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REVIEW ARTICLE

Comprehensive review of liquid chromatography methods for fumonisin determination, a 2006–2022 update

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Abstract Fumonisins are mycotoxins present worldwide. They are mainly found in corn and its derived foods; however, they also have an important presence in other grains, fruits, and vegetables. Their consumption in excessive amounts can affect animal and human health. The most abundant of these is fumonisin B_1, associated with a range of toxicological effects in animals, including equine leukoencephalomalacia, porcine pulmonary edema, and rodent carcinogenicity. In humans this mycotoxin has been shown to increase rates of esophageal cancer. The International Agency for Research on Cancer has classified FB_1 within the 2B group, considering it a possible human carcinogen. Thus, analytical methods that identify/quantify fumonisins become a necessity to ensure adequate control of food and crops. An analytic method needs to be sensitive, selective, and robust to provide reliable data that can aid in monitoring risk assessment, quality control, and research. Recently, colorimetric methods which use immunologic and molecular approaches based on dyes, enzymes and aptamers have gained attention; some of these using nanomaterials. However, these methods are still in development. Currently, chromatographic methods remain the most confident and robust analytic tool, especially for quantification purposes. There is a great deal of information reported in the literature regarding these methods; despite this, there has not been a compilation of the methods for fumonisin analysis to facilitate its consult since 2005. Being the most common method for fumonisin detection worldwide, the present review focuses on the compilation of liquid

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chromatography methods published between 2006 and 2022 organized by matrix, analytes, instrument, and method conditions, using diverse detectors including MS, fluorescence, and an evaporative light scattering detector. Additionally, These techniques have been applied to diverse matrices, namely food and beverages, including grains, milk, meat, beer, wine; as well as biological samples such as urine, plasma, serum, and tissues. Other aspects pertaining to legislation, extraction, cleanup (selective pressurized liquid extraction, strong anion-exchange, immunoaffinity chromatography, and QuEChERS), derivatization procedures, limit of detection and quantification of fumonisins are also included. This review had compiled and organized 88 chromatographic methods for fumonisins analysis, and the analysts can consult all the procedures with detail.

1. Introduction

Despite the current improvement in processing, packing and labeling activities, food safety is still an important concern, not only for human consumption, but also for crop control, fresh food quality and safety. Fungi contamination of these and other products is a paramount problem, as it can cause diverse ailments to humans and animals, as well as compromise production yield of the different crops and livestock. Mycotoxins are small secondary metabolites (molecular weight - MW- $\sim$ 700) produced by microfungi; these are naturally occurring substances that are responsible for detrimental effects to the host, and are, for the most part, resistant to food processing (Bullerman and Bianchini, 2007, Turner et al., 2009). These compounds can be carcinogenic, nephrotoxic, hepatotoxic, neurotoxic, immunosuppressant, and can modify estrogen production (Jia et al., 2014). An important aspect pertaining to the consumption of mycotoxins is their ability to accumulate within an organism. Thus, different sources such as grains: wheat (Headley, 2022 in graphical abstract), oats, rice (Toro 2022 in graphical abstract), barley, and corn (Diogo 2011 in graphical abstract), fresh vegetables (Cumming 2022 in graphical abstract) and fruits (apples, raisins, and nuts) contribute to increase the amount of accumulated toxins in the host. This phenomenon continues in livestock whereby the ingestion of contaminated food sources increases the levels of toxins within their organisms, and are passed on to their derivatives (i.e. meat, milk, eggs, among others). As a result, human consumption of these products multiplies the chain of transmission, as crops and livestock (Embrenhar 2022 in graphical abstract) become saturated of mycotoxins from different sources; this is known as a carryover effect (Marasas 2001). Hence, contamination by mycotoxins has been recognized as a health problem, with special attention being put on aflatoxins, ochratoxins and fumonisins by their direct or accumulated toxicity (Requena et al., 2005).

Mycotoxins are generally characteristic to a specific genus. Some of the main genus producing mycotoxins are *Aspergillus* (aflatoxins and ochratoxins), *Penicillium* (patulin, ochratoxin A, citrinin, penicillic acid, cyclopiazonic acid, and penitrem), and *Fusarium* (trichothecenes and fumonisins) (Grajewski et al., 2012). Among aflatoxins, ochratoxins, and fumonisins, these last ones have been associated with important human diseases such as esophageal cancer (Marasas 2001), with an increased incidence of human immunodeficiency virus (HIV) infection (Williams 2010), liver and kidney disease, and growth impairment (Chen 2018). Some reviews have compiled the toxicity and mechanism of action of FB (Chen 2021, Stockmann-Juvala 2008). It has been estimated that mycotoxins are present in at least a quarter of the world's agricultural products, and their stability at high temperatures guarantee their integrity even after passing through cooking and industrial procedures (Williams 2010). Despite these considerations, not all countries have legislation that regulate their concentration in food. The number of mycotoxins that are known to exert a toxic effect on human and animal health is constantly increasing, for this reason, generation and observance of legislation that ensures minimization of mycotoxins exposure is needed to ensure the quality of food (Bueno 2015). Diverse detection methods have been used to evaluate fumonisins, and some new methods have a promising future for easier and faster methodologies. Enzyme-linked immunosorbent assay (ELISA) methods based on antigens are specific and commercially available, however these have expiration date and need to be stored under refrigeration. Some enzymes have been proposed for colorimetric methods intended for more analytes, however these demonstrate low selectivity. Nanomaterials have arisen as a promising tool for mycotoxin detection, using immunoreactions or aptamers for detection. Despite this, for research purposes, characterization of nanomaterials is required, and instrumentation is expensive. Thus, this method may only prove favorable for future commercial applications if a high specificity, especially in real samples, can be achieved. These techniques have been recently reviewed (Majdinasab et al., 2021) and remain out of the scope of the present paper. In general, the most extensively used technique for mycotoxin determination is liquid chromatography associated with different detectors (Bueno 2015). This is because it has a well established and robust methodology that has been proven for all kinds of matrices. There is a considerable number of articles regarding fumonisin analysis (including reviews); however, there has been no compilation of this information available since 2006. This review aims to compile and organize the advances in the field from 2006 to 2022 in a single document including liquid chromatography coupled to mass spectrometry (LC-MS) and ultra-performance liquid chromatography (UPLC) methods currently used. Additionally, matrices, pretreatment procedures and instrument conditions are also reported, so that readers can easily find a method close to their needs in a single article.

2. *Fusarium* genus

Fusarium genus (syn *Giberella*) was first described by Link in 1803. It belongs to the Nectriaceae family and is widely spread in soil. *Fusarium* includes more than 150 species of filamentous fungi, classified into nine categories, and is considered one of the most mycotoxigenic genus. *Fusarium* phylogeny and morphology has been recently reviewed generating an online identification database (Crous 2021). It is of agricultural concern for its capacity to grow on plants, particularly crops, but also in fruits, contaminating food and feed (Tapia 2014, Grajewski et al., 2012). Approximately 20 species are considered pathogenic for their capacity to produce mycotoxins that affect plants, animals, and humans. *F. verticillioides* and *F. proliferatum* are the main producers of fumonisins (Gelderblom 1988); *F. solani* and *F. oxysporum* have been reported to cause minor health problems directly to humans, producing keratitis, endophthalmitis, onychomycosis, cutaneous and subcutaneous infections, sinusitis, arthritis and mycetoma. In immunocompromised patients, however, especially those with hematological disorders, they can cause severe disseminated infections that can reach mortalities of almost 100% ("Fungal

Infections. Fusarium Solani" https://www.life-worldwide.org/fungal-diseases/fusarium-solani; "Fungal Infections. Fusarium Oxysporum," https://www.life-worldwide.org/fungal-diseases/fusarium-oxysporum). Prolonged exposition to these fungi can also lead to chronic diseases such as cancer (Shier 2000). The distribution of *Fusarium* species has been studied mainly in commercial substrates, and particularly for certain geographical areas such as *F. graminearum* and *F. culmorum* in Europe (Pasquali 2016), *F. oxysporum* in Israel and Middle East (Maymon 2020), and *F. oxysporum* worldwide (Dita 2018).

3. Fumonisins

The first report regarding fumonisins was published in 1988 when they were first isolated by Gelderblom *et al* (Gelderblom 1988). The chemical structure of these mycotoxins was first proposed in the same year as a result of the collaboration between the Programme on Mycotoxins and Experimental Carcinogenesis (PROMEC) and the Council for Scientific and Industrial Research (CSIR) (Marasas 2001). Structurally, fumonisins are characterized by a long chain of polyhydroxy alkylamines containing two propane tricarboxylic acid moieties (tricarballylic acid, TCA) that are esterified to hydroxyl groups on adjacent carbon atoms. Currently twenty-eight different structures of fumonisins have been described (Agriopoulou 2020), which have been classified into four series: Series-A corresponds to amides, Series-B exhibits a free amine group and a terminal methyl, Series-C includes a terminal amine group, and Series-P incorporate an 3-hydroxypiridinium residue in their structures (Yazar 2008, Braun 2018).The fumonisins most frequently isolated from *Fusarium* are illustrated in Fig. 1.

Within these groups of natural compounds, fumonisins B (FB_1, FB_2, FB_3) are the most relevant because they have been found on various food products and crops (Arranz 2004). FB_1 is the most abundant and toxic fumonisin of the group. Its chemical structure is a 2*S*-amino-12*S*,16*R*-dimethyl-3*S*,5*R*,10*R*,14*S*,15*R*-pentahydroxyeicosane, in which hydroxyl groups at C-14 and C-15 are substituted with a propane-1,2,3-tricarboxylic acid (TCA) residue. FB_2 does not have the hydroxyl group at C-10. FB_2 and FB_3's structural isomers, differ only in the location of an hydroxyl group (Fig. 1) (Bryła 2013). The *FUM* genes have been identified as the responsible for fumonisin biosynthesis (Alexander 2009).

3.1. Fumonisins in food

Fumonisins are present in a wide number of food products around the world. Cereals are the group with the highest documented concentration of these toxins (Kamle 2019). Maize, and maize-based products are particularly affected (Stępień 2011), with as much as an estimated 50% of products contaminated in varying degrees (Pagliuca 2005), depending mainly on agroclimatic and storage conditions (Bryła 2013). In particular, FB_1 has been found in different types of food such as asparagus, garlic (Seefelder 2002), barley (Park 2002), beers (Kawashima 2007), dried figs (Heperkan 2012), and milk (Gazzotti 2009). Additionally, FB_1 and FB_2 have been reported in 'black oats' feed from Brazil, and forage grass in New Zealand. They have also been found in home-grown corn consumed in rural areas of Southern Africa, and in commercial corn-based human food products from retail outlets (Norhasima 2009).

Concentrations of FB_1 and FB_2 vary widely between products. They have been found in corn meal up to 2.98 μg FB_1/g and 0.92 μg FB_2/g, and in corn grits up to 2.55 μg FB_1/g and 1.07 μg FB_2/g, respectively. In contrast, Switzerland, the United States, and South Africa have reported very low concentrations of these toxins, being lower than 0.06 μg/g, in products such as corn breakfast cereal (Norhasima 2009). A *meta*-analysis including contamination of cereal-based foods

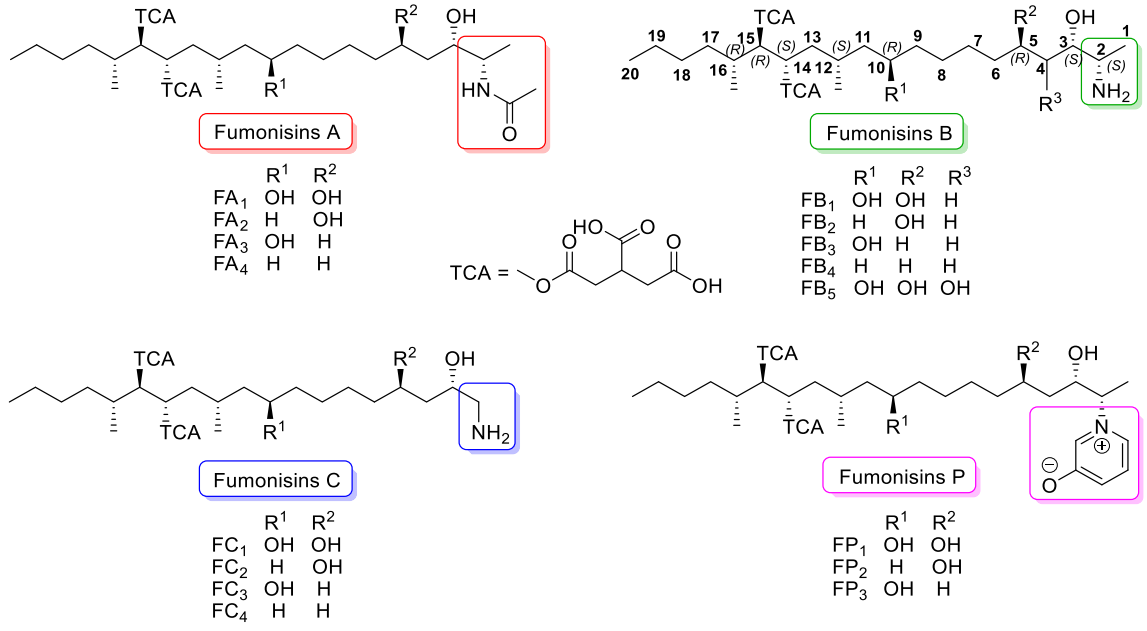

Fig. 1 Selected chemical structures of fumonisins.

revealed the highest concentration of fumonisins in corn-based products, followed by wheat-based products, other cereals, and barley-based foods. Regarding the occurrence, it was reported widely in other cereal-based foods, followed by corn-based foods, rice-based foods, and wheat-based foods (Farhadi 2021).

3.2. Stability

The integrity of fumonisins depend on a combination of conditions that include temperature, pH, humidity, biotic or abiotic conditions, matrix and, time in these conditions. Several studies on fumonisin stability were performed in the 90′s. It has been shown that FB_1 is partially hydrolyzed at acidic or basic conditions, or at 100–125 °C, and completely degraded at 200 °C for 60 min in the absence of a matrix (Jackson 1996). Thus, the extent of FBs degradation, and their toxicity in food depend primarily on the cooking and processing conditions (Humpf 2004). FBs are known to be relatively heat stable and are minimally affected during food processing techniques such as baking, frying, broiling or extrusion cooking, where temperatures can reach 150–200 °C (Humpf 2004). In maize flour, at neutral and acidic conditions, FBs were reported stable at temperatures greater than 220 °C (25 min) (Bryła 2017). Selection and disposal of damaged grains, along with soaking and/or washing corn reduced the concentration of FBs by eliminating it from food material (Saunders 2001). Dry milling has been shown to maintain FB_1 mostly intact (Kamle 2019), however, wet milling has been shown to produce products suitable for animal and human consumption (gluten, fiber, germ, and starch), as the water used in the process causes FB_1 deterioration (Saunders 2001). Fumonisins can also interact with aminoacids, proteins or reducing sugars to form covalent bonds during heat processes. For instance, FB_1 reacts with D-glucose, present in corn grits, during extrusion cooking at 160–180 °C and forms the reaction product *N*-(carboxymethyl) fumonisin B_1 known as NCM (Seefelder 2002, Taylor 2012).

3.3. Toxicological effects

Fumonisin has been proven to induce growth and lipid disruption in plants, animals, and humans, especially FB_1. Additionally, immunotoxicity, organ toxicity (liver, kidney, intestinal tract, heart, lungs, brain) and reproductive toxicity has been reported (Chen 2021). Structural similarity between sphingosine, sphinganine and fumonisin (*e.g.* FB_1, Fig. 2) is cited as the key for their toxic effects, however oxidative stress, endoplasmic reticulum stress and altered tumor necrosis factor (TNF) signaling pathway, has also been recognized as a mechanisms of their toxicity (Chen 2021; Stockmann-Juvala 2008).

In banana plants, FB_1 decreases the activity of certain enzymes such phenylalanine ammonia lyase (PAL), β-1,3-glucanase (GLU), and chitinase (CHI). It also enhances reactive oxygen species like malondialdehyde (MDA) and hydrogen peroxide, as well as transcription of genes associated to cell death (Xie 2021). In maize, FB_1 competitively inhibits ceramide synthetase (CerS) disturbing lipid equilibrium and cell protection (Beccaccioli 2021).

In animals, the presence of FBs has been found to impair immune function, cause liver and kidney damage, decrease weight and increase mortality rate (Akande 2006). Fumonisins can cause an ample range of animal diseases, including leukoencephalomalacia (LEM) in horses (Lockett 2022 in graphical abstract) and rabbits, hemorrhage in rabbits, pulmonary edema in pigs, and liver cancer in rats. In addition, they are toxic to turkey poults and have been associated with diarrhea and reduced body weight in broiler chicks (Ghiasian 2009). Different species of fish are affected by FB_1, in general, they induce weight and hematocrit reduction, as well as liver and kidney damage similar to other animal species (Oliveira 2020).

Fumonisins are associated with an increased risk of esophageal and liver cancer in humans (Liu 2017), and with a general increase of cancer incidence in regions where maize is the population's dietary base (Martins 2012). The inhibition of CerS causes the accumulation of the sphingoid bases sphinganine (Sa) and sphingosine (So), and a decrease of complex sphingolipids (Cano-Sancho 2012). Currently, the interference with sphingolipid biosynthesis remains the main cause of toxicity in humans and animals (Soriano del Castillo 2007). Sphingolipids have recently been associated with control of cell growth and proliferation of cancer cells. Ceramide has an important role in limiting cancer progression by inducing cell death (Ogretmen and Avenue 2018). Thus, its inhibition by fumonisins can potentially enhance the development of cancer, which is why the International Agency for Research on Cancer (IARC) has classified FB_1 as a probable carcinogenic to humans (group 2B) (Duarte-Vogel 2006). Exposure to fumonisins has also been shown to increase the risk of neural tube defects (NTD) in humans (Seyed Amir Ghiasian 2006). Furthermore, some studies have suggested a possible link between exposure to fumonisins and an increase in the mortality of infection by human immunodeficiency virus (HIV) in sub-Saharan Africa (Williams 2010). More recently, a preliminary study has demonstrated the presence of hydrolyzed FB_1 (aminopentol) in the urine of women infected with human papillomavirus (HPV) and its absence in healthy women (Ramírez-Cisneros 2020).

Fusarium produces fumonisin to facilitate its entrance to the cell by producing lipid disruption in the host cell. As a corollary, cells affected by fumonisins become a target for other infection agents such as viruses. Additionally, this lipid disruption leads to alterations in cell metabolism that can lead to cancer and cell death.

Hydrolyzed fumonisins are structurally more similar to Sa and So, however their toxic effects are still unknown. Toxicodynamic studies, especially in humans are necessary to establish dose–response of fumonisins and their hydrolyzed forms.

3.4. Toxicokinetics

The bioavailability, distribution, and toxicokinetic studies in several animal species including laboratory rodents, primates, swine, ruminants, and poultry have shown that fumonisins are poorly absorbed and have a very low bioavailability. However, little amounts of fumonisins accumulate in tissues and organs (Shier 2000). The bioavailability for FB_1 administered orally in non-human primates has been reported as < 5 % of the dose with $T_{max} = 1.02$ h. Elimination half-live was found to be $T_{1/2} = 3.15$ h for plasma, $T_{1/2} = 4.07$ h for liver and $T_{1/2} = 7.07$ h for kidney. In contrast, when administered

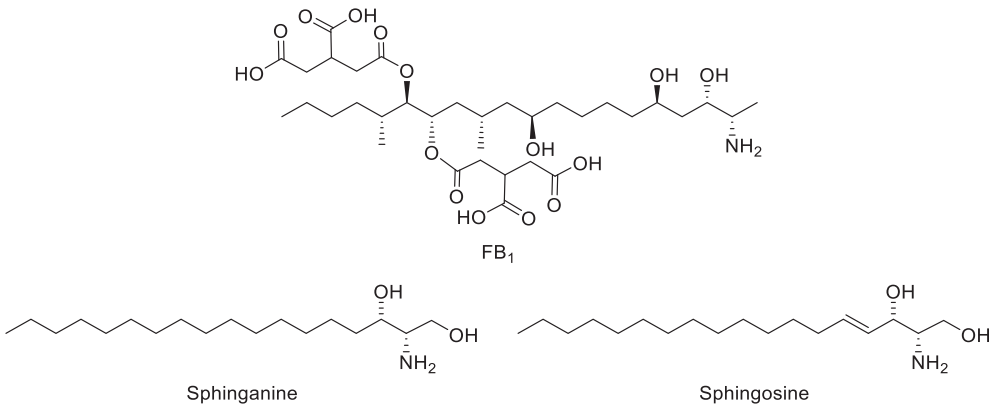

Fig. 2 Chemical structures of sphinganine, sphingosine and FB_1.

with feed, concentrations in the kidneys increase approximately 10-fold compared to liver concentrations; suggesting an increase in the rate of elimination (Voss 2017). Bioavailability studies have demonstrated that, of the total concentration of FBs (FB_{1+2+3}) in the liver or kidney of rats, FB_1 shows the highest concentration, finding FB_2 and FB_3 in very minor concentrations (Voss 2017). In contrast, FB_1 is only detected in plasma and tissues at low levels, suggesting that its absorption is negligible.

Indeed, in cows and laying hens, systemic absorption of orally given FB_1 is < 1% (Bouhet 2007). Fumonisins were mostly excreted, almost unchanged, in feces and only a small percentage was excreted in urine. Nevertheless, urine is the most acceptable, and easiest, medium to investigate compared to feces (Van Der Westhuizen 2013).

Even though fumonisins have poor absorption, they have been demonstrated to be an important factor in the development of livestock and human diseases (Shier 2000). This poses the interesting question of why they have proven toxic effects despite their low bioavailability. Several investigations have tried to explain this phenomenon, including *in vitro* studies using Caco-2-cells to prove the absorption of FB_1 in enterocytes. A study has established that the only form readily absorbed corresponds to the completely hydrolyzed form of FB_1 (aminopentol). Another study using radiolabeled FB_1, performed in nonhuman primates, demonstrated that after 24 h of administration, the intestinal epithelial cells contained 25% of the dose (Shephard 1992). Furthermore, recent data has indicated an interaction between FB_1 and cholesterol and/or bile salts, which may lead to the incorporation of FB_1 into mixed micelles. Thus, the metabolism of fumonisins could lead to an increased bioavailability (Bouhet 2007).

Some aspects of fumonisin toxicokinetics remain unknown, however, and pigs have been suggested as a model because of its similarity with fumonisin metabolism in humans (Schelstraete 2020).

4. Limits and legislation

Removal of mycotoxins from food products has proven to be a difficult process; therefore, maximum acceptable levels have been established for human consumption to ensure the safety of these products. Guidelines have been published in response to this need, that dictate the maximum concentration of these compounds that can be tolerated. There is a varied range of permissible amounts of mycotoxins in food according to different guidelines, encompassing ranges from 200 to 4000 μg/kg (Ponce-García 2018). Many organizations worldwide oversee strict regulations for mycotoxin control, and possible food contamination. Some of these are global organizations such as the Joint Expert Committee on Food Additives (JECFA); the scientific advisory board of the World Health Organization (WHO) and the Food and Agriculture Organization (FAO). Others are limited to geographical areas such as the European Food Safety Authority (EFSA) in the European Union, which gives counseling to European Commission; and the Food and Drug Administration (FDA) in the United States of America (Pereira 2014).

In 1997, fumonisins as a subgroup of mycotoxins, were subject to regulations in only one country (FAO, 1997). In 2005, the number of countries regulating fumonisins increased to six, and the limit for their presence in maize was established as a maximum of 3000 mg/kg (Panel 2015).

Currently, many countries have implemented several regulations to control the presence of fumonisins in food products by implementing prescribed acceptable and maximum limits (WHO-Department of Food Safety and Zoonoses 2018). The JECFA established a maximum tolerable daily intake (PMTDI) of 2 μg/kg b.w./day for FB_1, FB_2, and FB_3 (alone or in combination). On the other hand, the European Union (EU Regulation 1126/2007) and the US, proposed acceptable upper limits of 4000 μg/kg for FB_1 and FB_2 (Agriopoulou 2020). These established safe limits are not homogenous as different countries change them mainly in relationship to food products. For example, the maximum permissible levels (MPL) for the combination of FB_1 + FB_2 is 4000 μg/kg for unprocessed maize; whereas for maize intended for direct human consumption is 1000 μg/kg; 800 μg/kg for maize-based breakfast cereals/snacks; and 1400/2000 μg/kg for maize milling fractions of particle size greater/< 500 μm respectively. The Codex Alimentarius Commission on Food Contaminants recommends a limit of 5000 μg/kg for combined FB_1 + FB_2 + FB_3 MPL for unprocessed corn grain and 2000 μg/kg MPL for processed maize-based products including flour (Bryła 2013) (WHO-Department of Food Safety and Zoonoses 2018). The main purpose of these legislations is to prevent the consumption of food that is potentially contaminated with mycotoxins, ensuring the protection of the inhabitants of developed coun-

tries (Alberts 2017). At present, there are limits established for raw maize (4000 μg/kg), as well as for maize flour and semolina (2000 μg/kg) (Alimentarius 2019). The European Commission has regulated acceptable levels of fumonisins with its most recent modification in 2010 indicating 2000 μg/kg for raw maize, 1000 μg/kg for maize products for coction, 400 μg/kg for direct ingest maize products and, 200 μg/kg for babies and kinder food (European Comission 2007). In contrast, countries with emerging economies lack similar regulations or have poor standards; this can lead to problems with over-consumption of food with high levels of mycotoxins, including fumonisins (Ponce-García 2018). To control and/or verify fumonisin presence in food and feed products, analytical methods are needed for a wide variety of matrices. These have been proven to affect fumonisin stability and thus, bioavailability (Tables 1-3).

5. Analytical methods

There are a lot of reported methods for fumonisin analysis. These have been mainly developed to analyze their presence in grains and grain-based products as there is a high concern for their presence in these types of matrices. However, other matrices such as fruits, vegetables, animal tissues, cereals and beverages should also be considered, as their carry over and cumulative effects ensure their presence in these types of food products. Moreover, analysis in human matrices is of special importance to completely establish toxicokinetics, as well as to elucidate the mechanisms by which fumonisins relate to some diseases.

This review compiles and organizes 88 analytical methods for fumonisins between 2006 and 2022, including liquid chromatography coupled with MS detectors (single quadrupole -sQ-, triple quadrupole -QQQ- and time of flight -TOF-, with or without ion tramp), fluorescence and light scattering. The workflow for fumonisin determination includes 1) extraction, sometimes followed by 2) clean up or derivatization, and finally 3) separation and detection (Fig. 3), being the first and third steps the fundamental ones. The detailed methodology used depends on the matrix analyzed, as well as the instrumentation available (Ridgway 2012). Matrices included in this work were classified as maize and corn-based products (34 methods), other cereal and seeds (11 methods), beverages (12 methods), products of animal origin (17 methods) and other samples (14 methods). Instrumentation used and conditions are detailed. Table 1 includes methods describing extraction and separation/detection using chromatography coupled to mass detectors without clean-up procedure; Table 2 shows those methods that include a clean-up stage after extraction, followed by separation/detection using chromatography coupled to mass detectors; Table 3 refers to methods describing extraction and separation/detection using chromatography coupled to fluorescence or light scattering detectors.

5.1. Extraction

Extraction is needed to obtain the enriched extract with the desired analytes, and to enhance sensitivity of the method, diminishing interferences with other components of the sample. Organic solvents, such as chloroform and hexane, which are commonly used in other mycotoxin extraction, are not recommended for FBs determination (Patel et al., 2011); this is due to the structure of FBs, which includes multiple hydroxy, amine and carbonyl groups that make polar solvents necessary for its extraction (Scott 1993). Therefore, a mixture of water and acetonitrile (ACN) or methanol (MeOH) is the most used solvent. However, some matrices are aqueous rendering these mixtures useless as the matrices are miscible with these solvents.

