TOPIC 1
ATMOSPHERIC PHOTOCHEMISTRY and
AIR POLLUTION

Field Project & Instrumentation:
CO, O₃, NO, NO₂, CO₂, aerosols, UV
ATMOSPHERIC PHOTOCHEMISTRY and AIR POLLUTION
Field Campaign on Top of Bldg. 54

On the top of the building you will measure ultraviolet radiation (UV), CO, O₃, NO, NO₂, CO₂, wind speed (u), temperature (T) and aerosols (1, 2.5, and 10μm diameter filters) (we will use aerosols as tracers of nearby combustion).

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Gas absorption and scattering
BEERS LAW

$I(x) = I(0) \exp(-\sigma[i]x)$

$I = \text{photon flux (photons / m}^2\text{)}$

$\sigma = \text{absorption cross section at 4.3\,\mu m (m}^2\text{ / molecule)}$

$x = \text{photon pathlength from source (m) (total path = 2.5m)}$

$[i] = \text{gas concentration (molecule / m}^3\text{)}$
Measuring CO$_2$: Teledyne Model 360E Analyzer, contd.
Measuring CO: Teledyne 300E Carbon Monoxide Analyzer (similar to the 360E CO₂ Analyzer)

Beer-Lambert Law

\[ I = I_0 \exp\left(-[CO] \sigma_{CO} \ell_{cell}\right) \]

\[ [CO] = \ln\left(\frac{I_0}{I}\right) / (\sigma_{CO} \ell_{cell}) \]

- Band pass filter at 4.7μm with 14 m pathway
- GFC wheel with CO to cancel interfering gases (H₂O, CO₂, N₂O, CH₄)
- Low CO cannot be accurately measured with high concentrations of interfering gases

Calibration: Zero/Span

Zero and Span gases should match chemical composition of sample

Span gas with concentration ~80% of full measurement range

Traceable to NIST standard
Ozone has an absorption maximum at 254 nm, coincident with the principal emission wavelength of a low-pressure mercury lamp.

Only potential interferences from organic compounds in highly polluted air.
Measuring O₃: Dual Beam Ozone Monitor, contd.

Solenoid valves switch in unison to alternately send ozone-scrubbed air and unscrubbed air through the two absorption cells. The intensity of light passing through ozonescrubbed air ($I_0$) is measured in Cell 1 while the intensity of light pass through unscrubbed air ($I$) is measured in Cell 2. Every 2 seconds, the solenoid valves switch, changing which cell receives ozone-scrubbed air and which cell receives unscrubbed air. The 2 values are averaged.

Beer-Lambert Law

$[O_3] = \ln\left(\frac{I_0}{I}\right) / (\sigma_{ozone} \ell_{cell})$

$I = I_0 \exp[-[O_3] \sigma_{ozone} \ell_{cell}]$

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In principle, the measurement of ozone by UV absorbance requires no external calibration; it is an absolute method.

However, non-linearity of the photodiode response and electronics can result in a small measurement error (Model 306 versus standard). Therefore, each instrument is compared with a NIST-traceable standard.
Scrubs ozone from ambient air to produce zero air and air with ozone mixing ratios 30-1000 ppb, up to 10 concentration steps.

**O₃ concentration depends upon:**
- lamp intensity
- O₂ concentration (P and T)
- sample time in cell (cell volume and flow rate)

Benefits: portable & source of ozone with same humidity, P, etc as air to be measured

Factory calibrated against NIST-traceable ozone standard

Uses same chemistry that produces ozone in the stratosphere

\[
O_2 + h\nu \rightarrow O + O \\
2 [O + O_2 + M] \rightarrow 2 [O_3 + M]
\]

\[
3 O_2 + h\nu \rightarrow 2 O_3
\]

Low pressure mercury lamp photolyzes oxygen at 185 nm (monitored by photodiode)
Measuring NO: Nitric Oxide Monitor
(2B Technologies Model 400)

NO + O₃ → NO₂ + O₂ + chemi-luminescence*

- Stoichiometric reaction
- Adequate concentration of O₃ added to the sample stream
- Decrease in the concentration of O₃ is measured by absolute UV absorption (as in the Ozone Monitor, 254nm)

Beer-Lambert Law

\[ C_{O₃} = \frac{1}{\sigma l} \ln \left( \frac{I_o}{I} \right) \]

\[ C_{NO} = C_{O₃, ref} - \frac{F_{total}}{F_{total} - F_{ozone}} \left( C_{O₃-NO} \right) \text{det} \]

\[ F_{total}/(F_{total} - F_{ozone}) \] is dilution correction factor ($F =$ flow rate)

*Alternative chemi-luminescence analyzer:* Detects the small amount of light produced. Higher sensitivity & faster response time but requires more frequent calibration
Measuring NO: Nitric Oxide Monitor, contd.

Reference cell to correct for ambient O$_3$
Adequate reaction time 3.5 - 4.5s

Light intensities measured for:
Sample air and reference
NO scrubbed sample air and reference

Ozone production by low pressure mercury lamp at 185nm to photolyze O$_2$ (same as Ozone Calibration Source)
Corrections for incomplete reaction and dilution by added ozonized air

Courtesy of 2B Technologies, Inc. Used with permission.
Measuring \([\text{NO}_x](= [\text{NO}] + [\text{NO}_2]) \) & \([\text{NO}_2]\)

(*2B Technologies Model 401 “NO\(_2\) Converter”*)

Air stream (containing both NO and NO\(_2\) ) passes through a molybdenum catalytic converter which converts NO\(_2\) into NO prior to the air entering the “NO Monitor”.

Thus the “NO Monitor” gives a measurement of \([\text{NO}_x]\).

Then \([\text{NO}_2] = [\text{NO}_x] – [\text{NO}]\) where [NO] is value obtained by “NO Monitor” without using the Converter
Continuous sample stream illuminated with laser light at 780 nm
Smallest detectable particle 0.1μm
Light scattering in all directions, focusing lens and photo-detector at 90 degrees
Fixed sensing volume
Can choose 1.0μm, 2.5μm, and 10μm inlet nozzles

*Optics kept clean by surrounding aerosol stream in a sheath of filtered air*
Measuring Aerosols: DustTrak, contd.

Mie light scattering theory

Scattered light by aerosols dependent upon:

- Particle size parameter [ratio of circumference (πD) to laser wavelength (λ)]
- Index of refraction of aerosol material
- Aerosol light absorption properties \( \varpi = \frac{\sigma_{abs}}{\sigma_{abs} + \sigma_{scat}} \)

Collected light \( \propto \) Total scattered light \( \propto \) Aerosol mass concentration

Calibration and Zeroing

Internal calibration constant relates this linear response. Determined from the ratio of voltage response to the known mass concentration of a test aerosol (ISO 12103-1, A1 Arizona Test Dust) that has a wide size distribution representative of a variety of ambient aerosols

Optional recalibration for each specific aerosol type

Zero calibration daily with zero inlet filter
4μm is internationally accepted as the 50 percent cut-off size for respirable aerosol diameter. Particles larger than 4 μm impact onto the surfaces of the upper respiratory tract and cannot reach the lungs.

10mm Nylon **Dorr-Oliver Cyclone (2)** included with the aerosol monitor can be used to discriminate between the respirable fraction and other portions of the ambient aerosol.

Particle-laden air sample swirls inside the **Cyclone** body. Larger (higher mass) particles cannot follow the air stream and become trapped, while smaller particles stay in the air stream and pass through. When using the **Cyclone**, you can assume that all particles smaller than the cut-off size pass through and all larger particles become trapped in the grit pot.