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Review

Challenges in the Analytical Preparation of a Biological Matrix in Analyses of Endocrine-Disrupting Bisphenols

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Abstract: Endocrine-disrupting chemicals (EDCs) are xenobiotics presented in a variety of everyday products that may disrupt the normal activity of hormones. Exposure to bisphenol A as EDC at trace and ultra-trace levels is associated with adverse health effects, and children are recognized as the most vulnerable group to EDCs exposure. In this review, a summary is presented of up-to-date sample preparation methods and instrumental techniques applied for the detection and quantification of bisphenol A and its structural analogues in various biological matrices. Biological matrices such as blood, cell-free blood products, urine, saliva, breast milk, cordial blood, amniotic and semen fluids, as well as sweat and hair, are very complex; therefore, the detection and later quantification of bisphenols at low levels present a real analytical challenge. The most popular analytical approaches include gas and liquid chromatography coupled with mass spectrometry, and their enhanced reliability and sensitivity finally allow the separation and detection of bisphenols in biological samples, even as ultra-traces. Liquid/liquid extraction (LLE) and solid-phase extraction (SPE) are still the most common methods for their extraction from biological matrices. However, many modern and environmentally safe microextraction techniques are currently under development. The complexity of biological matrices and low concentrations of analytes are the main issues for the limited identification, as well as understanding the adverse health effects caused by chronical and ubiquitous exposure to bisphenols and its analogues.

Keywords: bisphenol A; blood; endocrine disruptor; sample preparation techniques; urine

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1. Introduction

Bisphenols (BPs) are widely used chemicals in industrial, commercial and domestic appliances. The most used monomer is bisphenol A (BPA), while the other molecules with two p-hydroxyphenyl functional groups in their structure are known as BPA analogues and are applied as BPA alternatives [1]. BPA is used in the production of polycarbonate plastics and epoxy resins and it can be found in plastic bottles, cans, toys, thermal paper, but also in dental fillings and medical devices [2,3]. Bisphenol S (BPS), bisphenol F (BPF) and bisphenol AF (BPAF) are the most frequently used alternatives. BPS is used in thermal paper, can coating, epoxy glue and dyes additive; BPF can be found in food packages coating, in liners, lacquers and varnishes [4]; while BPAF is added in electronic materials, in optical fibers and waveguides, as well in food processing equipment [5]. Both BPA and its analogues can be detected in surface water, wastewater, sediments or air [6–14]. Human exposure to BPs is mainly a result of oral ingestion and dietary sources due to BP leaking from plastic packaging or coatings into foods and beverages [15–18]. Although BPA is the most detected compound in comparison to other analogues, in spite of the type of food container, BPs are also present in both canned and non-canned products [19]. However, the EU Commission set the maximum allowed migration level for BPA as 0.05 mg per kg of food [20]. Other routes of exposure include inhalation and dermal absorption. Once BPA

enters the human body, it undergoes conversion into glucuronide and sulphate conjugates in the gastrointestinal tract and the liver. Up to 84–97% of bisphenol A is eliminated through urine dominantly in conjugated form [21]. Unconjugated BPA ("free" or aglycon BPA) circulates in a very low concentration in the human body, and it is difficult to detect. Usually, the total BPA concentrations, both in conjugated and unconjugated forms, are measured in biomonitoring studies. BPA has been detected in various human matrices such as urine, saliva, serum, plasma, breast milk, follicular fluid, amniotic fluid, semen, placental tissue and umbilical serum. Although there are innumerable reports about BPA as a biomarker in environmental studies, data regarding the detection of its analogues in human samples are scarce and usually focused on a few, such as BPB, BPS, BPF and/or BPAF [22].

The simultaneous determination of BPA alternatives is pivotal for observing the effects of joint exposure to these very ubiquitous substances. Reliable and sensitive analytical methods for synchronously detecting and quantifying low BP concentrations in human matrices are necessary. Aside from the difficulty in developing a method to determine low (trace and ultra-trace) levels of structurally similar compounds from biological samples, the matrices per se are challenging in BP biomonitoring studies. Pre-concentration is usually required because BP levels in biological matrices are mostly in the ranges of ng/mL and ng/g. In addition, biological samples contain endogenous chemicals that may be co-extracted and affect the result of both the identification and quantification of analytes. Furthermore, external contamination of the samples is possible during sample collection, preparation and analysis, since BPs are ubiquitous and can be found not only in daily life products, but also in laboratory materials and equipment. Procedures that include the washing and rinse-up of laboratory glassware with various organic solvents, the application of high-purity chemicals, and blank analysis are standard steps in BP biomonitoring studies [23,24]. Thus, the sample preparation can be considered crucial in BP biomonitoring and include sample treatment, clean-up and preconcentration, before separation, detection and quantification. In order to obtain extracts that are suitable for further quantitative analysis, the key step is the adequate extraction and enrichment of the structurally similar analytes with high recovery, as well as the removal of potential interfering compounds. As the most tedious procedure that takes up to 80% of the total time for analysis, the sample preparation is referred to as the bottleneck in the method development [25]. After appropriate extraction, the BP separation, detection and quantification can be performed using selective, specific and sensitive methods. The method for BP determination requires proper analytical validation, which includes satisfactory accuracy, linearity range, method precision (repeatability and intermediate precision) and method robustness, as well as a low limit of quantitation, and a limit of detection that will provide an evaluation of trace BP levels [26]. Human BP exposure evaluation can be only conducted if reliable analytical methods are developed and validated.

In this paper, a comprehensive overview of the methods applied for BP determination in various human samples is presented, focusing on the challenges for extract preparation from the observed biological matrices. Original research articles and review papers published in the English language were searched using the Google Scholar and PubMed databases up to February 2023, with a focus on BPA and its analogues investigated in urine, blood and cell-free fractions, saliva, cordial blood, amniotic fluid, breast milk, semen/seminal plasma, sweat and head hair.

2. Biological Matrices

The most sensitive methods for determining BPA and its analogues in each matrix are summarized in Table 1.

Table 1. The most sensitive methods for determining BPA and its analogues in each matrix.

