

WHITE PAPER

Methods for traceable calibration of gas phase components

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Introduction

The transition from using fossil fuels to using green fuels, along with the potential to capture, store and use carbon, should occur with a minimum of additional and potentially more harmful compounds emitted into the atmosphere. The transition from fossil fuels to green fuels should not only consider the reduced emissions of carbon, but also reducing the emissions in general. The introduction of both green fuels for combustion processes along with carbon capture (CC) plants will result in a changed composition of emissions from plants and sources, and this should be considered in the environmental permit and measured accordingly.

The emissions from CC plants depend on the technology (e.g., the type of solvent used) used. CC plants may result in the emission of complex and potentially harmful chemical compounds. To conduct real-time measurements using, e.g. Proton Transfer Reaction Time of Flight (PTR-ToF-MS) or Fourier Transformed Infrared spectroscopy (FTIR), the equipment requires calibration prior to measurements. For the calibration of more complex and problematic compounds, gas standards may not be available as accredited or certified gases. Therefore, the production of gases or gas mixtures for calibration in the laboratory or on-site becomes highly relevant to ensure high-quality and reliable measurements.

This whitepaper summarises available methods applicable for the generation of calibration gases and gas mixtures. Table 1 - Table 4 shows different approaches for generating calibration gases with known concentrations.

- **Static dilution:** the functional principle of static dilution is constituted of injection of liquid and evaporation of the liquid within an enclosed container with a defined and static volume [6, 12].
- **Dynamic dilution:** the functional principle of dynamic dilution is constituted of a continuous flow of diluting gas through the generation system and mixture with the vapour at a known rate of generation [5, 12].



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Table 1

Permeation method for producing gas phase components for calibration.

Type: Dynamic dilution

Description	Advantages	Limitations	Literature
<p>Permeation tubes containing the analyte of interest are placed in an oven and kept at a stable temperature.</p> <p>The analyte will permeate through the walls at a rate governed by temperature and tube geometry.</p> <p>Analyte will be mixed with a carrier gas and potentially several other analytes to obtain a mix.</p> <p>Estimated time aspect to obtain for steady state conditions¹: Minimum 24 hours.</p>	<p>Permeation methods are considered an effective and accurate way of preparing low-concentration test gas.</p> <p>Permeation tubes are inherently safe compared to gas cylinders—they operate at low pressures and contain a small quantity of chemicals.</p> <p>Permeation rate reaches a constant value if it is kept at a constant temperature.</p> <p>The method can be used to generate standard gas mixtures for a wide range of substances, including substances not suitable for other methods.</p> <p>Portable equipment is available.</p>	<p>Permeation processes are highly sensitive to fluctuations in temperature.</p> <p>Long initial time for reaching permeation equilibrium (up to 24 hours).</p> <p>Procurement costs are relatively high.</p> <p>Potentially high costs related to the purchase of permeation tubes.</p> <p>The generation of standard gas is sensitive to changes in factors of the permeation tubes over time.</p> <p>May require several weeks for stabilisation before calibration can be performed with sufficient accuracy.</p> <p>Different compounds might require different temperatures when placed in the oven, resulting in difficulties related to the preparation of complex mixtures by only using permeation.</p> <p>The process of permeation requires a high level of accuracy prior to the production of a gas for calibration, as the tubes continuously must be weighed (over longer periods) to ensure the generation of the correct concentration when producing a gas for calibration.</p>	<p>[3]</p> <p>[5]</p> <p>[11]</p> <p>[12]</p> <p>[13]</p> <p>[14]</p> <p>[15]</p> <p>[18]</p>

Table 2

Evaporation methods for producing gas phase components for calibration. Unless otherwise specified, the description within the table relates to both types of methods.

