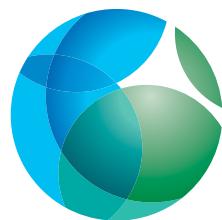


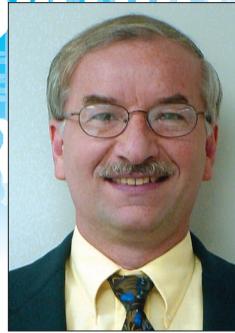
Calibration Standard Gases Are Key to Reliable Measurements



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by Ronald C. Geib

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Accurate, repeatable measurements are possible only when an analytical instrument is calibrated properly.

Quantitative analytical measurements are a critical component in achieving accuracy in laboratory and manufacturing applications that include petrochemical processes, natural gas, environmental compliance, and health and safety programs. Where the measurement hardware is not calibrated, there can be no certainty in the measurements conducted. Enter calibration gases.

The calibration gas standard establishes a known analyzer response to a certified chemical component concentration. This enables sample responses to be converted to a concentration whose accuracy can be determined. This article offers an in-depth review of how calibration standard gases are manufactured, certified, and properly maintained.

Ordering Calibration Standard Gases

The specialty gas industry is made up of specialists that manufacture and supply calibration standard gases. Before a specialty gas company can produce a calibration gas standard, specific information is required from the end-user. This information includes a list of components that make up the calibration gas: concentrations, units, balance gas, cylinder size, blend tolerance, and analytical accuracy.

While all specialty gas companies offer standard product grades that have defined blend tolerance and analytical accuracy,

customers must be aware that grade names, blend tolerances, and accuracy are not uniform throughout the industry. Thus, careful evaluation of suppliers and specifications is essential to ensure value, consistency, and technical satisfaction.

Blend Tolerance

Blend tolerance is the concentration range that includes the mixture's minor component(s) and concentration(s). For example, a supplier's primary standard grade may claim one percent accuracy and two percent blend tolerance. For a 100 ppm concentration, the blend tolerance indicates that the component certified concentration will be in the 98 to 102 ppm range. The end-user, however, must be careful in defining the blend tolerance that is acceptable for his analyzer and calibration requirements. Should there be a need for a calibration gas that is at the top of the instrument range (span gas), then the mixture should be ordered with a maximum

concentration specified because there is no use for a calibration gas standard that exceeds full scale.

If a minimum of calibration adjustments is desired from standard-to-standard, then the end-user should consider a homogeneous batch, or, alternately, find a supplier that has the capability to blend with very narrow blend tolerances, such as less than one percent relative.

Accuracy

Accuracy is defined as the agreement of a measured value with its true value. Common synonyms for accuracy are analytical accuracy, analytical uncertainty, and certification accuracy. All calibration standard gases should have a certified component concentration, along with an expression of the accuracy of the certified value. Analytical accuracy is a statistically derived value. The generally accepted formulae for calculating accuracy are published in International Standard Organization (ISO) and U.S. institute papers. Basically, accuracy is calculated using a propagation of error model, commonly referred to as the square root of the sum of the squares of the common error factors. In measurements, the common error factors for supplier certification of a calibration gas standard are the reference standard error, the calibration curve error, the imprecision of the measurements, and the instability of the gas mixture. For a gas mixture certifica-



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tion directly against a reference standard, the mathematical expression is as follows (assuming no instability over time):

$$\text{Accuracy} = k[(\text{std error})^2 + (\text{precision})^2 + (\text{cal. curve})^2]^{1/2}$$

At the 95 percent confidence level, coverage factor $k = 2$

Example:

Standard Error at 1RSD = 0.5 percent

Precision at 1RSD = 0.5 percent

Calibration Curve Error at
1RSD = 0.5 percent

The result of this calculation is 1.7 percent, which a supplier may round to plus or minus two percent accuracy. A word of caution here: *the specialty gas industry does not uniformly apply accuracy calculations—some suppliers may use alternative calculations, or base their calculations on gravimetric additions.*

The end-user of the calibration standard gas must determine the measurement accuracy that is needed for his specific application. If a process control chart is available, the user could assess the impact of having deviations up to twice the reported accuracy. (Keep in mind that plus or minus two percent on individual certified standards could result in a range of cylinder values of minus two to plus two percent or four percent for repeat orders.) Environmental regulations may specify the accuracy required of measurements and even the correct certification procedure, such as EPA Protocol Gases for environmental instrument calibration. The accuracy propagation of error calculation is also fundamental to any process or laboratory analyst's understanding of the measurement accuracy of his analytical technique.

Traceability to National Standards

A traceability definition is taken from ISO Guide 25 (currently ISO 17025):

“ . . . the property of a measurement result, whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons.” In the U.S., gas



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phase national standards are provided by the National Institute of Standards and Technology, NIST. In the field of gaseous measurements, NIST traceability is complicated by the fact that a limited number of gases are available as standard reference materials by NIST.

Many U.S. environmental regulations require traceability of the specified minor components through measurement versus a NIST SRM (Standard Reference Material) or NIST NTRM (NIST Traceable Reference Material). Where available, end-users should request NIST gas traceability. Also, the traceability information must be reported on the certificate of analysis as proof of the NIST traceability. For the hundreds of chemical species that may be needed as gas standard minor components, NIST traceability is achieved through gravimetric weight calibrations, or other mechanisms (including titrimetry), which should also be reported on the certificate of analysis. For non-NIST SRM traceable chemicals, the end-user should request information on how the supplier guarantees the accuracy and traceability of the minor component(s). This will provide assurance that the calibration gas standards will be consistent over time, and also meet the ISO 9000 certification requirements.

