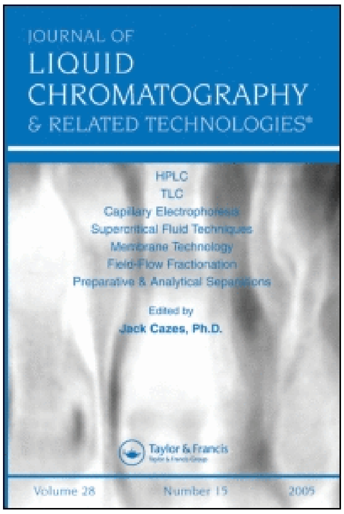

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LIQUID CHROMATOGRAPHIC ANALYSIS OF HYDRAULIC FLUIDS

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ABSTRACT

Liquid chromatographic test methods are developed to fingerprint hydraulic fluids and to quantitatively analyze specific fluid components. Petroleum-base and synthetic hydrocarbon-base hydraulic fluids conforming to existing Military Specifications and used by the Army Materiel Command are considered. Detailed methods and test procedures are developed for the analysis of a MIL-H-6083D hydraulic fluid. The precision and accuracy of each method is evaluated.

INTRODUCTION

Most hydraulic fluids are complex chemical mixtures of a petroleum or non-petroleum base-stock component formulated with various additives which may be present in trace amounts or constitute up to 20% by weight of the fluid. The additives in hydraulic fluids include viscosity-temperature coefficient improvers, oxidation inhibitors, antiwear agents, as well as corrosion and rust inhibitors. Furthermore, the fluids are susceptible to contamination and may undergo chemical changes during use or storage as evidenced by loss of volatiles, sludge formation, color changes, and hydraulic system failures.

The performance, stability, compatibility, toxicity, and flammability of a hydraulic fluid are directly related to its chemical composition. Although variations or changes in a fluid's formulation may adversely affect hydraulic system performance and limit the operational lifetime of a fluid, the chemical composition of the fluid base-stock and additives generally are not well-specified. Indeed inspection procedures tend to address the performance of a fluid rather than its chemical composition.

The purpose of this paper is to show how various liquid chromatographic (LC) techniques might be applied to the problem of monitoring hydraulic fluid composition. Test methods are developed to "fingerprint" the overall chemical composition and to quantitatively analyze specific fluid components. High performance gel permeation chromatography (GPC), reverse bonded-phase chromatography and adsorption chromatography techniques are applied. A variety of fluids are examined and a case study is performed on a MIL-H-6083D hydraulic fluid of known formulation.

MATERIALS

The hydraulic fluid samples are identified by their Military Specification number rather than the manufacturers' designation; and fluids with the same Specification number but obtained from different manufacturers are denoted, for example, as 46170-1 and 46170-2. According to their Specifications, 5606C, 6083C and 6083D consist of a petroleum base oil stock with viscosity index (VI) improvers (polymeric materials not to exceed 20 wt%), an antiwear agent (0.5 ± 0.1 wt% tricresyl phosphate), and oxidation or corrosion inhibitors; but no pour point depressants are permitted. Oxidation inhibitors in 5606C and 6083D may not exceed 2 wt%; while the concentration of corrosion inhibitors in 6083C and 6083D is whatever quantity is necessary to comply with the corrosion property requirements. The fluids 83282A and 46170 consist of a synthetic hydrocarbon base oil (alpha-olefin) stock with no limitations on the additives used except for those specifically restricted. The oxidation inhibitors in 83282A are not to exceed 2 wt%, and no pour point depressants or VI improvers are allowed in 83282A and 46170.

A MIL-H-6083D fluid was obtained with samples of the base oil stock and additives used in its formulation. The compositions of the supplier's fluid 6083D-0 and fluids formulated 6083D-1 and -2 and off-formulated 6083D-3 to -7 in the laboratory are given in TABLE 1. The base oil is designated as a mineral oil. Tricresyl phosphate (TCP) is the antiwear agent and di-tert-butyl-p-cresol (BPC) is the oxidation inhibitor. The rust inhibitor consists of a 50 wt% solution of barium dinonylnaphthalene sulfonate in solvent extracted castor oil.

Distilled in glass 2,2,4-trimethylpentane (C8) and methylene chloride were obtained from Burdick & Jackson Labs, Muskegon, MI. Tetrahydrofuran (THF) was dried with molecular sieves and distilled from calcium hydride. The water was freshly distilled and not retained longer than one day. All solvents were filtered (0.45 Millipore) to degas and remove particulates and were stirred continuously to ensure homogeneity during analysis.

