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Original Article

Rapid and sensitive UHPLC-MS/MS methods for dietary sample analysis of 43 mycotoxins in China total diet study

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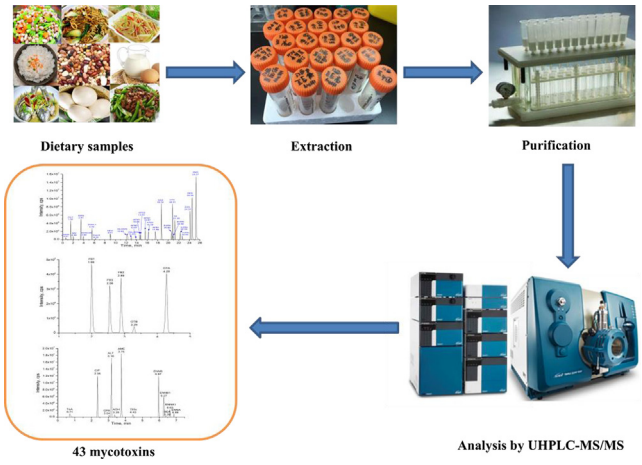
HIGHLIGHTS

- A strategy comprising three UHPLC-MS/MS methods was developed for measuring 43 mycotoxins.
- Method validation was evaluated for all 43 mycotoxins in 12 complex food matrices.
- The methods were applied for 72 dietary samples collected from the sixth China total diet study.
- The most detected mycotoxins were DON, SMC, FB1, ZEN, BEA, ENNB1, and ENNB.
- The 43 mycotoxins were accurately investigated in a total diet study for the first time.

GRAPHICAL ABSTRACT



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ABSTRACT

Introduction: Mycotoxins are toxic metabolites produced by fungi that commonly contaminate foods. As recommended by the World Health Organization, total diet study (TDS) is the most efficient and effective way to estimate the dietary intakes of certain chemical substances for general populations. It requires sensitive and reliable analytical methods applicable to a wide range of complex food matrices and ready-to-eat dishes.

Objectives: A novel strategy with high selectivity and sensitivity, incorporating three methods based on ultra-high-performance liquid chromatography coupled with tandem mass spectrometry (UHPLC-MS/MS), was designed for measuring 43 mycotoxins in dietary samples in a China TDS.

Methods: The 43 mycotoxins were divided into 3 groups for analysis to achieve better performance. For each group, an UHPLC-MS/MS method was developed to determine the target compounds after clean-up by solid phase extraction. A total of 21 isotope internal standards were employed for accurate quantitation. Method validation in terms of linearity, selectivity, sensitivity, accuracy, and precision was performed for all the 43 mycotoxins in 12 complex food matrices.

Results: The limits of detection (LODs) and limits of quantitation (LOQs) were 0.002–1 ng mL^{-1} and 0.006–3 ng mL^{-1}, respectively. The method recoveries of the 43 mycotoxins spiked in 12 food categories were in the range of 60.3%–175.9% after internal standard correction, with relative standard deviations (RSDs) below 13.9%. For practical application, this method was utilized for 72 dietary samples collected

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from 6 provinces in the 6th China TDS. More than 80% of the samples were found contaminated by mycotoxins. DON, SMC, FB_1, ZEN, BEA, $ENNB_1$, and ENNB were most detected.
Conclusions: The proposed methods with high sensitivity, accuracy, and robustness provide powerful tools for multi-mycotoxin monitoring and dietary exposure assessment, allowing 43 mycotoxins, including some emerging mycotoxins, to be accurately investigated in a total diet study for the first time.

Introduction

Mycotoxins represent toxic secondary metabolic products synthesized by filamentous fungal species. They are naturally occurring and widely found in various food types. Plant-based foods can be directly infested by the mycotoxin producing fungi. Other food products may become contaminated because of carry-over from feeds or raw materials. The general population is primarily exposed to common mycotoxins through their diet [1,2]. Consumption of mycotoxin-contaminated foods may lead to acute or chronic effects, such as cytotoxicity and immunosuppression, as well as hepatic, gastrointestinal, and carcinogenic diseases [3,4]. The World Health Organization (WHO) has described mycotoxins as one of the major causes of foodborne illnesses that pose a potential threat to animal and human health [5].

A total diet study (TDS) is jointly recommended by the WHO, the Food and Agriculture Organization (FAO), and the European Food Safety Authority (EFSA) as the most efficient and cost-effective method for evaluating dietary intakes of certain chemical compounds for population groups through cooked and ready-to-eat diets, [5,6]. Incorporating the impact of cooking and preparation on less stable chemicals and on the formation of new ones, a TDS gives a more accurate estimation of dietary exposure. The analytical methods required to conduct a TDS must meet high requirements not only for sensitivity and reliability, but also for the practical applicability to a wide range of complex food matrices and ready-to-eat dishes.

Mycotoxins have been investigated in several TDSs conducted around the world, such as the French TDS (21 mycotoxins) [7–9], Netherlands TDS (37 mycotoxins) [10–12], Spanish TDS (18 mycotoxins) [3], Lebanese TDS (4 mycotoxins) [13], Canada TDS (1 mycotoxin) [14], Australia New Zealand TDS (11 mycotoxins) [15], Vietnam TDS (3 mycotoxins) [16], Ireland TDS (16 mycotoxins) [17], Regional Sub-Saharan Africa TDS (14 mycotoxins) [18,19] and Hong Kong TDS (13 mycotoxins) [20]. A variety of analytical methods have been employed in TDSs, among which the LC-MS/MS technique is increasingly applied as a highly selective and a sensitive tool for multi-mycotoxin analysis in complex food matrices.

China has successfully conducted five TDSs since 1990 [21,22]. The 6th China TDS (2016–2020) was further expanded to 24 provinces, representing the dietary habits of multiple geographical regions and covering most of the population (greater than2/3). In the 6th China TDS, daily consumed foods were classified into 13 categories: cereals and their products, legumes and their products, potatoes and their products, meats and their products, eggs and their products, aquatic foods, milk and dairy products, vegetables and their products, fruits and their products, sugar, water and beverages, alcohols, and condiments (including cooking oils). Cooking oil and condiments were put into the other 12 categories during the preparation and cooking of TDS samples, which further complicated the chemical compositions versus raw products, requiring an advanced analytical method.

The present study developed a sensitive, accurate, and robust strategy for detecting 43 mycotoxins, i.e. aflatoxin B_1 (AFB_1), aflatoxin B_2 (AFB_2), aflatoxin G_1 (AFG_1), aflatoxin G_2 (AFG_2), aflatoxin M_1 (AFM_1), aflatoxin M_2 (AFM_2), ochratoxin A (OTA), ochratoxin B (OTB), deoxynivalenol (DON), nivalenol (NIV), 3-acetyl-deoxynivalenol (3A-DON), 15-acetyldeoxynivalenol (15A-DON), fusarenon-X (Fus X), 3-glucose-deoxynivalenol (DON-3-G), deepoxy-deoxynivalenol (DOM-1), HT2 toxin, T2 toxin, 4,15-diacetoxyscirpenol (DAS), neosolaniol (NEO), sterigmatocystin (SMC), citrinin (CIT), cyclopiazonic acid (CPA), moniliformin (MON), zearelenone (ZEN), zearalenone (ZAN), α-zearalenol (α-ZOL), β-zearalenol (β-ZOL), α-zearalanol (α-ZAL), β-zearalanol (β-ZAL), fumonisin B_1 (FB_1), fumonisin B_2 (FB_2), fumonisin B_3 (FB_3), patulin (PAT), beauvericin (BEA), enniatin A (ENNA), enniatin A1 ($ENNA_1$), enniatin B (ENNB), enniatin B1 ($ENNB_1$), tenuazonic acid (TeA) alternariol (AOH), altenuene (ALT), alternariol monomethyl ether (AME), and tentoxin (TEN), in all 12 food categories from the 6th China TDS by isotope dilution UHPLC/MS/MS. Considering the diversity of their physicochemical properties, the 43 mycotoxins were classified into three groups, with specific sample preparations and instrumental conditions for each group, to achieve the best performance. The methods were validated in terms of linearity, specificity, accuracy, LOD, LOQ, and intra- and inter-day variability, and then practically used to test 72 samples covering all 12 food categories. This versatile multi-mycotoxin and multi-matrix strategy with high sensitivity and broad applicability enables 43 mycotoxins, including *Alternaria* toxins and emerging toxins, to be included in a TDS for the first time and serves as a potent tool that will help monitor mycotoxins and assess dietary exposure.

Materials and methods

Chemicals and materials

LCMS-grade acetonitrile, methanol, ammonia acetate, formic acid, ammonia water, ammonium hydrogen carbonate and ammonium dihydrogen phosphate were commercially obtained from Fisher Scientific (USA). Mycotoxin standards for AFB_1, AFB_2, AFG_1, AFG_2, AFM_1, AFM_2, HT2, T2, 3A-DON, 15A-DON, FB_1, FB_2, FB_3, OTA, OTB, AOH, AME, TeA, BEA, TEN, ALT, MON, DON, NIV, Fus X, ZEN, ZAN, α-ZOL, β-ZOL, α-ZAL, β-ZAL, PAT, DON-3-G, DOM-1, NEO, DAS, SMC, CIT, and CPA were obtained from Biopure (Austria). ENNs ($ENNA_1$, ENNA, $ENNB_1$, and ENNB) were supplied by PriboLab (Singapore). A total of 21 labeled internal standards were utilized, with ^{13}C-DON, ^{13}C-3-ADON, ^{13}C-NIV, ^{13}C-AFB_1, ^{13}C-AFB_2, ^{13}C-AFG_1, ^{13}C-AFG_2, ^{13}C-AFM_1, ^{13}C-ZEN, ^{13}C-T2, ^{13}C-HT2, ^{13}C-PAT, ^{13}C-DAS, ^{13}C-SMC, ^{13}C-FB_1, ^{13}C-FB_2, ^{13}C-FB_3, ^{13}C-OTA, and ^{13}C-CIT provided by Biopure, ^{13}C-TeA supplied by Fluka (USA), and TEN-d_3 obtained from TRC (Canada). Ultrapure water was obtained on a Milli-Q system (Millipore, USA). The MycoSep 226 Aflazon+ multifunctional cartridge and MultiSep 211 Fum column were supplied by Romer Labs (Austria). The Oasis HLB SPE column (200 mg, 6 mL) was purchased from Waters (USA).

Preparation of standard solution

The choice of mycotoxin concentration is based on their sensitivity on the instrument and initial concentrations in commercial

standard solutions. The mixed standard solution A contained 5 μg mL^{-1} of MON, PAT, ZEN, NIV, Fus X, DON, 3A-DON, 15A-DON, T2, and HT2; 2.5 μg mL^{-1} of NEO, DAS, DON-3-G, and DOM-1; 0.5 μg mL^{-1} of ZAN, α-ZOL, α-ZAL, β-ZOL, β-ZAL, and SMC; 0.1 μg mL^{-1} of AFB_1 and AFG_1; 0.025 μg mL^{-1} of AFB_2, AFM_1, AFM_2, and AFG_2. The mixed internal standard solution A contained 25 ng mL^{-1} of ^{13}C-AFB_1, ^{13}C-AFB_2, ^{13}C-AFG_1, ^{13}C-AFG_2, and ^{13}C-AFM_1; 50 ng mL^{-1} of ^{13}C-T2; 0.5 μg mL^{-1} of ^{13}C-HT2, ^{13}C-DON, ^{13}C-3-ADON, ^{13}C-NIV, ^{13}C-PAT, ^{13}C-DAS, and ^{13}C-SMC; 0.15 μg mL^{-1} of ^{13}C-ZEN.

The mixed standard solution B contained 2.5 μg mL^{-1} of FB_1, FB_2, and FB_3 along with 0.5 μg mL^{-1} of OTA and OTB. The mixed internal standard solution B contained 0.5 μg mL^{-1} of ^{13}C-FB_3 and ^{13}C-OTA along with 0.25 μg mL^{-1} of ^{13}C-FB_1 and ^{13}C-FB_2.

The mixed standard solution C contained 5 μg mL^{-1} of *Alternaria* Toxins, CPA and CIT along with 0.5 μg mL^{-1} of ENNs and BEA. The mixed internal standard solution C contained 25 ng mL^{-1} of ^{13}C-AFB_2 and 0.5 μg mL^{-1} of ^{13}C-TeA and TEN-d_3.

Stock solutions A and C were prepared in acetonitrile, and stock solution B was prepared in acetonitrile–water (1:1, v/v). All the solutions were stored at −40 °C in the dark and diluted with the initial solvents for UHPLC-MS/MS analysis.

Food samples

In total, 72 dietary samples in the 12 categories were collected from six provinces (Hebei, Beijing, Jilin, Hubei, Guangdong, and Guizhou) in the 6th China TDS. Food sampling was designed similar to previous China TDSs [21,22]. The 12 types of dietary samples were clustered in accordance with the local dietary recipes and consumption of local residents. After cooking, the prepared food was mixed to form a provincial composite sample for each food category. All samples were transferred to the laboratory as soon as possible through the cold chain and stored at −20 °C prior to analysis. The 72 samples were only used for method development and pre-screening purposes. The result is not sufficient to present the contamination level of studied mycotoxins in China.

Sample preparation

The 43 mycotoxins were assigned to 3 groups for detection. Group A included 26 mycotoxins (AFB_1, AFB_2, AFG_1, AFG_2, AFM_1, AFM_2, HT2, T2, 3A-DON, 15A-DON, MON, DON, NIV, Fus X ,ZEN, ZAN, α-ZEL, β-ZEL, α-ZAL, β-ZAL, PAT, DON-3-G, DOM-1, NEO, DAS, and SMC). Group B included 5 mycotoxins (FB_1, FB_2, FB_3, OTA, and OTB). Group C included 12 mycotoxins (AOH, AME, TeA, ALT, TEN, BEA, $ENNA_1$, ENNA, $ENNB_1$, ENNB, CIT, and CPA).

Group A. Homogenized food samples of exactly 2 g (2 mL of water or beverage) in a 50-mL centrifuge tube were added to 40 μL of mixed isotope internal standard A (^{13}C-AFB_1, ^{13}C-AFB_2, ^{13}C-AFG_1, ^{13}C-AFG_2, ^{13}C-AFM_1, ^{13}C-T2, ^{13}C-HT2, ^{13}C-DON, ^{13}C-3-ADON, ^{13}C-NIV, ^{13}C-PAT, ^{13}C-DAS, ^{13}C-SMC, and ^{13}C-ZEN) and 9 mL of extraction solution (acetonitrile/water solution; 84:16, v/v). The mixture was incubated at room temperature for 0.5 h, ultrasonicated for 0.5 h, and centrifuged at 9000 rpm for 10 min. The supernatant was then obtained for purification.

Exactly 5 mL of the supernatant was purified by passing through a MycoSep 226 Aflazon+ multifunctional cartridge. Then additional 3 mL of acetonitrile solution (acetonitrile/water; 84:16 v/v) was added to the cartridge to push out the remaining sample solution. All the effluent was collected, nitrogen-dried at 40 °C, and reconstituted in 1 mL of acetonitrile/0.2% formic acid in water (1:9 v/v). After vortex mixing for 30 s, the solution underwent centrifugation at 20000 rpm for 30 min for sample injection.

Group B. Food samples of exactly 2 g (2 mL of water or beverage) in a 50-mL centrifuge tube were added to 40 μL of mixed isotope internal standard B (^{13}C-FB_1, ^{13}C-FB_2, ^{13}C-FB_3, and ^{13}C-OTA) and 10 mL extraction solution (acetonitrile/water; 1:1 v/v), shaken for 1 h at room temperature, and centrifuged at 9000 rpm for 10 min. Precisely, 5 mL of the resulting supernatant was adjusted to pH 6–9 with 0.1 mol L^{-1} NaOH solution, and added to 10 mL methanol/water (3:1 v/v).

The resulting mixture was allowed to pass through a MultiSep 211 Fum cartridge, which was subsequently washed with 10 mL methanol/water (3:1 v/v) to remove interfering compounds. After drying the cartridge, the analytes were eluted with 10 mL 0.1% formic acid methanol, nitrogen-dried at 40 °C, and reconstituted in 1 mL acetonitrile/0.2% formic acid in water (1:4 v/v). After vortex mixing for 30 s, the solution was centrifuged at 20000 rpm for 30 min prior to analysis.

Group C. Sample preparation of group C was the same as described in our previous publication [23]. Briefly, food samples of 2 g (2 mL of water or beverage) in a 50-mL centrifuge tube were added to 40 μL of mixed isotope internal standard C (^{13}C-TeA, TEN-d_3, and ^{13}C-AFB_2) and 9 mL extraction solution (acetonitrile/methanol/water; 45:10:45 v/v/v, pH 3.0 NaH_2PO_4), incubated for 0.5 h at room temperature, ultrasonicated for 0.5 h, and centrifuged at 9000 rpm for 10 min. Then, 5 mL of the resulting supernatant was added to 15 mL of 0.05 mol L^{-1} phosphate buffer (pH 3). After vortexing for 30 s, the supernatant was obtained for purification.

The resulting mixture was loaded onto an Oasis HLB SPE column that had been preconditioned with 5 mL of methanol/acetonitrile (1:1 v/v) followed by 5 mL of phosphate buffer (0.05 mol L^{-1}, pH 3). The cartridge was then washed with 5 mL of methanol/water solution (1:4 v/v) and eluted with 5 mL each of methanol and acetonitrile. The eluate was nitrogen-dried at 40 °C, and reconstituted in 1 mL acetonitrile /water (1:9 v/v). After vortexing for 30 s, the solution underwent centrifugation (20000 rpm, 30 min) for sample injection.

UHPLC-MS/MS

UHPLC-MS/MS analysis was performed on an Exion LC AD™ System (SCIEX, USA) coupled with a Triple Quad 6500+ mass spectrometer (SCIEX, USA). The Analyst®1.6.3 and MultiQuant™3.0.2 were utilized for instrument operation and data processing.

Group A. The 26 major mycotoxins were separated on a CORTECS™ UPLC® C18 Column (2.1 × 100 mm, 1.6 μm, Waters). Water (A) and methanol/acetonitrile (1:1 v/v) (B) were used as the eluent with the following gradient: 5% B (initial), 5%–11% B (1–3 min), 11% B (3–12 min), 11%–28% B (12–12.1 min), 28% B (12.1–17 min), 28%–42% B (17–19 min), 42%–48% B (19–26 min), 48%–100 % B (26–27 min), 100% B (27–30 min), 100%–5% B (30–30.1 min), and 5% B (30.1–32 min). The flow rate was 0.4 mL/min. The column temperature was kept at 50 °C, and 5 μL of each sample was injected for analysis.

The MS/MS parameters in multi-reaction monitoring (MRM) mode under positive or negative ionization were optimized for each analyte as listed in Table 1. Other settings were as follows: ion spray voltages, −4500 V and +5500 V, respectively; source temperature, 550 °C; curtain gas, 20 psi; sheath gas, 50 psi; drying gas, 40 psi; collision gas (nitrogen), medium.

Group B. Chromatographic separation of FBs (B_1, B_2, and B_3) and OTs (OTA and OTB) was performed on a CORTECS™ UPLC® C18 Column (2.1 × 100 mm, 1.6 μm, Waters) with a mobile phase consisting of 0.1% formic acid (A) and acetonitrile (B) at a flow rate of 0.4 mL/min. The following elution gradient was applied: 30% B (initial), 30%–45% B (0–2 min), 45%–55% B (2–5 min), 55%–100%

Table 1
MS/MS parameters on the precursor, quantification and confirmation daughter ion, declustering potential, and collision energy of 43 mycotoxins in the MRM mode.

Analyte	Precursor	Quantification ion	DP/CE[a]	Confirmation ion	DP/CE[a]
15A-DON	337.1(-H)	150.1	−20/−20	277.1	−20/−12
3A-DON	339.1(+H)	137.1	60/15	231.1	60/20
AFB_1	313.1(+H)	240.9	120/55	284.9	120/28
AFB_2	315.0(+H)	287.1	120/40	259.2	120/38
AFG_1	329.1(+H)	311.1	125/33	243.3	125/38
AFG_2	331.0(+H)	245.0	120/44	257.0	120/42
AFM_1	329.2(+H)	259.1	135/35	273.2	135/32
AFM_2	331.0(+H)	257.0	120/42	245.0	120/44
ALT	292.9(+H)	275.1	30/13	257.0	30/25
AME	270.9(-H)	256.0	−110/−29	228.0	−110/−39
AOH	258.8(+H)	185.1	150/43	213.0	150/37
BEA	784.5(+H)	244.2	220/38	262.3	220/34
CIT	250.9(+H)	232.8	50/40	205.1	50/37
CPA	334.9(-H)	140.0	−120/−36	180.1	−120/−37
DAS	384.2(+$NH4^+$)	307.1	20/15	247.1	20/20
DOM-1	281.1(+H)	233.0	30/20	109.0	30/17
DON	297.1(+H)	231.0	40/20	249.0	40/15
DON-3-G	297.1(-$C_6H_{11}O_6$)	231.0	40/20	249.0	40/15
ENNA	682.3(+H)	210.0	220/34	228.2	220/37
$ENNA_1$	668.2(+H)	210.0	200/32	228.2	200/33
ENNB	640.3(+H)	196.4	180/34	214.2	180/33
$ENNB_1$	654.4(+H)	196.0	180/33	214.1	180/35
FB_1	722.3(+H)	704.2	40/41	334.3	40/55
FB_2	707.2(+H)	689.3	50/40	337.4	50/52
FB_3	707.2(+H)	337.3	50/50	355.3	50/46
Fus X	353.4(-H)	262.9	−50/−15	204.6	−50/−18
HT2	447.1(+Na)	345.0	100/25	285.1	100/28
MON	97.0(-Na)	40.8	−40/−21	–	–
NEO	400.1(+$NH4^+$)	305.1	30/17	215.2	30/23
NIV	311.2(-H)	281.0	−20/−20	205.0	−20/−13
OTA	404.1(+H)	239.1	50/34	358.1	50/20
OTB	371.1(+H)	205.9	40/31	188.1	40/35
PAT	152.8(-H)	109.0	−60/−12	81.0	−60/−16
SMC	325.1(+H)	310.0	120/35	280.9	120/52
T2	489.1(+Na)	387.2	150/30	245.1	150/36
TeA	196.2(-H)	139.0	−50/−28	112.2	−50/−34
TEN	415.3(+H)	312.2	120/29	301.9	120/19
ZAN	319.3(-H)	275.0	−130/−25	205.0	−130/−28
ZEN	317.2(-H)	175.1	−140/−40	131.3	−140/35
α-ZAL	321.2(-H)	277.0	−150/−30	303.2	−150/−30
α-ZOL	319.3(-H)	274.9	−135/−30	160.0	−135/−39
β-ZAL	321.2(-H)	277.3	−155/−30	303.1	−155/−30
β-ZOL	319.2(-H)	275.3	−150/−25	159.8	−150/−40
^{13}C-AFB_1	330.3(+H)	301.2	115/31	255.2	115/57
^{13}C-AFB_2	332.0(+H)	303.2	100/38	273.1	100/45
^{13}C-AFG_1	346.3(+H)	328.2	70/30	257.1	70/40
^{13}C-AFG_2	348.2(+H)	330.2	55/39	259.3	55/45
^{13}C-AFM_1	346.1(+H)	288.1	100/32	273.0	100/30
^{13}C-CIT	264.2(+H)	246.2	60/24	217.1	60/38
^{13}C-3A-DON	356.3(+H)	245.2	60/15	145.2	60/45
^{13}C-DAS	403.2(+$NH4^+$)	244.3	30/23	213.2	30/24
^{13}C-DON	312.2(+H)	263.2	60/17	245.1	60/15
^{13}C-FB_1	756.3 (+H)	738.5	50/56	356.4	50/43
^{13}C-FB_2	740.4 (+H)	358.4	50/53	722.4	50/42
^{13}C-FB_3	740.4 (+H)	358.3	75/53	376.4	75/47
^{13}C-HT2	469.3(+Na)	362.2	120/29	300.3	120/26
^{13}C-NIV	326.1(-H)	295.1	−67/−15	183.2	−67/−45
^{13}C-OTA	424.1 (+H)	250.0	50/34	377.3	50/20
^{13}C-PAT	160.1(-H)	115.0	−160/−13	86.2	−160/−15
^{13}C-SMC	343.3(+H)	297.2	100/35	327.0	100/50
^{13}C-T2	513.1(+Na)	406.3	163/33	334.2	163/32
^{13}C-TeA	198.2(-H)	141.0	−50/−28	114.0	−50/−36
^{13}C-ZEN	335.0(-H)	185.2	−150/−30	140.0	−150/−35
TEN-d_3	418.2(+H)	314.9	140/30	305.4	140/19

[a] DP, declustering potential (V); CE, collision energy (eV).

