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IDENTIFICATION AND QUANTIFICATION OF HYDROCARBON PRODUCTS IN EF--ETC(U)
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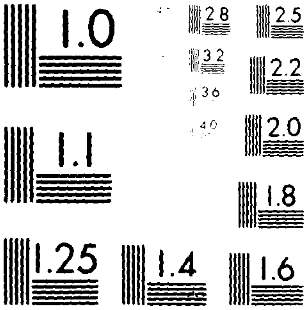

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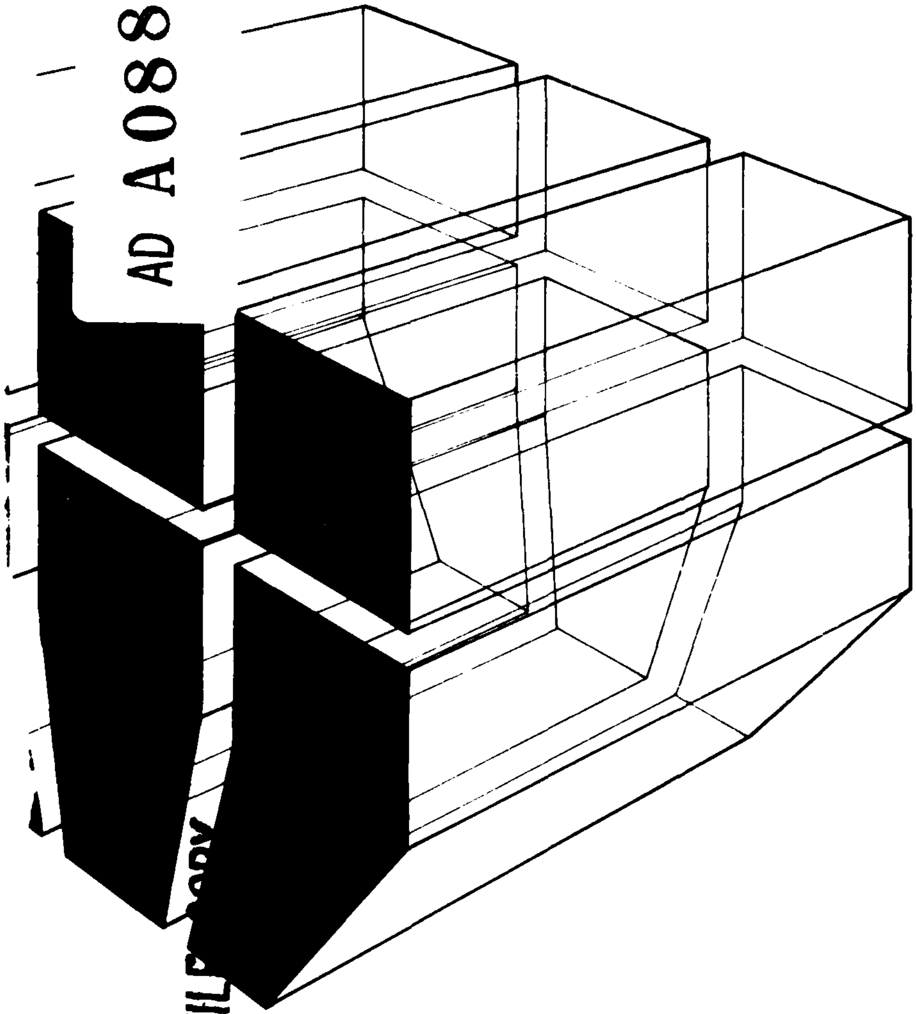
INTERIM REPORT N-91
May 1980
Oil Pollution Control at Military Installations

IDENTIFICATION AND QUANTIFICATION OF HYDROCARBON PRODUCTS IN EFFLUENTS



by
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This report documents interim results of a study to (1) investigate the capability of infrared (IR) spectroscopy for the identification of specific hydrocarbon products in effluents from washracks and other vehicle service operations at Army installations, and (2) make a comparative evaluation of the Environmental Protection Agency's (EPA) gravimetric (STORET 00556) and IR (STORET 00560) methods of quantifying "total hydrocarbons" in wastewater.

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Results have shown that IR spectroscopy can provide a basis for the identification of hydrocarbon products for which reference samples are available. In the initial phase of the work, a scheme of sequential discriminant analysis and pattern recognition was used with reference to a file of military specification (MIL SPEC) hydrocarbon products used in servicing wheel- and track-type Army vehicles. The complexity of IR data reduction was shown to increase rapidly with the number of hydrocarbon products present in a given sample -- a result of a similarity in the hydrocarbon components' molecular structure. The use of gas-liquid chromatography (GLC) in conjunction with IR spectroscopy provided additional discrimination and simplified data reduction.

A comparative investigation of the gravimetric vs IR methods for the quantification of "total hydrocarbons" in wastewater showed that the IR method was capable of higher precision than the gravimetric method at hydrocarbon concentrations less than 10 mg/ℓ, and could provide information on chemical composition and consequently the origin of the hydrocarbon product. However, quantification of "total hydrocarbons" by the infrared method required greater skills and technical background of the analyst than the gravimetric method.

FOREWORD

This report was prepared for the Directorate of Military Programs, Office of the Chief of Engineers (OCE), under Project 4A762720A896, "Environmental Quality for Construction and Operation of Military Facilities"; Task Area 02, "Pollution Abatement Systems"; Work Unit 009, "Oil Pollution Control at Military Installations." The applicable QCR is 3.01.00A. The OCE Technical Monitor is Mr. W. Medding, DAEN-MPO-U.

The report was prepared by the Environmental Division (EN) of the U.S. Army Construction Engineering Research Laboratory (CERL). Dr. E. Novak is Acting Chief of EN.

COL Louis J. Circeo is Commander and Director of CERL, and Dr. L. R. Shaffer is Technical Director.

A

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IDENTIFICATION AND QUANTIFICATION OF HYDROCARBON PRODUCTS IN EFFLUENTS

1 INTRODUCTION

Background

Operations essential to the maintenance, servicing, and washing of military wheel- and track-type vehicles generate large volumes of wastewater which contain variable concentrations of hydrocarbon products. Federal regulations require that such hydrocarbon concentrations be monitored when they are contained in effluents discharged into waterways;[1]* military installations could be liable for restoration costs if environmental pollution is caused by military-generated outfalls which exceed established hydrocarbon concentration limits.[2]

Methods for the quantification of "total hydrocarbons" have been developed and approved by the Environmental Protection Agency (EPA); however, these methods cannot be used to identify specific hydrocarbon products.[3] Thus, it is difficult to track a given hydrocarbon pollutant to its source. Therefore, the U.S. Army Construction Engineering Research Laboratory (CERL) is attempting to develop a reliable method of identifying specific hydrocarbon products in washrack effluent.

Objective

The overall objective of this study is to (1) develop methods that can be used to identify specific hydrocarbon products in wastewater from vehicular service and washrack areas at Army installations; and (2) evaluate the effectiveness of infrared (IR) spectroscopy vs gravimetric procedures for quantifying "total hydrocarbons" in wastewater.

The objective of this report is to document initial investigations into (1) and (2) above.

Approach

This phase of the study included (1) an extensive literature search, (2) IR spectroscopy and gas-liquid chromatography (GLC) of reference materials and an actual field sample from an Army installation, (3) redesign and fabrication of experimental equipment, and (4) revisions to testing.

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* Superscript numbers refer to reference list beginning on page 52.

The hydrocarbon products to be included for identification in this study were limited to those products used to service and maintain military vehicles -- e.g., lubricating oils and greases, hydraulic fluids, coolants, and solvents. Also included for the purpose of identifying contributing hydrocarbon pollutant sources other than vehicular service areas were plant/animal-derived hydrocarbon types that are present in wastewaters from mess halls or other domestic activity areas.

Scope

The ecological scope of this study is limited to effluent streams or accumulations which potentially could find paths through surface and ground water into aquifers. The study does not include atmospheric components.

Mode of Technology Transfer

Research findings on the identification and quantification of hydrocarbon products in wastewater will be compiled and published as a Technical Bulletin. This research supports on-going work on the development of source control and treatment systems for wastewater discharges from Army tactical equipment maintenance operations. Facility design criteria developed and results of field evaluations will be published both as a laboratory technical report and as an Engineer Technical Letter. True technology transfer will not occur until the submitted guidance is incorporated into Design Guide DG 1110-3-80, *TOE Vehicle Maintenance Complexes*.

2 APPROACH

The value of IR spectroscopy for characterizing organic species with regard to molecular composition and structure is well known. However, the task of translating spectral information on molecular structure so proprietary hydrocarbon products in a mixture of such hydrocarbon products can be identified becomes increasingly complex as the number of constituents in the mixture increases. To limit the possible combinations of analyte variables to reasonable numbers, CERL's analytical approach was designed to be specific for and limited to the identification of hydrocarbon products used at Army vehicular services areas (Table 1).

Extensive research and development efforts by other agencies and independent groups have been directed toward methods of analytically characterizing petroleum products. A number of techniques have been used, including infrared spectroscopy,[3-16] absorption and fluorescence spectrophotometry,[17-22] GLC,[16,23-41] and trace-elemental analysis.[5,16,42,43] Reviews of recent applications of these methods are given by Bentz; Brown, et al.; Kawahara; Adlard; and Gruenfeld.[7,8,32,44,45]

Table 1

Hydrocarbon Products To Be Identified in Washrack Effluents

Description	Specific Gravity (25°/25°)
10W Oil	0.880
30W Oil	0.904
90W Oil	0.899
GAA Grease	--
Antifreeze	1.125
Brake Fluid	1.0149
Hydraulic Fluid	--
Solvent Type II	0.800
Kerosene	0.808

However, the general focus of these studies was identification of a crude oil or petroleum derivative as the single component in an accidental or clandestine marine spill. Former work in this area has not addressed itself to identifying multicomponent mixtures of hydrocarbon products.

Three methods of IR data reduction were evaluated for use in this study:

1. The multivariate statistical approach effectively used by Mattson, et al., to fingerprint a given crude oil specimen to determine its source.[50] However, with equipment initially available at CERL, this method was not readily adaptable to mixtures of hydrocarbon products in which the relative concentrations of the constituents were variable.

2. Linear discriminant function analysis used by Kawahara and Yang to discriminate between given specimens of a single petroleum product to identify the geographical origin of the material.[51] This method was also found not to be directly applicable to mixtures of proprietary hydrocarbon products.

3. Work by Vogel in identifying and quantifying trace constituents in a complex matrix by means of a limited number of appropriately chosen spectral band combinations unique to each given constituent.[52] This method seemed adaptable to the CERL study, and seemed likely to provide sufficient information to allow discrimination among the hydrocarbons listed in Table 1.

To test how this approach might work in practice, an "evaluationary" experimentation procedure was used. First, a data file of IR reference spectra from samples of nine military specification (MIL SPEC) materials obtained from the Logistics Center, Fort Lewis, WA (Table 1) and reference spectra from an animal- and a vegetable-derived oil such as those used in food preparation were recorded under controlled conditions. Table 2 summarizes a peak-by-peak log of these reference spectra. This log was searched for absorption bands at wavenumbers unique to each given hydrocarbon material. As was expected, the similarity in molecular structure of a majority of the products was reflected in both the universal occurrence of the CH_2 (2930/cm) band used for quantifying "total hydrocarbons," and the similarity of the majority of the other principal bands. Consequently, minor peaks were required to provide the necessary spectral information for differentiating the hydrocarbon products.

A major portion of the initial experimental work focused on optimizing the operating parameters of the available IR spectrophotometer. Such optimum parameters were essential to insure that the absorption spectra of the reference materials would be accurately recorded.

