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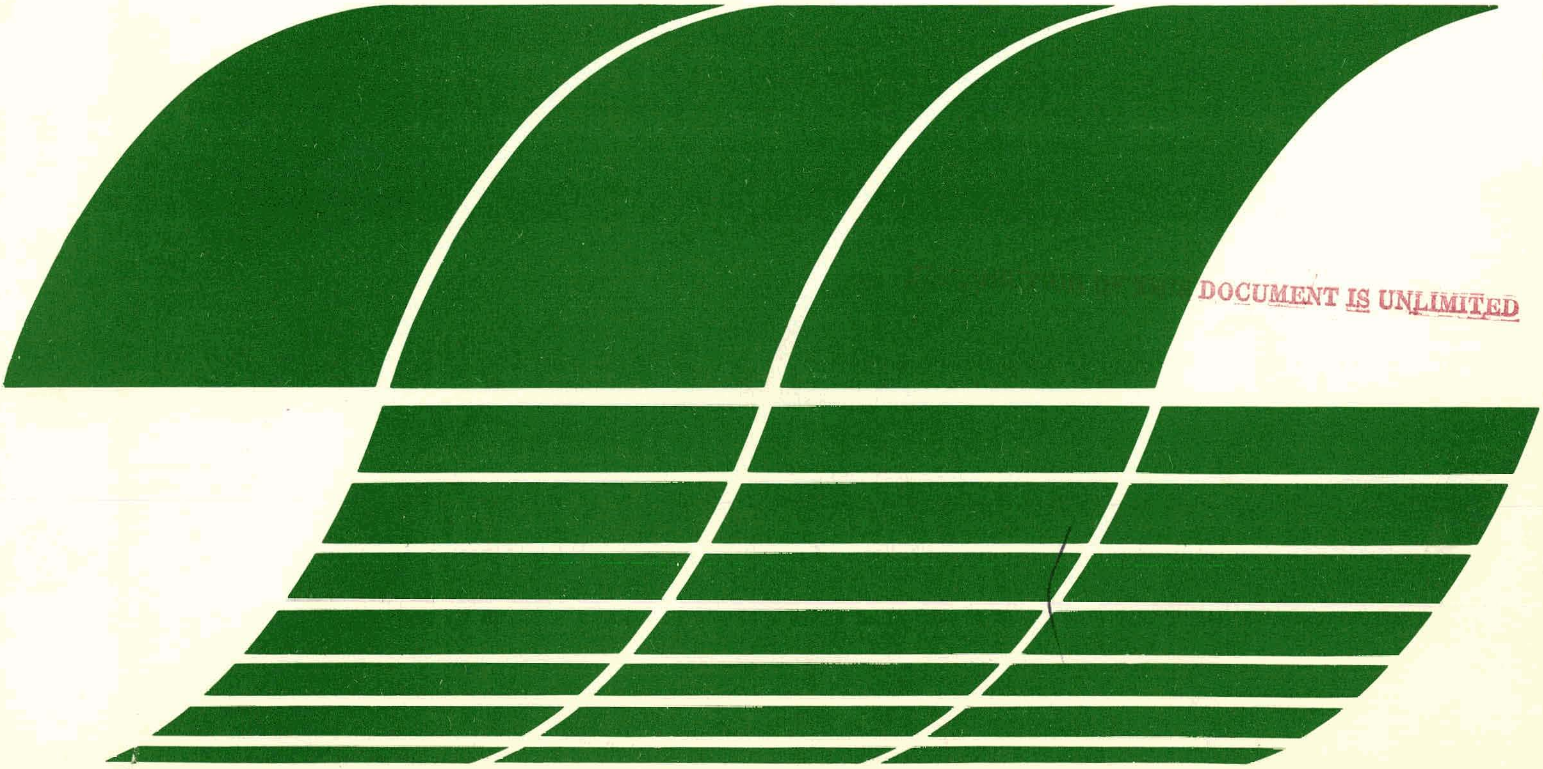
Research and Development

# Trace Organics Variation Across the Wastewater Treatment System of a Class-B Refinery

MASTER

## Interagency Energy/Environment R&D Program Report



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WATER RESOURCES RESEARCH PROGRAM

# TRACE ORGANICS VARIATION ACROSS THE WASTEWATER TREATMENT SYSTEM OF A CLASS-B REFINERY
and
# Estimate of Removal of Refractory Organics by Add-On Mixed-Media Filtration and Granular Activated Carbon at Pilot Scale

by

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# TRACE ORGANICS VARIATION ACROSS THE WASTEWATER TREATMENT SYSTEM OF A CLASS-B REFINERY
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# Estimate of Removal of Refractory Organics by Add-On Mixed-Media Filtration and Granular Activated Carbon at Pilot Scale

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## ABSTRACT

Wastewater at SOHIO's Toledo refinery was sampled every four hours for four successive days in December, 1976. Effluents from the full-scale system (dissolved-air-flotation [DAF] unit and final clarifier for the activated-sludge unit) and an add-on pilot-scale unit (mixed-media filter and activated-carbon columns) were sampled for analysis of common wastewater parameters and trace organic compounds. Grab samples taken every four hours were composited daily. Organics were isolated into acid, base, and neutral fractions. Four-day composites of these daily extracts were analyzed by capillary-column gas chromatography/mass spectrometry. Some 304 compounds were identified in the neutral fraction of the DAF effluent and removal of these organics by the activated-sludge and add-on treatment units was estimated. Numerous data for the approximate concentration of organic compounds are presented. Common wastewater parameters are also presented for comparison to specific organics concentration data.

The activated-sludge unit removed aromatic compounds better than it did nonaromatics whereas the activated-carbon unit was better at removal of nonaromatic compounds. Average percentage removal of those organics present in the DAF effluent was: >99% (activated sludge), ~0% (mixed-media filter), and <1% (activated carbon). Of the ~1% of trace organics remaining in the final-clarifier effluent, 81% (by weight) were removed by the activated carbon. Because of variations in extraction efficiencies, amount of sample injected, losses on the GC column and transfer lines, and other sources of error, these are only approximate removal estimates.

## EXECUTIVE SUMMARY

This report presents the results of research conducted by Argonne National Laboratory jointly for the U.S. EPA's Robert S. Kerr Environmental Research Laboratory and for the U.S. DOE's Division of Environmental Control Technology, Office of Assistant Secretary for Environment. The primary aim of the research was to evaluate the efficiency of pilot-scale granular activated carbon for the removal of organic compounds refractory to the activated-sludge treatment system of a Class B petroleum refinery that met BPT ("best practicable technology") in 1977. In order to achieve this goal, it was necessary to characterize the trace organic compounds present not only in the effluent from an add-on mixed-media/activated-carbon pilot-scale unit, but also those compounds in the effluents from two of the wastewater treatment steps (the dissolved-air-flotation and activated-sludge treatment steps) that preceded the pilot-scale unit. The research approach that was adopted and the major results are as follows.

### a) Add-on pilot-scale setup at Class-B refinery

Argonne assisted the Robert S. Kerr Environmental Research Laboratory (RSKERL) in setting up its mobile, pilot-scale equipment at SOHIO's Toledo refinery, a 120,000 BPSD refinery having crude topping, catalytic cracking, and coking. The RSKERL pilot-scale equipment consisted of two 6-in.-ID glass, up-flow carbon columns, with a total bed depth of 6 ft, preceded by one 6-in.-ID, mixed-media filter. A constant flow rate of 0.25 gpm was maintained and a carbon analyzer was used to confirm that TOC breakthrough (carbon-column overloading with organics) did not occur.

### b) Wastewater sampling and organics extractions

Grab samples of wastewater taken every 4 hr were composited every 24 hr at each of the four sampling points mentioned earlier (the effluents from the dissolved-air-flotation, final-clarifier, mixed-media-filtration, and activated-carbon units). Each day's composite samples were iced and air shipped to RSKERL for extraction. This procedure was followed for four consecutive days. Organic compounds were isolated by a liquid-liquid extraction technique using methylene chloride followed by extract concentration and ampuling for shipment. RSKERL supplied Argonne with 1-mL solutions of the acid, base, and neutral fractions composited over the 24-hr sampling periods.

### c) Identification of wastewater organic compounds

The 12 fractions of the composited extractions were analyzed by gas chromatography/mass spectrometry (GC/MS), using capillary columns of the wall-coated variety and Grob-type splitless injection. Comprehensive identification of organics in the effluent from the dissolved air flotation (DAF) unit was undertaken. Over 300 compounds were identified in the neutral fraction using (primarily) single-ion chromatograms. The concentrations of the organics in the final clarifier (FC), mixed-media filtration (MMF), and activated-carbon (AC) effluents were so low that a special procedure had to be instituted for their identification. It was necessary to assume that each organic compound identified in the DAF effluent was present also in the FC, MMF, and AC effluents, but at much lower concentrations. This assumption was equivalent to using the extract of the DAF effluent as a "standard mixture." Identification of each organic in the FC, MMF, and AC extracts was based on retention time, presence of major ions, and semi-quantification of the area or peak height of each major ion.

### d) Results (neutral-fraction organics)

Predominant types of compounds in the neutral fraction of the DAF effluent were n-alkanes, toluene, $C_2$, $C_3$ and $C_4$ benzenes, naphthalene, methyl naphthalenes and $C_2$-naphthalenes, phenanthrene, anthracene, and methyl phenanthrenes and anthracenes, present in concentrations of about 10-700 ppb (expressed as concentration in the wastewater, and not corrected for extraction efficiency).

There was extensive removal of trace organics by the activated sludge unit, no measurable removal by the add-on mixed-media filter unit, and varying removal, where measurable, of the remaining (refractory) organics by the add-on activated-carbon unit. With regard to the n-alkanes, $C_9$ through $C_{31}$, the percent removal by activated sludge was greatest for $C_{10}$ and fell off gradually as carbon number increased. With activated carbon, there was again a gradual decrease in percent removal as carbon number increased, due probably to less adsorption ability for higher alkanes.

Percent removals of branched alkanes by the activated sludge and by the activated carbon, where measurable, are in the same range as the n-alkanes.

Cycloalkanes (or alkenes) were removed by the activated-sludge unit in much the same way as the n-alkanes but none could be detected in the activated-carbon effluent, probably because of their extremely low concentrations in the final-clarifier effluent.

Alkylated benzenes were drastically removed by the activated sludge; additional removal by activated carbon appeared to be limited. Indan and tetralin-type molecules exhibited similar behavior.

Naphthalene and alkylated naphthalenes were substantially removed by activated sludge and only partially removed by activated carbon.

Alkylated benzothiophenes, dibenzothiophenes, PNAs, and alkylated PNAs were present in very small quantities and removal percentages were difficult to estimate.

In general, the activated-sludge unit removed aromatic compounds better than nonaromatic compounds whereas activated carbon showed greatest removal efficiency on nonaromatic compounds of the neutral fraction.

### e) Results (acid-fraction organics)

Over 30 phenols were found in the acid fraction of the DAF effluent, ranging in concentration from 1 to 50 ppb. Predominant phenols were phenol, the cresols, an unidentified xylenol, and 2,3-xylenol. The activated-sludge unit was very effective in removing phenols. Three alkylated phenols were removed at levels of >99.9%. A measure of the efficiency of the activated-carbon unit for removal of phenols was not possible due to the extremely low concentrations (or absence) of phenols in the effluent from the final clarifier.

### f) Results (base-fraction organics)

More than 70 compounds were found in the base fraction of the DAF effluent. Some of these were not organic bases, reflecting incomplete separations in the extraction process. Very small amounts of alkylated pyridines were present, such as picolines, ethyl pyridines, lutidines, ethyl picolines, collidines and ethyl lutidines. Small amounts of alkylated quinolines, $C_1$, $C_2$, and $C_3$s, and appreciable quantities of aniline and alkylated anilines were present. Although analysis of the data showed that the activated-sludge unit did remove base-fraction organics, little can be said owing to the very small concentrations involved.

### g) Results (common wastewater parameters)

Also reported herein are the results of a parallel effort at wastewater characterization that was conducted by SOHIO's Warrensville Research Center. Common wastewater parameters were run daily on composites of 4-hr grab samples collected in parallel with those taken for trace organics characterization. Average performance data for the 4-day study showed either no effect or only a minor effect of the mixed-media filter, but a major effect of activated-carbon unit, on final-clarifier effluent. The activated-carbon effluent was of a quality equal to or better than the plant intake water (from Maumee Bay) for all seven parameters measured. The final clarifier effluent was slightly higher in concentration with regard to cyanide, COD, BOD, and TOC and equal or better with regard to O + G and suspended solids than the intake water and activated carbon effluent. However, since only very low levels (ppb range) of organics were found by GC-MS analysis of the final clarifier effluent, the organics contributing to the BOD, COD, and TOC concentrations are compounds not amenable to extraction and/or GC-MS analysis and probably consist of high molecular weight compounds such as humic acids and natural by-products of bacterial action.

### h) Removal of trace organics by granular activated carbon (GAC) at pilot scale

A limitation of this study is that data were obtained from the pilot-scale GAC unit for only four days on *fresh* carbon. These data permit inferences about refractory organics removal only when a GAC adsorber is started up. It was not possible to speculate on 1) compound breakthrough characteristics with respect to percent GAC bed saturation as a function of TOC or COD adsorbing capacity or 2) when regeneration is necessary.

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# 1 INTRODUCTION

## 1.1 BACKGROUND

At the time this study was initiated, the 1983 BATEA model for wastewater treatment for the petroleum refining industry, as proposed by the Environmental Protection Agency (EPA), consisted of the following treatment sequence: biological treatment, mixed-media filtration, or its equivalent, and granular activated carbon. Thus, the proposed 1983 model consisted of fixed-bed activated-carbon adsorption added onto the 1977 "best-practicable-technology" (BPT) which consisted of biological treatment followed by final polishing. (The U.S. Court of Appeals Ruling of August 11, 1976, however, remanded for reconsideration by the EPA Administrator the 1983 guidelines for petroleum refining including the requirement for granular activated carbon in the treatment sequence.)

An important step in evaluating the efficacy of the BATEA model involves documentation of the ability of fixed-bed activated carbon to remove trace organic compounds that are refractory to the biological plus mixed-media treatment steps. This study was carried out to try to determine the relative organic compositions of the effluents from the biological, mixed-media (polishing), and granular-activated-carbon treatment steps. An effort was made to characterize the trace organic compounds in these effluents at a Class B refinery having treatment meeting BPT limitations. The results would serve primarily as guidance for determining the need for a larger-scale study and would not necessarily be used to predict the performance of a full-scale system.

## 1.2 STUDY OBJECTIVES AND SCOPE

The objectives of this study were

a) characterization of trace organic compounds across the full-scale wastewater treatment system at a Class B petroleum refinery that met BPT,

b) characterization of trace organics in effluents from add-on filtration and carbon adsorption at pilot scale, and

c) estimation of the ability to remove trace organics by the full scale and the add-on pilot-scale units.

The scope of the study involved taking water samples every four hours for four days at the following points (Fig. 1.1):

1) the refinery's raw-water intake main,
2) the effluent stream from the dissolved-air-flotation (DAF) unit,
3) the effluent stream from the final clarifier (FC),
4) the pilot mixed-media filter (MMF) effluent stream, and
5) the pilot activated-carbon (AC)-column effluent stream.

The four-hour grab samples were to be composited daily. Trace organics from the composited samples were to be extracted as acid, base, and neutral fractions for characterization by capillary-column gas chromatography/mass spectrometry (GC/MS).

Comparisons of the trace organic compositions of the effluents listed above were undertaken by

a) attempting a comprehensive identification of the organics in the DAF effluent,
b) determining the retention time and the major ions associated with each organic compound in the DAF effluent,
c) measuring the peak height (or area) of the major ions of each organic in the DAF effluent,
d) measuring, in the FC, MMF, and AC effluents, the peak height (or area) of the previously-determined major ions of each organic, and

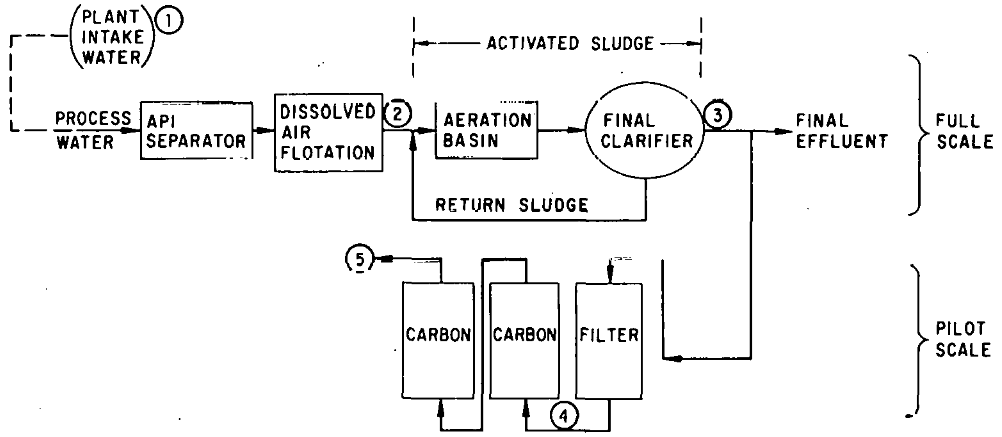

Fig. 1.1. Schematic Diagram Showing Proposed Sampling Points at the Plant Intake(1) and in the Full-Scale(2,3) and Pilot-Scale(4,5) Wastewater Treatment Systems of a Class-B Refinery

e) calculating the percent reduction of peak height (or area) of each major ion in going from the DAF to the FC, MMF, and AC effluents.

The above assumes that extraction efficiencies are equivalent (not necessarily 100%) for each organic compound in the DAF, FC, MMF, and AC effluents.

## 1.3 PREVIOUS WORK

Burlingame (1977) characterized the organic compounds in three grab samples of wastewater from an unspecified Class-B refinery. The wastewater samples were taken subsequent to the API separator, subsequent to the Pasveer oxidation ditch and clarifier, and subsequent to the non-aerated lagoons. Burlingame used capillary-column GC and high-resolution MS to identify and inventory the major compound types in the neutral fraction of the three samples. Pfeffer, Harrison, and Raphaelian (1977) reported on the preliminary results of the present work, for SOHIO's Class B refinery at Toledo, Ohio.

With the exception of these two preliminary studies, we are unaware of any published works that attempt to characterize all of the measurable trace organics across a full-scale refinery wastewater treatment system. Nor have we found any material in the literature regarding the removal efficiencies of activated carbon for trace or refractory organics in biologically treated refinery wastewater.

Matthews (1978) has prepared a comprehensive review of the treatment of selected industrial wastewaters, including petroleum refinery wastewater, with activated carbon. No studies such as the present were uncovered in Matthews' search of the literature.

## 1.4 REFINERY SELECTION

Considerable time was allocated to refinery selection, as there was sufficient funding to study only one refinery. Repeated discussions and meetings were held with members of the API's W-20 Task Group to arrive at a "representative" refinery; however, all agreed that a truly representative refinery did not exist. It was agreed to acquire permission from a Class B refinery whose final effluent quality met BPT. Other selection criteria included intake water quality and variability, refinery turnaround plans, final-effluent quality, raw-waste loading, and hydraulic detention times typifying the activated sludge process at a Class B refinery.

Agreement was reached in September 1976 to conduct the study at SOHIO's Toledo refinery. This is a Class B refinery (crude topping and catalytic cracking) with coking, having a crude capacity of 120,000 BPSD. The treatment train at that time consisted of an API Separator, a dissolved-air-flotation (DAF) unit, an extended aeration type activated sludge unit, and a final clarifier. The final effluent quality routinely satisfied BPT requirements with the exception of suspended solids. Following a 1-month turnaround period, the wastewater treatment system returned to steady state in November 1976, one month before sampling for this study began.

# 2 EXPERIMENTAL PROCEDURES

## 2.1 PILOT-SCALE EQUIPMENT

### 2.1.1 Setup

EPA's Robert S. Kerr Environmental Research Laboratory (RSKERL) furnished a mobile laboratory trailer that was positioned near the final clarifier. Facilities aboard the trailer included 6-in.-ID glass columns for filtration and carbon adsorption (Fig. 2.1), a TOC analyzer for monitoring organic carbon breakthrough, pumping and distribution capability, and sampling gear. The sampling equipment, pumps, and distribution lines were fabricated and so installed that the only materials in contact with water moving through the pilot treatment system were stainless steel, glass, Teflon, and polypropylene. A stainless-steel reservoir was used for backwashing (Fig. 2.2). Pumps had polyethylene impellers and housings. Sampling points 2 and 3 (Fig. 2.2) were removable steel plugs. A 25-ft inlet line connected the clarifier weir trough to the primary pump. Sampling points aboard the trailer were: 1) SOHIO's final clarifier effluent, 2) pilot mixed-media filter effluent, and 3) pilot carbon-column effluent (Fig. 2.2).

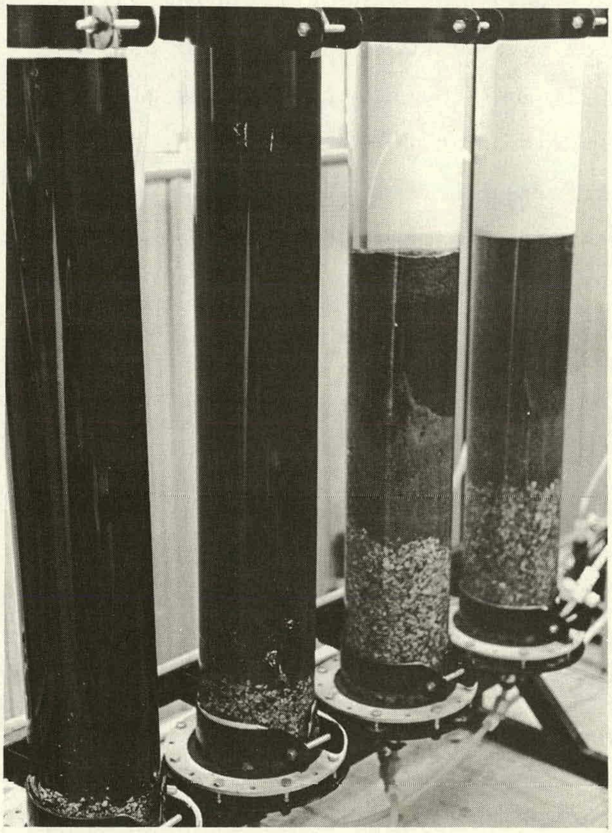

Fig. 2.1. Pilot-Scale Activated-Carbon Columns and Mixed-Media Filters

Two, parallel, down-flow mixed-media filters (Fig. 2.1) were used. While one was operating for 24 hr, the second, having been backwashed, was ready for use the next day. Figure 2.2 shows the configuration of the filtering bed: anthrafilt, washed ungraded sand, and washed gravel. Sand used had an Effective Size of 0.2 mm and a Uniformity Coefficient of 4.5.

Backwashing was accomplished by alternately pulsing with air and pumping carbon-column effluent.

Two up-flow carbon columns (Fig. 2.1) were packed as shown in Fig. 2.2 and operated in series to achieve a total bed depth of 6 feet. A constant flow rate of 0.25 gpm was maintained. The reactivated carbon used was Calgon's Adsorption Service Carbon. Calgon's analysis of a sample from the lot used at Toledo gave these results:

| | |
|---|---|
| Apparent Density[a] (g/cc): | 0.51 |
| Molasses Number:[b] | 282 |
| Iodine Number:[c] | 821 |
| Sieve Result (mesh) | 8x40 |

Column packing was accomplished by trickling material into each water-filled glass column.

### 2.1.2 Operation

Following packing, the filters were cleaned by back flushing with plant tap water for about one hour. Each filter was backwashed prior to usage by pulsing with air, to kick up the anthrafilt and the top few inches of sand, and then backwashing with final-clarifier effluent to sweep out the dislodged suspended solids. This operation was performed for about one hour. During the run, backwashing was performed in a similar manner using carbon effluent; then the column was allowed to stand for about 23 hours while full of the carbon-column effluent.

On the day prior to the study, the system was operated for about one hour on final-clarifier effluent and then shut down until the study. Flow control was accomplished by mechanical constriction (Fig. 2.2) on the carbon-column discharge line. This eliminated $H_2S$ bubbles released in the carbon

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[a] Weight per unit volume of homogeneous activated carbon.

[b] Calculated from the ratio of optical densities of the filtrate of a molasses solution treated with standard activated carbon and the test activated carbon. This is the test method of Pittsburgh Activated Carbon Co. Molasses number is assumed to reflect transitional-pore surface area.

[c] The milligrams of iodine adsorbed by one gram of carbon at an equilibrium filtrate concentration of 0.02N iodine. It is measured by contacting a single sample of carbon with an iodine solution and extrapolating to 0.02N via an assumed isotherm slope. Iodine number can be correlated with ability to adsorb low-molecular-weight substances and is assumed to reflect small-pore surface area.

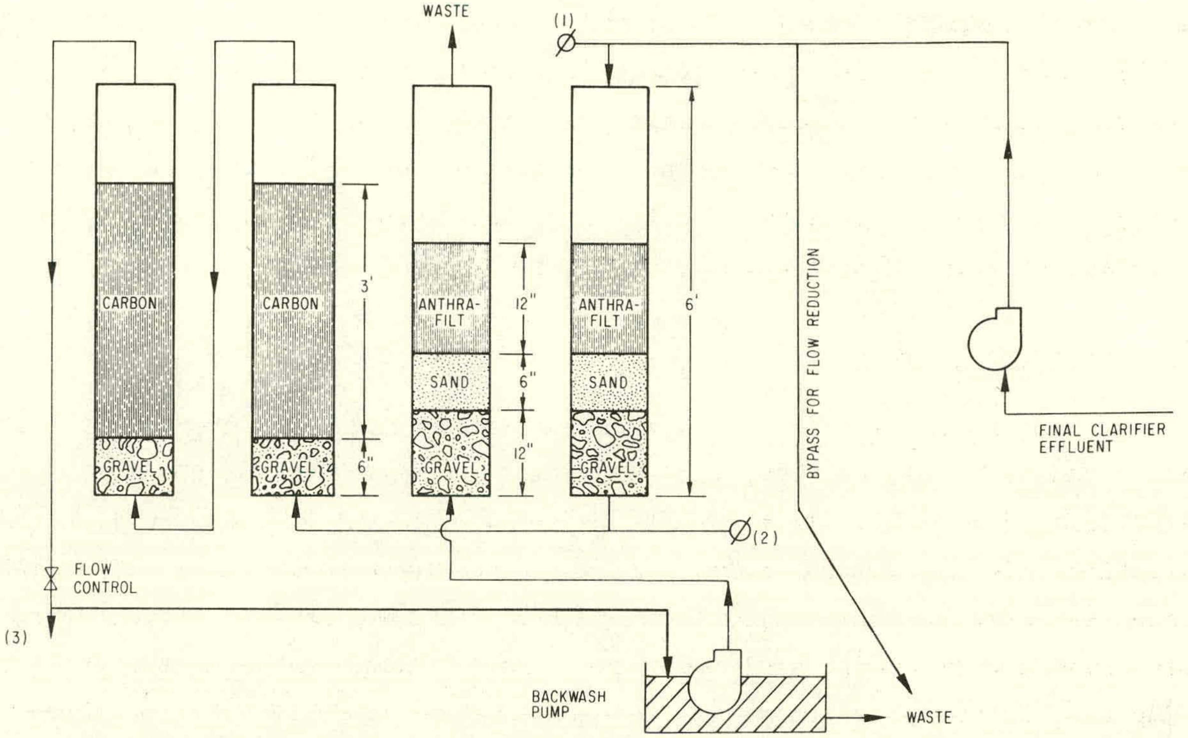


Fig. 2.2. Schematic of Add-On Treatment System and Sampling Points for Effluent from Final-Clarifier(1), Mixed-Media Filter Unit(2), and Carbon-Column Unit(3)

columns when flow control was attempted at the discharge side of the pump feeding final clarifier effluent to the filter.

The add-on treatment system was operated at 1/4 gpm, resulting in about 36 min contact time for the carbon at a surface loading rate of 1.27 gpm/ft$^2$. The residence time (36 min) is the empty-bed residence time, V/Q. No biological growth was noted on the carbon during the study.

Flow to the columns was initiated at 4:00 A.M. on the first day of the study. Following the 8:00 A.M. sampling each day, the system was shut down. The filters were reversed; the backwashed filter was switched to the filtration mode, and the previously used filter was plumbed for backwash. The columns were started again, and the flow adjusted. Total shut-down time was about 15 min.

During the study, there were no significant recorded changes in flow through the plant wastewater treatment system, as measured by the biofeed pumping rates (that is, the wastewater influent to the aeration basin). Note that, waste sludge being insignificant, the final-clarifier effluent and biofeed flows were assumed to be equal. Aeration time was of the order of 16-18 hours and mixed-liquor volatile suspended solids concentration in the aeration basin was 4440 mg/L, during the study. These values are noted here because the performance and operating conditions of the activated sludge unit can have a significant effect on the organics removal capabilities of granular activated-carbon columns (Kim, et al., 1976).

## 2.2 WASTEWATER SAMPLING

Samples of wastewater (~420 mL each) were taken and iced every four hours (8A, 12N, 4P, 8P, 12M, and 4A) at each of the five locations given in Sections 1.2 and 2.1. Plant intake water was sampled at a wet well on the negative side of the pump that lifts water to the process units. The well receives water by gravity flow from Maumee Bay, Lake Erie. Effluent from the dissolved air flotation (DAF) unit was sampled from a valve on the discharge pump that lifts DAF effluent to the aeration basin. This valve remained open during the 4-day study.

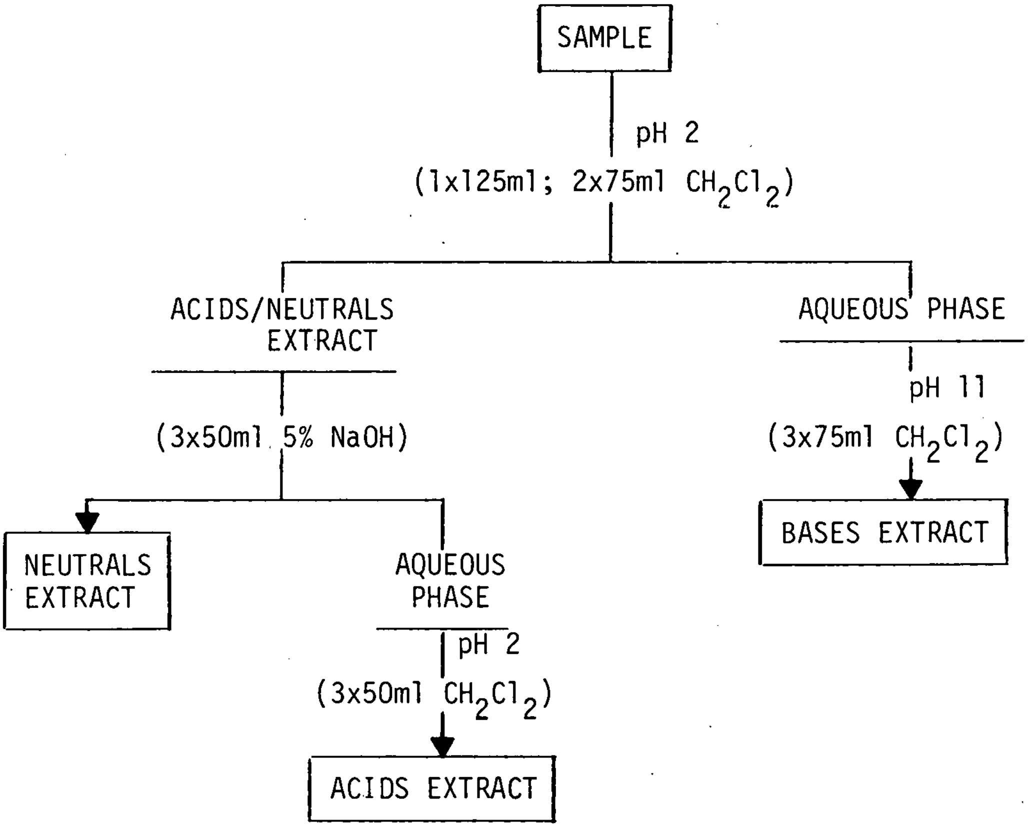
Every 24 hr a composite sample (~2.5 L) was made up, from the previous day's 4-hr individual samples, for each of the five sampling points. Each daily set of composited samples was transported in ice chests to Detroit for air shipment to Ada, Oklahoma. The samples arrived at RSKERL in Ada within 9 hr of final compositing in Toledo.

Attention was given to decontaminating material coming in contact with water samples. All glassware was cleaned by firing, maintaining 550°C for 1 hour. Sample-bottle caps contained Teflon liners which had been cleaned by Soxlet extraction with methylene chloride, the solvent later used in the laboratory for extracting the organics from the water samples.

Two problems occurred which should be noted. The 12N grab was missed during the first 24-hr compositing period owing to a power failure. Secondly, the validity of the composite sample of carbon-column effluent for the first day and for 1/6 of the second day is somewhat doubtful owing to an error in sampling. The flow being only 1/4 gpm and the total volume of sample required for SOHIO and Argonne analyses being over 2 gallons, the flow restriction was removed during sampling. The flow was probably 1 gpm at this time. However, soluble total organic carbon values recorded before and after this point showed no appreciable differences. Total organic carbon values were measured to assure that no break-through occurred during the study. (Samples were taken of the final-clarifier, mixed-media, and carbon-column effluents (usually at 8:00 A.M. and 12:00 N) for determination of soluble total organic carbon.)

## 2.3 ISOLATION OF ORGANICS

Personnel at EPA's RSKERL prepared the composited water samples for GC/MS analysis by Argonne. This involved the following tedious liquid-liquid extraction sequence using methylene chloride.



Again, all glassware was fired for organics decontamination. A major problem was emulsion formation, requiring emulsion breaking and phase separation by various techniques. Each organic extract was dried by passing through anhydrous sodium sulfate and the solvent was stripped, resulting in 1 mL of concentrated extract which was sealed in a glass ampul. A period of 9 man-hours was involved in preparing each sample to the ampul stage; there were 20 samples requiring this preparation.

Of the 24-hr-composited 3780-mL water samples from each of the sampling points, 2500 mL were extracted to give 200 mL each of neutral, acid, and base fractions. Of the 200-mL extract of each fraction, 125 mL were concentrated to 1 mL extracts (one for each of 4 days, 3 fractions, and 5 sampling points - a total of sixty 1-mL extracts). For use in GC/MS analysis, 0.2 mL of each of four 1-mL extracts (one for each day) were combined to give a 4-day composite extract which was evaporated in a 1-mL, cone-shaped vial to 50 μL.

## 2.4 GC/MS ANALYTICAL PROCEDURES

### 2.4.1 General Description of the GC/MS System

Analysis of the specific organics in the extracts was performed on a Hewlett-Packard 5982A GC/MS equipped with a Hewlett-Packard 5933A Data System consisting of a 2100S Computer with 16K, 16-bit-word core memory, 7900A Dual Disc Drive with 2.5M bytes/disc memory, 5948A A/D Converter, 6131C D/A Converter, and a Tektronix 4012 Display Terminal. A 5930 HP GC was used in place of the 5700 Series HP GC normally delivered with the 5982A GC/MS. Peripheral equipment included a Tektronix 4631 Hard Copy Unit and a Zeta 130-10 Incremental Plotter. Discs with the Aldermaston AWRE Spectral Library, the HP Contributed Libraries, and the EPA/NIH Spectral Library were also available along with an Anderson Jacobson AD 342 Acoustic Coupler for connecting to the Cyphernetics Mass Spectral Search System in Ann Arbor, Michigan. During the course of the study, it was found that the time required for analysis and workup of data far exceeded that required for collection of data. This was due partly to the great complexity of the samples and partly to the high resolution of peaks by the capillary columns used. Thus, a time sharing data system, the HP 5934A, was obtained; it consisted of a 21MX Computer with 32K, 16 bit word core memory, 7900A Dual Disc Drive with 2.5M bytes/disc memory, 5948B Data Subsystem (A/D and D/A Converters), and a Tektronix 4012 Display Terminal. With this data system, data could be collected during GC/MS runs while previously collected data could be analyzed. Also, the 5933A Data System could be used for analyzing previously collected data.

### 2.4.2 Capillary-Column GC/MS

Due to the anticipated complexity of samples that were to be analyzed, it was felt that capillary columns of the wall-coated variety should be used to afford the greatest resolution possible. Although support-coated open tubular (SCOT) type columns are simpler to use, the wall-coated open tubular (WCOT) columns were used because of their greater resolution, less susceptibility to tailing due to adsorptive effects, and their ability to pass higher-boiling components such as PNAs, which were of interest in this study. With WCOT columns, leak-proof and low-dead-volume connections are required to avoid tailing of peaks and care was taken to ensure that this was the case. A modified split/splitless Hewlett-Packard Grob-type injection system was used for the capillary columns. The end of the column was connected to glass-lined stainless-steel tubing with an ID of 0.5 mm. The glass-lined stainless-steel tubing was connected directly to a line going to the mass spectrometer source. Since no separator, such as a jet or membrane separator, was used, all components of a mixture exiting the column entered the mass spectrometer. Therefore, there could not be discrimination in the amount of each component reaching the mass spectrometer as there is with separators. Assuming the individual components are not lost in the injection system, the column, or the glass-lined stainless-steel-tubing transfer line, the amount of each component in the mixture reaching the source of the mass spectrometer is a true representation of the quantity injected on column.

The glass-lined stainless-steel-tubing transfer line was wrapped carefully with insulated nichrome wire, insulated with glass wool and glass electrical tape. With this method of heating, the transfer line could be left at lower temperatures due to the more uniform heating and compounds passing through the transfer line were less likely to decompose due to hot spots typically found in commercial instruments where other devices are used for heating the transfer line. As a result, gains in sensitivity, particularly of the higher boiling components, are noticeable.

Since the sample extracts consisted of small amounts of organics in a solvent, it was found necessary to use Grob-type splitless injection. As opposed to split operation, the Grob system avoids the loss of large amounts of the sample and the discrimination of components of the mixture. Also, peaks tend to be sharper due to the so-called "solvent" effect whereby the plug formed at the beginning of the column is smaller because the solvent acts as a barrier to diffusion of the plug and tends to concentrate the plug. Moreover, in splitless operation, the septum is continuously purged during the run thereby avoiding components of the septum to enter the column. However, it was found that, between runs, septum-bleed would enter the column, deteriorating the resolution of the column during runs. Thus, a modification of the system was made whereby the injection port was automatically put into the purged state between runs or overnight.

Aside from the well-known increased resolution of capillary columns over packed columns, there are other aspects of capillary column GC/MS that make the use of capillary columns desirable. First, since in mass spectrometry, the mass spectrum, or abundance of each ion, is recorded at a specific instant, there is no integrating effect. Thus, even if one can see a total-ion chromatographic peak, one does not necessarily get an interpretable mass spectrum. With capillary column GC/MS, because of the narrowness of the peak, the actual amount of compound reaching the source per unit time is considerably higher than with packed columns and, therefore, sensitivity is increased and possible interpretation is enhanced. Second, capillary columns have drastically reduced column bleed as compared to packed columns. Although present data systems are equipped with methods for subtracting background, this procedure never works very well, particularly with trace amounts of organics. From the outset, it is better to have as little background as possible. Third, all the compound exiting the capillary column enters the mass spectrometer, whereas with packed columns, only part (typically less than 50%) gets through the separator to the mass spectrometer source. There are certain high-boiling compounds that never get through packed columns due either to adsorptive effects or to decomposition. On the other hand, capillary columns pass the same high-boiling compounds at considerably lower temperatures.

### 2.4.3 Specific Problems Encountered in the Analysis of Extracts

In initial capillary column GC/MS studies of the neutral fraction of the DAF, FC, MMF, and AC samples, it was found that, whereas there were appreciable amounts of organics in the DAF samples, the concentration of organics in the FC, MMF, and AC was well below the detection limit by typical GC/MS procedures, except for a very few organics. For example, a major component in the DAF is n-pentadecane; it was present at a concentration of approximately 240 ng on column (that is, when injected onto the column at 100 times dilution). It was reduced by the activated sludge to approximately 90 ng on column and, by the activated carbon, to approximately 8.1 ng on column. The majority of organics in the DAF have a lower concentration than that of n-pentadecane. Since the lower limit of detection under ideal conditions by typical GC/MS procedures is approximately 10 ng on column, it would appear that a study of the reduction of the organics in the DAF effluent by the activated-sludge and activated-carbon units might be impossible with the possible exception of a very few compounds. Even with single-ion techniques (mass fragmentography), the detection of most of the organics would at best be difficult in the FC and AC effluents. Also, due to the large number of different organics (over 300) in the DAF, the use of single-ion techniques would be cumbersome; present-day data systems for GC/MS are set up for monitoring only a limited number of ions and are, therefore, adaptable to looking at only a few compounds during a run. Based on these observations, it appeared that the identification of organics in the FC and AC samples would be impossible.

Because of the foregoing problems an assumption had to be made; namely, those organics that are present in the DAF effluent are present also in the FC and AC effluent, but at much lower concentrations. Under such an assumption, one can examine the FC- and AC-effluent GC/MS data for those specific organics present in the DAF effluent. This method is equivalent to using the extract of the DAF effluent as a "standard mixture," and requires a comprehensive identification of the organics in the DAF-effluent extract and documentation of the mass spectrum, major ions, and retention time of each component. The identification of the organics in the FC and AC effluents is, therefore, based on retention time and the presence of major ions and the semi-quantification on the area or peak height of the major ions. (Of course, in identifying a component in the FC and measuring its concentration, one can not differentiate between whether the component had arisen from incomplete removal by the activated sludge or from bacterial decomposition of another component.) Although the method is simple in principle, it is difficult to carry out because most of the more than 300 components in the DAF effluent are present in only minute quantities and, in many cases, there is an overlap of peaks even with the use of high resolution capillary columns. (An exhaustive analysis by massgrams indicates that there are probably 400-600 components in the DAF effluent and many of the components overlap in high resolution capillary column GC/MS.)

However, with the use of capillary columns, the identification of small quantities of organics is enhanced since the background due to column bleed is low and background due to other compounds is often absent because of the high resolving power of capillary columns. Also, the probability of overlapping peaks having the same major ions is low, and there are, in practice, relatively few instances in which interferences take place.

### 2.4.4 Techniques for Identifying Organics in the Extracts

It was found that the major components in the DAF effluent were benzene, toluene, all isomers of $C_2$, $C_3$ and $C_4$-benzenes, naphthalene, alkylated naphthalenes, alkanes and alkenes. There were also many indans, anthracenes, phenanthrenes and fluorenes. It would appear that standards would be of use in identifying what is present in the DAF effluent. However, it was found that the commercially available standards are only those simpler compounds that are easily identifiable by GC/MS such as n-alkanes and alkylated benzenes up to $C_3$ or $C_4$-benzenes and a few indans, naphthalenes, anthracenes, phenanthrenes, and branched alkanes. One is familiar with the great number of isomers possible with alkanes up to $C_{25}$ but listings of aromatic compounds are less frequently available. A very limited listing of such aromatics, along with the number actually found in the neutral fraction of the DAF effluent, is found in Table 2.1.

The retention times of isomers of hydrocarbons occur in groups when chromatographed on a non-polar column, since separation takes place predominantly according to the boiling point of each compound. A representation of this effect is shown in Fig. 2.3, which is taken from data of a GC/MS run of the DAF-effluent neutral fraction on a 50-m OV-101 column programmed from 20°C to 240°C at 2°C/minute with 2-min hold at 20°C.

The identification of the type of isomer within a group is relatively easy since the fragmentation pattern of isomers is fairly predictable. For example, take the $C_3$-benzene isomers; Table 2.2 is a listing of approximate abundances of key ions useful for differentiating between these isomers. If one assumes a tendency to reach the stable tropylium ion (from $C_6H_5CH_2^+$) and that the loss of an alkyl group is preferred to the loss of hydrogen, one can explain the patterns that arise with these $C_3$-benzenes. For example, to reach a tropylium ion from an ethyl toluene, either a methyl or hydrogen ion could

Table 2.1. Number of Possible Isomers of Alkylated Benzenes and Some PNAs Commonly Found in the Neutral DAF Fraction

| | Possible Isomers | Found in DAF |
|---|---|---|
| Benzene | 1 | 1 |
| Toluene | 1 | 1 |
| $C_2$-Benzenes | 4 | 4 |
| $C_3$-Benzenes | 8 | 8 |
| $C_4$-Benzenes | 22 | 19 |
| $C_5$-Benzenes | 50 | 19 |
| $C_6$-Benzenes | 135 | 16 |
| Indan | 1 | 1 |
| $C_1$-Indans | 7 | 2 |
| $C_2$-Indans | 29 | 4 |
| Tetralin | 1 | 1 |
| $C_1$-Tetralins | 4 | 1 |
| $C_2$-Tetralins | 16 | 2 |
| Naphthalene | 1 | 1 |
| $C_1$-Naphthalenes | 2 | 2 |
| $C_2$-Naphthalenes | 12 | 7 |
| Phenanthrene/anthracene | 2 | 2 |
| $C_1$-Phenanthrenes/Anthracenes | 8 | 5 |
| $C_2$-Phenanthrenes/Anthracenes | 51 | 9 |
| Fluorene | 1 | 1 |
| $C_1$-Fluorenes | 7 | 3 |
| $C_2$-Fluorenes | 29 | 7 |
| Benzothiophene | 1 | 1 |
| $C_1$-Benzothiophenes | 6 | 4 |
| $C_2$-Benzothiophenes | 21 | 7 |
| Dibenzothiophene | 1 | 1 |
| $C_1$-Dibenzothiophenes | 7 | 2 |
| $C_2$-Dibenzothiophenes | 28 | 1 |

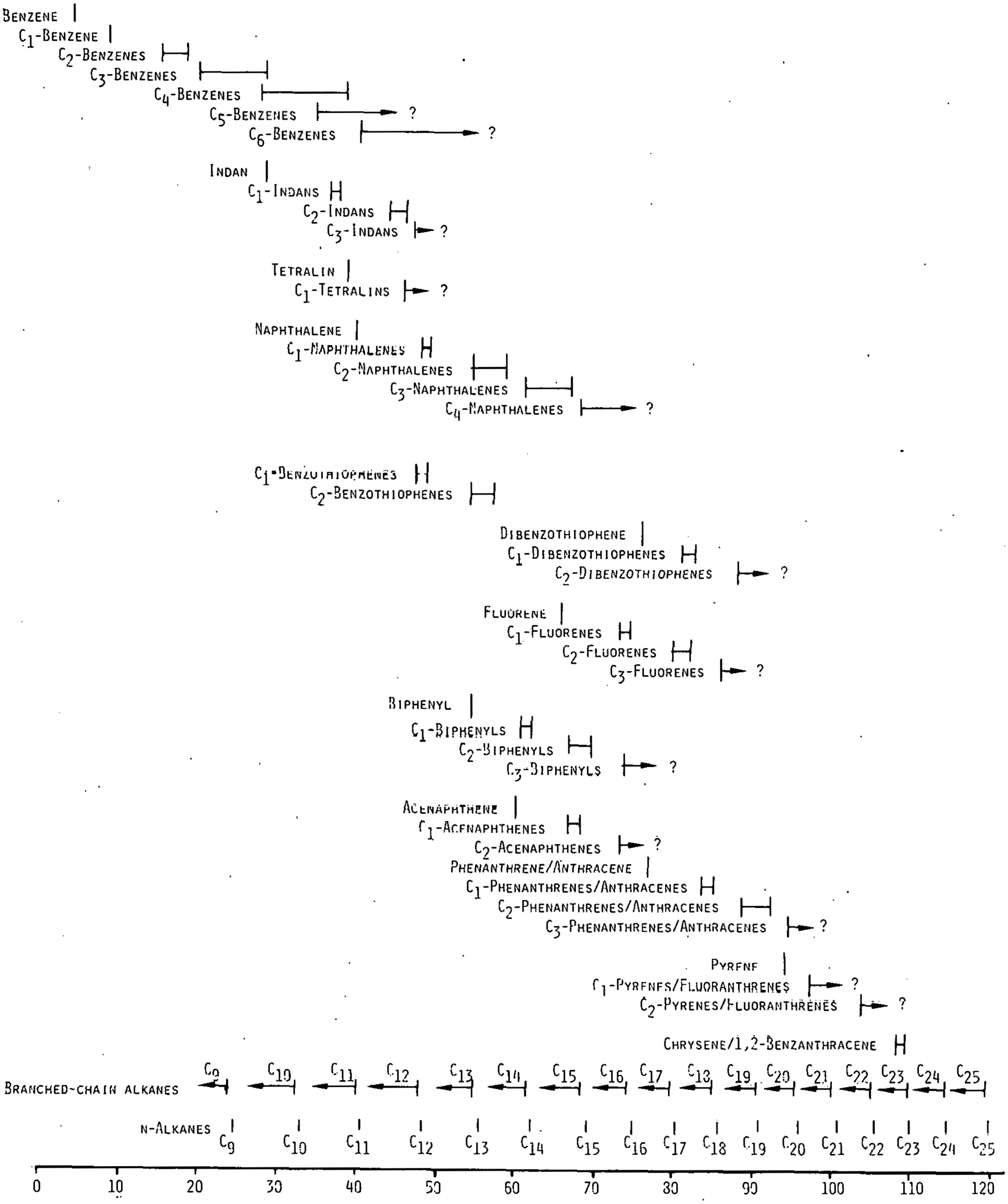


Fig. 2.3. Groupings of Major Classes of Compounds Present in the Neutral DAF Fraction as a Function of Retention Time, Chromatographed on a 50-m OV-101 Capillary Column Programmed at 2°C/Min from 20-240°C with 2-Min Hold at 20°C

Table 2.2. Abundances of Key Ions of $C_3$-Benzenes

| | Ions | | | |
|---|---|---|---|---|
| Compounds | 91 | 105 | 119 | 120 |
| 1,2,3-Trimethyl benzene | 5 | 100 | 10 | 45 |
| 1,2,4-Trimethyl benzene | 5 | 100 | 10 | 50 |
| 1,3,5-Trimethyl benzene | 5 | 100 | 10 | 60 |
| o-Ethyl toluene | 5 | 100 | Trace | 25 |
| m-Ethyl toluene | 5 | 100 | Trace | 25 |
| p-Ethyl toluene | 5 | 100 | Trace | 25 |
| n-Propyl benzene | 100 | 85 | None | 45 |
| i-Propyl benzene | 5 | 100 | None | 25 |

be lost but methyl loss is preferred and only a trace of the 119 ion is formed. With i-propylbenzene, the loss of a methyl group is further enhanced with the formation of a relatively stable secondary carbonium ion, and thus there is no perceptible 119 ion. With n-propyl benzene, the loss of ethyl leads to the tropylium ion with a mass of 91. Finally, with the trimethyl benzenes, there are appreciable amounts of 119 formed due to the loss of a hydrogen. These patterns (Table 2.2) can be seen nicely in the 91, 105, 119, and 120 massgram plots of the DAF in Fig. 2.4. The trimethyl benzenes (numbers 16, 18, and 25) have appreciable amounts of the 119 ion. The n-propyl benzene (number 13) has an appreciable 91 ion. The ethyl toluenes (numbers 14, 15, and 17) have predominantly the 105 ion and traces of the 119 ion. Finally, i-propyl benzene (number 13) has a 105 ion but no 119 ion.

