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

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ABBREVIATION

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

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

Thus, green micro-extraction techniques are rapidly evolving in several fields such as bioanalytical, forensic (Borden et al., 2020), and food applications (Agrawal et al., 2021; Hansen & Pedersen-Bjergaard, 2020; He & Concheiro-Guisan, 2019; Soares da Silva Burato et al., 2020; V. Soares Maciel et al., 2018). In agro-food analysis, the determination of flavor and fragrances in food and beverages has become a hot research topic, mainly because of their massive consumption worldwide (Martins et al., 2021; V. Soares Maciel et al., 2018). The accurate identification and quantification of the characteristic odor-active compounds in wine, beer, and spirits are crucial for obtaining a well-balanced product appreciated by consumers (Van Opstaele, De Causmaecker, et al., 2012). Because of that, research activities focused on beverage aroma are out of the most dynamic topics in food chemistry (Lyu et al., 2021). Just by browsing the literature produced up to the time this review was written and searching for the name of the beverage (wine, 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).
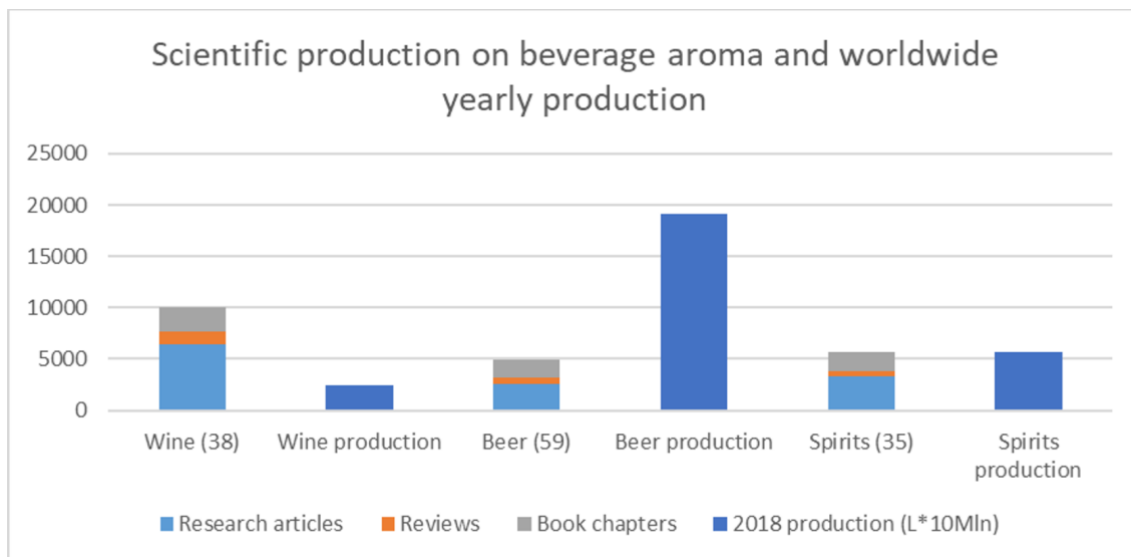
124   **FIGURE 1**. Scientific production (ScienceDirect, 2021) on beverages aroma (in brackets the number of

125   patents currently deposited) and the 2018 yearly worldwide production (Conway, 2020).

127   However, analysis of such complex matrices is still challenging, requiring at least one sample

128   preparation step to balance matrix effects, and overcome false quantitative results. Generally,

129   sample preparation procedures for alcoholic beverages combine several processes such as

130   extraction, preconcentration, fractionation, and isolation of targeted compounds, including

131   copious amounts of organic solvents (Marín-San Román et al., 2020a). Nowadays, micro-

132   extraction techniques are helpful to eliminate or minimize the amounts of solvents and reagents

133   used, matching GAC requirements as well as the needed sample treatments. Moreover, these

134   techniques consider the recovery of the extractant solvents, their reuse (Namiesnik, 2000), and in

135   some instances, the use of less toxic solvents. Non-chlorinated organic compounds, novel solvents

136   such as ionic liquids (ILs)(Hallett & Welton, 2011; Pacheco-Fernández & Pino, 2019; Trujillo-

137   Rodríguez et al., 2013), eutectic point solvents ultra-low (DESs) (Cunha & Fernandes, 2018;

138   Smith et al., 2014), supramolecular solvent (amphiphilic solvents) (Ballesteros-Gómez et al.,

139   2010; Melnyk et al., 2014), or supercritical fluids (Jose A. Mendiola, Miguel Herrero, Maria

140   Castro-Puyana, 2013) are the new trend in the micro extraction applications. The following

141 sections illustrate the current scenario of the mostly used green microextraction techniques to

142 determine specific aroma compounds, the volatile odor active molecules (VOAs) in popular

143 alcoholic beverages.

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A. Role of VOAs in alcoholic beverages

146 From the chemical point of view, wine, beer, and spirit aromas are complex mixtures of volatile

147 molecules derived from raw materials, transformation steps, ageing phenomena, and, sometimes,

148 undesired side reactions. These compounds are often part of articulated equilibrium involving

149 phase transitions (physical equilibrium), bond cleavage or redox reactions (chemical equilibrium),

150 and many bio catalyzed steps that make them just the tip of an iceberg (Gabrielli et al., 2021; Luo

151 et al., 2020; Polášková et al., 2008; Schieberle, 1995; Vanderhaegen et al., 2006). Among the

152 multitude of intrinsic components of alcoholic beverages, VOAs are the first compounds reaching

153 the consumers, even before drinking (odor); together with the ones received through the retro

154 nasal way (aroma), they compose the flavor (Ibáñez & Cifuentes, 2015; Özay et al., 2019). Odor,

155 and especially aroma are also the quality aspects that are most directly related to taste, satisfaction

156 and healthiness (Morrin & Tepper, 2021). Several groups of compounds are related to

157 characteristics scents such as esters for fruity (Niu et al., 2019), terpenes for floral (Yang et al.,

158 2019), six carbon chain alcohols and aldehydes for herbaceous (Sun et al., 2020),

159 four/six/eight/ten carbon chain linear saturated fatty acids for cheesy (Katarína et al., 2014; Selli

160 et al., 2006). Contrarily, strong identity molecules can be directly associated with specific good

161 like 1,1,6-trimethyl-1,2-dihydronaphthalene for kerosene (Dobrydnev et al., 2020), furaneol for

162 strawberries (Ferreira et al., 2003), diacetyl for butter (Anderson et al., 2019) and so on. This

163 composition is characteristic for fermented beverages such as wine, beer, spirits, and all those

164 beverages that are produced using microbiological transformations (Anjos et al., 2021; Garde-

165 Cerdán & Ancín-Azpilicueta, 2006; Pissarra et al., 2005). In addition, beverages whose

166 production occurs a barrel refining, are involved in a sorption equilibrium between the liquid

167 phase and the wood, from which many compounds can be extracted or adsorbed (Martínez-Gil et

168 al., 2018). Hence, VOAs are an heterogeneous class of compounds whose concentrations varies

169 from a few ng·L^{-1} to hundreds of mg·L^{-1} who are enclosed in complex and compositionally

170 variable matrices in which interfering macro-components such as polyphenols, ethanol,

171 polysaccharides, and fermentative compounds can modulate their volatility (Andujar-Ortiz et al.,

172 2009; Castro-Vázquez et al., 2011; Davis & Qian, 2019).

173 These characteristics highlighted the complexity of VOAs analysis that requires dedicated sample

174 preparation procedures to allow an accurate quantitative determination. The most critical step lies

175 in selecting an extraction method capable of isolating the desired analytes without resulting in the

176 formation of artifacts (Thompson-Witrick et al., 2015). Moreover, each alcoholic beverage matrix

177 remarkably varies one from the other, making many methods suitable only for a specific class of

178 products. Therefore, the need for specific methods for each matrix, often associated with laborious

179 pretreatments or further operations is mandatory. In fact, because of the diversity of VOAs, an

180 ideal method that can concentrate and recover all targeted compounds is not available (Zhang et

181 al., 2020). Accordingly, this review article covers the widely used microextraction techniques in

182 the determination of VOAs in alcoholic beverages, with particular emphasis on the greenest

183 methodologies.

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185 ## B. Sample preparation for determining VOAs

186 Classical sample preparation techniques for the determination of VOAs in wine, beer, and spirits

187 include Static (S-HS) or Dynamic Head-Space extraction (D-HS) (Rosillo et al., 1999), Liquid–

188 Liquid Extraction (LLE) (Costa Freitas et al., 2012; Mamede & Pastore, 2006; Mayr et al., 2014),

189 and Solid-Phase Extraction (SPE) (Cabrita et al., 2007; Remedios Castro et al., 2008; López et

190 al., 2002). Extraction techniques based on S-HS and D-HS are efficient for analyzing compounds

191 with very high vapor pressure values. One of the most significant advantages of S-HS is the

192 absence of required sample pretreatment, but it is characterized by a minimal sample capacity,

193 leading to poor sensitivity. D-HS technique allows the concentration of the head space volatile

194 compounds in a cold trap (or sorbent) under the action of a gas flow. Then, the trap is rapidly

195 heated, allowing the transfer of trapped compounds into the chromatographic system, generally

196 by quickly heating the trap. However, these two techniques are being replaced by modern

197 headspace sampling techniques with a greater enrichment factor.

198 Strategies based on LLE are effective, allowing the determination of a broad range of compounds

199 with very different polarities (Andujar-Ortiz et al., 2009; R. Castro et al., 2004). However, they

200 are quite tedious, time-consuming and with a significative consumption of hazardous solvents

201 (Silvestre et al., 2009); these drawbacks resulted in changing this technique in favor of others.

202 SPE widely replaced LLE methods, mainly because it allows a significative improvement in

203 enrichment and selectivity reducing in the meanwhile the use of solvents. The optimization of

204 several parameters such as selected sorbents, the solvent used for conditioning, sample flow rate,

205 and the eluting solvent is crucial to obtain a reliable extraction leading to more complicated

206 procedures instead of LLE (Fornells et al., 2019; Ochiai et al., 2008). In addition, these techniques

207 involve the use of a large amount of sample, which means that these methods are neither

208 environmentally sustainable nor cheaper (Marín-San Román et al., 2020a).

209 Microextraction techniques with reduced or no solvent consumption are well-established green

210 alternatives to exhaustive solvent-based or sorbent-based methods (Spietelun et al., 2013). They

211 can integrate several activities such as sampling, extraction, and enrichment of the targeted

212 analytes in fewer steps than the traditional ones. Like conventional techniques, these green

213 alternatives are classified as solvent-free, such as Solid Phase Micro-Extraction (SPME), Stir Bar

214 Sorptive Extraction (SBSE) that are based on sorbents as SPE derivatives, and the solvent-based

215 techniques where a solvent is used as extraction media as the LLE principle (Soares da Silva

216 Burato et al., 2020). Because of the null consumption of organic solvent and the applicability of

217 several compounds, the determination of VOAs in alcoholic beverages is largely performed by

218 solvent-free techniques. Less volatile compounds can be extracted with Liquid Phase Micro

219 Extraction (LPME) techniques, that describes the LLE with a downscaled solvent volume

220 (microliters). The theory of "like dissolves like" is on the basis on the success of these micro

221 extraction procedures, that can be optimized varying solvent system composition, and/or pH

222 value. These modifications can be performed accordingly to the distribution coefficient of the

223 analyte/matrix allowing best and fastest extraction. LPME is usually divided into three main

224 groups: (a) Dispersive Liquid-Liquid Micro-Extraction (DLLME), (b) Hollow-Fiber LPME (HF-

225 LPME), (c) Single Drop-Micro-Extraction (SDME) (Pena-Pereira et al., 2009; Soares da Silva

226 Burato et al., 2020). However, this review limits the discussion on the DLLME coupled to mass

227 spectrometry (MS) which is the technique currently available in the literature comprising the

228 specific determination of VOAs in alcoholic beverages.

229

230 ## C. Separation and detection techniques for VOAs determination

231 The achievement of the GAC goals is made possible as a result of the evolution of extraction

232 techniques described in this review as well as the technological progress of the analytical

233 instrumentation. The increased sensitivity provided by the last developed mass spectrometers is

234 the key to reliably detect and quantitate trace analytes using reduced amount of sample. Non-

235 bonded VOAs compounds are molecules whose physical characteristics perfectly fit for gas

236 chromatography (GC). In GC the separation takes place in gas form so the best MS source for the

237 analysis of vapor-phase molecules is Electron Ionization (EI). This hard ionization is a physical

238 process that involves a significative amount of energy (mostly 70 eV) generating a widespread

239 fragmentation that provides many structural information (Famiglini et al., 2021). In addition, EI

240 has no polarity limitation so it can be used for every class of volatile compound and, since it's not

241 based on a chemical reaction, matrix effects due to ionization interferences are limited (Famiglini

242 et al., 2018). Currently, most EI mass spectrometers are coupled to low resolution analyzers such

243 as quadrupole (Q) or triple quadrupoles (QqQ); however, ion traps (IT) and especially time-of-

244 flight (TOF) analyzers are used in particular for untargeted applications where the knowledge of

245 the exact mass is a precious information (Eichhorn et al., 2012; Saito-Shida et al., 2018). Finally,

246 GC-EI-MS perfectly fits the HS-SPME working-flow.

247 Simplifying the preparation step, either minimizing volumes or replacing solvents with safer ones,

248 it is often paid by a reduction of the sample purity; this lack can be balanced using high

249 performance chromatography and robust MS detectors such as EI based ones (Armenta et al.,

250 2020). Based on what was stated above, EI is a powerful tool for compound discovery, especially

251 when coupled to bi-dimensional chromatography like GCxGC, and a reliable source for

252 quantitative experiments in complex matrices (Herrero et al., 2009).