Matrix	Analytes	Preparation Technique (Sorbent/Extraction Solvent)	Instrumental Analysis	Recovery (%)	RSD (%)	The Lowest LOD	The Lowest LOQ	Reference
URINE								
	BPS, 2,4-BPS, BPSIP, BPS-MAE, BPS-DAE, TGSA, DBSP, DPS, DDS, DD-70, TDP	LLE (ethyl acetate)	LC-MS/MS	62–95	2–14	6–7 pg/mL	Data not reported	[27]
	BPA, BPF, BPS, BPB	SPE (HLB)	LC-MS/MS	98–118	7–25	0.004–0.01 ng/mL	0.05–0.5 ng/mL	[28]
	BPA	SPE (not reported)	GC-MS/MS	104.4	1.5–9.7	0.05 ng/mL	Data not reported	[29]
	BPA, BPS, BPF, BPZ, BPP, BPAF, BPAP	DLLME (acetonitrile)	LC-MS/MS	90–112	1.9–14.8	0.005–0.2 ng/mL	0.02–0.5 ng/mL	[30]
	BPAF, BPF, BPE, BPA, BPB, BPS, BPZ, BPAP	DLLME (acetonitrile + tetrachloroethylene + acetic anhydride)	GC-MS	62–103	1–20	0.03–4.55 ng/mL	0.1–2.5 ng/mL	[4]
	BPA	HF-LPME (octanol)	GC-MS	Data not reported	13.9–17.1	1.82 ng/mL	3.04 ng/mL	[31]
	BPA	Salting out-LLME (tetrahydrofuran)	LC-MS/MS	95–108	6	0.1 ng/mL	0.2 ng/mL	[32]
	BPA	Restricted-access volatile SUPRAS-based microextraction (hexanol + tetrahydrofuran)	LC-MS/MS	96–107	4.5	0.015 ng/mL	0.025 ng/mL	[33]
	BPA	Micro-QuEChERS + dSPE (acetonitrile + C18 and magnesium sulphate)	GC-MS	74–118	3–10	0.13 ng/mL	0.43 ng/mL	[34]
BLOOD and CELL-FREE FRACTIONS								
	BPA, BPS, BPC, BPE, BPF, BPG, BPM, BPP, BPZ, BPFL, BPBP	LLE (acetonitrile)	LC-MS/MS	87.6–134.6	1.2–15	0.008–0.039 ng/mL	0.024–0.12 ng/mL	[1]
	BPA	LLE (ethyl acetate)	GC-MS	Data not reported	Data not reported	0.01 ng/mL	0.10 ng/mL	[35]
	BPA, BPS, BPF, BPB, BPAF	MSPE (core-shell structured magnetic covalent organic framework nanocomposite)	LC-MS/MS	93–107.8	1.2–6.9	0.1–78.4 ng/mL	3.2 −260.3 ng/mL	[36]
	BPA	SPE (polymer divinylbenzene)	GC-MS/MS	83.31–104.01	5.97–15.25	Data not reported	1 ng/mL	[37]
	BPS, BPF, BPAF, BPB, BPP, BPZ, BPAP, TBBPA, TBBPS, TCBPA	UAE + SPE (MCX)	LC-MS/MS	66.6–101	0.8–14	0.001–0.197 ng/mL	0.002–0.658 ng/mL	[38]
	BPA, BPB, BPE, BPF, BPS, BPAF, BPZ, TBBPA	UAE + QuEChERS (acetonitrile + primary secondary amine + C18 + magnesium sulphate + graphitized carbon black)	LC-MS/MS	62–91	2.6–5.5	0.1–1.0 ng/mL	0.3–2.5 ng/mL	[39]
	BPA, BPB, BPE, BPF, BPP, BPS, BPZ, BPAP, BPAF, MCBPA, DCBPA, TriCBPA, TCBPA, BADGE, BADGE × H_2O, BADGE × $2H_2O$, BADGE × HCl, BADGE × 2HCl, BADGE × H_2O × HCl, BFDGE, BFDGE × $2H_2O$	SUPRAS-based microextraction (hexanol + tetrahydrofuran)	LC-MS/MS	72–107	1–10	Data not reported	0.019–0.19 ng/mL	[40]
	BPA, BPS, BPF, BPB, BPAF, BPZ, BPE, BPAP	DLLME (acetonitrile + tetrachloroethylene + acetic anhydride)	GC-MS	74–116	2–17	0.03–4.55 ng/mL	0.1–15 ng/mL	[4]
SALIVA								
	BPA	LLE (acetonitrile)	LC-MS/MS	Data not reported	2.8–4	0.1 ng/mL	Data not reported	[41]
	BPA	HF-LPME (octanol + ethyl octanoat)	GC-MS	93	7.36–13.02	0.07 ng/mL	0.24 ng/mL	[42]
	BPA, BPS, BPAF, BPAP, BPP, BPZ	DLLME (acetone + chloroform)	LC-MS/MS	85–114	2–19	0.01–0.1 ng/mL	0.1–0.4 ng/mL	[43]
	BPA, BPB, BPE, BPF, BPP, BPS, BPZ, BPAF, BPAP, MCBPA, DCBPA, TriCBPA, TCBPA	SUPRAS-based microextraction (hexanol + tetrahydrofuran)	LC-MS/MS	95–105.6	0.6–16	0.012–0.049 ng/mL	0.024–0.098 ng/mL	[44]