A Waters Associates ALC/GPC-244 instrument with 6000A solvent delivery system, 660 solvent programmer, U6K injector, 440 dual wavelength UV absorbance detector and R400 refractive

TABLE 1. 6083D Fluid Formulations (Wt%)

Sample	Base Oil	VI Improver	TCP	BPC	Rust Inhibitor
6083D-0	79.7	13.3	0.5	0.9	5.6
6083D-1	79.6	13.39	0.503	0.90	5.59
6083D-2	79.6	13.40	0.502	0.90	5.59
6083D-3	83.1	11.10	0.416	0.748	4.66
6083D-4	73.7	19.78	0.463	0.833	5.18
6083D-5	79.3	13.23	0.964	0.896	5.57
6083D-6	79.0	13.18	0.496	1.78	5.55
6083D-7	75.2	12.55	0.472	0.849	10.95

index (RI) detector was used with μStyragel, μPorasil and μBondapak C_{18} columns. For direct data analysis, the LC detectors were interfaced with a Spectra Physics SP4000 data system which included SP4020 data interfaces, SP4050 printer/plotters and an SP4010 disc memory module. The 440 UV detector absorbance output (0-2 volts) and the R400 RI detector output (0-100 millivolts) were interfaced to the SP4020 modules using a 0-10 volt and a 0-1 volt input card, respectively. For RI detection, both the RI detector sensitivity (e.g., 32X) and the SP4050 attenuation (e.g., ATTN 10) are specified in the test methods.

The hydraulic fluids were completely soluble in THF and methylene chloride. All samples were filtered (0.45μ Millipore) prior to injection and analyses were run at ambient temperature. For solvent programming, the gradient was initiated upon sample injection.

TEST METHODS

GPC fingerprinting

Sample - filtered hydraulic fluid
Injection volume - 5μl
Mobile phase - THF
Flow rate - 2 ml/min
Columns - μStyragel 10^3, 500, 500, 100, 100 Å
Pump pressure - 1500 psi
Detector - UV 280 nm, ATTN 10
RI 32X, ATTN 10
Chart speed - 0.5 cm/min
Analysis time - 25 minutes

Reverse bonded-phase chromatography fingerprinting

Sample - filtered hydraulic fluid
Injection volume - 10μl
Mobile phase - 60% H_2O/40% THF to 100% THF
15 minute gradient 6
Flow rate - 2 ml/min
Column - μBondapak C_{18} (30 cm X 3.9 mm)
Pump pressure - 2500 to 700 psi
Detector - UV 280 nm, ATTN 50
Chart speed - 1 cm/min
Analysis time - 20 minutes

VI improver analysis

Sample - filtered hydraulic fluid
Calibration - hydraulic fluid standard or set of acryloid polymer solutions
Injection volume - 5μl
Mobile phase - THF
Flow rate - 2 ml/min
Column - μPorasil (30 cm X 3.9 mm)
Pump pressure - 1100 psi
Detector - RI 8X, ATTN 50
Chart speed - 1 cm/min
VI improver retention time - 58 seconds
Analysis time - 2 minutes
Calculations - wt% VI improver $= A \cdot C_s/A_s$ (1)

where C_s is the concentration (wt%) of VI improver in the standard, A_s and A (H_s and H) are the peak areas (heights) for the VI improver in the standard and sample being analyzed.

TCP analysis

Method 1

Sample - filtered hydraulic fluid
Calibration - Sample Spiking. Calibration sample is prepared by weighing $w_x = 0.1g$ TCP with $w = 20g$ of the hydraulic fluid and mixing in a 50-ml beaker.
Injection volume - 5μl
Mobile phase - methylene chloride
Flow rate - 2ml/min
Column - μPorasil (30 cm X 3.9 mm)
Pump pressure - 1100 psi
Detector - UV 254nm, ATTN 10
Chart speed - 1cm/min
Retention time - TCP, 275 seconds
Analysis time - 5 minutes
Calculation - wt% TCP $= \dfrac{w_x \cdot A}{w \cdot (A_s - A)} \cdot 100\ \%$ (2)

where A_s and A (H_s and H) are the peak areas (heights) for TCP in the spiked and unspiked samples.

Method 2

Sample - Prepare a solution of concentration C (μg/μl) by weighing w=20g hydraulic fluid in a 100-ml volumetric flask and diluting to 100-ml with the internal standard stock solution.
Internal standard stock solution - pipet 4-ml benzyl alcohol into a 1-liter volumetric flask and dilute with methylene chloride to 1-liter.

Calibration - prepare a set of standard TCP solutions (0.5 to 2.0μg/μl) by adding weighed TCP to 100-ml volumetric flasks and diluting with the internal standard stock solution. Analyze each standard and plot peak area as a function of TCP (μg) injected.

Injection volume - V = 25μl

Other conditions are identical to those in Method 1.

Benzyl alcohol retention time - 550 ± 5 seconds.

$$\text{Calculation - wt\% TCP} = \frac{W\cdot \bar{A}_{IS}}{C\cdot V\cdot A_{IS}}\cdot 100\% \qquad (3)$$

where W is the weight (μg) of TCP determined from the TCP peak area and the standard calibration plot. $\bar{A}_{IS}$ is the average internal standard peak area and A_{IS} is the area of the internal standard peak obtained with the analysis of the fluid sample solution.

Base oil, rust and oxidation inhibitors analysis

Sample - filtered hydraulic fluid

Calibration - hydraulic fluid standard or by sample spiking

Injection volume - 5μl

Mobile phase - 100% C8 to 80% C8/20% THF
5 minutes gradient 6

Flow rate - 2 ml/min

Column - μPorasil (90 cm X 3.9 mm)

Pump pressure - 1500 to 1400 psi

Detector - UV 280 nm, ATTN 10

Chart speed - 1 cm/min

Retention times - base oil peak, 357±2 seconds
rust inhibitor, 308±1 seconds
BPC, 496±2 seconds

Analysis time - 15 minutes

Calculations - Eq. 1 or Eq. 2, where $w = 10$g and $w_x = 2$, 0.5, or 0.1g for samples spiked with base oil, rust inhibitor or BPC, respectively.

