Sorbent-Based Microextraction of Natural Toxins from Food Samples

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Natural toxins are chemical substances that are not toxic to the organisms that produce them, but which can be a potential risk to human health when ingested through food. Thus, it is of high interest to develop advanced analytical methodologies to control the occurrence of these compounds in food products. Current trends in sample preparation involve moving towards “greener” approaches by scaling down analytical operations, miniaturizing the instruments and integrating new advanced materials as sorbents. The combination of these new materials with sorbent-based microextraction technologies enables the development of high-throughput sample preparation methods, which improve conventional extraction and clean-up procedures.

Keywords: natural toxins ; food analysis ; sample preparation ; sorbent materials ; microextraction

1. Introduction

Natural toxins are chemical substances naturally produced by living organisms (animal, plants or microorganisms) that are not toxic to them, but which can be potential health hazards to humans when ingested through food. These substances may naturally occur in food endogenously (toxic compounds that are implicit constituents of food resulting from the metabolism of a genus, species or strain, e.g., glycoalkaloids in potato or tetradotoxin in pufferfish) or exogenously (toxic compounds resulting from the metabolism of living organisms that occur in food as contaminants as they are not intentionally added, e.g., mycotoxins produced by molds grown in different products and toxins produced by algae that may be accumulated in edible marine organisms) [1][2]. The World Health Organization (WHO) encourages national authorities to monitor the most relevant natural toxins in the food supply. In this context, natural toxins of exogenous origin have received the most attention because of their potential harmful health risks and their involvement as natural contaminants. With respect to international organisms, these natural toxins of exogenous origin can be grouped in mycotoxins, phycotoxins (or marine toxins) and plant alkaloids [1][3][4]. Mycotoxins are toxic metabolites produced by certain types of molds, which can grow on a large number of foodstuffs such as cereals, dried fruits, nuts and spices. Most of these mycotoxins are chemically stable and survive food processing. The most common are aflatoxins (B1, B2, G1, G2 and M1), ochratoxins (A, B and C), patulin and fusarium toxins (deoxynivalenol, nivalenol, T-2 toxin, HT-2 toxin, zearalenone and fumonisins) [5]. On the other hand, marine toxins are produced during blooms of particular naturally occurring microalgae species in the ocean and fresh water. Thus, these toxins can be retained and bioaccumulated in shellfish and fish or contaminate drinking water. Their intake can be a potential hazard to consumers, since they are not eliminated by cooking or freezing, and might cause several adverse effects [6]. Conversely, in recent years, awareness about alkaloids of plant origin, such as pyrrolizidine, tropane and opioid alkaloids, has raised because of their occurrence as contaminants in different food products and the lack of data and knowledge about their exposure through food. These alkaloids are secondary metabolites of some plants, which can grow in fields as weeds and contaminate food crops appearing throughout the production of plant-derived products and finally be ingested, being toxic to humans [4][7][8][9][10][11][12]. The control of all these exogenous natural toxins in food is of high importance since they can cause from mild disorders (headache, vomiting, diarrhea, etc.) to serious situations (neurological disorders, carcinogenic, teratogenic or/and mutagenic effects, hepatic and renal damage, etc.) and can even be lethal. Moreover, they may cause the appearance of chronic diseases due to their harmful effects after a long-term exposure at high levels [1][2][3][4][5][6][7][8][9][10][11][12]. Therefore, food safety plays an essential role in reducing the risks related to the presence of harmful substances in food in order to protect consumers. In fact, the WHO in collaboration with the European Food Safety Authority (EFSA), the Food and Agriculture Organization (FAO) and the Codex Alimentarius Commission have established a legislation for mycotoxins and marine toxins [13][14], whereas pyrrolizidine, tropane and opioid alkaloids are in the process of being legislated, and at the moment only recommendations have been established for them [15][16][17]. In this sense, maximum residue limits (MRLs) for many of these natural toxins have been established in these guidelines to control the occurrence of these compounds in food [13][18].

Nonetheless, to achieve these limits and ensure the health of consumers it is important to develop high-throughput, sensitive and selective analytical methods to determine in a feasible way the presence of these natural toxins in foodstuffs [19]. However, the analysis of these compounds in food samples constitutes a challenging task because of the extreme complexity of these matrices, which considerably hinders the selective extraction of the target analytes and decreases the sensitivity of the method [20]. Despite significant advances in analytical instrumentation, particularly with respect to the combination of mass spectrometry and chromatographic separation, these techniques are not sensitive enough for direct analysis of complex matrices. Therefore, sample preparation is still a crucial step in food analysis in order to achieve an effective isolation and/or preconcentration of the analytes and provide an adequate clean-up of matrix interferences prior to instrumental analysis [21].

