

IDENTIFYING THE RIGHT PERMEATION TUBE FOR YOUR APPLICATION



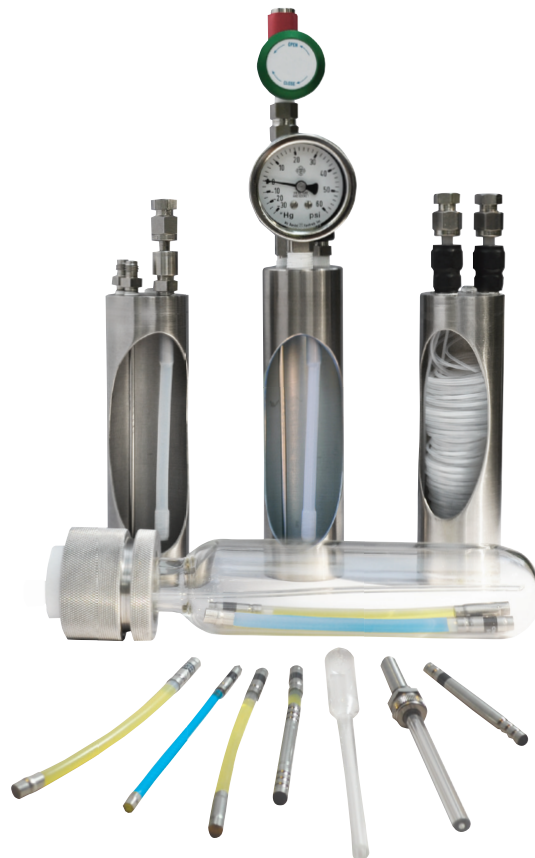
Permeation tubes have been used for many years in various applications for creating trace concentration gas standards for calibrating gas analytical devices such as a gas chromatograph. Permeation tubes create NIST traceable gas standards because they are held at a stable temperature and are certified via gravimetric weight loss method where both the temperature and weight loss are measured by fundamental traceable standards (4). Creating NIST traceable gas standards for calibration is not the only use for these highly underrated small devices, it just may be the most likely use for them. Permeation tubes can be used for more than routine calibration of gas analytical devices and understanding how they work, and the different types of permeation tubes available aids users in identifying the right permeation tube needed for a specific application. This article provides a basic understanding of different types of Trace Source™ permeation tubes and how to identify the right permeation tube to generate a precise trace concentration for a specific application.

“Any application that would require a trace gas standard or known accurate amount of trace gas concentration to be dynamically generated will benefit from the use of some type of permeation tube.”

What is a Permeation Tube?

As stated, a permeation tube is simply that – a tube, or a cylinder that consists of a polymeric membrane, typically Teflon® tubing that is permeable to a chemical compound (6). Pure analyte is contained within the tube and the tube is sealed in a way that pure analyte passes through the membrane at a stable measured rate. In the case of Trace Source™ Permeation Tubes, there are different types, and each type varies depending on the requirement of the application and chemical property. The most important thing to consider about permeation tubes is that when held at a stable temperature, they are extremely effective in controlling a very low stable flow of pure gas across the membrane that would otherwise be difficult to measure by conventional flow measurement devices (5). In operation the small flow of gas that passes across the tube membrane is determined by measuring the weight loss of the device over time and establishing the “emission rate” of the gas as the tube is held at a known temperature. The mechanism of permeation of a compound through a membrane is defined as the product of the solubility of the compound in the membrane and the diffusivity of the compound through the membrane, both of which are functions of temperature (5) Trace Source™ permeation tube emission rates are measured in nanograms per minute (ng/min) or nanoliters per minute (nl/min) and are used in a calculation that yields concentration based on dilution flow rate (sccm) and other determining factors.

There are two specific categories of Trace Source™ Permeation tubes available for achieving low ppm concentrations or higher ppm concentrations: **Disposable Permeation Tubes** and **Refillable Permeation Tubes**.



