

Monitor Sulfur Compounds In Petroleum Chemical, Environmental, and Other Samples, Using a Special-Purpose Capillary GC Column

Measurement of sulfur compounds is important to petroleum chemical analysts for several reasons, including a need to monitor odor problems and prevent catalyst poisoning. Sulfur compounds also are important to environmental analysts and to food, beverage and fragrance analysts, for similar reasons. Gas chromatography, using sulfur-specific detectors, is commonly used to quantify sulfur compounds, but the analysis can be complicated by the inability to resolve the sulfur compounds from the sample matrix, or from each other, or by analyte adsorption in the chromatographic column. We have developed a thick film, low phase ratio (low β) capillary GC column specifically for resolving sulfur compounds, ranging from the light gases to the dimethylbenzothiophenes. Analyses using an SPB-1 SULFUR column and sulfur-specific detection are shown here for sample matrices ranging from C1 through C24+ hydrocarbons. Analyses of petroleum hydrocarbon gas and liquid streams, using flame ionization detection, also are shown.

Key Words:

- sulfur gases
- sulfur compounds
- stack gases

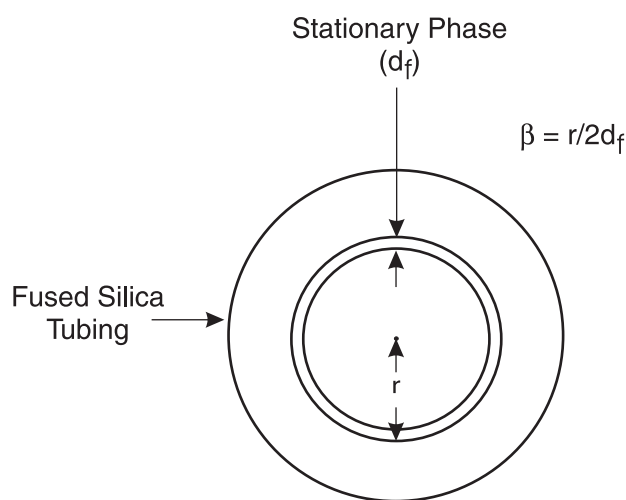
Analyses of sulfur compounds are important to analysts in several industries. In the petroleum chemical industry, analysts must analyze various hydrocarbon matrices for sulfur compounds, to monitor trace odor problems, determine the recovery of sulfur from crude oil, and prevent catalyst poisoning. Environmental analysts monitor sulfur compounds to monitor pollution and determine the origin and subsequent fate of various sulfur compounds. For example, analysts in the paper manufacturing industry monitor stack gases for sulfur compounds. Very low levels of sulfur compounds give certain foods and beverages their distinctive flavors, but in higher concentrations can create unappealing flavors and aromas. Consequently, analysts in food and beverage quality control laboratories also monitor sulfur compounds.

Although several methods can be used to monitor sulfur compounds in petroleum chemical and other samples, there are several important advantages to using gas chromatography for these analyses. In contrast to methods which simply indicate total sulfur levels, gas chromatography allows individual compounds to be identified and quantified in a wide variety of samples, often at sensitivities of parts per billion or less. Samples can be gaseous, liquid, or solid. The methodology is particularly well suited to analyses of volatile sulfur compounds, which often are the compounds most important to the analyst.

Because of the importance of accurate information on the sulfur compound content of so many samples, we developed a capillary GC column specifically for sulfur compound analyses. The SPB™-1 SULFUR column is a 30 meter, 0.32mm ID fused silica column coated with a very thick, 4.0 μ m, film of bonded, nonpolar (dimethylpolysiloxane) stationary phase. The column has a very low phase ratio, or beta (β) value (Figure A), of 20. Beta is a dimensionless number that defines the ratio between the gaseous phase and the liquid (stationary) phase in a capillary column. Lower β values indicate a higher relative amount of stationary phase, and thus greater ability to retain (and separate) lower molecular weight compounds. The very low β for the SPB-1 SULFUR column (β values for typical columns are between 100 and 400) makes it especially well suited for analyses of gaseous sulfur compounds.

Table 1 summarizes the conditions used to obtain the chromatograms in this bulletin. Several of these applications required a subambient initial column temperature, or a final temperature as high as 300°C. The split ratio varied from 10:1 to 100:1, depending on the sensitivity required for the application. As shown in Table 1, three detectors were used: flame photometric detection (FPD) and sulfur chemiluminescence detection (SCD) for monitoring the sulfur compounds and flame ionization detection (FID) for detecting hydrocarbon compounds.

Figure A. Beta Value



G000113

Table 1. Chromatographic Conditions for Applications in this Bulletin

Column:	SPB-1 SULFUR 30m x 0.32mm ID, 4.0µm phase
Column Temperature	
Initial:	-10°C to 35°C
Final:	200°C to 300°C
Program Rate:	5°C to 10°C/minute
Carrier Gas:	helium, 20cm/second
Injector Temperature:	250°C to 275°C
Split Ratio:	10:1 to 100:1
Detectors:	FPD, SCD, FID
Detector Temperature:	250°C to 300°C

Figure B shows the FPD and FID responses in an analysis of two gasoline samples. As is typical, gasoline #1 contains relatively high levels of many thiophene-type compounds, from thiophene through the methylbenzothiophenes. Thiophene is absent from gasoline #2, and the other thiophene-type compounds are present in smaller amounts than in gasoline #1. An SPB-1 SULFUR column, used with a flame photometric detector, easily allows this comparison to be made. Also note that while virtually no hydrocarbons were detected in either sample after 40 minutes (FID chromatograms), many sulfur compounds were detected after 40 minutes (FPD chromatograms).

For petroleum applications in which sulfur compounds are present in moderate quantities, an FPD provides accurate quantification. In quantitative analyses of trace amounts of sulfur compounds in the presence of high levels of hydrocarbons, however, an FPD may not be suitable, due to a phenomenon known as quenching. Figure C shows the FPD and FID responses in analyses of a qualitative reference naphtha sample and a qualitative reference alkylate sample. Ethanethiol is present at a high concentration in the naphtha; thus, a low FPD sensitivity can be used and the baseline is quite flat. Higher sensitivity is required for the alkylate analysis, however, because ethanethiol and propanethiol are present at very low levels. Note that at the higher sensitivity negative peaks are observed in the FPD chromatogram, corresponding to elution times for some of the major hydrocarbons. Although their presence is not indicated on the chromatogram, these compounds “quench” the FPD, creating the negative responses. Figure D shows how this quenching effect can adversely affect quantification. The negative peak just prior to propanethiol on the FPD tracing could lead to an inaccurate area measurement for the sulfur compound.

Other sulfur-specific detectors, notably the Hall® electrolytic conductivity detector (HECD) and the sulfur chemiluminescence detector (SCD), are less sensitive to quenching. Figure E shows the SCD and FID responses for a natural gas condensate. Although a significant amount of propane elutes at the same time as the trace amounts of carbonyl sulfide (COS) and sulfur dioxide (SO₂), the SCD chromatogram shows no evidence of quenching.

Figure E was obtained by using an initial temperature of -10°C to resolve COS and SO₂ on the nonpolar phase. If separation of these two compounds is not required, an ambient initial temperature can be used. Figure F shows the SCD and FID responses for natural gas with an initial temperature of 35°C. Sulfur compounds present in quantities as small as 4ppm (hydrogen sulfide, H₂S) are easily detected. Thus, the combination of an SPB-1 SULFUR column and an SCD easily enables an analyst to see the differences in a “sour” natural gas sample (Figure G).

The combination of an SPB-1 SULFUR column and a sulfur chemiluminescence detector also ensures accurate quantification of higher molecular weight sulfur compounds. Figure H shows the

analysis of a C3 refinery gas sample, using an initial temperature of -10°C to resolve COS and SO₂. Larger sulfur compounds are detected in quantities as small as 20 picograms (benzothiophene). Figure I shows comparable results for an analysis of a butane feedstock, in which component levels as low as 0.06ppm (dimethylsulfide, diethylsulfide) could be quantified. Because COS and SO₂ are absent from the butane sample, the analysis was initiated at 35°C.

The SPB-1 SULFUR column also provides excellent chromatograms for heavier petroleum chemical samples. Figures J, K, and L show analyses of a naphtha feedstock, a catalytically cracked gasoline, and #2 diesel fuel, respectively, using a -10°C initial temperature (ambient temperature is equally suitable) and monitoring SCD and FID responses. In Figures J and K, note that hydrocarbons larger than C13 are eluted in less than 30 minutes; methyl naphthalenes are eluted in approximately 25 minutes. In Figure L, hydrocarbons up to C24 are eluted in less than 40 minutes, and the baseline rise is minimal. In Figures K and L, sulfur compounds ranging from sulfur dioxide to the dimethylbenzothiophenes are resolved and eluted in less than 30 minutes. Figure M shows an analysis of gasoline.

The SPB-1 SULFUR column also is useful for sulfur analyses in the environmental and food and beverage areas. Figure N shows an analysis of a mixture of 19 sulfur compounds, using an SCD. The compounds are typical of those monitored in stack gases, indoor air, and outdoor air. A subambient initial temperature was used to resolve COS and SO₂. On-column quantities in this analysis ranged from approximately 100 to 350 picograms of sulfur.

