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Organic Constituents in Sour Condensates from Shale-Oil and Petroleum-Crude Runs at Sohio's Toledo Refinery

Identification and Wastewater-Control-Technology Considerations

R. J. Wingender, W. Harrison, and L. A. Raphaelian

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ARGONNE NATIONAL LABORATORY
Energy and Environmental Systems Division

prepared for
U. S. DEPARTMENT OF ENERGY
under Contract W-31-109-Eng-38

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Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A06
Microfiche copy: A01

Distribution Category:
Oil Shales and Tar Sands
(UC-91)

ANL/PAG-4

ARGONNE NATIONAL LABORATORY
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Argonne, Illinois 60439

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R. J. Wingender, W. Harrison, and L. A. Raphaelian
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February 1981

work sponsored by

U.S. DEPARTMENT OF ENERGY
Assistant Secretary for Environment
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FOREWORD

Within the Department of Energy, the Environmental and Safety Engineering Division provides the Office of Environment with the data and information necessary for making independent and unbiased judgments relative to the efficacy and practicability of environmental control technologies for existing and emerging energy systems. As part of this program, literature data and field data acquired at energy facilities are evaluated to determine the status of environmental control options. These evaluations contribute to the development of policies for Department-wide compliance with existing and anticipated environmental regulations, guidelines, and standards. Additionally, the program provides guidance to Department of Energy research, development, and demonstration programs to ensure that environmental controls are produced in concert with emerging energy systems. Of particular importance are judgments on the practicability and cost of the various proposed options. One specific area of interest is the treatment of process waters and wastewaters derived from recovery and refining of liquid hydrocarbons, both naturally occurring hydrocarbons and those synthetically produced from other feedstocks.

Project Officer for this study was Henry F. Walter, US DOE Environmental and Safety Engineering Division, Environmental Control Technology Branch, Washington, D.C. 20545.

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FIGURES

TABLES

TABLES (Contd.)

LIST OF ABBREVIATIONS

A -- acid

A/D -- analog to digital

AMU -- atomic mass units

BK -- laboratory blank

B/N -- base/neutral

C_x -- alkyl substitution, $x = 1,2,3$, etc.

d_{10} -- ten deuterium atoms (instead of hydrogen atoms)

GC/MS -- gas chromatograph interfaced to a mass spectrometer

H-P -- Hewlett-Packard

m -- meter

µL -- microliter

ng -- nanogram

NIH -- National Institutes of Health

PET -- petroleum

ppb -- parts per billion

ppm -- parts per million

REF -- refinery

S.O. -- shale oil

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ABSTRACT

Samples of sour condensate generated from the continuous processing of both crude shale oil and petroleum crude were collected and extracted with methylene chloride. The extracts were analyzed using capillary-column gas chromatography/mass spectrometry at Argonne National Laboratory and Radian Corporation.

Qualitatively, the predominant types of organic compounds present in the shale-oil sour condensate were pyridines and anilines; semiquantitatively, these compounds were present at a concentration of 5.7 ppm, or about 78% of the total concentration of components detected. In contrast, straight-chain alkanes were the predominant types of compounds found in the sour condensate produced during isocracking of conventional crude oil. The approximate concentration of straight-chain alkanes, 8.3 ppm, and of other branched and/or unsaturated hydrocarbons, 6.8 ppm, amounted to 88% of the total concentration of components detected in the sour condensate from the petroleum-crude run.

Nitrogen compounds in the shale-oil sour condensate may necessitate alterations of the sour water and refinery wastewater-treatment facilities to provide for organics degradation and to accommodate the potentially greater ammonia loadings. This would include use of larger amounts of caustic to enhance ammonia removal by steam stripping. Possible problems associated with biological removal of organic-nitrogen compounds should be investigated in future experimental shale-oil refining runs.

1 INTRODUCTION

Shale-oil crude from the Paraho Development Corporation's commercial demonstration surface retort was processed continuously through an isocracker at the Toledo, Ohio, refinery of Standard Oil Company of Ohio (SOHIO) during the period of November 10 to December 12, 1978. The purpose of the run was to demonstrate the feasibility of producing on-spec military fuels, such as jet fuel and marine diesel fuel, from shale oil. During the run, 73,096 barrels of oil were processed. This unique opportunity was further exploited to obtain samples of the sour condensate. Characterization of organic compounds in this water provides preliminary information useful in anticipating the need for additional studies of wastewater control technology for shale-oil refining.

While the shale oil was being processed, samples of the sour condensate generated were collected directly from the isocracker, and extracted with methylene chloride. The extracts were preserved in sealed ampules stored at low temperature. In June of 1979, samples of sour water generated by conventional crude-oil refining were collected from the same sample point to provide comparative analyses. These sour-water samples were extracted and the extracts preserved in the same manner as the shale-oil sour condensates. The extracts were then analyzed using capillary-column gas chromatography/mass spectrometry (GC/MS) at Argonne National Laboratory during the latter part of 1979 and early 1980. Splits of the extracts analyzed by Argonne were analyzed simultaneously by nearly identical techniques at Radian Corporation. Because the Argonne data are more comprehensive, however, the results discussed in the body of this report are exclusively those obtained by Argonne.

The results of the analysis (Table 1) show that the majority of the organic compounds present in the isocracker shale-oil sour condensate are nitrogen-containing species. Of the nine different types of nitrogen compounds identified, the predominant types are pyridines and anilines.

In contrast, straight-chain alkanes are the predominant organic compounds found in the sour condensate produced in the isocracking of conventional crude oil. Whereas the concentration of organic constituents appears to be greater in the crude-oil sour condensate than in the shale-oil sour condensate, no organic-nitrogen compounds were detected in the former (Table 2).

Analyses of crude shale oil have shown that it has a much higher nitrogen content than conventional crude oils (Table 3). The principal nitrogen compounds in shale oil have been reported to be pyridines, pyrroles, amides, nitriles, indoles, quinolines, and other such materials. The distribution of these compounds in shale oil has been found to correlate closely with that in the shale-oil sour condensate. The significant exception to this is aniline. Aniline is not found in the raw shale oil and is believed to be produced during the refining process.

The following sections describe the method by which the shale oil was processed, the sampling procedures, the methods and results of the identification and quantitation of the extractable/chromatographable organic constituents, and present the wastewater-control technology considerations that should be addressed in future work.

2 SHALE-OIL PROCESSING AND SOUR-WATER HANDLING

The crude Paraho shale oil was shipped by rail to the SOHIO Toledo refinery. The crude oil consisted of a mixture of material that had been in storage at the retorting site for about a year and material that had been recently produced. It was noted that the older material was more viscous and more difficult to pump than the newer material. Analyses of the two crude oils were not available. The materials were combined in a new storage tank and were continuously mixed and steam heated during storage.

Table 1 Summary of Types of Compounds Identified in Sour Condensate from Refining Shale Oil

Name of Group	Concentration in Sour Water, ppb
Substituted Benzenes	472
Pyridines	4379
Piperidines	45
Anilines	1313
Indans	40
Tetralins	16
Naphthalenes	52
Tetrahydroquinolines	325
Quinolines	133
Indoles	69
Hydrocarbons	91
PNAs	5
Carbazoles	121
Tetramines	72
Sulfides	117
Phenols	12
Ketones	2
Pyrroles	2

Table 2 Summary of Types of Compounds Identified in Sour Condensate from Refining Crude Oil

Name of Group	Concentration in Sour Water, ppb
Substituted Benzenes	808
Straight Chain Alkanes (C_{10-19})	8260
Branched & Unsaturated Hydrocarbons	6810
Decalins	256
Tetralins	400
Indans	106
Cyclohexyl Compounds	416

Table 3 Properties of Various Crude Oils

	Paraho Shale Oil[a]	Dawson County, Texas[b]	Los Angeles County, California[b]
Gravity (°API)	19.3	38	26.2
Gravity (Specific)	0.934	0.835	0.897
Pour Point (°F)	85	5	45
Viscosity (SUS) @100°F	-	40	92
Weight % N	2.19	0.102	0.501
Weight % S	0.61	0.1	1.53

[a] TRW Corporation, *A Preliminary Assessment of the Environmental Impacts from Oil Shale Developments,* EPA-600/72-77-069 (1977).

[b] U.S. Department of Energy, *Analysis of 800 Crude Oils from United States Oil Fields,* BETC/R1-78/14 (1978).

The crude shale oil was processed through an isocracking unit, which is the process used by SOHIO for hydrocracking. This unit (Isocracker I) employs high temperatures and high hydrogen pressures in the presence of a catalyst to desulfurize and denitrify crude oils and crack the higher boiling materials into lighter, lower boiling products. In addition, some saturation of the olefins may be present. (Details of the operation of the isocracker and material balances for the period November 11-26, 1978, are given in Appendix I.)

As shown in Fig. 1, normal operation of the isocracker employs two reactor stages. The first stage is used primarily for desulfurization and denitrification, and the major portion of the hydrocracking is carried out in the second stage.

During the shale-oil run, only a single stage was used, as shown by the heavy lines in Fig. 2. This procedure was adopted because the goal of the test was to produce jet fuel, marine diesel fuel, and heavy fuel oil, all of which are considered middle and heavy products. While some cracking did occur, in this stage the main purpose for its use was the removal of sulfur and nitrogen from the crude shale oil. The final products were produced through distillation of the desulfurized and denitrified oil.

As shown in Figs. 1 and 2, the product leaving the reactor was mixed with water prior to entering the hydrodenitrification (HDN) high-pressure separator and water coalescer. The water was added to "wash" the product of H_2S, ammonia, and chlorides generated by the isocracking process. The separated water is the sour water or sour condensate. During the shale-oil run, the water injection rate was 20-25 gpm. The sour-condensate sample collected for analysis represented the combined flow from the HDN high-pressure separator and the water coalescer. The sample was collected at point 1, as shown in Fig. 2.

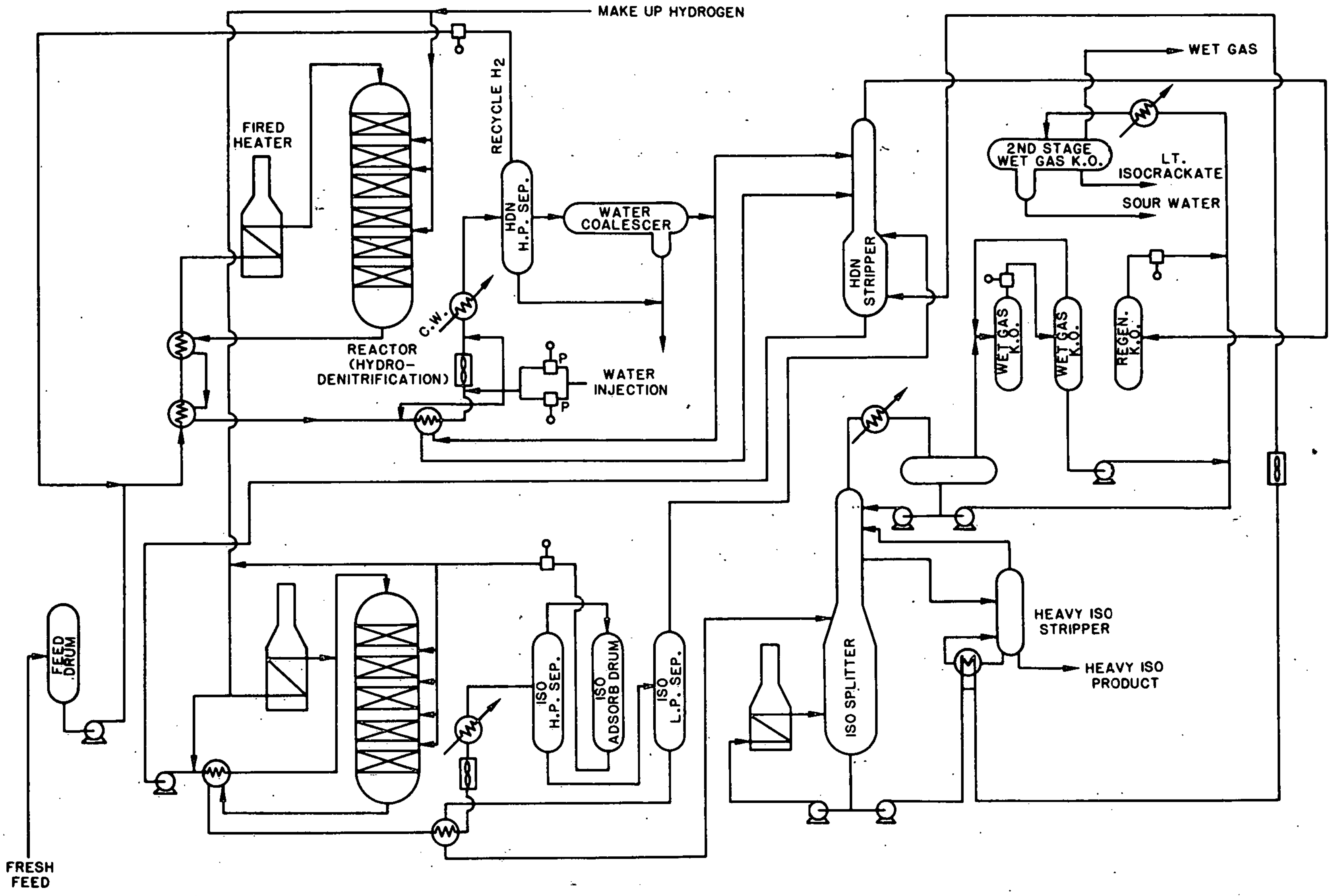

Fig. 1 Simplified Process Flow for Isocracker I

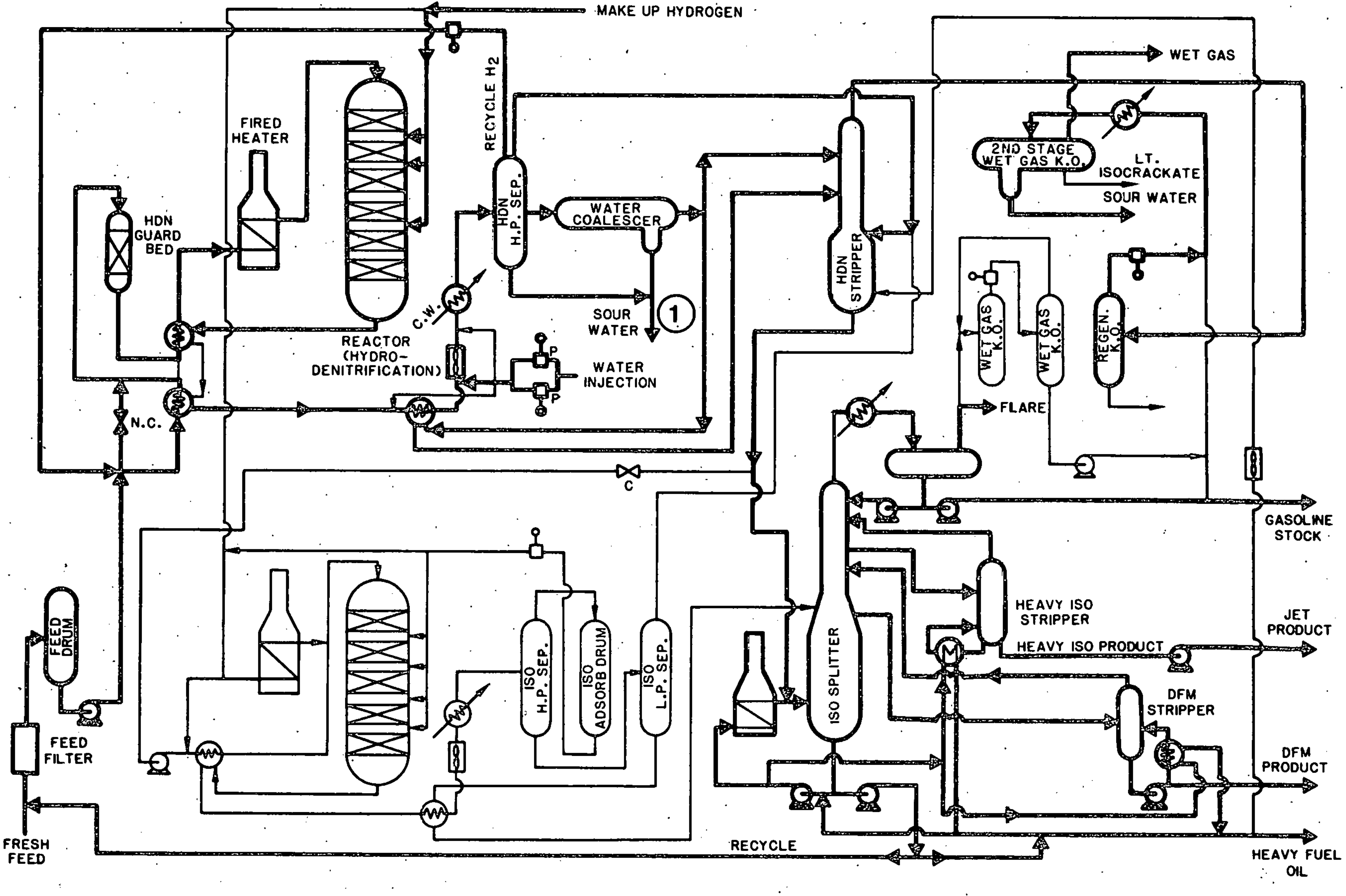

Fig. 2 Process Flow for Isocracker I during Shale-Oil Run

From this point on in the shale-oil processing, sour condensate from shale oil was combined with sour condensates from various other refinery sources and directed to a storage tank. The combined flow was then passed through a sour-water stripper for removal of H_2S and NH_3. The sour-condensate-stripper operation included an injection of caustic to raise the pH to about 9.0 to enhance removal of ammonia. The stripper bottoms then were discharged to the wastewater-treatment facility.

3 PROCEDURES FOR SOUR-CONDENSATE SAMPLING AND SAMPLE PREPARATION

One-gallon amber glass bottles with Teflon-lined lids were used as sample containers. The bottles were prepared by washing them first with methylene chloride and then with nitric acid, rinsing them twice with glass distilled water, and then autoclaving them. Samples were collected by throttling sour condensate through a 1/4" stainless-steel ball valve directly into the 1-gal bottles.

A set of samples consisted of:

- 1 gal wastewater, unpreserved, for semivolatiles analysis;
- 1 gal wastewater preserved with HNO_3 to pH 2, for total metals analysis;
- 1 gal distilled water, unpreserved, semivolatiles blank; and
- 1 gal distilled water, preserved with HNO_3, metals blank.

Each set was iced and sent via air express from Toledo, Ohio, to the laboratory for workup.

Organics were removed from all laboratory glassware used in sample preparation by holding the glassware at a temperature of 550°C for 3 hr in a cleaning oven. A general procedure was selected for preparing the water samples for semivolatiles analysis by GC/MS because the classes of compounds present were not known. The samples were prepared according to method number 625, as published in the Federal Register *44* (#23) 69540-69542 (Dec. 3, 1979). This method covers the determination of a number of organic compounds that are solvent extractable and amenable to analysis by GC/MS. A 1-L sample of sour condensate is extracted three times with 60-mL volumes of methylene chloride. The combined organic extract is dried by passing it through a column of anhydrous sodium sulfate and is concentrated in a Kuderna-Danish apparatus. Approximately equal portions of the 1-mL concentrate are transferred to three separate ampules that are then sealed under nitrogen and labeled as the "base/neutral" fraction.

The pH of the previously extracted water is adjusted to 2 or below with 6N H_2SO_4. The water is then serially extracted three times with 60-mL portions of methylene chloride. The extracts are combined and dried by passing them through a column of anhydrous sodium sulfate. After concentration in a Kuderna-Danish apparatus, the concentrate is proportioned equally among three ampules that are then sealed under nitrogen and labeled as the "acid" fraction.

A total of three water samples were processed and coded as follows: a BK-REF (blank for the refinery runs prepared by processing distilled water shipped in one of SOHIO's sampling bottles); an SO-REF (960 mL of foul water collected during the shale-oil refining); and a PET-REF (930 mL of foul water collected during petroleum refining). Two organics fractions were prepared from each of the three water samples: a bases/neutrals extract (B/N) and an acids extract (A). The final volumes of each extract ranged from 0.8-1.05 mL; each of the six total extracts was split into thirds, and the splits were glass ampuled under nitrogen and stored at 4°C. Volumes of the splits were measured before ampuling, using a 500-μL syringe. One complete set of the splits has been retained at 4°C.

Six extracts were retained by Argonne for characterization and semiquantitation of the components present. Splits of these extracts were also sent to Radian Corporation for characterization (see Appendix H), under subcontract to Argonne. The extracts sent to Argonne were identified as follows:

Sent September 25, 1979

S.O. REF B/N 0.3/1.0	2-14-79 FMP
S.O. REF A 0.3/0.9	2-14-79 FMP
BK REF B/N 0.3/0.9	9-20-79 FMP
BK REF A 0.3/1.05	9-20-79 FMP

Sent November 15, 1979

PET REF B/N 0.35/1.05	10-12-79 FMP
PET REF A 0.3/0.8	10-12-79 FMP

The meaning of the identification code for the first sample was as follows: shale-oil refinery run, base/neutral fraction; volume of extract is 0.3 mL of a total 1.0 mL extract prepared February 14, 1979. The letters FMP designated the chemist responsible for the extractions.

4 CHARACTERIZATION OF ORGANIC CONSTITUENTS

4.1 DESCRIPTION OF THE GC/MS SYSTEM

The organic compounds in the extracts were analyzed on a Hewlett-Packard 5993A GC/MS equipped with an H-P 1000 E series computer with 32K, 16-bit word core memory, 7900A dual disc drive with 2.5 M bytes/disc memory, and a Tektronix 4012 graphic display terminal. Peripheral equipment included a Tektronix 4631 hard copy unit and a Zeta 130-10 incremental plotter. With this system, data can be collected at the same time that previously collected data are being analyzed.

The parameters used for scanning were as follows: run time, 120 min; mass range, 35-450 AMU; A/D measurements per datum point, 1; scan rate, 362 AMU/sec; and threshold, initially 50, later reduced to 20 as column background decreased.

The mass spectrometer was tuned with perfluorotributyl amine each day using the AUTOTUNE program provided in the H-P 5993 software prior to making sample or standard runs. When necessary, the OVERRIDE program was also used to optimize mass-spectral parameters to enhance the abundance of the 219-mass ion. This procedure provided improved sensitivity of the mass spectrometer to the molecular weight range of the compounds anticipated in the samples.

4.2 DESCRIPTION OF THE CHROMATOGRAPHIC SYSTEM

A 50-m glass capillary column of the wall-coated, open tubular (WCOT) variety, coated with OV-101, was used in this study. The sample (4 μL) was introduced into the column via a Hewlett-Packard Model 18835B Grob-type split/splitless capillary inlet system operated in the splitless mode. In this mode, the injection port and septum/seal were continuously purged except during the injection interval when the injection port purge was turned off. A 0.6-min injection interval was used. A sequence timer controlled the timing and activation of a solenoid in the purge line. The end of the column was connected directly to a Swagelok tee. One port of the tee was connected to the inlet of the mass spectrometer source and the remaining port was connected to a second solenoid valve. When this valve was open, most of the column effluent was diverted from the mass spectrometer. In normal operation the second valve was actuated by the sequence timer to close 8 min after injection to force the column effluent to enter the mass spectrometer source after the solvent had eluted from the column. The advantages of this type of system for analysis of trace organic compounds have been described previously.[1] When derivatized samples were run, the timer was set to actuate the valve 16 min after injection to prevent the majority of the derivatizing reagent components from entering the mass spectrometer source.

A temperature program of 20°C to 240°C with a 2°/min rate and a 2-min hold at 20°C was employed. The 20° initial temperature was necessary to achieve a good "solvent effect," as described by Grob,[2] since the solvent used was methylene chloride.

4.3 REAGENTS AND STANDARDS

Standards used to provide reference spectra and retention characteristics were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. Four sets of standards were prepared: two sets of pyridines and anilines, one set of quinolines and tetrahydroquinolines, and one set of cyclohexanes.

Derivatizing reagents used were Pierce TRI-SIL -- Catalog #4899950 and Methyl-8 -- Catalog #4938025 obtained from Alltech Associates, Deerfield, Illinois.

The calibrating solution used was prepared from a 2000-ppm solution of anthracene-d_{10} obtained in an EPA consent-decree priority-pollutant standard kit prepared by Radian Corporation and purchased from Alltech Associates. The concentration of the calibrating solution was 100 ng/μL.

4.4 IDENTIFICATION PROCEDURE

Several criteria were used to make the identifications listed in the tables of Appendixes A, B, C, and D. They include:

1. Comparison of experimental mass spectral data to those presented in the Registry of Mass Spectral Data;[3]
2. Comparison of the mass spectra of authentic compounds to the observed mass spectra; and
3. Characterization based on retention time and the presence of two or more of the most prominent and most unique mass-spectral peaks.

When the observed and published mass spectra were identical, the compounds were identified with the positions of substitution indicated. This procedure was followed with the realization that the spectra obtained by different instruments could differ enough to make position assignments difficult if not impossible.

When the relative intensities in the observed mass spectra could not be matched to within 5-15% of the corresponding relative intensities in reference spectra, positions of substitution and identification of the substituent alkyl group(s) were not provided. Rather, the compound was characterized as a C_2-, C_3-, or C_x-homologue.

The chromatographic column used in this study was coated with OV-101, a nonpolar methyl silicone fluid, which accordingly provided separations based primarily on boiling point. Since the boiling point increases with increasing carbon number in a homologous series, the retention times of the homologues are a function of the number of CH_2 groups. Therefore, familiarity with the types of compounds present in a particular fraction, their retention characteristics, and the retention characteristics of authentic compounds, leads to the grouping of variously substituted homologues by carbon number. The grouping process is accomplished by inspection of massgram plots of key ions on the graphic display. For example, C_3-benzenes display key mass ions of 91, 105, and 120, and were observed to elute as a group within the 20- to 24-min range of retention times. Thus, compounds present in low concentration in a fraction providing at least two key ions within such a grouping can be tentatively identified as an alkyl substituted member of that group. For example, for a component observed to elute with a retention time of 21.2 min whose mass spectrum contains only 105- and 120-mass ions, a tentative identification as a C_3-benzene is permitted.

The key ions and retention time ranges from the alkyl substituted homologues of eight classes of compounds were empirically obtained. These data, presented in Table 4, were particularly useful in making tentative identifications of compounds whose concentrations were so low that only a few of the stronger mass ions were observed.

