

## ANALYTICAL DEVELOPMENT FOR THE STABILITY OF SUB-PPM NITROGEN OXIDE (NO<sub>x</sub>) MIXTURES IN CYLINDERS

E. Coffre<sup>a</sup>, M. Haouchine<sup>b</sup>, A. Grimberg<sup>a</sup>, V. Bossoutrot<sup>a</sup>, T. Jacksier<sup>b</sup>

<sup>a</sup> Air Liquide, Centre de Recherche Claude-Delorme, Les Loges-en-Josas B.P. 126  
78350 Jouy-en-Josas, France

<sup>b</sup> Air Liquide, Chicago Research Center, 5230 S. East Ave.  
Countryside, IL 60525 USA

Email: [Valerie.Bossoutrot@airliquide.com](mailto:Valerie.Bossoutrot@airliquide.com)

### Introduction

NO<sub>x</sub> is a generic term for a group of reactive gases containing both Nitrogen and Oxygen in varying amounts. These gases are released into the atmosphere when fossil fuels (coal, gasoline...) are burned at high temperature. The main sources of NO<sub>x</sub> are motor vehicles, electric utilities, and other industrial, residential, and commercial sources that burn fuel. NO<sub>x</sub> has been identified as the primary cause for the formation of ground-level ozone, which leads to serious respiratory problems. It is also responsible for a variety of other health and environmental hazards such as acid rain, global warming, toxic chemicals and atmospheric particle formation. (1)

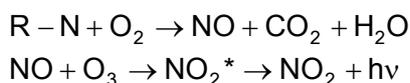
As a result, many countries and organizations around the world are increasingly regulating NO<sub>x</sub> emissions to the atmosphere. The primary regulations aim at drastically decreasing the amount of NO<sub>x</sub> released, especially by engines used in transportation and utility/industrial/residential boilers. Therefore, professionals not only have to find ways of limiting and/or controlling NO<sub>x</sub> emissions, but prior to that they must have reliable and precise means of measuring ever-decreasing concentrations. In this perspective, there have been considerable efforts by instrument manufacturers to lower detection limits to sub-ppm levels. Also important are the availability and reliability of the standards used to calibrate those instruments. In this paper, a method for low-level NO<sub>x</sub> analysis using a Nitrogen Chemiluminescence Detector coupled to a Gas Chromatograph (GC-NCD system) is developed. Finally, a proprietary cylinder treatment developed for the storage of low-level reactive compounds is shown to be successful in storing ppb levels of Nitrogen Oxide (NO) and Nitrogen Dioxide (NO<sub>2</sub>) for at least 11 months and 4 months respectively.

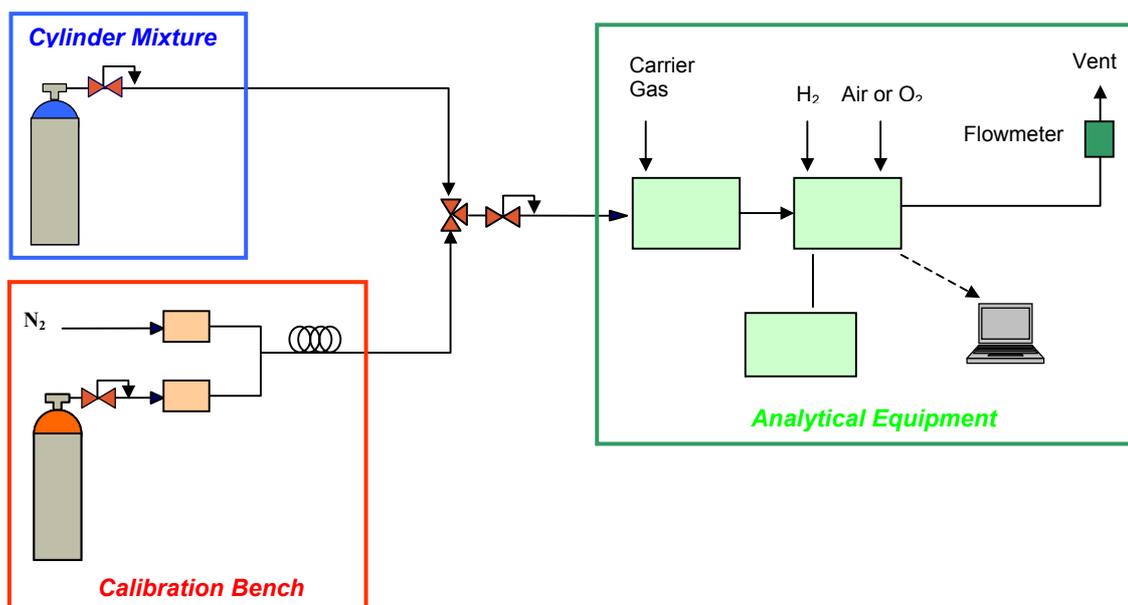
### Gas Chromatograph – Nitrogen Chemiluminescence Detector (GC-NCD)

