

UNITED STATES STEEL, LORAIN, OHIO, WORKS, BLACK RIVER SURVEY:
ANALYSIS FOR HEXANE ORGANIC EXTRACTABLES AND POLYNUCLEAR AROMATIC HYDROCARBONS

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SUMMARY

Three water and twelve sediment samples, collected at the U. S. Steel, Lorain, Ohio, works, were analyzed as part of an extensive biological and chemical survey of the Black River in the vicinity of the U. S. Steel site. Two water samples, taken from blast furnace effluents, were free of contamination. The coke sewer (002) sample did show the presence of small amounts of organic compounds, possibly paraffins, cycloparaffins, and/or olefins. The concentration of any individual component was less than 20 ppm (wt/v). Small amounts (<1 ppm) of polynuclear aromatic hydrocarbons (PAH) may have been present in the coke sewer sample. Water samples were analyzed by gas chromatography/mass spectrometry (GC/MS).

The sediment samples were extracted with n-hexane to determine organic solvent extractables - "Oil and Grease". Values ranged from 810 to 26,700 mg/kg based on dried sample weight. Highest values were at sampling sites in close proximity to the plant.

PAH were determined in sediment samples by gas chromatography (GC) and GC/MS. Liquid chromatography (LC) was used to separate PAH from other classes of organic compounds in hexane extracted residues. Quantitation of ten PAH in eight samples was then made by GC. These PAH represented an envelope of polynuclears of increasing ring complexity ranging from phenanthrene and anthracene (molecular weight 178) through two dibenzanthracenes

(MW 278). Several of the PAH quantitated are known carcinogens. Values of benz[a]- plus benz[e]pyrene ranged from 0.91 mg/kg (sample 19466) to 19 mg/kg (sample 19472). Values for dibenzanthracenes ranged from 0.37 (19467) to 12 mg/kg (19472). Sample 19472, collected just downstream from plant outfall 002, contained the largest concentrations of PAH; this sample was examined in detail by GC/MS. A broad spectrum of PAH was seen to be present; these included unsubstituted as well as methyl substituted polynuclears. Specialized GC/MS data system techniques were used to determine the presence of PAH. Isotope abundances were used to confirm molecular formulas.

INTRODUCTION

At the request of EPA Region V, NFIC-Cincinnati's Organic Chemistry Laboratories were asked to analyze twelve sediment and three water samples, collected by NFIC-Cincinnati personnel, at the U. S. Steel, Lorain, Ohio, works; this plant discharges into the Black River. This request is part of an extensive biological and chemical survey of the Black River in the vicinity of the U. S. Steel site in conjunction with EPA's pending court case against U. S. Steel. The sediment samples were to be analyzed for compounds extractable into an organic solvent; this procedure is better known as an Oil and Grease Determination. In addition the sediments were to be scanned for Polynuclear Aromatic Hydrocarbons (PAH). Certain PAH, for example benz[a]pyrene, are known to be powerful carcinogens. The three water samples were to be analyzed for the presence of organic compounds and in particular PAH. Chain of custody procedures were followed in handling the samples.

The request for PAH analysis arose out of the survey, conducted by Mr. Allen Lucas of these laboratories,¹ in which substantial concentrations of benz[a]pyrene (BaP) were found to be present in sediment samples collected at a U. S. Steel - Calumet site. Dr. Paul Clifford, who analyzed these samples, reported concentrations of BaP ranging from 1 to 380 mg/kg (dry sample weight) using gas chromatography/mass spectrometry (GC/MS) and fluorescence spectroscopy as analytical tools.

The approach taken in our laboratory to analyze for PAH in the Lorain sediment survey was different than in the Calumet case. In the latter

instance PAH were found as part of a general scan for organic compounds; phenanthrene, anthracene, and BaP were then selected as measures of PAH and carcinogenic content. In the Lorain case it was decided to analyze the samples for a broad spectrum of PAH from phenanthrene and anthracene (MW=178) to the dibenzanthracenes (MW= 278). It was felt that it would be of greater value scientifically to examine selected sediments for many individual PAH than all samples for, say, BaP. In fact a detailed PAH scan was obtained for eight of the twelve Lorain sediment samples.

EXPERIMENTAL

A. HEXANE EXTRACTABLES (OIL AND GREASE)

The method used for hexane organic extractables is essentially the same as outlined in the Standard Methods procedure.²

Samples were weighed into individual wide mouth porcelain crucibles. Before removal each sample was agitated in its original container to assure adequate mixing. A control was prepared. It contained 25 g of silica gel and 25 ml of water. Samples and the control, ca 50 g wet weight, were air dried at 30°C overnight in the individual crucibles. They were then crushed to fine particles and allowed to dry an additional two hours. Each residue was placed in a soxhlet thimble and extracted in individual soxhlet apparatuses into "distilled-in-glass" n-hexane for 10 hours. Hexane was evaporated to 15 ml by allowing a stream of nitrogen to flow over the solvent in the extraction flasks which were heated by a steam bath held at 80°C. The remaining sample and solvent from each flask were transferred to appropriate size vials. The extraction flasks were washed with small portions of n-hexane which were transferred to the vials. No apparent residue remained in the extraction flasks. A stream of nitrogen was allowed to flow over each sample vial, at room temperature, until the hexane solvent had evaporated. Checks were made to be certain that samples had reached a constant weight indicating complete hexane loss. Oil and grease is reported as mg, organic residue per kg, dry sample. It should be noted, that in all procedures, attempts were made to keep sample exposure to light in the laboratory to a minimum to prevent decomposition of compounds to be analyzed for in the residue.

B. LIQUID CHROMATOGRAPHIC FRACTIONATION

Polynuclear aromatic hydrocarbons were separated from other classes of organic compounds in the hexane extractable residues by a liquid chromatographic (LC) procedure given by Hoffmann and Wynder.³⁻⁵ In order to determine recovery of PAH from the LC column an experiment was performed.

Florisil, 60/100 mesh, was heated for an hour at 110°C and cooled in a dessicator. Forty grams of the activated Florisil was weighed and placed in a column chromatography tube whose dimensions were 40 X 2 cm (id). The volume occupied by the Florisil was 20.5 X 2 cm (id). Aluminum foil was placed around the column to prevent any possible photochemical reactions. With the stopcock in an open position, hexane was poured into the column. (It is imperative that the solid packing be uniform and without air bubbles). The initial hexane elutant was discarded. The volume of eluting solvent passing through the column was determined to be 37 ml. Five ml of a 1 mg/ml standard of BaP in cyclohexane was applied and adsorbed onto the column.

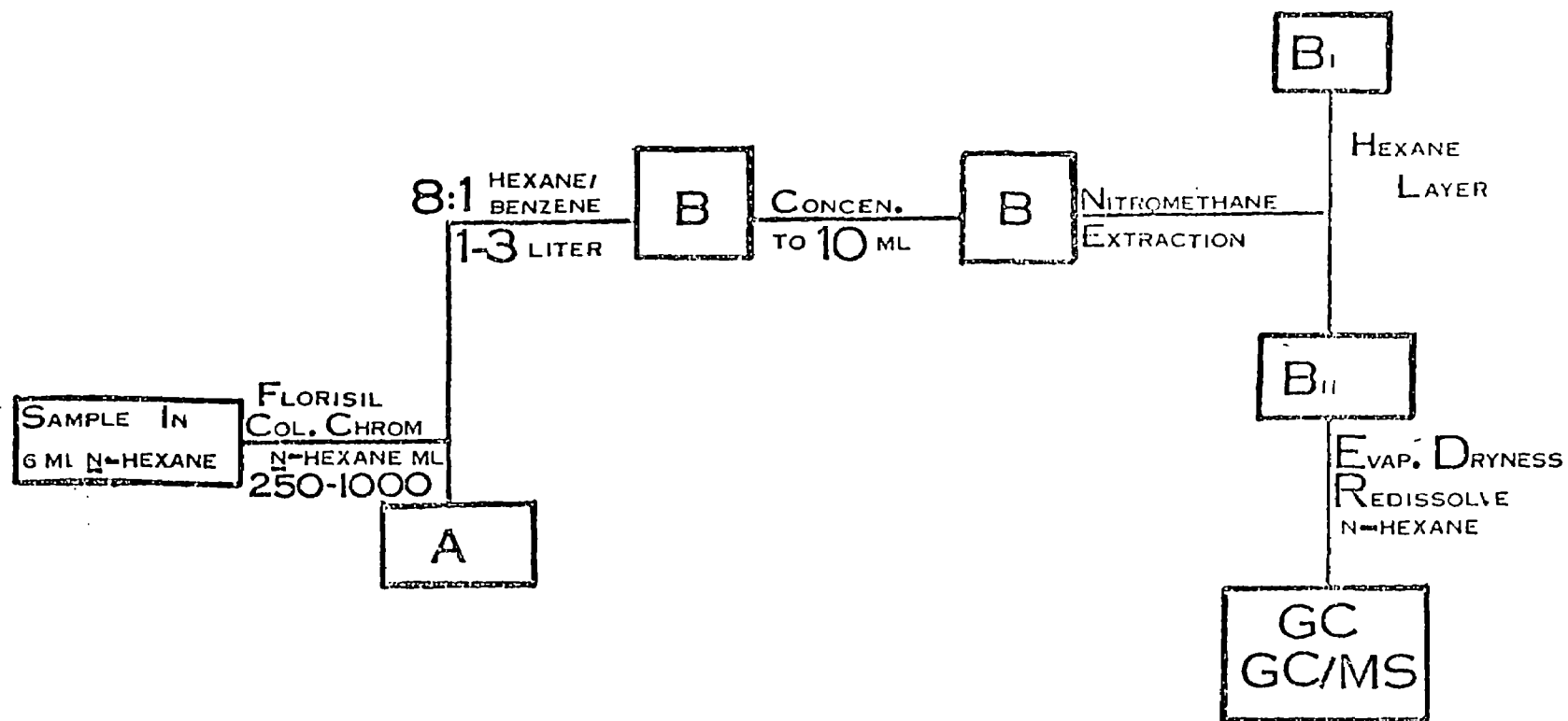
The first eluting solvent was n-hexane - 200 ml. The flow rate was 375 ml/hour. Twenty-five ml fractions were collected and viewed under ultraviolet (UV) light (long wavelength - 365 nm) and observed for fluorescence. No fluorescence was observed for all eight fractions.

The second eluting solvent was an 8:1 hexane/benzene (V/V) solution. The volume of this solution to be applied was determined experimentally. A critical variable which affects the total volume of the solvent used

is the flow rate (i.e., slower flow rates require less eluting volume). A flow rate of 340 ml/hour was established. Fifty ml fractions were collected in 100 ml reagent bottles. Each fraction collected was covered with aluminum foil and viewed under UV (365 nm) light. The total volume after which no further fluorescence was observed was 700 ml. The fractions were pooled and the total volume (700 ml) was concentrated in a 1 liter round bottom flask by use of a Büchi ROTAVAPOR-R. After the solvent was evaporated to approximately 30 ml, the concentrate was transferred to a 250 ml wide-mouth flask. The original container was washed with 8:1 hexane/benzene and the washings transferred to the 250 ml flask. Under a steam bath (at ca 70°C) and a gentle stream of nitrogen, the volume was further reduced to 2-5 ml. This solution was transferred to a 15 ml centrifuge tube and the 250 ml flask washed with 8:1 hexane/benzene; washings were added to the centrifuge tube and this volume was reduced to ca 2 ml and stored in a refrigerator until ready for analysis by GC.

Samples were chromatographed in a fashion similar to that in the BaP recovery experiment. The Scheme (Page 8) outlines the procedures used. The samples (i.e., hexane extractable organic residues) were dissolved in 6 ml n-hexane and applied to Florisil columns. n-Hexane was the first solvent; it was employed to elute non-polar paraffinic type material. Depending on the sample, 250 to 1000 ml of n-hexane were used. The n-hexane fraction is defined as fraction A. For one sample, number 19470, where a duplicate oil and grease determination was made, ten 100 ml fractions were collected

FLOWCHART OF TYPICAL SAMPLE WORKUP



SCHEME

in 125 ml Erlenmeyer flasks. No fluorescence was observed indicating no breakthrough of PAH. Fractions 2, 4, 6, and 10 were concentrated to ca 5 ml on a steam bath under a stream of nitrogen. The concentrates of these fractions were examined by gas chromatography.

After n-hexane, an 8:1 n-hexane/benzene (V/V) solution was used to elute fraction B which contains the PAH. As fractions were collected they were checked for fluorescence. Certain of the samples less concentrated in PAH, particularly in higher molecular weight PAH, displayed no fluorescence after ca one liter of solvent had been eluted from the column. For these samples elution was terminated when fluorescence was no longer observed. Other samples, for example 19472, displayed fluorescence after elution by 3.5 liters of solvent. For this sample eluate from 0-2500 ml and 2500-3500 ml were separated.

Fraction B was concentrated to 10 ml by previously described methods. It was then extracted four times with 10 ml portions of nitromethane (NM).^{3,4} The NM extracts (fraction B_{II} in Scheme) were pooled and evaporated to dryness and redissolved in n-hexane--1 to 5 ml depending on the sample.

C. GAS CHROMATOGRAPHY

A gas chromatographic (GC) method was employed to analyze for specific PAH, based on the system of Lao et al.⁶ A 10 ft X 1/8 in stainless steel column was employed which was packed with 6% Dexsil 300 on 80/100 mesh Supelcoport. A similar column packed with 3% Dexsil 300 was equally efficient and eluted compounds in a shorter time. A Varian 1400 GC equipped with a flame ionization detector (FID) and a Hewlett Packard Model 7100B, 1 MV recorder, were used. Injector temperature was 225°C and detector temperature 325°C. After injection the column was held at 165°C for two minutes then programmed at 4°C per minute to 295°C and held until the dibenzanthracenes had eluted. Total analysis time for the 6% and 3% Dexsil columns were ca 120 and 80 minutes, respectively. The carrier gas was helium and its flow rate 30 ml/min. The cylinder pressure regulator was set to deliver 80 psig to minimize pressure drop accross the column during the temperature program. Extreme care had to be taken to prevent helium leaks in the carrier gas line. A Gow-Mac Model 21-110 Leak Detector was useful in detecting leaks in gas lines.

