UNIVERSIDAD DE MURCIA

Targeted and non-targeted gas chromatography-mass spectrometry analysis of volatile compounds released from recycled and virgin polyethylene terephthalate polymer: Authentication study

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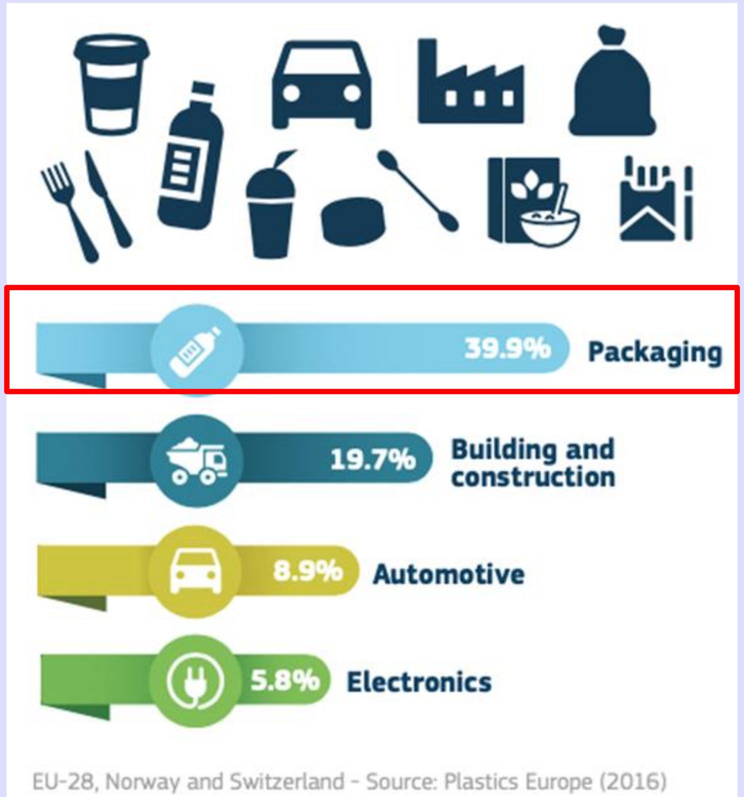
Plastic production has highly increased



Sustainable plastic packaging solution → Recycling

Recycling plastic packaging is needed to reduce plastic residue, BUT there is a need to control its quality

Recycling process → Degradation reactions

could lead to the generation of

Organic Volatile Compounds (VOCs)

Generate unpleasant odors

A risk for the consumer

VOCs monitoring is needed in recycled materials

Authentication of recycled packaging is required to avoid frauds.

Analytical strategy for VOCs determination and authentication of recycled plastic content

