beverages

Review

Advances in Extraction Techniques for Beer Flavor Compounds

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Abstract: Owing to the unique chemical properties exhibited by beer flavor compounds, different extraction methods have been utilized to extract these compounds from the sample matrix. Carbonyl compounds, which significantly contribute to flavor instability in beer, pose challenges in detection due to their low concentrations and reactivity. Consequently, the analysis of beer flavor compounds has focused on improving sensitivity and specificity through techniques that minimize sample preparation requirements and reduce interactions between factors involved in the analysis. Notably, extraction techniques such as headspace solid-phase microextraction (HS-SPME), stir bar sorptive extraction (SBSE), and gas diffusion microextraction (GDME) have been successfully applied to the analysis of carbonyl compounds in alcoholic beverages, including beer. Derivatization agents like 2,4-dinitrophenylhydrazine (DNPH) and O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) enhance the volatility and stability of analytes, facilitating their separation and detection in gas chromatography and high-performance liquid chromatography. Chromatographic separation methods, particularly gas chromatography and liquid chromatography, are extensively employed to identify and quantify aroma/flavor compounds in various foodstuffs, including beer. This review provides a comprehensive overview of extraction techniques and chromatographic methods used in the analysis of beer compounds.

Keywords: beer flavor; instability; off-flavors; extraction; detection; carbonyls

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1. Introduction

Sample preparation is a crucial step in the analytical process, accounting for a significant portion of the overall effort. Its main objectives are to eliminate sample interference, concentrate target analytes, and potentially convert analytes into a more detectable form through derivatization [1–3]. Various methods are employed for sample processing, such as homogenization, filtration, centrifugation, distillation, extraction, fractionation, and concentration. Traditional solvent-based techniques like liquid–liquid extraction have been commonly used but are being replaced by alternative methods such as solid-phase extraction [4]. The emergence of non-traditional extraction techniques offers advantages such as reduced sample volume, preparation time, and solvent usage, and the possibility of solventless approaches [5,6].

Due to the distinct chemical properties, such as volatility, polarity, and thermolability, exhibited by the compounds present in beer, various extraction methods have been employed to extract them from the sample matrix [7]. Table 1 presents a compilation of several extraction techniques that have been utilized for the analysis of flavor compounds in beer.

Table 1. Analytical techniques employed for the extraction of volatile compounds from beer.

Extraction Technique	Compounds	Bibliographic References
Liquid–liquid extraction (LLE)	Aldehydes; alcohols; ketones	[8–10]
Liquid–liquid extraction (LLE)	Aldehydes	[10]
Solvent drop microextraction (SDME)	Alcohols	[11,12]
Steam distillation	Aldehydes	[13–15]
Solvent-assisted flavor evaporation (SAFE)	Aldehydes	[8,16]
Headspace solid-phase microextraction (HS-SPME)	Aldehydes; volatile fraction; carbonyl compounds	[9,17–19]
Headspace solid-phase microextraction (HS-SPME)	Volatile compounds	[20,21]
Solid-phase microextraction (SPME, on fiber derivatization with PFBHA)	Aldehydes; ketones; esters; ethers	[7,8,18,22–28]
Stir bar sorptive extraction (SBSE, with derivatization with PFBHA)	Aldehydes;	[29,30]
Solid-phase extraction (SPE)	Ketones; amines	[31–33]
Solid-phase extraction (SPE)	Aldehydes; amines	[33–36]
Derivatization with PFBHA	Carbonyl compounds	[37,38]

Carbonyl compounds are the primary contributors to flavor instability in beer. Therefore, it is crucial to investigate the impact of these compounds on both the organoleptic characteristics and sensory changes of beer during aging. However, detecting these compounds is challenging due to their extremely low concentrations and high reactivity, attributed to the polar carbonyl group [18]. Carbonyls are often volatile and can be sensitive to heat; therefore, maintaining a lower temperature during extraction is crucial to prevent the loss or alteration of these compounds. High temperatures can lead to the thermal degradation or alteration of sensitive compounds. In the case of carbonyls, heat can cause them to degrade or react with other compounds, forming artifacts that were not present in the original sample, and leading to inaccurate results. Therefore, it is crucial to use methods that preserve the integrity of these volatile and sensitive compounds to achieve accurate and reliable results.

With this in mind, the analysis of beer flavor compounds has continuously been optimized to achieve improved sensitivity and specificity. The development of new techniques has focused on several aspects, including (1) minimizing sample preparation requirements, (2) encompassing a broad range of compounds within the same chemical group, and (3) reducing interactions between various factors involved in the technique [39]. Over the past decade, different extraction techniques such as headspace solid-phase microextraction (HS-SPME), stir bar sorptive extraction (SBSE), and gas diffusion microextraction (GDME) have been successfully applied to the analysis of carbonyl compounds in alcoholic beverages, including beer.

In addition, derivatization techniques have been utilized in conjunction with various extraction methods to enhance the volatility of semi-volatile compounds and improve the stability of several analytes. The derivatization reaction is particularly important in both gas chromatography (GC) and liquid chromatography (LC) because it enhances the detectability and improves the separation efficiency of analytes, making it easier to identify and quantify compounds with low concentrations or those with limited volatility or UV absorbance [40]. The most commonly used derivatizing agents for beer analysis are 2,4-dinitrophenylhydrazine (DNPH) and O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA). DNPH-derivatized compounds exhibit higher absorption coefficients and improved hydrophobic retention, enabling their easier separation by high-performance liquid chromatography (HPLC) and detection through ultraviolet (UV) spectroscopy [41] or voltammetry [42]. Furthermore, 4-hydrazinobenzoic acid (HBA) has been applied in the analysis of various carbonyl compounds in alcoholic beverages, including beer, followed by HPLC-UV analysis [43,44]. PFBHA is commonly employed as a derivatizing agent in gas chromatography analysis [17,22].

