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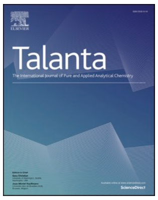

Quantitative determination of olefins in pyrolysis oils from waste plastics and tires using selective adsorption by Ag–SiO_2 followed by GC×GC-FID

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ABSTRACT

Determination of olefins in pyrolysis oils from waste plastics and tires is crucial for optimizing the pyrolysis process and especially for the further advanced valorization of these oils in terms of the circular economy. Identifying olefins, even using high-resolution techniques like GC×GC, is challenging without TOF-MS, which allows modification of the ionization step. Currently, the only method for determining olefins in plastic pyrolysis oils is GC-VUV, recently standardized as ASTM D8519. However, TOF-MS and VUV are not affordable instruments for many research teams working on plastics recycling. This paper introduces a simple method for the selective micro-scale adsorption of olefins over $AgNO_3/SiO_2$, followed by the GC×GC-FID analysis. Olefins are determined indirectly from the loss of chromatographic area in respective hydrocarbon groups before and after removal. Only 50 μL sample and 15 min of sample separation are needed. Our method was extensively validated and provides a reliable determination of olefin content in a wide range of pyrolysis oils from plastics and tires and their products after mild hydrotreatment. It is affordable to all researchers and industrial companies working on plastics recycling by thermochemical processes as it does not require an MS detector.

1. Introduction

Pyrolysis of waste plastics to produce pyrolysis oils represents one of the most promising methods for chemical recycling [1,2]. Oils derived from polyolefin plastics could potentially substitute a portion of the steam cracking feedstock [1,3]. Unlike fossil feedstocks, pyrolysis oil from plastics typically contains a high concentration of olefins (8–72 wt %), alongside heteroatoms [4]. Pyrolysis oils from scrap tires, aimed at aromatics and fuel production, also exhibit a notable olefins content [5,6]. These olefins play a significant role in increased coke formation and exchanger fouling during steam cracking, leading to a restriction of their content in steam cracking feedstock to 2 wt% [4]. The presence of olefins in pyrolysis oils from plastics results in low thermal and oxidative stability [7], posing challenges for storage and transportation. Understanding the olefin content in pyrolysis oils from plastics is crucial for advancing towards a circular plastics economy.

Several methods can be used for olefins determination in pyrolysis oils from plastics. Standard titration methods, such as bromine number [8]/index [9,10] and iodine value [11], represent the easiest and fastest methods, leveraging the reactivity of olefinic double bonds with halogens. These methods are widely employed for aliphatic double bonds determination in fossil gasoline fuel [8], biodiesel [11], and vegetable oils [11], and have also been applied to pyrolysis oils from polyolefins and tires [6,12,13]. The reactivity of various compounds is documented for the bromine number (see annexes A1 of ASTM D1159). However, when analyzing pyrolysis oils from plastics, determining double bonds via bromine number is affected by several factors. The lower reactivity of α-olefins and the non-reactivity of the second double bond in conjugated dienes can impede accurate determination. Conversely, the reactivity of polyaromatics [8] and heterocompounds, such as thiols [8], pyrroles [8], and phenoles [14], commonly present in oils from municipal waste plastics [15], can lead to overestimating results. Additionally, expressing results in grams of halogen per 100 g of sample is not as straightforward as wt%.

Gas chromatography (GC) methods are frequently employed for olefins determination in plastic pyrolysis oils. However, the use of 1D-GC methods is characterized by significant co-elution of thousands of analytes in pyrolysis oils, and single quadrupole MS does not exhibit a universal response despite GC-MS is the most used method. Since identifying olefins without their derivation is problematic due to the similar spectra of naphthenes and olefins, only the most abundant

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Abbreviations

$Ag–SiO_2$	silica gel impregnated by $AgNO_3$
DCM	dichloromethane
FID	flame ionization detector
GC	gas chromatography
GC×GC	comprehensive two-dimensional gas chromatography
IS	internal standard
LOQ	limit of quantification
MM	model mixture
MWP	mixed waste plastics
MS	mass spectrometer
PE	polyethylene
PP	polypropylene
RSD	relative standard deviation
SD	standard deviation
SPE	solid phase extraction
STPO	scrap tires pyrolysis oil
TOF-MS	time-of-flight mass spectrometry detector
VUV	vacuum ultraviolet (detector)

olefins can be identified using GC-MS. The problem of significant co-elution of analytes can be mitigated by utilizing comprehensive two-dimensional gas chromatography (GC × GC), which allows for almost complete separation of all analytes. However, even after peak-by-peak identification, which is very time-consuming, distinguishing all olefins from naphthenes can be very challenging [16]. Hang et al. [17] described the elution order of several olefinic groups in the GC × GC chromatogram. However, only the following approaches can be applied for reliable distinguishing of all olefins from naphthenes utilizing TOF-MS detector: (i) decreasing the energy of electron ionization [18,19], (ii) the use of soft ionization techniques like photoionization [20–22], and (iii) bromine addition to double bond [23]. However, these methods are very time-consuming and require a highly educated operator, as manual peak-by-peak identification of MS spectra not present in the library is needed. Moreover, the TOF-MS detector used for this purpose is costly and not affordable for many research groups working on plastics recycling.

The most reliable method for determining olefins likely involves GC-VUV (vacuum ultraviolet detector) [24,25], recently standardized for analyzing pyrolysis oils from plastics as ASTM D8519 [26]. In their latest work, Lazzari et al. [22] demonstrated that the results from VUV correlate with those from TOF-MS with soft ionization. However, GC-VUV is still a relatively new method commercially available since 2014 [24,27]. The instrument is quite expensive and thus quite rare in laboratories.

Our focus was to develop a method that only requires GC × GC-FID, a significantly more cost-effective equipment, for selective and reliable determination of olefins in weight percentages. To achieve this, we optimized the adsorption of olefins over silica gel impregnated by silver nitrate (hereafter called $Ag–SiO_2$). The phenomenon of complexation of π-electrons present in olefins to Ag(I) atoms is well-known and was leveraged for the selective identification of olefins in hydrocarbon samples using high-resolution mass spectrometry [28,29]. Furthermore, a specific silver-containing stationary phase for GC × GC, suitable for separating mixtures containing olefins, has recently been developed [30]. Typically, the complexation of π-electrons to Ag(I) is used to quantitatively determine saturated compounds in hydrocarbon-containing samples after sample elution over $Ag–SiO_2$ [31,32].

Aligned with the principles of green analytical chemistry, the isolation of olefins was downscaled to minimize the consumption of $Ag–SiO_2$ adsorbent, pyrolysis oil sample, and elution solvent. The method underwent optimization to enable quantitative adsorption of compounds containing an aliphatic double bond (aliphatic olefins and styrenes) and complete elution of saturated hydrocarbons and alkylbenzenes. Several model mixtures of olefins and aromatic compounds were used for this purpose. Three approaches were tested to determine olefin content based on GC × GC chromatographic peak area loss. The optimized method was validated using mixtures of model compounds and by spiking an olefins-free sample with an olefins mixture. Finally, the method was applied to analyze a wide range of pyrolysis oils from waste plastics and tires, along with their distillation fractions and hydrotreated products, encompassing a broad spectrum of olefins content.

