Evaluation of the Agilent 1260 LC system for analysis of base oils, as specified by ASTM D7419
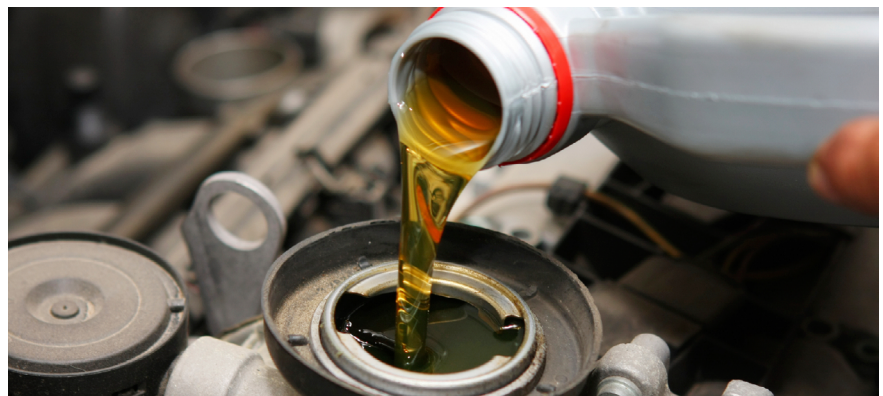
Application note

Petrochemical

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Introduction

Lubricants (oils and greases) used in industrial plants typically start off as a base oil. Most lubricant oils are formulated with 70%–99% base oil with the rest being additives to impart desirable characteristics. Greases typically have 70%–94% base oil. The American Petroleum Institute (API) has categorized base oils refined from petroleum crude oil into three categories based upon the properties of the product. The least refined, lowest performing products are classified as 'Group I' while the highly processed, most expensive, and highest performing products are 'Group III'.

The composition of the base oil has a significant effect on the quality, blending potential and possible applications for the product. While these oils may contain hundreds of individual compounds, it is typically sufficient to quantitate classes of compounds rather than identify and quantitate each compounds separately to ascertain quality. The most common method for these determinations in additive-free base oil is ASTM D7419 which measures total aromatics and total saturates using high performance liquid chromatography (HPLC) with refractive index detection.

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Experimental

Instrumentation

The Agilent 1260 Infinity HPLC system was used for this analysis. The following components were used:

- Agilent 1260 Infinity Quaternary Pump (G1311B)

- Agilent 1260 Infinity Standard Autosampler (G1329B)

- Agilent 1290 Infinity Column Compartment (G1316C) with valve drive installed (#058)

- Agilent 1200 Infinity Series Quick Change 2-position/6-port Valve (G4231A).

- Agilent 1260 Infinity Refractive Index Detector (G1362A)

- Agilent 1260 Infinity Variable Wavelength Detector (G1314F) s standards flow cell (G1314-60083)

- Open Lab Chromatography Data System

Columns

2 x Agilent ZORBAX SIL 9.4 x 250 mm, 5 µm,
Part number: 880952-201

1 x Agilent ZORBAX CN 9.4 x 250 mm, 5 µm, B12246

Mobile phase conditions

Heptane (HPLC Grade) @ 3.0 mL/min

Calibration standards and samples

Calibration standards and test samples were prepared as prescribed in ASTM D7419 using reagent grade hexadecane and octadecylbenzene in HPLC grade heptane with Class A volumetric glassware. An analytical balance capable of weighing to ±0.0001 g was used in the preparation of these solutions.

Flow paths

ASTM D7419 specifies columns in series with backflush after elution of saturates. The configuration used to achieve these conditions is shown in Figure 1. For the injection of the sample, the flow is directed through valve positions 4, 5 to the columns and then through valves 2, 3, 1 and 6 to the detector. In back flushing mode, the flow is directed through valves 4, 3, 1, 2 to the columns and then through valves 5 and 6 to the detector. Valve controls are configured in the Open Lab Chromatography Data System.
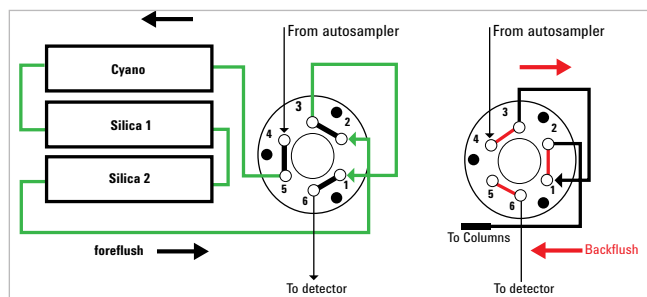