Figure O shows an analysis of sulfur compounds in wine. A sample of the headspace above the wine was injected onto the SPB-1 SULFUR column at 35°C. Trace quantities of these compounds could be monitored, using the SPB-1 SULFUR column and SCD. Analyses of five wine samples exhibiting differing, low concentrations of low molecular weight sulfur compounds are compared in Figure P. Concentrations of dimethylsulfide (DMS) as low as 0.3ppm were detected. Similarly, SO₂ in fruit juices and other beverages can be accurately monitored by headspace analysis methods.

Analyses shown in this bulletin confirm that an SPB-1 SULFUR capillary GC column, used in conjunction with a sulfur-specific detector, or with simultaneous detection on a sulfur-specific detector and an FID, provide excellent information for quantifying sulfur compounds in a wide variety of samples. Low molecular weight and higher weight volatile sulfur compounds can be monitored with equally good results.

Acknowledgment

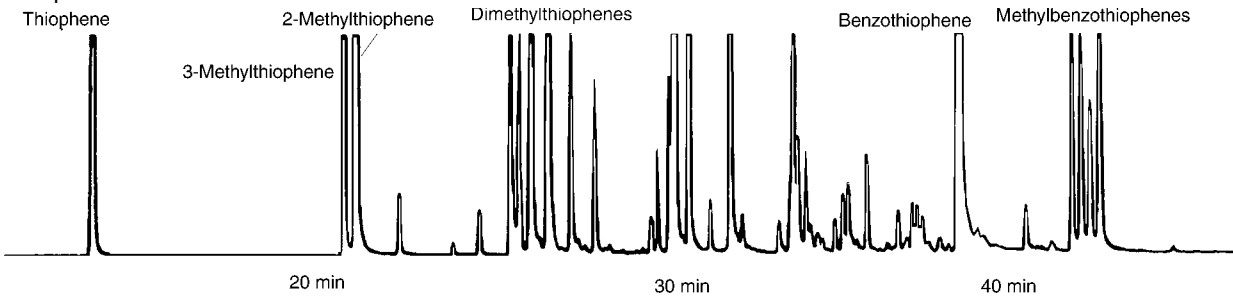
All chromatograms generated by using the sulfur chemiluminescence detector were donated by Sievers Research Inc., 1930 Central Avenue, Suite C, Boulder, Colorado 80301 USA (tel. 303-444-2009).

Sulfur chemiluminescence detectors are available from Sievers Research. We also are grateful to Sievers Research for cooperation and assistance in developing the SPB-1 SULFUR column.

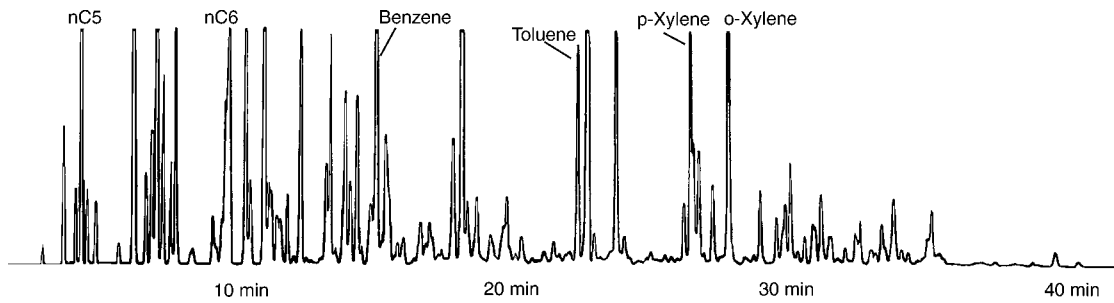
Figure B. FPD and FID Responses for Gasolines Reveal Differing Component Profiles

Gasoline #1

FPD Response

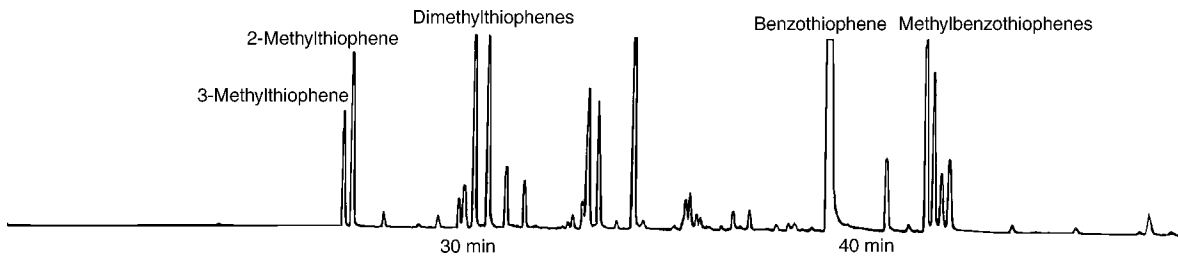


FID Response

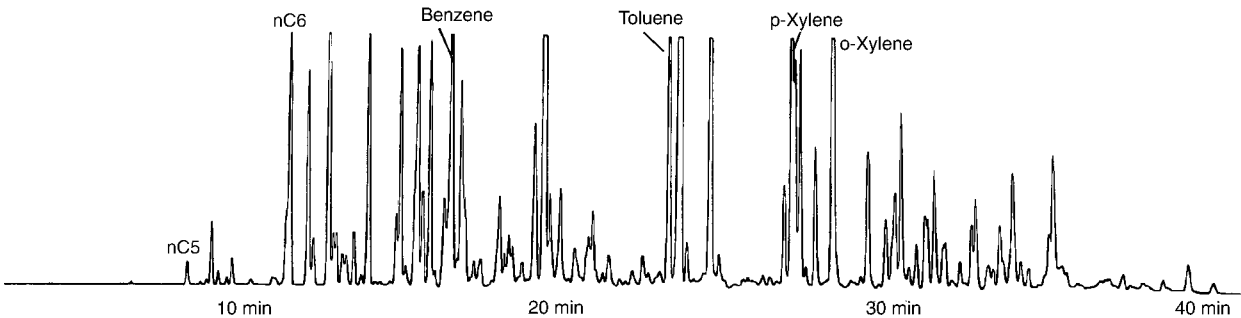


Gasoline #2

FPD Response



FID Response



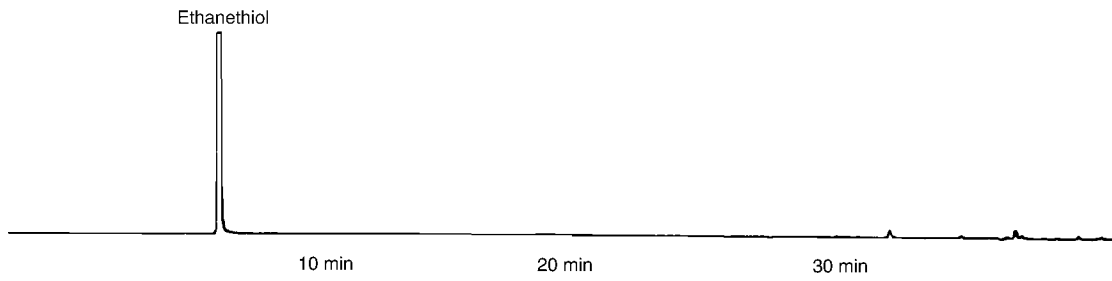
Oven: 35°C to 200°C at 5°C/min, Sample: 1µL gasoline, split 100:1.

G000121,122,123,130

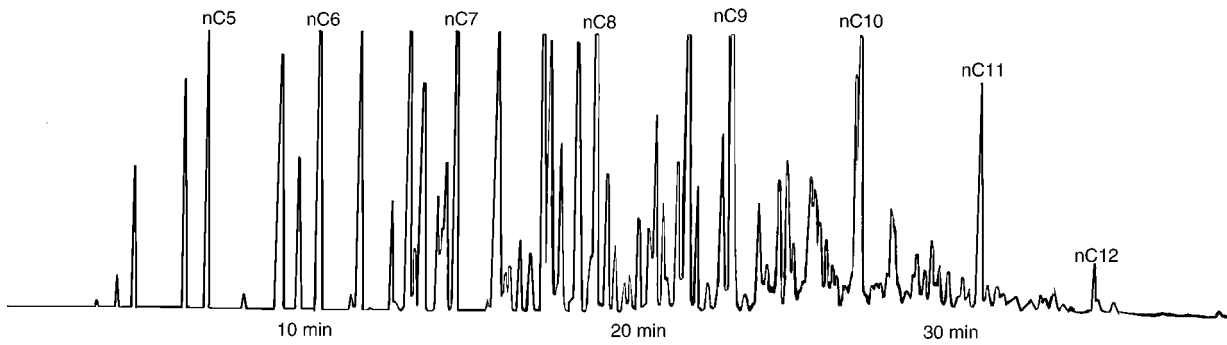
Figure C. Quenching Effect in the FPD Response

