

### 13. ORGANIC GEOCHEMISTRY ON LEG 104<sup>1</sup>

Keith A. Kvenvolden<sup>2</sup> and Thomas J. McDonald<sup>3</sup>

#### ABSTRACT

The Leg 104 organic geochemistry program consisted of monitoring (a) hydrocarbon gases, (b) organic and inorganic carbon, and (c) parameters resulting from Rock-Eval pyrolysis at three sites on the Vøring Plateau. The results amplify some of those obtained earlier on Deep Sea Drilling Project (DSDP) Leg 38. In a regional sense there is an inverse correlation between amounts of hydrocarbon gas and organic carbon. For example, significant concentrations of methane are present only at Site 644 in the inner part of the plateau where organic carbon contents are always less than 1%; in contrast, at Site 642 on the outer plateau, methane concentrations are very low (ppm range) whereas amounts of organic carbon approach 2%. Only at Site 644 are the environmental conditions such that methanogenesis is an active diagenetic process. Because of the importance of routine gas analyses to the Ocean Drilling Program (ODP), a procedure was devised to improve the use of Vacutainers for collection of gas samples.

Comparison of methods for determining organic carbon showed that at Sites 643 and 644 Rock-Eval TOC could be used as a measure of organic carbon, but not at Site 642. Although no liquid or solid hydrocarbons were encountered at any of the sites, a catalog of potential organic geochemical contaminants was developed in anticipation of such a discovery.

#### INTRODUCTION

In 1974, DSDP Leg 38 drilled six sites in the region of the Vøring Plateau, a prominent feature of the Norwegian continental margin. Three holes on the outer part and three holes on the inner part of the plateau defined the Eocene-to-Holocene sedimentary section (Talwani, Udintsev, et al., 1976). Of particular geochemical interest was Site 341 on the inner plateau where methane in high concentrations was found at sub-bottom depths below 50 m. Miocene sediment near the bottom of the hole (456 m) had a strong petroliferous odor and produced a bright yellow fluorescence (Morris, 1976).

The geochemical information from Leg 38 served as a background for further studies conducted on ODP Leg 104. Three sites tested the inner (Site 644), outer (Site 642), and foot (Site 643) of the Vøring Plateau (Chapter 1, this volume). At each of these sites a program of organic geochemistry was undertaken to (a) test procedures and methodologies, (b) determine the composition of hydrocarbon gases in sediments, (c) measure the content of organic and inorganic carbon with depth, (d) characterize the sedimentary organic matter by Rock-Eval pyrolysis, (e) catalog potential organic geochemical contaminants, and (f) interpret results. Information regarding each site can be found in the respective site chapters of Eldholm, Thiede, Taylor, et al. (1987).

#### PROCEDURES

The chemical laboratory aboard the *JOIDES Resolution* is well equipped to carry out basic studies in organic geochemistry. For our work we used two Hewlett-Packard (H-P) 5980A Gas Chromatographs for gas analyses; a Coulometrics 5030 Carbonate Carbon Apparatus, Perkin-Elmer (P-E) 240C Elemental Analyzer, and Carbonate Bomb to determine inorganic and organic carbon; and a Delsi Nermag Rock-Eval II with TOC (total organic carbon) option to characterize organic matter.

#### Gas Analyses

Hydrocarbon gases were extracted from sediment samples recovered at all three sites using methods adapted from Bernard et al. (1978) and Kvenvolden and Redden (1980). In addition, where high concentrations of core gas were encountered at Site 644, Vacutainers were used to collect the gas for shipboard and subsequent analyses (Claypool, et al., 1973). The procedure for gas extraction involved placing a sample of sediment (5-cm long, full round core, ~170 cm<sup>3</sup>) in a 1-pint (~0.5 L) can which had previously been prepared with septa-covered sampling ports. The can was filled with helium-purged (degassed) water, and a 100-cm<sup>3</sup> headspace was established by removing water from the can. The can was sealed, and the headspace purged with helium (250 mL/min for 10 min). The sample container was agitated for 10 min on a paint-can shaker to partition gases into the helium-filled headspace. A 5-mL sample of this headspace was withdrawn, and exactly 0.25 mL of the gas mixture was analyzed on a H-P 820 Natural Gas Analyzer, a special option for one of the H-P 5890A gas chromatographs. This option employs three columns (DC 200, Poropak Q, and Molecular Sieve 13X) and appropriate valve switching to provide for the determination of oxygen, nitrogen, carbon dioxide, methane, ethane, propane, the butanes, the pentanes and the total hexane + hydrocarbons. We monitored only the hydrocarbon gases.

Gases collected in Vacutainers and from the headspace of most canned samples from Site 644 were analyzed for methane utilizing the second H-P 5890A Gas Chromatograph equipped with 3.2 mm x 3.7 m Poropak Q (80-100 mesh) column and thermal conductivity detector. A typical injection volume was 0.2 mL. It was necessary to use this system for a rapid assessment of methane at high concentrations. In preparation for using Vacutainers, it was found that these commercial items contained an unacceptably high content of residual hydrocarbon gases. A method was devised to reduce the hydrocarbon "blank" of the Vacutainers as described later.

#### Carbon Analyses

Inorganic carbon was measured in two ways. In the first method, 1 g of dried sediment was placed in a Carbonate Bomb (Müller and Gastner, 1971) and digested with excess hydrochloric acid. The resulting pressure of carbon dioxide was measured

<sup>1</sup> Eldholm, O., Thiede, J., Taylor, E., et al., 1989. *Proc. ODP Sci. Results*, 104: College Station, TX (Ocean Drilling Program).

<sup>2</sup> U.S. Geological Survey, Menlo Park, CA 94025.

<sup>3</sup> Texas A&M University, College Station, TX 77843.

to determine the amount of inorganic carbon. In the second method, about 250 mg of dried sediment was treated with hydrochloric acid and gentle heating in the Coulometrics Carbonate Carbon apparatus (Huffman, 1977). In this apparatus the evolved carbon dioxide is transferred to a Coulometrics 5010 CO<sub>2</sub> Coulometer where ethanolamine is the indicator solution. As the evolved gas is passed through the solution, carbon dioxide is converted to a strong acid. Color change is monitored, and the results are reported in  $\mu\text{g C}$  and  $\% \text{CaCO}_3$ .

Organic carbon was determined either by digesting a sediment sample with acid to remove carbonate and analyzing the residual, dried, acid-free, carbonate-free material ( $\sim 15$  mg) on the P-E Elemental Analyzer. Alternately, the total carbon content of a nonacidified sample was measured on the P-E Elemental Analyzer, and the amount of organic carbon was determined by subtracting the content of carbonate carbon as measured by the Carbonate Bomb or the Coulometrics Coulometer.

### Rock-Eval Pyrolysis

Characterization of organic matter involved the programmed pyrolysis of 100 mg of dried, coarsely ground sediment in the Rock-Eval II with TOC option. The results of these analyses are presented in the individual site chapters of Eldholm, Thiede, Taylor, et al. (1987). Of interest to this paper are the TOC values which are compared with the organic carbon contents determined by combining information from the Carbonate Bomb, Carbonate Carbon apparatus, and Elemental Analyzer as discussed above.

### Potential Contaminants

To obtain gas chromatographic "fingerprints" of 35 potential organic geochemical contaminants, the following procedure was used: From 60 to 100 mg of each substance were weighed in glass vials. Each sample was dissolved in 5 -mL HPLC-grade *n*-hexane (Baker Analytical Reagent). Of the resulting mixture, 1  $\mu\text{L}$  (lesser amounts for specific materials) was analyzed with the H-P 5890A instrument configured for high-resolution, capillary gas chromatography. Conditions for gas chromatography are given in Table 1.

## RESULTS AND DISCUSSION

### Gas Analyses

Methane was the only hydrocarbon gas detected on the ship in samples from Sites 642 and 643 with one exception: Ethane in Section 104-643A-46-5 measured 2.1 ppm. The maximum concentration of methane was 23 ppm (volume of methane/volume of gas mixture). In contrast, at Site 644 below a sub-bottom depth of 22 m, concentrations of methane reach a maximum (as measured on the ship) of 51% (volume of methane/volume of gas mixture), and the methane was accompanied by higher molecular weight hydrocarbon gases. Table 2 compares the methane concentrations with depth at the three sites. Also for Site 644, concentrations of methane from Vacutainer samples are listed.

Average concentrations of methane extracted from sediment samples are:

Sites	643	642	644
CH <sub>4</sub> (avg.)	4.6 $\pm$ 3.5 ppm	8.7 $\pm$ 6.4 ppm	19.7 $\pm$ 16.6%

These concentrations are lowest in sediment at the foot of the Vøring Plateau (Site 643), a factor of two higher in sediment of the outer plateau (Site 643), and  $2 \times 10^4$  times higher in sediment of the inner plateau (Site 644). At Site 643, methane concentrations appear to be increasing with depth, probably due to dia-

**Table 1. Gas chromatographic conditions for analysis of potential organic geochemical contaminants.**

Instrument: HP-5890A Gas Chromatograph
Range — 0
Attenuation — 0
Injector temperature — 300°C.
Detector (FID) Temperature — 300°C.
Injection mode: Splitless
Purge B on after 0.8 min.
Column:
H-P Ultra Performance capillary
Phase: Cross-linked methyl silicone
Thickness: 0.11 microns
Internal diameter: 0.20 mm
Length: 25 m
Column pressure: 30 psi (helium)
Temperatures:
Initial: 40°C, 1 min.
30°C/min to 80°C.
Intermediate: 80°C
6°C/min to 300°C.
Final: 300°C, 15 min.

genesis and early catagenesis, but at Site 642 the amounts of methane decrease near the bottom of the hole as the basaltic basement is approached. In contrast, the concentrations are very high in samples at Site 644 below a sub-bottom depth of 22 m. Two maxima are present: 51.3% at 77.6 m and 41.4% at 235 m. In the upper part of the sediment section between about 80 and 150 m, gas expansion cracks were noted and sampled with Vacutainers. Methane composed between 45% and 89% (avg. =  $72.5 \pm 19.3\%$ ) of the gas mixture in the cracks; the remainder of the gas was likely air.

