INTERNATIONAL STANDARD

ISO 15337

First edition
2009-04-15

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

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

Reference number
ISO 15337:2009(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

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 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 15337 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 3, *Ambient atmospheres*.

Introduction

For ambient ozone (O_3) 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 O_3 gas mixture with excess nitric oxide (NO). When using this method, the generated O_3 calibration gases are traceable to a certified primary NO measurement standard.

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 (O_3) analysers. The method is applicable to the calibration of O_3 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*

3 Principle

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

$$NO + O_3 \rightleftharpoons NO_2 + O_2 \quad (1)$$

with a bimolecular reaction rate constant of $1{,}8 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} (or 0,44 µmol mol^{-1} 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 O_3 with excess nitric oxide (NO) in a dynamic flow system where, first, the NO and O_3 are mixed at relatively high concentrations (to effect essentially complete reaction of the O_3) 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 O_3; this is also equal to the nitrogen dioxide (NO_2) 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 O_3 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 O_3 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 (O_2) content shall be at the normal atmospheric concentration of 20,9 % ± 2 % volume fraction. No O_3, 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 NO_2 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 O_3 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 O_3 output.

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 O_3 at high concentration. This chamber shall be made of materials inert to O_3 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 O_3 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 O_3, 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 O_3 analyser, readable to within ± 0,5 °C.

5.7 Pressure meter, to indicate the pressure in the detection cell of the O_3 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 O_3 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 O_3 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, O_3 is generated to titrate some of the NO. The decrease in NO is equal to the added O_3. Finally, with the O_3 generator (5.1) still on, the NO flow is turned off so that the ambient O_3 analyser can measure the known O_3 concentration via the common manifold. By varying the O_3 generator output, other known O_3 concentrations can be generated in a similar manner. A linear least squares analysis of the O_3 analyser responses and corresponding calculated O_3 concentrations will produce a linear calibration function for the O_3 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 O_3 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).

