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Review

Phthalates: The Main Issue in Quality Control in the Beverage Industry

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Abstract: Phthalate esters (PAEs) are a group of chemicals used to improve the flexibility and durability of plastics. The chemical properties and the resistance to high temperatures promote their degradation and release into the environment. Food and beverages can be contaminated by PAEs through the migration from packaging material because they are not covalently bound to plastic and also via different kinds of environmental sources or during processing. For instance, alcoholic drinks in plastic containers are a particular risk, since the ethanol contained provides a good solubility for PAEs. According to its role as an endocrine disruptor compound and its adverse effects on the liver, kidney, and reproductive and respiratory systems, the International Agency on Research Cancer (IARC) classified di-(2-ethylhexyl) phthalate (DEHP) as a possible human carcinogen. For this reason, to control human exposure to PAEs, many countries prohibited their use in food as non-food substances. For example, in Europe, the Commission Regulation (EU) 2018/2005 restricts the use of DEHP, dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), and diisobutyl phthalate (DiBP) to a concentration equal to or below 0.1 by weight in plasticizers in articles used by consumers or in indoor areas. There are reports from the US Food and Drug Administration (FDA) that some beverages (and food as well), particularly fruit juices, contain high levels of phthalates. In some cases, the deliberate adulteration of soft drinks with phthalate esters has been reported. This paper would like to show the difficulties of performing PAE analysis in beverage matrices, in particular alcoholic beverages, as well as the main solutions provided for quality control in the industrial branches.

Keywords: phthalates; alcoholic beverage; non-alcoholic beverage; release; human hazards; analytical methods

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1. Introduction

Recently, plastic pollution has become one of the major threats to biodiversity, humans, and the environment. The increase in plastic production it is estimated to double by 2050 and triple by 2060, achieving 155–265 Mt/y by 2060 [1–3]. Data suggested by the European Chemical Agency (ECHA) have suggested that there are approximately 418 additives which are used from European industries to improve polymer plastic properties. PAEs are a class of synthetic chemicals used as plasticizers during plastic manufacturing, particularly for polyvinyl chloride (PVC), the most popular plastic after polyethylene [4,5]. PAEs, in addition to PVC materials, allow the polymers to slide against each other, improving their flexibility, durability, and stability [6]. Chemically, PAEs are dialkyl, alkyl, or aryl esters of 1,2-benzenedicarboxylic acid synthetized from the esterification of phthalic anhydride and specific alcohols (Figure 1) [7]. Their structure consists of a planar aromatic benzene ring

attached to two carboxyl group at the R and R′ positions (Figure 2) [8]. They are colorless, odorless liquids with low water solubility, high oil solubility, and low volatility [9]. The melting and boiling points range from −70 to 5.5 °C and from 230 to 486 °C, respectively. Water solubility, as well as the pressure vapor, shows a decreasing trend as the alkyl chain length or molar volume increases [10].

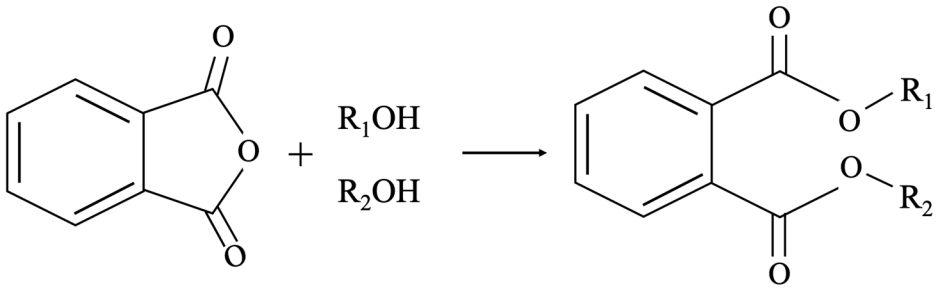

Figure 1. Esterification reaction of PAE synthesis.

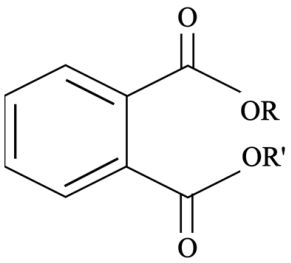

Figure 2. General structure of PAEs.

Owing to their physicochemical properties, PAEs have been used in a large volume of industrial applications since 1920. Low molecular weight (LMW) PAEs (1,2, or carbon in alkyl chains), i.e., dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DnBP), and di-isobutyl phthalate (DiBP), are mainly used in non-PVC products such as personal care products (PCPs), paint coatings, adhesives, and synthetic fragrances, while high molecular weight (HMW) PAEs (more than four carbons), such as DEHP, di-*iso*-nonyl phthalate (DiNP), and di-*n*-octylo-phthalate (DnOP), are mainly used in PVC products, e.g., PVC flooring, medical supplies, textiles, food packaging, and building materials [11–13]. PAEs are ubiquitous contaminants able to persist in different environmental media (e.g., soil, water, sediment, air) for a long time. They are quickly released through evaporation, leaching, and abrasion [14]. The use of plastic mulching films, pesticides, and fertilizers, as well as the presence of industrial discharge and sewage, can arise from PAE contamination in agricultural areas [15]. However, since they are not covalently linked but only bound to plastic polymers by hydrogen bonds or van der Waals forces, they may migrate from food packaging materials, mainly in oil or fat-containing food [16]. Food is a major route of PAEs, contributing about 67% of human exposure. The ingestion of contaminated food and beverages, as well as the inhalation of dust and dermal contact, promotes PAE migration within the human body [17,18]. In addition, the use of medical devices, such as infusion, transfusion, dialysis systems, or feeding tubes can be a considerable source of PAE exposure among patients in hospital settings [19]. For example, a study conducted on human exposure to PAEs during the COVID-19 emergency have suggested the presence of DEHP, DIBP, and BBP in facemasks at median concentration of 486, 397, and 92 ng g^{-1}, respectively [20]. However, PAEs are also applied as excipients and enteric coatings on drugs to control the oral administration and release of drugs into gastrointestinal tract. Guidelines published by the European Medicines Agency (EMA) and the U.S.-FDA have set limits for DEP and DBP exposure to 4.0 and 0.01 mg kg^{-1} day^{-1} and a less restrictive limit for DBP to 0.1 mg kg^{-1} day^{-1} [21,22]. A matter of high concern of PAEs is the exposure of them to infants and toddlers who can ingest these chemicals through toys, dust, and soil through

