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Direct analysis of aromatic hydrocarbons in purified mineral oils for foods and cosmetics applications using gas chromatography with vacuum ultraviolet detection

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ABSTRACT

Highly purified mineral oils are used in several pharmaceutical, foods and cosmetics applications. A fast and simple method was developed for the analysis of the total level of residual mineral oil aromatic hydrocarbons (MOAH) in these oils and in the intermediate oils that were sampled during the purification process. The method is based on gas chromatography with vacuum ultraviolet detection (GC-VUV) and relies on the spectral differences between the aliphatic and aromatic compounds in the sample. Because the detector provides a good selectivity for aromatics, direct quantification of the MOAH content is possible without the need for a laborious pre-separation of the mineral oil. The method was successfully applied for the direct analysis of the MOAH levels of 18 different mineral oil samples. The aromatics contents obtained by GC-VUV were similar to those obtained using two conventional methods (NPLC-GC-FID and SPE-GC-FID), with no statistically significant difference. The detector response was linear over the concentration range tested (0.5–20 mg/mL) and the repeatability (RSD value) was less than 8%, which is better than the typical values for the conventional methods (up to 15% RSD). The minimum MOAH level that can be determined with this method is approximately 0.13%, making the GC-VUV method sufficiently sensitive for the analysis of all but the highest purity mineral oils.

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1. Introduction

Highly refined and purified mineral oil fractions are widely used for elaboration of consumer products such as foods and cosmetics. These mineral oils (MO) are called 'white oils' and must meet very strict criteria in terms of residual levels of mineral oil aromatic hydrocarbons (MOAH) [1]. In addition to the deliberate use of these purified oils as ingredients for cosmetics or foods, mineral oil can also find its way into consumer products as a contaminant, e.g. through migration from recycled packaging materials or from the environment [2]. These contaminants can easily contain up to 30% and sometimes even up to 50% of MOAH and their concentration in consumer products ranges from 10 to 100 mg/kg [3,4]. Reliable methods for monitoring the total MOAH levels in MO are needed for the optimization of MOAH removal processes in white oil production, as well as for detecting MOAH contamination in quality assessment of consumer products. Ideally these methods

would also provide information on the composition of the MOAH fraction as this might affect both removal efficiency and toxicity of the MOAH [5].

Biedermann et al. developed a fully automated on-line normal phase liquid chromatography (NPLC) – gas chromatography-flame ionization detection (GC-FID) method with a silica column for the quantitative analysis of low levels of MOAH in foods and cosmetics. In this method, the NPLC step was used to perform a pre-separation of mineral oil saturated hydrocarbons (MOSH) and MOAH. Sensitive and universal quantification of the two fractions was then provided by the FID [6,7]. The Biedermann and Grob method is now widely used. However, because in many laboratories the instrumentation required is not available, also less automated approaches have been developed. A method using Solid Phase Extraction (SPE) for the pre-separation of MOSH and MOAH was developed by Moret et al. in 2011. To improve the MOSH/MOAH separation, the silica sorbent was replaced by silver-loaded silica making the determination of the cut point between MOSH and MOAH less critical [8,9]. Still, for samples with MOAH contents below 1% interferences of MOSH readily occur. For such samples the end of the MOSH band might overlap with the start of the later eluting MOAH fraction. Because

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the GC-FID quantification step provides no additional selectivity, traces of MOSH collected in the MOAH fraction result in incorrect MOAH levels. The need for this careful prefractionation makes the method time-consuming in routine analysis and faster methods with less sample handling steps are desired.

Recently a novel detector for GC has been introduced, the Vacuum Ultraviolet (VUV) detector. This detector measures the absorbance of gas phase compounds in the far UV wavelength range from 120 to 430 nm [10]. Essentially almost every compound absorbs strongly in this range of wavelengths [11]. Indeed the universal nature of the detector has been demonstrated with the analysis of a wide variety of compounds in different matrices [12–17]. The VUV detector has attracted significant attention for petrochemical analysis due to its ability to provide group-type information. In 2016, Groeger et al. found spectral differences between aliphatic and aromatics compounds in diesel fuel analysis [18]. At low wavelengths all compounds, aliphatic and aromatic, are detected, whereas at higher wavelengths only the aromatics and unsaturated compounds absorb. This is an extremely attractive feature in MOSH/MOAH analysis. If sufficiently selective, this would mean the GC-VUV combination would be able to quantify MOAH directly, i.e. without prior separation of MOSH and MOAH. This would be highly advantageous in terms of analysis cost and method ruggedness. Moreover, the chromatograms and spectra will contain information on the number of aromatic rings or the length and type of alkyl-moieties present, which could be relevant information for e.g. optimization of the MOAH removal processes in white oil production.

In this work a novel and rapid GC-VUV method for the determination of the aromatics content in mineral oil samples and intermediates from the white oil production process is described. Quantitative data obtained using the new direct GC-VUV method are compared with those from standard, off-line SPE-GC methods. Furthermore, the ability of the set-up for providing structural information on the molecules in the aromatic fractions from their VUV spectra is studied.

2. Materials and methods

Hexane and dichloromethane (DCM), both HPLC grade, were purchased from Biosolve BV (Valkenswaard, The Netherlands). *n*-undecane (C₁₁), bicyclohexyl (Cycy), *n*-tridecane (C₁₃), 5- α -cholestane (Cho), *n*-hexyl benzene (6B), 1-methyl naphthalene (1-MN), biphenyl (BP), 1,3,5-tri-*tert*-butyl benzene (TBB) and *n*-nonyl benzene (9B) were from Sigma-Aldrich (Zwijndrecht, the Netherlands). Silver-nitrate impregnated silica gel (230 mesh) loaded at approximately 10 wt.% was purchased from Sigma-Aldrich. Mineral oil samples from different stages in the purification process were obtained from a local supplier of white oils. The viscosities of the oils ranged from 10.32 to 153.4 cSt at 40 °C. The carbon numbers of the compounds ranged from 15 to more than 50.

