

# Unraveling different chemical fingerprints between a champagne wine and its aerosols

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**As champagne or sparkling wine is poured into a glass, the myriad of ascending bubbles collapse and radiate a multitude of tiny droplets above the free surface into the form of very characteristic and refreshing aerosols. Ultrahigh-resolution MS was used as a nontargeted approach to discriminate hundreds of surface active compounds that are preferentially partitioning in champagne aerosols; thus, unraveling different chemical fingerprints between the champagne bulk and its aerosols. Based on accurate exact mass analysis and database search, tens of these compounds overconcentrating in champagne aerosols were unambiguously discriminated and assigned to compounds showing organoleptic interest or being aromas precursors. By drawing a parallel between the fizz of the ocean and the fizz in Champagne wines, our results closely link bursting bubbles and flavor release; thus, supporting the idea that rising and collapsing bubbles act as a continuous paternoster lift for aromas in every glass of champagne.**

Fourier transform | ion cyclotron resonance | MS | bubbles | surfactants

In surfactant solutions, preferential adsorption of surfactants at the air-solution interface occurs as a result of the amphiphilic properties of surfactants, with the water-soluble moiety plunging into the solution and the hydrophobic component in contact with the air. In oceanography, enrichment of the sea-surface microlayer and atmospheric aerosols in surfactant materials has long been studied (1–3). Actually, bubbles trapped by the sea breakers action considerably increase exchange surfaces between the sea bulk and the atmosphere. Bubbles drag surfactants along their way through the liquid bulk, reach the sea surface, to finally burst and eject aerosol droplets into the atmosphere. Air bubbles trapped during rough sea conditions were found to increase specific organic concentrations in marine aerosols by several orders of magnitude compared with those found in the liquid bulk (4).

From a conceptual point of view, the situation found in glasses poured with champagne or sparkling wine is quite similar to that described above. Nevertheless, only quite recently, the tools of physical chemistry were used to identify the physical mechanisms behind the nucleation, rise, and collapse of bubbles found in champagne and sparkling wines (5–7). From a strictly chemical point of view, Champagne and sparkling wines are multicomponent hydro-alcoholic solutions supersaturated with CO<sub>2</sub>-dissolved gas molecules (formed together with ethanol during the fermentation process). Champagne and sparkling wines also hold hundreds of surface active compounds, some of them showing organoleptic interest. As soon as a bottle of champagne or sparkling wine is uncorked, the progressive release of CO<sub>2</sub>-dissolved gas molecules is responsible for bubble nucleation, the so-called effervescence process. It is worth noting that ≈5 L of CO<sub>2</sub> must escape from a typical 0.75 L champagne bottle. To get an idea of how many bubbles are potentially involved all along the degassing process, we can divide this volume of CO<sub>2</sub> to be released by the average volume of a typical bubble of 0.5 mm in

diameter. A huge number close to 10<sup>8</sup> is found, leading to an exchange surface ≈80 m<sup>2</sup>. Once champagne is poured into a glass, bubbles nucleated on the glass wall drag champagne surfactants along their way through the liquid bulk (6, 7). Surfactants finally reach the free surface and concentrate themselves at the air/champagne interface. At the free surface of a glass poured with champagne, the ever-increasing concentration of surfactants was indeed indirectly evidenced by observing the ever-increasing lifetime of bubbles with time (7). Actually, the ever-increasing surface concentration of surfactants progressively changes the boundary conditions on the bubble surface from slip to nonslip; thus, reducing in turn the drainage velocity and extending the lifetime of the bubble. The formation of adsorption layers of amphiphile macromolecules at the air/champagne interface was also directly evidenced through ellipsometry and Brewster angle microscopy (BAM) experiments (8, 9). Actually, bubbles bursting at the champagne surface radiate hundreds of tiny liquid jets every second, which quickly break up into a multitude of tiny droplets, as shown by use of high-speed photography, and laser tomography techniques very recently (Fig. 1) (5, 10). Based on a phenomenological analogy between the fizz of the ocean and the fizz in Champagne wines, it was hypothesized a few years ago that aerosols found in the headspace above a glass poured with champagne could considerably enhance the fragrance release of champagne by bringing chemical compounds to the taster's nostrils, showing both surface activity and organoleptic interest (7, 11). In the present work, an experimental proof is given using ultrahigh-resolution MS (Fourier Transform Ion Cyclotron Resonance Mass Spectrometer; FT-ICR-MS) as a nontargeted approach, to discriminate hundreds of surface active compounds, some of them showing indeed organoleptic interest, that are preferentially partitioning in champagne aerosols rather than in the champagne bulk. Thus, aerosols appear to hold the organoleptic essence of champagne.