Simple

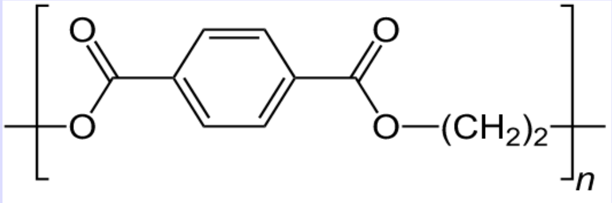
Automatized

Effective

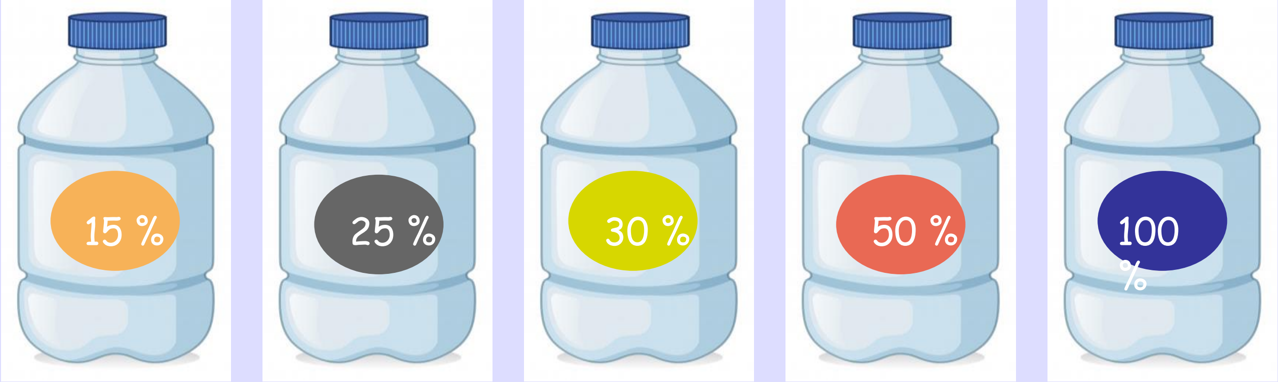
HS-GC-MS

VOCs fingerprint

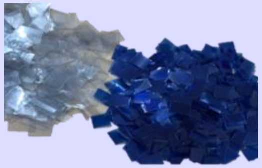
Chemometric (Principal Component Analysis & Partial Least Square correlation)



Polyethylene Terephtalate mineral water bottles: virgin & different recycled content



Quantification of some VOCs



0.3 x 0.4 cm

HS-GC-MS

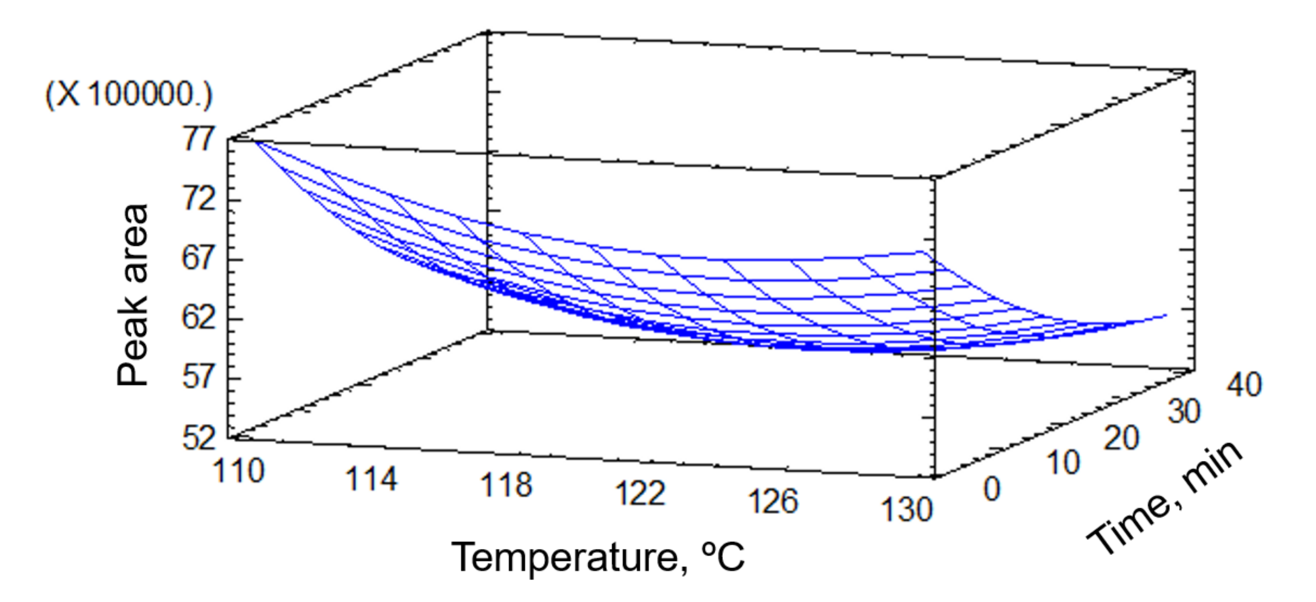
Volatile fingerprint

Chemometric (PLS) Authentication study

2 g of recycled PET sample
+ 2-chloroanisole (Internal Standard, IS)

Selection of the HS incubation temperature and time

Surface Response Design method (face-centered):



Higher analytical signals were obtained with 110 °C and 5 min.

