

L'utilisation du gaz vecteur Hydrogène en GCMS : application aux Arômes/Huiles Essentielles



24 Novembre 2023

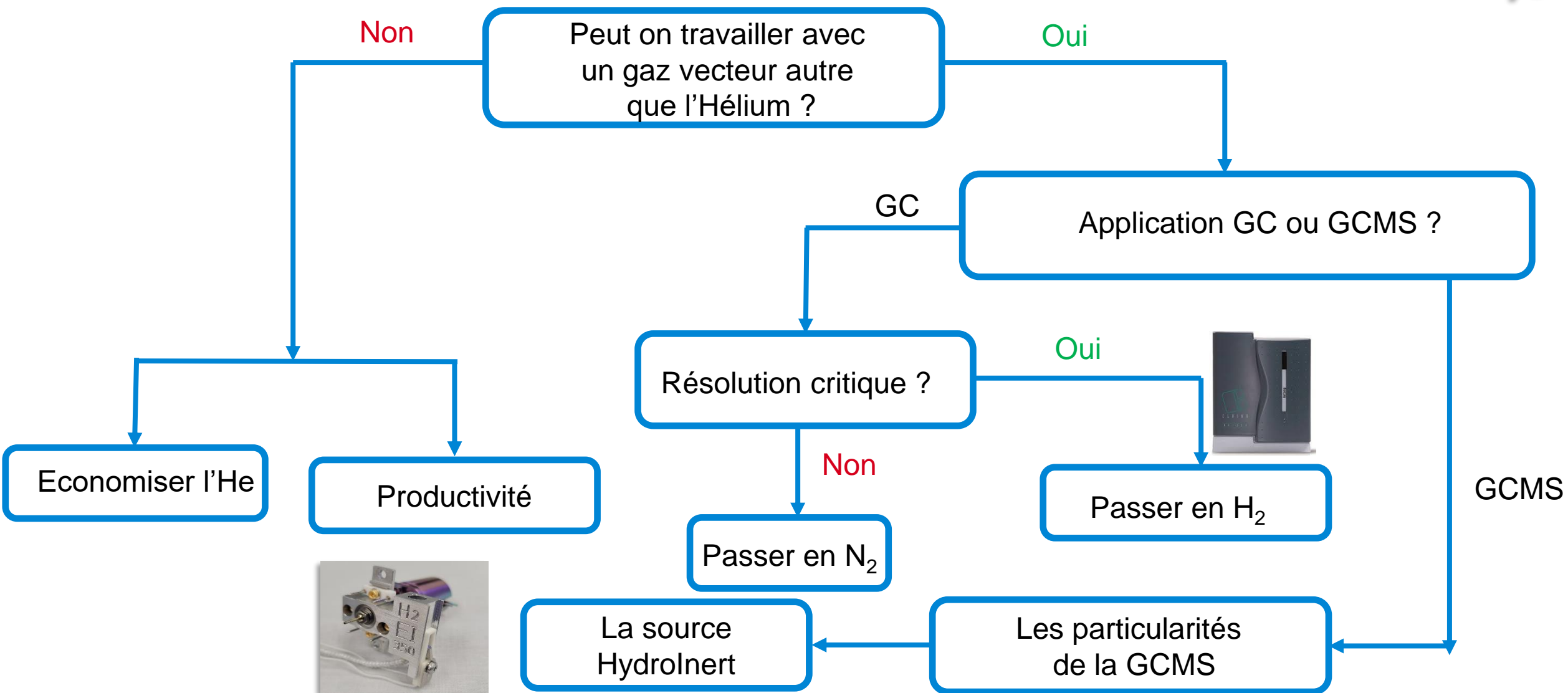
S. Decouflet
GC/MS Product specialist



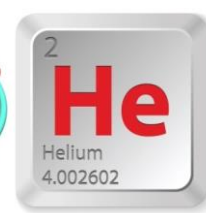
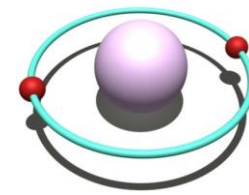
Choix du gaz vecteur : L'arbre de décision



https://explore.agilent.com/helium_shortage-ty



H2 versus He



Pourquoi des problèmes ?

- L'Hélium est une ressource minière finie
- Produit annexe des sources d'extraction de gaz
- Stock faibles et approvisionnement en baisse

Qu'est ce que cela implique ?

- Approvisionnement interrompu
- Coût en forte hausse
- L'Impact
 - Industrie de l'électronique
 - Tests médicaux
 - Recherche scientifique
 - GC & GCMS



H2 versus He



Helium

- Utilisé dans plus de 90 % des systèmes GC/MS
- Méthodes validées (temps de rétention, bibliothèques) : NIST
- Sensibilité suffisante pour répondre aux réglementations
- Augmentation des prix
- Difficultés d'approvisionnement

Hydrogen

- Utilisé avec succès dans l'analyse GC depuis des décennies
- Peut fournir une meilleure résolution chromatographique à une vitesse linéaire plus élevée
- Nécessite l'adaptation de la configuration et de la méthode de la chromatographie en phase gazeuse



Les Risques & objectifs : Maintenir la fidélité spectrale en gaz vecteur Hydrogène



- Eviter les perturbations dues aux pénuries d'Hélium
- Obtenir une **bonne fidélité spectrale** et éviter les réactions indésirables liés à l'Hydrogène dans la source
- **Tirez pleinement parti de l'hydrogène** en tant que gaz vecteur, notamment en réduisant les temps d'analyse, en améliorant la chromatographie et en bénéficiant d'une plus grande robustesse de la source
- **Travaillez en toute sécurité** grâce à l'utilisation d'un générateur d'hydrogène pour une sûreté maximale.
- **Pièces d'origine inchangées** et procédure d'assemblage déjà connue

Electron Ionization MS Sources

Conventional EI Extractor
(Inert Plus) Source

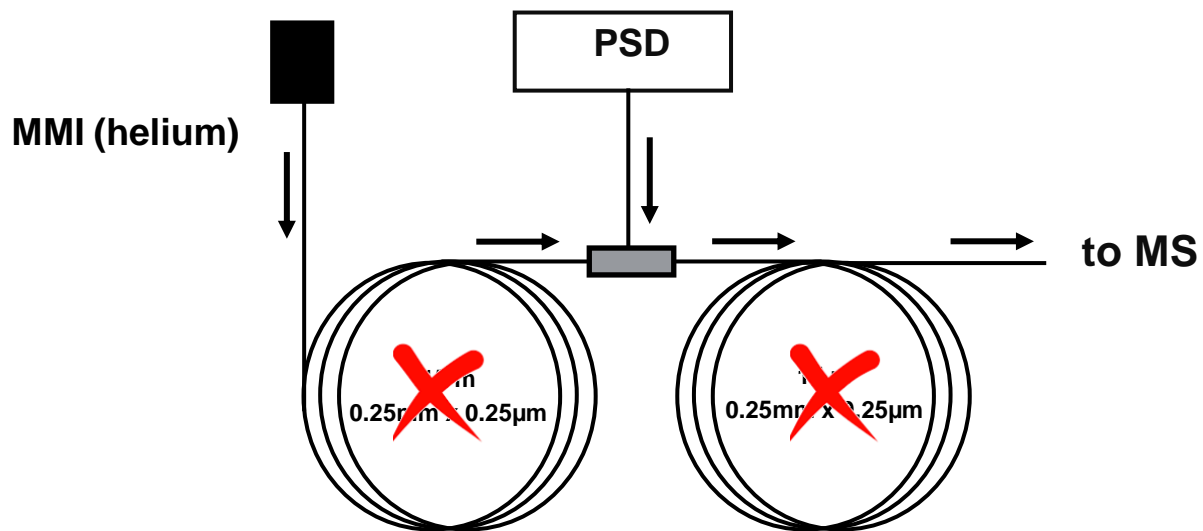
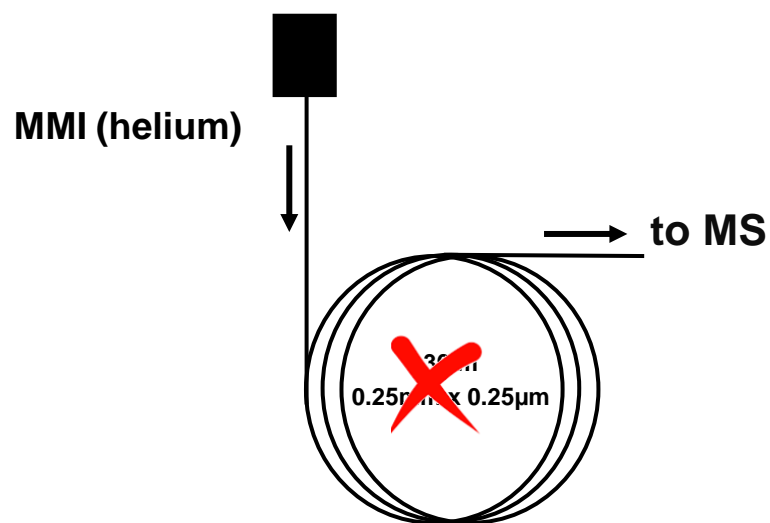
HydroInert
EI Source