Hamilton 10 µl syringes were employed for injection of standards and samples onto the GC column. Standards (1000 ppm) were prepared in Burdick and Jackson distilled-in-glass n-hexane using PAH obtained from commercial sources. Perylene was dissolved in benzene due to its low solubility in n-hexane. For quantitation, a standard mixture of ten PAH (see Results) was prepared in n-hexane. The standard mixture consisted of phenanthrene,

anthracene, fluoranthene, pyrene, benz[a]anthracene, benz[a]pyrene, benz[e]pyrene, perylene, dibenz[a,h]anthracene, and dibenz[a,c]anthracene. The concentration of each PAH in the standard was 50 ppm (wt/v) except for dibenz[a,h]anthracene which was 25 ppm. Concentrations of PAH in the samples were calculated by comparison with the standard mixture. Peak heights were used to compare the earlier eluting PAH (through benz[a]anthracene); peak areas were used for quantitations of BaP and BeP and later eluting compounds. In calculating concentrations of PAH components, corrections were applied for volumes of samples and standards analyzed and for total sample volumes. For comparison, the standard mixture was analyzed prior to sample analysis. When more than one sample was to be analyzed, the standard was run after every 2 - 3 samples.

In analyzing the paraffinic fraction A, a Perkin-Elmer Model 900 gas chromatograph equipped with a dual FID system and a Honeywell potentiometric recorder was employed. The GC was operated in the dual differential mode. Two 6 ft X 2 mm (id) glass columns packed with 3% OV-1 on 60/80 mesh Supelcoport were employed. Injector and detector temperatures were 220° and 320°C, respectively. The column was held at 80°C for five minutes after injection and then programmed at 10°C/minute to 220°C. The temperature was then held for ca 10 minutes.

D. GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

Analysis of standards and samples by GC/MS employed a Finnigan Model 1015 quadrupole GC/MS equipped with a System Industries Model 250 data system. Inasmuch as the GC on the Finnigan unit is a modified Varian 1400 instrument, columns could be interchanged with the GC possessing the FID.

The mass spectrometer (MS) was scanned by applying mass set voltages to the quadrupole rods from a 15-bit digital-to-analog convertor. At a given mass set voltage, only ions of a specific mass-to-charge ratio pass through the quadrupole field to the electron multiplier detector.⁷ The high mass range of the MS was used; the preamplifier setting was 10^{-7} amp/volt and 2600-2800 volts were applied to the electron multiplier.

Direct aqueous injection of water samples by GC/MS was accomplished using the method of Budde et al.⁸ A 6 ft X 2 mm id, glass column was packed with Chromosorb 101 and conditioned at 270°C for two days. Five μ l of sample was injected and the column oven held at 80°C for two minutes and then programmed at 4° or 8°C/minute to 220°C. The final temperature was held so that the total analysis time was 35-40 minutes. The MS ionizer and data system were turned on after water had eluted from the GC column and been pumped from the ion source. It was allowed to scan from 33-200 amu.

Water samples were also extracted and the extracts examined by GC/MS. One liter of sample was extracted twice with distilled-in-glass methylene chloride. The extracts were combined and dried by passage through two inches of

prewashed (with methylene chloride) anhydrous sodium sulfate in a glass column. After the combined extracts had been dried, 100 ml of distilled-in-glass acetone was poured through the column. The extract plus acetone was evaporated to 5 ml employing a Kuderna-Danish apparatus. In this way the methylene chloride (BP 39.8°C) was removed, leaving the sample dissolved in acetone (BP 56.1°C).

A 6 ft X 2 mm (id) glass column packed with 1.5% OV-17 + 1.95% QF-1 on Supelcoport, 100/120 mesh, was used to analyze extracted water samples. It was conditioned at 250°C for two days prior to analysis. Two to four µl of sample was injected onto the column and the MS was "turned on" after the solvent, acetone, had been pumped from the ion source, ca 1 to 2 minutes, and allowed to scan from 33-450 amu.

For sediment samples the 3% Dexsil column described in the section on gas chromatography was used. At the high temperatures needed for these analyses (ca 300°C) GS/MS separator and transfer lines had to be adjusted to 280°C and 230°C, respectively.

The System 250 data system has certain special features which were applicable to these analyses.⁹ These include choosing mass set voltages so that one can acquire data for selected ions of interest. This technique has the advantage of allowing the detection of compounds at 10-100 times lower concentrations than by normal scanning techniques. Another feature is being able to search the reconstructed gas chromatogram (RGC) for a limited number of ions. The RGC is a plot of ion current, normalized to 100% for the spectrum yielding the highest ion current against spectrum number.

The limited mass search allows the operator to ignore background and search for contributions to the ion current by selected ions of interest as a function of spectrum number.

RESULTS

A. WATER SAMPLES

Three water samples were received. The first was taken at the 1, 2, 5 blast furnace (east clarifier), the second at the 3, 4 blast furnace (west clarifier), and the third at the 002 discharge coke plant sewer. The samples were scanned for organic compounds, using the laboratory's gas chromatograph/mass spectrometer (GC/MS) unit. Two approaches were taken. First, a direct aqueous injection of sample was made into the GC/MS. This allows the determination of low molecular weight, volatile, organic compounds of varying types. The second procedure involved extraction of the sample into methylene chloride, addition of acetone, evaporation, and concentration (see Experimental Section).

The water samples were found to be essentially free of contamination. The direct aqueous injection technique showed that the two blast furnace effluents were free of lower molecular weight compounds though one of them probably contained a small amount of acetone. The coke plant sewer sample did show small quantities of organic compounds; the concentration of any individual component was likely less than 20 ppm (wt/v). While individual components were not identified, two or three classes of compounds were found possibly to be present; these are paraffins, cycloparaffins, and olefins. These classes were searched for by allowing the computer to scan the GC/MS reconstructed gas chromatograph for the presence of particular ions - m/e 43 and 57 for paraffins and m/e 55 and 69 for cycloparaffins and olefins.¹⁰

Few organic compounds were present in samples extracted with methylene chloride, even though the extraction procedures concentrated the samples some 200 fold. Blast furnace effluents showed no detectable compounds, while the coke plant sewer again showed small GC/MS peaks. For this sample the GC/MS was set to acquire data solely for ions corresponding to base peaks, which are also the molecular ions, of certain PAH. The ions were m/e 128 (naphthalene), 166 (fluorene), 178 (phenanthrene and anthracene), 202 (fluoranthene and pyrene), 228 (benz[a]anthracene and chrysene), and 252 (benz[a]pyrene and benz[e]pyrene).

GC/MS peaks were obtained, for the coke sewer extracted sample corresponding to m/e 166, 178, and 202 with 178 being the largest. These data indicate the presence of low concentrations (<1-5 ppm wt/v) of certain PAH. Phenanthrene and anthracene have a molecular weight of 178 and their presence would not be surprising, particularly since substantial amounts of these two PAH were found in sediment samples.

B. HEXANE EXTRACTABLES (OIL AND GREASE)

Table I presents data for the n-hexane extraction of organic compounds from the twelve sediment samples collected at the Lorain site. Table II gives a description of the sampling sites. Values ranged from 810 to 26,700 mg/kg based on the weight of samples dried overnight at 30°C. A blank containing 25 g of silica gel and 25 ml of water yielded no significant oil and grease. Five duplicate determinations were made and yielded excellent reproducibility.

TABLE I
"OIL AND GREASE" DATA
Lorain Sediment Samples

| Sample Number | Wet Sample Wt., Grams | Dry Sample Wt., Grams | Percent Volatiles | Weight Organic Residues, Grams | Oil and Grease, ppm mg/kg Dry Sample |
|---------------|-----------------------|-----------------------|-------------------|--------------------------------|--------------------------------------|
| Blank * | | | | 0.0031 | |
| 19465 | 70.46 | 30.79 | 56.4 | 0.0258 | 837 |
| 19466 | 50.83 | 25.62 | 49.6 | 0.0595 | 2,320 |
| 19467 | 53.02 | 28.84 | 45.6 | 0.1170 | 4,050 |
| 19467(A) | 52.98 | 28.85 | 45.6 | 0.0956 | 3,310 |
| 19468 | 51.96 | 33.35 | 35.9 | 0.0543 | 1,620 |
| 19469 | 60.43 | 34.53 | 42.9 | 0.3683 | 10,700 |
| 19469(A) | 57.82 | 33.30 | 42.5 | 0.3319 | 9,960 |
| 19470 | 52.67 | 32.69 | 38.0 | 0.3080 | 9,420 |
| 19470(A) | 49.70 | 30.83 | 38.0 | 0.3007 | 9,750 |
| 19471 | 49.57 | 20.46 | 58.8 | 0.2889 | 14,100 |
| 19472 | 55.53 | 36.74 | 33.9 | 0.9539 | 25,900 |
| 19472(A) | 55.27 | 36.09 | 34.8 | 0.9919 | 27,480 |
| 19473 | 49.08 | 29.08 | 39.6 | 0.5297 | 18,200 |
| 19474 | 64.79 | 39.26 | 39.5 | 0.9758 | 24,800 |
| 19474(A) | 62.34 | 36.31 | 41.8 | 0.9560 | 26,410 |
| 19475 | 50.83 | 31.26 | 38.7 | 0.2065 | 6,580 |
| 19476 | 73.05 | 37.25 | 49.1 | 0.2061 | 5,530 |

* Blank contained 25 g. Silica Gel and 25 ml. water

A - Duplicate determinations

TABLE II
DESCRIPTION OF BLACK RIVER SAMPLING STATIONS^a

| Sample Number | Sample Station | Mile Point | Site Description |
|---------------|----------------|------------|--|
| 19465 | 1 | - | Lake Water Treatment Intake |
| 19466 | 2 | - | Mouth of Harbor: Lake Erie-Black River |
| 19467 | 3B | 0.0 | Center of Black River (River Mouth) |
| 19468 | 4B | 1.0 | Center of River |
| 19469 | 5C | 2.5 | Right Hand Side of River, Looking Upstream |
| 19470 | 6B | 2.75 | Middle of Turning Basin Opposite Outfalls 003 and 004 |
| 19471 | 7B | 2.9 | Head of River Turning Basin - End of Commercial Navigation |
| 19472 | 8B | 3.4 | <u>ca</u> 500 ft. Downstream from Outfall 002 |
| 19473 | 9B | 4.0 | Near Plant Water Intake |
| 19474 | 10 | 5.0 | <u>ca</u> 0.2 mi. Downstream from Outfall 001 |
| 19475 | 11 | 0.2 | 0.2 mi Upstream on French Creek |
| 19476 | 12 | 5.3 | <u>ca</u> 0.2 mi. Upstream from Outfall 001 |

^aAll samples taken from the surface of the sediment layer.

C. POLYNUCLEAR AROMATIC HYDROCARBON ANALYSIS IN SEDIMENT SAMPLES

The organic residues obtained in the Oil and Grease determinations were used to analyze for PAH. These residues are complex mixtures of organic compounds of varying classes and a method of separating the PAH (fraction) was necessary. The largest body of information on the separation and analysis of PAH, other than in the air pollution field, lies in the tobacco smoke chemistry area. PAH determinations in organic residues obtained from sediments should be similar to determinations of PAH in tobacco tars. Separation of PAH was affected by the method of Wynder and Hoffmann.³⁻⁵ Several gas chromatographic (GC)¹¹⁻¹⁸ and gas chromatographic/mass spectrometric (GC/MS)¹⁹ methods of measuring PAH are available. Techniques for GC and GC/MS analysis advanced by Lao et al.⁶ appeared to be most applicable and were employed.

1. Liquid Chromatographic Separations of PAH

PAH were separated by the liquid chromatographic (LC) procedures outlined in the Scheme and detailed in the Experimental Section. Paraffinic type compounds are eluted from an LC Florisil Column by n-hexane (fraction A). The next solvent is an 8:1 hexane/benzene solution which elutes the PAH (fraction B). B is concentrated and PAH extracted into nitromethane (fraction B_{II}) to separate the PAH from other organic compounds that are eluted in fraction B.

Prior to analysis of the sediment organic residues an experiment was devised to measure PAH recovery from the LC column. Five ml of a 1 mg/ml (1000 ppm) benz[a]pyrene (BaP) solution was applied to a column and eluted

as in the Scheme except that the nitromethane (NM) extraction was omitted. The recovery of BaP was 97%.

It was determined that 1 liter of n-hexane was likely a sufficient amount of solvent to elute fraction A. For sample 19470 1 liter of n-hexane was eluted from the LC column with ten 100 ml fractions being collected. Fractions 2, 4, 6 and 10 were concentrated and examined by gas chromatography using OV-1 as the liquid phase; OV-1 is efficient for non-polar materials. Fractions 2 and 4 contained a broad envelope of paraffinic type material which eluted from the OV-1 column as temperature was programmed. Fraction 6 was free of GC peaks until a high column temperature was reached, ca 200°C. Reasonably, this indicates high molecular weight compounds which were late eluters from the LC column. Fraction 10 contained no GC peaks, thus signifying a complete separation of total fraction A.

Table III lists the volumes of n-hexane used to elute fraction A in each sample. Prior to GC analysis of the n-hexane cuts of sample 19470, it was felt that 200-400 ml of n-hexane would be sufficient to elute a total fraction A. Clearly this is not the case. Fortunately, however, any carryover of paraffinic material into Fraction B did not appear to adversely affect the final analysis; the nitromethane extraction apparently is almost exclusive for PAH, leaving behind other organic compounds in the hexane layer. For example GC/MS analysis of sample 19472 (see below) revealed only PAH; few other types of compounds were present. An exception was

TABLE III
 VOLUMES OF n-HEXANE USED TO ELUTE FRACTION A

| <u>Sample Number</u> | <u>Volume n-Hexane, ml</u> |
|--------------------------------|----------------------------|
| 19466 | 1000 |
| 19467 | 400 |
| 19469 | 400 |
| 19470 | 400 |
| 19471 | 1000 |
| 19472 | 200 |
| 19474 | 200 |
| 19476 | 1000 |
| 19470 (Duplicate) ^a | 1000 |

^aA second "Oil and Grease" determination was made on this sample - see Table I.

sample 19474 where an exceedingly high paraffin content (see explanation below) did interfere somewhat with PAH analysis. Elution of fraction A with greater than 200 ml of n-hexane was obviously necessary for this sample.

No fluorescence was observed in the 1 liter of n-hexane eluted for sample 19474. However, a low level of fluorescence was detected for samples 19466 and 19476. The possibility does exist that small amounts of low molecular weight PAH were lost.

