Zero Gas: A Concept in Search of a Definition

By Lisa Bergson

Zero gas has been the Holy Grail for the gas market for some 40 years. The irony is: definitions of zero gas, akin to the highest grade of gas reference material, are as ambiguous as its attainment is elusive. "It gets confusing if we name everything 'zero gas'," observed Paul Murphy, CTO of Japan's Takachiho Chemical Industrial Company, at last summer's Workshop on Zero Gas held at VSL, The Netherlands' national metrology institute, under the auspices of the European Union's Metrology of Chemical Pollutants in Air (MACPoll).

Used to calibrate a host of gas analyzers, zero gas is a moving target as its composition is determined by myriad factors, ranging from gas manufacturing capabilities to measurement methodologies to market needs and even national interests. In Japan, the focus on development of protocol gases is largely for the requirements of that nation's influential auto industry. There, the Chemicals Evaluation and Research Institute (CERI) has traceable zero standards for pollutants in the low parts per million.

In the U.S., among those Standard Reference Materials (SRMs) recently completed at the National Institute of Standards and Technology (NIST) is a hydrogen chloride standard to support emerging regulations for continuous emissions at coal-fired utilities and cement plants.

Developed by national institutes, such standards are typically duplicated and sold in portable cylinders by industrial gas companies, including Airgas Inc., Air Liquide Group and Praxair Inc., which periodically must submit samples of their product to the metrology institutes for validation. Notably, many institutes also provide calibration services for makers of analytical instrumentation, gas purifiers and gas generators, as well as for commercial labs. Used by industries worldwide, the reliability and consistency of standards have significant consequences.

As examples, these can range from human health and safety (consider medical gases and those used to test cylinders for divers and folks working in confined spaces) to manufacturing yields and process quality (costly and delicate semiconductor chips, for instance) to industrial emissions (such as U.S. power plants, where a poorly calibrated analyzer could generate incorrect reports and unwittingly cause a major emitter to incur sizable fines for falling out of compliance with the Clean Air Act).

One unifying theme is the growing demand for more stringent and consistent reference standards, "zero" or otherwise. These are needed to address the environmental and human health impacts of industrial emissions and greenhouse gases. They are needed to meet industry's quest for cleaner and more precise process control. Beyond that, our economic interdependence—with increased trade among nations and regions—mandates, to the extent possible, uniform standards to ease transactions and to protect consumers.

Defining Zero

The key attribute for any so-called zero gas is relevance. At the workshop, that issue was underscored by Rob Wessel, chair of the International Organization of Standardization (ISO) Technical Committee 158 on Gas Analysis, who spoke about a new ISO standard under development (ISO 19229), which addresses gas purity analysis and data treatment for calibration gases for general test purposes. The standard sets three criteria:

1. Is an impurity, such as H_2O, critical to the intended application?
2. Is traceable analysis required?
3. How do you estimate the uncertainties?

These questions preoccupied the workshop participants—drawn from a cross-section of gas manufacturers, national metrology institutes, and instrument and component makers—who gathered at the sleek VSL headquarters to discuss and, at times, heatedly debate MACPoll's value, meaning and methodology. It was a rare opportunity for participants to get an inside view of the machinations behind the adoption of an influential and wide-reaching new reference gas standard.

"Of course, zero gas depends on your application," stated Marta Doval Minarro, a workshop participant from the United Kingdom's National Physical Laboratory (NPL), with regard to the first criterion. "If there are impurities in the gas that do not affect your application, then it's still zero," she said. For its part, the European Union's MACPoll initiative calls out, variously, parts per billion (ppb) to parts per million (ppm) ranges of relevant impurities, comprising NO, NO_2, SO_2, NH_3, H_2O, H_2S, O_3 and CO_2 in nitrogen or pure air used for both "zeroing" analyzers and dilution purposes.

In its grandest sense, the three-year MACPoll project is part of a vast EUR 400 million European Metrology Research Program (EMRP) designed to coordinate research among Europe's national metrology institutes and "accelerate innovation and competitiveness." Driving the MACPoll effort are new EU clean air requirements that call for stepped up monitoring at over 6,000 stations across the continent. Given the absence of appropriate reference standards to calibrate approved monitors, however, the comparability of measurements from station-to-station and over time is challenging, to say the least.

