Introduction to Calibration Gases

What is calibration gas?

A calibration gas is a mixture of gaseous components used as a comparative reference in the calibration of analytical instruments, such as gas analysers or gas detectors.

Calibration is important for all testing instruments and the calibration gas is a means of establishing a known response to a certified chemical component concentration.

This paper looks at the key aspects to be aware of when procuring and using calibration gas. We will examine common terminology including metrological hierarchy, traceability, accreditation and units.

CAC GAS offers three ranges of specialty gas or liquid mixtures, depending on your requirements. Mixtures meeting CAC's high standard for quality will be classified into one of these three categories based on how they are made, tested, analysed, or certified.

Metrological Hierarchy

Metrology is defined by the International Bureau of Weights and Measures (BIPM) as "the science of measurement, embracing both experimental and theoretical determinations at any level of uncertainty in any field of science and technology".

Consumer assurance during the purchase of goods and services (such as natural gas or LNG) all depends on the confidence in the measurements made during these processes. This confidence is achieved by metrology's three basic activities: the definition of internationally accepted units of measurement, the realisation of these units of measurement in practice, and the application of chains of traceability (linking measurements to reference standards).

Forming the very foundation of the metrological hierarchy are the Primary Standard Materials (PSM) which are made to the highest metrological quality; are not subordinate to any others and are the definition or realization of their unit of measure. Historically, units of measure were generally defined with reference to unique artefacts which were the legal basis of units of measure.

For gas mixtures produced gravimetrically, the Primary Standard Material is the kilogram. The master kilogram is the primary mass standard for the International System of Units (SI) and is held by the International Bureau of Weights and Measures (BIPM) in Sèvres, France.

When it comes to calibration gas standards there are typically three levels: Primary Reference gas mixtures, Secondary Reference gas mixtures and working gas standards.

Primary Reference Gas Mixtures (PRGM)

Primary reference gas mixtures (PRGM) sit at the very top of the traceability chain. They are the highest quality standards available for use by commercial organisations. PRGM's are prepared by direct comparison to the Primary Standard Material and offer the best (lowest) uncertainties available. PRGM's are typically used by calibration laboratories and specialty gas manufacturers to establish the reference values of their own internal standards through analytical comparison with the PRGM.

Secondary Reference Gas Mixtures (SRGM)

Secondary reference gas mixtures (SRGM) are prepared gravimetrically and calibrated against PRGM's where the analytical value and analytical uncertainties are reported on the certificate. A SRGM balances low uncertainties with value for money especially when supplied in large volume cylinders. A lab offering SRGM's must be accredited to ISO17025 or equivalent.

Working Gas Standards

Working standards are calibrated with respect to secondary standards. Analysis is not underpinned by ISO17025 and are often determined by weight, not analysis. Buyers must rely on statements from the gas supplier that the mixtures are supplied as ordered.

What is ISO17025?

ISO17025 is an international standard that defines the "general requirements for the competence of testing and calibration laboratories". It is important to note it is the laboratory that holds the accreditation not the reference standards produced.

When using an ISO17025 calibration gas standard you can be sure that the mixture has been manufactured by different masses of components being weighed into a cylinder and the composition derived by ISO17025 accredited analytical methods.

The chemical traceability can be shown by comparison against national metrology institute reference gases (PRGM's) with analytical uncertainties on all components and to the mole, the SI unit for the amount of substance. Inaccurate, non-traceable calibration gases have the greatest potential for introducing errors into gas composition measurements and hence errors in calculated physical properties such as calorific value.

Traceability

Traceability has been defined as "the property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties" This definition has achieved global acceptance in the metrology community. All commercial reference standard manufacturers have the responsibility to establish traceability and the certificate of calibration should make it clear exactly how the manufacturer accomplished this traceability.

Accreditation

Accreditation means that testing and calibration laboratories; certification and inspection bodies have been assessed against internationally recognised standards to demonstrate their competence, impartiality and performance capability. Usually the reason for getting something independently evaluated is to confirm it meets specific requirements in order to reduce risks. Obvious examples are product failure, health risks, company reputation or to meet legal or customer requirements. Accreditation ensures that the selection of a laboratory, certification or inspection body is an informed choice and not a gamble. Accreditation provides confidence that the reference standard manufacturer has been successful at meeting the requirements of international accreditation standards.

Trust is placed with suppliers in a variety of ways: past experience, recommendation, brand preference and so on. The greater the familiarity, the more confident the purchasing decision. In today's large competitive business market it isn't always possible to buy from 'known' sources. Reassurance is needed to maintain trading confidence. Independent evaluation is the principle source of this reassurance and such confidence is underpinned by accreditation.

