

# A SIMPLE TEST METHOD FOR DETERMINATION OF WAXES IN CRUDE OILS AND BITUMENS

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## ABSTRACT

*Bitumen containing natural waxes and their effect on asphalt performance has been debated for many years. In determination of wax content, two European standard methods, EN 12606-1 (Method by distillation) and 12606-2 (Method by extraction), are currently used. The methods in general are very time-consuming and the waxes measured may differ from those actually present in the bitumen. The objective of this paper is to develop a simple method for determining waxes in bitumens and in crude oils. The method is based on thin layer chromatography with flame ionization detection (TLC-FID). In the test, a small amount of sample solution is spotted on a quartz rod coated with a thin layer of sintered silica. After the separation of saturates with n-heptane at room temperature, the rod is placed upside down in another chamber containing methyl-ethyl ketone (MEK) at a low temperature, typically -20 °C. The second development separates waxes that are insoluble in the cold MEK from other saturated compounds. The waxes are then quantified by FID. The method is verified using various model compounds, as well as commercial waxes. It has been satisfactorily applied to study a variety of crude oils and bitumens. Results showed that the new method for determining waxes is simple and quick, and has reasonable repeatability. A round robin test with three laboratory participants shows that there is a need to improve reproducibility of the test method. In addition, it is presumed that, by changing MEK temperature in the development chamber, waxes may be further characterized by TLC-FID.*

**Keywords:** wax, test method, thin-layer chromatography with flame ionization detection

## 1. INTRODUCTION

Wax in bitumens and in crude oils has been a subject of study for a long time. In crude oils, wax may crystallize upon cooling and precipitate as a solid material, causing problems in pipelines, and in production and processing equipments. In bitumen, the presence of natural wax was often believed to be detrimental to asphalt performance [1] [2] [3]. A previous study indicated that wax adversely influenced asphalt low temperature properties, but negative effects on wheel tracking resistance and moisture susceptibility were not shown [4]. Normally, wax is classified as paraffinic consisting of n-alkanes or microcrystalline wax containing isoalkanes and cycloalkanes. Paraffin waxes are highly crystalline materials with large crystal structures, whereas microcrystalline waxes are characterized by much finer crystals. In spite of the relatively simple definitions, the chemical compositions of waxes in petroleum materials are very complicated, and it is extremely difficult to make exact identification. Consequently, wax determination is always test-method related. One of the most relevant test methods is differential scanning calorimetry (DSC) which determines the amount of materials crystallized on cooling [5] [6] [7]. DSC measures energy change in the sample under a controlled heating or cooling rate. The content of crystallizing materials can be calculated providing that crystallization enthalpy is known. It is however dependent on molecular weight and structure and is usually not known, instead an average value must be estimated.

There are among others also two European standard methods for determination of wax content in bitumen, namely method by distillation [8] and method by extraction [9]. The first method determines the paraffin wax content of bitumen from a distillate obtained by a specified distillation process. The distillation takes place at very high temperatures (up to over 500°C) at which cracking of molecules may occur [5]. Another method involves three steps: extraction of asphaltenes with petroleum spirit, extraction of most aromatic compounds with oleum, and finally crystallization of wax in ether/ethanol mixture at -20°C. Both the methods are very time-consuming.

This paper presents a simple method for wax determination. It is based on thin-layer chromatography with flame ionization detection (TLC-FID), which is known as Iatroscan technique. The technique has traditionally been used to analyse bitumen generic fractions, i.e. saturates, aromatics, resins, and asphaltenes [10] [11]. The new method for wax determination involves two-step development with two solvents, n-heptane and methyl-ethyl ketone (MEK). The principle of the test method is first to separate saturates from other more polar components based on good solubility of saturates in n-heptane and weak interaction with the adsorbent. Waxes are then separated from the saturate fraction using a poor solvent MEK at such a low temperature that waxes are in solid state. The separated fractions are quantified with FID. By the new method, waxes are defined as the hydrocarbons that are soluble in n-heptane and insoluble in cold MEK. The method is validated by various model compounds and commercial waxes. It has been satisfactorily applied to a variety of samples of crude oils, residues and bitumens.

## 2. MATERIALS

**Model compounds:** A series of *n*-alkanes from *n*-hexadecane (*n*-C16) to *n*-hexatriacontane (*n*-C36) and an isoalkane squalane (C30H62) were selected for method validation. All the model compounds are of synthesis grade, and their melting points range from 18°C for *n*-C16 to 76.5°C for *n*-C36.

**Commercial waxes:** A number of refined waxes were selected. The commercial waxes were branded either as microcrystalline or paraffinic by respective producers. In Table 1, information provided by the producers is shown. Compared with the paraffinic waxes, the microcrystalline samples have higher melting points (MP, ASTM D 127) or congealing points (CP, ASTM D 938), indicating their molecular weight is considerably larger than the paraffinic waxes. The selected samples also included slack wax, a by-product of the de-waxing process of lubricating oil.

Source	Brand name	Type	CP or MP, °C
Sasol Wax	Sasolwax 5805	Paraffin	58–60 (CP)
	Sasolwax 5604	Paraffin	55–57 (CP)
	Sasolwax 5891	Microcrystalline	70–75 (CP)
	Sasolwax 0907	Microcrystalline	83–94 (CP)
Strahl & Pitsch	SP 173P	Paraffin	61 (MP)
	SP 19	Microcrystalline	81 (MP)
	SP 60	Microcrystalline	82 (MP)
Hans-Otto Schumann GmbH & Co	Terhell paraffin JA 201	Slack wax	42.5 (CP)

**Table 1: Characteristics of commercial waxes**

**Crude oils and residues:** Three crude oils of Venezuelan (Boscan) or Russian source and their residue were chosen (Table 2). Residue is obtained as a bottom fraction in a distillation process which separates crude oils into fractions by selective boiling points. It consists of the least volatile components at a specific boiling point (cut point). The cut points used for the three residues were 400°C for Boscan, 555°C for Russian A, and 560°C for Russian B. The yields determined by a simulated distillation using high temperature gas chromatography (HTGC) were estimated to 80% for Boscan crude oil, 22% for Russian A crude oil, and 15% for Russian B crude oil. Compared with the Boscan crude oil, the Russian crude oils are more paraffinic and contain more light fractions. The crude oils and residues were further characterized using a DSC procedure described in [5], and results are shown in Table 2.

