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Ambient air — Determination of the mass concentration of ozone — Chemiluminescence method

Air ambiant — Détermination de la concentration en mass d'ozone — Méthode par chimiluminescence

Reference number
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Foreword

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International Standard ISO 10313 was prepared by Technical Committee ISO/TC 146, *Air quality*, Sub-Committee SC 3, *Ambient atmospheres*.

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

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Ambient air — Determination of the mass concentration of ozone — Chemiluminescence method

1 Scope

1.1 General

This International Standard specifies a chemiluminescence method for the determination of the mass concentration of ozone in ambient air.

The method is applicable to the determination of the mass concentration of ozone between 2 µg/m^3 [0,001 ppm(V/V)] and 10 mg/m^3 [5 ppm(V/V)] at the reference conditions of 25 °C and 101,3 kPa.

Ultraviolet (UV) photometry is specified as the primary calibration method because of its proven accuracy and specificity to ozone. The use of transfer standards is allowed if they have been previously calibrated against the primary calibration method.

1.2 Limitations

The chemiluminescent reaction of ozone with ethylene is not subject to interference from any of the common air pollutants. However, particulate matter, if not removed, will accumulate in the sampling line and may cause a measurable destruction of ozone. If particulate matter is allowed to enter the reaction chamber of the analyser, it will not only scatter the emitted light but will also accumulate on the optical window, thereby causing further attenuation of the emitted light. Also, any nitrogen(II) oxide in the sampled air will to some extent react with the ambient ozone; therefore, the time during which the ambient air remains in the sampling line must be sufficiently short to keep this effect to a minimum.

NOTE 1 It has been reported by some researchers that, at about 80 % relative humidity and 22 °C, the responses for some commercially available chemiluminescence analysers were about 10 % higher than that for dry air. However, comparisons of ambient ozone measurements using commercially available chemiluminescence and UV-photometric analysers showed no significant differences. This suggests that, in practice, any errors associated with calibrations using dry air are compensated by other effects.

2 Definition

For the purposes of this International Standard, the following definition applies.

2.1 transfer standard: An apparatus (transportable) with associated operational procedures that is capable of accurately measuring or reproducing ozone concentration standards which are quantitatively related to the authoritative primary standard.

3 Principle

The air sample is drawn continuously, at a constant flow rate, through a particle filter before it enters the chemiluminescence analyser. It then flows into a reaction chamber where it is mixed with an excess flow of ethylene. Ozone and ethylene react instantaneously to produce light in the visible region with a maximum at a wavelength of about 400 nm. The emitted light intensity is proportional to the concentration of ozone in the air sample and is measured by a photomultiplier tube. The resulting voltage is amplified, displayed, and calibrated in terms of the ambient ozone concentration.

4 Reagents and materials

4.1 Sampling line

The sampling line shall be made of material that is inert to ozone, such as glass or fluorocarbon polymer, and it shall be as short as possible to keep the time the air sample remains there to a minimum. Any ambient nitrogen(II) oxide present in the air sample will react with some of the ozone during the time it remains in the sampling line. This decay of ozone is a complicated function of the mass concentration ratio, $\rho(O_3)/\rho(NO)$, and the difference in mass concentrations, $\rho(O_3) - \rho(NO)$. Calculations have shown that, if the residence time is less than 0,5 s, the decay in initial ozone will be less than 1 % for most ambient ozone and nitrogen(II) oxide concentrations encountered. Hence, it is recommended that the sampling line length and pumping speed be chosen such that the time the air remains within the sampling line is less than 0,5 s. However, in situations of routine monitoring, a time of up to 5 s is allowed.

Any sampling line or manifold preceding the filter shall be clean. Proper precautions shall be taken to prevent condensation inside the sampling line, for example, by heating the line.

4.2 Particle filter

The filter and its support shall be made of material inert to ozone, such as fluorocarbon polymer, and it shall remove all particles likely to alter the performance of the analyser. It shall be changed on a regular basis, depending on the concentrations of ambient particles at the sampling site. This is necessary because excessive accumulation of particles on the filter can cause loss of ozone from the air sample and an excessive pressure drop across the filter.

NOTES

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

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

4.3 Ethylene, of minimum purity 99,5 %.

WARNING — Ethylene has a lower explosive limit of 27,5 l/m^3. Any excess shall be vented outdoors or, if necessary, chemically removed, especially at sites where hydrocarbons are being measured. Observe standard safety precautions when using this flammable gas.

4.4 Zero air, required in the analyser calibration procedure.

It shall be free of ozone, nitrogen oxides and any other interfering substance that can cause an undesired positive or negative response in either the ultraviolet photometer or the chemiluminescence analyser.

