PERFORMANCE EVALUATION OF THE BIPM PRIMARY NO_2 FACILITY IN SUPPORT OF INTERNATIONAL EQUIVALENCE OF AIR QUALITY MONITORING

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The international equivalence of gas standards for air quality and greenhouse gas monitoring are major themes within the BIPM Chemistry Department programme which includes the coordination of comparisons of ozone, nitrogen monoxide, methane, formaldehyde and nitrogen dioxide gas standards. The nitrogen dioxide facility was recently used to underpin the international comparison CCQM-K74 designed to evaluate the level of comparability of the laboratory's measurement capabilities for nitrogen dioxide (NO_2) at a nominal mole fraction of 10 μmol·mol^{-1}. An in-depth study of the performance of the facility that combines gravimetry with dynamic generation of gas mixtures is presented in this document. The study details the main components of the facility such as the magnetic suspension balance, the flow control system for the dynamic generation of the gas mixtures, the flow control system for static nitrogen dioxide gas standards, the continuous gas analyzer ABB Limas and the FT-IR spectrometer facility.

1. INTRODUCTION

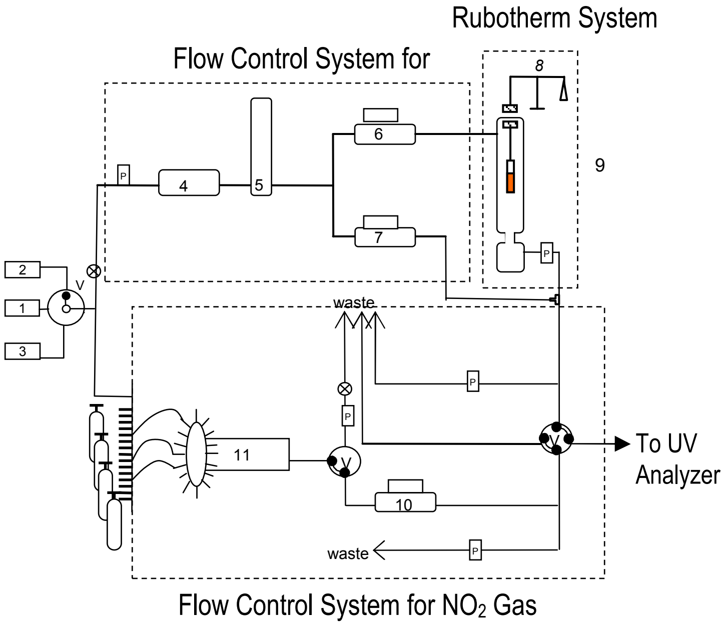
Internationally, there is a high priority attached to activities which reduce NO_x in the atmosphere. The current level of permitted emissions is typically between 50 μmol·mol^{-1} and 100 μmol·mol^{-1}, but lower values are expected in the future. Currently, ambient air quality monitoring regulations also require the measurement of NO_x mole fractions of 0.2 μmol·mol^{-1}. The production of accurate standards at these mole fractions requires either dilution of a stable higher concentration gas standard or production by a dynamic technique, for example, one based on permeation tubes (PT).

Several NMIs prepare static NO_2 mixtures gravimetrically in high pressure cylinders for the purposes of calibrating NO_2 analysers. Typically these have a certified uncertainty in x_{NO2} of the order of 0.5 %-1.0 % and a gravimetric uncertainty of the order of 0.05 %-0.15 %. Since NO_2 is a reactive gas it is important to ensure the stability of static mixtures containing NO_2 in high pressure cylinders, especially at mole fractions below 20 μmol·mol^{-1}.

The BIPM NO_2 facility provides an alternative mechanism for obtaining primary reference mixtures and a primary calibration method that combines gravimetry with dynamic generation of gas mixtures. The BIPM NO_2 facility also allows the comparison of dynamically generated mixtures with static NO_2 mixtures contained in high pressure cylinders, via the response of an NO_2 analyser to the mixtures. This allows either the comparison of dynamically-generated mixtures with static gravimetric mixtures, or the labelling of static secondary NO_2 mixtures with reference to the dynamically-generated mixtures. It also facilitates the direct comparison of static gravimetric mixtures sourced from different NMIs.