Spectral data from an unknown sample were correlated with that of standard reference materials, following a scheme of sequential

Table 2

Characteristic Absorption Peaks of Hydrocarbon Products Used in Servicing Military Vehicles or Present in Effluents at Military Installations (Operating Parameters Are As Listed In Table 3)

	MIL SPEC Product										
Wavenumber (cm-1)	10W Oil	30W Oil	90W Oil	Grease	Brake Fluid	Hydraulic Fluid	Anti-freeze	Solvent Type II	Kerosene	Animal Oil	Vegetable Oil
3410				M	VS		VS				
3220				M			VS				
3000										W	W
2920	VS	VS	VS	VS	VS	VS	VS	VS	VS	S	S
2850	VS	VS	VS	VS	VS	VS		VS	VS	S	M
2720	W	W	W	W	W	W		W	W		
1950					W	--	W				
1745						--				S	S
1700	W	W	W	W	--						
1650							M				
1604	W	W	W						W		
1575				S							
1460	S	S	S	S	S	S		S	S	M	M
1375	S	S	S	S	S	S		S	S		
1306	W	W	W								
1250					W	W-					
1230						W+					
1165	W	W	--					W	W	M	M
1140						M					
1027				W			S				
1090					VS						
960			W			W	M				
890			W								
810	W	W	W	M					W		
785			M			M					
723		M	M	M				M	W		
520					S						

Key to Relative Intensity of Absorption Peaks:

VS	transmittance less than 10%
S	transmittance between 10 and 50%
M	transmittance between 50 and 75%
W	transmittance greater than 75%

discriminant analysis and visual pattern recognition. Operations consisted of several stages of class characterization with reference to major peaks (group frequencies), followed by correlation of minor peaks by pattern recognition of intensity ratios in the unknown samples to the reference materials. By reducing the number of possible candidates in Table 1 through preliminary characterization, the probability of identifying or matching multiple components in the unknown sample with the known reference materials was enhanced. This multistage discriminant analysis approach seemed to lend itself to data reduction through either an appropriate computer program or a simple keysort card technique.

3 EXPERIMENTAL PROCEDURES

The Beckman Model IR-20 Infrared Spectrophotometer, used during the initial phase of this study, is an automatic-recording, filter-grating, double-beam instrument. Spectral information is presented as an analog plot of percent transmission vs wavenumber in the spectral range between 4000 to 240/cm on a formatted strip chart. Sample and reference cells used for hydrocarbon characterization were of the sealed demountable type, with Luer fittings and potassium bromide (KBr) windows spaced at a 0.05-mm path length.

Since most of the spectral information for hydrocarbon characterization would be obtained from minor peaks of greater than 75 percent transmission (while quantification of hydrocarbons would involve transmission measurement of peak and baseline values between 15 and 90 percent transmission), instrumental variables of the IR spectrophotometer needed to be critically balanced to record both major and minor peaks with minimum distortion and with high photometric accuracy and precision. To obtain this required performance, the four major instrumental variables (slit program, gain, response time, and scan rate) required systematic optimization. The interrelationship of these four variables on instrumental performance is shown in Figure 1. Optimization of these four variables involved a suitable balance between resolution, noise level, photometric accuracy, and time-related efficiency. Since an accurately represented spectrum is needed for intensity-ratio measurements (to identify hydrocarbons) and for peak height measurements (to quantify hydrocarbon concentrations), systematic efforts to establish instrumental parameters to maximize the accuracy of the recorded spectra were essential.

The procedure for optimizing the values of the instrumental parameters was an experimental one. Initial, realistically chosen values were successively refined to obtain the following performance criteria:

1. Spectral resolution of 4 to 7 wavenumbers/cm
2. Photometric distortion of 2 percent relative
3. Peak-to-peak maximum noise level of 0.5 percent transmission.

These experimentally established operating parameters, summarized in Table 3, were used as the basis for all succeeding spectral recording.

With the instrumental settings so established, absorption spectra were recorded for the nine MIL SPEC materials listed in Table 1; spectra of samples of vegetable-derived oil (safflower oil) and animal oil (lard) were also recorded. These absorption spectra are shown in Figures 2 through 10.

(1) Spectral Resolution $\propto \frac{E}{wNs}$

(2) Noise $\propto \frac{1}{w^2 r^{1/2}}$

(3) Servo Energy $\propto w^2 g$

where E is servo loop energy

w is monochromator slit width

N is noise

s is wavenumber scan rate

r is response time

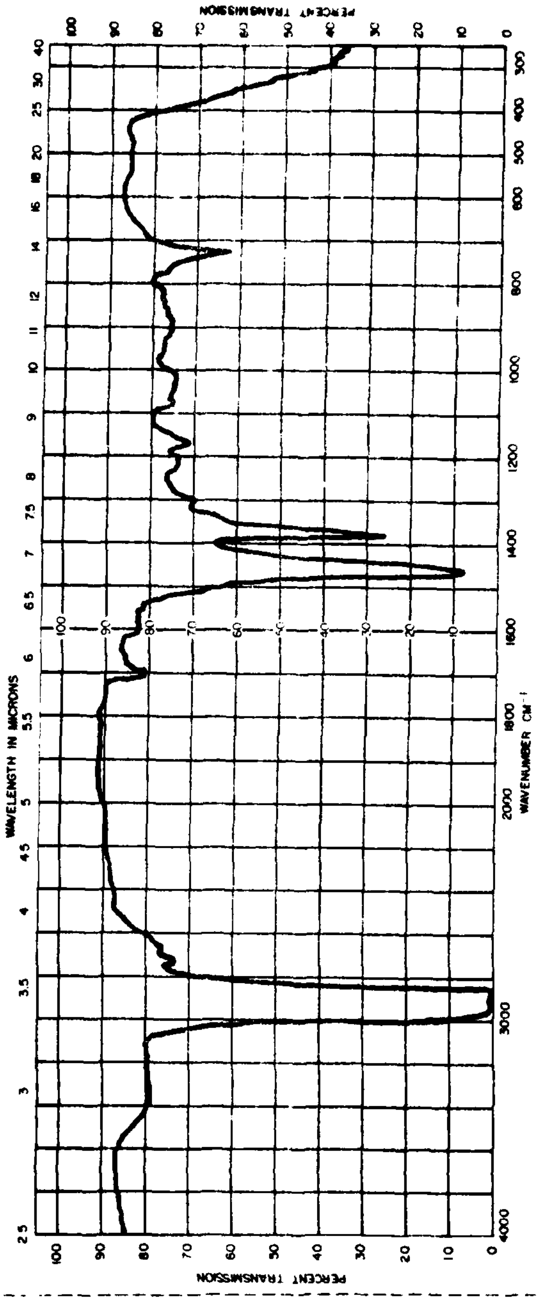
g is gain setting

Figure 1. Relationship between performance and instrumental variables in IR spectrophotometry.

Table 3

Optimized Operating Parameters for Beckman IR-20 Infrared Spectrophotometer

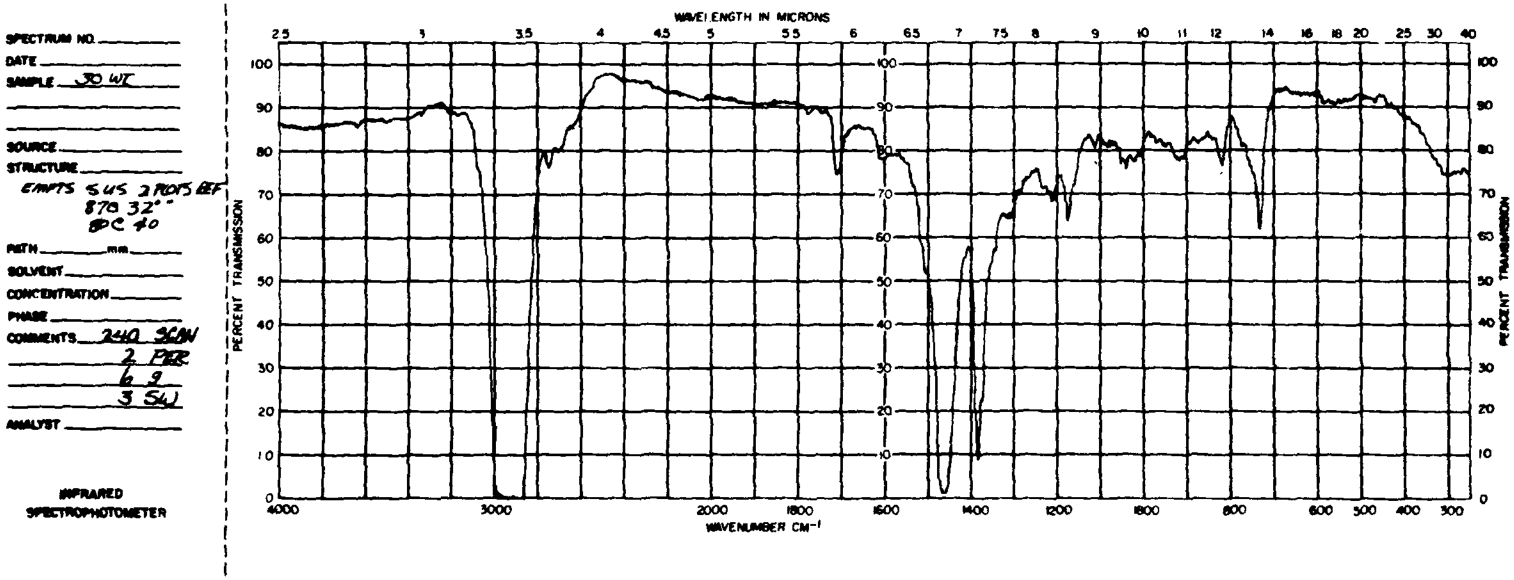
Mode:	Double beam
Spectral Range:	4000 to 250 cm^{-1}
Absorption Cells:	KBr plates spaced at 0.05 mm
Slit Program:	1
Gain:	6
Period:	1-second time constant
Scan Time:	240 minutes (17.2 cm^{-1}/min)



SPECTRUM NO. 1
DATE
SAMPLE 10W Oil
9150-00-191-2772
SOURCE
STRUCTURE
PATH 0.1 mm KBr
SOLVENT
CONCENTRATION
PHASE
COMMENTS
ANALYST

INFRARED SPECTROPHOTOMETER

Figure 2. IR spectrogram of 10W oil.



SPECTRUM NO.
DATE
SAMPLE 30 WT
SOURCE
STRUCTURE
EMPTS SUS 2 ROTS BEF
870 32°"
BC 40
PATH mm
SOLVENT
CONCENTRATION
PHASE
COMMENTS 240 SCAN
2 PER
6 9
3 SW
ANALYST

INFRARED
SPECTROPHOTOMETER

Figure 3. IR spectrogram of 30W oil.

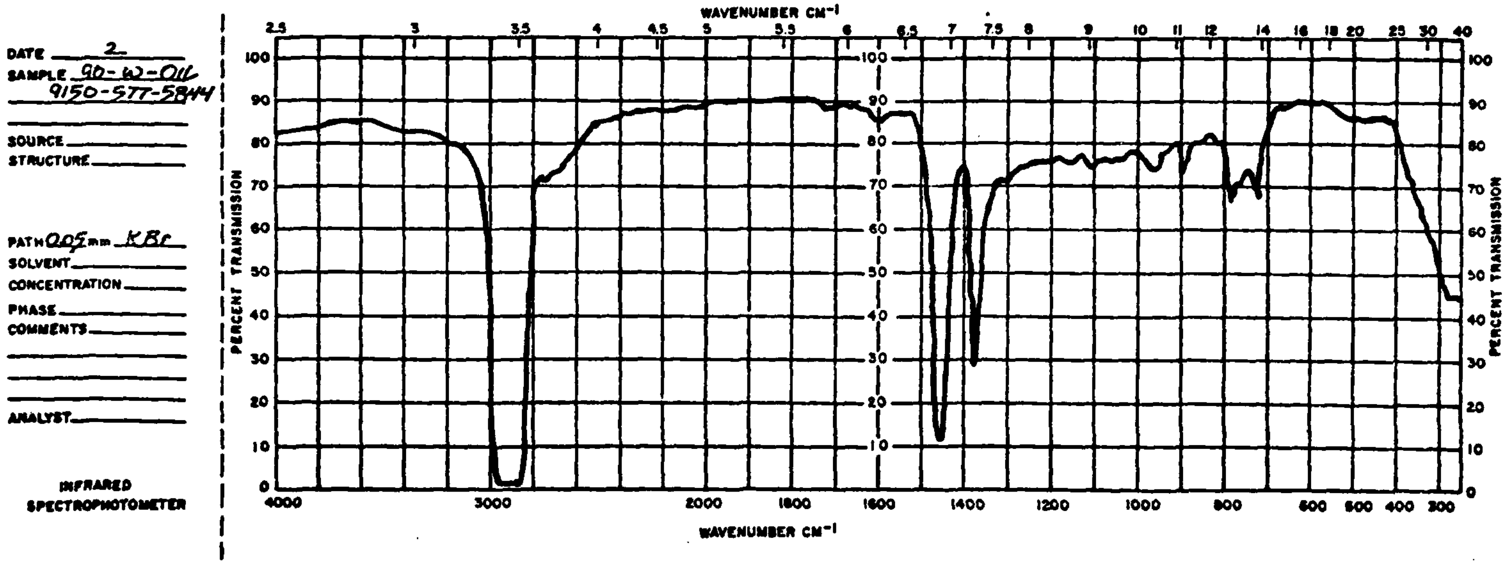


Figure 4. IR spectrogram of 90W oil.