GC Configuration and Method Considerations

~~Conventional 15m x 15m (or 30m)
0.25mm x 0.25 μ m~~

~~Cannot be used with H₂ carrier gas
because of insufficient inlet pressure~~

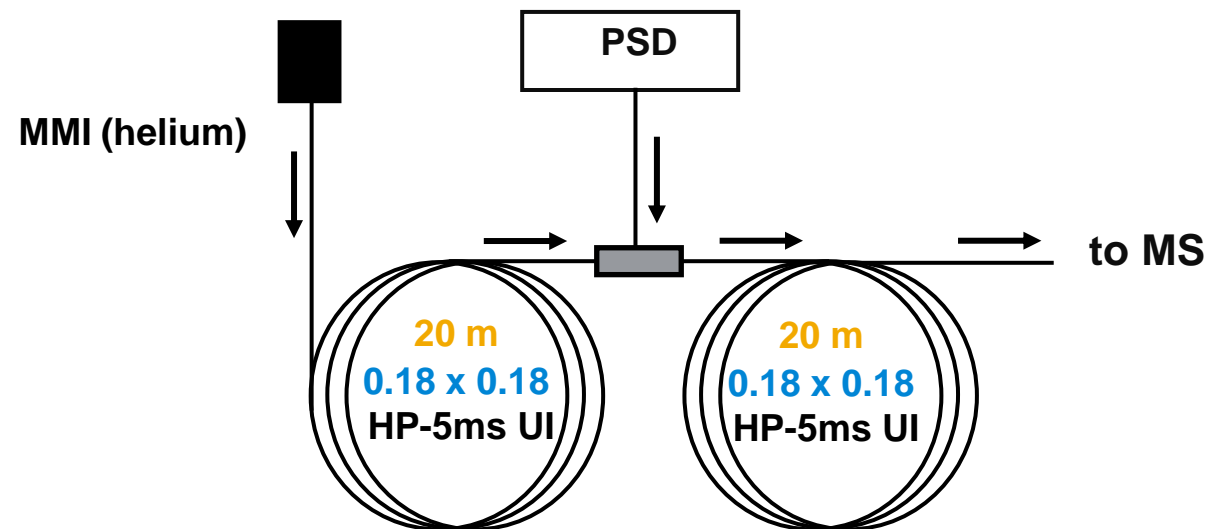


GC Configuration and Method Considerations

20x20m
0.18mm x 0.18 μ m

Compatible with H₂ carrier gas
Analysis time **20 min**

Exact matching of the RTs – 20-min analysis
with He using a 30m (or 15m x 15m) column



GC Configuration and Method Considerations

20x20m
0.18mm x 0.18 μ m

Compatible with H₂ carrier gas

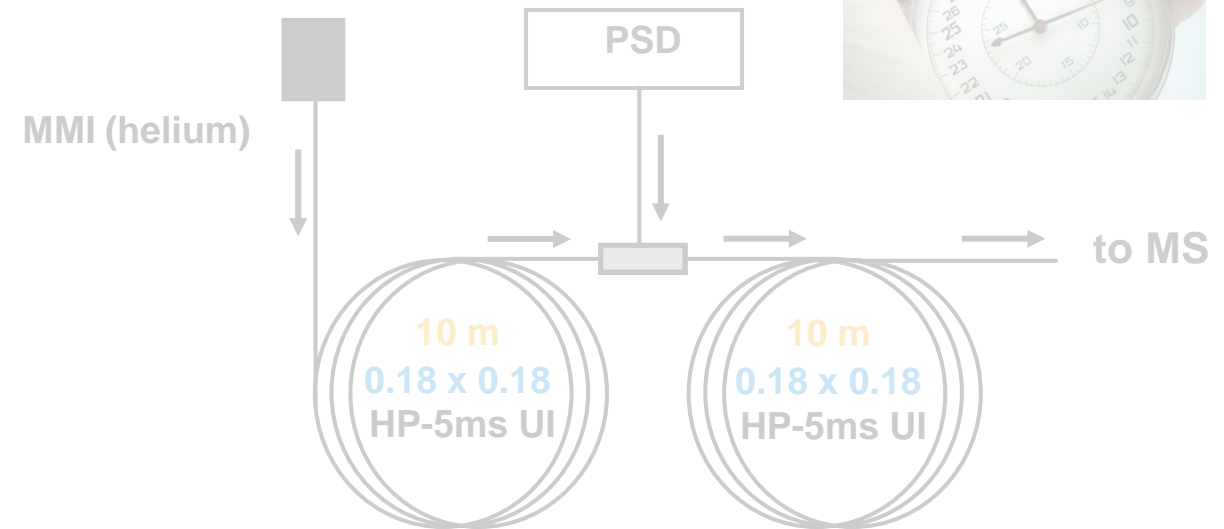
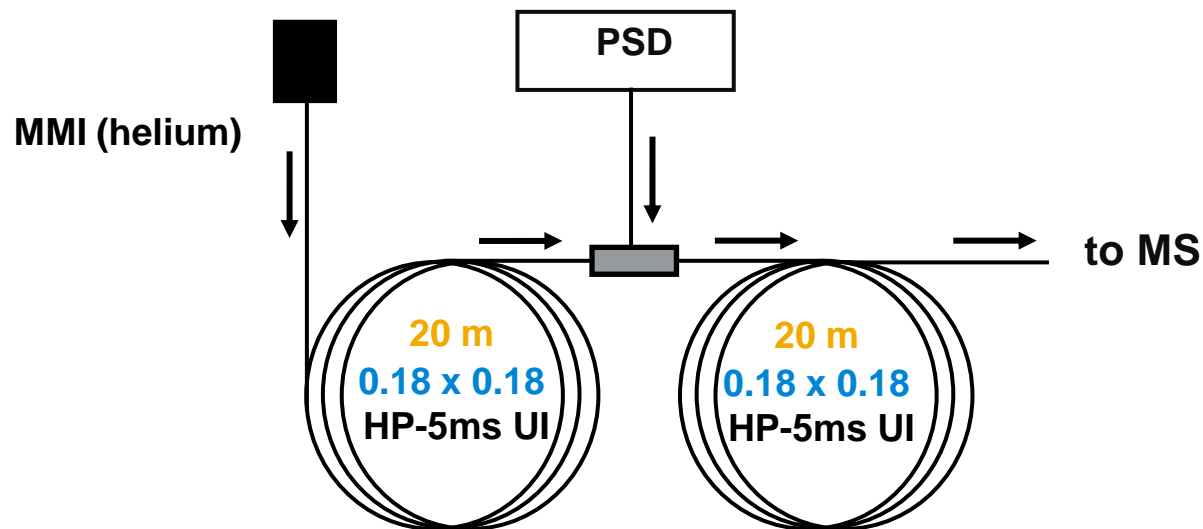
Analysis time **20 min**

