Actuality

More accurate measurement results for ground-level ozone

Since 1993, the METAS gas analysis laboratory has applied a harmonised method to calibrate ozone-measuring instruments using a primary ozone photometer. This method will now be adapted to the latest findings as part of an internationally coordinated process, reducing measurement uncertainties.

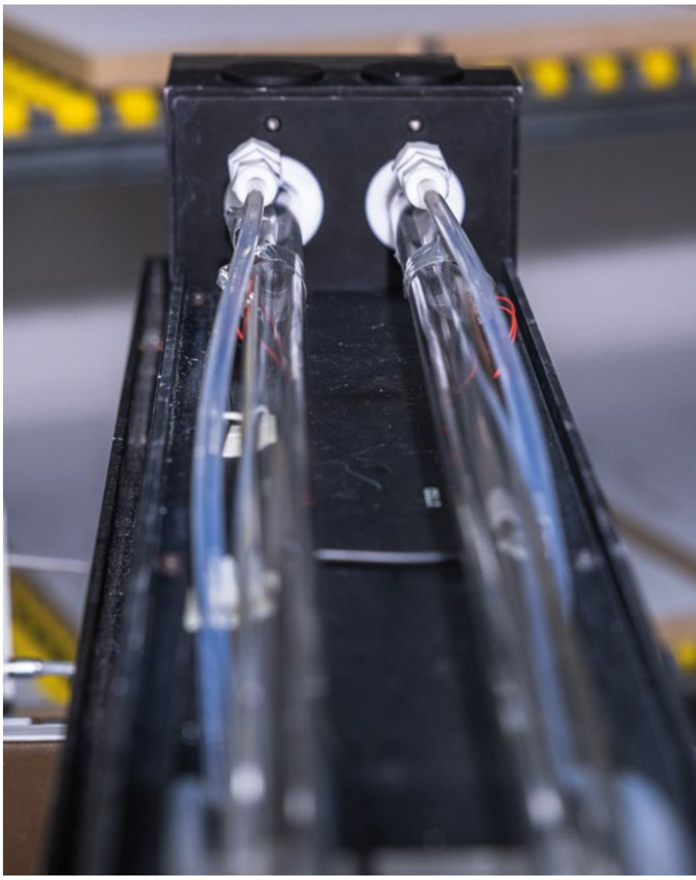
Bernhard Niederhauser

Measuring amount-of-substance fractions of ozone in the ground-level air has a long tradition in Switzerland. The measuring instruments used for air-quality monitoring and research are regularly calibrated following a standardised method. The process involves calculating the amount-of-substance fraction[1] of ozone in the air generated by a stable ozone generator through photometric measurement using a standard reference photometer (SRP). This ozone-air mixture is then simultaneously applied to a device under test to calibrate it accordingly.

$$x_{O3} = \frac{-1}{2 \cdot L_{opt} \cdot \sigma} \cdot \frac{R}{N_A} \cdot \frac{T_{mes}}{p_{mes}} \cdot \ln(D)$$

Formula for calculating the amount-of-substance fraction of ozone: x_{O3} is the amount-of-substance fraction of ozone; L_{opt} is the average optical length of the measuring cells; σ is the absorption cross section of an ozone molecule; R is the universal gas constant and N_A is the Avogadro constant. T_{mes} and p_{mes} are the measured temperature and pressure conditions and D is the product of the transmittances of both measuring cells.

The “Manifold” distributes the ozone-air mixture with the most stable amount-of-substance fraction to the reference and simultaneously to up to three test specimens.



The two 90 cm long measuring cells are alternately supplied with an ozone-containing mixture or zero air.

The absorption cross section has the biggest influence on this calculation and its uncertainty (see formula). The absorption cross section value currently used is from 1961[2] and is now being replaced internationally by a new, agreed value designated CCQM.O3.2019. From 2025, this value will allow for more accurate reference values and therefore more accurate measurement values.

A working group is coordinating the worldwide implementation

To ensure the change from the old to the new defined absorption cross section value proceeds as smoothly as possible and, above all, in a traceable manner, an international working group has been set up to coordinate the implementation and develop guidelines. The working group, which includes Swiss participants, has now published guidelines on the implementation and the harmonised use of metadata, as well as a series of reports on the facts and figures concerning the change.

Absorption characteristics

	Before the change	Conversion factor	After the change
Time period	Until Dec 2024		From Jan 2025
Name of reference	Hearn.1961		CCQM.O3.2019
Absorption cross section per molecule σ	$1.1476 \cdot 10^{-17}$ cm^2	1.01298	$1.1329 \cdot 10^{-17}$ cm^2 [4]
Rel. measurement uncertainty σ	1.06 %		0.31 %
Linear absorption coefficient α_x	308.32 cm^{-1}	1.01293	304.39 cm^{-1}
Rel. measurement uncertainty α_x	1.06 %		0.31 %

Table: The absorption values differ before and after the change. The value currently used is to be replaced by a new, somewhat lower value which is three times more accurate. Data not corrected according to CCQM.O3.2019 can be converted to the new reference using the conversion factor. Since the linear absorption coefficient is stored in the SRP, the line with the blue text is crucial for the conversion.

These and other insights are available on the International Bureau of Weights and Measures (BIPM)[3] information platform. Those interested can register to be notified of the latest updates. In addition, issues related to the adaptation of international, regional and national standards have been clarified and a timeline for implementation has been defined. Finally, a publication on the long-term effects of the change in different contexts is set to be prepared.

The procedure in Switzerland

In Switzerland, both calibration service providers, METAS and the Swiss Federal Laboratories for Materials Science and Technology (Empa) have agreed to only offer calibrations using the new absorption cross section from January 2025. Therefore, in the transition year 2025, all data based on a calibration certificate from 2024 or earlier can be converted to the new absorption cross section (see table).

Conversely, in 2025, all data from instruments that have been calibrated with reference to CCQM.O3.2019 can be corrected using the calibration function from the calibration certificate as usual. The procedure is expected to be completed by the end of 2025. After this point, it will only be possible to distinguish the new ozone measurement data sets by the detailed metadata.

Effects on the immission values

Because of the slight reduction in the absorption parameter by approx. 1.3 %, according to the Beer-Lambert Law (see formula) the measurement values will rise by the same amount. In rare cases, this may lead to additional instances where the immission limit values in accordance with the Air Pollution Control Ordinance are exceeded[5], as limit values are not adjusted accordingly and remain at the "round" numbers (e.g. 120 µg/m^3 for the one-hour average). Whether or not the change in absorption cross section causes other effects in other countries, or has a significant impact at all, will be laid out in future studies and publications on ozone time series.

1 For ideal gases, the amount-of-substance fraction is equivalent to the volume concentration.
2 Hearn, Proc. Phys. Soc., 78, 1961, DOI 10.1088/0370-1328/78/5/340; https://doi.org/10.1088/0370-1328/78/5/340
3 https://www.bipm.org/en/ozone
4 J T Hodges et al. 2019. Metrologia 56, 034001, https://doi.org/10.1088/1681-7575/ab0bdd
5 Ordinance on Air Pollution Control (OAPC, SR 814.318.142.1), https://www.fedlex.admin.ch/eli/cc/1986/208_208_208/en