

## Detecting single-digit parts-per-billion levels of moisture in ammonia gas

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**A**n increasingly important chemical used in the manufacture of electronic devices such as high-intensity light-emitting diodes (LEDs) is ultra-high-purity (UHP) anhydrous ammonia. However, the presence of residual trace moisture in UHP ammonia is a

process instrument with a single-digit parts-per-billion detection limit that can measure moisture in ammonia.

The challenge posed by moisture in ammonia has driven the development of continuous-detection instrumentation. Because ammonia and water are chemi-

cally similar, spectroscopic methods have proven to be the most promising option for detecting trace moisture in ammonia down to parts-per-billion levels. Since the mid-1990s, Fourier-transform infrared spec-

*Tests involving tunable diode laser absorption spectroscopy grapple with the problem of detecting moisture in ammonia gas, which can degrade LED device performance.*

troscopy (FTIR) has been the method of choice for detecting these low levels of moisture.<sup>1</sup> The performance of FTIR-based moisture measurement in ammonia has been enhanced by improved methods for handling ammonia samples and optimized spectral collection and data processing techniques.<sup>2,3</sup> Dual-cell near-infrared absorption spectroscopy using a tunable diode laser over a narrow spectral bandwidth is another

matter of concern. Especially in blue and white LEDs, there is a strong correlation between device performance and moisture content in the process ammonia used during manufacturing. In addition, increasing chemical consumption is forcing many facilities to use bulk storage tanks as a single supply source instead of cylinders as supply sources for individual tools. In light of these trends, it is imperative to have a robust, continuous

method for detecting trace spectroscopic levels of moisture in ammonia.<sup>4</sup>

This article describes the design and operation of a novel IR spectroscopic instrument, the DF-740 moisture analyzer, from Delta F (Woburn, MA). It also discusses the design of a calibration system for the generation of low levels of moisture in ammonia standards.

**Tunable Diode Laser Absorption Spectroscopy**

For use in process applications in which maintenance and user interaction are minimal and long-term reliability is required, the DF-740 uses a technique called tunable diode laser absorption spectroscopy (TDLAS), or wavelength modulation spectroscopy. Optically, the instrument couples a laser with a Herriott cell configuration that is packaged and thermally controlled to maintain alignment over extended time spans (i.e., years).<sup>5</sup> The sampling chamber that holds the Herriott optics receives a continuous flow of analyte gas via a downstream vacuum pump and valve that control cell pressures below one atmosphere. The TDLAS method used in the moisture analyzer is well known for providing trace sensitivity to moisture (and other analytes) in many different background gases.<sup>6,7</sup>

The tunable diode laser used in the TDLAS technique (a distributed-feedback InGaAsP laser) has linearly variable wavelength output with drive current. The laser wavelength

is both scanned and modulated. Scanning is conducted at 16 Hz to move the laser across a single-line moisture absorption, while modulation at 40 kHz is coupled to a lock-in amplifier in the detection signal process, which is set at 80 kHz (the second harmonic of the base modulation), providing the measured absorption signal. The output of the lock-in amplifier is conventionally called a 2f signal.

The advantages of this approach are the narrow-band filtering associated with the 80-kHz lock-in amplification, the zero baseline of the signal in the absence of absorption, and the higher-frequency detection that is removed from low-

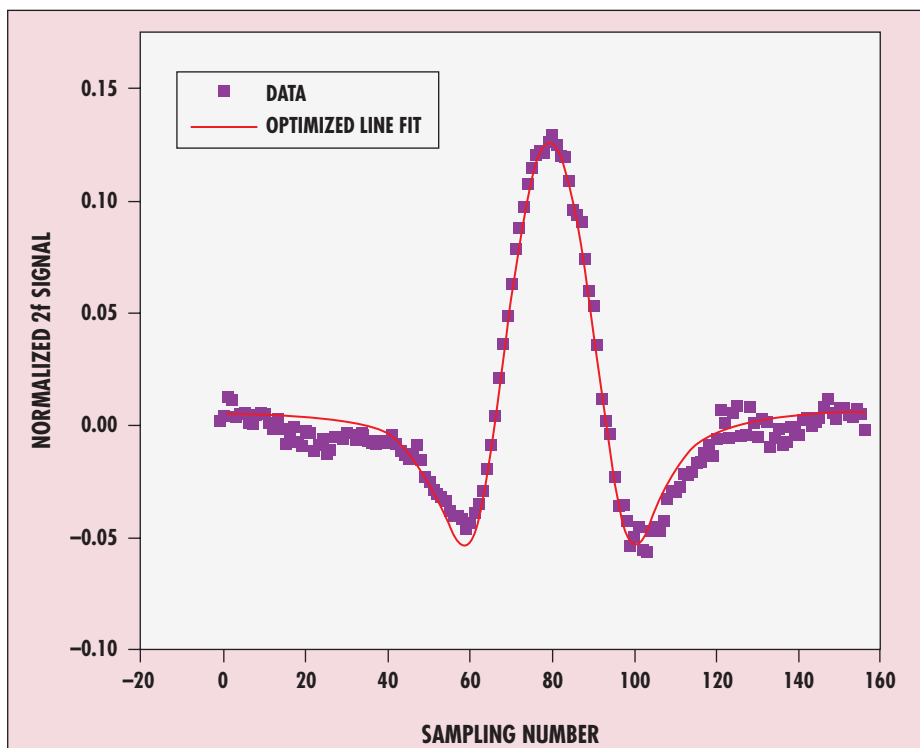


Figure 1: Typical spectrum with a line fit against an inert-gas background.