Table 1. *Cont.*

Matrix	Analytes	Preparation Technique (Sorbent/Extraction Solvent)	Instrumental Analysis	Recovery (%)	RSD (%)	The Lowest LOD	The Lowest LOQ	Reference
CORDIAL BLOOD								
	BPA	LLE (hexane + diethyl ether + perchloric acid)	HPLC-UV	96.1	1.99–7.53	0.13 ng/mL	Data not reported	[45]
	BPA, BPB, BPE, BPF, BPS, BPAF	LLE (dichloromethane)	LC-MS	Data not reported	Data not reported	0.14–2.5 ng/mL	Data not reported	[46]
	BPA	SPE (HLB)	GC-MS/MS	Data not reported	Data not reported	0.026 ng/mL	Data not reported	[47]
	BPA, BPF, BPS	SPE (HR-XAW)	LC-MS/MS	92–103	Data not reported	0.023–0.038 ng/mL	0.046–0.052 ng/mL	[23]
AMNIOTIC FLUID								
	BPA, BPAF, BPAP, BPB, BPP, BPS and BPZ	LLE (ethyl acetate)	LC-MS/MS	80–110	3–16	Data not reported	0.01–0.2 ng/mL	[48]
	BPF, BPE, BPAF, BPP, BADGE × 2HCl	DLLME (acetone + chloroform)	HPLC-FLD	76.5–113.3	5–12	2.04–7.50 ng/mL	6.17–22.72 ng/mL	[49]
	BPA	SPE (not reported)	LC-MS	Data not reported	Data not reported	0.1 ng/mL	0.3 ng/mL	[50]
	BADGE × $2H_2O$, BPE, BADGE·H2O, BPAF, BADGE, BPF, BADGE × H_2O × HCl, BPB, BPAP, BPP, BADGE × 2HCl	SPE (HLB)	HPLC-FLD	49–121	1.3–17.9	1.1–5.2 ng/mL	3.2–15.6 ng/mL	[51]
	BPA	SPE (not reported)	ELISA	Data not reported	Data not reported	0.2 ng/mL	Data not reported	[52]
BREAST MILK								
	BPA	LLE (acetonitrile + chloroform)	GC-MS/MS	85–115	Data not reported	0.2 ng/mL	0.5 ng/mL	[53]
	BPA, BPF, BPE, BPP, BADGE, BADGE × $2H_2O$, BADGE × 2HCl	DLLME (acetone + dichloromethane)	HPLC-FLD	67–110	7–17	0.5–2.1 ng/mL	1.4–6.3 ng/mL	[54]
	BPA, BPF, BPS	DLLME (acetone + chloroform)	LC-MS/MS	94.5–110.4	5.1–14.8	0.1 ng/mL	0.4–0.5 ng/mL	[55]
	BPA, BPAP, BPAF, BPE, BPF, BPSIP, 2,4-BPS, BPS-MAE, BPS-DAE, BPS-MPE, DDS, TDP, TGSA, DPS	SPE (HLB)	LC-MS/MS	63–109	Data not reported	0.3–37 pg/mL	Data not reported	[56]
	BPA, BPB, BPAP, BPAF, BPBP, BPC, BPCl2, BPE, BPPH, BPS, BPF, DHDPE, BPFL, BPZ, BP4,4′, BPM, BPP, BIS2, BP2,2′	SPE (polystyrene-divinylbenzene, molecularly imprinted polymers)	GC-MS/MS	90–109	13–20	0.001–0.030 ng/g	0.002–0.050 ng/g	[57]
	BPA	UA-MSPE (magnetic micro-meso porous activated carbon)	LC-UV	89.1–99.4	0.5–3.7	0.75 ng/mL	2.5 ng/mL	[58]
	BPA, BPB, BPC, BPE, BPF, BPM, BPP, BPS, BPZ, BPAP, BPAF, BPBP, BPFL, DHDPE, MCBPA, 3,5-DCBPA, 3,3-DCBPA, TriCBPA, TCBPA, TBBPA, MCBPF, DCBPF, TriCBPF, TCBPF, MCBPS, 3,5-DCBPS, 3,3-DCBPS, TriCBPS, TCBPS	QuEChERS (acetonitrile + EMR lipid powder)	LC-MS/MS	86.11–119.05	0.59–13.49	0.0003–0.067 ng/mL	0.001–0.200 ng/mL	[59]
	BPA, BPF, BPS, BPB, BADGE, BADGE × H_2O, BADGE × 2HCl	QuEChERS + dSPE (acetonitrile + sodium chloride and magnesium sulphate + zirconium-based sorbent and primary secondary amine)	HPLC-DAD	15–107	<10	142–693 ng/mL	430–2102 ng/mL	[60]

Table 1. *Cont.*

Matrix	Analytes	Preparation Technique (Sorbent/Extraction Solvent)	Instrumental Analysis	Recovery (%)	RSD (%)	The Lowest LOD	The Lowest LOQ	Reference
SEMEN/SEMINAL PLASMA								
	BPA	LLE (methyl tert-butyl ether)	LC-MS/MS	99.7–103.8	4.9	Data not reported	28.9 pg/mL	[61]
SWEAT								
	BPA	SPE (HLB)	LC-MS/MS	Data not reported	Data not reported	0.2 ng/mL	Data not reported	[62]
HEAD HAIR								
	BPZ, BPP, BPM, BPS, BPF, BDP, TBBPA, BPAP, BPAF, BPDP	SPE (HLB)	LC-MS/MS	86–101	3–9	0.04–0.5 ng/g	Data not reported	[63]
	BPA	SPE (HLB)	GC-MS/MS	106–112	6–16	5.47 pg/mg	50 pg/mg	[64]
	BPA	UAE + SPE (HLB)	LC-FLD	85	< 10	Data not reported	2.0 ng/g	[65]
	BPA	UAE	LC-MS	98	9.8–19.8	0.2 pg/mg	0.7 pg/mg	[66]