SPECTRUM NO 4
DATE
SAMPLE GREASE
80-0907

SOURCE
STRUCTURE

PATH 005 mm KBr
SOLVENT
CONCENTRATION
PHASE
COMMENTS

ANALYST

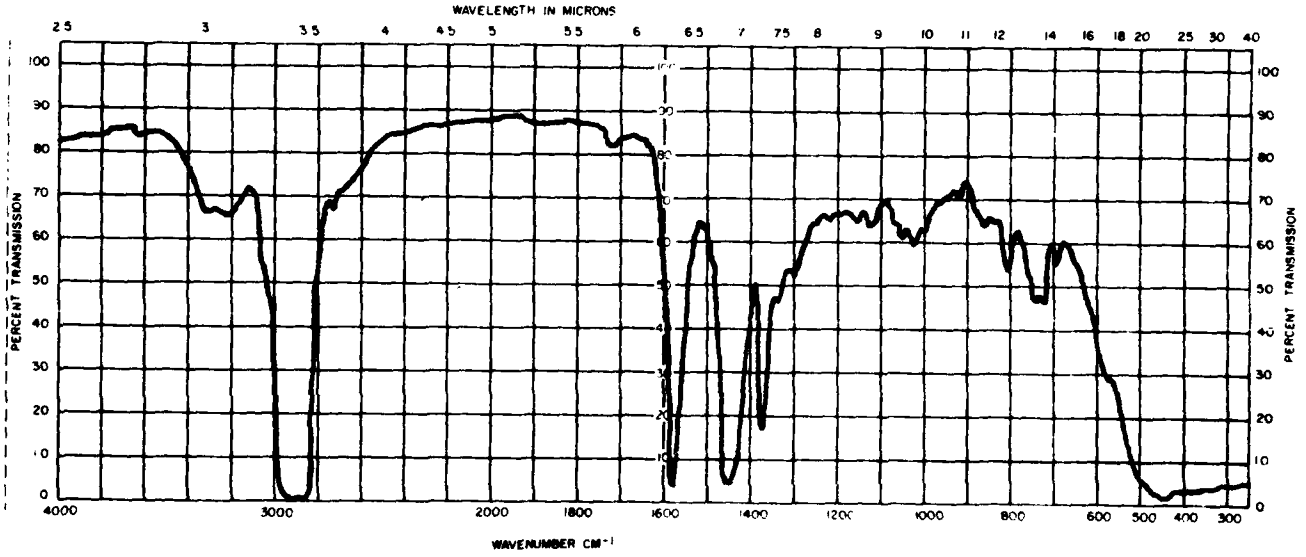


Figure 5. IR spectrogram of GAA grease.

SPECTRUM NO. 5
DATE
SAMPLE ANTIFREEZE
L493

SOURCE
STRUCTURE

PATH 0.025 mm KBr
SOLVENT
CONCENTRATION
PHASE
COMMENTS

ANALYST

INFRARED
SPECTROPHOTOMETER

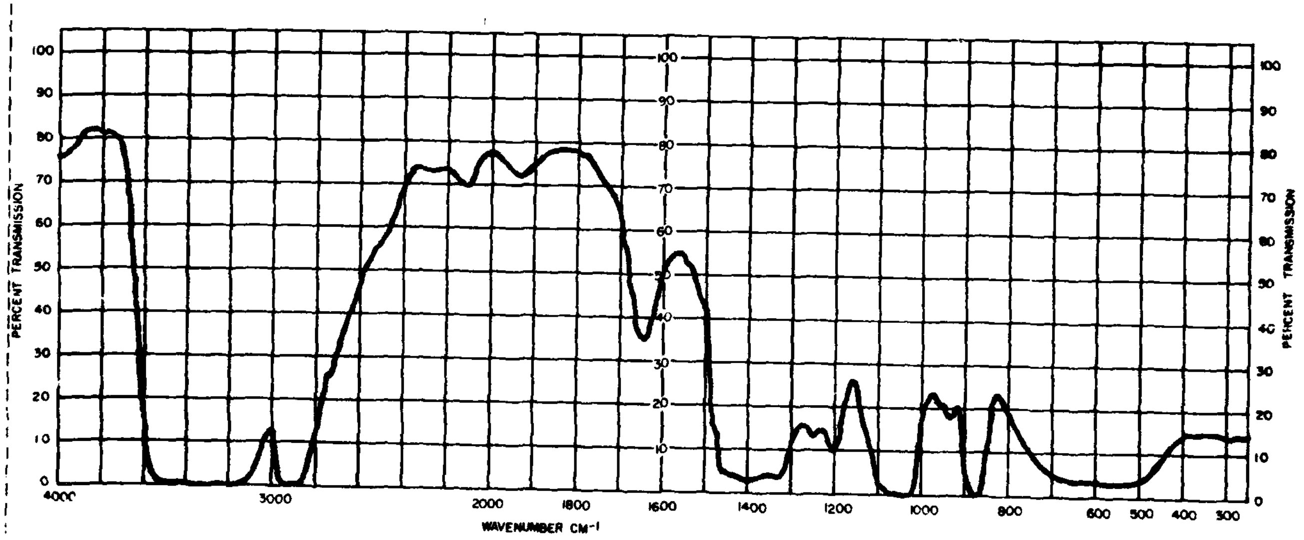


Figure 6. IR spectrogram of antifreeze.

SPECTRUM NO 6
DATE
SAMPLE BRAKE FLUID
231-9071
SOURCE
STRUCTURE
PATH ____ mm
SOLVENT
CONCENTRATION
PHASE
COMMENTS
ANALYST

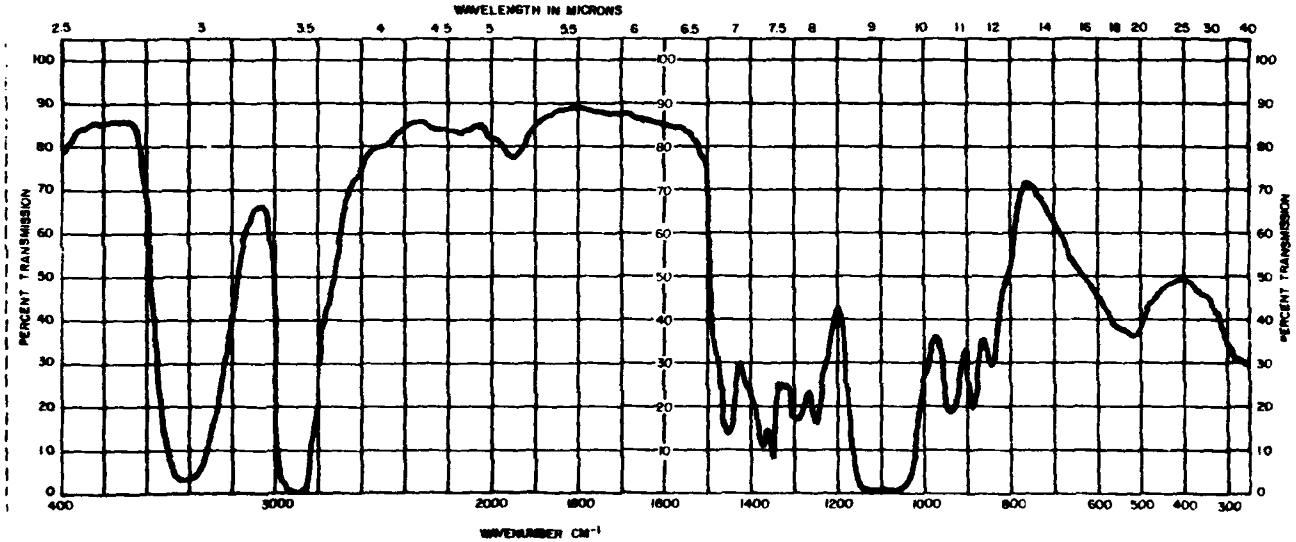


Figure 7. IR spectrogram of brake fluid.

SPECTRUM NO. 7
DATE
SAMPLE HYDRAULIC FLUID
9150-00-135-4805
SOURCE
STRUCTURE

PATH 0.05 mm ± 3c
SOLVENT
CONCENTRATION
PHASE
COMMENTS
ANALYST

INFRARED
SPECTROPHOTOMETER

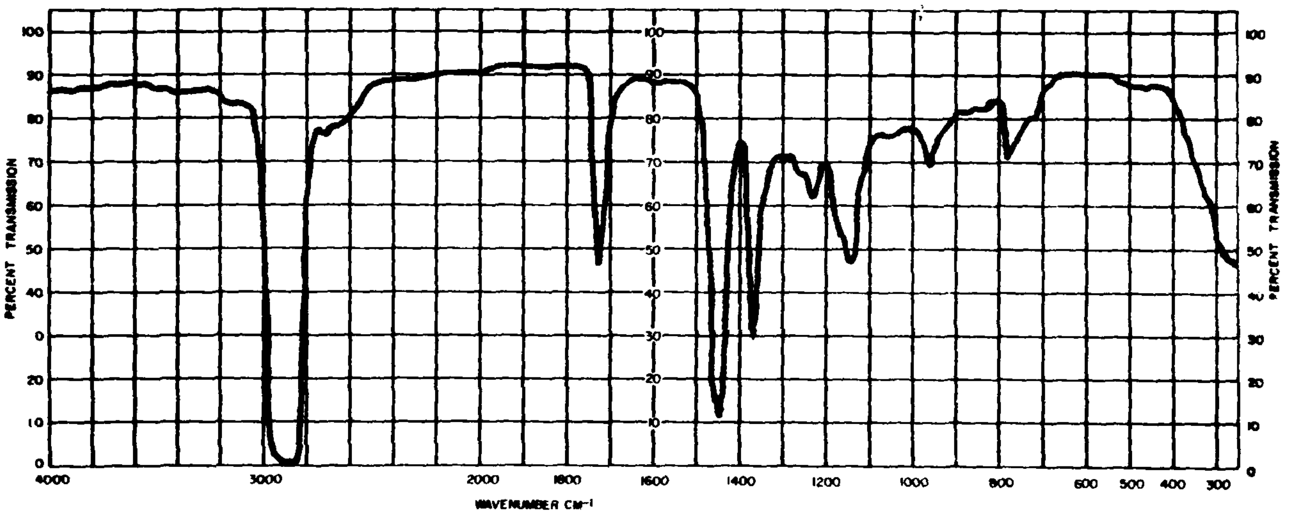


Figure 8. IR spectrogram of hydraulic fluid.

SPECTRUM NO 8
DATE
SAMPLE SOLVENT (TYPE II)
6850-637-6135

SOURCE
STRUCTURE

PATH ___ mm
SOLVENT
CONCENTRATION
PHASE
COMMENTS

ANALYST

INFRARED
SPECTROPHOTOMETER

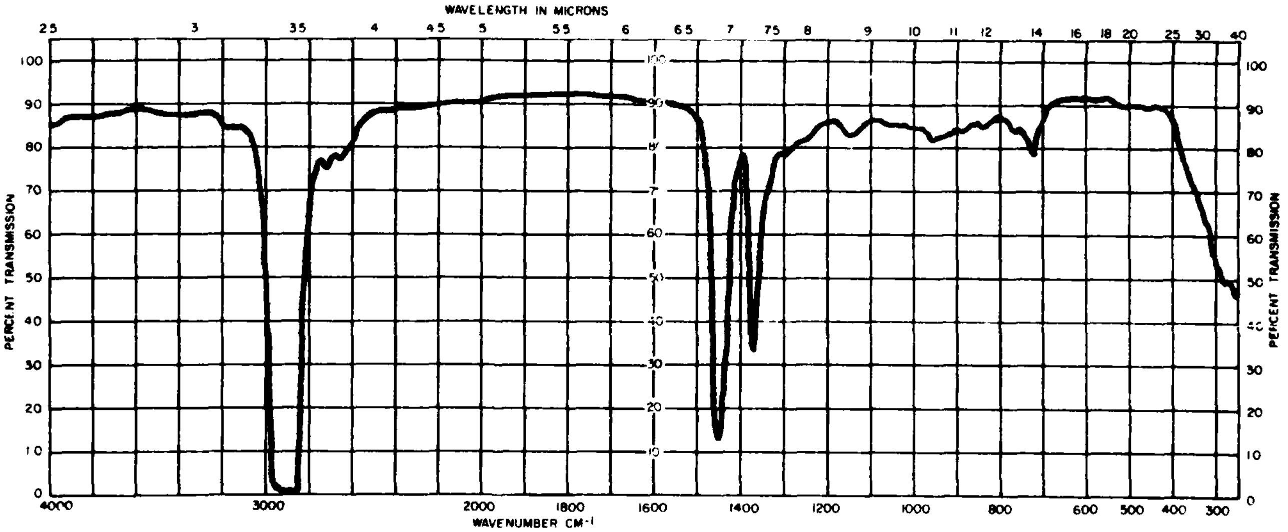


Figure 9. IR spectrogram of solvent type II.

