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Determination of ochratoxins in nuts and grain samples by in-tube solid-phase microextraction coupled with liquid chromatography–mass spectrometry

Keita Saito*, Risa Ikeuchi, Hiroyuki Kataoka

School of Pharmacy, Shujitsu University, Nishigawara, Okayama 703-8516, Japan

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ABSTRACT

A simple and sensitive method for the determination of ochratoxins A and B in nuts and grain samples was developed using an automated in-tube solid-phase microextraction (SPME) coupled with liquid chromatography–mass spectrometry (LC–MS). Ochratoxins were separated within 5 min by high-performance liquid chromatography using an Inertsil ODS-3 column with 5 mM anmonium acetate/acetonitrile (65/35, v/v) as the mobile phase. Electrospray ionization conditions in the positive ion mode were optimized for mass spectrometric detection of ochratoxins. The pseudo molecular ion $[M+H]^+$ was used to detect ochratoxins with selected ion monitoring (SIM) mode. The optimum in-tube SPME conditions were 20 draw/eject cycles of 40 μL of sample using a Carboxen-1006 PLOT capillary column as an extraction device. The extracted ochratoxins were easily desorbed from the capillary by passage of the mobile phase, and no carryover was observed. Using the in-tube SPME/LC–MS with SIM method, good linearities of the calibration curves ($r = 0.9993$ for ochratoxin A and $r = 0.9989$ for ochratoxin B) were obtained in the concentration range from 0.5 to 20 ng/mL. The detection limits (S/N = 3) for ochratoxins A and B were 92 and 89 pg/mL, respectively. The in-tube SPME method showed above 15–19-fold greater sensitivity than the direct injection method (10 μL injection). The within-day and between-day precisions (relative standard deviations) were below 5.1% and 7.7% ($n = 6$), respectively. This method was applied successfully to analysis of nuts and grain samples without interference peaks. The recoveries of ochratoxins spiked into extraction solution from nut samples were above 88%. Ochratoxins were detected at 0.7–8.8 ng/g levels in various nuts and grain samples.

1. Introduction

Ochratoxins A (OTA) and B (OTB) (Fig. 1) are naturally occurring mycotoxins produced by several species of the general Aspergillus and Penicillium like *Aspergillus ochraceus* or *Penicillium viridicatum* [1,2]. Ochratoxin is known to occur in commodities such as cereals, coffee, dried fruit and red wine. It has been shown to be hepatotoxic, nephrotoxic, teratogenic and carcinogenic to animals and is classified as a possible human carcinogen (category 2B) by the International Agency for Research on Cancer (IARC) [3]. Moreover, ochratoxin A is suspected to be the causative agent behind Balkan endemic nephropathy (BEN), a kidney disease encountered among the population of Southern Europe [4]. Therefore, ochratoxin contamination is a worldwide problem concerning food and feed safety and several countries have instituted ochratoxin restrictions in nuts and grain. The EC regulations have set a maximum tolerable limit for ochratoxin A at 3 μg/kg for all products derived from unprocessed cereals [5]. In view of the recognized adverse effects caused by ochratoxin and the need for regulatory control, monitoring of its level in nuts and grain samples is important to evaluate health risks due to human consumption of these products. Therefore, a sensitive, selective, and simple method to determine the presence and level of ochratoxin in nuts and grain samples is essential.

Analyses of ochratoxins have been carried out mainly by high performance liquid chromatography (HPLC)-fluorescence detection (FLD) [6–10], liquid chromatography–mass spectrometry (LC–MS) or LC–MS/MS [11–17], and immunological methods [18]. The details of the determination of ochratoxins in food samples have been summarized in some reviews [19–22]. LC–MS methods require derivatization of ochratoxins prior to analysis, although they are highly sensitive. HPLC with FLD detection is most widely used and has been adopted as the Association of Official Analytical Chemists (AOAC) official method [23]. However, HPLC methods reported previously are less sensitive.

LC–MS methods are specific and sensitive, and are becoming increasingly popular. However, most of the above methods require sample preparation steps, such as extraction, concentration, and isolation. Although ethyl acetate extraction and solid-phase extraction have been usually used as sample preparation techniques, most of these techniques are complicated and time-consuming.