253 Unfortunately, EI-MS has some limitation: it requires high vacuum conditions into the source so

254 it is mostly hyphenated with GC, and it is based on a a low efficiency ionization process with

255 negative repercussions in sensitivity. Sources with increased efficiency are Atmospheric Pressure

256 Ionization (API), mostly Electrospray (ESI); in this ionization molecules are transformed into

257 ions through a chemical acid/base reaction or the formation of adducts (Bruins & Niessen, 2019).

258 The energy involved is minimal so the fragmentation provides poor structural information but, on

259 the other hand, the molecule-to-ion efficiency is considerably higher, with a significative gain in

260 sensitivity. In the ESI, pH and elution conditions are crucial for the ionization so this source is

261 only coupled to Liquid Chromatography (LC). The lack of in-source fragmentation is offset by

262 the use of collision cell in tandem MS which use allows the access to structural libraries like.

263 Finally, LC-MS is the only technique for the analysis of bonded-VOAs.

264 Summarizing, most methods described in the next pages are based on GC-EI-MS as a

265 consequence to its suitability to the analysis of volatile compounds like VOAs (Pena-Pereira et

266 al., 2009; Savchuk et al., 2020); many GC systems, injectors, analyzers, and accessories are fitted

267 for tailoring its characteristics to the sample preparation method of choice. However, LC-ESI-MS

268 has a significative spread in many applications, especially when coupled to solvent-based

269 extraction techniques and derivatization processes. In the following sections the main extraction

270 techniques used in the analysis of VOAs in alcoholic beverages will be illustrated. Their main

271 features will be shown, as well as their advantages and disadvantages (Campillo et al., 2018).

272

273 ## II.   Solvent-free techniques for the analysis of VOAs

274 The best way to minimize the environmental impact of solvents is to avoid their use. Solvent-free

275 techniques have strongly spread their use in many analytical routes because represent an efficient

276 answer to the green issue (Sciarrone et al., 2015). In these techniques the molecules of interest

277 are sampled directly in the gas phase (D-HS, S-HS) or the extraction takes place using

278 heterogeneous phase like in the SBSE and SPME.

279

280   A. Head-space based techniques

281 HS techniques perfectly couple with aroma analysis since all VOAs molecules are available in

282 the gaseous phase in equilibrium with the matrix (Soria et al., 2015). The direct sampling and

283 injection of vapors produced by beverages is a good compromise to achieve a green method

284 without the requirement of further instrumentation. However, as a consequence of the variations

285 which affects the concentration of VOAs (from $ng*L^{-1}$ to $mg*L^{-1}$), and the strong interaction

286 between water matrix and functional groups, direct approaches are unsuitable for most analytes.

287 As a result of this evidence, to provide a strong and reliable enrichment, quantitative analyses are

288 used to be performed by head-space sampling using SPME (HS-SPME).

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

290 This extraction and pre-concentration technique was developed by Pawliszyn in 1989 (Arthur &

291 Pawliszyn, 1990). It is one of the most popular microextraction techniques. Its simplicity, ease of

292 automation, robustness, and the great sensitivity it achieves in most applications, make it a

293 powerful tool in analytical chemistry. The main configuration involves a sorbent phase coating a

294 metal tube support (Figure 2).
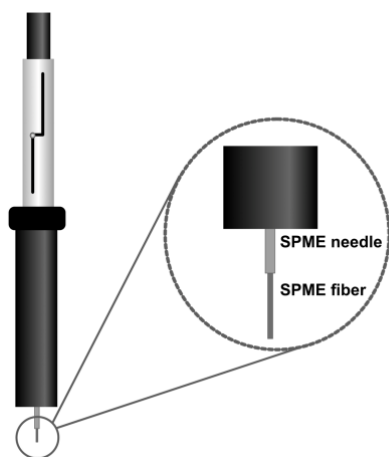
295

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

297   The fiber is usually 1 cm in length, and the sorbent (or stationary) phase thickness ranges between

298   7 and 100 μm. Several SPME devices are commercially available (*Restek*,.; *Supelco*,) which

299   differentiate by coating thickness, material and composition. The SPME presents two operation

300   modes depending on the nature of analytes and matrix; these are Head-Space SPME (HS-SPME)

301   and Direct Immersion SPME (DI-SPME) that are illustrated in Figure 3(a) and 3(b), respectively.

302
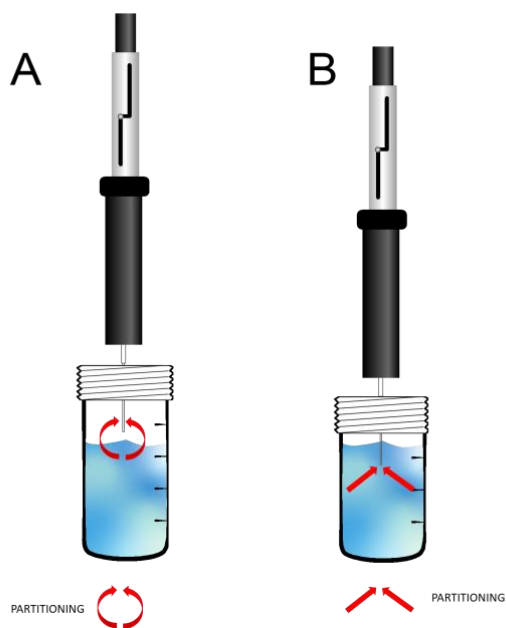
FIGURE 3. Extraction modes in solid phase micro extraction (SPME). (A) Head-Space (HS) SPME. (B) Direct immersion (DI) SPME.

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306   The first attempt of SPME analysis was presented in 1996 as a promising application for this

307   sample preparation strategy. Lay-Keow et. al. extracted several commercial vodkas with DI-

308   SPME using a 100 μm PDMS fiber coupled to GC-MS for the quantitation of as many analytes

309   as possible (comprising odor-active fatty acids, esters, furans, and others) (Ng et al., 1996).

310   Thanks to the amenable content of macromolecules, particles, and solids, it was possible to

311   directly soak the fiber into the sample.

312   HS-SPME is mostly used for determining volatile and semi-volatile compounds; in this

313   configuration, the fiber is exposed into the head-space between the sample and the cap of the vial

314   allowing gas-phase analytes to migrate from the sample to the sorbent. Once the compounds are

315   retained by adsorption/absorption mechanisms, they are desorbed for the instrumental analysis.

316   In solvent-free applications desorption is thermally performed directly into the GC injector with

high efficiency and avoiding the use of solvents; SPME fibers can be also subjected to elution with a small amount of organic solvent (<500 µL) (Płotka-Wasylka et al., 2015; SAS Wercinski, 1999) to make it suitable for LC methods.

Performing HS-SPME analysis in alcoholic beverages presents several limitations due to the matrix composition and different concentration of the odor-active molecules (López et al., 2002). Beverage vapor, especially for alcoholic ones, is mostly made of ethanol, water, and many other compounds like ethyl esters, phenols, higher alcohols, fatty acids, which are present at more than 0.1 mg/L (Ferreira et al., 2015). The matrix molecules and analytes are in a competition for interacting with the fiber affecting extraction efficiency, especially for trace compounds (Mestres et al., 1999). This behavior is more evident for DI-SPME because the fiber is also in contact with non-volatile analytes (Frago Ramos, 2016); this disadvantage balances the higher efficieny in the extraction of semi-volatile compounds that sometimes contribute to the beverage aroma. In this sense, HS-SPME gives better efficiency and quantitate the real amount present in the beverage. HS-SPME provides a significantly longer fiber life, increased performance stability, better representativeness of beverage odor, and longer instrumental maintenance intervals. In complex matrices like fermented beverages, HS-SPME showed also a better extraction efficiency for aroma compounds so it is preferred in most quantitative methods (Demyttenaere et al., 2003). Several parameters determine HS-SPME performance such as stirring, extraction time, temperature, coating thickness and phase-type. Since odor-active molecules have high volatility and most of them have a low molecular mass and reduced polarity, the extraction time and temperature are reduced if compared to methods developed for other analytes (Hiroyuki Kataoka, Heather L. Lord, 2000). Polydimethylsiloxane (PDMS) is a non-polar phase that has a high affinity for a-polar compounds and moderate for polar ones, if the extraction properties are optimized. Enhanced performance towards alcohols, esters and carbonyls can be achieved by using a more polar phase like polyacrylate (PA) with a consequent decrease of non-polar recovery (Remedios Castro et al., 2008). Mixed coatings, which have intermediate and complementary properties according to their polarity and retention capacity, are more suitable for aroma compound quantitation (Marín-San Román et al., 2020b). In addition, some of these phases are

345 more polar than PA, and better extract compounds with greater polarity such as esters, carbonyls

346 and alcohols.

347 Perestrelo et. al. developed an HS-SPME method for the determination of volatile compounds in

348 grapes. Using this procedure, it was possible to determine a broad class of compounds like 27

349 monoterpenes, 27 sesquiterpenes, 21 carbonyl compounds, 17 alcohols (of which 2 aromatics),

350 10 C13-norisoprenoids, and 5 acids. In this article, 6 different fiber coatings were evaluated

351 (polydimethylsiloxane (PDMS, 100μm), polydimethylsiloxane/divinylbenzene (PDMS/DVB, 65

352 μm), divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 50/30 μm),

353 carboxen/polydimethylsiloxane (CAR/PDMS, 75 μm), polyacrylate (PA, 85 μm), and

354 carbowax/divinylbenzene (CW/DVB, 70 μm) demonstrating that DVB/CAR/PDMS was the best

355 compromise to achieve suitable performance for all class of analytes(Perestrelo et al., 2011). Four

356 mL of sample were extracted in HS-SPME for 40 minutes at 40 °C under stirring (1100 rpm)

357 using sodium chloride (1.4 g) to enhance ionic strength. This procedure, which demonstrated to

358 be very versatile and efficient since it was able to quantitate 107 compounds coming from 6

359 different classes in just one run, was then extended to wine by Lukic et. al. for the evaluation of

360 the effects of six maceration treatments on volatile aroma profile of Teran red wine, and the study

361 of late and ice-harvest on Gewürztraminer odor composition (Lukić et al., 2016, 2017).

362 An in-depth study of SPME extraction for the determination of several odor-active molecules in

363 wine was presented by Metafa et. al. (Metafa & Economou, 2013). The authors explored 5

364 different fiber coatings (PDMS, PDMS/DVB, CAR/PDMS, and DVB/CAR/PDMS) both in DI

365 and HS operating mode. In this case, since further pre-treatments were scheduled, DI-SPME was

366 selected using a PDMS/DVB fiber to enhance the enrichment of analytes, necessary for the

367 detection with a single-quadrupole GC-MS. Twenty analytes including terpenes, terpenoids, and

368 norisporenoids were determined using 10 mL of sample extracted for 10 minutes at room

369 temperature at 1000 rpm of magnetic stirring.

370 SPME based sampling procedures were used also in beer for a similar purpose as wine. Cajka et.

371 al. developed an HS-SPME method coupled to GC–TOF-MS for the acquisition of aroma profile

372 in 265 beer samples (Cajka et al., 2010). Several SPME fibers were tested (100 μm PDMS, 65

373 μm PDMS/DVB, 65 μm CW/DVB, 50/30 μm DVB/CAR/PDMS, and 85 μm PA) and other

374 parameters such as extraction time, extraction temperature, salt addition were optimized. Four

375 mL of beer were extracted with 1.7 g of NaCl at 30 °C for 5 minutes, after 10 minutes of

376 incubation at 60°C using a 50/30 μm DVB/CAR/PDMS fiber.

377 Based on a similar procedure, Dennenlöhr et. al. developed and validated an HS-SPME-GC-

378 MS/MS methodology for quantification of selected hop aroma compounds in beer (Dennenlöhr,

379 Thörner, Manowski, et al., 2020). Hop aroma is the odor contribution of a particular mixture of

380 terpenes, terpenoids and esters, compounds that represent a key quality characteristic of many

381 popular beer styles such as "lager" and "IPA"(Anderson et al., 2019). The authors presented a

382 method that aimed to cover a wide concentration range (1–1000 mg/L) for 19 key odor-active

383 molecules and is applicable to the most significant beer styles, from light lagers to highly dry-

384 hopped beers. The method needed 1 mL of decarbonized beer sample, 0.4 g NaCl, and 7.5 minutes

385 of extraction time at 60 °C with a 50/30 μm DVB/CAR/PDMS fiber.

386 Another interesting procedure was presented by Riu-Aumatell et. al. focused on the determination

387 of key-odorant in low alcoholic beers (Riu-Aumatell et al., 2014). In this method, 5 mL of sample

388 were extracted at 45 °C for 40 minutes with a 50/30 μm DVB/CAR/PDMS fiber after the addition

389 of 1.75 g of NaCl. Fifty-nine analytes between fermentative compounds like esters, fatty acids,

390 and alcohols, varietal molecules such as terpenes and terpenoids, and many others related to the

391 ageing process (carbonyls and furans) were quantified. Thanks to the lower extraction temperature

392 and to a longer extraction time it was possible to efficiently extract 14 oxygen-containing

393 compounds coming from different categories (carbonyls, carboxyl acids, esters, and furans)

394 without derivatization, as usually did (Buiatti, 2008).