Trace Source™ Disposable Tubes

Trace Source™ Disposable Permeation Tubes consist of short lengths of Teflon™ tubing that are filled with a small amount of a pure chemical compound, for example pure Hydrogen sulfide, Benzene, or Acetone, etc. Over 550 compounds are currently available making permeation tubes an extremely versatile method for generating known trace gas concentrations (1). The disposable permeation tube is constructed using a polymeric membrane (typically Teflon®) as the active surface area through which really low analyte flow ("f") takes place. The tube is sealed at both ends with stainless steel end pieces and are plugged (See Figure 1). While most analyte vapor will escape the permeation tube through the walls of the tubing, in some cases it will also permeate through the end plugs. In such cases a stainless steel reservoir may be used to encapsulate the liquid component for longer tube life.

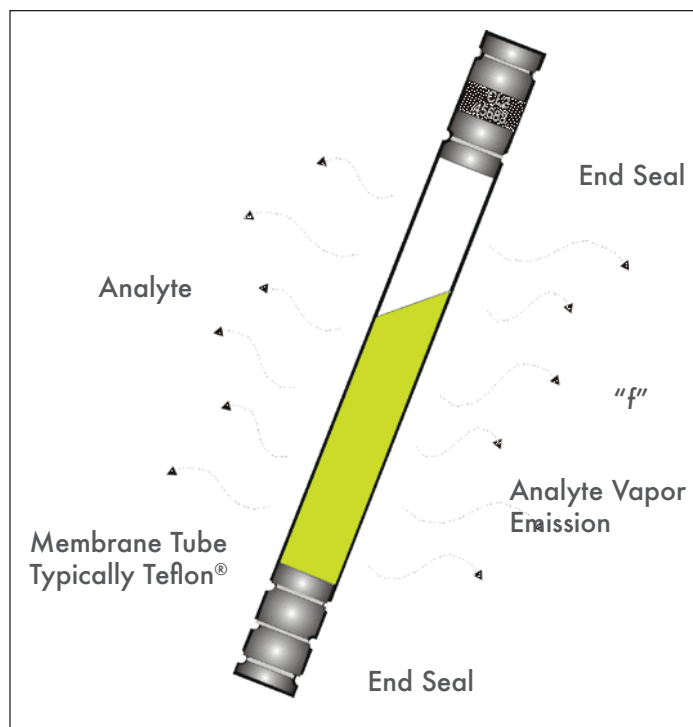


Figure 1 Typical Disposable Permeation Tube

Compounds such as Chlorine and Ammonia permeate rapidly in a disposable tube, while other compounds such as Formaldehyde may permeate much slower. Changes in operating temperature directly affect the permeation rate of the tube so it is important that the permeation tube be held at a stable temperature for accurate emission rate measurement. Depending on the temperature at which the tube is operated, the length or thickness of the tube material or the type of membrane used, various permeation rates are possible with disposable type tubes. This makes permeation tubes an excellent replacement to a cylinder gas for generating precision calibration gas standards. In general, disposable permeation tubes will provide low ppm to ppb ranges of concentrations and can be combined (if nonreactive to one another) to create gas mixtures. Up to 8 Trace Source™ Disposable Permeation Tubes can be used at the same operating temperature in one oven. Analyte permeation rates are manipulated by the construction of the device but the maximum lengths of typical disposable tubes are no longer than ~ 15 cm.

To provide a broad spectrum of permeation tubes to fulfill various applications, Trace Source™ Disposable Permeation Tubes are divided up into different types (See Figure 2).



Figure 2 Trace Source™ Disposable Permeation Tube Types

- 1 HRT (High Rate)** tubes consist of a thin tubing wall and generate moderate concentrations of low vapor pressure compounds. These compounds include C₂H₅SH, CCl₄, Acrylonitrile, Benzene, Styrene and Water. HRT tubes are also used for generating high concentrations of SO₂, CH₃SH and other moderate vapor pressure compounds. Typical emission rates yield concentrations of 1 to 20 ppm (depending on the compound, operating temperature and dilution flow rate) (7).
- 2 SRT (Standard Rate)** tubes have a different type of tube material and generate moderate concentrations of high vapor pressure compounds such as SO₂, H₂S, NH₃, Cl₂, etc. Additionally, SRT permeation tubes can generate very low concentrations of low vapor pressure compounds such as Carbon disulfide, Methylene chloride and Nitric acid. Typical emission rates yield concentrations of 1 to 10 ppm (depending on the compound, operating temperature and dilution flow rate) (7).
- 3 SRT-2 (Standard Rate 2)** consists of a thicker membrane material that slows down the permeation rate of the analyte and generates moderate concentrations of high vapor pressure compounds such as Cl₂, NO₂ and NH₃. These tubes are used up to 50°C and yield concentrations of sub-ppm to 5 ppm (depending on the compound, operating temperature and dilution flow rate) (7).
- 4 Extra life (EL)** Permeation Tubes are designed to have a longer operating life than other disposable tubes and are recommended for special compounds. The “EL” designation means the tubes are made with a reservoir to contain the chemical compound, but a short exposed active membrane provides a small surface area for permeation to take place (7).
- 5 Wafer type (EL-SRT2W)** is a combination of the “extra life” with a membrane of the SRT-2. They are basically an impermeable reservoir with permeation only from the ends. Generally, these are very long-life tubes (7).

