12.335/12.835 EXPERIMENTAL ATMOSPHERIC CHEMISTRY, FALL 2014

TOPIC 1
ATMOSPHERIC PHOTOCHEMISTRY and AIR POLLUTION

Field Project & Instrumentation: CO, O_3, NO, NO_2, CO_2, aerosols, UV

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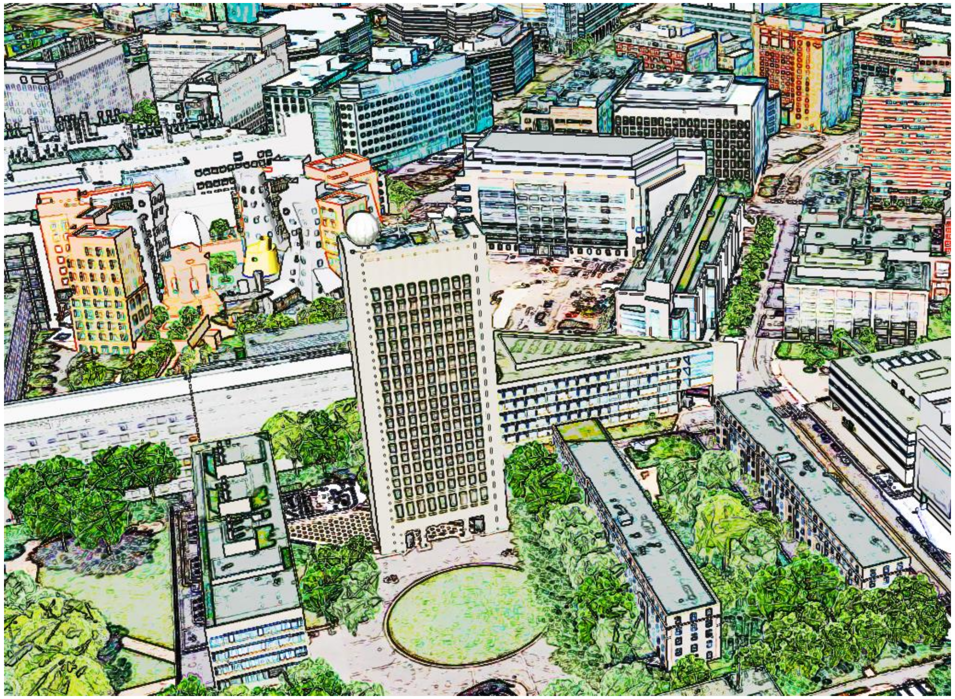
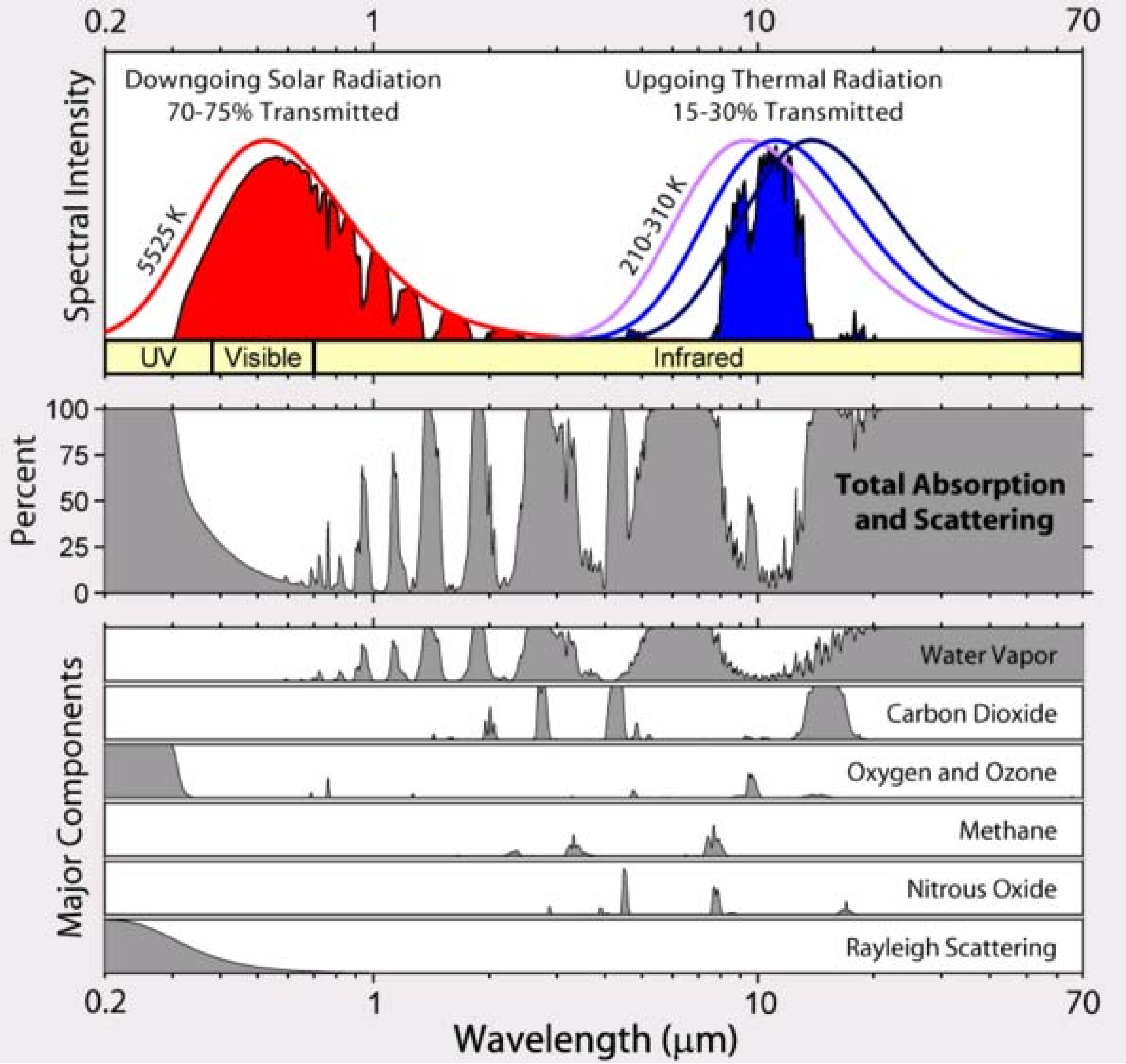
ATMOSPHERIC PHOTOCHEMISTRY and AIR POLLUTION Field Campaign on Top of Bldg. 54

