RSC Advances

PAPER

Cite this: *RSC Adv.*, 2024, **14**, 9892

Quantification of the composition of pyrolysis oils of complex plastic waste by gas chromatography coupled with mass spectrometer detector†

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Received 9th January 2024
Accepted 19th March 2024

DOI: 10.1039/d4ra00226a

rsc.li/rsc-advances

Waste valorisation through pyrolysis generates solid, liquid and gaseous fractions that need to be deeply characterised in order to try to recover secondary raw materials or chemicals. Depending on the waste and the process conditions, the liquid fraction obtained (so-called pyrolysis oil) can be very complex. This work proposes a method to quantitatively measure the composition of pyrolysis oils coming from three types of polymeric waste: (1) plastic packaging from sorting plants of municipal solid waste, (2) plastic rich fractions rejected from sorting plants of waste of electrical and electronic equipment and (3) end-of-life carbon/glass fibre reinforced thermoset polymers. The proposed methodology uses a gas chromatography (GC) coupled with mass spectrometer detector (MS) analytical technique, a certified saturated alkanes' mix, an internal standard and fourteen model compounds. Validation of the methodology concluded that the average relative error was between −59 wt% and +62 wt% (with standard deviations between 0 wt% and 13 wt%). Considering that the state-of-the-art scenario to quantify complex plastic pyrolysis oils as a whole is almost none and that they are usually evaluated only qualitatively based on the area percentage of the GC-MS chromatograms, the presented quantification methodology implies a clear step forward towards complex pyrolysis oil compositional quantification in a cost-effective way. Besides, this quantification methodology enables determining what proportion is being detected by GC-MS with respect to the total oil. Finally, the presented work includes all the Kováts RI for complex temperature-program gas chromatography of all the signals identified in the analysed pyrolysis oils, to be readily available to other researchers towards the identification of chemical compounds in their studies.

1. Introduction

Thermal and chemical recycling processes are being promoted in recent years in order to valorise plastic waste that is difficult to recycle mechanically. The pyrolysis process, which has been studied for several decades to recycle thermosets, thermoplastics and complex mixtures of plastics and other materials, is currently receiving unusual interest from industry and administration.[1] It is possible to return to the economy certain valuable products from non-recyclable waste that currently litters landfills around the world.[2,3] Pyrolysis generates three product fractions: solid, liquid and gas. When pyrolysing plastic (or plastic rich) waste, the liquid fraction (commonly known as pyrolysis oils) is usually the main and target product. It consists of a complex mixture of hydrocarbons of a broad range of carbon atoms, which, depending on the waste pyrolysed, may be accompanied by other heteroatomic organic chemicals (mainly nitrogen, sulphur, oxygen, halogens and metals) that could be considered pollutants.[4]

M. Kusenberg *et al.* presented a detailed review of the most common analytical techniques used to chemically characterise waste plastic pyrolysis oils.[5] As they reported, chromatography stands out as the most frequently used method for oil compositional analysis thanks to its versatility, as different detectors can be coupled and trace compounds down to ppb-s can be detected. The thermal conductivity detector (TCD) or the flame ionisation detector (FID) are reported to be currently the widest used in chromatography configurations.[5–7] In the case of the mass spectrometry detector (MS), the main advantage lies in its ability to identify unknown compounds. Indeed, TCD and FID could provide better signal quality results, but using these detectors would require prior knowledge of the nature of the chemicals present in pyrolysis oils, because identification is based on the comparison between the retention time of each chemical present in the oil and that of a standard substance. This is not an easy task, or even possible, when dealing with

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† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d4ra00226a

pyrolysis oils from real waste where thousands of chemical compounds could coexist as it has been reported for liquids obtained from the pyrolysis of biomass[8,9] or from petroleum fractions.[10] Combining the GC technique with mass spectrometry (MS) detectors could be a way to address coelution and complexity of the samples.[11] Gas chromatography coupled with mass spectrometry (GC-MS) provides a qualitative compositional analysis, based on the correspondence between the measured mass spectra and those available in the MS libraries[12] for volatile and semi-volatile compounds (typically weights up to 220 Da and/or boiling points below 350 °C), being possible to detect hundreds of compounds.[6,8,13] However, chromatographic techniques combined with additional detectors (GC-MS/FID, GCxGC/FID/MS and high-pressure liquid chromatography) are claimed as the most appropriate to characterise and quantify compounds in pyrolysis oils, based on a recent review about characterisation of pyrolysis oils from plastics.[11] Other powerful techniques such as gel permeation chromatography, ultraviolet-visible spectroscopy, Fourier-transform infrared spectroscopy, nuclear magnetic resonance and high resolution mass spectrometry are also mentioned as necessary in order to have a complete overview of the oil composition. These spectroscopic techniques have been successfully applied to classical petrochemical hydrocarbon streams (*i.e.* gasoline or diesel fuels). However, they are not enough if a detailed molecular characterisation is pursued and compositional differences exist between these fuels and pyrolysis oils from plastic waste. Despite the undoubtedly promising contribution to this research field of the mentioned techniques (with special mention to GCxGC), their use may not be as widespread as GC-MS yet, probably, due to the higher technical complexity as well as their higher cost.

Concerning quantitative composition of pyrolysis oils, during all these years the scientific community has normally used the "peak area percent" as the standard indicator for composition when using GC-MS.[14–21] However, the area percentage does not provide real information on the amount, because the signal intensity is not directly proportional to the concentration. Indeed, aspects such as the molecular weight of the species, the polarity, the selected chromatographic column, the volatility and the temperature influence the signal obtained. This "peak area percent" could be enough to be able to compare the compositional variations generated by the change in operating conditions and to know the approximate composition (aromatics, paraffins, olefins and others) of the oils that were proposed for use as alternative fuels or refinery blending mixtures.[6] However, individual quantification of each compound requires a laborious calibration procedure that is usually not cost-effective due to the large number, variability and diversity of chemicals implied.[7,13,22,23] A method is therefore needed that strikes a compromise between the cost in time/effort and the quality of the information obtained.

Apart from the challenge of quantification, there are also difficulties in identifying some chemicals present in pyrolysis oils. In fact, it is very common for a proportion, sometimes not negligible, of these oils to be defined as "unidentified". In this respect, it is possible to use mass spectral libraries such as those of NIST/EPA/NIH for identification.[24] However they are only partially useful if a complete identification and quantification of all peaks present is pursued.[22] The use of retention indices is the easiest way to identify chemicals because they perform better in peak identification than retention times (RT), due to their lesser dependency on GC parameters.[25] More precisely, the Kováts Retention Index (Kováts RI), defined as the relative retention time normalised to the near eluting *n*-alkanes,[26] is the most accepted one.[12,22] Updated databases (*i.e.* NIST 17 GC Method/Retention Index Library)[27,28] and specific software (*e.g.* MassFinder 4 (ref. 26)) do exist, where compounds and RI are related. What is missing is the availability of a systematic assignment of the Kováts RI to pyrolysis oils in research works, in order to feed and complete a global database where the identification of compounds based on this index would be simple and useful for both the scientific community and the industry.

This paper presents a methodology to identify and quantify by GC-MS the composition of pyrolysis oils produced from different kinds of real complex plastic waste: mixed plastics from packaging, mixed plastics from electronics and fibre reinforced thermosets. The idea is to provide with a better solution to all those research groups who analyse pyrolysis oils by GC-MS and report their results in area%.[29,30] The proposed methodology was successfully applied to twelve pyrolysis oils coming from the three mentioned plastic groups. The results of three of the pyrolysis oils have been explicitly included in this text and the results of the remaining nine have been included in the ESI† to limit the length of this paper. The non-isothermal Kováts RI (modification introduced by Van den Dool and Kratz)[31] of all the chemicals identified in the oils analysed are also included. The aim is to contribute to the existing databases[28] and to facilitate the identification of chemicals for the scientific community working on the pyrolysis of waste plastics.

2. Materials and methods

2.1. Pyrolysis oils

Three types of plastic waste were used as feedstock for the pyrolysis oil generation: post-consumer plastic packaging waste (Packaging), plastic fraction rejected from waste of electric and electronic equipment (WEEE) and fibre reinforced plastic waste (FRP). The intention was to produce pyrolysis oils of different chemical characteristics, in order to design a method that would be versatile. Thus, the so-called Packaging sample was a reject from the planar fraction obtained in mechanical–biological treatment plants of municipal solid waste and consisted mainly of polyolefins (polyethylene and polypropylene), which normally produces alkane and olefin-rich hydrocarbon mixtures in oils, and polystyrene. The WEEE sample was the plastic reject from a WEEE management and recycling plant and in this case consisted mainly of styrenic plastics (polystyrene, acrylonitrile-butadiene-styrene), which generate oils of aromatic nature. At last, the FRP waste was an end-of-life glass fibre reinforced polyester thermoset resin from the nautical sector, which produces oxygenated and aromatic oils with a significant proportion of unidentified compounds, some of them including

Table 1 Qualitative composition of the three analyzed pyrolysis oils, indicating retention time (RT), name, formula, CAS number and detected amount (in area%)

No.	RT (min)	Compound	Formula	CAS number	Area%
"Packaging": plastic packaging from sorting plants					
1	3.6	*n*-Hexane	C_6H_{14}	110-54-3	1.1
2	3.7	1-Hexene	C_6H_{12}	592-41-6	0.8
3	3.8	*n*-Heptane	C_7H_{16}	142-82-5	0.4
4	4.0	1-Heptene	C_7H_{14}	592-76-7	1.0
5	7.9	Toluene	C_7H_8	108-88-3	1.9
6	8.1	1-Octene	C_8H_{16}	111-66-0	1.8
7	8.3	Water	H_2O	7732-18-5	0.7
8	9.1	Cyclooctene	C_8H_{14}	931-88-4	0.1
9	9.9	Ethylbenzene	C_8H_{10}	100-41-4	2.8
10	12.9	Styrene	C_8H_8	100-42-5	38.1
11	14.5	Alpha-methylstyrene	C_9H_{10}	98-83-9	3.6
12	15.4	1-Undecene	$C_{11}H_{22}$	821-95-4	1.3
13	17.1	5-Dodecene, (*E*)-	$C_{12}H_{24}$	7206-16-8	1.1
14	24.5	5-Octadecene, (*E*)-	$C_{18}H_{36}$	7206-21-5	0.5
15	25.7	Nonadecane	$C_{19}H_{40}$	629-92-5	0.2
16	26.7	1-Nonadecene	$C_{19}H_{38}$	18435-45-5	0.8
17	27.8	Eicosane	$C_{20}H_{42}$	112-95-8	0.4
18	28.7	Cycloeicosane	$C_{20}H_{40}$	296-56-0	0.9
19	29.6	Heneicosane	$C_{21}H_{44}$	629-94-7	0.8
20	30.4	10-Heneicosene (*c*,*t*)	$C_{21}H_{42}$	95008-11-0	1.1
21	31.2	Docosane	$C_{22}H_{46}$	629-97-0	0.9
22	31.8	Benzene, 1,1′-(1,3-propanediyl)bis-	$C_{15}H_{16}$	1081-75-0	0.7
23	31.9	1-Docosene	$C_{22}H_{44}$	1599-67-3	1.4
24	32.6	Tricosane	$C_{23}H_{48}$	638-67-5	1.1
25	33.2	9-Tricosene, (*Z*)-	$C_{23}H_{46}$	27519-02-4	1.2
26	33.8	Tetracosane	$C_{24}H_{50}$	646-31-1	1.0
27	34.5	Cyclotetracosane	$C_{24}H_{48}$	297-03-0	1.2
28	35.0	Pentacosane	$C_{25}H_{52}$	629-99-2	1.3
29	35.6	*Z*-12-Pentacosene	$C_{25}H_{50}$	—	1.1
30	36.9	9-Hexacosene	$C_{26}H_{52}$	71502-22-2	1.4
31	37.5	Heptacosane	$C_{27}H_{56}$	593-49-7	0.8
32	38.9	Octacosane	$C_{28}H_{58}$	630-02-4	0.7
33	39.8	Cyclooctacosane	$C_{28}H_{56}$	297-24-5	0.9
34	40.6	Nonacosane	$C_{29}H_{60}$	630-03-5	0.7
35	41.7	*Z*-14-Nonacosane	$C_{29}H_{58}$	—	0.8
36	44.1	Cyclotriacontane	$C_{30}H_{60}$	297-35-8	0.7
37	45.2	Triacontane	$C_{30}H_{62}$	638-68-6	0.5
		Unknown			24.2
"WEEE": plastic fraction from waste of electric and electronic equipment					
1	6.1	Benzene	C_6H_6	71-43-2	0.3
2	7.2	2-Propenenitrile	C_3H_3N	107-13-1	0.3
3	7.4	2-Butenoic acid, methyl ester	$C_5H_8O_2$	18707-60-3	0.3
4	8.1	Toluene	C_7H_8	108-88-3	9.2
5	10.2	Ethylbenzene	C_8H_{10}	100-41-4	16.4
6	11.3	Benzene, (1-methylethyl)	C_9H_{12}	98-82-8	2.7
7	12.1	Benzene, propyl	C_9H_{12}	103-65-1	0.6
8	13.2	Styrene	C_8H_8	100-42-5	42.4
9	14.7	Alpha-methylstyrene	C_9H_{10}	98-83-9	11.8
10	25.8	Naphthalene, 1-methyl	$C_{11}H_{10}$	90-12-0	0.1
11	25.9	Phenol, 2,6-dimethyl	$C_8H_{10}O$	576-26-1	0.6
12	27.9	Phenol	C_6H_6O	108-95-2	8.2
13	29.4	Phenol, 2,3-dimethyl-	$C_8H_{10}O$	526-75-0	0.8
14	30.1	Benzenebutanenitrile	$C_{10}H_{11}N$	2046-18-6	1.2
15	30.9	Phenol, 3-ethyl	$C_8H_{10}O$	620-17-7	0.4
16	31.5	Phenol, 4-(1-methylethyl)	$C_9H_{12}O$	99-89-8	3.1
17	32.5	Phenol, *p*-*tert*-butyl	$C_{10}H_{14}O$	98-54-4	0.7
18	34.7	*p*-Isopropenylphenol	$C_9H_{10}O$	4286-23-1	0.5
		Unknown			0.6