FBs' ability to conjugate with proteins and sugars, allows it to be extracted with organic acids, the most commonly used are acetic acid (AcOH), formic acid (FA) and trifluoracetic acid (TFA); some authors have even used strong acids such as hydrochloric or sulphuric acid in the extraction of FBs (Zöllner and Mayer-Helm, 2006). To enhance the solubility of fumonisins in organic solvents, pressure has sometimes been used during extraction. Reported methods include liquid–liquid extraction (LLE) (Lucci et al., 2015), pressurized liquid extraction (PLE) (D'Arco 2008) and supercritical fluid extraction (Selim et al., 1996) (Tables 1-3). Matrix and analysis method defines the extraction method to be used and/or the extraction yield (Damiani et al., 2019.

Reported methods use an aqueous:organic proportion ranging from 10 to 85 % of organic solvent, however, typically more than 50% of MeOH or ACN and, from 0.1 to 3% of acid is used. Some mixes of ACN:MeOH:H_2O were used keeping the mentioned range for aqueous, and some used 100 % ethyl acetate (Monbaliu et al., 2009) for extraction. Immunoaffinity extraction was also reported for urine samples. Usually, suspension of sample into extraction solvents, was followed by shaking, for periods of time ranging from seconds up to 3 h, filtering or centrifugation, from 3,000 to 10,000 rpm for 2 to 15 min (Tables 1-3).

In 2012 Pietri and collaborators observed problems during the extraction step which resulted in unexpected low recoveries in maize flour samples due to the interactions between fumonisins and matrix components (Damiani et al., 2019).

5.1.1. Liquid-liquid extraction (LLE)

LLE is the most commonly used technique which, depending on the composition of the food matrix, uses a mixture of acidified solvents (Lucci et al., 2015). Examples include: methanol–water (Paepens et al., 2005), acetonitrile–water (Zitomer et al., 2008 or methanol–acetonitrile–water and a non-polar phase (Bryła et al., 2013. It is based on the distribution of toxin in immiscible phases (aqueous and organic phase). The non-polar contaminants (lipids and cholesterol) are removed with non-polar organic solvents such as hexane and cyclohexane, while polar toxin compounds are extracted in the aqueous phase. This method is useful for both liquid and solid samples, the latter are homogenized and remain suspended in a polar solvent. In both cases, centrifugation is carried out, after which drying is performed under a nitrogen atmosphere, and, finally, reconstitution is done in a mixture of the chosen solvent. LLE is suitable for several toxins at small-scale preparations, however, its main disadvantage is that it is time consuming and there can be loss of sample during handling (Nawaz 2017).

5.1.2. Pressurized liquid extraction (PLE)

PLE, also known as Accelerated Solvent Extraction (ASE), uses temperatures around 100–180 °C and 1500–2000 psi of pressure to modify the conditions of the solvent and the sam-

Table 1 LC-MS methods for FBs without clean up.

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions, Limits Mass Conditions / Limits
Maize and corn-based products					
(Zitomer et al. 2008)	B_1, B_2, B_3 Maize leaf	0.01	**Extraction:** 1.-Add 2 mL ACN/H_2O 1:1 (5% FA); 2.- Gently shaken for 3 h; 3.- Centrifugate to 15000 g; 4.- Filter; 5.- Dilute 1:10	**Metachem Inertsil ODS-3, 150 x3 mm, 5 μm** Inj vol 20 μL, A) H_2O/ACN/FA 97:2:1, B) H_2O/ACN/FA 2:97:1. 70-50% B in 9 min, 50-100% B in 2 min, keep 10 min; initial conditions for 10 min Flow: 0.20 mL/min, Time: t_{an} = 21 min, t_{Tot} = 31 min	**QTrap** CaT : 210°C LOD: 0.01 μg/kg all FBs
(De Girolamo et al. 2014)	B_1, B_2, PHF (B_1, B_2), HF (B_1, B_2) Maize based products	20	**Extraction:** 1.- 100 mL MeOH/ACN/citrate-phosphate buffer 25:25:50; 2.- Shake 1h; 3.- Dilute 1:10 with MeOH/H_2O 80:20 with 0.5% AcOH; 4.- Filter	**Gemini C_{18}, 150 x 2.0 mm, 5 μm at 40 °C** Inj vol 20 μL, A) H_2O, B) MeOH, both with 0.5% AcOH 40-60% B in 30 min, 60 to 40% B in 1 min; initial conditions for 9 min Flow: 0.2 mL/min, Time: t_{an} = 30 min, t_{Tot} = 40 min	**Orbitrap** CaV 45 V; SV 4 kV; RF Lens 75 V; ST 300 °C; CaT: 300 °C; SG 30 U; GF 10 skimmer V 18 V LOD: 5 μg/kg, LOQ: 10 μg/kg all FBs
(Beltrán et al. 2009)	B_1, B_2 Maize, kernel, dry pasta, baby food	2.5	**Extraction:** 1.- Add ACN/H_2O 80:20 + 0.1% AcOH, 2.-shake 90 min, 3.-centrifuge to 4000 rpm, 10 min; 4.-dilute 1:2 with H_2O, 5.-filter (0.22 mm nylon filter)	**Acquity UPLC BEH C_{18}, 50 x 2.1 mm, 1.7 μm at 40°C** Inj vol 20 μL, A) H_2O, B) MeOH, both with 0.5 mM AmAc and 0.1% AcOH 10-90 % B in 4 min, initial conditions for 3 min Flow: 0.3 mL/min, Time: t_{an} = 4 min, t_{Tot} = 7 min	**QQQ** CaV 3.5 kV; DGT 500°C; ST 120 °C; T 40 °C; DGF 1200 L/h, CoG 4 x 10^{-3} mbar LOD: 1 μg/kg, LOQ: 3.5 μg/kg
(C. Dall'Asta et al. 2008)	B_1, B_2, B_3 Maize, maize-based products	25	**Extraction LLE:** 1.- Add 100 mL H_2O/ACN/MeOH 50:25:25, 2.- blend (6000 rpm/5 min); 3.- take 4 mL; 4.- filter; 5.- dry N_2, 6.- reconstitute 1mL in H_2O/ACN 1:1; 7.- filter	**XTerra C_{18}, 250 × 2.1 mm, 5 μm at 30°C** Inj vol 10 μL, A) H_2O, B) MeOH, both with 0.1% FA 0% B for 3 min, 0-45% B in 2 min, keep 5 min, 45-85% B in 15 min, keep for 10 min, initial conditions for 10 min Flow: 0.2 mL/min, Time: t_{an} = 35 min, t_{Tot} = 45 min	**QQQ** CaV 3.2 kV; CV 30 V; EV 3 V; ST 120 °C; DGT 160 °C; CGF 70 L/h; DGF 650 L/h (N_2 for both) LOD: B_1, B_2 1 μg/kg, FB_3 8 μg/kg LOQ: B_1, B_2 5 μg/kg, FB_3 12 μg/kg
(Arroyo-Manzanares et al. 2018)	B_1, B_2 and other toxins Wheat, maize	2	**QuEChERS:** 1.-Add 8 mL of H_2O; 2.-shake 10 s; 3.-add 10 mL 5% FA in ACN; 4.-shake 2 min; 5.-add 4 g $MgSO_4$ + 1 g NaCl; 6.-shake 1 min: 7.-vortex 2 min; 8.-centrifuge to 4500 rpm, 5 min, 4 °C; 9.-take 5 mL; 10-dry under N_2 at 40 °C; 11.-reconstitute (0.2 mL MeOH/H_2O 1:1); 12.-centrifuge to 14000 g, 5 min, 4 °C	**ACQUITY HSS UPLC T3, 150 x 2.1 mm, 1.8 μm at 30 °C** Inj vol 10 μL, A) H_2O, B) MeOH, both with 0.3% FA and 5 mM AmF 5% B, keep 0.5 min, 5-94% B in 19.5 min, keep 1 min, 94-5% B in 3 min; initial conditions for 4 min Flow: 0.4 mL/min, Time: t_{an} = 21 min, t_{Tot} = 28 min	**QQQ** ST 150 °C; DGT 400 °C; NG 7 bar (N_2); CGF 150 L/h; DGF 1000 L/h LOD; 1.28 B_1, 0.25 FB_2, 0.27 B_3 μg/kg LOQ: 4.24 B_1, 0.82 FB_2, 0.89 B_3 μg/kg

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Table 1 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions, Limits Mass Conditions / Limits
(Chiara Dall'Asta, Galaverna, et al. 2009)	B_1, B_2, B_3 Corn-based products	5	**Extraction:** 1.- Add 50 mL H_2O/MeOH 30:70; 2.- Blend to 6000 rpm, 10 min; 3.- Stir for 60 min; 4.- re-extract the solid (same way); 5.- Filter; 6.- Dry 4 mL; 7.- Dissolve in 2 mL MeOH	**Xterra C_{18}, 250 x 2.1 mm, 5 μm, at 30 °C** Inj vol 5 μL, A) H_2O, B) MeOH, both with 0.2% FA 30% B for 2 min, 30-45% B in 3 min, 45-90% B in 20 min, keep for 10 min, 30% B in 1 min; initial conditions for 20 min Flow: 0.2 mL/min, Time: $t_{an} = 35$ min, $t_{Tot} = 56$ min	**QQQ** CaV 3.2 kV; EV 3 V; ST 120 °C; DGT 160 °C; CGF 70 L/h; DGF 650 L/h (N_2, both) LOD: FB_1 4 μg/kg, B_2, FB_3 8 μg/LOQ: B_1 B_2 5, B_3 12 μg/kg
(Chiara Dall'Asta, Mangia, et al. 2009)	B_1, B_2, B_3 Ground corn	5	**Extraction:** 1.- Add 50 mL H_2O/MeOH 30:70; 2.- Blend to 6000 rpm, 10 min; 3.- Stir for 50 min; 4.- Centrifuge to 3500 g, 15 min; 5.- Filter (2 mL)	**Xterra C_{18}, 250 x 2.1 mm, 5 μm at 30°C** Inj vol 10 μL, A) H_2O, B) MeOH, both with 0.1% FA 30 % B for 2 min, 30-45% B in 3 min, 45-90% B in 20 min, keep for 10 min; initial conditions for 15 min Flow: 0.2 mL/min, Time: $t_{an} = 35$ min, $t_{Tot} = 50$ min	**QQQ** CaV 4 kV; EV 2 V; ST 120°C; DGT 350 °C; CGF 50 L/h; DGF 600 L/h LOD: 5 μg/Kg
(Chiara Dall'Asta, Mangia, et al. 2009)	B_1, B_2, B_3 Corn-based products	5	**Extraction:** 1.- Add 2 ml H_2O/ACN/AcOH 20:79:1; 2.- Extract 90 min in rotatory shaker; 3.- Centrifuge 3000 rpm, 3 min; 4.- Take aliquot 350 μL and dilute 1:1 with extraction solvents	**Gemini C_{18}, 150 x 4.6 mm, 5μm at 25 °C** Inj vol 5 μL, A) H_2O/ACN/AcOH 89:10:1, B) H_2O/ACN/AcOH 2:97:1, both with 5 mM AmAc 0% B for 2 min, 0-100% B in 12 min, keep for 3 min; initial conditions for 4 min Flow: 1.0 mL/min, Time $t_{an} = 17$ min, $t_{total} = 21$ min	**QQQ** CaV 4.0 kV; EV 3 V; ST 550 °C; CUR 10 psi LOD: 8 μg/kg
(G. B. de Oliveira et al. 2017)	B_1, B_2 Maize	1	**Extraction:** 1.- Add 1 g Silica gel as dispersant; 2.- Mix in polypropylene cartridges, MSPD; 3.- Elute with 16 mL of 20 mM AmFo buffer:MeOH 9:1 (pH 7); 4.- Collect 2 mL fractions; 5.- Centrifuge to 4000 rpm, 10 min; 6.- Filter	**Poroshell, C_{18}, 100 x 3 mm, 2.7 μm, 40 °C** Inj vol 10 μL, A) Ultrapure H_2O, B) ACN, both with 0.1% FA 20-90% B in 3 min, keep 0.4 min, 90-20 % B in 0.1 min; initial conditions for 6 min Flow: 0.5 mL/min, Time: $t_{an} = 3.4$ min, $t_{Tot} = 9.5$ min	**QQQ** CaV 4.5 kV; EP 10 V; DGT 650 °C; NG 40 CUR 18 a.u, LOD: B_1 514, B_2 176 μg/kg LOQ: B_1 594, B_2 210 μg/kg
(D'Arco et al. 2008)	B_1, B_2, B_3 Corn-based baby food	3	**Extraction:** 1.- Add 100 μL of a 5 μg/mL Fbs solution (0.5 μg) and keep 15 min at RT; 2.-pack into 11 mL PLE pressure resistant stainless steel extraction cell; 3.-elute with 22 mL of MeOH 60% at 40°C and 34 atm, 2 min of preheating, 5 min of static time, 60 s of purge time; 4.- concentrate to 5 mL (40 °C and 80 mbar); 5.- transfer to a 15 mL conical tube; 6.-evaporate to dryness at 55°C with N_2 ; 7.reconstitute 1 mL MeOH/H_2O 50:50; 8.-filter	**Luna C_{18}, 150x4.6 mm, 5 μm (Temp NR)** Inj vol NR, A) H_2O, B) MeOH, both with 0.5% FA 65% B for 3 min, 65-95% B in 4 min, keep 3 min, initial conditions in 10 min Flow: 0.30 mL/min, Time: $t_{an} = 10$ min, $t_{Tot} = 20$ min	**QQQ** CaV 3.20 kV; CoV 50 V; EV 3 V; RF lens 0.2 V; ST 125 °C; DGT 300 °C; DGF 500 L/h; CGF gas 50 L/h LOD: 0.7 B_1 and B_2, 1.5 μg/kg B_3 LOQ: 2 B_1 and B_2, 5 μg/kg B_3

Table 1 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions, Limits Mass Conditions / Limits
(Chiara Dall'Asta, Mangia, et al. 2009)	B_1, B_2, B_3 Raw corn	100	**Extraction:** 1.- Add 50 mL KOH 2M; 2.- Centrifuge to 6000 rpm, 10 min; 3.- Stir (50 min); 4.- Add 50 mL ACN; 5.- Stir 10 min; 6.- Separate 20 mL and dry under N2; 7.- Redissolve in 50 mL KOH 2M; 8.- Centrifuge to 3500 rpm, 15 min; 9.- Dry under N2; 10.- Redissolve in H_2O/MeOH 30:70	**Hypersil C_{18}, 150 x 2.1 mm, 5 µm at 25°C** Inj vol 10 µL, A) H_2O, B) MeOH, both with 0.2% FA 20% B for 1 min, 20-100% B inwalnut 5 min, keep 3 min, initial conditions for 4 min Flow: 0.6 mL/min, Time: t_{an} = 8 min, t_{Tot} = 13 min	**QQQ QTrap** CaV 4 kV; CoV 50 V; ST 425°C; DGT 350°C; CGF 50 L/h; DGF 600 L/h (N_2, both) LOD: < 15 µg/kg
(Hu et al. 2019)	B_1, B_2 Raw maize	1	**Extraction:** 1.- 10 mL ACN/H_2O/AcOH 70:29:1; 2.- Shake 30 min; 3.- Centrifuge to 4500 rpm, 10 min; 4.- Filter supernatant; 5.- Take 1 mL; 6.- Add 10 µL, 1 µg/mL ^{13}C-34 FB_1 and ^{13}C-34 FB_2	**Luna C_{18}, 150 x 2 mm, 3 µm at 40°C** Inj vol 5 µL, A) H_2O, B) MeOH, both with 2 mM AmAc 40-90% B in 6 min, keep 1 min, 90-100% B in 1 min, keep 1 min, 100-40% B in 2 min; initial conditions for 4 min Flow: 0.2 mL/min, Time: t_{an} = 9 min, t_{Tot} = 15 min	**Qtrap** CaV 5.5 kV; EP 10 V; ST 600°C; CUR 40 psi; CoV 10 V; dwell time 100 ms LOD: 7 B_1; 6 B_2 µg/kg LOQ: 28 B_1; 27 B_2 µg/kg
(Bergmann, Hübner, and Humpf 2013)	B_1 Maize	10	**Extraction:** 1.- Add 20 mL ACN/H_2O 70:30 with 1% FA; 2.-Vortex 30 s; 3.- Sonicate 10 min; 4.- Shake 15 min; 5.- Centrifugate to 8000 g, 15 min, 25 °C; 6.- Dilute 1:1 1% FA; 7.- Filter if necessary	**Hyperclone C_8 BDS, 150 x 2.0 mm, 3 µm at 40° C** Inj vol 20 µL, A) H_2O, B) ACN, both with 1% FA 65% B for 4 min, 37.5% B for 0.5 min, 5% B for 2 min, keep for 0.5 min, initial conditions for 4 min Flow: 0.30 mL/min, Time: t_{an} = 7 min, t_{Tot} = 11 min	**QTrap** CaV 5.5 kV; DG 350 °C; NG 35 psi; DG 45 psi; CUR (N_2) 30 psi; CoG 5 x 10^{-5} Torr; QTrap CUR 20 psi LOD: 53 µg/kg, LOQ: 188 µg/kg
(de Matos et al. 2021)	B_1, B_2, HB_1, HB_2 Corn products	5	**Extraction:** 1.- Add ACN:H_2O:FA 75.24:1; 2.- shake for 2 min; 3.- sonicate for 10 min; 4.- centrifuge at 3000 rpm for 7 min; 5.-take 0.05 mL of extract; 6.- dilute with 0.95 mL 0.05% of AF in MeOH:H_2O 1.1; 7.- filter	**ACQUITY BEH C_{18} 100 x 2.1 mm, 1.7 µm at 35°C** Inj vol 5 µL, A) H_2O (0.1% FA), B) MeOH 65-80% B in 3 min, hold for 1 min, 100% B in 1 min, initial condition for 2 min Flow 0.3 mL/min, Time: t_{an} = 5 min, t_{Tot} = 7 min	**QQQ** CaV: 3kV; DGT: 400 °C; ST: 150 °C; CGF: 15 L/h; DGF:750 L/h LOD: (B_1: 0.43-1.98, FB_2 0.19-1.37, HB_1 0.72-1.39, HB_2 0.36-0.70) µg/Kg LOQ: (B_1:1.43-6.59, FB_2 0.60-4.60, $HB_1$2.40-4.60, HB_2 1.20-2.30) µg/Kg
(Lin et al. 2011)	B_1, B_2 Corn	5	**Extraction:** 1.- Add 25 mL MeOH/H_2O 3:1; 2.- Ultrasonic bath for 10 min at RT, output powder 120 W; 3.- Centrifugate to 5000 g, 5 min; 4.- Filter (0.22 mm nylon filter)	**Zorbax Eclipse XDB-C_{18}, 150 x 2.1 mm, 3.5 µm at 30°C** Inj vol 10 µL, MeOH/H_2O/FA 75:25:0.2 Flow: 0.20 mL/min, Time t_{an} = t_{Tot} = 4 min	**Q** CaV 3.5 kV; CoV 50 V; ST 120 °C; DGT 350°C; DGF 600 L/h LOD: 3.5 B_1, 2.5 µg/kg B_2 LOQ: 11.7 B_1, 8.3 µg/kg B_2
(A. S. Silva et al. 2019)	B_1, B_2	2	**Extraction:** 1.- Add 10 mL ACN 80%; 2.- Shake at 110 rpm, 1h; 3.- Centrifuge to 3000 rpm, 10	**Zorbax Eclipse Plus C_{18}, 2.1 x 50 mm, 1.8 µm at 30 °C**	**TOF** CaV 5.5 KV; ST 575 °C; CUR 30 psi; Gas 1

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Table 1 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions, Limits Mass Conditions / Limits
	Maize flour		min; 4.- Remove supernatant; 5.- Re-extract the solid, same way; 6.- Centrifuge to 3000 rpm, 10 min; 7.- Dilute 1:1 with H_2O; 8.- Filter	Inj vol 20 µL, A) 0.1% FA, B) ACN 10-70% B in 12 min, 70-90% B in 1 min, keep 1 min, 90-10% B in 1 min, initial conditions for 2 min Flow: 0.5 mL/min, Time: $t_{an} = 14$ min, $t_{Tot} = 17$ min	and Gas 2, 55 psi both; DP 100 V; Full scan 100-750 Da LOD: 62.5 µg/kg,LOQ: 125 µg/kg all FBs
Other cereal and seeds					
(Bartók et al. 2006)	B_1, B_2, B_3, its analogs Rice	3	**Extraction:** 1.- Add 25 mL of ACN/H_2O 75:25; 2.- Centrifuge to 13,500 rpm, 1 min; 3.- Shake 1 h; 4.- Centrifuge to 10,000 g, 10 min; 5.- Filter	**Supelcosil ABZ Plus, 250 x 2.1 mm, 5 µm at 40 °C** Inj vol 1 µL, A) H_2O, B) ACN, both with 0.1% FA 25-40 % B in 22 min, 40-100% B in 5 min, keep for 3 min. Flow: 0.3 mL/min, Time: $t_{an} = 27$ min, $t_{Tot} = 30$ min	**QTrap** CaV 3.5 kV; EV 200 V; HED Voltage 7 kV; NG 40 psi; DGF 9 L/min; DGT 350 °C; trap drive 53.9; max accumulation time 300 ms; full scan 50-1100 *m/z* LOD / LOQ: NR
(Soleimany, Jinap, and Abas 2012)	B_1, B_2 Cereals	10	**Extraction:** 1.- Add 40 mL H_2O/ACN/AcOH 20:79:1; 2.- Shake 60 min; 3.- Centrifuge the supernatant at 3000 rpm, 10 min; 4.- Dilute 1:1 in H_2O/ACN/AcOH 79:20:1; 5.- Filter	**Thermo Scientific C_{18}, 150 x 4.6 mm, 3 µm at 30°C** Inj vol 20 µL; A) H_2O, B) MeOH both with 0.1% AcOH 5% B for 8 min, 5-90% B in 14 min; 90-5% B in 3 min Flow: 0.25 mL/min, Time: $t_{an} = 22$ min, $t_{Tot} = 25$ min	**QQQ** CaV 3 kV; ST 120°C; DGT 400 °C; spray gas N_2 LOD: 20 ng/g, LOQ: 40 ng/g
(Rausch, Brockmeyer, and Schwerdtle 2020)	B_1, B_2, B_3 and other toxins Cereals	1	**QuEChERS:** 1.- Add 2 mL H_2O, 2.-mix 1 min, RT, 10 min; 3.- extract with 8 mL ACN/FA 75:5; 4.- Shake 15 min; 5.- add 4 g anhydrous $MgSO_4$, 1 g NaCl, 1 g Na_2HCit 1.5 H_2O, Na_3Cit 2 H_2O, 6.- Mix 1 min; 7.- Shake 15 min; 7.- Centrifuge to 2140 g, 2 min; 8.- Filter; 9.- Take 500 µL, dry; 10.- Redissolved in 250 µL MeOH/H_2O 20:80	**Raptor Fluoro Phenyl 50 x 2.1 mm, 2.7 µm in series with** **Raptor Biphenyl 50 x 2.1 mm, 2.7µm at 30 °C** Inj vol 10 µL, H_2O, 0.3% FA, B) MeOH, both with 5 mM AmFo 20% B for 0.6 min, 20-40 % B in 0.4 min, 40-90% in 8 min, keep 1 min, initial conditions for 3.5 min Flow: 0.4 mL/min Time: $t_{an} = 10$ min, $t_{Tot} = 13.5$ min	**QQQ** CaV 4.5 kV; ST 500 °C; CUR 40 psi; ISG 1 60 psi; ISG 2 65 psi LOQ: depending on the matrix, FBs 4-15 µg/kg
(Aurelien Desmarchelier et al. 2010)	B_1, B_2 and other mycotoxins Cereals	5	**QuEChERS:** 1.- Add 10 mL H_2O + 10 mL 0.5% AcOH in ACN; 2.- Shake at 300 rpm, 5 min; 3.- Add 5 g $MgSO_4$/NaCl 4:1, 4.- Shake; 5.- Centrifuge to 4000 g, 15 min, RT; 6.- Take 5 mL; 7.- Shake at 200 rpm, 5 min; 8.- Centrifuge to 4000 g, 1 min; 9.- Dry 1 mL at 40 °C (N_2); 10.- Add 75 µL MeOH; 11.- Sonicate; 12.- Add 75 µL H_2O, mix; 13.- Centrifuge to 8500 g, 10 min, RT; 14.- Dilute 60 µL with 140 µL H_2O; 15.- Centrifugate to 8500 g, 10 min, RT	**Zorbax Bonus-RP, 150 x 2.1 mm, 3.5 µm** Inj vol NR, A) H_2O 0.15% FA, 10 mM AmFo, B) MeOH 0.05% FA 15% B 0.5 min, 15-100% B 8.5 min, keep for 6 min, 15% B in 1 min, initial conditions for 9.5 min Flow: 0.25 mL/min, Time: $t_{an} = 15$ min, $t_{Tot} = 25.5$ min	**QTrap SRM** ST 550 °C; NG 50 psi; CUR 40 psi; TG 30 psi; CoG 1.2 x 10^{-4} psi LOQ: 50 µg/kg all FBs

Table 1 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions, Limits Mass Conditions / Limits
(Liao et al. 2013)	B_1, B_2 and other toxins Finished grain, nut products	1	**Extraction:** 1.-Add 5 mL H_2O/ACN 15:85; 2.-shake to 1550 rpm, 30 min; 3.-centrifugate to 4500 rpm, 5 min; 4.-take 500 µL; 5.-add 20 µL of ^{13}C-34 FB_1 (25 µg/mL) + 480 µL 20 mM FA; 6.-vortex 15 s; 7.-filter	**Ultra-Aqueous C_{18}, 100 x 2.1 mm, 3 µm, at 40 °C** Inj vol 10 µL, A) H_2O, B) MeOH, both with 0.1% FA + 10 mM AmFo 10 % B for 1 min, 10-100% B in 6 min, keep for 3 min, initial conditions for 5 min Flow: 0.5 mL/min, Time: t_{an} = 10 min, t_{Tot} = 15 min	**QTrap** Conditions NR LOD: FBs 2.2-2.9 µg/kg, LOQ: FBs 7.3-9.6 µg/kg, depending on the matrix
(Bartók et al. 2010)	Isomers of B_1 Rice	1	**Extraction:** 1.-8 mL MeOH/H_2O 75:25; 2.-homogenize 9,500 rpm, 4 min: 3.-centrifuge to 10,000 rpm, 10 min, 4.-filter	**YMC-Pack J'sphere ODS H80, 250 x 2.1 mm, 4 µm, 40 °C** Inj vol 1 µL, A) H_2O, B) ACN, both with 0.1% FA 24-40% B for 79 min, 40-100 % B for 15 min, keep for 10 min Flow: 0.20 mL/min, Time: t_{an} = 79 min, t_{Tot} = 104 min	**TOF, full scan MS** CaV 3.5 kV; Fragmentor 170 V; skimmer 70 V; DGT 350 °C; DGF 10 mL/min; NG 20 psi; full scan 100-1700; acquisition rate 250 ms/spectrum LOD/LOQ: NR
(Oueslati et al. 2012)	B_1, B_2 Cereals, derived products	5	**Extraction:** 1.- Add 10 mL ACN/H_2O 80:20; 2.-vortex 2 min, shake 60 rpm x 10 min; 3.-centrifuge to 5000 rpm, 5 min; 4.-filter 2 mL (0.20 µm, Millipore)	**Acquity UPLC BEH C_{18}, 100x2.1 mm, 1.7 µm at 30°C** Inj vol 5 µL, A) H_2O with 5 mM AmFo, B) MeOH 25-75% B in 3 min, 75-100% B in 2 min, keep for 1.5 min, 100-25% B in 1 min; initial conditions for 1 min Flow: 0.35 mL/min, Time: t_{an} = 6.5 min, t_{Tot} = 8.5 min	**QQQ** CaV 3.5 kV; CoV FB_1 45 V, FB_2 55 V; EV 3 V; ST 120 °C; DGT 350 °C; CGF 50 L/h; DGF 650 L/h LOD: B_1 and B_2 1 µg/kg LOQ: B_1 and B_2 5 µg/kg
(Rausch, Brockmeyer, and Schwerdtle 2021)	B_1, B_2, B_3, HB_1, HB_2, HB_3 Cereals	2.5	**Extraction:** 1.- Add ACN:H_2O:FA 79.20:1; shake for 15 min at RT; 3.- Add 20 µL of Deuterated internal standard; 4.- rotary agitation for 30 min; 5.- centrifuge at 1902 g, 6.- take an aliquot of supernatant, 7.- filter	**First dimension: YMC-Pack Diol-NP C_{18} 100 × 2.1 mm, 5 µm at 40 °C.** Vol. inj: 10 µL of sample, A) H_2O, B) ACN:H_2O 90:10 Both (0.1% FA, 10 mM AmFo) 100% B in 2.5 min, 100-90% B in 0.5 min, 90-20 % B in 0.8 min, hold for 3.8 min, 20-100% B in 0.20 min. initial condition for 17.20 min. Second dimension: 2 columns connected in series **Raptor FluoroPhenyl, 50 × 2.1 mm, 2.7 µm and Raptor Biphenyl 50 × 2.1 mm, 2.7 µm,** 5% B for 1.2 min, 5-0% B in 0.10 min, hold for 7.15 min, 0-5% B in 0.05 min, 5-50% B in 1.1 min, 50-70% B in 4.4 min, 70-85% B in 2.5 min, 85-100% B in 3 min, hold for 2 min, 100-5% B in 0.10 min, initial condition for 4 min	**QQQ** CaV: 4.5 kV; CUR: 40 psi; ST: 500 °C; LOQ: (B_{1-3}: 10, HB_{1-3}: 100) µg/Kg