One to three liters of 8:1 hexane/benzene was used to elute Fraction B. Table IV gives the volumes of solvent used. Elution of samples 19466 and 19476 was terminated at 1600 and 1250 ml respectively since fluorescence was no longer observed in solvent passing through the column. For sample 19472 2.5 liters of solvent were eluted; this was followed by elution with an additional liter which was separated from the initial 2.5 liters. Each was concentrated and extracted with nitromethane (NM); the NM extracts (fraction B_{II}) were evaporated to dryness, redissolved in n-hexane and analyzed by GC. All PAH through the dibenzanthracenes (MW 278) were found to be in the initial 2.5 liters fraction. Since fluorescence was observed in the 2.5 to 3.5 liter fraction, including the last 100 ml of this fraction, higher molecular weight, strongly fluorescing PAH are no doubt responsible for fluorescence at high elution volumes. Sample 19472 contained the highest amounts of PAH. Thus, it was acceptable to terminate elution after 2 liters of solvent on all other samples (see Table IV).

TABLE IV
VOLUME OF 8:1 HEXANE/BENZENE USED TO ELUTE FRACTION B

| <u>Sample Number</u> | <u>Volume 8:1 Hexane/Benzene, ml</u> |
|----------------------|--------------------------------------|
| 19466 | 1600 ^a |
| 19467 | 2000 |
| 19469 | 2200 |
| 19470 | 2100 |
| 19471 | 2000 |
| 19472 | 3500 |
| 19474 | 2050 |
| 19476 | 1250 ^a |

^a No fluorescence observed when these volumes had eluted.

2. Gas Chromatographic Analysis

Excellent separations of PAH were achieved employing Dexsil 3% and 6% columns. Figure 1 shows a gas chromatographic trace representing a typical analysis of a ten component PAH standard mixture. Table V gives the structures and properties of these compounds. Figure 2 shows a gas chromatographic trace representing the analysis of sample 19472; the sample represents the first 2.5 liters of 8:1 hexane/benzene from the LC column (see page 9).

In Figure 1 it can be seen that phenanthrene and anthracene (peaks 1 and 2) are partially separated, benz[a]pyrene (BaP) and benz[e]pyrene (BeP) (Peaks 6 and 7) are not separated and dibenz[a,h]- and dibenz-[a,c]-anthracene (peaks 9 and 10) are not separated. These observations reproduce the data of Lao et al.⁶

Components in the standard mixture were chosen to represent a PAH envelope that might be observed in sediment samples. Phenanthrene and anthracene are three ring PAH with molecular weights (MW) of 178. The dibenzanthracenes are five ring PAH with MW's of 278. In between there can be PAH with varying number of rings, ring structures, and substitutions on the rings. Over 100 PAH are known between MW 178 and 278. Effective separations are both critical and difficult; with caution they can be accomplished and compound assignments be made.

Figure 2 shows assignment of PAH to components of the standard mixture. In addition to comparing gas chromatograms of standards and samples, a comparison with the data of Lao⁶ was useful in chromatogram interpretation.

FIGURE I. Recorder trace of detector response in gas chromatographic analysis of PAH standard mixture using 6% Dexsil 300 column; Attenuation and amplifier settings are given in the figure as is recorder chart speed; Peak numbers correspond to the following PAH: 1. phenanthrene; 2. anthracene; 3. fluoranthene; 4. pyrene; 5. benz[a]anthracene; 6 and 7. benz[a]pyrene and benz[e]pyrene; 8. perylene; 9 and 10. dibenz[a,c]anthracene and dibenz[a,h]anthracene.

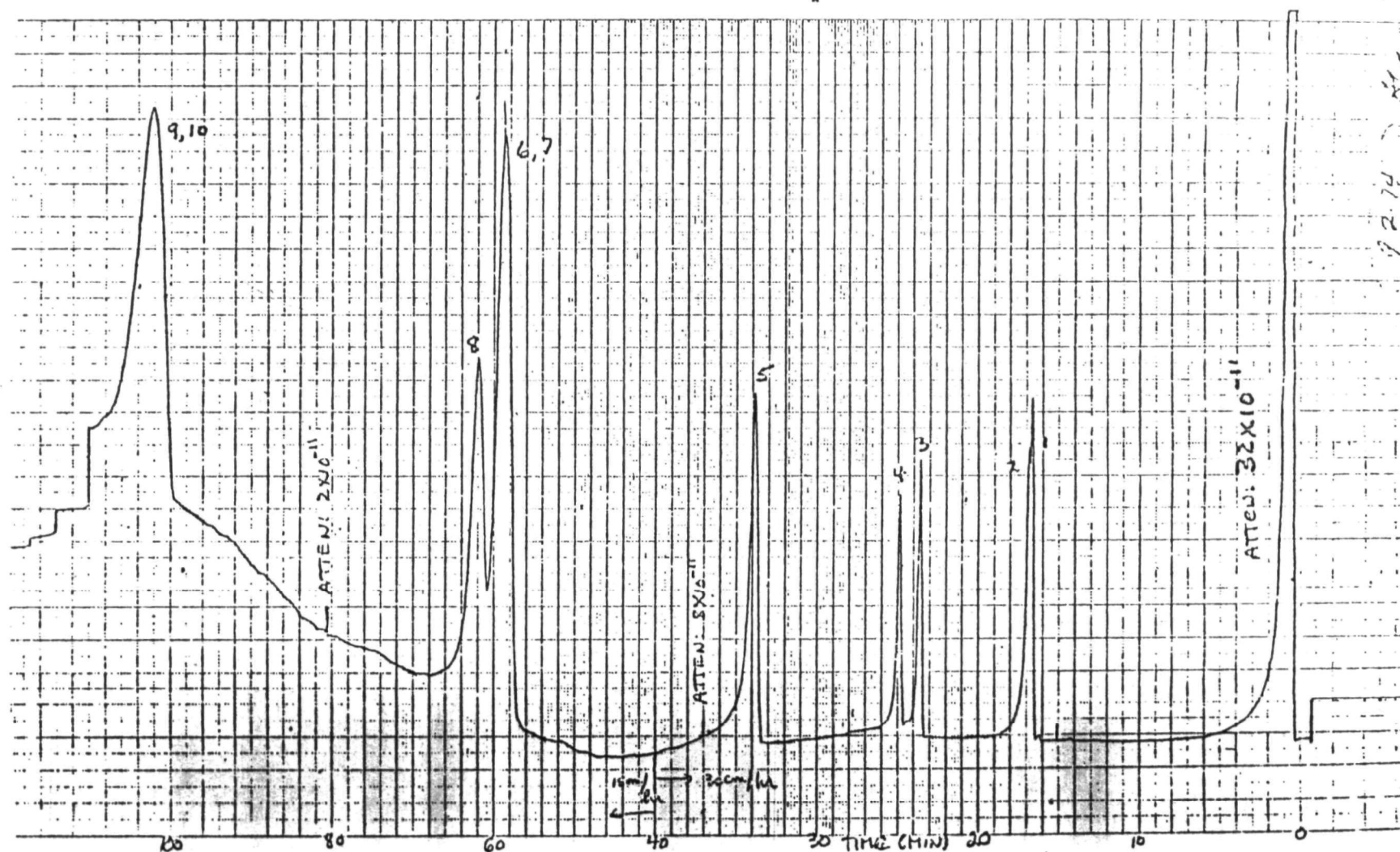


FIGURE II. GC trace for analysis of sample 19472, 0-2.5 liter, 8:1 hexane/benzene fraction. Attenuation, amplifier, and recorder settings are as indicated in the figure.

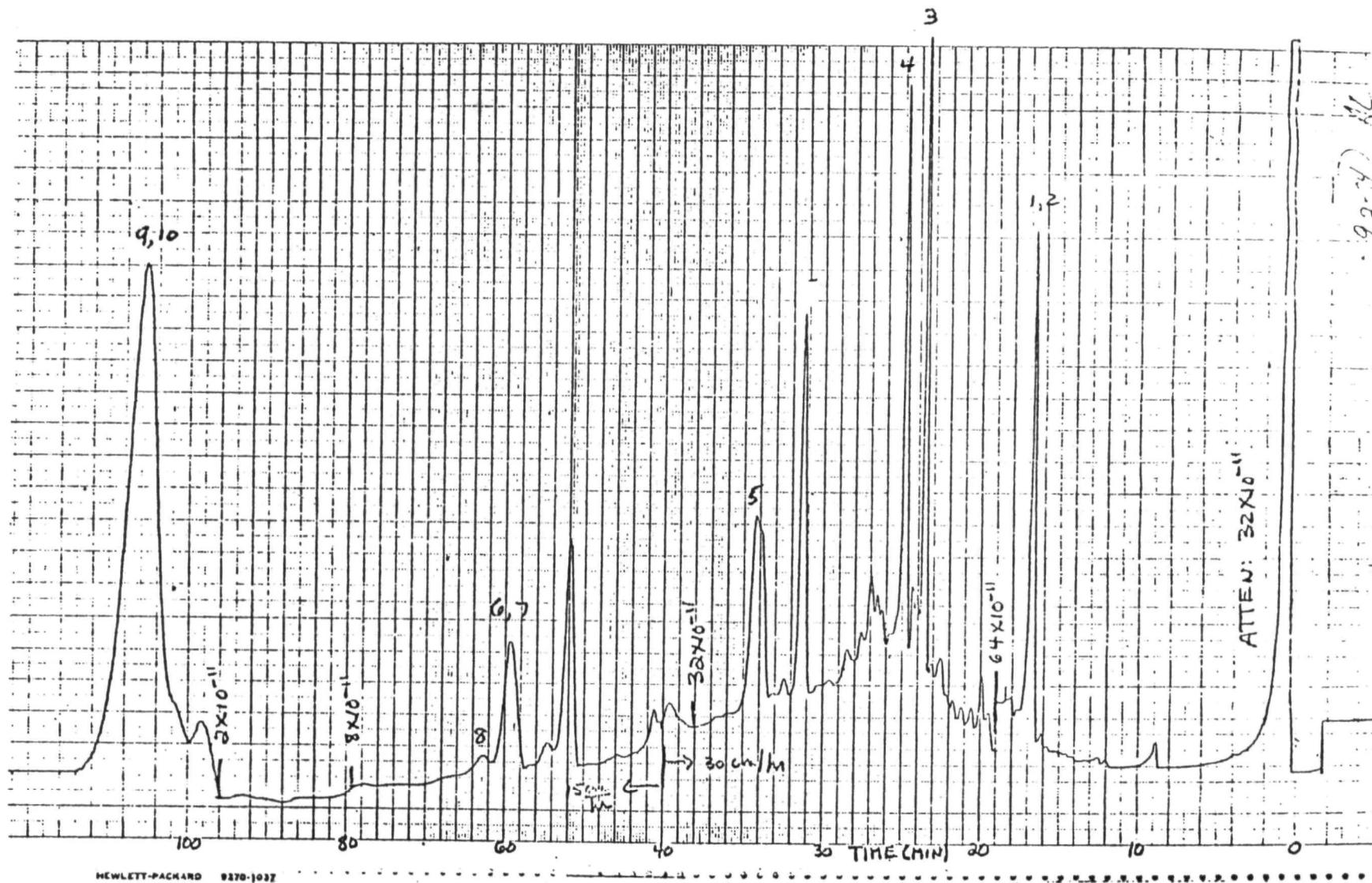
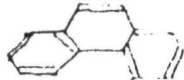
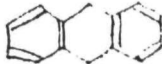
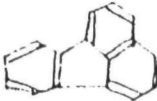
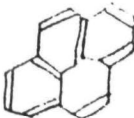
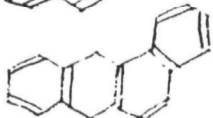
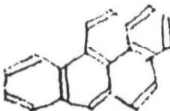
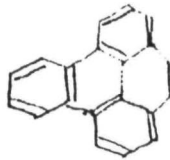
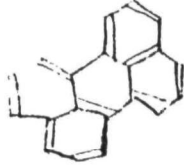
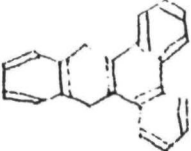
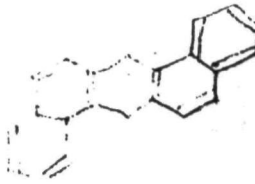


TABLE V

STRUCTURES AND PROPERTIES OF CERTAIN POLYNUCLEAR AROMATIC HYDROCARBONS

| PAH | Formula | Molecular Weight | Structure | Carcinogenic ^a Behavior |
|-----------------------|----------------|------------------|---|------------------------------------|
| Phenanthrene | $C_{14}H_{10}$ | 178 |  | - |
| Anthracene | $C_{14}H_{10}$ | 178 |  | - |
| Fluoranthene | $C_{16}H_{10}$ | 202 |  | - |
| Pyrene | $C_{16}H_{10}$ | 202 |  | - |
| Benz[a]anthracene | $C_{18}H_{12}$ | 228 |  | + |
| Benz[a]pyrene | $C_{20}H_{12}$ | 252 |  | ++++ |
| Benz[e]pyrene | $C_{20}H_{12}$ | 252 |  | ± |
| Perylene | $C_{20}H_{12}$ | 252 |  | - |
| Dibenz[a,c]anthracene | $C_{22}H_{14}$ | 278 |  | + |
| Dibenz[a,h]anthracene | $C_{22}H_{14}$ | 278 |  | +++ |

^a Ratings of carcinogenic behavior obtained from reference 20; (-) indicates not carcinogenic; (+) uncertain or weakly carcinogenic, (+) carcinogenic; (-+, ++, ++++) strongly carcinogenic.

The first major peak (labeled 1 and 2) in Figure 2 represents phenanthrene and anthracene. The assignment of these compounds is clear. However, since only one GC peak appeared it is probable that either phenanthrene or anthracene predominates. One cannot distinguish unequivocally between the two and quantitation must be made as the sum of phenanthrene and anthracene; this situation obtains for all other samples. For sample 19472 GC/MS experiments suggest that the major peak (1 and 2) is predominantly phenanthrene with a minor contribution from anthracene (see Figure 5, page 42).

The peaks labeled 3 and 4 can be assigned to fluoranthene and pyrene.⁶ Further support for these (and other) assignments will be given in the GC/MS data to be presented below. Peak 5 certainly represents at least two overlapping peaks. This is consistent with the observation of Lao et al⁶ which notes that benz[a]anthracene is not separated from chrysene and triphenylene using the Dexsil GC system. Peak 5, then, should be assigned to these three compounds; no other PAH of MW 228 elutes near these compounds⁶ and GC/MS data show that the peak is due to PAH having molecular weights of 228. Benz[a]anthracene and chrysene are carcinogens²⁰ while triphenylene is not.

