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Analysis of a Thioether Lubricant by Infrared Fourier Microemission Spectrophotometry

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ANALYSIS OF A THIOETHER LUBRICANT BY INFRARED FOURIER MICROEMISSION SPECTROPHOTOMETRY

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SUMMARY

An infrared Fourier microemission spectrophotometer was used to obtain spectra (wavenumber range, 630 to 1230 cm^{-1}) from microgram quantities of thioether lubricant samples deposited on aluminum foil. Infrared bands in the spectra were reproducible and could be identified as originating from aromatic species (1,3-disubstituted benzenes). Spectra from all samples (neat and formulated, used and unused) were very similar. Additives (an acid and a phosphinate) present in low concentration (0.10 percent) in the formulated fluid were not detected. This instrument appears to be a viable tool in helping to identify lubricant components separated by liquid chromatography.

INTRODUCTION

One of the first achievements of modern infrared interferometry was the recording of infrared emission spectra from moderately heated surfaces. The spectra of organic acids on flat metal surfaces were reported by Low (ref. 1). Griffith (ref. 2) showed spectra of thin (1 μm) coatings of grease on metallic mirrors. Bates (ref. 3), in a review paper, provides many other examples.

In concentrated contact lubrication, metal surfaces are exposed to liquid lubricants at high temperatures. These lubricants contain reactive species (additives) which form protective layers on the metal surfaces. The chemical composition of these surface films will provide important information about the mechanisms of additive action.

Most of the above studies involved unlimited radiating areas. However, in concentrated contact lubrication, contact diameters are always less than 500 μm and usually less than 100 μm. Therefore, a microspectrophotometer was developed (ref. 4) for dealing with the analysis of areas as small as 10 μm in diameter.

Another area of analytical interest is the determination of the chemical structure of eluted fractions of degraded lubricants separated by high performance liquid chromatography (ref. 5). Here, the very low concentrations of degraded lubricants in a large amount of liquid mobile phase makes conventional infrared analysis difficult.

Therefore, the objective of this investigation was to determine the ability of the Fourier emission infrared microspectrophotometer to elucidate the chemical structure of eluted fractions of a degraded high temperature liquid lubricant (thioether).

APPARATUS

The apparatus for Infrared Emission Fourier Microspectrophotometry is shown schematically in figure 1. The sample is shown below the heated metal block to which it is attached. The sample was a strip of aluminum foil, on which a drop of solution was allowed to evaporate, leaving a solid organic residue. The area analyzed in these experiments was 100 µm in diameter. It is exceedingly important to maintain the sample at constant temperature throughout to avoid a vertical temperature gradient within the residue. A temperature gradient could cause partial reabsorption of emitted radiation, making spectral analysis difficult, if not impossible.

The lens below the sample (fig. 1) is of Cassegrainian design. A small portion of the central section is blocked by a convex mirror which is facing downward, reflecting the radiation gathered by the larger concave mirror through a hole in its center into the rest of the instrumentation. A small planar mirror at 45° with the vertical, bends the radiation into the horizontal plane of the interferometer. However, immediately adjacent to the 45° mirror is the tuning fork chopper, whose reflecting tines are at a 45° degree angle with respect to the optic axis. In the open position of the chopper, sample radiation is passed through, while in the closed position, reference blackbody radiation is reflected and transferred downstream. The amplifier will detect only the difference between the sample signal and the blackbody signal after both have passed through the interferometer. After the Fourier transformation, a spectrum representing the difference between the sample and blackbody spectra is plotted by the recorder.

Figure 2 is a photograph of the inlet system and the sample holder. The lens looks at the bottom side of the sample held on a heatable mechanical stage allowing for x,y,z and rotational motion. Micrometer screws permit reproducible positioning of the sample. The rotating filter holder below the lens is connected to the large geared wheel in the foreground by a belt. This wheel has sectors painted white and black for the reflecting optical photocell pickup.

The blackbody is shown in figure 3. Radiation emerges from the hole in front. The flux can be controlled by the spring-loaded, adjustable wedge in front. The blackbody is shown schematically in figure 4. It can be both heated and cooled to a desired temperature and maintained there by a thermostatic control. The outer shell is always at ambient temperature. This blackbody differs from commercial ones of similar size because its temperature and flux intensity are separately variable at any time over a wide and continuous range.

