

Aroma determination in alcoholic beverages: green MS-based sample preparation approaches

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25 **Keywords:** sample preparation; volatile odor-active compounds; alcoholic beverages; green
26 extraction; mass spectrometry.

27

28 **ABBREVIATION**

29 GAC, green analytical chemistry; CW, carbowax; CAR, carboxen; DI, direct immersion; DI-
30 SPME, direct immersion solid phase micro extraction; DLLME, dispersive liquid-liquid micro
31 extraction; DVB, divinylbenzene; ESI, electrospray ionization; FEDHS, full evaporation dynamic
32 head space; GC, gas chromatography; HF-LPME, hollow fiber liquid phase micro extraction; HS,
33 head space; HS-SPME, head-space solid phase micro extraction; HPLC, high performance liquid
34 chromatography; LC; Liquid Chromatography; LLE, Liquid-Liquid Extraction; LPME, liquid
35 phase micro extraction; MS, mass spectrometry; OFD, on fiber derivatization (OFD); PA,
36 polyacrylate; PFBHA, o-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine; PDMS,
37 polydimethylsiloxane; SA-SBSE, solvent assisted stir bar sorptive extraction; SBSE, stir bar
38 sorptive extraction; SDME, single drop micro extraction; SPE, solid phase extraction; SPME,
39 solid phase micro extraction; Supercritical Fluid Extraction (SFE); VOA, volatile odor active
40 compounds (VOAs).

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71 **Abstract**

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73 Aroma determination in alcoholic beverages has become a hot research topic due to the ongoing
74 effort to obtain quality products, especially in a globalized market. Consumer satisfaction is
75 mainly achieved by balancing several aroma compounds, which are mixtures of numerous volatile
76 molecules enclosed in challenging matrices. Thus, sample preparation strategies for quality
77 control and product development are required. They involve several steps including copious
78 amounts of hazardous solvents or time-consuming procedures. This is bucking the trend of the
79 ever-increasing pressure to reduce the environmental impact of analytical chemistry processes.
80 Hence, the evolution of sample preparation procedures has directed towards miniaturized
81 techniques to decrease or avoid the use of hazardous solvents and integrating sampling, extraction,
82 and enrichment of the targeted analytes in fewer steps. Mass spectrometry coupled to gas or liquid
83 chromatography is particularly well suited to address the complexity of these matrices. This
84 review surveys advancements of green miniaturized techniques coupled to mass spectrometry
85 applied on all categories of odor-active molecules in the most consumed alcoholic beverages:
86 beer, wine, and spirits. The targeted literature consider progresses over the past 20 years.

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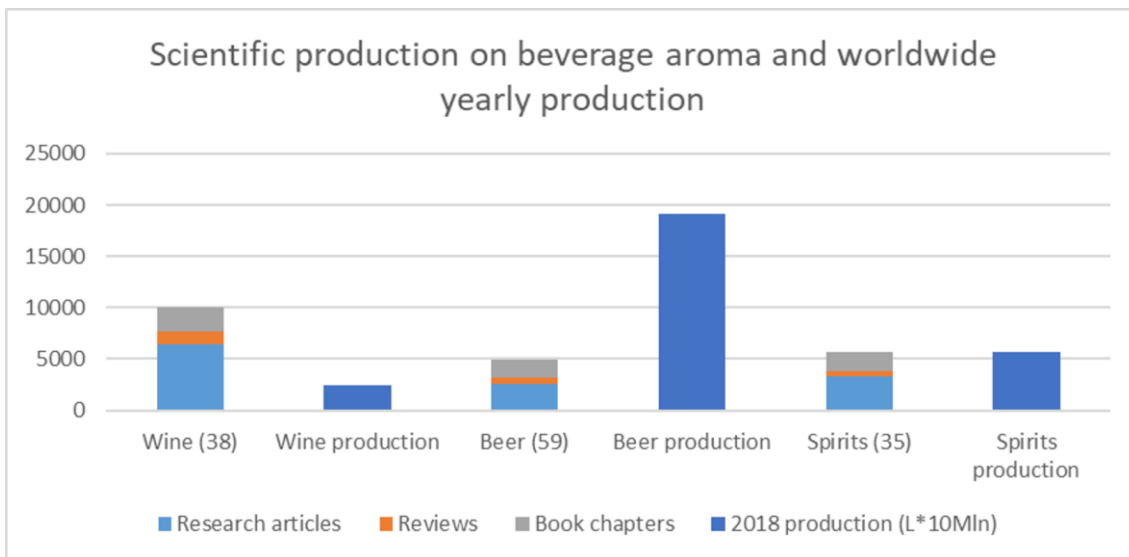
94 I. Introduction

95 Since the year 2000, when the “green chemistry” was introduced (Namiesnik, 2000), one
96 of the main efforts of analytical chemists has been implementing analytical methods to enhance
97 the eco-sustainability of the entire analytical process. One of the most effective ways to obtain
98 greener methodologies is to miniaturize each step of the analytical procedure (Agrawal et al.,
99 2021; Armenta et al., 2019). This miniaturization fulfills one of the fundamentals of Green
100 Analytical Chemistry (GAC), and include: (i) reducing the use of hazardous solvents from
101 hundreds of mL to a few μL to generate a tiny amount of toxic waste; (ii) using environmentally
102 friendly solvents (Sanchez-Prado et al., 2015; Vazquez-Roig & Picó, 2015); (iii) reducing the
103 amount of needed sample; (iv) using of miniaturized and automatized sample preparation
104 techniques to strongly decrease the energy consumption with comparable performance. From the
105 sample preparation point of view, the microextraction techniques offer a high-potential strategy.
106 These methodologies ensure adequate quality features, such as pre-concentration, accuracy, and
107 precision, with reduced or null solvent consumption coupled to lower risks for the operator and
108 the environment (Valcarcel, 1980).

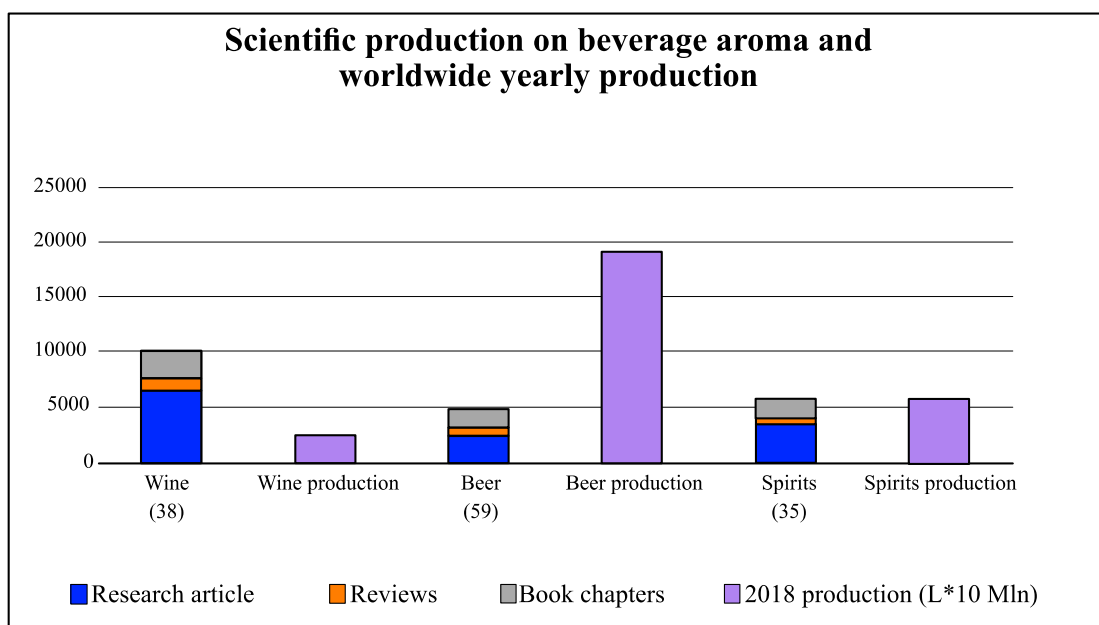
109 Thus, green micro-extraction techniques are rapidly evolving in several fields such as
110 bioanalytical, forensic (Borden et al., 2020), and food applications (Agrawal et al., 2021; Hansen
111 & Pedersen-Bjergaard, 2020; He & Concheiro-Guisan, 2019; Soares da Silva Burato et al., 2020;
112 V. Soares Maciel et al., 2018). In agro-food analysis, the determination of flavor and fragrances
113 in food and beverages has become a hot research topic, mainly because of their massive
114 consumption worldwide (Martins et al., 2021; V. Soares Maciel et al., 2018). The accurate
115 identification and quantification of the characteristic odor-active compounds in wine, beer, and
116 spirits are crucial for obtaining a well-balanced product appreciated by consumers (Van Opstaele,
117 De Causmaecker, et al., 2012). Because of that, research activities focused on beverage aroma are
118 out of the most dynamic topics in food chemistry (Lyu et al., 2021). Just by browsing the literature
119 produced up to the time this review was written and searching for the name of the beverage (wine,
120 beer, or brandy, rum, spirit, vodka, gin, and distillate for spirits) associated with the word

121 “aroma”, the number of outputted documents by the ScienceDirect database is remarkable (Figure
 122 1).

123



124



125 **FIGURE 1.** Scientific production (ScienceDirect, 2021) on beverages aroma (in brackets the number of
 126 patents currently deposited) and the 2018 yearly worldwide production (Conway, 2020).