For many years, liquid-liquid extraction (LLE) and solid-phase extraction (SPE) have been the most extensively used sample preparation techniques. Due to the inherent drawbacks of LLE (such as: time-consumption, limited ability to extract polar compounds, requirement of large volumes of solvents, etc.), SPE has become more popular, as it provides more efficient recoveries and lower solvent consumption than LLE [22]. Nevertheless, current trends in sample preparation involve moving towards “greener” approaches by scaling down analytical operations and miniaturizing the instruments [23] [24]. This has led in recent years to the development of different microextraction techniques for sample preparation procedures. In this sense, the SPE technique has been the axis of improving and creating even better and greener sorbent-based sample preparation techniques, which require less time and labor than SPE, such as: miniaturized solid-phase extraction (m-SPE), micro-dispersive solid-phase extraction (µ-dSPE), microextraction by packed sorbents (MEPS), pipette-tip solid-phase extraction (PT-SPE), solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE), and micro-solid-phase extraction (µ-SPE). These sorbent-based microextraction techniques have been proposed in recent years as an alternative to conventional sample preparation techniques to meet the Green Analytical Chemistry (GAC) requirements, as they involve advantages such as minimal solvent and sample consumption, fewer treatment steps, and reduction of waste generation [25]. Thus, they enable the development of cheaper, more cost-effective, and more environmentally friendly extraction and purification procedures.

On the other hand, the synthesis of new advanced materials for their application as sorbents in sample preparation has achieved considerable progress in the last decade, since these materials can play an important role in preconcentration processes and, in some cases, provide selective extraction of the target compounds [20][21][23][26][27]. Magnetic nanoparticles (MNPs), silica-based nanomaterials, metal-organic frameworks (MOFs), multiwalled carbon nanotubes (MWCNTs) and graphene oxide (GO) are currently the most used materials for the extraction of natural toxins from food samples, as they present large surface area and advanced physicochemical properties that enhance the efficiency, selectivity and sensitivity of the analytical procedures [21][27][28][29]. Additionally, the combination of these new materials with microextraction technologies enables the development of high-throughput sample preparation methods, which provide the advantages of both strategies leading to meet the GAC requirements and improving conventional extraction and clean-up technologies [23][30].

Some works in the literature have previously reviewed the determination of several natural toxins, such as phytotoxins [27] or mycotoxins [31], in food samples and other matrices. However, these works have just focused on one type of compounds but have not considered other natural toxins. On the other hand, other published reviews have addressed the development of new materials for their application to extract or detect chemical contaminants in order to ensure food safety [27][32][33].

2. Sorbent-Based Microextraction of Natural Toxins from Food Samples

The miniaturization of conventional sample preparation procedures has been proposed as an alternative for developing analytical methods with improved analytical characteristics (accuracy, precision, sensitivity, etc.) along with a decrease in sample and solvent consumption, reduction of hazardous reagents and wastes, and saving energy and time. As a result, new formats and configurations have arisen to carry out microextraction procedures, which overcome drawbacks of conventional techniques. **Table 1** collects the most relevant works published in the last decade dealing with microextraction techniques based on sorbent-adsorption, which have been applied for the isolation of natural toxins from different food samples. In this sense, Solid-Phase Microextraction (SPME) has been the most popular [34][35][36][37][38]. However, procedures based on the dispersion of the sorbent material, such as micro-dispersive solid-phase extraction (µ-dSPE) and micro-solid-phase extraction (µ-SPE) have also been used [39][40][41]. All the works reviewed were performed for the analysis of mycotoxins (ochratoxins, aflatoxins, zearalenone, fumonisins and patulin) in different food matrices (mainly, wine, cereals and nuts). Only three of the methodologies developed in these articles perform the simultaneous determination of different types of mycotoxins [37][39][40], while the other works only described the individual determination of a specific analyte [34][35][36][38][41][42]. Concerning detection mode, mass spectrometry (MS) and fluorescence detection

(FLD) were the techniques employed to detect these natural toxins (**Table 1**). Most of these works used MS detection, which is the most suitable technique to detect the presence of contaminants in food at trace levels thanks to its high sensitivity and to its structural elucidation capability, which enables the unequivocal identification and confirmation of the target analytes. In contrast, the FLD also provides high sensitivity and selectivity, but if the analytes do not show fluorescence it is necessary to carry out a derivatization process (pre-column or post-column derivatization) for their detection, which can sometimes be time consuming.

Table 1. Application of sorbent-based microextraction techniques for isolation of natural toxins in food samples (2009–2019).