TEST FLUIDS

Four liquid lubricant samples were studied in this investigation. They are described in Table I. Sample 1 was an unused thioether base fluid containing no additives. It is a mixture of polyphenyl ether and thioether components as shown in figure 5. Sample 2 was a formulated version of the thioether base fluid containing 0.1 wt % of 1-methylethyl-phenylphosphinate and 0.05 wt % trichloroacetic acid. Structures of these additives appear in figure 6. Sample 3 was a used sample of the formulated thioether from a high temperature bearing test which ran for 13 hr. Details of this test appear in reference 6. The final sample (4) is a concentration of the degraded products from sample 3 (the bearing test). Sample 4 was prepared by dissolving the bearing test sample in a mixture of acetonitrile and heptane. Two phases resulted with the nondegraded thioether concentrating in the heptane phase while the degraded thioether concentrated in the acetonitrile phase. The acetonitrile phase was then extracted and evaporated to dryness and reconstituted in 3 ml of chloroform. Samples 1, 2, and 3 were prepared by dissolving 40 μl of the lubricant in 3 ml of chloroform to simulate the concentration in an eluted fraction from a liquid chromatograph. One drop of these samples was allowed to evaporate on an aluminum foil surface (cleaned with carbon tetrachloride) for the infrared emission analysis. Evaporation took place at room temperature in a vacuum oven.

RESULTS

Infrared spectra obtained with the microspectrophotometer over a wavenumber range of 630 to 1230 cm^{-1} appear in figure 7. Figure 7(a) shows the emission spectra for the unused thioether base fluid (Sample 1). Figure 7(b) contains three different spectra from sample 2 (the unused formulated thioether base fluid). These spectra differ because of different sample and reference temperatures. Similar data for sample 3 (used formulated thioether from the bearing test) appear in figure 7(c). Figure 7(d) contains spectra for sample 4 (the concentrated degradation products from the bearing sample).

Spectra were also obtained over the spectral range of 1274 to 1851 cm^{-1}. However, the data in this range was not reproducible and therefore not included in this paper.

DISCUSSION

Comparison of Spectra

In order to compare bands from different spectra the following procedure was used. An approximate baseline was drawn for each spectrum. The areas of the prominent emission bands were approximated by (1) drawing a vertical line (height, h) from the peak to the baseline, marking the midpoint between peak and baseline and drawing another line (width at half height, w) parallel to the baseline through the midpoint until it intersects with the band contour and (2) by multiplying h and w. The band areas were thus approximated by triangles.

Since the spectra had been "normalized" (i.e., the highest band having the maximum possible ordinate), the band areas were corrected by multiplication with the greatest unnormalized amplitude (GUA). With this treatment, bands from different spectra can be compared. A summary of corrected band intensities for most of the spectra appears in figure 8.

Infrared Spectral Analysis

Before discussing these results, a few things should be pointed out. It is necessary to pay attention to these remarks in the context of the extremely weak signals recorded. The area concentration of sample on the foils is much less than a microgram/square centimeter. Ideally, the same spectral band (arising from the same vibration) should have the same energy, regardless of temperature. This is because the vibrational energy of a simple harmonic oscillator should not vary with temperature. However, deviations from this rule do occur and can be either experimental or physical.

Experimentally, the most important factors are the blackbody flux and temperature. Most of the spectra of this study represent differences between sample radiant energy and reference radiant energy. If the reference energy is higher than the sample energy, inversion of spectral bands may occur. Apparent absorption bands will be seen, rather than emission bands. If the reference temperature is different from the sample temperature, the baseline slope will not be horizontal. It may be positive in one spectral region and negative in another, as governed by the Planck's distribution law. This may results in the appearance of spurious satellite bands. This is because the level of the reference radiation is sometimes between the peak and the bottom of an emission band (fig. 9). Since only absolute values of the amplitude of the difference between sample and reference are calculated by the Fourier transformation, distorted spectra can result, as shown in figure 9. This previously described inversion can be difficult to recognize since correct emission bands may appear in one frequency range, but inverted bands in another. This problem can be minimized by (1) optically limiting the frequency range as much as possible and thereby reducing the slopes and (2) by obtaining duplicate spectra with slightly different reference temperatures. An example is shown in figure 10. Here, an emission spectrum of a polyphenyl ether was obtained with too high a reference temperature. Figure 10 shows an apparent absorption band at 720 cm^{-1}. Figure 11 shows an emission spectrum obtained under identical conditions of figure 10, except at a lower reference temperature. Here the correct emission band occurs at 690 cm^{-1}.