127

128 However, analysis of such complex matrices is still challenging, requiring at least one sample
 129 preparation step to balance matrix effects, and overcome false quantitative results. Generally,
 130 sample preparation procedures for alcoholic beverages combine several processes such as
 131 extraction, preconcentration, fractionation, and isolation of targeted compounds, including

132 copious amounts of organic solvents (Marín-San Román et al., 2020a). Nowadays, micro-
133 extraction techniques are helpful to eliminate or minimize the amounts of solvents and reagents
134 used, matching GAC requirements as well as the needed sample treatments. Moreover, these
135 techniques consider the recovery of the extractant solvents, their reuse (Namiesnik, 2000), and in
136 some instances, the use of less toxic solvents. Non-chlorinated organic compounds, novel solvents
137 such as ionic liquids (ILs)(Hallett & Welton, 2011; Pacheco-Fernández & Pino, 2019; Trujillo-
138 Rodríguez et al., 2013), eutectic point solvents ultra-low (DESs) (Cunha & Fernandes, 2018;
139 Smith et al., 2014), supramolecular solvent (amphiphilic solvents) (Ballesteros-Gómez et al.,
140 2010; Melnyk et al., 2014), or supercritical fluids (Jose A. Mendiola, Miguel Herrero, Maria
141 Castro-Puyana, 2013) are the new trend in the micro extraction applications. The following
142 sections illustrate the current scenario of the mostly used green microextraction techniques to
143 determine specific aroma compounds, the volatile odor active molecules (VOAs) in popular
144 alcoholic beverages.

145

146 [A. Role of VOAs in alcoholic beverages](#)

147 From the chemical point of view, wine, beer, and spirit aromas are complex mixtures of volatile
148 molecules derived from raw materials, transformation steps, ageing phenomena, and, sometimes,
149 undesired side reactions. These compounds are often part of articulated equilibrium involving
150 phase transitions (physical equilibrium), bond cleavage or redox reactions (chemical equilibrium),
151 and many bio catalyzed steps that make them just the tip of an iceberg (Gabrielli et al., 2021; Luo
152 et al., 2020; Polášková et al., 2008; Schieberle, 1995; Vanderhaegen et al., 2006). Among the
153 multitude of intrinsic components of alcoholic beverages, VOAs are the first compounds reaching
154 the consumers, even before drinking (odor); together with the ones received through the retro
155 nasal way (aroma), they compose the flavor (Ibáñez & Cifuentes, 2015; Özay et al., 2019). Odor,
156 and especially aroma are also the quality aspects that are most directly related to taste, satisfaction
157 and healthiness (Morrin & Tepper, 2021). Several groups of compounds are related to
158 characteristics scents such as esters for fruity (Niu et al., 2019), terpenes for floral (Yang et al.,

159 2019), six carbon chain alcohols and aldehydes for herbaceous (Sun et al., 2020),
160 four/six/eight/ten carbon chain linear saturated fatty acids for cheesy (Katarína et al., 2014; Selli
161 et al., 2006). Contrarily, strong identity molecules can be directly associated with specific good
162 like 1,1,6-trimethyl-1,2-dihydronaphthalene for kerosene (Dobrydnev et al., 2020), furaneol for
163 strawberries (Ferreira et al., 2003), diacetyl for butter (Anderson et al., 2019) and so on. This
164 composition is characteristic for fermented beverages such as wine, beer, spirits, and all those
165 beverages that are produced using microbiological transformations (Anjos et al., 2021; Garde-
166 Cerdán & Ancín-Azpilicueta, 2006; Pissarra et al., 2005). In addition, beverages whose
167 production occurs a barrel refining, are involved in a sorption equilibrium between the liquid
168 phase and the wood, from which many compounds can be extracted or adsorbed (Martínez-Gil et
169 al., 2018). Hence, VOAs are an heterogeneous class of compounds whose concentrations varies
170 from a few $\text{ng}\cdot\text{L}^{-1}$ to hundreds of $\text{mg}\cdot\text{L}^{-1}$ who are enclosed in complex and compositionally
171 variable matrices in which interfering macro-components such as polyphenols, ethanol,
172 polysaccharides, and fermentative compounds can modulate their volatility (Andujar-Ortiz et al.,
173 2009; Castro-Vázquez et al., 2011; Davis & Qian, 2019).

174 These characteristics highlighted the complexity of VOAs analysis that requires dedicated sample
175 preparation procedures to allow an accurate quantitative determination. The most critical step lies
176 in selecting an extraction method capable of isolating the desired analytes without resulting in the
177 formation of artifacts (Thompson-Witrick et al., 2015). Moreover, each alcoholic beverage matrix
178 remarkably varies one from the other, making many methods suitable only for a specific class of
179 products. Therefore, the need for specific methods for each matrix, often associated with laborious
180 pretreatments or further operations is mandatory. In fact, because of the diversity of VOAs, an
181 ideal method that can concentrate and recover all targeted compounds is not available (Zhang et
182 al., 2020). Accordingly, this review article covers the widely used microextraction techniques in
183 the determination of VOAs in alcoholic beverages, with particular emphasis on the greenest
184 methodologies.

185

186 B. Sample preparation for determining VOAs

187 Classical sample preparation techniques for the determination of VOAs in wine, beer, and spirits
188 include Static (S-HS) or Dynamic Head-Space extraction (D-HS) (Rosillo et al., 1999), Liquid-
189 Liquid Extraction (LLE) (Costa Freitas et al., 2012; Mamede & Pastore, 2006; Mayr et al., 2014),
190 and Solid-Phase Extraction (SPE) (Cabrita et al., 2007; Remedios Castro et al., 2008; López et
191 al., 2002). Extraction techniques based on S-HS and D-HS are efficient for analyzing compounds
192 with very high vapor pressure values. One of the most significant advantages of S-HS is the
193 absence of required sample pretreatment, but it is characterized by a minimal sample capacity,
194 leading to poor sensitivity. D-HS technique allows the concentration of the head space volatile
195 compounds in a cold trap (or sorbent) under the action of a gas flow. Then, the trap is rapidly
196 heated, allowing the transfer of trapped compounds into the chromatographic system, generally
197 by quickly heating the trap. However, these two techniques are being replaced by modern
198 headspace sampling techniques with a greater enrichment factor.

199 Strategies based on LLE are effective, allowing the determination of a broad range of compounds
200 with very different polarities (Andujar-Ortiz et al., 2009; R. Castro et al., 2004). However, they
201 are quite tedious, time-consuming and with a significant consumption of hazardous solvents
202 (Silvestre et al., 2009); these drawbacks resulted in changing this technique in favor of others.

203 SPE widely replaced LLE methods, mainly because it allows a significant improvement in
204 enrichment and selectivity reducing in the meanwhile the use of solvents. The optimization of
205 several parameters such as selected sorbents, the solvent used for conditioning, sample flow rate,
206 and the eluting solvent is crucial to obtain a reliable extraction leading to more complicated
207 procedures instead of LLE (Fornells et al., 2019; Ochiai et al., 2008). In addition, these techniques
208 involve the use of a large amount of sample, which means that these methods are neither
209 environmentally sustainable nor cheaper (Marín-San Román et al., 2020a).

210 Microextraction techniques with reduced or no solvent consumption are well-established green
211 alternatives to exhaustive solvent-based or sorbent-based methods (Spiegelun et al., 2013). They
212 can integrate several activities such as sampling, extraction, and enrichment of the targeted

213 analytes in fewer steps than the traditional ones. Like conventional techniques, these green
214 alternatives are classified as solvent-free, such as Solid Phase Micro-Extraction (SPME), Stir Bar
215 Sorptive Extraction (SBSE) that are based on sorbents as SPE derivatives, and the solvent-based
216 techniques where a solvent is used as extraction media as the LLE principle (Soares da Silva
217 Burato et al., 2020). Because of the null consumption of organic solvent and the applicability of
218 several compounds, the determination of VOAs in alcoholic beverages is largely performed by
219 solvent-free techniques. Less volatile compounds can be extracted with Liquid Phase Micro
220 Extraction (LPME) techniques, that describes the LLE with a downscaled solvent volume
221 (microliters). The theory of “like dissolves like” is on the basis on the success of these micro
222 extraction procedures, that can be optimized varying solvent system composition, and/or pH
223 value. These modifications can be performed accordingly to the distribution coefficient of the
224 analyte/matrix allowing best and fastest extraction. LPME is usually divided into three main
225 groups: (a) Dispersive Liquid-Liquid Micro-Extraction (DLLME), (b) Hollow-Fiber LPME (HF-
226 LPME), (c) Single Drop-Micro-Extraction (SDME) (Pena-Pereira et al., 2009; Soares da Silva
227 Burato et al., 2020). However, this review limits the discussion on the DLLME applied in MS-
228 based methods, -coupled to mass spectrometry (MS) which is which is -the extraction technique
229 currently available in the literature comprising the specific determination of VOAs in alcoholic
230 beverages.

231

232 C. Separation and detection techniques for VOAs determination

233 The achievement of the GAC goals is made possible as a result of the evolution of extraction
234 techniques described in this review as well as the technological progress of the analytical
235 instrumentation. The increased sensitivity provided by the last developed mass spectrometers is
236 the key to reliably detect and quantitate trace analytes using reduced amount of sample. Non-
237 bonded VOAs compounds are molecules whose physical characteristics perfectly fit for gas
238 chromatography (GC). In GC the separation takes place in gas form so the best MS source for the
239 analysis of vapor-phase molecules is Electron Ionization (EI). This hard ionization is a physical

240 process that involves a significant amount of energy (mostly 70 eV) generating a widespread
241 fragmentation that provides many structural information (Famiglioni et al., 2021). In addition, EI
242 has no polarity limitation so it can be used for every class of volatile compound and, since it's not
243 based on a chemical reaction, matrix effects due to ionization interferences are limited (Famiglioni
244 et al., 2018). Currently, most EI mass spectrometers are coupled to low resolution analyzers such
245 as quadrupole (Q), ~~or~~ triple quadrupoles (QqQ), and ion traps (IT). ~~however, ion traps (IT)~~ High
246 resolution mass spectrometer such as ~~and especially~~ time-of-flight (TOF) analyzers are used in
247 particular for untargeted applications where the knowledge of the exact mass is a precious
248 information (Eichhorn et al., 2012; Saito-Shida et al., 2018). Finally, GC-EI-MS perfectly fits the
249 HS-SPME working-flow.