Qualitative Reference Naphtha

FID Response



FID Response

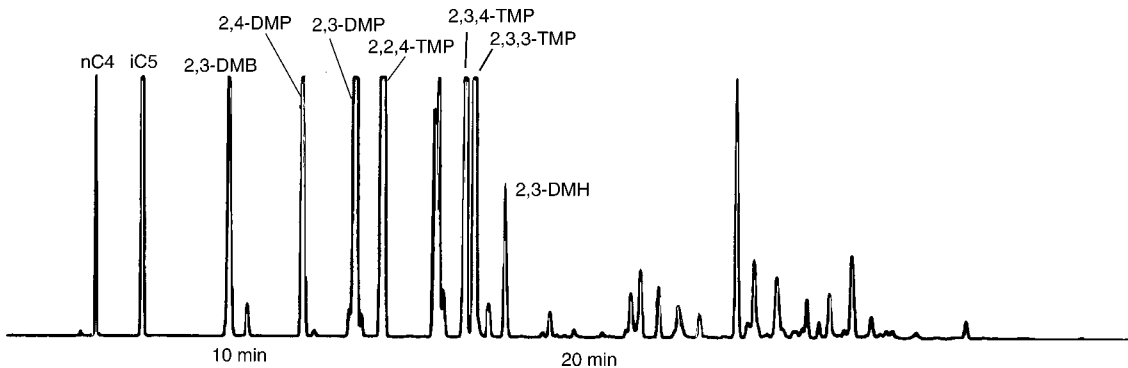


Qualitative Reference Alkylate

FPD Response



FID Response



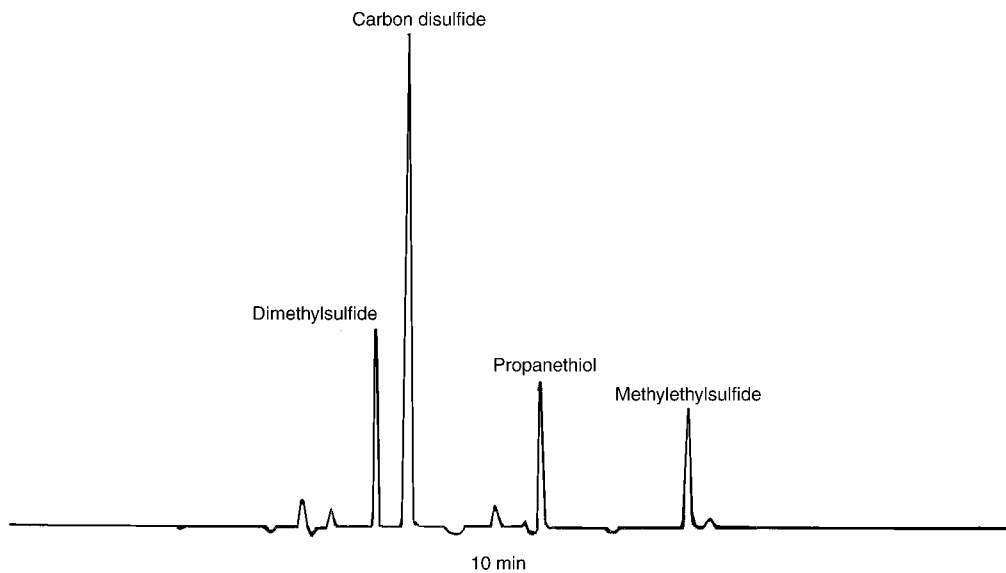
Oven: 35°C to 200°C at 5°C/min, Sample: 1µL naphtha, split 100:1.

G000126,127,128,129

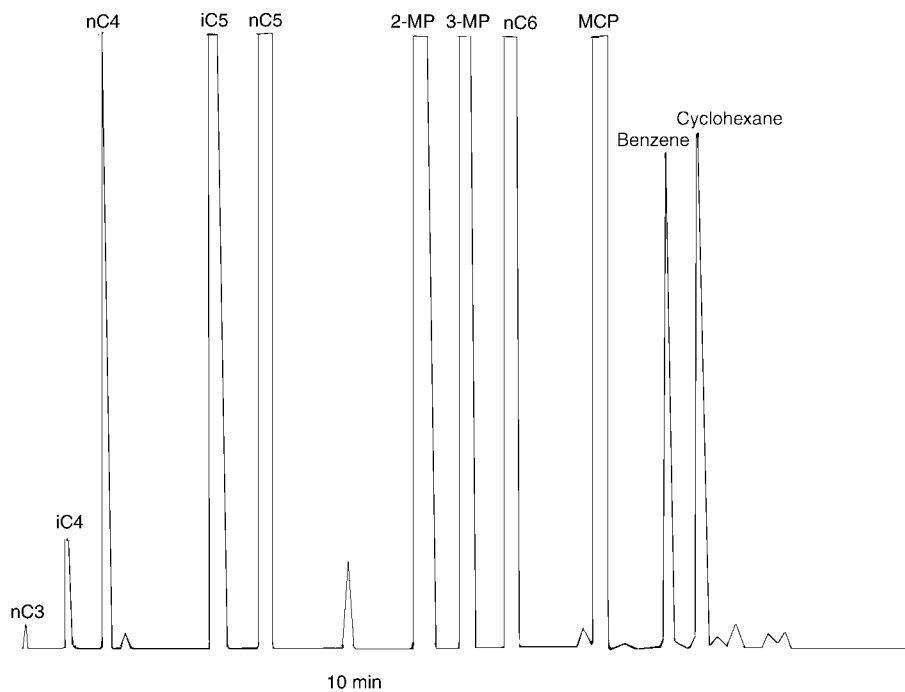
Figure D. FPD Quenching Can Affect Quantitative Analyses of Trace Sulfur Compounds

C5 Refinery Stream

FPD Response



FID Response



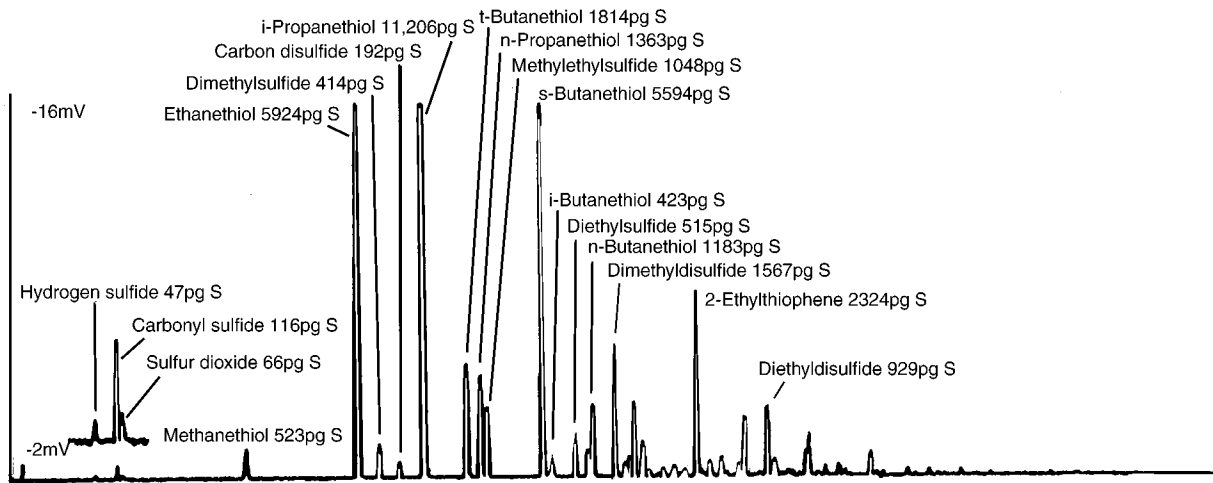
Oven: 35°C to 200°C at 5°C/min, Sample: 1µL C5 refinery stream, split 100:1.

G000131,132

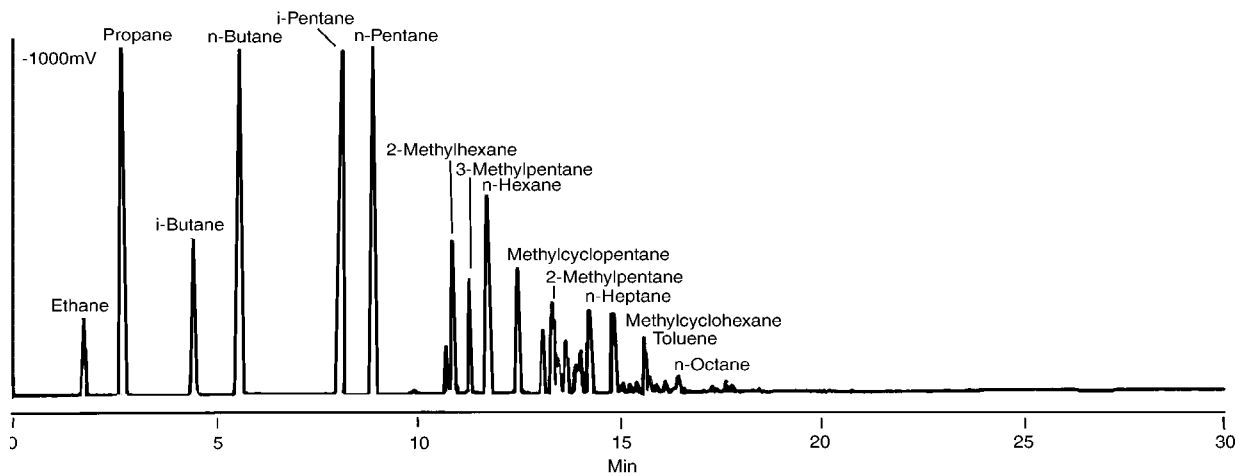
Figure E. SCD Response Shows No Evidence of Quenching