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Table 1 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions, Limits Mass Conditions / Limits
				Flow 0.2 mL/ min, 0.3 ml/min, Time: t_{an} = 7.6 min t_{Tot} = 25 min, Time: t_{an} = 15.50 min t_{Tot} = 25 min	
Other samples (Škrbić, Živančev, and Godula 2014)	B_1, B_2 and other toxins Crude extracts of nuts	10	**Extraction:** 1.- Add 40 mL ACN/H_2O/AcOH 79:20:1; 2.- Shake 1h; 3.- Filter; 4.- Take 20 mL; 5.- Add 20 mL hexane; 6.- Mix 2 min; 7.- Centrifuge to 5000 rpm, 5 min; 8.- Eliminate hexane phase. 9.- Filter aqueous phase	**Hypersil GOLD C_{18}, 50 x 2.1 mm, 1.9 μm at 25 °C** Inj vol 10 μL, A) H_2O, B) MeOH, both with 1% AcOH and 5 mM AmAc 5 % B for 0.5 min, 5-95 % B in 2.5 min, keep 2 min, 95-5% B in 1.2 min, initial conditions for 1.8 min Flow: 0.50 mL/min, Time: t_{an} = 6 min, t_{Tot} = 8 min	**QQQ** CaV 3.4 kV; ST 350 °C; SG 40 arbitrary units; aux gas 10 arbitrary units; CaT 270 °C LOD: 0.24 B_1, 0.05 B_2 μg/kg LOQ: 0.8 B_1, 0.17 B_2 μg/kg
(Yibadatihan, Jinap, and Mahyudin 2014)	B_1, B_2 and other toxins Palm kernel cake	5	**Extraction:** 1.- Add 20 ml H_2O/ACN/FA 20:79:1; 2.- Shake 60 min; 3.- Centrifuge supernatant to 3000 rpm, 10 min; 4.-Dilute 1:4 with water; 5.- Filter	**Symmetry C_{18}, 150 x 2.0 mm, 3μm, 30 °C** Inj vol. 25 μL, A) H_2O, 0.2% FA, B) MeOH 10% B for 8 min, 10-90 % B in 2 min, keep 7 min, from 90-10% B in 3 min, initial conditions for 5 min Flow: 0.20 mL/min, Time: t_{an} = 17 min, t_{Tot} = 25 min	**QQQ** CaV 3 kV; ST 120 °C; DGT 350 °C LOD both: Std 5.6 μg/kg LOQ both: Std 18 μg/kg LOD both: Samples 17.5 μg/kg LOQ both: samples 58 μg/kg
(Qian et al. 2018)	B_1, B_2 and other toxins Feed	2	**QuEChERS:** 1.- Add 1.5 g NaCl + 10 mL 3% AcOH in ACN/H_2O 80:20; 2.-Vortex 1 min, 3.- Ultrasound 20 min; 4.-Add 2 g anh $MgSO_4$; 5.- Vortex 1 min; 6.-Centrifuge to 8000 rpm, 5 min; 7.-Dry (N_2, 40 °C); 8.-Dissolve in MeOH:H_2O 1:1; 9.-Filter	**ACQUITY UPLC HSS T3, 100 x 2.1 mm, 1.8 μm at 40°C** Inj vol. 5 μL, A) H_2O, 0.1% FA, 1 mM AmAc; B) MeOH} 0-10% B in 1 min, 10-20% B in 2 min, 20-99% B in 8 min, keep 2.5 min; 99-10% B in 0.1 min; initial conditions for 5 min Flow: 0.3 mL/min, Time: t_{an} = 13.5 min, t_{Tot} = 18.5 min	QQQ CaV 5.5 kV; ST 550°C; Auxiliary gas 40 psi LOQ: 0.4 μg/kg for both B_1 y B_2
(Spanjer, Rensen, and Scholten 2008)	B_1, B_2, B_3 and other toxins Peanut, pistachio, wheat, maize, cornflakes, raisins, figs	25	**Extraction:** 1.- Add 100 mL ACN/H_2O 80:20, 2.- Shake 2h; 3.-Dilute 1:4 with H_2O; 4.- Filter if necessary (For raisins and figs use MeOH)	**Alltima C_{18}, 150 x 3.2 mm, 5 μm at 30 °C** Inj vol 20 μL, A) H_2O, B) ACN, both with 0.1% FA10-70% B in 12 min (curve 1), keep 4 min, 70-90 % B in 1.5 min (curve 6), keep 2.5 min, 90-10 % B in 1 min (curve 1) , initial conditions for 5 min Flow: 0.3 mL/min, Time: t_{an} = 20 min, t_{Tot} = 25 min	**QQQ** CaV 2.5 kV; CoV 75 V; DGT 450°C; CGF 100 L/h (N_2); DGF 600 L/h LOQ: depending on the matrix, B_1 5-100 μg/kg, B_2 1-100 μg/kg
(Aurélien Desmarchelier et al. 2014)	B_1, B_2 and other toxins	25	**Extraction:** 1.- Add 50 mL H_2O, 2.- Homogenize 1 min 10000 rpm, 3.-Take 5 g of sample (peanut, green cofee, cocoa, paprika) or 2 g (infant	**Zorbax Bonus-RP C_{18}, 150 x 2.1 mm, 3.5 μm at 50 °C** Inj vol 20 μL, A) H_2O, 0.15% FA, 10 mM AmFo,	**QTrap, QQQ** ST 550 °C; CUR 40 psi, Nebulizer 50 psi; Turbo gas 30 psi

Table 1 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions, Limits Mass Conditions / Limits
	Cereals, cocoa, oil, spices, infant formula, coffee, nuts		formula, sunflower oil), 4.-Add 100 µL of ^{13}C-FB standard (FB_1 and FB_2 each 10 µg/mL), 5.-Add 10 mL H_2O and 10 mL ACN, 0.5% AcOH, 6.-Add 5 g $MgSO_4$:NaCl 4:1 Centrifuge 4000g, 15 min, 7.-Defat 5 mL ACN phase with 5 ml hexane. 8.- Take 1 mL of ACN phase, dry, 9.-Reconstitute in 150 µL H_2O/MeOH 1:1, 10.-Centrifuge 8500 g, 10 min, 11.-Take 60 µL, add 140 µL H_2O, 12.-Centrifuge 8500 g, 10 min	B) MeOH, 0.05% FA 15% B for 0.5 min, 15-100 % B in 6 min, keep for 4.5 min, 100-15% B in 0.5 min, initial conditions for 7.5 min Flow: 0.35 mL/min, Time: t_{an} = 11 min, t_{Tot} = 19 min	LOD/LOQ: NR
(Shar et al. 2020)	B_1, B_2 and other toxins Feed, its ingredients	5	**Extraction:** 1.- Add ACN/H_2O/FA 79:20:1; 2.-Shake for 90 min to 180 rotations/s; 3.-Centrifuge to 4000 rpm, 2 min, 4.-Filter	**Acquity C_{18}, 100 x 2.1 mm, 1.8 µm, 40 °C** Inj vol 20 µL, A) H_2O, 1% FA, B) MeOH/H_2O/FA, 97:2:1, both with 10 mM AmFo. 0% B for 2 min, 0-50% B in 0.5 min, 50-100% B in 3.5 min, keep 1 min, initial conditions in 1 min, seal wash for 5 min Flow: 0.5 mL/min, Time: t_{an} = 7 min, t_{Tot} = 8 min	**sQ** CaV 2.79 kV; ST 150 °C; DGT 350 °C; CGF 50 L/h; CGF 600 L7h LOD B_1: 0.07 µg/kg,LOQ B_1: 0.22 µg/kg LOD B_2: 0.03 µg/kg,LOQ B_2: 0.08 µg/kg
(Frenich et al. 2009)	B_1, B_2 Maize, walnut, breakfast cereal, biscuit	5	**Extraction:** 1.- Add 10 mL ACN/H_2O 80:20 (for biscuit add 20 mL); 2.- Vortex 2 min; 3.- Shake to 60 rpm, 10 min; 4.- Centrifuge to 4500g, 5 min; 5.-Take and filter 2 mL	**Acquity C_{18}, 100 x 2.1 mm, 1.7 µm at 30°C** Inj vol 5 µL, A) H_2O with AmFo 5 mM, B) MeOH 25-75% B in 3 min, 75-100% B in 2 min, keep for 1.5 min, 100- 25% B in 1 min; initial conditions for 1 min Flow: 0.35 mL/min, Time: t_{an} = 6.5 min, t_{Tot} = 8.5 min	**sQ** CaV 3.5 kV; EV 3 V; ST 120°C; DGT 350°C; CGF 50 L/h; DGF 650 L/h (N_2 for both) LOD maize: B_1 0.1 µg/kg, B_2 0.2 µg/kg,LOQ maize: B_1 0.5 µg/kg, B_2 0.6 µg/kg; LOD breakfast cereal: B_1 2.1 µg/kg, B_2 0.7 µg/kg LOQ breakfast cereal: B_1 6.2 µg/kg, B_2 2.5 µg/kg
Beverages					
(Rubert et al. 2011)	B_1, B_2, B_3 and other toxins Beer	10 mL	**Extraction:** 1.- Sonicate 25 min, 2.-Condition SPE Oasis HLB cartridges with 5 mL ACN/MeOH 1:1; 3.- 5 mL H_2O; 4.- 10 mL sample into cartridge; 5.-Wash with 5 mL H_2O; 6.- Dry 30 min; 7.- Eluate with 4mL ACN:MeOH 1:1; 8.-Dry (N_2, 35 °C), 9.- Reconstitute in 1 mL (ACN/MeOH 1:1); 10.-Filter	**Gemini C_{18}, 150 x 2.0 mm, 5 µm, at 35 °C** Inj vol 10 µL, A) H_2O, 0.1% FA, B) MeOH, both with 5 mM AmFo 5-95% B in 10 min, 95-80% B in 5 min, initial conditions 5 min Flow: 0.2 mL/min, Time: t_{an} = 10 min, t_{Tot} = 20 min	**QQQ Orbitrap XL** CaV 30 V; SV 4 kV; Source Temp 275 °C; Capillary gas sheat 35 units; auxiliary gas 30 arbitrary units LOD: 30-35 µg/L, LOQ: 90-105 µg/L all Fbs depending of the beer type
(Huang et al. 2018)	B_1, B_2 and other toxins Liquorice	2	**QuEChERS:** 1.-Add 100 µL of D-atrazine (60 µg/L), 15 mL acetate buffer pH 3.0, 10 mL 5% FA in ACN; 2.- Shake; 3.- Extract with ultrasonic (53 KHz, 5 min, 20°C); 4.- Add 4 g $MgSO_4$ + 1 g NaCl + 0.5 g $Na_2HCit{\cdot}1.5H_2O$, 1 g $Na_3Cit{\cdot}2H_2O$; 5.- Shake to 1500 strokes/min, 5 min; 6.- Ice bath 10 min, 7.-Centrifuge to 18514 g, 10 min; 8.- Take 6.0 mL; 9.- Transfer supernatant	**Poroshell EC-C_{18}, 150 x 3 mm, 2.7 µm at 20°C** Inj vol 5 µL, A) H_2O, B) MeOH, 0.2% FA and 2 mM AmF 20% B for 2 min, 20-50% B in 2 min, 50-100% B in 7 min, keep 1 min, 100-20% B in 1 min, initial conditions for 2 min Flow: 0.45 mL/min, Time: t_{an} = 12 min, t_{Tot} = 15	**QQQ** CaV 5.5 kV; DP 150 eV; EP 10 eV; CUR 30 psi; GS1: 50 psi, turbo gas (gas 2) 50 psi, GT: 450°C LOD: B_1, B_2, 0.05 µg/kg LOQ: B_1. B_2, 0.125 µg/kg

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Table 1 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions, Limits Mass Conditions / Limits
			into 15 mL centrifugation tube containing 900 mg $MgSO_4$, 600 mg C_{18}, 150 mg PSA, 150 mg Si; 10.- Shake 5 min, 11.- Centrifuge 10 min; 12.- Take 2 mL, reduce volume <0.5 mL with N_2; 13.- Complete to 1 mL with H_2O/MeOH 80:20; 14.- filter	min	
(Tamura et al. 2012)	B_1, B_2, B_3 and other toxins Wine	5 mL	**Extraction:** 1.-Add 25 mL AmAc 10 mM, mix, 2.- wash in Oasis HLB SPE Cartridge conditioned with 5 mL AmAc 10 mM, 3.-elute with 5 mL AmAc 10 mM/ACN 1:1, 4.-elute 5 mL ACN, mix, dry N2 40°C, 5.-dissolve in 1mL H_2O, 6.-60 µL FA + 5 mL ACN, mix, 7.-apply to multistep #229 Ochra cartridge. 8.-Dry 4 mL of eluate with N_2 40°C, 9.-dissolve in 500 µL AmAc 10 mM/ACN 85:15, 10.-filter	**Acquity UPLC BEH C_{18}, 100 x 2.1 mm, 1.7 µm at 40°C** Inj vol 5 µL, A) H_2O; B) MeOH, with 2% AcOH, 0.1 mM AmAc 55-80% B in 5 min, initial conditions for 2 min Flow: 0.3 mL/min, Time: $t_{an}=5$ min, $t_{Tot}=7$ min	**QQQ** CaV 3 kV; ST 120°C; DGT 450 °C; CGF 50 L/h; DGF 800 L/h LOD: 0.30 µg/L, LOQ: 1 µg/L all Fbs
(Miró-Abella et al. 2017)	B_1, B_2 and other toxins Plant-based beverages	10 mL	**Extraction:** 1.- Add 10 mL 1% FA in ACN in a 50 mL centrifuge tube, 2.- Shake 3 min; 3.- Add 4 g $MgSO_4$ + 1 g NaCl; 4.- Shake vigorously 3 min; 5.- Centrifuge to 10000 rpm, 5 min, 20°C, 6.- dilute 1:1 with phase A 7.-filter	**Cortecs UHPLC C_{18}, 100 x 2.1 mm, 1.6 µm at 40°C** Inj vol 5 µL, A) H_2O, B) MeOH, both with 0.1% AcOH, 5 mM AmAc 10-50% B in 4.5 min, 50-95% in 7.5 min, keep 2.5 min Flow: 0.45 mL/min, Time: $t_{an}=$ 14.5 min, $t_{Tot}=$ NR	**QQQ** CaV 4 kV; DGF 18 L/min; DGT 160°C; nebulizer 35 psi; nozzle voltage 0.5 kV; Frag Vol 380 V LOD: 0.80; LOQ: 2.68 µg/kg all Fbs
(B. Zhang et al. 2018)	B_1 and other toxins Grapes, wines	5	**Extraction:** 1.- Add 5 mL distilled H_2O, 10 mL 1% AcOH in ACN; 2.- Shake to 3000 rpm; 3.- Add 1 g NaCl + 4 g $MgSO_4$, 4.- Centrifuge to 13000 rpm, 5 min, 10 °C; 5.- Transfer into 10 mL polypropylene tube containing 450 mg $MgSO_4$; 6.- Shake 30 s; 7.-Centrifuge to 5000 rpm, 5 min, 10 °C	**ZORBAX RRHD Eclipse Plus C_{18}, 50 x 2.1 mm, 1.8 µm at 30°C,** Inj vol 2 µL, A) H_2O, B) ACN, both with 0.1% FA 10-42% B in 2.4 min, 42-51% B in 3.6 min, 51-95% B in 0.2 min, 95-10% B for 0.8 min, initial conditions for 5 min Flow: 0.3 mL/min, Time: $t_{an}=6.2$ min, $t_{Tot}=$ 12 min	**QQQ** CaV 4 kV; DG temperature 350 °C; DG flow 10 L/min; Nebulizer 40 psi LOD: 1 µg/L, LOQ: 3 µg/L
(Pizzutti et al. 2014)	B_1, B_2, B_3 and other toxins Wines	5	**Extraction:** 1.- Add 5 mL H_2O, 10 mL 1% AcOH in ACN, 25 µg/mL of: FB_1 (ACN/H_2O 1:2), FB_2 (CAN/H_2O 1:3), and FB_3 (ACN); 2.-Mix to 300 rpm, 1 min; 3.- Add 3 g anh. $MgSO_4$; 4.- Shake 1 min; 5.- Centrifuge 13000 rpm, 5 min, 6.-Take 3 mL of superior phase; 6.- Mix with 450 mg anh. $MgSO_4$; 7.- Mix 10 s, centrifuge 4000 rpm, 4 min, 10 °C; 8.- Filter and dilute 1:1 with MeOH	**Acquity UPLC BEH C_{18}, 100 x 2.1 mm, 1.7 µm, 50 °C** Inj vol 5 µL A) H_2O, B) ACN, both with 0.1% FA 10-70% B in 10 min, 90 % B for 2 min, initial conditions for 1 min Flow: 0.4 mL/min, Time: $t_{an}=12$ min, $t_{Tot}=$ 13 min	**QQQ** CaV 2 kV; ST 120 °C; DGT 400 °C; DGF 100 L/h; CGF 700 L/h LOQ: 50 µg/kg all Fbs

Table 1 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions, Limits Mass Conditions / Limits
(Pérez-Ortega et al. 2012)	B_1 and other toxins Wine	4 mL	**Extraction:** Oasis HLB, Bond Elut Plexa 1.- SPE cartridges preconditioned with 4 mL MeOH, 2.- 4 mL H_2O at 2 mL/min; 3.- Add sample into cartridge; 4.- Elute with MeOH/H_2O 5:95; 5.- Dry in vacuum 1 min; 6.- Elute twice/4 mL MeOH, 1 mL/min; 6.- Evaporate (N_2, 37°C); 7.- Reconstitute (1 mL MeOH:H_2O 2:8); 8.- Filter	**Zorbax Eclipse XDB-C_{18}, 50 x 4.6 mm, 1.8 µm, temp NR** Inj vol 20 µL, A) H_2O, 0.1% FA; B) ACN 10 % B for 2 min, 10-50% B in 3 min, 50-100% B in 10 min, keep 3 min Flow: 0.5 mL/min, Time: t_{an} = 18 min, t_{Tot} = NR	**TOF** CaV 4kV; NGP 40 psi; DGF 9 L/min; DGT 325 °C; Frag Vol 190 V; range 50 -1000 LOD: 0.8 µg/L, LOQ: 2.68 µg/L
Samples of animal origin					
(Cao et al. 2018)	B_1, B_2 Urine, plasma 200 µL urine 200 µL plasma		**Extraction:** 1.- Add 50 µL β-glucuronidase + 20 µL SI ($^{13}C_{34}$-FB_1 1 mg/mL); 2.-incubate 37 °C overnight; 3.-centrifuge to 10000 rpm, 5 min; 4.- take supernatant, add 730 µL H_2O/ACN 90:10; 5.-filter1.- Add 50 µL β-glucuronidase + 20 µL SI ($^{13}C_{34}$-FB_1 1 mg/mL); 2.-incubate 27°C overnight; 3.-add 1mL ACN:AcOH 99:1; 4.- vortex 30 s; 5.-centrifuge to 5000 rpm, 10 min; 6.- dry at 45°C; 7.-reconstitute in 200 µL of H_2O: ACN 9:1; 8.-mix 30 s; 9.-filter	**Kinetex C_{18}, 100 x 2.1 mm, 2.6 µm, 40°C** Inj vol 10 µL A) H_2O, 0.2 mmol/L AcOH; B) MeOH 25% B for 1 min, 25-70% B in 2 min, 70-25% B in 0.5 min, initial conditions for 1.5 min Flow: 0.2 mL/min, Time: t_{an} = 3 min, t_{Tot} = 5 min	**QQQ, TISP** CUR 20 psi; CoG (CAD) 8 psi; GS1 20 psi; GS2 15 psi; GT 600°C; EP 10.0; CP 12.0 LOD B_1: urine 0.12 µg/L, LOQ B_1: urine 0.45 µg/L LOD B_1: plasma 0.19 µg/L, LOQ B_1: plasma 0.39 µg/L
(Devreese et al. 2012)	B_1 and other toxins Pig plasma	250 µL	**Extraction:** 1.- Add 12.5 µL ^{13}C-34 FB_1 (25 µg/mL in ACN) + 750 µL ACN (deproteinization); 2.-vortex 15 s; 3.-centrifuge to 8517 g, 10 min, 4°C; 4.-evaporate supernatant (N_2, 45 °C); 5.- reconstitute with 200 µL H_2O/MeOH 85:15; 6.- vortex 15 s, 7.-filter	**Hypersil Gold C_{18}, 50 x 2.1 mm, 1.9 µm at 45 °C** Inj vol 2.5-10 µL, A) H_2O with 0.1% AcOH, B) MeOH 35 % B for 1.5 min, 90 % B in 0.5 min, keep 1.5 min, 90-35 % B in 0.2 min, initial conditions 2.3 min Flow:0.30 mL/min, Time: t_{an} = 3.5 min, t_{Tot} = 6 min	**QQQ** CaV 4 kV, ST 300 °C; Aux gas 18 au; ISGP 4 au; SGP 23 au; VT 300 °C; LOD: 0.8 µg/L, LOQ: 1 µg/L
(Arroyo-Manzanares, García-Campaña, and Gámiz-Gracia 2013)	B_1, B_2 Milk thistle *Silybum marianum*	2	**QuEChERS:** 1.- Add 8 mL of 30 mM NaH_2PO_4 (pH 7.1); 2.-vortex 10 s; 3.-add 5 mL ACN with 5% FA; 4.- shake 2 min; 5.-sdd 4 g $MgSO_4$ + 1 g NaCl + 1 g NaCit + 0.5 g Na_2HCit 1.5 H_2O; 6.- shake 1 min; 7.-centrifuge to 4500 rpm, 5min); 8.- take 1 mL; 9.- dry; 10.-reconstitute with 1 mL MeOH/H_2O 1:1; 11.-filter	**Zorbax Eclipse C_{18}, 50 x 2.1 mm, 1.8 µm at 35 °C** Inj vol 5 µL, A) H_2O, B) MeOH, both with 0.3% FA, 5 mM AmFo 5-50% B in 1 min, 50-72 % B for 2 min, 72-80 % B for 2 min, 80-90 %B for 2 min, 90-5% B in 0.2 min Flow: 0.4 mL/min, Time: t_{an} = 7.2 min	**QQQ** ST 500 °C; CUR 30 psi; ISV 5 kV; gas 1 and gas 2 50 psi LOD: B_1 3.9 µg/kg,13.7 µg/kg LOQ: B_1 13.5 µg/kg, B2 45.7 µg/kg
(S. Zhang et al. 2022)	B_1, B_2, B_3 Broiler Chicken Feed and Excreta	5	**Extraction:** 1.- Add 20 mL of ACN:H_2O; 2.- shake for 30 min; 3.- ultrasonic for 30 min; 4.- take 50 µL; 5.- centrifuge at 8000 rpm for 15 min; 6.- add 950 µL of H_2O and vortex; 7.- take 50 µL; 8.- add 10 µL of IS ^{13}C-FBs; 9.- dilute with 850 µL of in MeOH:H_2O 1:9 (0.2 % -FA)	**CORTEX C_{18} 10 x 4.6 mm, 5 µm at 40 °C** Vol. Inj NR, A) H_2O B) MeOH both with 0.2 % -FA 10-90%B in 6 min; hold for 2 min; initial condition for 2 min Flow 0.4 mL/min, Time: t_{an} = 8 min t_{Tot} = 10 min	**QQQ** CaV 2.5 kV; CoG: 0.15 mL/ min, DGT 500 °C; DGF: 800 L/h; LOD: 50 µg/Kg all Fbs LOQ 160 µg/Kg all Fbs

