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# Comparison of three ionisation methods - electron ionisation, chemical ionisation and atmospheric pressure photoionisation - for the characterisation of volatile organic compounds (VOCs)

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## Abstract

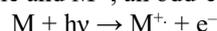
Different chemical classes of VOCs were analysed by three ionisation methods: the oldest gold standard, the electron ionisation (EI), was compared to chemical ionisation (CI) and to atmospheric pressure photoionisation (APPI), a more recent and rarest one. Methodological development on the APPI source coupled to an Orbitrap Fusion, was able to set the best parameters for VOCs high-resolution analysis. LODs calculation has shown a good sensitivity for EI and CI when methane was used as a reagent gas, but APPI, despite in-source fragmentation, is a promising technique for co-elution resolution problems.

*Keywords: EI, CI, APPI, high-resolution, in-source fragmentation*

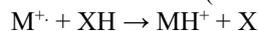
## Introduction

Gas chromatography (GC) is a reproducible, robust, selective, sensitive method to analyse volatile compounds and thermo-stable molecules in a wide range of applications. The separated analytes are generally analysed by mass spectrometry (MS) under vacuum conditions. The main ionisation method is the electron ionisation (EI). High kinetic energy (70eV) is commonly used. The electrons pass through the ionisation chamber by cutting the perpendicular flow of analytes. Energy exchanges occur causing molecular fragmentations [1]. CI is another ionisation method. A reactive gas, for instance, methane (CH<sub>4</sub>) or ammonia (NH<sub>3</sub>), is introduced into the source and is ionised by electron ionisation to form reactant ions that react with the analytes by proton transfer [2]. This type of ion-molecule reaction is less energetic than the electron ionisation. Thus, it limits fragmentations, however, it reduces sensitivity.

GC-MS can also be used coupled to Atmospheric Pressure Ionisation (API) conditions. The most recent API source is the APPI source. Photoionisation of molecules occurs if their ionisation potential is lower than the energy of the photons. APPI was introduced by Revel'skii [3]; the absorption of a photon by the molecule leads to the reaction below, where M is an ionisable molecule and M<sup>+</sup>, an odd-electron radical cation:



Moreover, hydrogen atom abstraction by the molecular radical cation 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 to a High Resolution Mass Spectrometer (HRMS) with an 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 three ionisation methods listed above. For this purpose, we used 6 VOCs of different chemical classes to determine the Limit of Detection (LOD) for each ionisation mode.

## Experimental

### Standards

Thirteen aroma compounds from different chemical classes (butanoic acid, 2-methylbutanoic acid, heptan-2-ol, 2-methylbutan-1-ol, 3-methylbutan-1-ol, 2-phenylethanol, linalool, heptanal, heptan-2-one, diacetyl, ethyl butanoate, isoamyl acetate) were purchased from Sigma Aldrich (Sigma Aldrich, France). They were chosen as representative key-aroma compounds in food. Concentrated solutions of each aroma compound were prepared in 99% dichloromethane (Fisher Scientific, France). For the evaluation of ionisation, each individual compound was prepared at various final concentrations from 0.1 to 200 ng/μL.

## Gas chromatography-Mass spectrometry

Chromatographic separation was performed on a DB-Wax capillary column (30 m x 0.25 mm x 0.5  $\mu\text{m}$ , Agilent Technologies, USA) with the following temperature program : 40°C to 240°C (held for 10 min), 4°C/min. The carrier gas (He) velocity was 40  $\text{cm}\cdot\text{s}^{-1}$ . Splitless mode at 240°C was used in the injection port (1  $\mu\text{L}$ ). GC-EI-MS and GC-CI-MS were conducted on a GC 7890A coupled to a quadrupole MS 5973 (Agilent Technologies, USA). The EI operating conditions were as follow: ion source at 230°C, electron ionisation mode at 70 eV, scan range from 29 to 350 m/z. For the CI operating conditions: ion source at 250°C, electron ionisation mode at 128 eV, chemical ionisation with ammonia and methane successively, scan range from 70 to 400 m/z. Data were recorded with MSD ChemStation (Agilent Technologies, USA). GC-APPI-HRMS was conducted on a GC Trace 1310 (ThermoScientific, USA) with the same above chromatographic conditions. Acquisitions in full scan and MS2 mode were performed on an Orbitrap Fusion instrument (ThermoScientific, USA) equipped with an APPI source developed by Mascom (Germany). The operating conditions were as follow: ion spray at 3500 V, scan range from 50 to 250 m/z. Data were recorded with Xcalibur.

