



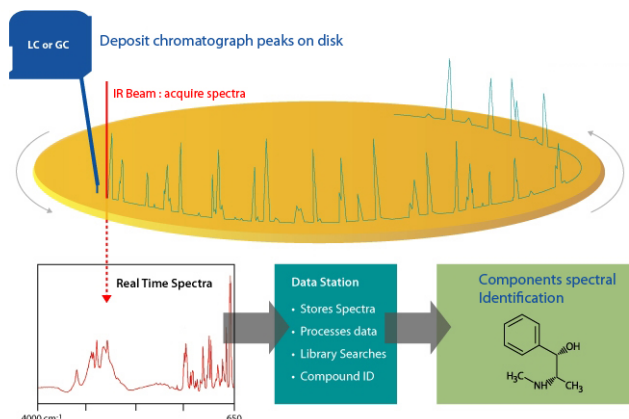
DiscovIR-LCTM

Deposition and Detection System

Application Note 028
May 2008

LUBRICANTS ANALYSIS

The DiscovIR-LC is a powerful new tool for materials analysis. When connected to the outlet of an LC column, the DiscovIR deposits LC eluants as a continuous track on an infrared transparent substrate. The built-in interferometer simultaneously captures a set of time-ordered infrared spectra from the deposited track. The result is a map of molecular structure of all sample components.



SUMMARY

This application note describes use of coupled GPC-FTIR to identify the polymeric additives in lubricants, and to characterize their molecular weight distribution. The same techniques described herein can also be applied to used lubricants, thus facilitating the measurement of:

- Additive shear degradation
- Additive loss.
- Oxidative and other chemical changes to polymer components.

INTRODUCTION

Both petroleum-based lubricants and synthetic lubricants contain additive packages, which enhance functional performance of the lubricant. These additives serve a variety of functions; including corrosion protection, antioxidation, reduction of acidity, control of lubricant viscosity, detergency, and wear protection of metal surfaces. The additives can be regarded as sacrificial, in that they are consumed in the fierce environment of engine lubrication. In the operation of an automotive engine, oil changes are not required due to the oil breakdown, but rather to the depletion and consumption of the additive package.



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Monitoring of lubricants during use is regularly employed in critical use situations and in high value equipment. The oil is regularly monitored for degree of oxidation, contaminant generated, and depletion of additives function. In some situations, certain additives will be added to a used oil, rather than doing a complete oil change-out. Common additive functions are listed in table I.

Viscosity modulators	Dispersants
Antioxidants	Buffers
Anti-wear agents	Solvents
Detergents	Corrosion inhibitors

Table 1 Oil Additive package components

Viscosity Index Improver (VII) and the Dispersant are both polymeric materials that typically comprise about 15% of the formulated lubricants. VIIs flatten out the viscosity-temperature curve of a lubricant. An engine oil provides optimum lubrication within a certain viscosity range, and fails to provide this lubrication when it is too hot or too cold. Depletion of a VII or functional deterioration will result in increased engine wear. The use of VIIs extends the safe operating temperature range of a motor oil.

Dispersants interact with particulate material produced or ingested during engine operation, preventing agglomeration that results in sludge that coats internal engine surfaces, and may plug oil passageways. The dispersants are complex small polymer chains that possess a polar chain-end group and an oil-philic end group. Polyisobutenyl succinimide and its variants is a commonly used dispersant. Being polymeric materials, the VIIs and the dispersants are subject to shear degradation within an operating engine, or other hydraulic applications that impose high liquid shear forces. Described below is a combined chromatography – spectroscopy method for identification and characterization of these polymeric components of a lubricant. The technique described is applicable to analysis of both new and used lubricants.

EXPERIMENTAL

Materials

Two unused samples of motor oil were obtained, and an analytical procedure was developed.
 Petroleum oil: Shell Rotella® T SAE 15W-40 Heavy duty oil for diesel engines

Synthetic oil: Mobil SAE10W-30 Motor oil for gasoline engines

These samples were injected onto a GPC column, which was connected to a UV detector and thence to the DiscovIR(S4H1) instrument.

Sample preparation

Each sample was prepared by dissolving in tetrahydrofuran (THF) at a concentration of 90 mg/ml.



GPC conditions:

Column: 25 x 1 cm Jordi Mixed Bed

Mobile phase: 100% THF, 1ml/min

Injection volume: 50 uL

Note: the polymer components are solid-phase, but the oil components are liquid, and tend to spread on the sample collection disk. A diverter valve was used to divert eluant flow from the DiscovIR-LC at a time just before the oil phase began to elute.

FTIR data collection

FTIR data collection conditions: Nebulizer 6W, Carrier gas 380, Disk Speed 3mm/min, Disk Temp. 20°C,

Pressure Chamber/Cyclone 6.40/400 torr Condenser (single) temp. (50C), Cyclone temperature: 260°C

Column flow terminated at 12.1 min to prevent small molecule mineral oil contaminate sample disk

RESULTS

Shell Rotella T 15W-40

This oil is designed for diesel engines and other heavy duty equipment.

