

NWRI CONTRIBUTION 90-106

**ANALYSIS OF FUELS FOR ORGANO
SULPHUR AND PHOSPHOROUS COMPOUNDS
USING AN ATOMIC EMISSION DETECTOR**

by

Brian F. Scott and Alain R. Cassista

**Canada Centre for Inland Waters
867 Lakeshore Road, P.O. Box 5050
Burlington, Ontario
L7R 4A6**

January 1990

**Analysis of Fuels for
Organo Sulphur and Phosphorous Compounds
using an Atomic Emission Detector**

by

Brian F. Scott¹ and Alain R. Cassista²

¹ Research and Applications Branch, National Water Research Institute, C.C.I.W., P.O. Box 5050 Burlington, Ont.

² National Water Quality Laboratory, C.C.I.W. P.O. Box 5050, Burlington, Ontario, Canada.

MANAGEMENT PERSPECTIVE

A new analytical technique combining separation by gas chromatography (GC) and detection by atomic emission (AED) was used to screen for sulphur and phosphorous organic compounds in fuels samples. This technique is gas chromatography with an attached atomic emission detector(AED). Studies on the linearity of the detector response, reproducibility, and the ability to discern spiked impurities in fuel samples at the 1 ppm level indicated the technique was ideally suited to detect contaminants in fuels. In total 332 fuel samples from across Canada were screened by the GC/AED technique. One sample from the Ontario Region and samples with the same series designation from the Quebec region were subjected to further analysis by GC/MS. A coal oil sample was found to contain high concentrations of benzo- and dibenzothiophene. The suspected sulphur compounds in some used oil samples could not be identified by GC/MS because of analysis interferences produced by the PAHs present in the samples. There were no suspected phosphorous-containing contaminants found in the samples.

PERSPECTIVE-GESTION

On a employé une nouvelle technique d'analyse pour déceler la présence de composés organiques soufrés et phosphorés dans des échantillons de carburant. Cette technique utilise un chromatographe en phase gazeuse (CG) muni d'un détecteur d'émission atomique (DÉA). Des études portant sur la linéarité de la réponse du détecteur, la reproductibilité des résultats et la capacité de déceler 1 ppm d'impuretés ajoutées aux échantillons de carburant ont révélé que cette technique convient parfaitement au contrôle des contaminants dans les carburants. Au total, nous avons contrôlé, à l'aide de cette méthode, 332 échantillons prélevés un peu partout au Canada. Un échantillon provenant de la région de l'Ontario ainsi des échantillons de la même désignation provenant de la région du Québec ont été soumis à une analyse plus approfondie par CG/SM. Un échantillon d'huile présentait des concentrations élevées de benzo- et de dibenzothiophène. Les composés soufrés dont on soupçonnait la présence dans certains échantillons d'huile usée n'ont pas été identifiés en raison de l'effet perturbant des hydrocarbures aromatiques polycycliques (HAP) que contenaient ces échantillons. Aucun contaminant phosphoré n'a été décelé dans les échantillons.

ABSTRACT

The GC/atomic emission detector (AED) technique is a new method that facilitates the analysis of environmental samples. This new method was used to investigate fuel samples for possible contamination by organo-phosphorous or sulphur compounds. Prior to the analysis of several hundred samples collected from across Canada, a series of preliminary studies were conducted including instrumental reproducibility, linearity of detector response, and dependence of the response on the compounds. In addition, extracts of uncontaminated fuels were analyzed to estimate the range of additives and indigenous compound which are normally found in these fuels. The reproducibility as measured by the coefficient of variance, was below 0.06% on the S channel and about 3X greater on the P channel. The response of the detector was linear over the range of 0.1 ng/uL to 10 ng/uL for the S channel. It was found that the response for the 26 compounds used as standards on either the S and P channel depended on the compound being analyzed, although the response was within a factor of 10 for all compounds on each channel. From the analysis of the fuels, there were more compounds detected on the S channel than on the P channel and at significantly higher concentrations.

RÉSUMÉ

La technique par chromatographie en phase gazeuse (CG) avec détection par émission atomique (DÉA) est une nouvelle méthode qui permet d'analyser plus facilement les échantillons environnementaux. On a utilisé cette méthode pour contrôler la présence de composés organiques phosphorés et soufrés dans des échantillons de carburant. Avant de procéder à l'analyse de plusieurs centaines d'échantillons prélevés un peu partout au Canada, on a effectué une série d'études préliminaires portant, entre autres, sur la reproductibilité des résultats obtenus, la linéarité de la réponse du détecteur et la relation entre la réponse et les composés. De plus, on a analysé des extraits de carburants non contaminés pour déterminer quels additifs et composés s'y trouvent normalement. La reproductibilité, qui a été mesurée à partir du coefficient de variation, était inférieure à 0,06 % sur la canal S et environ trois fois plus sur le canal P. La réponse du détecteur était linéaire dans la plage de concentrations de 0,1 - 10 ng/ μ L pour la canal S. La réponse des 26 composés utilisés comme étalons sur l'un ou l'autre des deux canaux dépendait du composé analysé, même si les réponses pour tous les composés sur chaque canal se situaient dans une fourchette correspondant à un facteur de 10. L'analyse des carburants a révélé que le nombre de composés décelés sur le canal S était plus élevé que le nombre de composés décelés sur le canal P, et que les concentrations mesurées étaient beaucoup plus élevées.

INTRODUCTION

A variety of organic contaminants can be illegally added to petroleum products. Consequently the analysis of fuels for possible contaminants requires a number of analytical techniques being used. Organochlorines including PCBs can be analyzed using dual capillary column GC with dual electron capture detectors (Scott & Onuska, 1989) or GC/MS. Organo-metallics can be analyzed using Atomic Absorption spectroscopy. The analysis of sulphur, phosphorous and nitrogen containing organics can be achieved by using flame photometric and nitrogen-phosphorous detectors. The thrust of the combined National Water Quality Laboratory (NWQL) and Research and Application Branch of the National Water Research Institute (NWRI) investigation was to develop a method to analyze a large number of samples for heteroatom compounds, especially organophosphorous and organosulphur compounds. The method had to be automated as a large number of samples had to be analyzed, it had to have a detection limit lower than 1 ppm and it had to be capable of being interfaced with a computer to assist in the data analysis. After evaluating existing methodologies utilized in the NWQL and NWRI laboratories to ascertain if any could meet the above criteria, it was decided that the on-site equipment did not have the necessary capabilities. Recent advances in analytical instrumentation were surveyed and the only system that could meet the above criteria was a gas chromatograph equipped with an Atomic Emission Detector (AED). Only one of these instruments existed in Canada, and it was secured for fuel analysis.

As this was a new technique, some development studies had to be conducted before the fuel samples could be analyzed. These included the reproducibility of the system, the relative responses of the two hetero-atoms (S and P) in different molecular structures, the linearity of the detector and the response of

spiked samples. Then a quick method for the screening of many samples had to be developed after which suspect samples could be further analyzed. At first, the sample is injected by splitless injection mode onto a capillary column housed in a gas chromatograph constructed so that the small potential amount of gas leakage at unions is minimal. The other end of the column is enclosed in a heated sleeve which is attached to the AED. By means of a discharge tube, the effluent of the column enters the microwave induced He plasma to undergo complete combustion (2000°C) and the elements of the effluent molecules are subjected to atomic spectroscopy. Each constituent element has a specific emission spectrum. The spectral emission lines are separated by a grating in the spectrometer portion of the detector, and a photodiode array monitors specific wavelengths of interest. The data are transferred to a work station where a small computer presents the data so that they can be more easily interpreted or manipulated by the operator.

Not all elements can be monitored at the same time, so that several injections of the samples may be necessary to obtain the total information required by the analyst. This results from two limitations of the instrument. First is that to optimize the response for different elements, different plasma conditions are necessary. Second, the photodiode array has a fixed length and cannot span the entire emission range. If one sample is to be analyzed for compounds containing the three elements S, P, and Cl, three injections are necessary. Sulphur requires a mixture of H₂ and O₂. Sulphur and chlorine require the same reagent gases but the diode array cannot span the range required to monitor S₁₈₁ and Cl_{479.5}. However C₁₉₃, N₁₇₄ and S₁₈₁ can be monitored in a single injection as can C₂₄₇ and Cl_{479.5}. To monitor S₁₈₁ and P₁₇₈ two injections are required. The results from the separate injections of a sample can be combined by the computer to present an overlay of spectral chromatograms, so that maximum information can be gleaned from the results.

Standards for calibration and other preliminary studies were prepared from available phosphorous and sulphur containing pesticides analyzed in the National Water Quality Laboratory. These were combined into three solutions. Also one of these standards was used regularly during the analysis of the fuels as a calibration standard.

Analysis of fuels is an extremely complex task. The only elements not generally found in petroleum are the halogens. All other elements can be found in at least trace amounts. At each step of petroleum processing, starting with removing the virgin oil from its reservoir, chemicals may be added to facilitate the flow and other handling characteristics. Once it is refined, other chemicals, which help the fuel to combust efficiently are added. These chemicals often contain heteroatoms. As the additives are commercial preparations, byproducts and other impurities are also added to the fuel although usually in smaller amounts. The oil in each reservoir is different from that found in other reservoirs, with the characteristics of the oil in any one reservoir changing as one goes from the surface of the reservoir to the bottom. At the refinery, the crude oil feed stock may be from several sources and the operating parameters of the refinery vary from day to day. This causes alterations in the product. Similar conditions exist for the manufacture of the additives. This serves to show that a wide variation in fuels of the same type is expected and there will be at least seven different types of fuels analyzed. One other factor is the change in formulation as well as the amount and types of additives included which are dependent on the time of year. Some additives are added in the range of low parts per hundred.

When analyzing fuels at a refinery operation, the focus is on quality control; when analyzing fuels at a forensic laboratory the focus is usually on the source of the oil, i.e. who is responsible for a spill. These analyses generally monitor the hydrocarbon

profile relying on a flame ionization detector. In analyzing for contaminants, especially when the contaminants contain heteroatoms, the analyst must first decide if a certain peak or peak pattern is a result of some indigenous constituents or is the result of a legal additive. Additives are usually chemical mixtures whose formulations are industrial secrets. The investigation of fuels for sulphur and phosphorous contamination was undertaken being cognizant of the difficulties mentioned above.