Also, as shown in Fig. 2.5, it can be seen that the retention time is related to the boiling point of the $C_3$-benzenes.

It can be shown that similar identifications, based on the fragmentation pattern and boiling point, can be made for other alkyl-substituted benzenes and alkyl-substituted naphthalenes, anthracenes, phenanthrenes, etc., provided a non-polar liquid phase is used for the GC column. [As the alkyl-substituted aromatic becomes more fully alkylated (such as $C_5$, $C_6$, etc.), correlations with boiling point break down because the molecules are more alkane-like and, therefore, similar to the liquid phase and partitioning with or solubility in the liquid phase is greater.]

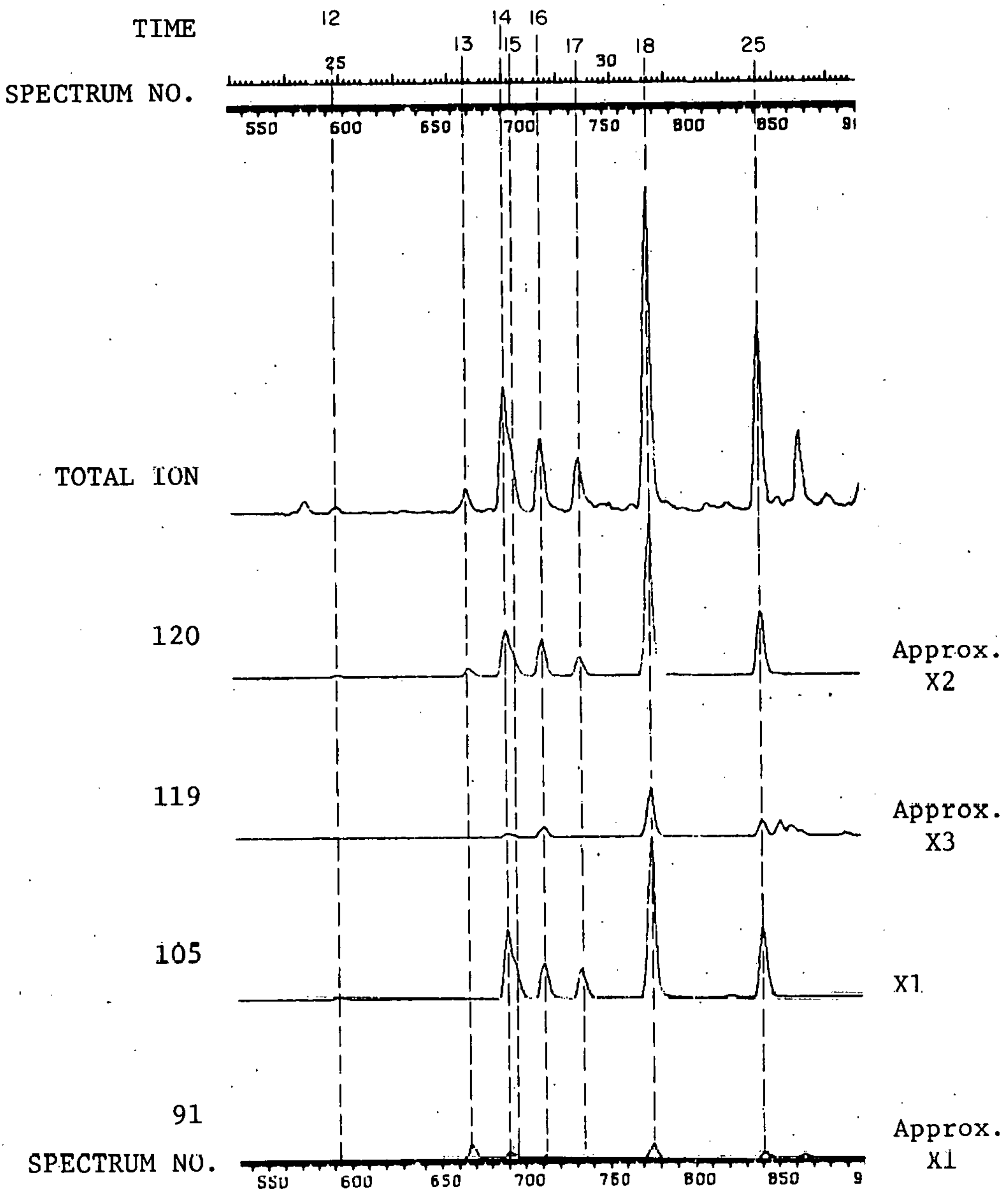


Fig. 2.4. Massgram Plots of Key Ions (91, 105, 119, and 120) of $C_3$-Benzenes used in Identifying the Specific Isomers

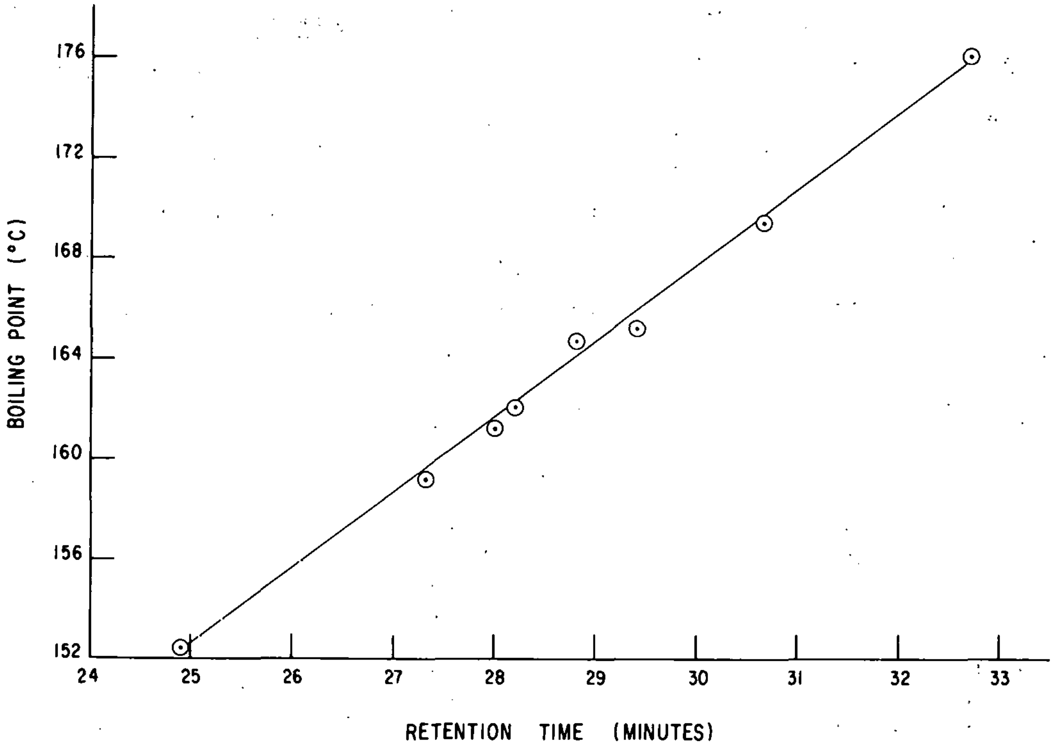


Fig. 2.5. Retention Time Versus Boiling Point of $C_3$-Benzenes

The major components of the neutral fraction of the DAF were identified by their mass spectra and the amount present was determined by measuring the peak area of the peak in the total-ion chromatogram and comparing it to the peak area of a standard from the same class of compounds. (Of course, it should be noted that generally GC/MS is not suitable for truly quantitative measurements and data generated must be considered only semi-quantitative. Also, percent recoveries with liquid-liquid extraction, stability, etc. are difficult parameters to determine, particularly with such complex mixtures as the neutral fraction of the DAF effluent.)

Whereas the amount of a major component in the neutral fraction of the DAF effluent was derived from the peak area of its peak in the total-ion chromatogram, the determination of the amount of the same compound in the FC and AC effluents was measured by determining the peak area of its major ion because, with the extremely low concentration of these compounds in the FC and AC effluents, major ions are more selective and impurities can be "filtered out."

In addition to identifying the major components in the neutral fraction of the DAF effluent by their mass spectra, an exhaustive massgram analysis of minor components was undertaken. It was found that most of the compounds in the DAF effluent were alkylated benzenes, naphthalenes, anthracenes, phenanthrenes, chrysenes, pyrenes, fluorenes, acenaphthenes, biphenyls, acenaphylenes, benzothiophenes, dibenzothiophenes, indans, and tetralins. There were also n-alkanes, branched alkanes and some cycloalkanes (or alkenes). Identification of alcohols was, at best, difficult because of their lack of molecular ion. It was found convenient to do a plot of four ions at a time:

| Ion | Identification |
|---|---|
| $M^+$ | molecular ion |
| $M^+ - 1$ | molecular ion minus one hydrogen |
| $M^+ - 15$ | molecular ion minus one methyl |
| $M^+ - 29$ | molecular ion minus one ethyl |

Most alkylated aromatics gave peaks of at least two of these ions and, in general, identification of the compound was not difficult. To make certain that the massgram peaks associated with a compound were, in fact, from the same compound, a line could be drawn through massgram peaks with relatively high accuracy since the Zeta plotter is accurate to one-hundred of an inch. If the peaks were coincident in retention time, it was assumed that those ions were from the same compound (see Fig. 2.4 for an example of this). Ions used for massgram plots are shown in Table 2.3.

In conclusion, the identification of organics in the neutral fraction of the FC and MMF/AC effluents by typical GC/MS procedures is difficult at best, since most of the compounds are present at concentrations approaching the limit of detection. However, by doing a comprehensive study, identifying each organic in the DAF efffluent and determining the retention times of the major ions associated with each organic in the DAF-effluent extract, it was found that organics in the DAF effluent also could be identified in the FC and MFF/AC effluents.

### 2.4.5 Column Effects and Semi-Quantitative Analysis of the Extracts

Whereas the analysis by capillary-column GC/MS of components in a mixture, with concentrations of each component ranging from 50-150 ng on column, is relatively simple, problems were encountered with the extracts because the range of concentrations was from well below 1 ng to 300 ng on column. It is

Table 2.3. Ions Used for Massgram Plots

| Ions | | | | Compound Type |
|---|---|---|---|---|
| Group 1 | | | | |
| 91 | 105 | 119 | 120 | $C_3$-benzenes |
| 105 | 119 | 133 | 134 | $C_4$-benzenes, benzothiophene |
| 119 | 133 | 147 | 148 | $C_5$-benzenes, $C_1$-benzothiophenes |
| 133 | 147 | 161 | 162 | $C_6$-benzenes, $C_2$-benzothiophenes |
| Group 2 | | | | |
| 117 | 118 | 131 | 132 | indan, $C_1$-indans, tetralin |
| 117 | 131 | 145 | 146 | $C_2$-indans, $C_1$-tetralins |
| 131 | 145 | 159 | 160 | $C_3$-indans, $C_2$-tetralins |
| Group 3 | | | | |
| 127 | 128 | 141 | 142 | naphthalene, $C_1$-naphthalenes |
| 127 | 141 | 155 | 156 | $C_2$-naphthalenes |
| 141 | 155 | 169 | 170 | $C_3$-naphthalenes |
| 155 | 169 | 183 | 184 | $C_4$-naphthalenes, dibenzothiophene |
| 169 | 183 | 197 | 198 | $C_5$-naphthalenes, $C_1$-dibenzothiophenes |
| Group 4 | | | | |
| 153 | 154 | 167 | 168 | biphenyl, acenaphthene, $C_1$-biphenyls, $C_1$-acenaphthenes |
| 153 | 167 | 181 | 182 | $C_2$-biphenyls, $C_2$-acenaphthenes |
| 167 | 181 | 195 | 196 | $C_3$-biphenyls, $C_3$-acenaphthenes |
| Group 5 | | | | |
| 151 | 152 | 165 | 166 | acenaphthylene, $C_1$-acenaphthylenes, fluorene |
| 151 | 165 | 179 | 180 | $C_2$-acenaphthylenes, $C_1$-fluorenes |
| 165 | 179 | 193 | 194 | $C_3$-acenaphthylenes, $C_2$-fluorenes |
| 179 | 193 | 207 | 208 | $C_4$-acenaphthylenes, $C_3$-fluorenes |
| Group 6 | | | | |
| 177 | 178 | 191 | 192 | phenanthrene/anthracene, $C_1$-phenanthrenes/anthracenes |
| 177 | 191 | 205 | 206 | $C_2$-phenanthrenes/anthracenes |
| 191 | 205 | 219 | 220 | $C_3$-phenanthrenes/anthracenes |
| Group 7 | | | | |
| 201 | 202 | 215 | 216 | pyrene,[a] $C_1$-pyrenes |
| 201 | 215 | 229 | 230 | $C_2$-pyrenes |
| Group 8 | | | | |
| 227 | 228 | 241 | 242 | chrysene,[b] $C_1$-chrysenes |
| 227 | 241 | 255 | 256 | $C_2$-chrysenes |
| Group 9 | | | | |
| 57 | 99 | 83 | 97 | alkanes, alkenes |

[a] Also includes fluoranthenes, aceanthrylenes, acephenanthylenes

[b] Also includes tetracenes, triphenylenes, tetraphenes

well known, in packed-column GC, that the peak height (or area) does not fall off linearly with the concentration, but that, as the concentration becomes low, the peak height (or area) falls off precipitiously. When no peak is observed with the injection of a small amount of compound, we say that the compound was lost in the column. Actually, what is really happening is that the compound is tied up by adsorption sites in the liquid phase or support and elutes gradually from the column, possibly with a long tail. It is, therefore, lost in the baseline. (Actually, the same phenomenon occurs with larger quantities of compound injected on the column, but the effect is not noticeable because the perecentage loss is small.) With capillary columns, adsorption can be a severe problem, since the glass surface is quite large relative to the amount of compound passing through the column. Thus, at low concentrations, measurements of concentration tend to be too low.

Additionally, a second problem can arise with capillary columns. Since the liquid phase is small per unit volume, band spreading can occur when a compound saturates the liquid phase and codissolves additional compound. Typically, an overloaded capillary-column GC peak rises slowly, reaches a maximum and quickly goes back to baseline much like a sawtooth wave. Thus, at higher concentrations, concentration can not be accurately measured by peak height. On the other hand, normally, area measurements are not affected. However, there are saturation effects that take place in a GC/MS system. Table 2.4 shows an example of this. The on-column concentration of the 100-fold diluted DAF-effluent sample of 2-methyl naphthalene is approximately 170 ng based on a 60 ng standard. This turns out to be approximately 380

Table 2.4. Area Counts of 50-Fold and 100-Fold Diluted Samples for Some Compounds in the DAF Effluent

| Compound | Ion | DAF 50-Fold Dilution | DAF 100-Fold Dilution | Ratio of Area Counts |
|---|---|---|---|---|
| 2-Methyl naphthalene | 142 | 82889 | 64351 | 1.29 |
| Naphthalene | 128 | 68867 | 56201 | 1.23 |
| 1-Methyl naphthalene | 142 | 50633 | 37639 | 1.35 |
| p,m-Xylenes | 91 | 45806 | 29896 | 1.53 |
| o-Xylene | 91 | 27903 | 17283 | 1.61 |
| Ethyl benzene | 91 | 12637 | 7516 | 1.68 |

counts per nanogram. It would be expected that the area counts would double in each case for the 50-fold versus the 100-fold dilution. However, as can be seen in Table 2.4, the ratio is low for high counts and increases for lower counts. Thus, at high concentrations the measurements of concentration tends to be low.

With the measurement of concentration being too low, at both high concentration due to overload and low concentration due to adsorption on the column, it would seem desirable to make corrections for these effects. However, since the DAF, FC, MMF, and AC effluent samples contain so many compounds, such an approach would be cumbersome. Also, it would seem feasible to dilute the sample to measure the strong peaks and concentrate the sample to measure the weak peaks. However, this introduces a new set of variables. In any case, considerable effort would be expended in doing standards at various concentrations and looking for interactions.

There are many techniques used for making capillary columns and these varied techniques lead to columns that are different in their resolution and adsorption. In this study, three capillary columns were used: a Perkin-Elmer 50-m OV-101, a Perkin-Elmer 50-m OV-17, and a LKB 20-m SE-30. The intention was to use the non-polar 50-m OV-101 for the neutral fractions, the 50-m OV-17 for the acid and base fractions, and the 20-m SE-30 for the higher boiling neutral compounds such as the PNAs.

### 2.4.6 Sources of Error in Determination of the Absolute Amount of Organics in the DAF, FC, and AC Extracts and the Percent Removal of Organics by Activated Sludge and the Add-On Treatment System

It is well known that measurement of the specific amount of each component in a mixture by GC/MS is at best semi-quantitative; however, this study required some idea of the effectiveness of full and pilot-scale treatment systems in removing trace organics from the wastewater stream. In determining organics removal from GC/MS data there are several potential sources of error; a few will be cited here. First, there is the problem of extraction efficiency. It would be expected that, in those samples with high concentrations of organics, such as the DAF effluent, extraction efficiency would be relatively high ("like dissolves like"). Thus, in samples with low concentrations of organics, such as the AC effluent, extraction efficiency would be relatively low. Moreover, the extraction efficiency would vary from compound to compound depending upon the solvent used, the concentration of the component to be extracted, and the polarity of the component. Second, the amount of sample injected, in this case 3 μL, can vary from sample to sample. This variation is usually in the range of ± 3% for a 3 μL injection. Third, in splitless operation, a small portion of the sample, usually less than 1%, is lost during purge. A more difficult parameter to measure, in this regard, is whether any discrimination has taken place in this loss. Fourth, in preparing the DAF extract, it was necessary to dilute the sample 100-fold relative to the FC and AC extracts. Fifth, as mentioned previously, the measurement of concentration tends to be low at both high concentrations (due to overload) and at low concentrations (due to adsorption on the column). As a result, at very low concentrations, there is often no measurable signal, although a compound may have been injected onto the column. Sixth, there is a peculiarity in the mass spectrometer and data system that leads to inaccuracies. The data system makes a comparison of the shape of a peak of an ion with a theoretical quadrupole peak shape (non-Gaussian). If that peak is similar and above a certain threshold in area (to reject noise), parameters set by the user, the peak is accepted. Since a typical peak in a quadrupole or, for that matter, in a magnetic-sector instrument, is truly a mixture of pulses of ions concentrated around the centroid of the peak, noise, and other types of pulses can destroy the shape of the peak and, thereby, the peak is rejected. An example of this can be seen in Table 3.9 (Section 3) in the 142 ion column under "Activated Carbon Effluent" where one sees unexpected zeros in the data: 12, 27, 56, 69, 50, 0, 24, 9, etc. These occurrences lead to inaccuracies in the measurement of the area of such a peak. They occur most often with weak and/or high mass peaks.

Taking into consideration all these sources of error, it would appear difficult to obtain an accurate or absolute measurement of the amount of each component in the extracts and, indeed, this is the case. However, within any one sample or injection, it is possible to make comparisons of the amounts of the various components. Also, it is possible to make comparisons of percent removal by activated sludge (or the add-on treatment system) for different components within a mixture since it would be expected that the errors introduced are generally the same for all components within said mixture. That is, although the actual values for percent reduction of each compound in a mixture might be quite inaccurate, comparisons of percent removal of compounds within a group and also of groups of compounds can be made. For example, whereas the reported percent removal of n-alkanes and alkyl benzenes might be inaccurate in an absolute sense, the relative removal of n-alkanes might be reasonably precise. Likewise, whereas the reported percent removal of each member of a series of n-alkanes might be inaccurate in an absolute sense, the relative differences in percent removal could be reasonably precise. To carry out these comparisons and to uncover trends, it was found necessary to report more significant figures than is warranted considering the potential sources of error. For example, a percent reduction of n-decane of 99.98% does not mean that it is accurate to four significant figures or even three significant figures. However, it is useful to use such a number for comparison with other n-alkanes such as n-octadecane (99.54%) and n-pentacosane (99.36%) showing a trend of reducing percent removal as the carbon number increases. Likewise, it is useful for comparison with branched alkanes which range from 99.73% to 99.96%, as described in the next section.

## 2.5 DETERMINATION OF ANCILLARY PARAMETERS

Personnel from the SOHIO Research Center, Warrensville, Ohio, collected samples for determination of standard wastewater parameters at the same times and locations as were sampled by Argonne and RSKERL personnel for the trace organics study. The SOHIO samples were iced and transported by car from Toledo to Warrensville each morning. All analyses were started within 5 hr after the daily composited samples left Toledo.

The following standard wastewater parameters were determined according to U.S. EPA-recommended procedures (U.S. EPA, 1974): oil and grease, cyanide, phenol, chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total suspended solids (TSS). Total organic carbon (TOC) was determined according to an ASTM procedure (American Society for Testing and Materials).

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# 3 RESULTS

## 3.1 NEUTRAL-FRACTION ORGANIC COMPOUNDS

Appendix A lists 304 compounds identified in the neutral fraction of the DAF effluent. Only a very few of these compounds could be identified directly by their mass spectra. However, with the use of massgrams, the majority of compounds were identified. (In certain cases, the exact isomer was not determined.) Appendix D presents massgram plots and tentative identifications of organics found in a GC/MS run with a 50-m OV-101 column programmed from 20° to 240°C at 2°C/min, whose total-ion chromatogram is shown in Fig. 3.1. Appendix E presents mass spectra for various compounds in the neutral fraction of the DAF effluent, listed according to increasing retention time.

It can be seen (Appendix A) that the predominant types of compounds in the neutral fraction of the DAF effluent were n-alkanes, toluene, $C_2$, $C_3$ and $C_4$-benzenes, naphthalene, methyl naphthalenes and $C_2$-naphthalenes, phenanthrene, anthracene, and methyl phenanthrenes and anthracenes. These compounds were present in the DAF effluent at concentrations from approximately 10 ppb to 700 ppb.

Generally, there was substantial removal of organics by the activated sludge unit, no measurable removal by the add-on mixed-media filter unit, and varying removal, where measurable, of many organics by the add-on activated carbon unit. (For purposes of this study, it will be assumed that all of the removal of organics by the entire add-on pilot-scale unit was due to the activated carbon. Therefore, all results referred to as percent removals by activated carbon represent, in fact, organics removal by the entire add-on treatment system.)

Tables 3.1-3.7 list the major organics found in the neutral fraction of the DAF effluent. In Table 3.1, which is a listing of the n-alkanes, $C_9$ through $C_{31}$, it can be seen that there is very significant removal of organics by the activated sludge (in the range of 99.33%-99.98% removal) and a substantial additional removal of organics by the activated carbon (in the range of 70.2%-97.9%). It is interesting to note that percent removal is greatest for $C_{10}$ and falls off gradually as the carbon number increases. It appears that either the bacteria are more efficient in degrading lower alkanes or there is

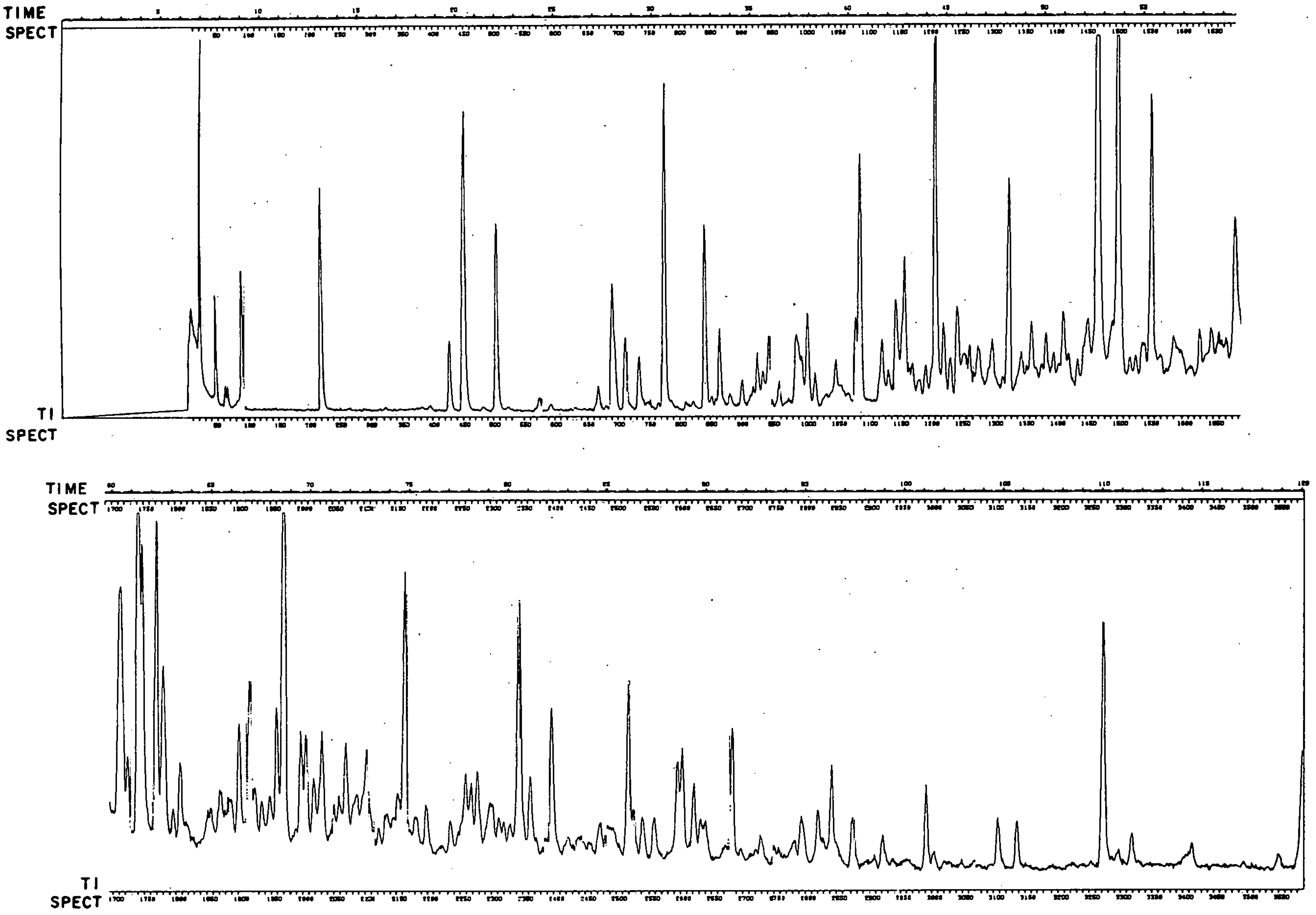

Fig. 3.1. Total-Ion Chromatogram of Neutral Fraction of DAF Effluent (Diluted 100-Fold) Made Using a 50-m OV-101 Column Programmed from 20-240°C with a 2-min Hold at 20°C.

wastage in sludge, or, possibly, there is considerable loss into the air of the lower alkanes due to their greater volatility. With the activated carbon, here again, there is a gradual decline in the percent removal as the carbon number increases. Apparently, the higher n-alkanes are less readily adsorbed onto the activated carbon. Possibly, as the size of the molecule increases, the molecule can not get into the pores of the activated carbon surface and is, therefore, less readily adsorbed.

In Table 3.2, branched alkanes are listed. Percent removals of these alkanes by the activated sludge and by the activated carbon, where measurable, are in the same range as the n-alkanes.

Cycloalkanes (or alkenes) are removed by the activated sludge in much the same way as the n-alkanes but none can be detected in the activated carbon effluent, possibly because of the low concentrations in the final-clarifier effluent.

The removal of alkylated benzenes (Table 3.3) by the activated sludge is drastic and ranges from 99.87-99.99%. Additional removal by activated carbon appears limited, ranging from 51.4-84.1%; however, data are scarce due to the low concentrations being measured. With indan and tetralin-type molecules, similar behavior is found (Table 3.4).

There is substantial reduction (99.69-99.99%) of naphthalene and alkylated naphthalenes by the activated sludge and varying reduction (37.7-91.7%) by the activated carbon (Table 3.5).

With alkylated benzothiophenes and dibenzothiophenes (Table 3.6), which were present in small quantities, the percent removal by the activated sludge was in the range of 99.81-99.93% and the percent removal by activated carbon was in the range of 71.4-82.9%.

With PNAs and alkylated PNAs (Table 3.7), the picture is not clear, since generally these compounds were present in very small quantities. Measurable removal figures for the activated sludge were in the 99.65-99.99% range and PNAs were not detectable in the activated-carbon effluent with the exception of phenanthrene and anthracene which were reduced 52.8% by the activated carbon.

The results in Tables 3.1-3.7 are summarized in Table 3.8. It can be seen by inspection of Table 3.8 that the percent removal by the activated

Table 3.1. Concentration of n-Alkanes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

| Compound | Concentration in DAF (ppb) | On-Column Concentration (ng)[a] | Percent Removal by Activated Sludge[b] | Percent Removal by Activated Carbon |
|---|---|---|---|---|
| n-nonane | 32 | 12 | NM | ND |
| n-decane | 128 | 48 | 99.98 | ND |
| n-undecane | 349 | 131 | 99.97 | T |
| n-dodecane | 544 | 204 | 99.83 | 97.9 |
| n-tridecane | 675 | 253 | 99.74 | 95.9 |
| n-tetradecane | 683 | 256 | 99.63 | 93.7 |
| n-pentadecane | 651 | 244 | 99.61 | 91.3 |
| n-hexadecane | 493 | 185 | 99.59 | 90.9 |
| n-heptadecane | 355 | 133 | 99.55 | 87.6 |
| n-octadecane | 261 | 98 | 99.54 | 86.9 |
| n-nonadecane | 205 | 77 | 99.55 | 88.4 |
| n-eicosane | 160 | 60 | 99.55 | 85.3 |
| n-heneicosane | 107 | 40 | 99.60 | 79.4 |
| n-docosane[c] | 64 | 24 | 99.40 | 80.3 |
| n-tricosane[c] | 61 | 23 | 99.55 | 82.6 |
| n-tetracosane[c] | 43 | 16 | 99.41 | 79.5 |
| n-pentacosane[c] | 32 | 12 | 99.36 | 70.2 |
| n-hexacosane[c] | 27 | 10 | 99.33 | 77.9 |
| n-heptacosane[c] | 19 | 7 | 99.43 | T |
| n-octacosane[c] | 13 | 5 | 99.36 | T |
| n-nonacosane[c] | 11 | 4 | NM | T |
| n-triacotane[c] | NM | NM | T | T |
| n-heneitriacotane[c] | NM | NM | T | T |

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of final-clarifier effluent.

[c] 20-m SE-30 column.

| | |
|---|---|
| T | Trace |
| NM | Not measurable due to interferences |
| ND | Not detectable |

Table 3.2. Concentration of Cycloalkanes and Alkanes Other than n-Alkanes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

| Compound (number) | Concentration in DAF (ppb) | On-Column Concentration (ng)[a] | Percent Removal by Activated Sludge[b] | Percent Removal by Activated Carbon |
|---|---|---|---|---|
| Alkanes | | | | |
| $C_{13}$-Alkane (97) | 159 | 60 | 99.92 | T |
| $C_{13}$-Alkane (117) | 77 | 29 | 99.94 | ND |
| $C_{14}$-Alkane (151) | 196 | 74 | 99.80 | T |
| $C_{14}$-Alkane (169) | 246 | 92 | 99.96 | 78.7 |
| Pristane | 157 | 59 | 99.73 | 78.1 |
| Phytane | 67 | 25 | 99.94 | 58.8 |
| Cycloalkanes[c] | | | | |
| (19) | 30 | 11 | 99.96 | ND |
| (21) | 21 | 8 | 99.94 | ND |
| (44) | 57 | 21 | NM | ND |
| (45) | 31 | 12 | 99.76 | ND |
| (49) | 41 | 15 | 99.98 | ND |
| (83) | 29 | 11 | 99.88 | ND |
| (86) | 27 | 10 | 99.86 | ND |
| (127) | 71 | 27 | 99.93 | ND |
| (129) | 42 | 16 | 99.95 | ND |
| (176) | 43 | 16 | 99.83 | ND |

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of final-clarifier effluent.

[c] Also includes alkenes.

| | |
|---|---|
| T | Trace |
| ND | Not detectable |
| NM | Not measurable due to interferences |

Table 3.3. Concentration of Alkylated Benzenes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

| Compound | Concentration in DAF (ppb) | On-Column Concentration (ng)[a] | Percent Removal by Activated Sludge[b] | Percent Removal by Activated Carbon |
|---|---|---|---|---|
| Toluene | 101 | 38 | 99.87 | 84.1 |
| Ethyl benzene | 35 | 13 | 99.95 | 66.7 |
| p and m-Xylenes | 187 | 70 | 99.97 | 76.6 |
| o-Xylene | 101 | 38 | 99.97 | 77.3 |
| i-Propyl benzene | 5 | 2 | ND | ND |
| n-Propyl benzene | 13 | 5 | 99.94 | T |
| m-Ethyl toluene | 93 | 35 | 99.98 | 71.2 |
| o-Ethyl toluene | 32 | 12 | 99.98 | T |
| 1,3,5-Trimethyl benzene | 43 | 16 | 99.97 | ND |
| 1,2,4-Trimethyl benzene | 176 | 66 | 99.98 | 44.9 |
| 1,2,3-Trimethyl benzene | 96 | 36 | 99.98 | 60.0 |
| n-Butyl benzene | 8 | 3 | T | ND |
| m-n-Propyl toluene | 19 | 7 | 99.97 | ND |
| o-n-Propyl toluene | 13 | 5 | 99.96 | ND |
| m-Diethyl benzene | 13 | 5 | T | ND |
| 1,3-Dimethyl-5-ethyl benzene | 29 | 11 | 99.98 | ND |
| 1,3-Dimethyl-4-ethyl benzene | 37 | 14 | 99.98 | ND |
| 1,2-Dimethyl-4-ethyl benzene | 43 | 16 | 99.99 | ND |
| 1,3-Dimethyl-2-ethyl benzene | 16 | 6 | ND | ND |
| 1,2-Dimethyl-3-ethyl benzene | 13 | 5 | T | ND |
| 1,2,4,5-Tetramethyl benzene | 27 | 10 | 99.98 | ND |
| 1,2,3,5-Tetramethyl benzene | 48 | 18 | 99.98 | T |
| 1,2,3,4-Tetramethyl benzene | 64 | 24 | 99.99 | 51.4 |

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of final clarifier effluent.

T Trace
ND Not detectable

Table 3.4. Concentration of Indan and Tetralin and Related Compounds and Their Alkylated Derivatives in the Neutral Fraction of the Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

| Compound (number) | Concentration in DAF (ppb) | On-Column Concentration (ng)[a] | Percent Removal by Activated Sludge[b] | Percent Removal by Activated Carbon |
|---|---|---|---|---|
| Indan | 93 | 35 | 99.98 | 50.0 |
| 1-methyl indan | 104 | 39 | 99.98 | T |
| 2-methyl indan | 61 | 23 | 99.99 | ND |
| Ethyl indan | 27 | 10 | T | ND |
| Dimethyl indan (100) | 61 | 23 | 99.98 | T |
| Dimethyl indan (106) | 11 | 4 | ND | ND |
| Dimethyl indan (111) | 35 | 13 | 99.97 | ND |
| Trimethyl indan (118) | 35 | 13 | T | ND |
| Tetralin | 11 | 4 | ND | ND |
| Methyl tetralin (104) | 64 | 24 | T | ND |
| Ethyl tetralin (126) | 27 | 10 | 99.93 | ND |
| Dimethyl tetralin (131) | 21 | 8 | T | ND |
| Ethyl styrene (39) | 19 | 7 | ND | ND |
| Ethyl styrene (41) | 48 | 18 | 99.98 | ND |
| $C_3$-Styrene (71) | 19 | 7 | T | ND |
| $C_3$-Styrene (72) | 72 | 27 | 99.99 | ND |
| $C_3$-Styrene (74) | 21 | 8 | 99.97 | ND |
| $C_3$-Styrene (77) | 53 | 20 | 99.99 | ND |

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of final clarifier effluent.

| | |
|---|---|
| T | Trace |
| ND | Not detectable |

Table 3.5. Concentration of Naphthalene and Alkylated Naphthalenes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

| Compound (number) | Concentration in DAF (ppb) | On-Column Concentration (ng)[a] | Percent Removal by Activated Sludge[b] | Percent Removal by Activated Carbon |
|---|---|---|---|---|
| Naphthalene | 197 | 74 | 99.99 | 37.7 |
| 1-Methyl naphthalene | 448 | 168 | 99.99 | 44.9 |
| 2-Methyl naphthalene | 259 | 97 | 99.99 | 33.3 |
| Ethyl naphthalene (146) | 77 | 29 | 99.98 | 55.8 |
| Dimethyl naphthalene (149) | 192 | 72 | 99.99 | 38.3 |
| Dimethyl naphthalene (153) | NM | NM | -- | -- |
| Dimethyl naphthalene (154) | 267 | 100 | 99.99 | 26.8 |
| Dimethyl naphthalene (155) | 203 | 76 | 99.99 | I |
| Dimethyl naphthalene (158) | 96 | 36 | 99.99 | 12.0 |
| Dimethyl naphthalene (160) | 45 | 17 | 99.94 | 37.5 |
| $C_3$-Naphthalene (166) | 24 | 9 | 99.74 | T |
| $C_3$-Naphthalene (168) | 21 | 8 | 99.69 | 87.7 |
| $C_3$-Naphthalene (172) | 160 | 60 | 99.91 | 91.7 |
| $C_3$-Naphthalene (173) | 45 | 17 | 99.76 | T |
| $C_3$-Naphthalene (174) | 37 | 14 | 99.90 | T |
| $C_3$-Naphthalene (175) | 51 | 19 | 99.95 | |
| $C_3$-Naphthalene (177) | 99 | 37 | 99.97 | 69.8 |
| $C_3$-Naphthalene (178) | 125 | 47 | 99.96 | 61.2 |
| $C_3$-Naphthalene (180) | 85 | 32 | 99.97 | 45.2 |
| $C_3$-Naphthalene (181) | 80 | 30 | 99.97 | T |
| $C_3$-Naphthalene (183) | 93 | 35 | 99.97 | T |

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of final clarifier effluent.

| | |
|---|---|
| NM | Not measurable due to interferences |
| T | Trace |
| I | Increase in concentration |

Table 3.6. Concentration of Alkylated Benzothiophenes and Dibenzothiophenes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

| Compound (number) | Concentration in DAF (ppb) | On-Column Concentration (ng)[a] | Percent Removal by Activated Sludge[b] | Percent Removal by Activated Carbon |
|---|---|---|---|---|
| Methyl benzothiophene (109) | 21 | 8 | T | ND |
| Methyl benzothiophene (114) | 16 | 6 | 99.91 | 71.4 |
| Methyl benzothiophene (119) | 13 | 5 | 99.87 | ND |
| Methyl benzothiophene (121) | 32 | 12 | 99.92 | 82.9 |
| Ethyl benzothiophene (156) | 11 | 4 | 99.85 | ND |
| Dimethyl benzothiophene (143) | 11 | 4 | 99.93 | ND |
| Dimethyl benzothiophene (148) | 16 | 6 | 99.91 | ND |
| Dimethyl benzothiophene (150) | 8 | 3 | 99.81 | ND |
| Dimethyl benzothiophene (152) | 8 | 3 | 99.83 | ND |
| Dibenzothiophene | 13 | 5 | T(N) | ND |

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of final clarifier effluent.

| | |
|---|---|
| T | Trace |
| N | Noisy, possibly due to column bleed |
| ND | Not detectable |

Table 3.7. PNAs and Alkylated PNAs Other than Naphthalenes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

| Compound (number) | Concentration in DAF (ppb) | On-Column Concentration (ng)[a] | Percent Removal by Activated Sludge[b] | Percent Removal by Activated Carbon |
|---|---|---|---|---|
| Phenanthrene/Anthracene | 168 | 63 | 99.97 | 52.8 |
| Methyl phenanthrene (250) | 72 | 27 | N | T |
| Methyl phenanthrene (251) | 80 | 30 | N | T |
| 1-Methyl anthracene | 27 | 10 | 99.98 | T |
| 2-Methyl anthracene | 27 | 10 | 99.99 | T |
| $C_2$-Phenanthrene/ Anthracene (262) | 5 | 2 | N | ND |
| $C_2$-Phenanthrene/ Anthracene (264) | 5 | 2 | N | ND |
| $C_2$-Phenanthrene/ Anthracene (265) | 16 | 6 | N | ND |
| $C_2$-Phenanthrene/ Anthracene (267) | 37 | 14 | N | ND |
| $C_2$-Phenanthrene/ Anthracene (268) | 40 | 15 | N | ND |
| $C_2$-Phenanthrene/ Anthracene (272) | 11 | 4 | N | ND |
| Fluorene | 27 | 10 | N | ND |
| Methyl fluorene (214) | 29 | 11 | 99.95 | ND |
| Methyl fluorene (216) | 35 | 13 | 99.93 | T |
| Methyl fluorene (218) | 16 | 6 | 99.91 | ND |
| Acenaphthene | 3 | 1 | I | ND |
| Methyl acenaphthene (186) | 35 | 13 | N | ND |
| Methyl acenaphthene (190) | 24 | 9 | N | ND |
| Methyl acenaphthene (193) | 16 | 6 | N | ND |
| Biphenyl | 24 | 9 | T(N) | T |
| Methyl biphenyl (164) | 19 | 7 | T(N) | ND |
| Methyl biphenyl (167) | 11 | 4 | T(N) | |
| Pyrene | 29 | 11 | 99.88 | 76.1 |
| $C_{17}H_{12}$ PNA (such as methyl pyrene) (287) | 11 | 4 | 99.67 | ND |
| Chrysene | 5 | 2 | 99.69 | ND |
| 1,2-Benzanthracene | 13 | 5 | 99.65 | ND |

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of the final clarifier effluent.

| | |
|---|---|
| N | Noisy, possibly due to unresolved interfering organics |
| T | Trace |
| ND | Not detectable |

Table 3.8. Comparison of Percent Removal by Activated-Sludge and Activated-Carbon Units for Various Classes of Organic Compounds

| Compound Class | Concentration Range in DAF Effluent (ppb) | Percent Removal Range by Activated-Sludge Unit | Average Percent Removal by Activated-Sludge Unit | Percent Removal Range by Activated-Carbon Unit | Average Percent Removal by Activated-Carbon Unit |
|---|---|---|---|---|---|
| Alkanes | 11-683 (27) | 99.33-99.98 | 99.65 (25) | 58.8-97.9 | 83.5 (18) |
| n-Alkanes | 11-683 (21) | 99.33-99.98 | 99.58 (19) | 70.2-97.9 | 85.9 (15) |
| Branched Alkanes | 67-246 (6) | 99.73-99.96 | 99.88 (6) | 58.8-78.7 | 71.9 (3) |
| Cycloalkanes | 21-71 (10) | 99.76-99.98 | 99.81 (10) | NM | NM |
| Alkylated Benzenes | 5-187 (23) | 99.94-99.99 | 99.97 (18) | 44.9-77.3 | 66.5 (8) |
| Toluene | 101 (1) | 99.87 | 99.87 (1) | 84.1 | 84.1 (1) |
| $C_2$-Benzenes | 35-187 (3) | 99.95-99.97 | 99.96 (3) | 66.7-77.3 | 73.5 (3) |
| $C_3$-Benzenes | 5-176 (7) | 99.94-99.98 | 99.97 (6) | 44.9-71.2 | 58.7 (3) |
| $C_4$-Benzenes | 8-64 (12) | 99.96-99.99 | 99.98 (8) | 51.4 | 51.4 (1) |
| Alkylated Indans, Tetralins | 11-104(18) | 99.93-99.99 | 99.98 (10) | 50.0 | 50.0 (1) |
| Alkylated Naphthalenes | 21-448 | 99.69-99.99 | 99.93 (20) | 12.0-69.8 | 49.4 (13) |
| Naphthalene | 197 | 99.99 | 99.99 (1) | 37.7 | 37.7 (1) |
| Methyl Naphthalenes | 259-448 | 99.99-99.99 | 99.99 (2) | 33.3-44.9 | 39.1 (2) |
| $C_2$-Naphthalenes | 45-267 | 99.94-99.98 | 99.98 (6) | 12.0-55.8 | 34.1 (5) |
| $C_3$-Naphthalenes | 21-160 | 99.69-99.97 | 99.89 (11) | 45.2-69.8 | 71.1 (5) |
| Alkylated Benzothiophenes & Dibenzothiophenes | 8-32 | 99.81-99.93 | 99.88 (8) | 71.4-82.9 | 77.1 (2) |
| Alkylated PNAs | 3-168 | 99.65-99.99 | 99.86 (10) | 52.8-76.1 | 64.5 (2) |

NM Not measurable
( ) Number of compounds

sludge of organics is greatest with aromatic compounds and relatively low with nonaromatic compounds. On the other hand, with activated carbon, greatest removal is with nonaromatic compounds. A striking example of this can be seen by looking at the raw data stored on disc (Table 3.9). In this table, the actual counts (or relative current generated by ions hitting the electron multiplier of the mass spectrometer) are recorded for 57, 97, and 142 AMUs for the final-clarifier effluent and the activated-carbon effluent. The 57 ion is typically used to look at alkanes, the 97 ion for cycloalkanes (and alkanes) and the 142 ion, here specifically for 2-methyl naphthalene (the first peak) and 1-methyl naphthalene (the second peak). The data are tabulated for successive scans and the 62 scans represent a little less than two minutes in the GC/MS run. It can be seen that the 142 peak for the final-clarifier fraction rises to 100 and then drops off and again rises to 55 and drops off, while in the activated-carbon fraction, the 142 ion rises to 69 and then drops off and again rises to 28 and drops off. One can visually inspect these data and see that there is only about a 30% removal for 2-methyl naphthalene and a 50% removal for 1-methyl naphthalene. Conversely, compared to the final clarifier, there are very large removals of alkanes (57) and cycloalkanes (97) by the activated carbon. In fact, looking at the raw data, one gets the impression that the activated carbon has adsorbed most of the organics and many of the organics that cannot be identified directly in the final clarifier because they are there in very small quantities. By adding up all the actual counts on the page, one can get a picture of what is happening. With ion 57, there are 15975 counts in the FC fraction and 449 counts in the AC fraction. This represents a "removal" of 97.2% of the 57 ion, presumably alkanes. With the 97 ion, there is a "removal" of 98.0%, representing cycloalkanes (and alkanes). These values are probably fairly representative of how effective the activated carbon is in removing organics. It seems to be relatively more effective in removing the nonaromatic compounds than aromatic compounds of the neutral fraction.