With disposable permeation tubes the pure chemical compound permeates from the inside to the outside of the active membrane. The purity of the chemical in a permeation tube is important to ensure a stable permeation/emission rate across the membrane otherwise impurities may cause errors in weight loss measurements. Permeation tubes are temperature dependent devices that require accurate and precise temperature control for repeatability, so they are placed in a precisely controlled oven such as one in a KIN-TEK Analytical, Inc. (KIN-TEK) Gas Standard Generator. The tubes are weighed periodically using a highly sensitive microbalance. The oven is calibrated with a NIST Traceable thermometer, and the microbalance calibrated with NIST traceable weights. Once the permeate flow (emission rate) is established, the output gas of the permeation tube may be diluted further with an inert or nonreactive carrier gas measured through a NIST Traceable flow meter/controller to create a known trace concentration standard (ppm, ppb, and ppt levels).

As seen in Figure 3, the component permeate flow (emission rate) across the permeation tube membrane is NIST traceable based on fundamental standards used in the weight loss and flow control measurement (4). When a NIST traceable mass flow meter or mass flow controller is used to measure the dilution gas, a NIST traceable gas standard is produced. KIN-TEK Analytical, Inc. permeation systems provide the oven, flow device, and other components that are required to generate an accurate NIST Traceable gas standard.