4.5 METHOD OF QUANTITATION

Measurement of the specific amount of any component in a mixture by GC/MS is only semiquantitative at best. A number of factors must be

Table 4 A Listing of Key Ions and Observed Retention Times for Several Groups of Compounds

	Carbon Number Substitution	Retention Times, Min
Group I Pyridines		
93, 92, 78, 66	1	10-13
107, 106, 92, 79	2	13-24
121, 120, 106, 79	3	20-30
135, 134, 120, 106	4	30-40
149, 148, 134, 120	5	34-45
163, 162, 148, 135	6	40-54
Group II Anilines		
93, 92, 66, 65	0	24
107, 106, 79, 77	1	30-35
121, 120, 106, 77	2	35-
135, 134, 120, 106	3	37-
Group III Tetrahydroquinolines		
133, 132, 118, 117	0	40-45
147, 146, 132, 118	1	43-52
161, 160, 146, 132	2	44-59
175, 174, 160, 146	3	50-
189, 188, 160, 146	4	53-
Group IV Quinolines		
129, 128, 102, 51	0	40
143, 142, 115, 89	1	45-50
157, 156, 142, 115	2	52-60
171, 170, 156, 142	3	60-
Group V Indoles		
117, 116, 90, 89	0	50
131, 130, 103, 77	1	54-
145, 144, 130, 115	2	54-60
159, 158, 144, 130	3	59-63
173, 172, 158, 144	4	72
Group VI Carbazoles		
167, 166, 140, 139	0	80
181, 180, 164, 152	1	84-
195, 194, 180, 152	2	88-
Group VII Benzenes		
92, 91, 65, 51	1	8
106, 105, 91, 51	2	13-16
120, 119, 105, 91	3	19-25
134, 133, 119, 105	4	28-
148, 147, 133, 119	5	35-
Group VIII Indans		
118, 117, 115, 91	0	26
132, 131, 118, 117	1	34-
146, 145, 131, 117	2	37-
160, 159, 145, 131	3	52-
Group IX Naphthalenes		
128, 127, 102, 51	0	32-
142, 141, 128, 127	1	44-
156, 155, 141, 127	2	52-

considered as sources of error in the quantitative data because several assumptions must be made. These factors include:

1. Efficiency of extraction of the organics from the water sample;
2. Errors in volumetric handling of the extract and calibrating solution;
3. The amount of sample lost during purge in splitless injection;
4. Variation in response due to the range of concentrations of components in the sample; and
5. Assumption that the response of each of the components is the same and equivalent to the response of the same quantity of the compound used for calibration purposes.

These factors are discussed more thoroughly in Section 5.

The amount of solvent plus solution injected on column was maintained at a relatively constant level of about 4 µL. An amount of fresh methylene chloride was drawn into the syringe followed by the desired quantity of sample solution to total 3 µL. Then, 1 µL of a 100-ng/µL solution of anthracene-d_{10} in methylene chloride was drawn into the syringe and the syringe contents were injected on column.

The area (response) of the base peak of each component detected by the mass spectrometer was measured, and the response of the anthracene-d_{10} in counts per nanogram was used to compute the semiquantitative results. Thus, a response factor of 1.0 was assumed for each compound detected.

4.6 DERIVATIZATION PROCEDURE

The general method followed to prepare derivatives of the polar compounds was to aliquot 5-10 µL the extract into the bottom of a 0.3-mL minivial (Catalog #95003, Alltech Associates) followed by 10-40 µL of the derivatizing reagent. The cap was fitted tightly onto the vial and the vial was then placed in a hot water bath maintained at 50°C for 20-30 min. The solution was allowed to cool before an aliquot was removed for injection into the GC/MS.

5 CHARACTERIZATION RESULTS

The procedure for the characterization of organics, as presented in Section 4, permits tentative identification if the specific compounds are well resolved and reference spectra are available. When components are present in high concentrations or in large numbers there is an increased likelihood for coelution. Coelution results in mass spectra that are combinations from two or more compounds, thereby complicating structural assignments.

The results of the characterizations presented in this section were achieved using manual interpretation methods. Use of the H-P EPA/NIH library search proved to be less accurate and more time-consuming, and reference spectra for the majority of the compounds detected were not available.

Quantitation was done by comparing the base-peak response of anthracene-d_{10} to the base-peak response of the individual compounds from a single determination. A response factor of 1.0 was used in this study. A more accurate approach utilizing the experimentally determined response factor of authentic material for each class of compounds detected was not adopted because the response factor changes as alkyl substitution changes. Attempts to improve quantitative accuracy by making replicate determinations with authentic materials available from chemical supply houses and custom synthesis laboratories would be far too tedious for this type of program, and the slight improvement in accuracy would not justify the expenditure in time or significantly alter the conclusion of the study.

The primary objective of this research was to compare the organic constituents of the shale-oil refinery and petroleum-oil refinery sour condensates. The comparison of the compounds observed and their concentration in the sour condensate is presented in Table 5. The following discussion gives a more detailed description of the constituents and their measured concentration from the analysis of the individual fractions.

5.1 COMPARISON OF COMPOUNDS IN THE BASE/NEUTRAL FRACTIONS

The shale-oil base/neutral (B/N) fraction contained about 98% of the total organic constituents identified (estimated 7123 out of 7266 ppb total) (Table 6). Some 207 compounds were characterized. Of the total concentration of compounds detected, 89% was due to nitrogen compounds (61% out of 89% attributable to pyridines). A complete listing of specific compounds is given in Appendix A. Selected spectra of some of the prominent components are presented in Appendix E.

The total-ion chromatograms obtained from the two B/N fractions are shown in Fig. 3. The large peaks appearing in the upper trace are due to the pyridine compounds present in the shale-oil B/N fraction. The large peaks in the lower trace appearing approximately every 7 min are due to the straight-chain alkanes present in the petroleum-oil B/N fraction.

A larger concentration of B/N components was found in the sour condensate from the petroleum-crude refinery run; however, these components were made up of straight-chain alkanes and branched and/or unsaturated hydrocarbons, as summarized in Table 7. Straight-chain alkanes accounted for 47% of the 17 ppm of B/N components in this sour condensate, and the branched and/or unsaturated components amounted to 43% of the total. No nitrogen-containing species, naphthalene, or substituted naphthalenes were observed in this sample. A total of 159 compounds was characterized in the petroleum-oil B/N fraction. These compounds are listed in Appendix B, and selected spectra of a few of the more prominent compounds are given in Appendix F.

Only four types of compounds were common to the two sour-condensate samples: substituted benzenes, indans, tetralins, straight-chain alkanes, and branched or unsaturated hydrocarbons. The concentrations of these compounds in the sour condensate from the shale-oil refinery run were 462, 40, 16, and 91 ppb, respectively, whereas the concentrations in the corresponding petroleum oil sample were 845, 107, 398, and 15,632 ppb, respectively.

Table 5 Comparison of Concentrations in ppb of Organic Compounds Characterized in the Shale-Oil and Petroleum-Crude Sour Condensate (numbers in parentheses indicate sums of the corresponding alkylated species in ppb)

	Shale Oil	Petroleum Oil
N-Alkanes	(67)	(8260)
C_{10}	-	180
C_{11}	-	600
C_{12}	-	1000
C_{13}	-	1300
C_{14}	6	1200
C_{15}	6	1200
C_{16}	6	1100
C_{17}	7	860
C_{18}	7	500
C_{19}	7	320
C_{20}	8	-
C_{21}	8	-
C_{22}	6	-
C_{23}	6	-
B/U* Hydrocarbons	(15)	(7372)
C_{10}	-	-
C_{11}	-	318
C_{12}	-	689
C_{13}	-	1495
C_{14}	1	1031
C_{15}	3	964
C_{16}	-	705
C_{17}	3	810
C_{18}	-	222
C_{19}	6	700
C_{20}	2	438
Pyridines	(4379)	-
C_1	67	-
C_2	817	-
C_3	1972	-
C_4	1070	-
C_5	451	-
C_6	2	-
Anilines	(1313)	-
C_0	400	-
C_1	615	-
C_2	91	-
C_3	94	-
C_4	109	-
C_5	4	-
Benzenes	(472)	(845)
C_1	156	-
C_2	149	47
C_3	139	485
C_4	15	313
C_5	13	-
Cyclohexanes	-	(416)
C_4	-	24
C_5	-	35
C_6	-	73
C_7	-	85
C_8	-	80
C_9	-	79
C_{10}	-	-
C_{11}	-	40

	Shale Oil	Petroleum Oil
Tetralines	(16)	(398)
C_0	16	67
C_1	-	167
C_2	-	107
C_3	-	57
Tetrahydroquinolines	(325)	-
C_0	28	
C_1	75	-
C_2	200	-
C_3	22	-
Decalins	-	(258)
C_0	-	16
C_1	-	87
C_2	-	77
C_3	-	29
C_4	-	49
Quinolines	(177)	-
C_0	4	-
C_1	37	-
C_2	90	-
C_3	46	-
Carbazoles	(121)	-
C_0	46	-
C_1	59	-
C_2	16	-
Indans	(40)	(107)
C_0	18	26
C_1	4	81
C_2	8	-
Indoles	(69)	-
C_0	7	-
C_1	20	-
C_2	26	-
C_3	14	-
C_4	2	-
Naphthalenes	(52)	-
C_0	26	-
C_1	23	-
C_2	5	-
Piperidines	(45)	-
C_1	10	-
C_2	35	-
Sulfides	(116)	-
C_2	2	-
C_3	114	-

*B/U ≡ branched and/or unsaturated

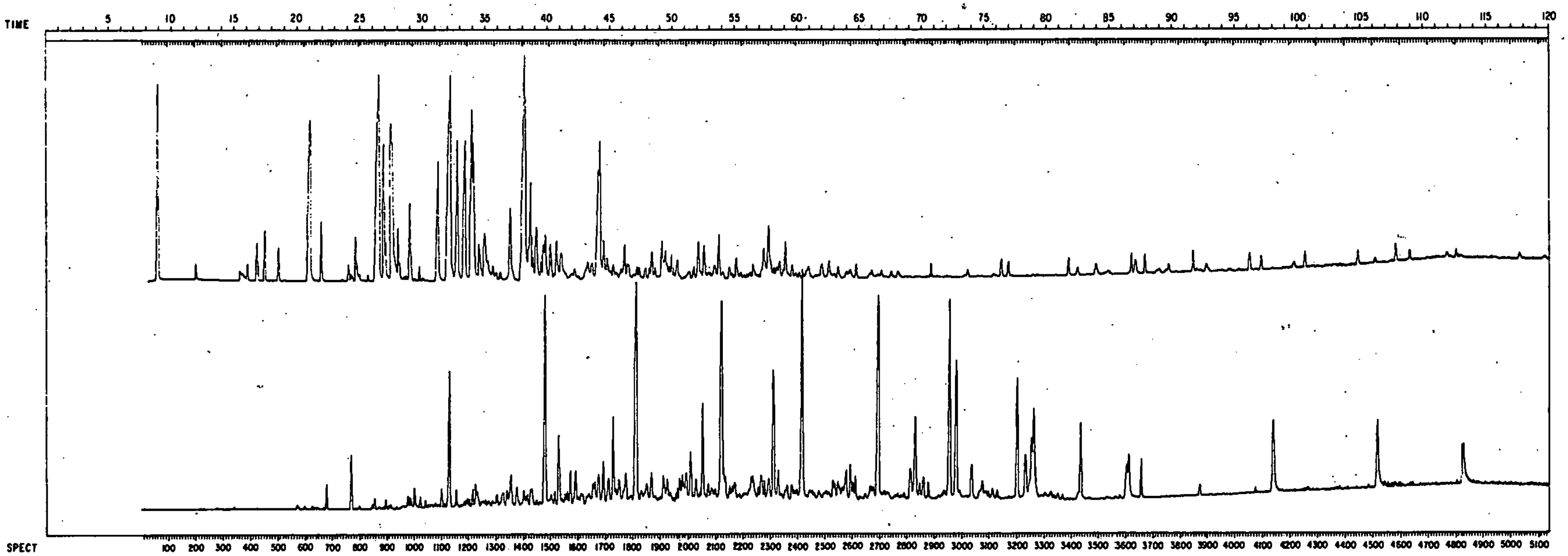

Fig. 3 Total-Ion Chromatograms of Compounds in the Base/Neutral Fractions. Upper Trace, Components of Shale-Oil Sample; Lower Trace, Components of Petroleum-Oil Sample (chromatograms normalized to 100%)

Table 6 Summary of the Types of Compounds Tentatively Identified in the Shale-Oil Base/Neutral Fraction

Name of Group	Concentration in Sour Condensate, ppb	Percent of Total Concentration
Substituted Benzenes	462	6.5
Pyridines	4379	61.5
Piperidines	45	0.6
Anilines	1313	18.4
Indans	40	0.6
Tetralins	16	0.2
Naphthalenes	52	0.7
Tetrahydroquinolines	325	4.6
Quinolines	133	1.9
Indoles	69	1.0
Hydrocarbons	91	1.3
PNAs	5	<0.1
Carbazoles	121	1.7
Tetramines	72	1.0
Total Concentration	7123	

Table 7 Summary of the Types of Compounds Tentatively Identified in the Petroleum-Crude Base/Neutral Fraction

Name of Group	Concentration in Sour Condensate, ppb	Percent of Total Concentration
Substituted Benzenes	845	4.8
Straight Chain Alkanes (C_{10-19})	8,260	46.8
Branched and Unsaturated Hydrocarbons	7,372	42.7
Decalins	258	1.5
Tetralins	398	2.2
Indans	107	0.6
Cyclohexyl Compounds	416	2.4
Total Concentration	17,656	

Derivatization of aliquots of these two fractions did not provide any additional information about the presence of other compounds that are not readily chromatographable due to their polar character.

5.2 COMPARISON OF COMPOUNDS IN THE ACID FRACTIONS

As received, both acid (A) fractions contained some precipitated matter that appeared to be sulfur. The shale-oil A fraction contained considerably more of this material than did the petroleum-oil A fraction.

The shale-oil A fraction contained only about 2% of the total organic concentration (estimated 143 out of 7266 ppb total). Most of the organic material in the shale-oil A fraction was due to organic sulfur compounds (82%). Phenol was also identified in the fraction after an aliquot was derivatized with TRI-SIL. Its concentration in the sour condensate was estimated to be only 12 ppb, or about 0.2% of the total. Phenol was the only derivatizable constituent observed in this acid fraction. Surprisingly, no alkyl phenols were found. A summary of these data is presented in Table 8, with a complete listing given in Appendix C. Selected spectra are presented in Appendix G.

The petroleum-crude A fraction contained very little organic material. Only some hydrocarbon carryover was detected. No further information was obtained after derivatization of an aliquot from the fraction. A 50-μL aliquot was concentrated to 5 μL to facilitate identification of components. A portion of this concentrate was also derivatized with TRI-SIL. However, no additional compounds were detected. The types of compounds detected in this fraction are summarized in Table 9. Acidic compounds were not observed in this fraction, and the compounds that were detected, listed individually in Appendix D, resulted from slight carryover of neutral components from the B/N fraction.

5.3 RESULTS FROM EXAMINATION OF LABORATORY BLANKS

The base/neutral and acid fractions obtained from the extraction of distilled water were included to provide a means to determine whether contamination took place during the extraction process. GC/MS examination of aliquots of these fractions indicated that if contamination did occur, it was below the detection limit of the instrumentation. No compounds were observed in these two fractions.

5.4 COMPARISON OF COMPOUNDS OBSERVED IN THE SHALE-OIL REFINERY SOUR CONDENSATE WITH COMPOUNDS IDENTIFIED IN SHALE OIL

Most of the reported information on the composition of shale oil was obtained by distillation (analytical fractionation) followed by adsorption (a silica-gel-column chromatographic method that allows arranging the compounds in groups having similar adsorbabilities), spectrometric analysis (UV, visible, IR, and some MS), and chemical analysis.[4] Nevertheless, the compounds identified by these techniques correlate well with those identified in this study in the refinery sour condensate by capillary-column GC/MS.

Table 8 Summary of the Types of Compounds Tentatively Identified in the Shale-Oil Acid Fraction

Name of Group	Concentration in Sour Condensate, ppb	Percent of Total Concentration
Sulfides	117	81.8
Phenols	12	8.4
Substituted Benzenes	10	7.0
Ketones	2	1.4
Pyrroles	2	1.4
Total Concentration	143	

Table 9 Summary of the Types of Compounds Tentatively Identified in the Petroleum-Crude Acid Fraction

Name of Group	Concentration in Sour Condensate, ppb	Percent of Total Concentration
Hydrocarbons	0.6	16
Substituted Benzenes	0.08	2
Unclassified	3.0	82
Total Concentration	3.68	

It has been reported that the principal nitrogen-containing species in shale oil are pyridines and pyrroles and small amounts of amides, arylamines and nitriles.[5] Anilines are not observed in shale oil but are postulated to arise during hydrocracking from saturation of the hetero-ring in such fused-ring compounds as indole or quinoline, followed by rupture of the bond between the nitrogen and the aliphatic carbon.[5] Thus, the nitrogen bases typically found in hydrocracked shale oil are 64% pyridine, 33% aniline, and 3% quinolines and tetrahydroquinolines,[6] which is almost identical to the distribution of compounds observed in the shale-oil sour condensate analyzed here (see Table 6).

Structural information about the pyridines present in shale oil has been reported. For example, it was observed that the principal alkyl substituent groups on the pyridines are methyl and/or ethyl,[4] indicating that multiple short chains such as trimethyl or methylethyl would be much more abundant than a few long chains such as propyl or butyl.[6] Furthermore, it was found that of the C_1 through C_3 pyridines, 80% had α substitution, with the most prominent substitution being in the 2,4-positions; and of the C_4 through C_7 pyridines, the major substitution pattern was of the 2,4,6-type, with very little 3- or 5- substitution.[6,7,8] In fact, 2,4,6-trimethyl pyridine constituted 33% of the total pyridines identified in shale oil.[4] By contrast, the 2,4,6-trimethyl pyridine constituted only 17% of the pyridines identified in the shale-oil refinery sour condensate. This difference is probably due to the method of sample preparation; i.e., the crude shale oil was extracted first with 10% H_2SO_4, followed by fractional distillation of the neutralized extract, whereas the shale-oil sour condensate was extracted with methylene chloride using a typical acid, base/neutral separation, as described in Section 3.

The anilines have also been reported to be α substituted, which is consistent with their postulated mode of formation, whereby rupture of the bond between the nitrogen and adjacent carbon of the saturated hetero-ring in a fused-ring system is thought to occur during hydrocracking. Previous attempts to use mass spectroscopy to distinguish the anilines present in fractionated shale oil from the pyridines were complicated because their spectra are very similar. Therefore, infrared techniques were employed.[6] In this study, the chromatographic separation achieved using a capillary column was sufficient to distinguish the two types of compounds and 22 substituted anilines were detected (see Appendix A).

Although pyrroles and nitriles are readily observed in shale oil,[5] they were not observed in the shale-oil sour condensate. There is one exception; a pyrrole compound tentatively identified as 1,2-dipyrrolylethane was observed in the acid fraction.

In general, pyrroles and indoles appear to be N-unsubstituted and highly ring-alkyl substituted.[5] Carbazoles, on the other hand, are evenly split between N-substituted and N-unsubstituted types.[5] Reference spectra were not available to completely characterize the substituted carbazoles present in the sour condensate.

One nitrogen-containing compound observed in the shale-oil sour condensate that has not been previously reported in shale-oil samples is hexamethylene tetramine. No explanation can be offered for its presence in the sample.

Sulfur and oxygen compounds are also observed in shale oil. The sulfur occurs principally in thiophenic-type compounds and oxygen occurs mainly in phenols with minor amounts in carboxylic acids, amides, ethers,[5] alcohols, and ketones.[4] However, in the refining of shale oils by catalytic hydrogenation, both sulfur and oxygen are removed.[5] Correspondingly, only 1.6% of the compounds identified in the shale-oil sour condensate contained sulfur and only a trace contained oxygen. One oxygen-containing compound, β-tetralone [3,4-dihydro-2 (1H)-napthalenone] was identified in the B/N fraction.

5.5 DISCUSSION OF CHARACTERIZATION METHOD

Despite the high resolution capability of the capillary column, complete separation between each compound in the B/N fractions was not achieved. It was, therefore, necessary to utilize massgram plots of key ions together with retention characteristics to make the identifications, as described in Section 4. Other techniques were used as well to sort out the information provided by the mass spectrometer. These techniques included the use of authentic compounds to provide retention characteristics and reference spectra.

However, neither reference spectra nor authentic compounds were available for the majority of the more highly alkyl substituted compounds (C_3, C_4, C_5, C_6) observed. Characterization could be made by predicting the pattern anticipated from examination of the available spectra of lower alkyl substituted compounds (C_0, C_1, C_2). A compound characterized by this technique, however, can only be tentatively identified as a C_x-homologue. It would be an almost insurmountable task to synthesize all possible isomers up to and including C_6, for example, and to obtain their mass spectra. Conversely, it is also an impossible task to unequivocally identify each of the C_x-homologues that might be present in a sample. The number of isomers possible for substituted pyridines is shown on Table 10. Thus, a compound tentatively identified (see Appendix A) as a C_4 pyridine is shown by Table 10 to have 48 possible structures.

It is instructive to compare published mass spectra for authentic compounds obtained from chemical supply houses to those obtained experimentally. Such a comparison gives the investigator an idea of the differences and similarities between data obtained by his instrumentation and the instrumentation that produced the reference spectra. The use of authentic compounds is also necessary to establish retention-time data. Retention characteristics obtained for authentic compounds used in this study are presented in Table 11.

It has already been pointed out that retention time and carbon number can be correlated because the boiling point of a compound is a function of the latter. In Fig. 4, this correlation is demonstrated for six different types of authentic compounds. In spite of the differences in polarity between the compound types, the fact that the majority of the points fall on a straight line indicates that the column separated the compounds on the basis of boiling point alone. The straight line in Fig. 4 was drawn from a linear-regression analysis of the data and has a correlation coefficient of 0.96.

Figure 5 shows the correlation obtained for substituted cyclohexane compounds. This data was extrapolated and used to predict the retention time for cyclohexanes with carbon numbers greater than six. The tentative identifications of C_7 through C_{11} cyclohexanes observed in the petroleum-crude oil B/N fraction were aided by this technique.

Knowledge of particular boiling points is useful for characterizing isomers of compounds. For example, although the molecular ions were not obtained for the branched and/or unsaturated hydrocarbons, their carbon numbers could be predicted because they elute before the corresponding straight-chain alkanes that are easily identified. This behavior occurs because the boiling point decreases as the symmetry of the molecule decreases, as illustrated in Table 12 for a number of C_9-hydrocarbons.

Compounds such as the C_0-tetrahydroquinolines were also characterized from a consideration of boiling points. These compounds are expected to elute in the order:

1. Cyclohexenopyridine (5,6,7,8-tetrahydroquinoline),
2. 1,2,3,4-tetrahydroisoquinoline, and
3. 1,2,3,4-tetrahydroquinoline,

Table 10 Calculation of the Total Possible Number of Alkyl Isomers of Pyridine

Alkyl Substitution	Possible Alkyl Groups & Combinations	Number of Isomers
C_0	None	1 $C_0 = 1$
C_1	R = methyl	3 $C_1 = 3$
C_2	$R_1 = R_2$ = methyl	6
	R = ethyl	3 $C_2 = 9$
C_3	$R_1 = R_2 = R_3$ = methyl	6
	R_1 = methyl; R_2 = ethyl	12
	R_1 = propyl (x2)	6 $C_3 = 24$
C_4	$R_1 = R_2 = R_3 = R_4$ = methyl	3
	$R_1 = R_2$ = ethyl	6
	$R_1 = R_2$ = methyl; R_3 = ethyl	15
	R_1 = methyl; R_2 = propyl (x2)	24 $C_4 = 48$
C_5	$R_1 = R_2 = R_3 = R_4 = R_5$ = methyl	1
	$R_1 = R_2 = R_3$ = methyl; R_4 = ethyl	9
	R_1 = methyl; $R_2 = R_3$ = ethyl	15
	$R_1 = R_2$ = methyl; R_3 = propyl (x2)	30
	R_1 = ethyl; R_2 = propyl (x2)	24
	R_1 = methyl; R_2 = butyl (x4)	48
	R_1 = pentyl (x9)	27 $C_5 = 154$
C_6	$R_1 = R_2 = R_3 = R_4$ = methyl; R_5 = ethyl	3
	$R_1 = R_2$ = methyl; $R_3 = R_4$ = ethyl	19
	$R_1 = R_2 = R_3$ = ethyl	6
	$R_1 = R_2$ = propyl (x2)	12
	$R_1 = R_2$ propyl	12
	R_1 = propyl; R_2 = ethyl; R_3 = methyl (x2)	60
	R_1 = butyl; $R_2 = R_3$ = methyl (x4)	60
	R_1 = butyl; R_2 = ethyl (x4)	48
	$R_1 = R_2 = R_3$ = methyl; R_4 = propyl (x2)	18
	R_1 = pentyl; R_2 = methyl (x9)	108
	R_1 = hexyl (x23)	69 $C_6 = 415$

Total possible isomeric combinations through C_6 = 654.

Table 11 Retention-Time Characteristics of Authentic Compounds

Name	Retention Time, Min	Relative Retention Time[a]
2-Picoline	10.5	1.39
2,4-Lutidine	17.8	2.63
2,4,6-Collidine	22.3	3.53
t-Butyl pyridine	30.2	4.95
Aniline-d_5	23.9	3.69
N-Methyl aniline	28.6	4.66
o-Toludine	28.8	5.06
2,6-Dimethyl aniline	36.3	5.82
2,4,6-Trimethyl aniline	42.9	7.22
2,6-Diethyl aniline	47.4	8.01
p-n-Butyl aniline	50.9	8.64
Quinoline	41.7	5.09
1,2,3,4-Tetrahydroquinoline	46.4	8.45
Cyclohexenopyridine	38.4	6.91
Quinaldine	49.3	8.99
Lepidine	44.7	8.13
2,6-Dimethyl quinoline	52.4	9.61
Toluene	8.1	1.00
o-Xylene	15.8	2.29
1,3,5-Trimethyl benzene	21.2	3.34
p-Diethyl benzene	27.8	4.51
Methyl cyclohexane	8.6	0.79
cis-1,3-Dimethyl cyclohexane	11.1	1.12
Ethyl cyclohexane	14.1	1.50
Isopropyl cyclohexane	19.7	2.23
t-Butyl cyclohexane	24.4	2.84
Dicyclohexyl	47.6	5.86
Naphthalene	36.7	6.11
Anthracene	74.9	12.93
Pyrene	90.5	15.77
Carbazole	75.3	13.01

[a] Computed assuming a gas-holdup time of 2.5 min.

