

‘Keeping It Simple’

Gas Mixtures for Stack Emissions Monitoring



Stack Emissions Monitoring

The Stack Emissions Monitoring market has undergone substantial legislative and quality changes over the past several years and this has resulted in ever increasing pressures on organisations and individuals to deliver products and services to a higher level of acceptance. There is no hiding from the fact that documented guidance and information can be misinterpreted and this has been evident due to the different approaches that have been put into practice. To further complicate matters the demands on OEM's, Process Operators and Test Houses are quite different, so what meets the requirements of one, is not suitable for the other and this in itself has caused some confusion and has resulted in some instances in the incorrect selection of gases.



Looking specifically at gas mixtures, examples of common terminology frequently used are: Traceability, Accredited Gases & Non Accredited Gases and Uncertainty. But these terms in turn raise a host of frequently asked questions:-

Traceability

- What is traceability?
- What is the interpretation of (Inter) National Standards?
- Are you using traceable gases to comply with your standard?
- When do you need to use traceable gases?

Accredited & Non Accredited

- UKAS Accredited?
- ISO17025 Accredited?
- ILAC and Mutual Recognition?

Uncertainty

- What does the Certificate data actually mean?
- Are you using the lowest uncertainties available?
- Are you confident that you fully understand these terms and they are being applied correctly in your business?
- Choosing the correct gas mixture for your application can be simple!

EN14181 – Selecting the Correct Gas Mixtures

Below is a guide which will aid you to selecting the correct gas mixture when working in accordance to EN14181.

QAL1 – Equipment Manufacturers

Prior or during the AMS purchasing period

Evaluation of the suitable measurement procedure, with a required measurement uncertainty, in accordance to EN ISO 14956.

Gas Mixture Requirements for QAL1:

Not required to be Traceable/ISO17025 Accredited, however gas mixtures must be stable and have an uncertainty of +/-2%.

QAL 2 – Test Houses

Validation of the AMS

At least every 5 years for each AMS on site, or after a major change in plant operation or failure/repair of the AMS, conducted by Test Houses accredited to the ISO EN/IEC 17025 MCERTS performance standard.

Gas Mixture Requirements for QAL2:

Traceable/ISO17025 Accredited calibration gases.

QAL 3 – Process Operators

Maintain and demonstrate the quality of the measurement

Weekly checking that the zero and span characteristics are consistent with those determined in the QAL1

Gas Mixture Requirements for QAL3:

Not required to be Traceable/ISO17025 Accredited, however gas mixtures must be stable and have an uncertainty of +/-2%.

Annual Surveillance Test (AST) – Test Houses

Performance of the AMS is still valid and the calibration function remains as previously determined

Every year on the anniversary of the first QAL2 for each AMS on site, conducted by Test Houses accredited to the ISO EN/IEC 17025 MCERTS performance standard.

Gas Mixture Requirements for AST:

Traceable/ISO17025 Accredited calibration gases.

Compliance monitoring also requires the use of Traceable/ISO17025 Accredited calibration gas mixtures with the use of the Standard Reference Methods (SRMs).



Understanding Traceability

The term 'traceable' has a very specific definition. It means that there is an auditable chain of direct measurements linking the value of the calibration material (in this case the concentration of the calibration gas) back to primary standard gas mixtures and ultimately to the SI units.

Primary Standard Gas Mixtures (PSMs):

National Measurement Institutes (NMI) worldwide, for example, NPL in the UK, NIST in USA and NMI in the Netherlands, prepare gravimetric primary standards of gas concentration, which they retain in-house as their ultimate references for gas measurements. These standards are known as Primary Standard Gas Mixtures and sit at the highest echelon of gas standards.

Primary Reference Gas Mixtures (PRGMs) & Secondary Gas Standards (SGSs):

PRGMs and SGSs are certified by a National Measurement Institute (NMI) directly against a selection of PSMs using in-house validated analytical methodology which has demonstrated repeatability and linearity. PRGMs generally have smaller uncertainties than SGSs.