Following the extraction procedure, chromatographic separation methods undoubtedly serve as the most frequently employed analytical techniques to identify and quantify aroma/flavor compounds in various foodstuffs, including beer. Table 2 shows several applications of chromatographic techniques for the analysis of beer compounds.

Table 2. Extraction and separation techniques used to analyze flavor compounds in beer.

Extraction Technique	Separation Technique	Compounds	Bibliographic References
HS-SPME	GC-FID	Flavor compounds (aldehydes, ketones, alcohols, esters)	[45,46]
HS-SPME SBSE LLME SPE	GC-MS GC-O	Flavor compounds (aldehydes, ketones, alcohols, esters)	[22,39,47–64]
HS-SPME	GC-O	Flavor compounds (esters, hop aroma compounds)	[54,65,66]
SPE	LC-MS	Hop acids, aflatoxins, amines, oligosaccharides, semi-volatile compounds	[39,67,68]
GDME (with derivatization)	HPLC-UV	Aldehydes, amines	[43,44,69]
SPE	HPLC-MS	Maillard reaction products, polyphenols	[70,71]

Gas chromatography (GC) is widely used in food analysis, specifically for assessing the composition of food, including flavor and aroma compounds. It offers advantages such as high resolution, repeatable retention times, and accurate quantification based on peak area measurements [47]. Gas chromatography–flame ionization detection (GC-FID) and gas chromatography–mass spectrometry (GC-MS) are commonly employed for measuring volatile compounds in beer. Gas chromatography with olfactory detection (GC-O) is used to determine volatile compounds in beer, particularly esters, by involving the sensory evaluation of the eluate to identify active odor compounds [54,72,73]. Liquid chromatography (LC) is extensively used to analyze semi-volatile compounds in beer. High-performance liquid chromatography (HPLC) with ultraviolet/visible (UV/VIS) detection is commonly used for individual phenolic acid, polyphenol, and antioxidant compound determination [74]. HPLC-UV has been employed for carbonyl compound analysis with derivatization and extraction. LC combined with mass chromatography (MS) allows qualitative and quantitative analysis, particularly for compounds with lower volatility or that are difficult to convert from the condensed phase to the gas phase [75].

This review provides an overview of various methodologies for the extraction of volatile compounds coupled with detection techniques for the analysis of flavoring compounds in beer. Due to the distinct characteristics of extraction techniques, they are categorized as follows: (1) liquid-phase extraction, (2) solid-phase extraction, and (3) membrane-assisted extraction. Each category is discussed separately to highlight their unique features and applications.

2. Liquid-Phase Extraction Techniques

2.1. Liquid–Liquid Extraction (LLE)

Liquid–liquid extraction, along with Soxhlet extraction, is recognized as a classical sample preparation technique. It is widely employed as one of the most prevalent sample pre-treatments to enhance selectivity by isolating the analyte from the matrix or to improve sensitivity by concentrating the analyte from a large sample volume. The separation is based on the partition equilibrium of a species between the organic and aqueous phases, represented by the partition coefficient (k_i) [76,77]. Liquid–liquid extraction (LLE) has been extensively employed in sample preparation for the analysis of wine and beer aromas. For instance, Soares da Costa et al. [10] utilized LLE in combination with GC-MS analysis to monitor the levels of methional and phenylacetaldehyde, compounds associated with the aged aromas of lager-type beers. Additionally, they established a correlation between the quantities of these chemical substances and their sensory impact in beer, using GC-O. While liquid extraction is a traditional sample preparation technique, it is not without drawbacks. Several limitations may arise during its application, including incomplete phase separation, emulsion formation when working with aqueous samples, low recovery levels, and the requirement of significant amounts of organic solvents [4,78]. These challenges have prompted the development of alternative liquid-phase extraction techniques, as discussed below.

2.2. Liquid-Phase Microextraction (LPME)

Miniaturized versions of liquid–liquid extraction, such as liquid-phase microextraction (LPME), offer a solution to some of the challenges associated with conventional LLE, particularly solvent consumption. LPME represents a solvent-minimized approach to sample pre-treatment, where only a few microliters of solvent are needed to concentrate analytes from the samples. The primary objectives of implementing LPME are to minimize the use of organic solvents and enhance sensitivity [79]. In this technique, extraction typically takes place in a small volume of organic solvent (referred to as the acceptor phase) from an aqueous sample containing analytes (known as the donor phase). LPME can be carried out using different approaches, with the most straightforward one being single-drop microextraction (SDME). Other approaches include the use of hollow fibers (HF), membrane bags, or flat-sheet membrane modules [80], as depicted in Figure 1.

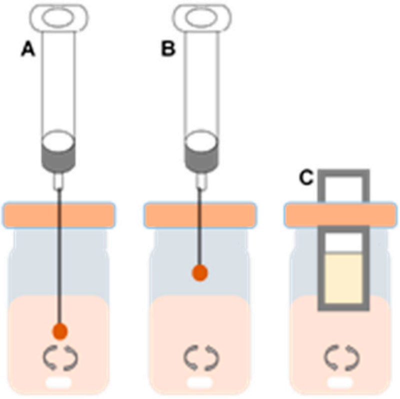

Figure 1. Scheme of (**A**) DI-SDME, (**B**) HS-SDME, and (**C**) HF-SPME.

