

Simultaneous Monitoring of Gaseous CO₂ and Ethanol above Champagne Glasses via Micro-gas Chromatography (μ GC)

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S Supporting Information

ABSTRACT: In champagne tasting, gaseous CO₂ and volatile organic compounds progressively invade the headspace above glasses, thus progressively modifying the chemical space perceived by the consumer. In this study, a novel, rapid, and noninvasive method aimed to simultaneously determine the content in gaseous CO₂ and ethanol above a glass poured with champagne, using a micro-gas chromatography technique coupled with a thermal conductivity detector, was presented. The simultaneous quantification of CO₂ and ethanol in the headspace of a champagne glass was monitored, in real tasting conditions, all along the first 15 min following pouring, depending on whether or not the glass shows effervescence. Both CO₂ and ethanol were found to be enhanced by the presence of ascending bubbles, thus confirming the close link between rising bubbles and the release of gaseous CO₂ and volatile organic compounds.

KEYWORDS: Champagne wine, CO₂, ethanol, micro-gas chromatography, effervescence

INTRODUCTION

Since the end of the 17th century, champagne has been a world-wide renowned French sparkling wine. From a strictly chemical point of view, Champagne wines are multicomponent hydro-alcoholic systems supersaturated with carbon dioxide (CO₂) dissolved gas molecules formed together with ethanol during the second fermentation process, called *prise de mousse*. During *prise de mousse*, bottles are sealed so that CO₂ molecules cannot escape and progressively dissolve into the wine.^{1–3} Actually, a standard 75 cL champagne bottle typically holds about 9 g of dissolved CO₂, which corresponds to a volume close to 5 L of gaseous CO₂ under standard conditions for temperature and pressure.^{1–3} This very significant volume of dissolved CO₂ is responsible for the formation of bubbles once the bottle is uncorked. When champagne is poured into a glass, there are indeed two pathways for progressive losses of dissolved CO₂ molecules: (i) into the form of heterogeneously nucleated bubbles, the so-called *effervescence* process, and (ii) by invisible diffusion through the free surface of the glass.^{1–5}

From the consumer point of view, the role of effervescence is essential in Champagne and sparkling wines, and to a great extent, in any other carbonated beverage. Without bubbles, champagne would be unrecognizable, and beers and sodas would be flat. However, the role of effervescence is suspected to go far beyond the solely aesthetical point of view. Effervescence and CO₂ impact champagne and sparkling wine tasting in terms of (i) visual perception, by the presence of dancing bubbles in the glass,^{1–5} (ii) taste and mouthfeel, by the fizzy and chemosensory excitation of nociceptors in the oral cavity (via the conversion of dissolved CO₂ to carbonic acid),^{6–8} and (iii) aromatic perception, as bubbles

release their content in gaseous CO₂ and volatile organic compounds (VOCs) above the champagne surface. Recently, by use of ultrahigh resolution mass spectrometry, it was indeed demonstrated that ascending bubbles radiate a cloud of tiny champagne droplets overconcentrated with compounds known to be aromatic or the precursors of aromas.⁹ Moreover, it was also recently demonstrated that the continuous flow of ascending bubbles strongly modifies the mixing and convection conditions of the liquid phase.^{10,11} Consequently, the release of dissolved CO₂ by invisible diffusion through the free air/champagne interface, as well as the release of the numerous VOCs, both of which strongly depend on the mixing flow conditions of the liquid medium, should be considerably enhanced in comparison with the release of dissolved gas species and VOCs from a liquid medium at rest.¹² Indeed, a link has been recently evidenced between carbonation and the release of some aroma compounds in water.^{13,14}

Among all the numerous VOCs found in wines, ethanol is obviously the one which is the most concentrated. Ethanol is an effective gustatory, olfactory and trigeminal stimulus.¹⁵ In recent studies, it has been shown that variation of wine ethanol content significantly contributes to the partitioning of odorant molecules in the wine headspace by modification of their solubility.^{16–18} Furthermore, from the taster's point of view, the perception of wine flavors was also found to be influenced by glass shape.^{19,20} Because of all the aforementioned reasons, no wonder that a very

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strong coupling therefore finally exists in champagne and sparkling wines tasting, among dissolved CO₂, the presence of rising bubbles, glass shape, CO₂ discharge, and VOCs release.

