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Recent Progress in the Analytical Chemistry of Champagne and Sparkling Wines

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Abstract

The strong interplay between the various parameters at play in a bottle and in a glass of champagne or sparkling wine has been the subject of study for about two decades. After a brief overview of the history of champagne and sparkling wines, this article presents the key steps involved in the traditional method leading to the production of premium modern-day sparkling wines, with a specific focus on quantification of the dissolved CO_2 found in the sealed bottles and in a glass. Moreover, a review of the literature on the various chemical and instrumental approaches used in the analysis of dissolved and gaseous CO_2, effervescence, foam, and volatile organic compounds is reported.

1. INTRODUCTION

Today, after more than three centuries and following continuous refining, champagne has become the most renowned French sparkling wine, praised worldwide for the fineness of its bubbles (1). Champagne and sparkling wines are elaborated through the same traditional method under high pressure from carbon dioxide (CO_2), as gas-phase CO_2 forms together with ethanol during a second in-bottle fermentation process promoted by adding yeasts and a certain amount of sugar in bottles hermetically sealed with a crown cap or cork stopper (2).

In sparkling beverages in general, and in champagne and sparkling wines in particular, the level of dissolved CO_2 found in the liquid phase is indeed a parameter of paramount importance because it is responsible for the visually appealing and very much sought-after repetitive bubbling process (the so-called effervescence). Another important visual attribute of champagne and sparkling wines, which has been thoroughly investigated over the past decades, is their foam quality, which is also dependent on the level of dissolved CO_2 (among many other parameters). Moreover, dissolved CO_2 is also responsible for the very characteristic tingling sensation in the mouth (3). Dissolved CO_2 acts on both trigeminal receptors (4–8) and gustatory receptors found in the oral cavity, via the conversion of dissolved CO_2 to carbonic acid (9, 10). Furthermore, the action of bursting CO_2 bubbles and subsequent projection of fast-traveling tiny droplets of wine were found to enhance the evaporation of volatile organic compounds (VOCs) dispersed in the liquid phase (11–13). Before going into more detail, suffice it to say that the presence of dissolved and gaseous CO_2 in glasses of champagne and sparkling wines largely impacts taste by modifying the neuro-physico-chemical mechanisms responsible for aroma release and flavor perception.

A better understanding of the strong interplay between the various parameters at play in a single glass of bubbly has been the subject of study for about two decades. After a short overview of the history of champagne and sparkling wines, this tutorial review presents the key steps involved in the traditional method leading to the production of premium sparkling wines that are supersaturated with dissolved CO_2 after refermenting the blends of still base wines in sealed bottles. Finally, a review of the literature on the various chemical and instrumental approaches used in the analysis of dissolved and gaseous CO_2, effervescence, foam, and VOCs is reported.

2. A BIT OF HISTORY

Many French regions claim to have made the very first sparkling wine, but the records are either ambiguous or unclear, as reported by Phillips in his latest book (14). The first bubbly is often wrongly attributed to Dom Pierre Pérignon, a monk appointed as the cellar master of the Abbey of Hautvillers, a small village in the region of Champagne (France), from 1668 to his death in 1715. On drinking a wine made sparkling by accident for the first time, he is said to have exclaimed, "I am drinking the stars!" (1). Nevertheless, it is now generally accepted that much of this story is indeed pure fiction. Stevenson (15) reported that the oldest recorded sparkling wine is Blanquette de Limoux, which was apparently invented in 1531 by Benedictine monks in the Abbey of Saint-Hilaire, near the French city of Carcassonne. They would have achieved this by bottling a still wine with residual sugars before alcoholic fermentation had ended.

The origin of champagne and sparkling wines as we know it today seems to date back to the early 1660s (16–18). In December 1662 (i.e., six years before Dom Pérignon became the cellar master of the Abbey of Hautvillers), an Englishman called Christopher Merret presented a paper on making sparkling wine to the newly formed Royal Society of London. He noted that adding sugar to barrels of still wines not only increased their alcohol content but also made them slightly

effervescent (18). As first reported scientifically by Merret, refermenting a wine in a closed space is indeed the key step that produces the delicate sparkle.

Champagne and sparkling wines elaborated through the same traditional method indeed mainly differ from still wines in their amount of dissolved CO_2 achieved through a second fermentation process undergone in sealed bottles. This method, developed and perfected in the Champagne region after more than three centuries of technical improvements and constant refining, has been progressively used throughout the entire world. Today, sparkling wines produced as such are labeled *méthode traditionnelle*. Indeed, many Italian, Spanish, North American, Brazilian, Australian, and South African sparkling winemakers use this method to elaborate their premium sparkling wines. This method involves several distinct key steps described below.

3. FROM HARVEST TO THE SEALED BOTTLE: THE *MÉTHODE TRADITIONNELLE* IN A FEW KEY STEPS

3.1. The First Alcoholic Fermentation

Three grape cultivars are grown in the 33,821 hectares of Champagne vineyards: Chardonnay (a white grape), Pinot Noir, and Meunier (both dark grapes). Until the early 2000s, grapes were usually harvested around mid-September. Nevertheless, for several years now, grapes are more often harvested around early September or even the end of August, as in the past few years, probably due to global warming (1). After manual harvesting, the grapes are pressed to release the juice, called grape must. After pressing, the must is transferred into open vats where yeast (*Saccharomyces cerevisiae*) is added. The key metabolic process during winemaking is alcoholic fermentation (i.e., the conversion of sugars into ethanol and gas-phase CO_2 by yeast), as described by the following relationship:

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2. \qquad 1.$$
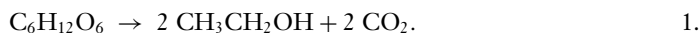
The process was first scientifically described by Joseph Louis Gay-Lussac in 1810, when he demonstrated that glucose was the basic starting point for producing ethanol (19–22). According to the equation, the amount of sugar found in the must determines the final level of ethanol after fermentation is achieved. In cool climates, such as Champagne, Alsace, and Germany (and even England more recently), where the vines struggle to ripen their grapes, sugar levels are indeed relatively low. In Champagne, for example, the must typically holds about 150 grams per liter (g L^{-1}) of sugars. Following Equation 1, with a must holding about 150 g L^{-1} of sugars, the wines often only reach 8–9% ethanol by volume after the first alcoholic fermentation is achieved. This level of ethanol is indeed insufficient to produce fine sparkling wines, such as those produced in the Champagne area. Under such circumstances, winemakers add sugar to the juice in a process called chaptalization [after Jean-Antoine Chaptal (1756–1832) who suggested the process]. Chaptalization involves adding pure cane or beet sugar to the must extracted from the grapes. Ideally, the first alcoholic fermentation should produce a base wine with between 10.5 and 11.5% alcohol (19–22). However, during exceptionally hot and sunny years (increasingly frequent due to global warming), the grapes have sugar contents high enough to reach the desired level of ethanol after the first alcoholic fermentation. Under such conditions, chaptalization may be unnecessary.

3.2. The Art of Blending

Because it is rare that a single base wine of a single vintage, vineyard, and grape variety will provide the perfect balance of flavor, sugar content, and acidity necessary for making a fine champagne or

sparkling wine, winemakers will often mix several different still (base) wines to create a single base wine. This is called the *assemblage* (or blending) step (1, 2). It is carried out shortly after the first alcoholic fermentation is complete. In Champagne, a cellar master will sometimes blend up to 80 different wines from various grape varieties, vineyards, and vintages to produce a single cuvee. The blend then undergoes a second in-bottle alcoholic fermentation (called *prise de mousse*), which is indeed the key step in transforming a still wine into a sparkling wine.