Physically, infrared emission bands are broadened as the temperature is increased (1) because of the excitation of additional rotational states and (2) because of a change of equilibrium between rotational isomers. This is because bands for two rotational states may be so close to each other that they are not resolvable.

In addition, the frequency of the band peak can also shift with temperature for both experimental and physical reasons. Experimentally, the primary reason is due to a change in baseline slope. Physically, frequency shifts may occur because of the lower spring constant at higher temperatures which would result in a lowering of the peak frequency. Hydrogen bonding and other intermolecular interactions may result in increases in frequency. These frequency shifts may be as great as ±5 cm^{-1}.

With the above comments in mind, the spectra obtained for the four different samples are now discussed.

Thioether base fluid (Sample 1). - The single beam spectrum (i.e., not referenced) for this fluid appears in figure 7(a). Strong emission bands occur at about 750 and 690 cm^{-1}. Moderate bands are seen at approximately 660, 790, 835, 880, 905, 965, 1005, and 1015 cm^{-1}. Weaker bands occur at 1025, 1135, and 1180 cm^{-1}. Most of these bands are representative of 1,3-disubstituted benzenes as compiled by Socrates (ref. 7). For example, bands at 690, 790, 880, and 965 cm^{-1} are due to aromatic (=C-H) out of plane deformation vibrations. Aromatic (=C-H) in plane deformations occur at 1075 and 1180 cm^{-1}. Other bands are associated with phenoxy (C-H) out of plane deformations (750 cm^{-1}) and C-S-C stretch (660 cm^{-1}). The remaining bands are not readily assigned. Aromatic (-S) stretch also occurs at 1075 cm^{-1}.

Formulated thioether fluid (sample 2). - Three spectra (800, 802, and 804) for this fluid appear in figure 7(b). All three spectra were taken at a sample temperature of 38 °C. Spectrum 800 was not referenced. Spectra 802 and 804 were referenced at temperatures of 28 and 31 °C, respectively. Taking into account variations among these spectra, bands appear at 670 to 690, 750 to 770, 800, 850 to 870, 920, 940, 990, 1050, 1130, and 1170 cm^{-1}. Most of these bands match those of the base fluid (sample 1) as would be expected. It does not appear that any new bands due to the additive content are detectable in this frequency range.

Degraded bearing test fluid (sample 3). - Spectra (810, 812, and 814) for this fluid appear in figure 7(c). Bands are observed at about 640, 665, 740, 795, 855, 910, 940, 980, 1025, 1055, 1125, and 1180 cm^{-1}. This was a degraded sample of lubricant taken at the conclusion of a 13 hr high temperature bearing test which was to have run for 100 hr. The test was terminated at 13 hr because of severe cage wear and high production of solids. The fluid was darkened and showed a viscosity increase of about 10 percent. Nevertheless, the spectra of this sample are very similar to those of the unused fluid. Previously, infrared spectra of high molecular weight products from polyphenyl ethers (ref. 8) have also been almost identical to the nondegraded fluid. Other results, using size exclusion chromatography (ref. 5), indicate that the degradation products of thioethers are essentially higher molecular weight homologs of the base fluid. Since these materials differ only in the number of aromatic rings, it is not surprising that their spectra are quite similar.

Concentrated degraded bearing test fluid (sample 4). - Since only a small percentage of a used lubricant is degraded, an extraction technique was used to concentrate these products. Although this concentration technique (described in the test fluids section) appeared to be visually successful, the spectra (fig. 7(d)) are the same as the nonconcentrated fluid (sample 3). In light of the discussion about the spectra from the nonconcentrated fluid, this is not surprising.

In conclusion, infrared emission microspectrophotometry appears to be a viable technique for helping to identify eluted components separated by liquid chromatography.

SUMMARY OF RESULTS

Four samples of a thioether lubricant were analyzed by infrared Fourier microemission spectrophotometry. The following results were obtained:

1. Infrared emission spectra (from 630 to 1230 cm^{-1}) were successfully obtained from less than microgram quantities of thioether lubricants deposited on surfaces of aluminum foil.

2. Infrared spectra from unused and degraded thioethers were essentially the same in the frequency range from 630 to 1230 cm^{-1}.

3. The technique was not able to detect two additives (an acid and a phosphinate) which were present at low concentration (0.1 wt %) in the base fluid.

