LECO France

«Innovations Analytiques » pour l'agroalimentaire, la parfumerie et la cosmétique» pour le CECM

GC-TOF/MS

GCxGC-TOF/MS

Hubert LATAPPY
Hubert_latappy@leco.com
06 50 60 79 27

Empowering results since 1936

LECO = “Laboratory Equipment Company”

Siège mondial à Saint-Joseph, Michigan, Etats-Unis

Présent dans le monde entier

Sommaire

Leco

- Gamme Sciences séparatives
- Principes et avantages du temps de vol

ChromaTOF

- Logiciel unique
- Data processing
  - Déconvolution
  - Recherche ciblée
  - Quantification

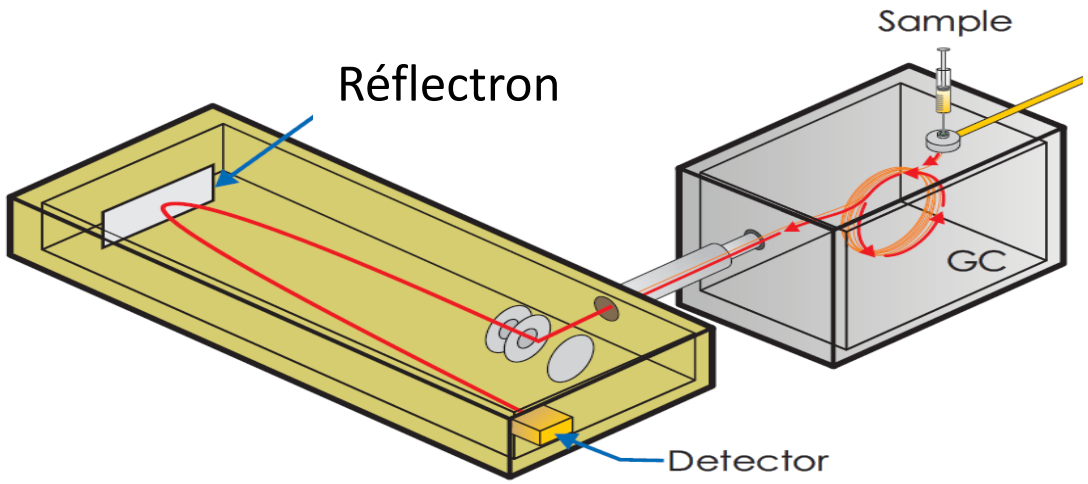
Principes de la GCxGC

- Exemple avec les allergènes
- La confirmation des MOSH-MOAH

Les autres innovations LECO

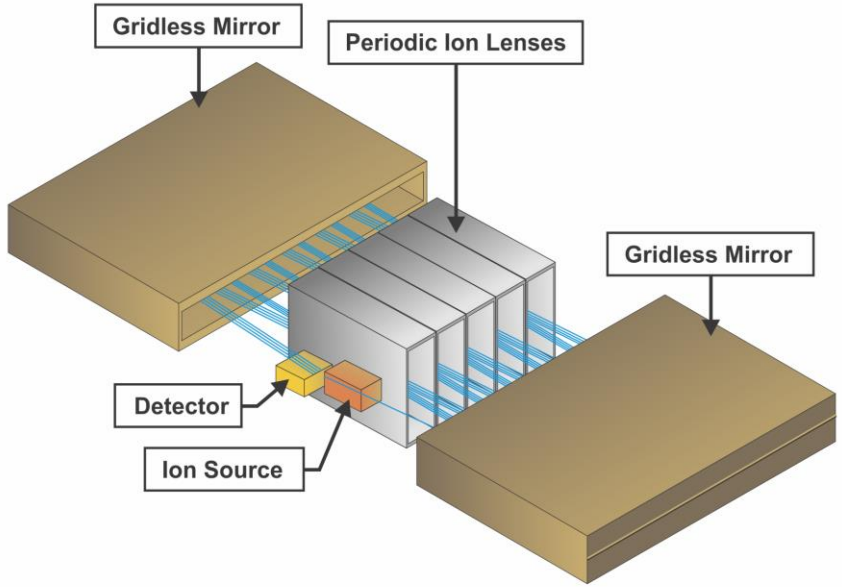
La gamme sciences séparatives

Moyenne Résolution



Résolution 0,1 Da

Haute Résolution



Résolution jusqu'à 50 000

➜ Vitesse d'acquisition élevée

➜ Full Screen

TOF compatible avec toutes librairies commerciales (NIST, Wiley, Fiehn…)

La gamme sciences séparatives

Temps de vol moyenne résolution

Pegasus BT

Pegasus BT 4D

GC → **Upgradable** → GCxGC

Temps de vol haute résolution

Pegasus HRT

Pegasus HRT 4D

Le Pegasus BT

GC-TOF/MS

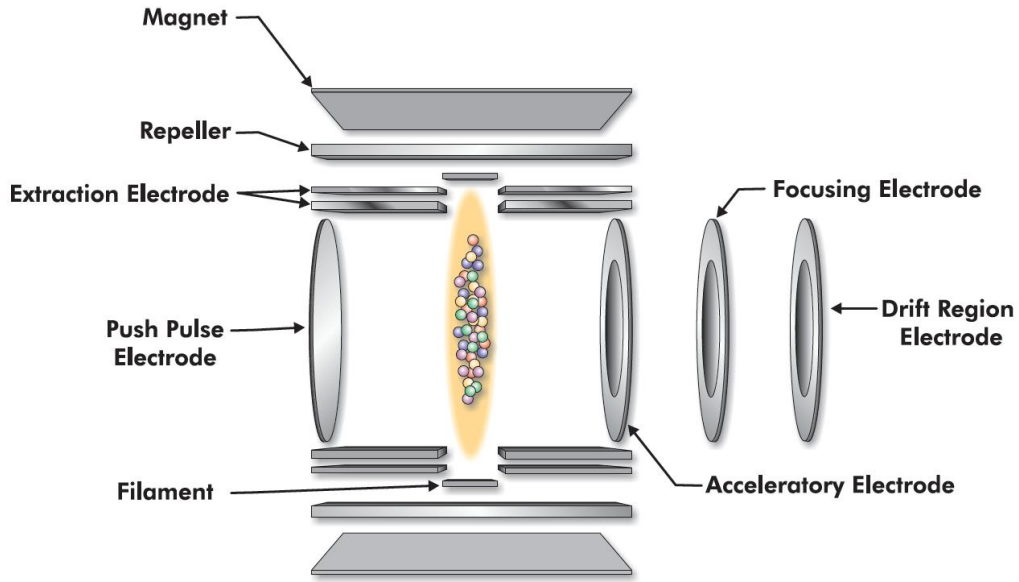
GC Agilent 8890 – TOF LECO – L-PAL3

Collaboration avec le RIC

ChromaTOF™

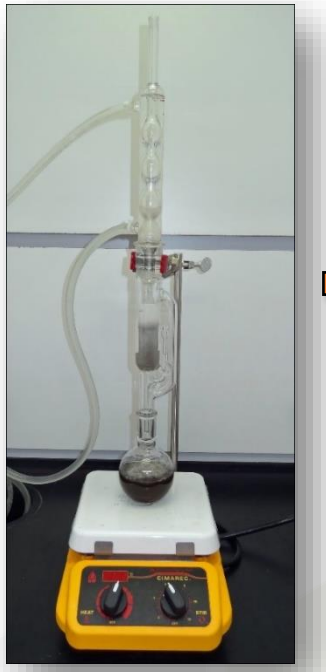
StayClean™ Ion Source

Le Pegasus BT : StayClean™ Ion Source



Ne se salit pas : ne se nettoie JAMAIS

Le Pegasus BT : StayClean™ Ion Source



Raw Sludge Sample

Soxhlet Extraction

Neat Sludge Extract

Sludge Extract Diluted 100:1

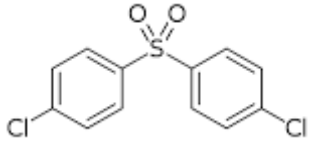
3000 injections
no change in performance !

Résolution et Sélectivité

Basse Résolution
< 1000
Ex: Quadripôle

Masse nominale
(ex : 238 m/z)

Fenêtre d'extraction : 0,5 Da

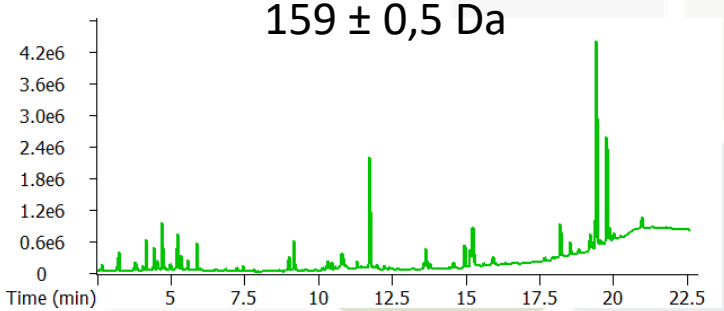


Moyenne Résolution
> 1500
Pegasus BT

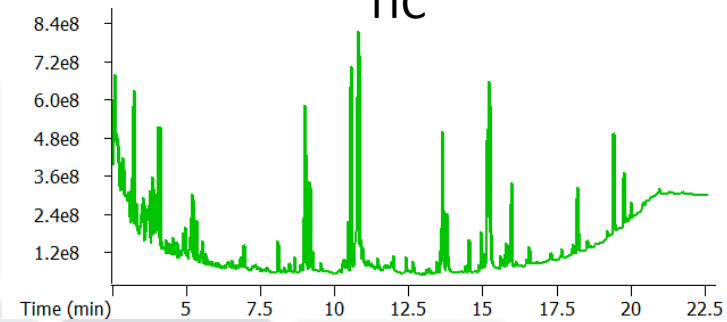
Masse 2 chiffres après la virgule
(ex : 238,23 m/z)