395 Yu Ping Zhao et. al. characterized the six most well-known distilled spirits using HS-SPME and

396 GC-MS (Y. P. Zhao et al., n.d.). Fourteen carbonyls, 2 lactones, 59 esters, 5 acetals, 26 between

397 terpenes and norisoprenoids, 22 alcohols, 6 furans, 2 carboxy acids, and 19 additional compounds,

398 for a sum of 155 analytes were quantitated or semi-quantitated in SIM mode. The extraction was

399 performed for 15 minutes at 50 °C consuming 5 mL of diluted sample (deionized water was added

to each liquor until 10% v/v ethanol), saturated with 1.5 g of NaCl and extracted using a 50/30

µm DVB/CAR/PDMS fiber.

A robust HS-SPME method for the determination of nitrogen-heterocyclic volatile aroma

compounds (i.e. pyrazines, quinones, and pirroles) in spirits was validated and presented by Picard

et. al.; this class of odor-active molecules are known to provide a complex aromatic bouquet

related to ageing in oak barrels that remove the immature character of raw distillate (Picard et al.,

2019). All parameters were explored and optimized obtaining the following procedure: 10 mL of

1:10 diluted spirit sample which pH was adjusted to 7, the addition of NaCl 3 g, 30 minutes of

extraction at 60 °C with an 85 µm CAR/PDMS coated fiber. The method demonstrated adequate

linearity since it provided R^2>0.99 in whisky through 10 calibration levels (0.5−1000 µg/L).

Intraday precision (RSD <10%) was evaluated acquiring 10 replicates of the same spirit spiked

at 50 µg/L whereas the interday precision (RSD <20%) was assessed by analyzing 12 replicates

at 50 µg/L in 1 month. Accuracy was calculated as a recovery percentage in spiked samples at 3

levels and ranged from 78.4% to 121.6%.

Niu et. al. extended the HS-SPME aroma determination to cocktails whose composition was based

on vodka (Niu et al., 2019). Eight mL cocktail with the addition of 2 g NaCl were extracted at

50°C for 45 minutes using a triphasic 50/30 µm DVB/CAR/PDMS fiber; 36 between esters,

terpens, terpenoids, norisprenoids, and alcohols were quantitated. The method showed good

linearity (R^2 >0.99) for a broad concentration range (approximately from few µg/L to mg/L).

Cognac is one of the spirits that better represents French tradition all over the world; its sensorial

impact is a fingerprint that strongly depends on the contribution of some age-related molecules

such as 3-methyl-2,4-nonanedione (3-MND). It is a well-known compound reminiscent of anise

or "dried fruit", according to its concentration, and gives a significative contribution to the

characteristic aroma of distilled wines where oxygen plays a key role, both in the production and

in the ageing process such as grappa, brandy, rum, vodka, and many others. (Luo et al., 2020; N.

Moreira et al., 2018; Plutowska & Wardencki, 2008; Vanderhaegen et al., 2006) Thibaud et. al.

developed a method based on HS-SPME that provided adequate performance for its quantitation

since the average concentration in the literature ranges from trace to 11.2 µg/L (Melnyk et al.,

428   2015; Thibaud et al., 2021). Ten mL of diluted sample (0.250 mL spirit + 9.750 deionized water)

429   were added to 5 g of ammonium sulphate and extracted at 50 °C for 25 minutes using a 65 μm

430   PDMS/DVB fiber. Quantitation was performed with GC-MS in chemical ionization mode using

431   methanol as a reagent gas.

432   MND is a diketone that belongs to the volatile carbonyl compounds family (VCCs). These

433   molecules, depending on their concentration, are related to pleasant nuances since the

434   winemaking of some oxidized wines like Vin Santo (Tofalo et al., 2009), Port (Prata-Sena et al.,

435   2018), Sherry (R. Castro et al., 2004), and Madeira (Pereira et al., 2011) or many distilled wine

436   spirits (Melnyk et al., 2015)) are tailored to emphasize their production (Manzocco et al., 2000).

437   However, in most cases, the presence of VCCs is a marker of long-standing undesired oxidation

438   related to aroma defects (Alañón et al., 2015; Gabrielli et al., 2021; Li et al., 2008). Carbonyls

439   quantification is sometimes used as a tool for the evaluation of complete fermentation and storage

440   monitoring (Tian et al., 2009). However, due to the significative polarity of carbonyls and the

441   establishing of strong hydrogen bonds with water and ethanol, VCCs (especially with higher

442   molecular weight) are often derivatized before the extraction via HS-SPME (Marín-San Román

443   et al., 2020a).

444   Many HS-SPME methods have been purposed with O-(2,3,4,5,6-pentafluorobenzyl)

445   hydroxylamine (PFBHA) on-fiber derivatization (Schmarr et al., 2008) and in solution

446   derivatization (Bueno et al., 2014; Nathalie Moreira et al., 2019), both with satisfactory results

447   but different simplicity of execution. On-Fiber Derivatization (OFD) strategy was used for the

448   determination of staling aldehydes in wort and beer samples (Dennenlöhr, Thörner, Maxminer, et

449   al., 2020). PFBHA was used as a derivatizing agent and GC-EI-MS/MS was the instrumentation

450   of choice due to its improved sensitivity and reduced matrix effects resulting from overlapping

451   PFBHA-oximes (PFBOs). Fifteen selected aldehydes were determined in wort and beer across a

452   wide concentration range (0.01-1000 μg/L). The presented method was extensively validated

453   through linearity assessment (R^2 >0.99), LOD/LOQ, precision (RSD <9.2%), and recovery (80-

454   118%). Extraction needed 3 mL of decarbonized beer, 1 g NaCl, and 10 minutes at 50 °C of fiber

455   exposure previously loaded with the PFBHA. A similar method was purposed by Schmarr et. al.

456   for the determination of many VCCs, such as alkanals, (E)-2-alkenals, (E,E)-2,4-alkadienals, and

457   others including S-containing ketones (Schmarr et al., 2008). In this case, the extraction needed

458   20 minutes at 40 °C using 10 mL of sample and no further preparation step.

459   On Solution Derivatization (OSD) was implemented into a new analytical method for the

460   determination of 18 carbonyl compounds in wines based on HS/SPME and GC-IT-MS (Pérez

461   Olivero & Pérez Trujillo, 2010). After exploring five fiber coatings, time and extraction

462   temperature, desorption time and temperature, pH, and ionic strength, content in tannins and

463   anthocyans, sucrose, SO_2, and alcoholic degree, the best extracting conditions were: 2 mL of wine

464   saturated with NaCl extracted with a 50/30 μm DVB/CAR/PDMS fiber for 45 minutes at 40 °C.

465   The method was validated over a wide range of concentrations showing good linearity (R^2>

466   0.998), remarkable repeatability and reproducibility (RSD <5.5%), and LOD ranging from 0.62

467   μg/L to 129.2 μg/L.

468   Moreira et. al. optimized an HS-SPME method coupled to GC-MS/MS with a prior in-solution

469   derivatization step with PFBHA to quantify 38 VCCs in different categories of Port wines

470   (Nathalie Moreira et al., 2019). Due to its winemaking and ageing process, Port is rich in

471   carbonyls so many issues such as carryover and fiber saturation must be considered. Optimal

472   extraction conditions were achieved with 2 mL of wine extracted using a 65 μm PDMS/DVB

473   fiber under stirring for 20 minutes at 32 °C. The method was also validated in terms of linearity,

474   repeatability, inter and intra-day precision and accuracy.

475   Similar methods have also been used to perform carbonyl quantitation in other beverages like

476   beer; Moreira et. al. presented a fully automated HS-ISD-SPME method using PFBHA as the

477   derivatizing agent like in most procedures for the determination of 45 different VCCs (Nathalie

478   Moreira et al., 2013a). Sixty-five μm PDMS/DVB fiber was used to extract 5 mL of beer at 45°C

479   for 20 minutes without salt addition. The proposed method showed to be linear, precise, accurate

480   and sensitive. LODs ranged from 0.003 to 0.510 μg/L, except for furans which were higher (1.54–

481   3.44 μg/L) whereas LOQs varied from 0.010 to 1.55 μg/L, except for furans (4.68 – 10.4 μg/L).

482   Good repeatability was achieved (RSD <17%) for all analytes. Accuracy was measured by

483   evaluating recovery in spiked samples which ranged from 88% to 114%.

484   HS-SPME with GC-MS was used for the determination of acrolein in alcoholic beverages. M.

485   Kächele et.al. developed a method using a fiber of 85 μm CAR/PDMS coating (Kächele et al.,

486   2014). Samples were prepared by weighing and mixing in an HS vial 2 g of NaCl, 5 mL of distilled

487   water and 0.125 g of beverage. The extraction was performed at 50 °C for 10 minutes. Since

488   acrolein is both an odor-active compound and a cytotoxic hazard for human health, its

489   determination is a very important task from more than one point of view. A very similar method

490   was developed for the quantification of carbonyl and furan derivates whose exposure could be a

491   risk for human health (Hernandes et al., 2019). A 50/30 μm DVB/CAR/PDMS fiber was used for

492   the extraction of 1 mL of sample with 30% NaCl (m/v) at 55°C for 1 hour. The fiber was

493   overcoated with PDMS to allow a simultaneous quantification of brewing compounds.

494   Performances were significant, especially for a SIM-mode quantification system (LOD ranging

495   from 0.03 μg/L for acrolein, to 1 μg/L for furfural).

496

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

498   Ionic liquids (ILs) are a particular class of non-molecular solvents also known as liquid, organic,

499   molten, or fused salts, which couple negligible vapor pressure and low melting point (usually

500   lower than 100°C) (F. Zhao et al., 2008). Most ILs are composed of nitrogen-based cations

501   (pyridine, pyrrolidine, imidazole and others) and a widespread variety of anions, spanning from

502   halides to more complex organic conjugated bases (Hallett & Welton, 2011). The main features

503   of ILs are their adjustable viscosity, significative thermal stability and the possibility to design

504   their formulation to enhance or reduce water miscibility (Mehrdad et al., 2019). Poly Ionic Liquids

505   (PILs) are organic polymers mainly obtained by the polymerization of unsaturated ionic liquid

506   monomers. The main advantage provided is the mechanical stability of polymers coupled to the

507   features of ILs that make PILs a promising coating for SPME fibers (Singha et al., 2018).

508   González-Álvarez et. al. used an imidazolium based PILs as a coating for SPME fiber used to

509   analyze beer aroma (González-Álvarez et al., 2013). Two different fiber materials were

510   synthetized by a free radical polymerization and assessed to provide high thermal and structural

511　　stability. The IL-1 butenyl fiber was compared to the conventional PDMS-DVB 65 μm and CAR-

512　　PDMS 75 μm fibers, showing a significant performance boost. Efficiency was evaluated in the

513　　analysis of lemon beer aroma by spiking real samples at 3 levels (100, 200, and 300 μg/L)

514　　obtaining satisfactory recoveries (78.4 – 123.6%) for all 8 compounds.

515　　Crucello et. al. evaluated some PILs coatings for the aroma characterization of novel Brazilian

516　　wines (Crucello et al., 2018). The best PILs-coated fiber was evaluated to be made a cross-linked

517　　imidazolium-based polymer which exhibited superior performance compared to

518　　DVB/CAR/PDMS. No quantitative data was provided but the comprehensive wine aroma profile

519　　obtained (up to 372 compounds identified) allowed a powerful evaluation of VOAs compounds

520　　available in the samples and could be a powerful tool for comparisons between different

521　　winemaking styles or vintages.

3.　Full Evaporation Dynamic Headspace (FEDHS)

523　　Full Evaporation Dynamic Head Space (FEDHS) is a solvent-free technique that can be coupled

524　　to GC–MS for the determination of volatile compounds at sub-ng*mL^{-1} level. In FEDHS a

525　　reduced amount of sample is fully vaporized without any liquid-to-gas equilibrium that

526　　maximizes sensitivity for semi-volatile compounds and ultra-trace ones (Figure 4).
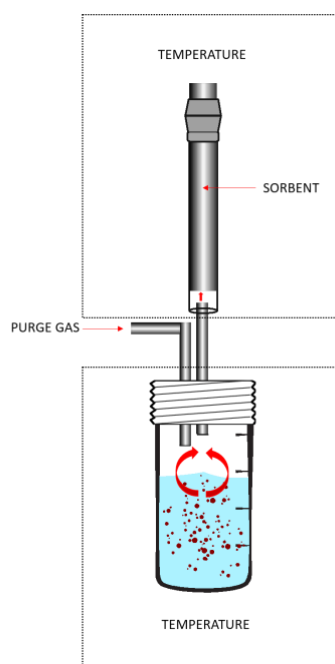
527

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

529 Compared to conventional D-HS and HS-SPME, FEDHS provides more uniform enrichment over

530 the entire polarity range for odor compounds in aqueous samples. Ochiai et. al. developed a

531 method for the analyses of key odor compounds (including hydrophilic and less volatile)

532 characteristics in whiskey (Ochiai et al., 2012). FEDHS was performed at 80°C using 3 L of purge

533 gas to allow the complete vaporization of 100 μL of whiskey. The developed method showed

534 high recoveries (85–103%) of the 18 odor-active compounds, separating them from most of the

535 low volatile matrix. Good linearity ($R^2 > 0.9909$) and high sensitivity (limit of detection: 0.21–

536 5.2 ng*mL^{-1}) were achieved. Phenolic compounds including vanillin were determined in the range

537 of 0.92–5.1 μg*mL^{-1} (RSD < 7.4%) in 6 single malt whiskey samples. Eight compounds including

538 12 potent odorants (e.g. coumarin, furaneol, indole, maltol, and pyrazine congeners) were

539 determined in the range of 0.21–110 ng* mL^{-1} (RSD < 10%).