DSC parameters	Venezuelan (Boscan)		Russian A		Russian B	
	Crude oil	Residue	Crude oil	Residue	Crude oil	Residue
Crystal. onset, °C	26.1	27.6	22.6	36.8	28.0	48.0
Melting out temp., °C	71.3	55.0	46.5	84.5	44.0	98.3
Wax content, %	4.1	0.4	12.2	2.1	9.4	4.8

**Table 2: DSC analysis of crude oils and corresponding residues**

**Bitumens:** Six samples of different sources and of different wax contents were selected. The bitumens are 70/100 or 160/220 pen grade. Typical parameters of the bitumen samples are shown in Table 3.

Bitumen	Source	Penetration, dmm	Softening point, °C	Vis. 135°C, mm <sup>2</sup> /s	Wax content, %	
					EN 12606-1	DSC
Bit-A	Venezuela	192	37.8	199	0.4	0
Bit-B	Venezuela	214	39.1	283	1.1	2.4
Bit-C	Middle East	205	39.2	225	1.3	4.2
Bit-D	Russia	180	40.1	202	1.5	4.1
Bit-E	Mexico	101	45.1	325	1.2	4.1
Bit-F	Unknown	86	46.4	181	1.7	6.2

**Table 3: Bitumen samples**

### 3. TLC-FID PROCEDURE

The TLC/FID system used was Iatroskan TH-10 TLC/FID analyser MK-4. Quartz rods (Chromarod, 10 in a rod holder) coated with a thin layer of silica were used for fraction separation. FID signals were collected and amplified in an in-house assembled amplifier. Data were analyzed using software Spectrum Viewer Basic 2.6. Peaks in the chromatograms were quantified by the area above a horizontal baseline drawn from one side of the peak to the other side or extrapolated from a distinct baseline in the chromatogram.

The principle of the TLC procedure for wax separation is illustrated in Figure 1. First, a sample solution (1% w/v) is prepared with chloroform and 1  $\mu$ L of this solution is spotted near the bottom of a rod. After evaporation of chloroform at ambient condition, the rod in a frame is placed in a lined development chamber containing *n*-heptane and only the very bottom of the rod is in contact with the solvent (solvent should not contact the sample spot). The rod is then developed for 35 minutes when *n*-heptane slowly rises up on the rod by capillary action. Due to good solubility in *n*-heptane and weak interaction with the adsorbent (silica), saturates are carried farther up, thus separated from other more polar components, which mainly stays at the application point.

After drying, the rod is turned upside down and hung inside the second development chamber containing MEK. This development tank is kept in a freezer or climatic chamber at a low temperature, for example -20°C. During temperature equilibrium, the rod is not in contact with MEK. After ten minutes, the rod (still upside down) is lowered into contact with solvent MEK and elution is proceeded for 25 minutes. During this step, some saturates move with MEK front, while solid waxes stay and are separated because of low solubility in MEK.

After the development in MEK, the rod, still in the frame, is left to dry at ambient condition for 40 minutes prior to FID analysis. The long drying time is necessary because water can condensate on the rod when it is transferred from the freezer into the ambient temperature. To remove traces of water, the rod is finally dried for about 2 minutes in an oven at 80°C.

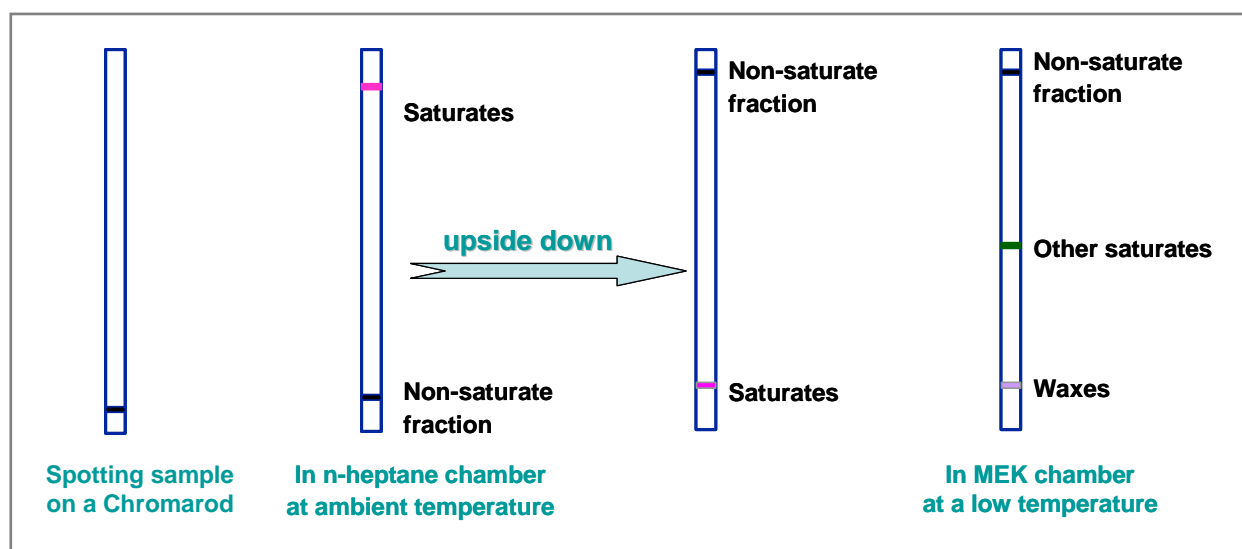


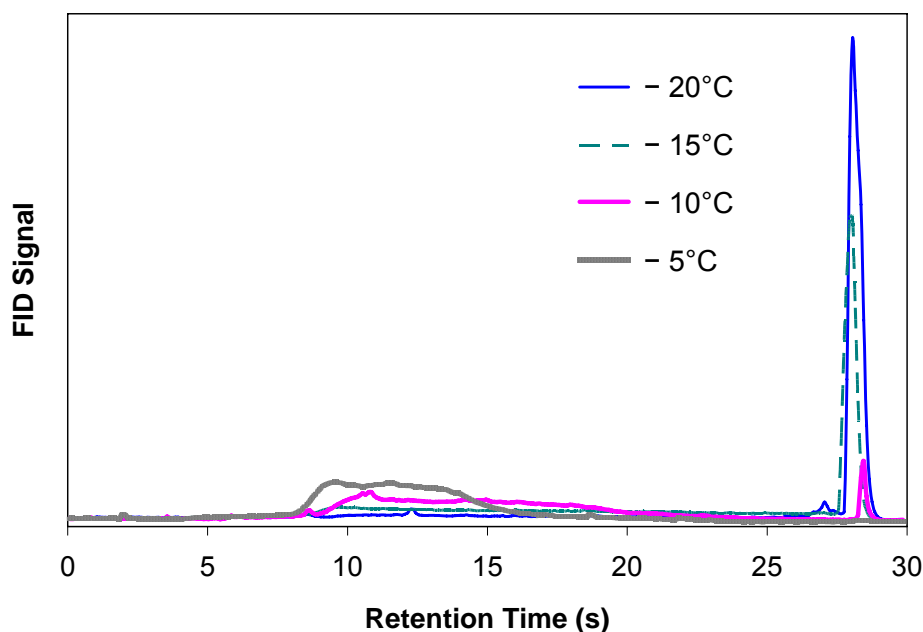
Figure 1: Principle of wax separation by thin-layer chromatography (TLC)