METHOD

The primary standards along with their formulae and molecular weight are listed in Table 1. The compounds were obtained as pure samples from the National Repository (Washington D.C.) and were made up in individual stock solutions using methanol as solvent. Three standard solutions were prepared at a concentration of 1 ng/ul per individual compound in isooctane. The first solution contained phosphamidon, crufomate, diazinon, parathion, methylparathion, ronnel, fenitrothion, dimethoate, phorate and ethion. Included in the second standard were guthion, ethylguthion, dimethoate, phosmet, carbophenothion and disulfoton. In the third standard was diallate, triallate, butylate, metribuzin, both endosulphans, phosphamidon and malathion.

The gas chromatograph was a Hewlett-Packard (HP) model 5890 which was specially fabricated so that there were minimal leaks at the unions of the fittings. Samples were injected by an HP7673a automatic sampler which delivered 1 uL of sample into a split/splitless injector operated in the splitless mode. The injector was maintained at 250°C and the purge time was 0.75 min. A capillary column (30mX0.25mm) with a 0.25u SE-52 XL liquid phase (HIRESKO, Mississauga, Ontario) was used for all determinations. Helium, with a column head pressure of 16 psi and an initial flow rate of 3 mL/min, was used as carrier gas. For the screening of

samples, the following oven settings were used: initial temperature of 80°C was maintained for 2 min, followed by a ramp of 10°C/min to 140°C, then the ramp was changed to 50°C/min until a maximum temperature of 260°C was reached and this temperature was held for 14 min. Each analysis takes 21.2 min. The temperature of the transfer line from the GC to the AED was maintained at 260°C. An HP5921a atomic emission detector was utilized for all the analysis. A solvent vent time of 2 min was initiated at 1.6 min to prevent the solvent from extinguishing the flame. After the first of two injections, the emission wavelengths of 193(C), 180.7(S) and 174.2(N) nm were monitored and after the second injection, the wavelength of 178.1(P) nm was monitored. The results were automatically transferred to the HP GC/AED/Data System at the work station.

For preliminary studies, fuel samples were treated as follows. A known amount of an uncontaminated fuel was weighed into a vessel and subjected to cleanup (Water Quality Methods Manual) and then a known aliquot of standard solution #1 was introduced. The volume was reduced to a known amount and placed in a vial ready for injection onto the GC/AED system.

Statistical studies were conducted using the results from 10 individual injections. For preliminary studies, isooctane blanks were injected as every third sample. Linear response range studies were made on concentrated or diluted aliquots of the standard solutions. Concentrated solutions were prepared by gently distilling off known volumes of solvent.

RESULTS

The first aspect that had to be examined was the reproducibility, with respect to retention time and response. Table 2 column 2, lists the means of the responses for each of the compounds used in the standard solutions, both for sulphur and phosphorous channels. Two of the compounds are listed twice as they were constituents in two solutions. Column 3 of Table 2 lists the coefficients of variance (CV) as percent, derived by dividing the standard deviation by the mean and multiplying by 100. Results from the S channel generally give a CV of 5%. Considering that these values were derived within a week of receiving the instrument and using splitless injections, these values are very good. The CV derived from the P channel are approximately three times greater than the values from the S channel. Even these higher values are reasonably good, considering that splitless injections are used. The poorer reproducibility on the P channel can be attributed to the combusting phosphorous interacting with the cavity, thereby producing longer tailing peaks. This is shown in Figure 1, which illustrates the response from the S and P channels for Standard #1. Despite this, the most striking feature of the values listed in column (2) is the range of values for different compounds in the S channel (1143 to 197) and the P channel (778 to 283). However as can be seen from the compound list in Table 2, several of the compounds have more than one of the same hetero atom. Therefore the equivalent response was calculated at the ng/uL concentration level. The resulting values are listed in column (3) of Table 2. The equivalent responses derived from the P channel have the same range as the mean responses with extremes of 778 and 32. For the responses derived from the S channel, the equivalent responses have a much smaller range than the mean responses, being reduced from 1143 and 115 to 388 and 57, excluding methylguthion. Both the mean response and the equivalent response at the lng/uL for each

compound was divided by the molecular weight of the compound to give the Molar response and Equivalent Molar response at 1 ng/uL. These values are listed in columns (5) and (6) of Table 2. Again there is a significant variation between the results obtained from either channel. The range encompasses a factor of 10. Since unknowns will be studied in a fuel matrix, this factor was considered small enough that high levels of compounds could be easily detected and their identification be established using GC-MS techniques. The variation in the response which is dependent on the compound is contrary to literature from the instrument manufacturers and their published work (Sullivan and Quimby, 1989). They state that the response on a particular channel, citing C_{247.8}, Cl_{479.5}, H₄₈₆ and O₇₇₇, is independent of the compound, and therefore manipulating the results could provide some clue as to the compound's formula. Based on the variation in response on the P and S channel for a series of compounds using splitless injection, the conclusion reported by Hewlett-Packard personnel cannot be applied to P and S compounds. Attempting to account for the variation in response by chemical structure proved to be complex.

Two compounds, dimethoate and malathion are present in two of the standard solutions. Dimethoate is in solutions #1 and #2, while malathion is in solutions #2 and #3. The values for dimethoate derived from both the S and P channels are within 10% of each other, while the values for malathion are within 4% of each other. No value is given for the CV of methylguthion from the P channel as its response was only present in two of the ten runs used for determining the mean response. The methylguthion from the S channel in Table 2 only refers to the retention time. This sulphur peak is weak at the concentrations used and it was below the value selected as noise over baseline.

Column (6) of Table 1 lists the retention times for the compounds in the standard solutions obtained under the operating conditions used. Values listed in the P channel agree with those

derived from the S channel, within ± 0.02 min. This small range of variation is necessary when investigating fuels for possible contaminants. The fact that there is such good agreement for the retention times is remarkable as during the analysis, the gc oven temperature was increased $50^{\circ}\text{C}/\text{min}$.

Table 3 contains the results for the linearity of response studies. Each value is the average of three injections per channel. For the S channel, the results exhibit good linearity over the concentration range studied. Results from the P channel exhibit considerable variation. This variation probably arises from the P interacting with the plasma cavity.

As the intent was to analyze fuel samples for possible S and P contaminants, it was necessary to examine fuels that were known to be uncontaminated and spike these fuels with one of the standard solutions. This serves two purposes. First, to ascertain if the spikes which were added as surrogate contaminants at the 1 ng/ul level could be detected in the resulting chromatograms. Second, as the concentration of each of the spiking components is known, to ascertain if it is possible to estimate the concentrations of unknowns within a factor of 10. Chromatograms for the unspiked fuels studied are shown in Fig. 2. These fuels include gasoline, #1 fuel, #2 fuel, diesel fuel, kerosene and #6 fuel oil. The most obvious difference between the result from the P and S channels for the same fuel is that there are more compounds detected with higher responses on the S channel than on the P channel. As the response for the S containing compounds are generally the same magnitude as the P containing compounds (Table 2), the concentrations of the various S compounds in the fuels are at least a factor of 10 greater than the P containing compound. This indicates that more S containing compounds are used as additives than those containing P. The chromatograms for the #6 fuel, more commonly called Bunker C, shows the least detector response activity of all the fuels examined. This fuel is generally the residue of the refining

operation and is used in heating plants and as fuel for large ships. The specifications for this fuel are not as stringent as for other fuels, so fewer additives are used. Chromatograms for the spiked fuels are shown in Fig. 2 and should be compared to those of the spiking solution, standard 1, shown in Fig. 1. All chromatograms obtained from the P channel exhibit the pattern of the P channel in Fig 1. Results of the spiking for the S channel are more complicated. Only in the chromatogram of the #6 fuel are all components of the spike solution discernible by simple inspection. In the other chromatograms the spike components are present but embedded in the peak pattern of the other S components. While analyzing this series of solutions it was evident that the chromatography was becoming poorer as indicated by the increasing retention times and more asymmetric peak shape on the S channel. This was caused by a faulty valve in the detector. Still it was possible to distinguish the components of the spiking solution. The relative responses of the peaks, as measured by the area, are what is anticipated. As the spike solution contains the constituents at the 1 ppm level, the P channel contains compounds at the ppm level and lower, while the S channel contains compounds at least at the 1 ppm level and usually higher.

More than 330 samples from various regions across Canada were analyzed and only two sets of samples required further investigation. The first was a coal tar sample whose chromatogram from the S channel is shown in Fig. 3(a). The initial two large peaks are considerably higher than any of the peaks observed in all the other samples, and these two peaks overwhelm all other peaks. To ensure that these two peaks represent chemicals that contain S, other features of the AED/Data System were utilized. This method involves using a "snapshot" and it can only be obtained from the data file that has just been collected. Before the instrument prepares the result files for the next sample, all the data for the previous result file are in the small computer and it has not been subjected to data reduction. These data can be envisioned as

consisting of a number of chromatographic overlays each collected at small time intervals, different from the others. For a particular time, in this instance at the maximum peak height for the suspected contaminant, the overlay is separated from the others. Then a second time is selected, just before that time when the emission peak was observed. The results in this overlay are subtracted from the first overlay to eliminate any background anomalies. For the two peaks of interest in Fig 3(a), the snapshots are shown in Fig 3(b) and 3(c). Each element usually has several emission spectral lines, and these can be used to confirm the presence of that particular element. Usually spectral measurements use the most prominent to determine the presence or concentration of an atom, as in the present case for S. The major S line occurs at 180.7 nm, but there are also two others, falling at 182.0 and 182.6 nm. These are the same peaks that are visible in Fig 3(b) and (c). Accordingly, the large peaks in Fig 3(a) are due to a S containing molecule. When the sample was subjected to GC/MS studies, considerable difficulty was encountered as PAHs interfered with the areas of interest. Eventually, MS patterns for benzothiophene and dibenzothiophene were obtained. An authentic sample of dibenzothiophene confirmed that these were the compounds of interest. Further analysis by GC/MS and AED estimated the concentration of these compounds at the percent level.

The second set was a series of used oil samples collected from the same source. A typical S channel chromatogram is shown in Fig. 4. This is quite different from the coal oil sample. These used oil samples were also subjected to GC/MS analysis, but a positive identification could not be made, because of interferences from high levels of PAHs.

DISCUSSION

The GC/AED system appears to be ideal for the screening of fuel samples for possible organo P and S contamination. The ease of operation of the instrument can be appreciated in that only two weeks were allowed for familiarization with the detector before the fuel samples were analyzed on the instrument. The system provides reproducible results both with respect to retention times and response. However, when there are problems on the instrument, such as was experienced with the faulty valve, useful results can still be obtained. If a supposed contaminant was found in any of the samples during the time when the valve was malfunctioning, those samples would have been reanalyzed when the fault was corrected.

