Ozone!
Introduction to Ozone Measurement

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David Wardle
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Beer’s law 1, 2
Ozone absorption
Slant path at 22 km; $\mu, m$ and $\sec \theta$
Rayleigh scattering
Langley plots 1, 2
Single wavelength attenuation expression
Dobson observations 1, 2
Performance Testing
Handbook

DOBSON
OZONE SPECTROPHOTOMETER

REPRODUCED FROM THE ANNALS OF THE INTERNATIONAL GEOPHYSICAL YEAR — VOLS. V & XVI, BY PERMISSION OF THE PERGAMON PRESS LTD.

Dobson's
Observer's Handbook
Beer’s Law

\[ \frac{\text{lost photons}}{\text{photons/s}} = \frac{\text{total optical depth}}{\text{Cross-section m}^2} \]

(e.g.: \(\text{Photons/s/m}^2\))

Total optical depth: \(\text{m}^2/\text{molecule} \times \text{molecules/m}^2\)

Lost photons: \(\text{photons/s}\)
Beer’s Law - 2

An integral derivation which emphasizes the restriction of there being no significant effects of reflection or scattering in the medium.

Consider: \( I = F(I_0, \text{stuff}) \)
Better: \( I = I_0 \times G(\text{stuff}) \)

\[ G(a+b) = G(a) \times G(b) \]
\[ G(\text{stuff}) = \exp(-\text{constant} \times \text{stuff}) \]

Or

\[ dI = -I \, dt \]

\[ I = I_0 \exp(-t) \]

O.K. if

The radiation is monochromatic and unidirectional.
‘Phenomenological’ Beer’s Law - 3

\[ I = I_0 \cdot \exp(-\mu \alpha x) \]

**stuff** - equivalent thickness of a layer of gas at standard temperature and pressure
  e.g. ‘total ozone’ or ‘column ozone’ (same)

**constant** - absorption coefficient \( \alpha \) \( \text{cm}^{-1} \) at s.t.p.

\[ x \text{ cm at s.t.p.} \]

\[ \alpha \text{ cm}^{-1} \text{ at s.t.p.} \]

‘Physical’

**stuff** - number of molecules per unit area

**constant** - absorption cross-section per molecule \( \sigma \) \( \text{cm}^2 \)

\[ n \text{ cm}^{-2} \]

\[ \sigma \text{ cm}^2 \]

\[ I = I_0 \cdot \exp(-\mu n \sigma) \]

Given \( L = \text{Loschmidt's number} \)

\[ = 2.687 \times 10^{19} \text{ molecules per cm}^3 \text{ at s.t.p.} \]

\( n / L = x \)

\( L \sigma = \alpha \)

(s.t.p. 0 C and 1 atmosphere)
Ozone Absorption - General

Ozone absorption coefficients
(cm at stp)-1

Dissociation if $\lambda < 1.1\mu m$

$O_3 + h\nu \rightarrow O_2 + O$

Excited states if $\lambda < 315\,nm$

$O_3 + h\nu \rightarrow O_2^* + O^*$

Note:

$O$ usually recombines with $O_2$

$O^*$ may make OH

$O_2^*$ may emit a 1.27$\mu$m photon
Ozone Cross-sections

Spectral regions used for ‘optical’ measurements by Huggins and Chappuis

Cross-sections as Measured in the Laboratory by the GOME FM.

GOME - Global Ozone Monitoring Experiment

FM – Flight Model
The tables show the standard Dobson measurement Wavelengths and the optical depths of a 1-cm ozone path.

The idea behind both the Dobson and Brewer measurements is that the absolute extinction on a wavelength pair from other things is similar, but the difference in ozone Absorption is large...
Ozone Absorption – Brewer Wavelengths

(The small absorption at 324 nm allowed this intensity to be used as a proxy for wavelengths longer than 325 nm in the original short-wavelength-range Brewer UV scans.)
Single-wavelength attenuation expression

\[
\log I = \log I_0 - (\mu ax + m\beta + \sec \theta \delta + \mu' a' y)
\]

where:

- \( I \) = radiation as measured by Brewer
- \( I_0 \) = radiation as would be measured by the Brewer above atmosphere
- \( \theta \) = solar zenith angle
- \( \mu \equiv \mu' \equiv m \equiv \sec \theta \) slant path factors
- \( a \) = ozone absorption coefficient
- \( x \) = ozone amount
- \( \beta \) = Rayleigh scattering coefficient
- \( \delta \) = amount of other absorption
- \( a' \) = \( SO_2 \) absorption coefficient
- \( y \) = \( SO_2 \) amount
Langley plot: single-wavelength measurement

A Langley plot is a graph of $\log I$ versus $\sec 2$ (or $\mu$).

