Stability and Traceability of Calibration Gases for EN 14181

The terms 'traceable' and 'stable' used to describe gas mixtures have long been a topic of debate, even confusion, since the EN 14181 standard was first published back in 2002. The objective of this article is to provide an explanation of these two terms as they relate to gas mixtures, and to enable users to select the correct calibration gases for their application with confidence.

"The calibration of analysers using binary mixtures can often lead to errors in the analysis of stack gases due to cross-sensitivity effects occurring within analysers, hence the value of these products in all aspects of EN14181 compliance."

By explaining the factors that affect mixture stability, and the various routes of traceability that exist for gas mixtures, the aim is to provide the required knowledge for those responsible for sourcing gas mixtures for emissions monitoring work; ultimately, to provide users with an ability to recognise the difference between a gas mixture which fulfils legislative obligations, and one that does not. The costs and the penalties of making a mistake in this area can be severe and have caught out many organisations over the years.

Gas Mixture Stability

The term 'stability' is perhaps the easier one to comprehend. It is a characteristic of a gas mixture. Stability is basically a declaration of how long the concentrations of components within a gas mixture will remain within the stated measurement uncertainty after they are originally certified by the manufacturer. In accordance with the ISO 6141 standard describing the requirements for certificates for calibration gases, it is mandatory that the stability of a gas mixture is stated on its accompanying certificate of analysis. It might also be expressed as a 'shelf life' or 'use by date'.

Accuracy and traceability of measurement is worth little if the analyst has no confidence in the stability of the standard they are using to calibrate their analytical equipment.

Most manufacturers of calibration gas mixtures invest heavily in the research and development of techniques that allow them to declare long mixture shelf lives. The factors that influence stability are many and include the following:

- Selection of optimum cylinder and valve materials
- Treatment of the internal surfaces of both the cylinder and the valve
- Segregation of cylinders into specific gas service
- Cylinder preparation before filling (heating, purging, evacuation)
- Selection of ultra high purity components
- Advanced filling technology
- Special analytical techniques
- Stability tests to prove stability

No single step leads to stable calibration gas mixtures. It is a combination of all these aspects and others that results in significantly improved mixture stability.

No matter what the traceability route is for the gas mixture, all reputable suppliers of calibration gas mixtures will declare a shelf life, albeit some longer than others. The EN 14181 standard demands that gas mixtures are used within their stated shelf life for all aspects of compliance. It's important to look carefully for this information to make sure the calibration gas being used has not expired.

Traceability of Gas Mixtures

Traceability of measurement requires an unbroken chain of comparisons to stated references, each with a stated uncertainty. The objective is to deliver national and international comparability, so it is easy to appreciate why there is such importance attached to this property of a gas mixture when it is used as part of EN 14181 compliance.

Traceable calibrations automatically provide users with the means to obtain consistent data over time, even when one mixture is replaced by another, and it allows full comparability of data obtained from similar measurements taken around the world.

Gas mixtures are traceable either to certified reference gas materials provided by national measurement institutes, or to the national mass standards.

Stephen Mellor, Product Specialist – Analytical, Air Products Plc, UK

The Source Testing Association (STA)
Unit 11 Theobald Business Centre,
Knowl Piece, Wilbury Way,
Hitchin, Herts SG4 0TY
United Kingdom
Tel: +44(0) 1462 457535
Fax: +44(0) 1462 457157
Email: General enquiries sam@s-t-a.org
Web: www.s-t-a.org

There are two main ways that commercial gas companies assign a certified value to a mixture of gas. One is by measuring the weight of gases added to the cylinder during the filling process. Traceability by weight involves comparing the weight of gas in the cylinder, via the aforementioned unbroken chain, to a weight that has been compared to the standard SI mass. If the manner in which these comparisons are made is documented and subject to audit, then, depending on the type of gas mixture, this can be an acceptable way to obtain traceability of the measurements taken to produce the gas mixture.

A second method is by analysing the contents of the cylinder after it has been prepared. Traceability is derived via a series of comparisons between gas samples from the filled cylinder, with gas sampled from a primary reference mixture (PRM) prepared by a national standards institute. Primary standard mixtures (PSMs) are maintained within the institution that made them and are used to produce the PRMs used by commercial gas companies as a comparison to certify their gas mixtures by analysis. National standards institutes all prepare primary reference materials by weight, thus forming the link with the SI unit of mass under tightly controlled and measured conditions of temperature, humidity and pressure.

When these comparisons are undertaken by a laboratory within the scope of its ISO 17025 accreditation awarded by a national accreditation body, it is considered traceable in accordance with the ILAC (International Laboratory Accreditation Cooperation) policy.

Regulatory Compliance

Having looked at the main routes of traceability for calibration gas mixtures, we can now link these to requirements set out in the EN 14181 standard.

For quality assurance levels QAL1, QAL2, and the annual surveillance tests (AST), the EN 14181 standard is clear in its prescription of calibration gas standards. For these aspects of compliance it is necessary to select a gas mixture which has been certified within the scope of an ISO 17025 accredited laboratory. That means that the gas mixture must have been certified analytically by comparison to a primary reference material.

When selecting gas mixtures for these applications, look for the following sign that it has been certified within the scope of an ISO 17025 accredited laboratory. Look for the mark of the national accreditation body awarding the accreditation to the laboratory, and the number of the certificate awarded to the organisation under which the gas mixture is supplied. It is also a good idea to keep on file a copy of the laboratory accreditation certificate so that it can be made available to auditors. Be suspicious of a certificate of analysis which makes reference to ISO 17025 but does not feature the mark of a national accreditation body.