2. Experimental

2.1. Model mixtures, pyrolysis oils, and their fractions, $Ag–SiO_2$

The list of model compounds used, purities, and suppliers is provided in Table S1. An overview of the composition of the studied model mixtures, labeled as MM**,** is shown in **Tables S2–S6**. 3-Chlorothiophene (>97.0 % pure) was purchased from TCI Chemicals. The solvents of p.a. purity were purchased from Lach-Ner, s.r.o.

Pyrolysis oils were produced from waste polyolefin plastics (sorted polyethylene (PE) and polypropylene (PP), or their mixture 50:50 m/m). Samples were labeled MWP (mixed waste plastics) when the origin was unknown. The second set of samples comprised pyrolysis oils from scrap tires (STPO). A summary of the studied pyrolysis oils and samples used for method validation is provided in Tables S7 and S8 and illustrated in **Fig. S1**.

The pyrolysis oils underwent hydrotreatment using a continuous flow laboratory-scale setup from CACTU Solutions (http://www.cactu.eu; UCT Prague). The hydrotreatment was performed at a constant pressure of 10 MPa and within a temperature range of 180–360 °C over a fixed bed of commercial sulfided $Ni–Mo/Al_2O_3$ catalyst. For further information regarding the hydrotreatment process and the fractional distillation of samples, see our previous publication [6].

Silica gels 60 for column chromatography with particle sizes (p.s.) of 0.040–0.063 mm, 0.015–0.040 mm, 0.063–0.200 mm, and 0.2–0.5 mm were purchased from Merck. Silica gel impregnated with $AgNO_3$ (hereafter called $Ag–SiO_2$) used for the olefins separation was prepared according to the procedure described in a previous study [32]. After impregnation, $Ag–SiO_2$ was activated in the oven at 160 °C for at least 12 h. Empty 3 mL SPE cartridges and respective bottom and top polyethylene frits were purchased from Altium International, s.r.o.

2.2. Analytical methods

2.2.1. Olefins separation over $Ag–SiO_2$

The following parameters were optimized to reach selective olefins separation, allowing their indirect quantification: (i) type of mobile phase, (ii) solvent volume, (iii) $Ag–SiO_2$ storability, (iv) $Ag–SiO_2$ load, (v) SiO_2 particle size, and (vi) elution of low boiling samples. More details can be found in the respective result section.

The optimized scheme for separating olefins over $Ag–SiO_2$ was as follows: A 3 mL SPE cartridge with a bottom frit was filled with 1.45 ± 0.03 g of hot (***freshly activated***) $Ag–SiO_2$ (p.s. 0.040–0.063 mm). This quantity corresponds to the two-level spoonful of the sorbent (using a stainless steel spoon, size 1.25 mL = ¼ teaspoon). The adsorbent was vibrated using a vortex (3000 RPM for at least 10 s), and the top frit was inserted. The sample (15 μL, approximately 12–14 mg) was injected onto the top frit. Dichloromethane (DCM) was dosed into the column in 0.6 mL portions, with each subsequent portion added after the previous one was absorbed. The first 1.8 mL effluent was collected into a 2 mL GC vial. Sample elution was solely supported by gravity. The separation procedure takes up to 10 min, and the parallel separation of multiple samples can significantly accelerate sample preparation. ***This***

separation scheme allows for the selective adsorption of compounds with an aliphatic olefinic group (e.g., olefins, limonenes, and styrenes) and complete elution of iso-alkanes, n-alkanes, monocycloalkanes, dicycloalkanes, tricycloakanes, and alkylbenzenes without an aliphatic olefinic group.

In the case of low-boiling samples (e.g., naphthas or pyrolysis oils containing light compounds), cooling the vial containing the effluent is necessary to prevent the evaporation of low-boiling compounds. A self-made holder for ten SPE columns and vials for effluent (Fig. S2) was used for this purpose. The cooling process itself was achieved by dry ice into the built-in reservoir.

2.3. Data processing – peak area normalization and olefins content determination

The measured data were processed in ChromSpace software. The content of olefins was determined based on the reduction in peak area (before and after olefins adsorption) in regions of iso-alkanes, *n*-alkanes, monocycloalkanes, dicycloalkanes, tricycloakanes, and alkylbenzenes. An overview of olefin types eluting in these regions is summarized in Table S9. Peak area normalization using an internal standard (IS) is crucial for precisely determining this reduction. Three approaches to normalization using different IS were tested: (i) ***n*-alkanes** present in the sample, (ii) **alkylbenzenes** present in the sample, and (iii) **3-chlorothiophene** – an externally added IS.

The optimized scheme for peak area normalization and determination of olefins content was as follows: A known mass (200 μL) of frozen (−18 °C) IS solution (3-chlorothiophene, 2.15–2.35 mg/g in DCM) was added to the 2 mL vial containing the collected DCM effluent from the SPE column after olefins adsorption. The sample (15 μL ≈ 12–14 mg), containing olefins (prior to their adsorption) and non-containing light fractions co-eluting with DCM solvent (initial boiling point >80 °C, as in the case of kerosene and gas oil fractions), was weighted into the 2 mL vial and dissolved in 1.8 mL of DCM. Similar to the sample after olefins adsorption, 200 μL of IS solution was added to this vial. For samples containing light fractions (such as whole pyrolysis oils and naphtha fractions), 30 mg of 3-chlorothiophene was directly added to 0.7–0.8 g of the respective sample. The vial was tightly closed, shaken, and injected into GC × GC under the conditions described in the supporting material.

For all samples of pyrolysis oils and derived fractions, analysis was conducted on the sample prior to olefins adsorption and on four samples devoid of olefins. Equations S1-S5 and S6 summarize the calculation of olefin content in the respective groups in the sample with the final boiling point of <360 °C and above 360 °C, respectively. To analyze these high-boiling samples, a tentative "cut" for fraction boiling up to 360 °C was made; the overview of the last groups included in this fraction is summarized in **Table S10**. The total content of aliphatic olefins represents the sum of olefins content in all respective aliphatic groups in the fraction boiling up to 360 °C. The classification according to carbon number and the compound group was created based on the MS data (see Fig. S3). However, even when only FID is available, the method published by Vozka et al. [33] can be used.

3. Results and discussion

The optimization of the method for determining olefin content based on their separation and final GC × GC-FID analysis consisted of three main steps.

i. Separation of olefins over Ag–SiO$_2$.
ii. Normalization of peak areas obtained by GC × GC-FID analysis.
iii. Validation of the optimized method using model mixtures, pyrolysis oils, and derived samples.

3.1. Optimization of olefins separation over Ag–SiO$_2$

3.1.1. Mobile phase composition

In the first step, an optimum mobile phase for the desired approach was sought. The SPE columns were filled with 1.45 ± 0.03 g of freshly activated Ag–SiO$_2$ (p.s. 0.040–0.063 mm), and the respective mobile phase was dosed to the SPE column with 1.8 mL of effluent was collected. Nine solvents and their mixtures, differing in polarity index (Table S11), were tested for the separation of model mixtures MM-1 (olefin-rich) and MM-2 (aromatic-rich). The results showed that the elution mechanism of different compounds over Ag–SiO$_2$ is a much more complex process than expected.