540 All relevant applications based on solvent-free analysis of aroma-active compounds in alcoholic

541 beverages are reported in Table 1.

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

Ext. technique	Matrix	Ext. volume	Instrumentation	Pro & Cons	Article
HS-SPME	Wine	4 mL	GC-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-MS	+ Strong validation, good performance - Only varietal compounds	(Metafa & Economou, 2013)
HS-SPME	Beer	4 mL	GC-TOF-MS	+ Fast, many analytes, reduced RSD, efficient - Only high concentrated analytes	(Cajka et al., 2010)
HS-SPME	Beer	1 mL	GC-MS/MS	+ Accurate quantitation (3 I.S.+MRM), reduced sample volume - High LOQ, non-commercial I.S.	(Dennenlöhr, Thörner, Manowski, et al., 2020)
HS-SPME	Beer	5 mL	GC-MS	+ 59 analytes, polar compounds without derivatization - Long extraction time	(Riu-Aumatell et al., 2014)
HS-SPME	Spirits	5 mL	GC-MS	+ 155 analytes from all categories	(Y. P. Zhao et al., n.d.)

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

				- **Long extraction time (40 min)**	
HS-SPME	**Wine**	**4.5 mL**	**GCxGC-MS**	**+ Performance, informations provided** **- No quantitative results provided, long extraction time (60 min)**	(Crucello et al., 2018)
SBSE	**Wine**	**20 mL**	**GC-MS**	**+ Flexibility, simplicity** **- Affected from ethanol, laborious**	(Caven-quantrill & Buglass, 2011)
SBSE	**Wine**	**20 mL**	**GC-MS**	**+ Simplicity, strong enrichment** **- Requires a previous SPE**	(Magali Picard, Celine Franc, Gilles De Revel, 2018)
SA-SBSE	**Beer**	**5 mL**	**GC-MS/MS**	**+ Strong enrichment, modularity** **- Effect of ethanol, heat-induced artifacts**	(Ochiai et al., 2016)
FEDHS	**Whiskey**	**0.1 mL**	**GC-MS**	**+ Minimized sample volume, sensitivity** **- Require instrumentation, unsuitable for reacting molecules, only few analytes**	(Ochiai et al., 2012)

544

B. Immersion-based techniques

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

In DI-SPME, the sorbent is directly exposed/immersed into the sample determining a higher interaction between analytes and fiber, and better recoveries for semi-volatile or non-volatile compounds (Figure 3 (b)). On the other hand, for the same reason, this configuration is affected by an increased matrix effect from complex samples that is also related to reduced fiber lifetime. Significative steps have been done through the development of new, more specific sorbent materials to overcome these restrictions (P. Rocío-Bautista, 2018) but currently DI-SPME is not the gold-standard in VOAs solvent-free analysis. Despite that, Tang et al. proposed a porous PILs to be used as a fiber coating for the analysis of organic acids in wine (Tang & Duan, 2017). An imidazolium-based coating was used and assessed to provide a significant performance increase. Samples were extracted with an on-fiber derivatization strategy using N-tert-butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA). All parameters including salt addition, pH, extraction temperature and time, derivatization temperature and time were explored in addition to the PILs

559   synthesis optimization, to achieve the best performances. An extensive validation demonstrated

560   good linearity (R^2>0.99) in the range 0.01 – 1 mg/L, satisfactory LOD (up to 0.07 µg/L), proper

561   repeatability (RSD<16%) and fiber-to-fiber reproducibility (RSD<20%). Recoveries in spiked

562   wine samples ranged from 78.19 to 98.11% and lifetime fiber durability was satisfactory.

563

564   ## 2. Stir-Bar Sorptive Extraction (SBSE)

565   An alternative to SPME which combines the absence on solvents and provides a simultaneous

566   enrichment and isolation of analytes, is represented by SBSE. These devices are bases in the

567   coating of a stir bar of PDMS with a potential extraction sorbent (Figure 5).

568
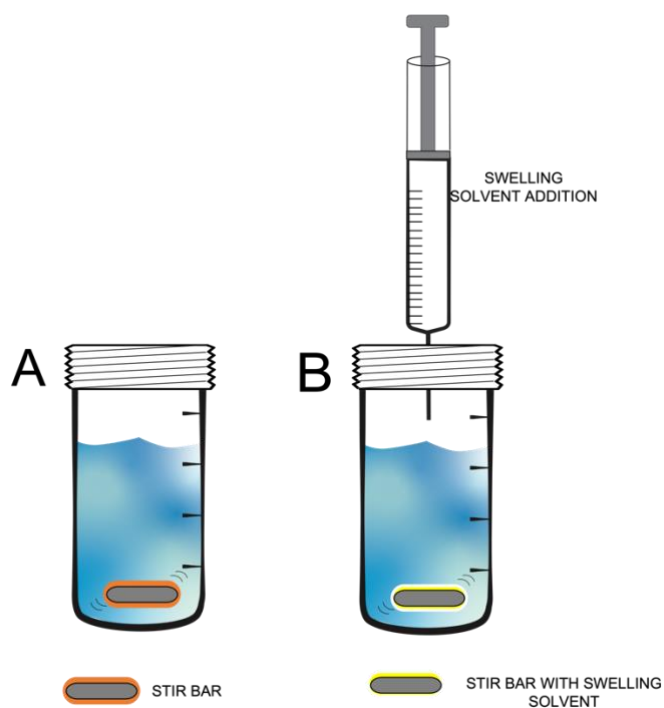
569   **FIGURE 5.** Extraction modes in stir bar sorptive microextraction (SBSE). (A) Classical SBSE extraction.
570   (B) Solvent assisted (SA) SBSE extraction

571

572   Contrary to HS-SPME or DI-SPME, in which the sorbent remains static throughout the overall

573   extraction process, the SBSE is a dynamic extraction. In this process, the sorbent is moving

574   through the solution, in this case, by a magnetic force (David & Sandra, 2007). This favors

575   analyte-sorbent interactions, and therefore requires much shorter extraction times than SPME.

Caven-Quantrill et. al. presented a study where SBSE was used in a comparison of volatile composition between grape juice and model wine (Caven-quantrill & Buglass, 2011). Twenty-four μL PDMS coated stir bar (length: 10 mm, film thickness: 0.5 mm) was used to extract 20 mL of sample at room conditions for 2 hours at 1100 rpm; the stir bar was then washed with pure water, dried and placed into the thermal desorption tube.

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

2.1 Solvent Assisted (SA)-SBSE

SBSE was used for the determination of 28 aroma compounds in beer in an innovative method presented by Ochiai et. al. (Ochiai et al., 2016). A commercial PDMS stir bar (63 μL; length: 10 mm; film thickness: 1 mm) was swollen in several solvents with log K_{ow} ranging from 1.0 to 3.5 while stirring for 30 min before extraction; this procedure is named Solvent-Assisted SBSE (SA-SBSE) and showed in Figure 5 (B). SA-SBSE demonstrated to provide better recoveries if compared to conventional SBSE depending on the solvents used in the stir bar preparation step and on the log $K_{ow} < 2.5$ of the analytes. Working with low-temperature thermal desorption (80°C) the formation of heat-induced artefacts was excluded and it was possible to optimize the method for the determination of 21 aroma active compounds in beer samples. Repeatability (RSD <8%) and linearity ($R^2 > 0.99$) were obtained for all compounds and that was a significant result. Similar procedures for the analysis of beverage with higher alcoholic percentage like wine and spirits

have not been published yet; this is reasonably due to the reduced polarity of ethanol compared to water those lower recoveries for low-polarity analytes.
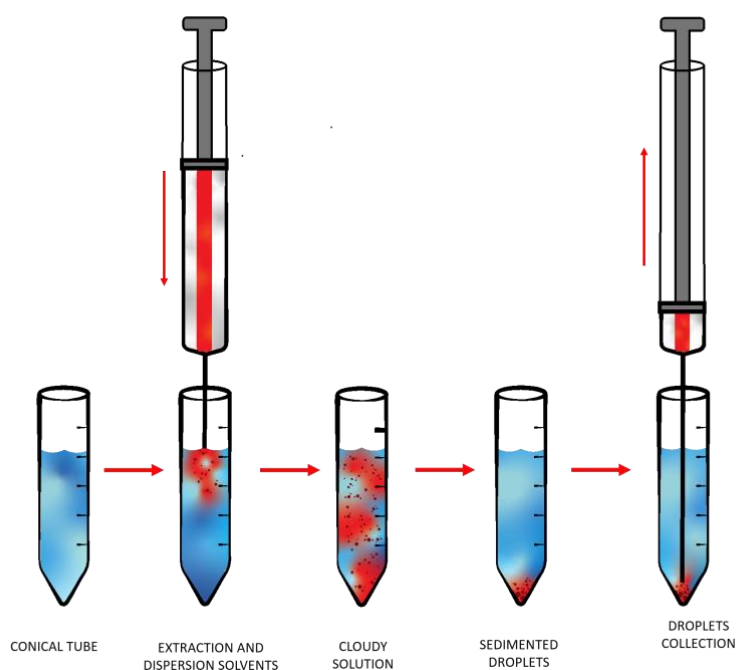
III. Solvent based techniques

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

A. Dispersive Liquid-Liquid Micro Extraction (DLLME)

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

628   DLLME employs a ternary system consisting of an extraction solvent (10-500 µL) immiscible in

629   water and a dispersion solvent (0.2-1 mL) miscible both with water and the extractant solvent,

630   which are quickly injected into an aqueous sample (2-10 mL). The basis of the technique is the

631   partition of the analyte between the sample and the extractant solvent. The contact of the three

632   components creates a cloudy solution in which the extraction solvent is dispersed in the sample

633   solution forming multiple organic microdroplets (Figure 6).

634

CONICAL TUBE   EXTRACTION AND   CLOUDY   SEDIMENTED   DROPLETS
                DISPERSION SOLVENTS   SOLUTION   DROPLETS   COLLECTION

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

636   Various strategies such as salt addition or ultrasound assistance can be used to boost recoveries.

637   A further centrifugation step ensures the phase separation which is followed by the droplet

638   collection and easy analysis by hyphenated or direct analytical methodologies. Several papers are

639   available in literature to demonstrate its applicability and performance level for VOAs analysis.

640   Zhou et al., used the conventional DLLME coupled with GC-MS to determine main higher

641   alcohols in fermented alcoholic beverages (Zhou et al., 2020). This method allowed to efficiently

642   quantify six alcohols in a characteristic chinese alcoholic beverage. The sample (3.5 mL) was

643   diluted 1:1 with water without any pH adjustment and using 2.1 mL of solvents (1.5 mL of

644   acetonitrile as dispersion and 0.6 mL of dichloromethane as extractant solvents, respectively).

Once optimized extraction conditions, only seven minutes (Zhou et al., 2020) are needed to perform the overall sampling process leading to a very rapid method with Enrichment Factors (EFs) spanning from 8.1 % and 9.1 % for selected compounds. Moreover, they compared DLLME with S-HS and HS-SPME, demonstrating the DLLME advantages in terms of recoveries, peak shape in the chromatographic separation, and time saving. Fariña et al.(Fariña et al., 2007), determined two volatile phenols, 4- ethyl guaiacol and 4-ethylphenol in wine using DLLME coupled with GC-MS. They used 5 mL of wine samples, to which were added 1 mL of acetone as a dispersion solvent and only 50 μL of carbon tetrachloride as extractant solvent. Results showed a very rapid procedure that takes less than six minutes for the extraction time with a minimum solvent usage. The comparison with other techniques conventionally used to determine volatile phenols in wine (LLE, SPE, HS-SPME, and SBSE) showed how this strategy reduced the analysis time and the required amount of sample. Fontana et al. (Fontana et al., 2018) characterized the profile of volatile and semi-volatile compounds in grape marc distillates extracted by DLLME and analyzed with a GC coupled to a time-of-flight accurate MS (TOF-MS). The extraction method was performed and optimized on a group of 17 compounds with different chemical functionalities (ketones, aldehyde, esters, alkanes, and alcohols) and response ranges in distillates. A selected volume of 2.5 mL of grape sample was diluted at 9 mL with water before extraction to reduce the adverse effect of the high percentage of ethanol (~ 40%) in the affinity of the compounds to extractant solvent. Acetonitrile (400 μL) and chloroform (100 μL) were selected as dispersive and extractant solvents, respectively. The obtained EFs were up to 52 times. The extraction efficiency of DLLME was compared with three SPME conditions: Direct-SPME at room temperature, HS-SPME at room temperature, and HS-SPME at 50 °C thermostated sample. The results showed that 12 out of 17 compounds are better extracted with the DLLME technique with low consumption of sample, solvent, and in a very faster sampling procedure (4 min). Oller-Ruiz et al., investigated for the first time the DLLME technique coupled to LC-MS/MS to determine five monoterpenes in hazelnut liqueur, red wine, wiskey, brandy, rum, and gin(Oller-Ruiz et al., 2017). No dilution in water was assessed because the ethanol content of each beverage was used as a dispersive solvent in a sample volume of 8 mL. Chloroform was chosen

673   as extractant solvent and 300 µL of it were rapidly added to unmodified beverages sample. The

674   enriched phase of chloroform was evaporated and reconstituted on 50 µL of water, a suitable LC-

675   MS solvent. The optimized method allowed to achieve EFs ranging from 12 and 88 using low

676   amounts of organic solvents in a very short extraction time (3 min).

