ABSOLUTE ZERO DEFINED

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The challenges of measuring absolute zero pollutants with existing calibration gases.

Above: Protocol test gases come in a variety of sized cylinders.

Before modern digital scales, old-fashioned balances with calibration weights on one side were commonly used to get accurate measures of objects' mass. An everyday illustration of this is the deli counter. If a customer ordered a pound of cheese, the calibration weight on the other side would weigh exactly one pound. When the two sides of the scale were even, the deli worker knew he had exactly one pound of cheese.

But what if the calibration weight fluctuated? The customer could wind up with more (or less) than a pound of cheese, without knowing it. And what if the scale had weight registering before anything was on the scale? The zero would be off and someone would get cheated even before the weighing started.

Understanding the Issues

Fluctuation in a calibration weight may not be a serious issue at the deli counter (who would ever complain about receiving extra cheese?), but it is a major issue when it comes to measuring air pollutants in gases. To accurately measure the pollutants in any gas mixture, it needs to be measured against a calibration gas, which should ideally have a definable zero measurement of pollutants. While it may be impossible to completely eliminate pollutants, an acceptable lower detection limit is necessary. It can be difficult to ensure that the calibration gas being measured against contains that lower limit of the pollutant. The calibration gas can become contaminated with trace amounts of pollutants if, for example, the zero gas itself is not made or properly analyzed, if the sample line was not thoroughly cleared of past pollutants before use, or if there was interference in the line. This means that the customer may wind up with a zero pollutant measurement that could already be measuring the constituent in the parts per million ranges.

One common way to help reduce pollutants is to use a gas (usually nitrogen) to purge the sample lines and regulator. Think of this as using a clean drinking straw to take a sip of water versus using a straw that was first used to sip soda. If one does not put clean, dry nitrogen through the lines and regulator, one could be introducing moisture or other interferants that could contaminate the cylinder and ruin the calibration gas. This can especially happen at very low-level pollutants of NO, NO_2, HCL or N_2O when measuring at levels below 10 parts per million. Slight amounts of moisture can react in the cylinder walls and ruin the mixture. Just like drinking through a clean straw, it is very important to purge the lines several times to ensure accurate measurement of low level pollutants with as little interference as possible. Some companies purge as many as nine times between calibrations.

It may seem like the obvious solution for achieving absolute zero would be to purge the line with another gas (for example, using SO_2 to clear a line for NO). However, the root issue still remains: Is it known for certain what is mixed with the nitrogen? What was previously in the container? Could there be low-level moisture on the cylinder walls? In short, there are many potential variables that can impact an attempt to obtain a zero calibration gas. The user is 100 percent dependent on the vendor because the regulation for CEM zero nitrogen gas or zero air (40 CFR 72.2) states the gas must be vendor certified to have less than or equal to 0.1 ppm SO_2, NO_X, total hydrocarbons, less than or equal to 1.0 ppm CO and equal to or less than 400 ppm CO_2.

The other part of the problem is getting the correct gas concentration to the low level required without compromising the accuracy. Just using a gas divider to get the concentration to the necessary level may unintentionally introduce other interferences into the mix, unless the interferences can be analyzed.

Consequences of inaccurate measurement

The main issue with inaccurate calibration gas measurements is that the EPA and individual states oversee low emissions permit requirements for criteria pollutants and other gases (such as hydrochloric acid, ammonia and formaldehyde), but may have trouble enforcing them. In theory, the EPA and state Title V permits allow for certain levels of pollutants, but the problem is, of course, that they are not able to properly enforce the low pollution emissions without an accurate and credible absolute zero point to accurately give a proper base line (starting point). Without accurate measurements, a Title V emitter could unknowingly be off and in violation of their Title V Emission permit from the start. This could lead to expensive fines and ultimately incorrect reporting of pollution emissions.