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TABLE I. - DESCRIPTION OF TEST SAMPLES

Sample	Fluid	Additive content
1	Unused thioether base fluid	None
2	Unused formulated thioether	0.1 wt % 1-methylethylphenylphosphinate 0.05 wt % trichloroacetic acid
3	Used formulated thioether from 13 hr high temperature bearing test[a]	Same as sample 2
4	Concentrated sample of degradation products from sample 3	------------------------------

[a] Reference 6.

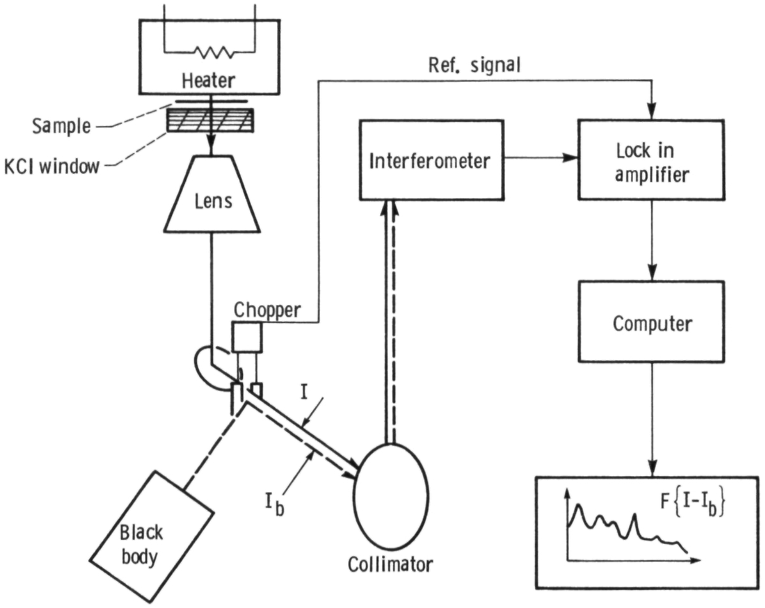

Figure 1. - Source unit for Fourier microspectrophotometry (operation with chopper and blackbody reference giving spectra representing the difference between source and blackbody signals).

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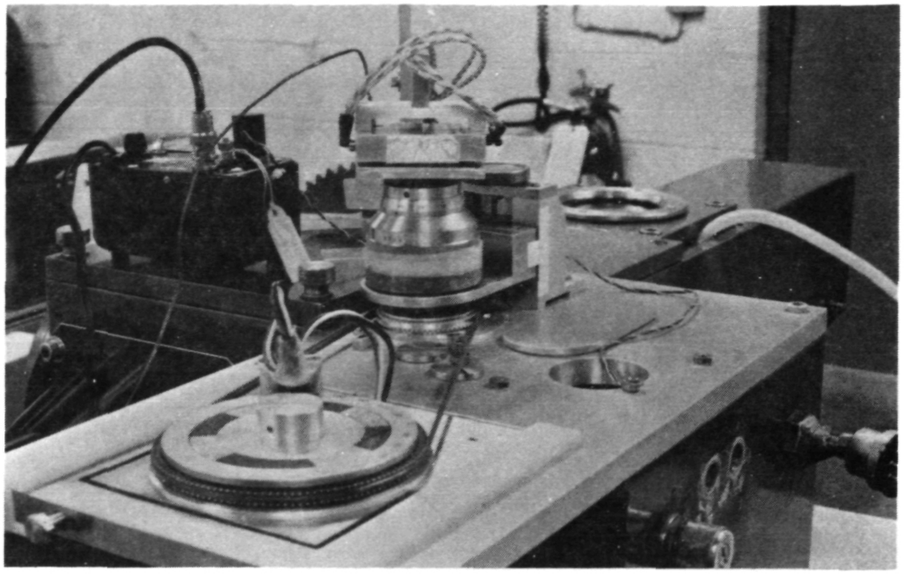


Figure 2. - View of apparatus to Record Emission Spectra. The heated sample holder is above the lens. The polarizer is rotated below the lens. Black and white sectors on the large gear in the foreground locate the angular polarizer postion for the photoelectric pickup. The opening in the interferometer cover below the polarizer is the entrance for the emitted radiation to be analayzed.