10x10m
0.18mm x 0.18 μ m

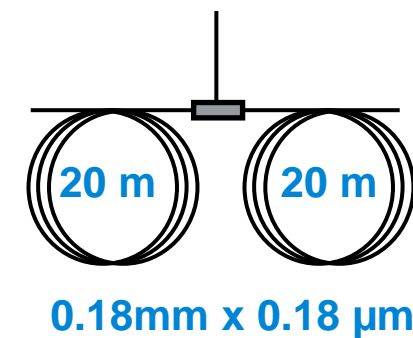
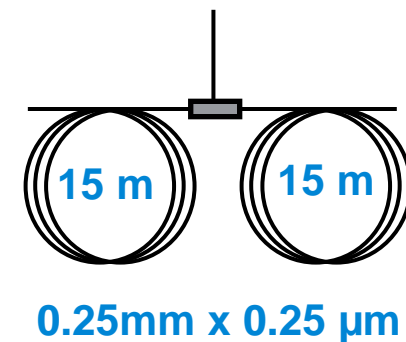
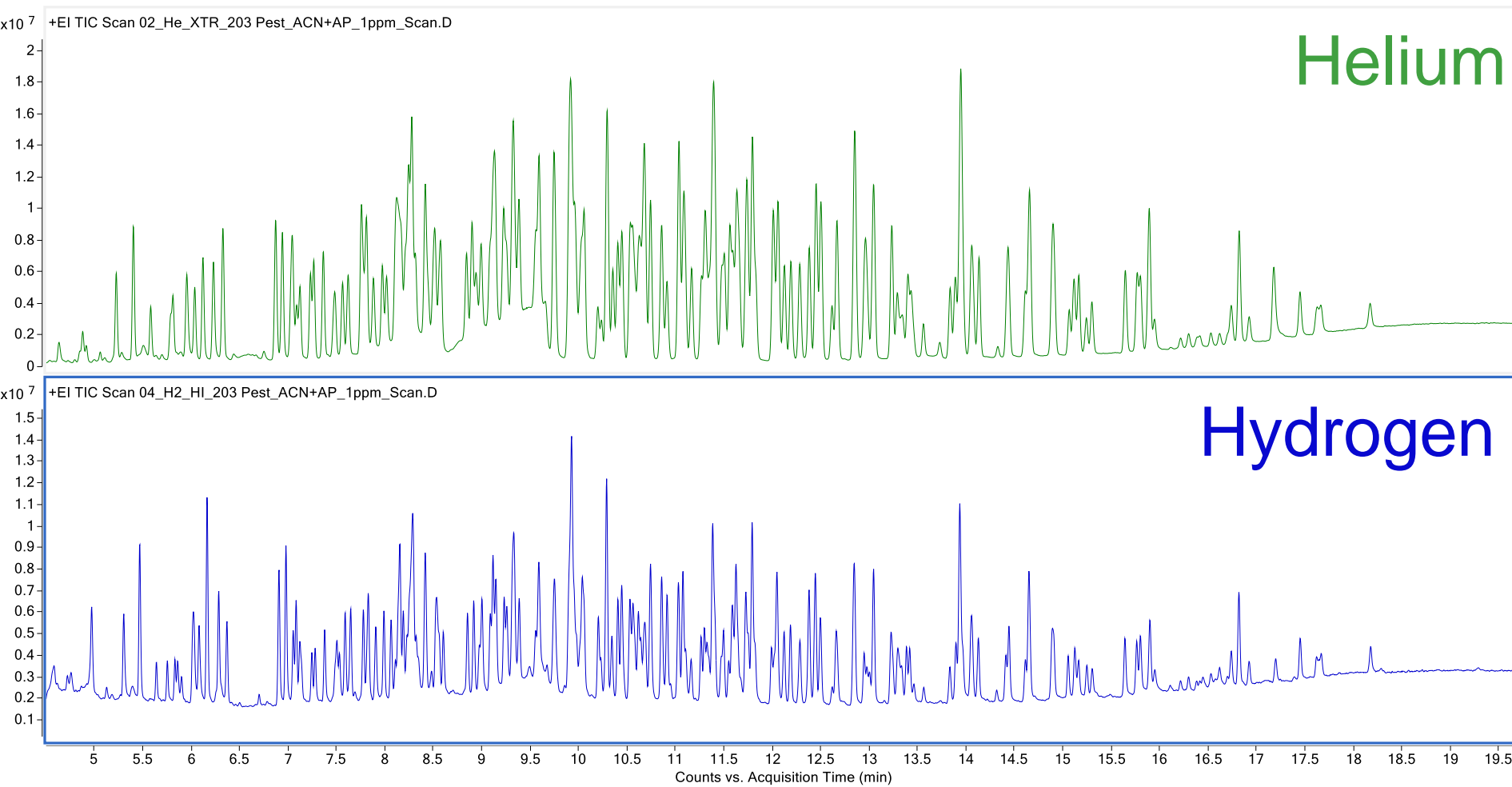
Compatible with H₂ carrier gas

Analysis time **10 min**

Exact matching of the RTs – 20-min analysis with He using a 30m (or 15m x 15m) column