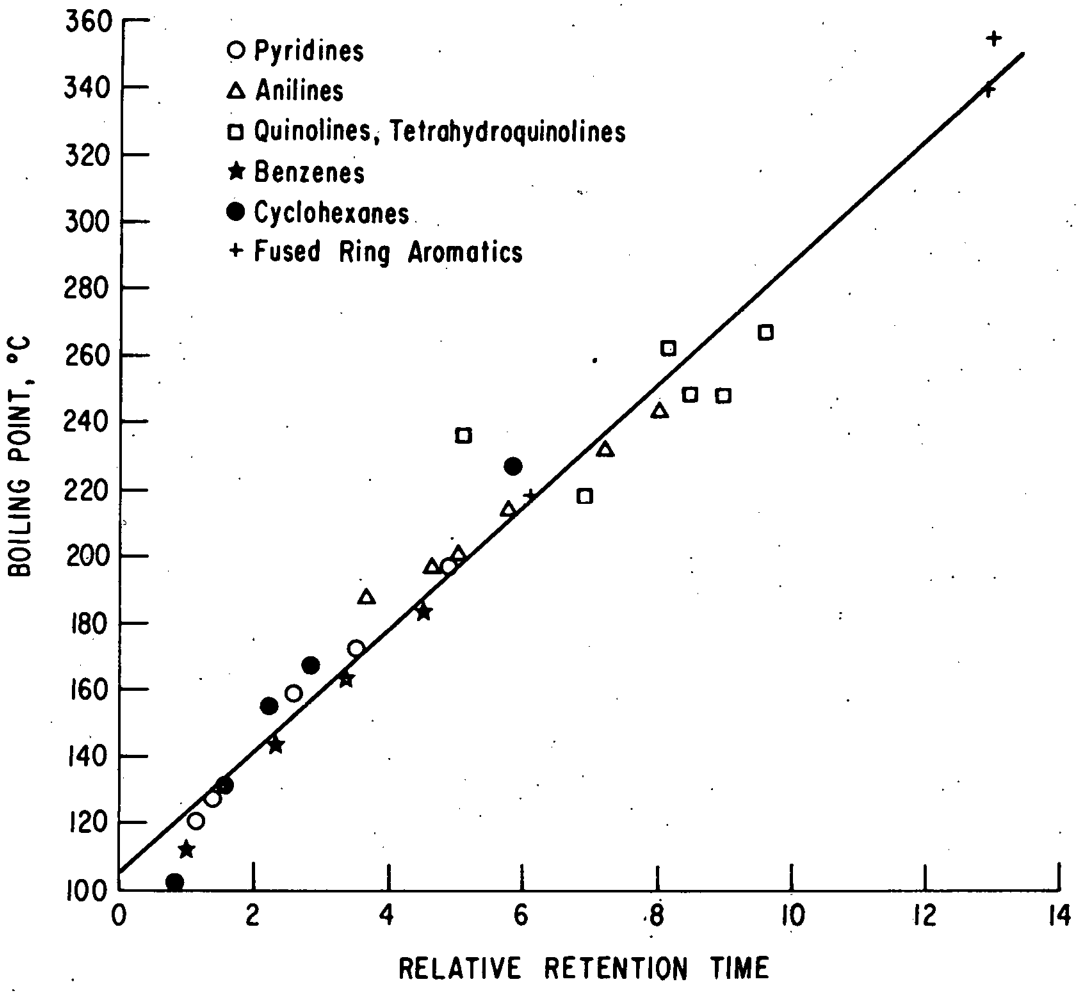

Fig. 4 Boiling Point Versus Relative Retention Time for Authentic Compounds (line drawn from linear-regression analysis)

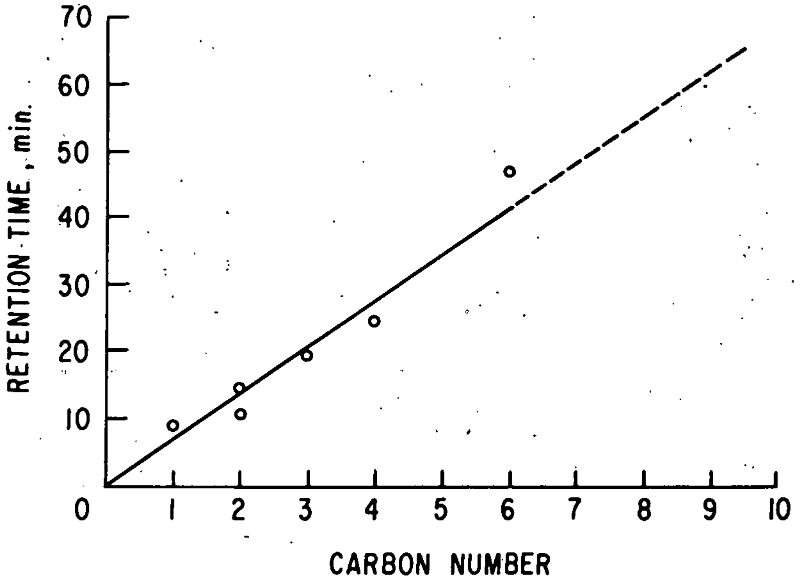

Fig. 5 Retention Time of Substituted Cyclohexanes Versus Carbon Number

Table 12 Boiling Points of a Number of C_9-Hydrocarbons

Name	Molecular Formula	B.P. °C
n-Nonane	C_9H_{20}	151
2-Methyl octadiene-4,6	C_9H_{16}	149
Nonene-2	C_9H_{18}	148-9
2,2-Dimethyl-4-ethyl hexane	C_9H_{20}	147
Nonene-1	C_9H_{18}	146
1,3-Dimethyl heptadiene-2,6	C_9H_{16}	145
3-Methyl octane	C_9H_{20}	144
2-Methyl octane	C_9H_{20}	143
4-Methyl octane	C_9H_{20}	142-3
4-Ethyl heptane	C_9H_{20}	141
2,2,3,3-Tetramethyl pentane	C_9H_{20}	140
2,3,4-Trimethyl hexane	C_9H_{20}	139
3-Ethyl-2-methyl hexane	C_9H_{20}	138
2,4-Dimethyl-3-ethyl-pentane	C_9H_{20}	137
2,5-Dimethyl heptane	C_9H_{20}	136
2,6-Dimethyl heptane	C_9H_{20}	135
3-Ethyl-2,2-dimethyl pentane	C_9H_{20}	134
2,2,3,4-Tetramethyl pentane	C_9H_{20}	133
2,3,5-Trimethyl hexane	C_9H_{20}	131
2,4,4-Trimethyl hexane	C_9H_{20}	130

since their boiling points are 218, 232-233, and 249°C, respectively. Thus, the C_4-tetrahydroquinolines probably were observed to elute before some C_2- and C_3-tetrahydroquinolines because the C_4 compounds are substituted cyclohexenopyridines that have a lower boiling point than the more symmetric C_2- and C_3-1,2,3,4-tetrahydroquinolines.

Characterization of more-polar compounds such as anilines and phenol was facilitated by derivatization techniques. Since the spectra of C_x-anilines are very similar to those of C_{x+1}-pyridines, the two cannot be distinguished by examination of spectra only.[6] However, they can be distinguished from a knowledge of their retention-time characteristics. The GC/MS data were therefore examined before and after derivatization with TRI-SIL. The differences specific to the anilines observed between the two GC/MS runs permitted determination of their retention characteristics.

One of the objectives of this study was to characterize and provide semiquantitative information on the priority pollutants in these samples. These data are compiled from Appendixes A, B, C, and D in Table 13.

5.6 POTENTIAL SOURCES OF ERROR INVOLVED IN SEMIQUANTITATIVE MEASUREMENTS

It was assumed that of the extraction of organic compounds from the sour-water-condensate samples was 100%. While this degree of efficiency

Table 13 Listing of the Compounds Identified as Priority Pollutants

Shale Oil		Petroleum Crude	
Name	Concentrations in Sour Condensate, ppb	Name	Concentrations in Sour Condensate, ppb
Toluene	146	Toluene	0.08
Ethyl benzene	29	Ethyl benzene	20
Phenol	12		
Naphthalene	26	Total Concentration	20
Anthracene	3		
Fluorene	2		
Total Concentration	218		

is not necessarily obtained, such an assumption has to be made in this type of study because the determination of each individual extraction efficiency would be too time-consuming. Moreover, the authentic compounds required for determining extraction efficiency are probably not readily available.

Since the solubility of the substituted benzenes and straight-chain alkanes and other hydrocarbons is very low in water, a 95-100% extraction efficiency for these compounds can be expected. However, it is more difficult to predict the extraction efficiency of polar nitrogen compounds -- such as pyridines, anilines, quinolines and tetrahydroquinolines -- that are somewhat soluble in water. The extraction efficiency of these compounds is sometimes improved by adjusting the pH of the aqueous solution to pH 12 before extracting, but the actual extraction efficiency for each compound is unknown.

Errors in quantitation can also occur from volumetric handling of the extract and calibrating solution. The samples were received in vials purged with nitrogen prior to sealing. The purging process caused evaporation of some of the methylene chloride solvent and possibly loss of the more volatile organic compounds. While the data presented were corrected for the amount of solvent lost, the measurement of this amount can be in error by 5-10%. Further manipulations such as dilution, concentration, derivatization, etc. contribute to the inaccuracies of the measurements because the solvent is very volatile and the working volumes are small. Thus, a small amount of solvent volatilization leads to a significant change in solution concentration and, therefore, a significant error in the semiquantitative data.

Analysis of components in a mixture by gas chromatography is optimally performed when the response of a component is very similar to that of the calibrating material, whether employed as an internal or external standard. Under actual conditions, this situation is seldom achieved due to the wide range of concentrations of components in samples of the type analyzed here. For example, the 218 components listed in Appendix A were observed to have concentrations ranging from <1 to 700 ng in the 0.5-)L aliquot of the shale-oil B/N extract injected on column. Measurements of concentration tend to be low at both low and high concentrations of material due to adsorption on the column at low concentration and saturation of the mass spectrometer at high concentration.

The amount of adsorption on a column depends on the molecular interaction of the compounds with the liquid phase. Hydrocarbon compounds behave more ideally with the OV-101 liquid phase than do polar compounds, because the hydrocarbons and liquid phase have similar attractive forces. Polar compounds, especially those containing nitrogen, undergo molecular interactions (hydrogen bonding) that lead to a decrease in the partition coefficient as the concentration increases and, therefore, the parts of the peak of high concentration tend to move faster than those of low concentration. This tendency is observed as peak tailing. Therefore, area measurements tend to be low depending on the amount of material lost in the tail. For identical concentrations of a hydrocarbon and a polar compound injected on column, a lower response would be measured for the polar material.

Moreover, it was assumed that the response measured for the base peak of any compound and that measured for the base peak of anthracene-d_{10} would be identical for identical concentrations injected on column (response factor + 1.0). This situation is seldom achieved in practice.[9] In Table 14, the actual amount of authentic materials injected on column is compared to the amount computed using the base peak response of the authentic materials and anthracene-d_{10}. The amount computed ranges from 0.22 to 1.15 of the actual amount injected, with an average value of 0.51. This value indicates that the response obtained for these compounds is roughly one-half of the value measured for an identical amount of anthracene-d_{10}.

6 WASTEWATER-CONTROL-TECHNOLOGY CONSIDERATIONS

6.1 EXPECTED EFFECTS OF SHALE-OIL SOUR CONDENSATE ON SOUR-WATER STRIPPER

In most refineries, sour condensate, after steam stripping to remove hydrogen sulfide and ammonia, ultimately goes to the wastewater-treatment plant. Two of the major sources of sour condensate present in a refinery are the hydrotreating and hydrocracking units. These units are designed to remove sulfur from the oil, by conversion to hydrogen sulfide, and nitrogen, by conversion to ammonia, so that S and N will not interfere with downstream refinery operations. Because shale oil has a high organic-nitrogen content (up to 20 times the nitrogen concentration of conventional crude oils), it is reasonable to assume that the sour condensates generated from hydrotreating and hydrocracking of shale oil will contain considerably more total nitrogen (ammonia and some organic nitrogen) than sour condensates generated from conventional crude oils.

A direct effect from the introduction of shale-oil sour condensate into a sour-water stripper designed for conventional crude-oil sour condensates could be an increased ammonia concentration in the stripped sour water (stripper bottoms). Since the stripper bottoms ultimately go to the wastewater facility and generally represent a significant fraction of the total wastewater flow, the presence of shale-oil sour condensate could add ammonia loading to the wastewater-treatment plant. Therefore, should a significant amount of crude shale oil be processed through a conventional

Table 14 Comparison of Actual Amount of Standard Compound Injected on Column to that Computed Using Anthracene-d_{10} as an Internal Standard

Compound Class	Name of Compound	ng Injected on Column	ng Found Relative to Anthracene-d_{10}	Ratio of Amount Found to Amount Injected
Pyridines	2-Picoline	95	48	0.50
	2,4-Lutidine (2,4-dimethyl pyridine	95	39	0.41
	2,4,6-Collidine (2,4,6-trimethyl pyridine)	75	43	0.57
Anilines	Aniline -d_5	89	35	0.39
	N-Methyl aniline	90	40	0.44
	o-Toluidine	95	50	0.53
	2,6-Dimethyl aniline	171	77	0.45
	2,4,6-Trimethyl aniline	141	74	0.52
	2,6-Diethyl aniline	154	111	0.72
	p-n-Butyl aniline	70	47	0.67
Quinolines & Tetrahydroquinolines	Quinoline	133	63	0.47
	1,2,3,4-Tetrahydroquinoline	69	22	0.32
	Cyclohexenopyridine (5,6,7,8-Tetrahydroquinoline)	166	37	0.22
	Quinaldine (2-methyl quinoline)	85	33	0.39
	Lepidine (4-methyl quinoline)	103	43	0.42
	2,6-Dimethyl quinoline	67	26	0.39
Substituted Benzenes	Toluene	51,73	32,58	0.63,0.79
	o-Xylene	84	97	1.15
	p-Diethyl benzene	59	42	0.71
Cyclohexanes	Methyl cyclohexane	79	17	0.22
	cis-1,3-Dimethyl cyclohexane	118	40	0.34
	Ethyl cyclohexane	102	40	0.39
	Isopropyl cyclohexane	93	34	0.37
	t-Butyl cyclohexane	97	61	0.63
	Dicyclohexyl	125	72	0.58

refinery, the sour-water stripper operations and design may have to be altered to handle the increased ammonia loading. Hence, a greater volume of stripping steam and higher pH levels (attained by adding caustic) might be required to control the stripper bottoms' ammonia concentration. It is possible that even considerably increased amounts of ammonia could be stripped from the condensate, thereby resulting in no increased ammonia loadings at the wastewater-treatment plant.

The effect of shale-oil sour condensate on the sour-water stripper could not be assessed during the SOHIO shale-oil run because the shale-oil sour condensates represented only about 2% of the total sour-water stripper feed and no samples of the stripper feed or bottoms were obtained. In addition, the shale-oil sour condensate itself was not analyzed for ammonia and the stripper was not operating normally due to problems with a part of the refinery sour-water-collection system. Further sampling and analysis of the stripper feed and product streams as well as the shale-oil sour condensate are required to assess the impacts.

A second, less-direct effect of refining shale oil is related to the major organic-nitrogen compounds identified by the shale-oil sour condensate analysis (pyridines and anilines). As shown in Table 15, these materials, like phenol, are somewhat water soluble, are steam distillable, have a relatively high vapor pressure, and have boiling points that are higher than the temperatures normally found in sour-water strippers (102-104°C). The SOHIO refinery normally adds caustic to the sour-water stripper to enhance ammonia removal, however, and it is expected that this action would assist in removal of the more volatile pyridines and anilines. Sour-water strippers generally remove 20%[13] to 60% (M. LaGraff, SOHIO, 1980, written communication) of the influent phenol. It is reasonable to assume that steam stripping will have a greater effect on the organic bases than it does on phenol because addition of caustic produces sodium phenolate, an ionic species. With sufficient addition of caustic, all bases are present in free base form, as opposed to ionic form (at pH >9.0), and bases like pyridines and anilines will be more susceptible to stripping. Because the stripper bottoms were not analyzed, the efficiency of this removal step cannot be measured and further sampling and analysis are required to quantitatively evaluate this step.

6.2 EXPECTED EFFECTS OF SHALE-OIL SOUR CONDENSATE ON A WASTEWATER-TREATMENT UNIT

As previously mentioned, stripped sour water in refineries normally goes to the wastewater-treatment unit, as is the case at SOHIO's Toledo refinery. During the shale-oil run, no sampling was done at the wastewater-treatment plant to determine the effect the shale-oil sour condensate might have on the facility. The shale-oil condensate represented a very small contribution to the total wastewater flow (<0.5%), and some unstripped sour condensate was being discharged to the treatment plant due to the upset described in Section 2. However, if the stripped shale-oil sour condensate has the characteristics described earlier, its effects on the wastewater-treatment plant may be projected.

Table 15 Properties of Organic-Nitrogen Compounds and Phenol

Compound	Boiling Point, °C	Water Solubility
Pyridine[a]	115-116	∞
Aniline	184-186	3.6 parts/100 parts H_2O @18°C
Quinoline	238	0.6 parts/100 parts H_2O @20°C
Phenol	184	8.2 parts/100 parts H_2O @15°C

[a] Stable in hot alkali.

Sources: *Perry's Chemical Engineers Handbook,* 4th ed. (n.d.); *Merck's Index,* 9th ed. (1976); and Elderfield, R.C., *Heterocyclical Compounds,* John Wiley & Sons (1980).

The major impact that the stripped shale-oil condensate would have on the wastewater-treatment plant would be a possibly increased ammonia contribution. This contribution would depend on the amount of condensate present due to shale-oil processing and the ammonia and organic-nitrogen concentrations of the stripped shale-oil sour condensate. It could be accommodated either through an increase in treatment time or an increase in effluent ammonia levels within permitted limits, depending on the system's ability to remove ammonia biologically. If a refinery were to process both shale- and conventional-crude oil, or change from conventional crude oil to shale oil, operating changes to increase the population of nitrifiers present in the wastewater facility would be necessary to facilitate ammonia removal. However, the actual effects and necessary actions can only be known through further test work. This effect would be site specific.

The other potential effect would be related to the concentration of extractable/chromatographable compounds in stripped shale-oil condensate. While these compounds typically are present in total concentrations less than 4 ppm in the unstripped shale-oil sour condensate, it is not known what effect they could have on a wastewater-treatment facility. Many have been identified in petroleum-refinery wastewaters, but these generally have concentrations of <1 ppb and treatment performance appears to be unaffected at such low concentration levels.[14]

The principal concern here is that these materials, should they be present in significant quantities in treatment-plant influent, could also increase effluent ammonia concentrations. Through treatability studies of coal-conversion wastewaters, it has been found that compounds such as pyridine, aniline, quinoline, and their derivatives are amenable to biological oxidation.[15] However, a product of this degradation is ammonia. Therefore, these materials could also contribute to the overall ammonia load or to increased effluent. Again, this cannot be confirmed by the SOHIO shale-oil run and further test work is necessary.

It was also shown in previous work[14] that, while most organic materials present in conventional refinery wastewaters show >99% removal by biological treatment, some of the organic-nitrogen compounds generally show only 90+% removal. It was also shown that these materials can be readily removed by activated-carbon adsorption, a procedure that could be considered as part of the wastewater-processing scheme should these compounds prove difficult to remove biologically. This treatment would be particularly important if these materials were identified as toxic and would have to be controlled.

Based on the preceding, it would appear that shale-oil sour condensate would have the greatest impact on wastewater-treatment systems that have the least flexibility of capacity for ammonia removal. The changeover from processing conventional crude oil to shale oil would probably require changes in the sour-water stripper and, possibly, in the wastewater-treatment plant operations. The necessity and extent of these changes would depend on such factors as the amount of shale oil processed, the volume and characteristics of shale-oil sour condensate generated, and the overall refinery-processing scheme.

The data from this project do not lend themselves to detailed projections of the effect that shale-oil sour condensate would have on the wastewater-treatment facility. More-extensive sampling and treatability tests are required to determine the exact nature of the shale-oil sour condensate treatment.

7 CONCLUSIONS

Good agreement on the types of compounds present in the shale-oil sour condensate and their relative concentrations was obtained by Argonne and Radian laboratories for shale oil, but not for petroleum-crude. The number of compounds detected by Argonne was 218, compared to 129 by Radian, in the former condensate, and 161 to 121 in the latter. The presence of tetralins, indans, and piperidines was reported by Argonne, whereas Radian reported a higher trithiolane concentration and n-alkanes through C_{29} in the shale-oil sour condensate. Because Radian did not detect any branched or unsaturated hydrocarbons in the extracts of the petroleum-crude sour condensate, a significant difference exists in the relative amounts of compounds between the Argonne and Radian data. On the other hand, Radian found larger concentrations of benzenes, tetralins, and indans and reported the presence of naphthalene, which Argonne did not detect. Because the Argonne data are more comprehensive, however, the conclusions that follow will be based exclusively on Argonne's identifications and semiquantitative results.

The prevailing types of compounds found in the sour condensate from the shale-oil run at SOHIO's Toledo refinery were pyridines and anilines. In contrast, straight-chain alkanes were the predominant types of compounds found in the condensate as a result of the petroleum refining run. Semiquantitative measurement of the pyridines and anilines in the sour condensate from the shale-oil refining run indicated that they are present in a concentration of 5.7 ppm, or about 78% of the total concentration of components detected. The concentrations of straight-chain alkanes, 8.3 ppm, and of other branched and/or unsaturated hydrocarbons, 6.8 ppm, amount to 88% of the total concentration of components detected in the sour condensate from the petroleum-crude refining run.

Very few priority pollutants were found in the samples under study; 3% of the total concentration of compounds characterized in the shale-oil sour condensate and 0.1% of those in the petroleum-crude sour condensate were on the priority-pollutant list. These compounds were predominantly substituted benzenes.

Based on the characteristics of the shale-oil sour condensate, it may be concluded that the presence of this condensate would affect the sour-water stripper operations. Actual effects may only be projected from the data generated by this project because the volume of shale-oil sour condensate represented only a small fraction of the total refining sour condensate (<2%). In addition, the samples obtained for organic-constituent analysis were of the unstripped-shale-oil sour condensate and the refinery was experiencing an upset of the sour-water stripper during the shale-oil run. Therefore, the analysis of additional samples is needed to confirm any projected effects. The effect that shale-oil sour condensate might have on wastewater-treating facilities will depend on such factors as the characteristics of the stripped condensate, the volume of shale-oil sour condensate present, the fate of the organic-nitrogen compounds in the sour-water stripper, the development of conditions encouraging the growth of bacteria capable of degrading the types of compounds in shale-oil sour condensate, and the ability of the wastewater-treatment facility to handle higher ammonia loadings and to oxidize the organic-nitrogen compounds.

It is possible that both the sour-water stripper and wastewater-treatment plants could be operated differently to increase the ammonia-removal efficiency. This change could involve greater stripping-steam requirements as well as higher pH levels to help remove the ammonia. The wastewater plant might have to be operated to enhance biological nitrification or to help control excess ammonia discharges through effluent treatment.

A final consideration bearing upon the speculations of the above two paragraphs is that shale crude oil may not be processed on a long-term basis in the same manner as was done in this experimental run.

ACKNOWLEDGMENTS

Alan Roberts, U.S. Navy Energy and Natural Resources R&D office, provided helpful information on details of the Navy's shale-oil processing studies. Tom Barrs, Mittelhauser Corporation, assisted with the wastewater-control-technology portion of the study.

The following SOHIO personnel are thanked for their assistance: Paul Tranquill, for providing information on the shale-oil processing run, and David Rulison and Michael LaGraff, for critical review of the manuscript. Vernon Snoeyink, Prof. of Environmental Engineering, University of Illinois/Urbana, and Donald Mackay, Prof. of Chemical Engineering, University of Toronto, also reviewed the manuscript and provided helpful comments.

Kathryn Macal edited this report and Sally Vargo prepared the manuscript for publication; both are members of Argonne's Energy and Environmental Systems Division.

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APPENDIX A

LISTING OF COMPOUNDS TENTATIVELY IDENTIFIED IN THE SHALE-OIL REFINERY BASE/NEUTRAL FRACTION

Retention Time, Min	Scan #	Tentative Identification	Base Peak	Base-Peak Counts	Concentration in Sour Condensate, ppb
7.9	22	Toluene	91	24,830	146
10.0	132	Picoline (methyl pyridine)	93	3,040	18
11.4	203	C_1-Piperidine	98	770	4
12.7	270	C_2-Piperidine	98	2,930	17
12.7	271	Picoline	93	6,360	37
12.9	279	Picoline	93	2,070	12
13.1	291	C_1-Piperidine	98	940	6
13.2	298	Ethyl benzene	91	4,970	29
13.9	330	Xylene	91	11,690	69
14.4	358	3,5-Dimethyl pyridine	107	10,280	60
15.0	386	C_2-Piperidine	112	2,880	17
15.3	405	Xylene	91	8,680	51
15.7	426	2-Ethyl pyridine	106	490	3
16.5	463	C_2-Piperidine	112	200	1
17.6	523	3,4-Dimethyl pyridine	107	78,490	460
18.4	565	2,5-Dimethyl pyridine	107	10,760	63
19.9	642	C_3-Benzene	91	920	5
20.4	667	2-Methyl-6-ethyl pyridine	120	5,110	30
20.5	674	C_3-Benzene	105	3,630	21
20.7	680	C_3-Benzene	105	1,300	8
20.9	693	C_2-Pyridine	107	10,400	61
21.2	705	C_3-Benzene	105	1,190	7
21.3	715	C_2-Pyridine	107	-	-
21.7	737	C_3-Benzene	105	2,150	13
22.6	779	2,4,6-Trimethyl pyridine	121	119,400	700
22.9	797	2,4-Dimethyl pyridine	107	29,000	170
23.1	805	C_3-Benzene	105	14,500	85
23.5	838	C_3-Pyridine	121	22,370	132
23.7	834	Aniline	93	68,400	400
24.1	858	Methylethyl pyridine	120	10,800	63
24.2	864	Methylethyl pyridine	120	2,930	23
24.5	881	Methylethyl pyridine	120	620	4
24.7	889	3-Ethyl-4-methyl pyridine	106	600	4
25.0	905	Trimethyl pyridine	121	11,730	69
25.7	939	Indan	117	3,140	18
27.2	1018	2,3,6-Trimethyl pyridine	121	27,880	160
28.0	1062	2,3,5-Trimethyl pyridine	121	96,660	570
28.3	1074	C_4-Benzene	119	580	3
28.7	1098	2,4-Dimethyl-6-ethyl pyridine	134	44,350	260
29.2	1122	Trimethyl pyridine	121	33,540	200
29.7	1147	C_4-Benzene	119	240	1
30.0	1160	N-Methyl aniline	106	61,300	360
30.1	1166	C_4-Pyridine	135	24,010	140

APPENDIX A (Contd.)