RESULTS

Fingerprinting

The primary purpose of a fingerprint is to establish whether the chemical composition of a fluid has changed or is different from that of another fluid sample. Generally, differences are apparent when chromatograms are overlaid. Notable fingerprint characteristics include (i) the number of peaks, (ii) peak retention times, (iii) peak heights or integrated peak areas, (iv) the ratio of a peak's height or area as determined with different detectors, (v) the ratio of the height or area of one peak to others in the same chromatogram, and (vi) differences in peak shape.

GPC provides a fingerprint dependent upon the relative size of the hydraulic fluid component molecules in solution. The chromatograms are highly reproducible such that, in replicate runs, peak retention times do not vary by more than 0.3% and peak heights agree within 2%. As shown in Figure 1, the GPC fingerprints of the petroleum base oil fluids are distinctly different from those based on synthetic hydrocarbons. When an RI monitor is used, there is little ambiguity in establishing whether polymeric VI improver is present. The VI improver starts eluting 11 minutes after injection; whereas other fluid components have retention times greater than 18 minutes. Except for VI improver detection, fingerprints obtained by UV monitoring offer more definition than those obtained using an RI monitor.

Reverse bonded-phase chromatography with gradient elution is an excellent technique for fingerprinting hydraulic fluid composition. Separation is based upon the distribution of the solute between the mobile and stationary phases such that solutes more soluble in the bonded-phase tend to have longer retention times. Solvent programming enhances resolution and promotes the complete elution of sample components. In general, the fingerprints (Figure 2) are more definitive but less reproducible than those obtained by GPC.

The fingerprints of petroleum base oil fluids are readily distinguishable from those based on synthetic hydrocarbons. The petroleum base oil elutes as a broad band of unresolved peaks over the region between 500 and 850 seconds; whereas sharp, well-resolved peaks are obtained for the synthetic hydrocarbon base oil. The synthetic base oil fluids are quite amenable to quantitative analysis; and, as shown in Figure 2, the fingerprints are definitive in discerning between MIL-H-46170 fluids obtained from different manufacturers.

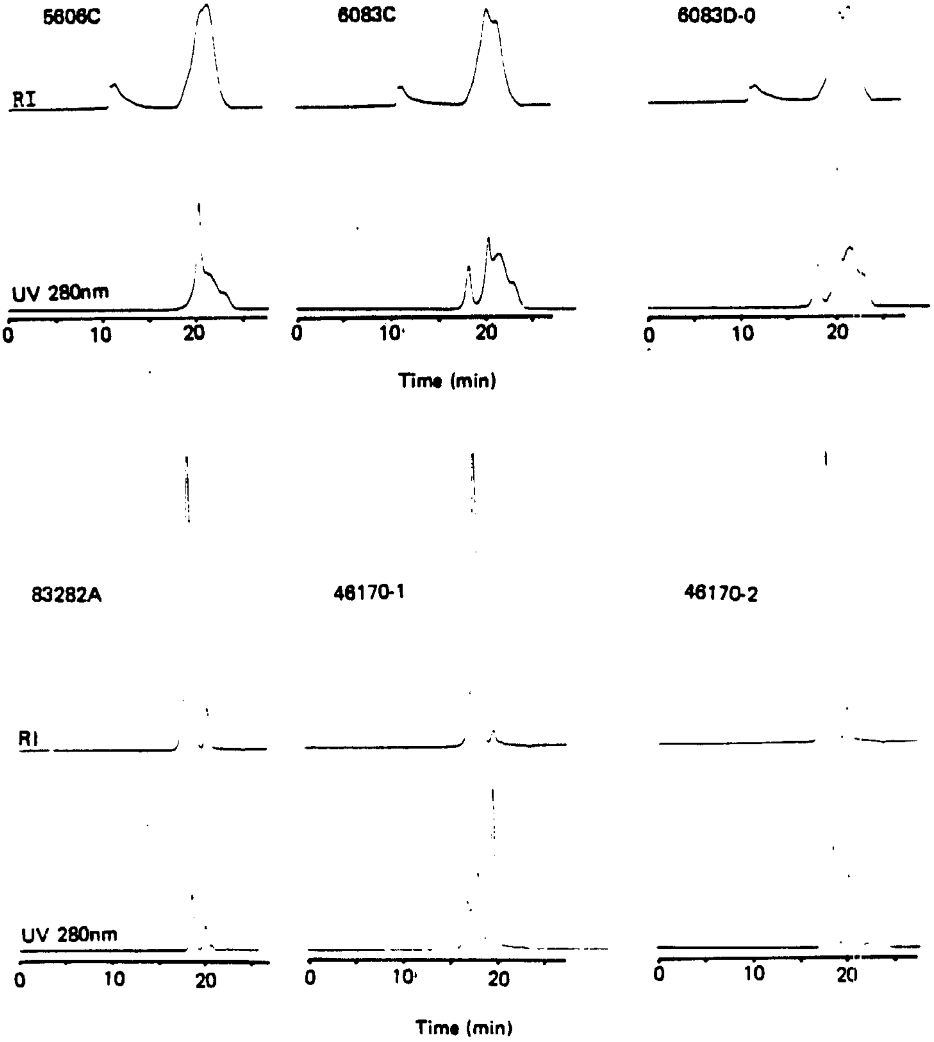


FIGURE 1. GPC fingerprinting

For 6083D-0, the oxidation inhibitor BPC elutes as a sharp peak along with the base oil at 650±4 seconds and the rust inhibitor elutes as a series of poorly resolved peaks during the first 500 seconds. The antiwear agent TCP and the VI improver are not

