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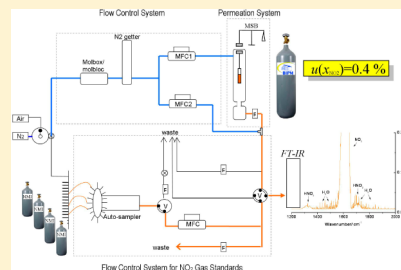
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Highly Accurate Nitrogen Dioxide (NO₂) in Nitrogen Standards Based on Permeation

Edgar Flores,* Joële Viallon, Philippe Moussay, Faraz Idrees, and Robert Ian Wielgosz

Bureau International des Poids et Mesures (BIPM), Pavillon de Breteuil, F-92312 Sèvres Cedex, France

ABSTRACT: The development and operation of a highly accurate primary gas facility for the dynamic production of mixtures of nitrogen dioxide (NO₂) in nitrogen (N₂) based on continuous weighing of a permeation tube and accurate impurity quantification and correction of the gas mixtures using Fourier transform infrared spectroscopy (FT-IR) is described. NO₂ gas mixtures in the range of 5 $\mu\text{mol mol}^{-1}$ to 15 $\mu\text{mol mol}^{-1}$ with a standard relative uncertainty of 0.4% can be produced with this facility. To achieve an uncertainty at this level, significant efforts were made to reduce, identify and quantify potential impurities present in the gas mixtures, such as nitric acid (HNO₃). A complete uncertainty budget, based on the analysis of the performance of the facility, including the use of a FT-IR spectrometer and a nondispersive UV analyzer as analytical techniques, is presented in this work. The mixtures produced by this facility were validated and then selected to provide reference values for an international comparison of the Consultative Committee for Amount of Substance (CCQM), number CCQM-K74,¹ which was designed to evaluate the consistency of primary NO₂ gas standards from 17 National Metrology Institutes.



1. INTRODUCTION

Nitrogen oxides (NO_x = NO + NO₂) emissions into the atmosphere constitute a major global air pollution issue. Currently, ambient air quality monitoring regulations² have as objectives the limiting of nitrogen dioxide (NO₂) concentrations to below 40 $\mu\text{g m}^{-3}$ to 200 $\mu\text{g m}^{-3}$ depending on the monitoring time, and lower values are expected in the future with the development of new NO_x reduction technologies in transport and industry.³ To support these monitoring requirements, highly accurate and traceable measuring systems are indispensable. A wide diversity of measuring systems is available and documented in the literature.^{4,5} Chemiluminescence is the most common method used to monitor NO_x and NO₂ air pollution, where NO₂ is not measured directly but calculated from the difference of nitric oxide (NO) and NO_x concentrations. Recent studies⁶ have shown that whereas total NO_x emissions have been dropping or stabilized in recent years, the proportion of NO₂ to total NO_x in the exhausts from vehicles has been increasing and the principal factor for this increase has been considered to be the increased use of oxidation catalysts and particle filters on light duty diesel vehicles. This together with the foreseen development of sensitive optically based methods^{7,8} for the direct measurement of NO₂ concentrations has led to the requirement for accurate standards of NO₂ in N₂ in addition to NO in N₂ standards. The current paper describes the development and performance of a dynamic facility for the generation of NO₂ in N₂ concentrations, as a fundamental step in the development of calibration standards for direct NO₂ concentration calibration and measurement. The facility utilizes a magnetic suspension balance system for mass loss measurements of a permeation tube and combines this for the first time with quantitative FT-IR measurements of both NO₂ and other nitrogen oxide

impurities, resulting in the production of highly accurate concentrations with a standard uncertainty of $\sim 0.04 \mu\text{mol mol}^{-1}$ ($k = 1$) at a mole fraction of 10 $\mu\text{mol mol}^{-1}$, a standard relative uncertainty of 0.4%. The performance of the BIPM facility has been demonstrated in the international comparison CCQM-K74¹ of NO₂ standards involving National Metrology Institutes (NMIs). In this comparison, the BIPM facility was used to value assign NO₂/N₂ gas standards contained in high pressure cylinders where, through careful quantitative purity analysis and as reported by previous similar studies,^{9,10} the presence of significant amounts of HNO₃ in the gas mixtures was confirmed.

In this paper, the operation and performance of the BIPM-NO₂ primary gas facility is described, including measurement equations and a comprehensive uncertainty budget that considers the uncertainty contribution of potential impurities measured by FT-IR.

2. BIPM-NO₂ PRIMARY GAS FACILITY

Instrumentation of the BIPM-NO₂ primary gas facility has been fully described elsewhere.¹ The facility combines gravimetry with dynamic generation of gas mixtures. It is comprised by three main modules: the Rubotherm system module (a continuous-weighing permeation equipment consisting of a permeation tube kept in a temperature-controlled enclosure, swept by carrier gas; the permeation tube is suspended from a weighing device and weighed continuously by a magnetic suspension balance), the flow control system for dynamic

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generation of the gas mixtures, and the flow control system module for static NO_2 gas standards (cylinders). Both static and dynamic sources of NO_2 mixtures are ultimately connected in series to a continuous UV-absorption gas analyzer (ABB LIMAS 11 AO2020), then to a FT-IR spectrometer. FT-IR analysis is preferred because a small but non-negligible amount of impurities is present in the mixtures generated by permeation. This technique was chosen since a survey of literature on NO_2 permeation devices, further described in section 2.4 (Other impurities), indicated that only infrared active impurities were possibly present in the mixtures.