Food Matrix (Amount)	Analytes	Sample Pretreatment	Microextraction Technique	Analysis	Recovery (%)	LOD	Ref.
Cereal flours (2 g)	AF (B1, B2, G1, G2)	Extraction with 10 mL of MeOH/phosphate buffer (80/20, *v*/*v*, pH 5.8). Evaporation to dryness and reconstitution with 4 mL of phosphate buffer. An aliquot of the extract (2 mL) subject to microextraction.	SPME Sorbent: Commercial fibers Elution: 0.1 mL MeOH	HPLC-FLD	49–59	0.035-0.2 µg/Kg	[34]
Nuts, cereals, dried fruits and spices (0.5 g)	AF (B1, B2, G1, G2)	Extraction with 1 mL of MeOH/H_2O (80/20, *v*/*v*). An aliquot of the extract (0.1 mL) mixed with 0.1 mL of 50 mM Tris buffer and brought to a total volume of 1 mL with H_2O before microextraction.	In-tube SPME * Sorbent: SUPEL-Q PLOT capillary	HPLC-MS	81–109	0.0021-0.0028 µg /L	[35]
Fruit juice and dried fruit (1 mL)	PAT	-	In-tube SPME * Sorbent: Carboxen-1006 PLOT capillary	HPLC-MS	> 92	0.023 µg /L	[36]
Nut and grain samples (0.5 g)	OTA, OTB	Extraction with 1 mL of MeOH/H_2O (80/20, *v*/*v*). Defatted with 3 mL hexane, supernatant discarded. An aliquot of the clean extract (0.1 mL) brought to a total volume of 1 mL with H_2O before microextraction.	In-tube SPME * Sorbent: Carboxen-1006 PLOT capillary	HPLC-MS	88	0.089-0.092 µg /L	[37]
Wine (0.05 mL)	OTA	-	In-tube SPME * Sorbent: Luna C18 particles	HPLC-MS/MS	61–73	0.02 µg/L	[38]

Food Matrix (Amount)	Analytes	Sample Pretreatment	Microextraction Technique	Analysis	Recovery (%)	LOD	Ref.
Powdered infant milk (3 mL) and mineral waters (50 mL)	ZEN, α-ZAL, β-ZAL, α-ZEL, β-ZEL, ZAN	Extraction of milk samples with 0.15 mL acetic acid and 6 mL ACN. Evaporation up to 2.5 mL and reconstitution with H_2O to 25 mL, pH adjusted to 3.0 before microextraction.	µ-dSPE Sorbent: 80 mg of MWCNTs Elution: 30 mL MeOH/Acetone (1/1, *v*/*v*)	HPLC-MS/MS	77–120	0.05–2.02 µg/L	[39]
Peach seed, milk powder, corn flour (0.2 g) and beer (0.2 mL)	AF (B1), OTB, T-2, OTA, ZEN	Microwave assisted extraction of solid samples with 0.2 g NaCl and 5 mL MeOH/H_2O (70/30, *v*/*v*). An aliquot of the extract (0.2 mL) brought to a total volume of 5 mL with H_2O before microextraction. Liquid samples diluted with H_2O up to 5 mL before microextraction.	µ-dSPE Sorbent: 12.5 µg zirconia nanoparticles Elution: 0.1 mL MeOH	UHPLC-MS/MS	84–105	0.0022–0.017 µg/L 0.0036–0.033 µg/Kg	[40]
Coffee (10 g) and grape juice (10 mL)	OTA	Extraction of coffee samples with 100 mL of carbonate. An aliquot of the extract (10 mL) adjusted to pH 1.5 before microextraction. Grape juice samples adjusted to pH 1.5 before microextraction.	µ-SPE Sorbent: 15 mg AFFINIMIP™ OTA Elution: 0.25 mL MeOH/Acetic acid (98:2, *v*/*v*)	HPLC-FLD	91–101	0.02–0.06 µg/Kg	[41]
Wine (0.35 mL)	OTA	-	MEPS Sorbent: 4 mg C18 sorbent Elution: 0.05 mL ACN/2% Acetic Acid (90/10, *v*/*v*)	HPLC-FLD	76–108	0.08 µg/L	[42]

* Elution performed with mobile phase (online system); ACN: Acetonitrile; AF: Aflatoxin; F: Fumonisin; HPLC-FLD: High performance liquid chromatography coupled to fluorescence; HPLC-MS/MS: High performance liquid chromatography coupled to tandem mass spectrometry; HPLC-MS: High performance liquid chromatography coupled to mass spectrometry; MeOH: Methanol; MEPS: Microextraction by packed sorbent; MWCNTs: Multiwalled carbon nanotubes; OTA: Ochratoxin A; OTB: Ochratoxins B; PAT: Patulin; SPME: Solid-phase microextraction; T-2: T-2 toxin; UHPLC-FLD: Ultra High performance liquid chromatography coupled to fluorescence; UHPLC-MS: Ultra High performance liquid chromatography coupled to tandem mass spectrometry; ZAL: Zearalanol; ZAN: Zearalanone; ZEL: Zearalenol; ZEN: Zearalenone; µ-dSPE: Micro-dispersive solid-phase extraction; µ-SPE: Micro-solid-phase extraction.

