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The Detection and Comparison of Sulfur Compounds in Petroleum Streams using Gas
Chromatography Coupled with Various Commercially Available Sulfur Detectors

by

Robert Ronald Wehman Jr.

A Thesis

Presented to the Graduate and Research Committee

of Lehigh University

in Candidacy for the Degree of

Master of Science

in

Chemistry

Lehigh University

May 1996

This thesis is accepted and approved in partial fulfillment of the requirements for the Master of Science

MAY 6, 1996
Date

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Thesis Advisor

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Co-Advisor

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Chairperson of Department

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ACKNOWLEDGMENTS

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ABSTRACT

Due to the new clean air laws, petroleum companies reduced the sulfur compounds in their products. With this reduction, many instrument companies entered the market place with new instruments to measure the levels of sulfur. These new instruments were targeted at the flamephotometric detector and the electrolytic conductivity detector. These latter instruments suffer from a lack of sensivity, low linear dynamic range, quenching and selectivity problems. These new companies all proclaim that their instruments solved these problems.

This study will address the problems mention above on four relativity new sulfur detectors. The Siever's Sulfur Chemiluminescence Detector both (flame and flameless) are compared with the Ankek flameless and Hewlett Packard's atomic emission detectors. Standards were prepared to test the conditions stated above and real world samples were also tested to determine if these instruments could equal the results of x-ray florescence. Instrument theory, functionality, mechanism and ease of operation will also be addressed. The data presented here helps to identify which detector will server one's own laboratory's need.

INTRODUCTION

Sulfur components are found in the foods and drink we consume, for example, in horseradish and coffee. They are also found in beer and wine. The pharmaceutical companies developed sulfur compounds for drugs and ointments during World War I, World War II and The Korean War. Sulfur drugs were use to fight infection in the wounded.[1] For several years, organic and inorganic sulfur containing compounds have become important components to be detected, identified and quantitated.

Sulfur compounds are of particular concern to the petroleum industry. Sulfur compounds poison catalysts and corrode pipelines.[1] In November of 1990, The Clean Air Act was passed requiring petroleum companies to reduce the levels of aromatics and volatile sulfur in petroleum products.[1] Gasoline sold in California must have sulfur levels below 40 parts per million, for example.[1]

With the developing need for sulfur detection, several instrument companies developed detectors for just this purpose. In the past, the Flame Photometric Detector (FPD) and the Electrolytic Conductivity Detector (ELCD) have been the instruments of choice. However, the FPD is not well suited for quantitative detection in complex hydrocarbon matrices. The FPD is non-linear and is not element specific. The FPD also displays hydrocarbon interferences and quenching. While ELCD is linear, it does suffer hydrocarbon interferences due to CO_2 response in the oxidative mode of operation. The ELCD requires significant routine maintenance and is not as sensitive as the more robust FPD.[2,3]

Recently, the scientific community has seen the emergence of the Hewlett Packard Atomic Emission Detector (AED), the Antek 705 Sulfur Chemilumenescence Detector and the Siever's Flame and Flameless Chemiluminescence Detector for the

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detection of volatile sulfur compounds. This paper illustrates how each instrument functions, and identifies similarities and differences for the determination of sulfur compounds in petroleum products. Specificity, selectivity, signal to noise ratios, linear dynamic range and the effects that accompany them are examined.

GAS CHROMATOGRAPHY

Gas chromatography is the physical separation of two or more compounds based upon their distribution or partition differences between the mobile gas phase and the stationary phase.[4] The stationary phase is either a solid or a high molecular weight liquid.[4] Figure 1 is a representation of a gas chromatograph and figure 2 is a schematic representation of a cross section of column construction showing both the solid and liquid phase. The sample is introduced into the injection port of the gas chromatograph by means of a syringe or by an automatic injection system.[4] The sample is vaporized in the injector and carried to the column as a vapor phase analyte. Once on the column, the sample is separated on a long narrow column with a non-volatile stationary phase. The separation is often aided with a programmable oven which encloses the column. Upon separation, sample molecules enter a detector. The detector functions as a transducer which generates an electrical signal that is measured and recorded.[4] The output is called a chromatogram, which is a plot of detector signal response versus time.[4] The response of the detector remains low or at the baseline until a component elutes from the column. Detected compounds produce peaks. The area of a peak represents the amount of each compound. In many cases, peak height is used instead of area. The retention time is a measure of the nature or identity of the compound.

Gas Chromatograph
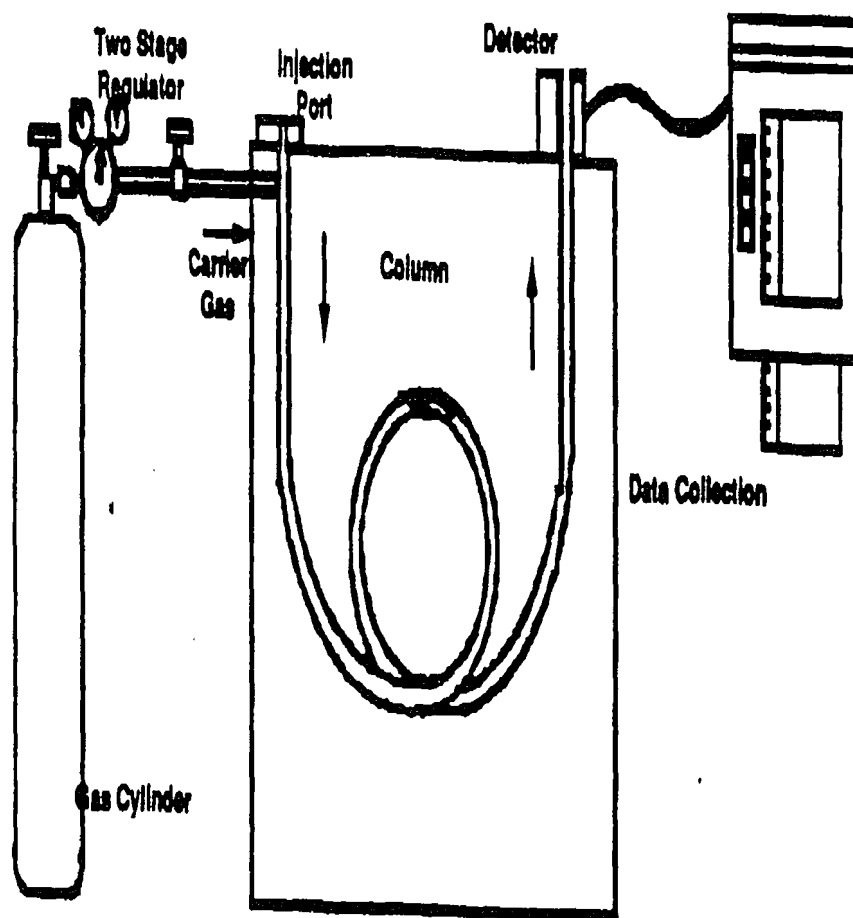
Figure 1. A typical gas chromatograph illustrating an injector, a column for separation and a detector.

Gas Chromatograph Columns
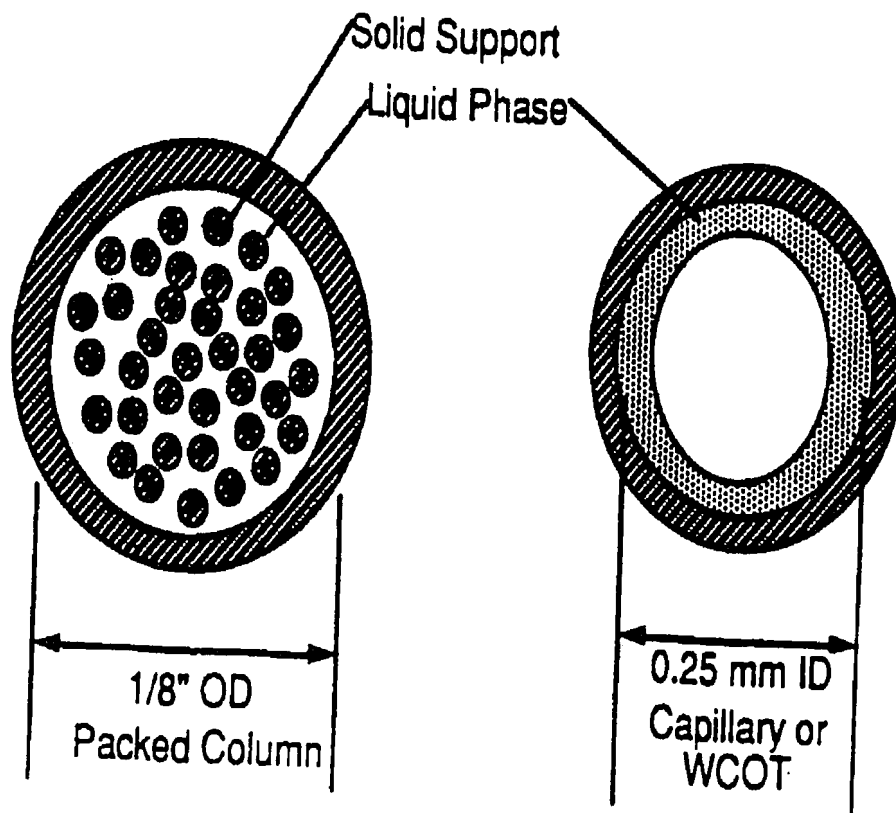
Figure 2. A packed and capillary column. Inside each are the solid and liquid phases. Also represented is the difference in size between packed and capillary columns.

THE SIEVERS FLAME CHEMILUMENESCENCE DETECTOR[5]

The Flame Sulfur Chemilumenescence Detector (SCD), see page 6, uses a ceramic probe which is housed in a probe interface assembly, as illustrated in figure 3. This assembly is mounted on top of a Flame Ionization Detector (FID). The ceramic probe is positioned approximately 4mm to 14mm from the FID jet. This assembly allows the probe to be engulfed in a hydrogen rich flame with vacuum drawing the flame products through a transfer tube (gas settings are discussed under experimental procedures). A transfer tube carries the effluent gas including SO from the flame to a reaction chamber. Inside this chamber, the effluent is combined with ozone, in-situ generated to convert SO to SO_2*, an activated molecule with an electron in a higher energy state. This SO_2* molecule is highly reactive and emits light as its electrons return to the ground state. This light is filtered through a wavelength-specific filter into a photomultiplier tube. Figure 4 illustrates a schematic of the SCD detector. These photons (light) are multiplied in a photomultiplier tube and the signal is sent to the detector for counting.[1,2,3] From the detector, the signal is converted from an analog signal to a digital signal by a Beckman Mark IV sixteen bit analog to digital converter. The signal is stored and processed by a Hewlett Packard 1000A mainframe computer which samples the data at a rate of fifteen readings per second; every three data points are averaged to make one point in the final data array. The reactions in the detector are represented by: 1,2,3. The difference between this detector and its' cousin the flameless is just the detector interface. This system uses the flame from the FID to pyrolyze the sulfur molecules and the flameless uses a burner. Both systems use the same detector box and electronics however, the experimental results are very different. For this study, they will be considered as two different detectors.

Sievers SCD Interface Assembly

HEX WRENCH

PROBE
INTERFACE
ASSEMBLY
(ASM 20600)

SET SCREW A

SET SCREW B

FID
COLLECTOR
ASSEMBLY

PROBE

FID JET

To install carefully slide the Probe Interface Assembly over the FID Collector Assembly.

Raise or lower Probe using Set Screw A.

clockwise = up.

0.64 mm per 360 degree turn or screw.