## 3.2 ACID-FRACTION ORGANIC COMPOUNDS

Over thirty phenols were found in the acid fraction of the DAF effluent. Also, several neutral compounds, which were present in large quantities in neutral fraction, were found in the acid fraction apparently due to incomplete separation during the extraction. A listing of compounds found in the

Table 3.9. Raw Data Output from GC/MS data System of 57, 97 and 142 ions Demonstrating the Pronounced Removal by the Activated Carbon of Alkanes (57 Ion) and Cycloalkanes (97 Ion) and Only Partial Removal of Methyl Naphthalenes (142 Ion)

| Spectrum No. | Final Clarifier Effluent (Neutral Fraction) | | | Activated Carbon Effluent (Neutral Fraction) | | |
|---|---|---|---|---|---|---|
| | Ion Counts/ 57 Ion | Ion Counts/ 97 Ion | Ion Counts/ 142 Ion | Ion Counts/ 57 Ion | Ion Counts/ 97 Ion | Ion Counts/ 142 Ion |
| 992 | 57- 110 | 97- 60 | 142- 0 | 57- 0 | 97- 0 | 142- 0 |
| 993 | 57- 130 | 97- 58 | 142- 0 | 57- 8 | 97- 0 | 142- 0 |
| 994 | 57- 139 | 97- 62 | 142- 0 | 57- 6 | 97- 0 | 142- 0 |
| 995 | 57- 132 | 97- 55 | 142- 0 | 57- 0 | 97- 0 | 142- 0 |
| 996 | 57- 131 | 97- 85 | 142- 0 | 57- 0 | 97- 0 | 142- 0 |
| 997 | 57- 221 | 97- 73 | 142- 11 | 57- 0 | 97- 0 | 142- 0 |
| 998 | 57- 375 | 97- 68 | 142- 0 | 57- 9 | 97- 0 | 142- 12 |
| 999 | 57- 543 | 97- 84 | 142- 29 | 57- 0 | 97- 0 | 142- 27 |
| 1000 | 57- 510 | 97- 98 | 142- 58 | 57- 0 | 97- 0 | 142- 56 |
| 1001 | 57- 350 | 97- 61 | 142- 100 | 57- 21 | 97- 0 | 142- 69 |
| 1002 | 57- 222 | 97- 54 | 142- 78 | 57- 11 | 97- 0 | 142- 50 |
| 1003 | 57- 147 | 97- 55 | 142- 99 | 57- 11 | 97- 0 | 142- 0 |
| 1004 | 57- 151 | 97- 75 | 142- 53 | 57- 19 | 97- 0 | 142- 24 |
| 1005 | 57- 131 | 97- 76 | 142- 45 | 57- 12 | 97- 0 | 142- 9 |
| 1006 | 57- 150 | 97- 89 | 142- 25 | 57- 0 | 97- 0 | 142- 14 |
| 1007 | 57- 128 | 97- 53 | 142- 27 | 57- 6 | 97- 10 | 142- 10 |
| 1008 | 57- 131 | 97- 62 | 142- 0 | 57- 0 | 97- 0 | 142- 0 |
| 1009 | 57- 98 | 97- 76 | 142- 0 | 57- 0 | 97- 0 | 142- 11 |
| 1010 | 57- 130 | 97- 77 | 142- 14 | 57- 0 | 97- 0 | 142- 6 |
| 1011 | 57- 188 | 97- 64 | 142- 0 | 57- 0 | 97- 7 | 142- 0 |
| 1012 | 57- 366 | 97- 58 | 142- 0 | 57- 0 | 97- 0 | 142- 0 |
| 1013 | 57- 602 | 97- 71 | 142- 0 | 57- 0 | 97- 0 | 142- 0 |
| 1014 | 57- 508 | 97- 81 | 142- 0 | 57- 0 | 97- 0 | 142- 0 |
| 1015 | 57- 293 | 97- 70 | 142- 0 | 57- 9 | 97- 0 | 142- 0 |
| 1016 | 57- 155 | 97- 79 | 142- 0 | 57- 21 | 97- 0 | 142- 7 |
| 1017 | 57- 90 | 97- 77 | 142- 0 | 57- 10 | 97- 0 | 142- 0 |
| 1018 | 57- 128 | 97- 81 | 142- 0 | 57- 0 | 97- 6 | 142- 0 |
| 1019 | 57- 163 | 97- 55 | 142- 0 | 57- 0 | 97- 0 | 142- 0 |
| 1020 | 57- 186 | 97- 72 | 142- 0 | 57- 0 | 97- 0 | 142- 0 |
| 1021 | 57- 245 | 97- 62 | 142- 0 | 57- 0 | 97- 0 | 142- 0 |
| 1022 | 57- 600 | 97- 88 | 142- 0 | 57- 14 | 97- 0 | 142- 0 |
| 1023 | 57- 1314 | 97- 109 | 142- 0 | 57- 8 | 97- 0 | 142- 0 |
| 1024 | 57- 1654 | 97- 120 | 142- 0 | 57- 18 | 97- 9 | 142- 0 |
| 1025 | 57- 1123 | 97- 96 | 142- 0 | 57- 35 | 97- 9 | 142- 0 |
| 1026 | 57- 382 | 97- 54 | 142- 0 | 57- 37 | 97- 0 | 142- 0 |
| 1027 | 57- 156 | 97- 55 | 142- 0 | 57- 33 | 97- 6 | 142- 0 |
| 1028 | 57- 164 | 97- 49 | 142- 0 | 57- 21 | 97- 0 | 142- 0 |
| 1029 | 57- 222 | 97- 54 | 142- 0 | 57- 18 | 97- 0 | 142- 0 |
| 1030 | 57- 232 | 97- 54 | 142- 0 | 57- 7 | 97- 0 | 142- 15 |
| 1031 | 57- 148 | 97- 48 | 142- 22 | 57- 7 | 97- 0 | 142- 13 |
| 1032 | 57- 142 | 97- 58 | 142- 28 | 57- 7 | 97- 0 | 142- 44 |
| 1033 | 57- 152 | 97- 56 | 142- 45 | 57- 11 | 97- 0 | 142- 28 |
| 1034 | 57- 167 | 97- 71 | 142- 55 | 57- 8 | 97- 7 | 142- 0 |
| 1035 | 57- 183 | 97- 72 | 142- 52 | 57- 0 | 97- 0 | 142- 18 |
| 1036 | 57- 256 | 97- 84 | 142- 21 | 57- 12 | 97- 0 | 142- 18 |
| 1037 | 57- 271 | 97- 87 | 142- 19 | 57- 10 | 97- 0 | 142- 16 |
| 1038 | 57- 232 | 97- 75 | 142- 18 | 57- 8 | 97- 0 | 142- 0 |
| 1039 | 57- 159 | 97- 62 | 142- 21 | 57- 6 | 97- 0 | 142- 0 |
| 1040 | 57- 172 | 97- 0 | 142- 0 | 57- 8 | 97- 0 | 142- 0 |
| 1041 | 57- 110 | 97- 87 | 142- 0 | 57- 0 | 97- 0 | 142- 7 |
| 1042 | 57- 132 | 97- 98 | 142- 0 | 57- 10 | 97- 0 | 142- 0 |
| 1043 | 57- 127 | 97- 114 | 142- 0 | 57- 9 | 97- 6 | 142- 0 |
| 1044 | 57- 157 | 97- 147 | 142- 0 | 57- 12 | 97- 0 | 142- 0 |
| 1045 | 57- 183 | 97- 207 | 142- 0 | 57- 0 | 97- 10 | 142- 0 |
| 1046 | 57- 181 | 97- 251 | 142- 15 | 57- 7 | 97- 0 | 142- 0 |
| 1047 | 57- 208 | 97- 148 | 142- 0 | 57- 0 | 97- 8 | 142- 0 |
| 1048 | 57- 145 | 97- 102 | 142- 0 | 57- 0 | 97- 8 | 142- 0 |
| 1049 | 57- 97 | 97- 86 | 142- 0 | 57- 0 | 97- 9 | 142- 0 |
| 1050 | 57- 143 | 97- 97 | 142- 0 | 57- 6 | 97- 0 | 142- 0 |

acid fraction of the DAF effluent can be found in Appendix B. It can be seen that, along with phenol itself, there are cresols, xylenols, ethyl phenols, $C_3$-phenols, $C_4$-phenols, and an unidentified plasticizer. The predominant phenols are phenol, the cresols, an unidentified xylenol, and 2,3-xylenol.

In Table 3.10, the approximate concentration in the acid fraction of the DAF effluent of these phenols is listed, along with percent removal by the activated sludge and activated carbon. The range of concentration in the DAF effluent is from below 1 ppb to about 50 ppb. Because of the extremely low concentrations of these phenols, it was difficult to find any phenols in the final-clarifier or activated-carbon effluents. Removal by activated sludge for three alkylated phenols was in the range of 99.89-99.98%. Most likely, the other phenols were practically completely degraded by the activated sludge. This is not unexpected, since phenols are oxidized readily not only by bacteria but also by oxygen, which was continuously fed into the activated-sludge unit. No evidence of the intermediates, such as quinones, was found in the neutral fraction of the final-clarifier effluent. With the great efficiency of removal of phenols by the activated-sludge unit, it was, of course, impossible to find any trace of phenols in the activated-carbon effluent. Thus, a measurement of percent removal by the activated carbon was not possible.

## 3.3 BASE-FRACTION ORGANIC COMPOUNDS

Over 70 compounds were found in the base fraction of the DAF effluent (Appendix C), several of which were not organic bases. Extraneous organics included those compounds present in large quantities in the neutral fraction of the DAF effluent, which apparently were not separated completely in the extraction process. In addition, there were considerable quantities of phenol and alkylated phenols such as cresols, ethyl phenol, and xylenols. These compounds probably formed acid salts with many of the organic bases present in the DAF effluent and were carried into the base fraction during extraction. This salt formation can sometimes cause problems during a GC/MS run. If the salts decompose during standing, or in the hot injection port, the retention time is not altered. If, however, decomposition takes place on the column or in the transfer line to the mass spectrometer, results are unpredictable.

Table 3.10. Phenols in the Acid Fraction of the DAF Effluent and Percent Removal by the Activated Sludge and Activated Carbon Units (50-m OV-17 Column, 3 μL Injection)

| Compound (Number) | Concentration in DAF (ppb) | On Column Concentration (ng)[a] | Percent Removal by Activated Sludge[b] | Percent Removal by Activated Carbon |
|---|---|---|---|---|
| Phenol | 22 | 83 | ND | ND |
| Cresol (2) | 33 | 124 | 99.98 | NM |
| p-Cresol | 50 | 186 | ND | ND |
| Ethyl phenol (6) | 4 | 16 | ND | ND |
| Ethyl phenol (10) | 7 | 26 | ND | ND |
| Dimethyl phenol (7) | 29 | 109 | ND | ND |
| 2,3-Dimethyl phenol (9) | 16 | 61 | 99.98 | ND |
| Dimethyl phenol (13) | 8 | 30 | ND | ND |
| n-Propyl phenol (11) | 1 | 5 | ND | ND |
| i-Propyl phenol (5) | 2 | 8 | ND | ND |
| i-Propyl phenol (12) | 4 | 15 | ND | ND |
| i-Propyl phenol (14) | 10 | 37 | ND | ND |
| i-Propyl phenol (15) | 1 | 3 | ND | ND |
| i-Propyl phenol (16) | 1 | 4 | ND | ND |
| n-Propyl phenol & methyl ethyl phenol (19,20) | 4 | 16 | ND | ND |
| n-Propyl phenol & methyl ethyl phenol (22,23) | <1 | 1 | ND | ND |
| Methyl ethyl phenol (17) | 2 | 9 | ND | ND |
| Methyl ethyl phenol (18) | 3 | 12 | ND | ND |
| 2,4,5-Trimethyl phenol | 3 | 10 | 99.89 | ND |
| Methyl ethyl phenol & $C_4$-phenol (24,25) | 1 | 4 | ND | ND |
| Methyl ethyl phenol & $C_4$-phenol (27,28) | <1 | 2 | ND | ND |
| $C_3$ and $C_4$-phenol (31,32) | 1 | 3 | ND | ND |
| $C_3$ and $C_4$-phenol (34,35) | 1 | 3 | ND | ND |
| Diethyl phenol (21) | 1 | 3 | ND | ND |
| Diethyl phenol (36) | <1 | 2 | ND | ND |

[a] Acid DAF fraction diluted 10 times.

[b] Acid fraction of the final clarifier effluent.

ND Not detectable
NM Not measurable

It was found that there was a variety of very small amounts of alkylated pyridines such as picolines, ethyl pyridines, lutidines, ethyl picolines, collidines, and ethyl lutidines and small amounts of alkylated quinolines, $C_1$, $C_2$, and $C_3$'s, and appreciable quantities of aniline and alkylated anilines (Tables 3.11, 3.12, 3.13). Although a few isolated values for percent removals by the activated-sludge and the activated-carbon units have been reported, because of the small quantities involved, not much confidence should be placed in the values. It can be said, however, that the activated sludge does reduce the amount of organic bases, but little can be said about the degree of removal.

## 3.4 TREATMENT-SYSTEM PERFORMANCE DATA

Performance of the full-scale biosystem and the add-on filtration/carbon train for the common wastewater parameters is shown in Tables 3.14 and 3.15, from Pfeffer, Harrison, and Raphaelian (1977). Some values are reported as less-than (<), reflecting lower limits of detectability as a function of the sampling and analytical protocol.

During the study, refinery crude oil throughput was 115,641 BPSD, the water inlet rate from Maumee Bay was 47.3 MGD, and the wastewater-treatment-plant throughput was 8.6 MGD. There were no significant recorded changes in flow through the plant wastewater treatment system, as measured by the biofeed pumping rates (that is, the wastewater influent to the aeration basin). Note that, waste sludge being insignificant, the final-clarifier effluent and biofeed flows were assumed to be equal. Aeration time was of the order of 16-18 hours and mixed-liquor volatile suspended solids concentration in the aeration basin was 4440 mg/L, during the study. Water temperature in the aeration zone averaged 76°F and settleable solids averaged 35% in the aeration zone and 95% on the clarifier recycle.

Table 3.11. Alkylated Pyridines in the Base Fraction of the DAF Effluent and Percent Removal by Activated Sludge and Activated Carbon Units (50-m OV-17 Column, 3 μL Injection)

| Compound (Number) | Concentration in DAF (ppb) | On Column Concentration (ng)[a] | Percent Removal by Activated Sludge[b] | Percent Removal by Activated Carbon |
|---|---|---|---|---|
| Picoline (1) | <1 | 2 | - | - |
| Ethyl pyridine (5) | <1 | 2 | ND | ND |
| 4-Ethyl pyridine (8) | <1 | 2 | 92.6 | ND |
| Lutidine (4) | <1 | 2 | ND | T |
| Lutidine (7) | 2 | 9 | 97.6 | ND |
| Ethyl picoline (9) | NM | NM | NM | ND |
| 2-Ethyl picoline (17) | 1 | 4 | ND | ND |
| Ethyl picoline (36) | 6 | 24 | ND | ND |
| 2,4,6-Collidine (14) | 2 | 8 | ND | ND |
| 2,3,6-Collidine (16) | <1 | 2 | ND | ND |
| 2,3,5-Collidine (18) | <1 | 1 | ND | ND |
| Collidine (28) | <1 | 2 | 67.0 | 99.6 |
| Collidine (38) | 2 | 9 | ND | ND |
| $C_3$-Pyridine (27) | <1 | 2 | ND | ND |
| $C_3$-Pyridine (29) | <1 | 1 | ND | ND |
| Ethyl lutidine (20) | 1 | 4 | ND | ND |
| Ethyl lutidine (22) | <1 | 1 | ND | ND |
| Ethyl lutidine (24) | 1 | 4 | ND | ND |
| Ethyl lutidine (26) | <1 | <1 | ND | ND |
| Ethyl lutidine (49) | <1 | 2 | ND | ND |

[a] Base DAF fraction diluted 10 times.

[b] Base fraction of the final clarifier effluent.

NM Not measurable due to interferences
ND Not detectable
T Trace

Table 3.12. Alkylated Quinolines in the Base Fraction of the DAF Effluent and Percent Removal by Activated Sludge and Activated Carbon Units (50-m OV-17 Column, 3 μL Injection)

| Compound (Number) | Concentration in DAF (ppb) | On Column Concentration (ng)[a] | Percent Removal by Activated Sludge[b] | Percent Removal by Activated Carbon |
|---|---|---|---|---|
| Quinoline (45) | 6 | 23 | ND | ND |
| Methyl quinoline (50) | 4 | 16 | ND | ND |
| Methyl quinoline (51) | 1 | 4 | ND | ND |
| Methyl quinoline (52) | <1 | 2 | ND | ND |
| Methyl quinoline (54) | <1 | 2 | 85.1 | ND |
| Methyl quinoline (56) | 2 | 8 | ND | ND |
| Methyl quinoline (58) | 1 | 4 | ND | ND |
| Ethyl quinoline (55) | <1 | 2 | ND | ND |
| Dimethyl quinoline (62) | 2 | 6 | 93.6 | 88.9 |
| Dimethyl quinoline (63) | 1 | 4 | ND | ND |
| Dimethyl quinoline (65) | 2 | 6 | ND | ND |
| Dimethyl quinoline (67) | <1 | 2 | ND | ND |
| Dimethyl quinoline (68) | 2 | 6 | 91.9 | ND |
| Dimethyl quinoline (69) | 1 | 4 | ND | ND |
| $C_3$-Quinoline (71) | 2 | 6 | 96.8 | ND |
| $C_3$-Quinoline (72) | 2 | 6 | 96.7 | ND |

[a] Base DAF fraction diluted 10 times.

[b] Base fraction of the final clarifier effluent.

ND Not detectable

Table 3.13. Alkylated Anilines in Base Fraction of the DAF Effluent and Percent Removal by Activated Sludge and Activated Carbon Units (50-m OV 17 Column, 3 μL Injection)

| Compound (Number) | Concentration in DAF (ppb) | On Column Concentration (ng)[a] | Percent Removal by Activated Sludge[b] | Percent Removal by Activated Carbon |
|---|---|---|---|---|
| Aniline (23) | 27 | 101 | 99.5 | T |
| o-Toluidine (31) | 29 | 109 | NM | ND |
| Toluidine (33) | 10 | 38 | NM | ND |
| N,N-Dimethyl aniline (25) | <1 | 2 | 88.6 | ND |

[a] Base DAF fraction diluted 100 times.

[b] Base fraction of the final clarifier effluent.

T Trace
ND Not detectable
NM Not measurable due to interferences

Table 3.14. Daily Performance for Common Wastewater Parameters[a]

| | mg/L Intake | | | | mg/L DAF Effluent | | | | mg/L FC Effluent | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Day 1 | Day 2 | Day 3 | Day 4 | Day 1 | Day 2 | Day 3 | Day 4 | Day 1 | Day 2 | Day 3 | Day 4 |
| Oil and Grease | <10 | <10 | <10 | 10 | 22 | 33 | 21 | 22 | <10 | <10 | <10 | <10 |
| Cyanide | <0.02 | <0.02 | <0.02 | <0.02 | 0.19 | 0.25 | 0.31 | -- | 0.16 | 0.12 | 0.20 | 0.10 |
| Phenol | 0.03 | <0.01 | 0.03 | 0.01 | 3.2 | 2.6 | 5.2 | 4.5 | 0.02 | 0.01 | 0.04 | 0.02 |
| COD | <15 | 18 | <15 | <15 | 122 | 172 | 154 | 154 | 49 | 50 | 51 | 44 |
| BOD | <10 | <10 | 14 | 10 | 82 | 127 | 108 | 96 | <10 | 15 | 21 | 24 |
| TOC | 19 | 19 | 17 | 15 | 39 | 56 | 72 | 60 | 22 | 29 | 27 | 17 |
| TSS | 35 | 29 | 11 | <10 | 31 | 56 | 37 | 30 | 12 | <10 | <10 | <10 |

| | mg/L MMF Effluent | | | | mg/L AC Effluent | | | |
|---|---|---|---|---|---|---|---|---|
| | Day 1 | Day 2 | Day 3 | Day 4 | Day 1 | Day 2 | Day 3 | Day 4 |
| Oil and Grease | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Cyanide | 0.16 | 0.15 | 0.20 | 0.10 | <0.02 | <0.02 | <0.02 | <0.02 |
| Phenol | 0.02 | 0.01 | 0.02 | 0.02 | <0.01 | <0.01 | <0.01 | <0.01 |
| COD | 42 | 38 | 51 | 44 | <15 | <15 | <15 | <15 |
| BOD | <10 | 11 | 22 | 27 | <10 | <10 | <10 | <10 |
| TOC | 19 | 26 | 23 | 18 | 10 | 12 | 11 | <5 |
| TSS | <10 | <10 | 12 | 12 | <10 | <10 | <10 | <10 |

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[a] The data of this table were provided by SOHIO's Warrensville, Ohio, Research Center. Rodger McKain (Study Leader), Robert Munko, David Rulison, and Jeffery Smola determined the parameters.

Table 3.15. Average Performance over 4-Day Study Period for Common Wastewater Parameters

| | mg/L Intake | mg/L DAF | mg/L FC | mg/L MMF | mg/L AC |
|---|---|---|---|---|---|
| Oil & Grease | <10 | 24 | <10 | <10 | <10 |
| Cyanide | <0.02 | 0.25 | 0.14 | 0.15 | <0.02 |
| Phenol | 0.02 | 3.9 | 0.02 | 0.02 | <0.01 |
| COD | <15 | 150 | 48 | 44 | <15 |
| BOD | <10 | 103 | 17 | 17 | <10 |
| TOC | 18 | 57 | 24 | 22 | 9 |
| TSS | 21 | 38 | <10 | <10 | <10 |

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# APPENDIX A

## Organic Compounds Found in Neutral Fraction of the Effluent from the Dissolved Air Flotation (DAF) Unit and Their Presence or Absence in the Effluents from the final Clarifier (FC)

| Compound Number | Retention Time (Min) | Compound Name | Relative Concentration in DAF Neutral Fraction | Presence(+), Absence(-) (FC Effluent) | Presence(+), Absence(-) (MMF/AC Effluent) |
|---|---|---|---|---|---|
| 1 | 7.0 | chloroform | high | + | + |
| 2 | 7.8 | 1,1,1-trichloroethane | high | + | + |
| 3 | 8.3 | benzene | medium | + | + |
| 4 | 8.4 | carbon tetrachloride | medium | + | + |
| 5 | 9.1 | cyclohexene | high | + | + |
| 6 | 13.1 | toluene | high | + | + |
| 7 | 19.7 | ethyl benzene | low | + | + |
| 8 | 20.4 | p-xylene | high | + | + |
| 9 | 20.4 | m-xylene | high | + | + |
| 10 | 22.1 | o-xylene | medium | + | + |
| 11 | 24.3 | n-nonane | low | + | - |
| 12 | 24.9 | i-propyl benzene | trace | + | - |
| 13 | 27.3 | n-propyl benzene | low | + | - |
| 14 | 28.0 | m-ethyl toluene | medium | + | - |
| 15 | 28.2 | p-ethyl toluene | medium | + | - |
| 16 | 28.7 | 1,3,5-trimethyl benzene | low | + | - |
| 17 | 29.4 | o-ethyl toluene | low | + | T |
| 18 | 30.65 | 1,2,4-trimethyl benzene | high | + | + |
| 19 | 30.8 | cycloalkane | low | + | - |
| 20 | 31.0 | cycloalkane | trace | T | - |
| 21 | 31.75 | cycloalkane | low | + | - |
| 22 | 31.9 | i-butyl benzene | trace | + | - |
| 23 | 32.05 | s-butyl benzene | trace | + | - |
| 24 | 32.65 | n-decane | medium | + | - |
| 25 | 32.7 | 1,2,3-trimethyl benzene | medium | + | + |
| 26 | 33.0 | m-isopropyl toluene | trace | T | |
| 27 | 33.3 | o-isopropyl toluene | trace | - | - |
| 28 | 33.3 | p-isopropyl toluene | trace | - | - |
| 29 | 33.4 | indan | medium | + | + |
| 30 | 33.6 | | trace | | |
| 31 | 33.95 | indene | trace | + | - |
| 32 | 35.1 | m-diethyl benzene | low | T | - |
| 33 | 35.35 | m-n-propyl toluene | low | + | - |
| 34 | 35.65 | p-n-propyl toluene | low | + | - |
| 35 | 35.7 | n-butyl benzene | trace | T | - |
| 36 | 35.9 | 1,3-dimethyl-5-ethyl benzene | low | + | |
| 37 | 36.4 | o-n-propyl toluene | low | + | - |
| 38 | 37.25 | 1,4-dimethyl-2-ethyl benzene | low | NM | NM |
| 39 | 37.25 | ethyl styrene | low | - | - |
| 40 | 37.4 | 1,3-dimethyl-4-ethyl benzene | low | + | - |
| 41 | 37.6 | ethyl styrene | medium | + | - |
| 42 | 37.9 | 1,2-dimethyl-4-ethyl benzene | low | + | - |

| Compound Number | Retention Time (Min) | Compound Name | Relative Concentration in DAF Neutral Fraction | Presence Absence(-) (FC Effluent) | Presence(+), Absence(-) (MMF/AC Effluent) |
|---|---|---|---|---|---|
| 43 | 38.25 | 1,3-dimethyl-2-ethyl benzene | low | - | - |
| 44 | 38.85 | cycloalkane | low | + | - |
| 45 | 39.1 | cycloalkane | low | + | - |
| 46 | 39.3 | 1,2-dimethyl-3-ethyl benzene | low | T | - |
| 47 | 39.3 | $C_5$-benzene | trace | NM | NM |
| 48 | 39.5 | $C_5$-benzene | trace | - | - |
| 49 | 39.7 | cycloalkane | low | + | - |
| 50 | 40.0 | $C_5$-benzene | trace | - | - |
| 51 | 40.35 | 1,2,4,5-tetramethyl benzene | low | + | - |
| 52 | 40.4 | $C_5$-benzene | trace | - | - |
| 53 | 40.6 | 1,2,3,5-tetramethyl benzene | medium | + | + |
| 54 | 40.6 | n-undecane | high | + | - |
| 55 | 40.85 | $C_5$-benzene | trace | NM | NM |
| 56 | 41.7 | 2-methyl indan | medium | T | 0 |
| 57 | 42.0 | $C_5$-benzene | trace | - | - |
| 58 | 42.35 | 1-methyl indan | medium | + | - |
| 59 | 42.5 | $C_5$-benzene | trace | - | - |
| 60 | 42.7 | $C_5$-benzene | trace | + | - |
| 61 | 42.9 | 1,2,3,4-tetramethyl benzene | medium | + | - |
| 62 | 43.05 | tetralin | low | - | - |
| 63 | 43.25 | $C_5$-benzene | trace | + | - |
| 64 | 43.6 | $C_5$-benzene | trace | + | - |
| 65 | 43.9 | $C_5$-benzene | trace | - | - |
| 66 | 44.2 | $C_5$-benzene | trace | + | - |
| 67 | 44.3 | $C_5$-benzene | trace | - | - |
| 68 | 44.45 | naphthalene | high | + | + |
| 69 | 44.8 | $C_5$-benzene | low | + | - |
| 70 | 44.9 | $C_6$-benzene | trace | + | - |
| 71 | 45.1 | $C_3$-styrene | low | - | - |
| 72 | 45.55 | $C_3$-styrene | medium | + | - |
| 73 | 45.6 | $C_6$-benzene | trace |  | - |
| 74 | 45.75 | $C_3$-styrene | low | + | - |
| 75 | 46.0 | $C_5$-benzene | trace | T | T |
| 76 | 46.05 | $C_6$-benzene | trace | T | - |
| 77 | 46.2 | $C_3$-styrene | medium | T | - |
| 78 | 46.35 | $C_6$-benzene | trace | + | - |
| 79 | 46.4 |  | trace | - | - |
| 80 | 46.6 | $C_5$-benzene | trace | - | - |
| 81 | 46.7 | cycloalkane | trace | + | = |
| 82 | 46.8 |  | trace | - | - |
| 83 | 47.0 | cycloalkane | low | + | - |
| 84 | 47.2 | $C_6$-benzene | trace | - | - |
| 85 | 47.3 | $C_5$-benzene | trace | - | - |

| Compound Number | Retention Time (Min) | Compound Name | Relative Concentration in DAF Neutral Fraction | Presence(+), Absence(-) (FC Effluent) | Presence(+), Absence(-) (MMF/AC Effluent) |
|---|---|---|---|---|---|
| 86 | 47.4 | cycloalkane | low | + | - |
| 87 | 47.45 | | trace | - | - |
| 88 | 47.8 | $C_5$-benzene | low | + | - |
| 89 | 47.8 | $C_6$-benzene | trace | + | - |
| 90 | 48.1 | $C_6$ benzene | trace | + | - |
| 91 | 48.2 | n-dodecane | high | + | + |
| 92 | 48.4 | | trace | - | - |
| 93 | 48.6 | $C_6$-benzene | trace | + | - |
| 94 | 48.7 | ethyl indan | low | - | - |
| 95 | 48.85 | $C_6$-benzene | trace | T | - |
| 96 | 49.05 | $C_5$-benzene | trace | T | - |
| 97 | 49.3 | $C_{13}$-alkane | high | + | - |
| 98 | 49.4 | | trace | - | - |
| 99 | 49.7 | | trace | - | - |
| 100 | 50.0 | dimethyl indan | medium | T | T |
| 101 | 50.1 | $C_6$-benzene | trace | - | - |
| 102 | 50.3 | | trace | - | - |
| 103 | 50.5 | $C_6$-benzene | trace | - | - |
| 104 | 50.85 | methyl tetralin | medium | T | - |
| 105 | 51.1 | $C_6$-benzene | trace | T | - |
| 106 | 51.2 | dimethyl indan | low | - | - |
| 107 | 51.6 | $C_6$-benzene | trace | - | - |
| 108 | 51.85 | $C_3$-indan | trace | - | - |
| 109 | 51.9 | methyl benzothiophene | low | + | - |
| 110 | 52.0 | $C_6$-benzene | trace | - | - |
| 111 | 52.15 | dimethyl indan | low | + | - |
| 112 | 52.2 | methyl ethyl indan | trace | - | - |
| 113 | 52.35 | $C_6$-benzene | trace | - | - |
| 114 | 52.45 | methyl benzothiophene | low | + | + |
| 115 | 52.55 | | trace | - | - |
| 116 | 52.7 | 2-methyl naphthalene | high | + | + |
| 117 | 52.8 | $C_{13}$-alkane | medium | + | - |
| 118 | 52.85 | trimethyl indan | trace | - | - |
| 119 | 53.0 | methyl benzothiophene | low | + | - |
| 120 | 53.1 | trimethyl indan | trace | - | - |
| 121 | 53.35 | methyl benzothiophene | low | + | T |
| 122 | 53.4 | trimethyl indan | trace | - | - |
| 123 | 53.4 | $C_6$-benzene | trace | - | - |
| 124 | 53.65 | $C_4$-indan/$C_3$-tetralin | trace | - | - |
| 125 | 53.7 | 1-methyl naphthalene | high | + | + |
| 126 | 53.8 | ethyl tetralin | low | + | - |
| 127 | 54.2 | cycloalkane | medium | + | - |
| 128 | 54.3 | $C_4$-indian/$C_3$-tetralin | trace | + | - |

| Compound Number | Retention Time (Min) | Compound Name | Relative Concentration in DAF Neutral Fraction | Presence(+), Absence(-) (FC Effluent) | Presence(+), Absence(-) (MMF/AC Effluent) |
|---|---|---|---|---|---|
| 129 | 54.55 | cycloalkane | low | + | - |
| 130 | 54.55 | ethyl tetralin | trace | NM | - |
| 131 | 54.95 | dimethyl tetralin | low | T | - |
| 132 | 55.05 | $C_4$-indan/$C_3$-tetralin | trace | T | - |
| 133 | 55.2 | $C_6$-benzene | trace | - | - |
| 134 | 55.4 | n-tridecane | high | + | + |
| 135 | 55.45 | | trace | + | - |
| 136 | 55.55 | $C_4$-indan/$C_3$-tetralin | trace | + | - |
| 137 | 56.4 | $C_4$-indan/$C_3$-tetralin | trace | - | - |
| 138 | 56.85 | $C_4$-indan/$C_3$-tetralin | trace | - | - |
| 139 | 57.6 | $C_4$-indan/$C_3$-tetralin | trace | - | - |
| 140 | 58.15 | $C_4$-indan/$C_3$-tetralin | low | - | - |
| 141 | 58.35 | biphenyl | low | + | T |
| 142 | 58.95 | $C_4$-indan/$C_3$-tetralin | trace | - | - |
| 143 | 59.1 | dimethyl benzothiophene | trace | + | - |
| 144 | 59.4 | ethyl benzothiophene | trace | + | - |
| 145 | 59.55 | dimethyl benzothiophene | trace | NM | - |
| 146 | 59.55 | ethyl naphthalene | medium | + | + |
| 147 | 59.95 | | trace | + | - |
| 148 | 60.05 | dimethyl benzothiophene | low | + | - |
| 149 | 60.4 | dimethyl naphthalene | high | + | + |
| 150 | 60.6 | dimethyl benzothiophene | trace | + | - |
| 151 | 60.75 | $C_{14}$-alkane | high | + | + |
| 152 | 61.1 | dimethyl benzothiophene | trace | + | - |
| 153 | 61.15 | dimethyl naphthalene | medium | NM | + |
| 154 | 61.3 | dimethyl naphthalene | high | + | + |
| 155 | 61.5 | dimethyl naphthalene | high | + | + |
| 156 | 61.6 | ethyl benzothiophene | trace | + | - |
| 157 | 62.25 | n-tetradecane | high | + | + |
| 158 | 62.55 | dimethyl naphthalene | medium | + | + |
| 159 | 63.0 | | low | - | - |
| 160 | 63.4 | dimethyl naphthalene | low | + | + |
| 161 | 64.75 | | low | - | - |
| 162 | 64.95 | acenaphthene | trace | + | - |
| 163 | 65.35 | | low | - | - |
| 164 | 65.45 | methyl biphenyl | low | + | - |
| 165 | 65.65 | | trace | - | - |
| 166 | 65.8 | $C_3$-naphthalene | low | + | + |
| 167 | 65.95 | methyl biphenyl | low | + | - |
| 168 | 66.3 | $C_3$-naphthalene | low | + | - |
| 169 | 66.4 | $C_{15}$-alkane | high | + | + |
| 170 | 66.5 | $C_3$-naphthalene | trace | + | T |
| 171 | 66.75 | $C_{14}$-alkane | trace | + | T |
| 172 | 66.9 | $C_3$-naphthalene | high | + | T |

| Compound Number | Retention Time (Min) | Compound Name | Relative Concentration in DAF Neutral Fraction | Presence(+), Absence(-) (FC Effluent) | Presence(+), Absence (-) (MMF/AC Effluent) |
|---|---|---|---|---|---|
| 173 | 67.2 | $C_3$-naphthalene | low | + | - |
| 174 | 67.45 | $C_3$-naphthalene | low | + | - |
| 175 | 67.85 | $C_3$-naphthalene | medium | + | - |
| 176 | 68.05 | cycloalkane | trace | + | NM |
| 177 | 68.25 | $C_3$-naphthalene | medium | + | T |
| 178 | 68.6 | $C_3$-naphthalene | medium | + | T |
| 179 | 68.65 | n-pentadecane | high | + | + |
| 180 | 69.45 | $C_3$-naphthalene | medium | + | + |
| 181 | 69.7 | $C_3$-naphthalene | medium | + | T |
| 182 | 70.1 |  | low |  |  |
| 183 | 70.55 | $C_3$-naphthalene | medium | + | T |
| 184 | 71.15 | fluorene | low | NM | NM |
| 185 | 71.35 | $C_3$-naphthalene | trace | + | - |
| 186 | 71.7 | methyl acenaphthene | low | NM | - |
| 187 | 71.75 | $C_3$-naphthalene | trace | + | - |
| 188 | 72.05 | $C_2$-biphenyl | trace | NM | - |
| 189 | 72.1 | methyl acenaphthene | trace | NM | - |
| 190 | 72.3 | methyl acenaphthene | low | NM | - |
| 191 | 72.6 | $C_2$-biphenyl | trace | + | - |
| 192 | 72.7 | $C_4$-naphthalene | low | + | - |
| 193 | 72.8 | methyl acenaphthene | low | + | - |
| 194 | 73.1 |  | trace | - | - |
| 195 | 73.35 |  | trace | - | - |
| 196 | 73.7 | $C_2$-biphenyl | trace | NM | - |
| 197 | 73.9 | $C_4$-naphthalene | trace | T | - |
| 198 | 74.1 |  | trace | - | - |
| 199 | 74.45 | $C_4$-naphthalene | trace | NM | - |
| 200 | 74.5 | $C_2$-biphenyl | trace | + | - |
| 201 | 74.6 | $C_4$-naphthalene | trace | + | - |
| 202 | 74.8 | n-hexadecane | high | + | + |
| 203 | 75.0 |  | trace | - | - |
| 204 | 75.2 |  | trace | - | - |
| 205 | 75.3 | $C_4$-naphthalene | trace | + | - |
| 206 | 75.8 | $C_4$-naphthalene | low | + | - |
| 207 | 76.6 | $C_4$-naphthalene | trace | NM | - |
| 208 | 77.0 | $C_4$-naphthalene | low | NM | - |
| 209 | 77.4 |  | trace | - | - |
| 210 | 77.5 |  | trace | - | - |
| 211 | 77.85 | $C_4$-naphthalene | low | + | - |
| 212 | 78.05 | $C_4$-naphthalene | trace | NM | - |
| 213 | 78.05 | $C_3$-biphenyl | trace | NM | - |
| 214 | 78.1 | methyl fluorene | low | + | - |
| 215 | 78.35 | $C_2$-acenaphthene | low | NM | - |
| 216 | 78.4 | methyl fluorene | low | + | T |

| Compound Number | Retention Time (Min) | Compound Name | Relative Concentration in DAF Neutral Fraction | Presence(+), Absence(-) (FC Effluent) | Presence(+), Absence(-) (MMF/AC Effluent) |
|---|---|---|---|---|---|
| 217 | 78.95 | $C_4$-naphthalene | trace | NM | - |
| 218 | 79.0 | methyl fluorene | low | + | - |
| 219 | 79.05 | $C_3$-biphenyl | trace | NM | - |
| 220 | 79.1 | | trace | - | - |
| 221 | 79.15 | $C_2$-acenaphthene | trace | NM | - |
| 222 | 79.2 | $C_4$-naphthalene | trace | NM | - |
| 223 | 79.45 | $C_2$-acenaphthene | trace | NM | - |
| 224 | 79.55 | $C_4$-naphthalene | trace | NM | - |
| 225 | 79.75 | $C_2$-acenaphthene | trace | NM | - |
| 226 | 80.05 | $C_2$-acenaphthene | trace | NM | - |
| 227 | 80.4 | $C_3$-biphenyl | trace | NM | - |
| 228 | 80.55 | n-heptadecane | high | + | + |
| 229 | 80.65 | dibenzothiophene | low | T | - |
| 230 | 80.7 | $C_3$-biphenyl | trace | NM | - |
| 231 | 81.1 | pristane | high | + | - |
| 232 | 81.35 | | trace | - | - |
| 233 | 81.8 | $C_3$-biphenyl | trace | NM | - |
| 234 | 82.2 | anthracene/phenanthrene | high | + | + |
| 235 | 82.95 | | trace | - | - |
| 236 | 83.5 | | trace | - | - |
| 237 | 83.6 | | trace | - | - |
| 238 | 84.05 | | trace | - | - |
| 239 | 84.6 | $C_2$-fluorene | low | NM | - |
| 240 | 84.95 | $C_2$-fluorene | low | NM | - |
| 241 | 85.3 | $C_2$-fluorene | low | NM | - |
| 242 | 85.55 | $C_2$-fluorene | trace | NM | - |
| 243 | 85.9 | $C_2$-fluorene | trace | NM | - |
| 244 | 86.0 | n-octadecane | high | + | + |
| 245 | 86.25 | methyl dibenzothiophene | low | NM | - |
| 246 | 86.3 | $C_2$-fluorene | trace | NM | - |
| 247 | 86.75 | phytane | medium | + | + |
| 248 | 86.9 | $C_2$-fluorene | trace | NM | - |
| 249 | 87.35 | methyl dibenzothiophene | low | + | - |
| 250 | 88.5 | methyl phenanthrene | medium | NM | T |
| 251 | 88.8 | methyl phenanthrene | medium | NM | T |
| 252 | 89.3 | methyl phenanthrene | trace | NM | T |
| 253 | 89.35 | | trace | - | - |
| 254 | 89.65 | 2-methyl anthracene | low | + | T |
| 255 | 89.95 | 1-methyl anthracene | low | + | T |
| 256 | 90.85 | $C_3$ fluorene | trace | + | T |
| 257 | 91.2 | $C_3$ fluorene | trace | + | - |
| 258 | 91.3 | n-nonadecane | high | + | + |
| 259 | 91.65 | | trace | - | - |
| 260 | 92.4 | | trace | - | - |

| Compound Number | Retention Time (Min) | Compound Name | Relative Concentration in DAF Neutral Fraction | Presence(+), Absence(-) (FC Effluent) | Presence(+), Absence(-) (MMF/AC Effluent) |
|---|---|---|---|---|---|
| 261 | 92.65 | $C_2$-dibenzothiophene | trace | - | - |
| 262 | 93.35 | $C_2$-phenanthrene/anthracene | trace | T | - |
| 263 | 93.55 | | trace | - | - |
| 264 | 94.1 | $C_2$-phenanthrene/anthracene | trace | T | - |
| 265 | 94.35 | $C_2$-phenanthrene/anthracene | trace | T | - |
| 266 | 94.4 | fluoranthrene | trace | NM | - |
| 267 | 94.7 | $C_2$-phenanthrene/anthracene | low | + | - |
| 268 | 95.6 | $C_2$-phenanthrene/anthracene | low | + | - |
| 269 | 95.9 | $C_2$-phenanthrene/anthracene | trace | T | - |
| 270 | 96.1 | $C_2$-phenanthracene/anthracene | trace | NM | - |
| 271 | 96.3 | n-eicosane | high | + | + |
| 272 | 96.5 | $C_2$-phenanthrene/anthracene | trace | NM | - |
| 273 | 97.2 | $C_2$-phenanthrene/anthracene | trace | NM | - |
| 274 | 97.4 | | low | - | - |
| 275 | 98.8 | $C_3$-phenanthrene/anthracene | trace | T | - |
| 276 | 98.9 | pyrene | low | + | - |
| 277 | 99.35 | | trace | - | - |
| 278 | 99.95 | $C_3$-phenanthrene/anthracene | trace | T | - |
| 279 | 101.1 | n-heneicosane | medium | + | + |
| 280 | 101.1 | $C_3$-phenanthrene/anthracene | trace | NM | - |
| 281 | 101.45 | $C_3$-phenanthrene/anthracene | trace | NM | - |
| 282 | 102.0 | $C_3$-phenanthrene/anthracene | trace | NM | - |
| 283 | 102.25 | $C_3$-phenanthrene/anthracene | trace | NM | - |
| 284 | 102.45 | $C_{17}H_{12}$ PNA | trace | NM | - |
| 285 | 103.5 | $C_{17}H_{12}$ PNA | trace | T | - |
| 286 | 104.4 | $C_{17}H_{12}$ PNA | trace | NM | - |
| 287 | 104.7 | $C_{17}H_{12}$ PNA | low | + | - |
| 288 | 105.65 | n-docosane | medium | + | + |
| 289 | 105.7 | $C_{17}H_{12}$ PNA | trace | + | - |
| 290 | 106.05 | $C_{17}H_{12}$ PNA | trace | NM | - |
| 291 | 109.1 | $C_{18}H_{14}$ PNA | trace | T | - |
| 292 | 110.0 | n-tricosane | medium | + | + |
| 293 | 110.0 | phthalate | high | + | + |
| 294 | 110.1 | $C_{18}H_{14}$ PNA | trace | T | - |
| 295 | 110.8 | | trace | - | - |
| 296 | 111.2 | $C_{18}H_{14}$ PNA | trace | T | - |
| 297 | 111.45 | | low | - | - |
| 298 | 113.9 | chrysene | trace | + | - |
| 299 | 114.2 | 1,2-benzanthracene | low | + | - |
| 300 | 114.45 | n-tetracosane | low | + | + |
| 301 | 117.05 | | trace | - | - |
| 302 | 118.8 | | trace | - | - |
| 303 | 119.75 | n-pentacosane | low | + | NM |
| 304 | 120.0 | phthalate | medium | + | + |

T Trace
NM Not measurable due to interferences

# APPENDIX B

## Organic Compounds Found in the Acid Fraction of the Effluent from the Dissolved Air Flotation (DAF) Unit and Their Presence or Absence in the Effluents from the Final Clarifier (FC) and Add-on Mixed-Media Filter/Activated Carbon (MMF/AC) Units

| Compound Number | Retention Time (Min) | Compound Name | Relative Concentration in DAF Acid Fraction | Presence(+), Absence(-) (FC Effluent) | Presence(+), Absence(-) (MMF/AC Effluent) |
|---|---|---|---|---|---|
| 1 | 49.0 | phenol | medium | - | - |
| 2 | 51.9 | cresol | high | - | - |
| 3 | 54.3 | naphthalene | trace | + | - |
| 4 | 54.8 | p-cresol | high | - | - |
| 5 | 56.9 | i-propyl phenol | trace | - | - |
| 6 | 57.2 | ethyl phenol | low | - | - |
| 7 | 57.7 | dimethyl phenol | medium | - | - |
| 8 | 58.5 | 2,4,5-trimethyl phenol | low | + | - |
| 9 | 60.6 | 2,3-dimethyl phenol | medium | + | - |
| 10 | 60.9 | ethyl phenol | low | - | - |
| 11 | 62.2 | n-propyl phenol | trace | - | - |
| 12 | 62.5 | i-propyl phenol | low | - | - |
| 13 | 62.7 | dimethyl phenol | low | - | - |
| 14 | 63.6 | i-propyl phenol | low | - | - |
| 15 | 64.2 | i-propyl phenol | trace | - | - |
| 16 | 64.4 | i-propyl phenol | trace | - | - |
| 17 | 65.4 | methyl ethyl phenol | trace | - | - |
| 18 | 65.9 | methyl ethyl phenol | low | - | - |
| 19 | 66.4 | n-propyl phenol | low | - | - |
| 20 | 66.4 | methyl ethyl phenol | low | - | - |
| 21 | 66.7 | diethyl phenol | trace | - | - |
| 22 | 68.0 | n-propyl phenol | trace | - | - |
| 23 | 68.0 | methyl ethyl phenol | trace | - | - |
| 24 | 68.9 | methyl ethyl phenol | trace | - | - |
| 25 | 68.9 | $C_4$-phenol | trace | - | - |
| 26 | 69.4 | dimethyl naphthalene | trace | - | - |
| 27 | 69.4 | methyl ethyl phenol | trace | - | - |
| 28 | 69.4 | $C_4$-phenol | trace | - | - |
| 29 | 70.2 | alkene | trace | + | - |
| 30 | 70.7 | dimethyl naphthalene | trace | - | - |
| 31 | 70.7 | $C_3$-phenol | trace | - | - |
| 32 | 70.7 | $C_4$-phenol | trace | - | - |
| 33 | 71.1 | dimethyl naphthalene | trace | - | - |
| 34 | 71.4 | $C_3$-phenol | trace | - | - |
| 35 | 71.4 | $C_4$-phenol | trace | - | - |
| 36 | 71.5 | diethyl phenol | trace | - | - |
| 37 | 73.6 |  | trace | - | - |
| 38 | 76.3 | n-heptadecane | trace | + | - |
| 39 | 77.2 | $C_6$-benzene | trace | + | - |
| 40 | 82.2 | n-octadecane | trace | + | - |
| 41 | 87.8 | n-nonadecane | trace | + | - |
| 42 | 93.2 | n-eicosane | trace | + | - |
| 43 | 99.4 | plasticizer | low | + | + |
| 44 | 100.0 | plasticizer | low | + | + |
| 45 | 100.4 | plasticizer | medium | + | + |