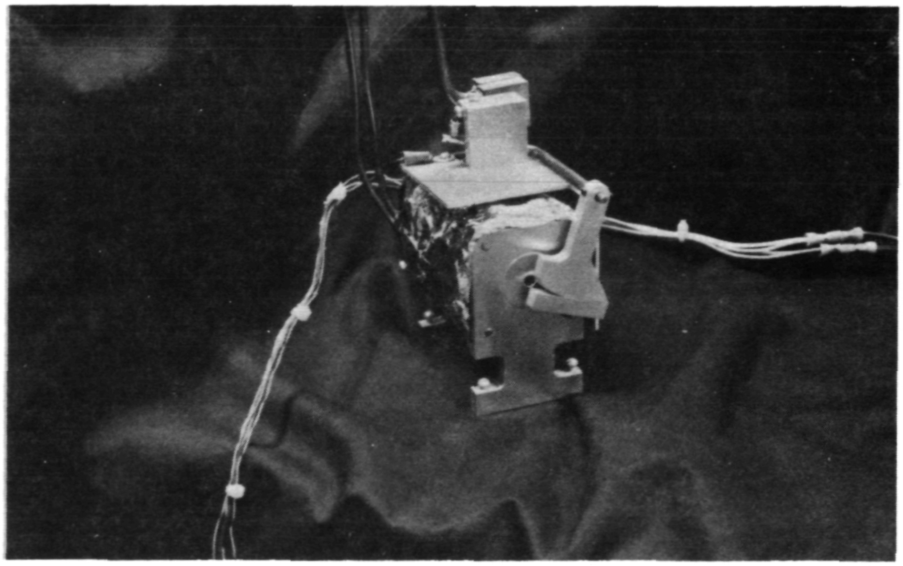


Figure 3. - Blackbody Reference Source. The radiation exits through the round hole and wedge in front.

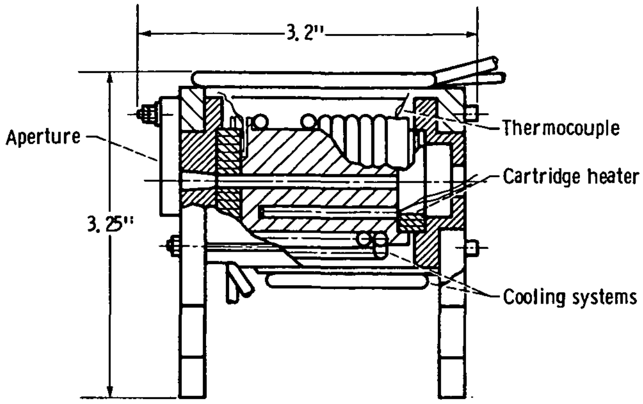
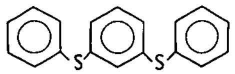
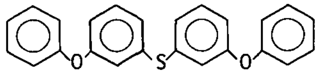


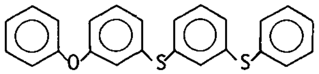
Figure 4. - Schematic of Blackbody reference source.



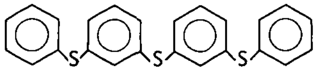
1,3-bis (phenylthio) benzene



1,1'-thiobis [3-phenoxybenzene]

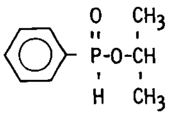


1-phenoxy-3-[[3-(phenylthio)phenyl]thio] benzene



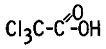
1,1'-thiobis [3-(phenylthio)benzene]

Figure 5. - Chemical structures of Thioether components.



