INNOVATIVE CALIBRATION STRATEGIES FOR ROUTINE QUALITY ASSURANCE AND QUALITY CONTROL OF ANALYZERS FOR REACTIVE TRACE GASES, WITHOUT THE NEED FOR PRIMARY STANDARDS

Reliable, sub-ppb trace gas measurements are essential for a range of industrial process and air quality monitoring purposes.

Picarro's Cavity Ring-Down analyzers (CRDS) have become the preferred technology for stable and continuous, high-precision trace gas measurements since the commercial release in 2005. Currently, they are used for a range of gas monitoring purposes, such as: fence line emissions near industrial facilities (HF, H_2CO, H_2S, EtO), air quality inside sterilized isolator spaces (H_2O_2), occupational exposure limits to toxic gases, stack emissions monitoring to comply with regulations and emissions (HF, H_2CO, H_2S, EtO), process control to improve yield (HF, SO_2, NH_3, H_2S, HCl), and many other applications.

A key feature of CRDS analyzers is their unprecedented stability and ease of use. This is thanks to the low calibration requirements, which is accomplished by the patented wavelength monitor. wavelength monitor tracks one or more well-defined spectral reference lines (most commonly: water), which guarantees the unmatched low drift. Therefore, the performance of Picarro's industrial trace gas analyzers only needs to be validated on an infrequent basis (e.g., during a yearly performance validation).

Commonly, a calibration of crucial gas measurement equipment is performed with commercially available and certified gas standards, specifically to determine the linearity and the zero value of the analyzer. Importantly, sourcing accurate standards for hazardous, corrosive, and reactive trace gases is challenging and often technically impossible. To overcome this limitation of such standards, Picarro established a three-fold approach: 1. Factory calibration with a golden analyzer, 2. Validation of the linearity of an analyzer using a surrogate gas approach, and 3. Accurate determination of the zero value of an analyzer.

1. Golden analyzer approach

The golden analyzer is a carefully calibrated inhouse reference instrument with exceptionally low drift that is used as a transfer standard to cross-calibrate production units. The golden analyzer is regularly checked against a non-reactive proxy gas (see point 2 'surrogate gas validation') and trusted, rare primary gas standards. It is important to note that the accuracy of the golden analyzers is not limited by the measurement precision of the trace gas standards, but rather the limited accuracy of available primary standards.

2. Surrogate gas validation

To offer a straightforward calibration strategy for reactive and hazardous gases, Picarro has developed the method of surrogate gas validation for gases such as ammonia (NH_3), hydrogen chloride (HCl), hydrogen peroxide (H_2O_2), hydrogen fluoride (HF), and formaldehyde (H_2CO) (see Table 1). The principle is that two adjacent adsorption lines of individual species behave in similar manners. As such, the accuracy and linearity of the analyzer can be validated using surrogate gases. Picarro selected these surrogate gases based on the spectroscopy for each analyzer. Key criteria for this selection process were: A. non-reactive gas, B. Commercially available certified cylinders, and C. Adsorption line adjacent to the primary gas.

For most analyzers, Picarro recommends that the linearity is verified by measuring three different surrogate gas concentrations, in addition to the zero-point measurement (see point 3 'accurate determination of zero value'). In practice, reactive trace gas analyzers from Picarro are assessed with a span accuracy of 5% or 10% (measured on the surrogate gas), reflecting the specified accuracy of the certified surrogate gas standards.

3. Accurate determination of zero value

As mentioned, the drift of Picarro's CRDS analyzers is constrained by the patented wavelength monitor which tracks one or more well-defined spectral reference lines. This impedes highly undesirable monotonical drift and thereby guarantees unmatched long-term stability. For most applications, the zero value only needs to be determined infrequently (e.g., together with the yearly span validation). An example of an exception to this is the measurement of ethylene oxide for ultra-low background monitoring purposes, where more frequent zero referencing delivers the desired low ppt performance.

One last aspect to keep in mind is that, depending on the trace gas of interest, accurate determination of the zero value is complicated because ultra-high purity (UHP) zero air may contain ppt to ppb amounts of the target gas. For this purpose, Picarro tested a range of scrubbing agents to assure convenient, reliable, and accurate determination of the zero value within an acceptable specification (e.g., phosphoric impregnated activated charcoal (PAIAC) is recommended for ammonia, activated charcoal and coconut shell for hydrogen chloride and hydrogen fluoride, manganese greensand for hydrogen peroxide, and DrieRite for formaldehyde).

For more information on best practices for QA/QC of reactive trace gas measurements, please download the Rapid Analyzer Validation Using a Traceable Surrogate Gas Approach paper.

Table 1: Hazardous, corrosive, and reactive primary gases, and the corresponding surrogate gases and concentrations that can be used to validate the performance of the Picarro CRDS analyzers. Note that the concentrations of the surrogate gases are usually higher than their natural abundances because the spectral features of the surrogate gases tend to be weaker.

Model	Primary Gas	Surrogate Gas	Surrogate Gas Concentrations
G2103	Ammonia (NH_3)	Carbon dioxide (CO_2)	0, 200, 1 000, 10 000 ppm
G2108	Hydrogen chloride (HCl)	Methane (CH_4)	0, 7, 50, 100 ppm
PI2114	Hydrogen peroxide (H_2O_2)	Methane (CH_4)	0, 7, 50, 100 ppm
G2205	Hydrogen Fluoride (HF)	Oxygen (O_2)	0, 20.94% (ambient)
G2307	Formaldehyde H_2CO)	Methane (CH_4)	0, 7, 50, 100 ppm

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