The rapid increase in concentration of methane below a sub-bottom depth of about 22 m follows a rapid decrease in the amount of sulfate in the pore waters (See site chapters in Eldholm, Thiede, Taylor, et al., 1987). In fact, there is an inverse correlation between methane and sulfate concentrations showing that the occurrence of methane is intimately tied to the absence of sulfate (Claypool and Kaplan, 1974). To account for these observations, the environment at Site 644 must be reducing, with methane resulting from the microbial reduction of carbon dioxide. The minimal concentrations of methane at Sites 642 and 643 suggest that the environments there are oxidizing.

In addition to methane, higher molecular weight hydrocarbon gases were also present at Site 644. In order of increasing depth ethane appeared first followed by propane, *n*-butane, and finally *n*-pentane. Overall there is a general increase with depth in the concentrations of these gases. Kvenvolden et al., (this volume) discuss in detail the geochemistry of hydrocarbon gases at the three sites. They report that not only are the higher molecular weight hydrocarbon gases present at Site 644, but also at Sites 642 and 643, based on laboratory studies onshore.

### Preparation of Vacutainers for Shipboard Use

#### The problem

Gas escaping from sediment is often manifest as gas expansion cracks or voids developed while the sediment is confined in the core liner. The gas in these voids is sampled by means of Vacutainers. The procedure involves a special tool consisting of a hollow point for penetrating the coreliner, a valve to control the release of gas, and a needle to let the gas pass into a Vacutainer. The procedure works well for collecting gas samples, but the Va-

Table 2. Comparison of methane concentrations at Sites 643, 642, and 644.

Site 643 Foot of Vöring Plateau			Site 642 Outer Vöring Plateau			Site 644 Inner Vöring Plateau			Vacutainers		
Hole- Core- Section	Sub-bottom depth (m)	CH <sub>4</sub> ppm	Hole- Core- Section	Sub-bottom depth (m)	CH <sub>4</sub> ppm	Hole- Core- Section	Sub-bottom depth (m)	CH <sub>4</sub> (%)	Hole- Core- Section	Sub-bottom depth (m)	CH <sub>4</sub> (%)
A-1-2	3.0	0.8	B-1-2	2.9	2.7	A-1-4	5.9	0.00			
A-4-4	30.3	5.2	A-1-3	5.7	11.0	A-3-4	22.1	0.08			
A-7-5	60.3	1.3	B-2-5	12.2	2.3	A-5-3	39.6	3.4			
A-10-5	88.7	3.0	B-4-4	26.6	1.7	A-7-2	57.1	39.8			
A-13-5	117.3	0.9	B-5-4	35.3	3.3	A-9-3	77.6	51.3	A-9-5	80.2	81.3
A-16-5	145.8	1.3	B-7-4	53.3	4.5	A-10-4	88.6	—	A-10-1	83.0	56.3
A-19-5	174.3	2.9	B-8-4	62.8	4.9	A-11-5	99.6	16.5	A-11-4	96.8	84.1
A-22-4	201.2	3.7	B-10-4	81.8	9.2	A-14-3	125.1	38.4	A-12-7	111.0	84.5
A-25-5	232.2	4.0	B-11-4	91.3	8.5	A-15-4	136.1	23.6	A-14-2	122.4	89.9
A-28-5	261.6	9.3	B-13-4	110.1	6.1	A-16-4	145.6	—	A-15-5	136.2	45.0
A-31-5	291.0	1.8	B-16-6	137.0	11.9	A-17-2	152.1	13.3	A-16-2	141.4	89.4
A-34-2	315.8	1.1	B-19-4	163.6	15.3	A-20-4	183.6	7.2	A-17-1	150.3	47.7
A-37-2	346.7	5.0	C-22-3	181.9	14.5	A-22-4	192.7	2.3			
A-44-5	417.5	5.5	B-22-4	192.6	23.0	A-23-4	200.0	1.0			
A-46-5	436.9	9.0	D-4-5	216.6	21.7	A-25-2	208.9	23.4			
A-49-4	464.4	4.9	B-25-4	219.0	12.9	A-28-2	219.0	31.7			
A-52-5	494.8	12.8	D-7-5	245.6	10.8	A-29-2	224.0	14.3			
A-56-5	533.5	9.7	D-10-5	274.5	5.8	A-31-2	235.0	41.4			
			D-13-2	299.1	1.4	A-34-4	251.9	27.4			

cutainers have a background of hydrocarbon gases which can interfere significantly in analyses, especially when the core gas itself contains low amounts of hydrocarbons. We made a brief study of the hydrocarbon gases in Vacutainers, and describe a simple way to clean up the Vacutainers so that they are acceptable for shipboard work.

#### Method

Vacutainers were selected randomly from Lot 4F093 (Exp. Date 07/15/86) supplied by B-D (Becton-Dickinson): Vacutainer Brand; Evacuated Blood Collection Tube; Red Stopper, 20 mL, 165 x 16 mm; 100 tubes per lot; Becton-Dickinson, Division of Becton, Dickinson and Co., Rutherford, New Jersey 07070.

We tested various ways to remove the hydrocarbon background from the Vacutainers. The H-P 5890A Gas Chromatograph with Option 820 (Natural Gas Analyzer) was used to detect and quantify the hydrocarbons. In all of our trials we employed the Labconco Freeze Dryer 8 as a vacuum source to remove hydrocarbons and to reestablish vacuum within the Vacutainers. For this purpose we plugged a port of the freeze-dryer with a Vacutainer stopper inserted backwards. A double-ended 20G needle (B-D Vacutainer Needle) was used to connect the plugged port of the freeze-dryer to a Vacutainer. In our first trials, we removed the stopper from the Vacutainer and flushed the open tube with helium. We reassembled the Vacutainer and evacuated with the freeze-dryer. We found this method could satisfactorily remove the hydrocarbons, but an alternate procedure worked just as well and was faster. In this alternate procedure, we simply took the Vacutainer as supplied and attached it to the freeze-dryer. Evacuating for a period of 10 min or longer essentially removed the hydrocarbon gases.

#### Results and Discussion

Vacutainers as supplied by B-D have a vacuum of about 510 to 610 mm Hg. With the freeze-dryer, a vacuum of about 640 mm Hg could be established in the Vacutainers. This latter vacuum could be detected with the Vacuum Leak Detector, commonly called a Tesla Coil, (for example, Thomas Scientific Cat. #9675-L10). In our survey of B-D Vacutainers, we found that only about three of 20 Vacutainers had sufficient vacuum to test

positively (bluish glow in a darkened room). When vacuum was reestablished in the Vacutainers by means of the freeze-dryer, this vacuum gave a positive test with the vacuum leak detector. A vacuum gage (for example, Alltech Cat. #8028) was used to measure the actual vacuum, but with each test the vacuum was reduced by 50 mm Hg.

We found that the reestablished vacuum varied after a 24-hr period. In our tests the vacuums ranged from 510 to 610 mm Hg after 24 hr, but one Vacutainer had atmospheric pressure. Because of this last result, we recommend that the Vacutainers with reestablished vacuums be used within 12 hr and that the vacuums be checked with a leak detector or gage immediately before use.

To test the hydrocarbon background in Vacutainers, we added an atmosphere of helium to each Vacutainer and removed 5 cm<sup>3</sup> for injection into the gas chromatograph. Figures 1A-1E illustrate by means of gas chromatograms the hydrocarbon background of the Vacutainers and the reduction of this background by the procedures just described. Figure 1A shows a standard mixture of hydrocarbons and is for reference. Figure 1B shows a typical hydrocarbon background in the Vacutainers of the lot supplied by B-D. Methane, ethane, propane, and *n*-hexane are present in concentrations ranging from 5 to 113 ppm. An unknown is also present at concentrations comparable to methane. (This unknown has a retention time between isobutane and *n*-butane.) After the Vacutainer was evacuated on the freeze-dryer, the hydrocarbon background was reduced (Fig. 1C) so that the only hydrocarbon detected was methane at 2 ppm. The unknown was also reduced significantly. Sometimes the hydrocarbon background was completely removed (Fig. 1D) and could not be distinguished from the helium blank (Fig. 1E). Thus, by reestablishing the vacuum in Vacutainers, the hydrocarbon background, except for methane, cannot be detected. Methane can be reduced to at least 2 ppm and often to lower concentrations.