The response of the ozone chemiluminescence analyser is affected by the oxygen content in the gas sample. Therefore, if synthetic air is used, the oxygen content shall be within ± 2 % of the normal atmospheric concentration of 20,9 %.

NOTE 4 Details on a scrubbing system for making zero air from ambient air may be found in [1] and [2] in annex B.

5 Apparatus

5.1 Chemiluminescence analyser, consisting of sample and ethylene flow inlet systems, a constant temperature reaction chamber coupled to a photomultiplier detector and accompanying signal processing electronics. A flowmeter, if it is not an integral part of the analyser, shall be available for verifying that the flow meets the specifications of the instrument.

A schematic diagram of a typical system is shown in figure 1.

5.2 Apparatus for calibration, an ozone calibration system shall be used. (See the simplified schematic diagram in figure 2.)

NOTE 5 An equivalent system would be one that uses only the air line with the ozone generator to bring zero and ozonized air to the manifold, hence eliminating the need for the four-ports two-way valve.

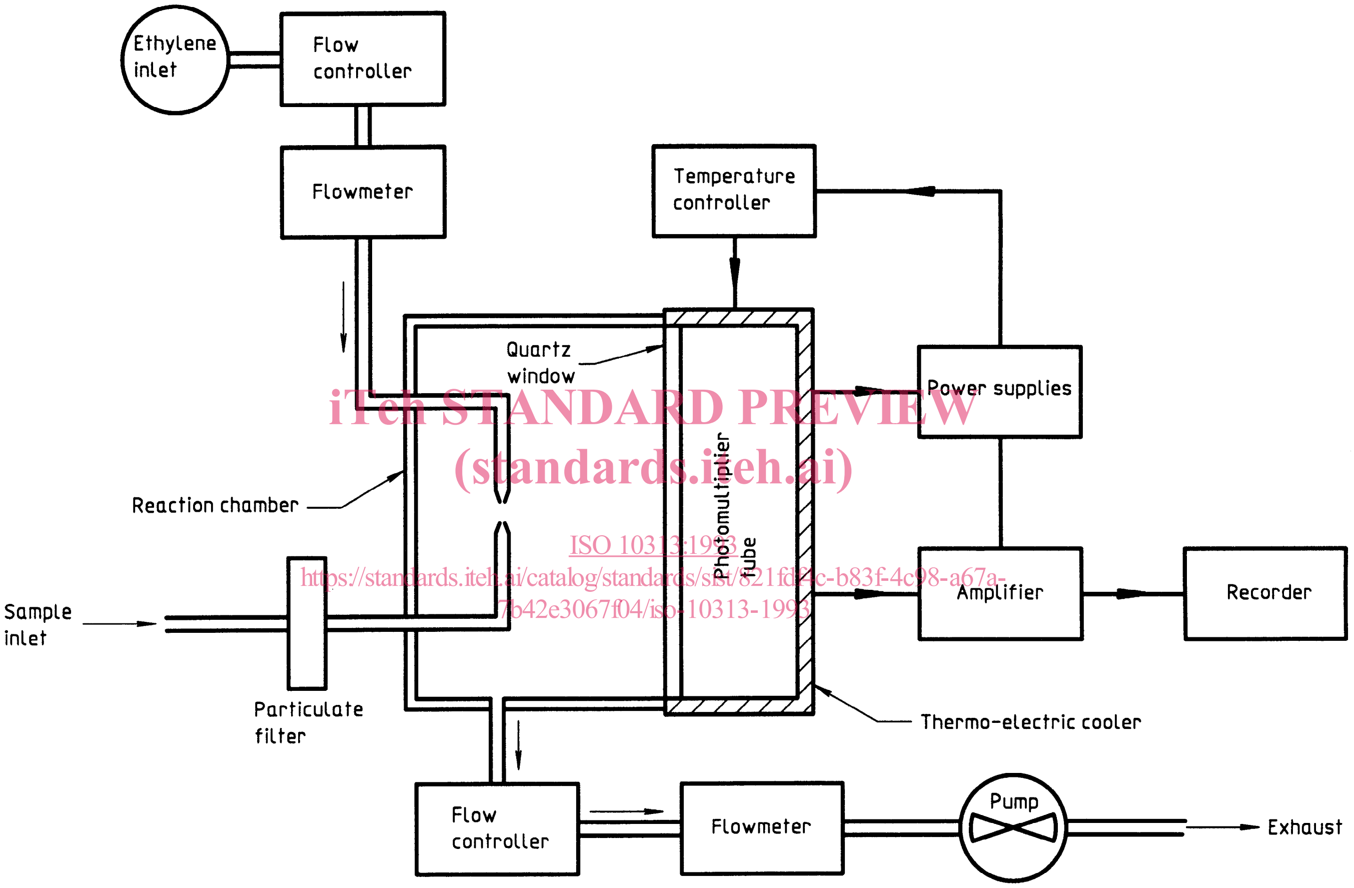