3. Integration of New Advanced Materials as Sorbents on Microextraction Techniques to Isolate Natural Toxins from Food Samples

Sometimes, the commercially available microextraction techniques and sorbent materials used limit the development of the analytical methodologies. One of the crucial parameters that determine success of sample preparation is the choice of the sorbent material. Depending on the analytes to be extracted, the sorbent material must have specific characteristics that allow obtaining the highest extraction efficiency. In addition, using minimal amounts of sorbents is one of the requirements of the Green Analytical Chemistry (GAC) when developing an analytical procedure [29]. Thus, the sorbent must have advanced functional properties to be able to potentially interact with the target analytes to achieve high extraction efficiency by using minimal amounts of it. In this sense, current trends in the development of analytical methods are focused on the synthesis of new advanced materials to apply them as sorbents in sample preparation procedures. Among these materials, magnetic nanoparticles (MNPs), silica-based nanomaterials, metal-organic frameworks (MOFs), multiwalled carbon nanotubes (MWCNTs) and graphene oxide (GO) have been the most employed for the extraction of natural toxins from food products (**Table 2**). The advanced properties of these materials, such as their large surface area, low resistance to diffusion, fast sorption kinetics and large adsorptive capability make them very suitable for sample preparation, as they improve the efficiency, selectivity and sensitivity of the analytical procedures. Moreover, the integration of these new materials in microextraction technologies enables developing high-throughput analytical methods with the advantages of both strategies. Thanks to this integration, conventional and commercially available procedures can be improved and GAC requirements can be accomplished. In this sense, in the last decade, different new materials have been used to extract natural toxins from food products by their combination with different microextraction techniques, such as m-SPE, in-syringe SPE, PT-SPE, µ-dSPE, µ-MSPE, µ-SPE, SPME and SBSE (**Table 2**). They have proved their efficiency in the extraction of several mycotoxins (mainly aflatoxins, ochratoxins, patulin and zearalenone) and marine toxins, which have been mainly extracted from cereals, drinks, dairy products and seafood (**Table 2**). Sometimes, these sorbent materials lack or have little selectivity during the extraction procedure, leading to the extraction of matrix interferences along with the analyte that may hinder its detection. To overcome this problem, MIPs can be synthesized as sorbents by polymerization processes [30]. In this sense, different MIPs have been applied in m-SPE, µ-MSPE and SBSE for the extraction of patulin, T-2 toxin, fumonisin, aflatoxins and ochratoxins from food samples (**Table 2**). Nevertheless, when developing multicomponent methods to simultaneously extract different compounds belonging to different chemical families in a single run, the lack of selectivity of the materials is desirable, since in this case the sorbent must be able to extract a wide range of compounds. Therefore, in these cases specificity is not required. On the other hand, the analytical procedures published in the last decade, which integrate new materials in microextraction techniques for the extraction of natural toxins from food, have been mainly combined with the detection of analytes by HPLC coupled to MS or FLD, and to a lesser extent with ultraviolet detection (UV), such as the diode array detection (DAD) (**Table 2**). In contrast, there are no works using GC as a separation technique instead of HPLC. Indeed, for the analysis of these natural toxins, it is more suitable to use HPLC, since they are not very volatile compounds. Therefore, sometimes, to achieve their analysis by GC it is necessary to perform a derivatization process, which is more complex and time consuming than the determination by HPLC.

Table 2. Application of new advanced materials on sorbent-based microextraction techniques to isolate natural toxins from food samples (2009–2019).