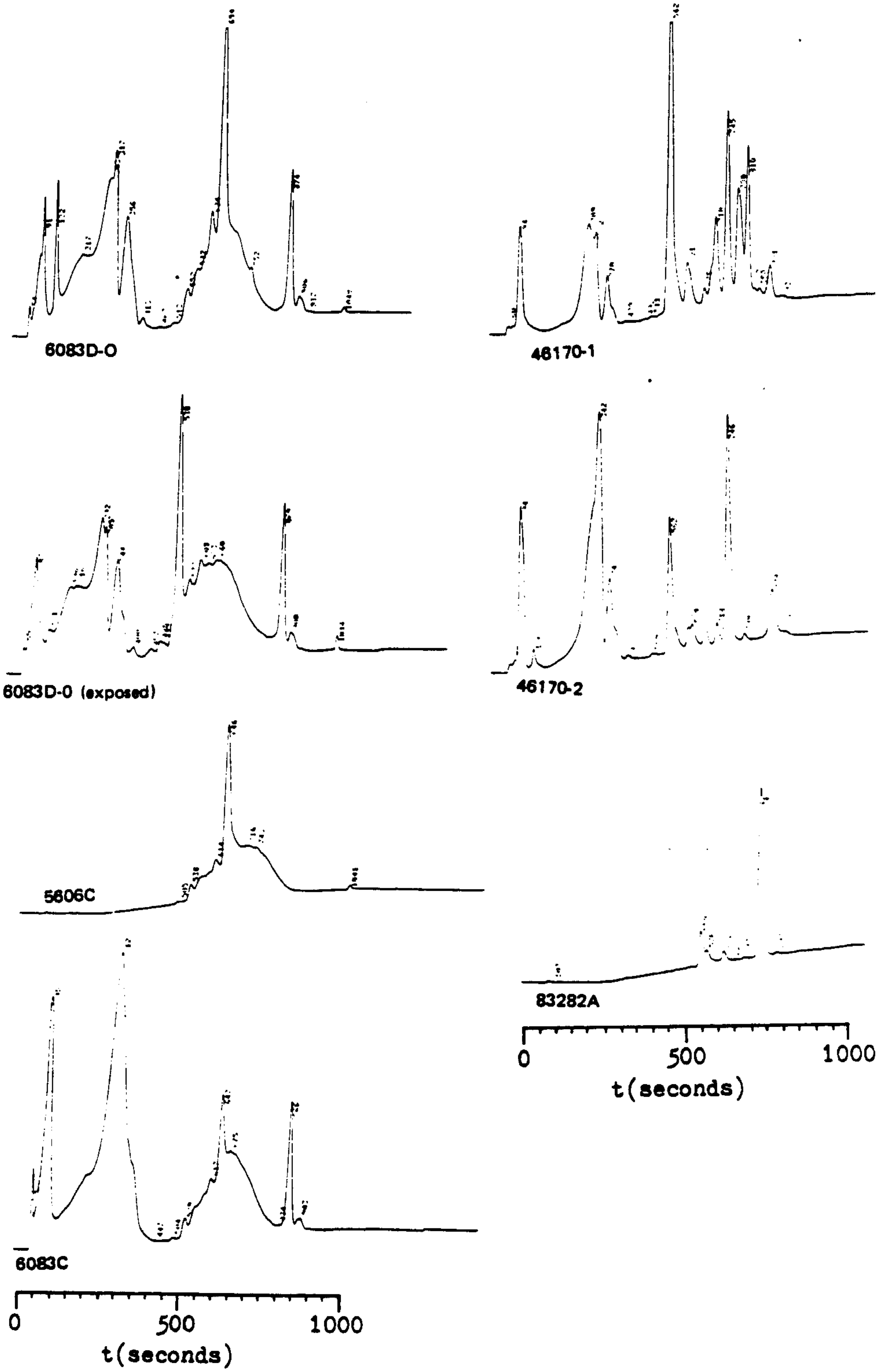


FIGURE 2. Reverse Bonded-phase chromatography

apparent since they do not absorb strongly at the monitoring wavelength. Exposing 6083D-0 to sunlight over a period of one month causes chemical changes detectable by fingerprinting. BPC and at least one other component (132 seconds) disappear; and a new peak, probably due to the product of the oxidation inhibitor reaction, appears at 538 seconds.

VI Improver Analysis

Polymers and copolymers of methacrylates, olefins, butadienes and styrene are used as VI improvers. GPC may be used to determine whether hydraulic fluids contain VI improvers, as well as quantitatively analyze and isolate VI improvers for subsequent chemical or molecular weight analysis.[1,2] In this paper a variation of the GPC method is developed. A polar, microporous substrate is used with a relatively polar mobile phase. The VI improver elutes as a sharp peak in the interstitial volume and is fully separated from other components which elute together as a single peak (Figure 3). The method is rapid, nondestructive and requires little sample.