# APPENDIX C

## Organic Compounds Found in the Base Fraction of the Effluent from the Dissolved Air Flotation (DAF) Unit and Their Presence or Absence in the Effluents from the Final Clarifier (FC) and Add-On Mixed-Media Filter/Activated Carbon (MMF/AC) Units

| Compound Number | Retention Time (Min) | Compound Name | Relative Concentration in DAF Base Fraction | Presence(+), Absence(-) (FC Effluent) | Presence(+), Absence(-) (MMF/AC Effluent) |
|---|---|---|---|---|---|
| 1 | 22.5 | picoline | trace | | - |
| 2 | 23.3 | | trace | | - |
| 3 | 25.7 | | trace | | - |
| 4 | 27.2 | lutidine | trace | - | T |
| 5 | 29.3 | ethyl pyridine | trace | - | - |
| 6 | 30.9 | $C_3$-benzene | trace | | T |
| 7 | 31.9 | lutidine | low | + | - |
| 8 | 33.4 | 4-ethyl pyridine | trace | + | - |
| 9 | 33.4 | ethyl picoline | trace | NM | NM |
| 10 | 33.7 | $C_3$-benzene | trace | - | - |
| 11 | 34.5 | n-undecane | trace | - | - |
| 12 | 34.8 | | trace | - | T |
| 13 | 35.2 | | trace | - | - |
| 14 | 36.2 | 2,4,6-collidine | trace | - | - |
| 15 | 36.8 | $C_3$-benzene | trace | - | - |
| 16 | 37.5 | 2,3,6-collidine | trace | - | - |
| 17 | 38.3 | 2-ethyl picoline | trace | - | - |
| 18 | 39.6 | 2,3,5-collidine | trace | - | - |
| 19 | 40.0 | | trace | - | - |
| 20 | 42.0 | ethyl lutidine | trace | - | - |
| 21 | 42.2 | n-dodecane | trace | - | - |
| 22 | 42.2 | ethyl lutidine | trace | - | - |
| 23 | 42.7 | aniline | medium | + | T |
| 24 | 43.6 | ethyl lutidine | trace | - | - |
| 25 | 43.6 | N,N-dimethyl aniline | trace | + | - |
| 26 | 43.9 | ethyl lutidine | trace | - | - |
| 27 | 44.3 | $C_3$-pyridine | trace | - | - |
| 28 | 45.4 | collidine | trace | + | + |
| 29 | 45.7 | $C_3$-pyridine | trace | - | - |
| 30 | 46.5 | | trace | - | - |
| 31 | 48.9 | o-toluidine | medium | NM | - |
| 32 | 49.2 | phenol | low | - | |
| 33 | 49.7 | toluidine | low | NM | - |
| 34 | 52.2 | p-cresol | low | - | - |
| 35 | 54.3 | naphthalene | trace | - | - |
| 36 | 55.0 | ethyl picoline | low | - | - |
| 37 | 55.1 | cresol | low | - | - |
| 38 | 55.7 | collidine | trace | - | - |
| 39 | 56.9 | n-tetradecane | trace | - | - |
| 40 | 57.4 | | trace | - | - |

| Compound Number | Retention Time (Min) | Compound Name | Relative Concentration in DAF Base Fraction | Presence(+), Absence(-) (FC Effluent) | Presence(+), Absence(-) (MMF/AC Effluent) |
|---|---|---|---|---|---|
| 41 | 57.8 | xylenol | trace | - | - |
| 42 | 60.7 | xylenol | trace | - | - |
| 43 | 60.9 | xylenol | trace | - | - |
| 44 | 61.1 | ethyl phenol | trace | - | - |
| 45 | 61.6 | quinoline | low | - | - |
| 46 | 62.2 | 2-methyl naphthalene | trace | - | - |
| 47 | 63.7 | n-pentadecane | trace | - | - |
| 48 | 63.9 | 1-methyl naphthalene | trace | - | - |
| 49 | 64.3 | ethyl lutidine | trace | - | - |
| 50 | 65.6 | methyl quinoline | low | - | - |
| 51 | 65.8 | methyl quinoline | trace | - | - |
| 52 | 66.9 | methyl quinoline | trace | - | - |
| 53 | 67.6 | | | | |
| 54 | 68.4 | methyl quinoline | trace | + | - |
| 55 | 68.7 | ethyl quinoline | trace | - | - |
| 56 | 69.3 | methyl quinoline | trace | - | - |
| 57 | 69.4 | dimethyl naphthalene | trace | - | - |
| 58 | 69.8 | methyl quinoline | trace | - | - |
| 59 | 70.2 | n-hexadecane | trace | - | - |
| 60 | 70.8 | dimethyl naphthalene | trace | - | - |
| 61 | 71.1 | dimethyl naphthalene | trace | - | - |
| 62 | 71.5 | dimethyl quinoline | trace | + | + |
| 63 | 71.8 | dimethyl quinoline | trace | - | - |
| 64 | 72.4 | dimethyl naphthalene | trace | - | - |
| 65 | 72.9 | dimethyl quinoline | trace | - | - |
| 66 | 73.9 | dimethyl naphthalene | trace | - | - |
| 67 | 74.6 | dimethyl quinoline | trace | - | - |
| 68 | 75.1 | dimethyl quinoline | trace | + | - |
| 69 | 75.5 | dimethyl quinoline | trace | - | - |
| 70 | 76.3 | n-heptadecane | trace | - | - |
| 71 | 78.7 | $C_3$-quinoline | trace | + | - |
| 72 | 79.6 | $C_3$-quinoline | trace | + | - |
| 73 | 82.2 | n-octadecane | trace | - | - |
| 74 | 87.8 | n-nonadecane | trace | - | - |
| 75 | 93.2 | n-eicosane | trace | - | - |
| 76 | 97.9 | plasticizer | trace | - | - |
| 77 | 98.2 | n-heneicosane | trace | - | - |
| 78 | 98.6 | plasticizer | trace | - | - |
| 79 | 98.6 | alkane | trace | - | - |

T Trace
NM Not measurable due to interferences

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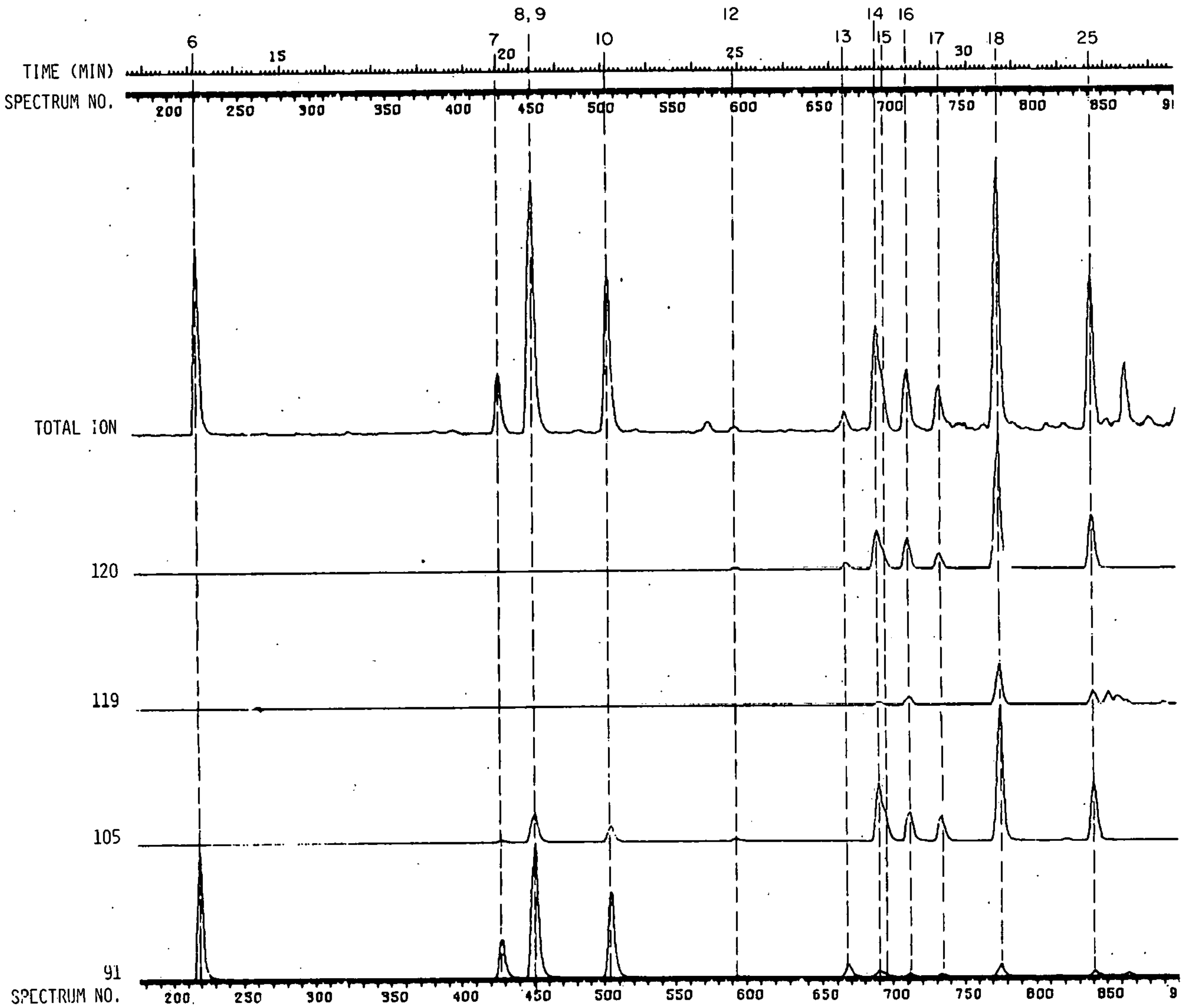
# APPENDIX D

## Massgram Plots for Compounds in the Neutral Fraction of the DAF Effluent

MASSGRAM PLOTS OF KEY IONS (91, 105, 119, AND 120) FOR IDENTIFYING TOLUENE, $C_2$-BENZENES, AND $C_3$-BENZENES



$C_1$-BENZENES

6 Toluene

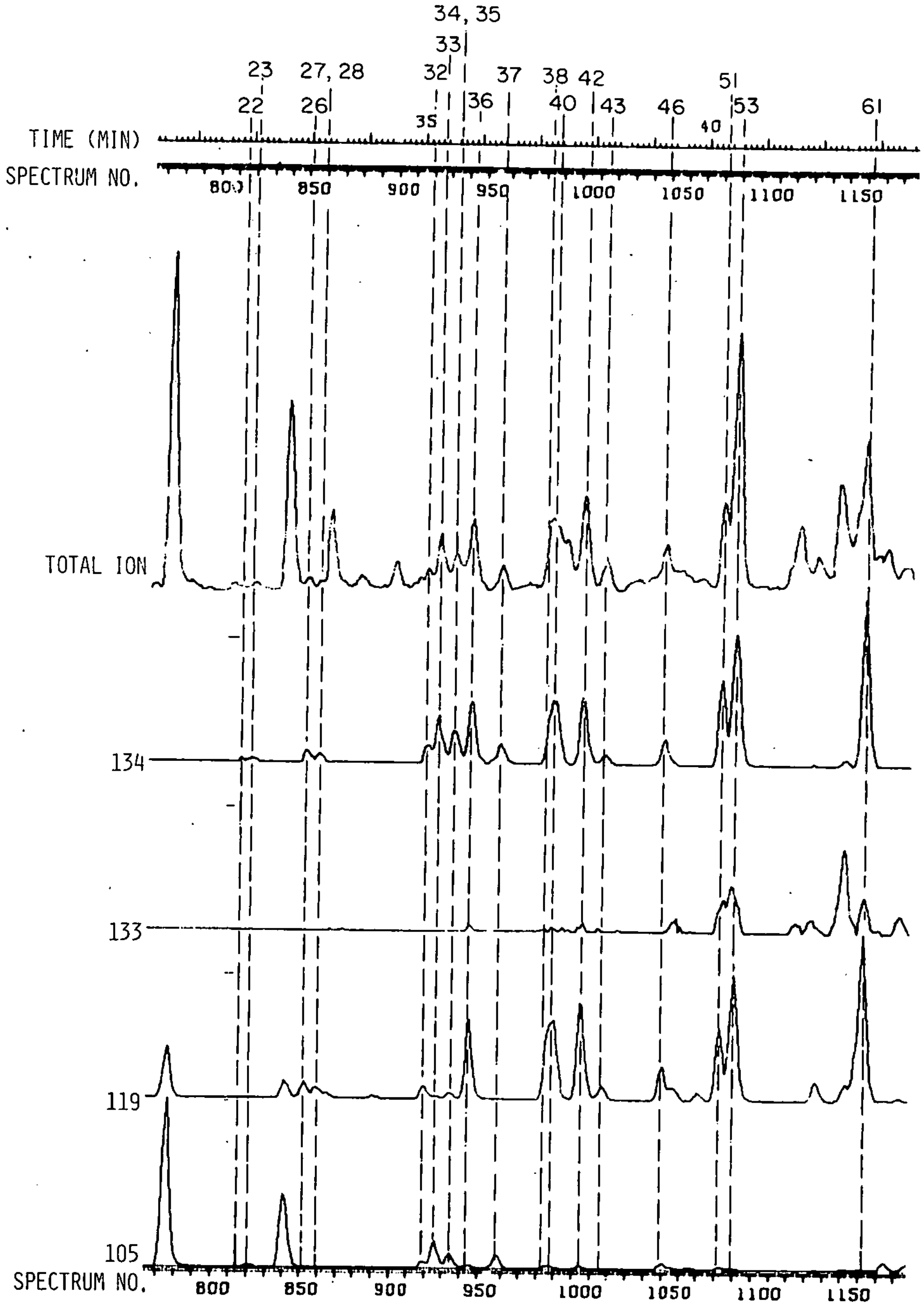
$C_2$-BENZENES

7 Ethyl benzene
8,9 p and m-Xylenes
10 o-Xylene

$C_3$ BENZENES

12 i-Propyl benzene
13 n-Propyl benzene
14 m-Ethyl toluene
15 p-Ethyl toluene
16 1,3,5-Trimethyl benzene
17 o-Ethyl toluene
18 1,2,4-Trimethyl benzene
25 1,2,3,-Trimethyl benzene

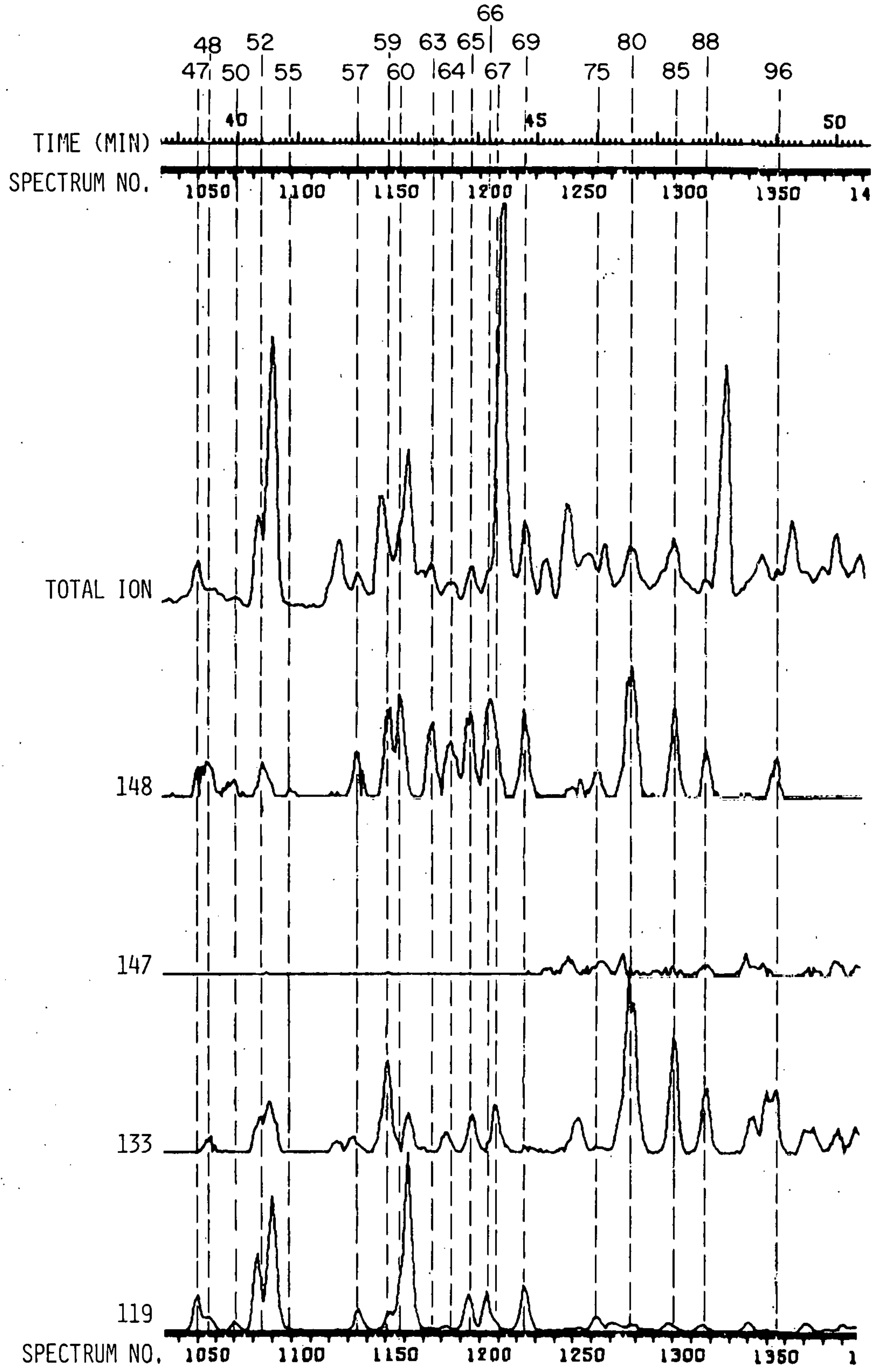
MASSGRAM PLOTS OF KEY IONS (105, 119, 133, 134) FOR IDENTIFYING $C_4$-BENZENES



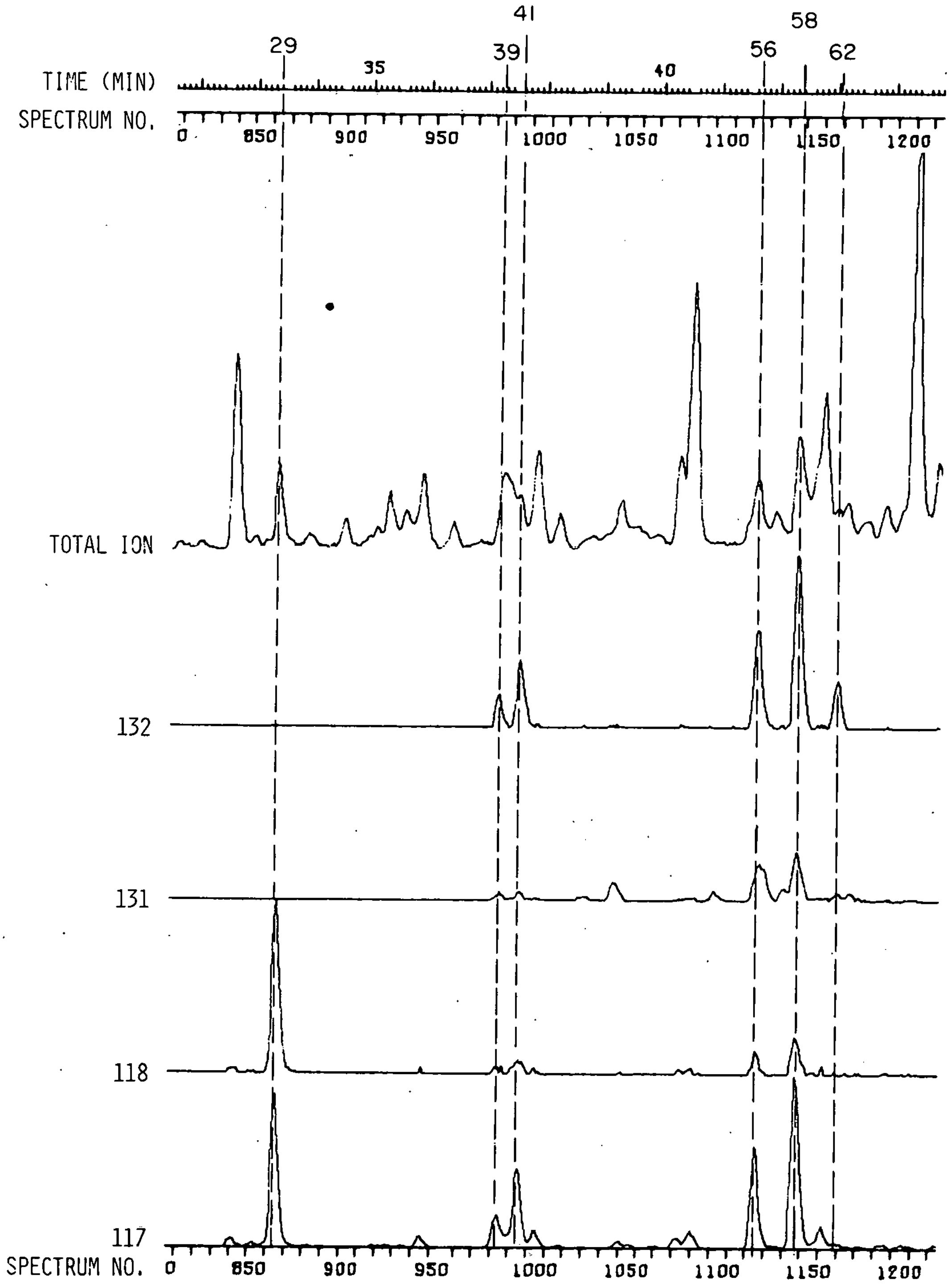
$C_4$-BENZENES

| | | | |
|---|---|---|---|
| 22 | t-Butyl benzene | 38 | 1,4-Dimethyl-2-ethyl benzene |
| 23 | s-Butyl benzene | 40 | 1,3-Dimethyl-4-ethyl benzene |
| 26 | m-Isopropyl toluene | 42 | 1,2-Dimethyl-4-ethyl benzene |
| 27,28 | p and o-Isopropyl toluene | 43 | 1,3-Dimethyl-2-ethyl benzene |
| 32 | m-Diethyl benzene | 46 | 1,2-Dimethyl-3-ethyl benzene |
| 33 | m-n-Propyl toluene | 51 | 1,2,4,5-Tetramethyl benzene |
| 34,35 | p-n-Propyl toluene and n-butyl benzene | 53 | 1,2,3,5-Tetramethyl benzene |
| 36 | 1,3-Dimethyl-5-ethyl benzene | 61 | 1,2,3,4-Tetramethyl benzene |
| 37 | o-n-Propyl toluene | | |

# MASSGRAM PLOTS OF KEY IONS (119, 133, 147, 148) FOR IDENTIFYING $C_5$-BENZENES



## MASSGRAM PLOTS OF KEY IONS (117, 118, 131, 132) FOR IDENTIFYING INDANS, ETHYL STYRENES, AND TETRALIN



INDANS

29 INDAN
56 2-METHYL INDAN
58 1-METHYL INDAN

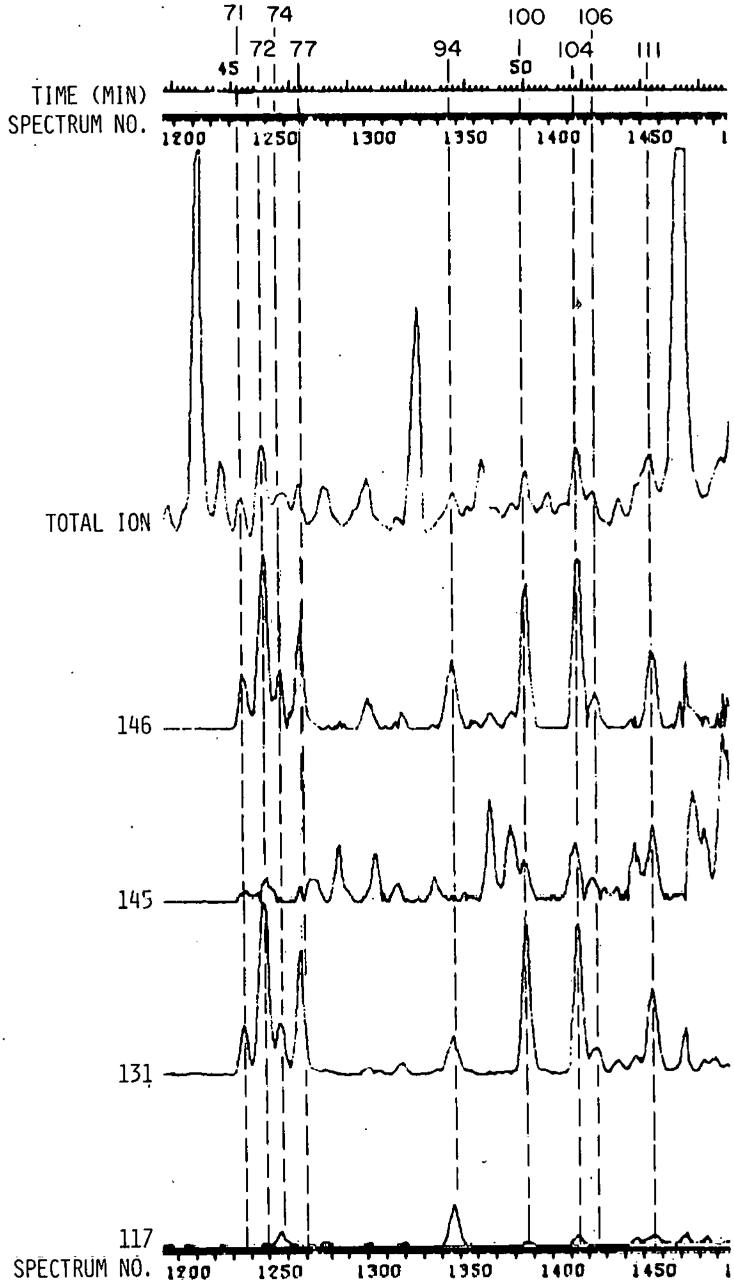
ETHYL STYRENES

39 ETHYL STYRENE
41 ETHYL STYRENE

TETRALINS

62 TETRALIN

## MASSGRAM PLOTS OF KEY IONS (117, 131, 145, 146) FOR IDENTIFYING $C_2$-INDANS, $C_3$-STYRENES, AND $C_1$-TETRALINS



$C_2$-INDANS

| | |
|---|---|
| 94 | Ethyl indan |
| 100 | Dimethyl indan |
| 106 | Dimethyl indan |
| 111 | Dimethyl indan |

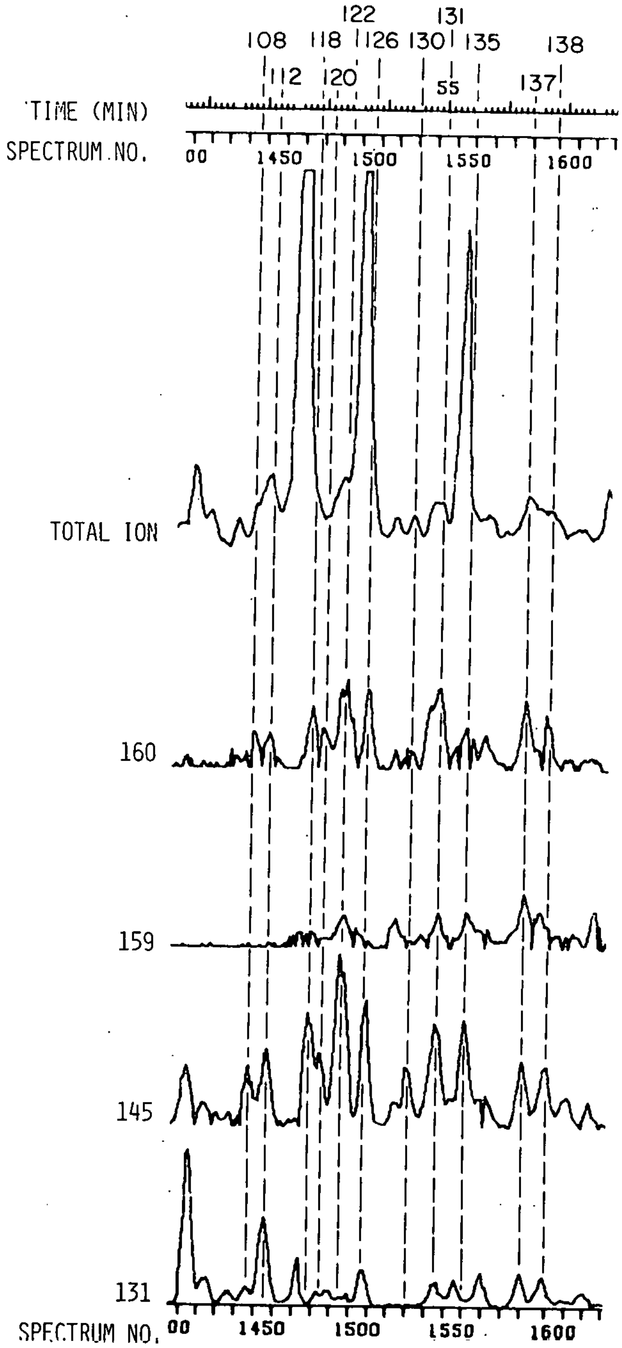
$C_3$-STYRENES

| | |
|---|---|
| 71 | $C_3$-Styrene |
| 72 | $C_3$-Styrene |
| 74 | $C_3$-Styrene |
| 77 | $C_3$-Styrene |

$C_1$-TETRALINS

104 Methyl tetralin

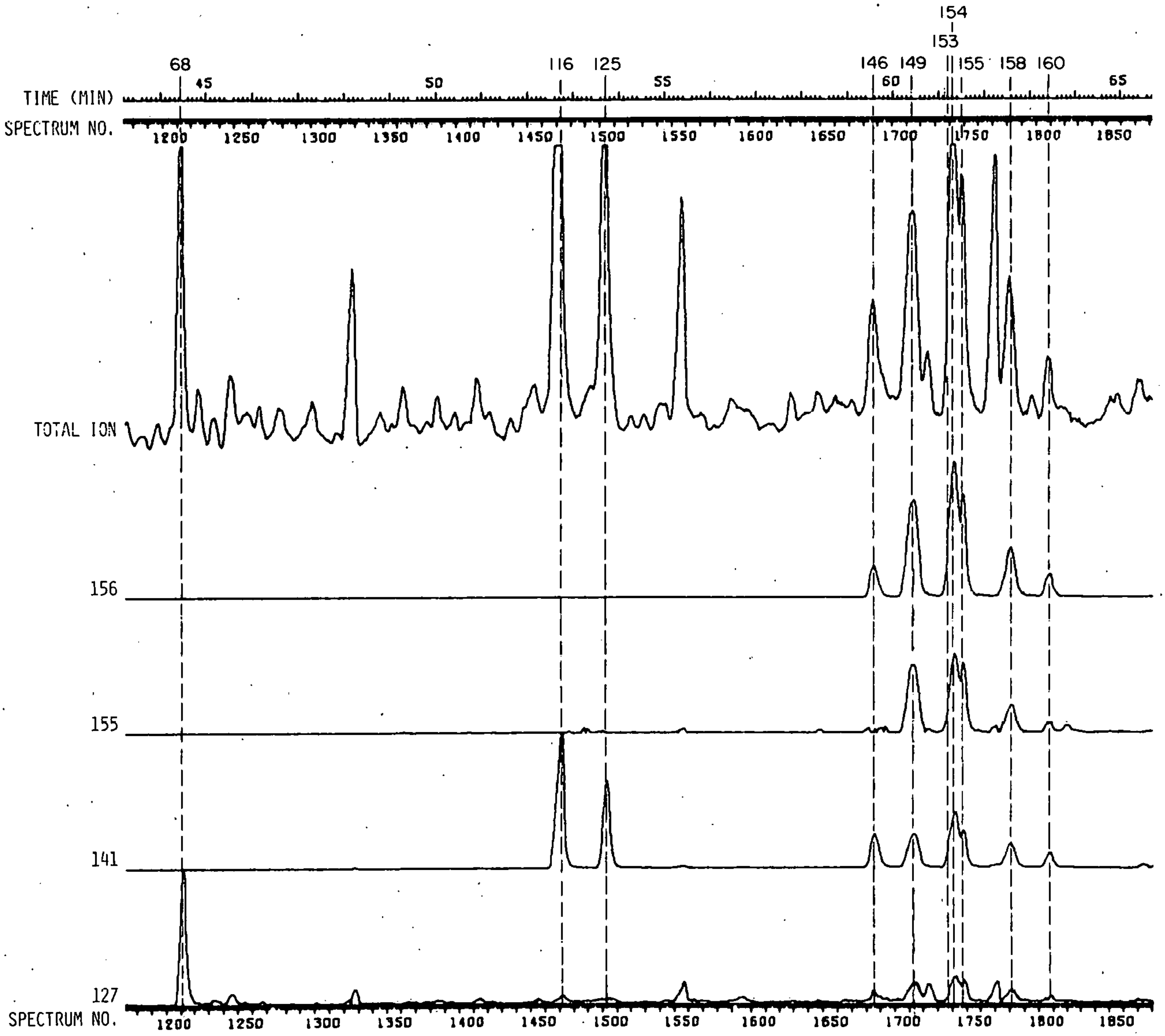
# MASSGRAM PLOTS OF KEY IONS (131, 145, 159, 160) FOR IDENTIFYING $C_3$-INDANS AND $C_2$-TETRALINS



| $C_3$-INDANS | |
|---|---|
| 108 | $C_3$-Indan |
| 112 | Methyl ethyl indan |
| 118 | Trimethyl indan |
| 120 | Trimethyl indan |
| 122 | Trimethyl indan |

| $C_2$-TETRALINS | |
|---|---|
| 126 | Ethyl tetralin |
| 130 | Ethyl tetralin |
| 131 | Dimethyl tetralin |
| 137 | Dimethyl tetralin |
| 138 | $C_2$-Tetralin |

MASSGRAM PLOTS OF KEY IONS (127, 141, 155, 156) FOR IDENTIFYING NAPHTHALENE, METHYL NAPHTHALENES, AND $C_2$-NAPHTHALENES



NAPHTHALENE

| | |
|---|---|
| 68 | Naphthalene |

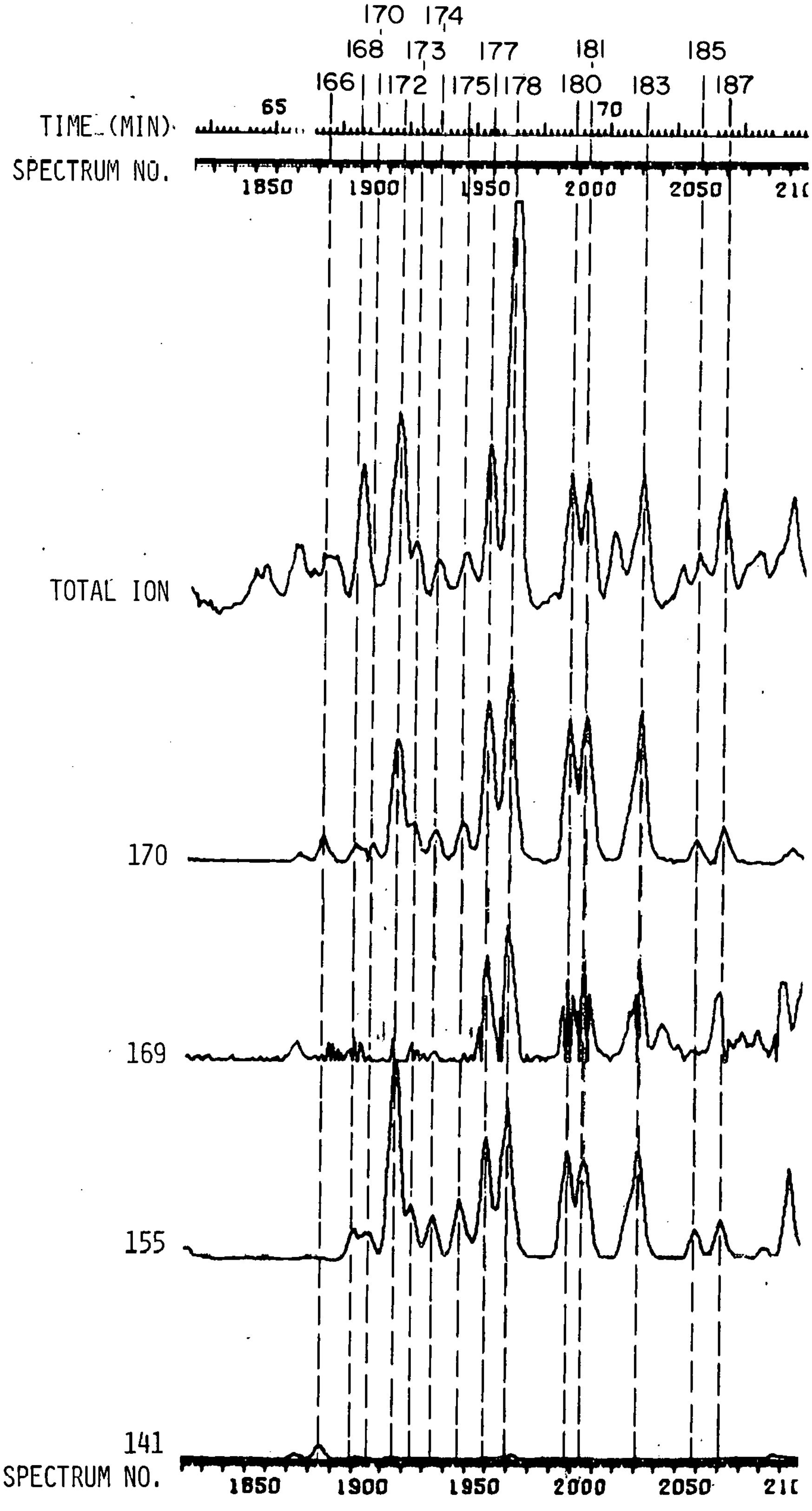
$C_1$-NAPHTHALENES

| | |
|---|---|
| 116 | 2-Methyl naphthalene |
| 125 | 1-Methyl naphthalene |

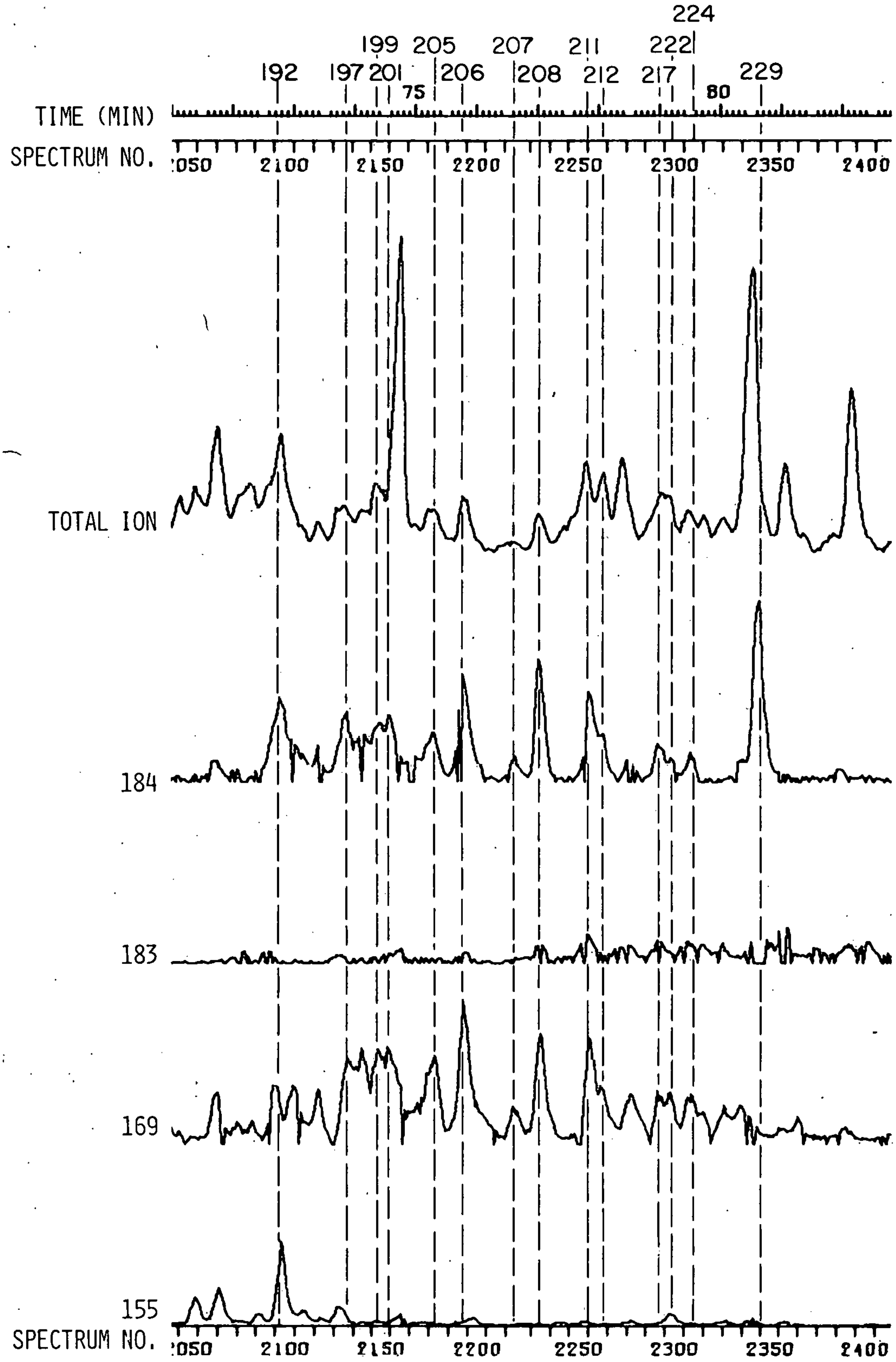
$C_2$-NAPHTHALENES

| | |
|---|---|
| 146 | Ethyl naphthalene |
| 149 | Dimethyl naphthalene |
| 153 | Dimethyl naphthalene |
| 154 | Dimethyl Naphthalene |
| 155 | Dimethyl naphthalene |
| 158 | Dimethyl naphthalene |
| 160 | Dimethyl naphthalene |

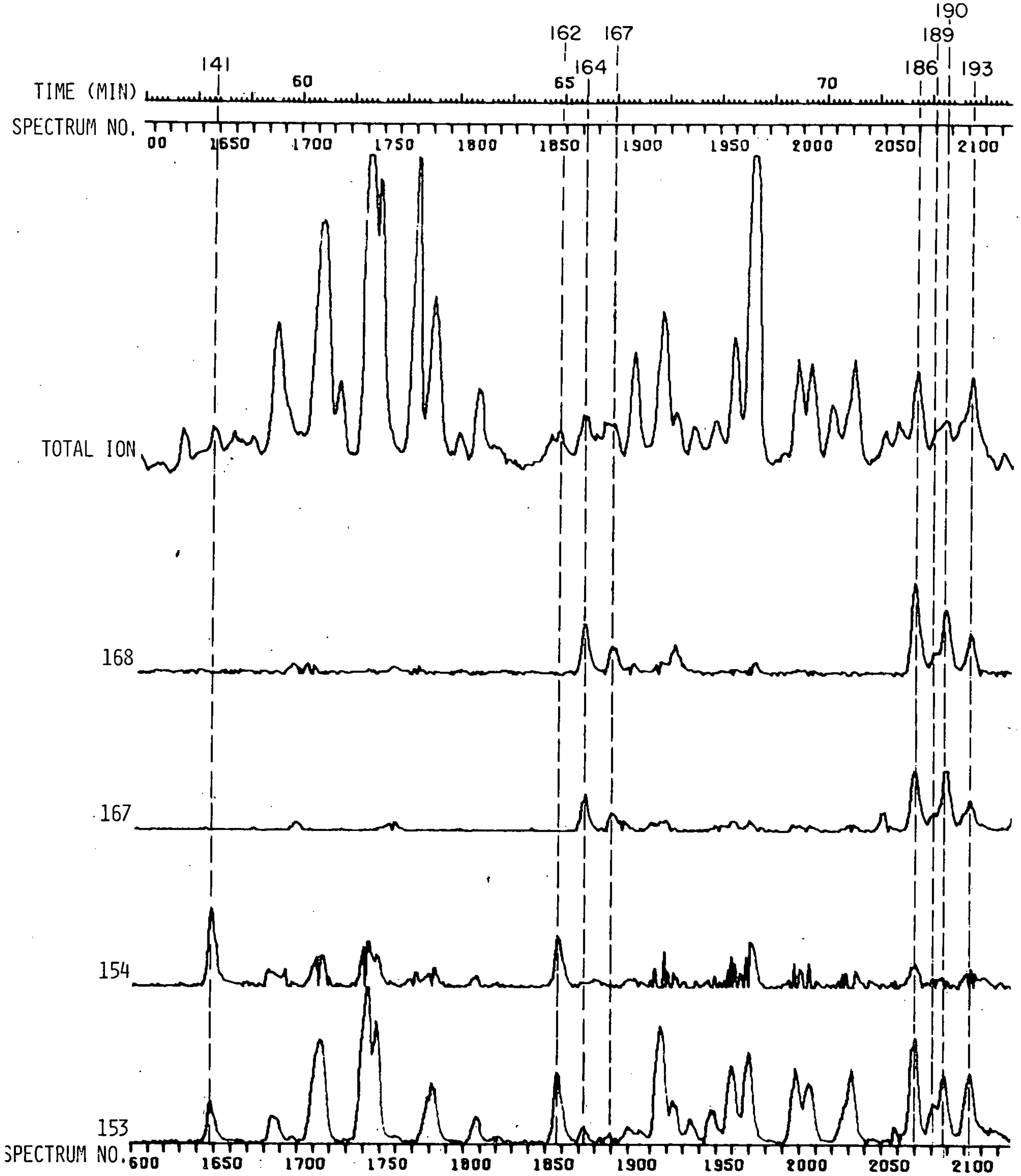
## MASSGRAM PLOTS OF KEY IONS (141, 155, 169, 170) FOR IDENTIFYING $C_3$-NAPHTHALENES



MASSGRAM PLOTS OF KEY IONS (155, 169, 183, 184) FOR IDENTIFYING $C_4$-NAPHTHALENES AND DIBENZOTHIOPHENE (NUMBER 229)

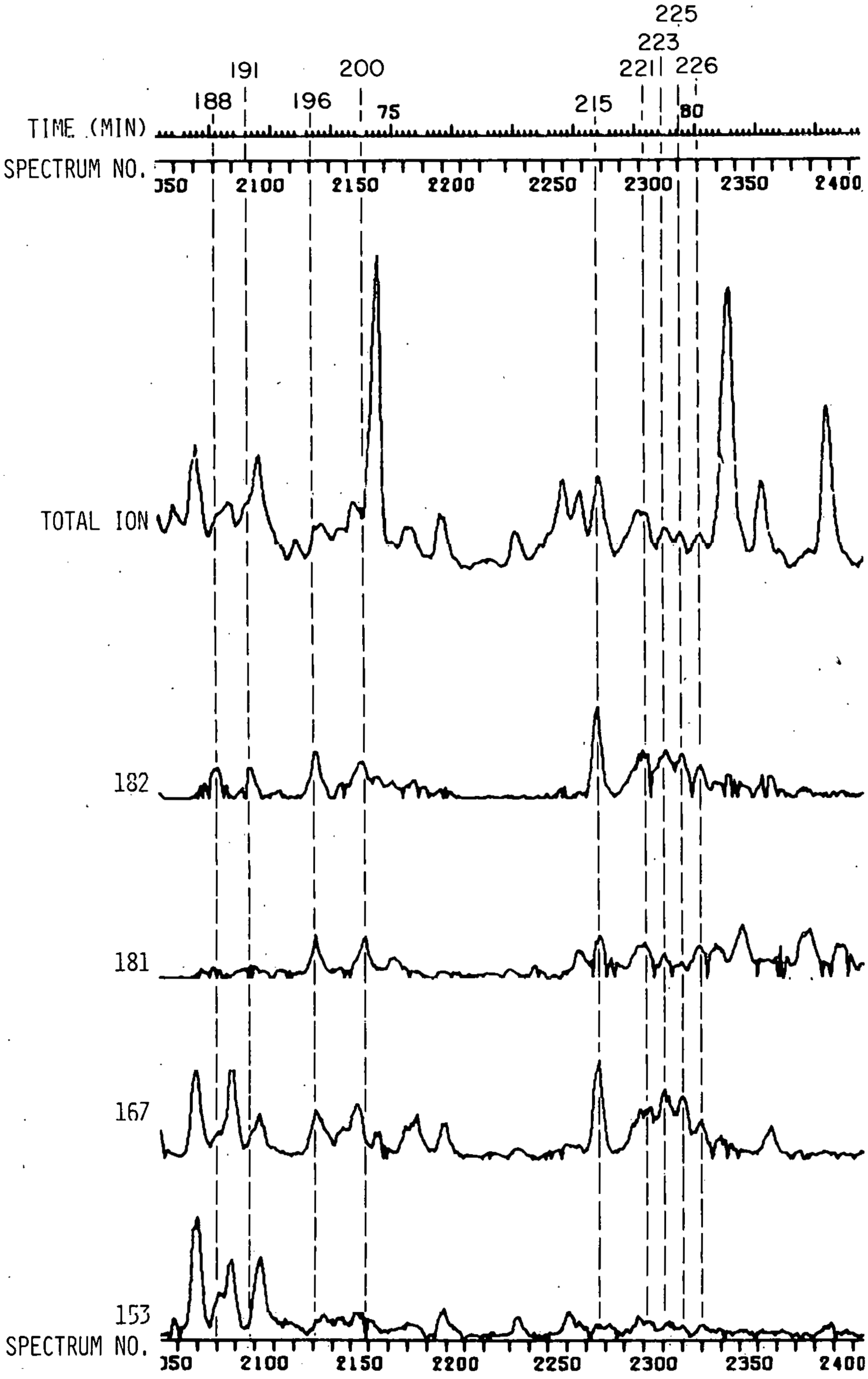


MASSGRAM PLOTS OF KEY IONS (153, 154, 167, 168) FOR IDENTIFYING BIPHENYL, ACENAPHTHENE, METHYL BIPHENYLS, AND METHYL ACENAPHTHENES



