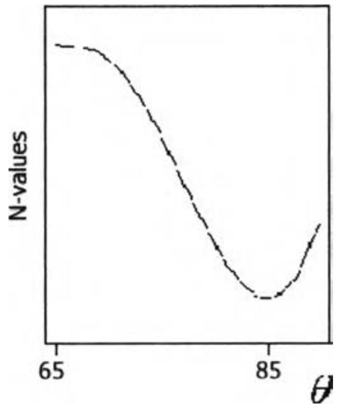

Fig 3.1 Umkehr curve [14]

Umkehr observations yield highly useful information of the vertical distribution of ozone in the atmosphere. A standard Umkehr observation consists of a series of short and long wavelengths made on the clear zenith sky during early morning or late afternoon between solar zenith angle 60 and 90 degrees. To be computing the vertical distribution of ozone, it is necessary to know the total amount of ozone present at the time of observations.

3.1 Umkehr Method

Umkehr method is a tool using in vertical distribution of ozone calculation. It comprises with algorithms for Umkehr measurements and model of the vertical ozone distribution which be emphatically in data analysis.

3.1.1 Umkehr Algorithm

The Umkehr algorithm comprised the forward and inverse model. The forward model will predict what the Umkehr measurement could be for given the ozone profile (first-guess, which represents typical ozone profile for the location and time of the year). The predicted measurements are compared against actual measurements and their difference is resolved into changes to the a priori ozone profile (climatological profile). This part is done in the inverse model where the adjusted profile is produced.

For this study, the Umkehr algorithm procedure mainly employs the inversion technique of Mateer and DeLuisi in 1992. The retrieval techniques of Rodgers in 1976 and 1990 which use the values of the ozone absorption coefficients and their temperature dependence (Bass and Paur, 1984) also describe as below.

Forward Model

The forward model is used to describe the relation between an Umkehr N-value and an ozone profile distribution. The Brewer zenith sky measurements reported in terms of N-values mathematically represented as:

$$N(\theta) = 100 \times \log\left(\frac{F_0^{/} \times K^{/} \times C^{/}}{F_0 \times K \times C}\right) \quad (3.1)$$

where F_0 is the extraterrestrial solar flux constant, K is the instrument constant and C is the photon-counts related to zenith-sky intensities at two wavelengths, where the prime denotes the longer wavelength. The instrument constants (K and K') are unknown because none of the instruments is calibrated in zenith-sky radiance mode. In addition, the extraterrestrial solar flux constants (F_0 and F_0') are not known accurately therefore a normalization procedure is used to cancel out the unknown parameters.

To make the retrieval insensitivity of the instrument in its response to light, tropospheric aerosols and surface albedo, the smallest zenith angle (usually at 60 degree) to be subtracted from the other zenith angles so called normalizing observation.

$$y(\theta) = N(\theta) - N(\theta_0) \quad (3.2)$$

where y (Θ) is normalized measurement, N is Umkehr measurement, Θ is one of nominal solar zenith angles (SZAs) and Θ_0 is the normalization solar zenith angle (SZA).

Light from the direct solar beam illuminates the atmosphere and is scattered by it. Observation of the zenith sky from the ground will include light that is simply scattered at some level in the atmosphere and then proceeds directly to the observation point, light which is reflected up from the ground and then scattered toward the instrument and light which has been scattered more than once and/ or reflected from the ground. In the Umkehr analysis it is assumed that light which is observed in the primary scattered plane will consist of single scattered light plus a fraction which is multiply scattered. For efficiency the total radiance (N_{TOT}) is break into four components as below:

$$N_{TOT} = N_{SS} + N_{MSC} + N_R + N_T \tag{3.3}$$

where N_{SS} is a single-scattered radiance, N_{MSC} is the higher orders of scattered radiances, N_R is refraction radiance and N_T is a temperature correction.

