Good Calibration Gas- Technical Paper for the Natural Gas and LNG Industry

A calibration gas is a reference gas mixture used as a comparative standard in the calibration of analytical instruments, such as gas analysers, gas chromatographs or other gas measurement devices. If it is important that the instrument is capable of making good measurements, then the reference standard used to calibrate it is equally important.

Throughout this paper we look at what makes a good calibration gas, the benefits it provides and how it all relates to the measurement of Natural Gas or LNG.

What is Natural Gas?

Natural Gas is a type of fossil fuel that is abundant throughout the world. It is colourless and in its raw form consists mainly of methane with smaller amounts of inert gases, sulphurs and other hydrocarbons.

What is LNG?

LNG is an acronym that stands for Liquefied Natural Gas. In order to liquefy the natural gas, it is cooled to -<162*C. At this temperature, the gas has entered into the liquid phase. Once liquefied, the LNG occupies approximately 600 times less volume than Natural Gas.

What is gas quality?

Natural Gas is made up of several component gases and is therefore subject to natural variation. This inconsistency affects the energy contained within a given volume of gas.

Gas quality is most commonly described based on the measurements taken of the heating value, also known as calorific value, the Wobbe Index, and relative density, amongst many others.

Why do we measure gas quality?

Gas quality is measured mostly for fiscal purposes. Fiscal measurement as a general term means "measurement for money" and may be performed for either allocation or custody transfer purposes.

Allocation is the numerical distribution of product between parties according to their equity share.

Custody transfer is typically contract driven. A custody transfer point does not necessarily imply a change of ownership. It may be that at this point a measurement of the natural gas is taken to ensure that the contractual obligation between buyer and seller is being met.

The obligation may require adherence to accuracy, linearity, repeatability or uncertainty standards as defined by the measurement standards they have agreed to operate under.

How do we measure gas quality?

Gas quality is most commonly measured with the use of a Gas Chromatograph.

A gas chromatograph is used to separate the components of a Natural Gas so that each major component can be quantified. The internal process consists of subsystems that inject the sample, separate the sample, detect the components and report the results.

Instrumentation and Calibration Gas

In its simplest form, the GC is simply a comparator. Similar to a high quality wrist watch, there is no point in it being precise if it is set to the wrong time!

For fiscal measurement of natural gas or LNG, the GC needs to be both precise and accurate, but the accuracy is primarily derived from the reference material (calibration gas) only.

The calibration gas is the principle driver of the accuracy of the instrument.

Inaccuracies in the calibration gas will produce biased stream gas measurements**. The uncertainties of both reference material and instrument will compound and can affect the results even further.

In both LNG and natural gas measurement, the GC is essentially a cash register. The data obtained from the instrument along with flow or volume data will determine the financial value of the product.

Considering the vast financial sums changing hands in these transactions, it is extremely important to ensure the most accurate measurement is made.

For this reason, using the best quality calibration gas available is one of the simplest, most cost effective and readily available methods of improving your measurements and reducing your uncertainties.

What makes a good calibration gas?

When discussing the quality of a calibration gas, the relationship between accuracy, precision and tolerance is often confused.

In general terms, accuracy refers to how close the measured value is to a known value.

Precision refers to how close two or more measurements are to each other. Precision is independent of accuracy, you can be very precise but inaccurate and you can also be very accurate but imprecise.

When talking about the accuracy of components within a calibration gas standard, the term tolerance is often used.

Tolerance is a term used to describe a manufacturing method's ability to meet the end user's requested nominal value for each component. The manufacturer will aim for the requested value, and the tolerance will determine the range into which this value will fall.

If it is a good quality gas standard, each component will then be analysed with a GC to verify this value.

For example, if an end user has requested a component to be 10ppm, and the manufacturing process has a +/- 2% tolerance, the final measured value may be anywhere between 8ppm to 12ppm and still be considered within tolerance. Let's assume the measured value is 9ppm.

Next, analytical uncertainty must be considered. Analytical uncertainly refers to the accuracy of the measured value. In our example, if the uncertainty on the measurement is +/-1%, then the 'true value' will fall between 8.91ppm and 9.09ppm.

A good quality calibration gas should always list the analytical value and uncertainty on that value. If the tolerance is +/-1% but the analytical uncertainty is +/-30% then what is the true value?

Many reference standard certificates will simply state blanket uncertainties, uniform across all components, determined without performing any analysis.

The different characteristics of each compound in the gas mixture make it virtually impossible for each component to have the same uncertainty.