B (5–6 min), 100% B (6–8 min), 100%–30% B (8–8.1 min), and 30% B (8.1–10 min). The column temperature was kept at 50 °C, and the injection volume was 5 μL.

The analytes were detected in positive MRM mode with parameters shown in Table 1. Other settings were as follows: ion spray voltage, +5500 V; source temperature, 550 °C; curtain gas, 25 psi; sheath gas, 55 psi; drying gas, 65 psi; collision gas (nitrogen) medium.

Group C. Chromatographic separation of the 12 mycotoxins in group C was carried out with a CORTECS™ UPLC® C18 Column (2.1 × 100 mm, 1.6 μm, Waters) as reported in our previous paper

[23]. The eluent was composed of 0.01% aqueous ammonia with 5 mmol L^{-1} ammonium acetate (A) and acetonitrile (B). The gradient elution was performed as follows: 10% B (0–1 min), 10%–35% B (1–4 min), 35%–76% B (4–6 min), 76% B (6–7.5 min), 76%–100% B (7.5–8 min), 100% B (8–10 min), 100%–10% B (10–10.1 min), and 10% B (10.1–12 min). The flow rate was set at 0.4 mL min^{-1}. The column temperature was kept at 50 °C, and 5 μL of each sample was injected for analysis.

The MS/MS parameters in multi-reaction monitoring (MRM) mode under positive or negative ionization were optimized for each analyte as listed in Table 1. Other settings were as follows: ion spray voltages of −4500 V and +5500 V, respectively; source temperature, 450 °C; curtain gas, 20 psi; sheath gas, 60 psi; drying gas 55 psi; collision gas (nitrogen), medium.

Method validation

Method validation was carried out following Commission Decision 2002/657/EC [24], EMEA [25], and FDA [26] guidelines. Validation parameters included selectivity, carry-over, linearity, accuracy (method recovery, R_M), precision (intra- and inter-day variabilities), and sensitivity (LOD and LOQ).

The selectivity of the method was investigated by comparing the chromatograms of 12 distinct blank food samples with samples spiked with a mixture of analytes. The carry-over was carried out by injecting blank samples after injection of a high concentration calibration standard; residues were not greater than the respective analyte LODs.

The LOD and LOQ of each analyte were evaluated using both the standard solution and spiked blank samples in low amounts. Signal-to-noise (S/N) ratios for LOD and LOQ were above 3 and 10, respectively. Calibration standard curves of analytes were prepared using internal standard method and 1/x weighted linear regression with at least six concentration points for each analyte, assessed by calculating the regression coefficient (R^2).

Apparent recovery (R_A) and matrix effects (M_E) were assessed using three sets of calibration curves without correction by internal standards. The values were determined as described below [23,27]:

$$M_E(\%) = B/A \times 100\%,$$

$$R_A(\%) = C/A \times 100\%,$$

where A represents the slope of a calibration curve prepared in neat solvent; B represents the slope of a matrix-matched calibration curve prepared by spiking blank samples after sample preparation; and C represents the slope of a matrix-matched calibration curve prepared by spiking blank samples before sample preparation.

The accuracy and precision of the method were evaluated by recovery experiments. R_M was investigated by spiking low, medium, and high concentrations of mycotoxin standards into 12 blank dietary matrices, which were corrected by internal standards. Method precision, expressed as intra-day and inter-day RSDs, was calculated using data from three different days in six replicates.

Results and discussion

This study aimed to develop a set of three methods for measuring 43 mycotoxins in 12 food categories with acceptable recoveries. This method combination can detect multiple mycotoxins with distinct characteristics in various food matrices. Applying the same sample preparation and analysis method to study all compounds is challenging because of the diverse and complex set of molecules that could potentially be found in ultra-trace amounts in dietary samples. Therefore, the 43 mycotoxins were divided into three groups for analysis.

MS/MS condition optimization

Optimization of MS/MS conditions was performed by direct infusion of individual standard of each analyte. Ionization mode, ion spray voltage, declustering potential (DP), curtain gas, source temperature, sheath gas, and drying gas were optimized stepwise to obtain the highest signal intensity of the precursor ion. ESI in negative and positive modes with ion pray voltages of −4.5 kV and +5.5 kV, respectively, were chosen. The collision energy (CE), a major factor that affects MRM transition, was optimized individually for each analyte to achieve the most sensitive and stable product ions. Two different MRM transitions per analyte were selected and optimized, except for MON. MON as a small molecule (molecular weight of 98 Da) yielded only one strong product ion. Thus, only one MRM transition (m/z 97 to m/z 41) can be programmed, as has been done in previous studies [28,29]. The MRM transitions together with their corresponding DP and CE are presented in Table 1.

Chromatographic separation

The main factors affecting chromatographic separation were assessed, including UPLC column, eluent, additives (e.g., formic acid, ammonium acetate, acetic acid, and ammonium hydroxide), elution gradient, flow rate, and column temperature. A CORTECS™ UPLC® C18 column (2.1 mm × 100 mm, 1.6 μm, Waters) was selected based on its performance in achieving good resolution and peak morphology for the analytes within a short runtime.

Mobile phase composition (organic modifier and additives) was evaluated to obtain higher sensitivity and separation efficiency for the analytes. As shown in Fig. 1a, the peak areas of the 26 mycotoxins are differently affected by the mobile phase composition. Aflatoxins had similar peak areas in acid, neutral and alkaline conditions. For T2, HT2, SMC, and DAS, the peak areas slightly increased in 0.1% formic acid, but dropped significantly in 0.1% aqueous ammonia. For DON, ZEN and their derivatives, the peak areas decreased apparently in both the acid and alkaline media. Therefore, mobile phase without any additives was chosen for group A.

The organic modifier (methanol or acetonitrile) in the mobile phase markedly affected chromatographic separation of analytes in group A. When a single organic modifier was used, adequate separation was hardly achieved for AFM_1 and AFM_2, ZAN and α-ZEL, and 3A-DON and 15A-DON, due to the high similarity of their structures and properties. Particularly, 3A-DON and 15A-DON as positional isomers presented a common precursor ion (m/z 337) and similar product ions. Complete separation was necessary to avoid peak overlapping and achieve accurate quantification of the two compounds. Different proportions of methanol and acetonitrile were tested for their separation efficiencies. By selecting methanol/acetonitrile (1:1 v/v) as the organic mobile phase, the satisfactory separation of the 26 mycotoxins in group A was achieved. Meanwhile, the isocratic elution at 11% B (3–12 min) and 28% (12.1–17 min), and a mild gradient elution program of 42–48% B (19–26 min) were essential to give optimal separation for DON derivatives, aflatoxins, and ZEN derivatives, respectively. MON and PAT are highly polar molecules having low interaction with the hydrophobic C18 column. Therefore, a gradient elution started from 95% water was applied to get acceptable retention of MON and PAT. A representative chromatogram of a standard mixture is shown in Fig. 2a.

For group B, formic acid greatly enhanced the sensitivity of ochratoxins and fumonisins (Table 1b), because it generates highly

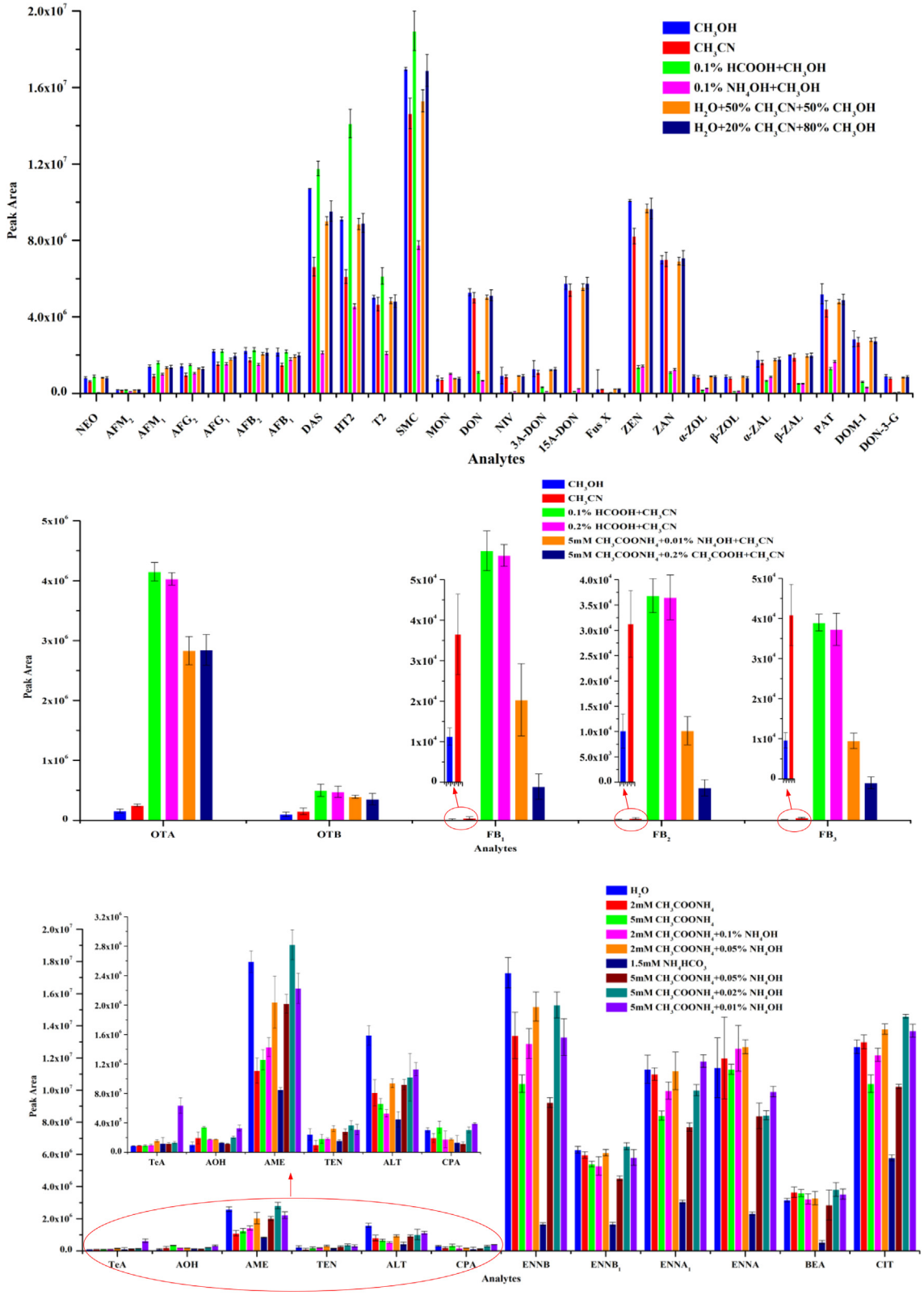

Fig. 1. Evaluation of the effects of additives in the mobile phase on the peak areas for (a) 26 analytes of group A, (b) 5 analytes of group B and (c) 12 analytes of group C (n = 3), with MON, PAT, ZEN, NIV, Fus X, DON, 3A-DON, 15A-DON, T2, HT2, CIT, CPA, TeA, AME, AOH, ALT, and TEN at 100 ng mL^{-1}; NEO, DAS, DON-3-G, DOM-1, and FBs at 50 ng mL^{-1}; ZAN, α-ZOL, α-ZAL, β-ZOL, β-ZAL, SMC, OTA, OTB, ENNs, and BEA at 10 ng mL^{-1}; AFB_1 and AFG_1 at 2 ng mL^{-1}; AFB_2, AFM_1, AFM_2, and AFG_2 at 0.5 ng mL^{-1}. Abbreviations: HCOOH, formic acid; CH_3COOH, acetic acid; CH_3COONH_4, ammonium acetate; NH_4OH, ammonia water solution; CH_3CN, acetonitrile; CH_3OH, methanol.

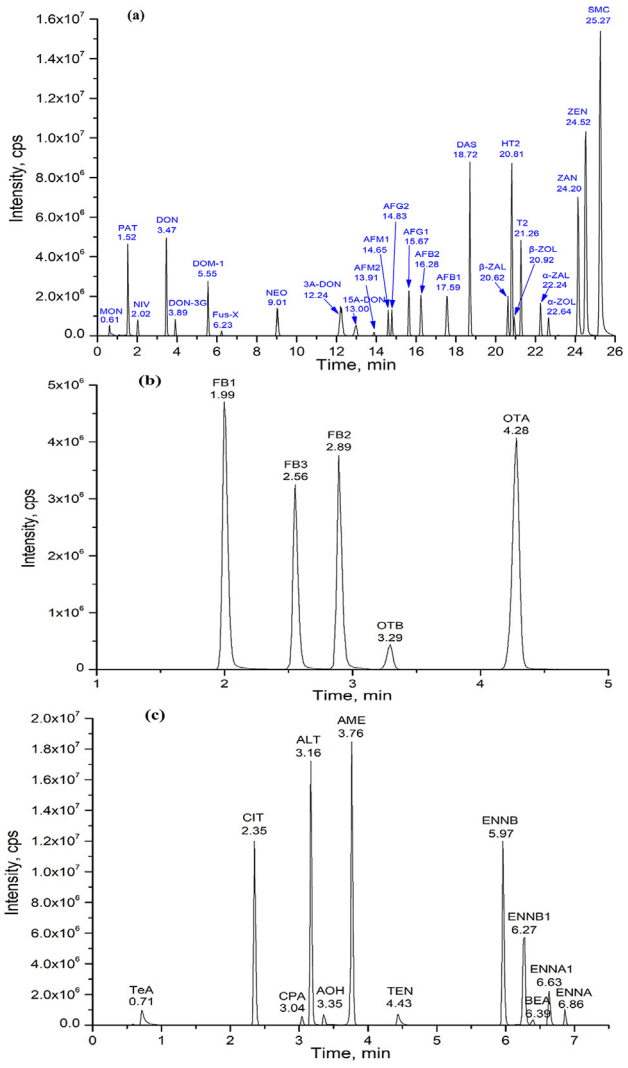

Fig. 2. Extracted ion chromatograms of UPLC separation of the 43 mycotoxins. (a) 26 analytes of group A, (b) 5 analytes of group B, (c) 12 analytes of group C. The concentration of each analyte is the same as in Fig. 1.

abundant hydrogen ions to assist positive ionization. Fortunately, the peak shapes of fumonisins were also improved in an acidic mobile phase. Acetonitrile was preferred as the organic modifier, due to the reduced background signals and higher elution ability compared with methanol. The complete separation of the 5 mycotoxins could be easily achieved with a mobile phase consisting of 0.1% formic acid (A) and acetonitrile (B) under a gradient elution (Fig. 2b).

Methods for detecting emerging mycotoxins, including *Alternaria* toxins, enniatins, and BEA have been optimized in our previous work [23]. Based on our study, inappropriate pH of the mobile phase and the use of methanol instead of acetonitrile can cause two peaks for TeA and peak splitting for AOH and ALT. Ammonia acetate as a modifier can result in the best peak shapes. In addition, additives in the mobile phase significantly affected the sensitivity of *Alternaria* toxins (Fig. 1c). Ultimately, 0.01% aqueous ammonia with 5 mmol L^{-1} ammonium acetate (solvent A) and acetonitrile (solvent B) were used as the mobile phase, which markedly enhanced the signals of TeA and AOH [23]. In addition, although CIT and CPA showed tailing peaks under neutral and acidic conditions, sharp peaks and good separation were obtained using the same chromatographic conditions as the emerging mycotoxins (Fig. 2c). Consequently, CIT and CPA were assigned to the group C.

Different column temperatures were tested, including 30, 40, and 50 °C. With the increase in column temperature, the analysis time decreased, and the separation efficiency and peak shape were improved. Therefore, 50 °C was selected for further experiments.

Different flow rates were also tested. No significant difference in sensitivity was observed when the flow rates were 0.3 mL min^{-1} and 0.4 mL min^{-1}. Further increase in flow rate caused high back-pressure. Therefore, a flow rate of 0.4 mL min^{-1} was selected, as the separation could be completed in a shorter time.

The sensitivity of the compounds increased with the increase of injection volume from 1 to 5 μL. Greater volume caused peak broadening because of sample dispersion and column saturation.

Sample preparation

Extraction and cleanup are critical steps in separating multi-mycotoxins, notably in complex food matrices, which comprise proteins, fats, pigments and carbohydrates with very different compositions.

The optimal extraction solvents were selected also according to the solubility of mycotoxins and the solvent recommended by the manufacturer of the cartridges. Water, methanol, acetonitrile, and their combinations were tested, and typical extraction solvents in the literature were also considered. For the 26 mycotoxins in group A, 84:16 (v/v) acetonitrile aqueous solution was the optimal extraction solvent. It has been widely used for the extraction of trichothecenes [30,31], zearalenone and its metabolites [32], and multi-mycotoxins [33]. Moreover, Malone et al. studied the extraction efficiency for mycotoxins in naturally contaminated commodities in detail [34], concluding that acetonitrile/water (84:16) was the most efficient solvent for aflatoxins extraction, and that 50%–80% organic solvent had similar efficiencies for extractions of OTA and fumonisins. Acetonitrile/methanol/water (45:10:45 v/v/v) was the optimal extraction solvent for emerging mycotoxins, and was also used to extract *Alternaria* toxins from vegetables [35,36]. To improve the recoveries of compounds possessing carboxyl groups, such as TeA and CPA, pH 3.0 NaH_2PO_4 was added to an acetonitrile/methanol/water (45:10:45 v/v/v) solution as the extraction solvent.

Solid-phase extraction (SPE) are commonly employed for reducing the matrix effect and obtaining a satisfactory recovery. Four cartridges, including MycoSep 226, MultiSep 211 Fum, Oasis HLB, and Oasis C_{18}, were assessed using the mixed standard solution of target compounds. MycoSep and MultiSep cartridges represent multi-functional columns comprising adsorbents specifically designed for mycotoxin purification. Fig. 3 depicts the recoveries by using various cartridges for 43 compounds.

The MycoSep 226 AflaZon+ cartridge used in this study is a one-step clean-up cartridge that retain interfering substances from complex samples and let target compounds through. According to the operating instructions, sample extract in acetonitrile/water (84:16) can be directly loaded onto the cartridge without any pre-conditioning before use. It is quite convenient for mycotoxin determination. After evaluation, 26 mycotoxins (group A) were found to have good recoveries using this cartridge.

Ochratoxins and fumonisins contain carboxyl groups, with strong water solubility and sensitivity to pH changes. Therefore, the clean-up of these toxins is mainly based on ion-exchange mechanism. MultiSep 211 Fum cartridge packed with mixed sorbent materials including ion-exchange resin exhibits strong retention of these compounds. According to the operating instructions, the loading buffer was Methanol/Water (3:1, pH 6–9). Under this condition, ochratoxins and fumonisins existed in ionic form and could be well retained in the cartridge. A wash step with the same

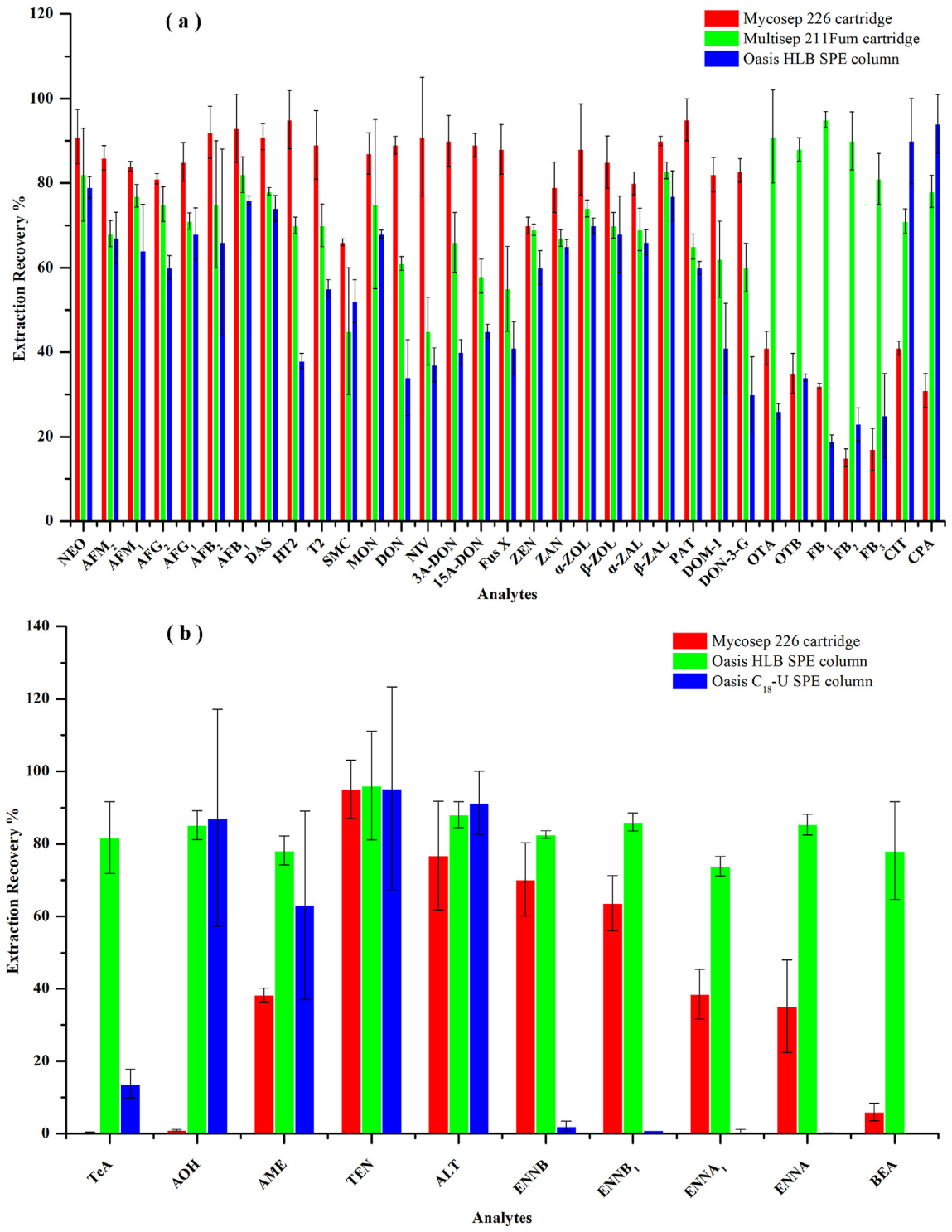

Fig. 3. Recovery by using Mycosep226 cartridge, Multisep 211Fum cartridge, Oasis HLB SPE column for 43 mycotoxins (n = 3). The concentration of each analyte is the same as in Fig. 1.

buffer (Methanol/Water, 3:1) was applied to remove sample matrices and interferences. Methanol containing 0.1% formic acid was used as eluting solvent. Under the acidic condition, these toxins changed into neutral form and thereby could be eluted from the cartridge and collected for further analysis.

