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Use of High Pressure Liquid Chromatography in the Study of Liquid Lubricant Oxidation

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NASA

USE OF HIGH PRESSURE LIQUID CHROMATOGRAPHY IN THE STUDY OF LIQUID LUBRICANT OXIDATION

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E-1409

ABSTRACT

The general principles of classical liquid chromatography and high-pressure liquid chromatography (HPLC) are reviewed, and their advantages and disadvantages are compared. Several chromatographic techniques are reviewed, and the analysis of a C-ether liquid lubricant by each technique is illustrated. An analysis by size exclusion chromatography of an ester lubricant, which had been degraded using a micro-oxidation apparatus, is illustrated to show how HPLC can be used in the study of high-temperature lubricant degradation.

INTRODUCTION

High-pressure (or performance) liquid chromatography (HPLC) is a relatively new separation method (the major developments occurring during the years 1965 through 1969) based on the classical separation technique, liquid column chromatography [1]. Chromatography, in general, is a method of physically separating a mixture of substances due to the equilibrium distribution of the substances between a stationary phase (or bed) and a mobile phase which percolates through the stationary phase. The mixture of substances (to be separated) are solutes in a solvent mobile phase.

In liquid column chromatography (classical or HPLC) the mobile phase is a liquid, whereas a gas mobile phase is employed in gas chromatography. Although HPLC is not used as extensively as gas chromatography, its advantage lies in the fact, that while only about 20 percent of all organic material is volatile enough to be examined by gas chromatography [2], a higher percentage of organic material can be dissolved in an appropriate solvent for examination by HPLC.

HPLC has been utilized at Pennsylvania State University to study the high temperature oxidation of ester-based lubricants [3,4], and has also been used in the analysis of space-qualified lubricants [5]. At NASA Lewis Research Center, HPLC is one of several laboratory instruments used to study the compositions, oxidative mechanisms, and kinetics of candidate high temperature lubricants. Understanding oxidation mechanisms is essential in facilitating a logical approach to the synthesis and formulation of new lubricants with improved high temperature stability in air.

Classical Liquid Column Chromatography

Fig. 1 represents the separation of a mixture of three substances (solutes) by classical liquid column chromatography. The column is an open tube which is commonly packed with alumina or silica. The mixture is separated by adsorbing the solute substances from a small volume of solvent onto the packed bed and then leaching the column with a sequence of solvents (the mobile phase) of increasing polarity. The eluant is then collected in fractions for examination [6].

Classical liquid column chromatography, although a valuable analytical tool, has several drawbacks: (1) It is a time consuming method of separation; (2) examination of the collected fractions is difficult because of poor resolution; (3) the manual operation of the column is greatly dependent on the operator's skill. HPLC, on the other hand, has several advantages: (1) Separation times are generally fast; (2) resolution is excellent; (3) there is less dependence on the operator's skill as a result of automation.

Modern High Pressure Liquid Chromatography

A modern HPLC system consists of four major components (Fig. 2):

1 A solvent delivery pump
2 A sample injection port
3 A separatory column (or columns)
4 A detector

The solvent delivery pump must provide a continuous, controlled flow of solvent (the mobile phase) through the separatory column and to the detector, and the sample injection port must provide the means of introducing the sample under study into the HPLC system without interruption of the solvent flow rate. The detector must be capable of detecting the separated solute substances that elute from the column.

The first step in separating a mixture of substances by HPLC is to dissolve a small quantity of the mixture into an appropriate solvent (the mobile phase). A small volume of the resultant solution is then injected into the HPLC system where it merges into the mobile phase (from the solvent delivery pump to the separatory column). Due to the packing of a column (the stationary phase generally consists of very fine particles), the HPLC system must operate at high-column inlet pressures to overcome the column resistance to the mobile phase flow. The mobile phase flow rate is controlled by adjustments to the solvent delivery pump; flow rates of 1-milliliter per minute are common. The mixture of substances in the sample are separated because of their different rate of passage through the column. Their presence is sensed by detectors at the downstream segment of the column. A refractive index detector and a fixed wavelength ultraviolet light detector are two popular optical instruments used to detect the separated substances which elude from the separatory column.

A refractive index detector is adjusted to the refractive index of the mobile phase solvent and responds to any eluted substance (in the mobile phase) that has a different refractive index from that of the mobile phase. A fixed wavelength ultraviolet light (UV) detector will respond to any eluted substance that is UV sensitive at that particular wavelength. The UV detector wavelength may be adjusted.

A modern HPLC system, because it overcomes the inherent difficulties of classical liquid column chromatography, has gained widespread use in the laboratory as a routine analytical instrument. In many instances its versatility has allowed it to be used as an on-line analyzer in industrial process plants [7]. It is also a valuable research tool in the study of chemical reaction mechanisms and kinetics and has been used extensively in our laboratory for the separation of the components of synthetic lubricants and for the separation of their oxidation degradation products.

MODES OF SEPARATION

Different types of separatory columns can be used in an HPLC system depending on the type of separation best suited for the particular mixture of substances being studied. The two main classes of separation are those separations affected by the physical characteristics (size exclusion) of the substances and those affected by the chemical nature (adsorption, partition) of the substances [8].

Size Exclusion Chromatography

This mode separates a mixture of substances according to their molecular size (geometry) differences by permeation into a solvent-filled matrix in the column (Fig. 3). This matrix can be either an inorganic (i.e., silica gel) or organic (i.e., styrene, divinyl benzene) stationary phase. The substances having the greater molecular size will tend not to permeate into the matrix pores as much as the smaller molecular size substances. Thus the order of elution from a size exclusion column is from the larger to the smaller molecular size substances.