Upon storage of the Vacutainers with reestablished vacuums for 24 hr, there appears to be an increase in the concentration of the unknown. Methane may also increase in amount, but as illustrated in the example on Figure 1F, the methane is present at less than 2 ppm. The source of the increasing compounds is likely the rubber stopper of the Vacutainer. Because of the possibility of continued outgassing from the stopper during a 24-hr

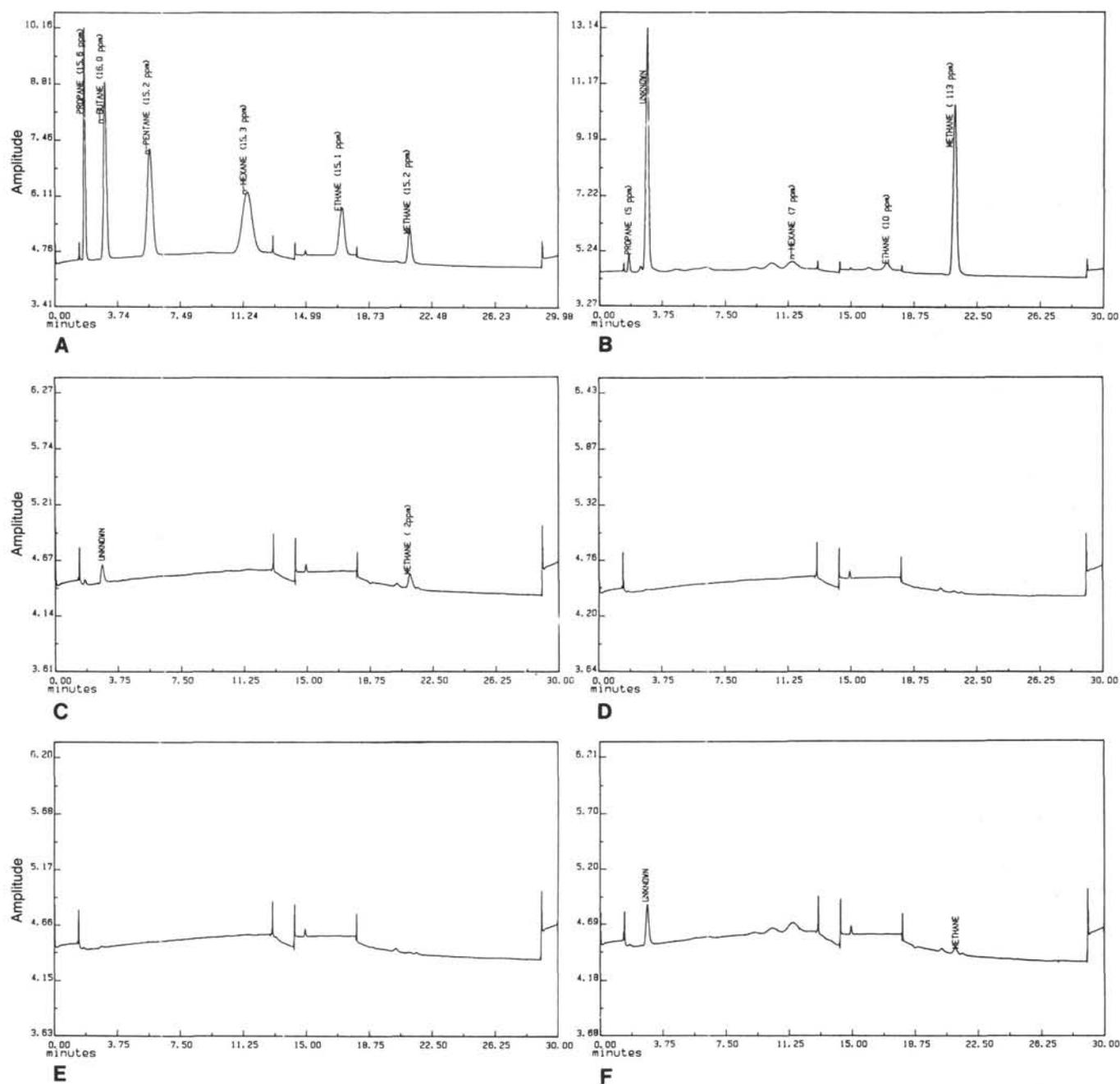


Figure 1. Gas chromatograms showing the clean-up of Vacutainers: A. Standard showing methane through *n*-hexane; B. Vacutainer background; C. Reduced background after treatment; D. Background removed; E. Helium blank; F. Vacutainer blank after treatment and storage.

storage under vacuum, we recommend that the Vacutainers be used within 12 hr of their preparation.

We also noted that if a prepared Vacutainer was stored with an atmosphere of helium inside for 24 hr, there was no obvious increase in the amounts of background components. This preliminary observation suggests that the cleaned-up Vacutainers can be used for long-term storage. For this purpose we recommend that RTV Silicone Sealant be used to coat the stopper where needle penetrations have been made. The use of these prepared Vacutainers for long-term storage should be investigated further before committing them for this purpose. For sample collection, however, the cleaned-up Vacutainers appear

to be adequate if precautions are taken to use the Vacutainers soon after the clean-up procedure.

#### Summary

The hydrocarbon background of shipboard B-D Vacutainers can be reduced significantly and in most cases below detection limits by simply evacuating the Vacutainer on the laboratory freeze-dryer for at least 10 min. The vacuum can be checked with a vacuum leak detector or vacuum gage which should read about 640 mm Hg. It is recommended that the Vacutainers be used within 12 hr of preparation to ensure that no new hydrocarbons have outgassed from the rubber stopper. The use of

these prepared Vacutainers for long-term sample storage needs further investigation.

### Carbon Analyses

The content of organic carbon is a fundamental property of sediments. This property was measured at the three sites, and the results are shown in Table 3. Average amounts of organic carbon at each site are:

Sites	643	642	644
$C_{org}$ (avg.)	$0.48 \pm 0.49\%$	$1.07 \pm 0.53\%$	$0.69 \pm 0.17\%$

Comparison of the information on Tables 2 and 3 and of the average values for methane concentrations and organic carbon contents show that there is little or no correlation between these geochemical parameters. At Site 642 where organic carbon is most abundant (avg.  $\sim 1.07\%$ ) the average concentration of methane is only about 9 ppm. In contrast, at Site 644 where high concentrations of methane are found (avg.  $\sim 20\%$ ) the average amount of organic carbon is only about 0.7%. The sediments at Site 643 have low average methane concentrations ( $\sim 5$  ppm) and low average organic carbon contents ( $\sim 0.5\%$ ). The results suggest that where there are reducing conditions and low sulfate concentrations as at Site 644, methanogenesis is active, and methane concentrations are high. At the other two sites the environmental conditions are likely oxidizing and sulfate is present (see site chapters in Eldholm, Thiede, Taylor, et al., 1987), thus limiting the amount of methane produced even though organic carbon is available. Therefore, in a regional sense an inverse correlation exists between amounts of methane and organic carbon; on the inner Vøring Plateau (Site 644) methane concentrations in sediments are high and organic carbon values are low whereas on the outer plateau (Site 642) the amount of methane is low and organic carbon contents are relatively high. At the foot of the plateau (Site 643) the amounts of both methane and organic carbon are low.

We investigated alternative ways of measuring organic carbon to try to find a reliable method for shipboard use. For Site 642 we acidified the samples and determined organic carbon ( $C_{org}$ ) directly with the Elemental Analyzer. The values for  $C_{org}$ , shown in Table 3, represent replicates and are believed to be good estimates of the organic carbon content of sediments at Site 642. Separate portions of nonacidified sediment samples were analyzed by Rock-Eval to determine TOC (Table 3). There was no agreement between  $C_{org}$  and TOC at this site. We believe the TOC values are in error because flow rates for the instrument may have been incorrectly set.

Because the acidification step was time-consuming and might result in contamination, we modified the procedure for determining organic carbon in sediments at Sites 643 and 644. We eliminated the acidification step and determined organic carbon by difference between the total carbon (from the Elemental Analyzer) and the inorganic carbon (from the Carbonate Carbon apparatus or the Carbonate Bomb). That this procedure was feasible was ascertained by reexamining some samples from Site 642 (Table 4). This comparison showed that at least for these kinds of sediments, organic carbon determined by difference provides a reasonable estimate of the organic carbon content.

Although Rock-Eval TOC values for sediments at Site 642 were not comparable with  $C_{org}$ , at the other sites there was reasonable agreement (Table 3). At Site 643 there was agreement between  $C_{org}$  and TOC for sediments from sub-bottom depths exceeding about 145 m; for the more shallow samples, there was no agreement. Values of  $C_{org}$  and TOC for sediments at Site 644 are comparable, with a few exceptions. Thus, Rock-Eval TOC values may be used with caution as an estimate of the organic carbon content of sediments.

**Table 3. Comparison of organic carbon ( $C_{org}$ ) and TOC (total organic carbon) from Rock-Eval pyrolysis.**

Hole-Core-Section	Depth (mbsf)	$C_{org}$ (%)	TOC (%)
Site 643			
A-1-2	3.0	0.25	0.08
A-4-4	30.3	0.22	0.11
A-7-5	60.3	0.42	0.06
A-10-5	88.7	0.11	0.72
A-13-5	117.3	1.05	0.35
A-16-5	145.8	0.19	0.18
A-22-4	201.2	0.62	0.55
A-25-5	232.2	0.66	0.67
A-28-5	261.6	0.73	0.74
A-31-5	291.0	0.80	0.74
A-34-5	315.8	1.08	1.06
A-37-5	346.7	1.78	1.72
A-44-5	417.5	0.11	0.10
A-46-5	436.9	0.09	0.11
A-49-4	464.4	0.05	0.08
A-52-5	494.8	0.05	0.06
A-56-5	533.5	0.00	0.07
Site 642			
B-4-4	26.6	0.34	0.00
B-7-4	53.3	0.44	0.10
B-10-4	81.8	0.83	0.16
B-13-4	110.1	0.66	0.03
B-16-6	137.0	1.43	0.10
B-19-4	163.6	1.50	0.11
C-22-3	181.9	1.74	0.28
B-22-4	192.6	1.84	0.01
D-4-5	216.6	1.17	0.39
D-25-4	219.0	1.25	0.29
D-7-5	245.6	1.00	0.30
D-10-5	274.5	1.31	0.22
D-13-2	299.1	1.34	0.12
D-18-2	326.4	0.06	—
Site 644			
A-1-4	5.9	0.37	0.38
A-3-4	22.1	0.64	0.56
A-5-3	39.6	0.68	0.72
A-7-2	57.1	0.96	1.05
A-10-4	88.6	0.46	0.42
A-14-3	125.1	0.77	1.08
A-16-4	145.6	0.81	0.13
A-20-4	183.6	0.64	0.61
A-25-2	208.9	0.82	0.49
A-29-2	224.0	0.73	0.67
A-34-4	251.9	0.69	0.71