CIT and CPA are acidic mycotoxins with strong polarity and are easily adsorbed by the MycoSep 226 cartridge, thereby resulting in poor recoveries. However, improved recovery was obtained for CIT and CPA using the Oasis HLB column. The 10 emerging mycotoxins (*Alternaria* mycotoxins, enniatins and beauvericin) have been optimally assessed in our previous work [23]. The performances of MycoSep 226, Oasis C18, and Oasis HLB were comparatively assessed, as well as their abilities to enrich these 10 analytes. As shown in Fig. 3, Oasis HLB column yielded improved recoveries and was selected for clean-up of the 12 mycotoxins in group C.

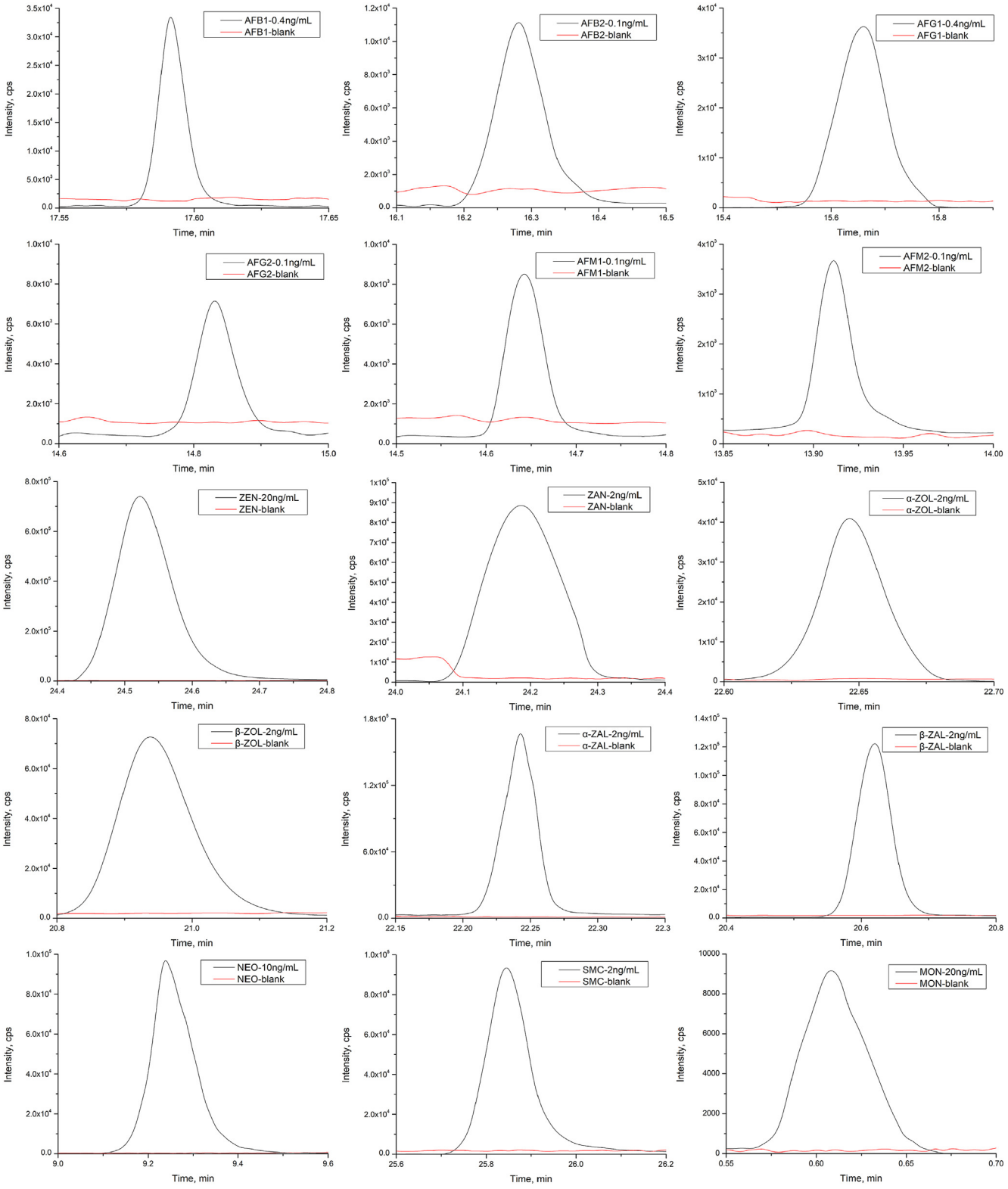

Fig. 4. LC-MS/MS extracted ion chromatograms of blank food samples and food matrices fortified with (a) AFB_1 and AFG_1 at 0.4 ng mL^{-1}, AFB_2, AFM_1, AFM_2, and AFG_2 at 0.1 ng mL^{-1}, ZEN and MON at 20 ng mL^{-1}, *β*-ZAL, *β*-ZOL, ZAN, α-ZAL, α-ZOL, and SMC at 2 ng mL^{-1}, NEO at 10 ng mL^{-1}; (b) DON, DON-3-G, 15A-DON, 3A-DON, Fus X, T2, HT2, PAT, CIT, and CPA at 20 ng mL^{-1}, DOM-1 and DAS at 10 ng mL^{-1}, NIV, OTA, and OTB at 2 ng mL^{-1}; and (c) FBs at 10 ng mL^{-1}, AME, AOH, ALT, TeA, and TEN at 20 ng mL^{-1}, ENNs and BEA at 2 ng mL^{-1}.

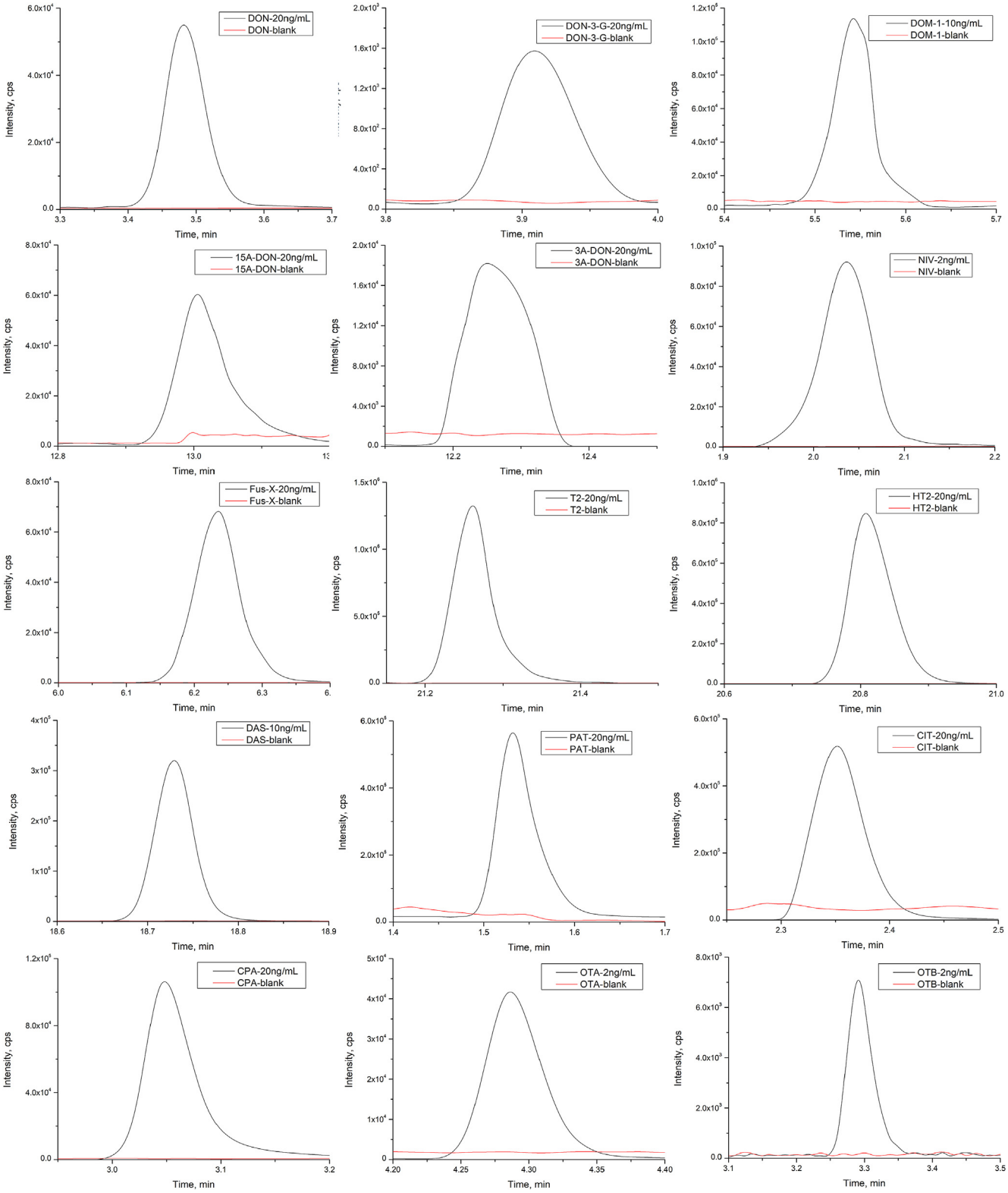

Fig. 4 (*continued*)

Different centrifugation speeds (5000 rpm, 7000 rpm, 9000 rpm) and durations (10 min, 15 min) were tested during sample extraction. A speed of 7000 rpm was not enough to completely separate the food matrix, especially for foods containing large amounts of fat and oil. After optimization, centrifugation at 9000 rpm for 10 min was selected to get a clear supernatant in a shorter time.

Filtration with a 0.22 μm filter is commonly required to remove the particles in tested sample solution before UHPLC-MS/MS analysis. However, some mycotoxins can partially bind to several types of filter membrane. Alternatively, a high-speed centrifugation at 20000 rpm for 30 min was applied prior to injection into the instrument.

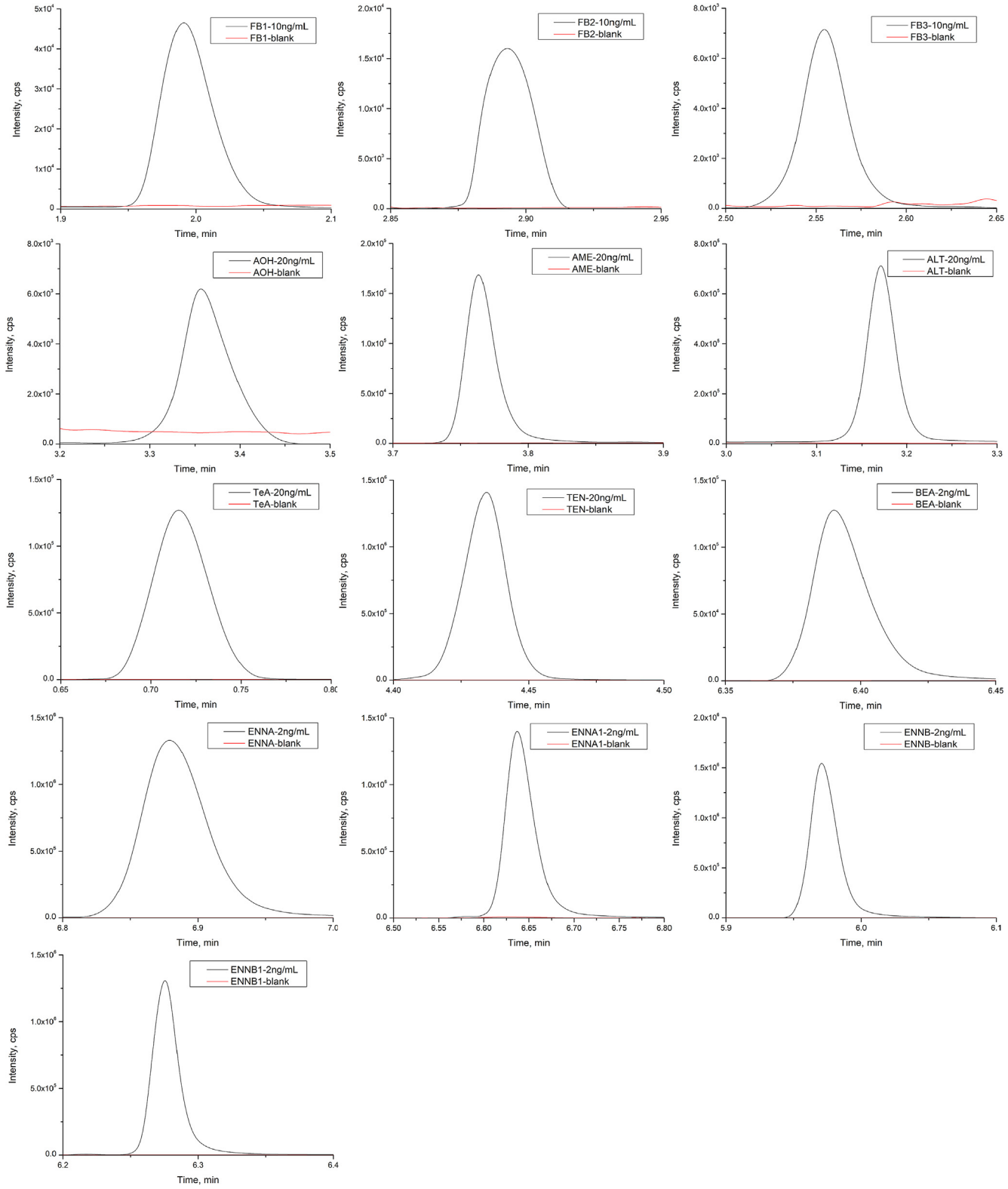

Fig. 4 (*continued*)

Method validation

As shown in Fig. 4, there were no peak interferences at the same retention times and *m*/*z* channels of the 43 target compounds, which indicated the absence of interfering endogenous substances, as well as good selectivity for the developed method. Carry-over experiments were conducted by injecting blank samples after a high concentration standard, and no sample-to-sample carryover was observed.

The LOD and LOQ of each analyte were measured first with the standard solution, giving the results as shown in Table S1. In addition, the LOD and LOQ were also evaluated with blank samples

Table 2
Matrix effect, apparent recoveries, LODs and LOQs of the 43 mycotoxins. Matrix effect and apparent recoveries are measured without internal standard correction. LODs and LOQs are measured using spiked blank samples in low amounts.

Analyte	Creals and their products				Legume and their products			
	Matrix Effect (%)	RA (Apparent recovery, %)	LOQ (μg kg^{-1})	LOD (μg kg^{-1})	Matrix Effect (%)	RA (Apparent recovery, %)	LOQ (μg kg^{-1})	LOD (μg kg^{-1})
15A-DON	92.0	82.2	0.3	0.1	82.6	83.0	0.3	0.1
3A-DON	87.3	66.1	0.6	0.2	66.5	66.8	0.6	0.2
AFB_1	99.1	62.8	0.006	0.002	90.6	75.0	0.006	0.002
AFB_2	67.9	56.7	0.006	0.002	62.4	54.0	0.006	0.002
AFG_1	87.0	61.7	0.01	0.004	77.8	62.9	0.01	0.004
AFG_2	85.9	60.2	0.01	0.004	68.5	60.0	0.01	0.004
AFM_1	102.7	47.1	0.01	0.004	60.0	51.6	0.01	0.004
AFM_2	75.8	50.0	0.01	0.004	75.2	51.4	0.01	0.004
ALT	105.1	90.1	0.6	0.2	101.3	77.3	0.6	0.2
AME	117.0	79.6	0.06	0.02	71.4	55.8	0.06	0.02
AOH	108.3	58.2	0.6	0.2	73.9	51.5	0.6	0.2
BEA	127.3	87.6	0.06	0.02	162.8	107.3	0.06	0.02
CIT	78.3	67.0	0.1	0.04	103.3	77.2	0.1	0.04
CPA	101.9	78.6	0.06	0.02	86.8	63.6	0.06	0.02
DAS	78.3	66.1	0.1	0.04	77.1	78.8	0.1	0.04
DOM-1	65.2	75.3	0.6	0.2	50.6	43.8	0.6	0.2
DON	150.2	61.4	0.6	0.2	43.6	58.3	0.6	0.2
DON-3-G	69.5	70.3	0.3	0.1	63.1	68.9	0.3	0.1
ENNA	127.1	80.6	0.06	0.02	145.1	95.6	0.06	0.02
$ENNA_1$	188.2	131.6	0.06	0.02	144.1	91.4	0.06	0.02
ENNB	164.1	111.3	0.01	0.004	166.1	89.7	0.01	0.004
$ENNB_1$	156.2	139.0	0.06	0.02	177.8	102.8	0.06	0.02
FB_1	113.7	87.1	0.03	0.01	68.9	113.6	0.03	0.01
FB_2	99.3	81.0	0.06	0.02	99.5	94.5	0.06	0.02
FB_3	105.5	89.2	0.06	0.02	80.5	101.5	0.06	0.02
Fus X	82.3	70.6	0.6	0.2	81.1	69.5	0.6	0.2
HT_2	76.4	70.9	0.2	0.08	63.3	65.7	0.2	0.08
MON	58.8	56.7	2.0	0.8	57.2	67.2	2.0	0.8
NEO	84.2	67.9	0.06	0.02	71.4	70.0	0.06	0.02
NIV	42.4	87.2	0.3	0.1	42.6	79.0	0.3	0.1
OTA	100.2	68.9	0.01	0.004	101.7	82.8	0.01	0.004
OTB	95.8	67.5	0.01	0.004	115.6	80.6	0.01	0.004
PAT	42.2	68.5	3.0	1.0	49.8	80.3	3.0	1.0
SMC	85.2	50.1	0.006	0.002	85.4	73.2	0.006	0.002
T_2	66.6	63.0	0.1	0.04	81.9	73.0	0.1	0.04
TeA	122.0	96.1	0.6	0.2	90.7	81.1	0.6	0.2
TEN	99.7	95	0.1	0.05	121.4	94.9	0.1	0.05
ZAN	148.3	116.2	0.06	0.02	126.2	70.0	0.06	0.02
ZEN	105.0	69.1	0.06	0.02	92.3	66.3	0.06	0.02
α-ZAL	96.2	76.0	0.06	0.02	91.5	59.0	0.06	0.02
α-ZOL	68.9	63.9	0.03	0.01	68.6	68.1	0.03	0.01
β-ZAL	84.1	79.2	0.03	0.01	84.9	70.3	0.03	0.01
β-ZOL	95.0	76.5	0.1	0.04	90.6	66.8	0.1	0.04

Analyte	Potatoes and their products				Meats and their products			
	Matrix Effect (%)	RA (Apparent recovery, %)	LOQ (μg kg^{-1})	LOD (μg kg^{-1})	Matrix Effect (%)	RA (Apparent recovery, %)	LOQ (μg kg^{-1})	LOD (μg kg^{-1})
15-ADON	41.6	89.4	0.3	0.1	89.8	88.5	0.3	0.1
3-ADON	78.5	92.3	0.6	0.2	74.9	68.1	0.6	0.2
AFB_1	95.8	85.5	0.006	0.002	75.9	47.4	0.006	0.002
AFB_2	74.2	87.9	0.006	0.002	55.7	43.5	0.006	0.002
AFG_1	87.8	85.8	0.01	0.004	73.6	49.6	0.01	0.004
AFG_2	66.5	120.6	0.01	0.004	68.1	45.4	0.01	0.004
AFM_1	77.6	98.6	0.01	0.004	71.5	46.4	0.01	0.004
AFM_2	71.1	67.5	0.01	0.004	134.5	44.4	0.01	0.004
ALT	147.8	133.6	0.6	0.2	149.2	137.7	0.6	0.2
AME	91.0	67.2	0.06	0.02	128.7	85.2	0.06	0.02
AOH	103.0	81.1	0.6	0.2	112.2	84.3	0.6	0.2
BEA	128.2	92.6	0.06	0.02	158.9	105.7	0.06	0.02
CIT	82.4	75.8	0.1	0.04	112.2	73.2	0.1	0.04
CPA	94.6	76.4	0.06	0.02	87.6	67.8	0.06	0.02
DAS	77.8	95.3	0.1	0.04	78.2	56.2	0.1	0.04
DOM-1	71.7	92.1	0.6	0.2	59.8	51.3	0.6	0.2
DON	50.5	92.0	0.6	0.2	43.2	49.7	0.6	0.2
DON-3-G	68.4	103.5	0.3	0.1	59.3	47.5	0.3	0.1
ENNA	153.3	107.8	0.06	0.02	132.5	80.4	0.06	0.02
$ENNA_1$	184.4	128.5	0.06	0.02	148.2	101.2	0.06	0.02
ENNB	137.7	100.2	0.01	0.004	134.5	97.1	0.01	0.004
$ENNB_1$	180.9	116.1	0.06	0.02	166.3	120.2	0.06	0.02

Table 2 (*continued*)

FB_1	69.7	92.0	0.03	0.01	85.7	77.4	0.03	0.01
FB_2	69.6	94.2	0.06	0.02	74.0	65.2	0.06	0.02
FB_3	68.2	101.6	0.06	0.02	69.3	65.2	0.06	0.02
Fus X	81.3	66.7	0.6	0.2	70.3	62.3	0.6	0.2
HT_2	67.8	97.3	0.2	0.08	88.2	73.2	0.2	0.08
MON	92.5	83.3	2	0.8	57.6	51.3	2	0.8
NEO	83.2	74.1	0.06	0.02	88.7	93.4	0.06	0.02
NIV	44.6	92.6	0.3	0.1	42.7	49.0	0.3	0.1
OTA	94.5	85.8	0.01	0.004	104.8	70.9	0.01	0.004
OTB	92.4	85.6	0.01	0.004	86.1	65.1	0.01	0.004
PAT	49.2	72.0	3.0	1.0	40.3	42.9	3.0	1.0
SMC	80.6	92.6	0.006	0.002	104.1	48.4	0.006	0.002
T_2	70.8	117.2	0.1	0.04	109.4	136.8	0.1	0.04
TeA	86.2	65.2	0.6	0.2	105.8	91.2	0.6	0.2
TEN	160.6	140.9	0.1	0.05	121.3	108.2	0.1	0.05
ZAN	80.7	67.6	0.06	0.02	101.7	55.3	0.06	0.02
ZEN	87.8	62.5	0.06	0.02	101.1	52.1	0.06	0.02
α-ZAL	88.4	70.1	0.06	0.02	83.2	60.9	0.06	0.02
α-ZOL	75.2	73.5	0.03	0.01	72.8	51.5	0.03	0.01
β-ZAL	86.8	116.6	0.03	0.01	85.7	52.6	0.03	0.01
β-ZOL	81.1	68.9	0.1	0.04	90.2	51.8	0.1	0.04