Fenêtre d'extraction : 0,05 Da

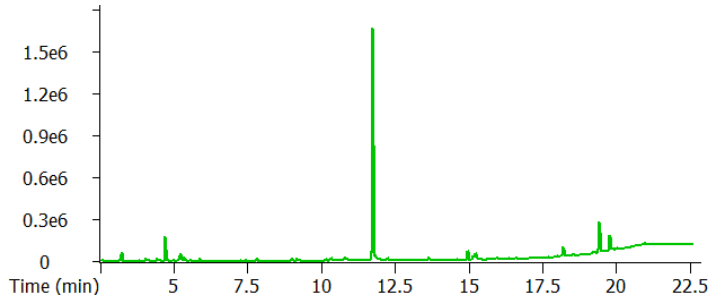
159 ± 0,5 Da



TIC

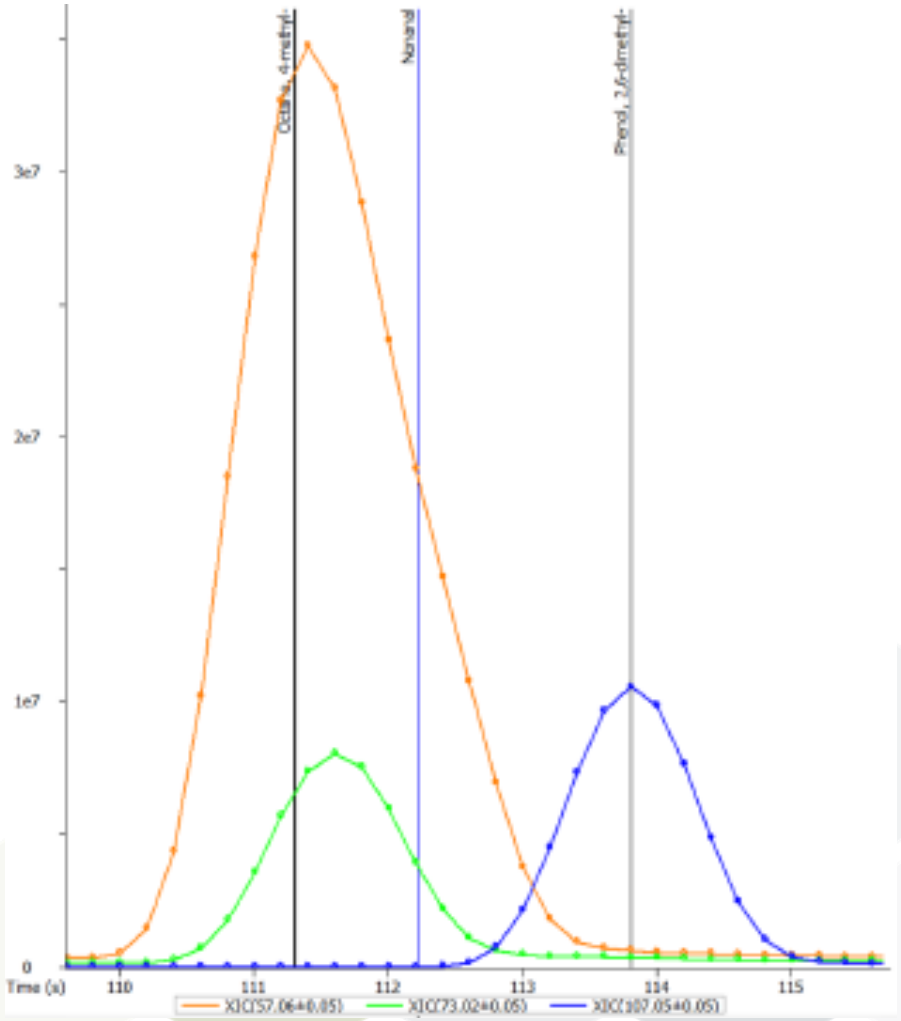


158.97 ± 0,05 Da

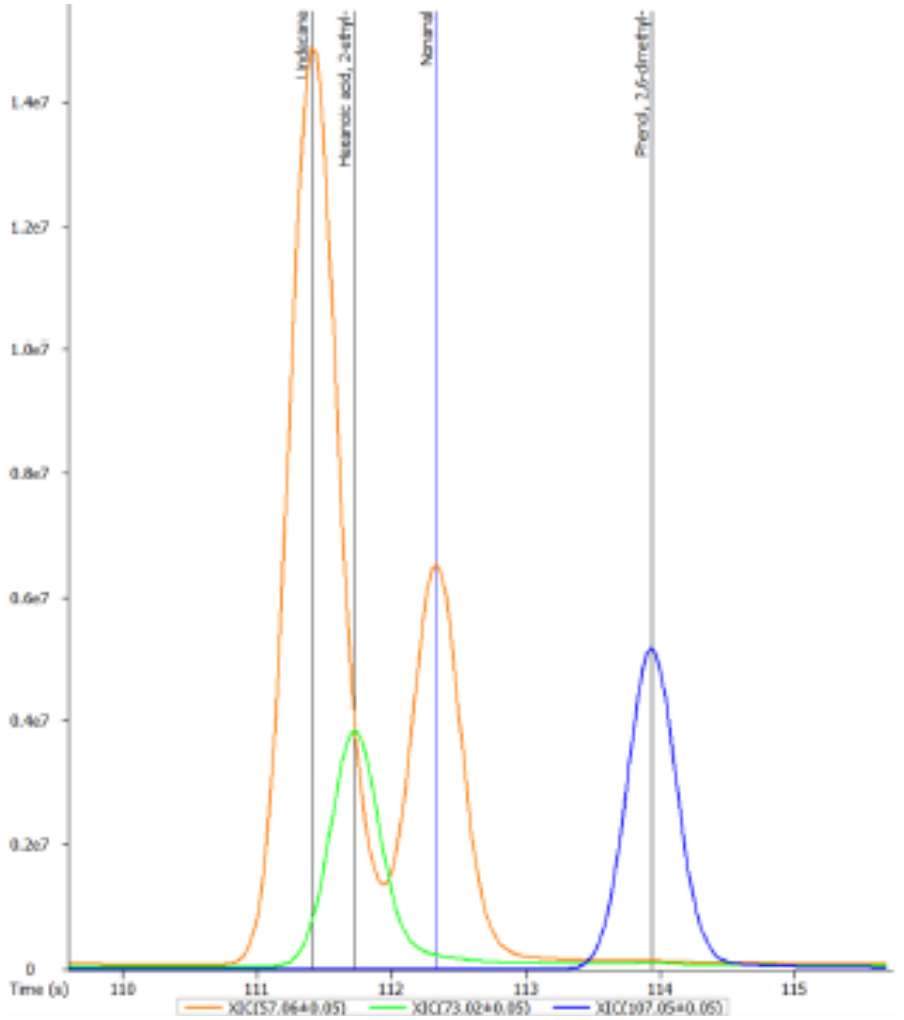


Impact vitesse d'acquisition

5 spectres/s



30 spectres/s



ChromaTOF

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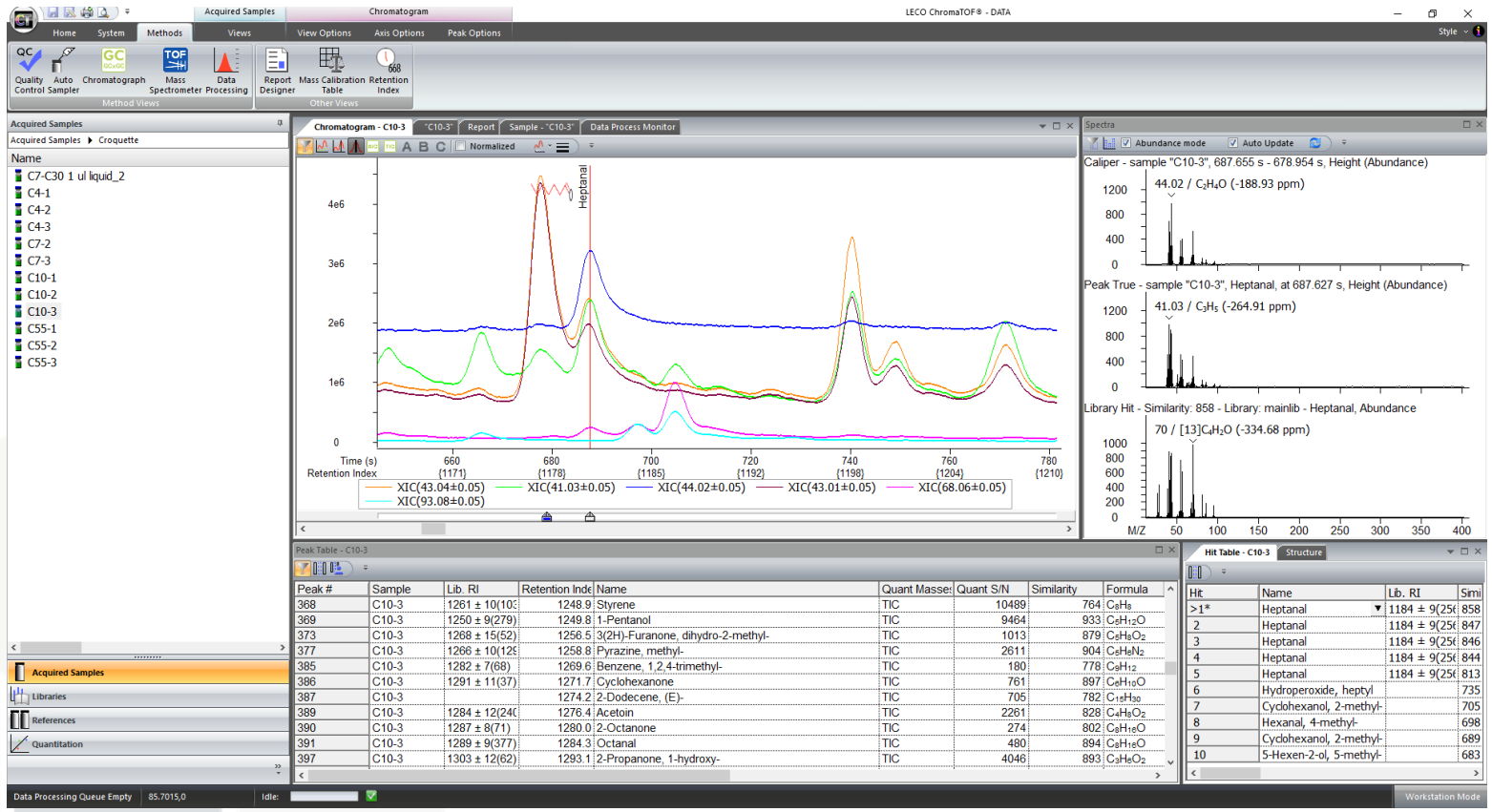
ChromaTOF

Acquisition

- Tune automatique
- Pilotage passeur
- Pilotage GC
- Pilotage MS
- Data processing



ChromaTOF

Acquisition

- Tune automatique
- Pilotage passeur
- Pilotage GC
- Pilotage MS

- Data processing

Juste après l'acquisition ou/et à posteriori

Déconvolution (Non target screening)

Comparaison à une ou plusieurs librairie

Comparaison aux indices de rétention

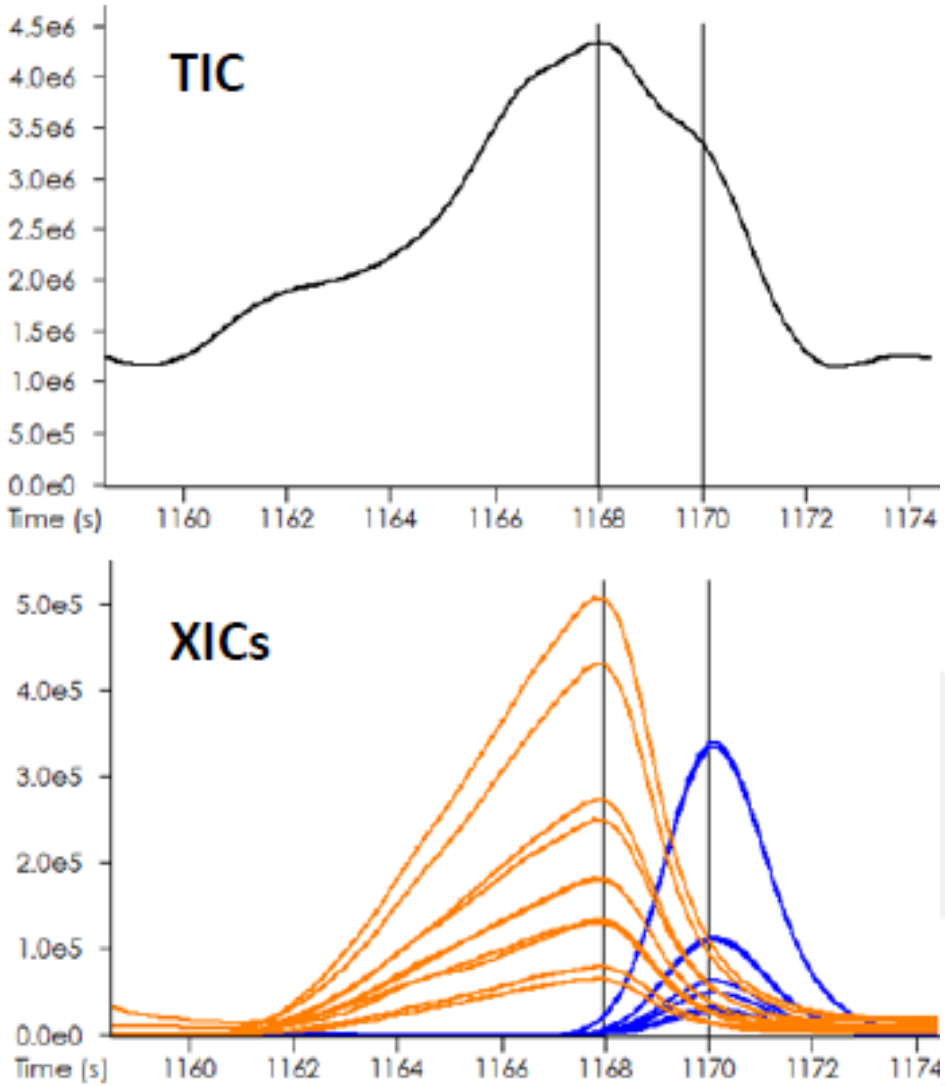
Recherche ciblée

Recherche ions ciblés dans fenêtre de temps de rétention

Quantification

Utilisation de courbes de quantification

Déconvolution automatique – non-AMDIS



2 paramètres à considérer :

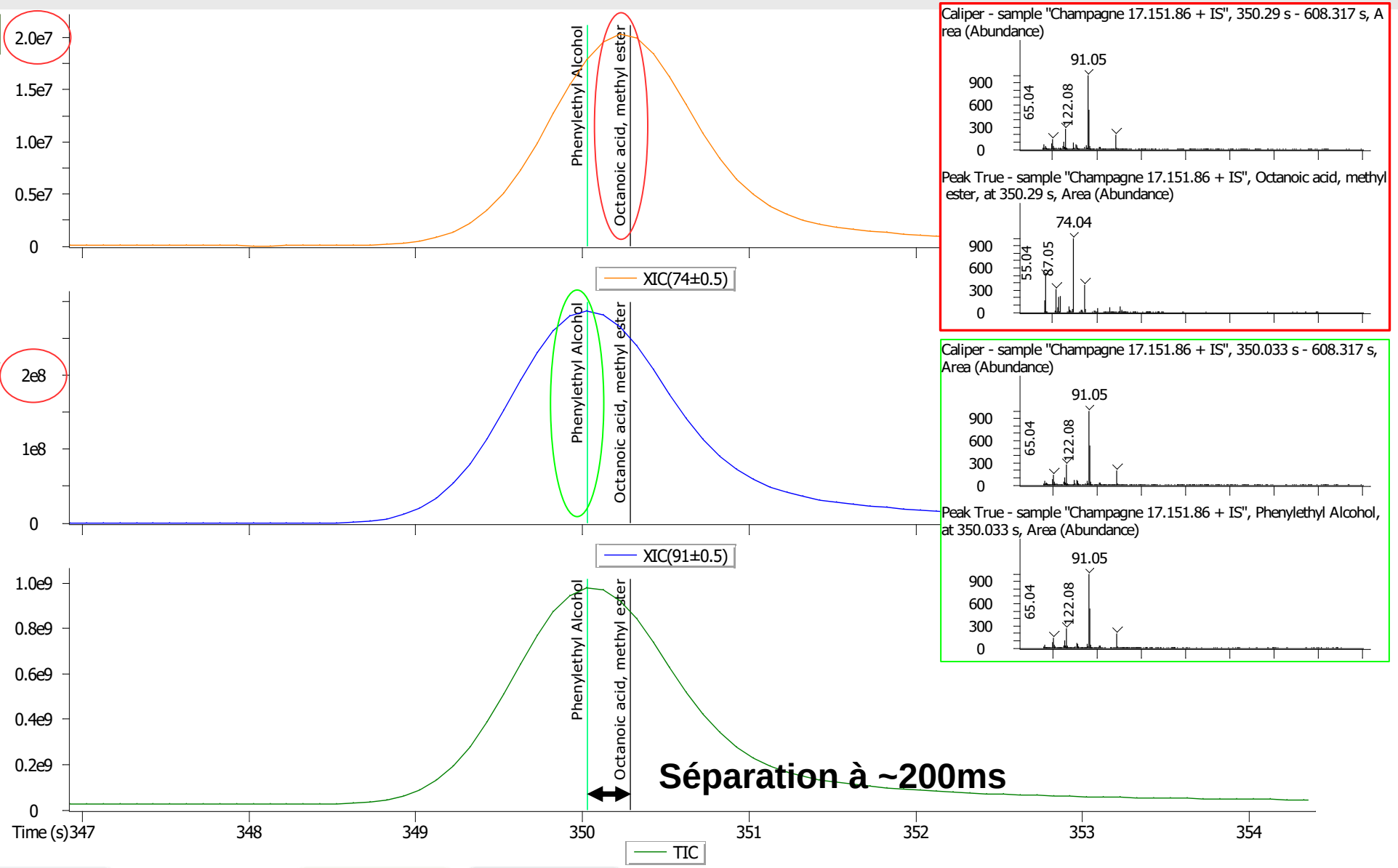
1) Rapport S/N minimum
2) Nombre d'ions minimum dans le spectre

