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. 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 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 are 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 within which will be the mixture minor component concentrations. For example, a supplier's primary standard grade may claim 1% accuracy and 2% blend tolerance. For a 100 ppm concentration, the blend tolerance says that the component certified concentration would be 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 adjusted from standard to standard, then the end user should consider a homogeneous batch or pursuing 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 formulas for calculating accuracy are in International Standard Organization (ISO) and U.S. Institute papers. Basically, accuracy is calculated using a propagation of error model that 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 both supplier certification of a calibration gas standard are the reference standard error, the imprecision of the measurements, and the instability of the gas mixture. The mathematical expression is as follows:

$$\text{Accuracy} = [(\text{std error})^2 + (\text{precision})^2 + (\text{stability})^2]^{1/2}$$

Example:	Standard Error	= 1%
	Precision	= 1%
	Instability	= 1%

The result of this calculation is 1.7% which a supplier would round to ±2% accuracy. A word of caution here is that the specialty gas industry does not uniformly apply accuracy calculations — some suppliers either do not report accuracy or base it on other calculations such as gravimetric additions. The end user of the calibration standard gas must determine the measurement accuracy that is needed for the specific application. If there were a process control chart, the user would 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). Often there is a clause in contracts that specifies the accuracy required of reported values. Finally, environmental regulations frequently 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 calculations is also fundamental to any process or laboratory analyst understanding the measurement accuracy of his/her process.

NIST Traceability

ISO Guide 25 defines traceability as: "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." Organizations that have achieved ISO 9000 certification must demonstrate that their measurements comply with the preceding definition. In the U.S., national standards are provided by the National Institute of Standards and Technology, NIST. In the field of chemical measurements, NIST traceability is complicated by the fact that only about 20 chemicals are addressed by NIST. See Table 1.

TABLE 1. NIST SRM Components

MINOR COMPONENT	BALANCE GAS	COMPONENT RANGES
Benzene	N_2	0.25 - 10 ppm
Bromobenzene	N_2	0.25 - 10 ppm
Carbon Dioxide	N_2	300 ppm – 16%
Carbon Dioxide	Air	330 – 380 ppm
Carbon Monoxide	N_2	10 ppm – 16%
Carbon Monoxide	Air	10 – 45 ppm
Chlorobenzene	N_2	0.25 – 10 ppm
Hydrogen Sulfide	N_2	5 – 20 ppm
Methane	Air	1 – 10 ppm
Methane	N_2	50 – 100 ppm
Nitric Oxide	N_2	5 – 3000 ppm
Nitrogen Dioxide	Air	100 – 2500 ppm
Nitrous Oxide	Air	300 – 330 ppb
Oxygen	N_2	2 – 21%
Propane	Air	0.25 – 500 ppm
Propane	N_2	100 ppm – 2%
Sulfur Dioxide	N_2	50 – 3500 ppm
Toluene	N_2	0.25 – 10 ppm

For many U.S. environmental regulations, traceability of the above minor components through measurement versus a NIST traceable gas standard is essential. Where possible, the end user should request NIST gas traceabilty, 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 traceabilty is achieved through gravimetric weight calibrations and other mechanisms that 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 of the minor component as this will ensure that the calibration gas standards will be consistent over time plus meet the ISO 9000 certification requires.

Storage and Shelf-Life Considerations

For any calibration gas standard with hydrocarbon minor components with mole % or higher concentration, the hydrocarbon dew point becomes important. The hydrocarbon dew point is that temperature where the most vapor pressure restricted minor component condenses from the gas phase into liquid. Condensation invalidates the certification. Specialty gas companies usually have a standard dew point temperature, and an example would be 32 degrees 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 experience significant condensation. The supplier and end-user must anticipate shipping and storage conditions and negotiate the proper dew point 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 dew point calculations because manual calculations can not take into consideration the molecular interactions that often reduce the allowable cylinder fill pressures. Mixture storage with respect to the mixture dew point has been discussed, the mixture self-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 validity
- 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 suppliers quality system provides the organization and control mechanism to provide the 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.

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 and classes are listed in Table 2.

TABLE 2. Reactive Chemical Species

1. H_2S
2. NH_3
3. NO
4. NO_2
5. SO_2
6. HCl
7. Phosgene Amines
8. Dienes
9. Ethers
10. Aldehydes
11. Organosulfurs
12. Ethylene
13. Propylene Oxide

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

Gravimetric certifications have the following limitations:

- Loss of reactive minor components due to surface absorption (example: chlorine in a steel container).
- Presence or addition of impurities in multicomponent mixtures (example: isobutene impurity in propane adding to isobutene weight in a Propane/Isobutane mixture).
- Reaction of impurities in the mixture with certified minor components (example: O_2 impurity with Nitric Oxide).
- Blunders, which may include addition of the wrong component, an erroneous weight, or even no component.

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 of laboratory certifications by technically proficient laboratories.

Laboratory Certification

Once the gas mixture has been blended, better grade gas mixtures and the better specialty gas suppliers will require laboratory certification of the components' concentrations. The laboratory must address the orders and advertised traceabilty requirements by conducting measurements against an appropriate reference standard, or reference standard mechanism. The highest NIST traceable standard is the NIST SRM. NIST and private industry also have an NIST Traceable Reference Material (NTRM) program that allows the copying of either the SRM or other NIST primary standards. The NTRM programs are essential for specialty gas suppliers to maintain directly NIST traceable certification programs.

For the hundreds of minor components that must be certified where there are no NIST SRM, the supplier has the responsibility to develop certification practices that can statistically validate the concentration on minor components in the cylinder. Some technology that is used includes wet titrations after quantitative collection of minor components of the gas phase into scrubbing solutions, multiple preparations of gravimetric standards and conducting 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 organization. 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.