

Low Level Nitric Oxide and Nitrogen Dioxide Cylinder Gas Stabilization and Analysis by FTIR

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Standards were prepared using state-of-the-art cylinder passivation and blending, and analyzed with FTIR to show successful packaging of low level NO, NO₂, and mixed component standards.

Introduction

Compressed gas cylinders have been used for well over one hundred years in a multitude of different applications and industries. Applications are as diverse as breathing oxygen mixtures for human use in medicine and diving, to highly reactive silane mixtures used in electronics chip manufacturing, to 65–100 component (and greater) mixtures at parts-per-billion levels for environmental monitor calibration. With increasing demand for exact low-level environmental monitoring of noxious materials, new challenges have arisen for providing stable mixtures of gases at extremely low concentration levels. Some of these gases are very reactive and require specialized procedures for handling and stable storage.

Two materials which elicit such interest are nitric oxide (NO) and nitrogen dioxide (NO₂). These gases are normally monitored individually, or the concentrations can be combined and reported as a total NO_x measurement depending on specific requirements. There are a number of analytical techniques for determining the concentration of the materials in a gas matrix, but the two most widely used methods are chemiluminescence and infrared absorption (Fourier Transform Infrared Spectroscopy – or more simply, FTIR). Both techniques are capable of measuring low concentrations of NO and NO₂ in a gas matrix down to low parts-per-billion (ppb) levels. However the FTIR is capable of analyzing numerous additional components in a single analysis.

Theory and Practice

Reactive gas stabilization in cylinders remains a topic that could easily fill a number of lengthy books; however the principles are straightforward. These technologies rep-

resent a significant amount of the intellectual property of specialty gas producers. The basic concept of reactive gas containment consists of correct material selection based

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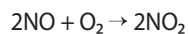
on the material of interest (aluminum or steel cylinder; stainless steel cylinder valve and regulation assembly, etc.) followed by correct preparation of the container.

A typical initial preparation of a compressed gas cylinder in the specialty gas industry includes a heat and evacuation cycle to remove atmospheric components and residual water from the cylinder's internal surfaces. Contamination, such as water, adsorbed on the cylinder wall is the primary cause of degradation of reactive gas mixtures across a wide diversity of materials. Obvious components susceptible to water induced degradation would be acid or base gases such as hydrogen chloride, hydrogen fluoride, ammonia, and others. A more important side-effect of this type of degradation is the formation of rust on some cylinder walls and a potential compromise of cylinder integrity. Less obvious components susceptible to this type of degradation would include nitric oxide, nitrogen

dioxide, sulfur dioxide, formaldehyde, and others. One degradation path associated with NO and NO₂ mixtures is the formation of nitric acid (HNO₃), which can be found in some higher level NO₂ standards either as a result of poor preparation or the advanced age of the standard.

Secondary treatment regimens for the stabilization of these materials vary with the company manufacturing the mixture. Passivation regimens available and currently in use include a number of different cylinder acid washes, abrasive polishing techniques, non-reactive metal coatings (such as nickel), polymer coatings, deactivation techniques borrowed from the gas chromatography column conditioning industry, anodizing, and simple cylinder pretreatment with the component of interest (known in the industry as "pickling"). All of these techniques can be used with varying degrees of success for one or more reactive species and, depending on implementation and process control, some are ultimately more effective than others.

Nitric oxide presents a unique challenge because of its high reactivity with oxygen. The following chemical reaction shows that one molecule of oxygen will react spontaneously with two molecules of NO to form two molecules of NO₂:



This means that a standard blended at a 10 ppm concentration of NO requires only 5 ppm of oxygen contamination to convert completely to 10 ppm of NO₂. Another implication of this reaction ratio is the requirement of a pristine environment used in handling the components of interest. The cylinder must be ultra clean as discussed above and, additionally, the blending manifolds and associated gas-handling systems must be non-reactive and contain no trace of oxygen contamination. Oxygen tends to have a ubiquitous presence

in all systems because of its high concentration in the air we breath. All other supply gases introduced into the cylinder (specifically the balance gas of the mixture) must also be oxygen free to a high degree of certainty. Therefore, the first challenge is to introduce the components into a pristine environment without initially causing a condition that will precipitate decomposition.