Because of the light which scattered down from the zenith- sky is combination of single-scattering and multiple-scattering therefore Marteer (1964) had constructed tables of the fraction of multiply scattered light which can be used to remove that component from the observed zenith-sky intensities to provide the total column amount of ozone. The radiative transfer equation is an algebraic representation of the relation between ozone vertical distribution and zenith-sky measurements at different solar zenith angles. The single-scattered zenith-sky intensity (I) at given wavelength can be described as following:

$$I_\lambda = I_\lambda^0 \times \beta \times P(\theta) \int_{p0}^{\infty} \exp[-\int_{p0}^{p} (\alpha_\lambda dx_3 + \beta_\lambda dp) - \int_{p}^{\infty} (\alpha_\lambda dx_3 + \beta_\lambda dp) \cdot ds / \Delta h] \cdot dp / \Delta p \tag{3.4}$$

where: I_λ^0 is the spectral radiance outside the earth's atmosphere, P (Θ) is scattering function, Θ is scattering SZA, α_λ and β_λ are ozone absorption and Rayleigh scattering coefficients (cm^{-1}) respectively, dx_3 (atm-cm) is ozone amount in layer dp, ds is slant path of incidence of direct beam in layer dp (atm) of thickness Δh (km), Δp is change in pressure of sub-layer (atm) and p_0 is the pressure altitude of the station.

In order to use the forward model we need to know how the N-values depend on ozone, aerosols, surface reflection, air refraction and multiple scattering assumptions.

The model requires information on ozone absorption and Rayleigh scattering cross-sections for the UV-part of solar spectrum.

The input dataset is based on ozone absorption cross-section (α) measured by Bass and Paur in 1984:

$$\alpha = C_0 + C_1T + C_2T^2 \tag{3.5}$$

where T is temperature, C_0 is ozone absorption at 0^0 C and C_1 and C_2 are linear and quadratic temperature correction coefficients respectively. The Rayleigh scattering cross-section (β) is from Bate (1984).

Inverse Model

As the forward model, the measurement vector elements y (Θ) consist of the observed N-values at the various solar zenith angles N(Θ), corrected for multiple scattering and refraction and with the value at the smallest zenith angle N(Θ_0) subtracted. The measurement vector y is expanded about the linearization point x_n as follow:

$$y = y_n + \frac{\partial y}{\partial x(x - x_n)} \tag{3.6}$$

$$y = y_n + K_n(x - x_n) \tag{3.7}$$

where y is the measurement vector, y_n is the vector of calculated observations for x_n and K_n is the matrix of weighting functions. The retrieval ozone profile is obtained iteratively using equation of Rodgers in 1976. The *n*th iteration retrieval x_{n+1} are obtained from x_n as follow:

$$x_{n+1} = x_0 + S_xK_n^T(K_nS_xK_n^T + S_e)^{-1} \times [y - y_n - K_n(x_0 - x_n)] \tag{3.8}$$

where x_{n+1} is the state of vector for the solution of the iterative equation, x_n is retrieved profile on the nth iteration, x_0 is a priori information, S_x is the a priori covariance matrix, S_e is the error covariance matrix for the measurements (= K_nX), K_n is the Jacobian matrix, y is the vector of observations, y_n is the vector of calculated observations for x_n, and the superscript T represents matrix transposition.

The solution starts with a first-guess profile x_1 from which the weighting function K_1 and measurements y_1 are evaluated and proceeds through n iterations until the retrieved profiles stop changing. The iterations are stopped when no more changes in profile or N-value namely the size of x_{n+1}-x_n must be less than 0.04 in all layers, the root mean square (R.M.S.) value of the change must be less than 0.01 and the R.M.S. value of the changes in the last square bracket of Eq. (3.8) is no grater than 0.15 N-units. When more than five iterations are required for convergence, it has been found that there is a poor fit and the observation should be rejected.

3.2 The Vertical Ozone Observations

The vertical distribution of ozone is routinely measured with the ground-based remote sensing instruments and satellite instruments which measure the intensity of UV or visible light at wavelengths in the absorption spectrum of ozone. The most commonly used ground-based instruments in the Global Ozone Observing System (GO_3OS) are Dobson Spectrophotometer, Brewer spectrophotometer and Ozone Sonde. While SAGE I and SAGE II are the satellite instruments.

The Umkehr Brewer raw data can get from Thai Meteorological Department (TMD), which in the ground-based of ozone monitoring network in the Global Atmospheric Watch (GAW) programme of the World Meteorological Organization (WMO). The vertical ozone measurements started in 1997 but the continuously data are between 2001 and 2003, using the Brewer spectrophotometer which located at Songkhla (B120). The instrument is maintained by the staff and calibrated with reference standard instrument. The Brewer instrument had been calibrated with traveling standard Brewer (B017) by International Ozone Service Limited. in April 2000 and in February 2004 respectively.

