Metrology for Nitrogen Dioxide

Best practice guide for the preparation of static primary NO_2 reference standards.

DELIVERABLE D1

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http://empir.npl.co.uk/metno2/

CONTENTS

1 OBJECTIVES 2

2 CHOICE OF CYLINDER (VALVE, CYLINDER MATERIAL, AND PASSIVATION) 2

2.1 CYLINDER VALVE 2
2.2 CYLINDER MATERIAL 2
2.3 CYLINDER PASSIVATION 2

3 GAS MIXTURE PREPARATION 3

4 PURITY OF THE MATRIX GAS 4

5 STORAGE AND USE OF THE GAS CYLINDERS 4

5.1 STORAGE 4
5.2 CONDITIONING OF GAS CYLINDERS 5
5.3 PURGING AND CONDITIONING PROCEDURE 5

6 RECOMMENDATIONS 5

7 REFERENCES 6

1 Objectives

The objective of this deliverable is to provide users with a best practice guide for the preparation of static primary NO_2 reference standards. The target amount fractions are within the range of 1-10 µmol/mol. The deliverable also addresses the issue whether the gravimetric value can be used for NO_2 standards or if a correction procedure is needed to account for the presence of NO_y impurity compounds.

After review, this report will be submitted to Euramet as D1: ’*Best practice guide for the preparation of static primary NO_2 reference standards*’.

2 Choice of cylinder (valve, cylinder material, and passivation)

NO_2 is a very reactive compound (in particular the reaction with H_2O is important). All the materials in contact with NO_2 (valve, cylinder wall, pressure regulator, sampling system) need to be compatible with NO_2.

2.1 Cylinder valve

At VSL it has been observed that using the same configuration (analyser, sampling system, and pressure regulator), there can be a significant difference in the observed time response for different cylinders. This difference is thought to be due to the cylinder valve. For a cylinder with a pressure regulator connected to it, keeping the cylinder valve open for a certain period (some hours up to 1 day) before analysis can drastically improve the time response for certain cylinders. A disadvantage of this procedure is that water can potentially enter the cylinder leading to the enhanced formation of NO_y inside the cylinder.

In general, it is recommended to use a cylinder valve with a low dead volume and a small wetted area. It is recommended to consult cylinder valve suppliers (e.g. Rotarex or GCE) to obtain the most suitable valve.

2.2 Cylinder material

Typically, there are two choices for the cylinder material: aluminium and stainless steel. For NO_2 mostly aluminium is used. An important benefit of aluminium cylinders is the much smaller mass. Within the framework of the MetNO2 project VSL tested 3 stainless steel cylinders (sausage type) with a SilcoNert 2000 coating. These cylinders showed high HNO_3 levels, possibly due to the inleak of water though the valves of this type of cylinder which are specified to have a much higher leak rate than the valves of commonly used gas cylinders.

2.3 Cylinder passivation

Within the framework of the project several cylinder treatments were tested. An overview of the cylinders tested by the different partners is shown in Table 1.

Table 1 Overview of the cylinders tested within the framework of the MetNO2 project and the performance as assessed by the partner.

Passivation	Manufacturer cylinder	Material	Water Volume (L)	Partner	Observed stability	Observed NOy	Performance (good stability, low NOy)	Remarks
AlphaTech (Air Liquide)	Luxfer	Aluminium	5 and 10	VSL	Good	~1%	Good	-
SilcoNert 2000	Swagelok	Stainless steel	3.6	VSL	Reasonable	High (up to 5%)	Bad	Probably valves are not suitable for NO_2 gas mixtures due to higher leak rate
Aculife III-IV (Scott)	Luxfer	Aluminium	5	TUBITAK	Good	-	Good	Aculife III-IV (Scott)
Experis (TC1 – Chemical treatment)	Luxfer (Air products)	Aluminium	10	LNE	Reasonable for NO_2 in N_2 Bad for NO_2 in air	-	Reasonable for NO_2 in N_2 Bad for NO_2 in air	Formation of HNO_3
NO_2 treatment (4 bars)	Luxfer (Air Liquide)	Aluminium	11	LNE	Reasonable for NO_2 in N_2 Bad for NO_2 in air	-	Reasonable for NO_2 in N_2 Bad for NO_2 in air	Formation of HNO_3
Spectraseal (BOC)	Luxfer	Aluminium	10	NPL	Reasonable	~ 1 %	Reasonable	Variable amounts of NOy observed
Megalife (Air Liquide)	Luxfer	Aluminium	10	NPL	Reasonable	~ 0.5 %	Reasonable	More consistent amounts of NOy observed

3 Gas mixture Preparation

There are two ways of preparing nitrogen dioxide standards: starting either from pure nitrogen dioxide or from pure nitrogen monoxide. Most NMI's and gas suppliers start from pure nitrogen monoxide as nitrogen dioxide is a liquid with a low vapour pressure and only available at relatively low purity (~99.5% as compared to 99.99% for nitrogen monoxide). Note that for pure nitrogen monoxide some instabilities have been reported (amongst others the formation of N_2O) and therefore it is best to use (relatively) new pure nitrogen monoxide as a source of the NO_2.

For the reasons stated above, within the MetNO2 project all partners opted to start from pure nitrogen monoxide. From the pure nitrogen monoxide, nitrogen monoxide mixtures are prepared in nitrogen. Typically, two or more steps are used to obtain the final premixture which will be in the higher µmol/mol range. To prepare nitrogen dioxide mixtures, first oxygen or a mixture of oxygen in nitrogen is added. In the final step nitrogen is added. As an example, to prepare a 10 µmol/mol NO_2 in nitrogen gas standard, one can start with a NO in N_2 premixture with a NO amount fraction up to a few hundred µmol/mol, to which an O_2 in N_2 mixture and finally nitrogen are added. The added amount of oxygen is so that the final amount fraction of O_2 left (after reacting with NO) is around 1000 µmol/mol.

