APPLICATION NOTE

GC Integrated Permeation Device

- **GC-integrated Design**
- **PPB to PPM Level Calibration**
- **No Cylinders or Regulators Required**
- **Option for Dual Ovens**
- **Cost Effective, Safe, Clean, Flexible, NIST Traceable**

Keywords:
Permeation Device, Sulfur Traces, Low Level Calibration

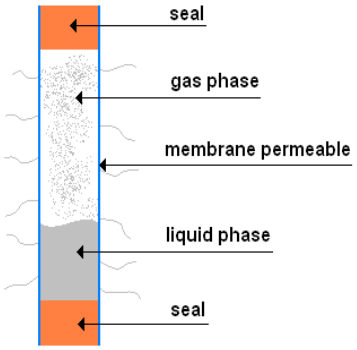


Figure 1. Schematic of a Permeation Tube

INTRODUCTION

Obtaining a reliable and accurate way of calibrating analyzers at low levels is often a challenge, particularly when the components of interest are reactive or tend to cling to contact surfaces (e.g. H_2S). Most of the times pressurized gas cylinders are used to deliver the required gas compositions but the use of gas cylinders have some distinct disadvantages like: high pressures, unstable/inaccurate composition, use of lab space, difficulties with shipment and delivery. Permeation devices provide an excellent method of producing known gas concentrations in the PPM and PPB level for calibration of analytical instrumentation, overcoming the disadvantages of gas cylinders.

A permeation device is a device based around a permeation tube which is contained within a highly accurate thermally controlled chamber and flushed by a stable accurate flow of inert gas.
A permeation tube is a sealed permeable membrane containing a chemical component, typically in liquid form, that permeates through the walls of the membrane at a constant rate (see Figure 1). This constant rate is referred to as the permeation rate.

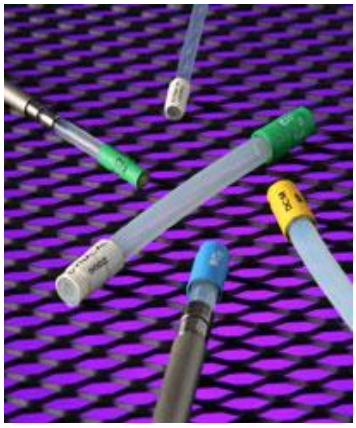


Figure 2. Examples of Permeation Tubes

The permeation tube is maintained at a constant temperature inside a permeation chamber to establish constant vapor pressure inside the device. This results in an equilibrium between the liquid and the vapor phase of the chemical component. The vapor escapes through the walls of the permeable membrane at a constant rate as long as the set point temperature is maintained. A stable known flow of an inert gas such as nitrogen, helium, argon etc. is passed through the permeation chamber to mix with the vapor resulting in a known volumetric concentration in ppm/ppb. By varying the dilution flow rate one is able to generate different concentrations using a single tube.

AC PERMEATION DEVICE CONFIGURATION

As mentioned the AC permeation device is integrated into AC Gas Chromatography Solutions, offering the following advantages:

- Small footprint
- Automated calibration at ppm and ppb level
- Automated variation of concentration over 1 decade by permeation gas flow variation
- Permeation gas can be created in different matrices
- Option to use 2 permeation ovens
- 3 tubes per permeation oven
- Optimal Gas composition stability
- Reduced risk

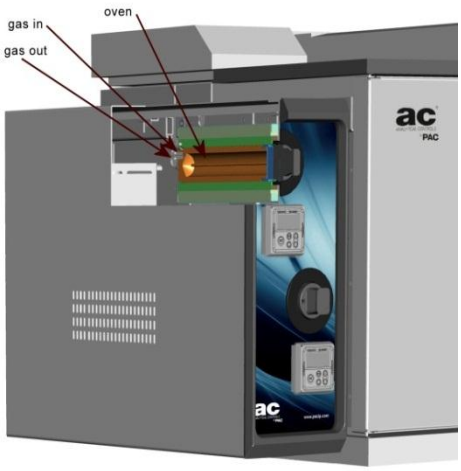


Figure 3. AC Integrated Permeation Device

The AC GC-integrated permeation device can be configured with either 1 or 2 permeation ovens. Using 2 permeation ovens provides the possibility to calibrate components that are not chemically compatible or to calibrate components that have certified permeation rates using different temperatures.