2,4-BPS = 2,4′-bis(hydroxyphenyl)sulfone; 3,3-DCBPA = 3,3-dichlorobisphenol A; 3,3-DCBPS = 3,3-dichlorobisphenol S; 3,5-DCBPA = 3,5-dichlorobisphenol A; 3,5-DCBPS = 3,5-dichlorobisphenol S; BADGE = bisphenol A diglycidyl ether; BADGE × $2H_2O$ = bisphenol A diglycidyl ether dihydrate; BADGE × 2HCl = bisphenol A diglycidyl ether dihydrochloride; BADGE × H_2O = bisphenol A diglycidyl ether hydrate; BADGE × H_2O × HCl = bisphenol A diglycidyl ether chlorohydroxy; BADGE × HCl = bisphenol A diglycidyl ether hydrochloride; BFDGE = bisphenol F diglycidyl ether; BFDGE × $2H_2O$ = bisphenol F diglycidyl ether dihydrate; BIS2 = bis-2(hydroxyphenyl)methane; BP2,2′ = biphenyl-2,2′ -diol; BP4,4′ = biphenyl-4,4-diol; BPA = bisphenol A; BPAF = bisphenol AF; BPAP = bisphenol AP; BPB = bisphenol B; BPBP = bisphenol BP; BPC = bisphenol C; BPCl2 = bisphenol Cl2; BPDP = t-butylphenyl diphenyl phosphate; BPE = bisphenol E; BPF = bisphenol F; BPFL = bisphenol FL; BPG = bisphenol G; BPM = bisphenol M; BPP = bisphenol P; BPPH = bisphenol PH; BPS = bisphenol S; BPS-DAE = bis(4-allyloxyphenyl)sulfone; BPSIP = 4-hydroxyphenyl 4-isoprooxyphenylsulfone; BPS-MAE = 4-{[4-(allyloxy)phenyl]-sulfonyl}phenol; BPS-MPE = 4-hydroxy-4-benzyloxydiphenyl-sulfone; BPZ = bisphenol Z; C18 = octadecyl modified silica phase cartridges; DBSP = 2,4-bis(phenylsulfonyl) phenol; DCBPA = dichloro-BPA; DCBPF = 3,5-dichlorobisphenol F; DD-70 = bis [2-(4-hydroxyphenylthio)ethoxy]methane; DDS = 4,4′-diaminodiphenylsulfone; DHDPE = 4,4-dihydroxydiphenyl ether; DLLME = dispersive liquid–liquid micro-extraction; DPS = diphenylsulfone; dSPE = dispersive solid-phase extraction; ELISA = enzyme-linked immunosorbent assay; EMR = enhanced matrix removal; GC-MS = gas chromatography tandem mass spectrometry; GC-MS/MS = gas chromatography tandem mass spectrometry/mass spectrometry; HF-LPME = hollow fiber liquid-phase microextraction; HLB = hydrophilic lipophilic balanced cartridges; HPLC-DAD = high-performance liquid chromatography with diode-array detection; HPLC-FLD = high-performance liquid chromatography with fluorescence detector; HPLC-UV = high-performance liquid chromatography with ultraviolet spectroscopy; HR-XAW = polystyrene-divinylbenzene copolymer with weak mixed-mode anion exchanger; LC-MS = liquid chromatography tandem mass spectrometry; LC-MS/MS = liquid chromatography tandem mass spectrometry/mass spectrometry; LLE = liquid–liquid extraction; LLME = liquid–liquid microextraction; LOD—limit of detection; LOQ—limit of quantification; MCBPA = monochloro-BPA; MCBPF = mono-chlorobisphenol F; MCBPS = monochloro-BPS; MCX = mixed-mode cation cartridges; MSPE = magnetic solid-phase extraction; QuEChERS = quick, easy, cheap, effective, rugged and safe; RSD—relative standard deviation; SPE = solid-phase extraction; SUPRAS = supramolecular solvents; TBBPA = tetrabromobisphenol A; TBBPS = tetrabromobisphenol S; TCBPA = tetrachlorobisphenol A; TCBPF = tetrochlorobisphenol F; TCBPS = tetrochlorobisphenol S; TDP = 4,4′-thiodiphenol; TGSA = bis(3-allyl-4-hydroxyphenyl)-sulfone; TriCBPA = trichloroBPA; TriCBPF = trichlorobisphenol F; TriCBPS = trichlorobisphenol S; UAE = ultrasound-assisted extraction; UA–MSPE = ultrasonic-assisted magnetic solid-phase extraction.

2.1. Urine

Urine is the most common human sample in biomonitoring studies to assess BP exposure due to its non-invasive and simple method of collection, which is comfortable for the participants. The main advantages of urine as a biological matrix are the opportunity to collect samples continuously, its suitability for long-term monitoring and the fact that it can be collected in large quantities. In addition, metabolite concentrations are usually higher in urine in comparison to blood and blood products; many compounds are more stable in urine and, if the content of certain compounds is low, a large amount of urine allows pre-concentration and their subsequent identification and quantification. Finally, in comparison to blood samples, urine as a matrix is less demanding in terms of storage, transportation and processing conditions [67]. On the other hand, urine samples have a relatively small window of detection, given the short half-life of BPA (~6 h). The BPA concentration variability in within-day spot samples, as well as within-person first morn-

ing voids, and 24 h collections, have also been reported [68]. To avoid these obstacles, the total BPA concentration is measured in urine as the most relevant and robust marker of exposure assessment [69]. Considering that contamination could consequently affect the total BPA content, field blank and reagent blank are recommended when total BPA concentration is used as a biomarker [21]. Therefore, enzymatic hydrolysis is a crucial pretreatment step before the extraction procedure [4]. The optimization of the hydrolysis step in terms of amount and enzyme type, time interval, temperature and buffer pH, is essential for accurate BP quantification in urine [70]. Usually, commercially available β-glucuronidase from *Helix pomatia* or *E. coli* is used for BP enzymatic hydrolysis. In addition, β-glucuronidase/arylsulfatase enzyme from *Helix pomatia* is an appropriate choice for the simultaneous determination of urinary BPA and its structural analogue levels because the enzyme mix ensures complete deconjugation of glucuronide and sulfate metabolites (i.e., BPA monosulfate and BPA disulfate) [4,71–73]. Generally, after a urine aliquot is transferred into a glass tube, ammonium acetate buffer (pH 5.0–6.5) is added with the proper amount of the enzyme and an internal standard. The mixture is then incubated at 37 °C for at least 90 min to several hours (usually 4 h), or even left overnight, in order to guarantee that conjugated BPs are completely hydrolyzed [30,73–76]. Additionally, internal standard calibration is recommended for BP quantification to diminish the urine matrix effects as well as the differences in the reproducibility, due to the analyte loss during treatment. Instead of the external calibration and standard addition method, a constant amount of appropriate internal standard is added before the incubation step to every sample, in order to improve the method precision. Namely, the numerous steps during the extraction procedure as well as the presence of different compounds in urine can significantly affect the acquired results. A compound with almost the same structure and MS ionizability as BPA is recommended as an internal standard. Hence, a stable isotope BPA analogue is considered an ideal internal standard that meets the requirements for identical response factors [77]. The application of $^{13}C_{12}$-BPA and d16-BPA as internal standards is well documented [30,78]. The sensitive analysis of BPA structural analogues in urine may also include d4-BPA, d10-BPF, $^{13}C_{12}$-BPAF [79], $^{13}C_{12}$-BPS [27,80] and d6-BPA diglycidylether [75]. Moreover, isotopically labeled conjugated BPA such as d6-BPA-glucuronide ensures the optimization of the enzymatic hydrolysis step and accurate quantification of BPA conjugated forms in urine samples [71,81]. The successful chemical synthesis of BPA mono- and di-glucuronide as well as BPA mono- and di-sulfate was reported and enabled the direct quantification of BPA metabolites in human urine [82]. The urinary BPA metabolites content might also be taken into account as a relevant biomarker owning to the higher detection frequency of glucuronides in urine, as well as the fact that the metabolite concentrations are generally unaffected by the external contamination [83]. In comparison to the total number of biomonitoring studies, data about the BPA glucuronide and sulfate metabolite levels in the urine of the general population are scarce [83–88]. The commercial development and distribution of various BPA structural analogues, related metabolites, as well as isotopically labeled counterparts are still an imperative and will enable the development of simultaneous methods for urinary BP quantification in a wide range.

