

Application Note

► Determination of hydrocarbon types in lubricating oil base stocks

| | |
|-------------|--|
| Category | Chemical Analysis |
| Matrix | Mineral oil |
| Method | NP chromatography |
| Keywords | Quality control, industrial by-products, gas oil, lubricating oil, saturated compounds, aromatic compounds, IP 368 |
| Analytes ID | Lubricating oil base stocks, gas oil VCH4_Mineral_Oil_IP368 |



Summary

This method covers the separation and determination of representative saturated and aromatic hydrocarbons in lubricating oil base stocks with a boiling point above 270 °C according to the European standard method IP 368. It can be applied to gas oils boiling in the range of 200 °C to 350 °C by substituting pentane for hexane in the described method. In contrast to similar methods¹ such as IP 391/07 which use representative model substances for calibration, this method uses fraction collection with subsequent gravimetric determination of the evaporated fractions. This method can be easily and affordably automated by using the KNAUER Smartline Analyzer 6550.

Introduction

When crude mineral oil is refined, a large part of the high boiling fractions are included. Even though most of these fractions are transformed into volatile compounds via crack processes, a smaller amount is still used for lubricating oil.

Despite the increasing distribution of fully synthesized lubricating oil base stocks, mineral oil based products are still of great importance. The most important characteristics of lubricating oil base stocks such as pour point, oxidative stability and temperature-dependent viscosity all depend on the ratio of aromatic and saturated products. Therefore all lubricating oil base stocks are classified into six groups² with a major property:

The group with the smallest fraction of aromatics has the highest quality and the highest price. The first group may contain more than 10 % aromatics and less than 90 % saturated compounds. The second group must contain less than 10 % aromatics and more than 90 % saturated compounds followed by the third group with less than 1 % aromatics and more than 90 % saturated compounds (the 4th to 6th groups include fully synthesized products without aromatics). The importance of determining hydrocarbon types becomes thereby apparent.

The representative separation of aromatic and saturated compounds is described in IP method 368³ by applying a normal phase separation in n-hexane with a column up to 2 m in length (realized by a serial column arrangement). The polarity of aromatic compounds is much higher than the polarity of saturated ones. Therefore the saturated compounds elute first and the aromatics elute much later. For a proper analysis time, an optimization step is recommended. A backflush procedure can be applied by using the switching valve in the Smartline Analyzer 6550. The valve is applied to inverse the column direction to obtain the aromatic hydrocarbons in a single large peak after emergence of the saturated hydrocarbons.

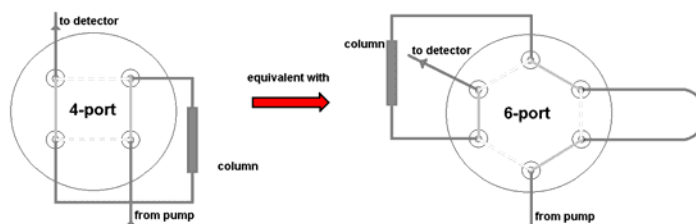
Experimental system overview

The system solution presented in this application is customized to fulfill the requirements of the European standard IP 368. It is equipped with additional switching valves which are integrated into KNAUER Smartline Assistant units (Figure 1). The first two 17-port-1-channel valves are used for the multi sample injection module. The samples can be loaded in 16 sample loops via a standard manual injection valve and the analysis can be done sequentially. In addition, a second manual valve is used for the calibration of the loops as described in IP 368. A 4-port valve is applied to backflush the columns after the saturated compounds have passed the column. This backflush valve function is easily realized by using a KNAUER 6-port valve as shown in Figure 2.



