

TD and GC × GC – HRTOFMS/FID for the identification of odorous compounds in complex polymer matrices

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Services

Analytical support
Problem solving
Out of Spec analysis
Regulatory assessment

Industrial projects

Product/process development
Product/process improvement

Collaborative projects

Competence development
Product development
Process development





Activities

ENVIRONMENT

Air quality | Health & safety | Energy | Circular Economy

MATERIALS TECHNOLOGY

(Bio-based) polymers & composites
Emissions and odours from materials
Lightweight materials
Mechanical Recycling

CHEMISTRY AND INDUSTRIAL PROCESSES

Intensified / continuous processes
Micro/Meso fluidic technologies
Catalysis and synthesis
Chemical Recycling

ANALYTICAL AND TECHNOLOGICAL SERVICES

Extended characterization platform / reverse engineering
Pilot equipment
Products and processes improvement

700 industrial contracts per year

40 employees

Since 2000, Certech has collaborated with 1400 companies

(Bio-based) polymers & composites

- Thermoplastic compounding
- Compatibilisation/dispersion
- **Biocomposite and biobased formulations**
- Lightweight materials
- Thermoset formulation
- High performance polymers for 3D printing
- Regulatory compliant materials

Barrier materials

- Selective controlled permeability
- Technical membranes
- Functional coatings

Emissions and odours from materials

- **Objective measurements and diagnostic**
- **Odour-chemistry correlation**
- **Remediation**
- Validation of materials and devices for indoor air purification

Mechanical Recycling (P to P)

- Thermoplastic compounding/processing
- Shredded composites valorisation
- Characterisation / technical data sheet
- **Odour management of recyclates**

- Consumer awareness has increased :
More stringent demands regarding quality life, e.g. comfort, safety
Information by public authorities, consumer organisations and health professionals
Press coverage
- Impact of environmental issues :
Compliance with legal requirements
- Compliance with customer requirements (pressure from end-users)
Labels and producers awareness
- Marketing issues (odourless and low VOC grades)



<http://www.air-tek.net>



<https://www.montgomerycountymd.gov>



<https://www.montgomerycountymd.gov>



<https://school.discoveryeducation.com>

Key expertise: Odour Analysis

4 components of odour:

- **Detectability** which corresponds to the detection threshold, odour quantification by dynamic olfactometer according to EN 13725
- **Intensity**, quantification based on a scale
- **Quality**, decomposition into fundamental notes, “champ des odeurs[®]” approach
- **Hedonic tone** (acceptability), subjective and global (annoyance, approach – pleasantness/unpleasantness)

I. Quantitative analyses of odour by Dynamic dilution olfactometry

- Standardized method (EN 13725) for the measurement of odour intensity based on « dynamic olfactometry at detection threshold »
- Calibration of the detector (human noses) which has to be representative of the whole population
- Definition of a universal unit for odour intensity « uo_E/m^3 »
- Very high quality criteria (repeatability, reproducibility ...)

Basic principles of measurement :

The scale (and units) is determined by the physiological response provided by a reference material : n-Butanol

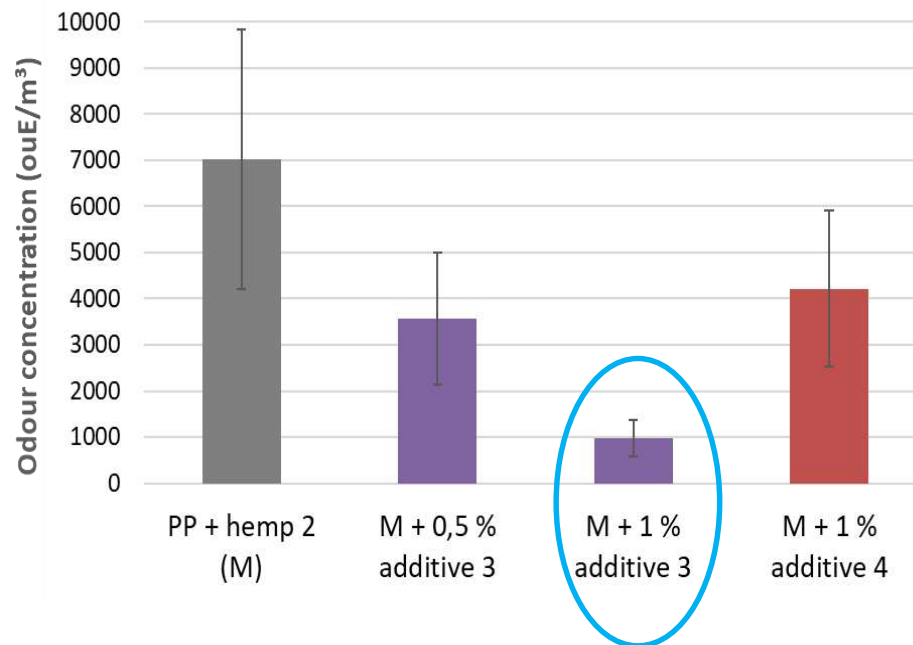


Test 400



I. Quantitative analyses of odour by Dynamic dilution olfactometry

Exemple: Comparison of odour remediation additives effect on biocomposite



→ A difference between olfactometric results is considered as significant when at least a factor 2 is observed between 2 evaluations

II. Quantitative and Qualitative analyses of odour by evaluation using intensity scale and descriptors according to the « champ des odeurs » with expert panels

- Direct evaluation of the odour under different temperature conditions (static)
- Odour quantification by rating on intensity scale
- Odour description according to a recognized methodology
- Trained panels are performing the tests
- Recording of performances and training of the panels
- References are used (n-Butanol at different concentrations)

16 experts Certech
(trained each week)



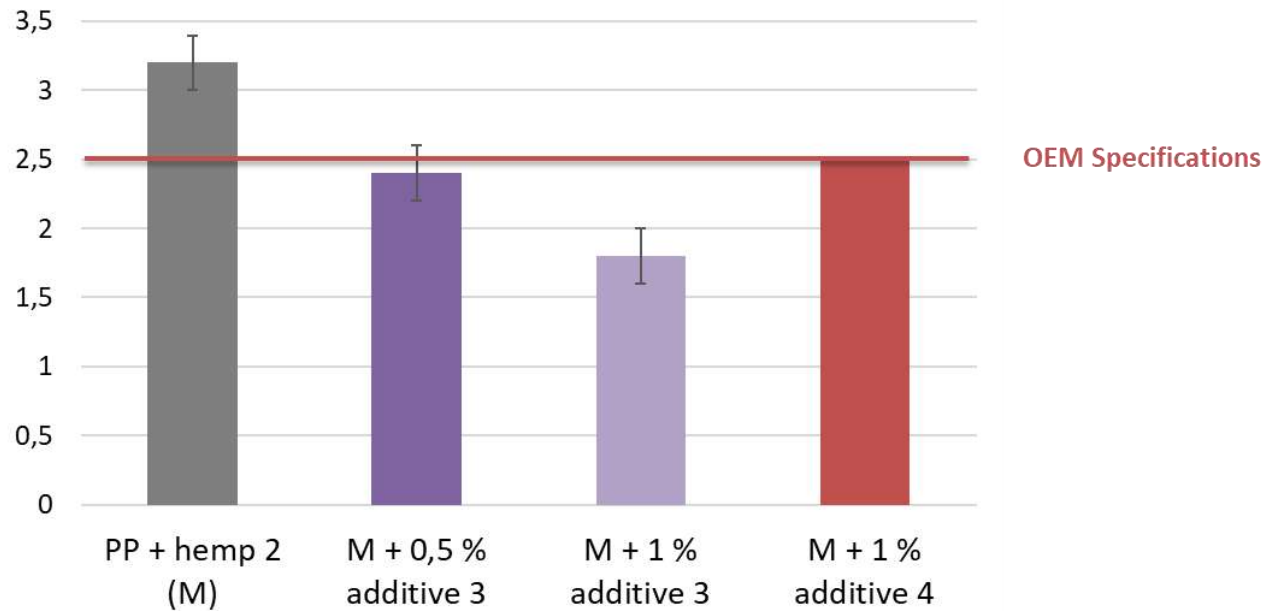
Accredited by french OEM
(ISO12219-7 and ISO5496)

PSA PEUGEOT CITROËN



II. Quantitative analyse of odour by intensity scale

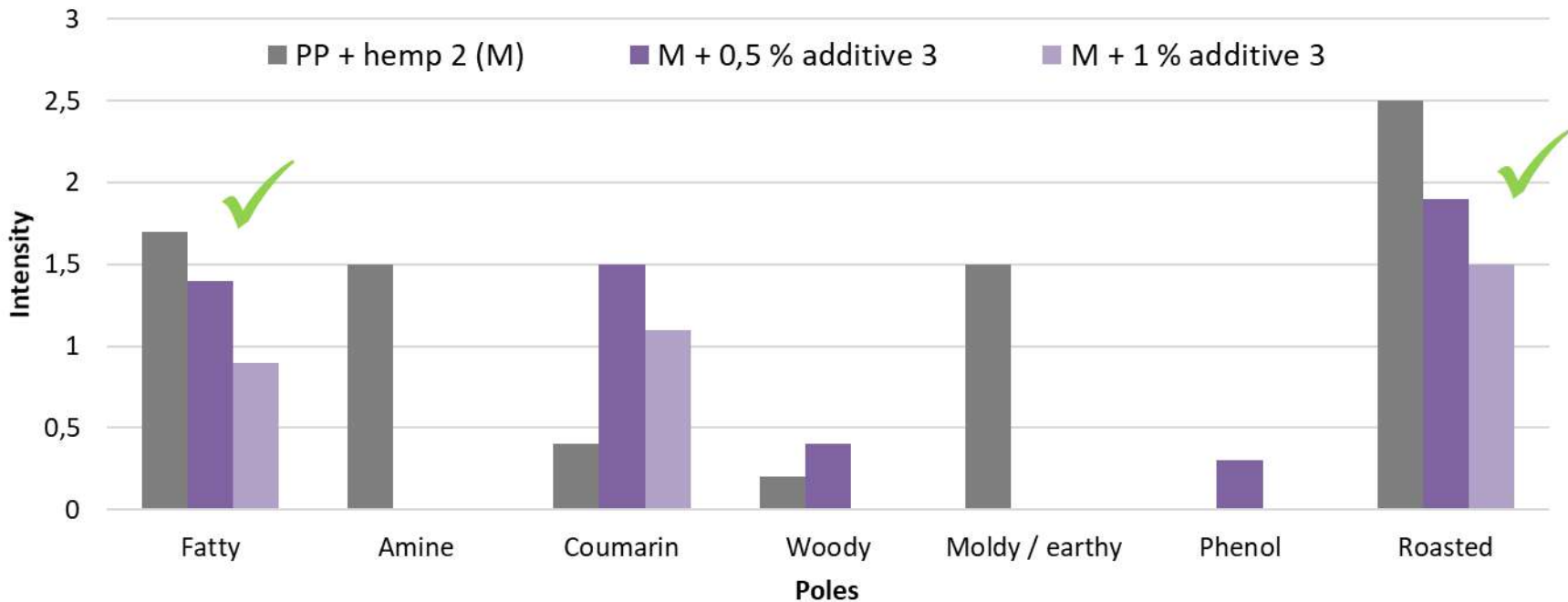
Exemple: Comparison of odour remediation additives effect on biocomposite



