ISSN 1061-9348, Journal of Analytical Chemistry, 2024, Vol. 79, No. 3, pp. 241–261. © Pleiades Publishing, Ltd., 2024.

REVIEWS

The article is dedicated to the 300th anniversary of St. Petersburg State University

Microextraction Separation and Preconcentration of Mycotoxins for Their Determination in Food Products

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Received June 3, 2023; revised July 21, 2023; accepted July 25, 2023

Abstract—Mycotoxins are among the most dangerous natural food contaminants. The review considers the principles of microextraction methods (liquid–liquid and solid-phase microextraction) used for the separation and preconcentration of mycotoxins from food products for their subsequent determination by various physicochemical methods of analysis. The capabilities and limitations of the considered methods, as well as examples of their application, are described.

Keywords: microextraction, mycotoxins, food products

DOI: 10.1134/S1061934824030109

Mycotoxins (from the Greek "mukes"—mushroom and "toxicon"—poison) are secondary metabolites of microscopic molds with pronounced toxic properties. Currently, many genera of molds are known (*Aspergillus*, *Penicillium*, *Fusarium*, *Claviceps*, *Neotyphodium*, *Myrothecium*, *Stachybotrys*, *Trichoderma*, and *Trichothecium*), producing more than 400 different types of toxins with diverse chemical structures [1]. Mycotoxins are distributed almost everywhere and can be found in the regions with both temperate and tropical climates, depending on the type of the fungi producing them. The most common targets for the fungal growth and the formation of toxins are cereals, dried fruits, nuts, beans, fruits, spices, and other food products.

Mycotoxins pose a serious risk to human and animal health [1]. Mycotoxins enter a human body as a result of eating food products of plant or animal origin contaminated with them, and animal bodies get mycotoxins with feed contaminated by them. Entering a body, such toxins cause a change in the composition of the microflora in the intestines, and when absorbed in the gastrointestinal tract, they have a negative effect on cells, organs, tissues, and the physiological state of humans and animals and provoke cancer and immunodeficiency.

Because of the negative impact of mycotoxins on the animal and human health, the quality of food raw materials, food products, and feed is currently monitored to identify these toxicants. In the Russian Federation and other countries, the maximum permissible concentrations of mycotoxins in various food products have been established, which vary from 0.025 to 1000 μg/kg [2–5].

Currently, chromatographic [6, 7] and immunochemical methods of analysis [8] are most widely used to determine mycotoxins in food products; less commonly, electrophoretic [9, 10] and fluorimetric [11] analysis is used (Fig. 1). Among the chromatographic methods, the most common is high-performance liquid chromatography in the reversed-phase version with photometric detection in the ultraviolet and visible spectral regions (**HPLC-UV**) [12–15], fluorimetric (**HPLC-FL**) detection [16–19], or tandem mass spectrometric detection (**HPLC-MS/MS**) [20–23]. The last two methods provide high sensitivity and selectivity with respect to the mycotoxins being determined. If the analytes do not absorb light in the ultraviolet and visible spectrum regions to a sufficient extent to achieve the required limits of detection or do not have intrinsic fluorescence, pre- [24] or post-column [25] derivatization is carried out for HPLC-UV and HPLC-FL analyses.

Food products are samples with complex matrices; therefore, in determining mycotoxins in them, sample preparation, as a rule, includes procedures for elimi-

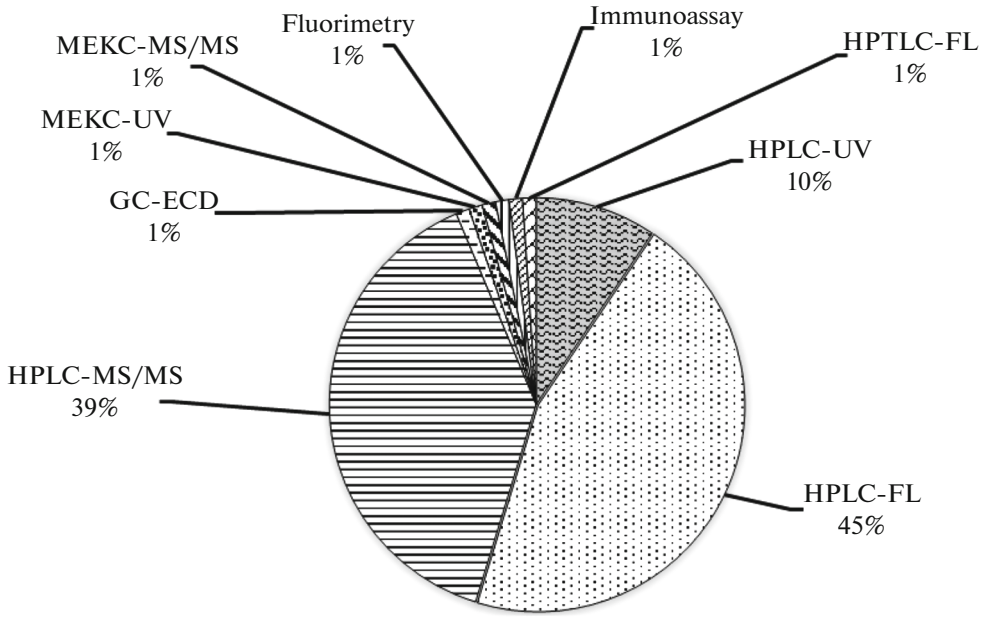

Fig. 1. Distribution of the number of publications published in 2000–2023, according to the analysis methods used (GC-ECD—gas chromatography with an electron capture detector; MEKC—micellar electrokinetic chromatography).

nating the interfering effects of matrix components and preconcentrating the analytes. To isolate trace amounts of mycotoxins from food, liquid–liquid and solid-phase extraction methods are most in demand [6, 26]. Recently, liquid–liquid (**LLME**) and solid-phase (**SPME**) microextraction (**ME**) methods have been rapidly developed, which make it possible to miniaturize the sample preparation stage and differ from the traditional methods in small volumes of the extractant and small amounts of the sorbent, and in some cases also in a higher rate of establishment of an interfacial equilibrium [26–30]. Microextraction is widely used to determine trace concentrations of mycotoxins in food products using modern analytical methods. This is confirmed by the growing number of publications (Fig. 2) on the use of ME methods for the determination of mycotoxins in food products. Among the LLME methods, dispersive (**DLLME**), membrane-based (**MLLME**), and supramolecular solvent-based (**ME into SUPRAS**) microextraction are popular, with the overwhelming number of works devoted to DLLME (Fig. 3). Single-drop ME (**SDME**) is much less frequently used. Among the SPME methods, dispersive, in-tube, and fiber-based SPME are most commonly used.

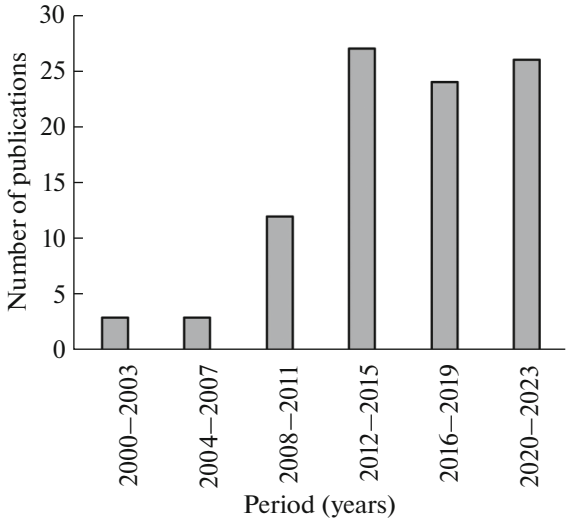

Fig. 2. Number of publications devoted to microextraction separation of mycotoxins from food products, published since 2000 (based on a search of literary sources in the Russian scientific electronic library eLibrary and the Scopus database).