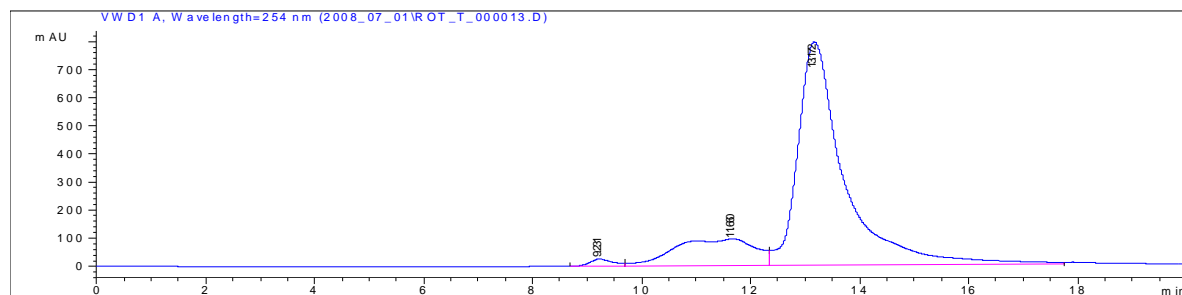


Figure 1 UV detector trace of Rotella T polymer fraction.

The UV trace shows a component eluting at 9.2 minutes, then a partially resolved set of eluants in the 10 – 12 min region. The very large peak eluting at 13 minutes is the base lubricant fraction.



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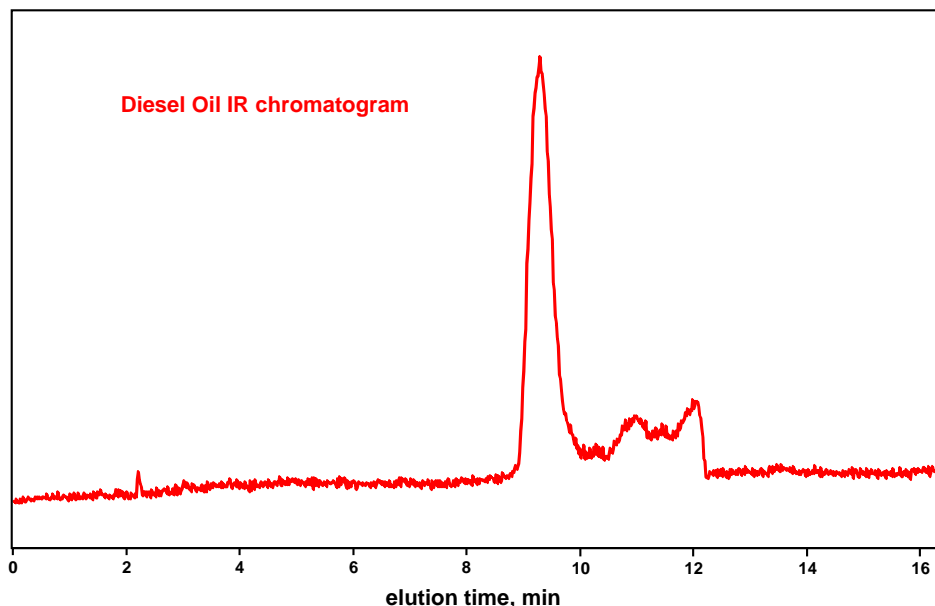


Figure 2 Infrared chromatogram of Rotella T polymer fraction

To generate the GPC-IR chromatogram, the eluant was diverted at 12.2 minutes. This was done to prevent the lubricant fraction from flowing on the collection disc, and over-running the deposited polymer fractions. The resultant IR chromatogram consequently does not have any of the base lubricant in the elution profile. As expected, the intensities of the eluted peaks differ from the UV chromatogram, but there is a good concurrence of elution order. The IR chromatogram shows a strong eluted peak at 9.2 minutes, followed by a broad elution band in the 10 -12 minute region.



