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**CHARACTERIZATION AND EVALUATION OF
HYDROCARBON FUELS IN
ENVIRONMENTAL SAMPLES BY GC/MS**

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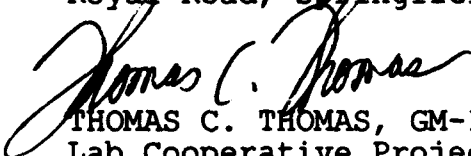
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13. ABSTRACT (Maximum 200 words) The complexity of hydrocarbon fuels and the need for identification of their components in environmental samples has created a need for a more specific analytical method. GC/MS was used to identify fuels and mixtures by establishing an n-alkane (C ₆ to C ₂₄) normalized ratio profile for each fuel. This data uses concentrations of the n-alkanes, C ₆ to C ₂₄ , found to be characteristic of petroleum fuels. The n-alkane normalization calculation gives a recognizable ratio pattern which may be used to discriminate between very similar fuels. This method has been used to identify the source of contamination through analyzing environmental samples.				
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CHARACTERIZATION AND EVALUATION OF HYDROCARBON FUELS IN ENVIRONMENTAL SAMPLES BY GC/MS

INTRODUCTION

The capillary gas chromatography method described by Roberts and Thomas (1) was modified to provide an analytically specific method for characterizing a wide spectrum of fuels and petrochemical solvents. This method can be particularly useful for rapid analysis to identify fuels, petrochemical solvents and various individual compounds present as contaminants in environmental groundwater, soil samples, and sludges from underground storage tanks, waste treatment plants, and various types of surface spills. The comparison of these samples is accomplished through establishing an n-alkane normalized ratio profile for the individual type of fuel, petrochemical solvent, or hydrocarbon. This data uses concentrations of the n-alkanes C_6 to C_{24} found to be characteristic of petrochemical solvents and fuels. This comparative process is accomplished by calibrating the GC/MS with mg/L amounts of the individual alkanes. The profile of the individual fuels is constructed by calculating the ratio of the individual ion peak areas of n-alkanes in the samples to the average ion peak areas of C_{10} through C_{13} n-alkanes in the same sample. The ratios of n-alkanes and their patterns are then compared to the ratios and patterns of reference standard fuels. The aromatic compounds in the fuels can be used as marker compounds in some cases to establish overall qualitative identification. The formula we used to calculate the n-alkanes normalization is shown in Table 1.

EXPERIMENTAL

Fuel and solvent bulk standards used in this study were supplied by U.S. Air Force bases. These base reference standard fuels were used to develop ratios and patterns and to identify the fuels and solvents found in environmental samples.

Reference fuel standards were diluted 1:1000 with Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane). Freon 113 is the solvent used by this laboratory for the total petroleum hydrocarbon extraction procedure, EPA Method 418.1 (2). All environmental samples were extracted using this procedure. To 0.5-mL aliquot of the standard stock solution (C_8 - C_{17}), diluted with Freon 113, was added the internal standard d_8 naphthalene giving a concentration of 50 mg/L for the internal standard and 37.5 mg/L of the standard hydrocarbon components for the daily check standard (Figure 1). A working standard screen (C_8 - C_{17}) was prepared by diluting stock standard solutions to 1 mL in a volumetric flask with Freon 113 to give concentrations of approximately 7.5 and 37.5 mg/L for a standard curve. A second qualitative curve, a qualitative full screen standard solution of

selected aromatic and branched chain alkane marker compounds (C_6 - C_{24}) consisting of 36 components was similarly prepared. The selection of deuterated d_8 -naphthalene as the internal standard was based on the presence of naphthalene in a wide spectrum of fuels. A stock solution of the internal standard was made up at a concentration of 2000 mg/L in Freon 113.

Samples were analyzed using a Hewlett-Packard (HP) Model 5890 gas chromatograph coupled to HP Model 5970 Mass Spectral Detector (MSD). All samples were analyzed by Electron Impact GC/MSD full scan data acquisition. The data from the GC/MSD was transferred to a Hewlett-Packard 1000 RTE/6 data system using the Aquarius software program. See Table 2 for instrument parameters, techniques, column, and conditions for the instruments. The GC/MSD was calibrated daily using perfluorotributylamine (PFTBA). Tuning ratios for the ions were approximately m/z 69(100%), m/z 219(75%), and m/z 502(7.5%). Maintaining uniform tune ratios and abundances gives reproducible results over long periods of time. Each day, a mid-level concentration calibration standard was ran and graphed to verify that the instrument met overall quality assurance criteria.