This review considers methods for the LLME and SPME of mycotoxins from food products for their determination using various physicochemical methods of analysis. The review was prepared on the basis of publications published between 2000 and 2023 in periodical journals and presented in the databases of the Russian Scientific Electronic Library (elibrary.ru) and Scopus.

LIQUID–LIQUID MICROEXTRACTION

The DLLME method is widely used for the separation and preconcentration of mycotoxins from food samples. In DLLME, a mixture of a non-polar

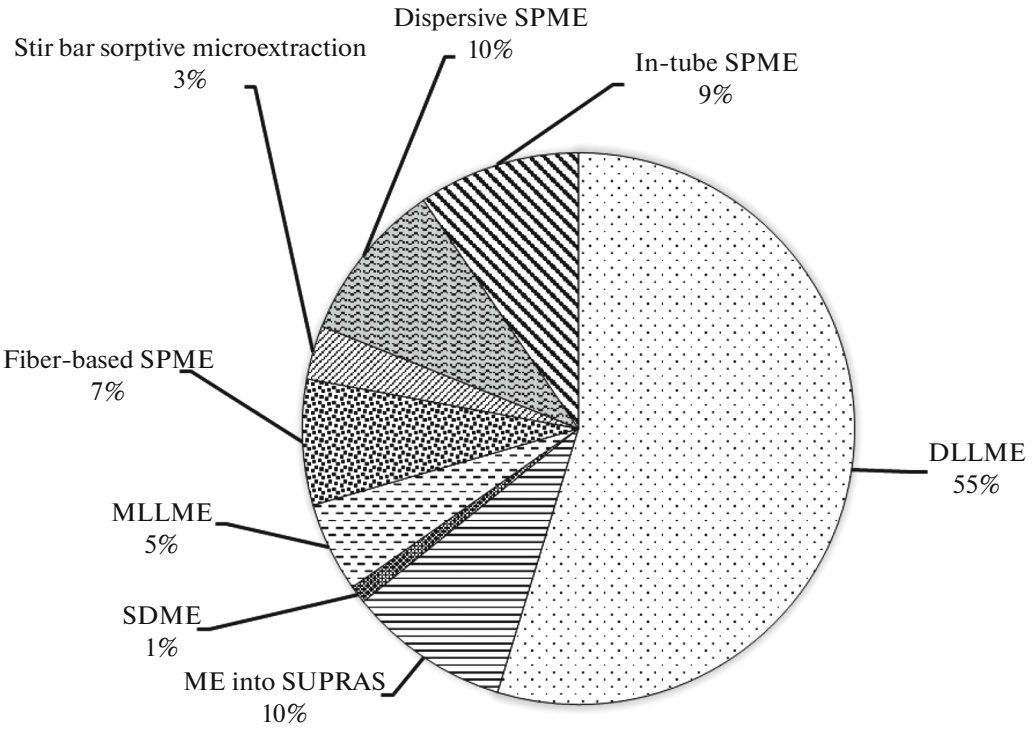

Fig. 3. Distribution of the number of publications published in 2000–2023, according to the liquid and solid-phase microextraction methods used.

extractant and a polar solvent (dispersant) is introduced into an aqueous solution being analyzed, as a result of which the extractant phase is evenly distributed in the aqueous phase as a fine emulsion [27]. The formation of a hydrophilic emulsion leads to a significant acceleration of mass transfer and the rapid (in no more than 1 min) establishment of an interfacial equilibrium due to the large phase contact area. After centrifugation, the extract is collected and analyzed. As a rule, liquid chromatography methods are used. Sometimes, to simplify the selection of an extract, extractants with low melting points are used (e.g., *n*-dodecanol with a melting point of 24°C) and their crystallization is carried out while cooling the extraction system [12]. In addition, a possibility of using magnetite magnetic nanoparticles (**MNP**) coated with a medium-chain carboxylic acid to separate the extract phase without centrifugation in determining aflatoxin M_1 in milk samples by the fluorimetric method in the presence of a nonionic surfactant Triton X-110 was shown [11]. The DLLME method has found application for preconcentrating the most common and dangerous mycotoxins (ochratoxin A [20, 31–34], patulin [9, 13, 14], deoxyvalenol [21], sterigmatocystin [20, 21], aflatoxins [16, 17, 20, 24, 35, 36], trichothecenes [37], fumonisins [20, 21], zearalenone [20, 38–40], citrinin [20], nivalenol [37]) from liquid foods and extracts from solid matrices. Aromatic (toluene [41]) and chlorine-containing organic solvents (chloroform [17, 24, 42], dichloromethane [37], trichloromethane [16]), fatty alcohols (*n*-heptanol [11], *n*-dodecanol [12]) and ethyl acetate [38, 43] are most often used as mycotoxin extractants, and methanol [21], acetonitrile [38], acetone [44], and isopropanol [9] are used as dispersants. If the extract is incompatible with the analytical equipment used to determine analytes, back extraction is carried out into a solvent immiscible with it (e.g., into the aqueous phase) [45] or the extract is evaporated with the further dissolution of the dry residue (solvent replacement) for the subsequent analysis [31]. For example, in [21], 13 mycotoxins were determined in rice bran using HPLC-MS/MS after extracting the analytes from the sample into an aqueous-organic mixture and preconcentrating them by the DLLME method in chloroform. The extract was evaporated in a stream of nitrogen and the dry residue was dissolved in the aqueous component of the mobile phase for the subsequent chromatographic analysis.

It is worth noting that the DLLME method allows one to achieve high preconcentration factors due to the use of a small volume of an extractant, which makes it the most effective for preconcentrating trace amounts of mycotoxins from food. However, there is a problem of reducing the distribution coefficients of analytes between the phases of the aqueous solution of a sample and the extractant in the presence of a disper-