REPEATABILITY

To demonstrate the stability of permeation gas, 3 permeation tubes (H2S, COS and DMS) were inserted into an AC permeation device that was fitted onto an Agilent 7890 GC (see figure 3). The content of the 3 sulfur components in the permeation gas was measured over a period of 4 days (200 analyses), displayed in figure 5. RSD on peak area over this period stayed well within 1.5 %, even for H2S (also see table 1).

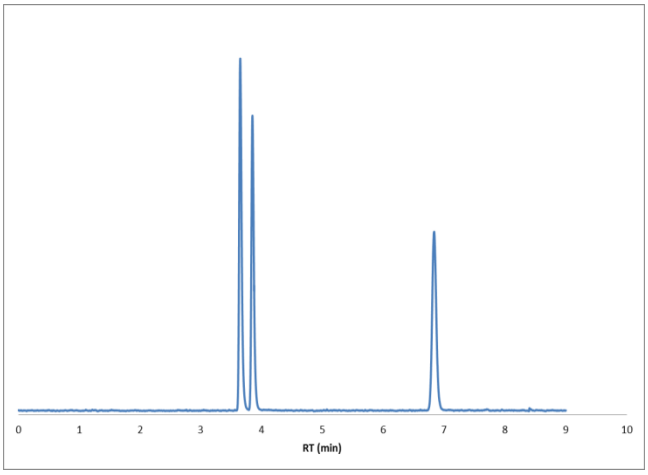
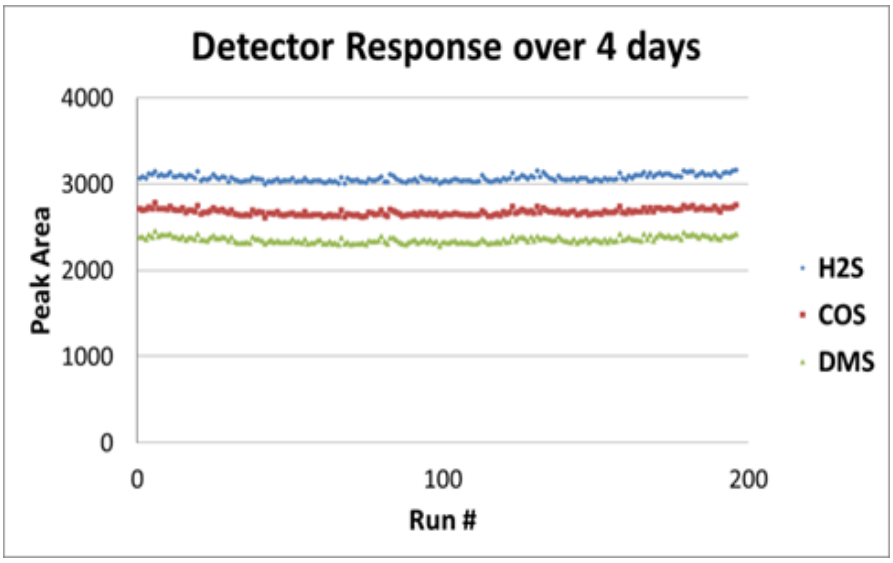


Figure 4. Chromatogram of Permeation Gas @ 5-7 ppm each on 7890GC with Antek 7090 SCD



Component	Conc. (ppm V/V)	RSD (%)
H2S	7.1	1.2
COS	5.4	1.3
DMS	5	1.5

Figure 5 with Table 1 included. Permeation Gas Stability over 4 Days

ACCURACY

To validate the accuracy of the GC system equiped with an AC permeation device, a certified reference gas (cylinder) composition was analyzed using the system calibrated with the dual oven permeation device. Certified values on cylinder were around 11 ppm for each component. Permeation Flow was varied between 20 and 200 ml/min to establish bias at both flows.
The relative bias between the determined value and the certified target value of this cylinder gas remained within an acceptable window of 10% for all components for both permeation flows (20 ml/min / 200 ml/min, see table 3).

