

# Ammonia takes the stage with bright LEDs

Tiger Optics describes the accompanying challenge of moisture detection.



*Aloha in situ at Air Products*

Careful attention to detail paved the way to success for global gas provider Air Products and Chemicals, Inc., when it recently took the bold step of building the world's first on-site, ultra-high-purity ammonia ( $\text{NH}_3$ ) facility, with a supply capacity of 2,000 metric tons per year. Designed to optimize its production for Anhui Sanan OptoElectronics Co. Ltd, a subsidiary of Sanan OptoElectronics (Sanan), one of China's largest LED (light emitting diode) makers, the on-site operation guarantees a steady and affordable supply of premium  $\text{NH}_3$  to Sanan's facility in the Wuhu Economic and Technological Development Area. Air Products elected to use advanced laser-based moisture analyzers from Tiger Optics, LLC to both optimize process control and validate product quality.

"Integrating the ammonia into the process is much more dynamic than simply checking the product quality before it enters the pipeline," says Bob Ford, Air Products' Bulk Specialty Gas manager.

The investment in quality and precision pays off, Air Products finds, when it comes to HB

(high brightness) LEDs.  $\text{NH}_3$  reacts with trimethyl gallium to form gallium nitride, the preferred nitrogen source for LED fabrication. But, even 10s of parts-per-billion (ppb) of moisture present in the process gas can relegate LEDs destined for high-value vehicle headlamp components to low-output Christmas lights and baubles for children's toys. Trouble is, oxygen compounds—in particular moisture—rob LED devices of luminosity by creating defects in the crystal. As Ford puts it, "That defect is not making light." Knowing the stakes, Air Products made moisture monitoring an integral part of the plant's design.

## Bright horizons

Toxic, flammable and corrosive, ammonia demands special treatment. It is stored and transported as a liquefied gas, but utilized as a vapor in the production of HB LEDs, which are increasingly employed across the consumer electronics industry. Prized for their clarity, cool temperature, long life and low power requirements, HB LEDs are 2.5 times more efficient than conventional fluorescent sources.

In 2010, HB LEDs became the favored "back lighting" source for TV and computer monitors. Worldwide HB-LED revenues jumped to \$11.2 billion that year, then climbed to \$12.3 billion in 2011, according to a recent report from Strategies Unlimited, the oft-cited California market research firm<sup>(1)</sup>.

Such growth prompts a voracious demand for ultra-high purity  $\text{NH}_3$ . Used to manufacture semiconductor compounds that form LEDs, a single metal-organic chemical vapor deposition (MOCVD) tool can consume eight to 10 pounds of ammonia per hour. Considering that an LED fabrication plant may operate 50 such tools, the gas requirements are challenges best met by a company with scale and experience. Yet Air Products anticipated the needs of the LED industry at least 10 years ago, Ford told Electronics Update, an Air Products publication, last fall<sup>(2)</sup>. The company set out to make the purification and distribution of ammonia a "core competency," he said. Distribution evolved from cylinders to bulk specialty gas systems (BSGS), to heated ISO containers to the on-site ammonia plant built for Sanan last year.

Meanwhile, Tiger Optics applied its patented technology to the challenge of ammonia analysis. Having introduced the world's first commercial "Continuous Wave Cavity Ring-Down Spectroscopy" (CW CRDS) analyzer in 2001, the Warrington, PA-based company developed its first low-pressure (LP) instrument for a Korean ammonia maker in 2004. Since that time, Tiger Optics has worked closely with gas manufacturers worldwide to resolve various issues associated with  $\text{NH}_3$  characterization. As a result, the company has earned renown as a world leader in specialty gas analysis, having placed nearly 200 units in service for ammonia alone.

In 2010, the company introduced the ALOHA- $\text{H}_2\text{O}$ <sup>TM</sup>, the world's first CW-CRDS ammonia analyzer dedicated to the HB-LED market. Despite its small footprint, the device facilitates detection of moisture in ammonia at levels of 10 ppb, with 5 ppb sensitivity, exceeding current market requirements. "We thought, 'Do we look at something new?'" recalls Derek Berger, the electronics specialty materials analytical project lead for Air Products.