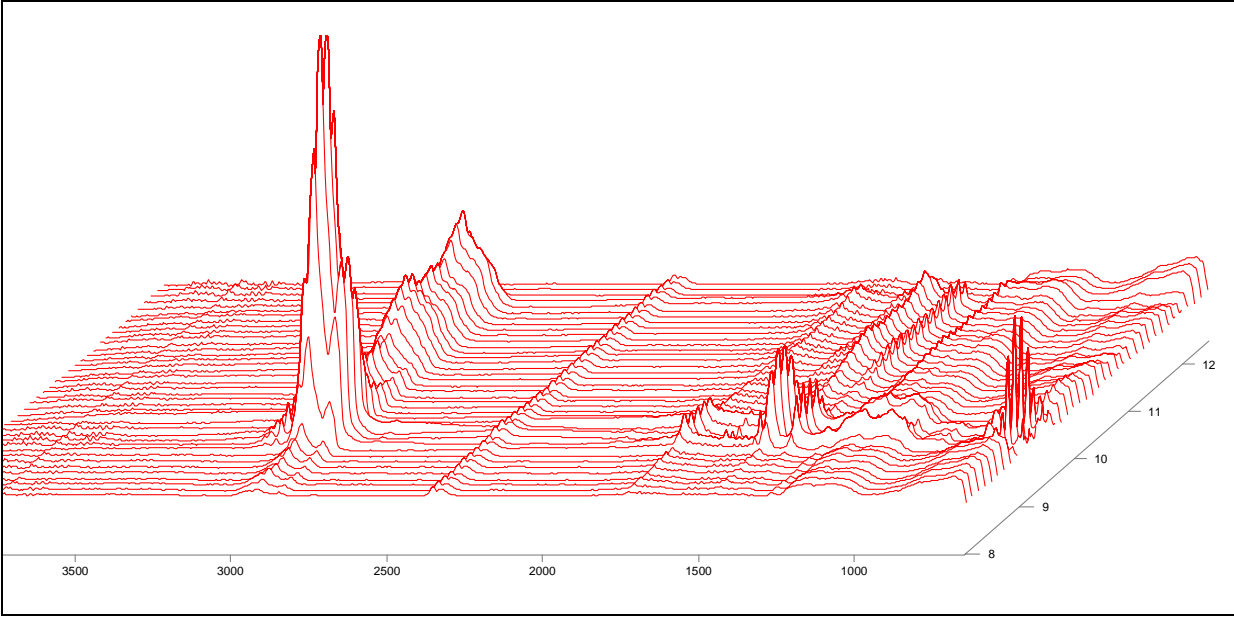


Figure 3 Time-ordered spectra from the GPC-IR analysis of Rotella T

Figure 3 provides a composite view of the spectral characteristics of the sample. The time-ordered spectra are stacked, with the earliest eluant in the foreground and the later eluant stretching into the background. The unique chemical structures of the components are apparent in this composite spectra-chromatography view.

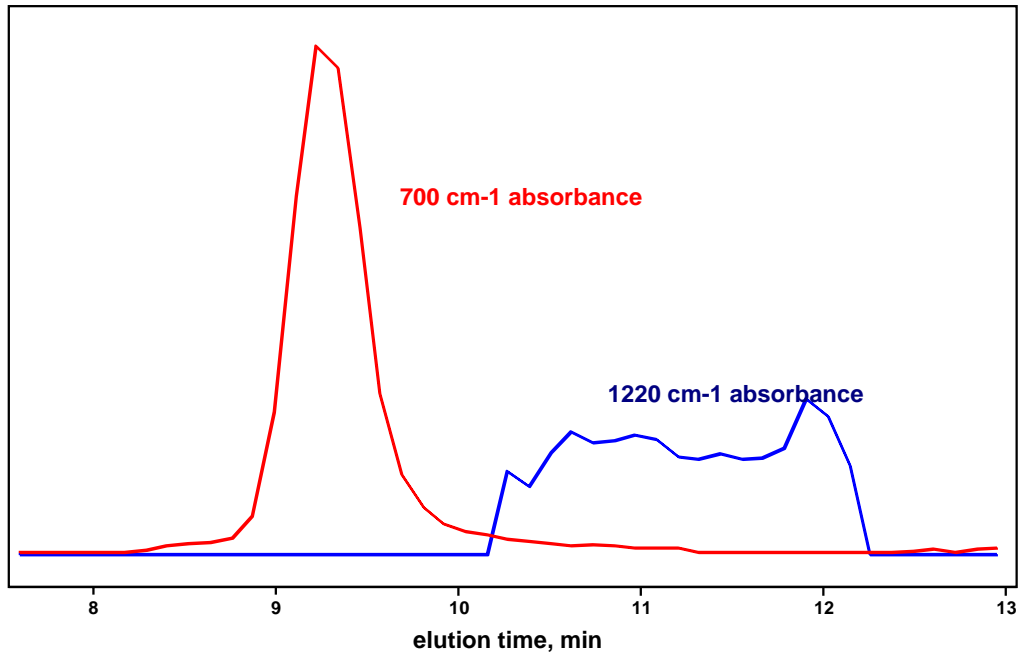


Figure 4 Function group chromatograms of Rotella components



Chromatograms generated from specific spectral bands are shown in Figure 4, and confirm two different chemical species in the sample. This technique can be especially useful in characterizing the elution distribution of non-resolved chromatographic eluants.

