Accurate measurements of ozone absorption cross-sections in the Hartley band

international bureau of weights and measures

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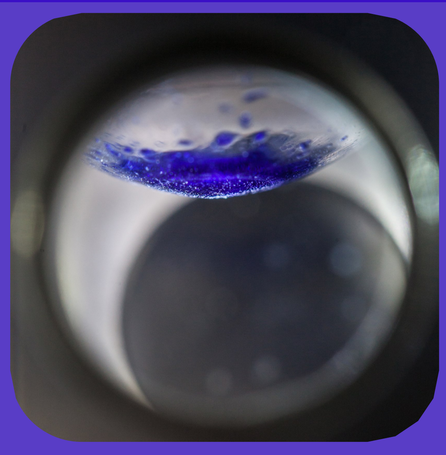
Ozone in the troposphere is monitored worldwide for its important impact on health. Levels of ozone are measured by networks using mostly Ultra Violet absorption instruments, with traceability to Standard Reference Photometers (SRP), relying on the UV absorption of ozone at the 253.65 nm line of mercury.

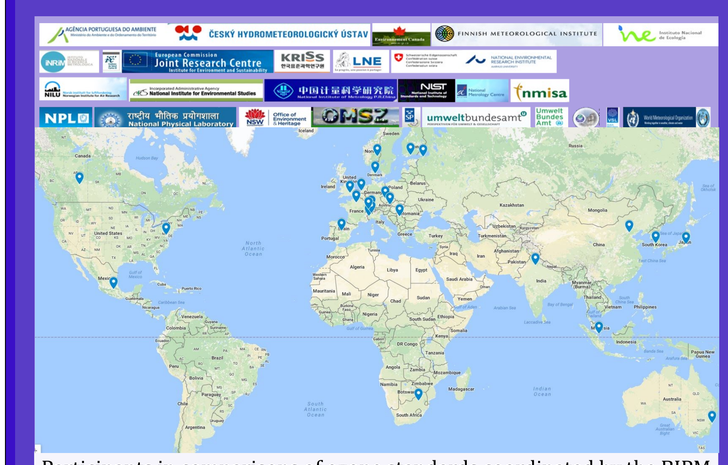


In 2014, new measurements of the ozone absorption cross-section in the Hartley band were performed on gaseous ozone samples generated from a sample of purified liquid ozone. The cross-section at the 253.65 nm line of mercury was determined by comparison with an SRP.

The SRP acts as the primary standard for numerous national and international ozone monitoring networks, such as the WMO Global Atmosphere Watch (GAW) Programme.

Several replicas of this instrument are maintained by the BIPM, one of which is the reference for the international comparison BIPM.QM-K1 of national ozone standards coordinated by the BIPM.

Traceability scheme for measurements of ozone at ambient levels



Participants in comparisons of ozone standards coordinated by the BIPM

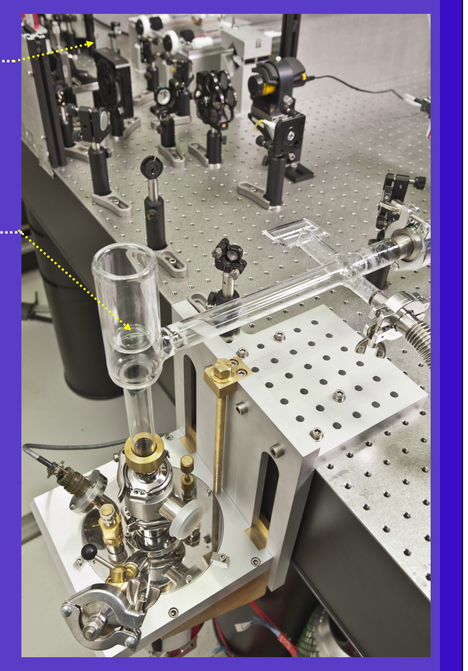
Ozone international comparisons

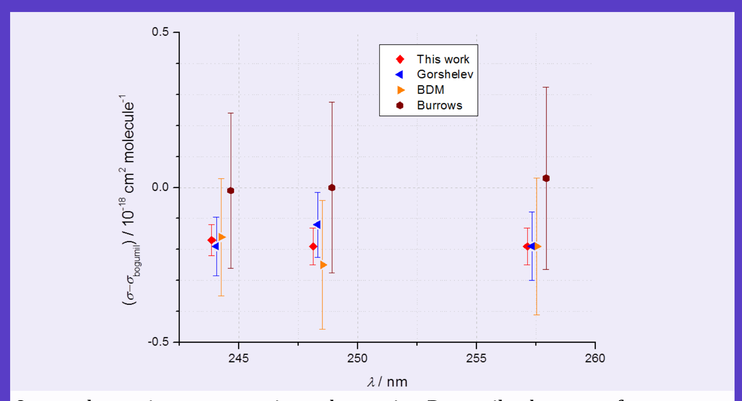
- Set of 3 SRP at BIPM
- Series of bilateral comparisons between participants and BIPM
- 28 Member States of the BIPM, 2 international organizations

