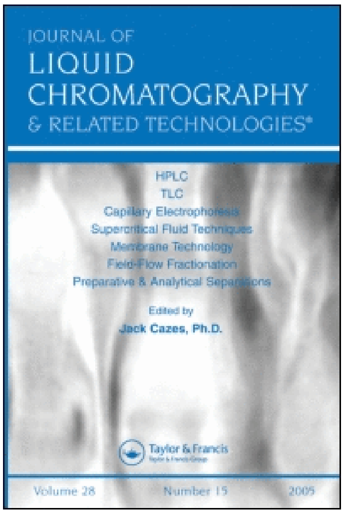

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Contaminant Determination in Cold Rolling Oil Using HPSEC with RI and PDA Detection

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CONTAMINANT DETERMINATION IN COLD ROLLING OIL USING HPSEC WITH RI AND PDA DETECTION

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ABSTRACT

A size exclusion liquid chromography (HPSEC) method using refractive index (RI) and photodiode array (PDA) detectors and a BASIC calculation program was developed for high molecular weight contaminant determination in the C_{15} linear paraffin-based cold rolling oil. Eight laboratory standards were analyzed to determine the new HPSEC/RI calibration factor for the C_{15} linear paraffin rolling oil. Three contaminants and thirteen standard solutions were evaluated to establish calibration curves. The HPSEC/RI/PDA method will quantitatively determine the concentrations of polyisobutylene-based hydrodynamic backup bearing lubricant, mist-applied extreme pressure gear oil for the workroll bearing and antiwear hydraulic oil in the cold rolling oil. Deviations for backup bearing lubricant, workroll bearing lubricant and hydraulic oil are approximately 3%, 4% and 7% of the contaminant concentration, respectively.

The BASIC calculation program can assist operators in reducing calculation error and improving speed and accuracy for the HPSEC method.

INTRODUCTION

Two types of lubricants are used in the cold rolling mills to produce aluminum sheet and foil. The cold rolling oil, which is composed of a hydrocarbon base oil and long chain, polar friction reducing additive, provides lubrication and cooling to the workroll and the aluminum sheet. The mechanical lubes, such as hydraulic fluid, bearing greases, and gear oils, are used to provide lubrication to the mechanical parts of the mill system. During the rolling process, the mechanical lubes of the mill system have the potential to contaminate the cold rolling oil through accidents or leaks. The contaminated cold rolling oil tends to generate "smut" and thermal stain on the sheet, decrease the rolling speed, and cause slippage of the workroll.

In practice, zero contaminants in the rolling oil is almost impossible to achieve in the plant. Determining the level of high molecular weight contaminants (tramp oil) in the rolling oils and providing this valuable information to the mill supervisor are a challenge to the plant's QA laboratory. Traditionally, infrared spectroscopy (IR) and viscosity measurement are most commonly used by the QA laboratory for a quick contaminant determination; however, both techniques have accuracy, sensitivity and characterization problems. Most of the time, IR analysis is very limited due the functional similarity of the rolling oil and mechanical lubes. The viscosity test cannot provide an accurate result for the contaminated rolling oil because it cannot distinguish between the type of mechanical lubricant contaminant and because the viscosities of the potential contaminants can cover a wide range (about 32 - 7,750 cSt @ 40°C).

High performance size exclusion chromatography (HPSEC), which is also known as gel permeation chromatography (GPC), has been well developed[1] and widely used in the polymer, oil, paper, and other industries for characterization and separation of polymeric materials[2], asphalts[3], cellulosics[4], pectins, chelate complex[5] and proteins[6]. Actually, size exclusion or gel permeation is a form of liquid chromatography in which the solute molecules are separated as a result of their diffusion into solvent-filled polymer matrixes in the column packing. Normally, these porous column matrices are formed by heavily cross-linked polymer chains. Large molecules can be excluded from the porous matrices of the packing due to their physical size in the mobile phase. Therefore, the large

Table 1

Chemical Composition of Standard Solution

Standard	Backup Bearing Lubricant (%)	Hydraulic Oil (%)	Workroll Bearing Lubricant (%)
	1	6	0 0
2	0	6	0
3	0	0	6
4	3	3	0
5	3	0	3
6	0	3	3
7	2	2	2
8	1	5	0
9	5	1	0
10	3	2	0
11	3	2	1
12	3	2	2
13	3	2	4

Table 2

SEC Calibration Factor for C_{15} Linear Paraffin SEC/RI Standards

Backup Bearing Lubricant (%)	Hydraulic Oil (%)	Workroll Bearing Lubricant (%)	Additive (%)	SEC/RI Time Slicing Data (%)	SEC Calibration Factor
-	-	-	8	0.80	-
6	-	-	-	16.98	0.35
-	6	-	-	12.66	0.47
-	-	6	-	15.15	0.40
3	3	-	-	14.56	0.41
3	-	3	-	15.0	0.40
-	3	3	-	13.58	0.44
2	2	2	-	14.48	0.41

Notes: 1. All standards were prepared using C_{15} linear paraffin as base oil.
2. Virgin C_{15} linear paraffin base oil was used as the baseline standard.

solute molecules are eluted from the GPC column before the smaller molecules, which have the opportunity to permeate into the porous, solvent-filled matrix. The order of elution from the GPC column will always be the largest molecules first, the smallest last[7].

Two of the most commonly used packing materials, Styragel™ and Poragel™, are highly cross-linked, polystyrene-divinyl benzene type polymers. They are hydrophobic and allow the chemist to separate molecular weight ranges from somewhere around 100 to about 50,000,000. There is a rough way to determine what pore size columns will be applicable for a given application. The 100 Å columns are used for compounds that have molecular weight of <700. The 500 Å gels are used to separate molecular weights between 12,000 and 700 or lower.

The highly viscous mechanical lubes have much higher molecular weight or size than the cold rolling oil. Therefore, HPSEC is a better choice for quantitative and qualitative determination of mechanical lubes in the cold rolling oil. An HPSEC method using UV and RI detection was developed by B. L. Riddle, et al..[8] in 1984. The method was able to demonstrate the capability of HPSEC for mechanical lube determination in cold rolling oil.