2.1. Mineral oil and standard solutions

Stock solutions of each mineral oil (at 500 mg/mL) and of the mixture of standard compounds (C₁₁, C₁₃, Cycy, Cho, 6B, 1-MN, BP, TBB and 9B at 1 mg/mL per compound), which are used as markers for the MOSH and MOAH separation, to evaluate losses of volatile compounds and for quantification, were prepared in hexane. For the off-line argentation normal phase liquid chromatography – gas chromatography – flame ionization detection (AgNPLC-GC-FID) analyses, samples for injection were obtained by combining 200 μ L of the mineral oil stock solution and 300 μ L of the standard mixture and filling the vial to 1 mL using hexane

(final concentrations of 100 and 0.3 mg/mL, respectively). For the off-line SPE-GC-FID, a 50 mg/mL solution of each mineral oil was prepared from the stock solution and 50 μ L of this solution were combined with 6 μ L of the standard solution and 444 μ L of hexane (5 and 0.012 mg/mL, respectively). For the GC-VUV analysis, mineral oil solutions of 5 mg/mL in hexane were prepared without the standard compounds.

2.2. AgNPLC fractionation

LC fractionation of the samples was conducted on a Waters Alliance 2695 LC instrument with a Waters 996 DAD detector (Waters, Etten-Leur, The Netherlands). The method was based on that described by Biedermann and Grob [19] with some modifications to increase the separation gap between the MOSH and MOAH fractions. Instead of a 250 \times 2 mm ID column packed with silica, two serially connected 100 mm \times 4.6 mm ID \times 5 μ m AgNO₃ loaded silica columns (Agilent, Amstelveen, The Netherlands) were used. The MOSH/MOAH separation was performed using a gradient starting with hexane held for 12 min, and then programmed to 30% DCM in 1 min, maintaining this composition until the end of the run (25 min) at a flow rate of 0.3 mL/min. Using these chromatographic conditions, the MOSH fraction elutes between 8 and 10.5 min, and MOAH from 13 min until the end of the run. Both fractions were concentrated to 0.5 mL prior to GC analysis. To avoid shifts in the elution window due to column contamination, the column was reconditioned after every run with 100% DCM for 5 min at 0.5 mL/min, followed by a 5 min rinse with hexane, also at 0.5 mL/min. 20 μ L of the mineral oil sample was injected into the system.

2.3. SPE fractionation

Empty glass SPE cartridges (Sigma-Aldrich) were packed with 0.5 g of silver impregnated silica gel. Conditioning was performed by heating the cartridges at 120 °C for 2 h, washing with 10 mL of DCM and with 4 mL of hexane. The volume of sample applied to the silver-silica SPE was 0.5 mL. Elution of the MOSH was achieved with 5 mL of hexane. The MOAH fraction was eluted with 8 mL of hexane/DCM (50:50 v/v). Both fractions were concentrated to 0.5 mL prior to GC analysis.

2.4. GC-FID

GC analysis of the MOSH and MOAH fractions obtained from SPE or LC was carried out using an Agilent 6890 N C instrument system with a Focus-PAL autosampler (GL Sciences, Eindhoven, The Netherlands). The sample (1 μ L) was injected in splitless mode (2 min splitless time) at 350 °C in a 4 mm ID liner packed with glass wool. The capillary column, 15 m \times 0.32 mm \times 0.1 μ m DB5-HT (Agilent), was used at a constant flow of 2 mL/min using helium as carrier gas. The temperature program ran from 60 °C (3 min) to 350 °C (3 min) at 15 °C/min. The FID temperature was set at 350 °C and the data collection rate was 200 Hz.

2.5. GC-VUV

A VGA-101 VUV detector (VUV Analytics, Cedar Park, TX, USA) was connected to an Agilent G1530 A GC system equipped with an Optic 3 injector and a Focus-PAL autosampler (GL Sciences). The chromatographic conditions were identical to those for the GC-FID analyses. The temperature of the transfer line and the flow cell of the VUV detector were set at 350 °C. Nitrogen was used as make-up gas at a pressure of 0.35 psi. The data collection rate was 100 Hz.