* Corresponding author. Tel.: +81 86 271 8388; fax: +81 86 271 8388.
E-mail address: ksaito@shujitsu.ac.jp (K. Saito).

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Table 1
Program for in-tube SPME process.

Sequence	Event	Switching valve	Vial	Draw/eject		
				Cycle[a]	Volume (μL)	Speed (μL/min)
1	Conditioning of the capillary	Load	MeOH	D/E (2)	40	200
2	Drawing of air into the capillary	Load	Empty	D (1)	50	200
3	Conditioning of the capillary	Load	Water	D/E (2)	40	200
4	Extraction of analytes into the capillary	Load	Sample	D/E (20)	40	200
5	Needle washing	Load	MeOH	D/E (1)	2	200
6	Desorption of analytes from the capillary	Inject	–	–	–	–
7	HPLC separation of analytes and return to sequence 1	Load	–	–	–	

[a] D, draw; E, ejection.

Complicated pretreatment methods may introduce errors, and the use of large volumes of organic solvent poses a health hazard to those performing the analyses and contributes to environmental pollution. One efficient pretreatment method is fiber solid-phase microextraction (SPME) method, but extraction and desorption of samples are difficult to automate [24]. Therefore, it is important to develop an efficient sample pretreatment method, and automation will reduce labor and cost. A routine analysis method will also facilitate the processing of large numbers of samples.

In-tube SPME, using an open tubular fused-silica capillary with an inner surface coating as the SPME device, is simple and can be easily coupled on-line with HPLC and LC–MS. In-tube SPME allows convenient automation of the extraction process, which not only reduces the analysis time, but also provides better accuracy, precision, and sensitivity than manual off-line techniques. We have developed an in-tube SPME method for the determination of various compounds in food samples by coupling with HPLC [25,26] and LC–MS [27–29]. The details of the in-tube SPME technique and its applications have been summarized in a number of reviews [30–35]. Here, we report an automated on-line in-tube SPME/LC–MS method for the determination of ochratoxins in nuts and grain samples.

2. Experimental

2.1. Materials

OTA and OTB were purchased from Sigma–Aldrich Japan (Tokyo, Japan) and dissolved in methanol to make a stock solution at a concentration of 1 mg/mL. The solutions were stored at 4 °C and diluted to the required concentrations with pure water prior to use. LC–MS grade acetonitrile and water used as mobile phases were purchased from Kanto-kagaku (Tokyo, Japan). All other chemicals were of analytical grade.

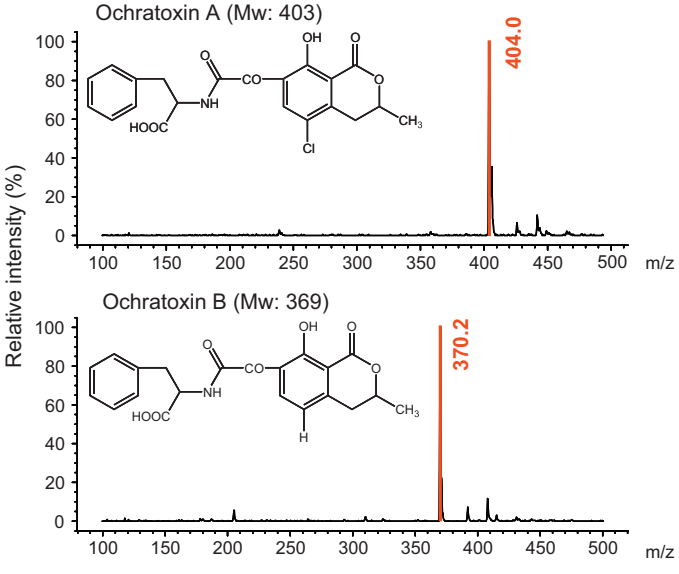

Fig. 1. ESI-mass spectra of OTA and OTB.