For each fuel type the chromatographic pattern, particularly from the S channel, was similar for samples collected across Canada. Samples, such as used oil or naphtha, presented more of a challenge. Used oils could come from many sources and the final transported solutions could be mixtures. For the majority of the fuels, the heteroatom compounds elute from the chromatograph during the elution of the major hydrocarbon fraction or slightly before. This is not surprising as the S or P containing compounds, when placed in the oil as additives to enhance the performance of the fuel or increase its fluidity, must conform to the same specifications of that fuel.

The AED technique presented here was intended as a screening method. Identification of any suspect contamination was to be undertaken by GC/MS. The identification of benzothiophene and dibenzothiophene was difficult because of interference by polynuclear aromatics but facilitated by the concentrations of the thiophenes being in the low percents or parts per hundred. If their

concentrations had been a factor of 10 less, the identification may not have been made. In the case of the used oil samples, the suspected compounds could not be identified. These unknowns were at lower concentrations than the thiophenes, but they dominated the chromatograms of the samples. The results from the AED were of little help to the GC/MS operator as a completely different oven temperature program was used as was a different capillary column liquid phase. Despite this, even if everything was identical, the MS may not have been able to distinguish the compounds of interest because of the large interference from the PAHs present. The next step to be taken in the AED screening procedure should be to chromatograph suspected samples at a lower temperature rate and compare the results with chromatograms of other S and P containing compounds. This data could then be given to the GC/MS operator so that the MS could be used in a confirmation mode rather than the identification mode.

REFERENCES

- Scott, B.F. and Onuska, F.I., J. MicrocolSep, 1, 69, 1989.
- Sullivan, J. J. and Quimby, B.D., J. High Res. Chrom., 12, 282, 1989.
- Water Quality Methods Manual, Water Quality Branch, Ontario Region, Burlington, Ontario.

ACKNOWLEDGEMENT

Environmental Protection of CPS is thanked for providing the necessary funds to purchase the equipment. The efforts of the management of the NWQL, in particular Mr. R. Sampson, were very much appreciated in providing foresight and encouragement to make the study a reality. Finally the assistance of Mr. J. Carron (NWQL) in operating the GC/MS, contributed significantly to this study.

TABLE 1

LIST OF COMPOUNDS USED IN THE STANDARD SOLUTIONS

COMPOUND	SOLUTION NUMBER	MOLECULAR FORMULA	MOLECULAR WEIGHT
Phorate	1	$C_7H_{17}O_2SP$	260.4
Diazinon	1	$C_{12}H_{21}O_3SN_2P$	304.4
Ronnel	1	$C_8H_8O_3SPCl_3$	321.6
Methyl parathion	1	$C_8H_{10}O_5SNP$	263.7
Malathion	2&3	$C_{10}H_{19}O_6S_2P$	330.6
Parathion	1	$C_{10}H_{14}O_5SNP$	291.3
Crufomate	1	$C_{12}H_{19}O_2PNC1$	275.7
Ethion	1	$C_9H_{22}O_4S_4P_2$	384.5
Carbophenothion	2	$C_{11}H_{16}O_2S_3PC1$	342.9
Guthion	2	$C_{12}H_{16}O_3S_2N_3P$	345.3
Disulfoton	2	$C_8H_{19}O_2S_3P$	242.3
Methylguthion	1&2	$C_{10}H_{12}O_3S_2N_2P$	317.3
Phosphamidon	3	$C_{10}H_{19}O_5PNC1$	299.7
Phosmet	2	$C_{11}H_{12}O_4S_2NP$	317.4
Fenitrothion	1	$C_{11}H_{16}O_5SNP$	305.3
Butylate	3	$C_9H_{19}OSN$	189.3
Diallate	3	$C_{10}H_{17}OSNC1_2$	270.2
Triallate	3	$C_{10}H_{16}OSNC1_3$	304.7
Metribuzin	3	$C_8H_{14}OSN_4$	214.3
Dimethoate	1&2	$C_5H_{12}O_3S_2NP$	229.3
Endosulphans	3	$C_9H_6O_3SC1_6$	407.0

TABLE 2

	(A) PHOSPHOROUS CHANNEL					
	(1) MEAN RESPONSE	(2) CV (%)	(3) EQUIV RESPONSE	(4) MOLAR RESPONSE	(5) EQ.MOL. RESPONSE	(6) RETENTION TIME
PHORATE	778.28	18.9	778.28	2.99	2.99	9.48
DIMETHOATE	411.74	23.1	411.74	1.81	1.81	9.66
DIAZINON	449.81	20.8	449.81	1.47	1.47	9.82
PHOSPHAMIDON	32.96	28.2	32.96	0.11	0.11	10.27
Me-PARATHION	299.42	19.3	299.42	1.14	1.14	10.47
RONNEL	295.04	13.5	295.04	0.97	0.97	10.64
FENITROTHION	325.37	16.7	325.37	1.07	1.07	10.74
PARATHION	283.60	17.4	283.60	0.92	0.92	11.02
CRUFOMATE	66.04	12.7	66.04	0.24	0.24	11.11
ETHION	619.66	17.1	309.84	1.61	0.81	13.56
DIMETHOATE	355.98	7.0	355.98	1.55	1.55	9.67
MALATHION	363.95	2.9	363.95	1.10	1.10	10.76
CARBOPHENOTHION	302.20	5.3	302.20	0.88	0.88	14.30
PHOSMET	140.29	12.3	140.29	0.44	0.44	16.45
METHYLGUTHION	81.06		81.06	0.26	0.26	18.25
GUTHION	131.36	11.5	131.36	0.38	0.38	20.12
MALATHION	337.07	6.0	337.07	1.02	1.02	10.75

	(B) SULPHUR CHANNEL					
	(1) MEAN RESPONSE	(2) CV	(3) EQUIV. RESPONSE	(4) MOLAR RESPONSE	(5) EQ.MOL. RESPONSE	(6) RETENTION TIME
PHORATE	1143.22	2.8	381.07	4.39	1.46	9.49
DIMETHOATE	426.33	6.0	213.06	1.86	0.93	9.68
DIAZINON	305.20	3.4	305.20	1.04	1.04	9.84
Me-PARATHION	202.47	6.9	202.47	0.77	0.77	10.49
RONNEL	197.60	4.6	197.60	0.65	0.65	10.66
FENITROTHION	196.82	8.1	196.82	0.71	0.71	10.77
PARATHION	231.17	5.5	231.17	0.79	0.79	11.04
ETHION	652.31	5.8	135.58	1.79	0.42	13.60
DIMETHOATE	337.78	4.9	337.78	1.47	1.47	9.69
MALATHION	324.39	2.4	162.19	0.98	0.49	10.79
CARBOPHENOTHION	406.81	3.8	135.60	0.98	0.33	14.35
PHOSMET	115.36	8.4	57.68	0.36	0.18	16.51
METHYLGUTHION						18.51
GUTHION	113.45	6.0	56.72	0.33	0.17	20.19
BUTYLATE	388.54	2.2	388.54	1.89	1.89	8.33
DIALATE	167.27	2.0	167.27	0.62	0.62	9.48
TRIALATE	304.81	2.6	304.81	1.00	1.00	10.11
METRIBUZIN	296.49	3.7	296.49	1.48	1.48	10.39
MALATHION	305.34	4.1	152.67	0.92	0.46	10.79
a-ENDOSULPHAN	170.13	1.8	170.13	0.42	0.42	12.50
b-ENDOSULPHAN	124.21	4.0	124.21	0.31	0.31	13.75

TABLE 3

Effect of Changing Concentration on the Area Response
of the Hetero Compounds

PHOSPHOROUS CHANNEL

MIXTURE #1	10X	5X	1X	0.5X	0.25X	0.125X
	Area	Area	Area	Area	Area	Area
PHORATE	6100	2925	397	186	86	45
DIMETHOATE	5924	2750	293	106	37	
DIAZINON	4151	997	248	128	54	21
PHOSPHAMIDON	1468	475	69			
Me-PARATHION	5011	2286	245	108	51	
RONNEL	4553	2318	238	108	49	20
FENITROTHION	5404	2660	270	127	49	20
PARATHION	4130	1861	164	76	26	
CRUFOMATE	3115	1311	100	38		
ETHION	9117	3908	457	172	84	51

SULPHUR CHANNEL

	Area	Area	Area	Area	Area	Area
PHORATE	9958	5144	1050	506	247	118
DIMETHOATE	6636	3383	556	207	84	36
DIAZINON	3033	1511	281	131	69	36
Me-PARATHION	3258	1628	282	127	64	33
RONNEL	2491	1263	239	116	55	28
FENITROTHION	3004	1514	270	123	57	28
PARATHION	2926	1488	263	115	53	29
ETHION	9389	4625	801	375	182	91

FIGURE 1.

RESPONSE FROM SULPHUR (a) AND PHOSPHORUS (b)
CHANNELS OF STANDARD #1.

