
**Ambient air — Gas phase titration —
Calibration of analysers for ozone**

*Air ambiant — Titration en phase gazeuse — Étalonnage des analyseurs
d'ozone*

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Introduction

For ambient ozone (O₃) analysers, the primary standard measurement principle for calibration is UV photometry. This International Standard provides an alternative secondary measurement principle and method based on gas phase titration of an O₃ gas mixture with excess nitric oxide (NO). When using this method, the generated O₃ calibration gases are traceable to a certified primary NO measurement standard.

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Ambient air — Gas phase titration — Calibration of analysers for ozone

1 Scope

This International Standard specifies the gas phase titration (GPT) method for the calibration of ambient air ozone (O₃) analysers. The method is applicable to the calibration of O₃ concentrations in the range 10 µg m⁻³ (5 nmol mol⁻¹ mole fraction) to 2 000 µg m⁻³ (1 000 nmol mol⁻¹ mole fraction). This International Standard uses the reference conditions of 25 °C and 101,325 kPa; however, reference temperatures of 0 °C and 20 °C are also acceptable.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 7996, *Ambient air — Determination of the mass concentration of nitrogen oxides — Chemiluminescence method*

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3 Principle

Gas phase titration (GPT) is based on the simple gas phase bimolecular reaction:



with a bimolecular reaction rate constant of $1,8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (or $0,44 \text{ } \mu\text{mol mol}^{-1} \text{ s}^{-1}$ when concentrations are expressed as mole fractions) at 298 K.

This reaction is fast, and equilibrium lies far to the right hand side of Expression (1) if the kinetic conditions specified in Annex A are satisfied. This International Standard is based on mixing O₃ with excess nitric oxide (NO) in a dynamic flow system where, first, the NO and O₃ are mixed at relatively high concentrations (to effect essentially complete reaction of the O₃) and, second, the reaction products and any excess NO are then diluted with zero reference gas (e.g. synthetic air) to final calibration concentrations. Since the reaction is stoichiometric, the molar decrease in measured NO is equal to the added O₃; this is also equal to the nitrogen dioxide (NO₂) reaction product.

The NO is obtained from a certified NO measurement standard, a calibrated gas mixture in a compressed gas cylinder. Other calibrated sources could be used (e.g. see VDI 2453-3 [11]), and adapted to the GPT calibration apparatus. The change in NO concentration at the GPT output manifold is measured by a chemiluminescence NO analyser. A stable O₃ generator is used to produce variable concentrations of the gas to cover the calibration range of interest.

4 Reagents and materials

4.1 Sample line and connectors, made of material that is inert to O₃ and NO, such as glass or fluorocarbon polymer [e.g. perfluoro(alkoxy alkane) (PFA), polytetrafluoroethylene (PTFE) or perfluoro (ethylene-propylene) plastic (FEP) are acceptable]; these shall be as short as possible to keep the residence time to a minimum.

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

4.2 Zero reference gas, for calibration of the GPT procedure. If synthetic air is used, the oxygen (O₂) content shall be at the normal atmospheric concentration of 20,9 % ± 2 % volume fraction. No O₃, nitrogen oxides or any other interfering substance that can cause an undesired measurable positive or negative response in the analysis shall be detectable in the zero air.

NOTE Details on a system for making zero air from ambient air can be found in ASTM D5011 [9].

4.3 NO measurement standard, stored in a compressed gas cylinder and containing a known concentration of NO in nitrogen, in the range 10 μmol mol⁻¹ to 100 μmol mol⁻¹, for use in the calibration procedure. This NO cylinder shall be traceable to a primary measurement standard (e.g. a certified reference material), and the NO₂ impurity shall be less than 0,5 % mass fraction of the NO concentration.

5 Apparatus

Usual laboratory equipment and, in particular, the following.

5.1 Ozone generator, capable of producing steady O₃ concentrations in the required range throughout the period of the calibration. Conventional UV low-pressure mercury vapour lamps are adequate for this purpose; however, both voltage and temperature regulation shall be provided for a stable O₃ output.

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CAUTION — Ozone is a toxic gas and good laboratory practice should limit indoor ozone concentrations to less than 200 μg m⁻³ (100 nmol mol⁻¹). Consult a reference text for more details on hazards of ozone and appropriate safety precautions. Any excess should be vented into an activated charcoal scrubber (with negligible back-pressure) or outdoors well away from any sampling intake. Comply with any local regulations currently in force for handling, use and disposal of ozone.