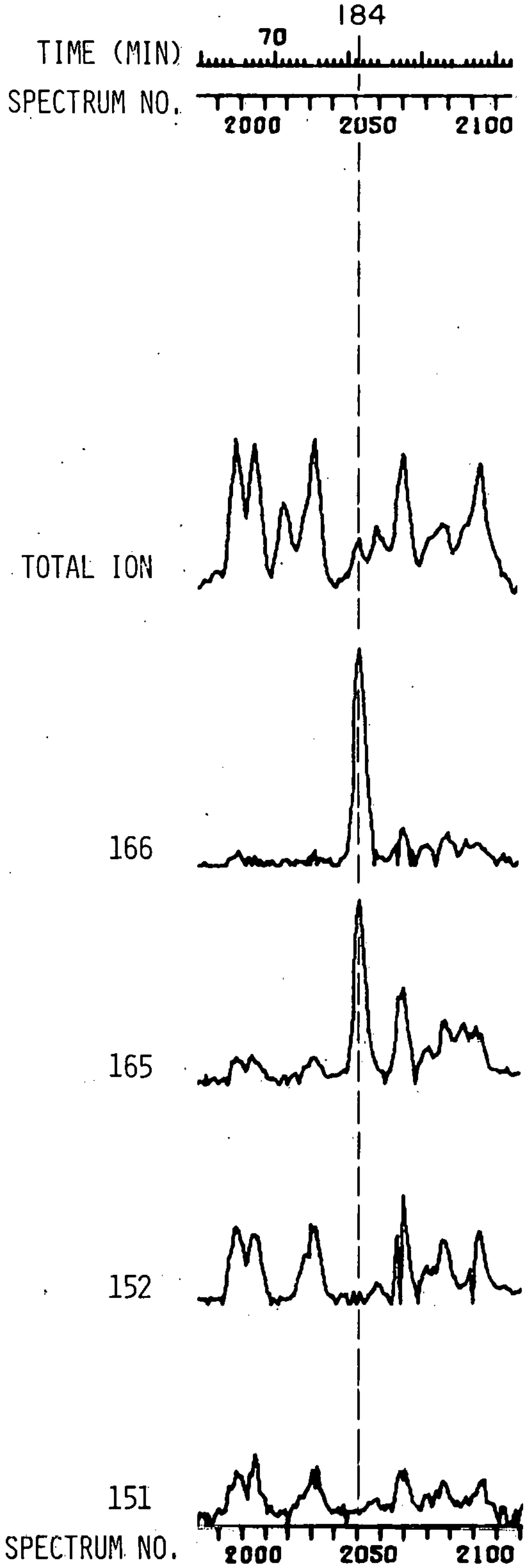
| BIPHENYL | METHYL BIPHENYLS | ACENAPHTHENE | METHYL ACENAPHTHENES |
|---|---|---|---|
| 141 | 164, 167 | 162 | 186, 189, 190, 193 |

MASSGRAM PLOTS OF KEY IONS (153, 167, 181, 182) FOR IDENTIFYING $C_2$-BIPHENYLS AND $C_2$-ACENAPHTHENES

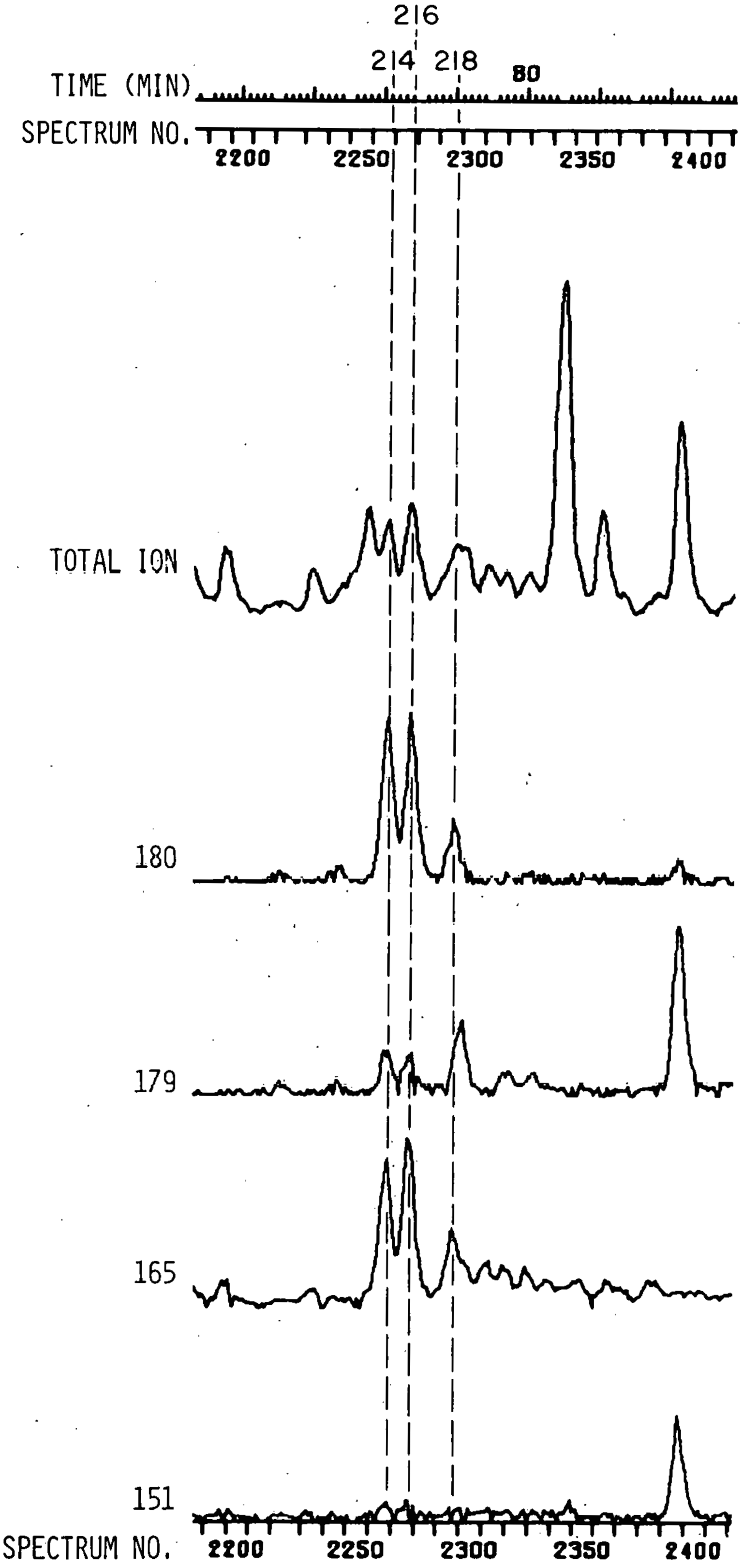


| $C_2$-BIPHENYLS | $C_2$-ACENAPHTHENES |
|---|---|
| 188, 191, 196, 200 | 215, 221, 223, 225, 226 |

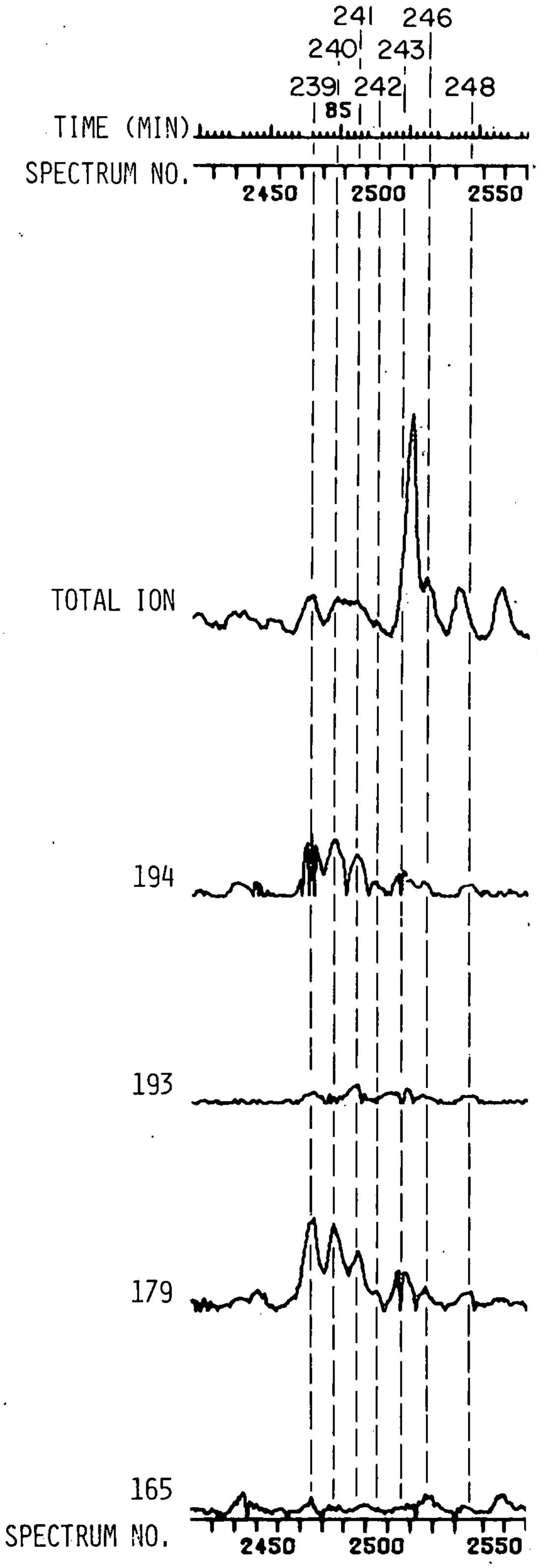
## MASSGRAM PLOTS OF KEY IONS (166, 165) FOR IDENTIFYING FLUORENE



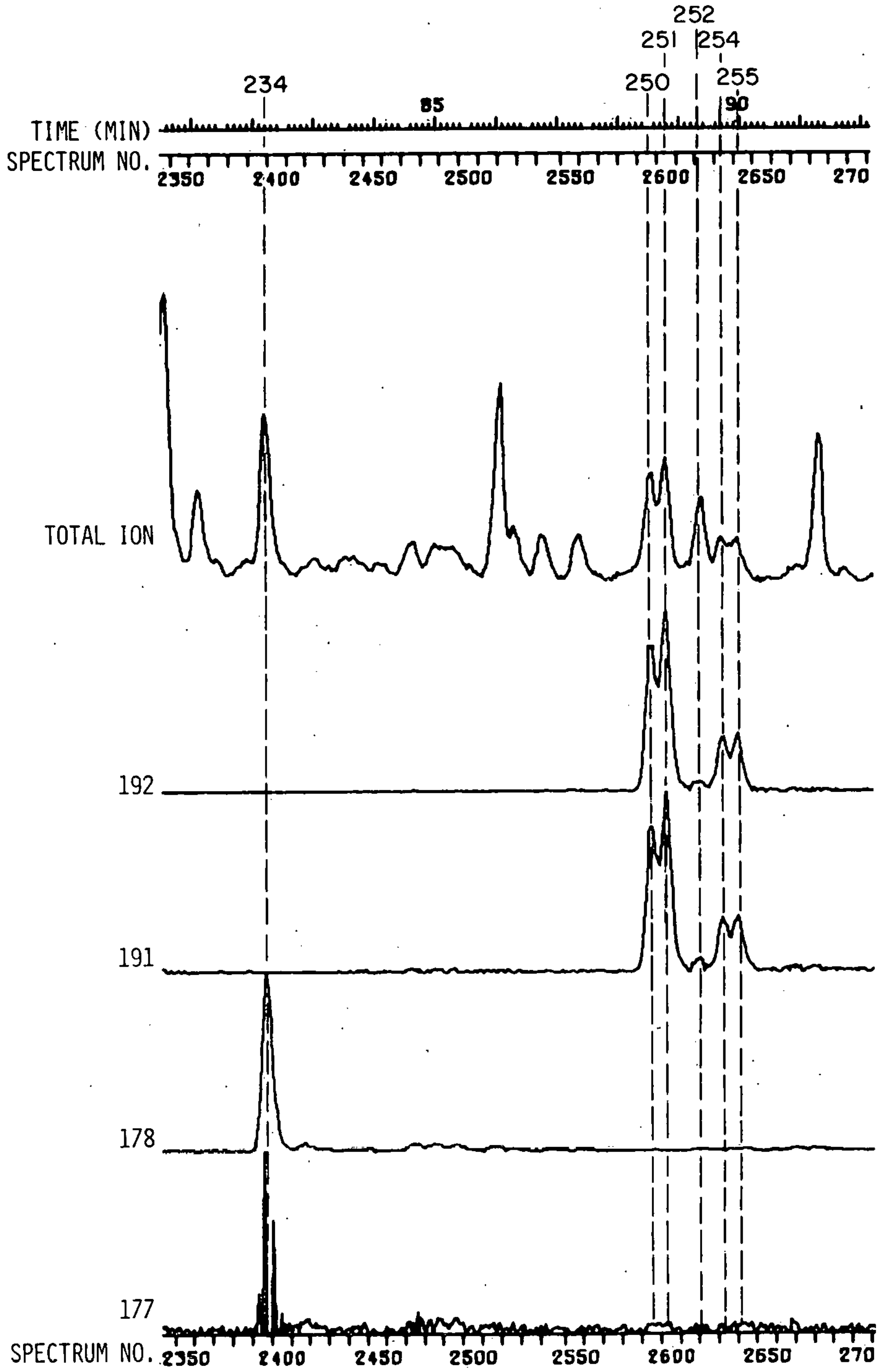
MASSGRAM PLOTS OF KEY IONS (151, 165, 179, 180)
FOR IDENTIFYING METHYL FLUORENES



MASSGRAM PLOTS OF KEY IONS
(165, 179, 193, 194) FOR
IDENTIFYING $C_2$-FLUORENES



## MASSGRAM PLOTS OF KEY IONS (177, 178, 191, 192) FOR IDENTIFYING PHENANTHRENE, ANTHRACENE, METHYL PHENANTHRENES, AND METHYL ANTHRACENES



<u>PHENANTHRENE/ANTHRACENE</u>

234 Phenanthrene/Anthracene

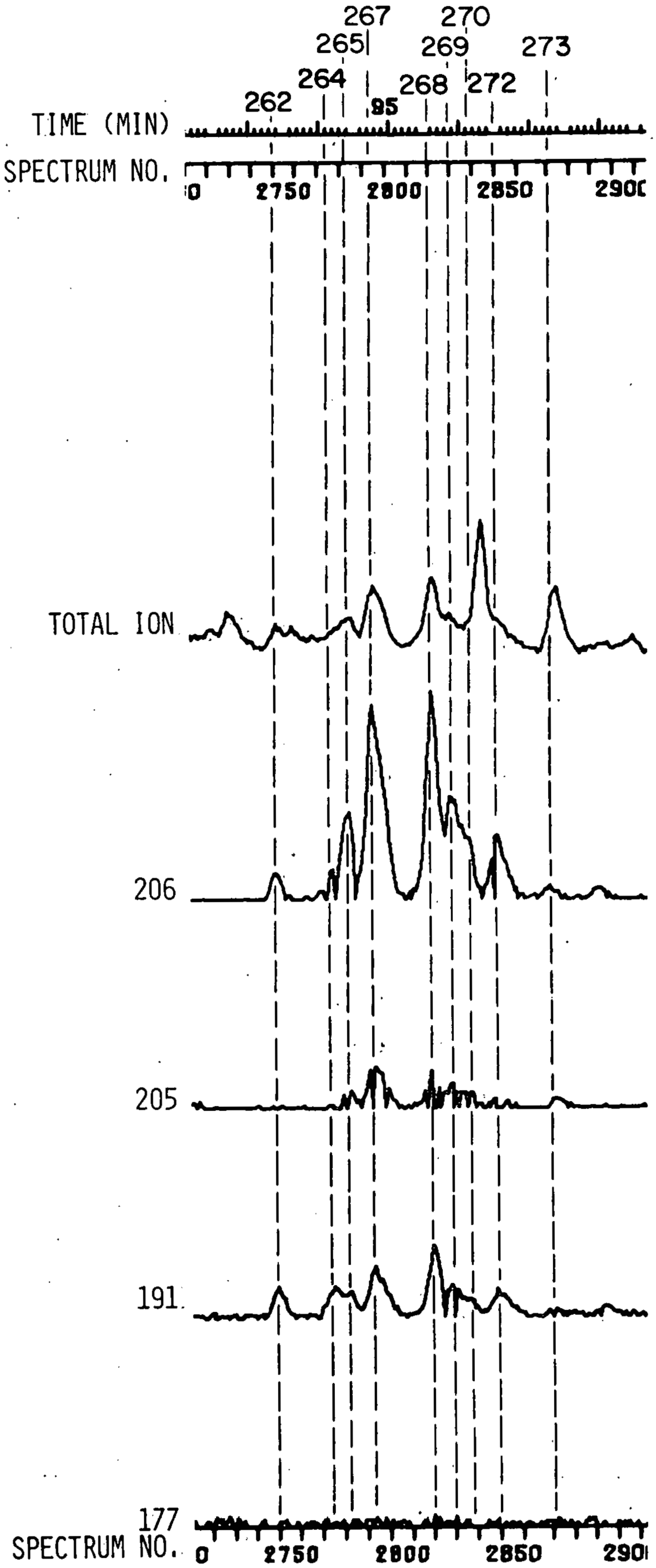
<u>METHYL PHENANTHRENES</u>

250 Methyl phenanthrene
251 Methyl phenanthrene
252 Methyl Phenanthrene

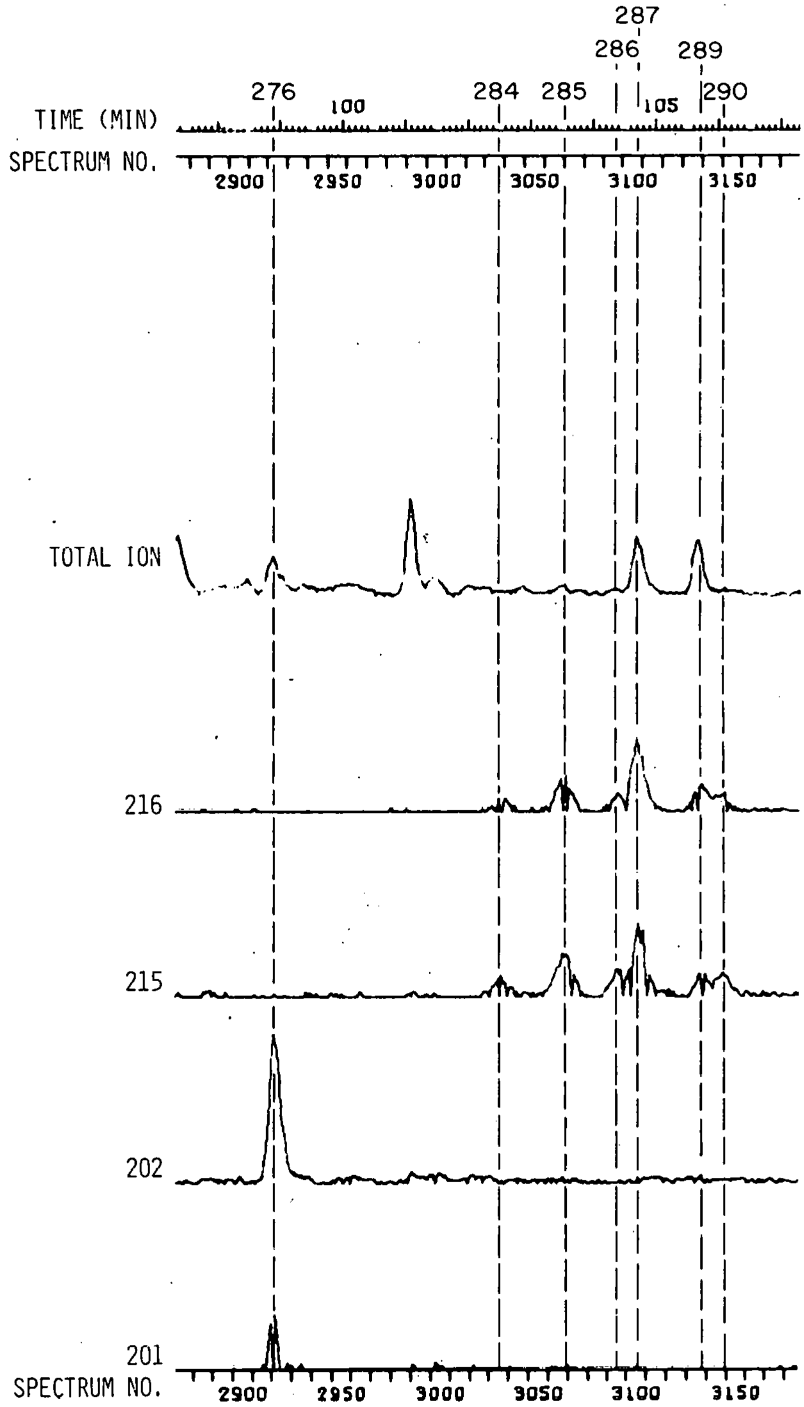
<u>METHYL ANTHRACENES</u>

254 2-Methyl anthracene
255 1-Methyl anthracene

# MASSGRAM PLOTS OF KEY IONS (177, 191, 205, 206) FOR IDENTIFYING $C_2$-PHENANTHRENES AND $C_2$-ANTHRACENES



# MASSGRAM PLOTS OF KEY IONS (201, 202, 215, 216) FOR IDENTIFYING PYRENE AND METHYL PYRENES (INCLUDES METHYL FLUORANTHENES, ACEANTHRYLENES, ACEPHENANTHRYLENES)



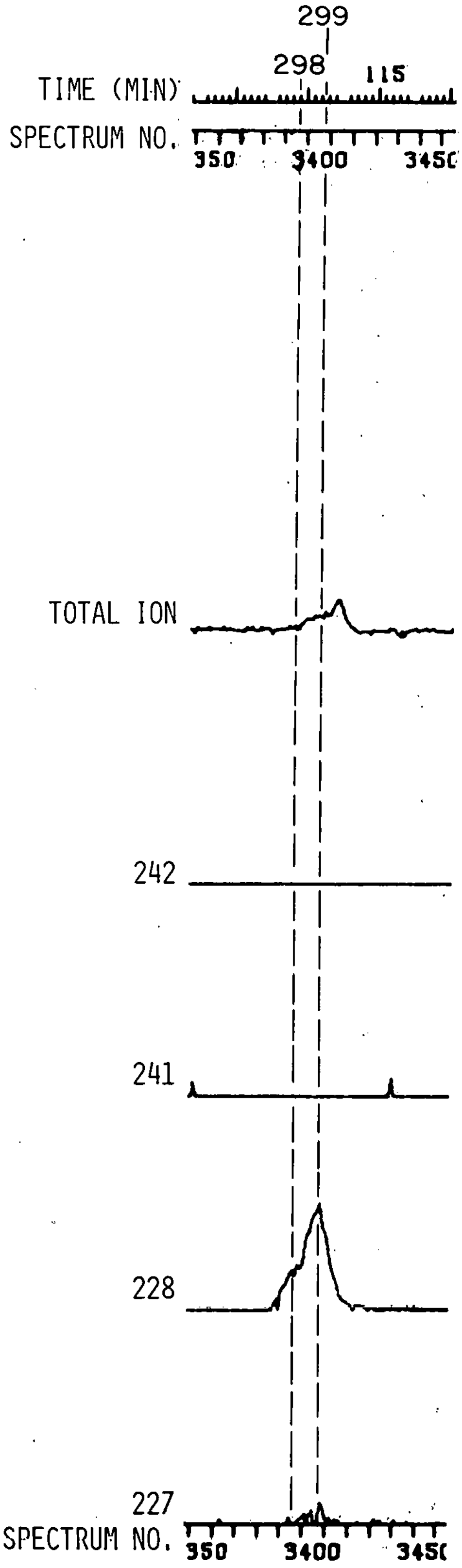
PYRENE

276

METHYL PYRENES, FLUORANTHENES, ACEANTHRYLENES, ACEPHENANTHRYLENES

284, 285, 286, 287, 289, 290

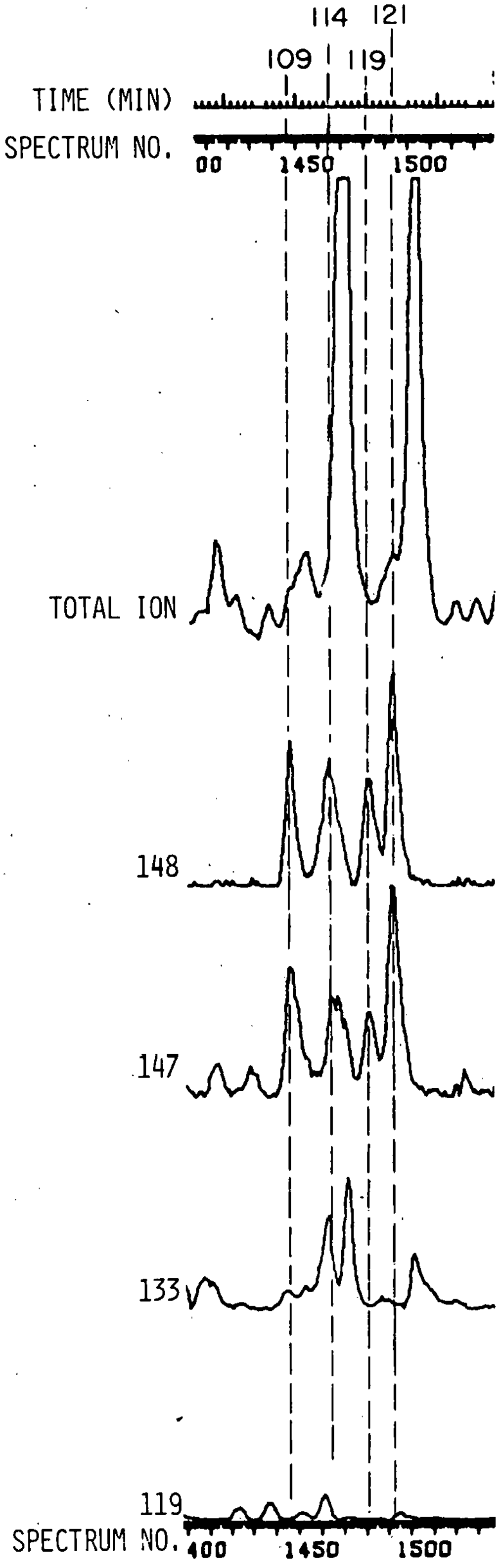
# MASSGRAM PLOTS OF KEY IONS (227, 228) FOR IDENTIFYING MISCELLANEOUS PNA's



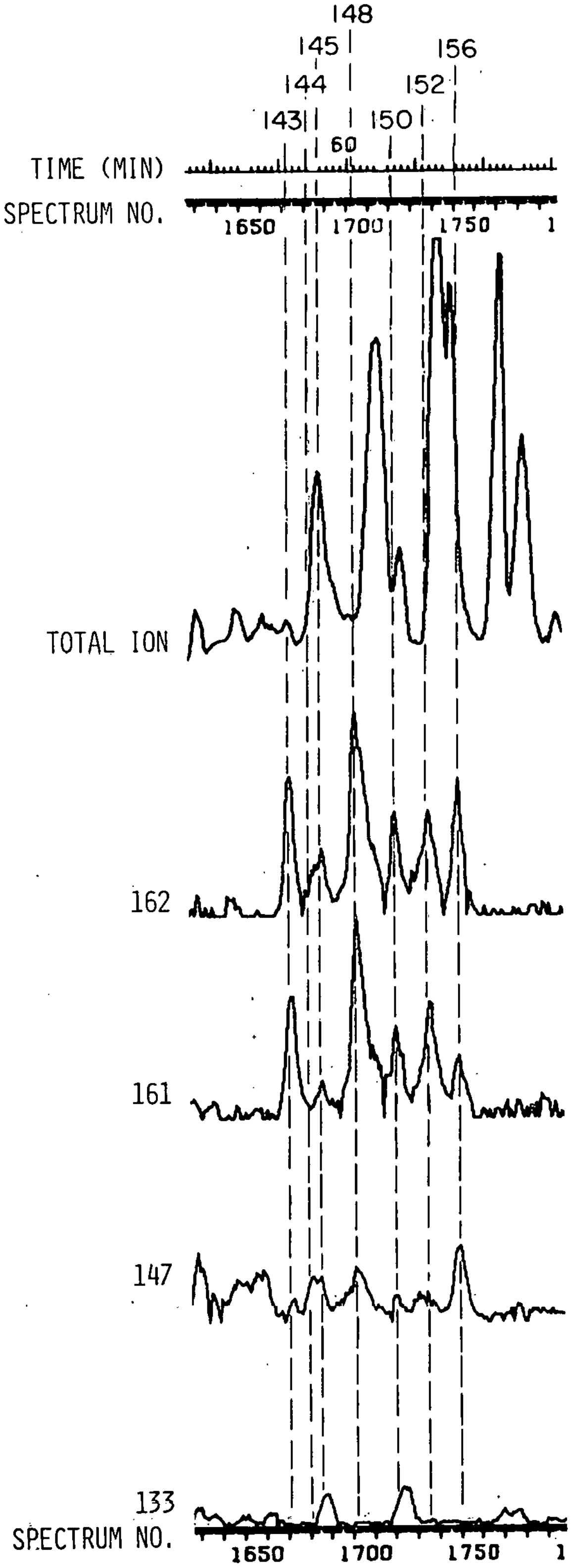
<u>MISCELLANEOUS PNA's</u>

| | |
|---|---|
| 298 | CHRYSENE |
| 299 | 1,2-BENZANTHRACENE |

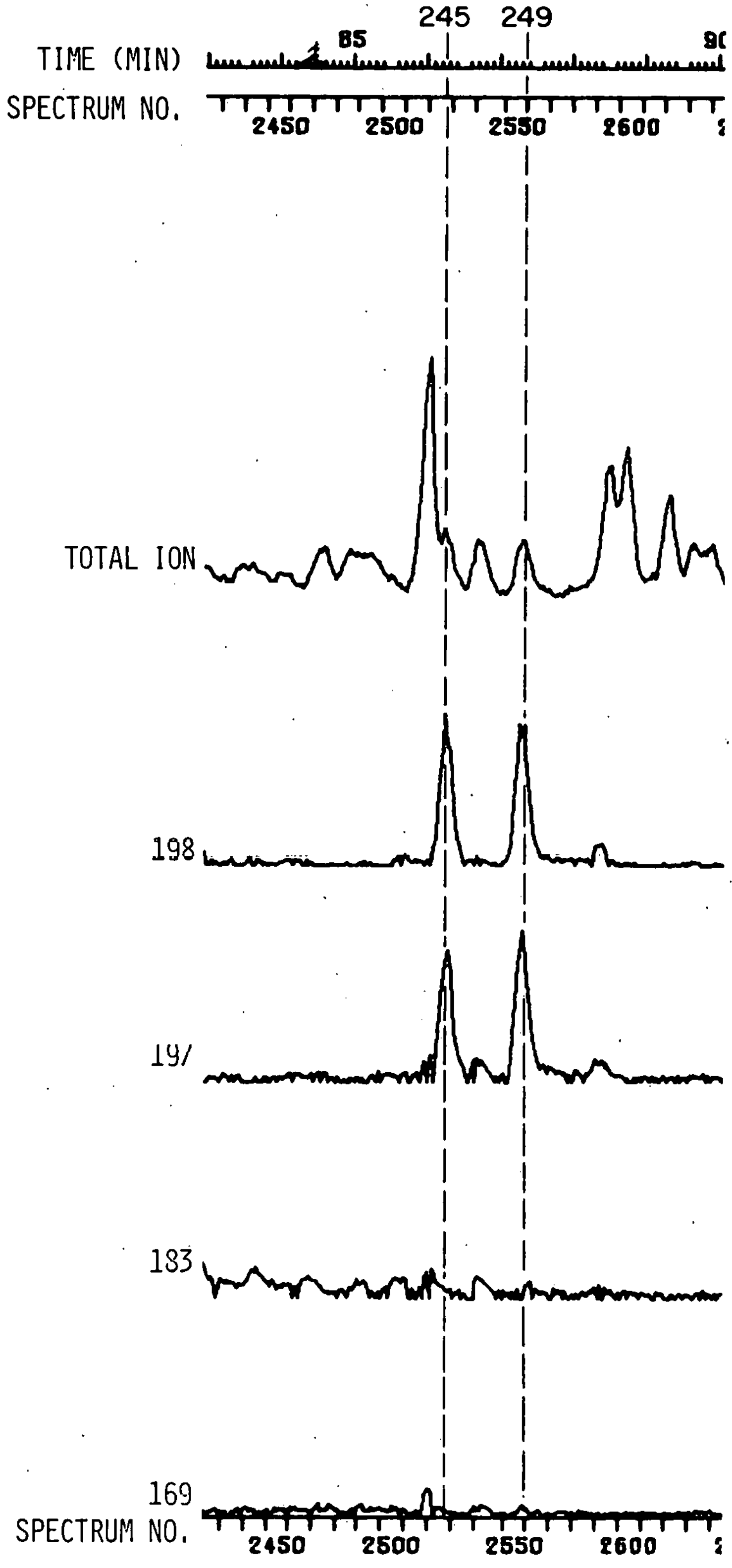
# MASSGRAM PLOTS OF KEY IONS (119, 133, 147, 148) FOR IDENTIFYING METHYL BENZOTHIOPHENES



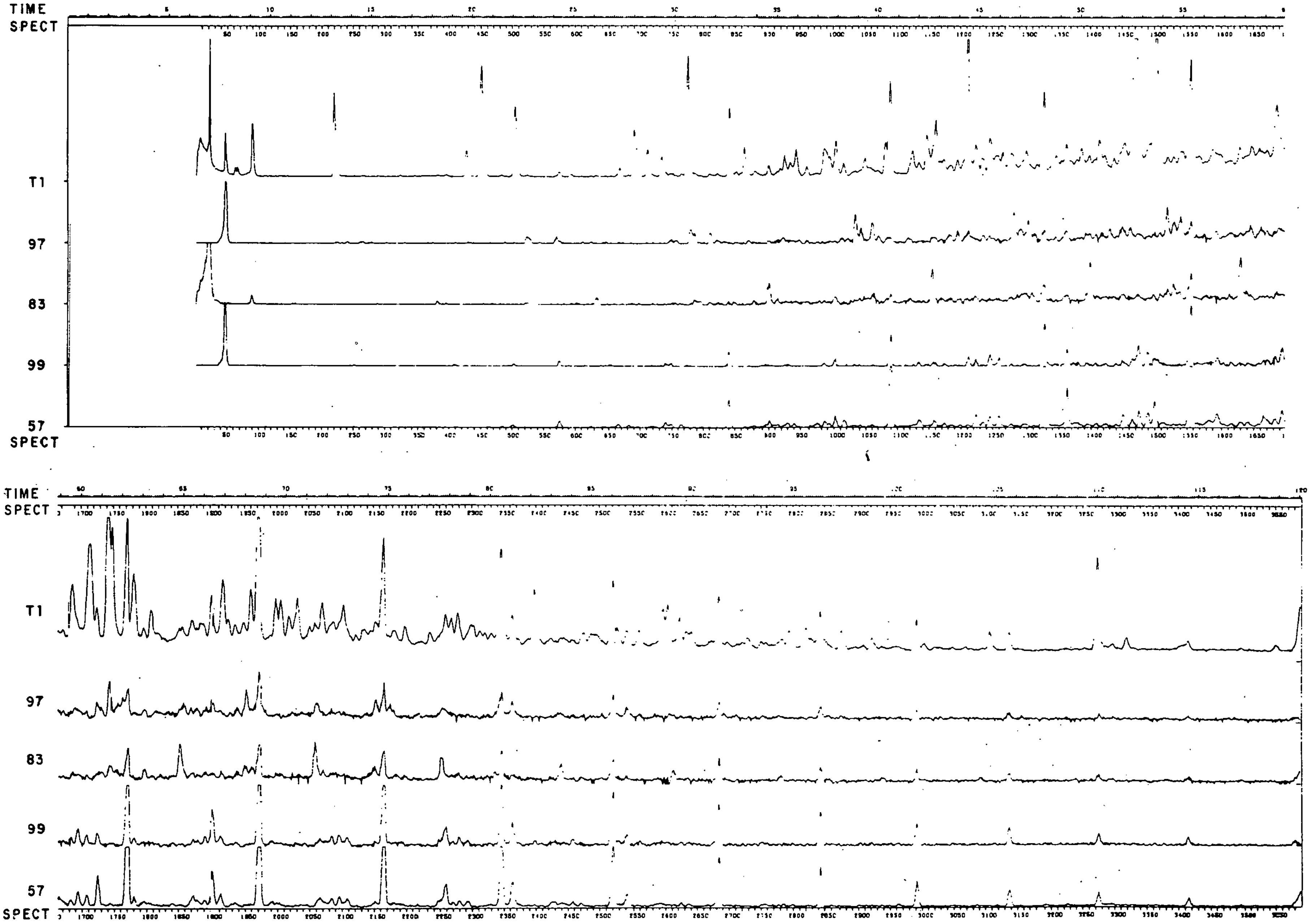
## MASSGRAM PLOTS OF KEY IONS (133, 147, 161, 162) FOR IDENTIFYING $C_2$-BENZOTHIOPHENES



## MASSGRAM PLOTS OF KEY IONS (169, 183, 197, 198) FOR IDENTIFYING METHYL DIBENZOTHIOPHENES



# MASSGRAM PLOTS OF KEY IONS (57, 99) FOR IDENTIFYING ALKANES AND KEY IONS (83, 97) FOR IDENTIFYING CYCLOALKANES



# APPENDIX E

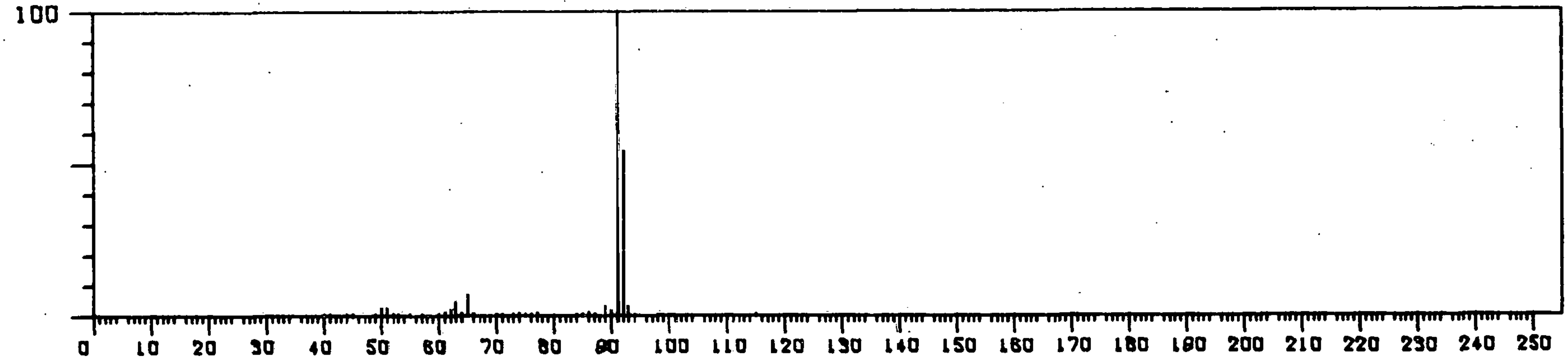
## Mass Spectra for Various Compounds in the Neutral Fraction of the DAF-Effluent Sample Listed According to Increasing Retention Time

| Retention Time (min.) | Compound Name | Page |
|---|---|---|
| 13.1 | toluene | E4 |
| 19.7 | ethyl benzene | E5 |
| 20.4 | p- and m-xylene | E6 |
| 22.1 | o-xylene | E7 |
| 27.3 | n-propyl benzene | E8 |
| 28.0 | m-ethyl toluene | E9 |
| 28.1 | p-ethyl toluene | E10 |
| 28.6 | 1,3,5-trimethyl benzene | E11 |
| 29.3 | o-ethyl toluene | E12 |
| 32.5 | n-decane & 1,2,3-trimethyl benzene (mixture) | E13 |
| 30.6 | 1,2,4-trimethyl benzene | E14 |
| 32.7 | trimethyl benzene | E15 |
| 33.4 | indan | E16 |
| 35.3 | m-n-proply toluene | E17 |
| 35.6 | p-n-propyl toluene & n-butyl benzene (mixture) | E18 |
| 35.9 | 1,3-dimethyl-5-ethyl benzene | E19 |
| 36.4 | o-n-propyl toluene | E20 |
| 37.3 | 1,4-dimethyl-2-ethyl benzene | E21 |
| 37.4 | 1,3-dimethyl-4-ethyl benzene | E22 |
| 37.9 | 1,2-dimethyl-4-ethyl benzene | E23 |
| 40.3 | 1,2,4,5-tetramethyl benzene | E24 |
| 40.5 | 1,2,3,5-tetramethyl benzene & n-undecane (mixture) | E25 |
| 42.8 | 1,2,3,4-tetramethyl benzene | E26 |
| 43.1 | tetralin | E27 |
| 44.4 | naphthalene | E28 |
| 44.7 | $C_5$-benzene | E29 |
| 48.2 | n-dodecane | E30 |
| 50.0 | dimethyl indan | E31 |
| 51.9 | methyl benzothiophene | E32 |

| Retention Time (min.) | Compound Name | Page |
|---|---|---|
| 52.2 | methyl ethyl indan | E33 |
| 52.7 | 2-methyl naphthalene | E34 |
| 53.0 | methyl benzothiophene | E35 |
| 53.7 | 1-methyl naphthalene | E36 |
| 55.3 | n-tridecane | E37 |
| 58.3 | biphenyl | E38 |
| 59.1 | dimethyl benzothiophene | E39 |
| 59.5 | ethyl naphthalene | E40 |
| 60.4 | dimethyl naphthalene | E41 |
| 60.7 | $C_{13}$-alkane | E42 |
| 61.3 | dimethyl naphthalene | E43 |
| 61.5 | dimethyl naphthalene | E44 |
| 62.2 | n-tetradecane | E45 |
| 62.5 | dimethyl naphthalene | E46 |
| 63.3 | dimethyl naphthalene | E47 |
| 64.9 | acenaphthene | E48 |
| 65.4 | methyl biphenyl | E49 |
| 66.0 | methyl biphenyl | E50 |
| 68.6 | n-pentadecane & some $C_3$-naphthalene | E51 |
| 71.1 | fluorene | E52 |
| 72.3 | methyl acenaphthene | E53 |
| 74.8 | hexadecane | E54 |
| 75.8 | $C_4$-naphthalene | E55 |
| 77.0 | $C_4$-naphthalene | E56 |
| 77.8 | $C_4$-naphthalene | E57 |
| 78.3 | methyl fluorene | E58 |
| 80.5 | n-heptadecane | E59 |
| 80.6 | dibenzothiophene | E60 |
| 82.2 | anthracene/phenanthrene | E61 |
| 84.6 | $C_2$-fluorene | E62 |
| 84.9 | $C_2$-fluorene | E63 |
| 85.2 | $C_2$-fluorene | E64 |

| Retention Time (min.) | Compound Name | Page |
|---|---|---|
| 86.0 | n-octadecane | E65 |
| 86.2 | methyl dibenzothiophene | E66 |
| 87.3 | methyl dibenzothiophene | E67 |
| 88.5 | methyl phenanthrene | E68 |
| 88.7 | methyl phenanthrene | E69 |
| 89.6 | 2-methyl anthracene | E70 |
| 89.9 | 1-methyl anthracene | E71 |
| 91.2 | n-nonadecane | E72 |
| 98.9 | pyrene | E73 |
| 101.1 | n-heneicosane | E74 |
| 105.6 | n-docosane | E75 |
| 113.9 | chrysene | E76 |
| 114.2 | 1,2-benzathracene | E77 |

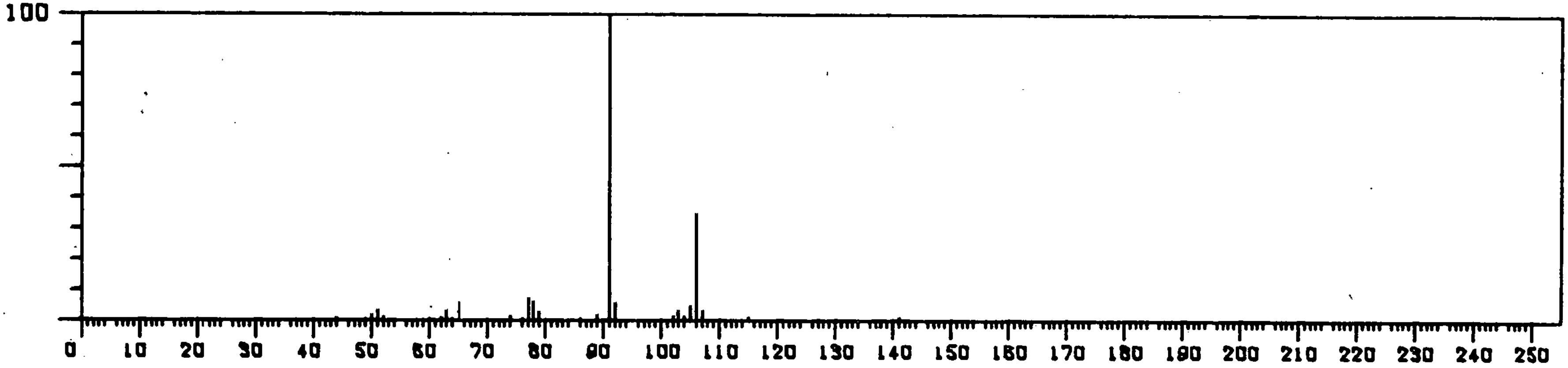
FRN 13201   SPEC 220      RET. TIME  13.  1            TOLUENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 428 RET. TIME 18. 7 ETHYL BENZENE

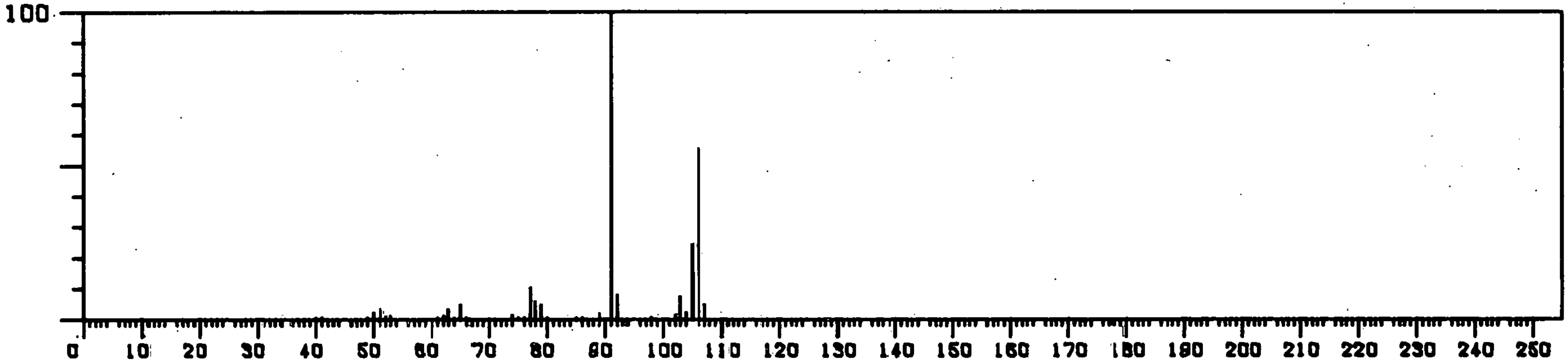


E5

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201   SPEC 452   RET. TIME  20.  4   P & M-XYLENE