$C_6H_5{-}P(=O)(H){-}O{-}CH(CH_3)_2$

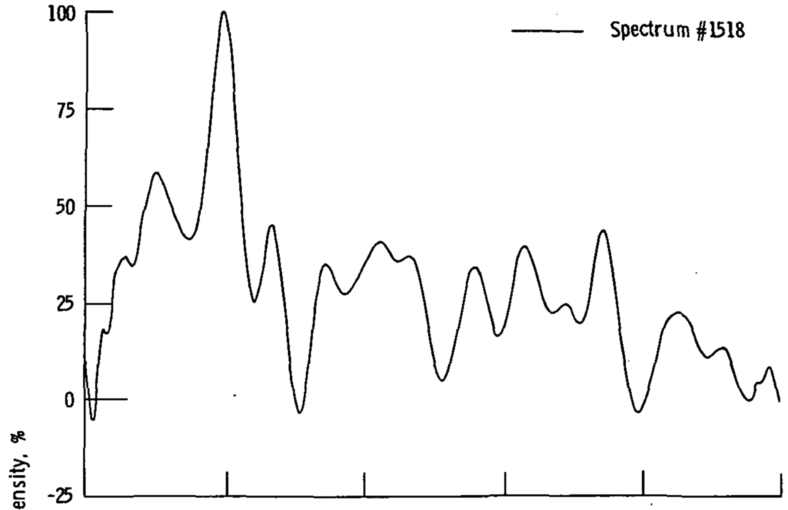
(a) 1-Methylethyl Phenylphosphinate



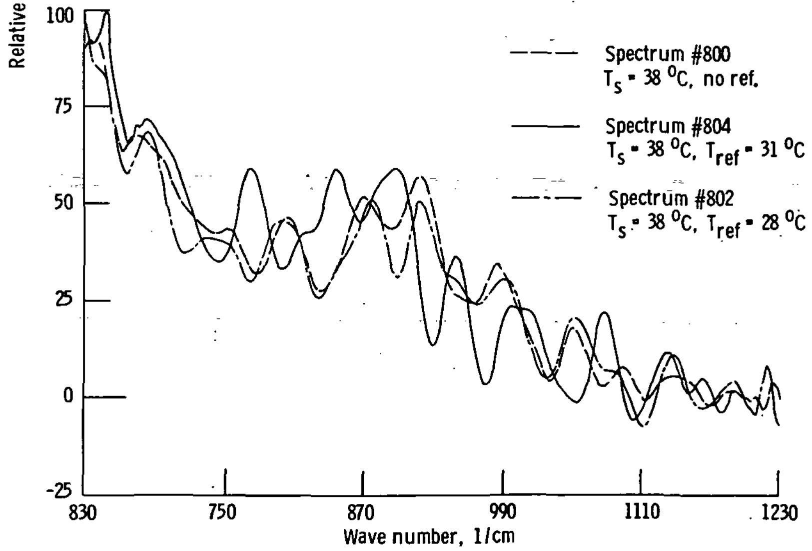
$Cl_3C{-}C(=O){-}OH$

(b) Trichloroacetic acid

Figure 6. - Structures of additives in formulated Thioether.

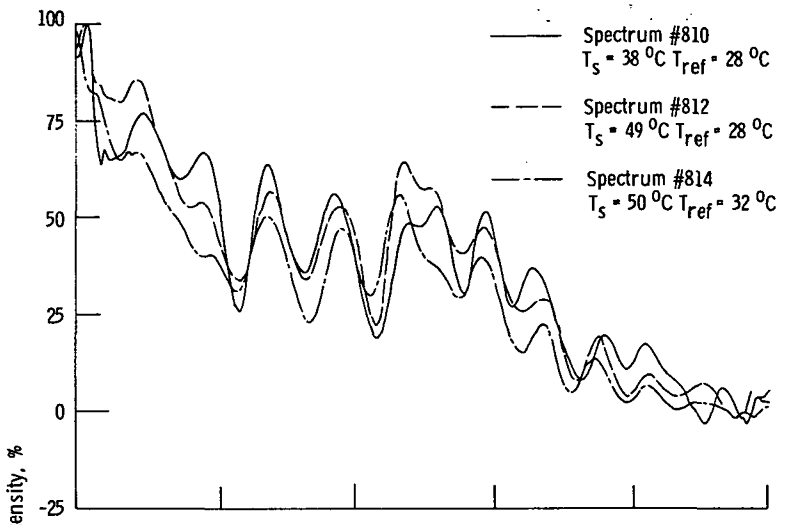


(a) Unused Thioether base fluid.

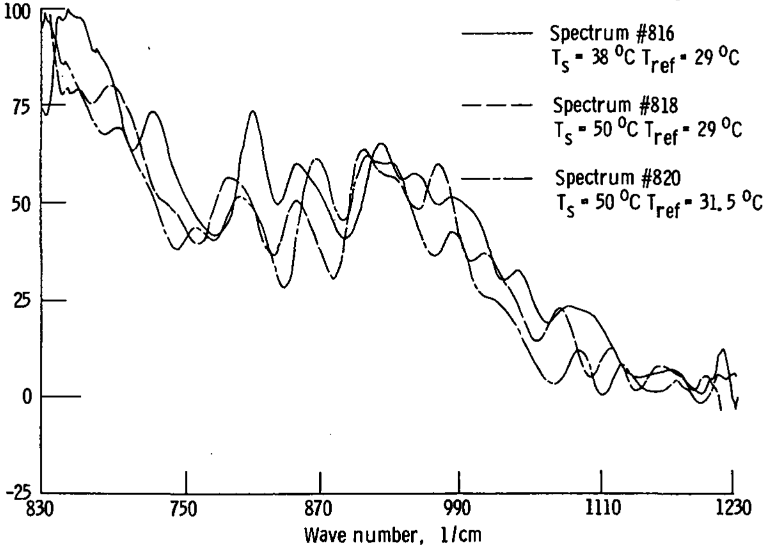


(b) Unused formulated Thioether fluid.