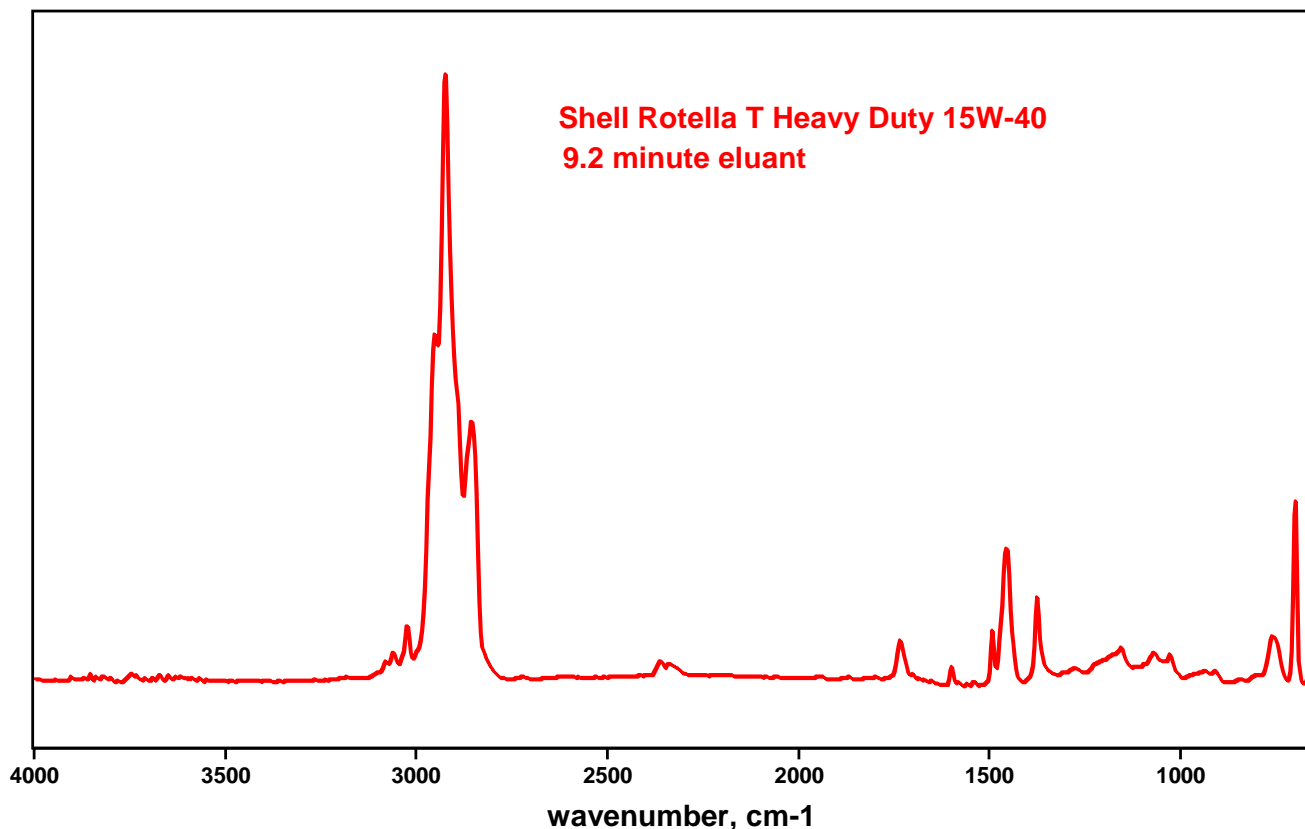


Figure 5 First elution peak spectrum

The initial elution peak has an average molecular weight of 600K, and is the Viscosity Index Improver for this oil. Both aromatic and ester functionalities are apparent. Bands associated with conjugated dienes are absent.

- Typical aromatic CH stretches (3082, 3061, 3027)
- Ring breathing modes at 1601, 1493
- Aromatic ring out of plane bends at 698, 756
- 1735 carbonyl
- C-O stretches in the 1200 -1000 region

There is little apparent drift in the [700cm-1/1735cm-1] bands ratio of this elution peak; indicating no great compositional variation. The spectra of this elution region appear to be those of a styrene-acrylate copolymer.