Natural Gas Condensate

Sulfur Chemiluminescence Detector Response



Flame Ionization Detector Response

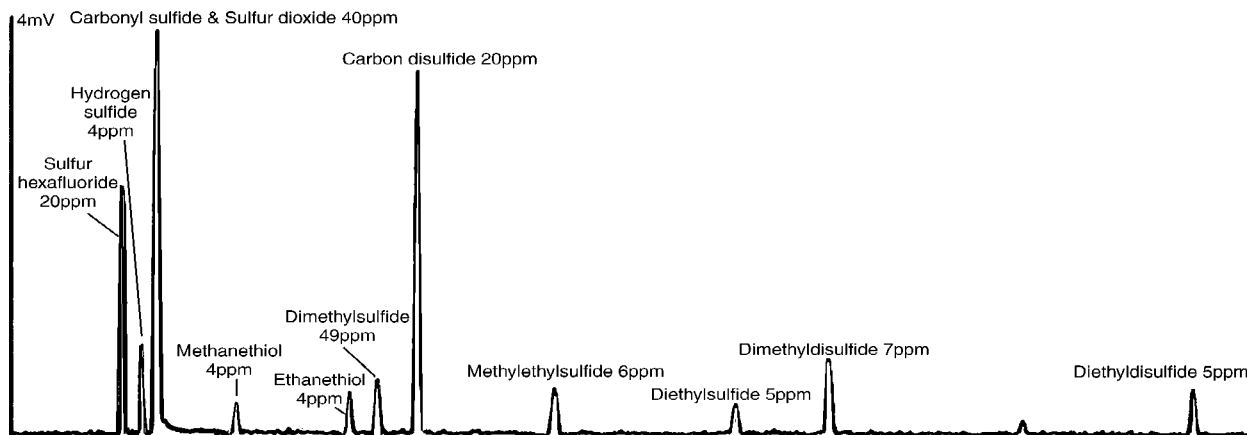


Oven: -10°C (3 min) to 300°C at 10°C/min, Sample: 0.5mL natural gas condensate, split 10:1.
Chromatograms provided by Sievers Research Inc., Boulder, Colorado, USA.

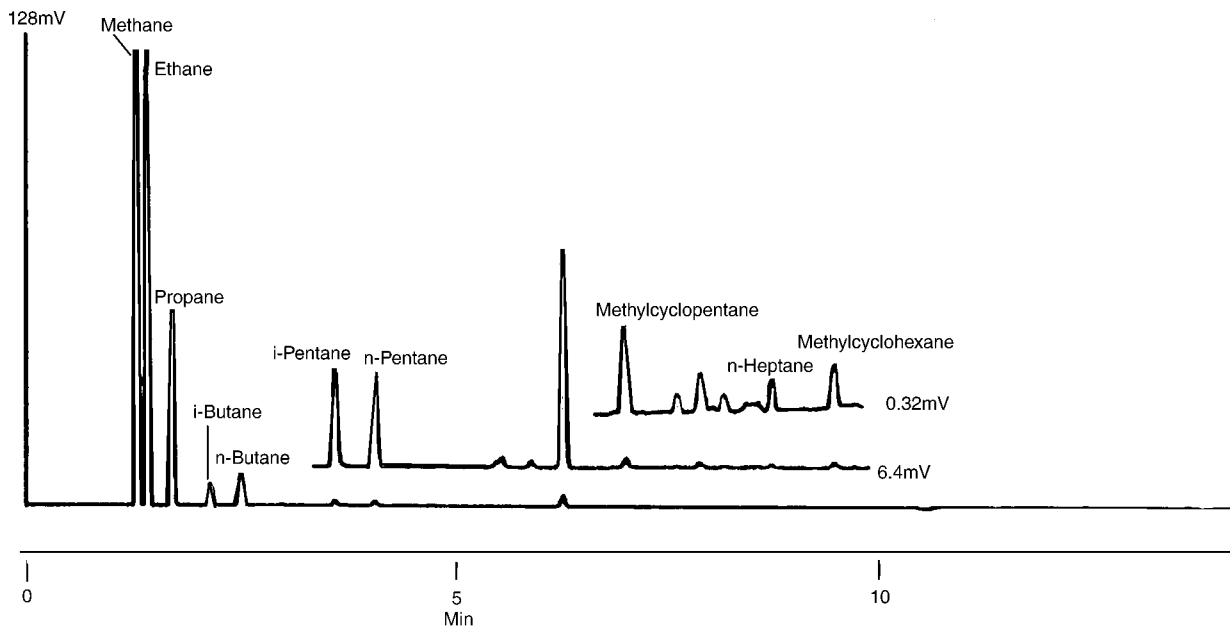
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Figure F. Sulfur Compounds in Natural Gas

Sulfur Chemiluminescence Detector Response



Flame Ionization Detector Response

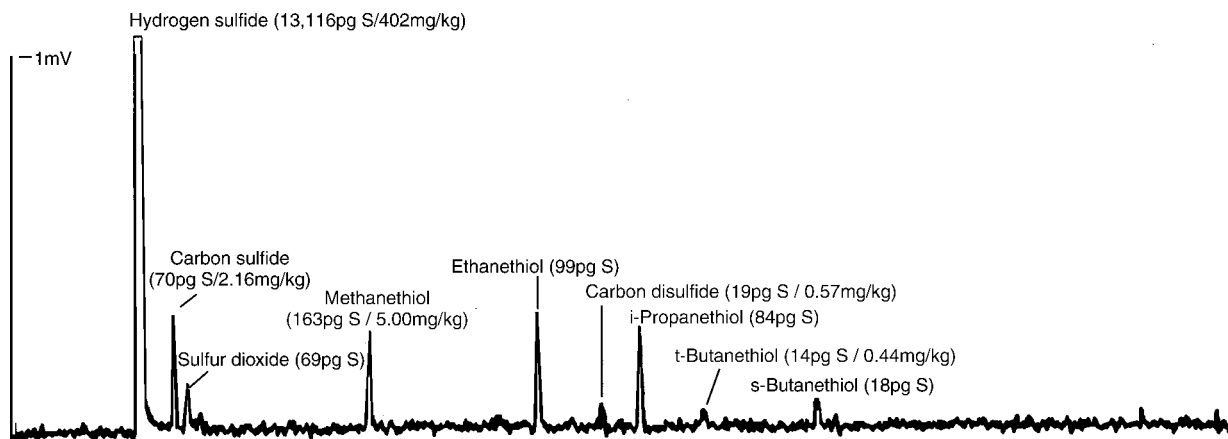


Oven: 35°C (1 min) to 250°C at 10°C/min, Sample: 0.5mL natural gas, split 10:1.
Chromatograms provided by Sievers Research Inc., Boulder, Colorado, USA.

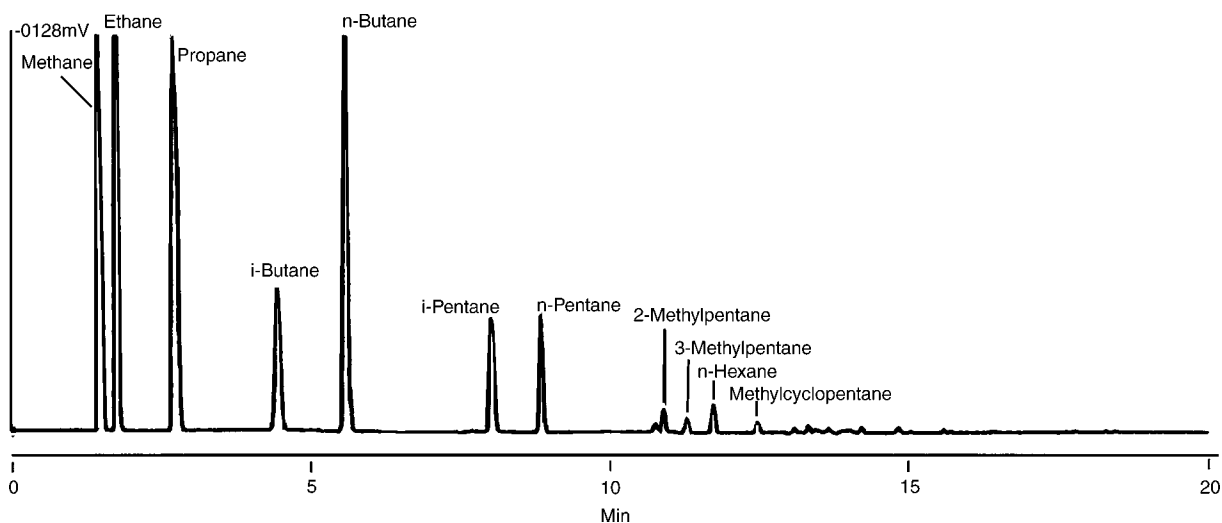
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Figure G. Quantities of Low Molecular Weight Sulfur Compounds Are Elevated in Sour Natural Gas