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Table 1 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions, Limits Mass Conditions / Limits
(Weiying et al. 2022)	B_1, B_2 Milk	1	**Extraction:** 1.- Add IS ($^{13}C_{34}$-FB_1 117 ($^{13}C_{34}$-FB_1), $^{13}C_{34}$-fumonisin B_2 ($^{13}C_{34}$-FB_2) mixed internal standard (25 µg/mL); 2.- add 5 mL of ACN:H_2O (2% FA); 3.- vortex for 10 min; 3.- Centrifuge at 3900 rpm for 3 min; 4.- evaporate to dryness at 40 °C under N_2; 5.- redissolved in 5 mL of H_2O; 6.- Add 6 mg of DSPME MIL-101 (Cr); 7.-ultrasonic for 10 min; 8.- centrifuge at 1200 rpm for 5 min; 9.- filter	**Shimadzu C_{18} 100 × 2.1mm, 1.8 µ m at 40 °C** Vol. Inj. 3 µL of sample, A) H_2O (1% FA), B) CAN 5% B for 1 min 5 -90 %B in 3.5 min; hold for 2.5 min; initial condition in 0.1 min; hold for 1.9 min Flow 0.4 mL/min, Time: t_{an} = 8 min t_{Tot} = 10 min	**Qtrap** CaV: 5.5 kV; CoG: 35 psi; CUR: 35 psi; GS2: 45 psi LOD: 1.5 µg/Kg all Fbs LOQ 5 µg/Kg all Fbs
(Flores-Flores and González-Peñas 2018)	B_1 B_2, B_3 Milk	1 mL	**Extraction LLE:** 1.- Add 4 mL 2 % FA in ACN, 2.-shake 15 min; 3.-centrifuge 5000 rpm, 10 min, 4.-take 4 mL supernatant, 5.-add 60 mg NaOAc, 6.-shake 15 min, 7.- centrifuge 5000 rpm, 5 min, 8.-take 3.5 mL of ACN phase, dry at 65°C, 9.- reconstitute in 200 µL of mobile phase, 10.-filter	**Ascentis Express C_{18}, 150 x 2.1 mm, 2.7 µm, 45°C** Inj vol 20 µL, A) H_2O, B) MeOH/H_2O 95:5, both with 0.1% FA and 5 mM AmFo 5-28% B in 5 min, 28-45 in 5.5 min, 45-60% B in 0.5 min, 60-90% B in 5 min, keep for 1 min, initial conditions for 13 min Flow: 0.4 mL/min, Time: 16 min	**QQQ** CaV 4 kV; DGT (high-purity N_2) 350°C; DGF 9 L/min; 275.8 Pa, dry gas 40 psi LOD/LOQ: FB_1 10 µg/L, FB_2 2.5 µg/L, FB_3 0.625 µg/L
(Song et al. 2013)	B_1 and other toxins Pig, human urine	5 mL	**Extraction:** 1.- Add 10 mL $MgSO_4$ (2 M) with EtOAc/FA 99:1, shake 15 min; 2.-centrifuge to 4000 g, 15 min; 3.-take aqueous phase, add 5 mL ACN/FA 99:1; 4.-repeat extraction; 5.-dry (N_2, 60°C); 6.-reconstitute with 500 µL 1:1 A:B; 7.-filter; 8.-centrifuge to 10000 g, 5 min	**Symmetry C_{18}, 150 x 2.1 mm, 5 µm at RT** Inj vol 20 µL, A) H_2O, B) MeOH, both with 0.3% FA, 5 mM AmFo 5% B for 1 min, 5-25% B in 4 min, 25-60%B in 2 min, 60-80% B in 8 min, 80-100 B in 1 min, keep 6 min, 100-5 % B in 3 min Flow: 0.25 mL/min, Time: t_{an} = 22 min, t_{Tot} = 25 min	**QQQ** CaV 3.2 kV; DGF 800 L/h; CGF 20 L/h; DGT 350 °C; ST 120 °C LOD: 0.05 ng/mL, LOQ: 0.17 ng/mL
(K. Zhang et al. 2013)	B_1, B_2, B_3 and other toxins Milk based infant foods	0.5	**Extraction:** 1.- Add 25 µL IS ($^{13}C_{34}$ FB_1, $^{13}C_{34}$ FB_2, $^{13}C_{34}$ FB_3 500 ng/mL); 2.- Vortex 30 s; 3.- Add 5 mL ACN/H_2O 1:1; 4.- Shake 10 min at 30-35 pulsations/min; 5.- Take an aliquot of 2 mL; 6.- Filter 2 mL; 7.-Centrifuge to 4500 rpm, 30 min	**Phenomenex Kinetex XB-C_{18}, 100 x 2.1 mm, 2.6 µm, 40°C** Inj vol 5 µL, A) H_2O, B) MeOH, both with 0.1% FA, 10 mM AmFo 5-40% B lineal in 2 min, 40-100% exponential B in 7 min, keep 2.5 min, 100-5% B in 0.5 min, initial conditions for 3 min Flow: 0.3 mL/min, Time: t_{an} = 11.5 min, t_{Tot} = 15 min	**QQQ-IT** CaV 5.5 kV; CUR 30 psi; ST 450 °C; gas 1 and gas 2 60 psi LOQ B_1: 2 µg/kg all fbs
(Abia et al. 2013)	B_1, B_2 and other toxins Urine	1 mL	**Extraction:** 1.- Centrifuge to 5600 g, 3 min; 2.- take 100 µL 3.-add 900 µL H_2O/ACN 9:1	**Gemini 150 x 4.6 mm, 5 µm** Inj vol 5 µL, A) H_2O, B) ACN, both with 0.1% AcOH 5 % B for 2 min, 5-30 % B in 8 min, 30-96 % B in 4 min, keep 1 min, initial conditions for 2.25 min Flow: 0.6 mL/min, Time: t_{an} = 15 min, t_{Tot} = 17.25 min	**QTrap** ST 650 °C, CUR 30 psi, SG 80 psi, DG 80 psi LOD: B_1 and B_2 0.5 µg/L, LOQ: B_1 and B_2 1.7 µg/L

Table 1 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions, Limits Mass Conditions / Limits
(Nualkaw et al. 2020)	B_1, B_2 and other toxins Swine, Poultry, Dairy Feeds	1	**QuEChERS:** 1.-Add 10 mL H_2O 1% FA, 2.-soak 30 min; 4.-add 10 mL ACN: 5.-shake to 240 rpm, 30 min; 6.-add 1 g NaCl + 4 g $MgSO_4$; 7.-shake 30 s: 8.-centrifuge to 10000 rpm, 5 min; 9.-take 2 mL; 10.-add 0.1 g silica C_{18} + 0.3 g $MgSO_4$; 11.-mix; 12.-centrifugate 1 min; 13.-dry at 40 °C, 14.-reconstitute in 960 µL MeOH 20% + 40 µL (250 ng/mL ^{13}C-34 FB_1 + 50 ng/mL ^{13}C-34 FB_2); 15.-filter	**Accucore C_{18}, 100 x 2.1 mm, 2.6 µm, 25 °C** Inj vol 3 µL, A) deionized H_2O, 0.1% FA, 5mM AmF; B) MeOH 0-20% B in 4 min, 20-40% B in 5.5 min; 40-100% B in 10.5 min, keep 2.5 min; initial conditions for 3 min Flow: 0.4 mL/min, Time: t_{an} = 22.5 min, t_{Tot} = 25.5 min	**Qtrap** Needle voltage 4.5 kV; CUR 30 psi; nebulizer (Gas1), turbo gas (Gas2) 55 psi; turbo gas temperature 500 °C LOD: B_1 15 µg/kg, B_2 4.5 µg/kg; LOQ: B_1 30 µg/kg, B_2 9 ng/kg
(Osteresch et al. 2017)	B_1 and other toxins Blood or serum	100 µL	**Extraction LLE:** 1.-Spott 4 times on filter paper; 2.-dry overnight at RT, 3.-Extract with 1 mL H_2O/acetone/ACN 30:35:35 in 2 mL safe-lock tubes; 4.-Sonicate 30 min; 5.-Take 800 µL; 7.-Dry at 50°C under reduced pressure; 8.-Reconstitute with H_2O/ACN/AcOH 95:5:0.1; 9.-Centrifuge to 22000 g, 10 min	**Gravity SB C_{18}, 100 x 2.0 mm, 3 µm at 45°C** Inj vol 30 µL, A) H_2O, 0.1% AcOH, B) ACN, 2% AcOH 3-15% B in 3 min, 15-55% B in 1.5 min, keep for 1.5 min, 55-100% B in 2 min, keep 10 min, initial conditions 1.5 min Flow: 0.75 (0-6), 0.85 (6.1-10), 0.75 (10.1-11.5) mL/min, Time: t_{an} = 10 min, t_{Tot} = 11.5 min	**QTrap** CaV 5.5 kV; ST 500 °C; DP 125 V; CUR 40 psi; GS1 45 psi; GS2 50 psi LOD: 0.521 ng/L LOQ: 2.5 ng/mL

(ACN) Acetonitrile, (AcOH) Acetic acid, (AE) Appearance energy, (AmAc): ammonium acetate, (AmFo) Ammonium formate, (CaV) Capillary voltage, (CaT) Capillary temperature, (CGF) Cone gas flow, (CoG) Collision gas, (CUR) Curtain gas, (DG) Drying gas, (DGF) Desolvation gas flow, (DGT) Desolvation gas temperature, (EV) Extractor voltage, (FA) Formic acid, (Frag Vol) Fragmentor Voltage, (GF) Gas flow, (GT) Gas Temp, (LIT) linear ion tramp, (MeOH) Methanol, (MSPD) Matrix Solid Phase Dispertion, (NG) Nebulizer gas, (NR) Not reported, (PLE) Pressurize Liquid Extraction, (RT) Room temperature, (ST) Source temperature, (SV) Source voltage, (t_{an}) analysis time, (t_{Tot}) total time including column conditioning.

Table 2 LC-MS methods for FBs with clean up.

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions Mass Conditions / Limits
Maize and corn-based products					
(Ren et al. 2011)	B_1, B_2, B_3 Maize	2.5	**Extraction:** 1.- Add 200 µL of IS (2.5 µg/mL $^{13}C_{34}$- FB_1, 1 µg/mL $^{13}C_{34}$-FB_2, $^{13}C_{34}$-FB_3); 2.- Add 10 mL ACN/H_2O 1:1; 3.- Extract with ultrasonic 1h; 4.- Centrifuge to 15 000 rpm, 6 min; 5.- Adjust pH to 7-9 with NaOH; 6.- Take an aliquot of 3 mL; 7.-Dilute with MeOH/H_2O (66.7:33.3) **Clean up:** 1.- Load the dilute sample in MultiSep 211 FUM cartridge; 2.-Pass 8 mL of MeOH/H_2O (66.7:33.3); 3.- Pass 10 mL of MeOH (1% AcOH), collect; 4.- Transfer 10 mL to a tube; 5.- Dry (N_2, 50°C); 6.- Redissolve in 1 mL of MeOH:AmAc 10 mM/L (1:1); 7.- Shake 30s; 8.- Filter	**BEH C_{18}, 100 x 2.1 mm, 1.7 µm, 35°C** Inj vol 2 µL, A) H_2O, 0.1% FA, B) ACN/MeOH 1:1 30-70% B in 2.3 min, 70% B for 1.7 min, 70-100% B in 0.2 min, keep for 0.6 min, 100-30% B in 0.2 min., re-equilibrate for 2 min Flow: 0.3 mL/min, Time: t_{an} = 4.8min, t_{Tot} = 7 min	**QQQ** CaV 3.5 kV; CoV 45 V; ST: 120; CGF: 50L/h DGT 350°C; DGF 500 L/h LOD: (B_1 0.45, FB_2 0.50, B_3 0.10) µg/kgLOQ: (B_1 1.50, FB_2 1.65, B_3 0.40) µg/kg
(L. Silva et al. 2009)	B_1, B_2 and other toxins Corn-based products	25	**Extraction:** 1.- Add 40 mL MeOH/H_2O 80:20; 2.- Centrifuge to 2500 g, 15 min 3.- Extract the remaining solid with 30 mL MeOH/H_2O 80:20; 4.- Filter **Clean up:** 1.- Dilute 10 mL of filtrate with 40 mL of PBS; 2.- Take 20 mL 3.- Add to a FumoniTestTM immunoaffinity; 4.- Wash with 10 mL PBS; 5.- Eluted twice with 1.5 mL of MeOH; 6.- Evaporate (N_2, 60 °C); 7.- Reconstitute in 50 µL MeOH/H_2O (1:1)	**Luna C_{18}, 250 x 4.6 mm, 5 µm** Inj vol 10 µL, A) H_2O, B) MeOH both with 0.5% FA 65% B for 4 min, 65-95% B in 4 min, keep 7 min Flow: 0.50 mL/min, Time: $t_{an} = t_{Tot}$ = 15 min	**QQQ** CaV 4 kV, GT 350°C; DGF 13 L/min; NG 30 psi LOD: 40 µg/kg, LOQ:110 µg/kg all Fbs
(Cavaliere et al. 2007)	B_1, B_2 and other toxins Maize	1	**Extraction:** 1.- 10 mL ACN/H_2O 75:25; 2.- homogenize 15s; 3.- Transfer on cartridge (6 mL) with 100 mg of C_{18}; 4.-Wash the extract with 7 mL of ACN/H_2O 75:25, twice; 5.- Collect 25 mL; 6.- Take 5 mL; 7.- Dilute with 500 mL of H_2O. **Clean up:** 1.- Load sample dilute on SPE-Carbograph-4 (500 mg); 2.- Wash with 10 mL of H_2O; 3.- Pass 0.3 mL of MeOH; 4.- Elute with 1 mL MeOH and 8 mL of DCM:MeOH 8:2 (50 mM of FA); 5.- Evaporate to 100 µL; 6.- Add IS (FB_1, FB_2 in MeOH/H_2O 1:1 (1 mg/mL); 7.- Evaporate to 100 µL; 8.- Dilute with 100 µL of LC mobile phase	**Alltima C_{18}, 250 x 2.1 mm, 5 µm, 45 °C** Inj vol 20 µL, A) H_2O, B) MeOH, both containing 25 mmol/L FA, adjusted to pH 3.8 with ammonia 60% B for 3 min, 60-90% B in 5 min, 100% for 10 min Flow: 0.2 mL/min, Time: t_{an} = t_{Tot} = 18 min	**QQQ** CoV 5.5 kV; CUR 35; GS1 35; GS2 40; GT 350 °C LOD/LOQ: 10 mg/kb for FB1 and 5ng/kg FB_2
(Lattanzio et al. 2007)	B_1, B_2 and other toxins Maize	10	**Extraction:** 1.- Add 50 mL de PBS; 2.- Shake 60 min; 3.- Centrifuged to 3000 g, 10 min; 4.- filtrate 35 mL of PBS (extract A); 5.- Add 35 mL of MeOH, to the remain solid, containing 15 mLPBS; 6.- extract again 7.- Shake 60 min; 7.- Centrifuge to 3000 g, 10 min; 8.- Dilute 10 mL of extract with 90 PBS (extract B); 9.- Filter **Clean up:** 1.-Load 50 mL of extract B to the IAC; 2.- Wash with 20 mL of PBS; 3.- Add 5 mL of extract A; 4.- Wash with 10 mL of water; 5.- Eluate both extracts with 1.5 mL MeOH twice; 6.- Dry at 50 °C; 7.- Reconstitute with 200 μL MeOH/H_2O 4:6 (1 mM AmAc and 0.1% AcOH)	**Gemini C_{18}, 150 x 2 mm, 5 µm, 40°C** Inj vol 20 µL, A) H_2O (0.5% AcOH, 1 mM AmAc) B) MeOH (0.5% AcOH, 1 mM AmAc 20-40% B in 3 min, 40-63% B in 35 min, keep constant for 11 min, initial conditions for 10 min Flow: 0.200 mL/min, Time: t_{an} = 49 min, t_{Tot} = 59 min	**QTrap** GT 350 °C; CUR 30 PSI; CoV: 4.5 kV: GS1: 10 psi, GS2 30 psi. LOD: B_1 1.1 µg/kg, B_2 0.4 µg/kg
(Y. Wang et al. 2013)	B_1 and other toxins Maize	10	**Extraction:** 1.- Add 50 mL of ACN/H_2O/AcOH (79:20:1); 2.- Stir for 10 min; 3.- Filter; 4- Evaporate 10 mL to dry; 5.- Redissolve in 100 µL of MeOH; 6.- Vortex 1 min; 7.- Add 1.9 mL of H_2O 8.- Vortex again for 1 min	**Shimadzu XR-ODS 75 x 3.0 mm, 2.2µm, 30°C** Inj vol 20 µL, A) H_2O, B) MeOH both with 0.1% AcOH, 1 mM AmAc 50% B for 5 min, 50-10% B in 5 min, keep constant	**QTrap** GT 450°C; CUR 10 psi; GS1 50 psi; GS2 50 psi; SV 5.5 kV

Table 2 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions Mass Conditions / Limits
			Clean up: 1.- Active the Oasis HLB SPE cartridges with 2 mL of MeOH; 2.- Equilibrate with MeOH/H_2O (05:95); 3.- Load sample; 4.- Wash with 2 mL MeOH/H_2O (05:95); 5.- Elute with 2 mL of MeOH; 6.- Dry (N_2, 50°C); 7.- Redissolve in 1 mL MeOH/H_2O (2:8)	for 10 min, 10-50% B in 1 min, keep constant for 4 min Flow: 0.30 mL/min, Time: t_{an} = 21 min, t_{Tot} = 25 min	LOD: 0.64 µg/kg, LOQ: 2.12 µg/kg
Other cereals and seeds					
(Bryła, Renata, et al. 2013)	B_1, B_2, B_3 Cereal products	25	**Extraction:** 1.-Add 100 mL ACN/MeOH/H_2O (25:25:50); 2.- Stir 30 min; 3.- Centrifuge to 10730 g, 10 min; 4.- Dilute the supernatant 1:1 with 10 mL deionized H_2O **Clean up:** 1.- Transfer 8 mL of dilute extract to a FumoZon cartridge; 2.- Preconditionate with 4 mL of MeOH and H_2O; 3.- Wash with 6 mL ACN/H_2O (25:75); 4.- Eluate with 4 mL of 2% FA in MeOH; 5.- Evaporate to dry; 6.- Redissolve in 1 mL of MeOH/H_2O/AcOH (1:8.9:0.1)	**Kinetex PFP, 100x2.1mm, 2.6µm** Inj vol 25 µL, A) MeOH:H_2O:AcOH (20:79.9:0.1) B) MeOH:H_2O:AcOH (79:19.9:0.1) 20% B for 4 min, 20-55% B in 6 min, keep constant for 15 min, 55-100% in 5 min, keep constant for 10 min, initial conditions for 20 min Flow: 0.15 mL/min, Time: t_{an} = 40 min, t_{Tot} = 60 min	**IT** GF 45 a.u.; AGF 10 a.u.; CoV 4.5 kV; CaV 40 V; ST 260 °C LOQ: 25 µg/kg all FBs
(Vaclavikova et al. 2013)	B_1, B_2, B_3 and other toxins Cereals, nuts	5	**Extraction:**1.- Add 20 mL of ACN/H_2O/AcOH (79.5:20:0.5) for 60 min; 2.- Centrifuge to 5000 rpm, 2 min; 3.- Dilute 2 mL of sample with 33 mL of PBS **Clean up:** 1.- Load the aliquot on IAC; 2.- Wash with 10 mL of ultrapure H_2O; 3.- Elute with 3 mL of MeOH, evaporate; 4.- Reconstitute in 0.5 mL of MeOH/H_2O (0.5% AcOH) (1:1); 6.- Filter	**Acquity UPLC HSS T3 RP 100 x 2.1 mm, 1.7µm, 40°C** Inj vol 10 µL, A) H_2O, B) MeOH both with 5 mM AmAc 5-50% B in 1 min, 50-100% B in 6 min, keep 1 min, initial condition for 2 min. Flow: 0.4 mL/min, Time: t_{an} = 8 min, t_{Tot} = 10 min	**QTrap** ST 450°C; CaV 4.5kV; CUR 20 a.u.; GS1 55 a.u, GS2: 55 a.u LOD: 5 µg/kg, LOQ: 10 µg/kg all FBs
(Arroyo-Manzanares et al. 2014)	B_1, B_2 and other toxins cereals, spelt, rice	2	**QuEChERS:** 1.- Add 8 mL H_2O into test tube; 2.- Shake for 10 s; 3.- Add 10 mL 5% FA in ACN; 4.- Shake 2 min; 5.- Add 4 g $MgSO_4$, 1 g NaCl, 1 g sodium citrate, 0.5 g Na_2HCit 1.5 H_2O; 5.- Shake for 1 min; 6.- Centrifuge to 4500 rpm, 5 min; 7.- Transfer 2 mL of upper layer to a vial; 8.- Evaporate; 9.- Reconstitute with 1 mL of MeOH/H_2O 50:50; 10.- Filter	**Zorbax Eclipse Plus RRHD C_{18}, 50 x 2.1 mm, 1.8µm, 35°C** Inj vol 5 µL, A) H_2O, B) MeOH both with 0.3% FA, 5 mM AmFo 5% B for 1 min, 5-50% B in 1 min, 50-72% B in 2 min, 72-80% B in 2 min, 80-90% for 2 min, initial conditions in 0.2 min. Flow: 0.4 mL/min, Time: t_{an} = 8 min, t_{Tot} = 8.2 min	**QQQ** GT: 500°C; CUR: 30 psi; CaV 5 kV; GS1 and GS2 50 psi LOD: B_1 0.20, B_2 0.30 µg/kg LOQ: B_1 0.65, B_2 1.01 µg/kg
(Cendoya et al. 2019)	B_1, B_2 wheat-based products	25	**Extraction:** 1.- Add 50 mL of MeOH/H_2O 3:1; 2.- Shake for 30 min; 3.-Filter **Clean up:** 1.- Precondition with 5 mL of MeOH and 5 mL MeOH/H_2O 3:1; 2.- Load 10 mL of filtrated; 3.- Wash with 8 mL of MeOH/H_2O 3:1, 3 mL of MeOH; 4.- Elute with 14 mL of MeOH with 0.5% AcOH ; 5.- Dry (N_2, 40°C)	**XBridge™ C_{18}, 150 x 2.1 mm, 3.5µm, 20°C** Inj vol 45 µL, A) H_2O, B) MeOH both with 1% FA 9.5% B for 2 min, 9.5-50% B in 1 min, 50-97.5% B in 11 min, keep for 3 min, initial condition for 5 min. Flow: 0.2 mL/min, Time: t_{an} = 17 min, t_{Tot} = 22 min	**QQQ** CaV 3.0 kV; ST: 150 °C; DGT 200 °C; DGF: 726 L/h; GF 109 L/h LOD 0.01 µg/kg LOQ: 0.05 µg/kg all FBs
Products of animal origin					
(Gazzotti et al. 2009)	B_1 Bovine milk	10	**Extraction:** 1.- Centrifuge to 6000 rpm, 15 min; 2.- Dilute 5 mL of sample 1:1 with H_2O **Clean up:** 1.- Load the dilute sample to Vicam FumoniTestTM	**XTerra MS C_{18}, 150 x 2.15 mm, 5µm, 35°C** Inj vol 10 µL, A) H_2O/ACN (90:10) with 0.3% FA, B) ACN (0.3% FA)	**QQQ** CaV 3.25 kV; CoV 50 V; IST 140°C; DGT 400°C

(*continued on next page*)

Table 2 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions Mass Conditions / Limits
			Immunoaffinity at 1 drop/s; 2.- Wash with 20 mL of PBS buffer at 5 mL/min; 3.- Elute with 1.5 mL of MeOH; 4.- Pass 1.5 mL of H_2O, collect 3 mL; 5.- Evaporate 3 mL of eluate to 1 mL (40°C, N_2)	Elute isostatically with 75% A-25%B for 2 min, wash 80% B for 3 min Flow: 0.30 mL/min, Time: t_{an} = 2 min, t_{Tot} = 5 min	LOD: 0.003 µg/kg, LOQ: 0.1 µg/kg
(Gazzotti et al. 2011)	B_1 B_2, HFB_1 HFB_2 Pig liver	1	**Extraction:** 1.- Homogenize in 6 mL of MeOH/H_2O 80:20; 2.- Stir for 20 min; 3.- Centrifuge to 3000 rpm, 5 min; 4.- Wash twice with 6 mL of hexane; 5.- Evaporate aqueous phase; 6.- Reconstitute with 2 mL of aqueous buffer with 2% of AcOH, 0.1% Et_3N (pH 3.4) **Clean up:** 1.- Condition the Oasis HLB SPE cartridges with 2 mL of MeOH and 2 mL of H_2O; 2.- Load the sample; 3.- Wash twice: first 1 mL MeOH/H_2O (05:95), then 1 mL MeOH/H_2O/AcOH (05:94:01); 4.- Elute with 2 mL of MeOH; 5.- Evaporate to 200 µL; 6.- Reconstitute in 1mL of mobile phase of LC	**XTerra MS C_{18}, 150 x 2.15 mm, 5µm, 35°C** Inj vol 10 µL, A) ACN/H_2O (90:10); B) ACN both with 0.3% FA 25% B for 4 min, 25-40% B in 4 min, keep for 4 min, initial condition for 5 min Flow: 0.30 mL/min, Time: t_{an} = 12 min, t_{Tot} = 17 min	**QQQ** CaV 3.25 kV; ST 140 °C; GT 400 °C; GF 50 L/h; DGF 890 L/h LOD: 0.05 µg/kg, LOQ: 10 µg/kg all FBs and analogues
(Sørensen, Mogensen, and Nielsen 2010)	B_1, B_2 Meat products	0.7	**Extraction:** 1.- Add 140 µL of IS (^{13}C-FB_2 0.5 µg/mL), 4.5 mL of H_2O, 2.5 mL of ACN, 6 mL of pentane; 2.- Shake for 1 h; 3.- Centrifuge to 8000 g, 10 min; 4- Discard upper phase; 5.- Transfer 3.5 mL of lower phase; 6.- Add 9 mL of acetone; 7.- Shake; 8.- Centrifuge to 8000 g, 10 min; 10.- Collect 100 mL upper phase; 11.- Evaporate to 1.5 mL (45°C), reconstitute in 0.25 mL of MeOH **Clean up:** 1.- Load sample in Oasis (MAX) SPE cartridges; 2.- condition with 1 mL of MeOH followed by 1 mL of H_2O, wash with 1 mL of 1% aqueous ammonia; 1 mL of MeOH/H_2O/HCl 37% (40:59:1); 3.- elute with 2 mL of 2% AcOH in MeOH; 4.- evaporate (N_2, 45°C), re-dissolve in 200 µL ACN/H_2O (1:2).	**Gemini C6-phenyl 50 x 2 mm, 3µm, 40°C** Inj vol 1 µL, A) H_2O, B) ACN both with 20mM FA 20-55% B in 6 min, then 100% in 0.5 min, keep for 2.5 min. Flow: 0.30 mL/min, Time: t_{Tot} = 9 min	**QQQ** IST 120°C; DGF 700L/h; DGT 350°C LOD: B_1 64 µg/kg, B_2 6 µg/kg,LOQ: B_1 and B_2 150 µg/kg
(Liliana J.G. Silva et al. 2010)	B_1, B_2 Urine	10 mL	**Extraction:** 1.- Filter, 2.- Dilute 1:1 with 10 mL of PBS, 3.- Mix for 3 min **Clean up:** 1.- Load the sample in FumoniTestTM immunoaffinity column; 2.- Wash with 10 mL PBS; 3.- Elute with 5 mL of MeOH; 4.- Dry (N_2, 60°C); 5.- Redissolve in 1 mL of MeOH/H_2O (1:1)	**Luna C_{18}, 150 x 4.6mm, 5µm, 30°C** Inj vol 20 µL, A) H_2O, B) MeOH both with 0.5% FA 65% B for 3 min, 65-75% B in 4 min, keep for 8 min, initial condition for 10 min Flow: 0.50 mL/min, Time: t_{an} = 15 min, t_{Tot} = 25 min	**QQQ** CaV 3.20 kV; ST 125 °C; DGT 300°C; DG 500 L/h LOD: 5 µg/L LOQ: 10 µg/L all FBs
(Šarkanj et al. 2018)	B_1 and other toxins Urine	500 µL	**Extraction:** 1.- Centrifuge to 5600 g, 3 min; 2.- Incubate with 500 µL PBS (200 mM, pH 7.4) containing 3000 U of β-glucuronidase, 16 h, 37 °C **Clean up:** 1.- Precondition with 1mL MeOH, 1mL H_2O; 2.- Add sample to Oasis PRiME HLB; 3.- Wash twice with 500 µL H_2O; 4.- Eluate with 200 µL ACN x 3; 5.- Evaporated (N_2); 6.- Reconstitute with 470 µL of 10% ACN, 0.1% AcOH, add 30 µL IS (0.38 ng/mL ^{13}C-FB_1)	**Acquity HSS T3, 100 x2.1 mm, 1.8µm, 35°C** Inj vol 10 µL, A) H_2O, B) ACN, both with 0.1% AcOH 10% B for 2 min, 10-50% B in 13 min., 50-95% B in 5 min, hold 4 min, initial condition for 3 min. Flow: 0.1 mL/min, Time: t_{an} = 24 min, t_{Tot} = 27 min	**Qtrap** ISV 4.50 kV; ST 550°C; CUR 30 psi; SG 80 psi; DG 80 psi LOD: 0.001 µg/L, LOQ: 0.01 µg/L