UV laser - a stabilized Argon Ion laser with three lines in the Hartley band was used to measure the optical density in the gas cell filled with low pressure ozone. The path length of the absorption cell was determined by interferometry.

Ozone generator - ozone was generated from oxygen by discharges and cryogenic trapping at 75 K. Ozone was purified after evaporation at 135 K, recondensation and evacuation of residual oxygen.

Purity analysis - possible impurities in the ozone sample were analyzed by mass spectrometry and Fourier Transform Infrared spectroscopy. Ozone purity was between 98.1% and 99.6% depending on the pressure.



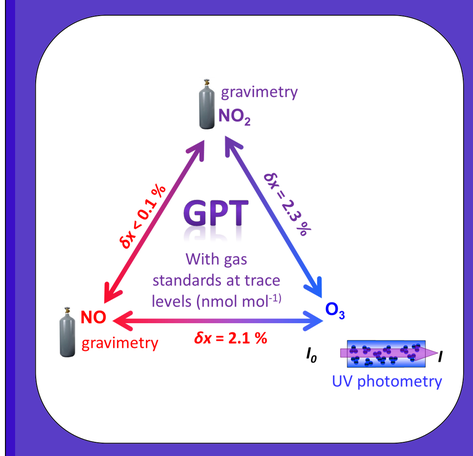


Ozone absorption cross-section values using Bogumil values as reference

(Wavelengths plotted with a 0.2 nm shift from each other)

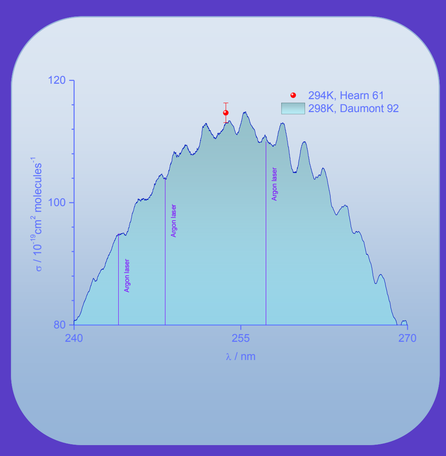
⇒ new measurements of absolute values of ozone absorption cross-sections with relative expanded uncertainties better than 0.7 %, for the wavelengths (in vacuum) of 244.06, 248.32, and 257.34 nm.

Published in Viallon et al. Accurate measurements of ozone absorption cross-sections in the Hartley band. *Atmos. Meas. Tech.* **2015,** *8* (3), 1245-1257)



In parallel, a Gas Phase Titration (GPT) experiment was conducted, using the reaction of O_3 at the nmol/mol level with NO resulting in NO_2 and O_2.

This allows measurements of O_3 anchored to NO and NO_2 standards of high accuracy produced by gravimetry.