VI improver concentration is directly proportional to the height or area of its peak. Selecting 6083D-0 as the standard with 13.3 wt% VI improver, multiple analyses were run on different formulations. The precision is ±0.2 and ±0.4 wt% for the peak area and height methods, respectively. The agreement between formulated and measured weight percentages is +0.2±0.4 and -0.1±0.7 wt% for the peak area and height methods, respectively. The major source of error is caused by the operator's inability to precisely inject identical amounts of sample. The error could be reduced by employing automatic injection or using an internal standard. Also, an error is introduced in measuring peak heights, ca. ±0.5mm or 0.3 wt%.

Analytical data from the hydraulic fluid analyses are shown in TABLE 2. As the VI improver concentration approaches 20 wt%, peak spreading becomes important and results in low values for determinations based on the peak height method. The somewhat

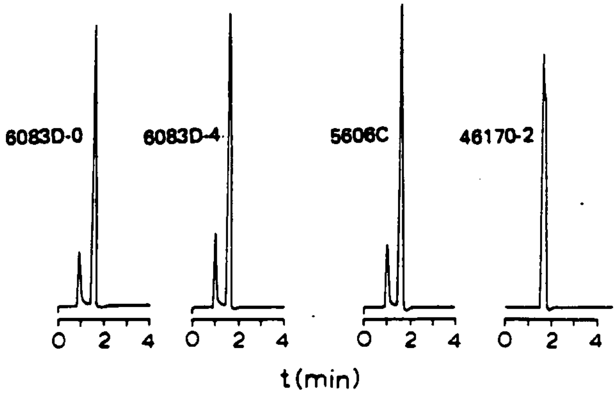


FIGURE 3. VI improver analysis

high concentration obtained for 6083D-0 (exposed) may be due to the loss of volatiles or to changes in the chemical structure of the VI improver during exposure to sunlight for 1 month. The results for 6083C and 5606C are suspect since in both cases the identity of the VI improver is unknown. Indeed the disparity

TABLE 2. VI Improver Analysis

WT %

Sample	Formulated	Measured by	
		Peak Area	Peak Height
6083D-0	13.3	13.3 ± 0.2	13.3 ± 0.4
-1	13.4	14.0	13.6
-2	13.4	14.0	13.6
-3	11.1	11.1	11.8
-4	19.8	19.6	18.3
-7	12.6	12.4	12.3
6083D-0 (exposed)	13.3	13.8	15.0
6083C	unknown	12.3	10.6
5606C	unknown	17.7	15.5
83282A	unknown	0	0
46170-1	unknown	0	0
46170-2	unknown	0	0

between the peak area and height values suggests that 6083C and 5606C may have a different type of VI improver than 6083D-0. Finally, as specified, neither 83282A nor the 46170 samples contain VI improvers.

TCP Analysis

Adsorption chromatography provides a rapid, quantitative method for TCP analysis. The analysis time is 5 minutes with TCP eluting as a single, well-resolved peak at 275 ± 2 seconds. If undiluted 6083D-0 is analyzed and spiked for calibration, its TCP concentration calculated from peak areas is 0.462 ± 0.014 wt%. The data in TABLE 3 were obtained using benzyl alcohol as an internal standard and injecting samples diluted in methylene chloride. The standard deviation shown for 6083D-0 is typical for this method. The precision is ±1.01% using peak areas and ±1.2% from peak height measurements. The accuracy as determined from the difference between formulated and measured values is +0.009 ± 0.012 and +0.01 ± 0.02 wt% for peak area and height measurements, respectively.

Chromatograms obtained with the TCP analyses (Figure 4) also provide fingerprints of fluid composition. Apparently TCP is not an additive in 83282A, 41670-1 or 46170-2. Perhaps the peaks at

TABLE 3. TCP Analysis-Adsorption Chromatography

	WT%		
	Formulated	Measured	
Sample		peak areas	peak heights
6083D-0	0.5	0.470 ± 0.004	0.49 ± 0.01
6083D-1	.503	.501	.48
6083D-2	.502	.504	.53
6083D-3	.416	.401	.40
6083D-5	.964	.963	.94
5606C	unknown	.615	.61
6083C	unknown	.661	.64
83282A	unknown	-	-
46170-1	unknown	-	-
46170-2	unknown	-	-

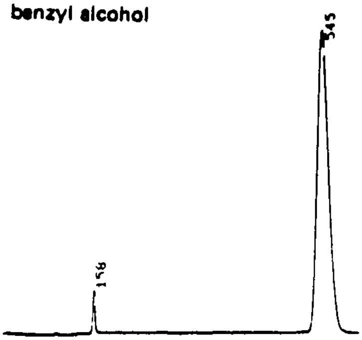
257-260 seconds represent other types of organo phosphate antiwear additives. Finally, it is noted that the TCP concentration in 5606C and 6083C exceed the specified limit.