#	1
Start Time*	Start of Run
Report Peaks	On
Min. S/N	10,0
Min. Stick Count	3

Déconvolution

Facteur 10

Large gamme spectrale



ChromaTOF

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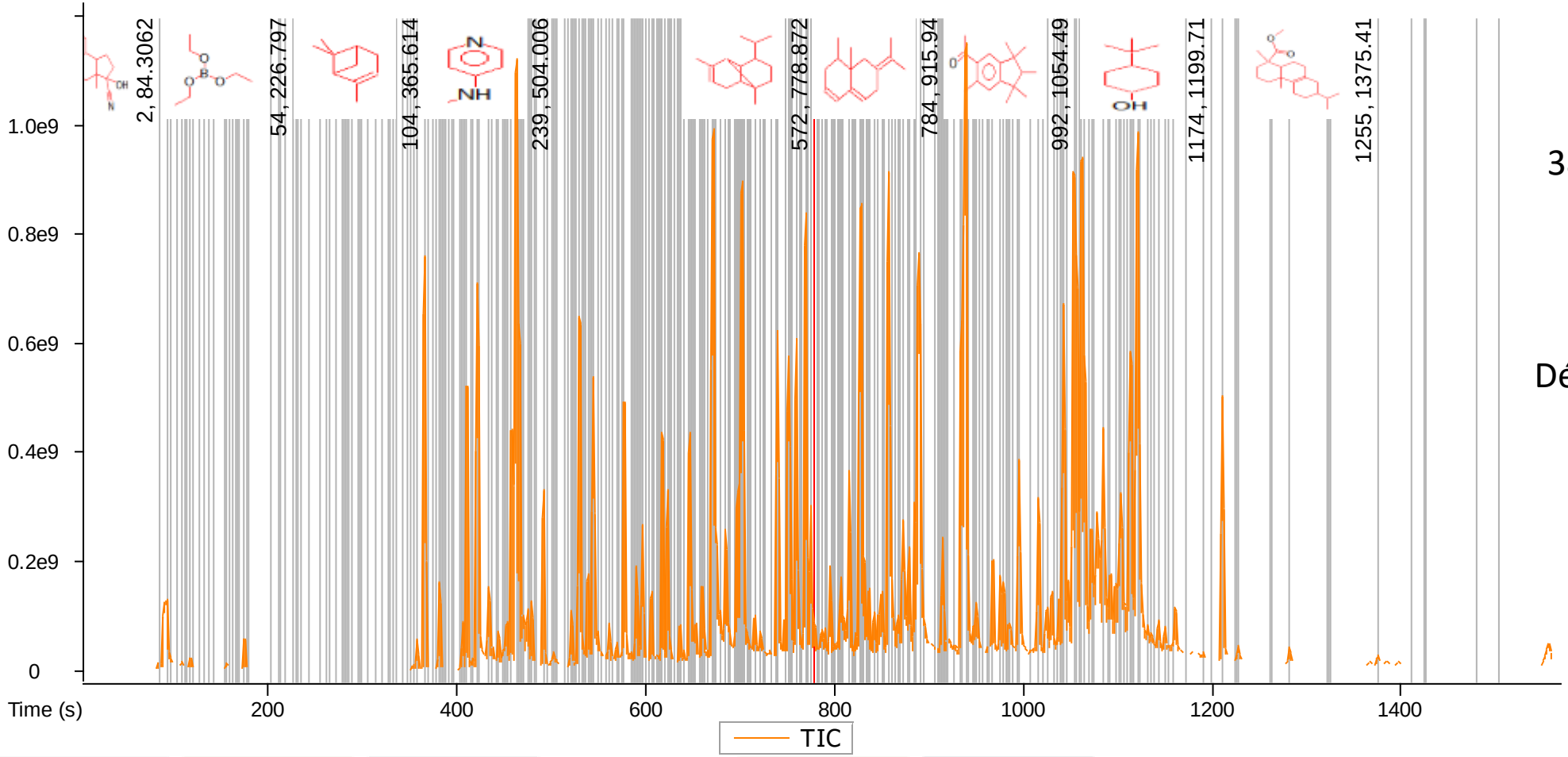
Déconvolution (Non target screening)

Echantillon de parfum



381 molécules identifiées

Avec similarité > 700

Déconvolution non-AMDIS

#	1
Start Time*	Start of Run
Report Peaks	On
Min. S/N	10,0
Min. Stick Count	3

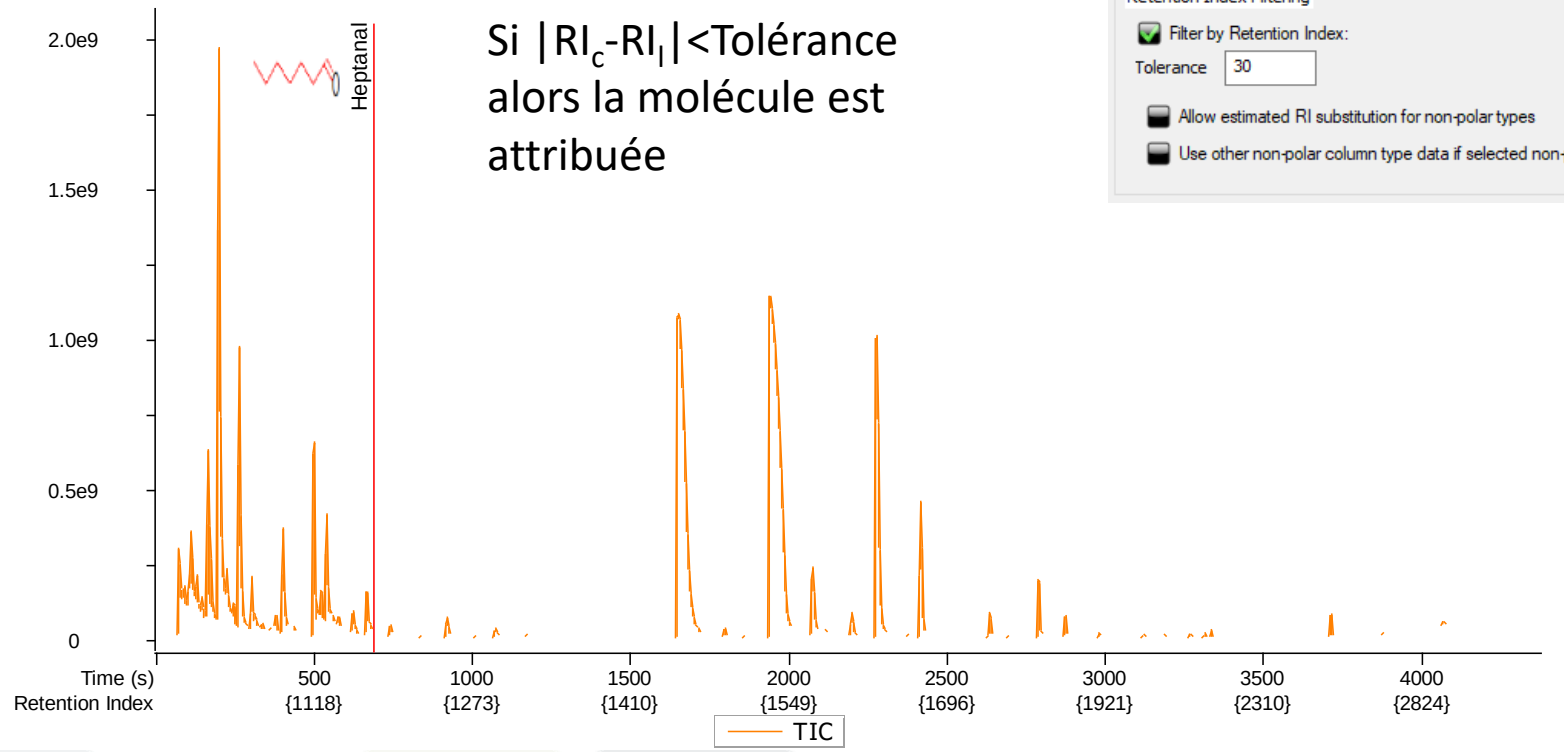
Utilisation indice de rétention

ChromaTOF compare l'indice de rétention calculé RI_c à l'indice de rétention de la librairie RI_l

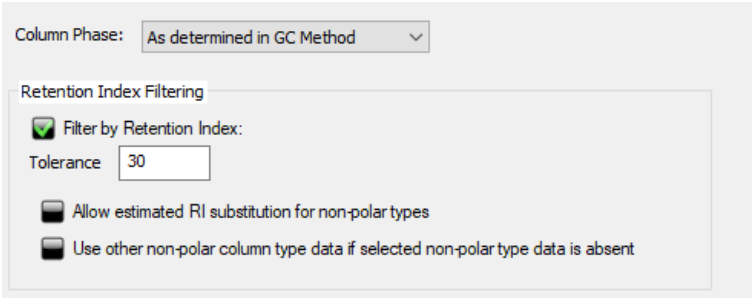
Retention Index Table - Leco C7-C30

Auto Select

#	Name	Absolute R.T.	Retention Ind
1*	C8	361.647	800.00
2	C9	484.912	900.00
3	C10	598.536	1000.0
4	C11	701.257	1100.0
5	C12	795.49	1200.0
6	C13	882.81	1300.0
7	C14	964.569	1400.0
8	C15	1041.48	1500.0
9	C16	1114.11	1600.0
10	C17	1183.01	1700.0
11	C18	1248.47	1800.0
12	C19	1310.7	1900.0
13	C20	1370.07	2000.0
14	C21	1426.83	2100.0
15	C22	1481.04	2200.0
16	C23	1533.18	2300.0
17	C24	1583.08	2400.0
18	C25	1631.16	2500.0
19	C26	1677.33	2600.0
20	C27	1721.85	2700.0
21	C28	1765.78	2800.0
22	C29	1813.61	2900.0
23	C30	1867.8	3000.0

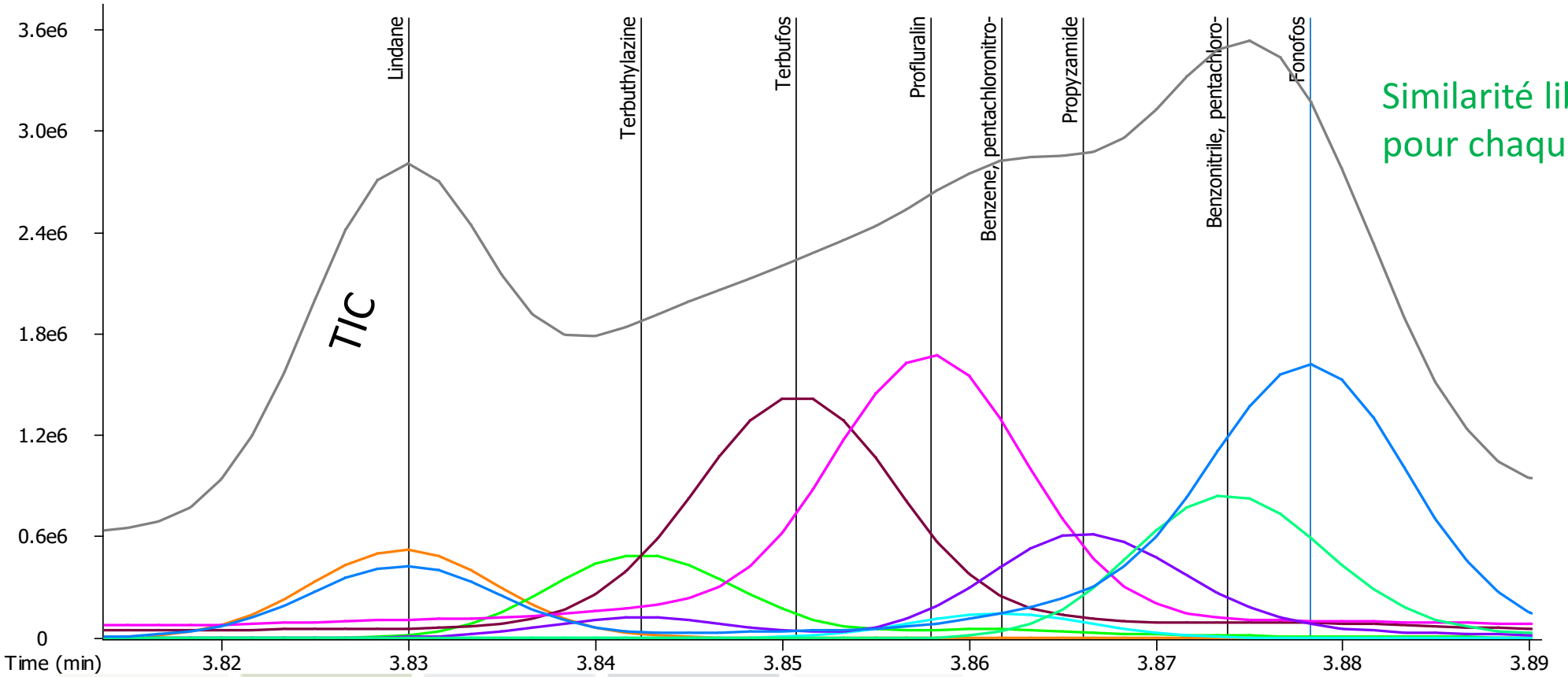


Si $|RI_c - RI_l| <$ Tolérance alors la molécule est attribuée



Quantification : 204 pesticides 8,55 min

Coélution de 8 pesticides sur 0,07min (env. 4 s)