The response control limits were required to be within 20% of the predicted value. If acceptable values were not obtained, the calibration was repeated using a fresh calibration standard.

RESULTS AND DISCUSSION

A chromatogram of the fuels n-alkane standard mixture (C_8 - C_{17}) for quantitation is presented in Figure 1. The complete n-alkane standard screen (C_6 - C_{24}) including aromatic compounds are eluted in 55 minutes. The chromatograms of military jet fuels (JP₄ and JP₈), diesel fuel, PD-680 solvent, and commercial Jet A fuel are shown in Figures 2-6. The total ion chromatograms of these fuels and solvent demonstrate the elution patterns of the n-alkane components characteristic of each type of hydrocarbon mixture. The addition of D_8 -Naphthalene as an internal standard has contributed to excellent reproducibility. The method provides a tool (normalization) seen in Table 3 that shows how this technique can be used to differentiate between specific hydrocarbon fuels and solvents for hazardous waste disposal, underground waste monitoring, spill sites, and other fuel related environmental contamination problems. The method has been used to trace the source of spills and groundwater contamination. An example of this method's application is shown on a sample received from an Air Force base. It was a quart of water taken from an area on a base lake that exhibited a constant oily sheen. Base officials did not know what was the source and concentration of the sheen and sent our laboratory the sample for hopeful clarification. The sample was extracted with Freon 113 as described earlier. A portion of the extract was injected into the GC/MS system; the resulting ion chromatogram is shown in Figure 7.

Analysis of the ion chromatogram showed peaks and normalization ratios as follows: $C_7=0.6$, $C_8=0.7$, $C_9=0.8$, $C_{10}=1.0$, $C_{11}=1.1$, $C_{12}=1.0$, $C_{13}=0.8$, $C_{14}=0.5$ and $C_{15}=0.2$. Although slight aging of the fuel distorted the ratio of the earlier peaks, a definite match to JP₄ can definitely be seen in Table 3. This conclusion is confirmed by comparison of patterns by the JP₄ standard (Figure 2) to the sample (Figure 7). When the identification as JP₄ fuel was reported back to the base; after a thorough search, they found a nearby fuel line that was leaking JP₄ that migrated through the soil to the lake area. Cleanup and repair began immediately.

CONCLUSION

Capillary column Gas Chromatograph/Mass Spectrometry can be used as the previous published GC/FID method for distinguishing between a variety of hydrocarbon fuels and solvents; however, it has the added dimension of identifying unknown organics that may be present in environmental samples. The n-alkane normalization calculation gives a recognizable ratios pattern which may be used to characterize very similar fuels.

This analysis method has been used to confirm responsibility for fuel spills and dumping and to identify the source of contamination by determining the specific fuel present in environmental samples. Tracing the contamination to single or multiple sources can be determined by the contribution from each type of fuel using the n-alkane normalization ratios and quantitation of the marker compounds, both aromatics and n-alkanes.

JP₄ fuels vary slightly in composition depending on the supplier and the particular blend purchased by each USAF base; however, they can easily be distinguished from other military fuels (JP₈), Jet A (commercial jet fuel), and diesel fuel in a sample. Results are more accurate if a standard of the fuel composition accompanies the samples. Matrix effects from high molecular weight hydrocarbons such as lubricants can interfere with the analysis. A reference standard fuel from the same area or possible suspected source would simplify the identification of contaminated wells or spills.

REFERENCES

1. Roberts, A.J. and T.C. Thomas. 1986. Characterization and Evaluation of JP₄, Jet A and Mixtures of these Fuels in Environmental Water Samples. Environ. Toxicol. Chem., 5:3-11 (1986).
2. U.S. Environmental Protection Agency. 1983. Methods for Chemical Analysis of Water and Wastes, Method 418.1, EPA 600/4-79-020, Cincinnati OH.