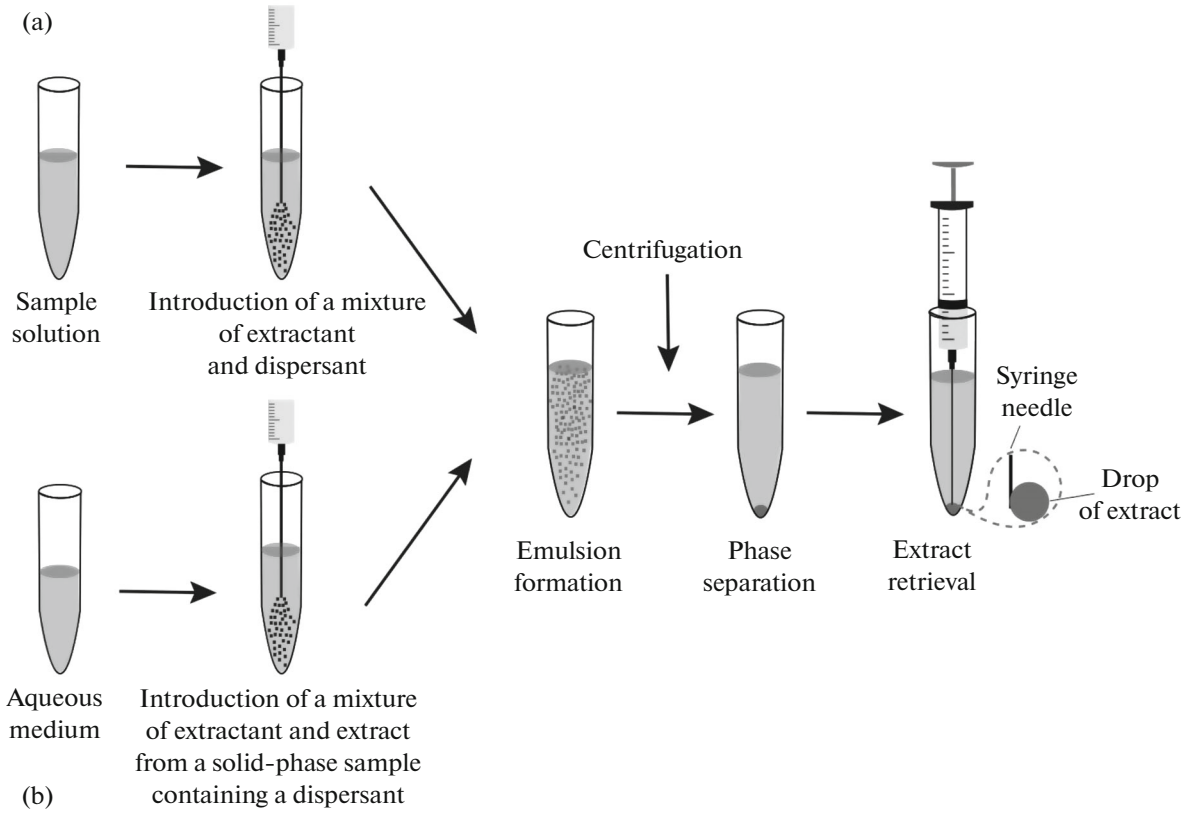

Fig. 4. Scheme of dispersive liquid–liquid microextraction when concentrating mycotoxins from an aqueous solution of a sample (a) or an extract from a solid-phase sample (b).

sant, which is associated with the higher solubility of mycotoxins in a mixture of a polar solvent and an aqueous solution compared to that in the initial aqueous solution. Currently, other methods for dispersing extractants that make it possible to partially or completely eliminate the use of dispersants, but require additional equipment were proposed. Among them are ultrasonic-assisted dispersion [12], alternate pumping from one syringe to another [15], or the use of a vortex mixer [44]. To isolate mycotoxins differing in polarity, double DLLME was proposed. Mycotoxins from the sample were extracted into the first extractant (e.g., ethyl acetate) in the presence of the first dispersant (e.g., acetonitrile), and then a mixture of the second extractant (e.g., chloroform) with the second dispersant (e.g., methanol) was added to the sample phase [38]. A disadvantage of this method is the dilution effect in mixing two extracts.

In determining mycotoxins in liquid samples predominantly consisting of water and containing small amounts of hydrophobic components (tea-based drinks [38], alcoholic drinks [31, 34, 44, 46, 47], juices [9, 13]), sample preparation may be minimal: e.g., ultrasonic degassing for malt alcoholic carbonated drinks [31] or filtration for wines [34] in determining ochratoxin A by HPLC-FL and high-performance thin-layer chromatography with fluorimetric detection (**HPTLC-FL**); centrifugation, filtration, and dilution of the filtrate with deionized water to analyze apple juice for patulin content using HPLC-UV [13] or micellar electrokinetic chromatography with photometric detection (**MEKC-UV**) [9]; adding a salting-out agent (sodium chloride) to the aqueous extract from black, red, or green tea leaves for the HPLC-MS/MS determination of a number of mycotoxins [38]. To carry out DLLME and extract analytes, a mixture of an extractant and a dispersant is introduced into prepared aqueous sample solutions (Fig. 4a).

The analysis of milk [11, 16, 35] and liquid dairy products [35, 43] is often difficult because of the interfering effect of matrix components (fats and proteins); therefore, a polar solvent (e.g., acetonitrile) containing acetic acid or sodium chloride [35] is added to the sample [48] to precipitate proteins, and *n*-hexane is added to remove fats [48]. The polar solvent phase serving as a dispersant is removed, an extractant is added to it, and the mixture is added to wtaer to preconcentrate the analytes. A more sophisticated approach was used to separate zearalenone from milk and yogurt samples before its determination by micel-

lar electrokinetic chromatography with tandem mass spectrometric detection (**MEKC-MS/MS**). It consisted of removing the polar solvent by evaporation and dissolving the analytes in an aqueous solution of sodium chloride for the further DLLME [48]. In the case of edible oils [17], a liquid–liquid extraction of analytes (aflatoxins B_1, B_2, G_1, and G_2) was carried out into an aqueous-organic medium (a mixture of methanol, water, and sodium chloride); the analytes were sorbed on an immunoaffinity column and eluted with a polar solvent; and the eluate then acted as a dispersant in DLLME before the HPLC-FL determination of the analytes.

The DLLME method is also actively used for preconcentrating analytes from extracts obtained after extraction from solid matrices (wheat, rice, corn, and barley grains [24, 36], legumes [42], rice bran [21], sesame, apricot and lychee kernels [12], amaranth seeds [45], dried fruits [33], cheese [16]) into a polar solvent or its mixture with water. A hydrophobic extractant is added to the resulting extract and the resulting mixture is introduced into an aqueous medium to form a finely-dispersed emulsion (Fig. 4b). DLLME can also be combined with the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method. Extraction from a food product sample into a mixture of a polar solvent with water, extraction with salting out of the extractant, and separation of matrix components from the extract using a sorbent (e.g., silica with anion exchange and octadecyl groups) were performed [16, 37]. Thus, it was proposed to separate aflatoxins B_1, B_2, G_1, and G_2 from grain and feed samples using the QuEChERS method, preconcentrate them from the extract using DLLME in chloroform followed by the evaporation of the extractant in a stream of nitrogen, and then obtain iodine derivatives of the analytes (luminophores) in a methanol solution of iodine for an HPLC-FL analysis with limits of detection in the range 0.08–0.1 μg/kg [24]. A combination of the QuEChERS and DLLME methods was also used in the determination of trichothecene mycotoxins (T-2 and HT-2 toxins, deoxynivalenol and nivalenol) in grain and mixed feed using gas chromatography with an electron capture detector [37]. Volatile trifluoroacetyl derivatives of the target analytes were prepared using trifluoroacetic anhydride. The limits of detection ranged from 10 to 50 μg/kg. A method for the DLLME of deoxyvalenol and its deoxymetabolite from extracts of corn grains and pork was described in [49]. The analytes were extracted from solid samples into ethyl acetate (dispersant), after which they were mixed with *n*-hexane and the aqueous phase was introduced. Hydrophilic analytes passed into the aqueous phase, which was used for an HPLC-MS/MS analysis. The limits of detection ranged from 4 to 6 μg/kg.

One of directions for the development of LLME is the search for selective and environmentally friendly extractants [50]. Ionic liquids (**ILs**), deep eutectic solvents (**DESs**) and SUPRASs have been proposed as "designer" extractants, the composition of which can be varied depending on the task at hand.

Ionic liquids consist of an organic cation and an anion, are in a liquid state at room temperature and possess chemical and thermal stability and low volatility [51–53]. At the moment, a few studies have been published concerning the use of ILs for the DLLME of zearalenone, ochratoxin A, and aflatoxins from beer [39], wheat and corn grains [39, 54], wines [32, 55] and tea leaves [56] for the subsequent determination of analytes by HPLC-FL. In all the presented works, the extractants are hydrophobic imidazolium ILs: 1-hexyl-3-methylimidazolium hexafluorophosphate [32, 54, 55], 1-butyl-3-methyl- and 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imides [39], and also a salt of the 1-butyl-3-methylimidazolium cation and the $[FeCl_2Br_2]^-$ complex anion [56]. In the latter case, the ionic liquid has magnetic properties; therefore, centrifugation is not required to separate the phases. Polar solvents (methanol, ethanol, a mixture of acetonitrile with methanol) are used as dispersants.