Since then, the method has been modified several times in our laboratory due to improvement of the GPC instrument and changes in column technology, the data handing software and the detection system. The modified HPSEC not only meets the challenge from the complexity of the cold rolling oil but also provides more specific and accurate information to the mill supervisor.

The modified HPSEC method[9] using refractive index (RI) and photodiode array (PDA) detectors and a BASIC program was developed for high molecular weight contaminants determination in the C_{15} linear paraffin rolling oil. Three major contaminants from the cold rolling mill were evaluated using HPSEC with RI and PDA detectors to determine if the HPSEC method can quantitatively and qualitatively detect these contaminants in the C_{15} linear paraffin rolling oil. These contaminants are polyisobutylene-based hydrodynamic bearing lubricant, an extreme pressure petroleum-based gear oil used to mist lubricate the mill's antifriction workroll bearing and a petroleum-based hydraulic fluid.

Thirteen standard solutions with various concentrations of the contaminants in the C_{15} linear paraffin base oil were prepared. Chemical composition of the standard solutions are listed in Table 1. The backup bearing

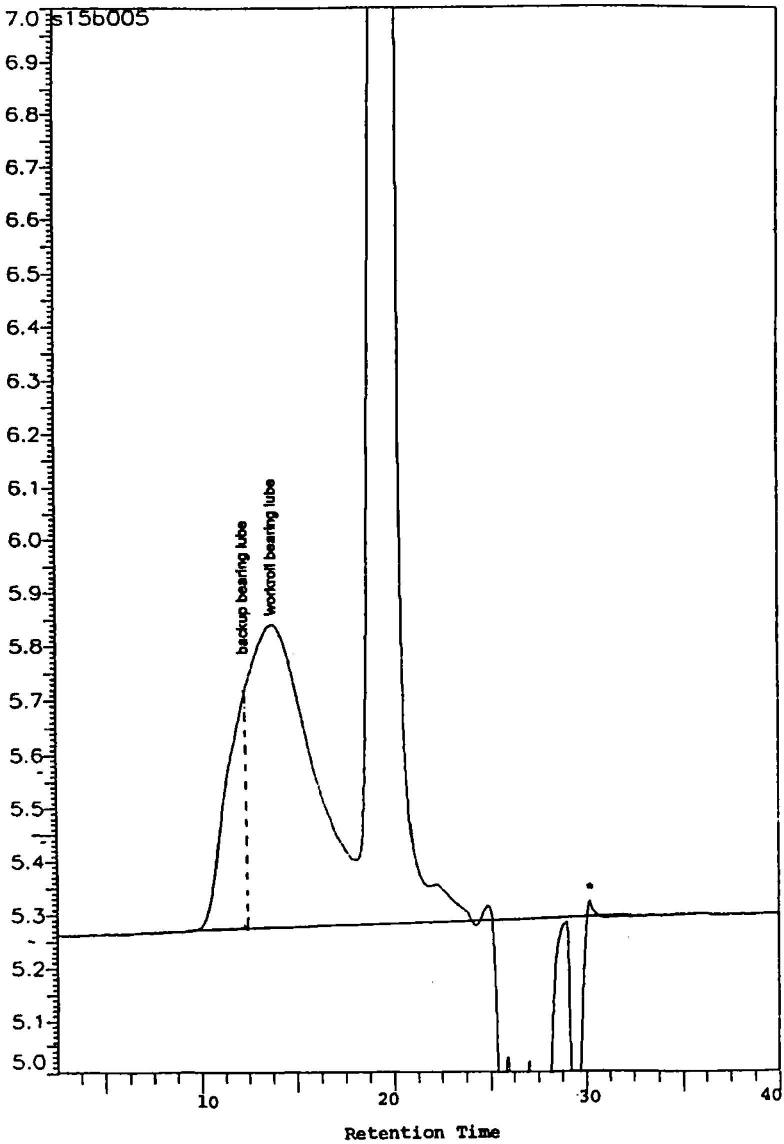


Figure 1. GPC/RI chromatogram of 3% backup bearing lube and 3% workroll bearing lube in C_{15} linear paraffin oil.

lubricant standard used in the study is a mixture of polyisobutylene H-95 and H-25 in a 1:2 ratio.