Peaks labeled 6 and 7 are assigned to BaP and BeP; peak 8 is assigned to perylene. GC/MS data show these peaks to have molecular weights of 252. The doublet consisting of a large and a small peak eluting before BaP and BeP also have molecular weights of 252 (see below). Based on the data of Lao⁶ the compounds represented by these peaks may be the benzo-fluoranthene isomers.

Peaks 9 and 10 are assigned to the dibenzanthracenes. Other PAH which elute in the dibenzanthracene region⁶ and which may be present in certain samples are the benzochrysenes, picene, the benzoperylenes, o-phenylenepyrene, and the benzoetraphenes.

Table VI reports the concentrations of PAH determined in sediment samples (from fractions E_{II}). Matching of individual components in the samples was not always as simple as in 19472 described above and in Figure 2. For samples where certain components could not be compared with the standard mixture a value is not reported in Table VI.

Samples 19466 and 19476 display the lowest levels of PAH. This is consistent with their low oil and grease values and the fact that fluorescence terminated after 1-1.5 liters of solvent in collecting fraction B. It is also consistent with the locations of these two sampling sites. Sample 19472 being just downstream from outfall 002 shows by far the highest concentrations of PAH. No explanation can be offered for the absence of lower molecular weight PAH in sample 19471.

Sample 19474 was different than all other sediments collected. Fraction A showed an apparently high paraffinic content. This was observed by analysis of fraction A employing the Dexsil column. Fractions A of several samples were scanned for qualitative information as to paraffinic content. Sample 19474 contained at least a ten fold higher paraffinic level than any other sample examined. In addition examination of Fraction B_{II} for PAH showed a different shaped GC elution pattern. The GC trace in Figure 2

TABLE VI
CONCENTRATIONS OF PAH DETERMINED IN LORAIN SEDIMENT SAMPLES

| Sample Number | Concentration, mg/kg (dry sample weight) ^a | | | | | | |
|---------------|---|--------------|--------|-------------------|-------------------------------|----------|-------------------|
| | Phenanthrene & Anthracene | Fluoranthene | Pyrene | Benz[a]anthracene | Benz[a]pyrene & Benz[e]pyrene | Perylene | Dibenzanthracenes |
| 19466 | 0.43 | b | b | 0.83 ^d | 0.91 | 0.10 | 0.67 ^c |
| 19467 | 2.8 | 2.5 | 2.9 | 1.6 ^d | 1.5 | 0.04 | 0.37 |
| 19469 | 2.6 | 3.9 | 5.2 | 2.9 ^d | 4.6 | e | 2.6 |
| 19470 | 3.2 | 3.3 | 4.4 | 2.8 ^d | 2.9 | e | e |
| 19471 | b | e | e | 3.1 ^d | 4.7 | 3.9 | 3.9 |
| 19472 | 18 | 29 | 30 | 24 | 19 | 2.0 | 12 |
| 19474 | ~3 ^b | b | b | b | 1.1 | e | e |
| 19476 | 0.68 | 0.75 | 0.61 | 1.2 ^d | 1.5 | 0.35 | 0.66 ^c |

^a Data calculated by comparison of PAH in the sample fraction B_{II} and a standard mixture of ten PAH.

^b Overlapping peaks in the gas chromatogram precluded analysis of this PAH.

^c Other major peaks occurred in the dibenzanthracene area of the GC. Concentration reported represents only GC peak at retention time of dibenzanthracenes in the standard mixture.

^d The GC peak clearly represents more than one compound, as reported in reference 6. The values given are for the total PAH present based on the benz[a]anthracene standard.

^e Less than detectable.

for 19472 is typical of samples analyzed except 19474. Consistent with our observations concerning sample 19474 is the fact that U.S. Steel apparently discharges waste oils from outfall 001; sample 19474 was taken 0.2 miles downstream from this outfall.

3. Gas Chromatographic/Mass Spectrometric (GC/MS) Analysis

Sample 19472 was examined in detail by GC/MS. In addition the ten component PAH solution was analyzed. Both analyses employed the 3% Dexsil column. The "real-time" and reconstructed gas chromatogram (RGC) for the standard mixture showed separations to be identical to these shown in Figure 1. Mass spectra for the standard compounds were consistent with spectra for known PAH.^{6,21,22}

Figure 3 shows the "real-time" gas chromatogram for the analysis of sample 19472. (All further mass spectral data reported are for this sample). The GC is essentially the same as the trace shown in Figure 2. In GC/MS analysis the total ion current is plotted, as in Figure 3, after each spectrum scan during the run. Over sixty peaks can be counted. Figure 4 shows the reconstructed gas chromatogram (RGC) of the same run shown in Figure 3. The data system has normalized the largest peak in the RGC to an amplitude of 100. Because of the way the data system acquires and processes information relative peak heights between the "real-time" and reconstructed chromatograms are not always the same. Further explanation cannot be given in this section, owing to space limitations.

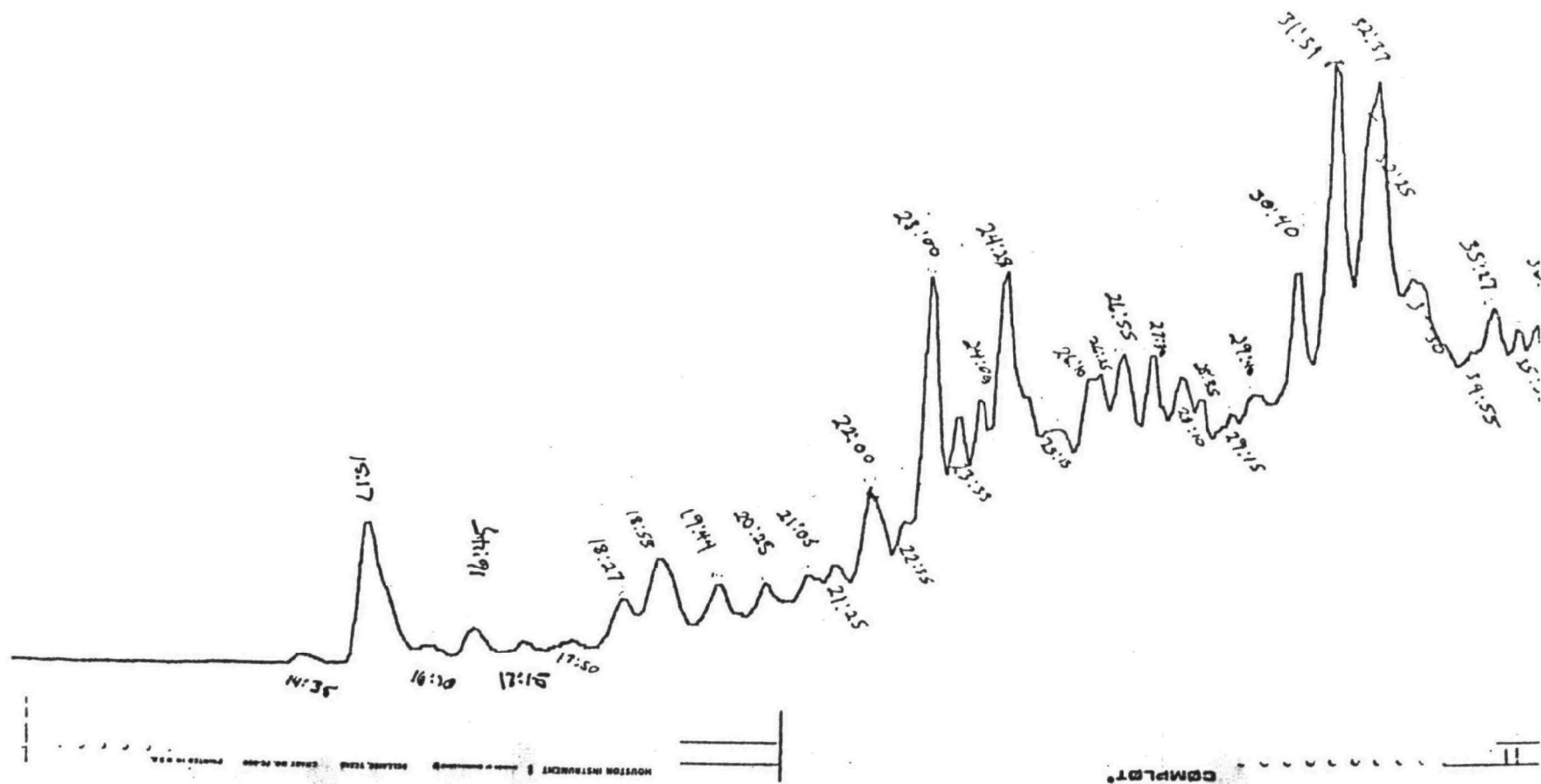
FIGURE 3: "Real-time" gas chromatogram of GC/MS analysis of sample 19472.

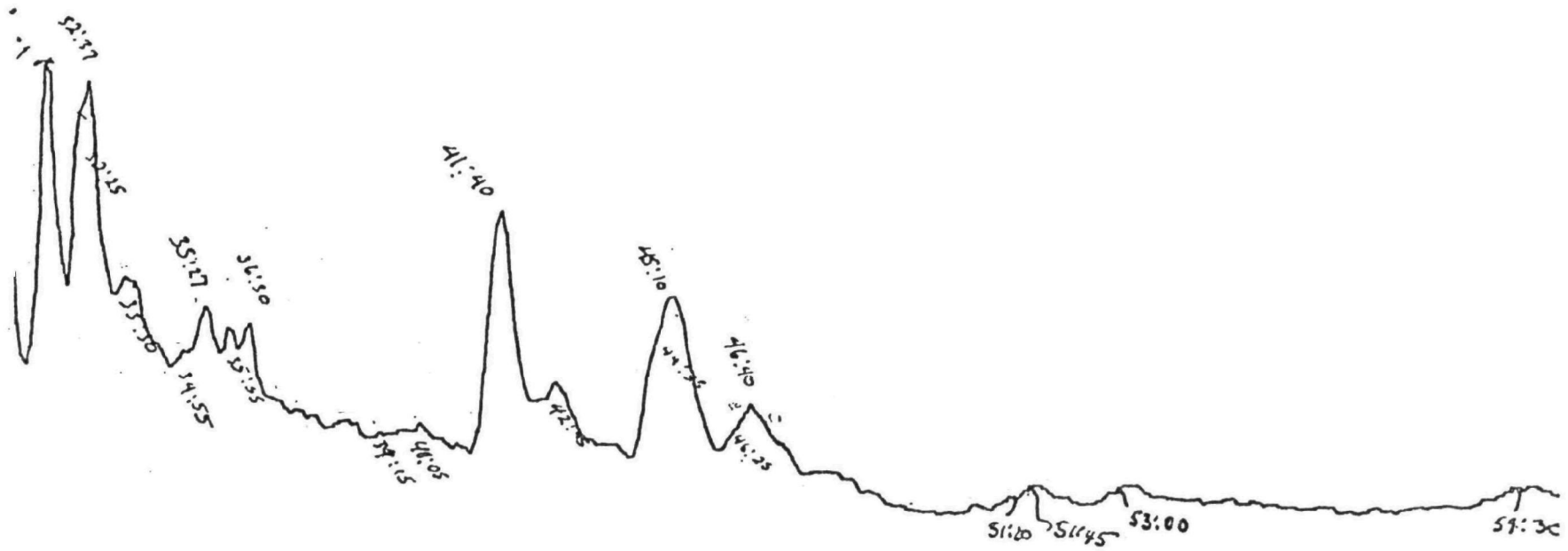
Times in minutes and seconds written above each peak represent retention times of the eluting components.

FIGURE 4: Reconstructed gas chromatogram for GC/MS analysis of sample 19472.

FIGURE 5: Reconstructed gas chromatogram for GC/MS analysis of sample 19472 employing a limited mass search for ions m/e 178, 202, 228, 252, and 278.

FIGURE 6: Reconstructed gas chromatogram for GC/MS analysis of sample 19472 employing a limited mass search for ions m/e 192, 216, 242, 266, and 292.