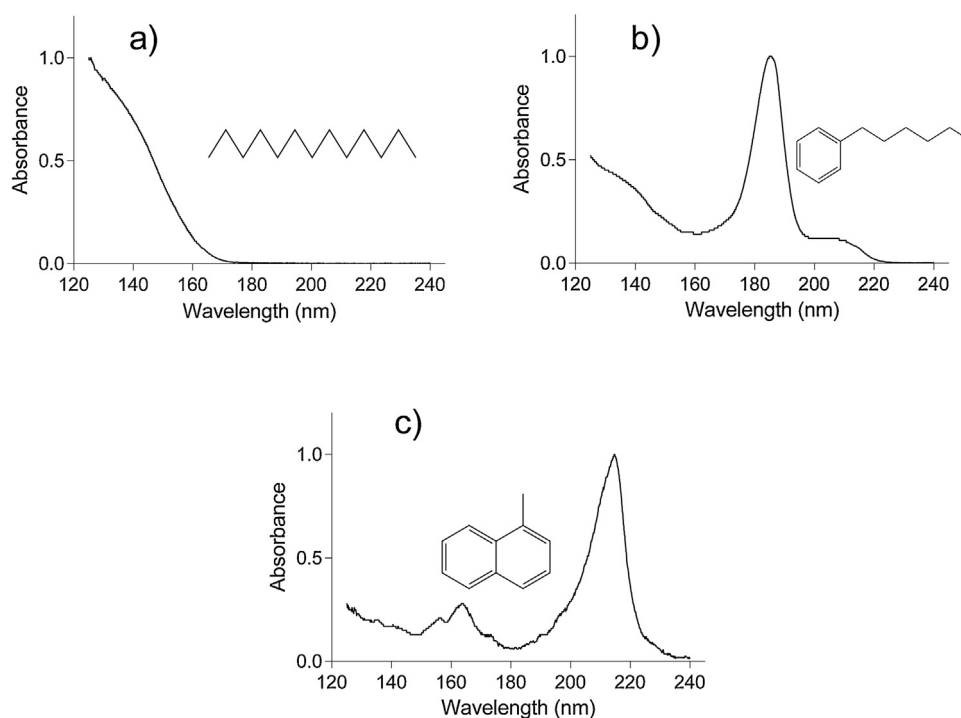


Fig. 1. GC-VUV absorbance spectra of a) C_{13} , b) 6B and c) 1-MN.

3. Results and discussion

3.1. VUV spectroscopic differences of MOSH and MOAH

The VUV spectra of compounds can differ significantly depending on the different functional groups present in the molecules [10]. Fig. 1 shows a few representative GC-VUV absorbance spectra of a number of aliphatic and aromatic compounds containing the typical structural elements of MOSH/MOAH compounds. Clear differences are observed between the different spectra. For the saturated compound, representing the MOSH fraction of the mineral oil, the spectrum monotonously decreases moving from the lowest wavelength of 125 nm to longer wavelengths. For these compounds no absorbance is observed at wavelengths above 180 nm (Fig. 1a). The aromatic compounds show a different behaviour (Fig. 1b and c). For these compounds one or more distinct maxima occur. The exact locations of these maxima and their band width depend on the number of aromatic rings and the way these are linked [11]. Molecules with one ring show an absorbance maximum around 185 nm. This maximum shifts to higher wavelengths when the number of rings in the molecule increases. For MOAH, which are basically alkylated aromatic compounds with one or more isolated or fused aromatic rings, the absorbance spectrum will consist of two regions, one adsorption band characteristic for the aromatic part, and a monotonously decreasing part originating from the aliphatic substituents.

To study the spectral differences between real MOSH and MOAH fractions, eight different mineral oil samples were separated using SPE. Fig. 2 shows the overall averaged VUV absorbance spectra obtained for the MOSH and MOAH fractions from these 8 oils. Since the absorbance spectra of all the mineral oils analyzed did not present any significant response at wavelengths higher than 240 nm, only data up to this value are presented. Because the levels of MOSH and MOAH in the samples were different, spectra were normalized to allow easier comparison, i.e. intensities at a specific wavelength were set equal. Normalization was performed

at 125 nm for MOSH, and at 125 nm or 195 nm for MOAH. From the comparison of the Figs. 1 and 2 it is clear that the MOSH and MOAH fractions show similar absorbance spectra as the individual model molecules. The aliphatic fractions show no response above 180 nm and the shape of the spectra for the eight MOSH fractions is very similar (Fig. 2a). When comparing the spectra of the aromatic fractions from the eight different mineral oils, two main differences become noticeable. In the spectra normalized at 125 nm, for the comparison of the aliphatic zone (125–180 nm), differences occur in the 160–180 nm region. Normalization at 195 nm, for the comparison of the aromatic zone, emphasizes the differences in the region of 190–240 nm. These two differences among the eight MOAH fractions are related to the structural differences in the molecules present in the different fractions. The first region, reflecting the aliphatic substituents of the aromatic rings, differs because of differences in the structure (linear, cyclic or branched) and length of the alkyl substituents. The second region where differences occur, i.e. the 190–240 nm region, reflects differences in the number and interconnectivity of the aromatic rings in the molecules. Mono-, di- or polyaromatic compounds with fused rings or rings closely together all have (slightly) different absorbance maxima.

3.2. Structural information of MOAH

In the previous section, clear differences were observed between the VUV spectra of MOAH fractions from different mineral oils. In a second series of experiments, changes in the spectra were studied over the GC elution window of a MOAH fraction. This was done by examining spectra collected at different times in the chromatographic run. The spectra obtained are shown in Fig. 3. These absorbance spectra can provide structural information on the compounds forming the aromatic fraction. The main differences seen are related to the alkyl part of the MOAH. In the spectra collected at longer retention times, i.e. for the heavier analytes, the aliphatic response (125–180 nm) increases. This is an indication of