3.3. The *Prise de Mousse*: A Second Alcoholic Fermentation in Sealed Bottles

Once the blend of still base wines is created, sugar (classically about 24 g L^{-1}) and yeast are added. The blend is put in thick-walled glass bottles and sealed with crown caps or premium natural cork stoppers (most often for prestige cuvees). The bottles are then placed in a cool cellar (12–14°C), where the blend is allowed to slowly ferment for a second time, producing ethanol and CO_2 again. Following Equation 1, adding 24 g L^{-1} of sugar to the blend leads to the production of 8.8 g of CO_2 (i.e., 0.2 mol) in every standard 750-mL bottle during the *prise de mousse*. Due to the molar mass of CO_2 (44 g mol^{-1}), and the molar volume of an ideal gas (close to 24 L mol^{-1} at 12°C), it can be deduced that close to 5 L of gas-phase CO_2 are physically trapped into a single 750-mL bottle (1, 2). Moreover, the added sugar also leads to the production of 12.3 g of ethanol (per liter of wine) within each bottle. This gain of ethanol increases the ethanol content up to about 12.5% by volume.

During the second in-bottle fermentation process, the bottles are sealed so that gas-phase CO_2 cannot escape and progressively dissolves into the wine. Because the capacity of CO_2 to become dissolved in wine is ruled by the so-called Henry's law equilibrium, the concentration C_L of dissolved CO_2 in the liquid phase is proportional to the pressure of gas-phase CO_2 in the headspace of the sealed bottle. Therefore, the following relationship classically applies (23):

$$C_L = \frac{n_L}{V_L} = k_H P, \qquad\qquad 2.$$

with n_L being the mole number of dissolved CO_2 in the liquid phase, V_L the volume of the liquid phase in the sealed bottle, k_H the strongly temperature-dependent Henry's law constant of gas-phase CO_2 in the liquid phase (i.e., its solubility), and P the partial pressure of gas-phase CO_2 in the sealed bottle.

In the sealed bottle, a volume V_G of gas phase (the headspace) cohabits with the volume V_L of wine (i.e., the liquid phase), as exemplified in the scheme displayed in **Figure 1**. For the sake of simplicity, we suppose that both volumes remain constant during the *prise de mousse* (i.e., minute changes of the liquid volume due to the progressive dissolution of CO_2 are neglected). In the pressure range of interest (a few bars), we may safely predict that the gas phase is ruled by the ideal gas law. Thus,

$$PV_G = n_G RT, \qquad\qquad 3.$$

with T being the wine temperature (in K), n_G the number of moles of gas-phase CO_2 in the bottle headspace, and R the ideal gas constant (8.31 J K^{-1} mol^{-1}).

Moreover, in the bottle hermetically sealed with a crown cap or cork stopper, the total CO_2 mole number produced during the *prise de mousse* (i.e., n_T) is a conserved quantity that decomposes into n_G moles in the gaseous phase and n_L moles in the liquid phase. Therefore,
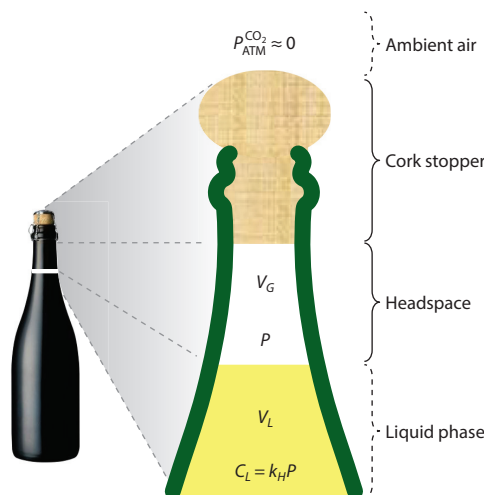
$$n_T = n_G + n_L. \qquad\qquad 4.$$

Figure 1

Schematic of a corked bottleneck with a compilation of the various parameters involved in the thermodynamic equilibrium of dissolved and gas-phase CO_2 in the sealed bottle, with C_L being the concentration of dissolved CO_2 in the liquid phase, V_L the volume of the liquid phase, k_H the Henry's constant of gas-phase CO_2 in the liquid phase, P the partial pressure of gas-phase CO_2 in the sealed bottle, V_G the volume of gas phase in the sealed bottle (i.e., the headspace), and the subscript ATM referring to the atmosphere.

By combining Equations 2–4, the following relationship was determined for the concentration of dissolved CO_2 found in the liquid phase after the *prise de mousse* (subscript *PDM*) was achieved (23):

$$C_{PDM} = k_H P_{PDM} \approx \frac{n_T k_H RT}{V_G + k_H RT V_L},$$

5.

with P_{PDM} being the partial pressure of gas-phase CO_2 in the headspace (expressed in Pa), and k_H being conveniently expressed in mol m^{-3} Pa^{-1}.

Thermodynamically speaking, in champagne and sparkling wines, the temperature dependence of k_H can be conveniently expressed with a Van't Hoff–like equation as follows:

$$k_H(T) = k_{298K} \exp\left[-\frac{\Delta H_{\text{diss}}}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right],$$

6.

with k_{298K} being the Henry's law constant of dissolved CO_2 (its solubility) at 298 K ($\sim 2.75 \times 10^{-4}$ mol m^{-3} Pa^{-1}), and ΔH_{diss} being the dissolution enthalpy of CO_2 molecules in the liquid phase ($\sim -24{,}800$ J mol^{-1}) (24).

By following Equation 5 combined with Equation 6, at a cellar temperature of 12°C, for standard bottles with $V_L = 75$ cL, a gaseous volume in the headspace of $V_G = 25$ mL, and a total number of CO_2 moles trapped per bottle $n_T \approx 0.2$ mole, a theoretical concentration of dissolved CO_2 close to 12 g L^{-1} forced by a pressure of gas-phase CO_2 close to 6 bar is to be expected after the *prise de mousse* is achieved.

3.4. Aging on Lees, Riddling, and Disgorging

In champagne, the second in-bottle fermentation is followed by a minimum aging period of 15 months in contact with dead yeast cells (a process called aging on lees). The yeasts undergo autolysis during this aging period. During autolysis, the yeasts release different compounds that modify

the wine's organoleptic properties, contributing roundness and its characteristic aroma and flavor (25, 26). More details about the chemical and biochemical features involved in sparkling wine production (from a traditional method to an improved winemaking technology) can be found in two reviews (27, 28).

After aging on lees, the procedure developed to remove the dead yeast cells from the bottle is known as *remuage*, or riddling. The process of riddling involves placing the bottles in specially designed racks that keep their necks tilted downward (19–22). This titling forces dead yeast cells into the necks of the bottles. The bottles then undergo disgorging. The necks of the bottles are frozen, creating a small ice plug that traps the sediment of dead yeast cells. The caps or corks are removed, and the plug of dead yeast cells next to the cap is ejected. A specific dosage, consisting of a mixture of sugar and aged wine, is then added to replace the bit of wine lost during disgorging. The wide variation in the levels of sweetness of a champagne—from *Brut nature* (very dry) to *Doux* (very sweet)—depends on the amount of sugar added at this step (19–22). It is worth noting that the volume of gas-phase CO_2 under pressure in the bottle headspace is inevitably lost at this step. The partial pressure of gas-phase CO_2 (initially found in the sealed bottle) therefore falls. The thermodynamic equilibrium of CO_2 is broken, but the bottle is then quickly recorked with a cork stopper. Dissolved and gas-phase CO_2 therefore quickly recover Henry's equilibrium, but with a newly defined total number of CO_2 moles in the recorked bottle (namely n_T^{CB}) equivalent to

$$ n_T^{CB} = n_T - n_G \approx n_T - \frac{P_{PDM} V_G}{RT}. \qquad 7.$$

After disgorging and recorking, the newly recovered equilibrium pressure of gas-phase CO_2 is therefore accessed by replacing n_T in Equation 5 with the newly defined total number of CO_2 moles in the corked bottle n_T^{CB}, defined in Equation 7. Accordingly, the newly subsequent concentration of dissolved CO_2 in the recorked bottles was theoretically determined as follows (23):

$$ C_{CB} = k_H P_{CB} \approx \frac{n_T k_H^2 (RT)^2 V_L}{(V_G + k_H RT V_L)^2}. \qquad 8.$$

Finally, by applying the latter equation, it can be concluded that the disgorging step slightly decreases the concentration of dissolved CO_2 in the liquid phase from about 12 g L^{-1} (after the *prise de mousse* is achieved) to about 11.5 g L^{-1} (after disgorging). As far as the level of dissolved CO_2 has to be accurately determined, the disgorging step must therefore be carefully taken into account.