Umkehr observations with the Brewer spectrophotometer instruments consist of measurements of the solar zenith radiation in eight wavelengths (306.3, 310.0, 313.5, 316.8, 320.1, 323.2, 326.4 and 329.5 nm). Log-intensity ratios are formed for the wavelength pairs (306.3, 323.2), (310.0, 326.4) and (313.4, 329.5). The observation controlled routinely under schedule operation in the early morning or late afternoon between solar zenith angles 60 and 90 degree (60, 65, 70, 74, 77, 80, 83, 85, 86.5, 88, 89, and 90 degree). Clear sky conditions are necessary for good results. The zenith prism is set skyward and the Brewer is oriented perpendicular to the solar azimuth. Observations must be terminated by the operator or by schedule of the next zenith angle entry transmitted solar radiation in the zenith direction in eight wavelength bands. Only six of these are used in the inversion procedure (306.3, 310.1, 313.5, 323.2, 326.4, and 329.5)

3.2.1 The Brewer Spectrophotometer

Though the Dobson instrument has served its purpose well since the 1930s, the Brewer spectrophotometer is today becoming the instrument of choice for ozone measurement. The first Brewer Spectrophotometer was designed by Alan Brewer (1948-1962) who worked at Sub-department of Atmospheric, Oceanic and Planetary Physics, University of Oxford. This instrument is designed for continuous outdoor operation to measures the light intensity for determination of total ozone, sulphur dioxide, nitrogen dioxide and UV spectra. A complete Brewer System is comprised as the following items:

a) Brewer Spectrophotometer
b) IBM PC or compatible microcomputer
c) Printer-dot matrix printer
d) Control software

The Brewer spectrophotometer is normally supplied with automated iris and filter wheel controls, azimuth, zenith trackers and a UVB monitor. The Brewer System is illustrated in Fig.3.2 as bellow:

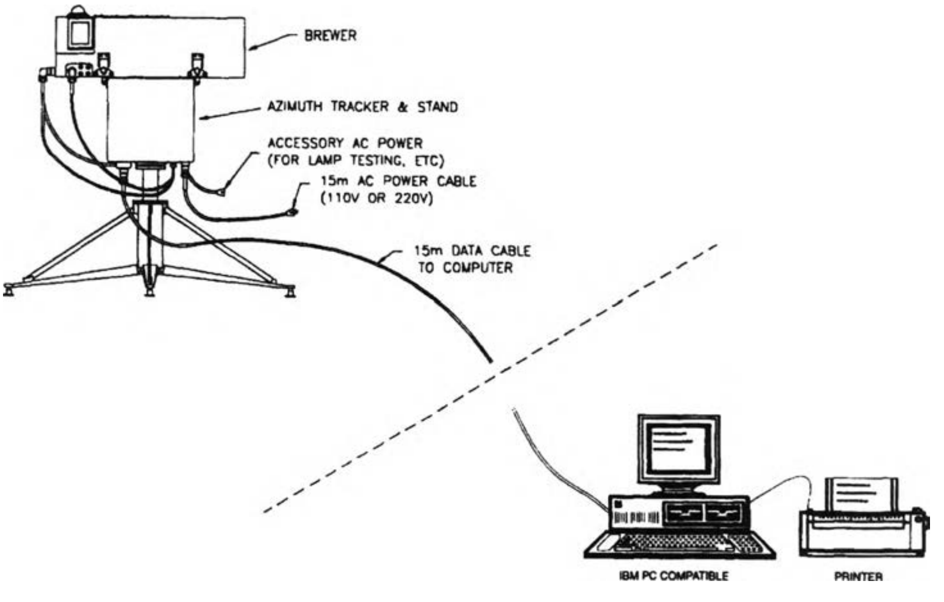

Fig 3.2 The Brewer spectrophotometer [15]

The routinely ozone profile is also measured by Ozone Sonde and satellite instruments, for Ozone Sonde, ozone profile is measured the concentration of ozone as a function of height by sampling ambient air during a balloon-borne ascent to an altitude typically between 30 and 40 km while satellite used solar occultation method (e.g., SAGE II), solar backscattered UV method (SBUV), infrared and microwave thermal emission technique respectively.

The Optical System

Basic component of the optical system of Brewer spectrophotometer are shown in Fig.3.3. For zenith sky observations, the solar radiation enters the instrument through the inlet window and through a movable prism. Then the radiation continues through foreoptics (iris, attenuation filters and entrance slit) to a mirror.