The use of ***toluene*** promoted the elution of all compounds containing aromatic rings and almost all olefins. The only compound adsorbed from the tested mixtures was limonene. Surprisingly, more polar ***chlorobenzene*** almost met our requirements. Besides the partial elution of α-pinene, the main drawback was the size of the chlorobenzene peak, which, due to co-elution, hindered the monitoring of the lightest compounds during used 1D-GC analysis.

The testing of four ***oxygen-containing solvents*** proved them unsuitable for the desired purpose, most probably due to their coordination/complexation with Ag(I) atoms, resulting in the elution of all compounds from tested mixtures except for 1-octyne. A similar effect of oxygenates on the separation of olefins and saturated compounds over an Ag(I)-modified membrane was observed by Zyl and Linkov [34].

The most promising results were proved for DCM and chloroform, characterized by almost complete elution of alkylbenzenes and perfect selectivity for adsorption of compounds containing aliphatic double bonds. The results are summarized in Table S12 and Table S13, respectively.

Based on the previous test, multiple binary mixtures of these most promising solvents were tested to describe the elution of compounds and identify the ideal solvent combination. As shown in **Fig. 1**, adding DCM and chloroform to *n*-pentane resulted in the desired effect. Surprisingly, the more polar chloroform proved less effective for the elution of aromatics. ***This test demonstrated that DCM is the optimal mobile phase for the complete elution of saturated hydrocarbons and alkylbenzenes and the selective adsorption of compounds containing the aliphatic olefinic group.*** The chromatographic separation of olefins using DCM is described in detail in the next section.

3.1.2. DCM solvent volume

For the detailed description of the olefins separation, model mixtures MM-1 (olefin-rich), MM-2 (aromatic-rich), and MM-3 (complex) were eluted with DCM, and 16 fractions with a total volume of 7.2 mL were collected (6 × 0.3 mL at first and 9 × 0.6 mL thereafter) and analyzed separately. The obtained results showed that the collection of 1.8 mL of effluent for all model mixtures ***was a perfectly chosen volume, as it allowed complete elution of all saturated compounds and alkylbenzenes while simultaneously achieving complete adsorption of all compounds containing aliphatic olefinic double bonds*** (Fig. 2 and **S4B**). Even α-pinene, an extreme example of an olefinic molecule characterized by a sterically hindered double bond, began to elute in the next 0.6 mL increment (1.8–2.4 mL). All other olefin group-containing compounds started to elute much later, and for several compounds like cyclohexene and α-terpinene, elution was not observed even after 7.2 mL of DCM (Fig. S5B).

3.1.3. Storability of Ag–SiO$_2$

The maximum activity of Ag–SiO$_2$ in this type of separation is crucial and can be decreased by exposure to air moisture. A set of tests was performed to check the necessity of using freshly activated (hot) adsorbent. Two different storage approaches over 27 days in a dark place of the freshly activated adsorbent were studied: (i) storing prefilled SPE columns ready to use in evacuated bags, and (ii) storing the adsorbent in an air-tight glass bottle and filling of SPE cartridges

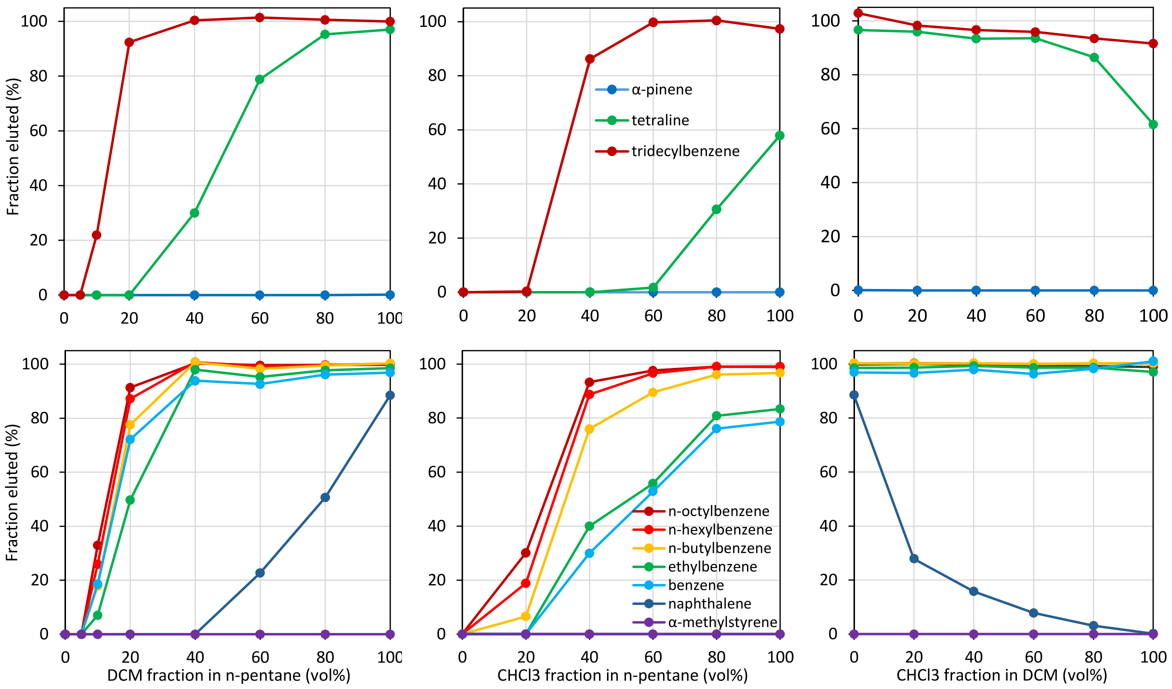


Fig. 1. The effect of mobile phase composition on the separation of MM-1 (top) and MM-2 (bottom).

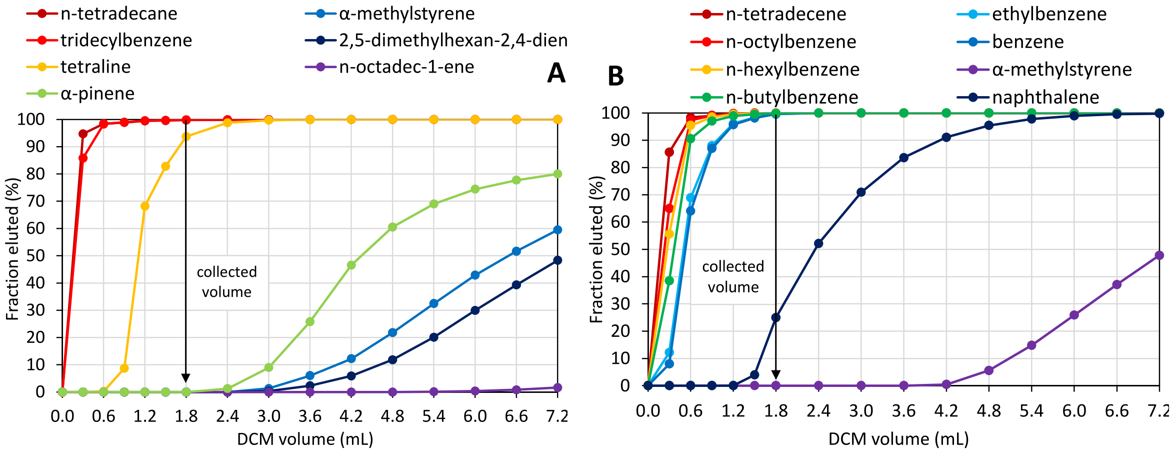


Fig. 2. Cumulative amount of compound fraction eluted for MM-1 **(A),** and MM-2 **(B),** not shown olefins which did not start eluting within 7.2 mL.

immediately before the separation.