Component	20 ml/min		200 ml/min	
	Bias (ppm v/v)	Bias %	Bias (ppm v/v)	Bias %
H2S	1.1	9.7	0.6	5
COS	-0.2	1.4	-0.1	-0.8
DMS	0.8	7.2	0.5	4.1
MeSH	0.3	2.2	0	-0.3
EtSH	0.1	0.6	0.1	0.5

Table 2. Accuracy at 20 and 200 ml/min Permeation Flows. Bias measured at target value of approximately 11 ppm v/v each component, expressed as Measured Value Cylinder – Measured Value Calibration Device

SYSTEM INERTNESS

One of the main challenges chemists face when working with gas cylinders is creating a decent and realiable calibration curve. Multiple point calibration curves require several cylinders, that often prove unavailable at the desired low concentrations, or a dilution system between a single source calibration gas cylinder and the analyzer, both making rather inflexible solutions.
Also the inertness of the sample path will prove extremely critical when creating a calibration curve . Poorly deactivated lines or connections will negatively impact Linear Dynamic Range and lower detection limits.
All lines in AC Permeation Device are deactivated specifically for calibrating and analyzing active components at low concetration levels. Furthermore, the flexible permeation flow and dual oven design allow for making a true multipoint calibration curve from up to two sets of 3 of permeation tubes, even at ppb levels of concentration:

Below chromatogram represents a CO_2 sample spiked with trace levels sulphur (5 components) at approximately 30 ppb per component level. Peak Elution order is as per table 3. Table 3 summarizes data from 3 runs, mean value measured and repeatability (N=3). Identifying the 5 sulfur component peaks is easy and accuracy/repeatability of quantification at this low level are great. LOD levels are typical.

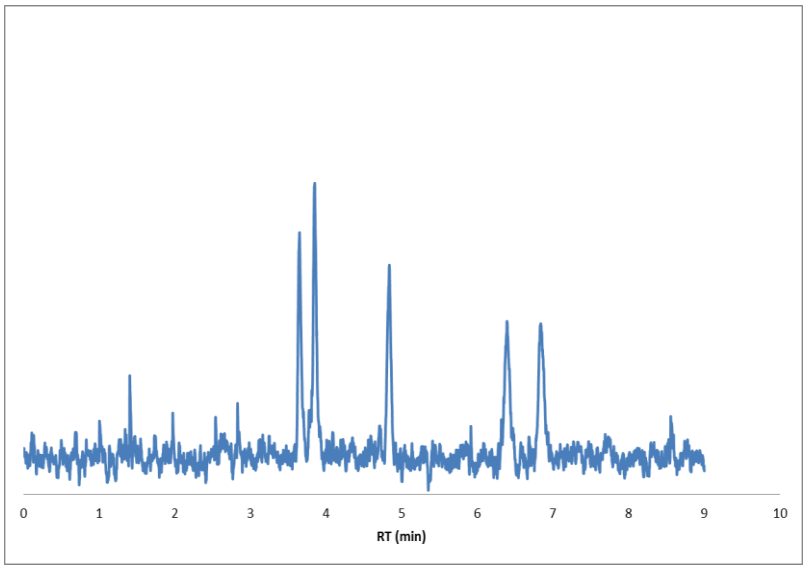


Figure 6. Low concentration Sulfur components in CO_2 : Chromatogram

Component	Run 1	Run 2	Run 3	Mean (n=3)	RSD %
	(ppb V/V)	(ppb V/V)	(ppb V/V)	(ppb V/V)	(n=3)
H2S	29	28	28	28	2.6
COS	36	24	31	30	19.2
MeSH	26	28	23	26	9.1
EtSH	29	29	25	28	8.1
DMS	27	24	31	27	13.6