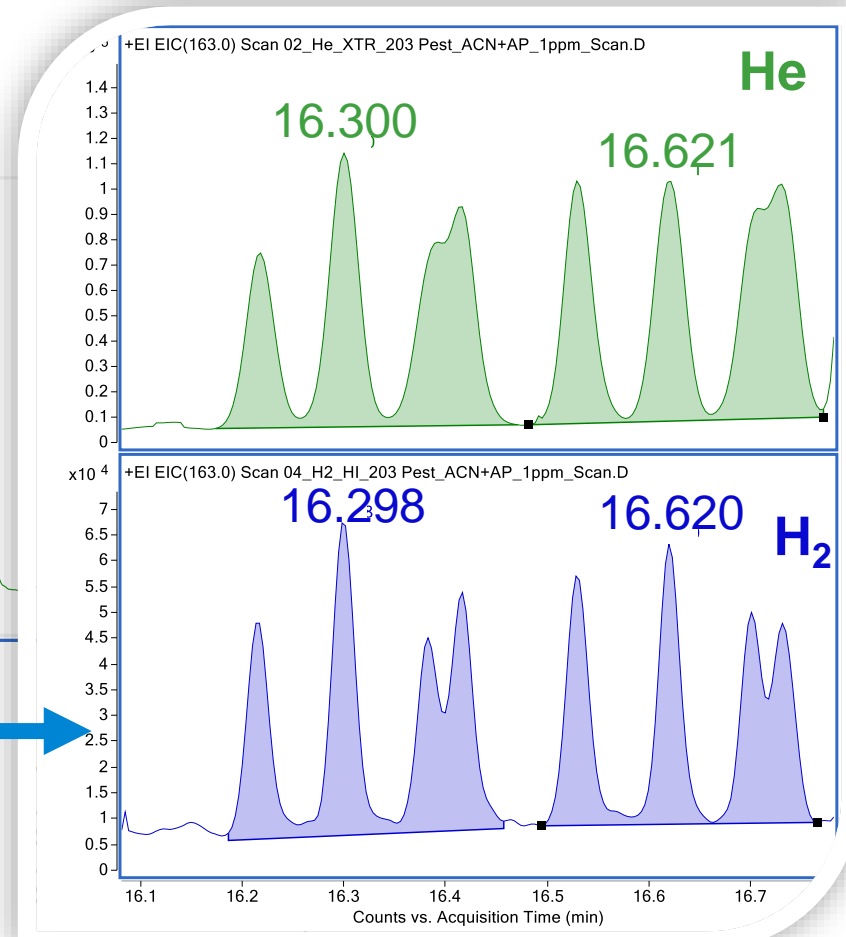
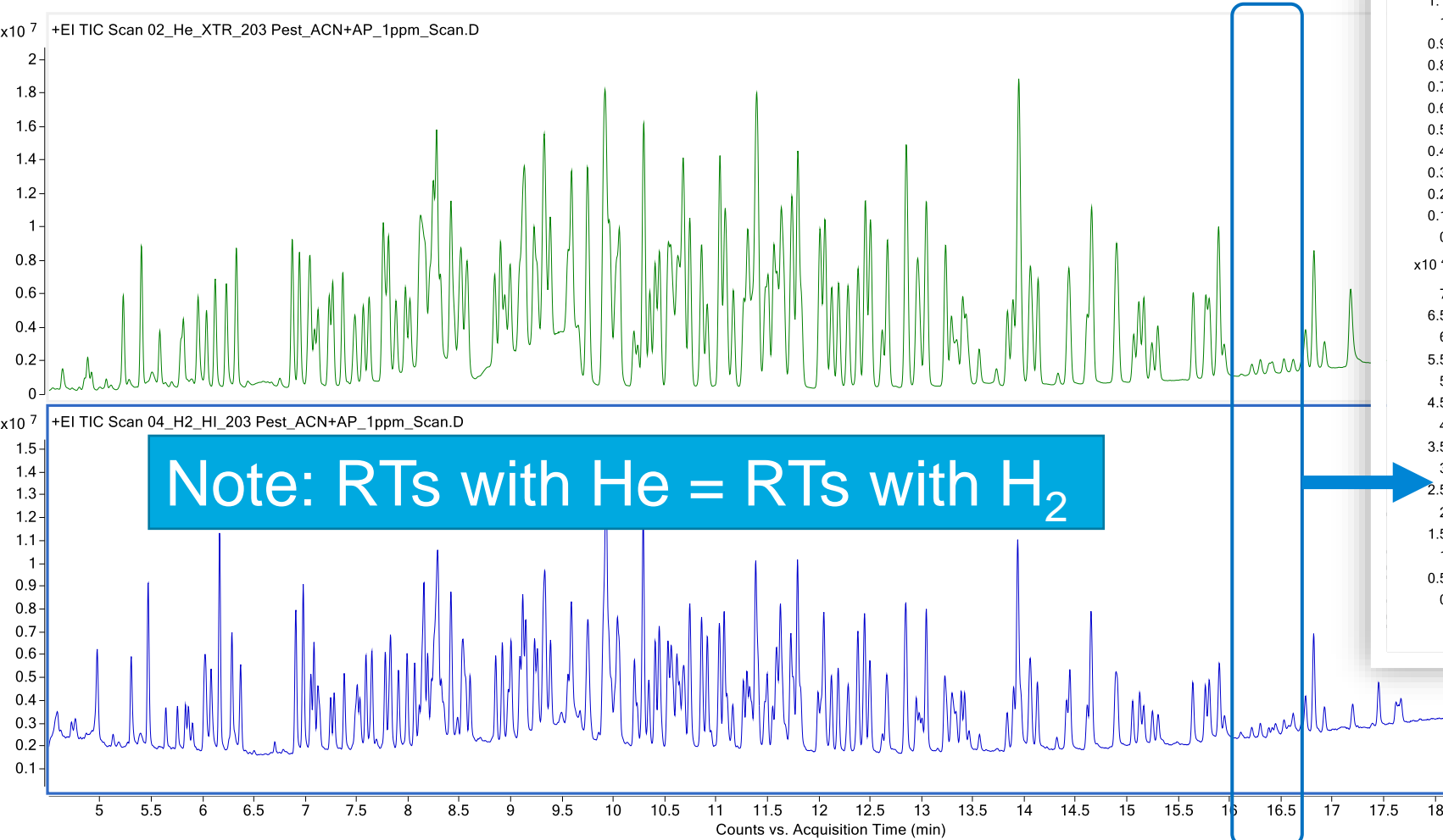


Exact Retention Time Matching Achieved with Method Translation and Retention Time Locking