2.2. Instrument and analytical conditions

The LC–MS system was a Model 1100 series LC coupled with an atmospheric pressure (AP) electrospray ionization (ESI) MS (Agilent Technologies, Boeblingen, Germany). An Inertsil ODS-3 column (50 mm × 2.1 mm, particle size of 4 μm; GL Science Inc., Tokyo, Japan) was used for LC separation under the following conditions: column temperature, 40 °C; mobile phase, 5 mM anmonium acetate/acetonitrile (65/35, v/v); and flow rate, 0.2 mL/min for 10 min run. ESI-MS conditions were as follows: nebulizer gas N_2 (50 psi); drying gas, N_2 (12 L/min, 350 °C); fragmentor voltage, 110 V; capillary voltage, 2000 V; ionization mode, positive mode; mass scan range, 100–500 amu; selected ion monitoring (SIM), *m/z* 404 (ochratoxin A) and 370 (ochratoxin B); and dwell-times for the ions in SIM, 289 ms. LC–MS data were processed with an HP ChemStation.

2.3. In-tube solid-phase microextraction

A GC capillary column (60 cm × 0.32 mm i.d.) was used as the in-tube SPME device, and placed between the injection loop and injection needle of the autosampler. The injection loop was retained in the system to avoid fouling of the metering pump. Capillary connections were facilitated by use of a 2.5 cm sleeve of 1/16-in polyetheretherketone (PEEK) tubing at each end of the capillary. PEEK tubing with an internal diameter of 330 μm was shown to be suitable to accommodate the capillary used. Standard 1/16-in stainless steel nuts, ferrules, and connectors were used to complete the connections. CP-Sil 5CB, CP-Sil 19CB (Varian Inc., Lake Forest, CA, USA), Supel Q PLOT and Carboxen-1006 PLOT (Supelco, Bellefonte, PA, USA) were tested for comparison of extraction efficiency. The autosampler software was programmed to control the in-tube SPME extraction, desorption, and injection. (A) *Sampling and extraction*: vials (2 mL) were filled with 1 mL of sample for extraction, and set into the autosampler programmed to control the SPME extraction and desorption technique. In addition, 2-mL autosampler vials with a septum, one containing 1.5 mL of methanol and another containing 1.5 mL of water, were set into the autosampler. The capillary column was washed and conditioned by two repeated draw/eject cycles (40 μL each) of these solvents, and then a 50-μL air plug was drawn prior to the extraction step. The extraction of ochratoxin onto the capillary coating was performed by 20 repeated draw/eject cycles of 40 μL of sample at a flow rate of 150 μL/min with the six-port valve in the LOAD position. After extraction, the tip of the injection needle was washed by one draw/eject cycle of 2 μL of methanol. (B) *Desorption and LC–MS analysis*: the extracted