2. DESCRIPTION OF THE BIPM NO_2 PRIMARY GAS FACILITY

The BIPM's facility comprises a magnetic suspension balance, a flow control system for the dynamic generation of the gas mixtures and a flow control system for static nitrogen dioxide gas standards. Both, static and dynamic sources of NO_2 mixtures are ultimately connected to a continuous UV gas analyzer, ABB Limas 11 (AO2020). Figure 1 shows a schematic of the BIPM NO_2 facility. The flow control system of the BIPM's facility is mainly comprised of a molbloc/molbox® system, a SAES® nitrogen purifier and two mass flow controllers. The magnetic suspension balance was developed by Rubotherm and the flow control system for high pressure cylinders is comprised by a multi-position valve with sixteen ports. The operation and automation of the equipment is achieved via a LabView® programme developed at the BIPM.



Flow Control System for Rubotherm

1. Zero air generator
2. Nitrogen Generator
3. Nitrogen Cylinders
4. molbloc (0-1000) mL/min
5. SAES Nitrogen purifier
6. Mass flow controller (0-100) mL/min
7. Mass flow controller (0-1000) mL/min

Rubotherm System (dynamic gas mixtures)

8. Magnetic suspension balance
9. NO_2 permeation tube

Flow Control System for NO_2 Gas Standards

10. Mass flow controller (0-1000) mL/min
11. Multi position valve (16-ports)

***Figure 1**: Schematic of the BIPM NO_2 facility.* P *indicates an electronic pressure controller and* V *a valve.*

3. THE NITROGEN DIOXIDE MOLE FRACTION DETERMINATION AND UNCERTAINTY BUDGET

The determination of the nitrogen dioxide mole fraction of the stream emerging from the facility is calculated using the following equation:

$$x_{NO2} = \left(\frac{P\cdot V_{\mathrm{mN2}}}{F\cdot M_{\mathrm{NO_2}}}\right) - \left(\frac{x_{\mathrm{HNO_3}}\cdot M_{\mathrm{HNO_3}}}{M_{\mathrm{NO_2}}}\right) \qquad (1)$$

where x_{NO2} is the nitrogen dioxide mole fraction; P is the nitrogen dioxide permeation rate; V_{mN2} is the molar volume of nitrogen at standard conditions (273.15 K, 101.3 kPa); $M_{\mathrm{NO_2}}$ is the molar mass of NO_2; F is the total flow of nitrogen given by the sum of carrier nitrogen and diluent nitrogen flows, at standard conditions (273.15 K, 101.3 kPa); x_{HNO3} is the HNO_3 mole fraction determined by FT-IR spectroscopy; and $M_{\mathrm{HNO_3}}$ is the molar mass of HNO_3.

The permeation standard uncertainty, considering a tube with a permeation rate equivalent to $P \approx 8357$ ng·min^{-1}, is $u(P)$ =4.18 ng·min^{-1} assuming that P follows a rectangular distribution of ± 6.2 ng·min^{-1}.

The uncertainty in NO_2 molar mass of 0.00047 g·mol^{-1}, 0.001 % relative, can be derived from the IUPAC Table of Atomic Weights. As for NO_2, the uncertainty in nitric acid molar mass, 0.000561 g·mol^{-1} (0.0009 % relative), was derived from the IUPAC Table of Atomic Weights.

The molar volume V_m of a real gas at standard conditions (T = 273.15 K, p = 101.325 kPa) is given by the formula $Vm=ZRT/P$ where Z is the compressibility factor and R is the gas constant, 8.314 472 J·mol^{-1}·K^{-1}, with relative $u(R)$ of 1.8×10^{-6}. Since they are defined by convention there is no uncertainty in T and p.

The compressibility factor of nitrogen obtained from the NIST Refprop database is Z_{N2} = 0.9995434 with relative $u(Z)$ of 15×10^{-6}. Thus the molar volume of nitrogen and its standard uncertainty are V_{mN2} = 22.4037 L·mol^{-1} $u(V_{\mathrm{mN2}})$ = 0.0003 L·mol^{-1}, or 1.5×10^{-5} relative.

The standard uncertainty of F is calculated by the formula proposed by DHI instruments(1):

$u_{\mathrm{combined}}(F_{\mathrm{total}})$ = 0.08 % of $rdg_{molbloc}$+0.005 % of FS

where rdg_{molbloc} (or F_{molbloc}) is the molbloc flow reading and FS its full scale.