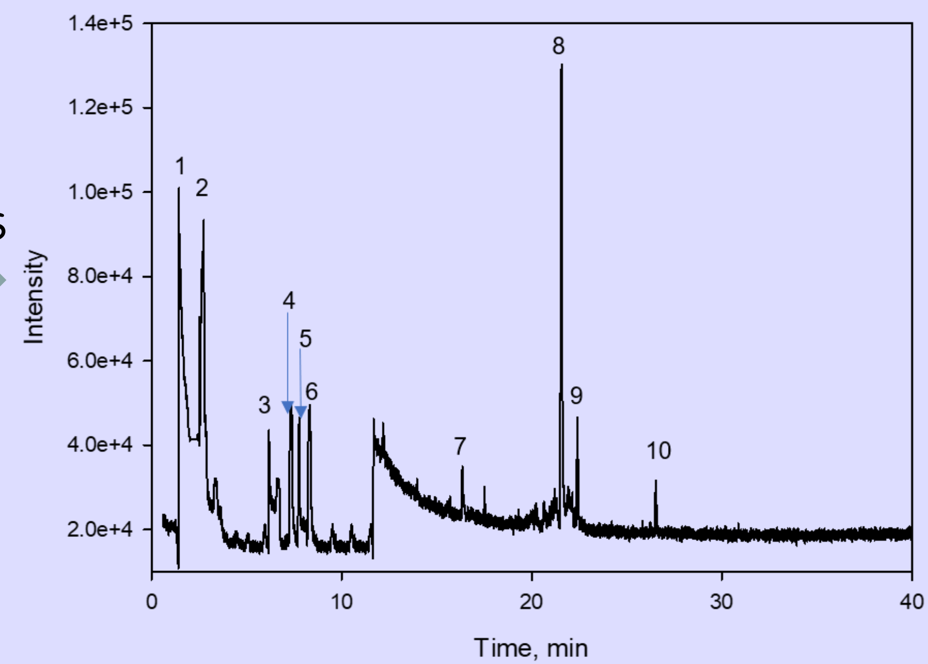
NON-TARGETED APPROACH FOR VOCs

Homemade database including VOCs from the literature

Compounds	ions (m/z)		
2,4-Ditertbutyl phenol (DBP)	57, 191, 206		
2-Ethyl-1,3-dimethylbenzene	91, 106, 107		
10-Methylnonadecane	57, 71, 282	Decanal	41, 43, 156
5-Methyl undecane	43, 57,156	1,2-dichlorobenzene	146, 148, 150
7-Methyl hexadecane	57, 71, 240	Toluene	91, 92, 93
Tritetracontane	57, 71, 606	1-octene	43, 55, 112
Tetratetracontane	57, 71, 619	2-undecanone	43, 58, 170
1-Chlorooctadecane	43, 57, 289	2-nonanone	43, 58, 142
Heptacosane	43, 57, 380	2-heptadecanone	43, 58, 254
Decane	43, 57, 142	2-heptenal	27, 41, 112
Hexadecane	43, 57, 226	2-octenal	41, 55, 126
Nonadecane	43, 57, 268	2-decenal	41, 43, 154
Dodecane	43, 57, 170	n-Acetic acid	43, 45, 60
Octadecane	43, 57, 254	n-Hexanoic acid	60, 73, 87
Tetradecane	43, 57, 198	Octadecanoid acid	43, 73, 284
Propyl octyl ether	43, 57, 71	Acetone	42, 43, 58
10-Methyleicosane	43, 57, 296	2,6-Dimethyl-nonane	43, 57, 156
3,8-Dimethyldecane	43, 57, 170	3-Methyl-5-propyl-nonane	57, 71, 184
2,6,10-Trimethyldodecane	57, 71, 212	4-Methyl-decane	43, 71, 156
1,1'-Oxybis dodecane	43, 57, 354	2-Methyl-decane	43, 57, 156
1,1'-Oxybis decane	43, 57, 298	3-Methyl-decane	57, 71, 156
Tetratriacontane	57, 71, 479	3,7-Dimethyl-decane	43, 57, 170
Benzophenone	77, 105, 182	3,6-Dimethyl-undecane	43, 57, 184
Dibutyl phthalate (DBP)	149, 150, 278	2-Methyl-dodecane	43, 57, 184
Diethyl phthalate (DEP)	149, 177, 222	2-butanamine	41, 44, 86
Heptanal	41, 70, 114	n-Propyl acetate	43, 61, 73
Dodecanal	43, 57, 184	Methyl benzene	91, 92, 93