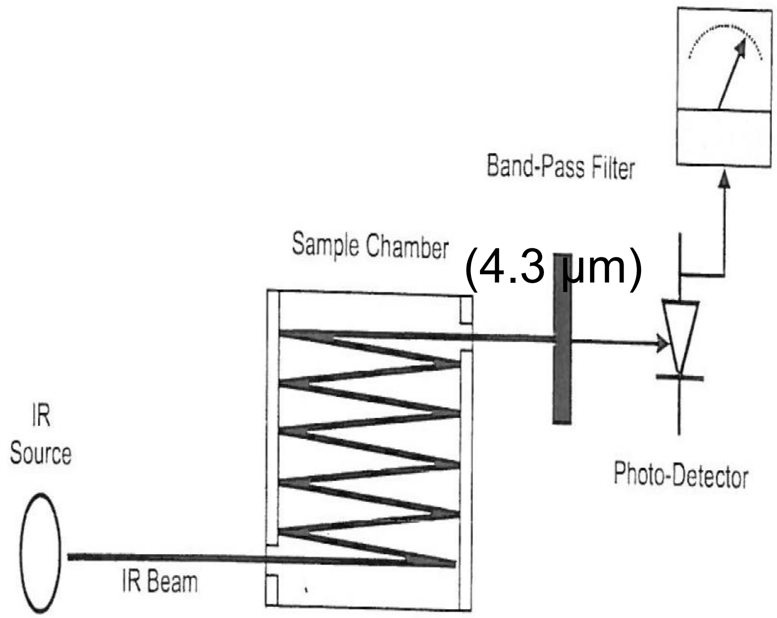
On the top of the building you will measure ultraviolet radiation (UV), CO, O_3, NO, NO_2, CO_2, wind speed (u), temperature (T) and aerosols (1, 2.5, and 10µm diameter filters) (we will use aerosols as tracers of nearby combustion).



Gas absorption and scattering



Measuring CO_2: *TELEDYNE Model 360E Gas Filter Correlation (GFC) Optical Analyzer*