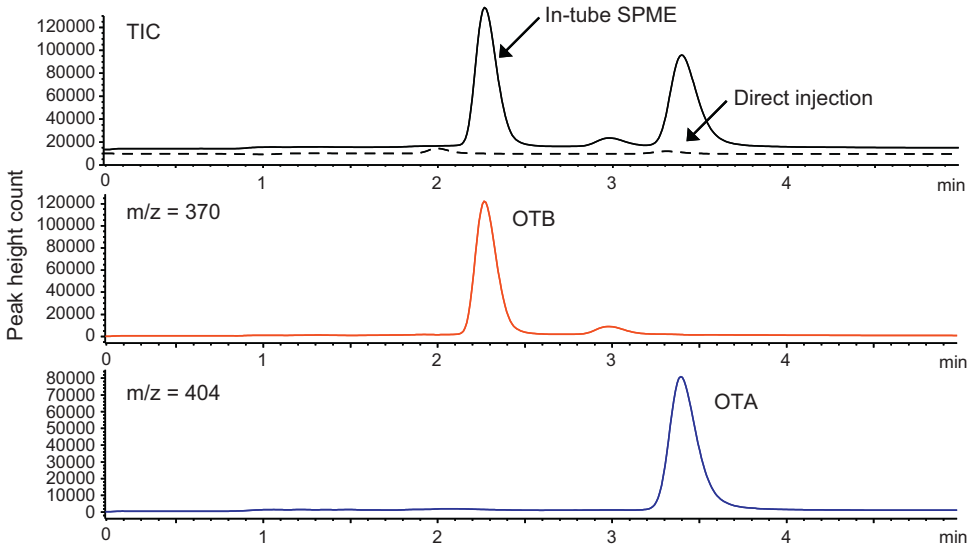

Fig. 2. Typical total ion and selected ion chromatograms obtained from standard OTA and OTB (10 ng/mL of each ochratoxin) by direct injection and in-tube SPME coupled with LC–MS in positive ion mode. *LC–MS conditions*: see Section 2.

compounds were desorbed from the capillary coating with the mobile phase and transported to the LC column by switching the six-port valve to the INJECT position, and detected with the MS system. During analysis, the SPME capillary was washed and conditioned with mobile phase for the next extraction. The extraction procedure is shown in Table 1. A description of the in-tube SPME/LC–MS system has been reported previously [27,32].

2.4. Preparation of nuts and grain samples

Nuts and grain samples were purchased from a local supermarket. All samples were stored in their original packaging under recommended conditions (either refrigerated or at room temperature) until use. Nuts and grain samples were homogenized to powder with a blender (Ace Homogenizer AM-7, Nissei, Tokyo,