Table 3. Low concentration Sulfur components in CO_2 : Repeatability and accuracy

OTHER PERMEATION DEVICE BENEFITS

- **NIST TRACEABLE, STABLE GAS COMPOSITIONS**

The permeation rates for permeation tubes can be certified using standards traceable to NIST by the most basic and accurate laboratory procedure – measuring the gravimetric weight loss over a known period of time at a known temperature.
Ccomponents in gas cylinders may react with each other or adsorb onto the cylinder walls causing the standard to become inaccurate and unreliable. Improper pressure regulators may aggrevate this and impact the calibration gas composition.
When using permeation devices the mixture is continuously created which leaves minimal time for reaction and the sample flow path is continuously flushed which deactivates all contact surfaces in the sample flow path.

- **REDUCING RISK**

Gas cylinders are big and heavy. They take up a lot of space (which often limits the number of standards in inventory), and shipment is slow and expensive. The AC permeation device is fully integrated into the GC and as such doesn't need to be handled and doesn't use any additional lab space. You can also forget about disposal fees and monthly rental charges.
Pressurized Gas cylinders can be a potential danger – a leak or broken connection can cause a sudden release of a large volume of toxic, corrosive, odorous, or otherwise hazardous gas.
Permeation devices contain low amounts of the pure substance, and are permanently sealed, virtually unbreakable, and safe to handle. The permeation device offered by AC is also protected against overheating which further limits risk.

- **HIGH FLEXIBILITY, EASY DELIVERY**

A Permeation Device may be incorporated in many types of analyzers or even be used to accommodate two different channels of analysis in one GC.
Hundreds of components are available in the form of permeation tubes, and rates for new components can easily be certified using NIST-traceable standards.
Shipment of gas cylinders to some countries is almost impossible and local supplies may not always provide the desired quality. Because of the limited quantity of chemicals used and its small weight and size, shipment of permeation tubes is much more convenient than shipment of gas cylinders.

CONCLUSION

The AC Integrated Permeation Device offers a powerful alternative to the use of certified gas cylinders for calibration in ppb/ppm range.

Permeation tubes are easier to ship, transport and store than gas cylinders, thus avoiding the need to deal with high pressure gases that are heavy and take up valuable lab space. The Permeation Device is specifically designed to allow calibrations ensuring full sample integrity, even at the lowest concentrations.
The Pereation device can be equiped with 2 permeation ovens, offering the flexibility required when permeation tubes used have different calibration temperatures. Using 2 ovens also allows for calibrating multiple components at a time.

Permeation tubes will never fully replace calibration gas cylinders but they are the preferred solution when calibrating at ppm or ppb levels. It offers an easy to use and cost-effective solution that provides better quality calibration even at lower levels, great flexibility towards components, while avoiding known issues commonly seen in Calibration Gas cylinder use.

Components	Most volatile components that can be determined by Gaschromtagraphy (e.g. H2S, COS, DMS, SO2) See: here for a complete list
Sample Matrix	Gas
Concentration Range	Low PPB to PPM
Temperature Range Perm Oven	35 – 80 ˚C
Perm Oven Temp. Accuracy	Better than 0.1 ˚C
Mass Flow Controller Range	20 – 200 ml/min
Mass Flow Control Accuracy	+/- 5%

Table 4. Specifications AC Integrated Permeation Device

AC Analytical Controls® has been the recognized leader in chromatography analyzers for gas, naphtha and gasoline streams in crude oil refining since 1981. AC also provides technology for residuals analysis for the hydrocarbon processing industry. Applications cover the entire spectrum of petroleum, petrochemical and refinery, gas and natural gas analysis; ACs Turn-Key Application solutions include the AC Reformulyzer ® , SimDis, Hi-Speed RGA and Customized instruments.