Table 2 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions Mass Conditions / Limits
Bevearages					
(Nakagawa et al. 2020)	B_1, B_2, B_3 Domestic wine	5 mL	**Extraction:** 1.- Add 0.1 mL of IS ($^{13}C_{34}$-FB1 0.2 mg/L in acetonitrile: water (1:1); 2.- adjusted volume at 10 mL with wine; 3.- mix; 4.- add 8mL of PBS (1% PEG, 5% $NaHCO_3$; 5.- mix; **Clean up:** 1.- Equilibrate with 3 mL of PBS; 2.- Load sample in cartridge; 3.- Wash 6 mL (3 mL x 2 times) of H_2O (0.5% $NaHCO_3$) and 6 mL (3 mL x 2 times) of 10 mM AmAc; 4.- Elute with 3 mL of MeOH (2% AcOH); 5.- evaporate to dryness; 6.- reconstitute in 0.2 mL ACN: H_2O 1:1.	**ZORBAX Eclipse XDB-C_{18} 250×3 mm, 5µm, 40°C** Inj vol 3–20 µL, A) H_2O, B) ACN, both with 0.1% FA 10% B for 3 min, 10-90% B in 15 min, hold for 5 min, initial conditions for 10 min. Flow: 0.3 mL/min, Time: t_{an} = 20 min, t_{Tot} = 30 min	**Qtrap** CaV 5 kV; CUR 10 psi; GS1 70 psi; SG 60 psi; ST 500°C LOD: 1 µg/Kg all Fbs LOQ 2
(Romero-González et al. 2009)	B_1, B_2 Beer	10 mL	**Extraction:** 1.- Sonicate for 20 min **Clean up:** 1.- Precondition with 5 mL ACN/H_2O (60:40) and 5 mL of H_2O; 2.- Load sample in C_{18} cartridge; 3.- Wash with 5 mL of H_2O; 4.- Elute 2 mL ACN/MeOH 60:40; 5.-Filter	**Acquity UPLC BEH C_{18}, 100 x 2.1 mm, 1.7µm, 30°C** Inj vol NR, A) H2O, B) MeOH both with 5 mM AmFo 25 to 100% B in 3.75 min, keep 1.25 min, 100 to 25% B in 0.5 min, initial condition for 1 min Flow: 0.35 mL/min, Time: t_{an} = 5.5 min, t_{Tot} = 6.5 min	**QQQ** CaV 3.5 kV; ST 120; DGT 350°C; CGF 80 L/h; DGF 600 L/min LOD: B_1 0.07, B_2 0.09 µg/kg; LOQ: B_1 0.23, B_2 0.30 µg/kg
(Tamzura, Uyama, and Mochizuki 2011)	B_1, B_2, B_3, and other toxins Beer-based drinks	10 mL	**Extraction:** 1.- Sonicate for 15 min, 2.- Add 10 mL ACN, mix, 3.- Add the content of dSPE citrate extraction tube; 4.- Vortex for 20 s, 5.- Centrifuge to 2380 g, 5 min **Clean up:** 1.- Precondition with 5 mL ACN; 2.- Load sample in InertSep C_{18}, SPE; 3.- Elute with 5 mL ACN; 4.- Evaporate to dryness; 4.- Dissolved with 500 µL of 10 mM AmAc aqueous/ACN (85:15); 6.- Filter	**Acquity UPLC BEH C_{18}, 50 x 2.1 mm, 1.7µm, 40°C** Inj vol 5 µL, A) H_2O, B) MeOH (2% AcOH, 0.1 mM AmAc) 55-80% B in 2 min Flow: 0.50 mL/min, Time: t_{an} = t_{Tot} = 2 min	**QQQ** CaV 3 kV; IST 120°C; DGT 450°C; CGF 50 L/h; DGF 800 L/h LOQ**:** 5 µg/L all FBs
Other samples					
(di Mavungu et al. 2009)	B_1, B_2, B_3 and other toxins Food supplements	1	**Extraction:** 1.- Add 25 mL of AcOEt/FA 95:5 for 30 min ; 2.- Centrifuge; 3.- Evaporate 20 mL to dryness; 4.- Reconstitute in 5 mL of H_2O/MeOH 1:1 and 10 mL Hex; 5.- Shake, 6.- Transfer aqueous fraction into a tube; 7.- Add H_2O/MeOH 1:1 (2 x 5mL); 8.- Evaporate; 9.- Reconstitute in 400 µL H_2O/MeOH 1:1; 10.- Centrifuge to 14000 g, 10 min; 12.- Take 250 µL, 13.- Filter; 14.- Dilute in 25 mL H_2O **Clean up: SPE:** 1.- Condition with 10 mL CH_2Cl_2/MeOH 8:2 with 50 mM FA, then 5 mL MeOH, 20 mL acidified H_2O (10 mM HCl), finally 10 mL H_2O; 2.- Add obtained solution to Oasis HLB SPE cartridge; 3.- Wash 10 mL H_2O; 4.- Elute with 1 mL MeOH and 4 mL CH_2Cl_2/MeOH 8:2; 5.- Evaporate; 6. Reconstitute in 100 µL injection solvent; 7.- centrifuge 14000g for 10 min.	**Symmetry C_{18}, 150 x 2.1 mm, 5µm, RT** Inj vol 20 µL, A) H_2O/MeOH/AcOH 94:5:1, B) MeOH/H_2O/AcOH 97:2:1 both with 5mM AmAc 5-65 % B in 7 min, 65-75% B in 4 min, 75-100% B in 2 min, keep for 2 min, 100-60% B in 1 min, 60-40% B in 6 min, 40-5% B in 1 min, hold 2 min. Flow: 0.3 mL/min, Time: t_{an} = 16 min, t_{Tot} = 25 min	**QQQ** CaV 3.2 kV; ST 150°C; DGT 350°C; CGF 20 L/h; DGF500 L/h LOD: B_1 1, FB_2 0.3, FB_3 1 µg/kg LOQ: B_1 3, FB_2 1, FB_3 3 µg/kg

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Table 2 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions Mass Conditions / Limits
(Khayoon et al. 2010)	B_1, B_2 Food, feed	10	**Extraction:** Add 40 mL ACN/H_2O (1:1); 2.- Shake 5 min; 3.-Filter **Clean up:** 1.- Take 1 mL of filtrate; 2.- Add 2.5 mL of 1% KCl; 2.- Precondition with 5 mL of MeOH, follow of 5 mL 1% KCl solution; 3.- Load in C_{18}, SPE; 4.- wash with 3 ml 1% KCl, followed by 2 mL of ACN/1% KCl 1:9; 5.- Elute with 2 mL of MeOH/H_2O (1:1)	**Inertsil ODS, 350 x 2.1mm, 3µm, 40°C** Inj vol 20 µL, A) H_2O, B) MeOH both with 0.2% FA 50-75% B in 4.0 min, 75-100% in 2.0 min, keep 6.5 min, B 100-50% in 3min Flow: 12.5 min 0.20 mL/min, 3 min 0.3 mL/min, Time: $t_{an} = 12.5$, $t_{Tot} = 15.5$ min	**QQQ** CaV 4 kV; DGF 600 L/h; DGT 350°C LOD: B_1 10, B_2 40 µg/kg LOQ: B_1 40, B_2 130 µg/kg
(Jerome Jeyakumar, Zhang, and Thiruvengadam 2018)	B_1, B_2 and other toxins Fungal cultures: Maize, Asparagus	NR	**Extraction:** 1.- Add 25 mL AcOEt to cultures, shake to 8000 rpm; 2.- After 2 h, mix with 5% acetone, isopropanol; 3.- Extracted with AcOEt 1:1; 4.- Collect upper layer, 6.- Evaporate; 7.- Reconstitute 10 mL isopropanol **Clean up SAX:** 1.- Add 10 mL sample into cartridge; 2.- Eluate 3 mL MeOH followed by 5 mL of 1% KCl; 3.- Collect into a 5-mL tube; 4.- Dry	**Supelco C_{18}, 250 x 2.1 mm, 5µm** Inj vol 10 µL, A) H_2O, 0.1% FA, B) CAN 15% B, 5 min, 15-100% B in 35 min, keep 10 min; 100-15 % B in 1 min, keep 9 min. Flow: 0.2 mL/min, Time: $t_{an} = 50$ min, $t_{Tot} = 60$ min	**Qtrap** CaV 5 kV; ST 200°C; DGT 300°C, NGF 2µmL/min LOD/LOQ: NR
(Facorro, Llompart, and Dagnac 2020)	B_1, B_2 Mixed Feed Rations	2	**QuEChERS:** 1.- Add 10 mL of ACN/FA 90:10; 2.- Shake for 1 h, 25°C; 3.- Add 0.5 Na citrate sesquihydrate + 1g NaCitrate + 1g NaCl + 4g $MgSO_4$; 4.- Shake for 1 min; 5.- Centrifuge to 3398 g, 5 min **Clean up:** 1.- Discard of supernatant; 2.- Load 1 mL in SPE Oasis PRiME HLB cartridge (3cc, 150 mg), collect; 3.- Transfer to a 2 mL dSPE tube; 4.- Add 150 mg $MgSO_4$ + 50 mg PSA + 30 mg C_{18} silica + 30 mg Al-N; 4.- Centrifuge to 2360 g, 2 min; 5.- Take 500 µL, evaporate; 6.- Reconstitute with 350 µL of MeOH	**Kinetex C_{18}, 50 x 2.1 mm, 2.6 µm, 40°C** Inj vol 10 µL, a) H_2O, B) MeOH, both buffered with 3 mM AmFo or AmAc., 10%-100% B in 8 min, keep 7 min Flow: 0.25mL/min, Time: $t_{an} = t_{Tot} = 15$ min	**QTOF** CaV 5.5 kV; ST 550 °C, CUR 50 a.u. **LOQ:** B_1 2.9, B_2 2.4 µg/L
(Jia et al. 2014)	B_1, B_2, B_3 and other toxins Dairy products	15	**Extraction:** 1.- Add 10 mL MeOH/H_2O (84:16) with 1% AcOH; 2.- Vortex 1 min, add 6 g $MgSO_4$ + 1.45 g sodium acetate anhydrous; 3.- Shake for 1 min; 4.- Centrifuge to 4000 rpm, 5 min **Clean up:** 1.- Add 8 mL of upper phase + 1.2 g $MgSO_4$ + 108 mg PSA + 405 mg C_{18} silica to dSPE tube; 2.- Shake for 1 min; 3.- Centrifuge to 4000 rpm, 5 min; 4.- Transfer 200 µL; 5.- Add 300 µL of MeOH + 500 µL 8 mM AmFo; 6.- Vortex 30 s; 7.- Filter 1 mL	**Thermo Accucore C_{18}, 100 x 2.1 mm, 2.6µm** Inj vol 5 µL, A) H_2O, B) MeOH, both 0.1% FA, 4 mM AmFo 0% B for 1 min, 0-100% B in 6 min, keep 5 min, 100-0% B in 1 min, initial condition for 2 min Flow: 0.30 mL/min, Time: $t_{an} = 12$ min, $t_{Tot} = 15$ min	**Q-Orbitrap** CaV 3kV; ST 320 °C; GT 350 °C; SG 18 L/min, Aux 3 L/min **LOD/LOQ:** NR
(Monbaliu et al. 2009)	B_1, B_2, B_3 and other toxins Sweet pepper	3	**Extraction:** 1.- Add 15 mL AcOEt, FA 1%); 2.- Shake 15 min; 3.- Centrifuge to 3300 g, 5 min; 4.- Filtrate; 5.- Repeat this process with 10 mL of the same mix solvent; 6.- Keep an aliquot (10 mL) for the SAX; 7.- Evaporate remaining part to 5 mL **Clean up:** 1.- SPE: pass remaining through the NH_2-SPE column; 2.- evaporate; 3.- Redissolve the evaporate in 3 mL of ACN/H_2O (84:16); 4.- Pass through the SPE; 3.-SAX, evaporate aliquot to dry; 5.- Redissolve in 5 mL MeOH/H_2O (75:25); 5.- Adjust pH at 5.8-6 with NaOH 0.25 M; 6.- Wash with 4 mL MeOH/H_2O (75:25) and then 4 mL of MeOH; 7.- Elute with 4 mL MeOH, AcOH 1%; 8.- Evaporate; 9.- Redissolve in 100 µL H_2O:MeOH:AcOH (57.2:41.8:1) and 5 mM of AmAc; 10.- Centrifuge to 14000 g, 15 min	**Symmetry C_{18}, 150 x 2.1 mm, 5 µm, 25 °C** Inj vol 20 µL, A) H_2O/MeOH/AcOH (94:5:1). B) MeOH/H_2O/AcOH (97:2:1) both with 5 mM AmAc 5-65% B in 7 min, 65-75% B in 4 min, 100% B for 2 min, initial conditions for 12 min Flow: 0.30 mL/min, Time: $t_{an} = 13$ min, $t_{Tot} = 25$ min	**QQQ** CaV: 3.2 kV, ST: 150 °C, DGT: 350 °C LOD: B_1 13, FB_2 6.5, B_3 8.4 µg/kg LOQ: B_1 27, FB_2 13, B_3 17 µg/kg

Table 2 (*continued*)

Ref	FBs Matrix	Sample (g)	Sample treatment Extraction procedure	LC conditions Column / Injection volume / Mobile Phase Flow / Analysis Time	MS conditions Mass Conditions / Limits
(de Smet et al. 2009)	B_1, B_2, B_3 Bell pepper, rice, corn flakes	1	**Extraction:**1.- Add 8 mL of ACN/H_2O 84:16; 2.- Shaker 30 min; 3.- Centrifuged to 2670 g, 20 min; 4.- Evaporate **Clean up:** 1.- Condition with 2 mL MeOH; 2.- Wash with MeOH/H_2O 75:25; 3.- Redissolve sample in 2 mL of MeOH/H_2O (75:25); 4.- Adjust pH 5.8-6.5 with 0.1M NaOH; 5.- Eluate with 2 mL MeOH/FA 95:5; 6.- Evaporate; 7.- Redissolve in 100 µL of H_2OACN 60:40 with 0.3% FA	**Altima C_{18}, 150 x 3.2 mm, 5µm** Inj vol 20 µL , H_2O/ACN (60:40) with 0.3% FA Isocratic condition Flow: 0.3 mL/min, Time: 12 min	**QQQ** CaV 3.6 eV; ST 140 °C; DGT 350 °C LOD: B_1 20, B_2 7.5, B_3 12.5 µg/kg LOQ: B_1 40, B_2 15, B_3 25 µg/kg

(ACN) Acetonitrile, (AcOH) Acetic acid, (AE) Appearance energy, (AmAc): ammonium acetate, (AmFo) Ammonium formate, (CaV) Capillary voltage, (CaT) Capillary temperature, (CGF) Cone gas flow, (CoG) Collision gas, (CUR) Curtain gas, (DG) Drying gas, (DGF) Desolvation gas flow, (DGT) Desolvation gas temperature, (EV) Extractor voltage, (FA) Formic acid, (Frag Vol) Fragmentor Voltage, (GF) Gas flow, (GT) Gas Temp, (LIT) linear ion tramp, (MeOH) Methanol, (MSPD) Matrix Solid Phase Dispertion, (NG) Nebulizer gas, (NR) Not reported, (PLE) Pressurize Liquid Extraction, (RT) Room temperature, (ST) Source temperature, (SV) Source voltage, (t_{an}) analysis time, (t_{Tot}) total time including column conditioning.

ple, and facilitate the extraction of analytes (Kou 2003). The sample is initially dispersed with an inert material and further loaded into an extraction cell where the solvent is pumped in. Then, the extraction cell is heated to the desired temperature (above 200 °C) for 5 to 9 min, and pressurized (D'Arco 2008).

5.1.3. Supercritical fluid extraction (SFE)

Supercritical fluids are helpful in the extraction of analytes from a matrix. Their unique properties (low density and viscosity) make them superior to conventional extraction solvents, facilitating the extraction of compounds in samples. The most used fluid is CO_2, however, analytes with polar characteristics do not adequately dissolve. To increase its efficiency towards polar analytes, modifiers such as methanol, ethanol or acetone are added. Limitations of this technique include high cost and the need for sophisticated equipment (Selim et al., 1996, Nawaz et al., 2017).

5.2. Clean-up

A great number of methods have included a clean-up step after extraction (Table 2). The aim is to eliminate major impurities like organic acids, polar pigments, sugars, among others. The most used are QuEChERS, solid-phase extraction (SPE) with reverse phase, strong anion exchange (SAX) cartridges, and immunoaffinity columns (IAC) (Damiani et al., 2019, Marschik et al., 2013). It has been shown that solvent temperature used in this process can deeply influence the recovery of fumonisins (Lawrence et al., 2000).

5.2.1. QuEChERS

QuEChERS is a technique initially developed by Anastassiades and collaborators in 2003 (Anastassiades 2003). They coined the acronym QuEChERS which stands for Quick, Easy, Cheap, Effective, Rugged and Safe. It involves microscale extraction with acetonitrile, followed by a cleanup based on a dispersive solid-phase extraction (d-SPE) (Wilkowska and Biziuk, 2011). In the extraction step, magnesium sulphate is used to reduce water in the sample, along with sodium chloride, while in the cleanup step, a primary secondary amine (PSA) or C_{18} is usually used as sorbent to retain co-extracted compounds such as sugar and fatty acids (Ridgway 2012, Zhang et al., 2012). Other salts such as magnesium chloride, sodium nitrate, sodium sulfate and lithium chloride have been used to eliminate water, finding magnesium sulfate as the most effective for separation of both phases, eliminating water from the organic phase. QuEChERS has become the most popular pre-treatment for some matrices like as corn, wheat, oats, rice, and other cereals, as it boasts several advantages such as the decrease in volume of solvent, materials, time, as well as a reduction in cost of analysis.

5.2.2. Solid phase extraction (SPE)

SPE is a variation of traditional chromatography, and thus, is based on the same principle, the use of a mobile and a stationary phase. Separation is performed according to affinity using small disposable cartridges packed with silica gel or bonded phases which are in the stationary phase. The sample is first dissolved and loaded into a cartridge, after which it is rinsed to remove most of the contaminants and is subsequently

Table 3 LC methods with different detectors.

[Ref]	FBs Matrix	Sample (g)	Sample treatment	LC conditions	Detector conditions, Limits
Maize and corn-based products					
(Wall-Martínez et al. 2019)	B_1, B_2 and other toxins *Tortilla*	25	**Extraction:**1.- Dry the *tortilla* at 60°C for 2.5 h; 2.- Milled and homogenize for 15 min at 30 rpm; 3.- Add 50 mL MeOH/H_2O 80:20; 4.- Shake for 2 min; 5.- Centrifuge to 4000 rpm, 10 min; 6.- Take 10 mL of supernatant; 7.- Dilute adding 40 mL of PBS **Clean up IAC R-Biopharm:** 1.- Precondition with 20 mL PBS (5.0 mL/min); 2.- Load 10 mL of sample diluted on the cartridge; 3.- Wash with 1.5 mL MeOH (0.5-1.0 mL/min) and 1.5 mL of H_2O **Derivatization:** Mix 100 µL of diluted extract with 100 µL OPA reagent (120 mg OPA, 3mL MeOH, 12 mL $Na_2B_4O_7 \cdot H_2O$ 0.1 M, 179 µL 2-mercaptoehtanol) prior to injection.	**Uptisphere type 5 ODB, ODS, 250 x 4.6 mm, 5µm, 40°C** Iny vol 10 µL, A) 99% H_2O, B) ACN both with 1 % AcOH 41 % B 9 min, 61 % B for 7 min, keep 4 min, initial conditions for 5 min Flow: 0.8 mL/min, Time t_{an} = 20 min, t_{Tot} = 25 min	**FDA** λex : 360 nm λem: 450 nm LOD: B_1 0.13, B_2 0.04 µg/kg LOQ: B_1 3.0, B_2 2.7 µg/kg
(Caldas and Silva 2007)	B_1, B_2 and other toxins Corn base food products	25 cornmeal, precooked corn flour, popcorn, sweet corn, corn flakes 12.5 corn snacks	**Extraction:** 1.- Add 100 mL MeOH/H_2O (3:1) (cornmeal, PCF, popcorn, corn snacks), 50 mLMeOH/H_2O (4:1) + 2.5 g NCl (sweet corn) 100 mL MeOH:0.4 M sodium tetraborate (3:1) (corn flakes), 2.- filter **Clean up SAX:** 1.- Precondition with 5mL MeOH:H_2O 1:1; 2.- Add 10 mL of filtrate on SAX column; 3.- Wash with 5mL MeOH:H_2O 3:1; 3.- Elute 12 mL MeOH/AcOH (99:1) + 4 mL MeOH:AcOH (95:5) (cornmeal, PCF, popcorn, corn snacks), 12 mL MeOH/AcOH (99:1) + 8 mL MeOH:AcOH (95:5) (sweet corn, corn flakes); 4.- Dry at 40°C; 5.- Reconstitute in 500 μL **Derivatization:** 1.- Add 480 μL of 0.05 M sodium borate buffer (pH 9.5), 170 μL sodium cyanide solution (0.013%) and 50 μL of 0.5 mg/mL naphthalene-2,3 dicarboxaldehyde (NDA) in MeOH; 2.- Vortex, 3.- Heat at 60 °C for 15 min, and cooled, 4.- Add 2.8 mL of 0.05 M phosphate buffer	**C_{18}, 150 cm x 4.6 mm, NR** Iny vol 10µL, A) H_2O, B) ACN both 2.5% AcOH 55-80% B in 5 min, keep 8 min, initial conditions for 1min Flow: 1 mL/min, Time: t_{an} = 13 min t_{Tot} = 14 min	**FDA** λex : 420 nm λem: 500 nm LOQ: 127-2040 µg/kg depending on the matrix
(Chiara Dall'Asta, Mangia, et al. 2009)	B_1, B_2, B_3 Ground corn	25	**Extraction:** 1.- Add 100 mL H_2O/ACN 1:1; 2.- Shake for 1h; 3.- Filter; 4.- Adjust to pH 6-9 with 0.5 N NaOH; 4.-Take 3 mL, place into test tube; 5.- Add 8 mL MeOH/H_2O 3:1 **Clean up SPE MultiSep 211 Fum:** 1.- Precondition with 5 mL MeOH, then 5 mL MeOH/H_2O 3:1; 2.- Load sample 3.-Wash with 8 mL MeOH/H_2O, then 3 mL MeOH; 4.-Elute 3:1 MeOH/AcOH 99:1; 5.- Dry at the eluate to 60°C; 6.- Reconstitute with 1 mL MeOH **Derivatization:** 1.- Add 1 mL sodium borate buffer (0.05 M, pH 9.5), 0.5 mL NaCN reagent (13 mg NaCN in 100 mL water) and 0.5 mL NDA reagent (25 mg NDA in 100 mL MeOH). 2.- Heat for 20 min in a 60°C water bath and cooling for 4 min at 8°C, 3.- Dilute with 7 mL of phosphate buffer (0.05 M, pH 7.4)/ACN (2:3)	**Brownlee C_{18}, 100 x 4.6, 5µm, NR** Inj vol 80 µL, H_2O/ACN/AcOH 52:47:1 Isocratic Flow: 0.2 mL/min, Time: NR	**FDA** λex: 420 nm λem: 500 nm LOD/LOQ: < 100 µg/kg
(L. J.G. Silva et al. 2007)	B_1, B_2 Maize base	25	**Extraction:** 1.- Add 40 mL MeOH/H_2O 4:1; 2.- Centrifuge 2500 g, 15 min; 3.- Extract remaining solid twice with 30 mL MeOH/H_2O 4:1; 4.- Filter **Clean up: FumoniTest TM IAC:** 1.- Dilute 10 mL sample with 40 mL	**Nucleosil 120, C_{18}, 250 x 4.6mm, 5µm, NR** Inj vol NR, ACN/H_2O/AcOH 61:38:1	**FDA** λex: 420 nm λem: 500 nm

Table 3 (*continued*)

[Ref]	FBs Matrix	Sample (g)	Sample treatment	LC conditions	Detector conditions, Limits
	products		PBS; 2.- Filter; 3.- Load 20 mL; 3.- Wash 10 mL PBS; 5.- Elute 2 x 1.5 mL MeOH; 6.- Evaporated at 60°C **Derivatization:** 1.- Reconstitute in 50 µL MeOH/H_2O 1:1; 2.- Add 500 µL 0.05M sodium borate buffer (pH 9.5 adjusted with 1N NaOH), 500 µL NaCN reagent, and 150 µL NDA reagent (0.5 mg/mL in ACN); 2.-Heat 15 min at 60°C, cold to room temp	Isocratic Flow: 1 mL/min, Time: t_{Tot}:14 min	LOD/LOQ: NR
(Muscarella et al. 2008)	B_1 maize-based foods	5	**Extraction:** 1.- Add 2x12.5mL of an ACN/MeOH/H_2O 3:3:4; 2.- Sonicate 20 min; 3.-Centrifuge at 2112 *g*, 10 min; 4.- Dilute 3 mL with 12 mL PBS **Clean up IAC FUMONIPREP:** 1.- Load 10 mL of dilute sample; 2.- Wash with 10mL of PBS; 3.- Elute with 4 mL of MeOH at 0.5 L/min; 4.- Evaporate; 5.- Dry, 40°C; 6.- Reconstitute in 0.5mL of MeOH/0.1M phosphate buffer at pH 3.15 3:2 **Derivatization: OPA:** NR	**Eurospher C_{18}, 150mm x 4.6mm, 3µm, 40 °C** Inj vol 100 µL, A) 0.1M phosphate buffer at pH 3.15, B) MeOH 60% B for 2 min; 60-65% B in 5 min, to 65-75% B 3 min; initial condition for 5 min Flow: 0.8 mL/min, Time: t_{an} = 10 min t_{Tot} = 15 min	**FDA** λex: 343 nm λem: 445 nm LOD B_1 4, B_2 5 µg/L LOQ: B_1 13, B_2 16 µg/L **
(Liu et al. 2017)	B_1, B_2 Maize	10	**Extraction:** 1.- Hydrate for 12 h with 10 mL ultrapure H_2O; 2.- Add 30 mL ACN, 3.- Shake 120 rpm, 1 h; 4.-Filter **Clean up SAX:** 1.- Precondition with 5 mL MeOH followed by 5 mL ACN /H_2O 3:1 at a flow rate 1 mL/min; 2.- Load 8 mL of sample; 3.- Wash with 5 mL MeOH; 4.- Elute with 10 mL AcOH/MeOH 1:99, 5.-Dry, 6.- Reconstitute in 2 mL ACN/H_2O 1:1 **Derivatization:** OPA post column in HPLC pump 1 (1% NaOH) 0.8 mL/min, pump 2 (3g OPA, 9 mL MeOH, potassium borate, 9 mL 2-mercaptoethanol) 0.6 mL/min	**Agilent C_{18}, 250 x 4.6 mm, 5µm, 40°C** Inj vol 50 µL, A) 0.05 M citric acid buffer (pH = 4), B) MeOH 55-65% B in 10 min, 65-70% B in 12 min, keep 3 min, 70-55% B in 3 min Flow: 1 mL/min, Time: t_{an} = 25 min t_{Tot} = 28 min	**FDA** λex: 335 nm λem: 440 nm LOD: B_1 6, B_2 7 µg/kg LOQ: B_1 20, B_2 23 µg/kg
(Sokolovic 2022)	B_1, B_2 Maize	20	**Extraction:** 1.- Add 100 mL of MeOH:H_2O 7:3; 2.- shake for 3 min; 3.- filter; 4.- dilute 1:20 with deionized H_2O **Derivatization: OPA:** NR	**Zorbax Eclipse C_{18} 125 x 4 mm, 5 µL** Vol. Inj: NR, A) 20 % H_2O (1% Na_3PO_4) B) 80% MeOH isocratic elution Flow: 1 mL/min,Time: t_{Tot} = 30 min	**FDA** λex: 335 nm λem: 440 nm LOD: 223 µg/kg for all FBs
(Gnonlonfin et al. 2008)	B_1 and other toxins Chips	10	**Extraction:** 1.- Add 50 mL of MeOH/H_2O 75:25; 2.- Mix for 1 min; 3.- Filter **Clean up SAX:** 1.- Precondition with 5 mL H_2O, 5 mL MeOH, and 5 mL MeOH/H_2O 75:25 at a flow rate of 1 mL/min; 2.- Apply 10 mL of sample; 3.- Wash 8 mL with 5 mL MeOH/H_2O 75:25 and 8 mL MeOH; 4.- Elute 14 mL MeOH/AcOH 99:1 at a flow 1 mL/min; 5.- Evaporate; 6.- Reconstitute in 1 mL of MeOH, 7.-Evaporate, 8.- Reconsitute in 200 µL MeOH	**Supercosil C_{18}, 150 x 4 mm, 3µm, 30°C** Inj vol 10 µL, MeOH/0.1 M sodium dihydrogen phosphate 80:20 adjust pH 3.35 with phosphoric acid Isocratic	**FDA** λex : 335 λem: 440 LOD: 0.025 µg/kg

