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Navy Fuels Analytical Chemistry

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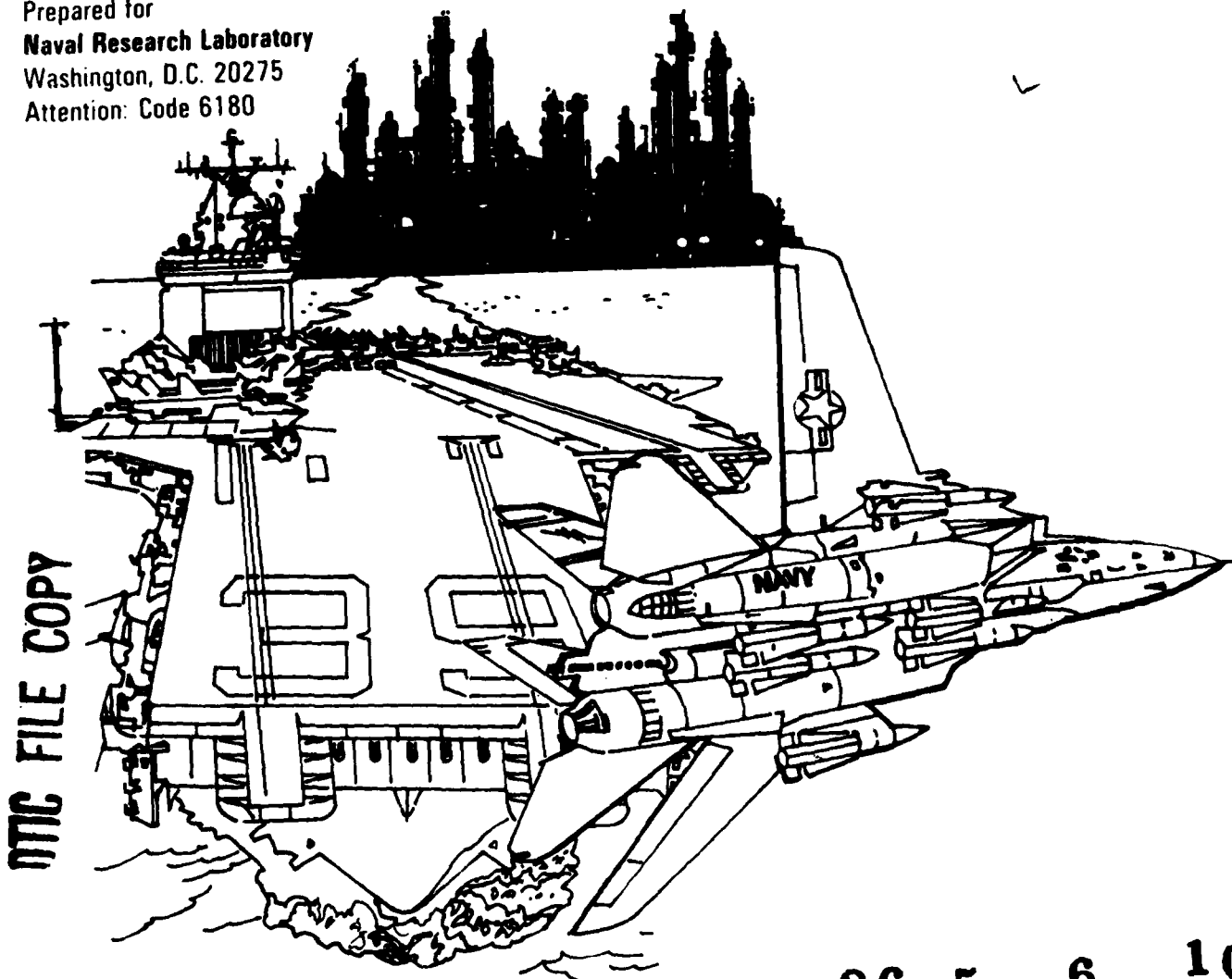
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FOREWORD AND ACKNOWLEDGEMENTS

This is the final report of an 18 month program performed by TRW's Chemistry Laboratory, a part of the Applied Technology Division under TRW's Space and Technology Group.

Dr. Martin Mach was Program Manager and Principal Investigator. He assumed responsibilities as Program Manager after Dr. Robert Beimer, the initial PM, left TRW in 1985. Important technical contributions to the program were made by Kevin B. Patzkowsky, Member of the Technical Staff.

We are pleased to acknowledge the interest and involvement of the Technical Monitor, Dr. Robert N. Hazlett of the Naval Research Laboratory. His guidance and understanding of trace sulfur analysis played a major role in the success of this program. In addition, we wish to thank Dr. George Mushrush of George Mason University, who provided technical and administrative continuity during Dr. Hazlett's sabbatical in Australia.

Finally, we owe a special debt of gratitude to Dr. Erwin Fishman, Program Manager for the initial 18 month program and, in our mind, the father of the Navy Fuels program. Although he transferred to another part of the company before the current program got underway, his interest and enthusiasm, for not only chemical research, but for music, art, good food, and life in general provided needed inspiration during several periods over the past 18 months. For that we are grateful.

ABSTRACT

TRW developed new and unique analytical methods in support of the Navy's program in mobility fuels analysis. These methods include 1) the separation and isolation of different classes of organosulfur compounds in JP-5 by high performance liquid chromatography with silver nitrate impregnated silica gel columns, 2) the separation and identification of individual sulfur compounds in the HPLC fractions by capillary gas chromatography with detection by a) simultaneous flame ionization and Hall electrolytic conductivity, and b) mass spectrometry, and 3) the quantitation of nanogram amounts of sulfur compounds in as-received fuel and the HPLC fractions using a TRW-developed ⁶integrating sulfur detector⁶ based on a modification of the Hall detector. This analytical scheme can be used to characterize the changes in sulfur compound distribution in JP-5 fuels arising from different crudes, refining conditions, aging, and thermal and oxidative stressing.

1.0 SUMMARY

This Navy Fuels Analytical Chemistry Program was a multi-pronged effort to characterize the organosulfur fraction in JP-5. It has shown notable success in the development of methods for the isolation, quantitation, and identification of these materials. The principal methods developed were:

- o the separation and isolation of different classes of organosulfur compounds in JP-5. TRW's method is based on high performance liquid chromatography (HPLC) using a silver nitrate/silica gel column, so-called "argentation chromatography". The two principal fractions isolated were the alkylbenzo- and dibenzothiophenes, and aliphatic sulfides [tentative assignment].
- o the separation and identification of individual sulfur compounds in the isolated HPLC fractions. The methods chosen were 1) capillary gas chromatography (CGC) with simultaneous detection of carbon compounds by a flame ionization detector (FID) and sulfur compounds by a Hall detector in the sulfur mode (HECD-S), and 2) CGC/mass spectrometry for compound identification.
- o the quantitation of nanogram amounts of sulfur compounds in the HPLC fractions using a TRW-developed integrating sulfur detector (ISD) based on a modification of the HECD-S. While the impetus behind the development of this method was the generation of sulfur mass balance data for the different organosulfur fractions, the method shows promise as a general laboratory procedure for trace sulfur in volatile samples.

These new methods permit the fractionation JP-5 fuels into sulfur classes, with subsequent analysis of each fraction for total sulfur by the ISD and for individual sulfur compounds by CGC/Hall and CGC/mass spectrometry (CGC/MS). The

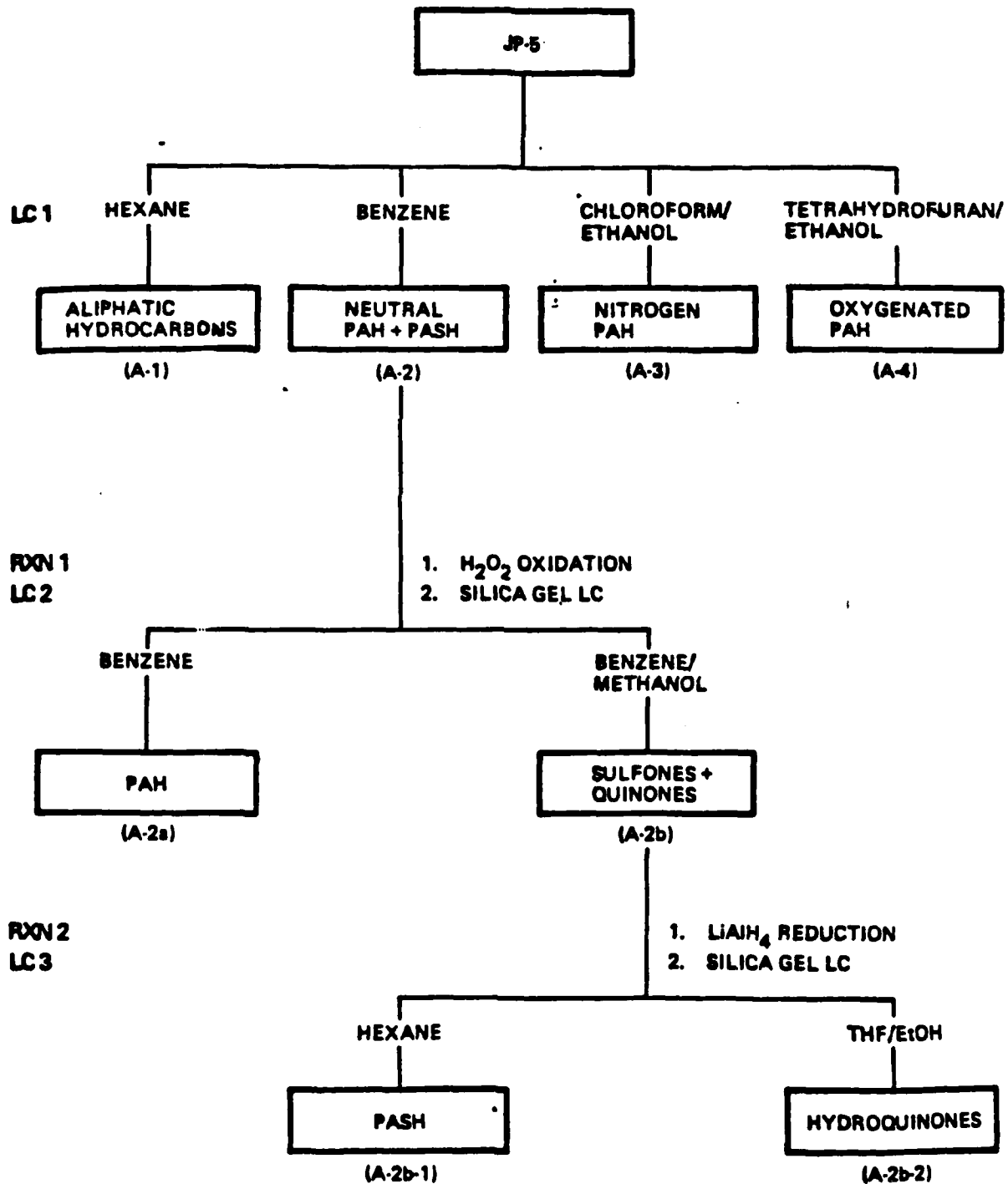
analytical scheme can be used to characterize the changes in sulfur compound distribution in JP-5 fuels arising from different crudes, refining conditions, aging, and thermal and oxidative stressing.

2.0 INTRODUCTION

Sulfur compounds have been linked to decreased thermal and oxidative stability of jet fuels. The problem has been compounded by economic factors which necessitate the use of higher sulfur, lower cost crudes. While sulfur compounds can be removed by hydrotreating and other methods, these processes lead to additional complications such as water formation. Removal of water by clay filtration then leads to the removal of other endogenous polar compounds, some of which are responsible for improved fuel lubricity. Thus, sulfur-free hydrotreated fuels usually have to be fortified with various additives to restore many of their original properties.

An alternate approach to the wholesale hydrotreating of all sulfur-rich fuels is to develop a detailed physico-chemical understanding of the role played by sulfur compounds in the different degradative processes and, based on these data, develop specific remedies to ameliorate their effects. Central to this task is the identification and quantitation of the different sulfur compounds present in JP-5 so that thermal or oxidative degradation can be related to specific compounds. This is not a simple task because the sulfur compounds, present in only trace amounts, must be separated from the welter of non-sulfur containing hydrocarbons that comprise over 99% of the fuel.

During the course of TRW's first program with the Naval Research Laboratory in JP-5 analysis and characterization, "Navy Mobility Fuels Evaluation" (Ref. 1), attempts were made to separate the polycyclic aromatic sulfur heterocycles (PASH, e.g., benzothiophenes (BT) and dibenzothiophenes (DBT)) from other hydrocarbons by a complex oxidation/reduction and chromatographic scheme developed by Lee (Ref. 2). According to this method (Scheme 1), JP-5 is fractionated into four classes of compounds by liquid



Scheme 1. Flow Diagram of Lee Method (Ref. 2) for Separation of Aromatic Sulfur Heterocycles

chromatography on alumina in step LC-1. The benzene eluate, containing the PASH plus co-eluting polycyclic aromatic hydrocarbons (PAH, e.g., naphthalenes (NP) and phenanthrenes (PH)) is oxidized with hydrogen peroxide (RXN 2), converting the PASH to the corresponding sulfones and oxidizing some PAH and PASH at sites other than sulfur to quinones and hydroquinones (HQ). The unreacted neutral PAH are removed from the polar sulfones, etc., in LC-2, and the oxidized compounds reduced with LiAlH_4 . This converts the sulfones back to the original, non-polar PASH, and reduces the quinones to HQs. The final step, LC-3, then separates the non-polar, reduced PASH from the quinones and HQ.

Analysis of the final PASH fraction by CGC with simultaneous detection by flame ionization (FID) and Hall electrolytic conductivity in the sulfur mode (HECD-S) showed a good correspondence between the FID and HECD-S traces, i.e., most of the CGC peaks are due to sulfur-containing compounds. However, similar analysis of the HQ fraction from LC-3 also showed a large number of sulfur containing peaks, attesting to the fact that a good deal of the PASH were irreversibly oxidized and "lost" to the HQ fraction. In addition, CGC/MS of the PASH fraction revealed the presence of likely artifacts such as a series of dihydro-BT, formed as a by-product in reduction RXN 2. The extreme complexity of the HQ fraction did not permit the elucidation of "key" structures that could be related to the original, unoxidized compounds.

In addition to the complications described above, the PASH isolation method suffers from the fact that the most "interesting" sulfur compounds, i.e., those most prone to oxidation and other degradative processes, will be those most likely lost because of side reactions. However, imperfect as these methods might be, they led to the isolation of gram amounts of sulfur-rich fractions relatively free of

hydrocarbon contaminants, and gave a preliminary view into the composition of the BT/DBT fraction.

Problems with the oxidation/reduction scheme led to TRW's second research proposal (Ref. 3) in which argentation chromatography (silver nitrate impregnated silica gel) would be used to separate BTs and DBTs from their PAH analogs NPs and PHs.

3.0 EXPERIMENTAL

3.1 SAMPLES

Fuel samples are designated as "NFP [Navy fuels program] -XX" for convenience. Most of the developmental work was performed using NFP-1. A brief description of the source of each fuel sample, along with several standards and solvents, is given in Appendix A.

3.2 CAPILLARY GAS CHROMATOGRAPHY (CGC)

Samples were analyzed on a Tracor 560 GC equipped as follows:

Injector: J&W inlet splitter with flow reversing quartz liner packed with DMCS/HMDS treated glass beads, operated at 280 C. Helium carrier gas at 16 psi (ca. 25 cm/sec (methane) at 60 C), split flow at 30 ml/min. Column effluent split to the HECD-S and FID using an SGE splitter union.

