
**Air quality — Determination of ozone
in ambient air — Ultraviolet photometric
method**

*Qualité de l'air — Dosage de l'ozone dans l'air ambiant — Méthode
photométrique dans l'ultraviolet*

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 13964 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 3, *Ambient atmospheres*.

Annexes A, B and C of this International Standard are for information only.

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Air quality — Determination of ozone in ambient air — ultraviolet photometric method

WARNING — This document calls for use of ozone gas. Ozone is a toxic gas and good laboratory practice should limit indoor ozone concentrations to less than $200 \mu\text{g}/\text{m}^3$ (volume fraction 1×10^{-7}). Consult a reference text for more details on hazards and safety of ozone. Any excess should be vented into an activated charcoal scrubber (with negligible back-pressure) or outdoors well away from any sampling intake.

1 Scope

This International Standard specifies an ultraviolet (UV) photometric method for the determination of ozone in ambient air. It is applicable to the determination of ozone concentrations in the range $2 \mu\text{g}/\text{m}^3$ (volume fraction of 1×10^{-9}) to $2 \text{ mg}/\text{m}^3$ (volume fraction of 1×10^{-6}). Furthermore, this International Standard uses the reference conditions of $25 \text{ }^\circ\text{C}$ and $101,25 \text{ kPa}$; however, reference temperatures of $0 \text{ }^\circ\text{C}$ and $20 \text{ }^\circ\text{C}$ are also acceptable.

For calibration, this International Standard specifies ultraviolet photometry as the primary reference procedure because of its proven accuracy and specificity to ozone. The use of secondary reference procedures (often called transfer standards), including non-UV methods, is allowed if they have been previously calibrated by the primary UV reference procedure (see ISO 6879 for definitions).

2 Interferences

The UV photometric method is not subject to interference from any of the common gaseous air pollutants at ambient concentrations less than $0,2 \text{ mg}/\text{m}^3$ (volume fraction of 1×10^{-7}). However, there are reported interferences of about $2 \mu\text{g}/\text{m}^3$ (volume fraction of 1×10^{-9}) and about $8 \mu\text{g}/\text{m}^3$ (volume fraction of 4×10^{-9}) in equivalent ozone for nitrogen dioxide and sulfur dioxide concentrations at a volume fraction of $0,5 \times 10^{-6}$, respectively. Additionally, there are some reported interferences for instruments using a manganese dioxide ozone scrubber; these are tabulated in annex A of this International Standard.

Particulate matter, if not removed, will accumulate in the sampling line and may cause a measurable destruction of ozone.

Ambient nitric oxide in the sample air will to some extent react with the ambient ozone during the residence time of the ambient air in the sampling line; corrections for this effect are given in annex B of this International Standard.

For ozone analysers with single absorption cells, any ambient pollutant that absorbs the photometer's UV radiation and that varies in concentration within the cycle time of the instrument may cause an interference. A similar limitation applies at a site where the ambient ozone concentration itself varies on this time scale, as for example, at traffic intersections.

NOTE In general, if interferences are suspected, it is preferable to use another method (for example, the chemiluminescence method using ethylene, see [2]) rather than attempting to scrub out the interfering agent, because the instability of ozone makes the testing and proving of scrubbers particularly difficult.

3 Principle

Sample air is drawn continuously through an optical absorption cell where it is irradiated lengthwise by monochromatic radiation, centred on 253,7 nm, from a stabilized low-pressure mercury (Hg) discharge lamp. The UV radiation which passes through the absorption cell is measured by a sensitive photodiode or photomultiplier detector and converted to a measurable electrical signal. Absorption of this radiation by the sample air within the absorption cell is a measure of the ambient ozone concentration. An ozone catalytic converter is used to selectively remove the ozone from the sample stream. This can be done either for the sample absorption cell (single-cell configuration) or a separate but identical reference absorption cell (dual-cell configuration); either configuration is acceptable.