IR SOURCE IS HOT FILAMENT

$$BEERS\_LAW$$

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

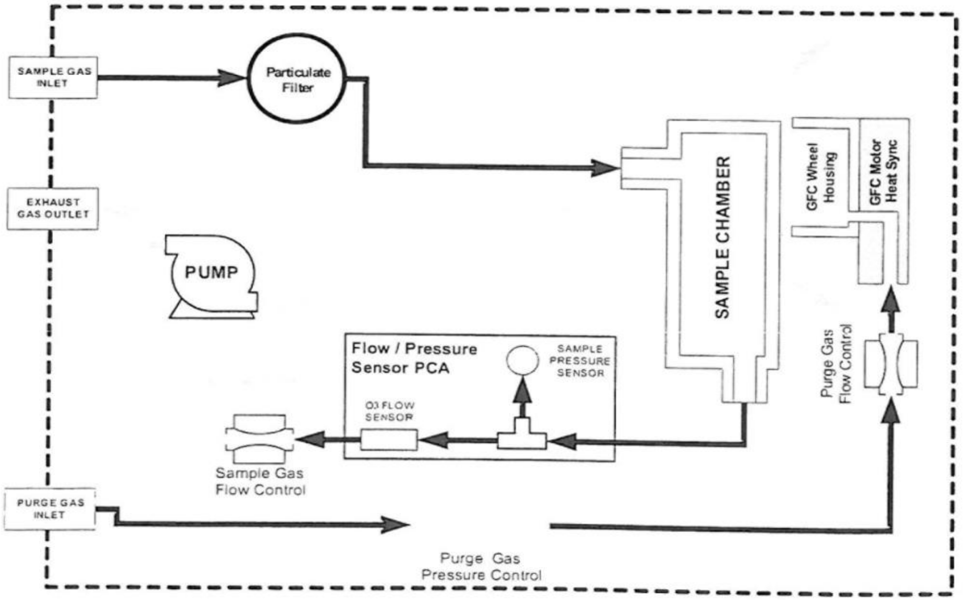
$$I = photon\ flux(photons / m^2)$$

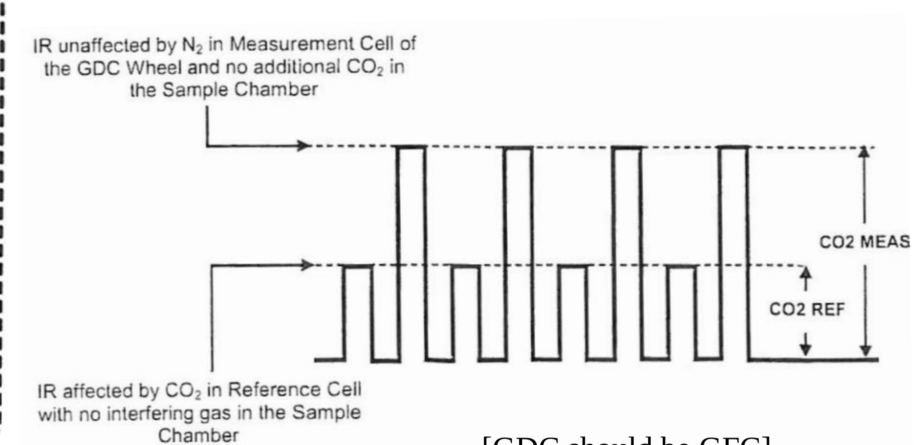
$$\sigma = absorbtion\ cross\ \sec tion\ at\ 4.3\mu m\ (m^2 / molecule)$$

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

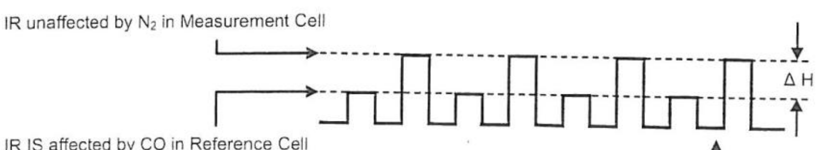
$$[i] = gas\ concentration\ (molecule / m^3)$$

Measuring CO_2: Teledyne Model 360E Analyzer, contd.

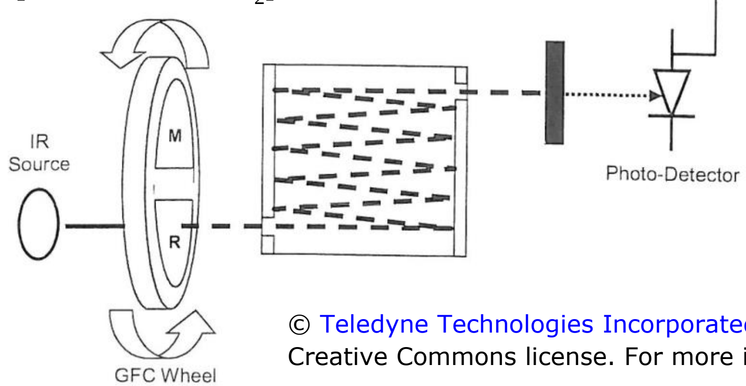


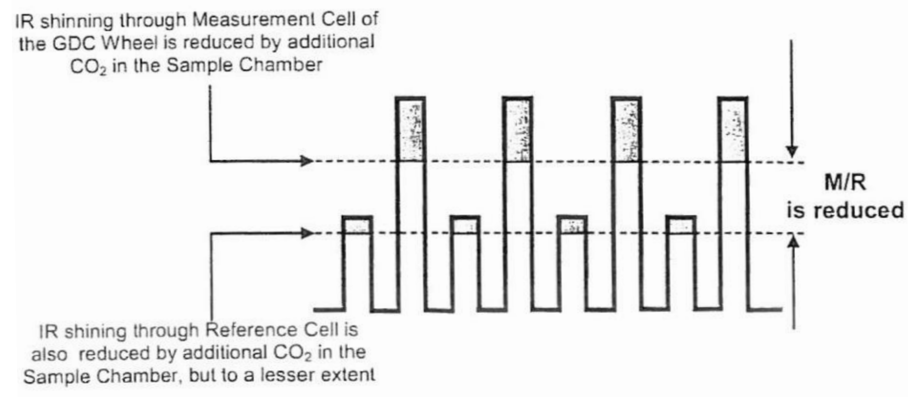


[GDC should be GFC]