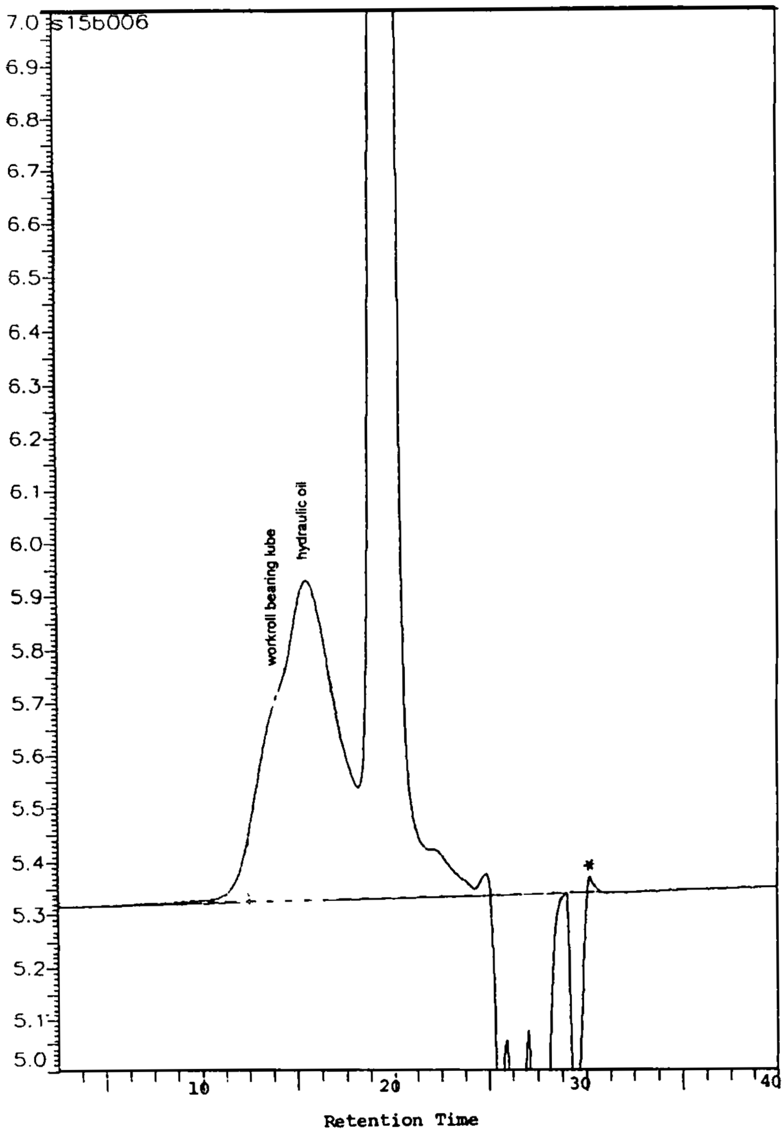


Figure 2. GPC/RI chromatogram of 3% workroll bearing lube and 3% hydraulic oil in C_{15} linear paraffin oil.

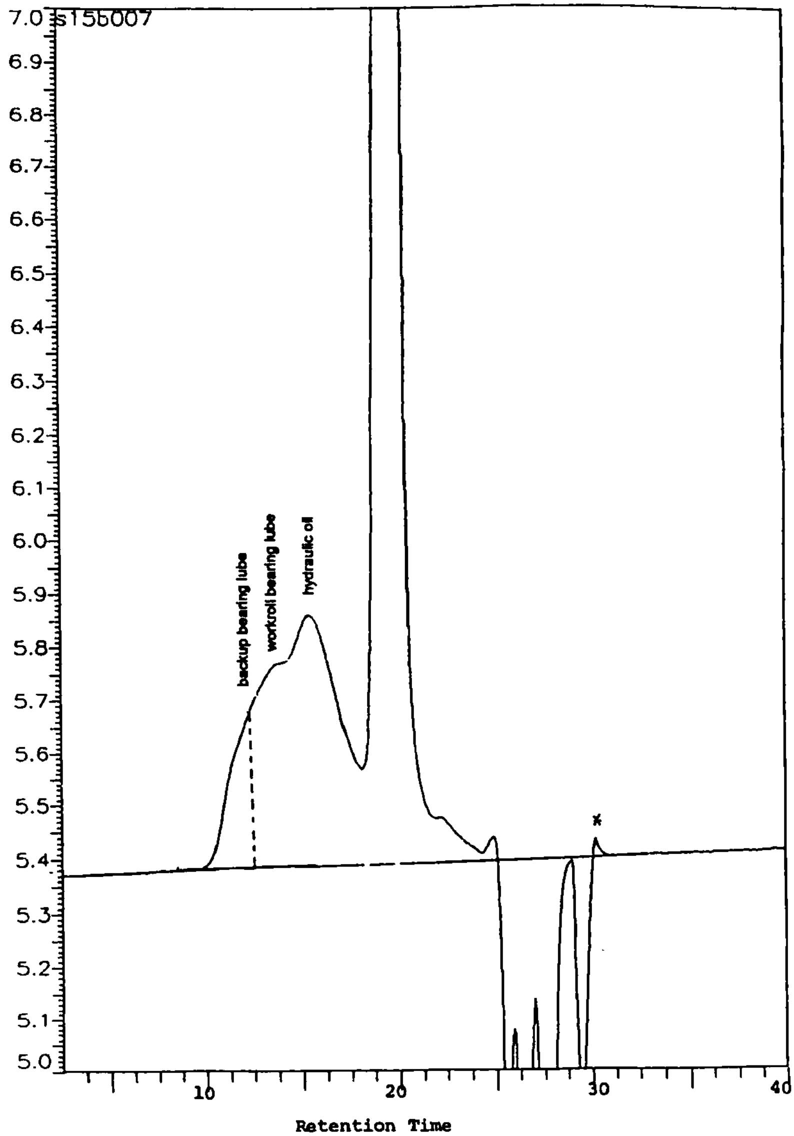


Figure 3. GPC/RI chromatogram of 2% backup bearing lube, 2% workroll bearing and 2% hydraulic oil in C_{15} linear paraffin oil.

EXPERIMENTAL

Chromatographic Conditions

GPC Column:	500, 100 and 100 Å Ultrastyragel columns from Millipore Co.
Mobile Phase:	Tetrahydrofuran (THF) w/o preservative
Flow Rate:	1.0 ml/minute
Injection Volume:	250 μl
Sample Concentration:	2% (wt/vol) in THF
Detectors:	▪ refractive index (RI) detector at 32X ▪ UV or photodiode array(PDA) detector @ 280 nm

RESULTS AND DISCUSSION

Determination of RI Response Factor

Linear paraffin base oils for cold rolling are highly refined and have a significantly narrower carbon number distribution than conventional middle distillate products, such as mineral seal oil. According to our experience, the C_{15} linear paraffin shows a very different response to the RI detector than mineral seal oil. It was not necessary to calibrate GPC/RI results for mineral seal oil due to the similar nature of mineral seal oil and the base oils used in mechanical lubricants. However, it was necessary to determine calibration factors for the C_{15} linear paraffin to calculate the actual percentage of high molecular contaminants. Eight laboratory standards were used for the evaluation. Calibration factors, calculated contaminant concentration and percentages of contaminants from a time slicing program are listed in Table 2.

