KIN-TEK
The Calibration Specialists

Tips on performing cylinder-free accurate gas calibrations for trace concentrations

Analysis of Volatile Organic Compounds (VOCs), Semi-VOCs, Hazardous Air Pollutants (HAPs), and many other gas component groups are common topics of interest in the gas analytical industry. Discussion of the methods and equipment used for analysis is typically provided for verification of analytical results or research performed. Some articles will mention the importance of accurate calibration and provide information related to the sources used for calibrating their analytical device, but more focus is given to specific analytical results and project criteria. While the quantitative analytical results are an important part of understanding the gas analyzed and the methods used, it is extremely important to perform proper calibration with accurate equipment and gas sources. This article provides tips on the equipment and methods for dynamically creating cylinder-free accurate calibration gas standards for ppmv and lower concentrations.

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Determine the Calibration Gas Requirement

The specifics of gas calibration and gas analysis relate directly to the user's application requirements. The first step is determined by the level of concentration and gases required to create a calibration curve. Typically, gas cylinders are used when calibration requires percent level volume concentrations but are not the best solution when calibration concentrations drop to ppmv and lower ranges. Loss of analyte to cylinder walls, storage of static blends, methods of filling the cylinder for trace concentrations mixes, temperature/pressure variances, and other characteristics contribute to inaccuracies that can exist when using a gas cylinder for lower concentration calibrations.

Permeation tubes and permeation systems offer a cylinder-free accurate solution for calibrating ppmv and lower concentrations. Without having to handle or store multiple large cylinder gases, permeation tubes are used to dynamically create a NIST Traceable simple gas standard or a complex gas mixture for calibrating a GC, GC/MS, IMS, or other analytical devices. Over 550 compounds are currently available making permeation tubes an extremely versatile method for generating known trace gas concentrations (1). Once the gas standard(s) and concentrations are determined to be in ppmv and lower concentration ranges, the permeation system and the modules are selected based on the required calibration scenario.

Determine the Calibration Equipment

Permeation tubes are temperature dependent devices that require accurate and precise temperature control for repeatability, and excellent flow control for accurately diluting and delivering the calibration gas. One permeation tube can replace several gas cylinders so incorporating a permeation system as a calibration solution saves space and long-term expenses. The next determining factor for performing cylinder-free calibration gas is selecting the equipment suitable for the application. The FlexStream™ permeation system is a modular approach to providing the right equipment for calibration scenarios that may exist. The "Flex" in the FlexStream™ name means the system is flexible enough to evolve with user requirements. Modules are selected based on component gases required in the calibration gas stream, the range of concentrations required, and if the calibration gas must be dry or humidified. Users can start simply with a single module FlexStream™ "Base" instrument and expand with other modules later if requirements grow. Automation and computer interface with FlexLink™ software (included with the system) makes it easy for users to automatically create an accurate concentration of calibration gas stream. Users plan their calibration requirements, easily install the permeation tube(s) required, and with a click of the mouse or tap of a stylus perform a full calibration curve.

As an example, think about creating a calibration curve for analyzing Methyl mercaptan (MeSH), Carbonyl sulfide (COS), and Hydrogen sulfide (H_2S) as a mixture in the same gas stream. With a target of 1 ppmv in an inert dilution gas flow of 500 standard cubic centimeters per minute (sccm), these three analytes can be combined into a single module FlexStream™ Base system with the internal oven operating at 40°C. Each permeation tube occupies the same oven inside a glass permeation tube adapter bottle connected within the system oven. A small flow of inert gas, typically Nitrogen, is always circulating through the glass bottle and picking up the gas permeated by the combination of the MeSH, COS, and H_2S, creating a sulfur gas mixture. Stepwise dilution of permeate gas dynamically creates the calibration gas curve with minimal effort almost instantaneously. For example, by selecting 1000 sccm for 0.5 ppm, 2000 sccm for 0.25 ppm, and 4000 sccm for 0.125 ppm and so on, variations of calibration scenarios are formed without changing out bulky gas cylinders, cylinder-free.

While it sounds extremely simple, it actually is if a few active tips are understood and followed.

Ten Simple Tips for Performing Cylinder-Free Calibrations

1 **Selection of equipment and permeation tubes should align with the application requirements.** If a complex gas mixture is needed, multiple modules in a series may be required. The FlexStream™ Base with extra ovens or secondary dilution capabilities may be needed to fulfill the complexities of the calibration. More than one permeation oven in a series provides flexibility to toggle on/off specific gases that may operate at different temperatures. Start with the right system to achieve the right scenario.

2 **When creating a low concentration gas mixture, good practice is to situate it as close as possible to the analytical device being calibrated to minimize loss of analyte to tubing walls or exposure to ambient conditions.** Situate the permeation system close to the gas analyzer or Device Under Test (DUT). Sticky analytes or those that easily condense may be lost if the flow path is much longer than a few feet. If it must be further away, allow serval hours for Span Gas to coat delivery tubing.