min. = 4 mm
max. = 14 mm

Figure 3. Sievers SCD flame assembly for an HP5890. Also shown is the distance between the probe and the flame and the hex wrench to adjust the height to flame ratio of the probe.
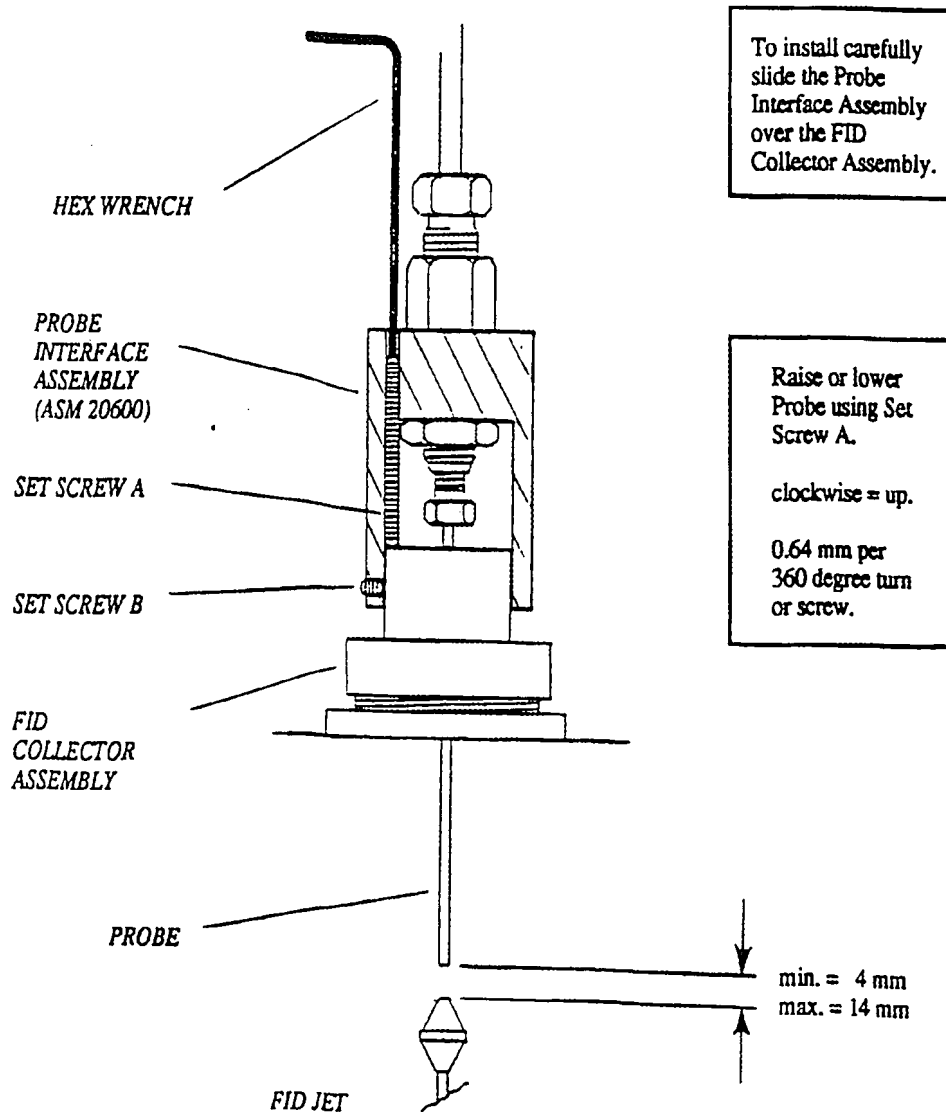
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Sievers Sulfur Chemiluminescence Detector
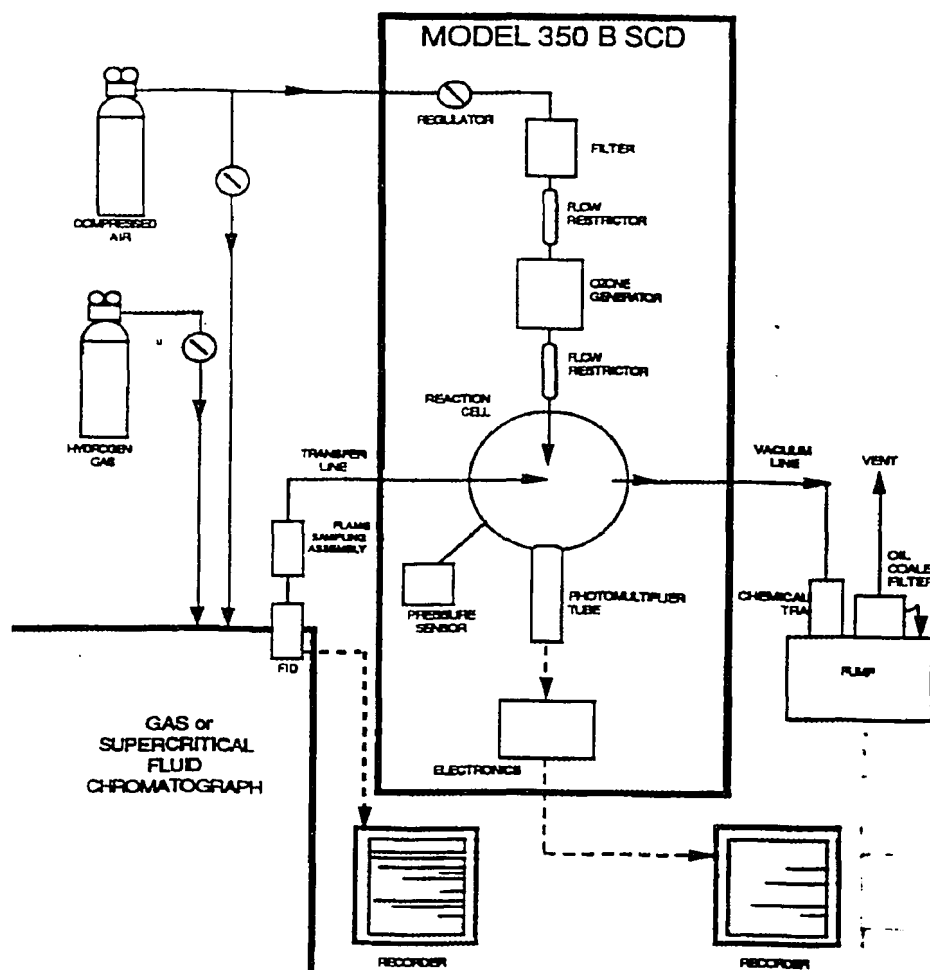
Figure 4. Siever's SCD schematic of the model 350 detector. Illustrated is the flow of column effluent, ozone generation and possible connection to gas chromatograph or supercritical fluid chromatograph.

$$\text{Sulfur Compounds} + H_2 / \text{Air Flame} \text{ ----- } SO + \text{Other Products} \quad (1)$$

$$SO + O_3 \text{ ----- } SO_2{}^* + O_2 + hv \text{ (400 nm)} \quad (2)$$

$$SO_2{}^* \text{ ----- } SO_2 + hv \text{ (400 nm)} \quad (3)$$
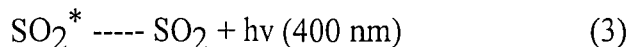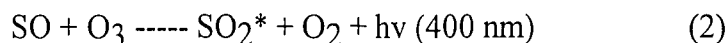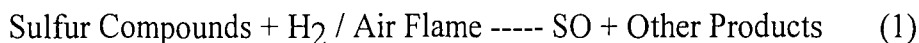
THE SIEVERS FLAMELESS CHEMILUMINESCENCE DETECTOR[5]

The Sievers Flameless Chemiluminescence Detector operates similar to its counterpart, the flame detector; however, the flameless unit uses a burner system for combustion as illustrated in figure 5. This burner houses a dual ceramic probe that is seated one inside the other. The column is inserted into a Valco zero dead volume fitting connected to a restrictor. The restrictor is used for maximum vacuum at the detector.

The burner is equipped with a thermocouple, furnace element and heater leads which are attached to a controller. This controller controls the hydrogen and air gas flows (gas flows are discussed under experimental procedures) as well as the temperature of the burner and gas safey shutoff. Inside the burner, sulfur compounds pyrolize to SO and other sulfur and non-sulfur species; a vacuum pump transfers the pyrolysis effluent to the reaction chamber where excess ozone is generated *in-situ*. SO reacts with ozone to form $SO_2{}^*$, which is an excited state species. As this molecule returns to the ground state it gives off light at 400 nm, which is detected with a photomultiplier tube and counted in the detector electronics. The signal from the detector is processed as described in the previous section.

$$\text{Sulfur Compounds (Analyte)} \text{ ----- } SO + H_2O + \text{Other Products} \quad (4)$$

$$SO + O_3 \text{ ----- } SO_2{}^* + O_2 \quad (5)$$

$$SO_2{}^* \text{ ----- } SO_2 + hv \text{ (400nm)} \quad (6)$$
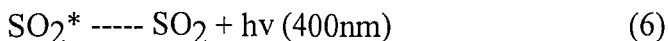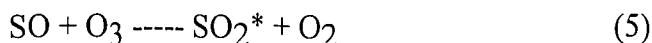
The goal of this design is to maximize reliability and sensitivity. The flameless detector is approximately ten times more sensitive than the flame detector due to the

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Sievers Flameless Burner Interface

Hydrogen inlet

Valco connector for →
SCD transfer line

1/16" Ceramic tube

Furnance element

1/8" Ceramic tube

Thermocouple

Heater leads

Cap-head bolts→

Adapter plate

1/4" Nut

1/16"(0.07" ID) SS Restrictor

Valco zero dead-volume fitting
(column connection)
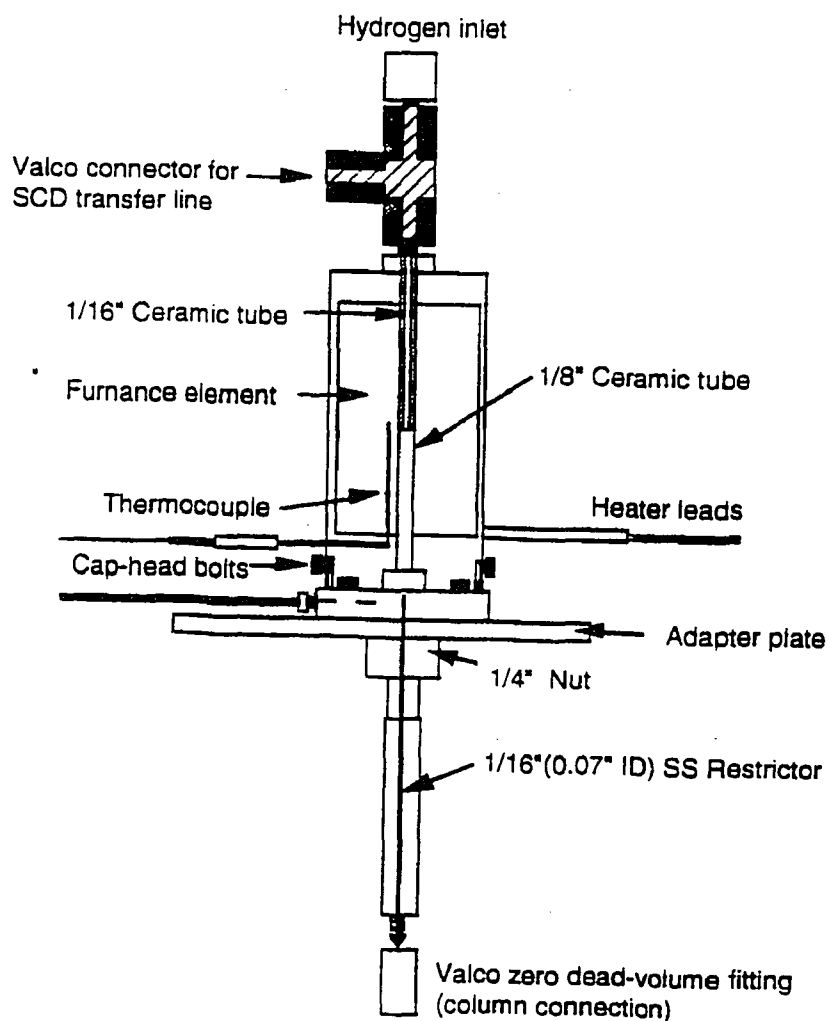
Figure 5. Siever's flameless interface showing
column connection, hydrogen inlet for
chemiluminescence reaction and the heater and
thermocouple leads.

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column insertion directly inside the burner. All the effluent is sent into the detector. In the flame version, many of the ions indiscriminately escape the probe and are not sent to the detector for processing.[2,3]

Both detector systems provide low level linear detection with no quenching for co-eluting hydrocarbon compounds.[2,3]

THE ANTEK SULFUR CHEMILUMINESCENCE DETECTOR[6]

The Antek sulfur chemiluminescence detector is a design similar to the Siever's flameless system discussed above. This system uses a furnace, mounted on top of the gas chromatograph as illustrated in figure 6. The capillary column enters the bottom of the assembly where analyte is reacted with oxygen to form SO_2 in the oxidative zone of the pyroreactor. This system also has a double probe system with one seated inside the other to allow hydrogen to enter the reaction chamber. Hydrogen is inserted around the inner 1/16" pyrolysis tube to interact with the SO_2 molecule traveling in the reductive zone of the reactor to produce H_2S. The H_2S enters a reaction chamber aided by a vacuum where H_2S reacts with ozone to generate SO_2^*. The SO_2^* emits light as it falls back to the ground state. The photons are detected by a photomultiplier tube and counted by the detector electronics. The signal is then processed as described previously. Figure 7 represents a flow diagram of the Antek detector illustrating flow from the gas chromatograph to the detector. The reactions in the detector are represented by:[5]

$$\text{Sulfur Compounds} + O_2 \text{ ----- } SO_2 + CO_2 + H_2O + \text{Oxides} \qquad (7)$$

$$SO_2 + H_2 \text{ ----- } H_2S + \text{Other Reduced Sulfur Species} \qquad (8)$$

$$H_2S + \text{Other Reduced Sulfur Species} + O_3 \text{ ----- } SO_2^* + O_2 \qquad (9)$$

$$SO_2^* \text{ ----- } SO_2 + hv \text{ (400 nm UV)} \qquad (10)$$

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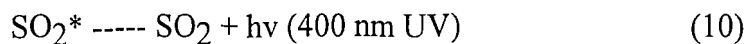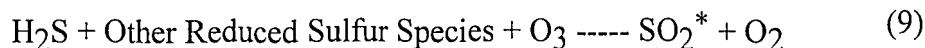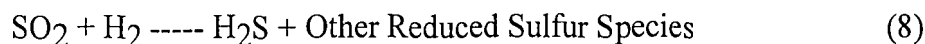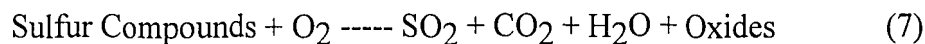
Anteks Flameless Interface
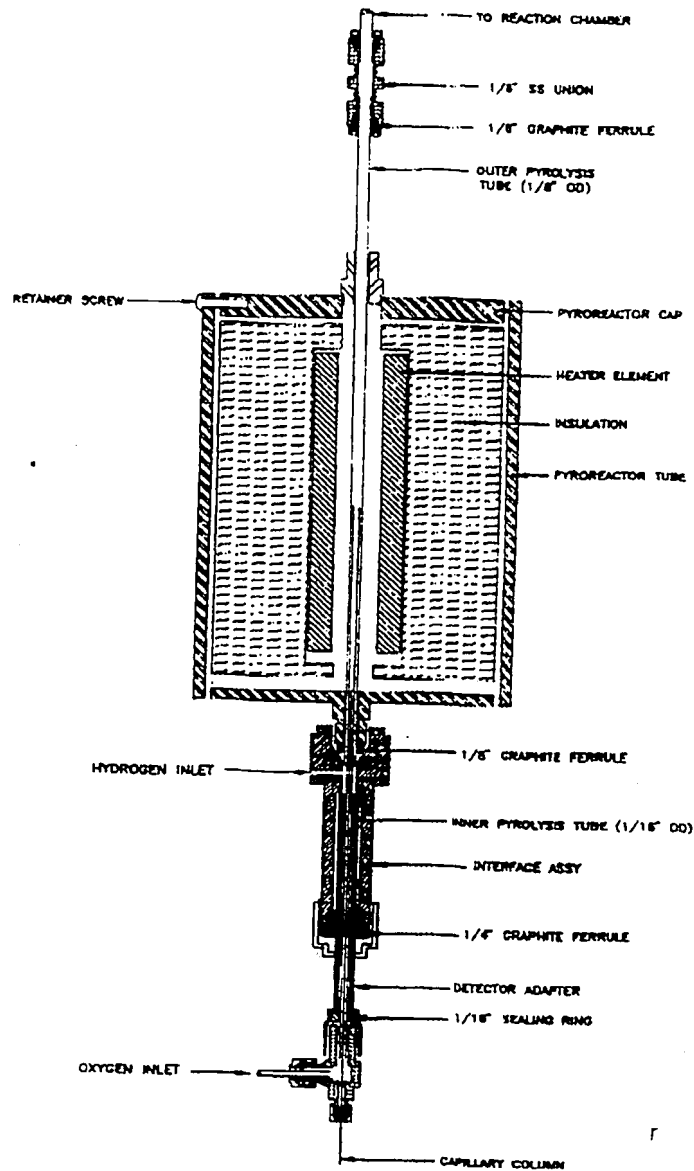
Figure 6. Antek's flameless interface illustrating oxygen and hydrogen inlets for chemiluminescence reaction and the pyroreactor to aid the reaction.