250 Simplifying the preparation step, either minimizing volumes or replacing solvents with safer ones,
251 it is often paid by a reduction of the sample purity; this lack can be balanced using high
252 performance chromatography and robust MS detectors such as EI based ones (Armenta et al.,
253 2020). Based on what was stated above, EI is a powerful tool for compound discovery, especially
254 when coupled to bi-dimensional chromatography like GCxGC, and a reliable source for
255 quantitative experiments in complex matrices (Herrero et al., 2009).

256 Unfortunately, EI-MS has some limitation: it requires high vacuum conditions into the source so
257 it is mostly hyphenated with GC, and it is based on a low efficiency ionization process with
258 negative repercussions in sensitivity. Sources with increased efficiency are Atmospheric Pressure
259 Ionization (API), mostly Electrospray (ESI); in this ionization molecules are transformed into
260 ions through a chemical acid/base reaction or the formation of adducts (Bruins & Niessen, 2019).
261 The energy involved is minimal so the fragmentation provides poor structural information but, on
262 the other hand, the molecule-to-ion efficiency is considerably higher, with a significant gain in
263 sensitivity. In the ESI, pH and elution conditions are crucial for the ionization so this source is
264 generally only coupled to Liquid Chromatography (LC) for the determination of more polar
265 compounds. The lack of in-source fragmentation is compensated by the use of collision cell in
266 tandem MS, where its use allows the access to structural libraries like EI ~~The lack of in source~~

267 ~~fragmentation is offset by the use of collision cell in tandem MS which use allows the access to~~
268 ~~structural libraries like~~. Finally, LC-MS is the only technique for the analysis of bonded-VOAs.
269 Summarizing, most methods described in the next pages are based on GC-EI-MS as a
270 consequence to its suitability to the analysis of volatile compounds like VOAs (Pena-Pereira et
271 al., 2009; Savchuk et al., 2020); many GC systems, injectors, analyzers, and accessories are fitted
272 for tailoring its characteristics to the sample preparation method of choice. However, LC-ESI-MS
273 has a significative spread in many applications, especially when coupled to solvent-based
274 extraction techniques and derivatization processes. In the following sections the main extraction
275 techniques used in the analysis of VOAs in alcoholic beverages will be illustrated. Their main
276 features will be shown, as well as their advantages and disadvantages (Campillo et al., 2018).

278 II. Solvent-free techniques for the analysis of VOAs

279 The best way to minimize the environmental impact of solvents is to avoid their use. Solvent-free
280 techniques have strongly spread their use in many analytical routes because represent an efficient
281 answer to the green issue (Sciarrone et al., 2015). In these techniques the molecules of interest
282 are sampled directly in the gas phase (D-HS, S-HS) or the extraction takes place using
283 heterogeneous phase like in the SBSE and SPME.

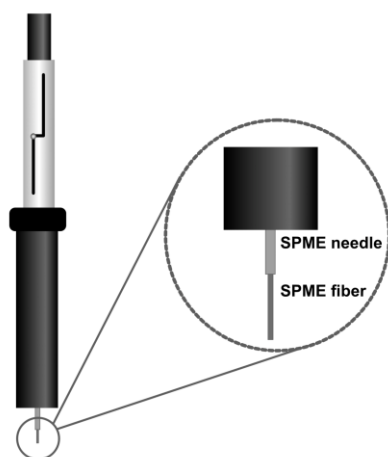
285 A. Head-space based techniques

286 HS techniques perfectly couple with aroma analysis since all VOAs molecules are available in
287 the gaseous phase in equilibrium with the matrix (Soria et al., 2015). The direct sampling and
288 injection of vapors produced by beverages is a good compromise to achieve a green method
289 without the requirement of further instrumentation. However, as a consequence of the variations
290 which affects the concentration of VOAs (from ng^*L^{-1} to mg^*L^{-1}), and the strong interaction
291 between water matrix and functional groups, direct approaches are unsuitable for most analytes.

292 As a result of this evidence, to provide a strong and reliable enrichment, quantitative analyses are
293 used to be performed by head-space sampling using SPME (HS-SPME).

294 1. Head Space Solid Phase Micro Extraction (HS-SPME)

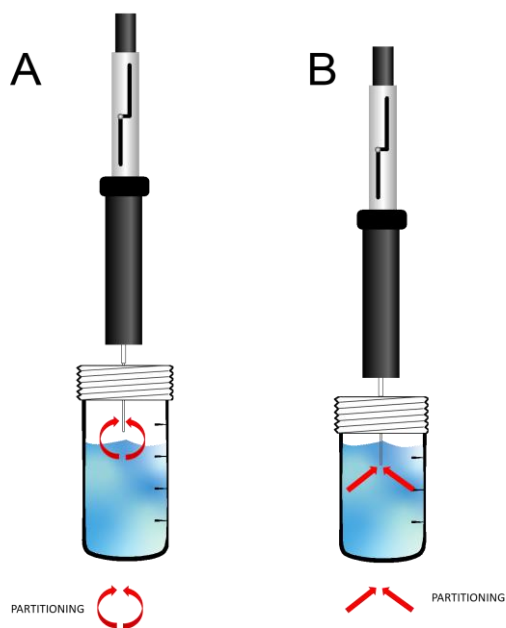
295 This extraction and pre-concentration technique was developed by Pawliszyn in 1989 (Arthur &
296 Pawliszyn, 1990). It is one of the most popular microextraction techniques. Its simplicity, ease of
297 automation, robustness, and the great sensitivity it achieves in most applications, make it a
298 powerful tool in analytical chemistry. The main configuration involves a sorbent phase coating a
299 metal tube support (Figure 2).



300

301 **FIGURE 2.** Schematic of SPME holder and fiber.

302 The fiber is usually 1 cm in length, and the sorbent (or stationary) phase thickness ranges between
303 7 and 100 μm . Several SPME devices are commercially available (*Restek*,; *Supelco*,) which
304 differentiate by coating thickness, material and composition. The SPME presents two operation
305 modes depending on the nature of analytes and matrix; these are Head-Space SPME (HS-SPME)
306 and Direct Immersion SPME (DI-SPME) that are illustrated in Figure 3(a) and 3(b), respectively.



307

308 **FIGURE 3.** Extraction modes in solid phase micro extraction (SPME). (A) Head-Space (HS) SPME. (B)
 309 Direct immersion (DI) SPME.

310

311 The first attempt of SPME analysis was presented in 1996 as a promising application for this
 312 sample preparation strategy. Lay-Keow et. al. extracted several commercial vodkas with DI-
 313 SPME using a 100 μm PDMS fiber coupled to GC-MS for the quantitation of as many analytes
 314 as possible (comprising odor-active fatty acids, esters, furans, and others) (Ng et al., 1996).
 315 Thanks to the amenable content of macromolecules, particles, and solids, it was possible to
 316 directly soak the fiber into the sample.

317 HS-SPME is mostly used for determining volatile and semi-volatile compounds; in this
 318 configuration, the fiber is exposed into the head-space between the sample and the cap of the vial
 319 allowing gas-phase analytes to migrate from the sample to the sorbent. Once the compounds are
 320 retained by adsorption/absorption mechanisms, they are desorbed for the instrumental analysis.
 321 In solvent-free applications desorption is thermally performed directly into the GC injector with
 322 high efficiency and avoiding the use of solvents; SPME fibers can be also subjected to elution
 323 with a small amount of organic solvent (<500 μL) (Płotka-Wasyłka et al., 2015; SAS Wercinski,
 324 1999) to make it suitable for LC methods.

325 Performing HS-SPME analysis in alcoholic beverages presents several limitations due to the
 326 matrix composition and different concentration of the odor-active molecules (López et al., 2002).

327 Beverage vapor, especially for alcoholic ones, is mostly made of ethanol, water, and many other
328 compounds like ethyl esters, phenols, higher alcohols, fatty acids, which are present at more than
329 0.1 mg/L^{-1} (Ferreira et al., 2015). The matrix molecules and analytes are in a competition for
330 interacting with the fiber affecting extraction efficiency, especially for trace compounds (Mestres
331 et al., 1999). This behavior is more evident for DI-SPME because the fiber is also in contact with
332 non-volatile analytes (Frago Ramos, 2016); this disadvantage balances the higher efficiency in the
333 extraction of semi-volatile compounds that sometimes contribute to the beverage aroma. In this
334 sense, HS-SPME gives better efficiency and quantitate the real amount present in the beverage.
335 HS-SPME provides a significantly longer fiber life, increased performance stability, better
336 representativeness of beverage odor, and longer instrumental maintenance intervals. In complex
337 matrices like fermented beverages, HS-SPME showed also a better extraction efficiency for
338 aroma compounds so it is preferred in most quantitative methods (Demyttenaere et al., 2003).
339 Several parameters determine HS-SPME performance such as stirring, extraction time,
340 temperature, coating thickness and phase-type. Since odor-active molecules have high volatility
341 and most of them have a low molecular mass and reduced polarity, the extraction time and
342 temperature are reduced if compared to methods developed for other analytes (Hiroyuki Kataoka,
343 Heather L. Lord, 2000). Polydimethylsiloxane (PDMS) is a non-polar phase that has a high
344 affinity for a-polar compounds and moderate for polar ones, if the extraction properties are
345 optimized. Enhanced performance towards alcohols, esters and carbonyls can be achieved by
346 using a more polar phase like polyacrylate (PA) with a consequent decrease of non-polar recovery
347 (Remedios Castro et al., 2008). Mixed coatings, which have intermediate and complementary
348 properties according to their polarity and retention capacity, are more suitable for aroma
349 compound quantitation (Marín-San Román et al., 2020b). In addition, some of these phases are
350 more polar than PA, and better extract compounds with greater polarity such as esters, carbonyls
351 and alcohols.