For example, consider having to monitor a gas-fired turbine with an $N0_X$ and CO permit with limits set at 2 ppm but the zero gas used has a zero span of zero to 20 percent. If the gas vendor did not test the gas and just stated that it meets the requirements of 40 CFR 72.2, while it is a legal gas, it may not have been properly made. There is also no audit requirement to catch bad zero gases as there is in the EPA protocol gas audits. In past incidents, the gases used as zero gas have been welding-grade gases, nitrogen or breathing air. In some cases, the gases have had $N0_X$ and CO levels up to 16 ppm (that is 160 times over the lower level permitted in zero nitrogen or air as defined in the regulations). This will invalidate the test with a bad lower value (a starting point) even before the test begins.

Current standards and protocols

Currently, the responsibility to certify that a calibration gas has an absolute zero measurement falls to the gas vendor. However, the user is ultimately responsible.

The vendor must carefully test the zero calibration gas to insure that it does not exceed the sub ppm level of pollutants required by the regulation.

For EPA protocol calibration gases, the vendors work with experts at a metrological association, such as the National Institute of Standards and Technology (NIST) in the United States, to verify its gases are traceable against a calibration gas, or standard, so that it will be reliable and accurate. In these cases, the process for testing an EPA Protocol Gas typically follows this path:

1. A gas vendor obtains an NIST Tracable Reference Material (NTRM) or Standard Referecne Material (SRM) from NIST, Primary Reference Material (PRM) or creates their own Gas Manufacturer Intermediate Standards (GMIS).
2. The analyzer is calibrated with the NTRM, SRM or GMIS standard for linearity.
3. The NIST traceable standard will then verify that the gas in the cylinder is what was claimed, similar to a one pound weight on a scale for the pollution concentration.
4. The vendor then repeats the analysis after a period of staging the cylinders to achieve the required stability before the certification of analysis can be put on the cylinder and it can be sold.

The difference here is that there are no NIST traceable gases to verify the lower limits of the criteria pollutants. Without them there is no standard for zero gas.

The process works very well when an EPA protocol gas is used to measure the concentration of the pollutant. The gas is traced from another gas that is "certified as accurate," within ±2 percent from the "tag value." The problem is that NIST does not have traceable gases for all the pollutants the industry needs to

EPA Guidelines for Measurement Procedures

Without a verifiably absolute zero calibration gas, the best thing that the gas industry can do is to make sure that gas purifiers are working well enough so that the gases can be measured on non-verified analyzers. This takes tremendous technical knowledge and requires gas vendors to make an investment into equipment to correctly produce the zero gas. But, even if the gas is properly generated, no one will know. Unlike EPA protocol gases, there are NO audit programs to spot check these important gases. So until there is a traceable zero gas, what can be done?

First, we depend upon the vendor's word that they are doing everything they can to maintain that the pollutants in the zero gas do not exceed the requirements of 40 CFR 72.2. Then, ask them for a walkthrough of their process to insure that they are taking prudent steps to avoid any cross contamination or problems with analysis.

Before long, the EPA will see this gap in the regulations and NIST will be able to start to produce some traceable zero materials soon. This, coupled with rolling the zero gases into the existing Protocol Gas Verification Program, will verify what is labeled as "zero" is absolutely zero.

Each cylinder of protocol gas mixture must come with an analytical certification.

measure. This is especially a problem for zero gas. NIST cannot make a standard and say with certainty that there are no trace pollutants in it, but they can make a standard that has the pollutants in a very small concentration, for example, less than 100 parts per billion, and verify that there is no more than that level of a criteria pollutant.

Looking forward

Many other countries, including Japan and the Netherlands, already have metrological standards in place for traceable zero gases. The U.S. is sorely lacking these standards. The good news is that reputable gas vendors are making great strides to convince the EPA and NIST that standards are critical to provide a more accurate measure of pollutants in gases so that the detection limits are clear. Gas vendors are also working to create the necessary calibration gases to monitor for new pollutants (HCL, ammonia, and formaldehyde) that are necessary to meet new EPA and state monitoring. There are considerations for zero gases for these new pollutants as well. ***PE***

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