The second challenge is to sta-

bilize the formulated material with respect to the interaction with the cylinder material thereby causing mid- and long-term degradation of the standard concentration. A proprietary combination of passivation technologies are currently used in our processes to render the surface of the cylinder non-reactive to the NO and NO₂ components.

There is also a widely held belief in the industry that NO and NO₂ cannot

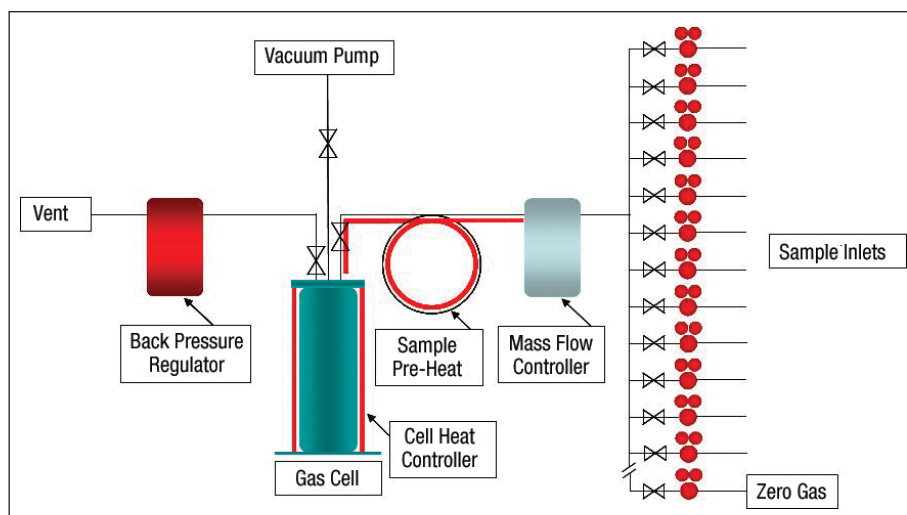


Figure 1. Typical configuration for an FTIR gas analytical delivery and control system including multiple sample inlet ports, flow control, pressure control, and temperature control systems

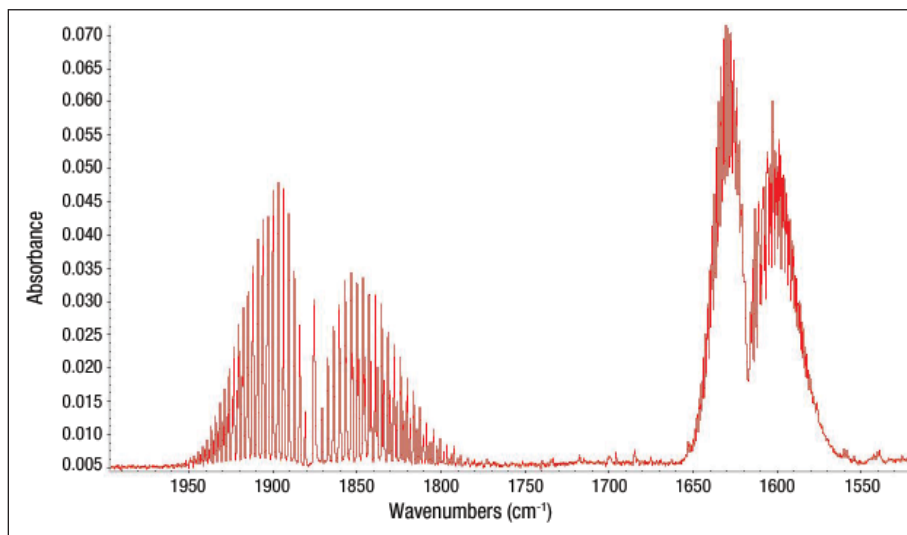


Figure 2. FTIR spectral data showing both nitric oxide and nitrogen dioxide in the same sample. The absorbances based around 1875 cm⁻¹ represents the nitric oxide component at 18.4 ppm concentration. The absorbances based around 1618 cm⁻¹ represents the nitrogen dioxide component at 3.5 ppm. As shown in this example, the nitrogen dioxide molecule is a much stronger absorber of infrared radiation than the nitric oxide molecule.

