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A first step towards the mapping of gas-phase CO₂ in the headspace of champagne glasses.

Anne-Laure MORIAUX, Raphaël VALLON, Clara CILINDRE, Frédéric POLAK, Bertrand PARVITTE, Gérard LIGER-BELAIR, Virginie ZENINARI*

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Abstract

Key upgrades to a previously developed CO₂-Diode Laser Sensor (CO₂-DLS) were done to monitor as accurately as possible the level of gas-phase CO₂ in champagne glasses. The upgraded CO₂-DLS allows to access a wide range of CO₂ concentrations (10-100 %). An additional set of mirrors with two pairs of galvanometer scanners was developed in order to provide simultaneous measurements of gas-phase CO₂ concentrations in the whole glass headspace. During the five minutes after pouring, the CO₂-DLS unambiguously unveiled horizontal homogeneity in the glass headspace in terms of gas-phase CO₂ concentrations. Nevertheless, a strong vertical gradient of gas-phase CO₂ was highlighted, with ever increasing CO₂ concentrations ranging from approximately 15 % to 50 % while moving away from the glass edge to the champagne interface. This strong vertical gradient was found to persist during the five next minutes following the pouring process, but with ever decreasing CO₂ concentrations as time elapses.

Keywords: gas sensor, CO₂, diode laser spectrometry, Champagne, effervescence

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Highlights

- Key upgrades to a CO₂ – diode laser sensor for enological applications are presented.
- Two off-axis parabolic mirrors with galvanometric mirrors are dedicated to the scanning.
- Monitoring gas-phase CO₂ in the headspace of a champagne glass was done, in space and time.
- Horizontal homogeneity and vertical stratification of gas-phase CO₂ above the champagne surface were highlighted.

Abbreviations

- CO₂ : carbon dioxide
- CO₂-DLS : CO₂-Diode Laser Sensor
- VOC : Volatile Organic Compound
- TDLAS : Tunable Diode Laser Absorption Spectrometer
- FP : Fabry-Pérot
- GM : Galvanometric mirrors
- D1 : Detector #1 ; D2 : Detector #2
- FPGA : Field-Programmable Gate Array
- FSIR : Full Scale Input Range
- DDS : Direct Digital Synthesizer
- INAO : Institut National des Appellations d'Origine or National Institute of Origin and Quality

1. Introduction

Nowadays, champagne has become the most renowned French sparkling wine, praised world-wide for the fineness of its effervescence. Champagne and sparkling wines elaborated through the same traditional method are under a high pressure of 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 a cork stopper [1, 2]. This second in-bottle fermentation process forced an amount equivalent to around $11\text{-}12\text{ g} \cdot \text{L}^{-1}$ of CO_2 to progressively dissolve into the wine, according to the so-called Henry's law [1]. From a strictly chemical point of view, Champagne wines can thus be seen as multicomponent hydroalcoholic systems, supersaturated with dissolved CO_2 , with a density close to unity, a surface tension and a viscosity about 50 % larger than that of pure water (mainly due to the presence of 12-13 % v/v ethanol) [1]. 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 since it is responsible for the visually appealing, and very much sought-after repetitive bubbling process (the so-called effervescence).

During Champagne or sparkling wine tasting, gas-phase CO_2 and volatile organic compounds (VOC) invade the headspace above glasses [1], thus progressively modifying the chemical space perceived by the consumer. Gas-phase CO_2 in excess can even cause a very unpleasant tingling sensation perturbing both ortho- and retronasal olfactory perception [3]. In recent years, both glass-shape and the CO_2 bubbling rates were found to play key roles concerning the rate at which dissolved CO_2 escapes from champagne, under standard tasting conditions [4–7]. Moreover, the temperature of champagne was also found to be a key parameter as concerns the losses of dissolved CO_2 from champagne glasses [8]. For all the aforementioned reasons, no wonder that the complex interplay between the level of dissolved CO_2 found in champagne, its temperature [8], the glass shape [4, 6, 7, 9], and the bubbling rate [5], finally impacts champagne tasting by modify-

28 ing the neuro-physico-chemical mechanisms responsible for aroma release and flavour
29 perception. Following these recent highlights, monitoring as accurately as possible the
30 level of gas-phase CO₂ above glasses is therefore a challenge of importance aimed at better
31 understanding the close relationship between the release of CO₂ and a collection of various
32 tasting parameters.

33 In many fields of research, gas-phase CO₂ must be accurately monitored, such as for
34 example in the field of biology [10, 11], environmental studies [12, 13], or in medicine
35 [14, 15]. In order to measure a molecule of interest in a non-invasive way, analytical
36 methods must be used to separate, identify and quantify it. The use of sensors and the
37 development of gas-phase CO₂ analysis methods in the food industry is widespread
38 [16], particularly in the analysis of food packaging [17] and the brewing industry [18, 19].
39 For example, the RoboBEER [20], aimed at measuring the release of gas-phase CO₂ by a
40 sensor (MG-811), is based on the principle of a solid electrolyte battery. However, this
41 sensor requires calibration and heating time, and it covers a small range of gas-phase CO₂
42 concentrations, between 0.04 and 1 %. A standard microgas chromatography can also
43 be used in order to measure gas-phase CO₂ [21, 22]. This method nevertheless requires
44 a calibration and it shows a low temporal resolution between successive measurements.
45 Gas-phase CO₂ can also be detected through a hyperspectral camera [23]. The system
46 requires a light source, such as a laser diode, adapted to the wavelength of absorption of
47 the gas of interest (CO₂). This method could allow the quantification of CO₂ in a wide
48 concentration range (0 to 100 %) but also requires an upstream calibration. Finally, in
49 the field of spectroscopy, the tunable diode laser absorption spectroscopy (TDLAS) is
50 predominantly used and seems to be the best solution to monitor gas-phase CO₂ [24]. It
51 allows the measurement of gas-phase CO₂ up to 100 % without requiring any calibration.
52 Based on the TDLAS, CO₂ gas sensors have been developed for atmospheric applications
53 [25, 26], power plant exhausts [27], combustion applications [28] and exhaled human breath
54 [29]. A CO₂-Diode Laser Sensor, namely the CO₂-DLS, dedicated to monitor gas-phase

55 CO₂ in the headspace of champagne glasses was recently developed [22, 30].

56 In this paper, an upgraded CO₂-DLS aimed at recording an ever increasing amount
57 of data is presented. Upgrading the CO₂-DLS has involved the modification of both data
58 acquisition and data management. Such modifications allowed to map, in space and time
59 and for the very first time, the precise concentration of gas-phase CO₂ in the headspace of
60 a champagne glass.

