Bureau International des Poids et Mesures

Ozone cross-sections (Hartley band)
Progress towards new accurate values

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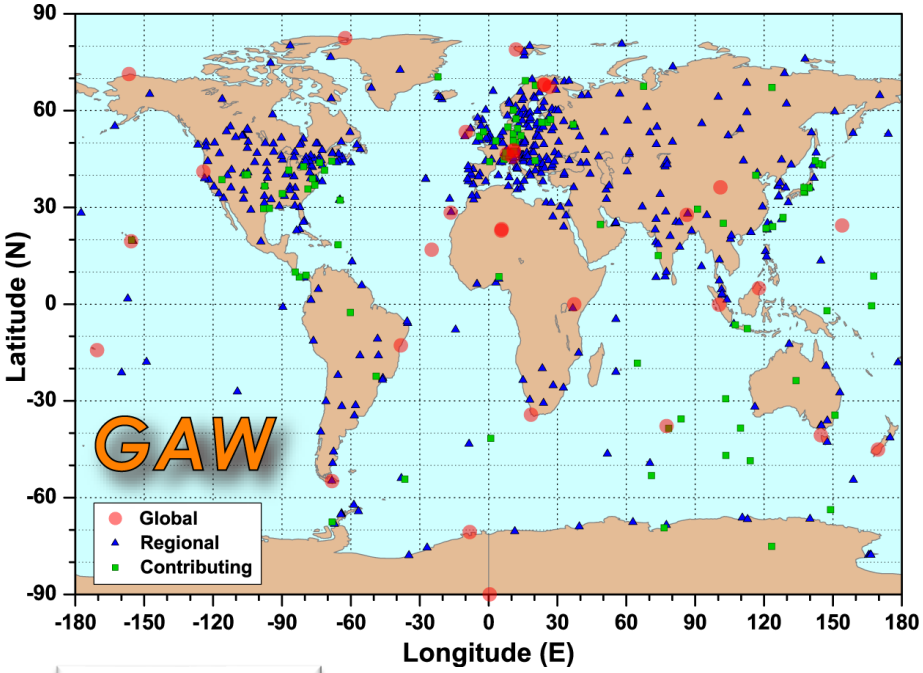
S. Lee and R.I. Wielgosz,

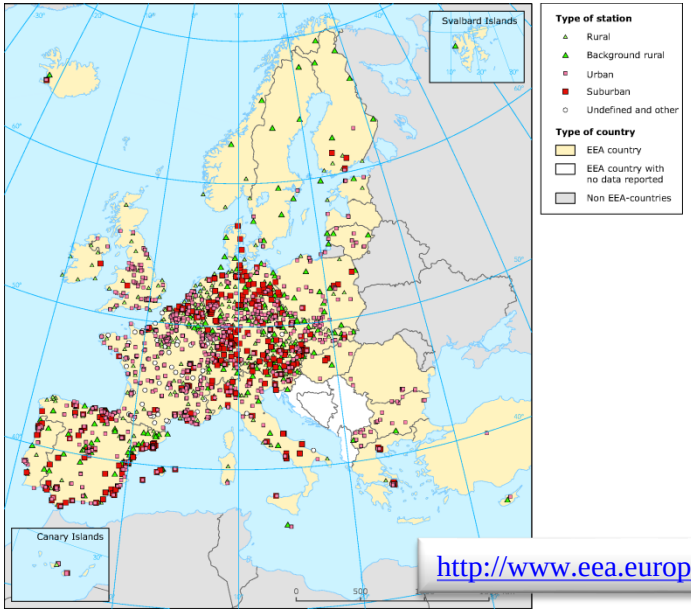
ACSO meeting
3-5 June 2013, WMO, Geneva

Surface ozone networks

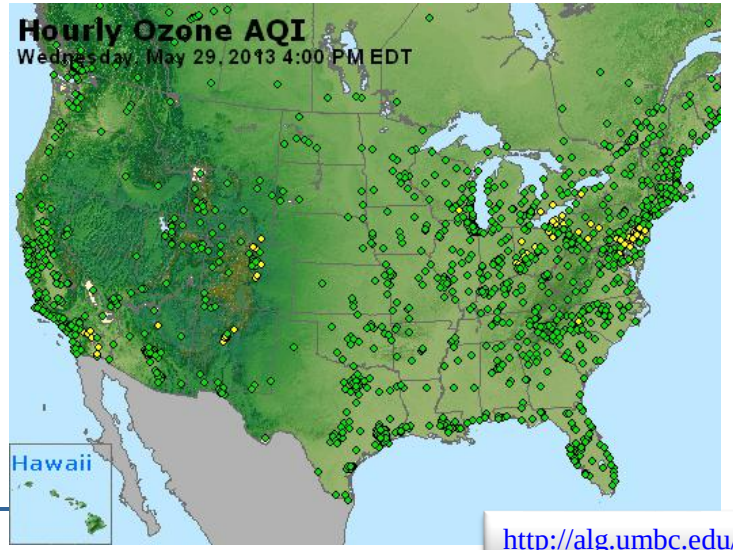
Global, regional and national ozone measurement networks = thousands of measurements of the surface ozone concentration every day