► His colleagues had already put extensive effort into validating Tiger's laser-based analyzers across a range of applications, from laboratory research to troubleshooting and routine quality assurance, and from measuring small specialty packages to large-volume air separation, within Air Products. Prior to shipment to China, however, Air Products subjected its ALOHA-H<sub>2</sub>O analyzers to stringent tests in its Allentown headquarters and Hometown specialty gas plant, where it operated side-by-side Tiger's HALO, a compact versatile analyzer first introduced in 2006.

Based on nine criteria, including linearity, specificity, and robustness, derived from the International Conference on Harmonization

(ICH), the ALOHA H<sub>2</sub>O's scored high marks. "We had two analyzers, and the results conformed closely, within a few ppb of each other," says James Scharadin, Air Products' global operations technical lead for gas spectroscopy.

Berger concurs. Expanding upon the group's comparison with older alternatives, he says Air Products saw "much better standard deviation between results." Noting his subsequent experience on-site, Berger adds, "Even over in Sanan in ammonia, when the instruments are side-by-side, they show very good agreement."

**On-site makes right**

By locating its distillation and analytical UHP NH<sub>3</sub> capacity on-site, Air Products overcame

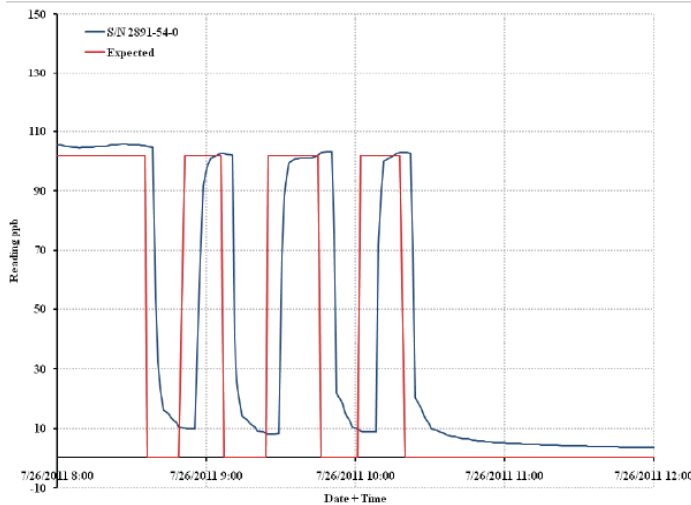
many hurdles associated with transport. "At these volumes it didn't make sense to constantly fill the trailer and send it out there," explains Scharadin. "It would have been a logistical nightmare." Specifically, the paradigm shift to on-site production took into account the following factors:

- **Complexity:** Specialty gases have multiple protocols tied to container hook-up, level monitoring, and container exchange schedules and maintenance.
- **Potential for contamination:** For gas suppliers and fab end-users, packaged gas delivery comes with the risk of gas contamination caused by poor execution of ►