LPME in the single-drop extraction mode does not necessitate specialized instrumentation. Most SDME approaches are manually performed, similar to conventional LLE methods, but they employ smaller amounts of extractor solvent. This technique revolves around a suspended drop of extractor solvent (1–10 μL) in the tip of a microsyringe. In practice, two primary approaches are employed for SDME: direct immersion (DI-SDME) or headspace (HS-SDME) (Figure 1) [81]. In DI-SDME, a drop of organic solvent is suspended directly from the tip of a microsyringe needle immersed in the aqueous sample. On the other hand, in HS-SDME, a microdrop of an appropriate solvent is positioned in the headspace of the sample solution [82]. SDME has primarily been used for GC analysis, as it allows for the use of the same syringe for both extraction and injection in the analytical chromatographic system [11]. One of the main drawbacks of SDME is the instability of the droplet, which can result in difficulties with extraction repeatability. Additionally, the selection of solvents is limited, and the volatility of the solvent is crucial. Solvents that are excessively volatile may not be suitable, while solvents with excessively high boiling points limit the applicability range [4]. To address the fragility of the organic solvent droplet used in SDME, the use of a hollow fiber (HF) has been employed to stabilize the extracting phase. The organic solvent is immobilized within the pores of the HF's wall, creating a supported liquid membrane. HF-LPME finds its primary application in the fields of bioanalysis and environmental analysis, with only a few applications observed in the realm of food analysis, primarily focused on contaminant and pesticide analysis [83].

In the context of beer analysis, LPME has been utilized by Fernandez et al. to determine aliphatic amines [84]. Tankeviciute and colleagues employed HS-SDME followed by GC analysis to detect various alcohols, such as propan-1-ol, among others, in beer [11]. Xiao et al., (2006) applied both DI-SDME and HS-SDME techniques to analyze sulfur compounds in beer, observing lower detection limits compared to headspace solid-phase microextraction (HS-SPME) [85]. Bolaños and coworkers applied HF-LPME for the determination of several pesticides, including those present in beer, followed by UHPLC-MS/MS analysis [86].

3. Solid-Phase Extraction Techniques

3.1. Solid-Phase Extraction (SPE)

Solid-phase extraction (SPE) is a widely used sample preparation technique that offers advantages over traditional methods. It is based on the principle of liquid–solid partitioning, where a solid sorbent material in disposable cartridges is used for extraction [87]. The sorbent, commonly silica, allows for surface modification, providing flexibility for using polar and nonpolar stationary phases and ensuring compatibility with various ligands [88]. The SPE procedure involves conditioning the sorbent, retaining analytes through specific interactions, washing to remove unwanted compounds, and eluting the target analytes for subsequent analysis. These steps ensure selective extraction and efficient sample cleanup, making SPE a valuable technique in analytical chemistry [89].

A visual representation of the complete SPE process, including these steps, can be found in Figure 2.

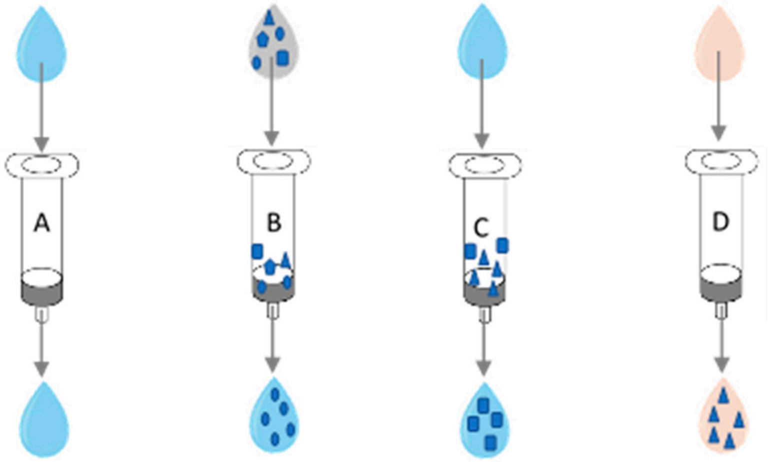

Figure 2. SPE operation steps: (**A**) washing/conditioning; (**B**) loading; (**C**) washing; and (**D**) elution.

SPE was developed as an alternative to LLE, offering several advantages over the traditional method. These include (1) higher recovery levels, (2) reduced analysis time by streamlining the procedure, (3) easy automation, (4) compatibility with chromatographic analysis, and (5) decreased organic solvent usage [78].

