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A Graphene Reinforced Fabric Phase Sorptive Extraction Method for Determination of Ochratoxin A in Food Samples

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Abstract
In the present study, a novel sorbent-based microextraction method was developed for the quick extraction of ochratoxin A from food samples. The extraction was performed based on graphene-reinforced fabric phase sorptive extraction (FPSE) followed by HPLC-FLD analysis. Chromatographic separations were performed on a C18 column with H_2O: ACN: acetic acid (49:49:2, v/v/v) as mobile phase at a flow rate of 1.0 mL/min and with fluorescence detection (λex= 333 nm and λem= 447 nm). The effect of graphene in the sol solution, extraction time, ionic strength, solvent extraction volume, desorption time, and desorption solvent type and volume were evaluated to obtain the maximum extraction efficiency. The optimum condition was obtained at pH=7, 40 mg of graphene per 10 mL of sol solution, 40 min for extraction time and 20 min for desorption time, the best solvent for desorption was 1.0 mL of ACN: HOAC (95:5 V/V) and extraction volume was 10 mL. The method showed a linear range of 2.0-17.5 ng/mL with a correlation coefficient greater than 0.97. The limit of detection and limit of quantification were found 0.49 ng/g and 1.49 ng/g, respectively with absolute good recoveries (67.7-104.0%) and low relative standard deviations. In addition, ochratoxin A was quantified with the developed method in wheat and chickpea samples and the results indicate the effectiveness of the presented method.

Keywords
Mycotoxin; Chickpea; Pre-concentration; Sportive extraction

1. INTRODUCTION

Ochratoxin A (OTA), the most-abundant food-contaminating mycotoxins, is produced by toxigenic mould species like Penicillium verrucosum, Aspergillus ochraceus, Aspergillus niger, and Aspergillus carbonarius. The species of A. ochraceus, Penicillium verrucosum, and A. carbonarius can grow at moderate, low, and high temperatures, respectively. So, OTA contamination is widely reported in different geographical regions and climates and various types of food such as cereals, cacao, coffee, wine, fruits, peanuts, cotton seed, corn, and rice [1]. OTA is a relatively heat-resistant compound that transferred to the human body through the food chain. It is likely to be potentially carcinogenic in humans and its determination in food samples is important [2-4]. Some of the newest and most sensitive techniques like non-enzymatic electro-chemiluminescence biosensors [5], Co-MOFs based dual signal ratiometric electrochemical aptamer sensor [6], peptide conjugated gold nanoparticles[7] ,electrospun Xene/polyvinylidene fluoride nanofiber composite [8] coupled with chromatographic methods were reported for OTA determination.

Extraction and pre-concentration of ochratoxin A are required before analysis. The analyte is normally extracted through solid-phase extraction [9], solid-phase microextraction (SPME) [10], liquid–liquid microextraction (LLME) [11], stir bar sorptive extraction (SBSE) [12], microwave-assisted extraction [13], and accelerated solvent extraction [14] methods. High organic solvent consumption [15], low sample capacity [16], and high cost [17] are the main limitations of these methods. Fabric phase sorptive extraction (FPSE) is a new extraction and pre-concentration method. In this technique, a sol-gel sorbent is coated on a substrate (like polyester, fibreglass, or cellulose) with a strong covalent bond. The advantages of this technique are high sample capacity and short sample preparation time [18]. Moreover, recent improvements in this sample preparation method increased the sensitivity and decreased detection limits in SPFE- HPLC analysis.

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The current study was designed to develop graphene reinforced FPSE technique for the extraction and pre-concentration of ochratoxin A followed by HPLC determination in different foodstuffs, including chickpea and wheat.

2. EXPERIMENTAL

2.1. Chemicals and reagents

Cotton fabric was purchased from Ardakan textile company (Yazd, Iran) and used a fabric phase sorptiove extraction (FPSE) media. Poly(tetrahydrofuran), methyltrimethoxysilane (MTMS), acetone, dichloromethane, sodium hydroxide, hydrochloric acid, HPLC grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany). Trifluoroacetic acid (TFA) and glacial acetic acid were obtained from Carlo Erba (Milan, Italy) and were used without further purification. Ochratoxin A powder was obtained from Sigma (St. Louis, USA). In all the experiments, double distilled water was used. Stock standard solution of ochratoxin A with concentrations of 100 µg ml^{-1} was prepared in methanol. Working standard solutions were prepared daily by diluting the stock solution with methanol: acetic acid (98:2 v/v). All of the working solutions were stored in darkness and refrigerator at 4˚C.