The FT-IR spectrometer was configured with a 48 ± 1.2 m optical-path White cell and then used to perform a purity analysis to determine and quantify the compounds present in mole fractions. These species cannot be neglected to correctly value assign the NO_2 mole fraction of the gas mixtures generated by the facility. Once the identification of the impurities is carried out, the FT-IR spectrometer is reconfigured with a 6.45 ± 0.08 m optical-path White cell and used as a transfer standard between dynamic and static mixtures and to monitor, in real time, the amount of the impurities present. We discuss these aspects further in sections 2.1 and 3.1.1. The operation and automation of the ensemble of instruments, including the FT-IR and ABB LIMAS 11, is achieved using LabView software.

2.1. Purity Analysis by FT-IR in High Concentration Mixtures. The FT-IR spectrometer was used for the identification and quantification of potential impurities contained in the gas mixtures generated by the BIPM- NO_2 primary gas facility. Identification of impurities by an accurate quantification method is essential to obtain nonbiased values of the NO_2 mole fraction produced. The FT-IR instrument used is a ThermoNicolet Nexus FT-IR spectrometer configured with a Mercury Cadmium Telluride (MCT) high D* liquid N_2 -cooled mid-infrared detector. For the quantification of impurities, the FT-IR was configured with a 48 ± 1.2 m path-length multipass White cell (Gemini Scientific Instruments, U.S.A.). The White cell has wetted surfaces of electropolished stainless steel and gold mirror coatings to minimize surface interactions with reactive gas phase species. To keep the internal optical path of the spectrometer free of any interference species, this ensemble is placed in a stainless steel enclosure that is constantly purged with pure N_2 (dewpoint $\sim -95^\circ\text{C}$, i.e., ~ 200 nmol mol^{-1} H_2O) flowing at ~ 15 L min^{-1} , produced by a nitrogen generator (FLO series, Claind, Italy) and purified by a getter system (Microtorr, SAES Pure Gas, Inc., U.S.A.). The gas sample from the permeation chamber flows from the NO_2 facility sampling manifold through the White cell, and then to waste. The sample flow rate is controlled upstream of the White cell at ~ 400 mL min^{-1} . The sample pressure and temperature are measured in real time by means of a calibrated barometer (Series 6000 Digital Pressure Transducer, Mensor, U.S.A.) and a calibrated 100 Ω RTD temperature probe introduced into the outlet gas flow line of the White cell. The spectrometer user interface is by means of the software IMACC (Industrial Monitoring and Control Corporation, U.S.A.). IMACC allows the automatic setting of all instrument parameters into the Thermo proprietary Omnic software for control, spectra acquisition, and online quantification.

To identify possible impurities generated in the dynamic mixtures, a smaller permeation chamber was configured with very low carrier gas flow rates, to increase the fractions of all compounds present in the mixtures. A carrier gas flow rate of

30 mL min^{-1} to 100 mL min^{-1} of N_2 was required for the preparation of the gas mixtures of NO_2 mole fraction between 50 $\mu\text{mol mol}^{-1}$ to 180 $\mu\text{mol mol}^{-1}$ and 10–13 h of constant measurements were needed to obtain a stable response of the FT-IR for each mole fraction. Because of the sticking property of HNO_3 , this flushing time period served to passivate all tubing and White cell walls,¹¹ minimizing any potential surface interaction.¹⁰ As further detailed in section 2.2, quantification of HNO_3 with two different White cells with an A/V (surface area/volume) ratio difference of 3 resulted in comparable mole fractions, demonstrating that no significant losses were caused by the cell inner surface, following the passivation process.

Background stability was achieved by means of the FT-IR enclosure box flushed with 15 L min^{-1} of pure N_2 , from the FLO generator. Temperature stability was achieved by the Rubotherm system bath. Flow stability was accomplished by a mass flow controller and verified by precise gas flow measurements with a commercial laminar flow element system named molbloc/molbox¹² recently calibrated by the National Metrology Institute of France (LNE) in the low flow range from 10 mL min^{-1} to 100 mL min^{-1} .

The mole fraction of NO_2 in this concentrated mixture was determined by the UV analyzer, which was specially calibrated for this mole fraction range by a gas dilution facility and a highly concentrated gas reference standard. According to the UV analyzer, the gas mixture contained (120 ± 1.2) $\mu\text{mol mol}^{-1}$ of NO_2 . Figure 1 plots the absorbance spectrum of a gas

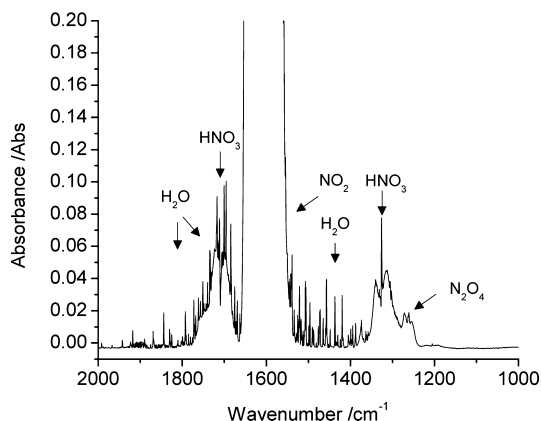


Figure 1. Infrared absorbance spectrum of a 150 $\mu\text{mol mol}^{-1}$ NO_2/N_2 gas mixture generated using the small NO_2 permeation device.

mixture generated by this small NO_2 permeation device using as carrier gas N_2 produced by the FLO generator that contains approximately 200 nmol mol^{-1} of H_2O . In addition to NO_2 and the expected HNO_3 and H_2O , dinitrogen tetraoxide (N_2O_4) was detected in the spectral region 1230 cm^{-1} to 1280 cm^{-1} .