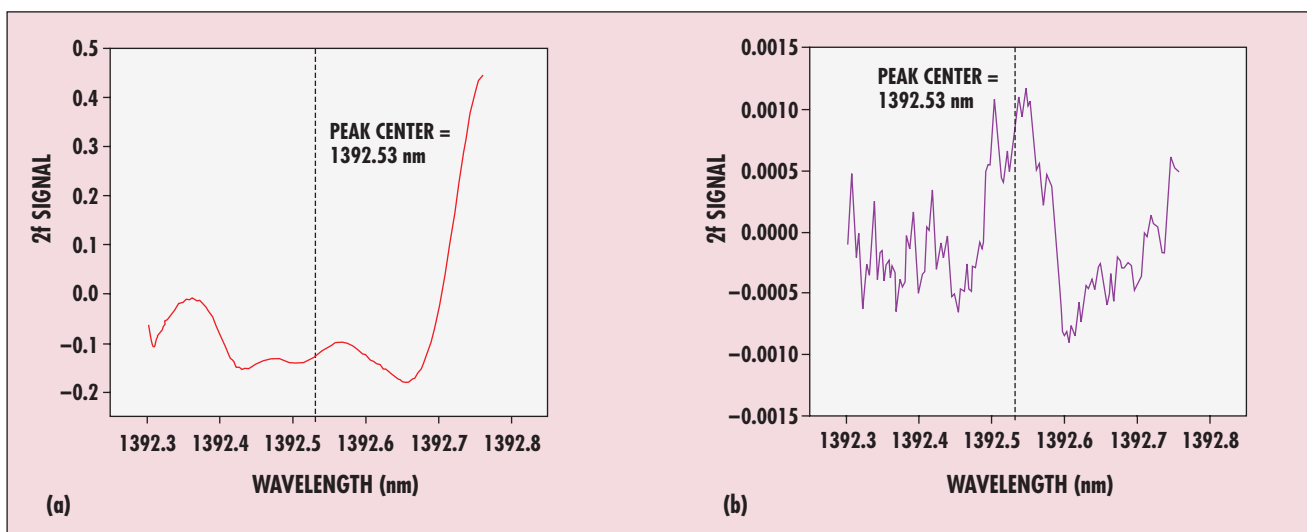


Figure 2: Moisture in ammonia absorption: (a) spectrum dominated by the ammonia absorption background, and (b) spectrum showing the actual comparative moisture content, which is approximately 7 ppb.

