

Application Note

Environmental

Determination of sulfur gases in natural gas with pulsed flame photometric detector.

Introduction

The presence of sulfur compounds in natural gas is undesirable since many of these compounds possess unpleasant odors, are unstable and corrosive and are poisonous to industrial catalysts.

In the analysis of trace sulfur containing gases in natural gas f things are important; complete separation from methane and to avoid adsorption of sulfur compounds on reactive surfaces in the analytical system. This note will focus on the chromatographic aspects only.

Three sulfur gases, hydrogen sulfide, carbonyl sulfide, and methyl mercaptan are isolated from natural gas components using a thick film PDMS column in combination with pulsed flame photometric detection (PDHID). The latter is known to provide equimolar response for sulfur components.

Experimental

The sample was introduced directly into the capillary column using an automated 6-port Valco gas sampling valve equipped with a 250 microliter deactivated metal loop. Chromatographic parameters as follows:

Column	0.53 mm x 60 m 5 µm film: SCION - 1, Part no. SC32165
Carrier Helium	6.1 cm ³ /min
Column Oven	30 °C for 1.0 min, 15 °C/min. to 200 °C; hold for 5 min.
PFPD	250 °, Range 10 Hydrogen: 13.4 cm ³ /min. Air 1: 17.3 cm ³ /min. Air 2: 9.7 cm ³ /min.

PFPD Operation

The PFPD houses two chambers (Figure 1). Ignition from a continuous igniter filament takes place in the ignition chamber and the flame propagates to a quartz tube in the combustion chamber to which a light pipe and photomultiplier tube and filter is connected. Hydrogen and air flow to the PFPD at rates such that a pulsing rather than a continuous flame is sustained at about 2 - 4 pulses per second. During each pulse background, chemiluminescent emissions associated with the hydrogen rich flame emit over a period of only 3 - 4 milliseconds while emissions from the S₂* species emit from about 4 to 16 milliseconds. This delayed emission is monitored by a delayed electrometer gate where gate delay and width are optimized for the sulfur emissions. Since the flame background is significantly eliminated, the sulfur signal is optimized. A detectivity of 1 pgS/s and a selectivity of 106 S/C are obtained and equimolar response is obtained irrespective of sulfur compound identity.

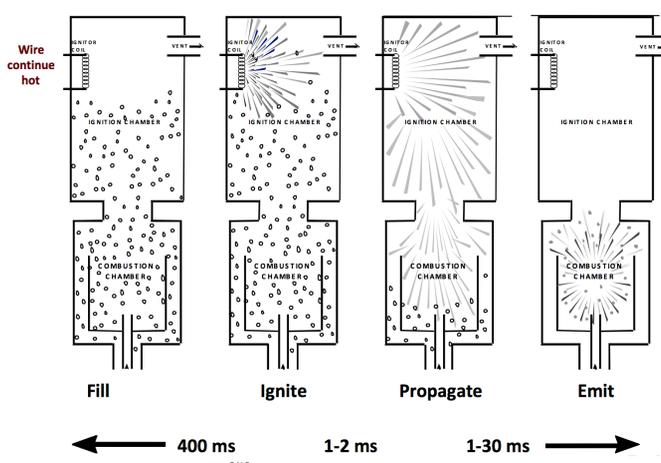


Figure 1: schematic operation of the PFPD

Results

Figure 2 shows the optimized separation under the conditions mentioned in the text. The sulfur species are completely separated from methane and the response is equimolar to sulfur.

ASTM method 5504 requires the retention time repeatability for the analytes of interest to be at or below 0.05 minutes. Four consecutive runs of the standard in natural gas were made with the following precisions: H₂S, 0.005 min, COS, 0.005 min, and CH₃SH, 0.004 min.

The PFPD provides equimolar response to sulfur independent of the compound in which it exists. Therefore, calibration factors for different components, based on sulfur content, are equal. Calibration factors for hydrogen sulfide and methyl mercaptan, which are certified calibration standards.

Compound	Concentration (S) (mg/m ³)	Area ^{1/2}	Factor (A ^{1/2} /C)
H ₂ S	2.48	569	229
CH ₃ SH	2.45	580	236

Conclusion

Following the guidelines of ASTM method 05504, sulfur gases may be resolved from major natural gas components on a long thick film capillary column of 0.53 mm id. Initial column temperature is critical to this separation. Excellent retention time precision is obtained and the PFPD provides selective and equimolar response for sulfur components.