Concentrations of dissolved CO_2 in a liquid phase can be easily accessed by using carbonic anhydrase (29), which is the official method recommended by the OIV (International Organisation of Vine and Wine) for measuring dissolved CO_2 in champagne and sparkling wines (30). Numerous experiments with early disgorged champagne bottles (having achieved their *prise de mousse* with 24 g L^{-1} of sugar) confirmed that the dissolved CO_2 concentration found in freshly opened 750-mL bottles is classically on the order of 11.5 g L^{-1} (31–35) and therefore in good agreement with the theoretical level of dissolved CO_2 modeled by Equation 8.

3.5. Chemical Composition and Viscosity

From the chemical point of view, after the *prise de mousse* is achieved, champagne and sparkling wines produced through the *méthode traditionnelle* can be viewed as multicomponent hydroalcoholic solutions, supersaturated with dissolved CO_2, with a density close to unity, a surface tension of $\gamma \approx 50$ mN m^{-1} and a viscosity close to 1.5–1.6 cP (mPa·s) (~50% larger than that of pure water because the liquid phase contains ~12.5% ethanol by volume) (2). In a wide range of temperatures

Table 1 Average chemical composition of a standard commercial *Brut*-labeled Champagne wine after a *prise de mousse* classically achieved with 24 g L^{-1} of sugar (37)

Compound	Concentration
Ethanol	~12.5% vol
Dissolved CO_2	~11.5 g L^{-1}
Glycerol	~5 g L^{-1}
Tartaric acid	~2.5–4 g L^{-1}
Lactic acid	~4 g L^{-1}
Sugars	6–12 g L^{-1}
Proteins	5–10 mg L^{-1}
Polysaccharides	~200 mg L^{-1}
Polyphenols	~100 mg L^{-1}
Amino acids	0.8–2 mg L^{-1}
Volatile organic compounds	~700 mg L^{-1}
Lipids	~10 mg L^{-1}
K^+	200–450 mg L^{-1}
Ca^{2+}	60–120 mg L^{-1}
Mg^{2+}	50–90 mg L^{-1}
SO_4^{2-}	~200 mg L^{-1}
Cl^-	~10 mg L^{-1}

from approximately 2°C to 22°C, the strongly temperature-dependent viscosity of a typical *Brut*-labeled champagne was measured with a standard Ubbelohde capillary viscometer (with samples of champagne first degassed) (36).

The average chemical composition of a typical *Brut* champagne wine is displayed in **Table 1** (37). *Brut* is indeed the most commonly consumed champagne style today (i.e., a Champagne wine with relatively low levels of sugar in the range of 6–12 g L^{-1}), although throughout the entire nineteenth century and into the early twentieth century, champagne was generally much sweeter than modern-day Champagne wines (38).

3.6. The Impact of Prolonged Aging on Lees on Dissolved CO_2

A misconception still lingers in the minds of some wine consumers that champagne and sparkling wines should not age much after this minimum period of 15 months in contact with dead yeasts. It is largely a myth and is certainly incorrect as far as the best cuvees are concerned. During prolonged aging on lees in contact with the dead yeast cells, complex chemical reactions take place, which bring complex and very sought-after aromas to champagne (25–28). Old vintages of the finest cuvees can even age on lees for several decades in bottles sealed with premium natural cork stoppers because of their remarkable impermeability to liquid and air, thus keeping the wine from oxidation (39, 40). Nevertheless, cork is a porous material with regard to gas transfers. As a result, gas species present on either side of the cork slowly diffuse through the cork stopper, along their respective inverse partial pressure gradients (41). In the past few years, different techniques issued from food packaging and wine analysis have been developed to measure gas permeation through various wine closures, including cork stoppers (42–49). Recently, X-ray tomography was demonstrated to be useful as a nondestructive technique for the visualization and identification of cork internal defects that could increase the risk of wine leakage, as well as the transfer of gas species through cork stoppers (50–52).
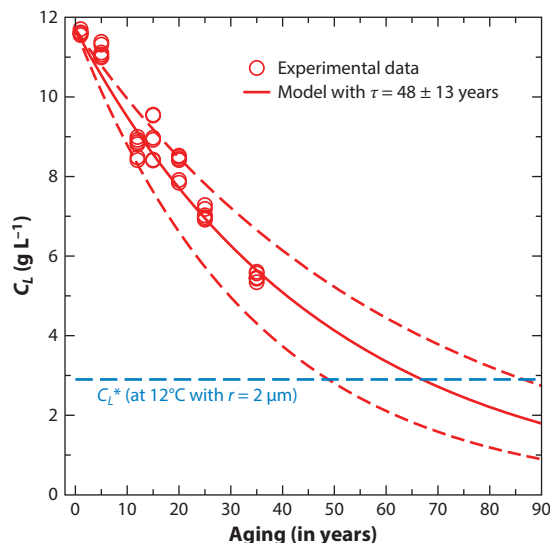
Figure 2

Concentrations of dissolved CO_2 found in the seven various vintages having experienced increasing periods of aging on lees (*red circles*) compared with an exponential-decay type model detailed in Reference 54, with a timescale of $\tau = 48 \pm 13$ years (*red solid* and *dashed lines*). The horizontal blue dashed line is the critical concentration of dissolved CO_2 below which bubbling becomes thermodynamically impossible (at a tasting temperature of 12°C, from typical bubble nucleation sites with radii of curvature on the order of 2 μm), as described in detail in Reference 56.

After the in-bottle fermentation, because the partial pressure of gas-phase CO_2 below the cork stopper reaches values close to 6 bar (at 12°C), gas-phase CO_2 can therefore slowly diffuse through the cork stopper, thus decreasing the level of dissolved CO_2 found in the liquid phase during prolonged aging on lees, as first observed by Liger-Belair & Villaume (53). Measurements of dissolved CO_2 were conducted on an outstanding vertical collection of seven vintages from a prestige cuvee showing increasing periods of aging on lees (namely 1, 5, 12, 15, 20, 25, and 35 years, respectively) (54). A classical amount of 24 ± 0.5 g L^{-1} of sugar was added in the blend to promote the *prise de mousse* of the seven various vintages. During the *prise de mousse* and aging on lees at 12°C, bottles were sealed with traditional premium cork stoppers (Amorim & Irmãos, Portugal). As shown in **Figure 2**, a global decrease in dissolved CO_2 was evidenced during aging on lees, with losses on the order of 6 g L^{-1} experienced by the oldest vintage after 35 years of aging. The losses of dissolved CO_2 evidenced for this prestige cuvee during aging on lees are indeed well described by an exponential decay-type model, with a timescale of $\tau = 48 \pm 13$ years (54).

Recently, the diffusion of gas-phase CO_2 through macro- and microagglomerated cork stoppers for champagne and sparkling wines was studied by a manometric technique (55). The results show that a small cork particle size, a high adhesive content, and a high level of cork compression favor the gas barrier properties of the cork stopper. Although the cork discs placed at one end of the stopper (in contact with the wine) present no resistance to gas transfer, the adhesive film between them constitutes the most efficient barrier to gas transfer. Satisfactorily, the global effective diffusion coefficients of gas-phase CO_2 through cork stoppers unveiled by this recent study are on the same order of magnitude as those indirectly approached by measuring the subsequent losses of dissolved CO_2 after prolonged aging on lees (53, 54).