Table 1 (*Contd.*)

No.	RT (min)	Compound	Formula	CAS number	Area%
"FRP": fibre reinforced polyester resin based plastic waste					
1	4.3	Propanal	C_3H_6O	123-38-6	1.9
2	6.1	Benzene	C_6H_6	71-43-2	2.3
3	7.7	1,3-Dioxolane, 2-ethyl-4-methyl-	$C_6H_{12}O_2$	4359-46-0	4.4
4	8.2	Toluene	C_7H_8	108-88-3	2.8
5	10.2	Ethylbenzene	C_8H_{10}	100-41-4	8.6
6	11.3	Benzene, (1-methylethyl)-	C_9H_{12}	98-82-8	1.4
7	13.2	Styrene	C_8H_8	100-42-5	19.9
8	32.2	Benzene, 1,1′-(1,3-propanediyl)bis-	$C_{15}H_{16}$	1081-75-0	11.2
9	34.6	Benzoic acid	$C_7H_6O_2$	65-85-0	9.4
10	35.1	Bicyclo[4.2.1]nona-2,4,7-triene, 7-phenyl-	$C_{15}H_{14}$	—	3.7
		Unknown			34.3

heteroatoms like nitrogen and halogens. In addition to this particular FRP waste, the method was also tested with oils from other glass and carbon fibre reinforced plastic waste, both based on polyester and epoxy. This information can be found in Table S1 of the ESI.†

Waste samples of *ca.* 100 g were pyrolysed in each case in a laboratory installation composed of a stainless steel non-stirred tank reactor electrically heated. The condensable compounds present in the generated pyrolysis vapours were cooled down and collected as liquids. As in the case of sample selection, oils from pyrolysis processes of different operating conditions were also selected. More precisely, for the post-consumer plastic packaging a single-step pyrolysis treatment was performed using a heating rate of 40 °C min^{-1} up to 640 °C without carrier gas but with pure N_2 purge. Regarding the WEEE sample, the selected oil came from a stepwise pyrolysis process (heating rate of 15 °C min^{-1}, 1 h isothermal step at 300 °C and a later heating till 500 °C) carried out with a continuous N_2 gas flow of 1 L min^{-1} (at 20 °C and 1 bar). In addition, before the condensation of oils, the generated pyrolysis volatiles were further thermally cracked at 400 °C in a fixed bed reactor in series, where a halogen adsorbent was placed. In this case, the proposed methodology was also applied for oils coming from the same sample (WEEE), but processed at different operating conditions (see Table S1 in ESI†). At last, the oil coming from the FRP waste sample (as well as those included in the Table S1†) was obtained through a single-step pyrolysis treatment using a heating rate of 3 °C min^{-1} up to 500 °C without N_2 purge nor inert carrier gas. Table 1 shows the summary of the qualitative composition by GC-MS (following the chromatographic programme described in Section 2.3) for the three pyrolysis oils analysed in the present work and employed as use-case (Packaging, WEEE and FRP).

2.2. Commercial reagents

The development of the analytical quantification methodology proposed in this work required the use of the following chemical compounds or mixtures:

(a) Mixture of saturated C7–C30 alkanes (alkane-mix) with reference number 49451-U from Supelco. This is a certified reference material with a concentration of 1000 μg mL^{-1} for each of the 23 components, which are dissolved in hexane. See Table S2 of the ESI.†

(b) 1-Propanol (purity 99.8%, CAS number 71-23-8, provided by Supelco) used as internal standard (IS).

(c) Six model compounds: cyclohexane (purity 99.5%, CAS number 110-82-7, supplied by PanReac-AppliChem), benzene (purity 99.8%, CAS number 71-43-2, supplied by Sigma-Aldrich), *o*-xylene (purity 99.0%, CAS number 95-47-6, supplied by Supelco), quinoline (purity 96.0%, CAS number 91-22-5, supplied by Honeywell Riedel-de Haën), *m*-cresol (purity 99.0%, CAS number 108-39-4, supplied by Sigma-Aldrich) and ethyl 4-aminobenzoate (purity 98.0%, CAS number 94-09-7, supplied by Thermo Scientific).

(d) Additional compounds needed to complete the calibration at low retention times: *n*-heptane (purity 99.0%, CAS number 142-82-5, supplied by PanReac-AppliChem) and cyclopentyl methyl ether (CPME) (purity 99.9%, CAS number 5614-37-9, supplied by Sigma-Aldrich).

(e) Chromatographic grade tetrahydrofuran (THF) solvent (purity 99.9%, product code 361736, supplied by PanReac-AppliChem).

(f) Chemical compounds used for the methodology validation: phenol (purity 99.5%, CAS number 108-95-2, supplied by Sigma-Aldrich), toluene (purity 99.5%, CAS number 108-88-3, supplied by Sigma-Aldrich), ethylbenzene (purity 99.0%, CAS number 100-41-4, supplied by Sigma-Aldrich), styrene (purity 99.9%, CAS number 100-42-5, supplied by Supelco), benzene-butanenitrile (purity 99.0%, CAS number 2046-18-6, supplied by Sigma-Aldrich). Additionally, nine of the alkanes contained in the alkane-mix that were not used as calibration compounds were used as validation compounds: nonadecane, eicosane, heneicosane, tricosane, tetracosane, pentacosane, heptacosane, nonacosane and tricontane. The selection of alkanes from the alkane-mix to be used in the calibration process will be further described in Section 3.1.

2.3. GC-MS analysis

The pyrolysis oils were prepared for analysis by diluting *ca.* 0.4 g of the oil in the case of "Packaging", *ca.* 0.1 g and 0.01 g for

Table 2 Pyrolysis oils dissolution preparation data prior to GC-MS analysis. Information included: liquid name, liquid identification number (ID#), liquid weight (g), dissolution volume (mL) and sample concentration (μg mL^{-1})

Name	ID#[a]	Pyrolysis oil weight (g)	Dissolution final volume (mL)	Total pyrolysis oil concentration (μg mL^{-1})
Packaging	ID12	0.3544	10 mL	35 440
WEEE	ID6	0.1004		10 040
WEEE (1/10)	ID6 diluted	0.0102		1020
FRP	ID1	0.0982		9820
FRP (×10)	ID1 concentrated	1.0020		100 200

[a] Identification number used in the complete pyrolysis oil list in the ESI Table S1.

"WEEE" and "WEEE (1/10)", respectively, and around 0.1 g and 1 g in the case of "FRP" and "FRP (×10)", respectively, in 10 mL of a THF solution (Table 2) that already included 1-propanol as internal standard (IS). A constant concentration of the IS was employed to work with a signal area in the same order of magnitude of the signals obtained in the analysed pyrolysis oils chromatograms and to minimise the instrumental variabilities. The samples were analysed on an Agilent GC-MS system with a gas chromatograph (6890) using a J&W DB-FFAP capillary column (60 m × 0.320 mm × 0.25 μm) coupled to a mass spectrometer (5973). Injector temperature was set at 300 °C. The analysis started at 40 °C for 5 minutes, ramped up by 8 °C min^{-1} to 150 °C and held at 150 °C for 5 minutes. It was then heated to 240 °C at 8 °C min^{-1} and maintained for 10 minutes. A 1 : 15 split was used with 1.5 mL per min helium as carrier gas flow employing an injection volume of 0.5 μL. The electron ionisation (EI) was set to 70 eV and the source temperature was set to 230 °C. The mass spectrometer measured from 0 min to 10 min in a range of 10–120 *m*/*z* with a threshold of 150 and 10.68 scans per s, and from minute 10 onwards in a range of 33–442 *m*/*z* with a threshold of 150 and 3.67 scans per s. The initial mass acquisition range (RT: 0–10 min) upper limit was set just six mass-charge units, 120 *m*/*z*, above the molecular weight of *n*-octane (114 Da), the highest molecular weight compound that was expected to appear in the studied oils at low retention times. The second mass acquisition range (RT: 10–47 min) mass-charge limit was set, in its lower limit 33 *m*/*z*, to avoid contamination from ions that can enter the analysis from the air dragged during the injection, nitrogen (28 Da) and oxygen (32 Da), and its upper limit corresponded to the highest molecular weight compound of the calibration mix, triacontane (C30, 442 Da). The difference in the mass acquisition range frequencies was set by the detector limitations for scanning a wide range of masess, as for a wider range of masses the scans per second decreases. The commercial NIST-08 mass spectral library was used for identification of the compounds. The acceptance criterion for identification was set at a minimum match quality of 85%. Each sample was analysed in triplicate in order to ensure the repeatability of the measurements.

On the other hand, the use of split type injection generates discrimination by molecular mass. This problem can be solved using other types of injections, such as on-column injection, headspace sampling, splitless injection, *etc.* However, regarding these mentioned injection possibilities, it was not possible to adopt them due to the available GC-MS configuration. In fact, the complexity of the samples analysed and the different concentration in some of their components (as high as 45 000 000 and as low as 450 000 (area units)) required the use of a split injection. Nonetheless, the molecular mass discrimination problem was addressed in this work by improving the heat transfer ahead of entering the column.[32,33] For that purpose, a deactivated glass-wool packed liner (Agilent 5183-4647) was selected to try to minimize the loss of volatile compounds during the injection.

To assess the possible differences between split and splitless injections due to molecular mass discrimination, the alkanes calibration mix used during this work was analysed by the chromatographic method proposed in this work and by an analogue with a splitless injection. The results, presented in Table S3 in ESI,† revealed that no discrimination was occurring during the 1 : 15 split injection.

3. Results and discussion

The state of the art calculates concentration of pyrolysis oils coming from plastic waste assuming equivalence of peak area percentage to weight percentage of compounds. The present approach introduces different response factors at different retention time intervals. In order to approach further accuracy of the quantitative method, a correction factor was used at each selected retention time intervals.

3.1. Development of the quantification method

The first step of the quantification method was to divide the chromatogram total duration into smaller time sections which were named as windows (W), strategy that has been previously reported in the quantification procedure of bio-oils.[34] The reason to dissect the chromatogram into smaller sections was to try to minimize the impact of all the aspects that have an influence on the area of the signals (*i.e.* molecular weight, polarity, solvent, chromatographic column). For the purpose of this paper, six windows were defined and applied to all the analysed pyrolysis oils: W1 from 0 min to 4.5 min, W2 from 4.5 min to 11 min, W3 from 11 min to 21 min, W4 from 21 min to 29 min, W5 from 29 min to 35 min and W6 from 35 min to 47 min. The selection of the number of windows was done as a compromise between introducing more than one calibration standard for the complete duration of the chromatogram and

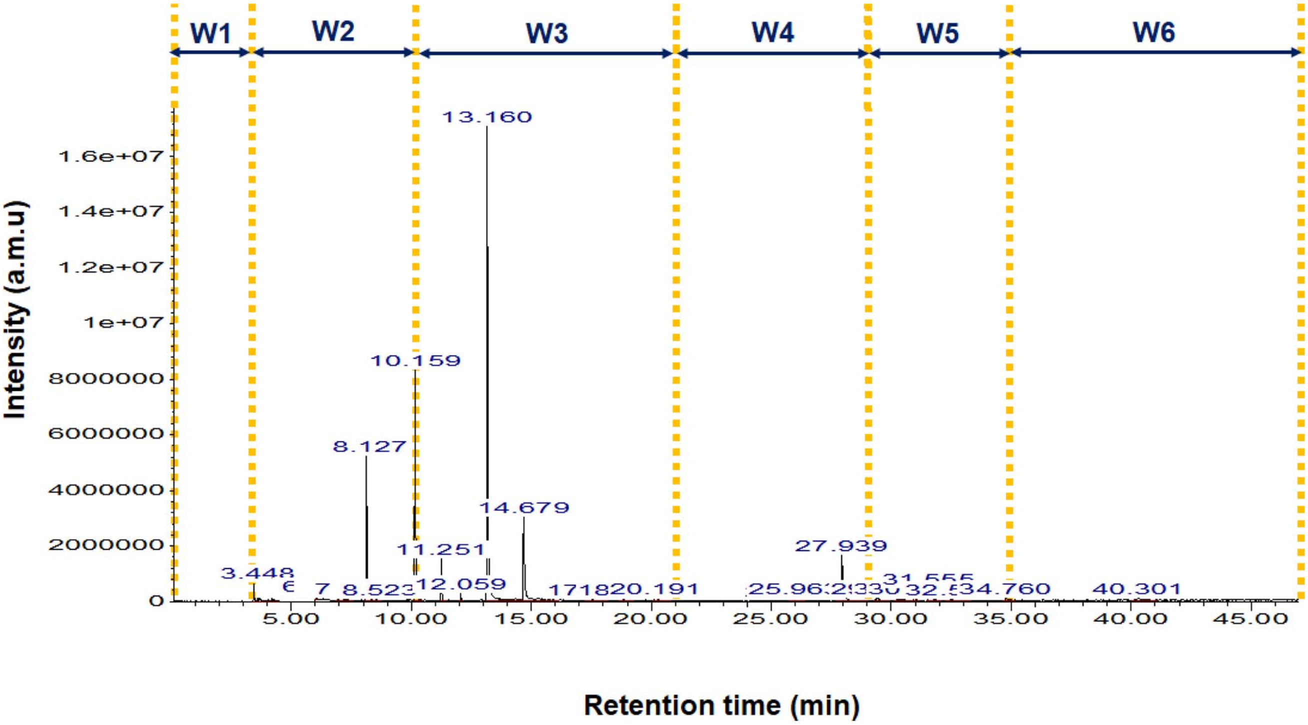

Fig. 1 Chromatogram sub-division in windows (W#), *e.g.* "WEEE" liquid (ID6).

the minimisation of the proposed methodology's tediousness when applying it. The time interval duration was adapted to adjust the validation compounds that we selected. Fig. 1 shows the chromatogram of "WEEE" liquid (ID6) with the windows retention time range limited with yellow vertical lines to illustrate the followed procedure.