## 4. RESULTS AND DISCUSSION

### 4.1 Verification with model compounds

In the first development step with *n*-heptane, it is generally agreed that the saturate fraction moves with the solvent front. In the second step, by selecting a proper low temperature for MEK, it is assumed that solid waxes will stick to the rod while other saturates move with the MEK front. To verify the above hypothesis, we used various model compounds which are typical of materials known to crystallize if present in crude oils and bitumens. Those included a series of *n*-alkanes, such as *n*-hexadecane (*n*-C16), *n*-eicosane (*n*-C20), *n*-tetracosane (*n*-C24), *n*-octacosane (*n*-C28), and *n*-hexatriacontane (*n*-C36). As a reference for a material known not to crystallize, squalane (2,6,10,15,19,23-hexamethyl-tetracosane) was also selected. As expected, in *n*-heptane at ambient temperature, all these compounds moved with the solvent front.

In MEK, experiments were made at temperatures varied in steps of 5°C from -40°C to 20°C. Examples of chromatogram at different temperatures are shown for *n*-C20 in Figure 2. This compound is practically stationary at the spotting site when temperature is -20°C, whereas at -5°C, it forms a large hump after the solvent front. Observations for other *n*-alkanes are summarized in Table 4. For the *n*-alkanes of larger size, the critical MEK temperature for immobilizing *n*-alkane is higher. In case of *n*-C36, such temperatures are higher than 20°C. The dependency of the critical MEK temperature upon *n*-alkanes is further illustrated by an excellent relationship to the melting point of *n*-alkane in Figure 3. The critical MEK temperatures are found to be approximately 58°C lower than the melting points of *n*-alkanes. As for squalane, movement with the MEK front can be seen at temperature as low as -40°C. This substance has the same carbon number as *n*-C30, but its melting point is -38°C, which is 104°C lower than that of *n*-C30. If the correlation shown for *n*-alkanes also is valid for isoalkanes, we may expect a very low MEK temperature (< -95°C) to immobilize squalane on TLC rod.



**Figure 2:** TLC-FID chromatograms showing development of *n*-C20 in MEK at different temperatures

Temperature, °C	Squalane	<i>n</i> -C16	<i>n</i> -C20	<i>n</i> -C24	<i>n</i> -C28	<i>n</i> -C36
-40	Y	N	N			
-35	Y	N*	N			
-30	Y	I	N			
-25		Y/I	N	N		
-20			N	N	N	
-15			I	N	N	
-10			I	N	N	
-5			Y	N	N	
0				N	N	N
5				Y/I	N	N
10				Y	N	N
15				Y	N*	N
20				Y	I	N

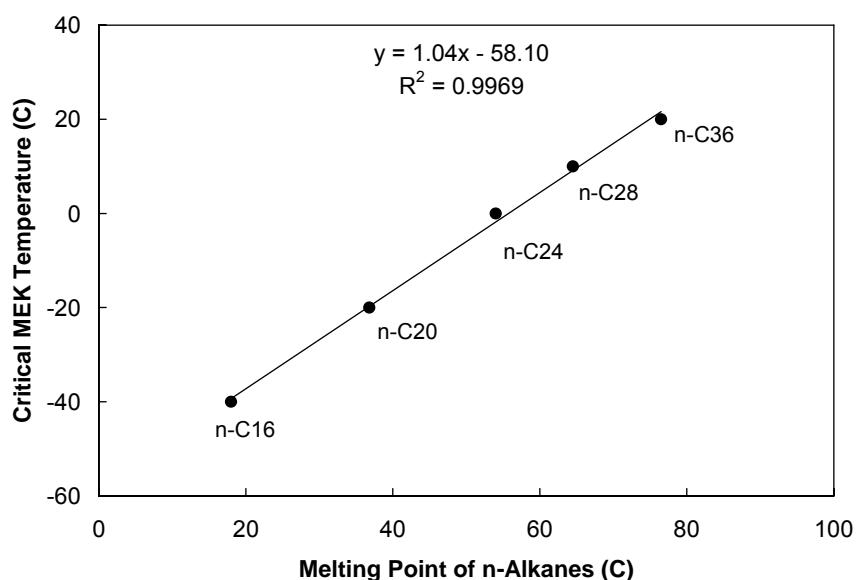
*N*- Stationary at the spotting site;

*N\**- Stationary but with obvious leakage;

*Y*- Movement with the solvent front;

*I* – Intermediate between *Y* and *N*.

**Table 4:** Behaviour of model compounds during development in MEK at different temperatures



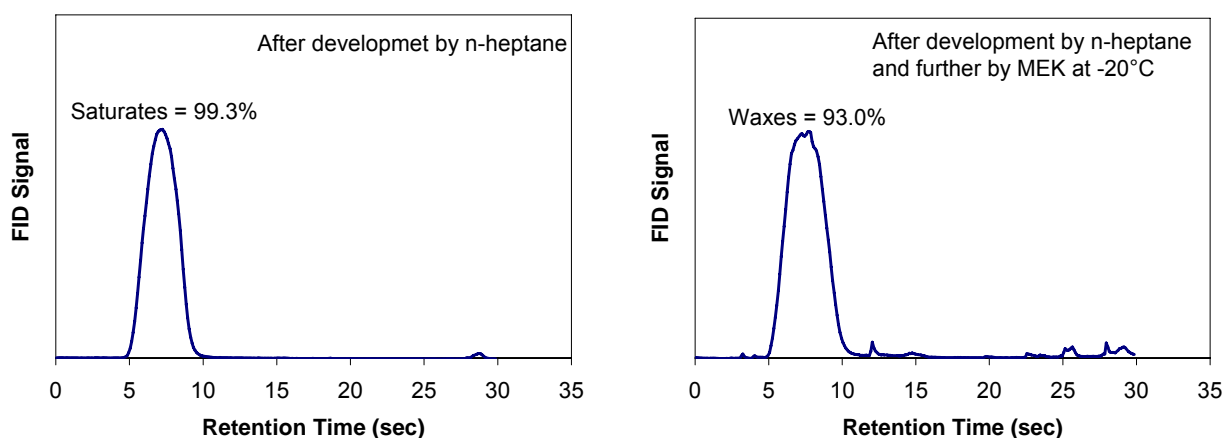
**Figure 3:** The critical MEK temperature as function of the melting point of *n*-alkanes

These results suggest that components of the wax as determined by the proposed method will depend on MEK temperature. If a temperature of  $-20^{\circ}\text{C}$  is selected, *n*-alkanes with less than 20 carbon atoms will probably not be captured as wax. There is also an upper limit for detecting heavy *n*-alkanes since those substances will not move as saturates but rather stay at the spotting site due to limited solubility in *n*-heptane. Experiments with *n*-C40 indicated that the limit is around this size of *n*-alkane. Thus, by the TLC-FID method and at MEK temperature of  $-20^{\circ}\text{C}$ , *n*-alkanes from C20 to C40 will be identified as waxes.

