CALIBRATION STANDARDS

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INTRODUCTION

Process measurements and analyzer calibrations are key components to bottom-line success in the Petrochemical and Industrial Gas market. Analytical results drive processes to higher yields by monitoring vital components and impurities that either achieve desired results or lead to costly reruns and downtime. Analyzers must be kept in constant calibration to eliminate senseless downtime, and calibration standards play an integral part in meeting that success.

This paper discusses the key elements in successfully ordering, manufacturing and maintaining a calibration standard. Once you fully understand the processes involved to produce calibration standards, you will have a greater appreciation for the efforts and labor associated with delivering a quality product that you can trust and rely upon to achieve your goals.

ORDERING CALIBRATION STANDARDS

There are several important factors to consider when ordering calibration standards. It is extremely important that a good understanding of what the customer desires is properly communicated to the calibration standard manufacturer. These factors include:

- Mixture phase
- Blend tolerance
- Accuracy
- Unit of measure

Mixture phase refers to the desired type of calibration standard the customer requires, such as a liquid or a gas blend.

Blend tolerance is the acceptable range for each of the components of the calibration standard. Example: Oxygen requested at 100ppm in nitrogen with +/-2% blend tolerance will allow an acceptable concentration of 98-102ppm for oxygen.

Accuracy is a statistical estimate of the maximum extent to which a measured value can deviate from the true value. Typical accuracy is +/-1, 2 or 5%. Example: If a component is certified at 100ppm with +/-1% accuracy, the end user should yield an analytical value of 99-101ppm for that component.

Unit of measure refers to the actual concentration of the components of the calibration standard in mole percent, weight percent or liquid volume.

Once the appropriate information has been properly communicated to the calibration standard manufacturer the production process will begin.

CYLINDER PREPARATION

Figure 1. *Cylinder bake out ovens used in the preparation of cylinders.*

During the production process of calibration standards, whether gas or liquid, the cylinder preparation step is a key element to the successful manufacturing of the standard. There are typically two types of cylinders used in the manufacturing of calibration standards, steel and aluminum. Both types of cylinders must be properly conditioned to deliver the contents consistently from full pressure to empty.

Depending on the contents of the calibration standard, cylinders may simply be heated, purged and vacuumed several times prior to being filled. For more complex component requests, a more rigorous preparation process is required to ensure the concentration of the gas in a cylinder is the same when it leaves the cylinder as it was when it was filled. This process begins by treating cylinders with a substance that passivates the internal surface of the vessel rendering it neutral or non-reactive to the components of the standard that it will eventually contain. The passivation process may require several days for the substance to properly bind with and absorb all reactive spots associated with the cylinder.

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BLENDING THE CALIBRATION STANDARD

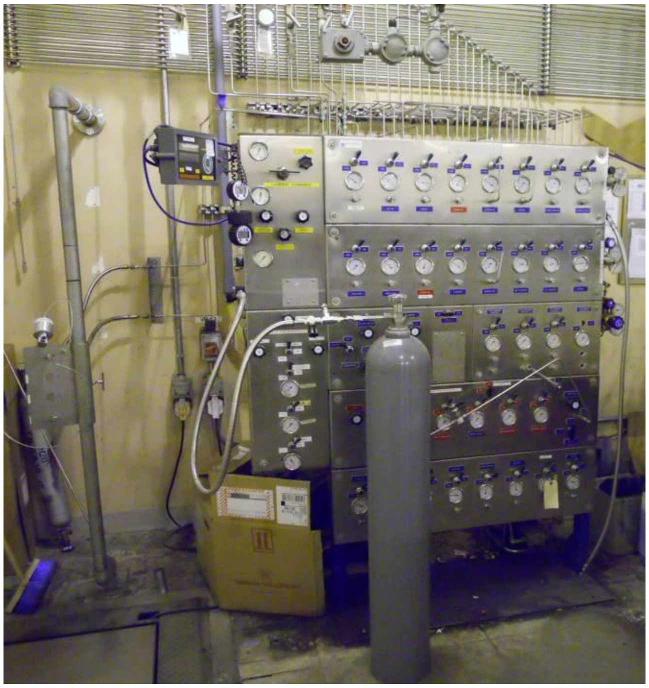

Figure 2. *Blending panel used in the gravimetric preparation of calibration standards.*

Once the cylinder has been properly prepped, the next step in the manufacturing process is calibration standard blending. Blending consists of introducing the components of the standard into the cylinder. The calibration standard can be certified by the blending process or by analytical certification from the lab.

Certifying the calibration standard by the blending process or by gravimetric values is an extremely accurate form of certification. The only element of uncertainty associated with the certification is the uncertainty of the scales. By applying a stringent QA/QC program in correlation with the calibration of the scales, an accuracy of +/-1% can be achieved and maintained with precise consistency.

There are several important factors that must be met before applying this process. First, the raw materials associated with the requested calibration standard must be properly validated through the QC program by being thoroughly analyzed for purity and all associated impurities found in the material. All components in the raw material must be accounted for and properly identified and quantified. Next, the gram adds for the components of the calibration standard must be large enough to achieve the desired accuracy of the standard requested by the customer. Floor scales and bench top balances may be used to achieve the accuracy specified by the customer. Once these requirements have been satisfied, the calibration standard may be certified by gravimetric values, or a more common term "Grav Numbers." If impurities are found in the raw material, they will be listed on the certificate of analysis. This "Grav and Ship" process will only succeed if there is a stringent QA/QC program in place for qualifying raw materials.

