

Recommendation of a new consensus ozone cross-section value for tropospheric ozone monitoring

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The propensity of ozone to strongly absorb UV radiation, notably in the Hartley Band, and the relative ease with which low-cost mercury lamps emitting at 253.65 nm (in air) can be used to interrogate this spectral region make the value of the ozone absorption cross-section at this wavelength particularly important to global ozone atmospheric monitoring. Back in the 1980's, developers of the NIST Standard Reference Photometer (SRP) equipped the instrument with a low-pressure mercury lamp and chose the ozone absorption cross-section value measured by Hearn in 1961 and recommended at the time by the EPA to compute the ozone concentration. Since that time, more than 60 NIST SRPs have been constructed and constitute primary standards for national and international ozone monitoring networks, such as the WMO Global Atmosphere Watch (GAW) Programme. Meanwhile, a growing body of evidence has led to a re-evaluation of the conventionally accepted value of the mercury line ozone absorption cross-section. On one hand, comparisons of UV absorption results based on measuring the density of pure ozone to those based on gas phase titration of ozone with nitrogen monoxide began to suggest the existence of a 2% to 3% bias. In addition, laboratory efforts to lower the uncertainty of the mercury-line ozone absorption cross-section in the UV as well as studies encompassing a wide range of spectral regions have continued, leading to a set of cross-section values lying about 2% below those agreed upon in the 1980's. This trend and its impact on stratospheric ozone measurements were recently acknowledged by the Absorption Cross-Section for Ozone (ACSO) committee, in which measurements performed by satellites, as well as those with Dobson and Brewer spectrophotometers were considered.

The case of tropospheric measurements still needs to be tackled, considering that recommended ozone cross-section values in different spectral ranges need to be consistent. To this aim, a Task Group was setup by the Gas Analysis Working Group of the Consultative Committee for Metrology in Chemistry and Biology (CCQM/GAWG), which has been the body organizing international comparisons of ozone standard instruments for ground-level measurements. Experts from this group were asked to review all measurements of the ozone cross-section value published since 1950, carefully considering measurement uncertainties. The goal of this effort is to recommend a consensus value and a combined uncertainty for the mercury-line ozone cross-section to be adopted in the use of standard instruments for tropospheric ozone measurements.

The outcome of this review will be presented, explaining how the different instrumental methods used to measure the ozone absorption cross-section were scrutinized, together with their metrological traceability and sources of uncertainties. The impact of recommending a new ozone cross-section value will be carefully considered, as tropospheric ozone is one of the most monitored and regulated gases worldwide.