2.1.1. H_2O . H_2O was present in all N_2 source gases used in the experiments in varying concentrations, at levels of 200 nmol mol^{-1} for FLO generated N_2 and below 20 nmol mol^{-1} in BIP N_2 (Air Products). Measurements of H_2O concentration before and after the glass permeation system (containing no permeation tube) were carried out and the water mole fraction was found to increase by 1 $\mu\text{mol mol}^{-1}$ due to diffusion of water into the system through the numerous glass connections of the chamber, as described in section 2.7. Measurements of H_2O mole fraction in the system with a permeation tube installed did not differ from the background levels determined by the method described above.

2.1.2. HNO_3 . Analysis of the absorbance spectra was performed using a classical least-squares (CLS)¹³ algorithm using synthetic calibration infrared spectra of HNO_3 generated by the Multiple Atmospheric Layer Transmission software (MALT)¹⁴ based on the line strength data within the HITRAN 2004 database. The spectral region used for the analysis was the region 1640 cm^{-1} to 1770 cm^{-1} . This region was chosen because of its good agreement to line strength values reported by Flaud et al.¹⁵ In this highly concentrated mixture, the mole fraction of HNO_3 was evaluated as 588 nmol mol^{-1} with a standard uncertainty of 37 nmol mol^{-1} . This value is non-negligible compared to the NO_2 fractions. Consequently, the quantification of HNO_3 fractions in the more diluted mixtures is required and is described in section 2.2.

2.1.3. N_2O_4 . In addition, due to the equilibrium reaction $\text{N}_2\text{O}_4 = 2\text{NO}_2$, the presence of N_2O_4 in highly concentrated gas mixtures, as reported by Fried et al.,⁹ was also anticipated. As no data on N_2O_4 line strength could be found in the databases, another method was used to evaluate its mole fraction in the mixtures. This method consisted of relating the ν_{11} band of N_2O_4 ¹⁶ that is located in the spectral region 1230 cm^{-1} to 1280 cm^{-1} to the HNO_3 absorption band located in the region 1286 cm^{-1} to 1360 cm^{-1} . The mole fraction of N_2O_4 was then estimated to be 60 nmol mol^{-1} . Due to the imprecision of the method used for its determination, a conservative standard uncertainty of 10% was assigned to the calculated mole fraction. In the next step, the facility was programmed to slowly increase the mole fraction of NO_2 from $60\text{ }\mu\text{mol mol}^{-1}$ to $170\text{ }\mu\text{mol mol}^{-1}$. As detailed in Flores et al.,¹ the N_2O_4 mole fraction increased quadratically with respect to NO_2 , from 5 nmol mol^{-1} to 140 nmol mol^{-1} . The nonlinearity in the decrease of the amount of N_2O_4 in diluted NO_2 mixtures ($10\text{ }\mu\text{mol mol}^{-1}$ of NO_2) means that the N_2O_4 concentration is negligible at these levels. This justifies the hypothesis that N_2O_4 can be considered as zero in mixtures normally produced by the facility, but with a nonzero uncertainty. The presence of N_2O_4 was also observed in one high concentration ($100\text{ }\mu\text{mol mol}^{-1}$) NO_2 gas mixture contained in the high pressure cylinder, exactly as reported by Fried et al.⁹

2.2. Real Time Monitoring of HNO_3 Mole Fractions. Since HNO_3 is present in the NO_2 gas mixtures produced by the BIPM- NO_2 primary gas facility under its normal operation mole fraction range, $5\text{ }\mu\text{mol mol}^{-1}$ to $15\text{ }\mu\text{mol mol}^{-1}$, it is quantified in a two-step process. For accurate quantification, HNO_3 is first quantified by configuring the FT-IR spectrometer with the $48 \pm 1.2\text{ m}$ path length White cell, then the $6.45 \pm 0.08\text{ m}$ path length White cell, with a volume of 0.75 L , is used to monitor the stability of the mole fraction of HNO_3 and also to perform the value assignment procedure for NO_2 . This White cell represents a good compromise between a sufficient detection limit and limited gas consumption. Figure 2 plots the HNO_3 mole fractions calculated using both White cells of four gas mixtures of NO_2 in N_2 with mole fractions of $8.8\text{ }\mu\text{mol mol}^{-1}$, $9.8\text{ }\mu\text{mol mol}^{-1}$, $10.8\text{ }\mu\text{mol mol}^{-1}$, and $11.8\text{ }\mu\text{mol mol}^{-1}$ produced by the BIPM facility. As can be observed, the mole fractions and stated uncertainties using the $6.45 \pm 0.08\text{ m}$ path length are consistent with those performed with the $48 \pm 1.2\text{ m}$ path length. As both cells had significantly different surface area to volume ratios, this confirmed that no HNO_3 decomposition was occurring at this mole fraction range (130 nmol mol^{-1} to 200 nmol mol^{-1}). The uncertainty associated with the determination of HNO_3 is described in section 2.4.

