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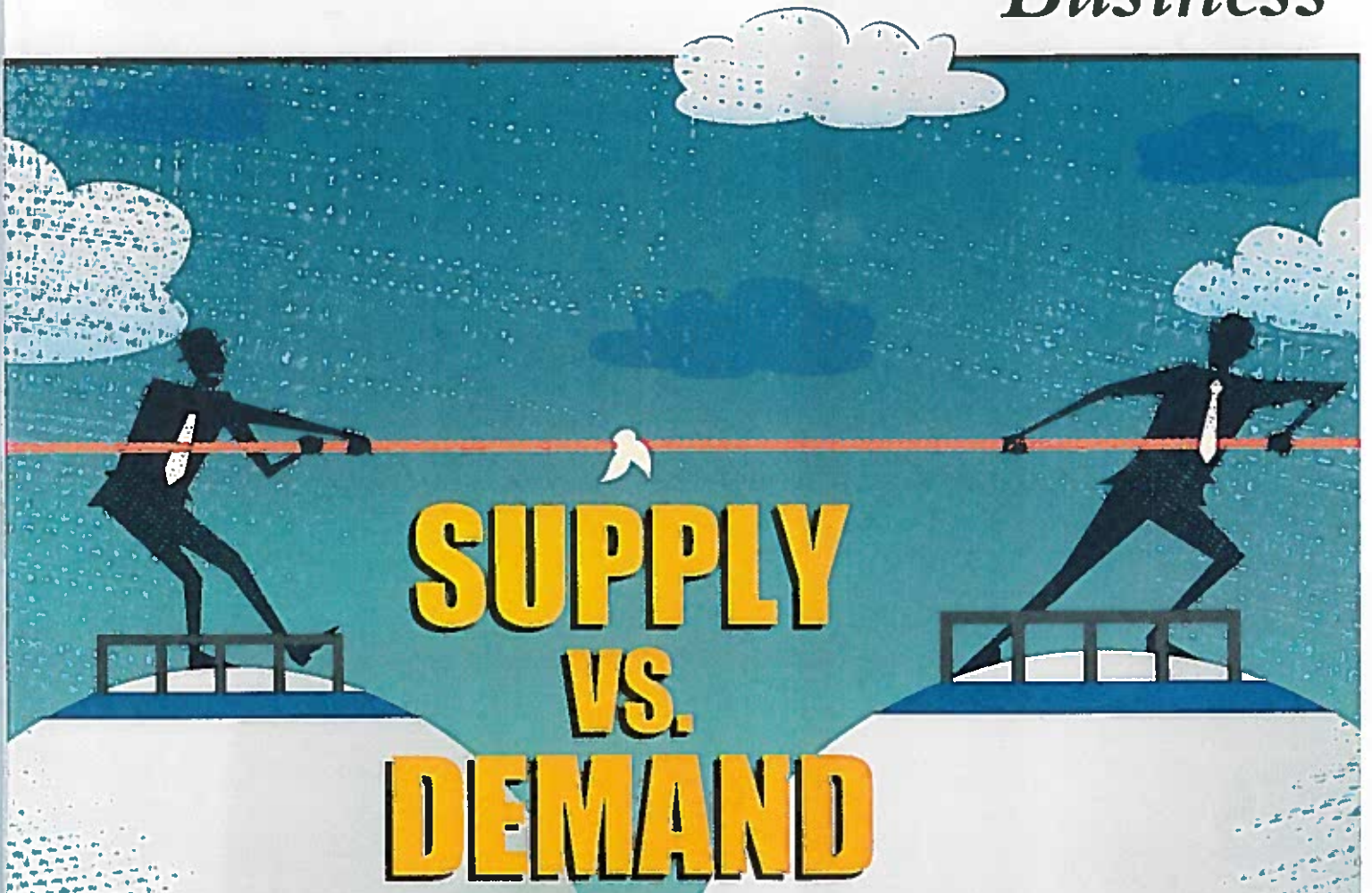