The gravimetric uncertainty is small (typical values are in the order of 0.02%). However, the actual uncertainty of NO_2 mixtures is typically 100 times higher. One of the largest sources of uncertainty in the preparation of static NO_2 standards is the presence of water which reacts with NO_2 creating nitric acid (HNO_3) [1], and therefore creates a discrepancy between the gravimetric and actual amount fractions. There are several reaction pathways possible including:

$$2\ NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

$$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$$

Due to the complicated reactions of nitrogen dioxide with water, it is possible to create several impurities, such as nitrogen monoxide and nitrous acid (HNO_2). During the preparation of nitrogen dioxide reference standards, it is important to minimise water through all parts of the preparation process. Measures which can be taken include the use of purifiers to dry gases and heating the materials used for the mixture preparation to remove adsorbed water. Further, during use of the gas standard measures should be taken to minimize the ingress of water (see section 5.3 for more details).

Note that for NO_2 amount fractions above around 100 µmol/mol the equilibrium with its dimer nitrogen tetroxide (N_2O_4) becomes relevant (for a 100 µmol/mol NO_2 mixture about 0.1% will be in the form of N_2O_4 while for a 1000 µmol/mol mixture this has increased to 1%).

4 Purity of the matrix gas

For NO_2 gas mixtures prepared in nitrogen (with typically around 1000 µmol/mol O_2 added) only the purity of nitrogen is important. Nitrogen is available at high purity, for example BIP Nitrogen from Praxair which contains less than 20 ppb H_2O, and other major companies supply nitrogen of similar quality. For NO_2 gas mixtures prepared in a matrix of air the purity of the used O_2 is of importance. O_2 is available at a much lower purity than N_2. In particular, the moisture level in O_2 is much higher (a short survey showed that for the best available pure O_2 the content of H_2O was <0.5 ppm). This relatively high moisture level will impact the formation of NO_y in the NO_2 gas mixture. Use of an additional purifier during the filling may help to lower the moisture level and hence reduce the formation of NO_y.

5 Storage and use of the gas cylinders

5.1 Storage

The storage and operation of gas mixtures in cylinders are often limited to certain temperature ranges. If the cylinder is stored at or exposed to temperatures below the stated range, some components may condense and lead to a possible change in the composition of the gas mixture.

It is recommended to avoid high temperatures (heating) close to the cylinder, e.g. from ovens or other intensive heat sources. High temperatures will result in higher pressures leading to potentially hazardous situations. In addition, elevated temperatures may result in the decomposition of thermally unstable species.

5.2 Conditioning of gas cylinders

Gas mixtures may need to be homogenized again if stored for long periods of time and if exposure to temperatures below the condensation point of one or more substances cannot be excluded. This may be done by bringing the cylinders up to ambient temperature and rotating them horizontally for an appropriate amount of time, which may depend on the matrix gas and the components.

It is further advised to store the cylinders for a minimum of 24 hours at laboratory temperature prior to their use.

5.3 Purging and conditioning procedure

The transfer line integrity, including the leak tightness and cleanliness of all of the components (pressure regulator, valves, transfer line, connections, etc.) shall be guaranteed to avoid contamination of the system and of the gas cylinder. In order to guarantee this appropriate equipment, choice of materials and purging procedures should be used. For reactive gases such as NO_2 it is advised to purge the transfer line with a flow higher than the flow to be used to generate the reference gas mixture. For adsorbing molecules like NO_2 conditioning the entire gas system with the gas mixture for an appropriate time (maximum two hours) saturates the adsorbing sites of the walls, resulting in more stable compositions.

It is recommended to sequentially pressurise, vent and evacuate all components of the transfer system with the gas mixture to be used by a membrane pump (ideally to ≤10 mbar). This method requires typically three cycles. In case evacuation is not possible, five to eight pressurising cycles are recommended. The insertion of a stop valve after the pressure regulator is recommended for safety reasons. An additional conditioning period of typically one to two hours followed by a final pressurising/venting cycle (not evacuation) further ensures the stability of the gas composition.

6 Recommendations

Currently several NMI’s use a correction factor for the gravimetric value for reactive compounds in cylinders like ammonia or ethanol. Such gases adsorb on the cylinder wall and for the loss a correction is applied (see e.g. CCQM-K93: Preparative comparison of ethanol in nitrogen [2]). In the case of NO_2 gas mixtures there might be some loss due to adsorption, but the main loss is due to the formation of NO_y compounds. Within this project only HNO_3 has been observed as an impurity and the amount fraction of this compound was in line with results of studies carried out by BIPM (CCQM-K74 key comparison [3]) and NIST (already done at the end of the 1980s [4]).

For NO_2 mixtures which were correctly prepared in suitable cylinders the HNO_3 amount fraction is about 1% which typically increases over time. It seems that the observed HNO_3 cannot account for all of the losses of NO_2 observed (more data is needed to substantiate this). Possibly some compounds are still on the cylinder wall or, less likely, other compounds are formed which have not been analyzed.

It is recommended to make a correction for the observed HNO_3. Note that better and faster measurement methods for HNO_3 are needed as it currently takes about 45 minutes (CRDS) or even more than 1 hour for FTIR in order to get a stable HNO_3 reading from a NO_2 mixture using a flow rate of 0.5 L/min.

7 References

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