→ The biocomposite + **additive 3 (1%)** is a candidate to meet OEM specifications in terms of odour intensity

II. Qualitative analyses of odour by the « champ des odeurs » methodology

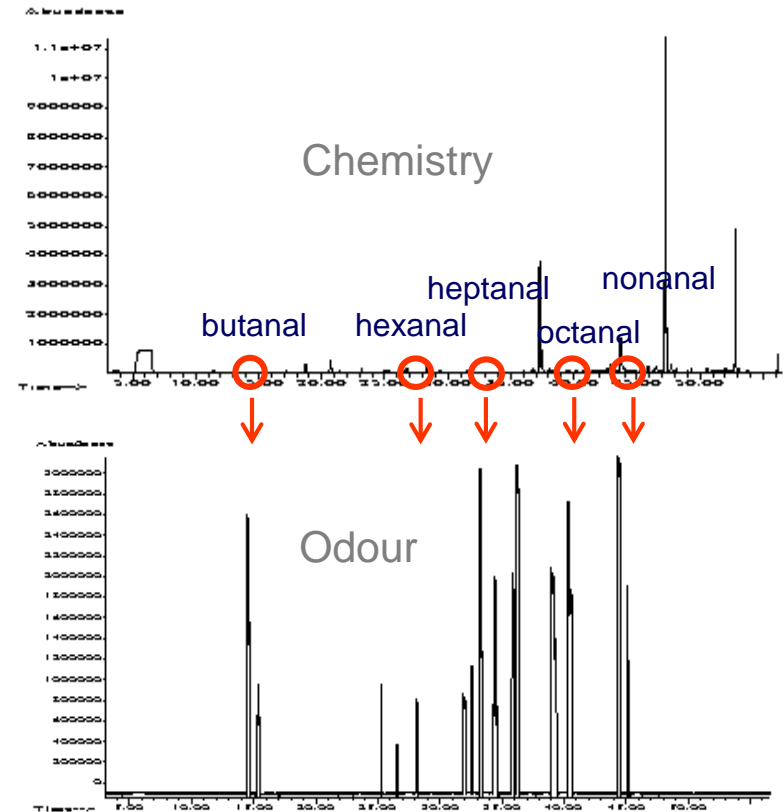
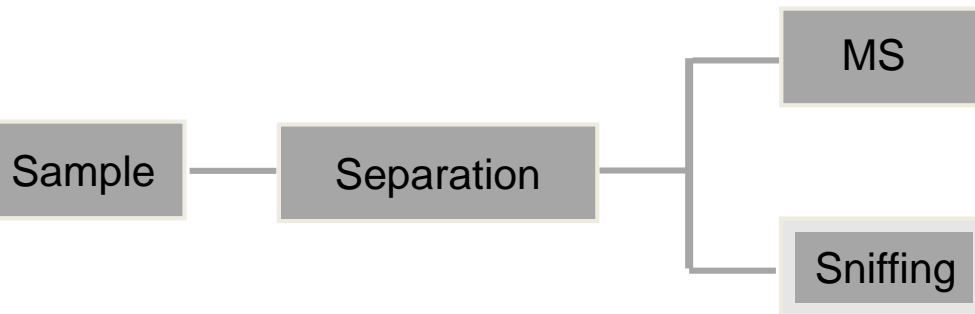
Exemple: Comparison of odour remediation additives effect on biocomposite



→ The **additive 3** decreases the fatty and roasted notes (confirmed with 2 experiments)

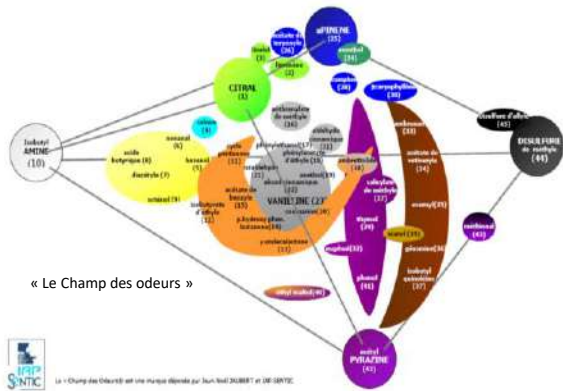
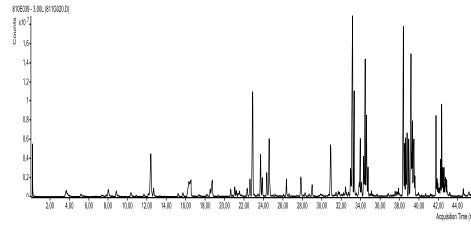
III. Correlation chemistry/odour by TD-GC-MS/Olfactometry (« sniffing »)

Identification of the causes - Diagnosis



III. Correlation chemistry/odour by TD-GC-MS/Olfactometry (« sniffing »)

Global odour assessment and decomposition



- Trained sensorial expert
- Descriptors + Intensity scale
- Continuous on-line analysis (45 min)
- Sensory room with purified air

T.R. (min)	N° CAS	Analyte	Standard	Conc. (µg/m³)	Références "Champ des Odeurs"	Evocation	Intensité
6,83	75-50-8	Triméthylamine	NA		Triméthylamine	note ammée, poisson	2,5
7,81	123-88-6	Propanal	NA		cis-3-Hexenal	note verte, herbe coupée	1,5
12,15	123-72-8	Butanal	Nonanal	4	Acide butyrique	note rance	2
12,41	431-03-8	2,3-Butanedione	MBK	50	Diacetyl	note grasse, beurrie	1,5
15,71	593-89-3	Butanal, 3-méthyl-	Nonanal	5	cis-3-Hexenal	note verte, herbe coupée	3
16,32	4170-30-3	2-Butenal	Nonanal	24	Isobutyrate d'éthyle	note fruitée, ananas	3
16,54	84-15-7	Acetic acid	Toluène	14	Acide acétique	note piquante	2
18,52	110-62-3	Pentanal	Nonanal	7	cis-3-Hexenal	note verte, herbe coupée	3
18,73	602-14-6	2,3-Pentanedione	MBK	20	Ethyl maltol	note douce, caramel	2,5
21,35	513-86-0	Acetoin	MBK	7	Phenol	note phénolée, anore	1,5
22,32	1576-87-0	2-Pentenal, (E)-	Nonanal	8	cis-3-Hexenal	note verte, herbe coupée	2
23,71	66-25-1	Hexenal	Nonanal	31	cis-3-Hexenal	note verte, herbe coupée	3
25,19	98-02-1	Furfural	Toluène	<1,7	Acide butyrique	note rance	2
26,89		Non identifié	Toluène	<1,7	Acétate de benzyle	note solvant, peinture	1,5
27,58		Non identifié	Toluène	<1,7	cis-3-Hexenal	note verte, herbe coupée	3
27,85	58-00-0 + 116-43-0	1-Forméthional + 2-Heptanone	Toluène	11	2-Acetyl pyrrazine + solvant	note grillée, cacahuètes + note solvant	2,5
28,29	111-71-7	Heptanal	Nonanal	4	Limonène	note fraîche, agrumes	3
29,23	5910-89-4	Pyrazine, 2,3-diméthyl-	Toluène	<1,7	2-Acetyl pyrrazine	note grillée, cacahuètes	2,5
29,71	129-52-4	Pentanoic acid	Toluène	<1,7	Acide butyrique	note rance	1,5
31,48	3777-63-3	Furan, 2-pentyl-	Toluène	<1,7	Limonène	note fraîche, agrumes	1,5
31,71		Alcane non identifié	n-Octane	3	1-Octen-3-ol	note fraîche, champignons	2,5
32,46		Alcane non identifié	n-Octane	6	solvant	note solvant	2
32,77	124-13-0	Octanal	Nonanal	5	Limonène	note fraîche, agrumes	3
34,61	112-40-3 + 108-95-2	Dodecane + Phénol	Toluène	35	Phenol	note phénolée, entre	2,5
35,13	120-51-6	Benzyl alcohol	Toluène	<1,7	Nonanal	note verte, concombre	3
35,61	98-86-2	Acetophenone	Toluène	<1,7	Ethyl maltol	note douce, caramel	2
36,11		Non détecté			2-Acetyl pyrrazine	note grillée, cacahuètes	2
37,14		Alcane non identifié	n-Undécane	<1,7	solvant	note solvant	3
37,35	18829-56-4	2-Nonenal, (E)-	Nonanal	<1,7	Nonanal	note verte, concombre	3
39,69		Non identifié	Toluène	<1,7	Undécenal	note verte, concombre	2
40,69		Non identifié	Toluène	<1,7	Eugénol	note épice, clou de girofle	2,5
41,20		Non identifié	Toluène	<1,7	b-Caryophyllène	note épice, safran	2,5
42,14		Alcane non identifié	n-Pentadécane	5	bois	note boisée	2,5
42,51		Alcane non identifié	n-Pentadécane	<1,7	bois	note boisée	2,5

IV. New instrumentation at Certtech

Minor compounds could be responsible of odour !