Column: J&W 30m x 0.25 mm i.d. DB-5 fused silica, 0.25 um coating thickness.

Temperature Program: 60 C (2 min hold) to 280 C at 8 C/min.

Detectors:

FID: 280 C

HECD-S:

Base: 280 C

Reactor tube: 850 C

Methanol flow: control knob at 12 o'clock

Vent open during solvent elution to minimize fouling of reactor tube.

Data System a) Spectra Physics Model 2000 (FID data),
b) Hewlett Packard Model 3385A (HECD-S data)

3.3 CAPILLARY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (CGC/MS)

DuPont 321 GC/MS with electron ionization source and INCOS data system

CGC conditions same as for the CGC runs except that all of the column effluent was directed to the MS.

3.4 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

DuPont 850 HPLC with DuPont variable wavelength UV detector and Waters refractive index detector.

Columns:

250 mm long by a) 10 mm i.d. (semi-preparative) or b) 3.9 mm i.d. (analytical) packed with 20% silver nitrate on R-Sil 5 (Applied Science Co.).

250 mm long by 3.9 mm i.d. packed with Zorbax silica (DuPont)

4.0 RESULTS AND DISCUSSION

Based on the initially encouraging results of the PASH isolation scheme, TRW proposed to improve upon the method by developing separation procedures that do not involve chemical reactions. Early in our development of an HPLC-based analytical scheme for sulfur compounds (Ref. 1), it was found that the most efficient and straightforward conditions for separation of JP-5 into its hydrocarbon class fractions (aliphatics + olefins, 1-, 2-, and 3-ring PAH) were normal phase HPLC on silica gel with isocratic pentane or hexane as an eluant. A number of reverse phase schemes were tried, but without success. Less polar solvents such as FC-72 (perfluorohexane, 3M Co.) were also tried in an attempt to increase the selectivity of the silica gel, but only resulted in an increase in retention times without any improvement in resolution.

A publication by Uden (Ref. 4) suggested that liquid chromatography on silica gel impregnated with silver nitrate would increase the selectivity of the normal phase system by selectively retarding sulfur compounds relative to their hydrocarbon homologs, e.g., BT/NP, DBT/PH.

This technique offered several potential advantages over the PASH separation scheme.

- o no chemical reactions are involved
- o the fuel is fractionated under mild conditions
- o the separation columns do not have to be specially prepared and activated for each sample
- o high resolution separations are attainable using HPLC instrumentation so that the elution "windows" of different fractions are readily obtained using suitable standards

- o separations are completed in an hour or two, compared to 4 - 5 days for the PASH scheme.

- o there is reduced risk of contamination of the final sample by solvents and reagents

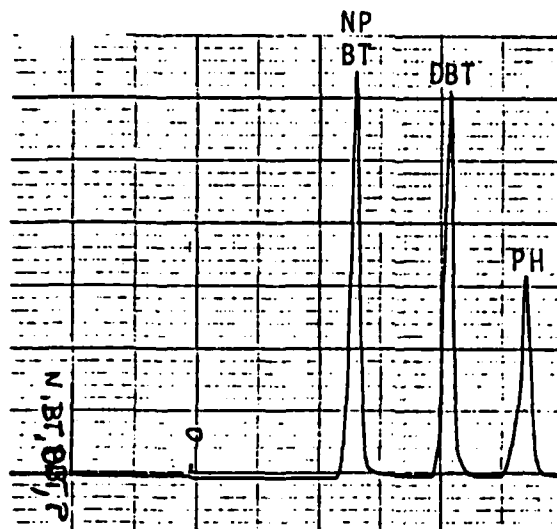
Consequently, so-called "argentation" chromatography was proposed as an all-chromatographic method of separating sulfur compounds from hydrocarbons (Ref. 3).

A second consideration involves the sample size required for compound identification. While the isolation of gram amounts of fractions has been the historical norm, modern instrumental methods of compound identification require only traces, not grams, of material. Therefore, it was felt that TRW's approach to sulfur compound isolation and analysis should take advantage of sensitive analytical techniques such as CGC and CGC/MS to reduce sample requirements to milli- or even micrograms of material.

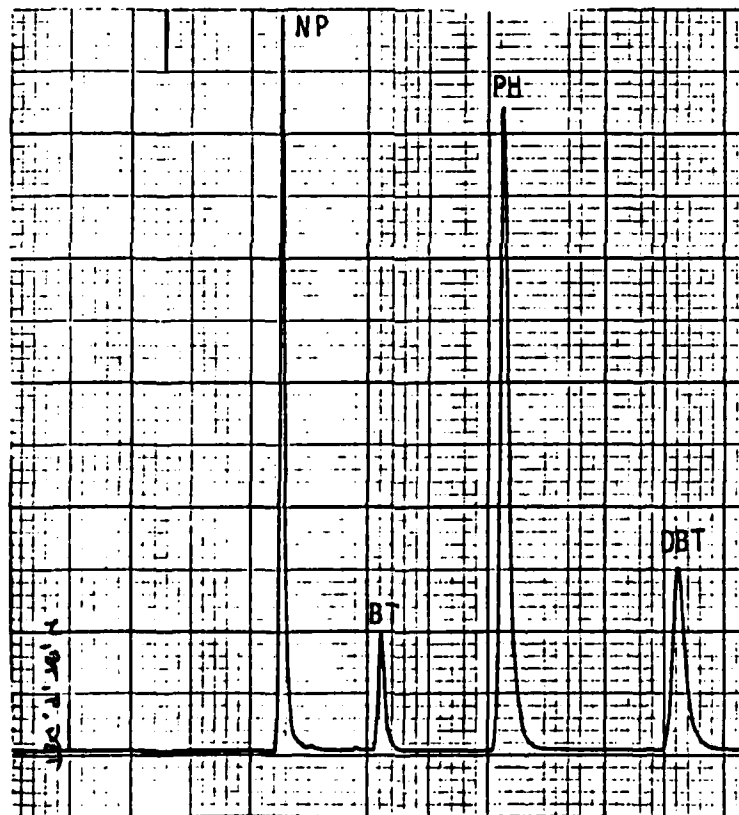
4.1 ISOLATION OF SULFUR CLASS FRACTIONS BY ARGENTATION HPLC

The method was tested using a 1/4" o.d. x 250 mm stainless steel column packed with 20% silver nitrate on R-Sil 5 (Applied Science Corp.) and either hexane or pentane eluant. The goal was to maximize the retardation of the BT/DBT retention time window relative to the NP/PH window. Initial results were not successful, giving varied retention times and non-reproducible data. After some further analyses, it was discovered that the silver nitrate column required long flow equilibration times before reproducible data were obtained. Once this occurred, retention times were reproducible to ca. 2 - 3%, peak resolution increased, and peak tailing decreased. Using this method, the BT/DBT window was retarded substantially relative to its NP/PH counterpart (Fig. 1).

High resolution and the reproducibility of retention times turned out to be especially important in the isolation of the



a)



b)

Figure 1. HPLC Separation of Naphthalene, Benzothiophene Phenanthrene and Dibenzothiophene

- a) Silica gel, pentane eluant
 b) 20% AgNO₃ on silica gel, 10% Benzene in Pentane eluant

BT and DBT fractions from JP-5. Because BT and DBT spikes are not visible in JP-5, this fraction had to be cut "blind" from the HPLC chromatogram (Fig. 2), based solely on retention time data from previous calibration runs with BT and DBT. Therefore, slight changes in retention times between calibration and sample runs would result in fractions containing varying amounts of the BT/DBT fraction, or the inclusion of large amounts of hydrocarbon impurities.

After investigating a number of column packings and eluants, it was found that 50 ul (ca. 40 mg) amounts of JP-5 fuels could be efficiently fractionated by 10% benzene in pentane on a 250 mm long by 10 mm i.d. column packed with 20% silver nitrate on silica gel. The column was allowed to equilibrate for some time with the eluant before retention time data for BT, NP, PH, and DBT were taken.

4.2 CGC ANALYSIS OF THE HPLC-SEPARATED FRACTIONS

The efficiency of the separation procedure was gauged by CGC analysis with simultaneous detection of the split column effluent using FID and HECD-S detectors. During the course of these studies, improvements were made in sulfur/carbon selectivity and GC resolution of the HECD-S. Using these improved methods, twelve fuels were separated, and the BT/DBT fraction analyzed by CGC.

4.2.1 Improved HECD-S Resolution

In our previous report (Ref. 1), it was seen that peaks in the HECD-S chromatogram were always more poorly resolved than those in the corresponding FID trace. This was ascribed to factors such as dead volume in the electrolytic conductivity detector and poorer chromatography of the more polar sulfur compounds. Discussions with technical personnel at Tracor, the GC manufacturer, indicated that traces of moisture in the reactor air could lead to broadened peaks. Installing a molecular sieve drying trap in the compressed air line led to

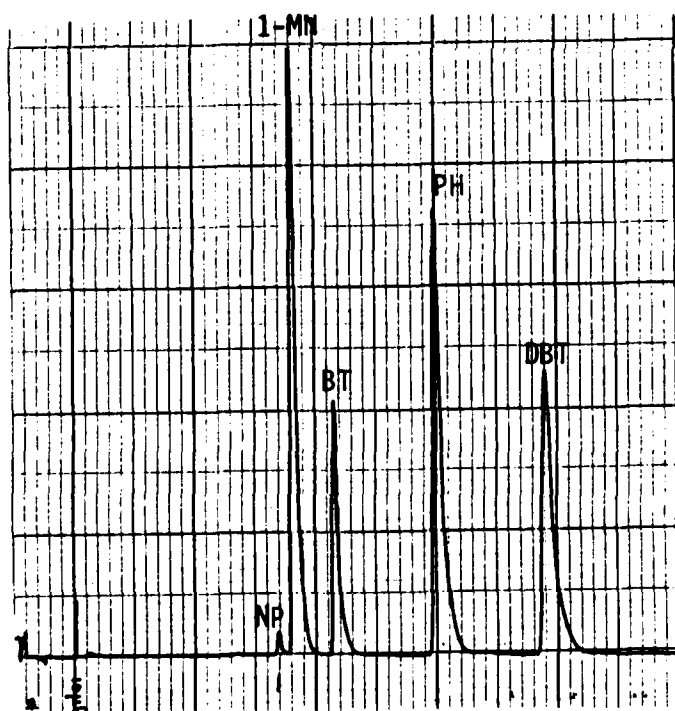
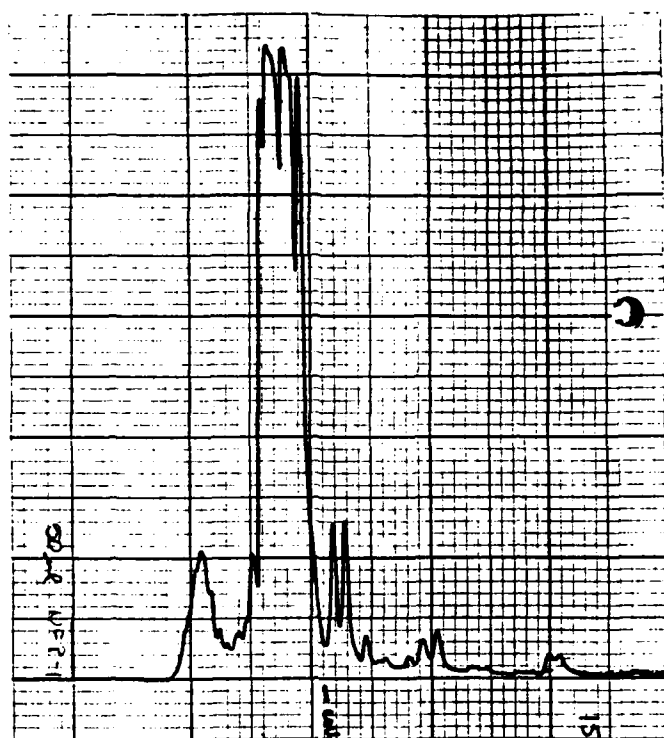


Figure 2. HPLC Chromatograms

a) NFP-1

b) Standard Mix (1-MN = Methyl-naphthalene)

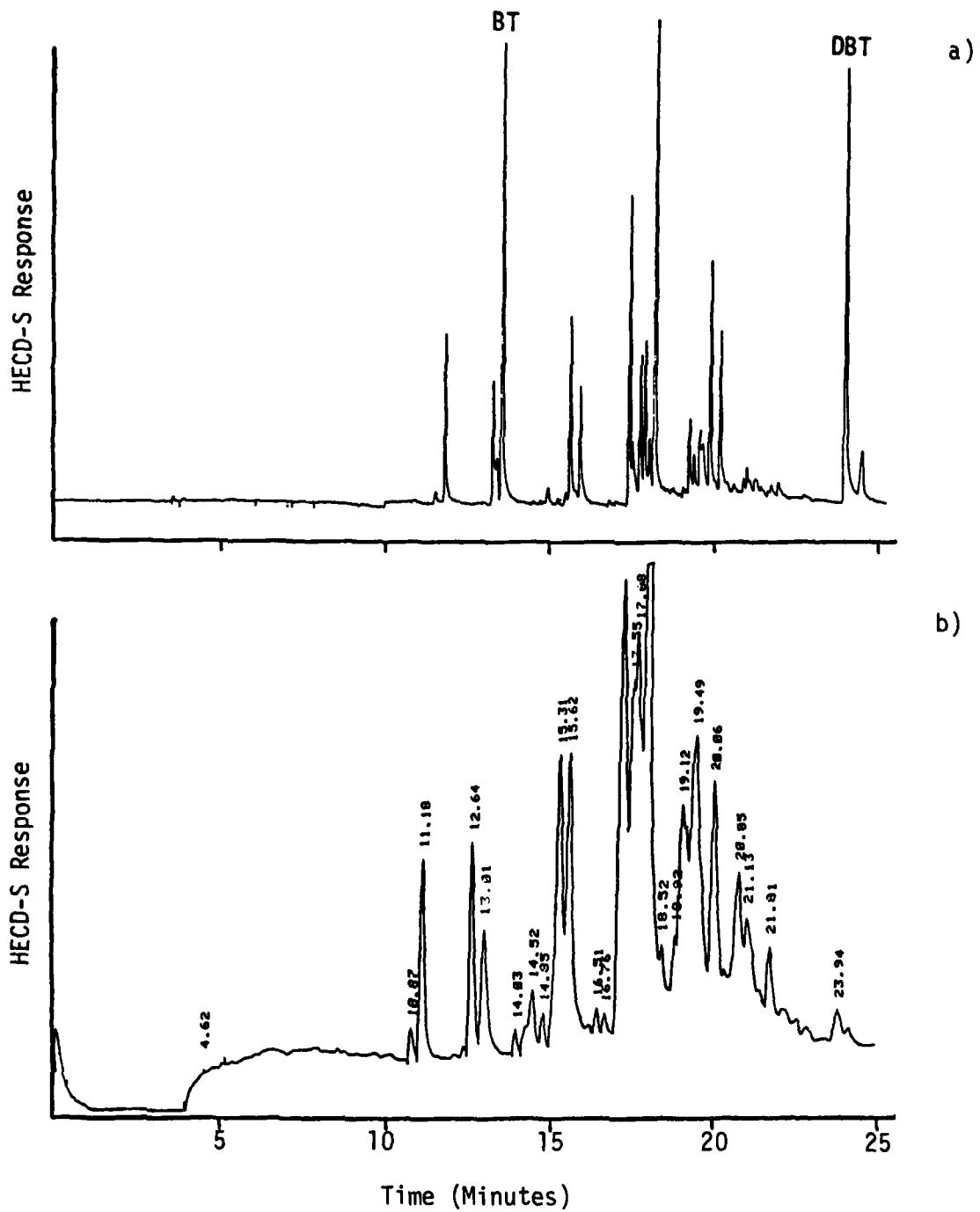


Figure 3. Capillary GC Chromatograms of NFP-1, HPLC on AgNO₃/silica gel, 1 pass.