Analyte	Eggs and their products				Aquatic foods and their products			
	Matrix Effect (%)	RA (Apparent recovery, %)	LOQ ($\mu g\ kg^{-1}$)	LOD ($\mu g\ kg^{-1}$)	Matrix Effect (%)	RA (Apparent recovery, %)	LOQ ($\mu g\ kg^{-1}$)	LOD ($\mu g\ kg^{-1}$)
15-ADON	99.1	93.0	0.3	0.1	88.2	108.4	0.3	0.1
3-ADON	117.4	123.8	0.6	0.2	81.3	117.6	0.6	0.2
AFB_1	113.8	62.7	0.006	0.002	80.8	62.7	0.006	0.002
AFB_2	86.0	59.1	0.006	0.002	56.5	59.1	0.006	0.002
AFG_1	116.5	66.2	0.01	0.004	78.8	66.2	0.01	0.004
AFG_2	80.4	57.1	0.01	0.004	64.7	57.1	0.01	0.004
AFM_1	84.1	46.8	0.01	0.004	64.7	46.8	0.01	0.004
AFM_2	65.4	48.6	0.01	0.004	58.6	55.8	0.01	0.004
ALT	115.9	139.9	0.6	0.2	133.1	112.7	0.6	0.2
AME	134.0	100.8	0.06	0.02	119.8	81.7	0.06	0.02
AOH	143.5	94.3	0.6	0.2	103.5	111.3	0.6	0.2
BEA	134.4	192.6	0.06	0.02	131.2	133.7	0.06	0.02
CIT	100.2	82.1	0.1	0.04	98.6	80.2	0.1	0.04
CPA	102.6	70.0	0.06	0.02	96.2	86.7	0.06	0.02
DAS	107.1	87.9	0.1	0.04	89.9	109.6	0.1	0.04
DOM-1	86.0	73.8	0.6	0.2	78.1	75.4	0.6	0.2
DON	73.4	66.8	0.6	0.2	41.7	66.8	0.6	0.2
DON-3-G	86.1	52.6	0.3	0.1	60.9	60.4	0.3	0.1
ENNA	117.0	182.1	0.06	0.02	134.2	134.5	0.06	0.02
$ENNA_1$	132.4	186.3	0.06	0.02	98.3	120.4	0.06	0.02
ENNB	131.1	88.1	0.01	0.004	151.9	98.6	0.01	0.004
$ENNB_1$	149.8	123.7	0.06	0.02	157.7	109.1	0.06	0.02
FB_1	103.7	81.6	0.03	0.01	101.7	92.7	0.03	0.01
FB_2	96.2	85.6	0.06	0.02	92.7	90.3	0.06	0.02
FB_3	85.3	96.9	0.06	0.02	79.8	72.4	0.06	0.02
Fus X	87.1	71.8	0.6	0.2	71.9	57.2	0.6	0.2
HT_2	70.5	67.2	0.2	0.08	76.7	65.0	0.2	0.08
MON	79.1	65.0	2.0	0.8	71.1	59.3	2.0	0.8
NEO	127.7	84.7	0.06	0.02	97.5	84.7	0.06	0.02
NIV	41.2	89.0	0.3	0.1	42.3	72.8	0.3	0.1
OTA	93.2	70.8	0.01	0.004	95.1	71.3	0.01	0.004
OTB	95.1	72.6	0.01	0.004	90.3	72.0	0.01	0.004
PAT	41.8	60.7	3.0	1.0	48.7	60.7	3.0	1.0
SMC	103.9	49.8	0.006	0.002	112.3	49.8	0.006	0.002
T_2	76.5	83.1	0.1	0.04	121.4	83.1	0.1	0.04
TeA	111.3	87.0	0.6	0.2	93.8	75.5	0.6	0.2
TEN	107.5	102.7	0.1	0.05	114	102.5	0.1	0.05
ZAN	120.7	84.9	0.06	0.02	159.5	84.9	0.06	0.02
ZEN	76.9	54.4	0.06	0.02	95.9	56.7	0.06	0.02
α-ZAL	70.1	57.7	0.06	0.02	86.7	59.0	0.06	0.02
α-ZOL	75.5	51.4	0.03	0.01	74.3	51.4	0.03	0.01
β-ZAL	76.7	59.5	0.03	0.01	71.5	57.0	0.03	0.01
β-ZOL	63.9	55.7	0.1	0.04	83.6	60.8	0.1	0.04

Table 2 (*continued*)

Analyte	Milk and their products				Vegetables and their products			
	Matrix Effect (%)	RA (Apparent recovery, %)	LOQ	LOD	Matrix Effect (%)	RA (Apparent recovery, %)	LOQ	LOD
			(μg kg^{-1})	(μg kg^{-1})			(μg kg^{-1})	(μg kg^{-1})
15-ADON	90.5	85.2	0.3	0.1	97.9	86.0	0.3	0.1
3-ADON	94.0	84.7	0.6	0.2	47.6	41.2	0.6	0.2
AFB_1	98.0	53.7	0.006	0.002	82.2	43.6	0.006	0.002
AFB_2	69.8	45.5	0.006	0.002	65.3	49.4	0.006	0.002
AFG_1	92.0	42.6	0.01	0.004	79.1	41.7	0.01	0.004
AFG_2	88.7	49.9	0.01	0.004	67.9	48.0	0.01	0.004
AFM_1	70.0	41.8	0.01	0.004	74.5	41.7	0.01	0.004
AFM_2	77.2	68.3	0.01	0.004	128.3	71.1	0.01	0.004
ALT	182.4	158.0	0.6	0.2	158.9	116.3	0.6	0.2
AME	122.4	76.4	0.06	0.02	97.4	73.5	0.06	0.02
AOH	104.3	86.0	0.6	0.2	98.8	82.1	0.6	0.2
BEA	141.8	99.3	0.06	0.02	86.7	58.8	0.06	0.02
CIT	96.6	92.1	0.1	0.04	116.3	80.1	0.1	0.04
CPA	102.2	82.5	0.06	0.02	85.6	78.5	0.06	0.02
DAS	85.1	86.1	0.1	0.04	78.0	61.5	0.1	0.04
DOM-1	71.9	67.1	0.6	0.2	49.0	57.8	0.6	0.2
DON	45.5	55.4	0.6	0.2	50.0	43.8	0.6	0.2
DON-3-G	59.1	42.2	0.3	0.1	62.4	42.7	0.3	0.1
ENNA	138.6	85.5	0.06	0.02	72.3	58.1	0.06	0.02
$ENNA_1$	122.6	81.2	0.06	0.02	71.4	63.8	0.06	0.02
ENNB	167.3	117.8	0.01	0.004	167.0	105.9	0.01	0.004
$ENNB_1$	196.7	128.4	0.06	0.02	127.6	83.5	0.06	0.02
FB_1	66.6	69.1	0.03	0.01	87.1	106.5	0.03	0.01
FB_2	67.2	87.6	0.06	0.02	86.5	95.1	0.06	0.02
FB_3	78.5	60.3	0.06	0.02	92.5	108.3	0.06	0.02
Fus X	77.6	89.3	0.6	0.2	90.8	76.6	0.6	0.2
HT_2	73.6	69.3	0.2	0.08	64.7	56.4	0.2	0.08
MON	58.3	52.5	2.0	0.8	46.0	42.5	2.0	0.8
NEO	101.5	90.4	0.06	0.02	78.2	64.7	0.06	0.02
NIV	42.1	42.9	0.3	0.1	32.5	48.1	0.3	0.1
OTA	85.0	79.9	0.01	0.004	93.3	66.7	0.01	0.004
TEN	108.5	108.0	0.1	0.05	162.7	132.4	0.1	0.05
ZAN	159.1	111.9	0.06	0.02	140.8	92.6	0.06	0.02
ZEN	101.0	69.9	0.06	0.02	94.9	58.4	0.06	0.02
α-ZAL	98.9	77.6	0.06	0.02	95.5	67.1	0.06	0.02
α-ZOL	75.4	51.9	0.03	0.01	80.2	49.3	0.03	0.01
β-ZAL	96.3	80.1	0.03	0.01	80	62.6	0.03	0.01
β-ZOL	103.8	82.6	0.1	0.04	88.2	66.6	0.1	0.04

Analyte	Fruits and their products				Sugar and their products			
	Matrix Effect (%)	RA (Apparent recovery, %)	LOQ	LOD	Matrix Effect (%)	RA (Apparent recovery, %)	LOQ	LOD
			(μg kg^{-1})	(μg kg^{-1})			(μg kg^{-1})	(μg kg^{-1})
15-ADON	89.3	81.2	0.3	0.1	87.6	82.6	0.3	0.1
3-ADON	52.6	48.9	0.6	0.2	52.6	47.8	0.6	0.2
AFB_1	81.3	63.7	0.006	0.002	88.6	73.9	0.006	0.002
AFB_2	63.8	55.5	0.006	0.002	60.3	52.6	0.006	0.002
AFG_1	82.3	51.6	0.01	0.004	83.6	71.3	0.01	0.004
AFG_2	70.2	47.9	0.01	0.004	66.5	53.9	0.01	0.004
AFM_1	71.8	58.8	0.01	0.004	61.4	62.5	0.01	0.004
AFM_2	79.5	62.3	0.01	0.004	57.6	54.2	0.01	0.004
ALT	190.7	144.4	0.6	0.2	98.5	84.5	0.6	0.2
AME	122.8	84.0	0.06	0.02	108.7	70.2	0.06	0.02
AOH	123.4	82.8	0.6	0.2	112.7	83.7	0.6	0.2
BEA	98.3	63.4	0.06	0.02	174.8	89.7	0.06	0.02
CIT	91.8	89.7	0.1	0.04	98.0	88.9	0.1	0.04
CPA	90.2	74.6	0.06	0.02	90.1	84.0	0.06	0.02
DAS	89.5	83.1	0.1	0.04	87.1	81.1	0.1	0.04
DOM-1	49.2	46.3	0.6	0.2	58.0	46.2	0.6	0.2
DON	41.8	43.7	0.6	0.2	49.7	42.3	0.6	0.2
DON-3-G	63.8	41.2	0.3	0.1	50.9	42.8	0.3	0.1
ENNA	129.5	89.4	0.06	0.02	121.9	66.4	0.06	0.02
$ENNA_1$	141.4	90.5	0.06	0.02	145.2	80.6	0.06	0.02
ENNB	122.0	135.1	0.01	0.004	170.0	100.8	0.01	0.004
$ENNB_1$	123.3	108.3	0.06	0.02	193.7	108.5	0.06	0.02
FB_1	60.4	91.7	0.01	0.03	84.5	80.8	0.03	0.01
FB_2	75.5	113	0.06	0.02	79.5	71.4	0.06	0.02
FB_3	88.1	98.1	0.06	0.02	71.4	72.0	0.06	0.02
Fus X	88.0	76.3	0.6	0.2	74.9	72.3	0.6	0.2
HT_2	71.2	84.5	0.2	0.08	64.7	69.6	0.2	0.08
MON	42.6	44.8	2.0	0.8	59.6	46.5	2.0	0.8
NEO	82.3	81.3	0.06	0.02	86.4	84.4	0.06	0.02
NIV	41.0	42.3	0.3	0.1	41.6	44.9	0.3	0.1

Table 2 (*continued*)

OTA	81.4	59.3	0.01	0.004	87.1	65.0	0.01	0.004
OTB	79.6	65.9	0.01	0.004	91.5	58.9	0.01	0.004
PAT	40.2	42.1	3.0	1.0	43.1	55.0	3.0	1.0
SMC	93.1	42.5	0.006	0.002	98.4	45.0	0.006	0.002
T_2	90.2	88.2	0.1	0.04	105.3	91.4	0.1	0.04
TeA	92.1	74.0	0.6	0.2	86.9	71.3	0.6	0.2
TEN	123.3	108.4	0.1	0.05	114.0	94.2	0.1	0.05
ZAN	120.6	81.9	0.06	0.02	147.8	103.7	0.06	0.02
ZEN	89.5	59.9	0.06	0.02	97.0	60.2	0.06	0.02
α-ZAL	92.3	76.6	0.06	0.02	97.2	73.5	0.06	0.02
α-ZOL	81.3	65.2	0.03	0.01	87.3	61.1	0.03	0.01
β-ZAL	92.5	76.1	0.03	0.01	92.3	69.8	0.03	0.01
β-ZOL	92.5	78.6	0.1	0.04	96.9	67.9	0.1	0.04

Analyte	Beverages and water				Alcohol beverages			
	Matrix Effect (%)	RA (Apparent recovery, %)	LOQ ($\mu g\ kg^{-1}$)	LOD ($\mu g\ kg^{-1}$)	Matrix Effect (%)	RA (Apparent recovery, %)	LOQ ($\mu g\ kg^{-1}$)	LOD ($\mu g\ kg^{-1}$)
15-ADON	97.4	59.7	0.3	0.1	95.2	75.4	0.3	0.1
3-ADON	85.6	47.4	0.6	0.2	112.4	85.9	0.6	0.2
AFB_1	96.0	49.0	0.006	0.002	104.4	69.3	0.006	0.002
AFB_2	85.3	47.5	0.006	0.002	76.4	56.2	0.006	0.002
AFG_1	96.2	52.4	0.01	0.004	108.9	61.0	0.01	0.004
AFG_2	95.3	107.5	0.01	0.004	90.8	57.4	0.01	0.004
AFM_1	89.2	62.4	0.01	0.004	88.0	46.0	0.01	0.004
AFM_2	89.5	71.4	0.01	0.004	67.7	48.5	0.01	0.004
ALT	183.7	151.0	0.6	0.2	140.8	144.3	0.6	0.2
AME	98.1	74.1	0.06	0.02	113.0	79.8	0.06	0.02
AOH	86.2	59.5	0.6	0.2	109.1	70.3	0.6	0.2
BEA	74.5	53.3	0.06	0.02	125.7	98.8	0.06	0.02
CIT	108.3	93.0	0.1	0.04	92.1	88.1	0.1	0.04
CPA	108.1	80.8	0.06	0.02	78.6	74.1	0.06	0.02
DAS	92.3	72.2	0.1	0.04	107.1	87.9	0.1	0.04
DOM-1	77.4	65.2	0.6	0.2	60.0	48.8	0.6	0.2
DON	46.9	72.2	0.6	0.2	60.7	49.7	0.6	0.2
DON-3-G	100.4	72.8	0.3	0.1	61.1	105.6	0.3	0.1
ENNA	75.5	48.4	0.06	0.02	126.4	90.0	0.06	0.02
$ENNA_1$	86.4	64.2	0.06	0.02	137.9	86.9	0.06	0.02
ENNB	115.7	74.4	0.01	0.004	155.5	112.3	0.01	0.004
$ENNB_1$	114.4	76.5	0.06	0.02	115.5	80.6	0.06	0.02
FB_1	72.3	92.3	0.01	0.03	67.8	69.3	0.03	0.01
FB_2	78.6	95.1	0.06	0.02	77.4	70.4	0.06	0.02
FB_3	70.2	105.5	0.06	0.02	78.9	75.2	0.06	0.02
Fus X	84.7	66.3	0.6	0.2	73.3	51.2	0.6	0.2
HT_2	76.1	56.9	0.2	0.08	84.6	74.0	0.2	0.08
MON	69.7	66.6	2.0	0.8	50.4	43.6	2.0	0.8
NEO	89.7	73.0	0.06	0.02	127.7	97.1	0.06	0.02
NIV	42.4	61.6	0.3	0.1	42.5	41.7	0.3	0.1
OTA	82.3	64.6	0.01	0.004	91.3	70.1	0.01	0.004
OTB	90.2	68.5	0.01	0.004	92.5	70.5	0.01	0.004
PAT	37.4	43.1	3.0	1.0	43.9	47.6	3.0	1.0
SMC	91.3	48.5	0.006	0.002	104	49.8	0.006	0.002
T_2	97.3	55.7	0.1	0.04	68.6	84.4	0.1	0.04
TeA	71.8	61.6	0.6	0.2	65.6	66.2	0.6	0.2
TEN	156.6	132.3	0.1	0.05	142.6	133.5	0.1	0.05
ZAN	121.8	97.3	0.06	0.02	76.1	57.2	0.06	0.02
ZEN	80.3	58.9	0.06	0.02	79.5	54.6	0.06	0.02
α-ZAL	80.3	72.4	0.06	0.02	81.6	58.8	0.06	0.02
α-ZOL	69.4	78.8	0.03	0.01	68.7	55.8	0.03	0.01
β-ZAL	79.2	101.9	0.03	0.01	72.0	60.4	0.03	0.01
β-ZOL	83.3	69.3	0.1	0.04	76.4	52.4	0.1	0.04

spiked at low amounts, and subjected to the whole analytical procedure. The results are shown in Table 2. In general, satisfactory values were achieved for all the 43 mycotoxins in the 12 food matrices. LOQs ranged between 0.006 $\mu g\ kg^{-1}$ (AFB_1, AFB_2, and SMC) and 3 $\mu g\ kg^{-1}$ (PAT). LODs between 0.002 $\mu g\ kg^{-1}$ (AFB_1, AFB_2, and SMC) and 1 $\mu g\ kg^{-1}$ (PAT).

Linearity was assessed with at least six concentration points for each analyte on three consecutive days (Table S1). The regression coefficients (R^2) of calibration curves were in the range of 0.9902–0.9995, except for BEA which had a R^2 of 0.9778. These findings indicated that the method had good linearity for the totality of analytes.

Matrix effects (M_E) and apparent recovery (R_A) were also investigated. Because of matrix complexity, M_E values ranged from 32.5% to 196.7%, and R_A ranged from 32.1% to 192.6% (Table 2). These results demonstrated that internal standard compensation is required to effectively analyze the compounds. Therefore, internal standards with comparable R_A values were chosen as reference internal standards for analytes without commercially available internal standards.

The accuracy and precision of the method were also examined by assessing blank food samples at three levels on 3 distinct days with six replicates performed per day. Accuracy ranged from

Table 3
Accuracy and precision data for determination of 43 mycotoxins at three levels in one day (n = 6) and three distinct days (n = 18). Method recoveries are corrected by internal standards.

Analyte	Spiked level (μg kg^{-1})	Cereals and their products				Legume and their products			
		Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%)		Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%)	
				Intra-day (n = 6)	Inter-day (n = 18)			Intra-day (n = 6)	Inter-day (n = 18)
15-ADON	2	2.33	116.8	3.2	2.6	2.22	110.9	4.2	6.5
	20	23.2	116.0	1.8	3.8	22.23	111.1	1.6	3.3
	200	233	116.5	2.7	6.5	252.9	126.4	4.3	6.9
3A-DON	2	1.96	97.8	1.4	6.2	2.07	103.4	6.0	4.5
	20	19.5	97.5	2.9	10.2	18.73	93.6	2.8	5.1
	200	183.4	91.7	4.8	2.8	186.8	93.4	10.5	6.9
AFB_1	0.04	0.038	94.9	1.2	3.9	0.038	94.8	5.0	8.1
	0.4	0.37	92.7	3.1	6.7	0.39	96.7	1.8	6.2
	4	3.68	92.0	5.4	10.1	3.71	92.7	4.7	7.2
AFB_2	0.01	0.009	91.0	1.6	3.6	0.009	92.8	8.2	10.9
	0.1	0.09	91.3	5.3	10.2	0.09	90.6	3.9	6.1
	1	0.94	94.9	5.1	6.4	0.97	97.4	8.3	6.3
AFG_1	0.04	0.038	95.0	9.4	10.1	0.04	91.1	6.0	8.1
	0.4	0.37	91.3	6.0	7.5	0.38	95.3	2.8	4.3
	4	3.81	95.3	6.6	7.8	3.71	92.8	10.5	6.8
AFG_2	0.01	0.01	100.0	7.5	9.2	0.007	69.7	7.9	6.1
	0.1	0.096	95.7	9.1	10.3	0.09	87.0	6.0	4.5
	1	0.96	96.1	1.9	5.7	0.94	94.4	5.5	6.9
AFM_1	0.01	0.01	100.4	6.6	6.2	0.008	89.1	8.0	9.1
	0.1	0.095	95.5	6.0	7.6	0.09	91.8	9.9	5.5
	1	0.98	98.1	4.7	6.9	0.98	98.7	5.4	6.2
AFM_2	0.01	0.011	110.1	10.4	11.1	0.008	80.0	7.3	9.1
	0.1	0.11	107.5	4.6	6.1	0.095	95.0	8.7	6.7
	1	1.06	106.4	2.6	3.8	0.94	94.2	10.8	11.2
ALT	2	2.25	112.4	2.4	5.6	2.28	114.0	1.6	5.8
	20	25.26	126.3	3.8	6.3	17.26	86.3	1.6	6.6
	200	257.2	128.6	4.2	6.8	156.6	78.3	6.5	7.8
AME	2	1.26	62.8	2.9	4.2	1.66	83.0	11.8	12.2
	20	14.47	72.3	1.2	5.2	14.79	74.0	4.8	6.6
	200	110	94.0	2.4	5.2	131.0	65.5	7.2	8.2
AOH	2	1.77	88.5	5.2	11.2	2.78	139.1	4.1	6.2
	20	14.72	73.6	8.5	10.9	13.65	68.3	11.1	12.3
	200	20.02	100.1	1.6	4.2	151.8	75.9	4.7	6.8
BEA	0.2	0.3	149.1	2.8	4.8	0.25	123.9	9.6	11.2
	2	1.96	97.8	2.5	4.1	1.37	68.4	7.7	9.6
	20	14.07	70.4	3.6	6.2	12.31	61.5	5.6	6.2
CIT	2	1.46	72.8	4.7	7.2	1.69	84.5	3.8	7.5
	20	17.96	89.8	5.5	8.3	15.79	79.0	4.7	8.1
	200	180.2	90.0	3.4	6.2	163.9	82.0	5.6	9.5
CPA	2	1.78	89.1	3.6	6.2	1.64	82.4	5.1	8.5
	20	16.54	82.7	2.5	4.3	17.66	88.3	3.2	5.9
	200	173.8	86.9	5.2	6.3	176.2	88.1	4.6	8.2
DAS	1	0.95	94.8	7.3	6.9	1.03	102.6	5.2	6.9
	10	9.39	93.9	4.5	6.1	9.07	90.7	6.5	8.3
	100	94.73	94.7	2.8	3.6	103.7	103.7	7.6	8.9
DOM-1	1	1.16	116.0	4.3	8.1	1.13	112.8	13.2	10.2
	10	11.85	118.5	1.1	2.6	11.11	111.1	3.9	5.3
	100	111.3	111.3	2.4	8.4	114.9	114.9	3.3	6.2
DON	2	1.97	98.5	2.0	2.5	1.95	97.5	2.0	2.6
	20	20.08	100.4	4.4	6.8	18.75	93.7	1.8	3.8
	200	201.9	101	1.0	7.5	193.3	96.7	4.7	5.5
DON-3-G	1	1.07	107.1	10.0	11.5	0.88	88.3	5.8	6.2
	10	10.26	102.6	5.4	6.9	10.27	102.7	7.6	10.3
	100	108.6	108.6	3.2	4.1	107.4	107.4	4.2	6.5
ENNA	0.2	0.33	164.4	6.5	8.8	0.13	64.3	5.4	9.5
	2	2.57	128.6	4.5	5.2	1.23	61.6	2.7	6.4
	20	18.72	93.6	10.1	12.0	13.96	69.8	9.9	12.1
$ENNA_1$	0.2	0.31	154.3	3.3	6.3	0.17	84.0	8.1	9.8
	2	2.05	102.4	2.6	7.8	1.41	70.2	3.5	3.9
	20	20.86	104.3	2.3	5.6	12.24	61.2	4.6	5.6
ENNB	0.2	0.28	138.8	2.6	4.2	0.15	72.8	4.2	9.5
	2	2.43	121.5	3.5	8.3	1.48	73.9	7.5	7.9
	20	25.37	126.9	5.8	8.5	12.16	60.8	1.9	2.3
$ENNB_1$	0.2	0.24	121.9	4.2	8.8	0.15	72.7	1.1	3.8
	2	2.2	110.0	9.1	10.2	1.55	77.5	1.7	3.6
	20	20.36	101.8	7.4	10.6	12.94	64.7	3.2	5.6
FB_1	1	0.86	85.9	5.4	7.3	0.86	85.7	4.3	2.5
	10	9.19	91.9	3.9	4.9	9.72	97.2	7.4	6.6
	100	98.19	98.2	9.7	5.6	91.46	91.5	5.7	7.3