Therefore, MACPoll aims to "improve the measurement and reduce the uncertainty" tied to the European Air Quality Directive 2008/50/EC, which references non-dispersive infrared (NDIR) fluorescence and chemiluminescence as the approved methods to measure CO, SO_2 and NOx, according to the CEN/TC 264 air quality standards developed by the European Committee for Standardization. Such relative methods require routine calibration and proper zero point calibration to assure accurate measurements. Otherwise, they can be prone to drift and temperature dependence, as is experienced with NDIR devices.

On the matter of estimating uncertainties, NIST research chemist George ("Jerry") Rhoderick expressed strong objection at the workshop to the fact that the MACPoll specifications were uniformly stated in terms of "less than or equal to." In a subsequent interview, he said, "NIST will not certify 'less than or equal to' values. We can't put an uncertainty on that," adding, "You can ask 20 people, and you're going to get varying opinions." Instead, he contends that the specifications should be stated in ranges high enough to apply set values.

Legislating Zero

"The definition of zero gas is a very tricky issue," acknowledged Annarita Baldan, the MACPoll project coordinator and VSL scientist, noting that the stated goal is to develop zero gas standards to "ensure the traceability and minimize the uncertainty of the measurements obtained with approved methods." To some attendees, these targets seemed a bit arbitrary however, with H_2O pegged at 150 ppm, despite the availability of many proven detection methods with far greater sensitivity. Meanwhile, for NH_3, SO_2, NO and NO_2, the specification is 1 ppb—a level that few, if any, commercial instruments can achieve. (See Figure 1.)

"It's very relaxed on moisture, but for SO_2, NO and NO_2, very strict," observed Wessel. "For CO_2, it's strangely high, which would pose problems with NDIR interference," he added. Peter Adam, director of Linde AG's Global Specialty Gases Customer Application & Engineering division, critiqued the specification for NO: "In synthetic air, 1 ppb is impossible. NO reacts immediately in the cylinder and becomes NO_2!"

The implications of such specifications are far from trivial. The onus is on those national metrology institutes (NMIs) participating in MACPoll to develop reliable means to produce, to validate and to handle the new standard. But, since NMIs are under more and more pressure to generate revenue, they may welcome the opportunity to offer expanded capabilities, like certifying commercial zero gas reference batches periodically for industrial gas companies.

That said, it will still be up to the makers and users of commercial gas standards for EU air quality monitoring to come into compliance. "Can environmental labs follow these guidelines is the big question," said Tatiana Macé of France's Laboratoire national de métrologie et d'essais (LNE). On that score, workshop speaker Francois Mathé of the Network of Air Quality Reference Laboratories (AQUILA) counseled, "Don't forget to be pragmatic."

Context

Species	Limit Value (nmol/mol)	Specification zero gas
NO	—	≤ 1 nmol/mol
NO_2	21 (calendar year)	≤ 1 nmol/mol
SO_2	47 (one day)	≤ 1 nmol/mol
NH_3	—	≤ 1 nmol/mol
H_2O	—	≤ 150 µmol/mol
H_2S	—	≤ 0.1 µmol/mol
CO_2	—	≤ 4 µmol/mol
O_3	60 (8 hours)	≤ 2 nmol/mol

Figure 1. Specifications for purity of zero gas as given by European standards for the measurements of NOx (EN14211) and SO_2 (EN14212) in air. Shown are relevant impurities in zero gas : NO, NO_2, SO_2, NH_3, H_2O, H_2S, CO_2, O_3 in order to meet the requirements of European standards for zero gas. (Figure 1 courtesy of MACPoll "Workshop Zero Gases" and EMRP)

Making Zero Gas Standards

The fact is, when it comes to zero gas, defining it is one thing; manufacturing and qualifying it, quite another. Regardless of application, the implementation of zero gas-based regulations relies on commercially available reference standards, along with appropriate instrumentation and zero air generators to verify their consistency.

In a presentation at the MACPoll workshop, VSL researcher Stefan Persijn depicted a wide disparity in the quality and availability of zero air generators. Used by most air monitoring networks and labs, generators are sold by a host of suppliers and utilize free samples (air). Yet when the workshop participants considered 21 different brands, a poll found that none of the products came close to generating zero air, particularly since the source material depends on local air quality. "In Lapland and Finland, they can use ambient air from the Arctic. But in cities, it's more of a problem," Persijn stated.