### Catalog of Potential Organic Geochemical Contaminants

At least 35 different organic and organic-related substances in use aboard the *JOIDES Resolution* can become incorporated in cores during the sampling procedure. For the most part, these contaminants do not interfere with scientific studies of the core material; however, certain investigations in organic geochemistry can be seriously affected by the presence of these substances. For example, naturally occurring bitumen is of special importance to petroleum geochemists. Bitumen, also called extractable organic material (EOM), is recovered from sediments by solvent extraction, but the contaminants that have found their way into the cores will also be extracted by the solvent. Therefore, in the analysis of bitumen in oceanic sediment collected through the Ocean Drilling Program, it is essential that distinction be made between naturally occurring bitumen and organic contaminants. The purpose of this catalog is to provide a guide

**Table 4. Comparison of organic carbon percentages determined by difference and by direct measurement of acidified samples from Site 642.**

Site 642 Hole-Core Section	Sub-bottom depth (m)	(a) % Total carbon elemental analyzer	(b) % Carbonate carbon	(c) % Carbonate carbon (Bomb)	% Organic carbon (difference a-b)	% Organic carbon (difference a-c)	% Organic carbon (acidified) elemental analyzer
B-4-4	26.6	1.15	0.86	0.84	0.29	0.31	0.34
B-7-4	53.3	0.46	0.01	0.00	0.45	0.46	0.44
B-10-4	81.8	1.26	0.49	0.00	0.77	1.26	0.83
B-13-4	110.1	2.60	2.00	1.92	0.60	0.68	0.66
B-16-6	157.0	2.76	1.66	1.80	1.10	0.96	1.43
B-19-4	163.6	2.95	1.83	1.56	1.12	1.39	1.48
B-22-4	192.6	1.78	0.01	0.00	1.77	1.78	1.84
D-4-5	216.6	1.28	0.00	0.00	1.28	1.28	1.17
D-7-5	245.6	1.14	0.02	0.00	1.12	1.14	0.98
D-10-5	274.5	1.28	0.01	0.00	1.27	1.28	1.31
D-13-2	299.1	1.34	0.03	0.00	1.31	1.34	1.34

to shipboard substances that can contaminate cores and become a potential problem for organic geochemistry.

The collection and analysis of potential organic geochemical contaminants was begun on ODP Leg 103 (Dunham, 1987). Nine substances were identified and analyzed by gas chromatography. We have now assembled a collection of 35 potential organic geochemical contaminants. The following information is provided for each of these materials: common or trade name, product description, manufacturer, and general usage during drilling, coring, and laboratory operations. The substances have been organized into four groups according to the probability of the material contaminating the core; the groups range from those materials with high probabilities of being contaminants to those that have very little chance of getting into the cores.

Each of the 35 substances was placed in *n*-hexane; most of the substances dissolved in this solvent, but some only partially went into solution. The mixtures were analyzed by capillary gas chromatography, and the resulting chromatograms are "fingerprints" of 35 potential organic geochemical contaminants. These chromatograms form the basis of this catalog. Figure 2A shows a gas chromatogram of a standard *n*-alkane mixture, prepared onboard from kits (Poly Science Corporation), with compounds ranging from *n*-C<sub>16</sub> to *n*-C<sub>36</sub>. Figure 2B is a gas chromatogram of the hexane blank which shows the background that must be present in the gas chromatograms of the samples reported here.

Descriptions of the 35 potential organic geochemical contaminants, along with the quantity of each that was placed in hexane, appear on Tables 5, 6, 7, and 8, which list, respectively, the substances having high, medium, low, and very low probabilities of contaminating the cores. Chromatographic "fingerprints", as obtained through the LAS-CPLLOT computer system, are shown in Figures 3 through 6. These chromatograms were prepared using the same enlargement factor (3.0) to facilitate comparison of the various "fingerprints." The figures are arranged in the order given on Tables 5 through 8. Compounds in the standard (Fig. 2A) will be used for discussion of some of the "fingerprints" of the potential contaminants.

Eleven substances with the greatest opportunity to be core contaminants are listed in Table 5 (Figs. 3A-3K). Of these materials, two kinds of Pipe Dope (lead- and zinc-based), Line Tar, and Cable Coating are likely to get into the core during the actual drilling process. The two types of Pipe Dope, used on drill pipe and drill collar connections, are manifest chromatographically as unresolved, complex mixtures spanning a broad range of molecular weights (Figs. 3A and 3B). Line Tar, with which the manufacturers coated sand lines and logging lines, also contains a complex mixture with discrete compounds in the range from *n*-C<sub>16</sub> to *n*-C<sub>37</sub> (Fig. 3C). The typical Cable Coating, which

is sprayed on sand lines and logging lines, is composed mainly of compounds with retention times less than *n*-C<sub>13</sub> but also has a complex mixture of high molecular weight compounds (Fig. 3D). 3-in-One Oil, which is a rust inhibitor (Fig. 3C), and Parker O-Lube, which is an O-ring grease (Fig. 3F), both contain unresolved complex mixtures of compounds spanning different molecular weight ranges, with Parker O-Lube having heavier compounds. The Silicone O-ring Grease (Fig. 3G) and the Marking Pencil (Fig. 3H) contain high molecular weight silicone compounds which extracted into the hexane solvent. WD-40 (Fig. 3I) could be particularly troublesome for organic geochemistry because it contains discrete compounds of both low and intermediate molecular weights and is used generously on the coring equipment and in the laboratory. GO-JO Hand Cleaner (Fig. 3J) has mainly low molecular weight components. Core liners are often coated with this material to aid insertion through the O-ring seals and into the core barrel; therefore, GO-JO can easily get into the cores. Also, GO-JO is commonly used as a hand cleaner and thus could be transferred to cores that have been touched with bare hands. Super Agitene (Fig. 3K), from the parts-cleaning tank, contains mainly low molecular weight compounds with retention times less than *n*-C<sub>13</sub>.

Nine substances were identified which have a medium probability of contaminating the cores (Table 6). Many of these materials are thread lubricants. Multigrease (Fig. 4A), Jet Lube (Fig. 4B), Lubriplate (Fig. 4C), Never-Seez (Fig. 4D), Aqua Lube (Fig. 4E), and all-Purpose Lube Oil (Fig. 4F) are composed mostly of unresolvable, complex mixtures of compounds having wide ranges of molecular weights. E-Z Break contains discrete compounds with retention times near *n*-C<sub>26</sub> (Fig. 4G). The chromatogram of the Compensator Oil shows a number of resolved compounds (Fig. 4H), and 7-11 Oil (Fig. 4I) is made up of mainly low molecular weight compounds with retention times less than *n*-C<sub>13</sub> but also contains some heavier molecular weight components.

Eleven substances have a low probability of being incorporated into the cores (Table 7). Hydraulic fluid (Fig. 5A) and Molybde (Fig. 5B) are composed mainly of complex mixtures of compounds, most of which are not resolved by gas chromatography. Chromatograms of Tapeze (Fig. 5C), rig wash detergent (Fig. 5D), and CO Contact Cleaner (Fig. 5C) are simple and are similar to the chromatogram of the hexane blank (Fig. 2B); these substances should pose few problems for organic geochemistry. Bakerlok (Fig. 5F), Silicone Lubricant #111 (Fig. 5G), and Vaseline Hand Lotion (Fig. 5H) also produce simple chromatograms with a few well-resolved peaks. The chromatogram for Contact Cleaner #2-26 (Fig. 5I) is much more complicated than that of the CO Contact Cleaner (Fig. 5E). The #2-26

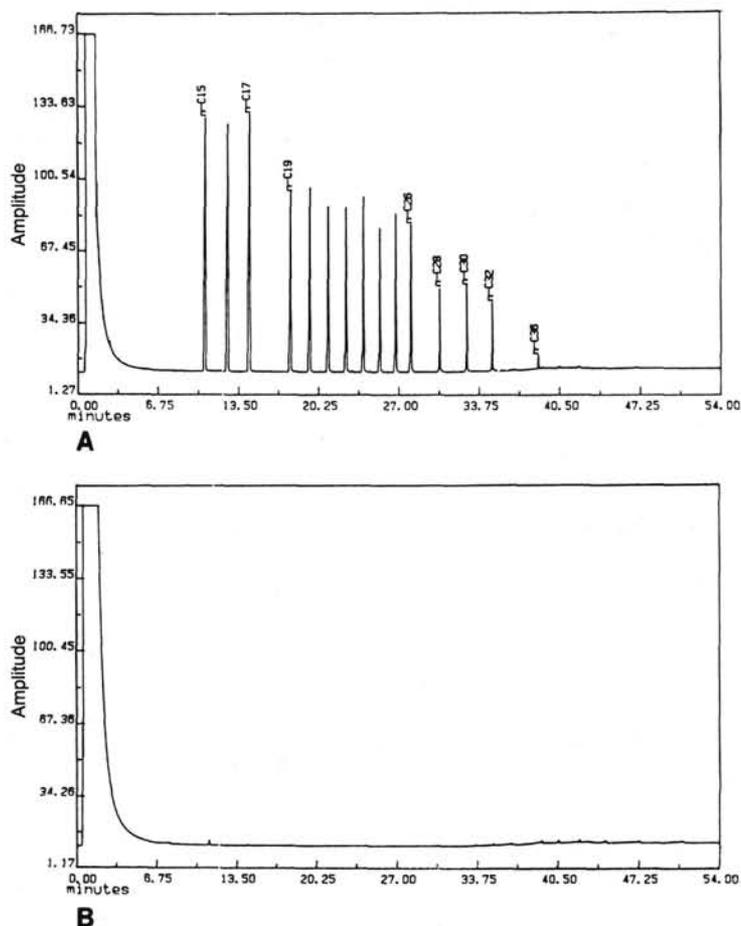


Figure 2. A. Gas chromatogram showing standard alkane mixture; B. Gas chromatogram of helium blank.