The ideal size exclusion process is illustrated in Fig. 4. There are three regions of importance: The total exclusion region, the selective permeation region, and the total permeation region. In the total exclusion region, all substances above a certain molecular size (M_t) will be excluded from permeation into the stationary phase matrix; these substances will elute at the same time, T_t (the total exclusion time). In the selective permeation region, substances having a molecular size smaller than M_t will permeate into the stationary phase matrix and elute at increasing times greater than T_t. In the total permeation region, all substances below a certain molecular size (M_p) will be small enough to travel throughout the stationary phase matrix with the mobile phase molecules; these substances will elute at the same time, T_p (the total permeation time).

A calibration curve can be constructed for a size exclusion column by plotting the log of the molecular weights of known substances (molecular weight is proportional to molecular size) versus their retention times. Figure 5 is a calibration curve constructed from known standards. By measuring the retention time of an unknown substance, its approximate molecular weight can be calculated.

Adsorption Chromatography

In adsorption chromatography, chemical interactions (hydrogen-bonding, dipole interactions) between the solute substances and the stationary phase affect separation of a mixture of substances. The solutes are reversibly adsorbed from a nonpolar mobile phase (i.e., heptane) onto the surface of a polar stationary phase. Silica gel, which has a high concentration of hydroxyl groups, is widely used as a stationary phase in adsorption chromatography (Fig. 6).

Figure 7 illustrates the mechanism of separation on a silica gel stationary phase. The phenol solute, because of its greater polarity, will interact more strongly with the stationary phase than will the hindered phenol solute. The phenol solute will be retained for a longer period of time, and thus will elute from the column after the hindered phenol solute has eluted.

Partition Chromatography

In this mode, the solute substances partition themselves between the mobile phase and a stationary organic phase which can be either coated or chemically bonded to a solid bed support (silica is commonly used). Separation of the substances is achieved because of the different equilibrium distributions (solubilities) of the substances between the mobile phase and the stationary phase. Partition chromatography can be classified as either liquid-liquid chromatography or bonded phase chromatography. In liquid-liquid chromatography, an organic liquid (the stationary phase) is coated onto the surface of a solid bed support (Fig. 8). The liquid stationary phase is normally a very polar substance such as B_1 B^1-oxydiproprionitrile, and the mobile phase a nonpolar substance such as heptane.

In bonded phase chromatography, an organic phase is chemically bonded to a solid bed support. Bonded phase chromatography can be further classified as either normal phase or reversed phase chromatography.

Normal phase chromatography results from chemically bonding a polar functional group, such as -CN, $-NH_2$ to a solid bed support (Fig. 9). The substances to be separated are dissolved in a nonpolar mobile phase (hexane, chloroform). Figure 10 illustrates a normal phase separation using a cyano (-CN) bonded phase column, with the result that the less polar substance elutes first.

Reverse phase chromatography is just the opposite of normal phase chromatography. A nonpolar functional group such as $-C_8$, $-C_{18}$ is chemically bonded to a solid bed support (Fig. 11), and the substances to be separated are dissolved in a polar mobile phase (methanol, water). Figure 12 illustrates a reversed phase separation using a C_{18}-bonded phase column, with the result that the more polar substance elutes first.

Gradient Elution

When a sample is a mixture of substances having a very wide variation of polarity, the separation of the sample becomes more difficult; Fig. 13 illustrates the problem. A sample containing six substances (of different polarity) is separated by adsorption chromatography. If a weak mobile phase is used (heptane), then all six substances may not be eluted (Fig. 13(a)). If a strong mobile phase is used (chloroform), then all six substances may not be completely separated (Fig. 13(b)). A blend of the weak and strong mobile phases may optimize the separation of the intermediate polar substances (the center) but the separation of the nonpolar and polar substances will be unsatisfactory (Fig. 13(c)).

If, however, the separation of the sample mixture is started with the weak mobile phase and then the strong mobile phase is gradually fed in, optimum separation of all six substances will be achieved (Fig. 13(d)). This separation method is called gradient elution chromatography as opposed to an "isocratic" chromatographic separation where the mobile phase composition is constant with time. Figure 14 depicts one way of obtaining a polarity gradient of the mobile phase. The most important variable in gradient elution is the mobile phase program, which varies the mobile phase composition with time.

Gradient elution is a powerful chromatographic technique generally used for the more difficult separations.

HPLC ANALYSIS OF A C-ETHER LUBRICANT

Figure 15 is the schematic of the HPLC system used to analyze a C-ether lubricant, which is a blend of four chemical components [9]. Figure 16 depicts the chemical composition of the lubricant. Four modes of chromatography were used to analyze the C-ether lubricant to illustrate and compare the more common chromatographic techniques.

Size Exclusion Analysis

A set of size exclusion columns (Fig. 17) consisting of a 500-Å μ-styragel column and two 100-Å μ-styragel columns were used to analyze the C-ether lubricant. This combination of columns allowed for the study of substances to molecular weights of 10 000. Chloroform was used as the mobile phase at a flow rate of 1 ml/min. Twenty microliters (μl) of the lubricant was dissolved in 3 ml of chloroform, and 50 μl of this solution was injected into the HPLC system. Figure 18 is the chromatogram (the recorded separation) of this sample. Peak A was identified as the mixture of the 4-ring phenyl components (components A1, A2, and A3 of Fig. 16) and peak B as the 3-ring phenyl component (component B of fig. 16). All peaks were identified by concentrating the sample with the four pure components of the C-ether lubricant (one component at a time), injecting the sample into the HPLC and noting which peak on the chromatogram increased relative to the other peaks.