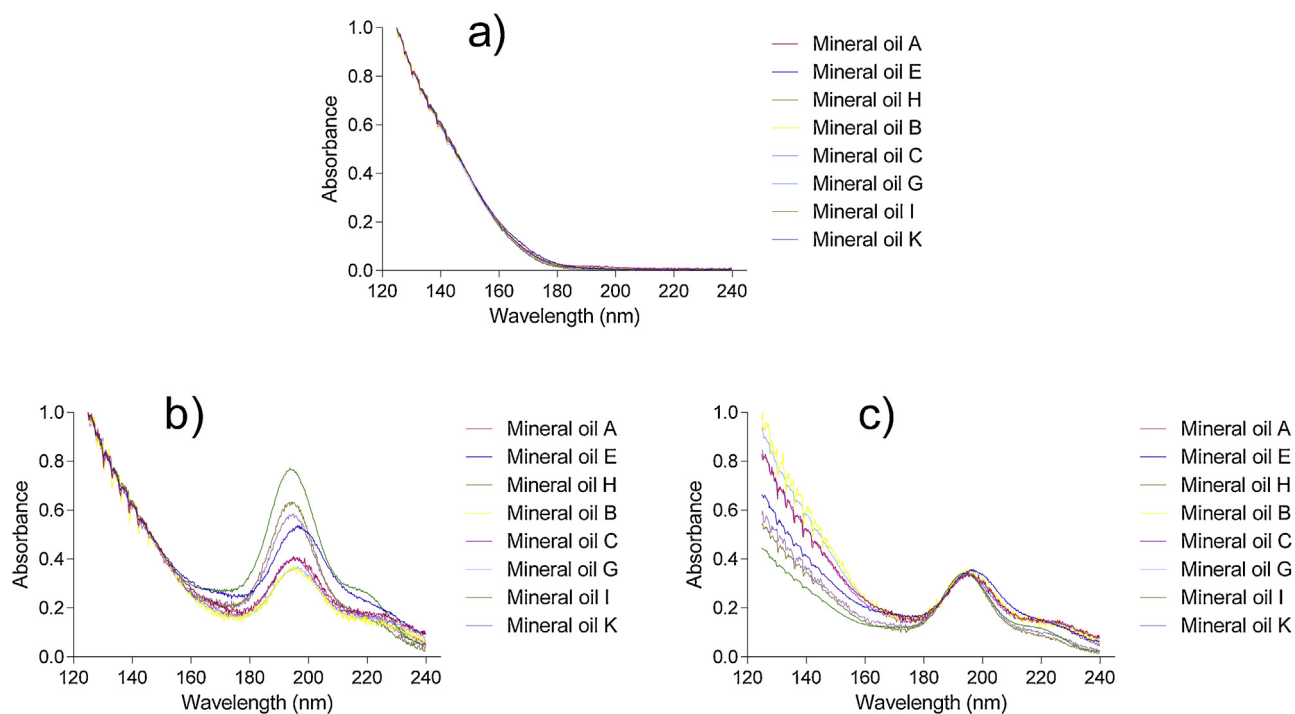


Fig. 2. GC-VUV absorbance spectra of a) MOAH normalized at 125 nm, b) MOAH normalized at 195 nm and c) MOAH normalized at 125 nm from eight different mineral oils. The noisy nature of the spectra (below 140 nm) is probably caused by variations in the pressure of the nitrogen in the flow cell.