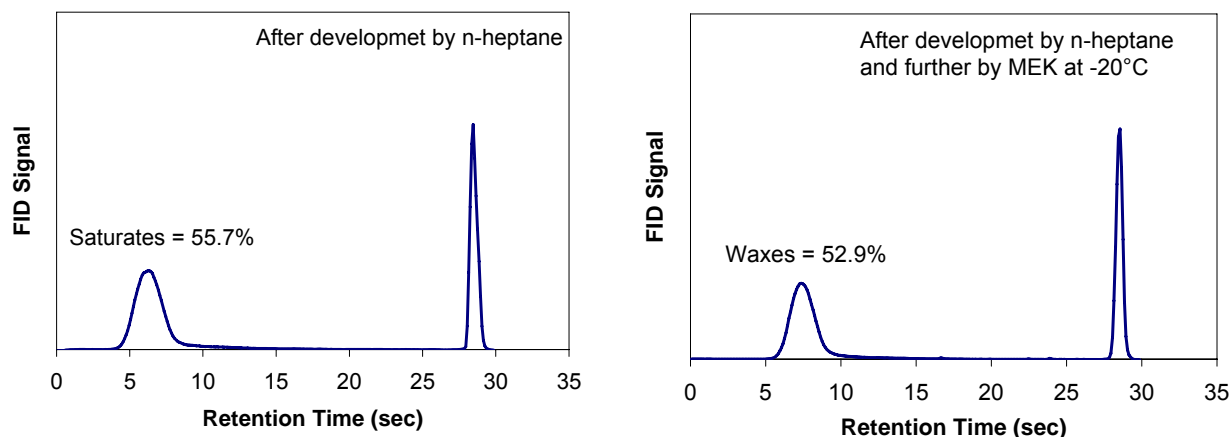
#### 4.2 Verification with commercial waxes

In order to further validate the TLC-FID method, eight commercial waxes were studied (Table 1). Three of the waxes are of paraffinic type and four branded as microcrystalline by the producers. The last wax studied was a slack wax, which is a mixture of oil and wax and is obtained as a by-product from the de-waxing process of lubricating oil.

Gas chromatography – mass spectroscopy (GC-MS) showed that the wax samples contain very small amount ( $< 0.2\%$ ) of *n*-alkanes smaller than C20. According to the observations made on model compounds, MEK temperature of  $-20^{\circ}\text{C}$  is selected for testing of the commercial waxes. Examples of TLC-FID chromatograms are shown in Figures 4 and 5 for a paraffin wax sample (Sasolwax 5805) and a microcrystalline wax sample (Sasolwax 0907), respectively. Test results, together with GC-MS data, are summarized in Table 5.



**Figure 4:** TLC-FID chromatograms of a paraffin wax (Sasolwax 5805) after the first (left) and the second step development (right)



**Figure 5:** TLC-FID chromatograms of a microcrystalline wax (Sasolwax 0907) after the first (left) and the second step development (right)

Wax samples	TLC-FID		<i>n</i> -alkanes (%) by GC-MS		
	saturates, %	waxes, %	< C <sub>20</sub>	C <sub>20</sub> – C <sub>40</sub>	> C <sub>40</sub>
Sasolwax 5805	99.4	93.6	0.1	84.8	1.1
Sasolwax 5604	98.0	97.6	0.1	91.3	0.6
Sasolwax 5891	62.6	64.0	0.0	14.1	1.9
Sasolwax 0907	52.9	53.3	0.1	26.1	5.8
SP 173P	98.4	98.3	0.0	89.0	0.0
SP 19	68.7	68.1	0.2	59.9	19.9
SP 60	59.5	49.4	0.0	9.9	2.1
JA 201	96.8	35.8	0.0	48.0	0.0

**Table 5:** Test results of commercial waxes

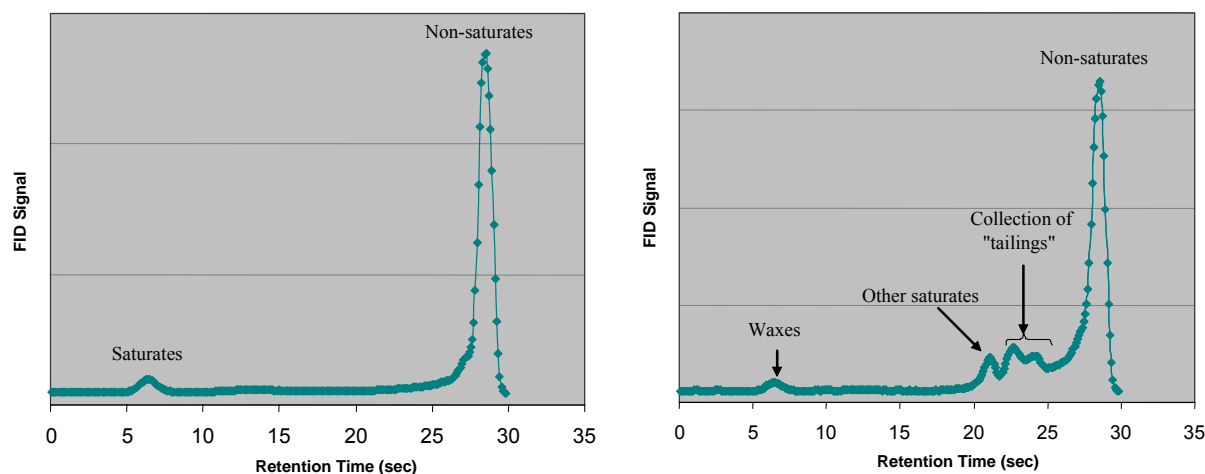
For the paraffin type wax samples (Sasolwax 5805, Sasolwax 5604, and SP 173P), the wax contents measured by the TLC-FID method are very close to the amount of *n*-alkanes estimated by GC-MS. Considering the microcrystalline type wax samples (Sasolwax 5891, Sasolwax 0907, and SP 60, except for SP 19), the wax contents are considerably higher than the amount of *n*-alkanes. This implies that other substances contribute to the wax fraction. Microcrystalline waxes are known to consist of saturated aliphatic hydrocarbons, particularly isoalkanes and cycloalkanes. Usually the melting point is lower for isoalkanes and cycloalkanes compared to *n*-alkanes of the same molecular weight. In this case, the microcrystalline waxes have higher melting points (Table 1), indicating considerably higher molecular weight. This is confirmed by the observation that a substantial fraction of the microcrystalline waxes are not soluble in *n*-heptane at room temperature and is thus retained at the spotting point on the rod. On the other hand, the fraction developed as saturates will solidify on cooling and be retained almost completely during the development with MEK and consequently identified as wax. We believe that the microcrystalline waxes produced from residues are more similar to the waxes in bitumen than paraffinic waxes. High amount of *non n*-alkanes in bitumen waxes has been shown in a previous study [5].