FIGURE 1. (a) S Channel
Standard

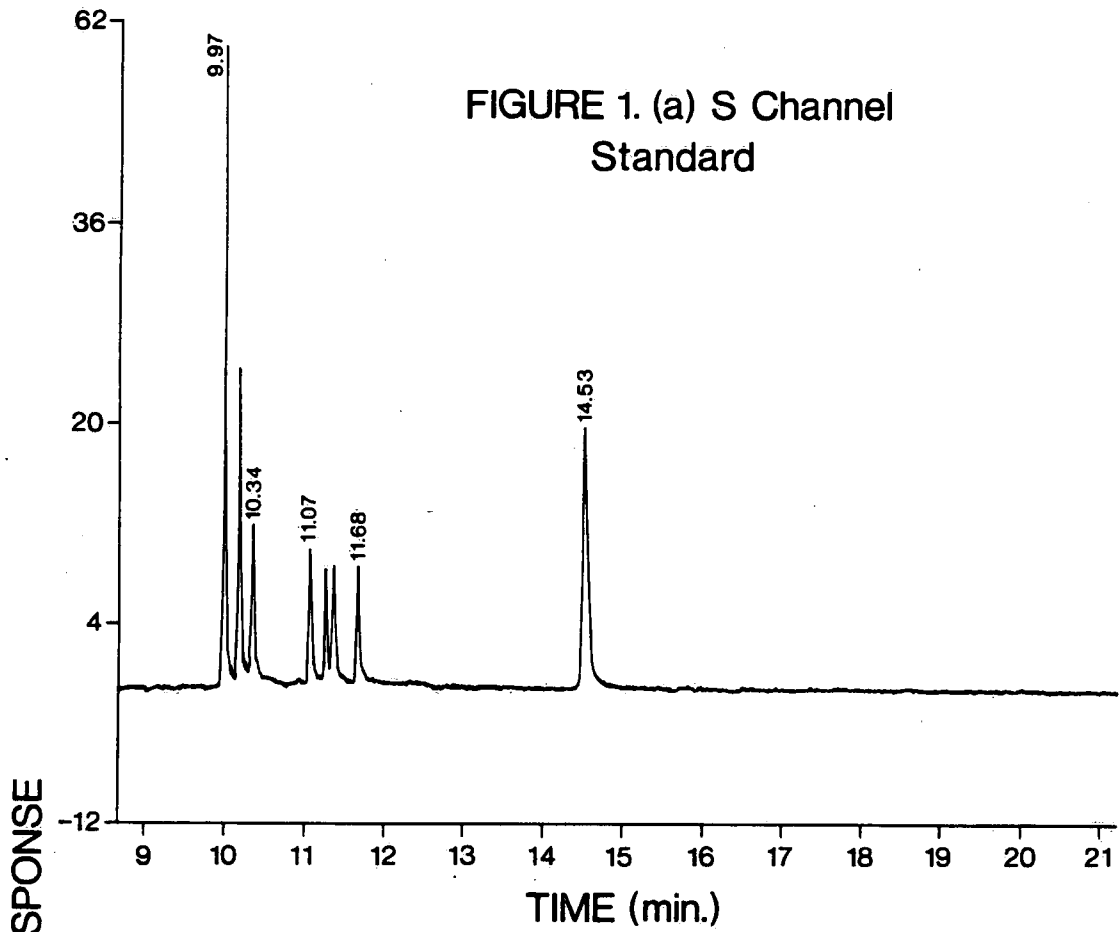


FIGURE 1. (b) P Channel
Standard

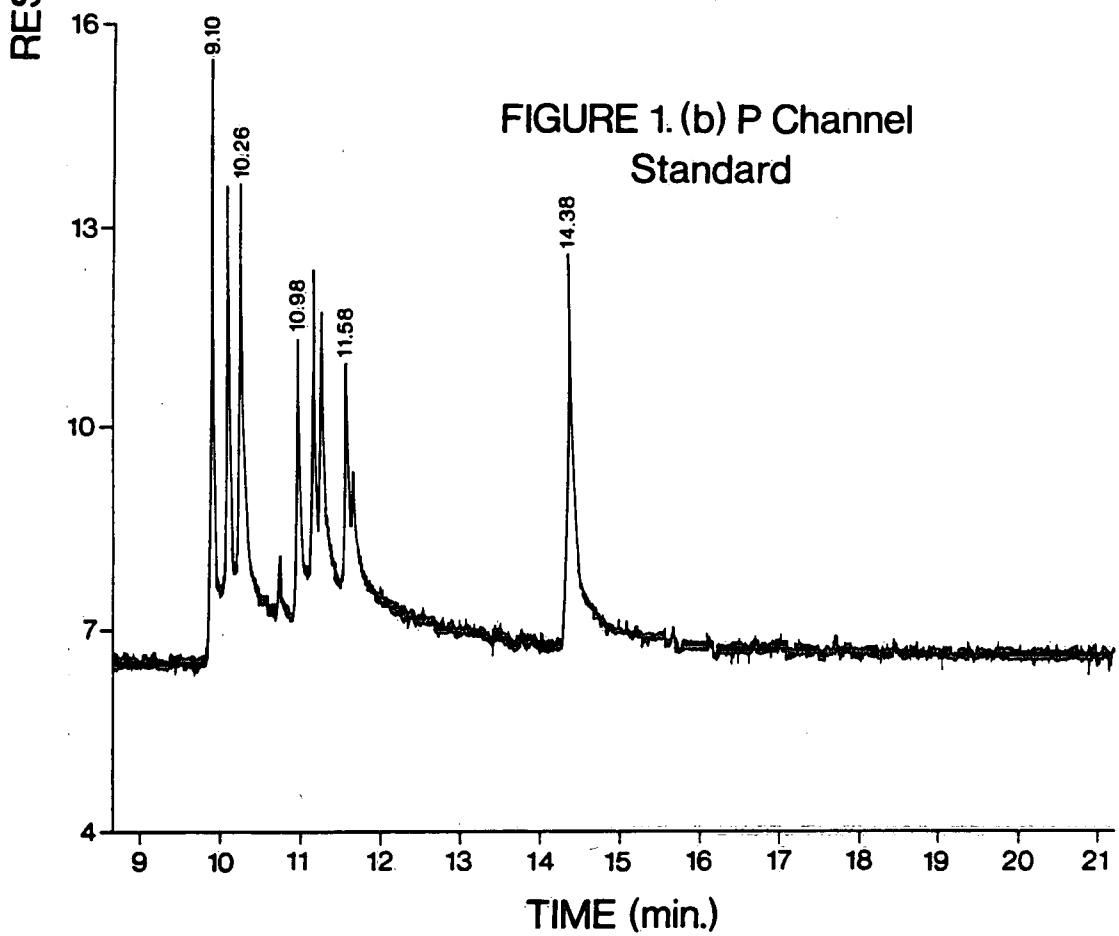


FIGURE 2.

RESPONSE FROM SULPHUR AND PHOSPHORUS CHANNELS
OF VARIOUS TYPES OF FUELS INVESTIGATED AS WELL AS
THE EFFECT OF SPIKING FUELS WITH STANDARD #1.