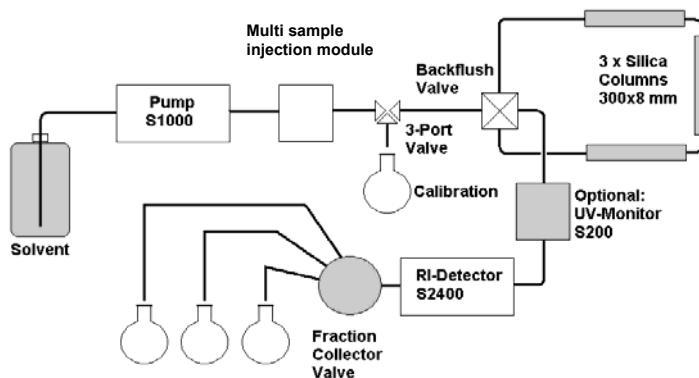
Fig. 1
Smartline Analyzer 6550

Fig. 2
Two types of backflush valves



Finally, a 16-port valve is used by the KNAUER Analyzer 6500 to carry out the fraction collection. A schematic overview of the complete system is shown in Figure 3. Three silica columns are used in series to increase the separation power. The columns must be connected to each other with low dead-volume connectors to avoid peak broadening effects and loss of theoretical plate numbers. Up to five silica columns with 2 m total column length, connected in series, may be necessary for the complete separation of heavy oils.

Fig. 3
Diagram of customized HPLC system



All of these features are realized by the KNAUER Smartline Analyzer 6550, which is equipped with the Smartline RI Detector 2400 and UV Detector 200 – both with a preparative flow cell (Figure 3).

Experimental: calibration

Since the collected fractions were weighed out after evaporation of hexane, no reference material was needed. The absolute volume of each sample loop must be determined only once. For this purpose a 3-port manual valve was implemented between the multi-loop injection valve and the backflush valve. By collecting the amount of an injection loop that was completely filled with the sample and transferring it into a tared dish (without passing through the columns), the total mass of injected sample {M} was determined after evaporating the solvent. This calibration is required only once for every sample loop. Here we only demonstrate the usage of two loops with the following correction factors. Up to 16 loops can be used for 16 different samples or lower sample numbers with double analysis.

| Loop | Total mass of sample injected (after evaporating) |
|------|---|
| 1 | 198.2 mg |
| 2 | 198.6 mg |

Experimental: sample preparation

About 5 g (4.9975 g) of the sample of a lubricating oil base stock were weighed out and transferred into a 50 ml volumetric flask, brought up to volume with hexane and shaken well until it was thoroughly mixed. Before injection the sample was filtered through a 0.45 µm syringe filter.

Chemical structure

Mineral oil fractions with a boiling range above 270°C contain long chain alkanes, cycloalkanes and high condensed aromatics with up to 70 C atoms. The precise chemical structure is difficult to determine because of the diversity of thousands and thousands of isomers and homologues. Therefore this method separates all compounds into aromatic and saturated compound groups. All compounds with higher polarity than the saturated ones, including those that contain sulfur, nitrogen or oxygen, were determined as aromatics as well.

Method parameters

| | |
|--------------------|---|
| Columns | Kromasil 100-16 Si, 300 x 8 mm ID (3 pieces, up to 5) |
| Eluent | hexane* |
| Flow rate | 6 ml/min |
| Injection volume | 2 ml (via sample loops) |
| Column temperature | Ambient |
| Detection | RI and UV at 254 nm (for aromatic compound group) |
| Analysis time | 45 min |

