Analysis of Extractable Total Petroleum Hydrocarbons (ETPH) Using Methylene Chloride Gas Chromatograph/Flame Ionization Detection

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1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for analysis of extractable total petroleum hydrocarbons (ETPH) in soil and water samples(i.e surface and ground water). The conditions used are designed to measure the C_9 to C_{36} range of hydrocarbons. This range represents the major components of a number of widely used petroleum products such as kerosene, jet and diesel fuels, No. 2 to No. 6 fuel oils and motor oil. This method is not used for quantitation of gasoline contamination, because the major components of gasoline are not retained in the sample extraction and concentration procedure.

1.2 The average response factors of C_9 to C_{36} alkanes and total peak area of the sample chromatogram are used to calculate the concentration of ETPH. An N-alkane mixture is run as a performance and calibration verification to ensure GC conditions are adequate to perform ETPH analysis. This also ensures that the initial calibration meets QC criteria. Capillary GC columns are recommended for the analyses.

1.3 This method is restricted for use by, or under the supervision of, analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.4 If the major contaminant is not ETPH, other tests should be performed in order to interpret data and characterize the contaminants.

1.5 This method is not intended to be used for the analysis of potable water.

2.0 SUMMARY OF METHOD

2.1 This method uses a gas chromatograph coupled with a flame ionization detector (FID) for the analysis of ETPH. Semi-volatile organic compounds other than petroleum hydrocarbons, which can be extracted and detected by FID, will be calculated as part of ETPH.

2.1.1 Soil and solid samples are extracted with methylene chloride using ultrasonic extraction or other appropriate preparatory methods to obtain necessary quantitation limits.

2.1.2 Water samples are extracted with methylene chloride using a separatory funnel or other appropriate preparatory methods to obtain necessary quantitation limits.

2.2 An appropriate column and temperature program, which can separate the solvent peak from C_9 alkane and is able to elute the last component, C_{36} alkane, in a reasonable time period (about 30 minutes) should be used. Detection is achieved by FID.

2.3 It is recommended that fused silica capillary columns be used for the analysis. Columns and conditions listed have been demonstrated to provide separation of the target analytes. Analysts may change these conditions as long as adequate performance is demonstrated.

2.4 Oil identification can be achieved by comparing the chromatograph of the sample to that of the known product.

3.0 INTERFERENCES

3.1 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. To reduce the potential for carryover, the sample syringe must be rinsed out between samples with an appropriate solvent. Whenever an unusually concentrated sample is encountered, it should be followed by injection of a solvent blank to check for cross contamination.

3.2 Those organic compounds that are extracted, eluted through the column and detected by FID may be calculated as ETPH. When interferences are present in significant amounts, irregular chromatograms may be observed.

4.0 APPARATUS AND MATERIALS

4 Gas chromatograph

4.1.1 Gas Chromatograph - A gas chromatograph with flame ionization detector (FID), capillary column inlet, liquid sample injector and data system. A data system that measures peak areas and is capable of performing baseline subtraction is recommended.

Recommended GC Columns:

4.1.2.1 Column 1 - 30 m x 0.53-mm inner diameter fused silica capillary column (DB-1, DB-5, or equivalent), 0.25 to 0.5 µm film thickness.

4.1.2.2 Column 2 - 30 m x 0.32-mm inner diameter fused silica capillary column (DB-1, DB-5, or equivalent), 0.25 to 0.5 µm film thickness.

4.1.2.3 Laboratories may use other capillary columns if they demonstrate method performance equal to or better than that provided with the method.

Detector - Flame ionization detector (FID)

4.2 Sample introduction - A Split/splitless, Grob, Direct or on-column GC injection port for the analysis of solvent extracts by direct injection.

4.3 Analytical balance - Capable of measuring differences of 0.0001g.

4.4 Top load balance - Zero -500 g capacity, capable of measuring differences of 0.01 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used whenever possible. Unless otherwise indicated, it is recommended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without diminishing the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in EPA SW-846 Chapter 1.

5.3 Methylene chloride, pesticide quality or equivalent - Store away from other solvents and test every batch with GC-FID to verify there are no extra peaks that could contribute to the ETPH measurement.

5.4 Fuel oil and other oil standards, e.g. diesel or jet fuel and motor oil - purchase from a commercial source. If available, obtain fuel from the source on site.

5.5 Alkane standard - The mixture should contain a range from C9- to C36 and may be prepared from pure standard materials or purchased as purchased as certified solutions. This N-alkanes mixture is used for establishing injection performance, calibration of response factor and retention times.

5.6 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methylene chloride.

5.6.1 Place a 10-ml tared, ground glass stoppered volumetric flask on the balance. Weigh the flask to the nearest 0.0001 g.

5.6.2 Using a 100-µL syringe, immediately add two or more drops of pure standard material to the flask, then re-weigh. The liquid must fall directly into the flask without contacting the neck of the flask.

5.6.3 Re-weigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.6.4 Some high molecular-weight hydrocarbons do not readily dissolve at room temperature. Moderate heat and sonication may assist in dissolution. Transfer the stock standard solution into a bottle with a Teflon-lined screw cap. Store, with minimal headspace, at 4°C and protect from light.

5.6.5 Standards must be replaced after six months (or sooner if comparison with check standards indicates a problem).

5.7 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards (as needed) that contain the compounds of interest, either singly or mixed. The stock solution should be allowed to equilibrate to room temperature, and should be inspected to determine that all solutes are completely dissolved. This step is particularly important for the alkanes standard mixtures. Secondary dilution standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.8 Calibration standards - Calibration standards at a minimum of five concentrations are prepared in methylene chloride from the secondary dilution of the stock standards. One of the concentrations should be at a concentration near, but above the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should cover the working

range of the GC. It is recommended that an N-alkane standard mixture with different concentrations be used as the calibration standard. Section 7.3 gives a typical example.

5.9 Surrogate standards - In this method surrogate standards are optional. If necessary, the analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and blank with one or two surrogate compounds which are not affected by method interference.

5.10 Silica gel, 60-200 mesh, Davison Grade 950 or equivalent. The gel should contain 1-2% water as defined by residue test at 139°C. Adjust by overnight equilibration if needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 General guidelines for semi-volatile sampling are applicable when sampling for ETPH. Soil and solid waste samples can be split off from samples taken for other semi-volatile analyses. These samples should be stored at 4°C, extracted within 14 days of sampling, and analyzed within 40 days after extraction. Water samples should be collected in separate bottles and stored at 4°C. When the sample is transferred for analysis, the sample bottle should be rinsed with solvent. Water samples should be extracted within 7 days of sampling and analyzed within 40 days of the extraction.

7.0 PROCEDURE

Sample Extraction

Methylene chloride is used as the extracting solvent. The following procedures are recommended. Nevertheless, any sample preparation method that is appropriate for the sample type and provides adequate performance may be used.

Soil and Solid Samples

Ultrasonic extraction (Method 3550) or Soxhlet Extraction (Method 3340) are the recommended extraction method for soil/solids. All results should be reported in dry weight.

7. Sonication Extraction - It is very critical that the method be followed explicitly to achieve an extraction efficiency that approaches that of the Soxhlet extraction. This requires that: (a) the necessary equipment be used (a ¾" horn and a minimum of 300 watts of power); the horn is properly maintained (tuned prior to use according to manufacturers instructions and that the tip of the horn is not worn); (b) the samples are properly prepared (Thirty grams of sample is thoroughly mixed with anhydrous sodium sulfate so that it exists as a free flowing powder prior to the addition of solvent); (c) the correct extraction procedure is followed (three extractions are performed with the methylene Chloride, the sonication is performed in the specified pulse mode and the tip is positioned just below the solvent surface but above the sample); and (d) there is visible observation of a very active mixing of the sample throughout the solvent when the energy pulse is on. The extracts are combined and are ready for silica gel clean up.

.2 Soxhlet Extraction – Thirty grams of solid sample is mixed with thirty grams of anhydrous sodium sulfate and placed in an extraction thimble and extracted with 300 mL of methylene chloride for 16-24 hours at 4-6 cycles/hour using a

Soxhlet extractor. Dry the extract by passing through a drying column containing approximately 10 cm of anhydrous sodium sulfate. The extract is then ready for silica gel clean up.

7.1.2 Aqueous samples

Both separatory funnel (Method 3510) and continuous liquid-liquid extraction (Method 3520) can be used for aqueous sample extraction.

7.1.2.1 Separatory Funnel – A measured volume of sample, usually 1 liter, at a neutral pH, is serially extracted three times with methylene chloride. The extracts are combined and are ready for silica gel clean up.

7.1.2.2 Continuous Liquid-Liquid Extraction – A measured volume of sample, usually 1 liter, at neutral pH , and extracted with methylene chloride for 18 to 24 hours. The extract is then ready for silica gel clean up.

7.1.3 Silica gel clean-up and concentration

Add 3 grams silica per 100 mls of sample. Stopper the flask and stir the solution for a minimum of 5 minutes on a magnetic stirrer. More silica gel may be added if necessary for dirty sample. The sample is then concentrated to 1 mL with a KD concentrator.