http://www.wmo.it



http://www.eea.europa.eu/

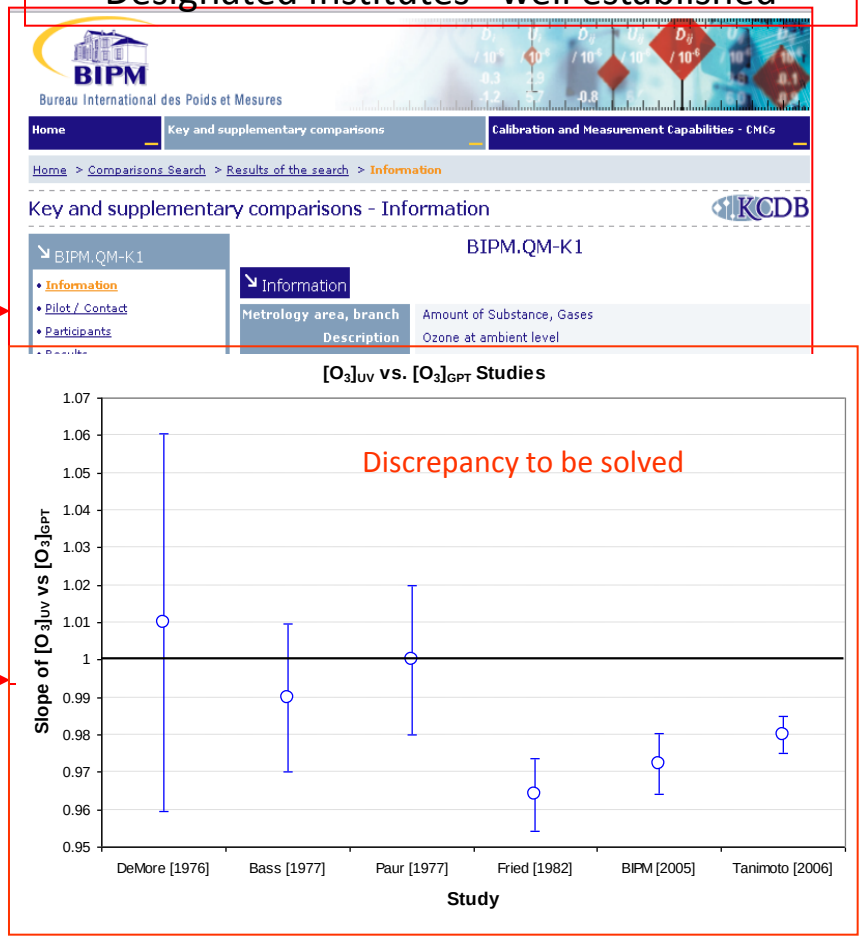


http://alg.umbc.edu/usaq/

Traceability of surface ozone measurements

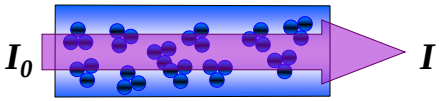
- **Chain of calibration to national standards**
- **Comparison between national standards**
- **Agreement between reference methods**

Role of National Metrology Institutes / Designated Institutes– well established



Resolving the discrepancy

UV photometry



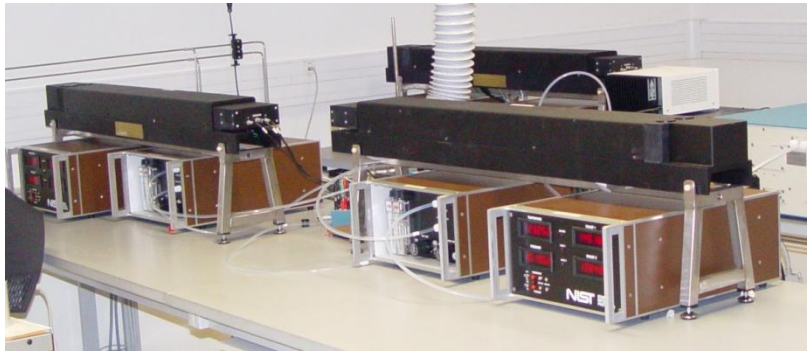
Reference instrument = NIST-SRP

⇒ BIPM maintains 5 replicates

⇒ Two sources of bias found (2006)

⇒ Comparability improved (2007)

⇒ Discrepancy not solved!



Gas Phase Titration

$$NO + O_3 \rightarrow NO_2 + O_2$$

Traceable to NO or NO_2

⇒ BIPM maintains both NO and NO_2 standards

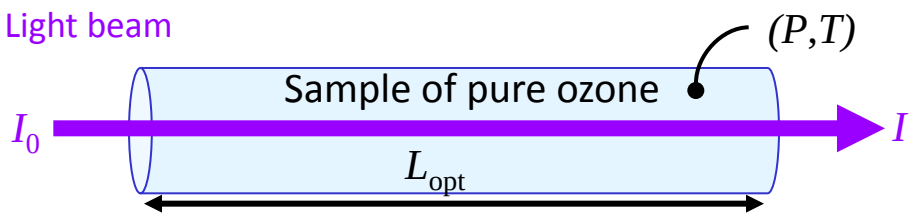
⇒ Both compared several times

⇒ Discrepancy not solved!

Need accurate measurements of the ozone cross-section

Relative or absolute measurements?

Absolute absorption measurements are performed in pure ozone, without reference to another absorption measurement

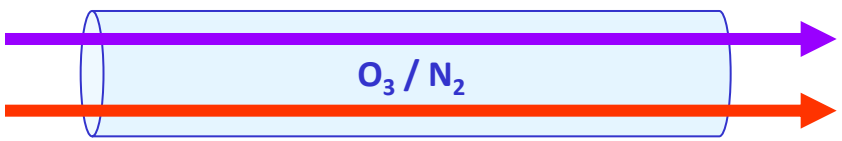


$$\sigma_{O3} = \frac{1}{L_{opt}} \frac{T}{P_{O_3}} \frac{R}{Na} \ln\left(\frac{I}{I_0}\right)$$

Difficult due to ozone reactivity

Relative absorption measurements are performed in a gas cell containing ozone/nitrogen

Reference = concentration deduced from UV absorption at 254 nm



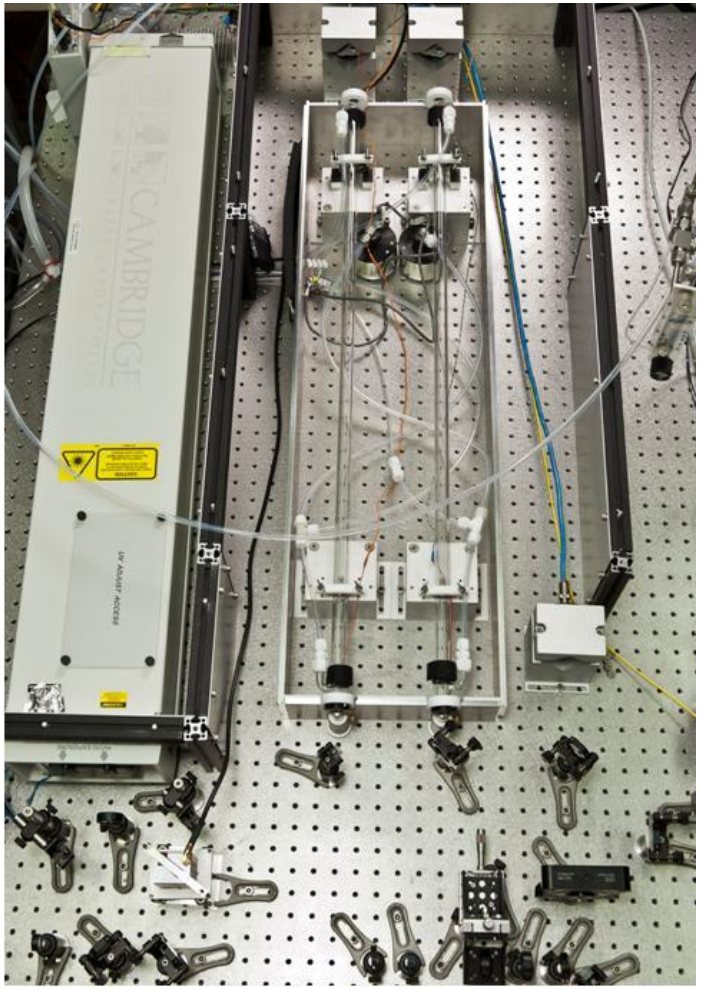
$$x(O_3) = \frac{1}{\alpha(\lambda = 254\text{nm}) L_{opt}} \frac{T}{T_{std}} \frac{P_{std}}{P} \ln\left(\frac{I}{I_0}\right)$$