3.7. Toward the Shelf Life Prediction of Corked Bottles of Sparkling Wines

Bubble formation is the hallmark of champagne and sparkling wines. The intensity of effervescence and the bubbles' size, two characteristics of paramount importance for sparkling wine lovers, both depend on the level of dissolved CO_2 found in the liquid phase (19–22). Nevertheless, below a critical level of dissolved CO_2, C_L^*, close to 3 g L^{-1} (at 12°C), a sparkling wine becomes thermodynamically unable to promote any bubble formation under standard tasting conditions (i.e., in a glass, with micrometric particles or glass anfractuosities acting as bubble nucleation sites), as described in detail by Liger-Belair (56).

Because the capacity of a sparkling wine to produce bubbles during tasting is crucial, the shelf life of corked bottles of sparkling wines could therefore be considered as being the time of aging needed to decrease the level of dissolved CO_2 in wine beyond the critical level on the order of 3 g L^{-1}. The precise knowledge of the subsequent diffusion coefficient of gas-phase CO_2 through the cork stopper used to seal a bottle during aging therefore becomes crucial to be able to correctly anticipate the progressive decrease of dissolved CO_2 in a corked bottle of sparkling wine. As illustrated in **Figure 2**, by extrapolating the dissolved CO_2 data time series well beyond the range of measurement (according to the exponential decay-type model), it can thus be suggested that very long aging on lees on the order of 70 ± 20 years should be needed to decrease the level of dissolved CO_2 in this prestige cuvee below the critical concentration required for bubbling. It is noteworthy that aging on lees rarely exceeds 30–40 years, even for the most prestigious cuvees. The critical aging period below which bubbling could become impossible through the lack of dissolved CO_2 should therefore never be reached for cuvees produced in bottles with narrow bottlenecks and sealed with premium natural corked stoppers.

In 2010, an outstanding collection of champagne bottles was discovered in a shipwreck at the bottom of the Baltic Sea. These bottles, produced in the early 1840s, spent 170 years in the seawater, at a constant temperature of about 4°C. The several bottles that have been uncorked were sadly unable to create bubbles, as reported by Jeandet et al. (38). Indeed, after such a long period of time, their dissolved CO_2 content fell much below the critical concentration C_L^* required for bubbling.

4. FROM THE TASTING GLASS TO YOUR SENSES

During champagne or sparkling wine tasting, CO_2 and VOCs are continuously released from glasses and, thus, progressively change the sensory characteristics of the product, for example, the effervescence and foam collar and olfactive and gustative attributes. Monitoring both dissolved and gas-phase CO_2 stagnating in the headspace above a glass of champagne or sparkling wine, studying factors that influence foam properties, and analyzing volatile compounds of champagne and sparkling wines have received much attention in the past decade and are discussed below.

4.1. Measurement and Perception of Dissolved CO_2 in the Glass

When tasting champagne and sparkling wines, the concentration of dissolved CO_2 found in the liquid phase is a crucial parameter because it is responsible for the visually appealing and very much sought-after effervescence brought about through nonclassical heterogeneous nucleation of CO_2 bubbles (2). Moreover, the presence of dissolved CO_2 in a liquid phase acts on both trigeminal receptors (10, 57) and gustatory receptors, via the conversion of dissolved CO_2 to carbonic acid (9, 58). As the concentration of dissolved CO_2 in champagne and sparkling wines is indeed the real key to the production of bubbles, numerous studies were dedicated to the precise determination of the dissolved CO_2 content found in champagne and sparkling wines (whether in the bottle or
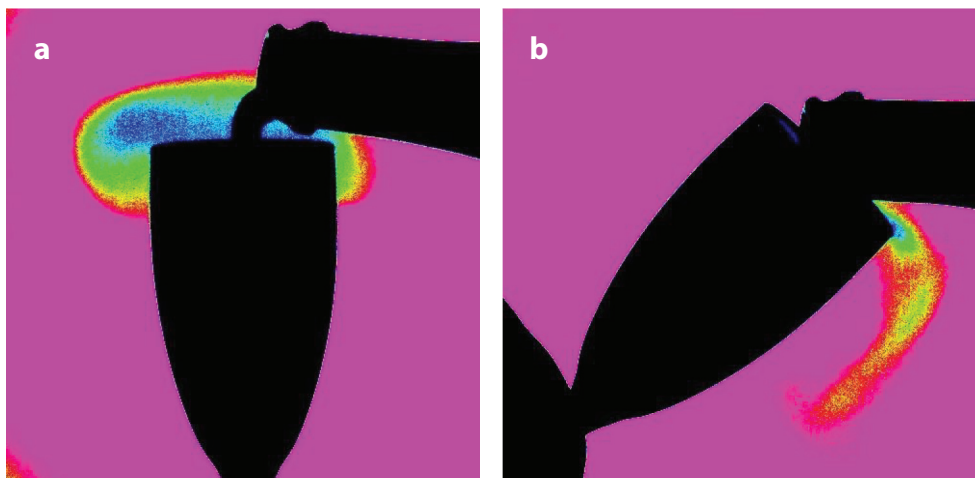
Figure 3

Snapshots created through infrared imaging, unveiling the massive losses of gas-phase CO_2 experienced by a Champagne wine during the pouring step, whether it is served in a (*a*) vertically oriented or (*b*) tilted flute. Photos provided by Université de Reims Champagne-Ardenne.

in the tasting glass). Several methods were used, from a nonintrusive one based on ^{13}C magnetic resonance spectroscopy (31) to the more usual one recommended by the OIV (30) using carbonic anhydrase (31–35). Some other intrusive methods have also been used to access the dissolved CO_2 content found in still and sparkling wines. Examples include the CarboQC (Anton-Paar) beverage carbonation meter (59, 60), the ORBISPHERE thermal conductivity sensor for CO_2 (available up to 10 g L^{-1} of dissolved CO_2) (61), and spectrophotometric detection with a flow injection (from 0.5 up to only 4 g L^{-1}) (62). Recently, a cyclic olefin copolymer–based continuous flow microanalyzer that integrates the spectrophotometric detection of CO_2 (from 0.25 to 10 g L^{-1}) was designed to analyze sparkling wines and beers (63).

Immediately after uncorking a bottle of sparkling wine, the thermodynamic equilibrium between gas-phase and dissolved CO_2 is broken, and the liquid phase becomes supersaturated with CO_2. Dissolved CO_2 must therefore progressively desorb from the liquid phase. As first observed by Liger-Belair et al. (33), massive losses of dissolved CO_2 are indeed experienced by a Champagne wine during the pouring step, because turbulences and eddies vigorously agitate the liquid phase as champagne progressively invades the glass. Immediately after pouring champagne into a glass, the dissolved CO_2 concentration (close to 11.5 g L^{-1} in the sealed bottle) falls to a level in the range of about 6 and 9 g L^{-1}, depending on several parameters such as the champagne temperature (33), bottle type (34), or glass shape (64). Nevertheless, it is worth noting that this range of dissolved CO_2 concentration of 6–9 g L^{-1} remains well beyond the minimum level C_L^* of dissolved CO_2 required for the production of bubbles in your glass (close to 3 g L^{-1} at 12°C). Moreover, the consequences of two different pouring methods were tested (33). Tilting the flute was found to have significantly less impact on the concentration of dissolved CO_2 than the former method because the "beer-like" way of serving champagne is gentler. Pouring champagne straight down the middle of a vertically oriented glass produces turbulence and traps air bubbles in the liquid, both of which force dissolved CO_2 to escape more rapidly from the liquid phase. These findings were corroborated through infrared imaging, by visualizing the cloud of gas-phase CO_2 escaping during the pouring process (33), as shown in the photographs in **Figure 3**. In order to

better preserve the dissolved CO_2 content and to prolong effervescence, champagne and sparkling wines should rather be dispensed in tilted glasses.