The storage experiments demonstrated that the freshly activated adsorbent completely separated α-pinene and α-methylstyrene from the model mixture (Fig. S6). No effect of amylene presence in DCM (2-methyl-2-butene, used as a free radical scavenger) on olefin adsorption was observed (Table S14 and S15). After 24 h from Ag–SiO_2 activation, traces of α-pinene from the MM-1 (olefin-rich) began to pass through the adsorbent. In the first days of storage, storage in a bottle showed poorer results (Fig. S6A), but over time, storage of the adsorbent in prefilled SPE columns in evacuated bags proved to be a significantly worse approach (Fig. S6B). After 27 days, the prefilled adsorbent retained almost no α-pinene and α-methylstyrene, and almost 50 % of 2,5-dimethyl-2,4-hexadiene eluted through the adsorbent. Insufficient adsorption was observed for 1-octadecene, an example of α-olefins present in significant amounts in pyrolysis oils from polyolefins [35]. ***The use of adsorbent, which was freshly activated at 160 °C and dosed into SPE cartridges while still hot, has proven to be a crucial approach, which is 100 % reliable and characterized by perfect reproducibility and maximal activity for olefins adsorption.***

3.1.4. Effect of Ag–SiO_2 load

Up to this point, a constant mass of adsorbent (p.s. of 0.040–0.063 mm), specifically 1.45 ± 0.03 g, was utilized in the SPE cartridge, along with an injection of 15 μL (≈12–14 mg) of the sample. When the adsorbent load was reduced to 1.38, 1.30, and 1.20 g (while maintaining a constant sample injection volume of 15 μL), only negligible deterioration of adsorption activity was observed, which was not clearly related to adsorbent mass (Table S16). Although a lower adsorbent mass did not significantly affect the separation efficiency, ***we recommend using the adsorbent mass of 1.45 ± 0.03 g to ensure sufficient adsorbent capacity***. We validated that the less precise volumetric dosing of adsorbent using a spoon of defined volume (as described in section 2.2.1) is practical, as it can significantly expedite the SPE column preparation process.

3.1.5. *Effect of Ag–SiO_2 particle sizes*

SiO_2 with a p.s. of 0.040–0.063 mm was used for all previous tests. As expected, the elution tests of MM-3 (complex) model mixture over Ag–SiO_2, prepared from SiO_2 with three other commercially available p. s. (0.015–0.040, 0.063–0.200, and 0.2–0.5 mm), showed that the use of SiO_2 with larger particles significantly accelerates the effluent elution (Fig. 3A). However, this elution acceleration came at the cost of worse adsorption effectiveness for several olefins (Fig. 3B). On the other hand, using the finest particles (0.015–0.040 mm) excessively prolonged the elution to more than 30 min, which could increase the evaporation risk of the low boiling compounds (see section 3.2.6). Moreover, the high dustiness made manipulating such fine powder very uncomfortable and dangerous. Nevertheless, the finest tested p.s. was the most effective for olefin adsorption (Figs. S5 and S6). The acceleration of elution by applying slight overpressure to complete it within approximately 60 s significantly worsened the effectiveness and reproducibility of olefin adsorption (Fig. 3B–Table S17). Based on all the above-mentioned observations, the ***p.s. of 0.040–0.063 mm was considered the best for this separation.***

3.1.6. *Separation of low-boiling samples*

Our method for determining olefins relies on their disappearance from the chromatogram after their selective adsorption over Ag–SiO_2. A critical assumption is that all saturated and monoaromatic compounds are entirely eluted. However, the decrease in peak area for low boiling non-olefinic compounds after elution may be due to their evaporation during the 10 min of elution at laboratory temperature. To simulate this potential issue and validate its possible mitigation, we designed an SPE column stand that cools vials using dry ice inserted into a built-in reservoir (see Fig. S2B). This study used a model mixture of 11 saturated hydrocarbons (**MM-CH**, Table S6) with boiling points ranging from 36 to 253 °C. The model mixture was pre-cooled in the freezer to −18 °C, and the effluent was collected at a temperature of +25 °C compared to −20 °C. The results revealed that ***vial cooling during effluent collection is crucial for low-boiling samples, especially those containing C5 and C6 hydrocarbons.*** We demonstrated that almost 25 % of *n-pentane* can evaporate during sample collection. However, even with vials cooled to −20 °C, evaporation of C5 compounds cannot be entirely eliminated (**Fig. S7**), which implies that the determination of C5 olefins by this method may lead to overestimated values.

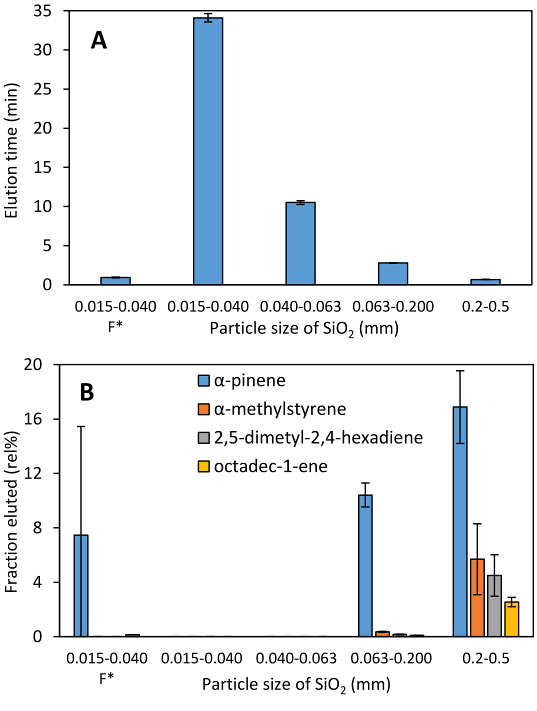


Fig. 3. Effect of SiO_2 particle size at constant Ag–SiO_2 mass on elution time (**A**) and adsorption of olefins (**B**), F* = elution accelerated by constant slight overpressure.

Conversely, vial cooling can significantly reduce the evaporation of C6 hydrocarbons, thus aiding in the developed method's more accurate determination of C6 olefins. However, cooling broad distillation range waxy oils from PE pyrolysis before their injection into the SPE column can pose a challenge as long-chain paraffins can crystalize even at 4 °C. For such samples, it is necessary to account for the slight overestimation of olefin content in the C5 and C6 groups due to the inability to cool the samples. Nevertheless, the content of the lightest hydrocarbons (C5 and C6) in these waxy samples is usually negligible (<5 %) [36], if present at all [4].