The Beer-Lambert law on light absorption is used to relate the measured UV transmittance to the path length of the absorption cell, the ozone absorption coefficient at 253,7 nm and the ozone concentration. The following equation gives this relationship:

$$\text{Transmittance} = I/I_0 = \exp(-aCd) \quad (1)$$

where

- I/I_0 is the transmittance of the ozone sample, i.e. the ratio of the irradiance (commonly called light intensity) falling on the detector when the absorption cell contains sample air to the irradiance when the cell contains ozone-scrubbed air;
- a is the ozone absorption coefficient at 253,7 nm, in square metres per microgram; ($a = 1,44 \times 10^{-5} \text{ m}^2/\mu\text{g}$; see [3]);
- C is the mass concentration of ozone, at the sample temperature and pressure in the absorption cell, in micrograms per cubic metre;
- d is the optical path length, in metres.

Most modern commercial ozone analysers measure the temperature and pressure of the sample air in the absorption cell. Using this data, an internal microprocessor automatically calculates the measured ozone concentration relative to some chosen reference condition. For analysers without this automated pressure and temperature compensation, the concentrations need to be corrected manually to the chosen reference condition (T_{ref} °C and 101,25 kPa) according to the following equation:

$$C_{\text{ref}} = \frac{101,25}{P} \cdot \frac{(T + 273,15)}{(T_{\text{ref}} + 273,15)} \cdot C \quad (2)$$

where

- C_{ref} is the mass concentration of ozone, at the reference temperature (T_{ref}) and pressure (101,25 kPa), in micrograms per cubic metre;
- T is the sample temperature of the absorption cell, in degrees Celsius;
- P is the sample pressure in the absorption cell, in kilopascals;
- T_{ref} is the reference temperature, in degrees Celsius;
- C is the mass concentration of ozone from equation (1), at the sample temperature (T) and pressure (P) in the absorption cell, in micrograms per cubic metre.

4 Reagents and materials

4.1 Sample line, made of material that is inert to ozone, such as glass or fluorocarbon polymer, and shall be as short as possible to keep the residence time to a minimum. Any ambient nitric oxide present in the sample air will react with some of the ozone during the residence time in the sampling line. This decay of ozone is a function of the ambient ozone and nitric oxide concentrations (see note below). Calculations have shown that if the residence time is less than 0,5 s, then the decay in initial ozone will be less than 1 % for most ambient ozone and nitric oxide concentrations encountered. Hence, it is recommended that the sampling line length and flowrate be chosen such that the residence time within the sampling line be as short as possible; a residence time of up to 5 s is allowed.

It is recommended that a particle filter (see 4.2) be installed at the sampling inlet to keep the whole inlet system clean. In case there is a sample line or manifold preceding the inlet particle filter (see 4.2), it shall be clean. Proper precautions shall be taken to prevent condensation inside the sample line, for example, by appropriate heating of the line.

NOTE 1 Annex B describes the correction for the reaction of ambient ozone with nitric oxide in the sampling line.

NOTE 2 Whenever a sampling line is cleaned or replaced, it may take several hours to equilibrate with ambient conditions.

4.2 Particle filter and its support, made of material inert to ozone, such as polytetrafluoroethylene (PTFE), and capable of removing all particles likely to alter the performance of the analyser. It shall be changed on a regular basis, depending on the ambient particle concentrations at the sampling site; however, the period between filter changes should not exceed 14 days. This is necessary because excessive accumulation of particles on the filter can cause loss of ozone from the sample air.

NOTE Frequently, a filter pore size of 5 µm is used.

NOTE Generally, new filters need some time to be conditioned by the ambient atmosphere. As a result, measured ozone concentrations have been observed to decrease temporarily by 5 % to 10 % for periods of 5 min to 15 min immediately following filter changes.

4.3 Zero air, required in the analyser calibration procedure. If synthetic air is used, the oxygen content shall be at the normal atmospheric concentration of $(20,9 \pm 2)\%$.

The zero air shall be free of ozone, nitrogen oxides and any other interfering substance that can cause an undesired measurable positive or negative response in the UV photometer. Different zero air supplies may have different remnant impurities and, in turn, these can cause different UV transmittances of the air samples. Hence, the zero air supplied to the photometer during the I_0 measurement [see equation (1)] shall be the same as that used for generation of the calibration ozone concentrations.