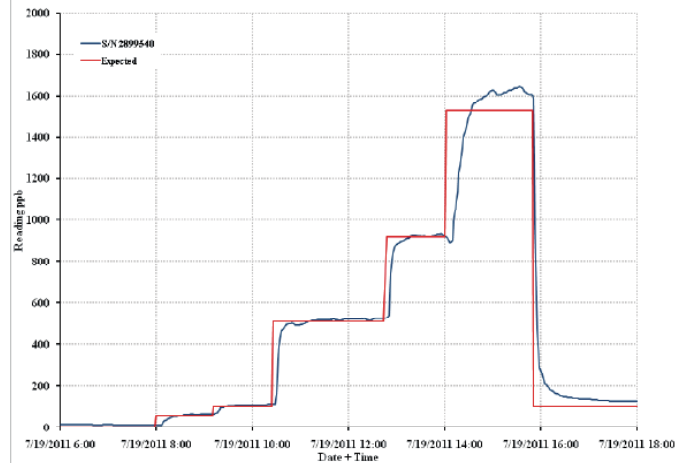
**Moisture analyzer performance**

**data collected by Air Products**

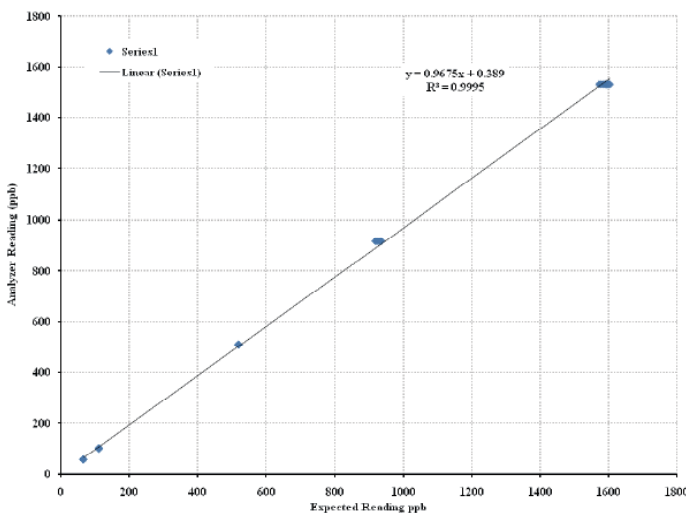
**ALOHA Instrument Repeatability**



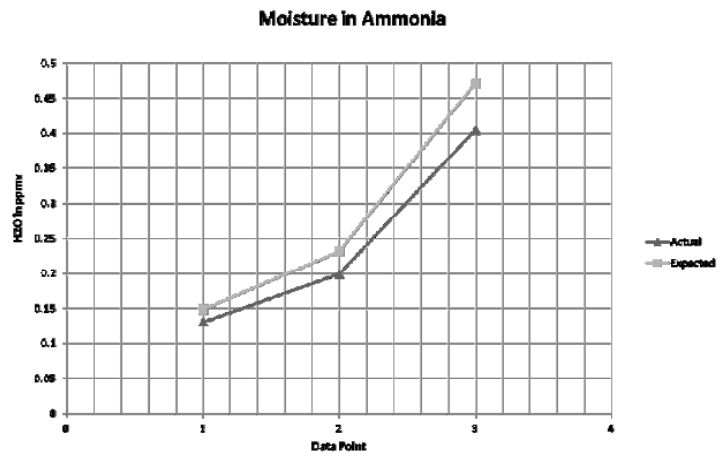
**ALOHA Instrument Step Challenge**



**ALOHA Instrument Linearity**



**ALOHA Moisture Response in Ammonia**  
(NOTE: Offset Due to Small Nitrogen % from Permeation Device)



- ▶ container connection, loss of line integrity due to regular connecting and disconnecting of fittings, intrusion of ambient air during transfer, and other challenges associated with routine package exchange.
- **Variability:** The scheduling of package exchange also introduces the threat of product run out, or a “bad batch” of product bringing a critical process to a halt. Plus, there is inherent variability package-to-package.
- **Cost:** Great numbers of standardized containers would be required, along with more manpower, if Air Products delivered such volumes to Sanan by conventional means.
- **Safety Issues:** The human health risk rises with exposure to ammonia in the process of connecting and disconnecting fittings, and other process steps.

Also, there is more waste  $\text{NH}_3$  from using supply containers instead of on-site. Drawing gas phase ammonia from a liquefied supply concentrates the moisture in the remaining liquid. When the supplier re-fills the tank, this

remaining  $\text{NH}_3$  has to be dumped or moisture mixes into the new in-spec liquid, potentially contaminating the product.

To prevent any mishaps, gas suppliers seek to minimize the distance the molecules must travel and the number of container transfers they undergo. “You want to eliminate variables and promote quality, safety, and cost-savings,” is Ford’s philosophy. With its on-site facility, Air Products distills the purified ammonia and sends it directly to Sanan via pipeline.

**Challenges of moisture analysis in hydrides**

Tiger Optics’ CW-CRDS technique relies on a fundamental spectroscopic principle: a molecule’s characteristic to absorb light at specific optical wavelengths, and not to absorb light at others. Based upon the Beer-Lambert law, Tiger’s technology precisely calculates the concentration of an analyte on-line and in real time. Tuned to the target molecule’s particular wavelength, laser light is beamed into an optical cavity as sample gas flows through it. Put simply, once the light builds to a predetermined intensity, which happens in a matter of milliseconds, it shuts off, and the measurement begins. Thereafter, the time it takes for the light to decay or “ring down” is equivalent to the presence of the target molecule in the gas.