3.2. *Olefins determination – peak normalization*

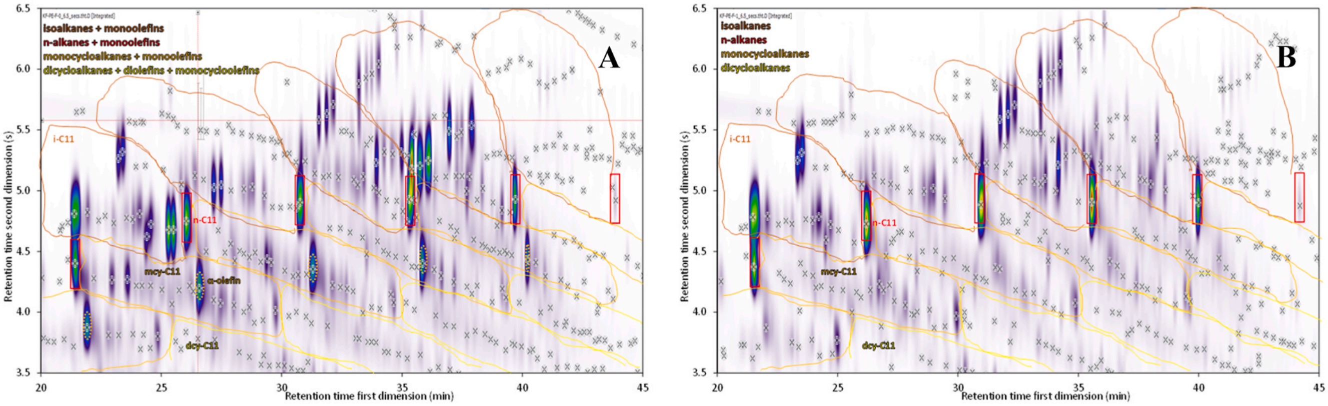
The method relies on monitoring area losses in the respective groups, and ensuring reliable monitoring of area loss involves normalizing the area of the respective groups before and after the selective removal of olefins. Theoretically, selected compounds already present in the sample and characterized by complete elution from Ag–SiO_2 could serve as a "native" internal standard (IS). Three alternative IS were tested for normalization: (i) ***n*-alkanes** present in the sample, (ii) **alkylbenzenes** present in the sample, and (iii) **3-chlorothiophene** – an externally added IS.

The native IS approach can only be applied to specific samples characterized by higher abundance (1–5 wt%) of these compounds. Pyrolysis oils from polyolefins often do not contain significant amounts of respective alkylbenzenes, and pyrolysis oils from tires are characterized by very low amounts of *n*-alkanes. While the classification for *n*-alkanes is usually commonly prepared, an appropriate alkylbenzene molecule applicable for this purpose must be found first. Based on our experience, cumene, characterized by an isolated peak (Fig. S8) and present at higher concentrations in studied pyrolysis oils from both polyolefins and tires, was a perfect example of alkylbenzene IS. *n*-Alkanes can be used as a native IS only for very few samples, as not only their low concentration in tire oil is a problem but also, with increasing PP content in plastic polyolefin waste, the number of iso-alkanes and especially iso-alkenes co-eluting with *n*-alkanes increases. ***The co-elution of iso-alkenes with n-alkanes, which would be hardly possible to identify using an MS detector, was easily determined by our method based on the n-alkane peak area loss after sample separation over Ag–SiO_2*** (see Fig. 4).

The only versatile solution applicable for all samples without the need for validation of the approach's suitability is using an externally added IS. As no hydrocarbon exists that would not be present in the pyrolysis oils samples and would elute completely from Ag–SiO_2, a known amount of 3-chlorothiophene was added to the sample before and after the olefins separation. The optimized procedure for peak normalization and olefins content determination is summarized in experimental section **2.3.** The use of different internal standards for peak area normalization before and after the separation of olefins was compared. The results summarized in **Table S18** showed only minimal differences in the results when IS was present at higher concentrations (>0.5 wt%).

3.3. *Validation of the method*

Currently, the only reliable method for determining olefins in weight percentages in pyrolysis oils from plastics (and possibly tires) is GC-VUV, using the newly established ASTM D8519 published in July 2023. However, like most research teams working on recycling plastics and tires, we are not equipped with this pricy instrument. Consequently, we are unable to validate our method using reference method data.



n-alkane content (wt%)	C10	C11	C12	C13	C14	C15
apparent with olefins (A)	2.65	3.16	3.34	5.05	1.86	0.07
real without olefins (B)	2.12	3.00	3.24	3.27	1.84	0.06

Fig. 4. Composition of crude pyrolysis oil from waste PP/PE mixture with olefins (**A**), after olefins separation over Ag–SiO_2 (**B**) obtained via GC × GC-FID.

Therefore, our optimized method of olefins determination was validated by analyzing several model mixtures, real pyrolysis oils, and derived samples.

3.3.1. JET-A1 kerosene spiked by MM-4

The initial validation of olefins determination in real hydrocarbon mixtures involved adding a known quantity of a mixture of 18 model olefin compounds, available in sufficient purity (**MM-4**), to olefins-free fossil kerosene (JET-A1). The **MM-4** model mixture contained only compounds boiling between 110 and 300 °C, thus representing olefins that can entirely evaporate in the GC injector. Additionally, due to their higher initial boiling point, co-elution with the DCM solvent is eliminated. Seven spiking concentrations ranging from 0.5 to 35 wt% olefins were prepared (Table 1).

As shown in Table 1, the results of the optimized method for these model samples correlated reasonably well with the reference value (obtained by weighing) up to the sample with approximately 2.5 wt% of olefins. For higher olefins content (>5 wt%), the measurement demonstrated relatively good precision (RSD <5 %) and excellent accuracy (relative difference of value from weighing vs. measuring <3 %). However, a significant deterioration of repeatability was observed for the sample containing 4.37 wt% of olefins, although the accuracy remained quite good. For even lower olefins content, the method's repeatability and accuracy deteriorate considerably, with results showing up to 50 % discrepancy from the reference value for the sample with ~1 wt% of olefins. To estimate upper range limitation, pure MM-4 (not diluted, 98.3 wt% olefins) was eluted over Ag–SiO_2. Only traces of α-methylstyrene (<0.01 %rel.) and 1.2 %rel. of 3-ethyl-5-methylhex-2-ene from the injected sample were determined in the effluent (**Table S19**). These observations provide the basis for the perfect suitability of the method for analyzing crude plastic pyrolysis oils characterized by high olefins content (8–72 wt%) [4].

Table 1
Results for JET-A1 sample spiked by olefinic model mixture MM-4 (n = 4).

MM-4 in JET-A1 (wt%)	Aliphatic olefins content			
	Prepared (wt %)[a]	Determined (wt %)	RSD (%)	Difference (rel. %)
40.71	34.90	35.88	0.4	2.8
20.46	17.54	17.55	1.7	0.1
9.80	8.41	8.35	3.3	−0.6
5.09	4.37	4.29	9.0	−1.7
2.71	2.32	2.17	21.1	−6.5
1.09	0.94	0.49	31.6	−47.5
0.50	0.43	−0.67	–	–
0	0.00	−0.03	–	–

[a] as prepared by weighing of JET-A1 and MM-4.