Cross-section relative measurement at wavelength λ

$$\alpha(\lambda) = \frac{-1}{x(O_3) L_{opt}} \frac{T}{T_{std}} \frac{P_{std}}{P} \ln\left(\frac{I}{I_0}\right)$$

Result depends on reference cross-section α(254 nm) – Usually value measured by Hearn in 1961

Laser ozone photometer



Step 1 – relative measurements of the ozone cross-section

- Light source = frequency doubled argon-ion laser
- 3 different wavelengths in the Hartley band: 244.06 nm, 248.32 nm and 257.34 nm.
- Intensity stabilised with Acousto-Optic Modulator

Laser ozone photometer performances validation

- **Linearity versus ozone mole fraction**
  - Tested against SRP31
  - No non-linearity observed
- **Linearity versus laser light power**
  - Light power density with laser ~ 10 μW cm^{-2} (< 1 μW cm^{-2} with lamp)
  - Tested on range 10 μW cm^{-2} to 60 μW cm^{-2} : no non-linearity.
- **Stability**
  - Laser system always been more noisy than lamp system
  - **<u>Intensive stability tests!</u>**

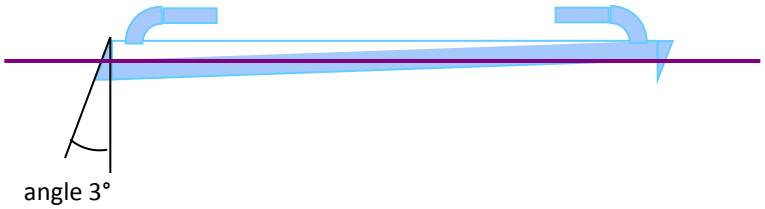
Laser ozone photometer uncertainty budget

Parameter	value	Standard uncertainty	Relative uncertainty
Temperature T	295 K	0.061 K	2.1 10^{-4}
Pressure P	1000 mbar	0.64 mbar	6.4 10^{-4}
Optical length L_{opt}	893.9 mm	0.4 mm	4.5 10^{-4}
Product of transmittances D	0.95	1.2 10^{-5}	2.6 10^{-4}
Combined relative uncertainty (without the absorption cross-section)			8.5 10^{-4}

Major improvement compared to SRP = reduced uncertainty on the path length.

3 mm diaphragm before/after cells to help laser alignment

Cells windows not perpendicular to laser beam

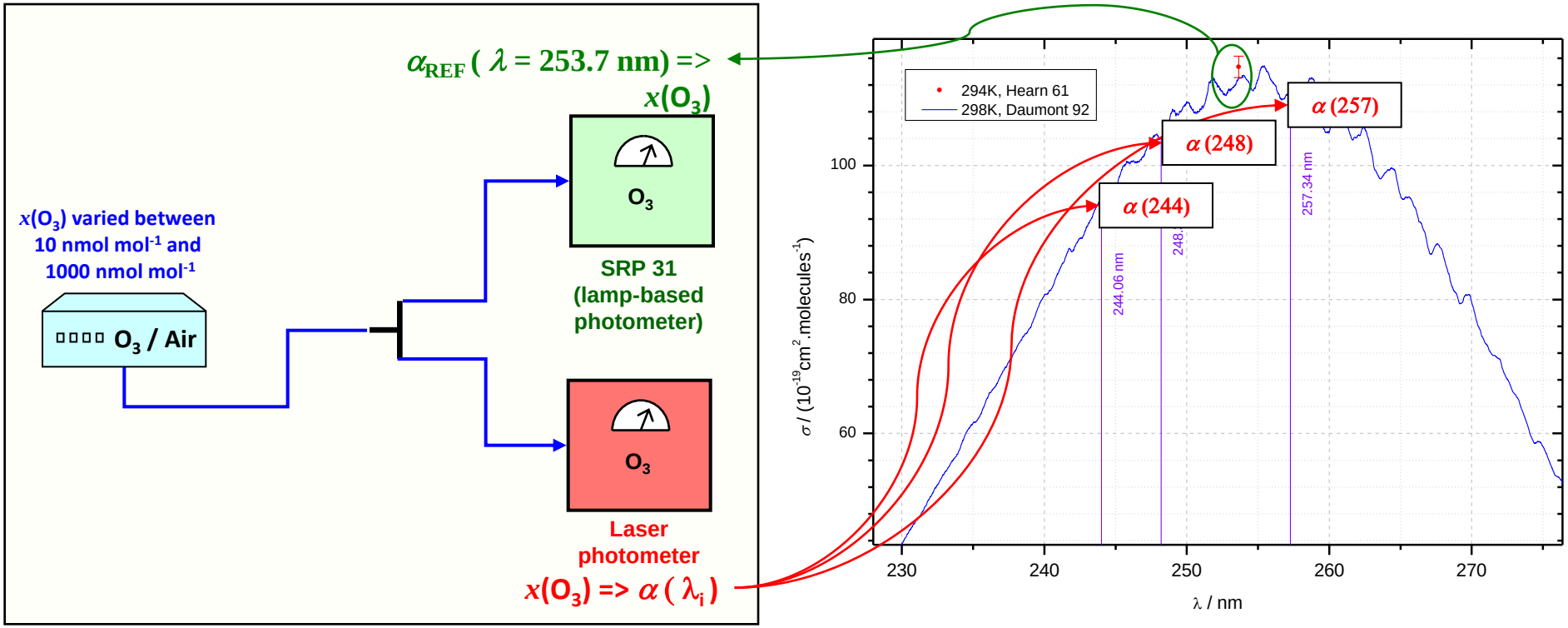


L_{opt} = cell length as measured by NIST

Relative measurements of the ozone cross-section with the UV laser ozone photometer