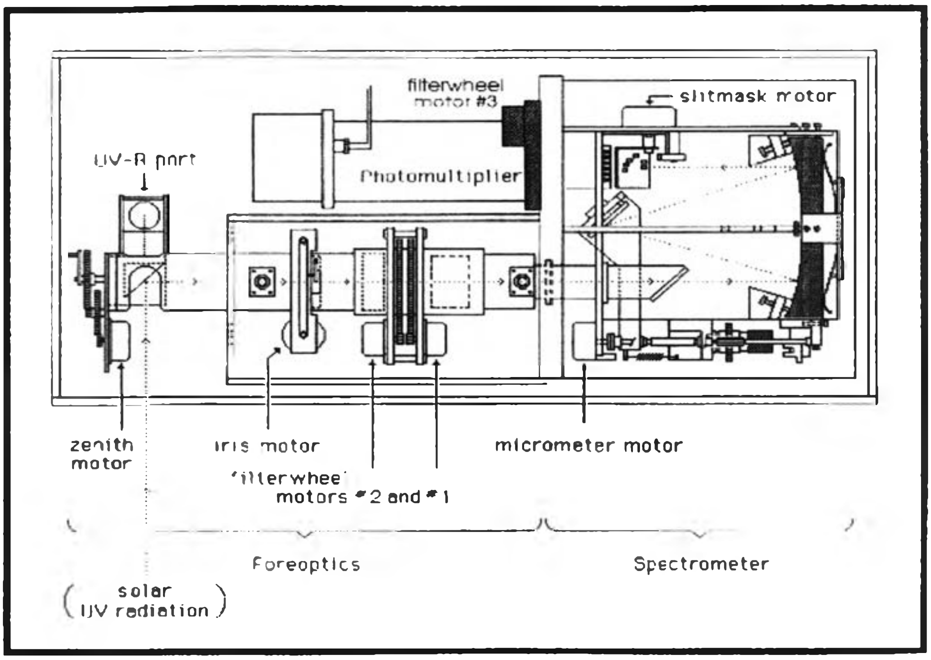

Fig 3.3 The optical system of the Brewer spectrophotometer [15]

After reflection on the mirror it falls on the movable holographic grating (1,800 lines/mm) where the radiation is decomposed and a second order spectrum is created. Spectral lines are then reflected and focused by the mirror on the plane of six exit slits. The dimension of the slits combined with the position of slots on a rotated chopper mask allows penetration of only selected wavelengths to fall on the photomultiplier where the irradiances are converted into photon counts. All movable parts of the optical system are precisely positioned with stepping motors and they are controlled by the connected computer.

3.2.2 The Units of Ozone Measurements

Ozone measurements are typically reported in one of four units.

Total Column Amount in Dobson Units (DU)

The total amount of ozone is measuring by the Dobson instruments and the Dobson units are always used. Dobson unit refers to a layer of ozone that would be 0.01 mm thickness. For example, if the ozone layer over Thailand were compressed to standard temperature and pressure (0°C and 1013.25 mb), it would be about 2.6 mm thick. So, this makes the average thickness of the ozone layer over Thailand come out be about 260 DU. In the general, 1 DU can be written as:

$$
\begin{aligned}
1 \text{ Dobson unit} \quad &= 1 \text{ milli-atmosphere- centimetre (m-atm-cm)} \\
&= 10^{-5} \text{ m of ozone at STP} \\
&= 2.687 \times 10^{16} \text{ molecules cm}^{-2} \\
&= 1 \text{ part per million metre (= 1.0 ppmm at STP)}
\end{aligned}
$$

Number Density (molecules/cm^3)

Number density refers to the absolute concentration as the number of ozone molecules per cubic centimeter where 10 DU/km is equal to 2.69×10^{24} molecules/cm^3 (number density). The vertical distribution of ozone measurements which made with the Brewer instruments and satellite instruments usually measured in this unit.

Partial Pressure in Nanobars (nb)

Partial pressure refers to the fraction of the atmospheric pressure at a given altitude for which ozone is responsible. Balloon borne measurement (Ozone Sondes) and Light Detection and Ranging Laser measurement (LIDAR) are usually reported in partial pressure. The partial pressure and number density profiles are very similar. This similarity is due to the fact that the partial pressure of ozone can be expressed as a function of the number density.

$$P_{ozone} = (\text{number density})\ kT$$

where P_{ozone} is the number density, k is Boltzman's constant (1.38×10^{-23} J/K) and T is temperature measured in degrees Kelvin.

Mixing Ratio in Parts (ppmv)

Surface ozone observation always represent in unit of mixing ratio in parts per million by volume relates the fractional concentration of ozone as the number of ozone molecules per million air molecules. The most commonly used instruments for measuring surface ozone are the UV photometric ozone analyzer and the Dasibi-type ozone monitor.