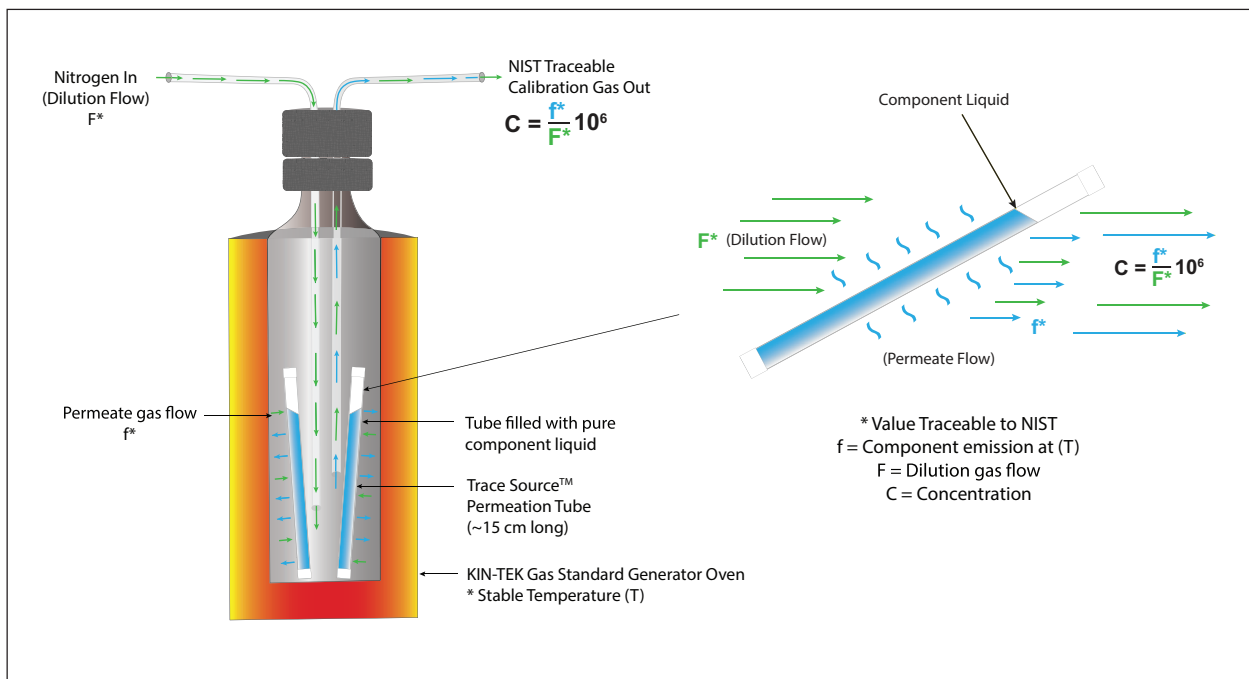


Figure 3 Trace Source™ Permeation Tube – How it Works

While Trace Source™ Disposable Permeation tubes can provide a broad range of concentrations or capabilities, their size prohibits reaching higher concentrations and only a small amount of analyte can be contained within the tube. To extend the concentration range to higher ppmv levels, often times it is necessary to use a refillable type of permeation tube. The next section explains different types of Trace Source™ Refillable Permeation Tubes.

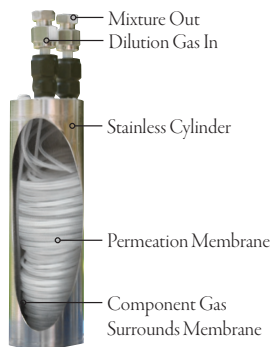
Trace Source™ Refillable Permeation Tubes



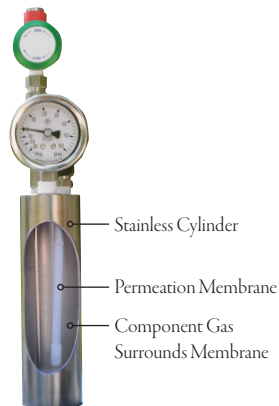
There are many applications that require the use of refillable permeation tubes to create known concentrations. The use of atmospheric or high vapor pressure gases (gases that cannot be liquified), the requirement for higher ppm level concentrations of liquid or condensable compounds, or the desire for using a permeation tube that can be refilled periodically are some criteria for using Trace Source™ Refillable permeation tubes. The pure compound and the required concentration typically dictate the type of Trace Source™ Refillable Tube needed.

Like the disposable tubes, permeation across the polymeric membrane takes place at a measured rate based on temperature, but for refillable type tubes, the liquid or gas is contained within the tube and crosses the membrane from the outside to the inside of the tubing where a flow of carrier or dilution gas circulates through the membrane and picks up the permeate gas and carries it out of the tube for further dilution (6). The cylinder body size is 6 inches in height and 1 ¾ inches in diameter. This provides broader capabilities for containing liquid or gas, as needed for longer tube life and for creating higher concentration ranges. One refillable tube would occupy the entire oven of a KIN-TEK permeation system, therefore higher concentration mixtures of analytes would mean more ovens needed in the series.

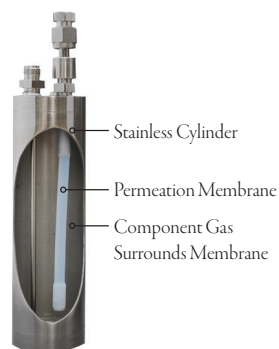
There are different categories of Trace Source™ Refillable Tubes – Liquid Filled, Gas Filled, or Gas Fed (See Figure 4). All three types are constructed as a stainless steel, or Monel™, cylinder with fittings that provide attachment directly into a KIN-TEK Permeation System for operation. In some special cases, other alloys, Teflon® or glass containment is used depending on chemical properties (3).



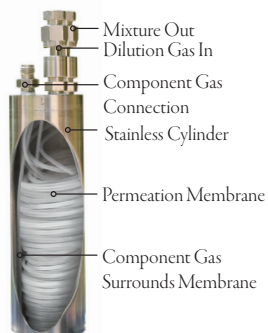
LFH - (Liquid Filled High rate) Permeation Tubes are typically stainless-steel (or other alloy) cylinders that contain the pure chemical standard and a coiled permeation membrane. Between 12 centimeters to 2000 cm of coiled membrane can fit inside the cylinder allowing much higher emission rates possible from a permeation tube. The expanded surface area of the longer membrane provides a broader range of permeation to take place across the membrane and the capacity of the cylinder allows higher fill volumes limited only by shipping allowances. Most liquid compounds, condensable gases, and subliming solids can be provided in an LFH (3).