If during the blending process the requested accuracy from the customer cannot be achieved by the gram add from the floor scale or tabletop balance, the gravimetric weighing data will be recorded on the blending paperwork, but the calibration standard will not be certified by gravimetric values. Instead, the standard will be sent to the lab for analytical certification. The gravimetric data will be used later as a guide point for the analytical evaluation.

LABORATORY CERTIFICATION

Figure 3. *Typical gas chromatograph (GC) used for analytical certification of calibration standards.*

Most calibration standards that require laboratory analysis usually have components at very low concentrations, ppm or ppb levels. With component concentrations that low, gravimetric values are not a reliable source to guarantee certification; therefore, analytical certification is employed to accurately assign the correct value of the components of the calibration standard.

Other types of calibration standards that require analytical certification are those that contain reactive components such as sulfurs, alcohols and other unsaturated hydrocarbons that have reactive potential associated with their bonding properties.

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A gas chromatograph (GC) is the most common analytical instrument used to perform the analytical certification of the calibration standard. A validated and qualified laboratory standard will be used to measure the instruments performance and then the candidate calibration standard will be run to certify the components of the standard. The gravimetric values that were recorded during the blending process will be used as a target for the analytical certification.

MAINTAINING THE CALIBRATION STANDARD

Once the calibration standard has been certified and shipped to the customer's site, maintaining the standard is very critical for performance and adherence to the guaranteed shelf life of the standard. Calibration standards will come in two different phases as stated earlier: a gas phase or a liquid phase.

A gas calibration standard will be manufactured at a specific dewpoint, usually 32°F or 40°F. What this implies to the customer is, during the use of that calibration standard, the cylinder should not be exposed to temperatures below the dewpoint value. Since many of the calibration standards used in today's Petrochemical and Industrial Gas market are composed of liquefiable hydrocarbons, manipulations of dewpoints are very common to allow for greater top pressure to be achieved when limitations are encountered due to vapor pressure properties of the heavier hydrocarbons. In such instances, the dewpoint calculation may be elevated to 70°F, and as long as the cylinder is not exposed to temperatures below 70°F for an extended period of time, the standard will maintain its integrity.

Figure 4. *Cylinder heating blanket.*

If the calibration gas standard is exposed to temperatures lower than the calculated dewpoint for an extended period of time, there is a high probability that the heavier liquefiable hydrocarbons will fall out of the gas phase and into a liquid within the cylinder. Because of this, it is recommended that the gas calibration standard be placed in a hot box or wrapped in a heated blanket, pictured above, for a minimum of 24 hours and then rolled for at least 30 minutes prior to being used. Once the calibration standard has been reheated and rolled and analyzed, if the heavier hydrocarbons are no longer present the standard may need to be returned the manufacturer for remake.

If, after being exposed to temperatures below the calculated dewpoint, there are no efforts to reheat and roll the cylinder to convert its contents back to a gas phase and the cylinder is opened and gas withdrawn from it, the certified gas calibration standard is at risk of being compromised. If there is a possibility of the exposure, it is best to treat the calibration standard as worse case scenario and reheat in accordance to the steps mentioned previously prior to opening and releasing any gas from within the cylinder. Once the cylinder has been opened and gas released, the contents cannot be adjusted to meet their original certification.

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To maintain a liquid calibration standard requires a very good understanding of the product ordered and the valve type that is associated with the cylinder. Liquid calibration standards will be equipped with a dual port valve; the liquid port is associated with the liquid material inside the cylinder and the gas port is used to maintain the pressure pad in the headspace of the cylinder.

The liquid calibration standard is withdrawn from the cylinder via the liquid port. A dip tube is connected to the liquid port and extends down into the cylinder to approximately one inch from the bottom. As the liquid valve is opened, the calibration standard material will exit the cylinder being forced up the dip tube by the pressure pad. The pressure pad is a very important element in the proper use and maintenance of the liquid calibration standard.

The gas port extends down into the cylinder a few inches directly below the valve near the top of the cylinder; this port does not extend into the liquid material. This port is used to apply the pressure pad of gas, usually helium, onto the top of the liquid material to help compress the liquefiable hydrocarbons into a liquid phase as requested by the customer. Typically the pressure pad is around 200-240psig. To properly withdraw the liquid calibration standard, a cylinder of helium should be connected and regulated to deliver the same amount of pressure as the pressure pad in the liquid standard. As the liquid is withdrawn for the cylinder, the helium will fill the voided space and maintain the constant pressure pad. If the pressure pad is not maintained while liquid material is being withdrawn from the cylinder, the pressure pad will fall in pressure and the liquefiable hydrocarbons will flash into a vapor phase up into the headspace. When this occurs, the integrity of the certified liquid calibration standard will be compromised. It is very critical that the pressure pad be maintained at its manufactured pressure during the entire use of the liquid calibration standard.

CONCLUSION

Success in the Petrochemical and Industrial Gas market is directly related to analyzer performance and an analyzer is only as good as its calibration standard. A good understanding of the ordering process and communication between customer and supplier is the first step in the successful use of a calibration standard. Knowledge of the manufacturing process will be a key indicator in determining the type of calibration standard needed to properly address the end users needs. Finally, appropriate maintenance of the calibration standard will be vital in achieving accurate measurements that will yield bottom line success in a highly competitive and challenging industry.