The used urine volume during the preconcentration step significantly varies (from 100 µL to the most common 5 mL) according to the applied sample preparation method and available instrumentation for quantification [2,4,27,33,71,81,82,89–92]. Considering that some BPs have higher octanol–water partition coefficients ($\log K_{ow}$) than BPA ($\log K_{ow}$ 3.43) [93], the development of an appropriate sample preparation method strongly depends on the targeted BPs properties so that the demand for high recoveries are met. The protocol for urinary BPA analysis in biomonitoring studies still involves classical methodology such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE), which are commonly applied for the elimination of interfering substances and preconcentration. LLE and SPE are multi-step techniques that are time-consuming and require experienced personnel to avoid possible external contamination, to handle manually small sample volumes and to prevent the high possibility of losing ultra-trace analytes. After LLE, SPE is

sometimes proposed as an additional clean-up step [81,82]. Generally, large quantities of organic solvents are needed for LLE, although this method is considered less expensive when compared to others [94]. Acetonitrile, dichloromethane, methyl tert-butyl ether and ethyl acetate are commonly used as solvents for the extraction of BPA, BPF, BPS and related analogues [72,74,75,81,92,95]. In contrast to LLE, SPE requires the optimization of an appropriate sorbent type, elution solvent, as well as the sample volume and pH adjustment, so that the clean preconcentrated sample with high BPs recovery is obtained. During the SPE procedure, the urine sample is loaded after the conditioning step, which also requires organic solvents. It is recommended to wash cartridges with pure water (and buffer solution, pH 6) to remove matrix interreferences [91] before the elution. The elution step might involve a single solvent or a solvent mixture (e.g., methanol, acetone, dichloromethane, ethyl acetate) if simultaneous analysis of different BPs is required. Different SPE sorbents have been applied for BPA and structural analogues preconcentration. The most popular sorbent for BPs enrichment is still silica-based C18, which can retain non-polar and moderately polar compounds, as well as hydrophilic–lipophilic balanced sorbent (HLB) consisting of lipophilic divinylbenzene and hydrophilic N-vinyl pyrrolidinone, which make them universal material for different kinds of analytes [28,81,91,96–100]. Florisil cartridges are sometimes recommended for the clean-up step [82]. Bearing in mind the reproducibility and stability issues that might occur with silica-based SPE cartridges, polymer-based sorbents should be used to overcome those problems. Hence, MAX and WAX mix-mode polymeric sorbents have also been applied for the isolation and enrichment of urinary BPs [79,101,102]. Additionally, there are a few examples of molecularly imprinted polymers (MIPs) application for urinary BPA extraction and/or clean-up. The application of MIP-SPE reduces the matrix effects and results in satisfactory BPA recovery [103,104]. Generally, in comparison to standard LLE, the SPE method is considered to ensure better selectivity, higher recoveries and, ultimately, a cleaner extract that usually has fewer interfering substances [24], although a significant loss of trace analytes might occur during both methods. The development of selective sorbents towards BPA and its analogues is still imperative.

As a green alternative to LLE, liquid-phase microextraction (LPME), particularly hollow fiber-based-liquid-phase microextraction (HF-LPME) and salting-out liquid–liquid microextraction (SALLME), together with dispersive liquid–liquid microextraction (DLLME), are a focus today. The combination of LLME with non-enzymatic microwave-assisted hydrolysis was proposed as a rapid and economical alternative method for urinary BPA determination [105]. HF-LPME and SALLME were successfully applied as an enrichment step in the analysis of BPA, whereas the DLLME technique has been proposed as a fast and simple alternative for the routine monitoring of BPA and its structural analogues (bisphenol B, BPS, BPF, BPZ, BPAP and BPAF) in human urine, as well as their conjugates [4,30–32,89,106,107]. A novel type of HF-LPME reinforced with graphene oxide nanoribbons was introduced for the determination of 5 BPs (BPA, BPS, BPF, bisphenol B and bisphenol AF) [108]. Restricted access-volatile supramolecular solvents have also been tested for urinary BPA analysis to achieve cleaner extracts in comparison to standard methods [33]. Nevertheless, solid-phase micro-extraction (SPME), which was developed as a solvent-free SPE procedure, as well as stir bar sorptive extraction (SBSE), are not common for BP extraction from urine.

Keeping in mind the urine matrix complexity and ultra-low levels of BPs (ng/mL), highly sophisticated instrumentation is needed for the sensitive and selective determination of BPA and its structural analogues in urine. Although numerous analytical methods have been developed, liquid chromatography (LC) and gas chromatography (GC) undoubtedly remain the most common methods for the analysis of BPA and its analogues [21,24,94,109,110]. Particularly, mass detectors (triple quadrupole, quadrupole ion trap or quadrupole time-of-flight) are unequivocally the first choice for the BP identification and quantification. LC-MS/MS as well as GC-MS ensure a low limit of detection. Prior to identification and quantification, the derivatization step of sampling is usually performed to increase the sensitivity (the limit of the detection, LOD) and selectivity of