Sulfur Chemiluminescence Detector Response



Flame Ionization Detector Response

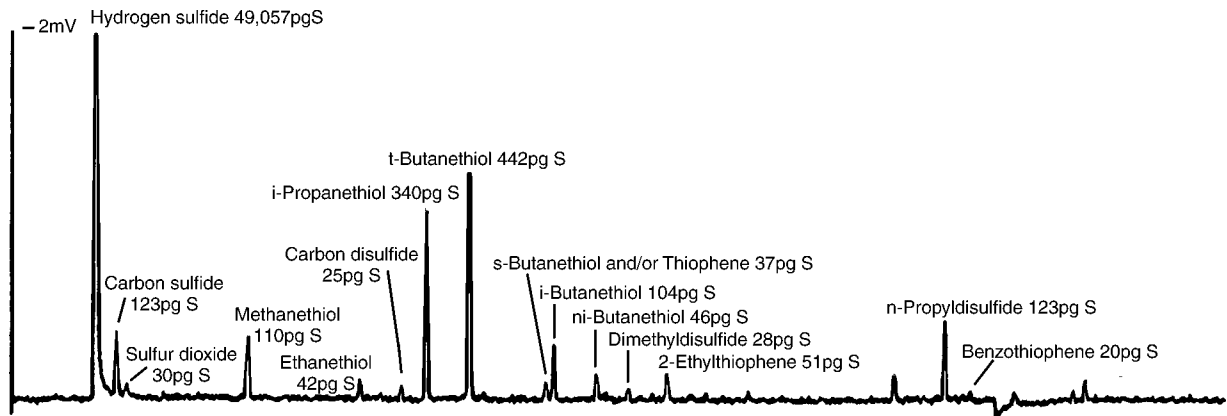


Oven: -10°C (3 min) to 300°C at 10°C/min, Sample: 2.0µL liquified sour natural gas, split 10:1.
Chromatograms provided by Sievers Research Inc., Boulder, Colorado, USA.

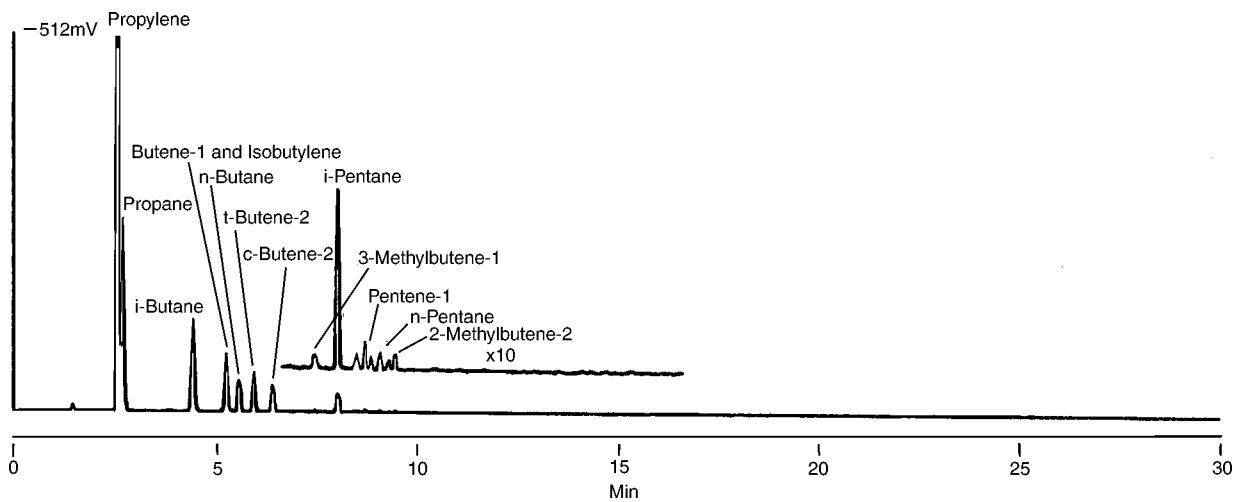
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Figure H. Low Weight and High Weight Sulfur Compounds In Refinery Gas

Sulfur Chemiluminescence Detector Response



Flame Ionization Detector Response

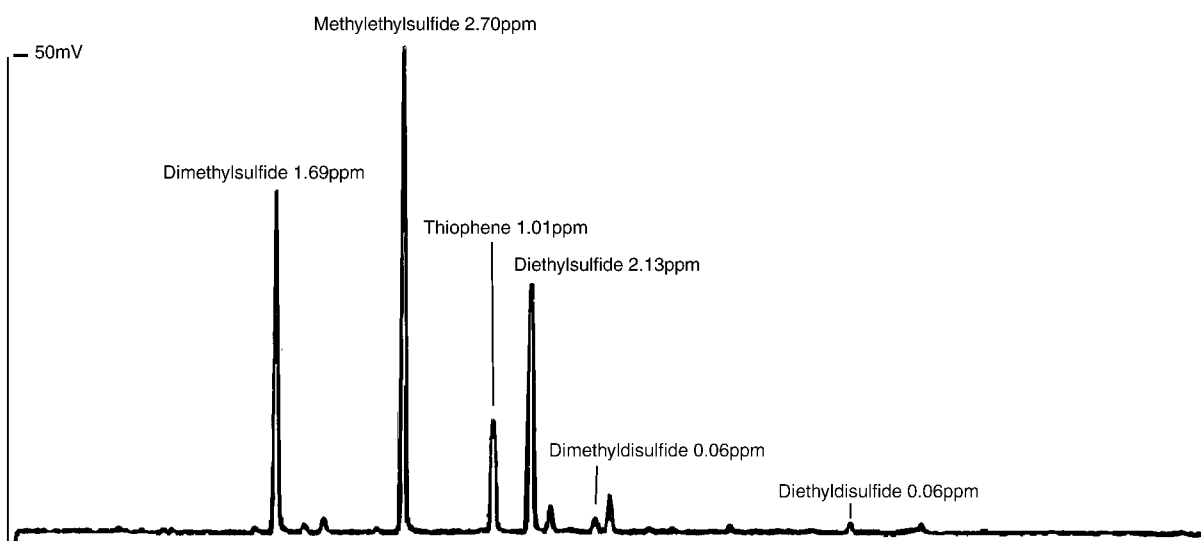


Oven: -10°C (3 min) to 300°C at 10°C/min, Sample: 0.1mL refinery gas, split 10:1.
Chromatograms provided by Sievers Research Inc., Boulder, Colorado, USA.

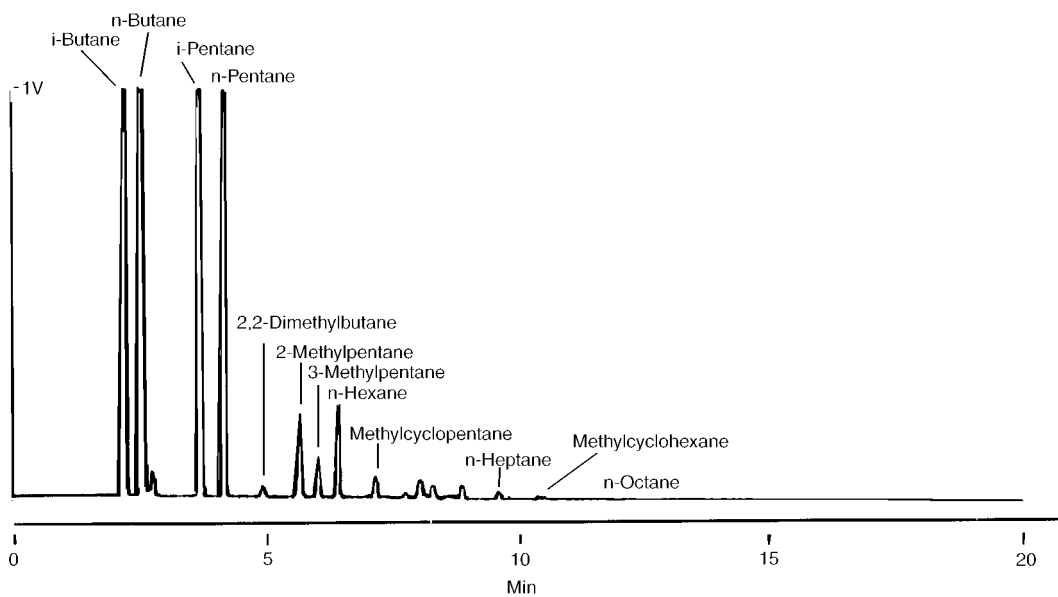
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Figure I. Trace Amounts of High Weight Sulfur Compounds in Butane Feedstock

