

Application Note for Specialty Gases.

The Preparation and Certification of a 30 ppt Calibration Gas Mixture.



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Abstract

Challenges in the preparation and certification of a 30 parts per trillion (ppt), also referred to as 30×10^{-12} , sulfur hexafluoride gas calibration mixture used as a transfer standard for the determination of anthropogenic carbon dioxide are described. 30 ppt equals to about 1.5 minutes out of every hundred thousand years.

Anthropogenic carbon dioxide in the oceans cannot be measured directly and a variety of tracers can be used instead to estimate the water mass age and therefore act as a proxy for the absorption of human derived carbon dioxide. Sulfur hexafluoride is increasingly being used in this application to obtain information about air-to-sea gas transfer processes which are important in climate change research.



1. Introduction

To improve our knowledge of the global carbon cycle is crucial to understanding and predicting climate change. Since the industrial revolution the world’s oceans have absorbed approximately 30% of all the anthropogenic ‘man-made’ carbon dioxide emitted into the atmosphere¹. Pre-industrial levels of atmospheric carbon dioxide are estimated to be ca 280 parts per million (ppm) however in 2010 the concentration had risen to 389.69 ppm². Carbon dioxide is the reference gas against which other greenhouse gases are measured and therefore has a Global Warming Potential (GWP) of 1³.

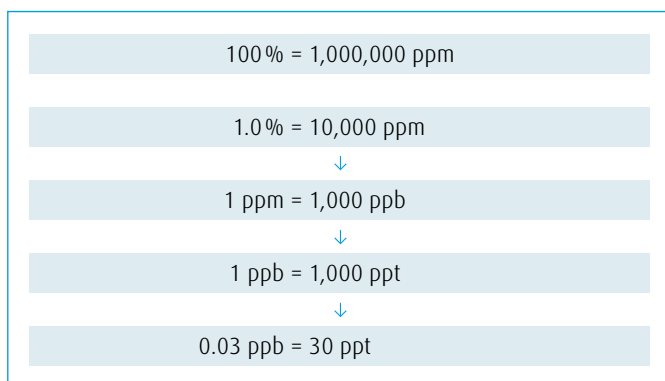
The role of the southern ocean in the uptake and storage of anthropogenic carbon dioxide is the subject of much research^{4,5}, and it has been recognised as a key region for the long term storage of gases from the atmosphere. As global emissions continue to rise the uptake of carbon dioxide increases, however, there are concerns about the oceans’ continued ability to absorb carbon dioxide. The Weddell Sea is a particularly important area where wintertime heat loss and sea ice formation increase the density of surface water, which then sinks taking with it gases such as carbon dioxide, effectively removing them from the atmosphere.

Anthropogenic carbon dioxide cannot be measured directly; however, scientists have adopted several strategies to estimate anthropogenic carbon concentrations including ‘back calculations’ using measurements of inorganic carbon^{6,7,8} and the use of tracers such as chlorofluorocarbons (CFCs)^{9,10} and sulfur hexafluoride (SF₆)¹¹. These tracers can be used to estimate water mass age and act as a proxy for the absorption of human derived carbon dioxide. Sulfur hexafluoride is increasingly used to obtain information about air – to – sea gas transfer processes.

The global warming potential of sulfur hexafluoride is 23,900, making it the most potent greenhouse gas the Intergovernmental Panel on Climate Change (IPCC) has evaluated³. It is a colourless, odourless, nontoxic, nonflammable gas with excellent dielectric properties and is used for insulation and current interruption in electric power transmission and distribution equipment, in semiconductor manufacturing to create circuitry patterns on silicon wafers and as a tracer gas for leak detection.

Measurements show that its global average concentration has increased by about 7% per year during the 1980s and 1990s, from less 1 ppt (1 x 10⁻¹²) in 1980 to almost 4 ppt in the late 1990s¹². Current tropospheric concentrations of sulfur hexafluoride are estimated to be ca 6 ppt. 1 ppt equals to about three seconds out of every hundred thousand years.