* Eluent continuously sparged with helium

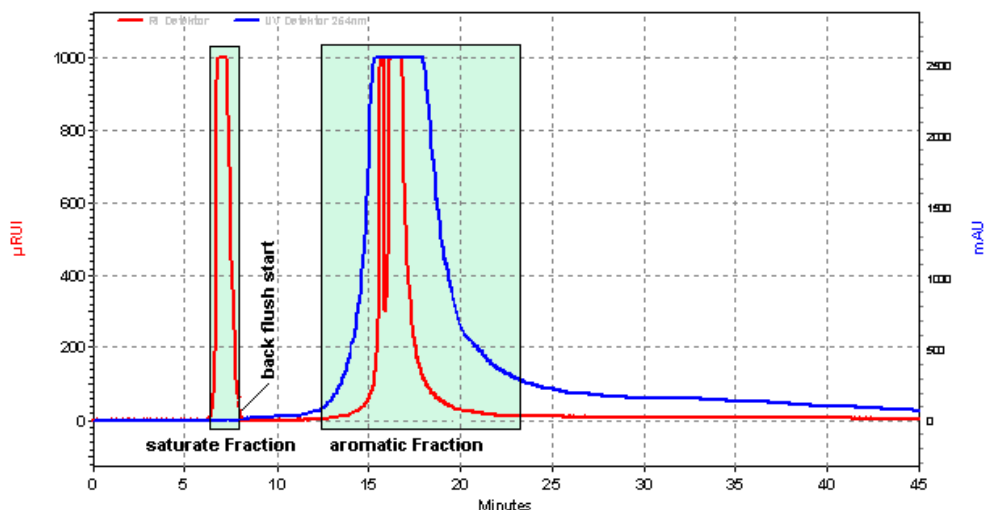
Results

The separation chromatogram of a lubrication oil sample in hexane is shown in Figure 4. The detection of the separated saturated and aromatic components was realized by refractive index and additional UV detection to recognize the aromatic fraction. After elution of the saturated fraction in the front of the chromatogram, the backflush valve is switches the flow across columns to elute the aromatic fraction as a single large peak with acceptable retention time. By using the automated fraction collection (FRC) functions of KNAUER's ClarityChrom Prep software, up to eight samples can be analyzed automatically in one sequence. By integrating an additional 17-port valve, the sample capacity can be enlarged to up to 16 samples in one sequence. The solvent in the collected fractions was evaporated and the nonvolatile residue was determined gravimetrically as shown in the table below.

| Sample loop | 1st fraction* (saturated) | 2nd fraction* (aromatics) | Recovery | Saturated compounds | Aromatic compounds |
|-------------|---------------------------|---------------------------|----------|---------------------|--------------------|
| 1 | 39.5 mg | 158.0 mg | 99.6 % | 19.9 % | 79.7 % |
| 2 | 39.7 mg | 157.2 mg | 99.1 % | 20.0 % | 79.2 % |
| Average: | | | | 19.95 % | 79.45 % |

* fraction collection according to RI signal

Fig. 4
Chromatogram of lubricating oil sample
(red: RI trace; blue: UV trace)



Method performance

| Oil | Repeatability* | Reproducibility* |
|---------------|----------------|------------------|
| Distillate | 0.7 % mass | 2.1 % mass |
| Bright stocks | 1.3 % mass | 5.0 % mass |

*These precision values were calculated from inter-laboratory results.

Conclusion

Using the KNAUER Analyzer 6550, specially adapted for oil analysis, hydrocarbon types in lubricating oil base stocks according to the European standard method IP 368/01 could be determined automatically, without the need for an autosampler unit. A combination of three silica columns in serial configuration was used to separate the aromatic from the saturated hydrocarbon group. The system described can be loaded with up to 8 different samples to automate the analysis. By adding a second 17-port fraction collection valve, up to 16 samples could be automatically analyzed. The volume of the sample loops according to the IP 368 method is 2 ml. If other volumes are needed, the sample loops can be easily adapted. The application presented clearly shows the advantage of an automated system for processing several samples, all in one very price attractive solution.

References

1. KNAUER, Application Note, VFC3, May 2010, at www.knauer.net
2. Zplus™ Tech Brief #10 at www.zddpluss.com
3. European Standard, IP 368/01 (2006)

Authors

Silvia Marten, Head of Columns and Applications Department, KNAUER
Elmar Tepper, Columns and Applications Department, KNAUER

Physical properties of recommended column



| | |
|------------------------------|-----------------------|
| Stationary phase | Kromasil 100-16 Si |
| USP code | -- |
| Pore size | 100 Å |
| Pore volume | 0.98 ml/g |
| Specific surface area | 320 m ² /g |
| Particle size | 16 µm |
| Form | spherical |
| Surface area | 330 m ² /g |
| Endcapping | no |
| Dimensions | 300 x 8 mm |
| Order number | 30GE000KSR |

Recommended instrumentation

The presented application was performed on the KNAUER Analyzer 6550 equipped with isocratic Smartline pump 1000, 10ml pump head, 2 ml sample loops, RI Detector 2400 and fixed wavelength UV Detector 200. Both detector units used were equipped with a preparative flow cell.

| Description | Order No. |
|----------------------------|-----------|
| Smartline Analyzer 6550 | A5004V18 |
| ClarityChrom Prep software | A1685 |

Contact information

Wissenschaftliche Gerätebau
Dr. Ing. Herbert Knauer GmbH
Hegauer Weg 38
14163 Berlin, Germany

Tel: +49 (0)30 / 809727-0
Fax: +49 (0)30 / 8015010
E-Mail: info@knauer.net
Internet: www.knauer.net