Certified Reference Gas Mixture (CRGM):

CRGMs may be prepared and supplied by a commercial gas company that have an ISO17025 laboratory with a calibration accreditation. The CRGMs are prepared using audited methods to compare the gas concentration to Metrology PRGMs or SGSs.

CRGMs have a valid traceability in terms of the ISO17025 and MCERTS Accreditation and the analytical result is stated on the Calibration Certificate with a calculated uncertainty of the measurement.

This uncertainty measurement is very important with regards to adhering to the standard reference methods (SRMs) whilst conducting QAL2 and AST procedures.

The UKAS Technical Policy Statement, TPS41, states *"Calibration certificates from accredited laboratories should display the accreditation mark of the relevant accreditation body and all calibration certificates should display a statement of uncertainty (and/or compliance if appropriate)"*¹

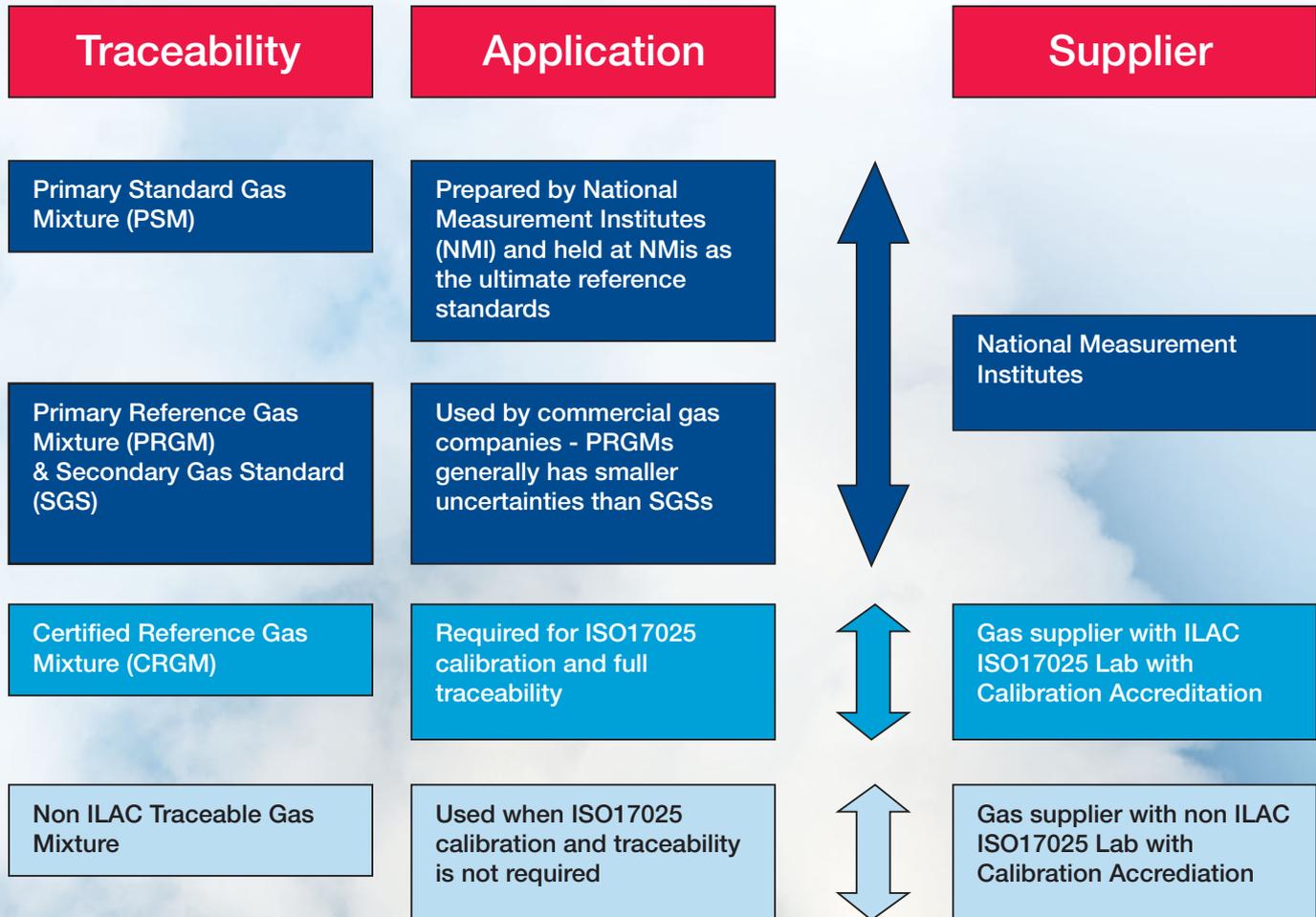
Unfortunately there is history of Traceability Claims and these tend to be made by some commercial gas companies. If your gas species analysis application requires Traceability it is important to determine the full traceability capabilities of your gas supplier, don't be misled by the misuse of the term Traceability, it could result in a costly mistake. It is also important to note that Traceable gas standards are referred to as ISO17025 Accredited gas standards.