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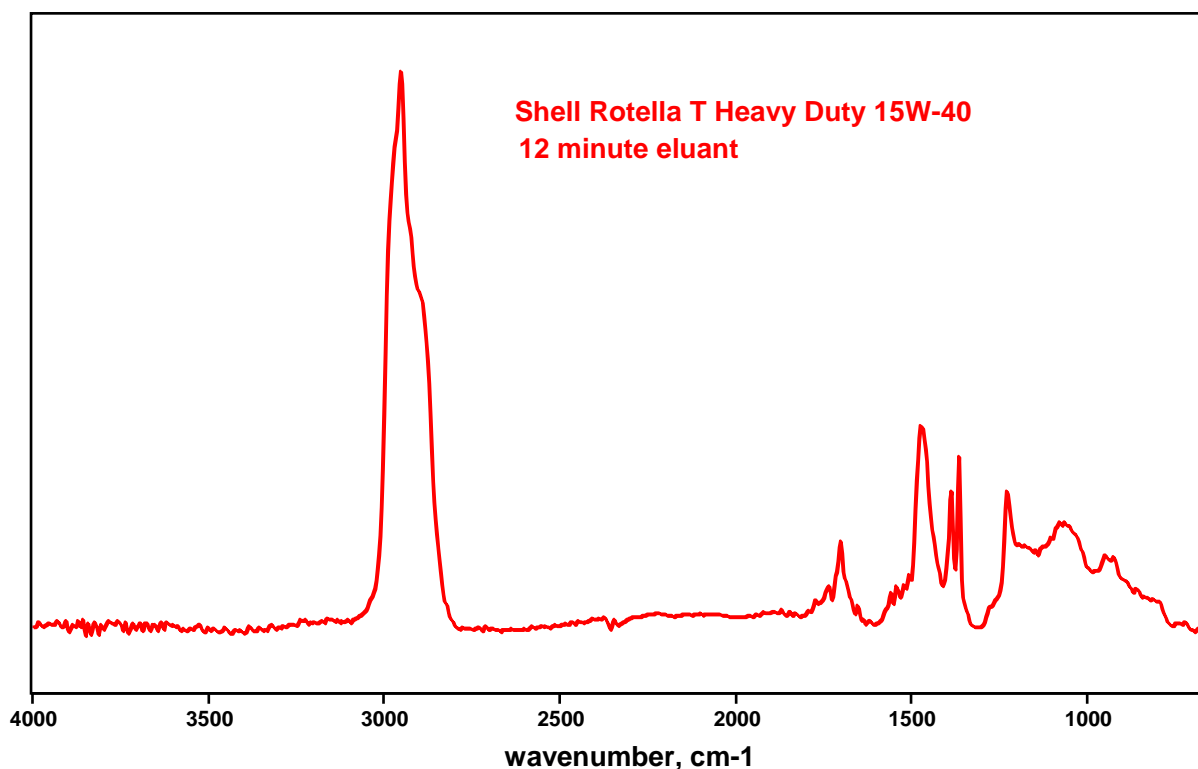


Figure 6 Spectrum of the 10 - 12 min eluant fraction.

The broad eluant profile in the 10 – 12 minute elution timeframe provided a spectrum that is shown in figure 6. Spectral variation across this region is minimal, and is indicative of a homogenous chemistry, with a broad variation of molecular weight (30,000 – 8000mw). This spectrum is characteristic of the dispersant polyisobutenyl succinimide (PIBS). The broad elution profile of this material suggests a heterogeneity of molecular weight in this fraction, but no clear evidence of compositional drift in the comonomers. The [dimethyl (1367 cm⁻¹) / imide (1700 cm⁻¹)] ratio decreases by only about 10% across the elution range of 10.5 – 12.2 min.

Mobile 1 10W-30 Synthetic

The synthetic lubricants are increasingly being utilized in passenger car engines, and are claimed to provide superior performance to petroleum based oils.



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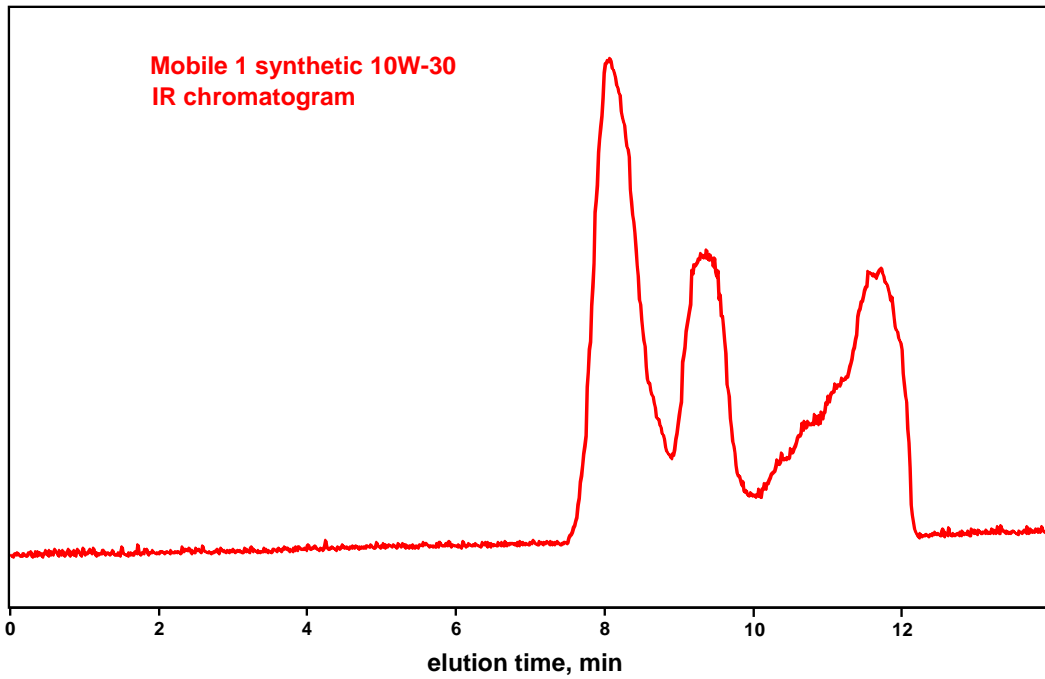