The average calibration factor calculated for the HPSEC/RI and the C_{15} linear paraffin rolling oil is 0.40. The actual percentage of high molecular weight contaminants used in the C_{15} linear paraffin rolling should be calculated by multiplying the HPSEC/RI time slicing data of the oil by 0.40. Another factor we should consider is the concentration of additive in cold rolling oil. Normally, a control standard is analyzed along with used oil sample for baseline correction. As the time slicing data in Table 1 show, the baseline of 8% additive in the C_{15} linear paraffin oil increases 0.8% when the virgin C_{15} linear paraffin oil without the additive was used as the control standard. It suggests that the amount of additive will affect the time slicing result when the

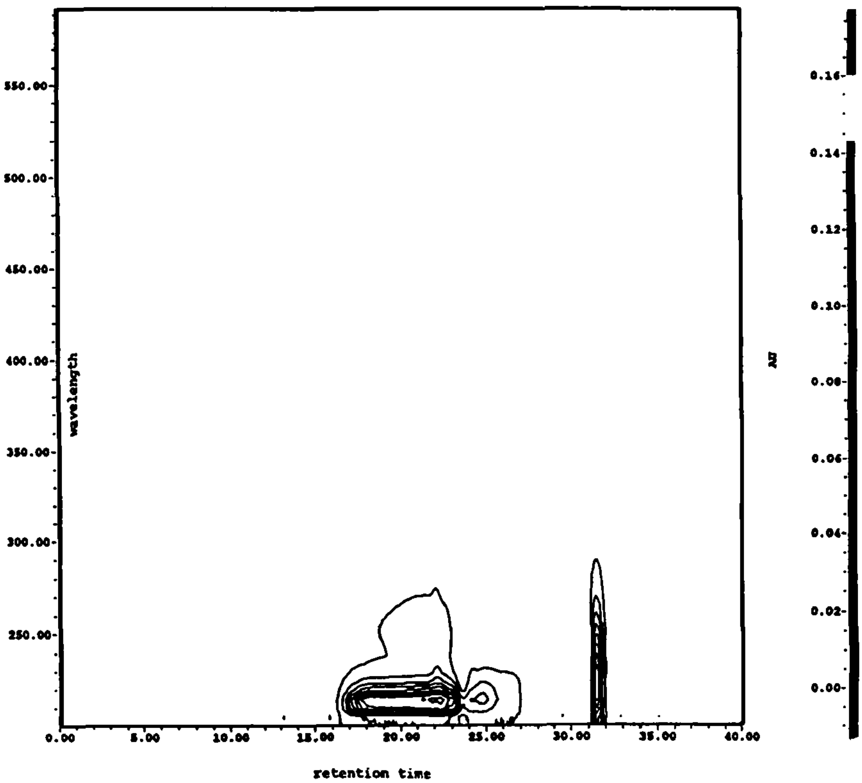


Figure 4. PDA contour plot of 6% backup bearing lube in C_{15} linear paraffin oil.

additive concentration changes. The change of baseline for the additive is about 10% of additive concentration (%) in the C_{15} linear paraffin rolling oil. For the future HPSEC/RI analysis, 8% additive in the C_{15} linear paraffin will be used as the baseline standard for cold rolling oil analysis.

SEC/RI and SEC/PDA Analysis of Standard Solution

Initially the HPSEC/RI method was conducted to investigate the contaminants in laboratory-prepared standard rolling oils. As the RI chromatograms in Fig. 1-3 show, the chromatographic separation between backup bearing lubricant / workroll bearing lubricant, workroll bearing

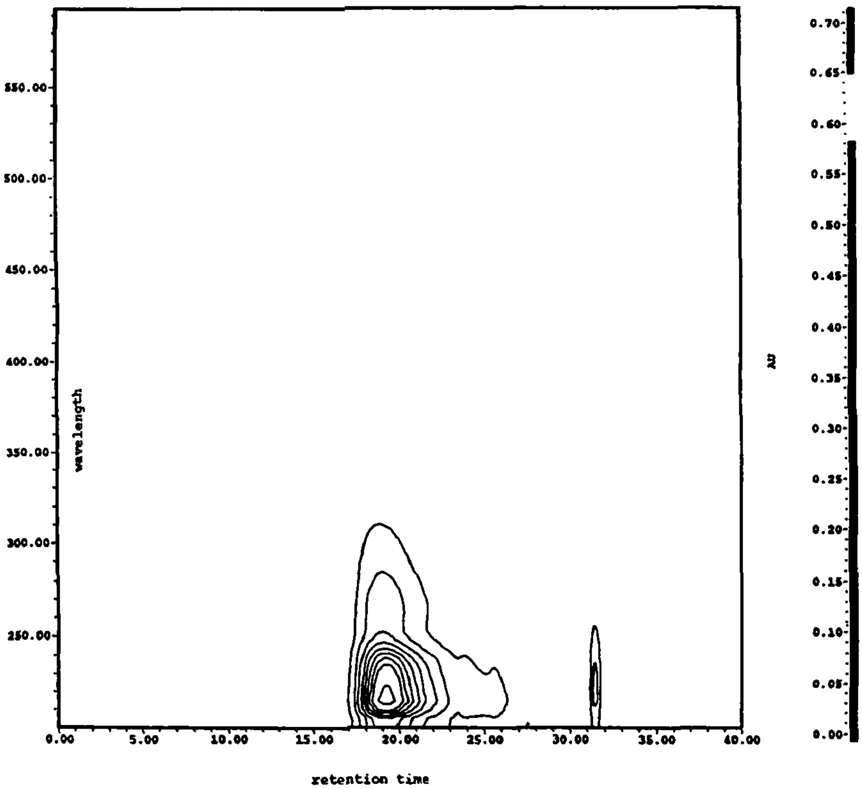


Figure 5. PDA contour plot of 6% workroll bearing lube in C_{15} linear paraffin oil.

lubricant/hydraulic oil and backup bearing lubricant/workroll bearing lubricant/hydraulic oil are very poor. The results suggest that HPSEC/RI alone is not a good method to quantitate the contaminants in rolling oil. However, the PDA or UV detector can help us solve the quantitation problem.