frequent hand-to-mouth transfer and saliva [23,24]. Concerning this, Directive 2009/48/EC set the maximum limit concentration of 0.1% (*w*/*w*) for DiNP, DEHP, and DBP in toys or childcare article because their harmful effects on the human reproductive system [25]. Moreover, pregnant women's exposure to PAEs and their subsequent permeation through the placental barrier can be deleterious for fetuses, inducing adverse outcomes, such as preterm birth, fetal sex hormone disruption, fetal anogenital distance abnormalities, and neonatal disease [26,27]. PAEs are recognized as "endocrine-disrupting chemicals" (EDCs) because their interaction with steroid hormone receptors. Epidemiological studies show the association between DEHP and DBP with adverse male reproductive outcomes (e.g., testicular cancer, cryptorchidism, hypospadias incidences, low sperm quality), the impairing of DEHP and mono-(2-ethyl-hexyl) (MEHP) on the folliculogenesis, maturation of oocytes and embryo development, and cardiometabolic diseases (e.g., obesity, impaired glucose tolerance, type 2 diabetes, T2D, and cardiovascular disease, CVD). Furthermore, children's exposure to low doses of EDCs may cause harmful effect on the brain, affecting the quality of life, the ability to learn, memory, and neurobehavioral development [28]. On the basis of these observation, the European Food Safety Authority (EFSA) used the reduction in fetal testosterone to group some phthalates (i.e., DEHP, DBP and BBP), considering DEHP as the index compound for relative potency factors, and to set a group tolerable daily intake (TDI) of 50 μg kg^{-1} bw^{-1}, which was based on a no-observed-adverse-effect level (NOAEL) of 4.8 mg kg^{-1} bw^{-1} day^{-1} for anti-androgenic effects in a multigenerational reproductive study in male rats [29–33]. DEHP is the most commonly applied plasticizer in the manufacture of plastic products, especially PVC, and also in the production of lubricants, glues, paints, inks, pharmaceutics, cosmetics, perfumes, and pesticides. Because of its teratogenic, reproductive, and toxic effects, DEHP is classified in the Group 2B carcinogen "Possibly Carcinogenic to humans" by the IARC [34,35]. Also, the Environmental Quality Standards Directive of the Eu Water Directive regulated the use of DEHP, decreasing its market share in Europe from 42% in 1999 to 10% in 2014 [36]. Six PAE congeners, including DEHP, DnBP, DEP, DMP, BBP, and DnOP, are listed as priority hazardous pollutants by the United States Environmental Protection Agency (USEPA), the European Union (EU), and China [37]. Moreover, the Commission Regulation (EU) 2018/2005, amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and the council concerning the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH), sets the concentration of DEHP, DBP, BBP, and DiBP equal to or below 0.1 by weight of the plasticized material [38]. Actually, numerous alternative plasticizers are used or are in development. For example, 1,2-cyclohexanedicarboxylic acid diisononyl ester (DiNCH) and bis-2-ethylhexyl terephthalate (DEHT) are the two primary PAE replacements. Subsequently, trimellitates, citrates, and adipates, including tris-2-ethylhexyl trimellitate (TOTM), tributyl-O-acetyl citrate (ATBC), diisobutyl adipate (DIBA), acetyl tributyl citrate (ATNC), di-(2-ethylhexyl) adipate (DEHA), and di-(2-ethylhexyl) sebacate (DEHS), are used as PAE substitutes in a wide variety of applications (electronic, apparels, and building materials). Meanwhile, di (2-ethylhexyl) tetrahydrophthalate (DEHTH), di (2-ethylhexyl) cyclohexane-1,4-dicarboxylate (1,4-DEHCH), and di(2-ethylhexyl) cyclohexane-1,2-dicarboxylate (1,2-DEHCH) are the new generation of PAE alternatives used in food contact materials and children's toys [39,40]. The present paper would like to show the analytical challenges of PAE analysis in beverage matrices, particularly alcoholic beverages, because of the ethanol activity on PAE adsorption. Several extraction and chromatographic methods are revised to provide promising solutions for quality control in the agri-food industries.

2. Analytical Procedures

The analysis of PAEs is highly difficult due their throughout and ubiquitous presence. Their adsorption in several complex matrices represents a challenge for their determination at low-level traces. In the following sections, the authors focuse their attention on the main extraction and chromatographic techniques for PAE detection in alcoholic and no-alcoholic beverages. For example, solid-phase extraction (SPE) and liquid–liquid extraction (LLE)

are the dominant techniques used for sample pretreatments, followed by qualitative and quantitative PAE assessments through gas chromatography (GC) or liquid chromatography analysis (LC) methods. Moreover, PAE contamination within the laboratories and accessories before implementing the analysis approaches are discussed to increase the attention on this problem during the analysis and to avoid false outcomes and inconveniences.

2.1. Analytical Issue

The ubiquitous presence of phthalates in the laboratory environment poses an analytical challenge known as the "phthalate blank problem" which is difficult to control [41]. Laboratory materials such as pipette tips, plastic containers, solvents, sorbents, analytical instrument, gloves, and plastic tubing contain PAEs. Moreover, they are also spread out in the air and dust, contaminating all surfaces, glassware, reagents, laboratory equipment, and skin. The blank problem represents a big issue because of the increase in the cross-contamination of PAEs in all stages of the analytical process (Figure 3). The occurrence of some discussed PAEs such as DEHP and DBP and the aseptic environment are still lacking, leading to their difficult determination at low-level contents and causing false positives or the overestimation of results. Therefore, to avoid contamination during the whole analysis, a series of strategies and precautions are necessary to be adopted by the analyst. It is preferable that the analysis of PAEs is carried out in a different area of the laboratory equipped with an air filter. Plastic materials can be replaced with glass, Teflon, PTFE, aluminum, or stainless steel. Several clean procedures are necessary to be applied: (i) glass materials should be washed with solvents with oxidizing agents or organic solvents such as cyclohexane, n-hexane, isooctane, methanol, or 2,2,4-trimethylpentane and heated to 400 °C for several hours; (ii) glass materials that cannot be cleaned by heating should be washed with pure solvents taken from containers to which aluminum oxide has been added; and (iii) the material of the analysis (e.g., sample vials) should be stored in desiccators containing aluminum oxide and/or covered with aluminum foil or stored also in glass or polytetrafluoroethylene (PTFE) containers to prevent PAE adsorption from the air. In addition, the use of PAE-free gloves and pipette tips and avoiding the use of PAE personal care products by laboratory staff are recommended. Before starting the analytical procedure, it is necessary to check PAE contamination in the inlets and caps of vials in the detection equipment and to track all possible contamination routes performing analytical blanks for each stage of the analytical procedure simultaneously, with the set of samples preferably analyzed in triplicate. To ensure aseptic conditions and to minimize the error of quantification during the procedure, the blank should be free from the target analyte. Therefore, if a high contamination level is estimated, it is necessary to raise the number of procedural blanks [41–43]. Finally, the standard addition method is another measure required for the PAEs' quantification to standardize the analysis, reducing the matrix-effect artefacts. This calibration method is time-consuming due to the need to construct a calibration graph for each sample. However, the addition of internal standards is also proposed as an alternative option to correct the potential loss of the target analytes, the variation in the injected volume, the detector response, and matrix effects. Therefore, it is necessary to find a similar compound to the analyte detected because the source of variation should affect both the analyte and internal standard in the same way and should be not present in the matrix. For this purpose, to improve the accuracy and the precision of the analysis, isotopically labeled standards are used because of their similar physical and chemical properties to their unlabeled analogues [43].