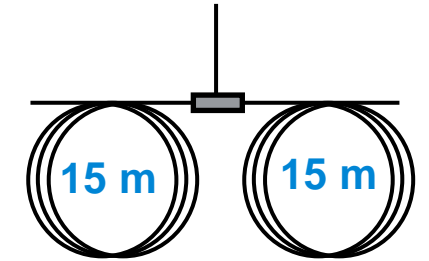
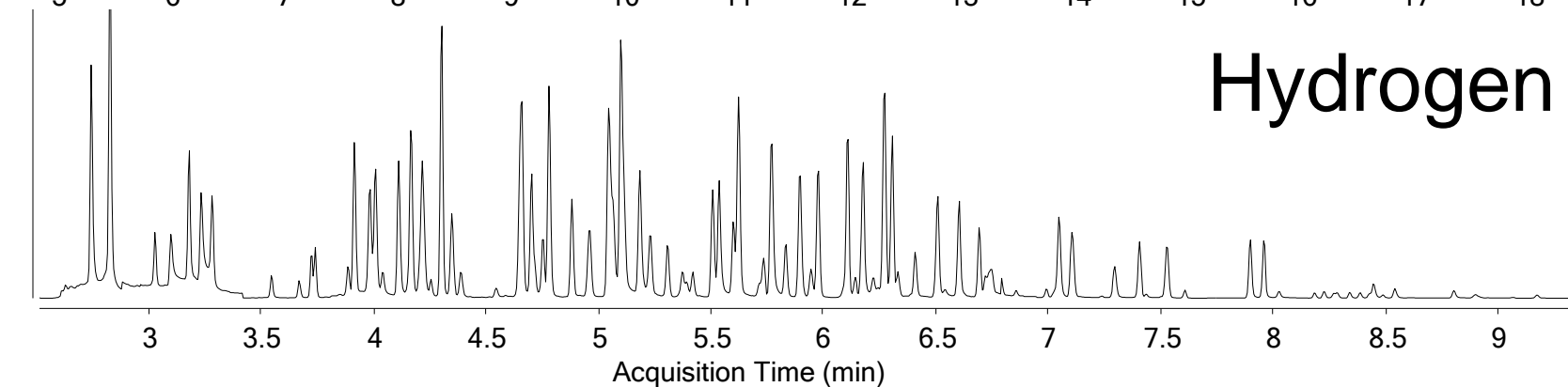
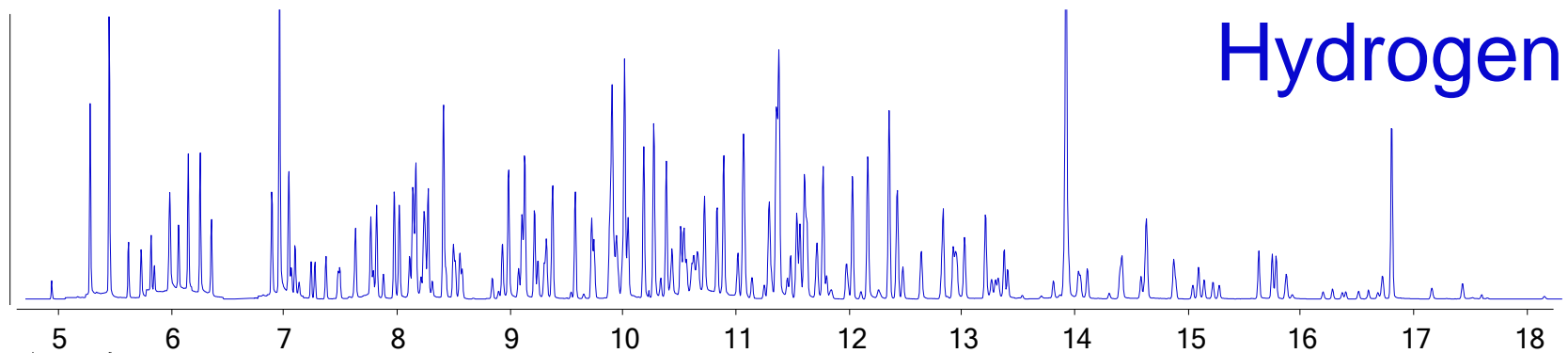
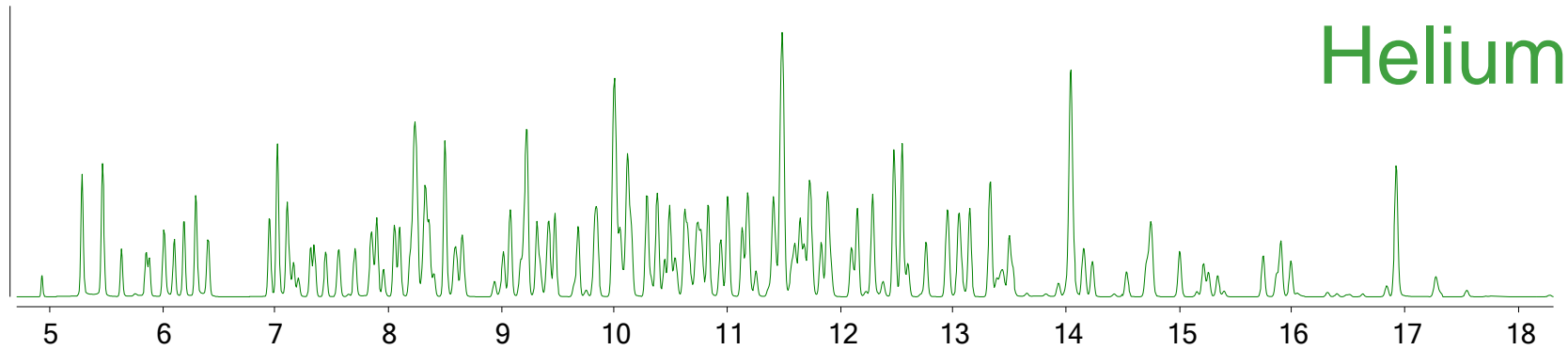
Superior Resolution with Hydrogen

EIC 163

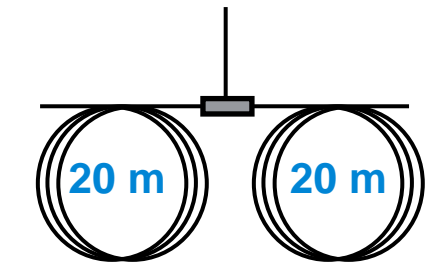


Cyfluthrins Cypermethrins

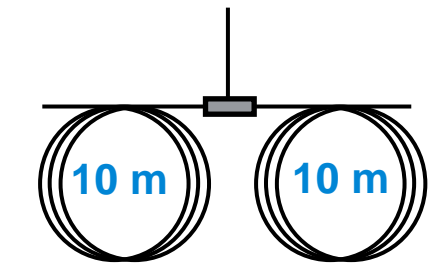
Proof-of-Concept: 10-Minute with Hydrogen