HS-GC-MS

Chromatogram of an unspiked real sample to which the IS was added (50 ng g^{-1})

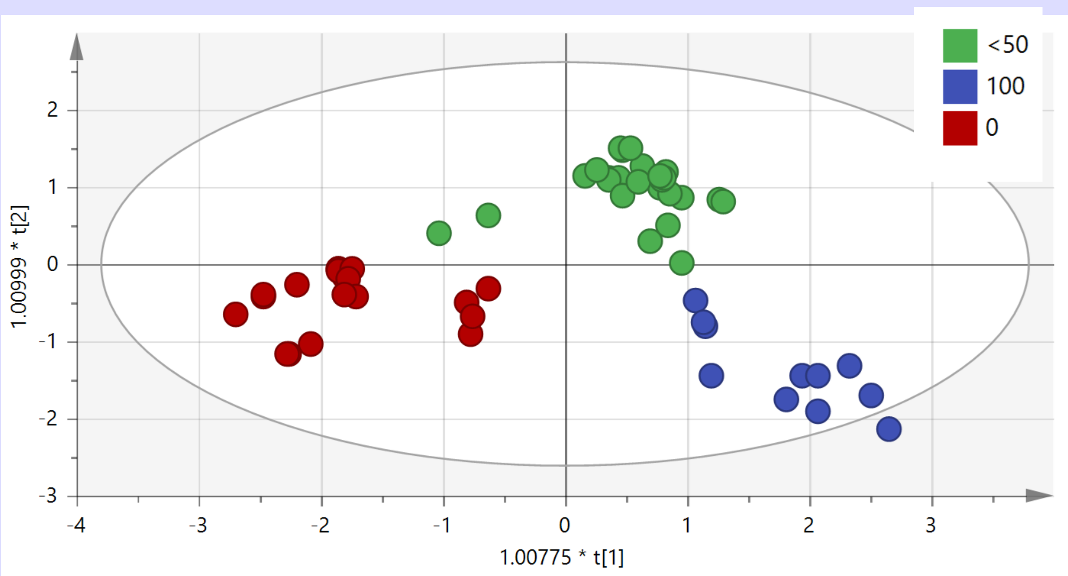


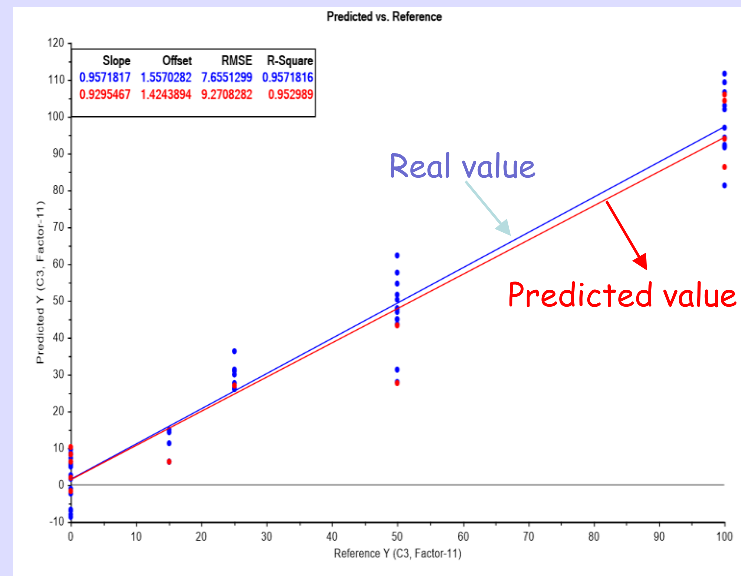
(1) Ethyl acetate, (2) 2-Methyl-1,3-dioxolane, (3) Propyl acetate, (4) Pentanal, (5) Hexanal, (6) Heptanal, (7) Nonanal, (8) Decanal, (9) IS and (10) 5-Methyl undecane