A Varian 3800 Gas Chromatograph was connected to an Ionics Sievers 255 Nitrogen Chemiluminescence Detector. This system (GC-NCD system) was then optimized for the analysis of sup-ppm levels of Nitric Oxide (NO). The main parameters that were optimized during our study are presented in the following sections.

#### *Experimental Set-up*

The set-up used is presented on Figure 1. A three-way valve allowed the selection between a calibration bench and a cylinder with unknown concentration to be directed to the analytical equipment. The NCD is a detector specific to Nitrogen compounds. It operates using the chemiluminescence reaction of Nitric Oxide with Ozone:





**Figure 1** : GC-NCD system set-up

**GC and NCD Conditions**

The main conditions used for this system are given in Table 1. The system was optimized in order to increase the sensitivity and reproducibility of the analysis. Several parameters were adjusted on both the GC and the NCD, and in the following section, optimization details are provided for some of these parameters.

**Table 1** : GC and NCD conditions

Gas Chromatograph	
Column Pressure	55.2 KPa *
Carrier Gas	2 mL/min *
Oven Temperature	80°C
Sample Flow Rate	18 mL/min
Sample Loop Volume	100 µL
Capillary Column	GS-200

\* for a 30m x 0.53mm column

Nitrogen Chemiluminescence Detector	
High Voltage Gain	1000 V
Peltier Cooler	-16°C (±1°C)
Gas for Ozone generator	Air at 41.4 KPa
Burner Pressure	< 26.7 KPa
Burner Temperature	800°C
Burner Gas	H <sub>2</sub> at 5 mL/min O <sub>2</sub> at 10 mL/min

**- Burner Conditions**

The Hydrogen and Oxygen plasma in the combustion tube converts all Nitrogen compounds into Nitric Oxide. The formed Nitric Oxide then reacts with Ozone to produce electronically excited Nitrogen Dioxide, which emits light when relaxing to its stable state. Oxygen is supplied to the burner either as pure Oxygen or as compressed air. Also, the burner temperature can be controlled and adjusted up to about 1000°C.

The detector was first tested with a set of conditions for the burner that was given by the literature as being standard conditions for Nitrogen Oxides analysis. These conditions are given in Table 2.

**Table 2** : Original burner conditions

Burner Pressure	< 26.7 KPa
Burner Temperature	1000°C
Burner Gas	Hydrogen at 5 mL/min and Air at 60 mL/min

In order to assess the performance of the detector at given conditions, five runs were performed and averaged. The relative standard deviation (RSD) was calculated as well as the Response Factor (RF):

$$RSD = \frac{\text{Standard Deviation (Area)}}{\text{Average Area}} \times 100 \%$$

$$RF = \frac{\text{Average Area}}{\text{Concentration(ppb)}} \quad (\mu\text{V}\cdot\text{min})/\text{ppb}$$

The results for each set of conditions are given on Table 3.