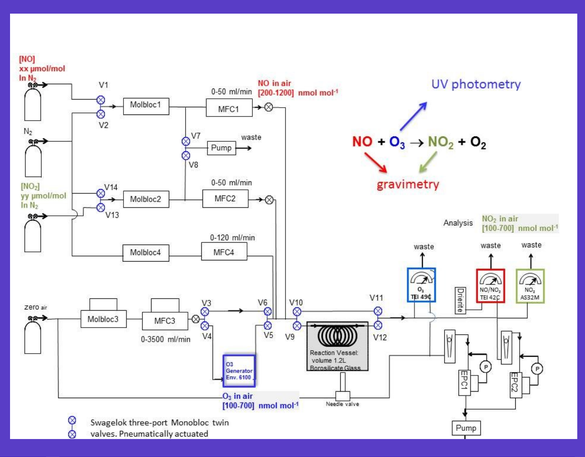


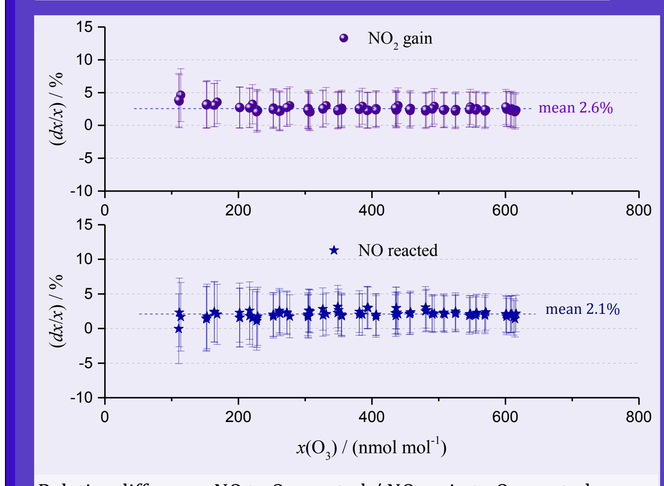
Those new results, together with published papers on ozone cross section measurements at 253.65 nm, will be reviewed by a Task Group recently established by the Gas Analysis Working Group of the CCQM (Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology).

NO reacted measured by chemiluminescence, in line calibration with diluted NO standards validated during comparisons

NO_2 gain measured by CAPS, in line calibration with diluted NO_2 standards FTIR analysis : HNO_3 mole fractions at (0.2 to 1) µmol mol^{-1} in standards at (10 to 40) µmol mol^{-1}.

O_3 reacted measured by UV photometry, calibration with BIPM SRP.





Relative difference NO to O_3 reacted / NO_2 gain to O_3 reacted.

⇒ Constant relative bias of

2.1% between NO and O_3 reacted

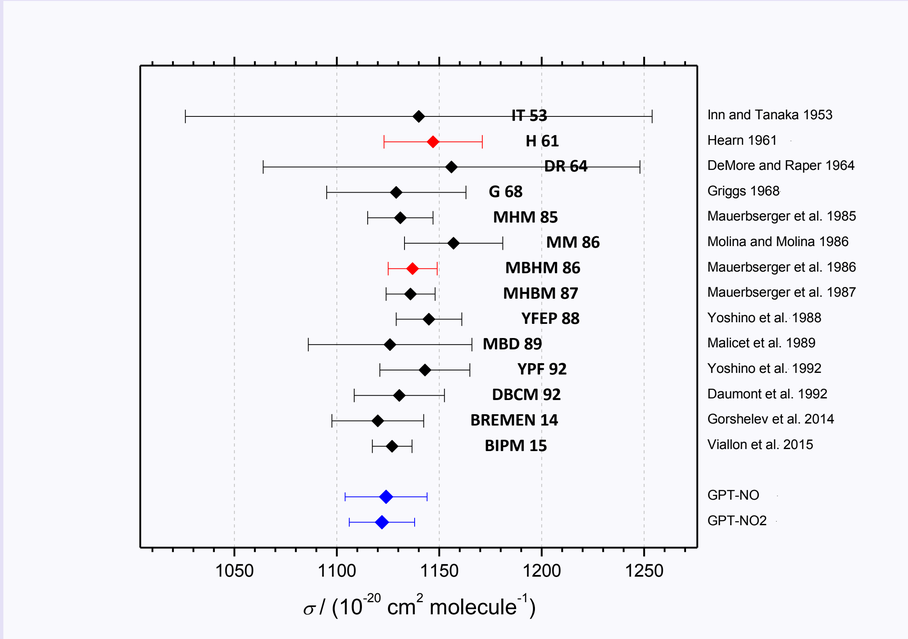
2.3% between NO_2 gain and O_3 reacted

attributed to a bias in the ozone absorption cross-section value at 254 nm.

⇒ Data used to deduce two other values of the absorption cross-section with expended uncertainty better than 1.8%.

From Viallon et al, Ozone cross-section measurement by gas phase titration, *submitted to Analytical Chemistry on 23 August 2016*

This group is in charge of recommending a value and uncertainty for the ozone cross section at 253.65 nm to be used in ozone reference photometers and for comparisons of these standards in the on-going international comparison BIPM.QM-K1.



Published values of the ozone absorption cross-section at the mercury line (253.65 nm), plus the two values obtained by GPT. Modified from the graph published in Orphal et al, Absorption cross-sections of ozone in the ultraviolet and visible spectral regions: Status report 2015. *J. Mol. Spectrosc.* **2016.**

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