Table 1. Calculation of n-alkane normalization ratios from C₆ through C₂₂

$$C(\text{Ave ion peak area}) = \frac{(C_{10} + C_{11} + C_{12} + C_{13})}{4}$$

Individual n-alkane ratio calculation using C₉ as an example

$$R(\text{ratio } C_9) = \frac{(\text{ion peak area of } C_9)}{C}$$

Table 2. HP 5890 GC and HP 5970 MSD GC/MS Instrument Parameters

Ionization Technique: Electron Impact

Scanning Method: Full Scan Spectrum

Sample Introduction Technique: Gas Chromatography

Injection Mode: Splitless-Capillary, Direct

GC Column: HP-5, 0.32mm I.D., 0.11mm WC, 50 M length

GC Injection Port Temp.: 260 degrees Centigrade

Carrier Gas: Helium

Mass Analyzer-Ion Source Temp.: 175 degrees Centigrade

GC Column Oven Temp. Program: 35-290 degrees Centigrade,

14-Minute Solvent Delay at 35 degrees C. Program (35 to 290) at 10 degrees C/min.

Column Head Pressure: 15 PSI

Table 3. Normalization ratios of n-alkanes for fuels and solvents

n-alkanes	JP ₄	Jet A	Diesel Fuel	JP ₈	PD 680 Solvent
C ₆	0.7	-	-	-	-
C ₇	1.1	-	-	-	-
C ₈	1.0	-	-	-	-
C ₉	0.9	0.3	-	0.2	-
C ₁₀	1.1	0.8	0.2	0.8	0.4
C ₁₁	1.1	1.1	1.0	1.1	3.1
C ₁₂	1.0	1.1	1.2	1.1	0.2
C ₁₃	0.9	1.0	1.6	0.9	-
C ₁₄	0.7	0.9	2.2	0.4	-
C ₁₅	0.3	0.6	2.5	-	-
C ₁₆	-	0.2	2.3	-	-
C ₁₇	-	-	1.9	-	-
C ₁₈	-	-	1.4	-	-
C ₁₉	-	-	1.2	-	-
C ₂₀	-	-	0.8	-	-
C ₂₁	-	-	0.5	-	-
C ₂₂	-	-	0.2	-	-