677

678   ## B. Supercritical Fluid Extraction (SFE)

679   Supercritical Fluid Extraction (SFE) is a sample preparation technique where a supercritical fluid

680   is used as extraction solvent (Figure 7).
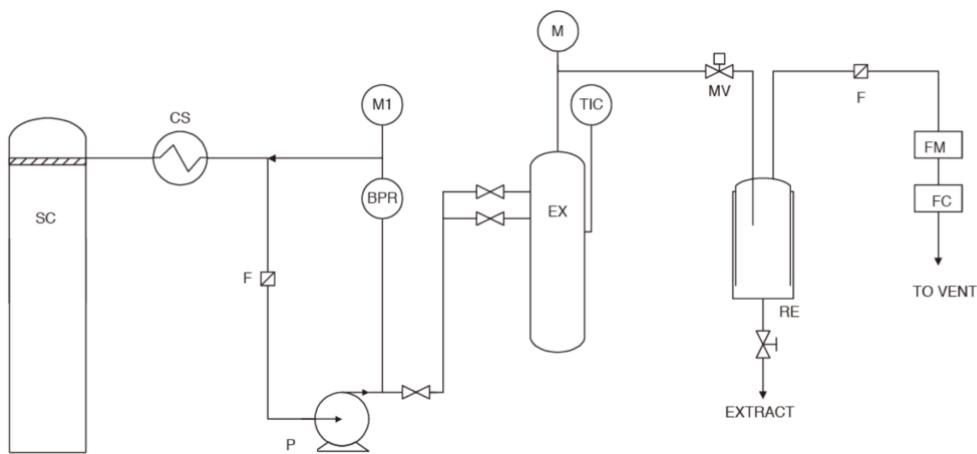
681

682   **FIGURE 7.** Schematic representation of SFE extraction and the equipment used (Gracia et al., 2009).
683   Reprinted with permission from I. Gracia, M.T. García, J.F. Rodríguez and A. de Lucas, 2009, copyright
684   year [2022].

685

686   The supercritical state is a combination of high temperature and high pressure which both exceed

687   their critical values. As a consequence, the solvent properties gradually change showing a gas-

688   type viscosity coupled to a density similar to that of the liquid state (Sakai et al., 2019). In terms

689   of polarity, supercritical fluids are known to be non-polar and their use as extracting solvent gives

690   the best efficiency with nonpolar or low polar substances. However, the characteristics mentioned

691   above can be tuned by adjusting temperature and pressure making supercritical fluids a non-toxic,

692   flexible, and selective alternative to conventional organic solvents. In addition, it's important to

693   highlight that in SFE methods the supercritical fluid can be easily removed from the extract and

694   recirculated, making the extraction simple, clean, solvent efficient, and environmentally

695 sustainable (Lang & Wai, 2001). The aspects pointed above allow supercritical fluids to be

696 included in the group of green solvents and SFE to be labelled as a GAC procedure. Currently,

697 CO_2 is the most used supercritical fluid, sometimes coupled with co-solvents such as ethanol or

698 methanol to adjust its polarity (Macedo et al., 2008).

699 Even though SFE was, especially in the last 20 years, an emerging GAC technique, Namieśnik

700 et. al. (Wiśniewska et al., 2015) published a review in 2014 where only one study was presented

701 for the determination of ethanol, which is not an VOAs compound, in spirit based alcoholic

702 beverages (Señoŕns et al., 2001). Up to now, SFE is used as a promising technology of aroma

703 compound extraction for industrial purposes (Van Opstaele, Goiris, et al., 2012), or as a treatment

704 for off-flavor removal (Gernat et al., 2020).

705 Carro et. al. developed an SFE based on supercritical CO_2 for the extraction of many free VOAs

706 in wine and must aroma (Carro et al., 1996). This paper can be considered a vanguard work since

707 it was presented in 1996 when the GAC principles were still not presented yet. However, despite

708 being over twenty years old, the authors developed an efficient SFE method that can be considered

709 "green" if compared to other used in those years. The sample (50 mL) was first extracted with

710 3.94 g of Amberlite XAD-2 in the extraction chamber, spiked with methanol (used as modifier),

711 extracted with supercritical CO_2, and finally eluted with 2 mL dichloromethane. Forty free volatile

712 compounds including terpenes, terpenoids and norisoprenoids were tentatively identified and

713 quantified after a brief validation (repeatability, correlation coefficient, and linearity range).

714 As concerns the spirits, Gracia et. al. presented an SFE method for the isolation of VOAs in sugar

715 cane spirits using supercritical CO_2. In this experiment, SFE was evaluated as a promising

716 technology for concentrating aroma compounds but since the extracts were analyzed, it can be

717 also considered for analytical purposes (Gracia et al., 2007). Twenty mL of extracts were diluted

718 1:1 with standard ammonium sulphate solution and extracted with 5 mL of diethyl ether/hexane

719 mixture (2:1). The organic layer was collected, concentrated under a nitrogen flow, filtered, and

720 used for GC-MS analysis. Up to 24 VOAs compounds were identified in crude and aged sugar

721 can spirits. The same research group extended the same procedure to fast aged rum with the same

722 purpose (Gracia et al., 2009).

723 All the discussed applications of VOAs analysis in alcoholic beverages using green miniaturized

724 solvent-based techniques are reported in Table 2.

725

726 **TABLE 2.** List of solvent-based methods for the analysis of odor active compounds in alcoholic beverages

727 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)

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IV. Conclusions

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

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

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

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

756 be the optimization focused for coupling these sample preparation methods with LC-MS analysis.

757 Succeeding in this task means to reach the goal of extending the best GAC extraction techniques

758 to trace-compounds, to better determine mid-volatile analytes and to significative improve limits

759 of detection and quantification of each other.

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References

778 Abdolmohammad-Zadeh, H., & Sadeghi, G. H. (2010). Combination of ionic liquid-based dispersive

779   liquid-liquid micro-extraction with stopped-flow spectrofluorometry for the pre-concentration and

780   determination of aluminum in natural waters, fruit juice and food samples. *Talanta*, *81*(3), 778–785.

781   https://doi.org/10.1016/j.talanta.2010.01.012

782 Agrawal, A., Keçili, R., Ghorbani-Bidkorbeh, F., & Hussain, C. M. (2021). Green miniaturized

783   technologies in analytical and bioanalytical chemistry. *TrAC - Trends in Analytical Chemistry*, *143*,

784   116383. https://doi.org/10.1016/j.trac.2021.116383

785 Alañón, M. E., Pérez-Coello, M. S., & Marina, M. L. (2015). Wine science in the metabolomics era.

786   *TrAC - Trends in Analytical Chemistry*, *74*, 1–20. https://doi.org/10.1016/j.trac.2015.05.006

787 Anderson, H. E., Santos, I. C., Hildenbrand, Z. L., & Schug, K. A. (2019). A review of the analytical

788   methods used for beer ingredient and finished product analysis and quality control. *Analytica*

789   *Chimica Acta*, *1085*, 1–20. https://doi.org/10.1016/j.aca.2019.07.061

790 Andujar-Ortiz, I., Moreno-Arribas, M. V., Martín-Álvarez, P. J., & Pozo-Bayón, M. A. (2009). Analytical

791   performance of three commonly used extraction methods for the gas chromatography-mass

792   spectrometry analysis of wine volatile compounds. *Journal of Chromatography A*, *1216*(43), 7351–

793   7357. https://doi.org/10.1016/j.chroma.2009.08.055

794 Anjos, O., Pedro, S. I., Caramelo, D., Semedo, A., Antunes, C. A. L., Canas, S., & Caldeira, I. (2021).

795   Characterization of a spirit beverage produced with strawberry tree (Arbutus unedo L.) fruit and

796   aged with oak wood at laboratorial scale. *Applied Sciences (Switzerland)*, *11*(11), 1–16.

797   https://doi.org/10.3390/app11115065

798 Armenta, S., Esteve-Turrillas, F. A., Garrigues, S., & de la Guardia, M. (2020). Green Analytical

799   Chemistry. In *Comprehensive Foodomics*. Elsevier. https://doi.org/10.1016/B978-0-08-100596-

800   5.22800-X

801 Armenta, S., Garrigues, S., Esteve-Turrillas, F. A., & de la Guardia, M. (2019). Green extraction

802   techniques in green analytical chemistry. *TrAC - Trends in Analytical Chemistry*, *116*, 248–253.

803   https://doi.org/10.1016/j.trac.2019.03.016

804   Arthur, C. L., & Pawliszyn, J. (1990). Solid Phase Microextraction with Thermal Desorption Using Fused

805   Silica Optical Fibers. *Analytical Chemistry*, *62*(19), 2145–2148.

806   https://doi.org/10.1021/ac00218a019

807   Ballesteros-Gómez, A., Sicilia, M. D., & Rubio, S. (2010). Supramolecular solvents in the extraction of

808   organic compounds. A review. *Analytica Chimica Acta*, *677*(2), 108–130.

809   https://doi.org/10.1016/j.aca.2010.07.027

810   Borden, S. A., Palaty, J., Termopoli, V., Famiglini, G., Cappiello, A., Gill, C. G., & Palma, P. (2020).

811   Mass Spectrometry Analysis of Drugs of Abuse: Challenges and Emerging Strategies. *Mass*

812   *Spectrometry Reviews*, *39*(5–6), 703–744. https://doi.org/10.1002/mas.21624

813   Bruins, A. P., & Niessen, W. M. A. (2019). Mass spectrometry | Atmospheric pressure ionization

814   techniques. In *Encyclopedia of Analytical Science* (Third Edit, Vol. 6, Issue 2018). Elsevier.

815   https://doi.org/10.1016/B978-0-12-409547-2.00311-5

816   Bueno, M., Zapata, J., & Ferreira, V. (2014). Simultaneous determination of free and bonded forms of

817   odor-active carbonyls in wine using a headspace solid phase microextraction strategy. *Journal of*

818   *Chromatography A*, *1369*, 33–42. https://doi.org/10.1016/j.chroma.2014.10.004

819   Buiatti, S. (2008). Beer composition: An overview. *Beer in Health and Disease Prevention*, *iii*, 213–225.

820   https://doi.org/10.1016/b978-0-12-373891-2.00020-1

821   Cabrita, M. J., Costa Freitas, A. M., Laureano, O., Borsa, D., & Di Stefano, R. (2007). Aroma compounds

822   in varietal wines from Alentejo, Portugal. *Journal of Food Composition and Analysis*, *20*(5), 375–

823   390. https://doi.org/10.1016/j.jfca.2006.12.006

824   Cajka, T., Riddellova, K., Tomaniova, M., & Hajslova, J. (2010). Recognition of beer brand based on

825   multivariate analysis of volatile fingerprint. *Journal of Chromatography A*, *1217*(25), 4195–4203.

826   https://doi.org/10.1016/j.chroma.2009.12.049

827   Campillo, N., López-García, I., Hernández-Córdoba, M., & Viñas, P. (2018). Food and beverage

828   applications of liquid-phase microextraction. *TrAC - Trends in Analytical Chemistry*, *109*, 116–123.

829   https://doi.org/10.1016/j.trac.2018.10.004

830   Carro, N., García, C. M., & Cela, R. (1996). Supercritical Fluid Extraction of Free Fraction Components

831   of Aroma in Wines and Musts. *Journal of Microcolumn Separations*, *8*(7), 453–460.

832   https://doi.org/10.1002/(SICI)1520-667X(1996)8:7<453::AID-MCS1>3.0.CO;2-0

833   Castro-Vázquez, L., Alañón, M. E., Calvo, E., Cejudo, M. J., Díaz-Maroto, M. C., & Pérez-Coello, M. S.

834   (2011). Volatile compounds as markers of ageing in Tempranillo red wines from La Mancha D.O.

835   stored in oak wood barrels. *Journal of Chromatography A*, *1218*(30), 4910–4917.

836   https://doi.org/10.1016/j.chroma.2010.12.094

837   Castro, R., Natera, R., Benitez, P., & Barroso, C. G. (2004). Comparative analysis of volatile compounds

838   of "fino" sherry wine by rotatory and continuous liquid-liquid extraction and solid-phase

839   microextraction in conjunction with gas chromatography-mass spectrometry. *Analytica Chimica*

840   *Acta*, *513*(1), 141–150. https://doi.org/10.1016/j.aca.2004.02.002

841   Castro, Remedios, Natera, R., Durán, E., & García-Barroso, C. (2008). Application of solid phase

842   extraction techniques to analyse volatile compounds in wines and other enological products.

843   *European Food Research and Technology*, *228*(1), 1–18. https://doi.org/10.1007/s00217-008-0900-

844   4

845   Caven-quantrill, D. J., & Buglass, A. J. (2011). Comparison of volatile constituents extracted from model

846   grape juice and model wine by stir bar sorptive extraction – gas chromatography – mass

847   spectrometry. *Journal of Chromatography A*, *1218*(7), 875–881.

848   https://doi.org/10.1016/j.chroma.2010.12.078

849   Conway, J. (2020). *Alcoholic Beverages Industry - Statistics & Facts*. Statista.

850   https://www.statista.com/topics/1709/alcoholic-beverages/

851   Costa Freitas, A. M., Gomes da Silva, M. D. R., & Cabrita, M. J. (2012). Sampling techniques for the

852   determination of volatile components in grape juice, wine and alcoholic beverages. In

853   *Comprehensive Sampling and Sample Preparation* (Vol. 4). Elsevier. https://doi.org/10.1016/B978-

854   0-12-381373-2.00126-5

855   Crucello, J., Miron, L. F. O., Ferreira, V. H. C., Nan, H., Marques, M. O. M., Ritschel, P. S., Zanus, M.

856   C., Anderson, J. L., Poppi, R. J., & Hantao, L. W. (2018). Characterization of the aroma profile of

857   novel Brazilian wines by solid-phase microextraction using polymeric ionic liquid sorbent coatings.