The second step was to calibrate the certified saturated *n*-alkanes mix (hereafter the alkane-mix). Fig. 2 shows the chromatographic response (signal intensity *vs.* retention time) of the alkanes of the alkane-mix for a concentration of 1000 μg per mL per alkane. A red line has been added to the graph to highlight the variability of peak signal intensity in function of retention

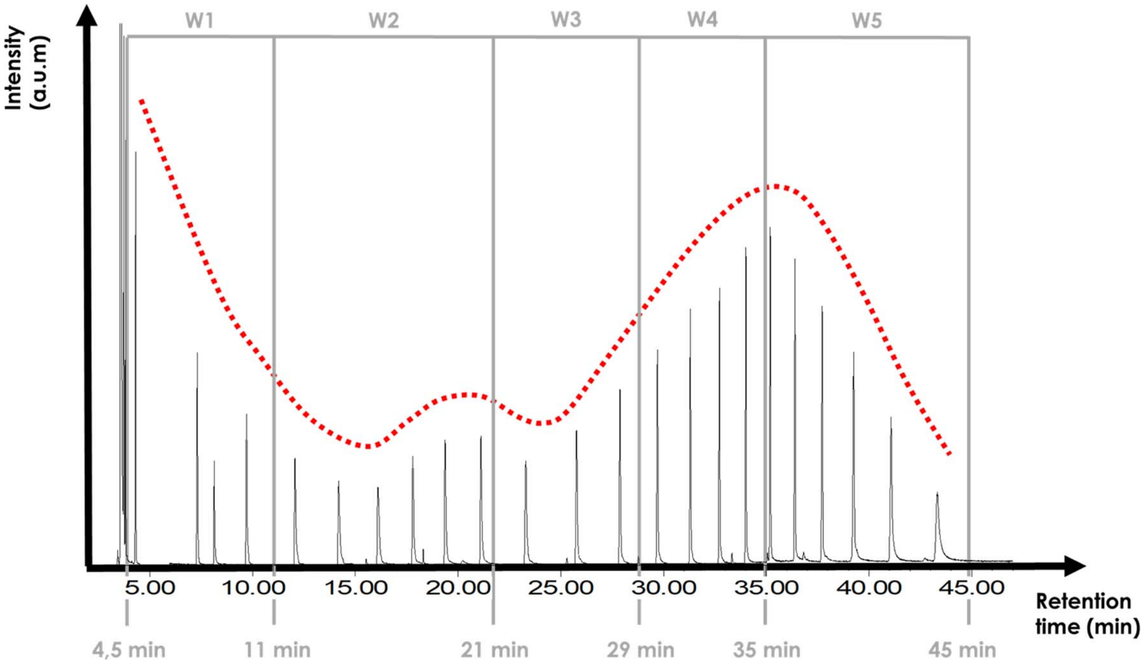

Fig. 2 Chromatographic area distribution for the alkane-mix (C7–C30, 1000 μg per mL per alkane).

time for different alkane compounds with the same concentration. The approach of dissecting the chromatogram in windows and the use of one calibration compound per window seeks to capture better the response factor variation along the chromatogram typically found when using mass selective detectors. Calibration was performed with four different concentrations, dissolving the mix in THF. In addition to the alkane-mix, the compounds heptane and cyclopentyl methyl ether (CPME) were also employed to have other compounds at low retention times, due to the poor solubility of the low retention time compounds from the alkane-mix (see Fig. S1†). The four calibration concentrations used were: (a) alkane-mix in THF: 900 μg mL^{-1}, 700 μg mL^{-1}, 500 μg mL^{-1} and 300 μg mL^{-1}, (b) heptane in THF: 873 μg mL^{-1}, 679 μg mL^{-1}, 485 μg mL^{-1} and 291 μg mL^{-1} and (c) CPME in THF: 837 μg mL^{-1}, 651 μg mL^{-1}, 465 μg mL^{-1} and 279 μg mL^{-1}.

In this calibration process a response factor (RF) was obtained by linear regression between the peak area and concentration for each alkane of the alkane-mix, for heptane and for CPME. Details of the calibration for all compounds, response factors and the R^2 linear fitting quality can be reviewed in Table 3. Eqn (1) shows the determination of the mentioned response factors obtained in the calibration process, where "alkane" applies to every alkane present in the alkane-mix, to heptane and to CPME. Note that the area of the alkane is referred to the area normalised to the internal standard (IS) area which has been employed to minimise the variability of the measured peak areas due to instrumental errors. Integrated areas were determined considering the total ion chromatogram (TIC).

$$\mathrm{RF} = \frac{\text{concentration alkane}}{\text{area alkane}_{\text{normalised to the IS area}}} \tag{1}$$

Table 3 Response factor (RF) of the chemical compounds present in the C7–C30 saturated-alkane-mix, heptane and CPME obtained in the conventional calibration procedure (RT: retention time, R^2: linear fitting quality)

Compound	Formula	RT (min)	RF	R^2
Heptane	C_7H_{16}	3.51	43.2	0.9823
Cyclopentyl methyl ether (CPME)	$C_6H_{12}O$	6.03	35.5	0.9915
Octane[a]	C_8H_{18}	4.31	28.4	0.9982
Nonane[a]	C_9H_{20}	7.31	25.7	0.9956
Decane[a]	$C_{10}H_{22}$	9.71	25.5	0.9957
Undecane[a]	$C_{11}H_{24}$	—	—	—
Dodecane[a]	$C_{12}H_{26}$	12.06	25.7	0.991
Tridecane[a]	$C_{13}H_{28}$	14.18	25.6	0.9936
Tetradecane	$C_{14}H_{30}$	16.10	23.9	0.9909
Pentadecane	$C_{15}H_{32}$	17.80	23.1	0.9911
Hexadecane	$C_{16}H_{34}$	19.37	21.3	0.9801
Heptadecane	$C_{17}H_{36}$	21.11	19.2	0.991
Octadecane	$C_{18}H_{38}$	23.30	19.6	0.9924
Nonadecane	$C_{19}H_{40}$	25.77	18.0	0.9866
Eicosane	$C_{20}H_{42}$	27.88	16.8	0.9912
Heneicosane	$C_{21}H_{44}$	29.70	15.5	0.9897
Docosane	$C_{22}H_{46}$	31.30	14.2	0.9899
Tricosane	$C_{23}H_{48}$	32.72	14.0	0.9919
Tetracosane	$C_{24}H_{50}$	34.01	13.3	0.9891
Pentacosane	$C_{25}H_{52}$	35.19	13.0	0.9828
Hexacosane	$C_{26}H_{54}$	36.39	12.6	0.9865
Heptacosane	$C_{27}H_{56}$	37.72	12.2	0.9896
Octacosane	$C_{28}H_{58}$	39.26	11.0	0.9902
Nonacosane	$C_{29}H_{60}$	41.07	11.6	0.9934
Triacontane	$C_{30}H_{48}$	43.32	12.5	0.9989

[a] Poor solubility.

The third step was to select, between the chemicals listed in Table 3, a representative calibration substance per window (hereafter calibration compounds). The aim was that the concentration of all substances belonging to the same window of the chromatogram was calculated using the response factor of the corresponding representative substance. For that, selected chemicals from the alkane-mix + heptane and CPME were: heptane in W1, CPME in W2, pentadecane in W3, octadecane in W4, docosane in W5 and octacosane in W6. These calibration compounds were selected trying to choose the compound located in the centre of each corresponding window. The fourth step was to establish a correction factor (CF) to calculate the concentration of such substances that could be present in pyrolysis oils but could be of very different chemical nature compared to the calibration compounds (alkanes + CMPE), for instance, naphthenic, aromatic and heteroatomic organic compounds. For that, six chemicals (hereafter model compounds) were selected: cyclohexane in W1, benzene in W2, *o*-xylene in W3, quinolone in W4, *m*-cresol in W5 and ethyl 4-aminobenzoate in W6. The correction factor (CF) calculation in each window is described in eqn (2), showing that the area of the model compound selected per window is divided by the area of the calibration compound per window. This CF value will be applied to all the detected signals in the chromatogram. Table 4 compiles the obtained results. Note that the area of the representative substance and the area of the model compound is referred to the area normalised to the IS area and it is calculated as the average of three measurements as aforementioned. Integrated areas were determined considering the total ion chromatogram (TIC).

$$\mathrm{CF} = \frac{\text{area of model compound}_{\text{normalised to the IS area}}}{\text{area of calibration compound}_{\text{normalised to the IS area}}} \tag{2}$$

The fifth and last step consisted of calculating the concentration of the compounds detected in the chromatograms of the pyrolysis oils, as described in eqn (3). For that, the window to which each compound belonged was initially defined according to its retention time (RT). Then, the area of the compound was multiplied by the response factor (RF) (eqn (1)) per window and by the correction factor (CF) (eqn (2)) of that window too. Note that the area of the compound is referred to the area normalised to the IS area. Integrated areas were determined considering the total ion chromatogram (TIC).

$$[\text{Compound}] = \text{area of compound}_{\text{normalised to the IS area}} \times \mathrm{CF} \times \mathrm{RF} \tag{3}$$

3.2. Determination of the relative error of the proposed quantification methodology

The proposed quantification methodology was evaluated through comparison with conventional calibration of fourteen chemical compounds (five of aromatic nature and nine of aliphatic nature) present in the pyrolysis oils (hereafter the validation compounds). Validation compounds were present in all the pyrolysis oils studied in this work and they were calibrated following the conventional procedure: preparing known concentrations of the compounds, analysing them in the GC-MS, and getting a response factor from the comparison of concentration and areas. Aromatic nature validation compounds were: toluene, ethylbenzene, styrene, phenol and benzenebutanenitrile, and aliphatic nature ones were: nonadecane, eicosane, heneicosane, tricosane, tetracosane, pentacosane, heptacosane, nonacosane and triacontane. The selection of the validation compounds was made trying to have them distributed along the complete duration of the chromatogram. In Table 5 the validation compounds are listed, together with the window of the chromatograph (W) in which each compound appears, the calibration concentration range, the response factor (RF) obtained per compound through conventional calibration and the R^2 linear fitting quality. It can be observed that the conventional calibration was successfully performed with all the validation compounds, with a R^2 value higher than 0.95.

The validation of the proposed quantification methodology was done based on the absolute and relative errors obtained applying eqn (4) and (5), respectively. The prepared concentration (named as $[\,]_{\text{prepared}}$ (μg mL^{-1})) refers to the concentrations prepared for conventional calibration with the validation compounds, while the calculated concentration (named as $[\,]_{\text{calculated}}$ (μg mL^{-1})) refers to the concentrations calculated by applying the quantification methodology proposed in this work.

$$\text{Absolute error } (\mu\text{g mL}^{-1}) = [\,]_{\text{prepared}}\ (\mu\text{g mL}^{-1}) - [\,]_{\text{calculated}}\ (\mu\text{g mL}^{-1}) \quad (4)$$

$$\text{Relative error (wt\%)} = 100 \times \text{absolute error } (\mu\text{g mL}^{-1})/[\,]_{\text{prepared}}\ (\mu\text{g mL}^{-1}) \quad (5)$$

Additionally, the concentrations of these validation compounds were also calculated following the proposed quantification methodology, but without applying the correction factor (CF). This was done in order to assess the impact of the nature of the quantified compounds and whether there was a need to implement a correction factor (CF) through the use of model compounds. Finally, the concentration of these validation compounds was also calculated considering that the area percentage was equal to weight percentage. The aim was to assess the hypothesis that the area percentage was equal to the weight percentage, and whether this could be an acceptable approach when only the order of magnitude of the concentration of the chemical compounds in the pyrolysis oils is pursued. In Fig. 3, the relative errors of these three quantification approaches are graphically represented (including average value and standard deviation). The average and the standard deviation values have been calculated considering the three pyrolysis oils used as use-case in this work (Packaging, WEEE, FRP) and the two additional liquid dissolutions (WEEE (1/10), FRP (×10)), as well as the additional nine pyrolysis oils studied and included in the ESI.† See Tables S4–S6† for detailed numerical data of the quantification of validation compounds for all the tested pyrolysis oils.