Antek's Chemiluminescence Detector
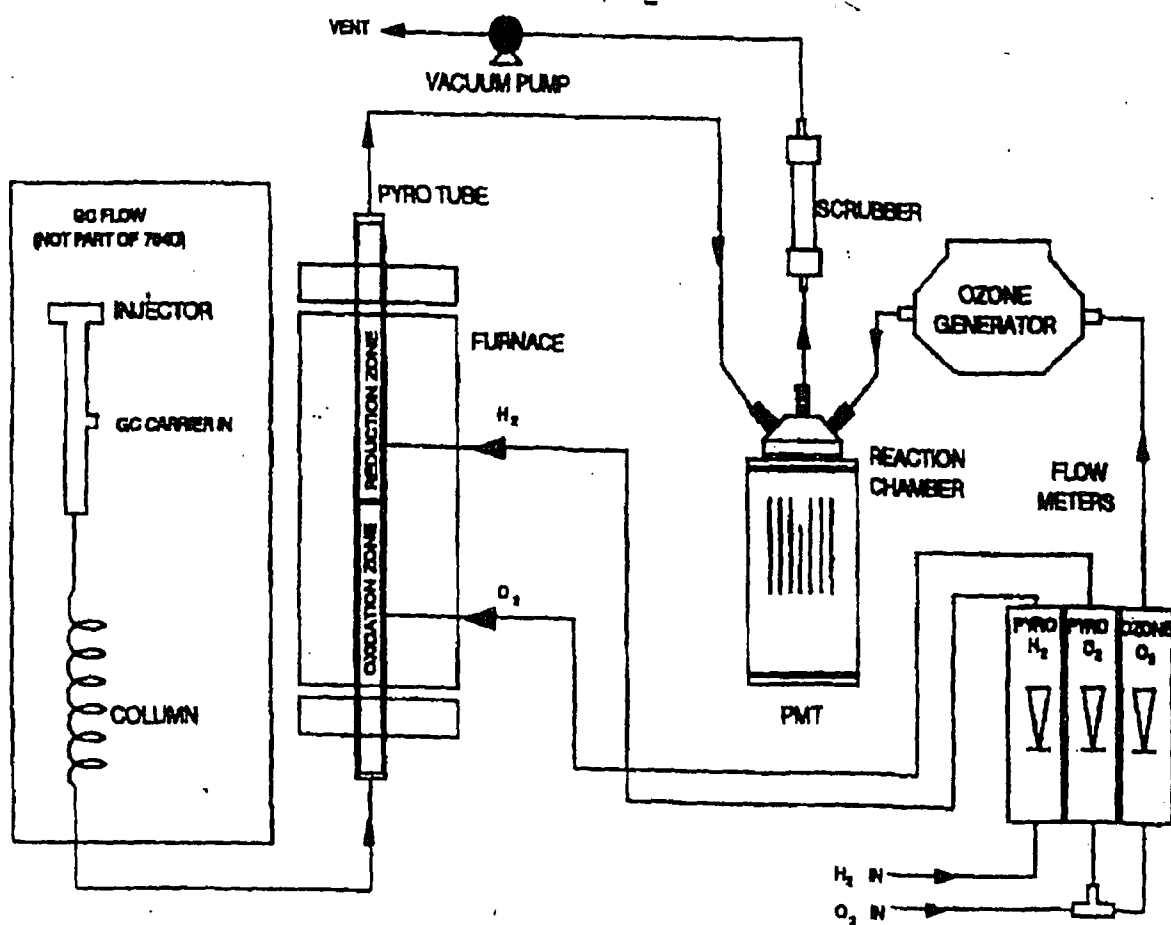
Figure 7. The flow diagram of the Antek Sulfur
– Chemiluninescence Detector including rotovalves
for gas adjustments.

The Antek furnace also contains a thermocouple, furnace element and heater leads which are attached to the main body of the detector to control conditions. This controller regulates the hydrogen and air gas flows as well as the temperature of the furnace and gas safey shutoffs.

THE HEWLETT PACKARD ATOMIC EMISSION DETECTOR[7]

The Atomic Emission Detector (AED), as illustrated in figure 8 receives the effluent from the gas chromatograph column, however it does not use a flame or furnace to pyrolyse the effluent. The column is connected to the AED via a heated and insulated transfer line. The column enters a helium microwave plasma where components are atomized. These atoms are excited and as they fall back to the ground state light is emitted. The light is sent through a spectrometer. The fixed grating focuses light to a moving diode array and a signal is detected. Data is stored and manipulated by a Pascal based Chemstation.[8,9]

MECHANISMS OF SULFUR CHEMILUMINESCENCE DETECTION

There are two opposing theories of the correct mechanism for sulfur chemiluminescence detection. There is significant controversy as to the correct mechanism for sulfur detection. Therefore it is important to understand the two proposed mechanisms occurring in the Sievers SCD and the Antek SCD, with the experimental data that supports each claim.[2,3,6,10]

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Hewlett Packard Atomic Emission Detector
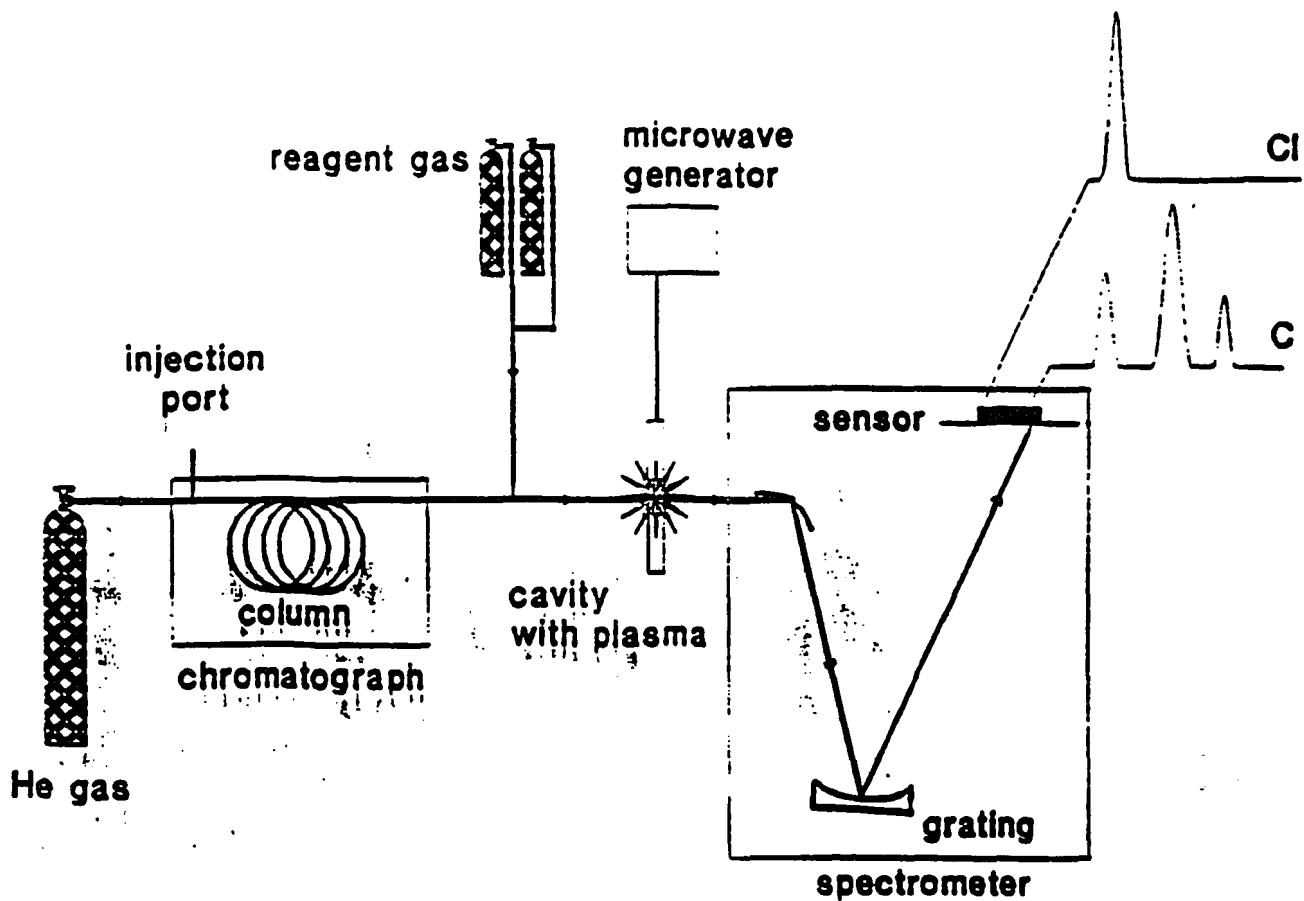
Figure 8. Hewlett Packard Atomic Emission Detector showing the cavity, spectrometer and photo dioda aray.

SIEVERS MECHANISM OF SCD DETECTION

The first theory of sulfur chemiluminescence detection is the Sievers mechanism stated below.[2,3,10,11] The Siever's instrument setup is similar to Antek's construction, and both instruments produce worthy results. However, the postulated intermediates for detection are different and the experiments conducted to prove which intermediates are important are stated below.[2,3,10]

$$Sulfur\ Compounds + H_2\ /\ Air\ Flame\ or\ Furnace\ \text{-----}\ SO + Other\ Products \quad (11)$$

$$SO + O_3\ \text{-----}\ SO_2^* + O_2 \quad (12)$$

$$SO2^*\ \text{-----}\ SO2 + hv\ 400\ nm \quad (13)$$
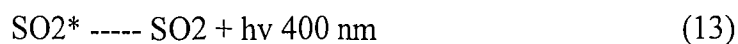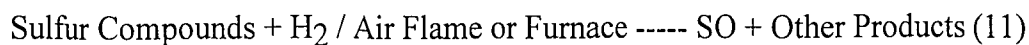
ANTEK'S MECHANISM FOR SCD DETECTION

The second theory for how sulfur compounds are detected using chemiluminescence techniques is Antek's mechanism. Their mechanism is slightly different than the mechanism describe above. The difference involves an H_2S intermediate and is shown below. At this time experimental evidence to support this mechanism is not available from the vendor or in the literature due to pending litigation.[6] However, one must not conclude that either mechanism is incorrect until all evidence is available and is considered.[6]

$$Sulfur\ Compounds + O_2\ \text{-----}\ SO_2 + CO_2 + H_2O + Oxides \quad (14)$$

$$SO_2 + H_2\ \text{-----}\ H_2S + Other\ Reduced\ Species \quad (15)$$

$$H_2S + Other\ Reduced\ Sulfur\ Species + O_3\ \text{-----}\ SO_2^* \quad (16)$$

$$SO_2^*\ \text{-----}\ SO_2 + hv\ (400\ nm - UV) \quad (17)$$
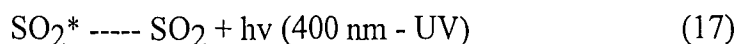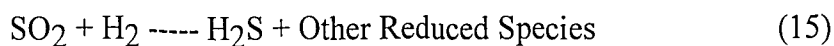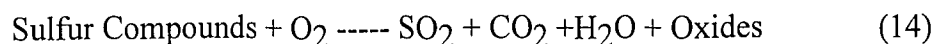
EXPERIMENTS TO DEFINE MECHANISM

Benner and Stedman at the University of Colorado Denver conducted four experiments to explain the above Sievers mechanism.[11] An emission spectrum test was designed with a standard flow tube. Sulfur gas and ozone were diffused through this tube to a microwave plasma. The emission from the plasma showed no detectable bands at 384 nm or 394 nm demonstrating that sulfur atoms do not dominate the reaction $S + O_3$ ----- $SO + O_2$. At the same time, in another flow tube, $H_2S + SO$ were also tested in the same fashion as described above; these did show emission at 384 nm and 394 nm. This experiment does not support one mechanism over another however this does illustrate that both H_2S and SO are components present in post flame gases.[11]

A rate constant experiment was performed next using a microwave discharge plasma, ozone and SO_2 as a source of SO. The rate constant for the reaction $SO + O_3$ ----- $SO_2^* + O_2 + h\nu$ was determined to be $5.0 (+-0.2) \times 10^{-13}$ molecules $cm^{-3}s^{-1}$. The microwave discharge was removed and the flame assembly described in the flame detector section was installed. The rate constant for this setup was calculated to be $4.7 (+-0.4) \times 10^{-13}$ molecules $cm^{-3} s^{-1}$. This indicates that SO was the dominant sulfur species in each experiment.[11]

The third experiment to establish that SO is the dominant species was performed by gas phase titration. Known amounts of NO_2 were added to SO_2 gas and titrated with ozone directly ahead of a photomultiplier tube; The emission was monitored at 350 nm. The experiment was performed three times with a 36 ms, 90 ms and 150 ms reaction time. The 36 ms experiment did not have sufficient time for reaction. Both the 90 ms

and the 150 ms experiment showed an end point at approximately 0.147 ml/min NO_2. This suggests that SO combined with O_3 as a function of NO_2 to produce SO_2^*.[11]

The simplest experiment was performed by using post flame H_2S gas and ozone. H_2S was mixed with ozone in front of a photomultiplier tube and a filter calibrated at 350 nm. No emission was observed. These experiments confirm the Sievers mechanism that SO and not H_2S is the dominant species used for chemiluminescence in the detection of sulfur compounds.[11]

EXPERIMENTAL PROCEDURES

Instrumentation: During this study, all separations were performed with an Hewlett Packard 5890A or 5890II Gas Chromatograph (Wilmington, DE) equipped with an HP 7673 auto sampler (Wilmington, DE). The detectors used were a Sievers 350A sulfur chemiluminescence detector (Boulder, CO), a Sievers 355 flameless burner (Boulder, CO) an Antek 705 sulfur chemiluminescence detector (Houston, TX), and an Hewlett Packard atomic emission detector 5921A equipped with electronic pressure controls. Separations were achieved with a 30 meter x 0.32 millimeter I.D., 4 micron film thickness SPB-1 capillary column from Supelco (Bellefonte, PA). Data were acquired, stored and processed by a Hewlett Packard 1000A mainframe computer (PaloAlto, CA) using Beckman CIS CALS software (Allendale, N.J.). The atomic emission detector computer system is an Hewlett Packard 332 Pascal Chemstation (Wilmington, DE).

Methyl sulfide, butylmercaptan, thiophene benzothiophene and dibenzothiophene were used to evaluate signal-to-noise ratios, selectivity, linearity and quenching. For example a 1%, by weight, stock solution of the various sulfur compounds was diluted in toluene. Aliquots were taken to make solutions ranging from 1000 ppm S to 0.1 ppm S.

These sulfur compounds were of highest purity, 98% or better, purchased from Aldrich Chemical Company (Milwaukee, WI.) and no other purifacation steps were used. Gasolines and diesel fuels were used to examine how accurate the detectors are to total sulfur as compared to x-ray fluorescence. X-ray fluorescence was analyzed according to AM-S 90-694.[12] These fuels used are commerically available from service stations in the New Jersey area. Gas chromatograph and other detector conditions are listed in tables 1 through 5.