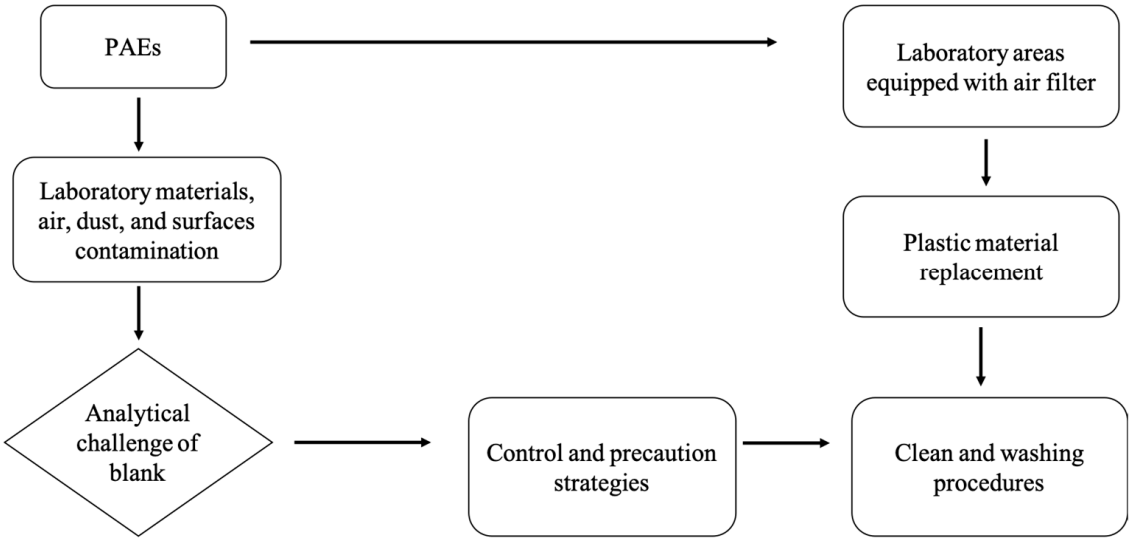

Figure 3. Analytical challenges of PAE analysis.

2.2. Analytical Procedures for the Extraction and Detection of PAEs

The identification of PAEs is still considered an analytical challenge because of their low-level traces in complex matrices. For this reason, the selection of a green and efficient sample preparation or pretreatment to avoid possible artefacts during the analysis is needed. Several pretreatment techniques followed by chromatographic analysis have been developed to extract PAEs from different samples: LLE, SPE, solid-phase microextraction (SPME), and liquid-phase microextraction (LPME). Traditional LLE methods are used because of their simplicity, cost-effectiveness, and feasibility in different fields (environment, food, and biological analysis). They consist in the process of transferring a dissolved substance from one liquid phase to another (immiscible or partially miscible) liquid phase in contact with it. However, there are a lot of drawbacks such as the long time of the analysis, large amounts of organic solvents, and analyte loss, which have promoted the use of more efficient extraction approaches [41]. SPE provides better selectivity and higher recovery, using a volume of solvent less than LLE. The selective retention of the analyte on a specific adsorbent makes it useful for the preconcentration and clean-up of samples before the analysis. However, its versatility could be compromising for the selectivity because different analytes may be simultaneously extracted by the same sorbents. The use of a stationary phase coated on a support for the SPME allows the combination of all steps of sample preparation in one step with fast extraction times, minimal solvent usage, and better sensitivity and selectivity for the analytes investigated. However, this approach requires a high cost of analysis and could be sensitive to the presence of interference in the sample matrix, which could affect the precision and accuracy of the results. The LPME techniques are a miniaturized form of LLE in which the extracting organic phase is limited to a few microliters for the extraction of the analytes. It is based on the use of low volumes of immiscible solvents which act as an acceptor phase for the extraction of compounds from the aqueous phase (donor phase). This technique includes three extraction techniques that were later developed, i.e., single-drop microextraction (SDME), hollow-fiber LPME (HF-LPME), and dispersive liquid–liquid microextraction (DLLME) [41]. SDME is a rapid and cost-effective sample preparation technique which involves the use of a single drop of extraction solvent to extract the analytes from the matrix. HF-LPME is carried out using a hydrophobic porous hollow fiber that consists of a liquid membrane, and the acceptor phase is introduced into the fiber. It allows one to reach high extraction efficiencies though the detection and quantification of a wide class of analytes at low levels. In addition, it requires a small sample volume, making it a cost-effective and eco-friendly technique. In the DLLME approach, the extracted solution is added to the dispersant solvent, which rapidly infuses into the aqueous phase, resulting in a cloudy solution with an increased surface

of contact between the sample and extractant, followed by centrifugation to obtain the analyte. However, there are different forms of DLLME like ultrasound-assisted dispersive liquid–liquid extraction (UA-DLLME), ultrasound–vortex-assisted dispersive liquid–liquid microextraction (USVA-DLLME), and magnetic stirring-assisted dispersive liquid–liquid microextraction (MSA-DLLME), which differ according to the media and which promote mechanical stirring for the extraction of the analyte by the extracting solvent [8].

Moreover, the selection of a suitable instrumental technique based on the physicochemical characteristics of the target analytes and their sensitivity levels is needed for their accurate identification and quantification.

Several studies have reported the assessment of PAEs in beverages and food using GC and LC as the mainly chromatographic methods [44–47]. These analytical methods are used for the detection and the quantification of trace amounts of different analytes, showing high precision, reproducibility, and versatility. However, taking into the account their disadvantages related to the blank values, sensitivity, specificity, and expansive cost of instrumentation, a combination of detection systems based on magnetic material, noble metal nanoparticles, and aptamers have been successfully applied for the determination of PAEs [48]. For example, immunoassay techniques such as the enzyme-linked immunosorbent assay (ELISA) and fluorescent polarization immunoassay (FPIA) have been applied for the detection of BBP, DiBP, and DEHP in food and environmental samples [49–52]. In addition, molecular imprinting technology based on the use of amphiphilic magnetic adsorbents (e.g., Fe_3O_4-GPS-A, Fe_3O_4@MIPs@Ag, and Fe_3O_4@NIPs@Ag) have been investigated for the determination of DBP, DOP, and DMP in environmental samples [53,54]. All these strategies apparently represent an advantage over conventional analytical methods because of their rapid separation, purification, accuracy, selectivity, low cost, simplicity, and high performance of analysis [55,56]. Nonetheless, they also show some difficulties due to the reproducibility, universality, and stability of the sensor.

3. Beverages

PAEs are not chemically bonded to plastic polymers. During the manufacturing or storage phases, they can easily migrate and contaminate food and beverages in contact. For this reason, the international safety authorities have set the maximum permissible concentrations for DBP (0.3 mg kg^{-1}), BBP (30.0 mg kg^{-1}), DEHP (1.5 mg kg^{-1}), and DiNP (9.0 mg kg^{-1}), considering a conventional daily consumption of 1 kg by a person of 60 kg bodyweight (kg-bw) and food packaging container of 6 dm^2 surface area releasing PAEs [57].

The presence of PAEs in food is widely investigated. However, the number of studies focused on the determination of PAEs in alcoholic beverages is still limited. A search on the Scopus database yielded only 64 documents published between 1978 and 2024, using the keywords “phthalates” and “alcoholic beverages” (Figure 4). The interest in PAE identification in alcoholic matrices is due to the potential risk of contamination during fermentation processes. The cultivation of grapes and other fruit is the first point of PAE contamination. The next point can be derived from the use of plastic material (packaging, pumps, and tubing), additives, and technological co-adjuvants during the fermentation, maturation, and bottling processes [58,59]. However, the relative molecular mass of the polymer, the thickness and amount of the plasticizer, the duration of plasticization and stabilization of the plastic material used for the fermentation tank, the type and composition of beverages, the total contact time and temperature combined with the lipophilic properties of PAEs, and the high ethanol content of beverages can accelerate their release during processing, transport, and storage [60,61].