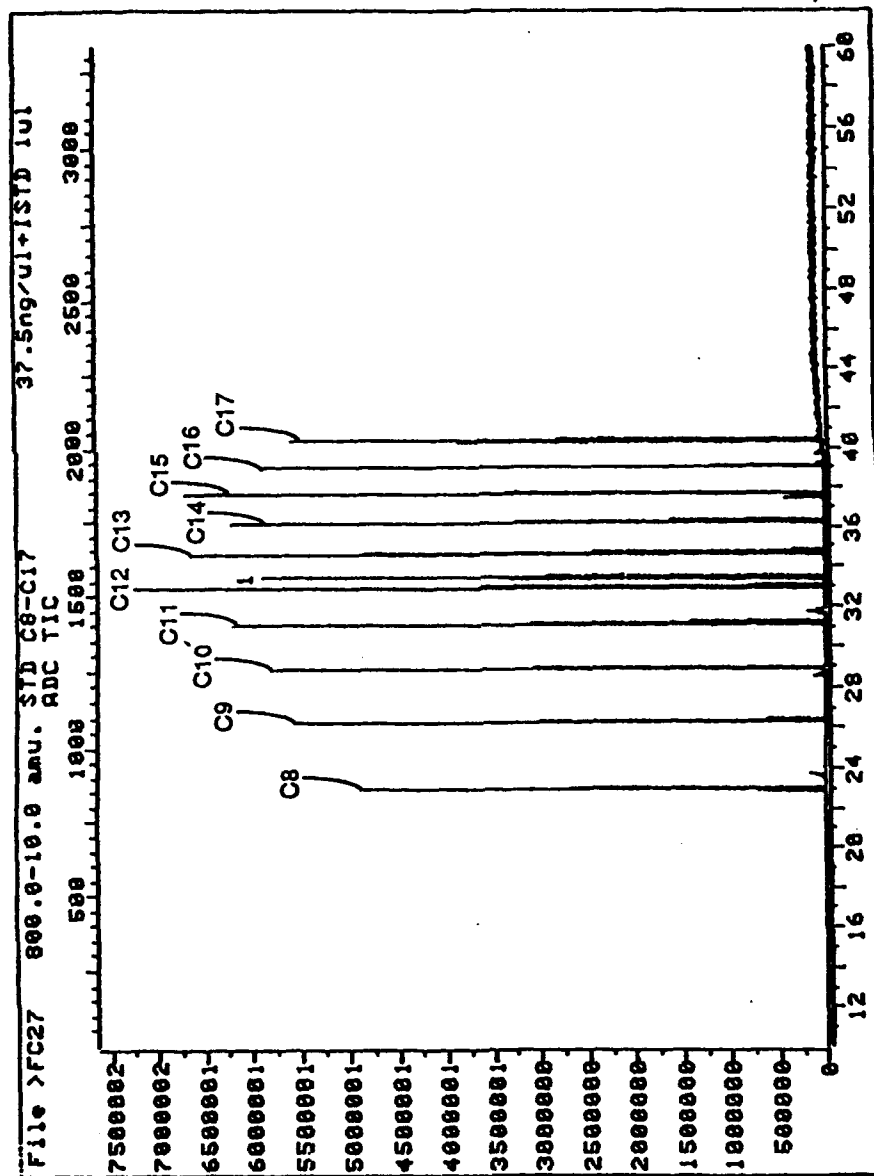


Figure 1. Total ion chromatogram of standard stock solution (C₈-C₁₇).

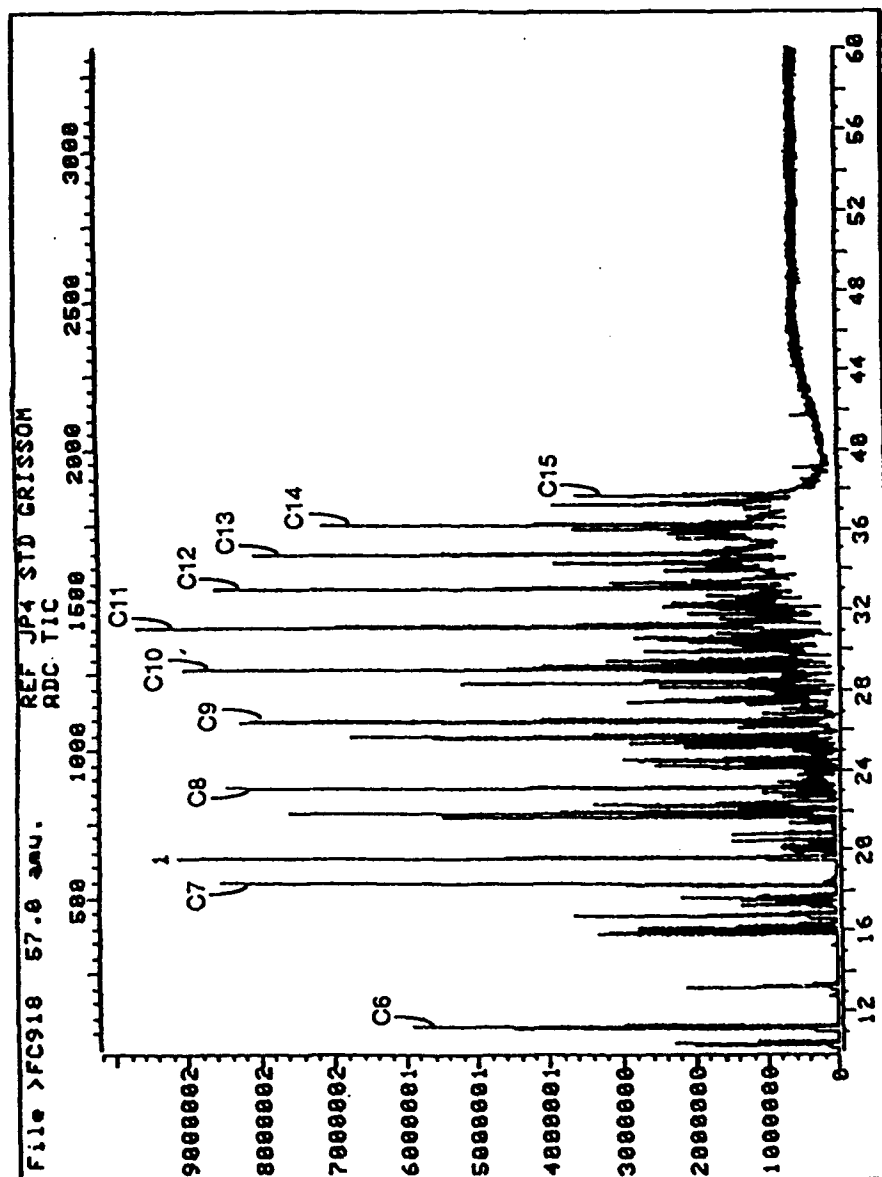


Figure 2. Total ion chromatogram of military jet fuel (JP₄).