## Data analysis

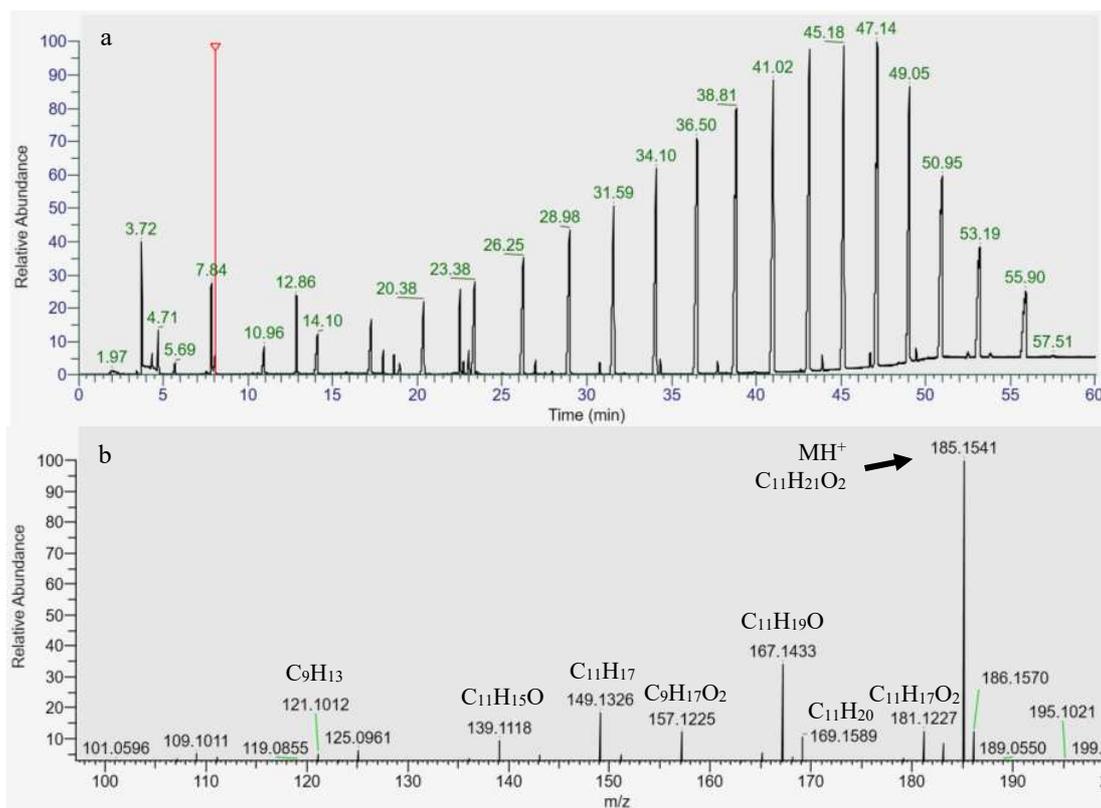
Each compound was validated by its identification based on its retention index (RI) and EI mass spectrum. RI values were calculated using the Van den Dool and Kratz formula [4] from the retention times of n-alkanes (C10-C30) on the same column. RI values were compared with RIs from the literature. The mass spectra were compared with those from databases: NIST, WILEY and INRAMASS (internal database achieved using standard compounds). For LOD comparison, standard solutions were analysed in triplicate. 4 to 7 points were chosen in the compound linearity domain and 1 to 3 ions were selected for each ionisation method. The sum of the abundances of these ions, for each triplicate and each solution, was calculated first, then the average and the standard deviation. LOD calculation was used to determine the minimal concentration detectable for each ionisation method and each compound.