The determination of styrenes showed a slight overestimation of the results, even for the sample with the highest styrenes concentration (Table S20). This discrepancy can be attributed to the higher polarity of alkylbenzenes with shorter alkyl substituents. Even though the elution of ~98–99.9 % of respective alkylbenzenes can be reached, it may still not be sufficient for accurately determining styrenes using our indirect method. It is improbable that the JET-A1 sample, without added olefins, would contain any styrenes. These findings suggest that the determination of styrenes throughout our indirect method would only apply to crude pyrolysis oils characterized by a higher content of styrenes. The main benefit of this method could be to validate that no other styrenes besides styrene and α-methylstyrene are present in the sample.

The above-mentioned observations are not surprising, as a lower decrease in peak area due to lower olefin content would naturally result in lower accuracy and precision in determining these smaller differences. The model samples contained a limited number of olefins, leading to relatively high peak areas even at lower total olefin concentrations. Therefore, it is highly probable that for real pyrolysis oils characterized by a much higher number of olefinic compounds, the limit of quantification (LOQ) lies around 5 wt% of olefins in the sample. The dilution approach was used to simulate this problem, as described in the following section.

3.3.2. Dilution of kerosene fraction of pyrolysis oil from polyolefins

To evaluate the reliability of the method for samples with lower total olefins content spanning hundreds of compounds, a kerosene fraction of raw pyrolysis oil from PE (PE-KE-feed) was diluted with kerosene of the same oil after deep hydrotreatment at 360 °C at 10 MPa (PE-KE-360/10) without olefins. The results of this test, summarized in **Table 2**, demonstrate that 5 wt% of olefins approximately represent the reliable LOQ of our method. The repeatability of determination increased beyond 5 %, and the measured value exhibited a relative difference of nearly 11 % from the prepared one.

3.3.3. Hydrotreated pyrolysis oil spiked by MM-4

Previous validations utilized kerosenes, which can completely evaporate to GC, with none of their compounds co-eluting with DCM. The final method validation approach involved spiking pyrolysis oil from a waste PP and PE mixture after deep hydrotreatment at 360 °C and 10 MPa (PP/PE-360/10) with an olefins mixture **MM-4**. This hydrotreated pyrolysis oil contained about 8 wt% of the fraction boiling above

Table 2
Results for PE-KE-feed diluted by PE-KE-360/10 (n = 4).

Sample name	Dilution[a]	Aliphatic olefins (wt%)[b]	RSD (%)	Dilution[c]	Difference (rel%)
PE-KE-feed	0	30.86		0	
PE-KE-A	0.508	15.68	4.8	0.506	−0.35
PE-KE-B	0.340	10.20	3.9	0.331	−2.85
PE-KE-C	0.170	4.68	7.1	0.152	−10.78
PE-KE-D	0.079	2.03	70.3	0.066	−16.52

[a] as prepared by weighing of PE-KE-feed and PE-KE-360/10.
[b] as determined by optimized method, the value for PE-KE-feed represents the average determined by the alternative approaches (see Table S18).
[c] as determined from the results of the optimized method.

360 °C (Fig. S1), posing challenges for GC analysis with a split injector. To determine the olefins content in the fraction boiling up to 360 °C, **Equation S(6)** was used utilizing the known content of this fraction from SIMDIST (Table S7). As can be seen from **Table S21**, for both spiking concentrations of 8.54 and 34.88 wt% of olefins, the results showed an acceptable correlation with the reference value obtained by sample preparation. Acceptable repeatability was observed for both aliphatic olefins and styrenes determination. However, similar to spiking the JET-A1 sample, an overestimation of the styrene content was noted, and it increased as their content decreased.

3.4. Real samples analysis

The analysis of raw pyrolysis oils from plastics and tires revealed that for olefins contents exceeding 1 wt%, both total and individual olefin groups exhibited excellent repeatability, with RSD much lower than 5 %. Illustrated by the various pyrolysis oils from tires, it is possible to observe whether olefins are mainly presented in limonene-like structures (eluting in tricycloalkanes region) or other groups, see Table 3. Additionally, a perfect correlation was observed between the results of olefins content in the calculated fraction boiling up to 360 °C based on the SIMDIST results (STPO 3*) and the result determined for this fraction isolated by distillation (STPO 3 fr.<360 °C). This observation further validates our approach to whole sample analysis.

The results for other analyzed pyrolysis oils are summarized in Tables S22 and S23. The results for individual groups make it possible to glean valuable information about the sample's origin. Despite both samples of pyrolysis oil from mixed waste plastics (MWP) exhibiting comparable total olefins contents of 58.4 vs. 53.1 wt% (MWP 1 vs. 2), they significantly differed in the content of iso-alkenes (which primarily elute in iso- and *n*-alkanes) and linear alkenes (eluting in monocycloalkanes). From the significantly higher content of iso-alkenes in MWP 1 (33.6 wt%) compared to MWP 2 (6.8 wt%), we can estimate that a larger proportion of PP was present in the feedstock from which the sample MWP 1 was produced.

The developed method for olefins determination is suitable for monitoring olefins in crude pyrolysis oils and their distillation fractions. Additionally, it can be employed to monitor olefins in products after hydrotreatment. To demonstrate this application, we analyzed kerosene fractions of pyrolysis oil from waste PP/PE mixture and scrap tires before and after hydrotreatment over Ni–Mo/Al$_2$O$_3$ catalyst at various temperatures while maintaining a constant pressure of 10 MPa. Fig. 5 illustrates differences in olefin hydrogenation at different temperatures for two different pyrolysis oils. More detailed results for olefins content in individual groups are shown in Tables S24 and S25. These tables revealed an increasing error in olefins determination (shown as RSD) with decreasing amounts of olefins.

3.5. Weaknesses of the method

Our method offers a straightforward approach for accurately determining olefins content in pyrolysis oils from plastics and tires, utilizing affordable instrumentation. Thanks to its simplified design, we are well aware of several factors influencing olefins determination.

(i) The method ***can provide reliable results*** for determining olefins content >5 wt%.
(ii) The method ***cannot determine*** olefins eluting in iso-C7, *n*-C6, and C6-monocycloalkanic groups due to their co-elution with the DCM (solvent) peak. Like other GC methods employing split/splitless injectors, our method reliably determines only olefins boiling up to 360 °C.
(iii) ***Overestimation*** of low-boiling point olefins in C5 and C6 groups ***cannot be entirely eliminated,*** even when the vial with effluent is cooled (see section **3.2.6**). It has to be pointed out that these light olefins can be easily determined by GC-FID utilizing the PONA column.
(iv) ***Overestimation*** of the olefins content can also result from several ***heterocompounds*** eluting in their respective regions of the GC chromatogram. These compounds will be adsorbed on Ag–SiO$_2$ along with olefins. If present in the sample, aliphatic alcohols, ketones, thiols, sulfides, amines, and nitriles will be determined

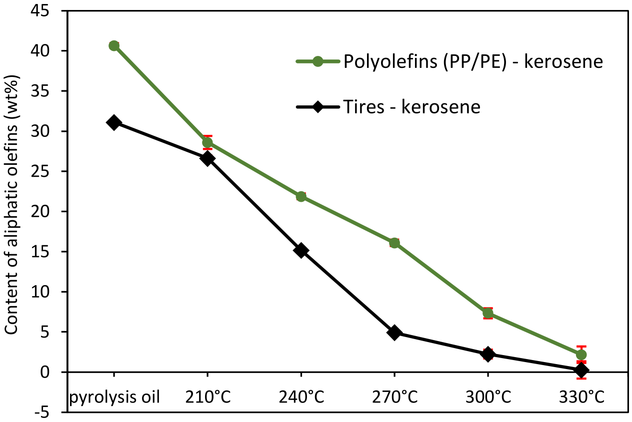


Fig. 5. Kerosene fraction of PP/PE and tires pyrolysis oil before and after hydrotreatment at different temperatures.