Similarité librairie > 800/1000 pour chaque composé

XIC

15 m x 0.25 mmID x 0.25 µm df Rxi-5MS

Pegasus BT4D – GCxGC-TOFMS

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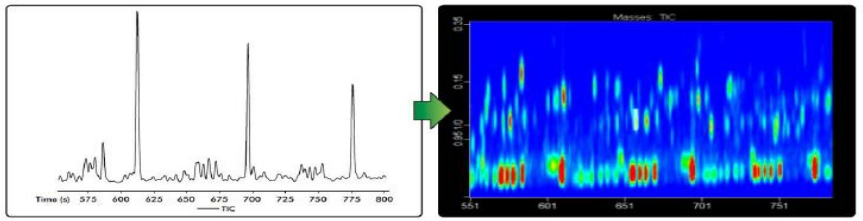
GCxGC-TOF MS de paillasse

LECO® Simply GCxGC™

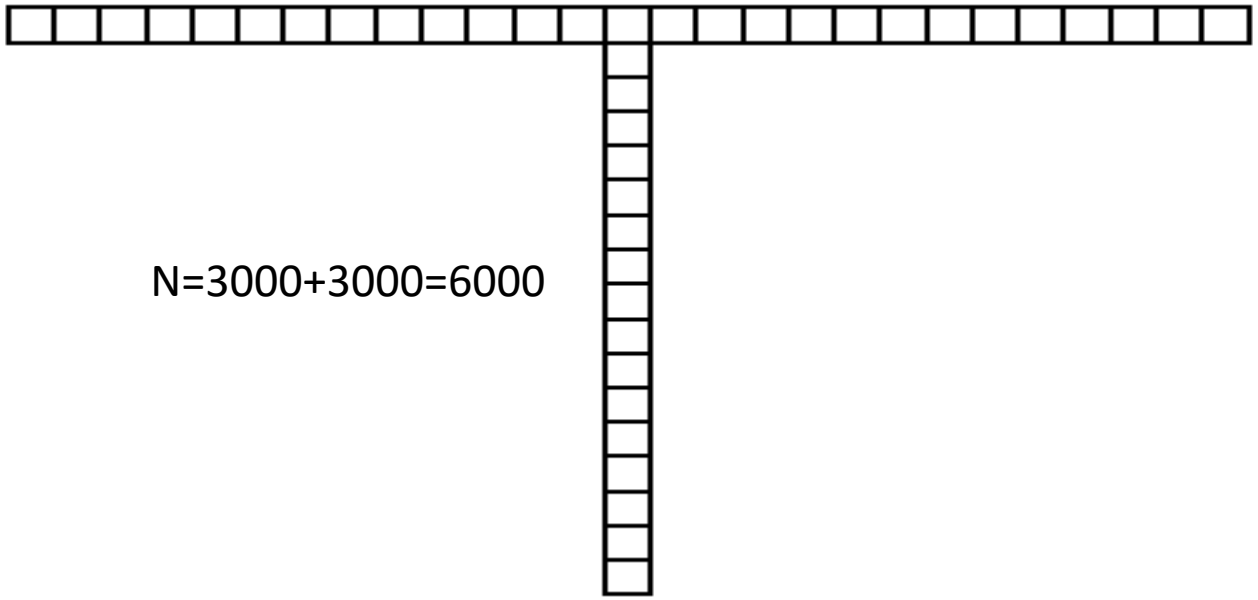


Techniques séparatives en GC

GC 1D

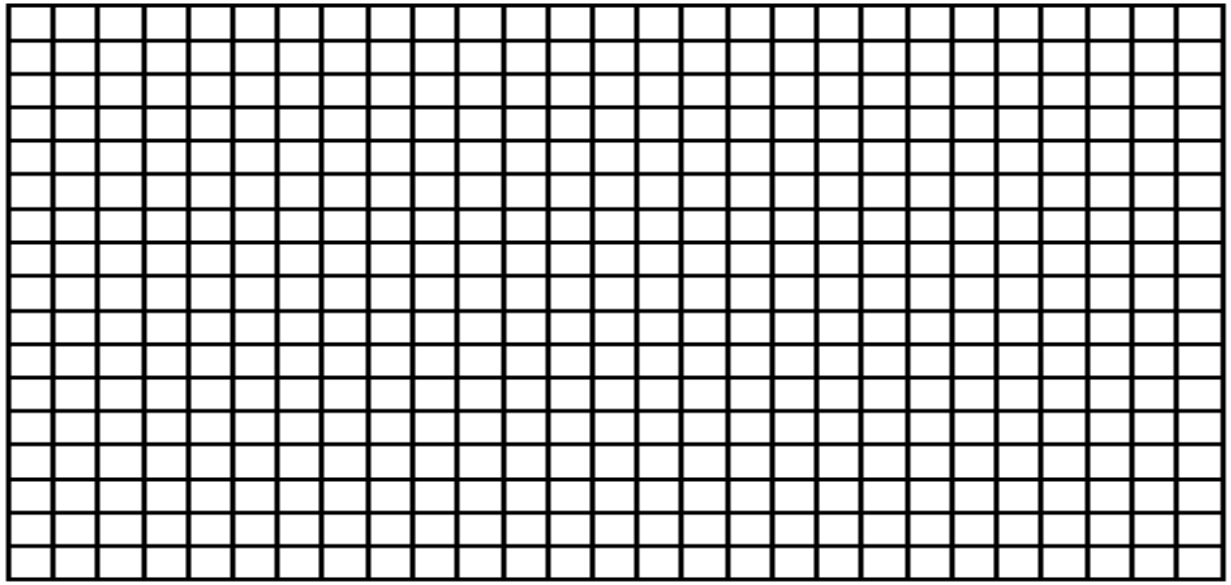
N=3000

GC 2D type Heart Cut



N=3000+3000=6000

GC 2D Compréhensive (GCxGC)