During the several minutes following the pouring of champagne in the glass, the roles of both temperature (65) and bubbling intensity (35) were also examined and found to be key parameters involved in the progressive losses of dissolved CO_2 from champagne glasses. Moreover, the glass shape also played a key role concerning the rate at which dissolved CO_2 escapes from champagne under standard tasting conditions (32). From a sensory point of view, McMahon et al. (66) have highlighted that a minimum concentration of 1.2 g L^{-1} of dissolved CO_2 is required to detect mouthfeel attributes of carbonation and bite by consumers of sparkling wines. Thirty minutes after having poured 100 mL of champagne in a standard narrow flute, the concentration of dissolved CO_2 still remained well beyond this minimum level of 1.2 g L^{-1} required to feel a carbonic bite (whatever the champagne temperature between 4°C and 20°C) (56). Furthermore, two recent studies have highlighted the CO_2 temporality profiles of sparkling wines (66) and beers (67) through the Temporal Check-All-That-Apply (TCATA) evaluation. The TCATA curves showed that the oral perception of carbonation (i.e., tingly sensation, carbonation bite) rose during the first 10 s of sensory evaluation, then an exponential decrease is observed (66, 67).

4.2. How Many CO_2 Bubbles Are in a Glass of Bubbly?

Thermodynamically speaking, bubble formation in a liquid phase is limited by an energy barrier to overcome. In order to nucleate and grow freely, CO_2 bubbles need preexisting gas cavities, immersed in the liquid phase, with radii larger than a critical radius on the order of several tenths of a micrometer (68). Closer inspection of glasses poured with champagne or another sparkling beverage revealed that most of the bubble nucleation sites were located on preexisting gas cavities trapped within hollow and roughly cylindrical cellulose fibers with cavity mouths of several micrometers (69, 70), as shown in **Figure 4**. In recent years, glassmakers proposed to champagne and beer drinkers a new generation of laser-etched glasses especially designed to trigger artificial standardized conditions of effervescence (56). In laser-etched glasses, bubble nucleation is most often triggered at the bottom of the glass with a ring-shaped structure constructed with adjoining laser beam impacts.

We have recently attempted to provide an accurate scientific answer to the question of how many bubbles are likely to form in a single glass of bubbly by using mathematical models that combine both the dynamics of ascending bubbles and mass transfer equations (71). As one might expect, the number of bubbles likely to form per glass depends on both the wine and the glass itself. If 100 mL of champagne (at 10°C) is poured straight down the middle of a vertically oriented flute, about one million bubbles are likely to nucleate if you resist drinking from your flute. Otherwise, champagne served more gently by pouring down the wall of a tilted flute (a technique that better preserves the concentration of dissolved CO_2 in the liquid phase) will yield tens of thousands more bubbles before it goes flat.

4.3. Monitoring of Gas-Phase CO_2 in the Headspace of a Glass

As soon as champagne or sparkling wine is poured into a glass, gas-phase CO_2 invades the headspace, thus progressively modifying the chemical space perceived by the consumer. High levels of gas-phase CO_2 can sometimes cause an unpleasant tingling sensation, perturbing both ortho- and retronasal olfactory perceptions (57). This is why monitoring as accurately as possible the level of gas-phase CO_2 in the headspace of champagne and sparkling wine glasses has received much attention in the past decade. Using micro-gas chromatography (μGC), Cilindre et al. (72)
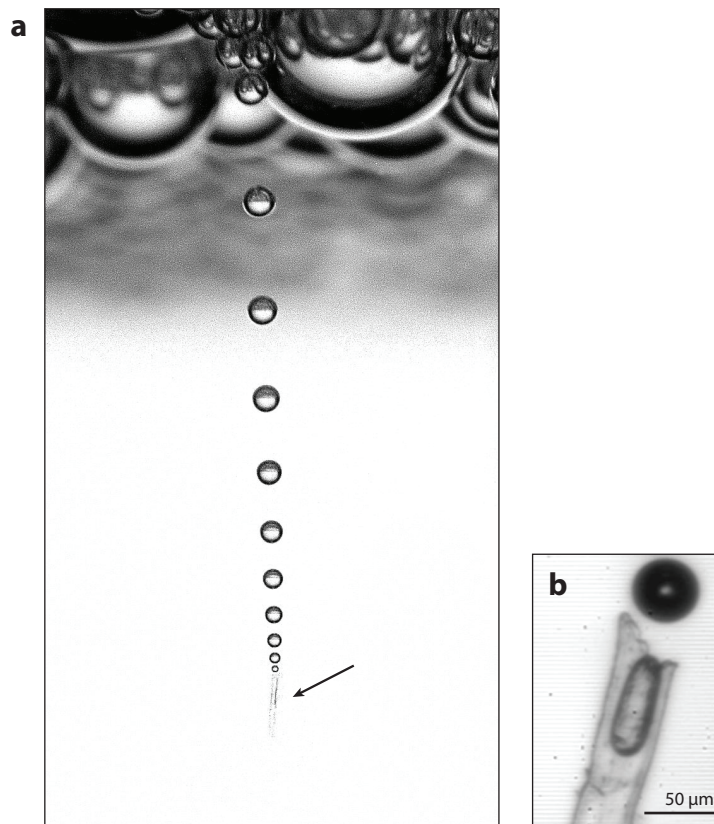
Figure 4

(*a*) High-speed photograph showing the repetitive CO_2 bubble nucleation process from the tip of a tiny cellulose fiber stuck on the wall of a champagne glass. (*b*) Micrograph showing a close-up view of the fiber. Photos provided by Gérard Liger-Belair/Université de Reims Champagne-Ardenne.

were able to measure the gas-phase CO_2 concentration in the headspace of a glass in real tasting conditions but with a relatively low time resolution (about 0.02 Hz). Indeed, the gas-phase CO_2 concentrations measured in the headspace above a flute or a coupe poured with champagne were found to progressively decline all along the first 15 min following pouring (64). Gas-phase CO_2 was found in nearly twice the concentration above the flute compared to above the coupe. Our results are consistent with sensory analyses of Champagne wines conducted by human tasters, as it is generally accepted that the smell of champagne and sparkling wines is more irritating when they are served in a narrow flute than in a wide coupe. Infrared imaging was also used to visualize gas-phase CO_2 escaping from both glass types and confirmed the tendency of flutes to hang on to concentrated quantities of gaseous CO_2 (64, 73).

More recently, several major improvements were made to an instrument named the CO_2-diode laser sensor (CO_2-DLS) (which combines two infrared lasers coupled with an optical fiber), which monitors in real time gas-phase CO_2 above carbonated beverages, with a high time resolution (about 13 Hz) (74). This instrument is based on the noninvasive technique called tunable diode laser absorption spectroscopy (TDLAS) (75), which had proved to be an effective tool to provide accurate gas-phase CO_2 concentration measurements. Moreover, compact laser sensors using new-generation diode lasers, similar to those used in the CO_2-DLS, have been developed for the
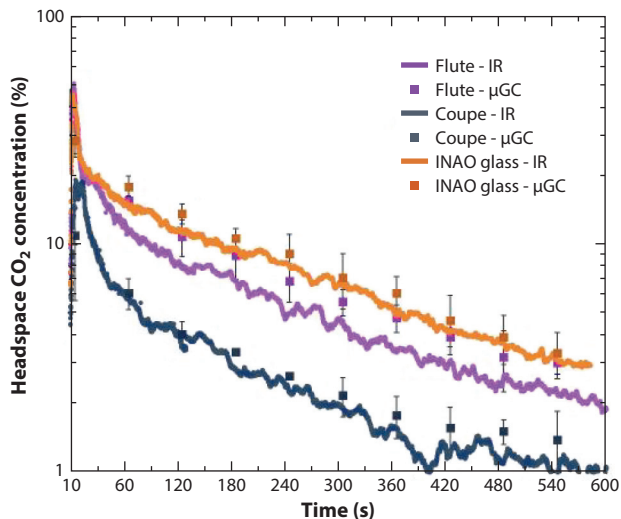
Figure 5