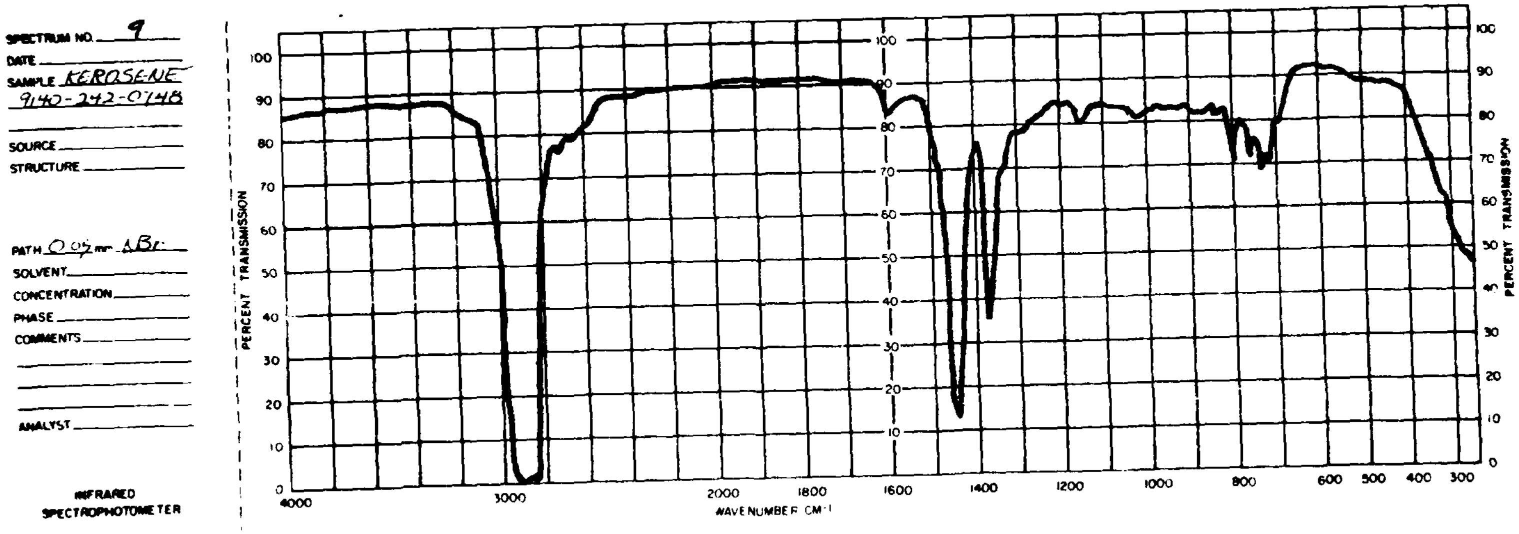

SPECTRUM NO. 9
DATE
SAMPLE KEROSENE
9140-242-0148
SOURCE
STRUCTURE
PATH 0.05mm KBr
SOLVENT
CONCENTRATION
PHASE
COMMENTS
ANALYST
INFRARED
SPECTROPHOTOMETER

Figure 10. IR spectrogram of kerosene.

Although the recording of IR spectra is straightforward, careful attention to established operating procedures and techniques of cell manipulation was necessary to insure valid and reproducible results. To avoid cross-contamination between samples, cells were flushed with five successive 100-μℓ portions of Freon 113. Cells were vacuum dried after each spectral scan. Since Luer fittings are potential reservoirs for traces of a previously contained sample, meticulous attention was paid to both external and internal surfaces of the Luer fittings and to the cell windows when cells were rinsed between samples.

It was determined that the conventional method of using a syringe to inject samples into absorption cells entailed an unacceptable risk of cross-contamination (in addition to contaminating exterior surfaces when highly volatile solvents such as Freon were used). Therefore, an improved, though unorthodox, manipulation technique was chosen. Cells were loaded using a 100-μℓ Eppendorf pipette assembly; the pipette's plastic tip provided a liquid-tight connection with the capillary orifice at the base of the Luer fittings. The calibrated 100-μℓ volume did overfill the 0.05-mm pathlength cell, and the disposable pipette tip insured against sample cross-contamination. The KBr cell windows remained matched within experimental error over the duration of spectral-data gathering.

Sample Preparation

Field hydrocarbon samples were typically skim samples consisting of an oily phase containing solid debris and occluded water overlying an aqueous phase. Since even trace amounts of water cause strong spectral interference and etch alkali-halide cell windows, complete separation of the organic phase from the aqueous phase and debris was necessary. This was accomplished on a physical basis, without the addition of solvent, by centrifugation of 2- to 5-mℓ portions of a sample in tapered 20-mℓ tubes in a clinical-type centrifuge. A portion of the supernatant organic layer was then carefully drawn off with a Pasteur pipette. The cycle was repeated until a clear organic phase was obtained. Gravity filtering of the separated organic phase through anhydrous sodium sulfate reduced the remaining traces of water to levels that could not be detected in the recorded spectra.

The conventional method of extracting the organic solvent from the original sample, followed by evaporation of the solvent, was not used because of (1) the inevitable addition of interfering solvent peaks if evaporation was performed at low temperatures, and (2) the loss of relatively volatile fractions of the organic phase if the solvent evaporation was conducted at higher temperatures. Residual solvent peaks were partially cancelled by using differential spectroscopy with pure solvent in the reference beam in a variable pathlength cell, except when the concentration of residual solvent in the sample extract required a cell pathlength less than the mechanical limit of the variable pathlength cell.

Petroleum-based oils and vegetable/animal oils in the presence of each other are quantified by evaluating infrared absorption measurements made at selected infrared frequencies specific to each class of material. In the work reported by Kahn, et al., monoglycerides, diglycerides, triglycerides, and other fatty acid esters which constitute a significant portion of the vegetable- and animal-derived oils and which are essentially absent in petroleum-derived oils, are represented at an absorption band at 1745 cm^{-1} (C=O). (Both petroleum and vegetable/animal-based oils absorb at a wavenumber of 2903 cm^{-1}; this measure is used in the official EPA quantification of "total hydrocarbons."[54]) Petroleum-based oils can be partitioned from vegetable/animal-based oils in an unknown sample before absorption measurements are made by simply contacting an oil sample dissolved in CCl_4 with silica gel. Vegetable/animal-based oils are selectively adsorbed;* the petroleum-based oils remain in solution.

Weathering Effects

When oils or other hydrocarbons are discharged into an aqueous effluent and are exposed to the atmosphere as emulsions or films overlying an aqueous phase, changes in physical and chemical characteristics are caused by the effects of solar irradiation, temperature, agitation, adsorption on solids, bacterial action, and chemical interaction with other chemical compounds in the effluent. This so-called "weathering" must be taken into account in analytical methods based on comparison of standard reference materials with the same components in a recovered sample that has undergone environmental exposure. The changes that occur in weathered hydrocarbons are reflected in the differences between the analytical response of a given off-the-shelf petroleum product and the same product present in a sample recovered from an effluent stream.

On the assumption that a state of equilibrium is approached in the weathering process, techniques to simulate environmental weathering have been developed. The U.S. Coast Guard, the Department of the Interior, the EPA, and others concerned with the fingerprinting of crude oil and petroleum products in marine and terrestrial environments have devoted considerable research and development effort to studies of the compositional changes caused by weathering, and to the development of techniques for simulating weathering of reference samples to compensate for the environmental weathering effect on the unknown sample.[5,6,56-63]

The reliability of analytical fingerprinting methods improves when synthetically weathered standards are used to identify recovered crude oil or petroleum products. Methods developed and adopted by the Energy Research and Development Agency** and the American Society for Testing and Materials (ASTM) for the synthetic weathering of crude oil involve a

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* adsorbed = bound on particle surfaces.
**Superseded in 1977 by the Department of Energy.

distillation (under reduced pressure) of the suspect and recovered oil samples, and collection of the 275°C (atm) fraction; this fraction is then analyzed.[17,22] This distillation technique rejects the light fractions of petroleum components having n-paraffin carbon numbers of 15 or less. This loss of the low carbon-number fraction does not hinder the identification of crude oils containing a homologous n-paraffin series extending to C_{40} or more. However, such synthetic weathering methods may be unsuited to the synthetic weathering of recovered samples that may contain diesel fuel, solvent, and other light hydrocarbon products such as might be encountered in effluent streams at Army installations. More applicable synthetic weathering techniques must be found so environmental weathering can be simulated without extensive loss of low-boiling hydrocarbons. Ultraviolet irradiation and aeration of standard reference materials at temperatures below 40°C offer potentially useful alternatives.[48,54]

Preliminary Results

Two effluent stream samples were analyzed by IR spectroscopy through spectral correlation of absorption peaks with those of the known reference materials listed in Table 2, using discriminant analysis and pattern recognition of analog data. In a field sample (a contaminated outfall sample from Flora Road outfall, Fort Lewis, WA), two constituents -- motor lubricating oil and diesel fuel or kerosene -- were identified by IR spectroscopy and confirmed by GLC as the principal hydrocarbon products present. Other minor peaks only slightly above threshold intensity were observed, but were not sufficiently defined to be analytically useful, since the Beckman IR-20 Spectrophotometer did not have the capability for scale expansion in the analog presentation of absorption values. Facilities for scale expansion and analog-to-digital data conversion would be required for accurate representation of minor peaks and for peak-rationing techniques.[64]

4 GAS-LIQUID CHROMATOGRAPHY

Over the past 10 years, GLC has gained a prominent place in analytical methods which fingerprint crude oil samples recovered from oil spills.[60] This has been due, in part, to the unique ability of GLC to differentiate between hydrocarbon species having similar structures. Petroleum crudes have a predominant component of n-paraffin hydrocarbons in an homologous series of carbon numbers to C_{40} or more. The chromatogram of a typical crude petroleum sample is characterized by a periodic sequence of approximately equally spaced peaks representing unit increments in carbon numbers of the n-alkanes contained in the given sample. The relative concentration of each n-alkane is a function of the area under the corresponding peak; information about peak height distribution of the respective n-alkanes allows recovered crude oil samples to be matched to known reference samples of the suspect petroleum.[64]

GLC was used during this study to complement IR spectroscopic techniques. The GLC carbon-number criterion made it possible to identify both the low-boiling n-paraffin fractions (carbon numbers less than 11) which characterize kerosene and diesel fuel and the higher-boiling n-paraffin fractions which constitute motor lubricating oils. However, weathering of n-paraffin series hydrocarbons results in partial loss of lower-boiling components; this loss is reflected in an attenuation or absence of the lower carbon-number peaks. As in the case in IR measurements, weathering effects must be taken into account when chromatographic data on field samples are interpreted.

Experimental Procedures

GLC information was collected using a Hewlett-Packard 5754 Gas-Liquid Chromatograph equipped with temperature programming and a flame ionization detector. Data output was through a Hewlett-Packard 3380A recording integrator which provided (1) an analog plot of the chromatogram (with retention times at each recorded peak), and (2) a table of the respective peak areas as percent of the total (for quantifying individual molecular species).

Optimum GLC operating conditions were established by experimenting with various liquid phases and values of instrumental parameters with respect to the sample materials to be analyzed (Table 4). Although other liquid phases might have given equal performance, Dexsil 300 was chosen for its thermal stability and its capability to provide reasonable resolution of peaks in a real-life sample.

After these analytical conditions were established, chromatograms were obtained from the 13 reference materials listed in Table 5. The recorded chromatograms appear in Figures 11 through 23.