Figure 7 Elution profile of polymer components of Mobile 1 synthetic oil

This sample shows three distinct polymeric elution peaks, and the possibility of multiple species co-elutants within these peaks.



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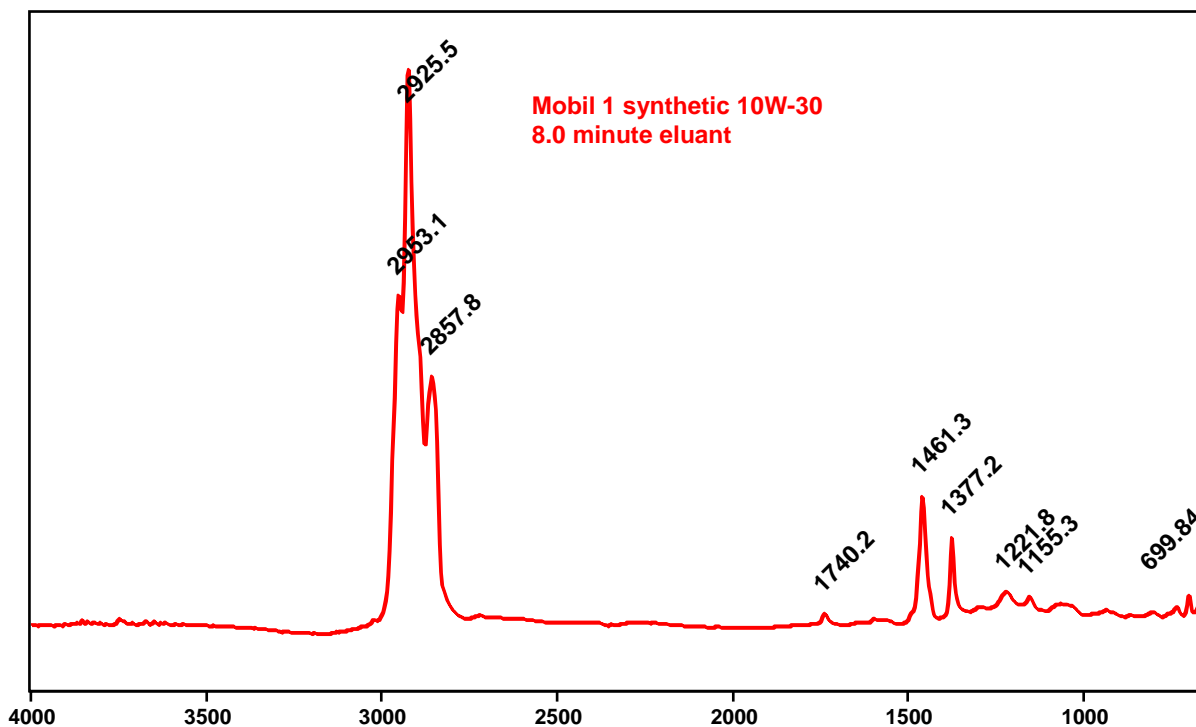


Figure 8 Mobile 1: first elution peak

GPC elution time indicates that this peak corresponds to a molecular weight of approximately 250K Daltons. It is an ethylene propylene copolymer, which also has a low styrene content (700 cm⁻¹ band and 3023 cm⁻¹ aromatic C-H stretch bands are observed), An weak ester carbonyl is also observed.



