

Trace sulfur calibration for various chromatography methods using an automated permeation system



Analyzing trace sulfurs in various applications is important to avoid damage to processes, expensive catalysts, and to prevent unwanted odors. Different techniques exist for analyzing trace sulfurs and each technique typically requires calibration to accurately quantify unknown samples. The presence of sulfurs even at very low concentrations can be harmful and corrosive to equipment [1, 2]. Catalysts used in refineries and petrochemical processes as well as fuels are adversely affected by the presence of sulfurs even in parts per billion (ppbv) levels. The reactive and unstable nature of sulfur compounds makes calibration challenging with gas cylinders when molecules can be lost to the storage vessel and calibration could be inaccurate [3]. Consideration should be given to standards, equipment, and materials for calibration to ensure accuracy and reliability of the gas standard for proper analysis. Disposable type permeation tubes used in an automated permeation system provide a reliable method for delivering accurate and traceable gas standards for trace sulfur calibration when the right equipment and parameters are understood. An overview of methods of analysis is presented with recommended techniques and equipment for dynamically generating various trace level sulfur compounds and gas mixtures.

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Many analytical methods outline analysis techniques of trace sulfurs in fuels and gases and cover a broad list of different sulfurs [1]. The reactivity of sulfur compounds causes them to adsorb to internal vessels and sampling lines [4]. Calibrations should be done with dynamic gas mixtures when working with very low component sulfur concentrations [5]. Analyzing sulfurs in Natural Gas using gas chromatography with a sulfur chemiluminescence detector (GC-SCD) or for light petroleum liquid analysis with Gas Chromatography and Sulfur Selective Detection (GS-SSD) are two examples of methods that require detection of trace sulfur compounds [1, 2]. Additionally, analyzing sulfurs in natural gas by Gas Chromatography and Pulsed Flame Photometric Detection (GC-PFPD) is uniquely advantageous over other detectors due to increased sensitivity and selectivity against hydrocarbon matrices [6]. For sulfur compounds in the sub-ppmv to ppbv and lower concentrations, dynamically generated gas standards prevent the need for storing reactive and unstable components. Permeation tubes with emission rates such as those shown in Table 1, provide a freshly generated source of calibration gas if properly calibrated and maintained at a constant stable temperature. High purity chemical compound is sealed in each permeation device, and each is gravimetrically certified at a stable temperature to determine emission rate of the chemical source. Weight loss is recorded over time to precisely determine the rate of pure component gas emission at a stable controlled temperature. Multiple tubes are easily combined within a permeation system and held at the required temperature for creating a complex gas mixture. Table 1 designates those sulfurs that are known to be available in disposable type Trace Source™ permeation tubes that provide low emission rates in corresponding nanogram per minute values at the listed temperature. These compounds are mentioned in ASTM methods and are referenced for use in calibration methods where controlling factors provide a constant source of accurate gas standard [5, 7]. Concentration in ppmv is the result of multiplying the emission rate of permeation tube by the given K factor and dividing by the total measured dilution flow. For example, a typical calculation is provided below:

$$\text{Concentration ppmv} = \frac{\text{Emission rate} \times K_0}{\text{Total Dilution Flow}}$$

Where Emission rate is given in ng/min, K0 is 24.41/MW of the component, and Total Dilution Flow is measured in standard cubic centimeters per minute (sccm). Given the list in Table 1, seven components are listed to give known emission rates at 30°C, while eight of the components are listed to provide a given emission rate at 60°C. Using two stable ovens in a series allows for a multi-component mixture to be created and a broad range of concentrations created by changing dilution flow.

Table 1

Name	Formula	MW g/mol	CAS #	Vendor Code	Emission Rate (ng/min)	Oper. Temp °C	Conc ppmv	Flow sccm
Sulfur dioxide	SO ₂	64.06	7446-09-5	1001	714	30	0.50	500
Hydrogen sulfide	H ₂ S	34.08	7783-06-4	1002	381	30	0.50	500
Carbonyl sulfide	COS	60.075	463-58-1	1003	670	30	0.50	500
Methyl mercaptan	CH ₃ SH	48.11	74-93-1	1004	536	30	0.50	500
Carbon disulfide	CS ₂	76.15	75-15-0	1005	850	30	0.50	500
Dimethyl sulfide	(CH ₃) ₂ S	62.14	75-18-3	1006	693	30	0.50	500
Dimethyl disulfide	C ₂ H ₆ S ₂	94.20	624-92-0	1007	525*	60	0.25	500
Ethyl mercaptan	C ₂ H ₆ S	62.14	75-08-1	1010	693	30	0.50	500
Diethyl sulfide	C ₄ H ₁₀ S	90.19	352-93-2	1012	1008	60	0.50	500
Methyl ethyl sulfide	C ₃ H ₈ S	76.16	624-89-5	1013	850	60	0.50	500
n-Propyl mercaptan	C ₃ H ₈ S	76.16	75-33-2	1014	850	60	0.50	500
n-Butyl mercaptan	C ₄ H ₁₀ S	90.19	109-79-5	1015	1008	60	0.50	500
Isobutyl mercaptan	C ₄ H ₁₀ S	90.19	513-44-0	1016	504*	60	0.25	500
Diethyl disulfide	C ₄ H ₁₀ S ₂	122.3	110-81-6	1017	546*	60	0.20	500
Tert-Butyl mercaptan	C ₄ H ₁₀ S	90.19	75-66-1	1019	302*	60	0.15	500

NOTE: For a full list of sulfur permeation tubes, visit www.kin-tek.com/chemical-compound-list. * Adjusted emission rate value to operate at 60°C.