be reliably packaged in the same cylinder due to the chemical reaction shown previously. However, this would result in an unstable mixture only if the reaction proceeds in both a forward and reverse direction to an appreciable extent. In chemical reactions the reverse reaction can always occur but the reaction of NO and oxygen is highly favored to move only in the forward direction. In other words, if there is any free oxygen in the container it will react completely with the NO to form NO₂. We have developed the methodology to successfully and accurately formulate low concentrations of NO (with a zero to negligible presence of NO₂), NO₂, and mixtures of NO and NO₂ at low levels.

All cylinders formulated in our facility are blended using gravimetric addition and serial dilution. This method involves the addition of gases into a cylinder in a controlled manner by weight. Ensuring that weight additions are greater than 40 grams allows control of the blending procedure to much better than ± 1% target accuracy even with multiple serial dilutions. With correct implementation and control, this methodology produces the highest quality and accuracy of any formulated gas standards.

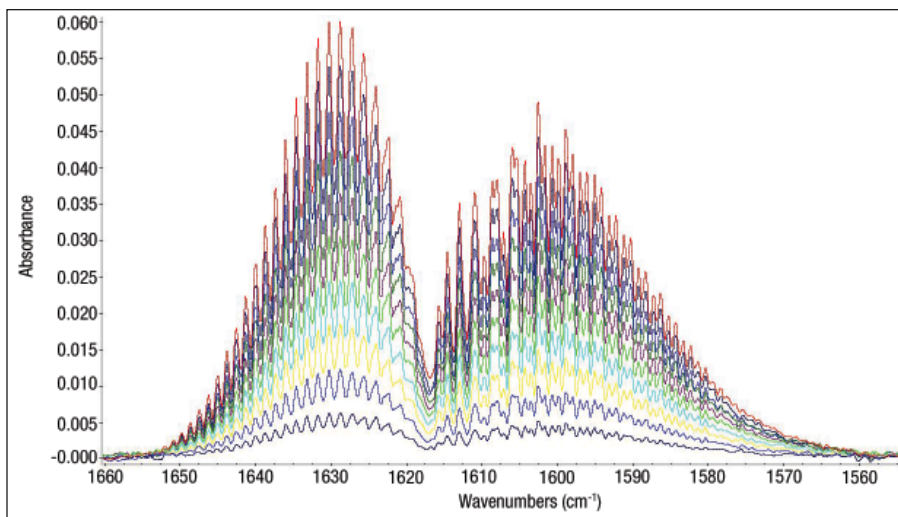


Figure 3. Nitrogen dioxide FTIR spectral data presented in an overlay showing the calibration series used to generate the data in Table 1.

Experimental

Accurate standards were prepared using gravimetric blending and serial dilution technology in our facility to target concentrations. A number of NO test cylinders were prepared to 0.67 ppm (670 ppb) concentration with a target specification for the NO₂ of less than 0.03 ppm (30 ppb). Combination standards were prepared using similar

PEAK AREA	ACTUAL PPM Concentration	PREDICTED PPM Concentration	% ERROR
0.000	0.00	-0.010	N/A
0.224	0.35	0.352	+0.6
0.417	0.67	0.661	-1.3
0.641	1.00	1.021	+2.1
0.840	1.33	1.341	+0.8
1.050	1.67	1.679	+0.5
1.246	2.00	1.993	-0.2
1.442	2.33	2.303	-0.9
1.658	2.67	2.655	-0.6
1.870	3.00	2.997	-0.1
2.088	3.33	3.346	+0.5

Table 1. FTIR analytical data used to calculate the calibration curve regression fit for the nitrogen dioxide analysis from 0 to 3.33 ppm. Also included in the data are the returned values for the actual data points from the linear regression and the error associated with the fit for each point.

