

## Determination of Total Aromatics and Total Saturates in Lube Basestocks by HPLC-RID as per ASTM D7419

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### User Benefits

- ◆ An analytical scale HPLC method for determination of total aromatics and total saturates
- ◆ Improved separation and simple operation

### Introduction

The composition of lubricating oil has a large effect on their characteristics and uses. The determination of, aromatics, saturates, and polar compounds is a key analysis of the lube basestock. The characterization of the composition of lubricating oils is also important for the evaluation of, for example, their interchangeability for use in blending<sup>1</sup>.

This application covers the determination of total aromatics and total saturates in additive-free lube basestocks using high performance liquid chromatography (HPLC) with refractive index (RI) detection. The high sensitivity and reproducible method was developed on Nexera HPLC system shown in Figure 1. This method is applicable to samples containing total aromatics in the concentration range from 0.2 to 46 mass % in the lube basestock.



Figure 1. Nexera HPLC system

### Experimental

#### System performance standards:-

(A) Prepared a system performance standard (SPS) by weighing hexadecane (1.0 ± 0.1 g) and octadecylbenzene (1.0 ± 0.1 g) into a 10 mL volumetric flask and diluting up to the mark by heptane as a diluent.

(B) Prepared a detection limit standard (DLS) by weighing 0.01g octadecylbenzene into a vial and adding 5.00 g hexadecane. This made a 0.2 mass % aromatics standard.

(C) Prepared a 0.1 mass % mixture of octadecylbenzene in hexadecane by weighing 0.01 g of octadecylbenzene in 10.0 g of hexadecane.

**Standard calibration levels:-** Prepared five calibration standards namely A, B, C, D, and E by weighing accurately octadecylbenzene and hexadecane in separate 10mL volumetric flasks and made up to mark by heptane, as given in Table 1. The resultant concentrations of both the compounds are shown in the same table.

**Sample preparation:-** Weighed 2.0 g of sample into a 4.0 mL vial and added 2.0 mL heptane. Shaken thoroughly to mix. Transferred the solution to 1.5 mL HPLC autosampler vial for the analysis. The instrument analytical conditions are given in table 2.

Table 1. Calibration standards.

Calibration standard	Hexadecane (g/10 mL)	Octadecylbenzene (g/10 mL)
A	0.01	0.01
B	0.1	0.1
C	1	0.5
D	2	1
E	5	3

Nexera LC system equipped with RID-20A and SPD 40 was used for the analysis. A set of two 250 mm Silica and Cyano columns were used in series. An automatic flow change-over valve was used with the system which was capable to backflush both the columns at the set time. The valve and mobile phase flow diagram is shown in figure 2A and 2B.

The backflush time was critically set, and the valve position changes were added in the time program. RID-20A was capable of faster stabilization to give very reproducible response with minimum drift in baseline. UV detector signal was also helpful in backflush and monitoring the aromatic signal.

Table 2. HPLC Analytical Conditions

Column	: 1. Ultra Silica 5µm 250 x 4.6 mm x 2 nos. 2. Shim-pack GIS CN 5µm 250 x 4.6 mm X (P/N 227-30263-07)
Mobile phase	: n- Heptane
Detector	: Refractive index detector (RID-20A) & UV Visible (SPD-40)
Mode	: Isocratic
Flow rate	: 1.5 mL/min
Column temperature	: 40 °C
Injection volume	: 100 µL
Flow cell temp.	: 40 °C
Run time	: 20 min
11.5 mins	Position 0 >> 1
24.5 mins	Position 1 >> 0

### Results

Injected 10  $\mu$ L of SPS containing 10% of both hexadecane and octadecylbenzene in foreflush mode. Hexadecane eluted early around 10 mins, followed by octadecylbenzene around 13.5 mins. The chromatogram of SPS in the foreflush mode is shown in figure 3. The resolution for both peaks was found to be 6.224 which was greater than the specified criteria by the official ASTM method.