Sulfur Chemiluminescence Detector Response



Flame Ionization Detector Response

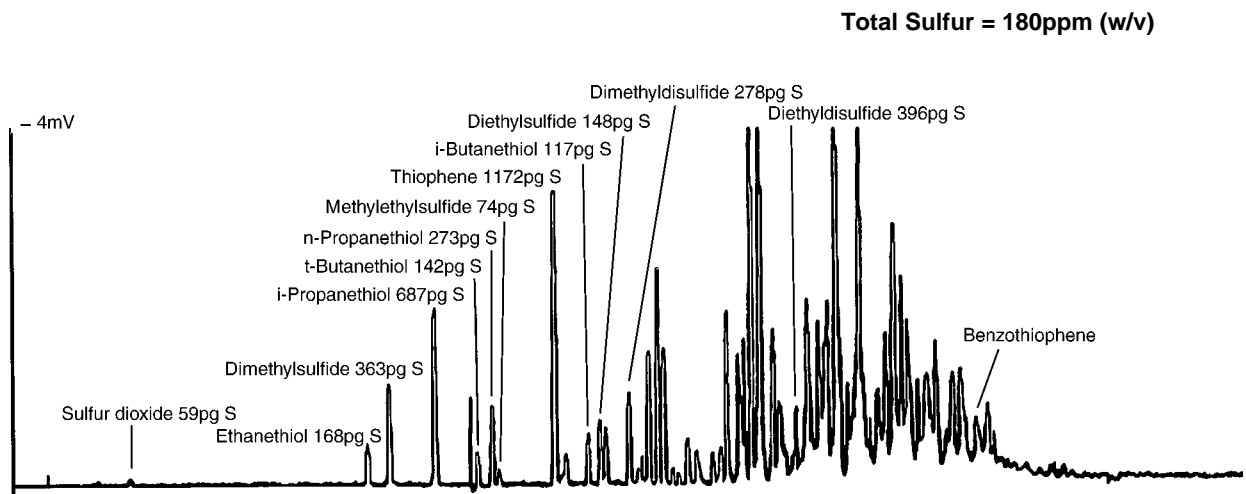


Oven: 35°C (1 min) to 300°C at 10°C/min, Sample: 1.0mL butane feedstock, split 10:1.
Chromatograms provided by Sievers Research Inc., Boulder, Colorado, USA.

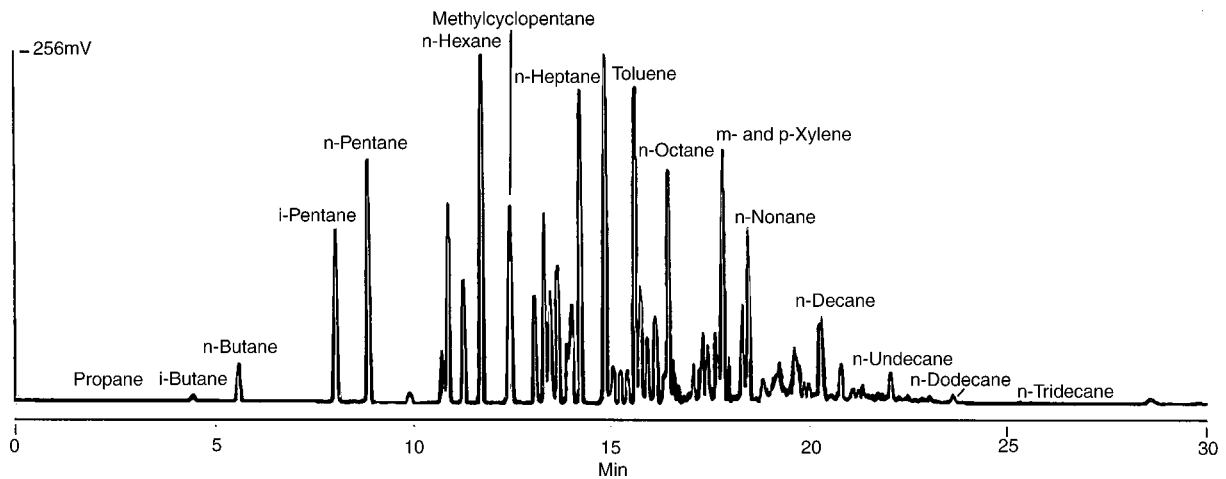
G000141,142

Figure J. Hydrocarbons and Sulfur Compounds In a Naphtha Feedstock

Sulfur Chemiluminescence Detector Response



Flame Ionization Detector Response

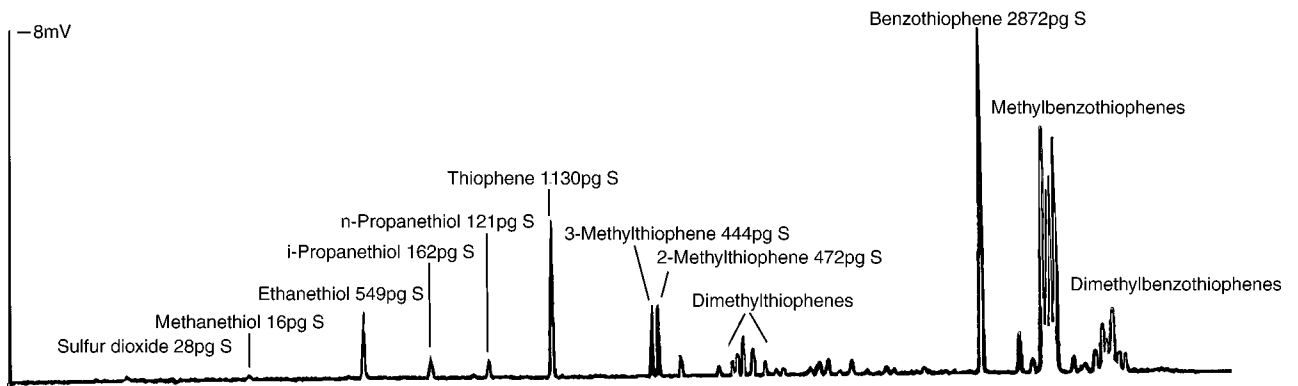


Oven: -10°C (3 min) to 300°C at 10°C/min, Sample: 2.0µL liquid naphtha, split 10:1.
Chromatograms provided by Sievers Research Inc., Boulder, Colorado, USA.

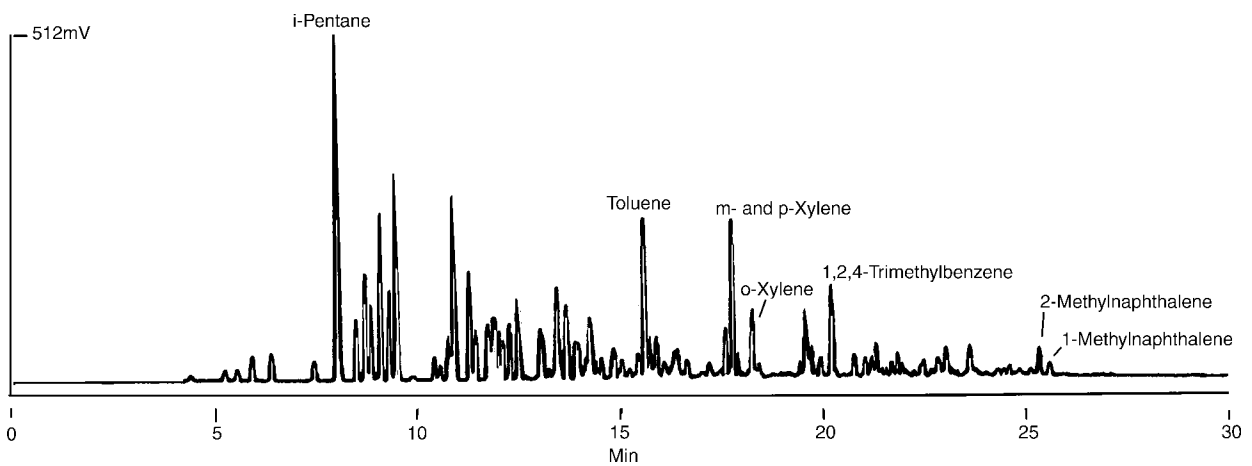
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Figure K. Hydrocarbons and Sulfur Compounds In Catalytically Cracked (FCC) Gasoline

Sulfur Chemiluminescence Detector Response



Flame Ionization Detector Response

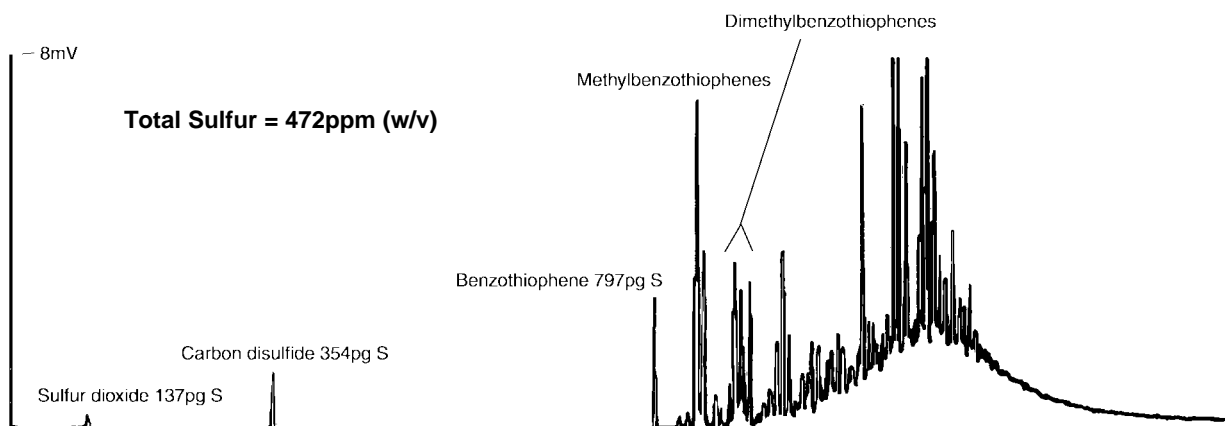


Oven: -10°C (3 min) to 300°C at 10°C/min, Sample: 2.0µL liquid gasoline, split 10:1.
Chromatograms provided by Sievers Research Inc., Boulder, Colorado, USA.