Cleaner is composed of low and intermediate weight compounds whereas the CO Contact Cleaner apparently contains only compounds that elute with the *n*-hexane solvent. Diesel Fuel #2 (Fig. 5J) is dominated by a mixture of *n*-alkanes ranging up to about *n*-C<sub>28</sub> and Liquid Wrench (Fig. 5K) appears to contain *n*-alkanes up to about *n*-C<sub>21</sub> among other compounds.

Table 8 lists four substances which have a very low probability of contaminating the cores. Gear Oil (Fig. 6A) contains an unresolved, complex mixture of compounds with retention times greater than about *n*-C<sub>25</sub>. Carboline Thinner #10 (Fig. 6B) appears to be a simple mixture of compounds with molecular weights near that of the *n*-hexane solvent. RTV Silicone Rubber (Fig. 6C) is composed of a series of silicone compounds spanning a broad molecular weight range. Finally, the Martin Decker Fluid (Fig. 6D) is made of a complex mixture of components with retention times less than about *n*-C<sub>17</sub>.

The substances having high and medium probabilities of contaminating the cores are grouped in Table 9 according to three categories of usage: drilling, core equipment, and laboratory. Those substances used in drilling are inadvertently incorporated into the core, and this kind of contamination cannot readily be controlled. Some control can be exercised, however, in the preparation of coring equipment, but because lubrication of these parts is necessary, contamination of the core by lubricants is always a possibility. In the laboratory, careful practice and attention to detail can minimize the contamination occurring there. One possible path of contamination goes from the roughnecks' gloves to the core liner to the marine technicians' hands to the core itself.

The chromatographic "fingerprints" shown in Figures 3 through 6 should be useful in distinguishing shipboard-related, petroleum-like substances from naturally occurring, petroleum-related materials that may be encountered during core recovery and processing. The conditions under which these 35 potential contaminants were prepared and analyzed have been described explicitly so that unknown samples can be analyzed in the same manner. This catalog should be helpful in safety monitoring and should provide organic geochemists with a preliminary means of detecting contaminated samples during cruise and postcruise studies.

## SUMMARY

Based on previous geochemical studies from DSDP Leg 38 (Talwani, Udintsev, et al., 1976) we predicted that high concentrations of gaseous hydrocarbons would be found at Site 644 but not at Sites 642 and 643. This prediction was realized. Only methane, not exceeding 25 ppm, was found at Sites 642 and 643, whereas at Site 644, below a sub-bottom depth of 22 m, methane, reaching a maximum of 51% was extracted from sediments. This methane was accompanied by increasing concentrations of the higher molecular weight hydrocarbon gases.

At none of the sites did we find evidence for liquid or solid hydrocarbons although we prepared for this eventuality by developing a catalog of potential geochemical contaminants that might be confused chemically with naturally occurring hydrocarbons. At DSDP Site 341, where high concentrations of methane were found (Morris, 1976), evidence for possible petroleum hydrocarbons was noted only in the Miocene section. Our ana-

**Table 5. Substances with a high probability of contaminating cores.**

Common/trade name	Product description	Manufacturer	Usage	Wt(mg)
Pipe Dope, Lead Based (Fig. 3A)	Drill Collar Compound SEDCO L-60, 60% Lead (Pb) 293-W-7258	SEDCO, Inc. Dallas, Texas	Drill Collar and BHA connections	80
Pipe Dope, Zinc Based (Fig. 3B)	Drill Collar Compound SEDCO ZN-50, 50% Zinc (Zn) 293-R-1226	SEDCO, Inc. Dallas, Texas	Drill pipe connections	70
Line Tar (Fig. 3C)	Unknown	Greening Donald Ltd. Rochester Corporation Victor Cable Company	Coating on sand lines and logging lines. Applied during manufacturing	50
Cable Coating (Fig. 3D)	CCX-77	Certified Laboratories Division of NCH Forth Worth, Texas	Sprayed on sandlines and logging lines to inhibit corrosion	50
3-in-One Oil (Fig. 3E)	Household Oil Spray	Boyle-Midway, Inc. New York, New York	Rust inhibitor on "Super Saw"	100
Parker O-Lube (Fig. 3F)	Barium Base, O-ring grease	Parker Seal Company	Greasing O-rings and seals on coring equipment	70
Silicone O-ring Grease (Fig. 3G)	Dow Corning 4-Compound	Dow Corning Corporation Midland, Michigan	Greasing O-ring and seals on coring equipment	70
Marking Pencil (Fig. 3H)	"Phano" China Marking Pencil	Joseph Dixon Crucible Co. Writing Products Div. Jersey City, New Jersey	Marking bottom of hard rock cores	50
WD-40 (Fig. 3I)	WD-40	WD-40 Company San Diego, California	Loosen rusted threads on coring and lab. equipment "Super Saw" blades	80
GO-JO Hand Cleaner (Fig. 3J)	GO-JO Stock #1111	GO-JO Industries, Inc. Akron, Ohio	Hand Cleaning and for greasing APC core liners during insertion	70
Super Agitene (Fig. 3K)	Parts Cleaning Fluid Super Agitene M-5005-5	Graymills Corporation Chicago, Illinois	Parts cleaning tank in the tool room	60

log Site 644, where high methane concentrations occur, was terminated before reaching the Miocene, to minimize the chance of recovering petroleum-like substances.

Our studies have shown that the occurrence of methane on the Vøring Plateau can be predicted; that is, high concentrations of methane can be expected on the inner plateau where sediments apparently are reducing, whereas sediments of the outer plateau contain very little gas. Regionally there is an inverse correlation between the amounts of methane and organic carbon; on the inner plateau where methane concentrations are high, organic carbon contents are low. On the outer plateau (Site 642) the opposite is true.

Methods for determining organic carbon were evaluated. For the kinds of sediments found at these sites, organic carbon values can be most efficiently determined by taking the difference between total carbon and carbonate carbon. Total organic carbon (TOC), as determined by Rock-Eval pyrolysis, can also be used as a measure of organic carbon content but with caution.

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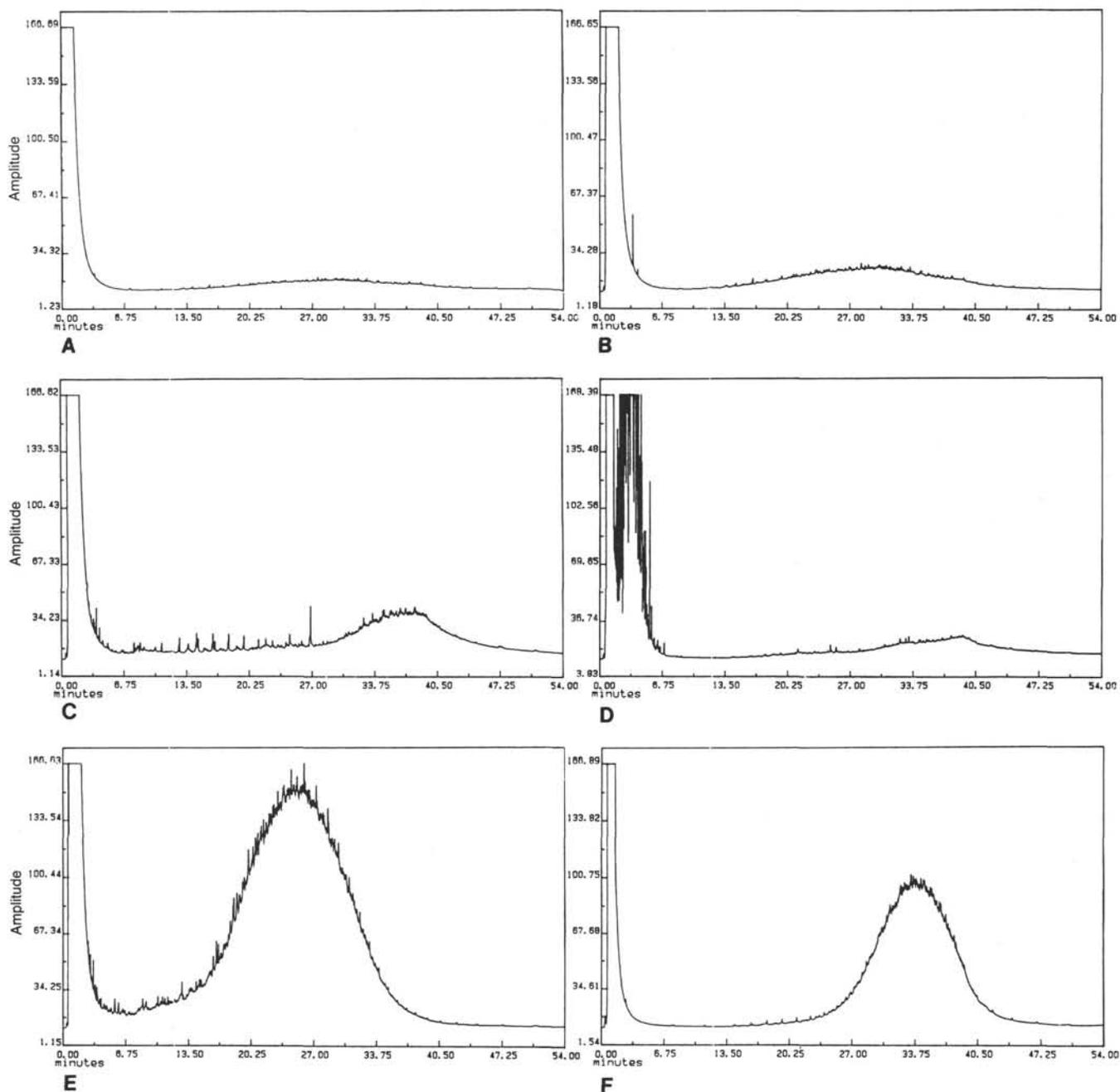


Figure 3. Gas chromatogram of substances with high probability of contaminating cores (Table 5): A. Pipe dope, lead based; B. Pipe dope, zinc based; C. Line tar; D. Cable coating; E. 3-in-one oil; F. Parker 0-lube; G. Silicone 0-ring grease; H. Marking pencil; I. WD-40; J. GO-JO hand cleaner; K. Super Agitene.