SPE is not only valuable for isolation and quantification purposes, but it also enables concentration of analytes for trace analysis, as they are eluted from the column in a small volume of solvent. Furthermore, SPE serves as an effective tool for sample cleanup to remove interfering compounds [90]. For instance, Santos et al. applied SPE to extract

E-2-nonenal from beer samples, achieving high recovery rates [36]. Similarly, Guido et al. utilized SPE to simultaneously extract *E*-2-nonenal and *β*-damascenone from beer, obtaining significant recovery factors [15]. SPE has also been employed for the extraction of carbonyl compounds in beer. Rodrigues et al. used SPE coupled with GC-MS analysis to investigate the variation in volatile compounds during beer deterioration, observing an increase in compounds such as furfural and 5-hydroxymethylfurfural (5-HMF) with beer deterioration [61]. Li et al. employed a novel solid-phase extraction column (polar-enhanced polymer, PEP-SPE) combined with HPLC-UV analysis to quantify furfural in beers. The PEP-SPE column demonstrated higher selectivity for furfural compared to a common C18-SPE column. They detected furfural levels ranging from 10 to 32 μg/L in beers, with an increase observed in artificially aged beers [35]. Additionally, Pejin et al. successfully used SPE extraction coupled with GC-MS detection to simultaneously extract diacetyl and 2,3-pentanedione from numerous beer samples [63].

3.2. Solid-Phase Microextraction (SPME)

In recent years, the focus of analytical chemists has shifted towards preparation techniques that minimize the use of organic solvents. Among these techniques, solid-phase microextraction (SPME) has emerged as a promising solventless approach [91]. SPME is a variation of solid-phase extraction (SPE) that addresses two significant drawbacks of traditional SPE methods: (1) lengthy extraction times and (2) the requirement for organic solvents [92].

SPME involves two key processes: partitioning of analytes between a coated fiber and the sample until equilibrium is reached, and desorption of the concentrated analytes into an analytical instrument [45,59,93,94]. During the first step, the coated fiber is exposed to the sample, allowing the target analytes to be extracted from the sample matrix and retained in the coating. In the second step, the fiber is transferred to an instrument for desorption, followed by separation and quantification [93]. By visually representing the SPME extraction device and the adsorption (A) and desorption (B) processes, the schematic diagram in Figure 3 provides a clear overview of the fundamental steps involved in SPME and aids in understanding the extraction mechanism.

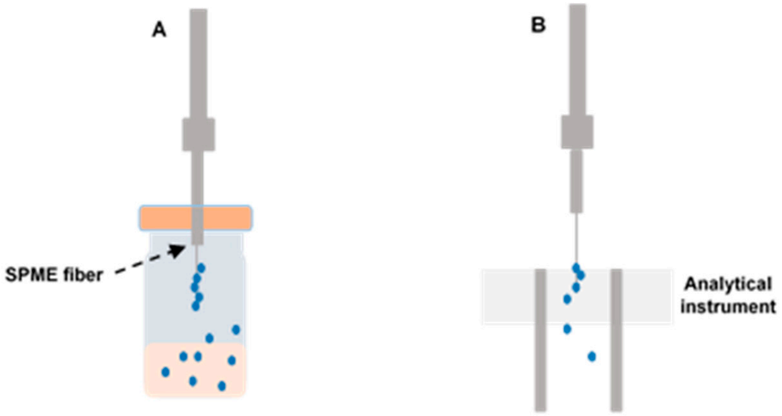

Figure 3. Schematic diagram depicting the SPME extraction device, illustrating the essential components and the sequential steps of adsorption (**A**) and desorption (**B**) processes.

SPME offers three distinct modes of microextraction to the stationary phase, depending on the positioning of the fiber relative to the sample: (1) direct extraction—immersion (DI), (2) headspace extraction (HS), and (3) extraction with a membrane process. In the DI mode, the coated fiber is immersed in the liquid sample matrix with agitation to enhance the extraction process. The HS mode, on the other hand, involves placing the fiber in a non-contact position with the sample, allowing SPME to be used with any matrix, be it liquid or solid. This mode leverages the volatility of analytes, enabling their release from the matrix. In the third mode, a selective membrane separates the fiber from the sample, allowing the analytes to pass through while blocking interferences.

The selection of the appropriate fiber coating is crucial, as it determines the affinity for the analyte based on the principle of "like dissolves like". A range of fiber coatings are available on the market, catering to different analyte types, particularly for applications in food sample analysis (refer to Table 3) [91,95,96]. The specific fiber used can vary depending on the specific compounds of interest in a given study, but divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fibers are commonly used for analyzing beer flavor compounds, as they exhibit a broad polarity range that allows them to adsorb a wide range of flavor compounds, making them quite versatile for beer analysis.

Table 3. Applications of SPME fiber for volatile determination in alcoholic beverages.

Fiber Type	Food Samples	Analyte(s)	Bibliographic Reference
PDMS	Beer	Non-polar flavor compounds; carbonyls; furan derivatives	[97,98]
	Wine	Volatile compounds; terpenes; aldehydes	[99–102]
PDMS-DVB	Beer	Aldehydes; ketones; esters; alcohols; carboxylic acids; hydrocarbons; E-2-nonenal	[7,9,17,103–107]
CAR-PDMS	Beer	Esters; alcohols; aldehydes; ketones; fatty acids; ethers; hydrocarbons; sulfur compounds; aromatic compounds; alicyclic compound; heterocyclic compounds E-2-nonenal	[9,108–110]
	Wine	Heterocyclic compounds	[111]
DVB-CAR-PDMS	Beer	Aldehydes; ketones; alcohols; esters; terpenes; carboxylic acids; volatile compounds fingerprint	[45,56,64,112–115]
	Wine	Sulfur compounds; volatile compounds	[116,117]
PA	Beer	Alcohols and esters	[118]
	Wine	Aroma volatiles	[119]

Solid-phase microextraction (SPME) is a sample preparation technique with several advantages. It is a solventless method that eliminates the use of toxic organic solvents. SPME allows for the quantification of numerous volatile compounds with low detection limits and achieves excellent linearity, extraction, and concentration of analytes in a single step. It requires minimal sample preparation and significantly reduces preparation time, making it cost-effective compared to other techniques [120,121]. SPME's high sensitivity enables the use of smaller sample volumes, protecting the separation column from excessive water or solvent exposure [122]. This makes SPME a versatile technique applicable to various sample types (liquid, gas, and solid) with complex matrices, allowing for the determination of analytes at trace and ultra-trace levels [92]. However, SPME has limitations, including a limited recommended operating temperature range, potential instability in inorganic solvents, and the possibility of fiber breakage [81].