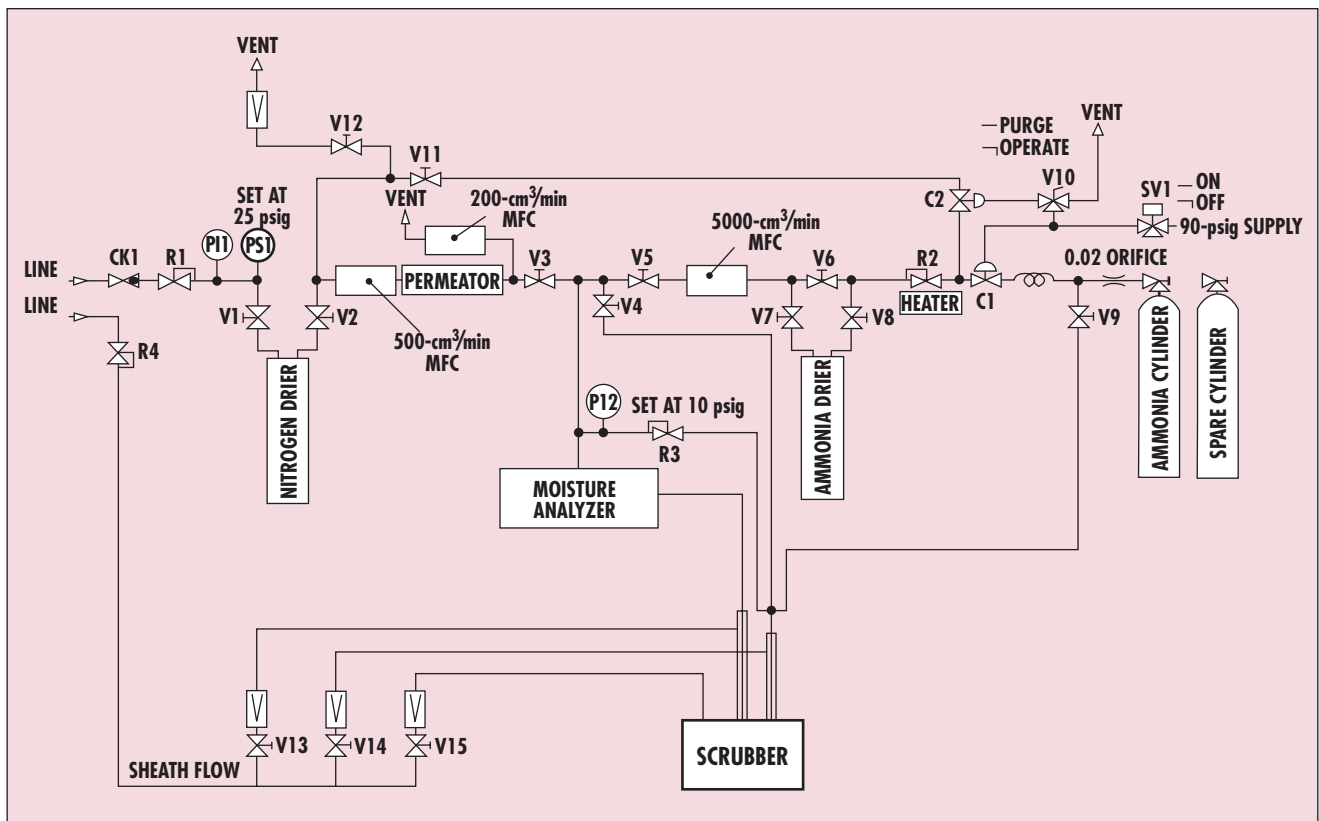


Figure 3: Schematic diagram of the experimental station that is used for generating purified ammonia and calibration-standard moisture.

frequency output noise from the laser. Because of these advantages, the instrument's absorption sensitivity is  $1 \times 10^{-6}$  absorbance units (au), compared with .01 au for a conventional spectrophotometer using Beer's Law. Indeed, since the TDLAS technique maintains Beer's Law, it also maintains the linearity and accuracy associated with conventional absorption experiments.

Because of the mathematical extraction associated with second-harmonic lock-in detection, the absorption peak is presented as a second-derivative profile after signal processing.<sup>6</sup> This profile is explicitly modeled according to the known spectroscopic parameters of laser tuning rate and pressure-induced line broadening of the specific absorption, as shown in Figure 1, which shows a typical spectrum with a line fit against an inert-gas background. In fact, the line-fit coefficient from a moisture-model peak in a linear regression interprets the strength of the moisture signal.

Key to implementing a line fit successfully is to identify the pressure-induced broadening of the moisture line correctly. In different gas matrices, varying amounts of broadening occur. Hence, each gas must be associated with a unique line measurement or calibration. Understanding that direct line-broadening determinations (e.g., from a strong line absorption) are linearly consistent with calibrations is critical for assessing line broadening in ammonia, since isolated measurement of a moisture absorption line shape in ammonia is impossible because of interference. In addition, broadening responds proportionately to the different components of

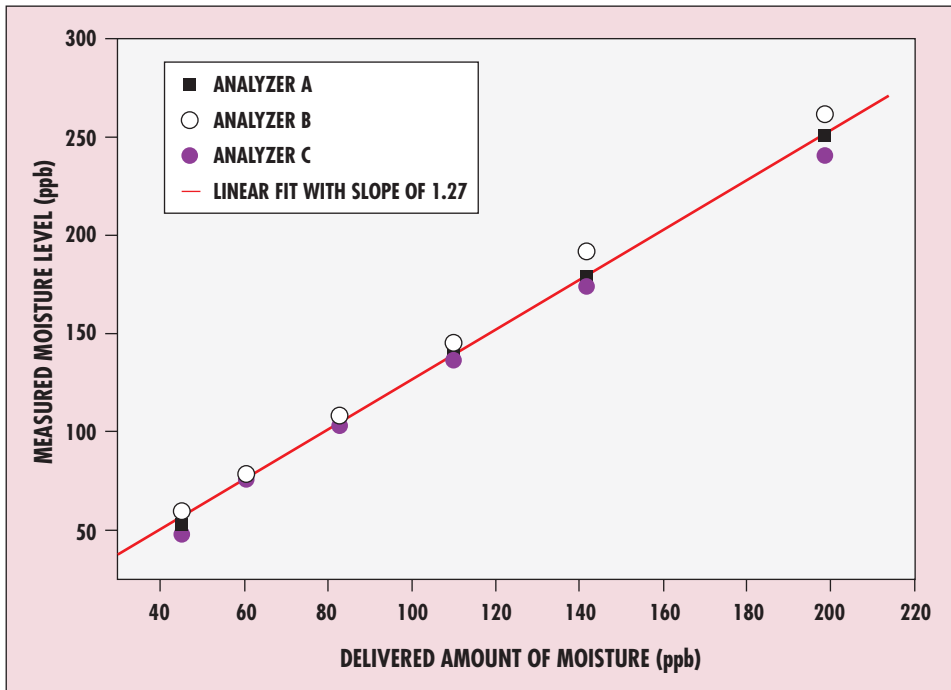
mixed gases. For example, a 50:50 mixture of nitrogen and argon broadens an absorption according to the 50:50 linear combination of the coefficients of the independent bulk gases.