61 2. Materials and methods

62 2.1. Instrument design: a new scanning part

63 In order to perform the measurement of the gas-phase CO₂ concentration at various
64 points, in the headspace of a champagne glass, for a very short time, the evolution of the
65 CO₂-DLS was required. A schematic representation of the CO₂-DLS with its new part
66 dedicated to the scanning of the headspace of champagne glasses, is presented in Fig. 1.

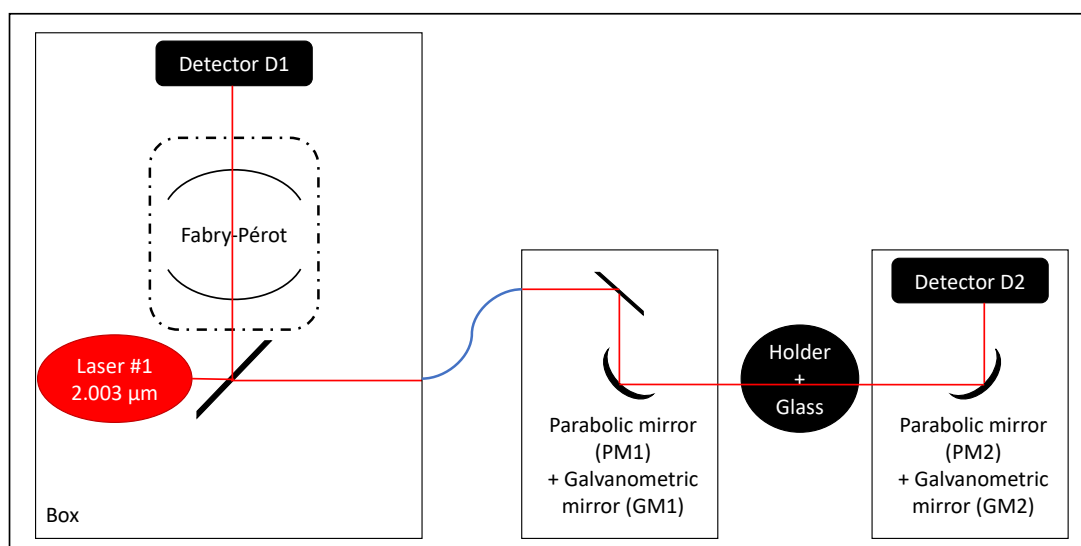


Fig. 1: Schematic representation of the optical set-up.

67 The optical part, with the laser sources and optical elements for collimation and control,
68 is identical to the one fully described in a precedent work [30]. This set-up is composed by
69 two laser diodes emitting at 2.68 μm (Nanoplus, Germany) and 2.003 μm (EP2004-0-DM,
70 Eblanaphotonics, Ireland), which allow the instrument to cover a wide range of gas-phase
71 CO_2 concentrations. The 2.003 μm laser monitors a weak CO_2 absorption line (R20 line
72 of the $(20^01)_2 \leftarrow (00^00)_1$ band of CO_2 , Intensity $1.206 \times 10^{-21} \text{ cm}^{-1} / (\text{molec} \cdot \text{cm}^{-2})$) and
73 allows to measure gas-phase CO_2 between 10% and 100%. The 2.68 μm laser monitors a
74 stronger CO_2 absorption line, allowing the measurement of gas-phase CO_2 below 15%. The
75 present work concerns the technical validation of the CO_2 -DLS with a recently developed
76 enological application part dedicated to the scanning of the glass headspace, located on
77 an independent board (3D representation in Fig. 2a). The technical validation has been
78 carried out with the 2.003 μm laser, in order to cover the largest range of gas-phase CO_2
79 concentrations, between 10 and 100 %.

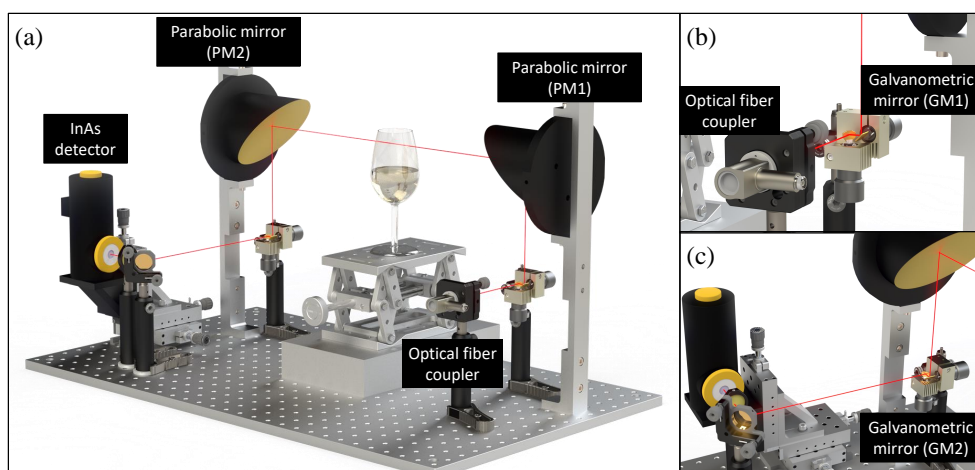


Fig. 2: Global view of the optical set-up created from SolidWorks (Dassault Systèmes, France) (a), with the red line showing the infrared beam, and panels showing both couples of galvanometric mirrors dedicated to the scanning of the glass headspace (b and c).

80 The scanning part of the CO₂-DLS includes a reflective fiber coupler red (Thorlabs Inc.,
81 USA) allowing the connection of the optical fiber, from the optical part of the CO₂-DLS,
82 and the beam collimation (Fig. 2b). A first couple of galvanometric mirrors (GM1, in
83 Fig. 2b model 6210H from Cambridge Technology, USA) is placed at the focus of an off-axis
84 parabolic mirror (PM1) to allow a laser beam translation to a set of (x,y) coordinates of
85 the scanning points in the glass headspace. In this experiment, a $\pm 1.5^\circ$ rotation angle
86 on the first mirror of GM1 allow a ± 1.5 cm beam translation on the horizontal axis (x), a
87 $\pm 1.5^\circ$ rotation angle on the second mirror of GM1 allow a ± 2.25 cm beam translation on
88 the vertical axis (y). PM1 is a 101.6 mm diameter, 152.4 mm focal length off-axis parabolic
89 mirror (model 83976, Edmund Optics, USA). Symmetrically, PM2 and GM2 (same model as
90 PM1 and GM1) allow to balance beam translation in order to detect laser light with a single
91 element cryogenic InAs photodiode (Fig. 2c). A pre-amplifier model DLPCA-200, Femto,
92 Germany) has been added after the cryogenic photodiode (Teledyne Judson Technologies,
93 USA) and the gain has been fixed at 10^6 . The use of this new detector, compared to the one
94 used in the previous set-up [30], has improved the signal quality by reducing the noise.