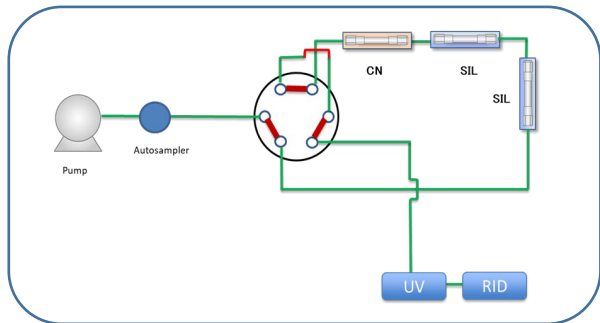


Figure 2A. Foreflush mode

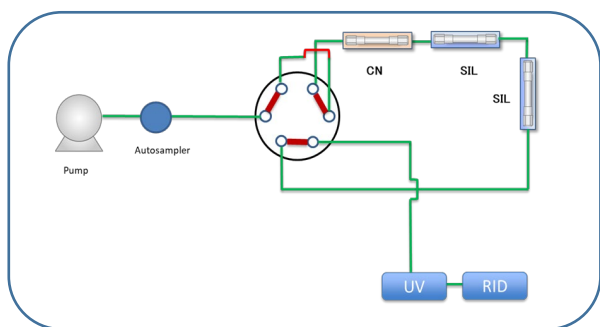


Figure 2B. Backflush mode

The back flush time was set based on the retention time of hexadecane in foreflush mode. The SPS was reinjected in the backflush mode where flow channel was switched to the reverse direction for both the columns in series. This resulted in the shift of octadecylbenzene peak to 23.5 mins. This was confirmed by the response of the UV detector. The chromatogram for the backflush is shown in figure 4.

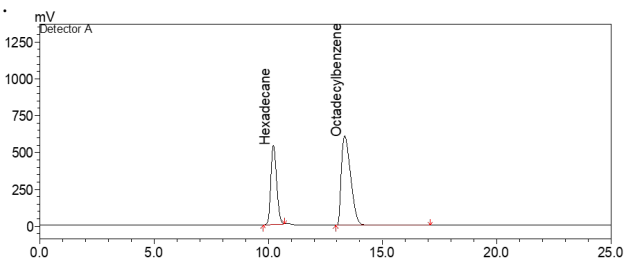


Figure 3. SPS in foreflush mode

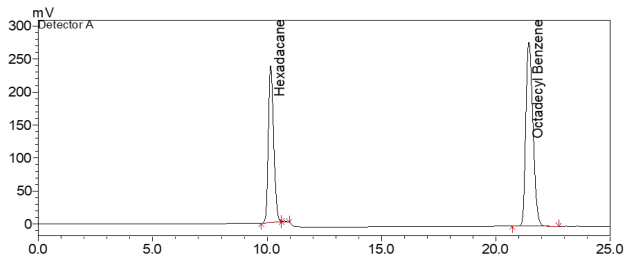


Figure 4. SPS in backflush mode

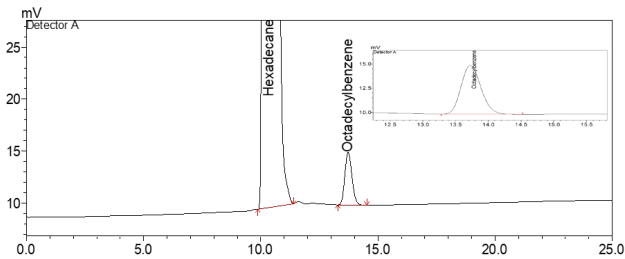


Figure 5. DLS solution

The DLS was then injected in the foreflush mode and ensured that the octadecylbenzene was detected with a signal/noise (S/N) of at 40. In compliance with the ASTM requirement, S/N should be greater than 8. figure 5. shows the DLS chromatogram with calculated S/N. 0.1% Octadecylbenzene in hexadecane was injected to check the Minimal Response Test (MRT) to verify that the minimal response was obtained at the low concentration. The MRT chromatogram is shown in figure 6.