Storage and Shelf-life Considerations

Mixture storage relative to the mixture shelf-life or stability should also be considered. For ISO 9000 compliance, and also for gas standards made to comply with environmental regulations, a shelf-life must be reported on the certificate of analysis. U.S. EPA specifies EPA Protocol

mixture shelf-lives. All other mixtures require the study and reporting by the individual supplier. For many reactive gas species at concentrations less than 1,000 ppm, the mixture stability depends on the technology of the supplier; the mixture stability can vary significantly.

Specialty Gas Industry Processes

Once the end-user has resolved all of the gas mixture specifications with the specialty gas supplier, an order is entered into the supplier's manufacturing process. If the mixture is a supplier catalog item, most of the production and laboratory procedures are routine and, in most cases, defined. Many gas and liquid mixtures are non-catalog or custom, and many challenge the technology and know-how of the respective gas supplier. In the engineering of a catalog and custom item, the gas manufacturer must address the following issues:

- Cylinder material, such as steel vs aluminum
- Cylinder preparation technology
- Raw material grades and impurities
- Chemical compatibility
- Blending technology
- Blending measurements vs blend tolerance
- Laboratory instruments and procedures
- Certificate of Analysis
- Shipping

Role of the Quality System in Specialty Gas Industry

The preceding paragraph identified nine key areas that must be addressed in the successful preparation and certification of a calibration gas standard. All of these activities must be systematized to ensure the end-user that a reliable calibration standard gas will be provided. The supplier's quality system defines the quality organization and control mechanisms that provide assurance of a reliable supplier. A common quality system is ISO 9002, but other programs exist, such as Laboratory Accreditation processes. The end-user should verify that the prospective supplier has sufficient quality systems to meet the

end-user's reliability expectations.

Specialty Gas Manufacturing Process

Successful gas mixture manufacturing requires reliable cylinder preparation and cylinder surface treatment technology. Different suppliers apply unique terminology to their cylinder treatment processes, and the proof of their utility is whether the supplier can back up his treatments with shelf-life studies of challenging mixtures. Reactive chemicals at concentrations less than 10 ppm raise challenges to the suppliers' technology. These challenging chemicals include ammonia, dimethyl disulfide, hydrogen chloride, hydrogen sulfide, nitric oxide, and nitrogen dioxide. However, there are many more chemicals. Also, concentrations of interest are often sub-ppm.

Once the proper cylinder and cylinder treatment have been identified, the supplier can forward the cylinder for blending. Depending on the grade of the mixture, as defined by the blend and analytical tolerances, the manufacturer may select from a number of blending options:

- Gravimetric
- Volumetric
- Dynamic

Gravimetric blending is quite common for high accuracy and tight blend tolerances. The purchaser of a calibration standard gas must be aware that some suppliers may base their certifications on the gravimetric quantity weighed into the cylinder only.

Gravimetric certifications have the following limitations:

- Loss of reactive minor components due to surface absorption (example: chlorine in a steel cylinder)
- Presence or addition of impurities in multi-component mixtures (example: isobutane impurity in propane, adding to the isobutane weight in a propane/isobutane mixture)
- Reaction of impurities in the mixture with certified minor components (example: oxygen impurity with nitric oxide)
- Mistakes, which may include addition of the wrong component or erroneous

weight additions.

For these reasons, most end-user measurements should be conducted with mixtures that have been verified using laboratory measurements.

The reliability of gravimetric concentrations is also subject to the purity of the raw materials. Also, the stability of the mixture is frequently dependent on the raw material impurities. Some raw materials do not include major impurities in their specifications, so the individual supplier may not be aware that they are present. For example, pure nitrogen frequently has several hundred ppm of argon; pure helium may have 20 ppm or more of neon; and carbon monoxide may have 0.7 percent argon. These examples also point out the value added through laboratory certifications by technically proficient analysts.

Laboratory Certification

Once the gas mixture has been blended, a certified gas mixture will likely require laboratory certification of all component concentrations. The laboratory must address the customer's traceability requirements by conducting measurements against an appropriate reference standard, or reference standard mechanism. NIST's gaseous traceable standard is the NIST SRM. NIST and private industry also have a NIST Traceable Reference Material (NTRM) program that allows the copying of either the SRM or other NIST primary standards.

For the hundreds of minor components that have no NIST SRM, the supplier has the responsibility to develop certification practices that can statistically validate the concentration of minor components in the cylinder. Some alternative certification technologies that are used include wet



Gas Mixture Blending Panel

titrations of minor components collected into scrubbing solutions, multiple preparations of gravimetric standards used in calibration curve studies, and working with regulatory and industry sources to prepare and certify mutually acceptable standards.

The Role of Quality Assurance Processes

Quality Assurance functions typically sponsor and assess the quality system within the supplier and end-user organizations. Granted that the supplier/customer relationship involves quantitative measurements, the quality assurance programs must include the support and evaluation of the measurement programs. In this regard, the application of the best available NIST traceable reference standards by the supplier is essential. Both the supplier and customer should participate in industry "round-robbins" that confirm the conformance of measurements to the industry. The supplier also needs to organize internal round robins to ensure the uniformity of multiple locations. The most important quality assurance function is to organize data interpretation and corrective action processes.

Conclusions

Considering how critical calibration standard gases are to leading industrial measurement processes, this article has gone into detail to identify the key variables for both the user of calibration standard gases, and the suppliers of calibration standard gases. If the end-user adheres to stringent application of the principles that need to be addressed, it follows that the end-user will be able to identify a reliable supplier.

Ron Geib is currently the Specialty Gas Product Manager with Matheson Tri-Gas, Inc. He has worked in the specialty gases field for 20 years, during which time he has held positions in Quality Assurance, Applied Technology, and Marketing. He can be reached at RGeib@matheson-trigas.com