CHEMOMETRIC ANALYSIS OF THE VOLATILE FINGERPRINT

Classificatory purposes: OPLS-DA (Orthogonal partial least squares model):
UV scaling without logarithmic transformation

Quantitative approach:
PLS regression model





100% recycled, ≤ 50% recycled and virgin PET samples showed some differences in their VOCs and formed three different regions in the PCA score plot related to their VOCs fingerprint

Good fit between reference (real) and predicted value :
Correlation 97.7%

Analytical characteristics of the developed HS-GC-MS method for VOCs quantification

Analytical characteristics of the method

Compound	Linearity range (ng g^{-1})	QL[a] (ng g^{-1})	RSD, %	RSD, %
Ethyl acetate	10-1000	10.4	3.6	4.2
2-Methyl-1,3-dioxolane	1.25-100	1.3	2.4	2.0
Pentanal	12.5-1000	12.5	1.6	1.9
Hexanal	1.25-100	1.3	7.2	8.0
o-xylene	2-100	2.0	2.3	1.9
Ethyl benzene	10-1000	10.4	6.0	6.8
Styrene	2-100	2.0	3.7	4.9
p-xylene	2-100	2.0	4.6	5.7
Cumene	25-100	2.0	3.1	4.1
Alpha-pinene	12.5-1000	12.5	3.9	4.9
Benzaldehyde	12.5-1000	12.5	6.9	7.7
Octanal	10-1000	10.4	5.4	4.8
Alpha-terpinene	10-1000	10.4	2.4	3.2
Limonene	25-1000	25	8.9	8.1
Linalool	12.5-1000	12.5	4.5	4.7
Nonanal	1.25-100	1.3	8.7	8.1
Naphthalene	12.5-1000	12.5	3.2	5.1
Butylhydroxytoluene	12.5-1000	12.5	9.3	11.5

Virgin PET sample fortified at 50 ng g^{-1} with all analytes including the IS (n=10)

100% recycled PET sample fortified at 50 ng g^{-1} with all analytes including the IS (n=10)

RECOVERY STUDIES:

- Two 100% recycled PET samples
- Spiked at two levels (25 and 100 ng g^{-1})
- Recovery values: 90-110%

[a] Calculated for Signal/Noise=10 → from 1.3 to 25 ng g^{-1}

Relative standard deviation → from 1.6 and 11.5 %, corresponding to pentanal and butylhydroxytoluene, respectively.

