New consensus ozone cross-section value for tropospheric ozone monitoring
Ozone is mainly measured by light absorption using the Beer-Lambert law

Ozone is normally measured in air (ambient or synthetic), with typical mole fractions around 30 nmol mol\(^{-1}\) (clean air) to 100 nmol mol\(^{-1}\) (polluted troposphere).

\[ I_0 e^{-\sigma n L} \]

\( I_0 \) is the light intensity before absorption (or without ozone). It is a measured quantity.

\( n \) is the number concentration of ozone (molecules cm\(^{-3}\)).

\( \sigma \) is the absorption cross-section at the wavelength of the input light.

\( L \) is the light absorption path length.

In many measurements, this is considered as being equal to the length of the gas cell. This is an approximation which may be corrected for most accurate measurements.

\( \sigma \) is the absorption cross-section at the wavelength of the input light.

Its value needs to be measured independently, and this was done by many groups since 1930. A consensus value based on past measurements is the best way to ensure comparability of world-wide measurements.
Ozone has a strong absorption peak in the UV. Low pressure mercury lamps emit light with a strong and sharp peak at 253.64 nm. It was chosen as light source in the first Standard Reference Photometer built at NIST in 1982. The ozone absorption cross-section value measured by Hearn in 1961 was chosen, and is still being used in most ozone UV photometers.

Cross-section measurements require PURE ozone

Ozone almost always produced by discharge in oxygen and trapped in liquid phase

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

**Pressure**: pressure sensors measure total pressure \( P_T \), not partial pressure \( P_{O_3} = x(O_3) P_T \)

**Purity** = assessment of impurities
- condensables \( x_C \)
- non-condensables \( x_{NC} \)

More accurate equation
Because of its detrimental effects on public health and the environment, ozone is one of the most monitored compounds at ground level.

Local, national, regional and even global networks rely on proper calibrations. Most of them are ultimately traceable to an ozone Standard Reference Photometer.

The SRP itself depends on the ozone absorption cross-section in the UV, at 253.65 nm.
Since the first version in 1982, more than 60 NIST SRPs have been constructed and act as primary standards for local, regional and international ozone monitoring networks.

The BIPM runs an on-going programme of comparison to demonstrate agreement between all national standards.
The most commonly used method to measure Ozone (ground level) is by UV photometry. UV photometry is anchored to the ozone absorption cross-section at a specific wavelength.

Ozone can also be measured by Gas Phase Titration: reaction with NO to produce NO₂.

Ozone measured by Gas Phase Titration is traceable to NO and/or NO₂, generally known by gravimetry.

Gas Phase Titration and UV photometry comparisons highlighted a bias in the absorption cross-section, when using the conventionally agreed value of Hearn-61.
### Review of 14 selected published values

<table>
<thead>
<tr>
<th>Identification</th>
<th>Author(s)</th>
<th>Year</th>
<th>Traceability</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFCRC-59</td>
<td>Inn and Tanaka</td>
<td>1959</td>
<td>Total pressure</td>
</tr>
<tr>
<td>Hearn-61</td>
<td>Hearn</td>
<td>1961</td>
<td>Decreasing ozone pressure</td>
</tr>
<tr>
<td>JPL-64</td>
<td>De More and Raper</td>
<td>1964</td>
<td>Oxygen pressure in gas buret after full conversion</td>
</tr>
<tr>
<td>Griggs-68</td>
<td>Griggs</td>
<td>1968</td>
<td>Total pressure</td>
</tr>
<tr>
<td>JPL-86</td>
<td>Molina and Molina</td>
<td>1986</td>
<td>Total pressure</td>
</tr>
<tr>
<td>UniMin-87</td>
<td>Mauersberger et al.</td>
<td>1987</td>
<td>Total pressure</td>
</tr>
<tr>
<td>HSCA-88</td>
<td>Yoshino et al.</td>
<td>1988</td>
<td>Total pressure</td>
</tr>
<tr>
<td>UniReims-93</td>
<td>Brion et al.</td>
<td>1993</td>
<td>Decreasing ozone pressure</td>
</tr>
<tr>
<td>UniBremen-99</td>
<td>Burrows et al.</td>
<td>1999</td>
<td>NO₂ cross-section via titration of O₃ with NO</td>
</tr>
<tr>
<td>UPMC-04</td>
<td>Dufour et al.</td>
<td>2004</td>
<td>Total pressure via IR absorption and LNE-SRP comparison</td>
</tr>
<tr>
<td>NIES-06</td>
<td>Tanimoto et al.</td>
<td>2006</td>
<td>NO gravimetric standards via titration and SRP comparison</td>
</tr>
<tr>
<td>UniBremen-14</td>
<td>Gorshelev et al.</td>
<td>2014</td>
<td>Total pressure</td>
</tr>
<tr>
<td>BIPM-15</td>
<td>Viallon et al.</td>
<td>2015</td>
<td>Total pressure via UV laser and SRP comparison</td>
</tr>
<tr>
<td>BIPM-16</td>
<td>Viallon et al.</td>
<td>2016</td>
<td>NO gravimetric standards via titration and SRP comparison</td>
</tr>
</tbody>
</table>

### Different traceabilities:

**Total pressure**: absorption measurement on pure ozone, including purity or not.

**Decreasing ozone pressure**: absorption measurement on ozone, assuming decomposition to oxygen only.

**Titration**: ozone concentration deduced after gas phase titration with nitrogen monoxide (NO). Absorption cross-section recalculated after comparison with a UV photometer.
How well can we measure the absorption cross-section?

Each published measurement was scrutinised to re-evaluate its uncertainty. This was an important part of the job as weights are inversely proportional to uncertainties.