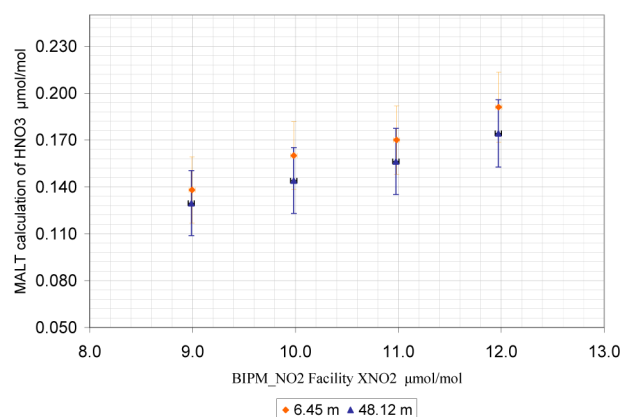


Figure 2. Calculated HNO_3 concentration obtained by FT-IR with a $6.45 \pm 0.08\text{ m}$ and a $48 \pm 1.2\text{ m}$ multipass White cell.

2.3. Measurement Equation. Since HNO_3 is emitted from the permeation tube, it contributes to its loss of mass, and the mole fraction of NO_2 generated by the facility is calculated using the following measurement equation:

$$x_{\text{NO}_2} = \frac{PV_m}{q_v M_{\text{NO}_2}} - \sum \frac{M_{\text{HNO}_3} x_{\text{HNO}_3}}{M_{\text{NO}_2}} \quad (1)$$

where x_{NO_2} is the NO_2 mole fraction; P is the NO_2 permeation rate; V_m is the molar volume of N_2 under standard conditions (273.15 K , 101.3 kPa); $M_{\text{NO}_2} = 46.0055\text{ g mol}^{-1}$ is the molar mass of NO_2 ; q_v is the total flow of the gas mixture; x_{HNO_3} is the mole fraction of HNO_3 quantified by FT-IR; and M_{HNO_3} is its molar mass.

2.4. Uncertainty Contributors. **2.4.1. Permeation Rate (P).** In principle, the permeation rate is the mass loss divided by time. In practice, the mass loss over 8 h of measurements is modeled using a second degree polynomial function. The permeation rate is calculated as the difference between the modeled mass loss at time t (m_{Loss_t}) and at time $t - 8\text{ h}$ ($m_{\text{Loss}_{t-8h}}$) divided by the time difference (8 h). To calculate the permeation rate uncertainty, the peak to peak spread of the residuals between the modeled and measured mass losses is evaluated. The spread is then used as the limits of a rectangular distribution of the uncertainty of the mass loss, giving $u(m_{\text{Loss}_t}) = 5/\sqrt{3} = 2.9\text{ }\mu\text{g}$. Then, the standard uncertainty associated with the mass difference during 8 h is equal to

$$u(m_{\text{Loss}_{8h}}) = \sqrt{u(m_{\text{Loss}_t})^2 + u(m_{\text{Loss}_{t-8h}})^2} = 4.1\text{ }\mu\text{g} \quad (2)$$

Considering a typical permeation rate of $P = 8357.32\text{ ng min}^{-1}$ calculated over 8 h, as explained above, the standard uncertainty is then $u(P) = 4.18\text{ ng min}^{-1}$ or 0.05% relative uncertainty.

2.4.2. Flow Rate (q_v). The molbloc/molbox systems used to measure the flow of ultrapure N_2 (BIP, Air Products) in the production of the NO_2 gas mixtures was calibrated by LNE. The expanded relative uncertainty ($k = 2$) of the flow measurements were taken from the LNE's calibration certificate No. K20869/1 equivalent to $U(q_v) \approx 0.2\%$.

2.4.3. Molar Volume (V_m) and Molar Mass (M_{NO_2}). The NO_2 (HNO_3) molar mass uncertainty equals to 0.0014 g mol^{-1} or 0.003% relative (0.0017 g mol^{-1} or 0.003% relative), as derived from the IUPAC Table of Atomic Weights 2007.¹⁷ The molar volume V_m of a real gas under standard conditions ($T =$

273.15 K, $p = 101.325$ kPa) is given by the formula $V_m = ZRT/p$ where Z is the compressibility factor and R is the gas constant, $8.314\,472\text{ J mol}^{-1}\text{ K}^{-1}$, with relative standard uncertainty $u(R) = 1.8 \times 10^{-6}$. Since these are defined by convention, there is no uncertainty in T and p . The compressibility factor of N_2 obtained from the National Institute of Standards and Technology (NIST) Refprop database is $Z_{N_2} = 0.9995434$ with a relative standard uncertainty $u(Z) = 15 \times 10^{-6}$. Thus, the molar volume of N_2 and its standard uncertainty are $V_m(N_2) = 22.4037\text{ L mol}^{-1}$ and $u(V_m(N_2)) = 0.0003\text{ L mol}^{-1}$, or 1.5×10^{-5} relative.

2.4.4. HNO_3 Mole Fraction (x_{HNO_3}). The uncertainty budget used to calculate the uncertainty in the determination of HNO_3 in the spectral region 1240 cm^{-1} to 1400 cm^{-1} is the subject of an independent publication recently submitted elsewhere.¹⁸ Three principal components of uncertainty were considered in this calculation: the FT-IR response stability that includes statistical noise and cell passivation, $u_{\text{stab}_HNO_3} = 20\text{ nmol mol}^{-1}$, the radiative transfer code (MALT) used to produce the synthetic infrared spectra used as references, $u_{\text{Calc}_HNO_3} = 0.017x$, and the molecular database HITRAN 2004, $u_{\text{HITRAN}_HNO_3} = 0.05x$. The final combined uncertainty associated with the FT-IR/MALT/CLS measurements of HNO_3 at a mole fraction (x) ranging from 100 nmol mol^{-1} to 200 nmol mol^{-1} with the $48 \pm 1.2\text{ m}$ optical path White cell is determined by the following equation, with values expressed in $\mu\text{mol mol}^{-1}$:

$$u(x) = \sqrt{(0.02)^2 + (0.05x)^2 + (0.017x)^2} \quad (3)$$

2.4.5. Other Impurities. Although HNO_3 was the only impurity detected in the gas mixtures produced by the BIPM- NO_2 primary gas facility, in non-negligible amounts, the possibility that some other compounds were present at levels lower than the FT-IR limit of detection was also considered. Based on purity analysis of NO_2 permeation tubes by Hughes et al.¹⁹ and Fried et al.⁹ the impurities considered as possibly permeating from a NO_2 permeation tube were dinitrogen tetroxide (N_2O_4), dinitrogen pentoxide (N_2O_5), nitrous acid ($HONO$), peroxyntitric acid (HO_2NO_2), and dinitrogen trioxide (N_2O_3), all infrared active. The possibility of detecting such impurities with the FT-IR spectrometer was evaluated by comparing their integrated line intensities reported in the literature (N_2O_3 ,²⁰ N_2O_5 ,²¹ $HONO$,²² and HO_2NO_2 ,²³), against the HNO_3 integrated band intensity reported by Chackerian et al.²⁴ in the spectral region 1640 cm^{-1} to 1770 cm^{-1} . As explained in detail in Flores et al.,¹ the integrated line intensities were used to calculate effective limits of detection for each potential impurity in a mixture of $10\text{ }\mu\text{mol mol}^{-1}$ of NO_2 in N_2 by using a ratio to the detection limit of HNO_3 . As a result, very low limits of detection (always below 1 nmol mol^{-1}) were found. This translates as negligible contributions to the total uncertainty presented in the following section.

2.5. Uncertainty Budget. It follows that the uncertainty budget for a NO_2/N_2 mixture having a nominal concentration of $8.8\text{ }\mu\text{mol mol}^{-1}$, calculated according to the Guide to the Expression of Uncertainty in Measurement (GUM),²⁵ is that shown in Table 1. The standard uncertainties in the range from $5\text{ }\mu\text{mol mol}^{-1}$ to $15\text{ }\mu\text{mol mol}^{-1}$ of NO_2 mole fractions produced with our facility can be finally modeled by the following linear function (numerical values in $\mu\text{mol mol}^{-1}$):

Table 1. Uncertainty Budget for a $8.86\text{ }\mu\text{mol mol}^{-1}$ NO_2/N_2 Primary Mixture Generated with the BIPM Facility^a

quantity	typical value	standard uncertainty	relative uncertainty
P	$8.3573\text{ }\mu\text{g min}^{-1}$	$4.18 \times 10^{-3}\text{ }\mu\text{g min}^{-1}$	5×10^{-4}
V_m	$22.4038\text{ L mol}^{-1}$	$0.34 \times 10^{-3}\text{ L mol}^{-1}$	1.52×10^{-5}
q_v	452 mL min^{-1}	0.455 mL min^{-1}	1.00×10^{-3}
M_{NO_2}	$46.0055\text{ g mol}^{-1}$	$1.40 \times 10^{-3}\text{ g mol}^{-1}$	3.04×10^{-5}
x_{HNO_3}	$0.104\text{ }\mu\text{mol mol}^{-1}$	$0.021\text{ }\mu\text{mol mol}^{-1}$	2.02×10^{-1}
M_{HNO_3}	63.013 g mol^{-1}	$1.17 \times 10^{-3}\text{ g mol}^{-1}$	1.86×10^{-5}
$x_{N_2O_4}$	0 nmol mol^{-1}	$0.866\text{ nmol mol}^{-1}$	N.A.
quantity	value	standard uncertainty	
x_{NO_2}	$8.86\text{ }\mu\text{mol mol}^{-1}$	$0.03\text{ }\mu\text{mol mol}^{-1}$	

^aNote: The NO_2 standard uncertainty presented in this table was calculated by means of the software GUM Workbench V.2.3²⁵.

$$u_{PT}(x_{NO_2}) = 0.00136x_{NO_2} + 0.020818 \quad (4)$$

2.6. Covariance between the Calibration Gas Mixtures. When using the facility to calibrate an analytical instrument, several NO_2/N_2 mole fractions are generated. All dynamic mixtures are derived from the same BIPM facility; an error in the analyte content in one gas is considered to propagate to all gas mixtures in a positive correlated fashion therefore nonzero covariances, $u_{PT}(x_{NO_{2,i}}, x_{NO_{2,j}})$, must be included in the uncertainty calculations. The covariance between two calibration gas mixtures i and j is described as follows:

$$u_{PT}(x_{NO_{2,i}}, x_{NO_{2,j}}) = \gamma(u(x_{NO_{2,i}}))^2 \quad (5)$$

where $u(x_{NO_{2,i}})$ is the standard uncertainty of the more concentrated mixture as given by eq 4 and

$$\gamma = \frac{q_j}{q_i} \quad (6)$$

is the dilution factor of the total gas flows q_j and q_i (with $q_j > q_i$). Note that as the NO_2 calibration gas mixtures generated with the facility are distributed over a small range of mole fractions (typically $8\text{ }\mu\text{mol mol}^{-1}$ to $12\text{ }\mu\text{mol mol}^{-1}$), then the dilution factor is often close to 1, and the covariances are often close to the variances $u(x_{NO_{2,i}})$.²