Today, DESs attract much attention from researchers because of their availability, ease of preparation, low toxicity, and biodegradability [57–59]. DESs precursors in many cases are of natural origin, which makes them environmentally friendly. The process of obtaining DESs in a laboratory is usually reduced to a simple mixing of a hydrogen bond donor and an acceptor upon heating. Combinations of initial precursors can be different, which is why they are classified as "designer" extractants. The melting points of DESs are lower than those of its precursors, and, therefore, it is usually in a liquid state at room temperature. The extraction properties of DESs depend on the nature of the precursors, which opens up wide possibilities for obtaining solvents with the required characteristics. Based on their solubility in aqueous media, DESs are classified into hydrophilic, quasi-hydrophobic, and hydrophobic [60]. Currently, there are individual examples of using quasi-hydrophobic (a mixture of choline chloride, 4-chlorophenol and α-terpineol [61], a mixture of ethylmethylammonium chloride [62] or diethanolammonium chloride [63] and the terpenoid carvacrol) and hydrophobic (a mixture of menthol and *n*-hexanol [40] or decanoic acid [64]) DESs for the extraction and preconcentration of aflatoxins, zearalenone, and ochratoxin A from solid (grain [40], cheese [63], rice [62]) and liquid (soy milk [61]) food products with the subsequent determination of analytes by HPLC-FL. Quasihydrophobic

DESs consist of precursors significantly differing in polarity, which causes the destruction of the solvent upon its contact with the aqueous phase. Essentially, extraction in this case proceeds to a phase containing predominantly one of the components of the DES. Hydrophobic DESs are most convenient for separating target analytes from aqueous samples. Such DESs are stable in the presence of water. Nevertheless, in aqueous-organic media, the stability of hydrophobic DESs decreases, and the phase released during DLLME may not correspond to the initial extractant in composition, as was noted in [40]. The use of hydrophilic DES (mixture of choline chloride with ethylene glycol) as dispersant for DLLME was described in [62]. Quasi-hydrophobic DES based on ethylmethylammonium chloride and carvacrol was added to a rice extract obtained after the extraction of aflatoxins B_1, B_2, G_1, and G_2 into hydrophilic DES, and the mixture was introduced into an aqueous medium for DLLME, followed by an HPLC-FL analysis of the extract. The limits of detection ranged from 0.02 to 0.07 μg/kg.

Supramolecular solvents (the term was proposed by Professor Rubio [18]) formed from isotropic (micellar) solutions of amphiphiles (surfactants) as a result of successive processes of self-organization and coacervation upon introducing phase separation initiators into the system or changing the temperature of the system in the form of a separate phase enriched with an amphiphile are also actively used, and the processes in such systems are supramolecular in nature [65, 66]. Supramolecular solvents were used in micellar extraction and ME to separate analytes by solubilizing them within supramolecular aggregates (micelles or vesicles) formed by amphiphiles in the sample solution, followed by the formation of a two-phase system [67]. To separate mycotoxins from food samples, only ethoxylated octylphenol (commercial name Triton X-114) [68, 69], which is a nonionic surfactant, and medium- and long-chain carboxylic acids (decanoic [18, 70, 71], tetradecanoic [72], and oleic [73]), which exhibit properties of both nonionic and anionic surfactants, were studied as amphiphiles. In the first case, phase separation occurred when an isotropic solution with direct micelles, obtained by mixing a sample with a surfactant solution upon the addition of salts (potassium nitrate, sodium chloride), is heated to a temperature of 50 to 55°C. At that, the extract has a too high viscosity for direct injection into a liquid chromatograph, and dilution with polar solvents (methanol, acetonitrile) is required. Extraction was previously carried out [69]; liquid–liquid [68] or solid-phase extraction on an immunoaffinity column [69] was used to separate aflatoxins B_1 and B_2, tenuazonic and cyclopiazonic acids from the analyzed sample (tomato juice [68], peanuts and peanut butter [69]). In the second case, coacervation occurred by two mechanisms: the first one consisted of the formation of "reverse" micelles of carboxylic acids in a mixture of an aqueous medium (pH 2.7–3.5) with tetrahydrofuran with the release of a SUPRAS [70, 71], the second one was the formation of a SUPRAS during the conversion of the carboxylic acid into an anionic form upon the addition of tetrabutylammonium hydroxide [74]. For micellar ME from samples of white, red and rose wines, the samples were acidified and a solution of carboxylic acid in tetrahydrofuran was introduced, and the separation of ochratoxin A and aflatoxin B_1 in the SUPRAS was observed. Analytes in the extracts were determined by chromatographic [71] or immunochemical [72] analysis. A direct analysis of the extract in the latter case was impossible due to the interfering effect of the extract components; therefore, tetrahydrofuran (a coacervation agent) was removed and the analytes were extracted into a phosphate buffer solution. Ochratoxin A, aflatoxin B_1, decoxivalenol, zearalenone, and fumonisins B_1 and B_2 were extracted from solid matrices (wheat, corn and bread grains [70, 72, 73], raisins [74], spices (ginger, turmeric, paprika, black pepper, nutmeg walnut) [72, 75]) by shaking samples with a previously obtained SUPRAS [72, 73] or with a micellar solution, followed by the in situ separation of the SUPRAS phase [70].

Single-drop ME is carried out by immersing a drop of an extractant at the tip of a microsyringe into a liquid sample. After separation, the drop is taken back for the further, usually chromatographic analysis [28, 76]. To separate patulin from apple juice, a three-phase version of single-drop microextraction was used, the essence of which was in the preliminary extraction of the analyte into an extractant immiscible with the sample, followed by its back extraction into a drop of an aqueous phase [22]. A juice sample and an extractant (ethyl acetate) were placed in a flat-bottomed flask with a long neck, and the mixture was shaken. A drop of water (5 μL) was injected into the upper organic layer using a microsyringe for the back extraction of the analyte and the subsequent HPLC-MS/MS analysis. The limit of detection was 0.5 μg/L. In SDME, the sample volume significantly exceeds the volume of the extractant, which usually makes it possible to achieve high preconcentration factors, and a possibility of directly introducing the extract into the analytical device reduces the total sample preparation time and the number of operations. The disadvantages of the SDME method include the low stability of the extractant drop under stirring, a possibility of the partial dissolution of the extractant phase, and the slow mass transfer of the analytes.

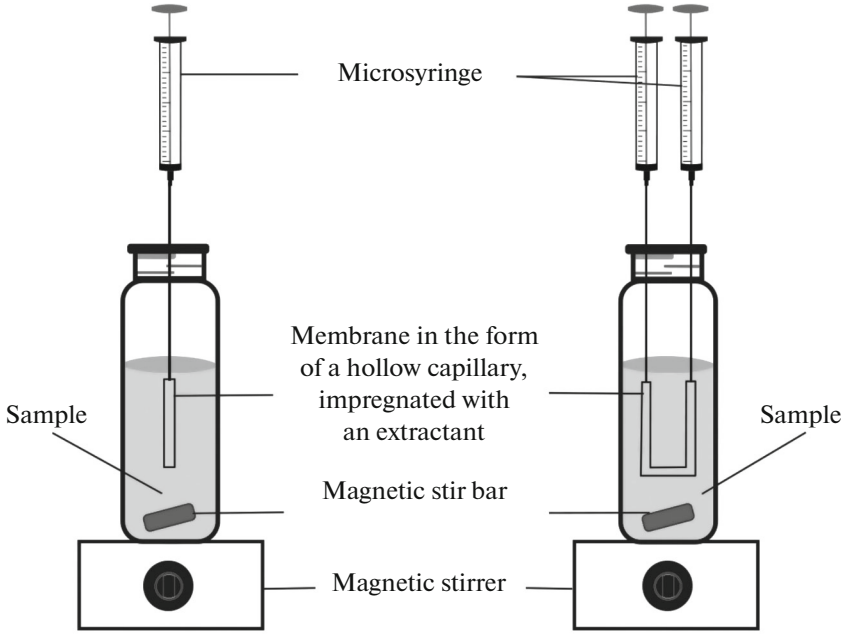

Fig. 5. Scheme of membrane-based liquid–liquid microextraction.