57S Prefilled Gas Permeation Tubes are stainless-steel (or other alloy) cylinders that are provided with a pressurized pure gas contained inside. An analog gauge shows the pressure of the gas inside that is surrounding the short length of Teflon® membrane. In operation, the Trace Source™ 57S Prefilled Permeation Tube would be connected via an adapter for installation into a KIN-TEK Gas Standard Generator and heated to a stable temperature. The diluent/ carrier gas of the Gas Standard Generator circulates through the adapter and into the inner tube membrane to carry the permeating gas back out to the system for calibration. Over time, the tube gauge pressure will drop with continuous use and the emission rate at the new pressure is calculated or the tube is returned for refill at the factory. Trace Source™ 57S Prefilled Gas Permeation Tubes are used in KIN-TEK Gas Standard Generators to create gas standards ranging from <50 ppb to 5 ppm for Arsine and other hydride gases, as well as highly reactive gases such as HCl, HBr, and Oxygen. Other gases such as NO, CO, CO₂, Nitrogen, Hydrogen, etc. are also available in the 57S Prefilled tube but at low concentrations (2).



57H or 57S Gas Fed Permeation Tubes are stainless-steel (or other alloy) cylinders that are certified with pure component gas but are evacuated (emptied) before shipment. Trace Source™ Gas Fed tubes are used within a KIN-TEK Gas Feed Module which is required for proper operation. The module is equipped with controls for the user to “feed” the pure component gas from a cylinder source directly into the permeation tube as it is operated and then vent excess (or purge it clean) to a safely between uses. The gas fed tube would occupy the permeation system oven as the user fills the tube from an external pure cylinder. The Gas Feed Module holds the tube at a stable temperature and a set pressure slightly above ambient condition. Once filled and stabilized, the component gas surrounds the internal membrane and works the same as any other Trace Source™ Refillable Permeation Tube in that the gas permeates across the polymeric membrane and is picked up by the inert diluent/carrier gas circulating through the system.



Trace Source™ 57H Gas Fed Permeation Tubes are constructed with an internal membrane of 12 cm to 2000 cm in length. The expanded surface area of the membrane length allows for reactive or high vapor pressure gases to be used for creating higher ppmv concentrations (~10 to >1000ppm). The Trace Source™ 57S Gas Fed tube holds an internal membrane of up to 10 cm and is used when lower concentration high vapor pressure or reactive gases are needed (ppb to about 10ppm). The Trace Source™ 57S Gas Fed tube would only be used in instances where a prefilled tube depletes too rapidly for feasible operation. Otherwise, the Trace Source™ 57S Prefilled Permeation Tube would be recommended.

Typical Applications Using Permeation Tubes

Any application that would require a trace gas standard or known accurate amount of trace gas concentration to be dynamically generated will benefit from the use of some type of permeation tube. A few are mentioned below:



Moisture Analysis: Trace moisture analysis in manufacturing and industrial applications is important for quality assurance. Water (trace moisture) permeation tubes used in a KIN-TEK Moisture Generator dynamically generate a very accurate standard for calibrating highly sensitive moisture analyzers such as tunable diode laser absorption spectrometers (TDLAS) and quartz crystal microbalances.

Gas Chromatograph/Mass Spectrometer Calibration:

Permeation tubes are often used for calibrating a GC/MS for determining unknown components and quantities of gas mixtures. With over 550 chemical gas standards available, many are VOCs (Volatile Organic Compounds) that are available in some type of Trace Source™ Disposable Permeation Tube to calibrate a GC/MS or build a library of gases used in analysis. A FlexStream™ Modular Permeation System allows the use of all types of Trace Source™ Permeation Tubes available and provides the user the tools needed for generating the precision gas. The Span Pac Industrial Permeation System also employs both disposable and LFH refillable tubes for calibrating a process GC or GC/MS.