Table 1. **GAS CHROMATOGRAPHIC CONDITIONS**

Oven	30 °C
Oven Heating Rate	10° Per Minute
	275 °C Final Temperature
	30 Minute Hold
Injector	250 °C
Flows	
Helium	1.3 mL/min - 1.5 mL/min Column
Velocity	23 cm/min - 26 cm/min Linear
Split Ratio	75 : 1 Split Flow
Injection	1 uL

Table 2.   <u>SIEVERS FLAME DETECTOR CONDITIONS</u>

Flows

Hydrogen	200 mL/min
Air	400 mL/min
Detector Temperature	Unknown
Detector Pressure	6 Torr - 8 Torr
Ceramic Probe	0.5 mm I.D.
	1.3 mm. O.D.
	105 mm length
	5 mm - 14 mm above jet
	HP Packed Column Jet
Transfer Line Temperature	Ambient

Table 3.   **SIEVERS FLAMELESS DETECTOR CONDITIONS**

Flows

Hydrogen	100 mL/min
Air	40 mL/min
Furnace Temperature	780 $^{\circ}$C
Detector Pressure	6 Torr - 8 Torr
Transfer line Temperature	Ambient
Ceramic Probe	
Outer Probe	3.17mm O.D. at 125 mm length
Inner Probe	1.6 mm I.D.at 105 mm length
	0.14 mm space between probes

Table 4.   **ANTEK FLAMELESS DETECTOR CONDITIONS**

Flow

Pyro Oxygen	75 mL/ min
Ozone Oxygen	50 mL/min
Hydrogen	150 mL/min
Detector Temperature	1000 ^{o}C
Detector Pressure	6 Torr - 8 Torr
Transfer Temperature	Ambient
Ceramic Probe	
Inner Probe	1/16 inch O.D. at 230 mm
Outter Probe	1/8 inch O.D. at 305 mm

Table 5.   **HEWLETT PACKARD ATOMIC EMISSION DETECTOR CONDITIONS**

Transfer Line Temperature	275 ^{o}C
Cavity Block Temperature	275 ^{o}C
Microwave Plasma Temperature	3000 ^{o}C
Flows	
Helium	60 psi
Nitrogen	25 psi
He Detector Make Up	60 psi
Oxygen Reagent Gas	25 psi
Hydrogen	70 psi
Spectrometer Purge	2 L/min
Sulfur Wavelength	181 nm
Carbon Wavelength	194 nm

RESULTS AND DISCUSSION

Until recently, trace analysis of sulfur compounds in petroleum products have been difficult. Analysis becomes difficult due to the fact that some sulfur molecules are polar in a non polar matrice . Therefore, sulfur compounds often adhere to the walls of reaction chambers and glassware.[10] With the recent development of the detectors described above volatile sulfur compounds have been identified, separated, quantified, and catalyst poison questions have been addressed.[1] It is important to understand the working parameters of the instruments to determine if it meets one's needs. Each of the instruments was evaluated for sensitivity, signal-to-noise ratios, dynamic range, quenching, and selectivity by using both standards and petroleum streams. Table 6 represents a summary of experimental results as they compare to the literature or the specifications set by the instrument companies.

SENSITIVITY / LIMIT OF DETECTION

One of the most common concerns when deciding if an instrument meets one's needs is the limit of detection sensitivity. Most of the instruments tested were able to achieve approximately 300 fg S / ul or 120 fg S / sec with the conditions described previously at a signal to noise ratio of 3 : 1. Table 7 illustrates the data used to calculate limits of detection. The formulas used to calculate these values are found in Appendix 1. Although most of the literature states a lower level of detectability, other conditions must be changed to get lower than achieved in this study. The Siever's SCD Flameless detector literature states a level of 25 fg S / s.[2,3] In order to achieve this level, one must first revise the instrument for on column injection. Allowing for on column injection in

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Table 6 Summary of Experimental Results

		Sievers Flame SCD	Sievers Flameless SCD	Antek Flameless SCD	Hewlett Packard AED
A	Lowest Level of Detection Lit 2,3,10	1-5 pg S / Sec	.05-.5 pg S / Sec could be as low as 25 fg S / Sec	1 pg S / Sec	.6 pg S / Sec
	Lowest Level of Detection Exp	50 pg S / Sec	120 fg S / Sec	121 fg S / Sec	128 fg S / Sec
	Lowest Level of Detection Exp	180 pg S / ul	337 fg S / ul	340 fg S / ul	322 fg S / ul
B	Dynamic Range Literature 2,3,6,10	3-4 decades	3-4 decades	4 decades	3-6 decades
	Dynamic Range Experimental	5 decades	5 decades	5 decades	6 decades
C	Quenching Literature 2,3,6,10	None	None	None	Some but backed out
	Quenching Experimental	None	None	None	Some but backed out with software
D	Selectivity Literature 2,3,6,10	10 e7	10 e7	10 e7	10 e7
	Selectivity Experimental	<10 e7	<10 e8	<10 e8	10 e8

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Table 7. __LOWEST LEVEL OF DETECTION SUMMARY AND DATA__

Detector	ppm S[1]	Signal to Noise Ratio (mv)	Height mVolts	L.O.D.[2]	Peak Width at 1/2 height (sec)	L.O.D	Selectivity
Seivers Flame	.1494	1.68	5.32	180 pg S / ul	3.6	50 pg S / sec	10^7
Seivers Flameless	.1494	1.76	31.2	337 fg S / ul	2.8	120 fg S / sec	10^8
Antek Flameless	.5186	.36	21.9	340 fg S / ul	2.8	121 fg S / sec	10^8
H.P. AED	.1494	.58	10.74	322 fg S / ul	2.5	128 fg S / sec	10^8

[1]A Split Ratio of 75 : 1

[2]At Signal to Noise of 3 : 1

these experiments would only improve the lowest limit of detection by the split ratio set in these experiments, which has already been accounted for in determining the above values. Changing the flow of oxygen and hydrogen allows for lower levels of detection however, there is a loss of resolution and possible instrument damage. Increasing the injection size would decrease the lowest level of detection. There was a loss of sensitivity over time observed in the flame system. This was due to crystalline deposits building up inside the probe. This is not as large a concern as it first appears. Cleaning the probe with an insertion tool readily restores sensitivity. However, one must judge when sensitivity has diminished below an acceptale level for routine operation. Both flameless systems do not appear to be affected by crystal formation. Combustion products travel through the inner and outer probes before reaching the hydrogen and oxygen areas where chemiluminescent species are formed.[3,10]

Both flameless systems and the H.P. AED provide better sensitivity because they operate at lower atmospheric pressure than the open flame system. The chemiluminescence of sulfur compounds depends inversely with pressure thereby increasing sensitivity at lower pressures.[2,3,10] Another factor that increases the sensitivity of these systems is that all of the column effluent enters the reaction chamber or the microwave plasma. The flame system loses some column effluent around the probe because the probe is positioned in the flame so some molecules get around the probe. All these factors add up to approximately one order of magnitude better sensitivity than the flame system.

Two effects from using the column effluent are peak broadening and asymmetrical peak shapes as demonstrated in figure 9. This is not due to adsorption or reaction of sulfur monoxide with the transfer line wall or the reaction cell wall.[1,3] The

Band broadening and Asymmetric Peak Shapes

FID   SCD

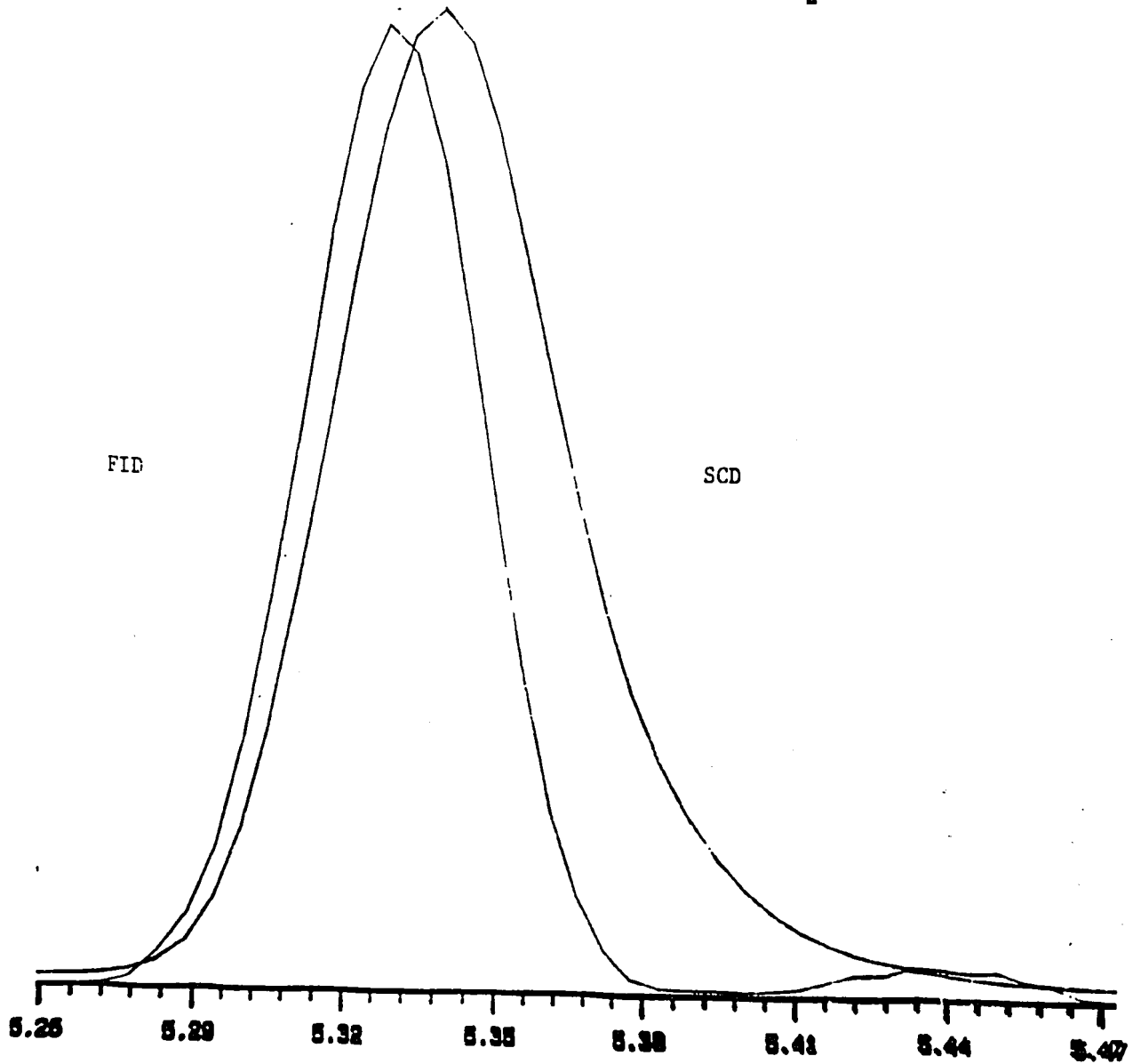| 5.26 | 5.29 | 5.32 | 5.35 | 5.38 | 5.41 | 5.44 | 5.47 |

Figure 9. Peak broadening of the SCD due to sulfur
    adsorption.

change in time occurs from the travel of compounds from the FID detector to the reaction cell through a lengthy transfer line of approximately 1 meter. The peak broadening is due to the turbulence as the sulfur compounds elute from a capillary column into the larger diameter transfer tube. It may also be due to the time it takes for the sulfur compounds to transit the reaction chamber. Figure 9 also illustrates the broadening of a peak from an FID compared to the flame SCD. Comparing the two peaks in skewness, a value of 1.0 is a perfect gausian peak.[6,8] The FID peak was slightly larger or fronted at a value of 1.11. However the SCD detector exhibits a large tail, discussed above, with a skewness value of 0.73. The formula for calculating skewness is found in Appendix 1. Fast flow rates of hydrogen, oxygen and the use of a vacuum reduces this effect. When this detector is used with the correct flow rates, the response from the SCD is actually better than without the faster flow rates. High flow rates of hydrogen and oxygen reduce the FID response by one to two orders of magnitude.

Another factor which can cause one system to give a larger response for one sample as compared to another SCD instrument is the photomultiplier tube. One photomultiplier tube could be different from another by a factor of two or three. This could be due to age of the tube condition, and even the brand of tubes.

A second concern in choosing a detector is the signal-to-noise ratio (S/N). Signal-to-noise ratios were calculated using a sample containing 0.1494 ppm S of methyl-sulfide. The results agree with what is expected from the literature. The Sievers flameless and the H.P. AED signal-to-noise ratios were calculated to be five times greater than that of the flame system[3]. The literature also states that the signal-to-noise ratio for SCD detection could be as great as ten times higher than the flame. The Antek SCD

gives the best possible signal-to-noise ratio at ten times greater than the flame detection system.

During these experiments, the detector used to represent the Sievers system was a model 350A SCD. Sievers also produced a 350B model which was available a few years later with improvements made to the "A" version. One improvement that could affect the signal-to-noise ratio is a construction flaw on the "A" series. The detector sends an analog signal to a digitizer, which takes data points at a predetermined rate. When the detector senses a signal the detector counts data points faster, in effect lowering noise around a given signal. The "B" model uses a digital signal that counts data points at this faster rate throughout the entire time data is taken. Therefore the peak- to-peak noise may be somewhat lower raising the signal-to-noise ratio.

Another condition that affects signal-to-noise ratio in the flameless and flame systems, not including the AED, is changing from air to oxygen for the reaction in the probe.[3] Changing from air to oxygen can increase the signal-to-noise ratio by approximately ten to twenty percent. However changing from air to oxygen has disadvantages. Pure oxygen causes the probes in both systems to burn hotter. This increase in temperature can cause detector failure. One would have to decide if the increase in signal-to-noise ratio for one set of important experiments is worth possible instrument damage.

LINEAR DYNAMIC RANGE

The data from the standards were plotted to establish the linearity and compare to the dynamic range listed in the literature. All of the detectors' performance was superior

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than the literature or specifications with a linear regression cofficient squared greater than 0.999. The detectors were all capable of five decades of linearity before the detector became saturated and the signal actually dropped as concentration increased. The Hewlett Packard AED faired better then the SCD's in this set of experiments. The AED was capable of six decades of linear response measured under the same set of conditions which is stated in the experimental section. The dynamic range was calculated by dividing the highest limit of detection by the lowest limit of detection where the linearity deviated from theoretical by five percent. The linear dynamic range is considered as the ability to detect a small and large signal and be in a linear operating area of the detector. A set of operating conditions is required so that one is operating in the linear region of the detector. Figures 10 through 13 demonstrate an upper most level of approximately 700 ppm S for all compounds, before the detector became saturated and the point where the slope of the curve changed by five percent. The Antek detector became saturated at 730 ppm S, while the AED was capable of going to a level of approximately 3000 ppm S. The AED system may have a larger linear range due to the data system. As mentioned above, the AED uses a Pascal Chemstation which may be able to handle more data at one time. Since the instrument uses a photo diode array it may be able to count photons faster than a photomultiplier tube or the mainframe computer our lab employs. This point may warrant some futher experiments.