352 Perestrelo et. al. developed an HS-SPME method for the determination of volatile compounds in
353 grapes. Using this procedure, it was possible to determine a broad class of compounds like 27
354 monoterpenes, 27 sesquiterpenes, 21 carbonyl compounds, 17 alcohols (of which 2 aromatics),

355 10 C13-norisoprenoids, and 5 acids. In this article, 6 different fiber coatings were evaluated
356 (polydimethylsiloxane (PDMS, 100 μ m), polydimethylsiloxane/divinylbenzene (PDMS/DVB, 65
357 μ m), divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 50/30 μ m),
358 carboxen/polydimethylsiloxane (CAR/PDMS, 75 μ m), polyacrylate (PA, 85 μ m), and
359 carbowax/divinylbenzene (CW/DVB, 70 μ m) demonstrating that DVB/CAR/PDMS was the best
360 compromise to achieve suitable performance for all class of analytes(Perestrelo et al., 2011). Four
361 mL of sample were extracted in HS-SPME for 40 minutes at 40 °C under stirring (1100 rpm)
362 using sodium chloride (1.4 g) to enhance ionic strength. This procedure, which demonstrated to
363 be very versatile and efficient since it was able to quantitate 107 compounds coming from 6
364 different classes in just one run, was then extended to wine by Lukic et. al. for the evaluation of
365 the effects of six maceration treatments on volatile aroma profile of Teran red wine, and the study
366 of late and ice-harvest on Gewürztraminer odor composition (Lukić et al., 2016, 2017).

367 An in-depth study of SPME extraction for the determination of several odor-active molecules in
368 wine was presented by Metafa et. al. (Metafa & Economou, 2013). The authors explored 5
369 different fiber coatings (PDMS, PDMS/DVB, CAR/PDMS, and DVB/CAR/PDMS) both in DI
370 and HS operating mode. In this case, since further pre-treatments were scheduled, DI-SPME was
371 selected using a PDMS/DVB fiber to enhance the enrichment of analytes, necessary for the
372 detection with a single-quadrupole GC-MS. Twenty analytes including terpenes, terpenoids, and
373 norisoprenoids were determined using 10 mL of sample extracted for 10 minutes at room
374 temperature at 1000 rpm of magnetic stirring.

375 SPME based sampling procedures were used also in beer for a similar purpose as wine. Cajka et.
376 al. developed an HS-SPME method coupled to GC-TOF-MS for the acquisition of aroma profile
377 in 265 beer samples (Cajka et al., 2010). Several SPME fibers were tested (100 μ m PDMS, 65
378 μ m PDMS/DVB, 65 μ m CW/DVB, 50/30 μ m DVB/CAR/PDMS, and 85 μ m PA) and other
379 parameters such as extraction time, extraction temperature, salt addition were optimized. Four
380 mL of beer were extracted with 1.7 g of NaCl at 30 °C for 5 minutes, after 10 minutes of
381 incubation at 60°C using a 50/30 μ m DVB/CAR/PDMS fiber.

382 Based on a similar procedure, Dennenlöhner et al. developed and validated an HS-SPME-GC-
383 MS/MS methodology for quantification of selected hop aroma compounds in beer (Dennenlöhner,
384 Thörner, Manowski, et al., 2020). Hop aroma is the odor contribution of a particular mixture of
385 terpenes, terpenoids and esters, compounds that represent a key quality characteristic of many
386 popular beer styles such as “lager” and “IPA”(Anderson et al., 2019). The authors presented a
387 method that aimed to cover a wide concentration range (1–1000 mg/L) for 19 key odor-active
388 molecules and is applicable to the most significant beer styles, from light lagers to highly dry-
389 hopped beers. The method needed 1 mL of decarbonized beer sample, 0.4 g NaCl, and 7.5 minutes
390 of extraction time at 60 °C with a 50/30 µm DVB/CAR/PDMS fiber.

391 Another interesting procedure was presented by Riu-Aumatell et al. focused on the determination
392 of key-odorant in low alcoholic beers (Riu-Aumatell et al., 2014). In this method, 5 mL of sample
393 were extracted at 45 °C for 40 minutes with a 50/30 µm DVB/CAR/PDMS fiber after the addition
394 of 1.75 g of NaCl. Fifty-nine analytes between fermentative compounds like esters, fatty acids,
395 and alcohols, varietal molecules such as terpenes and terpenoids, and many others related to the
396 ageing process (carbonyls and furans) were quantified. Thanks to the lower extraction temperature
397 and to a longer extraction time it was possible to efficiently extract 14 oxygen-containing
398 compounds coming from different categories (carbonyls, carboxyl acids, esters, and furans)
399 without derivatization, as usually did (Buiatti, 2008).

400 Yu Ping Zhao et al. characterized the six most well-known distilled spirits using HS-SPME and
401 GC-MS (Y. P. Zhao et al., n.d.). Fourteen carbonyls, 2 lactones, 59 esters, 5 acetals, 26 between
402 terpenes and norisoprenoids, 22 alcohols, 6 furans, 2 carboxy acids, and 19 additional compounds,
403 for a sum of 155 analytes were quantitated or semi-quantitated in SIM mode. The extraction was
404 performed for 15 minutes at 50 °C consuming 5 mL of diluted sample (deionized water was added
405 to each liquor until 10% v/v ethanol), saturated with 1.5 g of NaCl and extracted using a 50/30
406 µm DVB/CAR/PDMS fiber.

407 A robust HS-SPME method for the determination of nitrogen-heterocyclic volatile aroma
408 compounds (i.e. pyrazines, quinones, and pirroles) in spirits was validated and presented by Picard
409 et al.; this class of odor-active molecules are known to provide a complex aromatic bouquet

410 related to ageing in oak barrels that remove the immature character of raw distillate (Picard et al.,
411 2019). All parameters were explored and optimized obtaining the following procedure: 10 mL of
412 1:10 diluted spirit sample which pH was adjusted to 7, the addition of NaCl 3 g, 30 minutes of
413 extraction at 60 °C with an 85 µm CAR/PDMS coated fiber. The method demonstrated adequate
414 linearity since it provided $R^2 > 0.99$ in whisky through 10 calibration levels (0.5–1000 µg/L).
415 Intraday precision (RSD <10%) was evaluated acquiring 10 replicates of the same spirit spiked
416 at 50 µg/L whereas the interday precision (RSD <20%) was assessed by analyzing 12 replicates
417 at 50 µg/L in 1 month. Accuracy was calculated as a recovery percentage in spiked samples at 3
418 levels and ranged from 78.4% to 121.6%.

419 Niu et. al. extended the HS-SPME aroma determination to cocktails whose composition was based
420 on vodka (Niu et al., 2019). Eight mL cocktail with the addition of 2 g NaCl were extracted at
421 50°C for 45 minutes using a triphasic 50/30 µm DVB/CAR/PDMS fiber; 36 between esters,
422 terpens, terpenoids, norisprenoids, and alcohols were quantitated. The method showed good
423 linearity ($R^2 > 0.99$) for a broad concentration range (approximately from few µg/L⁻¹ to mg/L⁻¹).

424 Cognac is one of the spirits that better represents French tradition all over the world; its sensorial
425 impact is a fingerprint that strongly depends on the contribution of some age-related molecules
426 such as 3-methyl-2,4-nonanedione (3-MND). It is a well-known compound reminiscent of anise
427 or “dried fruit”, according to its concentration, and gives a significative contribution to the
428 characteristic aroma of distilled wines where oxygen plays a key role, both in the production and
429 in the ageing process such as grappa, brandy, rum, vodka, and many others. (Luo et al., 2020; N.
430 Moreira et al., 2018; Plutowska & Wardencki, 2008; Vanderhaegen et al., 2006) Thibaud et. al.
431 developed a method based on HS-SPME that provided adequate performance for its quantitation
432 since the average concentration in the literature ranges from trace to 11.2 µg/L⁻¹ (Melnik et al.,
433 2015; Thibaud et al., 2021). Ten mL of diluted sample (0.250 mL spirit + 9.750 deionized water)
434 were added to 5 g of ammonium sulphate and extracted at 50 °C for 25 minutes using a 65 µm
435 PDMS/DVB fiber. Quantitation was performed with GC-MS in chemical ionization mode using
436 methanol as a reagent gas.

437 MND is a diketone that belongs to the volatile carbonyl compounds family (VCCs). These
438 molecules, depending on their concentration, are related to pleasant nuances since the
439 winemaking of some oxidized wines like Vin Santo (Tofalo et al., 2009), Port (Prata-Sena et al.,
440 2018), Sherry (R. Castro et al., 2004), and Madeira (Pereira et al., 2011) or many distilled wine
441 spirits (Melnik et al., 2015) are tailored to emphasize their production (Manzocco et al., 2000).
442 However, in most cases, the presence of VCCs is a marker of long-standing undesired oxidation
443 related to aroma defects (Alañón et al., 2015; Gabrielli et al., 2021; Li et al., 2008). Carbonyls
444 quantification is sometimes used as a tool for the evaluation of complete fermentation and storage
445 monitoring (Tian et al., 2009). However, due to the significative polarity of carbonyls and the
446 establishing of strong hydrogen bonds with water and ethanol, VCCs (especially with higher
447 molecular weight) are often derivatized before the extraction via HS-SPME (Marín-San Román
448 et al., 2020a).