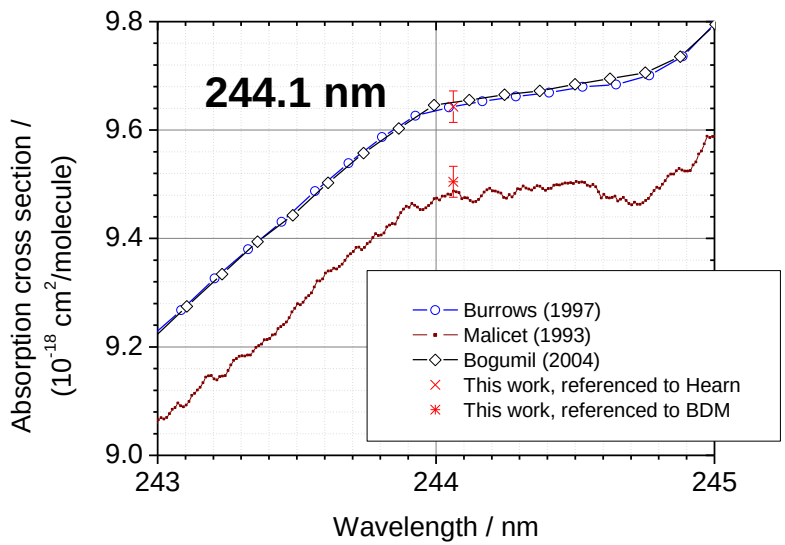
Comparison between SRP31 and the laser ozone photometer

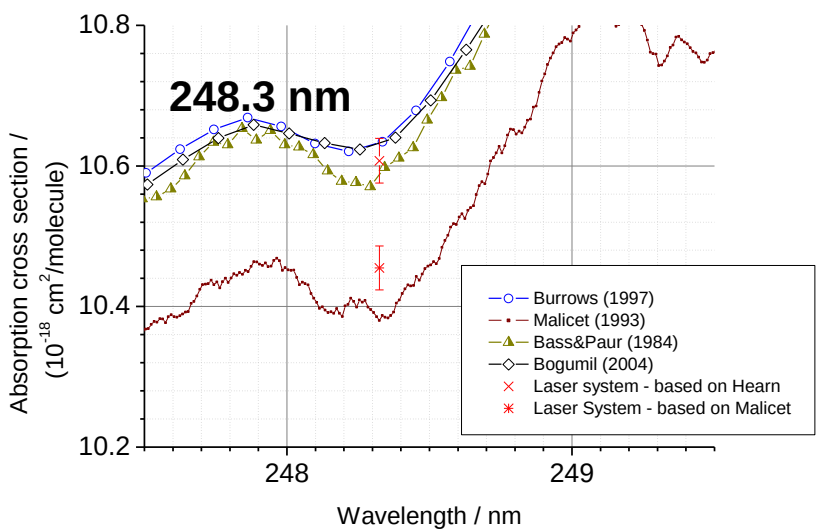
Deduce relative absorption cross-section at three wavelengths

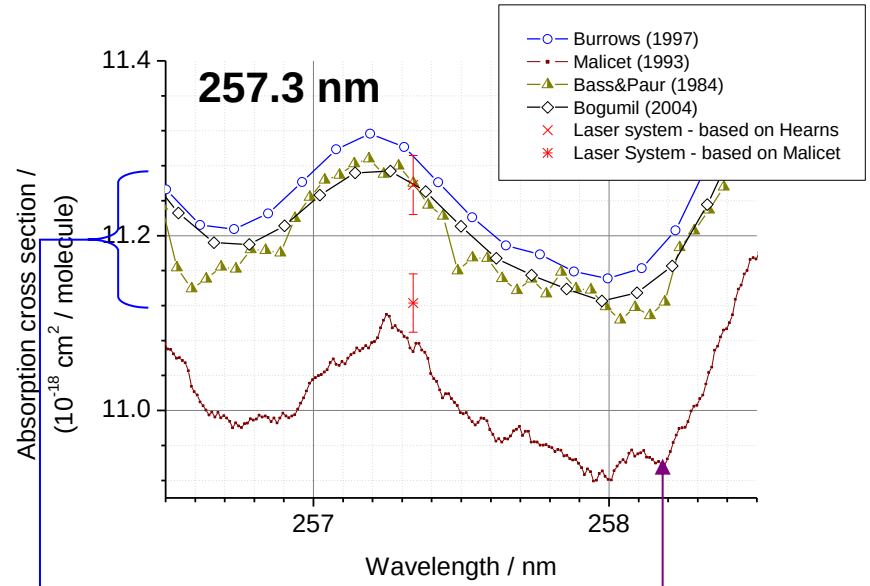


Petersen M., Viallon J., Moussay P. and Wielgosz R.I., 2012, **Relative measurements of ozone absorption cross-sections at three wavelengths in the Hartley band using a well-defined UV laser beam,** J. Geophys. Res., 117, D05301

Relative measurements of the ozone cross-section with the UV laser ozone photometer