FIGURE 2. (a) S Channel
Gasoline

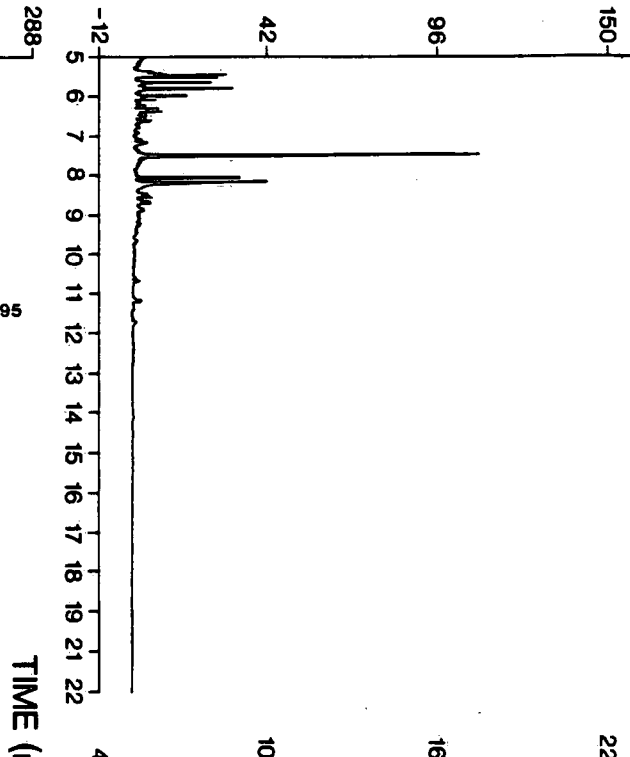


FIGURE 2. (a) P Channel
Gasoline

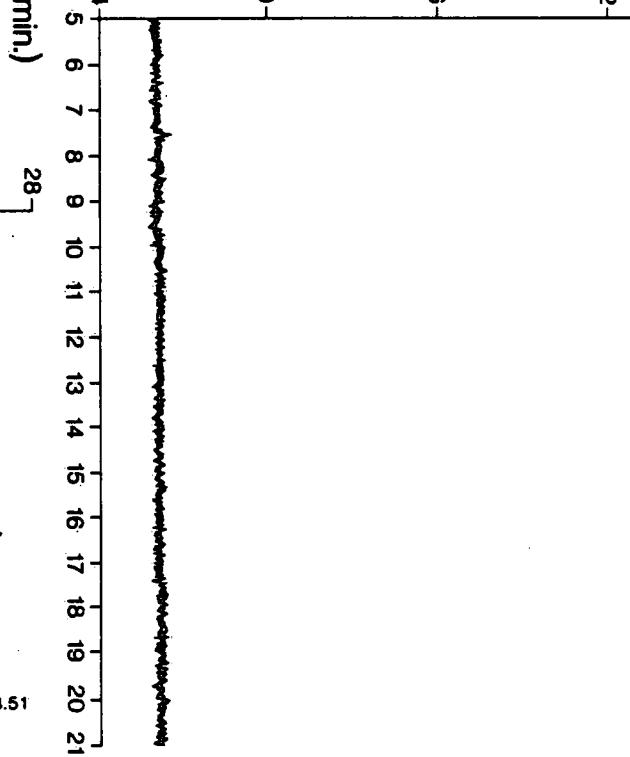


FIGURE 2. (b) S Channel
Gasoline Spiked

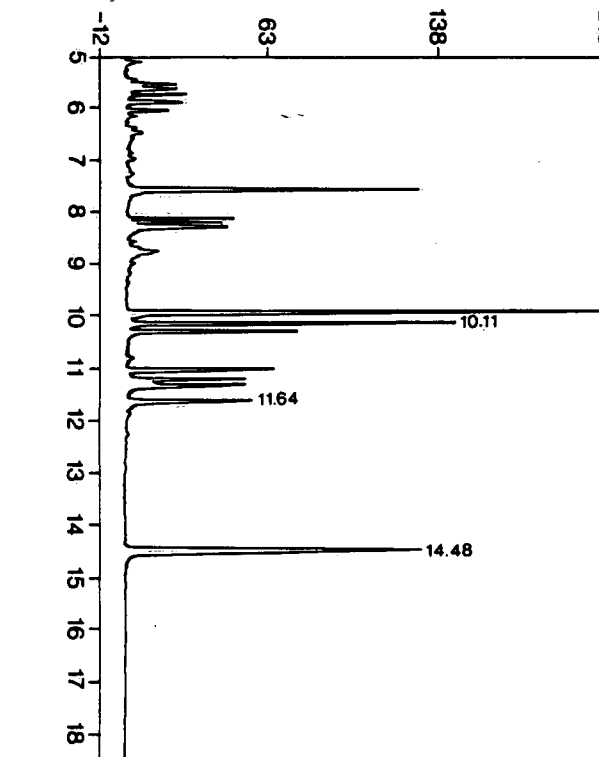
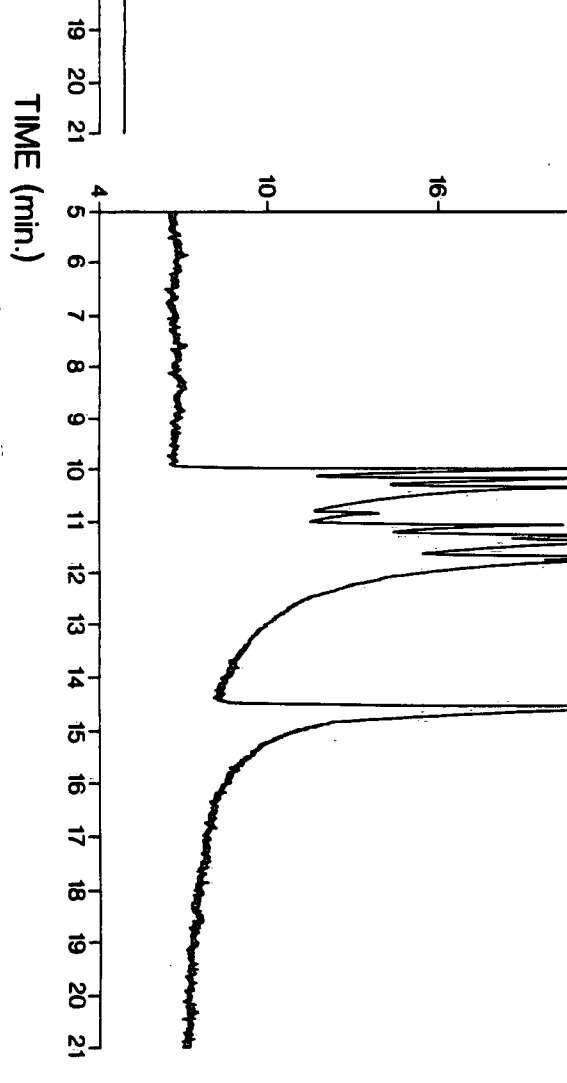
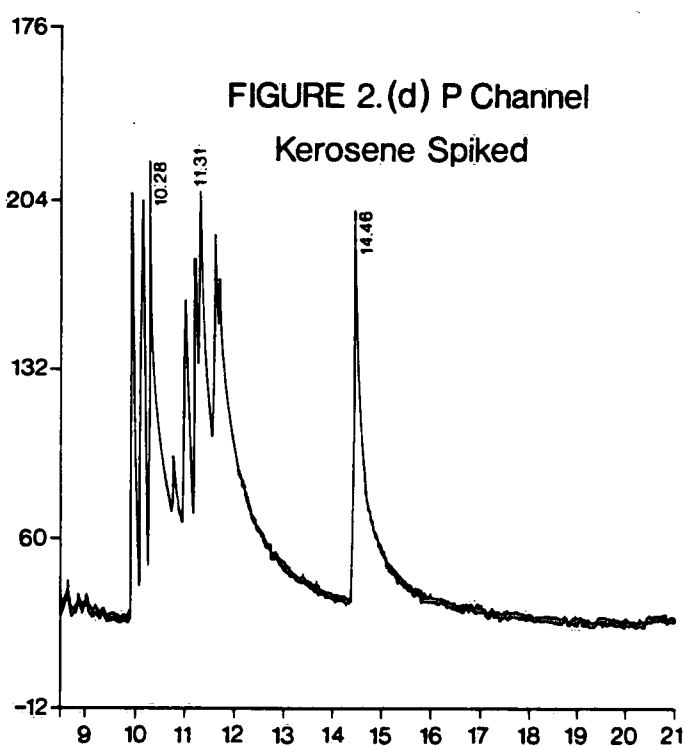
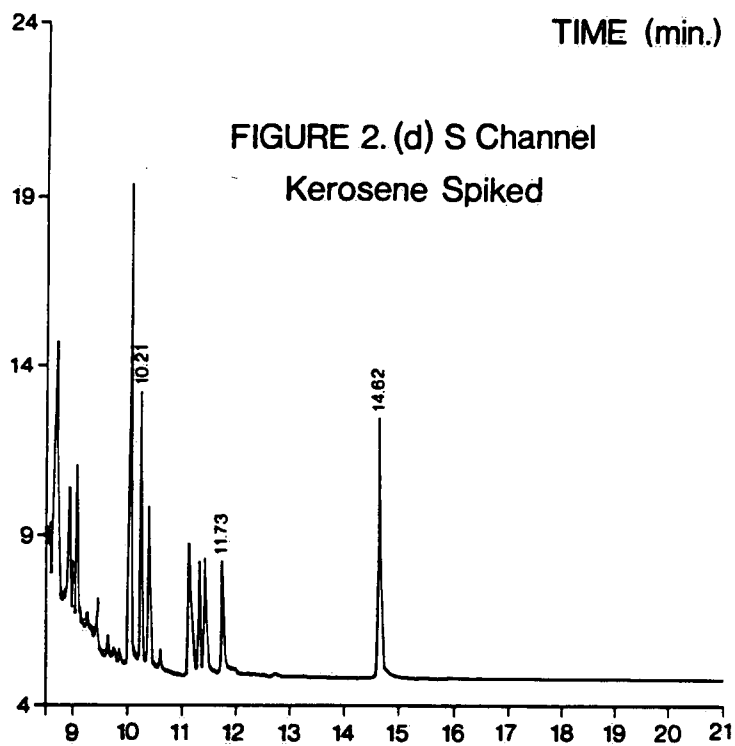
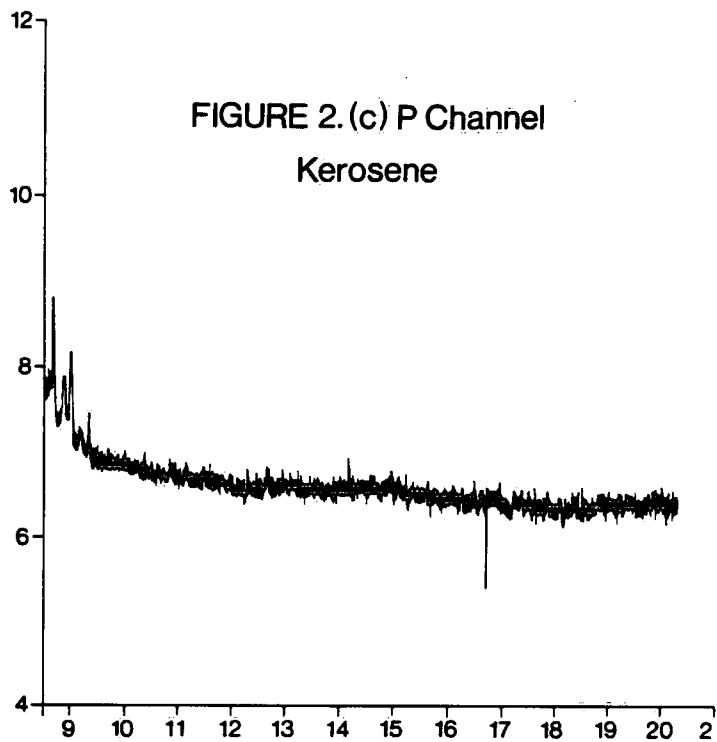
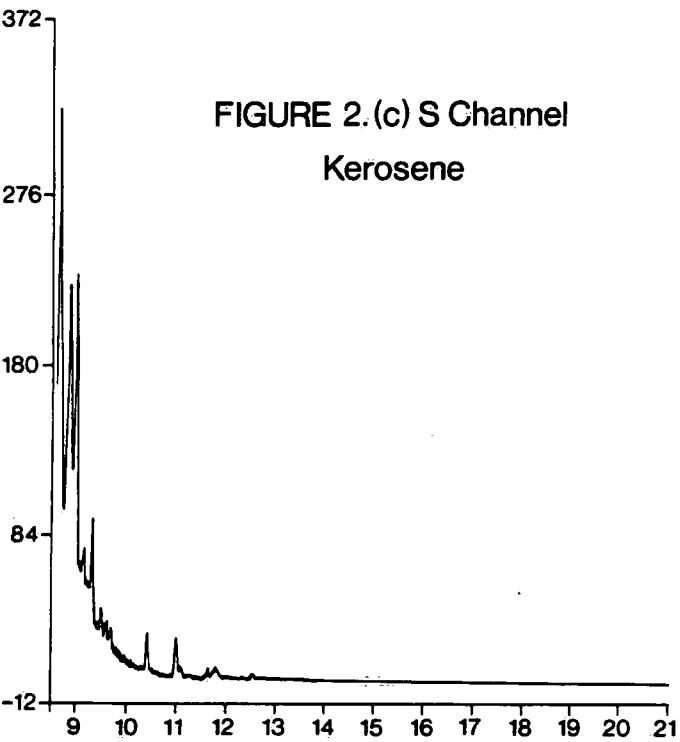
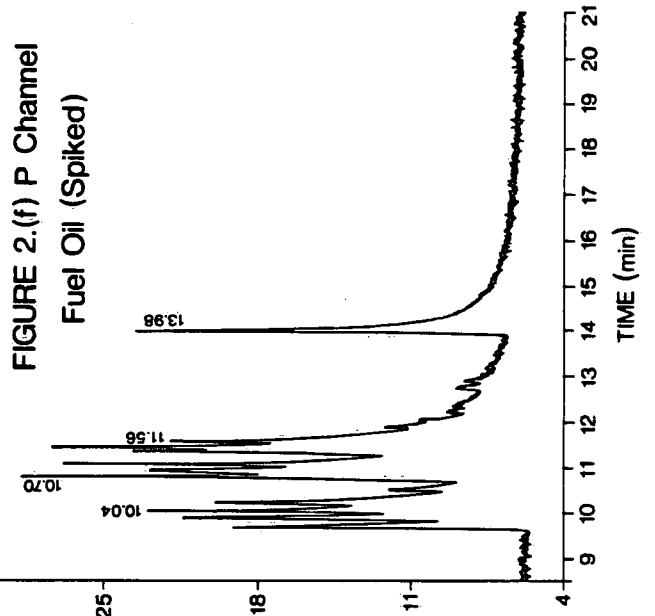
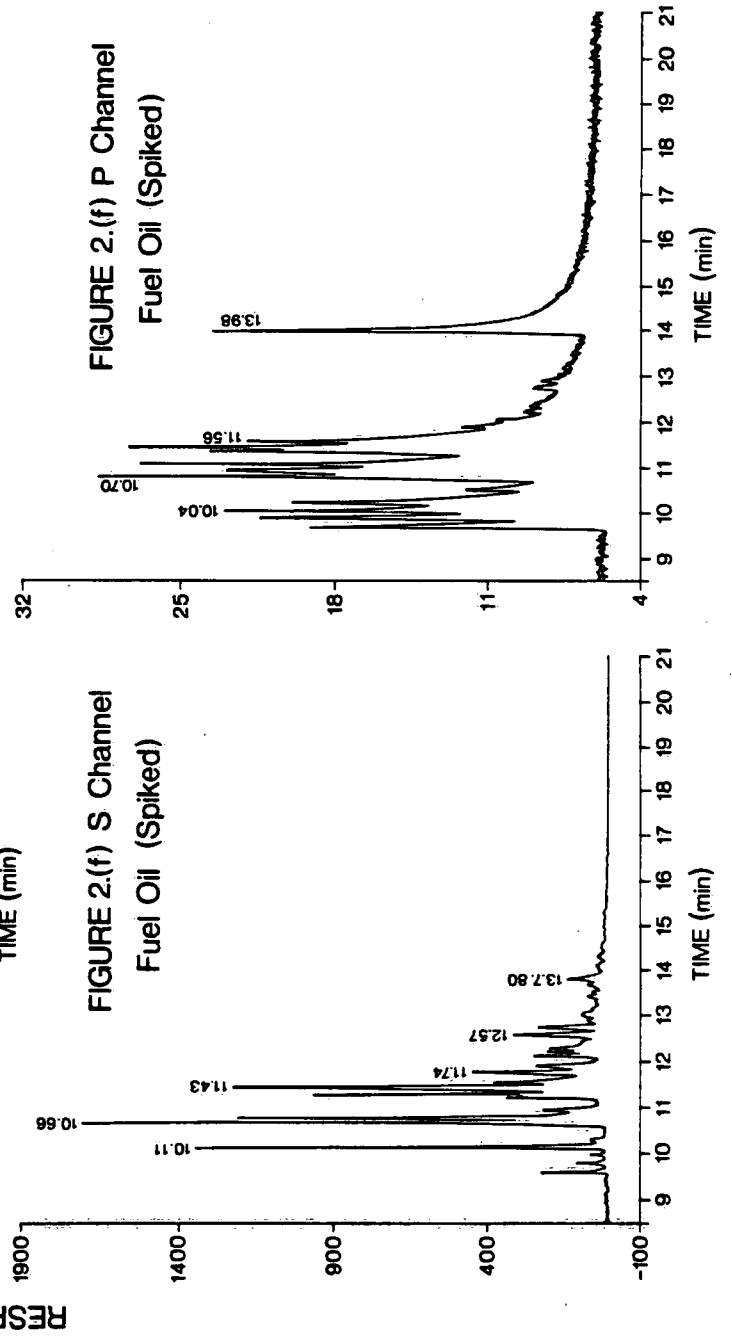
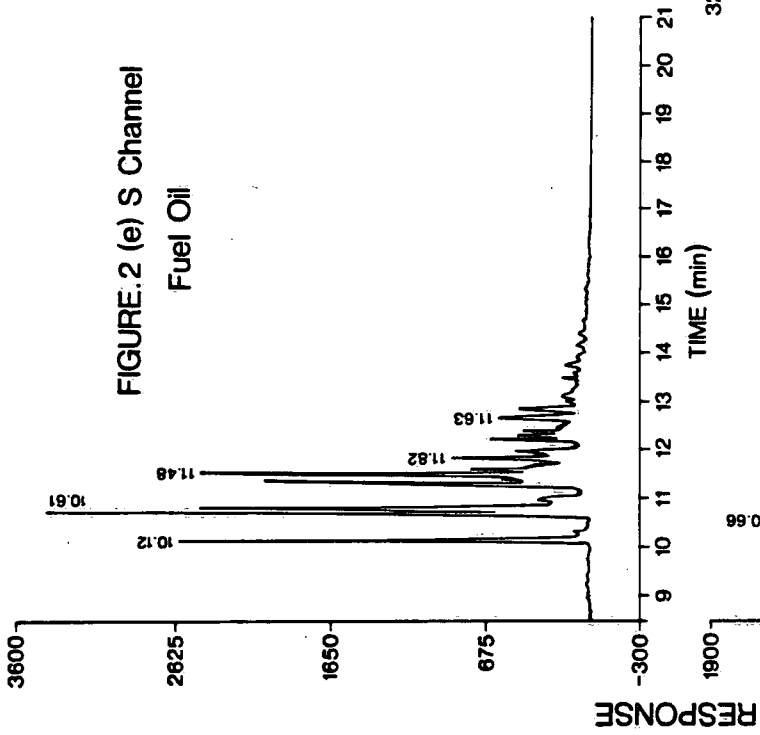