7.2 Chromatographic conditions (recommended)

Column 1

Carrier gas (Helium) flow rate:	5 ml/min
Oven Temperature program:	
Initial temperature:	40°C, hold for 0.5 minutes
Program:	40°C to 290°C at 15°C/min
Final temperature:	290°C, hold for 10 minutes.
Injector Temperature:	290°C
Detector Temperature:	300°C
Make-up gas:	25 ml/min

Column 2

Carrier gas (Helium) flow rate:	1-2 ml/min
Oven Temperature program:	
Initial temperature:	40°C, hold for 0.5 minutes
Program:	40°C to 290°C at 15°C/min
Final temperature:	290°C, hold for 10 minutes.
Injector Temperature:	300°C
Detector Temperature:	300°C
Make-up gas:	30 ml/min

7.2.3 Performance Verification

This method is based on the fact that the response factors of hydrocarbons are essentially the same, provided the GC system does not have discrimination when the sample is introduced. The

method relies on using the average response factor of alkanes to convert the total peak area of a sample chromatogram to a ETPH concentration. It is critical to maintain the gas chromatograph without significant sample introduction discrimination. The N-alkane mixture also serves other functions: a) to demonstrate sufficient separation between the solvent and C_9-alkane peak, b) to ensure that the last component, C_{36}, is eluted within a reasonable amount of time (30 minutes), and c) to serve as a retention time marker for oil identification. Performance is verified at the beginning of a GC analysis batch and whenever any changes are made to the system or operational parameters. Analyze the N-alkane mixture (C_9 to C_{36}) using the identical procedure to be used for the analysis of samples. Calculate the response factor for each N-alkane in accordance with the equation below:

$$Fi = Ai/Ci$$

Where:

Fi = response factor of an individual alkane

Ci = the mass (μg) of the alkane injected into column.

Ai= response in area counts for the individual alkanes.

Use the following equation to calculate the average response factor of N-alkanes:

$$Fa = (\Sigma Fi)/n$$

Where:

Fa - the average of the response factor.

n - the number of the alkanes used in the calculation.

The deviation of an individual response factor to the average response factor is calculated using the following equation:

$$\%D = [(Fi-Fa)/ Fa]100$$

If the response factors for the alkane standards are not within +/- 20%, then a new initial calibration must be prepared for a standard mix. Common causes of sample introduction discrimination include an injection liner that is dirty or has an activated surface, inappropriate column installation to the injection port, incorrect sample injection (especially when using the manual injection technique), dirty column, or an injection port leak. Performance failure may result when the N-alkane mixture is not completely dissolved in the solvent. It is very important to maintain the integrity of the N-alkane solution.

7.3 Initial calibration

7.3.1 Use the N-alkane mixture at different concentrations (concentration equaling the sum of individual alkane concentrations). The concentrations should correspond to the expected range found in real samples or should cover the working range of the detector. As an example, concentrations of 50 μg/ml, 100μg/ml, 200μg/ml, 500μg/ml and 1000μg/ml would be appropriate.

7.3.2 Introduce each calibration standard by matching the technique used to introduce the actual samples into the gas chromatograph. Tabulate peak area responses under the resolved peaks against the mass injected.

7.3. Calculate the average response factor according to sec.7.2.3 for each concentration level.

7.3.4 Calculate the average and relative standard deviation of response factors over the five concentrations. If the percent relative standard deviation (%RSD) of the response factor is less

than 30% over the working range, linearity through the origin can be assumed, and the average response factor can be used in calibration.

7.4 Quantitation range

7.4.1 The retention time range for a particular fuel is defined during initial calibration. The retention time range is the period between the mean retention time of the initial rise of the first major eluting peak and the mean of the final descent of last major eluting peak in the fuel pattern. Major peaks are at least 10% of the height of the largest peak in the fuel pattern.

7.4.2 The retention time range for an unknown sample is defined during initial calibration using the range shown by an nC_9 - nC_{36} standard.

7.5 Calibration verification

7.5.1 The response factor and retention times must be verified at the beginning of each 12-hour work shift as a minimum requirement. Verification is accomplished by analysis of an N-alkane standard that falls in the middle of the range of concentrations chosen. It is strongly recommended that additional analyses of the verification standard(s) be run throughout a 12-hour shift.

7.5.2 If the average response for the standard is within ±30% of the response obtained during the initial calibration (using initial response factor as 100%), then the initial calibration is considered still valid. If the response factor varies from the predicted response by more than ±30% in these additional determinations, corrective action must be taken to restore the system or a new calibration curve must be prepared.

7.5.3 All N-alkanes in the calibration verification analyses must fall within previously established retention time windows.

7.5.4 Solvent blanks and any method blanks should be run with calibration verification analyses to confirm that laboratory contamination does not cause false positives.

7.6 Gas chromatographic analysis

7.6.1 The sequence begins with a solvent blank followed by performance/calibration verification standard(s), then method blank and finally the sample extract analyses. A verification standard is also necessary at the end of each analytical batch. The sequence ends when the entire set of samples has been injected or when retention time and/or percent difference QC criteria are exceeded.

Note: If the criteria are exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before recalibrating and proceeding with sample analysis. All sample analyses performed using external standard calibrations must be bracketed with acceptable data quality analyses (e.g., calibration and retention time criteria). Therefore, all samples that fall between the standard that exceeded criteria and the last standard that was acceptable must be reanalyzed.

7.6.2 Samples are analyzed with the same instrument configuration as is used during calibration. It is recommended that same sample extract be split into two autosampler vials. The second vial can be stored for 24 hours to ensure that an uncompromised sample is available for

analysis or dilution, if the analysis of the first sample is unsuccessful or if results exceed the calibration range of the instrument.

7.6.3 Sample concentrations are calculated by comparing sample response data with the initial calibration (Sec. 7.3). Therefore, if sample response exceeds the limits of the initial calibration range, a dilution of the sample must be analyzed. Extracts should be diluted so that all peaks are on scale, as overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, is acceptable as long as calibration limits are not exceeded.

7.6.4 Second column confirmation is generally not necessary for petroleum hydrocarbon analysis. However, if analytical interferences are indicated, analysis using another method is required.

7.6.5 The performance of the entire analytical system should be checked every 12 hours, using data gathered from analyses of blanks, standards, and replicate samples. Significant peak tailing must be corrected.

7.7 Integration and Calculations

7.7.1 To measure the total area of the samples, construct the baseline of the sample chromatogram so that it starts at the beginning of the n-C_9 alkane peak and terminates at the end of the n -C_{36} peak. Evaluate the total peak area above the baseline to make sure it reasonably represents the sample response. It may be possible to achieve complete peak integration by using software-specific automatic integration parameters. If this cannot be done, manual integration may be necessary.

7.7.2 Baseline subtraction may generate better integration results, especially when a sample concentration is low or when column bleed contributes significantly to the baseline. Baseline subtraction may be performed directly on the gas chromatograph (provided the GC has this capability) or with the data acquisition software which runs the GC. Figure 7 in the Appendix illustrates the effect of baseline subtraction.

7.7.3 The concentration of ETPH of a sample is calculated as follows:

7.7.3. Aqueous samples

Concentration ($\mu g/L$) = $[(A_x/Fa)(V_t/ V_i)D]/ V_s$
where:

A_x	=	Response for the analyte in the sample, in total peak area counts.
Fa	=	Average response factor of alkane standard, count/μg
V_i	=	Volume of extract injected into GC in mls.
D	=	Dilution factor. If no dilution is made, D=1.
V_t		Volume of extract in mls.
V_s	=	Volume of sample extracted in L.

7.7.3.2 Nonaqueous and solid samples

Concentration (µg/kg) $=[(A_x/Fa)(V_f/ V_i)D]/ W$
where:

W — Weight of sample extracted, kg. The wet weight or dry weight may be used, depending upon the specific applications of the data.
Note: The injection volume of sample extract must be the same as that of the calibration standard.

7.8 Instrument Maintenance:

7.8.1 Injection of sample extracts from waste sites often leaves a high boiling point residue in the injection port area or the injection port end of the chromatographic column. Such samples may also splatter. This residue affects chromatography in many ways (i.e., peak tailing, retention time shifts, analyte degradation, etc.). In addition, residue buildup in a splitter may limit flow through one leg and therefore change the split ratios. If this occurs during an analytical run, the quantitative data may be incorrect. Instrument maintenance is therefore very important. Proper cleanup techniques will minimize the problem. Instrument QC will indicate when instrument maintenance is required.

8.0 QUALITY CONTROL

8. The laboratory should maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff is trained or significant changes in instrumentation are made.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a Laboratory Control Sample (LCS).