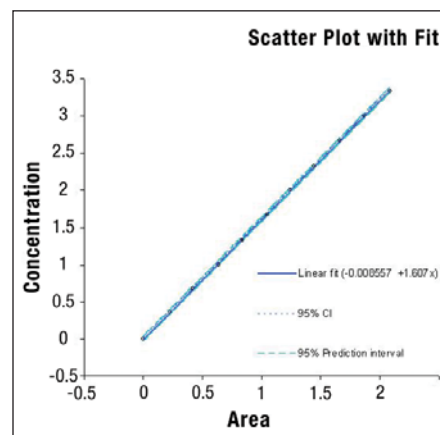


Figure 4. Regression analysis scatter plot data for the nitrogen dioxide calibration curve for 0 to 3.33 ppm showing a true linear data function to a high degree of accuracy

techniques at the 18.4 ppm NO/3.5 ppm NO₂ target concentration. All NO and NO/NO₂ mixtures were made in nitrogen. All NO₂ standards were formulated in an air balance gas. Other standards were formulated to various concentrations as test and calibration mixtures.

All analyses were performed using a Thermo Nicolet Magna 750 FTIR spectrometer fitted with an 8.4 meter folded path gas cell supplied by Gemini Optics (see Figure 1 for a typical FTIR sampling system design). The resolution of the spectrometer was set to 0.5 cm⁻¹ and 128 scans were accumulated.

The sample introduction and control (pressure = 1000 torr, flow = 3 liters per minute, and temperature = 25°C) were achieved by a delivery system designed and built in our facility to reproducibly sample gas streams for FTIR analysis. Dilution calibration curves were generated by a computer controlled dilution system designed and implemented by Custom Gas Solutions. The NO concentration was monitored by IR absorbance in the spectral region of 1960–1780 cm^{-1} and the NO₂ concentration was monitored by IR absorbance in the spectral region of 1660–1550 cm^{-1} (see Figure 2). There were no interferences in the absorbance assigned in these regions. The limit of detection on the NO in the experimental configuration is approximately 50–100 ppb. The limit of detection of the NO₂ is approximately 5–10 ppb. As evidenced by this comparison, NO₂ is a much stronger absorber of IR radiation than NO, making its detection at ultra-low levels easier.

Results

The FTIR system was calibrated for NO₂ with a ten point calibration curve from 3.33 ppm to 0.35 ppm, and the results were fit with a linear regression function to a high degree of accuracy as demonstrated in the attached table (see Table 1). The FTIR spectra data for the NO₂ component is shown as an overlay in Figure 3. The actual overlay of the fitting function with the data is shown in Figure 4. The calibration for the NO can be demonstrated with similar results. As demonstrated in this discussion, FTIR is a highly capable instrument for quantitative analyses of gaseous mixtures.

Six NO standards were blended to 0.67 ppm and showed no detectable NO₂ by FTIR immediately after blending. The cylinders were held for two weeks to allow any residual oxygen to react with the blended NO. There was still no detectable degradation of the NO component and no detectable NO₂ presence. These mixtures will continue to be monitored for stability over time.

The mixtures of NO and NO₂ were analyzed immediately after blending and found to match the gravimetrically determined concentration to within an error of approximately $\pm 2\%$. They were then analyzed at

two weeks of age to determine short term stability. There has been no change or variance in these standards to date.

Conclusion

Current technology and methods used in our facility were successful in packaging low level NO, NO₂, and mixed component standards. NO and NO₂ were used here to demonstrate the issues that can arise with any compressed gas standard. All standards in the specialty gas industry are subject to these concerns to a greater or lesser degree. The critical production/process components lending credibility over time to any calibration gas standard must be stringently specified and controlled through the entire production process from the selection of materials used in the package to the final hold times and



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analytical release processes. Best practices and current state-of-the-art technologies are quite capable of producing reliable materials for the calibration-sensitive laboratory and, in many cases, FTIR should be the method of choice for high precision quantitative analysis.

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