(*continued on next page*)

Table 3 (*continued*)

[Ref]	FBs Matrix	Sample (g)	Sample treatment	LC conditions	Detector conditions, Limits
			Derivatization OPA: 1.- Mix 50 µL sample with 200 µL OPA (40 mg OPA in 1 ml of methanol followed by addition of 5 ml of 0.L M sodium borate solution and 50 µL of 2-mercaptoethanol.)	Flow: 1 mL/min Time: NR	
(Tardieu et al. 2008)	B_1 Animal tissues, liver, kidney	1	**Extraction:** 1.- Homogenize in 2 mL of distilled H_2O (Liver, 500 rpm; breast muscle 3000rpm, 20 s) with a teflon Potter, 2.- Precipitate proteins with 2 mL of MeCN/MeOH 1:1 and 25mg of NaCl; 3.-Stir to 300 rpm, 120 min; 4.- Centrifuge 3000 g, 15 min; 5.- Take 3 mL of supernatant; 6.-Add 4 mL Hex; 7.- Centrifuge 3000 g, 15 min; 8.- Take 2 mL aqueous phase; 9.- Dilute with 8 mL PBS **Clean up: IAC FUMONIPREPC:** 1.- Pass the sample through cartridge; 2.- Wash 10 mL of PBS (pH 7.4); 3.-Elute 1.5 mL of MeOH, 1.5mL of H_2O; 4.- Evaporate, 40°C; 5.-Reconstitute with 200 µL ACN/H_2O 1:1 **Derivatization OPA:**1.- Add to 50 µL of sample: 50 µL of OPA, 50 µL of 0.1M borate buffer at pH 8.3, and 50 µL of H_2O	**Prontosil C_{18}, 250 x 4.6mm, 5µm** Inj vol 20 µL, MeOH/NaH_2PO_4 0.1M pH 3.35, 75:25 Isocratic Flow: 1 mL/min Time: t_{Tot} 15 min	**FDA** λex : 335 λem: 440 LOD: 10 µg/kg LOQ: 13 µg/kg
(Kawashima, Vieira, and Valente Soares 2007)	B_1 and other toxins Beer	> 50 mL NR	**Clean up: SAX:** 1.- Adjust pH 5.8-6.5 with 1N NaOH; 2.- Filter; 3.- Precondition with 10 mL of MeOH, 10 mL MeOH/H_2O 3:1; 4.- Load 50 mL; 5.- Apply into SAX; 6.- Wash with 10 mL MeOH/H_2O 3:1 and 6 mL MeOH; 7.- Elute with 20 mL MeOH/AcOH 95:5; 8.-Dry with N_2 at 60°C **Derivatization: OPA:** 1.- Reconstitute in 500 µL ACN/H_2O 1:1; 2.- Take 100 µL; 3.- Add 200 µL OPA reagent (40 mg *O*-ftaldialdehyde in 1 mL ethanol diluted with 0.1 M borate buffer and 50 µL 2-mercaptoethanol; 4. Ultrasonic bath at 5-15 °C, 30 sec	**Spherisorb ODS-2, 250 x 4.6 mm 2, 5µm** Inj vol 20 µL, ACN/H_2O/AcOH 54:46:1 Isocratic Flow: 1 mL/min, Time: t_{Tot} 19 min	**FDA** λex : 335 λem: 440 LOD/LOQ: NR
(Jerome Jeyakumar, Zhang, and Thiruvengadam 2018)	B_1, B_2 and other toxins Sugarcane	NR > 50 mL	**Extraction:** 1.- Add 25 mL AcOEt to the culture; 2.- Shake to 8000 rpm; 3.- Filtrate after 2h; 4.- Mix with 5% acetone, isopropanol; 5.- Extract liquid phase with AcOEt in a 1:1 ratio; 6.- Collect upper phase, 7- Evaporate; 8.- Reconstitute in isopropanol. All x 3 **Clean up SAX:** 1.- Load 10 mL; 2.- Wash with 3 mL MeOH followed by 5 mL of 1% KCl; 3.- Collect into 5 mL tube; 4.- Evaporate **Derivatization OPA:** 1. Pre-column derivatization [50 mg of OPA in 1.25 mL of methanol + 50 µL of 2-mercaptoethanol + 11.2 mL of 0.1 M sodium borate buffer (pH 9.5)]; 2.- Mix 100 µL of sample with 25 µL of OPA; 3.-incubate 2 min to rt.	**C_{18}, 250 x 4.6 mm, 5µm** Inj vol 20 µL, Isocratic, MeOH/ 0.1 M sodium dihydrogen phosphate buffer pH 3.3; 75:25 Flow: 0.3 mL/min, Time: 16 min	**FDA** λex: 335 nm λem: 440 nm LOD/LOQ:NR
(Piacentini et al. 2017)	B_1 and other toxins Beer	> 50 mL 25	**Clean up:** 1.- Adjust pH 5.8-6.5 with 1N NaOH; 2.- Filter; 3.- Precondition with 10 mL of MeOH, 10 mL MeOH/H_2O 3:1; 4.- Load 50 mL; 5.- Apply into SAX; 6.- Wash with 10 mL MeOH/H_2O 3:1 and 6 mL MeOH; 7.- Elute with 5 mL MeOH/AcOH 95:5; 8.-Dry with N_2 at 60°C, 7.- Reconstitute in 300 µL ACN/H_2O 1:1, 8.-Filter **Derivatization OPA:** 1.-Take 500 µL; 2.-Add 200 µL OPA reagent	**Luna C_{18}, 150 x 4.60 mm, 5 µm, Temp NR** Inj vol 20 µL, ACN/H_2O/AcOH 520:480:5 Isocratic Flow: 1 mL/min, Time: 15 min	**FDA** λex: 335 nm λem:440 nm LOD: 2 µg/L, LOQ: 6.3 µg/L

Table 3 (*continued*)

[Ref]	FBs Matrix	Sample (g)	Sample treatment	LC conditions	Detector conditions, Limits
			(40 mg *O*-ftaldialdehyde in 1 mL ethanol diluted with 5 mL 0.1 M borate buffer and 50 µL 2-mercaptoethanol.		
(Smith et al. 2017)	B_1, B_2 Feed	25 10	**Extraction:** 1.- Add 50 mL MeOH/ACN/H_2O 1:1:2; 2.-Vortex for 30 s; 3.-Shake 20 min, 3.-Filter, 4.-Dilute 1:5 with 0.01 M PBS **Clean up SPE:** 1.- Take 5 mL aliquot; 2.-apply into SPE column; elute rate approximately 1-2 drops/s, 3.-Wash with 10 mL 0.01 M PBS, 4.-Removed solvent (vacuum, 5 min), 5.-Elute with 1.5 mL MeOH then 1.5 mL H_2O **Derivatization Fmoc:** 1.- Take 500 µL, 2- Add boric acid (1 M, pH 7.5, 125 µL), control pH during derivatization; 3.- Add Fmoc (125 µL, 0.12 g Fmoc, 40 mL ACN, 2.88 g citric acid, 1.10 g tetramethylammonium chloride in 1 L distilled and deionized water), mix and wait 10 min, 4.- vortex; 5.-Add 1 mL anhydrous pentane, 6.- vortex and allowed to separate; 7.- discard the organic (top) layer; 8.- transfer aqueous (bottom) layer to a amber autosampler vial for HPLC-FLD analysis.	**Acclaim 120 C_{18}, 4.6 x 150 mm; 3 µ, 35°C** 10 µL of sample, A) citrate buffer (pH 4.7): ACN (70:30)], 20% B [citrate buffer (pH 4.7): ACN (30:70) 20-95% B in 20 min post-injection, keep 5 min, 95-20 % B in 1 min, initial conditions for 4 min Flow: 1 mL/min, Time: t_{an}25 min, t_{Tot}: 30 min	**FDA** λex: 263 nm λem: 313 nm LOQ: B_1 7.55, B_2 8.5 µg/L
(J. Wang, Zhou, and Wang 2008)	B_1 corn products	10	**Extraction:** 1.- Add ACN/H_2O 1:1; 2.- Shake over night; 3.- Filter; 4.-Take 10 mL; 5.- Place on the ice for 15 min; 6.- Centrifuge to 7000 rpm, 10 min at 4 °C **Clean up:** 1.- Preconditione with 2 mL of MeOH, 2.- Transfer 50 mL of sample; 3.- Apply to centrifugal tube with 300 mg of amberlite XAD-4; 4.- Stir for 5 h; 5.- Wash with 40 mL with deionized H_2O; 6.- Elute with 3 mL MeOH; 7.- Collect 8.- Dry 65 °C, 9.- Reconstitute	**Alltima C_{18}, 250 x 4.6 mm, 5µm** 20 µL of sample, A) H_2O/TFA, B) ACN/FA 0-20% B from 0 to 5 min, 20-40% B from 5 to 10 min, 40-80% B from 10 to 15 min, 80% B from 15 to 20 min, 80-0% B from 20 to 25 min Flow: 1 mL/min, Time: 25 min	**ELSD** 45°C of drift tube temperature, 2.0 L/min N_2 gas flow, gain value of 1 in the impactor-on mode LOD/LOQ: 3000 µg/L

(ACN) Acetonitrile, (AcOH) Acetic acid, (AE) Appearance energy, (AmAc): ammonium acetate, (AmFo) Ammonium formate, (FA) Formic acid, (Hex) Hexane, (MeOH) Methanol, (MSPD) Matrix Solid Phase Dispertion, (NR) Not reported, (PBS) Phosphate Buffer Solution, (PLE) Pressurize Liquid Extraction, (RT) Room temperature, (t_{an}) analysis time, (t_{Tot}) total time including column conditioning.

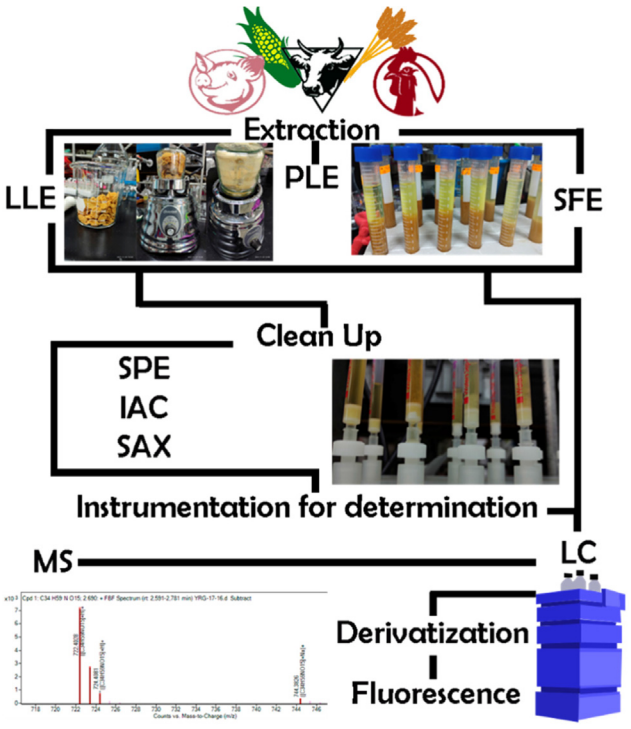

Fig. 3 Workflow for fumonisin chromatographic analysis.

extracted from the cartridge with a polarity compatible solvent. All this is done under reduced pressure. The SPE cartridges contain different binding phases, for example silica gel, C_{18} (octadecylsilane), floredil, phenyl, aminopropyl, ion exchange (anionic and cationic) or SAX, immunosorbents, and molecular imprinting polymers. These last two are affinity materials which provide them with a high binding capacity for small molecules making them excellent candidates for cleanup in terms of specificity, however, they have a high cost, and are not compatible with organic solvents, limiting their use to aqueous systems. This is a disadvantage compared to more common binding phases such as SAX or C_{18} (Turner et al., 2009).

Regarding fumonisin analysis, C_{18} is the most used stationary phase for SPE due to its easy acquisition, low costs, and the possibility of extraction of hydrolyzed forms. The second most used phase are SAX resins, whose efficiency is based on the interaction with fumonisin carbonyl groups, making them not appropriate for hydrolyzed forms (Zöllner and Mayer-Helm, 2006). Its elution has been reported with MeOH acidified with 0.05% AcOH achieving a pH $<$ 7. When ion exchange resins are used for this purpose, it is necessary that the analyzed mycotoxin be in its ionic form and in an aqueous solvent. For this reason, pH regulation of the medium is an important factor. This methodology has been used for the extraction of fumonisins and moniliformin. SAX columns consist of resins with weakly basic functional groups, such as NH_2, $NHCH_3$ or $N(CH_3)_2$, or with quaternary ammonium strongly basic groups ($N(CH_3)OH$) in which OH is replaceable by mycotoxin. Several types exist in both, anionic and cationic phases. SAX is the favored material for mycotoxin extraction (Turner et al., 2009).

IAC uses antibodies, present in the stationary phase, that bind selectively to mycotoxins present in the extract. This poses an important advantage, as there is a specific interaction between the antibody and the analyte, resulting in a greater speed of interaction. After antibody binding, mycotoxins are recovered by elution with a miscible solvent or by antibody denaturation. Disadvantages of this process include the necessity of combination with other techniques such as LLE or SPE for complex samples; and the requirement for the extract to be in aqueous solution containing little or no organic solvents, as their presence, even in low concentrations, can denature antibodies (Pereira et al., 2014). Recently, a rapid and sensitive method for determination of seven mycotoxins (including FB_1) using immunomagnetic (monoclonal antibodies conjugated with CNBr) solid-phase extraction (IMPSE) coupled to UPLC-MS/MS has been developed for peanut, maize, and wheat matrices (Wang et al., 2022).

5.3. Derivatization

The main objective of derivatization is to change the chemical and physical properties of compounds by modifying their chemical structure (Qi et al., 2014). Thus, derivatization reagents react with target compounds containing various functional groups, including carbonyl (O'Brien-Coker et al., 2001 hydroxyl (Barry et al., 2003), carboxyl (Santa et al., 2009), amine (Vanhoenacker et al., 2009, and thiol (Vichi et al., 2013.

This strategy has been of utmost importance in the development of new methodology for the detection of fumonisins, as these compounds are not capable of developing fluorescence or absorbance in UV–VIS light, due to their lack of a suitable chromophore or fluorophore group for detection. Derivatization with fluorescent derivatives including 9-fluorenylmethylchloroformate (FMOC-CL), 4-flouro-7-nitrobenzofurazan (NBD-F), o-phthaldialdehyde (OPA), naphthalene-2,3-dicarboxaldehyde (NDA) and dansyl chloride (DnS-Cl) (Ndube et al., 2011, Ndube 2009, Silva et al., 2009) allows for fumonisin detection with HPLC coupled to fluorescence or UV-Vanhoenacker et al., 2009), albeit with a low sensitivity. Despite these limitations, UV detection is still used although the methods are not new (Cardinael et al., 2015). Out of the fluorescent derivatives, OPA is the most used due to its low detection limits (50 ng/g), followed by NBD-F which is detected at 100 ng/g. NDA has an even lower detection limit than OPA, however, its use is generally avoided as potassium cyanide is required during derivatization, representing a high health risk (Table 3).

5.4. Instrumentation for determination

Once the sample is obtained, extracted and, in some cases purified or cleaned-up, different instrumentation can be used for fumonisin analysis; being HPLC and UPLC the most frequently employed. Chromatographic column is used in a reverse phase, most commonly with C_{18} as a stationary phase; nevertheless, diphenyl, amide and C_8 may also be used. The chromatographer can be coupled with a fluorescence (Table 3) or ESI source with mass spectrometry detectors (Tables 1-2). For these last ones, QQQ is the most widely used analyzer, although sQ and TOF analyzers had also been utilized. These are all used in positive mode and all acquisition modes are reported, full scan, single reaction mode (SRM) or multiple reaction mode (MRM). Some analyzers use an Ion Trap array.

5.4.1. Separation

Fumonisins have a higher molecular weight (around 721.83 g/mol) compared to other mycotoxins such as Ocratoxin A (403.81 g/mol), Zaralenone (318.36 g/mol) or Patulin (154.12 g/mol). Because of their high polarity, reverse phase LC is an excellent option for its separation. Previous extraction methods involve an aqueous phase, which is included as mobile phase (Tables 1-3). Different proportions of solvents are used for the composition of the mobile phase, MeOH: H_2O is preferred, followed by ACN:H_2O, especially when derivatization is used to provide better sensibility (Velázquez et al., 2000). There is a clear tendency of using a greater proportion of organic solvents in these mixtures with gradients reaching 100 % organic concentration, as well as the addition of FA or AcOH, and in some cases ammonium salts. This is done to enhance the ionization process necessary for mass detection, to control pH, and to increase the efficiency of separation.

Temperature used for these analyses vary between 10 and 45 °C for MeOH as mobile phase and 30–50 °C for ACN; flows from 0.1 to 1 mL/min are reported. Column dimension is another important aspect to consider when analyzing fumonisins. According to the literature compiled in the present article, there is a great variation between column dimensions, ranging from 50 to 250 mm in length, diameters going from 2.0 to 4.6 mm, and particle size ranging from 1.6 to 5 µm. The most used, however, oscillate between 100 and 150 × 2 mm, with a particle size of 4.6 µm.

A recent work by Sultan et. al. evaluated the efficacy of 5 columns with different dimensions and particle sizes. FB_1 and FB_2 were analyzed using liquid–liquid extraction, followed by a cleaning procedure using SPE, and fluorescence detection, using OPA as a fluorophore group. They conclude that the use of reverse phase SPE, followed by derivatization with OPA is an effective method for the determination of fumonisins, which agrees with the information gathered by this review. In that work the comparison between columns Nucleosil Cronus (150 mm × 4.6 mm, 5 µm) and Poroshell (75 mm × 4.6 m, 2.7 µm) yielded similar results regarding time and solvent use. However, it is of note that the use of columns with porous particles or those with a solid nucleus affect separation. Similarly, both the diameter of the column, and particle size used are also important parameters to determine in fumonisin analysis (Sultan et al., 2022).

5.4.2. Detection

Although many methods for fumonisin detection exist, such those based in fluorescence, the methods based on MS are the most sensitive. Among the methods included in this work, the lowest FB_1 LOD for fluorescence detector was 0.025 versus 0.0005 µg/Kg obtained with MS QTrap detector. Besides, MS detectors offer a great advantage as they do not require derivatization (Tables 1-2).

FDA methods depend on the presence of a chromophore or fluorophore that allows for the correct detection of the analytes, as has been mentioned previously, various derivatizing agents exist (see section 4.3), despite this disadvantage, these methos are still commonly used due to their low costs, and their applicability to a great number of matrices including beer, maize, and biological fluids, among others. Fumonisins can be detected at the following longitudes: λex: 420 nm, λem: 500 nm.

On the other hand, mass spectrometry for the detection of fumonisins is carried out with an ESI interphase, and IT, orbitrap, QQQ and TOF analyzers used in positive mode. In this analysis, the ion $[M + H]^+$ has been found to be the most abundant, with or without a high grade of fragmentation. Additionally, in negative mode, the formation of doubly charged molecular ions has been reported. The positive mode is used more frequently, although some authors have reported that it favors the formation of adducts that may present a problem with sensitivity. Despite this, the positive mode is still the most used mode as the $[M + H]^+$ ion is three times more abundant than $[M - H]^-$.

According to the present review, various mass analyzers such as sQ, QQQ, and TOF have been used, some of them with an ion trap (IT). IT methods are theoretically more sensitive, yet, not all ion trap (IT), Trap or QTrap methods reported here have been the most sensitive, with some QQQ or even sQ methods being able to detect lower concentrations (Tables 1 and 2).

Lower limits for FB_1, FB_2, and FB_3 have been reported by different authors, including Šarkanj *et al* for urine analysis (0.001 µg/L FB_1 and FB_2) (Šarkanj 2018), Zitomer *et al* regarding maize tissues analysis (0.01 µg/kg for FB_1 and FB_2) (Zitomer et al., 2008), Huang *et al* for liquorice (0.05 µg/L FB_1 and FB_2) (Huang et al., 2018). Among the different fumonisins analyzed, the most reported is FB_1, with $[M + H]$ 722.2 m/z being the most abundant ion. Additionally, the 334.3 and 352.3 m/z product ions can also be obtained by using a collision energy of 38–56 and 38–40 eV respectively (Table 4).

A light scattering method has also been reported. Even though its reported LOD and LOQ are high, these limits approach those that are permissible. Thus, it may prove useful in screening, as detection by this method correlates with level above the permissible limits (Ramalho et al., 2022, Mirón-Mérida et al., 2021).

5.4.3. Non chromatographic methods for fumonisins detection

Aside from conventional chromatographic methods, there is a wide variety of methods for fumonisin determination. These can be classified into two groups: immunological and molecular (Table 5) (Deepa and Sreenivasa, 2019).

Table 4 Transitions for FBs.

FB_1,			
Transitions (m/z)	CE	DP	CoV
722.2 → 704.3	31	70–76	50
722.2 → 352.3	38–40	70–76	50–60
722.2 → 334.3	38–56	70–76	50–65
FB_2/FB_3			
706.2 → 354.4	37	68–75	50
706.2 → 336.5	40–47	68–75	50–55
706.2 → 318.4	40–55	68–75	50–65

(CE) Collision Energy, (CoV) Cone Voltage, (DP) Declustering potential, all in *V*.

Table 5 Non-chromatographic methods for detection of fumonisins.

Immunological methods	Molecular methods
Enzyme Linked Immuno Sorbent Assay (ELISA)	Internal transcriber spacer (ITS)
Dipstick	Intergenic spacers (IGS)
Biosensor	Polyketide synthase
Immunoaffinity	FUM genes
Colloidal gold immune assay	Microarray
	Polymerase chain reaction (PCR)

(Majdinasab, Aissa, and Marty 2021; Deepa and Sreenivasa 2019; Gong, Jiang, and Chen 2015; Mirón-Mérida, Gong, and Goycoolea 2021).

The immunological methods are based on the interaction between the mycotoxin and a specific antibody. These antibodies act by recognizing specific chemical groups; as such, they can recognize structural analogs. To facilitate antibody detection, a marker is added which can be radioactive, chromogenic or fluorogenic in nature. The most popular, commercial, immunological method for fumonisin detection is enzyme-linked immunosorbent assay (ELISA) (Pereira et al., 2014). This method has been used to determine fumonisin concentration in corn and other cereals (Wang et al., 2006fresh and dehydrated commercial garlic (Tonti 2017); during industrial cornflakes processing (Castells et al., 2008); and maize and gluten meal (Coronel et al., 2016). Techniques such as time-resolved immunochromatographic assays, enzyme-linked aptamer assays, chemiluminescence immunoassays, fluorescence immunoassays, fluorescence resonance energy transfer immunoassays, and metal-enhanced fluorescence assays have been implemented in the detection of mycotoxins (Majdinasab et al., 2021, Chauhan et al., 2016).

Although molecular methods do not directly determine the presence of fumonisins, they are nonetheless important as they allow rapid detection of fumonisin-producing species. These DNA-based identification methods are fast, sensitive, and reliable (Deepa and Sreenivasa, 2017) because they are independent of the morphology and cultivability of the fungi. Of these, PCR is the most frequently used technology for detection of mycotoxin-producing *Fusarium* species (Gong et al., 2015). Today, aptamer-based methods are having a great impact in the detection of mycotoxins. Due to their exceptional affinity and specificity, they can be comparable to antibodies, with certain advantages such as easy nucleobase and chemical modification, and exponential self-amplification (Mirón-Mérida et al., 2021).

Also, these methods take advantages of nanomaterials to improve LOD, cost, analysis time, reduce instrument use for final users and overall, pretreatment and manipulation of samples. However, at a research level, nanomaterials need to be characterized, requiring instrumentation that is not common. Many of these technologies are still under development, with a large amount of research proposing them for fumonisin determination. Much of this information has been compiled over the years in various review papers (Majdinasab et al., 2021, Deepa and Sreenivasa, 2019, Gong et al., 2015, Mirón-Mérida et al., 2021). Until these methodologies achieve the robustness of chromatographic techniques, especially for absolute quantification, the latter techniques remain the techniques of choice.

6. Remarks

Fumonisins are mycotoxins widely distributed in food products, mainly due to the contamination of cereals (such as bread, bread, pasta, boxed cereals, flour, among others) by species of the *Fusarium* genus. Additionally, their presence in livestock feed, along with the eventual accumulation of these mycotoxins within their tissues, increases the transmission chain.

Fumonisins have a high capacity to withstand the processes used in the food industry. They have been found to be thermically stable, at a neutral pH, in temperatures ranging from 100 to 125 °C, only observing small degrees of degradation in alkaline or acidic mediums at temperatures above 175 °C. The analysis of the stability of its hydrolyzed forms in corn-based products indicates that their decomposition begins at temperatures above 250 °C, with the loss of the TCA groups. Even so, their decomposition does not exceed 20% of total fumonisins. The conjugation of fumonisins with sugars, proteins and even metals also occur in food products that are rich in these chemical entities. Currently there are no specific methodologies for analysis, detection, and quantification of hydrolyzed or conjugated forms of fumonisins for all the interest matrices, representing a niche of opportunity from an analytical and application point of view in the food industry. The basis of food in Mexico is corn; therefore, its population may be exposed to the consumption of *Fusarium* mycotoxins. Currently, there is a lack of legislation regulating the consumption of these compounds. The creation of new legislation is important to achieve adequate control and management of mycotoxin levels in food to ensure adequate food health in this regard.

Supporting material can be consulted at https://www.sciencedirect.com/journal/arabian-journal-of-chemistry and provides Tables 1-3 as excel file to facilitate the user experience by allowing the reader to sort by matrix, detector, LOD, LOQ, analysis time, etc.

7. Conclusion

Cheap, easy, and fast analytical methods for fumonisin detection are important worldwide, especially for countries where the content of these toxins is not regulated. Implementing regulation aids in the control of food products and contributes to food safety. Molecular, immunologic, and chromatographic methods can be used for fumonisin analysis. Molecular methods present the disadvantage of being only qualitative but widely used to identify fumonisin producer species. While immunologic and chromatographic methods can be utilized for both, qualitative and quantitative analysis. Immunologic methods are highly specific and useful for free fumonisins; however, these are not recommended for conjugated fumonisins. Immunological or molecular assays are still in development and could be a reasonable screening approach with final quantification being carried out by robust chromatographic methods, although some ELISA methods are commercially available. There are a wide variety of chromatographic methods. These are used for all kind of studies and applied to all kinds of samples because they can be coupled to different detectors. Chromatographic analysis of FBs can be qualitative or quantitative, another advantage is that they can analyze different FBs at the same

time. Among the chromatographic methods, different sensibilities can be reached thus, although ELDS presents LOD very close to the maximum permissible levels it is still a viable option as a screening method. The use of mass spectrometry analyzers provides a high sensibility and is appropriate when analyzing samples of different origin. UPLC and *HPLC* methods are reported, as well as different analyzers. Very low limits of detection can be achieved. Sample pretreatment can be sufficient by extraction with an organic solvent or mixtures of ACN, MeOH and water, sometimes using weak acids. Similarly, these mixtures are employed in a gradient elution with 0.1–0.3% of acid, however clean-up is suggested for these mixtures. Chromatographic methods have a greater versatility regarding the combination of columns and detectors that are available, which is part of the reason these methods are still employed generating more sensitive, shorter, and reliable results. The information of the chromatographic methods for fumonisin analysis developed in the last 16 years has been included in this review. This paper will facilitate to the reader to consider the methodological aspects of a method to analytical success. Thus, the readers will be able to combine and adapt these aspects between methods to their own necessity.