5.2 Gas flow controllers and meters: there are two options for controlling and measuring the gas flows; see 5.2.1 and 5.2.2. Electronic mass flow controllers (5.2.1) are recommended because of their inherent low measurement uncertainty and greater precision.

5.2.1 Electronic mass flow controllers, calibrated and capable of maintaining constant gas flow rates within ± 0,5 % throughout the calibration period. Components in contact with NO shall be of a non-reactive material.

5.2.2 Manual gas flow control and meters, capable of maintaining constant gas flow rates within ± 2 % throughout the calibration period. The gas flow meters shall be capable of measuring the required gas flows within ± 2 %.

5.3 Reaction chamber, to provide a suitable environment for the quantitative reaction between NO and O₃ at high concentration. This chamber shall be made of materials inert to O₃ and nitrogen oxides, such as borosilicate glass, PFA, FEP or PTFE. Its volume shall be limited so that the residence time of the gas mixture in this volume is less than 60 s (see Annex A for predetermining the volume for given flow conditions).

5.4 Dilution chamber, to provide a suitable environment for the mixing of reaction products and dilution air. It shall be made of materials inert to O₃ and nitrogen oxides, such as borosilicate glass, PFA, FEP or PTFE. Its volume should be sufficiently large to allow complete mixing of the gas components, but small enough to limit the residence time to less than 60 s.

5.5 Output manifold, to serve as a multi-port interface to allow sampling of the output from the GPT calibration system. It shall be made of materials inert to O₃, such as borosilicate glass, PFA, FEP or PTFE. It shall be of sufficient diameter and be vented to ensure an insignificant pressure drop from inside to outside the manifold. The vent outlet shall be located downstream of the other outlet ports so as to prevent intrusion of ambient air.

5.6 Temperature sensor, to measure the temperature of the detection cell of the O₃ analyser, readable to within $\pm 0,5$ °C.

5.7 Pressure meter, to indicate the pressure in the detection cell of the O₃ analyser, readable to within ± 2 hPa.

5.8 Chemiluminescence nitrogen oxides analyser, whose NO channel meets the requirements of ISO 7996. The purpose of this instrument is to determine quantitatively the decrease in NO response equivalent to the O₃ added in the GPT system.

NOTE Additional details on calibrating such an analyser can be found in VDI 2453-2 ^[10].

5.9 Pressure regulator for source gas cylinder, whose internal components are inert to NO.

6 Calibration procedure

6.1 Overview

A schematic diagram of a calibration system is shown in Figure 1. The following procedure is written for the option where

- a) both NO and O₃ analysers are simultaneously sampling the output manifold of the GPT system,
- b) concentrations are expressed as mole fractions, in nanomoles per mole.

A suitable and accurately known NO concentration in air is generated and measured with the chemiluminescence NO analyser (5.8). Then, O₃ is generated to titrate some of the NO. The decrease in NO is equal to the added O₃. Finally, with the O₃ generator (5.1) still on, the NO flow is turned off so that the ambient O₃ analyser can measure the known O₃ concentration via the common manifold. By varying the O₃ generator output, other known O₃ concentrations can be generated in a similar manner. A linear least squares analysis of the O₃ analyser responses and corresponding calculated O₃ concentrations will produce a linear calibration function for the O₃ analyser.

The linearity of the chemiluminescence NO analyser shall have been recently verified by means of a linear least squares analysis on its calibration data, and the calculated correlation coefficient shall be better than 0,99 for the NO calibration range of interest. (It should be noted that the calibration function for the NO analyser need not be used in the following calibration calculations.)

6.2 Calibration of the ambient ozone analyser

6.2.1 Install the instruments in a suitable location and provide temperature control of the measurement room to minimize any temperature dependence of the instruments. Follow the manufacturer's operating instructions for the analysers to set the various operating parameters correctly, including the sample flow rate and, if applicable, activation of the electronic temperature and pressure compensation on the O₃ analyser. Also, follow the diagnostic procedure as outlined in the manufacturer's operations manual to verify that instrument functions are within their performance specifications. The measured concentrations should be recorded by means of a suitable recording device (e.g. chart recorder or electronic data acquisition system).

