

THE APPLICATION OF IATROSCAN-TECHNIQUE FOR ANALYSIS OF BITUMEN

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Abstract. *Abstract: The analytical Iatroscan-technique is a thin film chromatography with FID-detection. The method for investigation of the structure of bitumen takes 3 hours instead of 2 days for the normal method with liquid chromatography. Therefore the Iatroscan-technique is a fast and very economical method. Another advantage is the possibility to correlate the saturated hydrocarbons with the paraffin content in regard to DIN 52015. The unsolubles in heptane can also be estimated from asphaltene content determined by Iatroscan.*

Key words: bitumen, Iatroscan, chromatography, paraffins

Introduction

Thin layer chromatography (TLC) combined with flame ionisation detection has become a common and widely used separation technique in laboratories in recent years. TLC is a simple and flexible technique because the detection system is not connected directly to the chromatographic system. Rod-shaped layers are used for the chromatography. They have mechanical and chemical properties which permit the detection of the separated components in an ionisation detector.

The TLC-FID method is based on work carried out in the 1960s. In the 1970s patents for the Japanese company Shionogi were published in which a procedure for manufacturing a TLC rod with a sintered silica gel layer reusable and suitable for flame ionization detection was described. At the beginning of the 1970s the Japanese company Iatron Inc. introduced Thinchrograph TFG10, which was replaced by the Iatroscan TH-10 Analyser, Mark II. In the 1980s the Mark III version appeared which is widely used throughout the world [1]. The analysis in our laboratory is done by the Iatroscan MK-5 Analyser controlled by an HP 3365 Series II Chemstation [2].

The TLC-FID method has become an important quantitative method and is used in medicine and biology for separation of chemical substances. Because it is a fast method and allows a high sample throughput it is particularly useful for series quantitative separations of mixtures of substances that can not analyzed by GC or HPLC because of their low volatility or the irreversible adsorption on a HPLC-column.

The advantages of TLC-FID are the reason why this method was tested for analysis of vacuum distillates and vacuum residues such as bitumen.

Analytical Methods for the Investigation of the Composition of Bitumen

Methods by Liquid Chromatography are standardized in ASTM D 2007 or ASTM D 4124. In these procedures first the asphaltenes are separated by precipitation with

solvents like heptane or pentane. In the second step the maltenes are separated into the fractions saturates, aromatics and resids by elution with different solvents on an LC-column.

The separated fractions must be dried and weighed. This takes a lot of time. The column packing must be renewed after each analysis. The consumption of material and solvents is high. The fractions are not pure and the overall yield is low.

The TLC-FID method is faster, cheaper and more accurate.

The determination of asphaltenes by extraction with solvents is also time-consuming. Less time is taken with a combination of UV-spectra and chemometric techniques of which the asphaltene content of heavy petroleum products can be derived. The asphaltene content of the IP 143 method can be correlated with the asphaltenes from the TLC-FID result.

Paraffines in bitumen can be obtained by distillation (DIN 52015) and ethanol-ether precipitation (AFNOR, EN 12606). Both methods consume much time and are difficult to automate. The estimation of the paraffin content by correlation with the saturates determined by TLC-FID takes less time.

TLC-FID Equipment and Procedure

The equipment for TLC-FID comprises:
a detection system such as FID
an integrator or other recorder system
accessories for sample application, elution and drying
Chromarods

Chromarods are placed in the rod holder, cleaned and activated in the flame of the detector of the Iatroscan instrument. Then the holder is removed and placed on the spotting guide. A small amount of sample (1-50 µg) in 0,2 to 2 µl of solution is applied to the start using a micropipette. The thin layers are eluted in the development tank, lined with a wick of chromatographic paper. Then the rods are dried for few minutes in a drying oven at 60 to

120°C, placed in the sliding frame of the Iatroscan Analyser and passed through an FID. The individual separated zones are ionized in the hydrogen flame and the ionization current is amplified and fed into the integrator and recorder.

In our experiments the samples were prepared by solution of 200 mg bitumen in 10 ml tetrahydrofurane or methylene dichloride (fresh distilled or stabilized, [3]). The rods (Chromrods SIII, supplied by SES GesmbH) were cleaned and activated in the FID-flame and stored at 40°C. 1 µl of sample solution (2%) was applied on the Chromarods and dried. The following mobile phases were used for the separation:

n-heptane

toluene: n-heptane (80:20)

methylene dichloride: methanol (95:5)

The solvents were used stepwise to elute first the saturates, then the aromatics and resins. The most polar asphaltenes remain at the original place.