8.4. Documenting the effect of the matrix should include analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch.

8.4.2 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix (such as clean sand) similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.5 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis, and the accuracy and precision obtained, will be determined by the sample matrix, sample introduction technique, and calibration procedures used. Table 4 contains MDL data for water samples. When a one-liter water sample is extracted with methylene chloride and concentrated to 1.0 ml, the MDL is 45 µg/l. Table 5 contains MDL data for spiked soil samples. For a 10-gram soil sample with a final extract volume of 1.0 ml, the MDL is 10 mg/kg. Table 6 shows MDL data for two low concentration soil samples. The MDLs for a 10-gram soil with final extract volume of 1.0 ml are 4.8 and 0.8 mg/kg respectively. Table 7.1 to Table 7.3 show the data for instrument detection limits for different fuel oil and N-alkane standards. The detection limits are from 0.5 to 6.8 µg/ml in methylene chloride solvent, depending on the reproducibilities and responses of fuel oils. In general, the MDL for a soil sample is 10 mg/kg with 10-g soil sample extracted and concentrated into 1-ml methylene chloride. The MDL for water samples is 50 µg/l with a 1000× concentration.

10. REFERENCES

1. ASTM, Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography, Designation: D 2887 - 93.

2. US EPA, Method 1664: N-Hexane Extractable Material (HEM) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry (Oil and Grease and Total Petroleum Hydrocarbons), October 1994.

3. US EPA, Method 8440: Total Recoverable Petroleum Hydrocarbons by Infrared Spectrophotometry, revision 0, January 1995.

4. US EPA, Method 8015B: Nonhalogenated Organics Using GC/FID, Revision 2, December 1996.

Appendix Tables and Figures

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Table-7.3 Instrumental Detection Limits for Five Typical Oils

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Table – SAMPLE CONTAINERS, PRESERVATION, TECHNIQUES, AND HOLDING TIMES

Analyte Class	Container	Preservative	Holding Time
Concentrated Waste Samples	125 ml widemouth glass with Teflon lined lid	None	Samples must be extracted within 14 days and extracts analyzed within 40 days following extraction.
Water Samples No Residual Chlorine Present	1-gal. or 2 x 0.5-gal.,or 4 x 1-L, amber glass container with Teflon lined lid	Cool, 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days following extraction.
Residual Chlorine Present	1-gal. or 2 x 0.5-gal., or 4 x 1-L, amber glass container with Teflon lined lid	Add 3 ml 10% sodium thiosulfate solution per gallon.[2] Cool, 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days following extraction.
Soil/Sediments and Sludges	250 ml widemouth glass container with Teflon lined lid	Cool, 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days following extraction.

Table - 2. Discrimination Check

Compound	BP (°C)	Conc.(µg/ml)	Area	RF	Fn	Average
Nonane (C9)	151	100	684,775	6.82E+03	1.00	
Decane (10)	174	104	708,733	6.84E+03	1.00	
Dodecane (12)	216	106	743,755	6.99E+03	1.02	
Tetradecane (14)	254	108	753,462	6.95E+03	1.02	6.91E+03
Hexadecane (16)	287	292	2,022,936	6.93E+03	1.02	(ml/µg)
Octandecane (18)	316	128	886,752	6.91E+03	1.01	
Eicosane (20)	344	166	1,142,315	6.90E+03	1.01	
Docosane (22)	369	99	687,081	6.97E+03	1.02	
Tetracosane (24)	391	100	663,940	6.64E+03	0.97	
Hexacosane (26)	412	95	648,943	6.80E+03	1.00	
Octacosane (28)	431	94	663,864	7.09E+03	1.04	
Triacontane (30)	449	73	508,007	7.00E+03	1.03	
Dotriacontane (32)	466	111	793,443	7.14E+03	1.05	
Tetratriacontane (34)	481	85	565,673	6.64E+03	0.97	
Hexatriacontane (36)	496	88	622,214	7.07E+03	1.04	

* Fn = The relative response factor of each n-paraffin to n-Nonane'

** Average RF was from n-C9 to n-C36

Table -3. Linearity of Alkanes by GC-FID

	Level 6	Level 5	Level 4	Level 3	Level 2	Level 1	Average	SD	RSD
Nonane	5,441	6,264	6,726	6,820	6,748	6,783	6,464	541	8.4
decane	7,016	6,975	6,815	6,841	6,749	6,753	6,858	113	1.6
Dodecane	7,165	7,128	6,984	6,990	6,894	6,902	7,010	113	1.6
Tetradecane	7,087	7,079	6,951	6,951	6,870	6,894	6,972	92	1.3
Hexadecane	7,072	7,046	6,928	6,928	6,852	6,881	6,951	89	1.3
Octadecane	6,969	6,967	6,885	6,906	6,824	6,897	6,908	55	0.8
Eicosane	6,907	6,909	6,832	6,898	6,862	6,917	6,888	34	0.5
Docosane	6,953	6,937	6,947	6,968	7,008	7,147	6,993	79	1.1
Tetracosane	6,848	6,840	6,654	6,639	6,570	6,433	6,664	160	2.4
Hexacosane	7,073	6,954	6,769	6,802	6,764	6,687	6,842	144	2.1
Octacosane	7,696	7,503	7,005	7,093	6,971	6,816	7,181	342	4.8
Triacontane	7,108	7,072	6,795	6,997	7,028	6,909	6,985	115	1.7
Dotriacontane	7,375	7,340	7,073	7,135	7,057	7,000	7,163	157	2.2
Tetratriacontane	6,813	6,748	6,591	6,639	6,629	6,558	6,663	98	1.5
Hexatriacontane	7,086	7,091	6,897	7,071	7,013	6,942	7,017	81	1.2

The higher RSD for Nonane might be caused by the tailing solvent peak

Table - 4. MethodPerformance For Spiked Water Samples

Sample:	DI Water		
n	Calculated Conc. (µg/ml)	Recovery (%)	RSD (%)
1	361	90	-10
2	350	87	-13
3	334	83	-18
4	382	95	-5
5	353	88	-12
6	334	83	-18
7	367	92	-9
8	339	85	-16
9	345	86	-15
10	405	101	1
Average	352	89	-12
SD	16	6	6
t - 0.99 (n = 9)	2.821		
DL (µg/ml)	45.4		
MDL (mg/L), 1 liter Water with Final Vol.= 100 ml	4.54		
MDL (µg/L), 1 liter Water with Final Vol.= 1.0 ml	45.4		

* A mix of #2 oil, #6 oil, Kerosene and Motor oil with 100µg/ml each was added to the water..
* Followed by liquid-liquid extraction and the final volume was 1.0 ml.
* All areas were baseline subtracted and autointegrated according to Method TPH06217.MTH.
* The sample's volume were 1 liter.
* RF (Oil Mix Oil - ml/µg) is the Response Factor of the mix of #2 oil, #6 oil, Kerosene and Motor oil with 100µg/ml each.

Table -5 Method Performance Data For Spiked Soil Samples

Sample ID	Calculated Conc. (µg/ml)	Recovery (%)	RSD (%)
S-11A	372	93	-7
S-11B	405	101	1
S-11C	461	115	14
S-11D	410	103	2
S-12A	357	89	-11
S-12B	405	101	1
S-12C	347	87	-14
S-12D	362	90	-10
S-14A	352	88	-13
S-14B	448	112	11
S-14C	490	122	20
S-14D	450	112	12
S-21A	463	116	15
S-21B	360	90	-11
S-21C	464	116	15
S-21D	454	113	13
Average	386	103	
SD	37	12	
t-0.99 (n = 16)	2.602		
DL (µg/ml)	97.5		
MDL (mg/kg-ppm), 10 g Soil with Final Vol.= 100 ml	975		
MDL (mg/kg-ppm), 10 g Soil with Final Vol.= 1.0 ml	9.75		

* RF (Oil Mix Oil - ml/µg) is the Response Factor of the mix of #2 oil, #6 oil, Kerosene and Motor oil with 100µg/ml each.
* The Oil mix was added to the soil samples and followed by sonication and the final volume was 100 ml.
* All areas were baseline subtracted and autointegrated according to Method TPH04067.MTH.
* The sample's amounts were around 10 grams.

Table - 6. Method Performance Data For Real Soil Samples

Sample ID:	Pile-1	S-26
n	Calculated Conc. (µg/ml)	Calculated Conc. (µg/ml)
1	63.9	18.4
2	47.1	9.9
3	58.4	14.3
4	68.3	17.3
5	94.3	17.3
6	72.3	19.9
7	45.3	16.1
8	67.8	17.9
9	88.6	17.2
Average	67.3	16.5
SD	16.6	2.881
t-0.99 (n = 9)	2.896	2.896
DL (µg/ml)	47.9	8.34
MDL (mg/kg-ppm), 10 g Soil with Final Vol.= 100 ml	479	83.4
MDL (mg/kg-ppm), 10 g Soil with Final Vol.= 1.0 ml	4.79	0.834

* The real sample's amounts were 10.1 gm for all Pile-1's and 10.0 gm for S-26-1 and 8.0 gm for the other S-26's.
* All areas were baseline subtracted and autointegrated according to Method TPH04067.MTH.
* Pile-1 is similar to #2 fuel oil and S-26 is #6 fuel oil

Table – 7.1 Preliminary Instrument Detection Limits for Five Typical Oils

Alkanes			kerosene		
	Peak Area (x 10e-3)	Calculated		Peak Area (x 10e-3)	Calculated
n	Total	Conc. (µg/ml)	n	Total	Conc. (µg/ml)
1	3177	345		685	50.0
2	3212	348		682	49.8
3	3232	351		684	50.0
4	3232	351		684	50.0
5	3247	352		684	50.0
6	3257	353		686	50.1
7	3232	351		688	50.3
8	3226	350		680	49.7
9	3221	349		687	50.2
Average	3226	350	Average	684	50.0
SD	23	2.47	SD	2	0.179
Conc. Injected (µg/ml)	350		Conc. Injected (µg/ml)	50	
	t-0.99 (n = 9)	2.896		t-0.99 (n = 9)	2.896
	DL (µg/ml)	7.14		DL (µg/ml)	0.52
DL (mg/kg-ppm), 10 g Soil with Final Vol.= 100 ml		71.4	MDL (mg/kg-ppm), 10 g Soil with Final Vol.= 100 ml		5.2
MDL (mg/kg-ppm), 10 g Soil with Final Vol.= 1.0 ml		0.714	MDL (mg/kg-ppm), 10 g Soil with Final Vol.= 1.0 ml		0.052
MDL (mg/L), 1 liter Water with Final Vol.= 100 ml		0.714	MDL (mg/L), 1 liter Water with Final Vol.= 100 ml		0.052
MDL (µg/L), 1 liter Water with Final Vol.= 1.0 ml		7.140	MDL (µg/L), 1 liter Water with Final Vol.= 1.0 ml		0.519

* All areas were multiplied by 10e-3 and without baseline subtraction.