Most of the previous studies about CO₂ in champagne wines were dedicated to the determination of dissolved CO₂ content found in the liquid phase (inside the bottle or as it is poured into a glass), using nonintrusive²¹ or mainly intrusive methods.^{22–26} The dissolved CO₂ content is generally determined by using carbonic anhydrase, which is the official method recommended by the OIV (namely, the International Office of Vine and Wine) for measuring the CO₂ content in Champagne and sparkling wines.²⁷ Otherwise, some others intrusive methods have been used in order to access the dissolved CO₂ content found in a liquid phase, such as for example, the ORBISPHERE thermal conductivity sensor for CO₂ (available up to 10 g/L of dissolved CO₂)²⁸ and spectrophotometric detection with a flow injection (from 0.5 to 4 g/L).²⁹ As far as we know, only one recent study has been dedicated to the measurement of gaseous CO₂ concentrations found in the headspace above champagne glasses, using a nonintrusive infrared laser spectrometer.³⁰

In the present article, a novel, rapid, and nonintrusive method aimed to simultaneously determine the concentration of gaseous CO₂ and ethanol found in the headspace above a champagne glass is presented. For this purpose, an analysis using a micro-gas chromatography (μ GC) technique coupled with a thermal conductivity detector (TCD) was developed. The simultaneous quantification of CO₂ and ethanol in the headspace of a champagne glass was monitored, in real tasting conditions, all along the first 15 min following pouring, depending on whether or not the glass shows effervescence.

MATERIALS AND METHODS

Champagne Samples. A standard commercial Champagne wine (with 12.5% v/v ethanol), elaborated in 2007 with the Chardonnay grape variety at the Nogent l'Abbesse cooperative (Marne, France), was used for this set of experiments. The concentration of CO₂ molecules dissolved in Champagne samples (before pouring) was determined using carbonic anhydrase (labeled C2522 Carbonic Anhydrase Isozyme II from bovine erythrocytes and provided by Sigma-Aldrich, US). This method is thoroughly detailed in two recent papers.^{22,23} Before pouring, champagne was found to hold a concentration of dissolved CO₂ of [CO₂] = 11.6 ± 0.3 g/L.

Glass Washing Protocol. To avoid the randomly located bubbling environment inevitably provided in glasses showing natural effervescence,³¹ we decided to use, for this set of experiments, a single standard flute engraved on its bottom (thus providing a standardized and artificial effervescence). More details on artificial bubble nucleation provided by laser engraving techniques can be found in ref 10. A second standard flute without any surface treatment was used for these experiments. Both flutes were cleaned with the same washing protocol in order to have a standardized effervescence or to be completely effervescence-free, for the engraved and nonengraved flute, respectively.

Between the successive pouring and time series data recordings, glasses were systematically thoroughly washed in a dilute aqueous formic acid solution, rinsed using distilled water, and then compressed air-dried. This drastic treatment eliminates the formation of calcium carbonate crystals on the glass wall as well as the adsorption of any dust particle acting as natural bubble nucleation sites. With such a surface treatment, the CO₂ bubble nucleation is either strictly restricted to the bubble nucleation sites of the ring-shaped engraving or forbidden in the flute

Table 1. Details of the Chromatographic Conditions for the Simultaneous Analysis of CO₂ and Ethanol above the Free Surface of a Champagne Glass, Using μ GC

	CO ₂	ethanol
channel	A	B
column	PPU	OV-1
Method Acquisition Parameter		
column temperature	140 °C	100 °C
carrier gas		helium
sampling time		10 s
injection time		50 ms
detector sensibility	low	high
detector		on
autozero		on
running time		60 s
Peak Integration Parameters		
slope sensitivity (μ V/s)		5.00
peak width (s)		0.50
integration OFF at time (s)	0.00	0.00
integration ON at time (s)	23.50	30.00

without any surface treatment. Therefore, differences in concentrations of gaseous CO₂ and ethanol evidenced above the glasses showing standardized effervescence or not are attributed only to the presence or absence of ascending bubbles.