To address the challenges of analyzing polar organic compounds using SPME, derivatization approaches have been employed [123]. Three derivatization methodologies can be implemented: (1) direct derivatization in the sample matrix, (2) derivatization in the SPME fiber coating, and (3) derivatization in the GC injector port [94]. In the first approach, the derivatizing agent is added to the sample vial, where the derivatives are formed and subsequently extracted for introduction into the analytical system [124]. For derivatization in the fiber coating, the fiber is impregnated with a derivatization agent and then exposed to the sample. The derivatization reaction takes place concurrently with the analyte extraction [125].

In beer analysis, due to the presence of lower quantities of non-volatile compounds, the extraction of volatile compounds from the headspace (HS) is advantageous [66,126]. The most commonly used extraction technique for beer analysis is HS-SPME, with or without derivatization, with PFBHA being the most frequently employed derivatizing agent. The oximes formed between carbonyl compounds and PFBHA exhibit relatively specific mass spectra and high sensitivity in different systems [7]. Horák et al. compared different extraction methods, including SPME, SPE, and stir bar sorptive extraction (SBSE), and found that SPME was the most advantageous technique due to its simplicity of use and low cost [60].

HS-SPME extraction coupled with GC analysis is commonly used for the analysis of volatile aroma compounds in beer, including free fatty acids, alcohols, acetates, and off-flavors such as diacetyl, pentanedione, acetoin, and acetaldehyde [39]. Campillo et al. employed HS-SPME to determine volatile sulfur compounds in beer, utilizing GC coupled with an atomic emission detector for subsequent measurements [109]. Charry-Parra et al. optimized HS-SPME coupled with GC-MS-FID to investigate volatile compound groups in beer, such as higher alcohols, esters, and aldehydes, some present at trace levels [59]. Jiao et al. utilized HS-SPME-GC-FID for beer volatile compound analysis and obtained chromatographic fingerprints of flavor in various beer samples, enabling classification by type, taste, and brewing origin [127]. Moreira et al. developed an HS-SPME methodology combined with GC-IT/MS detection to quantify a wide range of carbonyl compounds in beer, using PFBHA as a derivatizing agent. The method achieved very low detection (0.003 to 0.510 $\mu g \cdot L^{-1}$) and quantification (0.010 to 1.55 $\mu g \cdot L^{-1}$) limits, facilitating the identification of the main carbonyl compounds present at low concentrations in beer [7]. HS-SPME has also been employed for the extraction of beer flavor compounds, followed by analysis using GC-O. The combination of HS-SPME with GC-O/MS enables the comprehensive and accurate detection of trace compounds in beer. This approach allows the identification of low-threshold esters and improves the detection ability, with GC-O/MS providing information on aroma characteristics and olfactometry aiding in the detection of low-content esters that contribute to flavor [54]. Murakami et al. applied HS-SPME extraction followed by GC-O analysis to identify hop and aged aromas in beer [66]. Xu et al. investigated the flavor contribution of esters in lager beers using HS-SPME extraction and GC-O/MS analysis. The HS-SPME extraction enabled the identification of trace compounds, while GC-O/MS facilitated the detection and olfactory identification of numerous esters, including those with low-threshold values that significantly contribute to beer aroma and flavor [54]. The chemical and sensory characteristics of beer samples subjected to various storage conditions were evaluated by extracting volatile compounds using HS-SPME, while sensory analysis was performed by a sensory panel making use of the GC-O/TOF-MS combined techniques [64].

3.3. Stir Bar Sorptive Extraction (SBSE)

Stir bar sorptive extraction (SBSE), developed in 1999 by Sandra and colleagues at the Research Institute of Chromatography (RIC), is based on similar principles to SPME. However, instead of a polymer-coated fiber, stir bars are coated with polydimethylsiloxane (PDMS), a nonpolar polymeric phase that facilitates hydrophobic interactions with target molecules [92]. While polydimethylsiloxane (PDMS) is commonly used as a coating in SBSE, other coatings such as polyethylene glycol or polyacrylate can also be used, depending on the specific requirements of the analysis [128]. The use of PDMS coating in SBSE offers several advantages, including predictable enrichment, the absence of displacement effects, inertness, and rapid thermal desorption at mild temperatures [129]. The aroma recovery of beer flavors by pervaporation through commercial PDMS membranes has been tested in order to allow their recovery in nonalcoholic beers [130]. Similar to SPME, SBSE involves two main steps: extraction and desorption. The extraction process can occur in two modes: immersion or headspace (Figure 4).