Figure 1. Configuration for columns and valve for ASTM D7419

System performance

ATSM D7419 performance parameters for column resolution and capacity factor were established. The switching valve backflush time was calculated from the retention times obtained from the chromatograph of the System Performance Standard. The Backflush Switch Time was calculated from the performance standard as follows:

Backflush Switch Time $= t_1 + 0.1 \times (t_2 - t_1)$

$$= 12.703 + 0.1 \times (20.316 - 12.703)$$

$$= 13.463 \text{ minutes}$$

Where:
t_1 = retention time of hexadecane in minutes
t_2 = retention time of octadecylbenzene in minutes, refer to Figure 2.

Results and discussion

ASTM D7419 specifies a number of performance checks to insure that the instrument provides the precision needed for the determination of total aromatics and total saturates in the lube oil sample, as shown in Table 1.

Table 1. ASTM D7419 performance requirements

Performance area	Requirement	D7419-13 Section
Resolution	≥ 5	9.3
Capacity factor	≥ 0.4	9.3
Signal to noise at ≥ 10 µL injection volume	≥ 8	9.6
Short term precision fore flush mode	< 0.6% RSD	12.3
Calibration	Linear, forced through origin with a correlation coefficient > 0.999	10.4
Aromatic response factor	1.67–1.8	13.1
Std at 0.1 mass% analyses for octadecylbenzene	<0.15 mass %	9.7.3

A system performance standard was prepared according to section 9.3.1 of the ASTM method by weighing hexadecane (1.0 ± 0.1 g) and octadecylbenzene (1.0 ± 0.1 g) into a 10 mL volumetric flask and filling to the mark with heptane. This solution was then used to obtain the typical results for each of the quality checks that are shown below:

Requirement: Resolution ≥ 5
Resolution is calculated by:

$$\text{Resolution} = \frac{2 \times (T_2 - T_1)}{3 \times (y_1 + y_2)}$$

Where:

T_1 = Retention time of hexadecane peak

T_2 = Retention time of the octadecylbenzene peak

y_1 = Peak width at ½ height of hexadecane peak

y_2 = Peak width at ½ height of the octadecylbenzene peak

Substituting values obtained for the chromatogram in Figure 2 gives:

$$\text{Resolution} = \frac{2 \times (20.316 - 12.703)}{3 \times (0.11081 + 0.31815)}$$

$$= 12$$

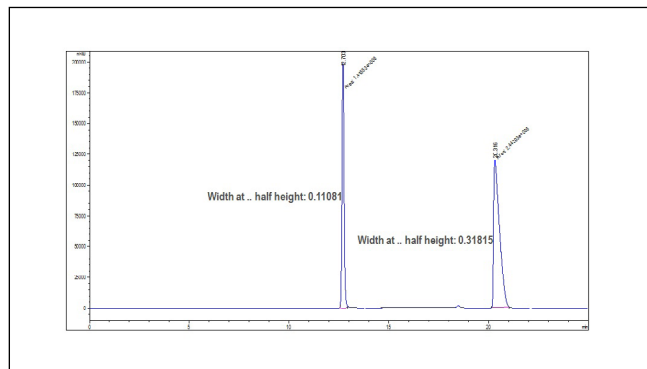Therefore, the system resolution exceeds the ASTM requirement.

Figure 2. Chromatogram of the system performance standard

Requirement: Capacity factor ≥ 0.4
The capacity factor (K) is calculated from the chromatogram using the equation:

$$K = \frac{T_2 - T_1}{T_1}$$

Where T_1 is the retention time of the hexadecane peak and T_2 is the retention time for the octadecylbenzene peak. Substituting values obtained from the chromatogram in Figure 2 into this equation gives:

$$= \frac{20.316 - 12.703}{12.703}$$

$$= 0.6$$

Therefore, the capacity factor exceeds the ASTM method requirement.