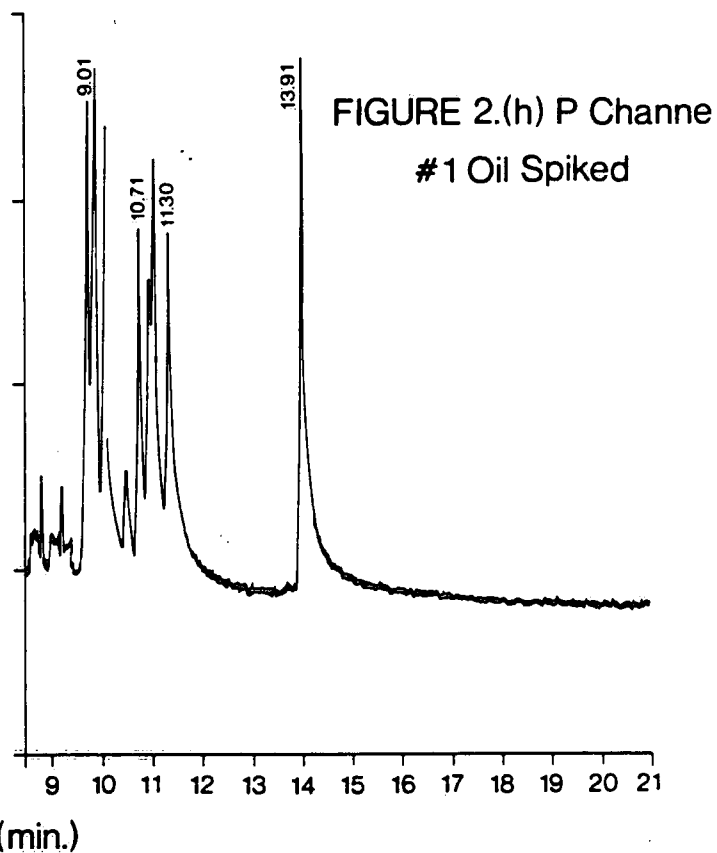
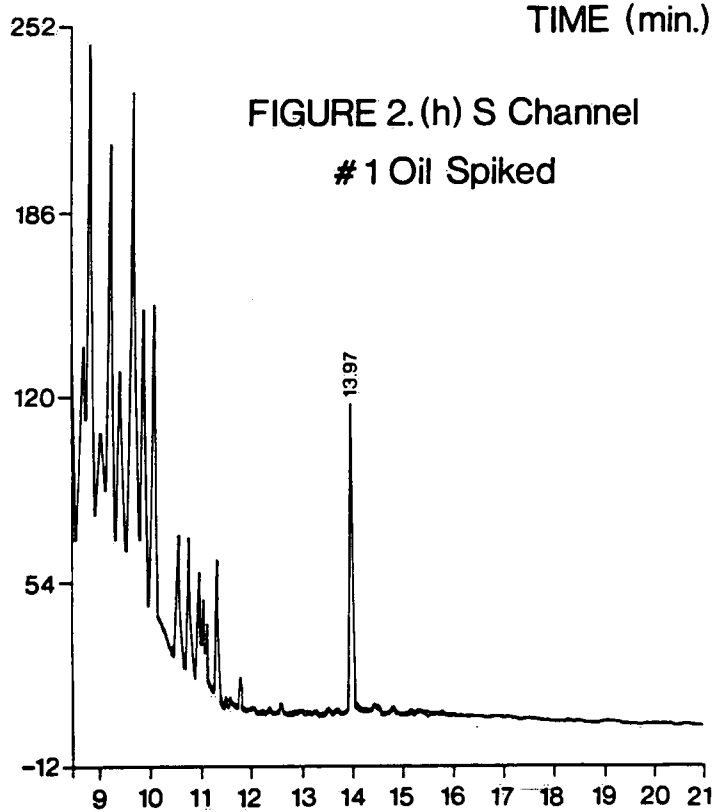
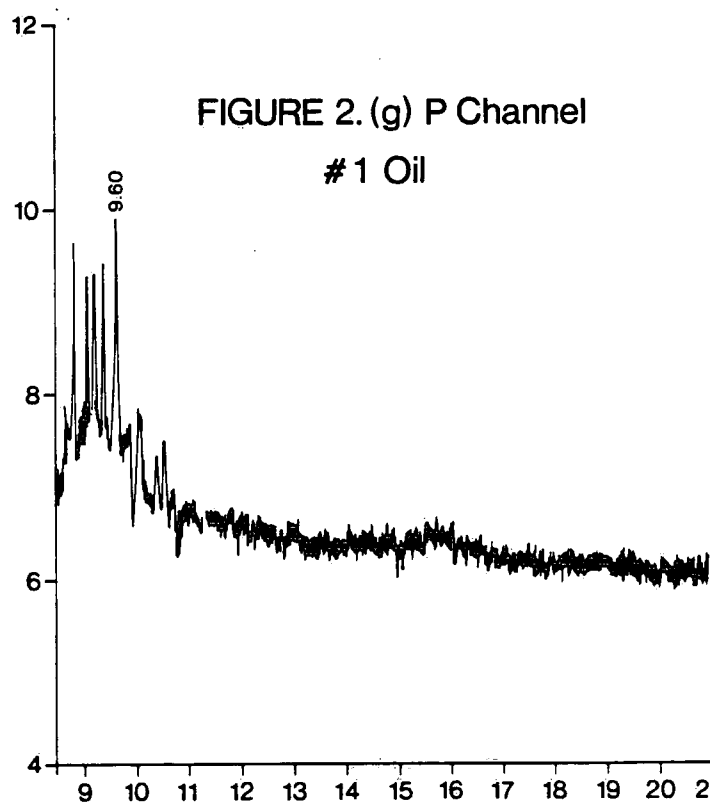
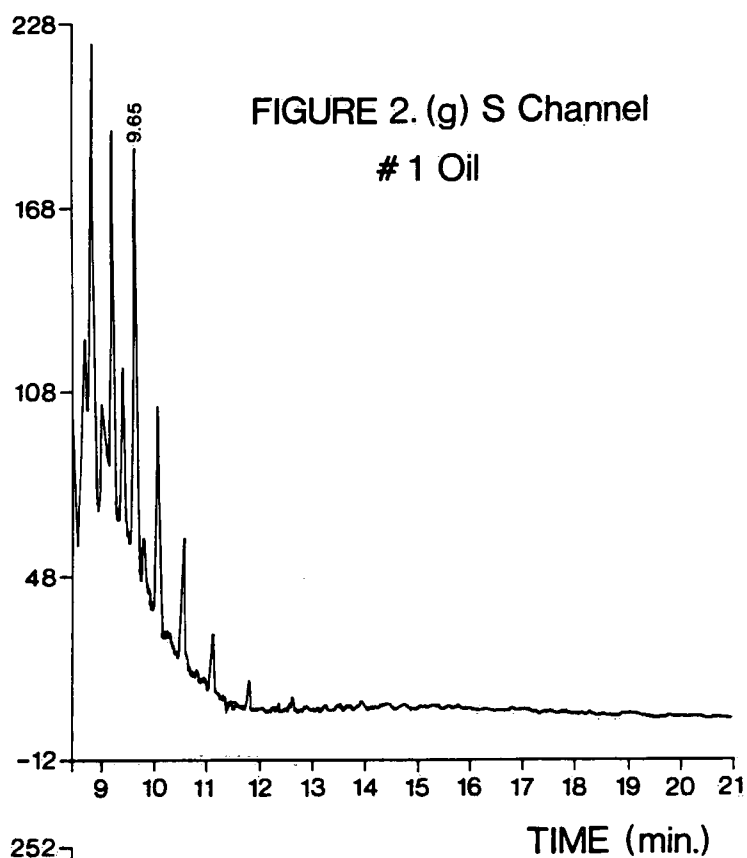
FIGURE 2. (b) P Channel
Gasoline Spiked





TIME (min.)