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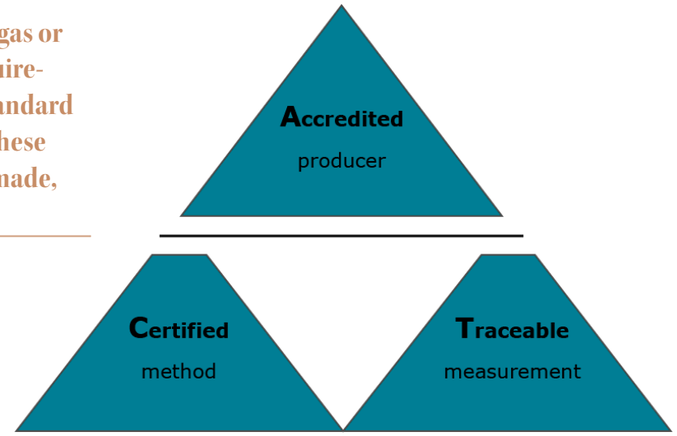

Manufacturing Gas Mixtures

Calibration gases by definition are mixtures of gaseous components from as little as 2 up to an indefinite number. There are two methods of manufacturing calibration gas mixtures, gravimetric and volumetric.

Volumetric Gas Mixtures

Volumetric mixtures are made by using a pressure gauge to determine how much of each component has been added. The accuracy of the mixture is largely determined by the accuracy of the pressure gauge.

Each gas in a mixture will occupy a certain amount of space at a certain pressure and temperature. The amount of space occupied by each gas is described using volume as a unit. This is inherently less accurate than the gravimetric method (using moles and grams). Each gas will expand and contract relative to pressure and temperature, at different rates, whereas moles and grams will always remain constant. This means that when using volume, depending on the environment in which you're using the mixture, the mixture ratios can change.

A volumetric certification is only accurate at the exact temperature and pressure specified on the certificate. If used outside of these conditions, the relative composition will change and will require a compressibility correction to be made. This can get complicated as the compressibility changes with composition and can effect natural gas type mixtures by up to 10%.

Gravimetric Gas Mixtures

Gravimetric gas mixtures are prepared by the weighing of each component of the mixture using accurate balances. Only mole and mass fractions are independent of both pressure and temperature, avoiding the need to make corrections at all.

The accuracy of a gravimetric gas mixture is determined by the accuracy of the balances. The only factors to correct for are the purity of the raw materials, something the manufacturer does on the customer's behalf. Traceability is obtained by mass through calibrated mass pieces. The highest quality calibration gas mixtures are manufactured by this method.

ISO 6142 specifies a gravimetric method for the preparation of calibration gas mixtures in cylinders with traceable values for the amount-of-substance fraction (amount fraction) of one or more components.

Units

The compositions of calibration gas mixtures are expressed in a number of different ways. These can change depending upon the mixture's method of manufacture, the type of components within the mixture or the process/analytical requirements.

In each case the units of measure and the ratio of these units relative to each other are listed on the certificate provided by the manufacturer.

Gas mixtures are commonly certified using the following units of measure:

mol (moles)
vol (volume)
mg/g/kg (milligrams/grams/kilograms)

These units are then given relative values using percentage ratios, which can be listed in a number of different ways. You may see one of these commonly used ratios:

ppb (parts per billion)
ppm (parts per million)
% (percentage)

On their own, these ratios are meaningless. We must combine them with a unit of measure to derive their significance. Some commonly used ways to display units & ratios together are:

mg/kg (milligrams per kilogram)
wt/wt (weight per total weight)
ppmv (parts per million, volume)
%vol, or %v/v (percentage of volume, percent volume per volume)
%mol (percentage of moles)

It is important to understand the reasons for using each of the various methods of measurement and to understand the difference between the different units of measure so we can be sure to recognise the most appropriate type for the measurement of natural gas.

Moles are commonly used when preparing gas mixtures gravimetrically. A mole is a unit of measure used to describe an amount of a chemical, based on its molecular weight, or molar mass. The molar mass is the weight of a single particle in its most elementary form. The atomic weight of each element is different and is expressed as the number of grams per mole.

This is important for gravimetrically prepared gas mixtures because all calculations are done based on the weight of each component added. When mixtures are described with moles, the total moles of all components are added together and then each component is listed as a ratio of the total moles in the mixture.

There are a number of factors to consider when manufacturing calibration gases.

Some of these can include:

- Material compatibility
- Ensuring corrosive gases such as Hydrogen Sulphide are only housed in aluminium cylinders (not steel)
- Gas compatibility -A good example being mixing Nitric Oxide (NO) and Oxygen (O2) together will cause them to react and create Nitrogen Dioxide (NO2)
- Flammability and Oxidant components. These have the potential risk of explosion during manufacturing.

An unavoidable fact is that many gases will contain other levels of gases as **impurities**. If these other gases are also present in the calibration gas mixture, then the amount of impurity must be taken into consideration when performing the calculations.

Compressibility is another factor that needs considering when designing or manufacturing a calibration gas. The term compressibility is a measure of how much a gas deviates from an ideal gas. The volume of an ideal gas in a cylinder can be calculated my multiplying the water volume of the cylinder (litres) by the pressure (bar)

For example, a 50L cylinder filled to 200 bar would contain 10,000L of gas, but Methane at 200 bar would actually contain 12,500L and Hydrogen 9,100L of gas. This deviation is due to the compressibility of the gases.

Consequences for the Customer

For measurement of natural gas or LNG, it's imperative the instrument being used is both precise and accurate, but the accuracy is primarily derived from the reference material (calibration gas).

In both LNG and natural gas measurement, the gas chromatograph 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.

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