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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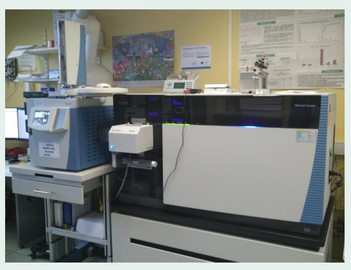
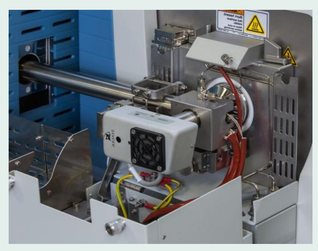
Introduction



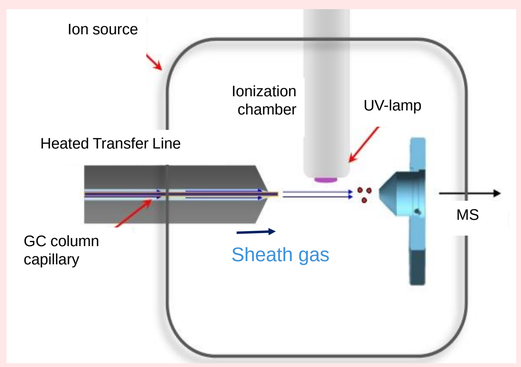
Gas chromatography - Mass Spectrometry (GC-MS) is the method of choice to identify and quantify VOCs in food. The main ionization method is the Electron Ionization (EI): high energy exchanges occur, causing reproducible molecular fragmentations. Chemical Ionisation (CI) is another ionization method where 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^+.



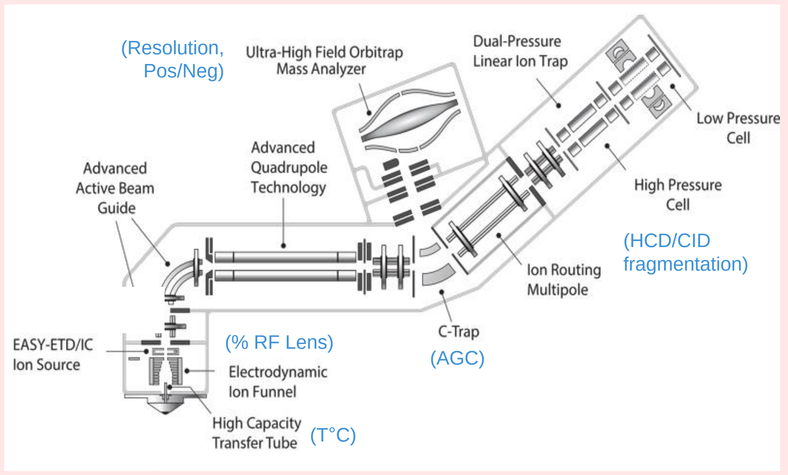
In our research platform, we recently coupled a GC Trace 1310 to a High Resolution Mass Spectrometer (HRMS) Orbitrap Fusion (ThermoScientific) with the APPI source developed by Mascom (Bremen, Germany). In this work, first, we present a general overview of the technical developments carried out on 13 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

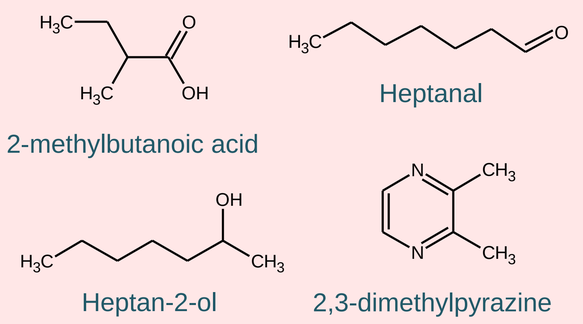
Compounds name	Chemical classes	MH+
Butanoic acid	Acids	88
2-Methylbutanoic acid	Acids	102
Heptan-2-ol	Alcohols	116
2-Methylbutan-1-ol	Alcohols	88
3-Methylbutan-1-ol	Alcohols	88
2-Phenylethanol	Alcohols	122
Linalool	Alcohols	154
Heptanal	Aldehydes	114
2,3-dimethylpyrazine	Pyrazines	108
Heptan-2-one	Ketones	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

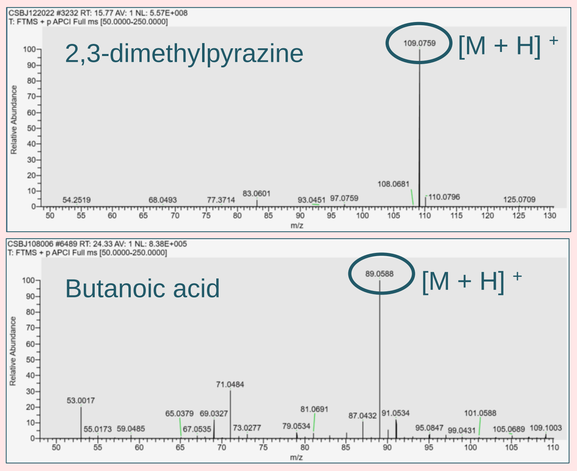


Figure 1 – MS profile in GC-APPI-HRMS for 3 VOCs.

- ✓ 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.

Table I – Optimized parameters for VOCs analysis.

MS	Optimum
Detector	Pos
AGC	2e5
Resolution	15000 (0.006 Da à 89 m/z)
% RF Lens	20 - 40
MS2	
HCD	20 % (best fragmentation)
CID	22 %
AGC	5e4
Resolution	15000
Sheath gas	2
Source T°C	150°C

LOD comparison

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

		LOD (ng/µL)			
Compound names	**Chemical classes**	**EI**	**CI (CH_4)**	**CI (NH_3)**	**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_4) are the most sensitive ionization methods for the studied acid, ketone and ester
- ✓ For the alcohol, EI is the best one while CI (CH_4) is most appropriate for the aldehyde
- ✓ Relatively high background noise in CI (NH_3) spectra compared to CH_4 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_4) 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.

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