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## GC-APPI-HRMS developments for the analysis of volatile organic compounds

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# Comparison of 3 ionization methods - electron ionization, chemical ionization and atmospheric pressure photoionization - for the characterization of volatile organic compounds (VOCs)

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## Introduction



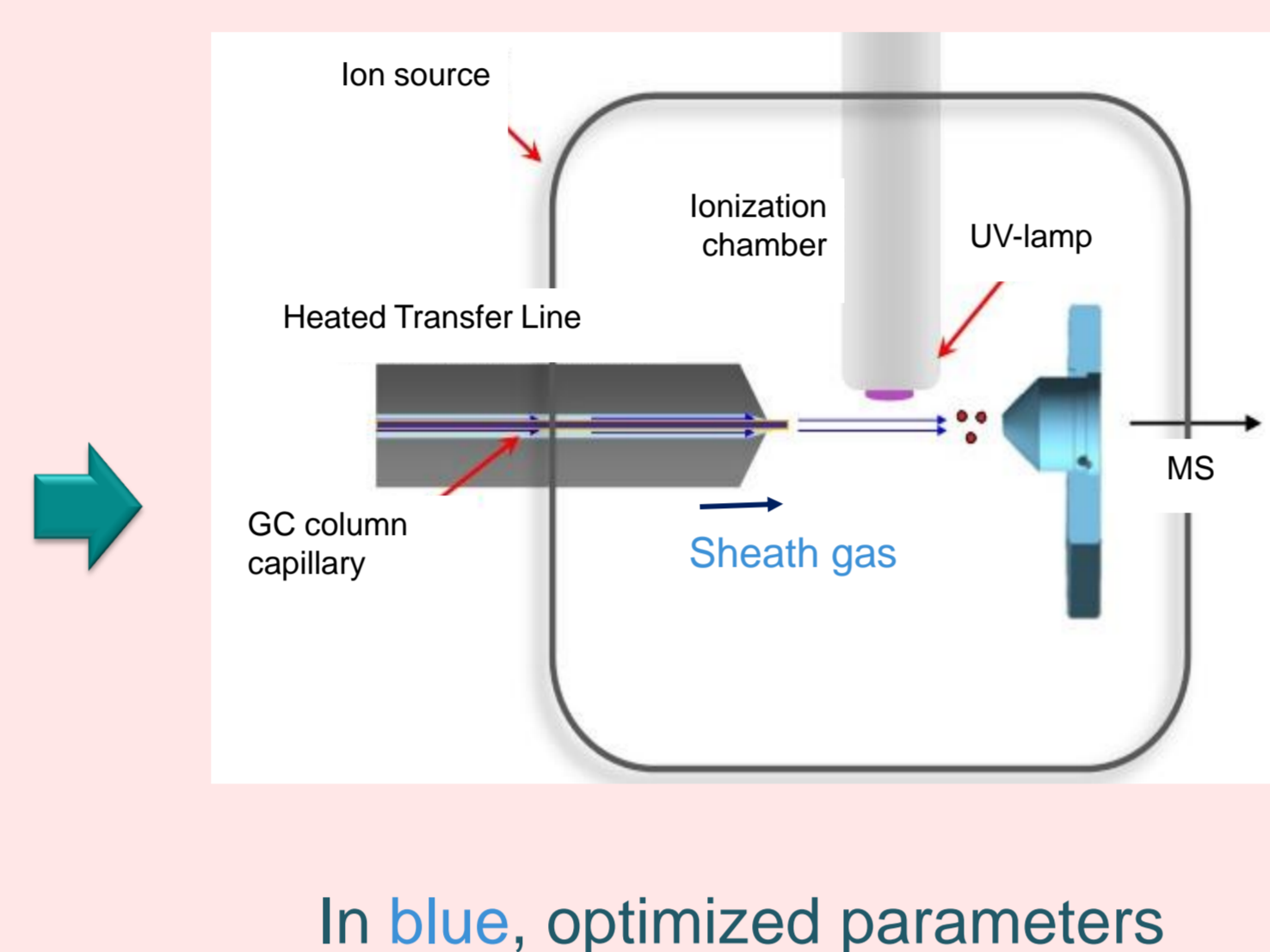
Gas chromatography - Mass Spectrometry (GC-MS) is the method of choice to identify and quantify VOCs in food. The main ionization method is the Electron Ionization (EI): high energy exchanges occur, causing reproducible molecular fragmentations. Chemical Ionisation (CI) is another ionization method where a reactive gas (i.e. methane or ammonia) is ionized to form reactant ions. These ions react with the analytes by proton transfer or charge transfer to produce quasi-molecular ions, sometimes accompanied by characteristic adduct ions. Atmospheric Pressure Photoionization (APPI) is the most recent source [1]. Emitted photons give rise to an odd-electron radical cation; hydrogen atom abstraction frequently occurs during in-source collisions, and produces a large quantity of protonated molecules, MH<sup>+</sup>.