Table 3 (*continued*)

Analyte	Spiked level (μg kg^{-1})	Cereals and their products				Legume and their products			
		Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%)		Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%)	
				Intra-day (n = 6)	Inter-day (n = 18)			Intra-day (n = 6)	Inter-day (n = 18)
FB_2	1	0.86	86.3	1.2	4.3	1.04	104.3	2.5	5.2
	10	10.24	102.0	1.3	5.2	9.13	91.3	3.3	4.1
	100	97.91	97.9	1.9	2.8	103.8	103.8	2.4	3.9
FB_3	1	1.06	106.2	1.1	3.9	1.05	104.5	2.1	7.1
	10	11.62	116.2	4.2	7.6	9.73	97.3	0.2	2.6
	100	98.42	98.4	3.2	4.8	103.4	103.4	2.4	4.3
Fus X	2	2.08	103.9	3.6	2.5	1.92	95.8	4.3	6.2
	20	20.06	100.3	4.5	5.8	18.74	93.7	2.3	7.3
	200	199.8	99.9	1.7	9.6	209	104.5	2.1	5.1
HT2	2	2.22	110.8	10	11.2	2.04	102.1	5.3	8.9
	20	20.22	101.1	1.4	2.4	20.75	103.8	3.5	6.1
	200	184.2	92.1	2.6	3.1	185.3	92.6	3.8	6.5
MON	2	1.79	89.5	8.2	10.8	2.06	103.5	10.2	11.8
	20	17.78	88.9	1.5	6.3	22.66	113.3	7.6	8.1
	200	183.2	91.6	7.7	6.1	187	93.5	10.0	6.5
NEO	1	0.95	95.3	0.7	2.9	0.97	96.9	4.8	5.1
	10	9.89	98.9	1.4	5.1	8.55	85.5	2.9	3.6
	100	100.3	100.3	3.2	4.5	94.57	94.6	3.3	4.9
NIV	2	2.044	102.0	5.6	6.8	1.74	87.0	8.4	7.4
	20	19.2	96.1	4.4	6.9	17.7	88.5	7.4	10.1
	200	182.5	91.3	2.1	7.2	181.1	90.6	5.9	6.8
OTA	0.2	0.18	92.6	1.1	2.5	0.2	100.8	2.0	3.5
	2	1.96	94.6	3.5	4.9	1.88	94.0	1.1	4.2
	20	18.12	94.2	3.8	5	19.05	95.3	4.2	8.3
OTB	0.2	0.17	85.0	0.7	2.6	0.18	90	2.9	6.3
	2	1.81	92.3	0.2	3.6	2.02	101	7.6	8.0.2
	20	18.17	90.2	2	8.2	19.87	99.4	1.1	2.1
PAT	2	1. 92	96.0	8.6	10.2	1.86	93.2	2.5	5.1
	20	19.05	95.3	11.8	12.5	18.96	94.8	4.0	10.8
	200	188.5	94.2	11.6	12.9	182.0	92.0	6.0	11.3
SMC	0.2	0.18	87.8	7.8	8.1	0.18	90.0	11.4	10.2
	2	1.92	96.2	5.4	6.3	1.92	96.1	4.7	6.5
	20	17.65	88.2	7.2	9.1	18.81	94.1	3.6	8.3
T2	2	2.16	108	9.2	10.2	2.26	113.1	1.2	3.3
	20	21.82	109.1	9.4	10.5	22.35	111.8	2.2	4.1
	200	214.6	107.3	9.8	11.8	214.4	107.2	2.7	3.5
TeA	2	2.45	122.5	3.4	5.6	1.93	96.3	4.3	6.5
	20	18.38	91.9	1.5	3.3	18.6	93.0	1.5	3.2
	200	180.6	90.3	0.9	3.2	176.5	88.2	5.2	6.6
TEN	2	2.49	124.6	5.9	10.8	2.02	101.1	9.5	11.8
	20	20.48	102.4	2.0	5.3	19.18	95.9	2.9	5.6
	200	184.8	92.4	1.9	3.4	168.8	84.4	1.9	2.3
ZAN	0.2	0.2	102	4.0	4.3	0.2	100.5	7.7	6.1
	2	1.96	98.0	2.6	4.9	2.04	101.8	2.1	3.5
	20	20.52	102.6	3.1	5.1	20.5	102.5	3.3	4.2
ZEN	2	2.02	101.0	3.4	5.2	1.94	97.4	7.2	8.2
	20	19.11	95.5	3.5	7.3	18.72	93.6	0.5	3.8
	200	199.3	99.1	4.2	6.8	198.9	99.5	2.8	4.5
α-ZAL	0.2	0.23	117.6	2.5	3.5	0.17	85.0	3.7	4.9
	2	2.15	107.4	2.5	4.9	1.63	81.5	5.4	8.5
	20	21.71	108.6	1.4	2.6	17.96	89.8	1.2	3.6
α-ZOL	0.2	0.16	80.0	10.2	11.6	0.18	90.6	6.5	8.1
	2	1.88	94.0	4.8	6.9	1.96	98.0	5.4	6.3
	20	18.6	93.0	2.2	3.5	19.01	95.1	1.2	3.8
β-ZAL	0.2	0.23	114.0	4.3	2.8	0.19	95.0	11.3	10.9
	2	2.21	110.4	5.2	8.2	2.03	101.5	2.4	3.6
	20	22.49	112.4	6.0	6.4	21.01	105.1	11.6	10.1
β-ZOL	0.2	0.22	110.0	6.9	8.2	0.21	105.0	9.2	11.2
	2	2.22	111.0	2.6	5.6	2.02	101.2	5.5	6.3
	20	23.23	116.2	3.1	6.8	20.19	100.9	6.1	5.1

Table 3 (*continued*)

Analyte	Spiked level (μg kg^{-1})	Potatoes and their products				Meats and their products			
		Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%) Intra-day (n=6)	Inter-day (n=18)	Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%) Intra-day (n=6)	Inter-day (n=18)
15-ADON	2	2.15	107.6	11.5	12.8	2.08	104.0	3.4	5.3
	20	20.09	100.5	5.3	6.4	22.12	110.6	1.2	4.1
	200	214.9	107.4	2.6	5.6	235	117.5	2.9	6.5
3A-DON	2	1.82	90.9	4.8	6.5	2.03	101.7	6.1	10.8
	20	18.47	92.3	3.3	4.6	18.24	91.2	0.6	5.1
	200	190.6	95.3	2.6	8.1	186.9	93.4	5.2	3.9
AFB_1	0.04	0.037	93.1	3.5	6.9	0.038	94.3	4.5	5.2
	0.4	0.34	85.5	2.7	4.2	0.37	91.4	5.3	3.6
	4	3.66	91.5	3.4	5.5	3.62	90.9	7.0	11.0
AFB_2	0.01	0.009	90.1	2.1	6.1	0.007	69.1	5.7	5.8
	0.1	0.087	87.9	1.8	3.7	0.093	93.1	9.5	12.6
	1	0.91	90.1	3.4	5.9	0.97	97.5	2.3	3.5
AFG_1	0.04	0.04	99.0	8.1	6.5	0.043	106.6	6.8	13.9
	0.4	0.34	85.8	3.5	6.6	0.39	98.3	6.1	8.3
	4	3.74	93.6	7.8	10.2	3.66	91.5	3.5	9.1
AFG_2	0.01	0.008	82.1	11.9	12.6	0.008	80.0	7.3	9.6
	0.1	0.1	99.4	4.1	5.7	0.087	86.9	3.6	5.7
	1	0.91	91.0	4.7	8.3	0.94	94.4	2.5	5.3
AFM_1	0.01	0.011	110.6	7.6	6.1	0.01	98.4	11	12.5
	0.1	0.09	98.6	3.2	4.8	0.1	100.2	9.8	10.3
	1	0.97	97.4	6.9	10.2	0.94	94.1	11.9	12.9
AFM_2	0.01	0.096	95.6	8.4	9.3	0.008	81.4	10.4	12.3
	0.1	0.087	87.5	5.2	11.9	0.08	80.5	9.3	10
	1	0.86	85.6	7.0	4.8	0.82	82.1	4.3	11.6
ALT	2	2.68	134.0	1.8	3.6	2.34	117.1	3.8	7.2
	20	25.25	126.2	6.6	8.8	22.68	113.4	4.6	8.2
	200	215.8	107.9	4.2	7.2	161.2	80.6	3.6	4.8
AME	2	1.46	72.9	3.8	4.6	1.53	76.5	2.2	8.2
	20	15.25	76.3	5.2	8.7	15.84	79.2	1.5	5.4
	200	167.4	83.7	4.5	9.5	164.6	82.3	7.3	9.2
AOH	2	2.39	119.3	8.1	10.3	1.44	72.3	4.5	8.6
	20	19.1	95.5	4.2	5.8	17.62	88.1	7.2	9.5
	200	225.9	112.9	9.8	10.2	165.9	83	1.5	6.9
BEA	0.2	0.17	84.4	7.5	8.6	0.28	141.2	1.5	6.8
	2	1.99	99.3	2.5	5.5	2.64	132.2	7.2	9.5
	20	16.77	83.9	3.2	5.3	22.35	111.8	4.3	8.2
CIT	2	1.66	83.6	4.5	8.1	1.75	87.5	6.8	9.4
	20	17.36	86.8	2.4	5.9	16.36	81.8	4.8	7.7
	200	161.5	80.1	6.5	4.3	173.6	86.8	6.3	8.5
CPA	2	1.63	81.4	3.5	8.5	1.52	76.7	5.2	6.8
	20	16.38	81.9	2.5	6.7	15.87	79.4	4.8	8.3
	200	191.7	95.8	3.1	7.9	162.6	81.3	4.2	5.9
DAS	1	1.01	101.1	4.3	6.7	1.06	105.6	6.3	8.2
	10	9.53	95.3	2.3	5.4	10.08	100.8	4.2	6.5
	100	93.68	93.7	8.3	9.3	91.42	91.4	1.1	7.3
DOM-1	1	1.11	111.4	8.5	11.8	1.08	108.3	13	10.5
	10	11.14	111.4	4.5	10.7	10.59	105.9	3.6	6.6
	100	115.1	115.1	1.7	11.1	106.2	106.2	10.7	9.3
DON	2	1.84	92.0	2.4	3.5	1.67	83.4	9.1	11.6
	20	20.18	100.9	1.7	5.1	18.11	90.5	10.2	12.3
	200	193.2	96.6	7.0	11.5	210.4	105.2	4.8	6.9
DON-3-G	1	1.12	112.1	5.5	12.9	0.91	91.0	6.8	5.1
	10	11.19	111.9	6.0	7.1	8.36	83.6	5.1	6.2
	100	103.5	103.5	2.3	5.3	93.2	93.2	10.2	11.3
ENNA	0.2	0.22	107.9	2.6	5.3	0.28	141.5	6.3	4.8
	2	2.66	133.1	2.8	4.8	2.39	145.3	3.2	4.3
	20	14.08	70.4	3.8	2.1	27.64	138.1	1.2	5.8
$ENNA_1$	0.2	0.3	150.3	4.5	7.8	0.25	125.6	1.5	5.5
	2	2.08	104.2	5.5	8.2	2.57	128.5	2.2	4.3
	20	15.16	75.8	7.4	10.3	26.81	134.1	9.2	11.5
ENNB	0.2	0.27	136.7	5.2	10.5	0.25	125.3	3.8	4.5
	2	2.03	101.7	1.3	5.6	2.53	126.5	2.8	6.3
	20	16.2	81.0	2.6	5.8	32.19	161.0	7.7	11.2
$ENNB_1$	0.2	0.31	154.9	3.2	5.2	0.16	79.2	4.5	6.4
	2	3.14	156.8	5.8	6.6	1.72	86.9	4.5	8.8
	20	16.37	81.9	6.8	6.9	23.66	118.3	6.2	10.6
FB_1	1	0.93	93.0	3.6	4.8	0.8	79.5	2.6	5.5
	10	10.44	104.4	0.9	5.5	7.27	72.7	0.2	4.3
	100	100.7	100.7	1.9	4.9	74.13	74.1	6.6	5.8
FB_2	1	1.09	109.5	5.0	5.8	1.18	117.5	7.6	8.2
	10	11.63	116.3	6.9	8.2	9.83	98.3	5.1	6.3
	100	111.7	117.1	5.4	4.3	89.25	89.3	7.0	8.1

Table 3 (*continued*)

Analyte	Spiked level (μg kg^{-1})	Potatoes and their products				Meats and their products			
		Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%) Intra-day (n=6)	Inter-day (n=18)	Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%) Intra-day (n=6)	Inter-day (n=18)
FB_3	1	1.04	103.8	1.1	3.9	0.84	84.3	7.9	9.2
	10	10.16	101.6	9.2	10.2	9.34	93.4	4.2	5.5
	100	101.8	101.8	4.7	5.8	95.58	95.6	0.8	3.8
Fus X	2	1.97	98.6	3.2	5.3	1.68	84.0	4.2	6.5
	20	18.87	94.3	4.4	6.1	16.92	84.6	3.3	6.9
	200	195.8	97.9	4.0	5.3	183	81.5	3.6	7.2
HT2	2	1.95	97.3	4.7	5.1	1.77	88.5	6.1	8.3
	20	19.84	99.2	10.1	11.2	20.3	101.5	5.9	6.5
	200	180.4	90.2	3.0	4.6	185.9	93.0	9.9	10.9
MON	2	1.86	93.0	5.6	6.9	2.01	100.5	4.3	6.1
	20	18.22	91.1	3.6	5.8	18.64	93.2	6.7	5.2
	200	180.9	90.4	6.3	5.7	186.7	93.3	1.8	3.1
NEO	1	0.85	84.5	2.4	6.3	0.93	92.5	3.9	10.3
	10	7.41	74.1	7.1	10.2	8.73	87.4	2.3	6.5
	100	74.39	74.4	6.6	8.1	79.87	79.9	7.0	10.2
NIV	2	1.79	89.4	5.0	8.1	1.91	95.5	7.6	8.3
	20	19.26	96.3	7.5	8.9	17.98	89.9	3.8	5.5
	200	185.2	92.6	3.3	5.2	177.9	88.9	3.3	7.8
OTA	0.2	0.18	90.1	1.6	3.5	0.19	96.0	1.9	5.2
	2	1.77	88.5	0.9	2.6	1.89	94.5	1.0	4.8
	20	19.96	99.8	3.5	4.3	17.44	87.2	0.3	3.9
OTB	0.2	0.17	83.5	2.1	5.2	0.22	112.0	3.0	8.2
	2	1.77	88.3	6.7	7.4	1.78	89.2	4.8	6.3
	20	16.84	84.2	1.5	6.3	18.92	94.6	3.5	4.8
PAT	2	2.27	113.7	7.0	11.2	1.75	87.5	8.9	7.5
	20	18.39	92	11.1	12.8	16.0	80.0	9.3	10.2
	200	183.1	91.6	6.2	10.3	181.5	90.8	7.3	8.1
SMC	0.2	0.18	90.1	8.7	6.2	0.19	95.0	8.1	9.3
	2	1.98	99.2	5.7	11.4	1.94	97.2	2.3	11.6
	20	18.52	92.6	9.1	12.8	19.49	97.5	7.9	6.5
T2	2	2.34	117.2	10.2	11.2	2.08	104.1	7.6	8.1
	20	22.83	114.9	10.8	11.9	21.57	107.9	4.2	6.3
	200	212.4	108.8	3.6	6.7	208.5	104.3	9.8	10.1
TeA	2	1.62	81.0	1.5	4.2	2.16	108.2	1.5	6.8
	20	19.69	98.5	8.2	8.6	20.25	101.3	4.6	8.3
	200	178.4	89.2	5.5	6.8	193.9	97.0	2.9	5.4
TEN	2	2.2	109.8	2.3	5.6	2.26	113.1	4.6	8.2
	20	23.39	117.0	1.2	3.3	22.58	112.9	3.5	10.8
	200	167.3	83.7	1.6	4.8	216.5	108.3	1.8	2.3
ZAN	0.2	0.2	99.2	2.2	3.2	0.22	109.9	2.4	9.6
	2	2.03	101.3	2.6	6.4	2.08	104.1	0.5	3.5
	20	20.23	101.1	1.1	3.5	21.75	108.8	9.3	6.1
ZEN	2	1.88	93.9	6.7	5.3	1.85	92.6	2.7	3.9
	20	18.43	92.1	3.4	6.1	18.85	94.3	4.3	5.2
	200	174.6	87.3	1.2	5.9	176.4	88.2	2.8	4.3
α-ZAL	0.2	0.25	105.1	4.1	5.6	0.21	105.1	4.1	12.1
	2	2.3	114.9	3.6	7.5	2.18	109.3	0.3	8.8
	20	21.75	108.8	0.9	3.9	23.62	118.1	5.5	8.7
α-ZOL	0.2	0.16	80.1	4.7	6.1	0.14	71.0	3.5	7.1
	2	1.71	85.5	2.4	5.8	1.57	78.4	3.2	6.5
	20	17.77	88.9	2.6	5.4	16.67	83.3	5.5	4.6
β-ZAL	0.2	0.24	117.5	6.5	5.9	0.22	110.1	9.6	5.1
	2	2.33	116.6	9.8	11.2	2.15	107.5	3.8	10.2
	20	23.5	117.5	5.5	6.9	20.61	103.1	0.3	11.2
β-ZOL	0.2	0.21	105.2	9.2	10.2	0.2	101.2	3.2	6.5
	2	2.11	105.7	2	6.5	2.09	104.6	4.5	4.1
	20	22.9	114.5	2.2	3.7	21.92	109.6	7.7	10.2

Analyte	Spiked level (μg kg^{-1})	Eggs and their products				Aquatic foods and their products			
		Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%) Intra-day (n=6)	Inter-day (n=18)	Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%) Intra-day (n=6)	Inter-day (n=18)
15-ADON	2	1.64	82.1	4.7	6.9	2.15	107.6	5.8	6.2
	20	16.83	84.1	1.2	5.3	20.85	104.3	4.1	10.3
	200	160.7	80.4	2.1	5.5	196.2	98.1	4.7	8.9
3A-DON	2	1.98	99.2	3.1	4.2	1.92	96.1	6.6	7.2
	20	19.12	95.6	5.8	6.9	18.96	94.8	1.5	5.4
	200	193.5	96.8	1.9	3.5	183.3	91.6	3	8.2
AFB_1	0.04	0.035	86.3	10.8	11.2	0.04	89.5	2.5	5.9
	0.4	0.36	91.1	9.8	10.6	0.35	86.7	4.8	5.8
	4	3.84	96.0	5.1	6.7	3.73	93.1	2.8	7.3
AFB_2	0.01	0.009	93.4	3.8	5.5	0.01	95.1	5.4	6.9

(*continued on next page*)

Table 3 (*continued*)

	0.1	0.09	91.1	12.2	12.7	0.09	94.3	5.4	9.1
	1	0.96	96.0	8.0	10.3	0.97	97.3	3.6	6.5
AFG_1	0.04	0.039	98.0	7.8	8.1	0.04	107.5	9.1	8.9
	0.4	0.41	103.2	10.9	13.8	0.35	88.6	4.8	8.6
	4	3.77	94.3	6.3	8.1	3.94	98.6	6.4	8.6
AFG_2	0.01	0.008	84.5	11.5	13.7	0.01	84.6	5.4	9.9
	0.1	0.097	96.9	7.1	6.5	0.06	84.3	9.3	10.5
	1	0.91	91.0	5.7	9.9	0.63	83.3	2.2	8.5
AFM_1	0.01	0.01	100.1	2.0	6.7	0.01	95.0	1.0	7.9
	0.1	0.094	93.8	11.3	13.6	0.09	89.0	4.9	6.1
	1	0.92	92.3	7.5	9.7	0.86	85.7	9.9	8.2
AFM_2	0.01	0.01	98.4	6.9	13.9	0.01	91.6	3.9	10.5
	0.1	0.067	67.3	5.3	12.8	0.11	108.2	3.2	6.3
	1	0.63	63.1	6.6	6.1	0.73	73.3	7.1	10.1
ALT	2	1.71	85.5	5.2	8.5	2.44	122.1	3.4	7.9
	20	22.78	113.9	2.4	9.9	20.68	103.4	7.8	9.3
	200	194.5	97.2	7.5	9.3	151.5	75.8	7.8	10.2
AME	2	1.54	76.9	5.8	10.5	1.63	81.4	1.2	5.5
	20	15.06	75.3	3.8	4.6	15.24	76.2	2.2	5.6
	200	166.3	83.1	2.8	5.2	154.6	77.3	6.5	7.7
AOH	2	1.41	70.7	4.5	7.2	2.88	143.8	3.4	6.4
	20	13.59	67.9	6.2	10.2	17.12	85.6	3.5	7.4
	200	136.2	68.1	1.6	9.2	162.8	81.4	3.6	7.2
BEA	0.2	0.27	134.8	7.3	9.9	0.23	113.7	2.8	10.8
	2	2.2	110.2	2.5	8.5	2.04	102.2	5.6	9.5
	20	23.94	119.7	5.6	8.8	24.75	123.8	2.9	10.9
CIT	2	2.24	112.2	3.2	6.6	1.64	80.2	1.8	5.3
	20	19.95	99.7	4.8	7.9	21.4	107	5.4	8.2
	200	214.7	107.3	4.2	6.2	213.4	106.7	4.7	5.5
CPA	2	1.64	81.8	4.5	5.2	1.55	77.5	2.2	3.8
	20	17.46	87.3	3.8	7.5	14.06	70.3	5.4	4.3
	200	192.3	96.1	2.6	5.3	153.3	76.6	2.8	5.6
DAS	1	0.98	97.7	3.2	5.5	1.01	101.3	7.5	8.3
	10	9.99	99.9	5.3	10.2	10.21	102.1	3.2	6.4
	100	101.1	101.1	7.5	11.3	94.31	94.3	3.9	9.6
DOM-1	1	1.67	167.3	4.5	6.2	1.54	153.9	2.6	7.9
	10	16.15	161.5	6.1	8	13.31	133.1	4.5	7.6
	100	151.7	151.7	1.9	3.6	156.9	156.9	5.3	6.8
DON	2	2.19	109.4	7.7	8.3	2.01	100.5	3.2	6.9
	20	20.22	101.1	7.2	9.1	17.79	88.9	5.8	8.1
	200	204.4	102.2	7.0	8.6	206.1	103.1	2.2	6.8
DON-3-G	1	0.89	105.2	2.5	5.1	1.12	112.4	7.8	10.2
	10	16.7	93.5	2.7	11.2	8.22	82.2	5.7	11.9
	100	88.29	86.4	4.2	6.5	82.34	82.3	3.9	6.3
ENNA	0.2	0.25	124.8	3.4	8.2	0.18	90.0	5.2	8.4
	2	2.06	102.9	3.6	6.3	1.99	99.4	3.8	6.2
	20	21.02	105.1	7.2	10.3	26.44	132.2	1.2	7.9
$ENNA_1$	0.2	0.25	127.2	6.8	9.2	0.21	102.6	2.2	6.3
	2	2.11	105.3	1.5	8.3	1.57	78.5	4.8	8.5
	20	20.14	100.7	5.2	8.4	25.41	127.0	3.6	6.4
ENNB	0.2	0.31	153.4	4.8	6.6	0.23	116.0	2.4	6.1
	2	1.88	94.0	2.3	9.2	2.35	117.4	8.2	9.6
	20	12.67	63.3	9.1	10.4	35.19	175.9	9.1	11.5
$ENNB_1$	0.2	0.3	147.6	4.9	8.5	0.16	78.8	2.5	4.3
	2	1.32	66.2	3.8	8.3	1.42	70.9	2.1	4.9
	20	15.41	77.1	2.8	5.3	26.66	133.3	3.8	9.1
FB_1	1	0.87	86.7	7.5	9.1	0.84	84.3	2.5	4.6
	10	8.16	81.6	2.9	3.5	8.55	85.5	4.1	8.2
	100	90.85	90.9	7.2	8.2	99.42	99.4	6.7	7.6
FB_2	1	0.96	98.6	5.1	6.7	0.82	82.3	4.5	6.3
	10	9.87	98.7	1.9	3.4	11.04	110.4	2.1	4.8
	100	85.61	85.6	7.2	8.2	105.6	105.6	2.5	5.2
FB_3	1	1.03	103.3	2.1	3.6	1.23	123.2	3.8	6.6
	10	11.88	118.8	1.5	4.8	12.37	123.7	4.2	4.8
	100	96.94	96.9	4.6	5.1	123.6	123.6	3.3	3.9
Fus X	2	1.75	87.5	3.1	5.5	1.71	85.4	2.9	8.5
	20	16.79	84.0	1.4	3.9	16.8	84.0	2.7	6.6
	200	167.8	83.9	3.9	6.1	156.6	78.3	6.6	9.1
HT2	2	2.11	105.7	3.2	6.6	2.23	111.7	5.6	8.9
	20	19.96	99.8	6.9	7.1	21.48	107.4	6.6	7.1
	200	194.0	97.0	2.7	4.5	192.6	96.3	2.5	6.5
MON	2	1.87	93.5	2.9	10.8	1.68	84.0	2.3	8.2
	20	17.72	88.6	5.3	11.3	17.25	86.3	4.8	8.7
	200	192.6	96.3	8.1	6.8	179.0	89.5	3.3	6.1
NEO	1	1.05	104.9	7.8	9.4	0.99	99.0	3.5	5.8
	10	10.85	108.5	7.6	8.2	9.96	99.6	5.4	6.7