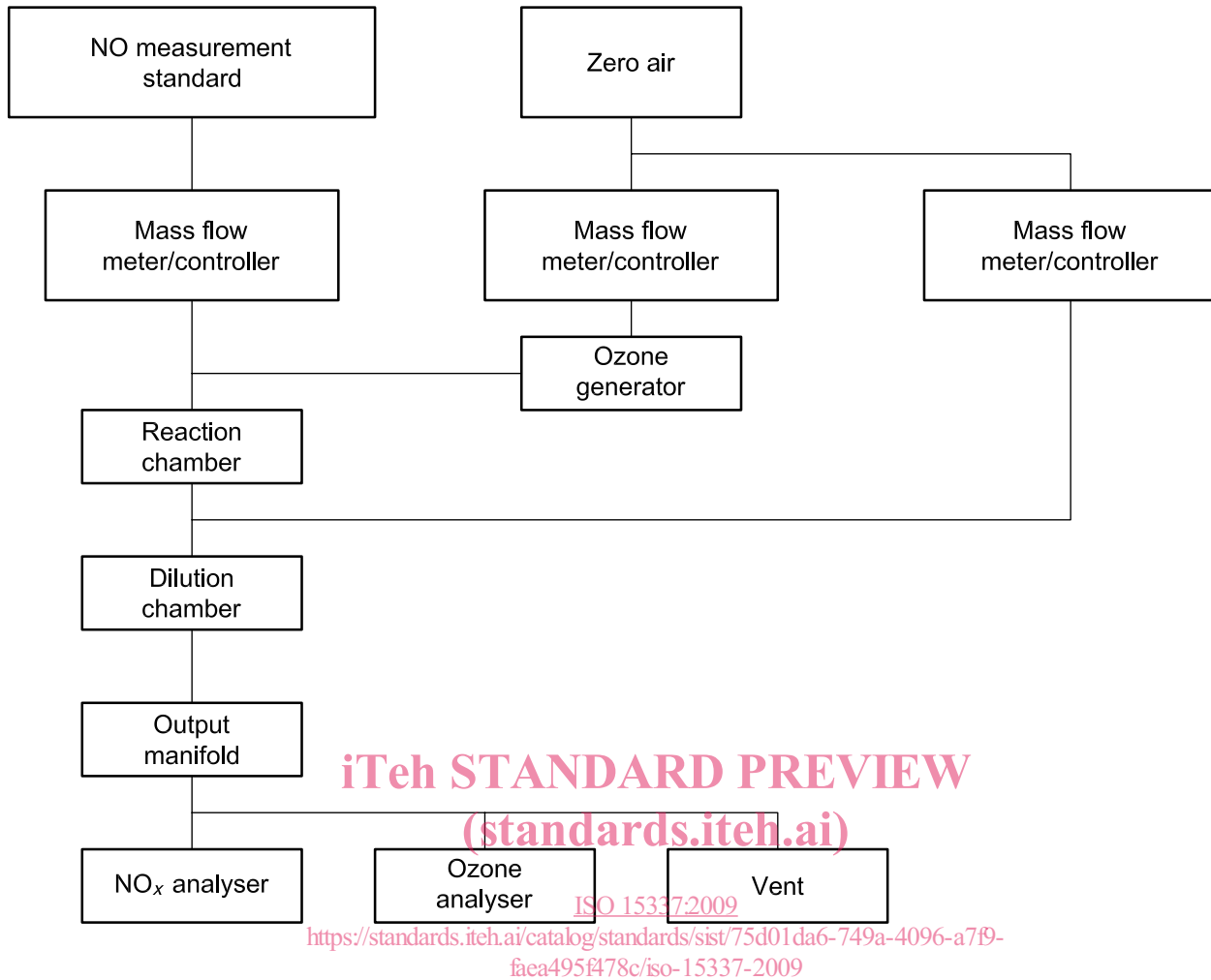


Figure 1 — Schematic diagram of a typical ozone calibration flow system for use with GPT

In the calculations to follow, concentrations are expressed as mole fractions. The calibration shall include measurements using zero air (see 4.2) and at least five O₃ concentrations, which should be reasonably spaced to cover the entire calibration range. For all calibrations, the input flow rate to the manifold shall exceed the total flow rate required by the instruments attached to the manifold by at least 10 %, with the excess appropriately vented at atmospheric pressure.

Carry out steps 6.2.2 to 6.2.11 in the calibration procedure.

6.2.2 Establish the GPT system parameters as set out in Annex A and assemble the apparatus as shown in Figure 1; ensure that the entire calibration flow system is free of leaks.

6.2.3 Introduce zero air (4.2) into the system and adjust the diluent air flow rate, q_d , and O₃ generator air flow rate, q_o . If necessary, change the zero control setting of the chemiluminescence NO and ambient O₃ analysers to indicate output readings close or equal to zero; record these “zero air” output readings.