2.2. Instrumentation

Different solutions were centrifuged with a Digicen 21 centrifuge (Orto Alresa, Madrid, Spain). A 2510 BRANSON Ultrasonic Cleaner (Branson Inc., USA) was used to prepare a bubble-free sol solution. FT-IR spectra were acquired on an AVATAR FT-IR spectrometer equipped with a universal ATR sampling accessory (Thermo, USA). Scanning electron micrographs were obtained by an LMU TESCAN BRNO- Mira3 Field Emission Scanning Electron Microscope (Oxford Instrument, England) equipped with an EDAX detector.

2.3. Chromatographic analysis

HPLC analyses were performed on an Agilent 1200 Series HPLC system (Agilent Technologies SL, Waldbronn, Germany) equipped with a binary pump and a 152 micro vacuum degasser, with attached 20 µL Rheodyne sample injector and a fluorescence detector set at 333 and 443 nm as excitation and emission wavelengths, respectively. Separations were carried out on a Waters Nova-pak® C18 analytical column (250 × 4.6 mm) operated at 30˚C. The mobile phase composition and flow rate were acetonitrile: water: acetic acid (49:49:2, v/v/v) and 1 mL/min, respectively. Data collection and analyzing as well as controlling the system operation was performed by Chemstation software.

2.4. Graphene synthesis

Graphene (G) was synthesized from graphite powders using a modified Hummer's method [19]. Briefly, graphite was added slowly into a cooled mixture of concentrated H_2SO_4/H_3PO_4 (9:1 v/v, 400 mL) under vigorous stirring to avoid agglomeration. Then, the mixture was cooled in an ice bath to keep the temperature below 20˚C and KMnO4 was gradually added. The reaction was continued at 50˚C for 12 h and the final mixture was poured onto about 400 mL of ice and continuously stirred to reach room temperature (23.0-25.0 ˚C). Then, H_2O_2 (30% w/w) was added to the mixture until the solution turned light yellow. The product was separated by centrifuging at 4000 rpm for 30 min, and the supernatant was decanted away. Finally, the mixture was filtered and washed with 5% HCl aqueous solution to remove metal ions followed by water until neutralization. The product was vacuum dried at 65˚C and the grey powder of graphite oxide was kept in a sealed container at room temperature.

An aqueous dispersion (0.05 %wt) of graphite oxide powder was prepared in deionized water. Exfoliation of graphite oxide to graphene oxide (GO) was achieved by ultrasonication for 1 h. Then, the obtained brown dispersion was subjected to centrifugation at 3000 rpm for 30 min to remove any unexfoliated graphite oxide. The resulting homogeneous dispersion was mixed with hydrazine solution (50 %wt in water, 12 mL) and ammonia solution (25 %wt, 14.2 mL). The mixture was vigorously stirred for a few minutes followed by refluxing at 98˚C for 24 h to reduce GO nanosheets to G. The products were then centrifuged, washed with water, and air-dried.

2.5. Pretreatment of cotton fabric

The cotton fabric (100% cellulose) was selected as the substrate for sol-gel sorbent coating. A fabric pretreatment was necessary for cleaning it and activating hydroxyl groups. Briefly, a piece of cotton fabric (10×10 cm) was soaked in distilled water and sonicated for 15 min. Then the fabric was immersed in a 1 mol/L NaOH solution for 1 h under constant sonication and followed by washing with a large amount of deionized water. Finally, it was immersed in an HCl solution (0.1 mol/L) and sonicated for 1 h. The fabric was rinsed with deionized water and placed in an inert atmosphere to dry overnight and was placed in a clean glass container for further process [20].

2.6. Preparation of FPSE media

The cotton cellulose fabric was coated with a sol solution prepared of poly-THF as the polymer, methyl-trimethoxysilane (MTMS) as the sol-gel precursor, trifluoroacetic acid (containing 5% water) as the sol–gel catalyst, and a 50:50 (v/v)

mixture of methylene chloride: acetone as the organic solvent. Graphene was also employed in the sol solution to increase absorption intensity of the resulting FPSE substrate..

The sol-gel coating and sol solution preparation process was described in detail elsewhere [21]. Briefly, 10 g of poly-THF and 10 mL of MTMS were mixed with 20 mL of methylene chloride: acetone and stirred by a magnetic stirrer. Then, 4 mL of TFA solution was added to the precursor solution followed by the addition of the pre-prepared graphene nanoparticles (136 mg). After that, the fabric was soaked in the prepared solution for 1 h. Subsequently, the fabric was dried in an inert atmosphere at ambient temperature for 24 h. The prepared FPSE media was cut into 2.0 × 2.5 cm pieces and was kept in a vacuum chamber to avoid contamination.