**Table 3** : Burner conditions optimization and results

Original Conditions			O <sub>2</sub> supply adjusted			Burner temp. adjusted		
NO (ppb)	RSD %	RF	NO (ppb)	RSD %	RF	NO (ppb)	RSD %	RF
10000	7.9	0.06	970	3.1	0.11	133	3.1	0.23
3300	17.3	0.04	530	7.3	0.14	106	5.7	0.23
1670	43.0	0.05	305	20.0	0.14	85	4.6	0.23
910	49.6	0.03						

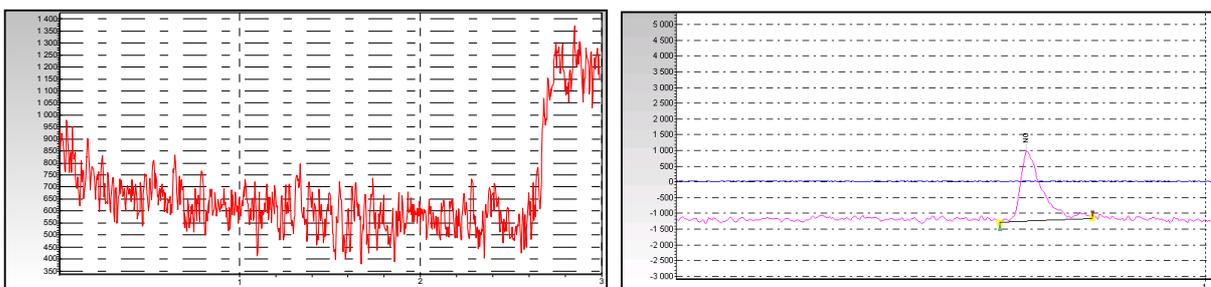
Air to pure O<sub>2</sub>
1000°C to 800°C

Using the original conditions listed in Table 2, the analysis proved to be very difficult owing to a very low sensitivity and low reproducibility. When air was switched to pure Oxygen, not only the response factor (RF) was improved by a factor of about three, but also the RSD was greatly improved, and sub-ppm analysis was then possible. Similarly, when the burner temperature was decreased, the response factor was doubled and the RSD was decreased to about 5%, even for concentrations below 100 ppb.

These improvements allowed detection limits lower than target of 100 ppb as well as stable and repeatable results to be achieved.

#### - Carrier Gas

In this study two different inert gases were considered for use as carrier gases: Nitrogen and Helium. A 10-ppm standard of Nitric Oxide in Nitrogen was run with Nitrogen as the carrier gas. The chromatogram is given on Figure 2a. It appeared that the baseline was very noisy and not stable. This was probably caused by the fact that a large amount of Nitrogen was injected in the burner (standard matrix gas and carrier gas), which may have triggered conversion of Nitrogen and created interferences with the signal.



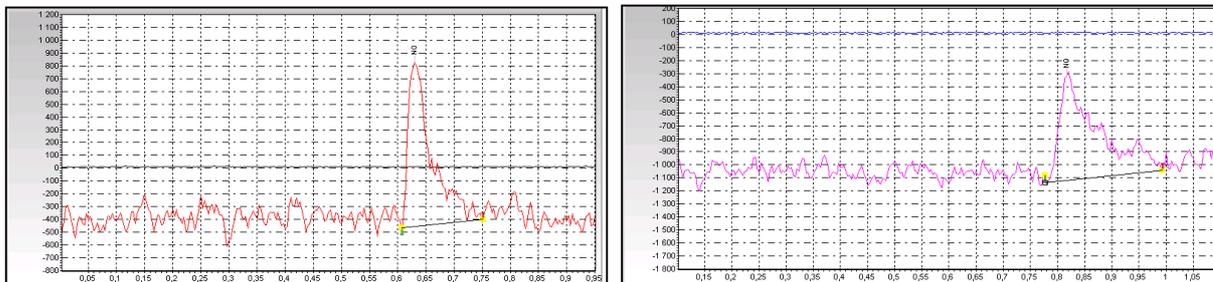
**Figure 2** : a) 10 ppm NO in N<sub>2</sub> with N<sub>2</sub> as carrier gas; b) 0.97 ppm NO in N<sub>2</sub> with He as carrier gas

A 970-ppb standard of Nitric Oxide in Nitrogen was then run with Helium as carrier gas. The chromatogram is given on Figure 2b. The baseline exhibited enhanced stability with a significantly lower noise level. Also, the peak for NO had a good shape that was easily integrated. Furthermore, when performing multiple injections, it was observed that the response was sufficiently repeatable. As a result, for the rest of the study, Helium was utilized as the carrier gas