the applied LC or GC method, due to the low volatility of BPA and/or the "ghosting" phenomenon of trace level phenols [111]. Sample derivatization is an additional step and, since undesirable derivatized by-products could be produced, an increase in quantification uncertainty might occur. Therefore, the derivatization step should be optimized in terms of type and amount of agent, temperature, time and pH value [31]. There are a wide range of derivatization methods that convert non-volatile compounds into volatile BPs derivatives, such as acylation, alkylation and silylation [2,64,107]. Even injection-port butylation was proposed for GC-MS BPA quantification in human urine with high precision and accuracy [112]. Nonetheless, N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and BSTFA with 1% trimethylchlorosilane (TMCS) are the most used derivatization agents that improve the physicochemical properties of BPs for GC quantification after the urine preconcentration and clean-up steps [31,82,90,113]. Considering the presence of a phenolic hydroxyl functional group, the negative electrospray ionization mode is selected for the LC-MS analysis of BPA and its conjugates, while the polarity is shifted and the positive mode is preferred if the derivatization step is included [21]. Sulfonyl chlorides are generally used for BPs derivatization when LC is applied for their quantification [28,114]. Moreover, LC-MS/MS could be coupled with online SPE for the routine monitoring of numerous urine samples [80]. Good separation LC protocol frequently includes C18 columns, whereas GC separation after the spitless/split mode commonly requires a 30 m long 5% phenyl/95% dimethyl polysiloxane column [4,82,89,91,92]. BPs are usually separated via LC using methanol–water or acetonitrile–water in the gradient mode with added stabilizers (e.g., formic acid, acetic acid, ammonium–acetate) as mobile phases, while helium is commonly applied as mobile gas in GC [4].

2.2. Blood and Cell-Free Fractions

Blood and its cell-free fractions, serum and plasma, are the biological matrices of choice in clinical, toxicological and epidemiological studies. They contain various biological information regarding the physiological and pathological features of the human body [5]. Serum clot as the platelets release proteins and metabolites, while fibrinogen cleaves into insoluble fibrin. During the centrifugation of fibrin clots, coagulation factors and blood cells are separated from the sample. Anticoagulants (i.e., EDTA, heparin, citrate) prevent the blood from coagulating when plasma is collected. In plasma, clotting factors are kept deactivated and fibrinogen, as well as anticoagulants, remain in the matrix after centrifugation and separation from the blood cells [115]. Numerous interferences, which may limit the identification and quantification of the analytes and affect the metabolite stability and composition, are attributed to the complexity of blood sample preparation. The detection window is narrow, as for urine samples. The obtained results are also affected by the choice of blood sample collection, since differences between serum, ACD plasma, citrate plasma, EDTA plasma, fluoride plasma, or heparin plasma are reported [116]. Serum not only differs from plasma in the anticoagulant content, but also in metabolites and lipoprotein composition. Generally, the metabolite levels are higher in serum in comparison to plasma, but serum collection tubes with separator gels create a barrier between the cells, and the serum and can also affect the composition and the content of the metabolites under analysis [117].

Although urine is generally considered the preferable matrix for the examination of BPA-related adverse effects in humans, blood is almost equally represented in biomonitoring studies [21]. Particularly, more studies are focused on serum as a matrix when compared to plasma and whole blood [24]. BPA mono-glucuronide is the dominant metabolite in the serum [118]. Despite relatively high BPA levels as aglycone being reported, contamination and deconjugation during all phases of the blood analysis (collection, storage, handling) might occur and impact the obtained results [119,120]. Based on the fact that total urinary BPA levels correlate well with plasma BPA content [82], it is recommended to measure the total BPA concentrations (free plus conjugated) in blood [4,113]. Consequently, enzymatic hydrolysis is a fundamental step in developing a reliable method for BP analysis in blood.

Analytical techniques commonly applied for the analysis of BPA and its structural analogues in serum and plasma are GC-MS, LC-MS and LC-MS/MS [1,4,26,35,36,121,122]. Although cross-reactivity is identified as one of the major limitations of the enzyme-linked immunosorbent assay (ELISA) method [109], there are examples of ELISA application in the assessment of BPA content in serum and plasma [123,124]. LLE and SPE remain the "golden standard" for sample preparation because they minimize the interference effect from the matrix [1,35,36,113,121,125]. Nevertheless, a simple protein precipitation procedure followed by LC-MS/MS has been proposed for BPA extraction from human plasma when handling a large number of samples is required [122]. Acetonitrile as well as hydrochloric acid are commonly used to precipitate the proteins in blood [1,126,127]. Non-polar solvents such as n-hexane could also be used in combination with other solvents (e.g., methyl tert-butyl ether, acetonitrile) for BPA isolation [128]. It is not rare for plasma or serum samples to be directly loaded onto an SPE column after water dilution and enzymatic hydrolysis [129]. Again, C18 and HLB sorbents are the most popular in SPE cartridges and both off-line and on-line SPE procedures have been documented [114,118,125,130,131]. Since BPs analogues significantly differ in $\log K_{ow}$ values, the development of an efficient extraction procedure that will ensure the elimination of all interferences is a challenging task. The simultaneous quantification of different BPs in human serum at the pg/mL level has been achieved with simple LLE, followed by the SPE clean-up step used as the sample preparation procedure [132]. Additionally, ultrasound-assisted extraction (UAE) might be employed together with the clean-up step on MCX columns for a preconcentration of up to 16 BP analogues in both plasma and serum [38,133]. The combination of UAE, which increases heat and mass transfer, with the quick, easy, cheap, effective, rugged and safe (QuEChERS) method, was also used for the simultaneous extraction of eight BPs in serum samples [39]. In contrast, hybrid the SPE–protein precipitation technique is proposed as a rapid serum pretreatment process for BPA analyses, since zirconium sorbent has potential to retain phospholipids, hence, reducing the number of steps during pretreatment [134]. Recently, a supramolecular solvent-based method was developed for the analysis of 21 BPs in both serum and urine [40]. Considering that the popularity of microextraction techniques is increasing, DLLME has been successfully applied with the GC-MS method for the evaluation of 8 BPs in whole blood and urine samples [4]. Simple and low-cost methods are an imperative; hence, in order to obtain quick results and the improved evaluation of BP levels, several attempts were made to develop sensitive and specific sensors for BPA quantification in the serum [135–138]. Although it is possible in 30 s to detect BPA in human serum, maternal and cordial blood at femtomolar levels, the high structural similarity of BPs still presents an issue for simultaneous quantification [137].