SELECTIVITY

Selectivity is the molar analyte response of sulfur divided by the molar analyte response of carbon.[1] Throughout these experiments all detectors were capable of

Figure 10 Calibration Curve for Thiophene using Siever's SCD Detector

Calibration Curve for Thiophene for Flame SCD

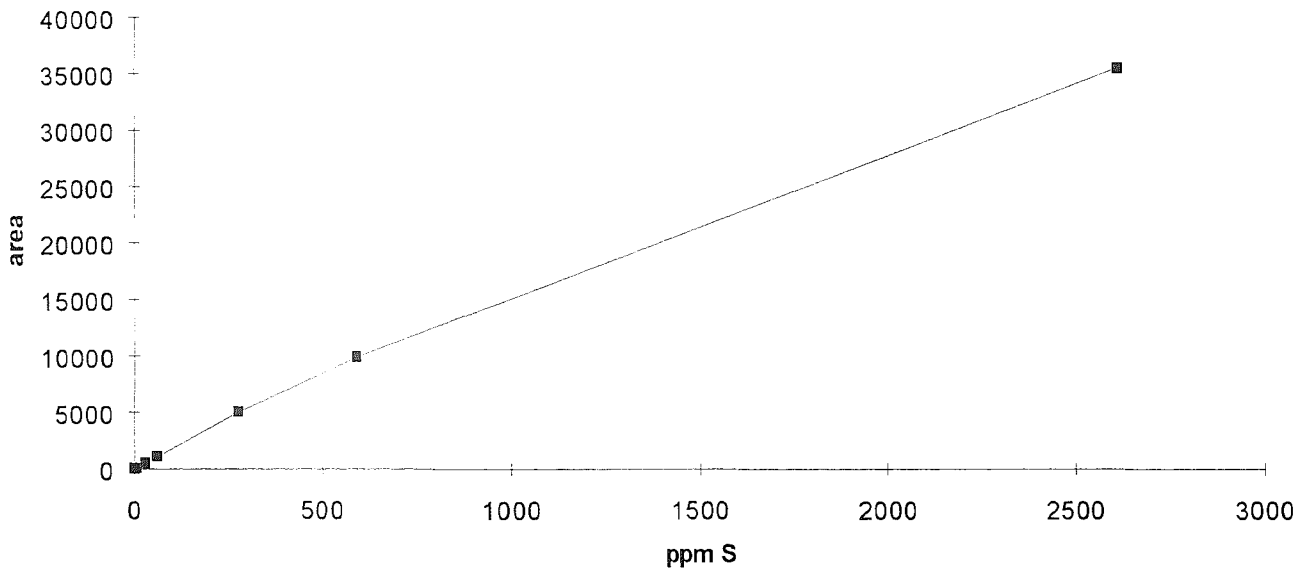# Figure 11 Calibration Curve for Thiophene using Siever's Flameless Detector

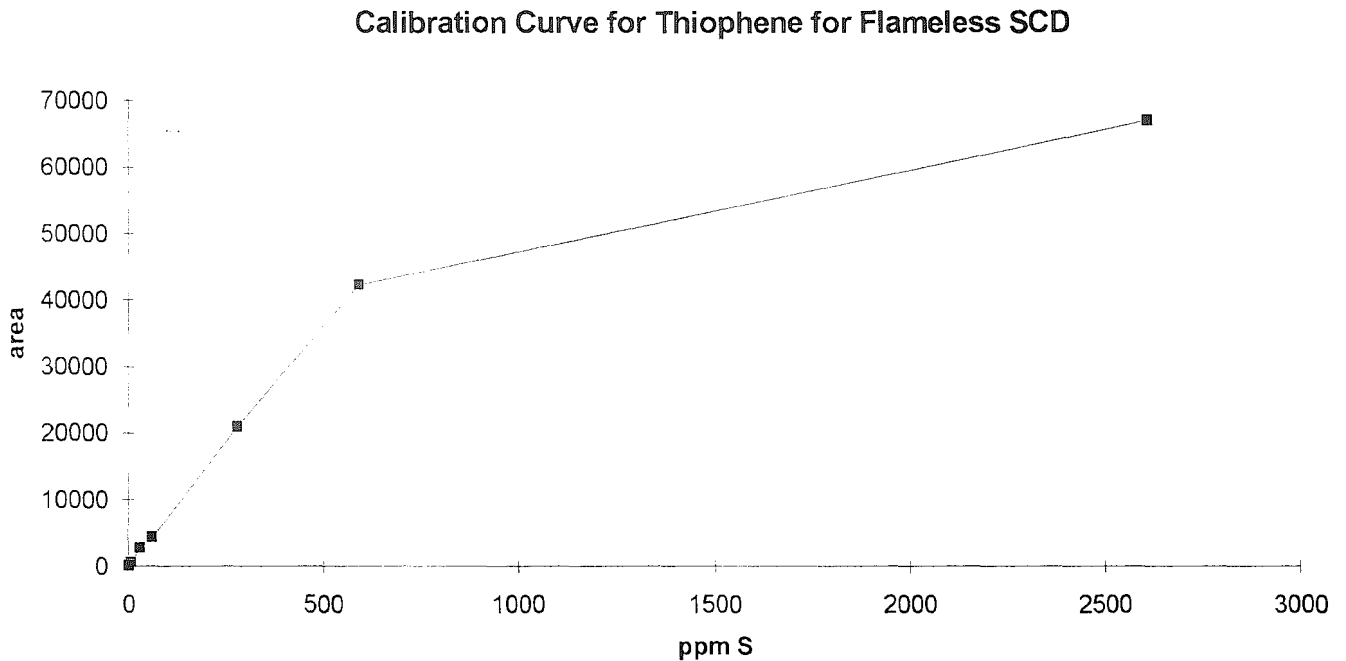Calibration Curve for Thiophene for Flameless SCD

Figure 12 Calibration Curve for Thiophene using Antek's Flameless Detector
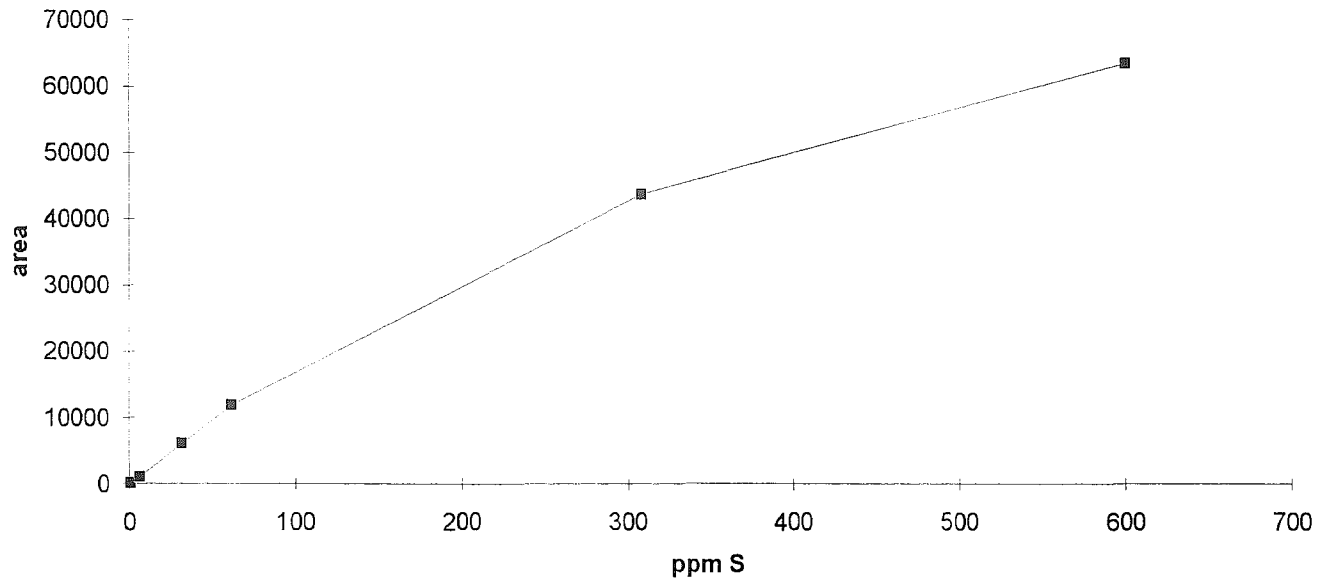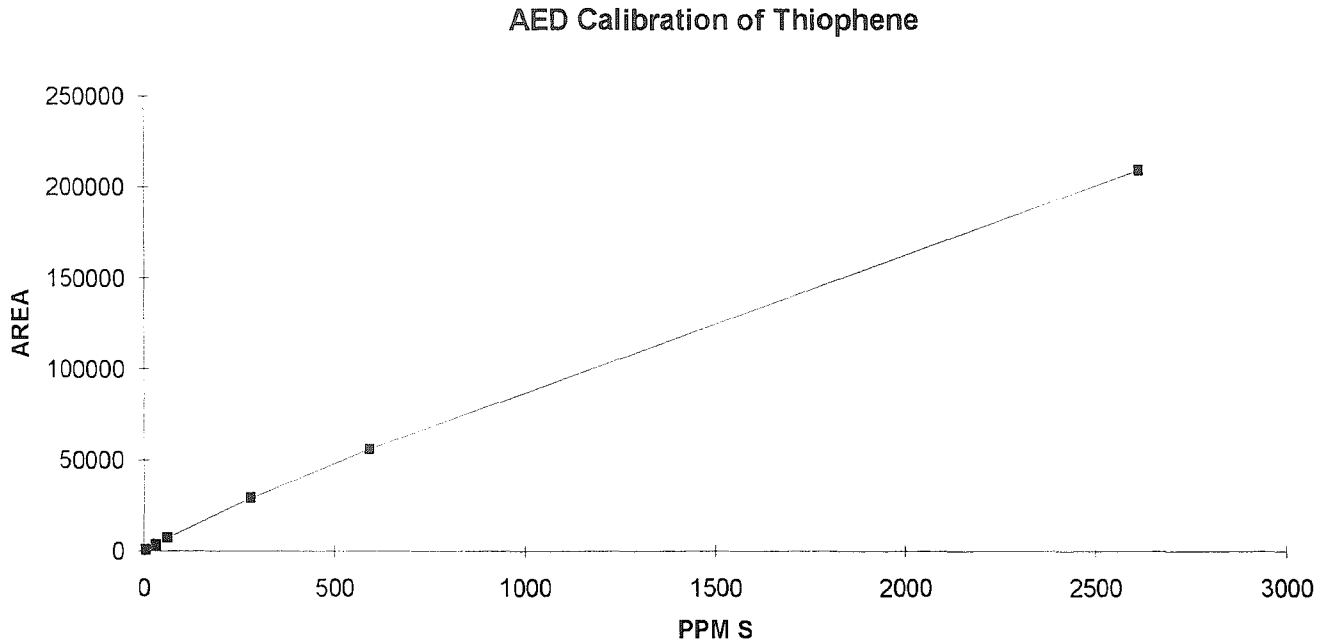

Calibration Curve for Antek Flameless For Thiophene

Figure 13 Calibration Curve for Thiophene using the Atomic Emission Detector

AED Calibration of Thiophene

achieving values of 10^7 or greater. Table 7 illustrates the selectivity values for each detector and the data used to calculate the values. In Appendix 1, the formula for the selectivity is given. Since there were no interferences detected from hydrocarbons, the signal-to-noise ratio was used as the maximum possible interference of hydrocarbons, and 1,000,000 ppm was used as the concentration of the of hydrocarobon. Selectivity was noticed to decrease if the flows were changed in the SCD instruments. By adjusting the oxygen and hydrogen it is possible to increase sensitivity and decrease selectivity. In the AED, there were some interferences from hydrocarbons. This is due to the emission of carbon being so strong carbon overtones are observed in other element channels as peaks. However, the AED software is equipped with the ability to back out this response with no effect on sensitivity or change in quantification results.

QUENCHING

Signal quenching was not observed in any of the systems. However, theoretically it is possible. Quenching is a loss of signal due to co-eluting hydrocarbon or a common solvent. Quenching would result from the loss of SO or H_2S radicals formed in the flame or furnace before they could be converted to SO_2.[3] Quenching could develop if the ozone generator was not functioning properly. The lack of ozone would cause a loss SO_2 conversion resulting in a loss of sensitivity and faulty quantification results.

COMPARISON WITH TOTAL SULFUR USING X-RAY FLUORESCENCE

All the properties discussed are important factors to be evaluated when trying to decide on a specific detector for a particular application. However, one must also evaluate the detector based upon how it performs when analyzing one's own samples. Seven petroleum samples in the naphtha, gasoline and diesel ranges were analyzed and compared to the total sulfur values obtained from x-ray fluorescence. Table 8 presents a summary sheet comparing performance of each instrument with the x-ray results. Figures 14 through 26 are chromatographs of different petroleum streams analyzed on the different sulfur detectors. Some chromatograms appear to be flat-topped. This is the result of enlarging the scale to observe the low levels of sulfur as well as the program in which the chromatogram was converted into a useful word processing form. The Antek chromatograms appear to be on a different x-scale. This is due to a slight difference in columns. At the time of this experiment the same column with a smaller diameter film thickness was used due to other pending analyses that could not be altered. This however did not change any of the areas that were examined. All instruments performed well. All detectors yielded a value within 10 percent of the x-ray value which is within an acceptable relative standard deviation for these analyses. A few samples gave deviations of more than ten percent. This is most likely the result of the computer integrating noise into the analysis. Also when the sulfur content is low the percent deviation is higher, though such cases may still be acceptable because the sulfur content is low.

All instruments were relatively easy to use. Once one determines each instrument's nuances or operation conditions, all the instruments in this evaluation are capable of being an important analytical tool for volatile sulfur analysis.