Requirement: Signal to noise at ≥ 10 µL injection volume is ≥ 8
A detection limit standard was prepared by weighing 0.01 g octadecylbenzene into a vial and adding 5.00 g of hexadecane to make the 0.2 mass% aromatics standard specified in the method. This was injected in the fore flush mode to obtain the chromatogram in Figure 3. The signal to noise ratio (S/N) is calculated as:

$$S/N = \frac{8.5 \text{ cm}}{0.9 \text{ cm}}$$

$$= 9.4$$

Therefore, the signal to noise ratio exceeds the ASTM requirement.

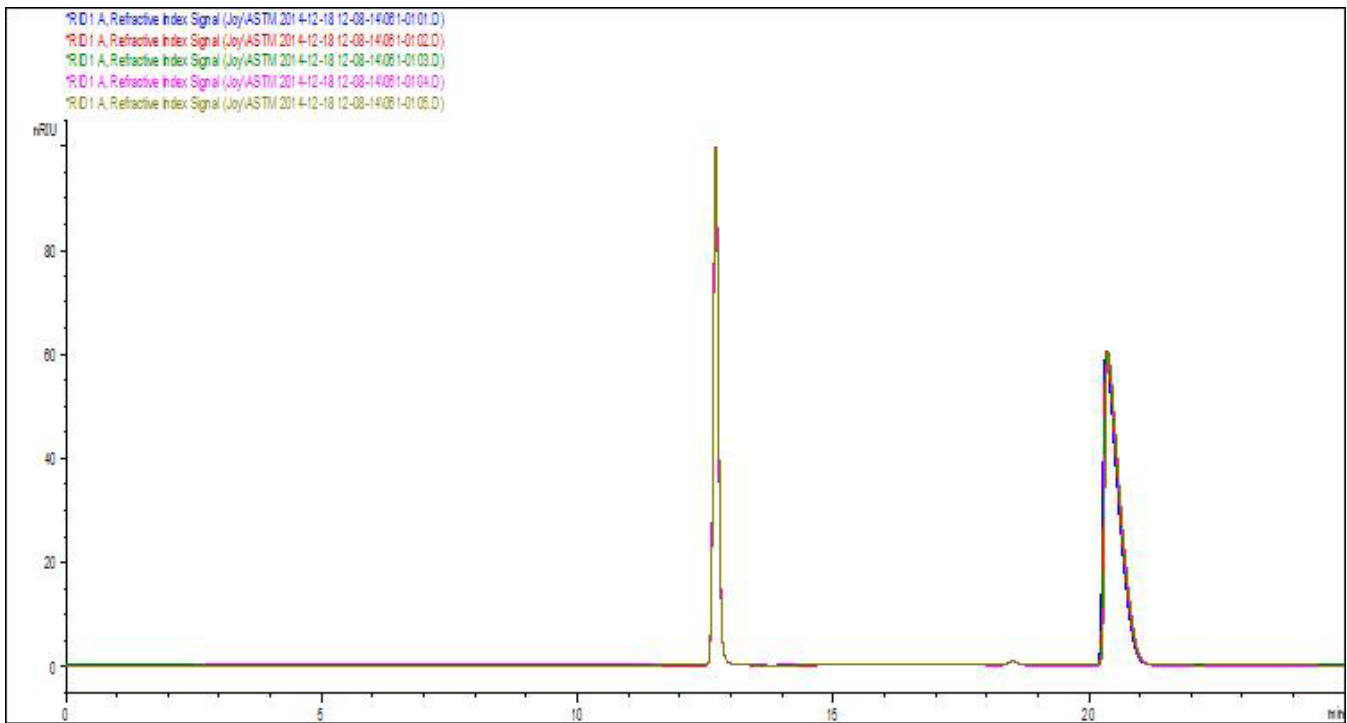**Figure 3**. Chromatogram for Signal to Noise Calculation

Figure 4. Overlay for 5 chromatograms of the system performance standard in fore flush mode

Requirement: Short term precision fore flush mode < 0.6% RSD
The ASTM method requires a short term precision study in the fore flush mode by injecting the system performance standard five times and determining that the relative standard deviations of the areas for the hexadecane and the octadecylbenzene components are less than 0.6%. An overlay of the chromatograms obtained for this study are shown in Figure 4 and the statistics obtained from the OpenLab Chromatography Data System are shown in Table 2 and Table 3.