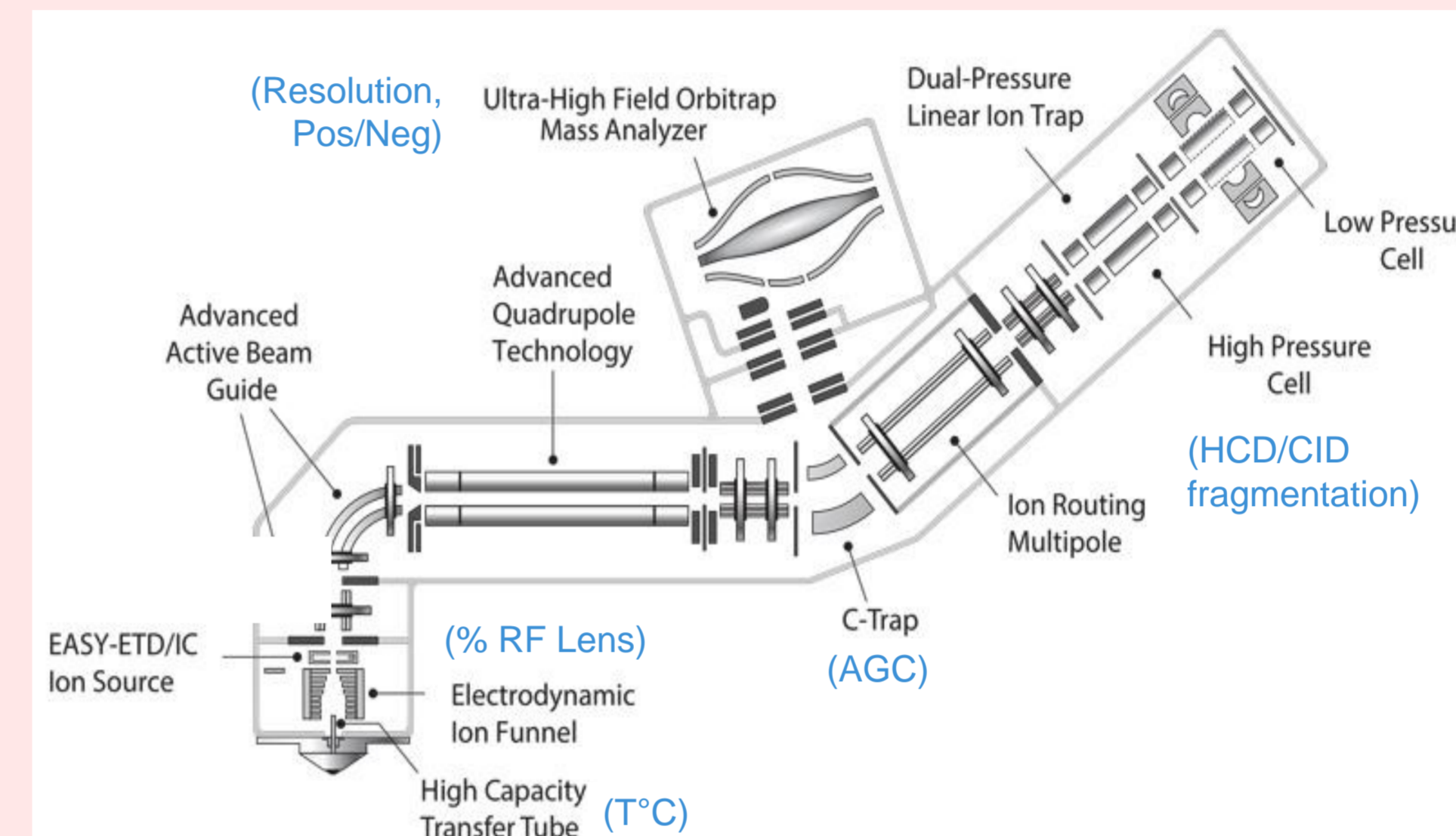
In our research platform, we recently coupled a GC Trace 1310 to a High Resolution Mass Spectrometer (HRMS) Orbitrap Fusion (ThermoScientific) with the APPI source developed by Mascom (Bremen, Germany). In this work, first, we present a general overview of the technical developments carried out on 13 VOCs with the GC-APPI-HRMS hyphenated technique. Secondly, we compare the ionization methods listed above. For this purpose, we used 6 VOCs of different chemical classes to determine the Limit Of Detection (LOD) for each source.