Food Matrix (Amount)	Analytes	Sample Pretreatment	Microextraction Technique	Analysis	Recovery (%)	LOD	Ref.
Cereals (5 g)	AF (B1, B2, G1, G2)	Extraction with 25 mL of MeOH/H_2O (80/20, *v*/*v*). Evaporation of the methanolic fraction of an aliquot of the extract (15 mL). Addition of Britton-Robinson buffer (pH 5.2) up to 3 mL. An aliquot of the extract (2 mL) subject to microextraction.	m-SPE Sorbent: 50 mg hyperbranched polymer Elution: 0.2 mL ACN	HPLC-FLD	83–103	0.012–0.120 µg/Kg	[43]
Apple juice (1 mL)	PAT	-	m-SPE Sorbent: 30 mg CD-based polymers Elution: 1 mL Diethyl ether/ACN (4/1, *v*/*v*)	HPLC-DAD	n.p.	n.p.	[44]
Apple juice (1 mL)	PAT	Dilution with 1 mL of H_2O before microextraction.	m-SPE Sorbent: 50 mg SiO_2maleicpolymer@MIP Elution: 5 mL de acidified ACN	HPLC-DAD	82–98	8.6 µg/L	[45]
Apple, apple juice, hawthorn, hawthorn juice, mixed juice, wines and tomato (10 g)	PAT	Extraction with 10 mL of ACN, 4 mg $MgSO_4$ and 1 g NaCl. An aliquot of the extract (1 mL) evaporated to dryness and reconstituted with 1 mL H_2O before microextraction.	m-SPE Sorbent: 30 mg dual dummy-MIP Elution: 3 mL MeOH	HPLC-MS/MS	81–106	0.05–0.2 µg/Kg	[46]

Food Matrix (Amount)	Analytes	Sample Pretreatment	Microextraction Technique	Analysis	Recovery (%)	LOD	Ref.
Bell pepper, rice and corn flakes (1 g)	F (B1, B2, B3)	Extraction with 6 mL ACN/H_2O (84/16, *v*/*v*). An aliquot of the extract (1 mL) evaporated to dryness and reconstituted with 1 mL ACN/H_2O (90/10, *v*/*v*) before microextraction.	m-SPE Sorbent: 20 mg MIP Elution: 1 mL MeOH/Acetic acid (95/5, *v*/*v*)	HPLC-MS/MS	62–86	4.5–44 µg/Kg	[47]
Maize, barley and oat (5 g)	T-2	Extraction with 25 mL of ACN/H_2O (84/16, *v*/*v*). For oat samples, after the solid-liquid extraction, the extract was additionally defatted with 10 mL of hexane. An aliquot of the sample extracts (1 mL) evaporated to dryness and reconstituted with 1 mL MeOH/H_2O (20/80, *v*/*v*) before microextraction.	m-SPE Sorbent: 50 mg MIP Elution: 3 mL MeOH/Acetic acid (95/5, *v*/*v*)	HPLC-MS/MS	60–73	0.4–0.6 µg/Kg	[48]
Milk (1 mL)	AF (B1, M1), OTA, ZEN, α-ZEL, β-ZEL, ZAN, α-ZAL, β-ZAL	Extraction with 5 mL ACN with 0.1% formic acid. Supernatant of the extract evaporated to dryness and reconstituted with 0.5 mL ACN/H_2O (20/80, *v*/*v*) and diluted up to 5 mL with 5 mL of H_2O before microextraction.	m-SPE Sorbent: 10 mg rGO/Au Elution: 5 mL MeOH/ACN/Formic acid (50/49/1, *v*/*v*/*v*)	UHPLC-MS/MS	70–111	0.01–0.07 ng/mL	[49]
Soy-based foods (2 g)	AF (B1, B2, G1, G2)	Extraction with 10 mL ACN/H_2O (75/25, *v*/*v*). Diluted up to 50 mL with 10% NaCl aqueous solution before microextraction.	In syringe SPE Sorbent: 30 mg 3DG@Fe_3O_4 Elution: 0.7 mL MeOH	HPLC-FLD	83–103	0.09–0.15 µg/Kg	[50]

Food Matrix (Amount)	Analytes	Sample Pretreatment	Microextraction Technique	Analysis	Recovery (%)	LOD	Ref.
Soy-based foods (2 g)	AF (B1, B2, G1, G2)	Extraction with 10 mL ACN/H_2O (75/25, *v*/*v*). Diluted up to 50 mL with 7% NaCl aqueous solution before microextraction.	In syringe SPE Sorbent: PU/GO nanofibers Elution: 0.75 mL MeOH	HPLC-FLD	76–101	0.09–0.15 µg/Kg	[51]
Maize (5 g)	AF (B1, B2, G1, G2)	Extraction with 20 mL ACN/H_2O (80/20, *v*/*v*). Evaporation to dryness and reconstituted with 0.1 mL MeOH. Diluted up to 10 mL with H_2O before microextraction.	In syringe SPE Sorbent: 15 mg β-CDPG Elution: 2 mL MeOH/DCM (2/1, *v*/*v*)	HPLC-FLD	91–105	0.0075–0.030 µg/Kg	[52]
Shellfish (0.2 g)	YTX, OA, DTX (1), GYM, SPX (1), PTX (2), AZA (1)	Extraction with 9 mL MeOH. An aliquot of the extract (0.1 mL) evaporated to dryness and reconstituted with 0.2 mL H_2O before microextraction.	PT-SPE Sorbent: 2 mg graphene Elution: 2 mL ACN with 0.5% ammonium hydroxide (for basic conditions) or with 0.5% formic acid (for acid conditions)	HPLC-MS/MS	78–90	0.1–1.5 µg/Kg	[53]
Peanut (50 g)	AF (B1, B2, G1, G2)	Extraction with MeOH/H_2O (80/20, *v*/*v*). An aliquot of the extract (8 mL) diluted with H_2O before microextraction.	µ-dSPE Sorbent: 5 mg GO Elution: 2 mL MeOH	HPLC-FLD	85–101	0.08–0.65 µg/Kg	[54]

