

# CALIBRATION STANDARD GASES

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## INTRODUCTION

Calibration standard gases are essential to quantitative analytical measurements in petrochemical processes, natural gas, environmental compliance, and health and safety programs – among others. The calibration gas standard establishes a known analyzer response to a certified chemical component concentration which enables the conversion of sample responses to a concentration with a determinable accuracy. In consideration of the criticality of calibration standard gases to valid measurements in chemical processes and environmental monitoring programs, the objective of this paper will be to provide an in-depth review of how calibration standard gases are manufactured, certified, and properly maintained.

## ORDERING CALIBRATION STANDARD GASES

The specialty gas industry has specialists in the provision of calibration standard gases and in the support gases essential to analytical measurement processes. Certain information is essential for the specialty gas company to provide the calibration standard that is required which is summarized as follows: minor components, concentrations, units, balance gas, cylinder size, blend tolerance, and analytical accuracy. All specialty gas companies will 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 in the industry so that careful evaluation of suppliers and specifications is essential to ensuring value and technical satisfaction.

### Blend Tolerance

Blend tolerance is the concentration range that will include the mixture minor component(s) concentration(s). For example, a supplier's primary standard grade may claim 1% accuracy and 2% blend tolerance. For a 100 ppm concentration, the blend tolerance indicates that the component certified concentration will be in the range 98 - 102 ppm. The end user must be careful in defining the blend tolerance that is acceptable for his analyzer and calibration practice. 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 are desired from standard to standard, then the end user should consider a

homogeneous batch, or finding a supplier that has the capability to blend with very narrow blend tolerances such as less than 1% 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, and the generally accepted formulae for calculating accuracy are in International Standard Organization (ISO) and U.S. institute papers. Basically accuracy is calculated using a propagation of error model which is 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 certification 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% confidence level, coverage factor  $k = 2$

Example: Standard Error at 1RSD = 0.5%

Precision at 1RSD = 0.5%

Calibration Curve Error at 1RSD = 0.5%

The result of this calculation is 1.7%, which a supplier may round to +/-2% accuracy. A word of caution here is that the specialty gas industry does not uniformly apply accuracy calculations - some suppliers may use alternative calculations, or base it on gravimetric additions. The end user of the calibration standard gas must determine the measurement accuracy that is needed for the specific application. If there is a process control chart, the user could assess the impact of having deviations up to twice the reported accuracy (remember that +/- 2% on individual certified standards could result in a range of cylinder values -2 to +2% or 4% for repeat orders). Environmental regulations may specify the accuracy required of measurements and even the correct certification procedure (example 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 process.

#### Traceability to National Standards

A traceability definition is taken from ISO Guide 25 (now 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 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 addressed as standard reference materials by NIST.

Many U.S. environmental regulations require traceability of the specified minor components through measurement versus a NIST SRM or NIST NTRM (NIST Traceable Reference Material). Where available, end users should request NIST gas traceability, plus 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, plus there are 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, plus meet the ISO 9000 certification standard expectations.

#### Storage and Shelf-life Considerations

For many calibration gas standards with hydrocarbon minor components at mole% or higher concentrations, the hydrocarbon dew point temperature is important. The hydrocarbon dewpoint temperature is where the most vapor pressure restricted minor component condenses from the gas phase into a layer or into a liquid. Condensation invalidates the certification. Specialty gas companies should manufacture to a standard dewpoint temperature, and an example would be 32 deg F. This is satisfactory in some geographic regions for most of the year, but in the winter in Minnesota, a complex gas mixture calculated at 32 degrees F will likely experience significant condensation. The supplier and end user must anticipate shipping and storage conditions and negotiate the proper dewpoint temperature for the geographic region; and this should be reported on the certificate of analysis as well. In some situations, unopened cylinders can be warmed to room temperature, and a condensed component(s) can be re-volatilized and re-mixed. However, data and a procedure from the supplier should be available to ensure that this will work. Also, a complex

mixture requires software to do dewpoint calculations because manual calculations can not take into consideration the molecular interactions which often reduce the allowable cylinder fill pressures. 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 1000 ppm, the mixture stability depends on the technology of the supplier, and 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 there are other programs such as Laboratory Accreditation processes. The end user should verify that the prospective supplier has sufficient quality systems to meet the end users reliability expectations. In addition, the supplier's understanding and use of technology and measurement science should be demonstrated by customer audit.

## Specialty Gas Manufacturing Process

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

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

- ◆ Gravimetric
- ◆ Volumetric
- ◆ Dynamic blending

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 multicomponent mixtures (example isobutane impurity in propane adding to isobutane weight in a Propane/isobutane mixture)
- ◆ Reaction of impurities in the mixture with certified minor components (example oxygen impurity with Nitric Oxide)
- ◆ Blunders that may include addition of the wrong component, an erroneous weight.

For these reasons, most end user measurements should be done with mixtures that have been verified using laboratory measurements, and the end user should confirm that the supplier includes laboratory certification in the mixture grade and pricing.

The reliability of gravimetric concentrations is also subject to the purity of the raw materials, plus the stability of the mixture is frequently dependent on the raw material impurities. Some raw materials do not include major impurities in their specifications and 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% 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 the components' 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 technology that is used includes wet 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. In 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 robins that confirm the conformance of measurements to the industry. The supplier also needs to organize internal round robins to challenge the uniformity of multiple locations. The most important quality assurance function is organizing data interpretation, and corrective action processes.

## CONCLUSIONS

In consideration of the criticality of calibration standard gases to leading industrial measurement processes, this paper has gone into detail identifying 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, then the end user will be able to identify a reliable supplier.