858   *Analytical and Bioanalytical Chemistry*, *410*(19), 4749–4762. https://doi.org/10.1007/s00216-018-

859   1134-3

860 Cunha, S. C., & Fernandes, J. O. (2018). Extraction techniques with deep eutectic solvents. *TrAC -*

861   *Trends in Analytical Chemistry*, *105*, 225–239. https://doi.org/10.1016/j.trac.2018.05.001

862 David, F., & Sandra, P. (2007). Stir bar sorptive extraction for trace analysis. *Journal of Chromatography*

863   *A*, *1152*(1–2), 54–69. https://doi.org/10.1016/j.chroma.2007.01.032

864 Davis, P. M., & Qian, M. C. (2019). Effect of ethanol on the adsorption of volatile sulfur compounds on

865   solid phase micro-extraction fiber coatings and the implication for analysis in wine. *Molecules*,

866   *24*(18). https://doi.org/10.3390/molecules24183392

867 Demyttenaere, J. C. R., Dagher, C., Sandra, P., Kallithraka, S., & Verhe, R. (2003). Flavour analysis of

868   Greek white wine by solid-phase microextraction–capillary gas chromatography–mass

869   spectrometry. *Journal of Chromatography A*, *985*, 233–246.

870 Dennenlöhr, J., Thörner, S., Manowski, A., & Rettberg, N. (2020). Analysis of Selected Hop Aroma

871   Compounds in Commercial Lager and Craft Beers Using HS-SPME-GC-MS/MS. *Journal of the*

872   *American Society of Brewing Chemists*, *78*(1), 16–31.

873   https://doi.org/10.1080/03610470.2019.1668223

874 Dennenlöhr, J., Thörner, S., Maxminer, J., & Rettberg, N. (2020). Analysis of Selected Staling Aldehydes

875   in Wort and Beer by GC-EI-MS/MS Using HS-SPME with On-Fiber Derivatization. *Journal of the*

876   *American Society of Brewing Chemists*, *78*(4), 284–298.

877   https://doi.org/10.1080/03610470.2020.1795478

878 Dobrydnev, A., Tarasov, A., Müller, N., Volovenko, Y., Rauhut, D., & Jung, R. (2020). An optimized

879   method for synthesis and purification of 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN). *MethodsX*,

880   *7*(December 2019), 56–61. https://doi.org/10.1016/j.mex.2019.12.009

881 Eichhorn, P., Pérez, S., & Barceló, D. (2012). Time-of-Flight Mass Spectrometry Versus Orbitrap-Based

882   Mass Spectrometry for the Screening and Identification of Drugs and Metabolites: Is There a

883   Winner? In *Comprehensive Analytical Chemistry* (Vol. 58). https://doi.org/10.1016/B978-0-444-

884   53810-9.00009-2

885 Famiglini, G., Palma, P., Termopoli, V., & Cappiello, A. (2021). The history of electron ionization in LC-

886   MS, from the early days to modern technologies: A review. *Analytica Chimica Acta*, *1167*.

887   https://doi.org/10.1016/j.aca.2021.338350

888   Famiglini, G., Palma, P., Termopoli, V., Cappiello, A., Tsizin, S., Seemann, B., Alon, T., Fialkov, A. B.,

889   & Amirav, A. (2018). Electron Ionization LC-MS: What Is It and Why Use It? *Comprehensive*

890   *Analytical Chemistry*, *79*(August 2018), 1–28. https://doi.org/10.1016/bs.coac.2017.06.008

891   Fariña, L., Boido, E., Carrau, F., & Dellacassa, E. (2007). Determination of volatile phenols in red wines

892   by dispersive liquid-liquid microextraction and gas chromatography-mass spectrometry detection.

893   *Journal of Chromatography A*, *1157*(1–2), 46–50. https://doi.org/10.1016/j.chroma.2007.05.006

894   Ferreira, V., Herrero, P., Zapata, J., & Escudero, A. (2015). Coping with matrix effects in headspace solid

895   phase microextraction gas chromatography using multivariate calibration strategies. *Journal of*

896   *Chromatography A*, *1407*, 30–41. https://doi.org/10.1016/j.chroma.2015.06.058

897   Ferreira, V., Jarauta, I., López, R., & Cacho, J. (2003). Quantitative determination of sotolon, maltol and

898   free furaneol in wine by solid-phase extraction and gas chromatography-ion-trap mass

899   spectrometry. *Journal of Chromatography A*, *1010*(1), 95–103. https://doi.org/10.1016/S0021-

900   9673(03)00963-4

901   Fontana, A., Rodríguez, I., & Cela, R. (2018). Dispersive liquid–liquid microextraction and gas

902   chromatography accurate mass spectrometry for extraction and non-targeted profiling of volatile

903   and semi-volatile compounds in grape marc distillates. *Journal of Chromatography A*, *1546*, 36–45.

904   https://doi.org/10.1016/j.chroma.2018.03.003

905   Fornells, E., Hilder, E. F., & Breadmore, M. C. (2019). Preconcentration by solvent removal: techniques

906   and applications. *Analytical and Bioanalytical Chemistry*, *411*(9), 1715–1727.

907   https://doi.org/10.1007/s00216-018-1530-8

908   Frago Ramos, S. (2016). Extracción y determinación de aromas en orujos de uva. *Universidad Pública de*

909   *Navarra*, 52.

910   Gabrielli, M., Fracassetti, D., Romanini, E., Colangelo, D., Tirelli, A., & Lambri, M. (2021). Oxygen-

911   induced faults in bottled white wine: A review of technological and chemical characteristics. *Food*

912   *Chemistry*, *348*, 128922. https://doi.org/10.1016/j.foodchem.2020.128922

913   Garde-Cerdán, T., & Ancín-Azpilicueta, C. (2006). Review of quality factors on wine ageing in oak

914   barrels. *Trends in Food Science and Technology*, *17*(8), 438–447.

915   https://doi.org/10.1016/j.tifs.2006.01.008

916   Gernat, D. C., Brouwer, E., & Ottens, M. (2020). Aldehydes as Wort Off-Flavours in Alcohol-Free

917   Beers—Origin and Control. *Food and Bioprocess Technology*, *13*(2), 195–216.

918   https://doi.org/10.1007/s11947-019-02374-z

919   González-Álvarez, J., Blanco-Gomis, D., Arias-Abrodo, P., Pello-Palma, J., Ríos-Lombardía, N., Busto,

920   E., Gotor-Fernández, V., & Gutiérrez-Álvarez, M. D. (2013). Analysis of beer volatiles by

921   polymeric imidazolium-solid phase microextraction coatings: Synthesis and characterization of

922   polymeric imidazolium ionic liquids. *Journal of Chromatography A*, *1305*, 35–40.

923   https://doi.org/10.1016/j.chroma.2013.07.012

924   Gracia, I., García, M. T., Rodríguez, J. F., & De Lucas, A. (2009). Application of supercritical fluid

925   extraction for the recovery of aroma compounds to be used in fast aged rum production. *Food*

926   *Science and Technology Research*, *15*(4), 353–360. https://doi.org/10.3136/fstr.15.353

927   Gracia, I., Rodríguez, J. F., García, M. T., Alvarez, A., & García, A. (2007). Isolation of aroma

928   compounds from sugar cane spirits by supercritical CO_2. *Journal of Supercritical Fluids*, *43*(1),

929   37–42. https://doi.org/10.1016/j.supflu.2007.04.010

930   Hallett, J. P., & Welton, T. (2011). Room-temperature ionic liquids: Solvents for synthesis and catalysis.

931   2. *Chemical Reviews*, *111*(5), 3508–3576. https://doi.org/10.1021/cr1003248

932   Hansen, F. A., & Pedersen-Bjergaard, S. (2020). Emerging Extraction Strategies in Analytical Chemistry.

933   *Analytical Chemistry*, *92*(1), 2–15. https://doi.org/10.1021/acs.analchem.9b04677

934   He, Y., & Concheiro-Guisan, M. (2019). Microextraction sample preparation techniques in forensic

935   analytical toxicology. *Biomedical Chromatography*, *33*(1), 1–12. https://doi.org/10.1002/bmc.4444

936   Hernandes, K. C., Souza-Silva, É. A., Assumpção, C. F., Zini, C. A., & Welke, J. E. (2019). Validation of

937   an analytical method using HS-SPME-GC/MS-SIM to assess the exposure risk to carbonyl

938   compounds and furan derivatives through beer consumption. *Food Additives and Contaminants -*

939   *Part A Chemistry, Analysis, Control, Exposure and Risk Assessment*, *36*(12), 1808–1821.

940   https://doi.org/10.1080/19440049.2019.1672897

941   Herrero, M., Ibáñez, E., Cifuentes, A., & Bernal, J. (2009). Multidimensional chromatography in food

942   analysis. *Journal of Chromatography A*, *1216*(43), 7110–7129.

943   https://doi.org/10.1016/j.chroma.2009.08.014

944   Hiroyuki Kataoka, Heather L. Lord, J. P. (2000). Applications of solid-phase microextraction in food

945   analysis. *Journal of Chromatography A*, *880*, 35–62. https://doi.org/https://doi.org/10.1016/S0021-

946   9673(00)00309-5

947   Ibáñez, E., & Cifuentes, A. (2015). Green extraction techniques 2015. *TrAC - Trends in Analytical*

948   *Chemistry*, *71*, 1. https://doi.org/10.1016/j.trac.2015.06.003

949   Jose A. Mendiola, Miguel Herrero, Maria Castro-Puyana, E. I. (2013). Supercritical Fluid Extraction. In

950   *Current Green Chemistry* (Vol. 1, Issue 1). https://doi.org/10.2174/221334610101131218100515

951   Kächele, M., Monakhova, Y. B., Kuballa, T., & Lachenmeier, D. W. (2014). Analytica Chimica Acta

952   NMR investigation of acrolein stability in hydroalcoholic solution as a foundation for the valid HS-

953   SPME / GC – MS quantification of the unsaturated aldehyde in beverages. *Analytica Chimica Acta*,

954   *820*(July 2013), 112–118. https://doi.org/10.1016/j.aca.2014.02.030

955   Katarína, F., Katarína, M., Katarína, Ď., Ivan, Š., & Fedor, M. (2014). Influence of yeast strain on

956   aromatic profile of Gewürztraminer wine. *LWT - Food Science and Technology*, *59*(1), 256–262.

957   https://doi.org/10.1016/j.lwt.2014.05.057

958   Lang, Q., & Wai, C. M. (2001). Supercritical fluid extraction in herbal and natural product studies - A

959   practical review. *Talanta*, *53*(4), 771–782. https://doi.org/10.1016/S0039-9140(00)00557-9

960   Li, H., Guo, A., & Wang, H. (2008). Mechanisms of oxidative browning of wine. *Food Chemistry*,

961   *108*(1), 1–13. https://doi.org/10.1016/j.foodchem.2007.10.065

962   López-Vázquez, C., Orriols, I., Perelló, M. C., & De Revel, G. (2012). Determination of aldehydes as

963   pentafluorobenzyl derivatives in grape pomace distillates by HS-SPME-GC/MS. *Food Chemistry*,

964   *130*(4), 1127–1133. https://doi.org/10.1016/j.foodchem.2011.07.140

965   López, R., Aznar, M., Cacho, J., & Ferreira, V. (2002). Determination of minor and trace volatile

966   compounds in wine by solid-phase extraction and gas chromatography with mass spectrometric

967   detection. *Journal of Chromatography A*, *966*(1–2), 167–177. https://doi.org/10.1016/S0021-

968   9673(02)00696-9

969   Lukić, I., Budić-Leto, I., Bubola, M., Damijanić, K., & Staver, M. (2017). Pre-fermentative cold

970   maceration, saignée, and various thermal treatments as options for modulating volatile aroma and

971   phenol profiles of red wine. *Food Chemistry*, *224*, 251–261.

972   https://doi.org/10.1016/j.foodchem.2016.12.077

973   Lukić, I., Radeka, S., Grozaj, N., Staver, M., & Peršurić, D. (2016). Changes in physico-chemical and

974   volatile aroma compound composition of Gewürztraminer wine as a result of late and ice harvest.

975   *Food Chemistry*, *196*, 1048–1057. https://doi.org/10.1016/j.foodchem.2015.10.061

976   Luo, Y., Kong, L., Xue, R., Wang, W., & Xia, X. (2020). Bitterness in alcoholic beverages: The profiles

977   of perception, constituents, and contributors. *Trends in Food Science and Technology*, *96*(July

978   2019), 222–232. https://doi.org/10.1016/j.tifs.2019.12.026

979   Lyu, J., Chen, S., Nie, Y., Xu, Y., & Tang, K. (2021). Aroma release during wine consumption: Factors

980   and analytical approaches. *Food Chemistry*, *346*(September 2020), 128957.