Table 8. Results from Petroleum Stream Analysis

Concentration of Sulfur, in ppm S								
SAMPLE	X-RAY	SCD FLAME		SCD FLAMELESS		ANTEK SULFUR		AED	
	Conc	Conc	%	Conc	%	Conc	%	Conc	%
LOW SULFUR GASOLINE	27	32	-18%	33	+ 22.2%	25	-7.4%	25	-7.4%
SUPREME GASOLINE	59	58	-1.6%	48	-18.1%	63	+ 6.3%	62	+ 5.1%
ASTM GASOLINE	393	374	-4.8%	361	-8.1%	406	+ 3.3%	360	-8.4%
LIGHT CAT NAPTHA	720	734	+ 1.9%	700	-2.7%	734	+ 1.9%	711	-1.3%
HEAVY CAT NAPTHA	1500	1518	+ 1.2%	1476	-1.6%	1500	-+ 0.0%	1488	-.8%
LOW SULFUR DIESEL	379	386	+ 1.8%	420	+ 10.8%	418	+ 10.3%	362	-4.5%
HEAVY SULFUR DIESEL	2210	2176	-3.6%	2200	-.4%	2136	+ 3.3%	2172	-1.7%
a) Relative difference between X - Ray Sulfur verse other Detectors									

Figure 14 Siever's Flame Analysis of Regular Gasoline
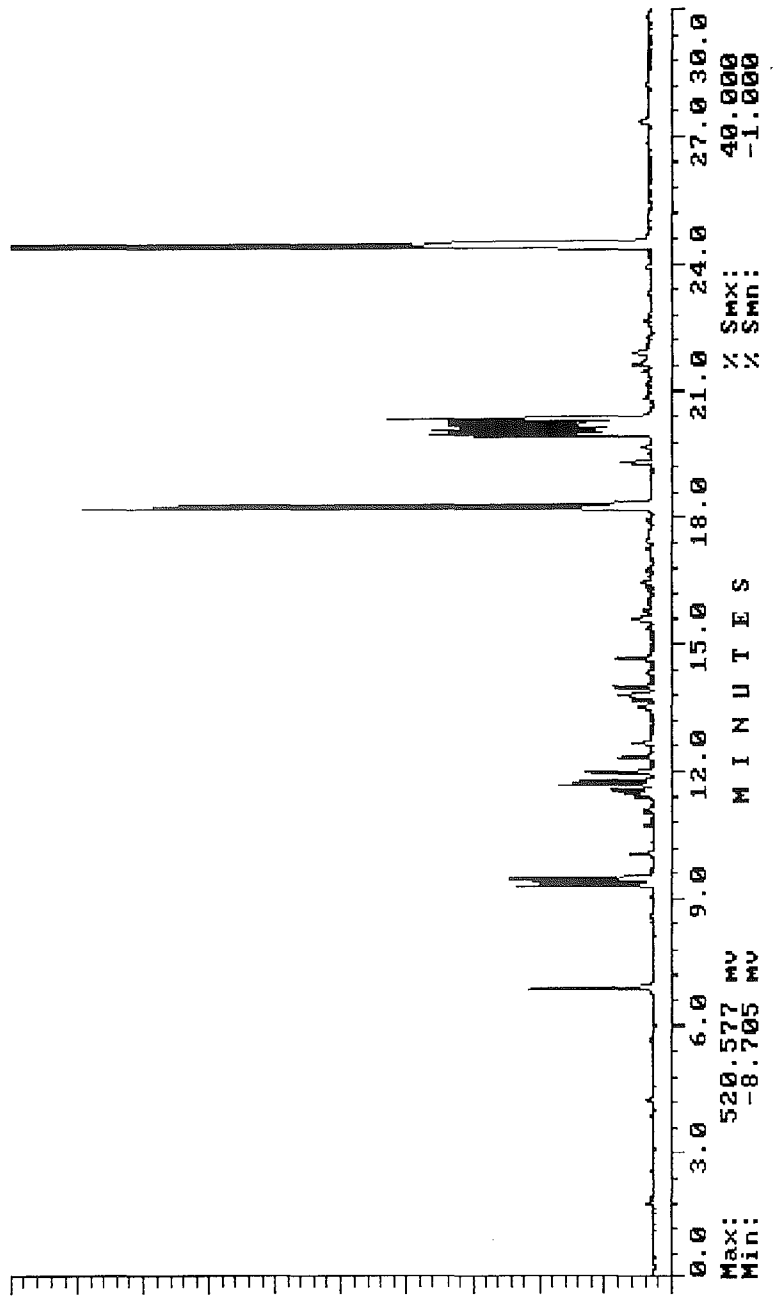
Figure 15 Siever's Flameless Analysis of Regular Gasoline

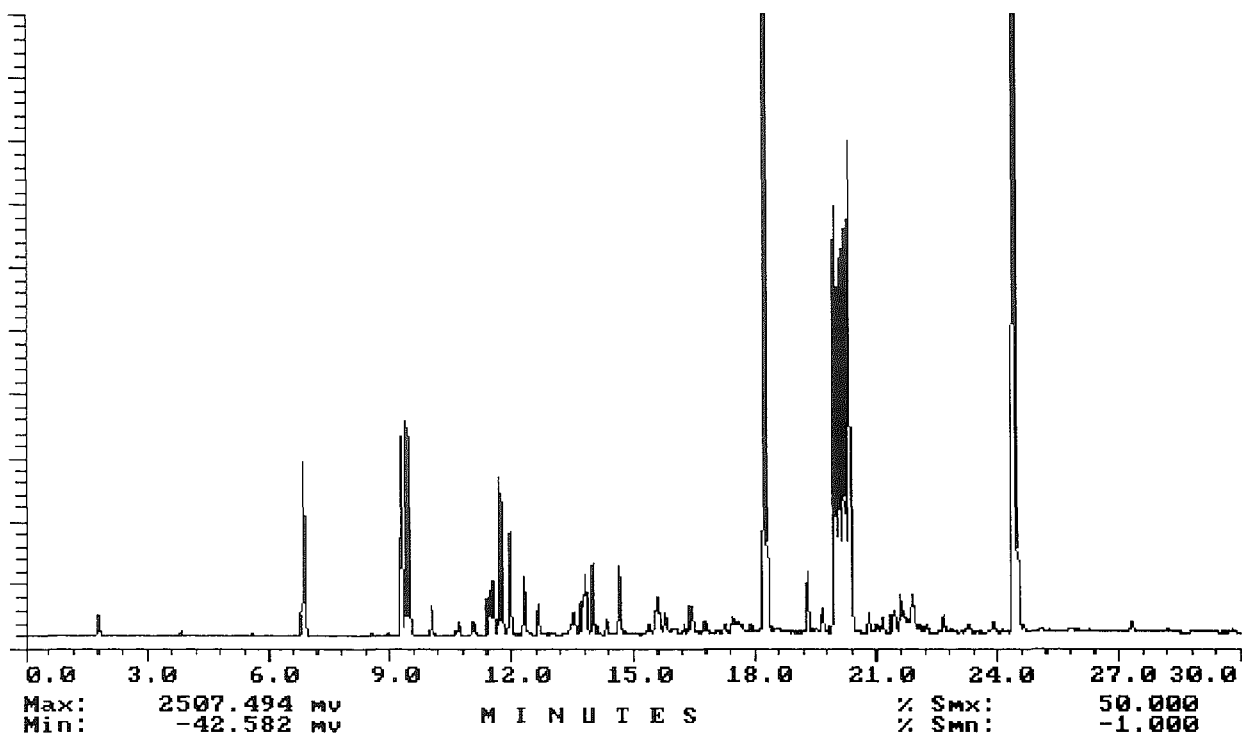|		
Max:	2507.494 mv	% Smx: 50.000
Min:	-42.582 mv	% Smn: -1.000

M I N U T E S

Figure 16 Antek's Flameless Analysis of Regular Gasoline

0.0	2.0	4.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0	20.0

Max: 5851.441 mv   % Smx: 100.000
Min: -6.457 mv   M I N U T E S % Smn: 0.000
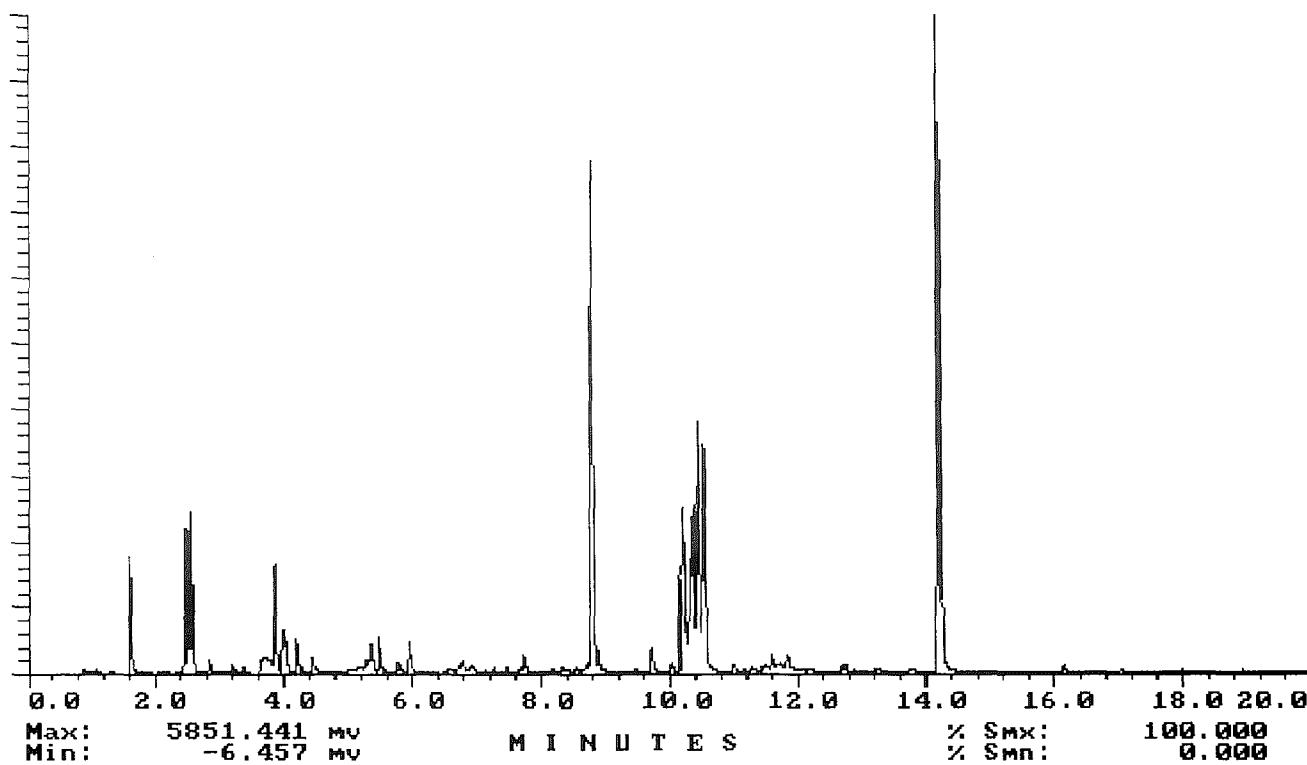
Figure 17 Atomic Emission Analysis of Regular Gasoline
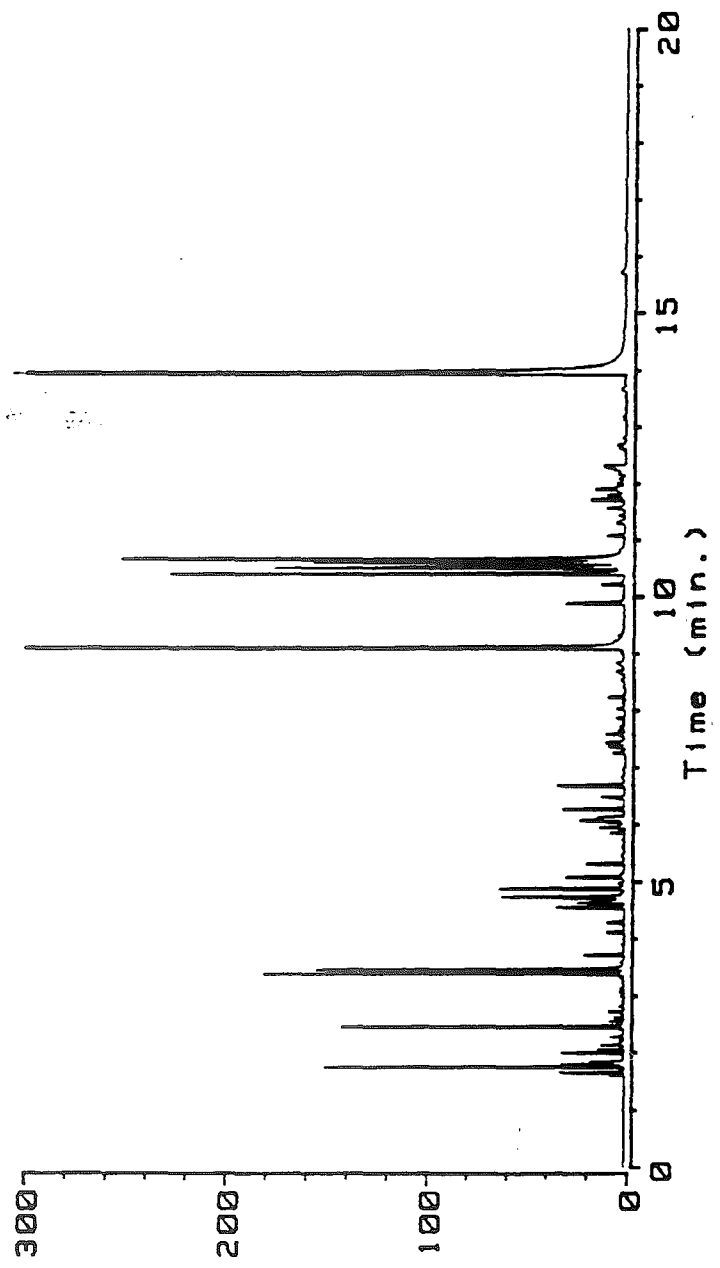
Figure 18 Siever's Flame Analysis of Heavy Cat Naphtha