- a) With drying tube on reactor air
- b) Without drying tube on reactor air

improved resolution and peak shape such that the HECD-S runs became equivalent in this regard to the FID data (Fig 3). All CGC/HECD-S data in this report were obtained with dried air.

4.2.2 Sulfur/Hydrocarbon Selectivity

A high sulfur/carbon selectivity is required for meaningful assessment of the efficiency of sulfur separation schemes. The HECD-S operates by mixing the GC effluent with air followed by oxidation in a heated (850 C) nickel tube to produce sulfur dioxide. The gas mixture is then introduced into an electrolytic conductivity (EC) flow cell using methanol as the flow solvent; the detector output is the conductivity of the methanol in the EC cell.

At relatively low levels of sulfur dioxide, the increase in conductivity imparted to the methanol is linear in sulfur dioxide concentration. However, several factors, some obvious and some not, can lead to questionable results.

At high concentrations, carbon dioxide formed by the combustion of hydrocarbons will produce an HECD-S response. While methanol was chosen as a solvent in the electrolytic conductivity cell to minimize response to non-sulfur compounds, large amounts of hydrocarbons can lead to false positive response. For example, the retention time of NP and PH spikes can sometimes be read directly from the HECD-S trace. Another factor is the condition of the heated nickel reactor tube. After a day or two at 850 C, the interior of the tube becomes oxidized and catalytically active, facilitating the oxidation of sulfur compounds to sulfur dioxide. However, its surface can be poisoned by excess hydrocarbons (which is why solvents are vented before they reach the tube), and its catalytic activity versus age and temperature are not clearly defined.

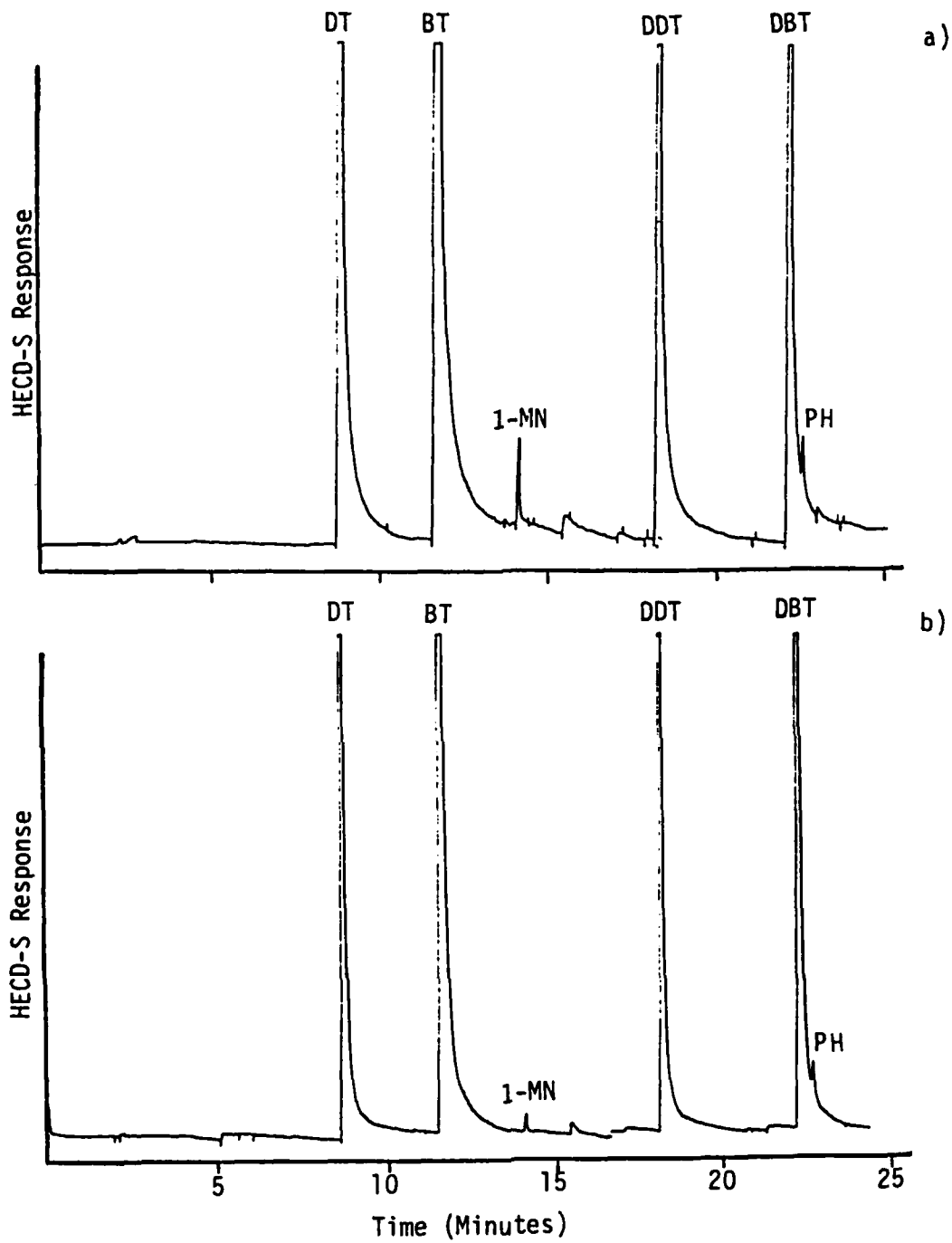


Figure 4. HECD-S Capillary GC Chromatograms of Sulfur Standard Mix

- a) Low S/C ratio, 530
- b) High S/C ratio, >1300

Consequently, a method was developed to standardize the HECD-S response, as well as gauge GC factors such as resolution and peak tailing, based on the injection of a test mixture of the following compounds:

- o Dithiane (DT)
- o BT
- o 1-Methylnaphthalene (1-MN)
- o Dodecanethiol (DDT)
- o PH
- o DBT

The resulting chromatograms were used as both a diagnostic tool to identify CGC problems such as a contaminated injector or a leaking effluent splitter, and as a means of calculating sulfur/carbon selectivity.

Sulfur/carbon selectivity is expressed as the HECD-S response to the amount of injected sulfur (in BT) to the amount of injected 1-MN:

$$S/C = \frac{\text{Peak area (HECD-S)/amt. of Sulfur injected (from BT)}}{\text{Peak area (HECD-S)/amt. of 1-MN injected}}$$

For this test mixture, BT/1-MN ratios of over 1000 were usually obtained, the equivalent of the HECD-S being approximately 250 times more sensitive to a molecule of BT than 1-MN. Chromatograms of high (>1300) and low (530) S/C selectivities are shown in Fig. 4. Note especially the larger 1-MN peak in the low S/C (upper) chromatogram.

4.2.3 GC Analyses

Both "one-pass" and "two-pass" samples were isolated and examined. Two-pass samples were obtained by isolating the one-pass fraction, concentrating it to a volume smaller than the HPLC injection loop, and reinjecting it taking care to place it in the HPLC injection loop between solvent "plugs",