The component values are often only based on measurements taken during the manufacturing process and the uncertainties are based on factors including historical data, uncertainty in weights & balances, or pressure/flow measurements. The process from which the uncertainties have been derived is often vague and unclear.

Of course, the measurements and data relating to the components going into the cylinder is a good place to start, but what goes into a cylinder is not always the same as what comes out. Despite the best cylinder preparation techniques, minor reactions between components can still take place within the cylinder, and many other effects must be taken into consideration, such as heavier hydrocarbons 'sticking' to the inside walls. The best way to ensure a quality measurement is to measure what is actually coming out of the cylinder with the use of a GC, calibrated to a primary reference standard**. When comparing gas standards side by side, be sure to be comparing apples with apples and be prepared to question the information provided on the certificates.

What can go wrong with calibration gas?

Methane reported as 'Balance'

Considering natural gas is made up mostly of methane; it is the most important component in terms of calculating the heating value, and thus the financial value. A good quality calibration gas manufacturer will be aware that the reference value and uncertainty for methane is necessary to determine the uncertainty of the overall gas quality measurement.

However, in many cases the methane component is simply referred to as 'balance' with no reference being made to the measured amount of methane in the standard or the accuracy / tolerance / uncertainty of this most important component. With Methane listed simply as 'balance' we cannot be confident in the uncertainty measurement of the heating value and the financial risk both buyers and sellers are under when trading.

Large or no uncertainties

It is a common misconception that measurement is an exact science. All measurements are merely estimates of the true value being measured and the true value can never be known. No matter how careful or accurate, every measurement result contains an independent amount of uncertainty. Therefore, if measurement is important, then measurement uncertainty is equally important.

In 2013 Australia produced approximately 2,467 Peta Joules of gas and the average price was $4.22 per Giga Joule bringing the total annual value to approximately $10,410,740,000. Considering the industry standard uncertainty limit when measuring gas is 1%, the financial uncertainty to this trading was approximately $104,107,400 for the year!

If your cash register, the gas chromatograph, is only as accurate as your calibration gas, it stands to reason that the lower the uncertainty of your calibration gas, the lower the uncertainty in your financial risk. If the calibration gas has no uncertainties at all or an even 1% across all components (scientifically very unlikely) then accurate calculation of this uncertainty is impossible.

Inappropriate units used (vol% or ppmv)

When discussing the amounts of each component in a gas mixture, it is important to use the correct units. When looking for a good calibration gas, ensure the values are reported using mole and mass fractions only (%mol/mol, ppm mol/mol)

Volumetric units (vol%, ppmv) are not independent of temperature and pressure. Any composition expressed in volumetric terms will require a compressibility correction to be made with respect to temperature and pressure. This can get complicated as the compressibility changes with composition and can effect natural gas type mixtures by up to 10%

Only mole and mass fractions are independent of both pressure and temperature, avoiding the need to make corrections at all.

Low temperatures (transport, storage, usage)

A calibration gas standard is a homogeneous mixture of components that have the same proportions of its components throughout a given sample.

A good analogy is like a cup of tea. If you were to add sugar to a cup of tea and not stir it, the sugar would sink to the bottom. As you drink the tea, it would be bitter at the beginning and get continually sweeter as you get to the bottom. In this case, the cup of tea would not be a homogenous mixture.

The same situation can occur with a calibration gas mixture. If not mixed correctly, the lighter components of a natural gas mixture (Methane, Ethane etc.) would be at the top and exit first when drawing a sample and heavier components would stay inside therefore not providing a clear representation of the sample.

When a calibration gas is prepared, it is rolled for a period of time after mixing to ensure it is homogenous, but these proportions can be altered when exposed to low temperatures during transport and storage.

If a hydrocarbon component calibration gas is exposed to temperatures below the minimum usage temperature, the heavier hydrocarbons can begin to move into the liquid phase, leaving the gas mixture as a two phase, non-homogenous gas standard. If used for calibration the instrument will be biased for higher hydrocarbons and a higher heating value.**

For this reason, it is important that the calibration gas is supplied with a phase diagram**, outlining the hydrocarbon dew point. This way we can identify when the standard has been exposed to low temperatures and also the minimum usage temperature. If indeed the cylinder has been exposed to a low temperature it is important that the standard is warmed and sufficiently rolled to ensure the mixture is homogenous again.

*****Look for our upcoming technical papers where we go in depth on Biased Stream Gas Measurements; Primary Reference Standards; Hydrocarbon Dewpoint Calculation; Bias and its Origins.***

Written by;
Matt Shaw, Business Development Manager
CAC Gas & Instrumentation

Resource information from EffecTech - UK