The PDA contour plots of backup bearing lubricant, workroll bearing lubricant and hydraulic oil are shown in Fig. 4-6. The PDA data reveal that all contaminants have UV absorbencies below 270 nm. Workroll bearing lubricant is the only contaminant that has a UV absorbance above 300 nm. The PDA evaluation suggests that (1) UV detection at 280 nm can be used to differentiate workroll bearing lubricant and hydraulic oil contaminant without a interference from backup bearing lubricant, and (2) UV wavelength of 300 nm can be used to analyze workroll bearing lubricant without the interferences from backup

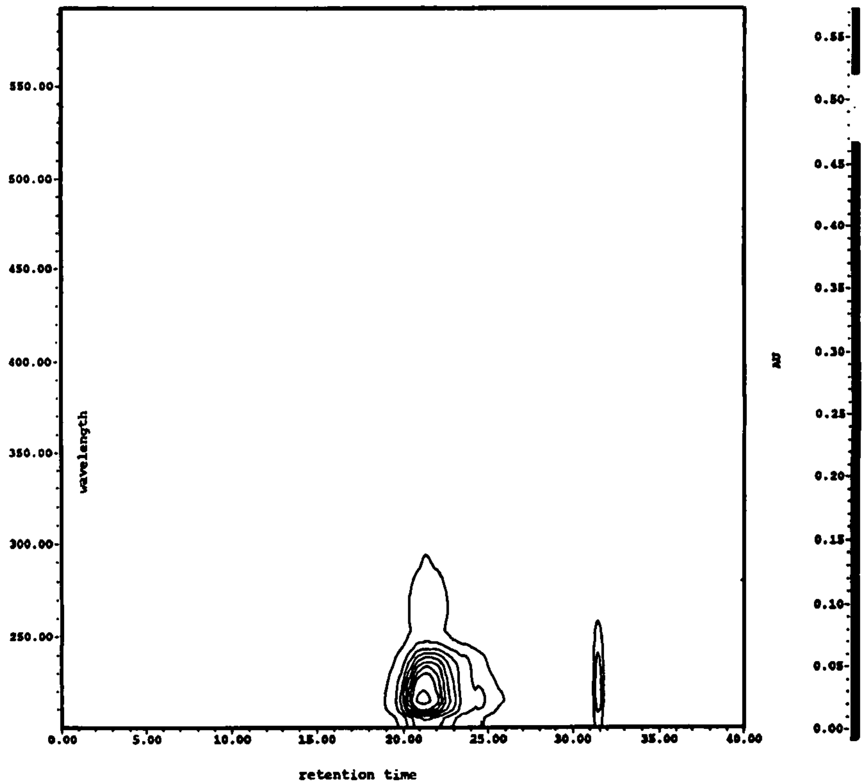


Figure 6. PDA contour plot of 6% hydraulic oil in C_{15} linear paraffin oil.

bearing lubricant and hydraulic fluid. A fair separation was observed in the GPC/UV chromatogram of workroll bearing lubricant and hydraulic fluid (Fig. 7). As the GPC/UV chromatogram in Fig. 8 show, the UV absorbance at 280 nm for backup bearing lubricant is very small compared to that of workroll bearing lubricant and hydraulic fluid (Fig. 9 and 10).

The PDA detector at 280 nm was used for workroll bearing lubricant and hydraulic oil determination. The concentration of backup bearing lubricant was determined using RI detection data. In order to avoid the possible retention time deviation of each run, the location of backup bearing lubricant, workroll bearing lubricant and hydraulic oil peaks are important. Listed below is the way to determine the location for each peak.

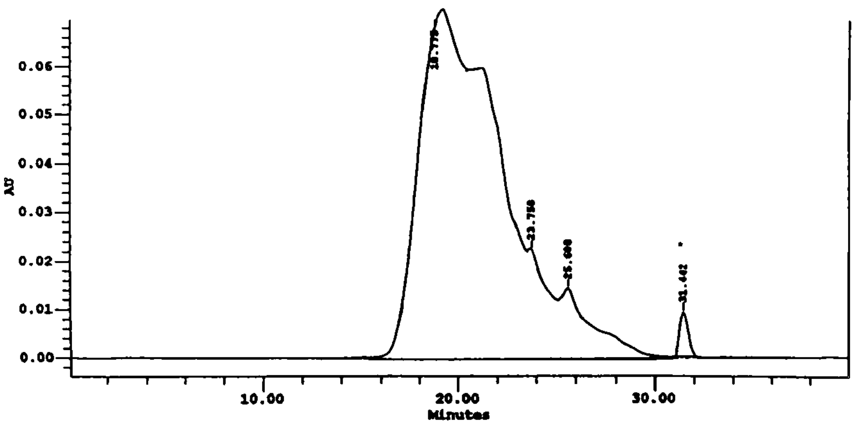


Figure 7. GPC/UV chromatogram of 3% hydraulic oil and 3% workroll bearing lube in C_{15} linear paraffin oil.

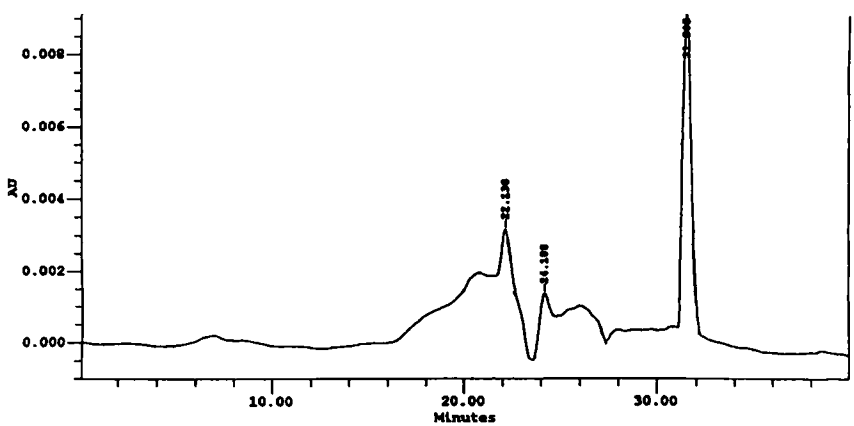


Figure 8. GPC/UV chromatogram of 6% backup bearing lube in C_{15} linear paraffin oil.