Figure 7. - Infrared emission spectra from 630 to 1230 cm^{-1}.

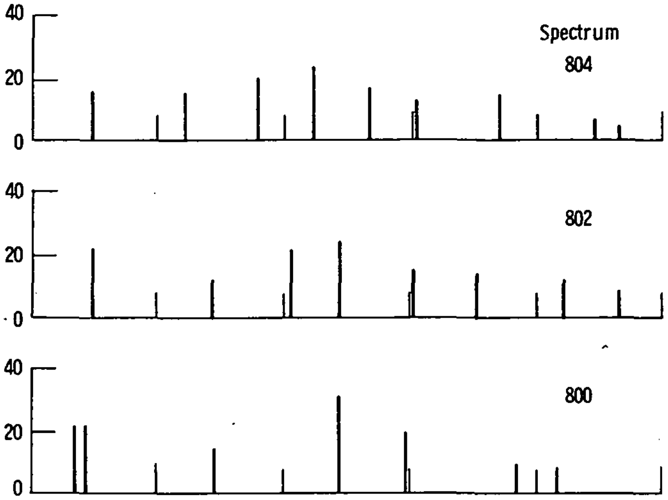


(c) Used formulated Thioether fluid from a 13 hr high temperature bearing test.

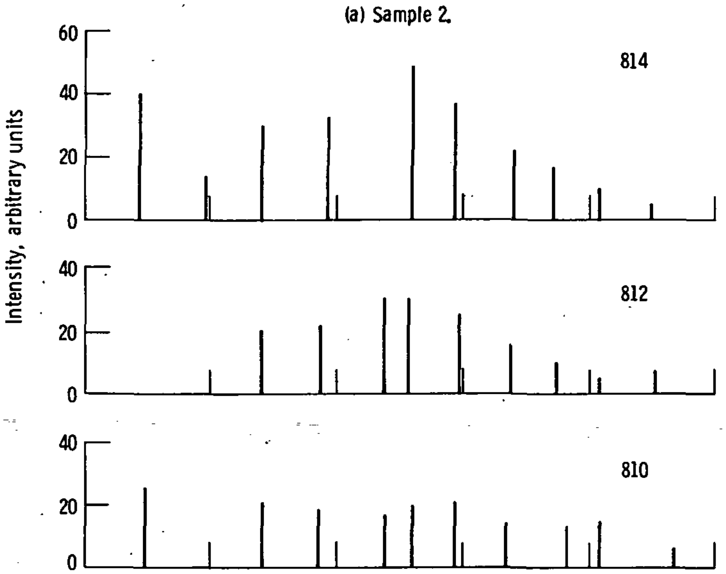


(d) Concentrated sample of degradation products from formulated Thioether fluid from a 13 hr high temperature bearing test.

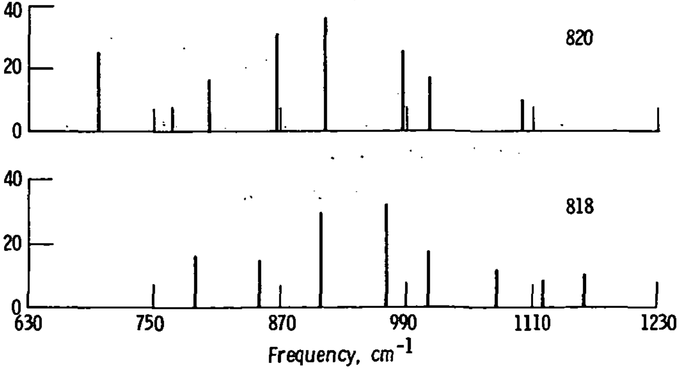
Figure 7. - Concluded.



(a) Sample 2.



(b) Sample 3.



(c) Sample 4.

Figure 8. - Normalized infrared emission bands for each sample.