Evolution of gas-phase CO_2 concentration in the headspace of various champagne glasses during the 10 min following the beginning of the pouring process. Champagne (100 mL) served at 20°C was dispensed in three types of glass (flute, coupe, and standard INAO tasting glass). To trigger a standardized effervescence, all glasses were etched with 20 laser beam points of impact. The squares correspond to the micro-gas chromatography (μGC) data, with an acquisition frequency equal to 0.02 Hz, whereas the dots correspond to the infrared (IR) CO_2-diode laser sensor (CO_2-DLS) data, with an acquisition frequency equal to 13 Hz. Figure adapted with permission from Reference 77.

fine detection of gas-phase CO_2 (76). Recently, the strong impact of glass shape, volume dispensed, and intensity of effervescence on the concentration of gas-phase CO_2 found in the headspace of various champagne glasses was unveiled through a new approach combining the CO_2-DLS and μGC (77). As shown in **Figure 5**, the headspace sampled simultaneously by both instruments at 5 mm below the edge of three types of glass (the flute, coupe, and INAO tasting glass) and during the 10 min of monitoring was significantly different between the three glass types in terms of the concentration of gas-phase CO_2. In the initial stage of monitoring, a strong increase in the gas-phase CO_2 concentration until a maximum of 50% for the flute as measured by the CO_2-DLS was observed at the end of the pouring step. Then, the gas-phase CO_2 concentration followed an exponential decay-type curve and finally decreased to a minimum below 5% at the end of monitoring (77). Even more recently, key upgrades of the CO_2-DLS were made to achieve real-time monitoring of gas-phase CO_2 at various points in the whole glass headspace (78, 79). Interestingly, these instrumental results on the evolution of gas-phase CO_2 concentration in the headspace of champagne glasses follow the same trend in the sensory perception of carbonation in sparkling wines and beers (66, 67), as mentioned above.

Quite recently, the release of gas-phase CO_2 above beer glasses was monitored by a CO_2 sensor based on the solid electrolyte cell principle (80). Nevertheless, the volume fraction of gas-phase CO_2 measured by this instrument ranged between 4×10^{-4} and 10^{-2}, which is much lower than the volume fractions of gaseous CO_2 typically found in the headspace of glasses poured with champagne or sparkling wines (72, 74, 77, 78).

Finally, it is noteworthy that the nasal irritation from CO_2 might be perceived from a concentration of 35.5%, as determined by Wise et al. (81). As seen in **Figure 5**, this concentration was reached at 5 mm below the edge of the flute and the standard INAO tasting glass during

the first few seconds following pouring, for a champagne served at 20°C. But a wider glass and a lower serving temperature will tend to significantly reduce the level of gas-phase CO_2 found in the headspace of the glass and therefore the risk of nasal irritation (77).

4.4. Monitoring Effervescence and Foam of Champagne and Sparkling Wines

It is worth noting that the concentration of dissolved CO_2 is a critical parameter in the ongoing natural effervescence process, which takes place in glasses served with a champagne or sparkling wine (2). Both the bubble size at the air–liquid surface and the frequency of bubble nucleation in the glass were found to increase with the level of dissolved CO_2 found in the liquid phase (24, 36). Thus, when the wine contains more dissolved CO_2 after pouring, the effervescence and foam will be more generous and likely to be perceived by the consumer (59).

The foaming properties of champagne or sparkling wines are related to the foam formation during the pouring of wine and then to the stability of the foam in the glass during the wine tasting. Since the early 1990s, numerous studies have been devoted to depicting each and every step of the traditional method (from the grape to the bottle) and each and every compound of champagne and sparkling wines that might enhance or reduce their foaming properties. Indeed, champagne and sparkling wines contain thousands of compounds, some of which have a significant influence on bubble stability and thus on the foam quality. Most compounds have been thoroughly reviewed by Kemp et al. (82, 83) and Martínez-Lapuente et al. (84) and authors cited therein. Nevertheless, one can note that most analytical approaches to assess foam formation and stability are done under in vitro conditions and very few under real tasting conditions (17). Indeed, the most commonly used method for foam analysis of champagne and sparkling wines is the Mosalux. This method was first proposed in 1990 by Maujean et al. (85). It was adapted from older methods widely used by brewers for decades [the methods of Bikerman (86) and Rudin (87)]. This method consists of producing foam by sparging a carrier gas (usually CO_2 air or nitrogen) in a liquid column. This gas sparging method enables the measurement of three foaming parameters, including the foamability (which corresponds to the maximum height of foam), foam stability (the height at which the foam stabilizes during gas injection), and time of stability (which corresponds to the time required for the foam to disappear once the gas injection is stopped).

Nevertheless, the main drawback of this gas sparging method relies on the fact that the wine samples have to be degassed prior to an experiment. The natural yeast-fermented level of dissolved CO_2 (responsible for the "natural" bubble nucleation process, which leads to the formation of foam in glasses poured with champagne and sparkling wines) is not considered. Such experimental conditions can finally be considered as too far from the real tasting conditions of champagne and sparkling wines. Indeed, the most recent analytical methods of foaming properties try to depict foam quality of champagne and sparkling wines under real tasting conditions.

Interestingly, in 1993, computer-assisted viewing equipment (CAVE) was first developed to assess, in real tasting conditions, the foaming properties of a sparkling wine. This apparatus was originally developed by Machet et al. (88) to quantify the evolution of the collar over time, with three cameras producing multi-angle point of views. The influence of base wine filtration was first studied (89). Later, a pouring robot that allows controlled repeatable pouring of champagne bottles was added to this CAVE system (90, 91). The CAVE allowed a thorough descriptive and quantitative analysis of foam during several seconds of the pouring process, and the height of the foam collar was also monitored during 6 min following the end of pouring. Only two applications of this instrument have been published in 2001 and 2010. The first study has shown that *Botrytis cinerea* infection of grapes induced important losses of foaming properties of Champagne wines (90). Then, a comparison of the foaming properties of champagnes elaborated from different grape

varieties and with different aging periods was made through the Mosalux and CAVE methods, which led to contradictory results, as the Mosalux method is far from real tasting conditions (91). A modification of the CAVE was recently proposed by Crumpton et al. (92, 93). This is a free-pour method that analyzes, through smartphone video recordings, foam height evolution and collar behavior of sparkling wines poured in an ISO standard tasting glass (with 80 laser-etched bubble nucleation sites).

A similar instrument was also recently developed in 2016 by Lima et al. (94): a portable and automated robotic pourer called the FIZZeye-Robot. The foaming properties are measured via the collection of images captured by a digital video camera during several minutes following the pouring process. The following parameters are quantified by the FIZZeye-Robot: foam volume (V_f), foam time (F_t), average foam lifetime (L_f), average collar lifetime (C_f), and collar time (C_t). With this method, the foaming properties and foam stability of a large number of champagne and sparkling wines have been assessed and compared under standard tasting conditions (94–98).

Thus, two distinct groups of analytical approaches can be applied to the analysis of foam of champagne and sparkling wines: One group, using artificial gas sparging methods (e.g., Mosalux), is far from real tasting conditions but has been widely used to depict each and every parameter of sparkling wines that might influence their foamability and foam stability (leading to some contradictory results). The other group, using real tasting conditions (e.g., CAVE, the free-pour method, FIZZeye-Robot), is closer to the consumer tasting conditions and might replace the sensorial analysis of foam that is quite difficult to perform due to the continuous and evolving foam behavior during the following minutes after the beginning of pouring. Notwithstanding the difficulties of the sensory evaluation of effervescence and foam, in 2004, Gallart et al. (99) were among the first to propose a protocol to make a detailed descriptive analysis of these inseparable organoleptic parameters of sparkling wines. They reported that most of the quantified descriptors related to effervescence and foam were correlated positively with foam parameters obtained by the Mosalux method. Since 2010, several studies have conducted visual evaluation of foam and effervescence with their own tasting conditions (100–104). Unfortunately, none have investigated the potential relationship between foam visual descriptors and the parameters measured by recent instrumental analysis methods (e.g., CAVE, the free-pour method, FIZZeye-Robot).