95 However, it can be noted that the mechanical constraints of the set-up require that
96 the laser beam goes through the focus of only one of the two mirrors of each pair of
97 galvanometric mirrors. The two couples of galvanometric mirrors are controlled each
98 by one external controller, and the motors of the x and y mirrors of each couple are
99 independent. Glasses are placed on a suitable holder (adjustable in height) between the
100 parabolic mirrors. Thus, the laser is reflected in a parallel manner by the off-axis parabolic
101 mirror (PM1) and the laser beam position is moved by GM1 while maintaining the same
102 direction. This device allows to impose a movement on the laser beam and to vary its
103 position horizontally and vertically. With the scanning part, the total optical path (optical
104 part + scanning part of the CO₂-DLS) is extended by 75 cm and the total optical of the
105 2.003 μm laser path is 175 cm. Thus the absorption by ambient CO₂ (400 ppm) over this
106 distance is less than 1% and the absorption by the ambient air can be considered as

107 negligible for the measurements realized by the laser.

108 2.2. *Upgrading data acquisition and processing*

109 The instrument is still fully managed using a laboratory made Labview software
110 (National Instruments, USA) driving a NI-7852R FPGA card (National Instruments, USA)
111 used for laser control (temperature set point, waveform generation for laser sweeping,
112 TTL trigger generation and data acquisition) and for the galvanometric mirrors engines
113 control. The FPGA card parameters used for the laser control are summarized in Table 1.
114 The corresponding input current applied to the 2.003 μm laser diode is a 90 mA peak to
115 peak sawtooth signal with an offset of 55 mA. With these parameters, the laser tuning
116 range is centered on the R20 line and is 0.75 cm^{-1} wide. The R20 line FWHM is 0.21 cm^{-1} .

Table 1: Technical characteristics and control parameters of the 2.003 μm laser.

Parameters	2.003 μm Laser @ 2.003 μm
Sample rate (kSamples/s)	1
Loop rate (kHz)	40000
DDS signal frequency (Hz)	42
Signal amplitude ramp (mV)	350
Offset ramp (mV)	350
Signal amplitude TTL (mV)	2500

117 In this update of the CO₂-DLS, the acquisition of signals is based on the use of a high
118 density digitizer (NI5105) (National Instruments, USA). Five signals are recorded : TTL
119 signal, D1 signal (Fabry-Pérot, noted FP), D2 signal (spectrum), the x mirror position of
120 GM1 and the y mirror position of GM1. The assignment of the full scale input ranges (FSIR)
121 has been adapted in function of each channel, in order to improve the saved data quality.
122 The selection of the different FSIRs is listed in Table 2.

Table 2: Assignment of the channels recorded by the acquisition card and the full scale input ranges assigned to each channel.

Channel	Recorded signal	Full scale input range (V)
0	x mirror position	10
1	y mirror position	10
2	TTL	10
3	D1 signal (FP)	2
4	D2 signal	1

123 The five channels are recorded with a frequency of $4 \cdot 10^6$ samples/s and a buffer memory
 124 system has been set up. All data, previously stored in ASCII format, are now stored in
 125 binary format to allow very high speed data transmission and to reduce the size of the
 126 generated files. The channels #0 and #1 corresponds to the positions of the mirrors x and
 127 y of GM1. The coordinate pair thus refers to a position for the measurement in the glass
 128 headspace, that is defined as a pixel. The recorded data thus correspond to a succession of
 129 files and each one of them consists of the succession of recorded channels over a regular
 130 time interval, i.e. a loop pattern, as in Fig. 3a.

131 The first step of the pre-treatment consists in rebuilding each channel recorded, as in
 132 Fig. 3b. Then, using the channels #0 and #1, the channels #2, #3 and #4 are reconstructed for
 133 each position in the glass headspace (i.e. pixel). The useful part of the signals (parts A and
 134 B on Fig. 3c) is taken to form a usable data set for each pixel. Finally, the data processing
 135 method used to obtain the gas-phase CO_2 concentration is the same as previously described
 136 by [30]. Nevertheless, the processing program has been adapted for the new binary format
 137 of the data. The measurement of the gas-phase CO_2 concentration is therefore always
 138 based on the result of a constrained non-linear fitting. An example of fitting is given in
 139 Fig. 4 which corresponds to a non-linear fitting for a spectrum of 50% of CO_2 mixture
 140 obtained with the $2.003 \mu\text{m}$ laser.

