The 2019 Ozone Cross-Section Consensus Value at 253.65 nm

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Implementing a Globally Coordinated Change in Ozone Cross Section Value for Surface Ozone Monitoring Virtual Workshop, (BIPM), October 5-9, 2020
O₃ measurements are linked to NIST-made SRPs maintained at NIST and BIPM

Over 60 SRPs are deployed world-wide

Basis for quantifying compliance with environmental regulations

Range (1 – 1000 nmol/mol) in air

Cross section has an uncertainty of 1.9 %.
SRP instruments are certified by comparison to primary SRPs for which the ozone mole fraction, $x_{O_3}$, and its combined uncertainty, $u(x_{O_3})$, are derived from the Beer-Lambert law and measured $T$, and $p$ of the sample; the Boltzmann constant, $k_B$; pathlength, $L$; and the 1961 Hearn value for the ozone absorption cross-section at 253.65 nm (air), $\sigma$. 

\[ I_0 e^{-n\sigma L} \]
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 were not corrected. Known bias was introduced via uncertainty; asymmetric components considered

• Uncertainties were evaluated according to GUM (1995). In some cases, this required introducing additional uncertainty not specified in the original publication
Studies Considered

Table 1. List of the fourteen independent publications selected to calculate the consensus value of the ozone absorption cross-section at 253.65 nm.

<table>
<thead>
<tr>
<th>Identification</th>
<th>Author(s)</th>
<th>Traceability</th>
<th>Sample purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFCRC-59 [35]</td>
<td>Inn and Tanaka</td>
<td>Ozone pressure</td>
<td>Assumed pure</td>
</tr>
<tr>
<td>Hearn-61 [3]</td>
<td>Hearn</td>
<td>Ozone pressure</td>
<td>Degradation to O₂ considered</td>
</tr>
<tr>
<td>JPL-64 [33]</td>
<td>De More and Raper</td>
<td>Oxygen pressure</td>
<td>Assumed full conversion of O₃ to O₂</td>
</tr>
<tr>
<td>Griggs-68 [34]</td>
<td>Griggs</td>
<td>Ozone pressure</td>
<td>Assumed pure</td>
</tr>
<tr>
<td>JPL-86 [39]</td>
<td>Molina and Molina</td>
<td>Ozone pressure</td>
<td>Assumed pure</td>
</tr>
<tr>
<td>UniMin-87 [37]</td>
<td>Mautersberger et al</td>
<td>Ozone pressure</td>
<td>Assessed by mass spectrometry</td>
</tr>
<tr>
<td>HSCA-88 [41]</td>
<td>Yoshino et al</td>
<td>Ozone pressure</td>
<td>Assumed pure</td>
</tr>
<tr>
<td>UniReims-93 [32]</td>
<td>Daumont et al</td>
<td>Ozone pressure</td>
<td>Degradation to O₂ considered</td>
</tr>
<tr>
<td>UniBremen-99 [31]</td>
<td>Burrows et al</td>
<td>* NO₂ cross-section via GPT</td>
<td>NA air sample/SRP</td>
</tr>
<tr>
<td>UPMC-04[44]</td>
<td>Dufour et al</td>
<td>Ozone pressure</td>
<td>Assumed pure</td>
</tr>
<tr>
<td>NIES-06 [10]</td>
<td>Tanimoto et al</td>
<td>* NO/N₂ standards via GPT</td>
<td>NA air sample/SRP</td>
</tr>
<tr>
<td>UniBremen-14 [45]</td>
<td>Gorshelev et al</td>
<td>Ozone pressure</td>
<td>Degradation to O₂ considered</td>
</tr>
<tr>
<td>BIPM-15 [26]</td>
<td>Viallon et al</td>
<td>Ozone pressure</td>
<td>Assessed by residual pressure measurements</td>
</tr>
</tbody>
</table>

*GPT: Gas-phase titration of the NO + O₃ → NO₂ + O₂ reaction
Uncertainties

Common to all measurements:
Type A: repeatability
Type B: pressure, temperature, optical pathlength, absorbance

\[ u_{r\text{tot}} = (u_{r,1}^2 + u_{r,2}^2 + \ldots )^{1/2} \]

Experiment-specific:
- sample purity. [(Mauersberger 1987, ... Viallon 2015)]
- GPT with gas standards: [Tanimoto (2006), Viallon (2015)]
- GPT with NO\textsubscript{2} absorption cross section: [Burrows (1999)]
- intensity of IR rovibrational transition of O\textsubscript{3}: [Dufour (2004)]
- effect of multiple reflections (Inn & Tanaka, Hearn, DeMore, Griggs, Molina Mauersberger, Yoshino, Brion, Gorshelev)
Final Monte Carlo & DerSimonian Laird Statistical Analysis

Monte Carlo method with skew-normal distribution accounted for asymmetric uncertainties

(DL) DerSimonian-Laird analysis indicated that inter-laboratory heterogeneity was negligible

\[
\begin{align*}
\langle \sigma \rangle &= 1.1329(35) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1} \\
U_{95}(\langle \sigma \rangle) &= 0.0069 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}
\end{align*}
\]

