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Original Research Paper

Thin layer chromatography performed in stages to identify the presence of aromatic like fraction in chosen bitumen modifiers

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HIGHLIGHTS

- The analysis of thin layer chromatography of bitumen performed in stages.
- The procedure to distinguish gilsonite in blends with bitumen is suggested.
- The hidden aromaticity of materials such as gilsonite and rejuvenators based on their response to a solvent is demonstrated.

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ABSTRACT

The organic modifiers are used to alter the rheology of the binder in the asphalt concrete at an added cost. For quality control purpose, recognizing if such material is present in the final blend is of an interest. The thin layer chromatography (TLC) using a flame photometric detector (FPD), in addition to the typical flame ionization detector, was demonstrated hereby as a potential analytical tool for this problem, differentiating between tall crude oil based anti-aging agent, polymer, oxidized bitumen and gilsonite. Gilsonite and anti-aging agent consists of the material soluble in solvent used in the development of the fraction referred to as aromatics. Due to the hindered mobility of modifier molecules on the stationary phase, the elution of aromatic fraction stops at position convoluted with polars I and polars II fraction regions, colloquially referred to as resins and asphaltenes. However, for the color of this fraction within gilsonite is different. The presence of gilsonite is thus identifiable visually after the second development bath, but also to an extent with FPD from the final chromatogram. The thin layer chromatography-flame ionization detectors (TLC-FID) procedure is suggested to be supplemented by infrared spectroscopy to discriminate between non-bituminous and bituminous modifiers of similar response during fractionation.

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1. Introduction

The addition of modifiers into the asphalt concrete occurs for multiple reasons and various types of modifiers are used in the asphalt concrete industry (Lu et al., 2008; Nciri et al., 2014; Presti, 2013; Shen et al., 2017; Yao et al., 2013; Zofka et al., 2015). The role of the modifier is to improve the performance of the mixture in some respect, or to provide environmental or economic benefit to the producer. Typically, the goal of modification is to improve the resistance to permanent deformation or fatigue, and that is achievable by alteration of the modulus of asphalt concrete. The stiffness modulus ($|E|$) of asphalt concrete (AC) can be influenced by multiple parameters (Christensen et al., 2003). Yet, for the identical mineral skeleton composition, it is the stiffness modulus of the binder that influences $|E|$ of AC (Pellinen et al., 2007). Hence the modifiers of bitumen, as strongly influencing the performance, are of practical importance.

The organic modifiers of similar solubility parameters to those of bitumen can alter the rheology of the blend compared with the unmodified binder by either decreasing the viscosity in the case of anti-aging agents (Zaumanis et al., 2019), or increasing it in the case of natural asphalts, waxes (Lu et al., 2008), polymers and organic based recycled solids (e.g., recycled asphalt shingles (RAS), crumb rubber) (Presti, 2013; Shen et al., 2017). The aging or oxidation of AC causes increase of the viscosity of the binder, which leads to the increase of the stiffness modulus of AC. Because of that, the different oxidized bituminous modifiers leading to the increase of the binder viscosity had been investigated over the years, e.g., natural asphalts (NA) (Ameri et al., 2011; Jahaniana et al., 2017; Ren et al., 2018; Themeli et al., 2017; Widyatmoko and Elliott, 2008), RAS (Abbas et al., 2013; Cascione et al., 2015), and recycled asphalt pavements (RAP) (Mangiafico et al., 2016). However, among the above mentioned, only the addition of NA is associated with an added production cost.

In case when certain modifiers such as NA mix with the bitumen, the detection of the modifier from the bitumen blend becomes challenging for the quality control and assurance purpose. Considering three blends (Fig. 1) with such modifiers added to straight run bitumen resulting in the equal stiffness of the binder, polymer modification (e.g., through RAS) is identifiable and quantifiable using infrared spectroscopy (FT-IR) (Kosińska et al., 2015; Yut and Zofka, 2011; Zofka et al., 2015), while sadly distinguishing between NA and aged bitumen with that technique presents a challenge. In Fig. 1, recognition of RAS is assumed in the situation when RAS contains polymer modification and is added to fresh unmodified binder. SBS stands for styrene-butadiene-styrene co-polymer, BAA stands for bio-based anti-aging agent, and mineral stands for mineral filler.

Both bitumen extracted from RAP and NA have oxidized species in their structure, therefore in infrared spectroscopy the signal in sulfoxide and carbonyl region is high for both materials (Jemison et al., 1992; Liu et al., 1996; Nciri et al., 2014). Likewise, results of fractionation of both of the materials are likely to result in increased asphaltenes and resins (Nciri et al., 2014; Siddiqui and Ali, 1999). The difference in fractional composition and infrared spectroscopy based indexes will depend on the level of oxidation in RAP or level of modification by NA in the blend.

Moreover, various NA based modifiers are available, such as trinidad lake asphalt (Liao et al., 2014) or Selenizza bitumen (Tartari, 2018). However, specifically gilsonite had been allowed as a modifier of asphalt concrete to improve resistance to permanent deformation in the Finnish Asphalt Specifications (Finnish Pavement Technology Advisory Council, 2017) starting from 1995 onwards (Finnish Pavement Technology Advisory Council, 1995). The design parameters for gilsonite modified materials for pavement structures are included in the Finnish Road Design Guidelines (Tiehallinto, 2004, 2005).

Gilsonite is a trade name for one of the natural asphalts, originally discovered as a vein in the USA (Nciri et al., 2014). Only recently, providers from other countries located in Asia had used the name, and it is worth mentioning that the material tested for hereby work was obtained before 2012 from USA. In the gilsonite modified AC, the ratio of bitumen to gilsonite by weight is approximately 90 : 10, due to the suggested additive content of 0.5 wt.% of the later per asphalt concrete mass. However, as noticed in the previous research it is quite complicated to establish post-mortem–using rheology and infrared spectroscopy – if the modification was in fact used (Makowska et al., 2014), and the problem deepens as the pavement ages.

Luckily, there is a chemical difference between the bitumen and NA, as both the straight run bitumen and the NA

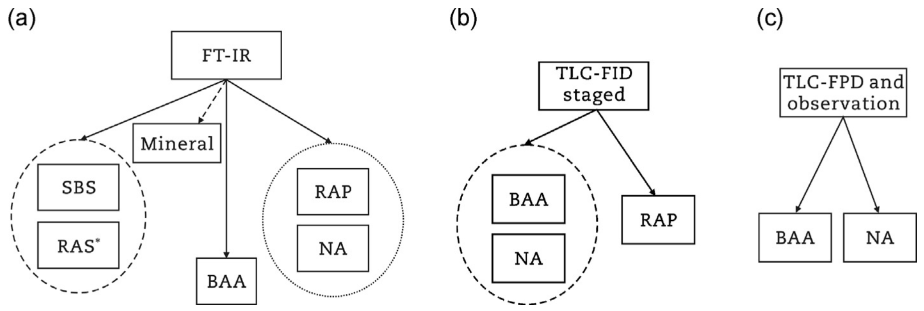

Fig. 1 – The possibilities for the qualitative recognition between modifiers allowed with the use of three blends. (a) FT-IR. (b) TLC-FID performed in stages. (c) TLC-FPD performed in stages and supported with observation.

differ in polarity as witnessed by their Hansen solubility parameters (HSP) (Hansen, 2007), at least as reported for gilsonite. In comparison, for the field aged bitumen samples, the HSP is similar to the fresh bitumen (Makowska and Pellinen, 2015; Redelius, 2000).