Availability of data and material

Not applicable.

Code availability

Not applicable.

For the present review, ethics approval, consent to participate and consent for publication are not applicable.

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Author contributions

Y.D.O.A. compiled all the methods parameters and wrote the first version of the manuscript, E.S.R. reviewed the medical and biological implications of fumonisins, M.Á.R.C. reviewed all methods parameters, M.Y.R. reviewed the general redaction of the complete manuscript. M.Á.R.C and M.Y.R. guided the complete work. All authors participated in the redaction of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2023.104716.

References

Abia, W.A., Warth, B., Sulyok, M., Krska, R., Tchana, A., Njobeh, P.B., 2013. Bio-monitoring of mycotoxin exposure in Cameroon using a urinary multi-biomarker approach. Food Chem. Toxicol 62, 927–934. https://doi.org/10.1016/j.fct.2013.10.003.

Agriopoulou, S., Stamatelopoulou, E., Varzakas, T., 2020. Advances in occurrence, importance, and mycotoxin control strategies: Prevention and detoxification in foods. Foods 9 (2). https://doi.org/10.3390/foods9020137.

Akande, K.E., Abubaka, M.M., Adegbola, T.A., Bogoro, S.E., 2006. Nutritional and health implications of mycotoxins in animal feeds: A review. Pak J Nut 5 (5), 398–403. https://doi.org/10.3923/pjn.2006.398.403.

Alberts, J.F., Lilly, M., Rheeder, J.P., Burger, H.M., Shephard, G.S., Gelderblom, W.C.A., 2017. Technological and community-based methods to reduce mycotoxin exposure. Food Control 73 (May), 101–109. https://doi.org/10.1016/j.foodcont.2016.05.029.

Alexander, N.J., Proctor, R.H., McCormick, S.P., 2009. Genes, gene clusters, and biosynthesis of trichothecenes and fumonisins in *Fusarium*. Toxin Reviews 28 (2–3), 198–215. https://doi.org/10.1080/15569540903092142.

Alimentarius, C., 2019. Norma general para los contaminantes y las toxinas presentes en los alimentos y piensos CXS 193–1995. WHO, FAO, pp. 1–76.

Anastassiades, M., Lehotay, S.J., Štajnbaher, D., Schenck, F.J., 2003. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and. J AOAC Int 86, 412–431. https://doi.org/10.2478/s11687-011-0011-9.

Arranz, I., Baeyens, W.R.G., Van Der Weken, G., De Saeger, S., Van Peteghem, C., 2004. Review: HPLC determination of fumonisin mycotoxins. Crit Rev Food Sci Nutr 44 (3), 195–203. https://doi.org/10.1080/10408690490441604.

Arroyo-Manzanares, N., García-Campaña, A.M., Gámiz-Gracia, L., 2013. Multiclass mycotoxin analysis in *Silybum marianum* by ultra high performance liquid chromatography-tandem mass spectrometry using a procedure based on QuEChERS and dispersive liquid-liquid microextraction. J. Chromatogr. A 1282, 11–19. https://doi.org/10.1016/j.chroma.2013.01.072.

Arroyo-Manzanares, N., Huertas-Pérez, J.F., García-Campaña, A. M., Gámiz-Gracia, L., 2014. Simple methodology for the determination of mycotoxins in pseudocereals, spelt and rice. Food Control 36 (1), 94–101. https://doi.org/10.1016/j.foodcont.2013.07.028.

Arroyo-Manzanares, N., De Ruyck, K., Uka, V., Di Mavungu, J., 2018. In-house validation of a rapid and efficient procedure for simultaneous determination of ergot alkaloids and other mycotoxins in wheat and maize. Anal. Bioanal. Chem 410 (22), 5567–5581. https://doi.org/10.1007/s00216-018-1018-6.

Barry, S.J., Carr, R.M., Lane, S.J., Waterhouse, I., 2003. Use of S-pentafluorophenyl tris(2,4,6-trimethoxyphenyl)phosphonium acetate bromide and (4-hydrazino-4-oxobutyl) [tris(2,4,6-trimethoxyphenyl)phosphonium bromide for the derivatization of alcohols, aldehydes and ketones for detection by liquid chromatograp. Rapid Commun. Mass Spectrom 17 (5), 484–497. https://doi.org/10.1002/rcm.933.

Bartók, T., Szécsi, Á., Szekeres, A., Mesterházy, Á., Bartók, M., 2006. Detection of new fumonisin mycotoxins and fumonisin-like compounds by reversed-phase high-performance liquid chromatography/electrospray ionization ion trap mass spectrometry. Rapid Commun. Mass Spectrom 20 (16), 2447–2462.

Bartók, T., Tölgyesi, L., Szekeres, A., Mesterházy, Á., 2010. Detection and characterization of twenty-eight isomers of fumonisin B1 (FB1) mycotoxin in a solid rice culture infected with *Fusarium verticillioides* by reversed-phase high-performance liquid chromatography/electrospray ionization time-of-flight and ion t. Rapid Commun. Mass Spectrom 24 (1), 35–42.

Beccaccioli, M., Salustri, M., Scala, V., Reverberi, M., 2021. The effect of *Fusarium verticillioides* fumonisins on fatty acids, sphingolipids, and oxylipins in maize germlings. Int J Mol Sci 22 (5), 1–17. https://doi.org/10.3390/ijms22052435.

Beltrán, E., Ibáñez, M., Sancho, J.V., Hernandez, F., 2009. Determination of mycotoxins in different food commodities by ultra-high-pressure liquid chromatography coupled to triple quadrupole mass spectrometry. Rapid Commun. Mass Spectrom 23 (12), 1801–1809.

Bergmann, D., Hübner, F., Humpf, H.U., 2013. Stable isotope dilution analysis of small molecules with carboxylic acid functions using 18O labeling for HPLC-ESI-MS/MS: Analysis of fumonisin B1. J. Agric. Food Chem 61 (33), 7904–7908. https://doi.org/10.1021/jf4022702.

Bouhet, S., Oswald, I.P., 2007. The intestine as a possible target for fumonisin toxicity. Molr Nut Food Res 51 (8), 925–931. https://doi.org/10.1002/mnfr.200600266.

Braun, M.S., Wink, M., 2018. Exposure, Occurrence, and Chemistry of Fumonisins and their Cryptic Derivatives. Compr. Rev. Food Sci. Food Saf 17 (3), 769–791. https://doi.org/10.1111/1541-4337.12334.

Bryła, M., Renata, J., Roszko, M., and Szymczyk, K., 2013a. Application of molecularly imprinted polymers to determine B 1 , B 2 , and B 3 fumonisins in cereal products., 578–584. doi:10.1002/jssc.201200753.

Bryła, M., Roszko, M., Szymczyk, K., Jedrzejczak, R., Obiedziński, M.W., Sekul, J., 2013. Fumonisins in plant-origin food and fodder - a review. Food Addit. Contam. - Chem. Anal. Control Expo. Risk Assess 30 (9), 1626–1640. https://doi.org/10.1080/19440049.2013.809624.

Bryła, M., Waśkiewicz, A., Szymczyk, K., Jędrzejczak, R., 2017. Effects of pH and temperature on the stability of fumonisins in Maize products. Toxins 9 (3), 1–16. https://doi.org/10.3390/toxins9030088.

Bueno, D., Istamboulie, G., Muñoz, R., Marty, J.L., 2015. Determination of Mycotoxins in Food: A Review of Bioanalytical to Analytical Methods. Appl Spect Rev 50 (9), 728–774. https://doi.org/10.1080/05704928.2015.1072092.

Bullerman, L.B., Bianchini, A., 2007. Stability of mycotoxins during food processing. Int J Food Microbiol 119 (1–2), 140–146. https://doi.org/10.1016/j.ijfoodmicro.2007.07.035.

Caldas, E.D., Silva, A.C.S., 2007. Mycotoxins in corn-based food products consumed in Brazil: An exposure assessment for fumonisins. J. Agric. Food Chem 55 (19), 7974–7980. https://doi.org/10.1021/jf0712898.

Cano-Sancho, G., Ramos, A.J., Marín, S., Sanchis, V., 2012. Occurrence of fumonisins in Catalonia (Spain) and an exposure assessment of specific population groups. Food Addit. Contam. - Chem. Anal. Control Expo. Risk Assess 29 (5), 799–808. https://doi.org/10.1080/19440049.2011.644813.

Cao, X., Li, X., Li, J., Ding, H., 2018. Quantitative determination of carcinogenic mycotoxins in human and animal biological matrices and animal-derived foods using multi-mycotoxin and analyte-specific high performance liquid chromatography-tandem mass spectrometric methods. J. Chromatogr. B: Analyt Technol Biomed Life Sci 1073, 191–200. https://doi.org/10.1016/j.jchromb.2017.10.006.

Cardinael, P., Casabianca, H., Peulon-Agasse, V., Berthod, A., 2015. Sample Derivatization in Separation. Science. https://doi.org/10.1002/9783527678129.assep063.

Castells, M., Marín, S., Sanchis, V., Ramos, A.J., 2008. Distribution of fumonisins and aflatoxins in corn fractions during industrial cornflake processing. Int. J. Food Microbiol 123 (1–2), 81–87. https://doi.org/10.1016/j.ijfoodmicro.2007.12.001.

Cavaliere, C., Foglia, P., Guarino, C., Berardo, N., 2007. Mycotoxins produced by Fusarium genus in maize: determination by screening and confirmatory methods based on liquid chromatography tandem mass spectrometry. Food Chem 105 (2), 700–710. https://doi.org/10.1016/j.foodchem.2006.12.057.

Cendoya, E., Nichea, M.J., Monge, M.P., Sulyok, M., Chiacchiera, S. M., Ramirez, M.L., 2019. Fumonisin occurrence in wheat-based products from Argentina. Food Addit Contam: Part B Surveillance 12 (1), 31–37. https://doi.org/10.1080/19393210.2018.1520308.

Chauhan, R., Singh, J., Sachdev, T., Basu, T., Malhotra, B.D., 2016. Recent advances in mycotoxins detection. Biosens Bioelectron 81, 532–545. https://doi.org/10.1016/j.bios.2016.03.004.

Chen, C., Mitchell, N.J., Gratz, J., Wu, F., 2018. Exposure to aflatoxin and fumonisin in children at risk for growth impairment in rural Tanzania. Environ Int 115 (March), 29–37. https://doi.org/10.1016/j.envint.2018.03.001.

Chen, J., Wen, J., Tang, Y., Long, M., 2021. Research progress on fumonisin b1 contamination and toxicity: A review. Molecules 26 (17), 1–21. https://doi.org/10.3390/molecules26175238.

Coronel, M.B., Vicente, S., Resnik, S.L., Alzamora, S.M., Pacin, A., 2016. Fumonisins in maize and gluten meal analysed in Argentinean wet milling industrial plants by ELISA compared with HPLC-FLD method. Food Control 67, 285–291. https://doi.org/10.1016/j.foodcont.2016.02.052.

Crous, P.W., Lombard, L., Sandoval-Denis, M., Thines, M., 2021. *Fusarium*: more than a node or a foot-shaped basal cell. Studies in Mycology 98,. https://doi.org/10.1016/j.simyco.2021.100116 100116.

Cumming, R., 2022. iNaturalist Mexico. https://www.inaturalist.org/observations/134863617. Last access February 7th, 2022.

D'Arco, G., Fernández-Franzón, M., Font, G., Damiani, P., Mañes, J., 2008. Analysis of fumonisins B1, B2 and B3 in corn-based baby food by pressurized liquid extraction and liquid chromatography/tandem mass spectrometry. J. Chromatogr. A 1209 (1–2), 188–194. https://doi.org/10.1016/j.chroma.2008.09.032.

Dall'Asta, C., Galaverna, G., Aureli, G., Dossena, A., and Marchelli, R., 2008. A LC/MS/MS method for the simultaneous quantification of free and masked fumonisins in maize and maize-based products. World Mycotoxin J, 1(3), 237–246. doi:10.3920/wmj2008.x040.

Dall'Asta, C., Mangia, M., Berthiller, F., et al. 2009b. Difficulties in fumonisin determination: The issue of hidden fumonisins. Anal. Bioanal. Chem, 395(5), 1335–1345. doi:10.1007/s00216-009-2933-3.

Dall'Asta, C., Galaverna, G., Mangia, M., Sforza, S., Dossena, A., and Marchelli, R., 2009a. Free and bound fumonisins in gluten-free food products. Mol Nut Food Res, **53**(4), 492–499. doi:10.1002/mnfr.200800088.

Damiani, T., Righetti, L., Suman, M., Galaverna, G., and Dall'Asta, C., 2019. Analytical issue related to fumonisins: A matter of sample comminution? Food Control, 95, 1–5. doi:10.1016/j.foodcont.2018.07.029.

De Girolamo, A., Lattanzio, V.M.T., Schena, R., Visconti, A., Pascale, M., 2014. Use of liquid chromatography-high-resolution mass spectrometry for isolation and characterization of hydrolyzed fumonisins and relevant analysis in maize-based products. J Mass Spectrom 49 (4), 297–305. https://doi.org/10.1002/jms.3342.

de Matos, N.A.V., de Moraes, M.H.P., Sartori, A.V., and do Couto J.S., 2021. Optimization and Validation of an Analytical Method for the Determination of Free and Hidden Fumonisins in Corn and Corn Products by UHPLC-MS/MS. Food Anal Methods, 14(8), 1611–1624. doi:10.1007/s12161-021-01984-8.

de Oliveira, G.B., de Castro Gomes Vieira, C.M., Orlando, R.M., and Faria, A.F., 2017. Simultaneous determination of fumonisins B1 and B2 in different types of maize by matrix solid phase dispersion and HPLC-MS/MS. Food Chem, 233, 11–19. doi:10.1016/j.foodchem.2017.04.091.

de Smet, D., Dubruel, P., van Peteghem, C., Schacht, E., de Saeger, S., 2009. Molecularly imprinted solid-phase extraction of fumonisin B analogues in bell pepper, rice and corn flakes. Food Addit. Contam. - Chem. Anal. Control Expo. Risk Assess 26 (6), 874–884. https://doi.org/10.1080/02652030902788920.

Deepa, N., Sreenivasa, M.Y., 2017. Fumonisins: A Review on its Global Occurrence, Epidemiology, Toxicity and Detection. J. Vet. Med. Res 4 (6), 1093.

Deepa, N., Sreenivasa, M.Y., 2019. Molecular methods and key genes targeted for the detection of fumonisin producing *Fusarium verticillioides* – An updated review. Food Biosci 32, (October). https://doi.org/10.1016/j.fbio.2019.100473 100473.

Desmarchelier, A., Oberson, J.M., Tella, P., Gremaud, E., Seefelder, W., Mottier, P., 2010. Development and comparison of two multiresidue methods for the analysis of 17 mycotoxins in cereals by liquid chromatography electrospray ionization tandem mass spectrometry. J. Agric. Food Chem 58 (13), 7510–7519. https://doi.org/10.1021/jf100891m.

Desmarchelier, A., Tessiot, S., Bessaire, T., Mottier, P., 2014. Combining the quick, easy, cheap, effective, rugged and safe approach and clean-up by immunoaffinity column for the analysis of 15 mycotoxins by isotope dilution liquid chromatography tandem mass spectrometry. J. Chromatogr. A 1337, 75–84. https://doi.org/10.1016/j.chroma.2014.02.025.

Devreese, M., De Baere, S., De Backer, P., Croubels, S., 2012. Quantitative determination of several toxicological important mycotoxins in pig plasma using multi-mycotoxin and analyte-specific high performance liquid chromatography-tandem mass spectrometric methods. J. Chromatogr. A 1257, 74–80. https://doi.org/10.1016/j.chroma.2012.08.008.

di Mavungu, J.D., Monbaliu, S., Scippo, M.L., de Saeger, S., 2009. LC-MS/MS multi-analyte method for mycotoxin determination in food supplements. Food Addit. Contam. - Chem. Anal. Control Expo. Risk Assess 26 (6), 885–895. https://doi.org/10.1080/02652030902774649.

Diogo, L., 2011. iNaturalist Mexico. https://www.inaturalist.org/observations/36434139. Last access February 7th, 2022.

Dita, M., Barquero, M., Heck, D., Mizubuti, E.S.G., Staver, C.P., 2018. *Fusarium* wilt of banana: Current knowledge on epidemiology and research needs toward sustainable disease management. Front Plant Sci 871 (October), 1–21. https://doi.org/10.3389/fpls.2018.01468.

Duarte-Vogel, S., Villamil-Jiménez, L.C., 2006. Micotoxinas en la salud pública. Revista de Salud Pública 8, 129–135.

Embrenhar, 2022. iNaturalist Mexico. https://www.inaturalist.org/observations/136754985. Last access February 7th, 2022.

Europea, C., 2007. Reglamento (CE) 1126/2007 de 28 de septiembre de 2007 que modifica el Reglamento (CE) no 1881/2006 por el que se fija el contenido máximo de determinados contaminantes en los productos alimenticios por lo que se refiere a las toxinas de Fusarium en el maí. Diario Oficial de La Unión Europea L 255, 14–17.

Facorro, R., Llompart, M., Dagnac, T., 2020. Combined (d)SPE-QuEChERS Extraction of Mycotoxins in Mixed Feed Rations and Analysis by High Performance Liquid Chromatography-High-Resolution Mass Spectrometry. Toxins 12 (3), 206–225. https://doi.org/10.3390/toxins12030206.

Farhadi, A., Fakhri, Y., Kachuei, R., Vasseghian, Y., Huseyn, E., Mousavi Khaneghah, A., 2021. Prevalence and concentration of fumonisins in cereal-based foods: a global systematic review and meta-analysis study. Environ Sci Pollution Res 28 (17), 20998–21008. https://doi.org/10.1007/s11356-021-12671-w.

Flores-Flores, M.E., González-Peñas, E., 2018. Short communication: Analysis of mycotoxins in Spanish milk. J Dairy Sci 101 (1), 113–117. https://doi.org/10.3168/jds.2017-13290.

Frenich, A.G., Vidal, J.L.M., Romero-González, R., Aguilera-Luiz, M.M., 2009. Simple and high-throughput method for the multi-mycotoxin analysis in cereals and related foods by ultra-high performance liquid chromatography/tandem mass spectrometry. Food Chem 117 (4), 705–712. https://doi.org/10.1016/j.foodchem.2009.04.045.

"Fungal Infections. Fusarium Oxysporum." n.d. http://www.life-worldwide.org/fungal-diseases/fusarium-oxysporum.

"Fungal Infections. Fusarium Solani." n.d. Accessed August 26, 2021. http://www.life-worldwide.org/fungal-diseases/fusarium-solani.

Gazzotti, T., Lugoboni, B., Zironi, E., Barbarossa, A., Serraino, A., Pagliuca, G., 2009. Determination of fumonisin B1 in bovine milk by LC-MS/MS. Food Control 20 (12), 1171–1174. https://doi.org/10.1016/j.foodcont.2009.02.009.

Gazzotti, T., Zironi, E., Lugoboni, B., Barbarossa, A., Piva, A., Pagliuca, G., 2011. Analysis of fumonisins B1, B2 and their hydrolysed metabolites in pig liver by LC-MS/MS. Food Chem 125 (4), 1379–1384. https://doi.org/10.1016/j.foodchem.2010.10.009.

Gelderblom, W.C., Jaskiewicz, K., Marasas, W.F., et al, 1988. Fumonisins–novel mycotoxins with cancer-promoting activity produced by Fusarium moniliforme. App Environ Microbiol 54 (7), 1806–1811.

Ghiasian, S.A., Maghsood, A.H., Yazdanpanah, H., et al, 2006. Incidence of *Fusarium verticillioides* and levels of fumonisins in corn from main production areas in Iran. J. Agric. Food Chem 54 (16), 6118–6122. https://doi.org/10.1021/jf061248w.

Ghiasian, S.A., Aghamirian, M.R., Maghsood, A.H., Shephard, G. S., Van Der Westhuizen, L., 2009. Occurrence of fumonisins in maize imported into Iran during 2001–2002. Mycotoxin Rese 25 (1), 25–28. https://doi.org/10.1007/s12550-008-0004-9.

Gnonlonfin, G.J.B., Hell, K., Fandohan, P., Siame, A.B., 2008. Mycoflora and natural occurrence of aflatoxins and fumonisin B1 in cassava and yam chips from Benin, West Africa. Int. J. Food Microbiol 122 (1–2), 140–147. https://doi.org/10.1016/j.ijfoodmicro.2007.11.047.

Gong, L., Jiang, Y., Chen, F., 2015. Molecular strategies for detection and quantification of mycotoxin-producing *Fusarium* species: A review. J Sci Food Agricult 95 (9), 1767–1776. https://doi.org/10.1002/jsfa.6935.

Grajewski, J., Blajet-Kosicka, A., Twaruzek, M., Kosicki, R., 2012. Occurrence of mycotoxins in Polish animal feed in years 2006–2009. Journal of Animal Physiology and Animal Nutrition 96 (5), 870–877. https://doi.org/10.1111/j.1439-0396.2012.01280.x.

Headley, J., 2022. iNaturalist Mexico. https://www.inaturalist.org/observations/143416143. Last access February 7th, 2022.

Heperkan, D., Güler, F.K., Oktay, H.I., 2012. Mycoflora and natural occurrence of aflatoxin, cyclopiazonic acid, fumonisin and ochratoxin A in dried figs. Food Addit. Contam. - Chem. Anal. Control Expo. Risk Assess 29 (2), 277–286. https://doi.org/10.1080/19440049.2011.597037.

Hu, L., Liu, H., Yang, J., Chen, X., 2019. Free and hidden fumonisins in raw maize and maize-based products from China. Food Addit Contam: Part B Surveillance 12 (2), 90–96. https://doi.org/10.1080/19393210.2018.1564371.

Huang, X., Wang, S., Mao, D., Miao, S., Hu, Q., Ji, S., 2018. Optimized QuEChERS method combined with UHPLC-MS/MS for the simultaneous determination of 15 mycotoxins in liquorice. Journal of AOAC International 101 (3), 633–642. https://doi.org/10.5740/jaoacint.17-0365.

Humpf, H.U., Voss, K.A., 2004. Effects of thermal food processing on the chemical structure and toxicity of fumonisin mycotoxins. Mol Nut Food Res 48 (4), 255–269. https://doi.org/10.1002/mnfr.200400033.

Jackson, L.S., Hlywka, J.J., Senthil, K.R., Bullerman, L.B., Musser, S.M., 1996. Effects of time, temperature, and pH on the stability of fumonisin B1 in an aqueous model system. J. Agric. Food Chem 44 (3), 906–912. https://doi.org/10.1021/jf950364o.

Jerome Jeyakumar, J.M., Zhang, M., Thiruvengadam, M., 2018. Determination of mycotoxins by HPLC, LC-ESI-MS/MS, and MALDI-TOF MS in *Fusarium* species-infected sugarcane. Microbial Pathogenesis 123, 98–110. https://doi.org/10.1016/j.micpath.2018.06.045.

Jia, W., Chu, X., Ling, Y., Huang, J., Chang, J., 2014. Multi-mycotoxin analysis in dairy products by liquid chromatography coupled to quadrupole orbitrap mass spectrometry. J. Chromatogr. A 1345, 107–114. https://doi.org/10.1016/j.chroma.2014.04.021.

Kamle, M., Mahato, D.K., Devi, S., Lee, K.E., Kang, S.G., Kumar, P., 2019. Fumonisins: Impact on agriculture, food, and human

health and their management strategies. Toxins 11 (6), 1–23. https://doi.org/10.3390/toxins11060328.

Kawashima, L.M., Vieira, A.P., Valente Soares, L.M., 2007. Fumonisin B1 and ochratoxin A in beers made in Brazil. Ciencia E Tecnologia de Alimentos 27 (2), 317–323. https://doi.org/10.1590/S0101-20612007000200019.

Khayoon, W.S., Saad, B., Salleh, B., Ismail, N.A., Manaf, N.H.A., Latiff, A.A., 2010. A reversed phase high performance liquid chromatography method for the determination of fumonisins B1 and B2 in food and feed using monolithic column and positive confirmation by liquid chromatography/tandem mass spectrometry. Anal Chimica Acta 679 (1–2), 91–97. https://doi.org/10.1016/j.aca.2010.09.008.

Kou, D., Mitra, S., 2003. Extraction of Semivolatile Organic Compounds from Solid Matrices. Sample Preparation Techniques in Analytical Chem 139–182. https://doi.org/10.1002/0471457817.ch3.

Lattanzio, V.M.T., Solfrizzo, M., Powers, S., Visconti, A., 2007. Simultaneous determination of aflatoxins, ochratoxin A and *Fusarium* toxins in maize by liquid chromatography/tandem mass spectrometry after multitoxin immunoaffinity cleanup. Rapid Commun. Mass Spectrom 21 (20), 3253–3261.

Lawrence, J.F., Niedzwiadek, B., Scott, P.M., 2000. Effect of temperature and solvent composition on extraction of fumonisins B1 and B2 from corn products. J AOAC Int 83 (3), 604–611.

Liao, C.D., Wong, J.W., Zhang, K., Hayward, D.G., Lee, N.S., Trucksess, M.W., 2013. Multi-mycotoxin analysis of finished grain and nut products using high-performance liquid chromatography-triple-quadrupole mass spectrometry. J. Agric. Food Chem 61 (20), 4771–4782. https://doi.org/10.1021/jf4000677.

Lin, H., Zhang, Y.W., Zheng, L.H., Li, Y.X., 2011. Anthracene and Anthraquinone Derivatives from the Stem Bark of Juglans mandshurica Maxim. Helv. Chim. Acta 94, 1488.

Liu, Y., Jiang, Y., Li, R., Pang, M., Liu, Y., Dong, J., 2017. Natural occurrence of fumonisins B1 and B2 in maize from eight provinces of China in 2014. Food Addit Contam: Part B Surveillance 10 (2), 113–117. https://doi.org/10.1080/19393210.2017.1280541.

Lockett, D., 2022. iNaturalist Mexico. https://www.inaturalist.org/observations/147363346. Last access February 7th, 2022.

Lucci, P., Castro-ríos, R., and Núñez, O., 2015. State-of-the-art in the analysis of fumosinins by liquid chromatography-mass spectrometry in: Evans C.M. (Eds.) Fumonisins: Natural Occurrence, Management Practices and Health Concerns, 116p, ISBN: 978-1-63482-789-8.

Majdinasab, M., Aissa, S.B., Marty, J.L., 2021. Advances in colorimetric strategies for mycotoxins detection: Toward rapid industrial monitoring. Toxins 13 (1), 13–47. https://doi.org/10.3390/toxins13010013.

Marasas, W.F.O., 2001. Discovery and occurrence of the fumonisins: A historical perspective. Environ Health Persp 109 (suppl. 2), 239–243. https://doi.org/10.1289/ehp.01109s2239.

Marschik, S., Hepperle, J., Lauber, U., Schwab-Bohnert, G., 2013. Extracting fumonisins from maize: Efficiency of different extraction solvents in multi-mycotoxin analytics. Mycotoxin Res 29 (2), 119–129. https://doi.org/10.1007/s12550-013-0163-1.

Martins, H.M.L., Almeida, I.F.M., Camacho, C.R.L., Santos, S.M.O., Costa, J.M.G., Bernardo, F.M.A., 2012. Occurrence of fumonisins in feed for swine and horses. Revista Iberoamericana de Micologia 29 (3), 175–177. https://doi.org/10.1016/j.riam.2011.07.005.