Table – 7.2 Preliminary Instrument Detection Limits for Five Typical Oils

#2 Fuel Oil			#6 Fuel Oil		
	Peak Area (x 10e-3)	Calculated		Peak Area (x 10e-3)	Calculated
n	Total	Conc. (µg/ml)	n	Total	Conc. (µg/ml)
1	1707	99.4			
2	1670	97.2			
3	1721	100			
4	1706	99.3			
5	1666	97.0			
6	1730	101			
7	1728	101			
8	1779	104			104
9	1749	101.8			99.2
Average	1717	100	Average	828	100
SD	36	2.08	SD	20	2.37
Conc. Injected (µg/ml)	100		Conc. Injected (µg/ml)	100	
	t-0.99 (n = 9)	2.896		t-0.99 (n = 9)	2.896
	DL (µg/ml)	6.02		DL (µg/ml)	6.85
MDL (mg/kg-ppm), 10 g Soil with Final Vol.= 100 ml		60.2	MDL (mg/kg-ppm), 10 g Soil with Final Vol.= 100 ml		68.5
MDL (mg/kg-ppm), 10 g Soil with Final Vol.= 1.0 ml		0.602	MDL (mg/kg-ppm), 10 g Soil with Final Vol.= 1.0 ml		0.685
MDL (mg/L), 1 liter Water with Final Vol.= 100 ml		0.602	MDL (mg/L), 1 liter Water with Final Vol.= 100 ml		0.685
MDL (µg/L), 1 liter Water with Final Vol.= 1.0 ml		6.023	MDL (µg/L), 1 liter Water with Final Vol.= 1.0 ml		6.853

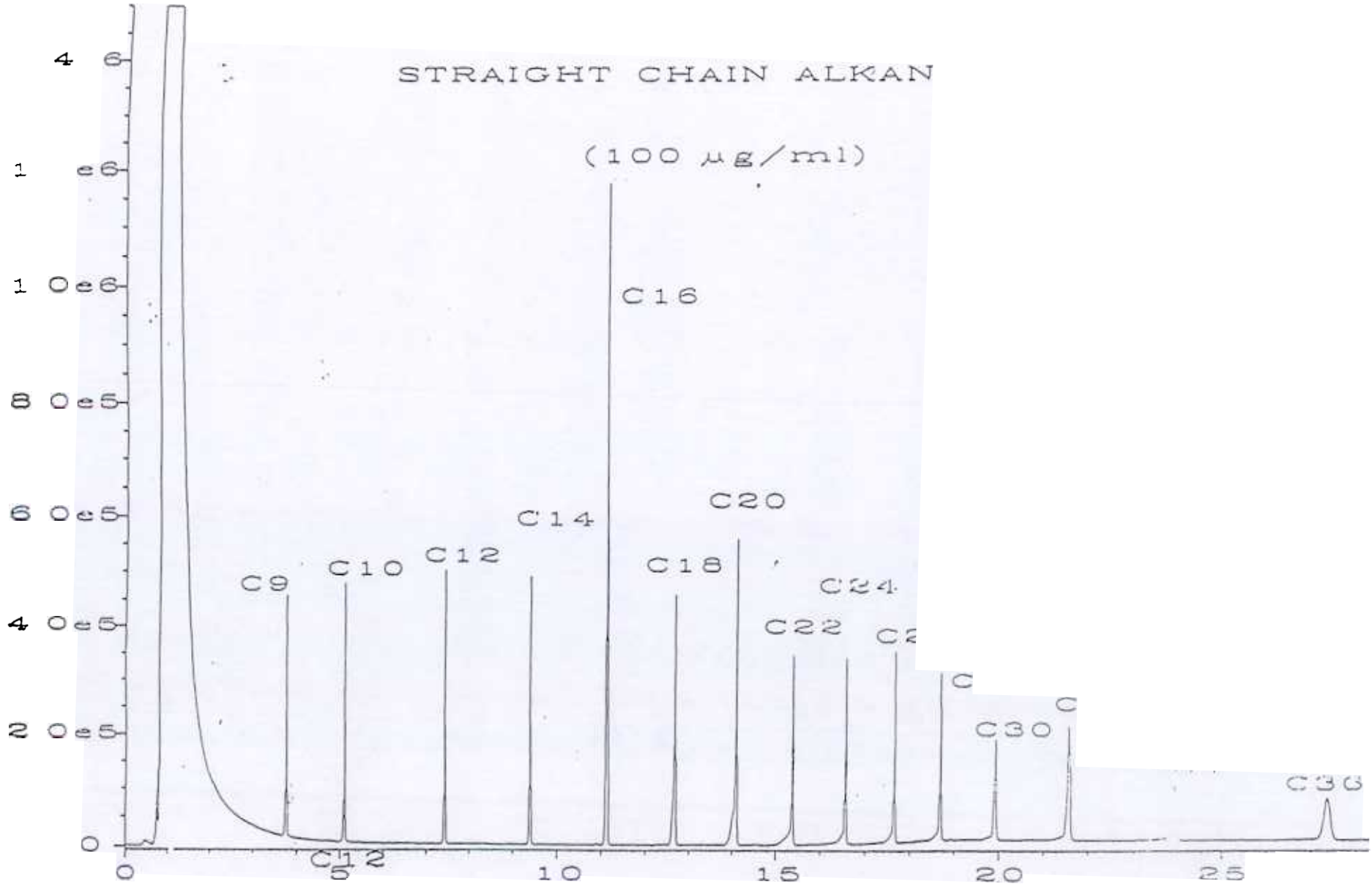
* All areas were multiplied by 10e-3 and with baseline subtraction.

Table – 7.3 Preliminary Instrument Detection Limits for Five Typical Oils

Motor Oil

n	Peak Area (x 10e-3) Total	Calculated Conc. (µg/ml)
1	1282	98.5
2	1304	100.2
3	1317	101
4	1262	97.0
5	1275	98.0
6	1287	99
7	1326	102
8	1345	103
9	1310	100.7
Average	1301	100
SD	27	2.045
Conc. Injected (µg/ml)	100	
	t-0.99 (n = 9)	2.896
	DL (µg/ml)	5.92
MDL (mg/kg-ppm), 10 g Soil with Final Vol.= 100 ml		59.2
MDL (mg/kg-ppm), 10 g Soil with Final Vol.= 1.0 ml		0.592
MDL (mg/L), 1 liter Water with Final Vol.= 100 ml		0.592
MDL (µg/L), 1 liter Water with Final Vol.= 1.0 ml		5.922

* All areas were multiplied by 10e-3 and with baseline subtraction.