2.3. Saliva

Saliva is another biological matrix that is easy to collect; the sampling does not disturb the integrity of the human body and is thus more easily approved by ethical boards. Saliva sample storage, transport and preparation is less complex when compared to blood [139]. However, the sample is diluted, which may require enrichment of the analytes; further, there are no data on whether the results differ if resting or stimulated saliva is collected. In addition, external contamination of the sample is possible and the detection window is short [140]. Acetonitrile is commonly used for the precipitation of saliva proteins, and both total and free BPA are quantified using internal standard calibration (d16-BPA) in approximately 100 µL of saliva with and without hydrolyzation, followed by LC-MS/MS [41,141]. Trace BPA levels might also be analyzed using GC-MS after preconcentration with SBSE and in situ acetic acid anhydride derivatization [142]. In line with the global trend of the reduction in organic solvent volumes, LPME and DLLME techniques are also applicable in BPA analysis in saliva [42,43]. In fact, DLLME and a supramolecular solvent-based microextraction method with LC-MS/MS instrumental analysis was developed for the determination of BPs analogues, such as BPS, BPF, BPAF, BPZ, etc. [44]. However, biomonitoring studies that use saliva as a sample are still rare.

2.4. Cordial Blood

Cordial blood, the neonatal blood from the umbilical cord at the time of delivery, is a commonly used sample in environmental studies since it provides valuable information about intrauterine exposure. It has the same advantages and disadvantages as other blood samples in terms of sample preparation, since cell-free matrices of serum or plasma must be obtained. The additional problem with cordial blood is the risk of maternal blood contamination during sample collection [143]. The neonatal blood provides unique data regarding the human maternal-to-fetal placental contaminants clearance and fetal/neonatal exposure to environmental pollutants, regardless of all the time-consuming and complex steps required for sample preparation [23,45]. To this day, the published biomonitoring studies focus on the examination of both free and total BPA, as well as BPA metabolites (BPA glucuronide and BPA sulfate) in whole cordial blood, plasma or serum [45–47,131,144–147]. Isotope-diluted LC-MS/MS [145,146] is proposed as a reliable analytical method, although ELISA, GC-MS/MS and LC coupled with a UV detector have also been successfully used [45,47,147]. LLE is still preferred as the preconcentration step. Particularly, if total BPA content is measured, incubation with β-glucuronidase from *Escherichia coli* or *Helix pomatia* with the addition of internal standard (d16-BPA or $^{13}C_{12}$-BPA) cannot be omitted before the addition of organic solvent [46,47]. Dichloromethane, as well as n-hexane and diethyl ether, are recommended organic solvents for the extraction of analytes from the cordial blood [45–47]. An online anionic exchange SPE procedure might be a convenient alternative for the analysis of BPA, BPS and BPF, as well as their glucuronides in the cordial plasma samples [23]. Despite all technological and analytical achievements, published reports about BPA and its structural analogue concentrations in cordial blood are sparse.

2.5. Amniotic Fluid

Amniotic fluid is a biofluid used to evaluate intrauterine exposure to environmental contaminants acquired by the mother, not only during pregnancy, but also before. It requires invasive collection by a trained physician with local anesthetic application and an ultrasound scan. The sample preparation of amniotic fluid is minimal [140]. Amniotic fluid in early gestation (the first half of pregnancy) is observed as a dialysate derived from fetal and possibly maternal compartments. Hence, the composition of the amniotic fluid may be close to both the fetal and maternal plasma with a reduced protein content. In the second half of pregnancy, the metabolic profile of the amniotic fluid differs from the maternal serum metabolic content; thus, amniotic fluid is recognized as the best matrix for the evaluation of fetal exposure [148]. Bearing in mind the high β-glucuronidase activity in human placental tissues, the quantification of both free and conjugated BPA levels in the amniotic fluid is preferable in order to better evaluate fetal BPA exposure during the gestation period [149]. However, the invasive sampling limits the suitability of amniotic fluid as a biological matrix, and only a few human studies related to BPA levels and analogues in amniotic fluid in the second and third trimester have been published [48,50–52]. In order to avoid cross-contamination during the sample collection, clinical-blank amniotic fluid that is kept separate from laboratory blanks should be evaluated [50]. LC combined with an MS or fluorescence detector is proposed for the quantification of BPA as well as analogues at low LOD [48–51]. In addition, the application of the EcoAssay Bisphenol A kit for the assessment of BPA content in amniotic fluids in the early second semester has been documented [52]. Simple LLE with ethyl acetate as a solvent might be used for the extraction of bisphenols (BPS, BPZ, BPAF, BPAP, BPP and BPB), including BPA [48]. Recently, the microextraction DLLE technique, as a more time-effective and environmentally friendly alternative, was developed with proper recoveries for BPF, BPE, BPAF, BADGE × 2HCl and BPP. Acetone miscibility with water and chloroform enables its application as an extraction solvent [49]. Almost at the same time, an SPE procedure using HLB columns after enzymatic hydrolysis with glucuronidase/sulfatase and extraction with acetonitrile was successfully tested for the enrichment of amniotic fluids and the later quantification of eleven bisphenols (e.g., bisphenol F, bisphenol E, bisphenol B) [51]. Aside

from extraction, acetonitrile ensures the removal of protein interferences from the sample. Despite the improvements in methodology and the fact that the evaluation of BPs in human amniotic fluid is essential to estimate gestational BP exposure levels, biomonitoring studies conducted with amniotic fluid are still very limited [48,51].