Measurements relative to Hearn

Absolute measurement by Malicet

Internal consistency of data sets confirmed

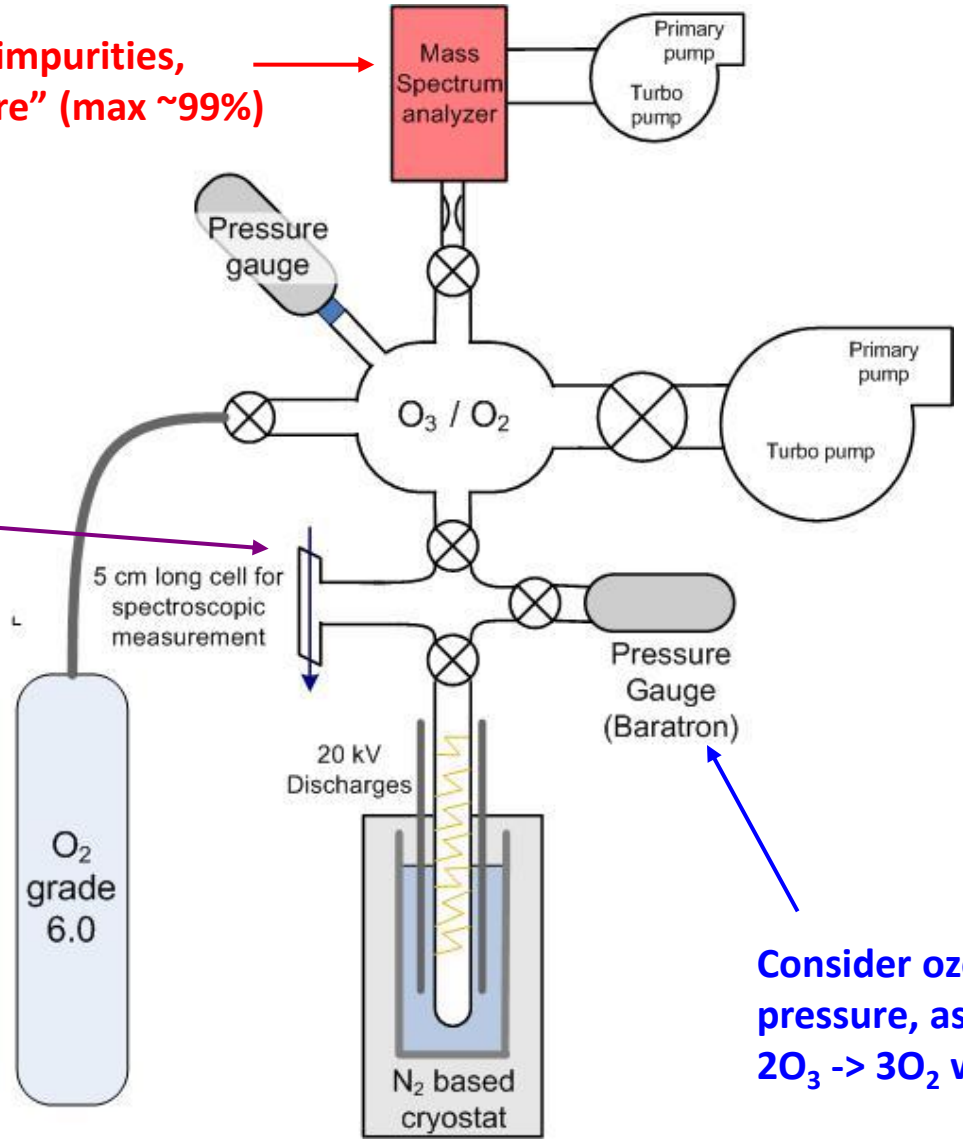
Discrepancies between data sets confirmed

Need more accurate reference!

Ozone cross-section, a measurement challenge

Measure O_2 and other impurities, as O_3 will never be "pure" (max ~99%)

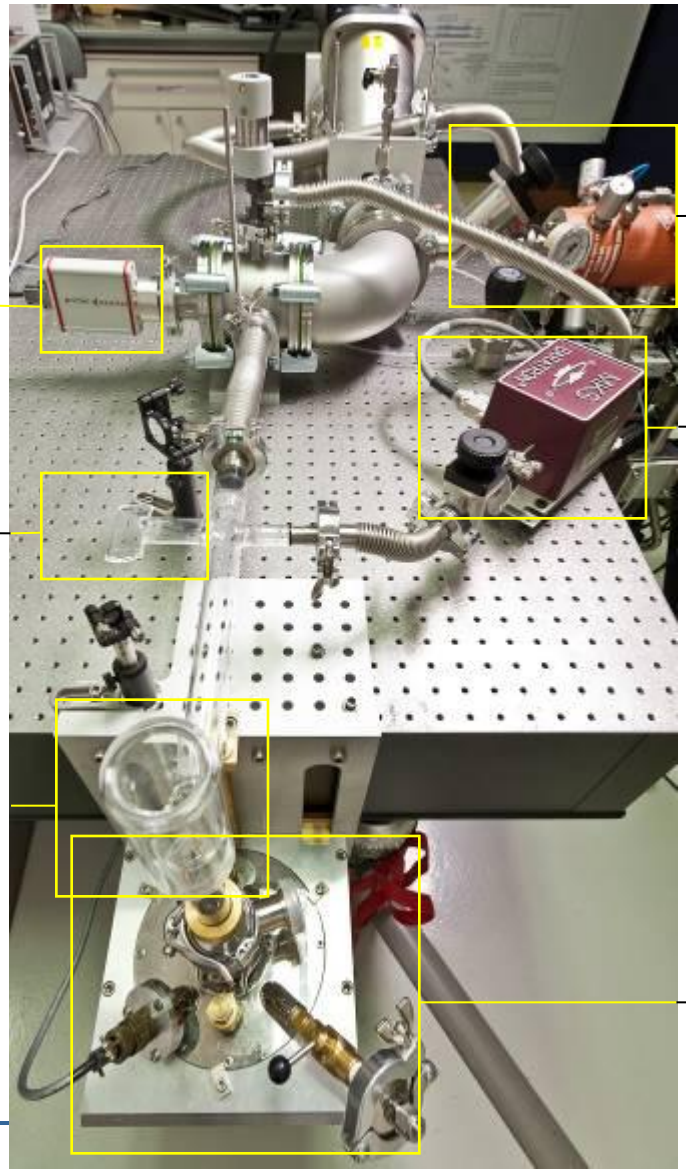
L_{opt} to be measured by interferometry



Consider ozone partial pressure, as decomposition $2O_3$ -> $3O_2$ will rapidly occur

The BIPM facility for ozone absorption cross-section measurements

Frequency doubled argon-ion laser with intensity stabilisation



Large range pressure gauge

5 cm absorption cell

Ozone generator (high voltage discharges)