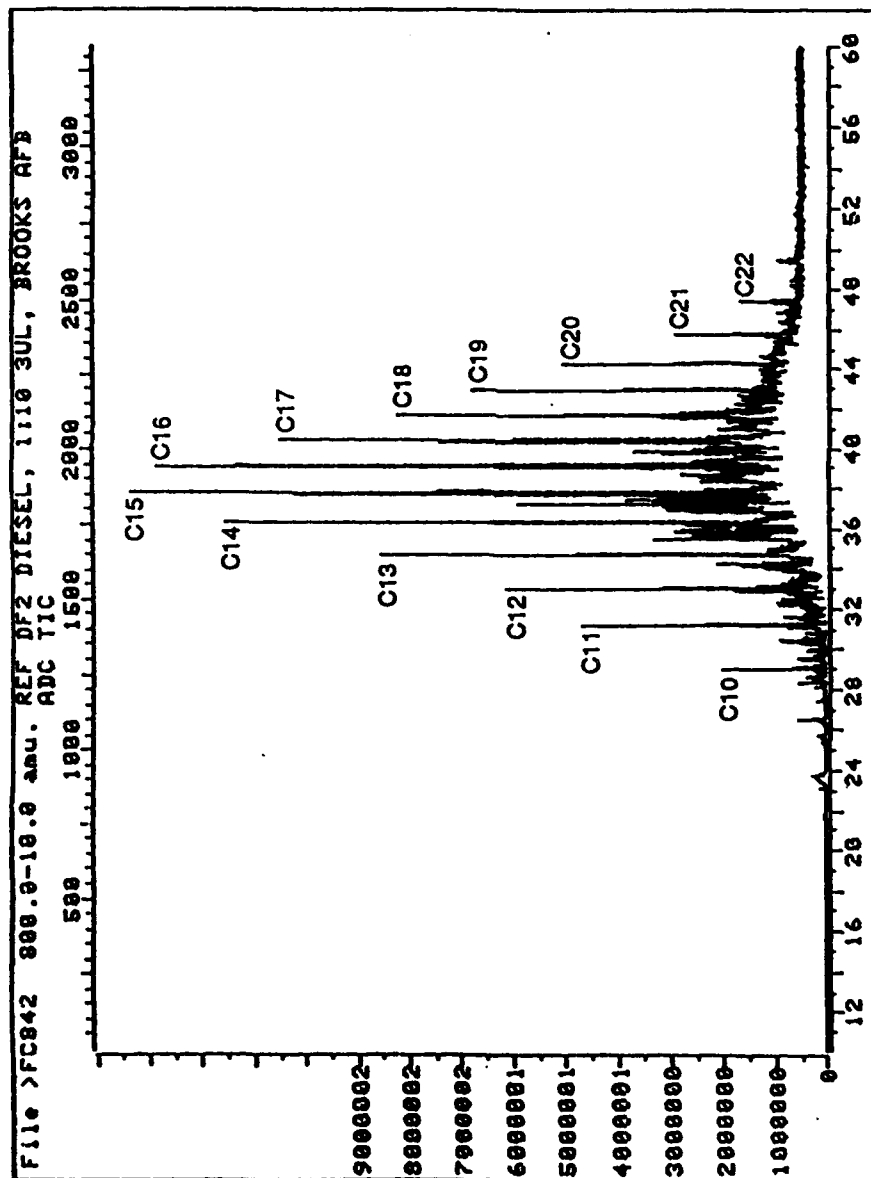


Figure 3. Total ion chromatogram of diesel fuel.