In theory, zero gas cylinders offer a better alternative. But, the absence of commercially available standards in the ranges prescribed leaves users with "no means to determine qualities of zero gases themselves," concluded Persijn. Hence, the need for the national metrology institutes to develop new gas protocols and, where needed, appropriate instruments for verification.

Case in point: VSL combines filters and scrubbers to first purify its gas, whether synthetic air or nitrogen, and then measures it with a house-made Cavity Enhanced Absorption Spectrometer (CEAS). Since this approach is likely to prove too expensive for field use, the institute plans to manufacture "zero gas" cylinders for both gas manufacturers and calibration of generators and gas analyzers.

Even so, some attendees doubted the costly new standards would be well received. "Our customers are not willing to pay for the effort we are putting into zero gases," lamented one gas industry insider. Chimed in another, "Customers may buy, but they will complain."

To Control, You Must Measure

At the MACPoll meeting, a wide divergence also emerged with regard to analytical equipment, based on a VSL survey completed by 23 instrument makers, gas suppliers, purifier makers and metrology institutes. Persijn, the VSL researcher, reported that when it comes to CO, NDIRs from Horiba Ltd. and Thermo Fisher Scientific Inc. are

Respondent	Detection Limits (ppb)			
	Air Quality labs	NMI 's	Instr. Manufacturers	Gas Producers
1.	0,5*	0,5	<1	5
2.	10	1	<2	20
3.	40	1	100	50/50
4.	<50	10		
5.	<80			
6.	<100			

*Figure 2. Analytical methods for CO-techniques based on frequency of use. Legend: NDIR (Horiba, Thermo Scientific) (blue); Gas chromatography (red); Laser spectroscopy (green): *NOAA is the National Oceanic and Atmospheric Administration. (Figure 2 courtesy of MACPoll "Workshop Zero Gases" and EMRP)*

Respondent	Detection Limits (ppb)			
	Air Quality labs	NMI 's	Instr. Manufacturers	Gas Producers
1.	~200 (technique)	5	1	10
2.		1300	1,5	20
3.			2	20
4.			<3000	100
5.				100
6.				100

Figure 3. Analytical methods for H_2O; CO-techniques based on frequency of use. Legend: Laser spectroscopy (CRDS/TDLS) (green); crystal oscillator (red); electrochemical (DL not indicated); dew point (blue), P_2O (orange): (Figure 3 courtesy of MACPoll "Workshop Zero Gases" and EMRP)

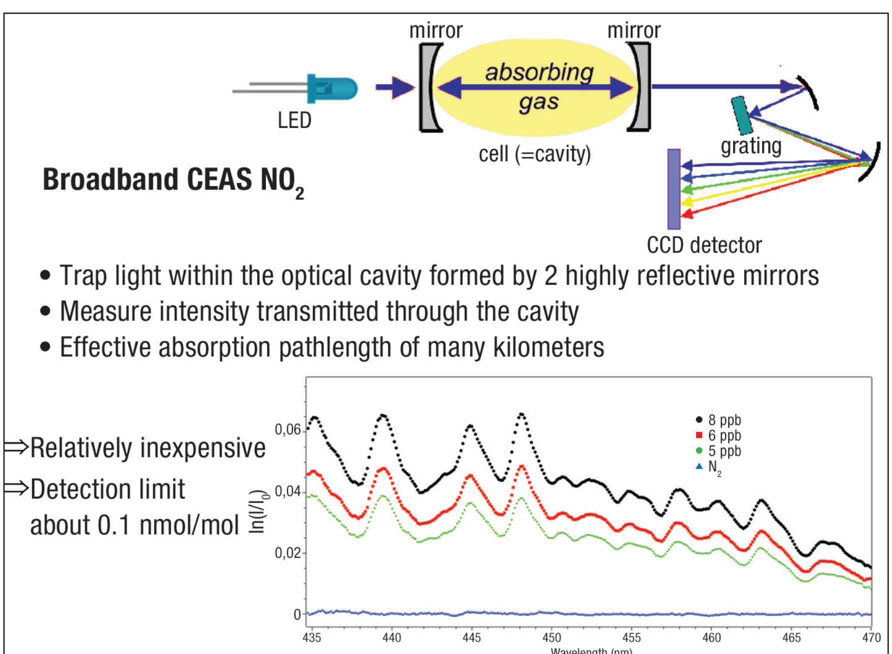

Figure 4. Absolute optical methods. (Figure 4 courtesy of VSL, MACPoll "Workshop Zero Gases" and EMRP)

the preferred method. (Please see Figure 2.) For SO_2, there are fluorescence devices from Horiba, Thermo, Teledyne Instruments Inc. and others. Chemiluminescence dominates NO, with Thermo, Environnement S.A., and Horiba in the lead.