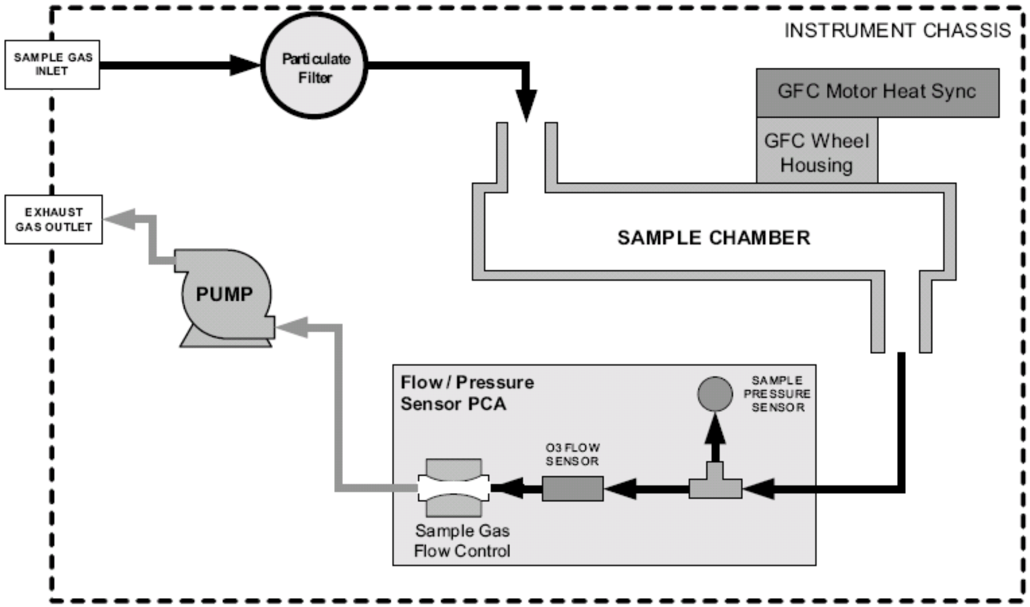
[CO should be CO_2]





Measuring CO: *Teledyne 300E Carbon Monoxide Analyzer*

(similar to the 360E CO_2 Analyzer)



Beer-Lambert Law

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

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

-Band pass filter at 4.7μm with 14 m pathway
-GFC wheel with CO to cancel interfering gases (H_2O, CO_2, N_2O, CH_4)
-Low CO cannot be accurately measured with high concentrations of interfering gases