Retention Time, Min	Scan #	Tentative Identification	Base Peak	Base-Peak Counts	Concentration in Sour Condensate, ppb
30.2	1172	C_4-Benzene	119	850	5
30.5	1186	o-Toluidine	106	7,940	47
30.9	1208	Toluidine	106	11,550	68
31.0	1215	Toluidine	107	24,200	140
31.5	1239	C_4-Pyridine	134	2,080	12
31.5	1241	C_4-Benzene	119	540	3
31.8	1252	C_4-Pyridine	134	1,070	6
32.2	1272	C_4-Pyridine	107	1,880	11
32.5	1290	C_4-Benzene	119	180	1
32.7	1303	C_4-Benzene	119	290	2
33.0	1317	C_4-Pyridine	135	18,790	110
33.9	1362	C_4-Pyridine	135	25,900	150
34.1	1374	C_4-Pyridine	135	44,070	260
34.4	1390	C_5-Pyridine	148	3,220	19
34.6	1397	C_4-Pyridine	134	15,740	92
34.6	1400	4-Methyl indan	117	2,410	14
35.0	1417	C_4-Pyridine	135	4,920	29
35.1	1424	C_5-Pyridine	121	6,150	36
35.1	1424	C_5-Benzene	134	2,300	13
35.3	1432	1,2,3,4-tetrahydronaphthalene (tetralin)	104	2,760	16
35.7	1452	C_5-Pyridine	148	9,440	56
35.8	1460	N-Ethyl aniline	106	9,640	57
36.1	1472	C_5-Pyridine	106	4,570	27
36.2	1477	Ethyl-methyl pyridine	121	2,890	17
36.4	1492	C_5-Pyridine	121	380	2
36.7	1504	C_5-Pyridine	121	6,860	40
36.8	1510	Naphthalene	128	4,520	26
37.1	1524	C_2-Aniline	121	5,860	34
37.7	1554	Dimethyl indan	131	550	3
37.9	1566	C_2-Aniline	121	-	-
37.9	1566	Dimethyl indan	131	-	-
38.1	1574	C_5-Pyridine	148	2,120	12
38.3	1584	C_5-Pyridine	121	-	-
38.3	1584	Dimethyl indan	131	350	2
38.9	1619	C_5-Pyridine	148	3,110	18
39.2	1629	C_5-Pyridine	121	2,060	12
39.3	1639	C_5-Pyridine	121	1,060	6
39.4	1641	β-Tetralone	104	460	3
39.7	1660	Hexamethylene tetramine	42	12,190	72
39.9	1669	C_5-Pyridine	148	12,300	72
40.0	1674	C_5-Pyridine	135	18,970	110
40.3	1691	C_5-Pyridine	148	2,770	16
40.5	1698	C_5-Pyridine	135	-	-
40.5	1698	5,6,7,8-Tetrahydroquinoline (2,3-Cyclohexenopyridine)	132	2,180	13
40.6	1702	Quinoline	129	680	4

APPENDIX A (Contd.)

Retention Time, Min	Scan #	Tentative Identification	Base Peak	Base-Peak Counts	Concentration in Sour Condensate, ppb
40.6	1705	C_5-Pyridine	148	360	2
40.9	1716	C_5-Pyridine	148	1,080	6
40.9	1716	C_6-Pyridine	163	–	–
41.1	1728	C_5-Pyridine	121	1,780	10
41.3	1741	C_5-Pyridine	121	1,130	7
41.8	1766	Propyl aniline	106	7,720	45
42.0	1777	N-Ethyl-o-toluidine	120	1,670	10
42.0	1777	C_6-Pyridine	162	410	2
42.2	1789	C_3-Aniline	121	2,840	17
42.2	1789	Tetrahydroisoquinoline (1,2,3,4)	132	794	5
42.5	1805	C_3-Aniline	120	–	–
42.8	1819	C_3-Aniline	120	1,300	8
43.0	1827	C_3-Aniline	120	2,410	14
43.0	1827	C_2-Indan	131	530	3
43.6	1859	Methyl tetrahydroquinoline	147	970	6
43.8	1870	Tetrahydroquinoline (1,2,3,4)	132	1,620	10
44.1	1883	Methyl tetrahydroquinoline	146	1,210	7
44.3	1896	Dimethyl tetrahydroquinoline	146	–	–
44.7	1919	C_3-Aniline	106	–	–
44.9	1927	Methyl tetrahydroquinoline	146	3,230	19
44.9	1928	Methyl napthalene	142	2,120	12
45.2	1942	C_4-Aniline	149	8,800	52
45.4	1951	C_3-Aniline	120	–	–
45.6	1963	Methyl quinoline	143	2,730	16
45.8	1971	C_4-Aniline	135	1,080	6
45.9	1980	Methyl napthalene	142	1,060	6
46.2	1993	Dimethyl tetrahydroquinoline	146	1,640	10
46.4	2003	C_3-Aniline	135	–	–
47.0	2036	Dimethyl tetrahydroquinoline	146	350	2
47.4	2057		145	180	1
47.7	2072	Dimethyl tetrahydroquinoline	146	3,070	10
47.8	2077	N-Butyl aniline	120	4,600	27
48.2	2098	Dimethyl tetrahydroquinoline	146	3,190	19
48.4	2107	C_4-Aniline	134	2,300	14
48.6	2116	Dimethyl tetrahydroquinoline	146	290	2
49.0	2138	Methyl quinoline	143	1,440	8
49.1	2144	C_4-Aniline	134	1,650	10
49.3	2158	Methyl tetrahydroquinoline	146	5,690	33
49.6	2168	Indole	117	1,130	7
49.7	2177	C_6-Pyridine	162	120	–
49.7	2177	Dimethyl tetrahydroquinoline	160	790	5
50.2	2199	Methyl quinoline	143	2,170	13
50.5	2216	Dimethyl tetrahydroquinoline	160	650	4
50.7	2230	Methyl tetrahydroquinoline	147	1,300	8
50.8	2234	C_5-Aniline	134	680	4
51.0	2244	Dimethyl tetrahydroquinoline	132	100	–

APPENDIX A (Contd.)

Retention Time, Min	Scan #	Tentative Identification	Base Peak	Base-Peak Counts	Concentration in Sour Condensate, ppb
51.2	2251	Methyl tetrahydroquinoline	146	350	2
51.4	2263	Dimethyl tetrahydroquinoline	146	290	2
51.6	2275	Dimethyl tetrahydroquinoline	161	-	-
51.8	2282	C_3-Indan	160	-	-
52.1	2301	Dimethyl tetrahydroquinoline	146	1,520	9
52.6	2324	C_2-Naphthalene	156	-	-
52.8	2338	C_4-Tetrahydroquinoline	188	-	-
52.9	2345	C_4-Tetrahydroquinoline	188	-	-
53.0	2347	C_2-Tetrahydroquinoline	161	3,450	20
53.1	2351	B/U C_{14} Hydrocarbon*	57	250	1
53.1	2352	C_1-Tetralin	146	-	-
53.4	2368	C_2-Tetrahydroquinoline	160	10,140	59
53.5	2370	C_2-Quinoline	157	2,020	12
53.7	2381	C_2-Naphthalene	156	880	5
53.7	2381	C_6-Pyridine	163	-	-
53.7	2381	C_2-Tetrahydroquinoline	160	-	-
54.3	2412	Methyl indole	130	3,410	20
54.3	2412	C_2-Tetrahydroquinoline	160	8,040	47
54.6	2425	Tetradecane (n)	57	1,060	6
54.7	2433	4,8-Dimethyl quinoline	157	8,160	48
54.9	2445	C_3-Tetrahydroquinoline	160	160	1
55.2	2457	2,6-Dimethyl quinoline	157	2,720	16
55.4	2473	C_2-Quinoline	157	400	2
55.8	2491	C_2-Tetrahydroquinoline	160	660	4
56.7	2535	C_3-Tetrahydroquinoline	160	1,270	7
56.8	2543	C_3-Tetrahydroquinoline	160	1,580	9
57.8	2593	5,8-Dimethyl quinoline	157	1,100	6
58.1	2609	C_2-Indole	144	3,890	23
58.4	2625	C_3-Tetrahydroquinoline	174	640	4
58.4	2625	C_2-Quinoline	157	300	2
58.7	2642	B/U C_{15} Hydrocarbon	57	500	3
59.1	2662	C_2-Tetrahydroquinoline	160	1,230	7
59.1	2662	C_3-Quinoline	171	620	4
60.1	2711	C_2-Quinoline	157	670	4
60.1	2711	C_2-Indole	144	510	3
60.7	2746	C_3-Naphthalene	170	40	-
61.0	2760	Pentadecane (n)	57	1,020	6
61.6	2793	C_3-Quinoline	171	-	-
61.8	2803	C_3-Quinoline	171	2,270	13
61.9	2810	C_3-Quinoline	171	2,420	14
62.4	2835	C_3-Quinoline	171	1,500	9
62.7	2848	C_3-Quinoline	171	680	4
63.4	2885	Fluorene	166	267	2
63.4	2885	C_3-Quinoline	171	420	2
63.7	2903	C_3-Indole	158	120	-
64.3	2930	C_3-Indole	158	2,400	14
67.1	3075	Hexadecane (n)	57	970	6

APPENDIX A (Contd.)

Retention Time, Min	Scan #	Tentative Identification	Base Peak	Base-Peak Counts	Concentration in Sour Condensate, ppb
68.2	3133	C_3-Indole	158	90	-
70.1	3232	B/U C_{17} hydrocarbon	57	520	3
71.9	3329	C_4-Indole	173	390	2
72.8	3374	Heptadecane (n)	57	1,180	7
73.4	3403	Pristane	57	970	6
74.3	3452	Anthracene	178	490	3
74.7	3474	Anthracene-d_{10}	188	33,068	
78.2	3654	Octadecane (n)	57	1,180	7
78.9	3690	Phytane	57	400	2
80.3	3763	Carbazole	167	7,760	46
83.4	3921	Nonadecane (n)	57	1,250	7
83.5	3926	Methyl carbazole	181	6,650	39
85.1	4012	Methyl carbazole	180	560	3
85.4	4025	Methyl carbazole	180	1,300	8
85.8	4046	Dimethyl carbazole	195	1,140	7
86.1	4062	Methyl carbazole	180	1,510	9
88.2	4174	Eicosane (n)	57	1,390	8
88.3	4176	Dimethyl carbazole	195	570	3
88.6	4192	Dimethyl carbazole	195	380	2
89.1	4219	Dimethyl carbazole	195	320	2
89.2	4224	Dimethyl carbazole	195	320	2
92.9	4416	Heneicosane (n)	57	1,370	8
97.4	4647	Docosane (n)	57	1,030	6
101.7	4869	Tricosane (n)	57	1,080	6
104.6	5020	**	129	930	5
109.4	5265	**	57	560	3
113.4	5471	**	57	250	1

*B/U ≡ branched and/or unsaturated.

**Too weak for tentative identification to be made.

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APPENDIX B

LISTING OF COMPOUNDS TENTATIVELY IDENTIFIED IN THE PETROLEUM-CRUDE REFINERY BASE/NEUTRAL FRACTION

Retention Time, Min.	Scan #	Tentative Identification	Base Peak	Base-Peak Counts	Concentration in Sour Condensate, ppb
13.5	278	*	91	390	18
14.9	342	Ethyl benzene	91	440	20
19.3	544	*	91	200	9
19.9	572	C_3-Benzene	105	1,490	69
20.0	577	*	105	500	23
20.5	599	C_3-Benzene	105	780	36
21.1	627	C_3-Benzene	105	820	38
22.3	681	C_3-Benzene	105	3,480	160
24.2	768	C_3-Benzene	105	2,070	96
24.2	771	Decane (n)	57	3,960	180
24.9	801	Indan	117	550	26
25.9	848	C_4-Cyclohexane	55	510	24
26.1	856	B/U C_{11} Hydrocarbon**	43	1,120	52
26.8	888	*	105	820	38
27.0	897	cis-Decalin (decahydronaphthalene)	41	350	16
27.2	909	*	57	343	16
27.4	915	C_4-Benzene	119	900	42
27.8	937	*	105	530	25
28.8	980	C_4-Benzene	119	720	33
28.8	980	B/U C_{11} Hydrocarbon	57	900	42
29.0	990	B/U C_{11} Hydrocarbon	43	800	37
29.3	1003	C_4-Benzene	119	1,110	52
29.3	1004	B/U C_{11} Hydrocarbon	43	1,720	80
29.7	1024	B/U C_{11} Hydrocarbon	57	940	44
30.2	1043	B/U C_{11} Hydrocarbon	55	730	34
30.9	1079	B/U C_{11} Hydrocarbon	55	280	13
31.5	1103	Methyl decalin (trans)	81	1,110	52
31.7	1114	C_4-Benzene	119	880	41
31.9	1124	C_4-Benzene	119	1,310	61
32.1	1133	Undecane (n)	57	12,870	600
32.6	1157	Methyl decalin (cis)	67	750	35
33.0	1173	Methyl indan	117	490	23
33.3	1186	*	81	50	2
33.5	1196	B/U C_{12} Hydrocarbon	57	1,400	65
33.7	1205	Methyl indan	117	1,230	58
33.9	1217	C_5-Cyclohexane	55	750	35
34.1	1226	C_4-Benzene	119	1,810	84
34.2	1227	B/U C_{12} Hydrocarbon	43	1,060	49
34.3	1235	1,2,3,4-Tetrahydronaphthalene (Tetralin)	104	1,530	67
34.3	1238	B/U C_{12} Hydrocarbon	41	630	29
35.9	1306	C_2-Decalin	41	370	17
36.3	1324	B/U C_{12} Hydrocarbon	57	2,500	120

APPENDIX B (Contd.)

Retention Time, Min	Scan #	Tentative Identification	Base Peak	Base-Peak Counts	Concentration in Sour Condensate, ppb
36.4	1328	B/U C_{12} Hydrocarbon	43	990	40
36.7	1342	B/U C_{12} Hydrocarbon	43	1,330	61
36.9	1351	C_2-Decalin	81	600	28
37.0	1356	B/U C_{12} Hydrocarbon	43	2,700	125
37.5	1378	B/U C_{12} Hydrocarbon	57	1,890	88
37.6	1384	C_2-Decalin	81	80	4
38.0	1404	B/U C_{12} Hydrocarbon	55	530	26
38.2	1414	B/U C_{12} Hydrocarbon	55	220	10
38.3	1417	B/U C_{12} Hydrocarbon	55	460	22
38.5	1427	Methyl tetralin	104	1,010	47
38.7	1434	B/U C_{12} Hydrocarbon	55	640	30
39.1	1451	B/U C_{12} Hydrocarbon	55	300	14
39.3	1463	B/U C_{12} Hydrocarbon	55	210	10
39.7	1482	Dodecane (n)	57	21,550	1000
40.1	1496	*	41	-	-
40.1	1496	*	117	327	15
40.2	1504	Dimethyl decalin	81	590	28
40.5	1518	B/U C_{13} Hydrocarbon	41	520	24
40.8	1532	2,6-Dimethyl undecane	57	7,920	370
41.1	1544	B/U C_{13} Hydrocarbon	57	500	23
41.4	1556	B/U C_{13} Hydrocarbon	57	470	22
41.5	1564	B/U C_{13} Hydrocarbon	41	230	11
41.8	1575	C_6-Cyclohexane	55	1,580	73
42.0	1586	B/U C_{13} Hydrocarbon	41	110	5
42.2	1594	Methyl tetralin	131	2,160	100
42.6	1614	B/U C_{13} Hydrocarbon	41	290	13
42.8	1620	B/U C_{13} Hydrocarbon	55	240	11
43.0	1632	B/U C_{13} Hydrocarbon	69	480	22
43.2	1641	B/U C_{13} Hydrocarbon	41	230	11
43.6	1657	Dimethyl undecane	57	2,880	130
43.7	1664	B/U C_{13} Hydrocarbon	43	1,240	58
43.9	1674	Methyl tetralin	131	450	20
44.0	1677	B/U C_{13} Hydrocarbon	43	1,660	77
44.0	1694	B/U C_{13} Hydrocarbon	57	3,320	150
44.8	1712	B/U C_{13} Hydrocarbon	57	2,480	120
45.2	1731	B/U C_{13} Hydrocarbon	57	8,670	400
45.4	1740	B/U C_{13} Hydrocarbon	43	320	4
45.7	1751	B/U C_{13} Hydrocarbon	55	780	36
46.0	1767	B/U C_{13} Hydrocarbon	41	180	8
46.2	1776	Dimethyl tetralin	118	1,690	78
46.6	1795	*	145	340	16
47.1	1815	Tridecane (n)	57	27,750	1300
47.4	1833	B/U C_{14} Hydrocarbon	55	170	7
47.9	1852	B/U C_{14} Hydrocarbon	57	710	32
48.3	1871	B/U C_{14} Hydrocarbon	57	1,970	91
49.2	1913	C_7-Cyclohexane	83	1,830	85
49.5	1927	C_3-Decalin	41	630	29

APPENDIX B (Contd.)

Retention Time, Min	Scan #	Tentative Identification	Base Peak	Base-Peak Counts	Concentration in Sour Condensate, ppb
49.8	1937	B/U C_{14} Hydrocarbon	55	130	6
49.9	1942	B/U C_{14} Hydrocarbon	57	100	5
50.0	1949	B/U C_{14} Hydrocarbon	55	130	6
50.3	1960	B/U C_{14} Hydrocarbon	55	330	16
50.5	1972	B/U C_{14} Hydrocarbon	57	1,760	82
50.7	1982	C_4-Decalin	41	420	19
51.1	1996	B/U C_{14} Hydrocarbon	43	1,270	59
51.1	1998	C_2-Tetralin	145	626	29
51.4	2012	B/U C_{14} Hydrocarbon	57	2,790	130
51.8	2031	B/U C_{14} Hydrocarbon	57	1,800	84
52.2	2045	B/U C_{14} Hydrocarbon	41	2,890	130
52.4	2056	B/U C_{14} Hydrocarbon	57	7,190	330
52.8	2075	B/U C_{14} Hydrocarbon	55	640	30
53.1	2088	B/U C_{14} Hydrocarbon	55	240	11
53.4	2101	B/U C_{14} Hydrocarbon	55	260	12
53.9	2125	Tetradecane (n)	57	25,240	1200
54.1	2132	C_4-Decalin	41	220	10
54.2	2139	B/U C_{15} Hydrocarbon	57	1,120	52
54.5	2154	C_3-Tetralin	57	620	29
54.7	2163	C_3-Tetralin	57	360	17
54.9	2172	C_3-Tetralin	57	240	11
56.2	2232	C_8-Cyclohexane	83	1,730	80
56.4	2239	C_4-Decalin	41	450	20
56.8	2258	B/U C_{15} Hydrocarbon	41	410	19
57.1	2269	B/U C_{15} Hydrocarbon	57	1,960	91
57.3	2280	B/U C_{15} Hydrocarbon	57	500	23
57.6	2295	B/U C_{15} Hydrocarbon	43	800	37
58.1	2314	B/U C_{15} Hydrocarbon	57	11,410	530
58.4	2330	B/U C_{15} Hydrocarbon	57	2,430	110
58.9	2355	B/U C_{15} Hydrocarbon	57	-	-
59.1	2363	B/U C_{15} Hydrocarbon	57	210	10
59.5	2380	B/U C_{15} Hydrocarbon	55	780	86
59.9	2397	B/U C_{15} Hydrocarbon	55	140	6
60.4	2420	Pentadecane (n)	57	26,000	1200
60.9	2443	B/U C_{16} Hydrocarbon	57	650	30
61.1	2454	B/U C_{16} Hydrocarbon	57	340	16
61.3	2462	*	57	550	26
61.7	2478	*	55	190	9
62.3	2505	*	41	220	10
62.8	2531	C_9-Cyclohexane	83	1,710	79
62.9	2537	*	55	290	13
63.2	2549	B/U C_{16} Hydrocarbon	57	1,280	60
63.3	2556	B/U C_{16} Hydrocarbon	57	1,550	72
63.5	2564	*	57	930	43
63.9	2579	B/U C_{16} Hydrocarbon	57	2,100	97
64.2	2594	B/U C_{16} Hydrocarbon	57	2,480	120
64.4	2604	B/U C_{16} Hydrocarbon	57	910	32

APPENDIX B (Contd.)

Retention Time, Min	Scan #	Tentative Identification	Base Peak	Base-Peak Counts	Concentration in Sour Condensate, ppb
64.6	2613	B/U C_{16} Hydrocarbon	57	1,900	88
65.4	2648	*	55	250	12
65.8	2668	*	55	910	42
66.0	2678	*	57	750	35
66.4	2695	Hexadecane (n)	57	23,620	1100
69.0	2815	B/U C_{17} Hydrocarbon	57	2,180	100
69.4	2832	B/U C_{17} Hydrocarbon	57	11,170	520
69.7	2847	*	57	870	40
70.1	2862	B/U C_{17} Hydrocarbon	57	1,670	77
70.5	2880	*	57	1,570	73
72.1	2957	Heptadecane (n)	57	18,430	860
72.7	2981	Pristane	57	15,010	700
73.8	3038	Anthracene-d_{10}	188	9,730	
74.5	3065	*	57	1,000	46
74.8	3075	*	57	1,630	76
74.8	3077	C_{11}-Cyclohexane	83	850	40
75.3	3099	*	43	400	18
75.6	3113	*	57	1,060	49
76.0	3131	*	57	710	33
77.6	3204	Octadecane (n)	57	10,790	500
78.2	3235	Phytane	57	4,550	210
82.6	3436	Nonadecane (n)	57	6,910	320
87.5	3659	B/U C_{20} Hydrocarbon	57	3,480	160
92.1	3873	*	57	1,460	68

*Too weak for tentative identification to be made.

**B/U ≡ branched and/or unsaturated.

APPENDIX C

LISTING OF COMPOUNDS TENTATIVELY IDENTIFIED IN THE SHALE-OIL REFINERY ACID FRACTION

Retention Time, Min	Scan #	Tentative Identification	Base Peak	Base-Peak Counts	Concentration in Sour Condensate, ppb
8.2	31	Toluene	91	10,010	10
9.1	72	Acetone	43	2,350	2
9.5	91	Methyl disulfide	45	2,390	2
15.0	349	*	43	960	1
16.4	410	*	55	440	<1
16.9	433	*	83	840	<1
19.0	528	Methyl trisulfide	45	-	-
19.7	562	Methyl trisulfide	45	4,830	5
20.0	575	Methyl trisulfide	45	11,260	11
28.5**	694	Phenol	151	12,680	12
29.7	1018	Trithiolane	45	100,000	98
49.8	1931	1,2 Dipyrrolyl ethane	81	1,680	2
74.3	3035	Anthracene-d_{10}	188	10,680	-

*Too weak for tentative identification to be made.

**Identified as the TRI-SIL derivative in separate run.

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APPENDIX D

LISTING OF COMPOUNDS TENTATIVELY IDENTIFIED IN THE PETROLEUM-CRUDE REFINERY ACID FRACTION

Retention Time, Min	Scan #	Tentative Identification	Base Peak	Base-Peak Counts	Concentration in Sour Condensate, ppb
10.1	95	Toluene	91	530	<0.1
48.6	1877	*	57	350	<0.1
55.2	2184	Tetradecane (n)	57	510	<0.1
59.4	2376	Pentadecane (n)	57	280	<0.1
61.6	2479	B/U C_{16} Hydrocarbon**	57	630	0.1
67.7	2757	Hexadecane (n)	57	600	<0.1
73.4	3023	Heptadecane (n)	57	520	<0.1
74.0	3049	Pristane	57	460	<0.1
75.5	3119	Anthracene-d_{10}	188	27,000	
78.8	3273	Phytane	57	370	<0.1
84.1	3519		64	17,700	3

*Too weak for tentative identification to be made

**B/U ≡ branched and/or unsaturated

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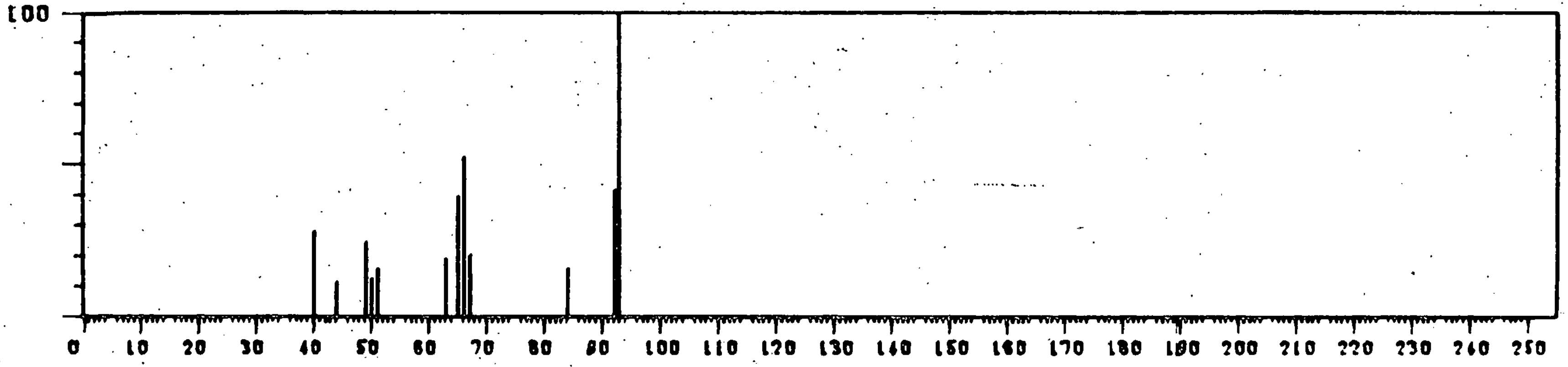
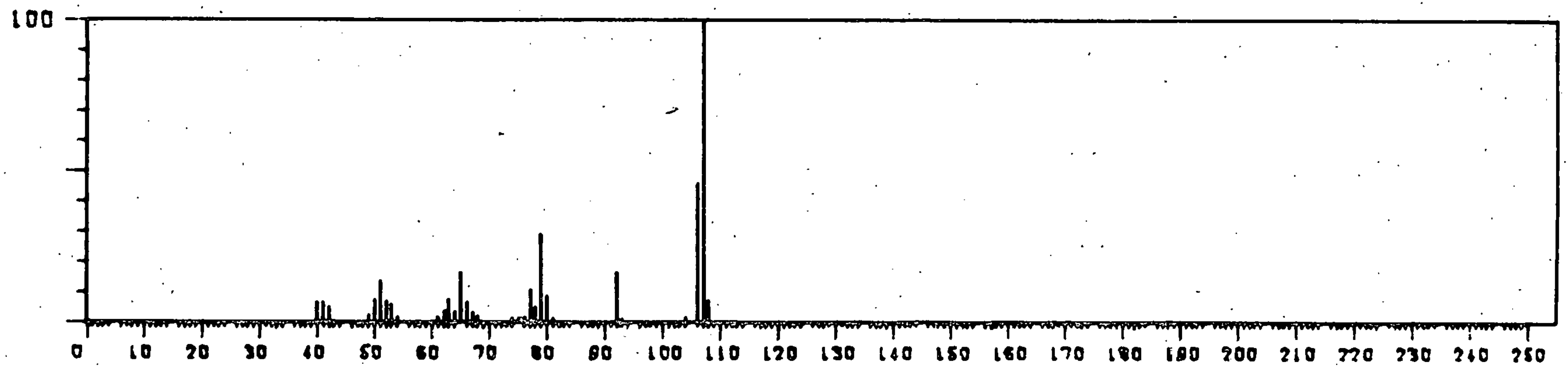
APPENDIX E