Figure 1 — Schematic diagram of a chemiluminescence ozone analyser

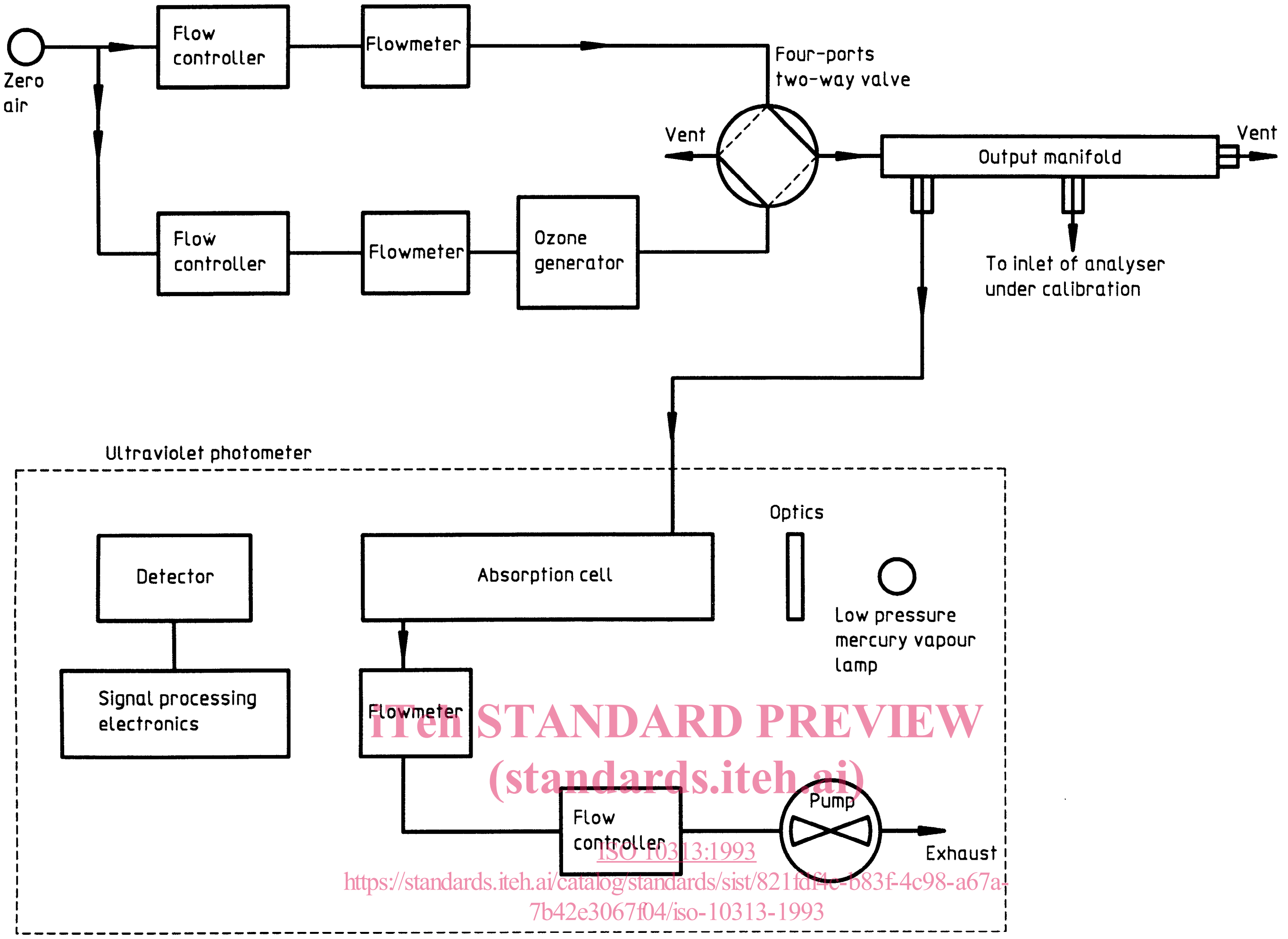

Figure 2 — Schematic diagram of a typical ultraviolet photometric calibration system

5.2.1 Ultraviolet photometer, for primary calibration only consisting of a low pressure mercury discharge lamp, a single or dual absorption cell, and detection and signal processing electronics. It shall be meticulously maintained. 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 line but transmit the 253,7 nm Hg measurement line. The detector shall be capable of measuring the transmittance through the absorption cell at a wavelength of 253,7 nm, with less than 0,5 % of the radiation detected being from other wavelengths (vacuum photodiodes with a caesium telluride sensitization meet this requirement). The length of the light path through the absorption cell shall be known to an accuracy better than 0,5 %, and the cell and associated plumbing shall be designed to minimize surface loss of ozone. Provision shall be made for measuring the temperature and pressure of the gas in the absorption cell (see 5.2.8 and 5.2.9). See the simplified schematic diagram of a photometer system in figure 2.