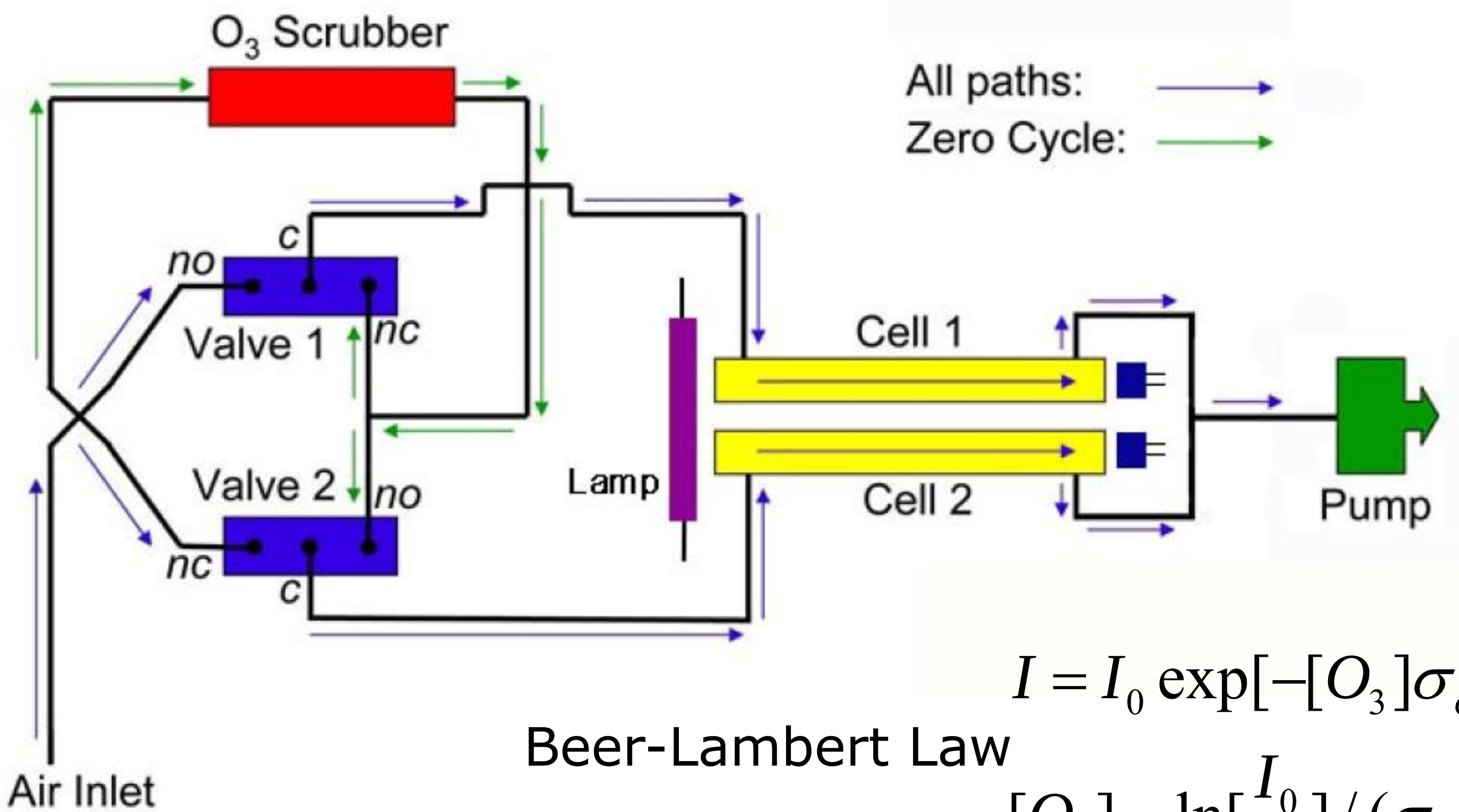
Calibration: Zero/Span

Zero and Span gases should match chemical composition of sample

Span gas with concentration ~80% of full measurement range

Traceable to NIST standard

Measuring O_3: *2B Technologies Model 205 Dual Beam Ozone Monitor*



Beer-Lambert Law

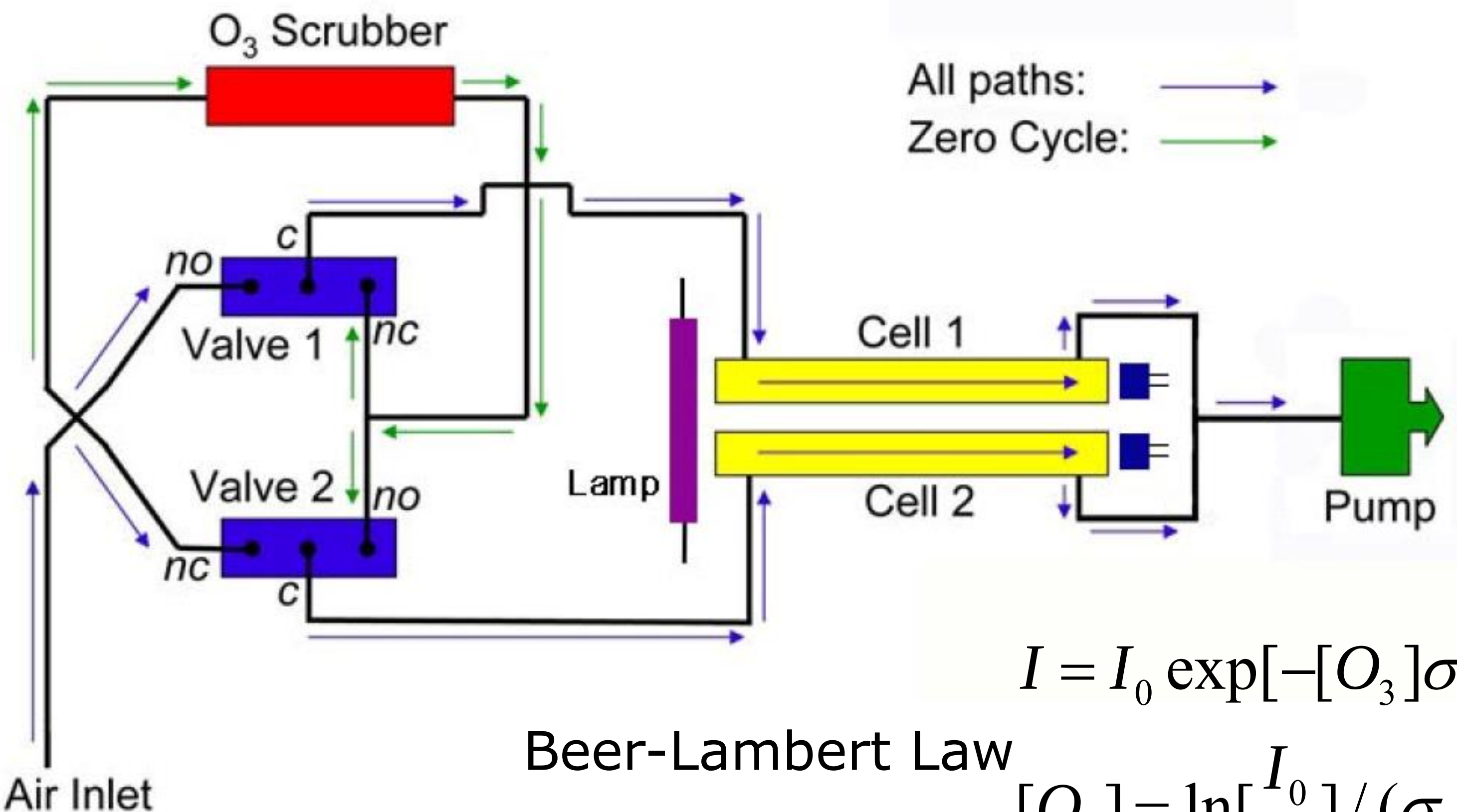
$$I = I_0 \exp[-[O_3]\sigma_{ozone}\ell_{cell}]$$

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

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 O_3: Dual Beam Ozone Monitor, contd.



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

Beer-Lambert Law

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

Courtesy of 2B Technologies, Inc. Used with permission.