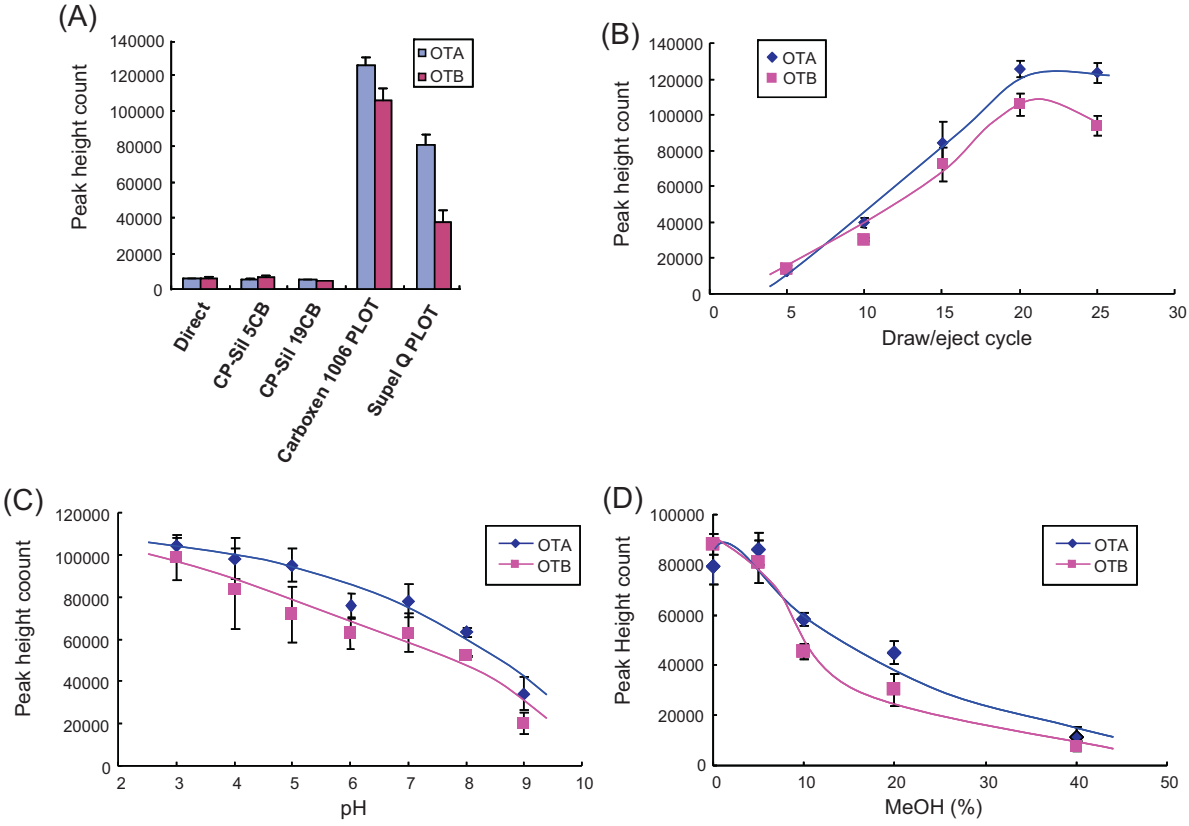

Fig. 3. Effects of (A) capillary coatings, (B) draw/eject cycles and (C) pH of sample, and (D) methanol concentration in the sample on in-tube SPME of ochratoxins. Ochratoxins were extracted by draw/eject of 40 μL of standard solution (10 ng/mL of each ochratoxin) at a flow rate of 200 μL/min.

Japan). Each sample of powder (about 0.5 g) was weighed into 10-mL Pyrex tubes with a PTFE-lined screw-cap, and extracted with 1 mL of 80% (v/v) methanol by shaking for 15 min. After centrifugation at 1000 × *g* for 5 min, the supernatant was washed three times with 1 mL of hexane to remove fat and then insoluble materials were removed by syringe filter (0.45 μm; Millipore, Billerica, MA). Aliquots (0.1 mL) of the filtered samples were pipetted into 2-mL screw-cap autosampler vials equipped with silicon/PTFE septa. After the total volume was made up to 1 mL with distilled water, the vials were set onto the sample tray in the autosampler.

3. Results and discussion

3.1. LC–MS analysis of ochratoxins

For mass spectrometric detection, AP and ESI were evaluated for determination of ochratoxins in both positive and negative ion modes. The ESI positive ion mode was most effective for ionization of ochratoxins. To select the monitoring ion for ochratoxins, ESI mass spectra were initially analyzed by LC–MS with direct liquid injection into the column. As shown in Fig. 1, each compound gave a very simple spectrum in scan mode for the mass range 100–500 *m*/*z*. Both compounds gave $[M+H]^+$ ions as base ions. The optimum fragmentor voltage was 110 V. Below this level, $[M+H]^+$ ion areas decreased.

LC separation of ochratoxins was performed using an Inertsil ODS-3 column. As shown in Fig. 2, OTA and OTB were eluted as a single peak using 5 mM ammonium acetate/acetonitrile (65/35, v/v) as the mobile phase, and each compound could be detected selectively by SIM.

3.2. Optimization of in-tube solid-phase microextraction and desorption

To optimize the extraction of ochratoxins by in-tube SPME, several parameters, such as the stationary phase of the in-tube SPME capillary column and number and volume of draw/eject cycles, were investigated. Four different capillary columns (CP-Sil 5CB, CP-Sil 19CB, Carboxen-1006 PLOT, and Supel Q PLOT) were evaluated for extraction efficiency. As shown in Fig. 3A, the porous polymer-type capillary column (Carboxen-1006 PLOT and Supel Q PLOT) showed better extraction efficiency than the other liquid-phase type capillary columns (CP-Sil 5CB and CP-Sil 19CB). As the Carboxen-1006 PLOT column has a large adsorption surface area, the amount extracted was greater than those obtained with the other liquid-phase type columns. In in-tube SPME, the extraction time, and flow rate are related to the amounts of compounds extracted. To monitor the extraction time profiles of ochratoxin by in-tube SPME, the number of draw/eject cycles was varied from 5 to 25 using a Carboxen-1006 PLOT capillary column. As shown in Fig. 3B, the extraction equilibrium of ochratoxin was reached with 20 draw/eject cycles of 40 μL of sample. Extraction efficiency was hardly changed in draw/eject rate at 50–250 μL/min. In this method, a draw/eject rate of 150 μL/min was used as the optimal flow-rate. Below this level, extraction requires an inconveniently long time, and above this level, bubbles tend to form inside the capillary column. The effects of the pH of the sample matrix on extraction of ochratoxins were examined using several buffer solutions. As shown in Fig. 3C, acetate buffer (pH 3) was most effective, and the optimal concentration of this buffer was 20 mM. As shown in Fig. 3D, there was a slight decrease in methanol extraction efficiency below 10%, but the effect was remarkable above 10%. Therefore, methanol concentration in samples was adjusted to <10%. The absolute amounts of ochratoxin extracted by the SPME capillary column were calculated by comparing peak area counts with the corresponding direct injection of the sample solution onto the LC column. At sample concentrations of 10 ng/mL, 6.21 ng (62.1%) of ochratoxin A and 6.64 ng (66.4%) of ochratoxin B were extracted onto the Carboxen-1006 PLOT column by in-tube SPME. Although the extraction yields of ochratoxins were relatively low, reproducibility was good due to the use of an autosampler.