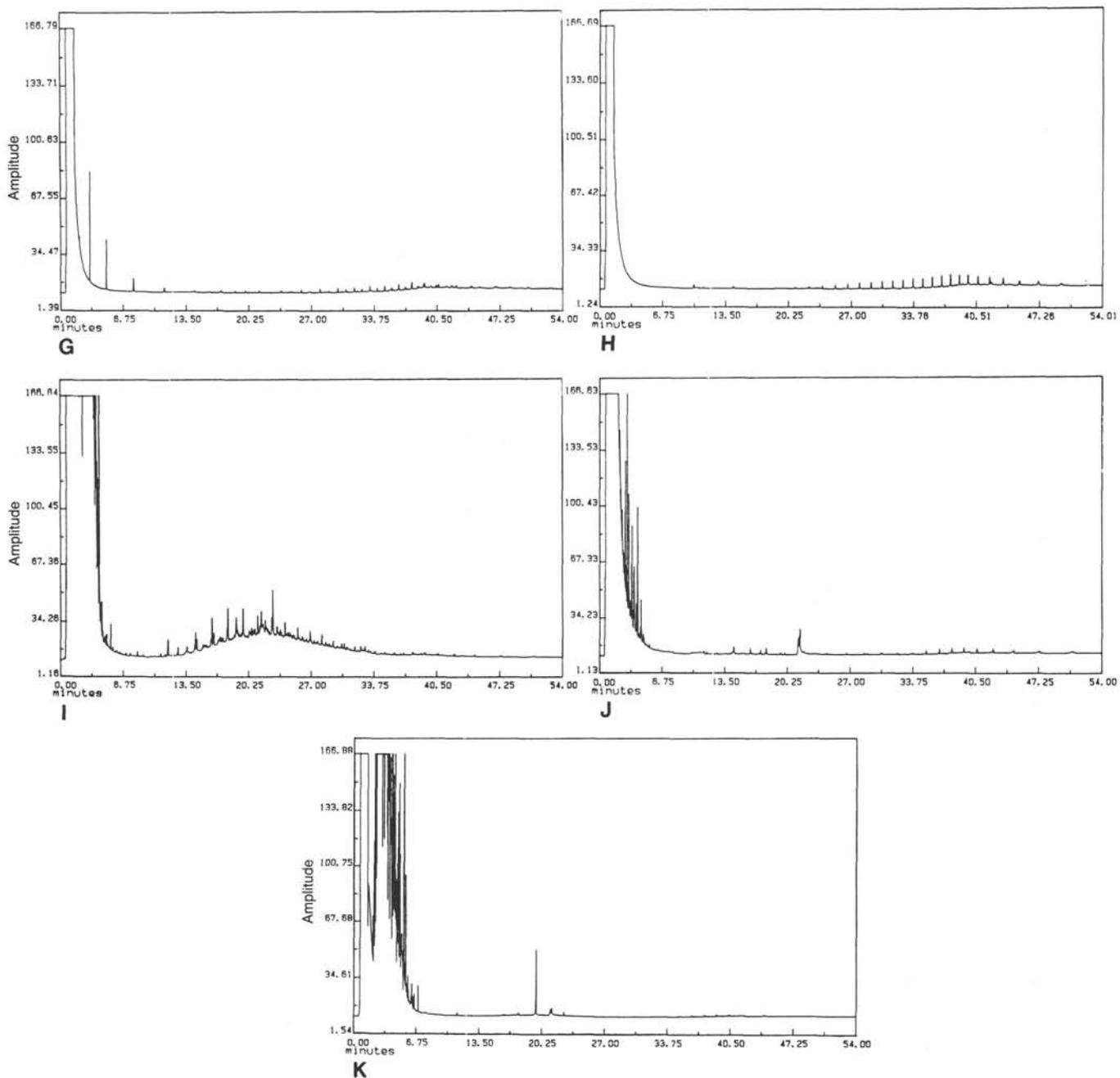


Figure 3 (continued).

**Table 6. Substances with a medium probability of contaminating cores.**

Common/trade name	Product description	Manufacturer	Usage	Wt(mg)
Multi-Grease (Fig. 4A)	Energrease BP LS EP 2	City Wide Petroleum Houston, Texas	Greasing rig equipment and core barrel swivels	60
Jet Lube (Fig. 4B)	SS-30 Jet Lube	Jet Lube, Inc. Houston, Texas	Thread corrosion inhibitor on some laboratory equipment	70
Lubriplate (Fig. 4C)	Lubriplate 630-2 PN 07201	Fiske Brothers Refining Co. Lubriplate Division Newark, New Jersey	Thread Lubricant on coring equipment and special tools	80
Never-Seez (Fig. 4D)	Anti-seize and Lubricating Compound, Pure Nickel Special	Never-Seez Compound Corp. Bostik Chemical Group Broadville, Illinois	Thread lubricant on coring equipment	80
Aqua Lube (Fig. 4E)	Aqua Lube	Far Best Corporation Allube Division Los Angeles, California	Water resistant lubricant for lab. equipment	60
All Purpose Lube Oil (Fig. 4F)	All Purpose Lubricating Oil	Watsco, Inc. Hialeah, Florida	Lubricating of saw on core cutter	60
E-Z Break (Fig. 4G)	High Temperature, Anti- seize and Lubricating compound	Markal Co./Lake Chemical Company Chicago, Illinois	Thread lubricant on coring equipment	70
Compensator Oil (Fig. 4H)	Quintolubric 822-TCF Synthetic Lubricant	Quaker Chemicals	Hydraulic Oil used in motion compensator	50
7-11 Oil (Fig. 4I)	#711-B Penetrat-Lubricant	Sprayon Products Inc. Industrial Supply Division Bedford Heights, Ohio	Corrosion inhibitor containing petroleum distillates for cleaning coring parts	60

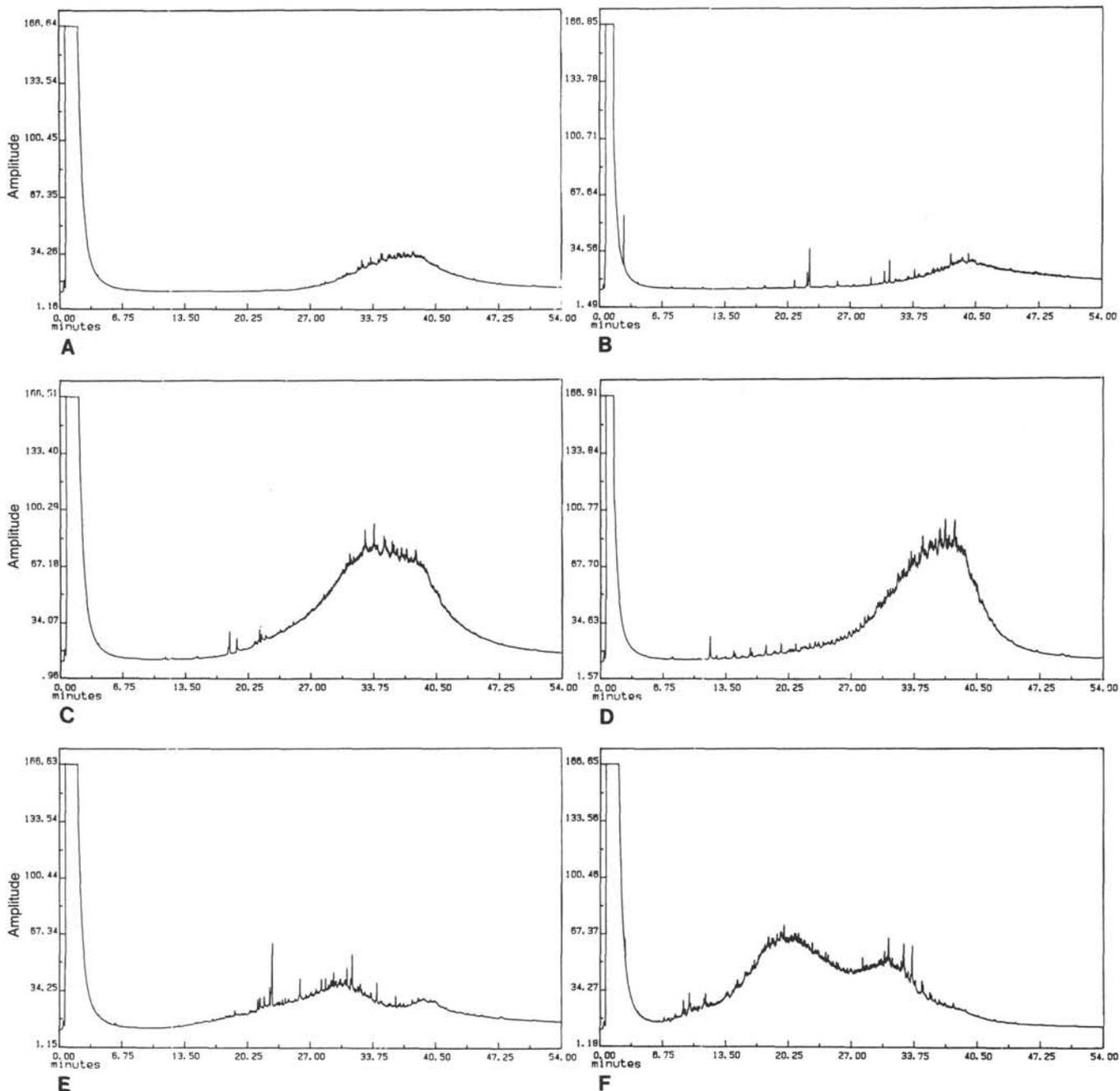


Figure 4. Gas chromatograms of substances with medium probability of contaminating cores (Table 6): A. Multigrease; B. Jet Lube; C. Lubriplate; D. Never-Seez; E. Aqua-Lube; F. All-purpose lube oil; G. E-Z Break; H. Compensator oil; I. 7-11 oil.