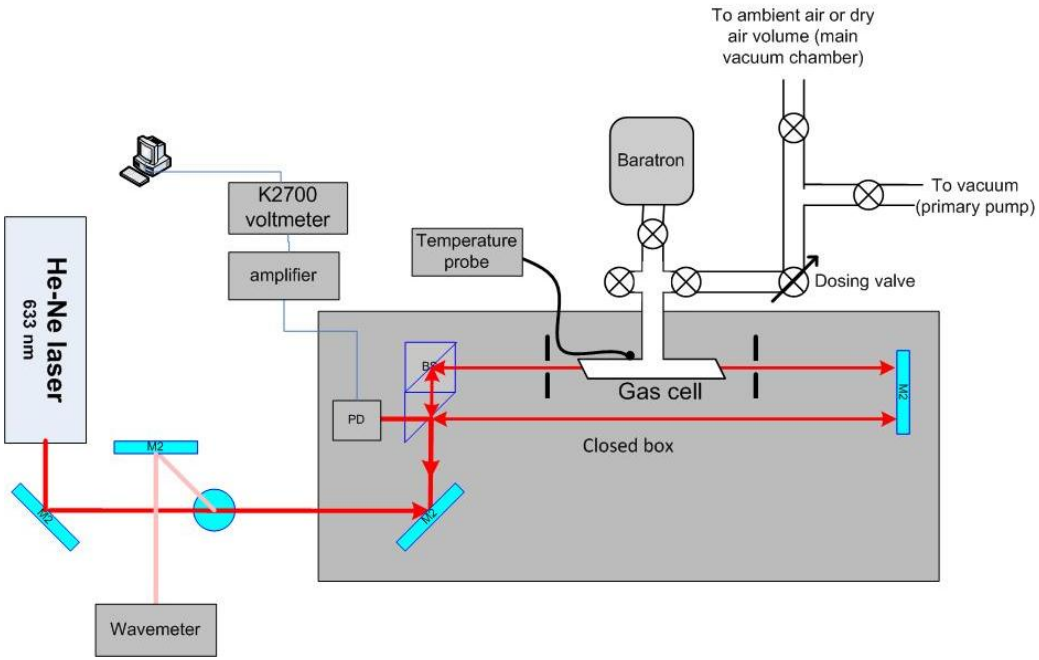
Mass spectrometer

High accuracy pressure gauge (Baratron) for $P < 1$ mbar

Temperature controlled cryostat

Absorption path length measurements by interferometry

Michelson interferometer to deduce L_{opt} in the cell in which the pressure is varied



Pressure in the cell: 1 bar -> 0.1 mbar

-> *F* fringes on the photodiode

-> Path length L_0

$$(n-1)\,L_0 = F\,\frac{\lambda_a}{2}$$

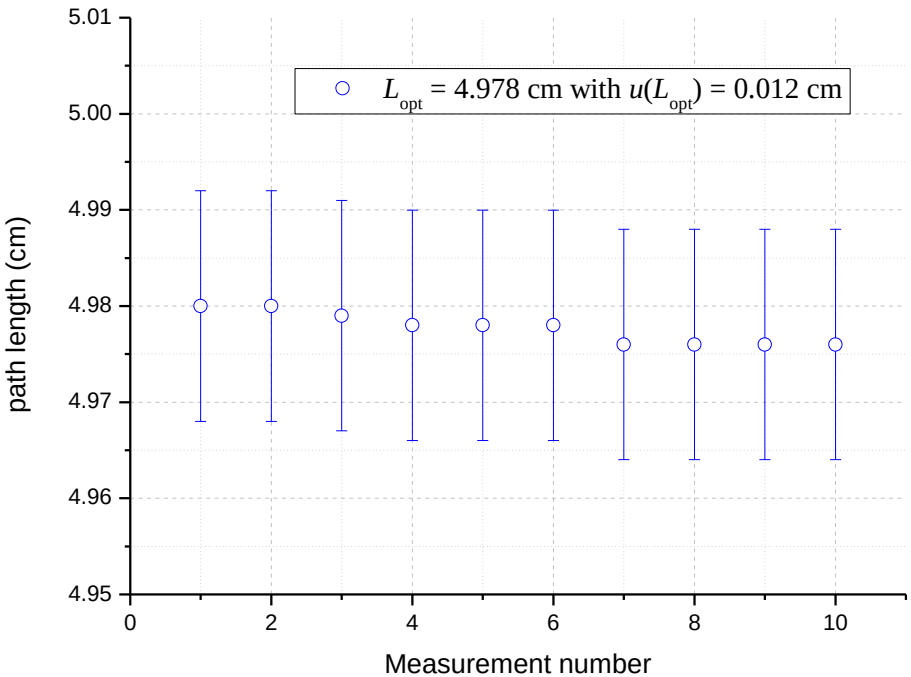
n	: index of refraction of air
L_0 / m	: light path length
F	: number of fringes
λ_a / m	: laser wavelength

Edlen formula for the air index of refraction at pressure *P* and temperature *T*

$$n-1 = \frac{p\cdot 10^{-8}\left[8342.54 + 2406147(130-\sigma^2)^{-1} + 15998(38.9-\sigma^2)^{-1}\right]\left[1+10^{-8}\cdot(0.601-0.00972T)\,p\right]}{96095.43\,(1+0.003661T)}$$