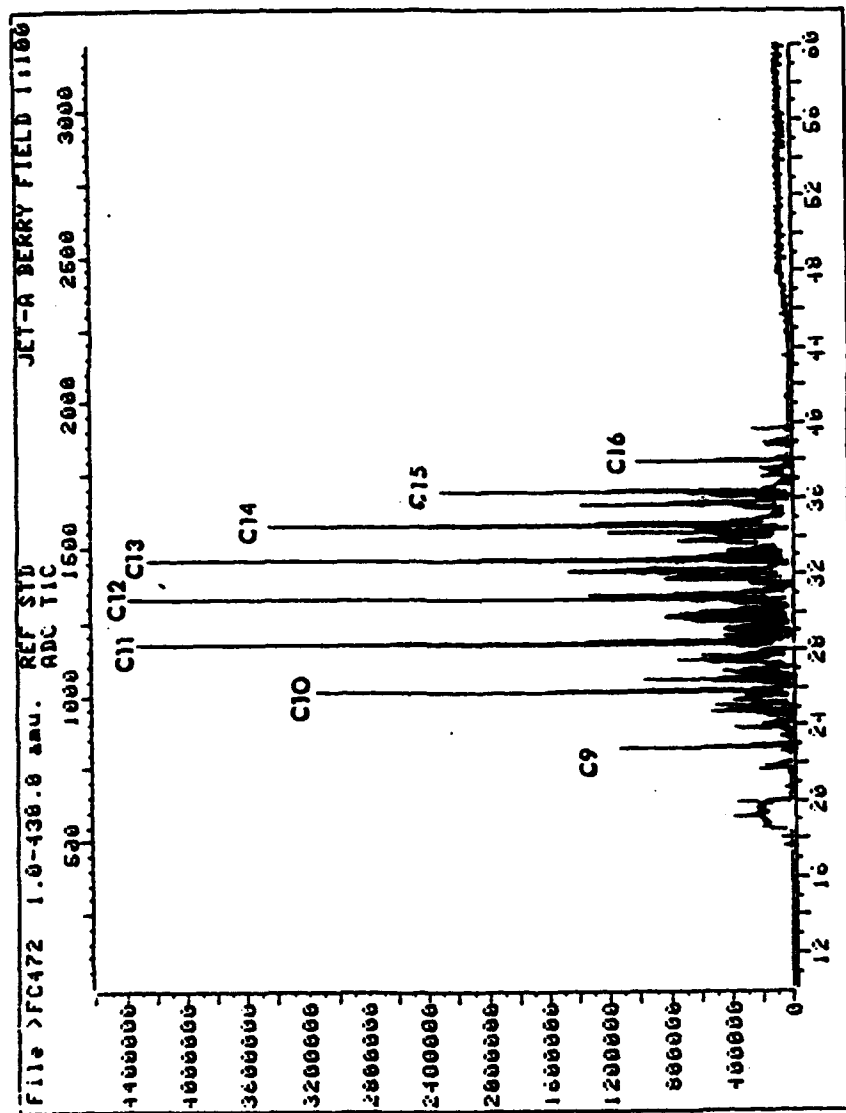


Figure 4. Total ion chromatogram of commercial jet fuel (Jet A).