SUPPLY VS. DEMAND

Storage has never been more important or as troublesome to the industry

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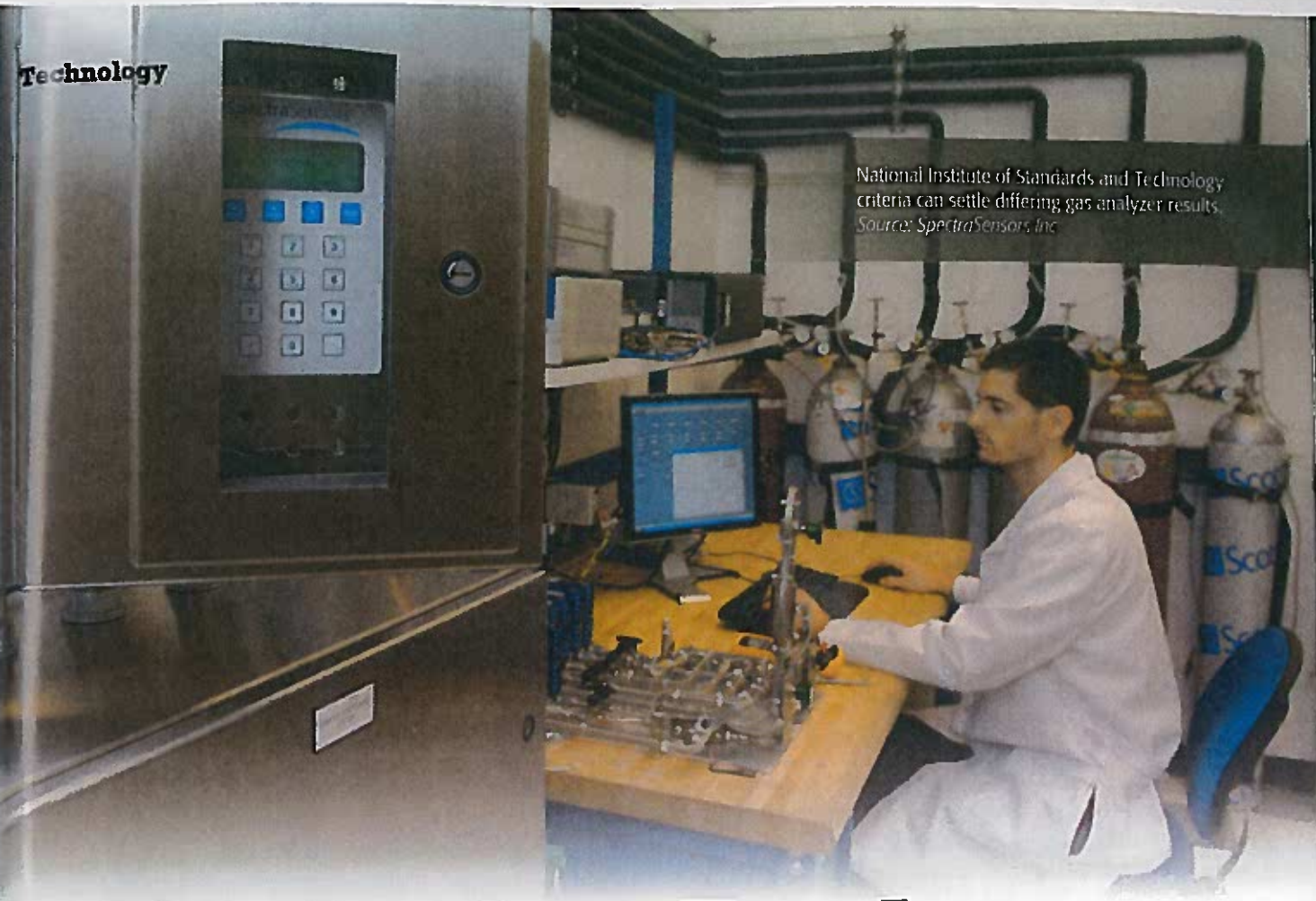

National Institute of Standards and Technology criteria can settle differing gas analyzer results. *Source: SpectraSensors Inc*

Analyzing Analyzers: Metrology In Gas Pipelines

Natural gas companies turn to standard traceability to end disputes on H_2S measurements.

By John Apgar

Upstream, you have producers and gas processors that deliver natural gas to fill the growing demand for the clean-burning fuel. Midstream, you have hundreds of miles of pipeline infrastructure to deliver the gas to market.

In between, at the points of custody transfer, are the multitudes of analyzers which ensure that contaminants such as hydrogen sulfide (H_2S) are low enough to safely protect the pipelines and the public. This critical measurement prevents corrosion that in the worst case can lead to pipeline rupture.

And what if the supplier and user each use a different analyzer?

Well, there is a saying in the natural gas industry: "If you have one analyzer you have a measurement; if you have two analyzers, you have an argument."

"Sometimes you will have a dispute when two different companies are using two different brands," said Hunter Brown, measurement control supervisor for Access Midstream, now a part of The Williams Cos., told *Midstream Business*. "The readings can be 2 parts per million (ppm) apart and that can mean a lot if the third party is reading 7 and the supplier is reading 5. In fact, it can result in a shut-in."

The reason accuracy is so important is simple: money. Neither supplier nor buyer can afford to halt any part of the 70 billion cubic feet of natural gas con-

sumed in the U.S. on a daily basis. If two analyzers show different readings in the same line, who wins the argument? Whoever can demonstrate the most accurate analyzer.

The final word

Fortunately there is a final word in accuracy at the National Institute of Standards and Technology (NIST), in fact it is the final word in all metrology. If an analyzer is calibrated with highly accurate gas, and that gas can demonstrate NIST traceability, the argument is over.

"Both calibration and validation are important. If either one is wrong, it's not going to read right," David Bromley with BP Plc told *Midstream Business*. "If I get that test gas in and it is reading 3 instead of 4 ppm, the question is, is it the test gas or the analyzer? One of them has to be wrong."

Increasingly, producers and processors are demanding greater accuracy through NIST traceability and that has led analyzer manufacturers to respond.