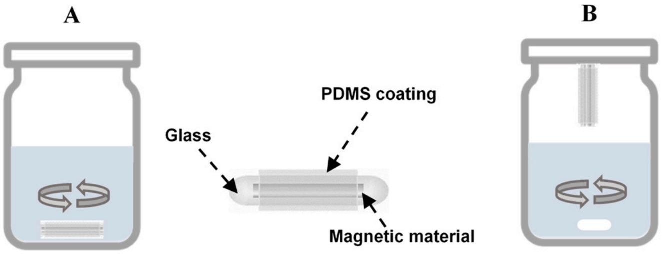

Figure 4. (**A**) Schematic representation of the apparatus illustrating the SBSE process through immersion. (**B**) Schematic representation of the apparatus illustrating the SBSE process through headspace.

In the immersion mode, the SBSE device is immersed in the aqueous sample and, under controlled physical and chemical conditions with stirring, the stir bar adsorbs the target organic compounds to be extracted [131,132]. Bicchi et al. expanded this technique to analyze samples in the vapor phase, known as headspace sorptive extraction (HSSE) [133]. In the headspace mode, similar to SPME, the coated stir bar is suspended in the headspace vial, allowing the polymer to come into contact with the vapor phase of a solid or liquid sample matrix [132]. An HSSE–GC–MS method was developed to identify 37 volatile compounds in various beer types (ale, lager, stout, and wheat). This optimized method was compared to a validated SBSE method, yielding similar concentration values for most compounds [134].

Following extraction, the stir bar is removed and subjected to thermal desorption or liquid retroextraction. Thermal desorption (TD) is performed at temperatures between 150 and 300 °C, typically taking 15 min, and is followed by gas chromatography (GC) to recover the accumulated analytes from the stir bar. This desorption procedure is typically carried out using a thermal desorption unit (TDU) connected to the GC system [135]. Liquid retroextraction (LRE) can be an alternative to TD. In LRE, the stir bar is placed in a small vial and desorption is performed using non-polar solvents (e.g., hexane) for GC analysis, or polar solvents (e.g., methanol, acetonitrile) for liquid chromatography (LC) analysis [129]. Benanou et al. demonstrated that loaded stir bars can be stored at 4 °C for up to 1 week without significant solute loss. Similarly to SPME, SBSE bars can be reused after thermal conditioning or solvent treatment [136].

SBSE has addressed certain limitations observed in SPME, as demonstrated by various researchers. With its pre-concentration capability, broad application range, and simplicity, SBSE is emerging as one of the most extensively investigated sample extraction techniques for organic compound analysis [131]. In a study comparing HS-SPME and SBSE, Castro and Ross found that SBSE exhibited higher recovery rates, indicating its effectiveness [106]. SBSE has been successfully employed for the extraction of various compounds in beer, as documented in Table 4. Although SBSE offers several advantages, it is important to acknowledge its limitations, which include (1) a restricted range of analyte polarities due to the available stationary phases, (2) susceptibility to strong matrix effects, and (3) the requirement for precise control of extraction conditions [92]. A recent study aiming to observe the impact of using different sample preparation techniques (dynamic headspace (DHS), vortex-assisted liquid–liquid microextraction (VALLME), multiple stir bar sorptive extraction (mSBSE), solid-phase extraction (SPE), and solid phase micro-extraction (SPME)) to figure out the most suitable sample preparation protocol for profiling the volatile organic compounds from fermented beverages showed that best coverage can be reached by using SPME together with SPE for beer, and VALLME for wine and cider [137]. A solvent-assisted stir bar sorptive extraction (SA-SBSE) was developed by using swollen PDMS for the enhanced recovery of polar solutes in aqueous samples. The performance of the SA-SBSE method using dichloromethane, diisopropyl ether, and cyclohexane was illustrated with analyses of aroma compounds in beer [138].

Table 4. Several applications of SBSE for beer analysis.

SBSE Extraction	
Analyte	**Bibliographic References**
Carbonyl compounds	[30,106,139]
Beer flavors	[140,141]
Esters	[106,139,142]
Aroma compounds	[143–147]
Off-flavors in aged beers	[148]
Terpenoids	[149]
Hop-derived bitter acids	[150,151]
Free fatty acids	[152]

4. Membrane-Assisted Extraction Techniques

In recent decades, membrane-assisted extraction techniques have emerged as alternatives to liquid–liquid extraction (LLE) or solid-phase extraction (SPE) methods due to their simplicity, selectivity, and reduced reliance on organic solvents. A variety of membrane-assisted techniques have been reported in the literature, but they all share a common principle. A membrane acts as a barrier between the sample solution (donor solution) and the acceptor solution. During the extraction process, analytes migrate across the membrane from the donor solution to the acceptor solution, establishing an equilibrium under the given conditions [153].

Membrane extractions can be categorized based on specific parameters, such as membrane porosity (porous or non-porous membrane) and number of extraction phases (one-, two-, or three-phase membrane techniques). Porous membrane techniques involve filtration and dialysis in various formats, while non-porous membrane techniques employ either a polymeric material or a liquid membrane to separate the donor and acceptor solutions. In most non-porous membrane extraction systems, the membrane forms a distinct phase between the donor and acceptor phases, resulting in a three-phase system [153]. Table 5 provides an overview of several membrane extraction techniques.

Table 5. Overview of different membrane extraction techniques.