Micro-gas Chromatography Procedure. μ GC is generally employed to monitor gases of environmental interest such as CO₂, N₂O, and CH₄.^{32,33} GC coupled with a thermal conductivity detector has been applied to the analysis of CO₂, N₂, and O₂ in beverage headspace. The quantity of each gas present was determined with a headspace sampler developed to puncture the beverage package (carbonated beverages or still wines).³⁴ In this study, analyses were conducted on a dual channel (A and B) micro-gas chromatograph equipped with a thermal conductivity detector (TCD) (MicroGC 200, Agilent, SRA Instruments, France). On channel A, a PorAPlot U (PPU) column was set at 140 °C for the determination of CO₂, while analysis of ethanol was performed on channel B with a OV-1 column at 100 °C. Helium was used as a carrier gas in the two columns. The injection time on both columns was 50 ms. Chromatograms were obtained every 60 s. Peaks areas were quantified using the SOPRANE software (version 2.6.5). The chromatographic conditions for the analysis of CO₂ and ethanol and the peak integration parameters are summarized in Table 1. The quantity of CO₂ was determined by means of a calibration curve using two bottles containing, respectively, 10% and 1% of standard CO₂ (supplied by Linde gas, France), and air (\approx 0.038% of CO₂) was used as a control (Supporting Information, Figure S1). Ethanol was quantified with a bottle of gas holding 0.25% of standard ethanol (supplied by Linde Gas, France) (Supporting Information, Figure S2). Calibration with the standard gas bottles were made with direct connection of the bottle to the μ GC sample injection valve using stainless steel tubing, avoiding any gas loss or any disturbing airstream, thus keeping constant the concentration of standard gas. The gas delivery pressure was also kept constant to 1 bar. Then, analyses and quantification of standard gases for calibration were made with the same parameters as those used for the samples (Table 1). Calibration curves plotted the relative area of CO₂ or ethanol versus the concentration of the standard. The procedure finally developed has shown a high reproducibility: 0.18% relative standard deviation (RSD) for 10% CO₂, 0.54% RSD for 1% CO₂, and 0.28% RSD for ethanol. RSD from six measurements for the following