449 Many HS-SPME methods have been purposed with O-(2,3,4,5,6-pentafluorobenzyl)
450 hydroxylamine (PFBHA) on-fiber derivatization (Schmarr et al., 2008) and in solution
451 derivatization (Bueno et al., 2014; Nathalie Moreira et al., 2019), both with satisfactory results
452 but different simplicity of execution. On-Fiber Derivatization (OFD) strategy was used for the
453 determination of staling aldehydes in wort and beer samples (Dennenlöhner, Thörner, Maxminer, et
454 al., 2020). PFBHA was used as a derivatizing agent and GC-EI-MS/MS was the instrumentation
455 of choice due to its improved sensitivity and reduced matrix effects resulting from overlapping
456 PFBHA-oximes (PFBOs). Fifteen selected aldehydes were determined in wort and beer across a
457 wide concentration range (0.01-1000 $\mu\text{g/L}^{-1}$). The presented method was extensively validated
458 through linearity assessment ($R^2 > 0.99$), LOD/LOQ, precision (RSD < 9.2%), and recovery (80-
459 118%). Extraction needed 3 mL of decarbonized beer, 1 g NaCl, and 10 minutes at 50 °C of fiber
460 exposure previously loaded with the PFBHA. A similar method was purposed by Schmarr et. al.
461 for the determination of many VCCs, such as alkanals, (E)-2-alkenals, (E,E)-2,4-alkadienals, and
462 others including S-containing ketones (Schmarr et al., 2008). In this case, the extraction needed
463 20 minutes at 40 °C using 10 mL of sample and no further preparation step.

464 On Solution Derivatization (OSD) was implemented into a new analytical method for the
465 determination of 18 carbonyl compounds in wines based on HS/SPME and GC-IT-MS (Pérez
466 Olivero & Pérez Trujillo, 2010). After exploring five fiber coatings, time and extraction
467 temperature, desorption time and temperature, pH, and ionic strength, content in tannins and
468 anthocyanins, sucrose, SO₂, and alcoholic degree, the best extracting conditions were: 2 mL of wine
469 saturated with NaCl extracted with a 50/30 µm DVB/CAR/PDMS fiber for 45 minutes at 40 °C.
470 The method was validated over a wide range of concentrations showing good linearity ($R^2 >$
471 0.998), remarkable repeatability and reproducibility (RSD <5.5%), and LOD ranging from 0.62
472 µg/L⁻¹ to 129.2 µg/L⁻¹.

473 Moreira et. al. optimized an HS-SPME method coupled to GC-MS/MS with a prior in-solution
474 derivatization step with PFBHA to quantify 38 VCCs in different categories of Port wines
475 (Nathalie Moreira et al., 2019). Due to its winemaking and ageing process, Port is rich in
476 carbonyls so many issues such as carryover and fiber saturation must be considered. Optimal
477 extraction conditions were achieved with 2 mL of wine extracted using a 65 µm PDMS/DVB
478 fiber under stirring for 20 minutes at 32 °C. The method was also validated in terms of linearity,
479 repeatability, inter and intra-day precision and accuracy.

480 Similar methods have also been used to perform carbonyl quantitation in other beverages like
481 beer; Moreira et. al. presented a fully automated HS-ISD-SPME method using PFBHA as the
482 derivatizing agent like in most procedures for the determination of 45 different VCCs (Nathalie
483 Moreira et al., 2013a). Sixty-five µm PDMS/DVB fiber was used to extract 5 mL of beer at 45°C
484 for 20 minutes without salt addition. The proposed method showed to be linear, precise, accurate
485 and sensitive. LODs ranged from 0.003 to 0.510 µg/L⁻¹, except for furans which were higher
486 (1.54–3.44 µg/L⁻¹) whereas LOQs varied from 0.010 to 1.55 µg/L⁻¹, except for furans (4.68 – 10.4
487 µg/L⁻¹). Good repeatability was achieved (RSD <17%) for all analytes. Accuracy was measured
488 by evaluating recovery in spiked samples which ranged from 88% to 114%.

489 HS-SPME with GC-MS was used for the determination of acrolein in alcoholic beverages. M.
490 Kächele et.al. developed a method using a fiber of 85 µm CAR/PDMS coating (Kächele et al.,
491 2014). Samples were prepared by weighing and mixing in an HS vial 2 g of NaCl, 5 mL of distilled

492 water and 0.125 g of beverage. The extraction was performed at 50 °C for 10 minutes. Since
493 acrolein is both an odor-active compound and a cytotoxic hazard for human health, its
494 determination is a very important task from more than one point of view. A very similar method
495 was developed for the quantification of carbonyl and furan derivatives whose exposure could be a
496 risk for human health (Hernandes et al., 2019). A 50/30 µm DVB/CAR/PDMS fiber was used for
497 the extraction of 1 mL of sample with 30% NaCl (m/v) at 55°C for 1 hour. The fiber was
498 overcoated with PDMS to allow a simultaneous quantification of brewing compounds.
499 Performances were significant, especially for a SIM-mode quantification system (LOD ranging
500 from 0.03 µg/L⁻¹ for acrolein, to 1 µg/L⁻¹ for furfural).

501

502 2. Poly Ionic Liquids (PILs) in HS-SPME

503 Ionic liquids (ILs) are a particular class of non-molecular solvents also known as liquid, organic,
504 molten, or fused salts, which couple negligible vapor pressure and low melting point (usually
505 lower than 100°C) (F. Zhao et al., 2008). Most ILs are composed of nitrogen-based cations
506 (pyridine, pyrrolidine, imidazole and others) and a widespread variety of anions, spanning from
507 halides to more complex organic conjugated bases (Hallett & Welton, 2011). The main features
508 of ILs are their adjustable viscosity, significant thermal stability and the possibility to design
509 their formulation to enhance or reduce water miscibility (Mehrdad et al., 2019). Poly Ionic Liquids
510 (PILs) are organic polymers mainly obtained by the polymerization of unsaturated ionic liquid
511 monomers. The main advantage provided is the mechanical stability of polymers coupled to the
512 features of ILs that make PILs a promising coating for SPME fibers (Singha et al., 2018).

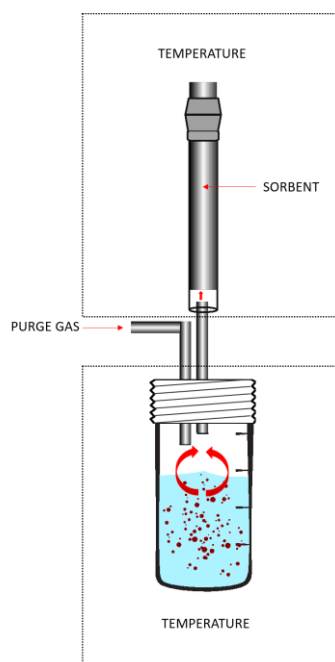
513 González-Álvarez et. al. used an imidazolium based PILs as a coating for SPME fiber used to
514 analyze beer aroma (González-Álvarez et al., 2013). Two different fiber materials were
515 synthesized by a free radical polymerization and assessed to provide high thermal and structural
516 stability. The IL-1 butenyl fiber was compared to the conventional PDMS-DVB 65 µm and CAR-
517 PDMS 75 µm fibers, showing a significant performance boost. Efficiency was evaluated in the

518 analysis of lemon beer aroma by spiking real samples at 3 levels (100, 200, and 300 $\mu\text{g/L}$)
519 obtaining satisfactory recoveries (78.4 – 123.6%) for all 8 compounds.

520 Crucello et. al. evaluated some PILs coatings for the aroma characterization of novel Brazilian
521 wines (Crucello et al., 2018). The best PILs-coated fiber was evaluated to be made a cross-linked
522 imidazolium-based polymer which exhibited superior performance compared to
523 DVB/CAR/PDMS. No quantitative data was provided but the comprehensive wine aroma profile
524 obtained (up to 372 compounds identified) allowed a powerful evaluation of VOAs compounds
525 available in the samples and could be a powerful tool for comparisons between different
526 winemaking styles or vintages.

527 3. Full Evaporation Dynamic Headspace (FEDHS)

528 Full Evaporation Dynamic Head Space (FEDHS) is a solvent-free technique that can be coupled
529 to GC–MS for the determination of volatile compounds at sub- $\text{ng}\cdot\text{mL}^{-1}$ level. In FEDHS a
530 reduced amount of sample is fully vaporized without any liquid-to-gas equilibrium that
531 maximizes sensitivity for semi-volatile compounds and ultra-trace ones (Figure 4).



532

533 **FIGURE 4.** Schematic of fully evaporation dynamic head space FEDHS extraction system.

534 Compared to conventional D-HS and HS-SPME, FEDHS provides more uniform enrichment over
535 the entire polarity range for odor compounds in aqueous samples. Ochiai et. al. developed a

536 method for the analyses of key odor compounds (including hydrophilic and less volatile)
 537 characteristics in whiskey (Ochiai et al., 2012). FEDHS was performed at 80°C using 3 L of purge
 538 gas to allow the complete vaporization of 100 µL of whiskey. The developed method showed high
 539 recoveries (85–103%) of the 18 odor-active compounds, separating them from most of the low
 540 volatile matrix. Good linearity ($R^2 > 0.9909$) and high sensitivity (limit of detection: 0.21–5.2
 541 $\text{ng}^*\text{mL}^{-1}$) were achieved. Phenolic compounds including vanillin were determined in the range of
 542 0.92–5.1 $\mu\text{g}^*\text{mL}^{-1}$ (RSD < 7.4%) in 6 single malt whiskey samples. Eight compounds including
 543 12 potent odorants (e.g. coumarin, furaneol, indole, maltol, and pyrazine congeners) were
 544 determined in the range of 0.21–110 $\text{ng}^*\text{mL}^{-1}$ (RSD < 10%).
 545 All relevant applications based on solvent-free analysis of aroma-active compounds in alcoholic
 546 beverages are reported in Table 1.