Finally the Chromarods were scanned. The separated zones were ionized in the hydrogen flame and the ionized current fed into the Chemstation.

The chromatogram of the vacuum residue shows a high peak for the aromatics. The air-blown bitumen contains less aromatic compounds and more resins and asphaltenes.

A. Influence of air and light

The resins and asphaltenes of vacuum residues from different crude oils determined by TLC-FID are higher

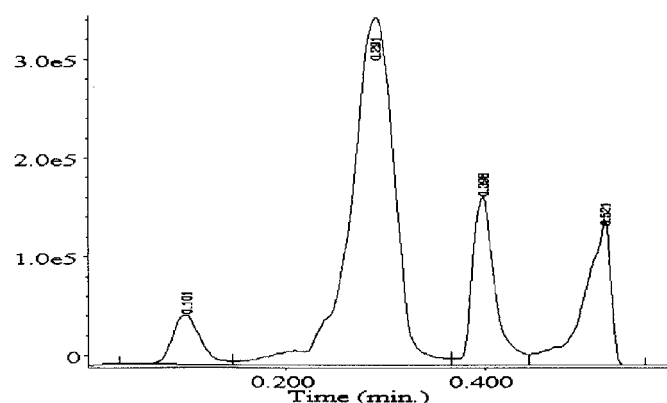


Figure 1. Chromatogram of vacuum residue

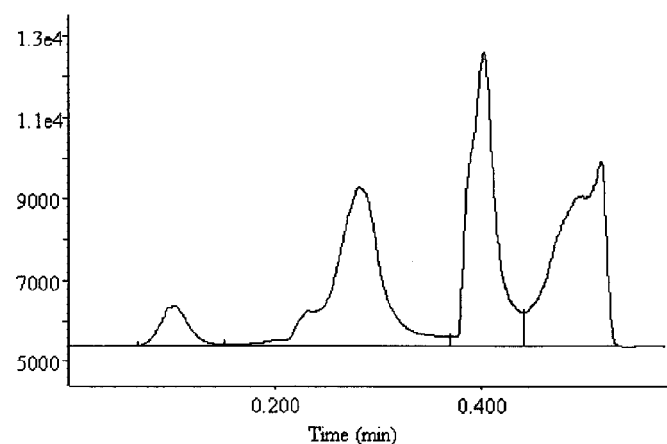


Figure 2. Chromatogram of air-blown bitumen

than the values investigated by column chromatography. Oxidation- and condensation reactions on the surface of the Chromarods are the reason for this phenomenon. To prove this we performed Iatroscan experiments in N₂-atmosphere and without light influence. The Figures 3 and 4 show the results of these attempts.

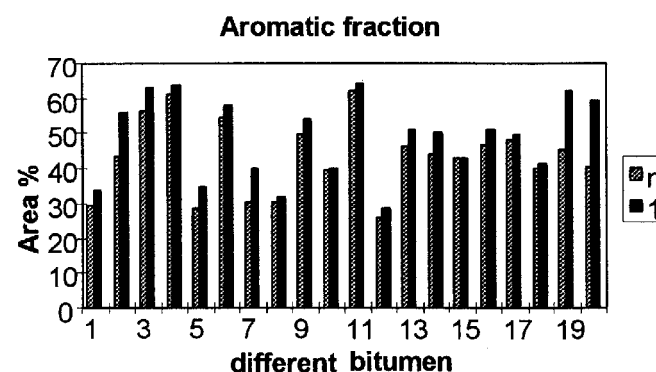


Figure 3. Aromatics, determined in air (n) and nitrogen atmosphere (1)

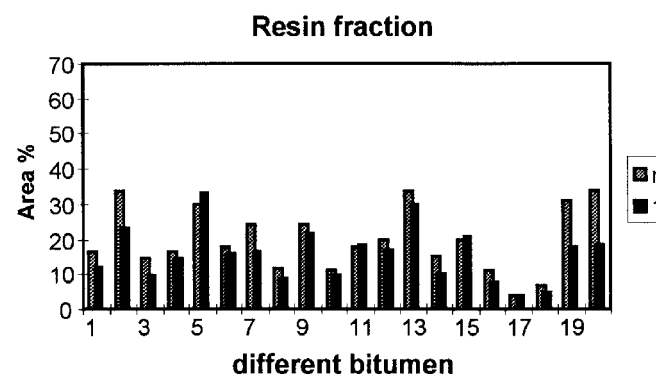


Figure 4. Resins in vacuum residues of different crude oils

The aromatic content determined in a N₂-atmosphere is higher than under conditions with air.