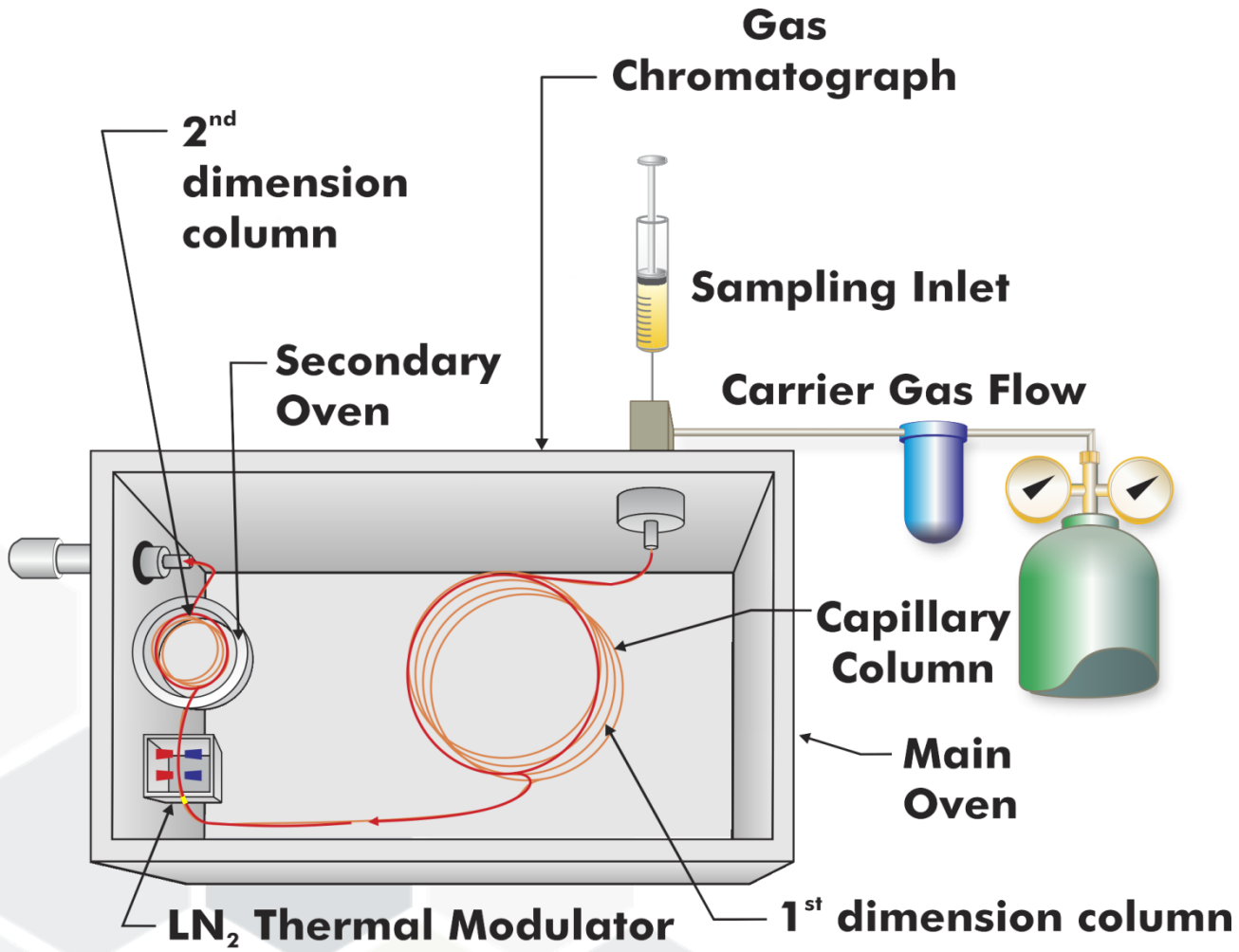


TOUT séparer en UNE injection

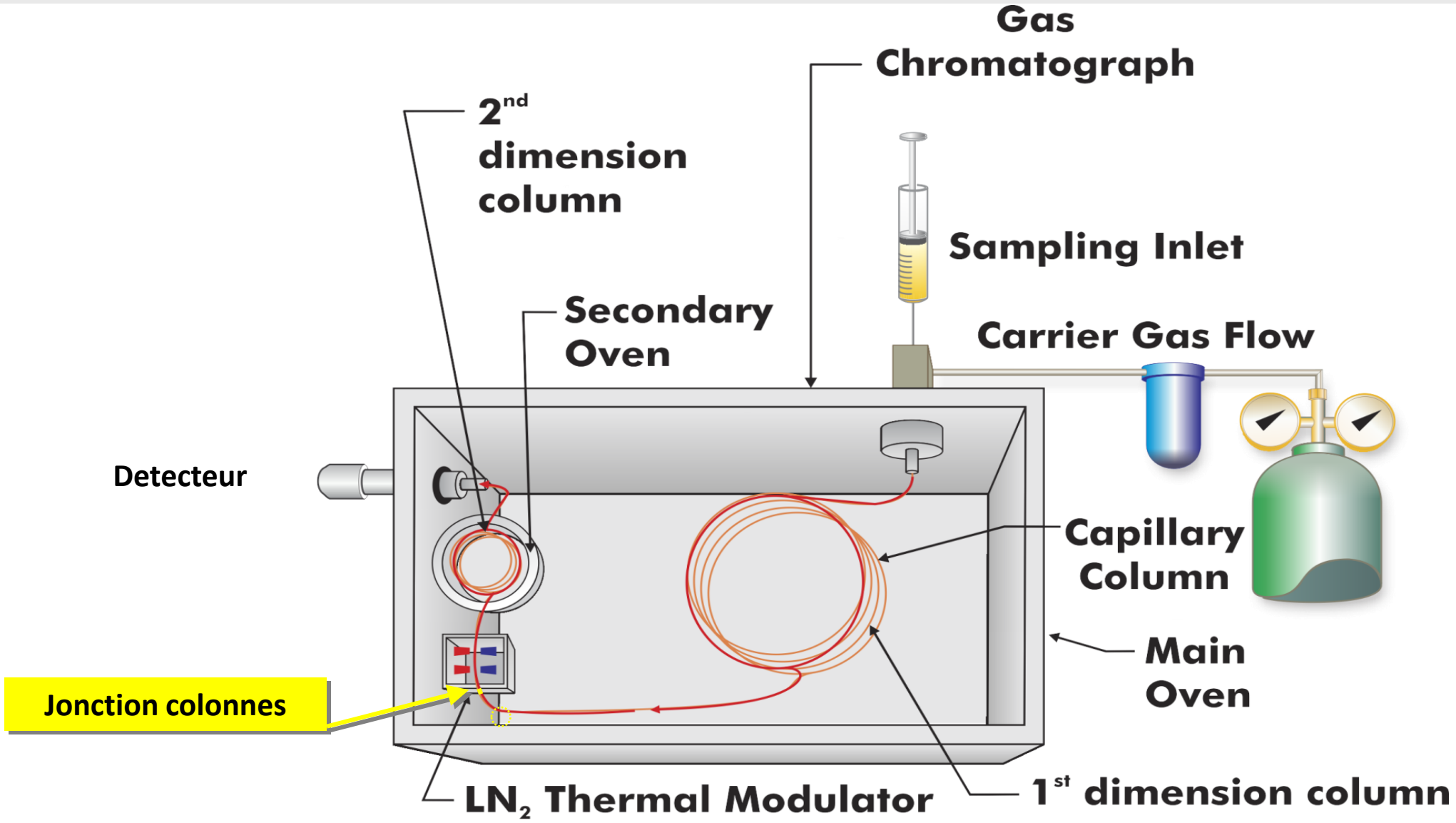
N=3000x200 = 600 000

L eq 1D = 6 km Tr = 1,5 ans

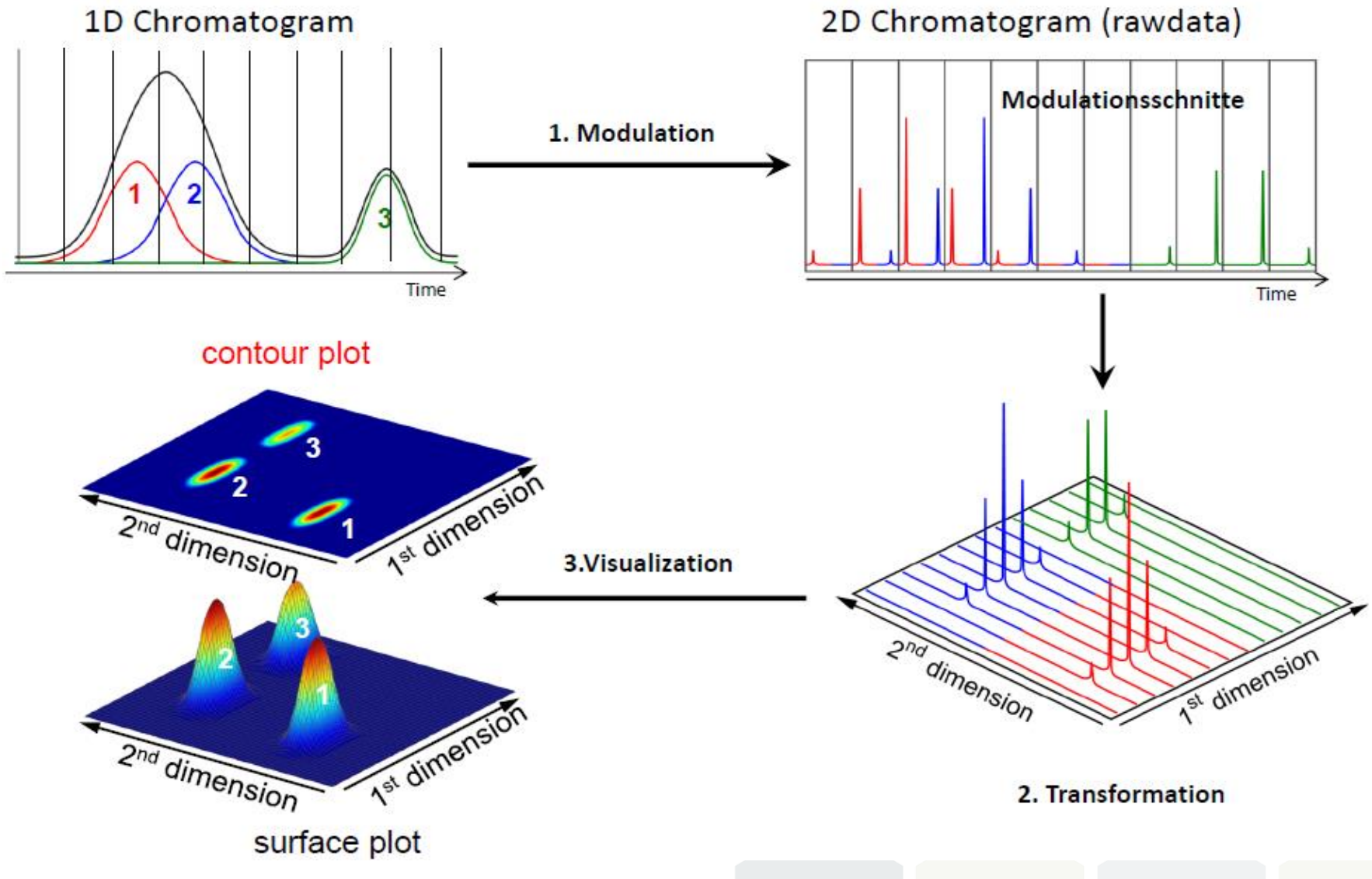
GCxGC Leco : Schema de la modulation



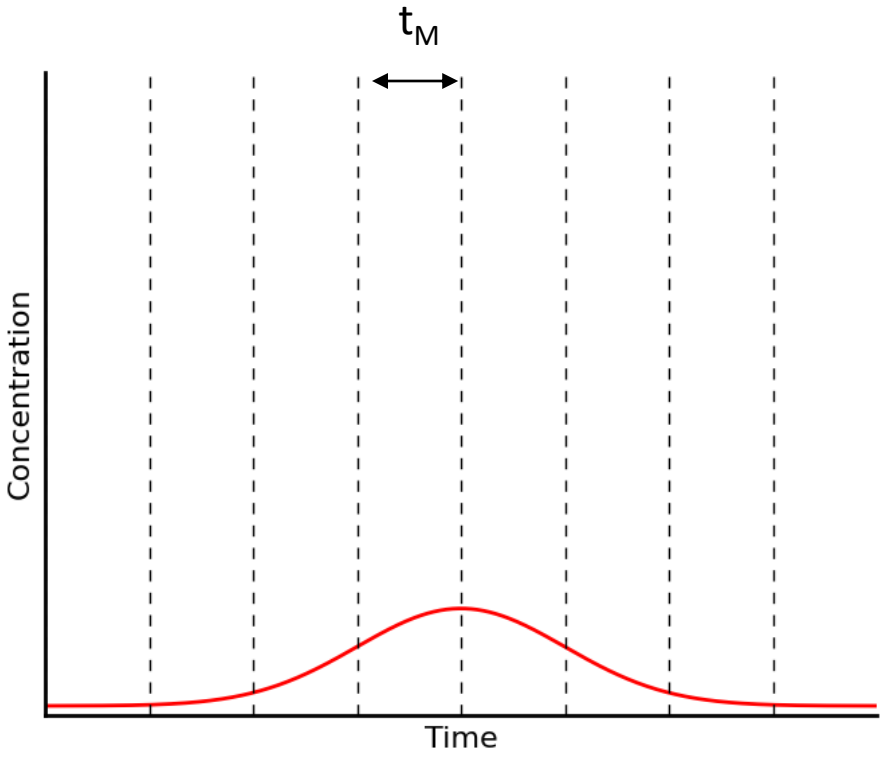
Principes

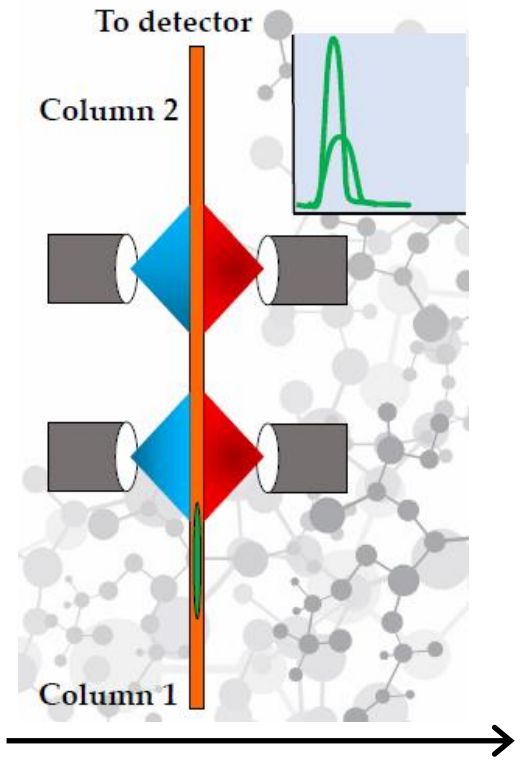

Gas Chromatograph
2nd dimension column
Sampling Inlet
Secondary Oven
Carrier Gas Flow
Detecteur
Capillary Column
Main Oven
Jonction colonnes
LN2 Thermal Modulator
1st dimension column

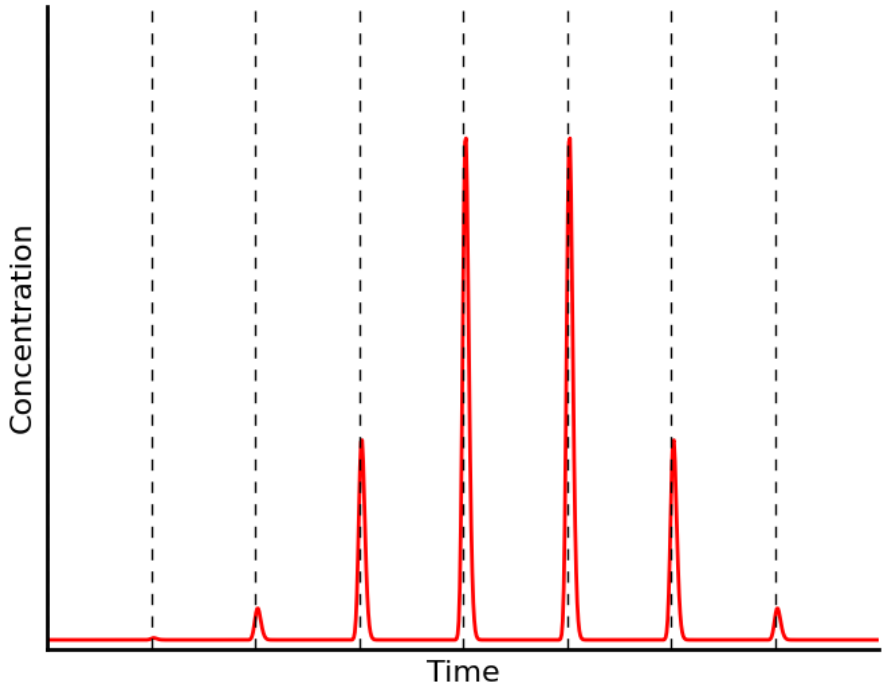
Principes


1D Chromatogram
1
2
3
Time
1. Modulation
2D Chromatogram (rawdata)
Modulationsschnitte
Time
2. Transformation
2nd dimension
1st dimension
3.Visualization
contour plot
surface plot

Principes : modulation thermique







t_M= Période de modulation

→ ***Facile à modifier***

→ ***Réglable pendant un run***

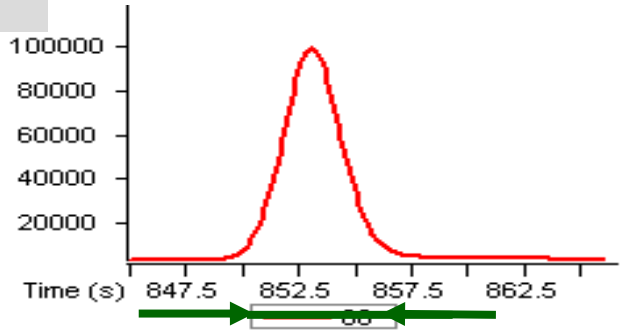
Gain en sensibilité

en modulation cryogénique

Principes : modulation thermique

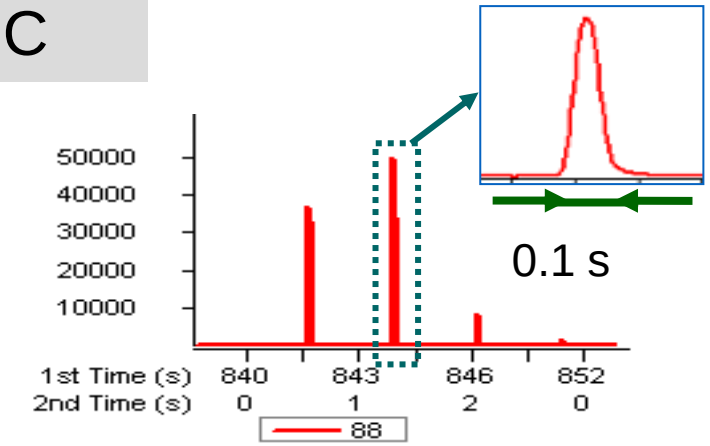
GC 1D

Pic large



7.5 s

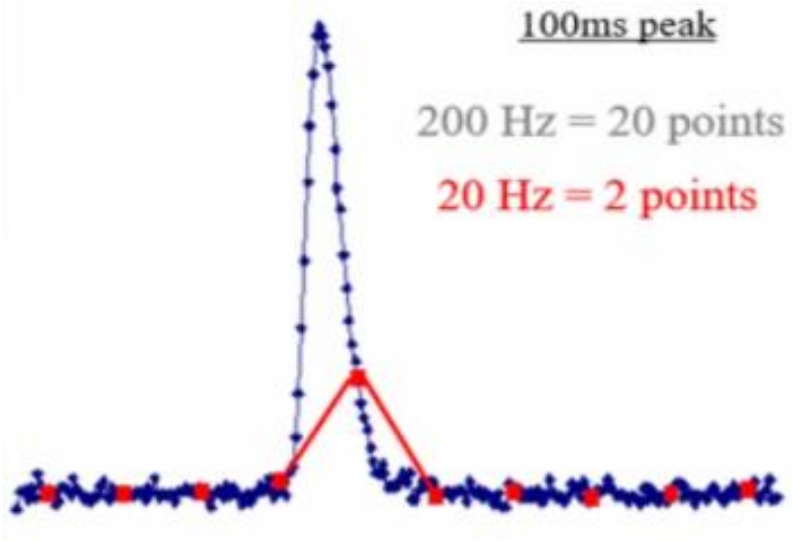
GCxGC



Pic très fin

0.1 s

Vitesse d'acquisition > 100 Hz
pour un pic 100 ms



TOF seul détecteur capable d'exploiter les pics très fins de GCxGC
(vitesse max d'acquisition = **500 spectres/sec**)