Table 4

GLC Operating Conditions

Instrument Type:	Hewlett-Packard 5754
Detector:	Flame ionization detector
Injection Port Temperature:	250°C
Detector Temperature:	300°C
Column:	365-m x 3.2-mm stainless steel column packed with 6 percent Dexsil 300 on 80/100-mesh Chromosorb WHP
Column Oven Temperature:	Programmed from 70 to 325°C at 4°C/minute. Held at 325°C
Carrier Gas and Flow Rate:	Helium at 30 cc/minute
Electrometer Range:	10^5
Chart Speed:	0.5 cm/minute
Sample Volume Injected:	1 to 5 μℓ as required

Table 5

Hydrocarbon Reference Materials for GLC

Reference Sample	Source
10W Oil	Fort Lewis
30W Oil	Fort Lewis
90W Oil	Fort Lewis
30W Oil	Fort Carson
Kerosene	Fort Lewis
Kerosene	Fort Carson
Hydraulic Fluid	Fort Lewis
Hydraulic Fluid	Fort Carson
Brake Fluid	Fort Lewis
Brake Fluid	Fort Carson
Diesel Fuel	Fort Carson
Antifreeze	Fort Lewis
Solvent Type II	Fort Lewis

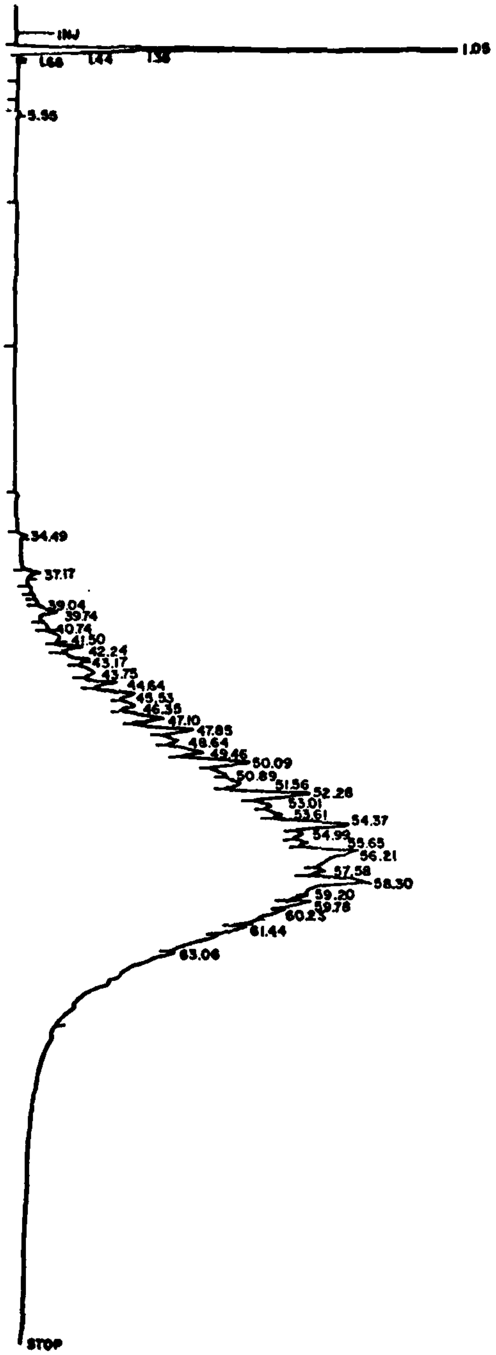

Figure 11. GLC chromatogram of 10W oil reference material.

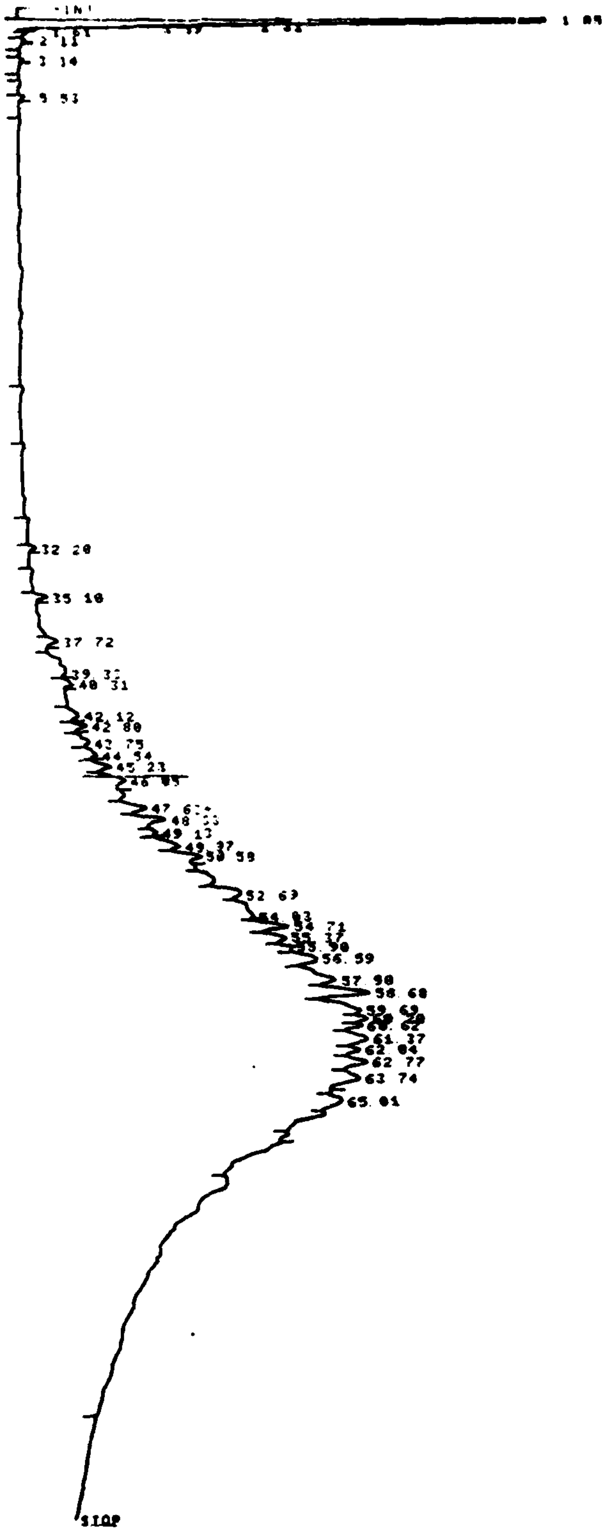

Figure 12. GLC chromatogram of 30W oil reference material (Fort Lewis).

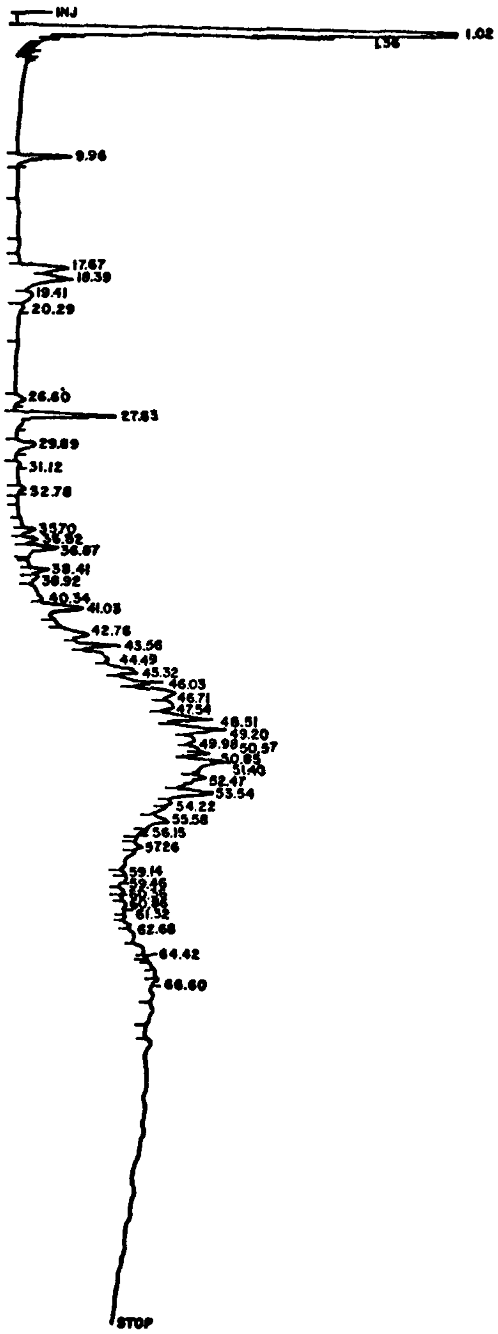

Figure 13. GLC chromatogram of 90W oil reference material.

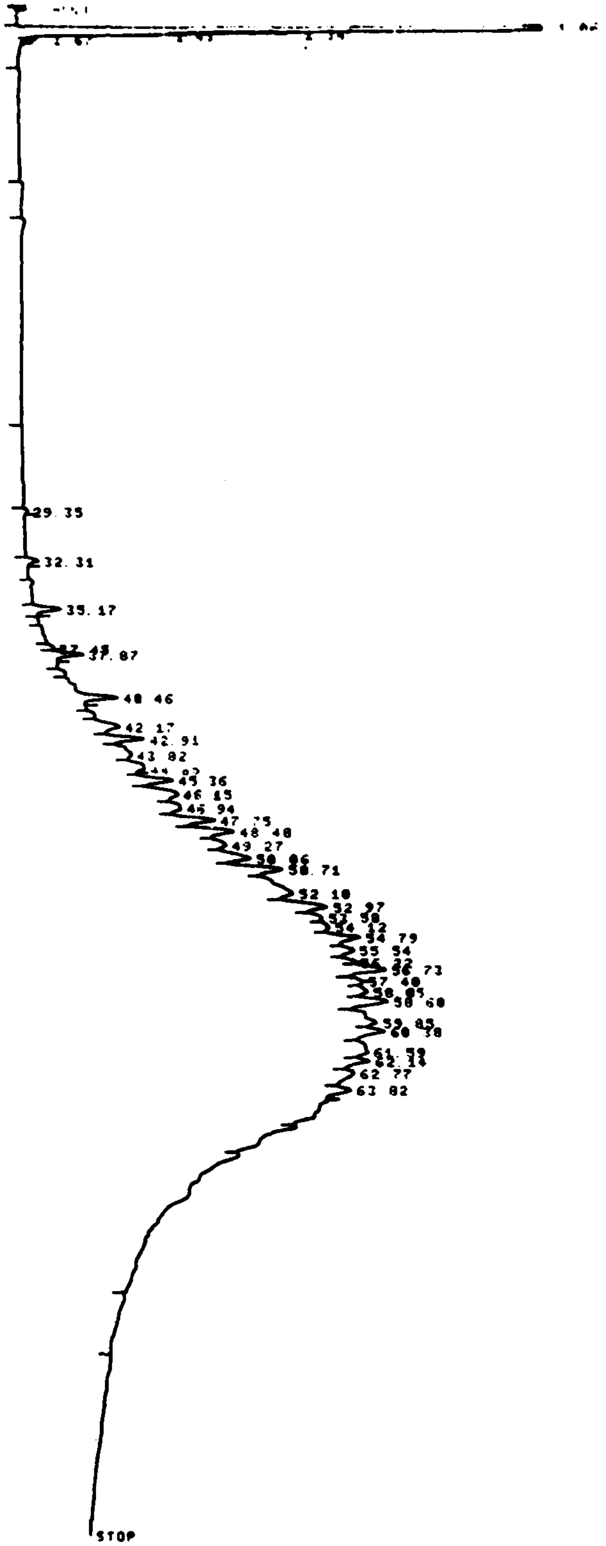

Figure 14. GLC chromatogram of 30W oil reference material (Fort Carson).

