BEYOND MEASURE

SCION INSTRUMENTS

Determination of Sulphur Gases in Natural Gas

Application Note AN0027

INTRODUCTION

The presence of sulphur compounds in natural gas is undesirable since many of these compounds possess unpleasant odours, are unstable, corrosive and poisonous to industrial catalysts. ASTM D6228 is the standard test method for the determination of sulphur compounds in natural gas by GC-PFPD (pulsed flame photometric detector).

In the analysis of sulphur containing gases in natural gas, it is vital that completes separation of methane is achieved whilst also avoiding adsorption of sulphur compounds on the reactive surfaces of the analytical system.

This application note focuses on the chromatographic aspects of the system. Three sulphur gases; hydrogen sulphide, carbonyl sulphide and methyl mercaptan were isolated from natural gas components using a thick PDMS column in combination with a PFPD.

EXPERIMENTAL

The sample was introduced directly into the capillary column using an automated 6-port Valco gas sampling valve equipped with a 250µL deactivated metal loop. The analytical conditions of the instrumentation can be found in Table 1.

Table 1. Analytical conditions of the GC PFPD system

Conditions	
Column	SCION-1 60m x 0.53mm x 5µm
Oven	30°C (1 min), 15°C/min to 200°C, 20°C/min (5 min)
Carrier Gas	Helium, 6.1cm^3/min
PFPD	250°C; H_2 13.4cm^3/min, Air 1 17.3cm^3/min, Air 2 9.7cm^3/min

PFPD OPERATION

The PFPD houses two chambers. 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 background, chemiluminescent emissions associated with the hydrogen rich flame emit over a period of 3-4 ms while emissions from the S2 species emit from 4 to 16ms.

This delayed emission is monitored by a delayed electrometer gate where gate delay and width are optimised for the sulphur emissions. Since the flame background is significantly eliminated, the sulphur signal is optimised.

A detectivity of 1pgS/s and a selectivity of 106 S/C are obtained and equimolar response is obtained irrespective of sulphur compound identity. Figure 1 details a schematic operation of the PFPD.

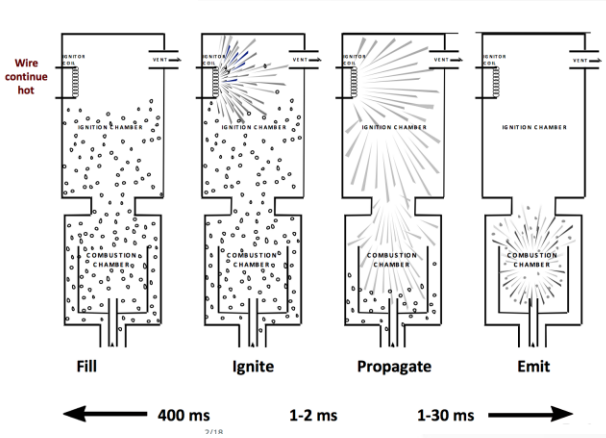

Fig 1. Schematic operation of the PFPD

RESULTS

Table 2 shows the optimised separation under the conditions mentioned in the text. The sulphur species are completely separated from methane and the response is equimolar to sulphur.

Table 2. Separation of hydrogen sulphide and methyl mercaptan

Compound	Conc (S) mg/m^3)	Area ($^{1/2}$)	Factor (A$^{1/2}$C)
H_2S	2.48	569	229
CH_3SH	2.45	580	236

Figure 2 shows the chromatogram of the PFPD analysis of H_2S, COS and CH_3SH.

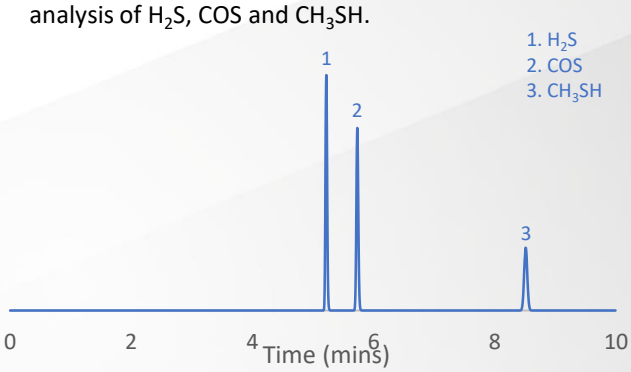

Fig 2. H2S, COS and CH3SH in natural gas

ASTM method 6228 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: H_2S 0.005, COS 0.005 and CH_3SH 0.004min. The PFPD provides equimolar response to sulphur independent of the compound in this is exists. Therefore, calibration factors for different components, based on sulphur content, are equal.

CONCLUSION

Following the guidelines of ASTM method 6228, sulphur gases may be resolved from major natural gas components on a long, thick film capillary column of 0.53mm internal diameter. Initial column temperature is critical to this separation. Excellent retention precision is obtained with the PFPD providing selective and equimolar response for sulphur compounds.

*The natural gas analyser can be configured with chemiluminescence detection for the determination of sulphur in natural gas as specified by ASTM D5504.

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