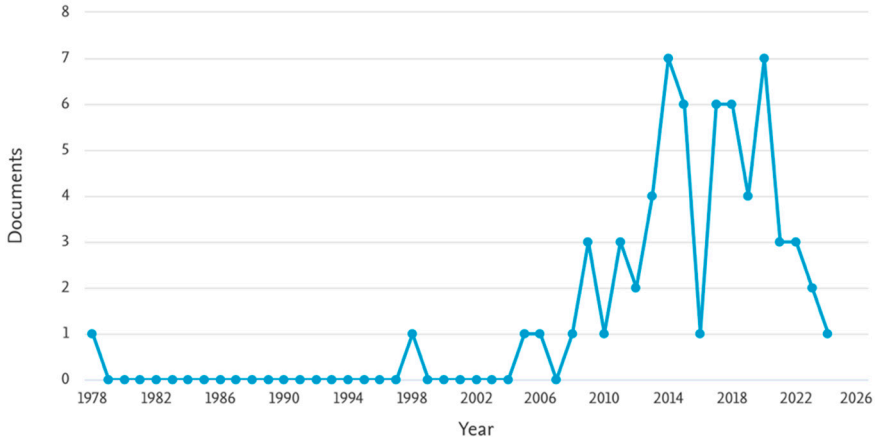

Figure 4. Studies on PAEs in alcoholic beverages available on the Scopus database in the temporal range 1978–2024.

3.1. Alcoholic Beverages

Alcoholic beverages are hedonic goods that have been consumed for a long time in societies for social, cultural, and behavioral purposes and also for the important role in diets by providing polyphenols and bioactive peptides [62].

The term alcoholic beverage refers to drinks containing ethyl alcohol or ethanol, produced by the fermentation of grains, fruits, and other starches [63]. Ethanol is the key component of alcoholic beverages which has effects on flavor perception. According to the alcohol content, alcoholic beverages may be differentiated into four categories: wines, beer, distilled beverages, and ciders and other unspecified fermented beverages (Table 1) [63,64].

Table 1. Class of alcoholic beverages based on typical ethanol concentration [63].

Beverage	Alcohol Concentration Range (% ABV)
Beer	5–12
Cider	1.2–8.5
Wine	8–14
Distilled beverages (whiskey, rum, tequila)	20–95

3.1.1. Wine

Wine is a beverage produced through the alcoholic fermentation of grapes. The alcohol content does not exceed 20% by volume [65]. During the winemaking process, wine could be significantly affected by PAE migration from plastic material generally used in the wine industry. Moreover, their high affinity with alcoholic solutions can increase their level of contamination as well [66]. DEHP, DBP, and BBP are common PAEs found in wine and in other food products. The Commission Regulation (EU) No 10/2011 of 14 January 2011 set the specific migration limit (SML) for DBP, DEHP, and BBP in wine at 0.3, 1.5, and 30 mg L^{-1}, respectively [66,67]. Several authors have studied the impact of PAEs in wine, developing a combination of extraction and detection methods for their identification and quantification at low concentrations (Table 2). Del Carlo et al. (2008) reported the determination of six PAEs in red and white wine samples using SPE on a C18 column coupled with gas chromatography–mass spectrometry (GC-MS) analysis [58]. The statistical evaluation of the total and single PAE concentration showed the detection frequencies of DBP and BBP (88% and 55%, respectively) in commercial wine probably added with adjuvants. On the other hand, no DBP and BBP have been detected in samples produced in stainless steel tanks, with no use of process adjuvants. A protocol based on USVA-DLLME for the determination of PAEs was proposed by Cinelli et al. (2013) and Montevecchi et al. (2017) [6,68]. The analysis by GC-MS showed a significant concentration of DBP in all wine samples analyzed (range: 33.3–312.4 pg μL^{-1}) [6], and the influence

of chemical nature on the behaviors of individual PAEs during the distillation process of wine showing amounts up to 0.62 ± 0.05 and 0.47 ± 0.04 mg for DBP and DEHP carried over and partially into the distillate, with DiNP accumulation only in the stillage (19.8 ± 1.7) [69]. A simple, low-cost, environmentally benign, and less time-consuming method based on ionic liquid dispersive liquid–liquid microextraction coupled with high-performance liquid chromatography (IL-DLLME-HPLC) was applied by Fan et al. (2014) for samples containing a high alcohol percentage (wine and white spirits). They studied the effect of the alcohol content on the performance of the proposed DLLME using a series of simulated samples. To achieve good extraction efficiency, an amount of ethanol content in the range of 16–23% was suggested for red wine, obtaining extraction recoveries (ERs%) for DiBP, DBP, BBP, and DEHP in the range of 99.1 ± 2.1 to 106.1 ± 5.5 [61]. A headspace solid-phase microextraction gas chromatography–mass spectrometry (HS–SPME–GC–MS) method validated by Carillo et al. (2007) [69] was applied by Perestrelo et al. (2020) for determining PAEs in wine [70]. According to Russo et al. (2012), the analytical method performance was affected by the increase in ethanol content [71]. It was observed that better limits of detection (LODs) and limits of quantification (LOQs) were achieved for 12% (*v*/*v*) ethanol in the range from 0.03 μg L^{-1} (DBP) to 0.07 μg L^{-1} (BBP) and from 0.09 μg L^{-1} (DBP) to 0.24 μg L^{-1} (BBP), whereas the LODs and LOQs values for 18% ethanol ranged from 0.04 μg L^{-1} (DBP) to 0.11 μg L^{-1} (2,2,4,4-tetrabromodiphenyl ether, BDE) and from 0.11 μg L^{-1} (DBP) to 0.36 μg L^{-1} (BDE), respectively. A novel procedure based on multi-walled carbon nanotubes (MWCNTs)/silica-reinforced HF-SPME coupled with GC-MS has been developed by Li et al. (2013) for a rapid analysis of PAEs in beverage (milk and juice) and alcoholic samples (wine). They optimized the parameters influencing the extraction efficiency, such as pH values (3.0), the ionic strength of the sample solution (NaCl 20% *w*/*v*), extraction time (50 min), temperature (40 °C), and desorption solvent (0.3 mL of diethyl ether) to achieve satisfactory recoveries of PAEs in all the analyzed samples [72]. Hayasaka (2014) used a HPLC system combined with a hold-back column to measure PAE concentrations in 10 selected commercial wines. This column allowed Hayasaka to retain the HPLC contaminants during HPLC column equilibrium time, avoiding their co-elution with PAEs from a wine sample and their influence on the quantification of PAEs in wine [67].