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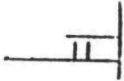
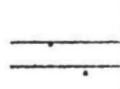


FIGURE 3 (CONT)

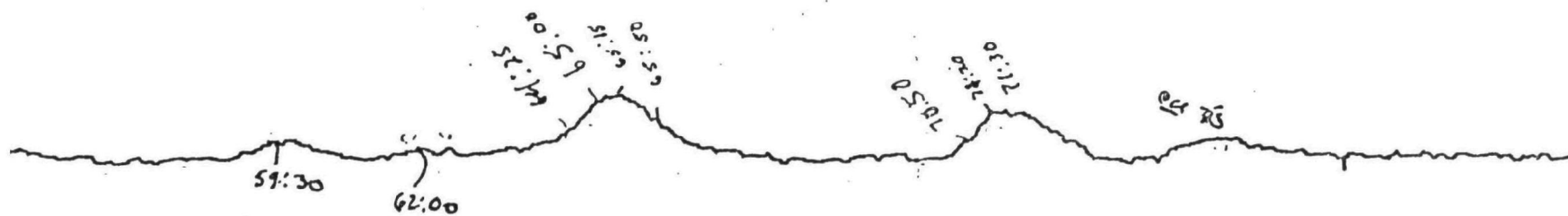
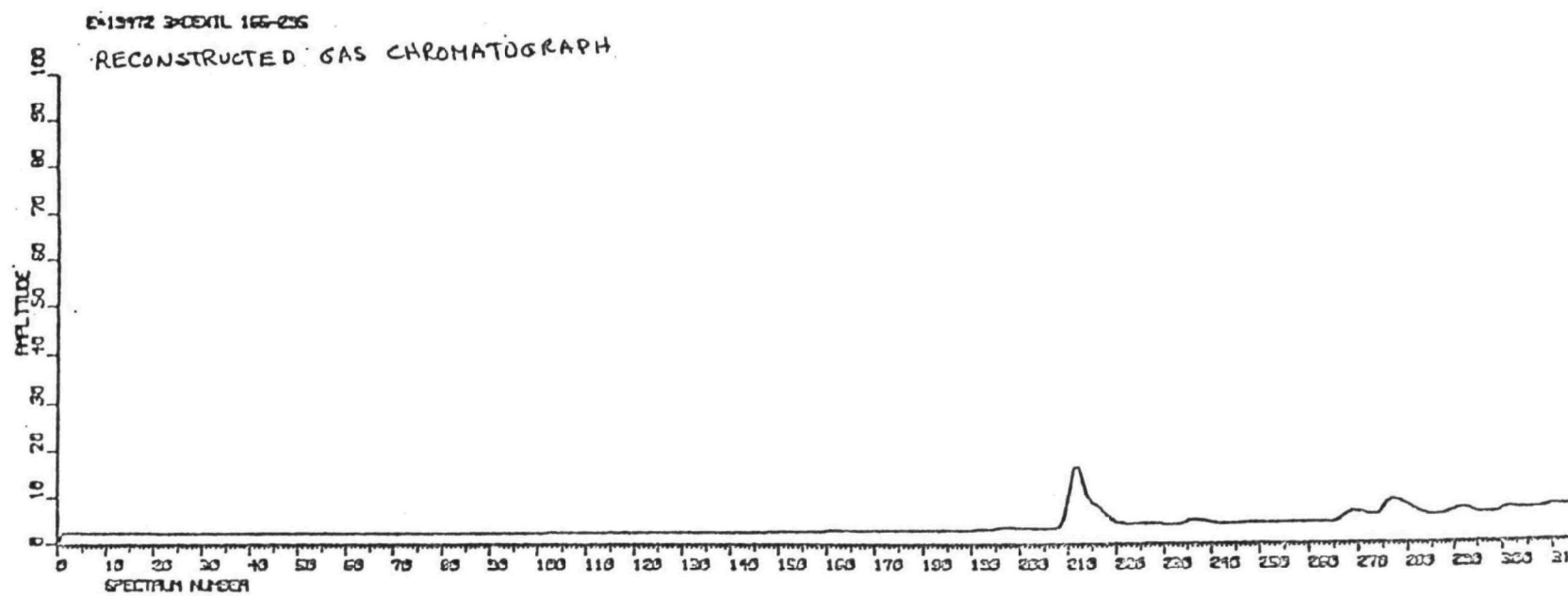
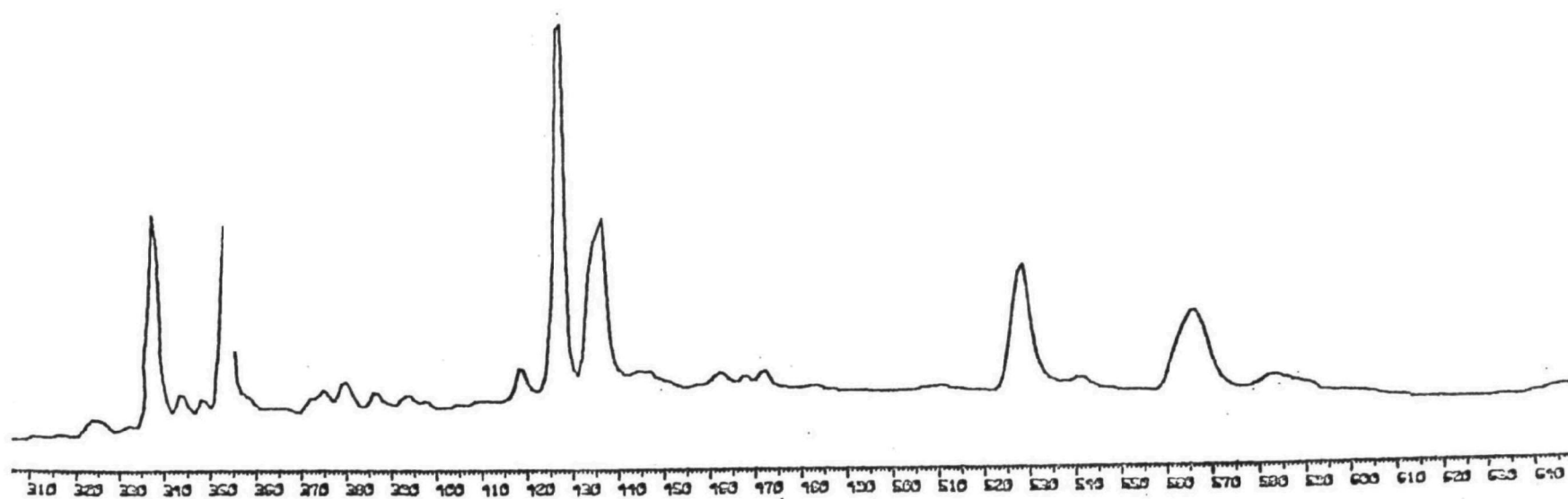


FIGURE 4



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FIGURE 4 (CONT)



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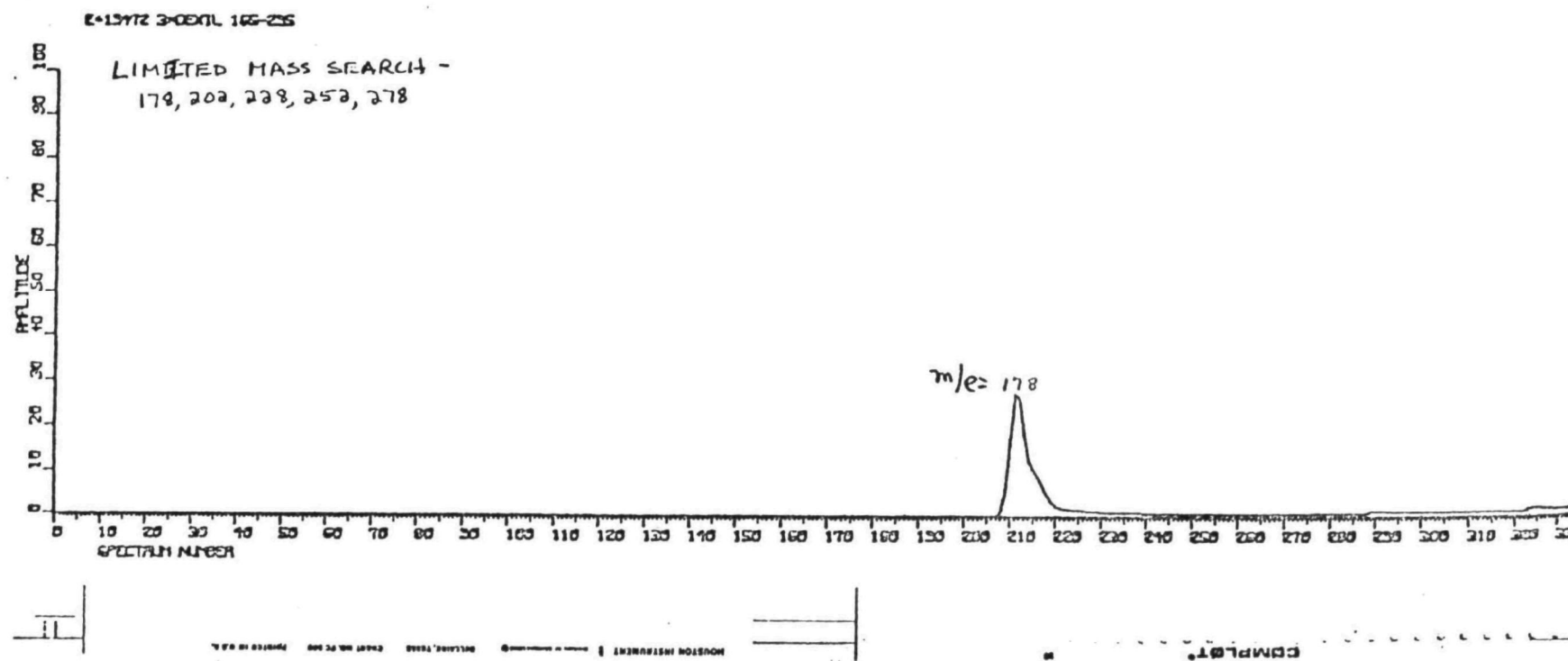
Figure 5 gives an RGC limited mass search for the parent ions corresponding to the compounds in the PAH standard mixture. The ions causing the RGC-peaks are indicated above each individual peak. A peak corresponding to m/e 278 is not observed since it is small compared to the 202 peak on which the RGC is normalized. The mass spectra of PAH almost always display intense parent ions. The parent is usually the base peak. Thus performing a limited mass search for the parent is an effective way of defining particular PAH. A cluster is often present about the parent representing the P-1, P-2, P-3, P+1, and P+2 masses; - that is the parent less one, two, and three and plus one and two amu.

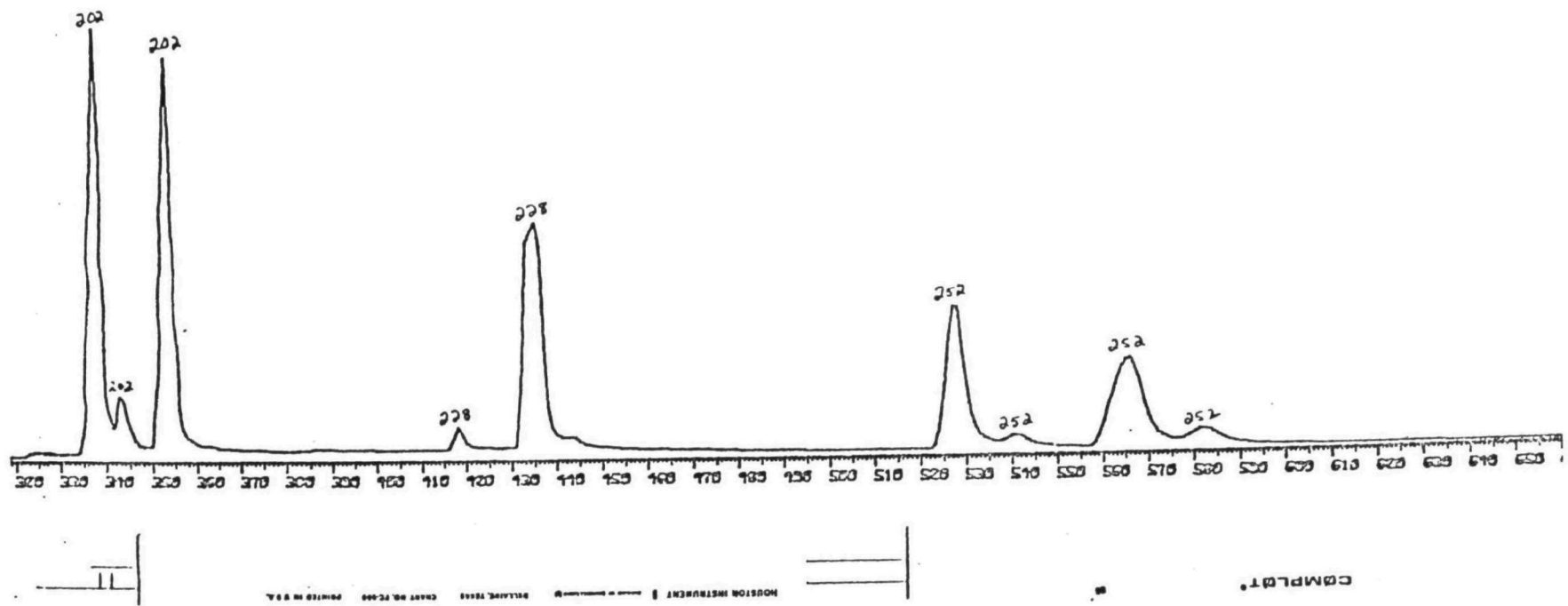
Figure 6 gives an RGC limited mass search for the methyl-substituted derivatives of compounds in the PAH standard mixture. Thus the unsubstituted parents +14 amu were searched. Again, the molecular ions causing the RGC peaks have been indicated.

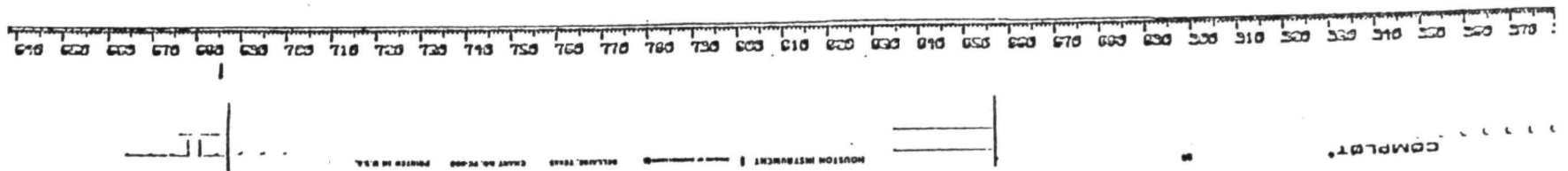
A limited mass search for dimethyl derivatives, the unsubstituted parents +28 amu, was made but the data were not conclusive and are not being presented.

Searching for unsubstituted ions in the standard and their methyl derivatives produced thirty-three separate GC/MS peaks indicating at least that many compounds. In certain cases two or more PAH were present for a specific RGC peak indicating more than one PAH was eluting from the Dexsil column into the ion source at the same time; this observation is quite reasonable. Searching for the dimethyl derivatives produced an additional eight distinct GC/MS peaks.