Normal Phase Analysis

A -CN bonded phase column was then used to analyze the C-ether lubricant. Heptane was used as the mobile phase at a flow rate of 1 ml/min. Twenty μl of the lubricant was dissolved into 3 ml of n-heptane and 50 μl of the resulting solution was injected into the HPLC system. Figure 19 is the chromatogram of the injected sample. Peaks A1, A2, and A3 were indentified as the 4-ring phenyl components and peak B as the 3-ring phenyl component.

Reversed Phase Analysis

Next, a C-18 bonded phase column was used to analyze the C-ether lubricant. A mixture of tetrahydrofuran (THF) and water (50 percent THF and 50 percent water by volume) was used as the mobile phase at a flow rate of 1 ml/min. Ten μl of the lubricant was dissolved into 3 ml of the solvent, and 20 μl of this solution was injected into the HPLC system. Figure 20 is the chromatogram of the injected sample. Peaks A1, A2, and A3 were identified as the 4-ring phenyl components, and peak B as the 3-ring phenyl component.

Adsorption Analysis

Finally, a silica adsorption column was used to analyze the C-ether lubricant. A mixture of n-heptane and chloroform (98 percent n-heptane and 2 percent chloroform by volume) was used as the mobile phase at a flow rate of 0.1 ml/min. Five μl of the lubricant was dissolved into 2 ml of the solvent, and 10 μl of this solution was injected into the HPLC system. Figure 21 is the chromatogram of the injected sample. Peaks A1, A2, and A3 were identified as the 4-ring phenyl components, and peak B as the 3-ring phenyl component.

Comparison of Results

The size exclusion analysis (Fig. 18) of the C-ether lubricant (a blend of four components) indicated the presence of only two components. The μ-styragel columns were able to separate the 3-ring phenyl component from the 4-ring components but were unable to separate the 4-ring components from each other.

The normal phase analysis (Fig. 19) of the lubricant indicated the presence of all four components. However, the -CN-bonded phase column was able to completely separate the 3-ring phenyl component from the 4-ring components but unable to completely separate the 4-ring components from each other.

The reversed phase analysis of the lubricant also indicated the presence of all four components. The C-18 bonded phase column, like the -CN-bonded phase column, was able to completely separate the 3-ring phenyl component from the 4-ring components but unable to completely separate the 4-ring components.

The optimum separation was obtained with the silica gel column used in the adsorption mode. It completely separated all four components.

HPLC ANALYSIS OF AN OXIDIZED ESTER LUBRICANT

An ester lubricant (trimethylol propane triheptanoate) was oxidized using a micro-oxidation technqiue, which is described in [3] to show how HPLC can be applied in the study of lubricant oxidation. The size exclusion mode was used in the ester oxidation analysis to present an overall view of the ester and its degradation products.

Figure 22 represents the micro-oxidation apparatus used to degrade the ester. Forty μl of the unused ester was placed onto the surface of a metal catalyst, keeping the apparatus at a constant temperature of 225° C. The ester was heated for 30 minutes under four different conditions:

1 An iron catalyst was used with a nitrogen atmosphere
2 An iron catalyst was used with an air atmosphere
3 A copper catalyst was used with a nitrogen atmosphere
4 A copper catalyst was used with an air atmosphere.

Figure 23 is the chromatogram of the unoxidized ester. Figure 24 shows the ester degradation under a nitrogen atmosphere using an iron catalyst. The loss of some ester as a result of evaporation is indicated by the decrease in the RI peak height, with the formation of decomposition product (or products) indicated by the broadening RI peak base and the detection of a UV peak.

Figure 25 shows the ester degradation under an air atmosphere using an iron catalyst. Along with the substantial loss of the initial ester (decrease of ester RI peak) is the formation of lower and higher molecular weight degradation material with the detection of at least three UV absorbing products.

Figure 26 shows the ester degradation under a nitrogen atmosphere using a copper catalyst. Evaporation of some ester occurred (see the RI peak) but broadening of the RI peak base did not, indicating no or very little formation of decomposition product. The UV detector was able to pick up at least three decomposition products.

Figure 27 shows the ester degradation under an air atmosphere using a copper catalyst. Unlike the air oxidization of the ester using an iron catalyst, no substantial loss of the ester occurred. The RI detector indicates higher molecular weight formation but not much. The UV detector also indicates very little decomposition product formation.

CONCLUDING REMARKS

It has been shown that HPLC, with the various separation modes available, can be used in the study of the high-temperature oxidative degradation of lubricants. With HPLC it is not only possible to monitor how a lubricant degrades with time (kinetic study), but also monitor the formation of degradation products and isolate these products for identification, hopefully providing a clue for the high-temperature improvement of the liquid lubricant.

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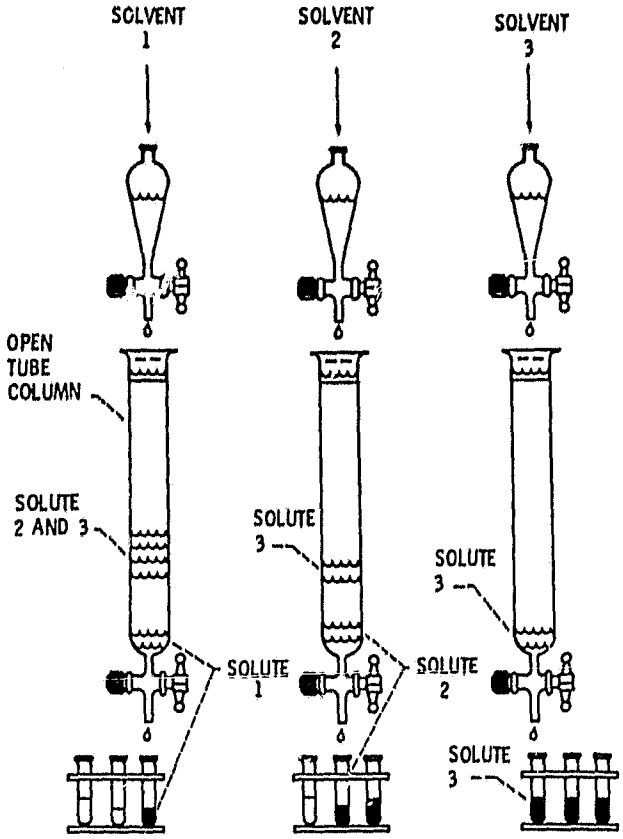

Figure 1. - Classical liquid column chromatography.