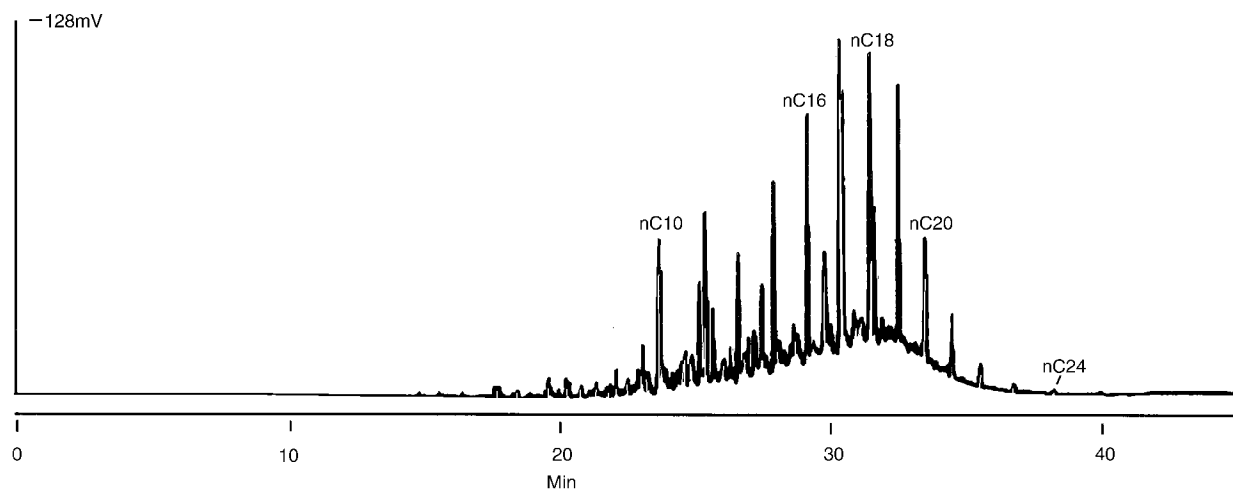
G000145, 146

Figure L. Hydrocarbons and Sulfur Compounds In #2 Automotive Diesel Fuel

Sulfur Chemiluminescence Detector Response



Flame Ionization Detector Response

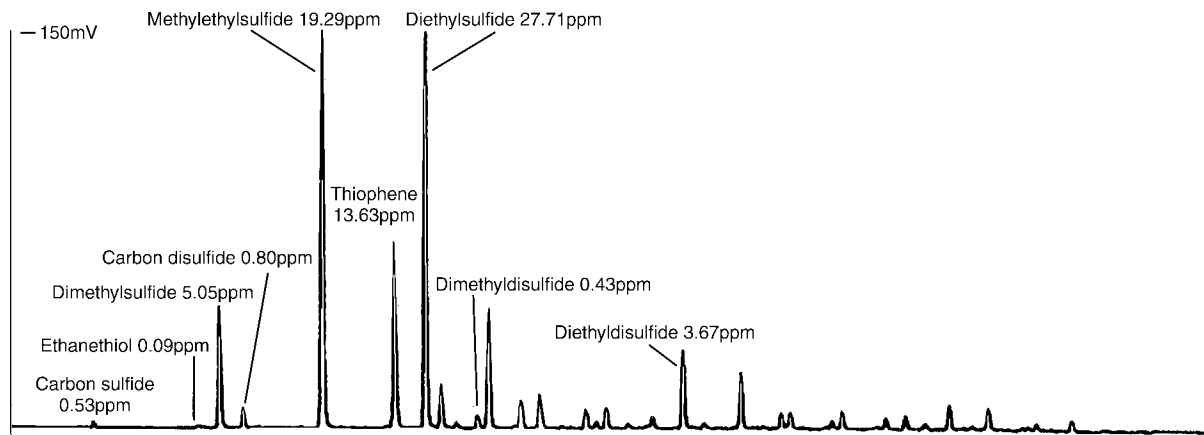


Oven: -10°C (3 min) to 300°C at 10°C/min, Sample: 2.0µL liquid diesel fuel, split 10:1.
Chromatograms provided by Sievers Research Inc., Boulder, Colorado, USA.

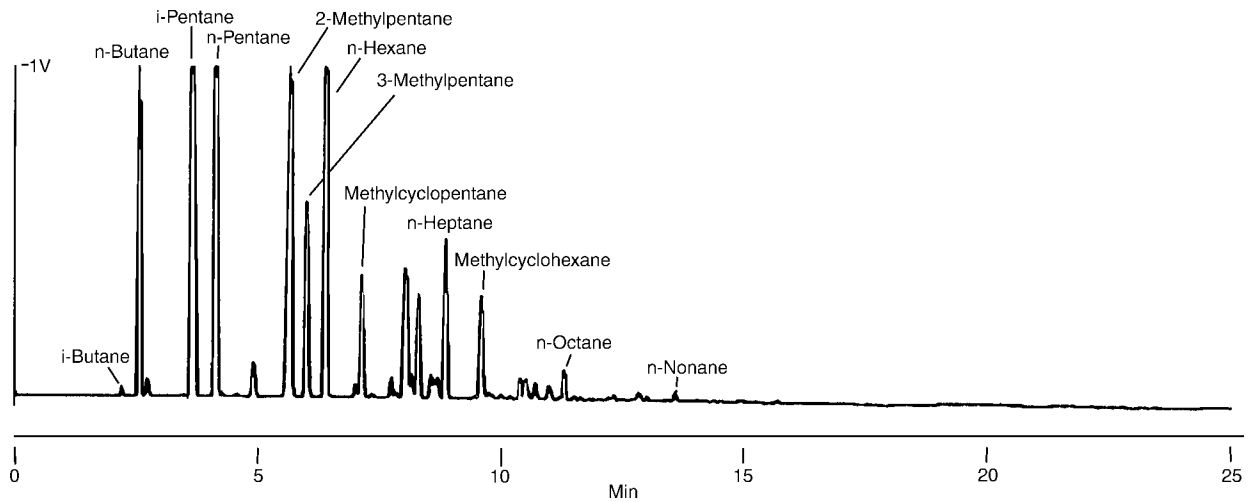
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Figure M. Gasoline Components

Sulfur Chemiluminescence Detector Response



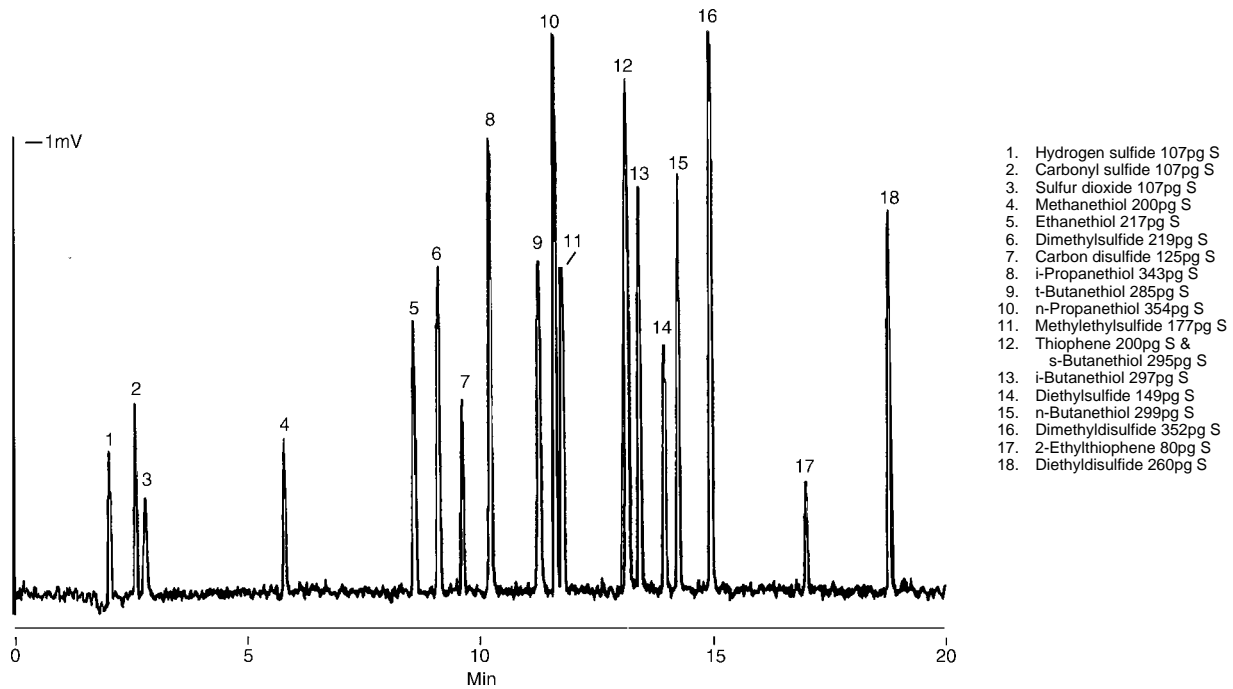
Flame Ionization Detector Response



Oven: 35°C (1 min) to 300°C at 10°C/min, Sample: 1.7µL liquid gasoline, split 10:1.
Chromatograms provided by Sievers Research Inc., Boulder, Colorado, USA.