Quantification of VOCs in the PET bottle samples

Analyte content[a] (ng g^{-1}) of PET mineral bottle samples

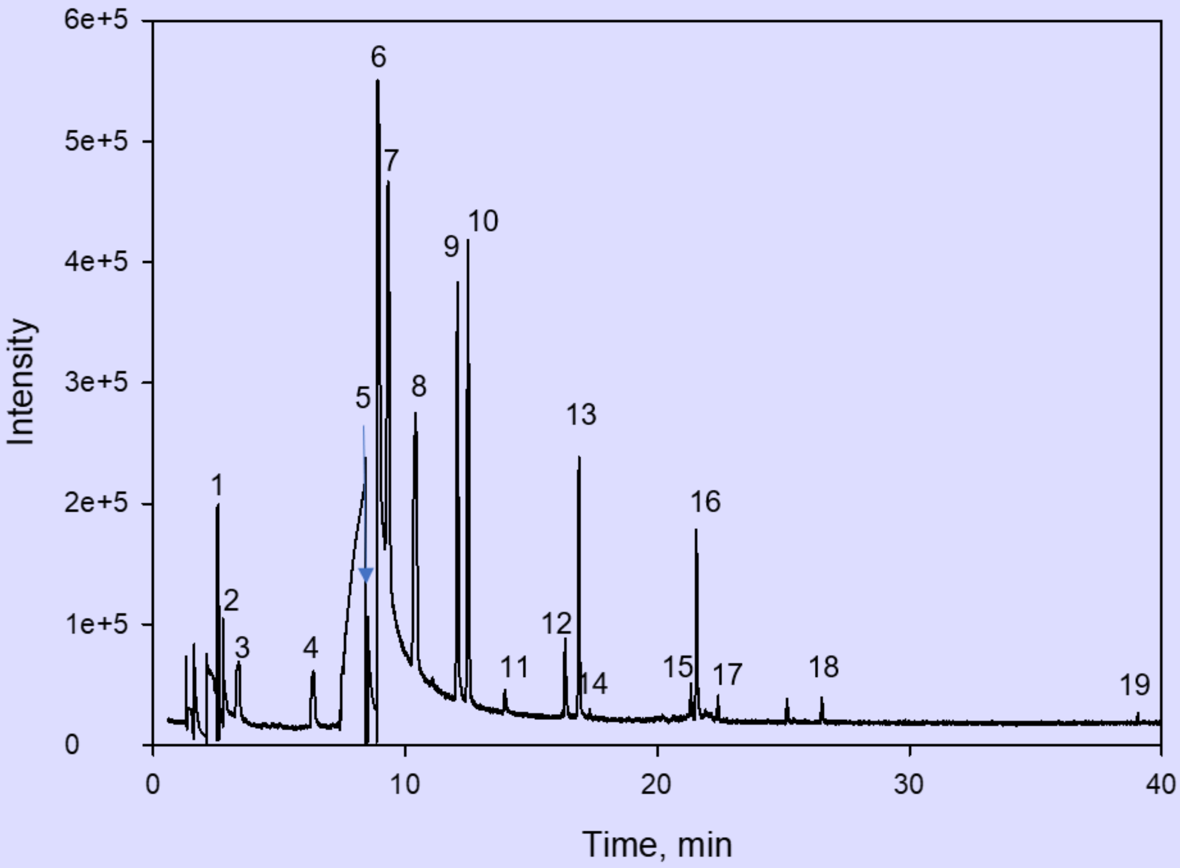
Samples	Ethyl acetate	2- methyl-1,3-dioxolane	Pentanal	Hexanal	Styrene	p-xylene	Benzaldehyde	Octanal	Nonanal
1A	ND	885 ± 78	ND	ND	ND	ND	ND	ND	144 ± 16
2A	ND	964 ± 101	ND	21 ± 1	ND	ND	ND	ND	87 ± 8
3A	ND	650 ± 61	ND	272 ± 36	ND	ND	ND	120 ± 3	874 ± 44
5A	ND	563 ± 12	ND	32 ± 5	ND	ND	ND	65 ± 6	91 ± 22
6A	ND	513 ± 53	ND	17 ± 4	ND	ND	ND	31 ± 1	149 ± 11
7A	72 ± 1	995 ± 180	70 ± 7	63 ± 11	ND	ND	ND	44 ± 20	235 ± 16
8A	ND	777 ± 31	ND	ND	ND	ND	ND	57 ± 1	206 ± 4
9A	ND	996 ± 99	ND	ND	ND	ND	ND	ND	42 ± 3
12A	ND	977 ± 141	ND	ND	ND	ND	ND	ND	91 ± 4
10B	ND	213 ± 17	222 ± 13	11 ± 3	ND	ND	ND	ND	56 ± 13
13B	ND	563 ± 80	ND	ND	ND	ND	ND	ND	27 ± 2
4C	ND	258 ± 9	ND	29 ± 2	ND	ND	ND	ND	160 ± 9
7C	267 ± 45	248 ± 53	182 ± 13	123 ± 3	ND	ND	ND	40 ± 11	25 ± 5
2D	ND	467 ± 48	ND	63 ± 27	ND	ND	ND	ND	187 ± 28
4D	ND	369 ± 40	ND	216 ± 13	ND	ND	99 ± 5	53 ± 1	545 ± 35
6D	ND	387 ±17	ND	28 ± 3	35 ± 1	ND	ND	62 ± 9	235 ± 25
7D	150 ± 1	381 ± 9	75 ± 6	164 ± 25	ND	ND	ND	48 ± 3	297 ± 66
11D	ND	154 ± 10	189 ± 7	88 ± 5	ND	ND	ND	22 ± 1	112 ± 7
2E	ND	94 ± 2	94 ± 2	139 ± 11	ND	ND	ND	ND	23 ± 1
5E	ND	85 ± 10	310 ± 68	ND	ND	ND	ND	ND	33 ± 13
6E	ND	142 ± 25	104 ± 3	212 ± 42	14 ± 0.7	ND	ND	ND	171 ± 19
7E	915 ± 90	146 ± 23	100 ± 8	54 ± 5	ND	ND	ND	35 ± 2	14 ± 0
11E	ND	108 ± 6	114 ± 9	117 ± 4	ND	10 ± 0.3	ND	46 ± 2	272 ± 7
14E	ND	58 ± 1	ND	79 ± 5	ND	ND	ND	ND	38 ± 2