Food Matrix (Amount)	Analytes	Sample Pretreatment	Microextraction Technique	Analysis	Recovery (%)	LOD	Ref.
Milk and yogurt (1.5 mL)	ZEN, α-ZEL, β-ZEL, ZAN, α-ZAL, β-ZAL	Extraction of milk samples with 3 mL ACN and 0.075 mL acetic acid. Evaporation of the supernatant until 1.5 mL and diluted with H_2O up to 25 mL, pH adjusted to 7 before microextraction. Extraction of yogurt samples with 4.5 mL and 0.075 mL acetic acid. The rest of the procedure the same as for milk samples.	µ-MSPE Sorbent: 80 mg Fe_3O_4@pDA Elution: 8 mL MeOH	HPLC-MS/MS	70–120	0.21–4.77 µg/L	[55]
Mineral and tap water (25 mL)	ZEN, α-ZEL, β-ZEL, ZAN, α-ZAL, β-ZAL	Adjustment of pH to 7 before microextraction.	µ-MSPE Sorbent: 60 mg Fe_3O_4@pDA NPs Elution: 6 mL MeOH	HPLC-MS/MS	70–119	0.02–1.1 µg/L	[56]
Red wine (50 mL)	AF (B1, B2, G1, G2)	-	µ-MSPE Sorbent: 4.4 mg PD-MNPs Elution: 0.25 ACN/MeOH (1/1, *v*/*v*)	HPLC-MS/MS	97–108	0.0012–0.0031 µg/L	[57]
Milk and dairy products (5 mL)	AF (M1)	Extraction with 5 mL hexane and 5 mL MeOH/2 mM NaCl aqueous solution (8/2, *v*/*v*) before microextraction.	µ-MSPE Sorbent: 8 mg AMNPs Elution: 2 mL DCM/MeOH/Acetic acid (80/19/1, *v*/*v*/*v*)	HPLC-FLD	97–116	0.2 ng/L	[58]
Shellfish (2 g)	AZA (1, 2, 3), OA, DTX (1, 2)	Extraction with 10 mL MeOH/H_2O (4/1, *v*/*v*). The supernatant mixed with 2 mL hexane, evaporated until 1 mL and addition of 4 mL of H_2O before microextraction.	µ-MSPE Sorbent: 50 mg MMM Elution: 2 mL Formic acid/MeOH (5/95, *v*/*v*)	UHPLC-MS/MS	83–119	0.4–1.0 µg/Kg	[59]

Food Matrix (Amount)	Analytes	Sample Pretreatment	Microextraction Technique	Analysis	Recovery (%)	LOD	Ref.
Maize (6 g)	ZEN, α-ZEL, β-ZEL, ZAN, α-ZAL, β-ZAL	Extraction with 24 mL of ACN/H_2O (75/25, *v*/*v*). The extract diluted up to 25 mL with H_2O before microextraction.	µ-MSPE Sorbent: 5 mg MNPs-MWCNT-nanoC18 Elution: 1 mL ACN	HPLC-MS	92–98	0.6–1.0 µg/mL	[60]
Rice, wheat and sesame (50 g)	AF (B1, B2, G1, G2)	Extraction of rice and wheat samples with 200 mL Acetone/H_2O (50/50, *v*/*v*). Elimination of the acetone fraction before microextraction. Extraction of sesame samples with 100 mL hexane and 200 mL Acetone/H_2O (50/50, *v*/*v*). The rest of the procedure the same as for rice and wheat samples.	µ-MSPE Sorbent: 10 mg MGNP Elution: 2 mL Acetone/H_2O (1/1, *v*/*v*)	HPLC-FLD	64–122	0.025–0.075 µg/Kg	[61]
Apple juice (5 g)	PAT	Extraction with 5 mL ethyl acetate/hexane (96/4, *v*/*v*), 1 g NaH_2PO_4 and 5 g Na_2SO_4. An aliquot of the organic phase (3 mL) mixed with 0.02 mL acetic acid, evaporated to dryness and reconstituted with 2 mL H_2O at pH 6.2 before microextraction.	µ-MSPE Sorbent: 30 mg MGO Elution: 1 mL ACN	HPLC-UV	69–83	2.3 µg/Kg	[62]
Milk (20 mL)	AF (B1, B2, G1, G2)	-	µ-MSPE Sorbent: 90 mg M/ZIF-8 Elution: 1 mL ACN/DCM (1/1, *v*/*v*)	UHPLC-MS/MS	79–102	2.3–8.1 ng/L	[63]