Assuming that attenuation is due only to Rayleigh scattering and ozone absorption (and that $m = \mu$), the Langley plot should follow:

$$\log I = \log I_0 - \mu(\alpha x + \beta) \quad \text{Signal} = RI$$

This same expression applies if $I$ signifies the instrument readings provided they are known to be proportional to the radiation; $I_0$ is then the reading the instrument would show if subjected to the radiation above the atmosphere. (Absolute irradiance calibration is not needed.)

The "long method" (terminology of G.M.B. Dobson) derives the ozone $x$ and the extra-terrestrial reading $I_0$ from the slope and intercept of the Langley plot. It uses several measurements obtained during any morning or afternoon to obtain single values for $x$ and $I_0$.

Changes in the ozone during the the day can cause significant errors!

The "short method" gives one ozone value for each measurement but requires a pre-determined value for the extra-terrestrial reading. Long-term drift in the instrument responsivity contributes an error in $I_0$ and, consequently, in $x$. 
Differential Measurements

(E.g.: Dobson or Brewer)

\[ I(\lambda_s) = I^0(\lambda_s) \exp[-\tau(\lambda_s)] \]
\[ I(\lambda_l) = I^0(\lambda_l) \exp[-\tau(\lambda_l)] \]

\[
\log\left( \frac{I(\lambda_s)}{I(\lambda_l)} \right) = \log\left( \frac{I(\lambda_s^0)}{I(\lambda_l^0)} \right) - \left[ \sigma(\lambda_s) - \sigma(\lambda_l) \right] \times m
\]

or

\[ F = F^0 - \Delta \sigma \times m \]

\[ X = \frac{(F^0 - F)}{(\Delta \sigma \times m)} \]

\[ m = 1.0 / \cos(SZA) \]

_Can be extended to 3 or more wavelengths with extra constraints..._
Langley plot – Short and Long Methods

**Long Method**

\[ \log I_0 \quad \text{vs} \quad \mu \]

- **Intercept**: \( \log I_0 \)
- **Slope**: \( a \times x + \beta \)

**Short Method**

\[ \log I_0 \text{ (given)} \quad \text{vs} \quad \mu \]

\[ OZONE = \frac{\log I_0 - \log I}{\mu a} - \frac{\beta}{a} \]

In practice, both methods applied to single-wavelength measurements give large uncertainties due to sources of attenuation other than air and ozone.

The uncertainties can be greatly reduced by using ratios of measurements at two or more wavelengths instead of measurements at any single wavelength.
Dobson Observation

The Dobson measures the ratio of intensities in the short and long channels of a pair, not the individual intensities.

There is a variable optical attenuator in the long channel. It comprises two optical wedges that are mechanically linked to a wheel so that the attenuation is determined by the rotation of the wheel, which is expressed in degrees and called the R-value.

The detector senses the difference between the responses to radiation in the two channels. A Dobson observation is made by adjusting the wheel so that this difference is zero. The R-value is then the result (or raw output signal) from the observation.

Dobson transmission functions *(nominal)*

<table>
<thead>
<tr>
<th>Wavelength settings (nm)</th>
<th>Short</th>
<th>Long</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-pair</td>
<td>305.48</td>
<td>325.14</td>
</tr>
<tr>
<td>B-pair</td>
<td>308.78</td>
<td>329.15</td>
</tr>
<tr>
<td>C-pair</td>
<td>311.46</td>
<td>332.39</td>
</tr>
<tr>
<td>D-pair</td>
<td>317.58</td>
<td>339.82</td>
</tr>
<tr>
<td>(C’- pair</td>
<td>332.39</td>
<td>453.6</td>
</tr>
</tbody>
</table>
Rayleigh scattering

i.e. the scattering of radiation by air molecules (elastic – no change in wavelength)

Rayleigh scattering causes unidirectional, monochromatic radiation, when passing through the atmosphere, to be attenuated by a factor:

$$\exp(m\beta)$$

where $m$ is the air mass ($\approx \mu$) and $\beta$ is the Rayleigh scattering coefficient

$$\beta \approx \frac{\text{pressure}}{1013} \frac{313.4^4}{\lambda^4}$$

i.e. $\beta = 1$ when $\lambda = 313.4\text{nm}$ and pressure = 1013 hPa

Thus for an atmosphere containing only air and ozone:

$$I = I_0 \cdot \exp(-\mu\alpha - m\beta)$$

$I$ is the direct solar irradiance in watts.m$^{-2}$.nm$^{-1}$

- the radiant energy originating from a small solid angle including the sun arriving at the earths surface (also in a small range of wavelength)