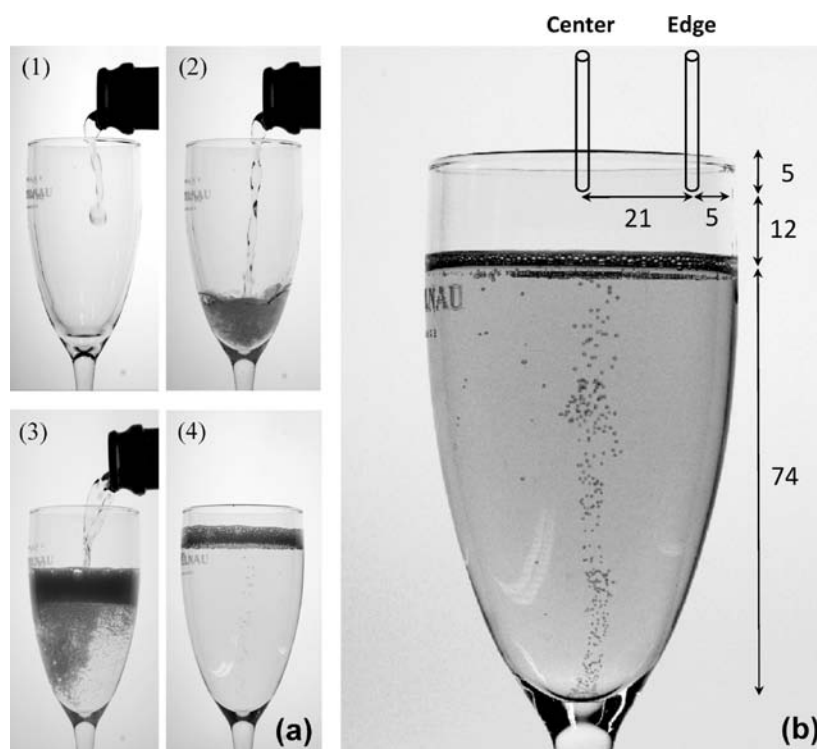


Figure 1. Time-sequence illustrating the standard-like way of serving 100 mL of champagne vertically into the flute (a) and scheme illustrating the two well-defined valve sampling positions in the headspace above the champagne surface, namely, on its axis of symmetry, or close to the flute's wall (dimensions are indicated in mm) (b). Photographs were taken by Gérard Liger-Belair.

samples are CO₂ in air, 1.84%; CO₂ at the edge of the engraved flute 1 min after the end of pouring, 18.38%; CO₂ at the edge of the engraved flute 15 min after the end of pouring, 12.59%; ethanol at the edge of the engraved flute 1 min after pouring, 7.25%; and ethanol at the edge of the engraved flute 15 min after pouring, 12.31%.

Experimental Setup and Procedure Used to Measure the Concentration of CO₂ and Ethanol above a Glass Poured with Champagne. Champagne (100 ± 5 mL) was carefully poured into the glass previously level-marked with 100 mL of distilled water. During the standard champagne-like way of serving, champagne vertically falls and hits the bottom of the flute (thus usually providing a thick head of foam, which quickly vertically extends and then progressively collapses during serving, as seen in the time-sequence displayed in Figure 1a). Immediately after pouring, the glass was manually placed at a well-defined position under the injection valve of the chromatograph (see the scheme displayed in Figure 1b). Then, the chromatographic analysis was started, and the sampling of champagne headspace above the glass was performed during 10 s and was repeated every 60 s, during 15 min following the pouring process. Figure 2 presents a global view, as well as a photographic detail of our experimental setup.

Experiments were conducted at room temperature (23 ± 2 °C). Champagne wines were stored at 20 ± 1 °C for one day before the experiment. Between the successive pourings, bottles were hermetically closed and stored at 20 ± 1 °C. To enable a statistical treatment, six successive pouring and data recordings on three distinct bottles (from the same batch) were done for each tasting condition. A comparison between two batches, corresponding to two vintages (2007 and 2008), was done, and the results are presented in Figures S3 and S4 (Supporting Information).

Statistical analysis was done by Student's *t* test (two-tailed, two sample unequal variance) to determine whether concentrations of CO₂

or ethanol were significantly different for each time after pouring. Differences at *P* < 0.05 were considered as significant.

RESULTS AND DISCUSSION

Influence of the Sampling Position on Gaseous CO₂ and Ethanol Content Found in the Headspace above the Champagne Surface: When the Tears of Wine Play Their Part. In this set of experiments, the flute showing standardized effervescence was used with the two well-defined headspace sampling positions shown in Figure 1b, namely, (i) above the center and (ii) close to the edge of the flute, respectively. In both cases, the sampling valve was located at the same distance from the wine surface. All along the first 15 min following pouring, Figures 3 and 4 show CO₂ and ethanol concentrations, respectively, according to these two aforementioned conditions of analysis. The CO₂ concentration shows a rather similar pattern whatever the position of the sampling valve (see Figure 3). The headspace above the champagne surface reached ≈15% of CO₂ early after pouring, and decreased to ≈1.5% of CO₂ 15 min later, whatever the position of the sampling valve. It is worth noting that inhaled concentrations of CO₂ above 2% can produce diverse toxicological effects, such as headaches, dizziness, hyperventilation, etc., and could even be lethal above 10% (depending on the length of time exposed).³⁵ Obviously, short time exposures to these high CO₂ concentrations (>10%) occur in usual champagne tasting conditions.