On the other hand, the effect of the oxidation of AC affects cracking and fatigue life negatively. The recycling of AC aims at lowering the viscosity of the binder in RAP by mixing with anti-aging agents (Cavalli et al., 2018; Zaumanis et al., 2019). Similar to the case of NA or polymer modifier, the addition of such agents is associated with the additional cost. Both polymer and anti-aging agents can be recognizable in FT-IR, provided there is a distinct marker peak different than those observed in straight run bitumen (Cavalli et al., 2018). On the other hand, those two materials can give similar response in the currently suggested thin layer chromatography-flame ionization detectors (TLC-FID) evaluated separation of bitumen into fractions. The objective of this study, as presented in Fig. 1, is to demonstrate a procedure to distinguish between the materials modified with those modifiers using FT-IR, staged IP469 (Energy Institute, 2006), staged IP469 (Energy Institute, 2006) analyzed with flame ionization detector (FID) as well as with flame photometric detector (FPD) in support to visual observation.

1.1. *Background*

Potentially, TLC could allow differentiation between the NA and RAP and even their blends, as it incorporates both information about solubility and polar interaction with the stationary phase (Spangenberg et al., 2011). At the same time, the signal can be quantified by the use of detectors. Since the separated compounds are organic, the FID is often integrated with the technique. It counts the carbon cations as a result of the change in conductivity of the exhaust gas (Holm, 1999; Lehto, 1988).

The Iatroscan TLC-FID Analyzer™ (Ogasawa et al., 2002) is the equipment suggested to perform the procedure specified in IP469 fractionation procedure (Energy Institute, 2006), and due to the limited number of competitors on the market, it is often the most used during the analysis. The equipment always contains the FID and optionally may contain FPD. The FPD is in essence an FID, extended by a filter for particular wavelength (hereby used filter for wavelength 394 nm) and a photomultiplier tube (Ogasawa et al., 2002) (Fig. 2).

Fig. 2 demonstrated the difference between the chromatograms obtained with both detectors. It can be seen that the FPD signal is typically much lower than FID signal. The distribution of peaks in FPD is also different to those of FID. The aromatic fraction gives the most abundant signal in FPD, which is clearly visible after spectra normalization (Fig. 2(b)). The potential reasons behind it are discussed further on.

Bitumen is a crude oil distillation product of high sulphur content (Lesueur, 2009). It was discussed previously that sulfoxyl group (a visible product of oxidation of sulphur containing compounds in bitumen) leads to the sudden

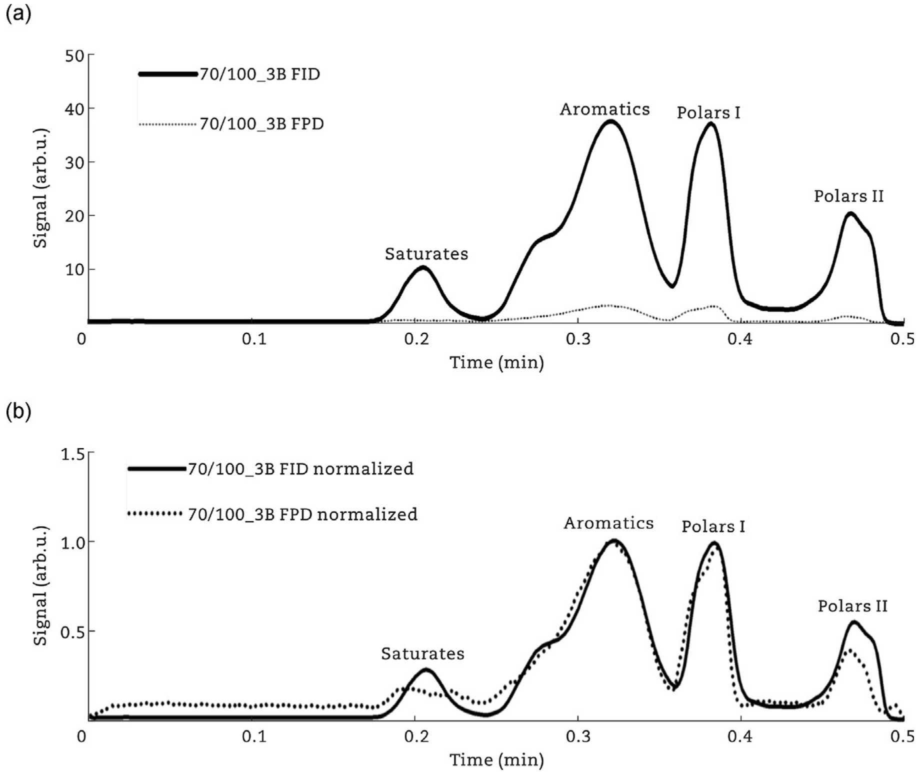

Fig. 2 – Typical densitograms obtained from FID and FPD detectors simultaneously from one rod. (a) Raw form. (b) After normalization.

increase in the viscosity during the short-term aging (Petersen, 2009). The importance of the sulphur compounds in step-wise oxidation during aging was proposed as an important parameter to follow in the bitumen (Makowska et al., 2017b). For that reason, using a combination of FID and FPD detectors would be of interest.

The sulphur content along the aromaticity in bitumen fractions is one of the parameters proposed as a differentiator between maltenes and asphaltenes (McKenna et al., 2013). In the recent studies on composition of bitumen fraction before and after laboratory aging procedures (Handle et al., 2017), it was reported that the sulphur content is the highest in the aromatics fraction, which would stay in line with the FPD signal of straight run bitumen. Ogasawa et al. (2002) suggest that FPD recognized sulphur when a filter for 394 nm wavelength is used (S-FPD). It is worth noting, tough, that not only sulphur containing compounds will absorb light in that region. For example, the anthracene, naphtacene or benzantracene based compounds also absorb certain amount of energy from the light at wavelengths below 400 nm, despite not having sulphur in their structures (Jones, 1943; Shimadzu Corporation, 2018). It is plausible that due to the sample overload on the rod, the aromatic or asphaltene molecule do not burn clean to small molecular cations of aliphatic nature (Holm, 1999). Only the aliphatic cations do not absorb energy within the considered wavelength range (Jones, 1943). In such case, the aromatic compounds could be present in the outflowing gas and contribute to the signal detected by S-FPD.