Sensitivity of human nose > Sensitivity of detector

=> Increase detector sensitivity (TOFMS) and VOC sampling combined with sniffing

→ New VOC multisampler-TD-GC-TOFMS/Olfactometry
(installation ongoing T4 2019)



IV. New instrumentation at Certech

Minor compounds could be responsible of odour !

Complex VOC profile, co-elutions with matrix, unknown degradation products

=> Increase chromatographic separation, sensitivity and specificity,
identification of compounds using High Resolution Mass Spectrometry

→ New VOC Multisampler-TD-GC×GC-HRTOFMS/FID

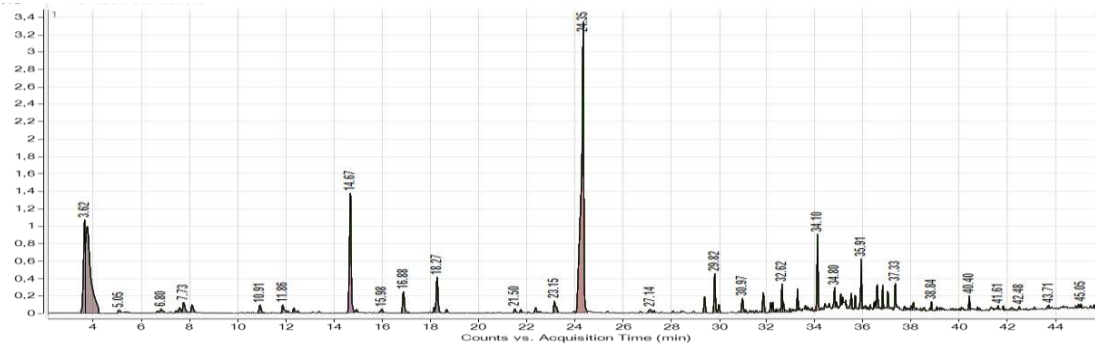


Characterization of complex polymer samples:

- Biobased/Biocomposite materials
- Recycled plastics

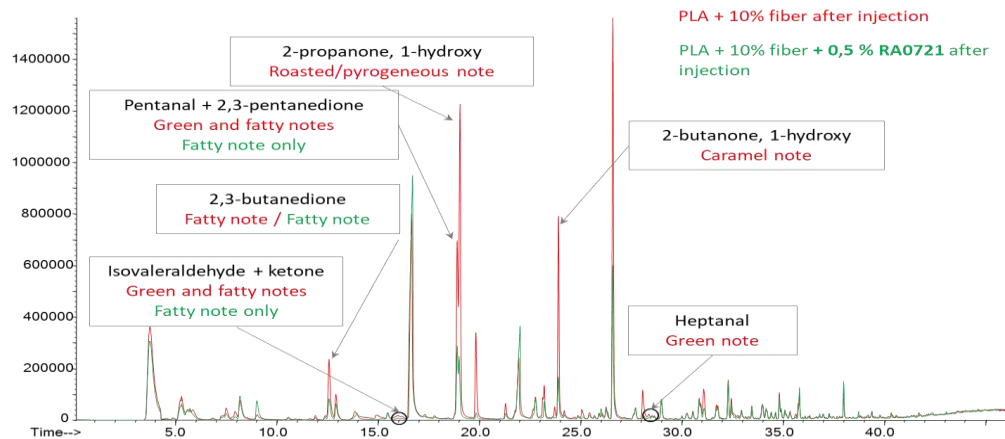


➤ TD-GC-MS/O analysis of odorous material



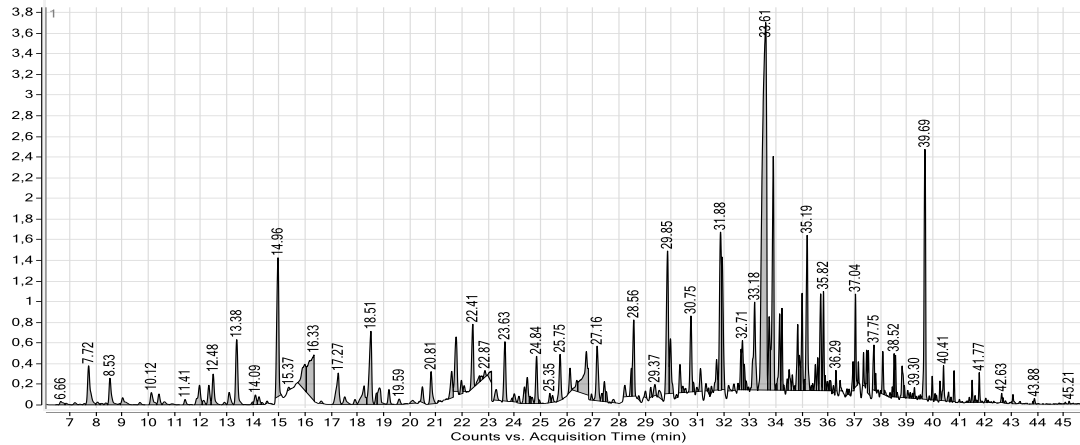
→ OK

➤ TD-GC-MS/O analysis of biocomposite PLA-cellulose



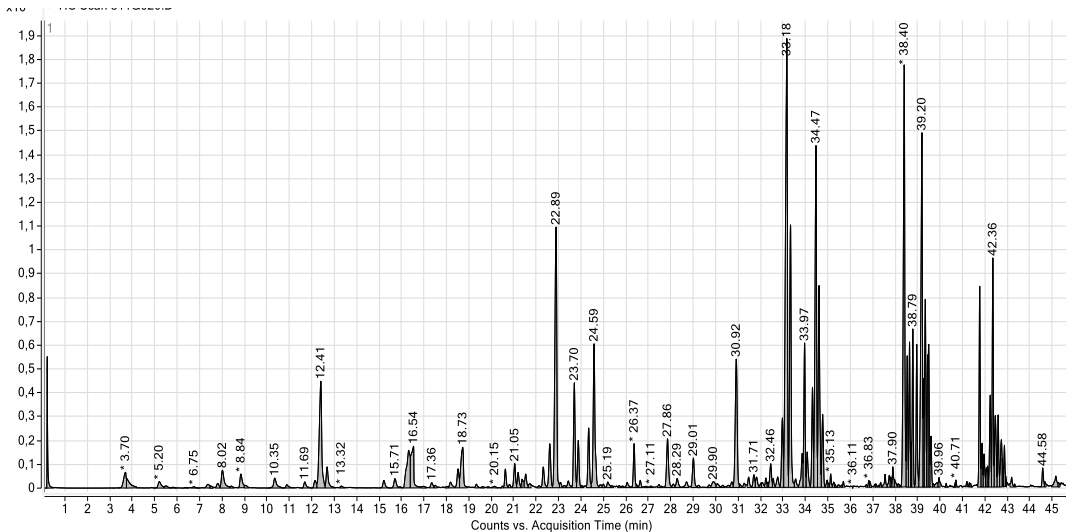
→ OK

➤ TD-GC-MS/O analysis of recycled plastic



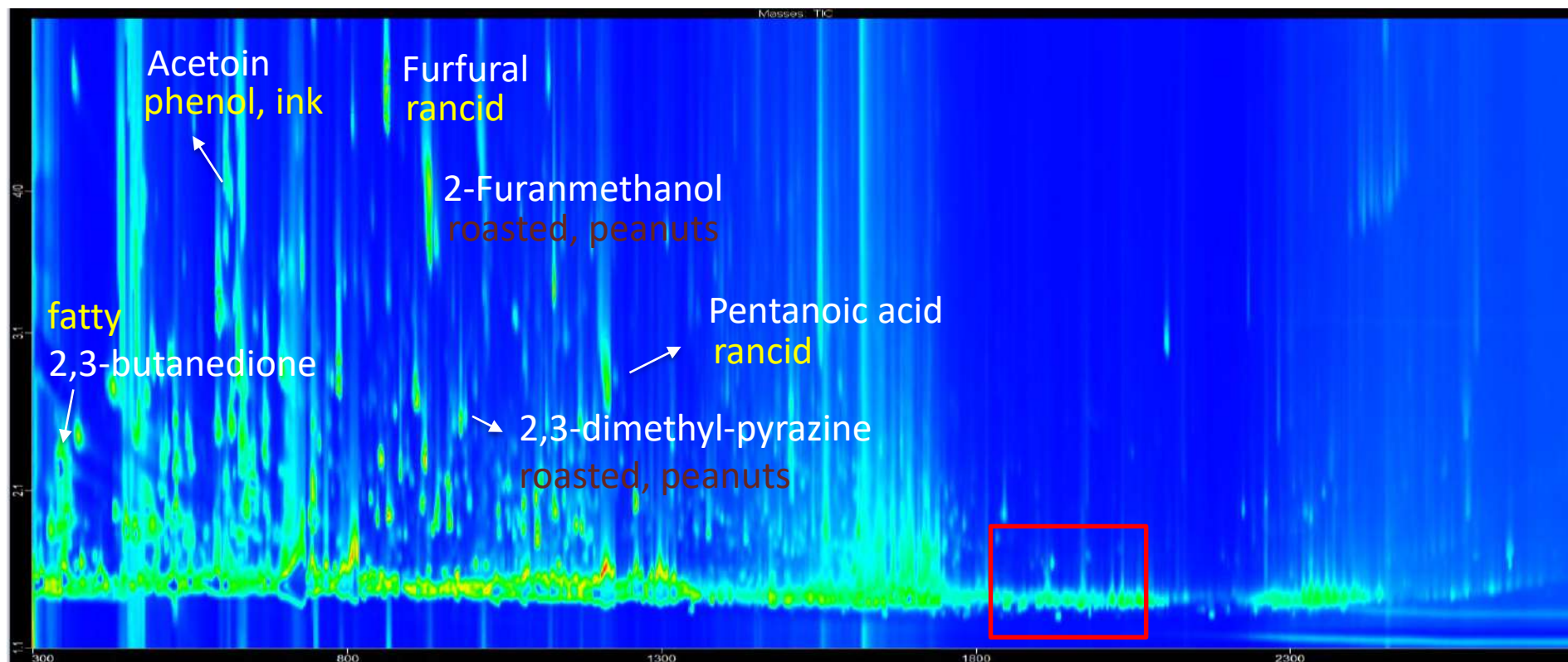
- ✓ Information of odorous compounds and characteristics VOCs
- ✓ Use of internal database