3.1.2. Spirits

Spirits are distilled alcoholic beverages containing the highest concentration of ethanol. They are produced through the distillation of raw ingredients (e.g., fruits, grains, or vegetables) followed by alcohol concentration by fractional distillation and maturation in charred barrels [65,73]. All these steps, as well as the high ethanol content, may increase the affinity for PAEs, introducing them into the beverages. Tequila is the main alcoholic beverage produced in Mexico from the distillation and fermentation of sugar from Agave tequilana Weber var. azul. Balderas-Hernández et al. (2020) monitored the PAEs' content in white, aged, extra-aged, and ultra-aged tequila by GC-MS analysis, determining their contamination level up to relating it to the age of maturation and to the year of tequila production. All PAEs detected did not exceed the admitted maximum limit for alcoholic beverages except for DBP (0.01–2.20 mg kg^{-1}) and DEHP (0.03–4.64 mg kg^{-1}), which exceeded the permissible limit of 0.3 mg kg^{-1} and 1.5 mg kg^{-1}, respectively, only in tequila produce in the year 2014 or before [57]. The USVA-DLLME approach for PAE identification was applied on a historical series of brandies by Montevecchi et al. (2017) [74]. According to Balderas-Hernández et al. (2020) [57], they detected a decreased level of DBP (from 0.27 mg kg^{-1} to 0.05 mg kg^{-1}) and DEHP (from 0.55 mg kg^{-1} to 0.30 mg kg^{-1}) in young brandy, confirming the effect of PAE concentration that occurs during the ageing process. Diamantidou et al. (2019) successfully developed a rapid, simple, and sensitive ultra-high-performance liquid chromatography–tandem mass spectrometry method (UHPLC-MS/MS) for direct PAE detection in Greek grape marc spirits. In this way, they directly injected the sample, by-passing the pretreatment step and reducing the PAEs'

contamination in laboratory materials. BBP (1.37–1526 μg L^{-1}), DBP (3.16–135.8 μg L^{-1}), and DEHP (6.92–113,220 μg L^{-1}) were the main analytes found, with DEHP levels above the legislative concentration (1.5 mg kg^{-1} food stimulant) limits in three of the samples [60]. The distribution and behavior of PAEs have been studied in Baijiu, Ouzo, and Peruvian pisco, traditional distilled alcoholic beverages consumed in China, Greece, and Peru. The results showed that the degradation tendencies of DEP (75%) and DEHP (93.0%) in Baijiu samples were affected by its own chemical nature, the ∑2PAE concentrations (0.046 to 0.317 mg kg^{-1}) below the maximum permissible levels mentioned above [75]. The validated high-performance liquid chromatography (HPLC) method with a UV detector proved suitable and reliable for the detection of DEHP found in the linear range 0.3–1.5 mg L^{-1} in the Ouzo samples [76], whereas the stir bar sportive extraction coupled with thermal desorption–gas chromatography–mass spectrometry (SBSE/TD-GC-MS) proved to be suitable for routine practice, with ranges of 101.7–938.1 μg L^{-1} and 297.1–1790.3 μg L^{-1} for DBP and hexahydrophthalate (BEHP) detected in most of the pisco samples [59]. Jurica et al. (2016) quantified seven PAEs from the five stages of plum spirit production, reporting concentrations of DBP (0.822 μg L^{-1}), BBP (0.122 μg L^{-1}), and DEHP (1.638 μg L^{-1}) higher than the limits established by the international regulation. This condition was due to the more acidic nature of the distillate which increased the PAEs' migration from the plastic and rubber equipment into the spirit samples [77]. Also, Wang et al. (2015), in the study of PAE determination in Chinese spirits, reported a significant concentration of DBP (range: 0.005–1.964 mg kg^{-1}) and DEHP (range 0.156–1.955 mg kg^{-1}), confirming the power of a high ethanol content for PAE extraction [78]. A spray-inlet microwave plasma torch–ionization tandem mass spectrometry (MPT-MS/MD) technique developed by Miao et al. (2018) proved to be highly reliable and sensitive for the online analysis of spirits and detection of nanogram levels of PAEs (range 1–100 ng g^{-1}) in low sample volumes (1 mL) within a few seconds [79]. Decanoic acid-coated Fe_3O_4 NPs were used by Wang et al. (2015) to analyze PAEs in liquor samples. This adsorbent applied to dispersive micro-solid-phase extraction (D-μ-SPE) showed excellent dispersibility in aqueous solution and PAE affinity thanks to the hydrophobic interaction with the carbon chain of decanoic acid. Among all compounds, only a DBP concentration at 29.47 ng mL^{-1} was found in the liquor samples analyzed [80]. In contrast, Wang et al. (2017) detected all 15 PAEs in liquor samples in the range from 0.0089 to 1.8190 μg mL^{-1}. This suggested that the lipophilic properties of PAEs, combined with the higher ethanol content, can accelerate migration and the accumulation in production processes [81]. While this may pose a minor risk for regulated alcohols, unregulated alcohols, especially those using DEP as a denaturing agent, could present a significant public health concern [82]. The performance of Amberlite XAD-2 resin for PAEs' determination in beverages with a wide alcohol range (10–40%) was investigated by Cinelli et al. (2014) [83]. The use of XAD-2 as a stationary phase showed excellent properties regarding the recovery of spiked PAEs both in hydroalcoholic solutions and in real samples (wine and liqueur beverages), confirming the widespread presence of DEHP in all samples analyzed (range: 6.5–22.4 pg μL^{-1}), except in red wine where no PAEs were found.

3.1.3. Beer

Beer is one of the most consumed beverages worldwide. It is produced via the alcoholic fermentation of barley or wheat with hops (or hops extract) in potable water, carried out by either brewer's yeast or a mixture of yeast and other microbes [65]. The contamination of beer by PAEs can end up from raw and plastic materials, containers, and processing equipment in contact. The study of Habshied et al. (2023) confirmed that beer in cans showed the highest maximum level of total PAEs (334.9 μg L^{-1}) compared to PET bottles (219.8 μg L^{-1}), with high concentration of DEHP (326.9 mg L^{-1}). On the other hand, a relatively high maximal value of DBP was found for PET bottle beers (17–92 μg L^{-1}), whereas low values of total PAEs were detected in glass-bottled beer (12.10 mg L^{-1}) [84]. Pereira et al. (2023) assessed the levels of phthalates and DEHA in commercial beer by means of DLLME coupled with GC-MS/MS analysis. The results suggested mainly the

presence of DEHA (205.4 μg L^{-1}), followed by DEHP, whereas DMP was not identified in any sample [85]. In agreement with Habshied et al. (2023) [84], the authors confirmed the higher presence of PAEs related to the alcohol content, higher average levels in beer packaged in aluminum cans, and human risks derived from various sources, which can lead to a cumulative effect after prolonged exposure.

3.1.4. Other Alcoholic Beverages

Finally, innovate methods based on membrane-assisted liquid–liquid microextraction (MALLE), chemometrics-assisted liquid chromatography with a simultaneous diode array and fluorescent detection (LC-DAD and LC-FLD), and the quick, easy, cheap, effective rugged, and safe (QuEChERS) method prior to GC-MS/MS were developed for the simple, fast, and low-cost analysis of PAEs in different kinds of alcoholic beverages [86–88]. The results reported that BBP was found in mostly in beer and grape juice (range: 0.14–0.19 μg L^{-1} and 1.2–1.5 μg L^{-1}), and bis(2-n-butoxyethyl) phthalate (DBEP), DnOP, and diisodecyl phthalate (DiDP) were quantified in beer samples stored in a plastic bottle (0.4, 0.9, and 1.1 μg L^{-1}, respectively), whereas DiNP was commonly found in cider samples stored in glass bottles (0.5–2.1 μg L^{-1}) [86]. Traces of DBP were also detected in brandy (65 μg L^{-1}), red wine (16–25 μg L^{-1}), sangria (30 μg L^{-1}), and beer (4.3–9 μg L^{-1}) [88]. As expected, alcoholic drinks showed higher concentrations of all analytes because of the extractive quality of ethanolic solutions which promote PAE migration [87].