Only for H_2O do the newer laser-based techniques, such as Cavity Ring-Down Spectroscopy (CRDS) and Tunable Diode Laser Absorption Spectroscopy (TDLAS), come to the fore. "Water is no problem at all," Persijn noted, with a nod to those techniques' detection capabilities. "Water would have been different five years ago, but now laser spectroscopy dominates," he said. (See Figure 3.)

In the absence of more certain methods for other target molecules, NMIs have embarked on the development of their own techniques, such as VSL's above-cited Broadband CEAS (see Figure 4), which measures to 0.1 ppb of NO_2. The U.K.'s NPL has developed Adjustable Gas Standards, based on chemiluminescence, while the French national institute is working on a novel technique, using commercial QCL-based absorption that measures SO_2 at 2.2 ppb, according to LNE's Macé. For spectroscopy buffs, one of the more unusual devices melds two different methods, TDLAS and CRDS, from Germany's PTB and Finland's MIKES, respectively. (See Figure 5.)

While several of the advanced systems presented are still in development, they show promise for direct, selective, and consistent measurement of three or more of the target species at a time. In a recent interview by email, Baldan, the MACPoll project coordinator, wrote that zero gas standards will be achieved by utilizing such "highly accurate measurements techniques, such as laser spectroscopy, which are highly sensitive and, if properly characterized, independent of calibration." The intent is that these be used in conjunction with more mature "classical techniques" to track impurities.

Packaging and Handling Zero Gas Standards

Measuring techniques are but one facet of this broad-based endeavor, which encompasses such related topics as cylinder treatment, filtration, purification and sample handling. Calibration gas can become contaminated with trace amounts of pollutants if, as examples, mistakes are made in the

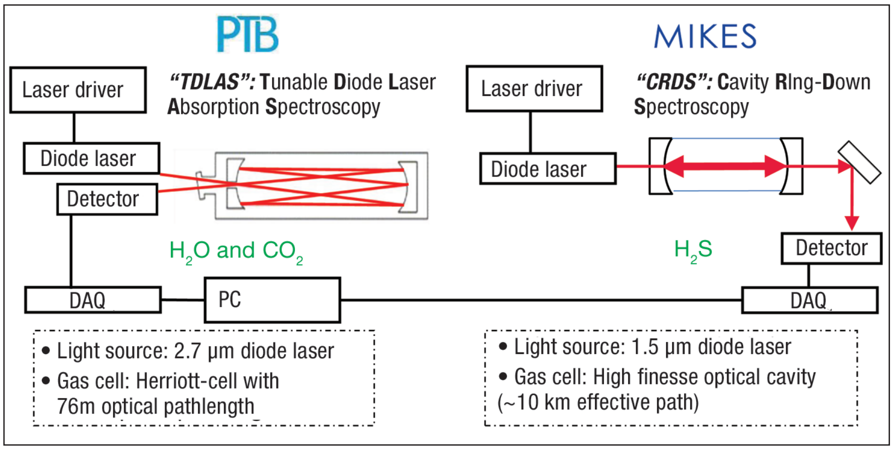

Figure 5. Multiplexing optical system: The two systems are combined through a common gas handling and data evaluation. (Figure 5 courtesy of MACPoll "Workshop Zero Gases" and EMRP)

filling process or the sample lines are inadequately purged and leak-checked. There were also recommendations that provisions be made for the shelf life of cylinders, which can change over time. In short, there are many potential variables impacting the integrity of zero and other calibration gases. Users may wind up with a zero pollutant measurement that could actually contain unwanted constituents in the ppm range.

Chasing Zero

Despite the challenges, if we are to effectively remedy health issues and environmental damage caused by pollution and greenhouse gases, we need viable means to impose regulations. As MACPoll progresses, the initiative will likely lead to a solid reference standard to validate air-monitoring equipment and thereby ensure credible data for enforcement. In so doing, a slew of exciting new instrumentation and related developments will come to the fore. In this sense, the quest for zero is ultimately a juggernaut for progress.

***LISA BERGSON** is CEO of Tiger Optics LLC. She can be reached at lbergson@tigeroptics.com*