➤ TD-GC-MS/O analysis of biocomposite PP + Hemp

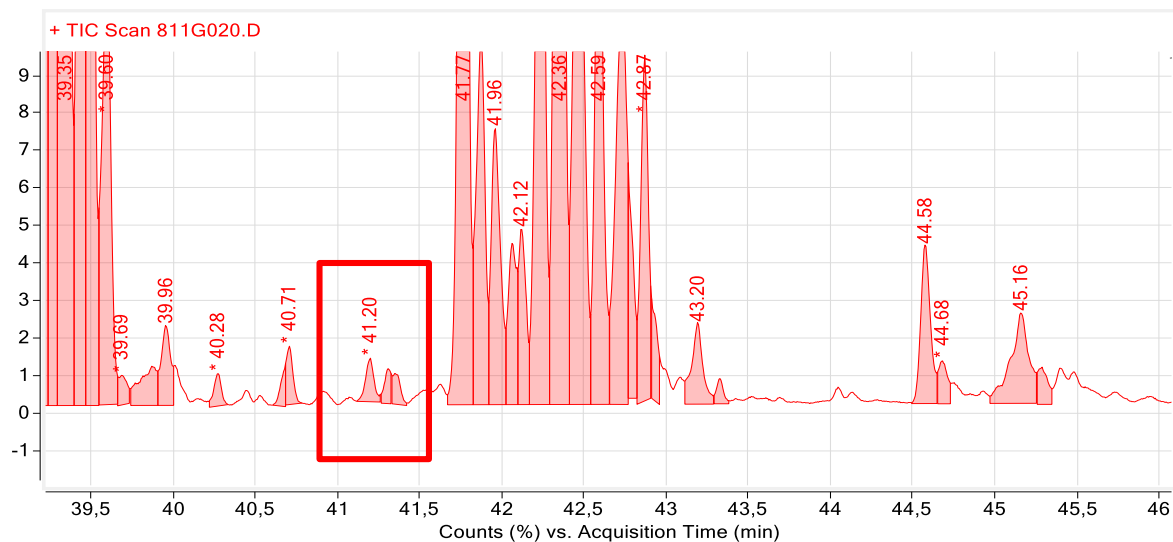


- ✗ Interesting information might be missing

➤ TD-GC×GC-HRTOFMS/FID analysis of biocomposite PP + Hemp



➤ TD-GC-MS/O analysis of biocomposite PP + Hemp



37,14		Alcane non identifié	n-Undecane	<1,7	solvant	note solvant	3
37,35	18829-56-6	2-Nonenal, (E)-	Nonanal	<1,7	Nonanal	note verte, concombre	3
39,69		Non identifié	Toluene	<1,7	Undecanal	note verte, coriandre	2
40,69		Non identifié	Toluene	<1,7	Eugenol	note épicée, clou de girofle	2,5
41,20		Non identifié	Toluene	<1,7	b-Caryophyllene	note épicée, cèdre	2,5
42,74		Alcane non identifié	n-Pentadecane	9	boisé	note boisée	2,5
42,91		Alcane non identifié	n-Pentadecane	<1,7	boisé	note boisée	2,5

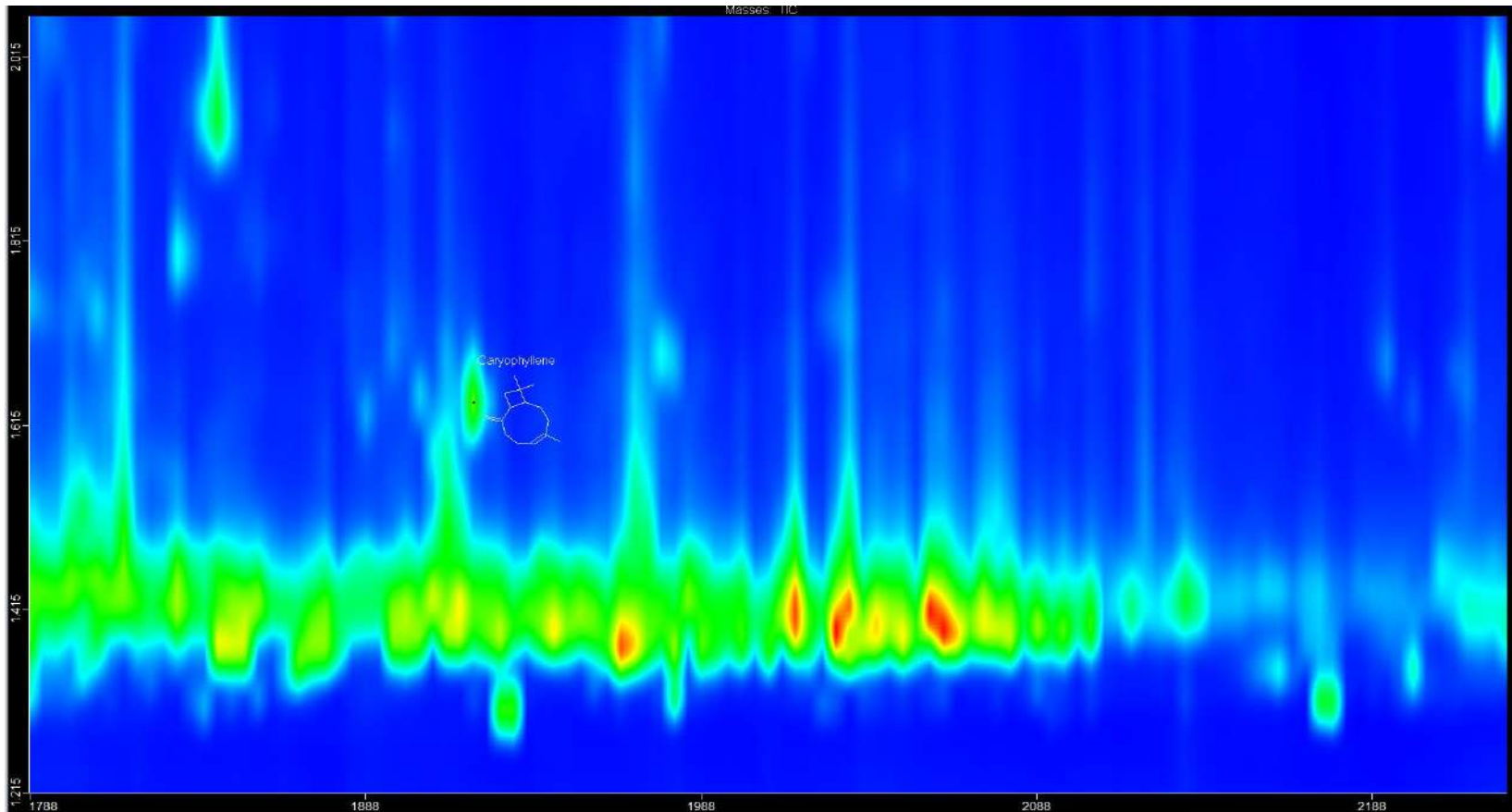
➤ TD-GC-MS/O analysis of biocomposite PP + Hemp

Best	Name	Formula	Score	RT	Mass
<input checked="" type="radio"/>	Hexadecane, 1-chloro-	C16H33Cl	66.43	41.2	
<input type="radio"/>	Octadecane, 1-chloro-	C18H37Cl	65.75	41.2	
<input type="radio"/>	1-Octadecanesulphonyl chloride	C18H37Cl...	65.32	41.2	
<input type="radio"/>	Octadecane, 1-chloro-	C18H37Cl	65.28	41.2	
<input type="radio"/>	Hexadecane, 1-chloro-	C16H33Cl	65.27	41.2	
<input type="radio"/>	Carbonic acid, eicosyl vinyl ester	C23H44O3	64.16	41.2	
<input type="radio"/>	Tetradecane, 1-chloro-	C14H27Cl			
<input type="radio"/>	Nonadecane, 1-chloro-	C19H39Cl			
<input type="radio"/>	2-Isopropyl-5-methyl-1-heptanol	C12H24O			
<input type="radio"/>	Carbonic acid, tridecyl vinyl ester	C19H37O2			

