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SULFUR COMPONENTS ANALYSIS IN HYDROCARBON MATRIX BY GAS CHROMATOGRAPHY

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INTRODUCTION

Determination of low concentrations of sulfur-contalning gases has received considerable attention in recent years (1-6). The need is particularly acute in the petroleum industry, since the trace amounts of sulfur compounds cause corrosion and poison catalysts. Because of their reactivity and labile nature, as well as diversity of stream composition, determination of sulfur components in hydrocarbon matrix is a complex and intricate task. This paper presents a method for GC analysis of trace levels (0-200 ppm) of sulfur compounds in gaseous hydrocarbon streams.

EXPERIMENTAL

Chromatography

Varian Model 3700 Gas Chromatograph equipped with a Dual Flame Photometric and a Flame Ionization Detector (FPD and FID, respectively) and Vista 401 Dual Channel Data System was employed. Material used for sample transfer lines, 1 cc gas sample loop and the column was high grade, acetone-washed nickel. The gas sample was introduced onto the column via a six port teflon Valco valve. Two certified standard gas blends, compressed in an aluminum gas cylinder from Scott Specialty Gases, were used as calibration gases. Standard 1 contained: hydrogen sulfide, methyl mercaptan, ethyl mercaptan, dimethyl sulfide and dimethyl disulfide in nitrogen matrix. Standard 2 contained: dimethyl sulfide, methyl ethyl sulfide, diethyl sulfide and diethyl disulfide in nitrogen matrix. The concentration of each component was certified within $\pm$ 2%. Ultra high purity He was used for the carrier gas and high purity hydrogen and air for the flame gases in the two detectors. The optimal flow rates for the flame photometric detector fuel gases were found to be: H_2, 142 ml/min; air #1, 80 ml/min; air #2, 170 ml/min. In the first flame, decomposition of the sample takes place. Combustion products from sulfur-containing compounds will produce optical emission in the second flame from the S_2 radicals formed. The Varian flame photometric detector employs a filter with maximum optical transmission at 365 nm for sulfur detection. For the flame ionization detector, the fuel gas flow rates were: H_2, 30 ml/min; and air, 300 ml/min. The carrier gas flow rate was 26 ml/min.

The type of column packing material used for trace sulfur analysis depends on the stream composition and the hydrocarbon concentration. For most applications, a complete separation of various sulfur species as well as resolution between hydrocarbons and sulfur compounds such as H_2S, C_1 and C_2 mercaptans, sulfides and disulfides was achieved using a 6' x 1/8" acetone-washed nickel column packed with oxi-propionitrile/Porasil C - Durapak 80-100 mesh. However, when analyzing H_2S in propylene rich streams (propylene concentration greater than 10%), there is no longer a baselne separation between H_2S and propylene with this column. A phenomenon referred to as "quenching effect" takes place in the detector, whereby the decrease in sulfur response is apparently due to inactivation of the excited S_2 species by its combination or collision with a hydrocarbon and its degradation products (5, 7). Silicone, QF-1 (5%) on Porapak QS column packing material will provide the necessary separation in the H_2S region when high propylene concentration is expected (6).

An effluent splitter (ratio 50:50) is placed on the outlet of the column to send identical gas streams to the FPD and the FID, thereby allowing detection of components on both detectors simultaneously. The temperature programming profile suitable for most applications was: initial temperature, 70°C; final temperature, 100°C; hold, 45 min.; rate 10°C/min. Retention times for various sulfur compounds obtained using the chromatographic conditions described above are presented in Table I.

Calibration and Analysis

For quantitative analysis of sulfur species, an external standard method was used for calibration. After the sample loop had been purged with the calibration gas for several minutes, the sample of calibration gas was injected, at atmospheric pressure, by means of a six-port injection

valve. The temperature program and data aquisition were then activated simultaneously. After the calibration run was completed the response factors were generated or updated (8).

TABLE I

Compound	Mol. Wt	B. P. (°C)	Retention Time, min.
Hydrogen sulfide	34.08	-60.7	0.71
Methyl mercaptan	48.11	6.2	1.99
Ethyl mercaptan	62.13	35.0	3.38
Dimethyl sulfide	62.13	37.3	4.98
Methyl ethyl sulfide	76.16	66.6	9.05
Dimethyl disulfide	94.20	109.7	9.63
Methyl propyl sulfide	90.19	95.5	14.79
Diethyl sulfide	90.19	92.1	16.90
Methyl isobutyl sulfide	104.22	112.5	21.88
Diethyl disulfide	122.25	154.0	30.89
Dipropyl sulfide	118.24	142.4	46.62

Providing that the flow rates of the fuel gases to the flame photometric detector have not changed, there should be no need for frequent recalibration. However, the calibration blend is analyzed daily to assure optimal performance of the system. Following calibration, a hydrocarbon sample from a high pressure gas cylinder is purged through the sample loop and injected in the same manner. Figure 1 presents a typical chromatogram for sulfur analysis in a hydrocarbon matrix.

