INTRODUCTION

The gas standards manufacturing industry is driven by such terms as quality, accuracy and traceability. Many times these terms become confusing and are often incorrectly interpreted and used by individuals who do not fully understand their meaning. It is true that all three are interrelated and when correctly referenced represent a pinnacle of a product that can be used as a reference for measurement in its field of expertise.

The following paper will discuss the “Elements of Gas Mixture Production” and the many complex terms and measurements involved to accurately deliver a product that can perform to its expectations. By understanding the processes and terminology used to produce these industry standards, the users may better understand what it is they are requesting and the true quality of product that they desire.

DEFINITION OF TERMS

NIST — National Institute of Standards and Technology. A government agency that is responsible for establishing and providing standards of all types, including gas reference standards.

SRM — Standard Reference Material. The highest pedigree gas reference material manufactured and certified by NIST.

MIXTURE ATTRIBUTES

When ordering a gas standard, there are several important attributes that must be identified and properly understood by the user so that the appropriate product can be provided. Such elements include:

- Concentration of Components
- Blend Tolerance
- Accuracy
- Urgency of Delivery
- Cost

Concentration of components refers to the actual value desired for each of the items found in the standard. These values can be reflected as weight percent, mole percent or liquid volume percent.

Blend Tolerance is the acceptable range of the individual components of the standard that a user will allow for the manufacturing of the standard. Example: Methane requested at 500ppm, with a 5% blend tolerance. The user will accept methane at a concentration between 475-525ppm.

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%. The source of true value is referred to as traceability, which will be discussed later.

Urgency of delivery is probably one of the simplest yet overlooked steps in correctly ordering a gas standard. Typical lead-time for a common gas standard is 10 days, but somehow in the dialogue at the time of ordering this information is forgotten. Requests for rush production can be provided to fit user’s needs.

Cost is a term that weights heavily in one’s mind when choosing a gas standard. Everyone must pay close attention to this term when ordering their standards. This is what makes it so very important for the user to fully understand exactly what type of gas standard they need. This term takes us into another very important aspect of gas standards . . .

WHAT IS A GAS STANDARD?

Gas standards have many different uses and depending on what the end user’s needs are primarily what determines the type of gas standard needed. It is very critical that this information is communicated with the gas standards manufacturer at the time of order.

Standards may be used for any of the following:

- Calibration of analytical instruments.
- Used to measure components in a process or stream.
- Used to identify the presence of particular components in a process or stream.

Standards that are used to calibrate analytical instruments must have the proper accuracy and traceability needed to yield the desired results that are sought by the end user. The accuracy of the standard value is very critical to the actual numbers that are generated by the analytical instruments. These values may be used for custody transfer of product, or to monitor yields from reactors in product synthesis. In any case, the true value expressed by this type of standard is extremely vital in yielding accurate measurements. These types of standards are more labor intensive and therefore carry a greater cost.
Standards used to measure components in a process or stream, but their exact values are not critical, can be met with less labor involved, therefore reducing their cost.

Standards that are used to simply identify the presence of particular components and not necessarily the quantitative amounts are non-labor intensive and low cost.

**TRACEABILITY**

Traceability refers to the pathway back to the source of true value. It's the relationship between a measured value and an established element of the National Measurement System. In the gas standards manufacturing business there are three types of recognized reference standard materials:

- Gas Reference Standards
- Mass Standards
- Pure Materials

**Gas reference standards** are products that are Metrology Institute Standards such as NIST, SRM's, or Registered Internal standards used for instrumental analysis.

**Mass standards** refer to NIST Class 1 registered weights, which are used for gravimetric analysis.

**Pure Materials** are more of an archaic method of blending using very pure products that have been NIST certified.

**STEPS IN PREPARING A GAS STANDARD**

There are several important factors, which affect the blending of a gas standard. All of these factors contribute to the successful preparation and shelf life of the intended gas standard. These factors are:

- Cylinder Preparation and Cylinder Choice
- Raw Material Analysis
- Blending
- Laboratory Analysis

**Cylinder preparation** is a very important part of all gas standards. Contrary to popular belief, everything you put into a cylinder is not necessarily what is going to come out. The inside of cylinder walls have reactive sites and depending on the type of material that has been requested to go into the standard, some of them tend to react inside of the cylinder with these reactive sites and never come out. Manufacturers have to segregate the types of cylinders in their inventory to properly match them to allow for the successful filling of requested materials so as to prevent this type of reaction within the gas cylinders. Many cylinders will be chemically treated to deactivate the reactive sites within the cylinders and help eliminate the chemistry that takes place when specific standards are being manufactured. Not only are active sites a problem for cylinders but the presence of moisture and oxygen can also be devastating to standards as well. Moisture and oxygen will react with any type of reactive component to yield undesirable products within the gas standard. Over time, these reactions will shorten the shelf life of the standard as well as alter their concentrations.