5.2.2 Ozone generator, which generates stable ozone concentrations that, in turn, are measured by the calibrated photometer (5.2.1). The ozone generator shall be capable of producing steady ozone concentrations in the range of measurement, at the required flow rate, and throughout the period of calibration. If a variable ozone generator is not available, the calibration system shall include a means of suitably diluting the ozone with additional zero air (see 4.4). In such a case, a mixing chamber shall be installed before the output manifold.

WARNING — Ozone is a toxic gas with a threshold limit value in air of 0,1 ml/m^3, and any excess should be vented into an activated charcoal scrubber or outdoors (well away from any sampling intake).

5.2.3 Airflow controllers, capable of maintaining steady airflows throughout the period of calibration.

5.2.4 Airflow meters, of any type that is suitable for measuring the required airflows.

NOTE 6 The actual airflows are not used in the calculations but are used only for achieving the nominal concentrations required in the calibration procedure.

5.2.5 Air pump, used to draw the required sample flow through the absorption cell.

5.2.6 Output manifold, made of materials inert to ozone, such as glass or fluorocarbon polymer. It shall be of sufficient diameter and be vented to ensure equal atmospheric pressure inside and outside the manifold. The vent shall be located so as to prevent intrusion of ambient air.

5.2.7 Four-ports two-way valve, with interior surfaces made of a material inert to ozone, such as a fluorocarbon polymer.

When a calibration system such as that shown in figure 2 is used, a four-ports two-way valve or some equivalent system of valves shall be used for switching the manifold flow between zero air and the ozone test atmosphere.

5.2.8 Temperature indicator, capable of measuring temperature with an accuracy of 0,1 °C.

5.2.9 Pressure indicator, capable of measuring pressure with an accuracy of ± 0,1 kPa.

6 Procedure

6.1 Operation of chemiluminescence analyser

Install the instrument in a suitable location. Follow the manufacturer's operating instructions for the specific analyser in use to set the various parameters, including sample and ethylene flow rates. Check to ensure that the manufacturer's performance characteristics are met or exceeded. If necessary, the location shall also be temperature controlled, so as to minimize the effect of the temperature dependence of the instrument. (See annex A for typical performance specifications.) Introduce the air sample into the instrument and record the ozone concentration by means of a suitable recording device (for example, chart recorder, electronic data acquisition system, etc.).

NOTE 7 During continuous operation of the instrument, it is recommended that a multipoint calibration be carried out every 3 months. In addition, frequent operational checks on the instrument zero and span should be made, usually once a week.

6.2 Calibration of the chemiluminescence analyser

6.2.1 Principle

A schematic diagram of an ultraviolet photometric calibration system is shown in figure 2. Various ozone concentrations (in air) are generated and accurately measured with a primary calibration ultraviolet photometer. These ozone calibration atmospheres are simultaneously sampled by the chemiluminescence analyser via a common manifold. The analyser responses are plotted against the ozone concentrations measured by the ultraviolet photometer. Alternatively, a calibration method using a transfer standard can be calibrated against the ultraviolet photometer and used to calibrate the chemiluminescence analyser at the sampling location.

NOTE 8 See [2] in annex B for details on the principles of operation of the ultraviolet photometer.

6.2.2 Calibration procedure using the primary UV standard

During the calibration procedure, the chemiluminescence ozone analyser shall be operated at its correct flow rate and temperature. The calibration includes measurements using zero air (see 4.4) and at least four ozone concentrations (using the ozone generator described in 5.2.2) which shall be reasonably spaced to cover the range being measured. For all measurements, the input flow to the manifold shall exceed, by at least 10%, the total flow required by the instruments attached to this manifold, with the excess appropriately vented at atmospheric pressure.

Carry out the following steps in the detailed calibration procedure.