SELECTED SPECTRA OF COMPOUNDS TENTATIVELY IDENTIFIED IN THE SHALE-OIL BASE/NEUTRAL FRACTION

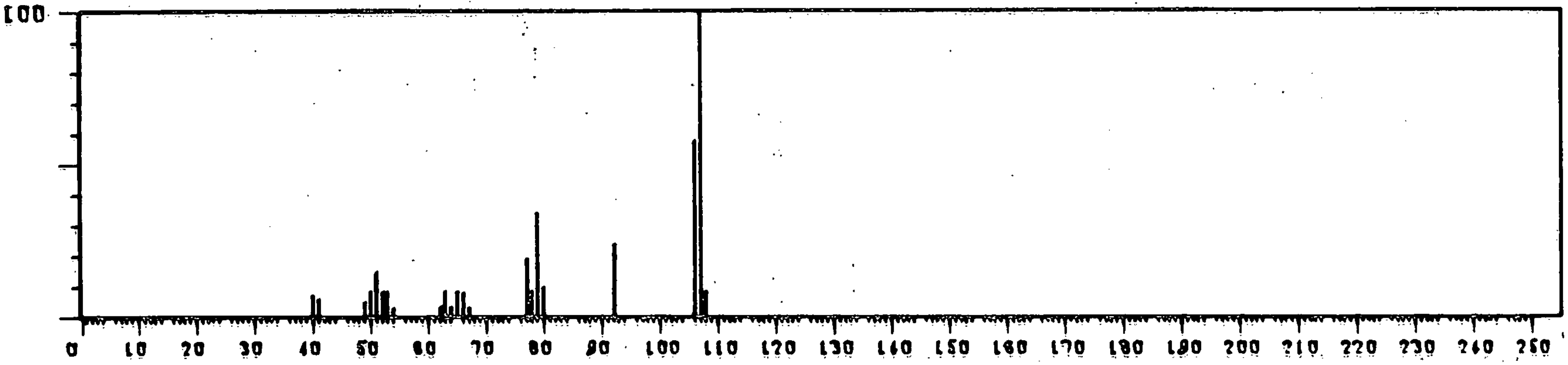
FRN 22102 SPEC 391 RET. TIME 15.3 Picoline



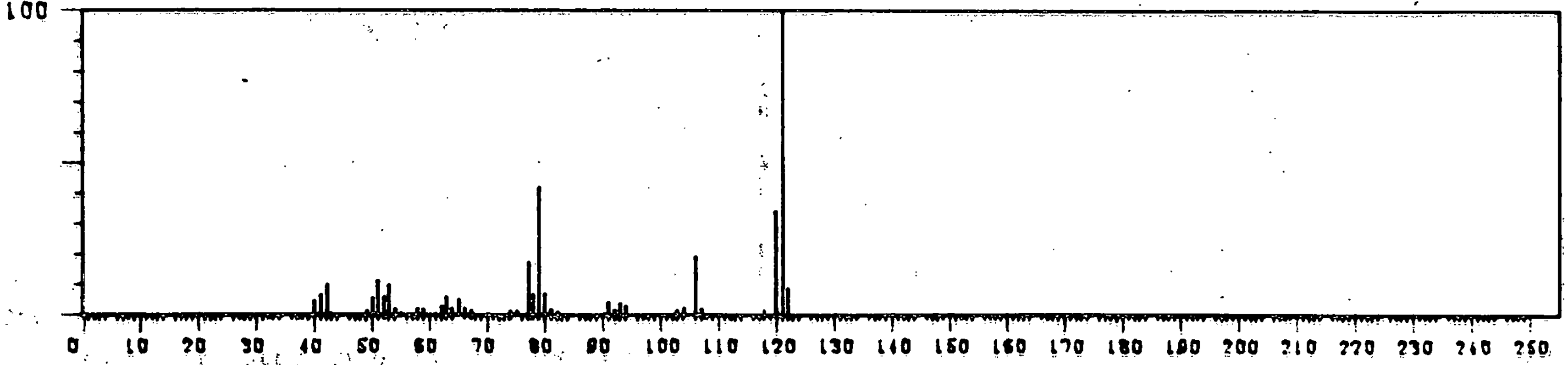
FRN 22102 SPEC 684 RET. TIME 20.9 2,4 - Dimethyl pyridine



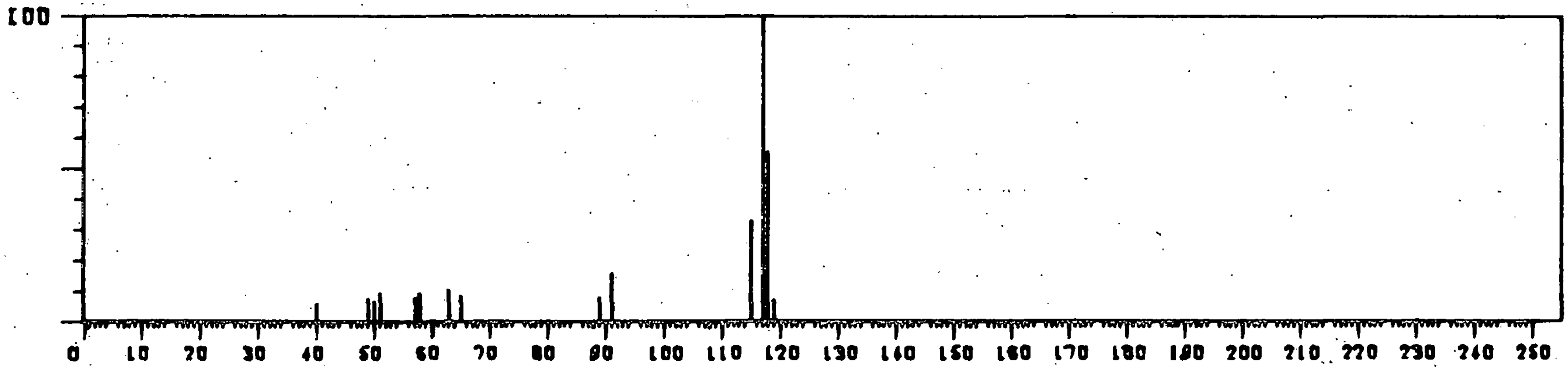
FRN 22102 SPEC 872 RET. TIME 24.5 3,5 - Dimethyl pyridine



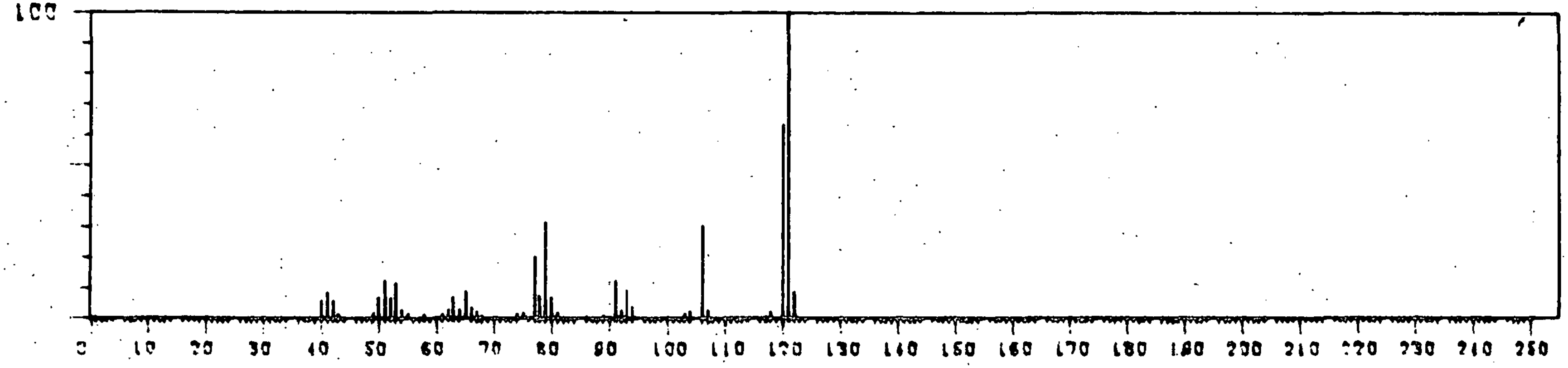
FRN 22102 SPEC 971 RET. TIME 26.4 2,4,6 - Trimethyl pyridine



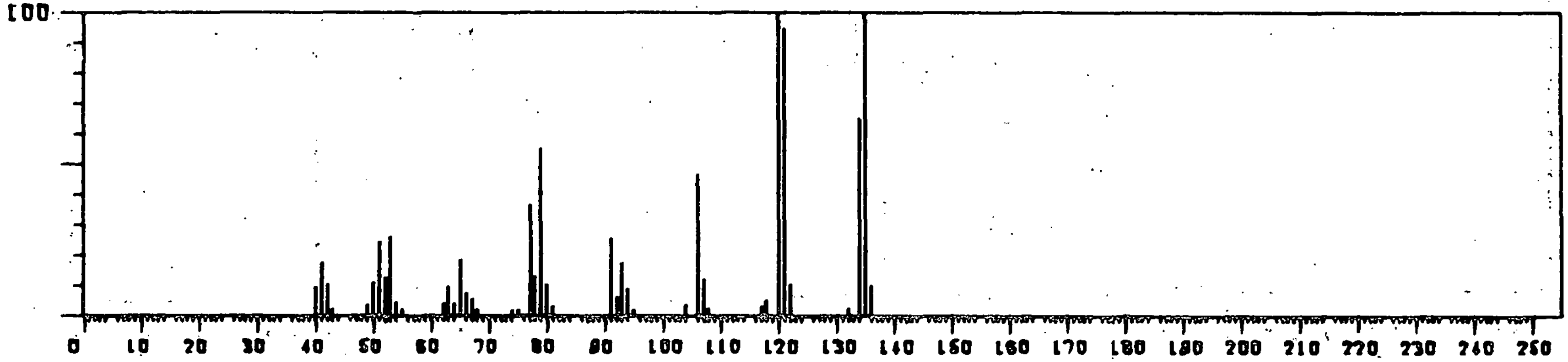
FRN 22102 SPEC 1138 RET. TIME 29.6 Indan



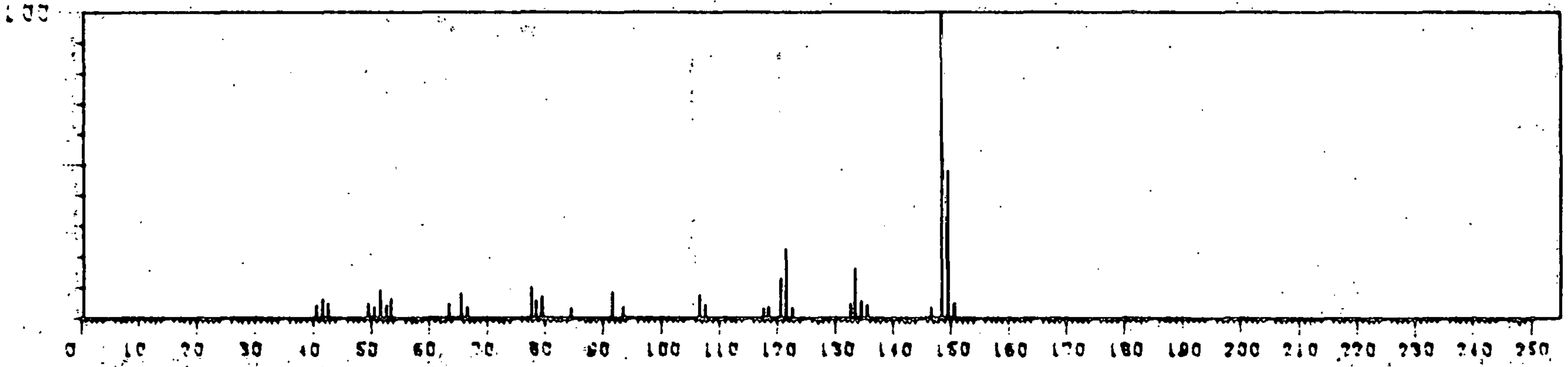
FRN 22102 SPEC 1271 RET. TIME 32.1 2,3,5 - Trimethyl pyridine



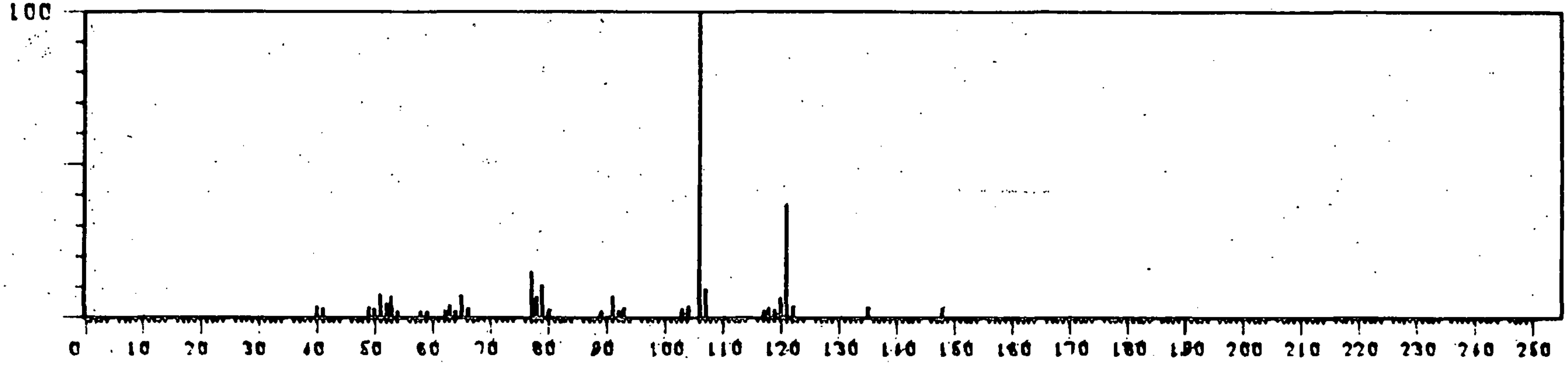
FRN 22102 SPEC 1586 RET. TIME 38.1 C_4 - Pyridine



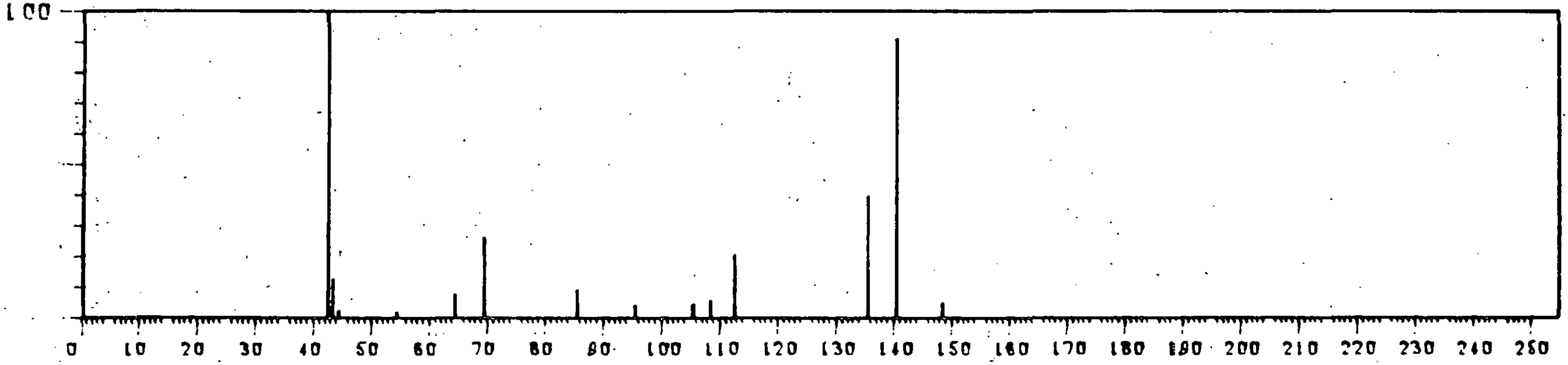
FRN 22102 SPEC 1661 RET. TIME 39.6 C_5 - Pyridine



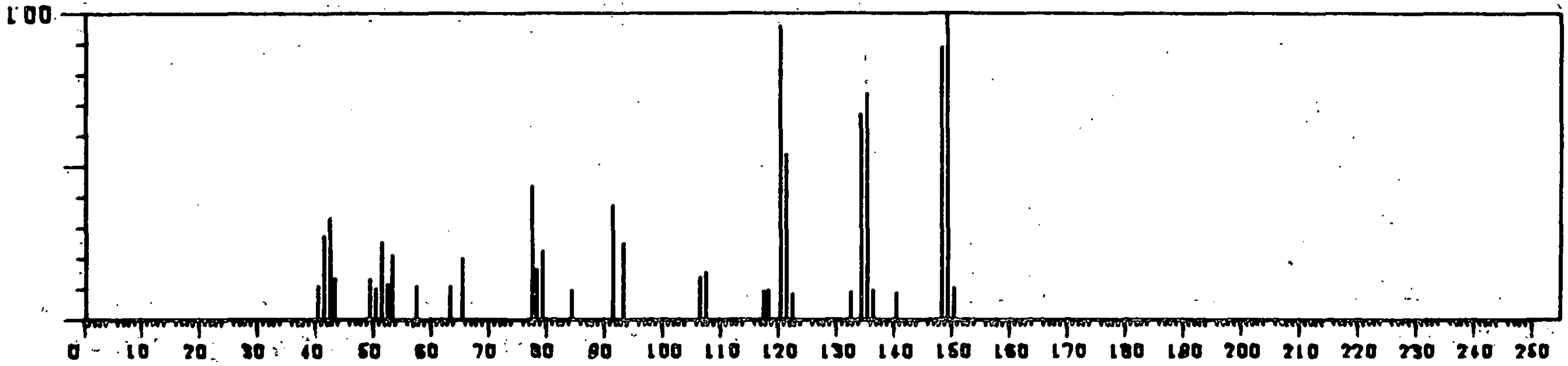
FRN 22102 SPEC 1670 RET. TIME 39.7 N - Ethyl aniline



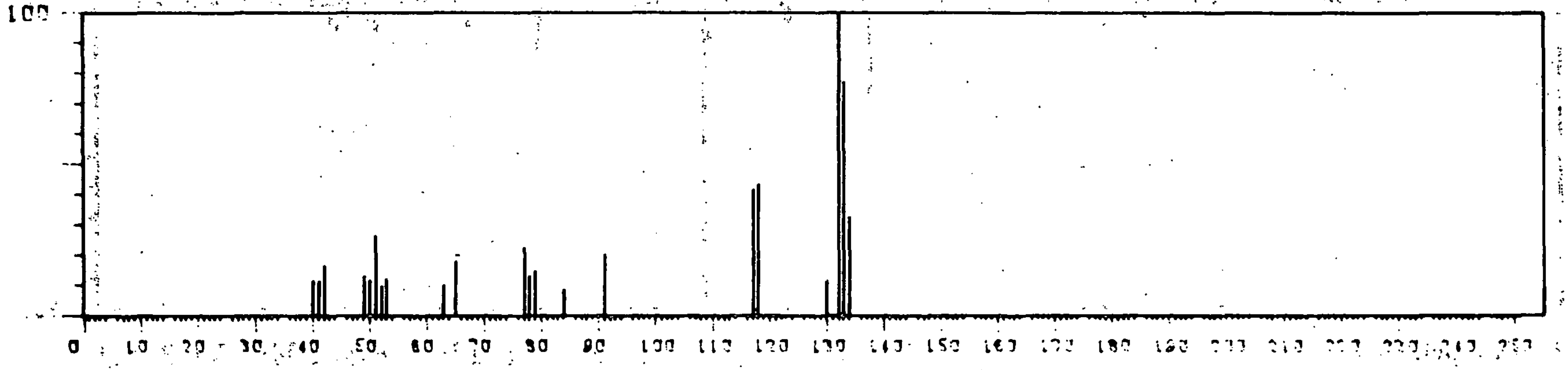
FRN 22102 SPEC 1902 RET. TIME 44.2 Hexamethylene tetramine



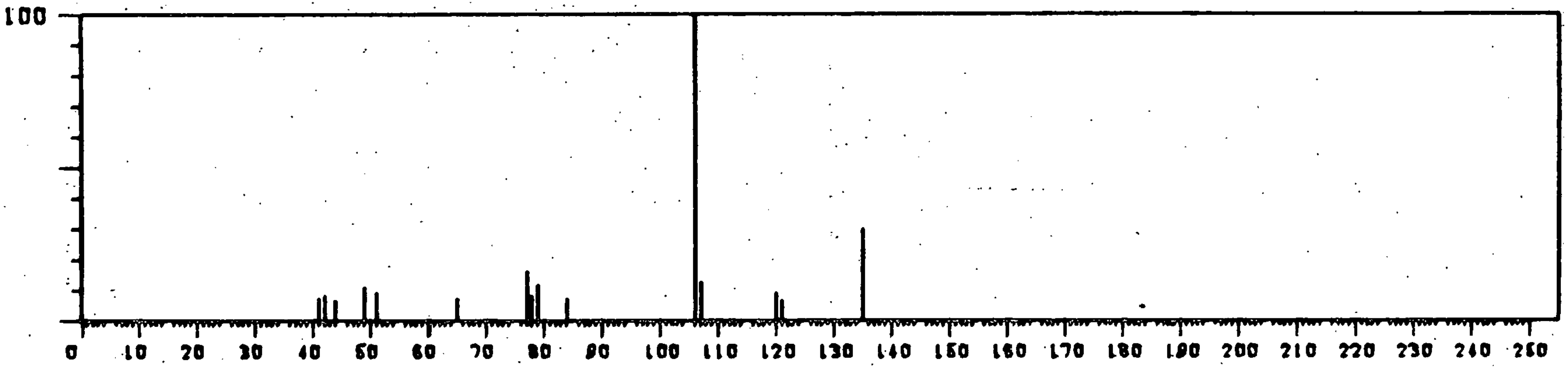
FRN 22102 SPEC 1916 RET. TIME 44.4 C_5 - Pyridine



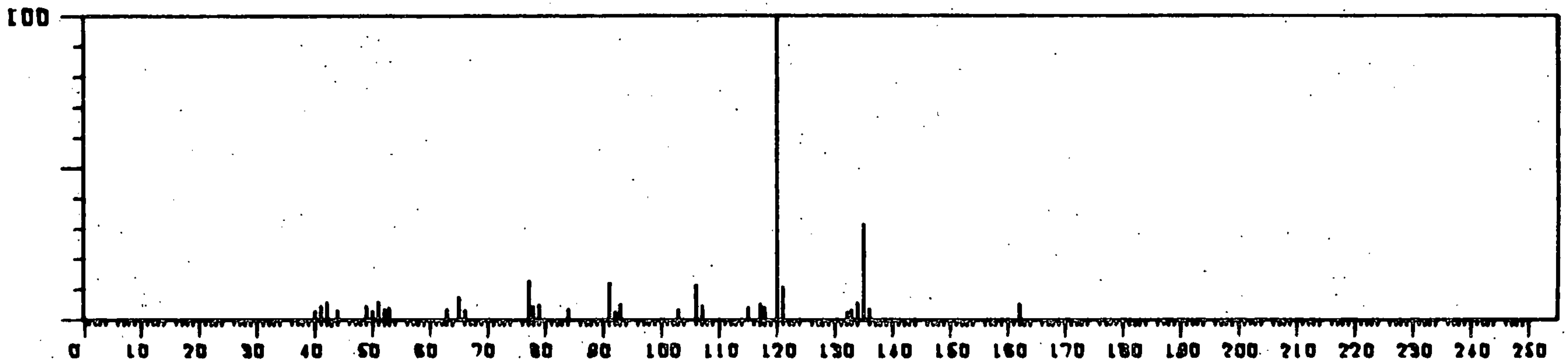
FRN 22102 SPEC 1930 RET. TIME 44.7 1,2,3,4-Tetrahydroquinoline



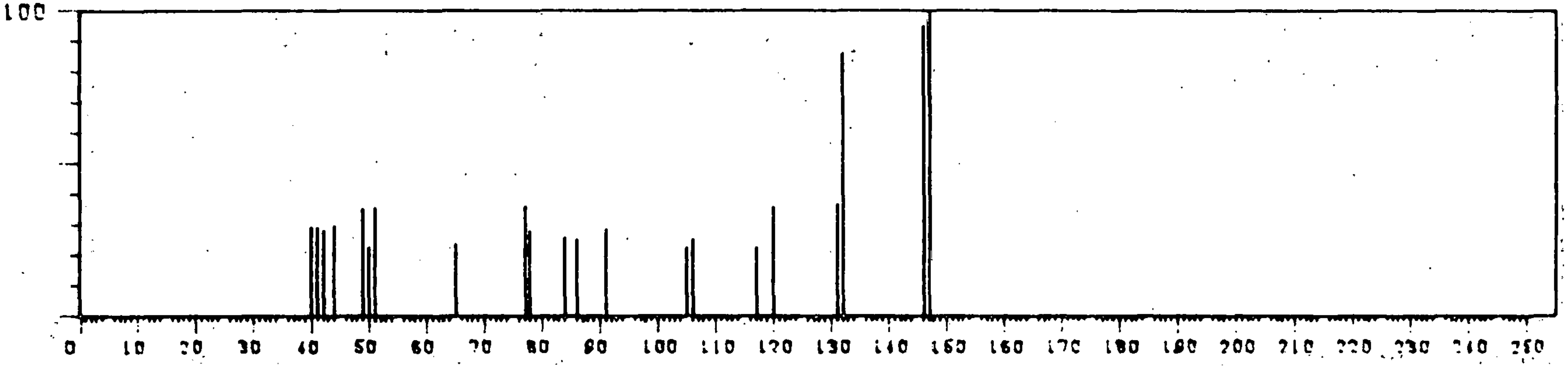
FRN 22102 SPEC 1989 RET. TIME 45.8 n - Propyl aniline