For the extraction of mycotoxins (aflatoxins, ochratoxin A and T-2 toxin) from food samples (beer and wine [77], rice, wheat, sesame seeds [19], a mixture of soy milk and apple juice [41], apple, orange, grape and pomegranate juice [23], milk [78]) MLLME is also used, which involves the extraction of the target analytes into the extractant phase located in the pores of a polymer membrane (Fig. 5), most often in the form of a hollow capillary made of polypropylene [28, 79]. This approach solves the problem of the stability of the extractant phase with respect to external influences inherent to SDME, e.g., it allows the extraction of aflatoxins B_1, B_2, G_1, and G_2 from a mixture of soy milk and apple juice, which is an emulsion [41]. The membrane is soaked with a suitable extractant (*n*-octanol [19, 23, 41, 77]), fixed to a needle or a metal rod, and immersed in the sample. Upon stirring, mass transfer of the analytes occurs into the extractant phase, which is then washed off with acetonitrile, methanol, or a mixture of acetonitrile with water for subsequent analysis. It is worth noting that in using MLLME, significant time is required to extract mycotoxins from samples (up to 4 h in the case of the separation of ochratoxin A and T-2 toxin from wine and beer samples into *n*-octanol [77]). To achieve higher recoveries and accelerate the process of mass transfer of mycotoxins from the samples, it was proposed to disperse nanomaterials (composite particles of graphene oxide and polyvinylpyrrolidone) in the extractant [19] or combine MLLME with DLLME [23, 41]. The first approach allows the simultaneous extraction of analytes using the LLME and SPME mechanisms. The second one involves introducing a mixture of an extractant (toluene) with a dispersant (acetone) into the aqueous phase of the sample and immersing a membrane impregnated with *n*-octanol into the resulting emulsion. In this case, microdroplets of toluene containing an analyte are transferred through the membrane. The automation of MLLME is possible [78]. HPLC-FL and HPLC-MS/MS are used to determine analytes after MLLME.

SOLID-PHASE MICROEXTRACTION

SPME is based on the sorption of analytes on the surface of milligram quantities of nano-sized sorbents or thin films with a thickness of tens to hundreds of microns [26, 30]. The efficiency of the sorption is determined by the affinity of the analyte to the sorbent or the film material. Suitable conditions are created for mass transfer by adjusting acidity, ionic strength, and mixing intensity. The analytes are then eluted and, as a rule, the eluate is introduced directly into the chromatographic system without changing the solvent. Various SPME methods have been proposed for the separation of mycotoxins from food.

Fiber-based SPME involves the sorption of target analytes on a polymer phase immobilized on the surface of a steel, a quartz, or a glass rod [80, 81]. A carbon-coated polymer film immobilized on a steel rod and pre-exposed to an aqueous solution of hydrochloric acid was used as a sorption phase (fiber) to extract

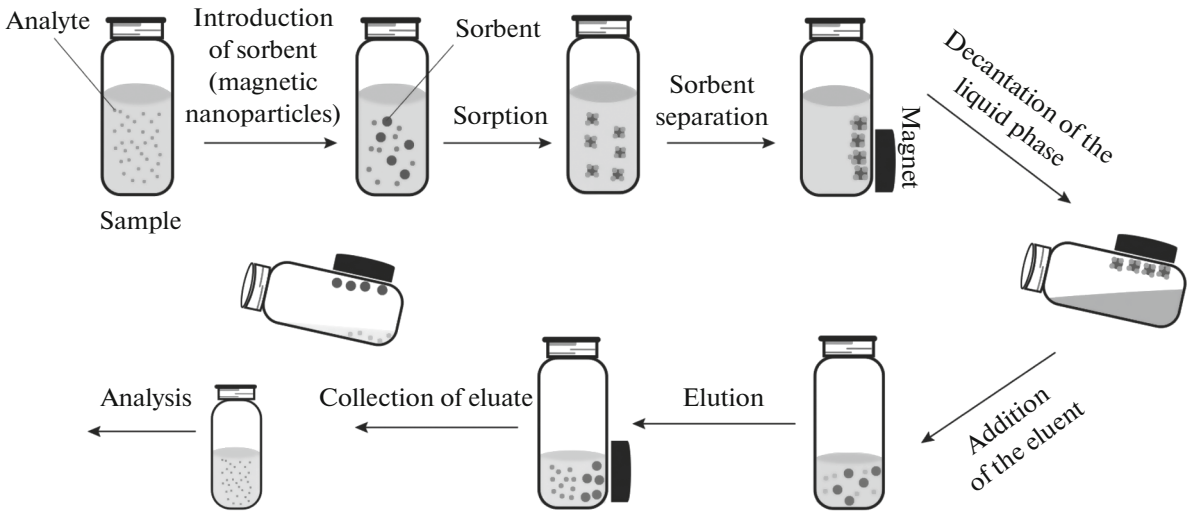

Fig. 6. Scheme of dispersive solid-phase microextraction using magnetic nanoparticles.

ochratoxin A from cheese samples [82]. The rod was directly introduced into the cheese sample so as to ensure a complete contact of the sorbent layer with the sample, after which it was left in this position for 20 min to separate ochratoxin A. The presence of an acid in the sorption layer ensured the mass transfer of the analyte in a molecular form. After sorption, the remaining sample was removed from the film and the analyte was eluted with methanol for a subsequent HPLC-MS/MS analysis. The proposed method is simple and does not require large solvent volumes. Fiber-based SPME is also used for the extraction of mycotoxins (ochratoxin A, cyclopiazonic, mycophenolic, and tenuazonic acids) from liquid samples (beer [83], wine [84]) or from extracts from solid samples (cheese [85, 86], corn flakes [87]) using sorbents based on polydimethylsiloxane and divinylbenzene (thickness 60 μm) or polyethylene glycol Carbowax and TPR-100 resin (thickness 50 μm). Analytes are determined by HPLC-UV and HPLC-FL methods.

A more effective method is ME using a magnetic molecularly imprinted stir-bars, the capabilities of which were demonstrated in the HPLC-MS/MS determination of aflatoxins in milk powder for baby food [88]. After the extraction of the analytes into an aqueous solution of formic acid in an ultrasonic field and liquid–liquid extraction into chloroform, the extractant was evaporated in a stream of nitrogen. The dry residue was dissolved in water and a magnetic stir bar made of a molecularly imprinted polymer containing magnetite MNP introduced during synthesis was placed into the resulting solution. Sorption occurred during the rotation of the stir bar in the magnetic field. Mycotoxins were desorbed from the polymer with a mixture of methanol and acetic acid. The eluate was evaporated in a stream of nitrogen, the residue was dissolved in the mobile phase, and aflatoxins were determined by liquid chromatography. Limits of detection in the range from 0.3 to 2 ng/kg were achieved.

A significant acceleration of mass transfer compared to the two methods discussed above is observed in the dispersive SPME method using milligram quantities of nano-sized sorbents based on carbon materials, metals, and metal/non-metal oxides [89, 90], uniformly distributed throughout the sample volume and having large surface areas due to small sizes. Thus, to preconcentrate aflatoxins B_1, B_2, G_1, and G_2 from polar media, zirconium oxide nanorods modified with IL—1-hexyl-3-methylimidazolium hexafluorophosphate—were used [91]. After extracting the analytes from red hot pepper and peanut samples into a mixture of acetonitrile with water, the resulting extract was shaken with the sorbent (1 min) on a vortex mixer, the analytes were eluted with acetonitrile, and the eluate was analyzed by HPLC-FL. The limits of detection were 0.01 μg/kg and higher. For the additional preconcentration of analytes after their elution from the sorbent (nitrogen and sulfur doped soot [92], iron-containing metal-organic framework structures [64]), DLLME with quasi-hydrophobic and hydrophobic DESs as extractants was used. At that, elution in the second case was carried out using hydrophilic DES based on choline chloride and ethylene glycol, which subsequently served as a dispersant for hydrophobic DES based on menthol and decanoic acid. Thus, it was possible to do without the use of classical, more toxic polar and non-polar organic solvents.