Table 2. Scientific studies on PAE determination and quantification in alcoholic beverages: comparison among the main analytical parameters. N/A: not available.

Beverage	Analytes	Extraction Procedure	Analytical Technique	Recovery (%)	LOD (pg μL^{-1})	LOQ (pg μL^{-1})	Ref.
Red and white wine	DMP, DEP, DBP, BcEP, BBP, DEHP	USVA-DLLME	GC-FID	85–100.5	0.022–0.1	0.075–0.335	[6]
Tequila	DEP, DBP, BBP, DEHP, DiNP	Extraction with methanol solvent	GC-MS	N/A	4–400	13–990	[57]
Red and white wine	DMP, DEP, DEHP, iBP, DBP, BBP	SPE with C18 sorbent	GC-MS	Red wine: 33–109 White wine: 65–92	Red wine: 15–18 White wine: 18	Red wine: 24–29 White wine: 29	[58]
Peruvian pisco (distilled from fermented grape musts spirits)	DMP, DEP, BEHP, BBP, DBP, DiDP, DiBP	SBSE	TD-GC-MS	91–124.4	1.3–21	4.2–70	[59]
Greek grape marc spirits	DMP, DEP, DPP, DPhP, BBP, DBP, DEHP, DiPP, DnPP, DnOP, DiNP, DiDP	–	UHPLC-MS/MS	81.6–109.6	0.3–33.3	1–100	[60]
White spirits and red wine	DiBP, DBP, BBP, DEHP	IL-DLLME	HPLC-DAD	White spirits: 88.5–103.5 Red wine: 91.6–104.6	White: 3.1–4.2 Red: 1.5–2.2	White: 10.3–14.0 Red: 5.0–7.3	[61]
Red and white wine	DMP, DEP, DiBP, DnBP, BBP, DEHP, DOP, DiNP, DiDP	Extraction with methanol solvent	HPLC-MS/MS	60.7–121.5	White: 500–4800 Red: 600–8800	White: 1600–14,600 Red: 1700–26,600	[67]
Brandy	DBP, DEHP, DiNP	USVA-DLLME	GC-MS	78.7–100.8	3–300	11–1000	[68]
Wine, juice, and milk	DEP, DBP, DEHP	HF-SPME	GC-MS	68–115	0.006–0.3	0.02–0.1	[72]
Wine	DBP, DEHP, DiNP	USVA-DLLME	GC-MS	N/A	N/A	N/A	[74]
Baijiu (distilled alcoholic Chinese beverage)	DMP, DEP, DPrP, DiBP, DnBP, BMEP, BMPP, BEEP, DAP, DnHP, BBP, DCHP, DEHP, DnOP	QuEChERS or VSLLME methods	GC-MS	83.4–122.3	0.05–10.0	0.125–20.0	[75]
Ouzo (Greek alcoholic beverage)	DEHP	Extraction with n-hexane solvent	HPLC-UV	90–97	N/A	60	[76]
Plum spirit	DMP, DEP, DiBP, DBP, BBP, DEHP, DOP	Extraction with DCM solvent	GC-MS	92.3–98.6	1.17–4.30	3.90–14.32	[77]

Table 2. *Cont.*

Beverage	Analytes	Extraction Procedure	Analytical Technique	Recovery (%)	LOD (pg μL^{-1})	LOQ (pg μL^{-1})	Ref.
Spirits	DMP, DEP, DiBP, DBP, DMEP, BMPP, DEEP, DPP, DHXP, BBP, DBEP, BBP, DBEP, DCHP, DPhP, DEHP, DNOP, DNP	LLE	ID-GC-MS/MS	94.3–105.3	1–10	3.3–33	[78]
Alcoholic spirits	BBP, DEP, DPP, DiDP	–	MPT-MS/MS	96.7–103	10–2400	20–7900	[79]
Liquor	BBP, DBP, DCHP, DnOP	D-μ-SPE	HPLC	88.9–105.4	0.91–2.43	3.02–8.25	[80]
Liquor	DMP, DEP, DPP, BMPP, DEEP, DEHP, BBP, DBEP, DCHP, DPhP, DnOP, DiBP, DBP, DHXP, DMEP	DLLME	GC-MS	72.6–115.5	0.003–0.57	0.010–1.861	[81]
Alcoholic beverage and unrecorded alcohol	DMP, DEP, DAP, DiBP, DBP, DEHA, BBP, DEHP, DHP, DnOP, d4-DEHP	LLE	GC-MS	103.9–110.4	700	2600	[82]
Red and white wine, hydroalcoholic food beverage (grappa and vodka)	DMP, DEP, DBP, BcEP, BBP, DEHP	SPE with Amberlite XAD-2 sorbent	GC-FID	94–103	1.21–2.51	2.42–5.03	[83]
Beer	DMP, DEP, DiBP, DBP, DEHP, DnOP	QuEChERS method	GC-MS	N/A	0.30–1.41	1.01–4.69	[84]
Beer	DMP, DEP, DiBP, DBP, BBP, DEHP	DLLME	GC-MS/MS	N/A	0.3–1.5	1–5 μg L	[85]
Beer, cider, and grape juice	DPP, DMEP, DiPP, DEEP, DnPP, BBP, DBEP, DCHP, DnOP, DiNP, DiDP	QuEChERS method	GC-(QqQ)-MS/MS	75–120	N/A	0.034–1.415	[86]
Beer, wine, and distilled beverage	BPA, DEP, DBP, DEHP	SPE	LC-DAD and LC-FLD	90–100	0.04–0.38	0.12–1.10	[87]
Brandy, wine, sangria, and beer	DMP, DEP, DBP, DPP, BMEP	LLE	GC-MS	N/A	0.1–0.4	0.3–1	[88]
Light alcoholic drink (beer)	DMP, DEP, DiBP, DBP, BBP, DEHP, iBcEP	SPE	GC-IT/MS	94.6–102.1	0.2–20	0.6–4	[89]
Light alcoholic drink (beer)	DMP, DEP, DiBP, DBP, BBP, DEHP, iBcEP	SPE	GC-IT/MS	95.6–99.6	0.03–0.10	0.11–0.28	[90]

3.2. Non-Alcoholic Beverages

Non-alcoholic beverages are one of the most consumed products in a modern diet since they provide consumers with refreshment, hydration, enjoyment, and the convenience of consumption [91]. They are divided into carbonated and non-carbonated drinks. Carbonated drinks are beverages to which carbon dioxide has been added intentionally. They represent the highest portion of non-alcoholic consumed beverages including non-alcoholic liquor, sodas, cola, lemonade, tonic, and other common beverages [92]. The non-carbonated drinks include vegetable and fruit juice, prepared or embedded water-based beverages, such as coffee and tea, and dairy products [93]. The consumption of soft drinks packaged in plastic containers represents a serious concern for PAEs' migration within them. For example, it was observed that PAE migration in soft drinks is 5–40 times higher than migration in mineral water likely due to the difference in pH (soft drinks = pH < 3 and mineral water = pH < 5) [94]. The content of PAEs in soft drinks as well as the best approaches of extraction and detection methods are investigated by several authors (Table 3). Russo et al. (2014) [89,90] analyzed the PAE content in soft drinks (up to 0.5% alcohol content) and light alcoholic drinks (up to 6% alcohol content), comparing two analytical procedures developed by them. The results obtained through the SPE-GC-IT/MS method were comparable with the USVA-DLLME-GC-IT-MS method, showing a difference < 5%. DEP, DiBP, DBP, BBP, and DEHP were present in almost all the beverages (0.15–1.5 pg L^{-1} vs. 0.16–0.99 pg L^{-1}, 0.16–2.38 pg L^{-1} vs. 0.24–2.45 pg L^{-1}, 1.99–5.70 pg L^{-1} vs. 1.93–5.66 pg L^{-1}, 0.28–0.85 pg L^{-1} vs. 0.05–0.81 pg L^{-1}, and 1.18–99.9 pg L^{-1} vs. 1.23–101.5 pg L^{-1}, respectively), confirming the applicability, ac-