0.25mm x 0.25 μ m

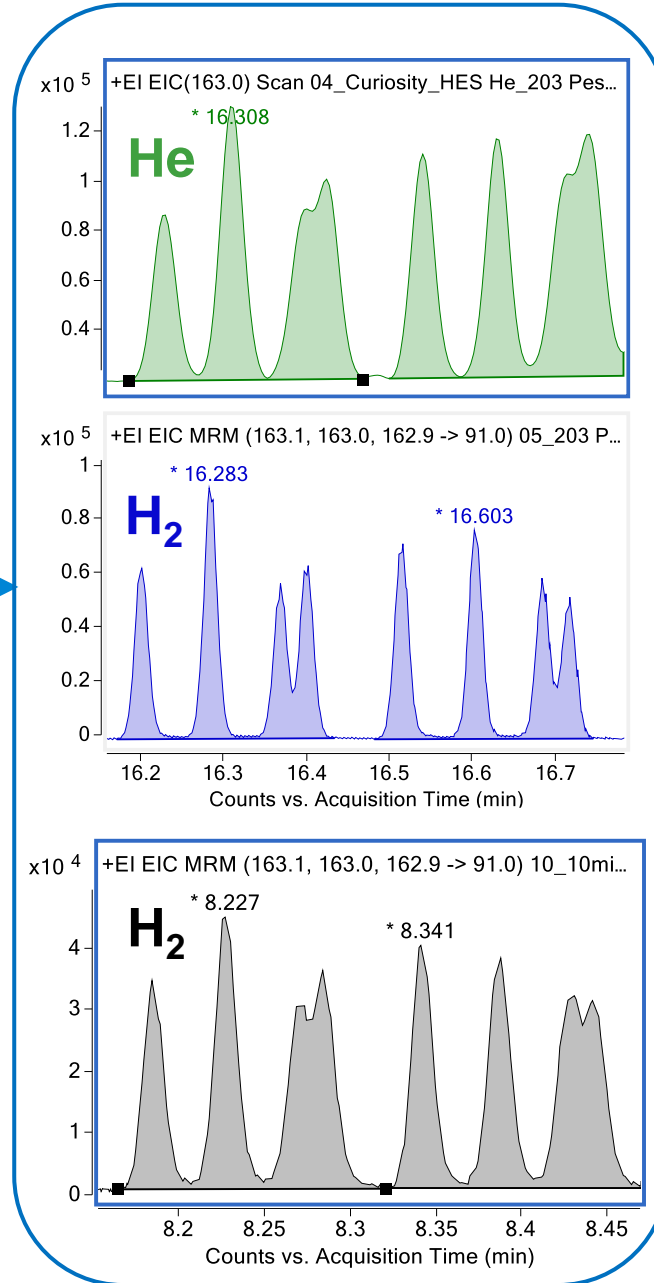
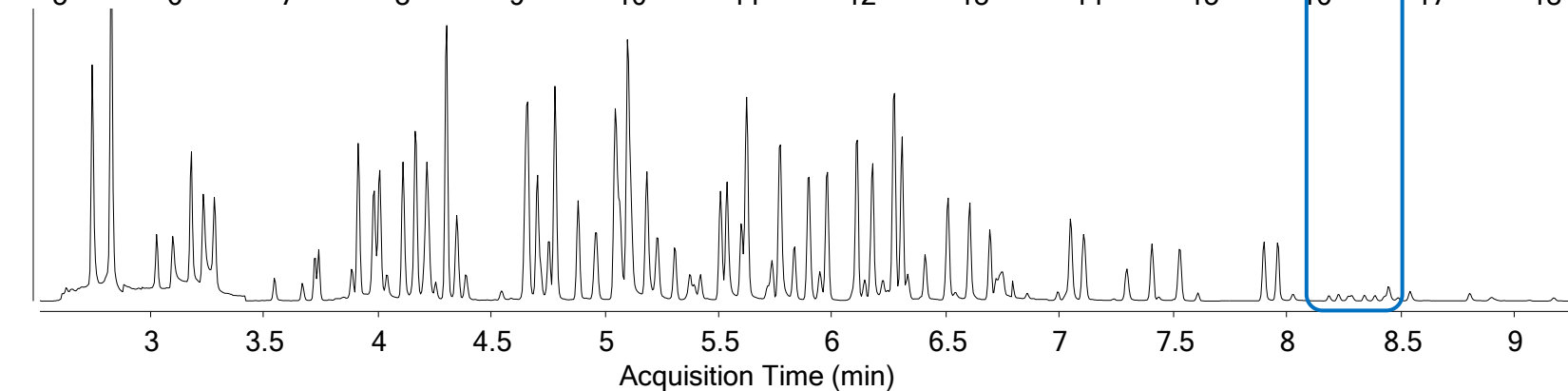
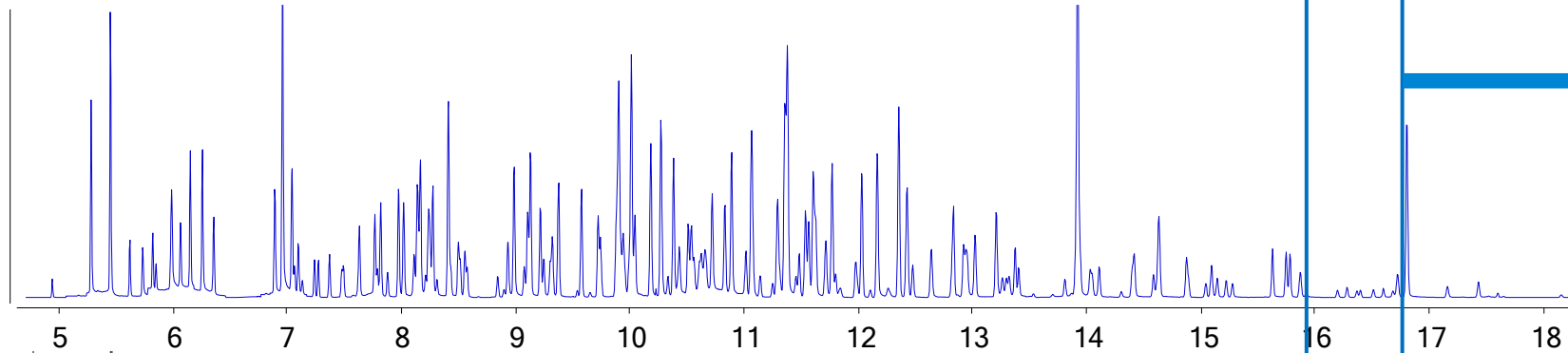
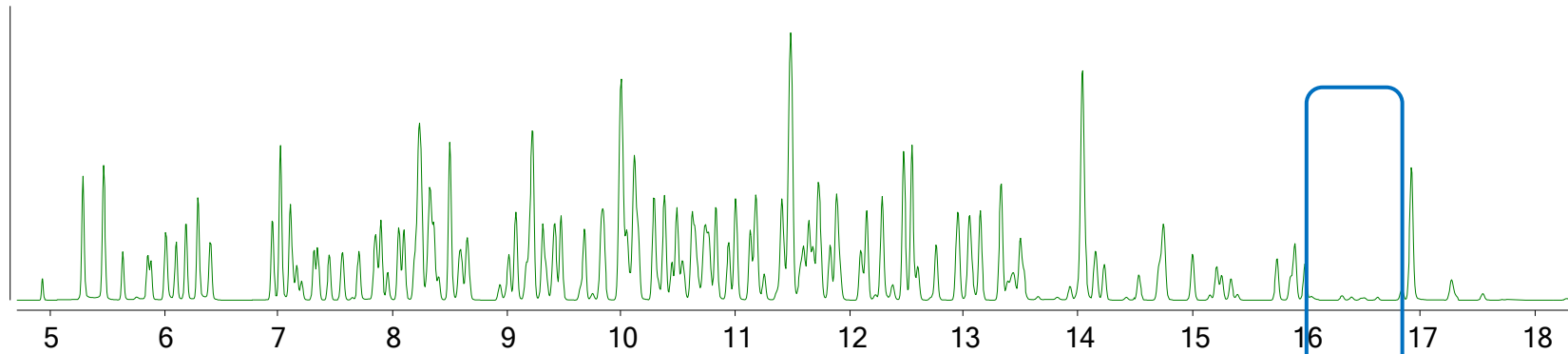


0.18mm x 0.18 μ m

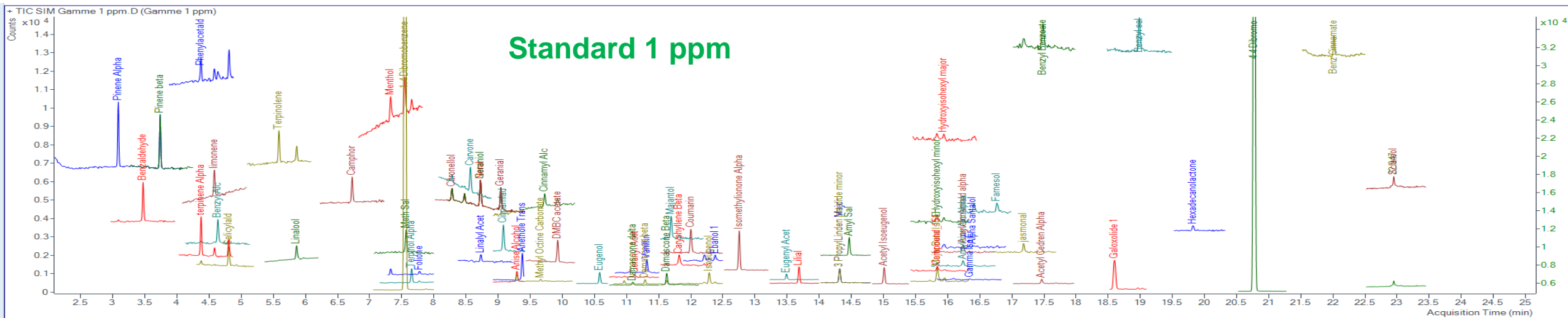
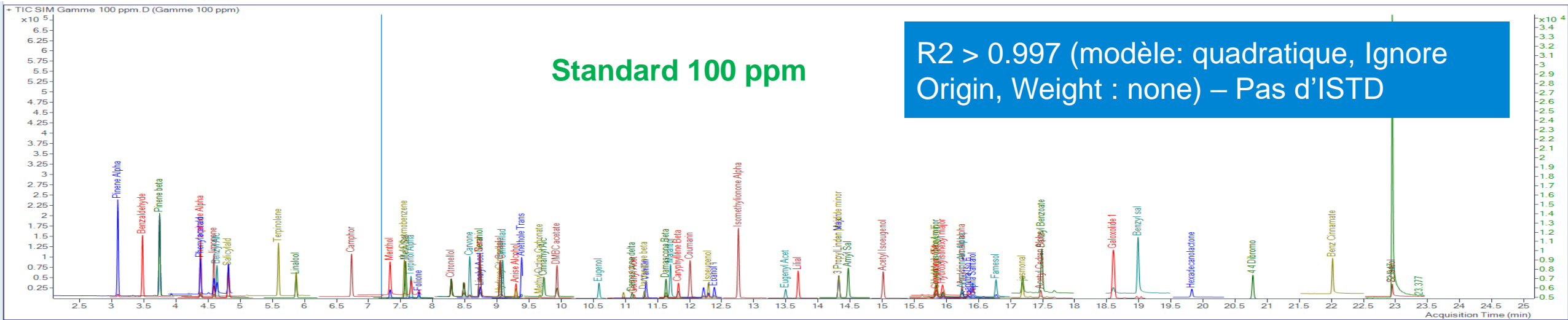