ISO 17025 accredited stack teams must calibrate instruments used for MCERTS testing or for carrying out EN 14181 – QAL2 or AST parallel measurements using gases that are traceable according to the policy of ILAC. If a multi-point gas divider is used to reduce the number of calibration gases required to make a calibration curve, the gas divider must also be calibrated by an ISO 17025 accredited laboratory that has this function within the scope of its accreditation.

ISO 17025 accredited stack teams must also check the span of instruments whilst undertaking QAL2 monitoring work. Working span gases that have traceability not according to ILAC policy are allowed since the purpose is to verify that the traceable calibration is still valid.

For operators needing to comply with the QAL3 element of EN 14181, traceability according to the ILAC policy is not strictly necessary, as stability of the gases is the primary requirement. Gases are used only as control gases and not used to calibrate the instrument. However, it is prudent that these control gases are of suitable quality to give consistent measurements that validate the instrument remains within the Shewart or Cusum control limits, and also produce concurrent results with the QAL2 or AST parallel measurements. Gas mixtures certified outside an ISO 17025 scope are deemed acceptable for QAL3 work.

As suppliers of calibration gas mixtures continue their efforts to serve customers in the field of emissions monitoring, and facilitate compliance with legislative requirements, it's inevitable that new product offerings and new solutions will come on line.

The last few years have already seen the availability of multi-component mixtures for emissions monitoring certified within an ISO 17025 accreditation scope. For example, mixtures with all of the components CO, SO_2, NO and CO_2 in the same cylinder.

The calibration of analysers using binary mixtures can often lead to errors in the analysis of stack gases due to cross-sensitivity effects occurring within analysers, hence the value of these products in all aspects of EN 14181 compliance. Calibration using binary mixtures often requires a large number of calibration cylinders and often do not take into account cross sensitivity effects. Such errors due to cross sensitivity can also prove expensive during any emissions trading process.

Another positive change is the advancement in cylinder preparation and treatment technology, resulting in shelf lives up to 10 years for some mixture types. Frequent gas cylinder changeovers are burdensome for any organisation, not least because of the cost of gas mixtures, the amount of site work involved, and administrative implications. Also, when working with any type of control chart, cylinder changes bring another added complexity, so it is easy to see the value of these developments to all parties involved in compliance work.

References:

Source Testing Association (STA) Quality Guidance Note QGE-005-2013 - Traceability in Calibration Gases

The Source Testing Association

The Source Testing Association (STA) was established in 1995 the membership comprises representation from process operators, regulators, equipment suppliers and test laboratories. The STA is a non-profit making organisation.

The STA is committed to the advancement of the science and practice of emission monitoring and to develop and maintain a high quality of service to customers.

Its aims and objectives are to:

(i) contribute to the development of industry standards, codes, safety procedures and operating principles;

(ii) encourage the personal and professional development of practicing source testers and students;

(iii) maintain a body of current sampling knowledge;

(iv) assist in maintenance of a high level of ethical conduct;

(v) seek co-operative endeavours with other professional organisations, institutions and regulatory bodies, nationally and internationally, that are engaged in source emissions testing.

The Associations headquarters are based in Hitchin, Hertfordshire with meeting rooms, library and administration offices.
The Association offers a package of benefits to its members which include:

- Technical advice relating to emission monitoring
- Conference and exhibition opportunities
- Seminars and training on a variety of related activities
- Representation on National, European and International standards organisations
- Training in relation to many aspects of emission monitoring
- Liaison with regulators, UK and International, many of whom are members.

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Stack VOC Determination using a Portable, Cutting Edge Analyser

The problem - Emissions of Volatile Organic Compounds (VOCs) from industrial chimneys are becoming an issue of global importance, and to posess accurate knowledge about how to test VOC is a wise strategy. VOC emissions are quantified and monitored according to standard EN 12619, using an FID analyser which uses hydrogen and other reference gases in pressurised cylinder. Operators must then approach the sampling point, often placed several meters from the ground, climbing chimneys of industrial settlements with instruments and cylinders. Is it possible to make this job easier and safer?

Using the Polaris FID analyser, from **Pollution Srl** (Italy), it is possible to carry out VOC monitoring according to EN 12619 without lifting accessories and heavy weights typically involved with FID analysers.

So far, the portability of such analysers was a feature of FID designed for fugitive emissions from valves, flanges, gaskets, pumps or compressors monitoring. Moreover, when VOCs are measured in chimneys according to EN 12619, the analyser must be much more robust and fully heated to 180°C, leading to increase in size and weight.

Polaris' FID analyser complies with this standard regulation, but the real breakthrough is the unmatched portability and the next generation technology.

Polaris FID is a new concept and incorporates these important features: two rechargeable batteries that last more than three hours; a zero air cylinder for 10 hours of continuous measurement; a span gas cylinder useful for tens calibrations and, last but not least, an advanced metal hydrides cartridge for hydrogen storage to fuel the flame detector. However, the hydrogen source is not the usual pressurised cylinder, but a small steel cartridge that weighs only 500 grams, and which stores hydrogen for 30 hours of continuous measurements. Furthermore, as hydrogen is chemically bonded to a special metal alloy inside the cartridge, there is no risk of leakage and explosion: hydrogen cylinder will not be a concern anymore.

In conclusion, the Polaris FID incorporates everything needed for a measuring campaign in just 13 kg and a compact body, making it the best choice for the operators who have to climb on the chimneys of industrial settlements easily and safely.

For More Info, email: 30694pr@reply-direct.com