Unlike the case of gaseous CO₂ presented in Figure 3, ethanol concentrations appear significantly different according to the sampling valve position above the flute, as seen in Figure 4. Sampling above the center of the flute shows a decrease of

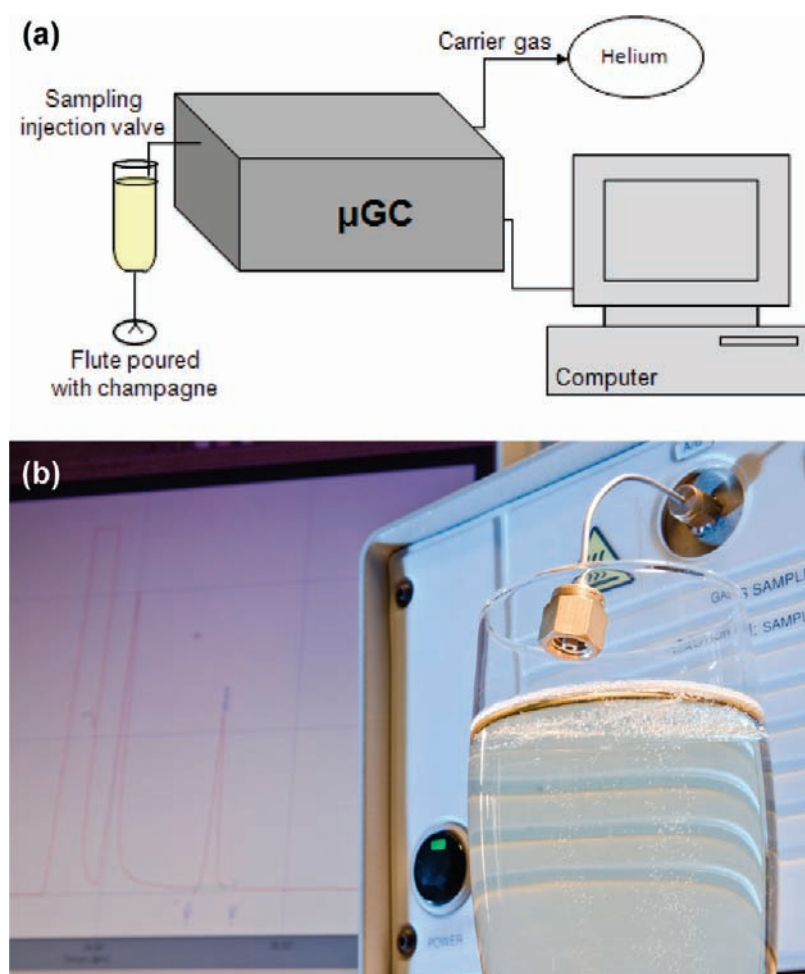


Figure 2. Scheme of the experimental setup used to simultaneously quantify the concentration of gaseous CO₂ and ethanol above a flute poured with champagne (a) and detail of the injection valve sampling gases in the headspace above the flute (b). The photograph was taken by Hubert Raguet.

ethanol concentration all along the analysis, from 0.4 to 0.14% of ethanol. Close to the edge of the flute, the concentration of ethanol keeps roughly constant (from 0.6 to 0.5 %). Moreover, it is worth noting that sampling close to the edge of the flute presents less dispersed values of both gaseous ethanol and CO₂ than sampling above the center of the flute. Indeed, the center of the flute might be less isolated from air movements in the room than the edge of the flute, thus leading to more variation of ethanol and CO₂ concentrations above the center of the flute. Therefore, it is worth noting that the headspace close to the edge of the flute is richer in vapors of ethanol than any that are far from any boundary above the center of the flute. We are therefore logically tempted to wonder why such differences exist between the behavior of gaseous ethanol and CO₂, depending on whether the sampling valve stands above the center or close to the edge of the flute. We propose an explanation based on a phenomenon commonly known as tears of wine, which is related to the formation and flow of wine drops on the internal walls of a glass.^{36,37}