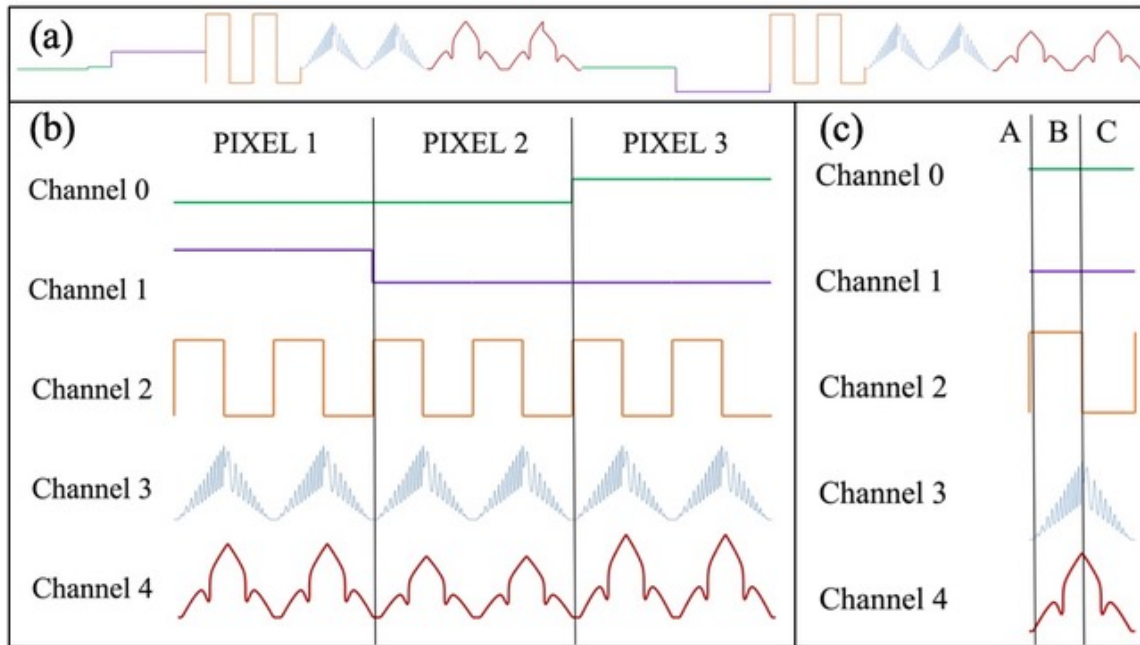


Fig. 3: Schematic representation of the signals, as recorded in the files, corresponding to successive accumulation of the 5 recorded channels (a). Schematic representation of the data recorded during the scanning of three pixels, with the position of the mirror x (Galvanometric Mirror GM1) in green on channel #0, the position of the mirror y (Galvanometric Mirror GM1) in purple on channel #1, the TTL signal in yellow on channel #2, the signal recorded by the detector D1 (Fabry-Pérot) in blue on channel #3 and the signal recorded by the detector D2 (spectra) in red on channel #4 (b). Zoom of the signals recorded during the scanning of a single pixel, in A the part below the laser threshold, in B the part used for the estimation of the intensity baseline (I_0) and for the transmitted intensity (I) and in C the part corresponding to the return of the laser at the initial frequency (decreasing part of the triangular laser control signal) (c).

141 2.3. Measurements of standard gas-phase CO_2 samples

142 A technical validation of the CO_2 -DLS, with its new part dedicated to the scanning of the
 143 headspace of a champagne glass, has been carried out. It has been highlighted, in a previous
 144 study [22], that during the pouring step, the gas-phase CO_2 concentration measured is
 145 in a large range, between 10 % and 100 %. Moreover, the aim of this upgraded device
 146 is to measure the gas-phase CO_2 concentration in the whole headspace of champagne

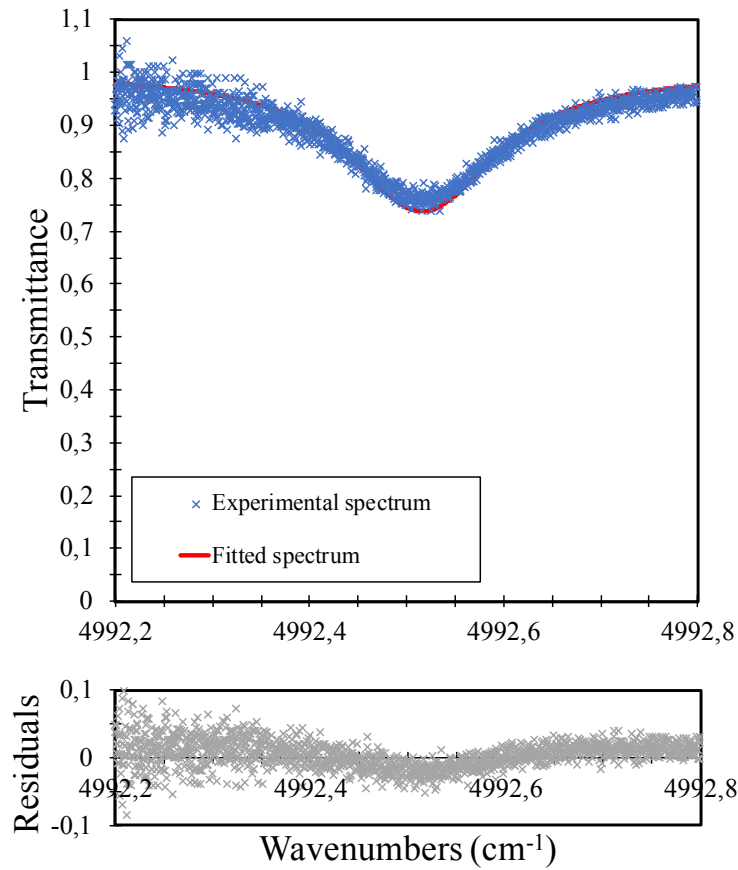


Fig. 4: Constrained non-linear fitting of a spectrum obtained with the laser emitting at 2.003 μm , of a 50 % concentration of gas-phase CO_2 .

147 glasses including close to the liquid surface, and it can be expected that the measured
 148 concentrations near the liquid surface even reach 100 %. This is why the technical validation
 149 has been done only with the 2.003 μm laser.

150 Various dry air/ CO_2 gas mixtures were prepared through a mass flow dilutor (Alytech
 151 GasMix), with increasing CO_2 concentrations ranging from 10 to 100 % (and with concen-
 152 tration errors varying between 0.001 % and 0.4 %, respectively). A gas cell analysis was

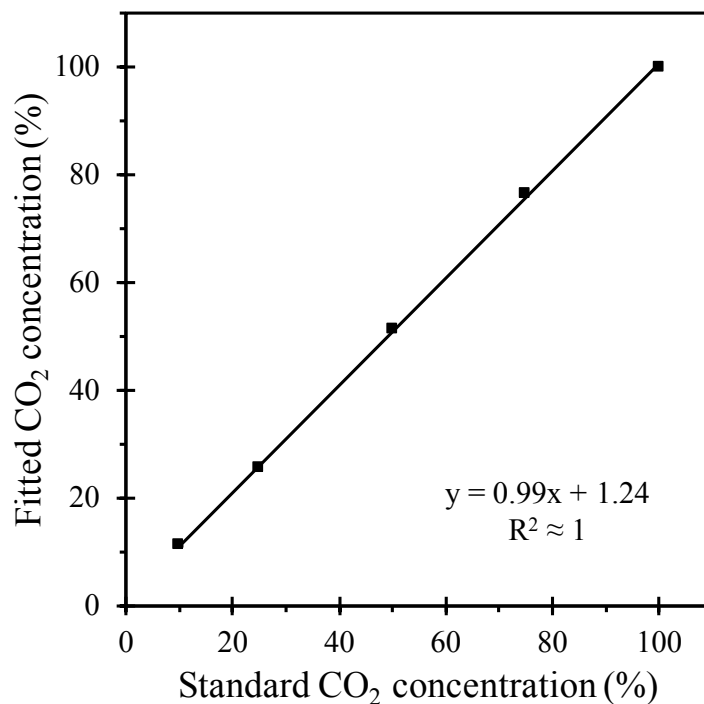


Fig. 5: Concentrations of gas-phase CO₂ as determined through the CO₂-DLS, fitted as a function of the dry air/CO₂ gas mixtures standards.