Houston-based SpectraSensors developed the first tunable diode laser analyzer to measure impurities such as H_2S and trace moisture in pipelines. On its own, the company soon realized that due to the inherent uncertainties in any measurement, a genuine accuracy claim must trace back to the metrology gatekeeper—NIST.

Originally, SpectraSensors used the same method other analyzer companies used, it simply ordered a calibrated gas bottle from a reliable source and used it to calibrate analyzers at the factory. Once calibrated, the unit was good to go. However, the company discovered that not all bottles are created equally and no one traced their standards back to NIST.

The problem was the company found a higher degree of uncertainty in the bottles than the manufacturers claimed, so it went looking for a company that would collaborate with them to solve the problem.

That company turned out to be Air Liquide.

"H_2S is a notoriously difficult component to blend into a gas mixture and have it remain stable," Dr. Stephen Miller, Air Liquide chief technical officer, told *Midstream Business*. "And that problem becomes progressively worse as concentrations become lower.

"In fact, there are anecdotal stories about chain of custody/monetary valuation arguments concerning the quantity of H_2S in a pipeline based on unresolved differences in the calibration of H_2S analyzers brought about by hidden discrepancies in the certified H_2S values on different calibration gas cylinders. Concentrations of the gas bottles can be a lot more variable than end users realize."

"If you truly care about the H_2S content in the pipeline, then all elements of your measurement system must be optimized. The sampling/ conditioning lines, the analyzer and the calibration gas must be free of errors and all work together as an integrated system."

— Dr. Stephen Miller,
chief technical officer, Air Liquide

Major commitment

Both companies realized it was going to take a major commitment of time and money to build the traceability path back to NIST. But the reward would be worth it.

"SpectraSensors showed us we could differentiate ourselves if we could solve this problem and their analyzer would have a strong case in any dispute," he added.

The H_2S concentration needed in the bottles was 4 ppm and 16 ppm, each of which had to be in a matrix gas of methane and nitrogen *and* everything had to be NIST traceable. The Air Liquide answer was "dual certification."

A common industry method to produce H_2S mixtures is to dilute H_2S down to 4 ppm and analyze it in a lab. But that process has accuracy risks, even if done with NIST reference standards, because there is no second check of the actual concentration and no indication of long-term stability. The Air Liquide dual certification process, which employs gravimetric and analytical procedures, both with full NIST traceability, requires these two independent methods come to the same result and agree with each other within close statistical boundaries.

"First, we determine the concentration and the accuracy of the mixture by mass alone using NIST primary references and stringent statistical methods," adds Miller. "Then, we analyze that same cylinder in the laboratory using instruments calibrated with NIST SRM's (standard reference materials). When these two independent processes agree with one another, we have high confidence in the certified H_2S concentration, and we have the required unbroken chain of comparisons within our measurements all the way back to NIST."

How does NIST know their values are correct? It's a three-step process that includes worldwide verification.

"When we create primary standards we design the procedure to develop a suite of standards that define a concentration range we wish to use to support for customers," Dr. Franklin Guenther with NIST told *Midstream Business*. "To verify the primary standards, we analyze the suite on an instrument with a well-defined instrument function, such as gas chromatography, which has a linear function. If all the primary standards fall on the linear response function of the instrument we are confident that the standards are self-consistent

and no blunders have occurred in the filling process. We then analyze them against past primary standards, and if they agree we are confident that our standards are historically consistent and that our measurement system has not shifted over time. Our third method of verification is to measure them against other National Metrology Institutes in a bilateral, or key, comparison."

The bottom line for everyone in the measurement business is that NIST is the standard, NIST traceability trumps all debates.

Total measurement system

Air Liquide's Miller sees it as a total measurement system.

"If you truly care about the H_2S content in the pipeline, then all elements of your measurement system must be optimized. The sampling/conditioning lines, the analyzer and the calibration gas must be free of errors and all work together as an integrated system. If you are not using a total measurement system then you risk making a less accurate measurement which leaves you susceptible to economic losses."

Bromley agrees.

"We have to have repeatability and accuracy in our measurement. If you are measuring 4 ppm you have to have repeatability and accuracy. Accuracy is the most important because I would hate to shut a valve on a company when they are not out of spec. We do get measurement disputes. When we see it go past 4 ppm we shut the valve down and the sender might say we don't see that over here. That's what they say to us. I know they don't have the type of analyzer we have and that can give you two different answers," he said.

SpectraSensors developed the first tunable diode laser analyzer for use in hydrocarbon streams. Since a laser beam is used, there is no physical contact between the gas stream and the sensor.

The analyzer is calibrated at the factory using the new, dual-certified NIST traceable H_2S calibration standards from Air Liquide. Termed the SSRM (SpectraSensors Reference Material), since it is a unique product developed for SpectraSensors, the blend is diluted in hydrocarbon streams through a dynamic blending station that uses mass flow controllers (MFC). Both the SSRM and the MFC are verified with NIST traceable flow references.

A customer can also validate the unit in the field, again, with an Air Liquide NIST traceable bottle. For natural gas suppliers and users, the end of the H_2S measurement argument at transfer points in pipelines could finally be in sight. ■