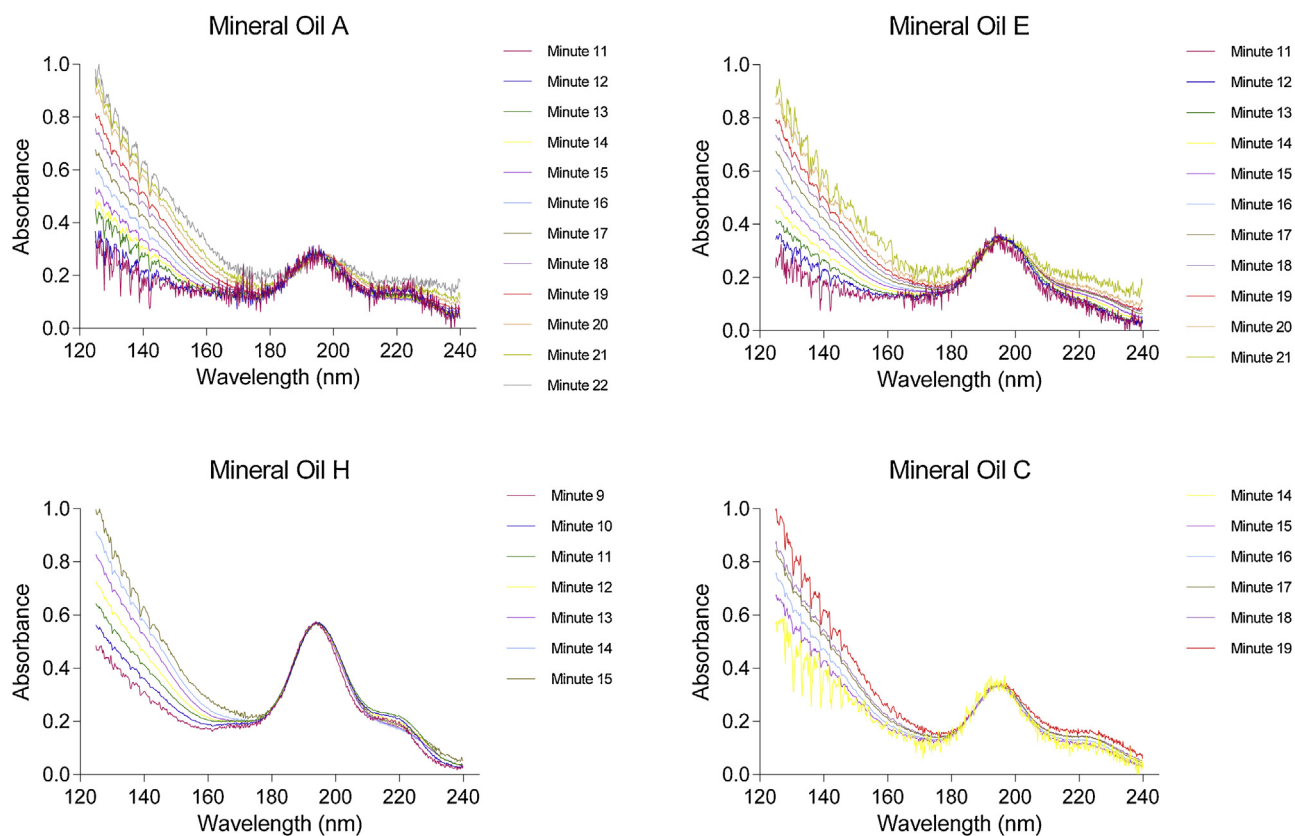


Fig. 3. Absorbance spectra of MOAH fractions from four different mineral oil. Each spectrum is the average of a 1 min slice of the chromatogram. For mineral oil A the hump starts at 9.29 min ($\approx C_{17}$) and finishes at 24.02 min ($\approx C_{52}$), for mineral oil E from 10.4 min ($\approx C_{18}$) to 23.21 min ($\approx C_{48}$), for mineral oil H from 7.46 min ($\approx C_{14}$) to 16.77 min ($\approx C_{31}$) and for mineral oil C from 13.66 min ($\approx C_{24}$) to 21.69 min ($\approx C_{44}$).

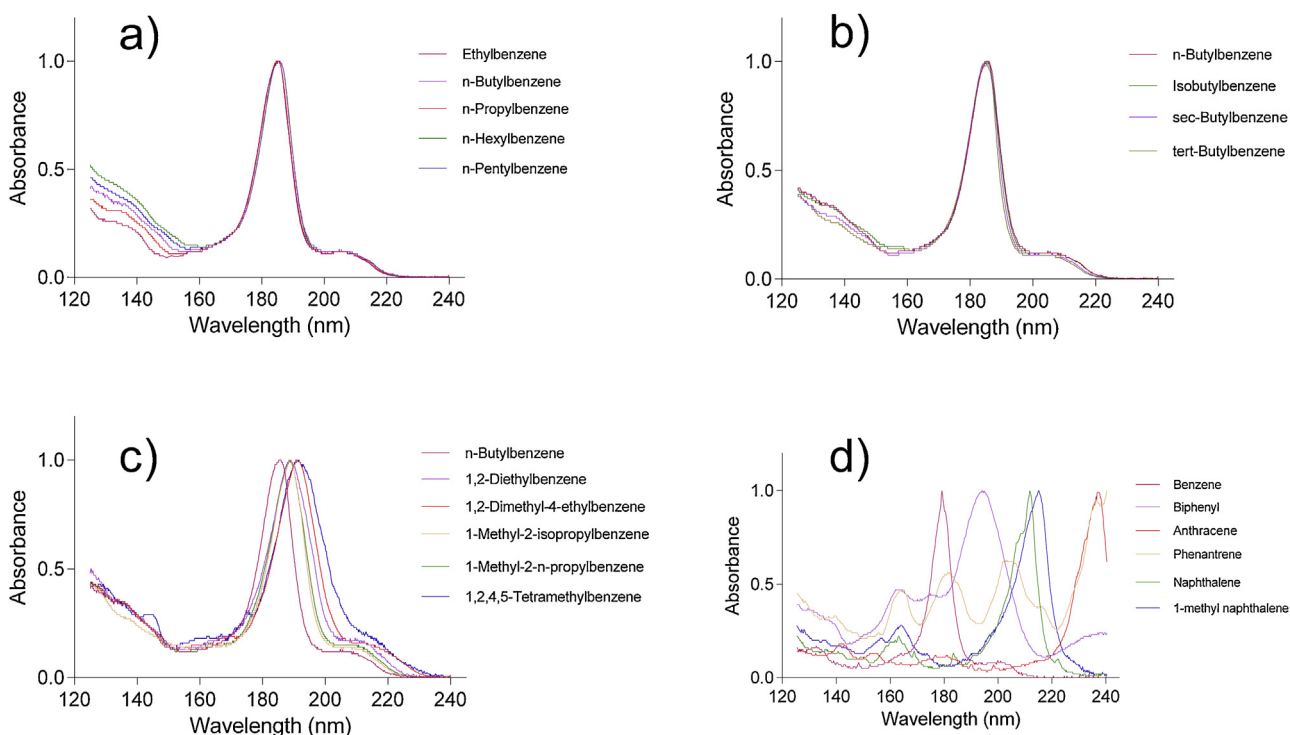


Fig. 4. GC-VUV absorbance spectra of different one-ring aromatic compounds.

the presence of longer chains or a higher degree of substitution on the aromatic core for the later eluting analytes. Furthermore, for the samples A, E and C differences are also seen in the aromatic part. The spectra obtained at longer retention times show higher responses in the 190–240 nm region than the ones obtained at the beginning of the chromatogram. This can be an indication of the presence of alkylated polyaromatic compounds.