ISO17025 Accredited? – International Choice

Calibration Gas Mixtures traceable to International Measurement Institutes are accepted by UKAS and the Environment Agency.

Worldwide, the national accreditation bodies have syndicated in the International Laboratory Accreditation Co-operation (ILAC), whose main objective is the creation of a network of agreements for the mutual recognition of calibration certificates and test reports of accredited laboratories. With a coalescing Europe the mutual recognition of national calibration certificates is essential and enables ISO17025 Accredited organisations a choice of supply. In Europe this is done by Multilateral Agreements (MLA) within the European Co-operation for Accreditation, which in the meantime almost all European accreditation bodies for calibration laboratories belong to.



Standard Reference Methods (SRMs) – Achieving the +/-2% uncertainty

“The expanded uncertainty shall be less than +/-2%”²

This statement is common in all of the Standard Reference Methods (SRMs) but how can you ensure both the correct traceability and uncertainty is achieved in accordance to the MCERTS Standard?

Option 1

Traceable/ISO17025 accredited gas mixtures, with an uncertainty of equal to or less than +/-2% can be taken to site and used directly to validate the analyser system.

Option 2

Traceable/ISO17025 Accredited gas mixtures can be used to cross check a non Traceable/ISO17025 gas mixture, also referred to as a Working Gas Mixture Standard, via a UKAS or ISO17025 accepted analytical procedure. The total uncertainty of the analytical procedure must demonstrate an uncertainty of equal to or less than +/-2%. To achieve this uncertainty the Traceable/ISO17025 Accredited gas mixtures required will have an uncertainty of +/-1%. The non Traceable/ISO17025 Accredited gas mixtures can then be used on site for the validation of the analyser. This method of cross checking does not allow the Test House Laboratory to supply an ISO17025 Calibration Certificate for the Working Gas Mixture Standard.

Both of the above options are practiced in the field, but there are a number of factors to consider prior to sourcing the best quality and cost effective solution for your organisation.

- Correct traceability
- Correct uncertainty
- Time spent performing the cross checking analytical procedure
- Cylinder holdings and rental
- Cylinder size
- Stability of the gas mixtures

The goal posts can move when it comes to using calibration gases and that is why it is important to work with a gas supply partner. Liaising with The STA, UKAS and The Environment Agency, you can trust that Air Liquide UK to be up to speed with all of the latest developments and will supply you the information that you require.

Constructing an offer that simplifies choices and gives you the right solution

Following its acquisition of Scott Specialty Gases, Air Liquide UK has further expanded its comprehensive range of ISO17025 Accredited calibration gases. Our product range offers very low uncertainties, +/-1%, a wide band of concentration ranges and a comprehensive choice of gas species. We are also proud to be able to supply Nitrogen Dioxide in Nitrogen, again with an uncertainty of +/-1% for concentrations greater than 10ppm. We believe this provides a choice which is unrivalled in the UK.

To complement the traceable gases, we have a comprehensive range of non ISO17025 traceable stable binary and multi component mixtures all supplied with Certificates of Analysis in accordance to ISO6141. For most working standards, delivery is less than 2 weeks, even for reactive gas mixtures such as nitric oxide, allowing customers to bring forward testing programs and reduce the required stock holding.