FIGURE 5







45

FIGURE 6

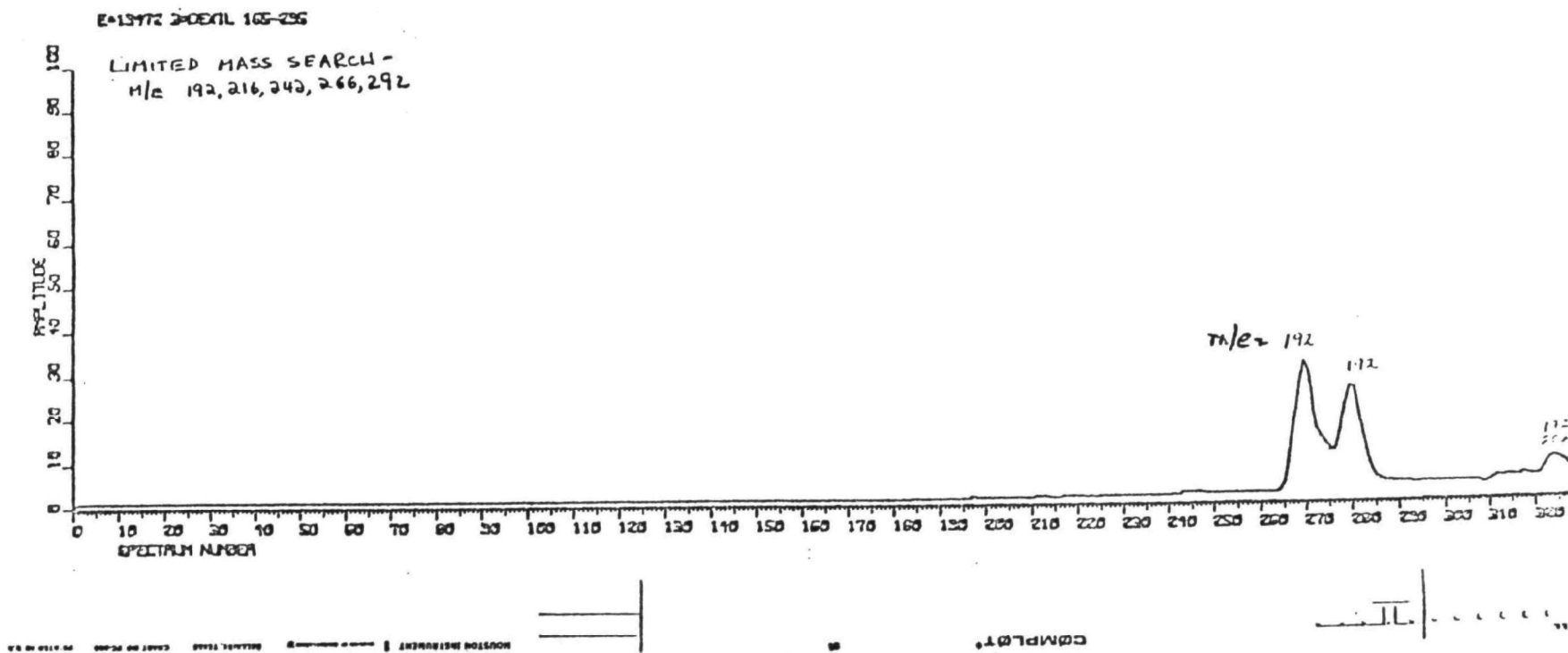
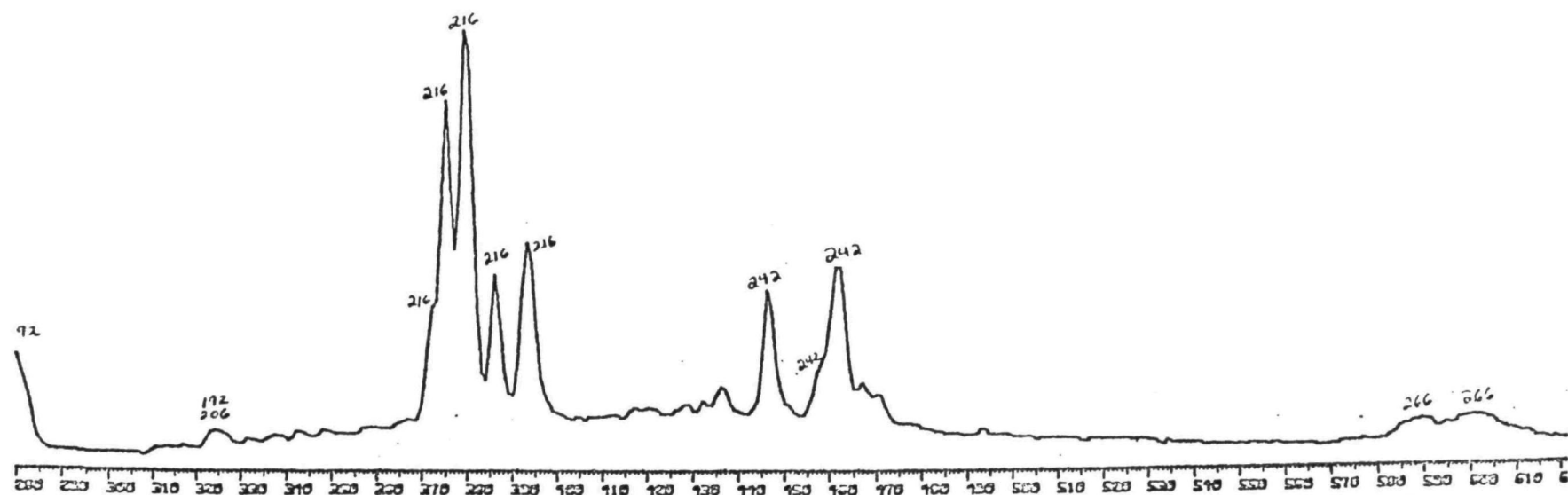


FIGURE 6(CONT)



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Mass spectral data show that the sample extract contained almost exclusively PAH. The largest peak in the RGC (Figure 4) was not a PAH but a phthalate derivative with a strong base peak of m/e 149. The presence of this compound cannot be explained.

Presentation of all mass spectra is precluded by space limitations. In Figure 5, however, it can be seen that peaks for phenanthrene + anthracene (m/e 178), fluoranthene (first m/e 202), pyrene (second large m/e 202), benz[a]anthracene and probably chrysene and tetraphene (large broad m/e 228), benz[a]- and benz[e]pyrene (large peak of second m/e 252 doublet) and perylene (last m/e 252 peak) are present. Comparison should be made with Figure 2.

Presentation of selected spectra is useful. Figures 7 through 11 show the mass spectra of major RGC peaks (Figure 5) having m/e 252 as the base peak - the benzfluoranthene, benzpyrene, perylene area. Figures 12 through 15 show the mass spectra of major RGC peaks (Figure 6) having m/e 242 as the base peak. These likely represent methyl-PAH which are not identified. Other unsubstituted PAH having molecular weights of 242 are possible but unlikely. It should be noted the computer was allowed to subtract background from spectra of interest. Thus in Figure 7 spectrum 526-520 signifies that spectrum 520 has been subtracted from 526.

Another method in identifying and confirming molecular formulas by mass spectroscopy employs isotope abundances of the common elements. For PAH one need consider only carbon and hydrogen. For every carbon atom,

FIGURES 7, 8, 9, 10, 11: Mass spectra of PAH having m/e 252 as the base peak in sample 19472.

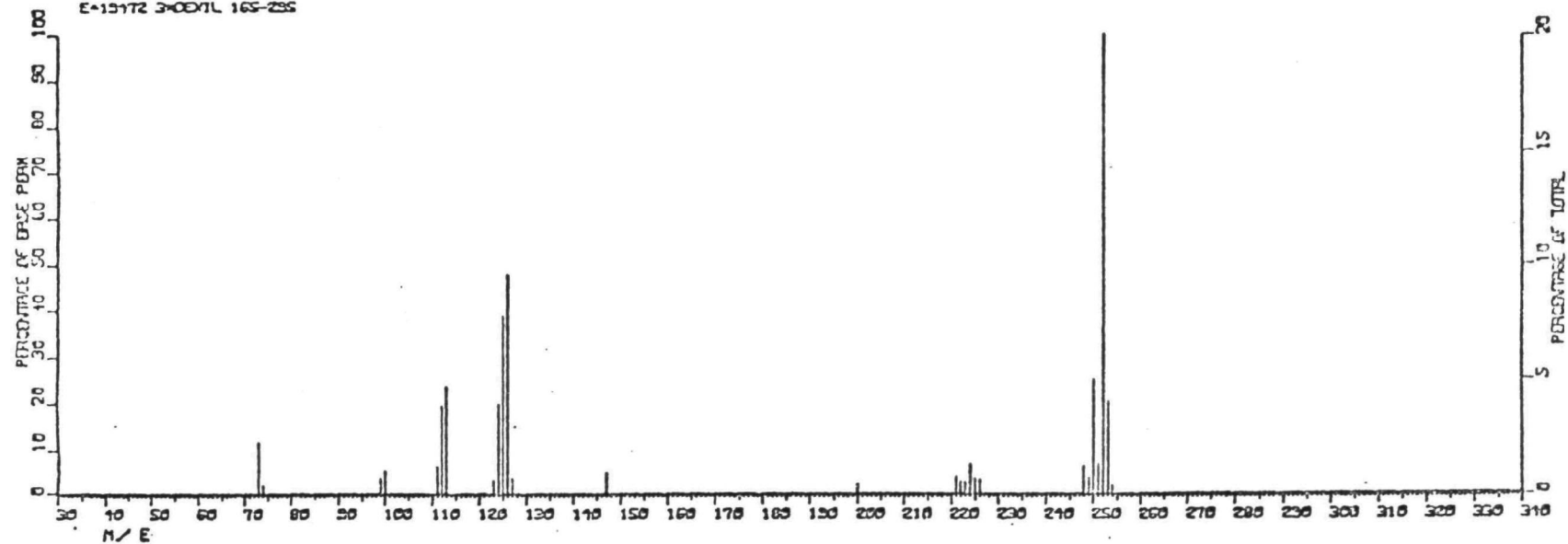
FIGURES 12, 13, 14, 15: Mass spectra of PAH having m/e 242 as the base peak in sample 19472.

FIGURE 7

TITLE: E-19472 3X0071L 165-285/4/M BOLD 10(-7)A/V PROOV
 SPECTRUM NUMBER: S26 - 520
 BACK PEAK: 238000
 TOTAL ION CURRENT: 1041904

SPECTRUM NUMBER S26 - 520

E-19472 3X0071L 165-285



50
FIGURE 8

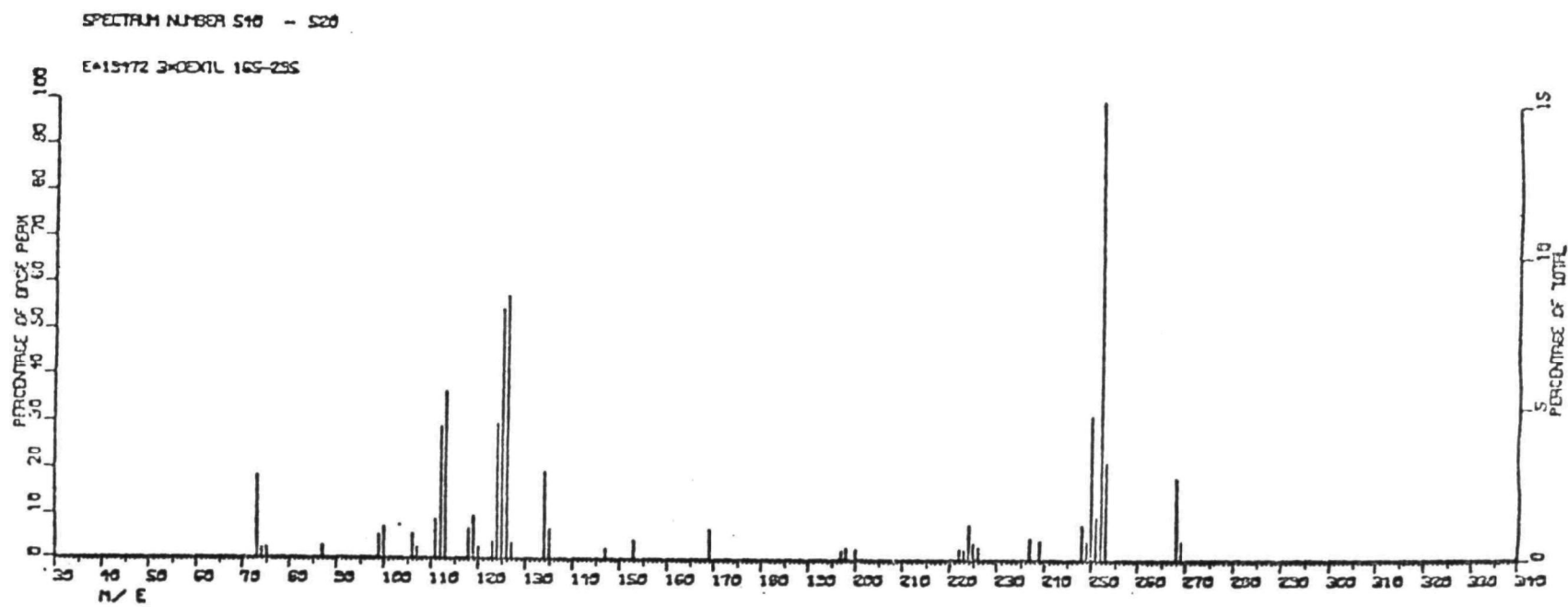


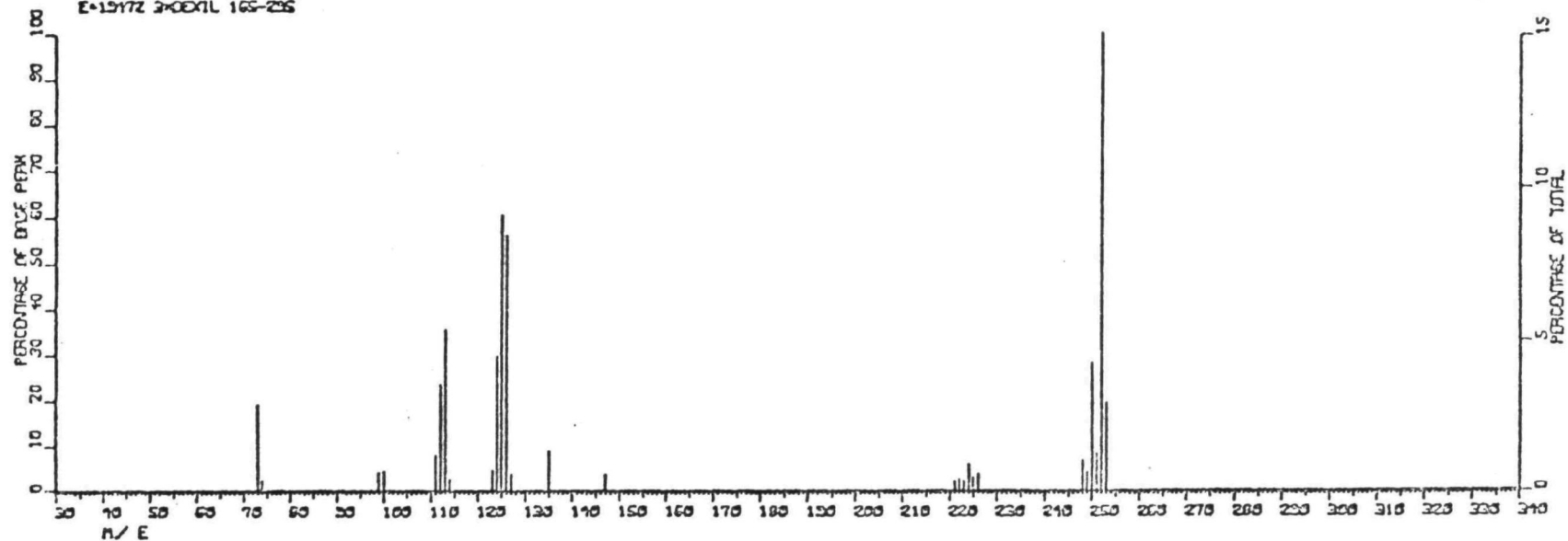
FIGURE 9

PPRINT 205
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TITLE: E-19472 3XOXIL 165-29504/M HOLD 10(-7)A/V 2800V
 SPECTRUM NUMBER: 563 - 557
 PLOT NAME: 146752
 TOTAL ION CURRENT: 748841

