Carbon Type Distribution of Petroleum Oils with SVM 4001 and Abbemat

Relevant for: Petroleum Industry - Research, production and incoming quality control of base oils, lube oils and process oils.

Measure the required parameters and calculate carbon distribution and ring content of oils according to ASTM D3238 in one go within minutes.

1 Why determine carbon type distribution?

The carbon type distribution serves to express the gross composition of the heavier fractions of petroleum into paraffinic, naphthenic, and aromatic components. It is one of the most important parameters for the qualification of base oils, lube oils, process oils, or plasticizer because it directly correlates to critical product performance properties.

According to the standard ASTM D3238, the carbon distribution and ring content of olefin-free petroleum oils is calculated from measurements of refractive index, density and molecular weight (n-d-M method). The mean molecular weight can be calculated following ASTM D2502 from viscosity measurements at 37.78 °C and 98.89 °C (100 °F and 210 °F).

So the following basic parameters are required:

- kinematic viscosity at 37.78 °C and 98.89 °C (obtained from SVM 4001)
- refractive index at 20 °C (obtained from the refractometer)
- density at 20 °C (calculated from the measured density values by the SVM software)

Further, the mean molecular weight is required. It is calculated from kinematic viscosity at 37.78 °C (100 °F) and 98.89 °C (210 °F) according to ASTM D2502.

From all these parameters, the carbon distribution (C_A, C_N, C_P) and ring content (R_T, R_A, R_N) are determined according to the formulas in ASTM D3238.

This report describes specifically how to test petroleum oils with the SVM 4001 (according to ASTM D7042, D4052 and D2502) in combination with an Abbemat refractometer to get the carbon type distribution according to ASTM D3238.

2 Which instruments are used?

For the viscosity and density measurement, the SVM 4001 with two measuring cells for simultaneous viscosity measurement at two temperatures is used. For the RI measurement, the Abbemat 550 is used. Connected via CAN interface, it is a module controlled by the SVM 4001 as master instrument.

Tip: Any other Anton Paar refractometer from the Performance/ Performance Plus Line (300/350 or 500) or from the Heavy Duty line (450/650) can be used.

3 Which samples are tested?

Five oil samples as listed below were tested:

Sample	
Nytro 4000X	Severely hydrotreated insulating oil
T110	Severely hydrotreated base oil
Nyflex 3150	Severely hydrotreated process oil
Nypar 315	Severely hydrotreated process oil

Samples were kindly provided by Nynas AB, Sweden.

4 Sample measurement

4.1 Instrument setup

Method: "SVM 4001 VI + Abbemat"

SVM 4001:

According to ASTM D7042, the following settings are predefined by default:

- Measuring temperatures:
  Cell 1: 37.78 °C, Cell 2: 98.89 °C
- Precision class "Precise"
- RDV limit 0.10 %
- RDD limit 0.0002 g/cm³
- 5 determinations
- Automatic prewetting: yes
- Sulfur correction: activated (enter the value if the sulfur content is 0.8 % or higher to improve the accuracy of the CTC calculation)
- Drying time: 150 s (built-in air pump)
  when using compressed air at 2 bar: 60 s

Abbemat refractometer:

The method SVM + Abbemat includes the following settings for the refractometer:

- Temperature: 20 °C
- Measurement accuracy "Most Precise"
- Hold time: 1 s
- Timeout: 200 s
- Wavelength: 589.3 nm (fixed parameter)

4.2 Calibration

Use only a calibrated instrument. The calibration shall be performed periodically using certified reference standards. According to ASTM D7042, the reference standards shall be certified by a laboratory, which meets the requirements of ISO/IEC 17025 or a corresponding national standard. Viscosity standards should be traceable to master viscometer procedures. The uncertainty for density standards must not exceed 0.0001 g/cm³. For each certified value the uncertainty should be stated (k = 2; 95 % confidence level). Use one or more standard(s) in the viscosity range of your oil sample(s). If required, apply a calibration correction to improve the reproducibility. To perform calibration (correction), refer to the SVM X001 Reference Guide.

For the refractometer perform at least a water check. For checks and adjustments of the Abbemat refer to the documentation of the Abbemat.

4.3 Sample preparation

If the sample is not freshly drawn from a production line or else, homogenizing the test specimen may improve the measurement repeatability. For some samples degassing may be required. Refer to the SVM X001 Reference Guide.

4.4 Filling

10 mL single-use syringes are recommended to have enough sample for refills. Never use syringes with rubber seals, as the rubber is chemically not resistant and these syringes tend to draw bubbles.