To simplify the dispersive SPME procedure, it was proposed to use MNP based on iron oxides (most

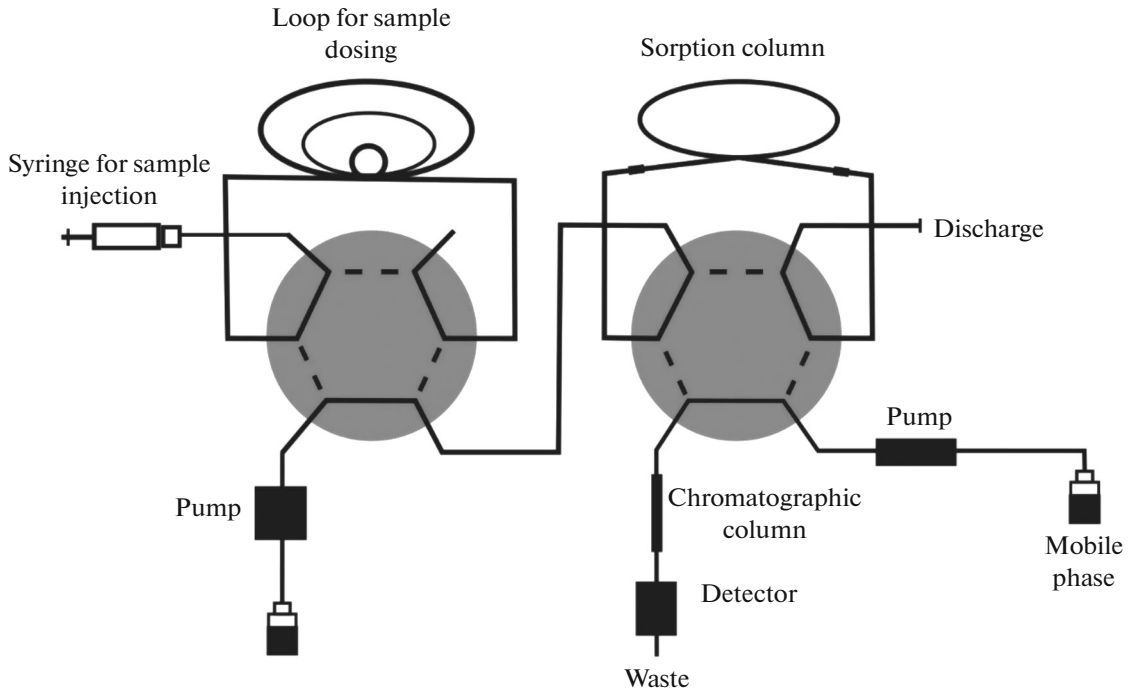

Fig. 7. Scheme of in-tube solid-phase microextraction.

often magnetite [93]). An advantage of such sorbents is a possibility of their separation from the liquid phase using an external magnet, which makes it possible to eliminate the centrifugation steps after the stages of sorption, washing the sorbent, and the elution of analytes (Fig. 6). To overcome the tendency of magnetite MNP to aggregation, improve their sorption properties, and increase the selectivity of the sorbent in separating mycotoxins of various classes from extracts from samples of wheat [94], vegetables, fruits and berries [95], spices [96], a composite material based on MNP and a molecularly imprinted polymer [94] was obtained or MNP were modified with polypyrrole [96] or covalent organic frameworks [95]. Analytes were determined by HPLC-UV and HPLC-MS/MS.

To automate the process of the sorption of analytes from samples and carry it out online, in-tube SPME in a capillary connected in series to a system for chromatographic analysis was proposed (Fig. 7) [30]. As a rule, the sorbent is placed in a capillary in a dispersed state [97], applied to the walls of the capillary [98, 99], or obtained in a capillary in situ as a monolith [100]. The eluate from the capillary is directly fed to a chromatography column. This approach was demonstrated in [100]. At the first stage, a carrier solution (an aqueous solution containing acetonitrile and trifluoroacetic acid) was passed through the system to condition the sorption column. Then, an aqueous-organic extract of a rice sample containing zearalenone, aflatoxin B_1, and sterigmatocystin was collected into the dosing loop. The sorption of analytes occurred in a capillary with the sorbent. Using a second pump, the mobile phase (acetonitrile and trifluoroacetic acid solution) was supplied to the capillary to elute the analytes; the eluate was sent to the system for HPLC-MS/MS analysis. The method made it possible to achieve high preconcentration factors (72–99). In [97], a capillary containing graphene-doped polymer nanofibers was used to separate zearalenone, citrinin, and ochratoxin A online from dairy products after deproteinization. Possibilities of using capillaries with particles of a carbon hydrophobic material (Carboxen) were shown in the HPLC-MS/MS determination of patulin in fruit juice and dried fruits [98], as well as ochratoxins A and B in samples of nuts, corn grains, rice, and wheat flour [99].

Characteristics of procedures for determining mycotoxins in food products, including the microextraction separation of analytes, are given in Table 1.

CONCLUSIONS

Mycotoxins are among the most dangerous contaminants of food and animal feed, the content of which is controlled to ensure safe products for consumers. In analytical practice, to determine trace concentrations of mycotoxins, it was proposed to use microextraction methods, which effectively eliminate the interfering effect of matrix components of the

Table 1. Characteristics of procedures for the determination of mycotoxins in food products, including liquid–liquid and solid-phase microextraction of analytes

Analytes	Test samples	Analysis method	Sample preparation	Extractant for LLME (extractant volume, μL) or sorbent/coating material (sorbent mass/coating thickness) for SPME	Sample volume (weight)	Limit of detection	Extraction recovery, %	Preconcentration factor	Reference
Aflatoxins, ochratoxin A, zearalenone, deoxyvalenol, patulin	Beans, sesame seeds, lotus seeds, apricot kernels	HPLC-UV/FL	Extraction of analytes into an aqueous-organic medium, DLLME, crystallization of the extract	1-Dodecanol (600)	1 g	0.02–0.5 μg/L	–	12–21	[12]
Aflatoxins, fumonisins, trichothecenes, ochratoxin A, citrinin, sterigmatocystin and zearalenone	Milk thistle seeds	HPLC-MS/MS	Extraction of analytes into an aqueous medium, extraction using the QuEChERS method, DLLME, solvent replacement	Chloroform (620)	2 g	0.5–459 μg/kg	62–99	–	[20]
Ochratoxin A	Malt beer	HPLC-FL	DLLME, solvent replacement	Chloroform (150)	5 mL	0.1 μg/L	–	–	[31]
Ochratoxin A	Raisin	HPLC-FL	Extraction into aqueous-organic medium, SPE, solvent replacement, DLLME, solvent replacement	Chloroform (200)	20 g	0.7 μg/kg	–	–	[33]
Ochratoxin A	Wine	HPTLC-FL	DLLME	Chloroform (100)	5 mL	0.009 μg/L	64	34.5	[34]
Patulin	Apple juice	HPLC-UV	DLLME, solvent replacement	A mixture of ethyl acetate and chloroform (250)	5 mL	2 μg/L	–	–	[13]
Patulin	Apple juice	MEKC-UV	DLLME, solvent replacement	Chloroform (1000)	5 mL	0.6 μg/L	75	–	[9]
Patulin	Apple juice	HPLC-UV	DLLME, solvent replacement	Chloroform (50)	7 mL	4 μg/L	97	–	[14]

Table 1. (Contd.)