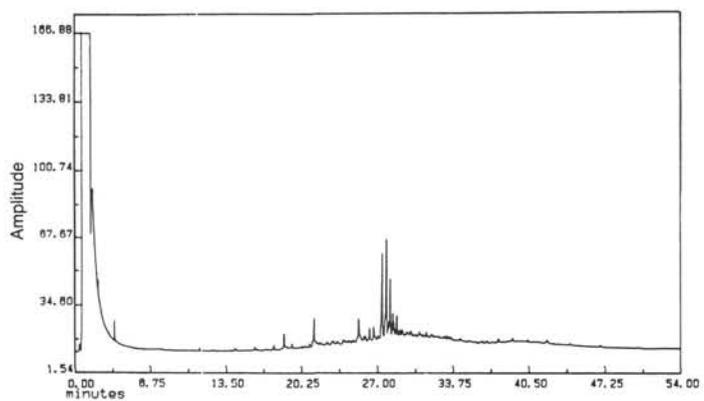
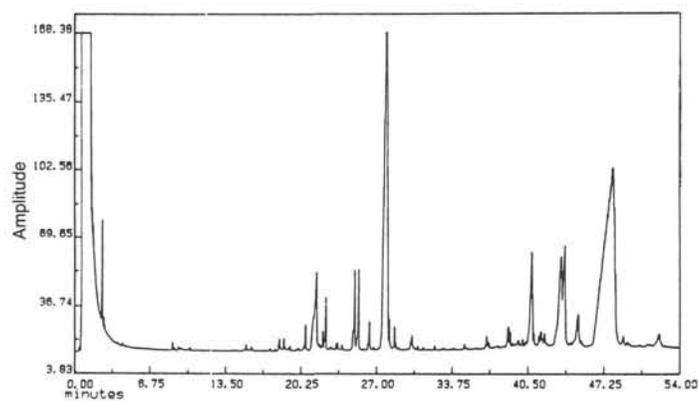
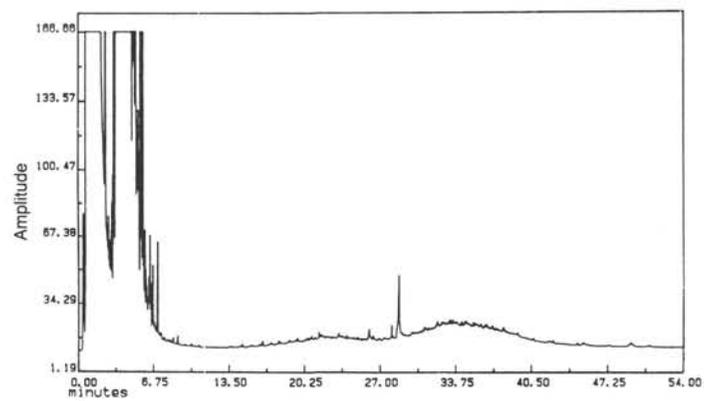
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Figure 4 (continued).

**Table 7. Substances with a low probability of contaminating cores.**

Common/trade name	Product description	Manufacturer	Usage	Wt(mg)
Hydraulic Fluid (Fig. 5A)	Mineral Based Hydraulic Oil, HLP-32	British Petroleum	Piperacker and most rig hydraulic systems	50
Molylube (Fig. 5B)	Molylube Grease Lithium base, 10% MoS <sub>2</sub> with EP Additives	Texaco, Inc.	Iron Roughneck and other rig equipment	70
Tapeze (Fig. 5C)	Cutting Fluid Contains Trichloroethane but not Carbon Tetrachloride	Le Dez Industries, Inc. Gonzales, California	Tapping threads in machine shop	80
Rig Wash Detergent (Fig. 5D)	SEDCO Rig Wash and Laundry Detergent PN SCN008101	SEDCO, Inc. Jacintoport Facility Channel View, Texas	Washing rig floor, decks, drilling equipment	50
CO Contact Cleaner (Fig. 5E)	CO Contact Cleaner #02016	CRC Chemicals U.S.A. Warminster, PA	Precision electronic cleaning solvent used occasionally to loosen rusted coring parts	80
Bakerlok (Fig. 5F)	Thread Locking Compound PN 199-50 Formula 'C'	Baker Oil Tools, Inc. Houston, Texas	Lock thread connections on coring parts, tools, etc.	60
Silicone Lubricant #111 (Fig. 5G)	Heavy Consistency #111 Compound	Dow Chemical Corporation Midland, Michigan	Occasional lubricant on coring and other drilling equipment	70
Vaseline Intensive Care Lotion (Fig. 5H)	Vaseline Intensive Care Hand Lotion	Chesebrough-Ponds, Inc. Greenwich, Connecticut	Hand lotion in tool room and chemical laboratory	90
Contact Cleaner (Fig. 5I)	Contact Cleaner Electrical Grade 2-26	CRC Chemicals U.S.A. Warminster, PA	Electronic cleaning solvent used occasionally to loosen rusted coring parts	60
Diesel Fuel #2 (Fig. 5J)	Marine Gas Oil/#2 Diesel, Cetane #50	Variable suppliers	Storing core equipment if 7-11 oil is not available	50
Liquid Wrench (Fig. 5K)	PH L1-16	Radiator Speciality Co. Charlotte, North Carolina	Penetrant for freeing rusted parts on coring equipment	50

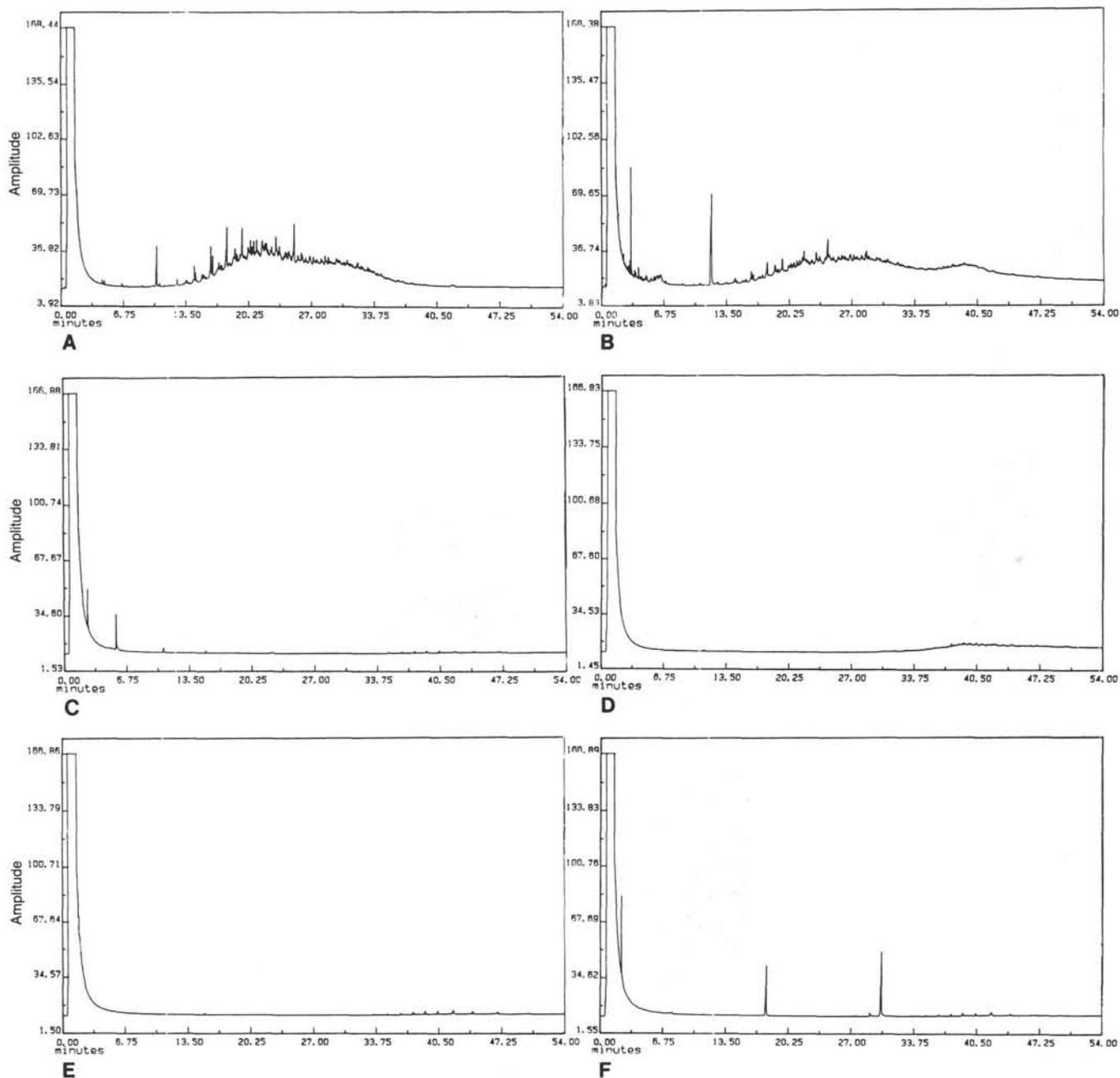


Figure 5. Gas chromatograms of substances with a low probability of contaminating cores (Table 7): A. Hydraulic fluid; B. Molylube; C. Tapeze; D. rig wash detergent; E. CO contact cleaner; F. Bakerlock; G. Silicone lubricant #111; H. Vaseline Intensive Care Lotion; I. Contact cleaner; J. Diesel fuel #2; K. Liquid Wrench.