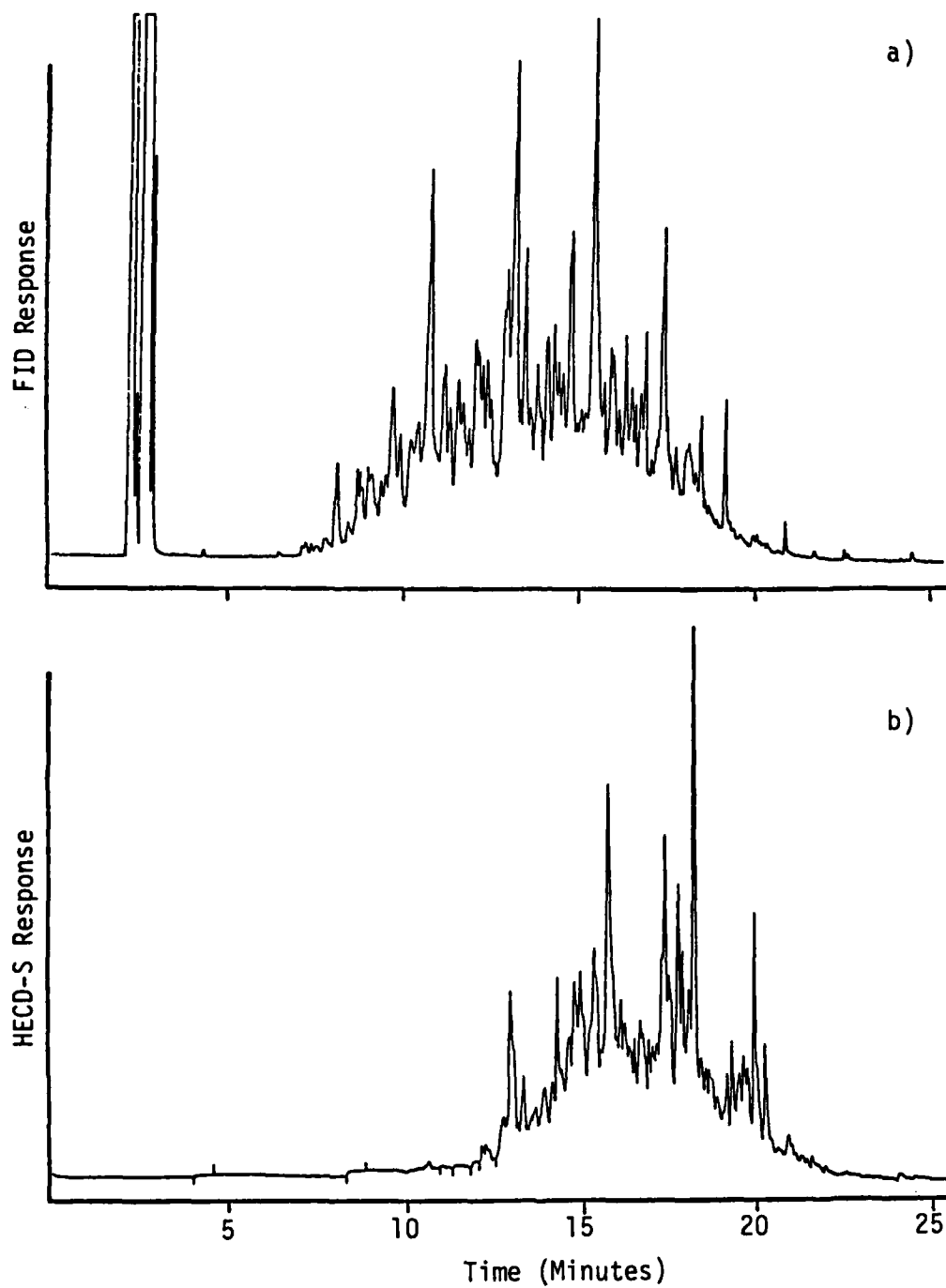


Figure 5. Capillary GC Chromatograms of NFP-3, As Received

- a) FID Trace
- b) HECD-S Trace

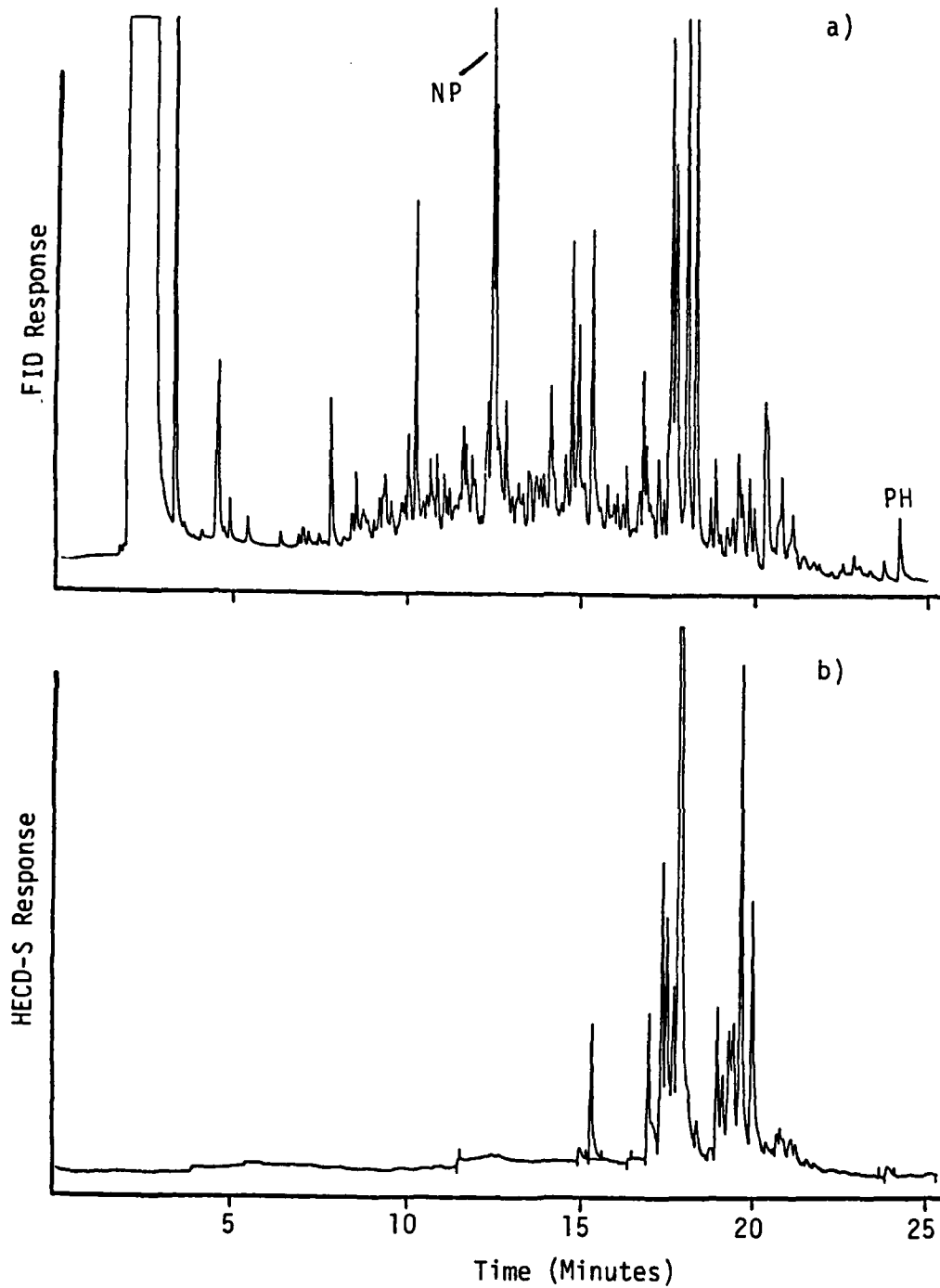


Figure 6. Capillary GC Chromatograms of NFP-3, HPLC on AgNO₃/Silica gel, 1 Pass

- a) FID Trace
- b) HECD-S Trace

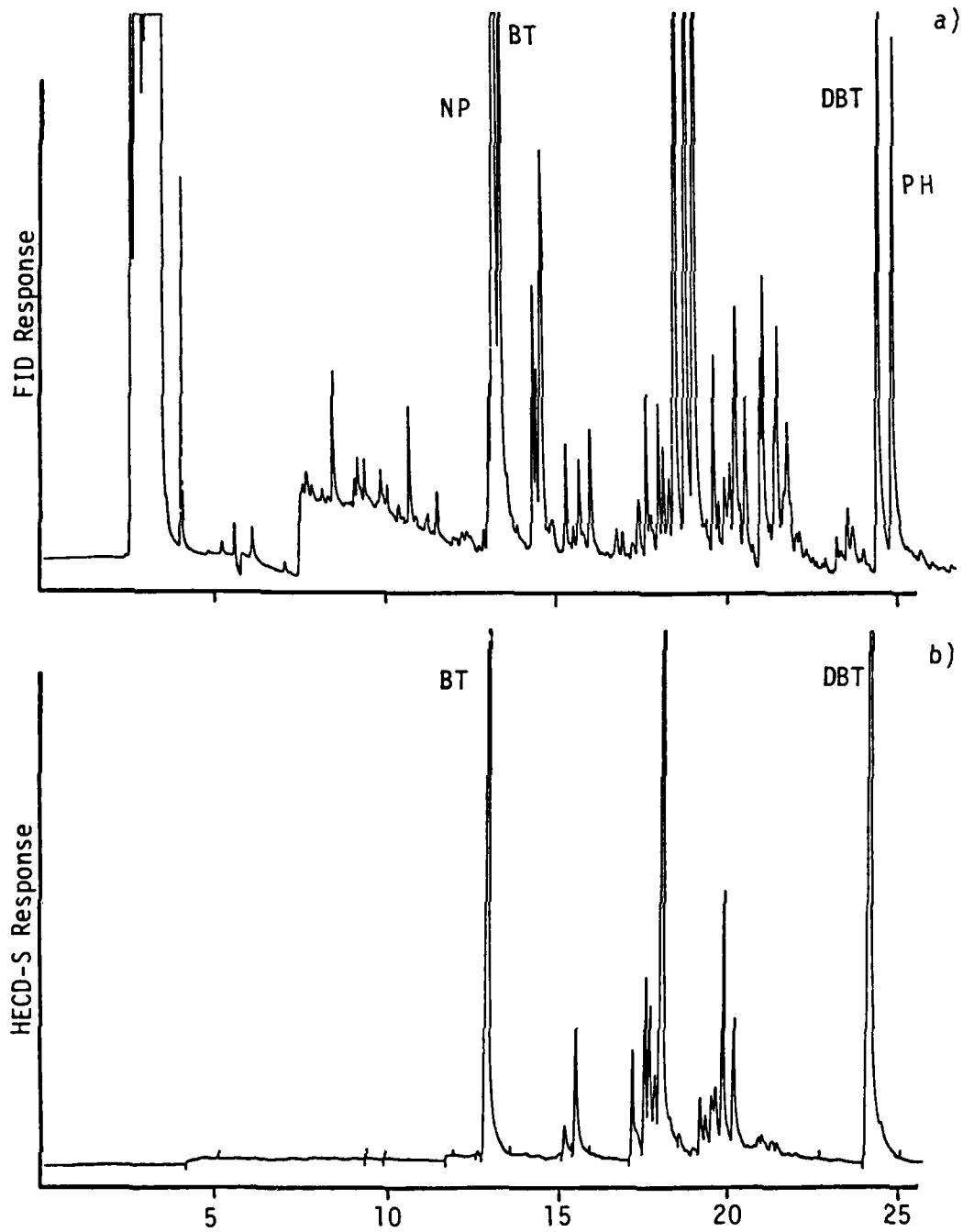


Figure 7. Capillary GC Chromatograms of NFP-3, HPLC on AgNO₃/Silica Gel, 2 Passes

- a) FID Trace
- b) HECD-S Trace

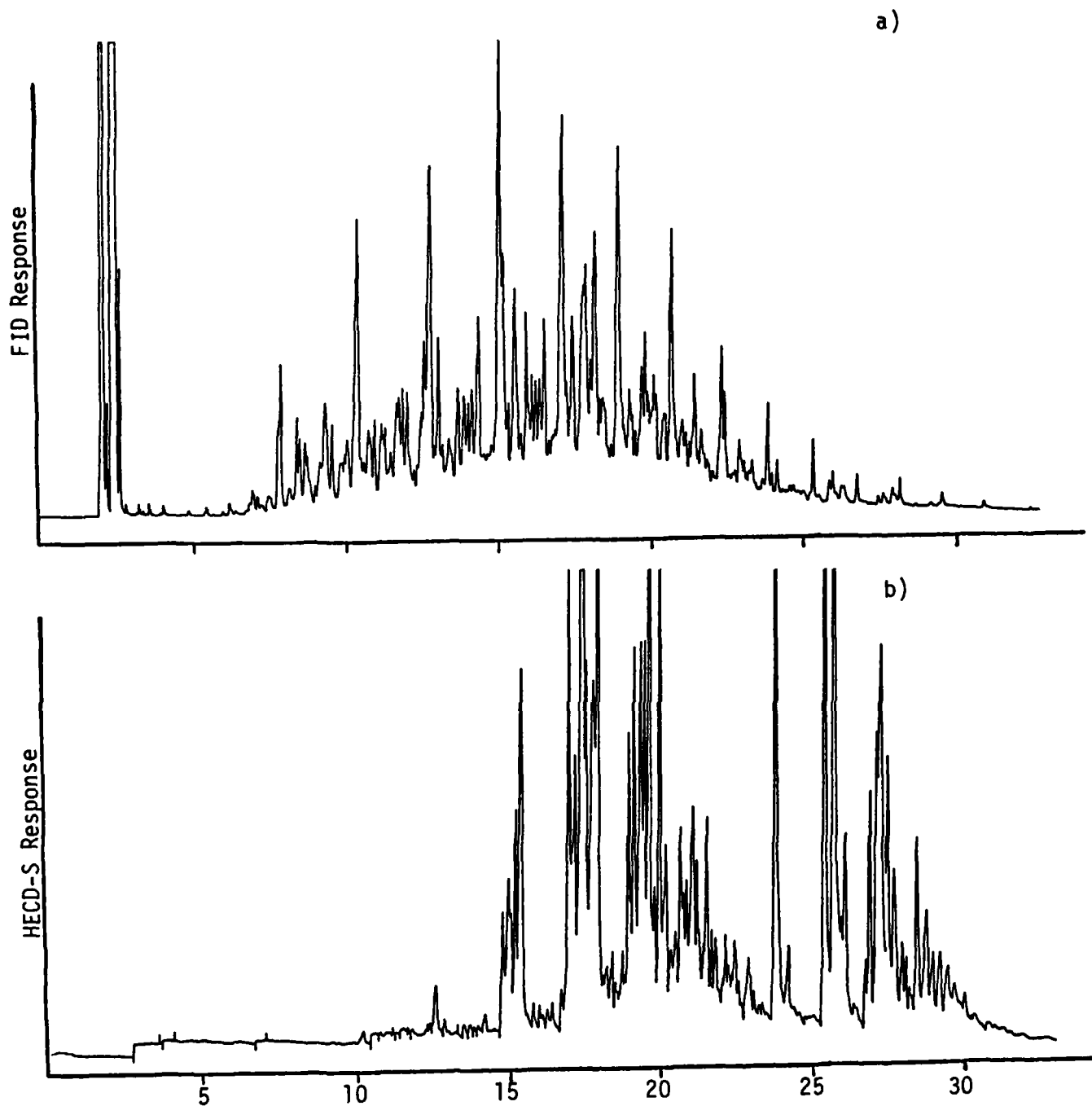


Figure 8. Capillary GC Chromatograms of NFP-12, As Received

- a) FID Trace
- b) HECD-S Trace

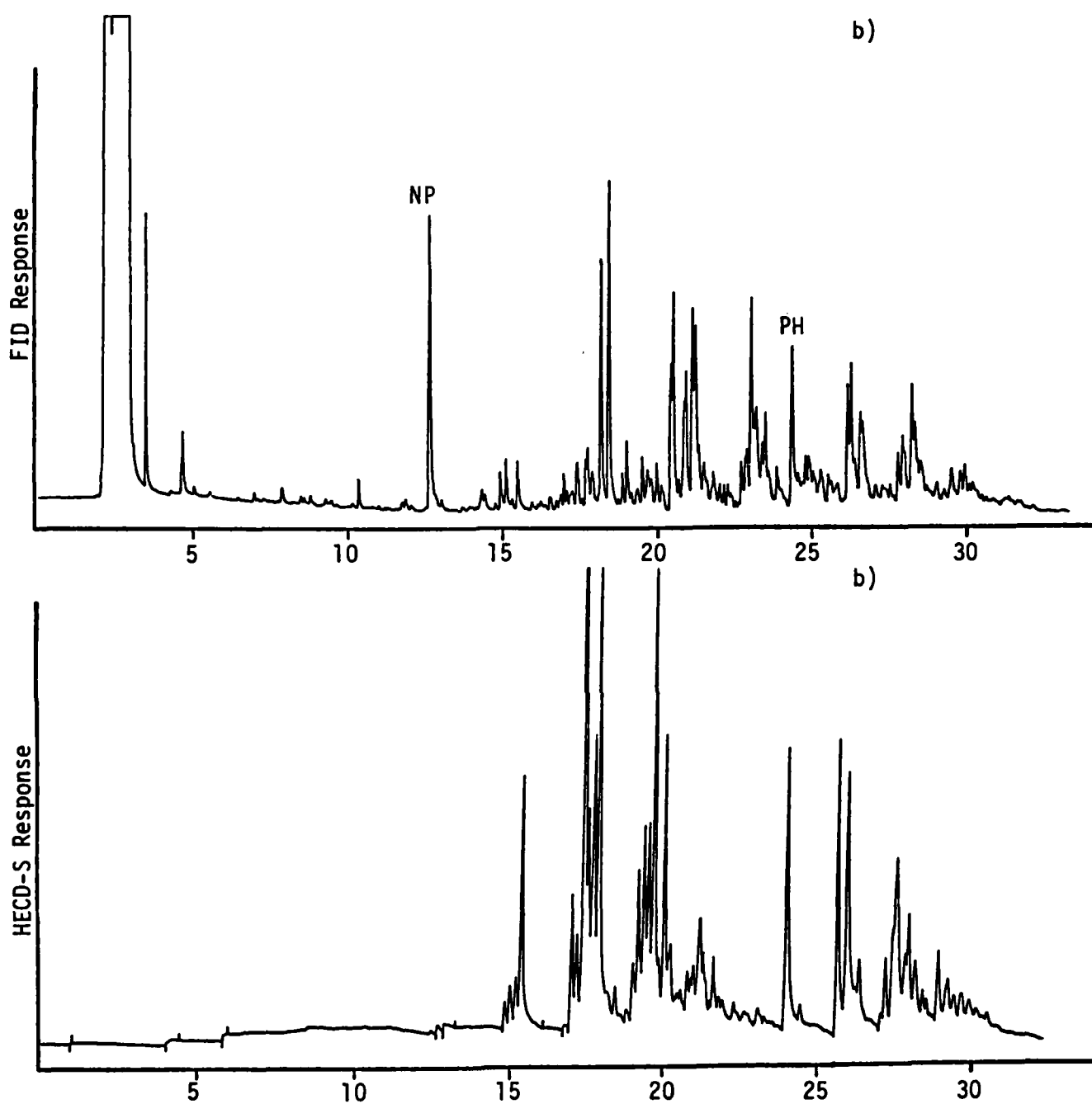


Figure 9. Capillary GC Chromatograms of NFP-12, HPLC on AgNO₃/Silica Gel, 1 Pass

- a) FID Trace
- b) HECD-S Trace

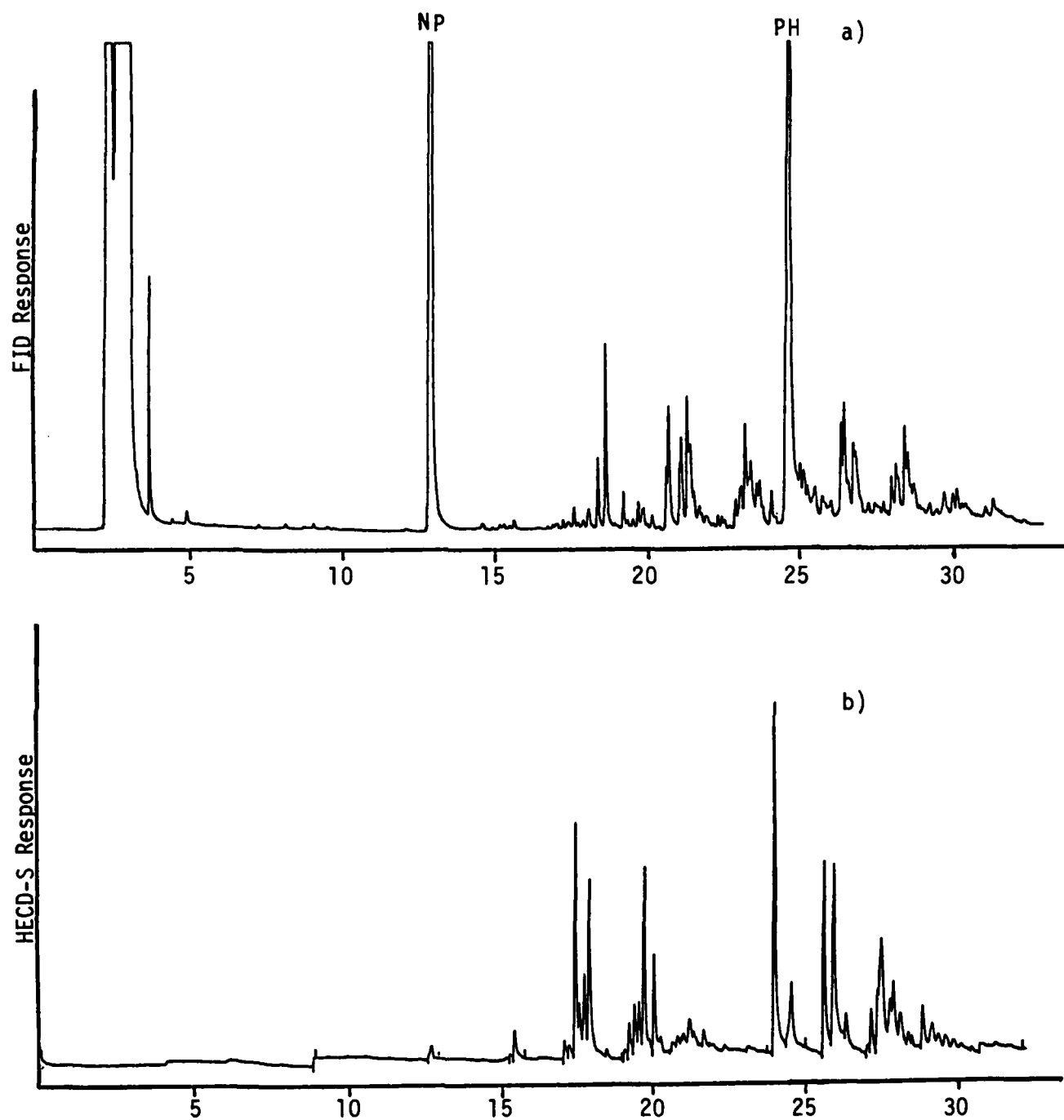


Figure 10. Capillary GC Chromatograms of NFP-12, HPLC On $\text{AgNO}_3/\text{Silica Gel}$, 2 Passes

- a) FID Trace
- b) HECD-S Trace

so as to insure that all of the sample was reintroduced. If the separation of sulfur compounds from PAH was ideal, there would be a correspondence between the FID and HECD-S peaks, i.e., all peaks contain sulfur and there are no extra hydrocarbon components.