A part of the aromatic compounds is oxidized to resins and asphaltenes during the determination in air. If the TLC-FID is performed in a N₂-atmosphere the resin content becomes lower.

The saturates are not influenced by air and there are no differences between the results with air and nitrogen atmosphere.

On average the aromatic content is reduced by 5% and the resins are increased by 3,9%. The asphaltenes raise by 1,7%. The extent of changes depends on the content of aromatics and resins and can reach in some cases much higher differences.

B. Composition of the TLC-FID fractions

The saturated fraction separated by TLC-FID contains only saturated hydrocarbons. This confirms the good separation between saturated and aromatic compounds. In contrary the saturated fraction determined by column chromatography is not pure and contains aromatic compounds.

The aromatics and resins exhibit a very similar hydrocarbon structure. But they show a different elemental

Table 1. Elemental composition of the fractions

	Saturates	Aromatics	Resins	Asphaltenes
C	86,0	85,0	82,2	83,3
H	13,9	10,4	9,6	7,5
N	<0,1	0,4	1,2	1,4
S	<0,1	4,1	3,7	6,2
O	<0,1	<0,2	2,8	1,5

composition. The resins contain more polar components and have more N- and O- atoms than the aromatics (Table 1).

C. Application of the TLC-FID for characterization of bitumen

The TLC-FID method is a major tool for quantitative analysis of asphalt composition. If suitable solvents are used, the results are quite similar and can be correlated with data of ASTM D 4124.

Another possibility is the estimation of the asphaltenes in vacuum residues. The determination of the asphaltenes in heavy petroleum products is done by the standard method IP 143. This precipitation method takes much longer than the TLC-FID analysis. Using chemometric methods the asphaltenes content can be derived with an reproducibility which is a little bit worse in comparison to the ÖNORM C 9220 or DIN 51595. The correlation between the asphaltenes content determined by ÖNORM C 9220 and asphaltenes of the TLC-FID method is shown in Figure 5.

The Iatroscan-asphaltenes give in the range 0 to 6% n-heptane-unsolubles below 1%. From 6% to 30% the TLC-FID asphaltenes eluted by a mixture of n-heptane:isopropanol correlate well with the asphaltenes from ÖNORM C 9220.

The paraffins of bitumen (DIN 52015) can be estimated with a similar result. The DIN-paraffin content can be calculated from the TLC-saturates by the following formula:

$$\text{DIN-Paraffin(\%M)} = 0,40 \cdot \text{SAT} - 0,44 \quad (1)$$

SAT = saturates determined by TLC-FID with the solvents n-heptane, toluene/heptane=80/20 and methylene dichloride/Methanol=95/5

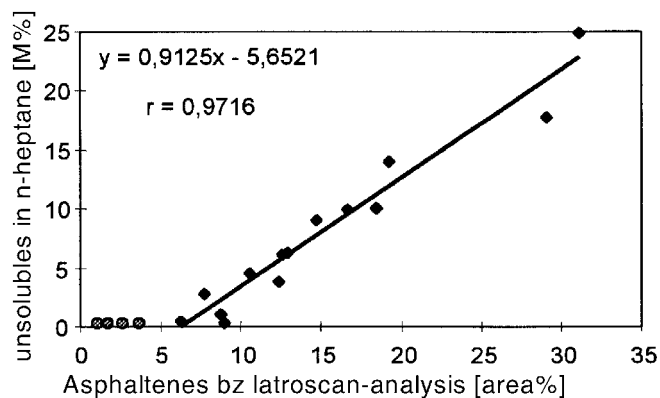


Figure 5. Correlation of the unsolubles in n-heptane with the Iatroscan-asphaltenes (95:5 = n-heptane:isopropanol)

Conclusions

Thin layer chromatography interfaced with flame ionization detector is a fast and effective tool for the determination of the composition of bitumen. The results are comparable with the results from methods which need more time (> 2 days) and material (> 5l).

The TLC-FID method can also be used for the estimation of the asphaltenes content and the DIN paraffines.

References

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