3 **Allow adequate time for the system to warm up and for the permeation tube to equilibrate before using (typically 4 or more hours depending on the analyte).** Permeation tubes are extremely temperature dependent and need time to warm up and equilibrate. Once stabilized the emission rate will remain constant and simple flow adjustments will provide variation in concentrations.

4 **Select a high purity, dry Nitrogen, or other inert gas to connected to the permeation system.** Low grade dilution gas with contaminants such as water or other impurities can interfere with calibrations. The FlexStream™ permeation system is equipped with highly accurate temperature control and an internal mass flow controller. Select a dilution gas that has very low contaminants or if possible, known contaminants to subtract.

5 **Use the best sampling method for the gas analyzer (DUT).** If the analyzer only needs a small flow and your calibration curve is based on larger flows, use a split flow method to send the gas needed to the analyzer while venting the rest of the flow. Do not build up pressure or create backpressure to the permeation system as that will create concentration fluctuations or inaccuracies. Allow the output gas to flow freely to the DUT by setting up a "Tee" fitting. If a specific flow measurement is required to the analyzer, incorporate a flow metering device to measure flow to the analyzer and allow the rest of the calibration gas to safely vent. A small pressure may be needed to divert the flow to the DUT.

6 **Establishing a baseline "zero" periodically contributes to accurate calibrations.** Practice incorporating a Zero flow setting periodically using the Zero mode allowed in the FlexStream™ or 491Flex™ permeation systems. A default flow rate can be used to verify baseline readings of dilution gas between calibrations and to minimize buildup in output lines.

7 **Use the Purge Mode before long shut down periods or Span with no permeation tubes installed.** When a long-term shutdown is planned, remove all permeation devices from ovens and run a clean dilution flow through the system flush/purge output lines before long shutdown periods. DO NOT perform a Purge mode with permeation tubes installed.

8 **Know the gas standards you are using.** Identify unique characteristics of the gases selected for calibration such as those that are light sensitive, air sensitive, or sticky and mitigate risks associated with each. Trace sulfurs may require special coating to be used on output tubing or those analytes that condense easily may require output tubing to be heat traced. Light sensitivity, air sensitivity, or analytes that absorb moisture may require special storage or operating conditions to minimize exposure to elements. Understanding the chemical characteristics will aid in longevity and repeatability of gas standards.

9 **Maintain certifications of equipment and permeation tubes.** It is recommended to have permeation tubes and calibration equipment certified annually to maintain traceability to NIST and ensure accuracy. Trace Source™ permeation tubes undergo weight loss analysis to accurately determine their emission rate. Specify certified Trace Source™ permeation tubes for best accuracy. Maintain annual calibrations/certifications of equipment to ensure performance accuracy to factory tolerance.

10 **Permeation tubes are shipped with a Safety Data Sheet (SDS) and information stating how they need to be stored when not being used.** Store all permeation devices according to the manufacturer's requirements. Some tubes deplete faster than others and may require a freezer or refrigerator to slow their permeation rates. Review all documentation received with equipment and permeation tubes and adhere to the storage requirements.

Common sense techniques for creating a calibration curve works whether the gas is created dynamically using a permeation system or when cylinders are used. However, with over 550 chemical gas standards available for use in small permeation tubes and the capability of replacing several gas cylinders with one permeation tube, it makes more sense to create custom mixtures without the need for cylinders.

Cylinder-free accurate gas calibrations can be done by incorporating a FlexStream™ permeation system and Trace Source™ permeation tube standards, and following a few general tips for best practice.

Solve Your Calibration Challenges with KIN-TEK Analytical Inc. Products

The Trace Source™ Permeation Tube technology is employed in KIN-TEK's Gas Standard Generators to provide accurate, NIST traceable calibration standards. KIN-TEK's products include a range of gas standard generators and permeation devices to fit almost any application that relies on the delivery of an accurate trace gas concentration. Individual gas generator modules can operate as stand-alone calibrators or be combined into a Gas Standard Generator System configured to solve the most complex applications. The System utilizes the FlexLink™ software that can log and export data for analysis and reference.

Contact a customer service representative now and discuss your specific application.

References:

1. KIN-TEK Analytical, Inc. (2023). Chemical Compound List. www.kin-tek.com. [Brochure] https://kin-tek.com/wp-content/uploads/2023/03/KIN-TEK-Chemicals-List_rev0006-rev-1-Web.pdf.

2. McKinley, J. and Majors, R.E., "The Preparation of Calibration Standards for Volatile Organic Compounds – A Question of Traceability", Sample Prep Perspectives, reprinted from LCGC, Volume 18, Number 10, October 2000.

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