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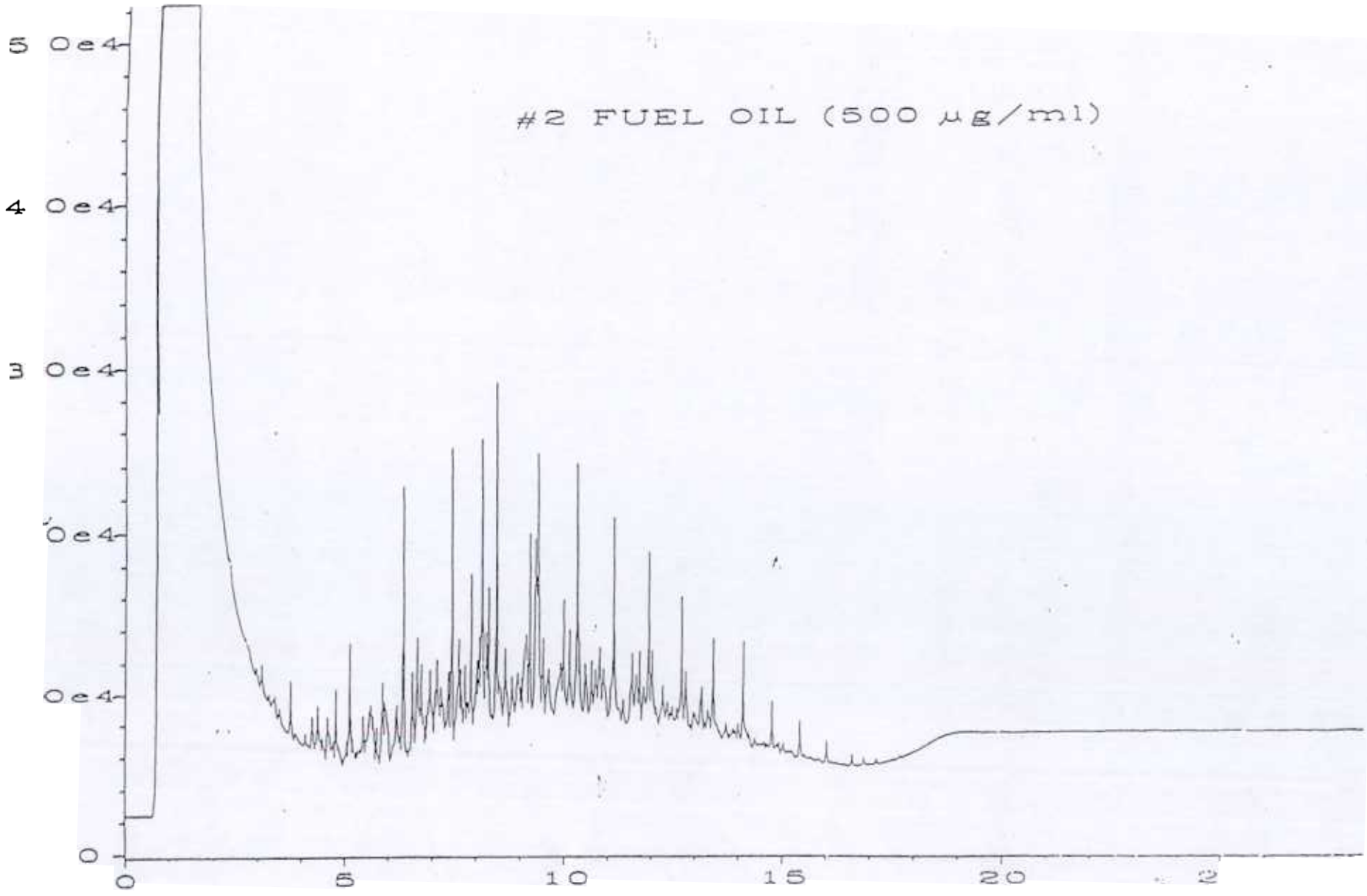
F ,ur Chrom ogram o tra gh Ch: n A 'kan