On the one hand, as observed in Fig. 3, the average relative error (wt%) when it is assumed that the area percentage was equivalent to the weight percentage (grey-colour bars) shows that lack of repeatability and high relative errors were generated for both aromatic and aliphatic compounds, although the latter showed the highest ones. This was an expected result based on the aspect of Fig. 2 where different areas are visually clear for same mass concentrations. Regarding the relative error with aromatic validation compounds was between 95 wt% to 191 wt% and the standard deviation between 67 wt% and 141 wt%. Regarding aliphatic validation compounds, no standard deviation is included because only one of the liquid-type

Table 4 Correction Factor (CF) for each window calculated based on the normalized average area (NAA) of the model compound (MC) and the calibration compound (CC). Response Factor (RF) per window used in the quantification methodology is also included

Compound	Type	Window (W)	Conc. (μg mL^{-1})	Normalised average area (NAA)	CF = NAA of MC/NAA of CC	RF per window
Cyclohexane	MC	1	490	13.9	1.2	43.2
Heptane	CC		490	11.3[a]		
Benzene	MC	2	540	12.5	0.8	35.5
CPME	CC		540	15.2[a]		
o-Xylene	MC	3	500	26.1	1.2	23.1
Pentadecane	CC		500	21.6[a]		
Quinoline	MC	4	670	38.4	1.1	19.6
Octadecane	CC		670	34.2[a]		
m-Cresol	MC	5	430	18.4	0.6	14.2
Docosane	CC		430	30.2[a]		
Ethyl 4-aminobenzoate	MC	6	480	21.4	0.5	11.0
Octacosane	CC		480	43.7[a]		

[a] Calculated using the response factor from the calibration (Table 3).

Table 5 Calibration points of validation compounds of aromatic and aliphatic nature (W: window, RF: response factor, R^2: linear fitting quality)

W	Compound	Concentration (μg mL^{-1})	RF	R^2
Aromatic compounds				
2	Toluene	170; 350; 650; 880; 900; 1200; 4270	20.4	0.9500
2	Ethylbenzene	270; 590; 900; 1212; 4640	20.2	0.9918
3	Styrene	240; 670; 800; 1520; 4508	17.5	0.9874
4	Phenol	300; 590; 930; 1230	27.8	0.9947
5	Benzenebutanenitrile	90; 330; 840	18.0	0.9983
Aliphatic compounds				
4	Nonadecane	300; 500; 700; 900	18.0	0.9866
4	Eicosane	300; 500; 700; 900	16.8	0.9912
5	Heneicosane	300; 500; 700; 900	15.5	0.9897
5	Tricosane	300; 500; 700; 900	14.0	0.9919
5	Tetracosane	300; 500; 700; 900	13.3	0.9891
6	Pentacosane	300; 500; 700; 900	13.0	0.9828
6	Heptacosane	300; 500; 700; 900	12.2	0.9896
6	Nonacosane	300; 500; 700; 900	11.6	0.9934
6	Triacontane	300; 500; 700; 900	12.5	0.9989

("Packaging" liquid) showed aliphatic compounds in it. In this case, aliphatic compounds showed relative errors between 284 wt% and 498 wt%. Therefore, in the light of these results, this quantification strategy (peak area% = weight%) can be considered useless from a quantification point of view, even for having an idea of the order of magnitude of the concentration of compounds in pyrolysis oils. This is an important remark because, as stated in the introduction of the article, the determination of the composition of pyrolysis oils through the area% obtained by GC-MS is a common and widespread practice in the scientific community.

In contrast, interesting results were observed when applying the proposed quantification methodology of this work, using the correction factor (light-blue-colour bars) and without using it (dark-blue-colour bars). Although the average relative errors were not negligible (they were between +62 wt% and −59 wt% using the CF and between +72 wt% and −29 wt% without using the CF) for all-type compounds, they were definitely lower than the peak area% approach. Moreover, taking into account that the currently employed procedures and standards for the quantification of organic compounds in bio-oils by GC-MS analytical technique assume variabilities around 20%,[35–37] it could be considered that the relative error of the proposed quantification methodology application fell within the assumable deviation for complex liquids as such. Also, regarding the standard deviation registered for the aromatic compounds, they could be considered more stable results due to its lower variability (between 0 wt% and +13 wt%). Surprisingly, the application of the quantification methodology without using the correction factor (CF) showed very similar results to those obtained when including it. It seemed that the adjustment proposed for the alkane-mix response factor by using model compounds only reduces the quantification error for the compounds appearing at the initial part of the chromatogram (*i.e.* toluene and ethylbenzene). Meaning that, the determination of correction factors could be avoided with the consequent simplification of the proposed methodology. Obviously, results related to the quantification of aliphatic compounds without using the CFs showed much lower relative errors because there is no need to adjust the response factor of the alkane mix in this case.

3.3. Quantification methodology application for concentration calculation

The proposed quantification methodology was applied to all the detected signals in the chromatograms of the studied pyrolysis oils following the steps described in Section 3.1. As a result, the concentration (in μg mL^{-1}) of each of the signals detected was obtained. Quantification results for each signal peak for the three use-case pyrolysis liquids (Packaging, WEEE and FRP) are included in Tables 6, 7 and 8, respectively, while the remaining nine pyrolysis oils, "WEEE (1/10)" and "FRP (×10)" can be found in the ESI (from Tables S7–S17†). The following information is included in the tables: (a) number of signal, (b) retention time (RT), (c) window (W), (d) compound name (in case quality match of the MS library search was equal or above 85%), (e) integrated area, (f) area percentage, (g) normalised area to the internal standard, (h) calculated concentration in μg mL^{-1} (calculated as normalised area of the compound multiplied by the correction factor (CF) and by the response factor (RF)), (i) calculated concentration in μg mL^{-1} (calculated as normalised area of the compound without (w/o) multiplying by the correction factor (CF) and multiplying by the response factor (RF)), (j) concentration in wt% (having used the CF), and (k) concentration in wt% (w/o using the CF). At the end of each table, the sum of the concentration of all the detected signals are included (in μg mL^{-1} and wt% referred to the total concentration of the oils described in Table 2). These values are further discussed in the next Section 3.4 where the influence of sample dilution, complexity of the oil composition and GC-MS analytical technique's limitations are related to the obtained results. Additionally, the total sum of the proportion of identified and unknown signals are also included. These results will be referred in Section 3.5, where Kováts Retention Index (KRI) is suggested as an additional compound identification strategy.

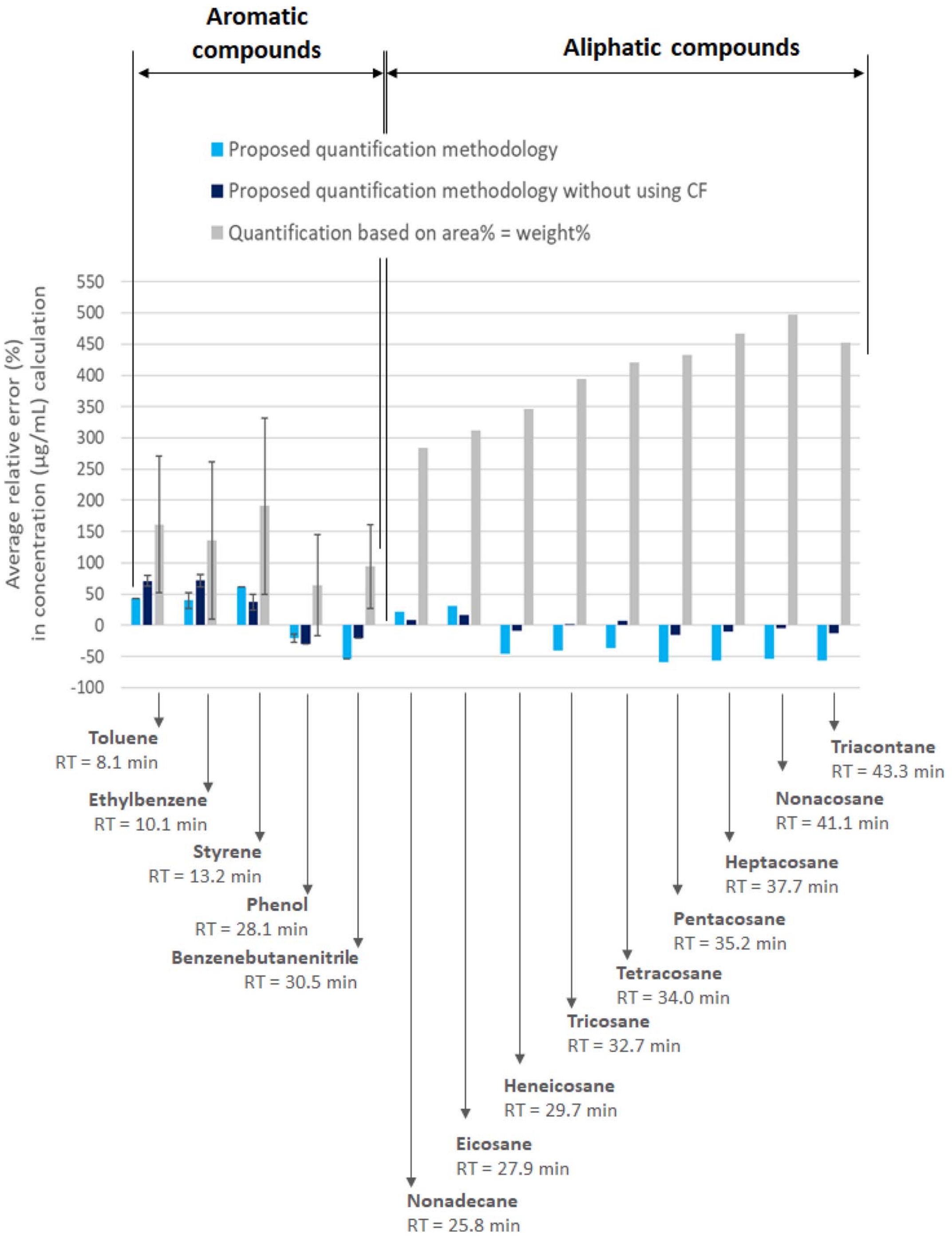

Fig. 3 Average relative errors (wt%) and standard deviation of the concentration (µg mL^{-1}) of validation compounds applying the proposed quantification methodology of this work (light and dark blue bars) and assuming area% equals weight% (grey bars).

From the quantification of the oils the following aspects could be highlighted. For Packaging, around the 33 wt% of the total concentration was detected by GC-MS and styrene was by far the main identified (12–15 wt%). This fact is related to the presence of polystyrene plastic in the original pyrolysed waste, whose monomer styrene is one of the major products when thermally cracking it.[38] Among the remaining detected signals, all presented weight percentages were below the 2 wt%. Regarding the composition, this oil was characterised by a mixture of aromatic and aliphatic compounds. In the case of FRP, similar overall quantification rate was obtained; 23–26 wt% of the total concentration was detected by GC-MS. In this case too, styrene was the compound with the highest yield (*ca.* 5 wt%) followed by other aromatic compounds such as ethylbenzene (*ca.* 3 wt%) and toluene (*ca.* 1.5 wt%). The aromatic nature of FRP oil was expected because polyester is an aromatic resin and additionally, styrene and styrene derivatives are typically used as reactive diluents in the manufacturing process of polyester thermoset