Ensure that the system (measuring cells and hoses) is leak tight, clean and dry.

For flow-through filling, inject approx. 4.5 mL as first filling. After prewetting refill at least 1 mL or until the sample in the waste hose is free of bubbles. The typical amount for valid results is approx. 7 mL, where the volume can vary depending on the sample.

4.5 Cleaning

4.5.1 Solvents

Ensure that the solvent starts boiling at a temperature higher than the measuring temperature. Otherwise a lack of cleaning in the hot upper cell may impact the measuring results.

Petroleum benzine 100/140 (aliphatic hydrocarbon solvent mixture with a boiling range of 100 to 140 °C respectively 212 to 284 °F) is a universal solvent, suitable for most oils.

Some oils may require an aromatic solvent, as they are not completely soluble in petroleum benzine. If so, use toluene or xylene as first solvent and the aliphatic hydrocarbon solvent as drying solvent.

Avoid using acetone or ethanol, as these solvents start boiling below the temperature of the upper cell and as they are not suitable for most oils.

For details, see the SVM X001 Reference Guide.

4.5.2 Cleaning Procedure

- Tap the cleaning button to open the cleaning screen. Observe it during cleaning to get information on the cleaning status of the SVM.
- Remove the sample from the cells (push through using an air-filled syringe).
- Fill approx. 5 mL of solvent using a syringe and leave the syringe connected (a 5 mL syringe for works well for cleaning purposes).
- Tap the motor speed button to improve the cleaning performance in the viscosity cell and stop it again.
- Move the plunger of the syringe back and forth (motor at filling speed) to improve the cleaning performance in the cells of SVM and Abbemat.
- Blow air for some seconds through the cells to remove the sample-solvent-mixture.
- Repeat the procedure until the liquid has reached approx. the solvent’s viscosity while the motor is turning at high speed.
- Perform a final flush with a drying solvent to remove any residues.
- Observe the cleaning screen. Dry the measuring cells until the cleaning value turns green and stays steadily green.
- Set a sufficiently long drying time to ensure that also the Abbemat cell (at 20 °C) is completely dry.

For details, see the SVM X001 Reference Guide.

5 Results

For this report, the measurement and calculation results obtained from SVM 4001 and Abbemat 550 and the reference values on the respective data sheets (PDS, CoA) are compared.

Carbon type analysis:

Carbon distribution:

Sample	C_A [%]	C_N [%]	C_P [%]
T110	13.80	34.73	51.40
Nypar 315	0.20	30.55	69.23
Nyflex 3150	9.63	29.03	61.30
Nytro 4000X	2.35	47.30	50.40

Table 1: ASTM D3238 (n-d-M) Carbon distribution (mean of 4 measurements)

Ring content:

Sample	R_T	R_A	R_N
T110	3.00	0.68	2.32
Nypar 315	1.58	0.01	1.57
Nyflex 3150	2.95	0.58	2.37
Nytro 4000X	1.96	0.08	1.88

Table 2: ASTM D3238 (n-d-M) Ring content (mean of 4 measurements)

Carbon distribution, deviations:

Sample	dev. C_A	dev. C_N	dev. C_P
T110	IR: -1.20 D2140: 2.80	4.28	-1.40
Nypar 315	Fulfilled **	3.45	4.22
Nyflex 3150	IR: 0.63 D2140: 2.63	-3.98	1.30
Nytro 4000X	IR: -1.65	IR: 2.30	IR: -0.60

*Table 3: Deviation to typical sample values * (dev. in percentage points)*

* Reference values / typical values were obtained by different methods. Where not mentioned, the value was determined by ASTM D2140.
** Value must be < 1.

Refractive Index:

Sample	RI meas. [nD]	RI typ. [nD]	Dev. [nD]
T110	1.5035	1.502	0.0015
Nypar 315	1.4681	1.468	0.0001
Nyflex 3150	1.4949	1.494	0.0009
Nytro 4000X	1.4746	n.a.	n.a.

Table 4: Refractive Index and deviation to typical values at 20 °C

ASTM D2502 Mean Molecular Mass:

Sample	[g/mol]	range	meets range value
T110	399.59	352 ... 408	OK
Nypar 315	371.59	368 ... 392	OK
Nyflex 3150	494.49	468 ... 505	OK
Nytro 4000X	273.01	n.a.	n.a.