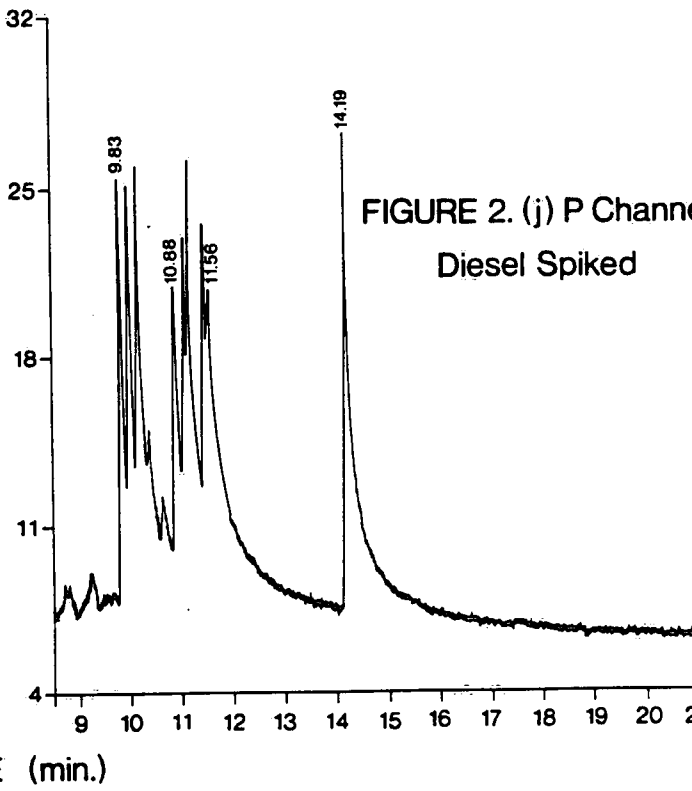
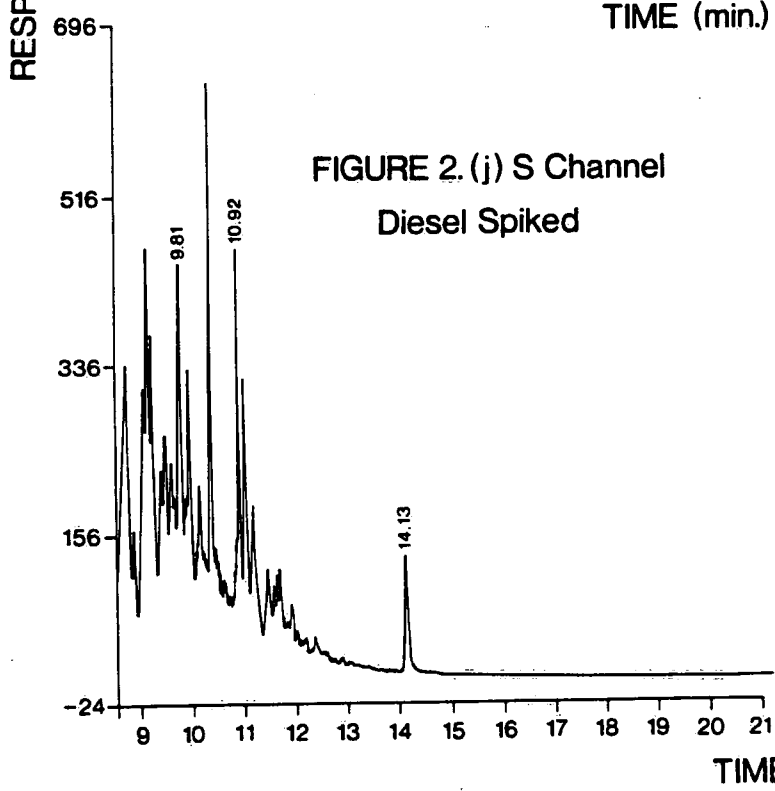
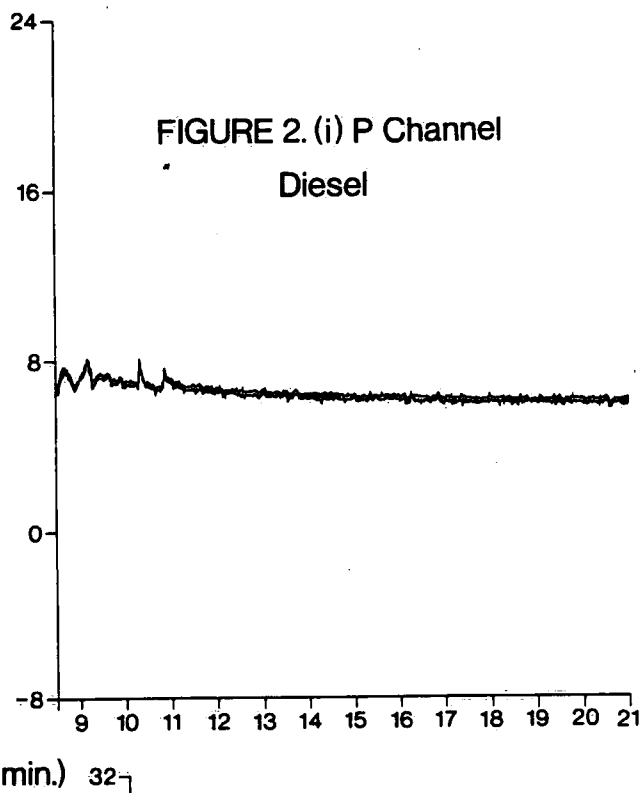
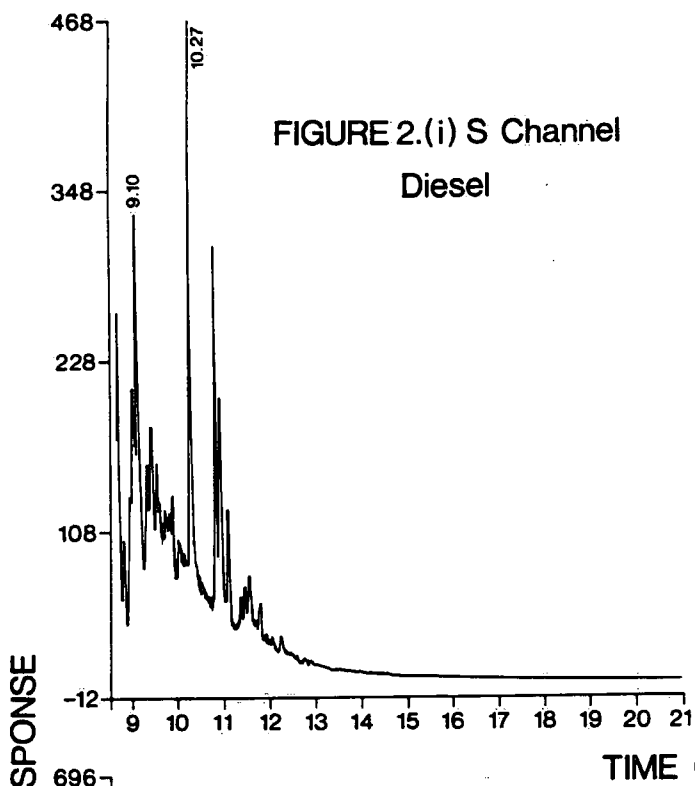