6.2.4 Adjust the flow rate from the NO measurement standard (4.3), q_{NO} , to obtain an NO output concentration of about 10 % to 20 % volume fraction higher than the maximum O₃ concentration required. Record the output reading of the nitrogen oxides analyser (5.8) and then determine the corrected output reading, V_i , by subtracting the “zero air” output reading (6.2.3). The mole fraction, $x_{NO,i}$, in nanomoles per mole, of the initial untitrated NO in the output manifold is calculated from:

$$x_{\text{NO},i} = \frac{q_{\text{NO}} x_{\text{NO},\text{std}}}{q_{\text{O}} + q_{\text{d}} + q_{\text{NO}}} \quad (2)$$

where

q_{d} is the diluent air flow rate, in cubic centimetres per second;

q_{NO} is the NO flow rate, in cubic centimetres per second, from the NO measurement standard (4.3);

q_{O} is the air flow rate, in cubic centimetres per second, through the O₃ generator;

$x_{\text{NO},\text{std}}$ is the mole fraction, in nanomoles per mole, of NO in the measurement standard.

6.2.5 Adjust the O₃ generator (while keeping flow q_{O} constant) to produce sufficient O₃ to decrease the NO output concentration to about 10 % to 20 % volume fraction of the original NO remains. Record the output reading of the nitrogen oxides analyser and then determine the corrected output reading, V_{f} , by subtracting the “zero air” output reading (6.2.3). At this point, the output reading of the O₃ analyser should remain unchanged within the expected output variability of the instrument from 6.2.4. A significant increase indicates that there is some unreacted O₃ in the output manifold. Eliminate this condition, otherwise the calibration is invalid. The O₃ mole fraction, $x_{\text{O}_3,\text{eq}}$, in nanomoles per mole, equivalent to the reacted NO, can be calculated from:

$$\left. \begin{aligned} x_{\text{O}_3,\text{eq}} &= x_{\text{NO},i} - x_{\text{NO},f} \\ &= \left(1 - \frac{V_{\text{f}}}{V_{\text{i}}}\right) x_{\text{NO},i} \end{aligned} \right\} \quad (3)$$

where

$V_{\text{f}}/V_{\text{i}}$ is the ratio of corrected output readings from the nitrogen oxides analyser, given by $x_{\text{NO},f}/x_{\text{NO},i}$;

$x_{\text{NO},f}$ is the final (excess) NO mole fraction, in nanomoles per mole, after titration with O₃;

$x_{\text{NO},i}$ is the initial untitrated NO mole fraction, in nanomoles per mole [Equation (2)].

6.2.6 Either divert the NO flow out of the system or temporarily shut it off and allow the untitrated O₃ to flow to the output manifold to be measured by the O₃ analyser. This calibration O₃ mole fraction, $x_{\text{O}_3,\text{cal}}$, is equivalent to that titrated by NO in 6.2.5 and is calculated from:

$$\left. \begin{aligned} x_{\text{O}_3,\text{cal}} &= x_{\text{O}_3,\text{eq}} \left(\frac{q_{\text{O}} + q_{\text{d}} + q_{\text{NO}}}{q_{\text{O}} + q_{\text{d}}} \right) \\ x_{\text{O}_3,\text{cal}} &= \left(1 - \frac{V_{\text{f}}}{V_{\text{i}}}\right) x_{\text{NO},i} \left(\frac{q_{\text{O}} + q_{\text{d}} + q_{\text{NO}}}{q_{\text{O}} + q_{\text{d}}} \right) \end{aligned} \right\} \quad (4)$$

where $x_{\text{O}_3,\text{cal}}$ is the calibration O₃ mole fraction, in nanomoles per mole.

NOTE Another option is to replace the NO flow with an equivalent zero air flow (easily done by switching in zero air gas to the NO flow controller) — in this case, the final O₃ mole fraction remains the same as calculated from Equation (3) during the NO titration step (6.2.5), and Equation (4) becomes unnecessary.

6.2.7 Record the O₃ analyser output and, if necessary, change the span control setting of the ambient O₃ analyser to indicate an output reading close to or equal to the O₃ concentration found from 6.2.6. If the span and zero settings are not independent, repeat steps 6.2.3 to 6.2.6.

If the span setting change is unexpectedly different from the last calibration, it is recommended that the source of this difference be investigated and rectified.