547 **TABLE 1.** List of solvent-free methods for the analysis of odor active compounds in alcoholic beverages
 548 and related highlights.

Ext. technique	Matrix	Ext. volume	Instrumentation	Pro & Cons	Article
HS-SPME	Wine	4 mL	GC- <u>EL</u> -MS	+ Wide range of analytes, high-optimization - Ion extraction chromatogram used for quantification	(Lukić et al., 2016, 2017; Perestrelo et al., 2011)
HS-SPME + DI-SPME	Wine	10 mL	GC- <u>EL</u> -MS	+ Strong validation, good performance - Only varietal compounds	(Metafa & Economou, 2013)
HS-SPME	Beer	4 mL	GC- <u>EL</u> -TOF-MS	+ Fast, many analytes, reduced RSD, efficient - Only high concentrated analytes	(Cajka et al., 2010)
HS-SPME	Beer	1 mL	GC- <u>EL</u> -MS/MS	+ Accurate quantitation (3 I.S.+MRM), reduced sample volume - High LOQ, non-commercial I.S.	(Dennenlöhner, Thörner, Manowski, et al., 2020)
HS-SPME	Beer	5 mL	GC- <u>EL</u> -MS	+ 59 analytes, polar compounds without derivatization - Long extraction time	(Riu-Aumatell et al., 2014)
HS-SPME	Spirits	5 mL	GC- <u>EL</u> -MS	+ 155 analytes from all categories - Poor validation data provided	(Y. P. Zhao et al., n.d.)
HS-SPME	Spirits	1 mL	GC- <u>EL</u> -MS	+ Robust quantitation of N-heterocycles, LOQ, sample volume	(Picard et al., 2019)

				- pH adjustment, only 1 class of analytes	
HS-SPME	Vodka cocktail	8 mL	GC- <u>EL</u> -MS	+ Broad calibration range, complex matrix	(Niu et al., 2019)
				- Large sample volume, only fermentative analytes	
HS-SPME	Cognac	0.25 mL	GC-CI-MS	+ Reduced sample volume, performance	(Thibaud et al., 2021)
				- Only MND, require CI	
HS-OFD-SPME	Beer	3 mL	GC- <u>EL</u> -MS/MS	+ Reduced LOD, extensive validation	(Dennenlöhner, Thörner, Maxminer, et al., 2020)
				- Complexity, only some aldehydes	
HS-OFD-SPME	Wine	10 mL	GC- <u>EL</u> -IT-MS	+ Broad range of carbonyls, no salt addition	(Schmarr et al., 2008)
				- Large sample volume, no real application presented	
HS-ISD-SPME	Wine	2 mL	GC- <u>EL</u> -IT-MS	+ Performance, robust validation, automatable	(Pérez Olivero & Pérez Trujillo, 2010)
				- Limited range of carbonyls	
HS-ISD-SPME	Wine	2 mL	GC- <u>EL</u> -MS/MS	+ Wide range of VCCs, robust validation, efficient, reliable	(Nathalie Moreira et al., 2019)
				- No diketone was quantified, used in analyte-rich matrix	
HS-ISD-SPME	Beer	2 mL	GC- <u>EL</u> -IT-MS	+ Strong validation, efficient, reliable	(Nathalie Moreira et al., 2013b)
				- Proof of application with a reduced number of samples	
HS-SPME	Beer, wine, many spirits	0.125 mL	GC- <u>EL</u> -MS	+ Performance, robustness, almost all beverages, minimized amount of sample	(Kächele et al., 2014)
				- Only 1 analyte	
HS-SPME	Beer	1 mL	GC- <u>EL</u> -MS	+ Wide range of polar analytes	(Hernandes et al., 2019)
				- Long extraction time, reduced productivity	
HS-SPME	Beer	8 mL	GC- <u>EL</u> -MS	+ Significant efficiency boost, good validation.	(González-Álvarez et al., 2013)
				- Only 8 compounds, only one matrix, validation in water	
HS-SPME	Wine	10 mL	GC- <u>EL</u> -MS	+ Full automatable, strong optimization and validation, good performance	(Tang & Duan, 2017)
				- Long extraction time (40 min)	
HS-SPME	Wine	4.5 mL	GCxGC- <u>EL</u> -MS	+ Performance, informations provided	(Crucello et al., 2018)

				- No quantitative results provided, long extraction time (60 min)	
SBSE	Wine	20 mL	GC- <u>EL</u> -MS	+ Flexibility, simplicity	(Caven- quantrill & Buglass, 2011)
				- Affected from ethanol, laborious	
SBSE	Wine	20 mL	GC- <u>EL</u> -MS	+ Simplicity, strong enrichment	(Magali Picard, Celine Franc, Gilles De Revel, 2018)
				- Requires a previous SPE	
SA-SBSE	Beer	5 mL	GC- <u>EL</u> -MS/MS	+ Strong enrichment, modularity	(Ochiai et al., 2016)
				- Effect of ethanol, heat-induced artifacts	
FEDHS	Whiskey	0.1 mL	GC- <u>EL</u> -MS	+ Minimized sample volume, sensitivity	(Ochiai et al., 2012)
				- Require instrumentation, unsuitable for reacting molecules, only few analytes	

549

550 B. Immersion-based techniques

551 1. Direct Immersion Solid Phase Micro Extraction (DI-SPME)

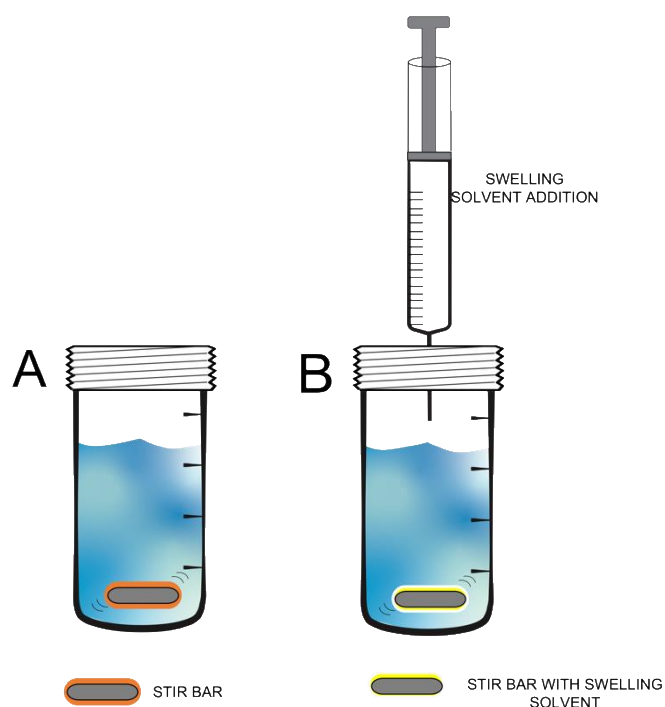
552 In DI-SPME, the sorbent is directly exposed/immersed into the sample determining a higher
553 interaction between analytes and fiber, and better recoveries for semi-volatile or non-volatile
554 compounds (Figure 3 (b)). On the other hand, for the same reason, this configuration is affected
555 by an increased matrix effect from complex samples that is also related to reduced fiber lifetime.
556 Significant steps have been done through the development of new, more specific sorbent
557 materials to overcome these restrictions (P. Rocío-Bautista, 2018) but currently DI-SPME is not
558 the gold-standard in VOAs solvent-free analysis. Despite that, Tang et al. proposed a porous PILs
559 to be used as a fiber coating for the analysis of organic acids in wine (Tang & Duan, 2017). An
560 imidazolium-based coating was used and assessed to provide a significant performance increase.
561 Samples were extracted with an on-fiber derivatization strategy using N-tert-butyltrimethylsilyl-
562 N-methyltrifluoroacetamide (MTBSTFA). All parameters including salt addition, pH, extraction
563 temperature and time, derivatization temperature and time were explored in addition to the PILs
564 synthesis optimization, to achieve the best performances. An extensive validation demonstrated
565 good linearity ($R^2 > 0.99$) in the range $0.01 - 1 \text{ mg/L}^{-1}$, satisfactory LOD (up to $0.07 \text{ } \mu\text{g/L}^{-1}$), proper

566 repeatability (RSD<16%) and fiber-to-fiber reproducibility (RSD<20%). Recoveries in spiked
567 wine samples ranged from 78.19 to 98.11% and lifetime fiber durability was satisfactory.

568

569 2. Stir-Bar Sorptive Extraction (SBSE)

570 An alternative to SPME which combines the absence on solvents and provides a simultaneous
571 enrichment and isolation of analytes, is represented by SBSE. These devices are bases in the
572 coating of a stir bar of PDMS with a potential extraction sorbent (Figure 5).



573

574 **FIGURE 5.** Extraction modes in stir bar sorptive microextraction (SBSE). (A) Classical SBSE extraction.
575 (B) Solvent assisted (SA) SBSE extraction

576

577 Contrary to HS-SPME or DI-SPME, in which the sorbent remains static throughout the overall
578 extraction process, the SBSE is a dynamic extraction. In this process, the sorbent is moving
579 through the solution, in this case, by a magnetic force (David & Sandra, 2007). This favors
580 analyte-sorbent interactions, and therefore requires much shorter extraction times than SPME.