Table 3 (*continued*)

	100	106	106	7.6	8.8	87.61	87.6	4.9	8.3
NIV	2	1.78	89	1.1	3.9	2.14	106.8	4.7	6.3
	20	18.38	91.9	1.1	2.5	18.38	91.9	1.2	8.1
	200	179.2	89.6	2.2	9.2	178.6	89.3	5.0	8.9
OTA	0.2	0.2	101.4	3.5	6.9	0.23	119.3	2.3	3.5
	2	1.92	96.2	2.4	4.6	2.18	109.1	4.2	5.2
	20	18.12	90.6	3.5	5.2	18.69	93.5	2.1	4.3
OTB	0.2	0.14	72.0	2.9	4.5	0.19	96.0	5.2	8.5
	2	1.4	70.2	6.8	7.2	1.99	99.6	4.8	7.6
	20	14.51	72.6	5.1	6.8	16.23	85.3	1.3	3.3
PAT	2	1.91	95.5	6.4	7.3	1.62	81.2	3.3	5.5
	20	22.69	113.5	5.7	6.3	17.82	89.1	2.4	4.9
	200	194.3	97.2	1.6	3.8	166.8	83.4	2.2	1.1
SMC	0.2	0.23	164.2	6.4	9.1	0.16	82.9	7.1	9.7
	2	18.14	95.1	1.4	5.3	1.83	91.6	6.9	8.4
	20	19.71	98.5	8.7	9.3	16.55	82.8	7.2	10.2
T2	2	2.31	115.5	7.5	9.3	2.36	117.9	6.5	8.1
	20	23.54	117.7	2.2	6.4	20.6	103.0	8.5	9.2
	200	217.9	112.2	7.6	8.1	188.8	94.4	6.9	11.3
TeA	2	2.58	129.1	4.2	6.3	2.06	102.8	3.2	5.5
	20	17.38	86.9	3.8	9.5	20.05	100.3	2.8	8.4
	200	179.9	89.9	2.4	6.4	183.9	92.0	2.5	6.2
TEN	2	2.3	115.1	2.8	4.4	2.4	120.1	3.8	4.9
	20	25.32	126.6	3.5	8.2	22.88	103.4	3.9	7.2
	200	229.8	114.9	3.6	7.8	210.9	75.8	5.3	6.5
ZAN	0.2	0.22	107.6	4.8	6.5	0.23	114.3	4.4	8.2
	2	2.06	103.2	2.8	3.9	2.12	106.1	2.0	7.3
	20	20.82	104.1	5.4	6.7	22.03	110.1	1.0	5.6
ZEN	2	1.86	92.9	3.6	5.3	1.84	92.0	5.9	6.1
	20	19.12	95.6	4.4	6.1	19.06	95.3	4.4	5.2
	200	182.6	91.3	6.5	10.3	187.3	93.7	2.1	9.6
α-ZAL	0.2	0.25	125.0	5.4	6.6	0.23	115.0	4.9	6.9
	2	2.49	124.6	2.4	3.7	2.07	103.6	5.5	7.2
	20	23.8	119.0	1.8	3.9	24.73	123.6	5.6	7.1
α-ZOL	0.2	0.21	103.3	3.4	4.8	0.17	83.4	5	6.5
	2	1.87	93.3	3.8	6.1	1.68	84.0	3.7	4.9
	20	18.28	91.4	4.2	10.6	17.46	87.3	6.9	7.6
β-ZAL	0.2	0.21	105.0	5.7	8.3	0.23	115.0	14.5	6.5
	2	2.22	111.1	2.8	5.3	2.22	111.0	5.3	6.9
	20	23.24	116.2	3.2	6.1	23.78	118.9	8.6	9.6
β-ZOL	0.2	0.23	115.0	6.7	6.8	0.23	114.8	3.4	6.3
	2	2.27	113.5	1.2	2.1	2.15	107.3	2.4	6.5
	20	23.32	116.6	0.8	5.7	23.56	117.8	3.4	5.9

Analyte	Spiked level ($\mu g\ kg^{-1}$)	Milk and their products				Vegetables and their products			
		Measured value ($\mu g\ kg^{-1}$)	R_M (Method recovery, %)	RSD (%)		Measured value ($\mu g\ kg^{-1}$)	R_M (Method recovery, %)	RSD (%)	
				Intra-day (n=6)	Inter-day (n=18)			Intra-day (n=6)	Inter-day (n=18)
15-ADON	2	1.99	99.4	4.4	8.5	2.18	108.9	5.5	9.3
	20	17.4	87	3.9	6.1	24.45	122.3	5.1	7.5
	200	182.9	90.6	5.3	6.6	252.3	126.1	2.1	6.3
3A-DON	2	2.00	100.2	1.9	6.1	1.86	93.1	5.1	8.3
	20	18.56	90.5	2.4	8.6	19.01	95.1	3.8	7.9
	200	184.3	92.1	4.3	7.6	181.7	90.8	2.9	5.1
AFB_1	0.04	0.03	85.8	6.1	9.3	0.036	90.8	6.7	9.6
	0.4	0.36	89.2	4.7	7.5	0.35	87.3	4.4	6.9
	4	3.36	84.0	6.4	8.8	3.45	86.3	4.5	8.2
AFB_2	0.01	0.009	90.6	3.0	6.3	0.01	109.1	8.7	10.5
	0.1	0.087	87.2	4.4	7.1	0.89	89.3	4.4	7.3
	1	0.89	88.6	5.4	9.2	0.88	88.1	4.5	6.3
AFG_1	0.04	0.04	93.8	1.1	6.2	0.036	64.1	9.1	10.2
	0.4	0.36	91.0	7.5	8.3	0.35	87.5	1.4	8.3
	4	3.59	89.7	5.9	7.2	3.45	86.6	4.2	6.5
AFG_2	0.01	0.009	89.7	8.9	10.1	0.01	100.4	3.7	5.5
	0.1	0.097	97.0	2.0	6.5	0.09	90.4	8.1	8.3
	1	0.91	90.6	11.1	12.3	0.88	93.9	4.7	6.9
AFM_1	0.01	0.01	96.6	9.5	8.6	0.01	96.5	9.8	11.2
	0.1	0.10	93.5	2.5	10.7	0.08	78.7	5.3	8.3
	1	0.74	84.1	5.4	6.5	0.92	91.7	3.9	4.5
AFM_2	0.01	0.01	117.4	2.1	5.5	0.01	93.0	10.7	11.2
	0.1	0.12	102.2	6.8	7.2	0.12	120.1	10.4	11.8
	1	0.74	73.7	8.6	9.3	1.12	111.8	3.3	6.5
ALT	2	1.83	91.5	2.6	8.5	2.69	134.6	8.1	10.2
	20	15.98	80.0	6.4	9.2	24.0	120.0	1.2	6.9
	200	218.5	109.3	3.5	6.3	199.5	99.8	3.5	4.3
AME	2	2.63	131.1	5.2	6.3	1.41	70.5	5.2	9.5

(*continued on next page*)

Table 3 (*continued*)

	20	21.86	109.3	5.1	8.6	14.36	71.8	2.5	6.6
	200	166.6	83.3	2.4	4.2	140.9	70.5	3.8	4.2
AOH	2	2.56	127.9	8.2	9.1	1.62	81.0	2.1	6.2
	20	19.57	97.8	6.5	8.2	24.16	120.8	3.5	6.4
	200	14.95	74.7	2.3	7.2	25.76	128.8	6.1	9.2
BEA	0.2	0.22	112.4	2.6	6.9	0.15	75.3	7.2	10.5
	2	2.84	141.9	3.5	7.6	1.99	99.7	2.4	7.1
	20	15.15	75.7	2.6	9.5	14.72	73.6	6.2	8.8
CIT	2	1.72	86.2	7.6	9.0	2.39	102.0	3.3	2.5
	20	18.32	91.5	1.3	2.2	18.23	91.1	1.9	3.8
	200	181.7	90.9	0.8	2.6	193.5	96.8	2.9	5.8
CPA	2	1.75	87.3	5.2	6.8	1.71	85.5	2.8	5.5
	20	18.6	93.0	4.3	8.9	21.94	109.7	5.8	4.2
	200	167.7	83.9	3.5	4.3	243.3	121.7	4.9	8.1
DAS	1	0.9	90.2	4.5	6.8	1.04	104.0	1.8	5.9
	10	8.43	84.3	9.7	10.2	9.79	97.9	3.1	6.3
	100	98.39	98.4	10.9	11.3	97.12	97.1	5.1	4.7
DOM-1	1	1.21	121.2	4.4	7.3	0.75	75.4	4.9	6.7
	10	12.56	125.6	3.7	8.3	9.23	92.3	1.2	7.2
	100	121.0	121	8.4	9.3	89.24	89.2	7.0	11.9
DON	2	1.98	99.1	3.2	6.5	2.12	105.9	2.8	5.5
	20	21.05	97.4	7.0	9.1	19.48	97.4	1.7	6.3
	200	205.6	102.8	3.6	5.5	205.2	102.6	3.0	8.1
DON-3-G	1	0.76	76.1	5.4	9.9	0.85	85.0	9.9	6.1
	10	7.18	71.8	2.5	8.3	8.68	86.8	6.5	8.3
	100	72.9	72.9	4.4	8.1	89.88	89.9	5.1	7.1
ENNA	0.2	0.26	130.5	3.4	7.2	0.15	75.5	3.2	10.1
	2	2.7	135.1	3.2	6.3	1.51	75.5	2.5	7.1
	20	26.02	130.1	8.2	11.3	14.23	71.2	7.2	11.2
$ENNA_1$	0.2	0.26	127.6	4.5	4.2	0.26	128.5	1.2	3.7
	2	2.02	100.8	1.3	6.3	1.83	91.4	2.4	2.5
	20	21.59	107.9	4.2	9.8	14.11	70.5	5.1	8.4
ENNB	0.2	0.19	93.9	5.2	7.6	0.14	71.9	4.1	6.6
	2	1.56	77.9	3.5	7.2	1.36	68.2	2.1	10.5
	20	18.01	90.0	5.8	11.4	16.73	83.7	5.8	6.3
$ENNB_1$	0.2	0.24	117.8	5.9	8.1	0.17	87.1	4.2	10.2
	2	1.97	98.4	2.4	6.3	1.95	97.4	3.1	5.8
	20	21.85	109.3	2.1	4.3	14.32	71.6	2.4	4.6
FB_1	1	0.97	97.0	2.7	4.8	1.0	100	2.4	4.9
	10	8.95	89.5	5.7	8.1	9.83	98.3	2.4	3.3
	100	91.22	91.2	5.9	6.3	90.4	90.4	5.6	6.6
FB_2	1	107.12	107.1	3.5	4.9	1.13	112.9	1.9	7.2
	10	10.33	103.3	4.1	5.2	8.9	89.0	1.3	2.3
	100	95.47	95.5	8.8	9.3	90.54	90.5	2.1	5.6
FB_3	1	0.93	93.3	1.5	2.8	1.08	108.4	4.4	3.9
	10	8.97	89.7	0.4	3.2	9.32	93.2	2.2	4.6
	100	90.09	90.1	7.5	9.4	91.94	91.9	2.7	6.1
Fus X	2	1.85	92.7	6.9	7.9	1.44	72.3	2.4	7.5
	20	15.62	78.1	5.3	6.8	21.9	109.5	5.1	9.2
	200	145.1	72.5	3.4	6.9	212.3	106.2	2.0	6.9
HT2	2	1.85	92.6	6.5	10.3	1.93	96.4	6.5	8.5
	20	19.5	97.5	2.3	7.5	20.69	103.4	1.8	2.9
	200	186.8	93.4	5.6	8.3	201.5	100.7	3.1	6.1
MON	2	1.76	88.0	7.6	7.6	1.65	82.5	2.7	5.5
	20	18.05	90.3	7.1	8.8	17.11	85.6	9.0	8.6
	200	183.4	91.7	3.5	10.5	171.5	85.8	2.0	10.5
NEO	1	0.80	80.0	2.0	9.6	0.92	91.9	3.6	5.5
	10	9.57	95.7	7.0	6.5	8.75	87.5	0.6	8.3
	100	96.33	96.3	3.8	4.6	82.19	82.2	10.8	11.1
NIV	2	1.77	88.6	3.1	8.1	1.56	78.2	5.6	5.1
	20	17.4	87.9	1.6	8.2	18.68	93.4	3.4	6.5
	200	181.2	92.3	4.2	7.5	189.2	94.6	1.1	4.9
OTA	0.2	0.21	104.0	0.9	2.1	0.2	97.9	6.5	8.3
	2	1.81	90.6	2.0	5.1	1.83	91.4	0.4	3.5
	20	17.71	88.6	1.1	3.2	18.28	91.4	2.2	4.6
OTB	0.2	0.17	84.7	0.4	4.6	0.18	91.5	6.3	8.2
	2	2.18	108.8	3.0	7.2	1.99	99.5	0.7	6.2
	20	16.82	86.1	2.6	6.5	18.96	94.8	2.4	3.5
PAT	2	1.22	68.8	9.0	11.9	1.94	97.1	9.4	9.3
	20	21.81	109.1	5.2	5.3	161.1	80.5	2.6	9.8
	200	182.9	91.5	3.5	6.2	181.8	90.9	2.9	6.7
SMC	0.2	0.16	78.5	5.1	8.3	0.21	106.6	2.5	4.7
	2	1.86	93.2	7.5	10.3	2.04	102.2	8.5	9.3
	20	20.43	102.1	6.8	8.9	21.07	105.3	8.0	10.2
T2	2	2.00	99.7	8.5	7.1	2.11	105.7	8.7	9.3
	20	20.31	101.6	8.8	9.6	18.59	93.0	9.0	7.8
	200	209.1	104.6	10.8	11.9	212.7	106.3	6.4	10.1

Table 3 (*continued*)

TeA	2	1.91	95.4	1.8	6.3	1.88	94.2	6.9	9.3
	20	18.63	93.2	3.5	5.9	17.5	87.5	3.2	5.5
	200	180.1	90.0	6.4	10.1	171.4	85.7	3.4	6.4
TEN	2	2.46	123.2	3.8	7.4	2.26	112.8	7.2	9.5
	20	21.5	107.5	5.2	10.2	20.06	100.3	2.8	3.2
	200	213.1	106.6	3.7	5.8	205.8	102.9	6.3	9.8
ZAN	0.2	0.20	98.5	2.9	5.1	0.17	83.5	0.7	4.3
	2	2.07	103.7	7.5	8.5	1.96	97.8	2.2	6.2
	20	21.81	109.0	2.3	7.9	20.52	102.6	3.5	4.5
ZEN	2	1.93	96.3	0.9	5.3	1.81	90.5	2.4	6.3
	20	18.57	92.8	2.6	6.1	17.89	89.4	0.5	4.1
	200	171.5	85.8	1.6	4.5	177.9	89.0	2.8	6.8
α-ZAL	0.2	0.24	120.1	2.3	6.1	0.17	85.3	2.1	5.9
	2	2.24	112.0	2.9	10.5	2.19	109.3	2.3	6.4
	20	22.89	114.4	2.1	6.2	21.17	105.9	0.5	8.1
α-ZOL	0.2	0.15	74.6	3.7	9.6	0.19	97.1	5.1	6.5
	2	1.53	76.4	0.8	6.7	1.54	76.9	1.1	7.8
	20	15.77	78.9	1.5	6.2	14.5	72.5	2.0	6.9
β-ZAL	0.2	0.23	115.0	5.0	8.9	0.21	103.1	5.7	8.1
	2	2.37	118.4	11.2	12.1	2.28	113.8	1.4	6.2
	20	24.73	123.6	0.6	6.3	23.24	116.2	2.2	7.6
β-ZOL	0.2	0.23	115.0	1.6	5.1	0.16	81.5	3.6	8.8
	2	2.35	117.3	1.8	10.3	2.11	105.3	0.7	7.5
	20	23.38	116.9	0.9	6.8	22.28	111.4	0.3	6.2

Analyte	Spiked level (μg kg^{-1})	Fruits and their products				Sugar and their products			
		Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%)		Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%)	
				Intra-day (n=6)	Inter-day (n=18)			Intra-day (n=6)	Inter-day (n=18)
15-ADON	2	1.79	89.5	6.5	9.3	2.06	102.8	7.2	9.3
	20	18.3	91.5	4.9	8.8	21.36	106.8	6.7	7.9
	200	181.7	90.9	5.3	7.9	230.8	115.4	3.3	5.1
3A-DON	2	2.05	102.5	5.2	6.0	1.91	95.4	5.7	6.2
	20	18.57	92.9	3.4	6.2	18.87	94.3	3.1	5.3
	200	184.3	92.1	4.1	5.8	190.5	95.2	6.6	5.9
AFB_1	0.04	0.03	75.4	5.8	6.1	0.04	99.5	0.2	4.2
	0.4	0.38	95.9	4.8	8.1	0.38	93.9	1.0	5.6
	4	3.46	86.5	7.4	6.5	3.68	92.1	5.7	8.9
AFB_2	0.01	0.009	90.7	6.2	4.1	0.008	82.2	4.4	6.1
	0.1	0.082	82.6	4.1	9.2	0.1	96.4	1.1	9.1
	1	0.83	83.8	5.3	5.5	0.72	91.8	2.9	4.8
AFG_1	0.04	0.04	92.6	7.2	9.1	0.037	92.1	7.5	10.9
	0.4	0.32	85.2	6.5	7.1	0.35	88.0	6.1	9.1
	4	3.69	92.3	5.9	8.2	3.83	95.6	7.5	5.6
AFG_2	0.01	0.009	92.5	5.2	6.5	0.01	97.6	8.3	9.9
	0.1	0.092	92.8	3.5	4.3	0.09	90.2	1.9	7.1
	1	0.83	83.4	2.1	4.6	1.00	99.7	6.9	8.5
AFM_1	0.01	0.01	92.4	8.5	9.1	0.09	87.8	1.2	6.1
	0.1	0.09	91.2	5.5	6.3	0.08	82.5	0.1	4.3
	1	0.84	84.8	5.8	8.1	0.83	83.2	9.8	6.1
AFM_2	0.01	0.01	85.9	3.9	6.1	0.01	95.6	2.4	8.2
	0.1	0.1	105.2	2.8	4.6	0.79	78.7	2.8	6.5
	1	0.84	84.8	4.9	7.1	0.7	70.4	7.5	10.8
ALT	2	2.17	108.7	2.4	10.5	2.54	126.9	2.8	6.5
	20	22.42	112.1	3.9	9.7	25.42	127.1	3.2	7.6
	200	252.4	126.2	2.1	4.4	232.5	116.2	2.4	6.9
AME	2	2.28	114.0	3.5	5.5	2.01	100.7	1.5	3.6
	20	14.69	73.3	2.4	3.6	19.19	95.9	3.2	8.6
	200	144.9	72.4	2.1	2.8	176.0	88.0	2.8	5.2
AOH	2	1.65	82.4	5.4	7.2	1.97	98.7	4.2	9.1
	20	23.33	116.7	3.6	8.1	15.29	76.5	2.4	8.2
	200	20.66	103.3	2.7	8.2	162.7	81.4	1.5	5.2
BEA	0.2	0.25	123.0	3.9	7.5	0.26	133.3	1.7	6.3
	2	1.31	65.3	2.6	7.9	1.54	76.8	3.8	9.2
	20	13.9	69.5	9.1	10.3	15.7	78.5	7.5	10.8
CIT	2	1.56	78.8	3.8	7.3	1.91	95.6	6.2	9.9
	20	17.35	86.8	5.2	7.7	17.18	85.9	1.4	5.8
	200	168.6	84.3	3,4	9.2	174.5	87.3	4.5	6
CPA	2	2.16	107.9	1.5	3.2	1.76	87.8	6.2	9.3
	20	16.03	80.2	4.8	6.9	14.97	74.9	4.2	6.8
	200	178.7	89.3	5.2	8.3	165.2	82.6	5.5	8.3
DAS	1	0.89	89.5	4.5	6.5	0.96	95.5	9.4	10.4
	10	8.73	87.3	7.7	8.1	10.86	108.6	6.0	6.7
	100	92.39	92.4	3.9	4.6	100.12	100.1	3.1	4.3
DOM-1	1	1.11	111.8	4.2	9.1	1.20	119.7	1.7	6.1
	10	11.96	119.6	2.7	4.6	12.37	123.7	9.0	8.5

(*continued on next page*)

Table 3 (*continued*)