981   https://doi.org/10.1016/j.foodchem.2020.128957

982   Macedo, S., Fernandes, S., Lopesio, J. A., de Sousa, H., Pereira, P. J., Carmelo, P. J., Menduiña, C.,

983   Simões, P. C., & Nunes Da Ponte, M. (2008). Recovery of wine-must aroma compounds by

984   supercritical co 2. *Food and Bioprocess Technology*, *1*(1), 74–81. https://doi.org/10.1007/s11947-

985   007-0002-5

986   Magali Picard, Celine Franc, Gilles De Revel, S. M. (2018). *Dual solid-phase and stir bar sorptive*

987   *extraction combined with gas chromatography-mass spectrometry analysis provides a suitable tool*

988   *for assaying limonene-derived mint aroma compounds in red wine. 1001.*

989   https://doi.org/10.1016/j.aca.2017.11.074

990   Mamede, M. E. O., & Pastore, G. M. (2006). Study of methods for the extraction of volatile compounds

991   from fermented grape must. *Food Chemistry*, *96*(4), 586–590.

992   https://doi.org/10.1016/j.foodchem.2005.03.013

993   Manzocco, L., Calligaris, S., Mastrocola, D., Nicoli, M. C., & Lerici, C. R. (2000). Review of non-

994   enzymatic browning and antioxidant capacity in processed foods. *Trends in Food Science and*

995   *Technology*, *11*(9–10), 340–346. https://doi.org/10.1016/S0924-2244(01)00014-0

996 Marín-San Román, S., Rubio-Bretón, P., Pérez-Álvarez, E. P., & Garde-Cerdán, T. (2020a).

997 Advancement in analytical techniques for the extraction of grape and wine volatile compounds.

998 *Food Research International*, *137*(September). https://doi.org/10.1016/j.foodres.2020.109712

999 Marín-San Román, S., Rubio-Bretón, P., Pérez-Álvarez, E. P., & Garde-Cerdán, T. (2020b).

1000 Advancement in analytical techniques for the extraction of grape and wine volatile compounds.

1001 *Food Research International*, *137*(April). https://doi.org/10.1016/j.foodres.2020.109712

1002 Martínez-Gil, A., Del Alamo-Sanza, M., Sánchez-Gómez, R., & Nevares, I. (2018). Different woods in

1003 cooperage for oenology: A review. *Beverages*, *4*(4). https://doi.org/10.3390/beverages4040094

1004 Martins, R. O., de Araújo, G. L., de Freitas, C. S., Silva, A. R., Simas, R. C., Vaz, B. G., & Chaves, A. R.

1005 (2021). Miniaturized sample preparation techniques and ambient mass spectrometry as approaches

1006 for food residue analysis. *Journal of Chromatography A*, *1640*, 461949.

1007 https://doi.org/10.1016/j.chroma.2021.461949

1008 Mashayekhi, H. A., Abroomand-Azar, P., Saber-Tehrani, M., & Husain, S. W. (2010). Rapid

1009 determination of carbamazepine in human urine, plasma samples and water using DLLME followed

1010 by RP-LC. *Chromatographia*, *71*(5–6), 517–521. https://doi.org/10.1365/s10337-009-1456-6

1011 Mayr, C. M., Geue, J. P., Holt, H. E., Pearson, W. P., Jeffery, D. W., & Francis, I. L. (2014).

1012 Characterization of the key aroma compounds in shiraz wine by quantitation, aroma reconstitution,

1013 and omission studies. *Journal of Agricultural and Food Chemistry*, *62*(20), 4528–4536.

1014 https://doi.org/10.1021/jf405731v

1015 Mehrdad, A., Taleb-Abbasi, M., & Rezaei, M. (2019). Miscibility behavior of hydroxyethyl

1016 cellulose/poly(vinyl pyrrolidone) blends in the presence of some imidazolium based ionic liquids.

1017 *Journal of Molecular Liquids*, *296*, 111844. https://doi.org/10.1016/j.molliq.2019.111844

1018 Melnyk, A., Namieśnik, J., & Wolska, L. (2015). Theory and recent applications of coacervate-based

1019 extraction techniques. *TrAC - Trends in Analytical Chemistry*, *71*, 282–292.

1020 https://doi.org/10.1016/j.trac.2015.03.013

1021 Melnyk, A., Wolska, L., & Namieśnik, J. (2014). Coacervative extraction as a green technique for sample

1022 preparation for the analysis of organic compounds. *Journal of Chromatography A*, *1339*, 1–12.

1023 https://doi.org/10.1016/j.chroma.2014.02.082

1024   Mestres, M., Sala, C., Martí, M. P., Busto, O., & Guasch, J. (1999). Headspace solid-phase

1025   microextraction of sulphides and disulphides using Carboxen-polydimethylsiloxane fibers in the

1026   analysis of wine aroma. *Journal of Chromatography A*, *835*(1–2), 137–144.

1027   https://doi.org/10.1016/S0021-9673(98)01050-4

1028   Metafa, M., & Economou, A. (2013). Chemometrical development and comprehensive validation of a

1029   solid phase microextraction/gas chromatography-mass spectrometry methodology for the

1030   determination of important free and bound primary aromatics in Greek wines. *Journal of*

1031   *Chromatography A*, *1305*, 244–258. https://doi.org/10.1016/j.chroma.2013.07.005

1032   Moreira, N., Lopes, P., Ferreira, H., Cabral, M., & Guedes de Pinho, P. (2018). Sensory attributes and

1033   volatile composition of a dry white wine under different packing configurations. *Journal of Food*

1034   *Science and Technology*, *55*(1), 424–430. https://doi.org/10.1007/s13197-017-2910-3

1035   Moreira, Nathalie, Araújo, A. M., Rogerson, F., Vasconcelos, I., Freitas, V. De, & Pinho, P. G. de.

1036   (2019). Development and optimization of a HS-SPME-GC-MS methodology to quantify volatile

1037   carbonyl compounds in Port wines. *Food Chemistry*, *270*(January 2018), 518–526.

1038   https://doi.org/10.1016/j.foodchem.2018.07.093

1039   Moreira, Nathalie, Meireles, S., Brandão, T., & De Pinho, P. G. (2013a). Optimization of the HS-SPME-

1040   GC-IT/MS method using a central composite design for volatile carbonyl compounds determination

1041   in beers. *Talanta*, *117*, 523–531. https://doi.org/10.1016/j.talanta.2013.09.027

1042   Moreira, Nathalie, Meireles, S., Brandão, T., & De Pinho, P. G. (2013b). Optimization of the HS-SPME-

1043   GC-IT/MS method using a central composite design for volatile carbonyl compounds determination

1044   in beers. *Talanta*, *117*, 523–531. https://doi.org/10.1016/j.talanta.2013.09.027

1045   Morrin, M., & Tepper, B. J. (2021). Multisensory marketing: effects of environmental aroma cues on

1046   perception, appetite, and consumption of foods and drinks. *Current Opinion in Food Science*, *40*,

1047   204–210. https://doi.org/10.1016/j.cofs.2021.04.008

1048   Namiesnik, J. (2000). Trends in Environmental Analytics and Monitoring. *Critical Reviews in Analytical*

1049   *Chemistry*, *30*(August 2013), 221–269. https://doi.org/https://doi.org/10.1080/10408340091164243.

1050   Ng, L., Hupe, M., Harnoisb, J., & Mocciab, D. (1996). *Characterisation of Commercial Vodkas by Solid-*

1051   *Phase Microextraction and Gas Chromatography / Mass Spectrometry Analysis*. 380–388.

1052 Niu, Y., Wang, R., Xiao, Z., Zhu, J., Sun, X., & Wang, P. (2019). Characterization of ester odorants of

1053   apple juice by gas chromatography-olfactometry, quantitative measurements, odour threshold,

1054   aroma intensity and electronic nose. *Food Research International*, *120*(October 2018), 92–101.

1055   https://doi.org/10.1016/j.foodres.2019.01.064

1056 Ochiai, N., Sasamoto, K., David, F., & Sandra, P. (2016). Solvent-assisted stir bar sorptive extraction by

1057   using swollen polydimethylsiloxane for enhanced recovery of polar solutes in aqueous samples :

1058   Application to aroma compounds in beer and pesticides in wine. *Journal of Chromatography A*,

1059   *1455*, 45–56. https://doi.org/10.1016/j.chroma.2016.05.085

1060 Ochiai, N., Sasamoto, K., Hoffmann, A., & Okanoya, K. (2012). Full evaporation dynamic headspace and

1061   gas chromatography – mass spectrometry for uniform enrichment of odor compounds in aqueous

1062   samples. *Journal of Chromatography A*, *1240*, 59–68. https://doi.org/10.1016/j.chroma.2012.03.097

1063 Ochiai, N., Sasamoto, K., Kanda, H., & Pfannkoch, E. (2008). Sequential stir bar sorptive extraction for

1064   uniform enrichment of trace amounts of organic pollutants in water samples. *Journal of*

1065   *Chromatography A*, *1200*(1), 72–79. https://doi.org/10.1016/j.chroma.2008.05.069

1066 Oller-Ruiz, A., Viñas, P., Campillo, N., Fenoll, J., & Hernández-Córdoba, M. (2017). Triple Quadrupole

1067   Mass Spectrometry with Liquid Chromatography and Dispersive Liquid-Liquid Microextraction for

1068   the Determination of Monoterpenes in Alcoholic Drinks. *Food Analytical Methods*, *10*(11), 3615–

1069   3622. https://doi.org/10.1007/s12161-017-0937-8

1070 Özay, H., Çakır, A., & Ecevit, M. C. (2019). Retronasal olfaction test methods: A systematic review.

1071   *Balkan Medical Journal*, *36*(1), 49–59. https://doi.org/10.4274/balkanmedj.2018.0052

1072 P. Rocío-Bautista, A. G.-S. and V. P. (2018). Solid-Phase Microextraction Coatings Based on Tailored

1073   Materials: Metal–Organic Frameworks and Molecularly Imprinted Polymers. In *Advanced Coating*

1074   *Materials* (Issue December). https://doi.org/10.1002/9781119407652.ch7

1075 Pacheco-Fernández, I., & Pino, V. (2019). Green solvents in analytical chemistry. *Current Opinion in*

1076   *Green and Sustainable Chemistry*, *18*, 42–50. https://doi.org/10.1016/j.cogsc.2018.12.010

1077 Pena-Pereira, F., Lavilla, I., & Bendicho, C. (2009). Miniaturized preconcentration methods based on

1078   liquid-liquid extraction and their application in inorganic ultratrace analysis and speciation: A

1079   review. *Spectrochimica Acta - Part B Atomic Spectroscopy*, *64*(1), 1–15.

1080   https://doi.org/10.1016/j.sab.2008.10.042

1081   Pereira, V., Albuquerque, F. M., Ferreira, A. C., Cacho, J., & Marques, J. C. (2011). Evolution of 5-

1082   hydroxymethylfurfural (HMF) and furfural (F) in fortified wines submitted to overheating

1083   conditions. *Food Research International*, *44*(1), 71–76.

1084   https://doi.org/10.1016/J.FOODRES.2010.11.011

1085   Perestrelo, R., Barros, A. S., Rocha, S. M., & Câmara, J. S. (2011). Optimisation of solid-phase

1086   microextraction combined with gas chromatography-mass spectrometry based methodology to

1087   establish the global volatile signature in pulp and skin of Vitis vinifera L. grape varieties. *Talanta*,

1088   *85*(3), 1483–1493. https://doi.org/10.1016/j.talanta.2011.06.025

1089   Pérez Olivero, S. J., & Pérez Trujillo, J. P. (2010). A new method for the determination of carbonyl

1090   compounds in wines by headspace solid-phase microextraction coupled to gas chromatography-ion

1091   trap mass spectrometry. *Journal of Agricultural and Food Chemistry*, *58*(24), 12976–12985.

1092   https://doi.org/10.1021/jf1034064

1093   Picard, M., Garrouste, C., Absalon, C., & Vivas, N. (2019). *Development of a Solid-Phase*

1094   *Microextraction-Gas Chromatography/Mass Spectrometry Method for Quantifying Nitrogen-*

1095   *Heterocyclic Volatile Aroma Compounds: Application to Spirit and Wood Matrices*.

1096   https://doi.org/10.1021/acs.jafc.9b05716

1097   Pissarra, J., Lourenço, S., Machado, J. M., Mateus, N., Guimaraens, D., & De Freitas, V. (2005).

1098   Contribution and importance of wine spirit to the port wine final quality - Initial approach. *Journal*

1099   *of the Science of Food and Agriculture*, *85*(7), 1091–1097. https://doi.org/10.1002/jsfa.2070

1100   Płotka-Wasylka, J., Szczepańska, N., de la Guardia, M., & Namieśnik, J. (2015). Miniaturized solid-phase

1101   extraction techniques. *TrAC - Trends in Analytical Chemistry*, *73*, 19–38.

1102   https://doi.org/10.1016/j.trac.2015.04.026

1103   Plutowska, B., & Wardencki, W. (2008). Application of gas chromatography-olfactometry (GC-O) in

1104   analysis and quality assessment of alcoholic beverages - A review. *Food Chemistry*, *107*(1), 449–

1105   463. https://doi.org/10.1016/j.foodchem.2007.08.058

1106   Polášková, P., Herszage, J., & Ebeler, S. E. (2008). Wine flavor: Chemistry in a glass. *Chemical Society*

1107   *Reviews*, *37*(11), 2478–2489. https://doi.org/10.1039/b714455p

1108 Prata-Sena, M., Castro-Carvalho, B. M., Nunes, S., Amaral, B., & Silva, P. (2018). The terroir of Port

1109   wine: Two hundred and sixty years of history. *Food Chemistry*, *257*, 388–398.