Samples of NFP-3 and NFP-12 were subjected to 1- and 2-pass HPLC fractionation. GC analysis of these fractions (Figs 5 - 10) shows that:

- 1) for as-received fuels (Figs. 5 and 8), the sulfur fraction (HECD-S trace) elutes at higher temperatures than the hydrocarbon components (FID trace), in agreement with earlier simulated distillation data (Ref. 1).
- 2) both NFP-3 (a distilled-only fuel) and NFP-12 (a blended fuel with a higher boiling point range than NFP-3) show a similar qualitative distribution of BTs and DBTs in their common retention time range, as shown in Figs. 6 and 9).
- 3) the characteristic HECD-S pattern of the BTs and DBTs (identities confirmed by CGC/MS analyses, see below) is seen to emerge in the 1-pass (Figs. 6 and 9) and somewhat more clearly in the 2-pass samples (Figs. 7 and 10). Hints of this distribution, such as the cluster of peaks at between 17 and 18 minutes, can be seen in the as-received fuel (Fig. 5).
- 4) based on the appearance of prominent FID but not HECD-S peaks in the 7 - 10 minute region of the as-received samples, it seems likely that there is a sulfur fraction in the as-received fuel that is not present in the collected BT/DBT fraction. If the peaks that obscure the "final" BT/DBT pattern in the HECD-S trace arose from spurious response to hydrocarbons due to a low sulfur/carbon selectivity, the early FID peaks should have also elicited an HECD-S response.

5) the 2-pass method does not appear offer significant improvements over the 1-pass method and might lead to some loss of sulfur compounds. In the case of NFP-12, comparison of Figs. 9 and 10 indicates a significant loss of material in the group of peaks eluting at between 14 and 22 minutes.

4.2.4 Retention Indices

Because of the large number of peaks in the capillary runs, a method was adopted for assigning retention indices (RIs) to each peak of interest, based on a scheme developed by Lee for BTs and higher sulfur heterocycles (Ref. 5). Samples are spiked with with small amounts of NP, PH, and chrysene (CH), which are assigned RIs of 2000, 3000, and 4000, respectively. The RI of any peak is calculated by interpolation between bracketing standards. As long as the same nominal GC conditions are employed, slight variations in program rate and column temperature will not significantly affect the RI values.

The PAH RI standards do not contain sulfur and therefore give very small or nonexistent peaks on the HECD-S trace. For the purposes of RI calculation, their retention times were determined by superimposition of the FID chromatograms.

Representative RI data for NFP-3, 5, 12, and 13 are given in Table 1. For convenience, the Table groups peaks present in high (>2 area-%), medium (0.5 - 2 area-%), and low (<0.5 area-%). Comparison of GC data from additional samples was done by superposition of the chromatograms on a light table. In general, all of the fuels showed a similar distribution of sulfur compounds in their BT/DBT fraction.

4.3 CGC/MS Analysis of the HPLC-Separated Fractions

The object of these analyses was to identify the sulfur compounds isolated from the fuels by the HPLC method.

TABLE 1

Retention Indices for HPLC-Isolated Sulfur Compounds

RI	Small Peaks (<0.5%)				Med. Peaks(0.5-2%)				Large Peaks (>2%)			
	HP-5	HP-3	HP-12	HP-13	HP-5	HP-3	HP-12	HP-13	HP-5	HP-3	HP-12	HP-13
2000	2012			2009								
2100												
2200		2211	2208				2221 2236			2240	2248	
2300	2248			2251								
2400	2388 2401 2430 2444			2390 2403		2419		2402		2404		
2500						2441		2432 2446		2417 2428 2444 2457	2419 2431 2446 2459	2428 2460
2600	2507 2588 2611	2508 2541	2509 2541	2508 2571								
2700					2506 2590				2557 2570		2559 2572	
2800				2626		2642		2640 2661		2613	2626 2612	2614
2900	2639 2680 2687							2643 2660		2646	2641	
3000		2709 2807					2684	2679 2687				
3100	2700 2710 2725		2717	2708 2725		2721	2712 2721	2706 2723				
3200					2761 2783		2748 2760	2743 2754			2738	
3300			2770	2773		2782		2779 2783				
3400	2799	2789 2807	2796	2798 2809		2809		2808				
3500				2842		2841		2837				
3600	2871		2867	2868		2862						

TABLE 1 (Con't)

RI	Small Peaks (<0.5%)				Med. Peaks (0.5-2%)				Large Peaks (>2%)			
	HP-5	HP-3	HP-12	HP-13	HP-5	HP-3	HP-12	HP-13	HP-5	HP-3	HP-12	HP-13
2900			2904	2908	2909							
	2924			2935								
	2950											
	2963											
3000			3020				3031			3065	3078	3083
										3039		
										3064		
	3083		3079									
3100	3093				3108							
										3136	3136	3134
										3165	3164	3163
3200							3202			3203		3201
	3235			3232								
	3243											
			3264		3268		3279			3288		3278
3300										3299		3298
										3311	3309	3309
										3336		3335
										3346	3345	3345
							3366			3367		3367
3400			3416		3391		3391	3391				
					3405		3401	3404				
					3415							
					3424							
							3436			3437		3436
3500					3484		3484			3486		3485
3600					3528		3529					3529
					3540							
					3553		3551	3553				
					3566							
					3583			3585				
					3597							
					3611			3614				
3700	3633											
	3652		3656									
	3674											
	3696											

One-pass HPLC fractions from NFP-3, -12, and 13 were analyzed by CGC/MS under the same conditions used for the CGC runs. Mass spectra were generated using electron ionization (EI). Small amounts of NP, PH, and, for NFP-12 and 13, chrysene (CH) were added as RI markers. Two types of data presentation were examined: total ion chromatograms (TIC) in which the total of all mass ions is plotted versus scan number (the CGC/MS equivalent of CGC retention time), and limited mass chromatograms (LMC) in which the occurrence of a specific ion is plotted versus scan number.

4.3.1 Total Ion Chromatograms

The BT and DBT peaks from the 1-pass HPLC runs were not seriously contaminated with PAH, and compound identification was possible. In contrast, CGC/MS analysis of as-received fuels did not reveal the presence of BTs because of their low relative concentrations. No structural or positional information was derived from inspection of the individual mass spectra of the different BTs or DBTs because of the similarity of the fragmentation patterns produced under EI conditions.

Alkylated compounds were identified generically as, e.g., "C-3 BT" (trimethyl-, propyl, etc.) or "C-2 NP". Fig. 11 is the TIC of "NFP-3, 1-pass", showing the occurrence of both BTs and NPs from C-0 to C-3 with traces of DBT. Both NFP-12 and -13 show C-1 to C-3 BTs plus C-0 to C-3 DBTs. The CGC/FID and CGC/MS chromatograms are qualitatively very similar (for example, Fig. 6 and 11, respectively, for NFP-3, 1-pass).

It is interesting to note that no dihydro-BTs were found. These types of hydrogenated compounds were found during CGC/MS analysis of the PASH fraction from the Lee method (Ref. 1). The absence of these compounds in the HPLC fractions supports the contention that significant chemical artifacts were introduced during the hydrogenation step.

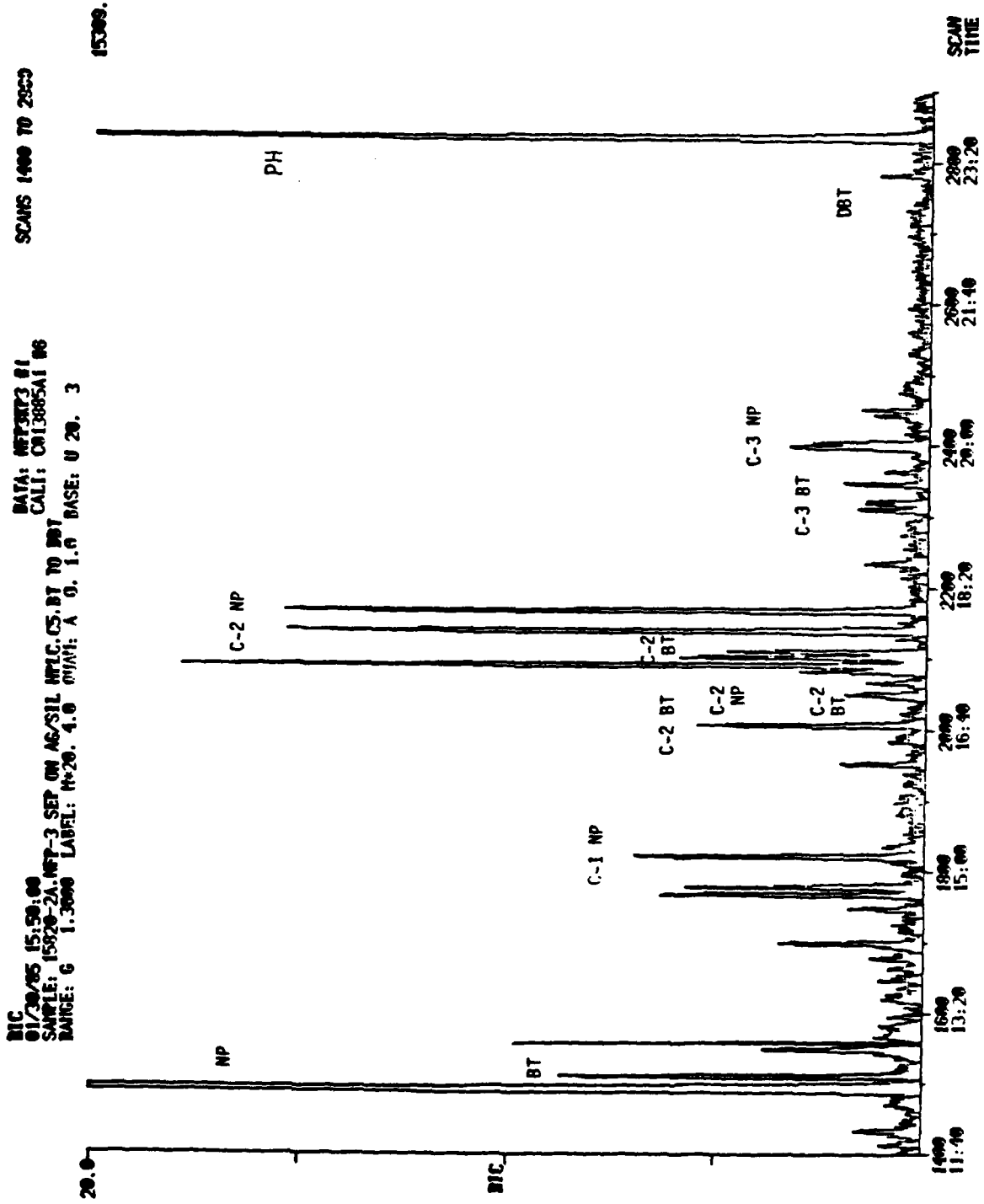


Figure 11. GC/MS TIC of NFP-3, 1-Pass Through Silver Nitrate/Silica Gel, Collected Fraction from BT to DBT.

4.3.2 Limited Mass Chromatograms

The occurrence of homologous series, e.g., C-1 to C-3 BTs, was determined with the help of LMCs generated from the TIC by the GC/MS data system. An LMC is a plot of a particular ion or selected ions versus retention time (scan number), rather than a plot of all ions as is the case for a TIC. The LMC technique takes advantage of the fact that a homologous series of alkylated compounds usually has a characteristic ion that increases by 14 amu per addition of each CH₂ group. The lower alkylated homologs of aromatic compounds tend to give the molecular ion as the base peak, or at least as a fairly intense ion. Thus, the alkylated homologs of BT (m/z 134) show ions at 148 (C1-BT), 162 (C2-BT), . . . , etc.. The similar series for NP is 128 (NP), 142 (C1-NP), 156 (C2-NP), . . . , etc.

Fig 12 shows a set of LMCs of "NFP-3, 1-pass" for C-0 through C-3 NPs and BTs, along with its TIC (vertically compressed compared to Fig. 11). Figs. 13 and 14 are similar sets of LMCs for NFP-12 and -13. Each trace is normalized to the highest peak, with that peak height (in relative units) at the right. In order of increasing retention time, the C-1 BTs can be assigned as the 7-, 2-, 5 and 6, and 3 and 4-methyl isomers (Ref. 6). A set of LMCs for the DBTs in NFP-12 and -13 are shown in Figs 15 and 16. As in the case of alkylated BTs, the mass spectra do not permit differentiation between isomers. However, Ref. 7 identifies the C-1 DBTs, in order of increasing retention time, as the 4, 2 and 3, and 1-methyl isomers.

4.4 SULFUR MASS BALANCE DETERMINATIONS

In order for the sulfur separation scheme to be validated, it must be shown that the sulfur content of all of the isolated fraction equals that in the as-received fuel itself. The relatively small samples obtained from the HPLC separations leads to problems not with compound analysis and

SCANS 1400 TO 2600

DATA: NFP3012 82837
CALL: 0813885A1 86

MIC + MASS CHROMATOGRAMS
01/20/85 15:50:00
SAMPLE: 15R20-2A, NFP-3 SEP ON AG/SIL HPLC, CS, BT TO DDT
RANGE: 6 1.3060 LABEL: H 0. 4.0 MIAMI: A 0. 1.0 MASE: U 20. 3