2.6. Breast Milk

Breast milk is useful to not only to determine infant exposure to xenobiotics and pollutants, but also to estimate the body burden of contaminants in the adipose tissue. Breast milk sampling is not invasive and allows considerable collection. It requires careful sample preparation due to its high lipids and proteins content [140]. Breast milk is a repository for environmental pollutants, but for relevant data, samples from at least two or three stages of lactation are required [150]. Regarding the easy collection, breast milk (after urine and blood) is considered an important matrix for biomonitoring studies that measure BP concentrations [24]. Considering the $\log K_{ow}$ value of BPA, it could be easily transported to breast milk following passive transport. Therefore, it is not surprising that BPA average values are usually above 1 ng/mL [151]. Hence, in the last few years, analysts have made significant efforts to develop reliable analytical methods for breast milk, since special precaution measures should be taken in order to control the contamination from the breast pumps and containers used for sampling. It is usually recommended to perform a migration study even if "BPA free" pumps are used, in order to avoid contamination [152]. LC coupled with an MS or tandem MS detector is by far the most used analytical approach for the detection and quantification of both BPA and its structural analogues in human breast milk [151–156]. Since breast milk is a complex matrix, the addition of internal standard ($^{13}C_{12}$-BPA, d16-BPA or d14-BPA) is needed [152–154]. Keeping in mind that total BPA concentrations were found to be much higher than free BPA in breast milk, enzymatic hydrolysis should also not be omitted [113,157]. Additionally, a decrease in the viscosity of the milk samples was observed after the addition of β-glucuronidase, which has a positive effect on the preparation procedure [60]. To date, BPA and its structural analogues have been isolated from breast milk using LLE [53], DLLME [54,55], UAE [158], SBSE [159] and both off-line and online SPE, using weak anion exchange cartridges, polystyrene-divinylbenzene, as well as MIP as a stationary phase [57,131,155,157,160]. Ultrasound-assisted magnetic SPE using the magnetic activated carbon as adsorbent is proposed as a fast and simple technique for the extraction of BPA from breast milk [58]. Nevertheless, until now, this technique has not been applied in biomonitoring studies. The precipitation of proteins and fats with acetonitrile or in combination with the metal salts in an acidic media is required during target compounds preconcentration and sample purification [159]. Special EMR–lipid-dispersed sorbents might also be used for fat removal [59,161]. Today, the QuEChERS methodology, which is commonly used for pesticides extraction from fruits and vegetables, is proposed for the removal of both proteins and fats as an important step in simultaneous BPs determination in breast milk [151,152,154,156,159]. Generally, the QuEChERS technique using acetonitrile as solvent is combined with dispersive SPE (d-SPE) to extract the analytes with satisfactory recovery rates and obtain purified preconcentrated samples. Recognized as environmentally friendly, QuEChERS/d-SPE has been used in biomonitoring studies that measure different BPA analogues (BPA, BPS, BPF and BPAF) in breast milk [151].

2.7. Human Semen/Seminal Plasma

Human semen is perceived as a sensitive and informative source of information regarding exposure to environmental pollutants. Namely, in some studies, pollutant metabolites were quantified in semen (seminal plasma), rather than the serum; thus, semen may be recognized as a biological matrix suitable for the quantification of persistent metabolites [162]. The self-collection may be the main limitation factor in the quality of collected matrices. Moreover, self-collection is always associated with a risk of external contamination and non-adequate storage. The sample preparation of seminal plasma requires several steps [163].

Particularly, LLE—with and without sonication, using acetonitrile or diethyl ether as solvents for the extraction—is the only proposed procedure for the BPA preconcentration and interference removal from seminal fluid for the later detection and quantification using LC-MS/MS [61,163]. Yet, there are no published methods regarding the sample preparation and analysis of BPA structural analogues in seminal fluid. The potential negative effects of BPA and its alternatives on male reproductive function are attracting growing attention, but until now, only the relationship between urinary BPA and BP levels and parameters of sperm quality have been examined [22,164,165].

2.8. Sweat

Sweat is hypotonic biofluid which can be collected easily and without harm to the integrity of the human body [140]. Sweat samples may differ if they are collected under stimulation (in a sauna, after physical activity, through the application of pilocarpine) in a short-term period [62] or with sweat-patches over a long-term period (at least a week). In addition, there are intra-individual differences that arise from sampling various body regions. The low secretion volume and the lack of protocols are the main limitations of sweat as a matrix, while the less demanding sample preparation in comparison to both blood and urine may be the main advantage. Simple sample dilution is often sufficient to avoid interference. Moreover, a longer time-detection windows in comparison to blood may be expected in some cases [166,167]. To the best of the authors' knowledge, only two studies have been performed that evaluate BPA in human sweat [62,168], and only one protocol has been developed up to now for the extraction and analysis of total BPA content (free BPA plus conjugates, monoglucuronide and monosulfate) from the sweat patches, using methanol as solvent for the extraction and LC-MS/MS for the quantification [168]. However, in order to propose sweat testing as an additional tool for BPA biomonitoring, further efforts need to be undertaken.

2.9. Head Hair

Usually, 150–200 hairs from the posterior vertex region of the scalp are collected as a biological sample. Collection from multiple sites from the vertex region is more acceptable for the subjects enrolled in the study, in order to avoid a visible bald patch. This method of collection has the largest window of detection (up to few months), but it is not suitable for determining recent exposure to environmental pollution. Although hair sampling is non-invasive, it is not comfortable for the participants. The risk of external contamination is high and clean-up needs to be conducted thoroughly [140]. The sample preparation method is complex and time-consuming [169], while the washing method is often pivotal for determining reliable data [170]. For the evaluation of BPA and its analogues in hair, stainless steel scissors are recommended for the collection of samples [171]. While hair as a matrix does not require enzymatic hydrolysis before extraction [172], hair samples need to be washed with water or sodium dodecyl sulfate solution and methanol using an ultrasonic bath, in order to remove both impurities (sebum, sweat, dust) and possible external BPA and the contamination of its analogues [63,64,171]. After drying, usually at room temperature, it is suggested to cut the hair into small pieces and add internal standard (d5-phenobarbital, $^{13}C_{12}$-BPA or d16-BPA) [63,169,171]. Methanol, ethyl acetate or an acetonitrile–water mixture might be applied for the BPA and the extraction of its analogues [63,64,169,172]. In addition, acidic hydrolysis might be employed before extraction with methanol for the successful isolation of BPA, BPS, BPF and their chlorinated derivatives [171]. LC or GC coupled with MS detectors are proposed for the identification and quantification of targeted bisphenols in hair [63,64].

3. Conclusions

The great progress in instrumental analytical chemistry enables the detection of BPA and its structural analogues in different biological matrices in ng/mL or an even lower range. LLE and SPE methods coupled with GC and LC–MS/MS are the favored techniques

for the simultaneous analysis of BPs. However, microextraction techniques such as LPME and DLLE have recently gained popularity. Urine is a preferable matrix to perform biomonitoring studies regarding rapid BP extraction and is a non-invasive method of collection. Currently, not all alternatives and conjugated forms of BP can be accurately measured because there is an absence of specific analytical standards. Potential external contamination is a result of the massive use and production of BPA and its structural analogues. Additionally, the complexity of the matrix and the coextracted components might affect the method performances in terms of sensitivity, reproducibility and accuracy. The development of fast, easily operated, accessible and economic procedures suitable for the selective and sensitive on-site analysis of different BPs without complicated instrumentations should still be addressed. Hence, the development and improvement of analytical separation methods remain pivotal for conducting epidemiological and toxicological studies regarding BP exposure.

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