The uncertainty in the calculated nitric acid mole fraction, x_{HNO3}, by FT-IR, is given by the numerical formula (with values in μmol/mol):

$$u(x_{HNO3}) = \sqrt{(0.02)^2 + (0.015x)^2 + (0.05x)^2} \qquad (2)$$

where x is the mole fraction of nitric acid predicted by FT-IR in the gas mixtures. Further details of the FT-IR methodology for the determination of HNO_3 by FT-IR spectroscopy will be presented in a forthcoming publication.

It follows that the uncertainty budget for a NO_2 mixture having a nominal concentration of ~10.0 µmol·mol^{-1} is as tabulated in
using nitrogen as the diluent gas.

3.1 The flow correlation contribution

All dynamic mixtures are derived from the same facility, therefore any error in the analyte content of a gas mixture, will also propagate to all gas mixtures in a positively correlated fashion. As a consequence a non-zero covariance, $u(x_{NO2j,}\ x_{NO2j+1})$ was included in the uncertainty calculation in addition to the standard uncertainties $u(x_{NO2j})$ and $u(x_{NO2j+1})$ of every dynamically created gas mixture *i*.
The non-zero covariance term is described as follows:

$$u(x_{NO_2,i}, x_{NO_2,i+1}) = \gamma\left[u(x_{NO_2,i})\right]^2 \qquad (3)$$

where γ is the dilution factor of the total gas flows F_i and F_{i+1}, and $u(x_{NO2})$ is the standard uncertainty of the analyte content x_{NO2}.

***Table 1**. Uncertainty budget for a NO_2 /N_2 primary mixture generated with the BIPM facility.*

	Estimate x_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient $c_i=\partial x_{NO2}/\partial x$	Uncertainty contribution $u_i(y)$ / mol·mol^{-1}	Index % /
P	8.3573 × 10^{-6}·g·min^{-1}	4.18 × 10^{-9}·g·min^{-1}	1.1	4.5 × 10^{-9}	14.2
V_{mN2}	22.4038 L·mol^{-1}	340.00 × 10^{-6} L·mol^{-1}	400 × 10^{-9}	140 × 10^{-12}	0.0
F	452 × 10^{-3}·L·min^{-1}	412.00 × 10^{-6} L·min^{-1}	-20 × 10^{-6}	-8.2 × 10^{-9}	47.1
M_{NO2}	46.0055 g·mol^{-1}	470 × 10^{-6} g·mol^{-1}	-190 × 10^{-9}	-91 × 10^{-12}	0.0
x_{HNO3}	104 × 10^{-9} mol·mol^{-1}	5.420 × 10^{-9} ·mol·mol^{-1}	-1.4	-7.4 × 10^{-9}	38.7
M_{HNO3}	63.005 g·mol^{-1}	561.10 × 10^{-6} g·mol^{-1}	-2.3 × 10^{-9}	-1.3 × 10^{-12}	0.0

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
x_{NO2}	8.86 µmol·mol^{-1}	0.27 % (relative)	2.00	95 % (normal)

4. PERFORMANCE EVALUATION OF THE BIPM NO_2 FACILITY

The performance evaluation of the facility was carried out by comparing the values of five nitrogen dioxide gas mixtures contained in high pressure cylinders using the UV Photometer gas analyzer, ABB Limas 11 (AO2020) as the comparator against the values of mixtures generated by the facility.

4.1 The UV Photometer gas analyzer

The analyser measurement uncertainty and optimum sampling period were calculated by time series analysis of the response of the instrument to a sequence of 8 dynamically generated primary gas mixtures, in the x_{NO2} range 4.5 µmol·mol^{-1} to 13.5 µmol·mol^{-1}. The noise of the instrument using τ_0=3s was confirmed to be white noise (see Figure 2).