SPECTRUM NUMBER 563 - 557

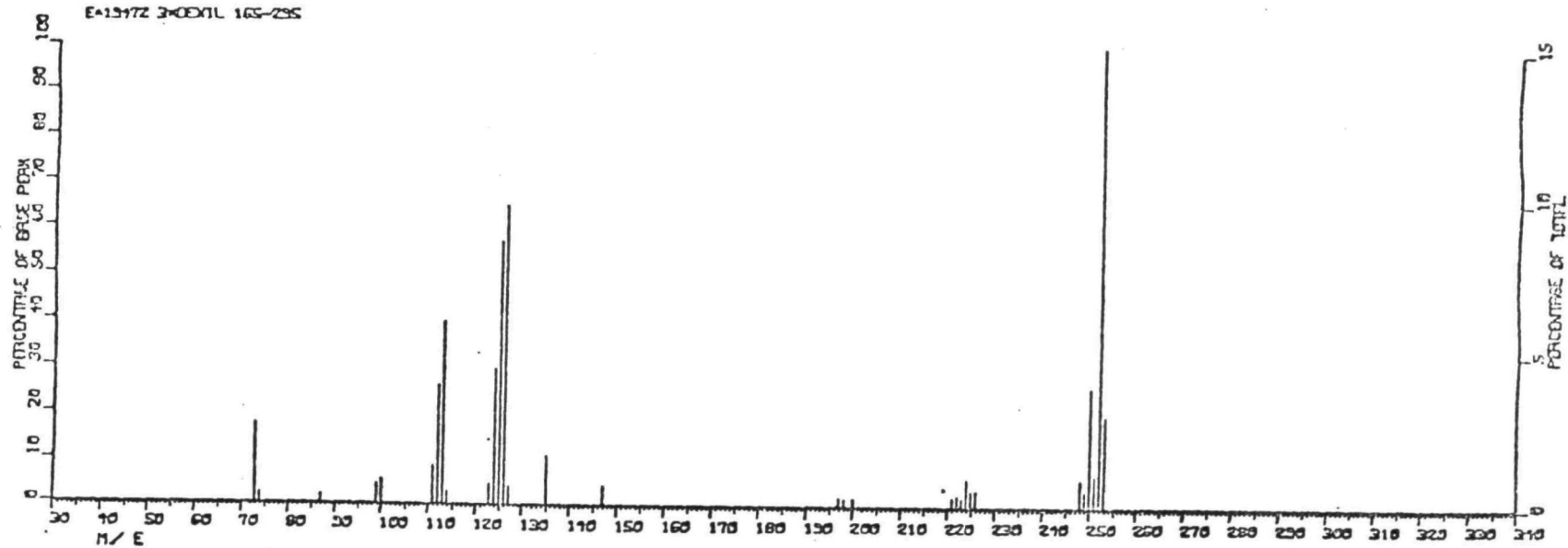
E-19472 3XOXIL 165-295



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FIGURE 11

TITLE: 1-10470 350V/11. 1A5-2050A/H HOLD 10(-7)A/V PH00V
 SPECTRUM NUMBER: 582 - 576
 BASE PLATE: 25049
 TOTAL ION CURRENT: 161366

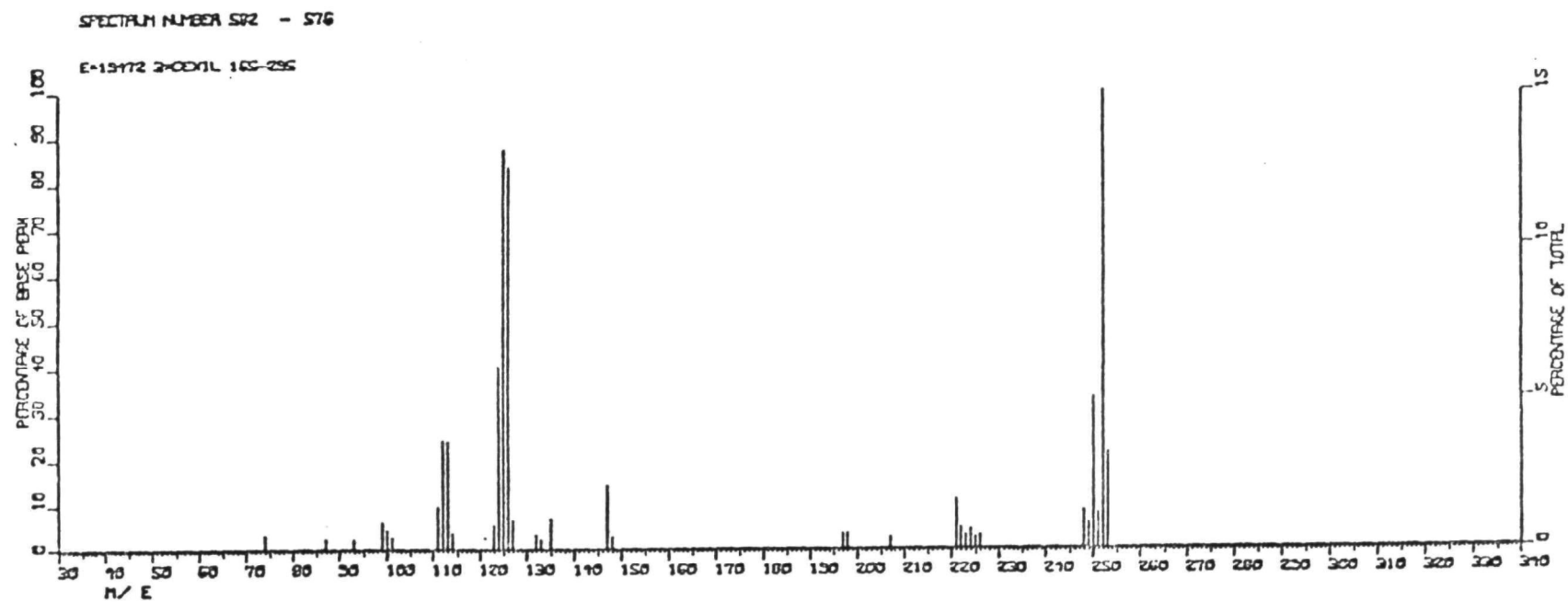


FIGURE 12

TITLE: E-19472 DIOXIL 165-295-235 HOLD 10(-7)A/V PRODU
 SPECTRUM NUMBER: 446 - 448
 SAGE PEAK: 24140
 TOTAL ION CURRENT: 112363

SPECTRUM NUMBER 446 - 448

E-19472 DIOXIL 165-295

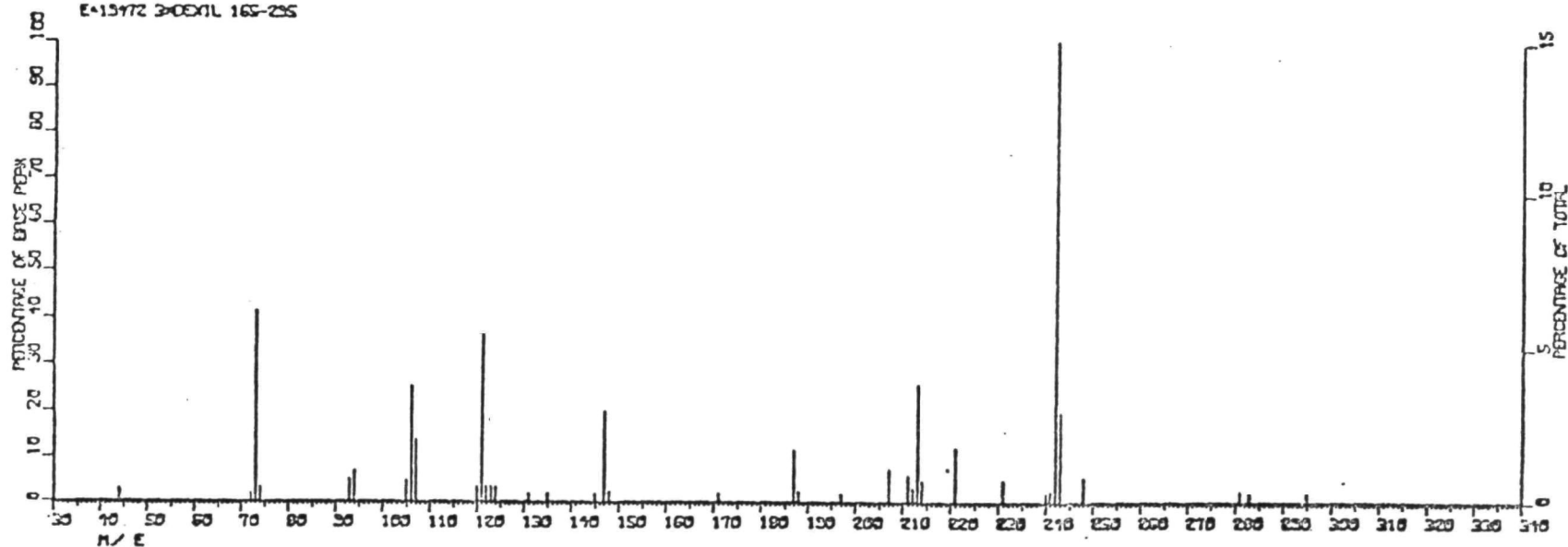


FIGURE 13

TITLE: E*10472 3-DEXYL 165-P9504/II HOLD 10(-7)A/V 2800V
 SPECTRUM NUMBER: 457 - 453
 BASE PEAK: 0000
 TOTAL ION CURRENT: 54760

SPECTRUM NUMBER 457 - 453

E*15472 3-DEXYL 165-235

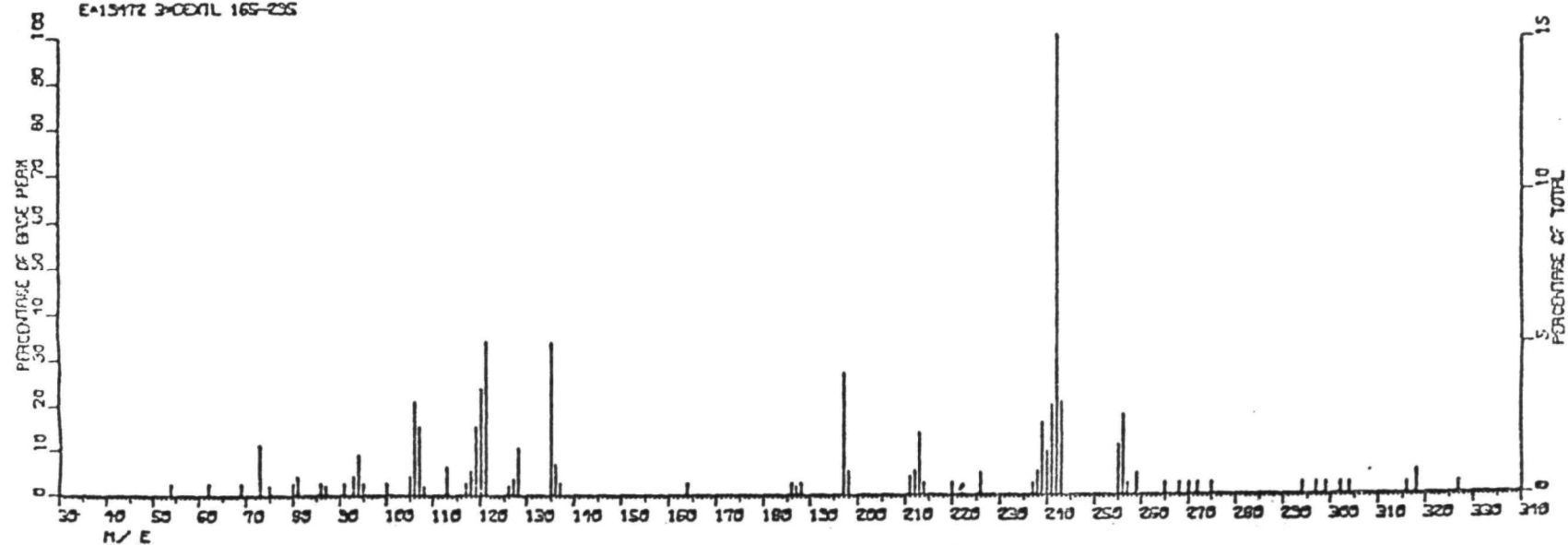


FIGURE 14

TITLE: E-10472 3-DEXIL 165-29504/M HOLD 10(-7)A/V 2000V
SPECTRUM NUMBER: 460 - 453
BASE PEAK: 20577
TOTAL ION CURRENT: 120165