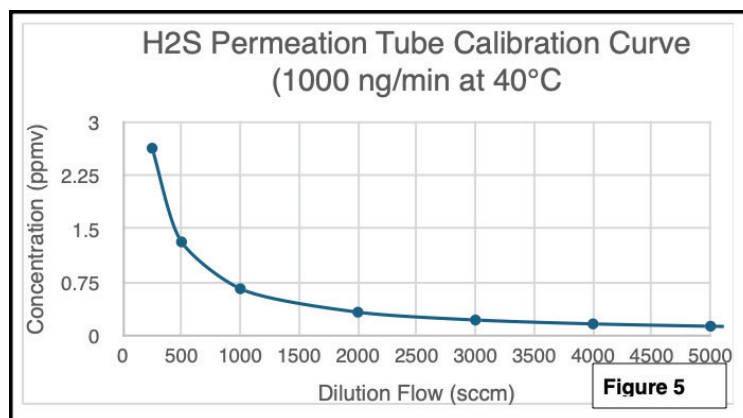
Research and Development (R&D): Improved methods of gas detection or analysis are always being researched for developing increased sensitivity to detect extremely low gas concentrations. Trace Source™ Disposable Permeation Tubes are a reliable method to dynamically generate ppb and lower NIST traceable gas standards for a variety of analytes such as BTEX: Benzene, Toluene, Ethylbenzene, and Xylenes for environmental gas analysis. Hazardous Air Pollutants (HAPs) that may be detected indoors such as Carbon Monoxide, Formaldehyde, Ammonia, and others are often researched for their effects on humans and animals. Creating known trace gas to determine exposure limits of filter materials, animal models, or absorbent materials also use both refillable and disposable types of permeation tubes to generate the various gases needed to quantify results. Depending on the research, KIN-TEK recommends the best permeation system and Trace Source™ Permeation tubes to use.

Trace Source™ Permeation Tubes are used in wide variety of applications that benefit from dynamically generating a quantitative NIST traceable gas standard. A fresh standard is created with every use and understanding the advantages of these devices adds value in the industry they serve.

Advantages of Permeation Tubes

Trace Source™ Permeation Tubes have many advantages.

1. They are small in size as most disposable tubes are less than 15 cm in length while refillable tubes are about 6-8 inches high.
2. They are reliable, easy to handle, easy to store, and safe to use with minimal possibility of exposure.
3. They provide a low concentration standard traceable to NIST.
4. Multiple disposable tubes can be used at the same temperature to easily create a mixture (Up to 8 Trace Source™ Disposable Permeation Tubes can be used within one KIN-TEK permeation tube bottle).
5. Permeation tubes dynamically generate a fresh gas standard with each use instead of using a static gas mixture in a big cylinder and one tube can replace several gas cylinders. Imagine a device the size of a pencil replacing a full gas cylinder!
6. When used in a KIN-TEK system and diluted properly, one permeation tube can provide several calibration points. For example, one Trace Source™ Disposable Hydrogen sulfide tube with a 1000 ng/min certified emission rate can produce a calibration point of 2.6 ppm in 250 sccm of inert dilution flow. Diluting the same tube's emitting gas by 5000 sccm provides a calibration point of 0.132 ppm (or 132 ppb). Hence, a calibration curve can easily be prepared with just one tube used in a KIN-TEK permeation system (See Figure 5).



7. Trace Source™ Permeation Tubes are easy to understand. Once the tube is constructed and certified, KIN-TEK Analytical, Inc. provides a Certificate of Calibration with the information needed to calculate the standard concentration at a given flow rate. Users can calculate the expected concentrations or rely on a KIN-TEK FlexStream™ System to calculate concentrations based on the tube emission rate and flow rate as needed at a set temperature. There is a simple calculation that is used once the tube is certified and the emission rate is established, for example:

Equation 1: Concentration in ppmv:

$$\frac{\text{Emission rate} \left(\frac{\text{ng}}{\text{min}} \right) \times K_0}{\text{Flow (sccm)}} = \text{Concentration (ppmv)}$$

Permeation Tube Technology has been around for many years but there is still a lack of understanding of the broad range of applications they serve. Understanding the different types of permeation tubes available helps to identify their use for a specific application. There are many applications in which these extraordinary little devices are used, and some are mentioned, but it would be hard to list them all. In general terms, whenever ppmv gas concentration (or lower) is present, is being analyzed, is being detected, or is needed for exposure testing, permeation tubes should be used to ensure the trace concentrations are quantified.



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.

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