Absorption path length measurements by interferometry

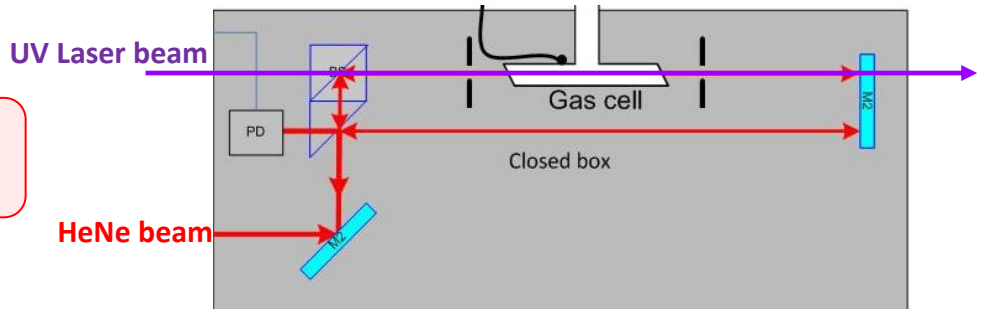
Measurements



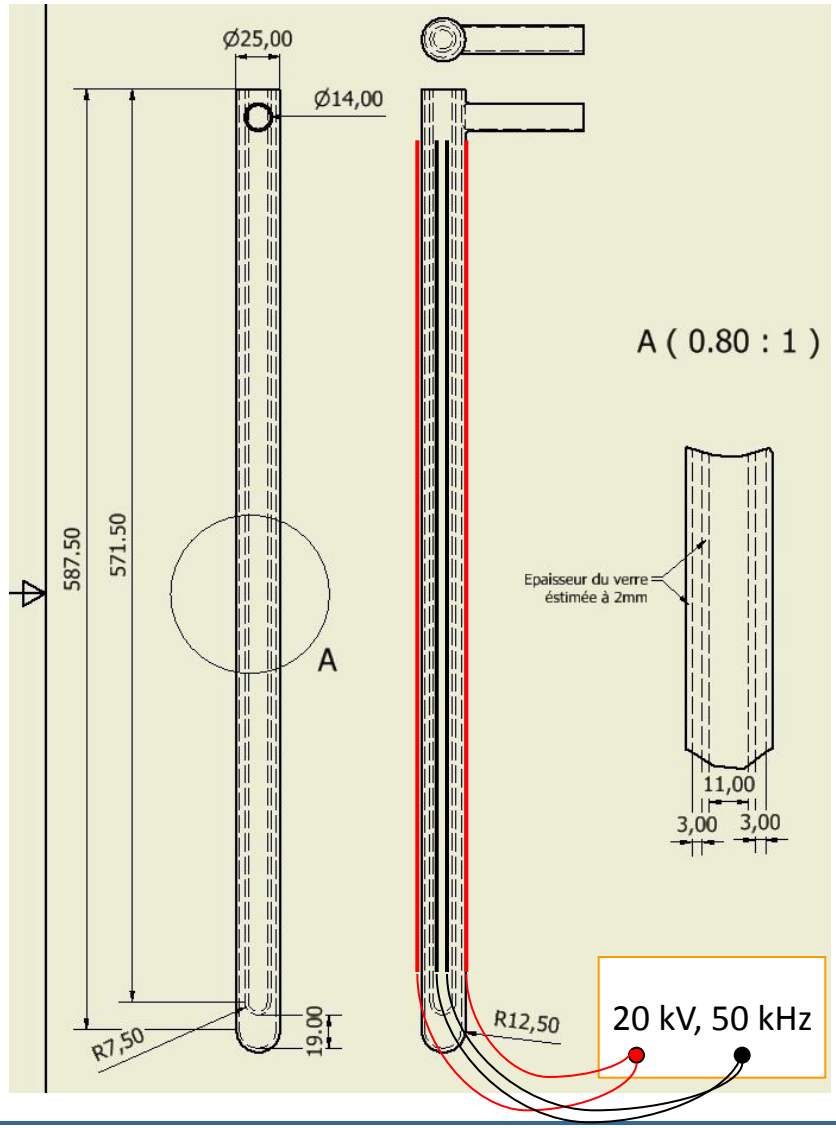
Uncertainty budget

Quantity	Value	Standard Uncertainty
F	42	0.102
T	22.3 °C	0.018 °C
P_a	1003.25 hPa	0.852 Pa
λ_a	0.632823 µm	3.47×10^{-6} µm
λ_v	0.632991 µm	0.29×10^{-6} µm
L_{opt}	**4.979 cm**	**0.012 cm**

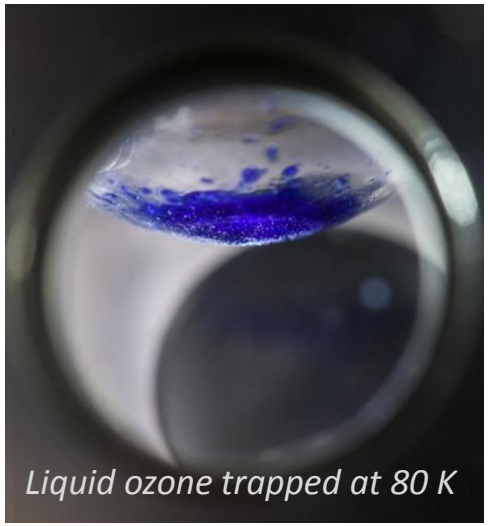
OK to be used for cross-section measurements, provided same laser path in the gas cell



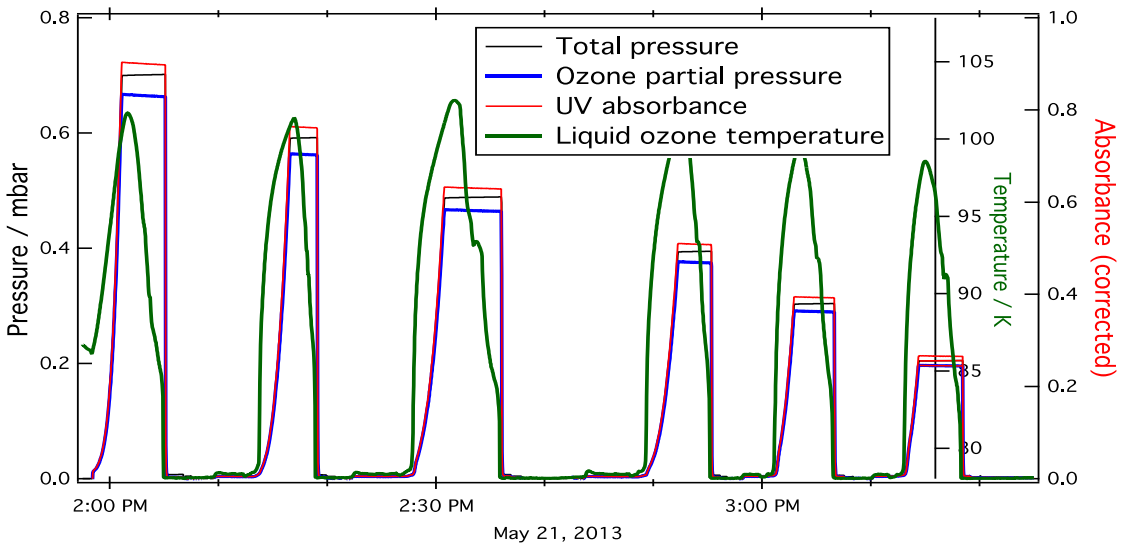
Ozone generator



- Ozone produced by discharges in pure oxygen
- generator = double wall cylinder in glass
- generation part inserted in cryostat
- controllable cryostat temperature from 74 K and above