2.7. Sample preparation

Chickpea and wheat samples were purchased from local markets in Mashhad (Khorasan Razavi, Iran) and tested for no contamination. Samples (500 g) were crushed into a fine powder with a resulting particle size of below 0.3 mm and stored at -20˚C for later analysis. Each grounded sample (5.0 g) was spiked with OTA stock standard solution and stored in the dark at ambient temperature for 30 min. The sample was mixed with 20 mL extraction solvent (methanol: water mixture, 50: 50, v/v) and stirred for 30 min. The mixture was filtered using a Whatman No. 4 filter and the filtrate (10 mL) was used for the FPSE experiment.

3. RESULTS AND DISCUSSION

3.1. Characterization of sol–gel PTHF coated FPSE media

3.1.1. Scanning electron microscopy

The surface morphology of the fabric substrate was studied by SEM images. Fig. 1 represents scanning electron micrographs of (a) uncoated cotton substrate, (b) sol–gel poly-THF coated, and (c) sol–gel graphene reinforced poly-THF coated fabric. An SEM image reveals numerous microfibrils along with bundles of microfibrils woven in such a way that it possesses well-structured macropores even after sol-gel PTHF coating. The SEM image also shows homogeneous and sponge-like porous thin PTHF sorbent coating around the cellulose microfibrils that allows rapid permeation of the sample matrix containing the target analyte and results in shorter extraction equilibrium time [22]. As shown in Fig. 1c, the graphene nanoparticles were successfully coated on the fabric surface.

3.1.2. FT-IR spectroscopy

The FT-IR spectra of the sol-gel reinforce poly-THF coated fabric are shown in Fig. 2. Characteristic absorption bands appeared in three peak areas between 3000 and 3300 cm-1; 1270 and 2900 cm-1; and 1020 cm-1 correspond to O–H, C–H and C–O bending vibration. The presence of a band in the FT-IR spectrum of sol–gel poly-THF coated FPSE media at 1100 cm−1 is indicative of Si–O–C bonds which showed successful incorporation of sol–gel poly-THF network to the cellulose substrate. The peak at around 1700 cm-1 is attributed to C=O vibrations and the peak at 2700 cm-1 corresponds to the C-H aromatic stretching vibrations. Also, considering the systematic reduction in the absorption bands between 3000 and 3300 cm-1 in the FT-IR spectrum of sol-gel graphene reinforce coated FPSE media, it can be stated that this reduction is due to the involvement of hydroxyl groups of cellulose substrate to the sol-gel network [23].

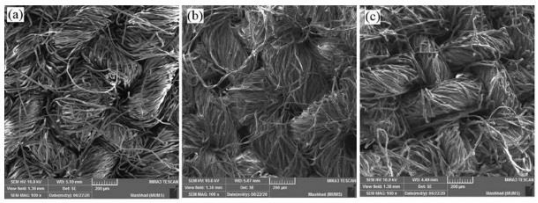

Fig. 1. SEM images of (a) uncoated cotton fabric, (b) sol–gel poly-THF coated fabric, and (c) sol–gel graphene reinforce poly-THF coated fabric

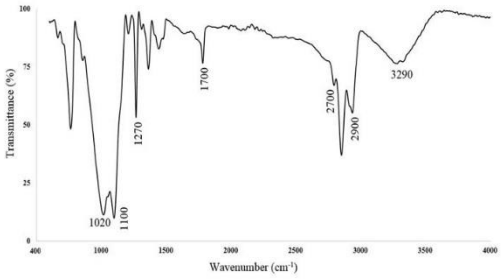

Fig. 2. FT-IR spectra of uncoated cellulose substrate sol–gel graphene-reinforced poly-THF coated fabric

3.2. FPSE procedure

The FPSE media was initially conditioned to remove undesirable impurities and eliminate the residues of organic solvents. Therefore, the FPSE media was soaked into 2.0 mL of methanol: acetonitrile mixture (50:50, v/v) for 5 min, and subsequently in 2.0 mL of ultrapure water for 3 min. In the adsorption step, a clean FPSE media was soaked into 10.0 mL of the sample solution containing 5.0 ng/mL of OTA. The vial was sealed, and the mixture was magnetically stirred for 40 minutes. Beyond that, the FPSE media was removed from the solution and air-dried at room

temperature. Subsequently, the FPSE media was soaked in the desorption solvent containing 1.0 mL of acetonitrile/acetic acid (95: 5, v/v) solution for 20 min. The solution was centrifuged at 9000 rpm for 5 min, filtered with a 0.45 µm syringe filter and subjected to HPLC analysis. To obtain high pre-concentration and extraction efficiency different parameters including graphene amount, extraction solvent type and volume, extraction time, ionic strength, desorption solvent volume and pH, and desorption time were studied and optimized.