For the fractionation procedure using TLC, the sample size applied on the rod was optimized originally linking the FID response to column chromatography fractionation results (Lehto, 1988; Ray et al., 1982; Teugels and Zwijsen, 1991), thus the ratio may be inappropriate for the S-FPD. The relationship between mass and signal may be outside of the linear range for S-FPD (Spangenberg et al., 2011).

The bitumen is fractionable with various techniques (ASTM International, 2018; Energy Institute, 2006), which utilize a range of the solubility parameters of subcomponents. Corbett proposed a separation procedure that is the most standard division into saturates, aromatics, resins and asphaltenes (SARA) (Lehto, 1988; Lesueur, 2009). Yet, the used names for the fractions were naphtene aromatics and polar aromatics, as opposed to the colloquially preferred aromatics and resins.

Overtime, the TLC-FID based fractionation technique (Energy Institute, 2006) became dominant due to its simplicity, shortness and low demand for hazardous solvents. However, the fractions of the column chromatography (ASTM International, 2018) (two types of stationary phase) are not exactly the same as those obtained in TLC-FID (one stationary phase). It was advocated that the products of those separations had a different name (Masson et al., 2001). In fact, the IP469 procedure specifically names the fractions: saturates, aromatics, polars I and polars II, after the work which proposed this procedure for the purpose of quality control in the petroleum industry (Ray et al., 1982) (Fig. 2). In that work, the authors referred to the peaks evolved in the third development bath and material remaining at the origin of the rod as resin A and resin B (Ray et al., 1982), noting that asphaltenes separated in IP143 procedure (Energy Institute, 2001), when tested in IP469 procedure, separate into two peaks as well. Additionally, the non-asphaltene fraction separated with IP143 also contributed to all four peaks in IP469 procedure. Recently, Jiang et al. (2008) also showed that analyzing with IP469 procedure, the fraction obtained in column chromatography for some bituminous products can contribute to more than one peak.

Furthermore, comparing the fractionation results from TLC-FID performed in different laboratories is challenging due to the use of the differing solvents and times of elution (often not reported in literature) (Higuerey et al., 2002; Lehto, 1988; Masson et al., 2001; Paliukaite et al., 2014; Tabatabaee and Kurth, 2017; Teugels and Zwijsen, 1991). The time of elution in each bath (development tank) is determined from the time it takes the solvent to reach a certain height specified in IP469. The development time is usually stable within a laboratory to assure the good repeatability and a comparison between samples. Though, it is worth noting that the position of the solvent front is also dependent on the temperature and humidity (Spangenberg et al., 2011), which may fluctuate in the laboratory during the year.

In order to reduce the costs of IP469 associated with the lower lifespan of the rods due to extensive cleaning, asphaltenes may be removed from the analyzed blend using IP143 procedure (Energy Institute, 2001) before performing IP469 procedure on separated maltenes (Tabatabaee and Kurth, 2017). Such procedure is also performed to ensure that the actual asphaltene (n-heptane insoluble matter) content is determined.

Another aspect worth mentioning is connected with the repeatability of the IP469 procedure, which allows large numerical differences between the fractions. Because of that, the procedure is not the best qualitative technique, especially to compare between different laboratories. However, the technique is useful for quality control purposes. Additionally, the bituminous materials from various refineries were distinguishable using the procedure (Paliukaite et al., 2014).

1.2. *Objective*

The hereby research was inspired by an observation of a different elution pattern from samples of bitumen modified with gilsonite in the consecutive development steps of fractioning through TLC technique according to the procedure IP469. Over the course of time, similar differences in the signal were observed during the analysis of other materials, i.e., some polymers and bio-based anti-aging agents.

In the development, in the so-called second bath, by toluene and n-heptane the ratio is 80:20 (vol.%), which for straight run bitumen elutes to the height of about 5 cm from origin, the gilsonite sample was staining the rods only close to the original spot (approximately to the height of 2–3 cm). It also had a different color (yellow for 70/100 and brown-red for GIL, while translucent for bio-based anti-aging agents and polymers). This observation could be helpful during the forensic analysis of the asphalt concrete samples in terms of identification of the possible presence of gilsonite as a modifier (Makowska and Pellinen, 2019).

Thus, this article presents how the incorporation of the S-FPD, the staged analysis of eluted material and visual observation, supports qualitative identification of gilsonite as a modifier in the bituminous blends. It additionally provides information about the fractions of gilsonite, anti-aging agents and polymer, that were currently understood as part of polars I and polars II fractions. Their solubility in the solvent used for the fractionation of aromatic compounds from the bitumen indicates mutual solubility with the aromatic fraction.

Because gilsonite is similar to a heavily aged bitumen, a material extracted and recovered from RAP (penetration 16 dmm) was used as a reference material (Makowska et al., 2017a). Additionally, a rejuvenator based on the tall crude oil was investigated with the same techniques to demonstrate the similarities and differences to gilsonite in response in both infrared spectroscopy and TLC fractionation. The ruberised styrene-butadiene-styrene block co-polymer was used as an example of a viscosity increasing modifier which is transparent to the observer.

The goal was to demonstrate a first step methodology to identify the possible presence of gilsonite in the blend. Because of the low reliability of the techniques discussed, the sample after initial analysis indicating potential presence, should be further studied with the more precise techniques to confirm the composition.

2. Materials and methods

The natural asphalt, namely gilsonite from the year 2012 (coded as GIL in Table 1), and paving grade bitumen 70/100 (coded as 70/100 in Table 1) were used in the analysis. A blend of 70/100 and GIL in proportion of 90:10 by weight (coded as BLEND in Table 1) was prepared as a reference for investigation.

As a material chemically similar to GIL, bitumen extracted with the use of dichloroethylene from RAP material from the field collected samples (coded as RAP in Table 1, as described in Makowska et al. (2017a), site 2, penetration: 16 dmm) were tested. A crude tall oil derived bio-based anti-aging agent (coded as BAA in Table 1) was tested to demonstrate similarities and differences to GIL. Additionally, a blend of RAP and BAA in 90:10 ratio was prepared for analysis as well (coded as RAP_BAA in Table 1).

Table 2 – Differences between IP469 and procedure adopted after work by Lehto (1988).