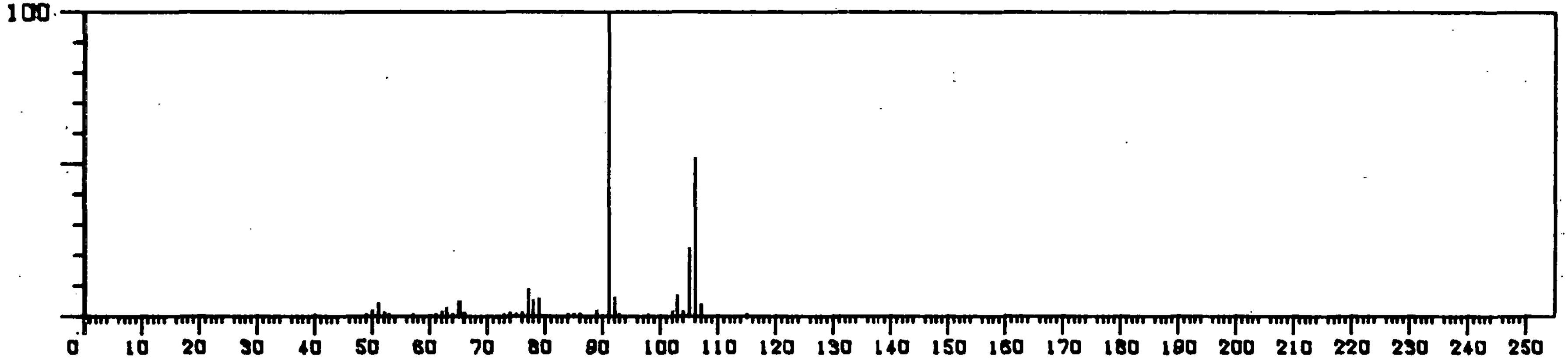


E6

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 505 RET. TIME 22. 1 O-XYLENE

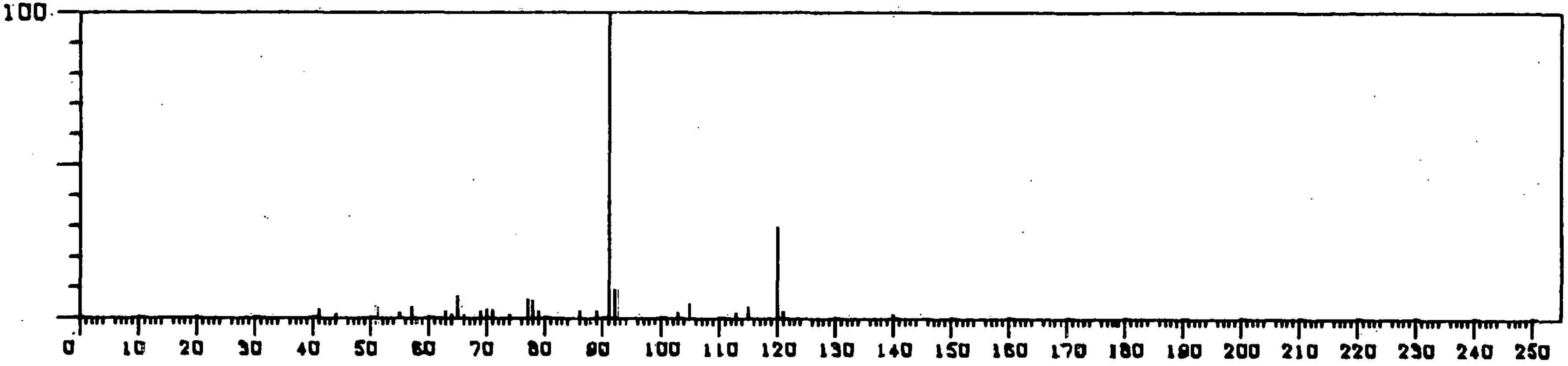


E7

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

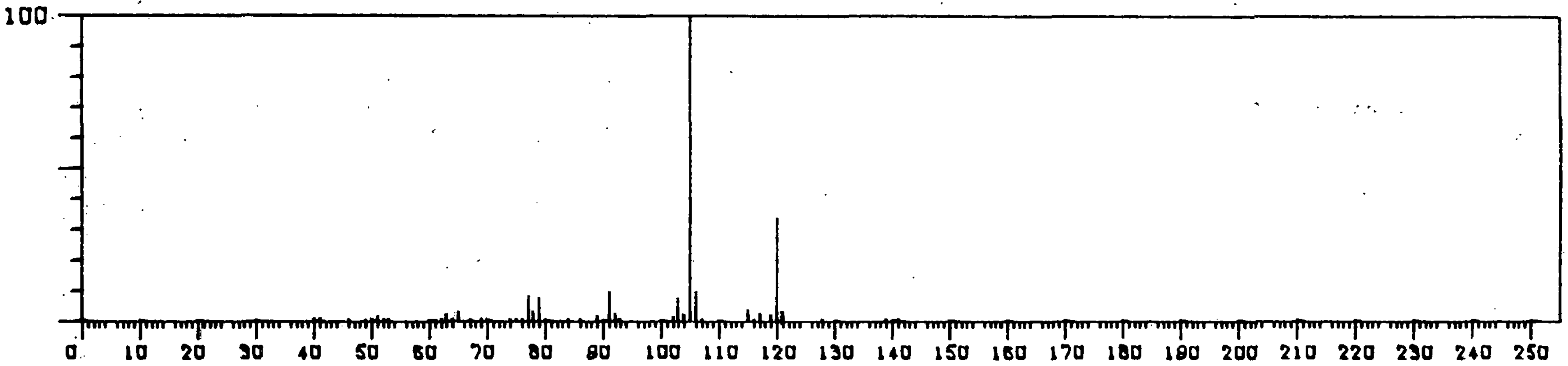
FRN 13201 SPEC 668 RET. TIME 27. 3 N-PROPYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

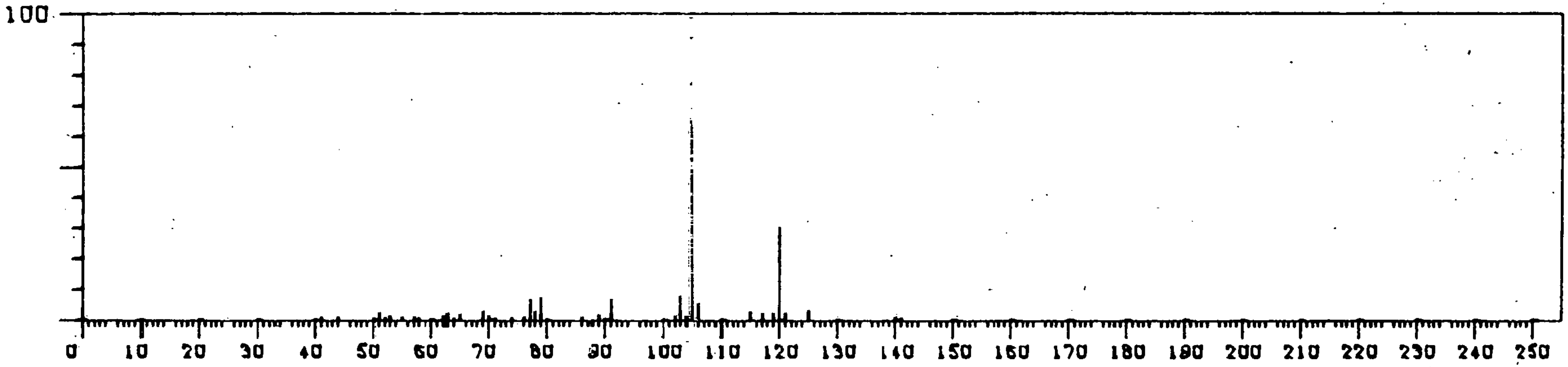
FRN 13201 SPEC 691 RET. TIME 28. 0 M-ETHYL TOLUENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 686 RET. TIME 28. 1 P-ETHYL TOLUENE

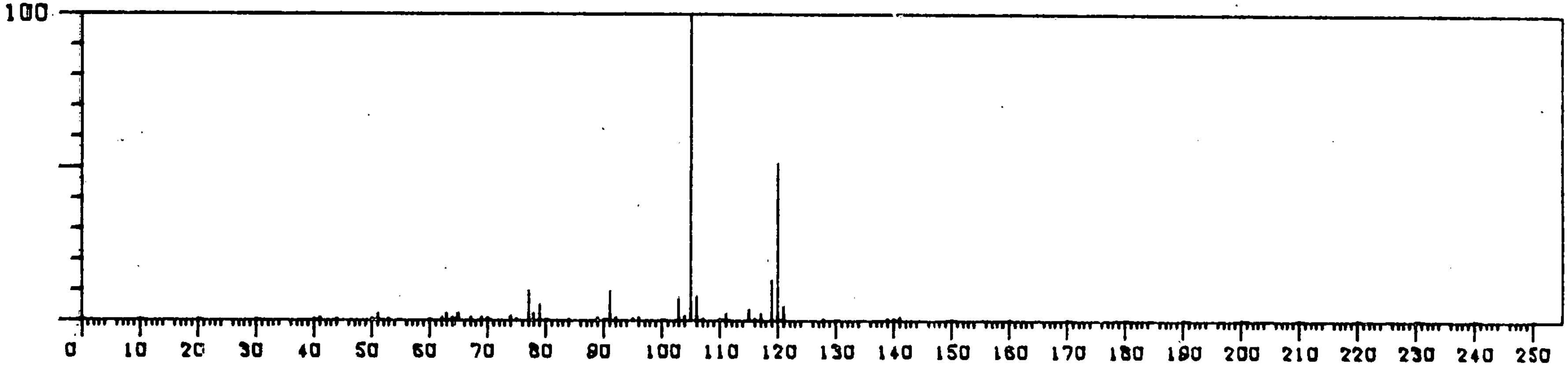


E10

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 712 RET. TIME 28. 6 1,3,5-TRIMETHYL BENZENE

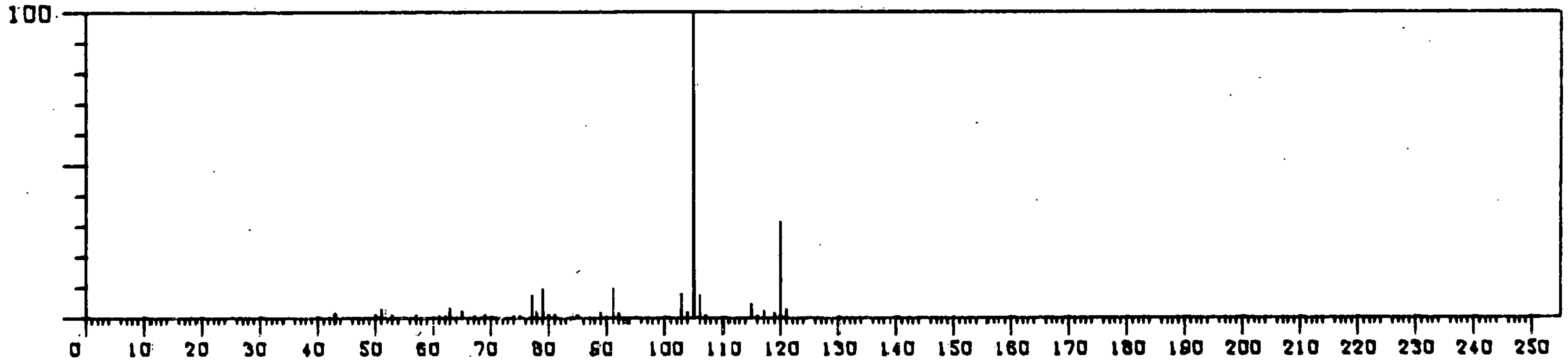


E11

DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

SOM OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

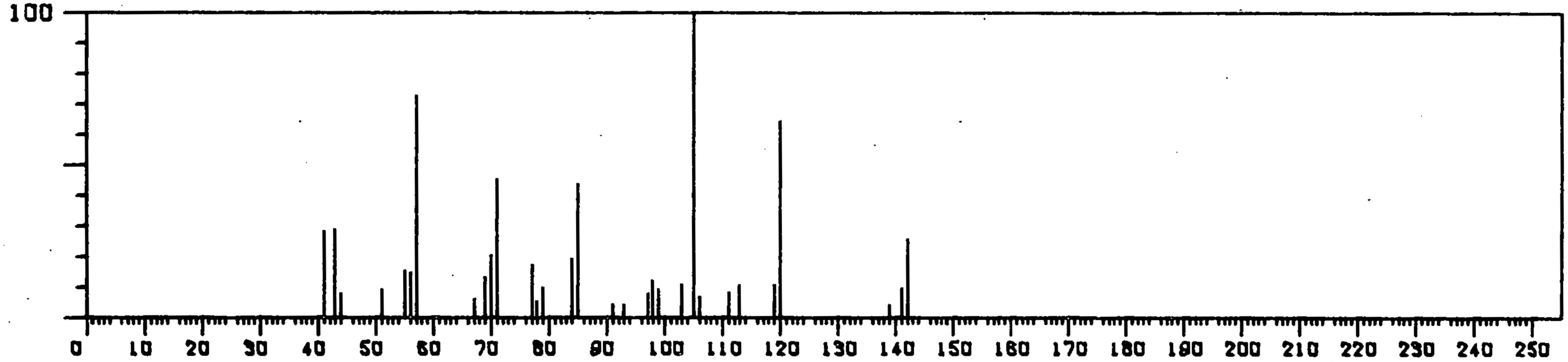
FRN 13201 SPEC 734 RET. TIME 28. 3 O-ETHYL TOLUENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

FRN 13201 SPEC 837 RET. TIME 32. 5 MIXTURE OF N-DECANE & 1,2,3-TRIMETHYL BENZENE

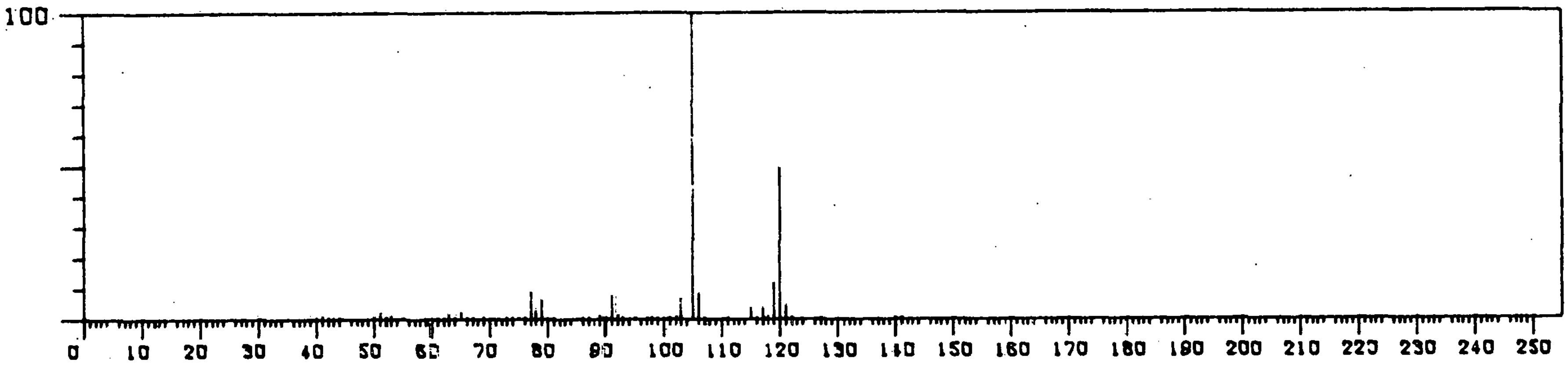


E13

DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

SOM OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

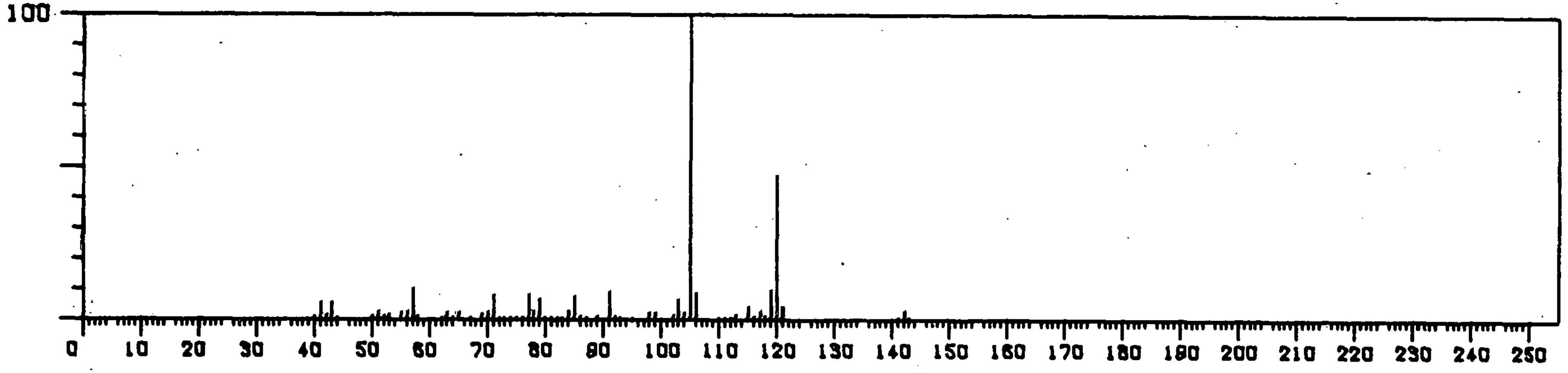
FRN 13201 SPEC 776 RET. TIME 30. 6 1.2.4-TRIMETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 842 RET. TIME 32. 7 1,2,3-TRIMETHYL BENZENE

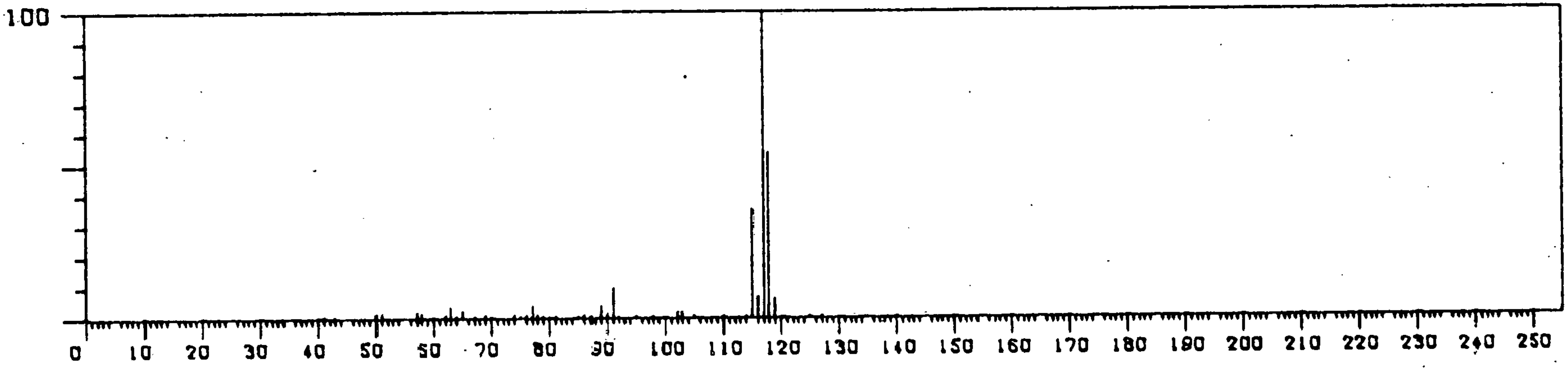


E15

DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

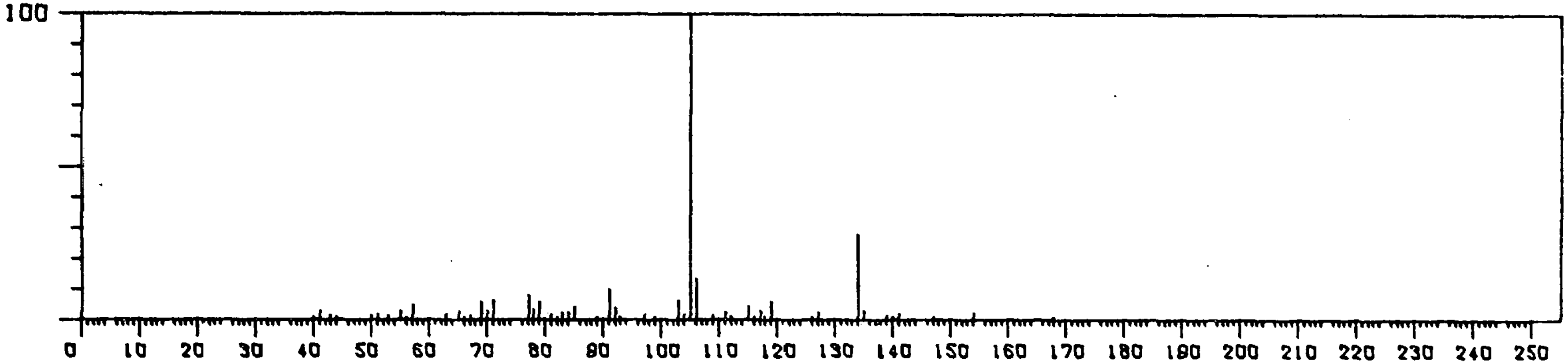
FRN 13201 SPEC 865 RET. TIME 33. 4 INDAN



DAF-1234-A-NEUTRAL/F-ME/CH2CL2,OIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

FRN 13201   SPEC 927      RET. TIME  35.  3            M-N-PROPYL TOLUENE

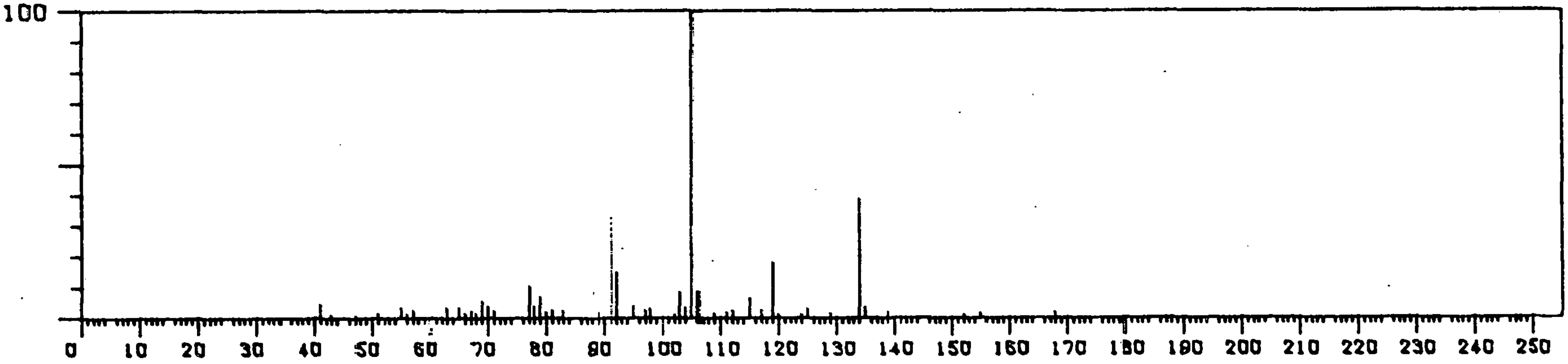


E17

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

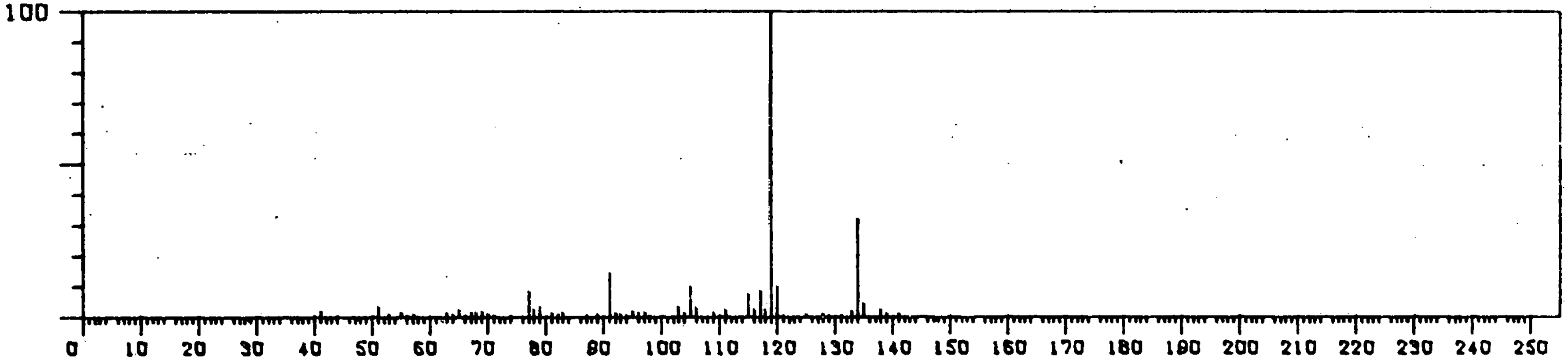
FRN 13201 SPEC 935 RET. TIME 35. 6 MIXTURE OF P-N-PROPYL TOLUENE & N-BUTYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

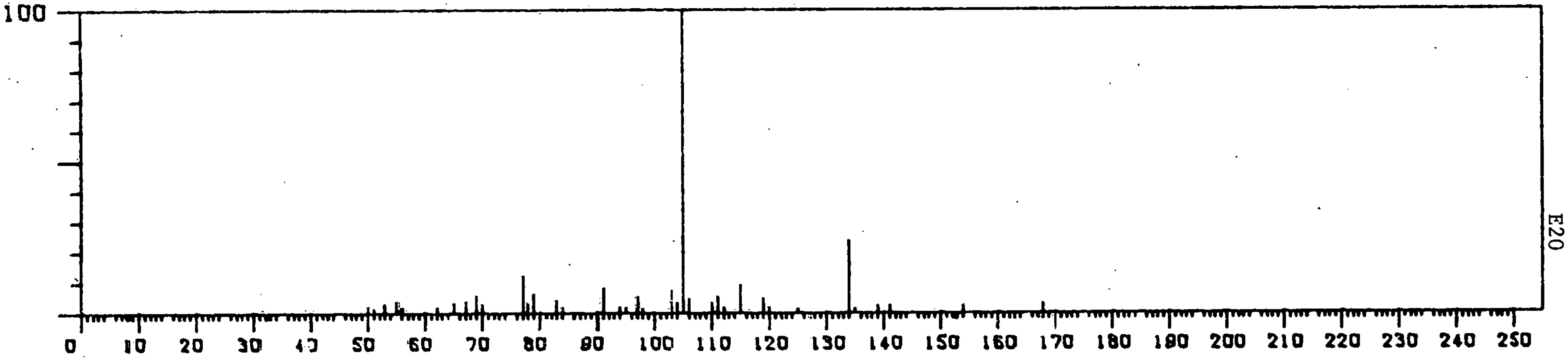
FRN 13201 SPEC 945 RET. TIME 35. 9 1.3-DIMETHYL-5-ETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

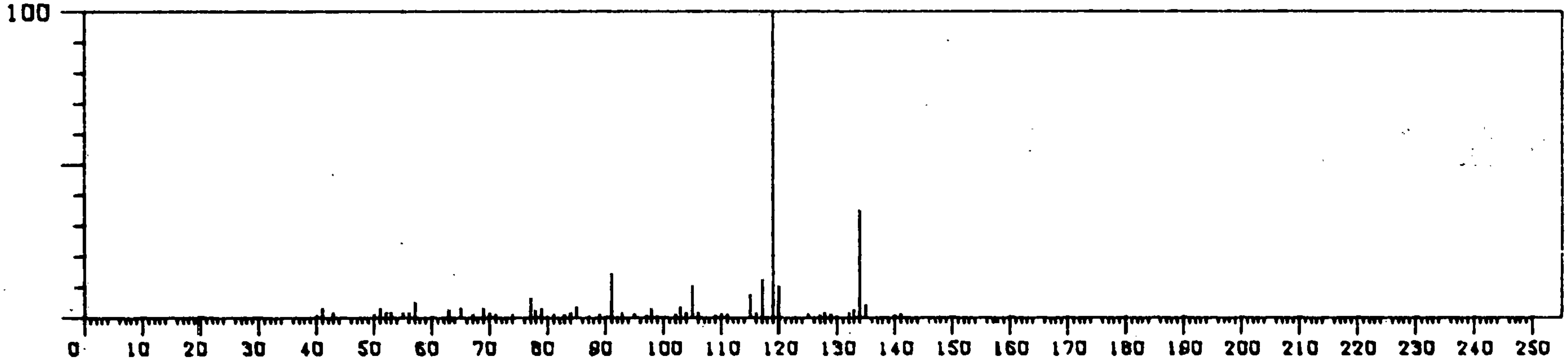
FRN 13201 SPEC 959 RET. TIME 36. 4 O-N-PROPYL TOULENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

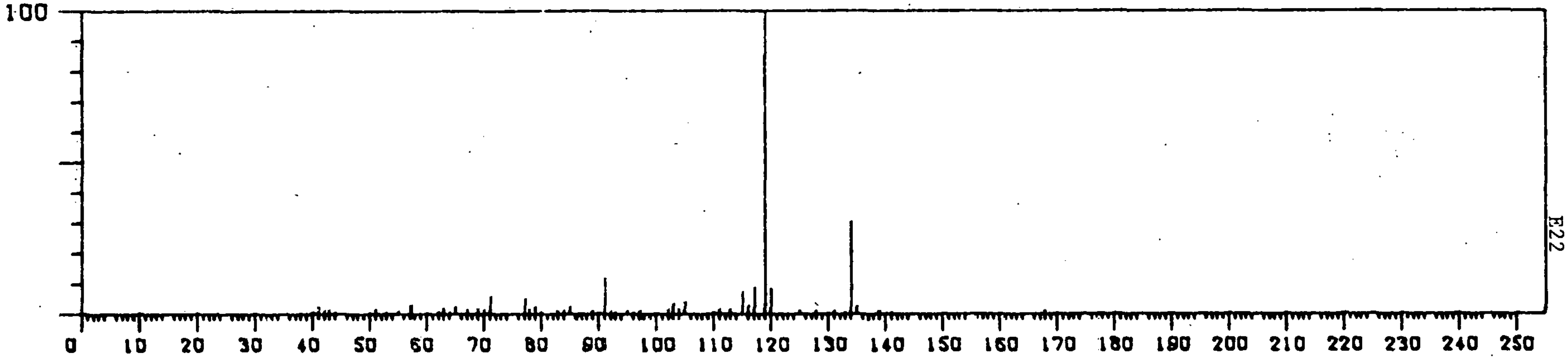
FRN 13201 SPEC 987 RET. TIME 37. 3 1.4-DIMETHYL-2-ETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

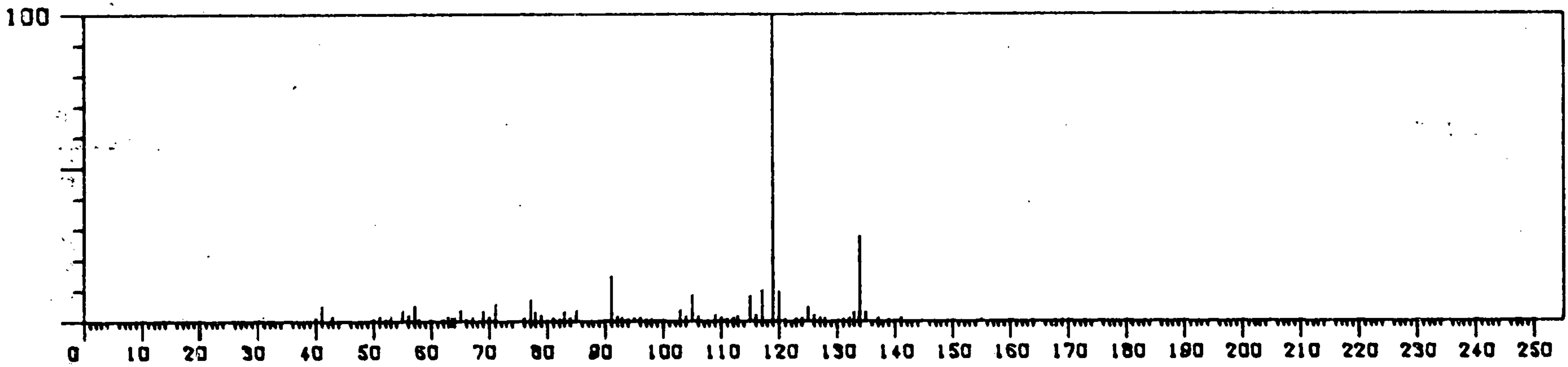
FRN 13201 SPEC 990 RET. TIME 37. 4 1.3-DIMETHYL-4-ETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1005 RET. TIME 37. 9 1.2-DIMETHYL-4-ETHYL BENZENE

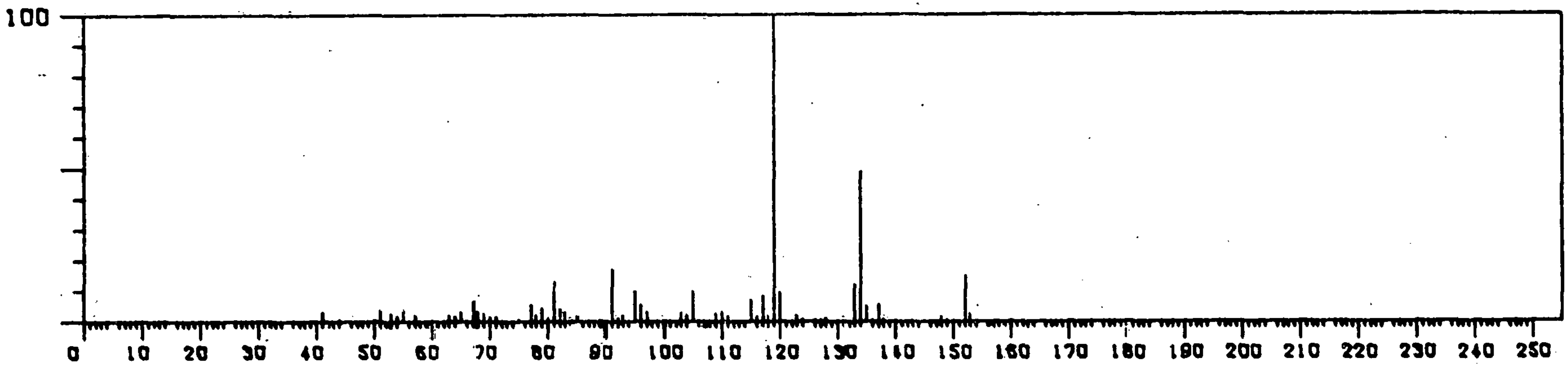


E23

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.OIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

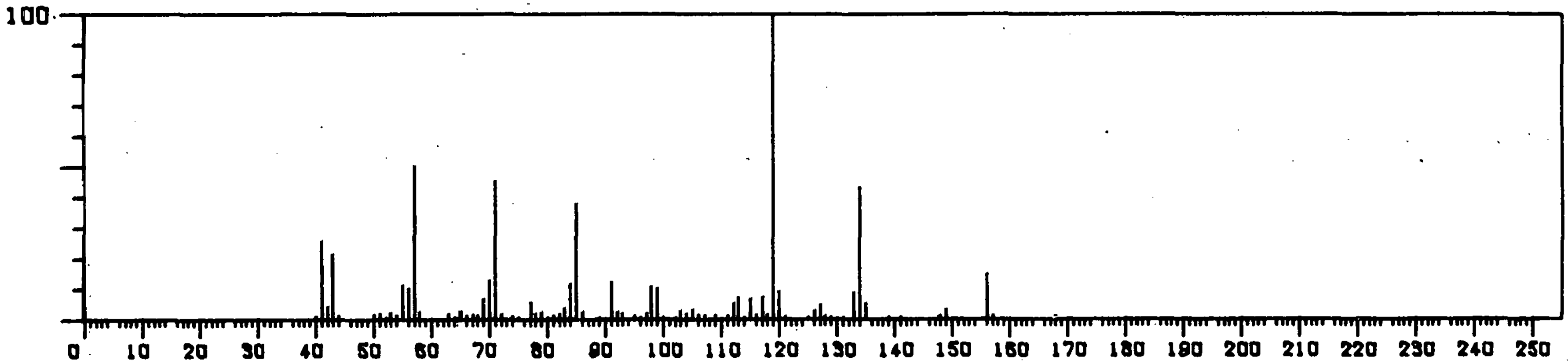
FRN 13201 SPEC 1082 RET. TIME 40. 3 1.2.4.5-TETRAMETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

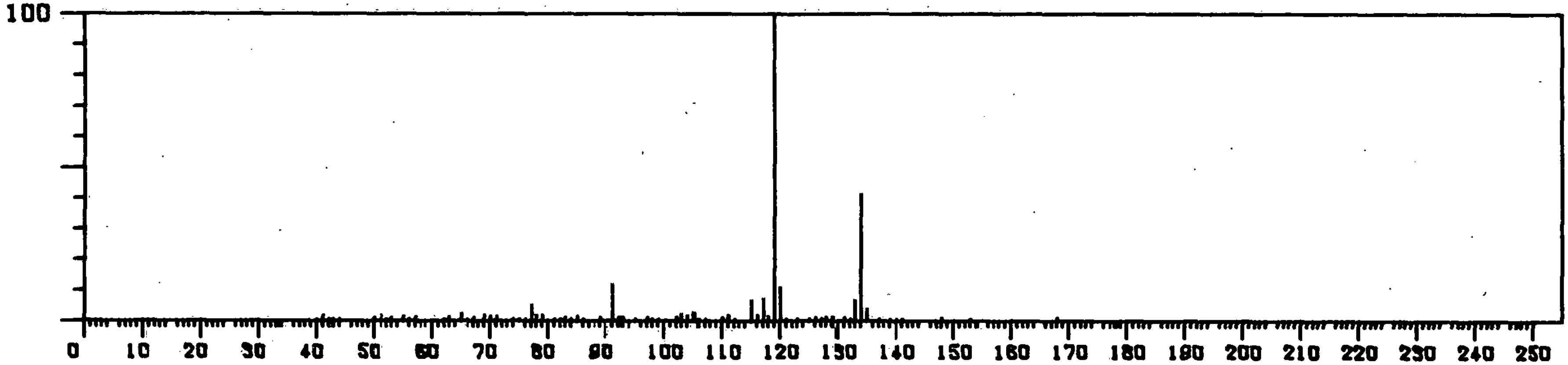
FRN 13201 SPEC 1080 RET. TIME 40. 5 MIXTURE OF 1,2,3,5-TETRAMETHYL BENZENE & N-UNDECANE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

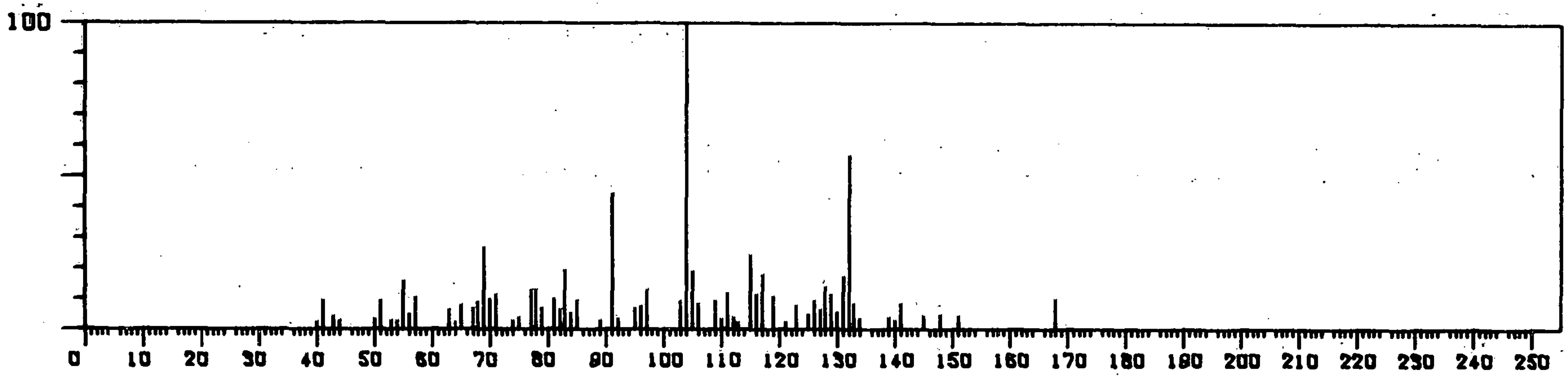
FRN 13201 SPEC 1162 RET. TIME 42. 8 1,2,3,4-TETRAMETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

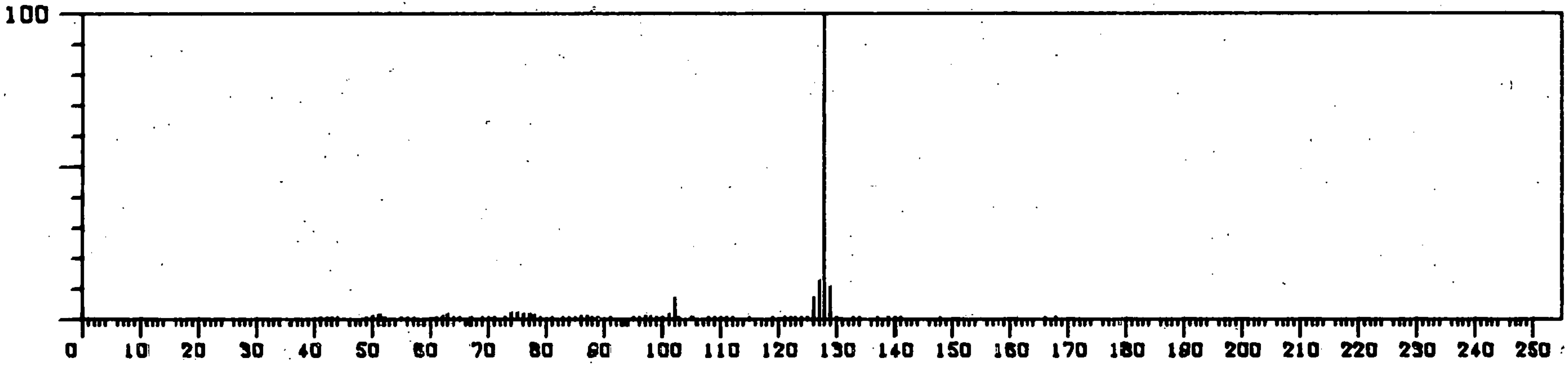
FRN 13201 SPEC 1170 RET. TIME 43. 1 TETRALIN



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

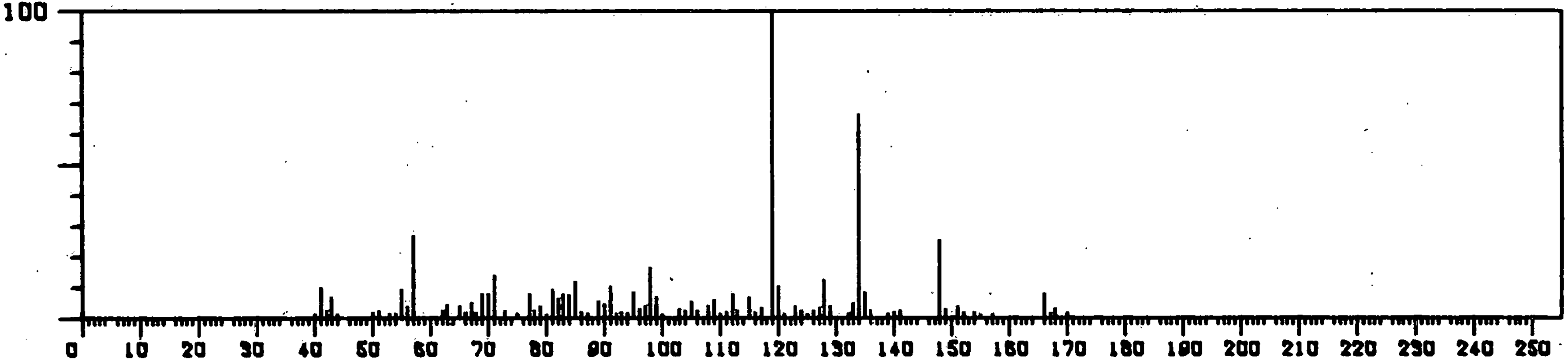
FRN 13201 SPEC 1213 RET. TIME 44. 4 NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1224 RET. TIME 44. 7 C5-BENZENE

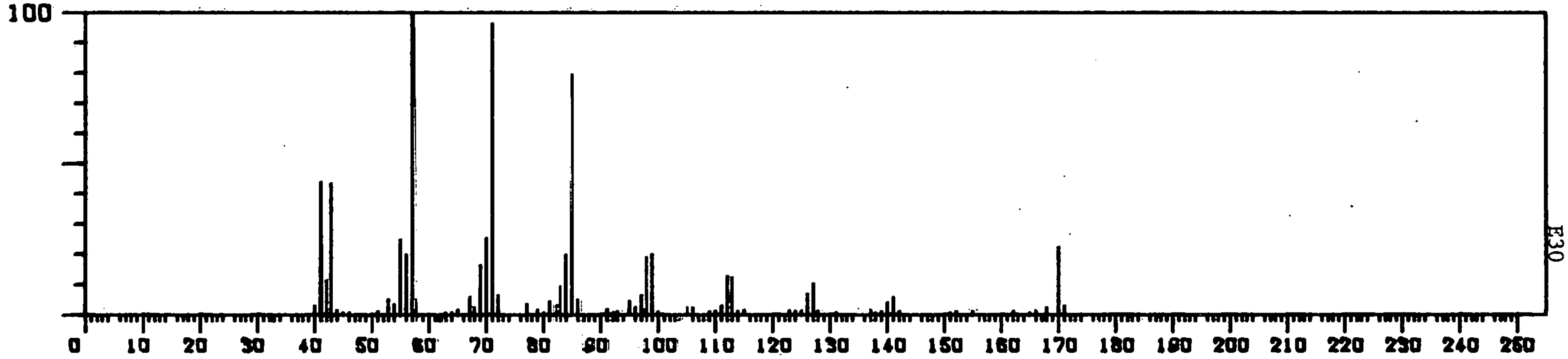


DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

SOM OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

E29

FRN 13201 SPEC 1328 RET. TIME 48. 2 N-DODECANE

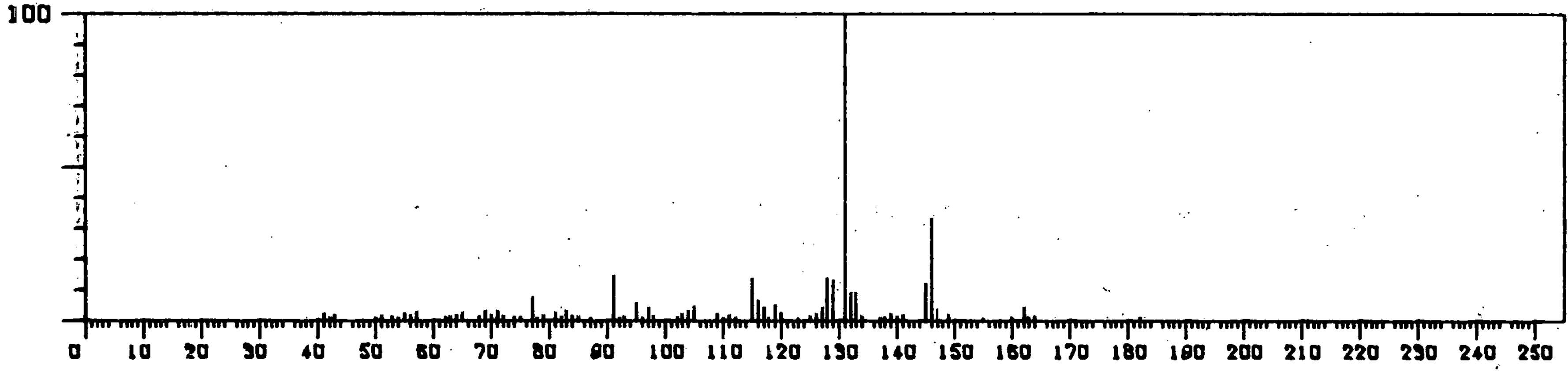


E30

DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

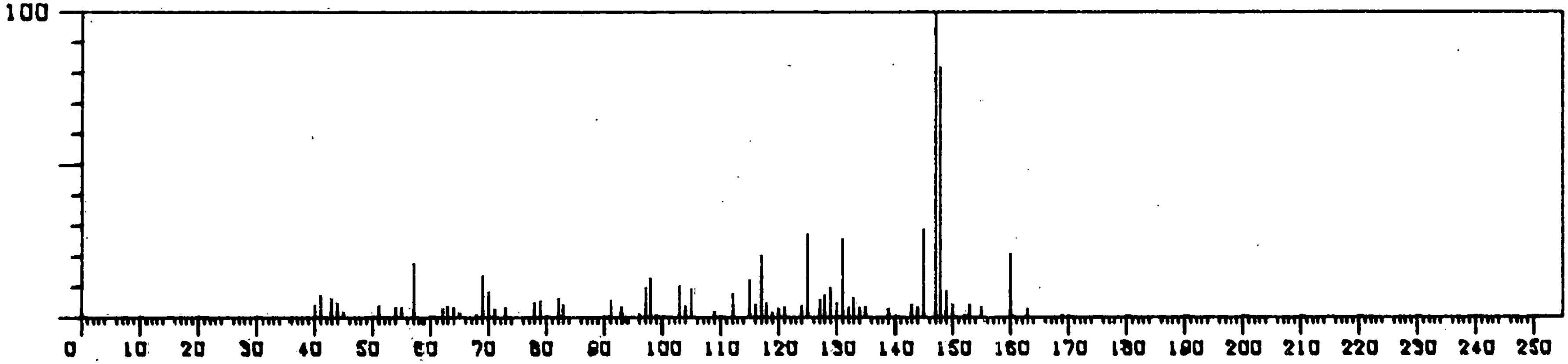
FRN 13201 SPEC 1387 RET. TIME 50. 0 DIMETHYL INDAN