In order to understand how the structure of the MOAH compounds affects the absorbance spectrum, VUV library spectra of different aromatic compounds were compared. Fig. 4a shows the spectra of one-ring aromatic species with increasing straight alkyl chain length. A steeper slope in the aliphatic region is related to the increment of the alkyl chain length. The aromatic region is not affected by the substituent length. On the other hand, Fig. 4b shows the spectral differences of four one-ring isomers with one alkyl chain with different levels of branching. Small changes are seen in the aliphatic part of the spectrum depending on the branching positions in the alkyl chain. Branched alkyl substituents give a slightly lower signal in the aliphatic part of the spectrum compared to the straight chain molecules. If the methyl groups are closer to the aromatic core, the aliphatic signal intensity is reduced. Finally, Fig. 4c shows the spectrum of one-ring isomers with increasing numbers of alkyl chains attached to the ring. For these isomers the aromatic part is affected more than the aliphatic part. For the compounds with more than one alkyl substituent the absorbance maximum of the aromatic part of the spectrum shifts to higher wavelengths. In other words, the location of the maximum could be an indicator for the degree of substitution of the aromatic compounds. However, it is important to emphasize that the presence of multiple aromatic rings in the structure will also shift the absorbance maximum of the aromatics to higher wavelengths, as is noticed in Fig. 4d. The absorbance spectra of benzene, naphthalene and anthracene demonstrate that an increase in the number of aromatic rings shifts the absorbance maximum to longer wavelengths [11]. Differences are also observed among molecules with the same number of aromatic rings. Naphthalene, biphenyl and 1-methyl naphthalene all

contain two rings; however, their absorbance spectra are different. Alkyl substitutions affect the absorbance spectrum in the same way as with the mono-aromatics. 1-MN shows a shift of the absorbance maximum to longer wavelengths and has a broader signal in the aromatic zone compared to naphthalene. On the other hand, the biphenyl absorbance spectrum is more similar to those obtained for one-ring species with an absorbance maximum at 195 nm.

Based on the information discussed above, it is possible to draw some preliminary conclusions on the type of MOAH species present in the different oil samples analyzed in Fig. 3. From the spectra it can be concluded that the aromatic cores of the different mineral oils are largely identical. From the ratios of the aromatic and aliphatic intensities (aromatic/aliphatic), it can be concluded that mineral oil A (0.820 - 0.426) contains the longest alkyl chains as substituents attached to the aromatic core, while mineral oil H (0.938 - 0.563) has the shortest chains. This statement is confirmed by the viscosity values of the mineral oils (91.21 and 10.32 cSt at 40 °C, respectively). For mineral oil A, E and C, an absorbance increase is observed in the region of the two-ring aromatic compounds, 205–240 nm, at longer GC retention times. This increment is more remarkable for mineral oil E indicating a higher content of polyaromatic compounds in this mineral oil. On the contrary, based on the spectra, mineral oil H seems to have the lowest content of polyaromatic compounds.

Fig. 5 shows a comparison of spectra obtained at the same retention time (15 min) for four mineral oil samples from different stages in the purification process. Because the spectra were recorded at the same GC retention time, they belong to compounds with similar volatility, and therefore similar molecular weight. The aliphatic response is highest for mineral oils A and C. This indicates the presence of multiple straight-chain alkyl substituents in these oils as compared to the minerals oil H and E. Based on the aliphatic response, mineral oil E seems to contain more branched alkyl chains. Furthermore, the aromatic region for this mineral oil shows a shift in the absorbance maximum to higher wavelengths and the absorbance band is wider than for the other three samples. These are additional indications for a higher degree of substitution.

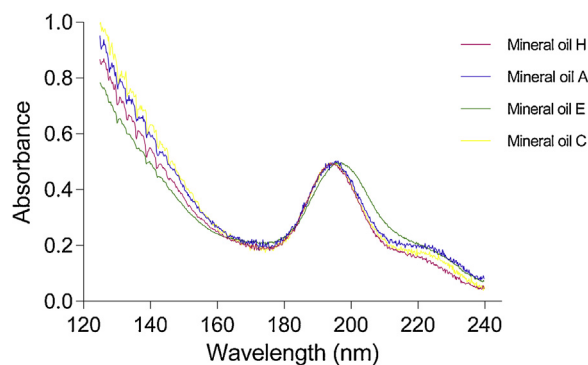


Fig. 5. GC-VUV absorbance spectra of the MOAH fraction of four mineral oils. The spectra were recorded at the same GC retention time.

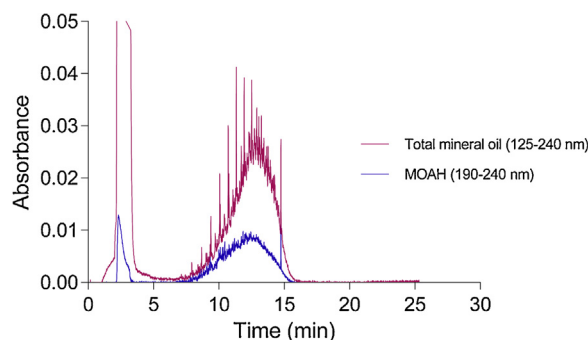


Fig. 6. Chromatogram of mineral oil H analysed on the GC-VUV system without previous prefractionation. The total mineral oil response was obtained using the entire wavelength range (125–240 nm), whereas the aromatic response was obtained with a 190–240 nm filter. The solvent peak (hexane) in both wavelength filters elutes at 2.5 min. The signal in the aromatic filter is either due to impurities in the solvent or limited detector selectivity. The sharp peak at 14.5 min is an impurity.

Apparently, sample E has more but shorter alkyl chains on the aromatic ring than the oils A, C and H. Regarding the aromatic region this corroborates the information previously mentioned about the type of aromatic species for each mineral oil and confirms the added value of VUV detection. The content of polyaromatic species is higher for mineral oil A and E, and low for oil H. However, for accurately estimating the percentages of these compounds in the mineral oil other analytical methods are needed like comprehensive LCxGC-MS [20].