0.18mm x 0.18 μ m

10-Minute with Hydrogen and Still Good Resolution

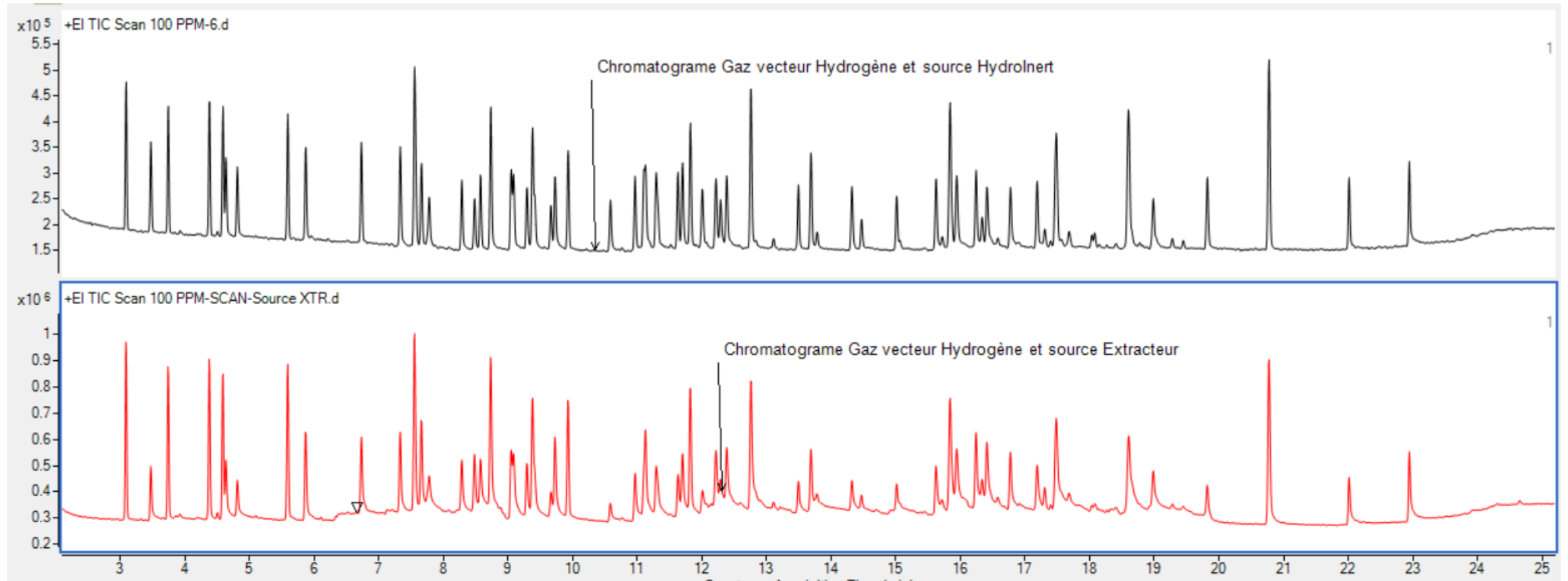


Méthode d'analyse : Profil chromatographique & Linéarité de la gamme



Analyse de composés inconnus

Comparaison des chromatogrammes obtenus



On observe un chromatogramme dégradé avec la source Extracteur et notamment de plus grandes trainées des pics par rapport au système en source HydroInert

Analyse de composés inconnus

Fenêtre de résultats Unknown Analysis

The screenshot displays the Unknown Analysis software interface. At the top, there is a menu bar with options: File, Home, View, Chromatogram, Tools, and Help. Below the menu is a toolbar with icons for Preset Layouts, Load/Save Layout, Print, Page Setup, Print Preview, Copy, and Clipboard. The main window is divided into several sections:

- Samples:** A table showing sample information.

Sample Name	File Name	Components	Hits
	100 PPM-6.D	708	65
- Chromatogram:** A Total Ion Chromatogram (TIC) plot showing detector response over time. The x-axis is labeled 'Acquisition Time (min)' and ranges from 3,000 to 22,000. The y-axis is labeled 'Counts x10^5' and ranges from 0 to 3.25. Numerous peaks are visible, each labeled with a chemical name such as Pinene <alpha>, Benzaldehyde, Terpinene <alpha>, Limonene, Salicylaldehyde, Terpinolene, Linalool, Camphor, Menthol, Citronellol, and many others.
- Components:** A table listing identified components with their retention times, names, match factors, and best hit status.

Component RT	Compound Name	Match Factor	Best Hit
3.0878	Pinene <alp...	96.3	<input checked="" type="checkbox"/>
3.4709	Benzaldehy...	97.3	<input checked="" type="checkbox"/>
3.7394	Pinene <bet...	96.0	<input checked="" type="checkbox"/>
4.3758	Terpinene <...	96.2	<input checked="" type="checkbox"/>
4.5031	Cymene <p...	71.3	<input checked="" type="checkbox"/>
4.5857	Limonene	95.4	<input checked="" type="checkbox"/>
4.6319	Benzyl alco...	96.0	<input checked="" type="checkbox"/>
4.8117	Salicylaldeh...	80.2	<input checked="" type="checkbox"/>
5.5900	Terpinolene	96.8	<input checked="" type="checkbox"/>
5.8668	Linalool	93.6	<input checked="" type="checkbox"/>
6.7286	Camphor	96.9	<input checked="" type="checkbox"/>
7.3299	Menthol	95.3	<input checked="" type="checkbox"/>
7.5531	Benzene, 1,...	98.2	<input checked="" type="checkbox"/>
7.5715	Salicylate <...	92.4	<input checked="" type="checkbox"/>
7.6569	Terpineol <...	95.6	<input checked="" type="checkbox"/>
7.7775	Oct-2-ynoat...	89.7	<input checked="" type="checkbox"/>
8.2830	Citronellol	92.7	<input checked="" type="checkbox"/>
- Major Ions:** A zoomed-in chromatogram showing three major peaks at retention times 3.06, 3.08, and 3.12 minutes. The peaks are color-coded and labeled with their component names: 93.0 (blue), 91.0 (green), and 92.0 (red).
- Molecular Structure:** A chemical structure diagram of Pinene <alpha>, showing a bicyclic ring system with two methyl groups (CH3) attached.
- Mass Spectra:** Two mass spectra are shown. The top one is the 'Spectrum' for component RT: 3.0878, showing relative intensity versus mass-to-charge ratio (m/z) from 30 to 140. The base peak is at m/z 93.0. The bottom one is the 'Spectre librairie' (reference spectrum) for Pinene <alpha> (FFNSC3.L), which closely matches the experimental spectrum.