1110   https://doi.org/10.1016/J.FOODCHEM.2018.03.014

1111 *Restek*. (n.d.). https://www.restek.com/it/

1112 Rezaee, M., Assadi, Y., Milani Hosseini, M. R., Aghaee, E., Ahmadi, F., & Berijani, S. (2006).

1113   Determination of organic compounds in water using dispersive liquid-liquid microextraction.

1114   *Journal of Chromatography A*, *1116*(1–2), 1–9. https://doi.org/10.1016/j.chroma.2006.03.007

1115 Riu-Aumatell, M., Miró, P., Serra-Cayuela, A., Buxaderas, S., & López-Tamames, E. (2014). Assessment

1116   of the aroma profiles of low-alcohol beers using HS-SPME-GC-MS. *Food Research International*,

1117   *57*, 196–202. https://doi.org/10.1016/j.foodres.2014.01.016

1118 Rosillo, L., Salinas, M. R., Garijo, J., & Alonso, G. L. (1999). Study of volatiles in grapes by dynamic

1119   headspace analysis: Application to the differentiation of some Vitis vinifera varieties. *Journal of*

1120   *Chromatography A*, *847*(1–2), 155–159. https://doi.org/10.1016/S0021-9673(99)00036-9

1121 Saito-Shida, S., Hamasaka, T., Nemoto, S., & Akiyama, H. (2018). Multiresidue determination of

1122   pesticides in tea by liquid chromatography-high-resolution mass spectrometry: Comparison

1123   between Orbitrap and time-of-flight mass analyzers. *Food Chemistry*, *256*(February), 140–148.

1124   https://doi.org/10.1016/j.foodchem.2018.02.123

1125 Sakai, M., Hayakawa, Y., Funada, Y., Ando, T., Fukusaki, E., & Bamba, T. (2019). Development of a

1126   practical online supercritical fluid extraction–supercritical fluid chromatography/mass spectrometry

1127   system with an integrated split-flow method. *Journal of Chromatography A*, *1592*, 161–172.

1128   https://doi.org/10.1016/j.chroma.2019.01.044

1129 Sanchez-Prado, L., Garcia-Jares, C., Dagnac, T., & Llompart, M. (2015). Microwave-assisted extraction

1130   of emerging pollutants in environmental and biological samples before chromatographic

1131   determination. *TrAC - Trends in Analytical Chemistry*, *71*, 119–143.

1132   https://doi.org/10.1016/j.trac.2015.03.014

1133 SAS Wercinski, J. P. (1999). *Solid phase microextraction theory*.

1134 Savchuk, S. A., Palacio, C., Gil, A., Tagliaro, F., Kuznetsov, R. M., Brito, A., & Appolonova, S. A.

1135   (2020). Determination of the chemical composition of alcoholic beverages by gas chromatography-

1136   mass spectrometry. *Journal of Food Processing and Preservation*, *44*(9), 1–15.

1137   https://doi.org/10.1111/jfpp.14676

1138   Schieberle, P. (1995). New Developments in Methods for Analysis of Volatile Flavor Compounds and

1139   their Precursors. *Characterization of Food*, 403–431. https://doi.org/10.1016/B978-044481499-

1140   9/50018-4

1141   Schmarr, H. G., Potouridis, T., Ganß, S., Sang, W., Köpp, B., Bokuz, U., & Fischer, U. (2008). Analysis

1142   of carbonyl compounds via headspace solid-phase microextraction with on-fiber derivatization and

1143   gas chromatographic-ion trap tandem mass spectrometric determination of their O-(2,3,4,5,6-

1144   pentafluorobenzyl)oxime derivatives. *Analytica Chimica Acta*, *617*(1–2), 119–131.

1145   https://doi.org/10.1016/j.aca.2008.02.002

1146   Sciarrone, D., Pantò, S., Ragonese, C., Dugo, P., & Mondello, L. (2015). Evolution and status of

1147   preparative gas chromatography as a green sample-preparation technique. *TrAC - Trends in*

1148   *Analytical Chemistry*, *71*, 65–73. https://doi.org/10.1016/j.trac.2015.02.024

1149   ScienceDirect. (2021). *ScienceDirect*. https://www.sciencedirect.com/

1150   Selli, S., Canbas, A., Cabaroglu, T., Erten, H., & Günata, Z. (2006). Aroma components of cv. Muscat of

1151   Bornova wines and influence of skin contact treatment. *Food Chemistry*, *94*(3), 319–326.

1152   https://doi.org/10.1016/j.foodchem.2004.11.019

1153   Señoŕns, F. J., Ruiz-Rodríguez, A., Ibañez, E., Tabera, J., & Reglero, G. (2001). Countercurrent

1154   supercritical fluid extraction and fractionation of alcoholic beverages. *Journal of Agricultural and*

1155   *Food Chemistry*, *49*(4), 1895–1899. https://doi.org/10.1021/jf001261v

1156   Silvestre, C. I. C., Santos, J. L. M., Lima, J. L. F. C., & Zagatto, E. A. G. (2009). Liquid-liquid extraction

1157   in flow analysis: A critical review. *Analytica Chimica Acta*, *652*(1–2), 54–65.

1158   https://doi.org/10.1016/j.aca.2009.05.042

1159   Singha, N. K., Hong, K., & Mays, J. W. (2018). CHAPTER 1: Polymerization in Ionic Liquids. *RSC*

1160   *Smart Materials*, *2018-Janua*(29), 1–22. https://doi.org/10.1039/9781788010535-00001

1161   Smith, E. L., Abbott, A. P., & Ryder, K. S. (2014). Deep Eutectic Solvents (DESs) and Their

1162   Applications. *Chemical Reviews*, *114*(21), 11060–11082. https://doi.org/10.1021/cr300162p

1163   Soares da Silva Burato, J., Vargas Medina, D. A., de Toffoli, A. L., Vasconcelos Soares Maciel, E., &

1164   Mauro Lanças, F. (2020). Recent advances and trends in miniaturized sample preparation

1165   techniques. *Journal of Separation Science*, *43*(1), 202–225. https://doi.org/10.1002/jssc.201900776

1166   Soria, A. C., García-Sarrió, M. J., & Sanz, M. L. (2015). Volatile sampling by headspace techniques.

1167   *TrAC - Trends in Analytical Chemistry*, *71*, 85–99. https://doi.org/10.1016/j.trac.2015.04.015

1168   Spietelun, A., Marcinkowski, Ł., de la Guardia, M., & Namieśnik, J. (2013). Recent developments and

1169   future trends in solid phase microextraction techniques towards green analytical chemistry. *Journal*

1170   *of Chromatography A*, *1321*, 1–13. https://doi.org/10.1016/j.chroma.2013.10.030

1171   Sun, Z., Cui, H., Yang, N., Ayed, C., Zhang, X., & Fisk, I. D. (2020). Enhancement of coffee brew aroma

1172   through control of the aroma staling pathway of 2-furfurylthiol. *Food Chemistry*, *322*(November

1173   2019), 126754. https://doi.org/10.1016/j.foodchem.2020.126754

1174   *Supelco*. (n.d.). https://www.sigmaaldrich.com

1175   Tang, Z., & Duan, Y. (2017). Fabrication of porous ionic liquid polymer as solid-phase microextraction

1176   coating for analysis of organic acids by gas chromatography – mass spectrometry. *Talanta*,

1177   *172*(February), 45–52. https://doi.org/10.1016/j.talanta.2017.05.032

1178   Thibaud, F., Peterson, A., Urruty, L., Mathurin, J., Darriet, P., & Pons, A. (2021). *Sensorial Impact and*

1179   *Distribution of 3 - Methyl-2,4-nonanedione in Cognacs and Spirits*.

1180   https://doi.org/10.1021/acs.jafc.1c00643

1181   Thompson-Witrick, K. A., Rouseff, R. L., Cadawallader, K. R., Duncan, S. E., Eigel, W. N., Tanko, J.

1182   M., & O'Keefe, S. F. (2015). Comparison of two extraction techniques, solid-phase microextraction

1183   versus continuous liquid-liquid extraction/solvent-assisted flavor evaporation, for the analysis of

1184   flavor compounds in gueuze lambic beer. *Journal of Food Science*, *80*(3), C571–C576.

1185   https://doi.org/10.1111/1750-3841.12795

1186   Tian, J., Yu, J., Chen, X., & Zhang, W. (2009). Determination and quantitative analysis of acetoin in beer

1187   with headspace sampling-gas chromatography. *Food Chemistry*, *112*(4), 1079–1083.

1188   https://doi.org/10.1016/j.foodchem.2008.06.044

1189   Tofalo, R., Chaves-López, C., Di Fabio, F., Schirone, M., Felis, G. E., Torriani, S., Paparella, A., &

1190   Suzzi, G. (2009). Molecular identification and osmotolerant profile of wine yeasts that ferment a

1191   high sugar grape must. *International Journal of Food Microbiology*, *130*(3), 179–187.

1192   https://doi.org/10.1016/J.IJFOODMICRO.2009.01.024

1193   Trujillo-Rodríguez, M. J., Rocío-Bautista, P., Pino, V., & Afonso, A. M. (2013). Ionic liquids in

1194   dispersive liquid-liquid microextraction. *TrAC - Trends in Analytical Chemistry*, *51*, 87–106.

1195   https://doi.org/10.1016/j.trac.2013.06.008

1196   V. Soares Maciel, E., de Toffoli, A. L., & Lanças, F. M. (2018). Recent trends in sorption-based sample

1197   preparation and liquid chromatography techniques for food analysis. *Electrophoresis*, *39*(13),

1198   1582–1596. https://doi.org/10.1002/elps.201800009

1199   Valcarcel, M. (1980). Principles of Analytical Chemistry. In *Analytical Chemistry* (Vol. 52, Issue 12).

1200   https://doi.org/10.1021/ac50062a780

1201   Van Opstaele, F., De Causmaecker, B., Aerts, G., & De Cooman, L. (2012). Characterization of novel

1202   varietal floral hop aromas by headspace solid phase microextraction and gas chromatography-mass

1203   spectrometry/olfactometry. *Journal of Agricultural and Food Chemistry*, *60*(50), 12270–12281.

1204   https://doi.org/10.1021/jf304421d

1205   Van Opstaele, F., Goiris, K., De Rouck, G., Aerts, G., & De Cooman, L. (2012). Production of novel

1206   varietal hop aromas by supercritical fluid extraction of hop pellets - Part 2: Preparation of single

1207   variety floral, citrus, and spicy hop oil essences by density programmed supercritical fluid

1208   extraction. *Journal of Supercritical Fluids*, *71*, 147–161.

1209   https://doi.org/10.1016/j.supflu.2012.06.004

1210   Vanderhaegen, B., Neven, H., Verachtert, H., & Derdelinckx, G. (2006). The chemistry of beer aging - A

1211   critical review. *Food Chemistry*, *95*(3), 357–381. https://doi.org/10.1016/j.foodchem.2005.01.006

1212   Vazquez-Roig, P., & Picó, Y. (2015). Pressurized liquid extraction of organic contaminants in

1213   environmental and food samples. *TrAC - Trends in Analytical Chemistry*, *71*, 55–64.

1214   https://doi.org/10.1016/j.trac.2015.04.014

1215   Viñas, P., Campillo, N., López-García, I., & Hernández-Córdoba, M. (2014). Dispersive liquid-liquid

1216   microextraction in food analysis. A critical review Microextraction Techniques. *Analytical and*

1217   *Bioanalytical Chemistry*, *406*(8), 2067–2099. https://doi.org/10.1007/s00216-013-7344-9

1218   Wiśniewska, P., Śliwińska, M., Dymerski, T., Wardencki, W., & Namieśnik, J. (2015). Application of

1219   Gas Chromatography to Analysis of Spirit-Based Alcoholic Beverages. *Critical Reviews in*

1220   *Analytical Chemistry*, *45*(3), 201–225. https://doi.org/10.1080/10408347.2014.904732

1221   Yang, Y., Jin, G. J., Wang, X. J., Kong, C. L., Liu, J. Bin, & Tao, Y. S. (2019). Chemical profiles and

1222   aroma contribution of terpene compounds in Meili (Vitis vinifera L.) grape and wine. *Food*

1223   *Chemistry*, *284*(October 2018), 155–161. https://doi.org/10.1016/j.foodchem.2019.01.106

1224   Zhang, P., Carlin, S., Lotti, C., Mattivi, F., & Vrhovsek, U. (2020). On sample preparation methods for

1225   fermented beverage VOCs profiling by GCxGC-TOFMS. *Metabolomics*, *16*(10), 1–10.

1226   https://doi.org/10.1007/s11306-020-01718-7

1227   Zhao, F., Meng, Y., & Anderson, J. L. (2008). Polymeric ionic liquids as selective coatings for the

1228   extraction of esters using solid-phase microextraction. *Journal of Chromatography A*, *1208*(1–2),

1229   1–9. https://doi.org/10.1016/j.chroma.2008.08.071

1230   Zhao, Y. P., Zheng, X. P., Song, P., Sun, Z. L., Tian, T. T., & Science, L. (n.d.). *Characterization of*

1231   *Volatiles in the Six Most Well-Known Distilled Spirits*.

1232   Zhou, Z., Ni, W., Ji, Z., Liu, S., Han, X., Li, X., & Mao, J. (2020). Development of a Rapid Method for

1233   Determination of Main Higher Alcohols in Fermented Alcoholic Beverages Based on Dispersive

1234   Liquid-Liquid Microextraction and Gas Chromatography-Mass Spectrometry. *Food Analytical*

1235   *Methods*, *13*(3), 591–600. https://doi.org/10.1007/s12161-019-01668-4