Parameter	IP469 procedure	Lehto procedure
Dispersive solvent	Toluene	Chloroform
Sample	1 μm of 2 vol.%	2 μm of 1 vol.%
Speed of burning (s/rod)	40	30

In order to demonstrate the response of a polymer in procedure IP469 and the positive S-FPD response of material which does not contain sulphur, a sample of radial styrene-butadiene-styrene co-polymer (coded as rSBS in Table 1) was analyzed.

The list of samples and corresponding tests performed on them is gathered in Table 1.

For the purpose of this analysis, both components in the prepared blends were weighted into the volumetric flask and then dispersed in the chloroform. This was performed to assure that there is no clustering or problems with dispersing the modifier in bitumen. The research was designed to comprise reference to the blends in the field. In samples extracted from asphalt concrete collected from the field, the bitumen and modifier would be dispersed in solvent after extraction step, thus homogeneity of the blend would be achieved due to such processing.

2.1. *Thin layer chromatography*

A solution of approximately 1 vol.% of material in chloroform was prepared, of which 2 μL drop was spotted on each rod, followed by drying in the nitrogen flow for 10 min. One reference rod is kept empty for the purpose of assurance of full solvent evaporation (Makowska and Pellinen, 2019).

Table 1 – Samples tested.

Sample code	Composition	One bath	Two baths	Three baths	FT-IR
70/100	Bitumen, grade 70/100	x	x	x	x
GIL	Gilsonite	x	x	x	x
BLEND	70/100 and GIL (90:10, wt.%)	x	x	x	x
RAP	Bitumen extracted from core (penetration: 16 dmm)	x	x	x	x
BAA	Bio-based anti-aging agent	x	x	x	x
RAP_BAA	RAP and BAA (90:10, wt.%)	x	x	x	x
rSBS	Radial styrene-butadiene-styrene			x	x

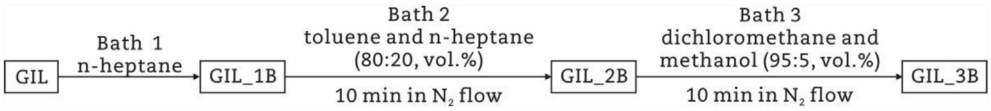

Fig. 3 – Schematic of the staged TLC procedure based on IP469 applied to the sample (using GIL as an example of the analyzed material).

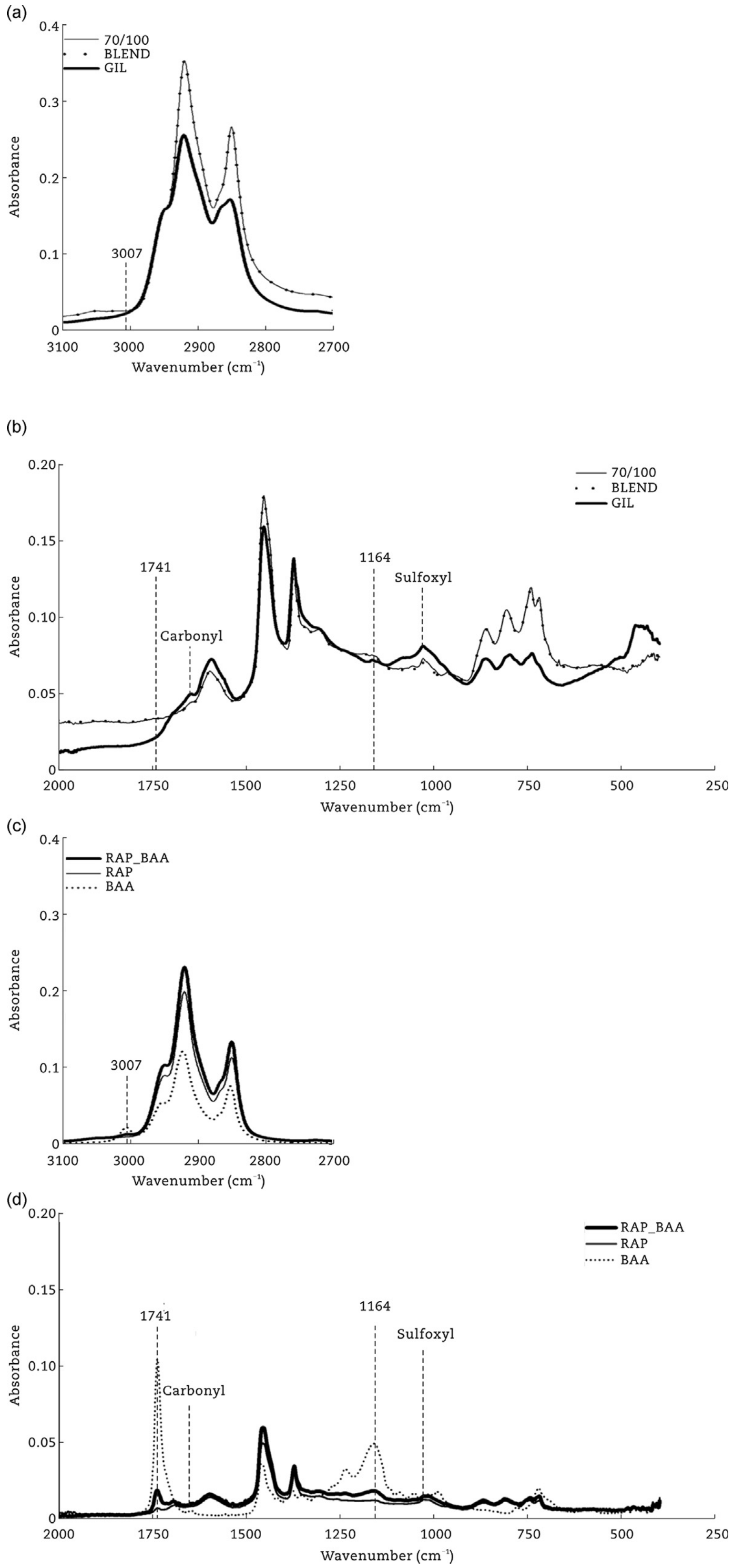

Fig. 4 – The absorbance spectra of each tested material in infrared light range. (a) Zoomed in for shorter wavelengths of BLEND. (b) Zoomed in for longer wavelengths of BLEND. (c) Zoomed in for shorter wavelengths of RAP_BAA. (d) Zoomed in for longer wavelengths of RAP_BAA.

A procedure described previously was applied to samples GIL, 70/100, BLEND, RAP, BAA and RAP_BAA (Makowska and Pellinen, 2019). The rSBS was analyzed only with the standard IP469 procedure (Energy Institute, 2006). Material pyrolyzed from rods (30 s/rod) after elution bath 1, bath 2 or bath 3 was given a suffix _1B, _2B, or _3B, respectively (Fig. 3).