153 designed from an INAO glass and filled with the various dry air/CO₂ gas mixtures at a
 154 pressure of 1 bar (absolute) (see [Appendix A](#) and Fig.A.10). The baseline was recorded
 155 with the empty cell. Then, a hundred spectra were recorded for each tested CO₂ concentra-
 156 tion. Finally, the results are displayed in Fig. 5, and fitted linearly with the concentration
 157 of standards in the whole range of CO₂ concentration varying between 10 % and 100 %.
 158 The slope of the regression line being equal to 0.99, the upgraded CO₂-DLS (with its new
 159 part dedicated to the scanning) therefore allowed to perfectly retrieve the standard CO₂
 160 concentration with a very good agreement (in the range between 10 and 100 %).

161 2.4. *Samples and enological application protocol*

162 2.4.1. *Champagne samples*

163 A commercial Champagne wine, in standard 75 cL bottles with a blend of Chardonnay,
164 Pinot Noir and Pinot Meunier base wines (champagne Nicolas Feuillatte, 12.5 %vol.) has
165 been used. Since their elaboration, bottles were stored in a cool cellar at 12 °C and the
166 champagne was poured at 12 °C. It was found to hold $(9.40 \pm 0.05) \text{ g} \cdot \text{L}^{-1}$ of dissolved
167 CO_2 before pouring, by using the analytical method described in [4].

168 2.4.2. *The glasses used and their washing protocol*

169 A machine-blown glass, called Absolu glass (Lehmann glass, Marne, France), was used
170 for this set of experiments. It is a hybrid glass, curved inwards at the top, with a total
171 volume of 380 mL and with a global shape similar to the one of a still wine glass. When
172 filled with 100 mL of champagne, the headspace is of 280 mL is still large. This is why it
173 has been chosen in order to study the gas-phase CO_2 distribution above champagne. A 3D
174 scheme of the Absolu glass is presented in Fig. 6a. Moreover, the set of glasses were laser-
175 etched champagne glasses, in order to promote standardized conditions of effervescence
176 (i.e., a rate of bubbling accurately controlled through laser beam-driven bubble nucleation
177 sites). To promote bubble formation, such glasses were simply etched on their bottom,
178 with several laser beam impacts. A sudden cooling after the laser beam impact causes a
179 network of crevices at the glass surface, as seen in the micrographs of adjoining laser beam
180 impacts displayed in Fig. 6b-d. As champagne is served in such laser-etched glasses, this
181 network of tiny crevices at the bottom of the glass surface enables the entrapment of tiny
182 air pockets. For a global overview of how laser-etched champagne glasses promote bubble
183 formation, see [1], and references therein. Finally, before each experiment, the glasses were
184 thoroughly washed using the protocol described in [22]. Thus, effervescence is strictly
185 restricted to the six artificial bubble nucleation sites, at the bottom of the glass.

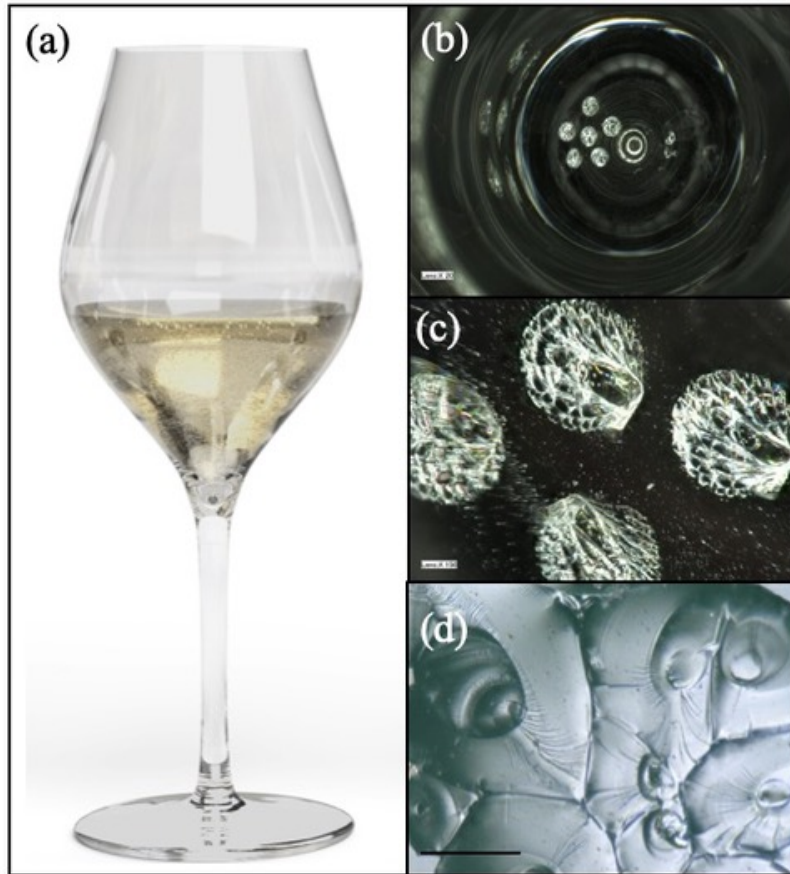


Fig. 6: Scheme (created from SolidWorks) of the Absolu glass filled with 100 mL of champagne (a). Micrographs of the six laser beam impacts found at the bottom of the laser-etched Absolu glass (b and c), one of them being enlarged in (d) and showing a network of crevices with characteristic open apertures close to $2\ \mu\text{m}$ (bar = $100\ \mu\text{m}$).