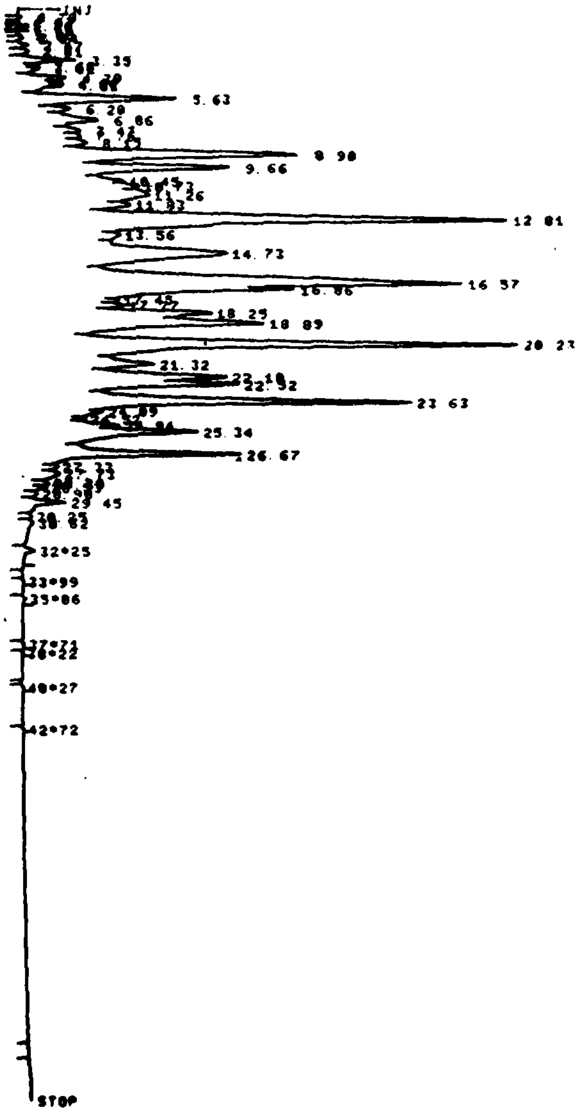

Figure 15. GLC chromatogram of kerosene reference material (Fort Lewis).

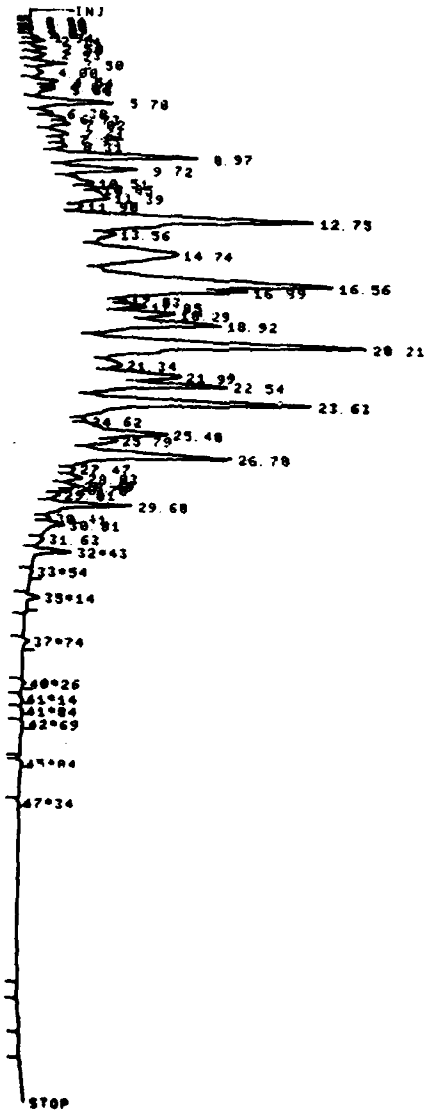

Figure 16. GLC chromatogram of kerosene reference material (Fort Carson).

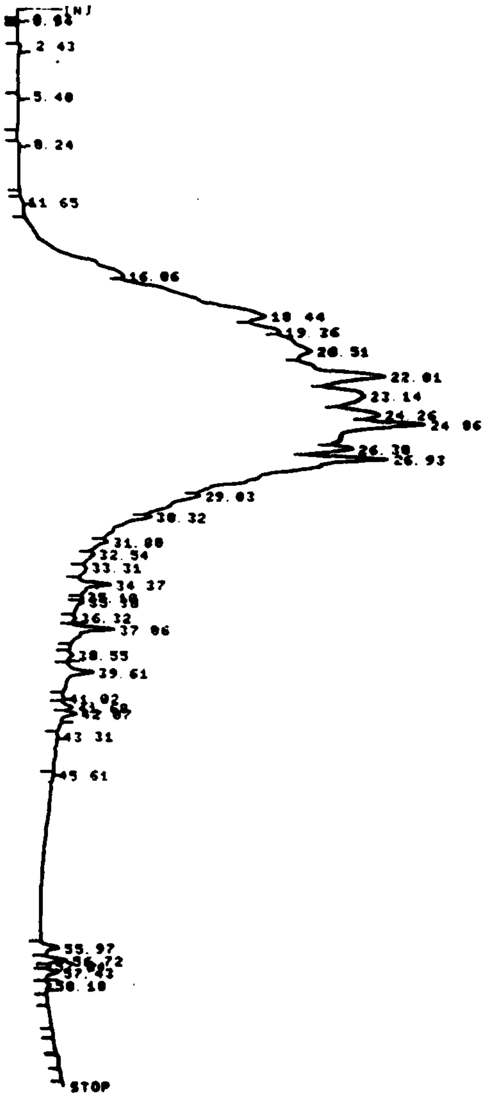

Figure 17. GLC chromatogram of hydraulic fluid reference material (Fort Lewis).

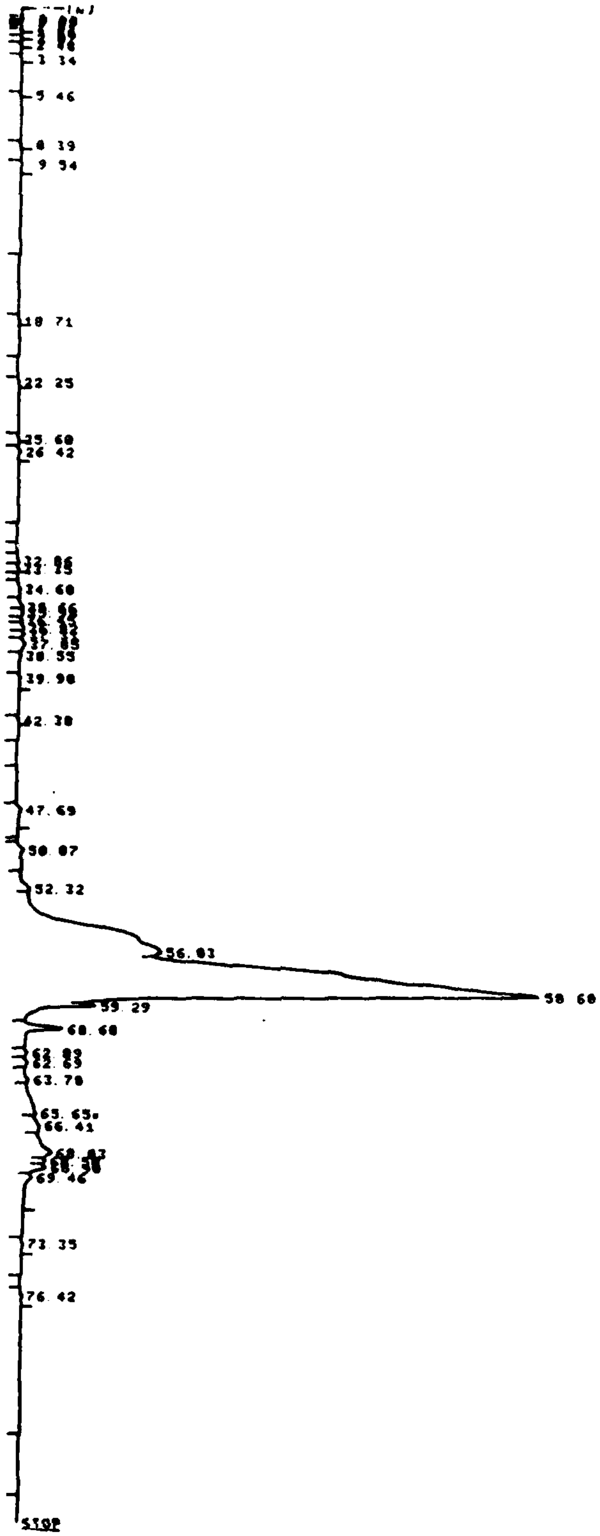

Figure 18. GLC chromatogram of hydraulic fluid reference material (Fort Carson).

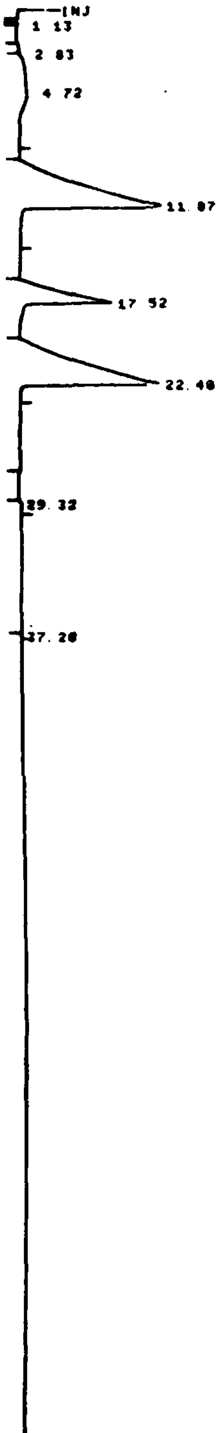

Figure 19. GLC chromatogram of brake fluid reference material (Fort Lewis).

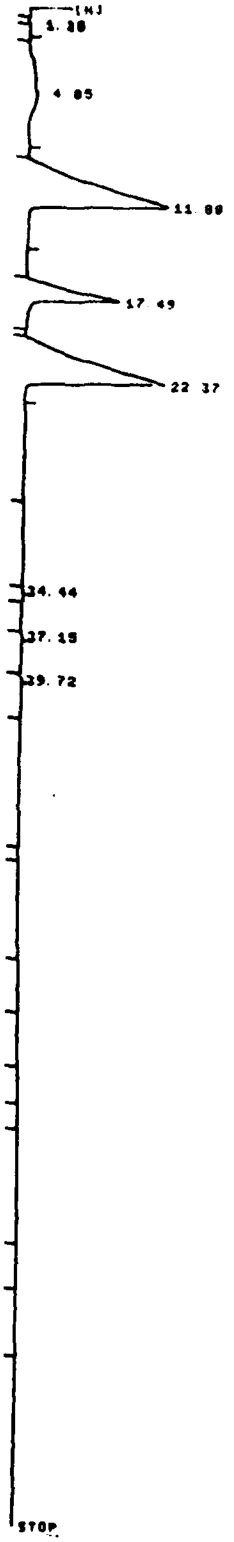

Figure 20. GLC chromatogram of brake fluid reference material (Fort Carson).

Figure 21. GLC chromatogram of diesel fuel reference material.

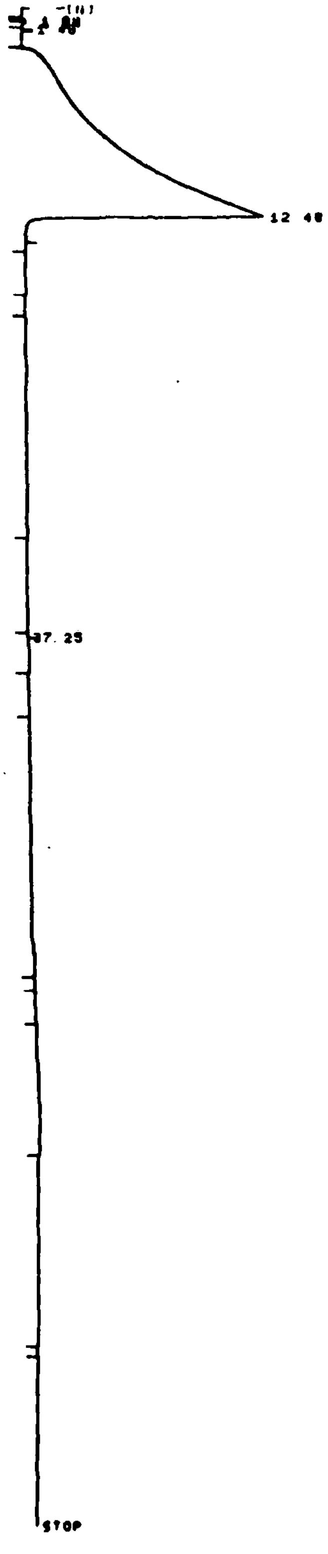

Figure 22. GLC chromatogram of antifreeze reference material.