3.3. Direct determination of the MOAH content by GC-VUV

The presence of absorbance bands specific for aromatics in the VUV spectra in principle enables direct quantitative assessment of MOAH levels in mineral oils without the need for a MOSH/MOAH prepreparation. To obtain the MOAH content from the GC-VUV data, two spectral filters were applied. The first filter covers the 190 to 240 nm region and detects only the MOAH species (Fig. 6). The second filter covers the entire range of wavelengths recorded (125–240 nm) and gives a (semi-)quantitative number for the total GC response of the mineral oil (MOSH + MOAH). This second filter is applied to be able to correct the data for differences in total mineral oil responses due to sample discrimination in the GC injection which was evaluated comparing the response of different mineral oils at the same concentration.

To be able to calculate the MOAH percentage directly from the GC-VUV chromatogram, the MOSH amount first needs to be calculated. This can be done from the peak area in the 125–240 nm region, corrected for the contribution of the aliphatic parts of the MOAH to this area. A good estimate of the correction factor can

be obtained from the MOAH spectra of the eight different oils shown in Fig. 2. These oils represent the typical mineral oils and intermediates encountered in industry. In these spectra, the total area is 1.38 ± 0.11 times higher than the area in the MOAH region (190–240 nm). Thus, the following equation can be derived:

$$MOAH_{125-240} = 1.38 \times MOAH_{190-240} \quad (1)$$

Because VUV spectroscopy follows the additivity principles of the Beer-Lambert law, the MOSH response can be calculated from:

$$MOSH_{125-240} = TR_{125-240} - MOAH_{125-240} \quad (2)$$

In these equations $MOSH_{125-240}$, $MOAH_{125-240}$ and $TR_{125-240}$ are the peak areas in the chromatogram of the MOSH, MOAH and total mineral oil, respectively, all calculated from the 125–240 nm signal. $MOAH_{190-240}$ is the corresponding area calculated from the 190–240 nm signal. The above areas can be converted into mass percentages of MOSH and MOAH in the mineral oil using the Eqs. (3) and (4):

$$MOAH \% = 100 \times \frac{MOAH_{125-240} \times RRF_{MOAH}}{(MOSH_{125-240} \times RRF_{MOSH}) + (MOAH_{125-240} \times RRF_{MOAH})} \quad (3)$$

$$MOSH \% = 100 - MOAH \% \quad (4)$$

Here RRFs are the relative response factors for MOSH and MOAH relative to methane. RRFs values for individual alkanes were determined in previous studies and it was found that they are remarkably independent of the length and structure of the alkyl chain [21]. In this work, an RRF_{MOSH} of 0.775 was used based on previous data [11]. For MOAH, an RRF_{MOAH} of 0.425 ± 0.055 was calculated. This value was obtained as an average of the RRF values for the eight different MOAH fractions described previously. Each RRF was calculated following Eq. (5), where A_{MOSH}/A_{MOAH} is the ratio of the areas of the two fractions:

$$RRF_{MOAH} = \frac{M_{MOAH} A_{MOSH(125-240nm)}}{M_{MOSH} A_{MOAH(125-240nm)}} RRF_{MOSH} \quad (5)$$

Once these RRF are established, they can be used for the direct GC-VUV MOAH quantitation in unknown mineral oil samples without the necessity of any MOSH/MOAH prepreparation, i.e. the laborious LC or SPE step can be avoided. This is reflected in the analysis time. While for the conventional methods a run takes 46 min, the proposed GC-VUV method is only 25 min.

To evaluate the performance of the direct GC-VUV method, some performance characteristics such as selectivity, linearity, repeatability, limit of detection (LOD) and limit of quantification (LOQ) were assessed using the two wavelength ranges described above and following the Eurachem guide for method validation [22]. This evaluation was done for three different mineral oils. One mineral oil was virtually free of aromatics (mineral oil N), whereas the other two contained significant MOAH levels (mineral oil A and H). Also the boiling point range of the three mineral oils was different (Fig. 7). The performance characteristics of the new method are shown in Table 1. The selectivity was evaluated by comparing the peak areas of equal injected amounts of MOSH and MOAH, isolated by SPE, in the MOAH region (i.e. 195–240 nm region). Equal amounts of MOSH and MOAH resulted in an approximately 3300 times higher response for MOAH than for MOSH. Or, phrased differently, for a MOAH free oil our direct GC-VUV method would report a MOAH level of 0.03%. A good linearity of VUV absorbance ($R^2 > 0.989$) versus concentration was seen at both wavelength ranges. The LOD and LOQ values at the current GC injection settings are similar for mineral oil N and H, both having a rather narrow boiling point range. Slightly poorer values were obtained for mineral oil A due to the broader volatility range, and hence broader chromatographic 'hump' of this oil. The LOD and LOQ values for the MOAH fraction were calculated based on the concentration of MOAH in mineral oil A and H (25 and 30% respectively). Thus, considering a

Table 1

Performance characteristics for three different mineral oil samples. MO 2 is aromatic free while MO A and H contain MOSH and MOAH.