**Cylinder choice** is another very important factor in successfully manufacturing gas standards. There are four typical package issues that users must always remember when placing standard orders:

1. Reactive components need to go into treated aluminum cylinders.
2. Acid-Base mixtures need to be in steel cylinders.
3. Heavy hydrocarbons need to go into aluminum.
4. Two-phase components need to go into constant pressure pistons unless the vapor pressures on the mixture components are similar down to the dewpoint of the mixture.

Reactive components are preferred in treated aluminum because it lessens the number of active cites inside of the cylinder to react.

Acid-base mixtures must be prepared in steel because of their corrosive properties. Aluminum is very susceptible to the corrosiveness of these types of chemicals.

Heavy hydrocarbons have a high affinity of getting absorbed into the walls of steel cylinders, therefore causing the standards to become invalid. By blending the heavy hydrocarbons in aluminum, the heavies are not absorbed and the standards remain stable throughout their intended shelf life.

The two-phase component statement refers to a mixture that contains components that if they are all at room temperature, some would be in a liquid phase and others in a gas phase. What makes these type blends difficult is that there must be enough constant pressure to keep the components in their requested phase. Typically these type blends are requested in liquid phase and a constant pressure piston cylinder is used. These piston cylinders allow for product on one side and constant pressure on the other. This constant pressure is what keeps the components in liquid phase.

**Raw material analysis** tends to be a much more tedious task to accomplish than it sounds. Gas standard manufacturers must have the analysis of all of their raw materials complete and accurate in order to begin to even think about successfully blending gas standards. The analysis of the raw material has to be known down to the last ppm to account for all cross-contamination that may occur from blending different components together to get the final mixture desired. As the blenders begin to mix the requested components of the customer's standard, they must account for all minor impurities that are present in the different components to accurately blend the requested mix.

**Blending** is a fine art of mixing different materials together to reach a final desired mixture. This is accomplished gravimetrically by using certified scales that have been
calibrated to yield precise measurements. The scales are certified against mass standards. The calibrations are performed on a regular schedule to maintain precise accuracy.

Laboratory analysis plays a very important role in the measuring and certifying process of gas standards. Once the standards have been gravimetrically blended their values are verified through laboratory analysis. This analysis is accomplished by the use of gas chromatographs (GC's) or process analyzers. The lab analysis is an independent non-bias verification of the gravimetric blending process that supports and defends the accuracy of the user's requested standard. The lab will use standards that have been certified by NIST or registered against NIST certified standards.

SOURCES OF UNCERTAINTY

During the manufacturing of gas standards, there are several sources of uncertainty that must be accounted for when applying the final accuracy to a mixture. The task of the manufacturer is to minimize these uncertainties as much as possible.

The gravimetric blending process has the following sources of uncertainty:

- Mass Standard Uncertainty
- Scale Resolution/Readability
- Scale Calibration Error
- Raw Material Purity
- Material Losses

All of these sources of uncertainty must be accounted for and minimized during the manufacturing of the gas standard. This is accomplished by specifying raw material requirements for minimum purity and accuracy.

The raw material delivery to the cylinder must be consistent and repeatable with no interference between components or reactions with the system. The scales must be statistically calibrated to determine precision and linearity, and all calculations must be consistent and corrected for all known biases. Finally, all system mechanical effects must be known and controlled.

The laboratory analysis is another area in which all sources of error must be identified and controlled. Their sources are:

- Reference Standard Uncertainty
- Calibration Error
- Instrument Precision

All of these sources must be minimized and controlled to allow for the proper certification of the gas standard. Standards of the lowest uncertainty must be obtained to allow for a minimum baseline of error to begin. Calibration error and instrument precision are maintained by rigorous verification and validation of calibration curves used to perform the analytical analysis.

CONCLUSION

Quality is a term that is so very important in an industry where accuracy is held in the highest regard. How quality is measured is dependent upon the individuals needs and requests. When ordering gas standards, it is very important to convey all the necessary information that will help manufacturers provide the product that is best suitable for the user's needs. There are many different types of gas standards available to the chemical and petrochemical industry and by properly understanding the terms and processes of standard manufacturing the appropriate standards can be provided to the end user.