Max:	442.467 mv	% Smx: 20.000
Min:	-17.078 mv	% Smn: -1.000

M I N U T E S
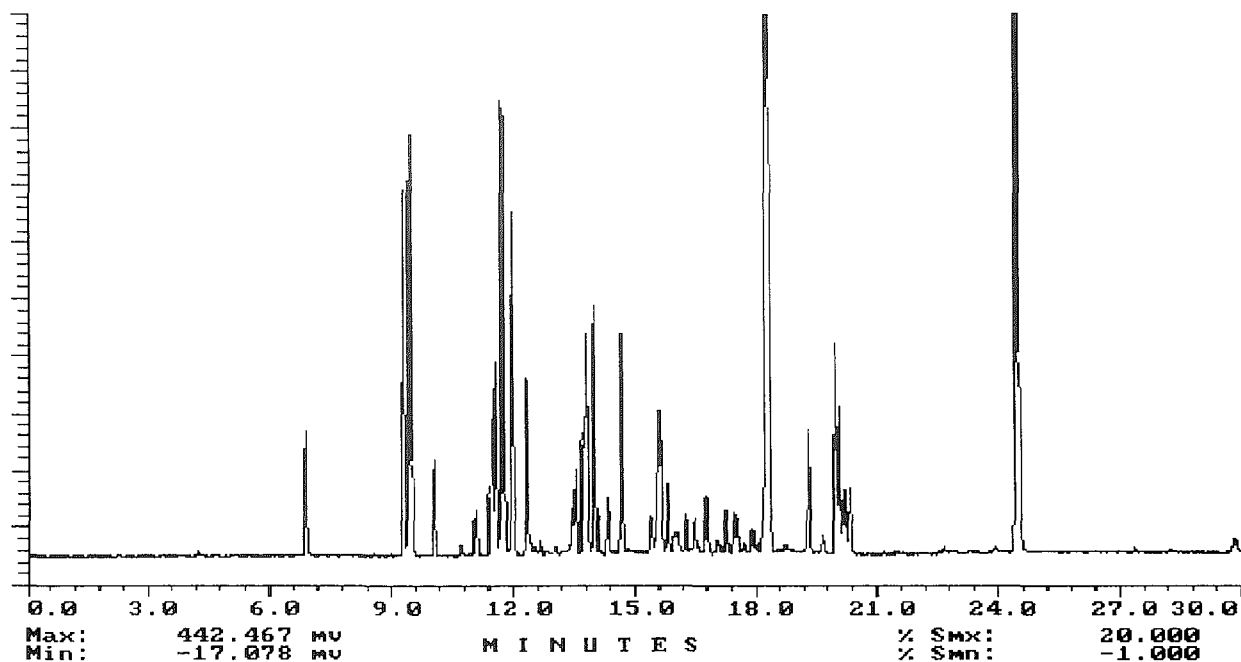
Figure 19 Siever's Flameless Analysis of Heavy Cat Naphtha

Max:	5776.978 mv	% Smx: 60.000
Min:	-96.283 mv	% Smn: -1.000

MINUTES
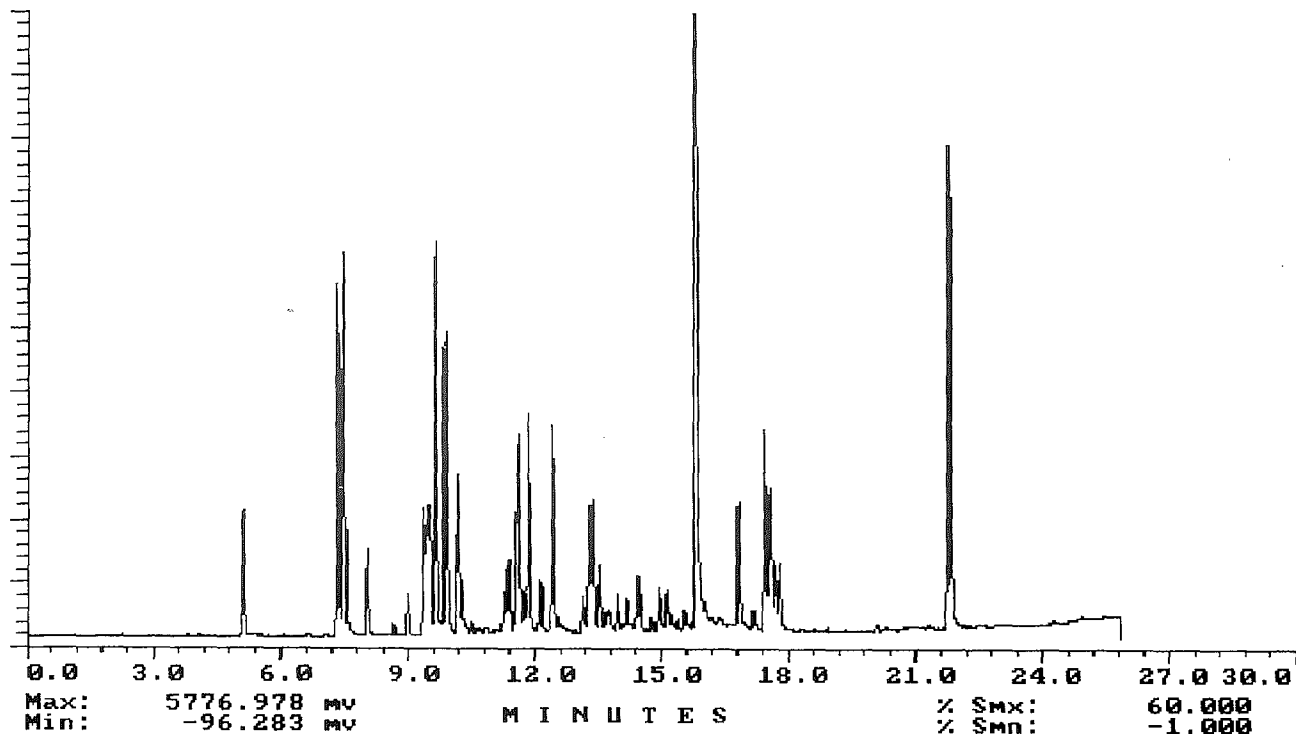
Figure 20 Antek's Flameless Analysis of Heavy Cat Naphtha

0.0	2.0	4.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0 20.0

Max: 7629.395 mv   % Smx: 100.000
Min: -7.985 mv   % Smn: 0.000

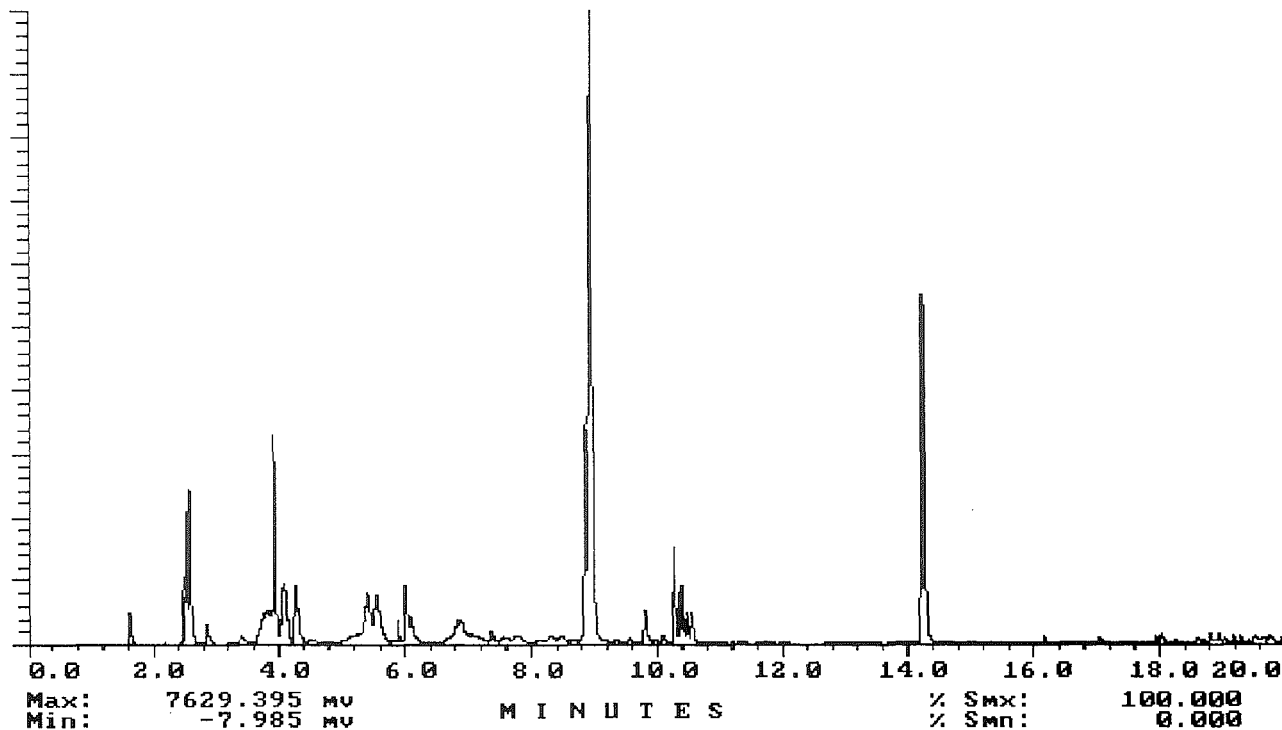M I N U T E S

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Figure 21 Atomic Emission
Analysis of Heavy Cat Naphtha
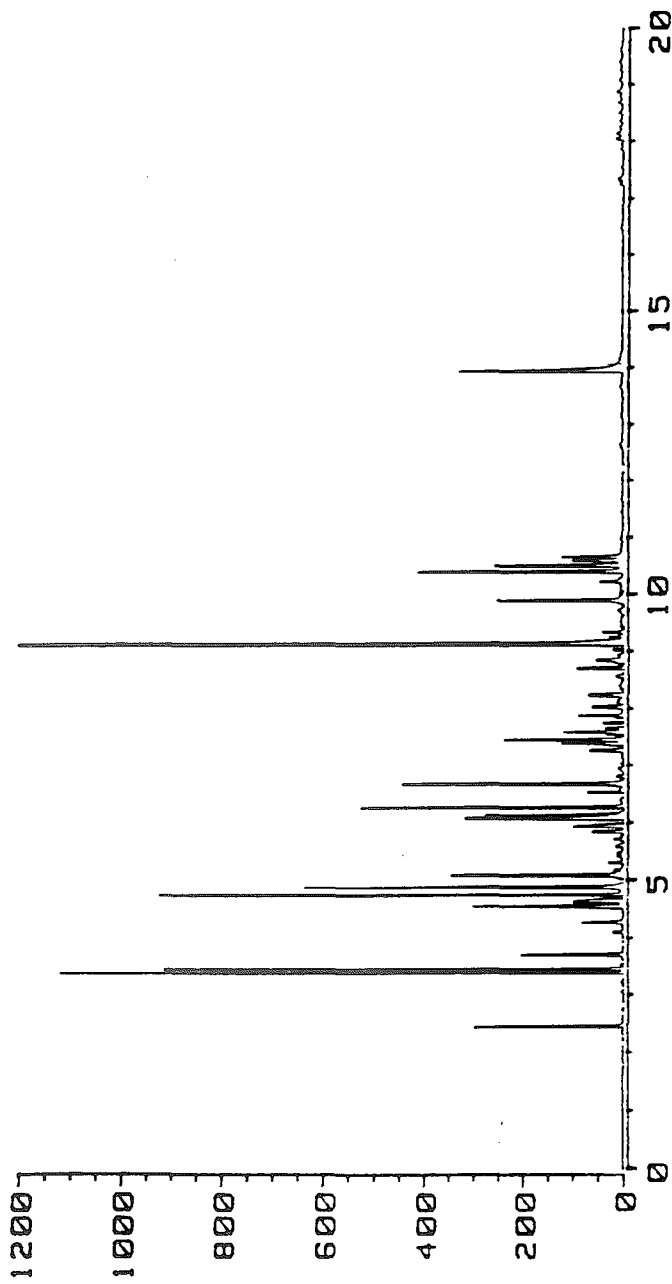
Figure 22 Siever's Flame Analysis of High Sulfur Diesel

Max:	627.185 mv	% Smx:	60.000
Min:	-5.443 mv	% Smn:	-1.000

MINUTES
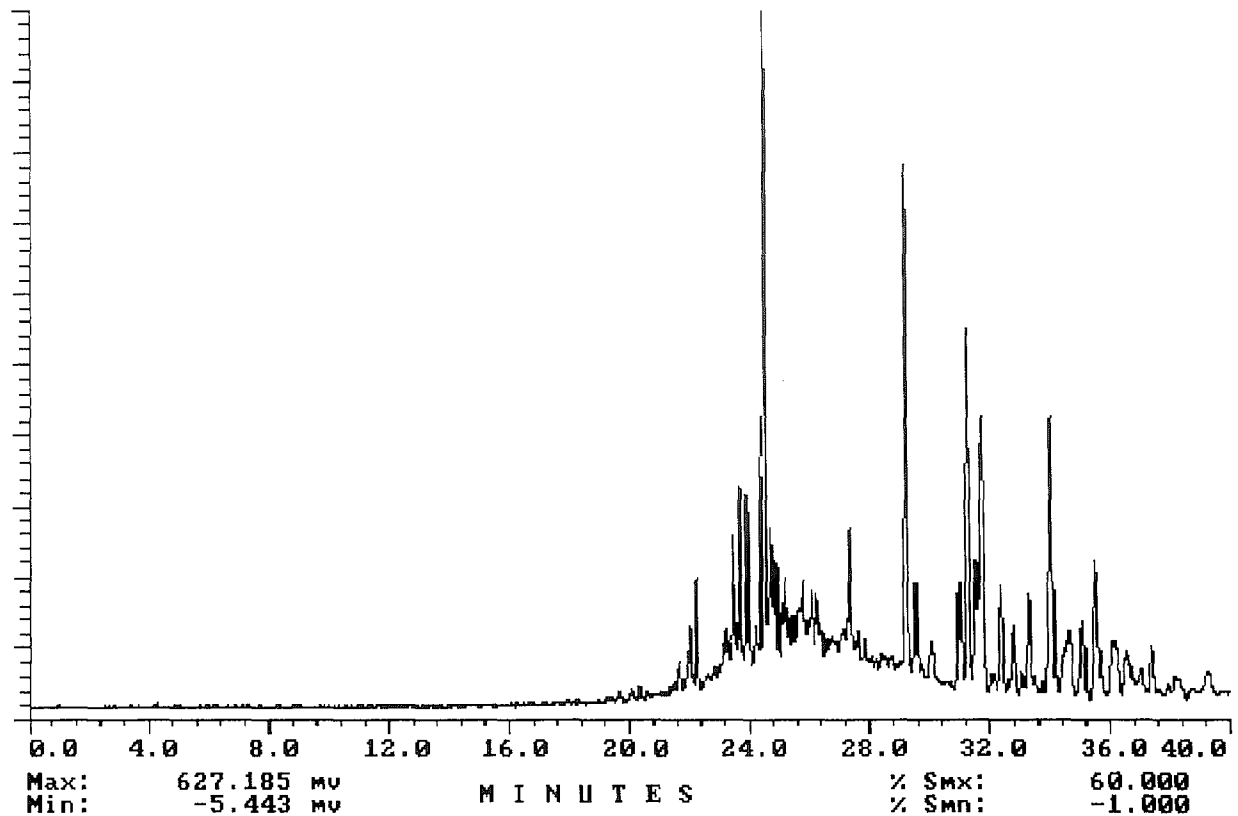
Figure 23 Siever's Flameless Analysis of High Sulfur Diesel