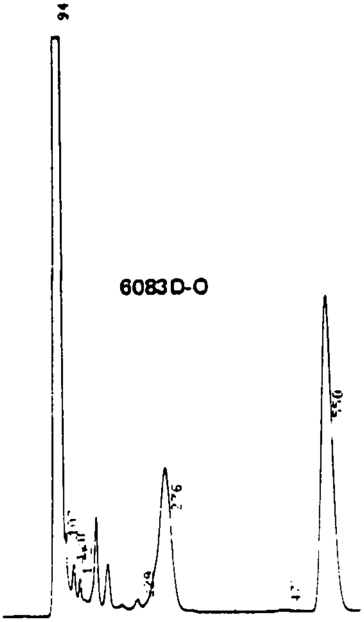
Base Oil, Rust and Oxidation Inhibitor Analysis

Adsorption chromatography with gradient elution is used to quantitatively analyze the base oil, rust and oxidation inhibitors in the 6083D-0 formulations (Figure 5). The rust inhibitor has a retention time of 308 ± 1 seconds and is followed by base oil components eluting from 315 to 600 seconds and the oxidation inhibitor BPC at 500 ± 6 seconds. The chromatograms are highly repeatable when run on the same day with the same column set and with no changes in solvent supply. On successive days, peaks at higher retention times may shift by as much as 10 or 15 seconds.

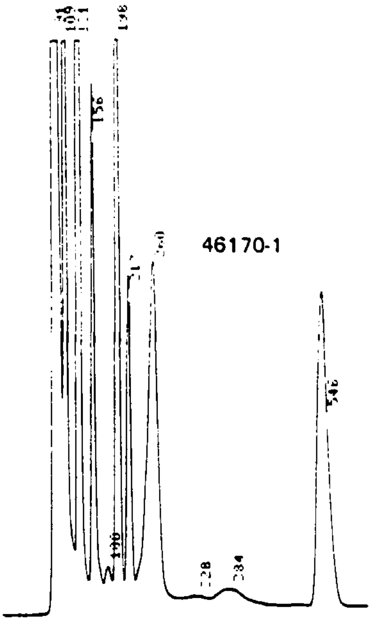
It is difficult, if not impossible, to analyze accurately the petroleum base oil in hydraulic fluids unless a standard of the actual base oil used in the formulation is available and unless the standard has at least one well-resolved peak that can be monitored without interference by other fluid components. The base oil in 6083D-0 has a component eluting at 357 ± 2 seconds that is sufficiently resolved for quantitative analysis. By spiking 6083D-0 with its base oil standard for calibration, the weight percentages of base oil in 6083D-0 and off-formulations of 6083D-0 were calculated and are compared with the formulated values (TABLE 4). The repeatability of each determination is ±2.4 wt%, whereas the agreement between the average values calculated and formulated are somewhat better. The low value for 6083D-0 (exposed) may be reflecting the loss of volatile base oil components or possibly chemical changes in the component eluting at 357 seconds.

The rust inhibitor barium dinonylnaphthalene sulfonate is fully resolved and elutes as a sharp peak at 308 ± 1 seconds. Using the peak spiking method for calibration, the average difference between the formulated and calculated values is +0.07 wt% with a standard deviation of ±0.55 wt%. The high value