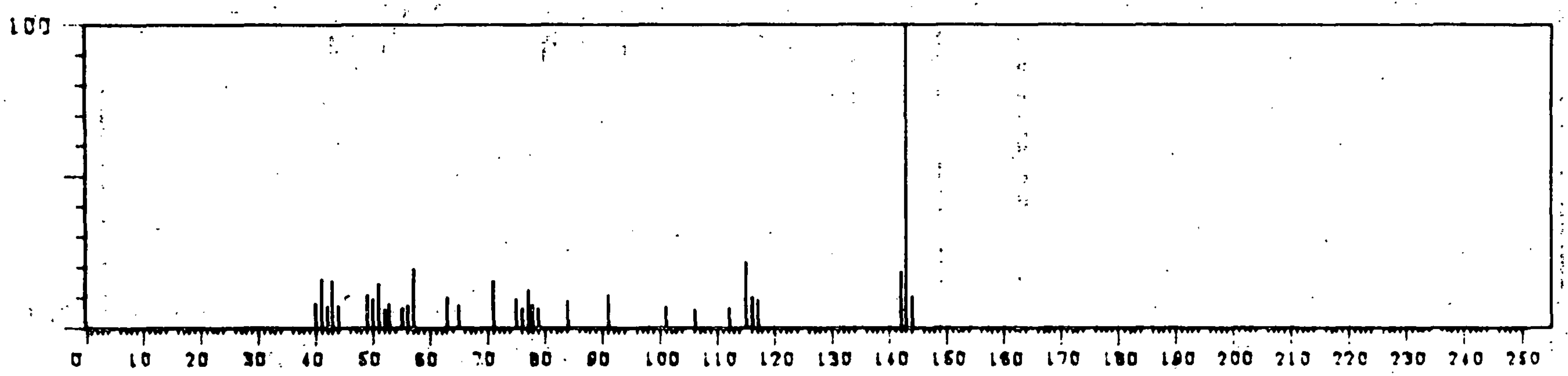
FRN 22102 SPEC 2005 RET. TIME 46.1 C3 - Aniline



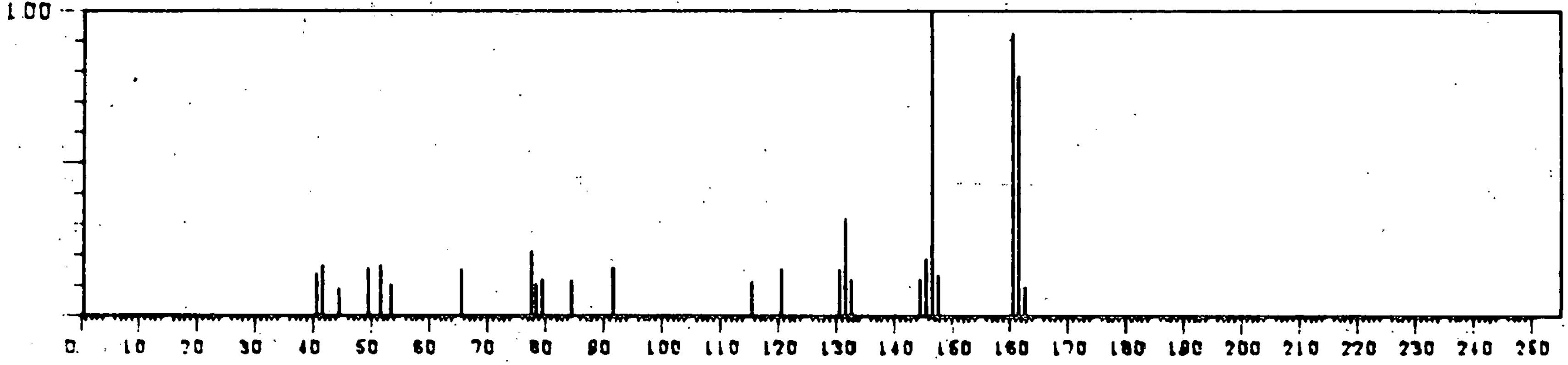
FRN 22102 SPEC 2089 RET. TIME 47.7 Methyl tetrahydroquinoline



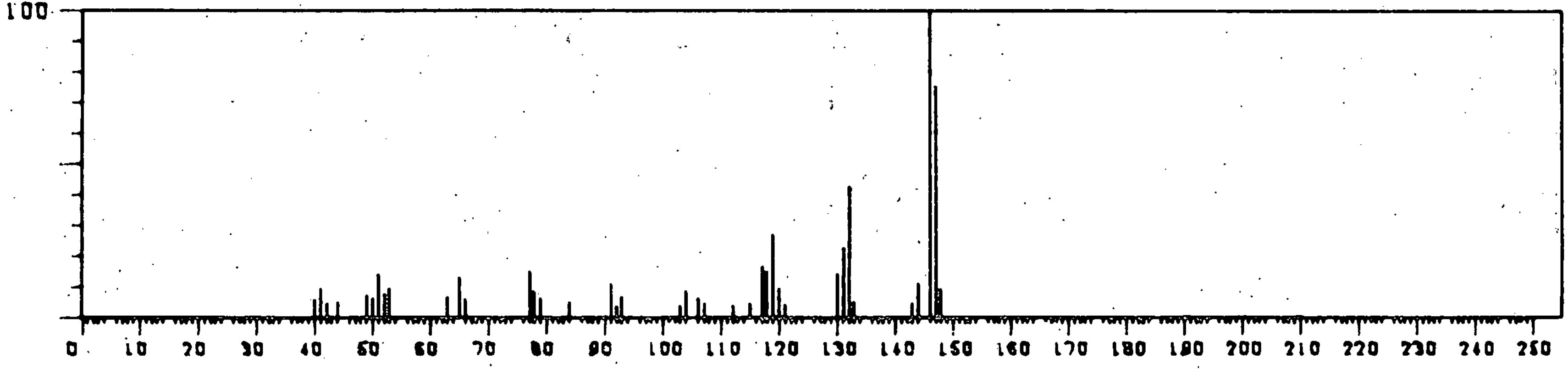
FRN 22102 SPEC 2206 RET. TIME 49.9 Methyl quinoline



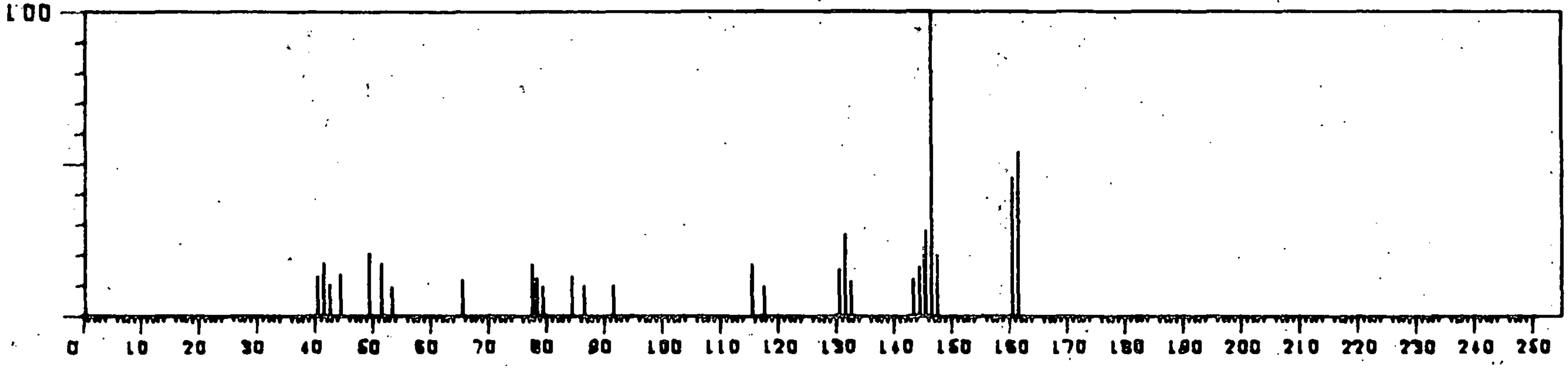
FRN 22102 SPEC 2230 RET. TIME 50.3 Dimethyl tetrahydroquinoline



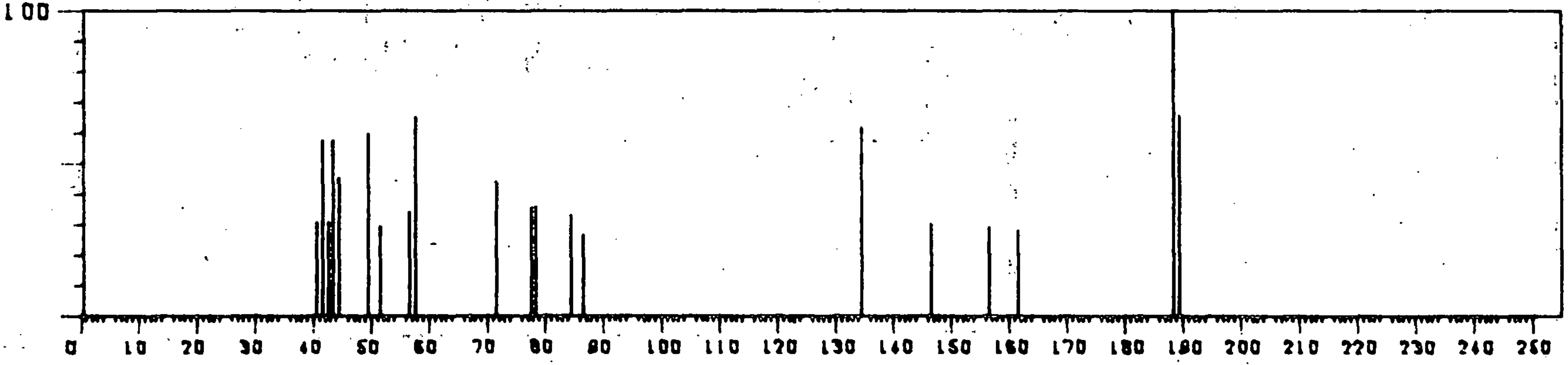
FRN 22102 SPEC 2405 RET. TIME 53.7 Methyl tetrahydroquinoline



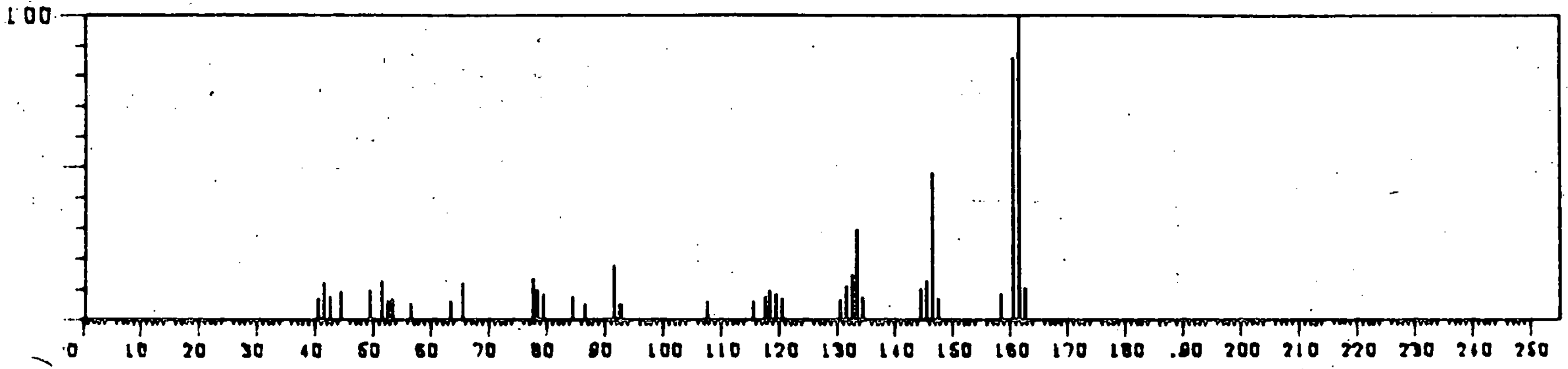
FRN 22102 SPEC 2549 RET. TIME 56.4 Dimethyl tetranydroquinoline



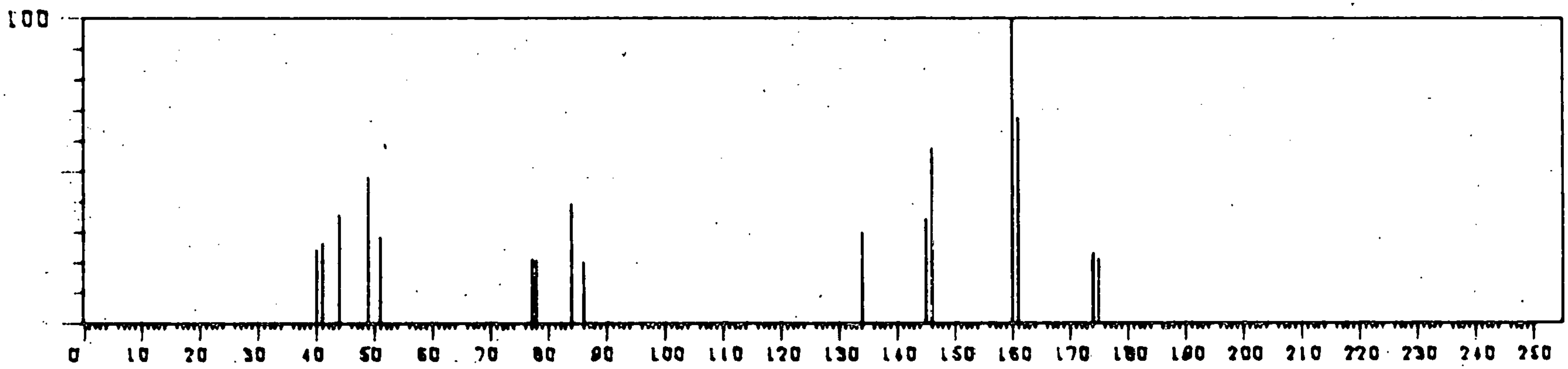
FRN 22102 SPEC 2584 RET. TIME 57.0 C4 - Tetrahydroquinoline



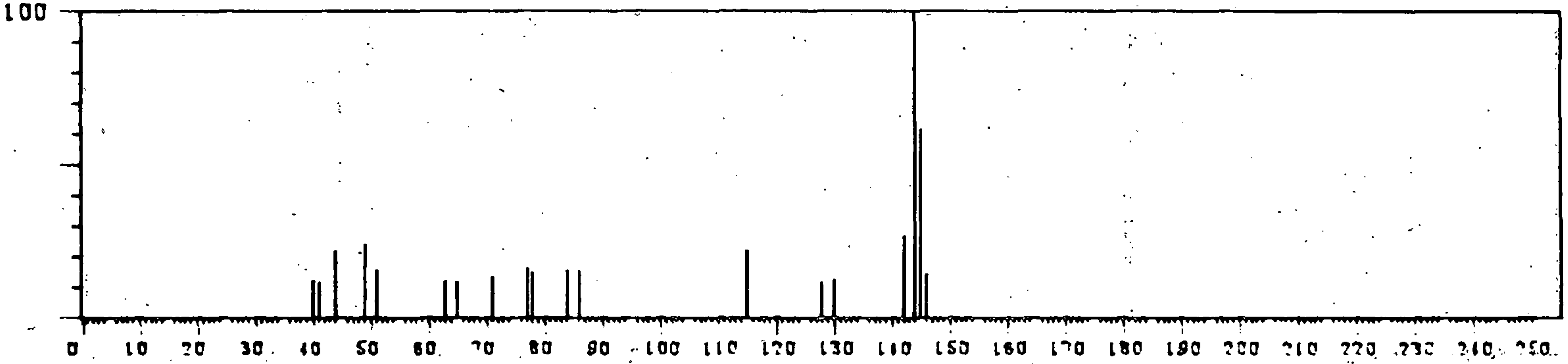
FRN 22102 SPEC 2596 RET. TIME 57.2 Dimethyl tetrahydroquinoline



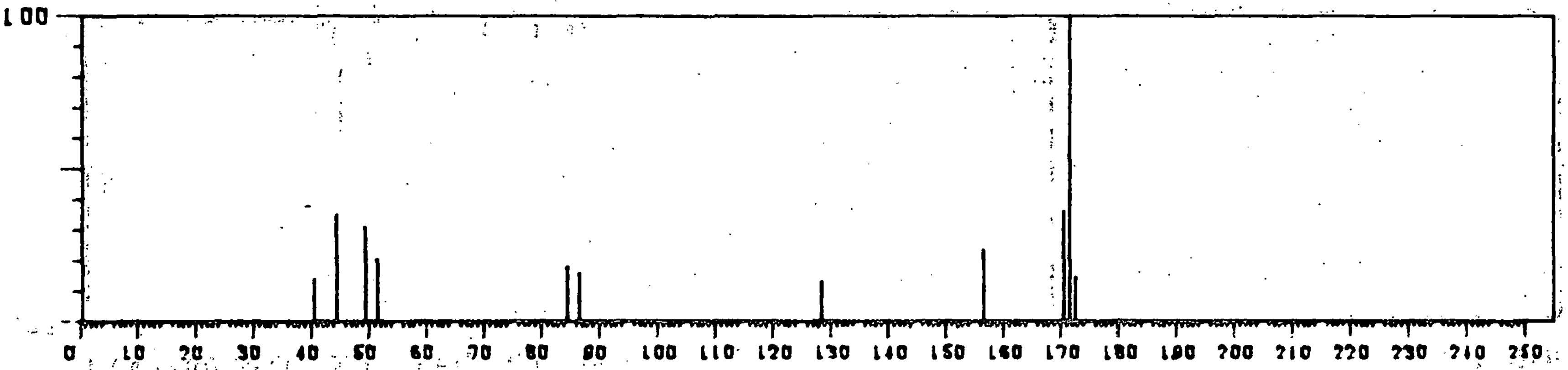
FRN 22102 SPEC 2745 RET. TIME 60.0 C3 - Tetrahydroquinoline



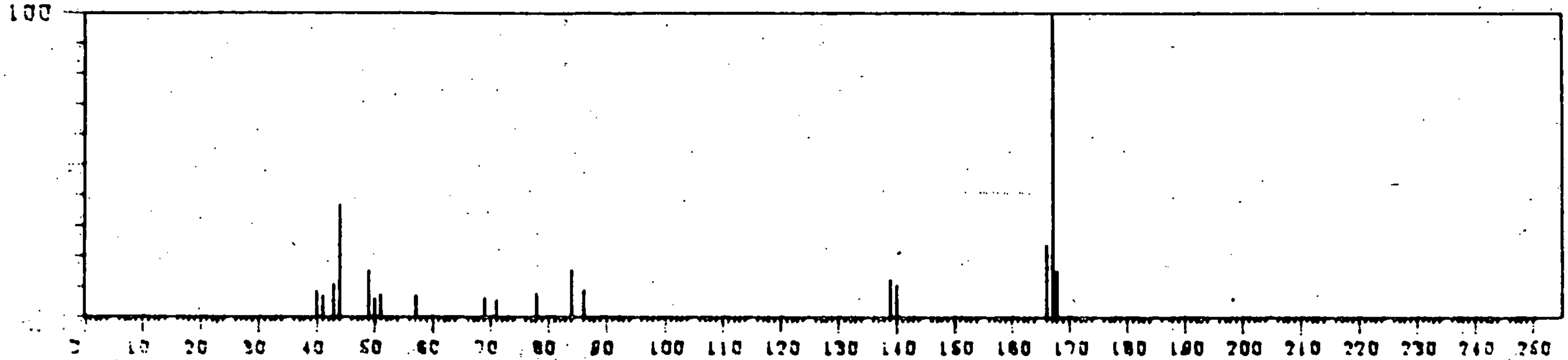
FRN 22102 SPEC 2843 RET. TIME 61.9 C2 - Indole



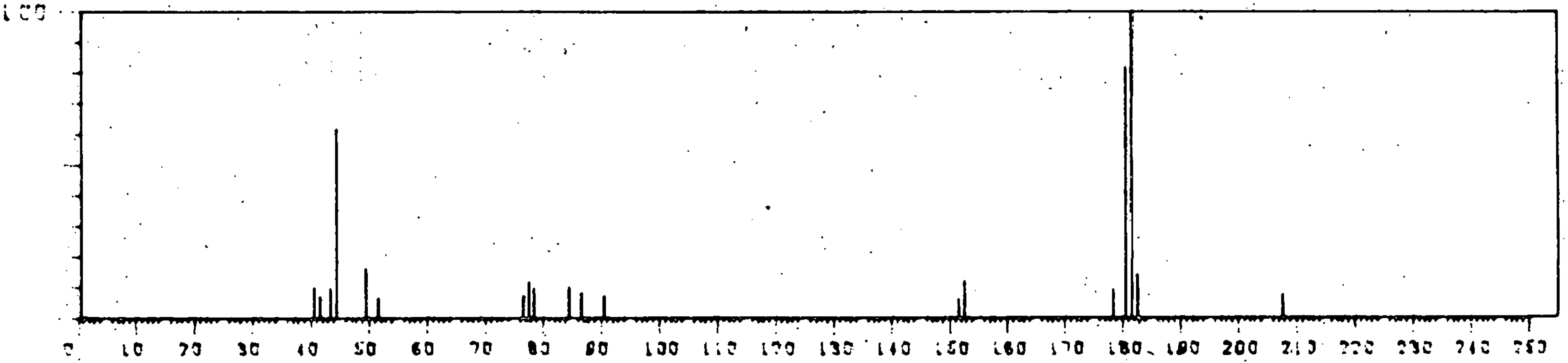
FRN 22102 SPEC 3047 RET. TIME 65.7 C3 - Quinoline



FRN 22102 SPEC 4015 RET. TIME 83.8 **Carbazole**



FRN 22102 SPEC 4184 RET. TIME 87.0 **Methylcarbazole**

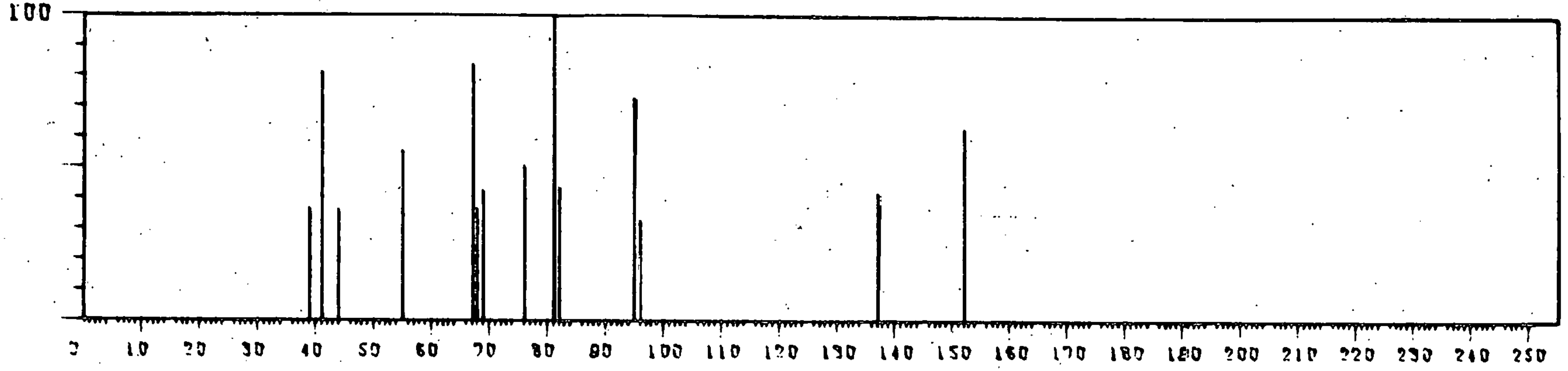


APPENDIX F

SELECTED SPECTRA OF COMPOUNDS TENTATIVELY IDENTIFIED IN THE PETROLEUM-CRUDE BASE/NEUTRAL FRACTION

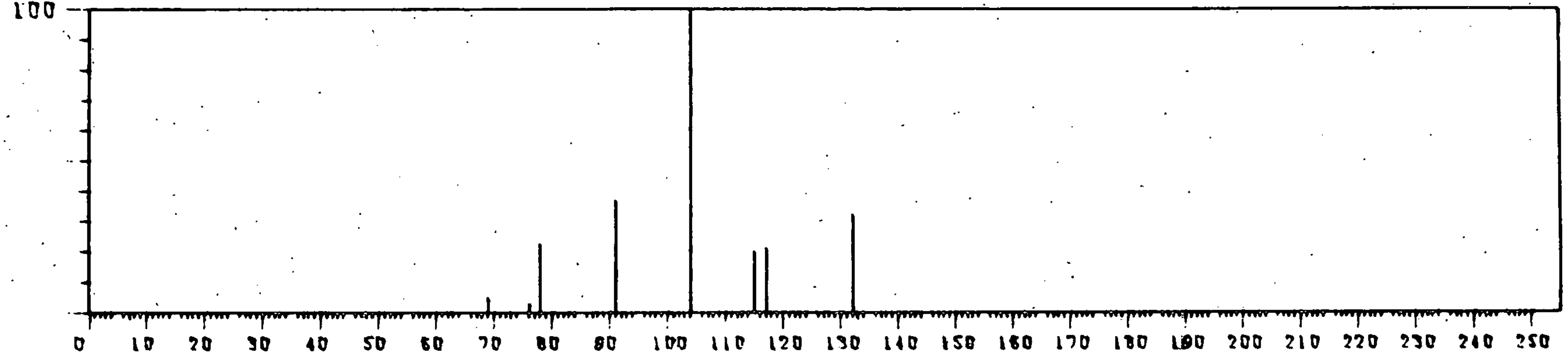
FRN 22404 SPEC 1103 RET. TIME 31.4

Methyl decalin (trans)