Food Matrix (Amount)	Analytes	Sample Pretreatment	Microextraction Technique	Analysis	Recovery (%)	LOD	Ref.
Seafood (5 g)	DA	Extraction with 20 mL MeOH/H_2O (1/1, *v*/*v*). The resultant sample extract subjected to microextraction.	µ-MSPE Sorbent: 1 mg Fe_3O_4 SPs@ZIF8/Zn^{2+} Elution: 0.4 mL 3 mM histidine solution	HPLC-MS/MS	93−102	0.2 ng/L	[64]
Shellfish samples (5 g)	DA	Extraction with 20 mL MeOH/H_2O (1/1, *v*/*v*). The resultant sample extract brought to a total volume of 25 mL with MeOH/H_2O (1/1, *v*/*v*) before microextraction.	µ-MSPE Sorbent: 1 mg Fe_3O_4@SiO_2@UiO-6 Elution: 1.5 mL ACN with 20% acetic acid	HPLC-MS/MS	91–107	1.45 µg/L	[65]
Beer (6 mL)	DON, ZEN, AF (B1, B2, G1, G2), F (B1)	Clean-up with a C18 sorbent. An aliquot of the clean sample (0.1 mL) evaporated to dryness and reconstituted with 0.48 mL ACN/H_2O/acetic acid (49/50/1, *v*/*v*/*v*) before microextraction.	µ-MSPE Sorbent: 25 mg MNM Elution: 0.5 mL ACN/H_2O/acetic acid (79/20/1, *v*/*v*/*v*)	UHPLC-MS/MS	87	n.p.	[66]
Corn (25 g)	AF (B1, B2, G1)	Extraction with 5 g NaCl and 125 mL MeOH/H_2O (7/3, *v*/*v*). An aliquot of the extract (15 mL) mixed with 45 mL of PBS before microextraction.	µ-MSPE Sorbent: 80 mg MNPC Elution: 1.2 mL ACN/H_2O (6/4, *v*/*v*).	HPLC-FLD HPLC-MS/MS	75–99	0.05–0.07 µg/L	[67]
Tea leaves and corn (5 g)	AF (B1, B2, G1, G2)	Extraction with 10 mL ACN/H_2O (60/40, *v*/*v*). 5 mL of the extract subjected to microextraction.	µ-MSPE Sorbent: 10 mg MMIP Elution: 1 mL ACN/formic acid (95/5, *v*/*v*).	UHPLC-MS/MS	76–95	0.05–0.1 µg/Kg	[68]

Food Matrix (Amount)	Analytes	Sample Pretreatment	Microextraction Technique	Analysis	Recovery (%)	LOD	Ref.
Rice (25 g) and wine (20 mL)	OTA, OTB, OTC	Extraction of rice samples with 100 mL ACN/H_2O (60/40, *v*/*v*) before microextraction. Wine samples diluted up to 25 mL with a solution of 2.5 M NaCl and 0.24 M $NaHCO_3$ before microextraction.	µ-MSPE Sorbent: 15 mg Fe_3O_4@PDA MIPs Elution: 1 mL ACN	HPLC-FLD	71–88	0.0018–0.018 µg/Kg	[69]
Grape juice	OTA	-	µ-MSPE Sorbent: 5 mg MMIP Elution: -	UV–vis	97	0.374 mg/L	[70]
Coffee (10 g) and cereals (5 g)	OTA	Extraction with 10 mL 1% carbonate aqueous solution. Sample extract adjusted to pH 1.5 before microextraction.	µ-SPE Sorbent: 10 mg LTL Elution: 0.4 mL MeOH	HPLC-FLD	92–101	0.09–0.3 µg/Kg	[71]
Cheese (0.05 g)	OTA	-	SPME Sorbent: Carbon-tape fiber Elution: 0.15 mL MeOH	HPLC-MS/MS	93	1.5 µg/L	[72]
Rice and wheat (10 g)	AF (B1, B2)	Extraction with 1 g NaCl and 100 mL MeOH/H_2O (80/20, *v*/*v*). Evaporation of the methanolic fraction of the extract and diluted with 40 mL H_2O. An aliquot of the extract (25 mL) subject to microextraction.	SPME Sorbent: 50 mg CNT Elution: 2 mL MeOH	HPLC-DAD	47–103	0.061–0.074 µg/L	[73]