Table 3
Olefins content in different pyrolysis oils from scrap tires (STPO).

Olefins in	STPO 1 (wt%)	RSD (%)	STPO 2 (wt%)	RSD (%)	STPO 3 (wt%)	RSD (%)	STPO 3[a] (wt%)	STPO 3 fr. <360 °C (wt%)	RSD (%)
n-alkanes	0.14	9.1	0.17	11.7	0.11	17.1	0.14	0.16	2.9
i-alkanes	0.70	23.6	0.34	4.2	0.52	7.7	0.68	1.71	1.7
monocycloalkanes	2.28	3.7	1.99	0.9	1.78	3.0	2.31	2.01	0.2
dicykloakanes	13.52	0.9	5.25	0.5	6.01	0.9	7.83	7.53	0.3
tricycloalkanes	11.13	0.1	1.61	0.6	3.58	0.4	4.66	4.73	0.1
Σ aliphatic olefins	27.76	1.4	9.36	0.5	12.00	0.9	15.62	16.14	0.3
Styrenes	4.37	3.2	2.86	6.9	4.01	5.4	5.23	3.75	2.2

[a] content of olefins in the fraction boiling up to 360 °C is based on its yield determined by SIMDIST.

as aliphatic olefins [15,17,37,38]. In our view, oxygenates present in pyrolysis oils from polyolefins can be considered the most problematic group in this regard. Phenols, cyclopentanones, and benzonitriles represent the most abundant heterocompounds in our samples. As these compounds elute out of the elution region of the aliphatic olefins, their presence does not affect the olefins determination by our method. Thiophenes and possibly other heterocompounds of similar polarity will be identified as styrenes. This is a significant challenge, particularly for pyrolysis oils from tires characterized by high sulfur content (≈1 wt%) [6, 39].

(v) ***Olefins, which are not fully adsorbed on Ag–SiO$_2$, will not be detected***, leading to ***an underestimation*** of the results. The method underwent extensive validation to detect even olefins characterized by three substitutions hindering the double bond. Testing numerous model compounds revealed only one olefin our method cannot identify. The double bond in the tetra-isobutylene molecule is hindered by several side methyl branches, and spatial hindrance of the whole molecule is likely responsible for limited adsorption over Ag–SiO$_2$ (Table S26).

Despite these known limitations, our method has the great potential to provide more accurate and reliable results than other commonly available methods. Its simplicity makes it ready for routine analyses of hydrocarbon mixtures rich in olefins, eliminating the need for time-consuming identification of MS spectra of unknown olefins by skilled experts. When detailed olefins analysis is of interest, the adsorbed olefins can be desorbed from the Ag–SiO$_2$ using, e.g., tetrahydrofuran or ethyl acetate and analyzed directly by GC × GC-MS. The removal of naphthenes from the olefin elution region can make compound identification easier.

4. Conclusions

The quantification of olefins in pyrolysis oils significantly advances the chemical recycling of waste polyolefins and tires. Our developed method relies on GC × GC-FID analysis of the sample before and after selective adsorption of olefins over Ag–SiO$_2$. It represents the most cost-effective approach for determining the olefins content (wt%) in these samples. Through extensive validation, we have demonstrated that the method yields precise and accurate results across a wide range of samples. Given the surge in plastics and tires chemical recycling in recent years, our method has the potential to accelerate this research by offering faster, more accessible, reliable, and affordable sample characterization. While our research primarily focused on determining olefins in pyrolysis oils from plastics and tires, the method holds applicability for both qualitative and quantitative monitoring of olefins in various samples despite the mentioned limitations.

CRediT authorship contribution statement

Miloš Auersvald: Writing – review & editing, Writing – original draft, Visualization, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Michal Šiman:** Investigation. **Petr Vozka:** Writing – review & editing, Methodology, Funding acquisition. **Petr Straka:** Writing – review & editing, Visualization, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Milos Auersvald reports financial support was provided by Ministry of Education Youth and Sports of the Czech Republic. Petr Straka reports equipment, drugs, or supplies was provided by Technology Agency of the Czech Republic. Petr Vozka reports financial support was provided by National Science Foundation. Petr Vozka reports financial support was provided by Cal State LA RSCA. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References

[1] O. Dogu, M. Pelucchi, R. Van de Vijver, P.H.M. Van Steenberge, D.R. D'Hooge, A. Cuoci, M. Mehl, A. Frassoldati, T. Faravelli, K.M. Van Geem, The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: state-of-the-art, challenges, and future directions, Prog. Energy Combust. Sci. 84 (2021) 100901.

[2] L. Dai, N. Zhou, Y. Lv, Y. Cheng, Y. Wang, Y. Liu, K. Cobb, P. Chen, H. Lei, R. Ruan, Pyrolysis technology for plastic waste recycling: a state-of-the-art review, Prog. Energy Combust. Sci. 93 (2022) 101021.

[3] M. Kusenberg, A. Eschenbacher, L. Delva, S. De Meester, E. Delikonstantis, G. D. Stefanidis, K. Ragaert, K.M. Van Geem, Towards high-quality petrochemical feedstocks from mixed plastic packaging waste via advanced recycling: the past, present and future, Fuel Process. Technol. 238 (2022) 107474.

[4] M. Kusenberg, A. Eschenbacher, M.R. Djokic, A. Zayoud, K. Ragaert, S. De Meester, K.M. Van Geem, Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: to decontaminate or not to decontaminate? Waste Management 138 (2022) 83–115.

[5] A. Quek, R. Balasubramanian, Liquefaction of waste tires by pyrolysis for oil and chemicals—a review, J. Anal. Appl. Pyrol. 101 (2013) 1–16.

[6] P. Straka, M. Auersvald, D. Vrtiška, H. Kittel, P. Šimáček, P. Vozka, Production of transportation fuels via hydrotreating of scrap tires pyrolysis oil, Chem. Eng. J. 460 (2023) 141764.

[7] N. Hassibi, R. Benrabah, Y.A. Vega-Bustos, B. Sirjean, P.-A. Glaude, G. Mauviel, V. Burklé-Vitzthum, Oxidative stability of hydrocarbons produced by pyrolysis of polypropylene, Fuel 358 (2024) 130121.

[8] ASTM D1159 - 23; Standard Test Method for Bromine Numbers of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration.

[9] ASTM D1492-21; Standard Test Method for Bromine Index of Aromatic Hydrocarbons by Coulometric Titration.

[10] ASTM D2710-20; Standard Test Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration.

[11] EN 14111; Fat and Oil Derivatives – Fatty Acid Methyl Esters (FAME) - Determination of Iodine Value.

[12] J. Walendziewski, Engine fuel derived from waste plastics by thermal treatment, Fuel 81 (4) (2002) 473–481.