#### - Sample Loop Volume

The sample loop allows the user to choose a sample volume to be injected into the column. Using a larger sample loop means that a larger amount of sample is passed through the column to the detector. As a result, it is expected that the signal obtained be larger. However, since a capillary column was used, column overloading may occur leading to a distorted

signal. Two sample loop volumes were examined in this study, 100  $\mu\text{L}$  and 250  $\mu\text{L}$ . The GC and NCD conditions were the same for both runs and the samples were 530 ppb NO in  $\text{N}_2$  and 478 ppb NO in  $\text{N}_2$  respectively. The chromatograms for each run are given in Figures 3a and 3b. The NO peak appeared to be much sharper when using the 100  $\mu\text{L}$  sample loop. The broadening effect observed in Figure 3b may be explained by the column overloading. Therefore, peak integration and NO quantification was easier and more precise with the smaller sample loop. The 100  $\mu\text{L}$  sample loop was chosen for the remaining of the study.



**Figure 3** : a) 530 ppb NO in  $\text{N}_2$  with a 100  $\mu\text{L}$  sample loop; b) 478 ppb NO in  $\text{N}_2$  with a 250  $\mu\text{L}$  sample loop

#### - Column Selection

Several capillary columns were tested for NO analysis. Since these columns had different stationary phases, very distinct results and column behaviors were expected. The list of columns that were investigated are given in Table 4, with corresponding dimensions and phase for each column.

**Table 4** : Tested Columns

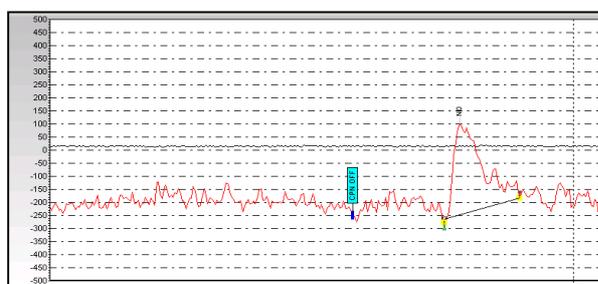
Manufacturer	Column Name	Dimensions	Stationary Phase
Varian	CarboPlot	25 m * 0.53 mm	Bonded Carbon Layer
Varian	CarboBond	25 m * 0.53 mm	Bonded Carbon Layer
J&W (Agilent)	MolSieve 5A	30 m * 0.53 mm	5Å Molecular Sieve
J&W (Agilent)	GS-Q	30 m * 0.53 mm	Porous Divinylbenzene Homopolymer
J&W (Agilent)	DB-200	30 m * 0.53 mm	(35% Trifluoropropyl)-methylpolysiloxane

#### - CarboPlot and CarboBond

After many attempts to passivate the inside column with a mixture of 10-ppm Nitric Oxide in Nitrogen, NO was still being retained by the column. Therefore, these columns are not suited for NO analysis, even at higher concentrations such as 10 ppm.

#### - MolSieve 5A

The column was conditioned by running multiple 10 ppm samples of NO in  $\text{N}_2$ , until the signal was constant. Then, an 85 ppb NO sample in  $\text{N}_2$  was run and the chromatogram obtained is shown on Figure 4. The peak was integrated and the area measured, however because 85 ppb is close to the detection limit with this column, the measurements were not repeatable.



**Figure 4** : 85 ppb NO in  $\text{N}_2$  on a MolSieve 5A column

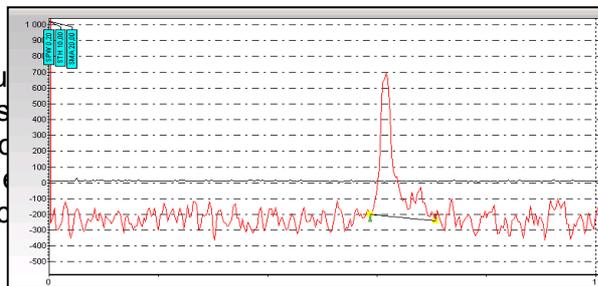
- GS-Q

This column widely used for NO measurement within different mixtures of light gases. After conditioning the column by injecting multiple samples of 10 ppm NO in N<sub>2</sub>, a 534 ppb sample of NO in N<sub>2</sub> was run and integrated. The chromatogram is shown on Figure 5. The peak was sharp and the measurements repeatable at that concentration. However, the detection limit was too high for analysis at levels below 100 ppb.