Precision data for 10 replicate runs of the two calibration blends is presented in Table II.

TABLE II

Compound	Level (ppm)	Std. Dev.	Retention Time (min.)	Std. Dev.
Hydrogen sulfide	15.4	0.2	0.71	0.03
Methyl mercaptan	16.2	0.1	2.00	0.04
Ethyl mercaptan	15.9	0.1	3.38	0.03
Dimethyl sulfide	15.7	0.1	4.99	0.03
Dimethyl disulfide	15.9	0.3	9.63	0.04
TOTAL	79.1	0.7		
Dimethyl sulfide	16.3	0.1	4.99	0.03
Methyl ethyl sulfide	16.1	0.1	9.05	0.04
Diethyl sulfide	15.9	0.1	16.90	0.04
Diethyl disulfide	15.3	0.4	30.89	0.04
TOTAL	63.6	0.7		

Sampling

During the course of the quantitative GC analysis of sulfur compounds in gaseous hydrocarbon streams it was observed that the light sulfur compounds (namely hydrogen sulfide and methyl mercaptan) were being depleted in the standard high pressure sampling cylinders.

Figure 2 presents the rate of H_2S depletion in standard 2250-ml stainless steel sampling cylinders (Cyls. No. 1 to 3). The cylinders were filled with Matheson certified standard containing 230 ppm H_2S in nitrogen. Within four minutes, 70% of the sulfur content was lost (cylinder No. 1). After 20 minutes no H_2S could be detected in the sample cylinder. Cylinder No. 1A is actually cylinder No. 1 that was steam cleaned, dried under house vacuum and refilled with the Matheson standard. A similar sulfur loss was confirmed by the Dohrman Sulfur Analyzer.

In another experiment, a clean sampling cylinder was filled with 290 ppm of H_2S in ethylene to determine if the hydrocarbon matrix affects the rate of sulfur loss. As illustrated in Figure 3 (curve I), the concentration of H_2S decreased 50% in less than 10 minutes. The same cylinder was flushed with helium, evacuated on a high vacuum line and refilled with the same amount of H_2S in ethylene. Although the number of active sites on the inner walls had been reduced, the passivation in this manner did not eliminate the problem entirely (curve II). After the initial drop in sulfur concentration, the rate of loss had reduced. Eventually, sulfur was lost completely overnight.

The same cylinder used in the above experiment was emptied but not cleaned and again refilled with 290 ppm H_2S in ethylene (Figure 4).