Far from any myth often linked to this observation, a clear explanation can be given with the knowledge of some chemical properties of the water–ethanol mixture. Since pure water has a much higher surface tension than ethanol (≈ 72 and ≈ 23 mN/m at 20 °C, respectively), a mixture of water and ethanol, such as

wine, has a lower surface tension than that of pure water. When ethanol, which is more volatile than water is, evaporates from the thinner region of the meniscus on the glass wall, a surface tension gradient is generated. This surface tension gradient (upwardly directed) forces the liquid phase to spontaneously climb along the glass wall, thus forming a thin film of wine.^{36,37} The film stops at a certain height (determined by the balance between surface tension gradient and gravity), where it accumulates into the form of drops which, when large enough, roll downward under the action of gravity, as seen in Figure 5. Because the surface tension gradient is kept by continuous evaporation of ethanol from the film, the upwardly directed wine flow self-propels until it finally stops after complete evaporation of the liquid. Such a phenomenon can be observed in any mixture where the more volatile compound has the lower surface tension. Tears of wine close to the glass wall therefore enhance the evaporation of ethanol compared to the evaporation of ethanol far from any boundary, which is finally consistent with the quantification of ethanol depending on the position of the μ GC sampling valve, as shown in Figure 4.

It is worth nothing that, in usual tasting conditions, the consumer rather sniffs at the edge of the glass. Therefore, we have decided to analyze CO₂ and ethanol concentrations above the champagne surface, close to the edge of the glass for the following experiments.

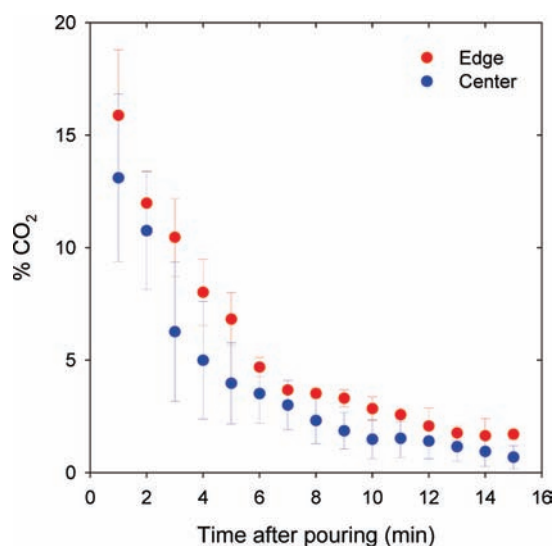


Figure 3. CO₂ concentrations in the headspace above the champagne surface, all along the first 15 min after pouring champagne, depending on the position of the sampling valve; each datum of each time series is the arithmetic average of six successive values recorded from six successive pourings; standard deviations correspond to the root-mean-square deviations of the values provided by the six successive data recordings.

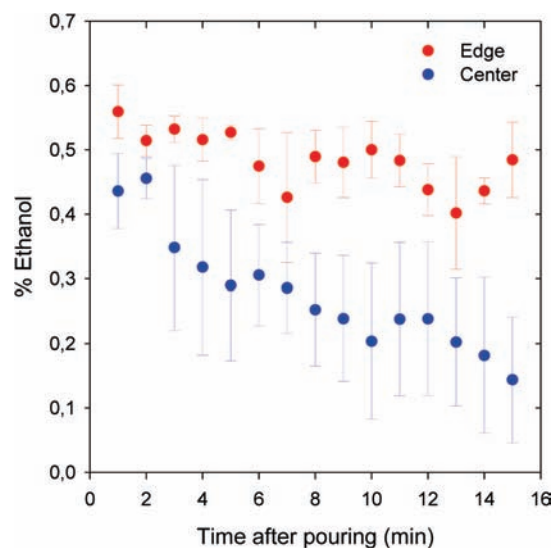


Figure 4. Ethanol concentrations in the headspace above the champagne surface, all along the first 15 min after pouring champagne, depending on the position of the sampling valve; each datum of each time series is the arithmetic average of six successive values recorded from six successive pourings; standard deviations correspond to the root-mean-square deviations of the values provided by the six successive data recordings.