Table 3

Measured Peak Height of Contaminants in Standard Solution

Standard	Detector	Backup bearing lubricant	Workroll bearing lubricant	Hydraulic oil
1	RI	0.710	(0.370)*	(0.200)*
	UV	0.001	(0.001)*	(0.002)*
2	RI	(0.01)*	(0.08)*	0.775
	UV	0	(0.01)*	0.066
3	RI	(0.200)	0.750	(0.360)*
	UV	0	0.135	(0.052)*
4	RI	0.355	-	0.500
	UV	-	-	0.0345
5	RI	0.450	0.570	-
	UV	-	0.064	-
6	RI	-	0.39	0.600
	UV	-	0.072	0.060
7	RI	0.300	0.380	0.470
	UV	-	0.045	0.038
8	RI	0.120	-	0.660
	UV	-	-	0.055
9	RI	0.575	-	0.320
	UV	-	-	0.0124
10	RI	0.350	-	0.370
	UV	-	-	0.023
11	RI	0.380	0.360	0.435
	UV	-	0.025	0.031
12	RI	0.280	0.390	0.475
	UV	-	0.047	0.040
13	RI	0.350	0.615	0.630
	UV	-	0.084	0.055

*Data shown in ( ) are the peak height interference to adjacent peaks.

backup bearing lubricant:	8.1 cm from the marked internal peak in HPSEC/RI chromatogram.
workroll bearing lubricant:	5.0 cm from the marked internal peak in HPSEC/UV chromatogram.
hydraulic oil:	4.2 cm from the marked internal peak in HPSEC/UV chromatogram.

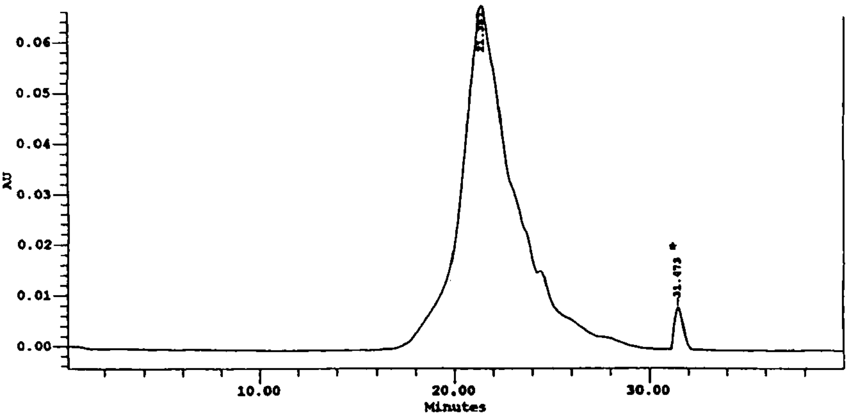


Figure 9. GPC/UV chromatogram of 6% hydraulic oil in C_{15} linear paraffin oil.

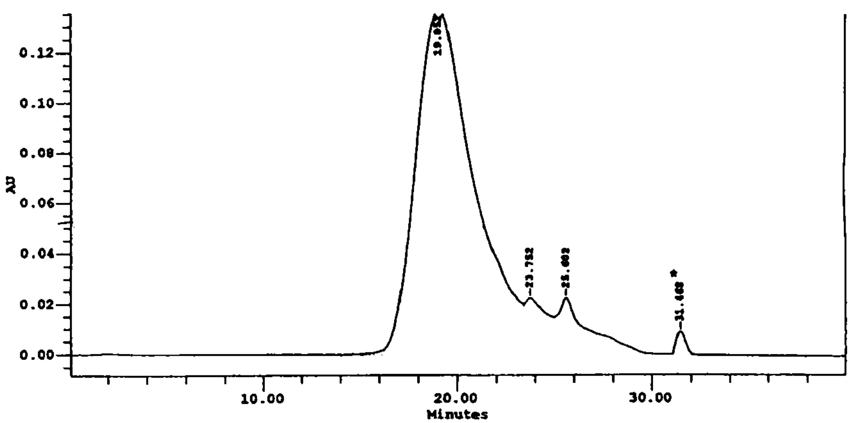
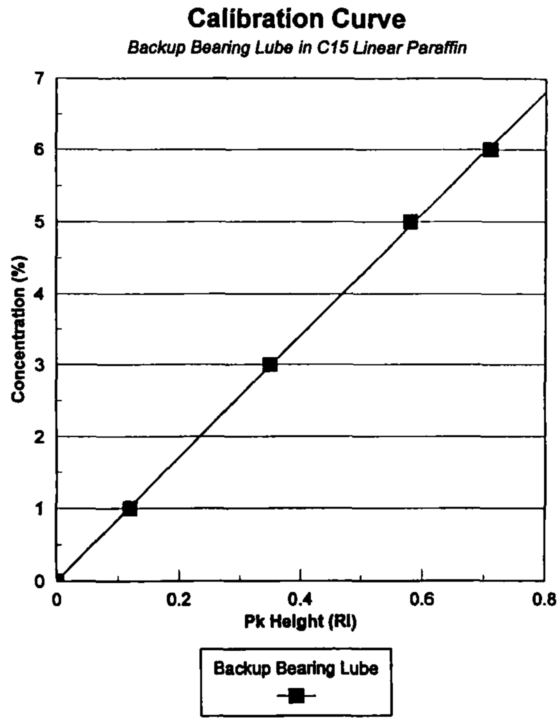


Figure 10. GPC/UV chromatogram of 6% workroll bearing lube in C_{15} linear paraffin oil.

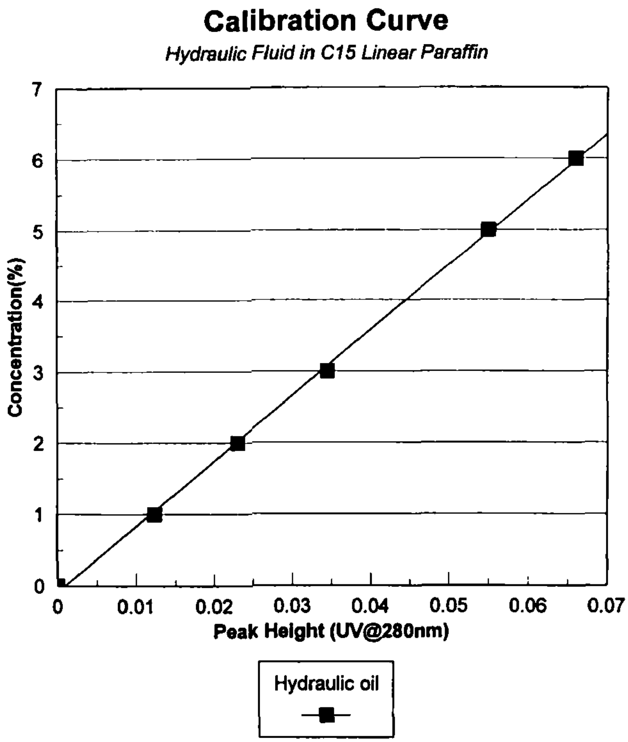


Conc. %	0	1	3	5	6
Pk Height	0	0.12	0.35	0.58	0.71

Figure 11. Calibration curve of backup bearing lube in C_{15} linear paraffin oil.