### Spectral Interference from Ammonia

In detecting trace levels of moisture in ammonia, there is a remarkable degree of overlap between moisture absorption lines and ammonia absorption lines. At the targeted detection limit of 10 ppb, even the very smallest ammonia absorption line intensities from the background gas exceed measured absorption from moisture. Moreover, the largest ammonia absorption lines distort the spectral baseline far from their peak centers.

In comparing moisture and ammonia absorption, there are no wavelength regions where moisture can be measured in isolation. Consequently, it is necessary to characterize or otherwise account for the interfering signal. While double-beam acquisition and subtraction can be used to characterize the signal, that method involves a daunting level of instrumental complexity.

Figure 2 demonstrates the difficulty of detecting moisture in an ammonia background. The background interferes with a moisture-absorption wavelength of 1392.5 nm at the center of the spectrum. While the 10-ppb moisture spike is not noticeable visually, explicit spectral subtraction renders it discernible, a feature that has been discussed elsewhere in the literature.<sup>4</sup>



**Figure 4: Multiple-point calibration results for three analyzers (A, B, and C) with a common permeation-tube delivery system. Zero levels were fixed based on line fits of individual data sets.**

A close inspection of the ammonia spectrum shows that multiple absorptions are occurring, making explicit and constrained spectral modeling of the ammonia background highly difficult. Therefore, arbitrary but stable functional sets were created to model the background independently from moisture. These sets are folded into the linear regression approach in combination with the explicit moisture absorption model to determine the true moisture content.

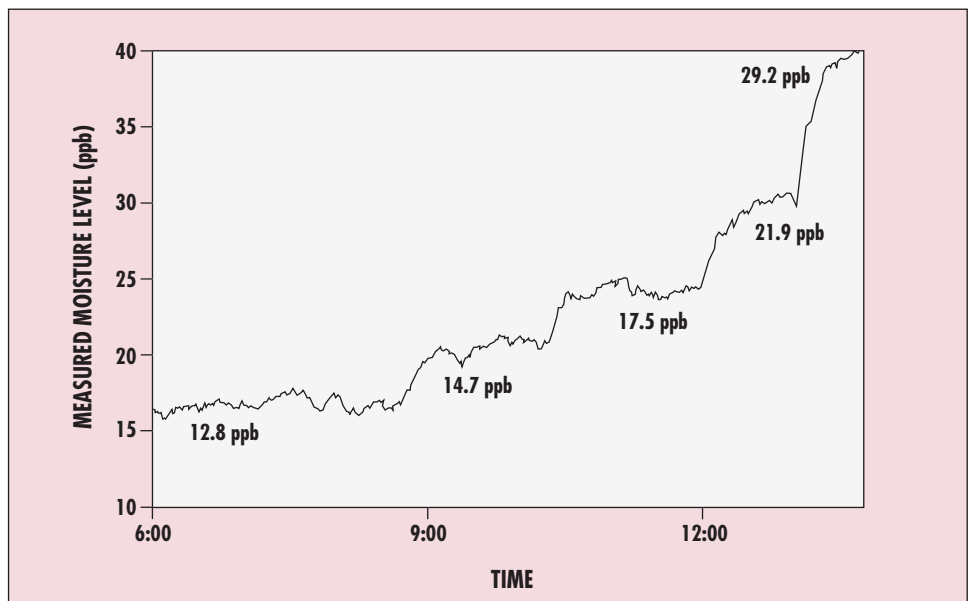
This approach has a three-fold outcome. First, the moisture response, as might be expected with any absorption experiment, is explicitly linear. Second, the zero baseline of the measurement is more arbitrary than if no other spectral structure were present beside the moisture absorption. Third, relatively tight pressure control is required in the sampling chamber to minimize the distortion of the spectral structure that results from pressure broadening.

**Experimental Station**

Most of the standards and samples discussed in this article were supplied to the analyzer

using the system presented in the schematic diagram in Figure 3. The system is designed to provide ammonia samples, dried ammonia “zero gas,” moisture standards in ammonia, and moisture standards in nitrogen. In addition, it can purge supply lines when ammonia cylinders are changed out and safely vent and scrub all ammonia flows using a strong sulfuric-acid solution. Cylinders containing approximately 50 lb of product sufficient for a month of testing were used to supply liquefied 5.5- or 6.5-grade ammonia.

An important component of the calibration system is a drier that provides ammonia zero gas and moisture-free nitrogen, which is used as diluent gas for the generation of standards. A proprietary molecular sieve with high affinity for moisture, even in the presence of excess ammonia, is used to dry ammonia, while a conventional high-capacity 13× molecular sieve is used to dry nitrogen. Although not critical, it is a good practice to avoid exposing the drier to nitrogen once it has been conditioned in ammonia. Therefore, valves V6, V7, and V8 in Figure 3 allow the ammonia drier to be bypassed whenever nitrogen is used in that portion of the system.