The minimum required repetitions as specified in the IP469 is three rods and this was performed. Unfortunately, one of the pure gilsonite repetitions in 3 baths failed (Makowska and Pellinen, 2018). Iatroskan MK-6/6S Analyzer™ equipped with FID and FPD was used for the collection of the chromatograms.

The precision (Energy Institute, 2016) of the TLC-FID supported fractionation method, based on the ranges allowed for repeatability and reproducibility, is low. In the past, the effort to establish the most optimal and repeatable procedure for separation was attempted (Lehto, 1988) for the Finnish industry and a certain set of parameters was chosen. Recently, a similar effort was attempted, where Simnofske and Mollenhauer (2017) reported that certain parameters are of high significance for repeatability and reproducibility of procedure described in IP469 and they included among others: the age of solution, the type of solvent, the concentration, the spot volume and the scan speed. Because the procedure after Lehto (1988) differs to that of IP469, the difference between parameters is provided in Table 2.

Additionally, the sample dries between the baths in nitrogen flow (non-oxidative ambient) at room temperature for 10 min, rather than in unspecified gas (air, oxidative agent as written in IP469) at high temperatures for 2 min, in order not to

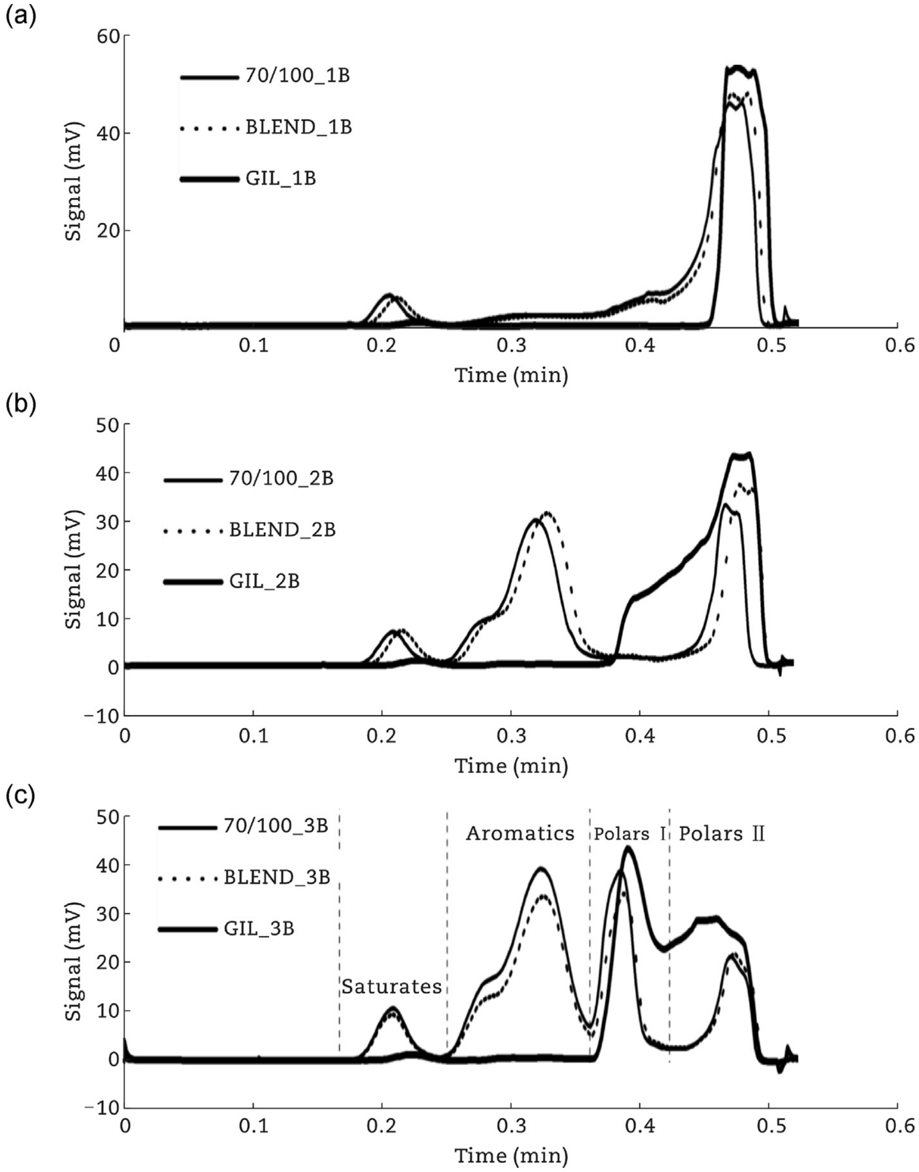

Fig. 5 — The chromatogram of 70/100, GIL and BLEND with visual division of fractions typically derived in the IP469 procedure. (a) After 1 bath. (b) After 2 baths. (c) After 3 baths.