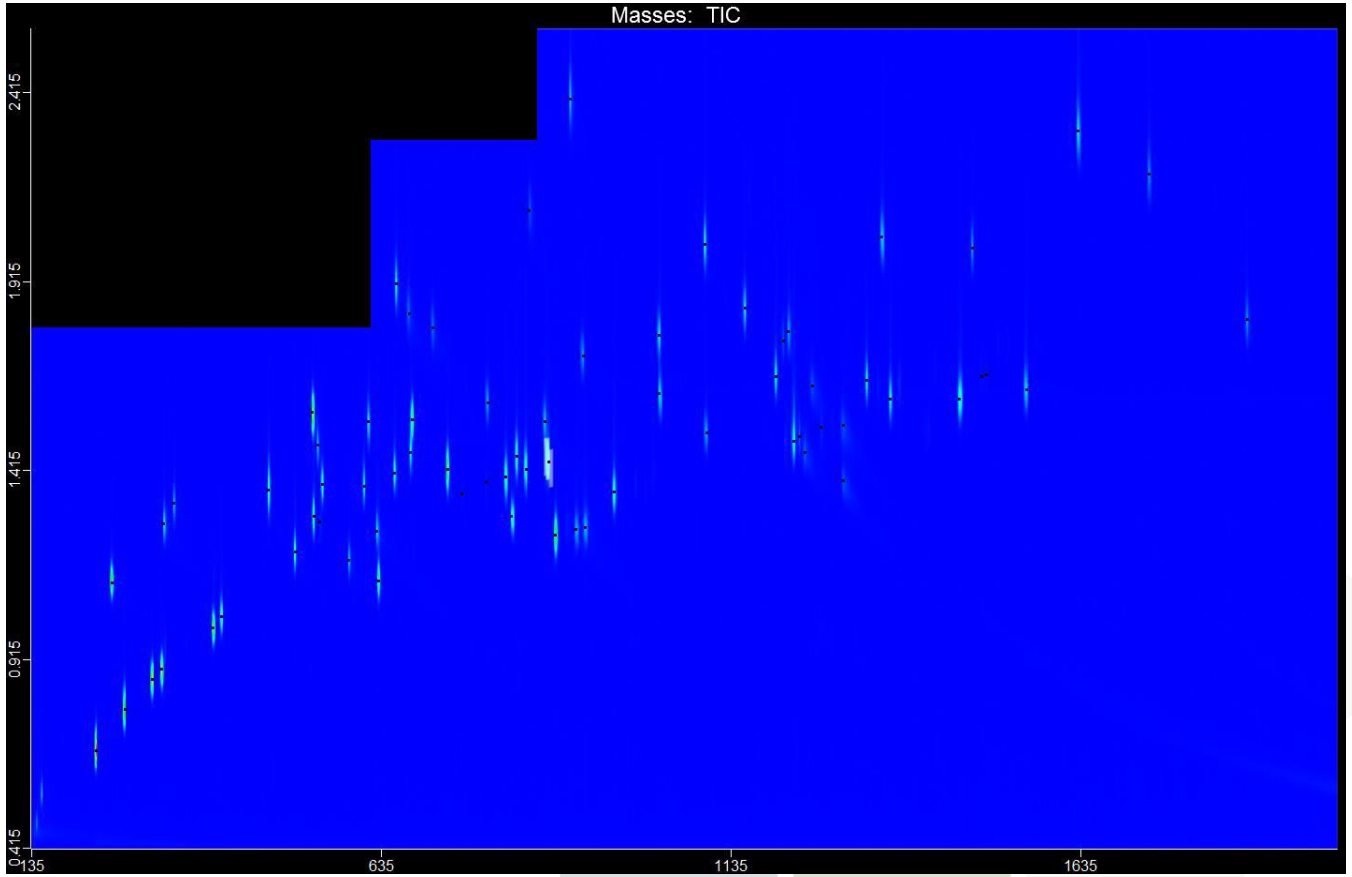
Exemple : Allergène

Cosmétiques : Problématique allergène
96 composés et isomères

Méthode : 31 minutes

Méthode recommandée :
GC-MS 2 colonnes avec 2 méthodes → 4 runs.

GCxGC : 1 seul run pour tout séparer



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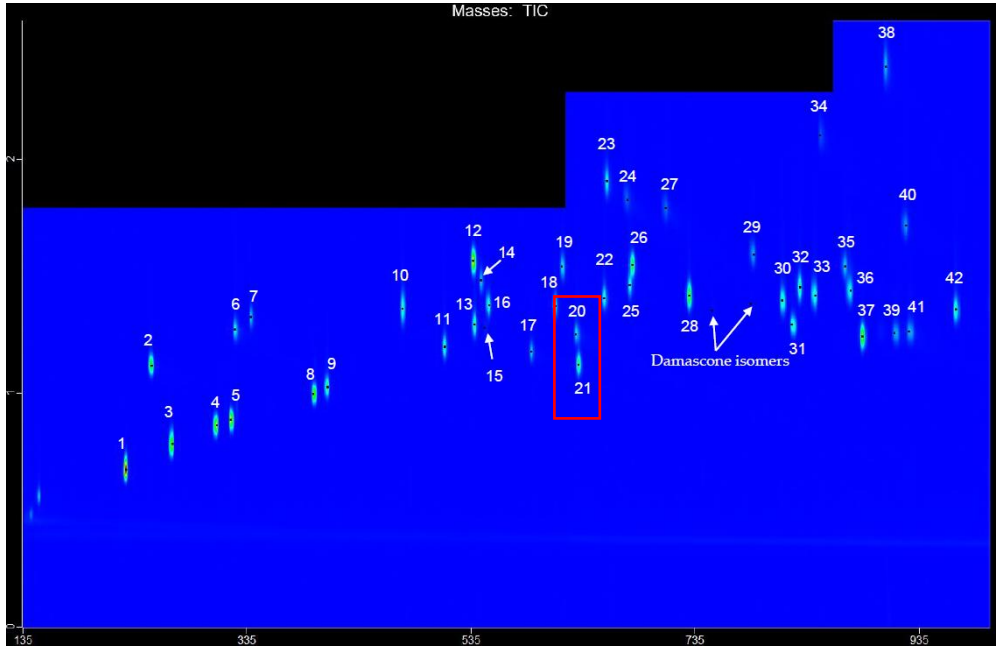

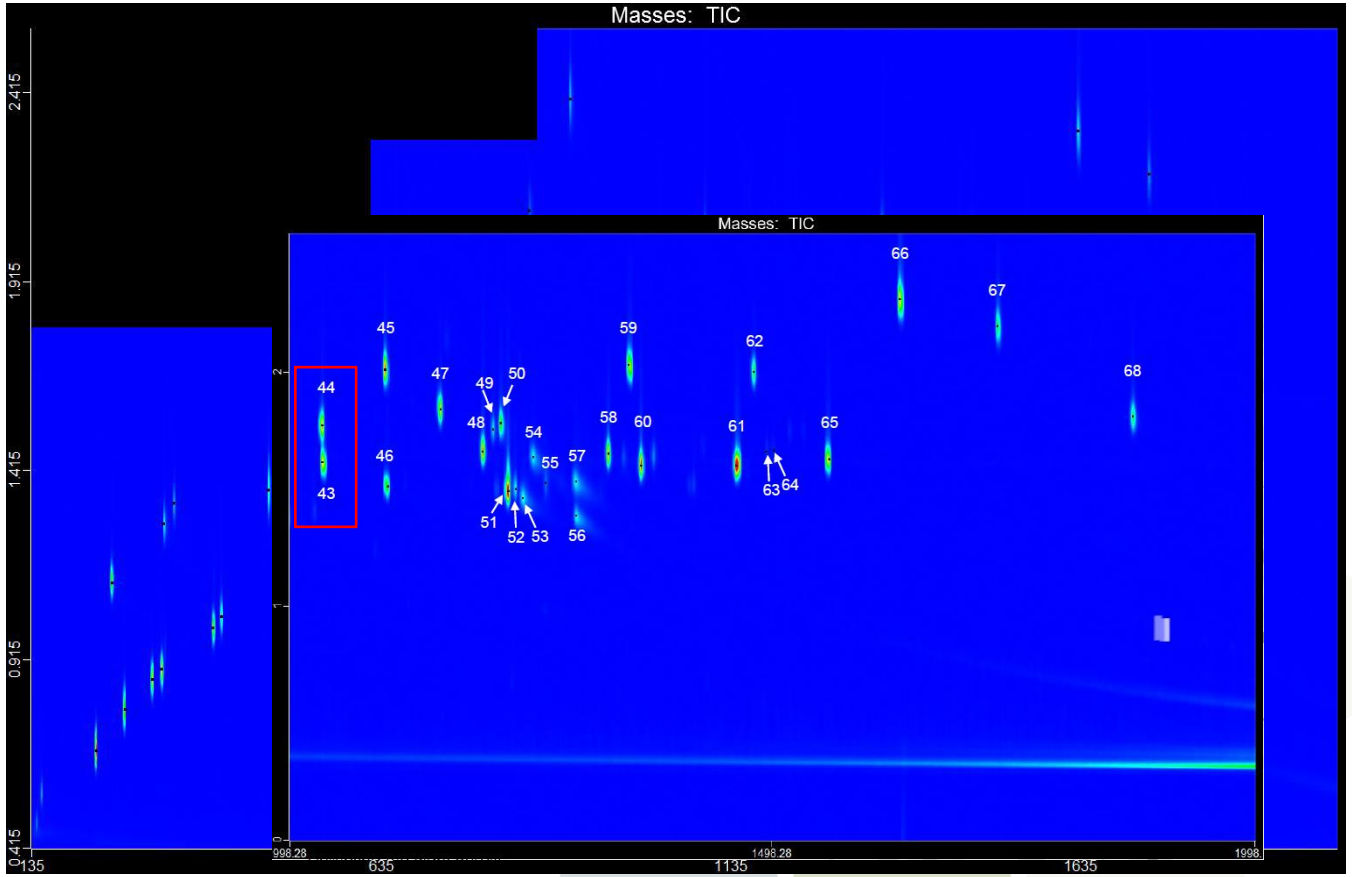

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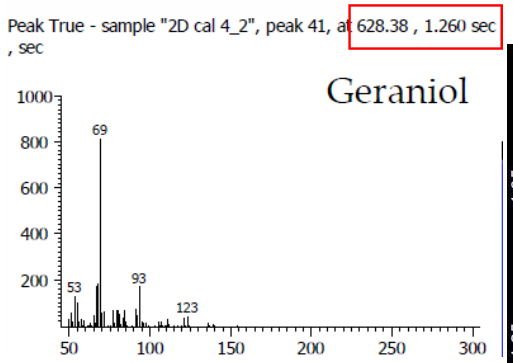
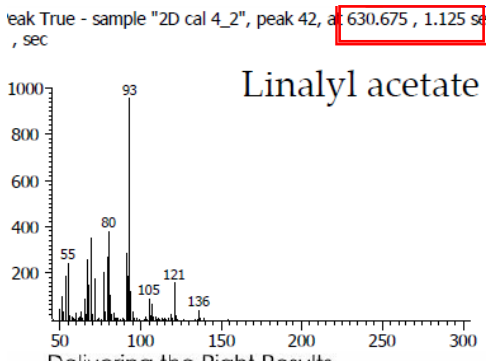
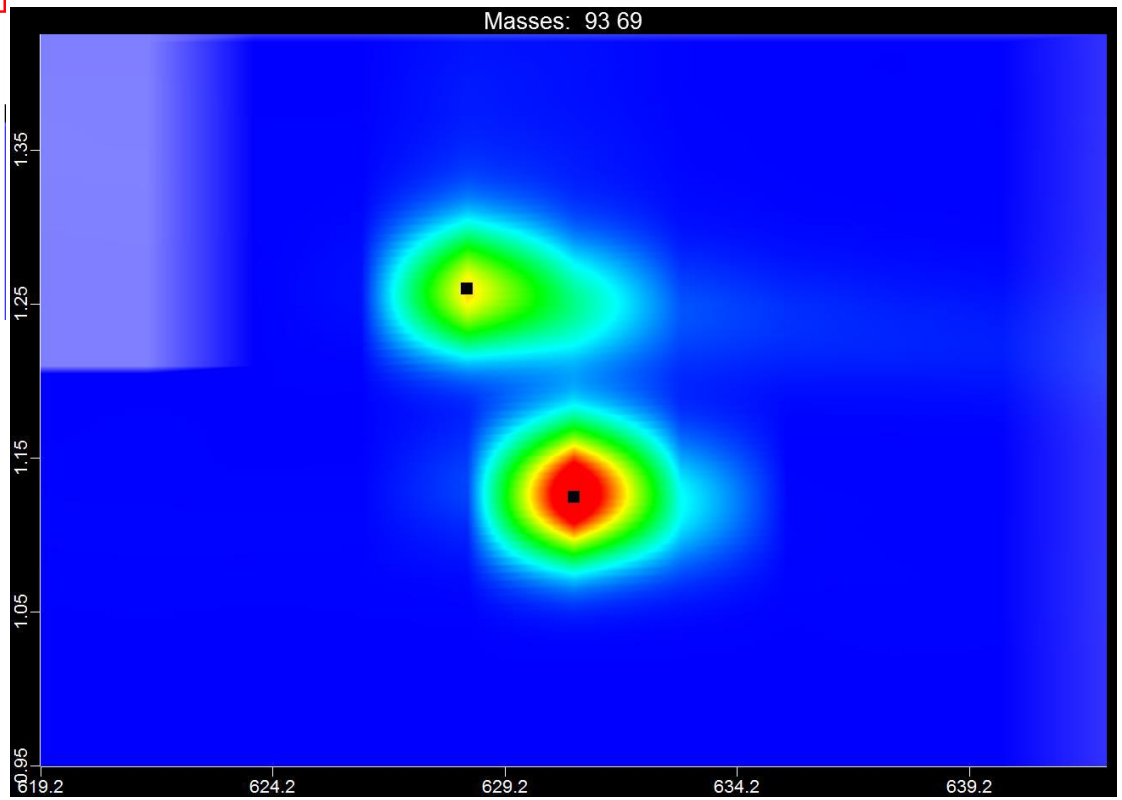
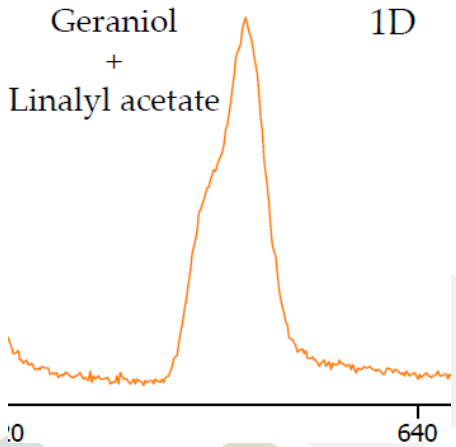