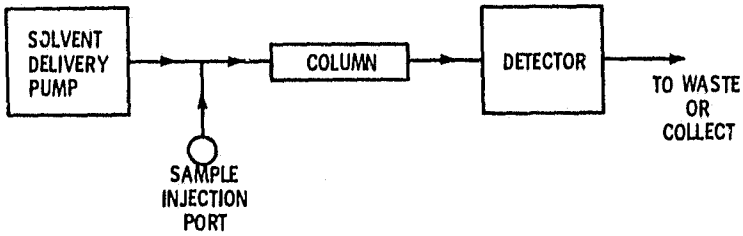

Figure 2. - Modern HPLC system.

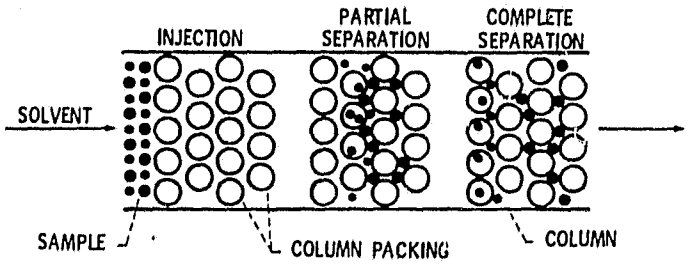

Figure 3. - Schematic diagram of size exclusion chromatography.

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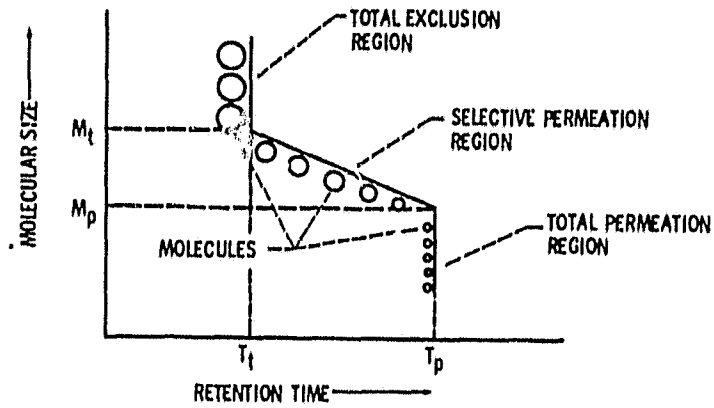

Figure 4. - The ideal size exclusion process.

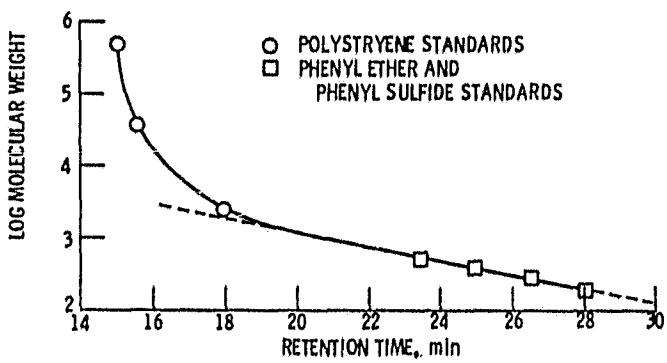

Figure 5. - Calibration curve for a size exclusion column set (one 500 Å and two 100 Å u-styragel columns). Flow rate, 1 milliliter/min; mobile phase, tetrahydrofuran.

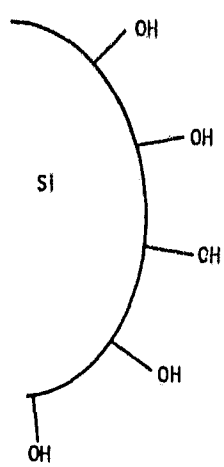

Figure 6. - Silica gel stationary phase.

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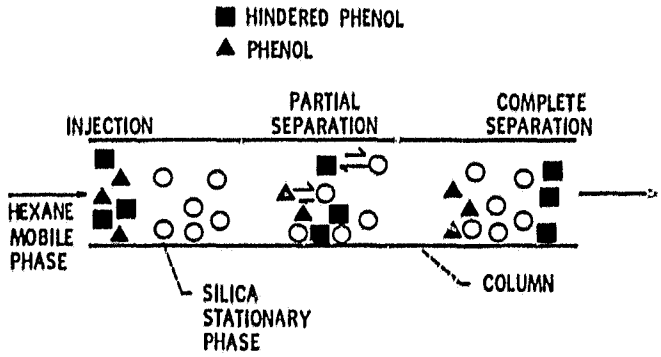

Figure 7. - Typical adsorption chromatographic separation.

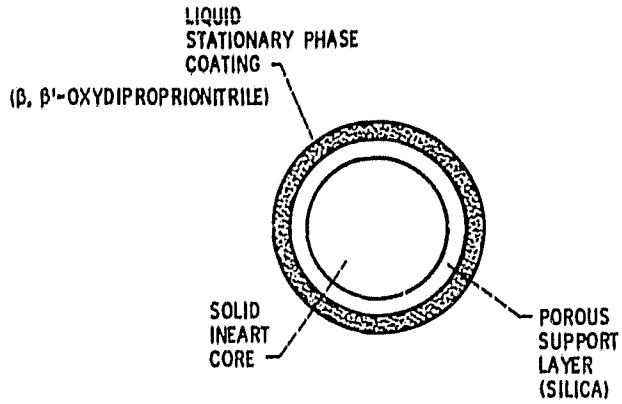

Figure 8. - Liquid-liquid chromatographic stationary phase.