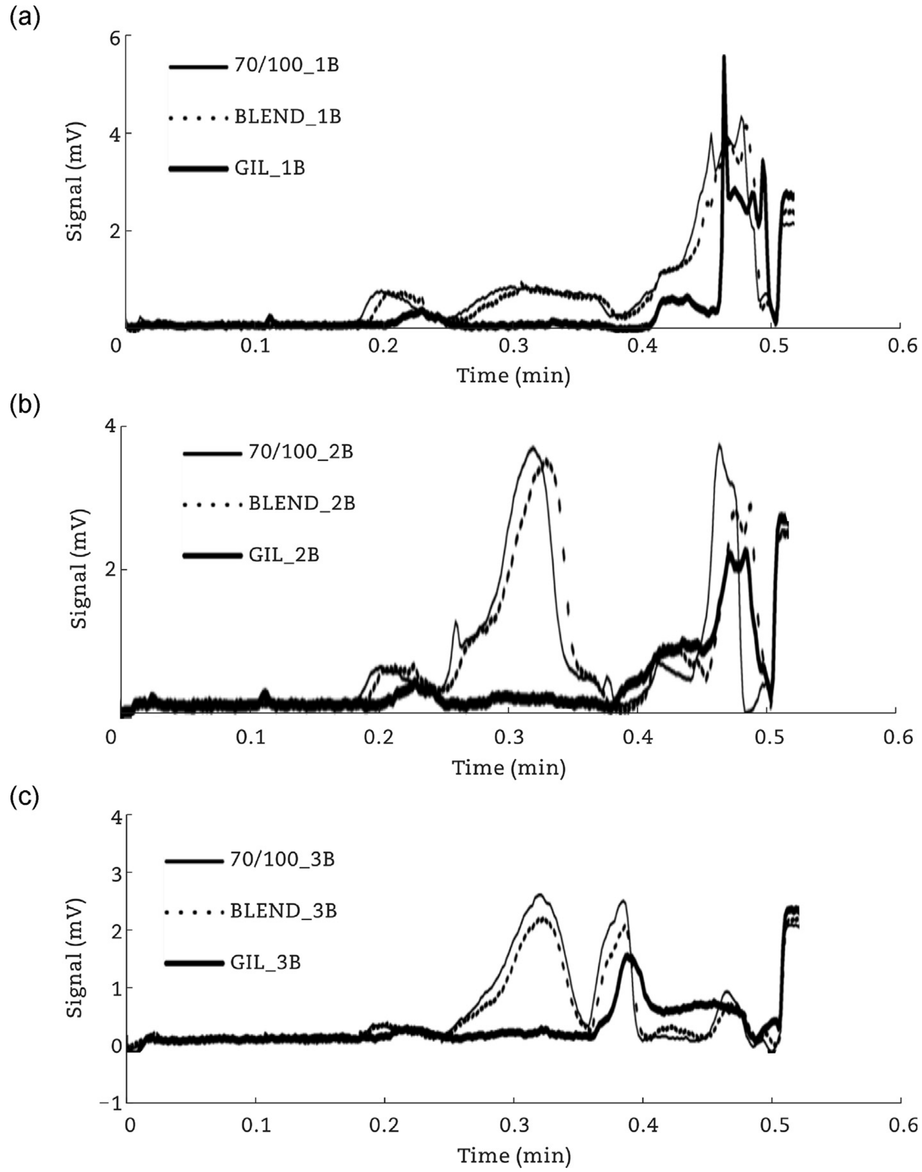

Fig. 6 – The chromatogram from TLC-FPD (sulphur) of bitumen, gilsonite and the blend of the two in the 90:10 ratio after elution. (a) After 1 bath. (b) After 2 baths. (c) After 3 baths.

oxidize the sample in uncontrolled way during the procedure. The prepared solutions are applied onto the rod only within the first day of preparation to prevent oxidation in dispersed state.

2.2. *Fourier transform infrared spectroscopy*

Analysis was supplemented by means of infrared spectroscopy, using Fourier transform infrared spectrometer (model iS50 by Thermo Fischer) with attenuated total reflectance (ATR) mode (Pyke GladiATR, diamond prism). The samples from solutions prepared for procedure IP469 as described above were spotted onto the diamond prism (2 μL), followed by short evaporation of chloroform in the ambient and measured at 4 cm^{-1} resolution (32 scans). The ATR correction comes automatically from the OMINC™ software.

3. Results and discussions

3.1. *Results from experiments*

Using the schema presented in Fig. 1, the first step investigation of the blend should easily provide information which divides the blends into modified by the polymer, flux or oxidized bitumen. Unfortunately, modification by RAS or RAP of the AC which originally was modified with the polymer, deems this division not as straight forward as

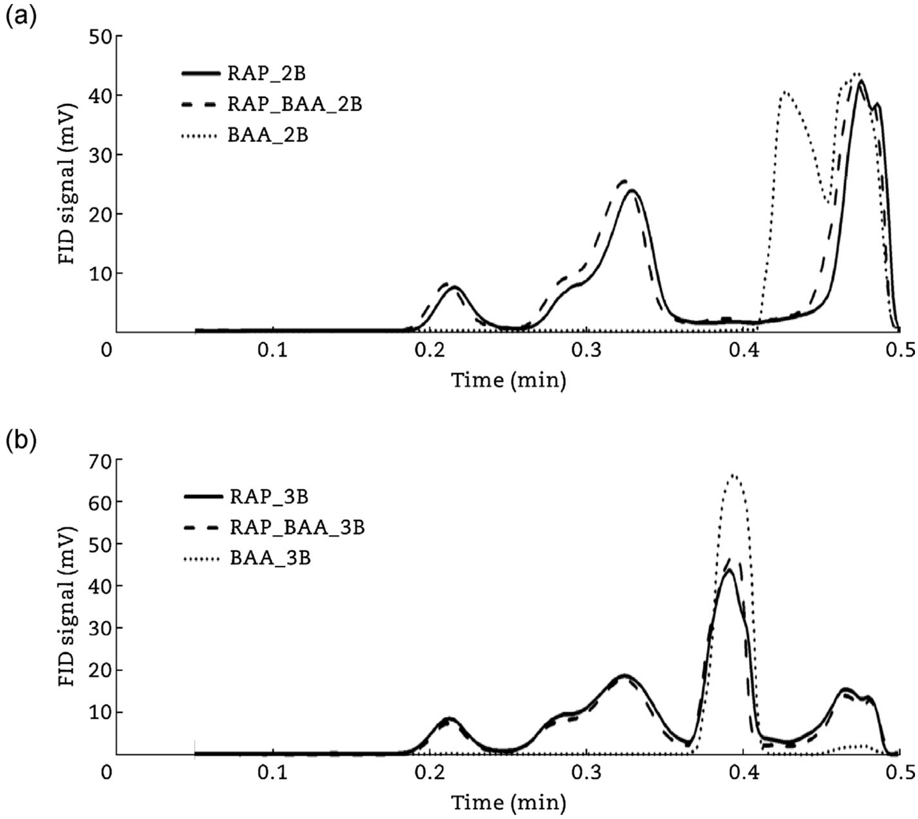

Fig. 7 – The FID chromatograms of RAP, RAP_BAA and BAA. (a) After 2 baths (upper frame). (b) After 3 baths (lower frame).