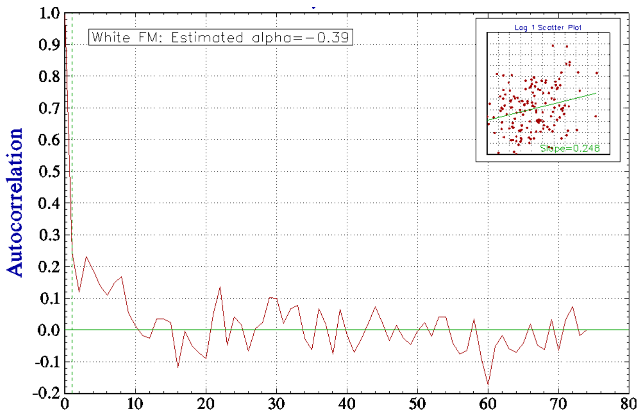


***Figure 2**. Autocorrelation after 150 points (τ_0=3s). x_{NO2}= 6.87µmol/mol*

By quantifying the Allan deviation (Figure 3) of the time series responses of the gas analyzer at various nominal nitrogen dioxide mole fractions, the optimum averaging time was calculated to be τ_{opt}=300 seconds with the analytical standard uncertainty below 12 nmol·mol^{-1}. To be conservative, the analytical uncertainty of the ABB Limas response was fixed at $u_{ABB}(x_{NO2})$=15 nmol·mol^{-1} for the nitrogen dioxide range 4.5 µmol·mol^{-1} to 13.5 µmol·mol^{-1}. The linearity of the gas analyzer was assessed by a comparison of thirty five dynamically generated primary gas mixtures, generated by the BIPM NO_2 facility, equally spaced in the x_{NO2} range 4.5 μmol·mol^{-1}-15.5 μmol·mol^{-1}. At each mixture concentration, the mixtures were allowed to flow through the analyzer for a period of 40 minutes. Only the last five minutes of flow and analyzer data were used to calculate 300 seconds average x_{NO2} and analyzer response values respectively. The measurement series were carried out in ascending and descending order (x_{NO2}). The Generalized Least Square calculation was implemented using B_LEAST[1], calibration and analysis functions were calculated for the UV analyzer response against the dynamically generated x_{NO2} data. Standard uncertainties associated with the nitrogen dioxide values provided by the dynamic facility (x-axis) and the response of the instrument (y-axis) were taken into account following the budget described previously. **¡Error! No se encuentra el origen de la referencia.** lists the parameters of the GLS fit of a linear analysis function to the observed x_{NO2} analyzer response data. The residuals of the subtraction of the calculated mixture mole fraction and the corresponding predicted UV analyzer response are plotted in Figure 4 as function of mole fraction.

4.2 Comparison of the BIPM NO2 facility gas mixtures against mixtures contained in high pressure cylinders

4.2.1 Characteristics of the primary gas mixtures contained in high pressure cylinders

The NO_2 standards used for the comparison were primary gas mixtures purchased from the National Metrological Institute in the Netherlands (VSL), produced for the CCQM-K74 comparison.

The standards had certified stability over a period of 6 months. Their mole fractions and certified uncertainties are listed in . The major impurities as estimated by the VSL are presented in . Once received at the BIPM, a purity analysis of the gas standards was undertaken by FT-IR spectroscopy using a 48 m ± 1.2 m multipath gas cell. The analysis of the infrared spectra was carried out using MALT, an acronym for Multiple Atmospheric Layer Transmission software developed at the University of Wollongong, used to generate synthetic FT-IR spectra of gas phase mixtures(2) and CLS software and the molecular database HITRAN(3) 2004. **¡Error! No se encuentra el origen de la referencia.** lists the nitric acid mole fraction found in each of the gas standards.

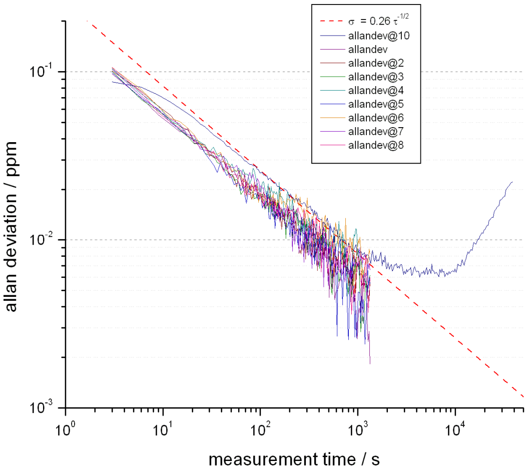


***Figure 3**. Allan deviation of the LIMAS analyser response to dynamically generated gas mixtures of NO_2/N_2 at various nominal mole fractions. The dark blue curve shows the same treatment performed on a time series of the FT-IR response to a dry air sample. The red dashed line shows the Allan deviation corresponding to white noise behaviour.*