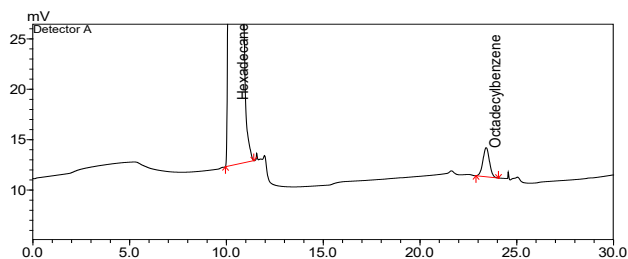


Figure 6. Chromatogram of 0.1% Octadecylbenzene in Hexadecane (MRT)

The calibration solutions from A to E were injected 10  $\mu$ L under the specified analytical conditions in backflush mode. The calibration curve was plotted in liner mode through the origin and found the coefficients of determination ( $r^2$ ) for hexadecane and octadecylbenzene were 0.995 and 0.999 respectively. The calibration curve information is shown in figure 7 and 8. The chromatograms for standard solutions A and E are shown in figure 9 to 13.

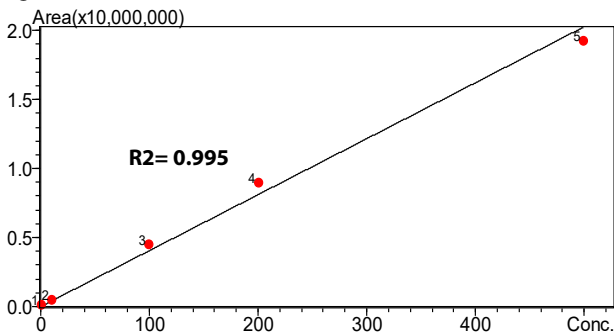


Figure 7. Calibration curve Hexadecane

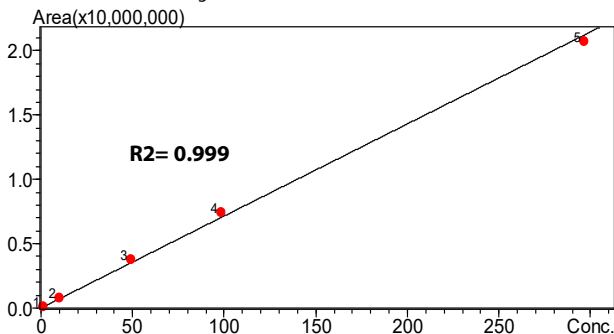


Figure 8. Calibration curve octadecylbenzene

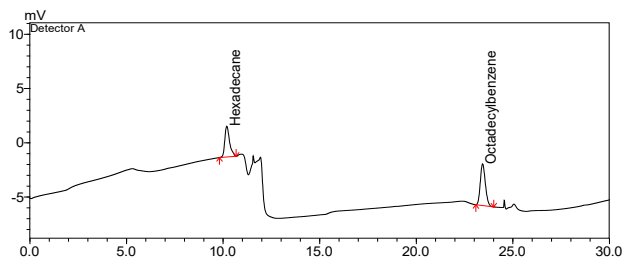


Figure 9. Standard A

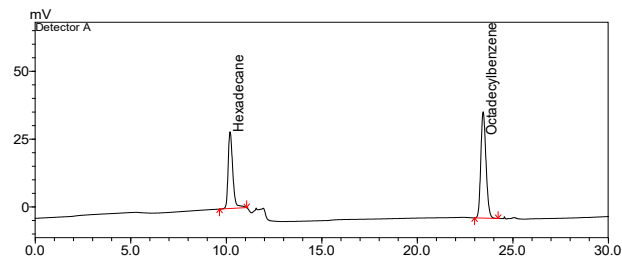


Figure 10. Standard B

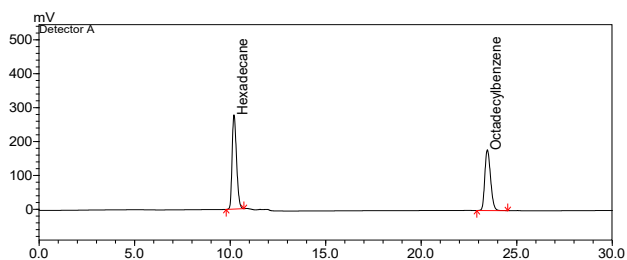


Figure 11. Standard C

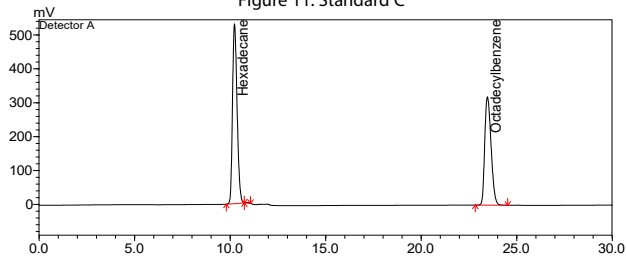


Figure 12. Standard D

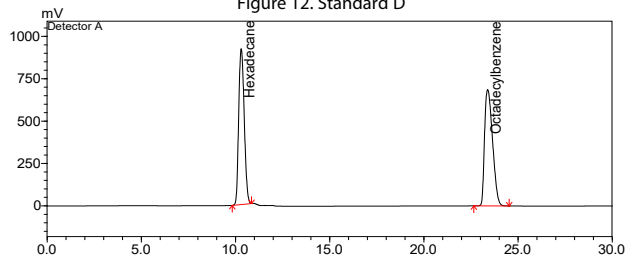


Figure 13. Standard E

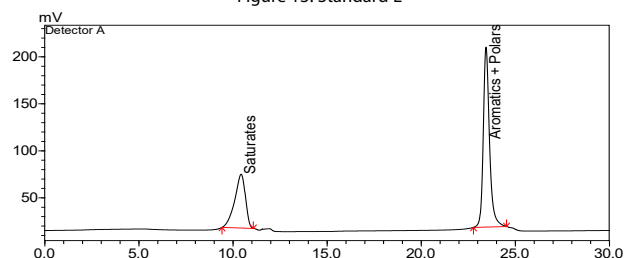


Figure 14. Sample 1

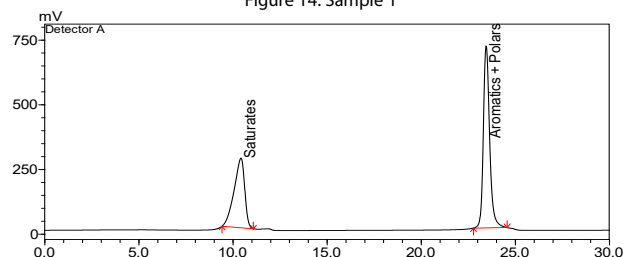


Figure 15. Sample 2

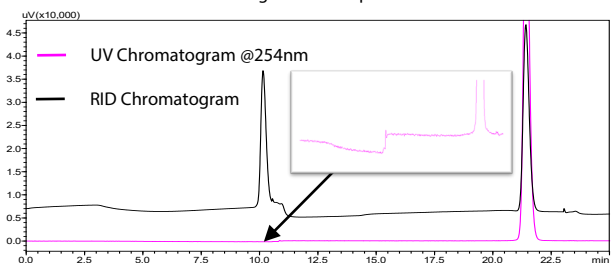


Figure 16. UV data comparison

The aromatic response factor was calculated by taking ratio of the slope of the calibration curve for octadecylbenzene and the slope of line for hexadecane.

The mass% of aromatics and mass% of saturates including polar compounds were calculated based on the formula provided in the ASTM D-7419 method. The calculated values are shown in Table 3. The sample chromatograms are shown figure 14 & 15. The optional UV detector at 254 nm can be utilized to monitor the overlap between aromatics and saturates in lube samples. The signal of the UV detector for saturates should be insignificant as compared to the signal of the aromatic peak. The UV and RID overlaid chromatograms are shown in the figure 16.

Table 3. Saturates and Aromatics + Polar results

Sample	Aromatic response factor	Total Saturates	Total Aromatics (+ Polars)
0.1% Solution	1.765	99.86%	0.14%
Sample 1	1.765	47.53%	52.47%
Sample 2	1.765	53.21%	46.79%

### Conclusion

This application note demonstrates the capability of Shimadzu's Nexera Series HPLC with RID-20A for the determination of total aromatics and total saturates in lube base stocks as per the procedure described in ASTM D-7419. The system suitability parameters were found to be within the acceptable limits laid down by ASTM. The analyzed samples produced results as per the requirement.

### Reference

- ASTM D-7419-07 Determination of Total Aromatics and Total Saturates in Lube Basestocks by High Performance Liquid Chromatography (HPLC) with Refractive Index Detection.

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