C PCHEM\2\DATA\040597\TPH0000 4 D

F gure Chromatogram of No fu o

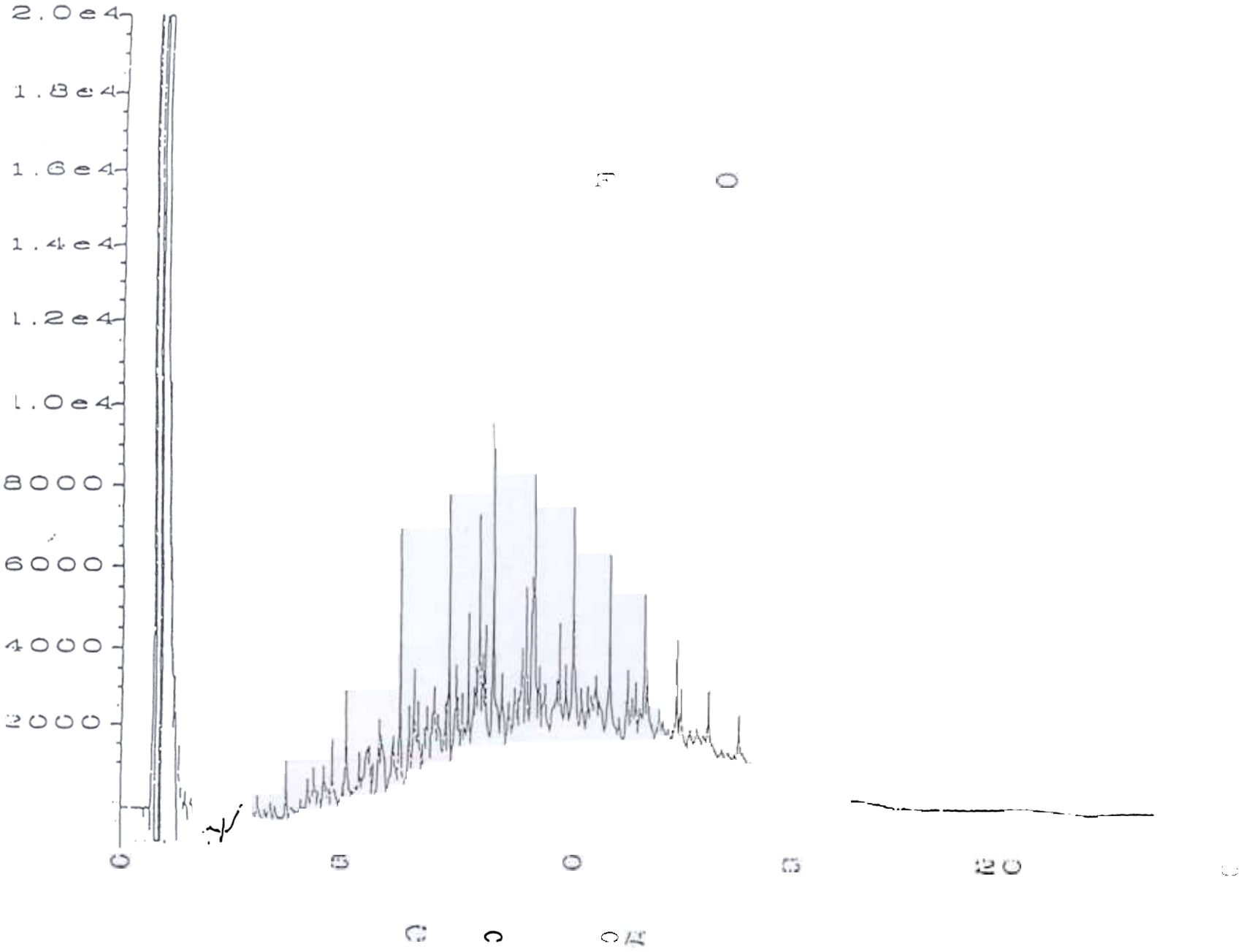


Figure Chromatogram of No fuel oil with baseline subtraction

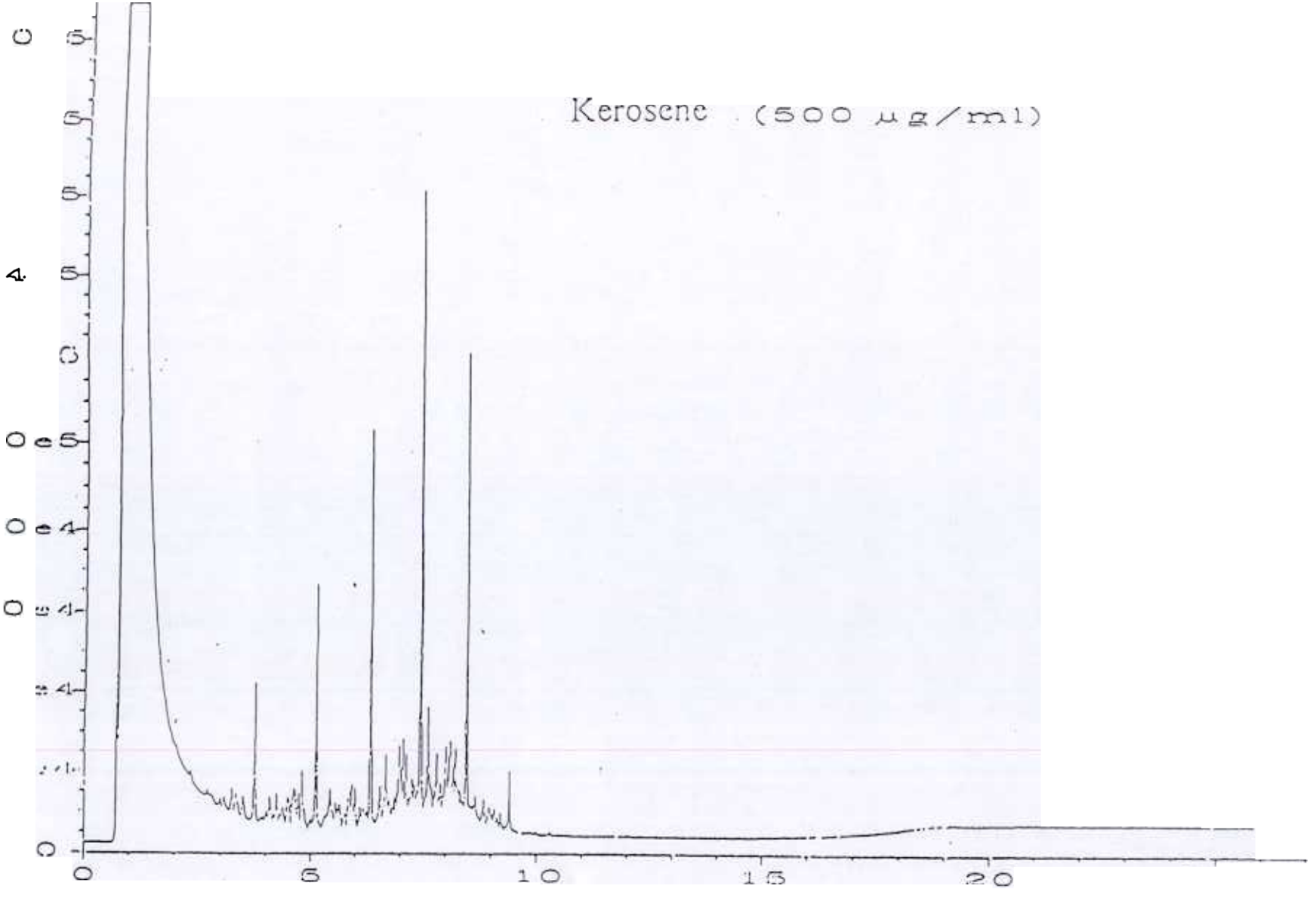
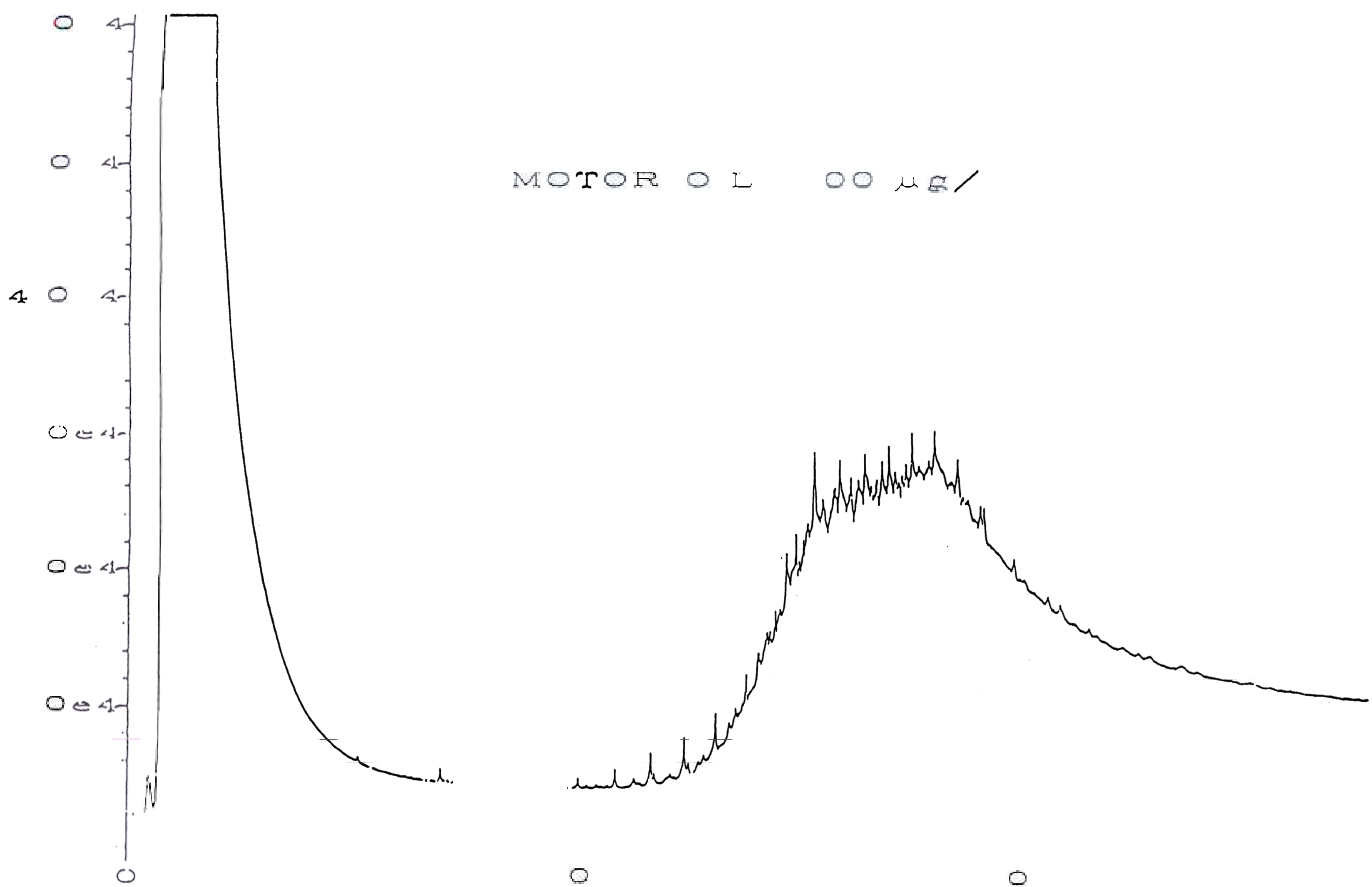