Type: Dynamic dilution or Static dilution

Description	Advantages	Limitations	Literature
<p>For dynamic dilution, the carrier gas is either passed through a liquid form of the compound of interest, where the liquid evaporates and mixes with the gas flow as the carrier gas bubbles through the liquid or the component for calibration is injected into a stream of carrier gas using a syringe.</p> <p>For static dilution, the component for calibration is injected into a stream of carrier gas and mixed in a mixing chamber, e.g. Tedlar® bags.</p> <p>Estimated time aspect to obtain for steady state conditions: Minutes.</p>	<p>The method is inexpensive when used as static dilution and has a short stabilisation period for the test gas generation compared to diffusion and permeation.</p> <p>A useful method to include a single or few volatile compounds in a wet gas stream.</p> <p>Has a wide applicability.</p> <p>Suitable for many compounds.</p>	<p>The determined accuracy of the test gas generated is lower than for the permeation and diffusion method.</p> <p>The concentration produced is highly variable, even if the setup is constant.</p> <p>The method is highly dependent on the vapour pressure of the compounds.</p> <p>Factors affecting the accuracy of the test gas are temperature variation and vapour pressure of the selected compound.</p> <p>Dynamic dilution may involve high procurement costs.</p> <p>Labour-intensive/high time consumption when using dynamic dilution, while static dilution is less time-consuming.</p> <p>Method limited to hydrophilic compounds if only applicable with aqueous solutions.</p> <p>For some systems, organic solvents can be used to generate a calibration gas.</p>	<p>[3]</p> <p>[4]</p> <p>[6]</p> <p>[9]</p> <p>[12]</p> <p>[16]</p>

Table 3

Diffusion method for producing gas phase components for calibration.

Type: Dynamic dilution

Description	Advantages	Limitations	Literature
<p>Diffusion of vapour of a liquid from a container through capillaries or directly from a capillary followed by mixing with a diluting gas flow.</p> <p>The constant concentration of test gas relies on temperature, pressure, concentration gradient, length and diameter of the capillary and the flow rate of the diluting gas.</p> <p>Estimated time aspect to obtain for steady state conditions: Hours.</p>	<p>It shares similar advantages as the permeation method.</p>	<p>Not applicable for preparation of multicomponent mixture in one diffusion vessel unless several vessels are applied.</p> <p>Share similar limitations as the permeation method, e.g., long calibration period and high dependence on temperature.</p> <p>Reduced ability to prepare standard gas mixtures of low-volatile compounds.</p>	<p>[3]</p> <p>[7]</p> <p>[11]</p> <p>[12]</p> <p>[17]</p>

Table 4

Gas cylinders for producing gas phase components for calibration.

Type: Dynamic dilution

Description	Advantages	Limitations	Literature
<p>Accredited gases with known concentrations, which can be coupled directly to monitoring equipment or be diluted prior to calibration.</p>	<p>Fast method for calibration: Steady state conditions may be obtained within seconds.</p> <p>The gas or mix of gases is often commercially available as accredited gas mixtures and awarded with a certificate.</p> <p>The responsibility for the accuracy of the concentration lies with the manufacturer of the accredited gases.</p> <p>A mix of gases can be dosed and measured simultaneously, which allows fast calibrations compared to other methods</p>	<p>The costs of mixed gases can be significant.</p> <p>Not all compounds of interest can be a part of a useful mixture of accredited gases.</p> <p>Cylinder gas mixtures may have relatively short expiration times (e.g. 12 months)</p>	<p>[8]</p>

The methods applicable for generating calibration gases listed above show a variety of advantages and limitations related to the method, which become crucial when considering the applicability of generating calibration gases for specific situations. As mentioned above, the emissions from CC plants differ between plants according to the solvent used, but amine-based solvents are common, and therefore, the ability to produce a calibration gas containing relevant amines is of high priority.

None of the listed methods above are applicable for generating a calibration gas containing all compounds of interest needed for a specific application. However, methods of permeation, diffusion, and evaporation are most suitable for a wide range of compounds monitored at CC plants, with evaporation being the method currently applicable to the highest number of amines.

Besides the ability to monitor and quantify the emissions from CC plants, determining the purity of the captured CO₂ is also of interest. A similar instrumentation is used for analysis of the purity of CO₂, requiring calibration methods as described above. The specifications for impurities in the captured CO₂ are set by the companies transporting and storing the CO₂, and the ability to ensure that specifications are met relies on the ability to sample pressurised CO₂.

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