The cylinder holdings at any site are also available for customers to view over a secure Internet link, allowing you to manage stocks effectively.

Dependant upon the gas mixture required, stabilities can range from 6 months to 36 months, with certified tolerances as low as +/-1%.

For example, for HCl we can offer a guaranteed stability of 36 months and bearing in mind the complexity of manufacturing and utilising this particular gas mixture, this achievement is unmatched by any other gas supplier. To complete the offer we have the capability to manufacture and supply the VOC Control Gas Mixture, required for annual checking of Flame Ionisation Detectors (FIDs) as required for BSEN12619, section 5.2.5.

All gases, whether it is calibration mixtures or pures for analyser operation, can be supplied in a choice of lightweight portable aluminium cylinders or larger cylinders for high gas volume demands.

Air Liquide's ISO17025 Scope of Accreditation

Gas	Matrix	Concentration Range	Relative Uncertainty (95% level of confidence)
Binary Gas Mixtures			
Carbon Monoxide	Nitrogen or Air	10ppm – 20%	+/-1%
Carbon Dioxide	Nitrogen or Air	10ppm – 20%	+/-1%
Methane	Nitrogen or Air	1ppm – 100ppm	+/-1% (<10ppm +/-2%)
Propane	Nitrogen or Air	1ppm – 3%	+/-1%
Sulphur Dioxide	Nitrogen	20 – 5000ppm	+/-1%
Nitrogen Dioxide	Nitrogen	3 - 1000ppm	+/-1% (<100ppm +/-2%)
Nitric Oxide	Nitrogen	1 – 2500ppm	+/-1% (<5ppm +/-2%)
Oxygen	Nitrogen	1 – 25%	+/-1%
Quaternary Gas Mixtures			
Carbon Monoxide	Nitrogen	0.2 – 5%	+/-1%
Carbon Dioxide		1.5 – 18%	+/-1%
Propane		150 – 1000ppm	+/-2%
Carbon Monoxide	Nitrogen	0.2 – 5%	+/-1%
Carbon Dioxide		1.5 – 18%	+/-1%
Propane		1000 – 5000ppm	+/-1%

Air Liquide also offers a unique range of services that ensure Test Houses and Process Operators remain in compliance. Calibration Certificates are available on-line ensuring these important records are always available during critical audits. Furthermore, an automated email notification system warns gas users when a calibration gas cylinder is approaching its expiry date, eliminating the non-conformance for using an expired gas.

The gas mixtures and cylinder choice are coupled with a portfolio of gas equipment and installation capabilities. For a continued gas supply we have a dedicated range of Change Over Manifolds which have the option of an alarm system and an LED which displays the cylinder contents. The LED display technology is very beneficial if your cylinders are away from a central location, at a glance you can decipher the contents of your cylinders. If portability is important there is the Selectable Flow Regulator, which delivers a preset pressure and allows the user to select 9 flow rates between 0-5l/min, these are available in both stainless steel and chrome plated brass. Our offer is completed by supplying the more traditional, single and dual stage regulators, available in a choice of materials specific for particular gas applications.

If training is regarded as a key aspect of your employee's development then you can choose from a range of specific courses, some of the most popular examples include Manual Handling and Transportation of Cylinders & Equipment.

The high quality and flexibility of our product range is a reflection of how Air Liquide UK are continuously developing product and service packages to meet the demands for the Stack Emissions Monitoring market. Most importantly we are determined to work with our customers as a gas partner who can correctly meet all your needs, but also keep you informed as to key requirements and changes in the market. To help our customers we have created a dedicated website on emissions offers which includes both technical advice on gases and information on health and safety. All of this is designed to help our customers to make the informed choices that will be right for their operations for both today's needs and also for the future. We have invested in growing a team of gas specialists who can work with our customers to demystify a complex subject.

Our aim is that the choice should be simple!

References

[1] TPS 41, Traceability of Measurement, Edition 3, June 2005

[2] BS EN 14789:2005, Stationary Source Emissions, Determination of Mass Concentration of Oxygen

Visit www.uk.liquide.com
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Stack Emissions Monitoring requirements:
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