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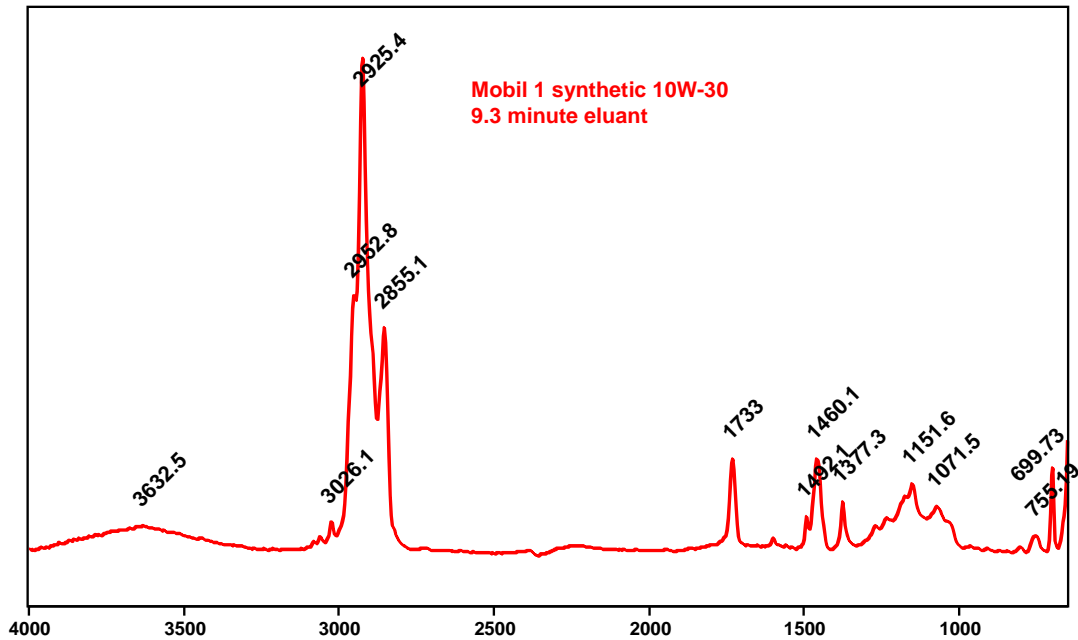


Figure 9 Mobil 1: 2nd elution peak

The second elution peak reveals a complex picture. Functional components indicate polyolefinic material, hydroxyl function (3625 cm⁻¹), an ester carbonyl (1733 cm⁻¹, 1151 cm⁻¹), and a styrenic (700 cm⁻¹, 1492 cm⁻¹, 1605 cm⁻¹, (C-H stretch bands above 3000 cm⁻¹). Average molecular weight of this peak is 50K Daltons.

A set of functional group chromatograms were prepared and are shown in the figure below which indicate that this peak is either a mixture of polymeric materials (VIIIs, pour point additives), or polymer(s) showing strong compositional drift.



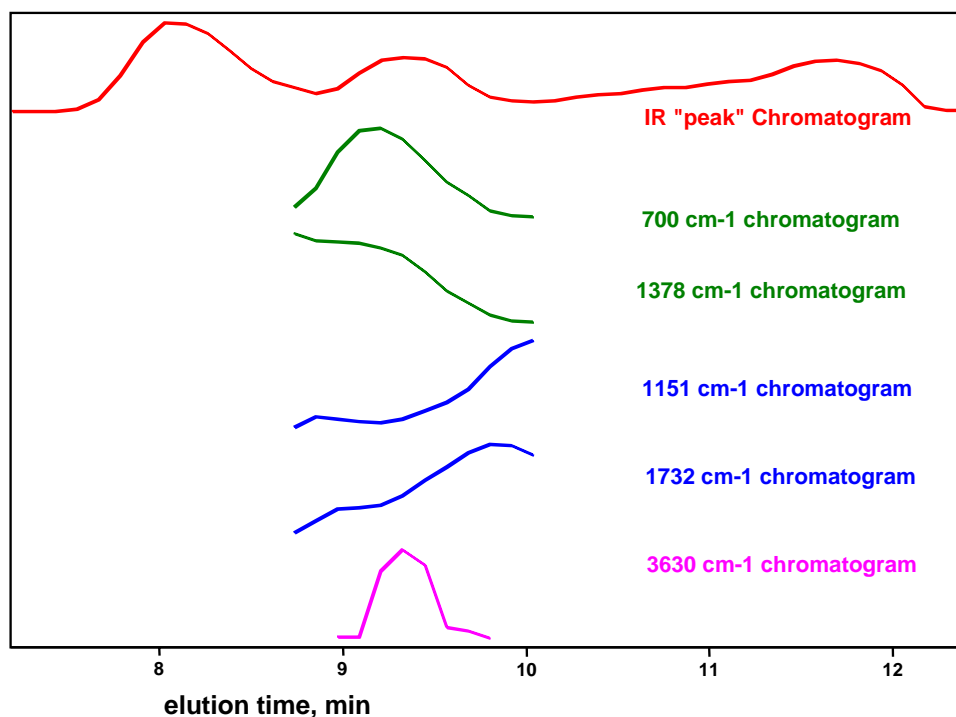


Figure 10 Functional group chromatograms of Mobile 2nd elution peak

As can be seen in Figure 10, the aromatic composition (green traces) of peak 2 decreases with elution time-molecular weight, while carbon-oxygen (blue traces) increases. These four traces are the values of the selected frequencies ratioed against the 2926 cm^{-1} C-H stretch frequency. This has the effect of cancelling out the varying deposit mass over the elution profile, and better reflecting *concentration* change of functional groups along the deposit track. We have assigned the appearance of a broad weak band centered at 3630 cm^{-1} to a hydroxyl containing material. The main material in this elution peak appears to be a PMA-PS copolymer. A mixture of individual co-eluting components cannot be ruled out. Collection of this GPC fraction and re-chromatographing in an adsorption chromatography mode would enable separation of discrete polymer species.