There is an exception observed for SP 19, which was also branded as the microcrystalline type. Unlike other microcrystalline waxes, the detected wax content (68.1%) in SP 19 is lower than the total amount of *n*-alkanes. SP 19 contains unusually high total amount of *n*-alkanes (80% as measured by GC-MS) for being a microcrystalline wax. Careful examination of GC-MS showed that it contains about 20% *n*-alkanes larger than C<sub>40</sub>, which are not identified as waxes by the TLC-FID method (Cf. Section 3.1). In the other samples, the amounts of *n*-alkanes larger than C<sub>40</sub> are found to be significantly low.

From above investigations on the microcrystalline waxes, it is concluded that the TLC-FID method also determines some isoalkanes and cycloalkanes of high molecular weight as waxes.

### 4.3 Analysis of crude oils, residues and bitumens

The TLC-FID method is used to determine wax contents in various crude oils, residues, and bitumens. The samples were selected to vary largely in wax content as shown in Tables 2 and 3. Examples of TLC-FID chromatograms of a waxy residue (Russian A) are shown in Figure 6. As expected, after the first step development in *n*-heptane at ambient condition, two fractions are obtained: one for saturates and another for non-saturated and large size saturate components. The tailing part between the two peaks indicates that some materials are partly soluble in *n*-heptane and thus move slowly with the solvent. When the rod is turned upside down for the second development in MEK at  $-20^{\circ}\text{C}$ , saturates are separated into waxes which are not eluted by MEK, and other substances (likely smaller isoalkanes and cycloalkanes) that move with the solvent. There are also peaks resulted from collection of the tailing part in the first step development.



**Figure 6:** TLC-FID Chromatograms of the Russian A residue after the first step development by *n*-heptane (left), and the second step development by MEK at  $-20^{\circ}\text{C}$  (right)

As already demonstrated with model substances, the temperature during the second development in MEK determines the size of the *n*-alkanes that crystallize. The *n*-alkanes of lower molecular weight crystallize at lower MEK temperature. At the same time, observations on the microcrystalline waxes samples show that, at sufficiently low temperature also *non n*-alkanes of high melting point may be solidified on the TLC rod and consequently determined as wax by the present method. In crude oils and residues, the temperature effect is reflected by a general increase in wax contents with decreasing MEK temperature (Figure 7). In some samples, discrepancy is observed at 0 and  $-10^{\circ}\text{C}$ , which is mainly attributed to low precision of the test method for determining low wax contents.

It is known that the residues selected in this study are obtained as bottom fraction in the distillation process. At the cut points, volatile components including majority of *n*-alkanes between C20 and C40 have been distilled. This is illustrated by a simulated distillation using HTGC in Figure 8. For this reason, one might expect lower wax contents in residues than in crude oils. Table 6 indicates that, for the Russian samples, wax contents of the residues are slightly lower than or equal to the wax contents found in the crude oils. This is surprising, since the major *n*-alkanes smaller than C40 are expected to be distilled at the indicated cut point. It seems reasonable to assume that the major part of the wax in the residue consist of isoalkanes and cycloalkanes. If portions of the residues in the crude oils are considered, it is possible to estimate amount of *n*-alkanes in the crude oils. For example, for the Russian A, the residue is about 22% of the crude oil at the cut point ( $555^{\circ}\text{C}$ ). At a MEK temperature of  $-20^{\circ}\text{C}$ , wax contents of the crude oil and residue are determined to be 1.9% and 2.0%, respectively. A back calculation suggests that 23% of the waxes in the crude oil are retained in the residue while the major part of the waxes (77%) has gone as distillates. Thus a rough estimation for the Russian A crude is that 23% of the waxes are high molecular weight isoalkanes or cycloalkanes and 77% are *n*-alkanes between C20 to C40. For the Boscan samples, wax contents both in the crude oil and residue are relatively low. In this case, the major part of the *n*-alkanes between C20 and C40 will be retained in the residue due to the low cut point ( $< 400^{\circ}\text{C}$ ).