Figure 1

Target emission rates are given based on concentrations of 0.5 ppmv in 500 sccm of dilution flow through the permeation system (unless otherwise noted). Increasing dilution flow will decrease output concentration of the gas standard thus allowing dynamic changes to gas concentration for creating a calibration curve. Typical dilution ratio is 20:1 in a base system but secondary dilution is possible. The vendor code shown in Table 1 refers to the compound code of Trace Source™ disposable tubes offered. Combining multiple tubes into one oven provides an easy way to create mixtures for calibration [8]. Once permeation tube parameters are met the key is precisely controlling oven temperature and dilution flow and designing effective means of gas delivery without loss of analyte to reactive surfaces [9].

An automated modular permeation system that provides ovens with the capacity to hold multiple permeation tubes and extends capabilities such as accurate and precise oven and flow control is available for calibrating using ASTM methods or other instances that require multiple trace sulfur analysis. The FlexStream™ Permeation System equipped with a Base Module, Permeation Module, and Secondary Dilution Module provides a simplified automated solution for generating calibration gases listed in Table 1. Figure 1 shows the suggested system for running all components listed in Table 1. The first two modules consist of the Base Module and the Permeation Module each of which have an internal high-capacity permeation oven that can hold up to 8 Trace Source™ disposable permeation tubes. Dividing those tubes listed at 30°C and those tubes listed at 60°C from Table 1 into each oven creates a mixture of all listed sulfurs. Hence, the Base Module oven will be set at 30°C and the PM Module will be set at 60°C. Users target the component of interest for the concentration to be delivered and the system auto-calculates flow requirements and auto-sets flow controllers to meet the requirements. Mode controls allow different scenarios to be selected by toggling one oven in to Standby Mode, or selecting both ovens to create Span Gas mixtures together; i.e. users easily toggle between ovens as needed. To enhance user interface there is an onboard local touchscreen or PC control using included FlexLink™ software that adds the capability of remote operation and data acquisition via computer with Ethernet or serial to USB connections. The primary dilution flow is controlled by a high precision mass flow controller that dilutes permeation tube emission rate output at a 20:1 ratio. Secondary dilution is used as needed when the system calculates the target concentration and initiates flow parameters for further dilution, activating secondary dilution capability.

In operation, a small amount of flow from the primary dilution gas mixture is diverted and then diluted further, creating the secondary phase dilution of the gas standards. This system can provide dilution ratios of 500:1 to 10,000:1 (when combined with the primary dilution ratio). Even higher emission rate tubes can be used when secondary dilution is one of the modules in the system to ensure better accuracy of delivered standard gas. In a FlexStream™ system, oven temperature is controlled to better than +/- 0.1°C and the accuracy of each mass flow controller is within +/- 1.5% of reading and/or +/-1% full scale, with NIST Traceability. The accuracy of the oven temperature combined with highly accurate flow control are excellent measurement controls, however the delivery of the trace level sulfurs to the analyzer is still an important factor to consider.

When analysis of single digit ppbv and lower concentrations of sulfurs are generated, even the slightest loss of molecules to active sites can create inaccuracies. Special features are needed to safeguard against component loss [4, 7]. The FlexStream™ Permeation System for trace sulfur calibration is optimized by the addition of Sulfinert® coated stainless steel output tubing that is heat traced. The entire output path to the analyzer can be treated to ensure delivery of highly accurate trace gas standards. Additionally, other configurations are possible that aid in interfacing with the analytical device depending on the calibration method. All parameters are recorded in data logging features of FlexLink™ software for later recall and reference for verification of performance parameters. Multiple concentrations and mixture scenarios are possible by interchanging various permeation tubes. Trace sulfur calibration is completely controlled, logged, and traceable and most disposable permeation tubes last over a year creating long term efficiency and cost savings without loss of accuracy. When not in use, the permeation tubes are removed from the system and easily stored in small containers, extending tube life further.

Permeation tubes have been around and used for creating low concentration standards since before 1970, but are still not a well-known solution. Analyzing for trace sulfurs for any of the mentioned methods or other requirements is challenging without the confidence of highly accurate calibration. Trace Source™ disposable permeation tubes for many sulfur species are available and provide a controlled and accurate method of creating a dynamic gas mixture of many proposed sulfurs. Dilution aspects and accurate temperature control using the FlexStream™ Permeation System with Base Module, Permeation Module, and Secondary Dilution Module provide ppbv and even lower gas standards. Additional features such as specially coated and or heat traced output tubing ensure delivery of molecules to the analyzer and greatly minimize loss of sulfur to active sites. The addition of FlexLink™ software simplifies the calibration process with extra control features, remote operation, and data acquisition capabilities making Trace Source™ disposable permeation tubes and the FlexStream™ system an excellent solution for trace sulfur calibration for various methods. Since many methods realize the advantage of using permeation tubes for trace sulfur calibration, there has been growing interest in both laboratory permeation systems and process/industrial permeation systems for calibrating various analytical devices as a long- term solution over gas cylinders.

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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.

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