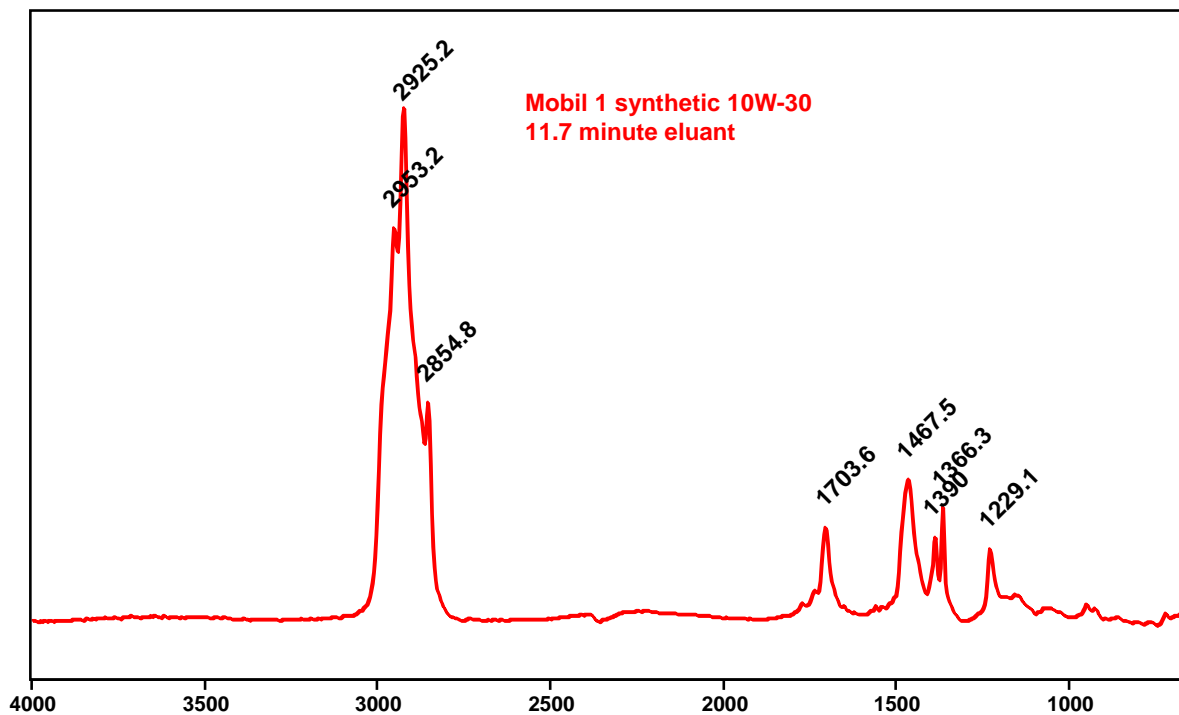


Figure 11 Mobile 1: 3rd elution peak

The third peak elutes over the 10 -12 minute time frame, presenting the same overall spectra within this elution time. It is also a PIBS material, and is quite polydisperse. Changes in the relative intensities of the C-H stretch frequencies of the later elution portion of peak 3 suggest changing influence of chain terminal groups of this fraction.

Comments

This is a rapid and powerful technique for the analysis of the polymeric components of lubricants. It avoids the vagaries of dialysis and traditional fractionation procedures. This analysis. If these techniques are applied to used oils, it is possible to characterize the changes to the VIIs, pour point additives, and dispersants. The technique finds application in quality control and manufacturing of lubricant formulations, as well as reformulation of products.

Polymeric lubricant components are inevitably subject to shear degradation in the operating environment. Shear degradation in turn causes loss of the protective properties of the additive package. Shear degradation and/or chemically induced breakdown reveals itself by increases in elution times of polymer components. It is beyond the scope of this present application note



to profile used engine oils, but polymer degradation is clearly recognizable as shifts in the time distribution of polymer components.

Polymer oxidation is revealed in C-O stretch band that occurs at 1160 cm^{-1} , while nitration gives rise to a band at 1604 cm^{-1} . The dispersants may also show spectral changes associated with their complexing to engine combustion by-products.

CONCLUSION

Many oil additive package components can be analyzed by discrete chemical tests for specific species. The polymeric additives are more complex, and not amenable to simple wet tests. By using the combination of Gel Permeation Chromatography coupled with infrared structural analysis it is possible to deformulate complex sets of polymer components, and to characterize the changes to these components when analyzing used oils.



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