

# KIN-TEK

The Calibration Specialists

## Calibration for Trace Sulfur in Olefins

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**Maintaining reliable standards for trace sulfur compounds in an olefin matrix is a common problem in industrial quality assurance. Using permeation tubes to dynamically blend the required mixtures offers a simple solution.**

Measurement of trace sulfur compounds is required throughout industry. In the manufacture of polyethylene and polypropylene, for example, even low ppb concentrations of some sulfur compounds will poison the catalyst, affecting yield and product quality. Because some compounds are more troublesome than others, speciation is required. Gas chromatography is generally the method of choice. Usually there is also a specification for total sulfur content, so either a second sample is run without speciation, or the individual compound concentrations are summed to provide the total sulfur number. In either case, a range of molecular weights and structures is needed to ensure accuracy of the total sulfur number.

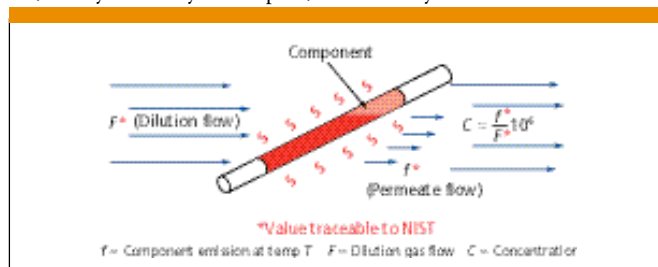
The high pressure static gas mixtures traditionally used for calibration have proven ineffective in low ppb sulfur applications. Permeation tubes have been successfully used to dynamically blend calibration mixtures for sulfur compounds.

### Experimental Conditions

Analysis of polymerization grade propylene provides a convenient example requiring a standard for trace sulfur compounds in an olefin matrix. Applications vary, but typical analysis requirements specify monitoring for carbonyl sulfide, hydrogen sulfide, methyl mercaptan, ethyl mercaptan, dimethyl sulfide, and some other "heavy" sulfur compound such as dimethyl disulfide, or thiophene. Some applications also monitor sulfur dioxide. Because the propylene peak may affect calibration, the matrix gas for the calibration mixture must be propylene.

Typical measuring ranges are 0–50 ppbw (or lower) for carbonyl sulfide, and 0–1 ppmw hydrogen sulfide and the other sulfur compounds. Plus, the total sulfur limit is 1 ppm.

To achieve the carbonyl sulfide concentration requires a permeation tube with a very low emission rate combined with a large dilution flow (or a secondary dilution step). The permeation rates of the various compounds are greatly different (see Table I), so two permeation ovens are needed to provide the full range of compounds. One oven, operating at 40 °C, is used for the carbonyl sulfide, hydrogen sulfide, sulfur dioxide, methyl and ethyl mercaptan, and dimethyl sulfide tubes. The other



**Figure 1:** The Perm Tube method. Traceable gas standards.

**Table I:** Comparative emission for sulfur compounds in nanograms per centimeter\*

Compound	40 °C	60 °C	80 °C
Carbonyl sulfide	>10,000‡		
Hydrogen sulfide	620‡		
Methyl mercaptan	769		
Ethyl mercaptan	185	715	
Dimethyl sulfide	190	788	
Dimethyl disulfide	18	100	303
Thiophene	80	330	1167

\*Data for TFE high rate tubes except as noted.

‡Special tube used to get low emission.

‡Type SRT-2 tube used.

oven, operating at 60 °C, is used for the dimethyl disulfide tubes.

Permeation tubes are equilibrium devices and must be continuously flushed with clean carrier gas (a small flow of the dilution gas) to keep their output steady. To reduce propylene consumption the system is equipped with a three-way valve on the inlet to switch from using specially purified propylene as the dilution gas during the calibration cycle to using nitrogen diluent for standby operation.

A much larger flow is required in the permeation system to create the trace concentrations than is needed for GC calibration. Also, the dilution flow must be varied to adjust the output concentration, so it is important to interface the permeation system to the GC in a way that allows the excess span gas to bypass the GC.

### Results

Using one tube each for carbonyl sulfide, hydrogen sulfide, sulfur dioxide, methyl mercaptan, ethyl mercaptan, and dimethyl sulfide operated at 40 °C, plus one dimethyl disulfide tube operated at 60 °C creates a mixture with 40–50 ppbw of carbonyl sulfide plus 0.8 ppmw of each of the other compounds when the dilution flow is 1 L/min.

Reducing the dilution flow to 800 cc/min raises the concentration of each component to 1 ppmw (50–62 ppb for COS). Raising the dilution flow to 5 L/min reduces the concentration of each component to 0.16 ppm, creating a total sulfur standard at 1 ppmw.

To account for error due to residual sulfur contamination in the propylene diluent the "method of standard additions is used." First the propylene "zero standard" is injected and the response to each component noted. The permeation tube emission is then added and the new response is observed. Calibration is based on the change in response due to the addition of the permeation tube emission.

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