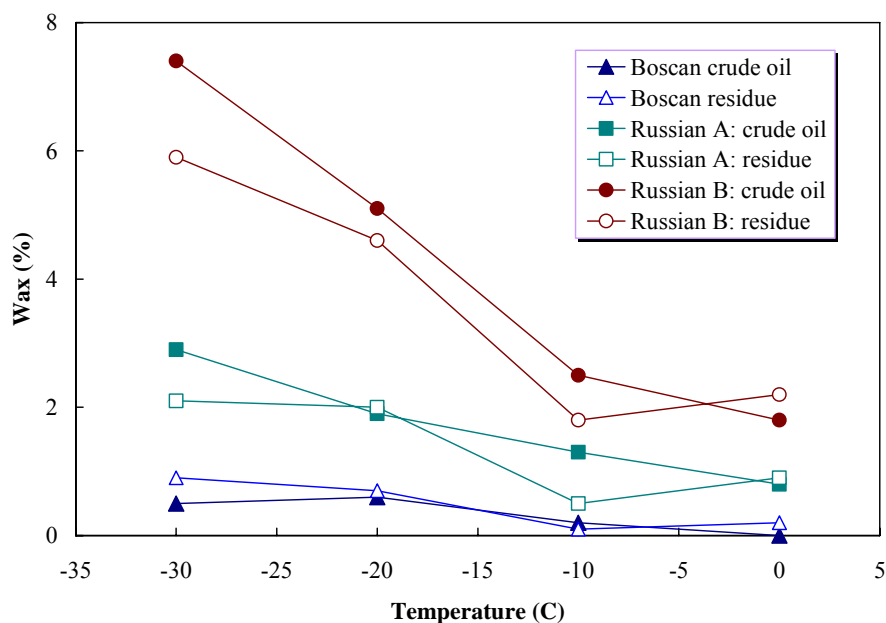


Figure 7: Effect of MEK temperature on determination of wax content

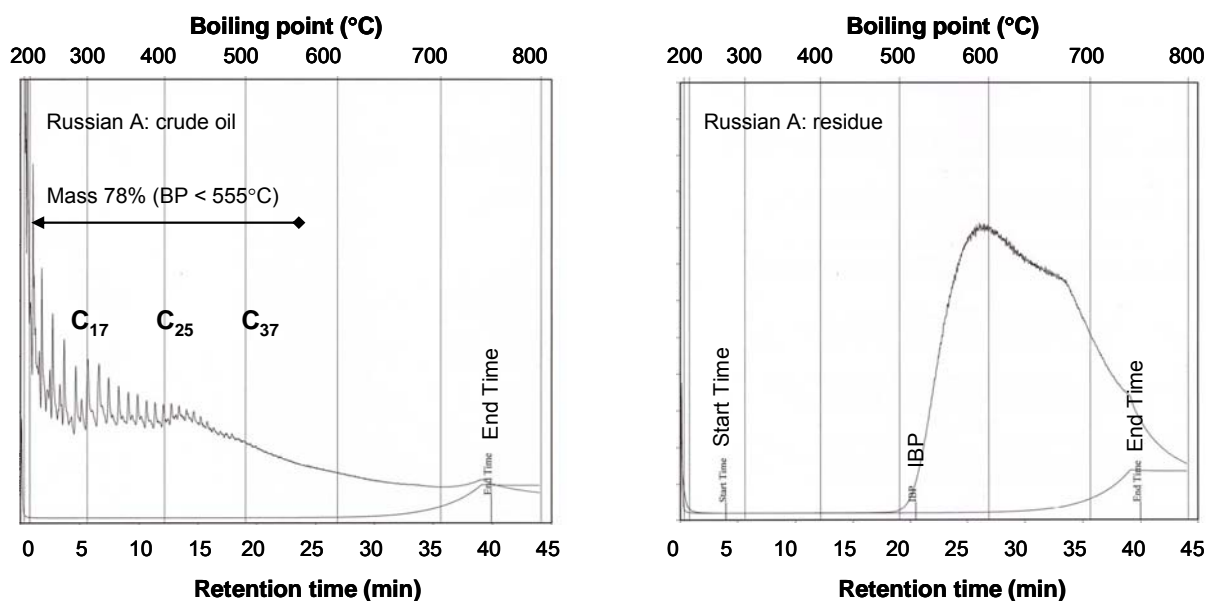


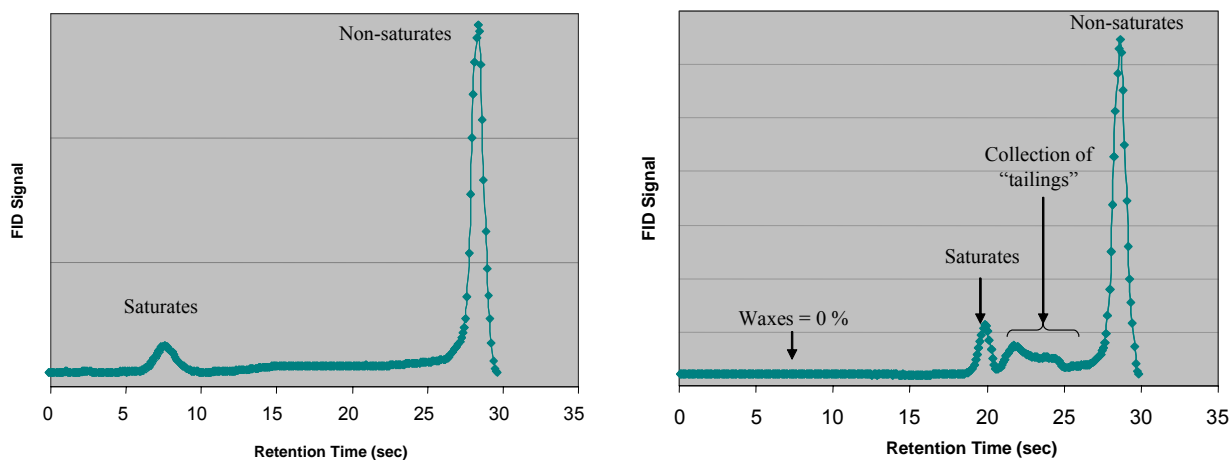
Figure 8: Examples of HTGC chromatograms for a crude oil and residue (A series of peaks reveal a characteristic pattern for n-alkanes, e.g. C<sub>17</sub>, C<sub>25</sub>, and C<sub>37</sub>)

The new method is finally applied to different bitumens with known wax contents (Table 3). Of the selected samples, Bit-A is considered as “wax-free” bitumen in spite of the wax content determined by EN 12606-1. In this sense “wax-free” refers to the lack of crystallizing materials during a cooling cycle in DSC. Figure 9 shows the TLC-FID chromatograms for Bit-A after the first and the second development. As illustrated, the non-waxy bitumen displays a distinct peak for saturates after the first step development in *n*-heptane. In the second development at -20°C, all saturates move with the solvent MEK, and no waxes are detected.

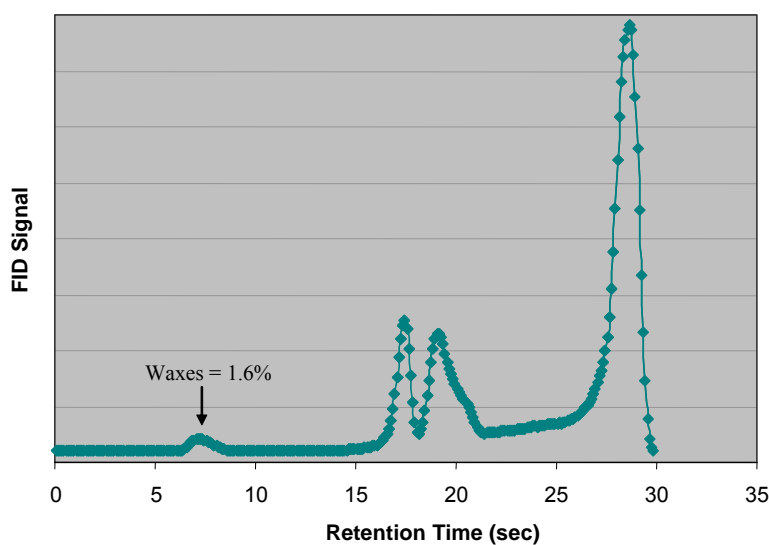
A further confirmation was made by adding a known amount of *n*-alkane to the non-waxy bitumen (Bit-A) and then determining wax content in the mixed sample. In Figure 10, TLC-FID chromatogram is shown for the non-waxy bitumen added with 3% *n*-octacosane. As indicated, 1.6% *n*-octacosane is detected as wax, which is slightly over 50%



of the added concentration. The reason for the low yield is not known, but we might speculate that *n*-octacosane is partly soluble in the saturate fraction moving with MEK.