581 Caven-Quantrill et. al. presented a study where SBSE was used in a comparison of volatile
582 composition between grape juice and model wine (Caven-quantrill & Buglass, 2011). Twenty-
583 four μL PDMS coated stir bar (length: 10 mm, film thickness: 0.5 mm) was used to extract 20 mL

584 of sample at room conditions for 2 hours at 1100 rpm; the stir bar was then washed with pure
585 water, dried and placed into the thermal desorption tube.

586 SBSE was also used as an enrichment step following a previous sample preparation technique to
587 make detectable trace analytes. Picard et. al. developed a method for the determination of 8
588 limonene derived monoterpenes related to the mint aroma in red wines (Magali Picard, Celine
589 Franc, Gilles De Revel, 2018). These molecules are not detectable without a complex sample
590 preparation so, in this application, SPE was followed by SBSE to make identifiable. A PDMS
591 coated stir bar (126 μ L; length: 20 mm; film thickness: 1 mm) was dropped into 20 mL of SPE
592 extract (diluted in Milli-Q water to a final ethanol concentration of 15% v/v) for 1 h at 20°C
593 stirring at 600 rpm. After a comprehensive optimization, the method was validated and
594 successfully applied to 15 Bordeaux red wines coming from different producers and vintages.

595 2.1 Solvent Assisted (SA)-SBSE

596 SBSE was used for the determination of 28 aroma compounds in beer in an innovative method
597 presented by Ochiai et. al. (Ochiai et al., 2016). A commercial PDMS stir bar (63 μ L; length: 10
598 mm; film thickness: 1 mm) was swollen in several solvents with log K_{ow} ranging from 1.0 to 3.5
599 while stirring for 30 min before extraction; this procedure is named Solvent-Assisted SBSE (SA-
600 SBSE) and showed in Figure 5 (B). SA-SBSE demonstrated to provide better recoveries if
601 compared to conventional SBSE depending on the solvents used in the stir bar preparation step
602 and on the log $K_{ow} < 2.5$ of the analytes. Working with low-temperature thermal desorption (80°C)
603 the formation of heat-induced artefacts was excluded and it was possible to optimize the method
604 for the determination of 21 aroma active compounds in beer samples. Repeatability (RSD <8%)
605 and linearity ($R^2 > 0.99$) were obtained for all compounds and that was a significant result. Similar
606 procedures for the analysis of beverage with higher alcoholic percentage like wine and spirits
607 have not been published yet; this is reasonably due to the reduced polarity of ethanol compared
608 to water those lower recoveries for low-polarity analytes.

609 III. Solvent based techniques

610 As mentioned before, SPME is the most utilized miniaturized sample preparation technique for
611 GC-MS determination of volatile and semi-volatile compounds in alcoholic beverage samples
612 (Fontana et al., 2018; López-Vázquez et al., 2012). However, less volatile and high water soluble
613 compounds, still amenable to GC analysis, are difficult to extract using this technique. Thus, there
614 is a demand for alternative sample preparation approaches capable of extracting a broad set of
615 volatile, semi-volatile, polar, and non-polar compounds in alcoholic beverages. As mentioned
616 before, LPME techniques fulfill these requirements allowing the high analyte pre-concentration
617 and the extraction with a volume lower than 100 μL simultaneously. It can be entirely injected
618 into the analytical instrumentation avoiding additional time-consuming procedures. Nowadays,
619 several LPME strategies are under investigation in beverages applications. However, these
620 researches are mainly focused on the determination and quantification of pesticides and
621 exogenous compounds rather than VOAs. To the best of our knowledge, only DLLME is
622 successfully applied to this specific application.

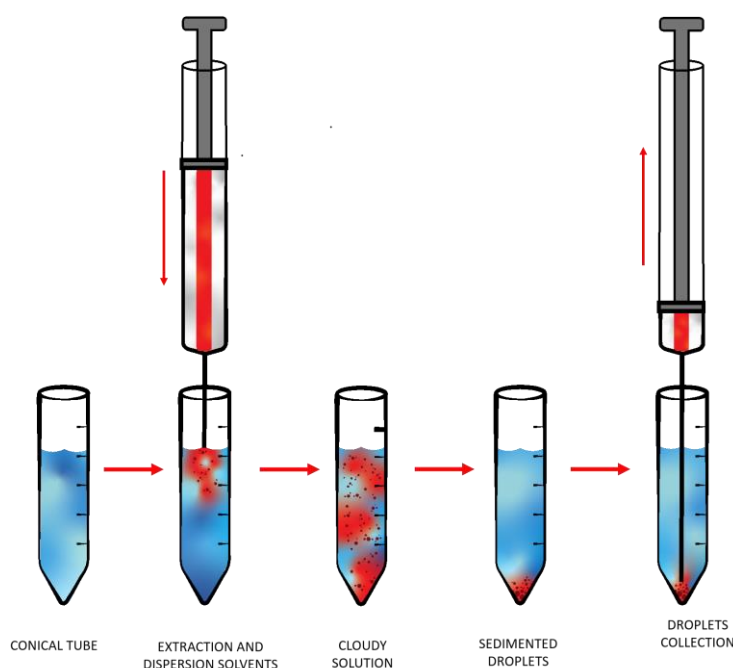
623

624 A. Dispersive Liquid-Liquid Micro Extraction (DLLME)

625 DLLME is an interesting microextraction technique used in broad application fields
626 (Abdolmohammad-Zadeh & Sadeghi, 2010; Mashayekhi et al., 2010), mainly because of its low
627 operational cost and simplicity of the required equipment (Oller-Ruiz et al., 2017). It can be
628 performed directly in standard conical tube obtaining an efficient preconcentration of the analytes
629 in a short time using few microliters of solvents (Viñas et al., 2014). For this reason, since it was
630 introduced in 2006 by Rezaee et al. (Rezaee et al., 2006), more than 2500 papers have been found
631 in the literature, making it a very active topic in sample preparation research studies (Hansen &
632 Pedersen-Bjergaard, 2020).

633 DLLME employs a ternary system consisting of an extraction solvent (10-500 μL) immiscible in
634 water and a dispersion solvent (0.2-1 mL) miscible both with water and the extractant solvent,
635 which are quickly injected into an aqueous sample (2-10 mL). The basis of the technique is the

636 partition of the analyte between the sample and the extractant solvent. The contact of the three
637 components creates a cloudy solution in which the extraction solvent is dispersed in the sample
638 solution forming multiple organic microdroplets (Figure 6).



639

640 **FIGURE 6.** Traditional dispersive liquid–liquid microextraction workflow.

641 Various strategies such as salt addition or ultrasound assistance can be used to boost recoveries.
642 A further centrifugation step ensures the phase separation which is followed by the droplet
643 collection and easy analysis by hyphenated or direct analytical methodologies. Several papers are
644 available in literature to demonstrate its applicability and performance level for VOAs analysis.
645 Zhou et al., used the conventional DLLME ~~coupled with~~ followed by GC-MS analysis to
646 determine main higher alcohols in fermented alcoholic beverages (Zhou et al., 2020). This method
647 allowed to efficiently quantify six alcohols in a characteristic chinese alcoholic beverage. The
648 sample (3.5 mL) was diluted 1:1 with water without any pH adjustment and using 2.1 mL of
649 solvents (1.5 mL of acetonitrile as dispersion and 0.6 mL of dichloromethane as extractant
650 solvents, respectively). Once optimized extraction conditions, only seven minutes (Zhou et al.,
651 2020) are needed to perform the overall sampling process leading to a very rapid method with
652 Enrichment Factors (EFs) spanning from 8.1 % and 9.1 % for selected compounds. Moreover,

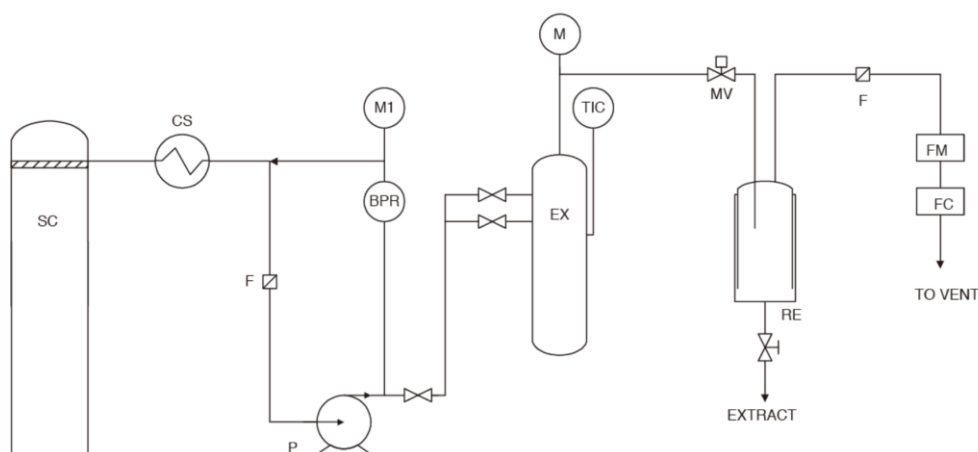
653 they compared DLLME with S-HS and HS-SPME, demonstrating the DLLME advantages in
654 terms of recoveries, peak shape in the chromatographic separation, and time saving. Fariña et al.
655 (Fariña et al., 2007), determined two volatile phenols, 4- ethyl guaiacol and 4-ethylphenol in wine
656 using DLLME ~~and coupled with~~ GC-MS. They used 5 mL of wine samples, to which were added
657 1 mL of acetone as a dispersion solvent and only 50 μ L of carbon tetrachloride as extractant
658 solvent. Results showed a very rapid procedure that takes less than six minutes for the extraction
659 time with a minimum solvent usage. The comparison with other techniques conventionally used
660 to determine volatile phenols in wine (LLE, SPE, HS-SPME, and SBSE) showed how this strategy
661 reduced the analysis time and the required amount of sample. Fontana et al. (Fontana et al., 2018)
662 characterized the profile of volatile and semi-volatile compounds in grape marc distillates
663 extracted by DLLME and analyzed with a GC coupled to a time-of-flight accurate MS (TOF-
664 MS). The extraction method was performed and optimized on a group of 17 compounds with
665 different chemical functionalities (ketones, aldehyde, esters, alkanes, and alcohols) and response
666 ranges in distillates. A selected volume of 2.5 mL of grape sample was diluted at 9 mL with water
667 before extraction to reduce the adverse effect of the high percentage of ethanol (~ 40%) in the
668 affinity of the compounds to extractant solvent. Acetonitrile (400 μ L) and chloroform (100 μ L)
669 were selected as dispersive and extractant solvents, respectively. The obtained EFs were up to 52
670 times. The extraction efficiency of DLLME was compared with three SPME conditions: Direct-
671 SPME at room temperature, HS-SPME at room temperature, and HS-SPME at 50 °C thermostated
672 sample. The results showed that 12 out of 17 compounds are better extracted with the DLLME
673 technique with low consumption of sample, solvent, and in a very faster sampling procedure (4
674 min). Oller-Ruiz et al., investigated for the first time the DLLME technique ~~followed by coupled~~
675 ~~to~~ LC-MS/MS to determine five monoterpenes in hazelnut liqueur, red wine, whiskey, brandy,
676 rum, and gin_ (Oller-Ruiz et al., 2017). No dilution in water was assessed because the ethanol
677 content of each beverage was used as a dispersive solvent in a sample volume of 8 mL.
678 Chloroform was chosen as extractant solvent and 300 μ L of it were rapidly added to unmodified
679 beverages sample. The enriched phase of chloroform was evaporated and reconstituted on 50 μ L