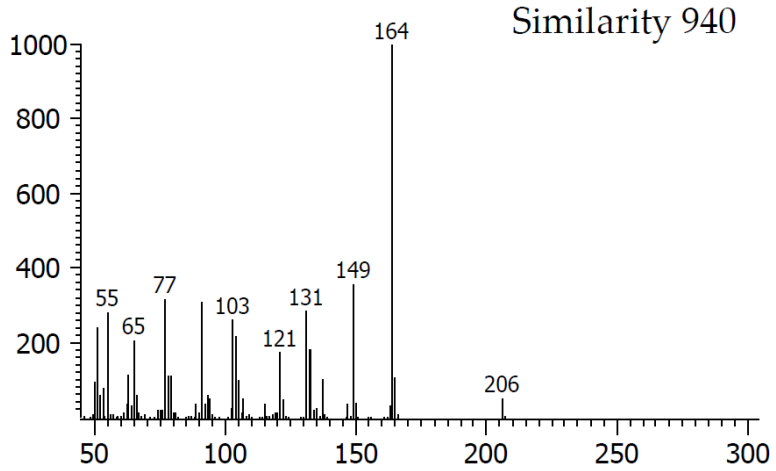


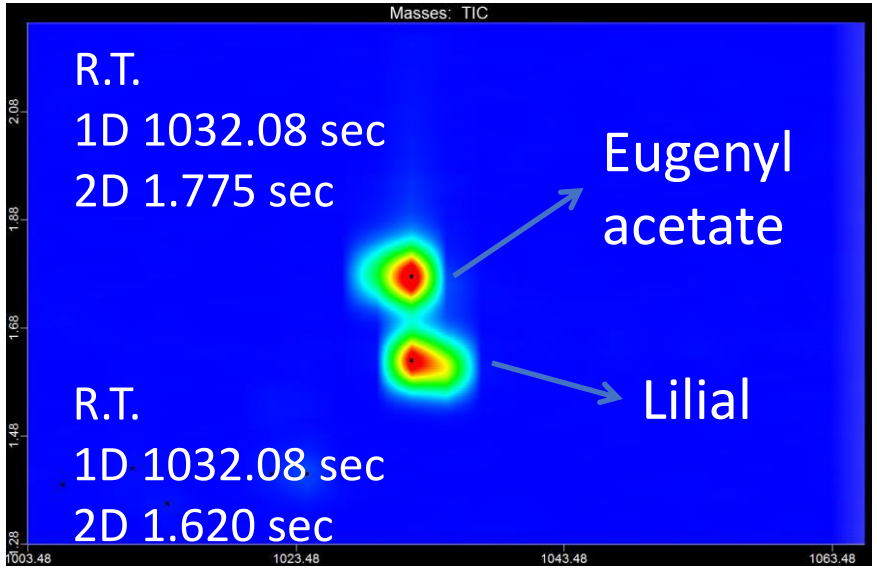




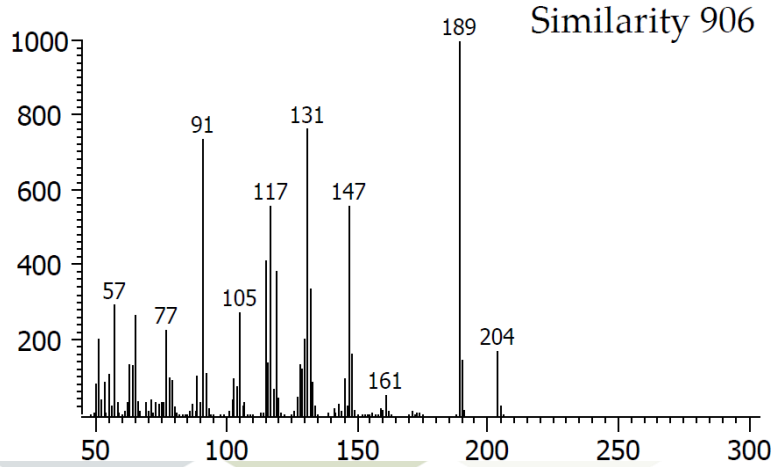
Exemple : Allergène

Peak True - sample "2D cal 4_2", peak 103, at 1032.08 , 1.775 s
ec , sec





Peak True - sample "2D cal 4_2", peak 102, at 1032.08 , 1.620 s
ec , sec



Exemple : MOSH/MOAH

What is MOSH/MOAH, why is it analysed?

- Mineral Oil (MOH) :

MOSH

Mineral oil saturated hydrocarbons

-n-alcane

- isoalcane

- cycloalcane

MOAH

Mineral oil aromatic hydrocarbons

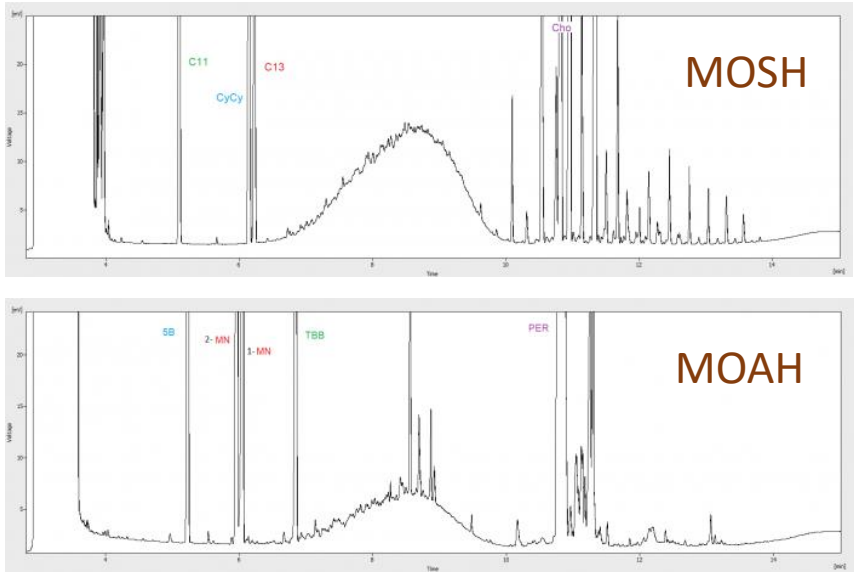
- principalement hydrocarbones aromatiques

Exemple : MOSH/MOAH

Analysis Challenges – What are Complexities?

- MOSH & MOAH sont séparés par LC ou SPE. Les extraits sont analysés par GC-FID

- Le nombre d'hydrocarbone saturé (MOSH) et d'hydrocarbone aromatique (MOAH) aboutissent souvent a des "humps"



Méthode de routine

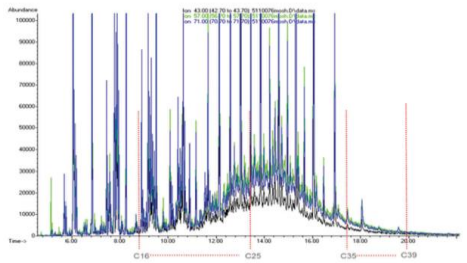
- La norme européenne propose l'utilisation de GC-FID après la séparation des deux fractions par LC/SPE (on-line ou off-line)
- FID est un détecteur non spécifique et tous les interférents dans ces chromatogrammes ne peuvent être vu
- Le risque est d'obtenir des résultats erronées (souvent faux positifs)

Exemple : MOSH/MOAH

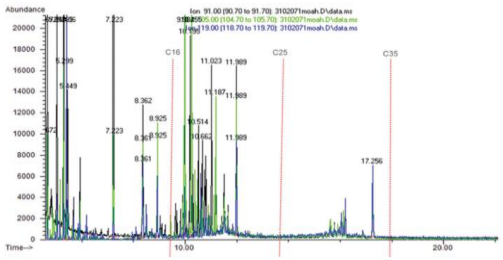
Interferences – MS!

- L'utilisation de la MS peut aider … seulement si aucun ion de la matrice ne vient interferer.

m/z 43, 57, 71, 85 → **MOSH** BUT = **Hydrocarbon of natural and/or synthetic origin**, like terpenes, natural waxes, oligomeric polyolefin **(POSH)**



m/z 91,105,119,133 → **MOAH** BUT = **Terpenes, terpenoids, carotenoids,etc**



Influence de la matrice

- FID sera précis sur des matrices légères ou les MOSH-MOAH n'auront pas d'interférence
- Analyse en 1D avec MS/FID va aider à confirmer –très dépendant du type de matrice notamment sur les matrices naturelles
- Comment résoudre le problème ……
  GCxGC-TOF-MS!

Exemple : MOSH/MOAH

GCxGC-TOF-MS for Confirmatory Analysis

- The needs for a confirmatory method is long accepted (EC/96/23, 2002)
- The latest scientific opinion recommends GCxGC (EFSA, 2012)

COMMISSION DECISION

of 12 August 2002

implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results

(notified under document number C(2002) 3044)

(Text with EEA relevance)

(2002/657/EC)

CONFIRMED

2.3. CONFIRMATORY METHODS FOR ORGANIC RESIDUES AND CONTAMINANTS

Confirmatory methods for organic residues or contaminants shall provide information on the chemical structure of the analyte. Consequently methods based only on chromatographic analysis without the use of spectrometric detection are not suitable on their own for use as confirmatory methods. However, if a single technique lacks sufficient specificity, the desired specificity shall be achieved by analytical procedures consisting of suitable combinations of clean-up, chromatographic separation(s) and spectrometric detection.

The following methods or method combinations are considered suitable for the identification of organic residues or contaminants for the substance groups indicated:

efsa

European Food Safety Authority

EFSA Journal 2012;10(6):2704

SCIENTIFIC OPINION

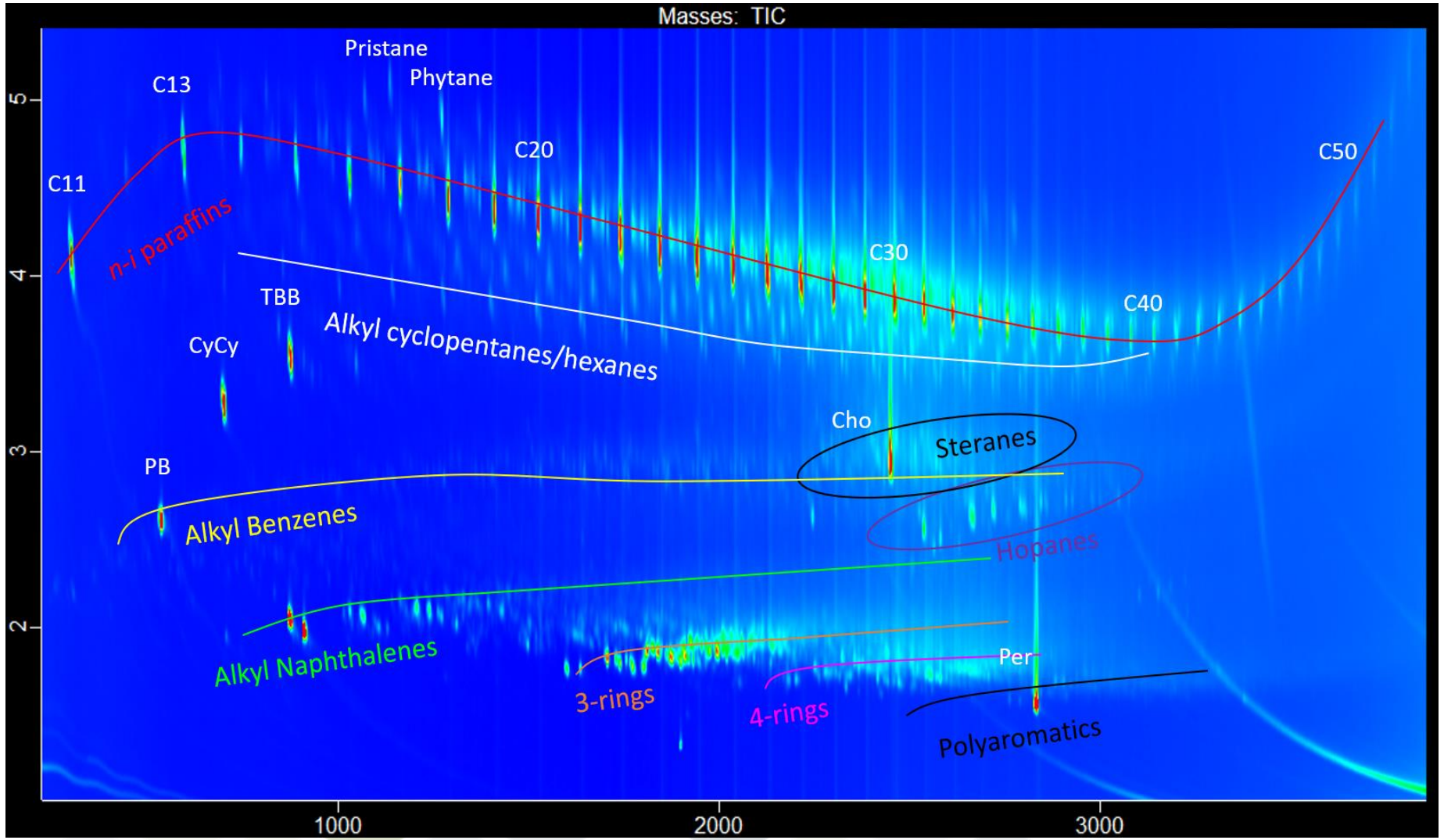
Scientific Opinion on Mineral Oil Hydrocarbons in Food[1]

EFSA Panel on Contaminants in the Food Chain (CONTAM)[2, 3]

Currently, the most efficient methods for analysis of MOSH and MOAH in food and feed comprise extraction followed by pre-separation by **high performance liquid chromatography (HPLC) on-line coupled to GC with flame ionisation detection (FID)**. Detection limits depend on the mass distribution, the sample matrix and any prior enrichment, and can be as low as 0.1 mg/kg. **Comprehensive GCxGC-FID** enables a rough separation and quantification of paraffins and naphthenes in the MOSH fraction, but it is of limited practicality for routine analysis. Contamination with polyolefin oligomeric saturated hydrocarbons (POSH), e.g. from plastic bags, heat sealable layers or adhesives, may interfere with MOSH analysis. Analytical capacity to distinguish the different MOAH subclasses in food is limited. For this purpose, **GCxGC appears to be the most effective method**. Due to the complexity and the variable composition of MOH mixtures, it is not possible to define certified standards of general applicability.