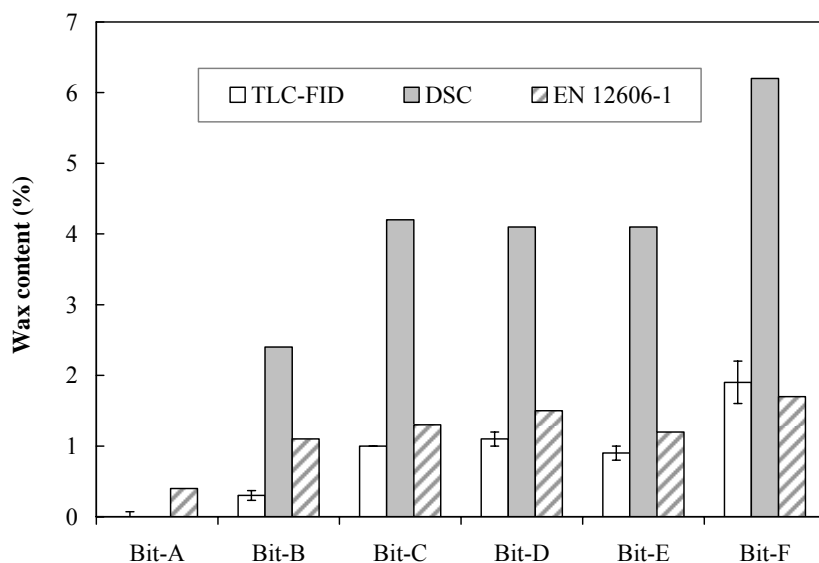


**Figure 9:** TLC-FID Chromatograms of Bit-A after the first step development by *n*-heptane (left), and the second step development by MEK at -20°C (right)



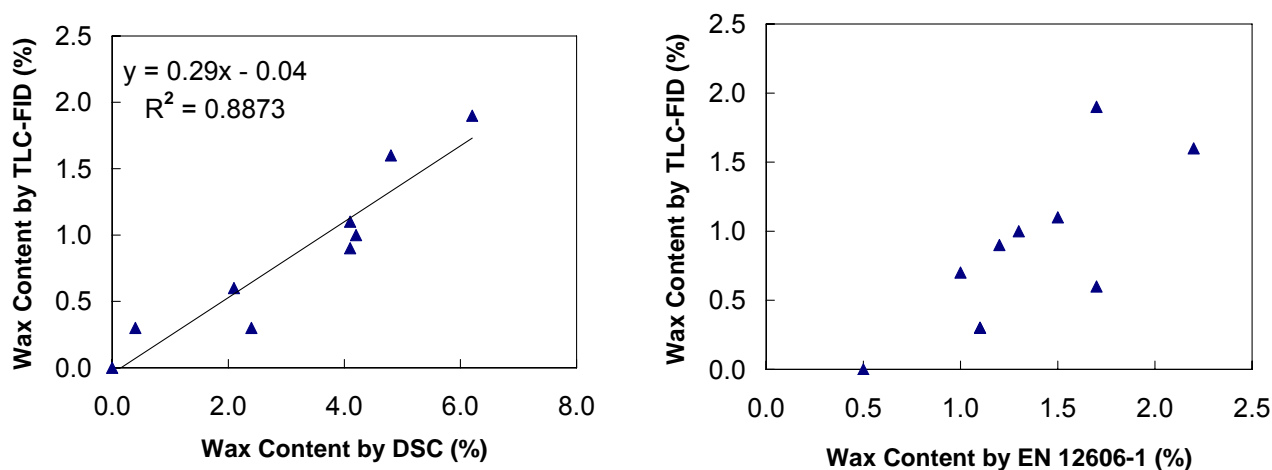
**Figure 10:** TLC-FID chromatogram for the now-waxy bitumen (Bit A) added with 3% *n*-octacosane after the first step development in *n*-heptane and the second step development in MEK at -20°C

Figure 11 shows the TLC-FID results for all the bitumen samples, together with the results obtained by DSC and CEN methods. Again the new method shows reasonable repeatability. It is also worth mentioning that the whole procedure of sample preparation, wax separation and FID detection takes less than 3 hours, and in each test run at least two samples (five rods for each sample) can be analyzed. This implies that the test method is much quicker compared to the current CEN standard method, which likely does not determine microcrystalline waxes.