## Methodology

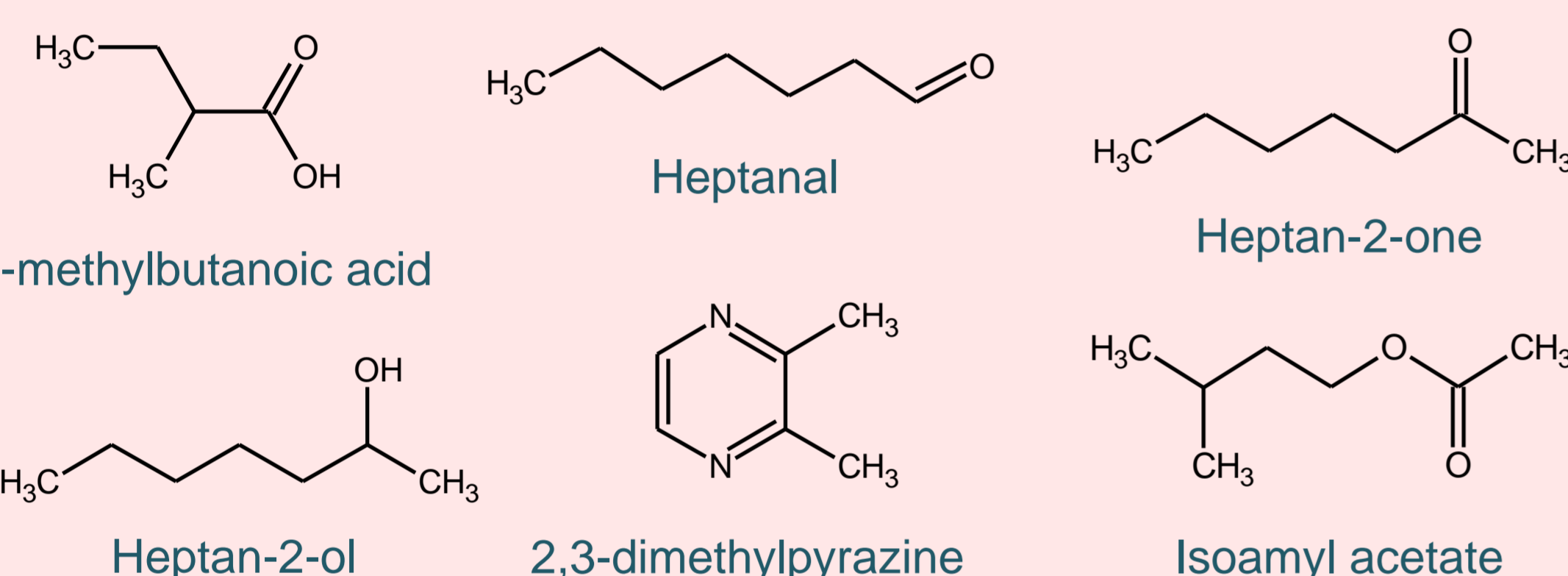
Compounds name	Chemical classes	MH <sup>+</sup>
Butanoic acid	Acids	88
2-Methylbutanoic acid	Acids	102
Heptan-2-ol	Alcohols	116
2-Methylbutan-1-ol	Alcohols	88
3-Methylbutan-1-ol	Alcohols	88
2-Phenylethanol	Alcohols	122
Linalool	Alcohols	154
Heptanal	Aldehydes	114
2,3-dimethylpyrazine	Pyrazines	108
Heptan-2-one	Ketones	114
Diacetyl	Ketones	86
Ethyl butanoate	Esters	116
Isoamyl acetate	Esters	130