benzyl alcohol
156
345


94
6083D-O
226
550


6083C
131
154
176
344


109
131
156
198
190
46170-1
328
334
546

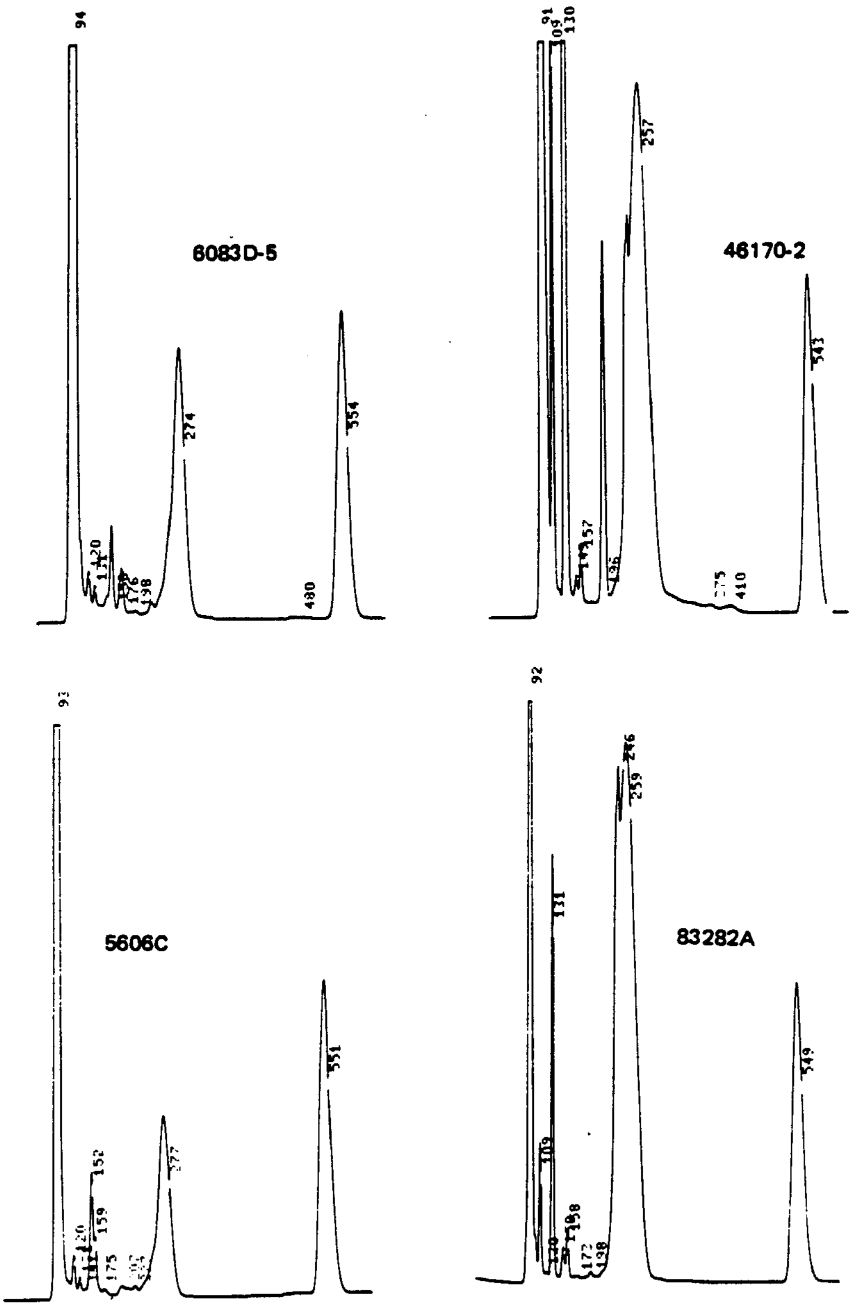
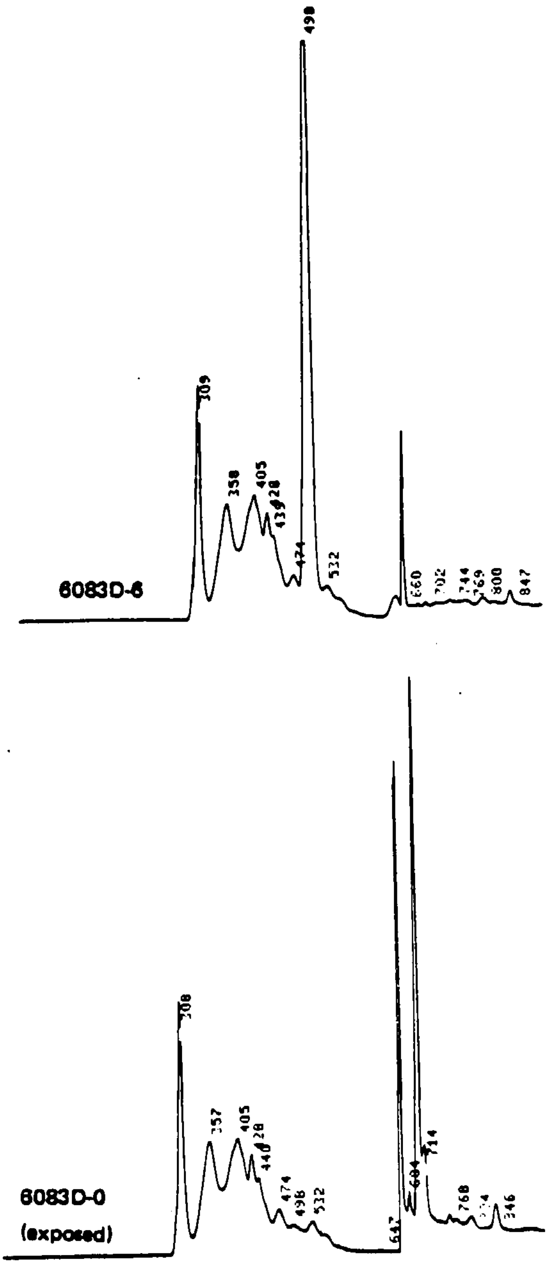


FIGURE 4. TCP analysis - adsorption chromatography


498
309
358
405
428
439
474
532
660
702
744
769
800
847
6083D-6
308
357
405
428
440
474
498
532
647
684
714
768
846
6083D-0
(exposed)