[13] J.M. Escola, J. Aguado, D.P. Serrano, L. Briones, Transportation fuel production by combination of LDPE thermal cracking and catalytic hydroreforming, Waste Management 34 (11) (2014) 2176–2184.

[14] M. Auersvald, M. Staš, P. Šimáček, Electrometric bromine number as a suitable method for the quantitative determination of phenols and olefins in hydrotreated pyrolysis bio-oils, Talanta 225 (2021) 122001.

[15] H.E. Toraman, T. Dijkmans, M.R. Djokic, K.M. Van Geem, G.B. Marin, Detailed compositional characterization of plastic waste pyrolysis oil by comprehensive two-dimensional gas-chromatography coupled to multiple detectors, J. Chromatogr. A 1359 (2014) 237–246.

[16] A. Lelevic, C. Geantet, M. Moreaud, C. Lorentz, V. Souchon, Quantitative analysis of hydrocarbons in gas oils by two-dimensional comprehensive gas

chromatography with vacuum ultraviolet detection, Energy & Fuels 35 (17) (2021) 13766–13775.

[17] H. Dao Thi, M.R. Djokic, K.M. Van Geem, Detailed group-type characterization of plastic-waste pyrolysis oils: by comprehensive two-dimensional gas chromatography including linear, branched, and di-olefins, Separations 8 (7) (2021).

[18] H. Burdová, D. Pilnaj, P. Kuráň, Application of low-energy-capable electron ionization with high-resolution mass spectrometer for characterization of pyrolysis oils from plastics, J. Chromatogr. A 1711 (2023) 464445.

[19] M.S. Alam, C. Stark, R.M. Harrison, Using variable ionization energy time-of-flight mass spectrometry with comprehensive GC×GC to identify isomeric species, Anal. Chem. 88 (8) (2016) 4211–4220.

[20] A. Giri, M. Coutriade, A. Racaud, K. Okuda, J. Dane, R.B. Cody, J.-F. Focant, Molecular characterization of volatiles and petrochemical base oils by photo-ionization GC×GC-TOF-MS, Anal. Chem. 89 (10) (2017) 5395–5403.

[21] M. Beccaria, M. Piparo, Y. Zou, P.-H. Stefanuto, G. Purcaro, A.L. Mendes Siqueira, A. Maniquet, P. Giusti, J.-F. Focant, Analysis of mixed plastic pyrolysis oil by comprehensive two-dimensional gas chromatography coupled with low- and high-resolution time-of-flight mass spectrometry with the support of soft ionization, Talanta 252 (2023) 123799.

[22] E. Lazzari, M. Piparo, C. Mase, L. Levacher, P.-H. Stefanuto, G. Purcaro, J.-F. Focant, P. Giusti, Chemical elucidation of recycled plastic pyrolysis oils by means of GC×GC-PI-TOF-MS and GC-VUV, J. Anal. Appl. Pyrol. 176 (2023) 106224.

[23] T.J. Trinklein, J. Jiang, R.E. Synovec, Profiling olefins in gasoline by bromination using GC×GC-TOFMS followed by discovery-based comparative analysis, Anal. Chem. 94 (26) (2022) 9407–9414.

[24] K.A. Schug, I. Sawicki, D.D. Carlton Jr., H. Fan, H.M. McNair, J.P. Nimmo, P. Kroll, J. Smuts, P. Walsh, D. Harrison, Vacuum ultraviolet detector for gas chromatography, Anal. Chem. 86 (16) (2014) 8329–8335.

[25] P. Walsh, M. Garbalena, K.A. Schug, Rapid analysis and time interval deconvolution for comprehensive fuel compound group classification and speciation using gas chromatography–vacuum ultraviolet spectroscopy, Anal. Chem. 88 (22) (2016) 11130–11138.

[26] ASTM-D8519, Standard Test Method for Determination of Hydrocarbon Types in Waste Plastic Process Oil Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection, GC-VUV), West Conshohocken, PA, 2023. www.astm.org.

[27] VUV Analytics Awarded, "Best new analytical instrument" at the gulf coast conference. https://vuvanalytics.com/vuv-analytics-awarded-best-new-analytical-instrument-at-the-gulf-coast-conference/, 2014. January 18th, 2024.

[28] Y. Zhang, C. Huang, F. Kong, Y. Wang, Q. Shi, L. Zhang, Selective molecular characterization of olefins in hydrocarbon mixtures by Ag+ complexation ESI high-resolution mass spectrometry, Fuel 319 (2022) 123760.

[29] S.D. Sherrod, A.J. Diaz, W.K. Russell, P.S. Cremer, D.H. Russell, Silver nanoparticles as selective ionization probes for analysis of olefins by mass spectrometry, Anal. Chem. 80 (17) (2008) 6796–6799.

[30] I.D. Souza, H. Nan, M.E.C. Queiroz, J.L. Anderson, Tunable silver-containing stationary phases for multidimensional gas chromatography, Anal. Chem. 91 (8) (2019) 4969–4974.

[31] B. Bennett, S.R. Larter, Quantitative separation of aliphatic and aromatic hydrocarbons using silver Ion−Silica solid-phase extraction, Anal. Chem. 72 (5) (2000) 1039–1044.

[32] P. Straka, D. Maxa, M. Staš, A novel method for the separation of high-molecular-weight saturates from paraffinic petroleum based samples, Org. Geochem. 128 (2019) 63–70.

[33] P. Vozka, G. Kilaz, How to obtain a detailed chemical composition for middle distillates via GC × GC-FID without the need of GC × GC-TOF/MS, Fuel 247 (2019) 368–377.

[34] A.J. van Zyl, V.M. Linkov, Influence of oxygen-containing hydrocarbons on the separation of olefin/paraffin mixtures using facilitated transport, J. Membr. Sci. 133 (1) (1997) 15–26.

[35] M.S. Abbas-Abadi, M. Kusenberg, A. Zayoud, M. Roosen, F. Vermeire, S. Madanikashani, M. Kuzmanović, B. Parvizi, U. Kresovic, S. De Meester, K.M. Van Geem, Thermal pyrolysis of waste versus virgin polyolefin feedstocks: the role of pressure, temperature and waste composition, Waste Management 165 (2023) 108–118.

[36] M. Kusenberg, A. Zayoud, M. Roosen, H.D. Thi, M.S. Abbas-Abadi, A. Eschenbacher, U. Kresovic, S. De Meester, K.M. Van Geem, A comprehensive experimental investigation of plastic waste pyrolysis oil quality and its dependence on the plastic waste composition, Fuel Process. Technol. 227 (2022) 107090.

[37] M. Auersvald, L. Kejla, A. Eschenbacher, H.D. Thi, K.M. Van Geem, P. Šimáček, Detailed characterization of sulfur compounds in fast pyrolysis bio-oils using GC × GC-SCD and GC–MS, J. Anal. Appl. Pyrol. 159 (2021) 105288.

[38] M. Staš, M. Auersvald, P. Vozka, Two-dimensional gas chromatography characterization of pyrolysis bio-oils: a review, Energy & Fuels 35 (10) (2021) 8541–8557.

[39] M.S. Abbas-Abadi, M. Kusenberg, H.M. Shirazi, B. Goshayeshi, K.M. Van Geem, Towards full recyclability of end-of-life tires: challenges and opportunities, J. Clean. Prod. 374 (2022) 134036.