NOTE Details on a system for making zero air from ambient air may be found in [4].

5 Apparatus

5.1 UV photometric ambient ozone analyser

The components of a typical UV photometric ozone measuring system with a single-cell configuration are shown schematically in Figure 1. When assembled, they become part of a UV photometric ambient ozone analyser with specifications conforming to those listed in annex C. Commercial instruments that meet these specifications are readily available in either single or dual cell configurations. The important components of such a system are as follows.

- a) **Ultraviolet absorption cell**, constructed of material inert to ozone, such as fluorocarbon polymer, borosilicate glass, fused silica or fluorocarbon-coated metal. It shall be mechanically stable so that any optical alignments are not affected by vibration or change in ambient temperature. Provision shall be made for measuring the temperature and pressure of the gas in the absorption cell [see 5.1 h) and 5.1 i)].

- b) **Ultraviolet source lamp**, i.e. a low-pressure mercury vapour discharge lamp that emits monochromatic UV radiation centred at 253,7 nm. The UV radiance of this lamp shall be electronically stabilized so that the analyser meets the required performance specifications (see annex C for typical values); any variation in lamp radiance during the measurement cycles will result in a measurement bias or noise. The lamp's mercury line at 185 nm (which photolyses oxygen to produce ozone) shall be eliminated by means of a high-silica glass enclosure or shield.

NOTE Spectral data show that ambient water vapour should not interfere in the UV wavelength region of interest here (about 200 nm to 300 nm). However, it has been observed in some analysers of one manufacturer that the quartz window of the UV source lamp was covered with a significant number of microscopic scratches. This resulted in a measurable variation in light scattering at the internal window surface due to changing humidity in the sample air. Replacement of such faulty windows eliminated this interference (see [1]).

- c) **UV detector**.

Quantitatively, 99,5% of the radiation sensed by the detector shall be at 253,7 nm. The response of this sensor and its associated electronics shall be sufficiently stable so that the analyser meets the required performance specifications.

NOTE Vacuum photodiodes with cesium telluride sensitization meet the requirement of sensitivity at 253,7 nm and negligible sensitivity at other mercury emission wavelengths. Other detectors, such as photomultiplier tubes, also satisfy this purpose.

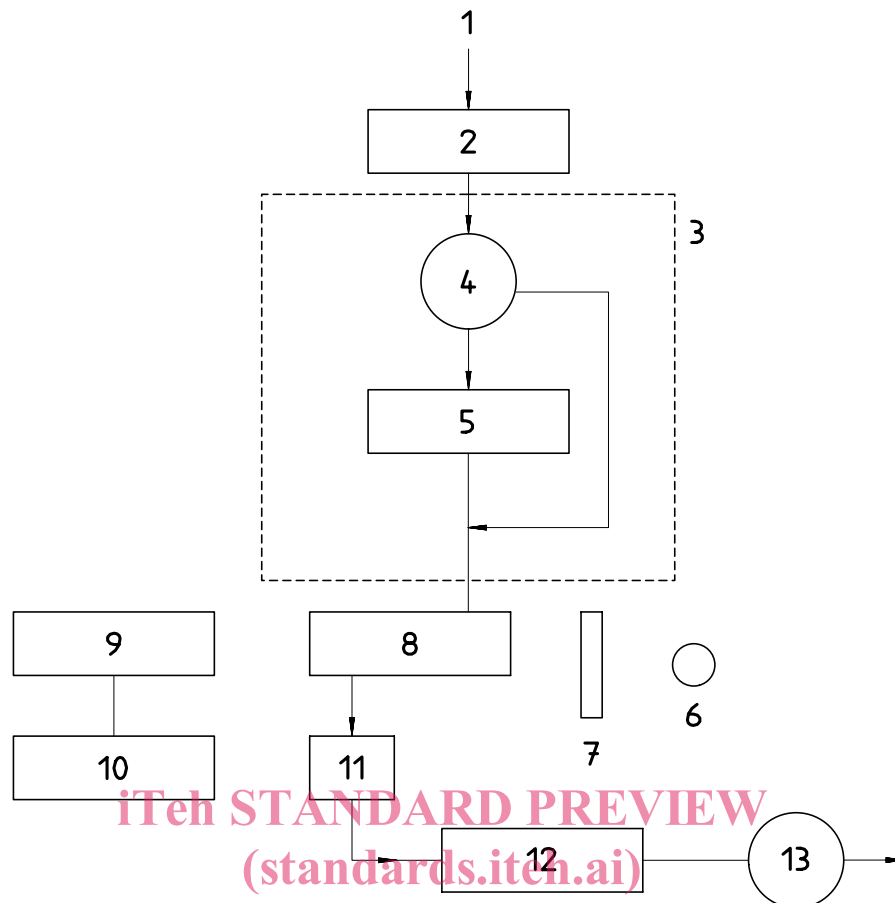
- d) **Ozone-specific scrubber (converter) with by-pass valve**, whose active component shall be a material that selectively catalyses the destruction of ozone in the ambient air sample stream.