Thirteen standard solutions were analyzed using the HPSEC/RI/PDA method. The UV and RI peak height data for the standard solutions are outlined in Table 3. Calibration curves and formulations for backup bearing lubricant, workroll bearing lubricant and hydraulic oil are shown in Fig. 11-13.

As the data in Table 3 show, peak interferences among the contaminants are present. To improve the method accuracy, these peak interferences should be considered in the concentration calculation. Due to the complexity of the HPSEC/RI/PDA method, a BASIC program was written to reduce operator error and improve the speed and accuracy of the analysis. The BASIC program (Appendix A) developed for the HPSEC/RI/PDA method is attached for your

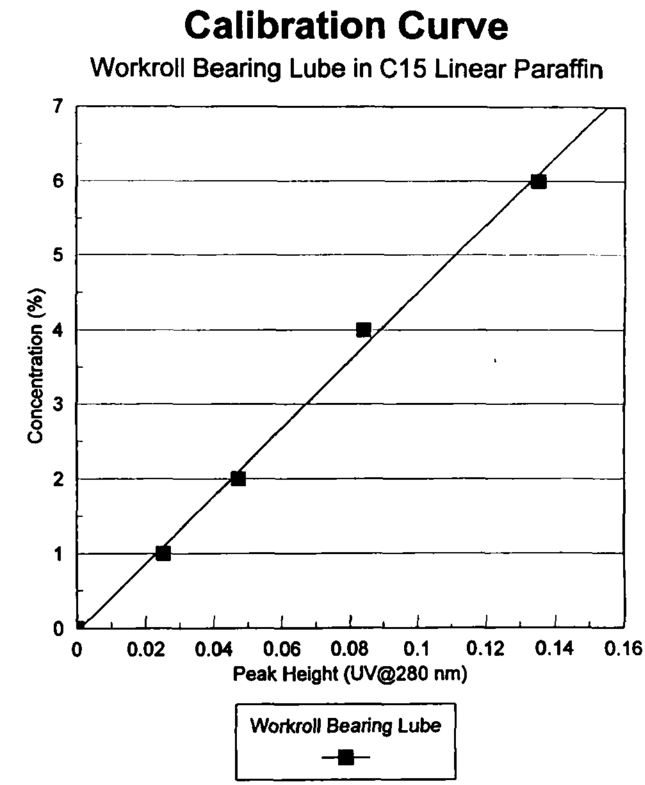


Conc. %	0	1	2	3	5	6
PK Height	0	0.0124	0.023	0.0345	0.055	0.066

Figure 12. Calibration curve of hydraulic oil in C_{15} linear paraffin oil.

information. Five standard solutions were used to test the accuracy of the calibration method. Their actual and calculated data are listed in Table 4.

The comparative concentrations for backup bearing lubricant, workroll bearing lubricant and hydraulic oil shown in Table 4 indicate that the HPSEC/RI/PDA method is a feasible analytical method for the study. The deviations for backup bearing lubricant, workroll bearing lubricant and hydraulic oil are about 3%, 4% and 7% of the contaminant concentration, respectively.



Conc. %	0	1	2	4	6
Pk Height	0	0.025	0.047	0.084	0.135

Figure 13. Calibration curve of workroll bearing lube in C_{15} linear paraffin oil.

Analysis of Used C_{15} Linear Paraffin Rolling Oil

A used cold rolling oil (12/03/93) was selected as an example to demonstrate the HPSEC/RI/PDA method. Peak heights measured for backup bearing lubricant, workroll bearing lubricant and hydraulic oil are shown in Fig. 14 and 15. Peak heights and calculated concentrations of backup bearing lubricant, workroll bearing lubricant and hydraulic oil are listed in Table 5.

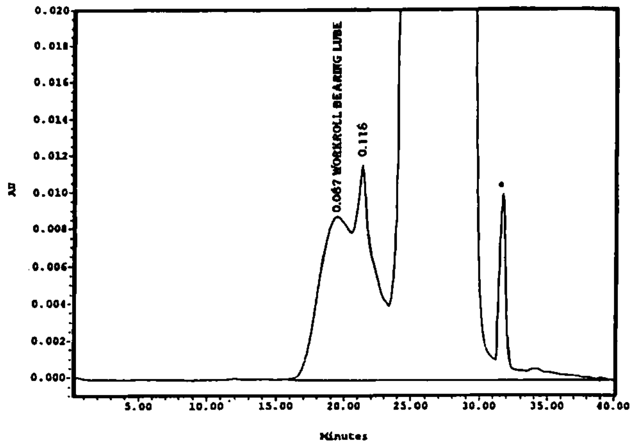


Figure 14. GPC/UV chromatogram of used cold rolling oil.

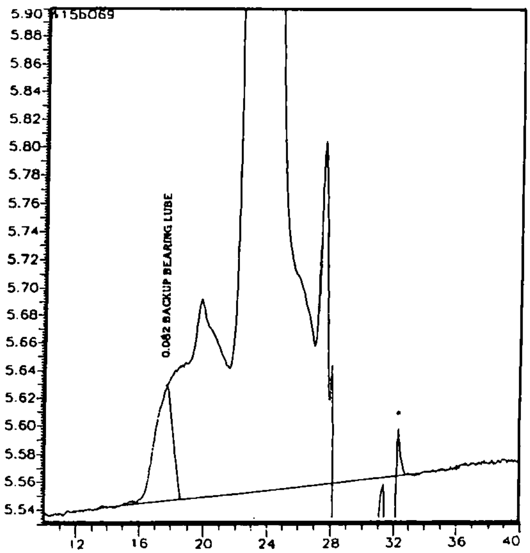


Figure 15. GPC/RI chromatogram of used cold rolling oil.