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_o) 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.

Measuring O_3: Ozone Calibration Source
(2B Technologies Model 306)

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

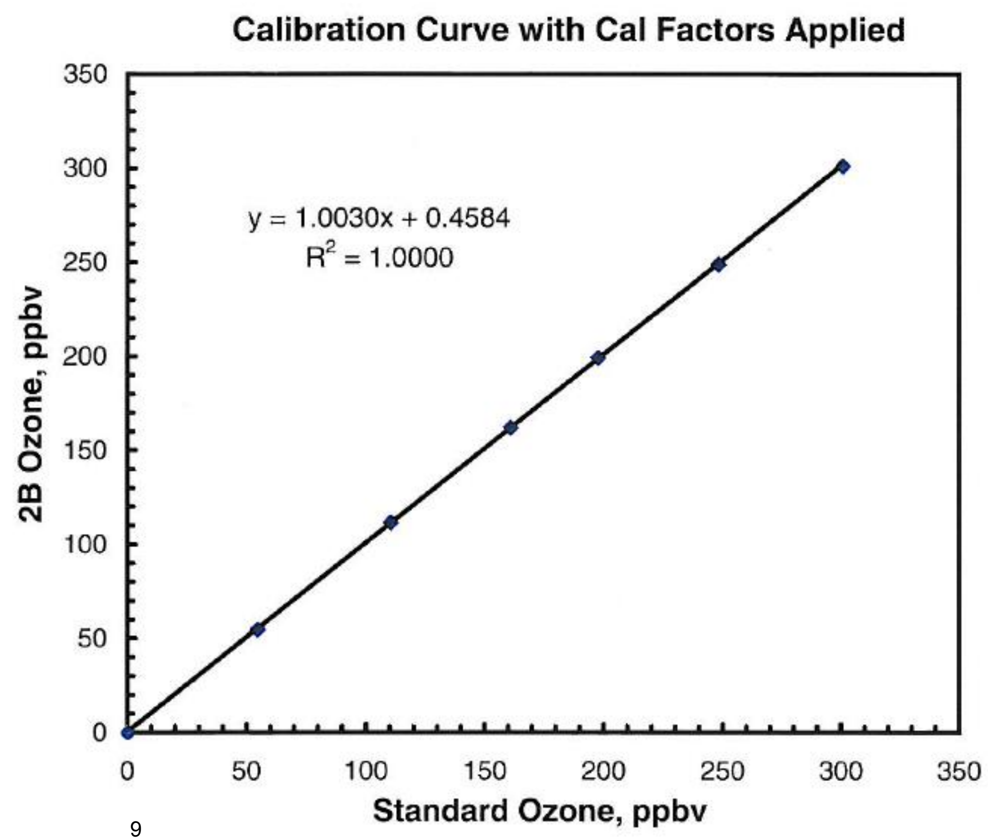
However, non-linearity of the photodiode response and electronics can result in a small measurement error (Model 306 versus standard). Therefore, each instrument is compared with a NIST-traceable standard

Serial No. 491 **08/24/07**

2B, ppbv	Std, ppbv	2B, corr	Deviation	% Dev.
289.1	300.7	301.4	0.7	0.2
238.7	248.1	249.0	0.9	0.4
191.0	197.5	199.4	1.9	1.0
155.3	160.9	162.3	1.4	0.9
106.7	110.4	111.7	1.3	1.2
51.9	54.6	54.8	0.2	
-0.7	0.0	0.0		

Average Precision, ppbv:	0.8
Avg. Precision at 1 Atm.:	0.7

Calibration Parameters:
Z = 1
S = 1.04



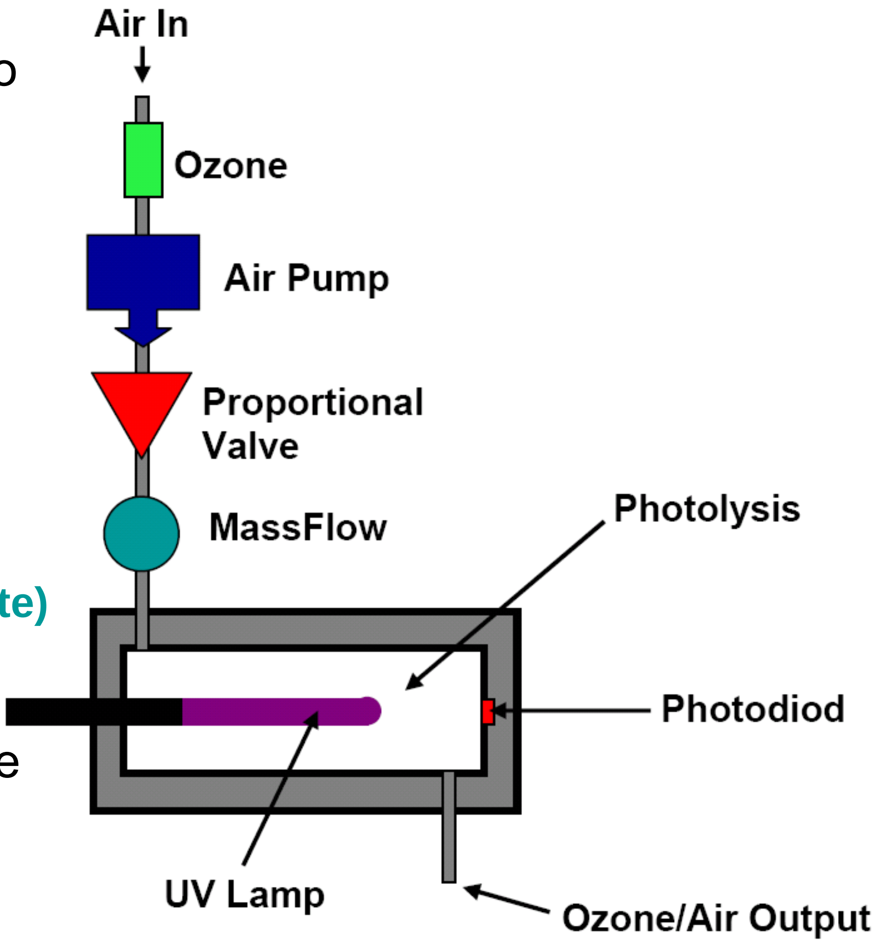
Measuring O_3: Ozone Calibration Source, contd