Table 6 Packaging pyrolysis liquid *composition details*

(a) No.	(b) RT (min)	(c) W	(d) Compound	(e) Area	(f) Area%	(g) Norm. area	(h) [ ] with CF (μg mL^{-1})	(i) [ ] w/o CF (μg mL^{-1})	(j) [ ] with CF (wt%)	(k) [ ] w/o CF (wt%)
1	3.464	1		13 342 390	1.0	5.2	276.1	225.1	0.8	0.6
2	3.515	1		815 406	0.1	0.3	16.9	13.8	0.0	0.0
3	3.545	1		1 019 872	0.1	0.4	21.1	17.2	0.1	0.0
4	3.608	1	Hexane	14 719 271	1.1	5.7	304.6	248.3	0.9	0.7
5	3.672	1	1-Hexene	10 791 387	0.8	4.2	223.3	182.1	0.6	0.5
6	3.731	1		1 341 412	0.1	0.5	27.8	22.6	0.1	0.1
7	3.831	1	Heptane	5 339 563	0.4	2.1	110.5	90.1	0.3	0.3
8	3.951	1		3 408 157	0.3	1.3	70.5	57.5	0.2	0.2
9	3.997	1	1-Heptene	13 005 024	1.0	5.1	269.1	219.4	0.8	0.6
10	4.142	1		2 091 863	0.2	0.8	43.3	35.3	0.1	0.1
11	4.210	1		1 277 172	0.1	0.5	26.4	21.5	0.1	0.1
12	4.263	1		2 347 386	0.2	0.9	48.6	39.6	0.1	0.1
13	4.364	1		2 153 487	0.2	0.8	44.6	36.3	0.1	0.1
14	4.422	1		5 572 419	0.4	2.2	115.3	94.0	0.3	0.3
15	4.494	1		839 856	0.1	0.3	17.4	14.2	0.0	0.0
16	6.071	2		16 889 821	1.3	6.6	192.4	233.9	0.5	0.7
17	6.192	2		3 420 349	0.3	1.3	39.0	47.4	0.1	0.1
18	6.295	2		1 258 393	0.1	0.5	14.3	17.4	0.0	0.0
19	6.898	2		2 389 174	0.2	0.9	27.2	33.1	0.1	0.1
20	7.233	2		5 283 845	0.4	2.1	60.2	73.2	0.2	0.2
21	7.928	2	Toluene	25 266 428	1.9	9.9	288	349.9	0.8	1.0
	7.920	2	1-Propanol (IS)	2 560 527						
22	8.121	2	1-Octene	23 863 565	1.8	9.3	271.9	330.4	0.8	0.9
23	8.317	2	Water	9 625 645	0.7	3.8	109.7	133.3	0.3	0.4
24	9.137	2	Cyclooctene	1 431 585	0.1	0.6	16.3	19.8	0.0	0.1
25	9.946	2	Ethylbenzene	37 138 223	2.8	14.5	423	514.2	1.2	1.5
26	10.343	2		1 958 923	0.1	0.8	22.3	27.1	0.1	0.1
27	11.000	3		3 761 669	0.3	1.5	40.9	34.0	0.1	0.1
28	11.331	3		1 049 600	0.1	0.4	11.4	9.5	0.0	0.0
29	11.821	3		4 514 524	0.3	1.8	49.1	40.8	0.1	0.1
30	12.917	3	Styrene	498 974 981	38.1	194.9	5430	4504.3	15.3	12.7
31	13.570	3		6 357 266	0.5	2.5	69.2	57.4	0.2	0.2
32	13.651	3		7 693 308	0.6	3.0	83.7	69.4	0.2	0.2
33	14.363	3		5 708 589	0.4	2.2	62.1	51.5	0.2	0.1
34	14.544	3	Alpha-methylstyrene	47 118 149	3.6	18.4	512.7	425.3	1.4	1.2
35	15.260	3		2 676 598	0.2	1.0	29.1	24.2	0.1	0.1
36	15.446	3	1-Undecene	16 420 651	1.3	6.4	178.7	148.2	0.5	0.4
37	16.198	3		3 898 518	0.3	1.5	42.4	35.2	0.1	0.1
38	16.298	3		925 401	0.1	0.4	10.1	8.4	0.0	0.0
39	16.325	3		1 958 906	0.1	0.8	21.3	17.7	0.1	0.0
40	16.996	3		5 110 306	0.4	2.0	55.6	46.1	0.2	0.1
41	17.145	3	5-Dodecene, (*E*)-	14 322 563	1.1	5.6	155.9	129.3	0.4	0.4
42	17.299	3		4 196 556	0.3	1.6	45.7	37.9	0.1	0.1
43	17.843	3		2 634 632	0.2	1.0	28.7	23.8	0.1	0.1
44	18.056	3		4 261 108	0.3	1.7	46.4	38.5	0.1	0.1
45	18.536	3		817 489	0.1	0.3	8.9	7.4	0.0	0.0
46	18.690	3		21 390 335	1.6	8.4	232.8	193.1	0.7	0.5
47	19.388	3		3 805 670	0.3	1.5	41.4	34.4	0.1	0.1
48	19.574	3		2 630 621	0.2	1.0	28.6	23.7	0.1	0.1
49	19.832	3		10 243 637	0.8	4.0	111.5	92.5	0.3	0.3
50	20.104	3		2 261 930	0.2	0.9	24.6	20.4	0.1	0.1
51	20.267	3		15 390 626	1.2	6.0	167.5	138.9	0.5	0.4
52	21.097	4		1 944 792	0.1	0.8	16.7	14.9	0.0	0.0
53	21.264	4		2 441 849	0.2	1.0	20.9	18.7	0.1	0.1
54	22.006	4		1 368 896	0.1	0.5	11.7	10.5	0.0	0.0
55	22.134	4		9 245 552	0.7	3.6	79.3	70.7	0.2	0.2
56	24.513	4	5-Octadecene, (*E*)-	6 240 398	0.5	2.4	53.5	47.7	0.2	0.1
57	25.633	4		3 191 486	0.2	1.2	27.4	24.4	0.1	0.1
58	25.742	4	Nonadecane	2 275 856	0.2	0.9	19.5	17.4	0.1	0.0

Table 6 (*Contd.*)

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)
No.	RT (min)	W	Compound	Area	Area%	Norm. area	[ ] with CF (μg mL^{-1})	[ ] w/o CF (μg mL^{-1})	[ ] with CF (wt%)	[ ] w/o CF (wt%)
59	26.738	4	1-Nonadecene	10 156 550	0.8	4.0	87.1	77.7	0.2	0.2
60	27.722	4		2 942 285	0.2	1.1	25.2	22.5	0.1	0.1
61	27.790	4	Eicosane	4 636 173	0.4	1.8	39.8	35.4	0.1	0.1
62	28.306	4		1 505 186	0.1	0.6	12.9	11.5	0.0	0.0
63	28.673	4	Cycloeicosane	11 601 316	0.9	4.5	99.5	88.7	0.3	0.3
64	29.566	5	Heneicosane	11 082 773	0.8	4.3	36.2	61.6	0.1	0.2
65	30.373	5	10-Heneicosene (*c*,*t*)	14 015 178	1.1	5.5	45.8	77.9	0.1	0.2
66	31.152	5	Docosane	11 630 086	0.9	4.5	38.0	64.6	0.1	0.2
67	31.474	5		2 272 213	0.2	0.9	7.4	12.6	0.0	0.0
68	31.755	5	Benzene, 1,1′-(1,3-propanediyl) bis-	8 525 223	0.7	3.3	27.9	47.4	0.1	0.1
69	31.873	5	1-Docosene	18 701 131	1.4	7.3	61.2	103.9	0.2	0.3
70	32.562	5	Tricosane	14 634 361	1.1	5.7	47.9	81.3	0.1	0.2
71	32.861	5		1 304 927	0.1	0.5	4.3	7.3	0.0	0.0
72	33.219	5	9-Tricosene, (*Z*)-	15 528 469	1.2	6.1	50.8	86.3	0.1	0.2
73	33.318	5		32 121 388	2.5	12.5	105.0	178.5	0.3	0.5
74	33.495	5		5 757 728	0.4	2.2	18.8	32.0	0.1	0.1
75	33.839	5	Tetracosane	13 419 496	1.0	5.2	43.9	74.6	0.1	0.2
76	34.030	5		3 663 006	0.3	1.4	12.0	20.4	0.0	0.1
77	34.460	5	Cyclotetracosane	15 199 698	1.2	5.9	49.7	84.5	0.1	0.2
78	34.642	5		3 347 340	0.3	1.3	10.9	18.6	0.0	0.1
79	34.737	5		3 565 549	0.3	1.4	11.7	19.8	0.0	0.1
80	35.036	6	Pentacosane	17 376 798	1.3	6.8	36.5	74.5	0.1	0.2
81	35.648	6	*Z*-12-Pentacosene	14 821 715	1.1	5.8	31.2	63.6	0.1	0.2
82	36.282	6		21 397 205	1.6	8.4	45.0	91.8	0.1	0.3
83	36.903	6	9-Hexacosene	18 136 731	1.4	7.1	38.1	77.8	0.1	0.2
84	37.496	6	Heptacosane	11 111 270	0.8	4.3	23.4	47.7	0.1	0.1
85	37.632	6		4 440 997	0.3	1.7	9.3	19.1	0.0	0.1
86	38.253	6		14 740 117	1.1	5.8	31.0	63.2	0.1	0.2
87	38.765	6		2 303 777	0.2	0.9	4.8	9.9	0.0	0.0
88	38.919	6	Octacosane	8 933 266	0.7	3.5	18.8	38.3	0.1	0.1
89	39.110	6		3 185 892	0.2	1.2	6.7	13.7	0.0	0.0
90	39.830	6	Cyclooctacosane	12 409 498	0.9	4.8	26.1	53.2	0.1	0.2
91	40.619	6	Nonacosane	9 456 695	0.7	3.7	19.9	40.6	0.1	0.1
92	40.863	6		3 086 064	0.2	1.2	6.5	13.2	0.0	0.0
93	41.738	6	*Z*-14-Nonacosane	10 295 018	0.8	4.0	21.6	44.2	0.1	0.1
94	42.191	6		2 425 556	0.2	0.9	5.1	10.4	0.0	0.0
95	42.667	6		7 487 853	0.6	2.9	15.7	32.1	0.0	0.1
96	43.025	6		1 518 568	0.1	0.6	3.2	6.5	0.0	0.0
97	44.058	6	Cyclotriacontane	9 005 564	0.7	3.5	18.9	38.6	0.1	0.1
98	45.213	6	Triacontane	5 978 784	0.5	2.3	12.6	25.6	0.0	0.1
99	45.671	6		2 051 534	0.2	0.8	4.3	8.8	0.0	0.0
100	46.954	6		3 473 024	0.3	1.4	7.3	14.9	0.0	0.0
Total detected signals							**12 019**	**11 508**	**33.9**	**32.5**
Identified signals							9242	8748	26	25
Unknown signals							2777	2760	7.8	7.9
Unknown% = 100 × unknown signals/total detected signals							23.1	24.0	23.0	24.3

resins.[39–41] Therefore, it is expected to recover them when thermally degrading it.[42–47] Finally, WEEE oil showed a much higher quantification yield for the detected compounds by GC-MS (around the 90 wt% of the total concentration). Moreover, a very interesting composition was obtained for this upgraded WEEE oil where around the 80 wt% of the total identified composition was made up by styrene (∼35–42 wt%), ethylbenzene (∼17–21 wt%), alpha-methylstyrene (∼10–12 wt%), toluene (∼10–12 wt%) and phenol (∼6 wt%); all of these chemicals with high market value. The remaining weight percentage was related to other phenolic compounds and aromatic hydrocarbons, mainly, although one nitrogenous compound and some unidentified ones were also detected.

3.4. Influence of the sample dissolution and complex nature in the obtained quantification results

Due to the high quantity of compounds present in the studied pyrolysis oils and the presence of unknown compounds, it was

Table 7 WEEE pyrolysis liquid *composition details*

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)
No.	RT (min)	W	Compound	Area	Area%	Norm. area	[ ] with CF (μg mL^{-1})	[ ] w/o CF (μg mL^{-1})	[ ] with CF (wt%)	[ ] w/o CF (wt%)
1	6.074	2		3 533 137	0.3	0.9	26.4	32.1	0.3	0.3
2	7.160	2		3 571 959	0.3	0.9	26.7	32.4	0.3	0.3
3	7.375	2		4 880 894	0.3	1.3	36.5	44.4	0.4	0.4
	8.146	2	1-Propanol (IS)	3 909 636						
4	8.136	2	Toluene	128 315 966	9.2	32.8	958.3	1164.7	9.5	11.6
5	10.162	2	Ethylbenzene	228 793 549	16.4	58.5	1707.7	2075.4	17.0	20.7
6	11.255	3	Benzene, (1-methylethyl)	37 591 576	2.7	9.6	268.1	222.4	2.7	2.2
7	12.061	3	Benzene, propyl	8 111 580	0.6	2.1	57.7	47.9	0.6	0.5
8	13.163	3	Styrene	592 506 672	42.4	151.6	4223.4	3503.5	42.1	34.9
9	14.689	3	Alpha-methylstyrene	165 247 441	11.8	42.3	1178.2	977.4	11.7	9.7
10	18.772	3		5 816 613	0.4	1.5	41.4	34.3	0.4	0.3
11	25.755	4	Naphthalene, 1-methyl	998 436	0.1	0.3	5.6	5.0	0.1	0.0
12	25.934	4	Phenol, 2,6-dimethyl	8 730 049	0.6	2.2	49.0	43.7	0.5	0.4
13	27.923	4	Phenol	114 487 078	8.2	29.3	643.1	573.2	6.4	5.7
14	29.368	5	Phenol, 2,3-dimethyl-	11 210 638	0.8	2.9	24.1	41.0	0.2	0.4
15	30.086	5	Benzenebutanenitrile	16 073 734	1.2	4.1	34.6	58.8	0.3	0.6
16	30.943	5	Phenol, 3-ethyl	6 332 514	0.4	1.3	11.3	19.1	0.1	0.2
17	31.504	5	Phenol, 4-(1-methylethyl)	43 139 189	3.1	11.0	92.4	157.1	0.9	1.6
18	32.471	6	Phenol, *p-tert*-butyl	9 133 589	0.7	2.3	12.6	25.7	0.1	0.3
19	34.711	6	Isopropenylphenol	7 347 303	0.5	1.9	10.1	20.6	0.1	0.2
20	40.301	6		3 013 257	0.2	0.8	4.4	9.0	0.0	0.1
Total detected signals							**9411.7**	**9087.7**	**93.7**	**90.5**
Identified signals							9276.2	8935.5	92.3	89.0
Unknown signals							135.5	152.2	1.4	1.5
Unknown% = 100 × unknown signals/total detected signals							1.4	1.7	1.5	1.7

not possible to calibrate all the detected signals to determine the quantification error for each of the studied oils. However, it was possible to compare the experimentally prepared concentration of the studied pyrolysis oils (see Table 2) with the total concentration of the pyrolysis oils determined by applying the proposed quantification methodology (included as "total value" in the last row of each table in Section 3.3). For that, it was assumed that the total concentration quantified through GC-MS for each pyrolysis oil was equal to the sum of the concentrations of all the detected signals in the chromatograms of each pyrolysis oil.

Fig. 4 compiles together the numerical values of the total concentrations for the three pyrolysis oils used as used-case in Section 3.3 (Packaging, WEEE and FRP) jointly with two additional liquid dissolutions (FRP (×10) and WEEE (1/10)), listed also in Table 2, with the aim to assess the influence of the prepared pyrolysis liquids' concentration in the obtained results. On the upper part of the figure, the absolute and the relative error were included (calculated based on (eqn (3)) and (eqn (4)), respectively) for the total concentration calculated experimentally and quantified based on the proposed methodology (for the blue colour bars). On the bottom of the figure, the number of detected signals per liquid were included together with the grade of sample concentration and the reference to the pyrolysis operating condition classifying the oils as raw and upgraded. Finally, in pink colour the total concentration of the validation compounds (prepared experimentally in dark pink and quantified applying the proposed methodology in light pink) were also added. The aim of showing together these four total concentrations' values was to bear in mind the capacity of the proposed methodology to quantify fairly well validation compounds (as explained in Section 3.2). Tables S18 and S19† include the detailed numerical data of Fig. 4.