Influence of Effervescence on Gaseous CO₂ and Ethanol Content Found in the Headspace above the Champagne Surface. Concentrations of gaseous CO₂ found above the wine surface were monitored during the first 15 min following pouring, as displayed in Figure 6, whether or not champagne was served into the flute showing effervescence. During the first 5 min after pouring, concentrations of gaseous CO₂ found close to the edge of the flute showing effervescence are about three times higher than those reached above the flute unable to



Figure 5. Evidence for the formation of tears (also called legs) on the wall of a glass poured with champagne; tears of champagne are expected to enhance the evaporation of ethanol close to the flute's wall. This photography was done by using the ombroscopy technique. This photograph was taken by Gérard Liger-Belair.

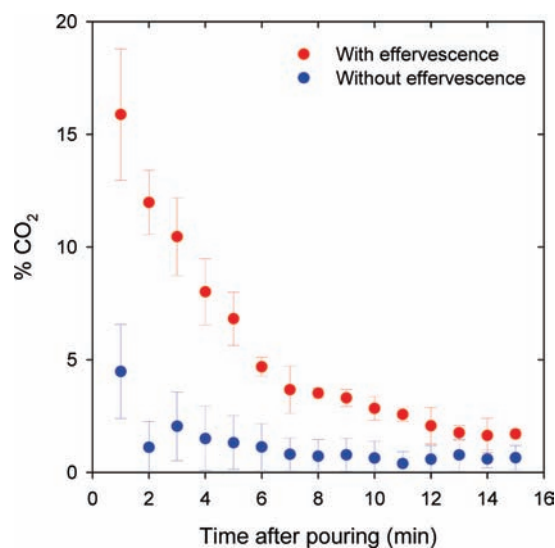


Figure 6. CO₂ concentrations in the headspace above the champagne surface, all along the first 15 min after pouring champagne, depending on whether or not the flute shows effervescence.

promote bubble formation. Indeed, in the flute showing effervescence, the CO₂ concentration reached $\approx 16\%$ 1 min after the beginning of pouring, declined to 3.5% 1 min later, and then decreased slowly until the end of analysis to reach a concentration close to 1.7%. Without effervescence, the maximum concentration of gaseous CO₂ reached 4.5% at 1 min after pouring, declined to 1.1% 1 min later, and then slowly decreased up to only 0.7% 15 min after pouring.

Simultaneously, the concentration of ethanol was monitored with the same successive samplings of the champagne headspace, analyzed with the second module of the μ GC. The successive levels of ethanol found in the headspace above both glass types, all along the first 15 min after pouring, are displayed in Figure 7. As expected, higher levels of ethanol were found, all along the analysis, above the flute showing effervescence than above the one showing no effervescence. As in the case of gaseous CO₂, the

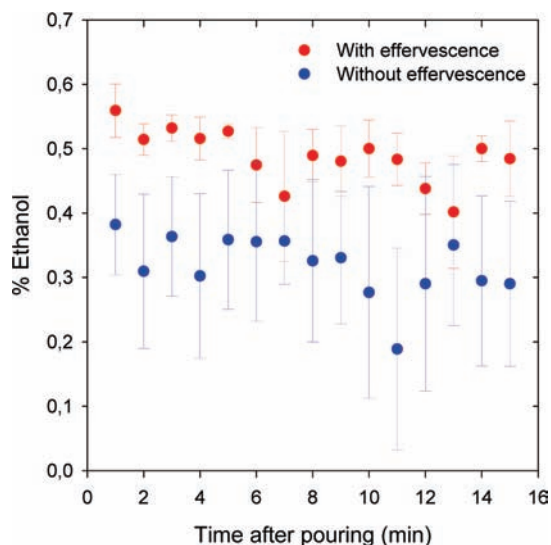


Figure 7. Ethanol concentrations in the headspace above the champagne surface, all along the first 15 min after pouring champagne, depending on whether or not the flute shows effervescence.

release of vapors of ethanol from champagne strongly depends on the presence of ascending bubbles.