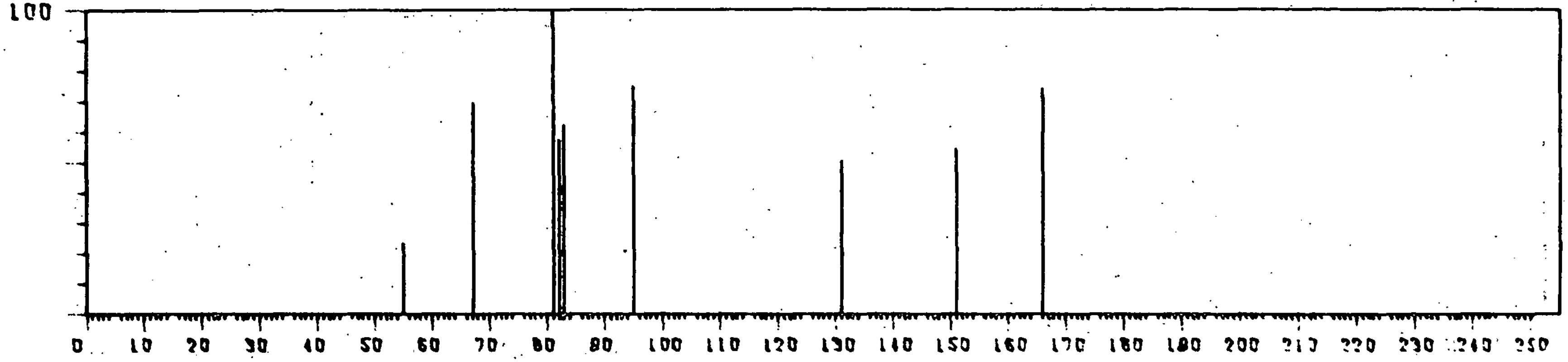


FRN 22404 SPEC 1234 RET. TIME 34.3

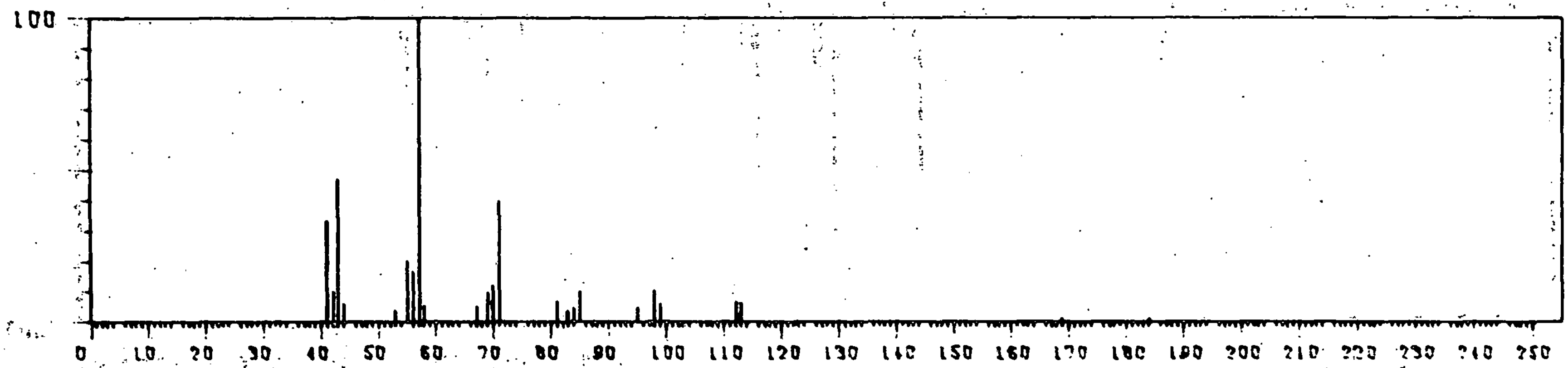
1,2,3,4 - Tetrahydronaphthalene (Tetralin)



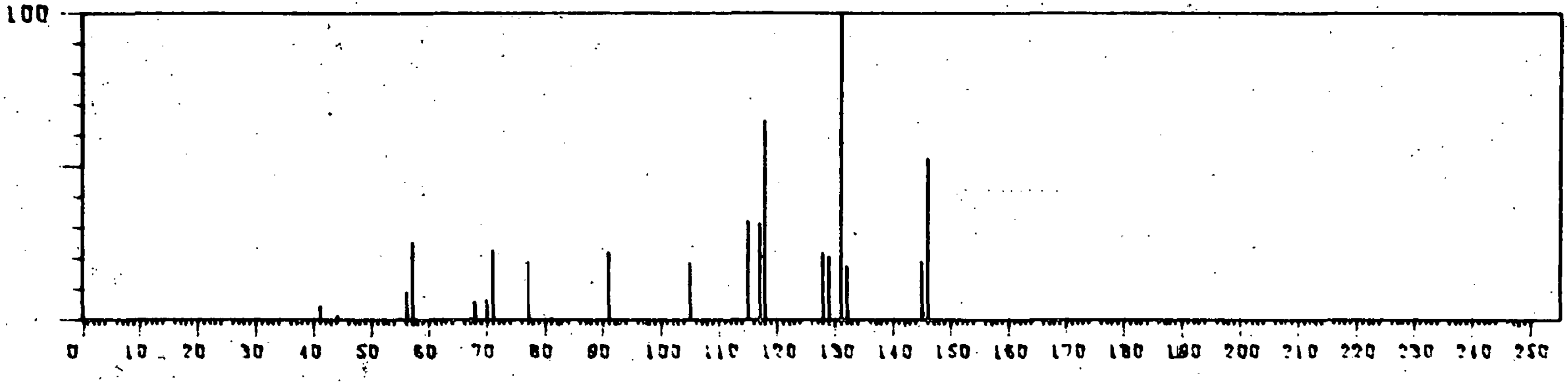
FRN 22404 SPEC 1351 RET. TIME 36.9 C2 - Decalin



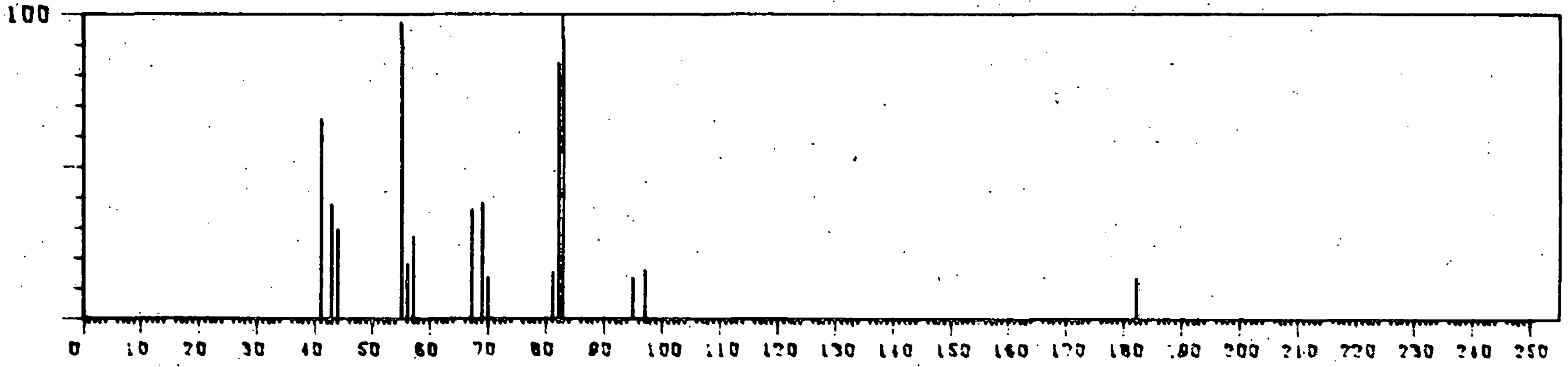
FRN 22404 SPEC 1532 RET. TIME 40.8 2,6 - Dimethyl undecane

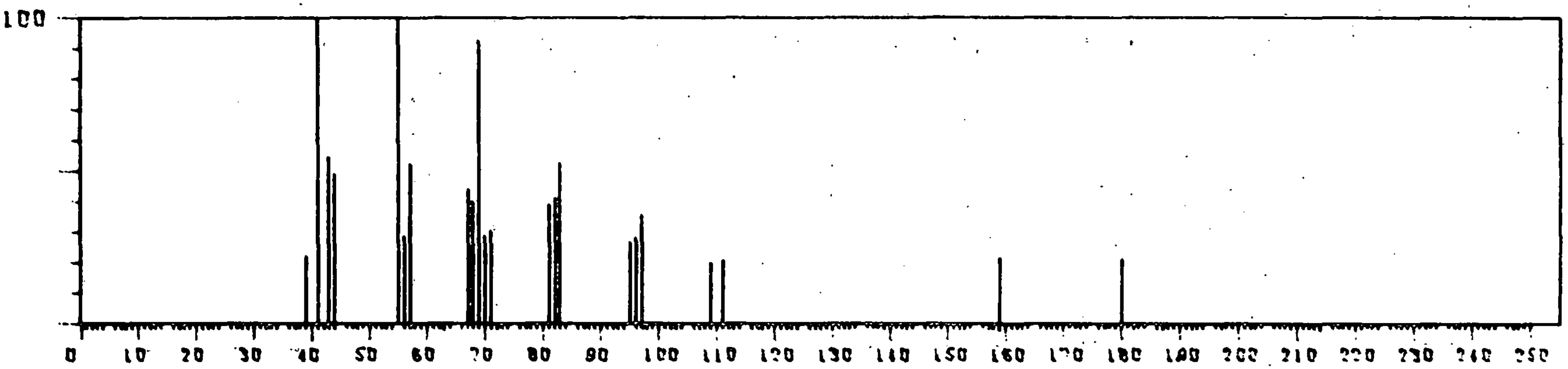


FRN 22404 SPEC 1594 RET. TIME 42.2 Methyl tetralin

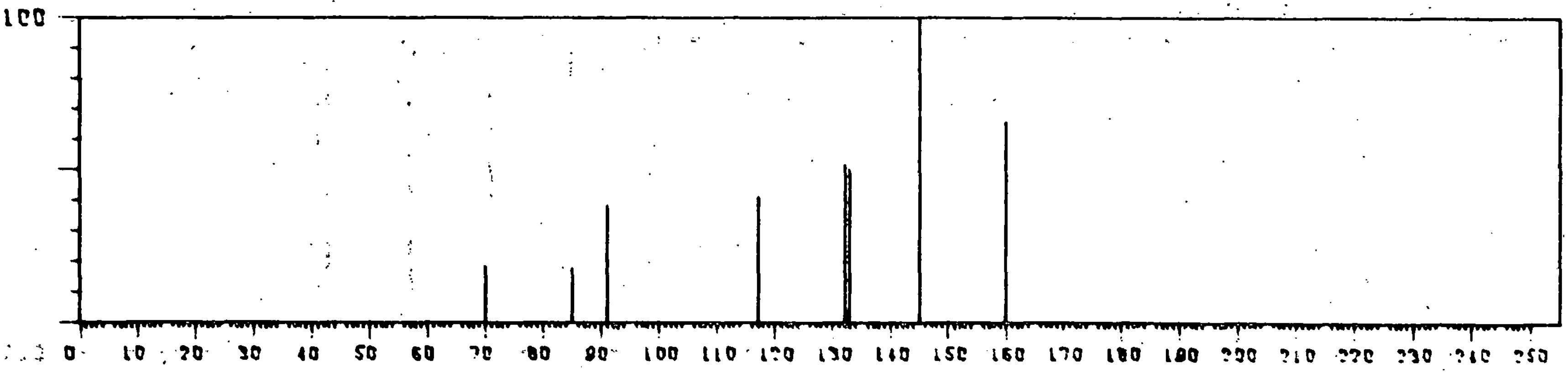


FRN 22404 SPEC 1913 RET. TIME 49.2 C7 - Cyclohexane



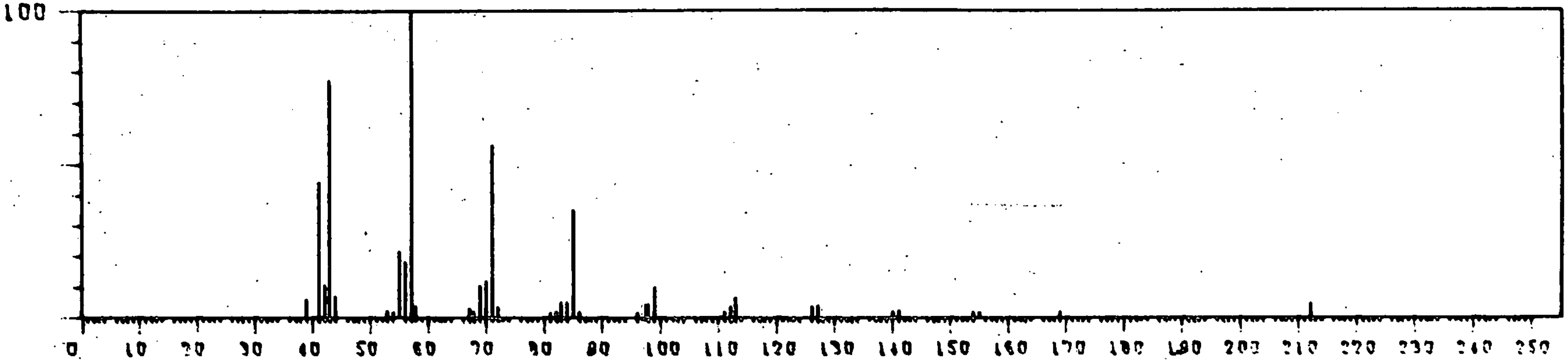

FRN 22404 SPEC 1927 RET. TIME 49.5

C3 - Decalin

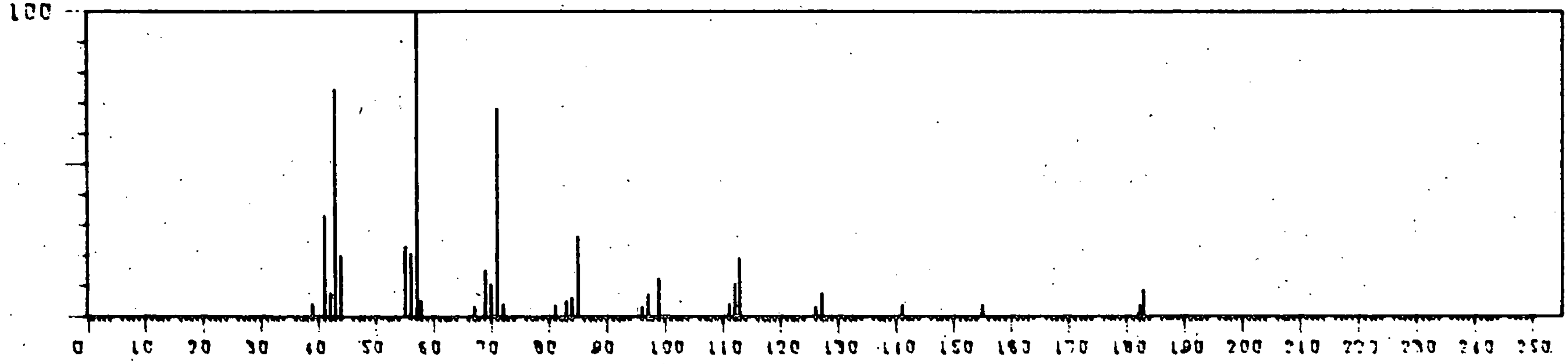

FRN 22404 SPEC 1998 RET. TIME 51.1

C2 - Tetralin

FRN 22404 SPEC 2420 RET. TIME 60.3 n - Pentadecane

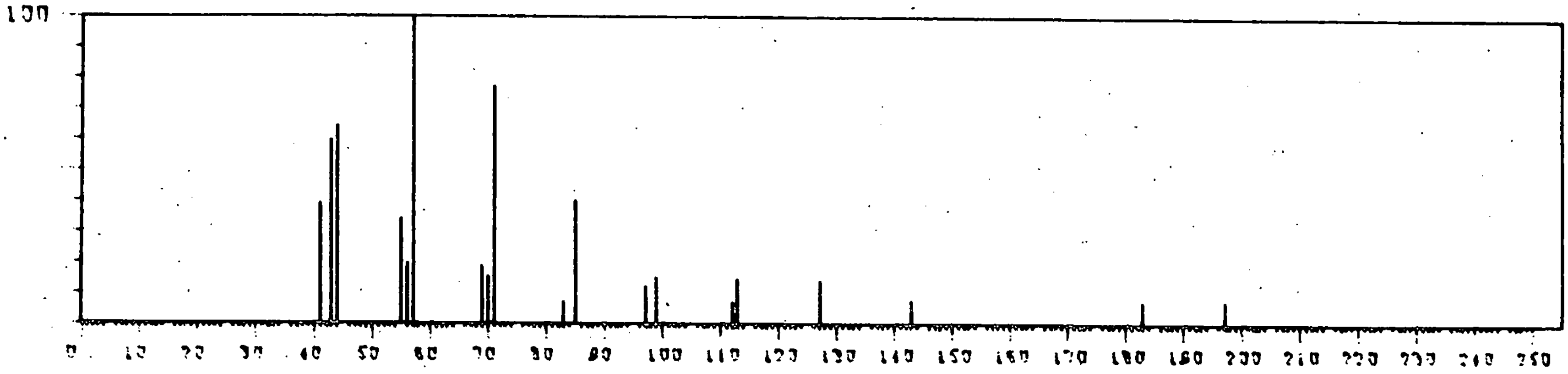


FRN 22404 SPEC 2981 RET. TIME 72.6 Pristane



FRN 22404 SPEC 3233 RET. TIME 78.2

Phytane



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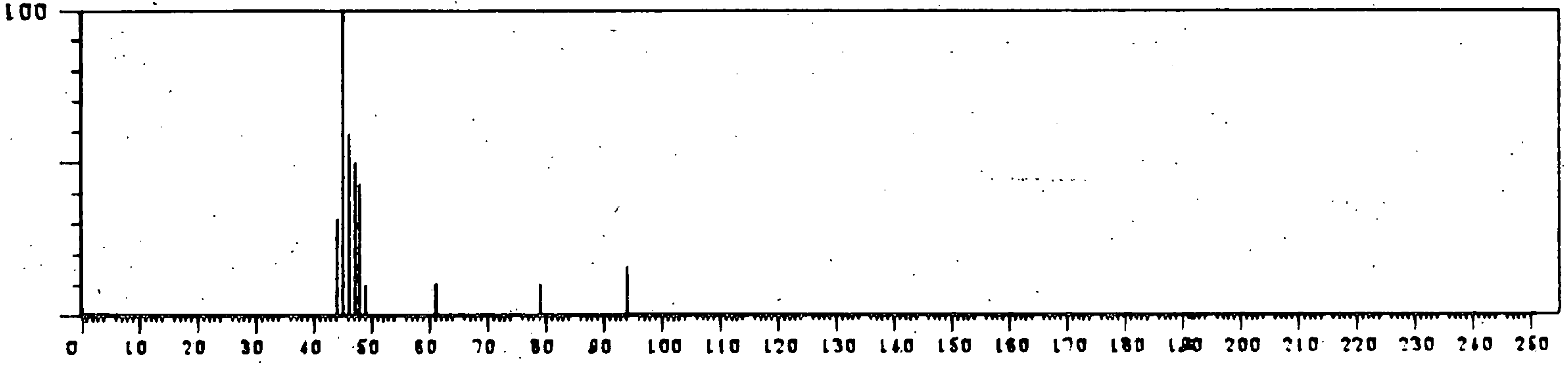
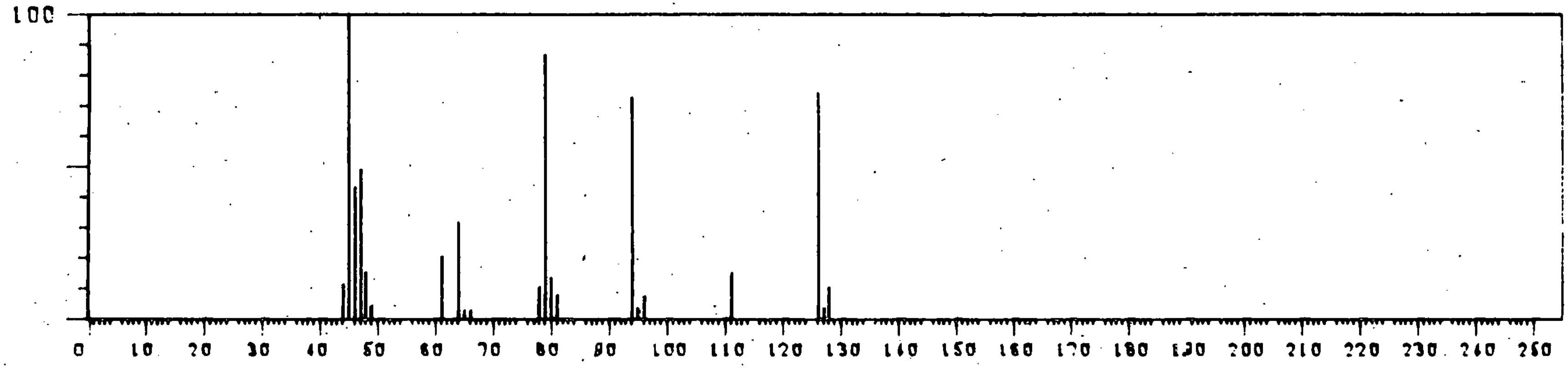
APPENDIX G

SELECTED SPECTRA OF COMPOUNDS TENTATIVELY IDENTIFIED IN THE SHALE-OIL ACID FRACTION

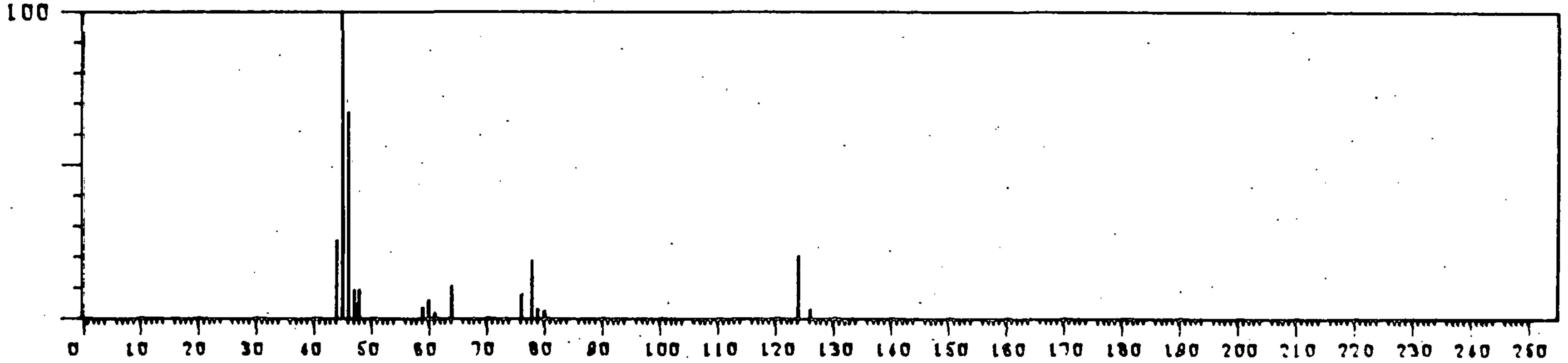
FRN 22401 SPEC 91 RET. TIME 9.4 Methyl disulfide



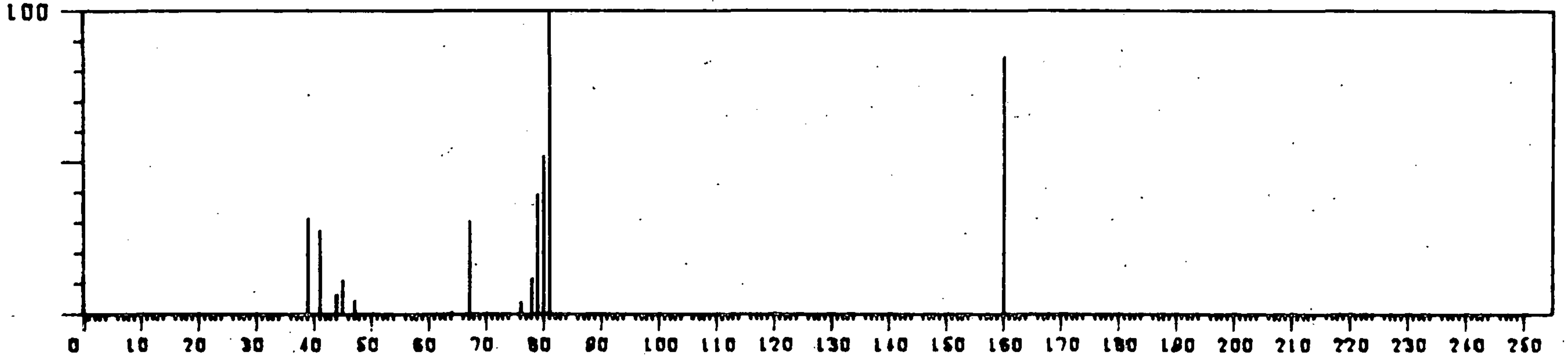
FRN 22401 SPEC 575 RET. TIME 20.0 Methyl trisulfide



FRN 22401 SPEC 1018 RET. TIME 29.6 Trithiolane



FRN 22401 SPEC 1931 RET. TIME 49.8 1,2, - Dipyrrolyl ethane



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APPENDIX H

PRESENTATION OF RADIAN CORPORATION'S REPORT

The DOE Project Officer for this study requested that Argonne National Laboratory (ANL) oversee a comparative analysis of the organic constituents in the sour-condensate samples. ANL chose Radian Corporation of Austin, Texas, because Radian's organics analytical group had experience in the analyses of complex samples from shale-oil production processes. Radian also used analytical equipment and techniques similar to those employed by ANL.

Split samples were sent to Radian and the results from the analysis of these samples were presented to ANL in a report included in its entirety in this appendix. The following discussion describes the similarities and differences between the ANL and Radian data.

In general, good agreement on the types of compounds and their relative concentrations was obtained by both laboratories for the shale-oil sour condensate. However, this was not the case for the petroleum-crude sour condensate. Radian reported the presence of a total of 129 compounds in the acid and base/neutral extracts of the shale-oil sour condensate and a total of 121 compounds in the acid and base/neutral extracts of the petroleum-crude sour condensate. The number of compounds detected by ANL was 218 and 161, respectively.

Despite the fact that Radian detected 89 fewer compounds in the extracts of the shale-oil sour condensate, agreement on the types of compounds characterized and their relative amounts is good. The Radian and ANL data are compared in Table H.1. Three types of compounds, tetralins, indans, and piperidines, found present in small concentrations by ANL were not reported by Radian. On the other hand, Radian reported a concentration of trithiolane three times greater than that measured by ANL, and the presence of n-alkanes through C_{29}, whereas ANL detected n-alkanes through C_{23}. Radian's ability to detect larger n-alkanes, however, is to be expected considering the types of capillary-columns employed and the chromatographic conditions used.

Because Radian did not detect any branched or unsaturated hydrocarbons in the extracts of the petroleum-crude sour condensate, a significant difference exists in the relative amounts of compounds between the ANL and Radian data (see Table H.1). There is no doubt that branched and unsaturated hydrocarbons are present. Isoprenoid substrates have been implicated as a significant source material in the formation of petroleum, resulting in a predominance of methyl-branched alkanes.[10] Pristane and phytane are two specific methyl-branched alkanes that have been identified in petroleum.[11,12] ANL found 770 ppm of pristane and 230 ppm of phytane in the B/N extract, significant concentrations that render them easily detectable.