Table 5: Mean molecular mass

6 Conclusion

The assembly of SVM 4001 with Abbemat is perfectly suitable for determining the carbon type analysis of petroleum oils, provided all requirements according to section 4, "Sample measurement" are fulfilled.

Figure 1: SVM 4001 with Abbemat 550

7 Literature

- ASTM D7042
- ASTM D3238: Standard Test Method for Calculation of Carbon Distribution and Structural Group Analysis of Petroleum Oils by the n-d-M Method
- ASTM D2502: Standard Test Method for Estimation of Mean Relative Molecular Mass of Petroleum Oils from Viscosity Measurements
- Anton Paar Application Report SVM 3001 with Abbemat for Transformer Oils Doc. No. D89IA013EN.

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APPENDIX

Appendix A. Carbon type analysis

Carbon-type analysis expresses the average amount of carbon atoms which occur in aromatic, naphthenic and paraffinic structures, reporting

- the percentage of the carbon atoms in aromatic ring structures (% C_A),
- the percentage in naphthenic ring structures (% C_N) and
- the percentage in paraffinic side chains (% C_P).

There are several physical property correlations for carbon type analysis.

In this application report the n-d-M method (refractive index – density – mean relative molecular mass), standardized as ASTM D3238, is described.

Besides, a further empiric procedure exists, the VGC-r_i method (viscosity gravity constant – refractivity intercept), standardized as ASTM D2140.

Why carbon type analysis?

Base oils, process oils and other petroleum oils are checked for their carbon type distribution. Oils with specified carbon type distribution are designed for different industries. Carbon type analysis according to ASTM D3238 is further used to determine the quantification of aromatics in diesel fuel.
Major groups for this kind of analysis are process oils. To know the carbon type analysis is important to improve product properties, the process efficiency and reliability. Process oils are used in various fields e.g.:

- as plasticizer in the rubber and polymer industry e.g. for automotive tires, sealants, footwear or other rubber products. Properties of the ready to use product like elasticity, grip, durability, low temperature performance, environmental sustainability on the one hand, further solvency and compatibility with the rubber compound during production highly depend on the used process oil. Such oils can be aromatic, naphthenic or paraffinic types.

- as textile auxiliary formulations in the production process of yarns. They are used to reduce respectively avoid dust formation, prevent wear and rupture of fibers, electrostatic charging and more. Such oils should have very low aromatic hydrocarbon content and a high viscosity index.

- in the production of cosmetics. Such oils need to have very low aromatic hydrocarbon content and must meet the requirements for medical white oil.

Nevertheless, there are also process oils, which are analyzed according to ASTM D2140.

ASTM D3238 (n-d-M)

“Standard Test Method for Calculation of Carbon Distribution and Structural Group Analysis of Petroleum Oils by the n-d-M Method”

This test method covers the calculation of the carbon distribution and ring content of olefin-free petroleum oils from measurements of refractive index, density and mean relative molecular mass.

The refractive index and density of the oil are determined at 20 °C. The mean relative molecular mass is estimated from measurements of viscosity at 37.78 °C and 98.89 °C (100 °F and 210 °F).

These data are then used to calculate

the **carbon distribution**
percentage of the total number of carbon atoms that are present in aromatic rings (% C_A), naphthenic rings (% C_N) and paraffinic chains (% C_P) or

the **ring analysis**
proportions of aromatic rings (R_A) and naphthenic rings (R_N), and paraffinic chains (C_P) that would comprise a hypothetical mean molecule.

ASTM D2502 - Mean relative molecular mass

"Standard Test Method for Estimation of Molecular Weight (Relative Molecular Mass) of Petroleum Oils From Viscosity Measurements”

The mean relative molecular mass is a fundamental physical constant that can be used in conjunction with other physical properties to characterize hydrocarbon mixtures.

This procedure covers the estimation of the mean relative molecular mass of petroleum oils or hydrocarbon fractions from kinematic viscosity measurements at 37.78 °C and 98.89 °C.

"SVM 4001 VI + Abbemat" Method

Beside the measurement results of the incoming parameters for the carbon type analysis and the analysis results according to ASTM D3238, this method offers a lot of additional useful parameters characterizing your oil:

- kinematic viscosity at 40 °C and 100 °C (extrapolated according to ASTM D341)
- Viscosity Index (according to ASTM D2270)
- Carbon type composition according to ASTM D2140 including the viscosity-gravity-constant (VGC) following ASTM D2501
- Density 20 °C
- API Spec. Gravity 15.56 °C (60 °F)
- Viscosity Gravity Constant according to ASTM D2501