Food Matrix (Amount)	Analytes	Sample Pretreatment	Microextraction Technique	Analysis	Recovery (%)	LOD	Ref.
Rice (2 g)	AF (B1), ZAN, STEH	Extraction with 10 mL ACN/MeOH/H_2O (51/9/40, *v*/*v*/v), 1.5 g $MgSO_4$ and 0.5 g NaCl. Evaporation to dryness and reconstituted with 3 mL 0.1% TFA/ACN (99/1, *v*/*v*) before microextraction.	SPME in-tube * Sorbent: MAA-co-DVB Elution:-	HPLC-PDA	78–103	0.69–2.03 µg/Kg	[74]
Milk (1 g) and baby foods (3 g)	AF (B1, B2, G1, G2, M1)	Extraction of milk samples with 3 mL 1% formic acid solution. Supernatant discarded and solid residue extracted with 6 mL chloroform. Evaporation to dryness and reconstitution with 4 mL H_2O before microextraction. Baby food samples dissolved with 1% formic acid solution. Supernatant discarded and solid residue extracted with 18 mL chloroform. Evaporation to dryness and reconstitution with 6 mL H_2O before microextraction.	SBSE Sorbent: 0.5 g MMIP-SB Elution: 3 mL MeOH/acetic acid (75/25, *v*/*v*)	HPLC-MS/MS	39–60	0.3–1.0 ng/Kg	[75]

* Elution performed with mobile phase (online system); ACN: Acetonitrile; AF: Aflatoxin; AMNPs: Aptamer-functionalized magnetic nanoparticles; AZA: Azaspiracid; CD: Cyclodextrin; CNT: Carbon nanotube; DA: Domoic acid; DAD: Diode array detector; DCM: Dichloromethane; DON: Deoxynivalenol; DTX: Dinophysistoxin; F: Fumonisin; Fe_3O_4 SPs@ZIF8/Zn^{2+}: Modified magnetic zeolite imidazolate framework-8; Fe_3O_4@PDA MIPs: Magnetic polydopamine-based molecularly imprinted polymer; Fe_3O_4@pDA NPs: Core–shell polydopamine magnetic nanoparticles; Fe_3O_4@SiO_2@UiO-6: Magnetite@silica core-shell magnetic microspheres; FLD: Fluorescence; GO: Graphene oxide; GYM: Gymnodimine; HPLC: High performance liquid chromatography; LTL: Zeolites linde type; M/ZIF-8: Magnetic zeolite imidazolate framework-8; MAA-co-DVB: Methacrylic acid-co-divinyl-benzene; MeOH: Methanol; MEPS: Microextraction by packed sorbent; MGNP: Magnetic-graphene nanoparticles; MGO: Magnetic graphene oxide; MIP: Molecular imprinted polymer; MMIP: Magnetic molecularly imprinted polymer; MMIP-SB: Magnetic molecularly imprinted stir-bars; MMM: Magnetic mesoporous microspheres; MNM: Magnetic nanostructured materials; MNPC: Magnetic nanoporous carbon; MNPs: Magnetic nanoparticles; MS: Mass spectrometry; MS/MS: Tandem mass spectrometry; m-SPE: Miniaturized solid phase extraction; MWCNTs: Multiwalled carbon nanotubes; n.p.: Not provide; OA: Okadaic acid; OTA: Ochratoxin A; OTB: Ochratoxin B; OTC: Ochratoxin C; PAT: Patulin; PBS: Phosphate buffer saline; PDA: Photodiode array; PD-MNPs:

Polydopamine magnetic nanoparticles; PT-SPE: Pipette-tip solid phase extraction; PTX2: Pectenotoxin-2; PU: Polyurethane; rGO: Reduced Graphene oxide; SBSE: Stir-bar sorptive extraction; SPE: Solid-phase extraction; SPME: Solid-phase microextraction; SPX1: Spirolides-1; STEH: Sterigmatocystin; TFA: Trifluoroacetic acid; T-2: T-2 toxin; UHPLC: Ultra high performance liquid chromatography; UV/vis: Ultraviolet/visible; YTX: Yessotoxins; ZAL: Zearalanol; ZAN: Zearalanone; ZEL: Zearalenol; ZEN: Zearalenone; β-CDPG: β-cyclodextrin supported on porous graphene nanohybrid; μ-dSPE: Micro-dispersive solid-phase extraction; μ-MSPE: Micro-magnetic solid-phase extraction; μ-SPE: Micro-solid-phase extraction; 3DG@Fe_3O_4: Magnetic three-dimensional graphene sorbent.

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