	Total mineral oil 125 – 240 nm			MOAH 190 – 240 nm		
	MO N	MO A	MO H	MO N	MO A	MO H
Linearity (0.5–20 mg/mL)	0.9931	0.9887	0.9979	NA	0.9886	0.9980
LoD (mg/mL)	0.026	0.0493	0.027	NA	0.018	0.008
LoQ (mg/mL)	0.088	0.1643	0.090	NA	0.061	0.026
Repeatability (CV%)	<7.96	<6.44	<6.18	NA	<2.89	<5.96

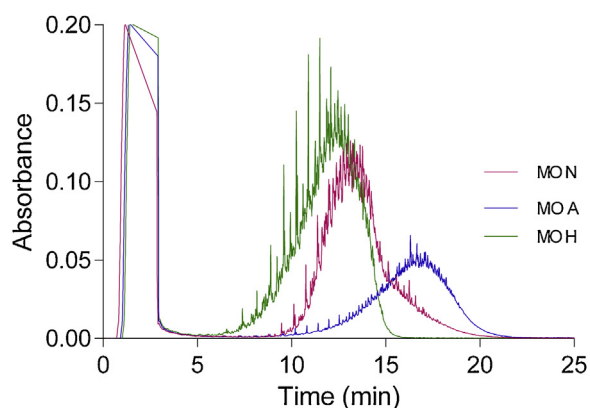


Fig. 7. GC-VUV chromatograms of the three mineral oils selected for the method validation. The chromatograms were obtained using the entire wavelength range (125 to 240 nm) and at the same concentration 10 mg/mL. The boiling point range of the mineral oils is different. Mineral oil N ranges from C₁₄ to C₄₀ (centered around C₂₃), mineral oil A ranges from C₁₇ to C₅₂ (centered around C₃₃) and mineral oil H ranges from C₁₄ to C₃₁ (centered around C₂₃).

mineral oil with a narrow range of volatilities, like mineral oil H, MOAH contents down to approximately 0.13% can be determined when working with a mineral oil concentration of 20 mg/mL, and a splitless injection of 1 μ L. In an experts discussion by the German Bureau for Risk Assessment in November 2016, typical MOAH levels in highly purified mineral oil end products were reported to be in the range of 0.025–1.7% [23]. This would make our method sufficiently sensitive for all but the highest purity samples. Finally, the repeatability of the method resulted in RSD values better than 8%. Unlike in the standard methods, on-line or off-line SPE-GC-FID or LC-GC-FID, these values are only related to the integration difficulties and deviations in the sample introduction because no other sample preparation steps are present.

3.4. Analysis of different samples

To determine the practical application limits of the newly proposed rapid GC-VUV method for MOAH analysis, a series of starting samples and intermediates of white oil production of different origins and different MOAH levels were analysed. Fig. 8 shows the MOAH content obtained for 18 different mineral oil samples using GC-VUV. Data from the standard methods (SPE-GC-FID and LC-GC-FID) are included to provide a frame of reference. The GC-VUV results are not statistically significantly different from those obtained by the two standard methods, which was evaluated by applying an analysis of variance (ANOVA) to each sample. At this point, it is important to mention that the repeatability of the MOAH measurements is much better for the GC-VUV method as compared to the standard methods. This is due to the absence of the complex manual sample pre-separation step. The samples analyzed in the comparison have MOAH contents from less than 0.13% to almost 50%. Their successful analysis clearly shows the applicability of the method to oils with both high and low aromatics content and fractions from different stages in the purification process. Mineral oil J shows the limitation of the standard methods. This mineral

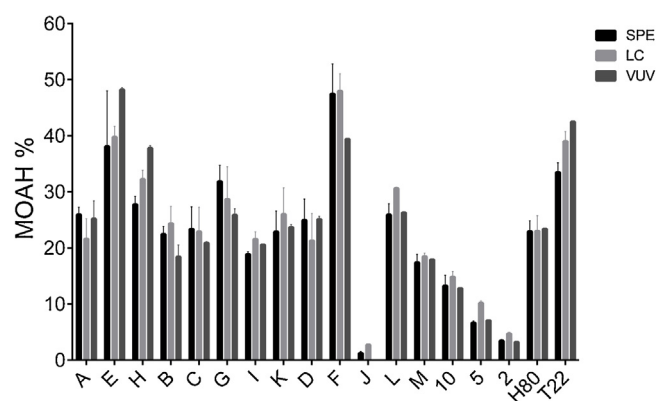


Fig. 8. Comparison of the aromatic percentage using GC-VUV and the two standard methods. The GC-VUV method presented the smallest variation due to the absence of pre-separation.

oil is free of aromatics, but even though a highly selective silver-loaded silica stationary phase was used, still some MOSH eluted in the time window where the MOAH would elute. This problem is related to the complexity of the sample. Sample J contains very high molecular weight compounds and, additionally, has a low content of aromatics. Because of the presence of the poorly soluble high molecular weight species there is an increased risk of MOSH compounds eluting in the MOAH fraction. Because in the next step a non-selective flame ionization detector is used for quantification, this immediately results in an overestimation of the MOAH level. This is not an issue in the GC-VUV analysis because no pre-separation is required.

4. Conclusions

A direct GC-VUV method for the determination of the MOAH content of purified mineral oil samples was developed. The method showed to be a good alternative for determining the aromatics content in mineral oil samples. Detection limits were around 0.13%, making the method sufficiently sensitive for all but the highest purity samples. The VUV spectra provide some structural information of the molecules present in the aromatics fraction. Thanks to the selectivity provided by the VUV detector no sample pre-separation is needed, which shortens the analysis time significantly and eliminates difficult experimental setups and/or manual sample handling steps. Additionally, the new method reduces the risks for errors, particularly when complex samples, i.e. samples with a low content of aromatics and a high molecular weight, have to be analyzed. This new method could potentially also be used for analysis of mineral oil in other consumer products such as food. However, sample preparation for reducing matrix interferences from e.g. triglycerides and olefins will still be needed.

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