Weak Library Match Score
No identification

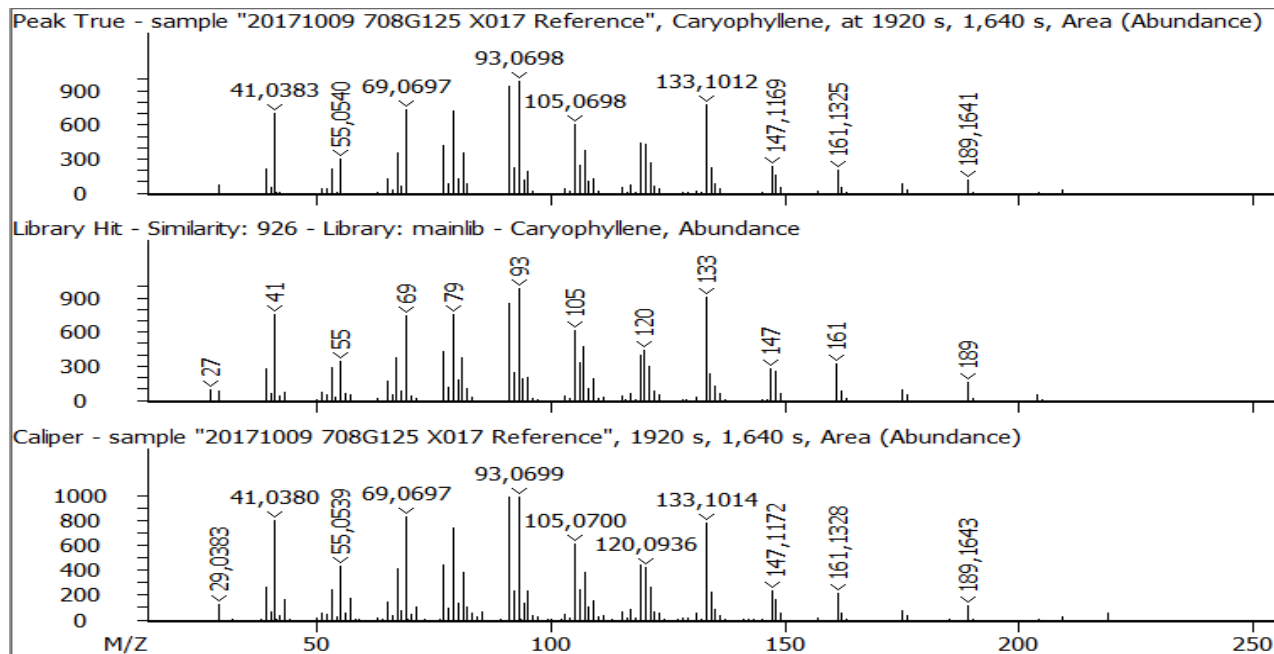


- TD-GC×GC-HRTOFMS/FID analysis of biocomposite PP + Hemp

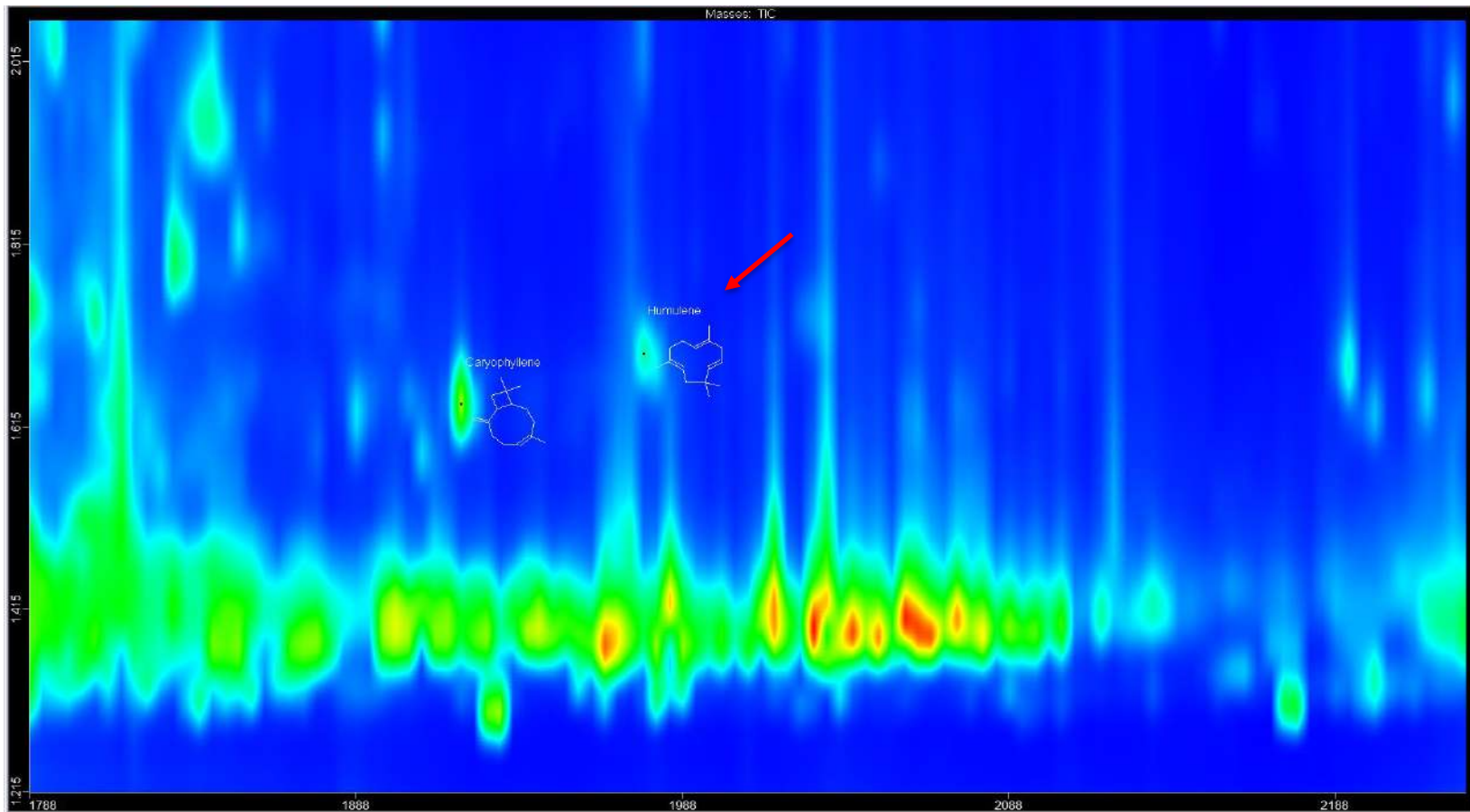


➤ TD-GC×GC-HRTOFMS/FID analysis of biocomposite PP + Hemp

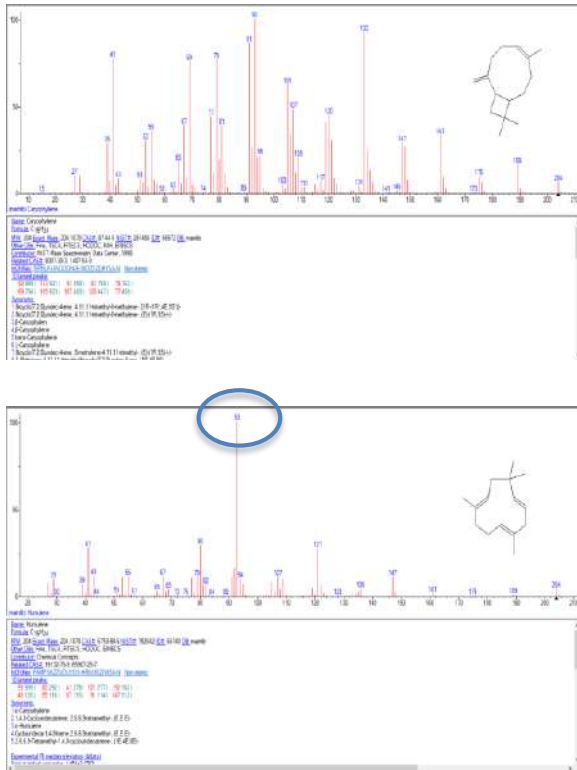
→ Identification of β -caryophyllene (spicy, woody odour)
(good match score library, chromatographic separation)



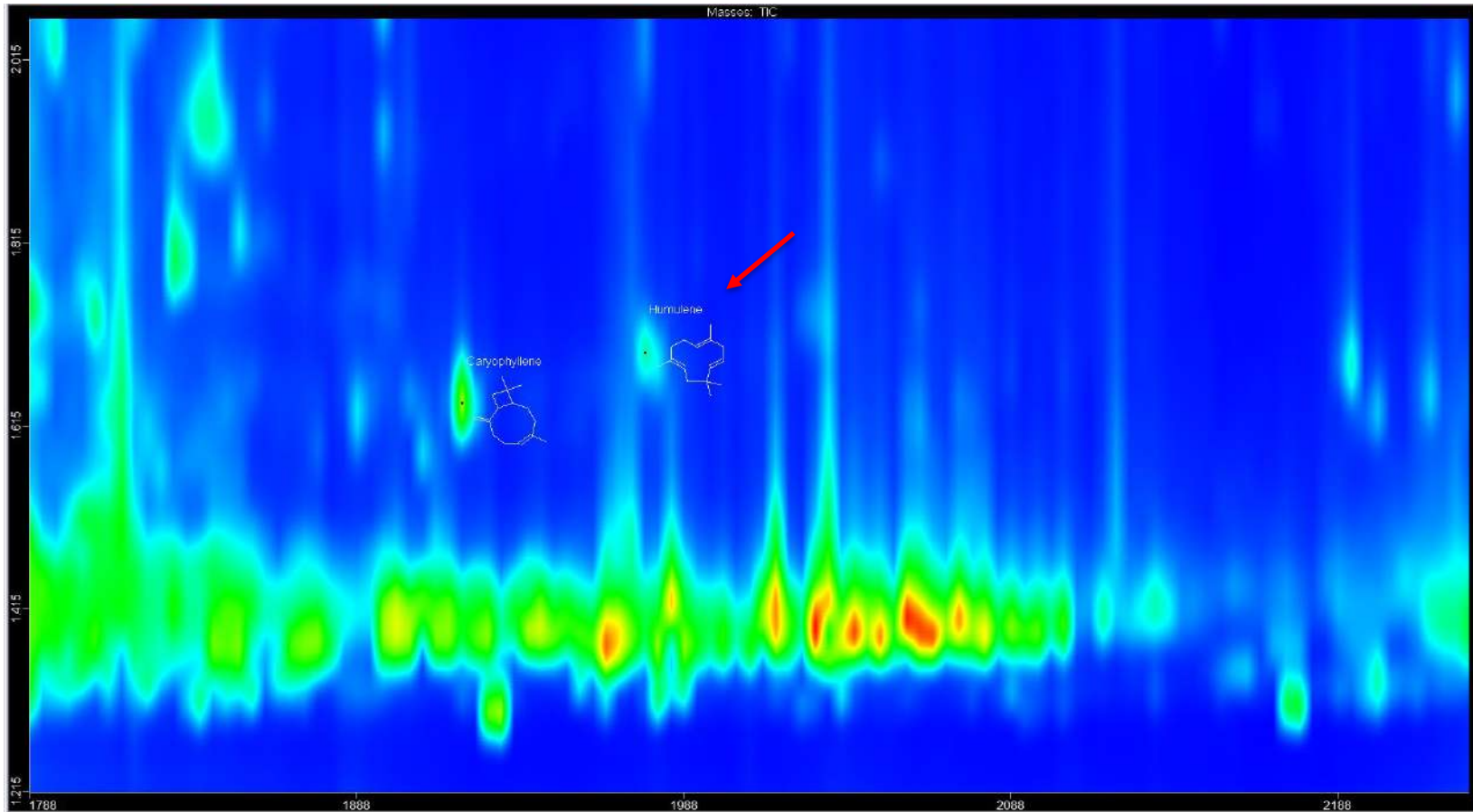
➤ TD-GC×GC-HRTOFMS/FID analysis of biocomposite PP + Hemp