**Figure 11:** Wax contents of bitumens determined by the TLC-FID, DSC and CEN methods

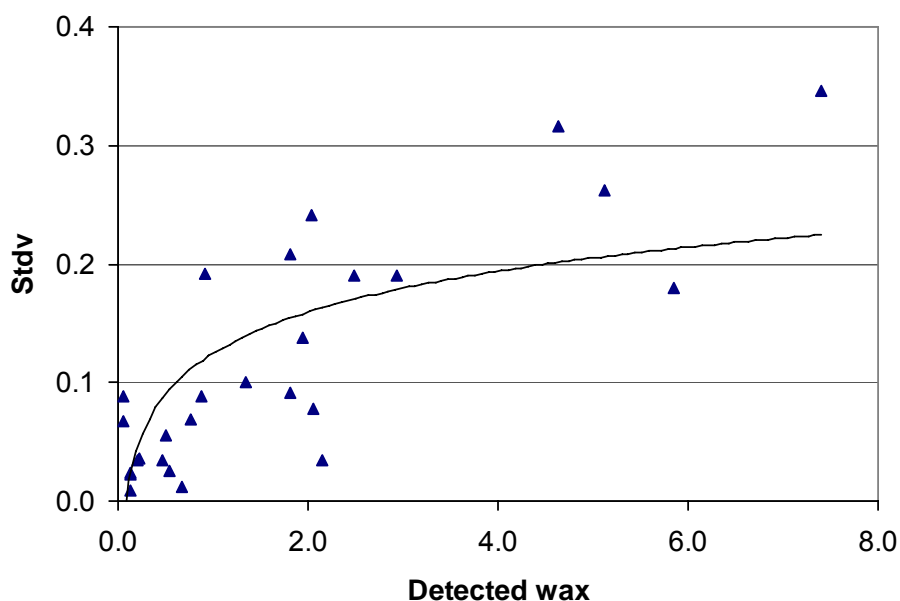
As already discussed, both the TLC-FID method and DSC determine the crystallized waxes in bitumens. Therefore correlation between the two methods would be expected. This has been confirmed by a high correlation coefficient between the two methods (Figure 12). In Figure 12, results obtained for three residues are included, and comparison is also made to the CEN standard method. It is found that correlation between the results of TLC-FID and EN 12606-1 is weak ( $R^2 = 0.63$ ). In fact, we should not expect correlation between TLC-FID and EN 12606-1, because EN 12606-1 is a destructive method that may artificially create small n-alkanes; at the same time it likely does not determine microcrystalline waxes. We believe that the new method is more relevant than EN 12606-1 in determination of the waxes which really exist and crystallize in crude oils and bitumens.



**Figure 12:** Comparison of TLC-FID, DSC and EN 12606-1 for determination of wax contents in bitumen and residue samples

#### 4.4 Repeatability and reproducibility

Repeatability of the TLC-FID method was extensively examined. In Figure 13, standard deviation as function of measured wax content is shown. In this figure, results of different runs by re-preparation of sample solutions for Russian crude oils and Bitumen F are also included. Relative standard deviations (RSD) of at least three measurements (rods) were found to be about 5% for a sample containing 4% waxes, and RSD did not exceed 15% for a sample containing 0.5% waxes.



**Figure 13: Standard deviation as function of wax contents measured by the TLC-FID method**

To determine reproducibility of the new method, a small round robin test was carried out in three laboratories (VTI, Neste, and Nynas). In Neste and Nynas, Iatroscan MK-6s was used. At VTI, two measurements (M1, M2) at different times were conducted with Iatroscan TH-10 TLC/FID analyser MK-4. The second measurement was made about half year later when FID data acquisition system was modified. The samples selected for the test were bitumen Bit-A, which is a wax-free based on DSC analysis, and the three pairs of crude oil and residue. Results are shown in Table 6. As indicated, the standard deviations between the results of different laboratories are relatively large, thus reproducibility is not satisfactory. Differences among the laboratories may be attributed to variations in data treatment (e.g. definition of base line) and in for example temperature control, sample load and elution time. The time of wax crystallization on TLC rods as well as age of the rods could also influence the results.

Laboratory	Bit-A	Venezuelan (Boscan)		Russian A		Russian B	
		crude oil	residue	crude oil	residue	crude oil	Residue
VTI (M1)	0	0.6	0.7	1.9	2.0	5.1	4.6
Nynas	0	0.6	0.8	1.5	1.1	3.2	4.1
Neste	0	0.4	0.2	1.1	0.8	2.8	1.5
VTI (M2)	0	0.3	0.3	1.9	0.6	4.6	1.6
Average	0	0.4	0.4	1.5	0.8	3.5	2.4
Stdv	0	0.2	0.3	0.4	0.3	0.9	1.5

**Table 6: Wax contents (%) determined by different laboratories**

## 5. CONCLUSIONS

- A new method based on TLC-FID is developed to determine wax content. It has been verified by various model compounds, including *n*-alkanes, isoalkane, as well as different types of commercial wax.
- The TLC-FID method detects waxes mainly composed of *n*-alkanes ranging from C20 to C40, and large isoalkanes and cycloalkanes of high melting point if those compounds are soluble in *n*-heptane.
- The new method is applicable to a variety of samples, such as crude oils, residues and bitumens. It is simple and quick, and has reasonable repeatability.
- Good correlation exists between wax contents determined by the TLC-FID and DSC methods.
- There is a need to improve reproducibility of the test method.

- It is presumed that, by changing MEK temperature in the development chamber, waxes may be further characterized by TLC-FID.

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## REFERENCES

- [1] Richter, F. "Effect of waxes on bitumen quality." *Oil Gas European Magazine*, No. 2, 2002, pp. 35-38.
- [2] Such, C., Planque, L., Lombardi, B., Planche, J.P., Gillet, J.P. "Seive A., Les paraffines dans les bitumes." *Proceedings of 2<sup>nd</sup> Eurasphalt & Eurobitume Congress, Barcelona, Sept. 20-22, 2000, Book 1*, pp. 846-854.
- [3] McKay, J.F., Branthaver, J.F., Robertson, R.E. "Isolation of waxes from asphalts and influence of waxes on asphalt rheological properties." *Preprints, Division of Petroleum Chemistry, ACS 210<sup>th</sup> National Meeting, Chicago, IL, August 20-25, 1995*, pp. 794-798.
- [4] Lu, X, Redelius, P. "Effect of bitumen wax on asphalt mixture performance." *Construction and Building Materials*, Vol. 21, 2007, pp. 1961-1970.
- [5] Lu, X, Redelius, P. "Compositional and structural characterization of waxes isolated from bitumens." *Energy Fuels*, Vol. 20, 2006, pp. 653-660.
- [6] Planche, J.P., Claudy, P.M., Letoffe, J.M., Martin, D. "Using thermal analysis methods to better understand asphalt rheology." *Thermochimica Acta*, No. 324, 1998, pp. 223-227.
- [7] Michon, L.C., Netzel, D.A., Turner, T.F., Martin, D., Planche, J.P. "A <sup>13</sup>C NMR and DSC study of the amorphous and crystalline phases in asphalts." *Energy Fuels*, Vol. 13, 1999, pp. 602-610.
- [8] European Standard EN 12606-1. "Bitumen and bituminous binders – determination of the paraffin wax content – part 1: method by distillation".
- [9] European Stand EN 12606-2. "Bitumen and bituminous binders – determination of the paraffin wax content – part 2: method by extraction".
- [10] Hartner, O. "Ermittlung des Gehaltes an Heptan-Unlöslichem und des Paraffinhaltes aus den Ergebnissen der Bitumenanalyse mittels DC-FID." *Bitumen*, No. 4, 1998, pp. 133-136.
- [11] Ecker, A. "The application of Iatroscaan-technique for analysis of bitumen." *Petroleum and Coal*, Vol. 43, 2001, pp. 51-53.