curacy, and efficiency of both analytical methods. Ortega-Zamora et al. (2021) applied, for the first time, the use of a natural deep eutectic solvent (NADES) consisting of L-menthol and acetic acid (1:1) for PAE extraction from soft drinks. The combination of this NADES with the dispersive liquid–liquid microextraction method based on the solidification of a floating organic drop (DLLME-SFO) allowed them to obtain an environmentally friendly methodology with an extraction efficiency comparable to the other extraction approaches. Therefore, the results of the HPLC-UV analysis showed concentrations of DBP (30.8 ± 5.8 μg L^{-1}) and DEHP (38.2 ± 10.4 μg L^{-1}) found in lime and lemon soft drinks and concentrations of DPP (49.7 ± 5.0 μg L^{-1}) found in green tea soft drinks [95]. According to Ortega-Zamora et al. (2021) [95], a vortex-assisted (VA)−DLLME protocol based on natural hydrophobic deep eutectic solvents (NaHDESs) was applied by Santana-Mayor et al. (2021) for the analysis of 14 PAEs and one adipate (DEHA) in tonic waters [96]. The results obtained by means of a ultra-performance liquid chromatography–tandem mass spectrometry system (UPLC-MS/MS) detected higher levels of DEHA (18.6 ± 2.3 μg L^{-1}) and DEHP (11.5 ± 1.3 μg L^{-1}) in the real samples, followed by DEP (0.08 ± 1.72 μg L^{-1}). Rafiei Nazari et al. (2018) studied the identification and quantification of PAE migration from plastic containers into non-alcoholic beer, observing a mean DEHP concentration between 0.6 and 2.9 μg L^{-1} [97]. These levels increased with the increasing of temperature and storage duration. The assessment of PAEs in non-alcoholic malt beverages has been also conducted by Rezaei et al. (2021) [98]. They extracted six PAEs using a magnetic adsorbent (MWCNTs-Fe_3O_4), followed by the injection of the extracted solution into a GC-MS system. The results showed the highest mean value for DEHP (5944.73 ± 2518.14 ng L^{-1}) which was lower than the EPA and WHO-EU standard levels (6000 ng L^{-1} and 8000 ng L^{-1}, respectively). The use of a magnetic particle (MP) adsorbent was previously applied by Moazzen et al. (2017) [99]. They prepared a novel multi-walled carbon nanotube modified with the catalytic nanoparticles of iron oxide and silver (MWCNTs-Fe_3O_4/Ag) by mixing the magnetic particles, using it as an SPE adsorbent. The novel magnetic solid-phase extraction technique combined with a gas chromatography/mass spectroscopy (MSPE-GC/MS) applied to the determination of PAEs from carbonated soft drinks reported the highest concentration of DEHP in four samples (6766.6, 9201, 9301.6, and 14,008 ng L^{-1}) which was higher than the standards defined by the EPA (6766.6, 9201, 9301.6, and 14,008 ng L^{-1}), but the mean values of all measured compounds were less than the standard values (6 μg L^{-1}). The QuEChERS-GC-MS/MS methodology, validated by Rodríguez-Ramos et al. (2020) for beer and cider, was also applied on grape juice, finding a concentration of BBP in the real samples of grape juice in the range of 1.2–1.5 μg L^{-1} [86]. The highest level of DBP (mean: 4.34 ng g^{-1}; median concentration: 3.59 ng g^{-1}) was found by Yang et al. (2016) in tea drink samples, followed by DEHP (mean: 3.60 ng g^{-1}; median concentration: 2.46 ng g^{-1}) [100]. The results of the estimated daily intake (EDI) by the Chinese population suggested that the concentration levels of PAEs investigated were not a risk, showing lower values than those suggested by the US EPA (20 and 100 μg kg-bw^{-1} d^{-1} for DEHP and DBP, respectively). Caldeirão et al. (2021) developed an eco-friendly DLLME-GC-MS/MS method for the extraction and quantification of six PAEs and one adipate (DEHA) from bottled herbal-based beverages [101]. The results reported the identification of PAEs in 13 out of 16 samples (81%), with levels of 36 μg L^{-1} and 63 μg L^{-1} quantified for DEP. Predominant DEHP levels were found in sport drinks (0.015–0.098 mg L^{-1}), tea (0.016–0.123 mg L^{-1}), coffee (0.028–0.159 mg L^{-1}), and fruit juices (0.022–0.126 mg L^{-1}) by GC-MS and SPE approaches validated by Wu et al. (2014) [102]. The release of PAEs from plastic bottles into the bottled beverages of fermented milk, fruit juice, and soft drinks was studied by Ahmed et al. (2017) [103]. They observed that DnOP was the major compound detected in all the tested beverages, which had the highest concentrations (0.52–0.82 μg mL^{-1}) and releasing rates (85.5–2116.7 μg $week^{-1}$), followed by DMP in juice (0.918 μg mL^{-1}), DBP in soft drink samples (0.520 μg mL^{-1}), and DEHP in fermented milk (0.437 μg mL^{-1}).

Table 3. Scientific studies on PAE determination and quantification in non-alcoholic beverages: comparison among the main analytical parameters. N/A = not available, [a] = ng kg^{-1}, [b] = ng.