As a time-based measurement, CW-CRDS is unaffected by fluctuations in either light intensity or environmental conditions, such as ambient humidity. It operates free of calibration, providing stable and reliable readings with minimal user intervention and no need for purifiers and calibration gases. Routine self-diagnostic sequences can be automated via the system’s software to run at the user’s convenience (typically once per month). Also, the required flow rate through the analyzers is less than 500 sccm, which reduces the amount of ammonia that is required for analyzing purposes compared to other technologies.

That said, moisture quantification in ammonia poses unique problems due to the chemical properties of ammonia and moisture, and the interactions between the two molecules in the gas phase. Tiger Optics Applied Research director Yu Chen explains the difficulty: “ $\text{NH}_3$  has strong, extensive spectral absorption features throughout the entire near IR region. To detect with adequate sensitivity and specificity, one needs to cleanly resolve and quantify the tiny absorption signal due to low ppb moisture against severe spectroscopic interferences from the 100 percent-pure  $\text{NH}_3$  background.” In sum, he says, “It’s like finding a needle in a haystack.”

In conjunction with their high sensitivity, noise is minimized in Tiger systems in part by controlling the conditions in the measurement

cell. Particularly in the ammonia matrix, due to ammonia’s highly active absorbance spectrum, small fluctuations in pressure can result in an increase in the background noise of the measurement. Therefore, thoughtful engineering was required to minimize the occurrence of this fluctuation.

While a vacuum pump is, therefore, required to measure moisture in ammonia, the type recommended by Tiger Optics requires no maintenance. The pump also draws less than 1.7 amps to operate. The savings due to reduced electrical consumption, when compared to other stand-alone pumps or house vacuum systems, typically justify the purchase of a dedicated pump for each analyzer. Combined, the savings achieved by obviating the need for calibration gases (and the cost of labor required to support such an effort), along with the reduced ammonia consumption, low maintenance, and low operating costs, provide the end-user with one of the lowest total costs of ownership in the industry.

**Sensitive, speedy and cost effective**

While initial cost was a key element in analyzer selection, the Air Products team was concerned about total cost of ownership, as well as performance. “We wanted analyzers that weren’t labor intensive, with ease of use, very low maintenance and high up-time,” says Scharadin.

Buoyed by the success of the innovative project, Ford sees on-site bulk specialty gas production as the wave of the future. Indeed, for Sanan, Air Products has already broken ground on a second high-purity  $\text{NH}_3$  plant with the same capacity, expected to be on-stream in the middle of 2012. [SGR](#)

- (1) See: [www.strategies-u.com/articles/reports/high-brightness-leds/high-brightness-led-market-review-and-forecast---2011.html](http://www.strategies-u.com/articles/reports/high-brightness-leds/high-brightness-led-market-review-and-forecast---2011.html)
- (2) <http://airproducts.com/~media/Files/PDF/industries/pv-electronics-update-fall-2011.ashx>

**TIGER SCIENTIFIC CORPORATION**  
**Accredited Humidity Calibration**  
**NVLAP Lab Code 207833-0**

**HumiCalc with Uncertainty**  
**Humidity Conversion Software**

Humidity	Relative Humidity	Dew / Frost Point	Volume Ratio, V (ppm)
0.05%	0.05%	-80 °C	0.1
100%	100%	70 °C	200,000

625 Wyoming Blvd. NE • Albuquerque, NM • 505-255-0444  
[www.tigeroptics.com](http://www.tigeroptics.com)  
 PH: 606.672.7728 • E-mail: sales@tigeroptics.com

**Lisa Bergson and Kimberly Reynolds**

Lisa Bergson (left) is CEO, Tiger Optics. Kimberly Reynolds (right) is global sales and product manager for the Gases & Chemicals Division, Tiger Optics. [www.tigeroptics.com](http://www.tigeroptics.com).