A remarkable aspect in Fig. 4 was related to the difference observed between the values obtained for the experimentally prepared samples (dark blue) and the values calculated applying the proposed quantification methodology (light blue). On one side, FRP (×10), Packaging and FRP samples presented significant differences. This fact confirms that a small part of raw pyrolysis oils (less than 40 wt% of the total sample in this case) were being detected by GC-MS. This result was somehow foreseeable, as the fraction of volatile and semi-volatile compounds that could be detected by GC-MS related to the total quantity of the raw pyrolysis liquid has been reported to be only a small part (prior to the application of upgrading processes).[6–8,13] On the other side, WEEE and WEEE (1/10)

Table 8 FRP pyrolysis liquid *composition details*

(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)
No.	RT (min)	W	Compound	Area	Area%	Norm. area	[ ] with CF (μg mL^{-1})	[ ] w/o CF (μg mL^{-1})	[ ] with CF (wt%)	[ ] w/o CF (wt%)
1	3.454	1		4 268 546	1.4	1.6	84.4	68.8	0.9	0.7
2	3.615	1		867 527	0.3	0.3	17.1	14.0	0.2	0.1
3	3.844	1		510 681	0.2	0.2	10.1	8.2	0.1	0.1
4	4.268	1	Propanal	5 878 351	1.9	2.2	116.2	94.7	1.2	1.0
5	6.069	2	Benzene	7 294 525	2.3	2.7	79.4	96.4	0.8	1.0
6	6.295	2		255 963	0.1	0.1	2.8	3.4	0.0	0.0
7	6.402	2		374 115	0.1	0.1	4.1	4.9	0.0	0.1
8	7.724	2	1,3-Dioxolane, 2-ethyl-4-methyl-	13 667 087	4.4	5.1	148.7	180.7	1.5	1.8
	8.150	2	1-Propanol (IS)	2 681 511						
9	8.146	2	Toluene	8 941 908	2.8	3.3	97.3	118.2	1.0	1.2
10	8.682	2		1 571 214	0.5	0.6	17.1	20.8	0.2	0.2
11	9.930	2		3 393 889	1.1	1.3	36.9	44.9	0.4	0.5
12	10.184	2	Ethylbenzene	27 058 674	8.6	10.1	294.4	357.8	3.0	3.6
13	10.577	2		1 091 676	0.3	0.4	11.9	14.4	0.1	0.1
14	11.277	3	Benzene, (1-methylethyl)-	4 288 186	1.4	1.6	44.6	37.0	0.5	0.4
15	11.634	3		1 296 036	0.4	0.5	13.5	11.2	0.1	0.1
16	12.098	3		681 737	0.2	0.3	7.1	5.9	0.1	0.1
17	12.786	3		1 104 503	0.4	0.4	11.5	9.5	0.1	0.1
18	13.203	3	Styrene	62 539 229	19.9	23.3	649.8	539.1	6.6	5.5
19	14.733	3		9 018 066	2.9	3.4	93.7	77.7	1.0	0.8
20	20.372	3		4 313 577	1.4	1.6	44.8	37.2	0.5	0.4
21	24.526	4		8 587 552	2.7	3.2	70.3	62.7	0.7	0.6
22	28.102	4		2 419 221	0.8	0.9	19.8	17.7	0.2	0.2
23	32.230	5	Benzene, 1,1′-(1,3-propanediyl)bis-	35 310 313	11.2	13.2	110.3	187.4	1.1	1.9
24	33.750	5		5 313 260	1.7	2.0	16.6	28.2	0.2	0.3
25	34.563	5	Benzoic acid	29 638 741	9.4	11.1	92.5	157.3	0.9	1.6
26	35.076	5	Bicyclo[4.2.1]nona-2,4,7-triene, 7-phenyl-	11 638 146	3.7	4.3	36.3	61.8	0.4	0.6
27	35.760	6		19 771 207	6.3	7.4	39.7	81.0	0.4	0.8
28	38.217	6		19 998 932	6.4	7.5	40.2	81.9	0.4	0.8
29	40.642	6		11 260 308	3.6	4.2	22.6	46.1	0.2	0.5
30	46.039	6		11 575 350	3.7	4.3	23.2	47.4	0.2	0.5
Total detected signals							**2256.8**	**2516.3**	**23.0**	**25.6**
Identified signals							1669.5	1830.4	17	18.6
Unknown signals							587.3	685.9	6.0	7.0
Unknown% = 100 × unknown signals/total detected signals							26.0	27.3	26.1	27.3

liquids showed very little difference between the prepared total concentration and the quantified one by the proposed method. This is most probably explained by the fact that these pyrolysis liquids were processed further; they were the outcome of an in-line upgrading process (step-wise pyrolysis plus adsorption step as mentioned in Section 2.1) of the volatiles generated during the pyrolysis process.

Fig. 4 shows also two additional pink-colour bars. On one hand, dark-pink colour bars correspond to the sum of the concentration of the validation compounds calculated by conventional calibration process. And, on the other hand, light-pink colour bars, show the sum of the concentration of the calibration compounds calculated applying the proposed quantification methodology. In all cases, light-pink bars show higher values than dark-pink bars, meaning there was some over-estimation in the concentration quantification. However, this was consistent with the relative errors reported for each validation compound in Fig. 3 in Section 3.2. On the one side, for the aromatic validation compounds tested, it could be inferred that for retention times below 28.1 min (RT for phenol), the proposed quantification methodology overestimated the concentrations, while above this retention time there was underestimation. On the other side, for the saturated alkane validation compounds, a similar trend was observed, with the exception of tricosane (RT = 32.7 min) and tetracosane (RT = 34.0 min) where a slight overestimation could be appreciated. Note that regarding alkanes, results without applying the correction factor were considered. This explains why the total concentration of the validation compounds estimated using the proposed quantification methodology was overestimated. The validation compounds present in the samples FRP, Packaging and WEEE were majorly present below the retention time 28.1 min. This means that the quantification error included in the quantification of these samples was mainly affected by overestimation errors.

Apart from that, results showed in Fig. 4 illustrates that the proposed quantification methodology was able to quantify the concentration of the compounds fairly well, independently of the type and dilution of the sample. Lastly, it was also noteworthy for FRP (×10), Packaging and FRP, the imbalance in the

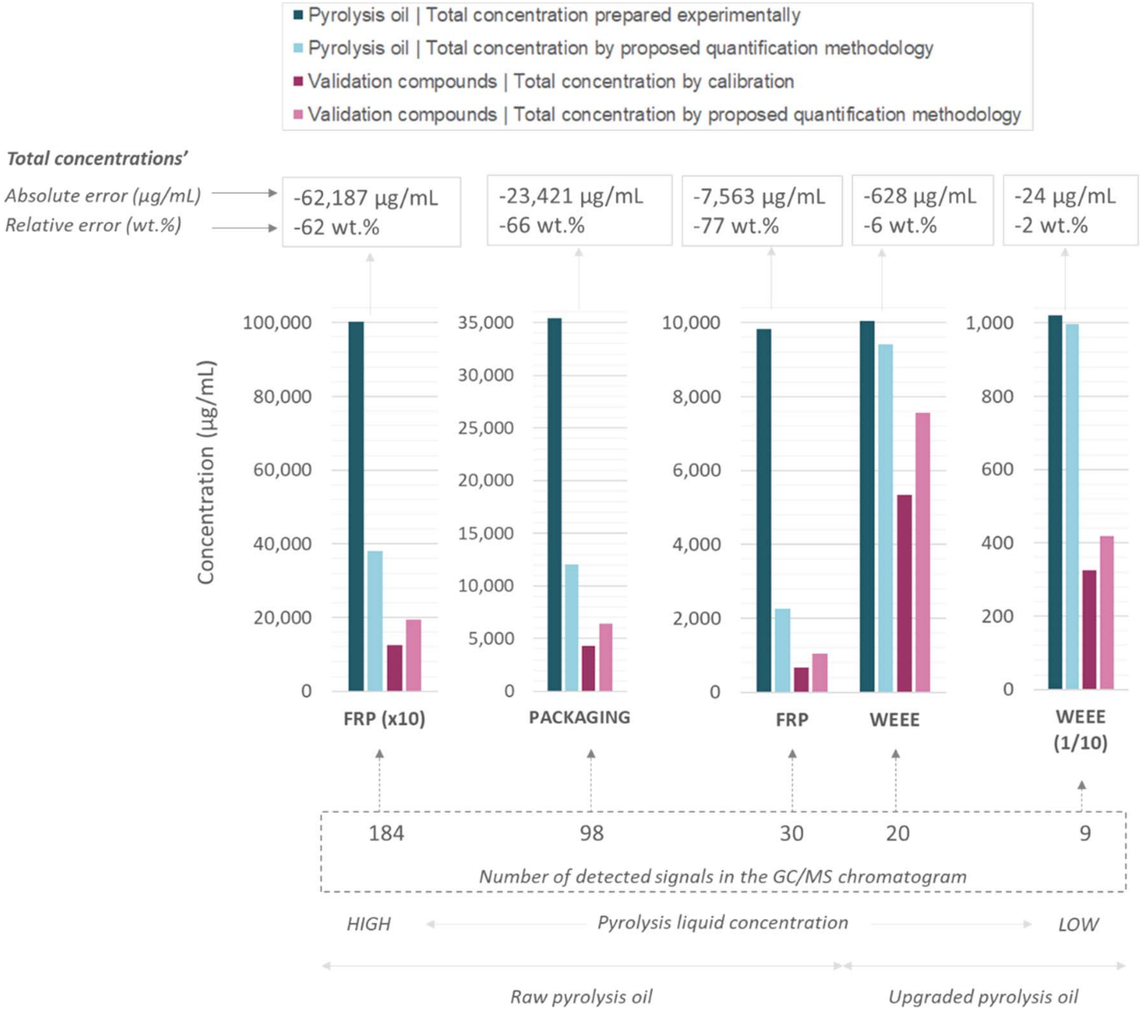

Fig. 4 Total concentration (µg mL^{-1}) of the use-case pyrolysis oils and of the validation compounds (experimental results *vs.* proposed quantification method results).

values obtained for the difference in the total concentration values for the pyrolysis liquid as a whole (blue-colour bars) and the difference in the total concentration values for the validation compounds (pink-colour bars). Blue-colour bars differ much more between them (dark-blue *vs.* light-blue) than the pink-colour bars (dark-pink *vs.* light-pink). This is not the case for WEEE and WEEE (1/10) due to the stated reasons.

The number of detected signals in GC-MS chromatograms seem to be influenced by the sample dilution. The obtained results indicated that, on the one hand, when the concentration of the sample FRP was increased from 9820 µg mL^{-1} to 100 200 µg mL^{-1}, the number of signals detected in the chromatogram increased too, from 30 to 184. However, the total concentration calculated applying the proposed methodology remained under-quantified (14 910 µg mL^{-1} *vs.* 100 200 µg mL^{-1}) with a −85 wt% of relative error. This result showed that, even though an increase in the concentration of the analysed pyrolysis oil by a tenfold enabled the detection of 154 new chemical compounds by the GC-MS, the quantification of the total concentration of this pyrolysis oil applying the proposed quantification methodology was again much smaller than the one prepared experimentally. Therefore, it could be inferred that the total number of compounds in the pure pyrolysis oil could be much higher and that many of them would appear in such small quantity that they were not detected.

Notwithstanding the fact that the proposed quantification methodology's error limits the precision of the calculated concentration values, there could be other reasons that lead to obtain very low total concentration values for some of the pyrolysis oils, mainly for Packaging and FRP. These high quantification differences were thought to be related to the incapacity of the GC-MS technique (in SCAN mode) to depict all the existing chemical compounds in the generated chromatograms. The reasons for not being able to capture all the compounds were thought to be four: (a) the incapacity to detect non-volatiles and high-molecular weight compounds using the GC-MS technique as stated in the previous section, (b) the presence of many chemical compounds in low concentrations, (c) the need to dilute the oil samples for their analysis leading to reduce the original concentration of the compounds to be

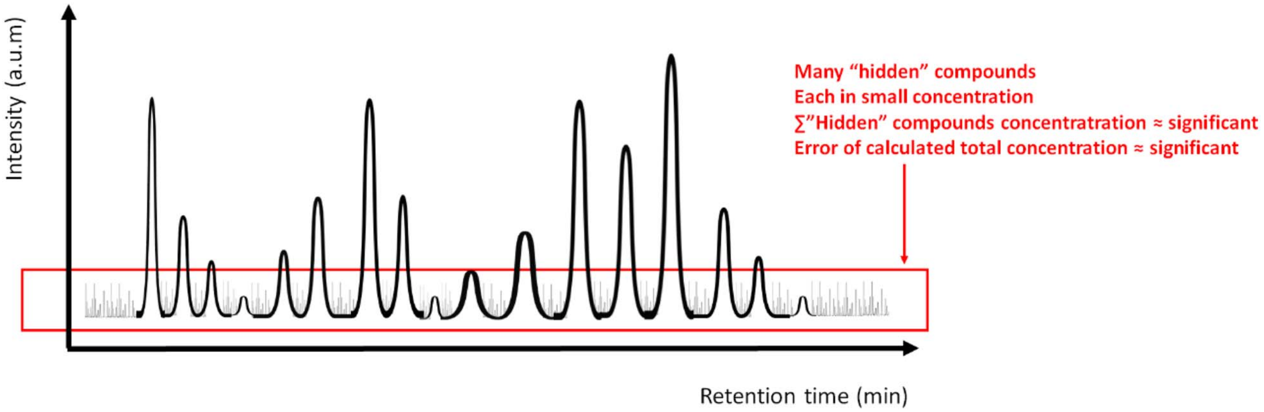

Fig. 5 Schematic representation of compounds lost in the GC-MS chromatogram baseline.

identified and (d) the sensitivity limit of the GC-MS analytical technique. Fig. 5 schematically illustrates this last hypothesis where many chemical compounds may be lost in the base line noise of the GC-MS chromatogram, and ignored in the quantification process, due to their low concentration. This idea is consistent with the number of detected signals in the GC-MS chromatograms for each analysed pyrolysis oil samples (Fig. 4). It could be hinder that it was directly related to the pyrolysis liquid concentration analysed, as the higher the concentration of the pyrolysis liquid in the solvent, the higher the number of detected compounds in the GC-MS chromatogram (FRP (×10) *vs.* FRP, WEEE *vs.* WEEE (1/10), and FRP (×10) > Packaging > FRP > WEEE > WEEE (1/10)). According to these results, it could be said that chemical compounds were lost in the base line of the GC-MS analytical technique when their concentration was low, leading to identify less volatile or semi-volatile compounds than those present in the liquids.