## Results and Discussion

**Describing the Chemical Spaces of Both Champagne Bulk and Aerosols.** Ultrahigh-resolution is the key in enabling the direct mass spectrometric comparison of bulk and aerosol spectra without need of absolute quantification. The combined advantages of the high mass accuracy (<200 ppb) and mass resolution (>500,000

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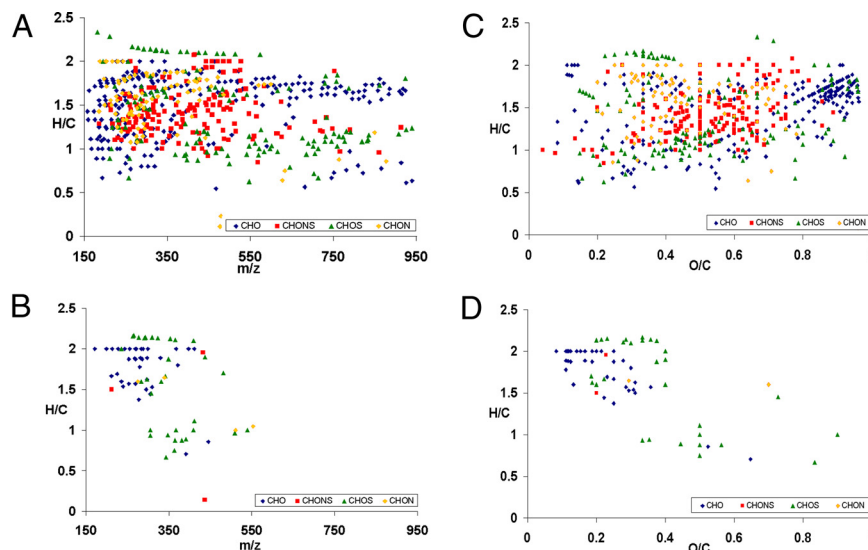
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**Fig. 5.** Van Krevelen diagrams of the bulk showing the presence of typical CHO, CHOS, CHON, and CHONS wine metabolites in the  $m/z$  range 150 to 500 and higher molecular weight carbohydrates (A and C); Van Krevelen diagrams of molecules concentrated in the aerosols only (with  $C_f > 2$ ) showing mainly CHO and CHOS highly saturated molecules with relative low oxygen contents (B and D). Color code: blue, CHO; green, CHOS; orange, CHON; red, CHONS.

297.2435 as ricinoleic acid (Table S1). Indeed, Pagot et al. (27) showed that peroxisomal  $\beta$ -oxidation of ricinoleic acid leads to  $\gamma$ -decalactone, a peachy aroma compound. Two other elemental formulas could be related to terpenoid glucose esters at  $m/z$  325.2024 and 345.1556 (28). The latter is a glucose ester of (E)-2,6-dimethyl-6-hydroxyocta-2,7-dienoic acid and was previously detected in Riesling wine (29). Picrocrocin could correspond to the  $[C_{16}H_{25}O_7]^-$  ionic elemental formula identified at  $m/z$  329.1605. This molecule is a glucoside of safranal and contributes to the bitter taste of saffron (30). Last, two alternative isomers at  $m/z$  171.1390 could correspond to monoterpene alcohols, which are considered as important aromas of wines from the Muscat grape variety (31).

In conclusion, we were interested in describing changes in the chemical complexity and diversity in champagne aerosols formation through ultrahigh-resolution MS, in the mass range 150–1,000. We were able to discriminate hundreds of chemical components that are preferentially partitioning in champagne aerosols rather than in the champagne bulk and could propose structural assignments for tens of them. By drawing a parallel between the fizz of the ocean and the fizz in Champagne wines, our study evidenced a relationship between bursting bubbles and the likely “exhausting aromas” effect often attributed to Champagne wines; thus, supporting the idea that rising and collapsing bubbles act as a continuous paternoster lift for aromas in every glass of champagne.

## Materials and Methods

**Champagne Bulk Sampling.** A standard Champagne wine was used for this set of experiments. Champagne was poured into glasses first thoroughly washed and rinsed by use of methanol. The champagne bulk was sampled directly from glasses, after champagne was poured. Samples were diluted 40  $\mu$ L/mL in methanol before flow injection in the FT-ICR-MS.

**Champagne Aerosols Sampling.** Microscope glass slides, also previously washed with methanol, were positioned at the top of glasses, 2 to 5 mm above the free surface of champagne. Champagne aerosols, originating from the myriad of bubbles collapsing at the air/champagne interface, progressively collect themselves by colliding the microscope glass slides. After 10 min of aerosols collection above champagne glasses, the slides were washed with methanol and ready for flow injection in the FT-ICR-MS. Depending on the sampling time and the amount of methanol needed for elution from the slides, the final concentration infused was different and uncontrollable due to relative evaporation on the glass slide surface.

**FT-ICR-MS Analysis.** Ultrahigh-resolution mass spectra were carried out on a Bruker APEX Qe FT-ICR-MS equipped with a 12 Tesla superconducting magnet and an Apollo II ESI source operated with 1,000 scan (1 MW) in the positive ion mode and 500 to 5,000 scan (4 MW) in the negative mode. Mass scan range was 150–2,000  $m/z$  for both modes. Spectra were externally calibrated on clusters of arginine (10 mg/L in methanol) and internally systematically on fatty acids [ESI(–)] and solvent diesters [ESI(+)]. The two ionization modes could be used complementary to differentiate components such as fatty acids [only ionisable in ESI(–)] and their corresponding isobaric ethyl esters [only ionisable in ESI(+)]. Samples were flow-injected straight forward in the ESI using a Hamilton 250  $\mu$ L syringe with a simple syringe injection pump at 0.12 mL/h.

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