186 2.4.3. *Definition of the pixels in the glass headspace*

187 In order to study the whole headspace of the glass, 100 mL of champagne at 12 °C were
188 poured and nine pixels were defined (Fig. 7a) on three different levels vertically, i.e. levels
189 A, B and C, and three different locations horizontally, including three pixels along the axis
190 of symmetry of the glass (i.e. #2) and three at 1.5 cm of the symmetry axis on each side, i.e.
191 #1 and #3. In Table 3, the distances between the pixels and the glass edge and the liquid
192 surface (100 mL), as well as the lengths of the optical path are given. As it can be seen in
193 Table 3, the path lengths for two pixels at the same measurement level on each side of the
194 symmetry axis, i.e. #1 and #3, is different because a slight deviation of the laser beam was
195 observed.

196 It can be noted that the minimum distance between the liquid surface and the measure-
197 ment level has been fixed at 2 cm. This distance between the wine surface and the laser
198 beam path has been chosen in order to limit a possible source of trouble for the measure-
199 ment caused by champagne aerosol droplets formed in the first ten seconds following the
200 beginning of the pouring.

201 In order to more deeply decipher the gas-phase CO₂ distribution above the champagne
202 surface, five pixels vertically arranged along the axis of symmetry of the glass were defined
203 in the glass headspace, as shown in Fig. 7b. The five pixels are located between 1 cm below
204 the glass edge (A2), and 2 cm above the champagne surface (C2). The relevant geometrical
205 parameters are presented in Table 4.

206 The two sets of experiments were performed in a thermo-regulated room (20 ± 1 °C).
207 The Absolu glass, was previously level-marked with 100 mL of distilled water, and placed
208 on its suitable holder. In order to limit the formation of foam and the presence of a liquid
209 film on the glass wall, 100 mL of champagne (at 12 °C) were poured carefully in the glass.
210 The pouring process lasts approximately 10-15 s. Actually, the presence of foam or a liquid
211 film on the glass wall may reduce or even stop the signal. The monitoring of gas-phase
212 CO₂ concentration begins 30 s before the beginning of the pouring process in order to

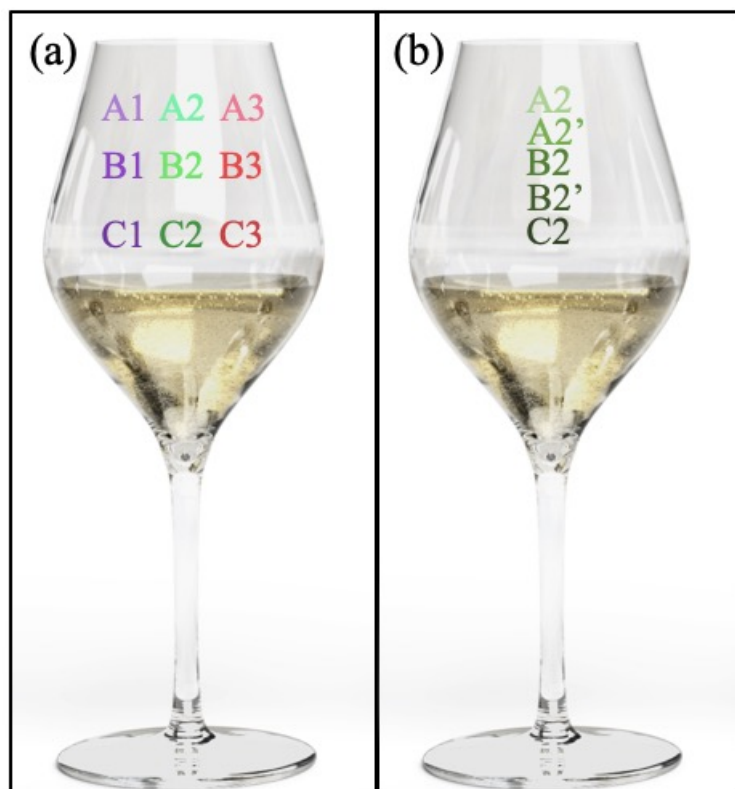


Fig. 7: Schemes (created from SolidWorks) of the Absolu glass filled with 100 mL of champagne, showing the respective location of the nine (a) and five pixels (b) dedicated to the simultaneous measurements of gas-phase CO₂ in the glass headspace.

213 record experimental baselines for each pixel while the glass is filled with ambient air.
214 The contribution of ambient CO₂ (400-1000 ppm in the lab) is considered to be negligible
215 compared to that of CO₂ degassed by the liquid ($\geq 10\%$) Four successive pourings from
216 two distinct bottles have been carried out then averaged for each experiment.

Table 3: Location and optical path length of the nine pixel, as defined in Fig. 7a, for the simultaneous measurement of gas-phase CO₂ in the headspace of the Absolu glass.

Pixels	Distance between the pixel and the liquid surface (cm)	Distance between the pixel and the edge of the glass (cm)	Optical path length (cm)
A1	6.5	1	4.8
B1	4.5	3	6.1
C1	2	5.5	7.3
A2	6.5	1	5.7
B2	4.5	3	6.7
C2	2	5.5	8
A3	6.5	1	5
B3	4.5	3	6.3
C3	2	5.5	7.6

Table 4: Location and optical path length of the five pixels vertically arranged along the axis of symmetry, as defined in Fig. 7b, for the simultaneous measurement of gas-phase CO₂ in the headspace of the Absolu glass.

Pixels	Distance between the pixel and the liquid surface (cm)	Distance between the pixel and the edge of the glass (cm)	Optical path length (cm)
A2	6.5	1	5.7
A2'	5.5	2	6.4
B2	4.5	3	6.7
B2'	3.5	4	7.5
C2	2	5.5	8

217 3. Results and discussion

218 3.1. Gas-phase CO₂ concentration measurement at nine different pixels in the glass headspace

219 During the pouring step, and within the five next minutes following pouring, the time
220 dependence of the gas-phase CO₂ concentration was simultaneously measured at nine
221 different pixels found in the glass headspace, as shown in the graph displayed in Fig. 8.
222 Regardless of the pixel at which gas-phase CO₂ measurement is performed, the global
223 shape described by the real-time monitoring of gas-phase CO₂ concentration is identical to
224 what was underscored in previous works [22, 30]. In the first stage of the monitoring, a
225 rapid growth of gas-phase CO₂ concentration is systematically observed, until a maximum
226 is reached only several seconds after the end of the pouring step. This rapid growth of
227 gas-phase CO₂ in the glass headspace during the pouring step is interpreted in light of
228 the huge losses of dissolved CO₂ unveiled during this stage. Actually, the turbulences of
229 the pouring step lead to the loss of several grams per liter of CO₂ from the liquid phase
230 supersaturated with dissolved CO₂ [5, 31, 32]. In a second step, a global decrease of gas-
231 phase CO₂ concentrations found in the headspace of the glass is observed. Interestingly,
232 a similar evolution of gas-phase CO₂ concentrations was measured by a CO₂ gas sensor
233 above beer glasses at concentrations below 1 % [20].