NOTE 1 Manganese dioxide on a metal substrate has been found to do this satisfactorily. Even though this particular compound does not remove any of the other more common pollutants, it has been found to partly remove some organic compounds which may be present in some ambient air. Annex A lists such interfering chemical compounds.

A three-way by-pass valve is used to direct ambient air alternately either through or around the ozone-specific scrubber. It shall be made of material that is inert to ozone, such as a fluorocarbon polymer.

NOTE 2 A significant decrease in response to ambient ozone of a UV ozone analyser may be an indication of scrubber failure. Normally, manufacturers give an average lifetime of such scrubbers; however, the actual lifetime will depend on the sampling location. For example, a city location, which is subject to higher pollutant concentrations than a remote location, may deactivate the scrubber prematurely.

- e) **Air pump**, installed at the end of the system (see Figure 1) to pull sample air through the instrument; capable of maintaining a flowrate of several litres per minute.
- f) **Air flow control device**, installed immediately ahead of the air pump so that the air flow through the analyser can be properly set.
- g) **Air flowmeter**, installed after the UV absorption cell (see Figure 1) to measure the sample flowrate in the instrument, capable of measuring air flow up to several litres per minute.
- h) **Temperature indicator**, capable of measuring the temperature of the sample air in the ultraviolet absorption cell with an accuracy of $\pm 0,5$ °C.
- i) **Pressure indicator**, capable of measuring the pressure of the sample air in the absorption cell with an accuracy of $\pm 0,2$ kPa.



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1 Air inlet	8 UV absorption cell
2 Particle filter	9 UV detector
3 Only for UV ambient ozone analyser	10 Signal processing electronics
4 Bypass valve	11 Flow meter
5 Ozone catalytic converter	12 Flow controller
6 UV source lamp	13 Pump
7 Optics	

5.2 Apparatus for calibration by primary reference procedure

A simplified schematic of an ozone calibration system is shown in Figure 2, and comprises the following.

NOTE An equivalent system would be one in which an extra zero air line, from the same zero air source, bypasses the ozone generator so as to facilitate switching zero or ozonized air into the manifold or directly into the UV calibration photometer. This would require additional inert gas lines, connections and valves.

- a) **Primary UV calibration photometer**, used for only that purpose and meticulously maintained under stable laboratory conditions.

Similar to the UV photometer of the ambient analyser, it shall consist of a low pressure mercury discharge lamp, a single or dual absorption cell, and detection and signal processing electronics. To prevent ozone generation within the absorption cell, a high-silica glass window (or equivalent) shall be inserted between the mercury lamp and the absorption cell to remove the 185 nm Hg wavelength (which photolyzes oxygen to produce ozone) and yet allow transmission of the 253,7 nm Hg measurement wavelength. The detector shall be capable of measuring the transmittance through the absorption cell at the 253,7 nm wavelength, with less than 0,5 % of the radiation detected being from other wavelengths (vacuum diodes with cesium telluride sensitization meet this requirement). The length of the light path through the absorption cell shall be known to