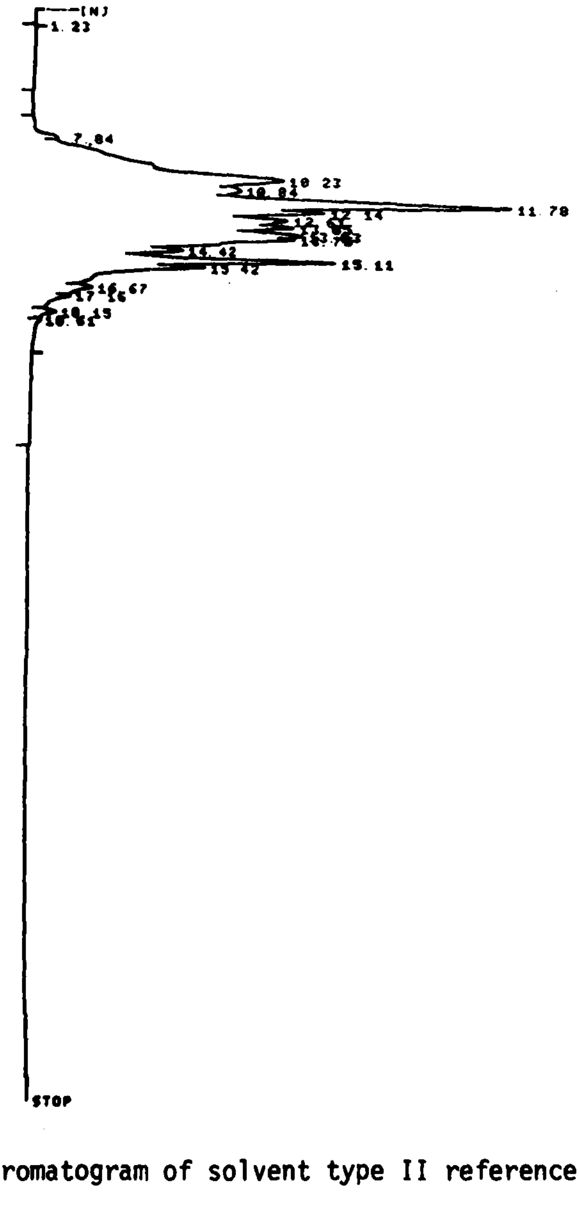

Figure 23. GLC chromatogram of solvent type II reference material.

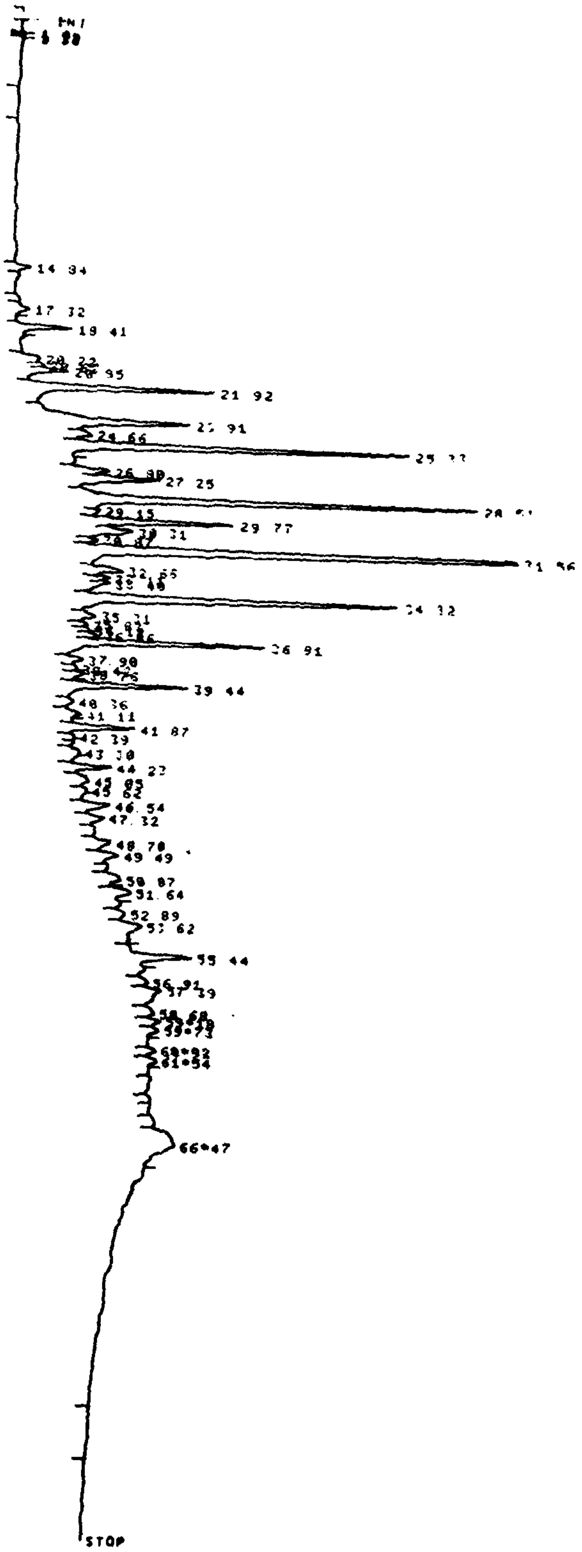

Figure 24. Chromatogram of field sample.

Preliminary Results and Discussion

At this phase of the study, visual pattern-recognition was used to categorize component classes. The presence of n-alkane homologous series was apparent in the kerosenes and lubricating oils in which the well-defined series of peaks are superimposed on an "unresolved envelope."[61] The lower carbon-number distributions in the kerosenes (with respect to the lubricating oils) were correlated to the respective boiling point ranges of the kerosene and motor-oil products. The dissimilarity between Fort Carson and Fort Lewis hydraulic fluid chromatograms denote different chemical compositions, although, according to MIL SPECS, the physical properties of these substances are the same. The brake fluid samples from the Fort Carson and Fort Lewis stores produced similar chromatograms, indicating that they had the same chemical formation. The "tailing" of the last three eluted peaks indicates highly polar compounds such as glycols or higher alcohols. The absence of the periodic-peak series of the n-alkanes in the chromatogram of solvent type II indicates it is not composed of n-paraffin hydrocarbons.

The field sample was used to test the analytical interdependence of GLC in combination with IR spectroscopy. The GLC operating conditions used in the preliminary tests on this sample were as given in Table 4, except that temperature programming was between 100 and 325^{o}C at a ramp rate of 10^{o}C per minute.

The outfall sample chromatogram (Figure 24) had a periodic series of peaks, indicating an homologous series which corresponded to the n-paraffin series in kerosene. Subsequent analysis by GLC/mass spectroscopy confirmed these peaks to be an homologous series of n-alkanes ranging from C14 to C24. The attenuation or absence of peaks for carbon numbers less than 12 in the field sample chromatogram (as compared to peaks of carbon numbers less than 8 in the reference sample of kerosene) indicated the expected losses of these lower-boiling n-alkanes through evaporation in the weathering process.

Since a sophisticated data-reduction system which would generate specific compound information was not available, GLC chromatogram patterns were visually screened to establish what classes of organic compounds may or may not be present. This step simplified the interpretation of IR spectra when the two techniques were used together, since a preliminary GLC screening reduced the population of probable components in a mixture of hydrocarbon products.

5 QUANTIFICATION OF HYDROCARBONS IN EFFLUENTS

General

The determination of oils and other hydrocarbons in effluents at military installations can provide information essential to the monitoring and control of environmental pollution by these substances.

CERL used the official EPA gravimetric method (STORET 00556) to determine "total hydrocarbons" in wastewater. This method is based on the weight of the residue on evaporation of a Freon extract of a given volume of a wastewater sample. Analytical results are expressed as milligrams of oil per liter. The stated analytical range is 5 to 1000 mg/ℓ.

An alternate EPA method (STORET 00560) uses IR spectroscopy and is based on the linear relationship of optical absorbance by the CH_2 band at 2930/cm, with concentration of the hydrocarbon.[65] The measured absorbance of a Freon extract of the sample is converted to concentration of "total hydrocarbons" in the original sample by means of an analytical curve prepared from absorption measurements of prepared standards of known concentrations of a standard oil in Freon. The analytical range is 0.1 to 40 mg/ℓ with conventional absorption cells. The upper limit can be extended several orders of magnitude by volumetric dilution of the Freon extract.

The EPA method using IR spectroscopy can provide information on composition as well as concentrations of the hydrocarbons, and therefore might be more appropriate in some cases than the nonselective gravimetric method.

Before CERL could evaluate the overall benefits and limitations of the IR and gravimetric methods with regard to precision, accuracy, procedural characteristics, and applicability to routine use, the Beckman IR-20 Infrared Spectrophotometer had to be retrofit with quartz-window cells of 1-, 10-, and 50-mm pathlengths for absorption measurements of solutions. The necessary cell holders of the dimension stability required for this purpose were not commercially available, and so prototypes were made at CERL (Figure 25). These prototypes were designed to accommodate the range of cells needed for both the initial phase of this study, and for planned investigations into low concentrations of hydrocarbons that would require relatively long pathlength cells.

Next, a "hands on" stepwise execution of the EPA IR procedure was conducted; critical attention was paid to procedural details of preparing and calibrating standards, development of the analytical curves, sample preparation, extraction techniques, absorption measurement methods, data reduction, and calculations.

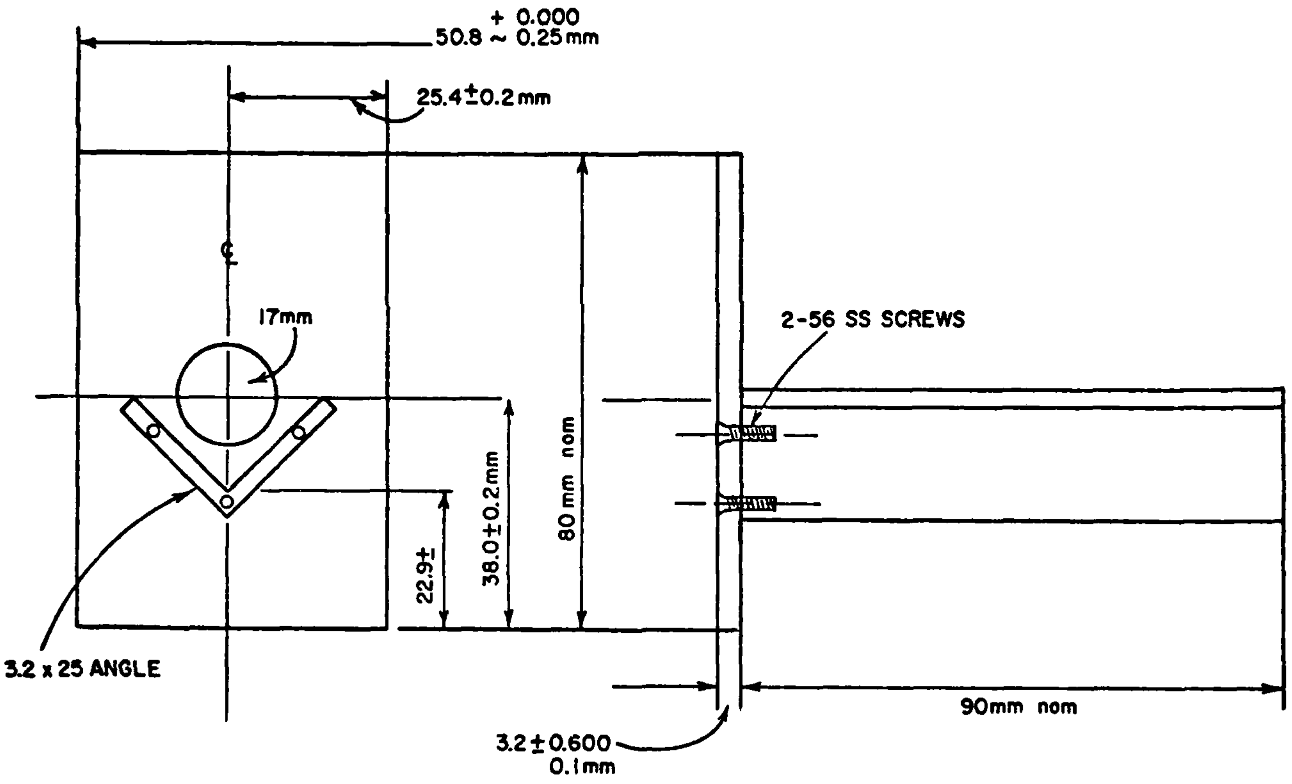

Figure 25. IR cell holder for absorption spectra of solutions.