SPECTRUM NUMBER 460 - 453

E-10472 3-DEXIL 165-295

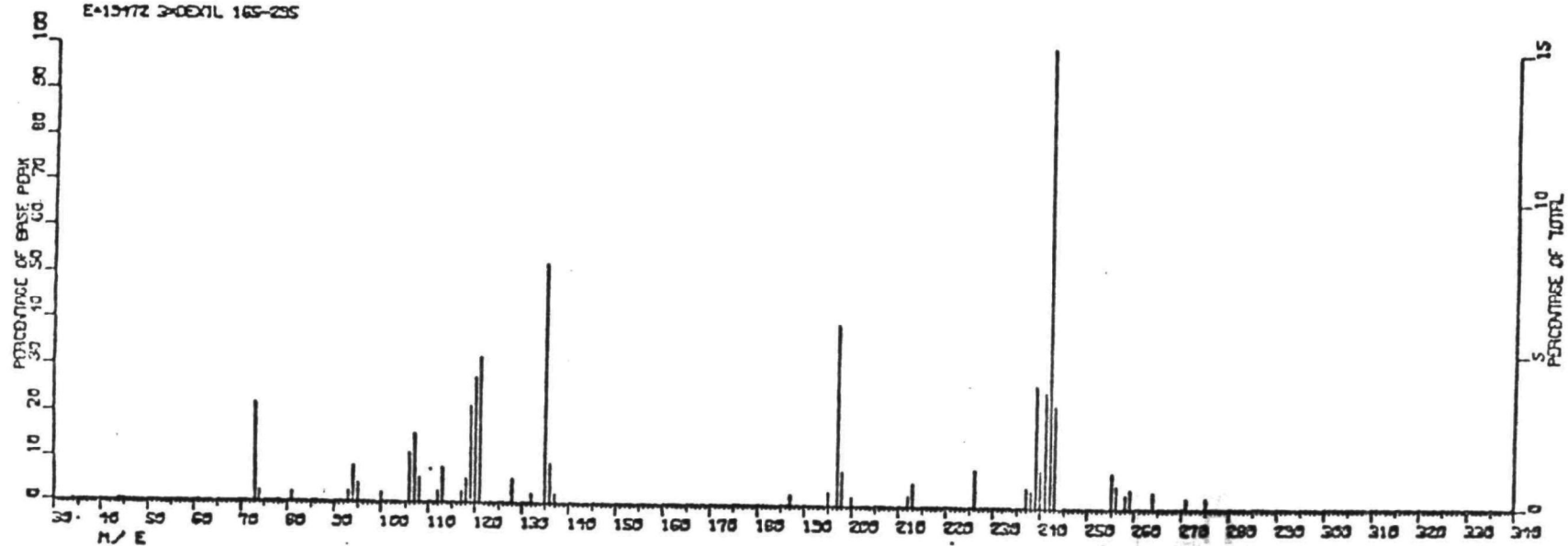
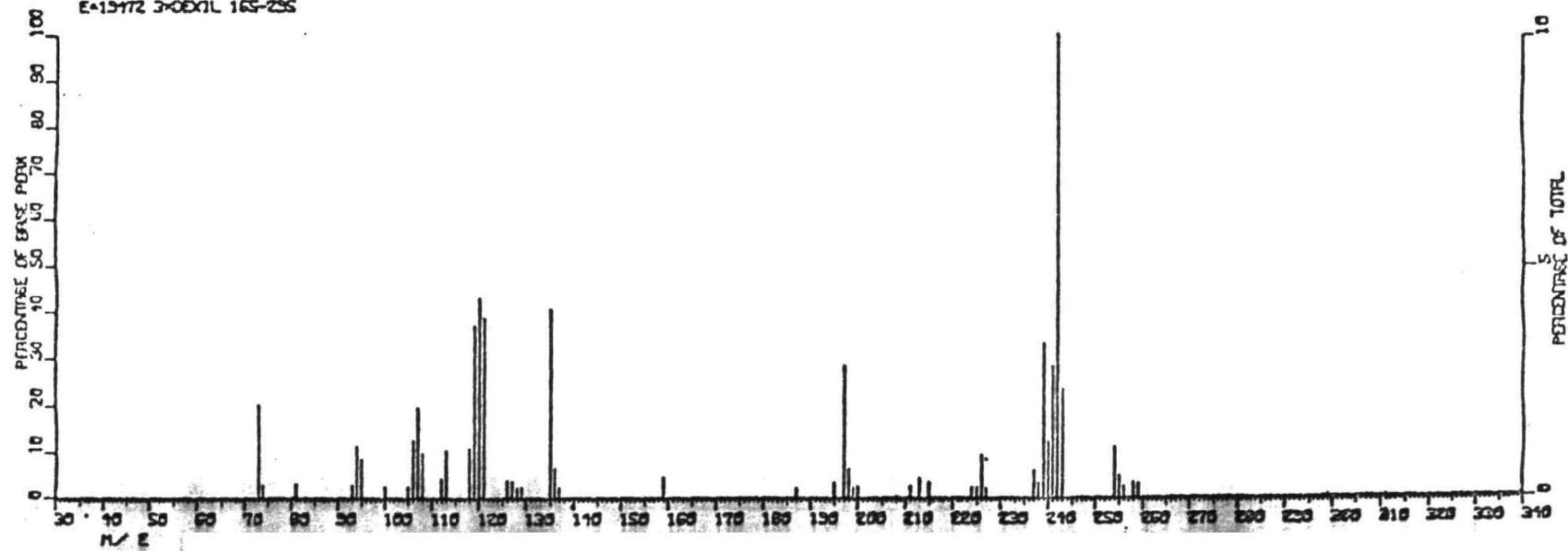


FIGURE 15

TITLE: F#19472 JXDXIL 165-R9504/M HOLD 10(-7)A/V 2000V
 SPECTRUM NUMBER: no2 - 453
 DATE: 08/01/81
 TOTAL ION CURRENT: 195191

SPECTRUM NUMBER 462 - 453

E=19472 JXDXIL 165-235



ca 1.08% of the molecules containing carbon possess a ^{13}C atom and produce a P + 1 (parent +1) peak. Each atom in an ion contributes an amount to the intensity of the isotope peak that is equal to the relative abundance of the isotope of that atom.²⁴ Thus if a strong molecular ion is present, as in the case of PAH, the P+1 abundance is useful in identifying a particular molecular formula.²⁴ The P+2 is also considered, for there exists a probability that two ^{13}C atoms exist in a single ion. Values of P+1 and P+2 have been calculated for the various molecular formulas and are presented in tables.^{23,25}

Table VII list P+1 and P+2 isotope abundances for selected PAH of interest. The values are theoretical except for two molecular formulas which represent experimentally determined literature data. Table VIII gives the P+1 and P+2 values for the PAH in the ten component standard mixture. Excellent agreement is observed.

Table IX gives the values found for certain major PAH present in sample 19472. The values were obtained from spectra defined by the reconstructed gas chromatograms shown in Figure 5 for unsubstituted and Figure 6 for methyl substituted PAH. Agreement for the unsubstituted PAH is good. In a sample containing often overlapping GC peaks one would not expect agreement to be ideal. This is especially true for the P+2 isotope abundances which is a second-order effect. In addition, spectra were defined by limited mass reconstructed gas chromatographic searches. Overlapping compounds present which are not seen in the limited mass search can easily

interfere with isotope abundance calculations. The total amounts of methyl substituted PAH present are considerably smaller than unsubstituted polynuclears. Thus, one would not expect isotope abundance calculations to be nearly as satisfactory for these cases; this is exactly the situation.

TABLE VII
ISOTOPE ABUNDANCES FOR MOLECULAR FORMULAS
CORRESPONDING TO PAH OF INTEREST^{a22,23,25}

| Formula | Molecular Weight | P+1 | P+2 |
|---------------------------------|------------------|-------|------|
| C ₁₄ H ₁₀ | 178 | 15.29 | 1.09 |
| C ₁₅ H ₁₂ | 192 | 16.40 | 1.26 |
| C ₁₆ H ₁₀ | 202 | 17.45 | 1.43 |
| C ₁₇ H ₁₂ | 216 | 18.56 | 1.62 |
| C ₁₈ H ₁₂ | 228 | 19.64 | 1.82 |
| C ₁₉ H ₁₄ | 242 | 20.76 | 2.04 |
| C ₂₀ H ₁₂ | 252 | 21.9 | 2.4 |
| C ₂₂ H ₁₄ | 278 | 23.5 | 3.2 |

^a Values are theoretical (reference 23) except for MW 252 and 278; these values are experimental findings (reference 25).

TABLE VIII
ISOTOPE ABUNDANCE FOR PAH STANDARD MIXTURE

| Compound Assigned | Formula | Molecular Weight | P+1 | P+2 |
|-------------------------|----------------|------------------|-------------------|------------------|
| Phenanthrene) | $C_{14}H_{10}$ | 178 | 15.2 ^a | 1.3 ^a |
| Anthracene) | | | | |
| Fluoranthene | $C_{16}H_{10}$ | 202 | 17.6 | 1.6 |
| Pyrene | $C_{16}H_{10}$ | 202 | 17.7 | 1.9 |
| Benz[a]anthracene | $C_{18}H_{12}$ | 228 | 19.7 | 2.1 |
| Benz[a]pyrene) | $C_{20}H_{12}$ | 252 | 21.1 ^b | 2.2 ^b |
| Benz[e]pyrene) | | | | |
| Dibenz[a,c]anthracene) | $C_{22}H_{14}$ | 278 | 23.5 ^b | 3.1 ^b |
| Dibenz[a,h]anthracene) | | | | |

^a Phenanthrene and anthracene were slightly separated as in Figure 4. Values for each side of the peak were calculated.

^b Values given are averages for several sections of each peak; each peak represents two compounds; see Figure 2.

TABLE IX
ISOTOPE ABUNDANCES FOR CERTAIN PAH FOUND IN SAMPLE 19472^a

| Spectrum | PAH Parent Peak | P+1 | P+2 |
|-----------------------|--------------------|------|-----|
| A. Unsubstituted | | | |
| 211-206 | 178 | 15.4 | 1.1 |
| 215-206 | 178 | 15.6 | 1.2 |
| 337-333 | 202 | 18.3 | 1.4 |
| 343-333 | 202 | 16.8 | 0.9 |
| 353-349 | 202 | 17.9 | 2.0 |
| 433-430 | 228 | 20.1 | 1.4 |
| 436-430 | 228 | 20.0 | 1.2 |
| 526-520 | 252 | 20.3 | 2.1 |
| 540-520 | 252 | 21.9 | 1.9 |
| 563-557 | 252 | 19.6 | 1.9 |
| 566-557 | 252 | 20.4 | 1.9 |
| 582-576 | 252 | 21.5 | 2.0 |
| 784-775 | 278 | 26.7 | e |
| 821-805 | 278 | 19.3 | e |
| B. Methyl Substituted | | | |
| 268-262 | 192 | 18.2 | 1.2 |
| 278-262 | b | b | b |
| 372-369 | 216 | 16.0 | c |
| 375-369 | 216 | 16.6 | 4.5 |
| 378-369 | 216 | 16.0 | c |
| 386-383 | 216 | b | b |
| 393-390 | 216 | b | b |
| 446-442 | 242 | 19.6 | c |
| 457-453 | 242 | 20.7 | c |
| 460-453 | 242 | 22.4 | c |
| 462-453 | 242 | 23.2 | cc |

TABLE IX (CONT)

- a. Refer to Figure 5 for unsubstituted PAH and Figure 6 for methyl substituted PAH.
- b. Overlapping of two or more compounds prevented analysis by this method.
- c. P+2 value small or not present.

DISCUSSION

A. SURVEY FINDINGS

Water samples were found not to be contaminated to any significant degree. The coke sewer (CO2) did show small quantities of organic compounds and likely contained lower molecular weight polynuclear aromatic hydrocarbons (PAH).

The data of Table I shows the presence of substantial amounts of hexane extractable organic residues in sediment samples. All Lorain sediments were surface samples. n-Hexane was used as the extracting solvent for two reasons. First it was felt that use of a halogenated solvent such as Freon would later interfere with gas chromatographic/mass spectrometric analysis of the residues for PAH. In addition, n-hexane was the extracting solvent used in the U. S. Steel Calumet survey and it was felt that comparisons between the two surveys would need to be drawn.

Calumet data²⁶ show "oil and grease" values as high as 120,000 ppm for one sample and over 60,000 ppm for many others; some of these were core samples. Lorain data show, overall, slightly lower oil and grease values. This could be consistent with the fact that the Black River has recently been dredged.

Reasonably, the highest "oil and grease" values in the Lorain survey were found in the vicinity of the plant discharge points. The lowest values determined were at the harbor mouth and 2-3 miles downstream from the outfalls. The low value for sample 19468 cannot be explained.

It is tempting to try to draw analogies between amounts of organic residue and particular classes of organic compounds present in sediment samples. In certain cases this can no doubt be done; however, caution must be exercised. For example while samples 19472 and 19474 yielded similar amounts of organic residue, their chemical compositions are quite different.

Table VI and other data presented in the Results section shows that a broad spectrum of PAH is present in the sediment samples. The highest concentrations are in the vicinity of the plant outfalls with the levels in 19472 being 2-10 fold greater, depending on specific PAH, than for any other sample analyzed. Lowest values are found for sample 19466 (harbor mouth), 19467 (center of the river mouth), and 19476 (0.2 miles upstream from outfall 001). It is reasonable that PAH were found in all samples since the sampling sites were in close proximity to the plant. A lake effect is known to occur carrying water upstream at least five miles from the river mouth.²⁷ Because this survey represented the first attempt in this laboratory to quantitatively analyze for many PAH, one probably should place wide tolerance limits on the accuracy of the data in Table VI. The data certainly reflect the levels of PAH in the analyzed samples; however, errors of $\pm 15\%$ would not be unexpected.

Many of the PAH found in the sediment samples are without question carcinogenic. These include not only compounds reported in Table VI (see also Table V). Since a broad envelope of PAH was shown qualitatively to be present, many unidentified compounds containing four or more rings, are no doubt carcinogenic. In particular are the methyl substituted PAH which have been shown to possess a high degree of carcinogenicity.^{5,20}

B. OTHER COMMENTS

The general philosophy taken at the outset of the survey was to analyze for a broad envelope of PAH rather than for one or two compounds. This approach proved to be successful and we believe that future surveys should be handled in a similar fashion.

The analysis for complex mixtures of PAH constitutes one of the most difficult determinations in organic chemistry; the data presented in this report are clear evidence of this fact. Optimum conditions for separating PAH from other classes of organic compounds had to be determined. GC and GC/MS analyses techniques had to be perfected. The PAH fraction (B_{II}) is complex and requires careful and detailed analysis and interpretation. These criteria were met and meaningful data were obtained.

In subsequent surveys, in other geographical locations, our capabilities will be extended. For example, we intend on obtaining a stock of PAH primary standards available from the Canadian Air Pollution Control Directorate, Department of the Environment, Ottawa.²⁸ These will allow us to quantitate upwards of 50 PAH.

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