**Figure 5: Real-time moisture step resolutions. Delivered concentrations, estimated with the permeation-tube source maintained at a low temperature, are presented numerically. The measured parts-per-billion values have not been corrected for offset and slope calibration.**

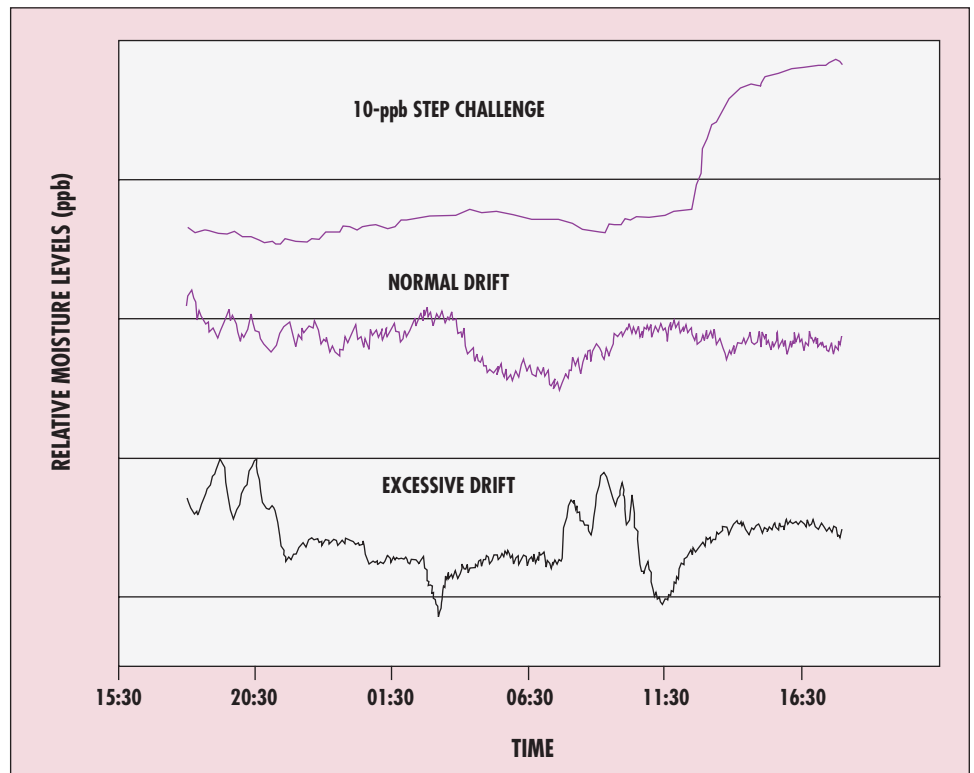
To provide a calibrated source of moisture, a conventional permeation tube is used. This well-known approach is the method of choice for generating low-level concentrations of moisture in inert gases. However, care must be taken to avoid exposing the tube to ammonia for two reasons. First, ammonia, like moisture, readily diffuses through the permeation tube, affecting the diffusion rate of the moisture through the tube's wall. Second, ammonia entering the permeation tube dissolves in the liquid water, affecting its vapor pressure. Both of these effects would cause the permeation tube to exhibit an emission rate different from that determined by the manufacturer during calibration.

To avoid these complications, the calibration system is designed to operate the permeation tube in a small amount of nitrogen, so that it can remain in the same environment in which it was calibrated by the manufacturer. During normal operation, the system delivers dry nitrogen through the two mass-flow controllers (MFCs) to the left of valve V3. Dry ammonia flows to the right of V5 and is controlled by a 5-L MFC. The two streams are mixed when V3 and V5 are open, generating the desired standard that is then made available to the analyzer.

To generate standards with lower concentrations, two MFCs are used on the nitrogen side of the system: a 500- and a 200-cm<sup>3</sup>/min unit. The 500-cm<sup>3</sup>/min MFC determines the amount of nitrogen that flows past the permeation tube. Changing the flow of gas from the first controller alone would not alter the final concentration of the standard appreciably. For example, while cutting that flow in half would decrease the dilution ratio by half, the moisture concentration from the permeation tube would double, leaving the resulting concentration essentially unchanged. Hence, the 200-cm<sup>3</sup>/min MFC is used to vent a portion of the permeation tube output before it reaches the ammonia diluent gas.

Under normal operating conditions, the calibration system delivers a constant total flow of gas that is somewhat greater than the flow required to operate the analyzer. The backpressure regulator R3 maintains the proper inlet pressure to the analyzer by exhausting excess gas. A set of flow calculations generate sets of moisture standards in the 40–500-ppb concentration range and constant fixed nitrogen concentrations of 1–5%.

To generate zero gas for the instrument, valve V3 is man-



**Figure 6: Breakdown of drifts versus moisture step responses over a 24-hour period. (Different operating conditions and corresponding drifts are shown on one scale for visualization purposes.)**

ually closed to prevent moisture from reaching the analyzer, since an MFC cannot be used as a positive shutoff device.