On the other hand, if the concentration of the sample WEEE was decreased from 10 040 μg mL^{-1} to 1020 μg mL^{-1}, the number of detected signals decreased consistently (from 20 to 9 chemical compounds). However, in this case the total concentration calculated applying the proposed methodology was fairly good (996 μg mL^{-1} *vs.* 1020 μg mL^{-1}). This result might be explained by the combination of two facts. On the one hand, the 11 signals that were not detected in the least concentrated sample (WEEE (1/10)) could represent a small weight percentage of the total sample. If so, they would impact mildly in the total concentration value. On the other hand, as showed in Section 3.2, the error added by the proposed quantification methodology could also provoke some over-estimation in the few detected signals. Finally, as mentioned before in Section 3.4, another plausible explanation for this low quantification relative errors could be related to the probably less complex nature of these WEEE liquids, what could also be inferred by the fewer number of compounds detected and shown previously in Table 7 compared to Packaging (Table 6) and FRP (Table 8), as well as the higher total concentration of the calibrated compounds (in dark pink in Fig. 4). This is consistent with the difference in the number of detected compounds between FRP and WEEE (30 *vs.* 20, respectively). They differed in number even though the same pyrolysis liquid concentration was prepared in both cases (around 10 000 μg mL^{-1}). In this case, complexity of the liquid composition should be considered together with the pyrolysis operation conditions. On the one hand, FRP was a pyrolysis liquid coming from a polyester based glass fibre reinforced plastic end-of-life waste. Due to the complex nature of polyester thermosetting resins,[40,48,49] it was expected that the applied thermal treatment (single-step pyrolysis at 3 °C min^{-1} heating rate up to 500 °C without N_2 gas flow) would generate higher quantity of chemical compounds. On the other hand, even though the plastic fraction from WEEE could be considered as complex as the plastic from FRPs, the pyrolysis treatment carried out to WEEE sample provoked higher cracking of the chemical compounds generated during the pyrolysis. In the case of WEEE, continuous N_2 gas flow was included in addition to a step-wise pyrolysis followed by a thermal cracking step in a fixed bed reactor in series, where an adsorbent upgraded the quality of the pyrolysis oil (as briefly described in Table S1†). Therefore, the higher number of detected signals for FRP compared to WEEE in the GC-MS chromatograms was consistent with the operating conditions of the pyrolysis process employed with each sample.

3.5. Kováts retention index calculation for temperature-programmed gas chromatography (Van den Dool and Kratz formula)

Depending on the complexity of the generated pyrolysis liquids (raw *vs.* upgraded) the proportion of the oil composition detected by GC-MS could be lower or higher. In the same way, among these detected compounds, the capacity to correctly identify chemical compounds by the MS library differs from oil to oil. In the presented work, in order to accept a compound as correctly identified by the MS library, the minimum quality match was set in 85%. Based on this criteria, 20% of the detected signals by the GC-MS were poorly identified in the case of Packaging (Table 6) and FRP (Table 8) and, therefore, no compound name was assigned to them. In contrast, it was possible to identify the remaining 80% of the detected signals. The case of WEEE sample was very different. In this case, the rate of unknown compounds was below the 2% (Table 7), which

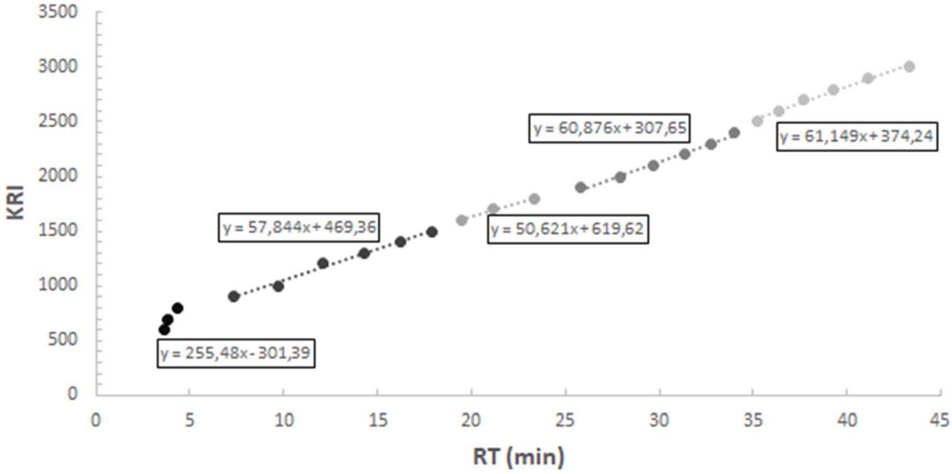

Fig. 6 Kováts Retention Index (KRI) in function of retention time (RT) and heating segment for the n-alkanes in the employed alkane-mix.

is consistent with the aspects previously discussed regarding the simpler composition of the upgraded pyrolysis oils.

In this sense, Kováts Retention Index (KRI) can be employed as a complementary information to identify the unknown compounds present in the pyrolysis oils. The use of the homologous series of n-alkanes is based on the knowledge that under isothermal conditions the retention times increase exponentially. This KRI relates the logarithm of the retention time value and the number of carbons of each alkane. The Kováts RI of these reference alkanes are calculated, by definition, multiplying the number of carbons of the alkane by 100 (for any stationary phase and at any column temperature). However, when non-isothermal chromatographic conditions are used, the modification introduced by Van den Dool and Kratz (eqn (6)) is a more appropriate approach.[31]

$$I_{\mathrm{TPGC,S}}^{\mathrm{ST.PH}} = 100 \times n \times \frac{t_{\mathrm{R}}(s) - t_{\mathrm{R}}(z)}{t_{\mathrm{R}}(z + n) - t_{\mathrm{R}}(z)} + 100 \times z \quad (6)$$

where "I" is the retention index, "t_{R}" is the retention time, "s" is the compound of interest, "ST. PH" is the stationary phase, "n" is the difference in carbon number of the two n-alkanes taken as reference and "z" and "$(z + n)$" are the n-alkanes with "z" and "$(z + 1)$" carbon numbers. Note that, in theory, this equation is strictly valid for linear temperature programs and its application to multi-linear temperature programming (as it is the case of this work) could lead to higher variabilities in the results.[31] One way to avoid these variabilities is to study every heating segment of the chromatographic method separately, attributing an independent equation to each isothermal and non-isothermal stage. In this sense, the KRI for each compound in the calibration mix is calculated for each heating segment mentioned in the Section 2.3.

Fig. 6 shows the linear regression between the non-isothermal Kováts RI of all the alkanes present in the employed alkane-mix and their retention times (RTs) for the temperature programme defined in Section 2.3. The linear regression equations fitting the n-alkanes' mix is shown in eqn (7)–(11).

Isothermal 40 °C:

$$\text{KRI } (y \text{ axis}) = 255.48 \times \text{RT } (x \text{ axis}) - 301.39 \ (R^2 = 0.9465) \quad (7)$$

Non-isothermal 40–150 °C:

$$\text{KRI } (y \text{ axis}) = 57.844 \times \text{RT } (x \text{ axis}) + 469.36 \ (R^2 = 0.9923) \quad (8)$$

Isothermal 150 °C:

$$\text{KRI } (y \text{ axis}) = 50.621 \times \text{RT } (x \text{ axis}) + 619.62 \ (R^2 = 0.9958) \quad (9)$$

Non-isothermal 150–240 °C:

$$\text{KRI } (y \text{ axis}) = 60.876 \times \text{RT } (x \text{ axis}) + 307.65 \ (R^2 = 0.9918) \quad (10)$$

Isothermal 240 °C:

$$\text{KRI } (y \text{ axis}) = 61.149 \times \text{RT } (x \text{ axis}) + 374.24 \ (R^2 = 0.9864) \quad (11)$$

In this way, identification of chemical compounds defined in the MS library with a low match quality level might be possible. The Kováts RI of all the signals detected on the chromatograms of the pyrolysis oils were determined following this procedure Table S20† compiles the KRI and the identified compound for all the analysed liquids to make them available to other researchers/databases who may find this information useful to identify their own compounds in their pyrolysis oils (taking into account the chromatographic column and temperature programme implemented, described in Section 2.3).

4. Conclusions

This paper presents an easy methodology that makes it possible to quantify the concentration of all the detected compounds by GC-MS, present in pyrolysis oils coming from streams of complex plastic waste from diverse nature. The quantification error is between +62 wt% and −59 wt% with a standard deviation between 0 wt% and + 13 wt%. So far, the state of the art for quantification of the concentration of compounds by GC-MS can be considered the one carried out for bio-oils (pyrolysis liquids generated from biomass) which reported variabilities around the 20%. Therefore, the error presented by the proposed quantification methodology would be in the same order of magnitude. The proposed quantification methodology provides a quantitative idea of the composition of the compounds present in the oils compared to the current situation, where results from the analysis of complex plastic pyrolysis oils using GC-MS are almost exclusively published and evaluated using the area percentage of identified compounds without questioning the representativeness of the obtained results. Moreover, the presented work also includes the evaluation of what would be the quantification error assuming that the area percentage was equal to the weight percentage of the compounds. As a result, it has been concluded that the average relative error for the validation compounds (between 284 wt% and 498 wt%) is higher than with the proposed quantification methodology. But, more importantly, the standard deviation is much higher (between 67% and 147%), meaning that reliable results could not be expected from this assumption. Definitively, the proposed quantification methodology is seen as a feasible approach to be easily implemented. It might not accurately determine every chemical compound present in the pyrolysis oil mixture when the complexity of the pyrolysis oils is high. However, it does provide a quantitative overview of the concentration of the main detected compounds by the GC-MS as well as a quantification value (as a whole) of those compounds that are not being visualised in the GC-MS chromatogram due to their low individual concentration, non-volatility or high molecular weight. Moreover, the difference between the value of the total concentration of the experimentally prepared pyrolysis oils and the value of the total concentration calculated applying the proposed quantification methodology could be an indicator of the complexity of the pyrolysis oil being analysed, by suggesting the presence of more or less chemical compounds.

Author contributions

A. Serras-Mallillos: conceptualization, investigation, methodology, writing, original draft preparation, B. B. Perez-Martínez: investigation, writing, reviewing and editing, A. Iriondo: supervision, reviewing and editing, E. Acha: funding acquisition, supervision, reviewing and editing, A. López-Urionabarrenechea: funding acquisition, supervision, writing, reviewing and editing, B. M. Caballero: funding acquisition, project administration, reviewing and editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Ministry of Science and Innovation of Spain [grant number PID2019-110770RB-I00/AEI/10.13039/501100011033]; the Basque Government [grant number IT1554-22 and ELKARTEK 2023 Program (NEOPLAST 2 Project, Reference KK-2023/00060)]. The authors thank for the technical and human support provided by SGiker (UPV/EHU, ERDF, EU). Authors are especially grateful to Luis Bartolomé from SGIker for the technical and human support provided.

References

1 I. S. Lase, D. Tonini, D. Caro, P. F. Albizzati, J. Cristóbal, M. Roosen, M. Kusenberg, K. Ragaert, K. M. Van Geem, J. Dewulf and S. De Meester, How much can chemical recycling contribute to plastic waste recycling in Europe? An assessment using material flow analysis modeling, *Resour., Conserv. Recycl.*, 2023, **192**, 1–19, DOI: 10.1016/j.resconrec.2023.106916.

2 T. Xayachak, N. Haque, R. Parthasarathy, S. King, N. Emami, D. Lau and B. K. Pramanik, Pyrolysis for plastic waste management: An engineering perspective, *J. Environ. Chem. Eng.*, 2022, **10**, 108865, DOI: 10.1016/j.jece.2022.108865.

3 S. Das, C. Liang and J. B. Dunn, Plastics to fuel or plastics: Life cycle assessment-based evaluation of different options for pyrolysis at end-of-life, *Waste Manag.*, 2022, **153**, 81–88, DOI: 10.1016/j.wasman.2022.08.015.

4 M. Kusenberg, M. Roosen, A. Zayoud, M. R. Djokic, H. Dao Thi, S. De Meester, K. Ragaert, U. Kresovic and K. M. Van Geem, Assessing the feasibility of chemical recycling via steam cracking of untreated plastic waste pyrolysis oils: Feedstock impurities, product yields and coke formation, *Waste Manag.*, 2022, **141**, 104–114, DOI: 10.1016/j.wasman.2022.01.033.