2.7. Potential Reactions and Losses in the Permeation Facility. The potential reactions and losses within the Rubotherm permeation chamber and pneumatic connections were investigated measuring with FT-IR a constant NO_2/N_2 gas mixture with a mole fraction of $10\text{ }\mu\text{mol mol}^{-1}$ passed through the Rubotherm system or sent directly to the FT-IR White cell. The infrared spectra collection was carried out every 5 min. As a result, it was noticed that, on average, mixtures flowing through the permeation chamber contained 20 nmol mol^{-1} less of NO_2 than gas mixtures flowing directly to the FT-IR White cell. Although noticeable, this difference is small and comparable to the standard uncertainty of the FT-IR response, as will be discussed in section 3.2.1. For this reason, it was concluded that an uncertainty component should be retained to cover the maximum changes in NO_2 concentrations observed in these experiments. Assuming a rectangular distribution with a half-width of 10 nmol mol^{-1} , the standard uncertainty due to potential losses of NO_2 can be written $u(x_{NO_{2,Losses}}) = 10/\sqrt{3} =$

5.7 nmol mol⁻¹. This uncertainty component is combined with the standard uncertainty associated with NO₂ mole fractions $u_{PT}(x_{NO_2})$ defined in section 2.5 as follows:

$$u_{PT,NO_2Losses}(x_{NO_2}) = \sqrt{(u_{PT}(x_{NO_2}))^2 + (u(x_{NO_2Losses}))^2} \quad (7)$$

This additional component increases the standard uncertainty from about 30 nmol mol⁻¹ to 36 nmol mol⁻¹.

No HNO₃ variations due to changing the flow path were detected confirming that this compound was not a product of reaction but actually permeating from the tube.

An increase of the H₂O mole fraction of about 1 μmol mol⁻¹ was observed when the NO₂/N₂ gas mixture was passed through the Rubotherm chamber (containing no permeation tube) compared to that passed through the tubing only, indicating that H₂O was diffusing into the system despite all the care given to avoid external contamination of atmospheric gases. Permanent background levels of H₂O were indeed observed in the facility with mole fractions found to lie between 1 μmol mol⁻¹ and 2 μmol mol⁻¹. This level of water was continually found in the system and not modified by the introduction of a permeation tube into the permeation chamber. Comparison with dry NO₂/N₂ cylinders confirmed that the NO₂ mole fraction determined by the BIPM's permeation system was correct and no other significant impurity than HNO₃, was needed to correct values based on the permeation device (see section 5).

3. ANALYTICAL INSTRUMENTATION AND UNCERTAINTIES

As previously described the BIPM-NO₂ primary gas facility is ultimately connected in series to the FT-IR spectrometer and the continuous UV gas analyzer. These instruments were used as transfer standards or "transfer measurement devices"²⁶ when value assigning NO₂ gas mixtures contained in high pressure cylinders. Ideally, the response of a transfer measurement device to an analyte must be very stable and linear, at least in the mole fraction range where the instrument will be used to minimize the uncertainty contribution in the value assignment procedure of the secondary standards. The characteristics of the FT-IR and UV analyzers were evaluated according to these principles. The results of this investigation are presented in section 3.1.

3.1. Analytical Instruments. 3.1.1. FT-IR Spectrometer.

For the acquisition of high quality spectra suitable for quantitative analysis of NO₂, 120 scans are coadded over a period of ~2 min to provide one single beam spectrum of a sample. This single beam spectrum is then ratioed with a similar spectrum of ultrapure N₂ collected under similar conditions to provide an absorbance spectrum of the gas sample (relative to ultrapure N₂). The White cell has a volume of ~750 mL, and the sample flows at ~400 mL min⁻¹. Assuming perfect mixing in the cell, we estimate that an initial sample at time $t = 0$ s has been 99.9% replaced after 10 min of flow and 99.9999% replaced after 20 min. Accordingly, to ensure complete exchange of the sample, spectrum acquisition started at $t = 0$ s but only the measured spectra obtained after flowing the sample through the White cell for 35 min were used for the mole fraction determination. It was also verified empirically that, after 30 min of flow, the sample was completely exchanged, within the bounds of measurement uncertainty. The absorbance spectra obtained following this procedure had

a very high signal-to-noise ratio, with the level of noise in the baseline being typically $\sim 2 \times 10^{-4}$ abs₁₀ peak/peak. By comparison, the main NO₂ peak had absorbance in the range (0.04–0.16) abs₁₀.

3.1.2. UV Analyzer. The UV gas analyzer ABB LIMAS 11 (series AO2020, Sweden) was used as a second analytical instrument for the NO₂ value assignment of the gas mixture contained in high pressure cylinders. The data acquisition was achieved through LabView. Before its use, the system was calibrated according to the instructions in the instrument manual.

3.2. Uncertainty Contributions of the Analytical Systems. The determination of the uncertainty contribution of the measuring devices was carried out by analyzing their responses to different mole fractions of NO₂ in the mole fraction range from 5 μmol mol⁻¹ to 15 μmol mol⁻¹. The gas mixtures used for this analysis were produced by the BIPM-NO₂ primary gas facility.