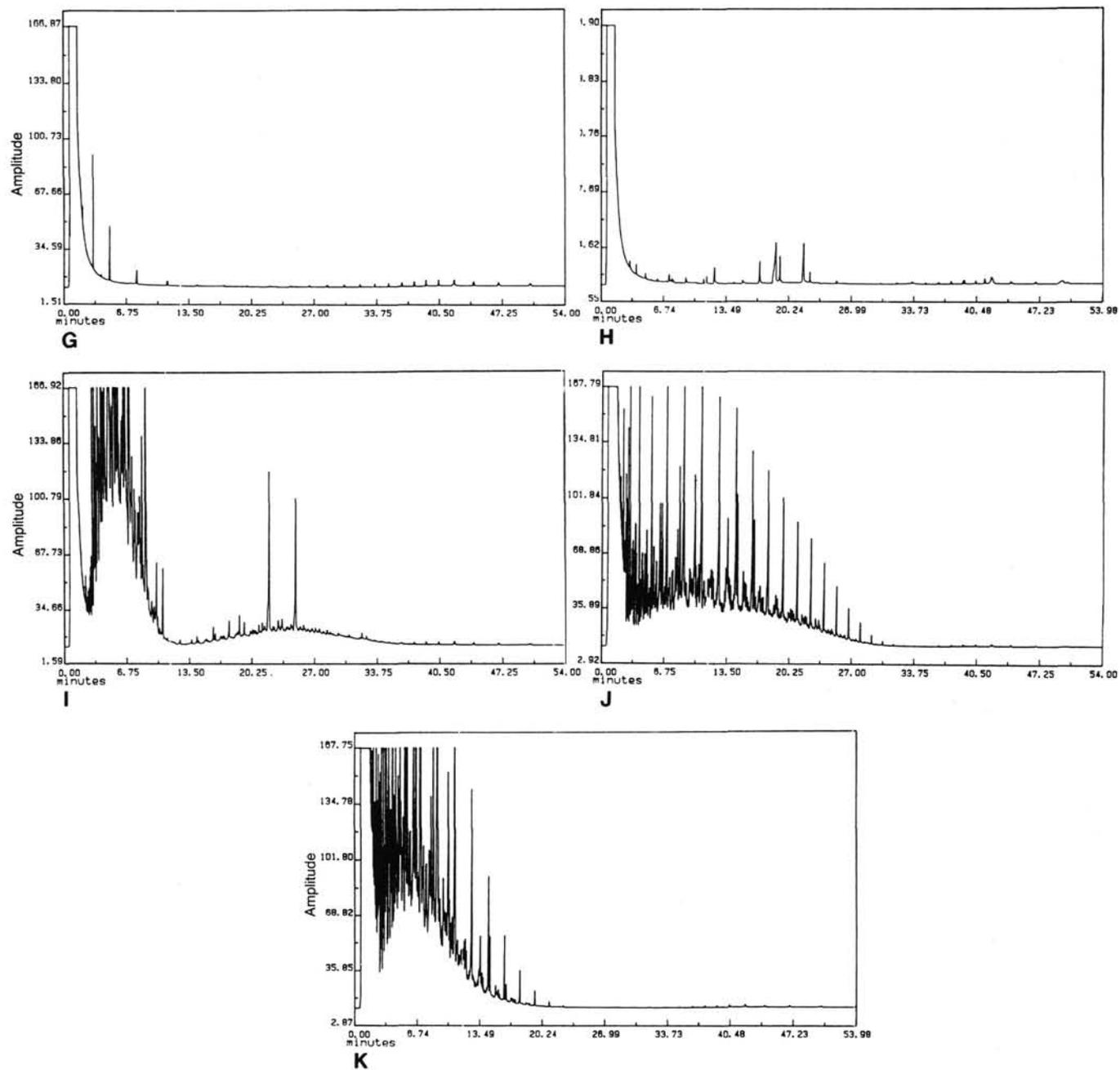


Figure 5 (continued).

**Table 8. Substances with a very low probability of contaminating cores.**

Common/trade name	Product description	Manufacturer	Usage	Wt(mg)
Gear Oil (Fig. 6A)	Lead-free E.P. Oil GRXB-220	British Petroleum	For piperacker and other rig equipment	60
Carboline Thinner (Fig. 6B)	Caroline Thinner #10	Carboline St. Louis, Missouri	Paint remover in tool room	70
RTV Silicone Rubber (Fig. 6C)	Adhesive Sealant	General Electric Company Silicone Products Division Waterford, New York	Seal pressure seals or fittings on deck equipment; rarely used down hole	50
Martin Decker Fluid (Fig. 6D)	Martin Decker Fluid	Martin Decker Dallas, Texas	Weight indicator sensors, lubricators on rig floor	50

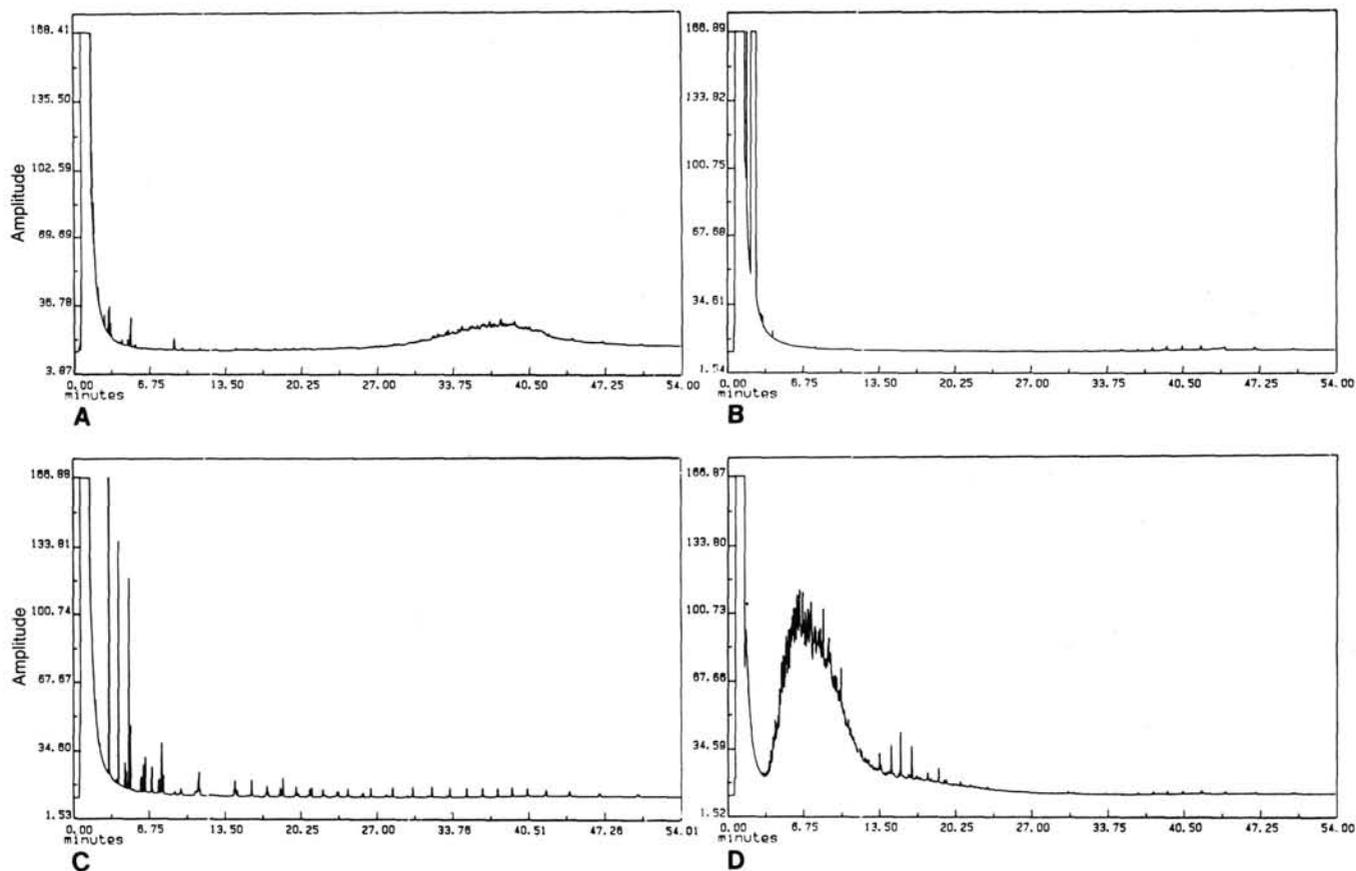


Figure 6. Gas chromatograms of substance with very low probability of contaminating cores (Table 8): A. Gear oil; B. Carboline Thinner; C. RTV Silicone Rubber; D. Martin Decker Fluid.

**Table 9. Potential contaminants classified by usage.**

Drilling	Core Equipment	Laboratory
Pipe Dope (Pb)	Parker O-Lube	3-in-One Oil
Pipe Dope (Zn)	Silicone O-ring Grease	WD-40
Line Tar	WD-40	Marking Pencil
Cable Coating	Super Agitene	Jet Lube
GO-JO Hand Cleaner	Multi-grease	Aqua Lube
Multigrease	Lubriplate	All Purpose Lube Oil
Compensator Oil	Never-Seez	GO-JO Hand Cleaner
	E-Z Break	
	7-11 Oil	