234 Moreover, as it can be seen in Fig. 8, the three different vertical levels of measurement
235 (i.e., A, B and C) clearly differ quantitatively from each other in terms of gas-phase CO₂
236 concentrations. The maximum concentration reached several seconds after the end of
237 pouring process is about 17 % at 6.5 cm above the liquid surface (pixels A1, A2 and A3),
238 against 32 % at 4.5 cm above the liquid surface (pixels B1, B2 and B3) and close to 50 % at
239 2 cm above the liquid surface (pixels C1, C2 and C3). Therefore, the closer one is to the
240 champagne surface, the higher the concentration of gas-phase CO₂ after the pouring step.
241 It is worth noting that this trend can be observed during the global decrease in gas-phase
242 CO₂ observed within the five next minutes following the pouring, as shown in Fig. 8.

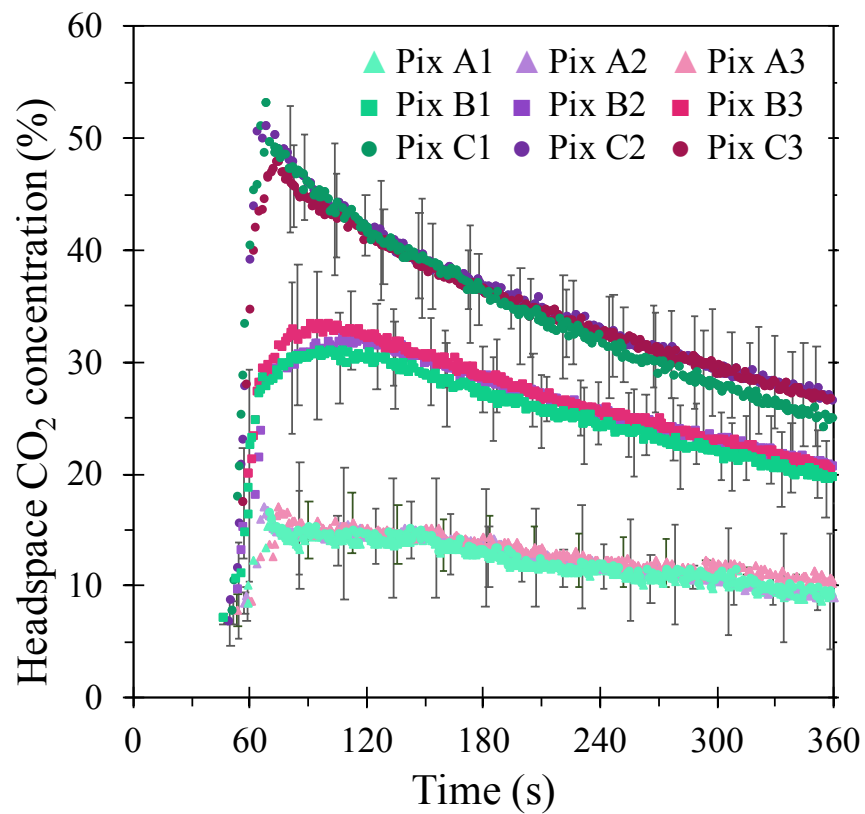


Fig. 8: Simultaneous measurements, as time elapses, of gas-phase CO₂ concentrations (in %) found at the nine pixels located in the headspace of the glass, as defined in Fig. 7a. The dots correspond to pixels C1, C2 and C3, the squares to pixels B1, B2 and B3, and the triangles to pixels A1, A2 and A3. The data resulting from four successive pouring were averaged. Error bars indicating standard deviation (n=4 except for A2, A3 and C1 n=3) were added to every 1/20 time point of the CO₂-DLS data. The acquisition data frequency is equal to 42Hz.

243 This set of data therefore allows to conclude that a strong vertical gradient of gas-phase
244 CO₂ quickly forms in the headspace of the glass, as soon as the pouring step is achieved.
245 This vertical gradient persists during the five next minutes following the pouring process.
246 Nevertheless, it is also noteworthy to mention that the gas-phase CO₂ concentrations
247 found in the glass headspace are very similar at the same horizontal level of measurement
248 (during the pouring step, and within the five next minutes of monitoring). The CO₂-DLS
249 therefore unambiguously unveiled horizontal homogeneity in the glass headspace, in
250 terms of gas-phase CO₂ concentrations.

251 3.2. *Close-up on the vertical gradient, along the symmetry axis of the glass headspace*

252 In order to better decipher the vertical stratification of gas-phase CO₂ in the glass
253 headspace, another set of data has been performed. During the pouring step and within the
254 five next minutes, real-time monitoring of gas-phase CO₂ was performed in the headspace
255 of the same glass, at five vertically arranged pixels (defined in Fig. 7b). Results are shown
256 in Fig. 9. Firstly, the time dependent gas-phase CO₂ concentrations clearly differ from one
257 pixel to another, thus unambiguously confirming the vertical gradient of gas-phase CO₂
258 unveiled through the CO₂-DLS. Secondly, it is worth noting that the averaged gas-phase
259 CO₂ concentrations measured in this experiment are slightly lower than those previously
260 retrieved and shown in Fig. 8. Actually, the manual pouring of champagne in the glass
261 leads to a lack of reproducibility and thus sometimes to slight differences between distinct
262 series of measurements, even under the same tasting conditions, with the same champagne
263 samples.