	100	121.0	121.7	6.4	5.2	114.9	115.0	4.6	7.8
DON	2	1.88	94.5	4.2	8.1	2.18	108.9	7.5	6.6
	20	18.05	90.3	3.2	6.5	19.75	98.8	0.8	5.2
	200	195.6	97.8	4.6	7.3	191.7	95.9	2.9	4.4
DON-3-G	1	0.86	86.0	8.4	6.6	0.86	86.2	6.8	8.8
	10	92.18	92.2	6.5	10.6	9.21	92.1	11.6	13.6
	100	92.8	92.8	3.4	7.1	94.6	94.6	4.6	6.4
ENNA	0.2	0.29	144.5	3.9	5.6	0.21	105.9	3.2	9.7
	2	1.54	77.1	3.7	8.3	1.6	79.9	4.8	2.3
	20	15.52	77.6	3.9	8.3	16.85	84.2	8.7	11.8
$ENNA_1$	0.2	0.25	123.5	2.1	2.4	0.19	94.2	6.2	8.8
	2	1.33	66.6	1.6	6.3	1.66	82.9	2.5	5.1
	20	14.92	74.6	5.1	4.4	16.88	84.4	5.1	7.3
ENNB	0.2	0.15	77.2	4.2	7.6	0.16	82.2	5.6	10.8
	2	1.32	65.9	5.1	6.2	1.6	80.0	2.1	4.3
	20	13.96	69.8	5.6	7.4	16.59	82.9	6.6	11.4
$ENNB_1$	0.2	0.23	114.9	5.2	9.4	0.21	105.3	2.3	9.5
	2	1.34	66.9	2.5	3.8	1.62	80.9	5.7	9.1
	20	14.12	70.6	2.1	6.3	14.0	70.0	3.6	5.1
FB_1	1	0.81	80.5	1.9	3.9	0.85	85.1	2.2	6.4
	10	8.80	88.0	1.9	4.6	8.55	85.5	5.1	8.2
	100	90.81	90.8	4.6	5.2	84.11	84.1	7.1	7.4
FB_2	1	90.41	90.4	2.6	6.3	1.02	102.2	2.9	3.8
	10	10.36	103.6	4.2	5.8	10.72	107.2	3.8	4.3
	100	90.22	90.2	4.8	7.3	102.0	102.0	2.0	6.5
FB_3	1	0.85	85.4	0.6	3.5	0.95	94.8	2.6	4.8
	10	9.62	96.2	5.1	6.9	10.08	100.8	3.7	7.1
	100	72.41	72.4	4.8	8.2	103.1	103.1	3.2	5.5
Fus X	2	1.82	91.4	2.9	5.6	1.75	87.5	4.3	6.7
	20	16.72	83.6	5.3	3.8	17.71	88.5	8.8	9.9
	200	152.4	76.2	8.4	9.1	168.8	94.4	3.8	7.2
HT2	2	1.83	91.5	6.5	7.4	1.95	97.5	8.7	10.9
	20	18.5	92.5	3.3	6.1	1.84	98.6	1.8	6.7
	200	176.4	88.2	5.6	7.6	179.8	89.9	11.8	10.1
MON	2	1.77	88.5	10.6	12.5	1.87	83	10.6	12.8
	20	19.14	95.7	8.1	3.6	17.76	88.8	3.8	8.2
	200	190.6	95.3	1.5	10.8	199.1	99.6	3.5	8.4
NEO	1	0.80	80.8	8.0	8.9	1.15	115.4	3.8	5.2
	10	9.17	91.7	7.5	10.2	11.76	117.6	0.8	4.9
	100	91.33	91.3	3.8	7.3	97.03	97	5.9	6.8
NIV	2	1.67	83.5	8.1	9.3	1.86	93.2	2.6	6.5
	20	16.3	81.5	2.6	5.5	16.71	83.6	5.8	7.9
	200	175.2	87.6	4.2	4.9	191.4	95.7	0.5	2.6
OTA	0.2	0.21	106.5	8.9	6.5	0.19	92.9	3.1	5.2
	2	1.86	92.9	5.4	6.8	1.83	91.3	3.6	6.3
	20	17.71	88.5	0.1	3.2	18.22	91.1	1.1	4.2
OTB	0.2	0.23	115.1	7.1	8.2	0.22	91.2	2.6	5.8
	2	1.85	92.6	2.3	4.5	1.7	84.9	4.2	6.9
	20	18.84	94.9	1.8	3.4	15.61	78.1	3.9	4.2
PAT	2	1.42	71.8	2	5.4	1.68	81.2	3.6	8.1
	20	17.51	87.6	6.2	10.2	16.84	84.2	0.3	4.6
	200	181.4	90.7	2.5	5.3	185	92.5	2.6	5.8
SMC	0.2	0.17	85.9	5.1	6.2	0.19	95.0	1.6	7.4
	2	1.86	93.4	3.5	4.3	1.82	91.1	6.5	8.2
	20	19.43	97.2	6.8	8.0	17.64	88.2	10.4	11
T2	2	1.8	90.1	5.5	10.2	1.7	85.1	4.6	5.2
	20	22.31	111.6	7.8	8.5	19.88	99.4	2.9	6.2
	200	209.0	104.5	4.8	6.3	192.8	96.4	12	12.8
TeA	2	1.98	98.9	3.3	5.3	1.92	96.0	3.4	9.3
	20	17.07	85.3	8.2	10.9	18.89	94.5	1.8	5.5
	200	173.2	86.6	6.1	7.6	179.8	89.9	6.4	7.8
TEN	2	2.41	120.6	2.5	6.4	1.87	93.5	3.2	4.6
	20	21.19	105.9	9.2	10.8	16.35	81.8	2.1	6.4
	200	209	104.5	3.5	9.8	176.8	88.4	3.1	7.1
ZAN	0.2	0.22	110.5	3.2	3.1	0.2	102.0	0.7	6.2
	2	2.17	108.5	8.5	7.7	2.07	103.4	2.6	5.5
	20	22.41	112.1	5.3	8.5	22.44	112.2	1.5	8.8
ZEN	2	1.83	91.5	2.3	6.5	1.87	93.5	3.0	4.6
	20	16.37	81.9	2.8	8.2	18.57	92.9	2.5	3.8
	200	182.3	91.2	1.6	3.1	175.8	87.9	2.8	6.2
α-ZAL	0.2	0.23	115.8	6.3	6.9	0.22	108.1	0.4	4.2
	2	2.14	107.4	4.9	7.7	2.29	114.5	1.5	2.4
	20	22.69	113.5	2.1	5.6	21.45	107.3	2.0	3.1
α-ZOL	0.2	0.16	80.6	2.7	4.7	0.16	82.0	1.0	2.5
	2	1.63	81.5	2.8	3.5	1.83	91.3	1.9	5.8
	20	16.77	83.9	6.5	4.9	18.24	91.2	4.1	8.5

Table 3 (*continued*)

β-ZAL	0.2	0.22	110.0	7.2	6.5	0.23	113.4	0.7	3.6
	2	2.37	118.5	8.2	9.2	2.51	125.7	2.6	4.9
	20	23.53	117.7	3.6	8.9	23.44	117.2	1.5	3.8
β-ZOL	0.2	0.25	125.0	3.6	7.3	0.26	130.0	0.4	7.5
	2	2.45	122.5	6.8	5.1	2.15	107.7	1.5	6.9
	20	24.28	121.4	0.9	3.8	22.67	113.3	2.0	4.1

Analyte	Spiked level (μg kg^{-1})	Beverages and water				Alcohol beverages			
		Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%)		Measured value (μg kg^{-1})	R_M (Method recovery, %)	RSD (%)	
				Intra-day (n=6)	Inter-day (n=18)			Intra-day (n=6)	Inter-day (n=18)
15-ADON	2	2	100.2	3.7	6.2	1.65	82.5	6.1	7.2
	20	22.38	112	2.5	7.6	16.18	80.9	5.6	6.3
	200	205.9	102.9	4.1	8.9	163.9	81.9	4.8	8.2
3A-DON	2	1.89	94.7	1.5	3.8	2.33	116.5	4.8	5.2
	20	19.58	97.9	3.8	8.5	20.23	101.1	3.8	4.1
	200	194.9	97.5	7.3	10.2	180.2	90.1	4.2	8.5
AFB_1	0.04	0.04	96.6	3.8	4.3	0.04	95.8	0.6	5.2
	0.4	0.37	92.2	3.7	5.2	0.36	89.2	2.9	4.1
	4	3.6	90.0	1.7	3.5	3.88	97.0	2.6	5.3
AFB_2	0.01	0.009	91.2	5.4	6.9	0.01	85.0	2.4	9.1
	0.1	0.09	89.8	3.9	6.4	0.1	100.1	6.5	8.5
	1	0.92	92.6	3.4	7.1	0.97	97.1	3.9	8.1
AFG_1	0.04	0.04	92.1	6.8	6.9	0.04	132.0	2.2	6.5
	0.4	0.39	97.3	3.2	7.8	0.54	135.4	2.1	7.8
	4	3.92	98.0	4.3	5.9	3.93	98.3	1.2	4.1
AFG_2	0.01	0.01	100.0	6.1	6.8	0.01	100.2	3.5	6.2
	0.1	0.09	86.8	1.6	6.3	0.11	106.5	0.4	7.2
	1	0.99	98.9	5.2	7.1	0.96	96.0	9.9	9.5
AFM_1	0.01	0.01	92.0	7.2	9.3	0.01	113.5	2.9	5.1
	0.1	0.09	92.6	6.7	8.8	0.12	117.2	7.0	8.2
	1	0.92	92.5	5.8	6.1	0.90	90.0	2.1	6.6
AFM_2	0.01	0.01	100.1	3.1	7.5	0.01	116.8	3.1	4.5
	0.1	0.11	110.0	3.0	5.9	0.13	130.3	1.9	3.1
	1	1.04	104.5	8.3	6.1	1.21	121.2	2.9	7.1
ALT	2	1.99	99.7	5.3	10.2	2.41	120.5	3.7	4.5
	20	17.45	87.2	8.4	11.3	24.31	121.6	4.5	6.9
	200	222.6	111.3	1.6	5.3	199.4	99.7	5.7	7.3
AME	2	1.46	73.2	3.1	5.4	1.31	65.5	4.8	6.5
	20	15.58	77.9	2.2	6.2	16.61	83.0	3.2	5.8
	200	149.8	74.9	7.6	10.3	157	78.5	6.2	8.2
AOH	2	1.57	78.6	2.2	4.8	2.67	133.4	4.8	6.2
	20	14.1	70.5	2.5	5.1	14.08	70.4	6	10.2
	200	136.7	68.3	3.5	6.2	166.4	83.2	1.5	3.2
BEA	0.2	0.15	75.3	2.8	5.8	0.13	63.1	7.4	8.9
	2	1.55	77.3	4.3	7.5	1.35	67.6	2	4.5
	20	14.94	74.7	2.1	5.9	12.69	63.5	6.5	8.8
CIT	2	1.43	71.7	6.9	8.3	1.58	78.9	5.1	7.9
	20	16.61	83.1	4.8	9.3	17.59	88.0	2.2	6.4
	200	163.6	81.8	6.2	8.2	159.5	79.8	4.5	8.5
CPA	2	2.1	105.9	1.2	3.5	1.52	75.9	4.5	8.2
	20	24.8	124,2	4.6	7.3	16.56	82.8	5.2	7.2
	200	205.7	102.9	2.8	6.3	150.3	75.1	6.2	8.6
DAS	1	1.01	100.7	3.7	7.5	1.12	112.1	4.4	7.8
	10	9.65	96.5	4.9	8.3	9.49	95.0	6.9	10.7
	100	87.08	87.1	11.9	9.1	84.94	84.9	1.6	3.1
DOM-1	1	0.77	77.2	9.8	11.1	0.68	68.2	4.6	6.9
	10	9.27	92.7	4.1	6.5	8.04	80.4	1.4	4.2
	100	86.1	86.1	10.7	11.6	84.65	84.7	6.9	8.1
DON	2	2.02	101.1	5.3	9.1	2.01	101.0	8.0	6.2
	20	19.29	96.5	1.4	4.5	20.13	100.7	7.9	8.5
	200	206.2	103.1	6.1	10.9	218.6	109.3	7.7	9.3
DON-3-G	1	1.02	102.1	1.6	8.5	1.21	121.0	6.8	8.1
	10	10.75	107.5	4.9	6.6	12.06	120.6	4.5	6.7
	100	101.8	101.9	3.5	7.1	120.4	120.4	5.8	8.2
ENNA	0.2	0.17	82.5	3.8	8.6	0.12	60.3	3.3	6.2
	2	1.54	77.2	1.3	3.5	1.30	64.8	2.7	5.3
	20	16.47	82.3	2.3	6.2	14.0	70.2	7.5	10.3
$ENNA_1$	0.2	0.18	89.7	1.8	4.5	0.13	64.5	8.1	10.2
	2	1.49	74.6	5.6	8.8	1.21	60.6	1.3	3.3
	20	17.15	85.8	2.4	6.9	12.22	61.1	2.5	5.4
ENNB	0.2	0.15	72.9	3.2	5.9	0.14	72.5	3.8	5.6
	2	1.35	67.3	5.5	10.2	1.77	88.8	10.3	11.2
	20	16.77	83.9	7.3	11.2	15.87	79.3	2.1	5.4
$ENNB_1$	0.2	0.17	84.6	1.4	5.5	0.17	84.2	3.9	5.5
	2	1.42	70.8	2.9	5.6	1.52	76.0	4.5	8.2

(*continued on next page*)

Table 3 (*continued*)

	20	16.91	84.6	1.4	8.3	15.1	75.5	8.4	11.3
FB_1	1	0.85	85.0	2.6	4.3	0.83	83.3	2.7	4.6
	10	8.83	88.3	4.2	5.3	8.65	86.5	5.1	5.2
	100	79.5	79.4	3.6	4.6	89.42	89.4	3.7	6.6
FB_2	1	0.86	85.9	3.8	7.1	0.85	85.3	6.5	4.3
	10	8.93	89.3	2.3	5.3	10.84	108.4	4.1	7.8
	100	90.75	90.8	4.1	3.6	112.6	112.6	3.5	5.7
FB_3	1	1.22	122.4	3.4	6.4	1.13	113.2	6.8	4.6
	10	9.12	91.2	5.2	6.7	11.35	113.4	3.2	3.5
	100	82.43	82.4	6.1	7.8	117.7	117.7	5.2	6.9
Fus X	2	1.8	90.2	5.1	3.6	1.48	74.0	8.2	9.3
	20	18.23	91.2	2.2	4.2	15.5	77.5	3.7	8.1
	200	194.3	97.1	3.2	6.6	136.4	68.2	1.8	3.5
HT2	2	1.95	97.5	2.7	10.3	2.01	100.5	3.7	8.1
	20	19.27	96.3	3.0	9.5	18.62	93.1	2.8	4.6
	200	184.5	92.2	1.8	6.3	189.0	94.5	7.8	10.9
MON	2	1.67	83.5	1.6	5.1	1.62	81	0.5	4.9
	20	16.21	81.1	5.5	7.5	17.22	86.1	2.1	6.1
	200	180.3	90.1	2.7	7.9	166.7	83.3	2.1	6.3
NEO	1	0.71	71.5	8.8	7.7	0.73	72.5	3.8	6.3
	10	7.76	77.6	3.2	6.2	7.27	72.7	8.2	10.6
	100	66.69	66.7	9.9	11.9	94.42	94.4	4.5	6.1
NIV	2	2	99.9	4.7	6.1	2.37	118.6	8.9	9.5
	20	18.36	91.8	2.5	6.7	20.59	102.9	3.9	6.1
	200	202.2	101.1	4.1	6.8	204.3	102.2	4.7	7.9
OTA	0.2	0.19	95.9	3.5	6.3	0.16	89.3	4.3	5.5
	2	1.75	87.4	2.4	5.2	1.65	89.1	4.1	6.3
	20	18.42	92.4	3.2	4.7	19.69	97.5	1.2	5.6
OTB	0.2	0.16	81.5	5.3	4.2	0.17	86.0	4.2	7.5
	2	1.86	89.5	0.9	5.2	1.89	95.6	3.8	5.6
	20	18.36	91.8	1.4	3.2	15.23	75.3	1.5	4.2
PAT	2	1.79	89.5	1.8	9.2	2.13	106.4	1.6	7.6
	20	17.42	87.1	3.5	6.3	22.2	111.0	9.6	9.8
	200	178.5	89.3	1.7	4.7	196	98.0	2.1	4.5
SMC	0.2	0.18	89.8	8.5	6.2	0.21	104.1	10.8	7.2
	2	1.77	88.4	4.3	9.8	1.79	89.9	7.0	9.3
	20	19.46	97.3	10.3	7.6	17.68	88.4	2.4	6.5
T2	2	2.25	112.5	3.2	6.2	2.09	104.5	5.0	7.9
	20	23.06	115.3	9.5	8.8	23.5	93.1	3.5	8.3
	200	222.6	111.3	5.6	4.2	239.5	94.5	9.0	6.9
TeA	2	1.77	88.46	2.4	6.4	2.53	126.4	1.2	3.3
	20	18.65	93.2	1.4	4.6	18.52	92.6	3.1	4.5
	200	178.5	89.3	7.8	10.5	172.7	86.3	2.7	6.4
TEN	2	2.06	103.1	2.3	5.5	2.52	125.9	2.2	5.4
	20	19.98	99.9	3.0	6.3	26.34	131.7	1.6	3.2
	200	222.8	114.2	4.4	5.8	232.9	116.4	2.6	8.8
ZAN	0.2	0.21	103.2	3.7	8.9	0.17	83.6	2.2	11.1
	2	2.02	101.2	7.0	9.3	2.01	100.7	4.6	8.3
	20	22.28	111.4	3.8	10.1	20.5	102.5	0.9	4.8
ZEN	2	1.87	93.5	2.7	4.9	1.96	97.8	2.8	4.2
	20	18.47	92.4	1.4	8.7	19.21	96.1	4.0	6.3
	200	181.2	90.6	3.3	6.1	181.6	90.8	0.9	4.5
α-ZAL	0.2	0.22	111.9	3.8	6.3	0.19	96.9	7.9	8.1
	2	2.18	108.9	0.4	4.1	1.91	95.5	1.5	3.5
	20	21.81	109.1	2.7	6.1	21.22	106.1	1.1	6.2
α-ZOL	0.2	0.16	78.2	6.3	7.5	0.21	102.9	0.5	4.1
	2	1.53	76.3	1.6	3.2	1.68	84.0	0.7	3.5
	20	16.6	83.0	4.9	4.0	16.77	83.8	1.7	4.2
β-ZAL	0.2	0.21	103.6	6.4	9.9	0.22	110.0	1.4	3.1
	2	1.92	96.1	5.0	7.1	1.93	96.4	3.9	4.2
	20	20.1	100.5	4.2	6.6	21.64	108.2	4.7	8.2
β-ZOL	0.2	0.19	95.8	5.7	7.9	0.17	85.2	9.3	10.9
	2	1.96	97.9	3.9	5.1	1.79	89.4	8.6	7.1
	20	17.65	88.3	5.5	8.5	19.82	99.1	2.2	6.3

60.3% to 175.9%; intra- and inter-day precisions (RSD) were 0.2%–12.2% and 2.1%–13.9%, respectively (Table 3).

Application to dietary samples

For practical application, the developed methods were utilized for detecting 43 mycotoxins in dietary samples collected in six provinces (Hebei, Beijing, Jilin, Hubei, Guangdong, and Guizhou) in the 6th China TDS. The levels of the 43 mycotoxins were obtained, and the results are presented in Table 4. Representative MRM chromatograms of naturally polluted samples are shown in Fig. 5. Among 72 dietary samples, 60 (83.3%) contained at least one mycotoxin. Overall, mycotoxin contamination varied significantly among food categories. ZEN (45.8%), FB_1 (30.6%), DON (26.4%), AFB_1 (22.2%), and emerging mycotoxins had high rates of detection, with values above 20%. Meanwhile, 15A-DON, DOM-1, AFM_1, AFM_2, AFG_2, OTA, AOH, MON, PAT, T2, HT2, DAS, NEO, CPA and CIT were not detected in any samples. Cereals, legumes, and their respective products were the main contaminated food types. In contrast, sugar, beverages and water were barely contaminated.

Table 4
The occurrence of 43 mycotoxins in 72 food samples from 12 food categories collected in six provinces for the 6th China TDS.

Food composites		Cereals	Legume	Potatoes	Meats	Eggs	Aquatic foods	Dairy products	Vegetables	Fruits	Sugar	Beverages and water	Alcohol beverages
15A-DON	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3A-DON	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	1/6	0/6	0/6	0/6	1/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	1.65	ND	ND	ND	2.74	ND	ND	ND	ND
AFB_1	Positive samples/ Samples analyzed (n/n)	3/6	3/6	1/6	3/6	1/6	3/6	0/6	2/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	0.02–0.07	0.11–1.38	0.04	0.02–0.05	0.05	0.02–0.08	ND	0.04–0.07	ND	ND	ND	ND
AFB_2	Positive samples/ Samples analyzed (n/n)	0/6	2/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	0.03–0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
AFG_1	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	1/6	0/6	0/6	0/6	0/6	1/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	0.02	ND	ND	ND	ND	0.02
AFG_2	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
AFM_1	Positive samples/ Samples analyzed (n/n)	0/6	2/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	0.02–0.03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
AFM_2	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
ALT	Positive samples/ Samples analyzed (n/n)	1/6	0/6	0/6	0/6	0/6	0/6	0/6	1/6	1/6	0/6	0/6	0/6
	Range (μg kg^{-1})	7.90	ND	ND	ND	ND	ND	ND	8.76	1.71	ND	ND	ND
AME	Positive samples/ Samples analyzed (n/n)	6/6	2/6	3/6	0/6	1/6	2/6	0/6	2/6	0/6	1/6	1/6	2/6
	Range (μg kg^{-1})	0.14–10.53	0.23–1.77	0.08–2.41	ND	0.72	0.17–0.38	ND	1.00–1.10	ND	0.12	0.16	0.27–1.00
AOH	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BEA	Positive samples/ Samples analyzed (n/n)	4/6	5/6	6/6	3/6	4/6	4/6	3/6	2/6	1/6	0/6	0/6	1/6
	Range (μg kg^{-1})	0.22–1.77	0.17–5.46	0.19–2.58	0.16–1.07	0.27–6.70	0.32–1.02	0.16–6.31	1.85–1.93	1.21	ND	ND	4.38
CIT	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0	0	0	0	0	0	0	0
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
CPA	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DAS	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DOM-1	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0	0	0	0	0	0
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DON	Positive samples/ Samples analyzed (n/n)	6/6	2/6	3/6	1/6	0/6	2/6	0/6	1/6	0/6	0/6	0/6	4/6
	Range (μg kg^{-1})	4.22–75.56	2.13–4.65	1.67–22.52	2.51	ND	0.94–1.84	ND	0.71	ND	ND	ND	0.73–11.79
DON-3-G	Positive samples/ Samples analyzed (n/n)	2/6	0/6	0/6	1/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	1/6
	Range (μg kg^{-1})	5.04–12.45	ND	ND	0.45	ND	ND	ND	ND	ND	ND	ND	3.33
ENNA	Positive samples/ Samples analyzed (n/n)	2/6	3/6	3/6	1/6	3/6	2/6	2/6	0/6	0/6	0/6	0/6	1/6
	Range (μg kg^{-1})	0.12–0.16	0.26–1.26	0.17–1.13	0.24	0.38–1.55	0.19–0.30	0.15–1.38	ND	ND	ND	ND	0.16
$ENNA_1$	Positive samples/ Samples analyzed (n/n)	2/6	3/6	2/6	1/6	3/6	2/6	1/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	0.10–0.22	0.22–0.29	0.15–0.18	0.23	0.24–0.51	0.18–0.21	0.25	ND	ND	ND	ND	ND
ENNB	Positive samples/ Samples analyzed (n/n)	5/6	6/6	5/6	5/6	5/6	6/6	2/6	5/6	2/6	0/6	0/6	1/6
	Range (μg kg^{-1})	0.21–0.69	0.05–2.10	0.21–2.38	0.05–3.45	0.07–3.75	0.07–4.88	0.02–0.09	0.11–0.29	0.05–0.83	ND	ND	0.13
$ENNB_1$	Positive samples/ Samples analyzed (n/n)	2/6	4/6	5/6	2/6	4/6	3/6	1/6	2/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	0.21–0.35	0.14–0.73	0.12–	0.11–	0.09–	0.22–	0.87	0.15–0.26	ND	ND	ND	ND