3.2.1. Stability. Allan variance analysis was applied to the time series obtained by the FT-IR spectrometer and the UV analyzer by means of the software Stable 32 (a frequency stability analysis software that allows the entry and editing of phase and frequency data, the calculation of stability statistics, and the plotting of phase, frequency and stability data). The Allan deviation is derived from the Allan variance or two-sample variances introduced by D. W. Allan to time and frequency metrology to characterize the stability of frequency standards.²⁷ When displayed as a function of the sampling time on a log–log plot, a system showing white noise behavior will typically be characterized by a linear decreasing function. Here, as can be seen in Figure 3, white noise behavior is observed with measurement averaging times up to 100 s with the FT-IR analyzer (t_{op_FTIR}) and 300 s with the UV analyzer (t_{op_UV}).

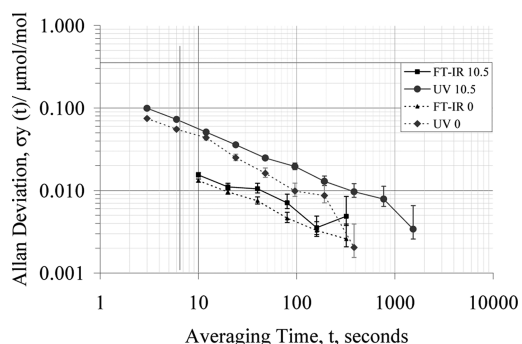


Figure 3. Allan deviation of the FT-IR spectrometer and UV analyzer responses to dynamically generated gas mixtures of NO₂/N₂ at 10.5 μmol mol⁻¹ nominal mole fraction. The dotted lines show the same treatment performed on N₂ only.

However, analyzing the instrument responses to ultrapure N₂, plotted in Figure 3, we observed that the noise coming from the instruments (dotted lines) is white noise for averaging times longer than the t_{op} used for the instrument. When analyzing dynamically generated gas mixtures of NO₂/N₂ at 10.5 μmol mol⁻¹ nominal mole fraction (solid lines), we observed additional noise attributed to instabilities in the gas mixtures produced by BIPM-NO₂ primary gas facility. From this study, the averaging times of both instruments were chosen as t_{op} and a conservative value of 20 nmol mol⁻¹ was kept as the standard uncertainty component due to instabilities in the instrument response of both instruments.

3.2.2. Linearity. The linearity of the FT-IR spectrometer and the UV analyzer was evaluated by analyzing the instrument response to NO₂ in the mole fraction range from 4 μmol mol⁻¹ to 15 μmol mol⁻¹ generated by the BIPM-NO₂ primary gas facility. The instrument responses were used to input into the Generalized Least Squares (GLS) algorithm described in ISO 6143:2001.²⁸ The responses of the FT-IR spectrometer at different mole fractions were obtained from the times series generated by IMACC. The responses of the UV analyzer were obtained from the raw value given by the instrument corrected for a zero drift. The uncertainty, $u(x_{\text{NO}_2})$, attributed to the x_{NO_2} value of the BIPM-NO₂ primary gas facility standards was calculated according to eq 4 from section 2.5.

Table 2 shows the parameters of the straight-line model analysis function produced as output by the GLS algorithm for

Table 2. Output from the GLS Algorithm in Its Analysis Mode^a

	FT-IR	UV analyzer
b_0 (μmol mol ⁻¹)	-0.28923	-0.20498
b_1	1.0182	1.0024
$u(b_0)$ (μmol mol ⁻¹)	0.02627	0.02596
$u(b_1)$	0.00260	0.00255
$\text{cov}(b_0, b_1)$ (μmol mol ⁻¹)	-0.00006	-0.00006
SSD rem	15.51	8.6
GOF	1.69	1.07

^a b_0 , b_1 , $u(b_0)$, $u(b_1)$, and $\text{cov}(b_0, b_1)$ are the parameters of a straight-line model calibration function for the FT-IR and UV analysers responses against x_{NO_2} .

each instrument for the same NO₂ gas mixtures generated by the facility. The goodness-of-fit (GOF) parameters in both cases, GOF_FT-IR = 1.69 and GOF_ABB = 1.07, indicate that the input data are consistent with a straight line model function and nonadditional uncertainty due to departure from linearity needs to be included.

4. CALIBRATION PROCEDURE FOR VALUE ASSIGNMENT

When the BIPM-NO₂ primary gas facility is used to value assign the NO₂ mole fractions of cylinders, such as for the international comparison CCQM-K74 (section 5), the typical procedure is as follows: on receipt, all cylinders are value assigned by the BIPM-NO₂ primary gas facility and are handled according the recommendations described in ISO 16664.²⁹ The cylinders are then sequentially analyzed using the 16-inlet automatic gas sampler connected to the BIPM-NO₂ primary gas facility, FT-IR spectrometer, and UV gas analyzer. For each analyzer, a calibration line is evaluated using GLS. The assigned BIPM NO₂ value is then equal to the predicted value from a calibration line calculated from a set of dynamic NO₂ primary gas mixtures obtained from the BIPM-NO₂ primary gas facility. When value assigning gas mixtures contained in high pressure cylinders with a mole fraction of 10 μmol mol⁻¹, the set of dynamic gas mixtures includes, as a minimum, four calibration standards with NO₂ mole fractions appropriately distributed over the range from 8 μmol mol⁻¹ to 12 μmol mol⁻¹. In the case of the international comparison CCQM-K74, a set of twenty dynamic gas mixtures was used.