The total concentration of contaminants calculated by the time slicing program and peak height measurement are 1.46% and 1.56%, respectively. The time slicing data of the oil is used to ensure the accuracy of the HPSEC method. If there are other contaminants which have very intensive UV absorbencies present in the used oil, the total contamination calculated from peak height will be greater than the time slicing data. The total contamination difference between time slicing and peak height results should be less than 20% of the time slicing data based on our experience.

Table 4

Comparative Data of Contaminants from HPSEC/RI/PDA Method

Standard Solution	Backup Bearing Lubricant (%)		Workroll Bearing Lubricant (%)		Hydraulic Oil (%)	
	Actual	**Calc.**	**Actual**	**Calc.**	**Actual**	**Calc.**
7	2.0	1.91	2.0	1.84	2.0	2.25
10	3.0	3.14	0.0	-0.25	2.0	2.11
11	3.0	3.07	1.0	0.96	2.0	1.97
12	3.0	2.91	2.0	2.02	2.0	2.08
13	3.0	2.99	4.0	3.80	2.0	2.21
Avg Dev:	0.08		0.11		0.14	

Table 5

Used C_{15} Linear Paraffin Cold Rolling Oil (12/03/93)

Contaminant	Backup Bearing Lubricant	Workroll Bearing Lubricant	Hydraulic Oil
Peak Height	0.082	0.087	0.118
Calc. Conc.	0.52%	0.27%	0.63%

CONCLUSION

The SEC/RI/PDA method can be used to determine the high molecular weight contaminants in any cold rolling oil. However, RI response factors for the rolling oil and the contaminants should be determined. Standard hydraulic oil, gear oil and bearing oil should be investigated as well for each of the rolling oils to quantitatively and qualitatively determine the amounts of the high molecular weight contaminants. A BASIC calculation program was written to reduce the operator error and to improve speed and accuracy of the HPSEC method. Since peak height is used for contaminant determination, the injection volume and concentration of oil sample are critical. Sample preparation using wt/wt or wt/vol concentration and a fixed volume sample loop are strongly recommended for the HPSEC method.

A UV detector can be used to replace the photodiode array (PDA) detector for the HPSEC study. Based on the PDA evaluation, a UV detector @ 280 nm can be used to differentiate workroll bearing lubricant and hydraulic oil contaminant without an interference from backup bearing lubricant. The UV wavelength @ 300 nm can be used to analyze workroll bearing lubricant without the interferences from backup bearing lubricant and hydraulic oil.

ACKNOWLEDGMENT

Discussions and comments from Mr. Carroll D. Davis, Supervisor of the Chemistry Section, and Mr. Barry. L. Riddle, Supervisor of the Lubrication and Surface Technology Section, are gratefully acknowledged.

APPENDIX A

```
1 REM COLD ROLLING OIL CONTAMINANT ANALYSIS
5 DIM x(20)
10 DIM y(10)
15 DIM z(10)
20 PRINT: PRINT TAB(6);"** COLD ROLLING OIL CONTAMINANT ANALYSIS **"
30 PRINT : PRINT TAB(15); "*** by C. B. HUANG, 12/02/93 ***"
40 PRINT : PRINT : INPUT "enter DATE of Cold Rolling Oil Sample, **/**/**"; D$
50 PRINT : INPUT "enter UV Peak Height of Workroll Bearing Lube"; x(1)
55 PRINT : INPUT "enter UV Peak Height of Hydraulic Oil"; x(2)
60 PRINT : INPUT "enter RI peak height of Backup Bearing Lube"; x(3)
62 PRINT : INPUT "enter the Total %Contamination calculated by time slicing program"; z(4)
65 LET y(1)=45.4789 * x(1)-.04687
70 LET x(4)=x(2)-y(1)*.008
75 LET y(2)=91.8231*x(4)-.0881
80 LET y(3)=8.62785*x(3)-.0543
```

```
82 IF y(1)/y(3)>.7 THEN GOTO 140
90 LET x(11) = x(1) - y(2) * .0017-y(3) * .0002
95 LET x(12) = x(2) - y(1) * .008 - y(3) * .0003
100 LET x(13) = x(3) - y(1) * .03 - y(2) * .0017
110 LET y(1) = 45.4789 * x(11) - .04687
120 LET y(2) = 91.8231 * x(12) - .0881
130 LET y(3) = 8.62785 * x(13) - .0543
140 LET z(1) = y(1) + y(2) + y(3)
150 LET z(5) = z(4) / z(1)
160 LET y(1) = z(5) * y(1)
170 LET y(2) = z(5) * y(2)
180 LET y(3) = z(5) * y(3)
200 LET z(1) = INT(z(1) * 100 + .55) / 100
210 LET y(1) = INT(y(1) * 100 + .55) / 100
220 LET y(2) = INT(y(2) * 100 + .55) / 100
230 LET y(3) = INT(y(3) * 100 + .55) / 100
235 INPUT "press 'retur' when printer is ready"; A$
240 LPRINT : LPRINT ; LPRINT "*** *** *** *** *** *** *** *** *** ***
*** ***"
250 LPRINT : LPRINT "Date of Cold Rolling Oil ** "; D$; " **"
260 LPRINT : LPRINT " % Backup Bearing Lube = "; y(3)
270 LPRINT : LPRINT " % Workroll Bearing Lube = "; y(1)
280 LPRINT : LPRINT " % Hydraulic Oil = ";
290 LPRINT : LPRINT " % Total Contamination by Time Slicing = "; z(4)
300 LPRINT : LPRINT " % Total Contamination by Peak Height = "; z(1)
310 Input "Do you want to calculate another sample? (y/n)"; A$
320 IF A$ = "y" THEN 40
400 END
```

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