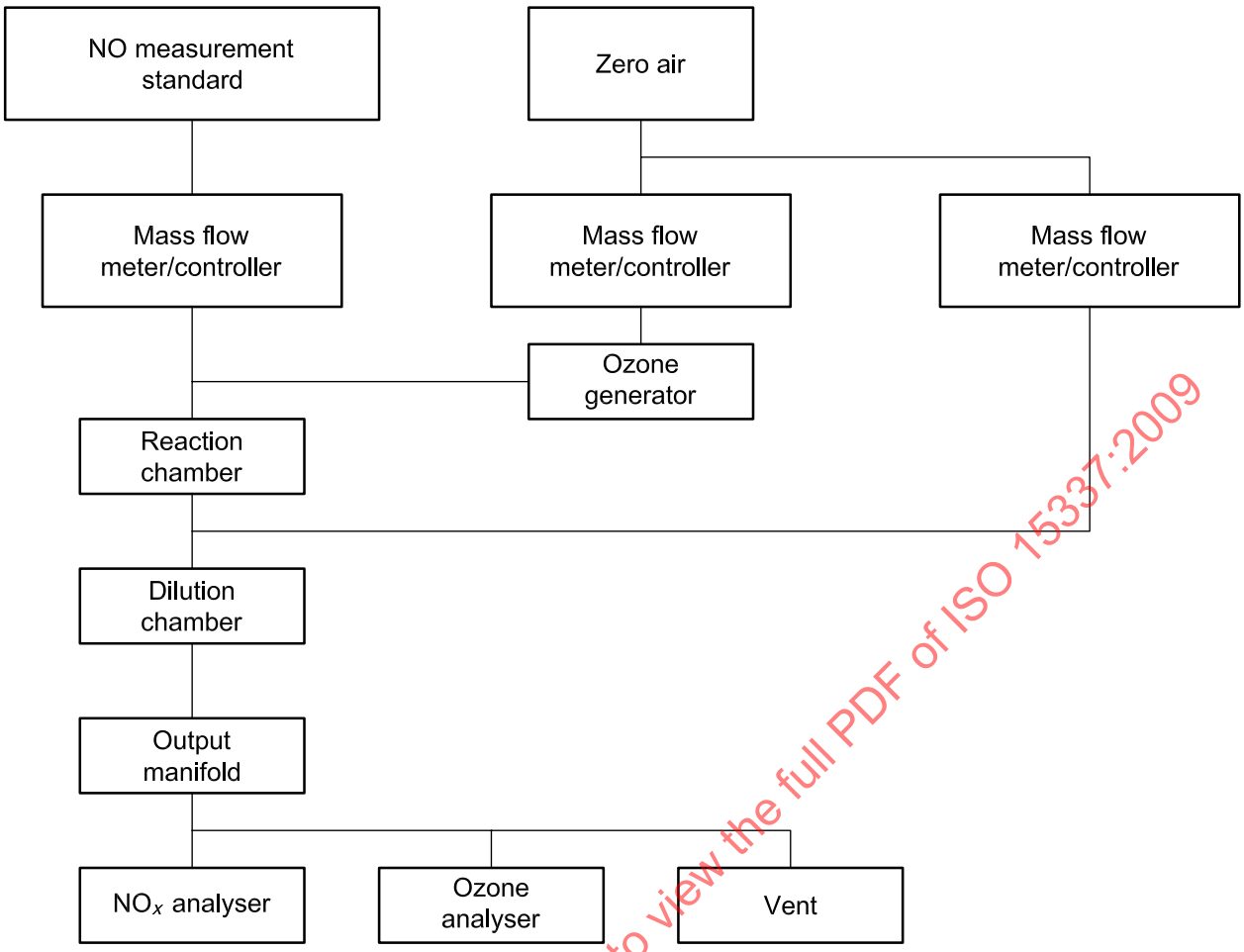

Figure 1 — Schematic diagram of a typical ozone calibration flow system for use with GPT

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 O_3 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 O_3 generator air flow rate, q_o. If necessary, change the zero control setting of the chemiluminescence NO and ambient O_3 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 O_3 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:

$$x_{NO,i} = \frac{q_{NO}\, x_{NO,std}}{q_o + q_d + q_{NO}} \quad (2)$$

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 O_3 generator;

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

6.2.5 Adjust the O_3 generator (while keeping flow q_o constant) to produce sufficient O_3 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 O_3 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 O_3 in the output manifold. Eliminate this condition, otherwise the calibration is invalid. The O_3 mole fraction, $x_{O_3,eq}$, in nanomoles per mole, equivalent to the reacted NO, can be calculated from:

$$\left.\begin{aligned} x_{O_3,eq} &= x_{NO,i} - x_{NO,f} \\ &= \left(1 - \frac{V_f}{V_i}\right) x_{NO,i} \end{aligned}\right\} \quad (3)$$

where

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

$x_{NO,f}$ is the final (excess) NO mole fraction, in nanomoles per mole, after titration with O_3;

$x_{NO,i}$ 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 O_3 to flow to the output manifold to be measured by the O_3 analyser. This calibration O_3 mole fraction, $x_{O_3,cal}$, is equivalent to that titrated by NO in 6.2.5 and is calculated from:

$$\left.\begin{aligned} x_{O_3,cal} &= x_{O_3,eq}\left(\frac{q_o + q_d + q_{NO}}{q_o + q_d}\right) \\ x_{O_3,cal} &= \left(1 - \frac{V_f}{V_i}\right) x_{NO,i}\left(\frac{q_o + q_d + q_{NO}}{q_o + q_d}\right) \end{aligned}\right\} \quad (4)$$

where $x_{O_3,cal}$ is the calibration O_3 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 O_3 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 O_3 analyser output and, if necessary, change the span control setting of the ambient O_3 analyser to indicate an output reading close to or equal to the O_3 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.

6.2.8 Keeping the flows constant at the values determined in 6.2.3 to 6.2.6, adjust the O_3 generator settings to generate O_3 concentrations for at least four other lower O_3 concentrations over the range of interest. Record the measured output readings of the analysers and calculate the corresponding calibration NO and O_3 mole fractions.

6.2.9 After the last O_3 calibration has been completed, turn the O_3 generator off while the NO flow is still off and measure the "zero air" output readings of the O_3 and NO analysers. If the change from initial to final "zero air" readings of the O_3 or NO analyser exceeds the manufacturer's zero drift specification, repeat the entire calibration procedure.

6.2.10 Plot the corrected O_3 analyser output readings versus the calculated O_3 mole fractions (or mass concentrations) at the chosen reference conditions of temperature and pressure.

6.2.11 Determine the linear calibration function of the O_3 analyser by means of a linear least squares analysis and report the appropriate response factor or slope (e.g. in nanomoles per mole volt or micrograms per cubic metre volt), the intercept or zero offset, their associated errors, and the correlation coefficient.

Repeating this calibration to estimate the repeatability of the calibration is optional.

6.3 Measurement precision

The measurement precision of this calibration method is expected to be less than 2 % (at the 95 % confidence level) for the generation and UV photometric measurement of O_3 calibration atmospheres when using electronic mass flow controllers (5.2.1).

6.4 Measurement uncertainty

The measurement uncertainty of the method is estimated to be better than ± 4 % of the measured concentration (at the 95 % confidence level).

7 Expression of results

Using the measured parameters of the GPT system, calculate the O_3 concentration in the manifold at standard reference pressure 101,325 kPa and the chosen reference temperature using Equation (4). For O_3, at 101,325 kPa, a mole fraction of 1 nmol mol^{-1} is equivalent to 2,141 µg m^{-3} at 0 °C, 1,995 µg m^{-3} at 20 °C, and 1,962 µg m^{-3} at 25 °C.