[a] Mean value ± standard deviation (n=3)
ND: No detected

- Samples named as:
  - A: 0% recycled PET
  - B: 15% recycled PET
  - C: 25% recycled PET
  - D: 50% recycled PET
  - E: 100 % recycled PET
- Different numbers correspond to different PET mineral water bottles suppliers.

- Most of the compounds present in the samples were aliphatic aldehydes.
- Benzene derivatives such as benzaldehyde, p-xylene and styrene were found in very few recycled samples

HS-GC-MS chromatogram of a spiked PET bottle sample (50 ng g^{-1})



1) Ethyl acetate
2) 2-Methyl-1,3-dioxolane
3) Pentanal
4) Hexanal
5) o-Xylene,
6) Ethyl benzene
7) Styrene
8) p-Xylene
9) Cumene
10) Alpha-pinene
11) Benzaldehyde
12) Octanal
13) Alpha-terpinene
14) Limonene
15) Linalool
16) Nonanal
17) 2-Chloroanisole (IS)
18) Naphthalene
19) Butylhydroxytoluene.

CONCLUSIONS

1. A novel non-targeted methodology based on HS-GC-MS and implying minimal sample preparation was developed to obtain the volatile fingerprint of virgin and recycled PET plastic bottles (containing different percentages of recycled plastic) from different suppliers.

2. The combination of chemometrics (OPLS-DA and PLS) with the data set obtained by HS-GC-MS methodology for PET samples has demonstrated to be a very useful tool to predict the percentage of recycled material in the PET bottle samples: AVOID FRAUDS.

3. Main contributors to the classification between virgin and recycled PET materials are 2-methyl-1,3-dioxolane which is present in higher amount in virgin PET bottles, and aliphatic aldehydes which are linked to secondary reactions occurring during recycling processes being, therefore, these compounds characteristics of recycled PET samples.

4. Seventeen VOCs were detected in the samples. Nine of them were quantified in the studied samples: ethyl acetate, 2-methyl-1,3-dioxolane, pentanal, hexanal, styrene, p-xylene, benzaldehyde, octanal and nonanal, being their concentrations ranging from 21 to 996 ng g^{-1} which corresponded to hexanal and 2-methyl-1,3-dioxolane, respectively.

Thank you for your attention