Conversion – percentage, ppm (parts per million), ppb (parts per billion) and ppt (parts per trillion):

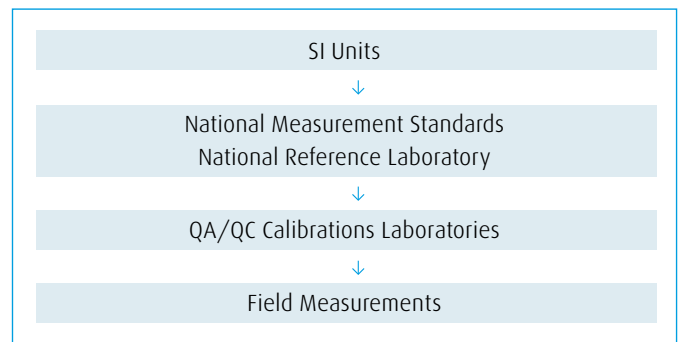


2. Preparation of gas calibration cylinders for use as transfer standards

The key attributes required in a gas calibration cylinder include:

- **Stability** – the calibration standard shall remain at the certified value throughout the specified shelf life and as the contents are depleted in use. In order to achieve stability cylinders may require the passivation of the internal surfaces¹³.
- **Accuracy** – the standard is ‘fit for purpose’ and the measurement uncertainty is consistent with identified requirements for use and customer needs.
- **Traceability** – traceability depends upon a chain of standards linked back to an international primary standard through a series of calibrations, i.e. inter-comparisons between 2 standards in the chain. The value of each standard in the chain must have a defined measurement uncertainty.

Therefore, to ensure measurement accuracy, stability, traceable calibration and defined measurement uncertainty are required.

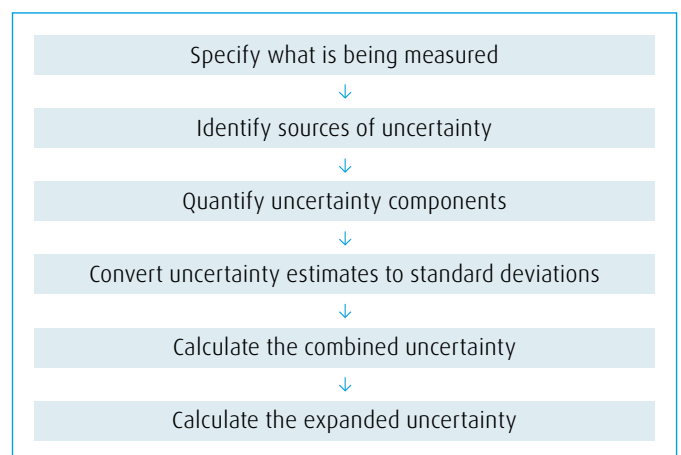


Traceability Model

The Guide to the Expression of Uncertainty in Measurement¹⁴, Quantifying Uncertainty in Analytical Measurement¹⁵ and the Expression of Uncertainty and Confidence in Measurement¹⁶ are all documents which give detailed guidance to enable the calculation of expanded uncertainties. The International Organisation for Standardisation (ISO) has defined measurement uncertainty as¹⁷:

‘A parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand.’

The stages in the evaluation of measurement uncertainty are illustrated below:



The uncertainty estimation process¹⁸

Sources of uncertainty in analytical procedures include:

- Sampling – homogeneity, the number of replicate samples taken, variations in temperature and pressure during sampling;
- Sample preparation – the presence of dilution errors or contamination;
- The presentation of certified reference material (CRM) to the measuring system – the uncertainty of the CRM;
- Calibration of the instrument;
- Analysis and data acquisition;
- Data processing, for example control of the rounding of results and the use of statistical treatments to derive results;
- The presentation and interpretation of results.

Gas calibration cylinders for use as transfer standards are normally manufactured from aluminium alloys. These cylinders are generally used for high integrity mixtures such as those used for ambient air pollution monitoring applications, e.g. nitric oxide/nitrogen and sulfur dioxide/air at parts per billion (ppb) concentrations.