Figure 4 Chromatogram Kerosene

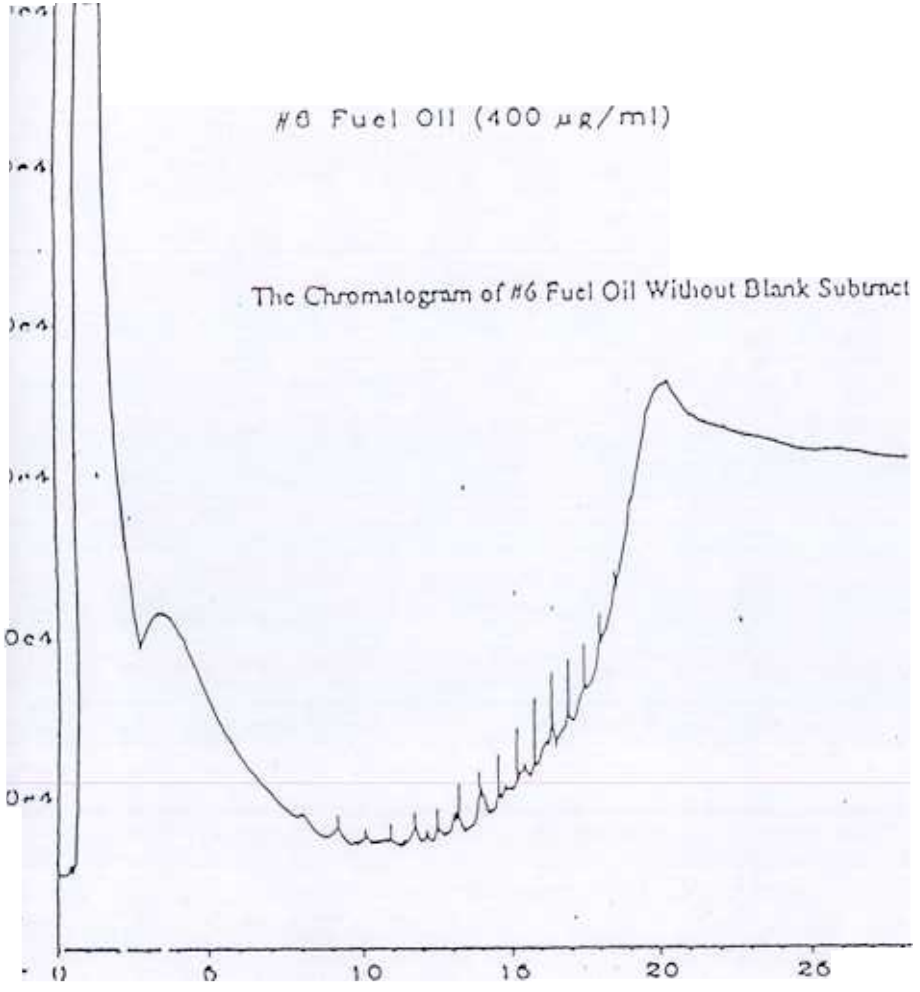
ur C Chom o r m ofNo u o



F u Chrom o mo moto o

Baseline Subtract is Necessary

Before



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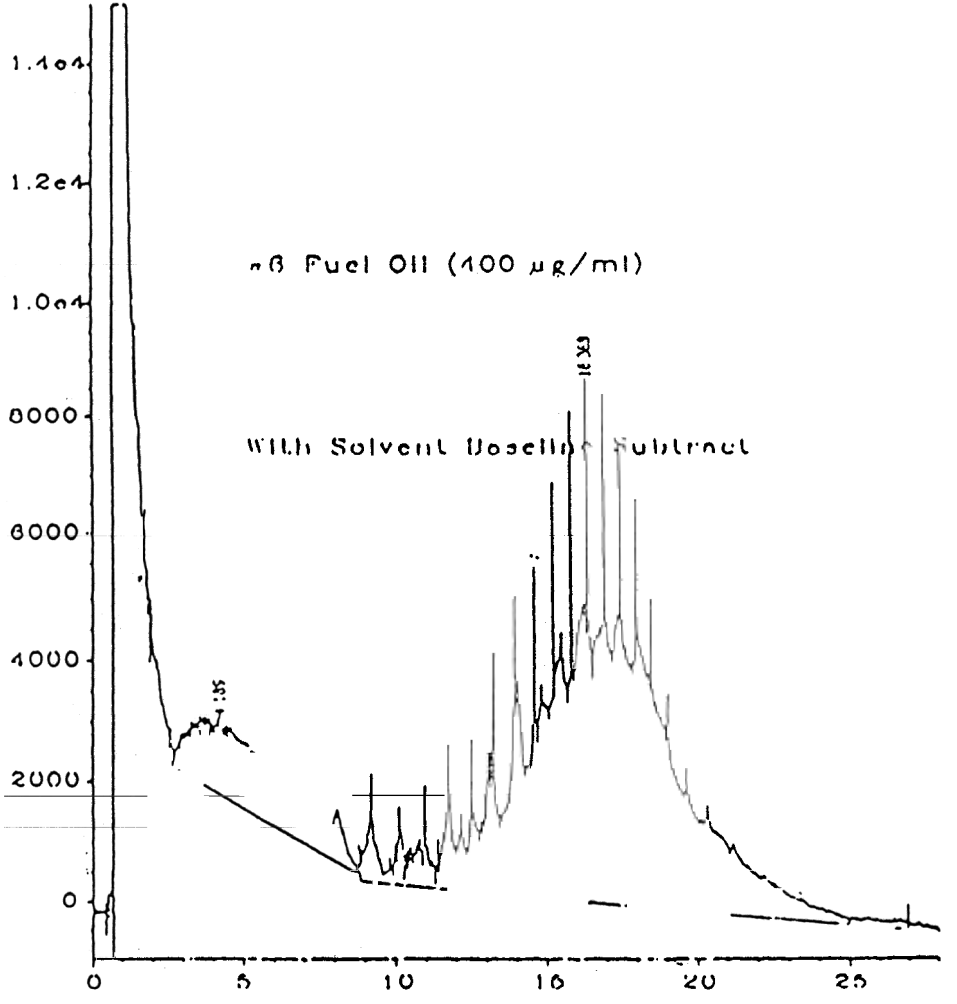
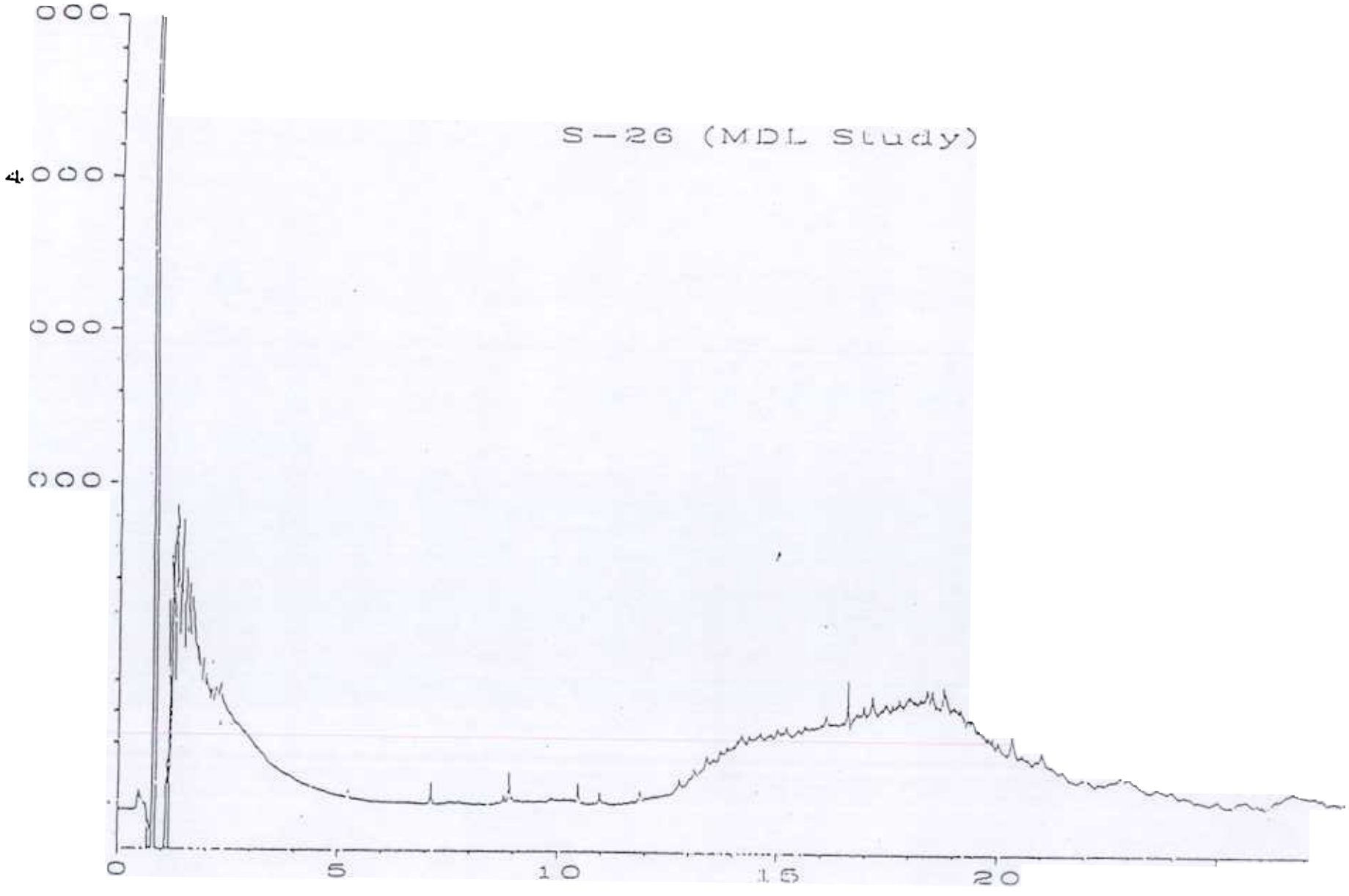
After



The Chromatogram of #6 Fuel Oil With Blank Subtract

Illustration of baseline subtraction



Chr m gr p D

F gu Chromatogram o o amp S 26 u d n the m t od d tect on m : udy

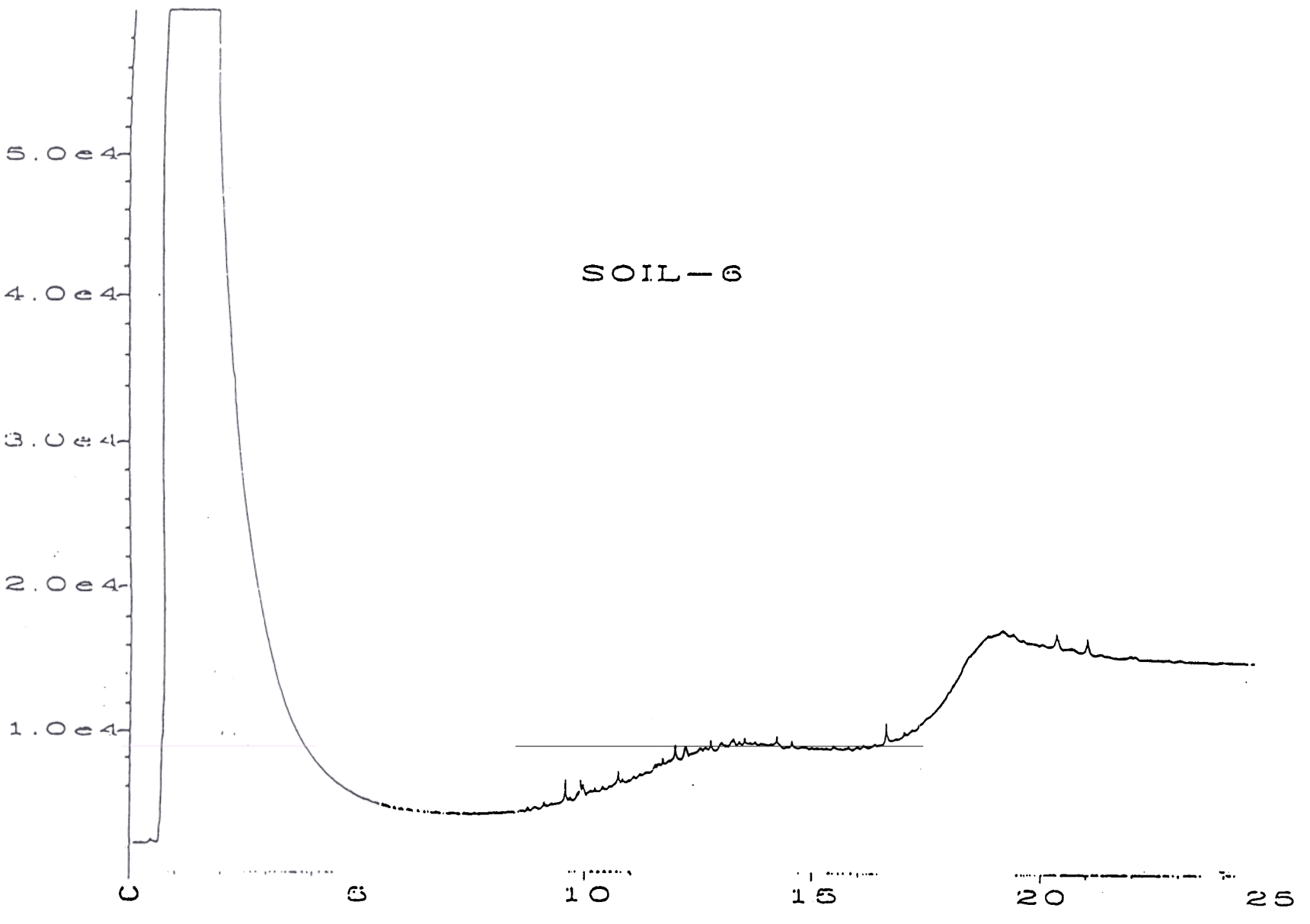


Figure -9 Chromatogram of soil sample (S-6)