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1447-1442 RET. TIME 51. 9 METHYL BENZOTHIOPHENE



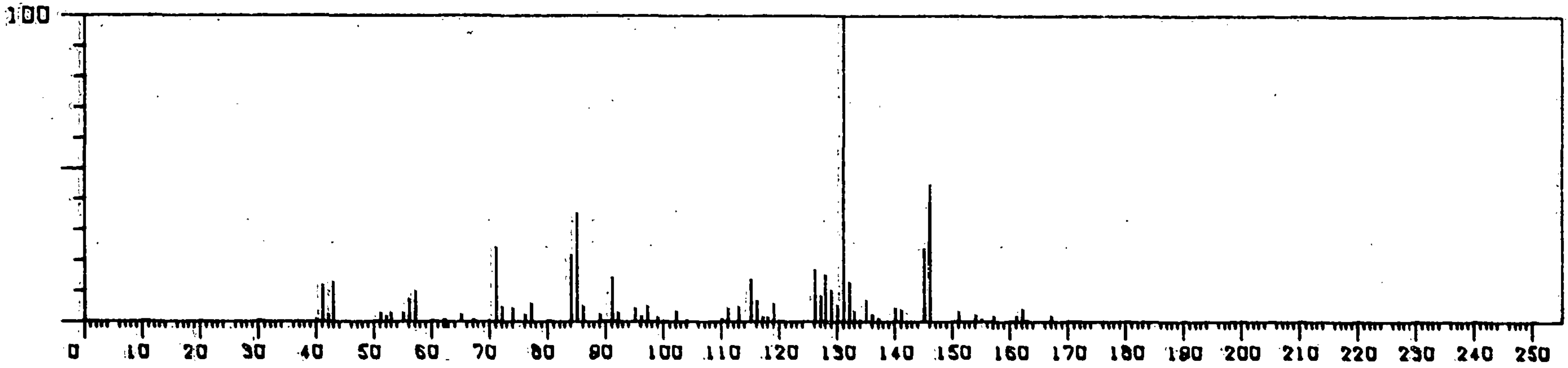
E32

AVGD SPECT

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 UL

FRN 13201 SPEC 1454-1447 RET. TIME 52. 2 METHYL ETHYL INDAN



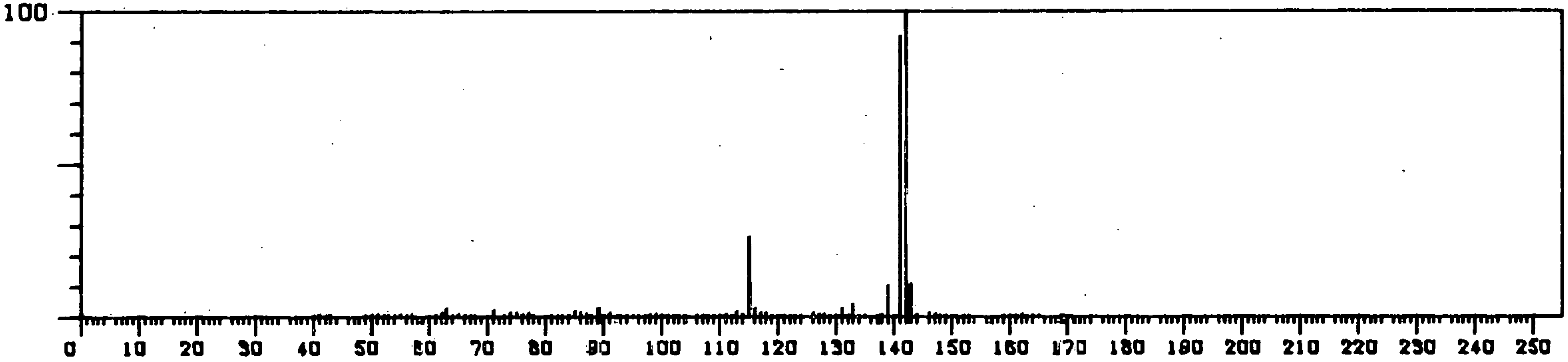
E33

AVGD SPECT

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 UL

FRN 13201  SPEC 1473    RET. TIME  52.  7          2-METHYL NAPHTHALENE

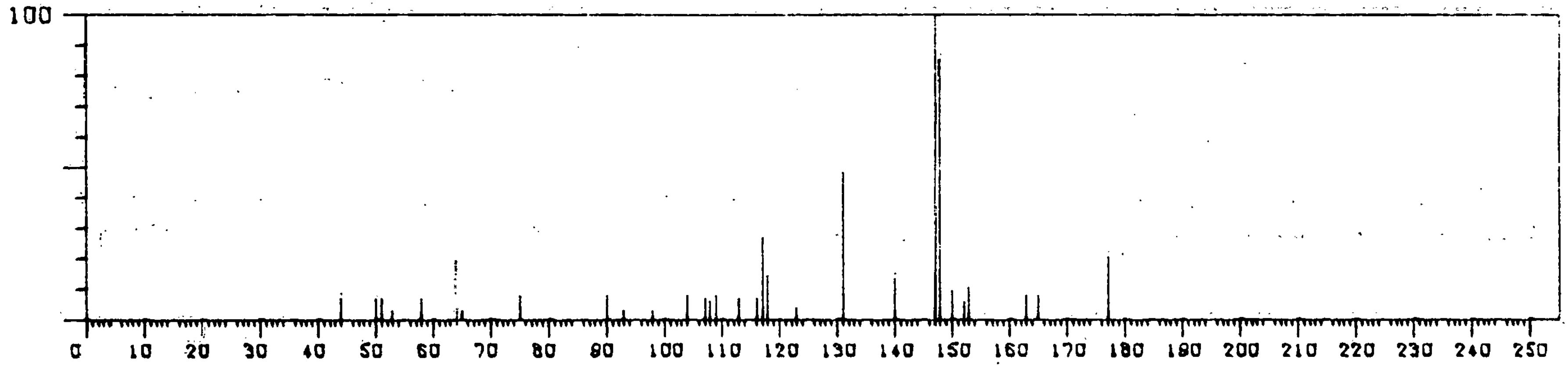


E34

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1483-1479 RET. TIME 53. 0 METHYL BENZOTHIOPHENE

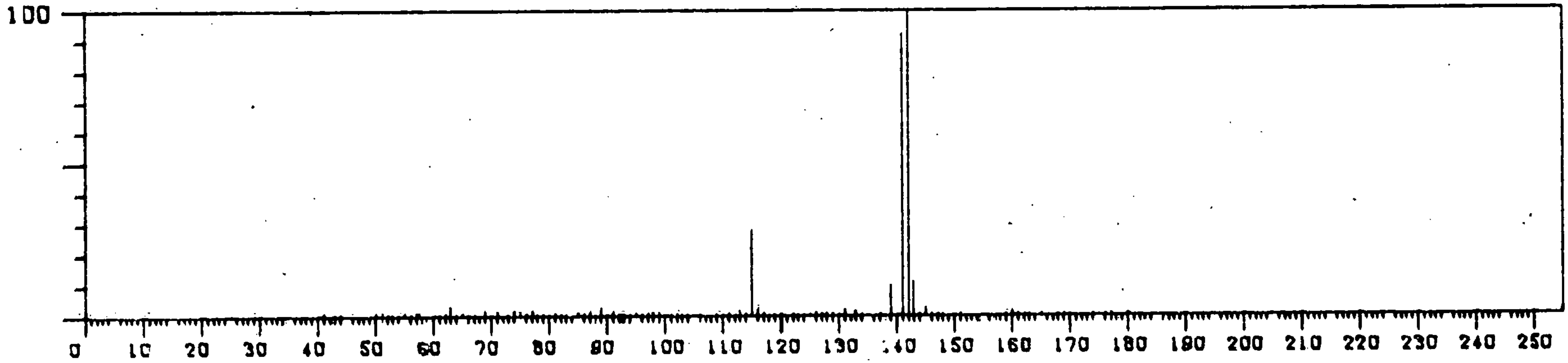


AVGD SPECT

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.OIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1:20:3 UL

FRN 13201 SPEC 1505 RET. TIME 53. 7 1-METHYL NAPHTHALENE

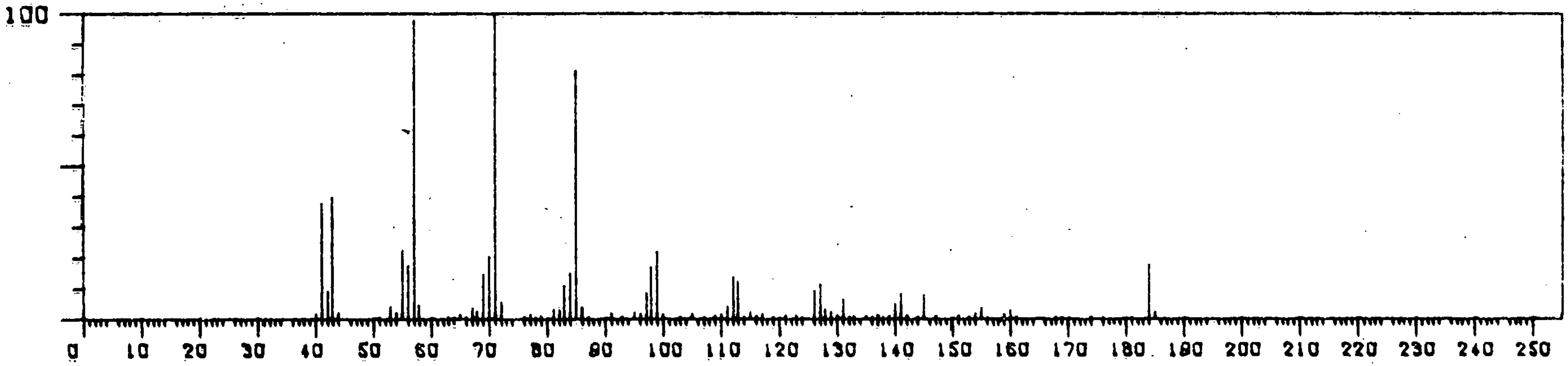


DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101;LP AT 2 DEG/MIN.TEMP 1.20.3 U

E36

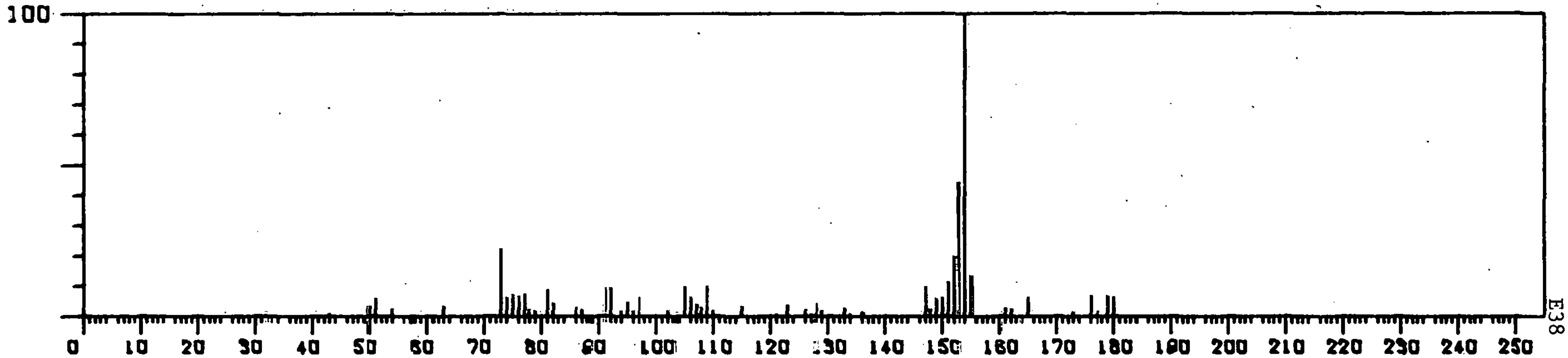
FRN 13201 SPEC 1557 RET. TIME 55. 3 N-TRIDECANE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201  SPEC 1648-1640  RET. TIME  58.  3  BIPHENYL

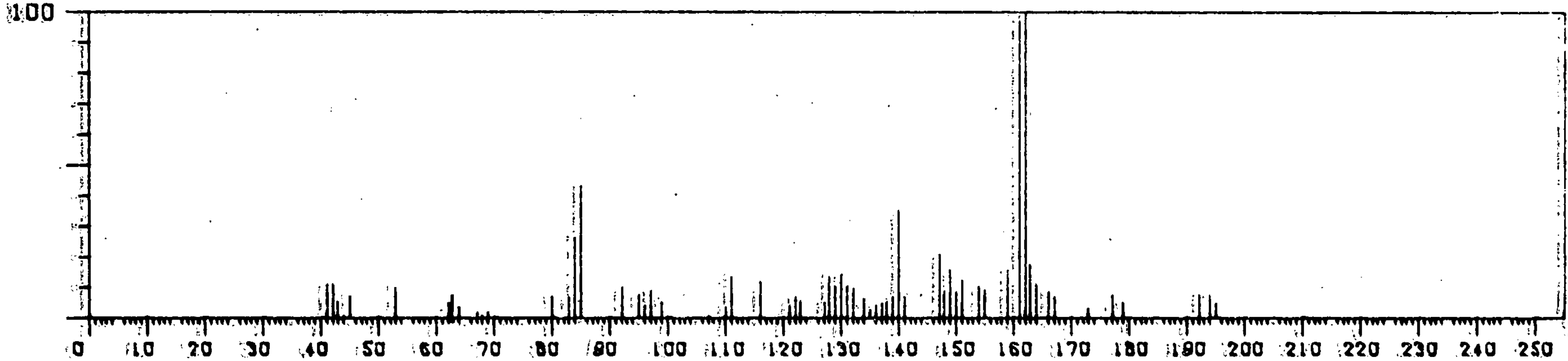


AVGD SPECT

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 UL

FRN 13201 SPEC 1672-1667 RET. TIME 59. 1 DIMETHYL BENZOTHIOPHENE



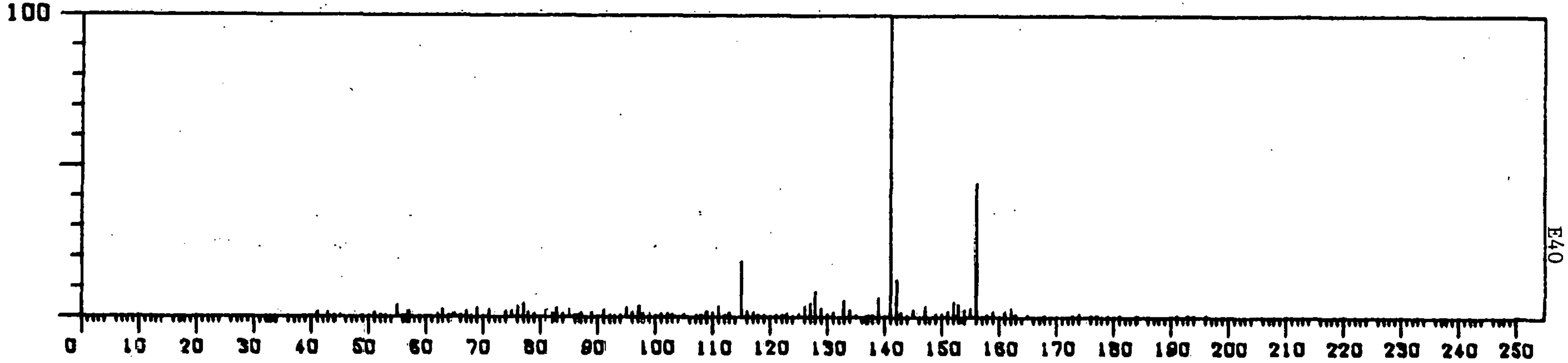
E39

AVGD SPECT

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 UL

FRN 13201 SPEC 1687 RET. TIME 58. 5 ETHYL NAPHTHALENE

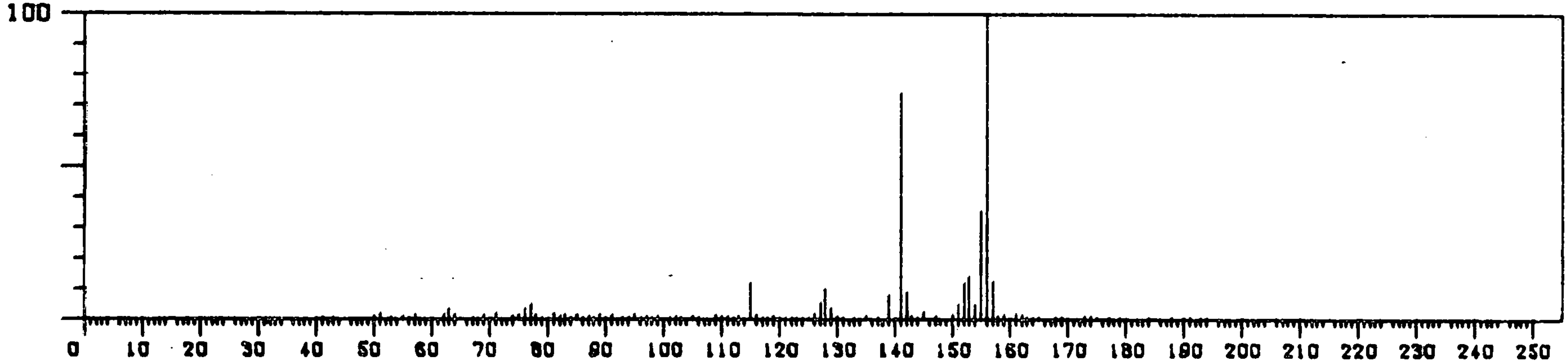


E40

DAF-1234-A-NEUTRAL/F-ME/CH2CL2,OIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

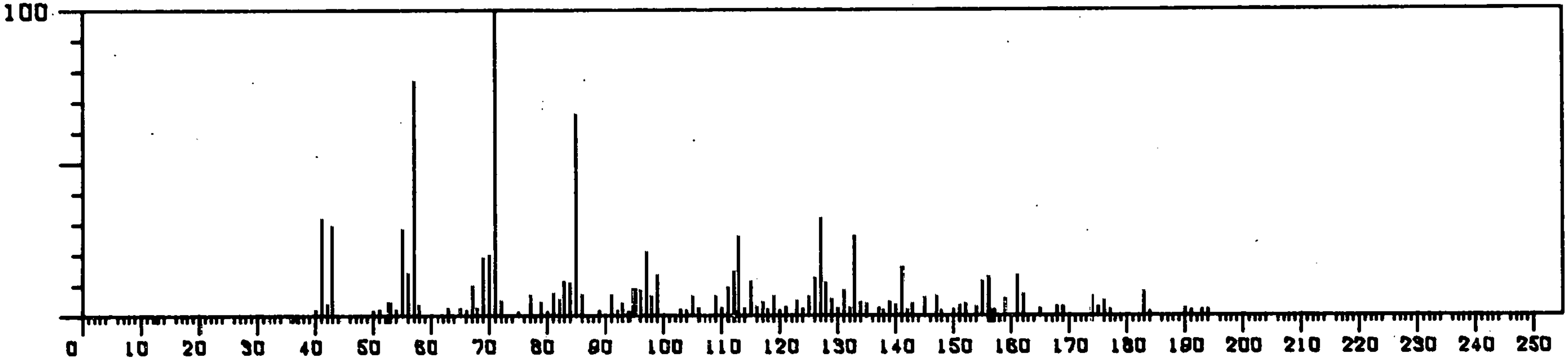
FRN 13201  SPEC 1714   RET. TIME  60.  4        DIMETHYL NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

FRN 13201   SPEC 1724     RET. TIME  60.  7            C13 ALKANE

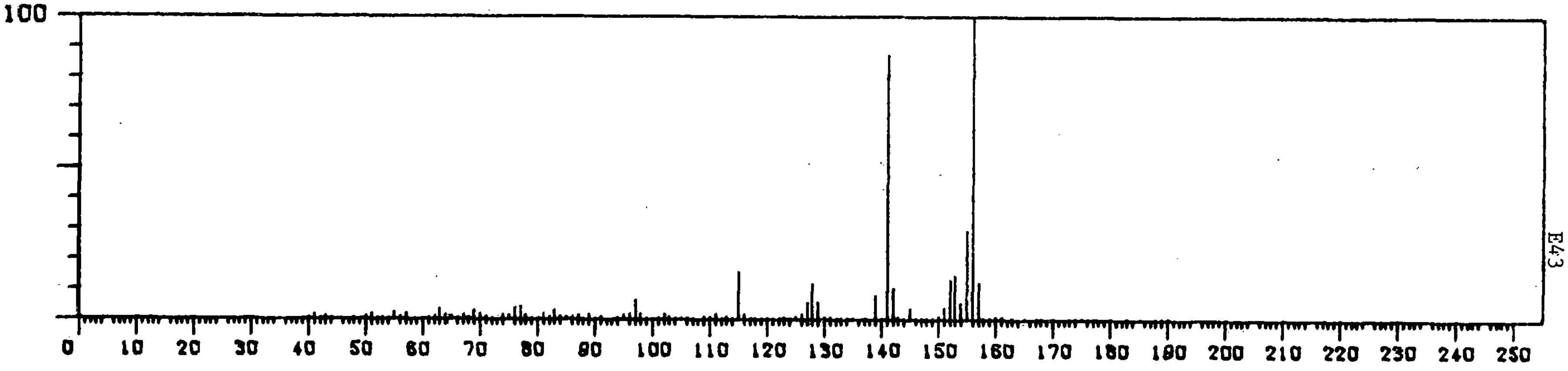


E42

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1,20,3 U

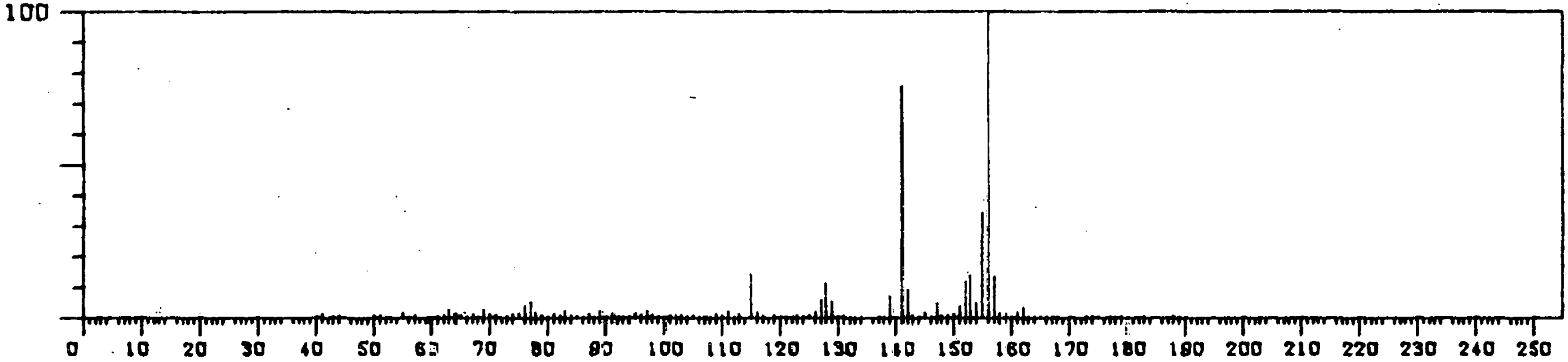
FRN 13201   SPEC 1743   RET. TIME  61.  3   DIMETHYL NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1748 RET. TIME 61. S DIMETHYL NAPHTHALENE

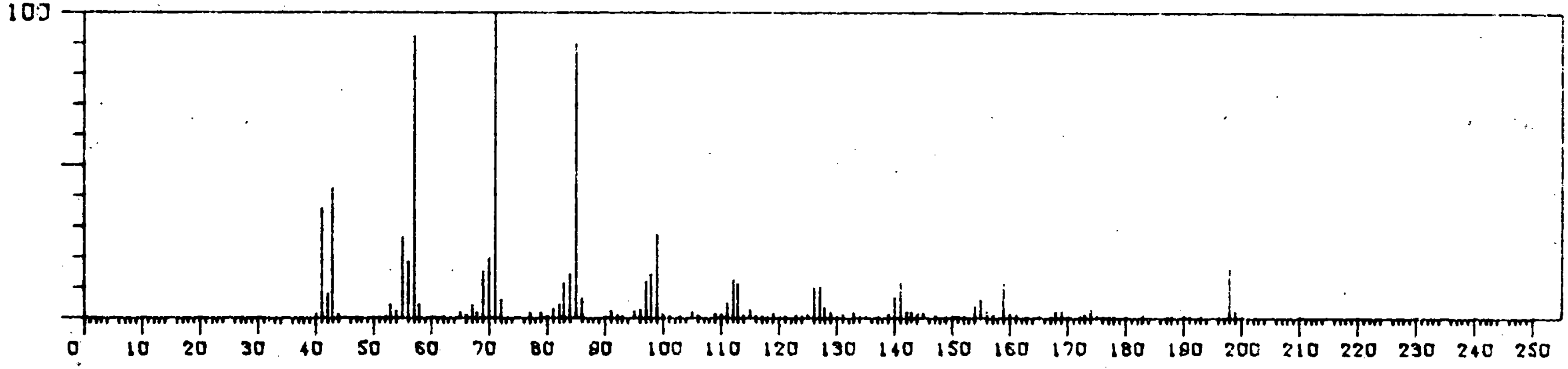


E44

DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

FRN 13201 SPEC 1772 RET. TIME 62. 2 N-TETRADECANE

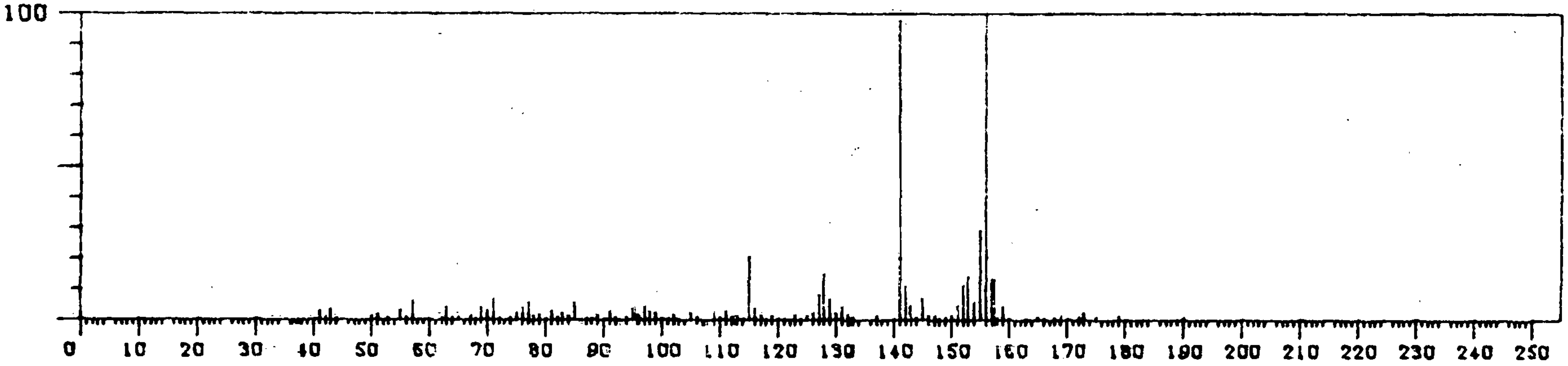


DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

E45

FRN 13201  SPEC 1782   RET. TIME  62.  5          DIMETHYL NAPHTHALENE

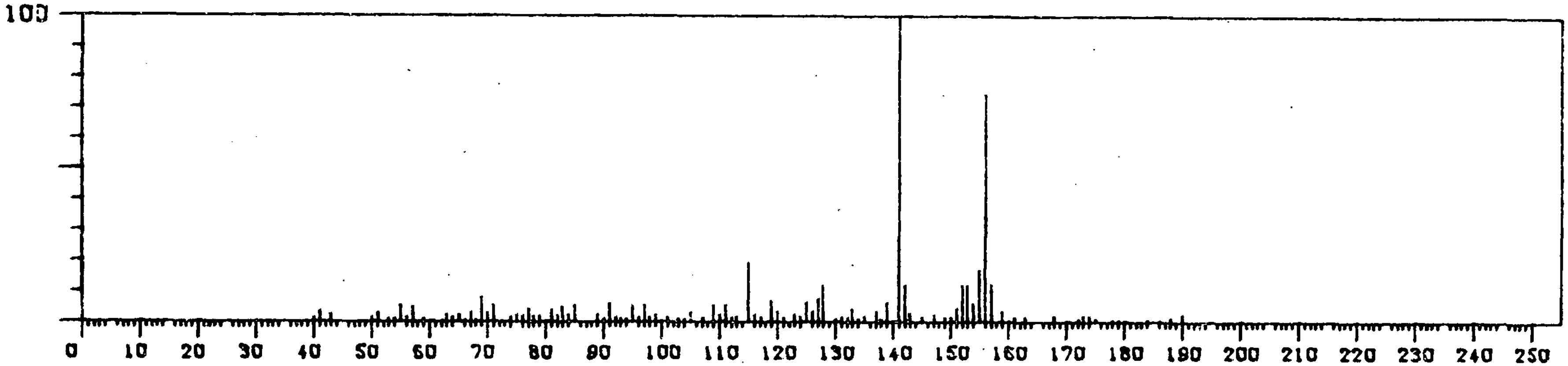


E46

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1.20.3 U

FRN 13201   SPEC 1808   RET. TIME  63.  3          DIMETHYL NAPHTHALENE

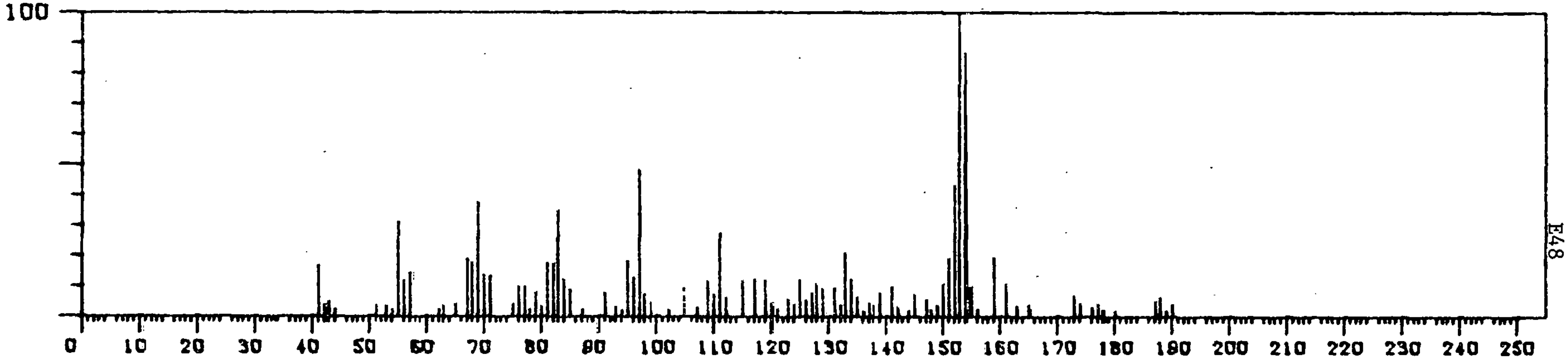


DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

E47

FRN 13201 SPEC 1858 RET. TIME 64. 9 ACENAPHTHENE

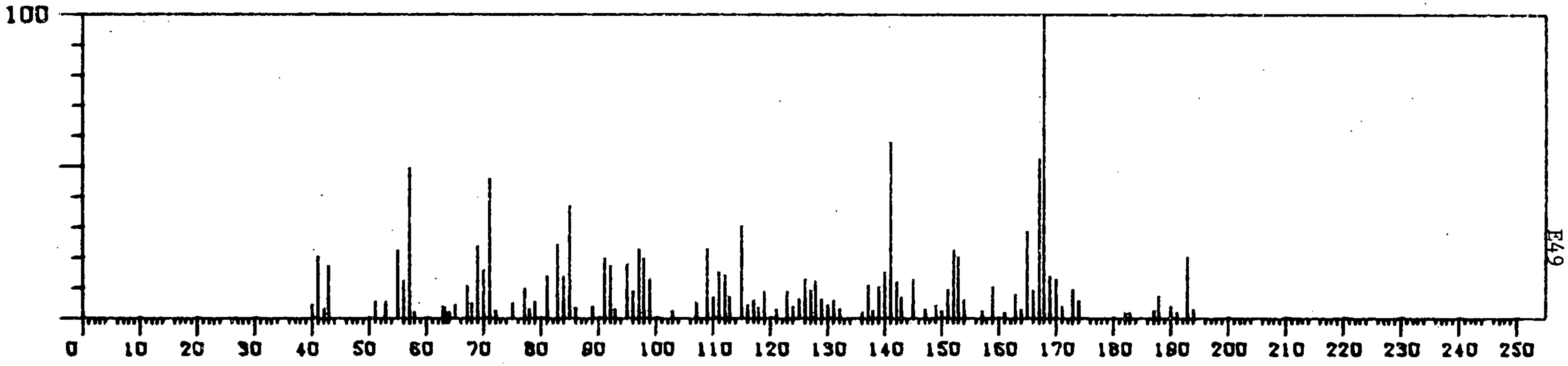


E48

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1872 RET. TIME 65. 4 METHYL BIPHENYL

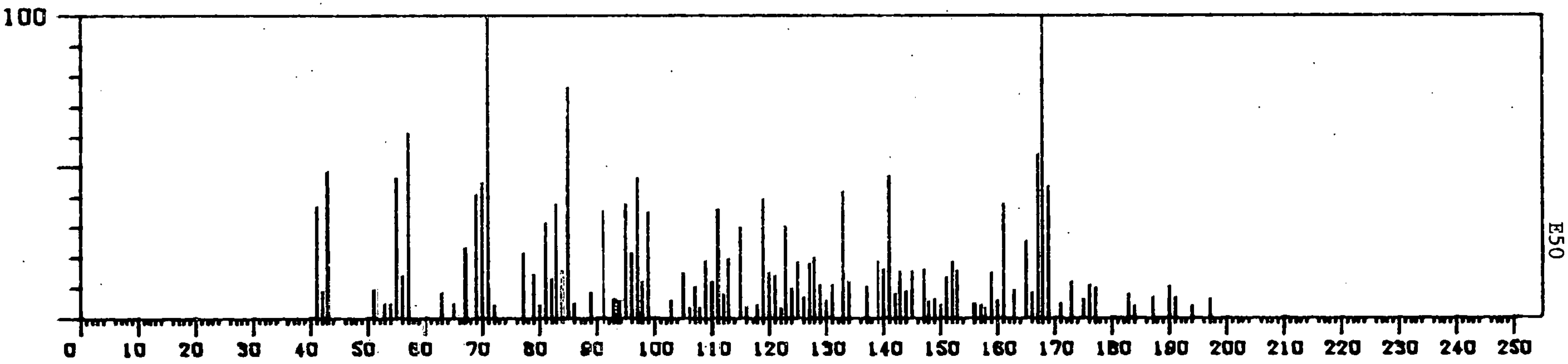


E49

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.OIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

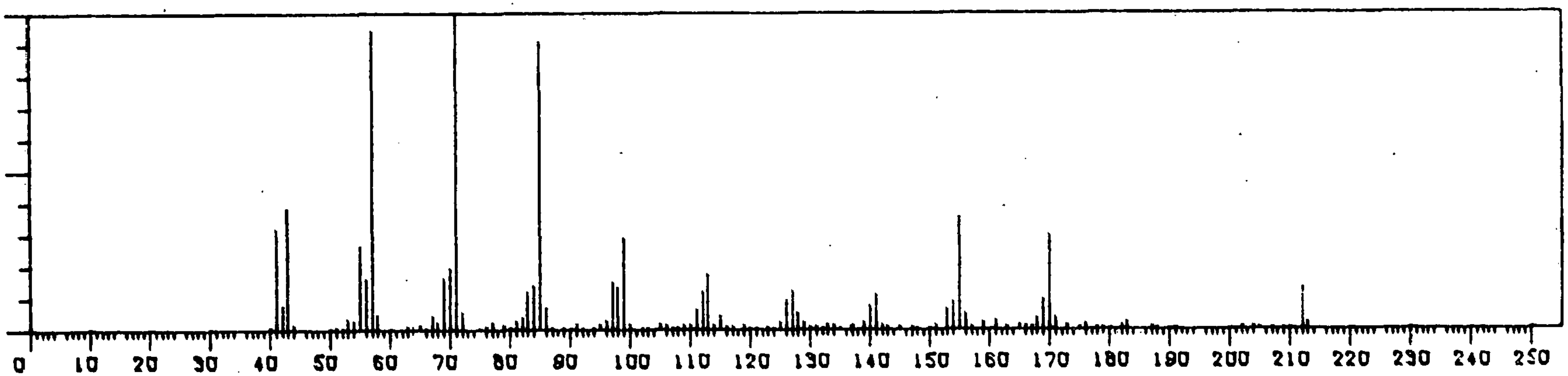
FRN 13201   SPEC 1891   RET. TIME  66.  0   METHYL BIPHENYL



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1973 RET. TIME 68. 6 N-PENTADECANE & SOME C3-NAPHTHALENE

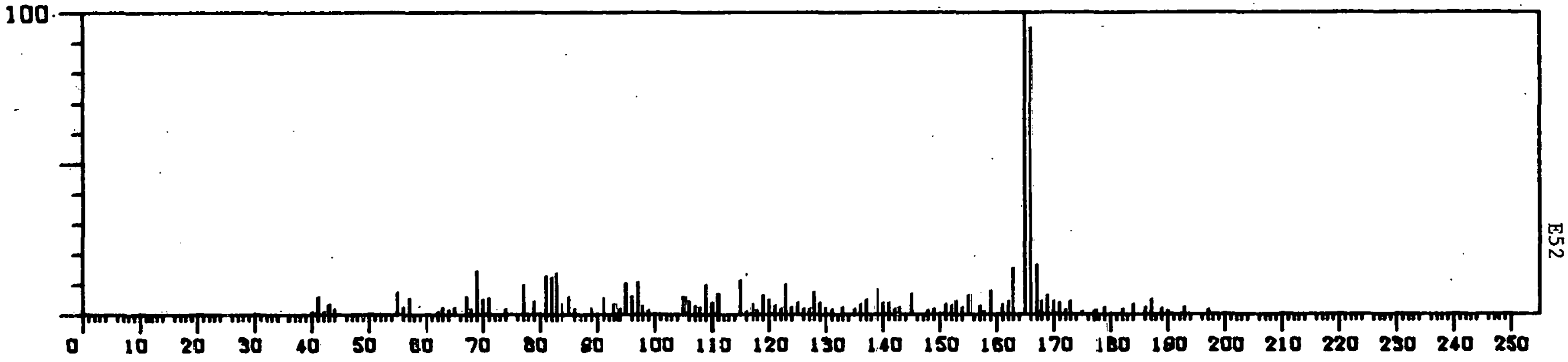


DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

E51

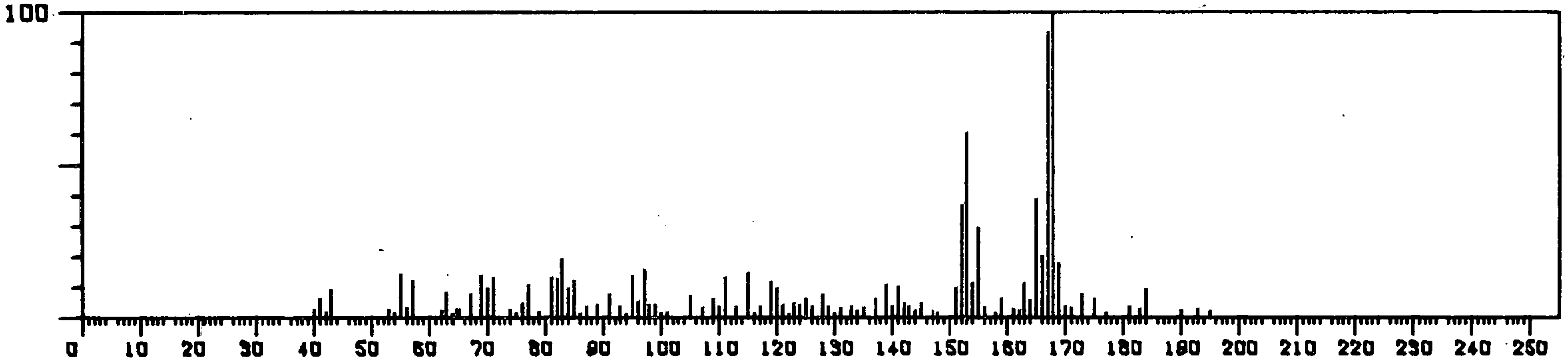
FRN 13201 SPEC 2052 RET. TIME 71. 1 FLUORENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 2089 RET. TIME 72. 3 METHYL ACENAPHTHENE

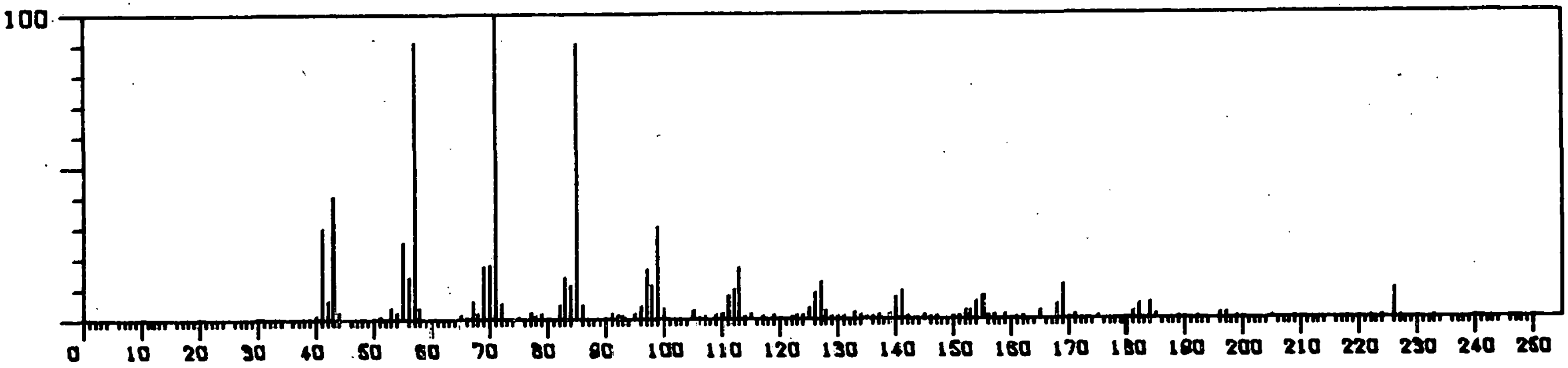


E53

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1,20.3 U

FRN 13201  SPEC 2167  RET. TIME 74. 8  HEXADECANE

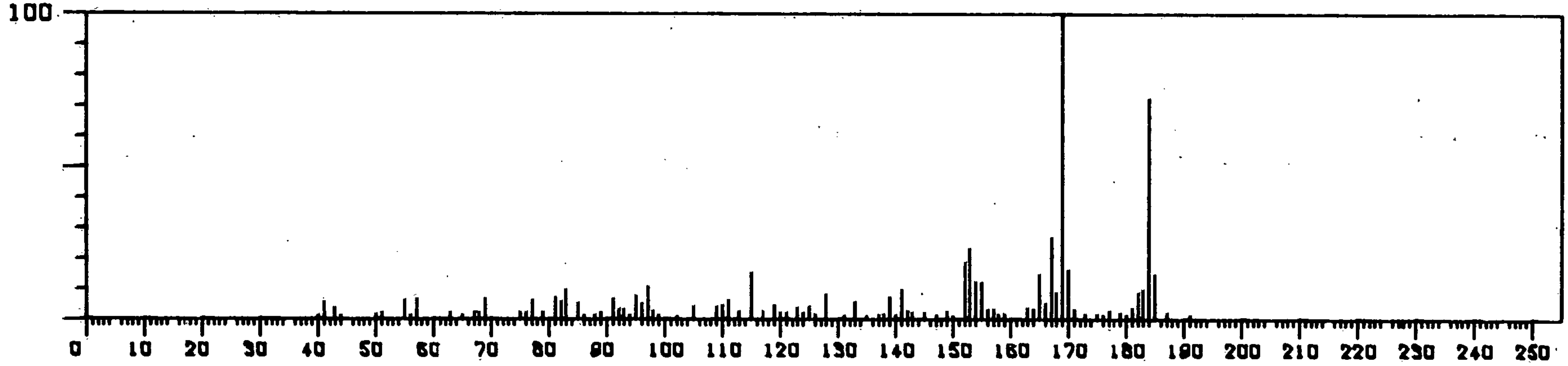


F.54

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

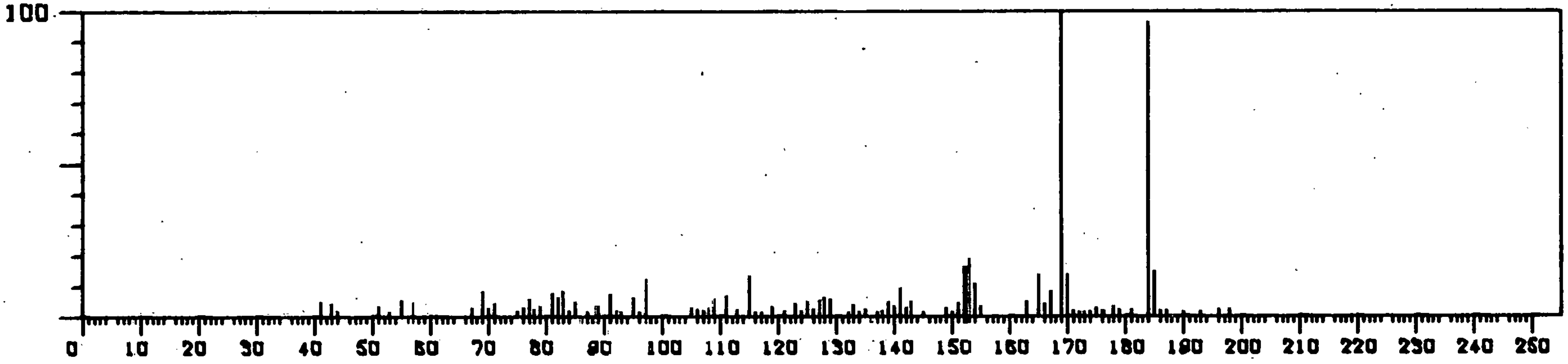
FRN 13201 SPEC 2188 RET. TIME 75. 8 C4-NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 2235 RET. TIME 77. 0 C4-NAPHTHALENE