These data show that the RSD for the hexadecane peak is 0.07 and 0.41 for the octadecylbenzene peak. Both of these values exceed the ASTM requirement.

Table 2. Statistics for short term precision study of hexadecane in a Test ASTM standard, with signal = RID1 A, refractive index signal

Inj#	RT (min)	Amount (g/mL)	Area	Height
1	12.704	0.9999	1431276.37500	198744.82813
2	12.705	1.0008	1432614.50000	198625.15625
3	12.703	0.9997	1430924.87500	198852.93750
4	12.703	1.0013	1433208.25000	198930.23438
5	12.708	1.0000	1431416.00000	198774.65625
Mean	12.705	1.0003	1431888.00000	198785.56250
Std Dev	0.00184	0.0007	974.08178	115.08447
RSD	0.014	0.0680	0.06803	0.05789

Table 3. Statistics for short term precision study of octadecylbenzene in a Test ASTM standard,, with signal = RID1 A, refractive index signal

Inj#	RT (min)	Amount (g/mL)	Area	Height
1	20.336	1.00490	2483405.50000	120883.35938
2	20.351	0.99657	2462828.00000	119829.09375
3	20.362	0.99576	2460811.50000	119717.38281
4	20.372	1.00383	2480753.25000	119932.14844
5	20.380	1.00000	2471300.50000	120158.43750
Mean	20.360	1.00021	2471819.75000	120104.08438
Std Dev	0.0175	0.00413	10202.20297	465.01175
RSD	0.086	0.41274	0.41274	0.38717

Requirement: Linear calibration with correlation coefficient > 0.999

The calibration curves obtained from standards made in accordance with the method are shown in Figure 5.

The correlation coefficients exceed the ASTM requirement for both hexadecane and octadecylbenzene.
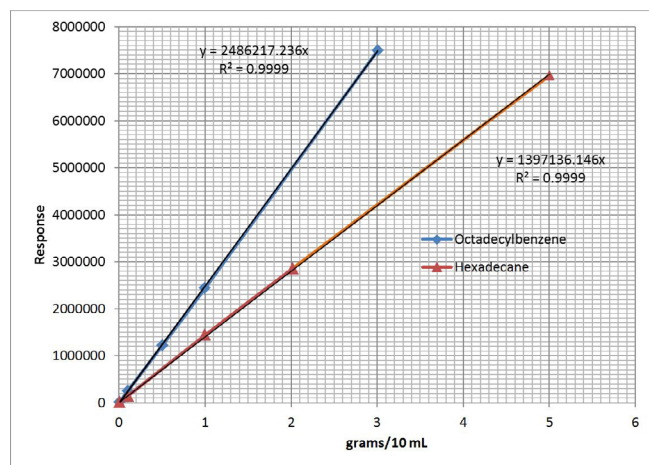

Figure 5. Calibration curves for hexadecane and octadecylbenzene

Requirement: Aromatic response factor is 1.67–1.80

The aromatic response factor is calculated by dividing the slope of the calibration line for octadecylbenzene by the slope of the calibration line for hexadecane. Using the slopes from Figure 5, gives:

$$\text{Aromatic response factor} = \frac{2486217}{1397136} = 1.78$$

Therefore, the aromatic response factor is in accordance with the requirements of the ASTM method.