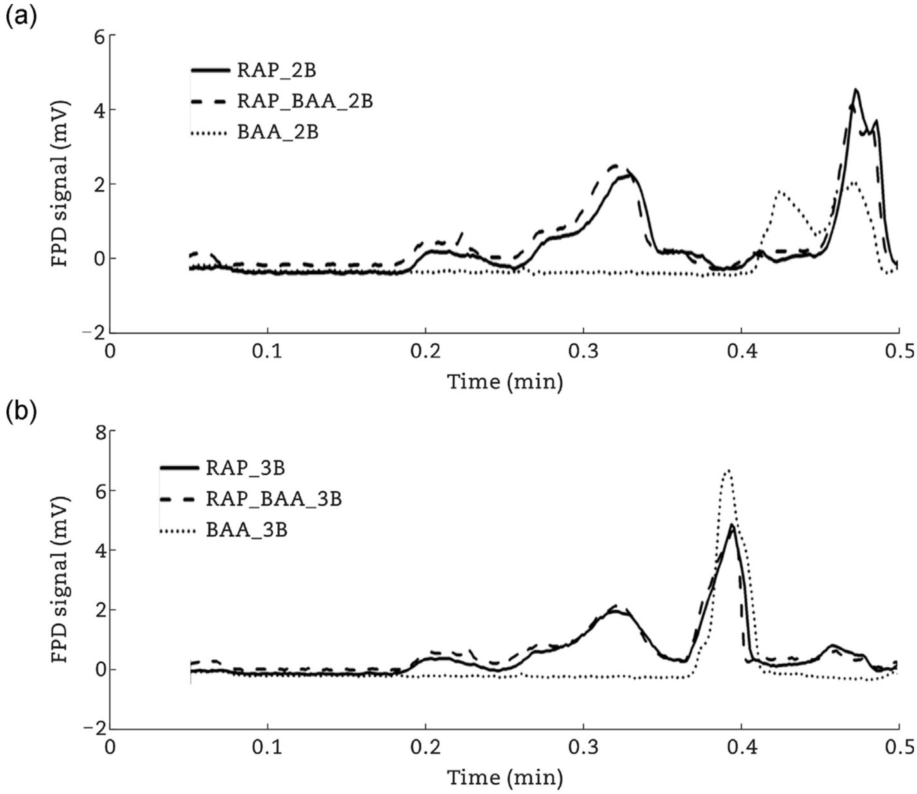

Fig. 8 – The FPD chromatograms of RAP, RAP_BAA and BAA. (a) After 2 baths (upper frame). (b) After 3 baths (lower frame).

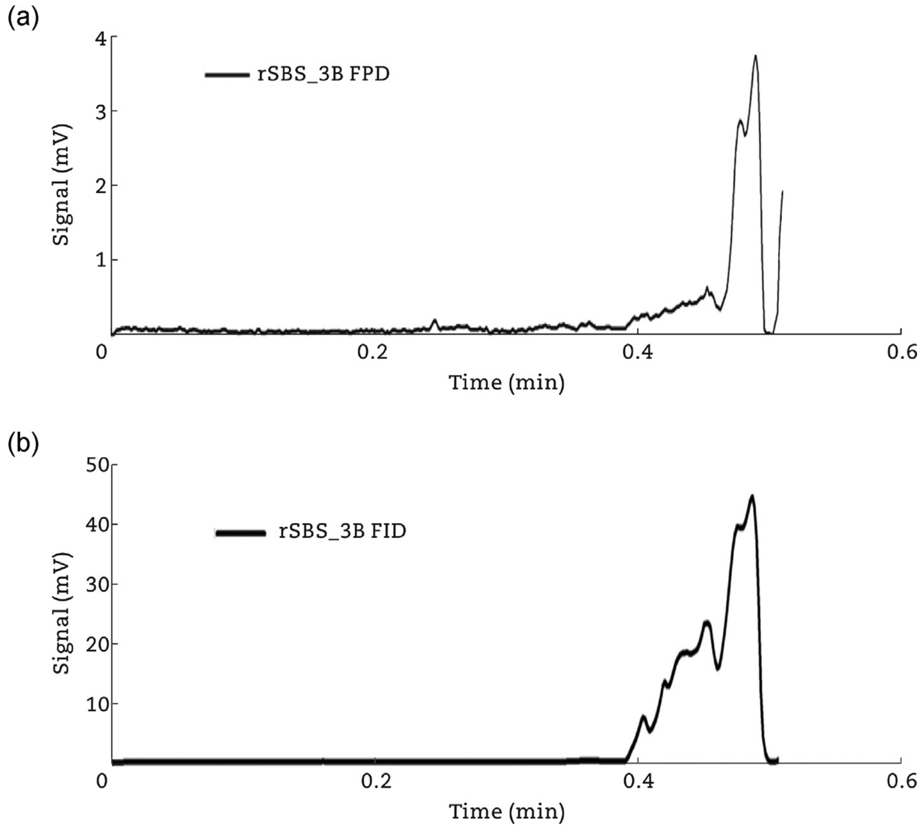

Fig. 9 – The chromatogram of radial SBS polymer after elution in 3 baths (rSBS_3B). (a) Analyzed using FPD (upper frame). (b) Analyzed using FID (lower frame).

would be desired. The polymer related peaks would be visible in the spectra in such cases. In the country in which the case of gilsonite recognition originally surfaced, the polymer modification for paving works is rare, thus presence of SBS in RAP is scarce.

Nevertheless, as witnessed with FT-IR spectroscopy (Fig. 4), the BAA in comparison to bitumen is expressing the peaks that allow it to be a distinguishable material, when blended. This is consistent with other reports, but caution is advised as not all anti-aging agents would have similar chemical composition allowing for an easy recognition (Cavalli et al., 2018). For these materials, three regions were identified as characteristic and assigned similarly as in food stuff oils (Liang et al., 2012), namely the peaks with maximum at 1164 cm^{-1} (C–O stretch; CH_2 bending), 1741 cm^{-1} (C=O stretch) and 3007 cm^{-1} (C–H stretch). Those peaks are observed in reference BAA and the absorbance intensity in those regions is visibly increased in the RAP_BAA. When we compare to fresh bitumen, the peaks at 1741 and 3007 cm^{-1} are more reliable markers, as during the aging of bitumen the peaks develop in the region between 1000 and 1200 cm^{-1} (Jemison et al., 1992; Liu et al., 1996; Makowska et al., 2017b). The BAA can be easily identified as a modifier in a fresh blend by infrared spectroscopy.

In terms of GIL and its blend (Fig. 4), the only significant difference between the spectra of 70/100 and BLEND is in the sulfoxyl region, as well as in the background shape. This is why the recognition of GIL in the sample cannot be performed based on FT-IR spectra alone. There is no reliable marker in infrared range.

In the regular TLC-FID analysis of material after the procedure IP469, the chromatogram has distinct four peaks assigned the name of saturates, aromatics, polars I and polars II (Fig. 2). The valley between polars I and polars II is in fact the region in which the GIL (Figs. 5 and 6), BAA (Figs. 7 and 8) and rSBS (Fig. 9) may elute into in the IP469 procedure.

Because the increase of the asphaltene fraction and resin fraction is associated with more pronounced aging (Siddiqui and Ali, 1999), this type of result for the BAA or polymer may lead to a conclusion that aging is inflicted during the addition of modifier, as the area of the peaks assigned to polars I and polars II (colloquially referred to as resins and asphaltenes) increases. However, that signal increases due to the fact that elution in the second bath for GIL and BAA has different retention factor. Material simply elutes to shorter distance from the origin than the aromatic fraction of bitumen. The mobility on the silica rod is a result of the size or polarity of the molecules. The above results indicate that those materials contain fractions of the solubility in the same solvent used to separate the aromatic fraction in bitumen. This may enhance the understanding of mutual solubility of bitumen, GIL, BAA and even polymers.

Looking into the region of the valley between polars I and polars II after three baths, allows for the identification of the presence of modifier. In this case, applying the staged TLC-FID/FPD combined with the visual observation of rods during the procedure and TLC-FPD reading in the above-mentioned valley, the identification of gilsonite should be possible by red/bordo tint to the rod. In case of doubt, eliminating the possible presence of BAA or a polymer is suggested by the FT-IR.