Analytes	Test samples	Analysis method	Sample preparation	Extractant for LLME (extractant volume, μL) or sorbent/coating material (sorbent mass/coating thickness) for SPME	Sample volume (weight)	Limit of detection	Extraction recovery, %	Preconcentration factor	Reference
Aflatoxins, ochratoxin A, deoxyvalenol, fumonisins, sterigmatocystin, T-2 and HT-2 toxin, diacetoxycirpenol, zearalenone	Rice bran	HPLC-MS/MS	Extraction of analytes into an aqueous-organic medium, DLLME, solvent replacement	Chloroform (200)	20 g	0.5–50 μg/kg	70–99	–	[21]
Aflatoxins	Milk, kefir, cheese	HPLC-FL	Extraction using the QuEChERS method, DLLME, solvent replacement	Trichloromethane (500)	5 g	0.01–0.1 μg/kg	–	–	[16]
Aflatoxins	Grain of wheat, corn, barley, compound feed	HPLC-FL	Extraction using the QuEChERS method, DLLME, solvent replacement, derivatization	Chloroform (300)	2 g	0.08–0.1 μg/kg	–	–	[24]
Aflatoxins	Liquid vegetable oils	HPLC-FL	LE, SPE, DLLME, solvent replacement	Chloroform (120)	5 g	0.0001–0.003 μg/L	75–95	–	[17]
Aflatoxins	Plant milk and products based on it	HPLC-FL	LE, DLLME, solvent replacement	Chloroform (1500)	5 mL	0.2 μg/L	–	–	[35]
Aflatoxins	Corn flour, rice, pasta	HPLC-FL	Extraction into an aqueous-organic medium, DLLME, solvent replacement	Chloroform (220)	25 g	0.01–0.17 μg/kg	67–92	–	[36]

Table 1. (Contd.)

Analytes	Test samples	Analysis method	Sample preparation	Extractant for LLME (extractant volume, μL) or sorbent/coating material (sorbent mass/coating thickness) for SPME	Sample volume (weight)	Limit of detection	Extraction recovery, %	Preconcentration factor	Reference
T-2, HT-2, deoxyvalenol, nivalenol	Corn, barley, oats, wheat	GC-ECD	QuEChERS extraction, DLLME, derivatization, solvent replacement	Dichloromethane (200)	2 g	3–15 μg/kg	90–95	–	[37]
Aflatoxins, nivalenol, HT-2 and T-2 toxins, zearalenone, ochratoxin A, deoxyvalenol	Drink based on black, red, green tea	HPLC-MS/MS	DLLME, solvent replacement	Ethyl acetate (620)	5 mL	0.05–10 μg/L	–	–	[38]
Aflatoxins, ochratoxin A, zearalenone	Rice, corn, wheat, beans, grain products	HPLC-FL	QuEChERS extraction, DLLME, solvent replacement	Chloroform (498)	2.5 g	0.03–11 μg/kg	76–84	–	[42]
Aflatoxins, ochratoxin A, sterigmatocystin, verruculogen	Rice wine	HPLC-MS/MS	DLLME, solvent replacement	Dichloromethane (800)	5 mL	0.05–0.5 μg/L	–	–	[44]
Deoxynivalenol	Rice	HPLC-UV	Extraction into aqueous-organic medium, DLLME	Chloroform (230)	25 g	24 μg/L	89	78	[15]
Zearalenone	Beer	HPLC-FL	DLLME	Chloroform (75)	5 mL	120 μg/L	83	43	[46]
Zearalenone	Beer	HPLC-MS/MS	DLLME	Toluene (550)	1 mL	0.4 μg/kg	86–95	–	[47]
Aflatoxin M_1	Milk	Fluorimetry	DLLME, SPME, solvent replacement	1-Heptanol (320)	10 mL	13 ng/L	–	–	[11]
Ochratoxin A	Drink based on orange juice and milk	HPLC-MS/MS	DLLME, solvent replacement	Ethyl acetate (620)	5 mL	–	–	–	[43]

Table 1. (Contd.)

Analytes	Test samples	Analysis method	Sample preparation	Extractant for LLME (extractant volume, μL) or sorbent/coating material (sorbent mass/coating thickness) for SPME	Sample volume (weight)	Limit of detection	Extraction recovery, %	Preconcentration factor	Reference
Zearalenone	Milk, yogurt	MEKC-MS/MS	Extraction into organic solvent, protein precipitation, fat removal, solvent replacement, DLLME, solvent replacement	Chloroform (110)	2 mL	12 μg/L	–	–	[48]
Deoxyvalenol, its deepoxy metabolite	Corn kernels, pork	HPLC-MS/MS	Extraction into organic solvent, DLLME	Water (100)	1 g	4–6 μg/kg	–	–	[49]
Deoxynivalenol, zearalenone	Amaranth seeds	HPLC-MS/MS	Extraction into an aqueous-organic medium, removal of fats, DLLME, reextraction	1-Dodecanol (100)	2 g	0.07–0.7 μg/kg	80–100	16–20	[45]
Zearalenone	Beer, wheat, corn	HPLC-FL	Extraction into organic solvent (for wheat and corn samples), DLLME	IL (1-butyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)imide) (200)	5 mL	0.25 μg/L	93	–	[39]
Ochratoxin A	Rice wine	HPLC-FL	DLLME	IL 1-hexyl-3-methylimidazolium hexafluorophosphate (100)	5 mL	0.04 μg/L	–	28	[32]
Zearalenone	Corn grain	HPLC-FL	Extraction into an aqueous-organic medium, DLLME, solvent replacement	IL 1-hexyl-3-methylimidazolium hexafluorophosphate (100)	10 g	0.3 μg/kg	–	–	[54]
Ochratoxin A	Wine	HPLC-FL	DLLME	IL 1-hexyl-3-methylimidazolium hexafluorophosphate (100 mg)	5 mL	5 ng/L	–	–	[55]

Table 1. (Contd.)

Analytes	Test samples	Analysis method	Sample preparation	Extractant for LLME (extractant volume, μL) or sorbent/coating material (sorbent mass/coating thickness) for SPME	Sample volume (weight)	Limit of detection	Extraction recovery, %	Preconcentration factor	Reference
Zearalenone	Bread, corn flakes, wheat grain	HPLC-FL	Extraction into a mixture of organic solvent and extractant, DLLME	DES (menthol–*n*-hexanol (2 : 1))	0.5 g	2 μg/kg	93	16	[40]
Aflatoxins	Rice	HPLC-FL	Extraction in DES, DLLME	DES (ethylmethylammonium chloride–carvacrol (1 : 2)) (90)	2 g	0.02–0.07 μg/kg	69–82	55–62	[62]
Aflatoxin M_1	Cheese	HPLC-FL	Extraction into an aqueous-organic medium, removal of fats, DLLME	DES (diethanolammonium chloride–carvacrol (1 : 2)) (64)	1 g	0.7 ng/kg	94	94	[63]
Cyclopiazonic acid, tenuazonic acid	Tomato juice	HPLC-UV	LE, solvent replacement, micellar ME	SUPRAS based on ethoxylated octylphenol (1400)	5 g	0.6–0.7 μg/L	40–95	–	[68]
Aflatoxins	Peanuts, peanut butter	HPLC-FL	Extraction into aqueous-organic medium, SPE, micellar ME	SUPRAS based on ethoxylated octylphenol (300)	10 mL 10 g	0.4 ng/mL 0.2 ng/mL	52–58	–	[69]
Ochratoxin A	Wort, vinegar, wine, beer	HPLC-FL	Micellar ME	SUPRAS based on decanoic acid (125)	15 mL	4–9 ng/L	–	–	[18]
Ochratoxin A	Wheat	HPLC-FL	Extraction into micellar solution, micellar ME	SUPRAS based on decanoic acid (220)	0.3 g	0.5 μg/kg	–	–	[70]
Ochratoxin A	Wine	HPLC-FL	Micellar ME	SUPRAS based on decanoic acid (125)	15 mL	5 ng/L	–	105	[71]
Ochratoxin A, aflatoxin B_1	Wine, spices	Immunoassay	Micellar ME, solvent replacement	SUPRAS based on tetradecanoic acid (340)	8 mL, 25 g	100–3100 μg/L	81–93	–	[72]
Deoxynivalenol, zearalenone, fumonisins	Cereal products	HPLC-MS/MS	Micellar ME	SUPRAS based on oleic acid (600)	0.3 g	8–15 μg/kg	–	–	[73]

Table 1. (Contd.)