In blue, optimized parameters



Methodological development in GC-APPI-HRMS



- ✓ Standard solutions in triplicate (0.1 to 200 ng/μL)
- ✓ 4 to 7 points in the compound linearity domain
- ✓ Selection of 1 to 3 ions for each ionization method
- ✓  $\sum$  abundances of these ions for each triplicate and each solution
- ✓ Average and standard deviation for each solution
- ✓ LOD calculation
- ✓ Calculation of minimal detectable concentration

LOD comparison according to the ionization method

## Results

### Methodological development in GC-APPI-HRMS

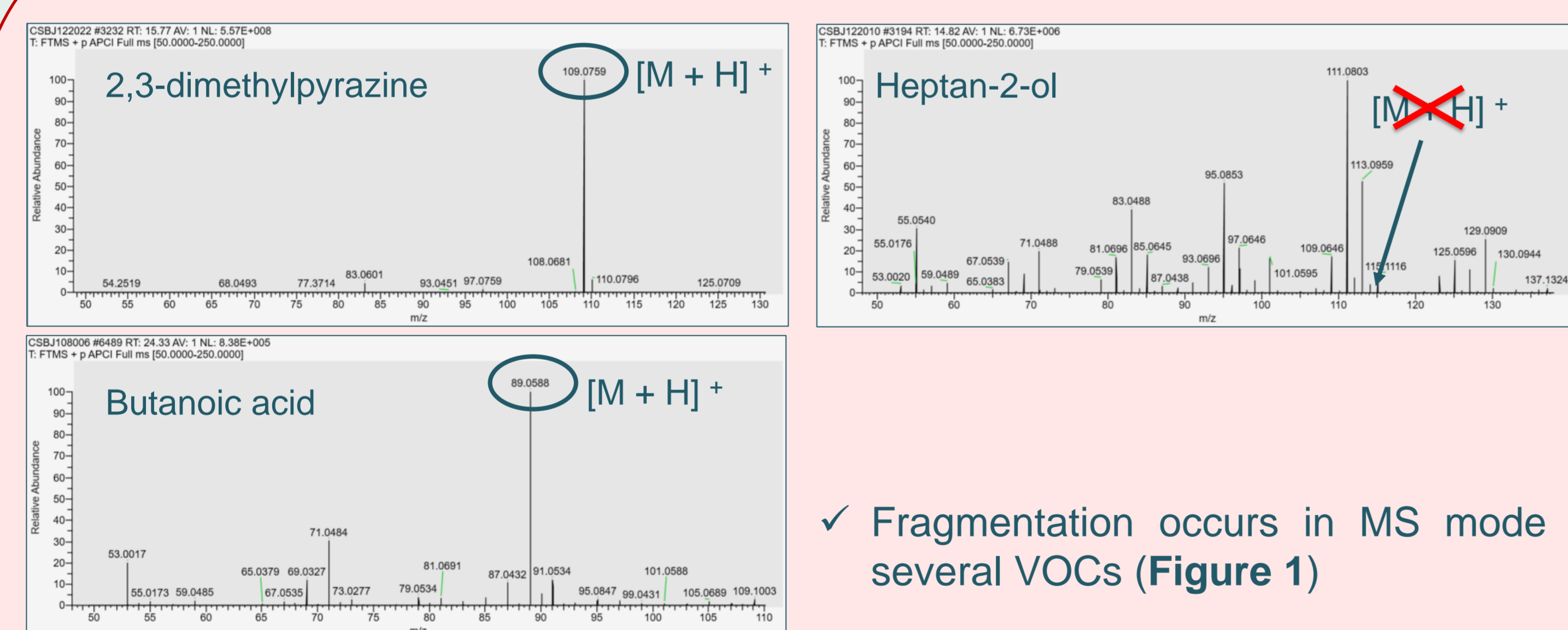


Figure 1 – MS profile in GC-APPI-HRMS for 3 VOCs.

Table I – Optimized parameters for VOCs analysis.

MS	Optimum
Detector	Pos
AGC	2 <sup>5</sup>
Resolution	15000 (0.006 Da à 89 m/z)
% RF Lens	20 - 40
MS2	
HCD	20 % (best fragmentation)
CID	22 %
AGC	5 <sup>4</sup>
Resolution	15000
Sheath gas	2
Source T°C	150°C

- ✓ Fragmentation occurs in MS mode for several VOCs (Figure 1)
- ✓ MS parameters have been optimized (Table I) to limit these fragmentations and to enhance the sensitivity
- ✓ In-source fragmentation remains important for several chemical classes: in fact, the radical cation of the linear oxygenated aroma compounds is subject to rearrangements that require very little activation energy. Ionization energy of oxygenated molecules is relatively low, then, fragmentations occur.

### LOD comparison

Table II – LOD (ng/μL) of different VOCs according to the ionization method.

Compound names	Chemical classes	LOD (ng/μL)			
		EI	CI (CH <sub>4</sub> )	CI (NH <sub>3</sub> )	APPI
2-Methylbutanoic acid	Acids	0.029	0.038	2.706	0.331
Heptan-2-ol	Alcohols	0.006	0.028	0.719	0.165
Heptanal	Aldehydes	0.023	0.008	6.872	0.052