Furthermore, it is worth noting from Figures 6 and 7 that the decrease of ethanol vapor concentration all along the 15 min following pouring was much less important than the decrease of gaseous CO_2 (whatever the flute type). This observation indirectly betrays the fact that the reservoir of ethanol (≈ 10 g per glass) keeps roughly constant during the first 15 min following pouring, whereas the small reservoir of dissolved CO_2 (≈ 0.7 g per glass after pouring) quickly decreases as time proceeds, thus decreasing in turn the rate at which gaseous CO_2 escapes from the champagne surface.

Molecular Mechanism Behind the Loss of Dissolved CO_2 .

Molecular diffusion is the mechanism behind the progressive desorption of dissolved gas species from the free surface area of a supersaturated liquid medium (as CO_2 molecules dissolved do from the free surface area of the champagne glass). Generally speaking, the desorption of dissolved gas species is ruled by pure diffusion or by diffusion–convection, whether the liquid medium is perfectly stagnant or in motion. In a purely diffusive case, a boundary layer depleted with dissolved gas molecules progressively expands near the free surface area so that the diffusion of gas species outgassing from the liquid medium inexorably and quickly slows down. In case of a liquid medium agitated with flow patterns, convection forbids the growing of the diffusion boundary layer by supplying the liquid near the free surface area with dissolved gas molecules freshly renewed from the liquid bulk.³⁸ Generally speaking, the higher the velocity of the mixing flow patterns, the thinner the thickness of the diffusion boundary layer and finally the higher the volume fluxes of gas species outgassing from the supersaturated liquid medium.

In the flute showing no effervescence, after the few tens of seconds following turbulences of the pouring process, champagne can be considered at rest. CO_2 molecules therefore slowly escape by pure diffusion. In the flute showing standardized effervescence, champagne is far from being stagnant, all along tasting. Actually, CO_2 bubbles nucleating and detaching from the ring-shaped engraving are driven by buoyancy. As they rise

through the liquid medium, bubbles act as exterior shear stresses on the surrounding fluid and induce the formation of large scale flow patterns, as already shown in previous papers.^{10,11} The desorption of CO_2 molecules outgassing from the champagne free surface area is therefore definitely under the influence of the mixing flow patterns found below the free surface and therefore obeys the laws of diffusion–convection which strongly increase the rate at which dissolved gas species escape from the liquid medium, as clearly shown in Figures 6 and 7.

In conclusion, the μGC technique proved to be a novel, rapid, and nonintrusive technique aimed to simultaneously access, in tasting conditions, the gaseous CO_2 and ethanol content found in the headspace above a glass poured with champagne. Effervescence was found to enhance the release of both gaseous CO_2 and vapors of ethanol above the champagne surface, thus confirming experimentally, and for the first time, a close link between ascending bubbles and the rate at which dissolved CO_2 and ethanol escape from the liquid phase. Moreover, since a close link between effervescence and ethanol release was evidenced, we are also tempted to extend our conclusions to the release of the other VOCs found in champagne and sparkling wines. The μGC technique presented here might therefore be used in order to quantify some other VOCs and progressively unravel the aromatic chemical headspace above a glass poured with champagne or sparkling wine, in real tasting conditions, by examining the influence of various parameters, such as the wine temperature and the glass shape, for example.

Furthermore, the conclusions of the present article could also be extended to alcoholic fermentation, which transforms the grape juice into wine in open tanks. Actually, it has long been known that the CO_2 production during alcoholic fermentation, into the form of myriad ascending bubbles, is responsible for the loss of up to 80% of the VOCs found in wines.³⁹ We could therefore imagine lowering the loss of VOCs during the fermentation process (monitored by μGC) by lowering the number of bubbles produced (and therefore their mixing effect) in the tank or by running fermentations at a constant CO_2 production rate.⁴⁰

■ ASSOCIATED CONTENT

S Supporting Information. Additional figures showing detailed information on calibration and a comparison between two champagne vintages. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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