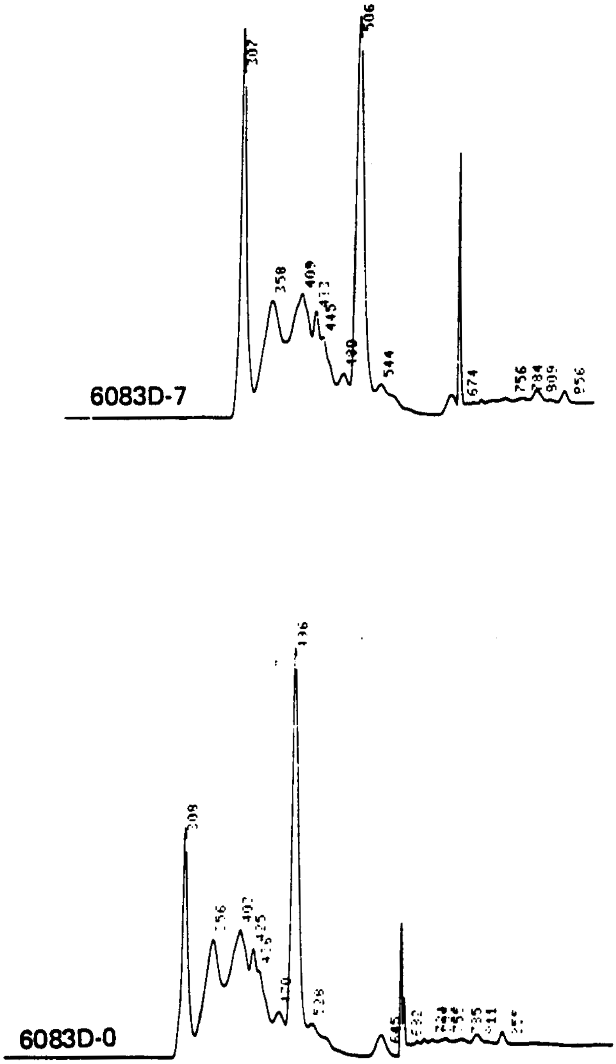


FIGURE 5. Adsorption chromatography with gradient elution - base oil, rust and oxidation inhibitor analysis

TABLE 4. 6083D Component Analysis*

Adsorption Chromatography Gradient Elution

	WT%		
Sample	Base Oil	Rust Inhibitor	BPC
6083D-0	78.5 (79.7)	5.2 (5.6)	0.90 (0.9)
6083D-1	79.6 (79.6)	6.1 (5.6)	.92 (0.90)
6083D-2	79.6 (79.6)	6.1 (5.6)	.88 (0.90)
6083D-3	84.5 (83.1)	3.7 (4.7)	.74 (0.75)
6083D-6	75.4 (79.0)	5.3 (5.6)	1.44 (1.78)
6083D-7	72.8 (75.2)	11.3 (11.0)	.97 (0.85)
6083D-0+ (exposed)	65.5 (79.7)	8.9 (5.6)	.063(0.9)

*Formulated compositions are given in parenthesis.

+An aliquot of 6083D-0 that was exposed to sunlight in an open container for one month.

determined for 6083D-0 (exposed) may be due to loss of the more volatile fluid components or to the formation of products which have retention times similar to that of the rust inhibitor.

The oxidation inhibitor BPC has a large molar absorptivity at 280 nm and therefore can be analyzed with a high degree of accuracy eventhough the BPC peak is not fully resolved from the base oil components at 500 ± 6 seconds. In 6083D-0, BPC peak areas may be analyzed with a high degree of precision ±2%. The agreement between the formulated and analytical BPC values in TABLE 4 is 0.04 ± 0.14 wt%. For 6083D-0 (exposed), as shown in Figure 5, the large BPC peak is no longer evident and a new peak appears at 714 seconds which is probably the BPC oxidation product. The actual wt% BPC in 6083D-0 (exposed) is probably lower than indicated in TABLE 4 since base oil components contribute significantly to the BPC peak area at low BPC concentrations.

CONCLUSION

Liquid chromatography is a viable analytical technique for monitoring the chemical compositions of hydraulic fluids.

Hydraulic fluids are sufficiently complex that differences in composition generally can be discerned by GPC and HPLC fingerprinting. Little or no sample preparation is required and analyses may be run in less than 30 minutes on microliter size samples.

Specific test methods were developed to fingerprint and quantitatively analyze the components in a MIL-H-6083D fluid formulation. Except for VI improver analysis, GPC is not as definitive in fingerprinting or as useful in quantitative analysis as the other HPLC modes. Reverse bonded-phase HPLC with solvent programming is excellent for fingerprinting but is limited in its usefulness for quantitative analysis of petroleum base fluids because of the poor resolution and interference of the base oil. Adsorption chromatography is the most versatile HPLC mode for hydraulic fluid analysis. Definitive fingerprints are obtainable and it is possible to quantitatively analyze all the known components in 6083D-0 using a single set of columns with modifications in the mobile phase. Total component analyses for the manufacturer's and three in-house formulations of 6083D are shown in TABLE 5. Accuracy is defined as the average differ-

TABLE 5. HPLC Analysis of 6083D Formulations

Component	WT %					
	6083D-0	6083D-1	6083D-2	6083D-3	precision	accuracy
V. I. improver	13.3	14.0	14.0	11.1	0.2	0.3
base oil	78.5	79.6	79.6	84.5	2.4	1.4
TCP	0.470	0.501	0.504	0.401	0.004	0.010
BPC	0.90	0.92	0.88	0.74	0.02	0.10
rust inhibitor	5.2	6.1	6.1	3.7	0.1	0.5
TOTAL	98.4	101.1	101.1	100.4		

ence between the formulated and measured values. Although different test methods were employed, the analytical values total to ca. 100 wt% within experimental error for each formulation.

Finally, certain limitations must be recognized and precautions taken in analyzing hydraulic fluids using liquid chromatography. Fluid components must be soluble and not react with the solvent(s), column substrate, or instrument seals and tubing. Precautions must be taken to prevent irreversible adsorption of sample components and solvent contaminants. Also, some components may prove too complex or be otherwise unsuitable (e.g., highly ionizable or associated species) to analyze by the methods described in this paper. Other limitations include the resolution and detection of specific fluid components. Such problems are fundamental in the application of any liquid chromatographic method and often are reconcilable by the modification of test conditions.

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