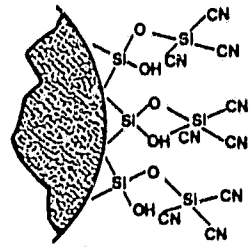

Figure 9. - Normal phase stationary phase.

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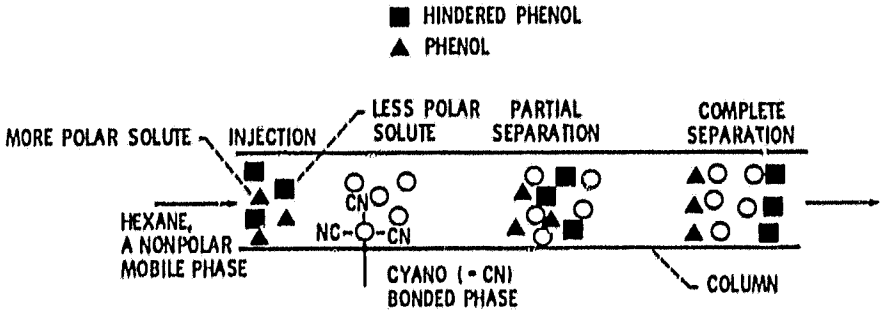

Figure 10. - Normal phase chromatography.

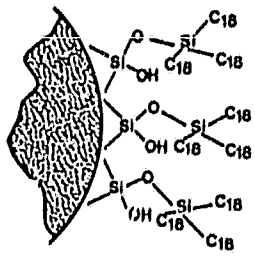

Figure 11. - Reverse phase stationary phase.

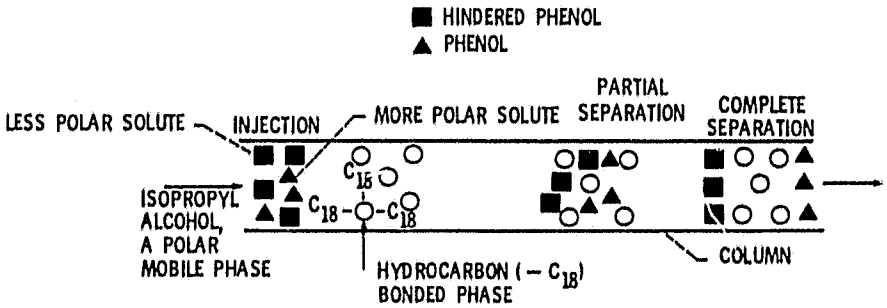

Figure 12. - Reverse phase chromatography.

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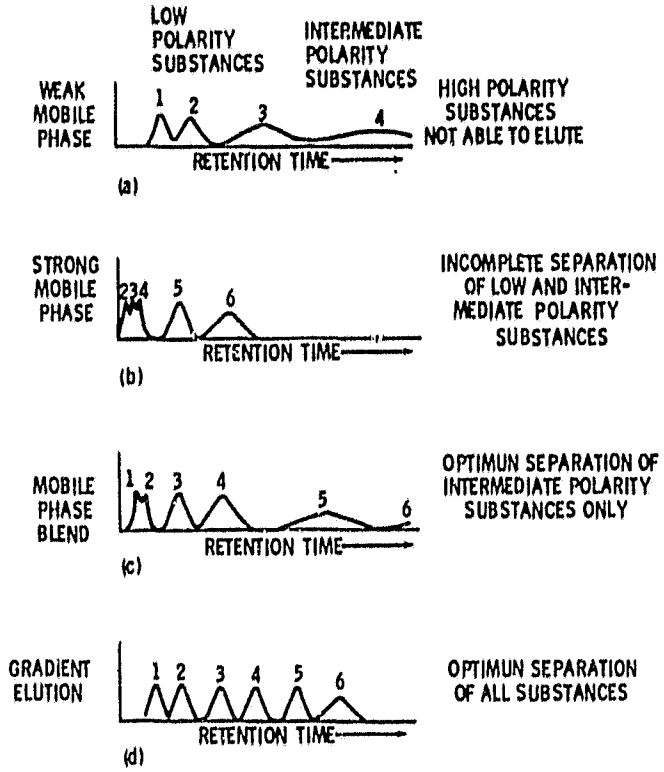

Figure 13. - Sample separation optimization.

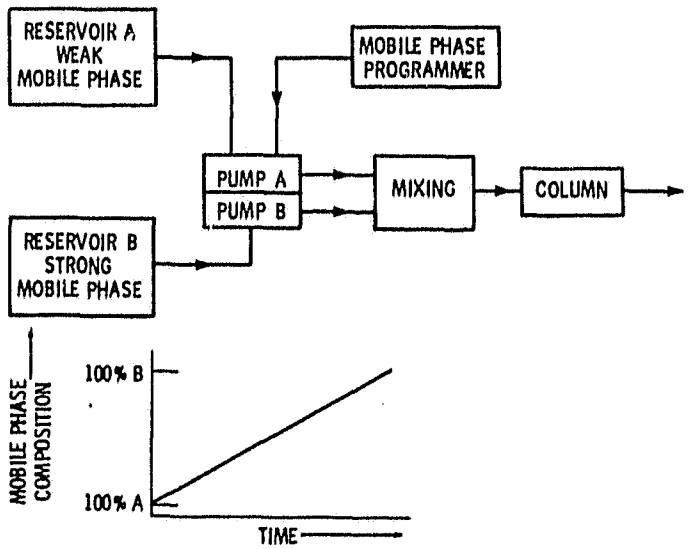

Figure 14. - Gradient elution chromatography.