**Figure 5** : 534 ppb NO in N<sub>2</sub> on a GS-Q column

- DB-200

As for the previous column, the chromatogram presented a sharp peak for an 85 ppb sample of NO in N<sub>2</sub>. The peak was the lowest out of the columns that were tested. Therefore, the DB-200 column from J&W was chosen.



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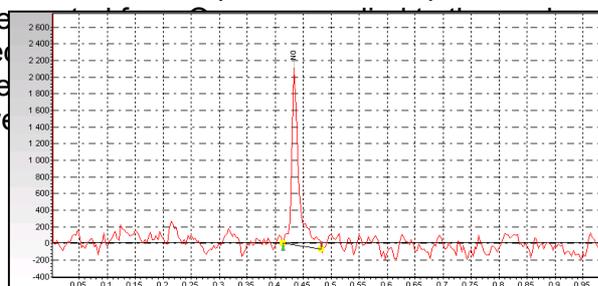
**Figure 6** : 85 ppb NO in N<sub>2</sub> on a DB-200 column

Summary

This GC and NCD system offers a good analytical solution for low-level Nitric Oxide measurement (100 ppb and below). This system is especially helpful for analysis of NO in various matrices (such as hydrocarbons) that may interfere with the chemiluminescence detection method. Since an effective separation is performed in the capillary column, these interferences may not affect the NO signal. However, analytical development is still needed for each matrix in order to optimize the performance of the system. Furthermore, this system proved to be very sensitive to any external disturbance and required regular tuning and maintenance. Thus, this system is well suited for being used in a laboratory environment; on the other hand, integration in a plant may prove to be very difficult and inappropriate.

**Environnement S.A. AC32M Online Analyzer**

The AC32M model from Environnement S.A. is a total NO<sub>x</sub> analyzer using the chemiluminescent reaction of Nitric Oxide with Ozone as a detection method. It also uses a NO<sub>2</sub> to NO converter in order to measure total NO<sub>x</sub>. The NO<sub>2</sub> concentration can then be accessed by subtracting the NO concentration from the total NO<sub>x</sub> concentration. Measurements were performed on samples at ambient pressure and temperature and, as for the NCD, ozone was generated on site. The manufacturer specifies a detection limit, stability and linearity of the analyzer. The performance figures were compared to the detection limit, stability and linearity of the analyzer. It was observed that the



analyzer was suitable for measuring levels below 100 ppb of NO and NO<sub>2</sub>. The stability and linearity also seemed to be very good for our application.

**Table 5** : Environnement S.A. Model AC32M Specifications

Noise Level ( $\sigma$ )	0.2 ppb
Lower Detectable Limit ( $2\sigma$ )	0.4 ppb
Response Time	Minimum 30 s
Linearity	$\pm 1\%$ of Full Scale
Sample Flow Rate	0.7 L/min

This total NO<sub>x</sub> analyzer exhibited very good performance such as detection limit, linearity and stability. Furthermore, the ease of use and the fact that it is a continuous analyzer make it very appropriate for plant operation. However, a few limitations for this system were identified:

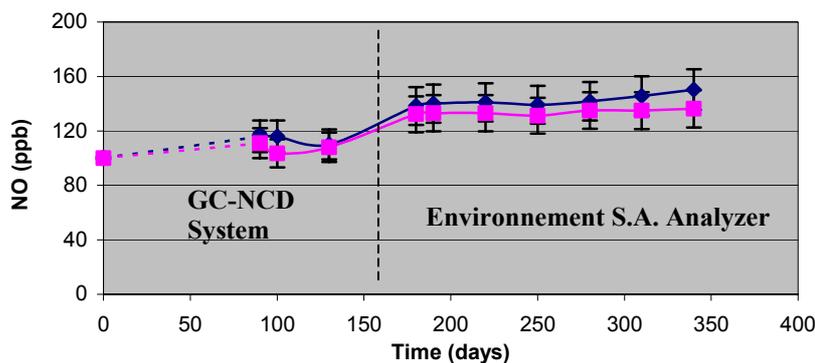
- Results for NO<sub>2</sub> quantification are not direct. No separation between compounds is performed; instead these results are based on calculation and may lead to higher errors.
- Because of some interference with the chemiluminescence reaction, measurement in hydrocarbon matrices is not possible.
- Owing to the high sample flow rate and the response time, the volume of sample needed for correct analysis appears quite high.