**Most underestimated uncertainties in direct absorption measurements**

- **Sample pressure ≠ ozone pressure**
  Many authors had assumed that their ozone sample was 100% pure. Purity between 92% and 99.6% for the most careful measurements is more reasonable.

- **Light path length ≠ gas cell length**
  Due to divergent light and/or reflections on the gas cell windows, the effective light path length is often larger than the gas cell length.
Dealing with asymmetric uncertainties

Biases not estimated by the authors were considered in an asymmetric uncertainty.

Example of bias on path length in UniMin-87

- underestimated path length
- over-estimated cross-section ($\sim 1/l$)
- enlarged negative component of the uncertainty
Advanced statistical tools to calculate a consensus value

The 14 selected values data are mutually consistent according to the conventional Cochran (chi-squared) test. To calculate a consensus value, a Monte Carlo and a DerSimonian-Laird procedure were compared and found equivalent.

The recommended value is 1.2% lower than the current value (Hearn-61) implemented in reference instruments for tropospheric ozone measurements.

Uncertainty 6 times smaller!
To reach a consensus, a Task Group was created and asked to review all published data. It was created within the Gas Analysis Working Group (GAWG) of the CCQM and is composed of:

6 GAWG members
Joseph Hodges (NIST) - Chairman
Joëlle Viallon (BIPM) – Executive Secretary
Robert Wielgosz (BIPM)

Sangil Lee (KRISS)
Paul Brewer (NPL)
Jari Walden (FMI)

+ 5 other experts
Antonio Possolo
Victor Gorshelev
Mary Ann Smith
Brian Drouin
Christof Janssen

NIST
LUP-Bremen
NASA
JPL
UPMC - Paris

statistics
UV-VIS FT spectroscopy of ozone
Infrared spectroscopy of ozone
Microwave spectroscopy of ozone
Pure ozone generation & UV-VIS spectroscopy
Statement of Work and Terms of Reference

“Recommend an SI-traceable value and uncertainty of the room-temperature O₃ cross section at the wavelength of 253.65 nm (air) which corresponds to Hg lamp emission sources used in ozone standard reference photometers (SRPs).”

Guidelines for Data Analysis & Review

- Identified a set of 14 independent, peer-reviewed 254-nm cross section measurements for O₃

Selection Criteria
- Publication dates 1950 – 2016
- Room temperature (295 K ± 2.5 K) cross section data
- Cross section explicitly indicated in publication or inferred via simple calculation
- For repeated measurements by a group, only the last published value will be used

- Data are not to be corrected. Known bias is to be introduced via uncertainty
- Uncertainties to be evaluated according to GUM (1995). May require introducing additional uncertainty not specified in the original publication
Motivation toward a change

- Current value appears biased:
  Comparisons between UV absorption and Gas Phase Titration methods highlighted a bias coming from the ozone absorption cross-section.

- Recommended change at other wavelengths by ACSO
  This committee of 49 researchers analyzed available dataset in the Huggins band and recommended a change from the so-called BP set (linked to Hearn-61) to a more recent set measured at IUP-Bremen.

Agreement in all bands is required to ensure agreements between instruments / atmospheric layers (satellite, Dobson, Brewer, Sondes).

Absorption cross-sections of Ozone in the ultraviolet and visible spectral regions – Status report 2015
July 2016Journal of Molecular Spectroscopy 327:105-121, DOI10.1016/j.jms.2016.07.007
Impact of recommending a NEW standard

- **Increase of reported ozone concentrations**
  shifting the ozone absorption cross-section down by **1.2%**
  will induce an increase of 1.2% in ozone measurements

\[ x(O_3) = \frac{1}{\sigma L T_{std}} \cdot \frac{P_{std}}{P} \cdot \ln \left( \frac{I}{I_0} \right) \]

Ozone mole fraction measurement equation when measured by UV photometry

- **Impact on compliance with air quality regulation**
  A study dated 2015 showed that a shift of 1.8% (based on BIPM-15 value) increases the number of non-compliant sites by **18 to 20%**.
Steps towards an accepted change

Discussion within GAWG – enough evidence for change

GAW Scientific Advisory Group on Reactive Gases

Absorption Cross Section of Ozone

Task Group recommended value published

Stakeholders consultation via meetings

Recommendation of new value with uncertainty + implementation plan and date

Environmental Protection Agencies, Via NMIs and DIAs?

Monitoring Networks AQUILA meeting, etc...

ISO 13964 (Ozone by UV photometry)

Ozone photometers manufacturers

2016

2018

2019

2020

2016

2018

2019
Atmospheric Ozone Measurements

- **At ground:** UV analysers
- **In aircrafts:** UV analysers
- **In satellites:** by spectroscopy using large spectrum
- **Ozone column from ground:** by spectroscopy in various regions
- **Balloons:** ozone sondes (calibrated with UV photometers)

![Diagram of atmospheric layers and ozone measurements](http://www.windows.ucar.edu)
Ozone absorption cross-sections in other bands

Agreement in all spectral bands is required to ensure agreements between instruments / atmospheric layers (satellite, Dobson, Brewer, Sondes).

Most lab IR measurements have been rescaled according to the 253.7 nm O$_3$ cross-section values.

HITRAN 2016 database will use Brion et al. temperature and wavelength dependence.
Thanks

CCQM/GAWG Task Group on Ozone Cross-Section members

Joseph Hodges (NIST - Chair)
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Brian Drouin (JPL)
Christof Janssen (UPMC)

Pure liquid ozone produced during the ozone cross-section measurements performed at the BIPM in 2014.

Paper submitted to Metrologia special issue
Focus on Advances in Metrology in Chemistry and Biology