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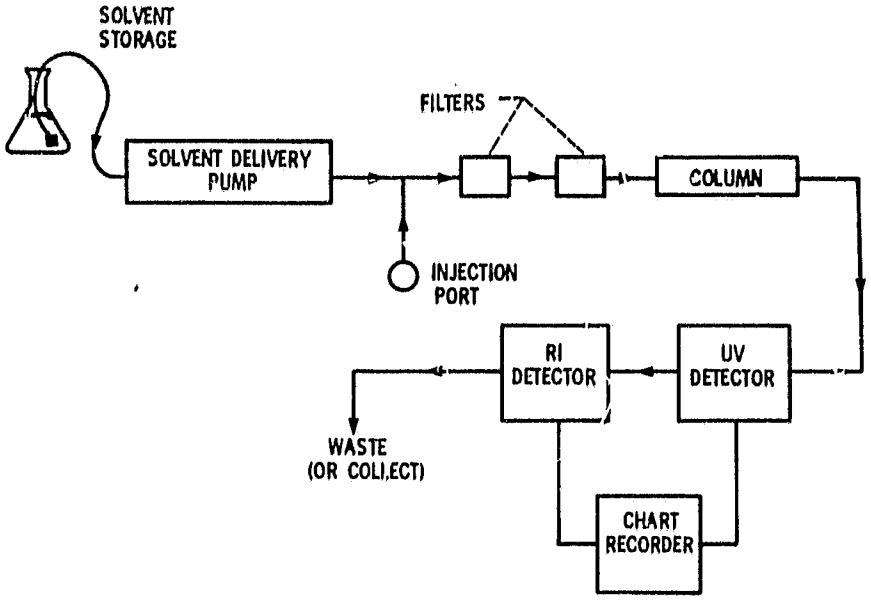
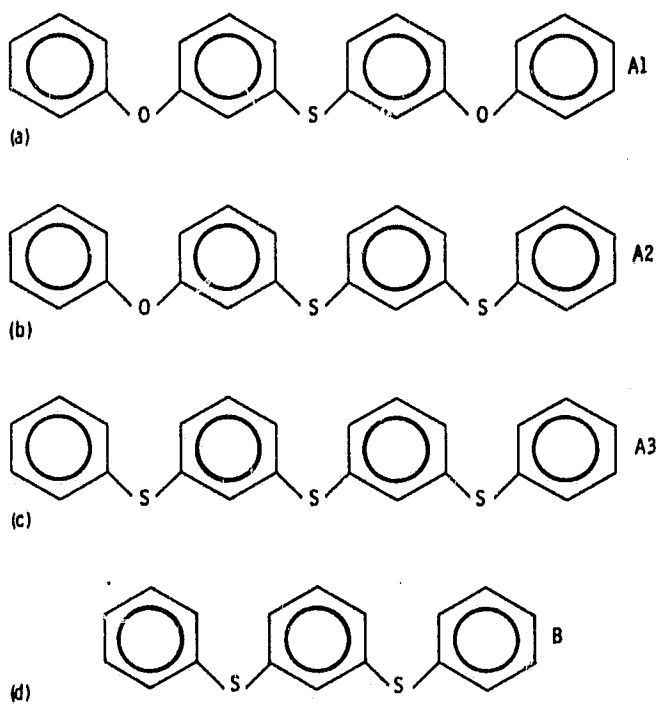


Figure 15. - HPLC system used in the analysis of the Thio-ether lubricant.



(a) 1, 1-thiobis [3-phenoxybenzene]; molecular weight, 370.
(b) 1-phenoxy-3-[[3-(phenylthio) phenyl] thio] benzene; molecular weight, 386.
(c) 1, 1-thiobis [3-(phenylthio) benzene]; molecular weight, 402.
(d) 1, 3-bis (phenylthio) benzene; molecular weight, 294.

Figure 16. - Chemical components of MCS 524 C-ether base fluid.

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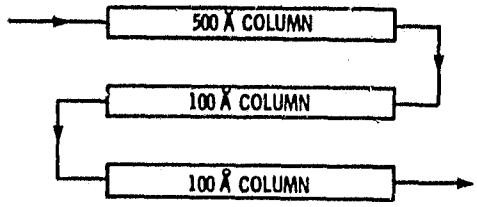

Figure 17. - Set of μ-Styragel size exclusion columns.

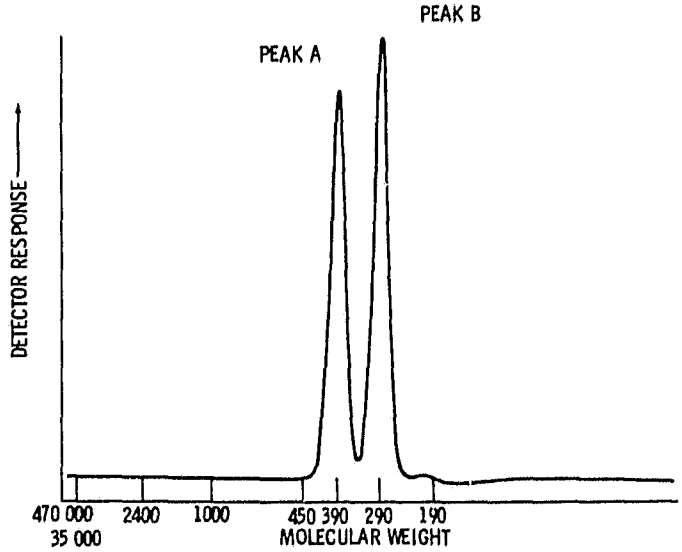

Figure 18. - Size exclusion chromatogram of C-ether lubricant using μ-styragel columns. Flow rate, 1.0 milliliter/min; mobile phase, chloroform; RI detector (8X).