Scrubs ozone from ambient air to produce zero air and air with ozone mixing ratios 30-1000 ppb, up to 10 concentration steps

O_3 concentration depends upon:
- **-lamp intensity**
- **-O_2 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



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Measuring O_3: Ozone Calibration Source, contd.

Uses same chemistry that produces ozone in the stratosphere

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

$$\mathbf{3\ O_2 + h\nu \rightarrow 2\ O_3}$$

Low pressure mercury lamp photolyzes oxygen at 185 nm (monitored by photodiode)

Measuring NO: Nitric Oxide Monitor
(2B Technologies Model 400)

$NO + O_3 \rightarrow NO_2 + O_2$ + chemi-luminescence*

- Stoichiometric reaction
- Adequate concentration of O_3 added to the sample stream
- Decrease in the concentration of O_3 is measured by absolute UV absorption (as in the Ozone Monitor, 254nm)

Beer-Lambert Law $$C_{O_3} = \frac{1}{\sigma l} \ln\left(\frac{I_o}{I}\right)$$

$$C_{NO} = C_{O_3,ref} - \frac{F_{total}}{F_{total} - F_{ozone}} \left(C_{O_3-NO}\right)_{\det}$$ molecules/cm^3

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

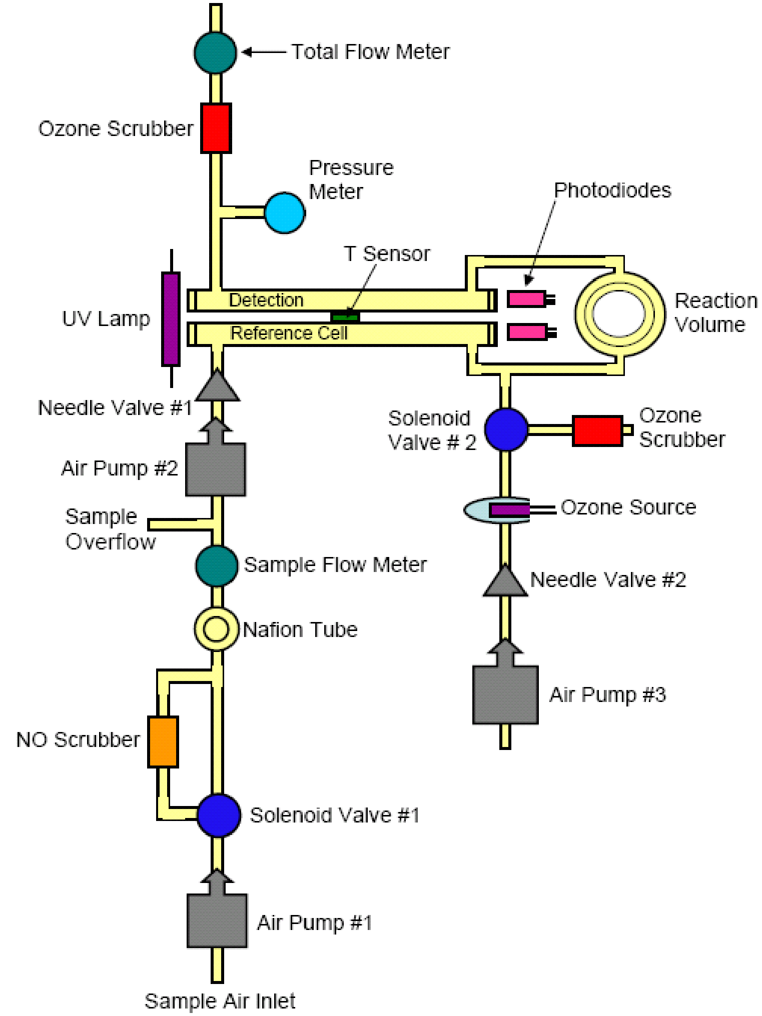
***Alternative chemi-luminescence analyzer:** Detects the small amount of light produced. Higher sensitivity & faster response time but requires more frequent calibration