The mobile phase was found to be suitable for desorption of ochratoxins extracted into the stationary phase of a capillary column. Dynamic desorption of these compounds from the capillary was readily achieved by switching the six-port valve. The desorbed ochratoxins were transported to the LC column by flow of the mobile phase. No carryover was observed because the capillary column was washed and conditioned by draw/eject cycles of methanol and mobile-phase prior to extraction. The extraction and desorption of ochratoxin by the in-tube SPME method were accomplished

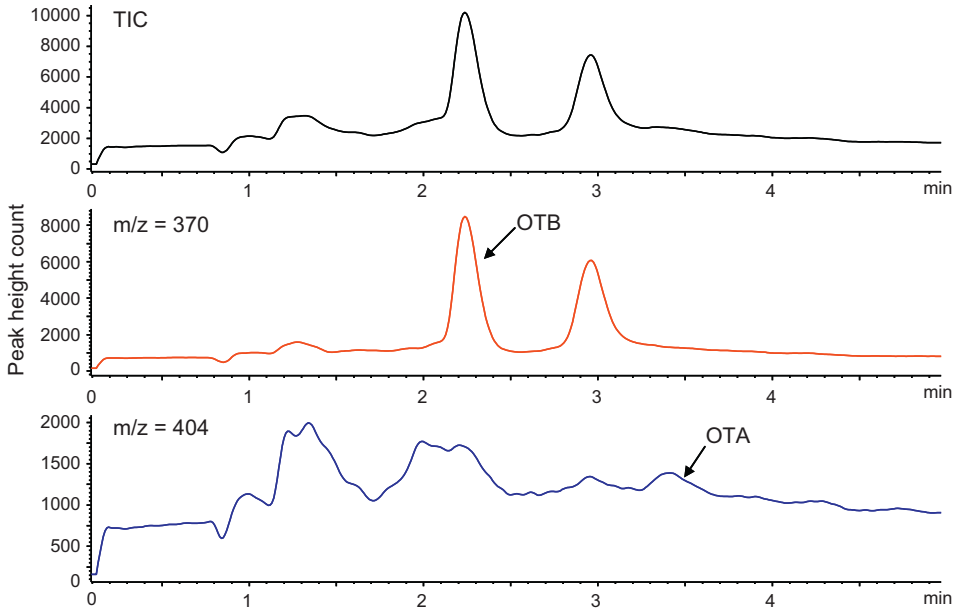

Fig. 4. Total ion and selected ion chromatograms obtained from cashew nuts by in-tube. SPME LC–MS. *LC–MS conditions*: see Section 2.

Table 2
Linear regression data, detection limits and within-day and between-day precisions of ochratoxins by in-tube SPME/LC–MS.

Compound	SIM (*m*/*z*)	Linearity[a]	Detection limit (ng/mL)[b]		D/I ratio[c]	Precision (RSD%)[d]	
		Correlation coefficient	Direct injection	In-tube SPME		Within-day	Between-day
OTA	404	0.9993	1.76	0.092	19.1	4.3	7.4
OTB	370	0.9989	1.37	0.089	15.4	5.1	7.7

[a] Calibration range: 0.5–20 ng/mL, 6-point ($n = 18$).
[b] S/N = 3.
[c] Sensitivity ratio of direct injection method against in-tube SPME method.
[d] $n = 6$.

Table 3
Recoveries of ochratoxins spiked into cashew nuts.