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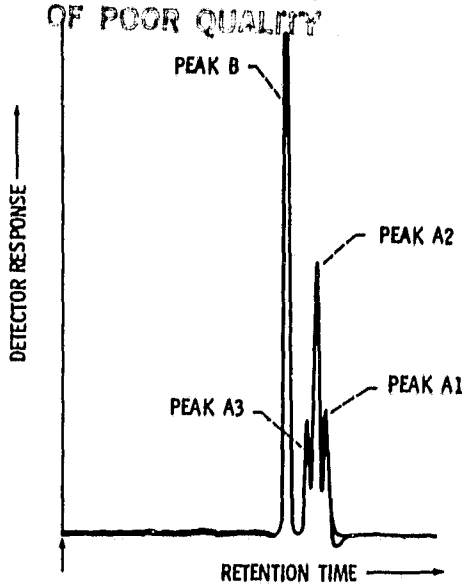

Figure 19. - Normal phase chromatogram of C-ether lubricant using a CN column. Flow rate, 0.50 milliliter/min; mobile phase, heptane; RI detector (8 X).

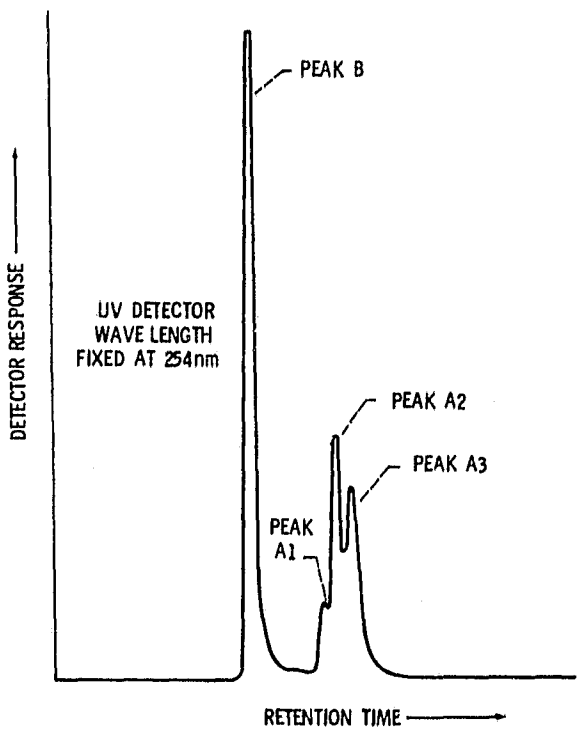

Figure 20. - Reverse phase chromatogram of C-ether lubricant using a C_{18} column. Flow rate, 0.5 milliliter/min mobile phase, water/tetrahydrofuran (50/50); UV detector (2.0 AUFS) set at 254 nm.

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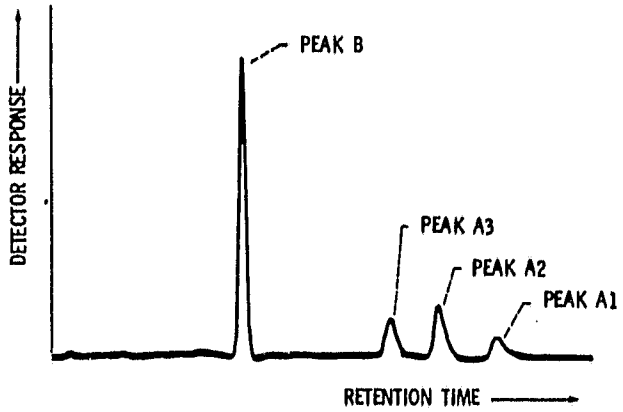

Figure 21. - Adsorption chromatogram of C-ether lubricant using a silica column. Flow rate, 0.1 milliliter/min; mobile phase, heptane/chloroform (98/2); RI detector (8X).

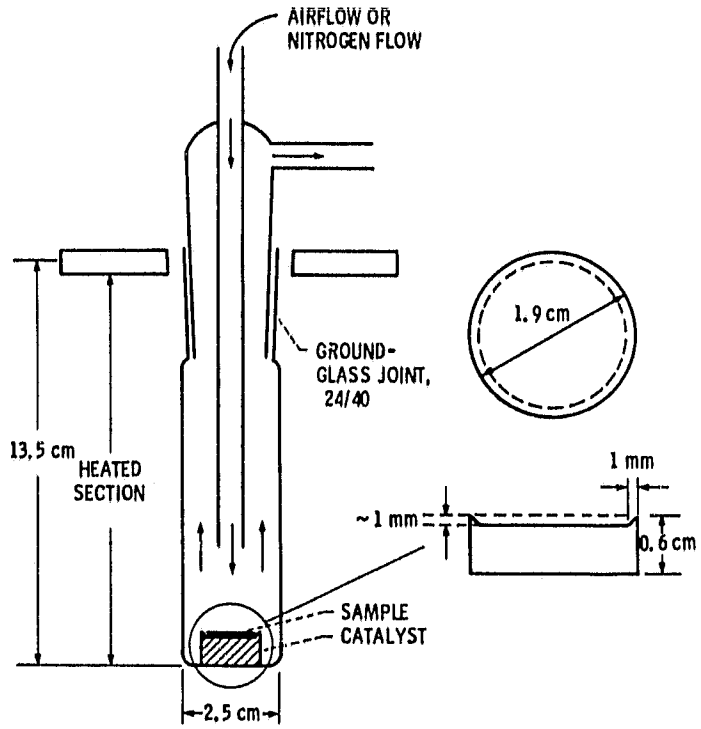

Figure 22. - Micro-oxidation apparatus.