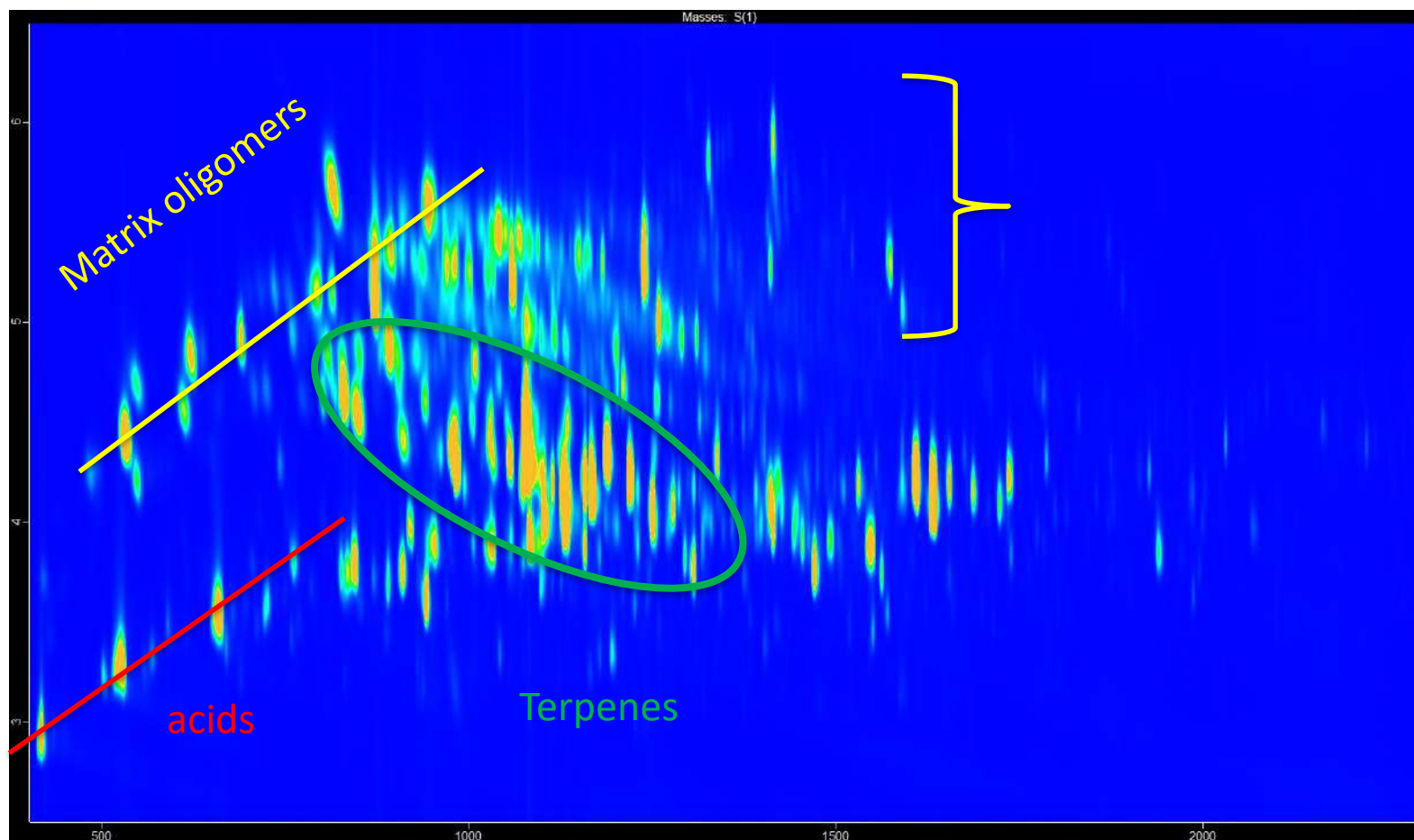
➤ TD-GC-MS/O analysis of biocomposite PP + Hemp



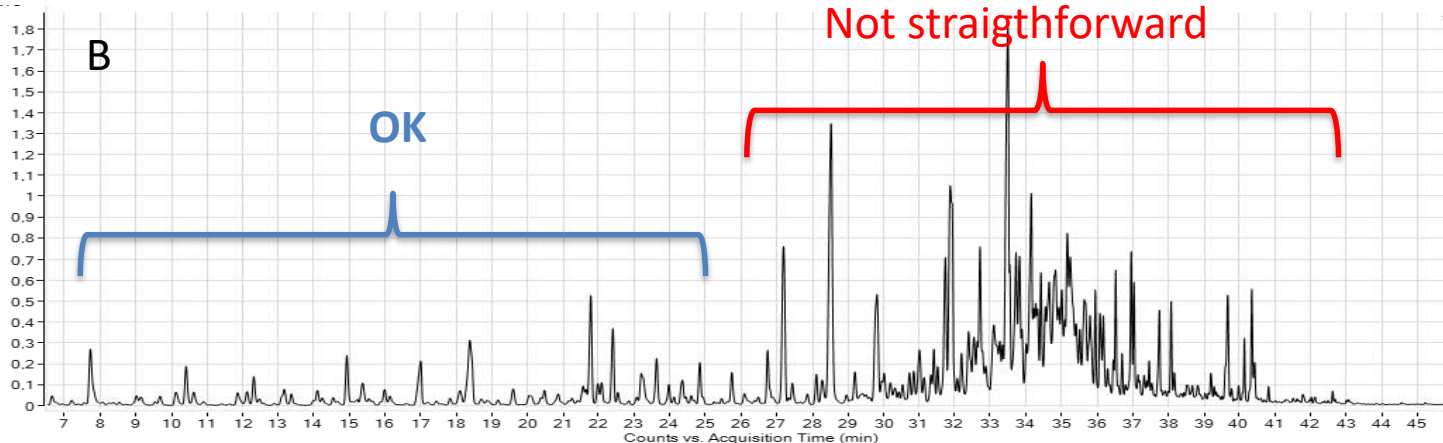
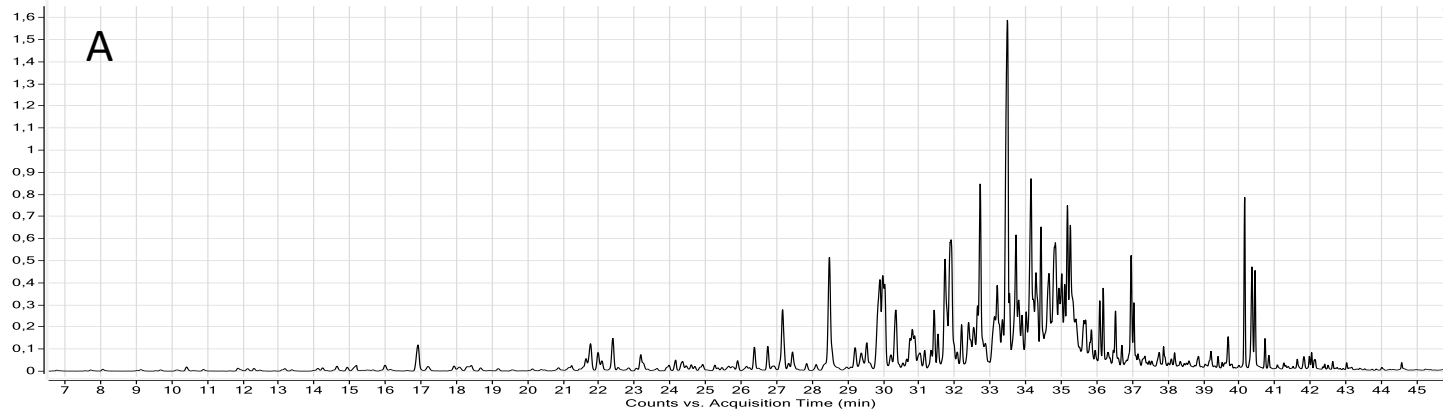
➤ TD-GC×GC-HRTOFMS/FID analysis of biocomposite PP + Hemp