Max: 4024.251 mv	% Smx: 100.000
Min: -27.978 mv	% Smn: -1.000

MINUTES
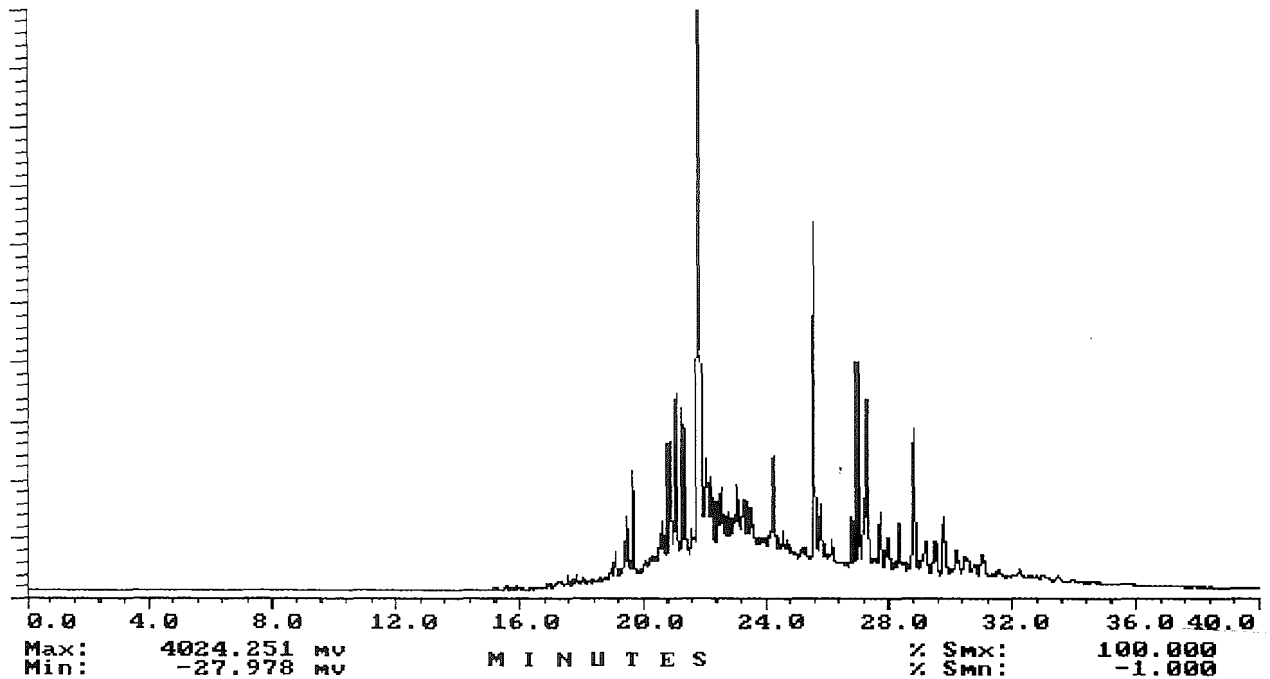
Figure 24 Antek's Flameless Analysis of High Sulfur Diesel

| 0.0 | 3.0 | 6.0 | 9.0 | 12.0 | 15.0 | 18.0 | 21.0 | 24.0 | 27.0 30.0 |

Max: 6707.520 mv
Min: -6.446 mv

M I N U T E S

% Smx: 100.000
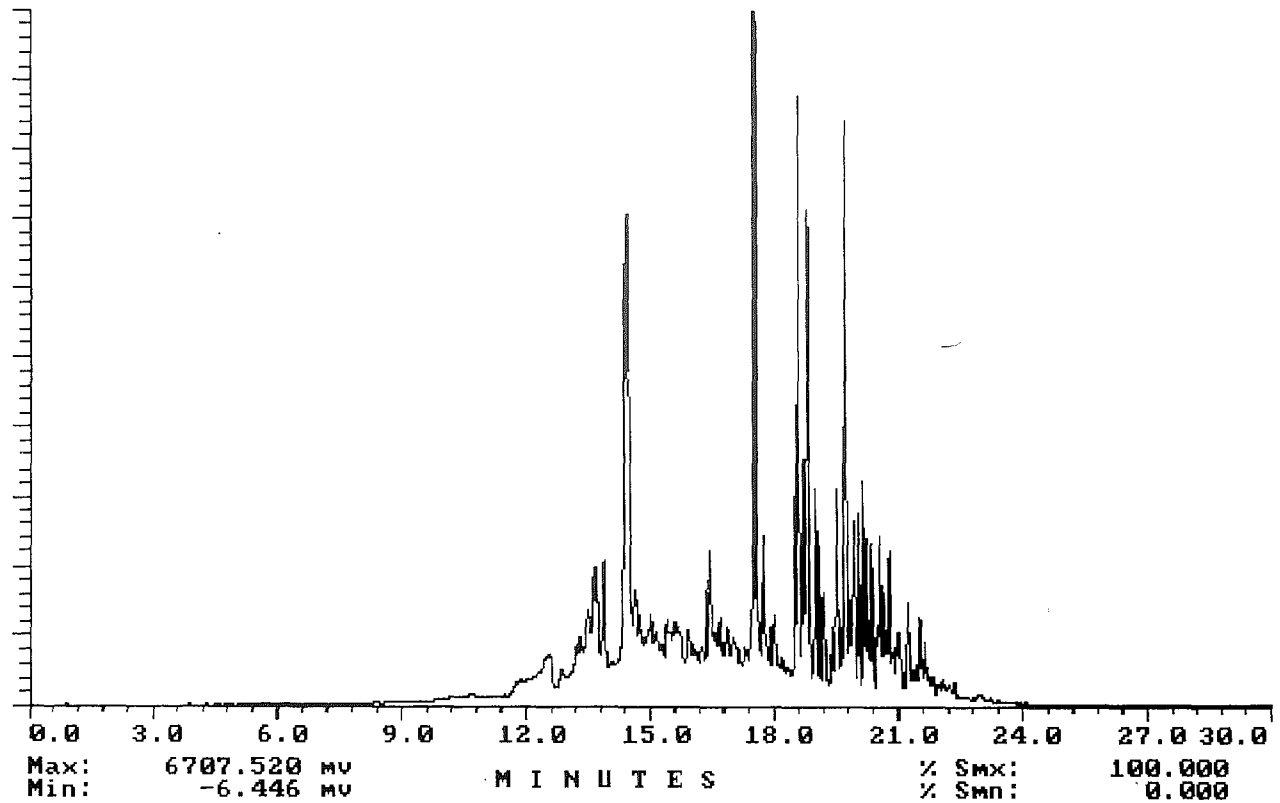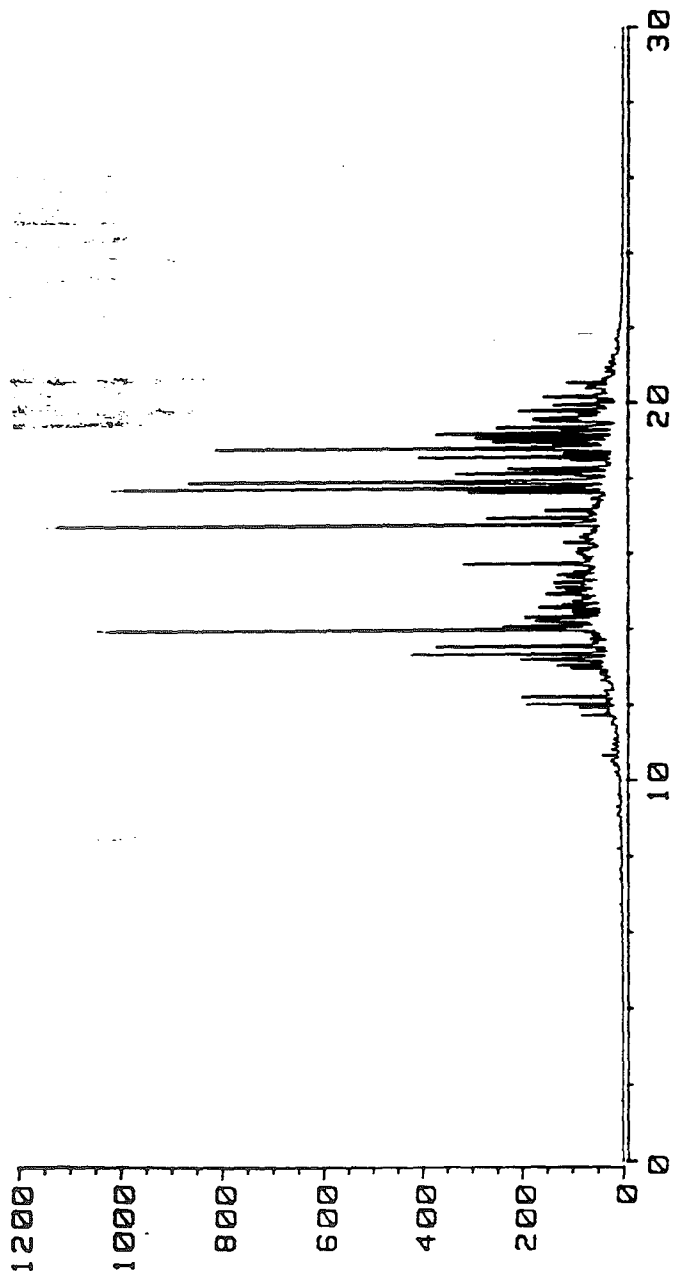% Smn: 0.000

50

Figure 25 Atomic Emission Analysis of High Sulfur Diesel

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CONCLUSION

The detectors described in this thesis will provide accurate sulfur analysis and short analysis times at a relatively low cost to the user. All the detectors provided low levels of detection with little or no interference from hydrocarbons. The flameless detectors provided a better ease of operation than the flame or the AED. They also provided the highest signal-to-noise ratios and lowest levels of detection during testing. However, the flameless systems are not capable of going to higher sulfur levels without changing the split ratio or diluting the sample. The flame system was prone to probe clogging. However this system provides the user with transfer ability from one instrument to another without modification to any standard gas chromatograph. The flameless systems require the mounting of the burner onto the top of the gas chromatograph. The flame system is capable of detecting high sulfur levels with little or no sample dilution. The atomic emission detector provides detection of most elements in the periodic table and can run up to eight elements in one automated method. However, the AED is more expensive. It also produced the largest dynamic range during our evaluation but it does have a lower selectivity. In most situations, hydrocarbon interferences can be subtracted using software. However, the AED does require skill and training for proper operation. The AED uses a glass discharge tube in the microwave plasma which does break periodically and needs to be changed. Although the replacement of this discharge tube is quick it is an inconvenience. If an analysts is using an external calibration, they do have to be re-analyzed after tube replacement because the discharge changes the response slightly. The AED software also provides simulated distillation data and gives a chemical formula for an unknown peak in the chromatogram.

In the first quarter of 1996, Hewlett Packard is expected to release a newer version reportedly with a new data system for easier use.

In order to meet the world demand for sulfur analysis in a time when sulfur emissions must be reduced, all four instruments described here will provide excellent capabilities. A user must choose which instrument meets the laboratory's needs and budget. Any detector selected from this study will be an asset.

REFERENCES

1. M. Dyson "The Sievers SCD 350 Detector." Analytical Proceedings. 30: 79-86 (Feb 1993).

2. Randall L. Shearer. "Development of Flameless Sulfur Chemiluminescence Detection Application to Gas Chromatography." Anal Chem. 64: 2192-2196 (1992).

3. Randy L. Shearer. "Gas Chromatography and Flameless Sulfur Chemiluminescence Detection." Anal Chem. 72 3258-3261 (1993).

4. Willard H. H., Merrit L. L., Dean J. A., Settle F. A. "Instrumental Methods of Analysis" Wadsworth Publishing Co. Bellmont California (1981). 540-554.

5. Sievers Instrument Company, Boulder CO.

6. Antek Instrument Company, Houston TX.

7. Hewlett Packard Company, Willington DE.

8. Thomas G. Albro, Peter A. Dreifuss, Richard F. Wormsbecher. "Quantitative Determination of Sulfur Compounds in FCC Gasoline's by AED." Journal of High Resolution Chromatography. 16: 13-17 (Jan 1990).

9. Bruce D. Quimby, Vincent Giarrocco, James J. Sullivan, Keith A. McCleary. "Fast Analysis of Oxygen and Sulfur Compound in Gasoline by GC-AED." Journal of High Resolution Chromatography. 15: 705-709 (1992).

10. Randy L. Shearer, Dee L. O'Neal, Ray Rios and David Baker. "Analysis of Sulfur Compounds by Capillary Column Gas Chromatography with Sulfur Chemiluminescence Detection." J.Chromatography. 28: 24-28 (1990).

11. Richard L. Benner, Donald H. Stedman. "Chemical Mechanisms and Efficiency of the Sulfur Chemiluminescence Detector." Applied Spectroscopy . 48: #7 848-851 (1994).

12. Analytical Methods Standard "The Determination of Total Sulfur in Gasolines, Diesel Fuel and Jet Fuel"

APPENDIX 1

Limit of Detection in wt S / ul

$$\frac{3 \ X \ S/N \ X \ Concentration}{5 \ \text{and height of peak in mv}}$$

Limit of Detection in wt S/sec

$$\frac{3 \ X \ S/N \ X \ Concentration}{5 \ X(\text{peak height in mv}) \ X \ (1/2 \ \text{peak width s})}$$

Dynamic Range

$$\frac{\text{Concentration of Highest Std}}{\text{Limit of Detection}}$$
At 5% diviation from linearity

Skew Value

$$\frac{\text{Time of A}}{\text{Time of B}}$$
At 95% peak height

Selectivity

$$\frac{\text{Height Analyte} \ X \ \text{ppm interference}}{\text{Height interference} \ X \ \text{ppm Conc Analyte}}$$

VITA

Robert R. Wehman Jr. was born on May 5, 1967 in the Bronx (New York) to Robert and Diane Wehman. After graduating Toms River High School East in 1985 he attended King's College in Wilkes Barre Pennsylvania. At King's Bob was a laboratory assistant for Dr. Chin Cu Lee. In 1989 he graduated with a Bachelor of Science Degree in Biology with a minor in Chemistry.

Later that year Bob accepted employment at Exxon Research and Engineering Company in Annandale New Jersey in the Gas Chromatography Laboratory of the Analytical Sciences Division, during this time he married Kim Hoff. He has received several divisional and company awards. His employment has taken him to far and remote places such as Billings Montana, Edmonton Canada and Sakai Japan.

During his employment at Exxon, he enrolled in Lehigh University, part time, to pursue a Masters Degree in Chemistry. After three-and-one-half years Bob received his Masters in June of 1996.

Bob is still employed at Exxon, and this degree promises more exciting challenges and responsibilities he waits to conquer.

END OF
TITLE