The SBS should not have sulphur in the structure, but the signal in the origin is very strong in the S-FPD. The typical polars II signal intensity is in the range of 20–30 mV (Fig. 2), but for rSBS this value is closer to 50 mV in FID (Fig. 9). This suggests quite a high load for the FID detector, which may mean that the sample is outside of the mass to signal linearity range for this material. As discussed in Section 1.1., the signal in S-FPD in such case may be visible due to not fully combusted aromatic parts of polymer present in the outflowing gas, which is suggested for exploration in the future. The aspects connected with the identification of SBS presence and its content as a modifier are explored elsewhere (Kosińska et al., 2015; Zofka et al., 2015), but it was important to underline that polymer may in fact give a similar result in TLC-FID as GIL after 3 baths elution while being translucent, supporting the need for visual observation during the procedures. This material also demonstrates that S-FPD should probably not be referred to as sulphur detector, yet it can be of supporting use to the typically applied FID.

Nevertheless, the SBS is hereby demonstrated to separate into fractions based on the solubility in the chosen solvents. Unfortunately, the height to which the material travels up on the silica rod, does not allow an analyst to cumulatively count it with other fractions. Even though the part of polymer moves in the solvents along the rod, the elution stops at heights typically assigned for the polars II fraction, often referred to as asphaltenes. Designing a separate chromatographic procedure for the polymers could in the future provide more information related to the mutual solubility of its components with the bitumen.

Noticeably, the strongest signal in S-FPD for bitumen is coming from the peak formed as a result of second bath (Fig. 2) (Ogasawa et al., 2002). Incidentally, it is the peak imposed in the mentioned valley region for GIL, BAA and polymer. Thus if the peak in the valley is more apparent in S-FPD than in FID evaluation, an indication of gilsonite presence should be considered. The blend of the GIL and the fresh bitumen is indeed giving a small peak by the S-FPD in that region (Fig. 6), which could prove promising for the qualitative recognition of GIL presence (Makowska and Pellinen, 2019).

When comparing the GIL to fresh bitumen, the signal by FPD indicates the presence of GIL in the BLEND (Fig. 6). However, for RAP extracted samples (Figs. 7 and 8) a similar smearing of the fraction in that region presents itself in the FPD signal alone. This is not coming together with the coloring on the column, though. The color in that region for RAP is similar to that observed for 70/100.

Interestingly, for tall oil based rejuvenator (BAA), the fraction soluble in the second solvent gets eluted to the position of the valley between the peaks assigned to polars I and polars II fraction (Fig. 6). The same procedure for bituminous products would position the molecules at different height (peak related to aromatic fraction). This is invisible to the naked eye, as the rejuvenator is almost transparent and only FID analysis between stages of elution allows us to see it.

In the third bath, all of the material is eluted to the normal (for bituminous materials) position of polars I peak (Fig. 5), thus the information about aromaticity in BAA is lost in IP469. For pure BAA, in FID signal after 3 baths, the peak is not sharp and above 50 mV, indicating overload of material for the FID. For the FPD signal the final peak is multimodal, indicating bad separation and overlap.

Using IP469 technique for blends with modifiers may lead to the wrong conclusions about the chemical nature of the components of the blends. To prevent the wrong assignment of the fraction and to allow for identification of the modifier, a staged analysis of the procedure is suggested as demonstrated above.

3.2. *Proposed future explorations*

As is demonstrated, some information about the modifiers, bitumens and blends may be lost when only the end result of TLC-FID fractionation is analyzed.

In the end, the slight coloring of the rod recorded by an operator, may be unconvincing to interested parties. The suggestion is, to start with the material at typical concentrations used for TLC-FID SARA fractionation in order to screen the products and then gradually increase concentration in the analyzed sample to establish if the gilsonite specific behavior is more visible. In principle, the TLC-FID allows for correlation with concentration, thus the quantitative analysis of the modifier's content in the blend should be achievable upon calibration between references. This was not attempted in this work.

Finally, the method presented here is considered a first step analytical procedure utilizing equipment available in asphalt research laboratories. In order to achieve a proof and confirmation, more precise techniques than TLC-FID and FT-IR should be applied. Those two techniques are well applicable to the analysis of pure substances, but in the considered case of blend evaluation the signals in them, as demonstrated above, may originate from multiple materials. Other methodologies which allow studies on blends could prove more informative, for example applying the inverse Laplace transform onto the nuclear magnetic resonance spin-echo signal decay. This technique follows the changes in microstructure upon the addition of modifiers, and already multiple additives have been tested with it (Rossi et al., 2015). However, ideally a marker molecule of modifier should be identified and its presence, or lack of, determined in the blend in case of legal dispute. Promising technique to achieve that, which could comprise the next analytical step, is testing of blends using high-field Fourier transform ion cyclotron resonance mass spectrometer (Handle et al., 2017; McKenna et al., 2013).

4. Conclusions

The results coming from the IP469 procedure analyzed with TLC-FID are questionable for blends with modifiers.

The analysis of BAA by fractionation procedure IP469 and analysis with TLC-FID indicates the modifier affects only the polars I fraction, while the aromaticity of the material remains unnoticed. This particular hidden solubility in the mixture of toluene and n-heptane (80:20, vol.%) solvent couple–characteristic for aromatics in bitumen which is similar for both BAA and GIL. The difference between them is in the interaction by the adsorption of the molecules onto the silica rod. For the BAA, the third bath solvent couple pushes all of the material with solvent front into the position of polars I. In case of GIL, the material remains on the rod and is visible in between the valley of polars I and II, also by coloring.

This previously hidden information (for BAA, GIL, SBS) is proposed to contribute to the future studies on mutual solubility of bitumen and its organic modifiers using the TLC-FID technique.

The use of flame photometric detector (394 nm) and analysis of results from the procedure at various stages in the procedure were proved to provide additional information about the blends of straight run bitumens with modifiers. The difference between gilsonite, the field aged bitumen and an anti-aging agent is observed by the color of the stain especially after the second elution bath, which allows for the qualitative identification of gilsonite as a modifier in the blend. The FPD detector was also demonstrated to give signal for materials, which do not contain sulphur in their structure. The suggestion is that the signal is of combined sulphurous compounds and inappropriately pyrolized aromatic compounds.

The added value of FT-IR for distinguishing between modifiers in combination with TLC-FID was demonstrated for material analysis.

A proof was provided on how the staged elution and analysis of TLC-FID fractionation procedure can supply additional insight into the understanding of the solubility of the modifiers in comparison to the bitumen.

Conflict of interest

The authors do not have any conflict of interest with other entities or researchers.

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