➤ TD-GC×GC-HRTOFMS/FID analysis of recycled plastic



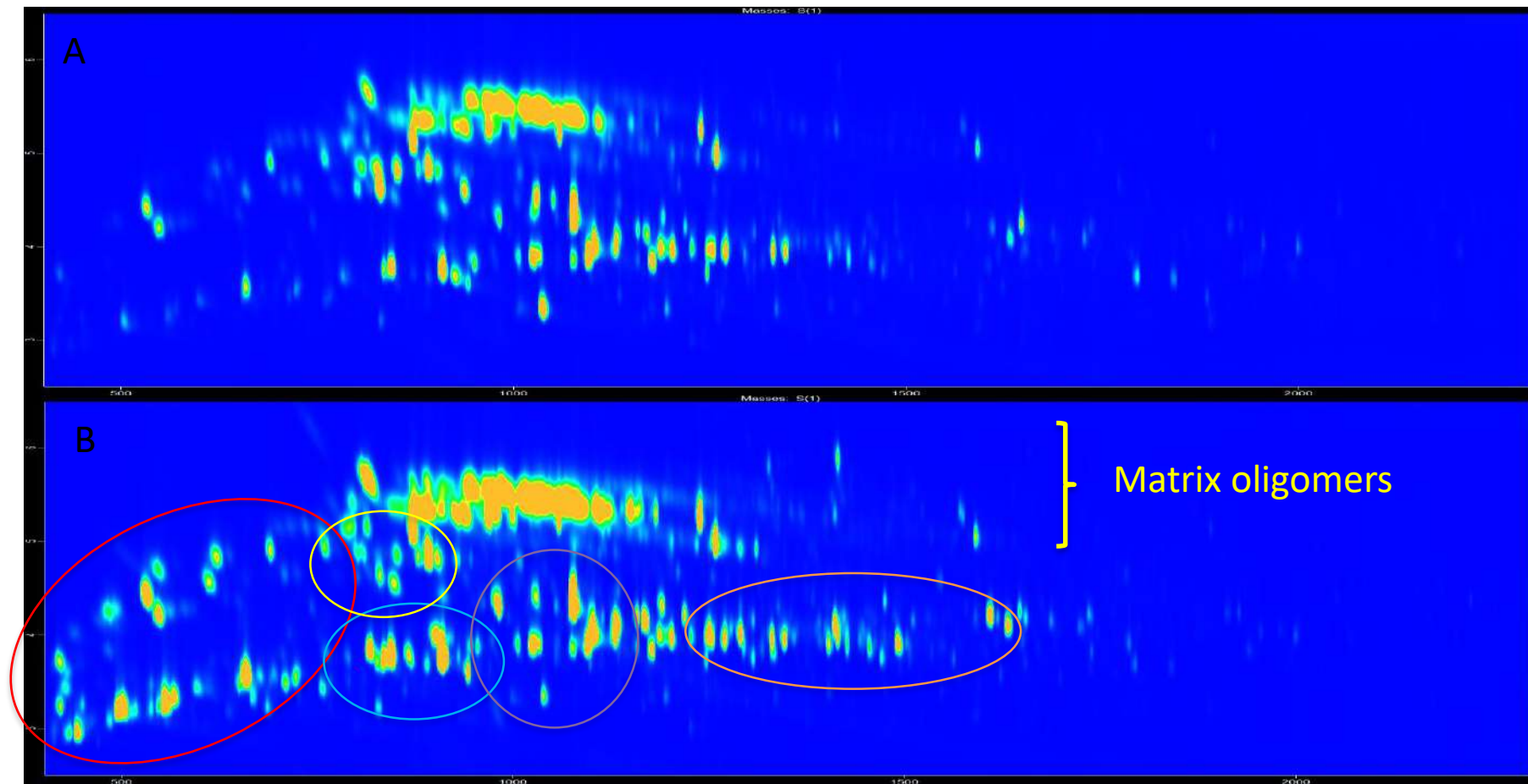
➤ TD-GC-MS/O analysis: comparaison of complex samples



✓ Comparison of odorous compounds and characteristic VOCs

✗ Important information might be missing

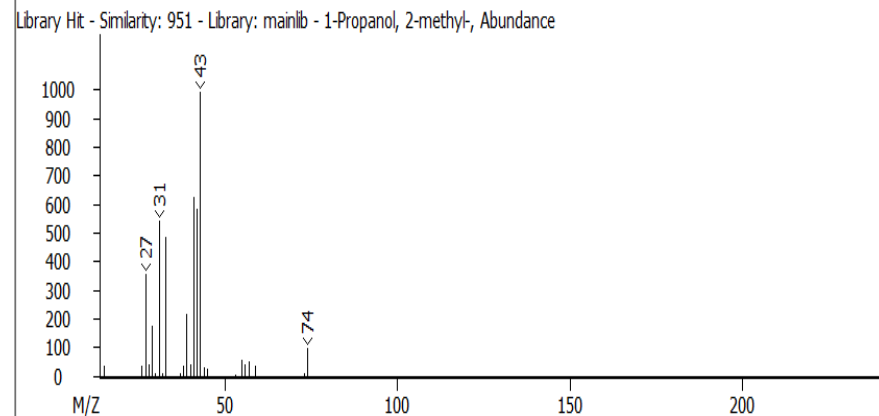
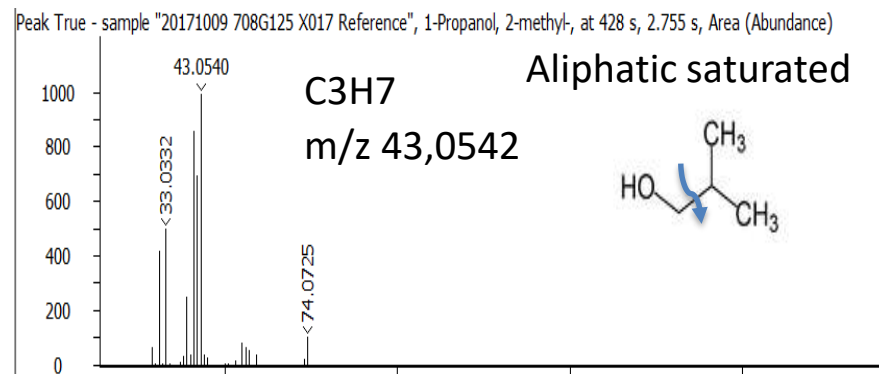
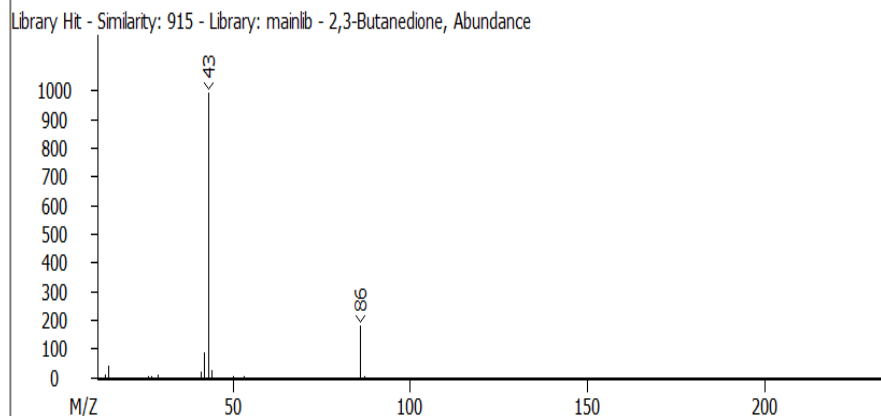
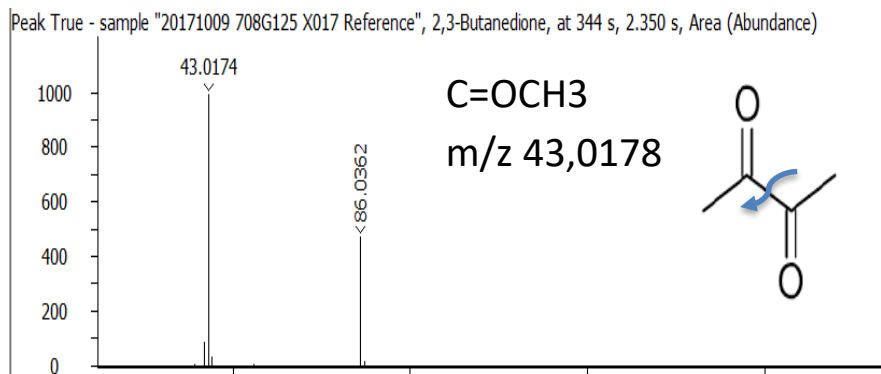
➤ TD-GC×GC-HRTOFMS/FID: comparaison of complex samples:



→ Exhaustive VOC characterization

✓ Full evaluation of increase vs decrease

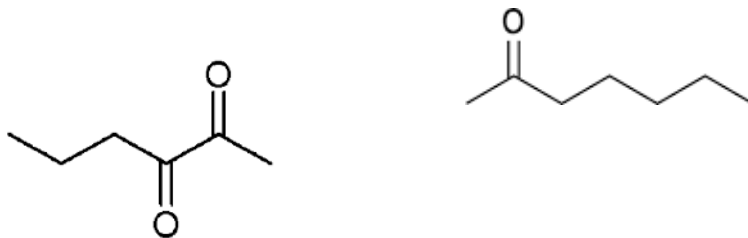
✓ TD-GC×GC-HRTOFMS/FID (R >25,000 FWHM, MA <1ppm)