2,3-dimethylpyrazine	Pyrazines	0.002	0.002	0.005	0.004
Heptan-2-one	Ketones	0.003	0.004	0.052	0.020
Isoamyl acetate	Esters	0.003	0.009	0.064	0.223

- ✓ Great disparity in sensitivity according to the chemical classes and the ionization method (Table II)
- ✓ EI and CI (CH<sub>4</sub>) are the most sensitive ionization methods for the studied acid, ketone and ester
- ✓ For the alcohol, EI is the best one while CI (CH<sub>4</sub>) is most appropriate for the aldehyde
- ✓ Relatively high background noise in CI (NH<sub>3</sub>) spectra compared to CH<sub>4</sub> is observed, which makes data processing very complex, and consequently, a higher LOD
- ✓ The studied pyrazine is the better-detected molecular species for the 4 considered methods
- ✓ LODs in APPI are better than those described in the literature, where the limit of detection in GC-APPI-MS is between 1 and 100 ng/μL [2]

## Conclusion & Perspectives

These preliminary results allowed to set up optimized parameters to better characterize VOCs by GC-APPI-HRMS.

LOD were calculated for different chemical classes and compared to other ionization methods. EI remains the most appropriate one to identify chemical compounds in databases, while CI (CH<sub>4</sub>) could provide supplementary information for molecular characterization. APPI, a promising technique to resolve co-elution problems, has to be improved, especially to reduce in-source fragmentation. The use of a dopant gas (acetone) should be tested in the near future.

## Contact

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[1] Raffaelli A. et al. (2003). Mass Spec. Reviews, 22, 318.  
[2] Revel'skii, I. A. et al. (2019). Journal of Analytical Chemistry, Vol. 74, No. 2, pp.192-197.