680 of water, a suitable LC-MS solvent. The optimized method allowed to achieve EFs ranging from
681 12 and 88 using low amounts of organic solvents in a very short extraction time (3 min).

682

683 B. Supercritical Fluid Extraction (SFE)

684 Supercritical Fluid Extraction (SFE) is a sample preparation technique where a supercritical fluid
685 is used as extraction solvent (Figure 7).



686

687 **FIGURE 7.** Schematic representation of SFE extraction and the equipment used (Gracia et al., 2009).
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689 year [2022].

690

691 The supercritical state is a combination of high temperature and high pressure which both exceed
692 their critical values. As a consequence, the solvent properties gradually change showing a gas-
693 type viscosity coupled to a density similar to that of the liquid state (Sakai et al., 2019). In terms
694 of polarity, supercritical fluids are known to be non-polar and their use as extracting solvent gives
695 the best efficiency with nonpolar or low polar substances. However, the characteristics mentioned
696 above can be tuned by adjusting temperature and pressure making supercritical fluids a non-toxic,
697 flexible, and selective alternative to conventional organic solvents. In addition, it's important to
698 highlight that in SFE methods the supercritical fluid can be easily removed from the extract and
699 recirculated, making the extraction simple, clean, solvent efficient, and environmentally
700 sustainable (Lang & Wai, 2001). The aspects pointed above allow supercritical fluids to be
701 included in the group of green solvents and SFE to be labelled as a GAC procedure. Currently,

702 CO₂ is the most used supercritical fluid, sometimes coupled with co-solvents such as ethanol or
703 methanol to adjust its polarity (Macedo et al., 2008).

704 Even though SFE was, especially in the last 20 years, an emerging GAC technique, Namieśnik
705 et. al. (Wiśniewska et al., 2015) published a review in 2014 where only one study was presented
706 for the determination of ethanol, which is not an VOAs compound, in spirit based alcoholic
707 beverages (Señoríns et al., 2001). Up to now, SFE is used as a promising technology of aroma
708 compound extraction for industrial purposes (Van Opstaele, Goiris, et al., 2012), or as a treatment
709 for off-flavor removal (Gernat et al., 2020).

710 Carro et. al. developed an SFE based on supercritical CO₂ for the extraction of many free VOAs
711 in wine and must aroma (Carro et al., 1996). This paper can be considered a vanguard work since
712 it was presented in 1996 when the GAC principles were still not presented yet. However, despite
713 being over twenty years old, the authors developed an efficient SFE method that can be considered
714 “green” if compared to other used in those years. The sample (50 mL) was first extracted with
715 3.94 g of Amberlite XAD-2 in the extraction chamber, spiked with methanol (used as modifier),
716 extracted with supercritical CO₂, and finally eluted with 2 mL dichloromethane. Forty free volatile
717 compounds including terpenes, terpenoids and norisoprenoids were tentatively identified and
718 quantified after a brief validation (repeatability, correlation coefficient, and linearity range).

719 As concerns the spirits, Gracia et. al. presented an SFE method for the isolation of VOAs in sugar
720 cane spirits using supercritical CO₂. In this experiment, SFE was evaluated as a promising
721 technology for concentrating aroma compounds but since the extracts were analyzed, it can be
722 also considered for analytical purposes (Gracia et al., 2007). Twenty mL of extracts were diluted
723 1:1 with standard ammonium sulphate solution and extracted with 5 mL of diethyl ether/hexane
724 mixture (2:1). The organic layer was collected, concentrated under a nitrogen flow, filtered, and
725 used for GC-MS analysis. Up to 24 VOAs compounds were identified in crude and aged sugar
726 can spirits. The same research group extended the same procedure to fast aged rum with the same
727 purpose (Gracia et al., 2009).

728 All the discussed applications of VOAs analysis in alcoholic beverages using green miniaturized
729 solvent-based techniques are reported in Table 2.

730

731 **TABLE 2.** List of solvent-based methods for the analysis of odor active compounds in alcoholic beverages
 732 and related highlights.

Ext. technique	Matrix	Sample volume	Ext. solvent volume	Ext. details	Instrumentation	Pro & Cons	Ref.
DLLME	Huangjiu (non-distilled alcoholic beverage)	2.5 mL	0.6 mL (dichloromethane)	Dispersive solvent Volume: 1.5 mL (acetonitrile)	GC-MS	+ rapid (1 min extraction time) -Dilution required to decrease ethanol percentage	(Zhou et al., 2020)
DLLME	Wine	5.0 mL	0.05 mL (carbon tetrachloride)	Dispersive solvent Volume: 1.0 mL (acetone)	GC-MS	+ rapid extraction -only two compounds detected	(Fariña et al., 2007; Gracia et al., 2007, 2009)
DLLME	Grape marc distillate	2.5 mL	0.1 mL (chloroform)	Dispersive solvent Volume: 0.4 mL (acetonitrile)	GC-HRMS	+ rapid extraction for a wide class of compounds -Dilution required to decrease ethanol content	(Fontana et al., 2018)
DLLME	Rum, Brandy, Mistela	8 mL	0.3 mL (chloroform)	---	LC-MS	+ Rapid extraction; disperser solvent not required -Evaporation to dryness required due to the LC-MS incompatibility of extraction solvent	(Oller-Ruiz et al., 2017)
SFE	Wine	50 mL	---	Ion resin adsorption prior to SFE	GC-MS	+ Efficient, linear - Use of ion resin and dichloroethane	(Carro et al., 1996)
SFE	Spirit, rum	20 mL	---	Micro-LLE on SFE extract	GC-MS	+ micro LLE - Need of LLE, only qualitative	(Gracia et al., 2007, 2009)

733

734 IV. Conclusions

735 Aroma is one of the most relevant aspects in beverage, so the analysis of VOAs is crucial, both
736 for product development and quality control. Since wine, beer and spirits are among the most
737 consumed beverages all over the world, the environmental impact of greening the analytical
738 process of their aroma is relevant. This result must be achieved with a simultaneous improvement
739 in terms of performance, because of the low concentration of many odor active compounds.

740 Miniaturized solvent-based techniques are a good answer for this issue since a strong reduction
741 of all volumes is the first goal to achieve for the GAC rule. LPME, such as DLLME allows to
742 combine a significative lowering of sample, solvents, and waste, without requiring specific
743 instrumentation; in addition, these techniques are the ones which better fits with LC-MS analysis.
744 However, since the extraction solvent must be immiscible with the matrix, finding a green one
745 with this characteristic is not an easy task. SFE is a promising extraction technique but currently
746 it has been used only for few MS based protocols.

747 On the other hand, nowadays solvent-free techniques could be addressed as the best solution for
748 coupling good recovery, high enrichment, and robustness without using energy and polluting
749 solvents. Currently, HS-SPME is the gold standard for GAC applied to VOAs analysis since it is
750 widely used for most aroma active compounds with excellent results, both with and without
751 derivatization; since it's used for sampling the head-space, HS-SPME is more representative of
752 the beverage aroma. SPME perfectly couple with GC-MS analysis and it's the most automatable
753 extraction technique. Many coatings have been developed, spanning from PDMS to PILs, which
754 allow to find a fiber suitable for most VOAs compound. SBSE could be assessed as a good
755 alternative instead of SPME, especially for mid-volatile compounds; since it works immersed in
756 the sample, extraction efficiency is not limited by molecules volatility. However, SBSE is limited
757 by a restricted choice of coatings if compared to SPME, lower life-time and is less automatable.
758 Currently, SBSE was employed only for low alcoholic grade beverages like beer.

759 The GAC principles are moving sample preparation towards solvent-free techniques, which
760 demonstrate to be the best choice for most analytes; however, a significative improvement should

761 be the optimization focused for coupling these sample preparation methods with LC-MS analysis.
762 Succeeding in this task means to reach the goal of extending the best GAC extraction techniques
763 to trace-compounds, to better determine mid-volatile analytes and to significantly improve limits
764 of detection and quantification of each other.

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