Exemple : MOSH/MOAH

The advantages of GCxGC-TOF-MS

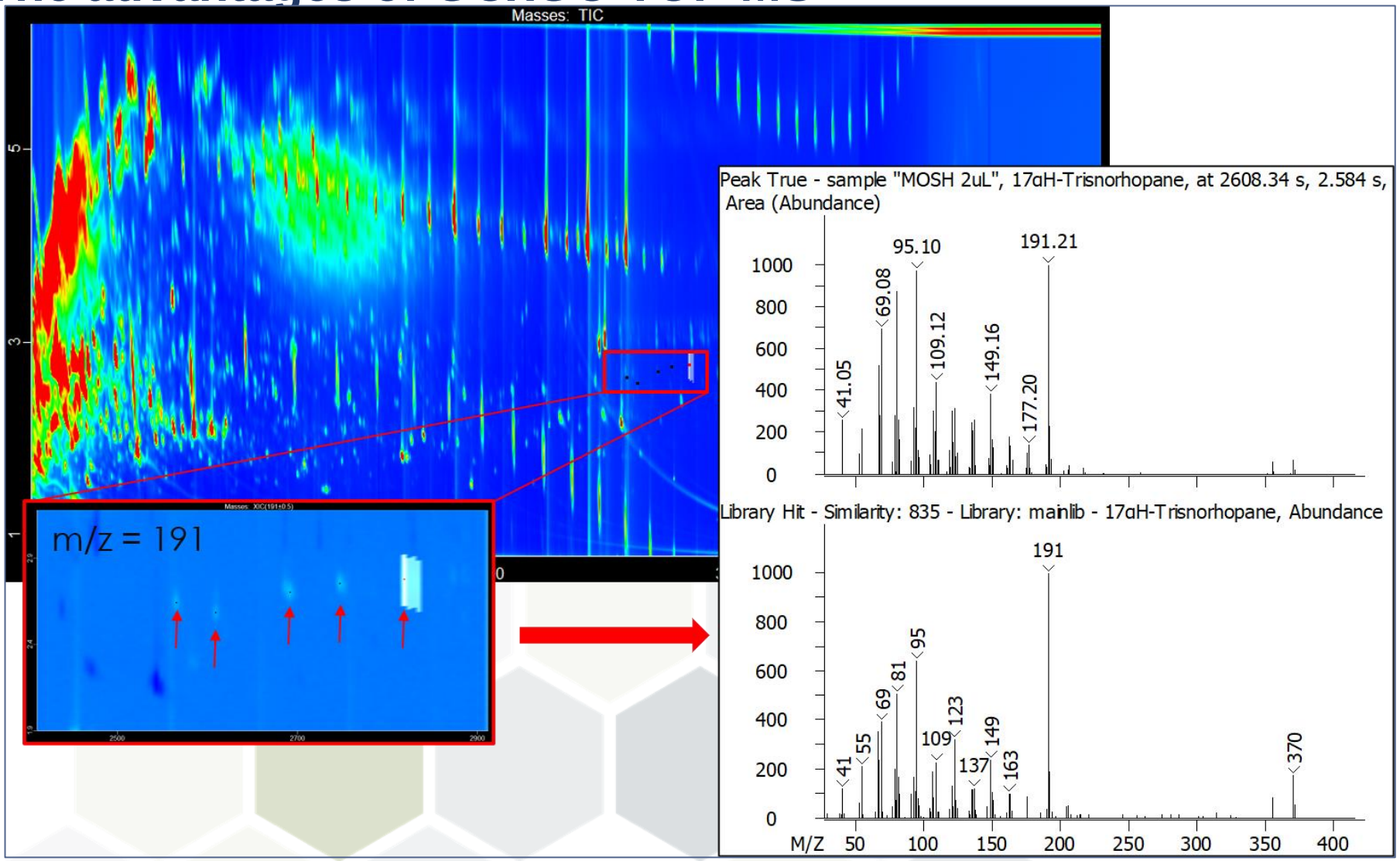


Huge Increase in Confirmation Confidence

- Multidimensional separation of different classifications from MOSH & MOAH
- Confirm presence of matrix interferences with confidence
- Tackle a greater variety of complex matrices (e.g. spices, milk formulas etc)
- Identify markers to confirm MOH (Hopanes)
- Ability to analyse upto C50

Exemple : MOSH/MOAH

The advantages of GCxGC-TOF-MS

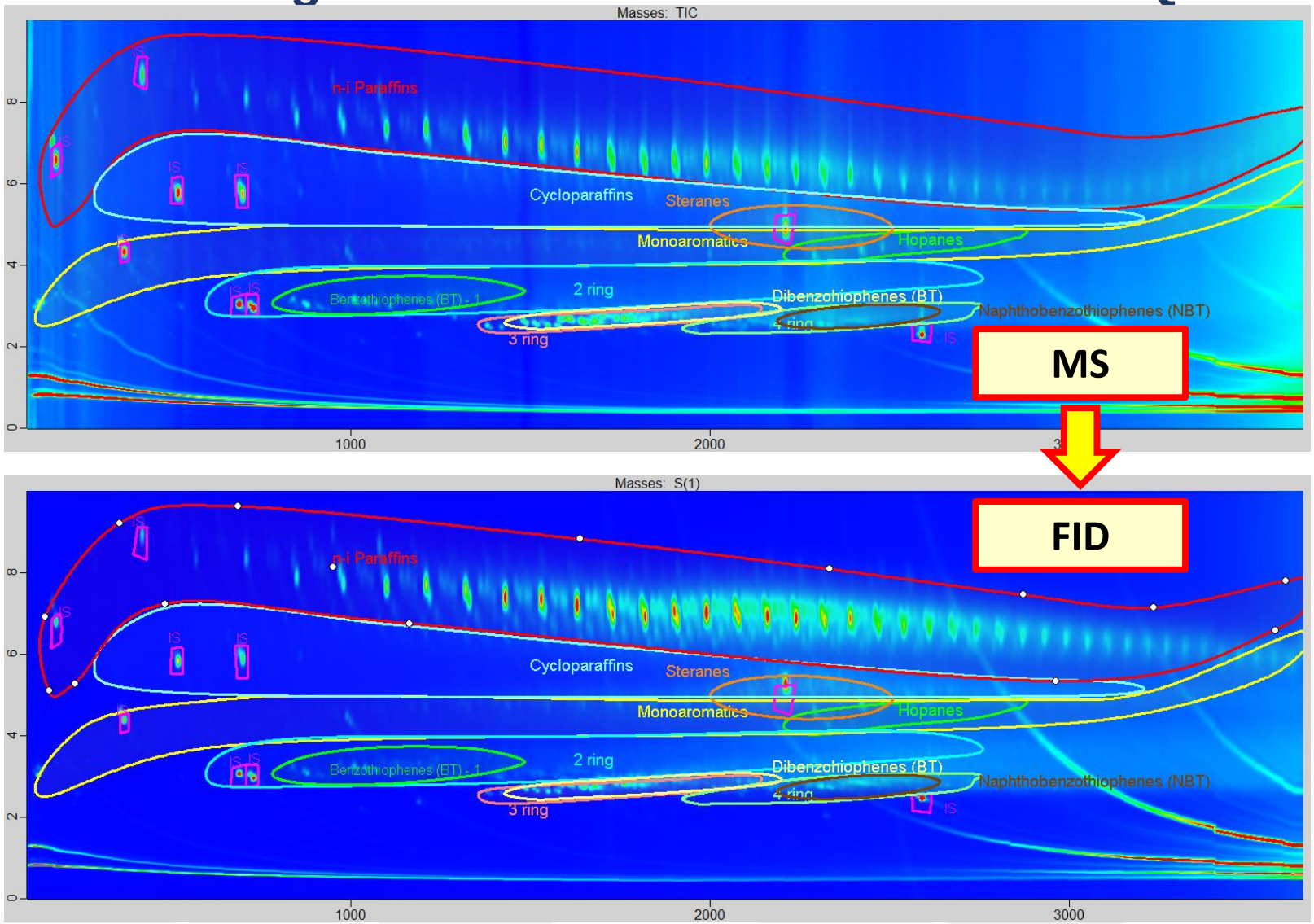


MOSH Fraction Example - Hopanes

- Hopanes considered as “proof,” of mineral oil contamination
- Hugely difficult to separate
- Often present at low levels
- Combination of GCxGC separation and the BT TOF-MS sensitivity allows hopanes to be identified with confidence

Exemple : MOSH/MOAH

The advantages of GCxGC-TOF-MS – Plus FID Quant



Translation of GCxGC TOF plots to GCxGC-FID plots

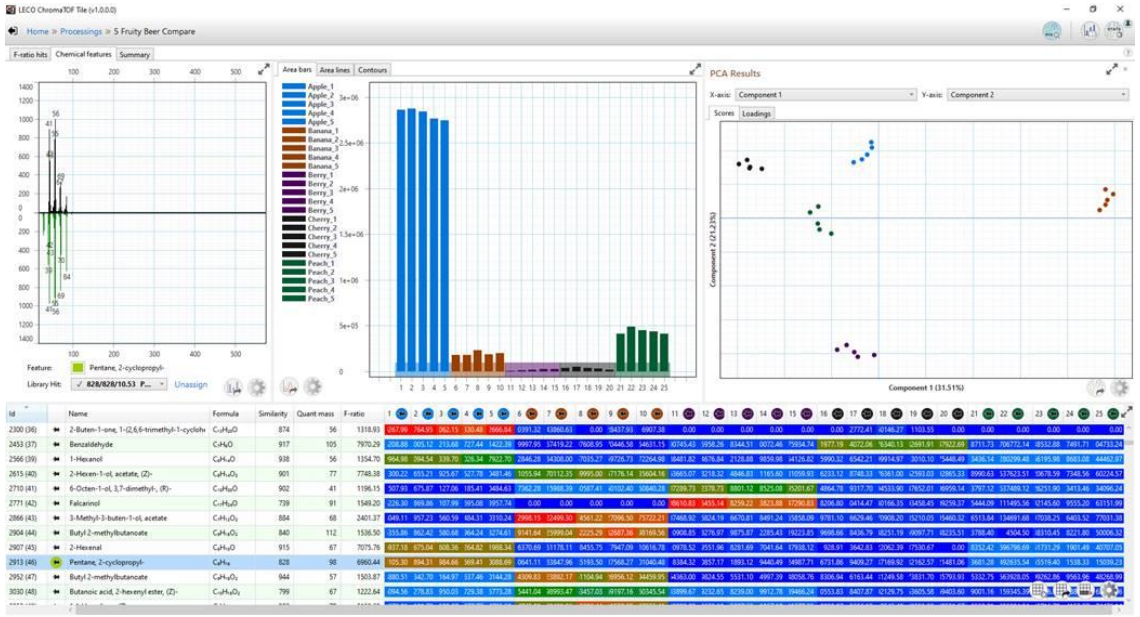
- The ability to correlate the TOF and FID plots, when similar GCxGC separation parameters are adjusted appropriately
- Allows classification groups to be quantified with FID with significantly higher accuracy/less error
- Challenge is to optimise differences in sensitivity of the two detectors and in turn the impact of injection mode & type (LC direct or inlet vs volume of injection
- Development stage – but could be the ideal future outcome!

Autres innovations

Comparaison statistique d'échantillons

Tile

- Etude process
- Etude vieillissement
- Origine géographique
- Contrôle production



Multi-mode source

1 sources → 3 modes d'ionisation (EI / PCI /NCI)

Acquisition Queue

	Type	Name	Folder	Status	Vial	Repet	Chromatographic Method	MS Method	AS Method	DS
1	Sample	2D Fish Sample in EI Mode	Fish Extract Data		12	1	2D Pesticide Analysis 2sec Mod	2D Pest MMS EI 250C	Solvent A 1uL	
2	Sample	2D Fish Sample in PCI Mode	Fish Extract Data		12	1	2D Pesticide Analysis 2sec Mod	2D Pest MMS PCI 165C	Solvent A 1uL	
3	Sample	2D Fish Sample in NCI Mode	Fish Extract Data		12	1	2D Pesticide Analysis 2sec Mod	2D Pest MMS NCI 165C	Solvent A 1uL	
4	Sample	2D Fish Sample in PCI Mode	Fish Extract Data		12	1	2D Pesticide Analysis 2sec Mod	2D Pest MMS PCI 165C	Solvent A 1uL	
5	Sample	2D Fish Sample in NCI Mode	Fish Extract Data		12	1	2D Pesticide Analysis 2sec Mod	2D Pest MMS NCI 165C	Solvent A 1uL	
6*	Sample	2D Fish Sample in EI Mode	Fish Extract Data		12	1	2D Pesticide Analysis 2sec Mod	2D Pest MMS EI 250C	Solvent A 1uL	

Sur HRT

R : 50000
MA < 1 ppm
F : 200 Hz

MERCI!

Questions & Discussion!

Hubert LATAPPY
Hubert_latappy@leco.com
06 50 60 79 27

SIMPLY GCxGC

www.leco.com/simply-gcxgc

Outil de développement de méthode **SIMPLE** sur GCxGC :

- ➜ Passer de la GC à la GCxGC
- ➜ Optimiser les performances GCxGC