\(\text{areas } \propto \text{weighting factors}\)
Composite Distribution Function

Weighted analysis leads to narrower, more-symmetric distribution

Final pdf is still slightly skewed
Studies Contributing to 90% of the Cumulative Weight

- BIPM-15
- UnivMin-87
- NIES-06
- HSCA-88
- JPL-86
- BIPM-16

Cumulative weight

Rank

1. Pure O₃
2. Assumed Pure O₃
3. Assumed Pure O₃
4. Assumed Pure O₃
5. GPT
6. BIPM-16
## Proposed Change in Ozone Cross-Section at 254 nm

<table>
<thead>
<tr>
<th>Ref.</th>
<th>( \sigma ) ( \times 10^{-17} \text{ cm}^2/\text{molecule} )</th>
<th>w.r.t. to Hearn</th>
<th>rel. std. unc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1)Hearn-61</td>
<td>1.147</td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>Hodges/CCQM</td>
<td>1.1329</td>
<td>-1.23 %</td>
<td>0.31</td>
</tr>
</tbody>
</table>

This work reduces uncertainty in the ozone absorption cross-section by factors of 6.1 and 2.6, respectively compared to those of Hearn and ACSO.

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Impact of New Cross Section on SRP uncertainty

**Current Situation**

- Uncert. in measured intensity ratio
- Uncert. in Hearn cross-section
- Uncert. in p, T, pathlength

**With New Cross-section**

- Uncert. in measured intensity ratio
- Uncert. in new cross-section
- Uncert. in p, T, pathlength

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**EPA O₃ Index (8 hr)**

- Good
- Very Unhealthy
- Unhealthy
- Unhealthy for Sensitive Groups
- Moderate
Figure 3. The percent increase in the number of sites that are out of compliance with air quality regulations due to the adjusted ozone abundances suggested by the new Viallon et al. (2015) cross section for the EU, the United States, and Canada between 1990 and 2012. Shaded regions indicate the uncertainty in the number of non-compliant sites associated with the 2 standard deviation uncertainty in the Viallon et al. cross section.

Based on BIPM-15, where $x$-sec = 1.8% less than the Hearn-61 value

The new consensus value for the $x$-sec is 1.23% less than the Hearn-61 value

Additional exceedances driven by reassignment of the $x$-sec will be $\sim 2/3$ that predicted by Sofen et al.
Measurements of Atmospheric Ozone across the Electromagnetic Spectrum

**Satellite:** OMI, TEMPO

**Ground:** Brewer-Dobson instruments, LIDAR, direct absorption

**ultraviolet-visible**

**thermal infrared**

**microwave**
Unifying the Spectroscopic Properties of Ozone

microwave Stark measurements of the permanent dipole moment of ozone; Mack and Muenter (1977) (unc. = 0.02 %)

photometric references

0.43 mm; intensities from Drouin et al. (2017) (unc. = 0.2 %)

254 nm; Hodges/GAWG (2019) Hartley band (x-sec unc. = 0.31 %)

325 nm; Janssen et al. (2018) Huggins band (x-sec unc. = 0.09 %)

FTS of 4.7 µm & 9.7 µm intensities

FTS of uv Hartley & Huggins bands

log wavelength, $\lambda$

100 nm 1 µm 10 µm 100 µm 0.43 mm 1 mm
Consistency of Cross Sections within the UV

New uv FTS measurements in agreement with Hodges/GAWG 254 x-sec to within 0.64 %

Consistency between 254 nm and 325 nm x-sec reference values demonstrated

FTS results provide improved temperature dependence over a wide spectral range for remote sensing applications

BDM = (Brion, Daumont, Malicet)

BDM – BW (3 % at 325 nm)
BDM – Janssen (2.4 % at 325 nm)

https://www.zenodo.org/record/1485588#.XFmO8FVKlCp

Birk & Wagner (2019)
Consistency between UV, IR and MW Measurements and with Theory

*Ab initio* calculations of O$_3$ cross-sections were compared to UV and IR measurements that were scaled by CCQM/Hodges value at 254 nm. Calculations agree with IR and MW measurements at 1% level, resolves 4% level discrepancies in IR and UV measurements, demonstrates consistency from UV to IR to MW regions, and IR databases (e.g. HITRAN) to be updated accordingly.
Summary

The Hodges/CCQM ozone absorption cross section at 254 nm is 1.23 % smaller than the current (Hearn) value, and therefore will increase field measurements of ozone mole fraction by 1.23 %

The uncertainty of this cross section has been reduced by a factor of 6 to ~0.3 %

This cross section is a key photometric reference point that contributes to SI traceability and a recently achieved percent-level consistency in laboratory ozone measurements and theory spanning the UV to MW regions of the electromagnetic spectrum.

Adoption of this cross section along with other reference values will help unify local and global measurements of atmospheric ozone.
Thanks !