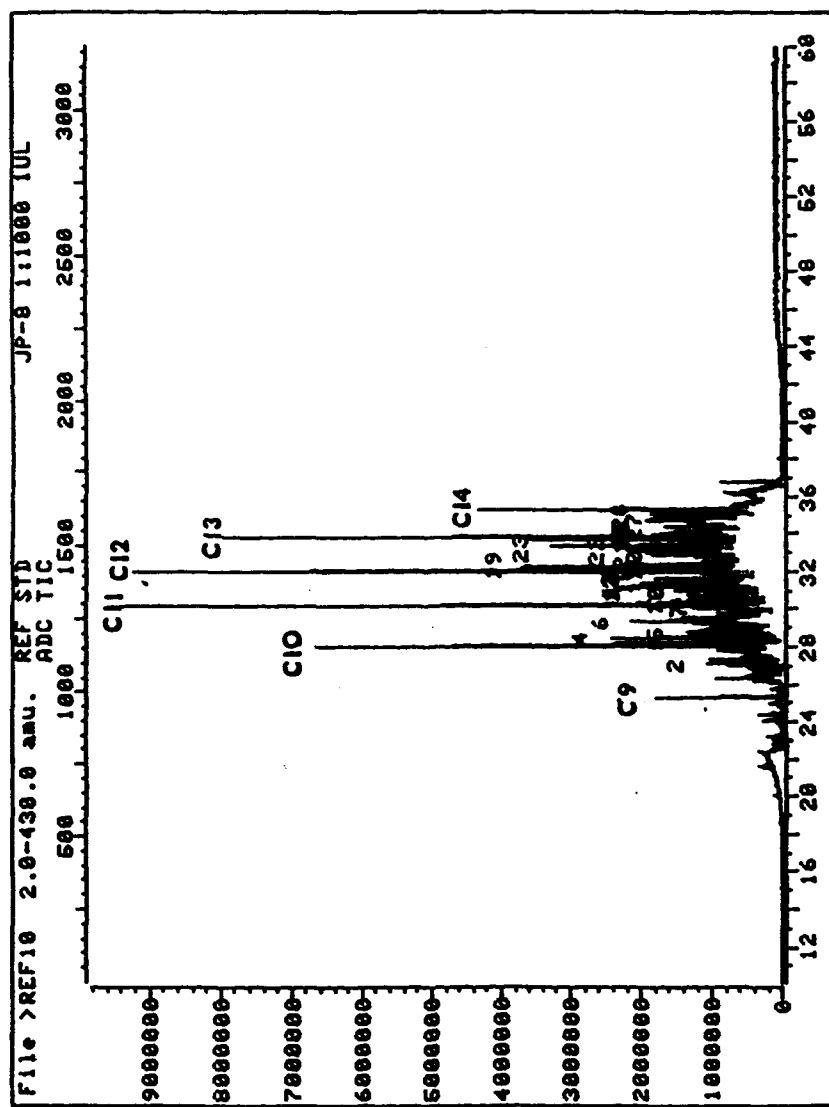


Figure 5. Total ion chromatogram of military jet fuel (JP8).