Analytes	Test samples	Analysis method	Sample preparation	Extractant for LLME (extractant volume, μL) or sorbent/coating material (sorbent mass/coating thickness) for SPME	Sample volume (weight)	Limit of detection	Extraction recovery, %	Preconcentration factor	Reference
Ochratoxin A	Raisin	HPLC-FL	Preparation of sample suspension, micellar ME	SUPRAS based on decanoic acid (500)	0.3 g	0.7 μg/L	100	–	[74]
Ochratoxin A	Spices	HPLC-FL	Micellar ME	SUPRAS based on decanoic acid (400)	0.2 g	0.5 μg/L	88–100	–	[75]
Patulin	Apple juice	HPLC-MS/MS	LE, SDME	Water (5)	10 mL	0.5 μg/L	–	3	[22]
Ochratoxin A, T-2 toxin	Beer, wine	HPLC-MS/MS	MLLME	*n*-Octanol	12 mL	0.02–0.09 μg/L	–	4–8	[77]
Aflatoxins	Soy milk and apple juice mixture	HPLC-FL	DLLME, MLLME, derivatization	*n*-Octanol	4 mL	0.01–0.03 μg/L	–	27	[41]
Aflatoxins	Sesame, wheat, rice	HPLC-FL	Extraction into an aqueous-organic medium, removal of fats, solvent replacement, MLLME	*n*-Octanol, containing composite particles of graphene oxide and polyvinylpyrrolidone	25 g	0.1–0.4 μg/kg	–	–	[19]
Aflatoxins, ochratoxin A	Fruit and berry juices	HPLC-MS/MS	MLLME, solvent replacement	*n*-Octanol	–	0.04–0.06 μg/L	–	723–765	[23]
Aflatoxin M_1	Milk	HPLC-MS/MS	MLLME	*n*-Octanol	10 mL	0.06 μg/kg	–	48	[78]
Ochratoxin A	Cheese	HPLC-MS/MS	Fiber-based SPME	Carbon coated polymer film (600 μm)	–	2 μg/L	93	–	[82]
Ochratoxin A	Beer	HPLC-FL	Fiber-based SPME	Copolymer of polymethylsiloxane and divinylbenzene (60 μm)	1.5 mL	20 μg/L	–	–	[83]
Ochratoxin A	Wine	HPLC-FL	Fiber-based SPME		1.5 mL	0.07 μg/L	–	–	[84]

Table 1. (Contd.)

Analytes	Test samples	Analysis method	Sample preparation	Extractant for LLME (extractant volume, μL) or sorbent/coating material (sorbent mass/coating thickness) for SPME	Sample volume (weight)	Limit of detection	Extraction recovery, %	Preconcentration factor	Reference
Cyclopiazonic acid	Cheese	HPLC-UV	Extraction into organic solvent, solvent replacement, fiber-based SPME	Polymer based on Carbowax polyethylene glycol and TPR-100 resin (50 μm)	0.5 g	7 μg/kg	–	–	[85]
Mycophenolic acid	Cheese	HPLC-UV	Extraction into an aqueous medium, fiber-based SPME		0.5 g	50 μg/kg	–	–	[86]
Ochratoxin A, cyclopiazonic, mycophenolic, tenuazonic acids	Cornflakes	HPLC-UV	Extraction into aqueous-organic medium, solvent replacement, fiber-based SPME	Copolymer of polymethylsiloxane and divinylbenzene (60 μm)	0.5 g	–	62–100	–	[87]
Aflatoxins	Powdered milk for baby food	HPLC-MS/MS	Removal of fats, LLE, SPME on magnetic stir bar, solvent replacement	Molecularly imprinted polymer (magnetite MNP introduced)	–	0.3–2 ng/kg	39–60	–	[88]
Aflatoxins	Red pepper, peanuts	HPLC-FL	Extraction into an aqueous-organic medium, dispersive SPME	Zirconium oxide nanorods modified with IL—1-hexyl-3-methylimidazolium hexafluorophosphate (10 mg)	5 g	0.01–0.07 μg/kg	95–100	–	[91]
Aflatoxins, ochratoxin A	Soy milk	HPLC-FL	Protein precipitation, dispersive SPME, DLLME	Nitrogen and sulfur doped carbon black (150 mg)	10 mL	0.1–0.8 ng/L	70–87	350–435	[92]
Ochratoxin A, aflatoxin M_1	Milk	HPLC-FL	Protein precipitation, dispersive SPME, DLLME	Iron-containing metal-organic framework structures (50 mg)	7 mL	0.3–0.8 ng/L	75–87	305, 263	[64]

Table 1. (Contd.)

Analytes	Test samples	Analysis method	Sample preparation	Extractant for LLME (extractant volume, μL) or sorbent/coating material (sorbent mass/coating thickness) for SPME	Sample volume (weight)	Limit of detection	Extraction recovery, %	Preconcentration factor	Reference
Zearalenone	Wheat	HPLC-UV	Extraction into aqueous-organic medium, dispersive SPME, solvent replacement	Composite material based on MNP and molecularly imprinted polymer (25 mg)	40 g	0.6 μg/kg	92	–	[94]
Aflatoxin B_1, ochratoxin A, zearalenone, tentoxin, altenuene, tenuazonic acid	Tomatoes, watermelon, melon, strawberries, hawthorn	HPLC-MS/MS	Extraction into aqueous-organic medium, dispersive SPME, solvent replacement	MNP modified with covalent organic frameworks (20 mg)	2 g	0.01–0.5 μg/kg	–	–	[95]
Aflatoxins	Paprika	HPLC-MS/MS	Obtaining a sample suspension, dispersive SPME, solvent replacement	MNP modified with polypyrrole (250 mg)	0.2 g	1 μg/kg	90–98	–	[96]
Zearalenone, aflatoxin B_1, sterigmatocystin	Rice	HPLC-MS/MS	Extraction into aqueous-organic medium, solvent replacement, in-tube SPME	Monolithic polymer sorbent based on methacrylic acid and divinylbenzene	2 g	0.7–2 μg/kg	–	72–99	[100]
Zearalenone, citrinin, ochratoxin A	Products based on plant milk	HPLC-FL	Protein precipitation, in-tube SPME	Graphene doped polymer nanofibers (25 mg)	40 mL	0.09–2 μg/L	–	–	[97]
Patulin	Fruit juice, dried fruits	HPLC-MS/MS	Extraction into organic solvent (for dried fruits), in-tube SPME	Particles of carbon hydrophobic material (Carboxen) deposited on the walls of the capillary	0.1 mL, 1 g	24 ng/L	–	83	[98]
Ochratoxins	Nuts, corn kernels, rice, wheat flour	HPLC-MS/MS	Extraction into aqueous-organic medium, removal of fats, in-tube SPME		0.5 g	0.18 μg/kg	–	15–19	[99]

Designations: SPE is solid phase extraction.

samples and preconcentrate analytes. An analysis of the published data has shown that microextraction methods are relatively easily combined with chromatographic, electrophoretic, and spectral methods in the determination of mycotoxins in food products. Recently, special attention has been paid to the use of ILs, DESs, and SUPRASs as effective extractants for separation and preconcentration of mycotoxins from various matrices. The main advantages of such methods are in the low consumption of extractants and small amounts of wastes generated; "designer" extractants are environmentally friendly and in many cases selective with respect to the substances being determined.

FUNDING

The authors express their gratitude to the Russian Science Foundation, project no. 21-13-00020, (https://rscf.ru/project/21-13-00020/).

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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Translated by V. Kudrinskaya