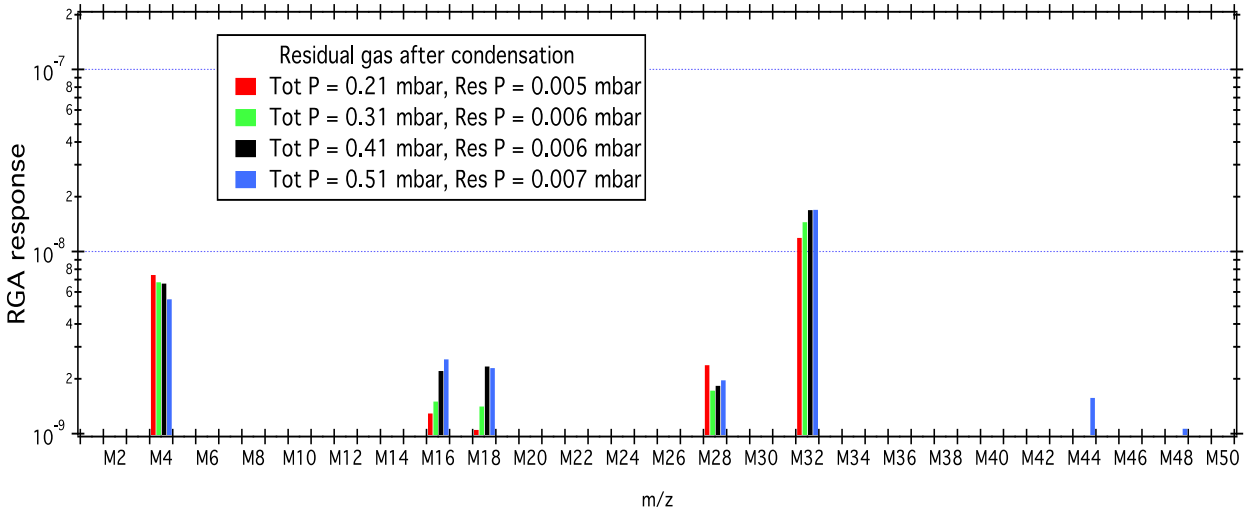


Ozone evaporation-condensation cycles



Ozone evaporated-condensed from generator at various pressures

Non-condensable impurities analysis with mass spectrometry



Ozone Pressure vs. Absorbance

Measurements with mercury lamp

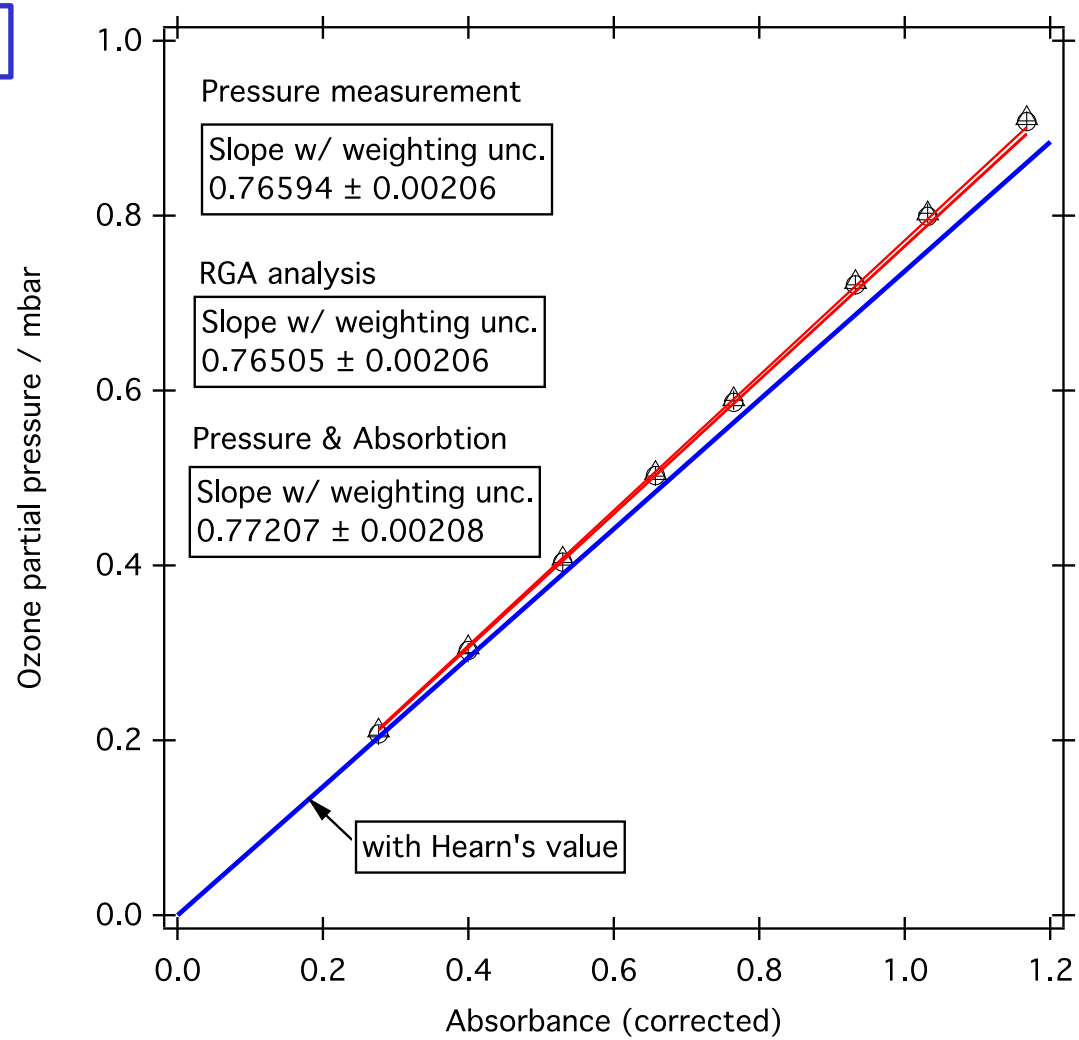
$$P_{total} = P_{O3} + P_{impurity}$$

$$P_{total} - P_{impurity} = P_{O3}$$

$$P_{total} - P_{impurity} = \frac{-\ln(I/I_0) R \times T}{s \times L_{optic} \times N_A}$$

$$P_{O3} = \underbrace{\frac{R \times T}{s \times L_{optic} \times N_A}}_{\text{Slope}} \times \left(-\ln(I/I_0)\right)$$

Preliminary value at 253.7 nm ~ 3% lower than Hearn value



Conclusion

- The BIPM provides the basis for a single, coherent system of measurements throughout the world, traceable to the International System of Units (SI).
- For ozone at ambient level, comparability is insured through International comparisons of ozone standard instruments (UV photometers)
- Traceability to the SI is under question as two reference methods do not agree
- To resolve this issue, new (more accurate) measurements of the ozone absorption cross-section in the Hartley band are undertaken
- Relative values at 3 laser wavelength were published in 2012
- Absolute values at the same wavelengths are coming soon