5 M. Kusenberg, A. Eschenbacher, M. R. Djokic, A. Zayoud, K. Ragaert, S. De Meester and 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 Manag.*, 2022, **138**, 83–115, DOI: 10.1016/j.wasman.2021.11.009.

6 M. Staš, D. Kubička, J. Chudoba and M. Pospíšil, Overview of analytical methods used for chemical characterization of pyrolysis bio-oil, *Energy Fuels*, 2014, **28**, 385–402, DOI: 10.1021/ef402047y.

7 M. Staš, M. Auersvald, L. Kejla, D. Vrtiška, J. Kroufek and D. Kubička, Quantitative analysis of pyrolysis bio-oils: A review, *TrAC, Trends Anal. Chem.*, 2020, **126**, 115857, DOI: 10.1016/j.trac.2020.115857.

8 M. Staš, J. Chudoba, M. Auersvald, D. Kubička, S. Conrad, T. Schulzke and M. Pospíšil, Application of orbitrap mass spectrometry for analysis of model bio-oil compounds and fast pyrolysis bio-oils from different biomass sources, *J. Anal. Appl. Pyrolysis*, 2017, **124**, 230–238, DOI: 10.1016/j.jaap.2017.02.002.

9 M. Staš, J. Chudoba, D. Kubička, J. Blažek and M. Pospíšil, Petroleomic Characterization of Pyrolysis Bio-oils: A Review, *Energy Fuels*, 2017, **31**, 10283–10299, DOI: 10.1021/acs.energyfuels.7b00826.

10 A. G. Marshall and R. P. Rodgers, Petroleomics: Chemistry of the underworld, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 18090–18095, DOI: **10.1073/pnas.0805069105**.

11 D. Zanella, M. Romagnoli, S. Malcangi, M. Beccaria, T. Chenet, C. De Luca, F. Testoni, L. Pasti, U. Visentini, G. Morini, A. Cavazzini and F. A. Franchina, The contribution of high-resolution GC separations in plastic recycling research, *Anal. Bioanal. Chem.*, 2023, **415**, 2343–2355, DOI: **10.1007/s00216-023-04519-8**.

12 S. Đurović, Application of the GC/MS technique in environmental analytics: Case of the essential oils, *Green Sustainable Process for Chemical and Environmental Engineering and Science: Analytical Techniques for Environmental and Industrial Analysis*, 2020, pp. 197–208, DOI: **10.1016/B978-0-12-821883-9.00005-9**.

13 A. Undri, M. Abou-Zaid, C. Briens, F. Berruti, L. Rosi, M. Bartoli, M. Frediani and P. Frediani, A simple procedure for chromatographic analysis of bio-oils from pyrolysis, *J. Anal. Appl. Pyrolysis*, 2015, **114**, 208–221, DOI: **10.1016/j.jaap.2015.05.019**.

14 D. K. Ratnasari, M. A. Nahil and P. T. Williams, Catalytic pyrolysis of waste plastics using staged catalysis for production of gasoline range hydrocarbon oils, *J. Anal. Appl. Pyrolysis*, 2017, **124**, 631–637, DOI: **10.1016/j.jaap.2016.12.027**.

15 N. Miskolczi, F. Buyong, A. Angyal, P. T. Williams and L. Bartha, Two stages catalytic pyrolysis of refuse derived fuel: Production of biofuel via syncrude, *Bioresour. Technol.*, 2010, **101**, 8881–8890, DOI: **10.1016/j.biortech.2010.06.103**.

16 N. Miskolczi, N. Borsodi, F. Buyong, A. Angyal and P. T. Williams, Production of pyrolytic oils by catalytic pyrolysis of Malaysian refuse-derived fuels in continuously stirred batch reactor, *Fuel Process. Technol.*, 2011, **92**, 925–932, DOI: **10.1016/j.fuproc.2010.12.012**.

17 A. López, I. de Marco, B. M. Caballero, M. F. Laresgoiti and A. Adrados, Pyrolysis of municipal plastic wastes: Influence of raw material composition, *Waste Manag.*, 2010, **30**, 620–627, DOI: **10.1016/j.wasman.2009.10.014**.

18 I. S. C. Carregosa, J. de C. Carregosa, W. R. Silva, T. M. Santos and A. Wisniewski, Thermochemical conversion of aquatic weed biomass in a rotary kiln reactor for production of bio-based derivatives, *J. Anal. Appl. Pyrolysis*, 2023, **173**, 106048, DOI: **10.1016/j.jaap.2023.106048**.

19 S. I. Okopi, J. Wang, W. Kong, Z. Yu, E. A. Ndudi, L. Che, Z. Gu and F. Xu, Valorization of food waste impurities by catalytic co-pyrolysis for production of pyrolysis oil with high energy potential, *J. Anal. Appl. Pyrolysis*, 2023, **170**, 105918, DOI: **10.1016/j.jaap.2023.105918**.

20 S. Vichaphund, P. Wimuktiwan, C. Soongprasit, K. Soongprasit, S. Phetchcrai, R. Sirichaivetkul and D. Atong, Study on pyrolysis behavior of polymeric coated aluminium scrap using TGA and Py-GC/MS, *J. Anal. Appl. Pyrolysis*, 2023, **172**, 105982, DOI: **10.1016/j.jaap.2023.105982**.

21 Z. Fu, F. Hua, S. Yang, H. Wang and Y. Cheng, Evolution of light olefins during the pyrolysis of polyethylene in a two-stage process, *J. Anal. Appl. Pyrolysis*, 2023, **169**, 105877, DOI: **10.1016/j.jaap.2023.105877**.

22 M. R. Djokic, T. Dijkmans, G. Yildiz, W. Prins and K. M. Van Geem, Quantitative analysis of crude and stabilized bio-oils by comprehensive two-dimensional gas-chromatography, *J. Chromatogr. A*, 2012, **1257**, 131–140, DOI: **10.1016/j.chroma.2012.07.035**.

23 P. Wenig and J. Odermatt, Efficient analysis of Py-GC/MS data by a large scale automatic database approach: An illustration of white pitch identification in pulp and paper industry, *J. Anal. Appl. Pyrolysis*, 2010, **87**, 85–92, DOI: **10.1016/j.jaap.2009.10.007**.

24 P. Ausloss, C. L. Clifton, S. G. Lias, A. I. Mikaya, S. E. Stein, D. V. Tchekhovskoi, O. D. Sparkman, V. Zaikin and D. Zhu, The Critical Evaluation of a Comprehensive Mass Spectral Library, *J. Am. Soc. Mass Spectrom.*, 1999, **10**, 287–299.

25 T. O. Melo, F. A. Marques and F. A. Hansel, Pyrolysis-gas chromatography–mass spectrometry Kováts retention index of pyrolysis products of lignocellulosic materials, *J. Anal. Appl. Pyrolysis*, 2017, **126**, 332–336, DOI: **10.1016/j.jaap.2017.05.013**.

26 S. C. Detlev Hochmuth, *Mass Finder 4*, 2010, **https://massfinder.com/wiki/MassFinder_4#Retention_index_feature**.

27 N. Mass Spectrometry Data Center, *NIST 17 GC Method/Retention Index Library*, 2020, **https://chemdata.nist.gov/dokuwiki/doku.php?id=chemdata:ridatabase**.

28 V. I. Babushok, P. J. Linstrom, J. J. Reed, I. G. Zenkevich, R. L. Brown, W. G. Mallard and S. E. Stein, Development of a database of gas chromatographic retention properties of organic compounds, *J. Chromatogr. A*, 2007, **1157**, 414–421, DOI: **10.1016/j.chroma.2007.05.044**.

29 H. Burdová, D. Pilnaj and P. Kuráň, Application of low-energy-capable electron ionization with high-resolution mass spectrometer for characterization of pyrolysis oils from plastics, *J. Chromatogr. A*, 2023, **1711**, 1–10, DOI: **10.1016/j.chroma.2023.464445**.

30 M. S. Klippel and M. F. Martins, Physicochemical assessment of waxy products directly recovered from plastic waste pyrolysis: Review and synthesis of characterization techniques, *Polym. Degrad. Stab.*, 2022, **204**, 1–17, DOI: **10.1016/j.polymdegradstab.2022.110090**.

31 G. Castello, Retention index systems: Alternatives to the n-alkanes as calibration standards, *J. Chromatogr. A*, 1999, **842**, 51–64, DOI: **10.1016/S0021-9673(98)00989-3**.

32 M. Trass, *Split Injections in Gas Chromatography: How to Reduce Inlet Discrimination by Using a Liner with Glass Wool*, 2008, pp. 1–2, **https://www.phenomenex.com**.

33 D. Rood, Gas chromatography problem solving and troubleshooting, *J. Chromatogr. Sci.*, 2004, **42**, 506–507, DOI: **10.1093/chromsci/42.1.54**.

34 J. H. Marsman, J. Wildschut, F. Mahfud and H. J. Heeres, Identification of components in fast pyrolysis oil and upgraded products by comprehensive two-dimensional gas chromatography and flame ionisation detection, *J. Chromatogr. A*, 2007, **1150**, 21–27, DOI: **10.1016/j.chroma.2006.11.047**.

35 E. Christensen and J. Ferrell, *Quantification of Semi-volatile Oxygenated Components of Pyrolysis Bio-Oil by Gas Chromatography/Mass Spectrometry (GC/MS)*, 2016, pp. 1–10, **https://www.nrel.gov/publications**.

36 ASTM, *ASTM D7544-12(2017) Standard Specification for Pyrolysis Liquid Biofuel*, 2012, p. 5, DOI: **10.1520/D7544-12R17**.

37 EPA, *Method 8270D Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry*, US EPA Arch, 2014, **https://archive.epa.gov/epa/sites/production/files/2015-12/documents/8270d.pdf**.

38 Y. Liu, J. Qian and J. Wang, Pyrolysis of polystyrene waste in a fluidized-bed reactor to obtain styrene monomer and gasoline fraction, *Fuel Process. Technol.*, 2000, **63**, 45–55, DOI: **10.1016/S0378-3820(99)00066-1**.

39 A. Kandelbauer, G. Tondi, O. C. Zaske and S. H. Goodman, *Unsaturated Polyesters and Vinyl Esters*, Elsevier Inc., 3rd edn, 2014, DOI: **10.1016/B978-1-4557-3107-7.00006-3**.

40 A. A. Athawale and J. A. Pandit, *Unsaturated Polyester Resins, Blends, Interpenetrating Polymer Networks, Composites, and Nanocomposites: State of the Art and New Challenges*, Elsevier Inc., 2019, DOI: **10.1016/B978-0-12-816129-6.00001-6**.

41 P. Penczek, P. Czub and J. Pielichowski, Unsaturated polyester resins: Chemistry and technology, *Adv. Polym. Sci.*, 2005, **184**, 1–95, DOI: **10.1007/b136243**.

42 N. Grittner, W. Kaminsky and G. Obst, Fluid bed pyrolysis of anhydride-hardened epoxy resins and polyether-polyurethane by the Hamburg process, *J. Anal. Appl. Pyrolysis*, 1993, **25**, 293–299, DOI: **10.1016/0165-2370(93)80048-5**.

43 A. Torres, I. De Marco, B. M. Caballero, M. F. Laresgoiti, M. A. Cabrero and M. J. Chomón, GC-MS analysis of the liquid products obtained in the pyrolysis of fibre-glass polyester sheet moulding compound, *J. Anal. Appl. Pyrolysis*, 2001, **58–59**, 189–203, DOI: **10.1016/S0165-2370(00)00122-4**.

44 F. A. López, M. I. Martín, F. J. Alguacil, J. M. Rincón, T. A. Centeno and M. Romero, Thermolysis of fibreglass polyester composite and reutilisation of the glass fibre residue to obtain a glass-ceramic material, *J. Anal. Appl. Pyrolysis*, 2012, **93**, 104–112, DOI: **10.1016/j.jaap.2011.10.003**.

45 L. Giorgini, C. Leonardi, L. Mazzocchetti, G. Zattini, M. Cavazzoni, I. Montanari, C. Tosi and T. Benelli, Pyrolysis of fiberglass/polyester composites: Recovery and characterization of obtained products, *FME Trans.*, 2016, **44**, 405–414, DOI: **10.5937/fmet1604405G**.

46 S. R. Naqvi, H. M. Prabhakara, E. A. Bramer, W. Dierkes, R. Akkerman and G. Brem, A critical review on recycling of end-of-life carbon fibre/glass fibre reinforced composites waste using pyrolysis towards a circular economy, *Resour., Conserv. Recycl.*, 2018, **136**, 118–129, DOI: **10.1016/j.resconrec.2018.04.013**.

47 S. M. Seraji, P. Song, R. J. Varley, S. Bourbigot, D. Voice and H. Wang, Fire-retardant unsaturated polyester thermosets: The state-of-the-art, challenges and opportunities, *Chem. Eng. J.*, 2022, **430**, 132785, DOI: **10.1016/j.cej.2021.132785**.

48 S. V. Levchik and E. D. Weil, Thermal decomposition, combustion and flame-retardancy of epoxy resins - A review of the recent literature, *Polym. Int.*, 2004, **53**, 1901–1929, DOI: **10.1002/pi.1473**.

49 T. Takeichi and N. Furukawa, *Epoxy Resins and Phenol-Formaldehyde Resins*, Elsevier B.V., 2012, DOI: **10.1016/B978-0-444-53349-4.00157-6**.