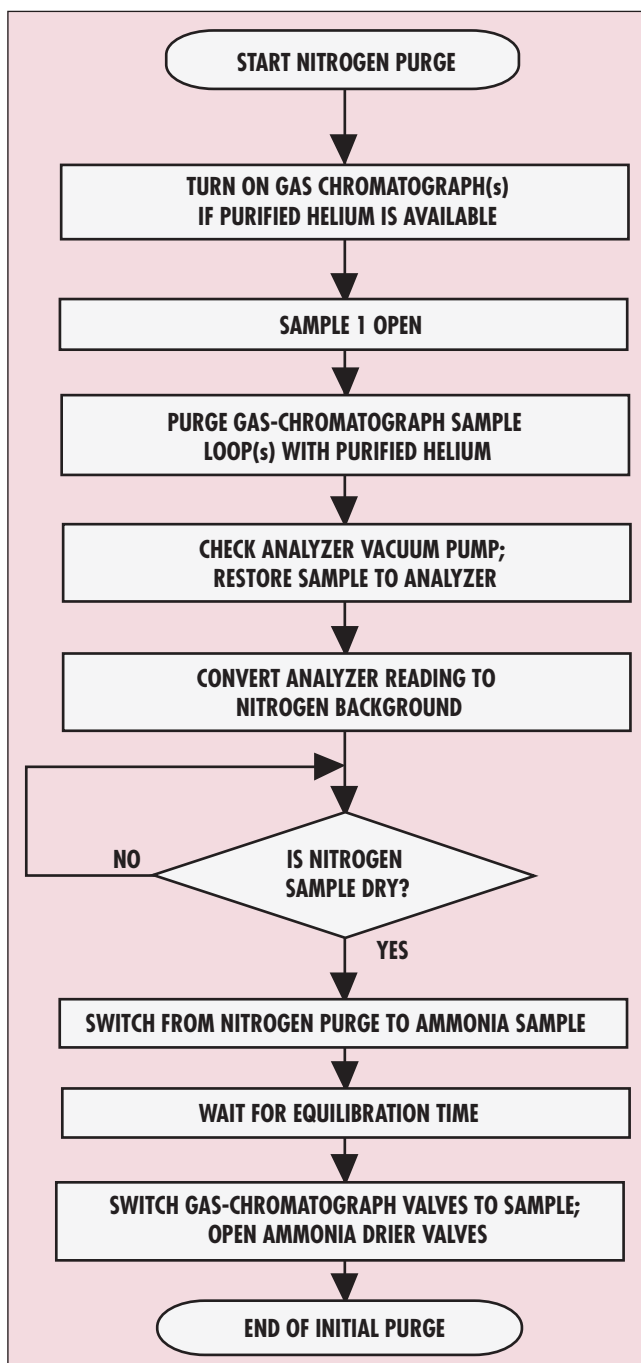
## Analytical Results

The capacity of the moisture analyzer was investigated on the basis of five criteria: moisture calibration, moisture response, drift performance, cell-pressure dependence, and the actual moisture content of purified ammonia at the nominal zero baseline. The investigation involved extended testing of four different instruments.

**Moisture Calibration.** Moisture calibration and response linearity were determined by creating a multiple-point calibration curve from varying moisture concentration levels generated by the permeation system. The results of this test using three analyzers are provided in Figure 4.

The analyzers were scrupulously calibrated in nitrogen gas using either a cylinder calibrated against a similar permeation tube system off-site at Delta F or within the experimental station. Ammonia line broadening, estimated to be  $8.26 \times 10^{-4}$  cm<sup>-1</sup>/torr, was entered into the analyzers, and the slopes in the ammonia background were determined to be 1.22, 1.26, and 1.32, yielding a mean of 1.27 with a standard deviation of 0.05. Based on these values, a corrected ammonia line broadening was determined to be  $6.50 \times 10^{-4}$  cm<sup>-1</sup>/torr.

During calibration, it was necessary to account for the potential effects of the nitrogen gas that was introduced to



**Figure 7: Flowchart showing the steps of a continuous-monitoring system. The process begins with a nitrogen purge and ends with the measurement of moisture in ammonia.**

operate the permeation tube, since nitrogen affects the broadening of the measured moisture and the background spectrum of the ammonia gas. In this case, the effect of the background spectrum of the ammonia gas was prominent, and the linear fits did not include the zero point taken in 100% dry ammonia. The lesser effect of nitrogen on broadening was within the experimental error range.

**Moisture Response.** Moisture response is demonstrated in Figure 5, which shows the real-time response to step challenges below 100 ppb. The instrumental response speeds as-

sociated with the various steps are approximately 15 minutes for upward transitions and approximately 5 minutes for downward transitions.