***Table 2** Parameters of the GLS fit of a linear analysis function to the observed nitrogen dioxide and analyser response data, for a thirty six hour period over the range x_{NO2}= (4.5-15.5) μmol/mol.*

b_0	b_1	$u(b_0)$	$u(b_1)$	Rem SSD	GOF
0.01681	1.0026	0.01167	0.00142	16.43	1.64

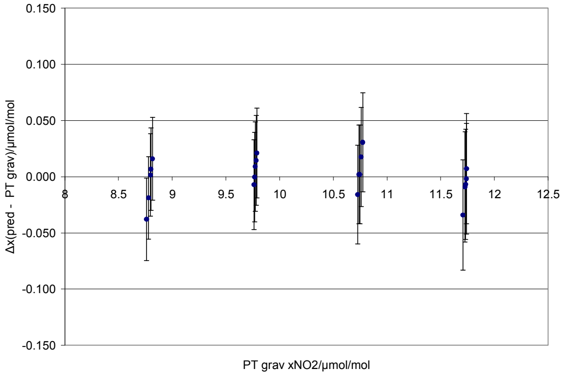


***Figure 4**. The residuals derived from the GLS self-prediction of the PT-derived standards listed in* ¡Error! No se

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[1] B_LEAST is a validated computer program that implements the recommended methods described in the International Standard ISO-6143 (Second edition 2001-0501). The program consists of the calibration module which implements the methods of determining the analysis or calibration function from calibration data, the explorer module which implements the methods of applying the analysis function parameters to measured response data (determination) and tools for production of function graphs and printing.

encuentra el origen de la referencia. *are plotted against nitrogen dioxide produced by the facility x_{NO2}.*

Table 3. *Characteristics of the VSL primary gravimetric mixtures, as provided by VSL.*

Cylinder ident.	Preparation date	Assigned NO_2 mole fraction /µmol·mol^{-1}	Certified standard uncertaint y /µmol·mol^{-1}
A	24/02/2009	10.604	0.105
B	18/03/2009	10.617	0.105
C	09/04/2009	10.608	0.105
D	09/04/2009	10.606	0.105
E	08/04/2009	10.609	0.105

Table 4. *Main impurities of the gas standards according to VSL.*

Cylinder Ident.	CH_4 / nmol·mol^{-1}	CO / nmol·mol^{-1}	CO_2 / nmol·mol^{-1}	H_2O / nmol·mol^{-1}
A	4	8	5	10
B	4	8	5	9
C	4	8	5	9
D	4	8	5	9
E	4	8	5	9

Table 5. *Mole fraction of nitric acid measured in the nitrogen dioxide gas mixtures acquired from VSL.*

Cylinder Ident.	MALT Calculated HNO_3 y / µmol·mol^{-1}	u(y) / µmol·mol^{-1}
A	0.348	0.027
B	0.214	0.023
C	0.114	0.021
D	0.155	0.022
E	0.237	0.024

4.2.2 Characteristics of the BIPM NO2 gas mixtures

From previous validation studies, nitric acid was also found to be the most important impurity in the nitrogen dioxide gas mixtures generated by the BIPM NO_2 facility.

lists the nitric acid mole fractions measured using FT-IR spectroscopy at different nitrogen dioxide mole fractions produced by the BIPM facility.

A second experimental configuration consisting of a (6.45 ± 0.08) m multipath gas cell was used to verify the mole fraction determination of nitric acid. Figure 5 plots the results of both sets of measurements demonstrating the consistency of measured values.

Table 6. *Nitric acid mole fractions calculated by MALT + CLS and the FT-IR configured with a 48 m ±1.2 m optical path gas cell.*

Pres	Temp	PT- Gravimetric x_{NO2}		Calculated HNO_3	
Torr	°C	x / µmol·mol^{-1}	u(x) / µmol·mol^{-1}	y / µmol·mol^{-1}	u(y) / µmol·mol^{-1}
795.94	25.42	9.00	0.02	0.141	0.021
795.65	25.80	10.00	0.02	0.158	0.022
795.42	26.04	11.00	0.03	0.174	0.022
795.26	25.82	12.00	0.03	0.176	0.022

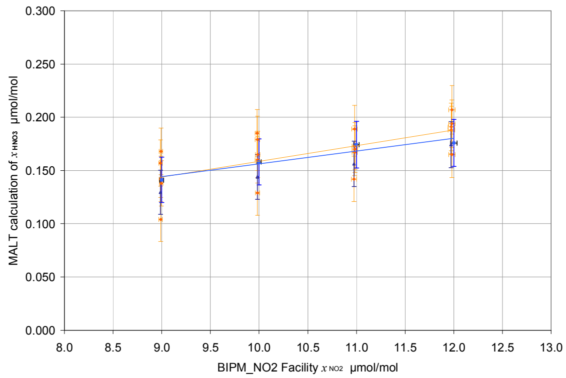

***Figure 5**. Calculated nitric acid concentration obtained by reconfiguring the FT-IR spectrometer with the a 6.4 m and a 48 m multi-pass white cells. The uncertainty bars (error bars) were calculated according equation 2.*