$I_0$ is the direct solar irradiance above the atmosphere
Slant path at 22 km; $\mu$ , $m$ and $\sec(\theta)$

$\mu = \sec\theta'$

$$\frac{\sin\theta'}{R} = \frac{\sin\theta}{R+h}$$

For ozone $h = 22 \text{ km}$

For air $\approx h \approx 6 \text{ km}$

With refraction ($n =$ refractive index),

$n(R+h)\sin\theta' = \text{constant along the path}$

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>0°</th>
<th>60°</th>
<th>75.52°</th>
<th>80.46°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sec\theta$</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>$\infty$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>1</td>
<td>1.980</td>
<td>3.81</td>
<td>5.39</td>
<td>12.1($a$)</td>
</tr>
<tr>
<td>$m$</td>
<td>1</td>
<td>1.994</td>
<td>3.94</td>
<td>5.81</td>
<td>38 ($b$)</td>
</tr>
</tbody>
</table>

$a$: with refraction = 12.6

$b$: neglecting refraction = 35

Brewer Approximation:

airmass = $1/\cos\{\sin^{-1}[R/(R+h)\sin(\theta)]\}$
Fery Spectrometer
Dobson Spectrophotometer

March 24 - 28, 2014  14th Biennial Brewer Workshop  Tenerife
Inside…

March 24 - 28, 2014
14th Biennial Brewer Workshop
Tenerife, China

18:18:44
Brewer Optics

To Photomultiplier Housing

Entrance Slit

~ 15 cm
Rectifier Phase

The Dobson was one of the first opto-electronic instruments to use phase-sensitive detection to improve signal-to-noise ratio and do a direct difference detection.

These tracings illustrate the phase setting adjustment made to synchronize the rectifier with the phase of the optical signal. The test is done with a large signal and high signal-to-noise ratio.
Brewer – SH Test

- For efficient operation the slits should be open as much as possible (design 7:8)
- Only one slit should pass light at one time
- Stepping motor must change positions as fast as possible
- It must not oscillate when stopped
- A non-resonant waveform is generated
- The SH test determines the time constant for the waveform
The Brewer – Run/Stop

- The Brewer multiplexes rapidly between multiple slits
- Photon counting is inhibited while changing slits so the electronics determines the timing interval
- The position of the slit mask must change fast with little oscillation to be accurate
- The Run/Stop test compares static measurements with dynamic measurements
Measurement Linearity

Dobson

• Issue largely avoided
• Detection of balance only at range of gains
• Optical wedge calibrated using 2-source test
• ‘N-tables’ used to translate R-values to logs
Linearity - Brewer

- Linearity tested explicitly
- 2-source test
  - Done using the DT test
  - Run with three slit positions
  - One has 2 slits open at once
- Measure: A, B and A&B
- Compare: A+B to A&B
- Solve for dt in:
  \[ A = A_o \exp(-A_o \ dt) \quad B = B_o \exp(-B_o \ dt) \]
  \[ A + B = (A_o + B_o) \exp[-(A_o + B_o) \ dt] \]
Sun Scans
The Brewer – SC Test

• The solar spectrum is observed under clear conditions (for stability)
• The grating angle is scanned by stepping the drive micrometer
• An extreme point in the ozone and SO$_2$ is identified near the nominal calibration step
• This step position is the calibration point for the instrument

(Note that the step number is a function of slant column ozone amount. Traditionally the cal step is chosen near 700 DU slant column ozone amount.)
Brewer Calibration

- Using direct regression against airmass
- Computer-calculated
- Station instruments done by comparison to traveling standard

Mauna Loa Observatory
Extraterrestrial Constant

L₀ analysis
From Oxford.
Brewer Langley Plot

Ozone ratio (R6) Langley plot

[Graph showing a line with data points]
The Formula...

Ozone = (F – Fo) / (mu * alpha)

If the ozone is constant,
Ozone * alpha = F / mu – Fo / mu

Plot F / mu against 1/ mu
The slope is Fo
Inverse plot

R6/amf Langley plot

![Graph showing the inverse relationship between R6/amf and 1/amf.](image)