After considering the numerous studies investigating the effervescence and foam quality of sparkling wines and champagne, we have decided to present a short synthesis of the main factors shown to impact their quality under real tasting conditions. **Table 2** summarizes the main factors influencing effervescence and foam quality evaluated in a glass of champagne or sparkling wine (through the CAVE or free-pour methods, FIZZeye-Robot, or visual evaluation) from recent results reported in the literature. As shown in **Table 2**, the sparkling wines produced through the traditional method together with a long aging on lees (>24 months) are positively correlated with foam and effervescence quality.

4.5. Analysis of Volatile Organic Compounds in Champagne and Sparkling Wines

Under standard tasting conditions, effervescence and CO_2 impact champagne and sparkling wine tasting in terms of aromatic perception, as collapsing bubbles release their content in gaseous CO_2 and VOCs above the wine surface. Moreover, 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 (107), as shown in **Figure 6**. Indeed, directly in a flute poured with champagne, it has been previously demonstrated through the use of ultrahigh-resolution mass spectrometry [Fourier transform ion cyclotron resonance–mass spectrometry (FT-ICR-MS)] that bursting

Table 2 Main factors positively or negatively influencing the main parameters of foam and effervescence evaluated under tasting conditions by instrumental analysis methods and visual evaluation from recent results reported in the literature

Factor	Foam quality						Effervescence		Analytical method	Samples (aging on lees)	Reference
	Foamability	Foam surface	Foam stability	Collar height	Collar surface	Collar stability	Bubble size	Bubble rate			
Grape variety											
Chardonnay	ND	ND	ND	ND	Increase	Increase	ND	ND	Collar extent pictures	Champagne, white	105
	Increase	ND	Increase	Increase	ND	ND	ND	ND	CAVE	Champagne, white	91
Verdejo	Increase	Increase	ND	Increase	ND	ND	ND	ND	Visual evaluation	SW, white and rosé, (0–9 months)	101
Prieto Picudo	Increase	Increase	ND	Increase	ND	ND	ND	ND			
Trepat	Normal	Full	ND	ND	Total	ND	Smaller	Slow	Visual evaluation	SW, white and rosé	103
Monastrell	Increase	Full	ND	ND	Total	ND	Smaller	Fast			
White (blend)	Normal	Full	ND	ND	Total	ND	Medium	Fast			
Production method											
TRAD	No effect	ND	ND	Increase	ND	ND	ND	ND	FIZZeye-Robot	25 SW	95, 96
Transfer	No effect	ND	ND	Lower	ND	ND	ND	ND			
Autolysis >24 months	No effect	ND	ND	ND	ND	ND	Smaller	ND			
TRAD (compared to Charmat, transfer, and carbonated)	No effect	ND	Increase	ND	ND	ND	ND	ND	FIZZeye-Robot	50 SW	98
Microencapsulated yeasts for the *prise de mousse*	Decrease	Partial	ND	ND	Partial	ND	No effect	No effect	Visual evaluation	SW, white, Riesling (6 months)	100
Mannoproteins added at tirage	No effect	Increase	ND	Increase	ND	ND	No effect	No effect	Visual evaluation	SW, white, Verdejo (9 months)	102
Aging on lees 0–12 months	No effect	ND	No effect	ND	ND	ND	No effect	No effect	Visual evaluation	SW, white, Pais (0–12 months)	104

(Continued)

Table 2 *(Continued)*

Factor	Foam quality						Effervescence		Analytical method	Samples (aging on lees)	Reference
	Foamability	Foam surface	Foam stability	Collar height	Collar surface	Collar stability	Bubble size	Bubble rate			
Chemical compounds added at disgorging step											
Alcohol	No effect	ND	No effect	Decrease	ND	ND	Bigger	ND	FIZZeye-Robot	SW, white, Chardonnay, Pinot Noir, Pinot Meunier, Pinot Gris (3 months)	97
Yeast invertase	Decrease	ND	Decrease	Increase	ND	ND	Smaller	ND			
Bovine serum albumin	Decrease	ND	Increase	Increase	ND	ND	Bigger	ND			
Mannoproteins	Increase		No effect	Increase	ND	ND	Smaller	ND			
Gallic acid	Increase		Decrease	No effect	Decrease	ND	Smaller	ND			
Asparagine	Increase		Decrease	ND	ND	ND	Bigger	ND			
Tryptophane	Decrease		Increase	Increase	ND	ND	Smaller	ND			
Yeast invertase + asparagine	Decrease		No effect	Decrease	Decrease	ND	No effect	ND			
Yeast invertase + gall	Decrease		No effect	ND	ND	ND	Bigger	ND			
Carboxymethyl cellulose	No effect		No effect	No effect	ND	ND	ND	ND	Free-pour method	SW, Seyval + Chardonnay (30 months)	92
Dosage (0–31 g L^{-1})	Decrease at 31 g L^{-1}	No effect	Decrease at 31 g L^{-1}	ND	ND	ND	ND	ND			
Sparkling wine chemical composition											
Protein content	No effect	ND	Increase	ND	ND	ND	ND	ND	FIZZeye-Robot	50 SW	95, 98
Titrable acidity	No effect	ND	Increase	ND	ND	Increase	ND	ND			94, 98
Alcohol	No effect	ND	Decrease	ND	ND	ND	ND	ND			98
Histidine	No effect	ND	Increase	ND	ND	ND	ND	ND			95, 98
Arginine	No effect	ND	Increase	ND	ND	ND	ND	ND			98
Tyrosine	No effect	ND	Increase	ND	ND	ND	ND	ND			95, 98
Asparagine	No effect	ND	Decrease	ND	ND	ND	ND	ND			95
Fatty acids	No effect	ND	No effect	ND	ND	ND	ND	ND			
Ethyl esters	No effect	ND	No effect	ND	ND	ND	ND	ND			
Wine price	Decrease	ND	Increase	ND	ND	Increase	ND	ND	FIZZeye-Robot	5 SW	94

Abbreviations: CAVE, computer-assisted viewing equipment; ND, no data; SW, sparkling wine; TRAD, traditional method.
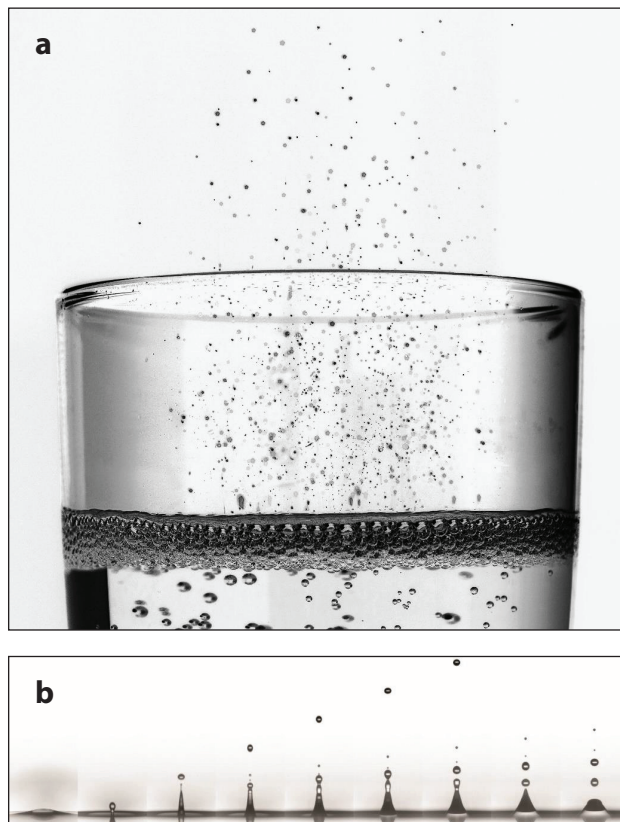
Figure 6

(*a*) Photograph revealing the myriad of tiny droplets forming a refreshing aerosol above the surface of a champagne flute and (*b*) a high-speed time sequence showing the action of a single millimetric bubble collapsing and propelling several droplets above the champagne surface. Photos provided by the Alain Cornu/Collection CIVC and Elisabeth Ghabache/Sorbonne Universités.

bubbles radiate a cloud of tiny droplets overconcentrated with tens of volatile compounds showing organoleptic interest or that are precursors of aromas (11). By drawing a parallel between the fizz of the ocean and the fizz in Champagne wines, the authors closely linked the action of 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 (11).