Radian, on the other hand, found larger concentrations of benzenes, tetralins and indans and reported the presence of naphthalenes that ANL did not detect. Examination of the total-ion chromatogram obtained from the run

Table H.1 Comparison of the Percent of Compounds Detected by ANL and Radian in Shale-Oil and Petroleum-Crude Sour-Condensate Extracts

	Percent of Compounds Detected			
	Shale Oil		Petroleum Crude	
Compounds	ANL	Radian	ANL	Radian
n-Alkanes	0.9	1.7	47	29
B/U Hydrocarbons	0.2	0.5	42	0
Pyridines	61	60.5	0	0
Anilines	18	18	0	0
Benzenes	6.6	4	5	28
Cyclohexanes	0	0	2	4
Tetralins	0.2	0	1	18
Tetrahydro-quinolines	4.5	5	0	0
Decalins	0	0	2	6
Quinolines	2.5	2.6	0	0
Carbazoles	1.7	1.6	0	0
Indans	0.6	0	0.6	12
Indoles	1	0.2		
Naphthalenes	0.7	2	0	2
Piperidines	0.6	0	0	0
Sulfides	1.6	5	0	0
	100.1	101.1	99.6	99

of the petroleum-crude B/N extract (Fig. 3), indicates that the more volatile compounds (including the early eluting, substituted benzenes reported by Radian) were not detected. A possible explanation is that the sample received by ANL could have received a more severe nitrogen purge before the ampule was sealed, causing loss by evaporation. This explanation is supported by the fact that toluene was observed in the petroleum-crude A fraction, probably as a result of carryover of the large quantity originally present in the petroleum-crude sour condensate, but was not observed in the B/N extract.

RADIAN CORPORATION
Radian Contract No. 219-038

SUMMARY OF SAMPLE ANALYSES
FOR
ARGONNE NATIONAL LABORATORY

February 28, 1980

Sumbitted to:

Dr. Ron Wingender
Argonne National Laboratory
EES-Building 12
Argonne, Illinois 60439

H1 INTRODUCTION

Three sets of samples were received for GC/MS analysis. Samples were extracts from petroleum refinery wastewater, from shale-oil refinery wastewater, and from blank water. Radian Corporation was subcontracted to perform these analyses by Argonne National Laboratory. Both Radian and Argonne National Laboratory concurrently analyzed split samples.

H2 ANALYTICAL METHODOLOGY

A description of the six samples submitted to Radian for capillary GC/MS analysis is presented in Table H.2. A detailed discussion of the analytical results obtained for the samples is presented in the following subsections.

H2.1 SAMPLE PREPARATION

Samples were received in sealed ampules and were transferred to septum sealed hypovials. Each sample was spiked with d_{10}-anthracene (an internal standard) at the 20- or 40-ppm level depending on the sample complexity.

After analysis by GC/MS, each sample fraction was derivatized with TRI-SIL to produce chromatographable derivatives from possible nonvolatile sample components containing heteroatoms such as oxygen, nitrogen, etc. The derivatization was accomplished by first removing the methylene chloride from the sample fractions under a stream of nitrogen. TRI-SIL (100 μL) was then added to each sample vial and allowed to stand for 20 hr at room temperature under dryness. Pyridine and volatile TRI-SIL by-products were then removed under a stream of nitrogen with gentle heating. Finally, the original volume of each fraction was restored with methylene chloride. Each derivatized sample was then reanalyzed by capillary GC/MS analysis.

H2.2 CAPILLARY GC/MS ANALYSIS

All samples were analyzed by capillary GC/MS using a computerized Hewlett-Packard 5985 GC/MS system. The capillary analytical column used for this study was a 0.5-mm ID x 60-m long glass capillary wall-coated SE-54 column.

Samples were injected into the GC/MS in the splitless mode of operation. Typically a 1-μL injection was employed. The GC column was programmed from 50°C to 260°C at 8°C per minute after an initial hold at 50°C. A helium carrier gas flow rate of 3.5 mL/min was employed.

The mass spectrometer was scanned from m/e 50 to m/e 500 and the instrument was operated in the electron impact mode at 70 eV. All mass spectral data were stored on magnetic disc for later interpretation and quantification.

Each sample fraction was analyzed in duplicate.

Table H.2 Samples Analyzed

Sample Designation	Fraction Type	Volume of Sample Received, mL	Total Volume of Sample, mL	Sample Date
BK REF	base/neutral blank	0.30	0.90	9/20/79
BK REF	acidic blank	0.45	1.05	9/20/79
SO REF	base/neutral	0.30	1.00	2/14/79
SO REF	acidic	0.30	0.90	2/14/79
PET REF	base/neutral	0.35	1.05	10/12/79
PET REF	acidic	0.30	0.80	10/12/79

H2.3 MANUAL INTERPRETATION OF DATA

In order to identify individual organic compounds present in a sample fraction, the stored mass spectral data were reviewed. For the most part, identification of compounds was accomplished by interpretation of individual mass spectra. However, knowledge of the chemical and physical properties of certain compounds was helpful, as well as certain gas chromatographic retention orders.

H2.4 QUANTIFICATION OF GC/MS DATA

Quantification of identified organic compounds in this program was accomplished based on integrated area measurements from GC/MS selected ion current profiles plots. Quantification was performed by the internal standard method using d_{10}-anthracene as the internal standard. For this study, the relative response factors for identified compounds relative to d_{10}-anthracene was taken as one.

The concentration of a compound in a sample extract was determined using the following equation:

$$\text{Conc.}_x = \frac{\text{Area}_x \times \text{Conc.}_{IS}}{\text{Area}_{IS} \times \text{RF}}$$

where

Conc._x = the concentration of a component (×) .

Area_x = the integrated peak area from a characteristic selected ion current profile plot for that compound.

Area_{IS} = the integrated peak area for the internal standard from its selected ion current profile plot.

RF = the relative response factor for compound x relative to d_{10}-anthracene.

H3 ANALYTICAL RESULTS

The results of this study are summarized in Tables H.3 and H.4. The data presented are semiquantitative in nature. All values were rounded to one significant figure. The compound identifications found in Tables H.3 and H.4 were accomplished by manual interpretation of the mass spectral data. Both the qualitative and the quantitative aspects of the reported data have been reviewed to minimize errors.

Table H.3 Petroleum Wastewater Extract

Compound	Retention Time, min.	Concentration, ppm	
		Analysis #1	Analysis #2
Ethyl Benzene	7.7	3	2
m/p-Xylenes	7.9	20	20
o-Xylene	8.5	20	20
iso-Propylbenzene	9.4	5	5
n-Propylbenzene	10.1	10	10
m/p-Ethyltoluenes	10.3	70	80
1,3,5-Trimethylbenzene	10.4	50	60
o-Ethyltoluene	10.7	30	40
1,2,4 Trimethylbenzene	11.0	150	160
Decane	11.1	80	90
iso-Butylbenzene/ sec-Butylbenzene	11.4	5	6
1,2,3 Trimethylbenzene	11.7	90	100
Cycloalkane	11.9	20	20
n-Butylbenzene	12.0	3	2
Indan	12.0	40	40
C_4-Alkylbenzene	12.3	8	9
Decalin	12.5	20	10
C_4-Alkylbenzene	12.5	40	40
Dimethylethylbenzene	13.0	60	60
Methyl indan	13.0	10	10
C_4-Alkylbenzene	13.1	60	60
Methyl indan	13.1	40	40
Dimethylethylbenzene	13.2	10	10
n-Undecane	13.3	80	190
C_4-Alkylbenzene	13.5	20	20
Methyldecalin	13.6	40	40
C_4-Alkylbenzene	13.6	20	20
C_4-Alkylbenzene	13.7	30	40
C_4-Alkylbenzene	13.8	60	60
Methyldecalin	14.0	30	30
Cycloalkane	14.2	20	30
C_4-Alkylbenzene	14.2	10	10
Methyldecalin	14.2	10	10
C_4-Alkylbenzene	14.3	40	40
Methyl indan	14.3	30	30
C_5-Alkylbenzene	14.5	60	40
Methyl indan	14.5	80	70
C_5-Alkylbenzene	14.6	30	30
Tetralin	14.7	100	80
C_5-Alkylbenzene	14.7	30	30
C_2-Alkyldecalin	14.8	20	20

Table H.3 (Contd.)

Compound	Retention Time, min.	Concentration, ppm Analysis #1	Concentration, ppm Analysis #2
C_5-Alkylbenzene	14.9	30	40
C_2-Alkyldecalin	15.1	40	40
C_2-Alkyldecalin	15.2	10	20
C_2-Alkyl indan	15.2	70	60
Naphthalene	15.2	20	20
Methyl tetralin	15.3	20	10
C_2-Alkyl indan/Methyltetralin	15.2	70	60
C_5-Alkylbenzene	15.3	20	10
n-Dodecane	15.3	320	170
C_2-Alkyl indan/ Methyltetratralin	15.4	40	40
C_5-Alkylbenzene	15.4	70	40
C_2-Alkyldecalin	15.5	20	20
C_5-Alkylbenzene	15.6	30	30
C_2-Alkyldecalin	15.6	10	20
C_2-Alkyldecalin	15.7	10	20
Methyltetralin	15.8	60	110
C_2-Alkylindan	15.8	10	10
C_5-Alkylbenzene	15.9	40	30
C_2-Alkyldecalin	16.0	30	30
C_2-Alkyl Indan/Methyltetralin	16.0	50	40
C_2-Alkylindan/Methyltetralin	16.1	9	10
Cycloalkane	16.1	40	30
C_5-Alkylbenzene	16.1	30	30
C_2-Alkyldecalin	16.2	20	20
C_2-Alkyldecalin	16.2	2	3
C_2-Alkylindan/Methyltetralin	16.4	30	30
C_5-Alkylbenzene	16.5	20	20
C_2-Alkyl indan/Methyltetralin	16.7	150	120
Methyltetralin	16.7	80	70
Methyltetralin	17.0	10	20
C_2-Alkyltetralin/C_3-Alkylindan	17.0	10	9
C_5-Alkylbenzene	17.0	70	60
C_2-Alkylindan/Methyltetralin	17.2	40	40
Methyltetralin	17.2	70	50
C_2-Alkyltetralin/C_3-Alkylindan	17.2	60	30
n-Tridecane	17.2	320	120
2-Methylnaphthalene	17.3	20	20
C_2-Alkyltetralin	17.4	20	20
1-Methylnaphthalene	17.6	10	20
Dimethyltetralin	17.7	100	110
C_2-Alkyltetralin	17.8	90	90

Table H.3 (Contd.)

Compound	Retention Time, min.	Concentration, ppm Analysis #1	Concentration, ppm Analysis #2
Cycloalkane	18.0	40	30
C_2-Alkyltetralin	18.1	50	50
C_2-Alkyltetralin	18.3	20	30
C_2-Alkyltetralin/C_3-Alkylindan	18.6	9	7
n-Tetradecane	18.9	300	120
C_2-Alkyltetralin	19.0	130	120
C_2-Alkylnaphthalene	19.2	10	10
C_2-Alkylnaphthalene	19.5	20	10
C_2-Alkyltetralin	19.6	40	30
Cycloalkane	19.7	30	20
C_2-Alkyltetralin	19.9	20	10
C_2-Alkylnaphthalene	19.9	6	3
n-Pentadecane	20.5	290	100
C_3-Alkylnaphthalene	20.8	4	2
C_3-Alkylnaphthalene	21.2	10	8
Cycloalkane	21.3	40	20
C_3-Alkylnaphthalene	21.5	7	9
C_3-Alkylnaphthalene	21.8	5	4
n-Hexadecane	22.0	260	110
Cycloalkane	22.9	30	20
n-Heptadecane	23.4	440	150
Cycloalkane	24.3	10	10
n-Octadecane	24.8	220	120
Cycloalkane	25.7	10	4
n-Nonadecane	26.1	180	90
n-Eicosane	27.3	100	80
n-Uneicosane	28.5	40	40
n-Doeicosane	29.6	20	20
n-Trieicosane	30.7	5	5

Table H.4 Shale-Oil Wastewater Extract

Compound	Retention Time, min.	Concentration, ppm Analysis #1	Concentration, ppm Analysis #2
Dimethyl disulfide	4.8	150	90
Toluene	5.2	180	160
$C_2H_4S_2$	6.3	100	60
2-Methyl pyridine	6.5	50	30
3- and 4-Methyl pyridines	7.7	110	100
Ethyl benzene	7.7	80	80
m/p-Xylenes	7.9	210	180
2,6-Dimethyl pyridine	8.3	170	150
o-Xylene	8.5	150	130
2,4-and 2,5-Dimethyl pyridine	9.5	1400	≥520*
2,3-Dimethylpyridine	9.8	250	220
$C_2H_6S_3$	10.5	40	90
3,5-Dimethyl pyridine	10.6	160	160
Aniline	11.0	880	620
2,4,6-trimethyl pyridine	11.0	2300	≥480*
3,4-Dimethyl pyridine	11.2	560	420
2,3,6-trimethyl pyridine	11.3	400	420
methylethyl pyridine	11.5	140	150
trimethyl pyridine	11.8	220	240
Phenol	12.0	6	10
2,3,5-trimethyl pyridine	12.4	600	440
trimethyl pyridine	12.6	1800	≥460*
C_4-Alkyl pyridine	12.7	360	140
2-Methyl aniline	12.7	170	40
4-Methyl aniline	13.0	680	≥380*
Dimethylethyl pyridine	13.1	480	680
3-Methyl aniline	13.1	560	300
Trithiolane, $C_2H_4S_3$	13.6	3000	≥440*
Dimethylethyl pyridine	14.0	330	280
Dimethylethyl pyridine	14.2	1100	≥340*
C_5-Alkyl pyridine	14.2	50	9
Dimethyl aniline	14.4	720	440
Dimethylethyl pyridine	14.4	200	100
C_5-Alkyl pyridine	14.5	70	60
C_2-Alkyl aniline	14.7	120	110
C_5-Alkyl pyridine	14.8	30	30
C_2-Alkyl aniline	14.9	230	250
C_2-Alkyl aniline	15.0	300	200
Naphthalene	15.2	120	100
n-Dodecane	15.3	10	8
Branched hydrocarbon	15.5	6	3
C_5-Alkyl pyridine	15.5	20	30

Table H.4 (Contd.)

Compound	Retention Time, min.	Concentration, ppm Analysis #1	Concentration, ppm Analysis #2
C_5-Alkyl pyridine	15.5	50	30
C_2-Alkyl aniline	15.6	70	70
C_2-Alkyl aniline	15.7	30	30
C_5-Alkyl pyridine	15.7	80	80
C_5-Alkyl pyridine	15.9	50	30
C_3-Alkyl aniline	16.0	640	350
C_2-Alkyl aniline	16.1	30	30
C_5-Alkyl pyridine	16.1	40	20
C_2-Alkyl aniline	16.3	30	20
C_3-Alkyl aniline	16.3	40	30
Quinoline	16.3	10	10
C_3-Alkyl aniline	16.4	60	50
Methyltetrahydroquinoline	16.6	30	20
C_3-Alkyl aniline	16.6	30	30
Branched hydrocarbon	16.6	6	4
C_2-Alkyl aniline	16.7	10	10
Methyltetrahydroquinoline	16.9	30	30
C_4-Alkyl aniline	17.1	2	2
Methyltetrahydroquinoline	17.1	60	50
n-Tridecane	17.1	20	10
C_3-Alkyl aniline	17.2	40	40
Methyltetrahydroquinoline	17.2	80	60
C_4-Alkyl aniline	17.2	120	120
2-Methyl naphthalene	17.3	40	30
Methyltetrahydroquinoline	17.4	20	20
C_2-Alkylaniline	17.4	6	6
Methylquinoline	17.5	40	40
1-Methyl naphthalene	17.6	30	30
$C_3H_6S_3$	17.7	20	70
Indole	17.7	40	20
C_3-Alkylaniline	17.8	4	4
C_3-Alkylaniline	17.9	10	10
C_3-Alkylaniline	18.0	20	10
Methyltetrahydroquinoline	18.1	100	90
C_3-Alkylaniline	18.2	10	4
Methylquinoline	18.4	20	30
Branched hydrocarbon	18.4	9	6
Methyltetrahydroquinoline	18.5	100	90
Methyltetrahydroquinoline	18.8	30	30
Methylquinoline	18.8	40	40
n-Tetradecane	18.8	20	10
C_2-Alkyl naphthalene	19.0	4	4

Table H.4 (Contd.)

Compound	Retention Time, min.	Concentration, ppm Analysis #1	Concentration, ppm Analysis #2
C_2-Alkyltetrahydroquinoline	19.1	10	
C_2-Alkylquinoline	19.2	10	10
C_2-Alkyl naphthalene	19.2	10	10
C_2-Alkyltetrahydroquinoline	19.4	80	110
C_2-Alkyquinoline	19.4	30	30
C_2-Alkyltetrahydroquinoline	19.4	130	110
Methyltetrahydroquinoline	19.4	10	20
C_2-Alkyl naphthalene	19.5	30	30
C_2-Alkyl naphthalene	19.8	30	30
C_2-Alkylquinoline	19.8	110	100
Branched hydrocarbon	19.8	10	8
C_2-Alkyltetrahydroquinoline	20.0	10	10
C_2-Alkyl naphthalene	20.0	20	
C_2-Alkylquinoline	20.3	10	20
n-Pentadecane	20.4	20	20
C_2-Alkylquinoline	20.7	20	30
C_2-Alkyltetrahydroquinoline	21.0	30	30
C_2-Alkylquinoline	21.1	10	8
$C_3H_6S_4$	21.2	200	140
C_2-Alkylquinoline	21.3	9	10
n-Hexadecane	21.9	20	20
Branched hydrocarbon	22.7	10	10
n-Heptadecane	23.4	20	20
Branched hydrocarbon	23.5	20	20
n-Octadecane	24.7	20	20
Branched hydrocarbon	24.9	10	9
Phenanthrene	25.0	3	
n-Nonadecane	26.0	20	20
Carbazole	26.0	70	70
Methyl carbazole	26.8	40	40
Methyl carbazole	27.3	20	20
n-Eicosane	27.3	20	20
Methyl carbazole	27.5	20	20
C_2-Alkylcarbazole	27.5	10	10
C_2-Alkylcarbazole	28.2	20	20
C_2-Alkylcarbazole	28.4	40	30
n-Uneicosane	28.5	20	20
n-Doeicosane	29.6	20	10
n-Trieicosane	30.7	20	10
n-Tetraeicosane	31.9	20	20
n-Pentaeicosane	33.4	10	10
n-Hexaeicosane	35.1	7	7

Table H.4 (Contd.)

Compound	Retention Time, min.	Concentration, ppm Analysis #1	Concentration, ppm Analysis #2
n-Hepteicosane	37.1	10	6
n-Octaeicosane	39.8	20	5
n-Nonaeicosane	43.2	7	3

*Detector Saturated

RADIAN
CORPORATION

March 6, 1980 219-038

Dr. Ron Wingender
c/o W. Harris/Argonne National Labs
9700 South Cass Avenue
EES-Building 12
Argonne, Illinois 60439

Dear Dr. Wingender:

Radian Corporation's report and my letter of February 28, 1980, failed to discuss the analysis of sample blanks which were important parts of the reported work. Both a refinery base/neutral and an acidic fraction blank were analyzed. These showed only minor residual baseline contamination. No sample components identified in the refinery sample were found in the corresponding blank sample. The values reported for the refinery sample, therefore, required no blank correction.

I am sorry for this oversight in our reporting. If you have any questions regarding this work, please do not hesitate to contact R. G. Oldham or me.

Sincerely,

Robert L. Spraggins, Ph.D.
Senior Scientist and
Group Leader GC-MS
Analysis

RLS/ds

8500 Shoal Creek Blvd./P.O. Box 9948/Austin, Texas 78766/(512)454-4797

APPENDIX I

SHALE-OIL PROCESSING SCHEME AND MATERIAL BALANCES FOR PERIOD NOVEMBER 11-26, 1978

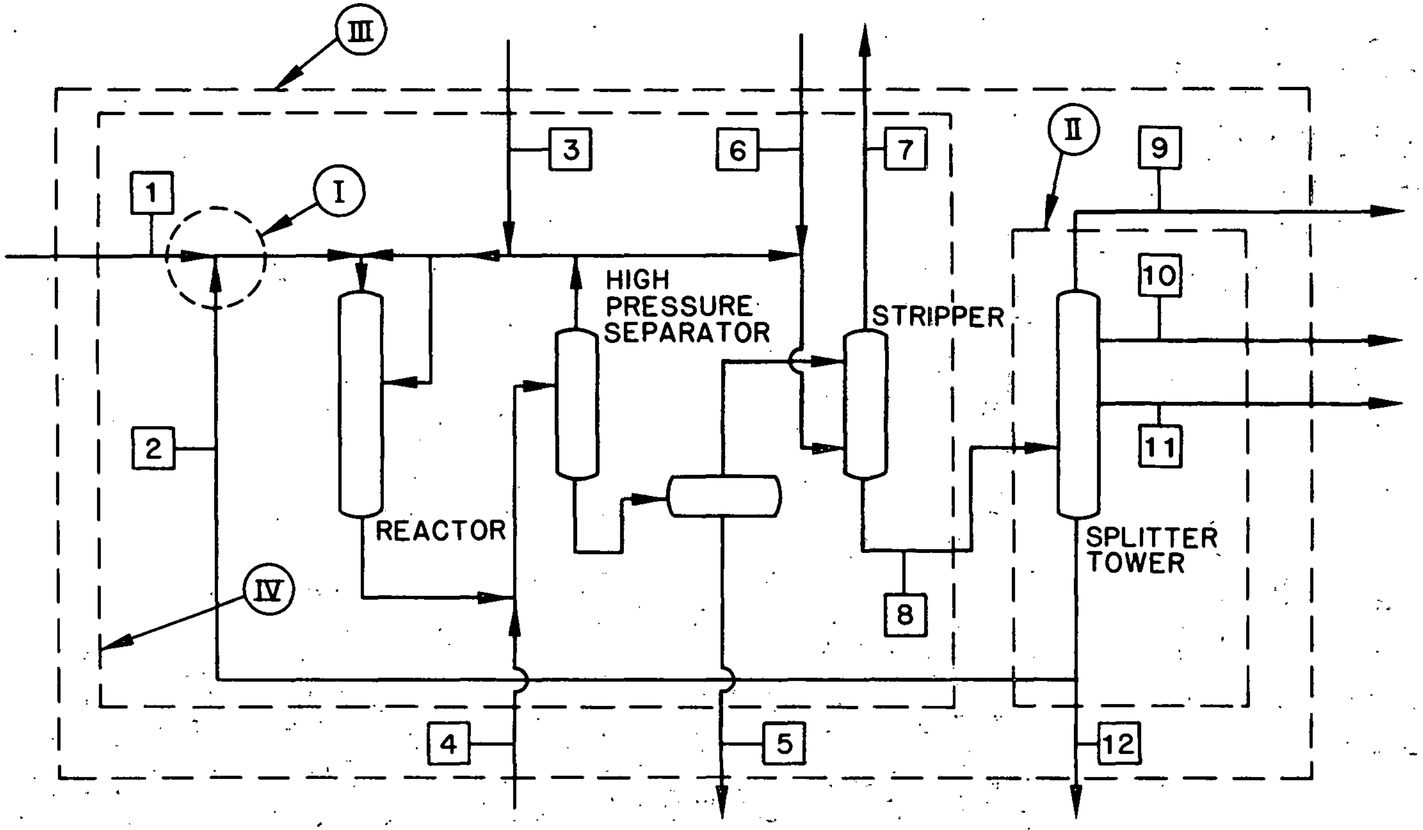
The following technical communication was provided by Dr. Alan Roberts, Headquarters Naval Material Command:

> Two processing units were utilized to refine crude shale oil into military fuels. The isocracker I unit accomplished the major portion of the refining and produced the basic jet and diesel fuels together with heavy fuel oil and a gasoline boiling range stock. An acid-clay treating unit was operated in series with the isocracker acting as a final polishing step to produce storage-stable jet and diesel fuels.
>
> In the isocracker I unit, filtered crude shale oil was charged directly with recycled hydrogen and heavy oil to a reactor containing a multiple number of catalyst beds after being preheated and passed through the guard bed (Fig. 1). The objective of the reaction section included the removal of heteroatoms and a selective cracking of the oil to produce an effluent maximized in the jet fuel and diesel fuel boiling ranges. Nitrogen, sulfur and oxygen were hydrotreated to ammonia, hydrogen sulfide and water, respectively. Hydrogen from the high pressure separator was recycled at various locations in the reactor to control the temperature increases associated with the exothermic reactions of the reactor. The reactor effluent was cooled by preheating reactor feed and stripper feed and was fed to a high pressure separator where hydrogen was removed for recycle to the reactor and reactor feed. Reactor effluent was also injected with steam condensate before being changed to the high pressure separator. Steam-condensate injection prevents salt fouling of equipment and removes much of the reactor effluent ammonia and hydrogen sulfide in a foul condensate stream. After separation of ammonia, hydrogen sulfide and hydrogen from the reactor effluent, the remaining hydrocarbon liquid phase was stripped of residual ammonia, hydrogen sulfide and light ends in the stripper column by the portion of high pressure separator overhead hydrogen not recycled to the reactor and any required make-up hydrogen. The stripped liquid hydrocarbon was finally fed to the splitter column where it was separated into the four basic products: heavy fuel oil, diesel fuel marine, jet fuel and gasoline boiling range stock. This column produced all four products continuously and was adjusted to product JP-5 and JP-8 at different times. JP-4 was to be produced by blending the jet fuel stream with a portion of the gasoline boiling range stock. JP-4 was not produced, however, since a steady flow of gasoline stock reliable for blending purposes could not be attained. Both diesel fuel and jet fuel sidestreams of the

splitter column were stripped of lighter boiling fractions to meet flash point specifications.

At this point, both diesel fuel and jet fuels were rundown to intermediate storage in tanks 65 and 64, respectively. At the conclusion of the ISO I operation, JP-5 and DFM were pumped from tanks 64 and 65 and treated separately in the acid-clay treater where residual fuel-bound nitrogen and color bodies were removed, making the finished products storage stable.

Because the emphasis of the present study is on the isocracker sour condensate, additional information on the processing scheme will go unreported here, with the exception of the material balance data of Figure I.1.



STREAM NO.	1	2	3	4-5	6	7	8	9	10	11	12
STREAM NAME	NET SHALE OIL FEED	LIQUID RECYCLE	MAKE-UP GAS	LOSS TO FOUL CONDENSATE	IMPORTED STR. GAS	WET GAS/ STR. OVHD.	SPLITTER FEED	GASO. STOCK	JET FUEL	DFM	HEAVY FUEL OIL
11 NOV.-26 NOV. CUMULATIVE TONS	7838.52	2595.85	971.47	338.81	-0-	1370.93	9600.29	714.99	965.09	1835.10	3489.49
CUMULATIVE BBL OR MSCF	48573.5	16998.0	90.15	-	-0-	52.81	63755.43	5421.61	6799.4	12462.	22850

Fig. I.1 Material Balances

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