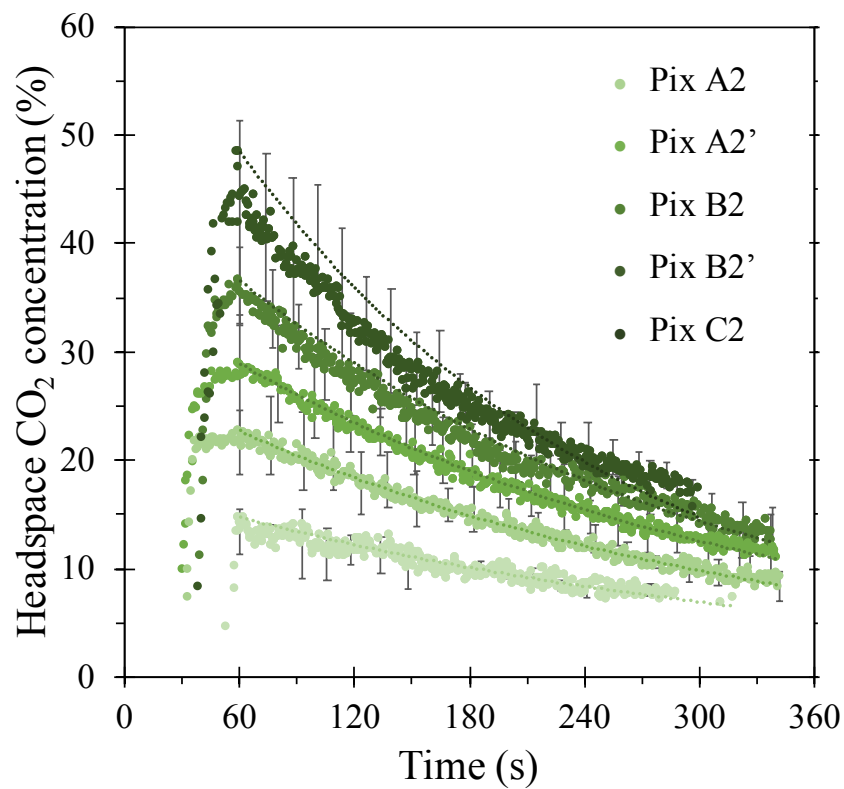


Fig. 9: Simultaneous measurements, as time elapses, of gas-phase CO₂ concentrations (in %) found at the five pixels vertically arranged along the axis of symmetry of the glass headspace, as defined in Fig. 7b. The data resulting from four successive pouring were averaged. Error bars indicating standard deviation (n=4 except for A2, A3 and C1 n=3) were added to every 1/20 time point of the CO₂-DLS data. The acquisition data frequency is equal to 42 Hz.

264 Moreover, and regardless the level at which the measurement is performed along the
 265 axis of symmetry of the glass headspace, the temporal decrease of the gas-phase CO₂
 266 concentration following the rapid growth observed during the pouring step (presented in
 267 Fig. 9) follows an exponential decay-type model described hereafter:

$$[\text{CO}_2](t) \approx [\text{CO}_2]_M \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

268 with $[\text{CO}_2]_M$ being the maximum average gas-phase CO₂ concentration reached several
 269 seconds after the pouring step (in %), t being the time (in s), and τ being the timescale of
 270 the exponential decay-type model (in s).

Table 5: Parameters of the exponential decay-type model fitting the temporal decrease of the average gas-phase CO₂ concentrations for the five pixels vertically arranged along the axis of symmetry of the glass headspace.

Pixel	$[\text{CO}_2]_M$ (%)	τ (s)	R^2
A2	14.5	312	0.92
A2'	22.5	282	0.99
B2	28.7	285	0.99
B2'	36.3	254	0.98
C2	48.1	200	0.98

271 Table 5 compiles the various parameters of the exponential decay-type model, for the
 272 five various pixels vertically arranged along the axis of symmetry of the glass headspace.
 273 This second set of data unambiguously confirms the formation of a strong vertical gradient
 274 of gas-phase CO₂ in the glass headspace at the end of the pouring step, with decreasing
 275 CO₂ concentrations while moving away from the champagne surface. This vertical gradient
 276 of gas-phase CO₂ persists during the five next minutes following pouring, but with ever
 277 decreasing CO₂ concentrations as time elapses. This vertical stratification of CO₂ betrays
 278 the fact that the density of gas-phase CO₂ ($\rho_{\text{CO}_2} \approx 1.8 \text{ g} \cdot \text{L}^{-1}$ at 20 °C) is approximately

279 1.5 times higher than the density of dry air ($\rho_{air} \approx 1.2 \text{ g} \cdot \text{L}^{-1}$ at 20°C). The cloud of
280 gas-phase CO_2 escaping from champagne during the pouring step and within the five next
281 minutes therefore tends to naturally stagnate and sediment above the champagne surface,
282 as already observed by [33] through infrared imaging.

283 **4. Conclusion**

284 Key upgrades to a previously developed CO_2 -Diode Laser Sensor (CO_2 -DLS) resulted
285 in an instrument well designed for accurate, simultaneous, and high-frequency measure-
286 ments of gas-phase CO_2 concentrations in the whole headspace of glasses poured with
287 champagne. Immediately after starting to dispense champagne into a glass, and within
288 the five next minutes following, real-time monitoring of gas-phase CO_2 was conducted at
289 different locations in the headspace of the glass, with a 24 ms time resolution. Immediately
290 after the pouring step, the CO_2 -DLS highlighted a strong vertical gradient of gas-phase
291 CO_2 above the champagne surface, thus unveiling a vertical stratification of gas-phase CO_2
292 in the headspace of the glass (with decreasing CO_2 concentrations while moving away
293 from the champagne surface, and as time elapses). Moreover, the sets of data unambigu-
294 ously unveiled horizontal homogeneity in the glass headspace in terms of gas-phase CO_2
295 concentrations. In a near future, this upgraded CO_2 -DLS will enable to further explore
296 the impact of various champagne tasting parameters on the gas-phase CO_2 concentrations
297 found in the headspace inhaled by champagne tasters, such as the tasting glass shape, the
298 champagne temperature, or the volume dispensed for example.

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416 **Appendix A. INAO Glass**

417 The term INAO means "Institut National des Appellations d'Origine". The INAO
418 glass is a certified tasting glass with a total volume capacity of 21 cL. Indeed, this tasting
419 glass meets the requirements of the French (NF V09-110 June 1971) and International
420 (ISO 3591:1977) standards regarding its physical and dimensional characteristics. The
421 INAO is widely used for still wines and sparkling wines tasting, by both professionals and
422 consumers. A photograph of the gas cell designed with an INAO glass is presented in Fig
423 [A.10](#).



Fig. A.10: Photograph of the gas cell designed with an INAO glass