5. CCQM-K74 INTERNATIONAL COMPARISON

The CCQM-K74 key comparison, carried out from June 2009 to May 2010, was designed to evaluate the level of comparability of NMIs measurement capabilities and standards for NO₂ at a nominal mole fraction of 10 μmol mol⁻¹. The CCQM-K74 key comparison was coordinated by the BIPM with the National Institute of Metrology of The Netherlands (VSL) given the responsibility to produce the NO₂ in N₂ gas mixtures for distribution between the participating laboratories. The key comparison reference values (KCRV), or “reference quantity value”²⁶ used in this comparison was allocated by the BIPM and based on the BIPM-NO₂ primary gas facility results. This value was decided by the Gas Analysis Working Group (GAWG) of the CCQM and based on the extensive work that the BIPM carried out to identify and quantify potential impurities contained in the BIPM-NO₂ primary gas facility gas mixtures (sections 2.1, 2.2, and 2.4) and the cylinder gas mixtures distributed by the participants, including stability analysis, as described in the following sections.

5.1. Stability of Cylinder Standards Used During the CCQM-K74. The gas mixtures distributed between the participants were produced by VSL using a special internal cylinder coating that prevents reactions within the standards. The mixtures were value assigned by the BIPM twice during an eight month period. Due to stability issues observed with similar gas mixtures,¹ an uncertainty component describing the stability of the cylinder over the period of the comparison was determined and taken into account in the general uncertainty calculation. This uncertainty component was determined using the maximum difference in the NO₂ values of the cylinders observed during this period. Assuming a rectangular distribution, the standard uncertainty due to possible drifts u_{Drift} associated with the NO₂ mole fraction (x_i) in the cylinder (i) was evaluated using the equation:

$$u_{\text{Drift}}^2(x_i) = \frac{(b_+ + b_-)^2}{12} \quad (8)$$

where b_+ and b_- are the upper and the lower boundaries for the NO₂ difference. The maximum difference between the BIPM assigned values for any particular cylinder was used so that b_+ and b_- were considered to be 37 nmol mol⁻¹ each, and by applying eq 8, $u_{\text{Drift}}(x_{\text{NO}_2}) = 21$ nmol mol⁻¹. Introducing this new uncertainty component in eq 7, the final standard uncertainty is given by the following equation:

$$u_{\text{BIPM}}(x_{\text{NO}_2}) = \sqrt{(u_{\text{PT}}(x_{\text{NO}_2}))^2 + (u(x_{\text{NO}_2\text{Losses}}))^2 + (u(x_{\text{NO}_2\text{Drift}}))^2} \quad (9)$$

This additional uncertainty component increased the relative standard uncertainty of the key comparison reference value to 0.4%.

5.2. CCQM-K74 Comparison Results. Results of the international comparison CCQM-K74¹ demonstrate the consistency between the participating laboratories results and the BIPM results in terms of a degree of equivalence (D) expressed quantitatively in two terms: its deviation from the BIPM reference value and the uncertainty of this deviation (at 95% level of confidence). Considering the challenges observed in early comparisons the results of this comparison indicate good consistency in the majority of measurement results ($\pm 3\%$). It was also concluded that a full interpretation of the

results of the comparison needs to take into account the presence of HNO_3 (in the range 100 nmol/mol to 350 nmol/mol) in the cylinders circulated as part of the comparison, as well as the possible presence of HNO_3 in the primary standards used by participating laboratories. HNO_3 is known to be a major source of systematic bias in chemiluminescence analyzers equipped with thermal converters in contrast to similar analyzers equipped with photolytic converters that use radiation between 350 nm to 400 nm to convert specifically NO_2 to NO as described by McClenny et al.⁵

Considering the different processes used to produce NO_2/N_2 mixtures in cylinders (by introducing NO into a matrix of nitrogen and oxygen) and by permeation (from liquid N_2O_4), the fact that the values of gas standard mixtures produced by the two methods are in agreement just when HNO_3 mole fractions are taken into account further confirms that this compound is the only non-negligible impurity present in the mixture.

6. CONCLUSION

The development of a highly accurate primary gas facility for the dynamic production of mixtures of NO_2 in N_2 based on continuous weighing of a permeation tube was successfully achieved incorporating an FT-IR based method for the accurate correction of the influence of impurities of nitrogen oxides and notably HNO_3 . It was demonstrated that the facility is able to produce NO_2 gas mixtures in the range from $5 \mu\text{mol mol}^{-1}$ to $15 \mu\text{mol mol}^{-1}$ with a standard relative uncertainty of 0.4%. To maximize the reduction of uncertainties, significant efforts have been made to identify and quantify potential impurities present in the gas mixtures, in particular HNO_3 , which is the only significant impurity identified. The mixtures produced by this facility were successfully used to provide reference values for the international comparison CCQM-K74,¹ which aims to accurately assign values to NO_2 concentrations determined in cylinders used as transfer standards. Seventeen NMIs participated in CCQM-K74. This work contributes toward a novel and complete uncertainty budget based on the analysis of the performance of the facility, including the use of a FT-IR and a nondispersive UV analyzer as the analytical techniques.

Future Work. This work illustrates that the most important uncertainty contributor of the NO_2 gas mixtures generated by the BIPM- NO_2 primary gas facility is the mole fraction determination of HNO_3 . To reduce the uncertainty in the mole fraction of HNO_3 , this would need to be determined directly from a dynamically generated concentration; therefore, the same BIPM facility will be used to dynamically generate HNO_3 gas mixtures. This approach is expected to much reduce the current uncertainty of these measurements which is based on traceability to the line strength of the HITRAN database 2004.

AUTHOR INFORMATION

Corresponding Author

*Phone: (33) 1 45 07 70 92. E-mail: edgar.flores@bipm.org.

Notes

The authors declare no competing financial interest.

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