The link between carbonation and the release of some aroma compounds has also been highlighted in other carbonated beverages. In 2009, using a proton transfer reaction–mass spectrometric (PTR-MS) technique, Pozo-Bayón et al. (106) and Saint-Eve et al. (108) unveiled a higher release of aroma compounds under both static and dynamic ("where the headspace is diluted by air at a constant rate") conditions above carbonated waters than above still waters. This link between carbonation and the release of volatile compounds was also evidenced in model beer through in vivo experiments (109).

VOCs are low-molecular-weight compounds that can become gases or vapors at room temperature, contrary to the nonvolatile constituents corresponding to macromolecules that remain in the wine matrix (110). More than 1,000 volatile compounds might contribute to the aromatic profile of wine. The chemical classes into which the wine volatile compounds are categorized

include (in alphabetical order) acids, alcohols, aldehydes, benzene derivatives, C_{13}-norisoprenoids, esters, ketones, phenolics, polyols, pyrazines, sulfur compounds, and terpenes. Most volatile compounds of wines contribute to their aromatic profiles once their concentration in the wine is above their respective odor detection threshold. Their concentrations in champagne and other sparkling wines range from ng L^{-1} to mg L^{-1} and are dependent on grape variety, fermentative conditions, and the post-fermentative process.

4.5.1. Ethanol. Among all of the numerous VOCs found in champagne and sparkling wines, ethanol is obviously the one that is the most concentrated (around 12.5% volume). Ethanol is an effective gustatory, olfactory, and trigeminal stimulus. Recent studies have shown that variation in wine ethanol content significantly contributes to the partitioning of odorant molecules in the wine (or model wine) headspace by modification of their solubility (110–114), thus affecting the global perceived sensory attributes of alcoholic beverages, including aroma, taste, and mouthfeel, as recently reviewed by Ickes & Cadwallader (115).

The concentration of gaseous ethanol in the headspace of champagne glasses was monitored for the first time in real tasting conditions through µGC coupled with a thermal conductivity detector (during the 15 min following pouring champagne in a glass) (64, 72). Those studies have demonstrated that lowering the serving temperature tends to decrease the ethanol vapor concentrations in the headspace of the glass, whereas vapors of ethanol were found to be enhanced by the presence of ascending bubbles. This confirms instrumentally for the first time the close link between rising bubbles and the release of gaseous CO_2 and VOCs. Recently, Wollan et al. (114) demonstrated how the evaporation of ethanol from commercial wines was strongly influenced by the glass shape and by the glass headspace in particular. Ethanol vapors were also recently monitored through infrared thermal imaging with a specific wavelength filter of 1,000–1,100 cm^{-1} to discriminate fresh grapes from decayed grapes (116). This novel, rapid, and nonintrusive technique facilitates the semiquantitative analysis of vapors from ethanol solutions ranging from 10% to 70%. In the near future, it might be interesting to combine this technique with the infrared thermal imaging technique previously used to visualize gaseous CO_2 above champagne glasses (33, 64, 73).

4.5.2. Volatile aroma compounds. Champagne and sparkling wines are complex mixtures of CO_2 and VOCs that are continuously released from the liquid phase once the wine is poured into glasses and, thus, progressively change the sensory attributes of the products smelled by the consumer. Even if dissolved and gas-phase CO_2 can now be precisely quantified under various tasting conditions, VOCs contributing to the aromatic profiles of champagne and sparkling wines are not, to date and to our knowledge, analyzed and identified in the headspace of glasses under standard tasting conditions. It will thus constitute an important challenge in the future to examine the aromatic profile of these wines more precisely.

Indeed, volatile compounds of champagne and sparkling wines are usually extracted under standardized analytical conditions using specific extraction methods such as solid phase extraction (SPE) (100), solid phase microextraction (SPME), stir bar sorptive extraction (SBSE) (117), or liquid–liquid extraction (LLE) (102) coupled with analytical techniques such as gas chromatography–mass spectrometry (GC-MS), gas chromatography–flame ionization detector (GC-FID), or even two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC × GC/TOF-MS) (118, 119). Thanks to its numerous advantages in terms of rapidity, ease of use, limited toxicity, cost, and sensitivity, SPME has been widely applied to the analysis of sparkling wine aromas since its first application to the study of aroma compounds from Cavas in 1999 (120) and Champagne wines in 2003 (121).

Most analytical approaches using SPME to extract aroma compounds from sparkling wines are made in the headspace of small sealed vials containing the degassed wine. The choice of the SPME fiber type is considered as a crucial factor. Indeed, different SPME fiber coatings offer a wide range of polarities and selectivity toward volatile and semi-volatile compounds of sparkling wines. For example, the triple-phase fiber, divinylbenzene-carboxen-polydimethylsiloxane (DVB-CAR-PDMS), is well adapted for volatile and semi-volatile compounds. Other factors also influence the extraction of aromas from sparkling wines, including the wine temperature (usually set between 35°C and 55°C), extraction time (from 10 to 52 min), sample agitation, ionic strength and, finally, the headspace/liquid ratio. For details on the main applications of headspace-SPME (HS-SPME) to analyze aroma compounds in various sparkling wines produced with the traditional method in the past decade, see **Supplemental Table 1**. One can note that not a single procedure exists to extract these volatile aroma compounds by HS-SPME, thus leading to different numbers of identified (and quantified) analytes, independent of the grape variety, winemaking conditions, or aging time.

Compared with that of still wines, the sensory analysis of carbonated beverages is much more complex to perform. Independent of the glass shape or serving temperature, the headspace composition above a sparkling wine, which is perceived by the consumer, should vary significantly during the first minutes after pouring. Indeed, the gaseous CO_2 and ethanol concentrations found in the headspace above a flute poured with champagne were found to decline during the 15 min following pouring (64, 72, 77–79). Moreover, Hirson et al. (122) have clearly demonstrated the time-dependent nature of the headspace volatile composition during the tasting of a still white wine. Therefore, the aroma sensory profile of a champagne or sparkling wine will undoubtedly change under real tasting conditions. In fact, the individual's sensory perception and the acceptance of a wine are strongly influenced by the container, including its shape, color, and material properties, as well as parameters related to the wine (e.g., temperature, volume), as recently reviewed by Spence & Wan (123). Examining the volatile aromatic profiles of champagne and sparkling wines more precisely, under real tasting conditions, is thus definitely an important challenge to overcome in the future.

5. CONCLUSION

Champagne and sparkling wine tasting may be seen as the pinnacle of glamor and frivolity to many people, but it should also finally be considered as a fantastic opportunity for chemists to explore the subtle processes hidden right under consumers' noses each time they enjoy a glass of bubbly. Sparkling winemaking is a more-or-less three-centuries-old art, but the pursuit of this art can still benefit from the latest advances in science. Examining the impact of swirling the wine in the glass (as tasters usually do before inhaling the headspace of their glass) on the spatial and temporal distribution of gas-phase CO_2 and VOCs within the headspace could be the focus of future research.

DISCLOSURE STATEMENT

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