Requirement: Std at 0.1 mass% analyses at <0.15 mass % for octadecylbenzene

A 0.1 mass% mixture was prepared by weighing 0.01 g of octadecylbenzene in 10.0 g of hexadecane and was analyzed in the backflush mode. The chromatogram obtained is shown in Figure 6 and the mass% of total aromatics + polars was calculated according to the equation:

$$(\text{Total Aromatics+Polars})(\text{mass\%}) = \frac{A_{ar}/ARF}{A_{na}+(A_{ar}/ARF)} \times 100$$

Where:
A_{ar} = area of the saturates peak
A_{na} = area of the aromatics + polars peak
ARF = aromatics response factor

Substituting in values from the chromatogram gives:

$$= \frac{2494.26/1.78}{2616560 + (2494.26/1.78)} \times 100$$

$$= \frac{1401.27}{2616560 + 1401.27} \times 100$$

$$= \frac{1401.27}{2617961.27} \times 100$$

$$= 0.054 \text{ mass\%}$$

Therefore, the total aromatics + polars measurement exceeds the ASTM requirement.
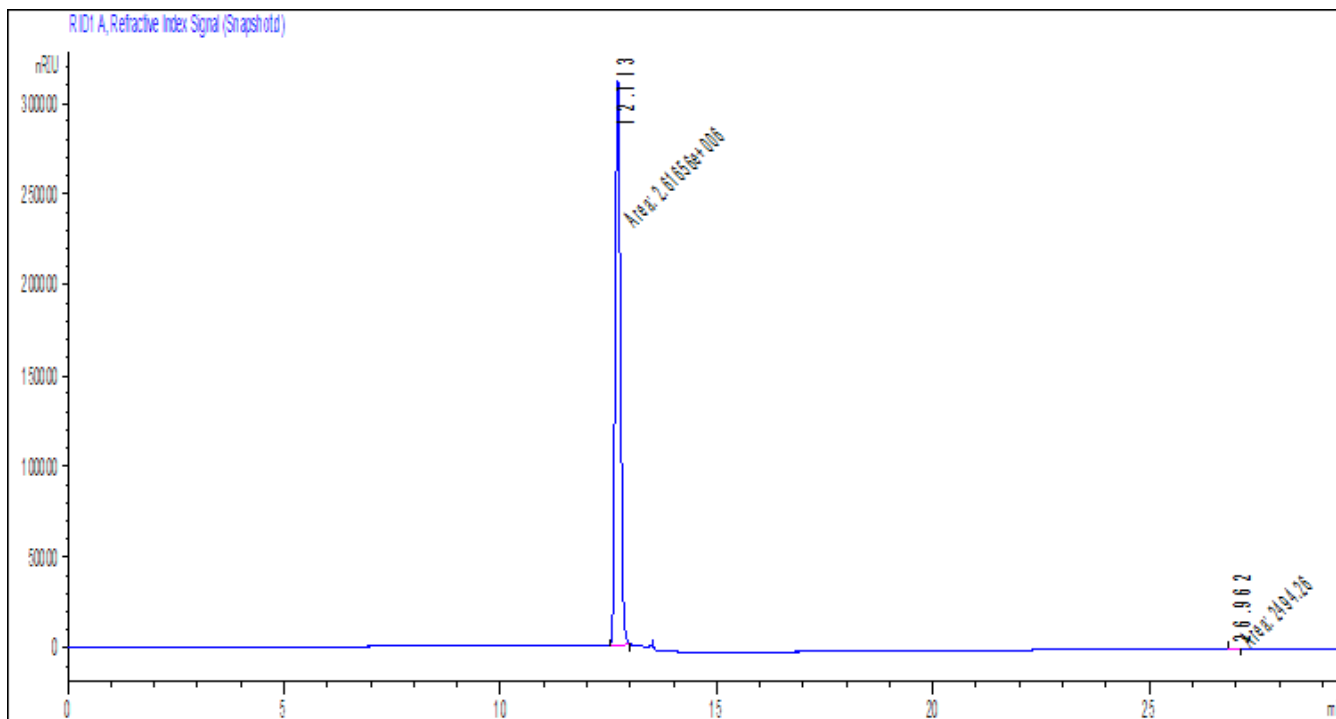
Figure 6. Chromatogram of 0.1 mass% mixture