Even with low (0.25-L/min) sample volumes of gas passing through the analyzer and limited heat tracing of experimental lines, the response time is very fast. The root cause of this phenomenon is that moisture, which otherwise might be adsorbed on the inner surfaces of the analyzer's delivery lines, is apparently gettered by ammonia. This effect is evident when initial drydowns are performed. In normal inert-gas operations, a drydown period is sometimes desirable after an analyzer is installed, depending on the isolation condition of the analyzer and dead spaces in the delivery lines before dry gas is delivered. In addition, a significant drydown process may be necessary if a delivery line or analyzer is inadvertently exposed to ambient air. Systems that have been exposed to ambient air have been found to achieve a stable and nominal zero baseline within 15 minutes after the introduction of ammonia, while a drydown period of hours would be expected with an inert gas such as nitrogen. No ammonia was introduced to an instrument before measured moisture in nitrogen had passed below 1 ppm.

**Drift Performance.** The analyzer's drift performance is considered key to establishing valid detection limits. Because interfering noise in optical instrumentation at the detection levels that are the subject of this study is not based on stochastic processes, long measurement time frames are of concern, since such time frames can involve drift. In such cases, real-time data are useful for assessing detection limits, since statistical evaluations can obscure the impact of drift, resulting in an overestimation of an instrument's true detection limit.

In an analytical sense, drift may actually reflect real moisture fluctuations from adsorbed surfaces or other points where moisture can gather, especially when heat tracing has not been performed. However, in the ammonia application under investigation here, moisture fluctuations are not considered to be significant because of the gettering effect of the ammonia gas.

Figure 6 compares drift over a 24-hour period under three different conditions: an actual small (10-ppb) moisture step challenge, normal operation, and a worst-case drift occurrence. If a worst-case drift is defined from the bottom trace as 10 ppb over a 4-hour period, it is apparent that an actual 10-ppb step, as reflected in the top trace, could still be assessed with confidence. That kind of determination over a short period of time represents a conservative estimate of the instrument's lower detection limit, since the measurement resolution of moisture is clearly below that threshold. Over extended periods of 7 days and more, total drift does not exceed 20 ppb.

The source of drift in the ammonia sensor undoubtedly has more to do with errors in the accounting of the background ammonia line spectra than with more-conventional optical signal interferences from the TDLAS technique, such as laser power nonlinearity and etalon interferences. Unintended distortions in background spectra, which dominate the moisture signal, are bound to affect the best-fit moisture coefficients in a linear regression. Improved modeling of the background to

handle such distortions may provide an opportunity to improve on the drift.

**Cell-Pressure Dependence.** The cell-pressure dependence of each analyzer was scrutinized. To optimize the moisture response, a median pressure level of 70 torr was used, which is roughly where the positive effect of having a moisture-absorption peak with a higher signal-integrated intensity intersects the negative effect of having lesser peak amplitude caused by pressure broadening.

The use of functional sets to model the background spectral contribution of ammonia presents a constraint when that spectral background undergoes significant change—for example, as a result of cell-pressure variance. The potential effect of such a change is an excessive shift in the offset reading of the ammonia gas (but not in the calibration).

A rigorous evaluation of the analyzers' response to cell pressure changes demonstrated that between 66 and 74 torr, there is no apparent offset response beyond normal instrumental drift. Changes that occurred when those pressure boundaries were exceeded were reversible. Throughout the experimental period, pressure did not drift beyond 2 torr of the set point once it had been set.

**Actual Moisture Content of Purified Ammonia.** Determining the actual moisture content of purified ammonia to achieve an accurate instrumental readout is analytically difficult. If a purifier does not remove moisture below 10–20 ppb, it is not possible to distinguish the true moisture content in ammonia from ammonia with no moisture content, given the excessive spectral dominance of the ammonia background.

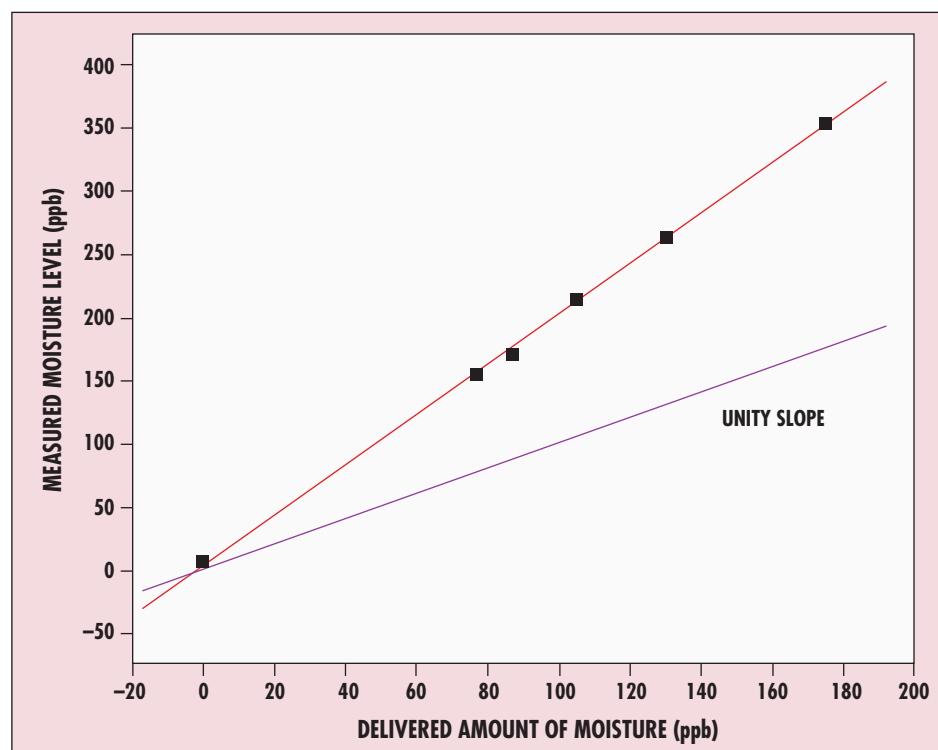
It is estimated that residual moisture in purified gas cannot