(*continued on next page*)

Table 4 (*continued*)

Food composites		Cereals	Legume	Potatoes	Meats	Eggs	Aquatic foods	Dairy products	Vegetables	Fruits	Sugar	Beverages and water	Alcohol beverages
				0.53	0.65	0.87	0.89						
FB_1	Positive samples/ Samples analyzed (n/n)	5/6	4/6	4/6	3/6	1/6	2/6	0/6	0/6	0/6	0/6	0/6	3/6
	Range (μg kg^{-1})	0.06–7.54	0.13–1.72	0.07–0.58	0.13–2.08	0.09	0.11–0.30	ND	ND	ND	ND	ND	0.22–2.16
FB_2	Positive samples/ Samples analyzed (n/n)	2/6	0/6	1/6	1/6	1/6	1/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	0.90–4.39	ND	0.22	0.14	0.10	0.80	ND	ND	ND	ND	ND	ND
FB_3	Positive samples/ Samples analyzed (n/n)	2/6	2/6	1/6	1/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	0.85–9.24	0.14–0.17	0.23	0.46	ND	ND	ND	ND	ND	ND	ND	ND
Fus X	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	1/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	6.92	ND	ND
HT2	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
MON	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
NEO	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
NIV	Positive samples/ Samples analyzed (n/n)	1/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	4.84	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
OTA	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
OTB	Positive samples/ Samples analyzed (n/n)	0/6	2/6	0/6	0/6	0/6	0/6	0/6	1/6	1/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	0.05–0.12	ND	ND	ND	ND	ND	0.09	0.25	ND	ND	ND
PAT	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
SMC	Positive samples/ Samples analyzed (n/n)	5/6	3/6	4/6	3/6	1/6	1/6	0/6	4/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	0.02–0.04	0.05–1.87	0.10–0.13	0.03–0.09	0.07	0.04	ND	0.09–0.17	ND	ND	ND	ND
T2	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TeA	Positive samples/ Samples analyzed (n/n)	6/6	1/6	0/6	1/6	1/6	2/6	2/6	1/6	0/6	0/6	0/6	4/6
	Range (μg kg^{-1})	2.17–15.17	0.86	ND	1.29	14.38	0.68–1.57	1.54–2.06	1.14	ND	ND	ND	2.45–17.62
TEN	Positive samples/ Samples analyzed (n/n)	4/6	2/6	2/6	1/6	2/6	2/6	0/6	3/6	1/6	1/6	1/6	3/6
	Range (μg kg^{-1})	0.73–7.70	0.28–0.43	0.15–0.35	0.32	0.15–0.26	0.66–0.68	ND	0.18–0.83	0.16	0.12	0.16	0.16–1.18
ZAN	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
ZEN	Positive samples/ Samples analyzed (n/n)	5/6	6/6	6/6	5/6	3/6	4/6	0/6	4/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	0.27–0.83	0.16–0.51	0.16–1.02	0.12–1.23	0.18–0.83	0.11–1.99	ND	0.23–0.99	ND	ND	ND	ND
α-ZAL	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
α-ZOL	Positive samples/ Samples analyzed (n/n)	1/6	0/6	0/6	1/6	0/6	0/6	0/6	1/6	1/6	0/6	0/6	0/6
	Range (μg kg^{-1})	0.07	ND	ND	0.06	ND	ND	ND	1.62	1.23	ND	ND	ND
β-ZAL	Positive samples/ Samples analyzed (n/n)	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	4/6	0/6	0/6	0/6
	Range (μg kg^{-1})	ND	ND	ND	ND	ND	ND	ND	ND	0.09–1.05	ND	ND	ND
β-ZOL	Positive samples/ Samples analyzed (n/n)	0/6	1/6	0/6	2/6	0/6	1/6	0/6	0/6	0/6	0/6	0/6	1/6
	Range (μg kg^{-1})	ND	0.17	ND	0.92–0.92	ND	0.93	ND	ND	ND	ND	ND	0.28

ND: level below LOD; positive sample refers to a sample with a result above the LOD.

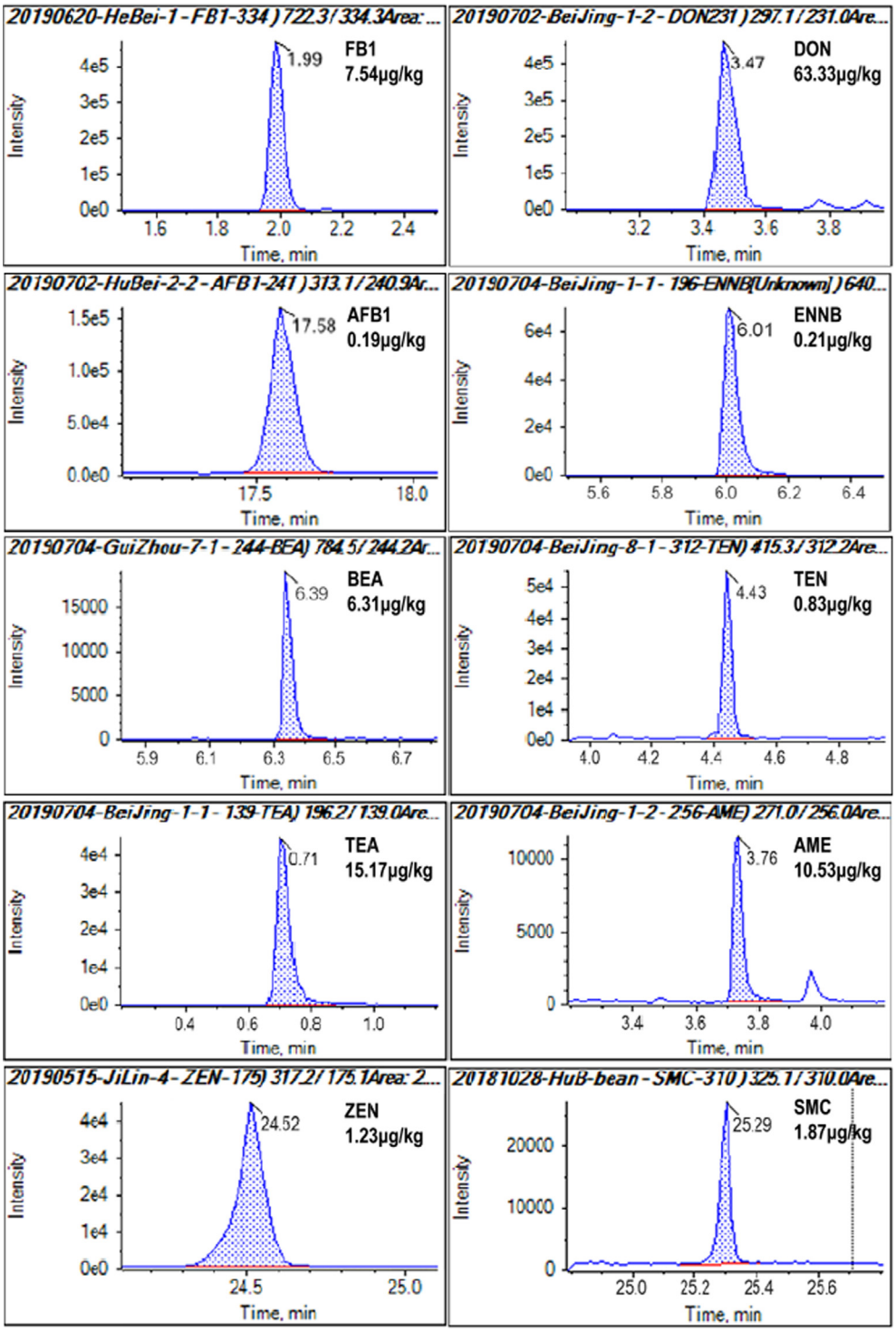

Fig. 5. Representative MRM-chromatograms of food samples with natural contaminations of mycotoxins.

Among ZEN and derivatives, ZEN showed the highest detection rate of 45.8%, followed by β-ZOL (6.9%), β-ZAL (5.6%), and α-ZOL (5.6%). ZAN and α-ZAL were not detected. ZEN was most frequently detected in cereals, legumes, potatoes, meats, eggs, aquatic foods and vegetables, with more than half of the samples testing positive.

Among DON and its derivatives, the detection rate of DON was 26.4%, with amounts ranging from 0.71 μg kg^{-1} to75.56 μg kg^{-1}. Cereals, legumes, potatoes, meats, aquatic foods, and alcohols, all showed mycotoxin presence, but the rates of positive samples were quite different among food categories. Cereals was the highest, with all the samples testing positive. DON contamination was greatly affected by climate, especially in the hot-humid area and the middle-lower reach of the Yangtze River, where the rain season was conducive to growth of mold and toxin production. The most elevated DON amounts were detected in cereals from Hubei at 75.56 μg kg^{-1}. DON-3-G (5.6%) and 3A-DON (2.8%) were rarely detected. Fus X and NIV were found only in one sample, and 15A-DON and DOM-1 were not detected in any samples.

Table 5
A summary of the mycotoxin analytical methods used in the different TDSs.

Country	Analyzed mycotoxins	Analyzed food	Food preparation	Analytical technique	Reference
France	AFB_1, AFB_2, AFG_1, AFG_2, AFM_1, OTA, PAT, ZEN, FB_1, FB_2, DON, NIV,3AcDON, 15AcDON, T-2, T-2 triol, HT-2, NEO, FUS-X, DAS, MAS	Vegetarians food; biscuits; breakfast cereals; breads; pasta; rice; cakes; chocolates; desserts; nuts and oilseeds; vegetables; pulses; eggs; sugars; breads, buns; butter; dairy products; coffee; meat; offal; fruits; soft drinks; alcoholic beverages; pizzas, salt cakes, quiches; sandwiches; soup; prepared dishes; salads; compotes	AFBG, AFM_1, OTA, ZEN, FB_1,FB_2: IAC; PAT: Sodium carbonate solution; Trichothecenes: Celite/carbon column.	AFBG, OTA,FB_1,FB_2: HPLC; PAT: HPLC-UV; Trichothecenes: GC–MS; AFM_1, OTA, ZEN: HPLC-FD	[7]
France	AFB_1, AFB_2, AFG_1, AFG_2, AFM_1, OTA, OTB, PAT, T-2, HT-2, NIV, DON, 3-Ac-DON, 15-Ac-DON, ZEN, α-ZAL, β-ZAL, α-ZOL, β-ZOL, FB_1,FB_2	Breads; breakfast cereals; pasta; rice; croissants; pastries; biscuits; cakes; milk; dairy products; eggs; butter; offal; delicatessen meat; vegetables; fruits; dried fruits; nuts and seeds; chocolate; non-alcoholic beverages; alcoholic beverages; coffee; pizzas; sandwiches; snacks; mixed dishes; desserts; compotes	AFM_1: IAC; FB_1, FB_2, OTA, PAT, TCTs A and B, ZEA: extraction without purification	AFM_1: IAC–LC–FD; FB_1, FB_2, OTA, PAT, TCTs A and B, ZEA: LC-MS/MS	[8,9]
Netherlands	AFB_1, AFB_2, AFG_1, AFG_2, AFM_1, AOH, AME, BEA, CIT, ENNA, $ENNA_1$, ENNB, $ENNB_1$, OTA, PAT, ZEN, α-ZOL, β-ZOL, STE, FB_1, FB_2, FB_3, DON, DON-3G,FUS-X, NEO, DAS, NIV, 3A-DON, 15A-DON, T-2, HT-2, MON, MPA, NPA, PeA, ROC and 13 Ergot alkaloids	Grains and grain-based products; legumes; meat and offal, nuts and seeds; oils and fats; soy products; tuber; vegetables	PAT: extraction without purification; AFB_1, AFB_2, AFG_1, AFG_2, AFM_1: IAC; Trichothecenes: SPE; Other mycotoxins: extraction without purification	PAT: HPLC-MS/MS; AFM_1: HPLC-FLD; AFB_1, AFB_2, AFG_1, AFG_2: HPLC-FLD; Trichothecenes: GC–MS/MS; Other mycotoxins: LC-MS/MS	[10,11,12]
Hong Kong (China)	AFB_1, AFB_2, AFG_1, AFG_2, OTA, FB_1, FB_2, FB_3, DON, AcDONs, ZEN, α-ZOL, β-ZOL	Cereals and their products, Vegetables and their products, Legumes, nuts and seeds and their products, Fruits, Meat, poultry and game and their products, Fats and oils, Beverages, alcoholic, Mixed dishes, Snack foods, Sugars and confectionery, Condiments, sauces and herbs	extraction without purification	UPLC-MS/MS	[20]
Spain	AFM_1	Milk; dairy products	IAC	HPLC-FD	[38,39]
Spain	AFB_1, AFB_2, AFG_1, AFG_2, OTA, ZEN, FB_1, FB_2, DON, NIV, 3A-DON, 15A-DON,T-2, HT-2, T-2 triol, NEO, Fus-X, DAS	Cereal and cereal products; olives; pickles; apple; pear; eggs; milk; milk shakes; custards; soya products; cheeses; grapes; alcoholic beverages; juices; oils	extraction without purification	UHPLC	[3]
Lebanon	AFB_1, AFM_1, OTA, DON	Bread and toast; biscuits and croissants; cakes and pastries, pasta and other cereal products; pizza and pies; rice and rice-based products; pulses; olive oil, sesame oil, and other oils; nuts, seeds, olives and dried dates; cheese; milk and milk-based beverages; milk-based ice cream and pudding; yogurt and yogurt-based products; caffeinated beverages; alcoholic beverages	Food samples (except for "Olive oil, sesame oil and other oils") extraction without purification; For "Olive oil, sesame oil and other oils", liquid–liquid extraction and IAC	LC-FD	[13]
Canada	OTA	Cereal and cereal products; alcohol drinks; coffee; tea; beans; fruits; sugars; chocolate; cheese; milk; eggs; dessert; meat; herb and spices; dried fruits; soya products; mixed dishes	IAC	LC-MS/MS	[14]
Australia New Zealand	AFB_1, AFB_2, AFG_1, AFG_2, AFM_1, AFM_2	Alcoholic and non-alcoholic beverages; cereal and cereal products; condiments; dairy products; eggs; fats; oils; fish; seafood; fish products; fruits; meat products; nuts and seeds; snacks; sugars; vegetables; infant food	—	HPLC-UV	[37]
Australia New Zealand	AFB_1, AFB_2, AFG_1, AFG_2, OTA	Alcoholic non-alcoholic beverages; cereal and cereal products; condiments; dairy products; eggs; fats; oils; fish; seafood; fish products; fruits; meat products; nuts and seeds; snacks; sugars; vegetables; infant food	—	—	[40]
Australia New Zealand	AFB_1, AFB_2, AFG_1, AFG_2, AFM_1, OTA, PAT, ZEA, FB_1, FB_2, DON	Alcoholic and non-alcoholic beverages; cereal products; condiments; dairy products; eggs; fats; oils; fish; fruits; meat; nuts; seeds; snacks; sugars; vegetables; infant food, beverages; fast food	—	—	[15]

Table 5 (*continued*)

Country	Analyzed mycotoxins	Analyzed food	Food preparation	Analytical technique	Reference
Viet Nam	AFB_1, OTA, FBs	Rice and products; Wheat and products; Other cereals; Tubes, root and products; Beans and products; Tofu; Oily seeds; Vegetables; Sugar, confectionary; Seasoning; Oil, fat; Meat and products; Egg and milk; Fish; Other aquatic products	extraction without purification	ELISA	[16]
Ireland	AFB_1, AFB_2, AFG_1, AFG_2, AFM_1, OTA, FB_1, FB_2, DON, 3A-DON, 15A-DON, DAS, T-2, HT-2, ZEN, PAT	Cereals, dairy, eggs, meat, fish, potatoes, vegetables, fruit, fruit dried, nuts seeds, herbs spices, soups,.sauces, sugar and preserves, confectionery, beverages, fats oils, snacks, composite	–	AFB_1, AFB_2, AFG_1, AFG_2, AFM_1, OTA, FB_1, FB_2, ZEN, PAT: HPLC DON, 3A-DON, 15A-DON, DAS, T-2, HT-2: LC/MS	[17]
Sub-Saharan Africa	AFB_1, AFB_2, AFG_1, AFG_2, FB_1, FB_2, FB_3, FB_4, STC, OTA, CIT, ZEN, Ergot Alkaloids, T2, HT2	cereals, tubers, legumes, vegetables, nuts and seeds, dairy, oils, beverages and miscellaneous	extraction without purification	LC–MS/MS	[18,19]

AFB_1 was found in 22.2% of the tested samples, at levels ranging between 0.02 and 1.38 μg kg^{-1}. Cereals, legumes, potatoes, meats, eggs, aquatic foods and vegetables, as well as their respective products, all showed aflatoxin contamination, at very low concentrations. AFB_2 was detected only in legumes (2.8%). AFG_1 was found in eggs and alcohols (2.8%). AFM_1, AFM_2, and AFG_2 were not detected in any samples.

Fumonisins were frequently detected in cereals, legumes, potatoes, meats, eggs and aquatic foods, with detection rates of 30.6%, 8.3%, and 8.3% for FB_1, FB_2, and FB_3, respectively. Among ochratoxins, OTB had a low rate of detection (5.6%), and OTA was not detected.

Emerging mycotoxins had high rates of detection, except AOH that was not detected. Enniatins occurred in more than half (58.3%) of the samples. BEA was found in 45.8% samples. Among *Alternaria* mycotoxins, detection rates were 30.6% for TEN, 27.8% for AME, 23.6% for TeA, and 4.2% for ALT. Cereals, legumes, potatoes and eggs showed the highest incidence rates, with most samples being positive.

Among the remaining mycotoxins, SMC was found positive in 29.2% of the samples, at concentrations below 2 μg kg^{-1}. MON, PAT, T2, HT2, DAS, NEO, CPA, CIT were not detected.

Serious contamination occurred for given food categories from certain mycotoxins. Overall, more than 80% of the samples were found contaminated by mycotoxins. DON, SMC, FB_1, ZEN, BEA, $ENNB_1$, and ENNB were most detected. These findings indicate the major points for further investigation.

Comparison

Table 5 summarizes the mycotoxin analytical methods in TDSs carried out in different countries, such as France, the Netherlands, Spain, Lebanon, Canada, New Zealand, Vietnam, Ireland, regional Sub-Saharan Africa, and Hong Kong. The number of mycotoxins analyzed varies from one mycotoxin to 37 mycotoxins. The study presented here developed a sensitive, accurate, and robust method for detecting 43 mycotoxins in the 6th China TDS, and the number of mycotoxins was the most studied at once. Compared with the 4th and 5th China TDSs, 10 emerging mycotoxins (AOH, AME, TeA, ALT, TEN, BEA, $ENNA_1$, ENNA, $ENNB_1$ and ENNB) were added into the 6th China TDS for the first time. Among the TDSs conducted in other countries, ENNs were investigated only in the Netherlands, while ATs, BEA, and TEN remain unexplored in other countries.

A variety of analytical methods have been employed in TDSs, including ELISA [16], LC-UV [7,37], LC-FLD [7,8,13,38], GC–MS [7], GC–MS/MS [10], and LC-MS/MS [8,10,14,18,20]. Among them, LC-MS/MS is increasingly applied as a highly selective and sensitive tool for multi-mycotoxin analysis in complex food matrices. A combination of different methods is still necessary in TDS to achieve satisfactory sensitivity and accuracy, especially when multiple mycotoxins were considered. Similarly, in this study, the 43 mycotoxins were classified into three groups due to their diverse properties, with specific testing methods for each group, to achieve the best performance. Recently, we reported a UHPLC-MS/MS method for analyzing 10 emerging mycotoxins (AOH, AME, TeA, ALT, BEA, TEN, $ENNA_1$, ENNA, $ENNB_1$, and ENNB) [23], presenting our staged research progress on mycotoxin determination in China TDS. The 10 emerging mycotoxins were also considered in this work (classified in group C), and after further investigation, two more mycotoxins (CPA and CIT) were included in group C.

Regarding the food categories, the foodstuffs involved in the China TDS were more complicated, which included not only 12 categories of goods, but also the preparation and cooking of TDS samples, further complicating chemical compositions versus raw products.

Since mycotoxins may occur in trace amounts in dietary samples, sensitivity plays a critical role in a TDS. In previous studies of TDSs in China and abroad, for some mycotoxins, the LODs were relatively high, and therefore, a considerable number of "not detected" values were obtained. In the Irish TDS, fusarium toxins were not detected in any of the samples tested; however, the respective LODs were relatively high (20 μg kg^{-1} for fumonisins, 10 μg kg^{-1} for zearalenone, and 50 μg kg^{-1} for all remaining fusarium toxins) [17]. When conducting exposure assessment, the non-detects are set to 0, LOD and LOD/2 to estimate the lower bound (LB), upper bound (UB), and medium bound (MB) of exposure, respectively. Therefore, a high value of LOD may affect the accuracy of exposure assessment. In the second French TDS [8], the mean daily exposure to T2 and HT2 ranged 8.93 ng kg^{-1} bw (LB) to 51.8 ng kg^{-1} bw (UB) for adults, and 14.5 ng kg^{-1} bw (LB) to 91.1 ng kg^{-1} bw (UB) for children. These UB estimates were very close to or exceeded the group provisional maximum tolerable daily intake (PMTDI) of 60 ng kg^{-1} bw day^{-1} due to uncertainty in analytical results (with LODs of 3 μg kg^{-1} for T2 and HT2). Similarly, in the 4th and 5th China TDSs, the detection rates of HT2 were 2.8% and 0% (with LOD of 0.8 μg kg^{-1}), but the MB of the exposure to T-2 and HT-2 was calculated to be 70 ng kg^{-1} bw day^{-1} and 52 ng kg^{-1} bw day^{-1}, respectively, representing 116.7% and 87% of the PMTDI value, which could not accurately reflect the real exposure level. In this study, by choosing the $[M + Na]^+$ as the precursor ion, the LOD of HT2 was greatly improved (0.08 μg kg^{-1}).

The proposed methods achieved a significant increase in sensitivity of multi-mycotoxins and could contribute to a more accurate estimation of dietary exposure.

Conclusions

The present work developed a highly sensitive and reliable strategy incorporating three UHPLC-MS/MS methods to determine 43 mycotoxins in dietary samples. The method recoveries for target compounds were 60.3–175.9%, with inter-day RSD below 13.9%, which are acceptable for analysis of multi-mycotoxins at trace levels. Upon optimization, LOQs were 0.0006–3 μg kg^{-1}, indicating high sensitivity. The method was validated and applied to the 6th China TDS with success. Of the 72 food samples, more than 80% were found contaminated by mycotoxins. The most detected mycotoxins were DON, SMC, FB_1, ZEN, BEA, $ENNB_1$, and ENNB. Based on these results, the screening of mycotoxins that are of high level and high detection rate can be considered higher priority in future risk assessment. This novel strategy provides a basis for monitoring mycotoxins in various foods and will help to assess dietary exposure to mycotoxins.

CRediT authorship contribution statement

Nannan Qiu: Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Funding acquisition. **Danlei Sun:** Formal analysis, Validation. **Shuang Zhou:** Methodology, Investigation, Validation, Writing – review & editing. **Jingguang Li:** Conceptualization, Investigation, Project administration. **Yunfeng Zhao:** Project administration, Resources, Supervision. **Yongning Wu:** Resources, Project administration.

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.

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Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jare.2021.10.008.

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