Beverage	Analytes	Extraction Procedure	Analytical Technique	Recovery (%)	LOD (pg μL^{-1})	LOQ (pg μL^{-1})	Ref.
Grape juice	DPP, DiPP, DEEP, DNPP, BBP, DEHA, DBEP, DCHP, DnOP, DiNP, DiDP	QuEChERS method	GC-(QqQ)-MS/MS	75–115	NA	0.034–1.415	[86]
Soft drink (soda, cola, bitter, tonic, beer, and a whisky and cola mix)	DMP, DEP, DiBP, DBP, BBP, DEHP, iBcEP	SPE	GC-IT/MS	95.5–100.6	0.2–20	0.6–41	[89]
Soft drink (soda, cola, bitter, tonic, beer, and a whisky and cola mix)	DMP, DEP, DiBP, DBP, BcEP, BBP, DEHP	USVA-DLLME	GC-IT/MS	94.2–99.6	0.03–0.10	0.11–0.28	[90]
Soft drink (green tea, tonic, and lime and lemon drink)	DPP, BBP, DBP, DiPP, DnPP, DCHP, DEHP, DiNP, DiDP	DLLME-SFO	HPLC-UV	71–125	1.1–15.3	3.5–33.3	[95]
Tonic water	BBP, DAP, DBEP, DBP, DCHP, DEEP, DEHP, DEP, DiNP, DMEP, DMP, DnOP, DnPP, DPP, DEHA	VA-DLLME	UPLC-MS/MS	71–124	NA	0.025–1.25	[96]
Non-alcoholic beer	DEHP	SPE	GC-MS	99–100	0.1	0.3	[97]
Non-alcoholic malt beverages	DnOP, BBP, DMP, DEP, DBP, DEHP	MSPE	GC-MS	94.2–104.3	0.013–0.03	0.039–0.09	[98]
Carbonated drinks (cola, orange, and lemon)	DMP, DEP, DBP, BBP, DEHP, DnOP	MSPE	GC-MS	96.2–103.3	0.012–0.025	NA	[99]
Purified water, mineral water, soda water, carbonated drinks, functional drinks, juice drinks, and tea drinks	DMP, DEP, DBP, DOP, BBP, DEHP	LLE with dichlorometane solvent	GC-MS	91.2–102	0.25–1.0 [a]	0.80–3.3 [a]	[100]
Herbal-based soft drinks (yerba mate and black tea)	DMP, DEP, DiBP, DBP, BBP, DEHA, DEHP	DLLME	GC-MS	82–111	5.0–13	20–35	[101]
Sport drinks, tea drinks, coffees, and fruit juice	DMP, DEP, DPP, DBP, BBP, DEHP, DOP	SPE	GC-MS	84–105	3–4	10	[102]
Fermented milk, fruit juice, and soft drink	DMP, DEP, DBP, DEHP, DnOP	Extraction with acetonitrile and ethyl acetate solvents	HPLC-DAD	Fermented milk: 75.77–82.95 Fruit juice: 77.68–80.51 Soft drink: 80.09–88.70	6.5 ± 2.5 [b]	20 ± 5 [b]	[103]

4. Conclusions

The significant use of PAEs as plasticizers in packaging and food containers became a relevant issue of public health, suggesting detrimental effects after the ingestion of contaminated foods and beverages. Their ubiquitous presence in manufacturing processes, laboratory material, and equipment, requires careful monitoring through cleaning protocols to avoid contamination and to ensure quality control during the analysis. Chromatographic techniques based on GC-MS and LC-MS have been discussed to detect PAEs' levels in alcoholic beverages. Although this kind of beverage is not largely discussed in the literature, it is important to understand the role of ethanol content on the adsorption of PAEs from packaging.

Studies on PAE migration highlighted the relevant effects and extraction properties of ethanol increasing in high alcoholic beverages. Likewise, interesting levels of PAEs have been revealed in soft drinks, particularly in carbonated drinks, which are the most beverages consumed. To improve the accurate, sensitive, fast, and economic determination of these target analytes, advanced methodologies based, for example, on immunoassays, molecular imprinting technology, and sensors have been suggested.

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Abbreviations

PAEs: phthalate esters; DEHP, di-(2-ethylhexyl) phthalate; DBP, dibutyl phthalate; BBP, benzyl butyl phthalate; DiBP, diisobutyl phthalate; PVC, polyvinyl chloride; LMW, low molecular weight; DMP, dimethyl phthalate; DEP, diethyl phthalate; DnBP, di-n-butyl phthalate; DiBP, di-isobutyl phthalate; HMW, high molecular weight; DiNP, di-iso-nonyl phthalate; DnOP, di-n-octylo-phthalate; ECDs, endocrine-disrupting chemicals; MEHP, mono-(2-ethyl-hexyl); DiNCH, 1,2-cyclohexanedicarboxylic acid diisononyl ester; DEHT, bis-2-ethylhexyl terephthalate; TOTM, tris-2-ethylhexyl trimellitate; ATBC, tributyl-O-acetyl citrate; DIBA, diisobutyl adipate; ATCN, acetyl tributyl citrate; DEHA, di-(2-ethylhexyl) adipate; DEHS, di-(2-ethylhexyl) sebacate; DEHT, di (2-ethylhexyl) tetrahydrophthalate; 1,4-DEHCH, di (2-ethylhexyl) cyclohexane-1,4-dicarboxylate; 1,2-DEHCH, di(2-ethylhexyl) cyclohexane-1,2-dicarboxylate; SPE, solid-phase extraction; LLE, liquid– liquid extraction; GC, gas chromatography; LC, liquid chromatography; PTFE, polytetrafluoroethylene; SPME, solid-phase microextraction; LPME, liquid-phase microextraction; SDME, single-drop microextraction; HF-LPME, hollow-fiber LPME; DLLME, dispersive liquid–liquid microextraction; ELISA, enzyme-linked immunosorbent assay; FPIA, fluorescent polarization immunoassay; SML, specific migration limit; GC-MS, gas chromatography–mass spectrometry; UA-DLLME, ultrasound-assisted dispersive liquid–liquid extraction; USVA-DLLME, ultrasound–vortex-assisted dispersive liquid–liquid micro-extraction; MSA-DLLME, magnetic stirring-assisted dispersive liquid–liquid microextraction; IL-DLLME-HPLC, ionic liquid dispersive liquid–liquid microextraction coupled with high-performance liquid chromatography; HS–SPME–GC–MS, headspace solid-phase microextraction gas chromatography–mass spectrometry; LOD, limit of detection; LOQ, limit of quantification; BDE, 2,2,4,4-tetrabromodiphenyl ether; HPLC, high-performance liquid chromatography; UHPLC-MS/MS, ultra-high-performance liquid chromatography–tandem mass spectrometry method; BEHP, hexahydro phthalate; SBSE/TD-GC-MS, stir bar sportive extraction coupled with thermal desorption–gas chromatography–mass spectrometry; MPT-MS/MD, microwave plasma torch–ionization tandem mass spectrometry; D-μ-SPE, dispersive micro-solid-phase extraction; GC-MS/MS, gas chromatography–mass tandem spectrometry; MALLE, membrane-assisted liquid–liquid microextraction; LC-DAD, liquid chromatography–diode array detection; LC-FLD, liquid chromatography–fluorescent detection; DBEP, bis(2-n-butoxyethyl) phthalate; DiDP, diisodecyl phthalate, BcEP, bis(2-chloroethyl) phosphate; iBP, isobutyl phthalate; DPP, dipentyl phthalate, DPhP, di(2-propylheptyl) phthalate; DiPP, diisopentyl phthalate; DnPP, di-n-pentyl phthalate; DPrP, dipropyl phthalate; BMEP, bis(2-methoxyethyl) phthalate; BMPP, bis(4-Methyl-2-pentyl)phthalate; BEEP, bis(2-ethoxyethyl) phthalate; DAP, diamyl phthalate; DnHP, d-n-hexyl phthalate; DCHP, dicyclohexyl phthalate; DMEP, dimethoxyethyl phthalate; BMPP, bis (4-methyl-2-pentyl) phthalate; DEEP, bis (2-ethoxyethyl) phthalate; DHXP, dihexyl phthalate; DHP, di-hexyl phthalate; BCEP, bis(2-chloroethyl) phosphate; BPA, bisphenol A; iBcEP, isobutylcicloexyl phthalate; DLLME-SFO, dispersive liquid–liquid microextraction method based on the solidification of a floating organic drop; VA-DLLME, vortex-assisted dispersive liquid–liquid microextraction; UPLC-MS/MS, ultra-performance liquid chromatography–tandem mass spectrometry system; MSPE-GC/MS, magnetic solid phase extraction technique combined with gas chromatography/mass spectroscopy.

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