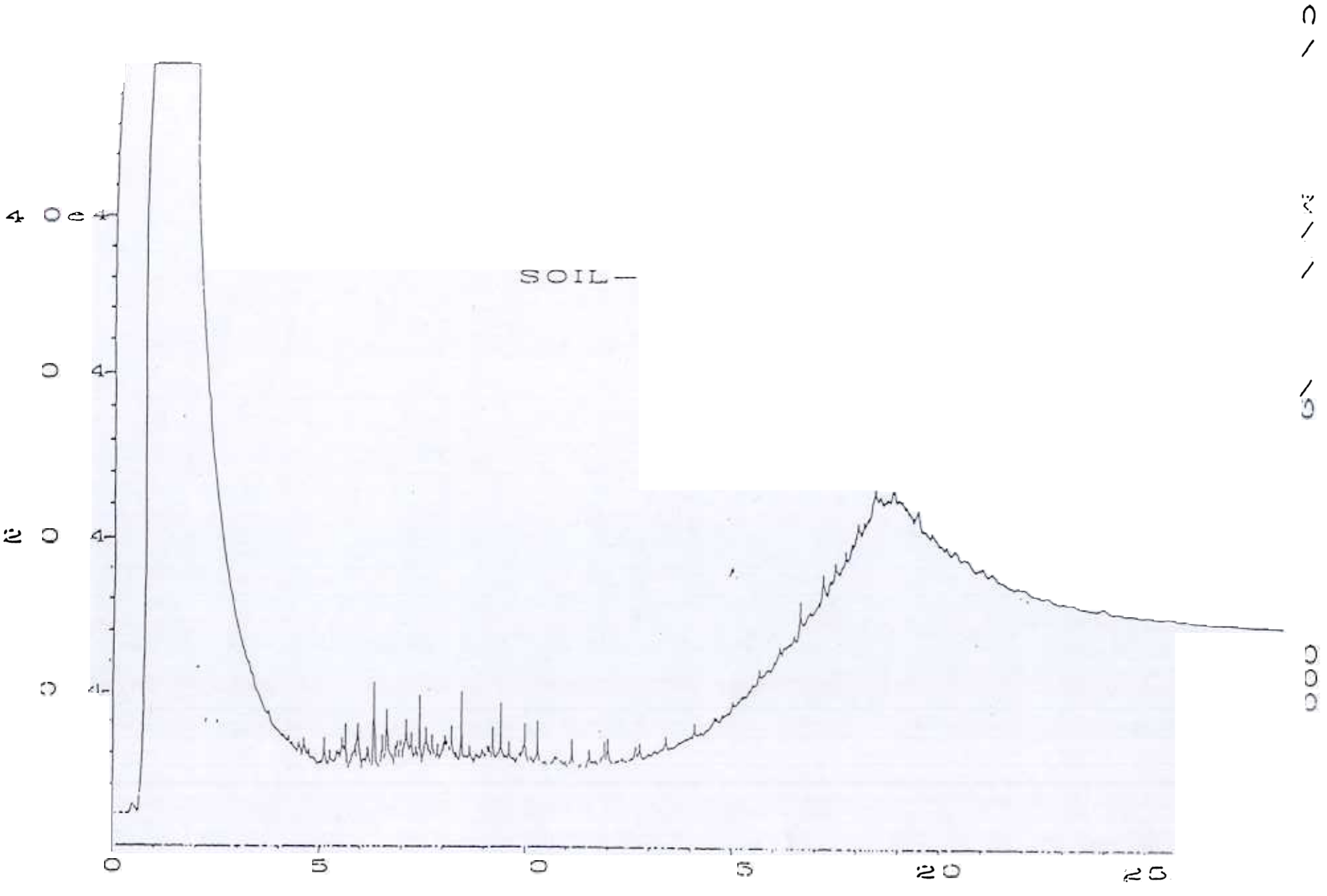


Figure Chromatogram of soil sample (S-23)

HPC E \2\ TAN04 \2\ P-00008

Chromatogram of impe

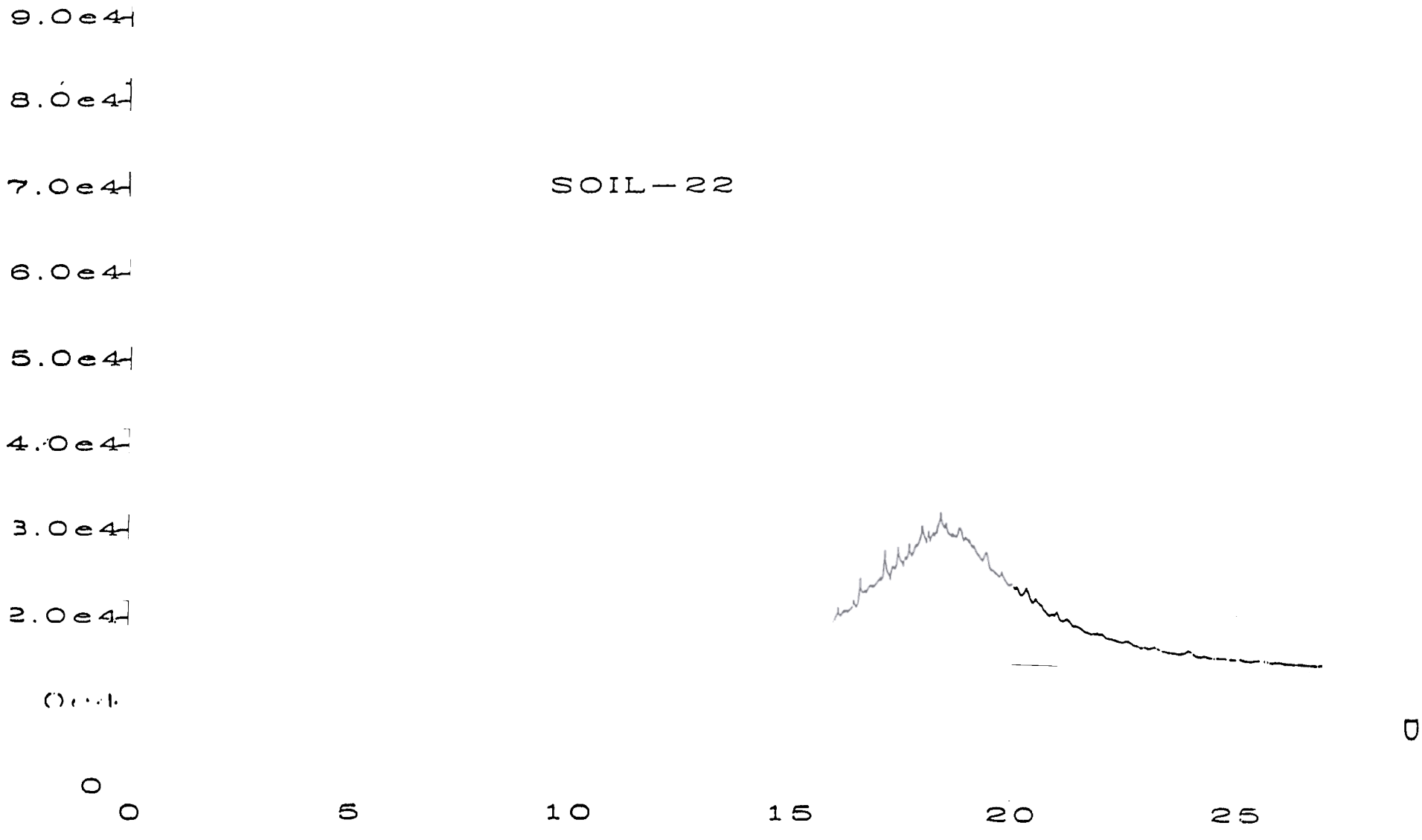


Figure 12 Chromatogram of soil sample (S-22)