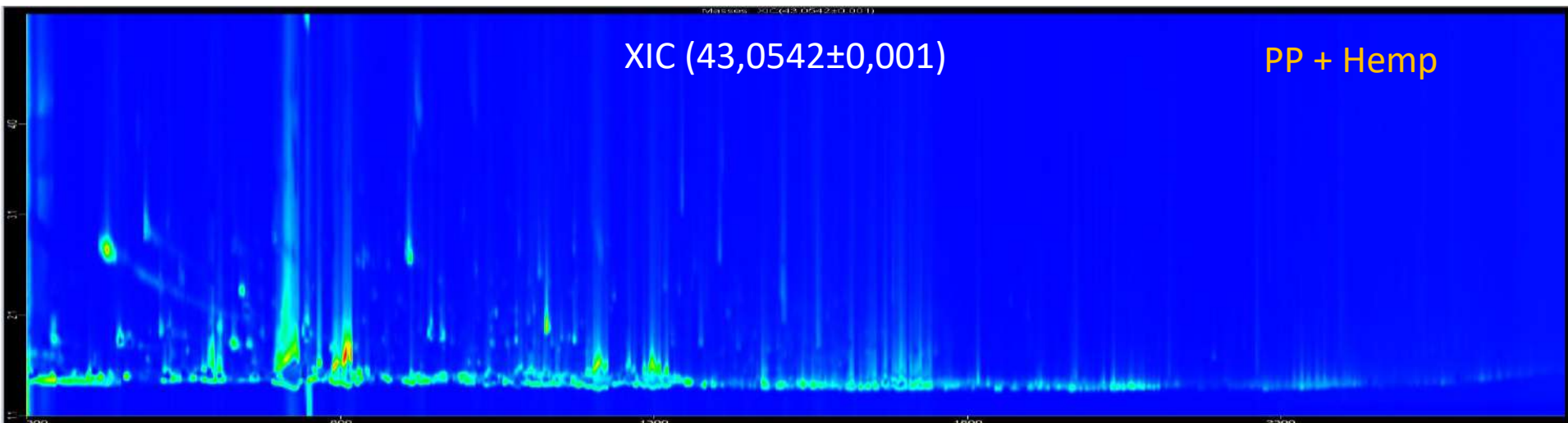
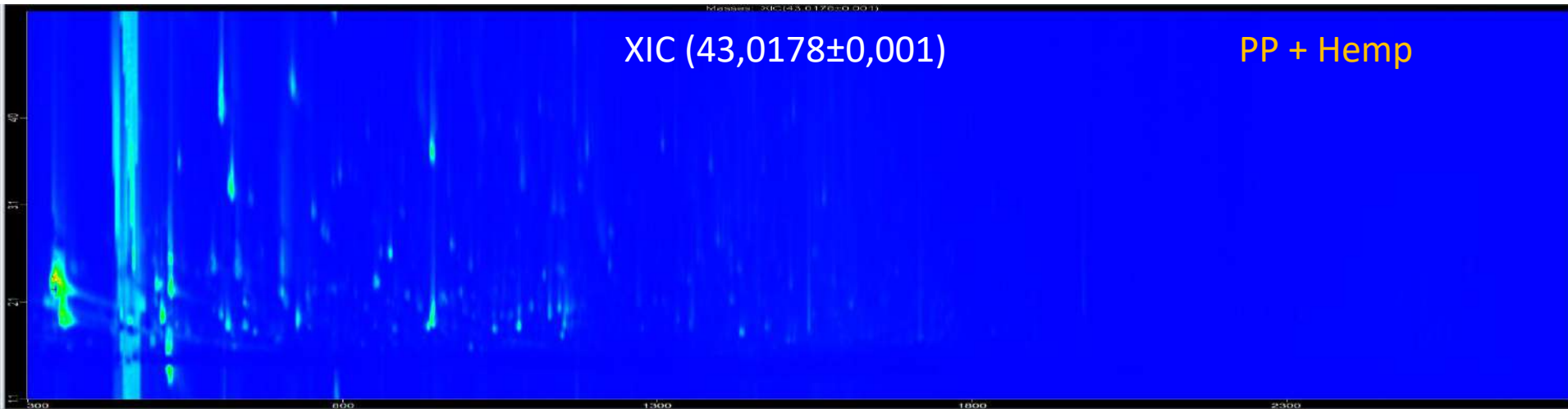


- Discriminate carbonyl compounds from aliphatic saturated hydrocarbons



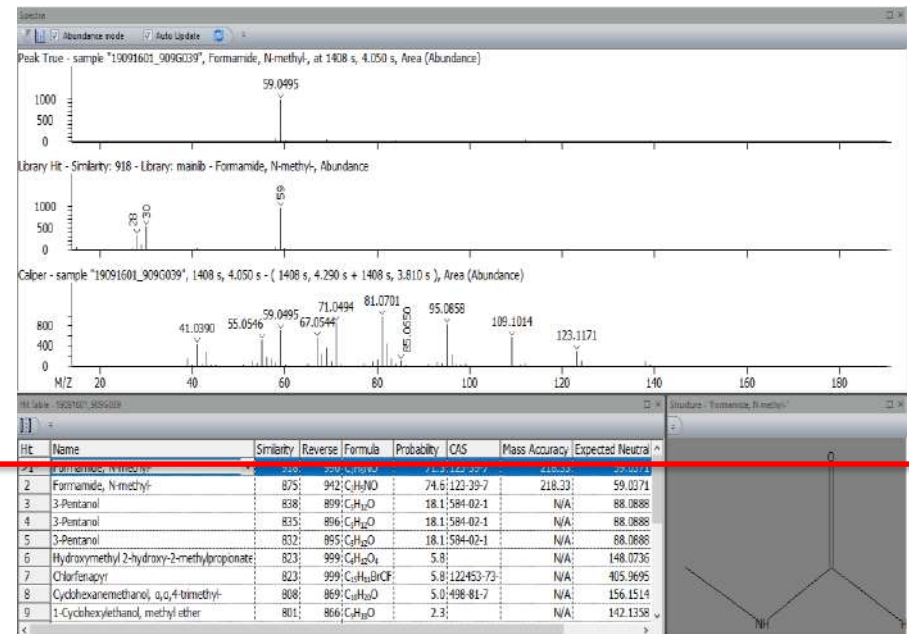
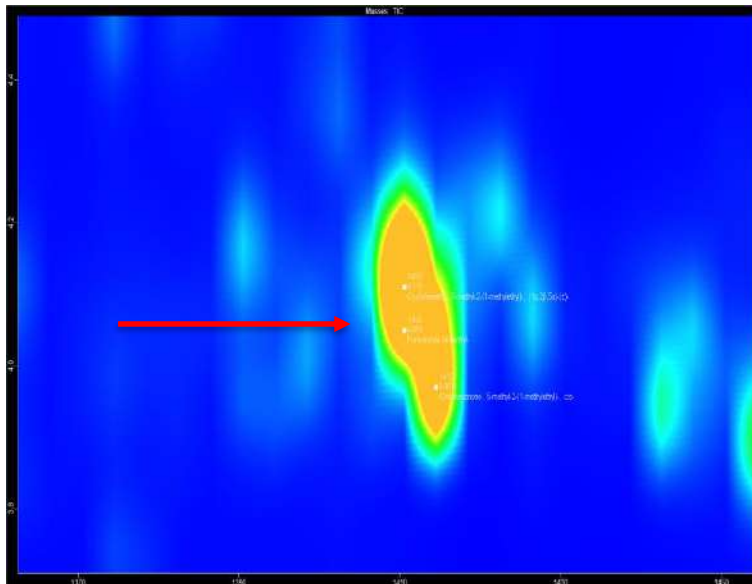
...or not...





✓ GC×GC-HRTOFMS (R >25,000 FWHM, MA <1ppm)

Deconvolution process found :
- N-methyl-formamide

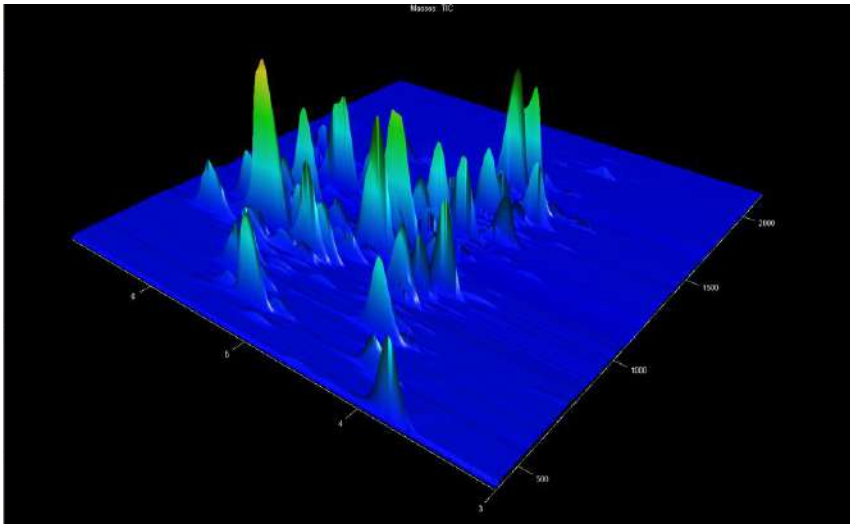


→ Good library Match score

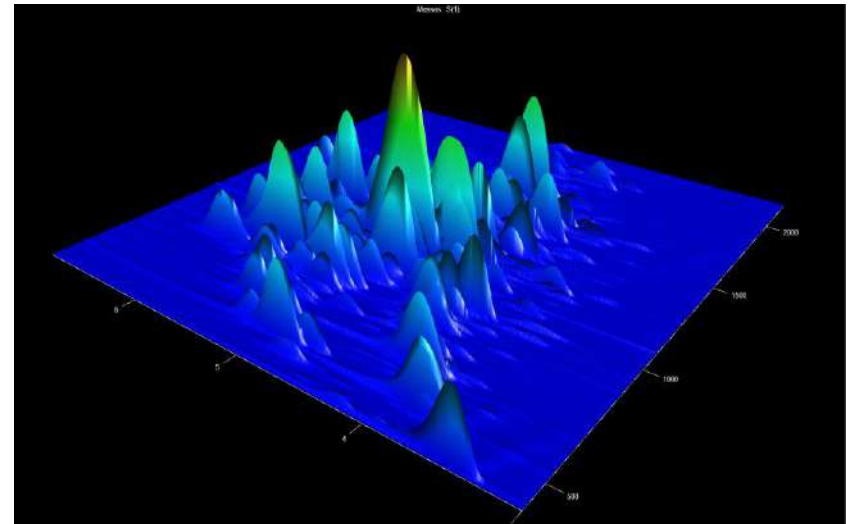
→ Easily excluded according to mass accuracy

- ✓ GC×GC-HRTOFMS/FID (dual detection)
 - Extended linear dynamic range (10^7)
 - Response factor

MS chromatogram



FID chromatogram (log scale)



- TD-GC×GC-HRTOFMS is a powerful tool for characterization of Odour and VOC emissions complementary to TD-GC-MS/Olfactometry
 - Complex VOC profiles emitted from biobased, biocomposite materials, recycled plastics
 - Correlation of Odour/VOC is not straightforward
 - Determination of specific VOC decrease
 - Undesirable compounds can be produced during the process
- Advanced characterization for selection of suitable additives for reduction of global odour, specific odour, TVOC or specific VOC emissions
- Interest for Formulation and Process development
- Evaluation of remediation after multi-stage process

Thank you!



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