- Assemble the apparatus as shown in figure 2.
- Introduce zero air into the manifold. Set the zero control of the ozone analyser being calibrated to indicate a reading of zero, and set the transmittance of the photometer at 100 %.
- Adjust the output of the ozone generator to generate the most concentrated ozone atmosphere required.
- Turn the valve to introduce the ozone atmosphere into the manifold.
- Note the transmittance on the photometer at 254 nm, and also the temperature and pressure in the photometric cell.
- Set the span on the ozone analyser being calibrated to the ozone concentration calculated using equation (1) (see 7.1).

- Generate and measure at least three other ozone concentrations over the scale range of the ozone analyser, by adjusting the ozone generator intensity.
- For each ozone concentration generated, record the ozone concentration and the corresponding analyser response.
- Plot the ozone analyser responses versus the corresponding ozone concentrations at standard conditions, and draw the ozone analyser calibration curve or calculate the appropriate response factor.

NOTES

9 Repeating this calibration to estimate the uncertainty in the calibration is optional.

10 A small fraction of the ozone may be lost upon contact with the photometer cell walls and other internal surfaces. Therefore, for maximum accuracy, such loss of ozone should be quantitatively determined and used to correct the output concentration. (See [2] in annex B.)

6.2.3 Calibration procedure for the transfer standard

Consider using a transfer standard whenever the primary calibration ultraviolet photometer is not readily available, for example at the site of the chemiluminescence analyser. Whenever such a procedure is used, follow the calibration procedure of 6.2.2 using the transfer standard instead of the primary UV-photometer standard.

The transfer standard shall meet the following requirements:

- its accuracy shall be established against the primary UV-photometric calibration method and this accuracy shall be maintained within ± 5 % between successive primary calibrations;
- traceability to the primary UV-photometric standard shall be established at least once per year.

NOTES

11 The recommended calibration method for the (portable) transfer standard is a second UV photometer system with its own zero air and ozone supply. Two other acceptable calibration methods for transfer standards, although less convenient than the UV-photometric method, are gas-phase titration of excess nitric oxide by ozone (or vice versa) and the laboratory-based neutral buffered potassium iodide-potassium bromide (KIBR) method (for example, see [3] and [4] in annex B).

12 There are other laboratory-based calibration methods for transfer standards that are less convenient or possibly less accurate (for example, see [5] in annex B). These include

- the neutral buffered potassium iodide-potassium bromide-thiosulfate (KIBRT) method;
- the boric acid buffered potassium iodide (BAKI) method;
- a stable ozone source with variable output.

7 Expression of results

7.1 Calibration ozone concentration

Calculate the mass concentration of ozone, $\rho(O_3)$, in micrograms per cubic metre, in the manifold at the reference conditions (25 °C and 101,3 kPa) using the following equation:

$$\rho(O_3) = \frac{-101{,}3 \times T \times \ln(I/I_0)}{298 \times 1{,}44 \times 10^{-5} \times b \times P} \qquad \ldots (1)$$

where

b is the optical path length, in metres;

I/I_0 is the transmittance of the ozone sample;

p is the pressure in the photometer cell, in kilopascals;

T is the temperature of the photometer cell, in kelvins;

$1{,}44 \times 10^{-5}$ is the absorption coefficient of ozone, in square metres per microgram.

7.2 Sample ozone concentration

Convert the chemiluminescence analyser readings to the mass concentrations of ozone by using the appropriate calibration curve. Report the results as micrograms per cubic metre (µg/m^3) at 25 °C and 101,3 kPa, or as parts per million by volume [ppm(V/V)]. For ozone, 1 ppm(V/V) is equivalent to 1 960 µg/m^3 at 25 °C and 101,3 kPa.

7.3 Precision

The overall precision at 95 % probability for the generation and UV-photometric measurement of ozone calibration atmospheres shall be better than 5 %; the same overall precision shall apply for the transfer standard calibration method.

NOTE 13 Studies have shown that the precision in UV-photometric ozone calibrations can be within ± 1 % if care is taken when operating the system. In combination with the chemiluminescence method and owing to variability in laboratory techniques, it is expected that the overall precision of the ozone analysis of ambient air will be within ± 3,5 %. (See [5] in annex B.)

7.4 Accuracy

The accuracy of the method is estimated to be better than ± 10 % of the measured concentration.

NOTE 14 The accuracy of the chemiluminescence method will be dependent on the photometer method to which it is referenced. The accuracy of the UV-photometer reference will be limited by the accuracy of the coefficient of absorption (± 1,5 %) and the measurements of the transmittance, pressure, temperature, ozone losses, etc. When a transfer standard is used, additional inaccuracies (inherent in the type of transfer standard) will be introduced.

8 Test report

The test report shall contain the following information:

a) a reference to this International Standard;

b) complete identification of the sample;

c) the results;

d) any unusual features noted during the determination.