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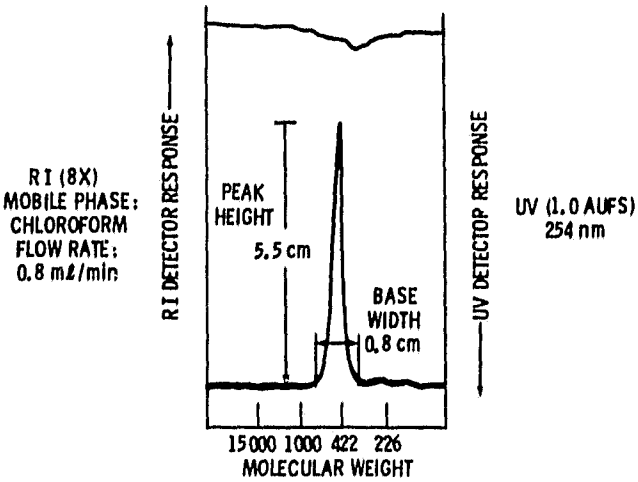

Figure 23. - Size exclusion analysis of unused Ester lubricant.

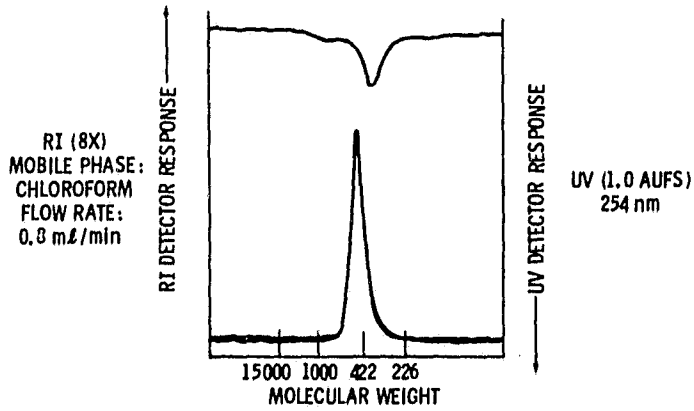

Figure 24. - Size exclusion analysis of degraded Ester lubricant-catalyst, iron; test atmosphere, dry nitrogen.

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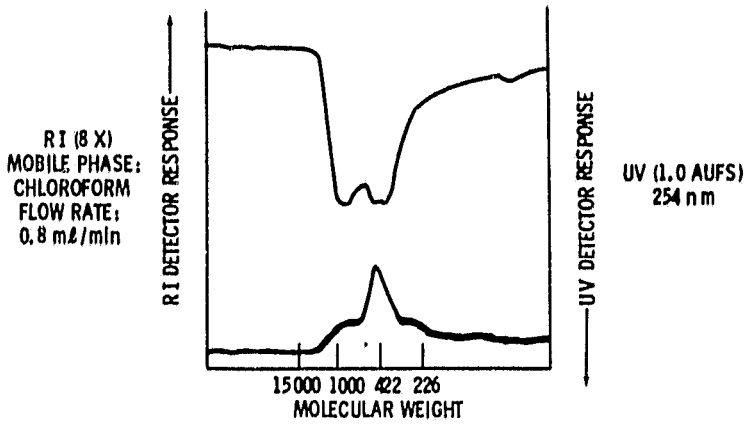

Figure 25. - Size exclusion analysis of degraded Ester lubricant-catalyst, iron; test atmosphere, dry air.

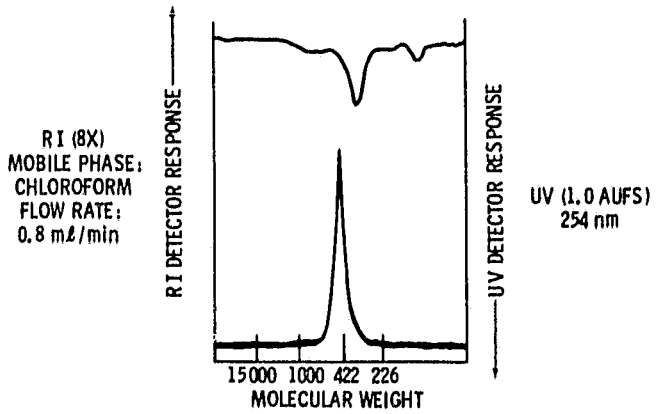

Figure 26. - Size exclusion analysis of degraded Ester lubricant-catalyst, copper, test atmosphere, dry nitrogen.

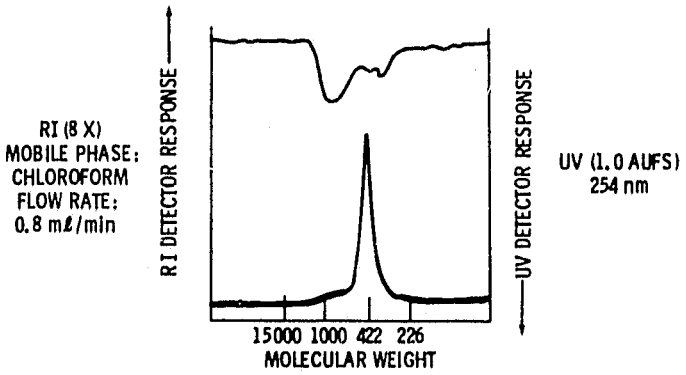

Figure 27. - Size exclusion analysis of degraded Ester lubricant-catalysis, copper; test atmosphere, dry air.