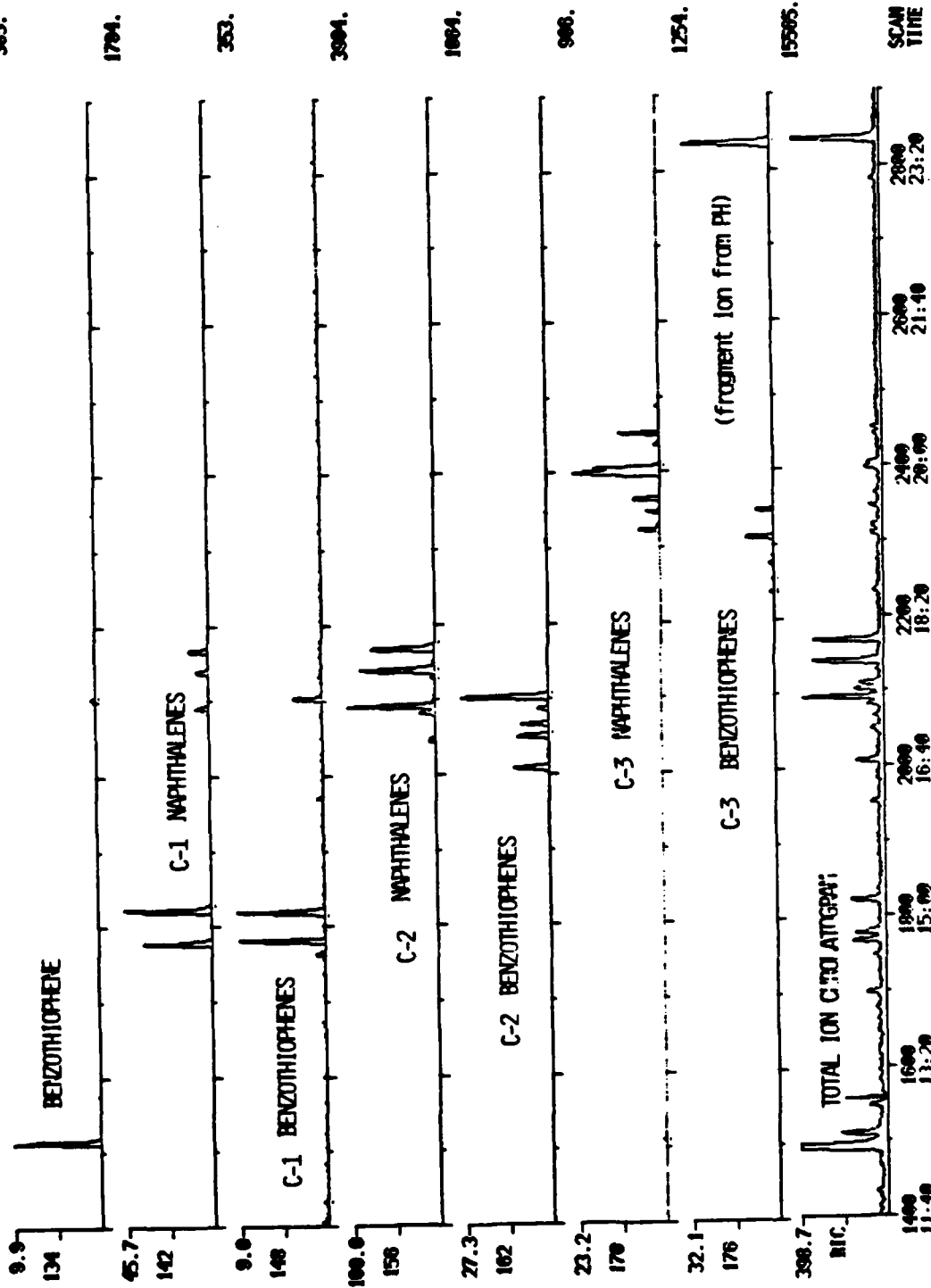


Figure 12. LMC of C-1 through C-3 Naphthalenes and BT plus C-1 through C-3 BT from the TIC of NFP-3 (1 Pass)

SCANS 1000 TO 1450

DATA: SIMULPI 01
CALL: C021505A 01

BIC + MASS CHROMATOGRAMS

02/07/85 9:29:00
SAMPLE: SURDOP A. 15820-7A. AG SII NPIC. IX
RANGE: 6 1.2710 LABEL: #13. 4.0 N1AH: A 0. 1.0 BASE: U 20. 3

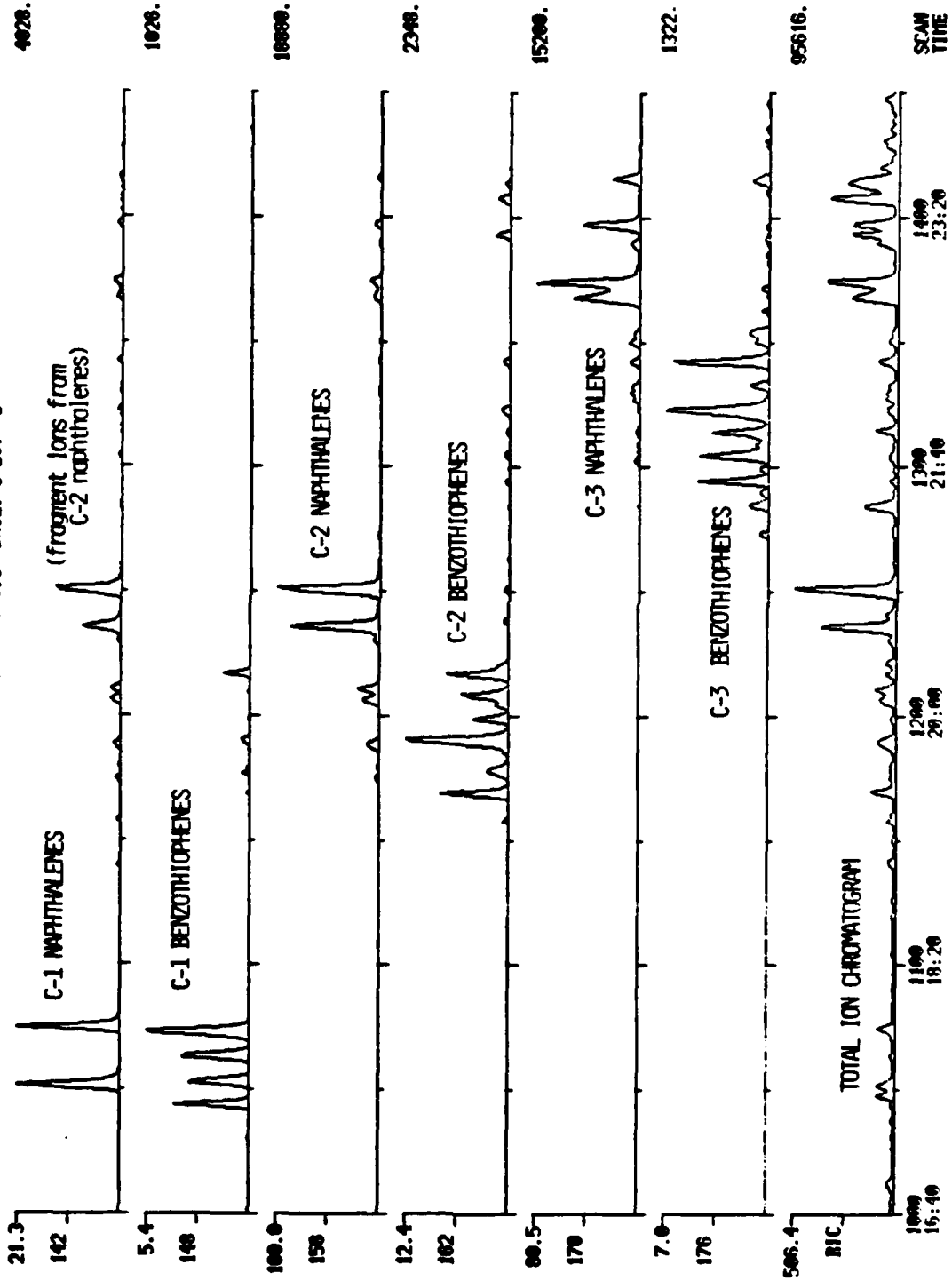


Figure 13. LMC of C-1 through C-3 NP and -BT, from the TIC of NFP-12, 1 Pass

BIC + MASS CHROMATOGRAMS
 02/15/85 14:01:00
 SAMPLE: 15820-8A, SUNDROP B, ACSIL, 1 PASS
 RANGE: 6 1.2200 LABEL: N-13, 4.0 OMAN: A 0. 1.0 BASE: U 20. 3

SCANS 850 TO 1250

DATA: SUNBKT1 01
 CALI: 0021595A 01

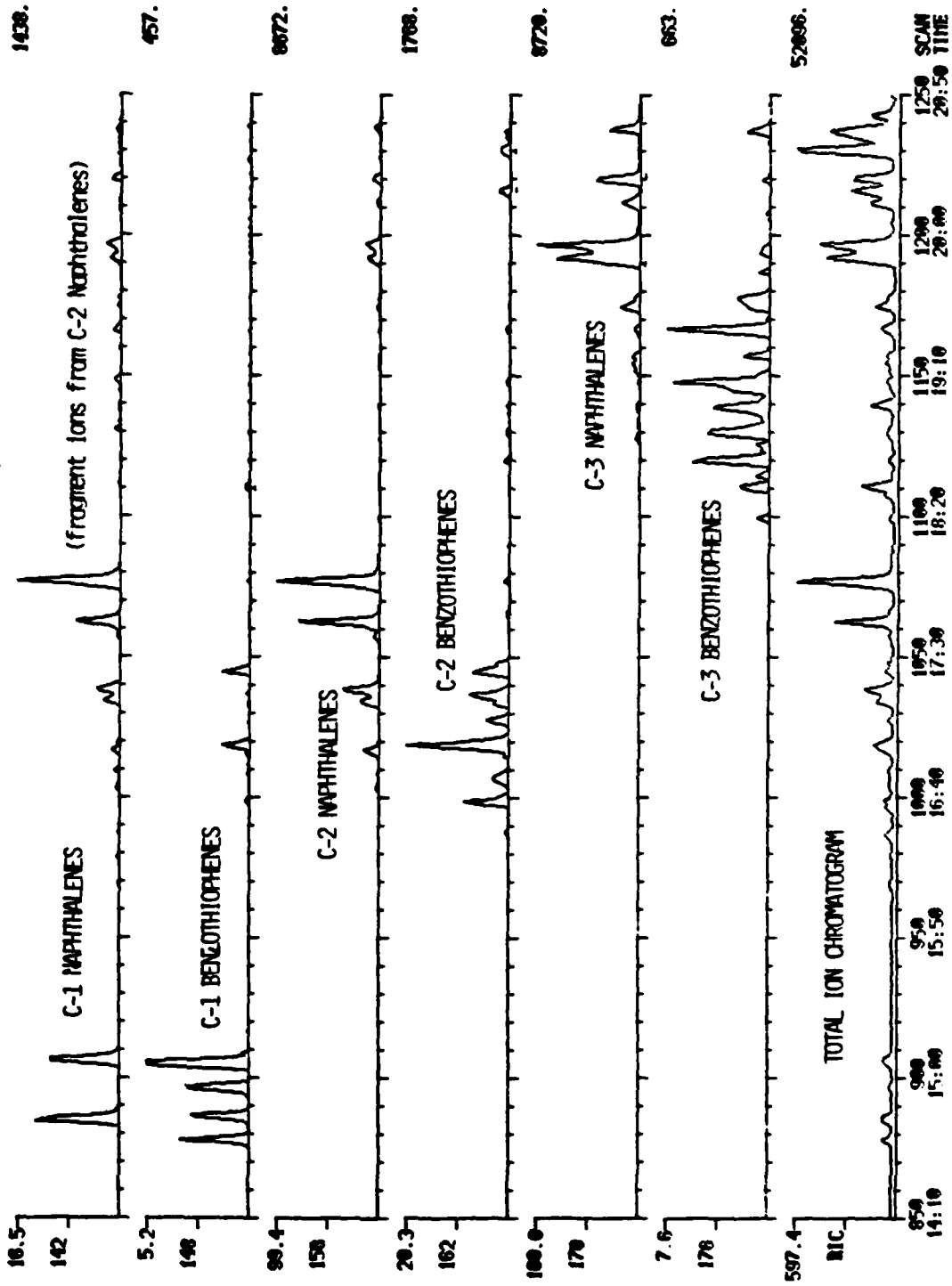


Figure 14. LMC of C-1 Through C-3 NP and -BT, from the TIC of NFP-13, 1 Pass

SCANS 1600 TO 2030

DATA: SUMMARY #1
CALL: C921585A #1

BIC + MASS CHROMATOGRAMS

02/07/85 9:29:00
SAMPLE: SUNCORD A. 15820-7A. AG SIL MPLC. 1X
RANGE: G 1.2710 LABEL: N 0. 4.0 OMAN: A 0. 1.0 BASE: U 20. 3