Compound	Spiked (ng/g)	Recovery (%)/mean ± SD ($n = 3$)		Spiked (ng/g)	Recovery (%)/mean ± SD ($n = 3$)	
		Average	RSD (%)		Average	RSD (%)
OTA	1.0	89.9 ± 6.8	7.6	10	88.8 ± 6.8	7.7
OTB	1.0	91.4 ± 7.6	8.3	10	94.6 ± 5.8	6.1

automatically within 30 min, and automated analysis of about 48 samples per day was possible by overnight operation.

3.3. Limits of detection and calibration curves

As shown in Table 2, OTA and OTB provided excellent response in SIM and the detection limit (S/N = 3) were 0.092 ng/mL and 0.088 ng/mL. The in-tube SPME method showed about 15–19-fold higher sensitivity than the direct injection method (10 μL), because ochratoxin in the sample solution was concentrated in the capillary column during draw/eject cycles. Sensitivity of this method was about five times higher than that of LC–MS methods reported previously [19]. The calibration curves for OTA and OTB were constructed from the peak height counts. A linear relationship was obtained for each compound in the range 0.5–20 ng/mL (six-point calibration) and the regression lines of OTA and OTB were $y = 13488x - 4228$ with $r = 0.9993$ ($n = 18$) and $y = 13297x - 2394$ with $r = 0.9989$ ($n = 18$), respectively (y, peak height; x, concentration (ng/mL) of ochratoxins; r, correlation coefficient). These correlation coefficients were above 0.999. The within-day and between-day relative standard deviations (RSDs) were below 5.1% and 7.7% ($n = 6$), respectively.

3.4. Application to the analysis of nuts and grain samples

Commercial nuts and grain samples were analyzed using the in-tube SPME LC/MS method. Ochratoxins were extracted easily with 80% methanol from each type of sample. Quantification limit of OTA and OTB in nuts and grain samples were both 0.18 ng/g (S/N = 10). To validate this method, known amounts of ochratoxins were spiked into extract from cashew nuts, and the recoveries were calculated. The overall recoveries of OTA were 89.9 ± 6.8% and 88.8 ± 6.8% at the concentration of 1.0 and 10 ng/g, respectively, and those of OTB were 91.6 ± 7.6% and 94.6 ± 5.8% at the concentration of 1.0 and 10 ng/g, respectively (Table 3). Fig. 4 shows typical chromatograms obtained from cashew nut samples. OTA and OTB were detected without interference peaks by SIM mode detection, although unknown peak was observed after elution of OTB. Data of ochratoxin analysis in 13 samples are shown in Table 4. Ochratoxins were detected at the concentration of 0.65–8.83 ng/g in several nuts samples.

Table 4
Contents of ochratoxins in nuts and grain samples.

Sample	Content (ng/g)/mean ± SD ($n = 3$)	
	OTA	OTB
Almond	3.75 ± 0.33	8.83 ± 1.52
Cashew nuts (raw)	0.65 ± 0.08	7.82 ± 0.22
Cashew nuts (roast)	ND	0.91 ± 0.02
Coconuts	ND	ND
Macadamia nuts	ND	ND
Peanuts	7.65 ± 2.47	2.56 ± 0.53
Peacan nuts	ND	ND
Pistachio nuts	ND	ND
Walnuts	ND	ND
Corn for pop corn	ND	ND
Giant corn	ND	ND
Faro flour	ND	ND
Rice	ND	ND

ND, not detectable.

4. Conclusions

The on-line in-tube SPME LC–MS method reported in the present study can continuously extract ochratoxins from nuts and grain sample extracts without pretreatment, which can then be analyzed by LC–MS. This method is automatic, simple, rapid, selective and sensitive, and can be applied easily to the analysis of nuts and grain samples. The in-tube SPME method showed above 15–19-fold greater sensitivity than the direct injection method (10 μL injection). This method was applied successfully to analysis of nuts and grain samples without interference peaks. The recoveries of ochratoxins spiked into extraction solution from nut samples were above 88%. The method described here will be a useful tool for contamination monitoring and determination of ochratoxins in nuts and grain samples.

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