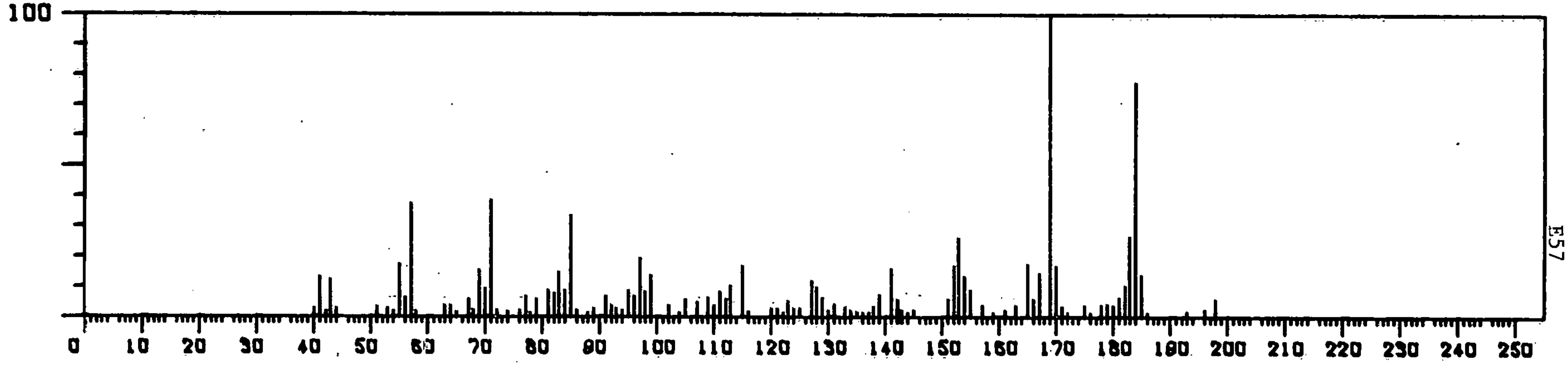


E56

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

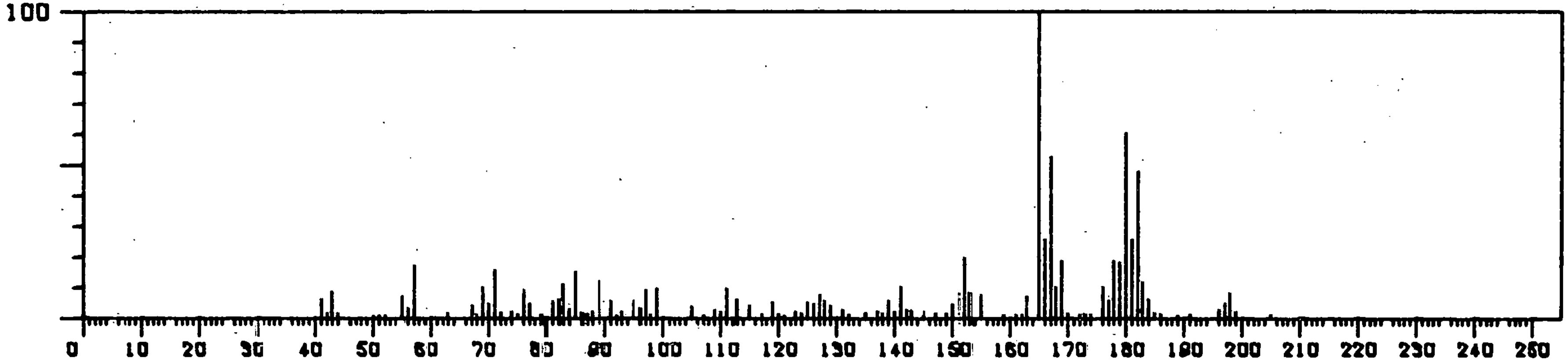
FRN 13201 SPEC 2261 RET. TIME 77. 8 C4-NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

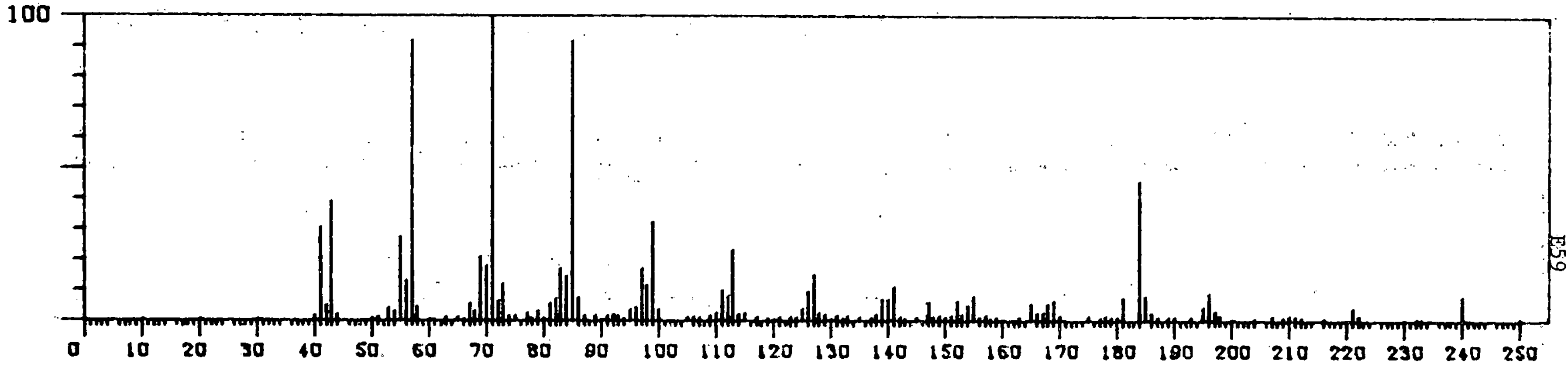
FRN 13201 SPEC 2278 RET. TIME 78. 3 METHYL FLUORENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

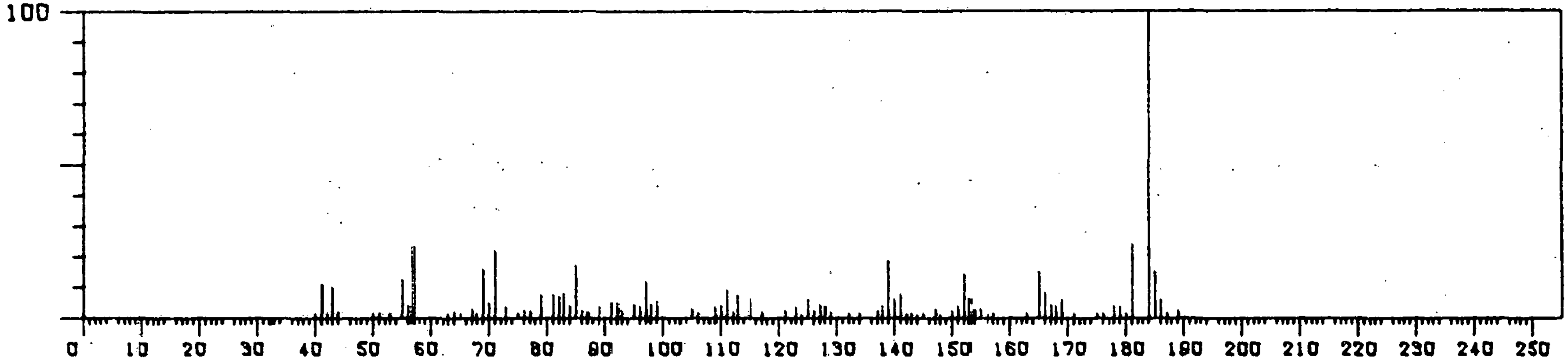
FRN 13201   SPEC 2347   RET. TIME 80. S   N-HEPTADECANE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

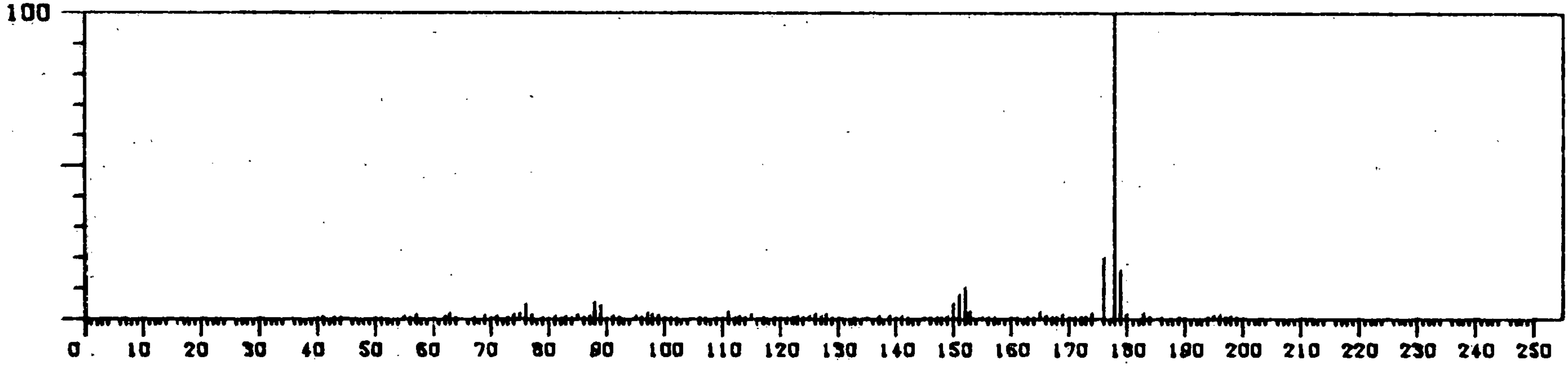
FRN 13201   SPEC 2350   RET. TIME 80. 6   DIBENZOTHIOPHENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

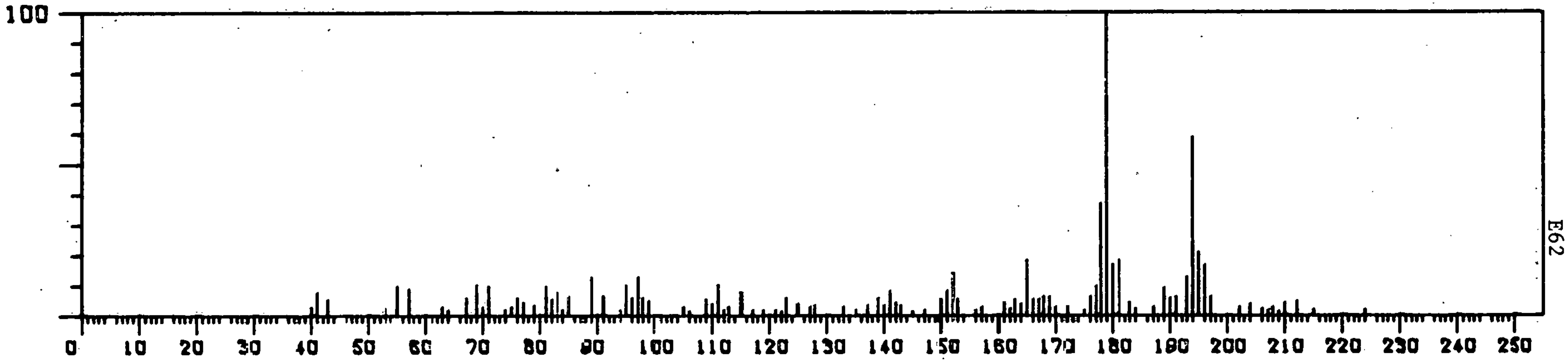
FRN 13201  SPEC 2399-  RET. TIME  82.  2  ANTHRACENE/PHENANTHRENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 2476 RET. TIME 84. 6 C2-FLUORENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

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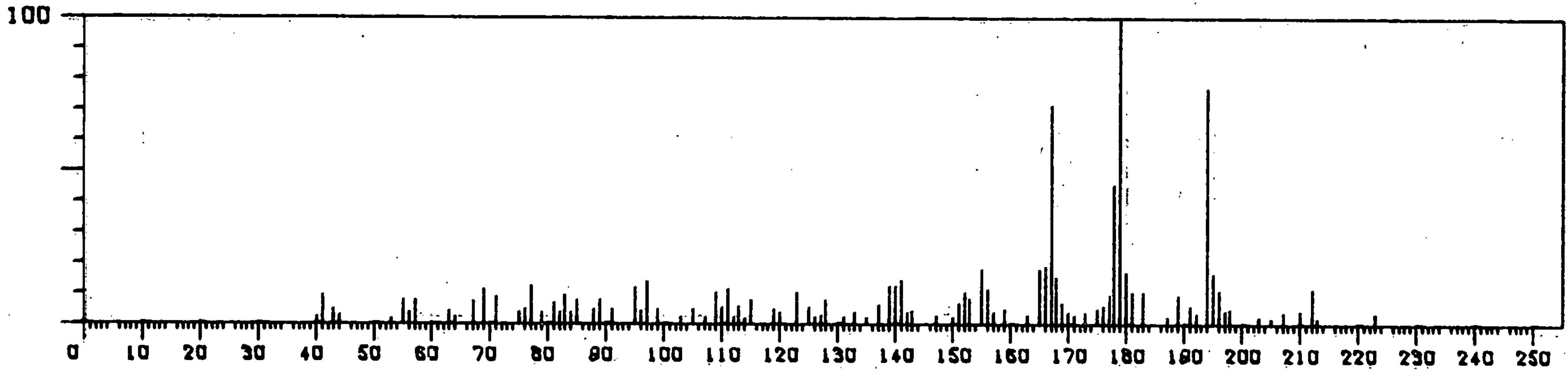
FRN 13201 SPEC 2487 RET. TIME 84. 9 C2-FLUORENE



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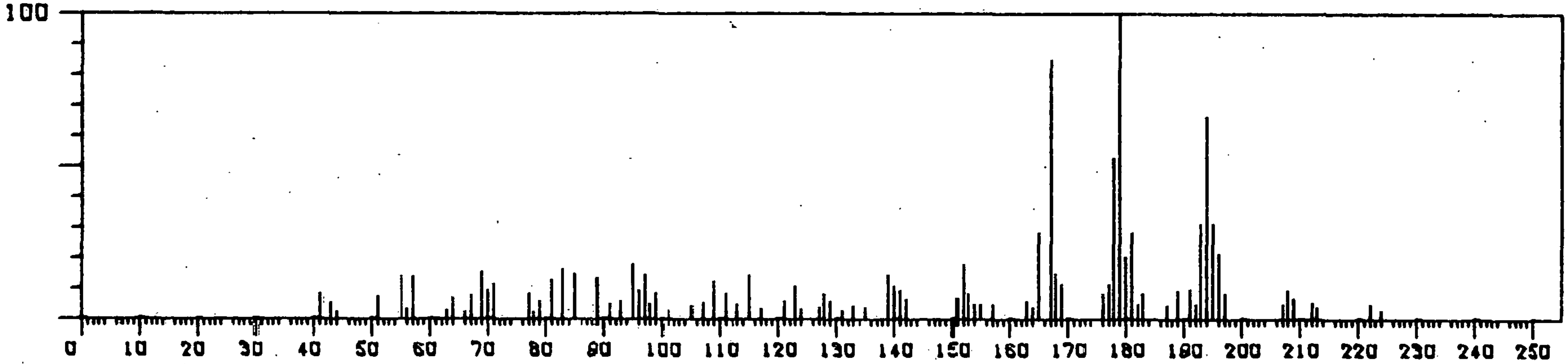
50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

FRN 13201 SPEC 2497 RET. TIME BS. 2 C2-FLUORENE



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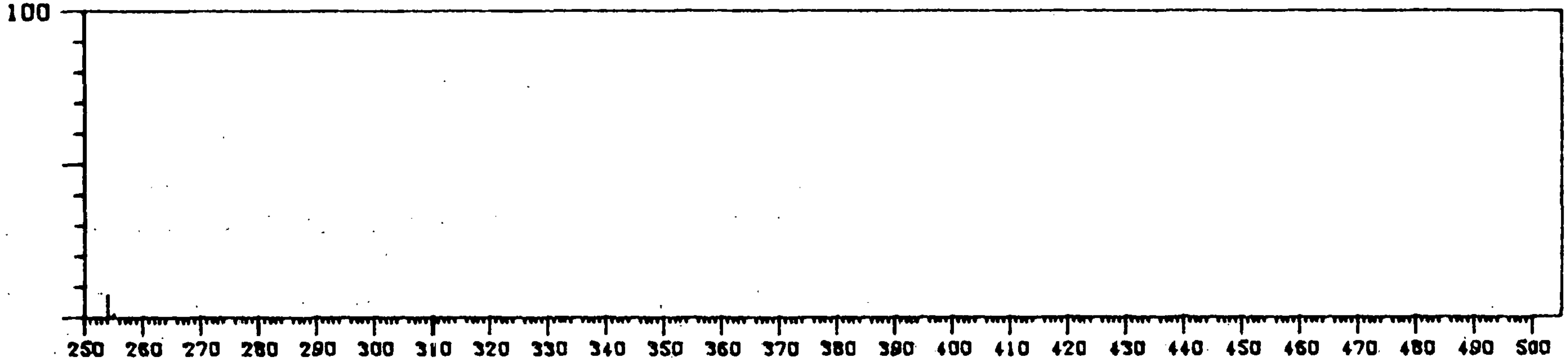
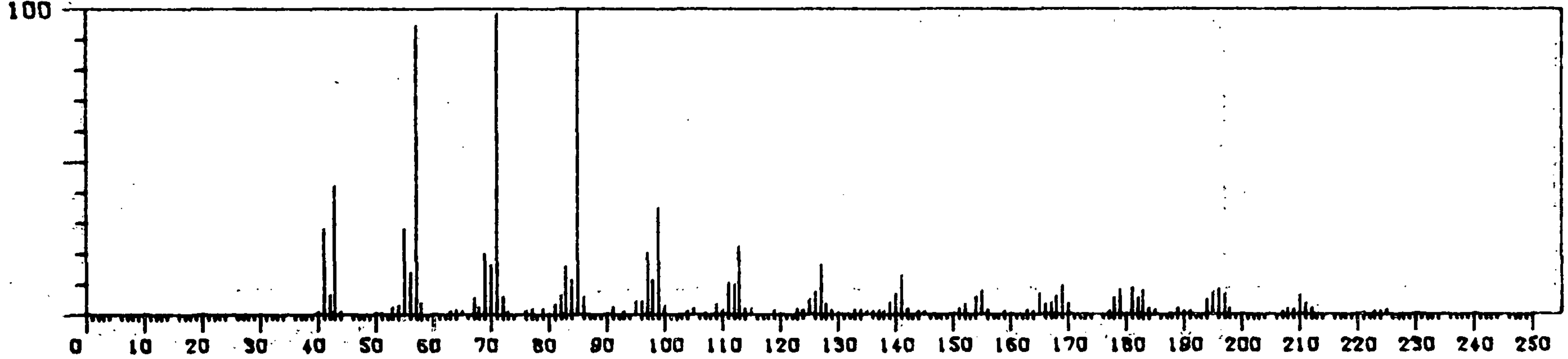
FRN 13201 SPEC 2521 RET. TIME 86. 0 N-OCTADECANE



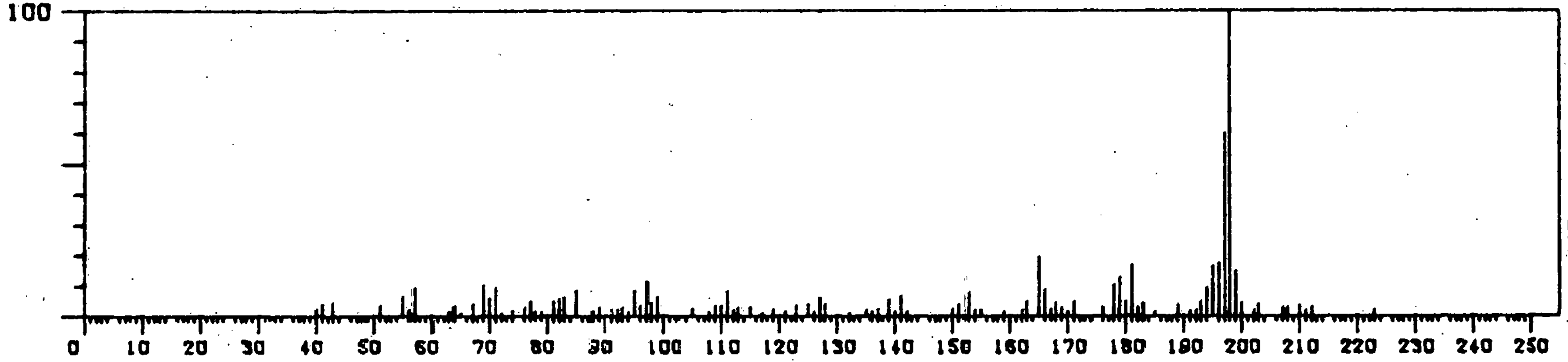
FRN 13201 SPEC 2521 RET. TIME 86. 0 N-OCTADECANE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 2528 RET. TIME 86. 2 METHYL DIBENZOTHIOPHENE



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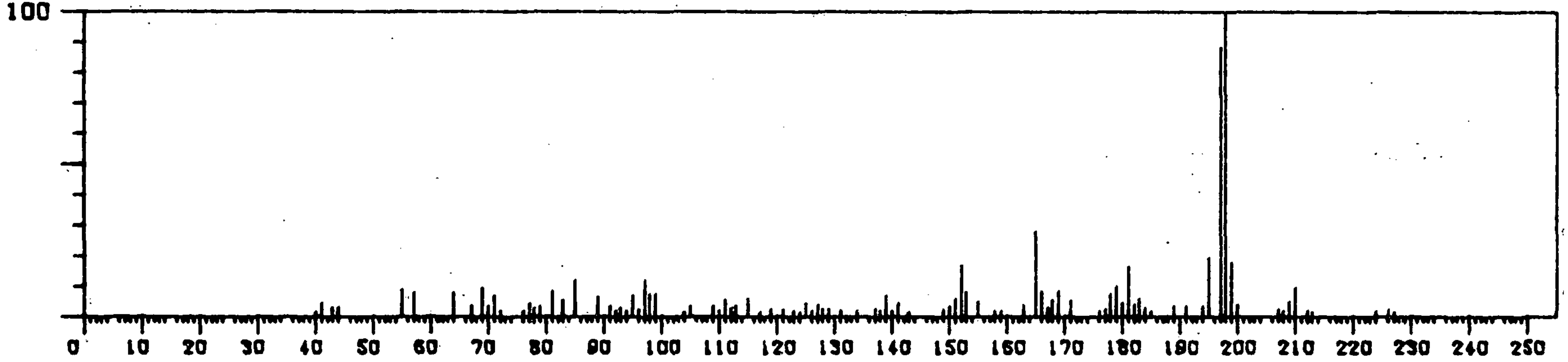
SOM OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

FRN 13201 SPEC 2558 RET. TIME 87. 3 METHYL DIBENZOTHIOPHENE

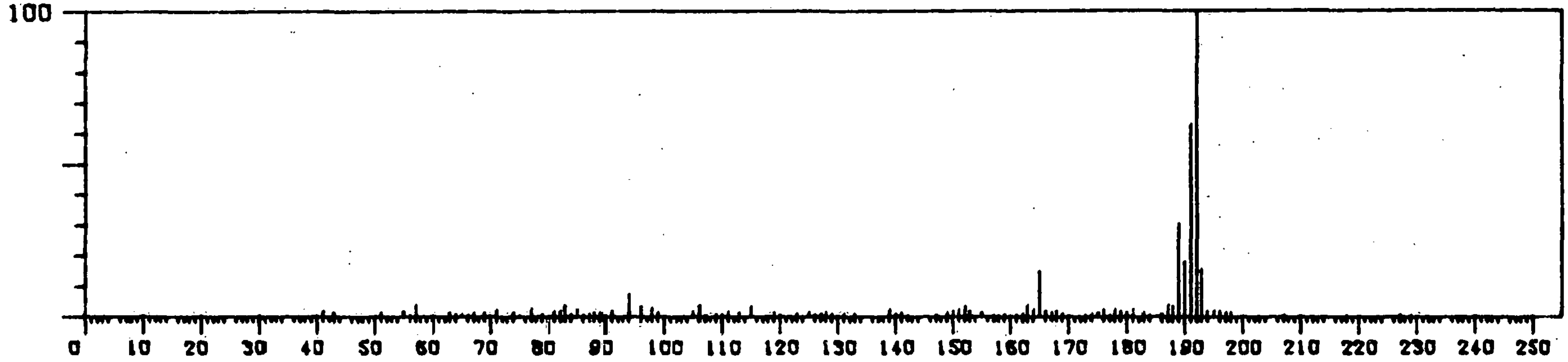


DAF-1234-A-NEUTRAL/F-ME/CH2CL2.OIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

E67

FRN 13201 SPEC 2597 RET. TIME 88. 5 METHYL PHENANTHRENE



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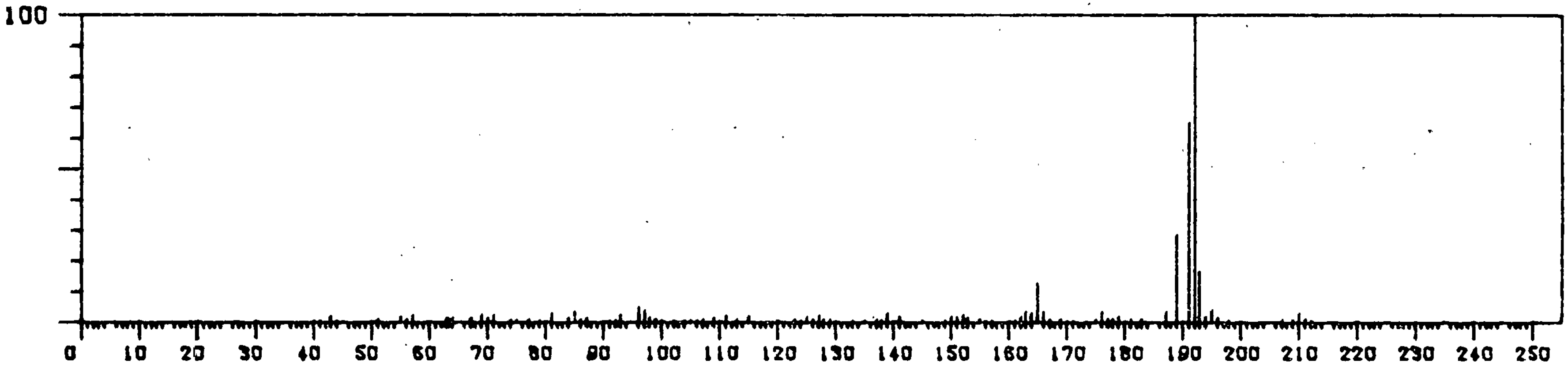
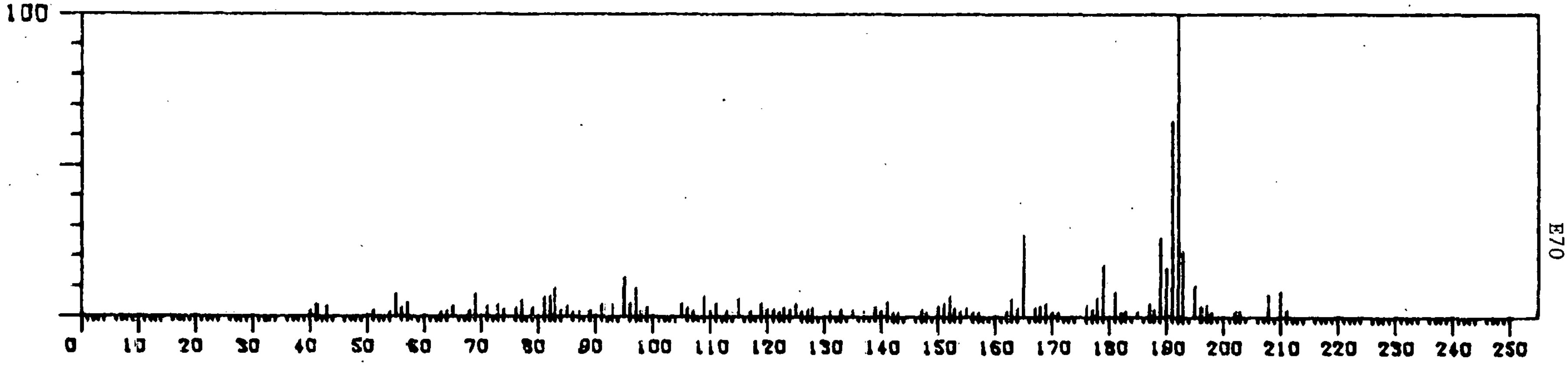
FRN 13201  SPEC 2605  RET. TIME 88. 7  METHYL PHENANTHRENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

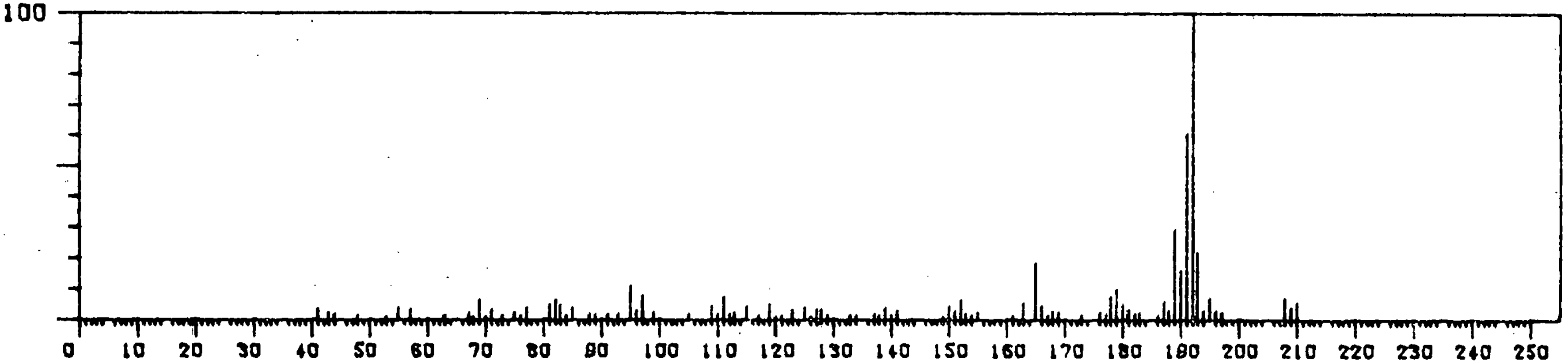
FRN 13201 SPEC 2631 RET. TIME 89. 6 2-METHYL ANTHRACENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201   SPEC 2641    RET. TIME  89.  9          1-METHYL ANTHRACENE



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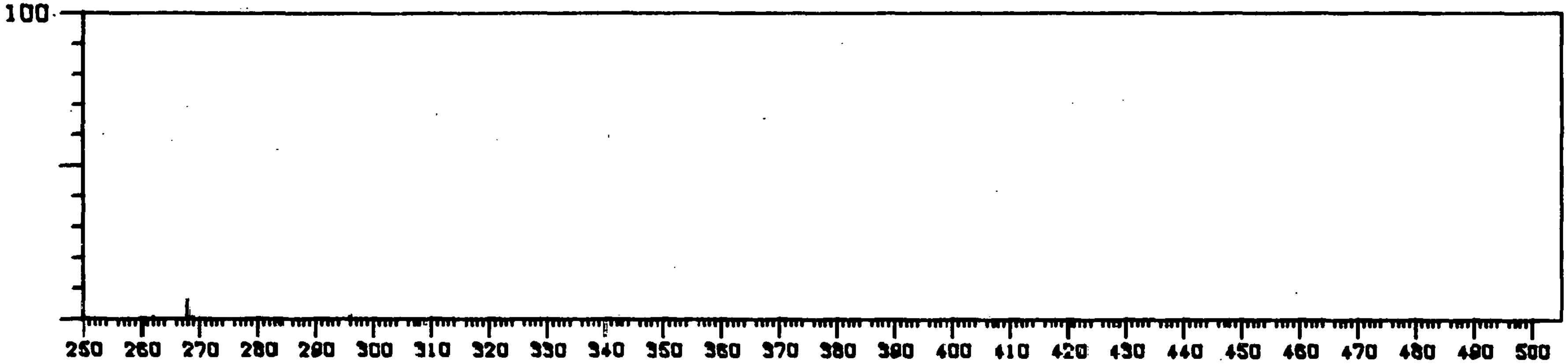
FRN 13201 SPEC 2684 RET. TIME 91. 2 N-NONADECANE



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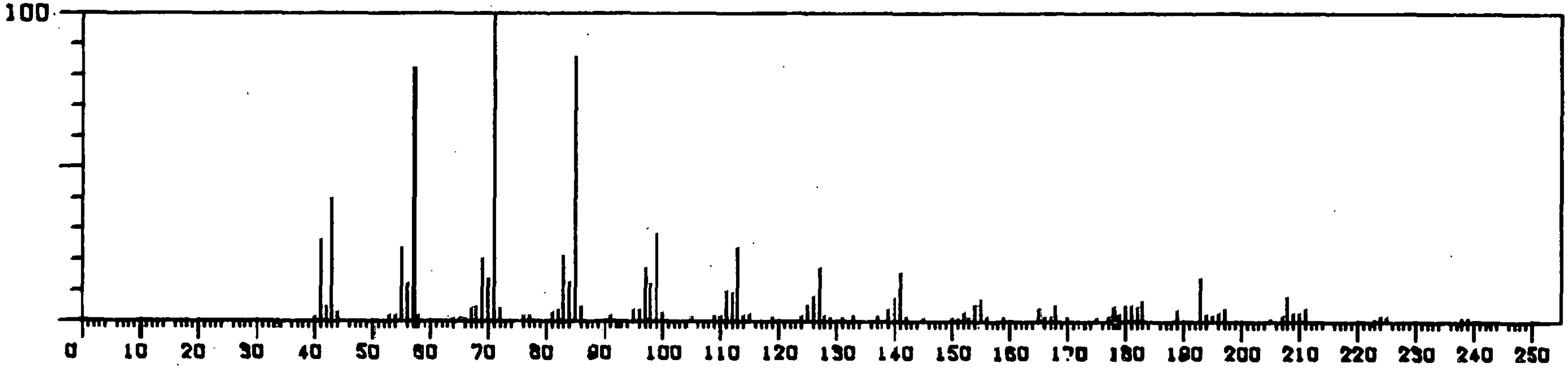

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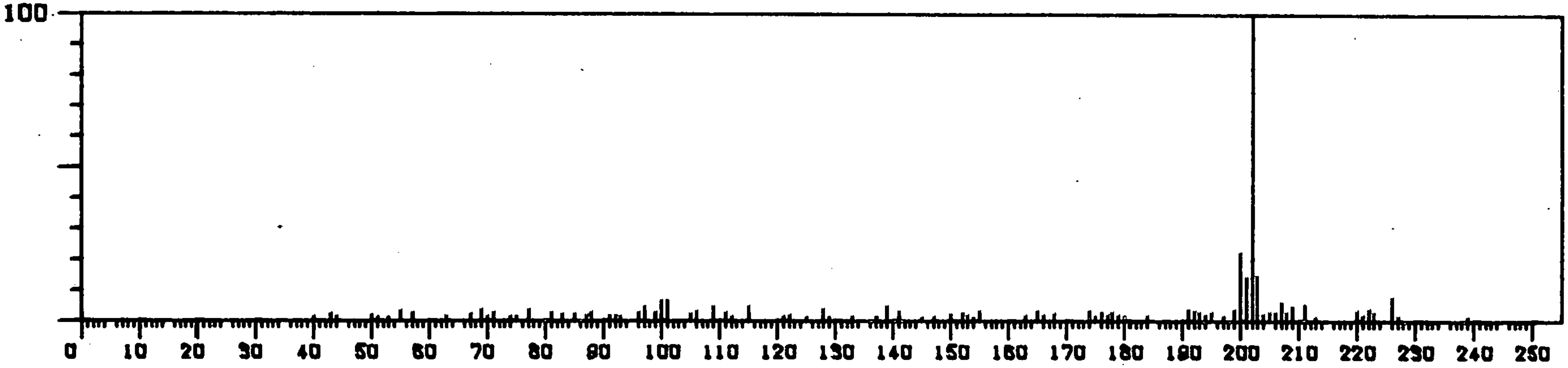
SOM OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

FRN 13201 SPEC 2823 RET. TIME 98. 9 PYRENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

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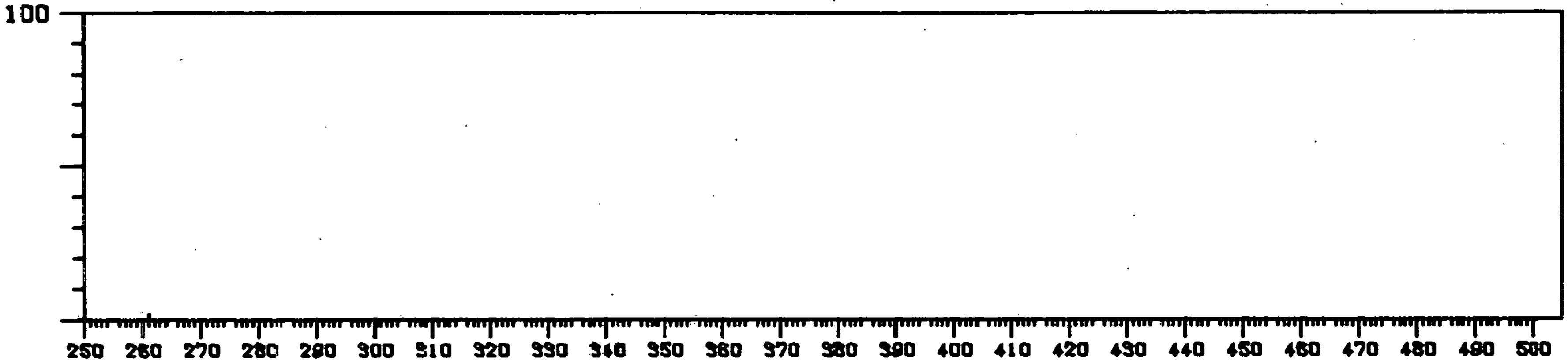
FRN 13201 SPEC -2980+2993+2993-3001 RET. TIME 101. 1 N-HENEICOSANE



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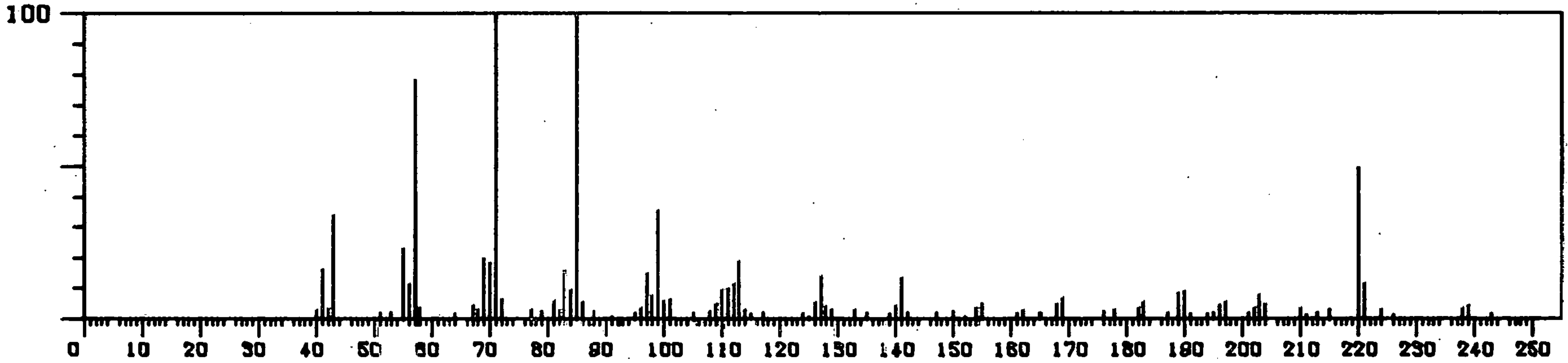
E74



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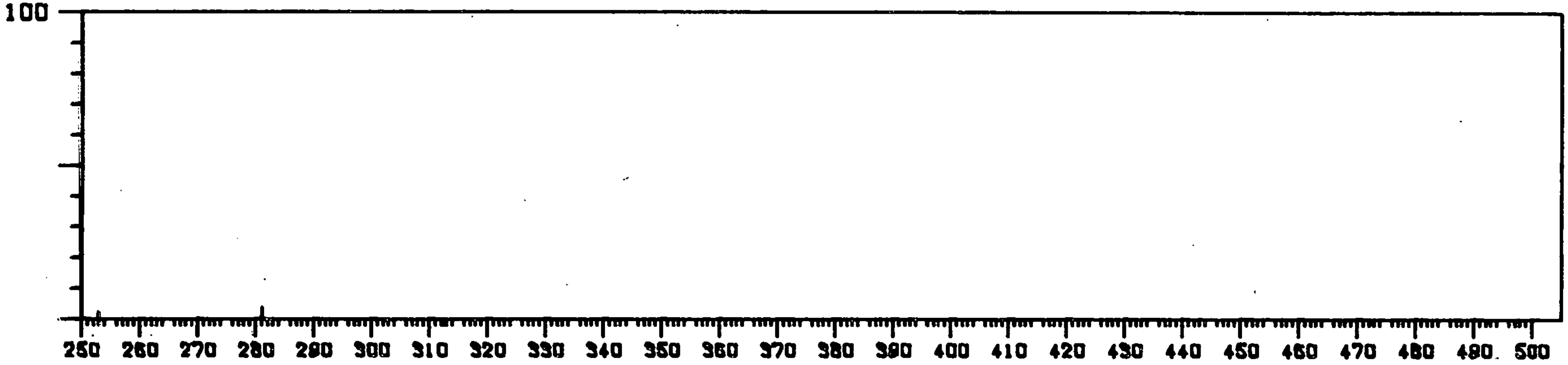
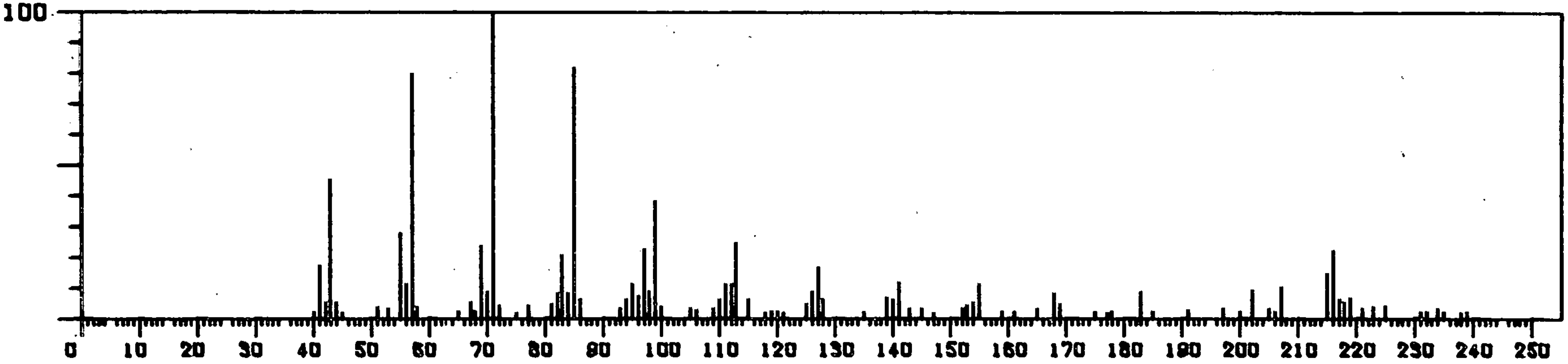
SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 UL

FRN 13201 SPEC 3138 RET. TIME 105. 6 N-DOCOSANE



FRN 13201 SPEC 3138 RET. TIME 105. 6 N-DOCOSANE



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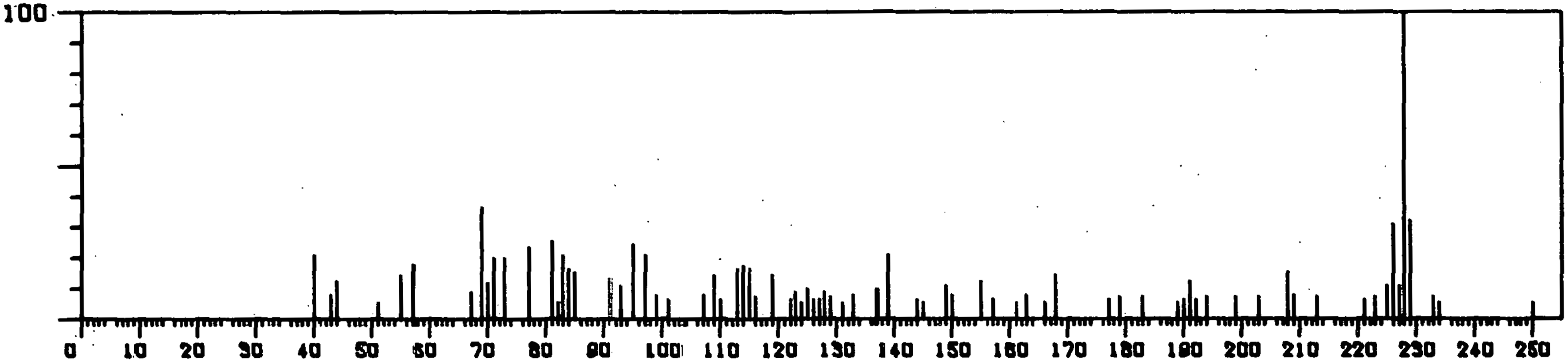
50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

FRN 13201 SPEC 3398 RET. TIME 113. 8 CHRYSENE

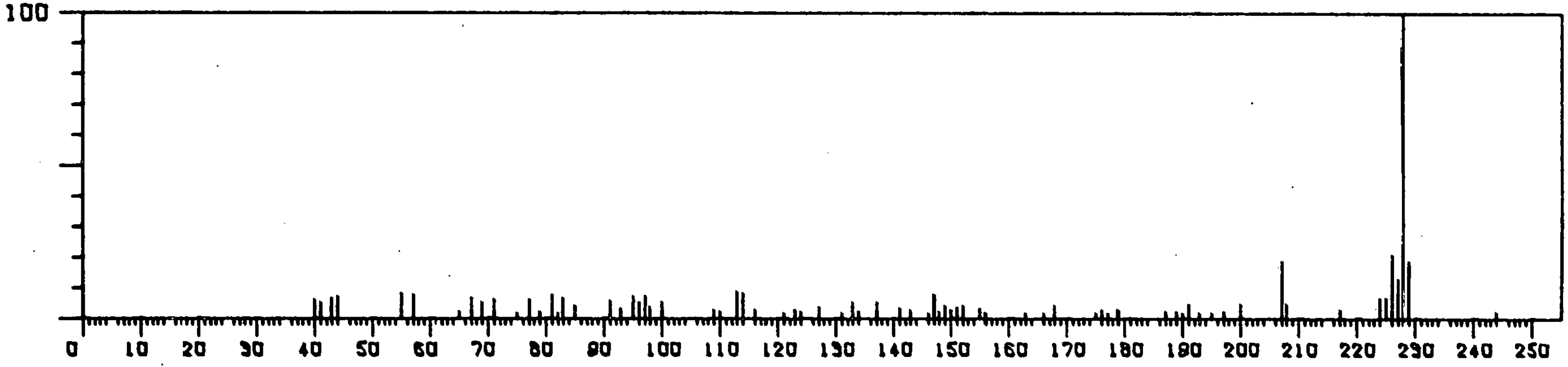


DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

E76

FRN 13201 SPEC 3407 RET. TIME 114. 2 1,2-BENZANTHRACENE



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16. ABSTRACT
Wastewater from a Class B refinery was sampled every 4 hours for 4 successive days in Dec., 1976. Effluents from the full-scale system (dissolved air flotation (DAF) unit and final clarifier for the activated sludge unit) and an add-on pilot-scale unit (mixed-media filter and activated-carbon columns) were sampled for analysis of common wastewater parameters and trace organic compounds. Grab samples taken every 4 hours were composited daily. Organics were isolated into acid, base, and neutral fractions. Four-day composites of these daily extracts were analyzed by capillary-column gas-chromatography/mass-spectrometry (GC/MS). Some 304 compounds were identified in the neutral fraction of the DAF effluent and removal of these organics by the activated sludge and add-on treatment units was estimated. The average percentage removal of organics present in the DAF effluent was greater than 99% for the activated sludge, approximately 0% for the mixed media filter, and less than 1% for the activated carbon. Numerous data for the approximate concentration of organic compounds are presented. Common wastewater parameters are also presented for comparison to specific organics concentration data.

17. (Circle One or More) KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|---|
| Activated Sludge<br>Activated Carbon<br>Chemical Engineering<br>Energy Conversion<br>Environmental Engineering | Energy Conversion<br>Mixed-Media Filter<br>Organic Chemistry<br>Refinery<br>Refining<br>Wastewater | Control Technology:<br>Energy Extraction<br>Processes & Effects:<br>Charac., Meas. & Monit.<br>Energy Cycle: Processing, Conversion<br>Fuel: Oil, Gas | 10A<br>97D-F |

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