Calibration mixtures at ppt levels require a very careful evaluation of feasibility and preparation techniques. Furthermore cylinder valve selection is also important particularly:

- Material compatibility to ensure mixture stability:
 - non reactive material surfaces;
 - use of stainless steel and passivation techniques and electro-polishing.

Amongst a range of techniques, Linde uses a proprietary process to render the aluminium surface of the SPECTRA-SEAL[®] cylinder chemically inert. Additional processes convert this passivation layer into a smooth, tightly adherent surface, with negligible adsorptive properties. As a result of these procedures, Linde can guarantee that SPECTRA-SEAL[®] calibration gas mixtures will remain stable, with a consistent analytical response for 5 years from their manufacturing date.

- And general design considerations to minimise inboard leakage or adsorption/desorption within the valve:
 - no elastomeric seals;
 - use of metal diaphragms.

Linde's REDLINE[®] represents premium Specialty Equipment including cylinder regulators and the full range of equipment required for fixed gas distribution systems installations. REDLINE[®] stretches from wall mounted automatic switch-over gas panels to shut off valves and furniture mounted point of use regulators. All REDLINE[®] components are designed for use with high purity specialty gases up to 6.0 grade and includes a welded panel option that can also be used for 7.0 grade gases.

Gas calibration cylinders are usually prepared volumetrically (manometrically), gravimetrically or by dynamic blending. Each technique has advantages and limitations.

Volumetric filling has a wide dynamic range and the filling accuracy is unaffected by low molecular weight gases such as hydrogen and

helium. However, limitations include pressure gauge accuracy and resolution, changing cylinder and gas temperatures during filling and errors due to the non-ideal behaviour of some gases.

Gravimetric filling techniques have the advantage of high balance accuracy and the use of reference masses directly traceable to the International System of Units (SI). The calibration and linearity of such balances can be undertaken by ISO/IEC 17025 accredited calibration laboratories. Gravimetric calibration mixtures are prepared by measuring the gas additions to a cylinder by the increase in mass of that cylinder. The composition of the gas mixture is calculated from the mass of each gas and a number of additional parameters, such as the purity of the gases used. A balance used for the preparation of calibration mixtures should have a total capacity suitable for weighing the mass of the cylinder, including the final gas content, and enough sensitivity to correctly weigh small amounts of gas.

3. Raw materials

The gaseous components used in the preparation of a calibration mixture require analysis to establish purity and ensure that any trace impurities present do not adversely affect the integrity of the mixture.

Contaminants are usually physically or chemically similar to the pure gas and may be difficult to separate, they also tend to be at low concentrations compared to the pure gas, e.g. 6.0 (99.9999%) specialty gases have not more than 1 ppm total reported impurity level and 7.0 (99.99999%) have 1 ppb total reported impurity level. The analysis therefore requires high sensitivity detectors.

Critical impurities are those which affect the final mixture concentration through chemical or physical means, for example trace oxygen in nitrogen used for the preparation of 500 ppb nitric oxide standards or some inert gases, such as argon, may be categorised as critical because of their molecular mass.

The HiQ[®] Nitrogen 7.0 used for the preparation of the parts per trillion (ppt) sulfur hexafluoride calibration mixture is manufactured by an air separation process and based on the fractional distillation of air at sub-ambient temperatures. The feed air to the single column system is treated as a mixture of oxygen, nitrogen and argon. Impurities such as water and carbon dioxide are removed in pre-purification steps. Sulfur hexafluoride has a boiling point of -63.9°C and is present in air at a concentration of approximately 6 ppt. Due to its ambient concentration and boiling point sulfur hexafluoride would concentrate in the least volatile product during the distillation of air, namely oxygen and not the nitrogen, furthermore it is anticipated it would be removed by plant clean up processes, absorbers etc.

Sulfur hexafluoride is unreactive, not attacked by water, acids or bases at ambient temperatures and stable in the presence of aluminium, stainless steel, copper, brasses and silver even at elevated temperatures.