The EPA IR method was then applied to the determination of hydrocarbons in a representative group of wastewater samples previously analyzed by the gravimetric method. Comparative results of the initial group of samples are listed in Table 6.

After a sufficient number of analytical results are accumulated (during the second phase of this study), these data will be analyzed and correlation statistics will be computed to assess bias between the IR and gravimetric methods. Accuracy and precision of the IR and gravimetric methods will be assessed through the use of synthesized wastewater samples containing known concentrations of the MIL SPEC hydrocarbon products (Table 1).

Experimental Procedures and Observations

The procedural details of the EPA IR method follow the solvent extraction and IR techniques used in the petroleum industry for monitoring refinery wastes and effluents.[46] Acidification of the sample to pH 2

Table 6

Comparative Analytical Results Between Gravimetric and IR Determination of Hydrocarbons in Wastewater

	Concentration (mg/ℓ)	
Sample Number	Gravimetric Method	IR Method
FB-4a	10.2	11.5
FB-4b	2.0	8.2
FB-5	11.0	9.5
FB-6	9.7	11.9
FB-8	5.6	6.1
FB-10	1.0	1.9
FB-15	21.5	23.5
FB-18	32.7	32.0

*Standardized with reference to 30W MIL SPEC motor oil.

or less with sulfuric acid at the time of sampling arrests biochemical changes and increases hydrocarbon extraction efficiency.[49] The use of Freon 113 as the extractant to replace the previously used carbon tetrachloride was a result of increased awareness during recent years of toxic substances, rather than for chemical reasons. The slight inconvenience of using the more volatile Freon 113 instead of carbon tetrachloride is compensated by the 100-fold lower toxicity of Freon relative to carbon tetrachloride.

The cell holder design shown in Figure 26 provided accurate and reproducible alignment of cylindrical cells of 1 to 10 cm pathlength with the optical axis of the Beckman IR-20 spectrometer. Precisely machined v-ways were used instead of conventional clamping devices to maintain accurate and reproducible positioning of the cells. This permitted convenient access for cell-filling operations and minimized mechanical stresses on the cells during their placement and removal.

In the selection of hydrocarbon compounds for preparation of the reference "oil" standard, the EPA IR procedure categorized hydrocarbons into two groups:

1. Known oils. These are oils in which the composition of the hydrocarbon material in the wastewater is known and a sample of the material is available for preparation of calibration standards.

2. Unknown oils. These are oils for which a sample of the material is not available for the preparation of standards.

In unknown oils, a hydrocarbon mixture consisting of 37.5 percent n-hexadecane, 37.5 percent isooctane, and 25 percent benzene (volume/volume basis) is given as the calibration material. However, the 0.769 specific gravity of that mixture is considerably less than the 0.900 average specific gravity of hydrocarbon products listed in Table 1 that might be present in washrack effluents, and consequently, would introduce a systematic error of approximately +18 percent in the analytical results. Therefore, it was decided to prepare calibration standards from a material of approximately 0.900 specific gravity. A MIL SPEC 30W motor oil with a 0.904 specific gravity was selected as the standard material; calibration standards were prepared over the range between 0.5 and 40 mg/ℓ.

Oil calibration standards were prepared according to conventional practices for serial dilutions of the MIL SPEC 30W motor oil with Freon 113. To minimize evaporation losses, the prepared standard series were stored in volumetric flasks sealed with latex caps over ground glass stoppers. Absorption spectra of the standards in the region of the 2930/cm band were recorded using the integral strip-chart recorder of the Beckman IR-20.

Data reduction required the conversion of the percent transmission readout of the IR-20 to absorbance. This was done graphically by means

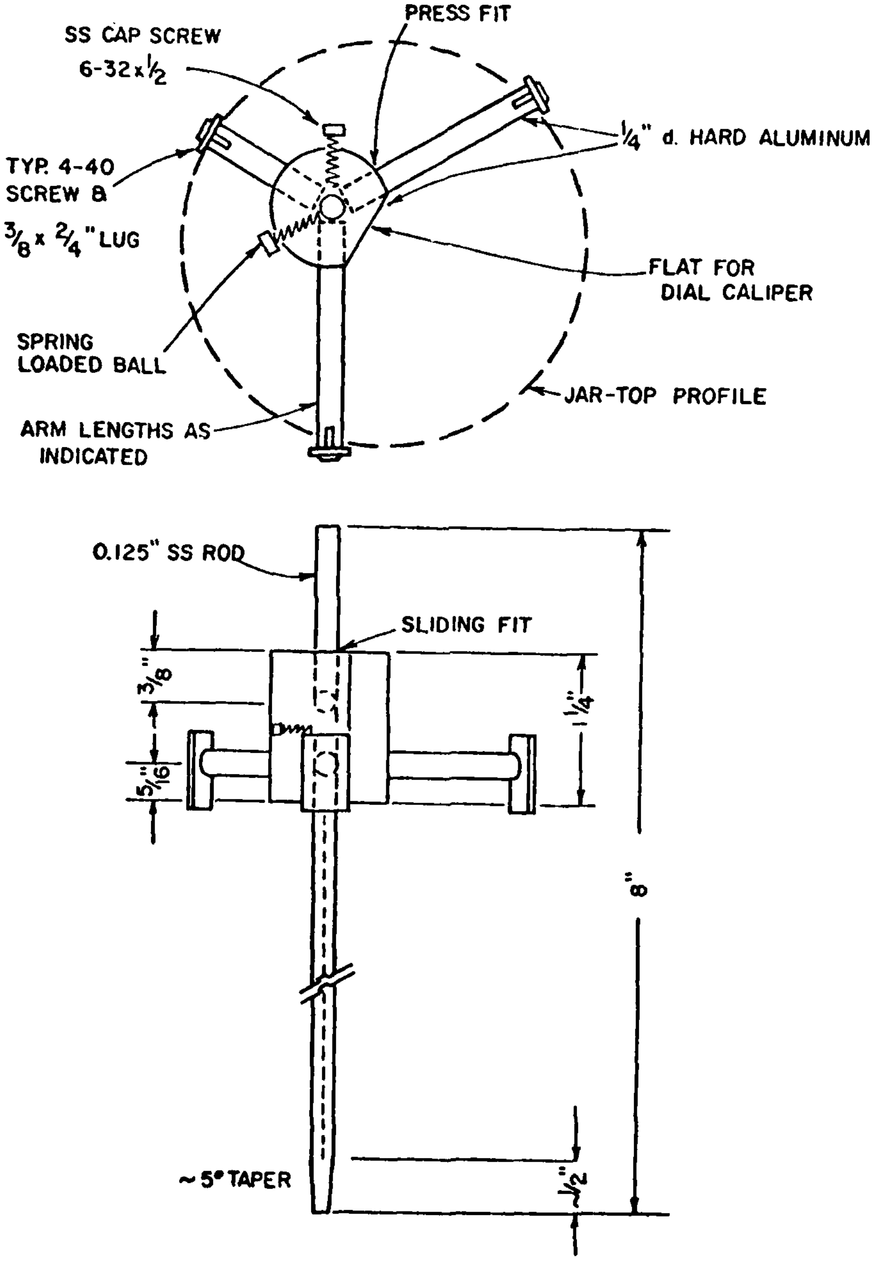

Figure 26. Reference gauge for determining sample volume for total hydrocarbon determination.

of a linear-function plot of percent transmission vs absorbance (%T vs A) on semilog paper, with absorbance on the linear axis and percent transmission on the logarithmic axis. The plotted intercepts were transmission = 100 vs absorbance = 0 (T = 100 vs A = 0), and transmission = 10 vs absorbance = 1 (T = 10 vs A = 1). Peak-height absorbance values were obtained from the strip-chart recording by subtracting the base-line absorbance value from the total absorbance value at peak center. The analytical curve of absorbance vs peak height was plotted in the conventional manner. In plotting the analytical curve, the use of log-log instead of the conventionally used linear-coordinate graph paper provided constant relative precision over the calibrated range when graphical data reduction methods were used.

Wastewater samples for oil determination were received in 1-quart "Mason jar"-type containers. Sample volume was established by attaching a tape reference mark on the jar at the liquid level, transferring the contents to a separatory funnel, rinsing with portions of Freon, refilling to the tape mark with water, then pouring the contents into a 1000-mℓ graduated cylinder and estimating the volume by visual interpolation between the 10-mℓ graduations on the cylinder. The uncertainty in establishing the liquid level in the sample jar and graduated cylinder through parallax and meniscus errors in routine operations was found to be approximately ±2 mm -- equivalent to ±20 mℓ of sample volume. The resultant error contribution to the analytical results was approximately ± 6 percent (for a sample volume of 300 mℓ).

A CERL-designed device was used to directly determine sample volumes through a liquid level vs volume calibration. This device provided both a measurement of sample volume four times more precise than the prescribed method and a significant reduction of operator time. To determine the sample volume, the device is placed on the Mason jar rim, then the depth from the rim to the liquid surface is measured with a vernier caliper integral with the device, and the sample volume is read directly from a previously prepared plot of sample volume vs measured depth from rim to liquid level. The relative error in the use of this method was approximately 1.5 percent for typical sample volumes.

The gravimetric method requires evaporation of the 100 mℓ of the Freon solvent from the extracted hydrocarbon at a temperature of 70°C and drying at 80°C. This results in partial losses of analyte fractions such as gasoline and other products having significant vapor pressure at those temperatures. Since the IR method does not require evaporation of the solvent from the hydrocarbon extract, losses of low-boiling hydrocarbon fractions are significantly lower than by the gravimetric method.

The determinative step of the gravimetric method requires oil residues to be weighed in 125-mℓ distilling flasks. The uncertainty of reproducing the tare weight of a vessel of this mass and volume after the necessary handling, evaporation, and drying operations is of the order of 10 mg, or approximately 200 percent or more of the reported value at oil concentrations below 5 mg/ℓ. While the relative precision of the gravimetric method varies inversely with oil concentration, the relative precision of the IR method is essentially constant over the calibrated range.

CERL's comparison of the gravimetric and IR methods included a consideration of the degree of expertise required to perform the analytical operations. The sampling and extraction operations of the two methods were identical -- assuming the EPA-prescribed separatory funnel technique was used. The weighing operations of the gravimetric method had to be carefully done to minimize tare changes in the flask containing the oil residue. However, since the determinative steps of the gravimetric procedure involve only an analytical balance, the procedure can be successfully performed by analysts who have minimum technical background. The infrared method, however, demands considerably more skill and technical background of the analyst. Technical judgment in selecting and preparing standards, generating analytical curves, establishing operating conditions and maintaining performance levels of the IR spectrophotometer, interpreting spectra, and recognizing spectral aberrations when they occur require that these operations be performed or supervised by a person competent in spectrochemical methods.

Future Work

The second phase of the study will generate enough comparative results from gravimetric and IR determinations to permit a statistical comparison. Phase 2 will also evaluate the effect of differences in absorptivity of specific hydrocarbons on observed concentrations by the IR method compared to the gravimetric method. Stability of spectral absorptivities of the various materials in Freon must also be examined, to assure validity of prepared standards stored over a given time interval. An analysis of variance of the procedural steps of the IR method will provide information on the relative attention required in sampling, extraction, solution preparation, standardization, and photometry for optimizing cost-effective operations.

6 CONCLUSION

As an initial step in developing methods for identifying hydrocarbon products in Army vehicular service and washrack effluents, IR spectroscopy and GLC methods were evaluated and tested.

Results have shown that IR spectroscopy may provide a basis for the identification of hydrocarbon products for which reference samples are available. In the initial phase of the work, a scheme of sequential discriminant analysis and pattern recognition was used with reference to a file of MIL SPEC hydrocarbon products used in servicing wheel- and track-type Army vehicles. The complexity of IR data reduction was shown to increase rapidly with the number of hydrocarbon products present in a given sample -- a result of a similarity in molecular structure of the hydrocarbon components. The use of GLC in conjunction with IR spectroscopy provided additional discrimination and simplified data reduction.

A comparative investigation of the gravimetric vs IR methods for the quantification of "total hydrocarbons" in wastewater showed that the IR method was capable of higher precision than the gravimetric method at hydrocarbon concentrations less than 10 mg/ℓ, and could provide information on chemical composition and, consequently, the origin of the hydrocarbon product. However, quantification of "total hydrocarbons" by the infrared method required greater skills and technical background of the analyst than the gravimetric method.

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