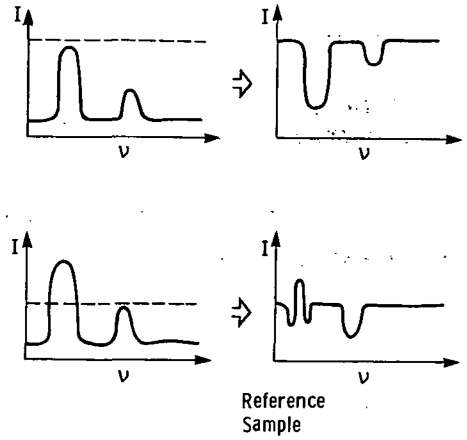


Figure 9. - Distortion of calculated emission bands as a result of a maladjusted reference level.

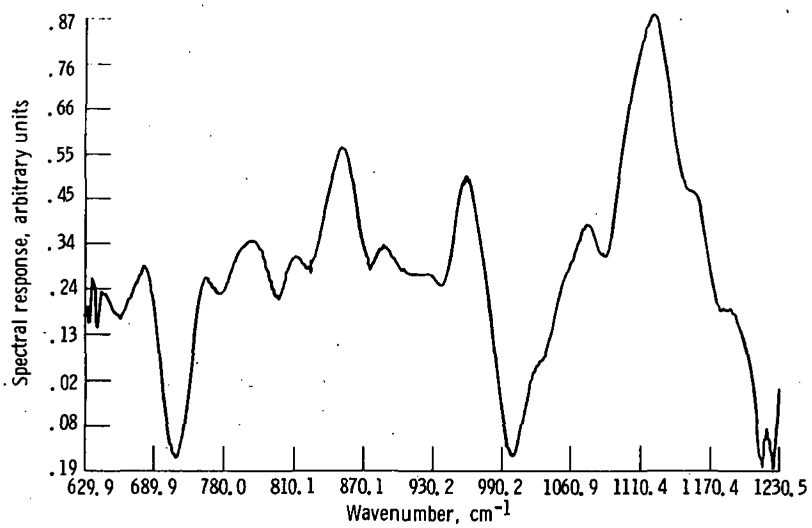


Figure 10. - Emission spectrum of a polyphenylether obtained with too high a reference temperature.

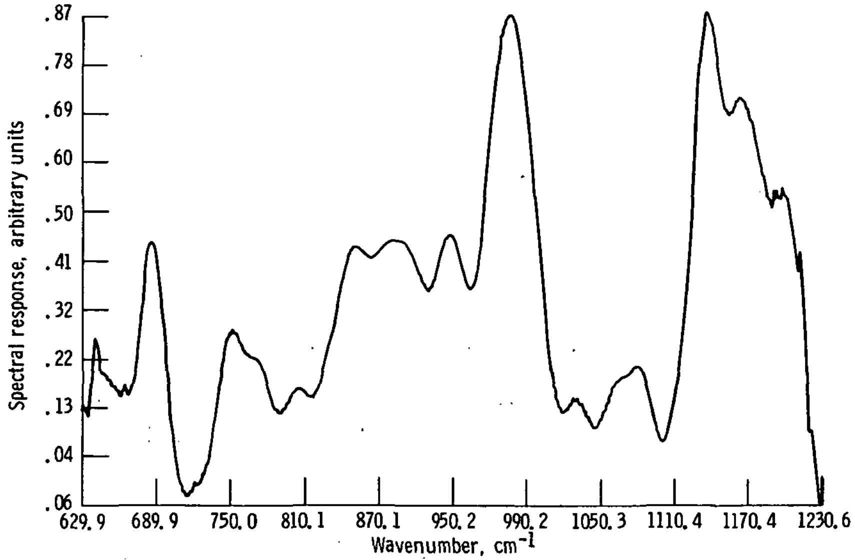


Figure 11. - Emission spectrum for the same conditions on those of figure 10, but obtained with a lower reference temperature.

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15. Supplementary Notes

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16. Abstract

An infrared Fourier microemission spectrophotometer was used to obtain spectra (wavenumber range, 630 to 1230 cm^{-1}) from microgram quantities of thioether lubricant samples deposited on aluminum foil. Infrared bands in the spectra were reproducible and could be identified as originating from aromatic species (1,3-disubstituted benzenes). Spectra from all samples (neat and formulated, used and unused) were very similar. Additives (an acid and a phosphinate) present in low concentration (0.10 percent) in the formulated fluid were not detected. This instrument appears to be a viable tool in helping to identify lubricant components separated by liquid chromatography.

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