be very high, since experiments lasting more than a year and involving the use of multiple analyzers to test gas from many cylinders have not detected incipient offset-level changes. Furthermore, evaluations of moisture calibrations conducted with varying concentrations of nitrogen added via the permeation-tube system indicate that residual moisture in purified ammonia may be <10 ppb. Because of the small impact of nitrogen on moisture broadening, calibration slopes based on different nitrogen concentrations can be generated to calculate a true-zero moisture level. However, assumptions associated with such an approach would benefit from more-rigorous experimental design and testing.

## Integrating Moisture Analysis into a Continuous-Monitoring System

The ability to acquire data and control the moisture analyzer through a serial interface are key features of a continuous-monitoring system. Although not as corrosive to piping, mechanical components, and instrumentation as acid gases, ammonia containing ~10 ppm of moisture can cause damage over time and overtax the getters and driers used in the continuous-monitoring system. To avoid that condition, the system is typically purged with dry nitrogen when trace-moisture levels are high, such as during initial drydowns. In addition, if a moisture excursion occurs in an ammonia process stream, the analyzer can protect the integrated system by setting off an alarm, after which another nitrogen purge can be conducted.

A diagram of the continuous-monitoring system's start-up



**Figure 8: Demonstration of the linearity and integrity of a nitrogen gas calibration in a moisture analyzer that has been calibrated with ammonia. The slope of the best fit is 1.99, and the ratio of the pressure-broadening coefficients is 2.06.**

and drydown procedure is presented in Figure 7. Included in the system are moisture analyzers and gas chromatographs, which are used to analyze other trace gases. These components are controlled and powered by an onboard computer, which selects one of the available sample ports in the analytical panel (represented by sample 1 in the figure). Each sample port can be purged with dry nitrogen or an ammonia sample, although dry nitrogen is used as the default purge gas at the onset of processing. During start-up, the fully powered moisture analyzer, which is equipped with a dedicated vacuum pump, is isolated from the rest of the system. Since the gauge for measuring internal analyzer pressure is downstream of the sensor cell valve, the integrity of the vacuum pump and downstream line can be checked at start-up. The onboard computer can then de-

liver a sample flow of gas to the moisture analyzer.

Although the moisture analyzer is configured and calibrated for ammonia service in the continuous-monitoring system, it can also measure the progress of the drydown process during nitrogen purge. Because the analyzer determines moisture content in a gas other than the calibration gas as a ratio of the broadening coefficients for moisture in the calibration gas, it maintains explicit linearity. This is illustrated in Figure 8, which shows the analyzer's response to a multiple-point calibration in nitrogen gas after having been configured for and calibrated in ammonia. Such a curve enables users to calibrate the moisture concentration in the nitrogen used during drydown at the level of the continuous-monitoring system because it is consistent with the linear scaling of broadening coefficients. Nitrogen purge continues until the analyzer demonstrates that the initial drydown process has been completed.

All the sample points then switch to ammonia process gas, so that sample 1 provides ammonia to the entire analytical panel. The onboard computer waits for an equilibration time to allow the short burst of moisture scrubbed off the tubing by the process ammonia to pass through the system. Gas chromatographs begin sampling ammonia at this stage, and the onboard ammonia getter/drier is opened to the process gas to perform process baseline checks. After this initiation process, future high levels of moisture will once again set off predetermined alarms, triggering a nitrogen purge.

### Conclusion

The fundamental issue underlying the work discussed in this article is that once the TDLAS approach demonstrated an analytical response to moisture in an ammonia background, two problems arose. One involved independently performing calibration in the presence of the ammonia background, and the other involved establishing the nonmoisture offset created by the ammonia background. Fortunately, the investigators found that these problems can be separated from each other, and they made considerable progress in developing an analyzer that is relatively free of operational pitfalls.

Another issue facing the investigation was whether the analyzer would be able to discern true zero-moisture conditions unambiguously. The marriage of the analyzer with the described integrated process control system represented a convincing first step toward achieving that goal and toward reliably identifying single-digit parts-per-billion moisture incursions.

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