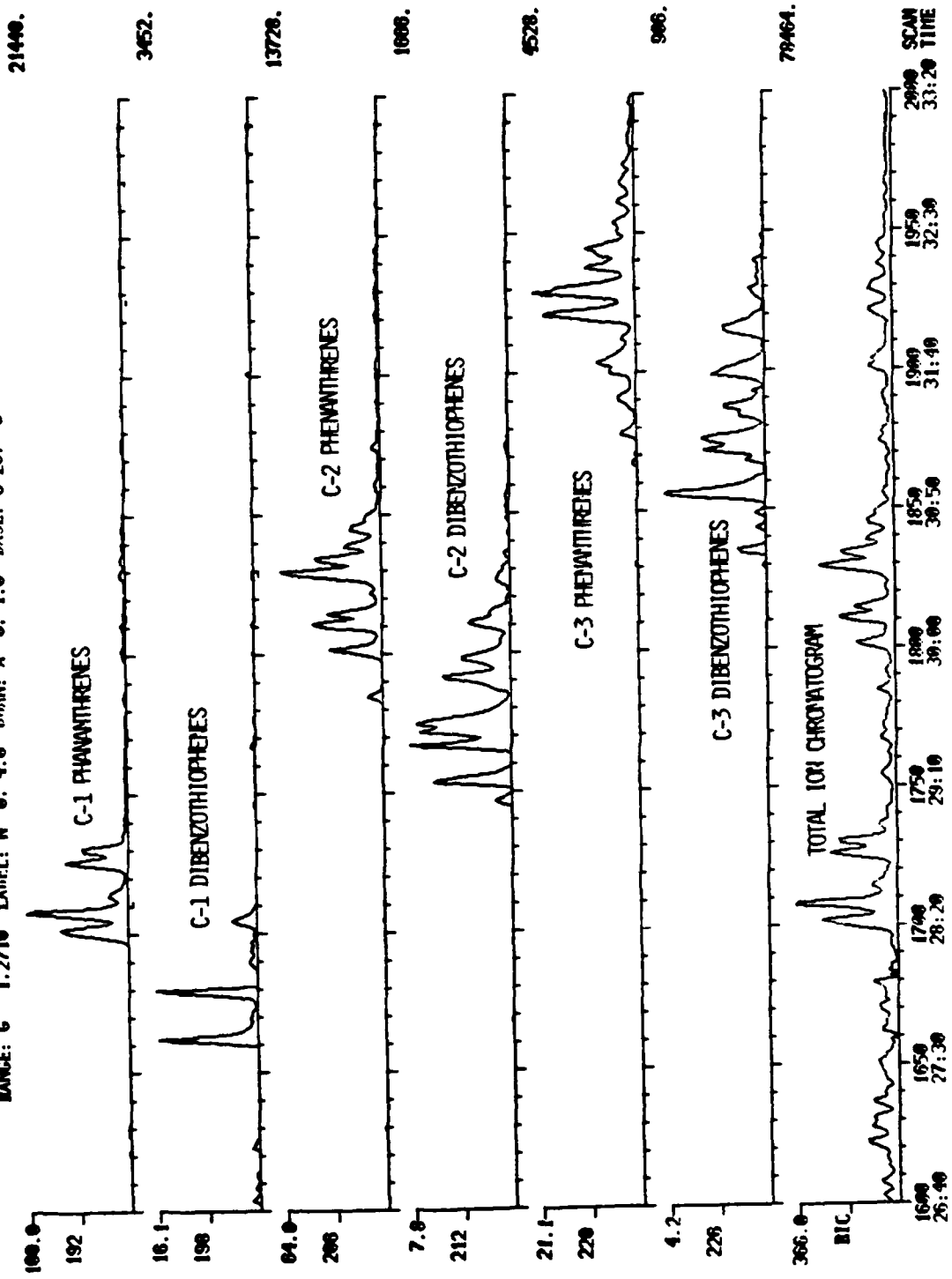


Figure 15. LMC of C-1 Through C-3 PH and DBT, from the TIC of NFP-12, 1 Pass

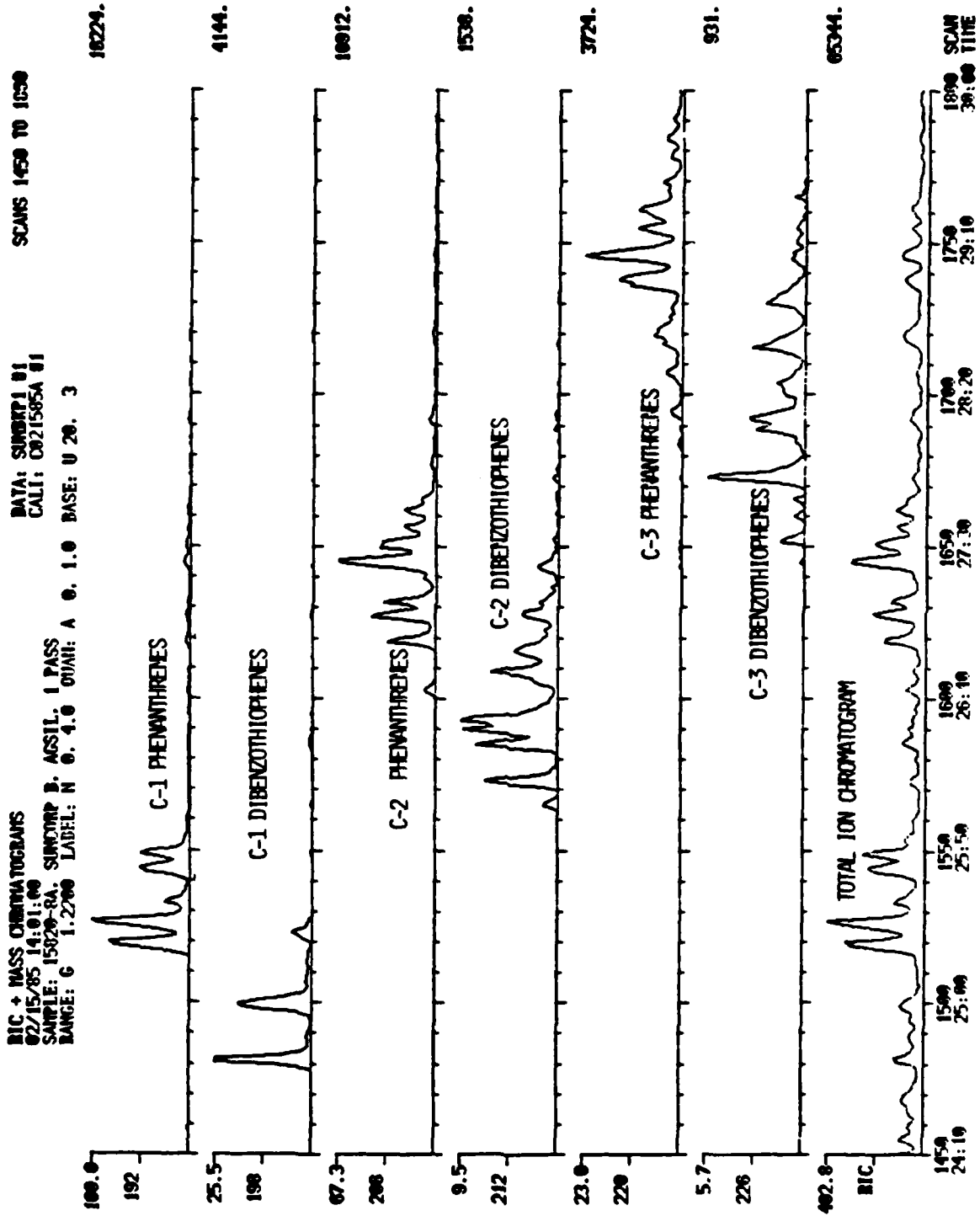


Figure 16. LMC of C-1 Through C-3 PH and DBT, from the TIC of NFP-13, 1 Pass

identification, but mass balance determinations. For example, a 50 ul (40 mg) sample of JP-5 with a sulfur titer of 0.2% contains 80 ug of sulfur. If the mass balance determinations on this sample are to be accurate to 2%, each analysis, whether on a high or low sulfur fraction, must have an accuracy of 1-2 ug, i.e., 0.02×80 ug. Lower sulfur fuels require correspondingly higher accuracies.

4.4.1 Conventional Combustion Bomb Analyses

While the amounts of material isolated by HPLC were adequate for CGC and CGC/MS analysis, the small absolute amounts of sulfur compounds in these fractions led to more stringent requirements for the total sulfur assays. Commonly used sulfur analyses such as the Lamp method (ASTM D1266-70) and X-ray fluorescence (ASTM D2622-77) are not amenable to the small samples isolated by HPLC.

Bomb calorimetry (ASTM D129-64) was investigated using several types of bombs with detection of the resulting sulfate ion by ion chromatography (IC). However, the method was found to suffer from high blanks, incomplete sample combustion, and the likelihood of introducing sulfur or sulfate contamination during sample handling and transfer steps. Some form of sulfur can be leached from the stainless steel bomb, and special care must be exercised in preventing these devices from being used for high sulfur assays. Other sources of sulfur include rinse and transfer solutions, the hydrogen peroxide or bromine water used to insure complete oxidation, and reduced sulfur compounds in reagents, etc. that are later oxidized to sulfate. Because there are a significant number of steps during which sulfur/sulfate contamination can be introduced, and no controlled method of distinguishing sample from blank sulfate, the efficacy of a bomb/sulfate assay must be open to question.

Incomplete combustion of the small samples will lead to low values due to incomplete conversion to sulfate. In extreme

cases, this phenomenon is accompanied by the formation of soot, especially, but not exclusively, when high aromatic content fuels are examined. The relatively high heat capacity of the sample pan, even when a 22 ml "mini-bomb" is used, is likely the principal cause of this problem. The use of burning aids would improve the situation, but at the risk of higher blank values. As was the case with inadvertant sulfate contamination, there is no foolproof method to either insure complete combustion or detect when the sample has not fully burned.

4.4.2 Specialized Sulfur Analyzers

A Dohrmann-Xertex low level sulfur analyzer was investigated as an alternative approach to the oxygen bomb/IC method for total sulfur analysis of the collected HPLC fuel fractions. Like the bomb method, the Dohrmann System 701 analyzer burns the sample in an oxygen-rich environment. Instead of an IC finish, however, the sulfur dioxide is determined conductometrically in a water flow cell. Because sulfur dioxide and trioxide, as well as the major product, carbon dioxide, would all give rise to a conductivity change, a trapping/conversion device is placed between the oven and the conductivity cell to effect a separation of the interfering species. The trap is a nickel oxide tube maintained at 500 C. At this temperature, sulfur dioxide and trioxide are converted to non-volatile nickel sulfate, while carbon dioxide passes through unretained. After the sample has been combusted, the trap is swept with a stream of dry nitrogen and heated to 900 C. At this temperature, sulfur dioxide is desorbed and measured. Thus, the conductivity cell sees only sulfur dioxide and accurate assays are possible without a need to know the dioxide/trioxide ratio.

4.4.3 Development of the Integrated Sulfur Detector (ISD)

The Dohrmann sulfur analyzer was able to quantitate ppb levels of sulfur in fuel samples via an oxidation/conductometric detection scheme. This is similar in principle to the Hall electrolytic conductivity detector in which the GC column effluent is oxidized in a heated, catalytic nickel tube and the sulfur dioxide detected conductometrically in a methanol flow cell. The principal difference between the Dohrmann and Hall detectors was the former's incorporation of a nickel oxide adsorber tube downstream of the oxidation chamber to trap the evolved sulfur dioxide. It seemed possible that the Hall detector could be modified to incorporate this trapping feature, while maintaining the advantages of sample introduction via a GC column.

Consequently, a trace sulfur analyzer was developed based on GC with a modified Hall detector, referred to as the integrated sulfur detector (ISD). In this method, sulfur compounds are oxidized to sulfur dioxide in the catalytic oven of the Hall detector, with the sulfur dioxide trapped downstream on a copper oxide trap maintained at 500 C. After the CGC run is completed, the trap is heated to 850 C, causing the sulfur dioxide to desorb and elute as an easily integrated, single peak, whose area is proportional to the amount of sulfur in the sample.

This one-step, ISD method has the following important features for the quantitation of very low sulfur levels:

- o reduced sample handling and contamination from rinse solvents, etc.
- o the ability to vent trace, low-boiling sulfur contamination that might be present in the HPLC solvent
- o sub-nanogram sensitivity
- o a typical analysis is completed in 15 minutes.

o the elimination of Hall detector response to carbon dioxide formed in the catalytic oven: carbon dioxide is not trapped on copper oxide at 500 C and thus is excluded from the post-run sulfur dioxide peak. This feature is very important in the analysis of low sulfur fractions, where response to hydrocarbons can give erroneously high sulfur values.

The successful development of the ISD was based on the following design philosophy:

- o residual HPLC solvent will be separated from the higher boiling JP-5 fractions in order to eliminate the possibility of contamination by trace amounts of solvent sulfur.
- o the conductivity flow cell should give reproducible and linear response to sulfur compounds
- o "blank" sulfur values must be low enough not interfere with trace sulfur measurements

Several components had to be separately evaluated to insure that the total device would perform accurately. Initial runs to determine the reproducibility of conductivity detector were performed with a short, packed column and a 1:50 dilution of NFP-1 in hexane. A 1.0 ul sample of the diluted fuel gave a peak area of 565,000 (22,000 counts/ng sulfur, based on a fuel density of 0.82 g/ml and a NRL assay of 0.16 wt-% sulfur) with a relative standard deviation of 4.0% (n = 5).

Sulfur dioxide was adsorbed and desorbed at 500 C and 850 C, respectively. Higher adsorption temperatures resulted in some sulfur dioxide "bleedthrough". The desorption temperature was high enough to release all of the trapped sulfur dioxide. Higher temperatures resulted in reduced heater life, and noisy, drifting baselines.

The effect of different adsorption temperatures is shown in Fig. 17. Fig. 17 (a) is the ISD trace of NFP-3 with the trap at 850 C; its FID trace is shown for comparison in (b). Fig. 17 (c) is the ISD trace with the trap at 500 C, followed by desorption at 850 C. In comparison with (a), very little breakthrough has occurred. The large, off-scale peak at 12 minutes is the sulfur dioxide that has desorbed in one step.

In addition, examination of chromatograms (a) and (c) shows that the peaks in (c) match the FID peaks in (b) more closely than the ISD peaks in (a). This suggests that the ISD response arises from carbon dioxide (which should not be trapped) rather than sulfur dioxide (which should).

The principal problem in the development of the ISD was high blanks. Traces of sulfur, sulfur dioxide, or other contaminants are trapped on the copper oxide and quantitated by the conductivity cell upon desorption. Through a fortuitous set of circumstances, initial runs gave blank values amounting to ca. 1 - 2% of the expected sample readings. However, later runs with different tanks of helium and air gave much higher readings. After determining by parametric analysis that the higher blanks were due, at least partially, to contaminants in the gases, scrubbers were installed just downstream of the cylinder regulators to remove the (presumed) low level of sulfur. The helium was scrubbed by passing the gas through a stainless steel trap containing activated charcoal and molecular sieves immersed in liquid nitrogen. The air was scrubbed first by passage through a column of nickel oxide on alumina catalyst heated to 650 C to oxidize all sulfur compounds to sulfur dioxide, with the sulfur dioxide then scrubbed from the air by a column of copper oxide at room temperature. These measures alleviated the problem somewhat, but it was found that traces of contaminants in the stainless steels, ferrules, connectors, etc., all contributed to the blanks.

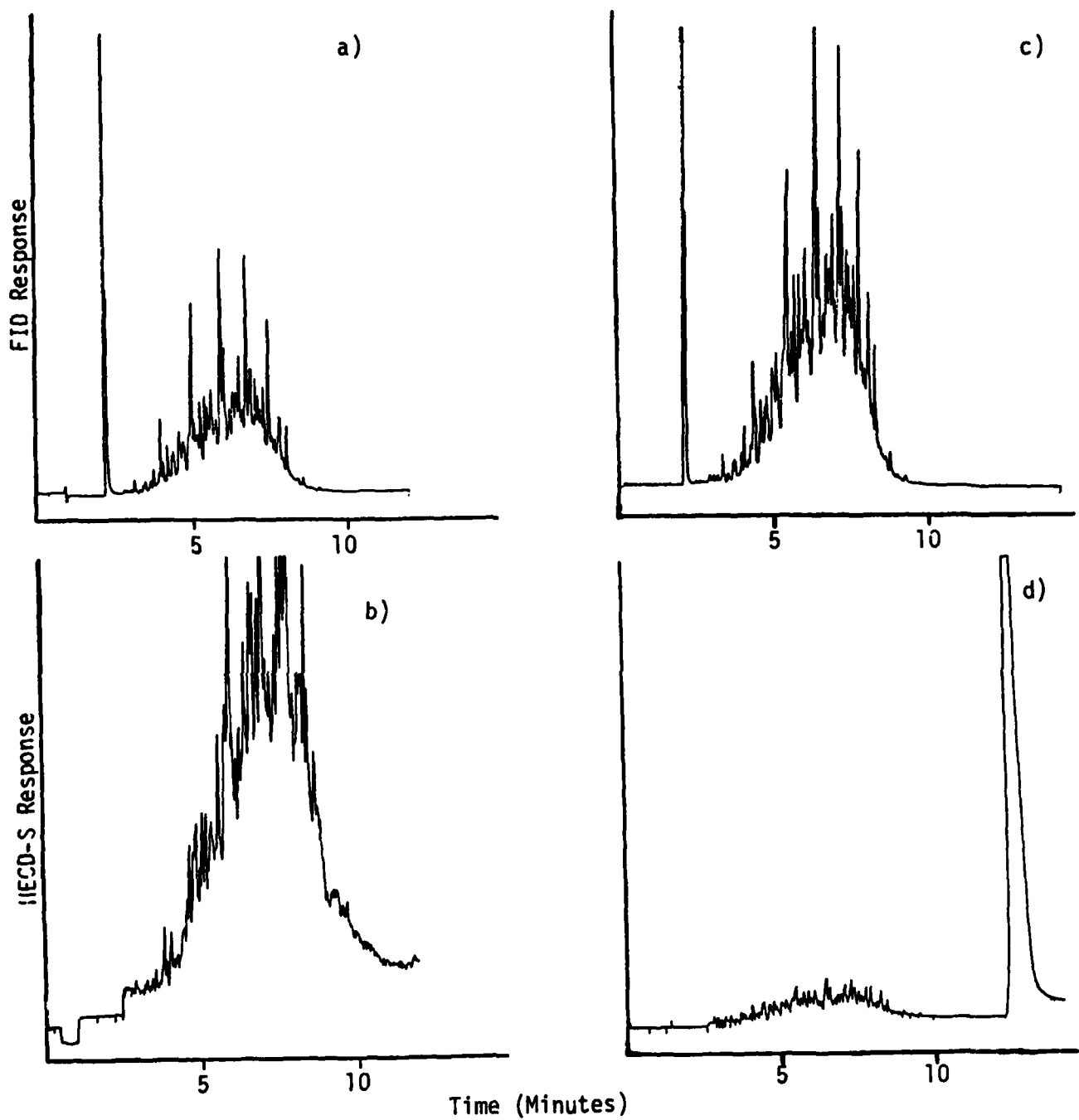


Figure 17. Capillary GC Chromatograms of NFP-3, As Received.
Upper Curves FID, Lower Curves HECD-S

- a), b) 1 μ l, CuO Tube at 850°C
 c), d) 2 μ l, CuO Tube at 500°C, then programmed
 to 850°C

Once the blank was reduced to manageable levels, linearity of response for the entire ISD was measured using standard solutions of BT and dodecanethiol in hexane. The plot of amount of sulfur injected versus ISD response, corrected for the blank value, is not linear (Fig. 18), but instead shows a higher slope at lower sulfur levels. Day-to-day variations in detector response were also found, but the general shape of the calibration curve was the same. In other words, the curve shifted up or down depending on detector response that particular day. Because this was found to be the case over a period of several days, sulfur assays on HPLC fractions were referenced to a calibration "anchor point", with the previously derived calibration curve shifted up or down to coincide with this value.