## Results and discussion

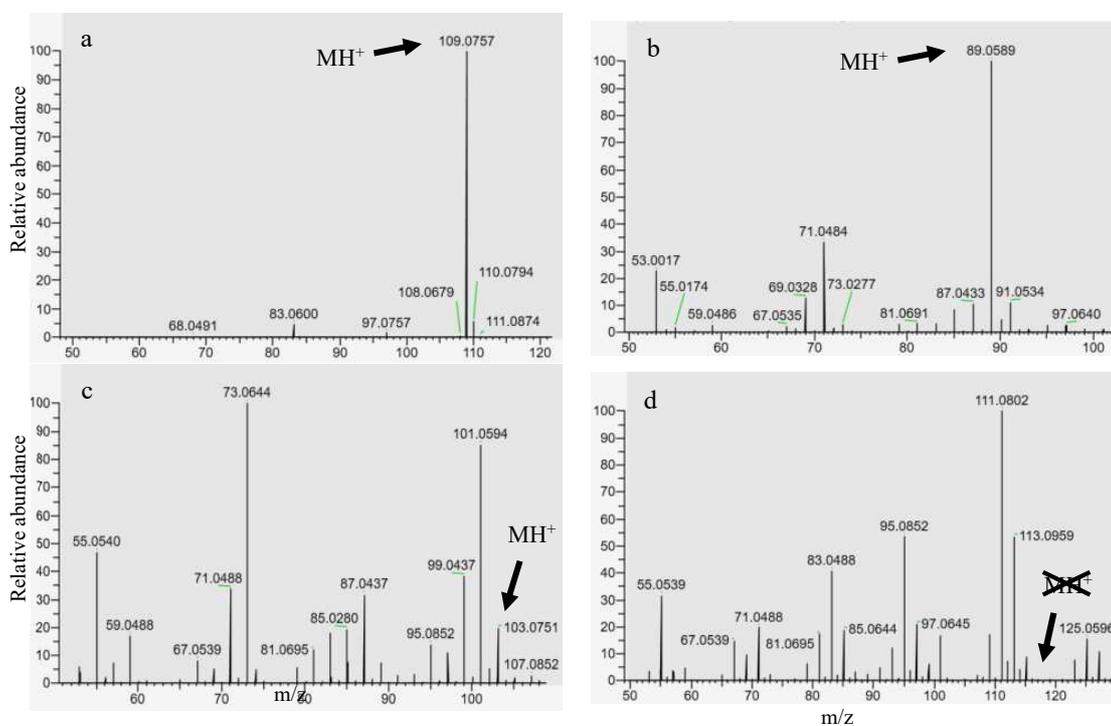
After analysis by GC-APPI-HRMS, adducts at + 27.959 Da were detected for each n-alkanes used to calculate RIs, without any molecular ion being observed. For example, the undecane, with a  $\text{C}_{11}\text{H}_{24}$  raw formula and a theoretical mass  $\text{MH}^+$  at m/z 157.195, was detected at m/z 185.154 with a  $\text{C}_{11}\text{H}_{21}\text{O}_2$  suggested raw formula (Figure 1). The same phenomenon was observed in the troposphere, alkanes coming from engines and industrial combustions react by photooxidation with OH radical at atmospheric pressure to form, for instance, + 27.959 Da adducts (ketone or furfural chemical classes have been suggested) [5].

Methodological development was performed on 13 VOCs of different chemical classes (acids, alcohols, aldehydes, pyrazines, ketones and esters); the goal was to adjust several instrument parameters to get the best sensitivity in our mass spectra. Critical parameters for the 13 VOCs studied were, first of all, the source parameters. Sheath gas flow needed to be very low to avoid dispersion of the molecules at the entry of the mass spectrometer. The transfer tube temperature was set to 150°C; higher temperatures gave rise to molecular dissociations while lower temperatures decreased sensitivity. Secondly, full scan mass parameters were investigated. Positive scan mode allowed the sensitivity to be doubled compared to negative mode. The Automatic Gain Control parameter (AGC) of the C-Trap was tested from 2E5 to 1E6 and the best performances were obtain with a low AGC value. Indeed, AGC regulates the ion stacks stored in the C-Trap before being shot into the Orbitrap. Large ion stacks lead to collisions between molecules, and dissociations occur. Resolution was set to 15,000. This resolution setting enabled to distinguish two ions separated by 0.006 Da, at m/z 89. A Radio Frequency (RF) Lens parameter from 20 to 40 % was optimal to promote the transmission of our low m/z ratio ions. Thirdly,  $\text{MS}^n$  parameters like fragmentation energies in CID (Collision-Induced Dissociation) and HCD (High-Collision Dissociation) were adjusted. HCD was more informative than CID, and low collisional energies were necessary to perform  $\text{MS}^n$  experiments on VOCs.