FIGURE 2.(k) S Channel
#6 Fuel

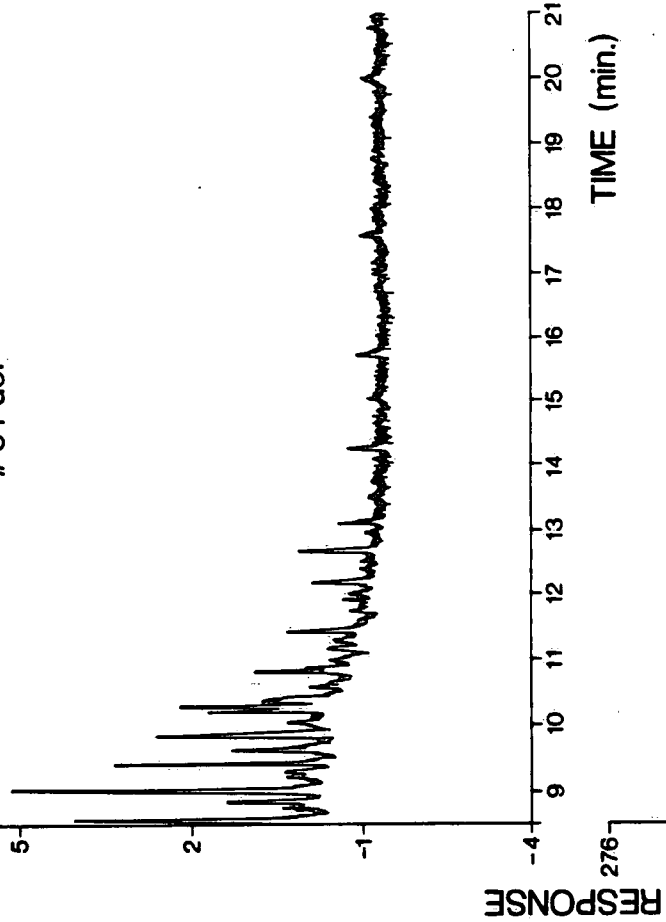


FIGURE 2.(k) P Channel
#6 Fuel Oil

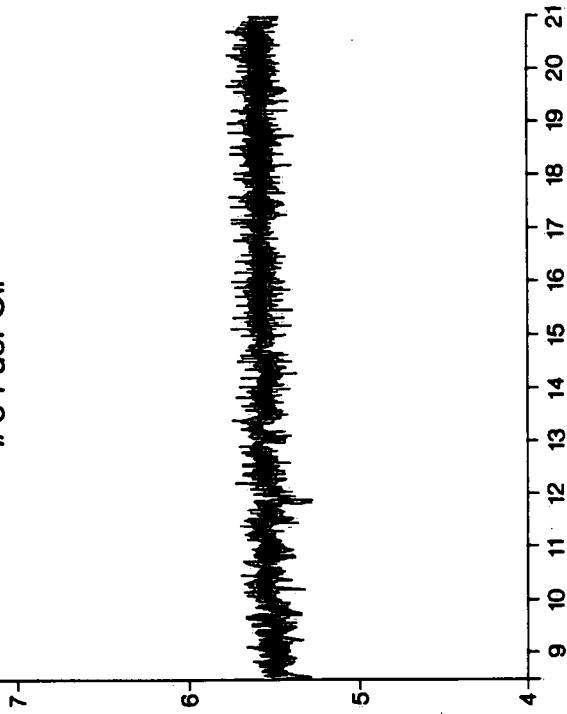


FIGURE 2.(l) S Channel
#6 Fuel Spiked

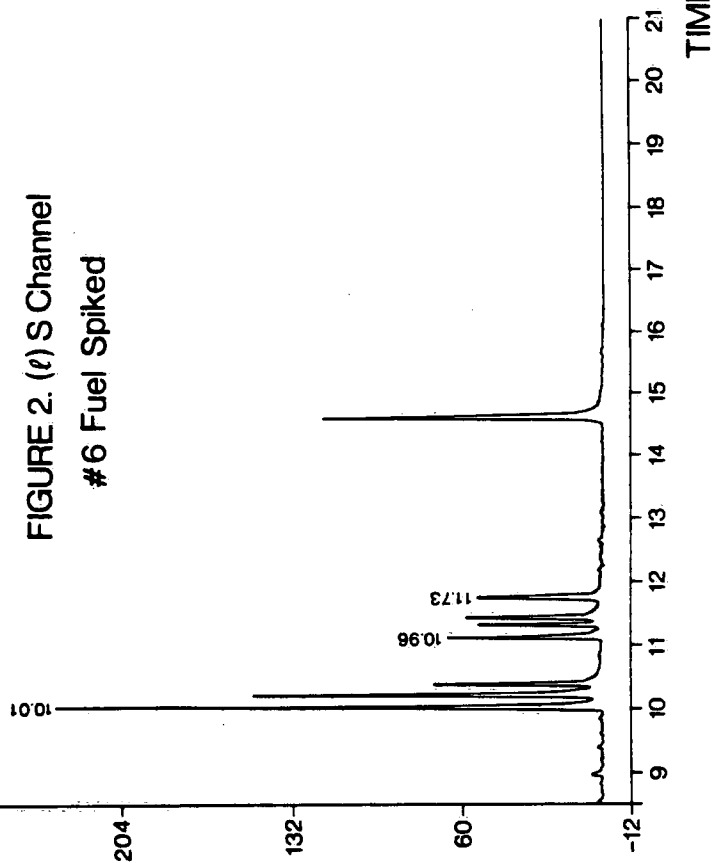


FIGURE 2.(l) P Channel
#6 Fuel Spiked

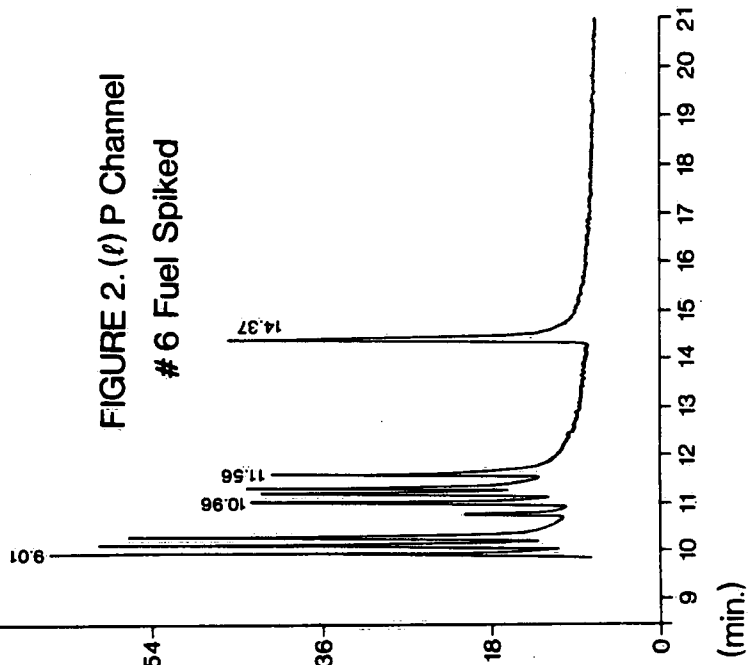
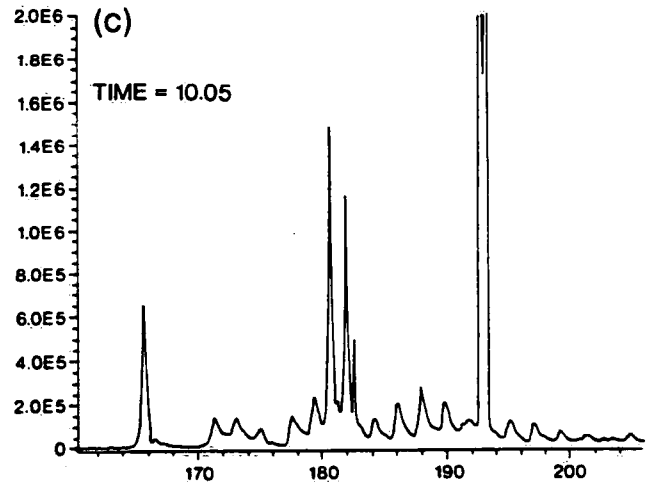
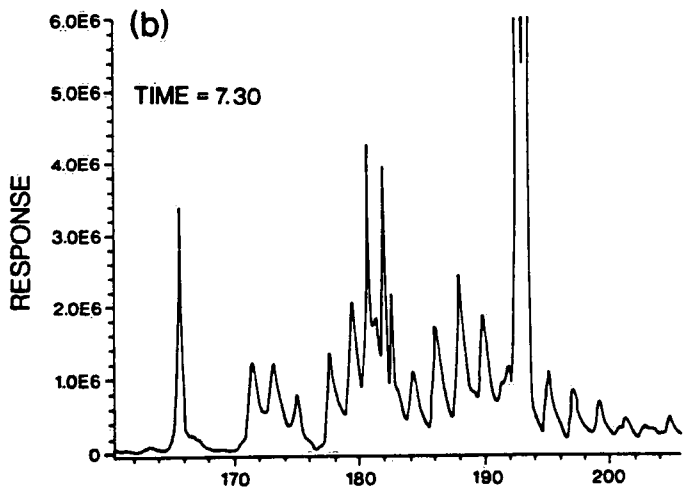
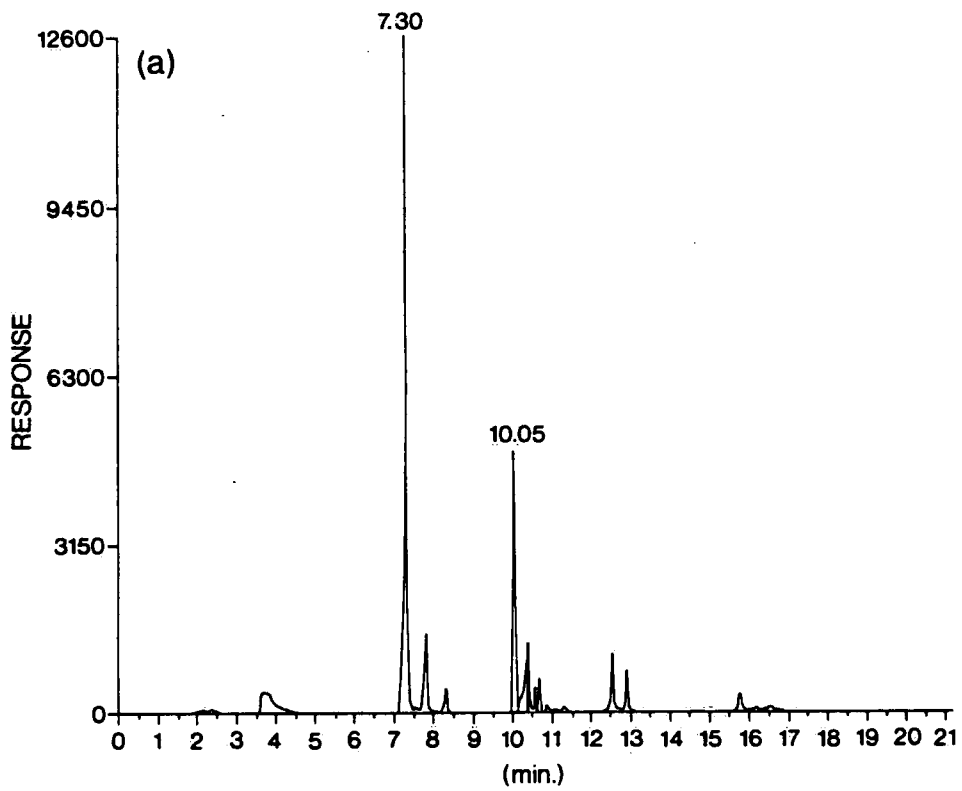


FIGURE 3.

SULPHUR CHANNEL RESPONSE FOR COAL OIL SAMPLE
WITH PRESENCE OF SULPHUR IN THE TWO MAJOR PEAKS
CONFIRMED BY SULPHUR SPECTRA ABOUT 181 nm IN (b) AND (c).



WAVELENGTH (nm)

FIGURE 4.

SULPHUR CHANNEL RESPONSE (a) FOR COAL OIL SAMPLE
WITH PRESENCE OF SULPHUR IN THE TWO MAJOR PEAKS CONFIRMED
BY SULPHUR SPECTRA ABOUT 181 nm IN (b) and (c).