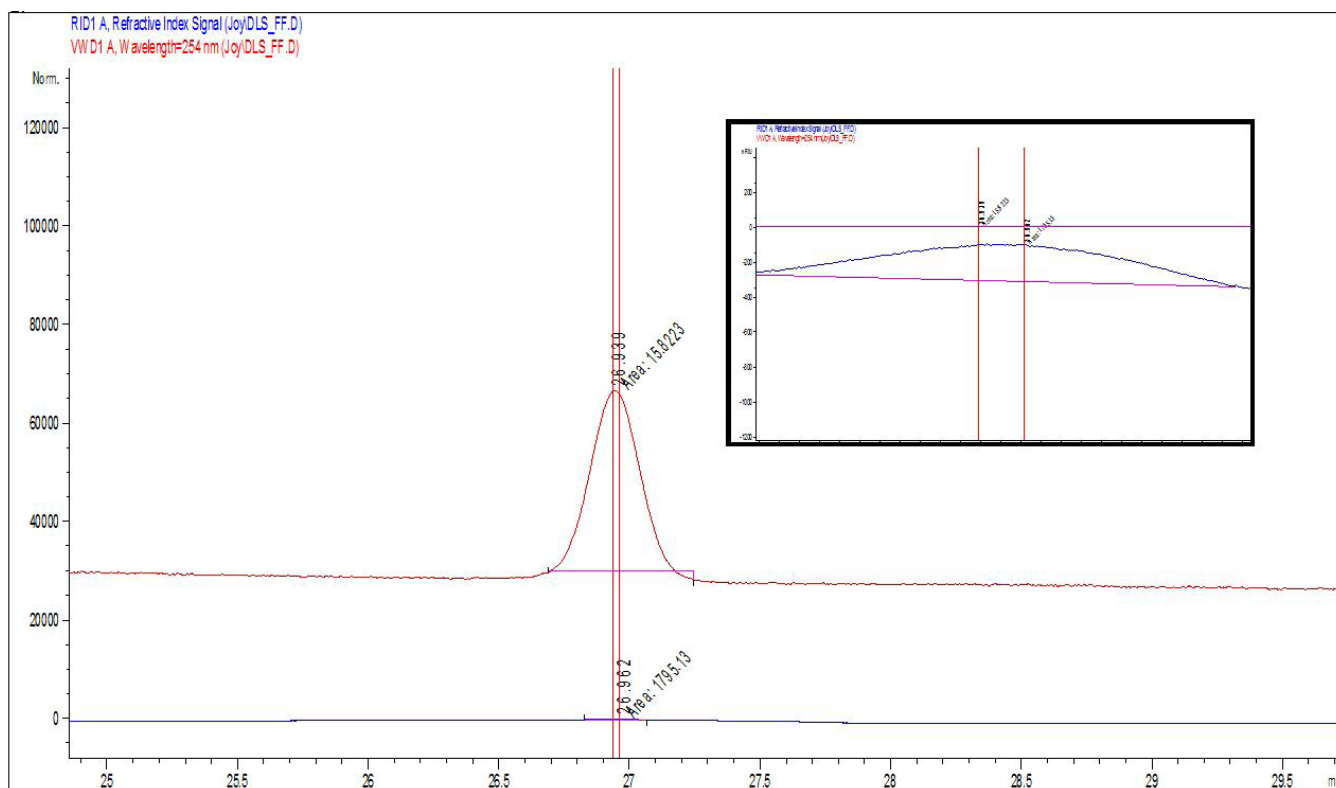

Figure 7. Chromatogram of octadecylbenzene peak of 0.1 mass% mixture using UV detection to verify retention time.

Conclusions

ASTM D7419 for the determination of total aromatics and total saturates in lube base oils is widely used to evaluate conformance to specifications that determine the value of products for commercial transactions or to determine product quality to support production decisions. To ensure that the data produced fulfills these requirements, a number of quality and precision checks are specified within the method. This study demonstrated that the performance of the Agilent 1260 LC System met or exceeded all of the specified requirements.

Reference

1. ASTM D7419-13, "Standard Test Method for Determination of Total Aromatics and Total Saturates in Lube Basestocks by High Performance Liquid Chromatography (HPLC) with Refractive Index Detection"

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