Despite these methodological developments, in-source fragmentation was observed on such chemical classes (Figure 2). 2,3-dimethylpyrazine spectrum presented a unique and intense protonated molecular ion.  $\text{MH}^+$  butanoic acid ion remained the most intense peak in the full scan mass spectrum, but fragment ions started to be observed in the background. The parent ion of 2-methylbutanoic acid was under-detected compared to fragment ions while  $\text{MH}^+$  heptan-2-ol was undetectable in the mass spectrum. Ionisation energy of oxygenated molecules is relatively low. The radical cation of the linear oxygenated aroma compounds is subject to rearrangements that require very little activation energy, and give rise to *in fine* fragmentation. When photoionisation occurs, the aroma compound recovers energy from the photons to lose its electron, and the difference is converted into internal energy which is available for the rearrangement and fragmentation processes.



**Figure 1:** (a) Total ion chromatogram of the *n*-alkanes. The red line is the undecane retention time. (b) Full scan mass spectrum of the undecane with a  $C_{11}H_{24}$  raw formula and a theoretical mass  $MH^+$  at  $m/z$  157.195. Elemental compositions are calculated by the FreeStyle software (ThermoScientific).



**Figure 2:** Full scan mass spectra of (a) 2,3-dimethylpyrazine (b) butanoic acid (c) 2-methylbutanoic acid and (d) heptan-2-ol. The arrows highlight the parent ion of each compound. Fragment ions appear for butanoic acid and are very abundant in the 2-methylbutanoic acid and heptan-2-ol mass spectra.

Six COVs were chosen to compare LODs in GC-APPI-HRMS with the two standard ionisation methods, EI and CI (methane and ammonia as reagent gas). Table 1 lists the minimal concentration detected for each aroma compound and each technique. A great disparity in sensitivity was observed according to the chemical classes and the ionisation method. EI and CI (CH<sub>4</sub>) were usually the most sensitive ionisation methods for the studied VOCs. The bad sensitivity obtained in CI (NH<sub>3</sub>) could be explained by a relatively high background noise in the spectra compared to CH<sub>4</sub>, which makes data processing more complex and consequently, gives higher LODs. Moreover, ionisation of molecules occurs if their proton affinity is lower than that of the reagent gas (204 Kcal/mol for NH<sub>3</sub> and 129 Kcal/mol for CH<sub>4</sub>). Except 2,3-dimethylpyrazine, whose proton affinity is around 219 Kcal/mol, our other VOCs are not able to give rise to MH<sup>+</sup> ions in CI NH<sub>3</sub>. However, adduct ions [M+NH<sub>4</sub>]<sup>+</sup> were systematically present in their spectra, the abundance of which was considered for LODs determination. The studied pyrazine is the best-detected molecular species for the four considered methods, maybe because of the good stability of the nitrogen cycle and its proton affinity very favourable. Even if APPI is not the most sensitive method in this experiment, APPI LODs are better than those described in the literature where the limit of detection in GC-APPI-MS is between 1 and 100 ng/μL [6].

**Table 1: Minimal concentration detected (ng/μL) for each volatile organic compound and each ionisation method. (EI) Electron Ionisation, (CI) Chemical Ionisation, (CH<sub>4</sub>) methane as reagent gas, (NH<sub>3</sub>) ammonia as reagent gas and (APPI) Atmospheric Pressure PhotoIonisation.**

VOCs	Ionisation method			
	EI	CI (CH <sub>4</sub> )	CI (NH <sub>3</sub> )	APPI
2-methylbutanoic acid	0.029	0.038	2.706	0.331
heptan-2-ol	0.006	0.028	0.719	0.165
heptanal	0.023	0.008	6.872	0.052
2,3-dimethylpyrazine	0.002	0.002	0.005	0.004
heptan-2-one	0.003	0.004	0.052	0.020
Isoamyl acetate	0.003	0.009	0.064	0.223

## Conclusion

These preliminary results allowed to set up optimised parameters to characterise VOCs better by GC-APPI-HRMS. LODs were calculated for different chemical classes and compared to other ionisation 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 characterisation. APPI, a promising technique to resolve co-elution problems, has to be improved, especially to reduce in-source fragmentation and enhance the efficiency of ion formation. Robb et al. [7] developed the use of a photo-ionisable dopant, working as an intermediate between the analytes and the photons; thereby, a reactant ionises the analytes by charge exchange or proton transfer, allowing a greater detection sensitivity. Acetone (m/z 59) as a dopant gas should be a good candidate for our applications, its low molecular weight being below the mass of interest of the VOCs.

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