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

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Surface ozone networks

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

Slope of $[O_3]_{UV} \text{ vs. } [O_3]_{GPT}$

Discrepancy to be solved

Resolving the discrepancy

UV photometry

\[ I_0 \rightarrow I \]

Reference instrument = NIST-SRP

⇒ BIPM maintains 5 replicates
⇒ Two sources of bias found (2006)
⇒ Comparability improved (2007)
⇒ Discrepancy not solved!

Gas Phase Titration

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]

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.

\[
\sigma_{O_3} = \frac{1}{L_{opt}} \frac{T}{P_{O_3}} \frac{R}{N_a} \ln\left(\frac{I}{I_0}\right)
\]

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

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

Result depends on reference cross-section \(\alpha(254\text{ nm})\) – Usually value measured by Hearn in 1961.
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 $\sim 10 \, \mu W \, cm^{-2}$ ($< 1 \, \mu W \, cm^{-2}$ with lamp)
  - Tested on range $10 \, \mu W \, cm^{-2}$ to $60 \, \mu W \, cm^{-2}$: no non-linearity.

- **Stability**
  - Laser system always been more noisy than lamp system
  - Intensive stability tests!
Laser ozone photometer uncertainty budget

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

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

angle 3°

$L_{opt}$ = 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

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

Internal consistency of data sets confirmed

Discrepancies between data sets confirmed

Need more accurate reference!
Ozone cross-section, a measurement challenge

Measure O₂ and other impurities, as O₃ will never be “pure” (max ~99%)

$L_{opt}$ to be measured by interferometry

Consider ozone partial pressure, as decomposition 2O₃ $\rightarrow$ 3O₂ 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
$\lambda_a / m$ : laser wavelength

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

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

Measurements

\[ L_{\text{opt}} = 4.978 \text{ cm with } u(L_{\text{opt}}) = 0.012 \text{ cm} \]

Uncertainty budget

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Standard Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F )</td>
<td>42</td>
<td>0.102</td>
</tr>
<tr>
<td>( T )</td>
<td>22.3 °C</td>
<td>0.018 °C</td>
</tr>
<tr>
<td>( P_a )</td>
<td>1003.25 hPa</td>
<td>0.852 Pa</td>
</tr>
<tr>
<td>( \lambda_a )</td>
<td>0.632823 μm</td>
<td>3.47×10^{-6} μm</td>
</tr>
<tr>
<td>( \lambda_v )</td>
<td>0.632991 μm</td>
<td>0.29×10^{-6} μm</td>
</tr>
<tr>
<td>( L_{\text{opt}} )</td>
<td>4.979 cm</td>
<td>0.012 cm</td>
</tr>
</tbody>
</table>

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

20 kV, 50 kHz

Liquid ozone trapped at 80 K
Ozone evaporation-condensation cycles

Non-condensable impurities analysis with mass spectrometry

Ozone evaporated-condensed from generator at various pressures
Ozone Pressure vs. Absorbance

Measurements with mercury lamp

\[ P_{\text{total}} = P_{O_3} + P_{\text{impurity}} \]

\[ P_{\text{total}} - P_{\text{impurity}} = P_{O_3} \]

\[ P_{\text{total}} - P_{\text{impurity}} = -\ln\left(\frac{I}{I_0}\right)R \times T \times L_{\text{optic}} \times N_A \]

\[ P_{O_3} = \frac{R \times T}{L_{\text{optic}} \times N_A} \left( \ln\left(\frac{I}{I_0}\right) \right) \]

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

Pressure measurement
Slope w/ weighting unc.
0.76594 ± 0.00206

RGA analysis
Slope w/ weighting unc.
0.76505 ± 0.00206

Pressure & Absorption
Slope w/ weighting unc.
0.77207 ± 0.00208

with Hearn's 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.