Composés identifiés

Ions majoritaires

Spectre déconvolué

Spectre librairie

Résultats de la recherche en librairie

Structure

Analyse de composés inconnus : Gaz Vecteur H2

	Component RT	Compound Name	CAS#	Match Factor en Source HI	Match Factor en Source Ext	Δ Match Factor
1	3.088	Pinene <alpha->	80-56-8	96.3	96.2	-0.1
2	3.471	Benzaldehyde	100-52-7	97.3	95.2	-2.1
3	3.739	Pinene <beta->	127-91-3	96.0	96.7	0.7
4	4.376	Terpinene <alpha->	99-86-5	96.2	86.8	-9.4
5	4.503	Cymene <para->	99-87-6	71.3	75.5	4.2
6	4.586	Limonene	138-86-3	95.4	92.8	-2.6
7	4.632	Benzyl alcohol	100-51-6	96.0	85.7	-10.3
8	4.812	Salicylaldehyde	90-02-8	80.2	Phenylacetaldehyde 61.8	Phenylacetaldehyde 61.9
9	5.590	Terpinolene	586-62-9	96.8	90.9	-5.9
10	5.867	Linalool	78-70-6	93.6	Linalyl acetate 86.4	Linalyl acetate 86.5
11	6.729	Camphor	76-22-2	96.9	93.8	-3.1
12	7.330	Menthol	1490-04-6	95.3	94.2	-1.1
13	7.553	Benzene, 1,4-dibromo-	106-37-6	98.2	94.5	-3.7
14	7.571	Salicylate <methyl->	119-36-8	92.4	90.2	-2.2
15	7.657	Terpineol <alpha->	98-55-5	95.6	91.5	-4.1
16	7.778	Oct-2-ynoate <methyl->	111-12-6	89.7	79.5	-10.2
17	8.283	Citronellol	106-22-9	92.7	93.6	0.9
18	8.480	Neral	106-26-3	86.1	Carveol 86.9	Carveol 86.10
19	8.572	Carvone	99-49-0	94.7	89.3	-5.4
20	8.729	Linalyl acetate	115-95-7	91.4	86.7	-4.7
21	9.046	Geranial	141-27-5	88.1	82.4	-5.7
22	9.084	Cinnamaldehyde <(E)->	14371-10-9	93.9	91	-2.9
23	9.291	Anisyl alcohol <para->	105-13-5	94.3	54.8	-39.5
24	9.378	Anethole <(E)->	4180-23-8	96.5	89.4	-7.1
25	9.412	Citronellal <hydroxy->	107-75-5	85.2	Citronellyl Butirate 74.7	Citronellyl Butirate 74.8
26	9.661	Non-2-ynoate <methyl->	111-80-8	92.0	Undecyne 74.5	Undecyne 74.6
27	9.726	Cinnamyl alcohol <(E)->	4407-36-7	90.8	Cinnamyl Formate 71.9	Cinnamyl Formate 71.10
28	9.929	1-ethanol, .alpha.,.alpha.-dimethyl-,	151-05-3	97.3	93.3	-4.0
29	10.583	Eugenol	97-53-0	95.4	87.3	-8.1
30	10.963	Damascone <delta->	57378-68-4	93.6	86.9	-6.7
31	11.100	Damascenone <(E)-, beta->	23726-93-4	77.6	86.9	9.3
32	11.126	1-anol, 1-methyl-4-(1-methylethenyl)-	10198-23-9	72.8	non identifié	non identifié

Analyse de composés inconnus : Gaz Vecteur H2

	Component RT	Compound Name	CAS#	Match Factor en Source HI	Match Factor en Source Ext	Δ Match Factor
33	11.288	Damascone <alpha-, trans->	24720-09-0	91.3	86.7	-4.6
34	11.318	Vanillin	121-33-5	50.0	56.7	6.7
35	11.628	Damascone <(E)-beta->	23726-91-2	92.1	89.2	-2.9
36	11.698	Majantol	103694-68-4	90.9	62.7	-28.2
37	11.820	Caryophyllene <(Z)->	118-65-0	92.1	92	-0.1
38	12.004	Coumarin	91-64-5	94.2	89.5	-4.7
39	12.214	Ebanol	67801-20-1	93.0	82.4	-10.6
40	12.289	Isoeugenol <Z->	5912-86-7	93.8	91.6	-2.2
41	12.382	Ebanol	67801-20-1	92.0	82.4	-9.6
42	12.757	Ionone <alpha-, isomethyl->	127-51-5	89.8	78.3	-11.5
43	13.493	Eugenyl acetate	93-28-7	94.0	85.3	-8.7
44	13.688	Lilial	80-54-6	91.2	77.9	-13.3
45	13.782	Salicylate <amyl->	2050-08-0	89.6	83.9	-5.7
46	14.321	Phthalide <3-propylidene->	17369-59-4	94.8	89	-5.8
47	14.470	Salicylate <amyl->	2050-08-0	93.4	83.9	-9.5
48	15.013	Isoeugenyl acetate	93-29-8	95.4	90.3	-5.1
49	15.622	Cinnamaldehyde <amyl->	122-40-7	88.9	83.5	-5.4
50	15.841	Iso E Super <gamma->	68155-67-9	77.1	64	-13.1
51	15.940	Lyril	31906-04-4	78.9	Amberonne 81.8	Amberonne 81.9
52	16.241	Amyl cinnamyl alcohol <alpha->	184900-07-0	86.6	71.2	-15.4
53	16.335	Iso E Super <alpha->	68155-66-8	79.8	non reconnu	non reconnu
54	16.408	Farnesol <2Z,6E->	3790-71-4	83.3	80.2	-3.1
55	16.577	Amyl cinnamyl alcohol <alpha->	184900-07-0	56.8	71.2	14.4
56	16.772	Farnesol <2Z,6E->	3790-71-4	85.9	80.2	-5.7
57	17.185	Cinnamaldehyde <alpha-hexyl->	101-86-0	92.4	83.6	-8.8
58	17.466	Vertofix coeur	68039-35-0	77.8	67.6	-10.2
59	17.487	Benzyl benzoate	120-51-4	95.1	83.5	-11.6
60	18.600	Galaxolide	1222-05-5	89.8	88.5	-1.3
61	18.984	Benzyl salicylate	118-58-1	90.5	85.6	-4.9
62	19.820	Hexadecanolact-16-one	109-29-5	82.5	83.3	0.8
63	20.774	1,1'-Biphenyl, 4,4'-dibromo-	92-86-4	92.4	77.3	-15.1
64	22.014	Cinnamate <benzyl->	103-41-3	93.7	79.6	-14.1
65	22.946	Labd-(13E)-8,15-diol	10267-31-9	79.6	62	-17.6

Conclusions

- L'utilisation de l'hydrogène avec une source extracteur classique montre une dégradation du profil chromatographique et une déformation des spectres de masses pouvant poser problème pour une bonne identification des composés en bibliothèque
- Le système proposé GC 8890 – MSD 5977C avec **source Hydro inerte** permet d'atteindre les seuils requis de sensibilité pour la détection des allergènes.
- La linéarité du système est satisfaisante sur la gamme étudiée (1 à 500 ppm)
- Il n'a pas été démontré d'impact notable de l'utilisation de H₂ en gaz vecteur combiné à la source HydroInert sur les spectres :
 - Possibilité de faire des analyses non-ciblés et des recherches en bibliothèque sans crainte de mauvaise identification.



Analyse des Allergènes : Nouvelle Réglementation Européenne

Webinaire | 18 janvier 2024 | 10h00