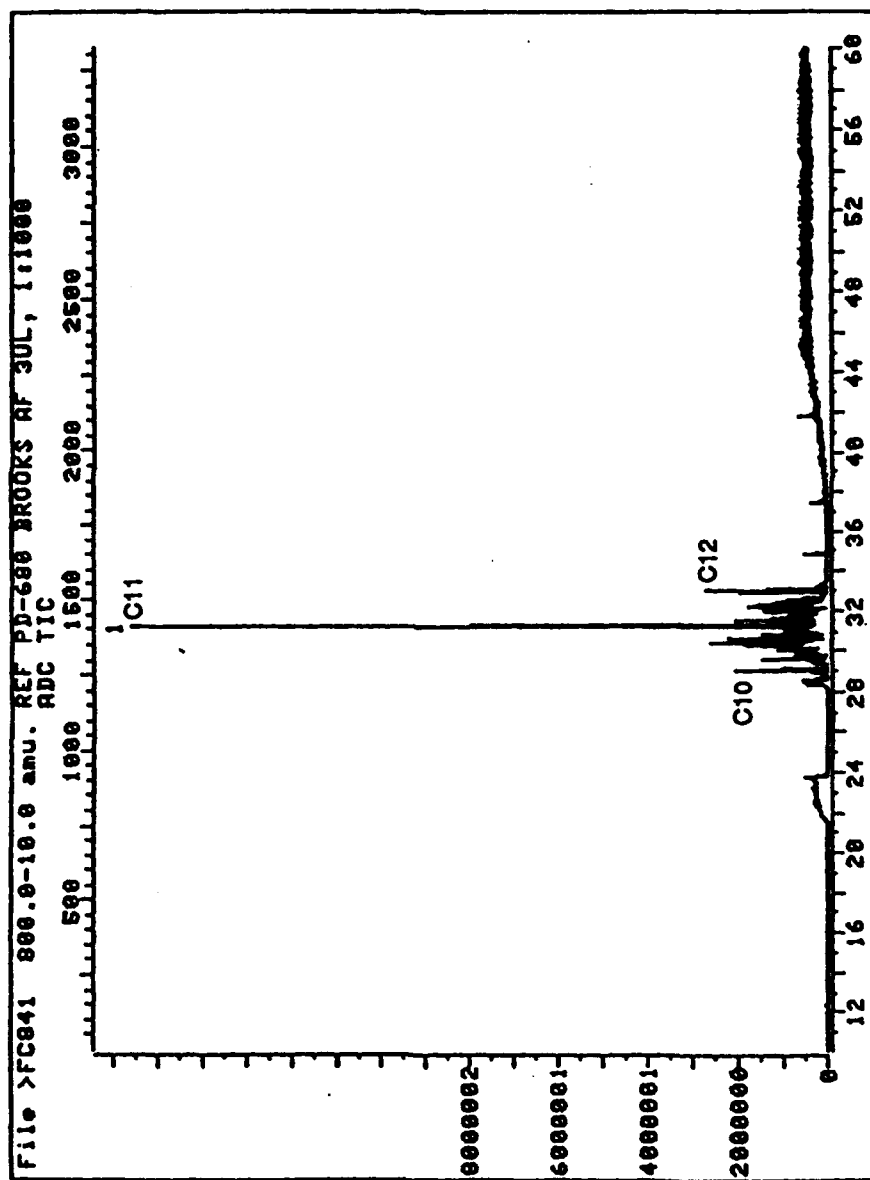


Figure 6. Total ion chromatogram of military supplied solvent (PD₆₈₀).

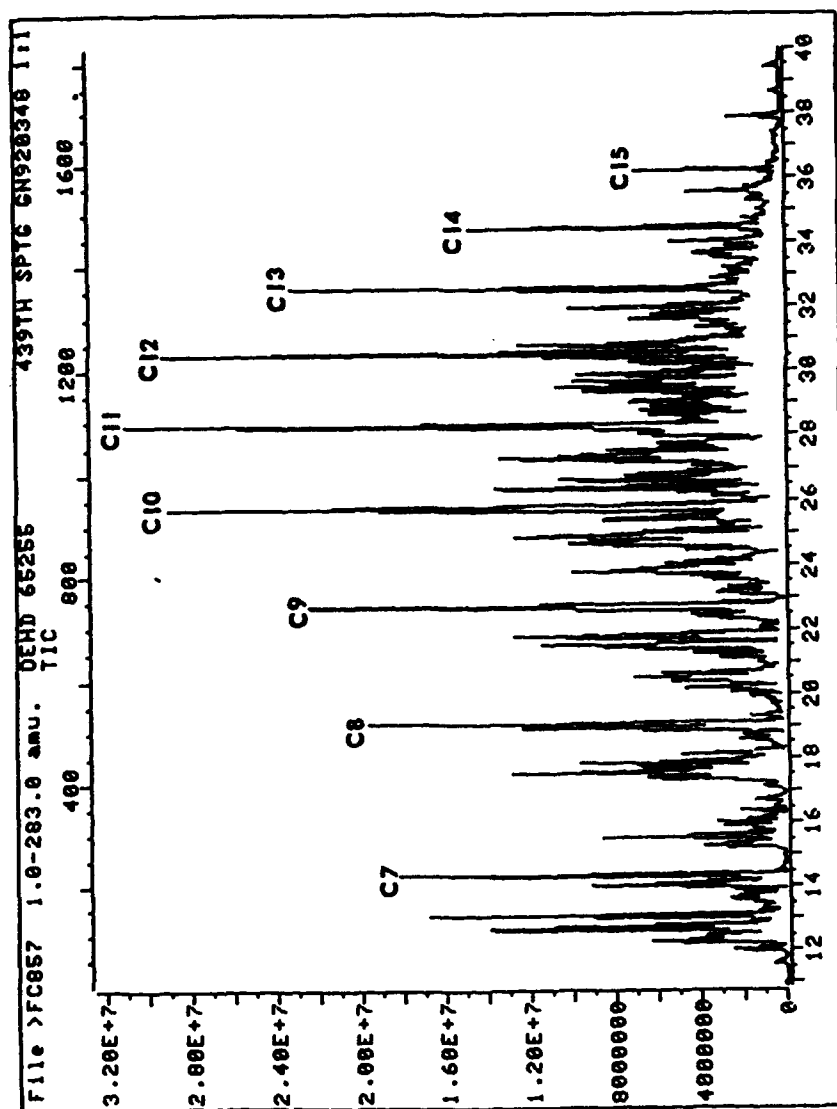


Figure 7. Total ion chromatogram of unknown hydrocarbons contaminating a base lake.