Concurrent with the above parametric studies, the following "working" ISD configuration was established:

- o the adsorber tube is constructed from a 5" length of alumina tubing containing a 1" charge of copper oxide held between quartz wool plugs. The tube is connected downstream of the nickel reactor tube by stainless steel Swagelok fittings and heated by several turns of Nichrome wire using two manually controlled Variacs in series for finer control. Temperature is monitored by a chromel-alumel thermocouple with digital readout.
- o samples are chromatographed on a 30m long DB-5 capillary column with split injection. After injection, the column is rapidly temperature programmed from 90 (2 minute hold) to 280 C (ballistic heaters) to separate solvent from sample.
- o all gases that will eventually enter the ISD are scrubbed before they enter the GC in order to reduce the problem of sample blanks.

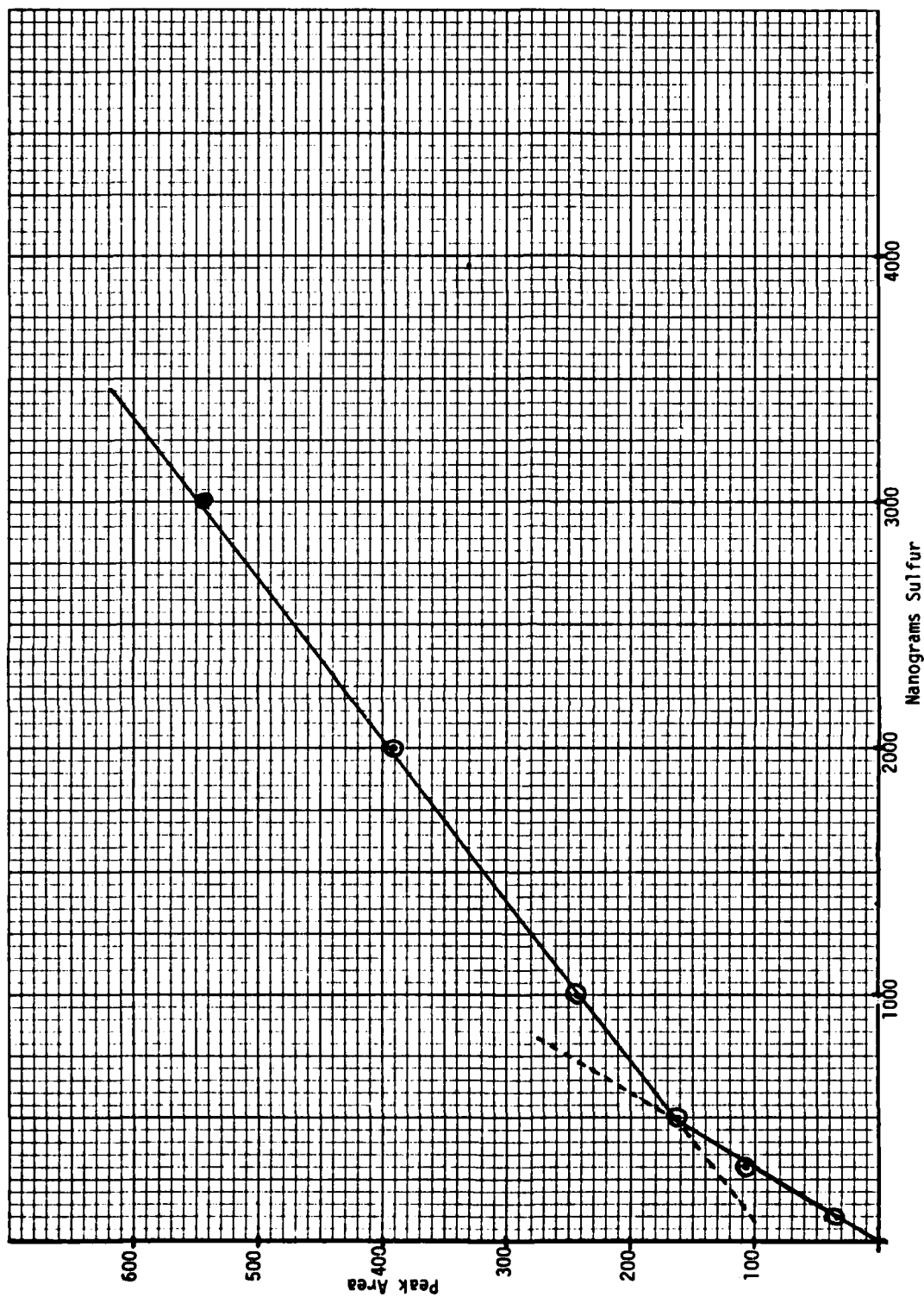


Figure 18. ng Sulfur Vs. Response, Peak Area for ISD.

- o The sulfur dioxide is trapped at 500 C and desorbed by quickly ramping the temperature to 850 C. With a little practice, the temperature can be ramped in approximately 60 seconds without substantial overshoot (less than 5 - 10 C) with the manually controlled Variacs.

4.4.4 Sulfur Assays Using the ISD

The instrument was calibrated with BT as an external standard, subtracting an average value for a system blank determined in previous runs. The calibration curve (Fig. 18) is not linear, and shows a higher normalized response at low sulfur levels. At this point, no effort was made to linearize or derive a mathematical expression for the detector response. Sulfur in the samples was quantitated by reading the values directly from the calibration curve.

The BT/DBT fractions from twelve fuel samples were separated and isolated by HPLC and sulfur mass balance relative to the unseparated, as-received fuel determined by the ISD. It should be emphasized that the ISD is still in the developmental stage, and accuracy cannot be guaranteed across the expected range of sulfur concentrations. The results (Table 2) show that the BT/DBT fraction accounts for ca. 30% of total fuel sulfur, with an as yet unidentified portion of the fuel likely accounting for most of the mass balance.

GC data confirms the absence of a substantial portion of the sulfur compounds. Comparison of the HECD-S chromatograms of the BT/DBT fraction and of as-received fuels (Fig. 5) shows that a large portion of the sulfur response is not accounted for in the BT/DBT fraction. Preliminary HPLC runs with NFP-1 in which the column was "stripped" with ethyl acetate gave a fraction that was very rich in sulfur compounds (Fig. 19) and tentatively identified by CGC/MS as aliphatic sulfides.

Visual comparison of the CGC/HECD-S chromatograms of as-received NFP-1 versus the BT/DBT and "sulfide" fractions

Table 2

Sulfur Mass Balance Assays for the BT/DBT HPLC Fraction
Using the ISDIntegrator Counts X 10⁻³

NFP Sample	As-Received	BT/DBT Fraction	Percent of Total
1	265	51.5	19.4
2	10.3	19.7	191
3	176	37.6	21.4
6	58.0	45.2	77.9
7	83.8	23.4	27.9
10	128	35.4	27.7
11	32.7	11.0	33.6
14	69.7	28.9	41.5
16	73.0	32.4	44.4
17	55.5	7.9	14.2
18	97.6	26.9	27.6
19	129	40.9	31.7

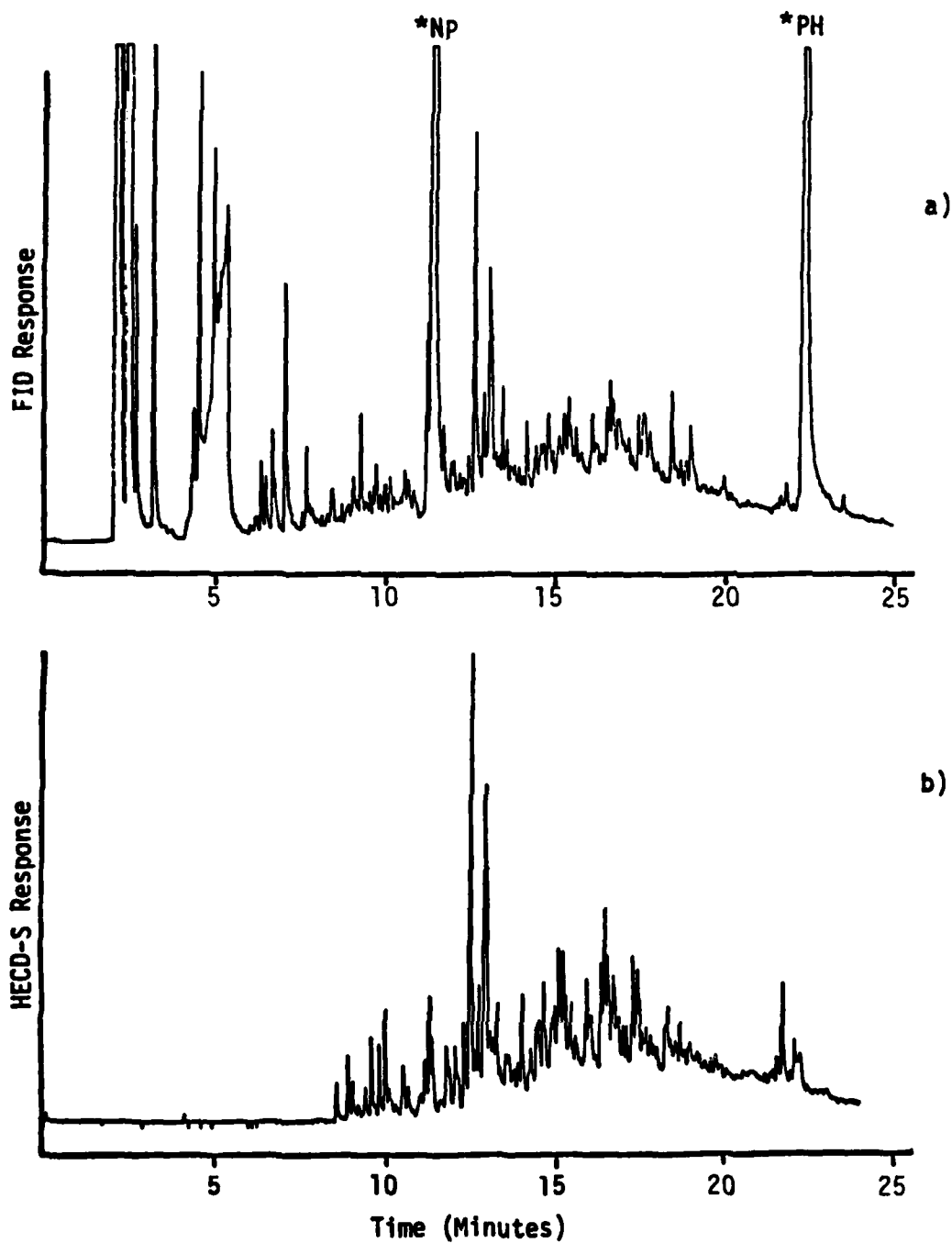


Figure 19 Capillary GC Chromatograms of the Ethyl Acetate Fraction of NFP-1.

- a) FID Trace
- b) HECD-S Trace

*Naphthalene (NP) and Phenanthrene (PH)
Standards Added

makes a plausible case for the sulfide fraction accounting for a good deal of the missing sulfur. Unfortunately, time and funds did not permit a more detailed investigation into the nature of this "sulfide" fraction.

4.5 THERMAL STRESS EXPERIMENTS

Preliminary experiments were initiated with NFP-1, 3, 5, 10, 11, and 13 to gauge the effects of thermal stressing, both in the presence or absence of air, on sulfur compound distributions. Glass ampules were charged with 0.2 ml of fuel, and the air samples sealed directly under ambient conditions. The anaerobic samples were subjected to several freeze/pump/backfill/thaw cycles using liquid nitrogen coolant and nitrogen backfill.

NFP-1 and -13 showed no change in their HECD-S chromatograms after heating for 1 day at 100 C. Similarly, heating at 100 C for 8 days did not significantly change the appearance of the GC data. It appears that higher temperatures and/or longer reaction times are necessary to produce a significant change in the sulfur compound distribution, at least as shown in the HECD-S chromatograms. Furthermore, it is not clear whether small observed changes in the chromatograms arise from detector variability or real changes in sulfur compound distribution. More significant changes in the chromatograms would have rendered this point moot, pending a detailed comparison of "before" and "after" GC/MS data to determine the identity of the GC peaks in question.

5.0 REFERENCES

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6. LIST OF ABBREVIATIONS

BT	Benzothiophene
CGC	Capillary gas chromatography
CH	Chrysene
DBT	Dibenzothiophene
DDT	Dodecanethiol
DT	Dithiane
EC	Electrolytic conductivity
EI	Electron ionization
FID	Flame ionization detector
HECD-S	Hall electrolytic conductivity detector in the sulfur mode
HPLC	High performance liquid chromatography
HQ	Hydroquinones
IC	Ion chromatography
ISD	Integrated sulfur detector
LMC	Limited mass chromatogram
1-MN	1-Methyl naphthalene
MS	Mass spectrometry
NP	Naphthalene
PAH	Polycyclic aromatic hydrocarbons
PASH	Polycyclic aromatic sulfur heterocycles
PH	Phenanthrene
RI	Retention Indices
TIC	Total ion chromatogram

APPENDIX A

Sample Fuel Designations

Fuel No.	Refinery	Date Rec'd	Comments
NFP-1	Powerine	10 Oct 1982	One gallon, high sulfur JP-5 shipped from NRL, designated 80-5
NFP-2	Exxon Banicia	15 Oct 1982	Five gallons JP-5 distilled from 90% North Slope 10% San Joachin Valley crude. Heavily hydrotreated. No A0-35 added
NFP-3	Powerine	10 Nov 1982	One gallon JP-5 picked up at refinery. Designated TL-88 by Powerine
NFP-4	Mobil	5 Sept 1981	One pint JP-4, picked up at refinery
NFP-5	Nat. Bur. of Stds.	-	NBS Std. 1624a, Sulfur in Diesel Fuel Oil
NFP-6	n.a.	10 Dec 1982	1 gallon JP-5 from NAPC
NFP-7	Powerine	-	5 gallons JP-5
NFP-8	Ashland	8 Mar 1983	Ashland 140 solvent, 5 gallons, similar b.p. range to JP-5, no additives
NFP-9	Shell	9 Mar 1983	Shell solvent 71, 5 gallons, similar to NFP-8
NFP-10	Beacon	10 May 1983	5 gallons JP-5

Fuel No.	Refinery	Date Rec'd	Comments
NFP-11	Mobil	10 May 1983	5 gallons JP-5, picked up at refinery in glass gallon jugs
NFP-12	Sun	Oct 1984	1 pint Suntech A from NRL
NFP-13	Sun	Oct 1984	1 pint Suntech B from NRL
NFP-14	n.a.	10 April 85	1 pint NAPC 81-9A, JP-5
NFP-15	n.a.	10 April 85	1 pint NAPC 81-19A, high aromatic JP-5
NFP-16		5 Aug 85	50 ml NRL 83-57 Exxon Baton Rouge
NFP-17		5 Aug 85	50 ml NRL 83-60 Gulf Port Arthur
NFP-18		5 Aug 85	50 ml NRL 83-62 Mobil Torrance
NFP-19		5 Aug 85	50 ml NRL 83-63 Fletcher Oil

END

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