8 Test report

The test report shall include at least the following information:

a) a reference to this International Standard;

b) documentation on the calibration method and NO measurement standard, including traceability to a primary NO measurement standard (see 4.3);

c) the calibration data, results, date and operator;

d) any peculiarities encountered during the calibration.

Annex A
(normative)

Gas phase titration apparatus parameter specifications

A.1 Calculation of dynamic parameter specification

A quantitative reaction between NO and O_3 in the GPT is ensured by a reaction chamber (5.3) of sufficient volume to allow the reactants sufficient time so that less than 1 % mole fraction residual O_3 remains. Laboratory studies have found that this will occur if the GPT dynamic parameter specification, P_r, in micromoles per mole per second, satisfies the condition in (A.1):

$$P_r = t_{rc}\ x_{NO,rc} > 165 \quad \text{(A.1)}$$

where

t_{rc} is the residence time, in seconds, of reactant gases in the reaction chamber, subject to Condition (A.2)

$$t_{rc} = \frac{V_{rc}}{q_o + q_{NO}} < 60 \quad \text{(A.2)}$$

in which

q_{NO} is the 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 O_3 generator;

V_{rc} is the volume, in cubic centimetres, of the reaction chamber;

$x_{NO,rc}$ is the reactant NO mole fraction, in micromoles per mole, in the reaction chamber, given by

$$x_{NO,rc} = \frac{x_{NO,std}\ q_{NO}}{q_o + q_{NO}} \quad \text{(A.3)}$$

in which $x_{NO,std}$ is the NO mole fraction, in micromoles per mole, of the undiluted NO measurement standard (4.3).

A.2 Determination of GPT apparatus parameter specifications

A.2.1 Procedure

A.2.1.1 To determine a suitable parameter specification for setting up a GPT system, proceed as in A.2.1.2 to A.2.1.10.

A.2.1.2 Select a suitable total flow rate, q_t, in cubic centimetres per second, at the output manifold; this flow rate is determined by the sample flows required by the analysers attached to the output manifold plus at least 10 % excess flow for venting.

A.2.1.3 Select a suitable volume, V_{rc}, for the reaction chamber; typically, this is in the range of 100 cm^3 to 500 cm^3.

A.2.1.4 Select an NO measurement standard (4.3) in the range of about 10 µmol mol^{-1} to 100 µmol mol^{-1} NO in nitrogen.

A.2.1.5 Establish $x_{NO,max}$ as the highest NO mole fraction, in micromoles per mole, which will be required at the output manifold; this shall be approximately 10 % higher than the upper range limit of the O_3 concentration required in the GPT calibration of the O_3 analyser. Determine the corresponding flow rate of the NO measurement standard (4.3), q_{NO}, from Equation (A.4):

$$q_{NO} = \frac{x_{NO,max}\ q_t}{x_{NO,std}} \tag{A.4}$$

A.2.1.6 Calculate the maximum acceptable flow rate, $q_{o,max}$, in cubic centimetres per second, through the O_3 generator, by equating the parameter P_r to 165 in the equation in (A.1), and solving for q_o using Expressions (A.1) to (A.3); the resulting equation is:

$$q_{o,max} = \left(\frac{x_{NO,std}\ q_{NO}\ V_{rc}}{165} \right)^{0,5} - q_{NO} \tag{A.5}$$

Any value lower than $q_{o,max}$ may be chosen for q_o in the GPT procedure.

A.2.1.7 Use Condition (A.2) to verify that t_{rc} is less than 60 s.

A.2.1.8 Calculate the diluent air flow rate, q_d, in cubic centimetres per second, from:

$$q_d = q_t - q_o - q_{NO} \tag{A.6}$$

A.2.1.9 Calculate the reactant NO mole fraction in the reaction chamber from Equation (A.3).

A.2.1.10 Calculate the GPT dynamic parameter specification by Equation (A.1) and verify that P_r is greater than 165 µmol mol^{-1} s^{-1}.

A.2.2 Example calculation

The example uses the following conditions and parameters:

a) the O_3 analyser has a sample flow rate of 35 cm^3 s^{-1};

b) the NO output of the GPT system is measured by a chemiluminescence NO analyser with a sample flow rate of 15 cm^3 s^{-1};

c) the calibration range is 0 µmol mol^{-1} to 0,500 µmol mol^{-1} O_3.

Calculate the minimum total flow rate, q_t, in cubic centimetres per second, required at the output manifold:

$$q_t = 35 + 15 + 5 = 55$$

where 5 is the value of the excess NO flow rate contribution.

Let us assume that a glass reaction chamber of volume, V_{rc} = 150 cm^3, is chosen and that an NO cylinder measurement standard of molar ratio, $x_{NO,std}$ = 50 µmol NO per mole of nitrogen, is available.