	Three-Phase Membrane Extraction					**Two-Phase Membrane Extraction**		**One-Phase Membrane Extraction**
	SLME *	**PME ***	**MESI ***	**MIMS ***	**GD ***	**MMLLE ***	**MASE ***	**Dialysis**
Donor	Aqueous	Aqueous/ Organic	Aqueous/ Organic/ Gaseous	Aqueous/ Gaseous	Aqueous	Aqueous	Aqueous	Aqueous
Membrane	Organic, liquid	Polymer	Polymer	Non-porous/ Porous	Pores	Solvent	Pores	
Acceptor	Aqueous	Aqueous/ Organic	Gas/Sorbent	Vacuum of MS spectrometer	Aqueous	Solvent	Aqueous/ Organic	Aqueous

* SLME—supported liquid membrane extraction; PME—polymeric membrane extraction; MESI—membrane extraction with sorbent interface; MIMS—membrane inlet mass spectrometry GD—gas diffusion; MMLLE—microporous membrane liquid–liquid extraction; MASE—membrane-assisted solvent extraction.

Supported liquid membrane extraction (SLME) is a three-phase extraction method that involves the transfer of analytes from an aqueous sample to another aqueous phase. This transfer occurs through the use of an organic liquid, which is positioned between the two aqueous phases. This process is chemically similar to the extraction and back-extraction techniques utilized in classical liquid–liquid extraction (LLE) [154]. SLME has found applications in food analysis, particularly in the successful extraction and quantification of nicotine in snuff, vanillin in various food samples such as chocolate, and caffeine in coffee and tea [155]. In polymeric membrane extraction (PME), a solid membrane, rather than a porous one, is employed to partition the donor and acceptor solutions. Silicone rubber is a commonly used material due to its hydrophobic nature, which results in high permeability for small hydrophobic molecules. The selectivity of PME is based on the variation in solubility and diffusion rates of different analytes within the polymer [156]. For optimal compatibility with gas chromatography, the most suitable approach involves employing a gaseous acceptor phase, which can be achieved through the membrane extraction with a sorbent interface (MESI) technique. This versatile method is applicable to both gaseous and aqueous samples. The MESI setup includes a membrane module equipped with a silicone rubber hollow fiber, acting as an extractor for analytes from the surrounding liquid or gaseous samples. Within the fiber, a gas flows and carries the analyte molecules from the membrane into a cooled sorbent trap, where they are subsequently captured [155]. The gas diffusion (GD) process relies on the mass transfer of volatile compounds from a donor solution, passing through a gas-permeable membrane, and finally reaching an acceptor solution. The two liquid phases are physically separated by a microporous hydrophobic membrane, which is impermeable to solvents but allows gas to pass through, preventing direct contact between the two liquids. The mass transfer occurs in three steps: (1) analytes are transferred from the donor solution to the vicinity of the membrane; (2) the species, in their gaseous form, diffuse through the membrane; and (3) the analytes are collected in either a liquid or gaseous acceptor phase [157]. Alternative methods for the determination of total SO_2 in beer, based on gas diffusion, have been applied. Bendtsen and Jorgensen applied flow injection analysis (FIA), using gas diffusion through a PTFE membrane, for the determination of total and free sulfite in beer [158]. Additionally, Firnandes and co-workers applied flow injection spectrophotometry using gas diffusion for the determination of total sulfur dioxide in beer [159]. Both authors found that the FIA system, coupled with gas diffusion, required no sample preparation, provided accurate and precise results with higher sampling rates, and reduced the consumption of p-rosaniline by ten-fold, when compared to the standard p-rosaniline method [158,159]. Membrane inlet mass spectrometry (MIMS) utilizes a membrane as the sole interface between a liquid or gaseous sample at atmospheric pressure and the vacuum environment of a mass spectrometer. This membrane, whether porous or non-porous, forms a secure seal between the two sides, allowing for accurate analysis. [29]. This technique was employed for the analysis of bitterness compounds and aliphatic amines in beer [160].

Microporous membrane liquid–liquid extraction (MMLLE) is a variation of membrane extraction that utilizes a microporous membrane to separate an aqueous phase and an organic phase. The microporous membrane allows for the diffusion of analytes through its pores, facilitating contact between the two phases [154]. In membrane-assisted solvent extraction (MASE), a hydrophobic or hydrophilic membrane is used to create a barrier between an aqueous solution and another liquid phase, enabling selective extraction near the membrane surface. This technique offers efficient extraction and separation capabilities. Dialysis, on the other hand, is a one-phase membrane extraction method where solutes migrate across a porous membrane from an aqueous donor solution to an aqueous receiving solution based on a concentration gradient. This process takes advantage of differences in solute diffusion rates, primarily influenced by molecular size [155] Dialysis is particularly effective for separating large molecules, such as proteins, from smaller ones, as their diffusion characteristics vary. This provides a means to efficiently remove large molecules from the sample [156]. Both MMLLE and dialysis are membrane-based extraction techniques that offer unique advantages for selective extraction and separation in analytical applications.

Gas Diffusion Microextraction (GDME)

Gas diffusion microextraction (GDME) is a hybrid technique that combines gas diffusion (GD) with microextraction. Microextraction involves the use of an extracting phase with a significantly smaller volume compared to the sample volume [161]. The concept of GDME was introduced in 2010 by Pacheco et al. as a method for the analysis of volatile and semi-volatile compounds [162]. The GDME device comprises a compact PTFE module with perforations, housing two distinct components with a membrane inserted in between.