Maymon, M., Sela, N., Shpatz, U., Galpaz, N., Freeman, S., 2020. The origin and current situation of *Fusarium oxysporum* f. sp. cubense tropical race 4 in Israel and the Middle East. Scientific Rep 10 (1), 1–11. https://doi.org/10.1038/s41598-020-58378-9.

Miró-Abella, E., Herrero, P., Canela, N., et al, 2017. Determination of mycotoxins in plant-based beverages using QuEChERS and liquid chromatography–tandem mass spectrometry. Food Chem 229, 366–372. https://doi.org/10.1016/j.foodchem.2017.02.078.

Mirón-Mérida, V.A., Gong, Y.Y., Goycoolea, F.M., 2021. Aptamer-based detection of fumonisin B1: A critical review. Anal Chimica Acta 1160. https://doi.org/10.1016/j.aca.2021.338395.

Monbaliu, S., Van Poucke, C., Van Peteghem, C., Van Poucke, K., Heungens, K., De Saeger, S., 2009. Development of a multi-mycotoxin liquid chromatography/tandem mass spectrometry method for sweet pepper analysis. Rapid Commun. Mass Spectrom 23 (1), 3–11.

Muscarella, M., Magro, S.L., Nardiello, D., Palermo, C., Centonze, D., 2008. Development of a new analytical method for the determination of fumonisins B1 and B2 in food products based on high performance liquid chromatography and fluorimetric detection with post-column derivatization. J. Chromatogr. A 1203 (1), 88–93. https://doi.org/10.1016/j.chroma.2008.07.034.

Nakagawa, H., Hashimoto, R., Matsuo, Y., Sago, Y., Yokoyama, K., Takahashi, H., 2020. Detection and Determination of Fumonisins B1, B2, and B3 Contaminating Japanese Domestic Wine by Liquid Chromatography Coupled to Tandem Mass Spectrometry (LC–MS/MS). Curr Microbiol 77 (10), 3057–3064. https://doi.org/10.1007/s00284-020-02113-0.

Nawaz, M.A.H., Rauf, S., Hayat, A., Catanante, G., Raza, R., Marty, J.L., 2017. Determination of Mycotoxins in Food. In: Wong, Y.C., Lewis, R.J. (Eds.), . In: Analysis of Food Toxins and Toxicants, 2 Volume Set, 139. John Wiley & Sons, Ltd, pp. 137–168. Online ISBN:9781118992685.

Ndube, N., Van Der Westhuizen, L., Shephard, G.S., 2009. Determination of fumonisins in maize by HPLC with ultraviolet detection of o-phthaldialdehyde derivatives. Mycotoxin Res 25 (4), 225–228. https://doi.org/10.1007/s12550-009-0031-1.

Ndube, N., van der Westhuizen, L., Green, I.R., Shephard, G.S., 2011. HPLC determination of fumonisin mycotoxins in maize: A comparative study of naphthalene-2,3-dicarboxaldehyde and o-phthaldialdehyde derivatization reagents for fluorescence and diode array detection. *J. Chromatogr. B: Analyt Technol Biomed.* Life Sci 879 (23), 2239–2243. https://doi.org/10.1016/j.jchromb.2011.06.007.

Nualkaw, K., Poapolathep, S., Zhang, Z., Poapolathep, A., 2020. Simultaneous determination of multiple mycotoxins in swine, poultry and dairy feeds using ultra high performance liquid chromatography-tandem mass spectrometry. Toxins 12 (4), 1–18. https://doi.org/10.3390/toxins12040253.

O'Brien-Coker, I.C., Perkins, G., Mallet, A.I., 2001. Aldehyde analysis by high performance liquid chromatography/tandem mass spectrometry. Rapid Commun. Mass Spectrom 15 (12), 920–928. https://doi.org/10.1002/rcm.324.

Ogretmen, B., Avenue, A., 2018. Sphingolipid metabolism in cancer signalling and therapy. Nature Reviews Cancer 18 (1), 33–50. https://doi.org/10.1038/nrc.2017.96.Sphingolipid.

Oliveira, M., Vasconcelos, V., 2020. Occurrence of mycotoxins in fish feed and its effects: A review. Toxins 12 (3). https://doi.org/10.3390/toxins12030160.

Osteresch, B., Viegas, S., Cramer, B., Humpf, H.U., 2017. Multi-mycotoxin analysis using dried blood spots and dried serum spots. Anal. Bioanal. Chem 409 (13), 3369–3382. https://doi.org/10.1007/s00216-017-0279-9.

Oueslati, S., Romero-González, R., Lasram, S., Frenich, A.G., Vidal, J.L.M., 2012. Multi-mycotoxin determination in cereals and derived products marketed in Tunisia using ultra-high performance liquid chromatography coupled to triple quadrupole mass spectrometry. Food Chem. Toxicol 50 (7), 2376–2381. https://doi.org/10.1016/j.fct.2012.04.036.

Paepens, C., De Saeger, S., Van Poucke, C., Dumoulin, F., Van Calenbergh, S., Peteghem, C.V., 2005. Development of a liquid chromatography / tandem mass spectrometry method for the quantification of fumonisin B1, B2 and B3 in cornflakes. Rapid Commun. Mass Spectrom. 19, 2021–2029. https://doi.org/10.1002/rcm.2022.

Pagliuca, G., Zironi, E., Ceccolini, A., Matera, R., Serrazanetti, G.P., Piva, A., 2005. Simple method for the simultaneous isolation and determination of fumonisin B1 and its metabolite aminopentol-1 in swine liver by liquid chromatography-fluorescence detection. *J. Chromatogr. B: Analyt Technol Biomed.* Life Sci 819 (1), 97–103. https://doi.org/10.1016/j.jchromb.2005.01.035.

Panel, E.C., 2015. Opinion of the Scientific Panel on Contaminants in Food Chain on a request from the Commission related to fumonisins as undesirable substances in animal feed. EFSA J 235, 1–32.

Park, J.W., Kim, E.K., Shon, D.H., Kim, Y.B., 2002. Natural co-occurrence of aflatoxin B1, fumonisin B1 and ochratoxin A in barley and corn foods from Korea. Food Addit Contam 19 (11), 1073–1080. https://doi.org/10.1080/02652030210151840.

Pasquali, M., Beyer, M., Logrieco, A., Vogelgsang, S., 2016. A European database of *Fusarium graminearum* and *F. culmorum* trichothecene genotypes. Front Microbiol 7 (apr), 1–11. https://doi.org/10.3389/fmicb.2016.00406.

Patel, S., Hazel, C., and Shah, I., 2011. Report Number : c03061 investigation of the loss of parent fumonisin mycotoxins during food processing. (March), 1–96. https://old.food.gov.uk/sites/default/files/C03061.pdf (accessed 8 Feb 2023).

Pereira, V.L., Fernandes, J.O., Cunha, S.C., 2014. Mycotoxins in cereals and related foodstuffs: A review on occurrence and recent methods of analysis. Trends Food Sci. Technol 36 (2), 96–136. https://doi.org/10.1016/j.tifs.2014.01.005.

Pérez-Ortega, P., Gilbert-López, B., García-Reyes, J.F., Ramos-Martos, N., Molina-Díaz, A., 2012. Generic sample treatment method for simultaneous determination of multiclass pesticides and mycotoxins in wines by liquid chromatography-mass spectrometry. J. Chromatogr. A 1249, 32–40. https://doi.org/10.1016/j.chroma.2012.06.020.

Piacentini, K.C., Rocha, L.O., Fontes, L.C., Carnielli, L., Reis, T.A., Corrêa, B., 2017. Mycotoxin analysis of industrial beers from Brazil: The influence of fumonisin B1 and deoxynivalenol in beer quality. Food Chem 218, 64–69. https://doi.org/10.1016/j.foodchem.2016.09.062.

Pizzutti, I.R., De Kok, A., Scholten, J., Da Silva, R.C., 2014. Development, optimization and validation of a multimethod for the determination of 36 mycotoxins in wines by liquid chromatography-tandem mass spectrometry. Talanta 129, 352–363. https://doi.org/10.1016/j.talanta.2014.05.017.

Ponce-García, N., Serna-Saldivar, S.O., Garcia-Lara, S., 2018. Fumonisins and their analogues in contaminated corn and its processed foods – A review. Food Addit. Contam. - Chem. Anal. Control Expo. Risk Assess 35 (11), 2183–2203. https://doi.org/10.1080/19440049.2018.1502476.

Qi, B.L., Liu, P., Wang, Q.Y., Cai, W.J., Yuan, B.F., Feng, Y.Q., 2014. Derivatization for liquid chromatography-mass spectrometry. TrAC - Trends Anal Chem 59, 121–132. https://doi.org/10.1016/j.trac.2014.03.013.

Qian, M., Yang, H., Li, Z., Xu, J., 2018. Detection of 13 mycotoxins in feed using modified QuEChERS with dispersive magnetic materials and UHPLC–MS/MS. J Separation Sci 41 (3), 756–764. https://doi.org/10.1002/jssc.201700882.

Ramalho, R.R.F., Pereira, I., da S. Lima, G., et al., 2022. Fumonisin B1 analysis in maize by Molecularly Imprinted Polymer Paper Spray Ionization Mass Spectrometry (MIP-PSI-MS). J Food Compost Anal, 107, 104362. doi:https://doi.org/10.1016/j.jfca.2021.104362.

Ramírez-Cisneros, M.Á., Rivera, V., Rios, M.Y., Vargas-De-León, C., Dávila, S., and Peralta, R., 2020. Hydrolyzed FB1 (aminopentol) detection on urine of HPV positive Mexican women: A preliminary study. 08 March 2021, PREPRINT (Version 2) available at Research Square (https://doi.org/10.21203/rs.3.rs-68390/v2).

Rausch, A.K., Brockmeyer, R., Schwerdtle, T., 2020. Development and Validation of a QuEChERS-Based Liquid Chromatography Tandem Mass Spectrometry Multi-Method for the Determination of 38 Native and Modified Mycotoxins in Cereals. J. Agric. Food Chem 68 (16), 4657–4669. https://doi.org/10.1021/acs.jafc.9b07491.

Rausch, A.K., Brockmeyer, R., Schwerdtle, T., 2021. Development and validation of a liquid chromatography tandem mass spectrometry multi-method for the determination of 41 free and modified mycotoxins in beer. Food Chem 338,. https://doi.org/10.1016/j.foodchem.2020.127801 127801.

Ren, Y., Zhang, Y., Han, S., Han, Z., Wu, Y., 2011. Simultaneous determination of fumonisins B1, B2 and B3 contaminants in maize by ultra high-performance liquid chromatography tandem mass spectrometry. Analytica Chimica Acta 692 (1–2), 138–145. https://doi.org/10.1016/j.aca.2011.03.005.

Requena, F., Saume, E., León, A., 2005. Mycotoxins: Risks and prevention. Zootecnia Tropical 23 (4), 393–410.

Ridgway, K., 2012. Sample Preparation for Food Contaminant Analysis. LC GC Europe 25, 1–8.

Romero-González, R., Vidal, J.L.M., Aguilera-Luiz, M.M., Frenich, A.G., 2009. Application of conventional solid-phase extraction for multimycotoxin analysis in beers by ultrahigh-performance liquid chromatography-tandem mass spectrometry. J. Agric. Food Chem 57 (20), 9385–9392. https://doi.org/10.1021/jf903154a.

Rubert, J., Mañes, J., James, K.J., Soler, C., 2011. Application of hybrid linear ion trap-high resolution mass spectrometry to the analysis of mycotoxins in beer. Food Addit. Contam. - Chem. Anal. Control Expo. Risk Assess 28 (10), 1438–1446. https://doi.org/10.1080/19440049.2011.595015.

Santa, T., Al-Dirbashi, O.Y., Yoshikado, T., Fukushima, T., Imai, K., 2009. Synthesis of benzofurazan derivatization reagents for short chain carboxylic acids in liquid chromatography/electrospray ionization-tandem mass spectrometry (LC/ESI-MS/MS). Biomed Chromatog 23 (4), 443–446. https://doi.org/10.1002/bmc.1124.

Šarkanj, B., Ezekiel, C.N., Turner, P.C., Warth, B., 2018. Ultra-sensitive, stable isotope assisted quantification of multiple urinary mycotoxin exposure biomarkers. Anal Chim Acta 1019, 84–92. https://doi.org/10.1016/j.aca.2018.02.036.

Saunders, D.S., Meredith, F.I., Voss, K.A., 2001. Control of fumonisin: Effects of processing. Environ. Health Perspect 109 (suppl. 2), 333–336. https://doi.org/10.1289/ehp.01109s2333.

Schelstraete, W., Devreese, M., Croubels, S., 2020. Comparative toxicokinetics of *Fusarium* mycotoxins in pigs and humans. Food Chem. Toxicol 137 (October 2019), 111140–111153. https://doi.org/10.1016/j.fct.2020.111140.

Scott, P.M., 1993. Fumonisins. Int J Food Microbiol 18 (4), 257–270. https://doi.org/10.1016/0168-1605(93)90149-B.

Seefelder, W., Gossmann, M., Humpf, H.U., 2002. Analysis of Fumonisin B1 in *Fusarium* proliferatum-infected asparagus spears and garlic bulbs from Germany by liquid chromatography-electrospray ionization mass spectrometry. J. Agric. Food Chem 50 (10), 2778–2781. https://doi.org/10.1021/jf0115037.

Selim, M.I., El-sharkawy, S.H., Popendorf, W.J., 1996. Supercritical Fluid Extraction of *Fumonisin* B1 from Grain Dust. J. Agric. Food Chem 44 (10), 3224–3229. https://doi.org/10.1021/jf940468j.

Shar, Z.H., Shar, H.H., Jatoi, A., Phanwar, Q.K., 2020. Natural co-occurrence of *Fusarium* toxins in poultry feed and its ingredients. Journal Fur Verbraucherschutz Und Lebensmittelsicherheit 15 (4), 341–350. https://doi.org/10.1007/s00003-020-01292-z.

Shephard, G.S., Thiel, P.G., Sydenham, E.W., Alberts, J.F., Gelderblom, W.C.A., 1992. Fate of a single dose of the 14C-labelled mycotoxin, fumonisin B1, in rats. Toxicon 30 (7), 768–770. https://doi.org/10.1016/0041-0101(92)90011-S.

Shier, W.T., 2000. The fumonisin paradox: a review of research on oral bioavailability of fumonisin B1, a mycotoxin produced by *Fusarium moniliforme*. J Toxicol: Toxin Reviews 19 (2), 161–187.

Silva, A.S., Brites, C., Pouca, A.V., Barbosa, J., Freitas, A., 2019. UHPLC-ToF-MS method for determination of multi-mycotoxins in maize: Development and validation. Curr Res Food Sci 1, 1–7. https://doi.org/10.1016/j.crfs.2019.07.001.

Silva, L., Fernández-Franzón, M., Font, G., Mañes, J., 2009. Analysis of fumonisins in corn-based food by liquid chromatography with fluorescence and mass spectrometry detectors. Food Chem 112 (4), 1031–1037. https://doi.org/10.1016/j.foodchem.2008.06.080.

Silva, L.J.G., Lino, C.M., Pena, A., Moltó, J.C., 2007. Occurrence of fumonisins B1 and B2 in Portuguese maize and maize-based foods intended for human consumption. Food Addit Contam 24 (4), 381–390. https://doi.org/10.1080/02652030601003811.

Silva, L.J.G., Pena, A., Lino, C.M., Fernández, M.F., Mañes, J., 2010. Fumonisins determination in urine by LC-MS-MS. Anal. Bioanal. Chem 396 (2), 809–816. https://doi.org/10.1007/s00216-009-3231-9.

Škrbić, B., Živančev, J., Godula, M., 2014. Multimycotoxin analysis of crude extracts of nuts with ultra-high performance liquid chromatography/tandem mass spectrometry. J Food Compost Anal 34 (2), 171–177.

Smith, L.L., Francis, K.A., Johnson, J.T., Gaskill, C.L., 2017. Quantitation of fumonisin B1 and B2 in feed using FMOC pre-column derivatization with HPLC and fluorescence detection. Food Chem 234, 174–179. https://doi.org/10.1016/j.foodchem.2017.04.142.

Sokolovic, M., 2022. HPLC and ELISA Methods for Detection and Quantification of Fumonisins in Naturally Contaminated Maize., Research Square, PREPRINT available at Research Square (https:// doi: 10.21203/rs.3.rs-1908427/v1).

Soleimany, F., Jinap, S., Abas, F., 2012. Determination of mycotoxins in cereals by liquid chromatography tandem mass spectrometry. Food Chem 130 (4), 1055–1060. https://doi.org/10.1016/j.foodchem.2011.07.131.

Song, S., Ediage, E.N., Wu, A., De Saeger, S., 2013. Development and application of salting-out assisted liquid/liquid extraction for multi-mycotoxin biomarkers analysis in pig urine with high performance liquid chromatography/tandem mass spectrometry. J. Chromatogr. A 1292, 111–120. https://doi.org/10.1016/j.chroma.2012.10.071.

Sørensen, L.M., Mogensen, J., Nielsen, K.F., 2010. Simultaneous determination of ochratoxin A, mycophenolic acid and fumonisin B2 in meat products. Anal. Bioanal. Chem 398 (3), 1535–1542. https://doi.org/10.1007/s00216-010-4059-z.

Soriano del Castillo, J.M., 2007. Micotoxinas en alimentos, Ediciones Díaz de Santos. ISBN: 978-84-7978-808-7.

Spanjer, M.C., Rensen, P.M., Scholten, J.M., 2008. LC–MS/MS multi-method for mycotoxins after single extraction, with validation data for peanut, pistachio, wheat, maize, cornflakes, raisins and figs. Food Addit. Contam. - Chem. Anal. Control Expo. Risk Assess 25 (4), 472–489. https://doi.org/10.1080/02652030701552964.

Stępień, Ł., Koczyk, G., Waśkiewicz, A., 2011. Genetic and phenotypic variation of Fusarium proliferatum isolates from different host species. J App Gen 487–496. https://doi.org/10.1007/s13353-011-0059-8.

Stockmann-Juvala, H., Savolainen, K., 2008. A review of the toxic effects and mechanisms of action of fumonisin B 1. Hum Exp Toxicol 27 (11), 799–809. https://doi.org/10.1177/0960327108099525.

Sultan, Y., Magan, N., Medina, A., 2022. Efficacy of different c18 hplc analytical columns in the analysis of fumonisins b1 and b2 in different matrices. Biointerface Res. Appl. Chem 12 (2), 1721–1734. https://doi.org/10.33263/BRIAC122.17211734.

Tamura, M., Takahashi, A., Uyama, A., Mochizuki, N., 2012. A method for multiple mycotoxin analysis in wines by solid phase extraction and multifunctional cartridge purification, and ultra-high-performance liquid chromatography coupled to tandem mass spectrometry. Toxins 4 (6), 476–486. https://doi.org/10.3390/toxins4060476.

Tamzura, M., Uyama, A., Mochizuki, N., 2011. Development of a multi-mycotoxin analysis in beer-based drinks by a modified quechers method and ultra-high-performance liquid chromatography coupled with tandem mass spectrometry. Anal Sci 27 (6), 629–635. https://doi.org/10.2116/analsci.27.629.

Tapia, C., Amaro, J., 2014. Género *Fusarium*. Rev Chilena Infectol 31 (1), 85–86. https://doi.org/10.4067/S0716-10182014000100012.

Tardieu, D., Auby, A., Bluteau, C., Bailly, J.D., Guerre, P., 2008. Determination of Fumonisin B1 in animal tissues with immunoaffinity purification. J. Chromatogr. B: Analyt Technol Biomed Life Sci 870 (1), 140–144. https://doi.org/10.1016/j.jchromb.2008.05.046.

Taylor, P., and Scott, P.M., 2012. Food Additives & Contaminants: Part A - Recent research on fumonisins : a review., (May 2015), 37–41.

Tonti, S., Mandrioli, M., Nipoti, P., Pisi, A., Toschi, T.G., Prodi, A., 2017. Detection of Fumonisins in Fresh and Dehydrated Commercial Garlic. J. Agric. Food Chem 65 (32), 7000–7005. https://doi.org/10.1021/acs.jafc.7b02758.

Toro, S., 2022. iNaturalist Mexico. https://www.inaturalist.org/observations/134863617. Last access February 7th, 2022.

Turner, N.W., Subrahmanyam, S., Piletsky, S.A., 2009. Analytical methods for determination of mycotoxins: A review. Anal Chim Acta 632 (2), 168–180. https://doi.org/10.1016/j.aca.2008.11.010.

Vaclavikova, M., Macmahon, S., Zhang, K., Begley, T.H., 2013. Application of single immunoaffinity clean-up for simultaneous determination of regulated mycotoxins in cereals and nuts. Talanta 117, 345–351. https://doi.org/10.1016/j.talanta.2013.09.007.

Van Der Westhuizen, L., Shephard, G.S., Gelderblom, W.C.A., Torres, O., Riley, R.T., 2013. Fumonisin biomarkers in maize eaters and implications for human disease. World Mycotoxin 6 (3), 223–232. https://doi.org/10.3920/WMJ2013.1589.

Vanhoenacker, G., Dumont, E., David, F., Baker, A., Sandra, P., 2009. Determination of arylamines and aminopyridines in pharmaceutical products using in-situ derivatization and liquid chromatography–mass spectrometry. J. Chromatogr. A 1216 (16), 3563–3570. https://doi.org/10.1016/j.chroma.2008.08.102.

Velázquez, C., Llovera, M., Plana, J., Canela, R., 2000. Effect of solvents on the fumonisins analysis by high-performance liquid chromatography with AccQ.Fluor as the derivatizing reagent. J. Chromatogr. A 870 (1–2), 469–472. https://doi.org/10.1016/S0021-9673(99)00908-5.

Vichi, S., Cortés-Francisco, N., Caixach, J., 2013. Determination of volatile thiols in lipid matrix by simultaneous derivatization/extraction and liquid chromatography–high resolution mass spectrometric analysis. Application to virgin olive oil. J. Chromatogr. A 1318, 180–188. https://doi.org/10.1016/j.chroma.2013.10.015.

Voss, K.A., Riley, R.T., Gardner, N.M., 2017. Fumonisins. *Reprod Dev Toxicol* 1, 925–943. https://doi.org/10.1016/B978-0-12-804239-7.00047-0.

Wall-Martínez, H.A., Ramírez-Martínez, A., Wesolek, N., Roudot, A.C., 2019. Risk assessment of exposure to mycotoxins (aflatoxins and fumonisins) through corn tortilla intake in Veracruz City (Mexico). Food Addit. Contam. - Chem. Anal. Control Expo. Risk Assess 36 (6), 929–939. https://doi.org/10.1080/19440049.2019.1588997.

Wan Norhasima, W.M., Abdulamir, A.S., Abu Bakar, F., Son, R., Norhafniza, A., 2009. The health and toxic adverse effects of *Fusarium* fungal mycotoxin, fumonisins, on human population. Am. J. Infect. Dis 5 (4), 280–288. https://doi.org/10.3844/ajidsp.2009.273.281.

Wang, S., Quan, Y., Lee, N., Kennedy, I.R., 2006. Rapid determination of fumonisin B1 in food samples by enzyme-linked immunosorbent assay and colloidal gold immunoassay. J. Agric. Food Chem 54 (7), 2491–2495. https://doi.org/10.1021/jf0530401.

Wang, Y., Xiao, C., Guo, J., Yue, T., 2013. Development and application of a method for the analysis of 9 mycotoxins in maize by HPLC-MS/MS. J. Food Sci. 78 (11), 1752–1756. https://doi.org/10.1111/1750-3841.12187.

Wang, W., Zhang, Q., Ma, F., Li, P., 2022. Simultaneous determination of aflatoxins, fumonisin B1, T-2 and cyclopiazonic acid in agri-products by immunomagnetic solid-phase extraction coupled with UHPLC-MS/MS. Food Chem 378,. https://doi.org/10.1016/j.foodchem.2021.132020 132020.

Wang, J., Zhou, Y., Wang, Q., 2008. Analysis of mycotoxin fumonisins in corn products by high-performance liquid chromatography coupled with evaporative light scattering detection. Food Chem 107 (2), 970–976. https://doi.org/10.1016/j.foodchem.2007.09.001.

Weiying, W., Weiwei, Z., Shunli, H., et al. 2022. Determination of fumonisins in edible vegetable oil by MIL-101(Cr) based dispersive solid phase microextraction combined with high performance liquid chromatography tandem mass spectrometry., 11, 133–143.

WHO-Department of Food Safety and Zoonoses (2018) Fumonisins. Retrieved February 28, 2021, from https://www.who.int/food-safety/FSDigest_Fumonisins_EN.pdf.

Wilkowska, A., Biziuk, M., 2011. Determination of pesticide residues in food matrices using the QuEChERS methodology. Food Chem 125 (3), 803–812. https://doi.org/10.1016/j.foodchem.2010.09.094.

Williams, J.H., Grubb, J.A., Davis, J.W., Robinson, A.G., 2010. HIV and hepatocellular and esophageal carcinomas related to consumption of mycotoxin-prone foods in sub-Saharan Africa. Am. J. Clin. Nutr 92 (1), 154–160.

Xie, L., Wu, Y., Wang, Y., Li, T., 2021. Fumonisin B1 induced aggressiveness and infection mechanism of *Fusarium proliferatum* on banana fruit. Environ. Pollut 288,. https://doi.org/10.1016/j.envpol.2021.117793 117793.

Yazar, S., Omurtag, G.Z., 2008. Fumonisins, trichothecenes and zearalenone in cereals. Int J Mol Sci 9 (11), 2062–2090. https://doi.org/10.3390/ijms9112062.

Yibadatihan, S., Jinap, S., Mahyudin, N.A., 2014. Simultaneous determination of multi-mycotoxins in palm kernel cake (PKC) using liquid chromatography-tandem mass spectrometry (LC-MS/MS). *Food Addit*. Contam. - Chem. Anal. Control Expo. Risk Assess 31 (12), 2071–2079. https://doi.org/10.1080/19440049.2014.978396.

Zhang, B., Chen, X., Han, S.Y., Zhu, X., 2018. Simultaneous analysis of 20 mycotoxins in grapes and wines from Hexi Corridor region (China): Based on a QuEChERS–UHPLC–MS/MS method. Molecules 23 (8). https://doi.org/10.3390/molecules23081926.

Zhang, L., Liu, S., Cui, X., Pan, C., Zhang, A., Chen, F., 2012. A review of sample preparation methods for the pesticide residue analysis in foods. Cent Eur J Chem 10 (3), 900–925. https://doi.org/10.2478/s11532-012-0034-1.

Zhang, K., Wong, J.W., Hayward, D.G., Vaclavikova, M., Liao, C. D., Trucksess, M.W., 2013. Determination of mycotoxins in milk-based products and infant formula using stable isotope dilution assay and liquid chromatography tandem mass spectrometry. J. Agric. Food Chem 61 (26), 6265–6273. https://doi.org/10.1021/jf4018838.

Zhang, S., Zhou, S., Yu, S., Zhao, Y., Wu, Y., Wu, A., 2022. LC-MS/MS Analysis of Fumonisin B1, B2, B3, and Their Hydrolyzed Metabolites in Broiler Chicken Feed and Excreta. Toxins 14 (2), 1–10. https://doi.org/10.3390/toxins14020131.

Zitomer, N.C., Glenn, A.E., Bacon, C.W., Riley, R.T., 2008. A single extraction method for the analysis by liquid chromatography/tandem mass spectrometry of fumonisins and biomarkers of disrupted sphingolipid metabolism in tissues of maize seedlings. Anal. Bioanal. Chem 391 (6), 2257–2263. https://doi.org/10.1007/s00216-008-2166-x.

Zöllner, P., Mayer-Helm, B., 2006. Trace mycotoxin analysis in complex biological and food matrices by liquid chromatography-atmospheric pressure ionisation mass spectrometry. J. Chromatogr. A 1136 (2), 123–169. https://doi.org/10.1016/j.chroma.2006.09.055.