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



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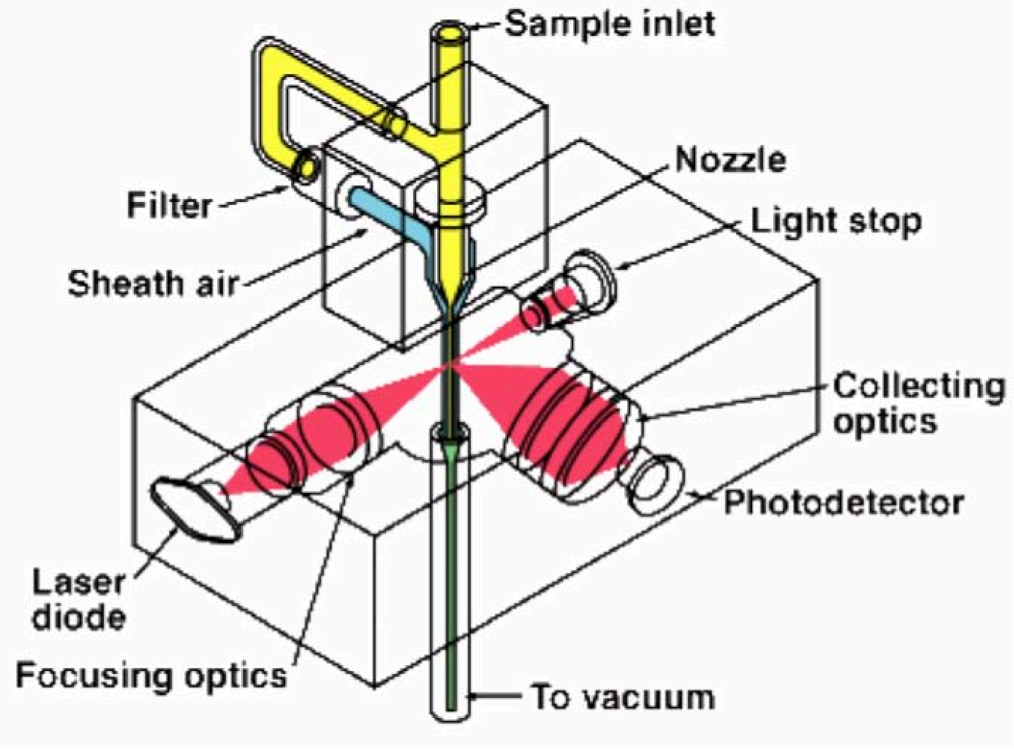
Measuring $[NO_x]$(= [NO] + $[NO_2]$) & $[NO_2]$
(2B Technologies Model 401 "NO_2 Converter")

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 $[NO_x]$.

Then $[NO_2] = [NO_x] – [NO]$ where [NO] is value obtained by "NO Monitor" without using the Converter

Measuring Aerosols: DustTrak Model 8520-1



Optics kept clean by surrounding aerosol stream in a sheath of filtered air

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

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 ($\varpi = \sigma_{abs}/(\sigma_{abs}+\sigma_{scat})$

Collected light $\propto$ Total scattered light $\propto$ Aerosol mass concentration

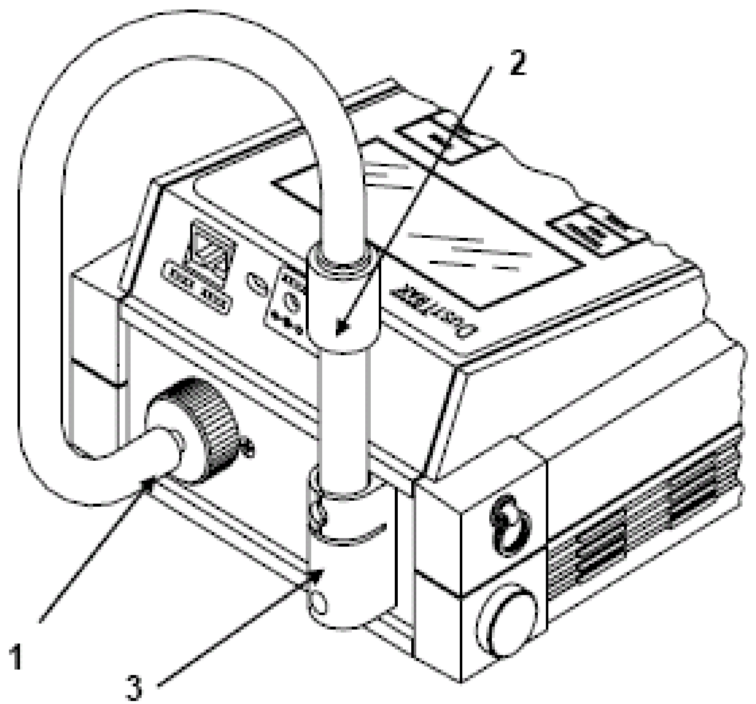
Calibration and Zeroing

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

Measuring Aerosols: DustTrak, contd.



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.