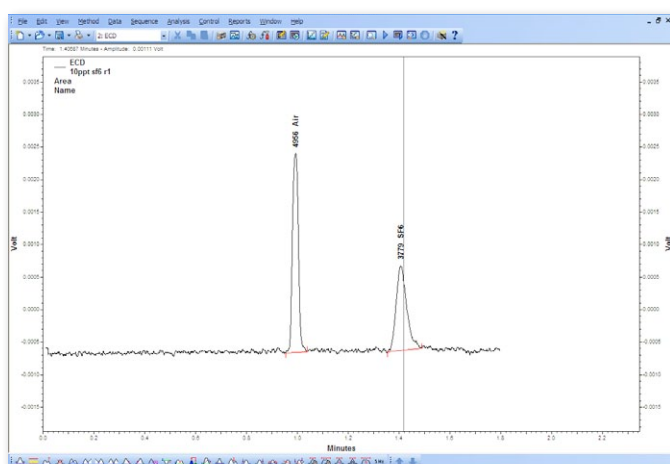
It is these physical and chemical properties of sulfur hexafluoride, particularly its stability and boiling point that allows the preparation of a 30 ppt sulfur hexafluoride in nitrogen calibration mixture. Its stability is also crucial in its use as a tracer compound.

4. Analysis and standardisation

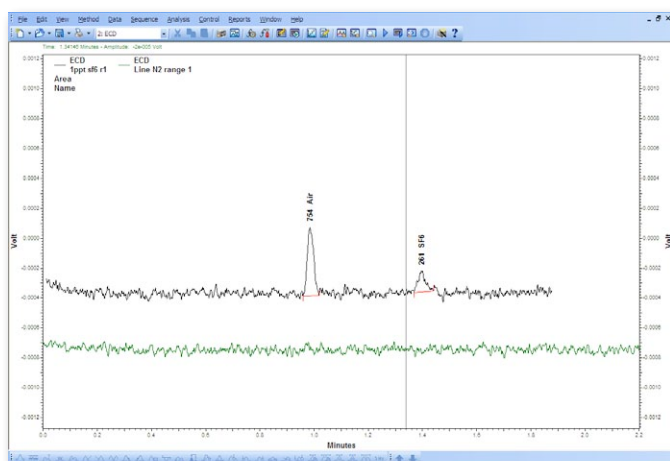
Experimental:

- Instrumentation: GC ECD
- Column: PoraPLOT Q 10 m x 0.53 mm
- Carrier and Make up gas: HiQ® Nitrogen 7.0
- Oven method: Isothermal 60 °C
- Injection Volume: 500 µL

The analysis of the 30 ppt sulfur hexafluoride calibration mixture was completed by gas chromatography using a gas chromatograph with an electron capture detector (ECD) and a 10 m x 0.53 mm PoraPLOT Q capillary column and HiQ® Nitrogen 7.0 carrier and make up gas. The gas chromatograph was operated isothermally with an oven temperature of 60°C and a gas sampling valve with a 500 micro-litre injection volume was used.



10 ppt SF₆



1 ppt SF₆ overlaid with high purity nitrogen

The electron capture detector detects electron absorbing species, i. e. those with high electro negativity, such as halogenated species. The ECD uses a radioactive beta particle (electron) emitter, typically a metal foil Ni63 radionuclide. The analyte concentration is proportional to the degree of electron capture, hence the background level of electrons change in the presence of electron absorbing species, e. g. sulfur hexafluoride. It is possible to detect halogenated compounds such as pesticides and chlorofluorocarbons (CFCs) at concentrations of 1 ppt. Electron capture detectors are commonly used for environmental monitoring.

5. Summary

In summary, it is possible to produce a stable 30 ppt sulfur hexafluoride gas calibration mixture for use as a transfer standard due to:

- the preparation of clean, dry and passivated aluminium alloy cylinders;
- the availability of high integrity valves and regulators with low internal volume, optimised flow paths and use of VCR fittings etc.;
- the production of very high purity nitrogen containing no sulfur hexafluoride for use as the carrier gas (analysis) and balance gas (mixture preparation);
- the physical properties of sulfur hexafluoride particularly its stability, unreactive nature and high sensitivity with respect to the electron capture detector which allows good analysis and standardisation procedures at the required concentration.

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