The extraction procedure of GDME is based on the mass transfer of analytes from the sample (donor phase) through a gas-permeable membrane. GDME often involves a derivatization reaction, which enhances the applicability, recovery, and selectivity of the technique [69]. Initially, GDME was tested for the determination of vicinal diketones (VDKs) in beer using HPLC-UV, with diacetyl and 2,3-pentanedione derivatized simultaneously with o-phenylenediamine (OPDA) during the extraction process. The standard procedure involved partially immersing the GDME module, with the membrane, into a thermostated cell containing the sample, with or without agitation. The derivatizing agent (acceptor solution) was placed inside the module (typically 0.5 mL), and the extraction commenced. After a specific duration, the acceptor solution was collected for instrumental analysis [162].

Over time, modifications have been made to this procedure depending on the sample matrix being analyzed. In the modified approach, the GDME module is attached to the cap of a glass flask, which is introduced into the headspace of the flask containing the sample, with or without agitation. The glass flask is placed in a water thermal bath, and analyte diffusion occurs in the headspace through the gas layer separating the sample and the acceptor solution [163]. Figure 5 provides a schematic representation of both the immersed and headspace extractions in GDME.

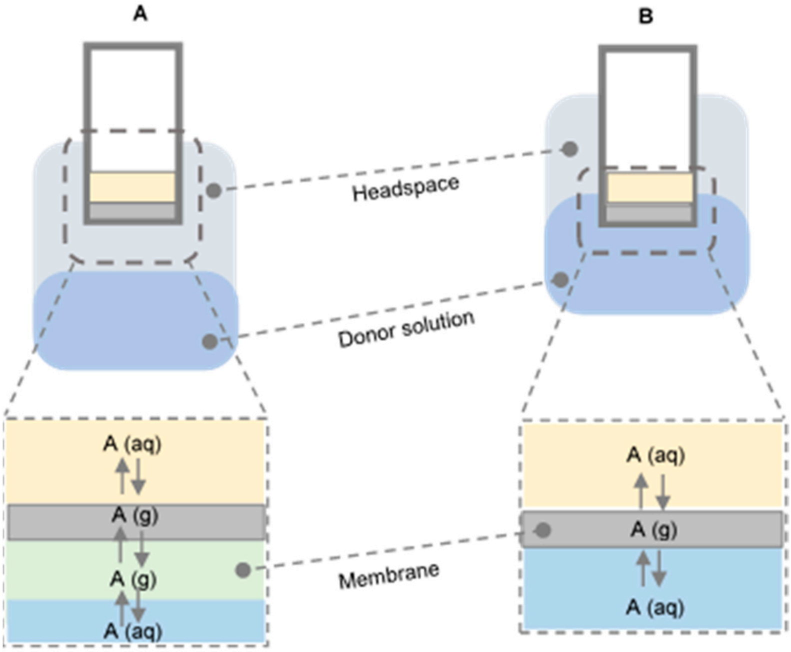

Figure 5. Illustration of the gas diffusion microextraction system in two configurations: (**A**) headspace and (**B**) immersed system.

In the immersed extraction mode, the transport of analytes from the donor solution to the acceptor solution occurs in three steps: (1) analytes pass from the donor solution to a gaseous phase within the membrane pores, (2) analytes diffuse through the membrane, and (3) analytes pass from the gaseous phase to the acceptor solution. In the headspace extraction mode, an additional step is involved, where the analytes first move to the headspace before undergoing diffusion through the membrane.

GDME has been successfully employed for the analysis of carbonyl compounds in various sample matrices, including alcoholic beverages such as wine [164,165], liquors, cachaça [43], and beer [43,44,69,162]. For instance, Gonçalves et al. utilized GDME in the chromatographic analysis of aldehydes in beer. Aldehydes, including acetaldehyde, furfural, and methylpropanal, were simultaneously extracted and derivatized with DNPH, and their identification was performed using HPLC [69]. Additionally, a GDME method incorporating simultaneous derivatization with HBA, followed by HPLC-DAD analysis, was established and validated for quantifying beer-staling aldehydes. Subsequently, this procedure was utilized to assess the effects of natural and forced aging on the concentrations of Strecker aldehydes, furfural, and acetaldehyde in beer [44].

In summary, GDME offers several advantages for the extraction of volatile and semi-volatile compounds. It is a versatile and straightforward technique with short extraction times [162], which can be applied to a wide range of analytes and sample matrices, and the extraction parameters can be tailored to suit specific matrix analysis. Furthermore, as the extracted material is in liquid form, GDME is compatible with most separation and detection analytical instruments.

5. Conclusions

This review highlights the significance of sample preparation in the analysis of flavor compounds in beer, aiming to eliminate interference, concentrate target analytes, and enhance detectability. Traditional solvent-based techniques like liquid–liquid extraction are being replaced by alternative methods such as solid-phase extraction (SPE) due to advantages like reduced sample volume, preparation time, and solvent usage. Various extraction techniques, including headspace solid-phase microextraction (HS-SPME), stir bar sorptive extraction (SBSE), and gas diffusion microextraction (GDME), have been successfully applied to the analysis of carbonyl compounds in beer. Derivatization techniques, employing agents like DNPH and PFBHA, enhance the volatility and stability of analytes, enabling easier separation and detection. Chromatographic techniques, particularly gas chromatography (GC) and liquid chromatography (LC), are widely used for aroma/flavor component analysis in beer, offering high resolution, accurate quantification, and the ability to measure volatile and semi-volatile compounds. This review provides an overview of extraction methodologies categorized as liquid-phase extraction, solid-phase extraction, and membrane-assisted extraction, discussing their unique features and applications in beer analysis.

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