G000149,150

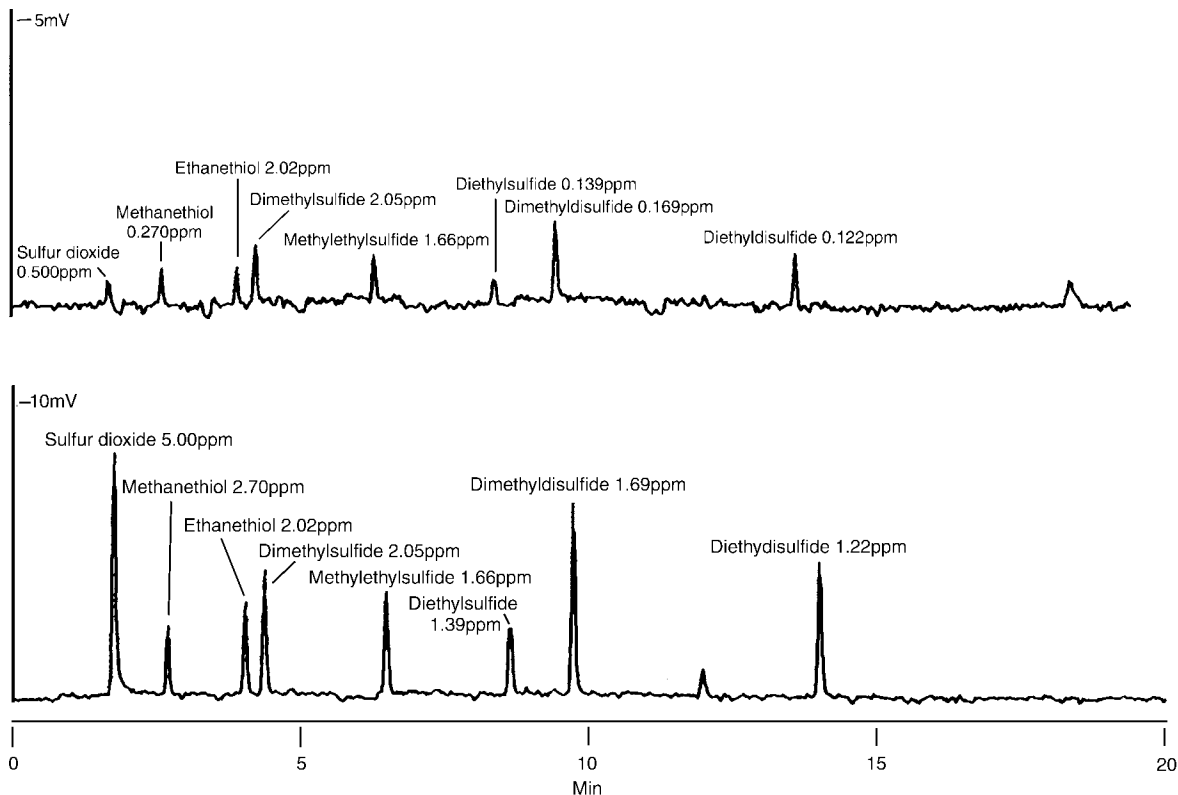
Figure N. Sulfur Compounds Typically Monitored In Stack Gases and Air



Oven: -10°C (3 min) to 300°C at 10°C/min, Detector: SCD, Sample: 0.1mL gas standards mixture, split 10:1. Chromatogram provided by Sievers Research Inc., Boulder, Colorado, USA.

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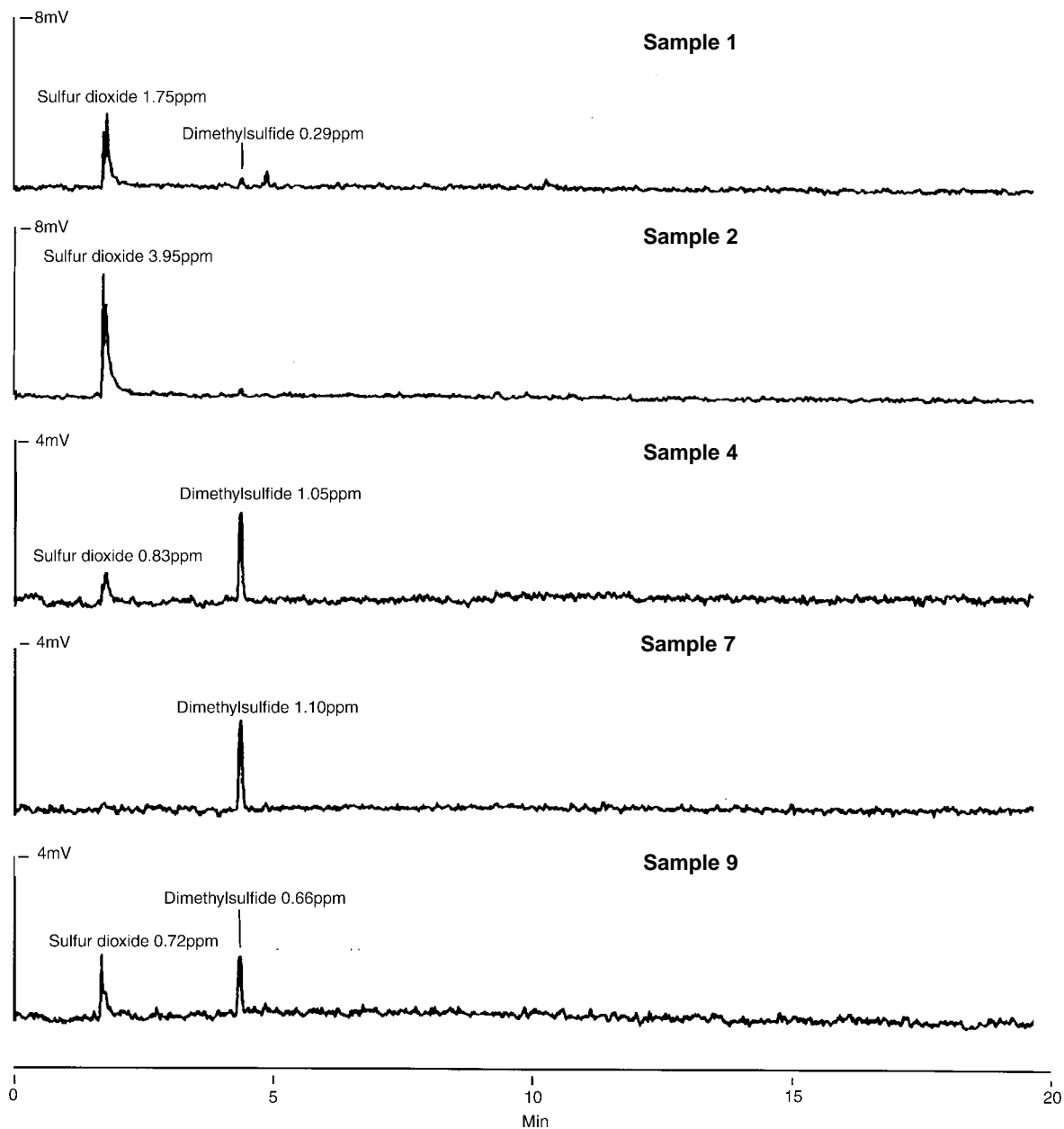
Figure O. Sulfur Compounds in Wine Headspace



Oven: 35°C (1 min) to 220°C at 10°C/min, Detector: SCD, Sample: 1.0mL wine headspace, split 10:1. Chromatograms provided by Sievers Research Inc., Boulder, Colorado, USA.

G000152,153

Figure P. Differences in Sulfur Compound Content of Wine Headspace



Oven: 35°C (1 min) to 220°C at 10°C/min, Detector: SCD, Sample: 1.0mL wine headspace, split 10:1.
Chromatograms provided by Sievers Research Inc., Boulder, Colorado, USA.

G000154

Ordering Information:

Description	Cat. No.
SPB-1 SULFUR Fused Silica Capillary Column 30m x 0.32mm ID, 4.0µm film	24158

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SPB, Supelco – Sigma-Aldrich Co.
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Fused silica columns manufactured under HP US Pat. No. 4,293,415.

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