### Low-Level NO<sub>x</sub> Storage in ALPHATECH™ Cylinders

ALPHATECH™ is a proprietary cylinder treatment\* that was developed for the storage of low-level reactive gas mixtures in compressed gas cylinders. It was the goal of this study to assess the applicability of this treatment to low-level NO<sub>x</sub> standards. Four cylinders were ALPHATECH™ treated and then two were filled with 100 ppb NO and two with 100 ppb NO<sub>2</sub> in Nitrogen balance. The shelf life of these cylinders was monitored over time using the GC-NCD system as well as the Environnement S.A. analyzer model AC32M described previously. The stability data is shown in Figure 7 for NO and in Figure 8 for NO<sub>2</sub>.

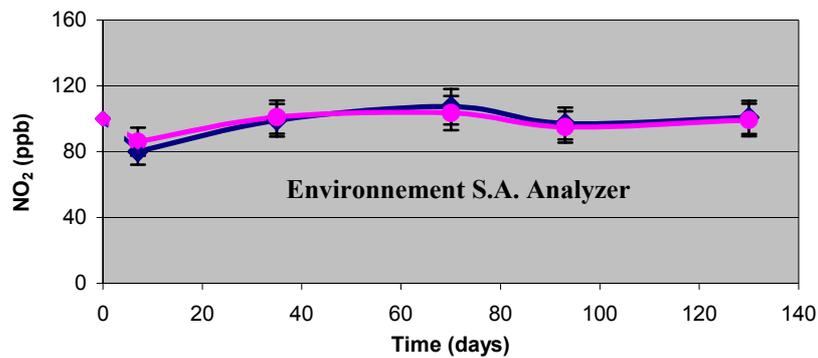
For both cylinders filled with NO, it appears that there was a discrepancy between the concentration measured by GC-NCD (around 110 ppb) and the one measured by the analyzer (around 140 ppb). This difference cannot be completely explained at the moment, however within the measurement made by one system, it seems that both cylinders remain stable for at least 11 months.

For the cylinders filled with NO<sub>2</sub>, only the analyzer from Environnement S.A. was used, and the data is very consistent throughout the monitoring period of about 4 months. The Relative Standard Deviation over that period was less than 11% for both cylinders.



**Figure 7** : Shelf-life of 100 ppb NO in N<sub>2</sub>

\* Patents pending



**Figure 8** : Shelf-life of 100 ppb NO<sub>2</sub> in N<sub>2</sub>

### Conclusions

A method for NO<sub>x</sub> analysis by GC-NCD has been developed and optimized in order to obtain low detection limits with repeatable and stable measurements. This method was compared to a total NO<sub>x</sub> analyzer, which is widely used in the industry. It was found that the GC-NCD system gave satisfactory results and could be utilized for NO<sub>x</sub> measurements in different matrices, especially in hydrocarbons, even though, because of its fine-tuning, high maintenance and high price, this system is best used in a laboratory setting. On the other hand the total NO<sub>x</sub> analyzer, which has a better detection limit, could be used in a plant environment since it is easy to use and requires a continuous sample flow. However, this analyzer does not allow measurement in diverse matrices (analysis not possible in hydrocarbon) and requires a high sample flow rate. Finally, it was also shown that ALPHATECH™ treated cylinders can be used for storage of sub-ppm level of NO and NO<sub>2</sub> in balance Nitrogen.

### Acknowledgements

The authors wish to thank Randy Shearer of Ionics Sievers for his useful discussions during the initial phases of this work. The authors also wish to extend their gratitude to Youssef Guillard for his significant contribution to this work.

### References

1. United States Environmental Protection Agency, "NO<sub>x</sub>, How Nitrogen Oxides affect the way we live and breathe", EPA-456/F-98-005, September 1998