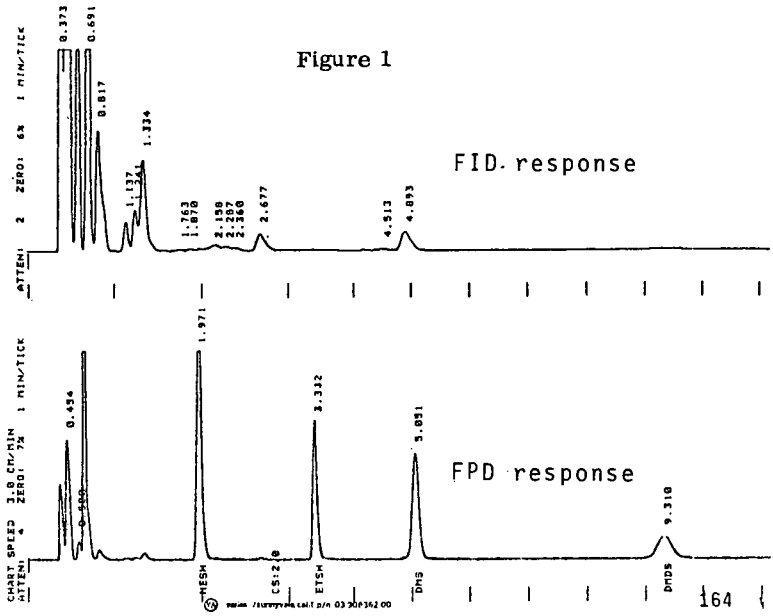


Figure 2. HYDROGEN SULFIDE IN NITROGEN MATRIX

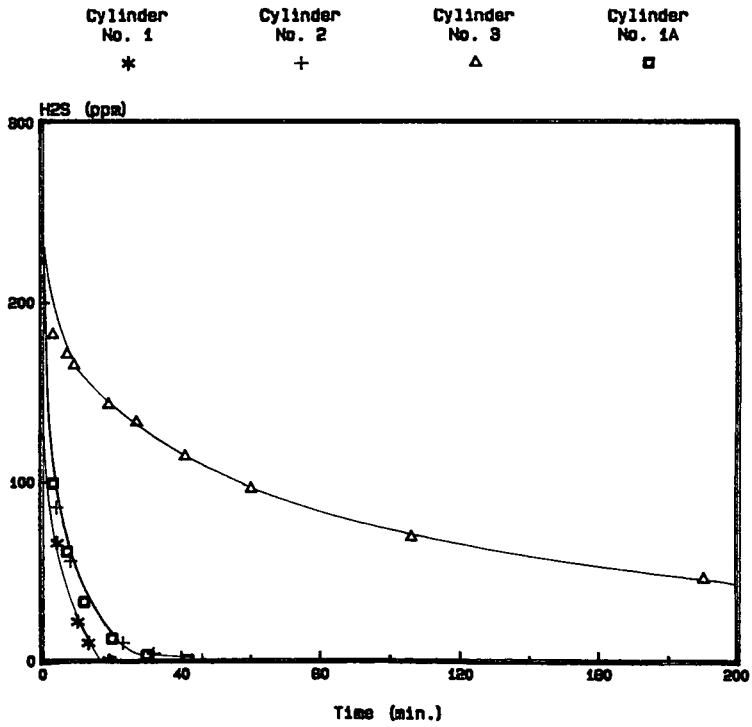


Figure 3. HYDROGEN SULFIDE IN HYDROCARBON MATRIX

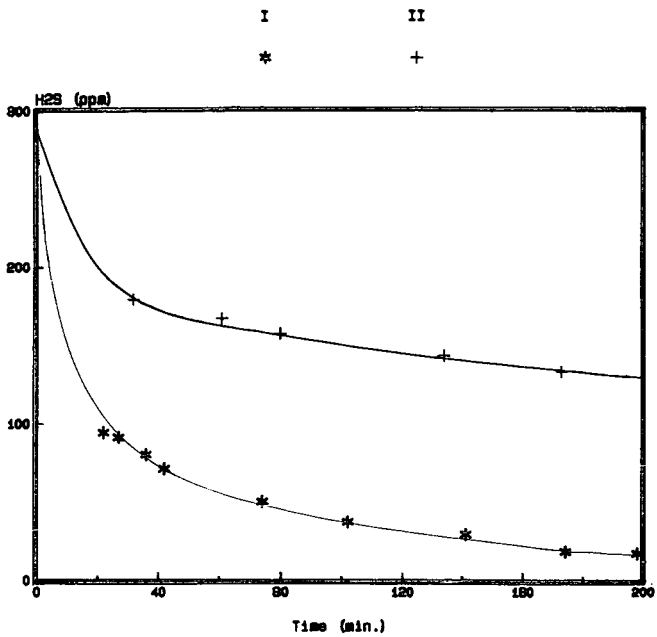


Figure 4. EFFECT OF MOISTURE

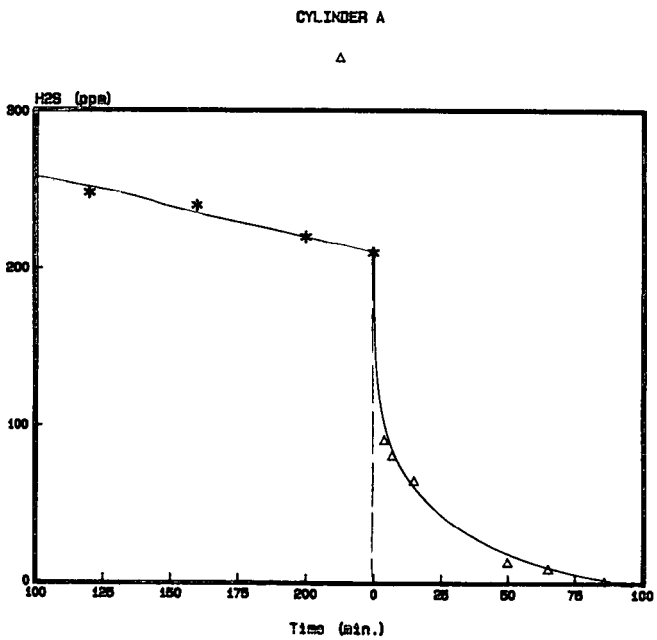


Figure 5. TEFLON-GRAPHITE COATING

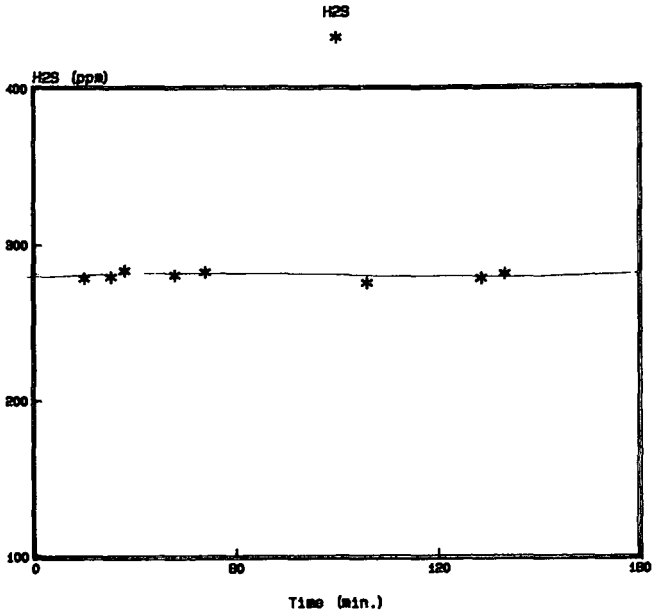
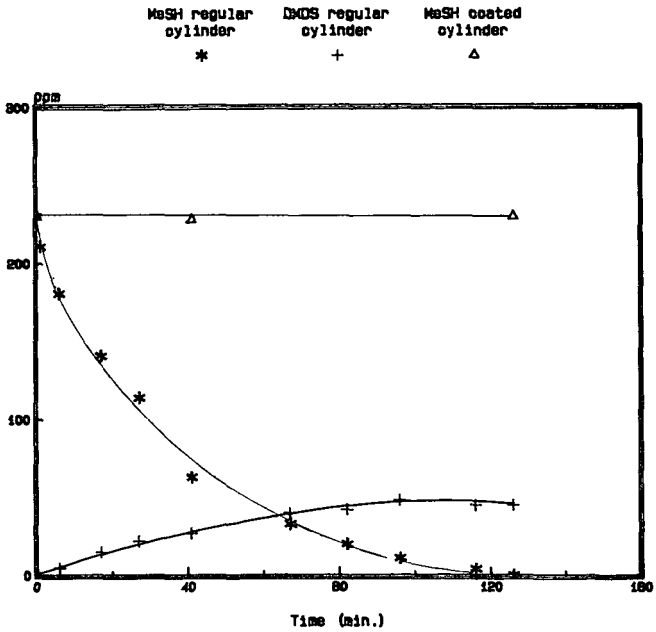


Figure 6. METHYL MERCAPTAN IN HYDROCARBON MATRIX



Presumably, the walls of the sample cylinder were further passivated, and the sulfur depletion rate was very low. After about 4 hours at a sulfur concentration of 210 ppm, the sample was transferred to a cylinder (passivated in the same manner) that contained 0.2 ml of water. A sudden drop in sulfur content (curve A) illustrates the high solubility of H_2S in water according to the reaction:

$$H_2S + H_2O \longrightarrow H_3O^+ + HS^- \qquad 1)$$

Provided a moisture-free environment is assured, adsorption on the metal walls appears to be the predominant cause for the decrease in sulfur concentration.

In an attempt to contain light sulfur compounds, a 2250 ml gas sample cylinder was lined with 0.0005 inch of teflon-graphite where the coating was baked onto the metal surface. The cylinder was tested with the same H_2S in ethylene mixture as in previous experiments (Figure 5). There was no apparent decrease in H_2S concentration over a period of 48 hours.

Figure 6 presents the comparative study of the two types of sample cylinders, i.e., teflon-graphite coated and regular (stainless steel) when methyl mercaptan is present in the hydrocarbon environment (ethylene matrix). Rapid oxidation of methyl mercaptan to dimethyl disulfide, reaction probably being catalized by the metal surface, as well as depletion on the walls is evident in the "regular" cylinder. However, in the teflon-graphite coated cylinder, the reaction did not take place and mercaptan content was unchanged over the time period indicated.

DISCUSSION

The unique and reactive properties associated with sulfur gases have presented difficult obstacles in attempts to contain low levels of these gases in high pressure cylinders (9, 10). Many factors are responsible for the apparent loss of sulfur content in the standard sample cylinders, such as, among others:

- Chemical reaction with, or promoted by, water molecules.
- Adsorption and/or reaction on the walls of the sampling cylinders.
- Oxidation of mercaptans to disulfides.

The results of this study indicate that gas mixtures containing low concentrations of sulfur compounds can exhibit stability if proper cylinder material and cylinder treatment techniques are used. Further evaluation of the teflon-graphite coated cylinders for their suitability in sampling of sulfur containing gases in various plant streams is under way. In addition, long term experience is being gathered.

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