4.2.3 The NO2 gas comparison

In order to determine the nitrogen dioxide analyser readings for each cylinder, dynamic mixtures and cylinders were sampled alternately. Each cylinder underwent a standard analysis between four dynamic standards. There were at least four permeation tube mixtures used in each measurement, with their x_{NO2} spanning that of the set of cylinder standards analysed. As described previously, one set of ABB analyser data was collected every three seconds and each dynamically generated mixture and cylinder mixture was analysed continuously for 20 minutes, following 20 minutes of sample line conditioning. Only the last five minutes of the ABB NO_2 measurements for each mixture were used in calculations for all the samples analysed, whether dynamic or static. Using B_LEAST, GLS calibration and analysis functions were calculated for the ABB analyser response versus dynamically generated x_{NO2} data. The uncertainty of 15 nmol·mol^{-1} was assigned to the 5 minutes average ABB response for each gas mixture. As described previously, all nitrogen dioxide gas mixtures generated by the BIPM NO$_2$ facility were corrected by subtracting the calculated nitric acid mole fraction (x_{HNO3}) from the nitrogen dioxide gravimetric value, x_{NO2} according to equation 1. The standard uncertainty used for the VSL gas mixtures was the uncertainty of the certified value as listed in Table 1.

4.2.3.1 Results

The parameters of the straight-line model analysis function produced as an output by the GLS algorithm are listed in ***¡Error! No se encuentra el origen de la referencia.***. The appropriate goodness-of-fit parameter, GOF = 1.54, indicates that the input data are consistent with a straight line model function.

Table 7 *Parameters of the GLS fit of a linear analysis function to the observed nitrogen dioxide and analyser response data, for a thirty six hour period over the range* x_{NO2}*= (4.5-15.5)µmol/mol.*

b_0	b_1	$u(b_0)$	$u(b_1)$
7.763E-02	9.375E-01	3.7773E-02	3.4061E-03

Rem SSD	GOF
14.5286	1.54

The calibration line thus obtained allowed predicted values of each of the five static gas mixtures to be calculated. The predicted values were corrected for the nitric acid mole fraction found in each cylinder and then compared to the certified values. The residuals are illustrated in Figure 6. The agreement between values within their stated uncertainties indicates the consistency of the two independent methods for producing NO$_2$ standards provided nitric acid impurities can be properly quantified.

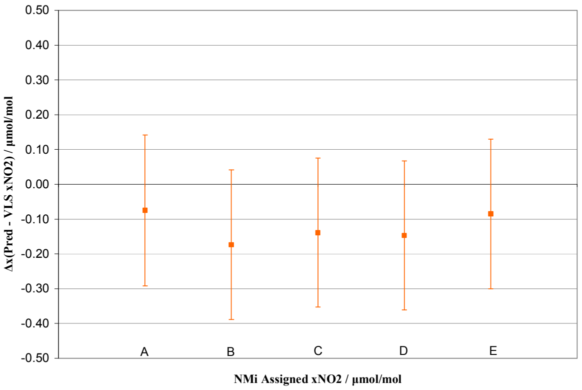

Figure 6*. Plot of the difference between values derived from GLS prediction and corrected for nitric acid against the VSL assigned* x_{NO_2}.

5 CONCLUSIONS

The BIPM NO$_2$ facility provides a reliable source of primary reference mixtures and facilitates the comparison with static NO$_2$ mixtures contained in high pressure cylinders. The expanded uncertainty of the nitrogen dioxide mole fractions generated by the BIPM NO$_2$ facility is 0.27 %. The quantification of the nitric acid mole fraction and the gas flow measurements represent 85 % of the global uncertainty. Residual water within nitrogen dioxide gas mixtures containing oxygen will lead to the formation of nitric acid. This effect appears in mixtures in high pressure cylinders, whereas permeation tubes could contain residual nitric acid which will permeate out of the tube. The BIPM's facility allows accurate measurement of nitric acid concentrations allowing corrections for the presence of this impurity.

6 FUTURE WORK

A nitric acid molecular database, traceable to the SI, will further reduce the uncertainty of nitrogen dioxide gas standards generated by the BIPM NO$_2$ facility.

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