3.2.1. pH effect of desorption solvent

The effect of different pH (3.0, 7.0, and 9.0) of the desorption solvent was studied on the recovery of OTA. The results showed the highest recoveries under approximately neutral conditions (pH=7). It is worth noting that the elution of the analyte most likely originated from its polarity (log Kow) and ionic state (pKa) at the elution conditions. In addition, the sol-gel network of the FPSE media remains so active for the highest interaction with the back extraction solution. Furthermore, we did not utilize harsh pH to keep the method simple and easy to apply in a routine laboratory.

3.2.2. Effect of graphene

The effect of different amounts of the graphene (0-50 mg per 10 mL of sol solution) was examined on the extraction efficiency of the OTA. As presented in Fig. 3a, the peak areas of AFs were increased by increasing the amount of graphene from 0 to 40 mg and remained nearly constant at higher amounts. Graphene has a very high surface-to-volume ratio, and it is natural that the increase of graphene increases the absorption of analytes. Therefore, 40 mg graphene nanoparticles was selected for the fabrication of the graphene-reinforced fabric phase.

3.2.3. Effect of extraction time

The distribution coefficient of the analyte affects the extraction and elution times. An adequate time is required to create an equilibrium between the sample solution and the FPSE medium [24]. The effect of the extraction time was considered to reach the maximum adsorption of the analyte on the FPSE media. As presented in Fig 3b, the maximum extraction efficiency was obtained at 40 min. No significant improvement was observed when contact time was extended. Increasing the contact time of the ochratoxin A solution with the fabric, increases the absorption of the analyte on the fabric, but after 40 min, the fabric was saturated and a equilibrium process occurs in absorption and desorption. Therefore, 40 min was considered the optimum time for extraction.

3.2.4. Effect of ionic strength

The addition of salt can simultaneously change the medium viscosity and analyte solubility. So, the effect of ionic strength was evaluated by the addition of sodium chloride (0-25 %w/v) to the extraction medium. An increase in NaCl concentration up to 25% caused a significant decrease in extraction efficiency (Fig. 3c), mainly due to an increase in viscosity and incomplete mass transfer of the analyte [3].

3.2.5. Desorption solvent type

Selecting an appropriate elution solvent is one of the effective factors to increase extraction efficiency. In this study, six different solvents were investigated to elute OTA from the fabric including MeOH: HOAC (95:5 v/v), MeOH: H2O (50:50 v/v), ACN: H2O (50:50 v/v), ACN: H2O: HOAC (49.5:49.5:1 v/v/v), ACN: MeOH (50:50 v/v), and ACN: HOAC (95:5 v/v). As presented in Fig 3d, the highest extraction efficiency or highest peak area was obtained with ACN: HOAC (95:5 v/v). The reason is that acidic acetonitrile has a polarity close to ochratoxin A and has a higher elution power than other solvents.

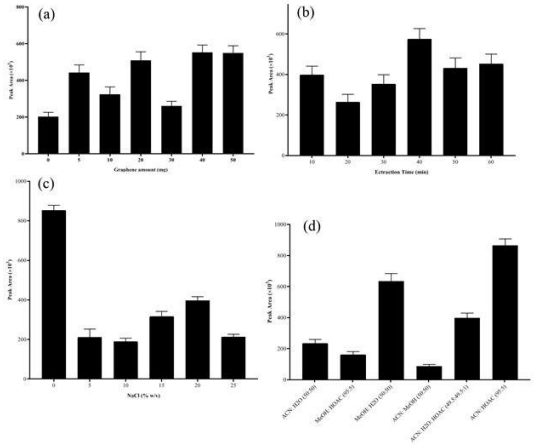

Fig. 3. Optimization of experimental conditions: (a) effect of the amount of graphene in sol solution; (b) effect of extraction time; (c) effect of ionic strength; (d) effect of extraction solvent type

3.2.6. Desorption time and volume

The FPSE media was placed in contact with the desorption solvent and the effect of desorption time was studied in 5-25 min intervals. The results showed an increase in peak area or enhancement in desorption efficiency at 20 and 25 min. However, no significant differences were observed between 20 and 25 min (Fig. 4a). So, adesorption time of 20 min was selected to ensure an equilibrium establish between the FPSE media and working solution.

The effect of desorption solvent volume (1.0-5.0 mL) was also studied. As presented in Fig. 4b, satisfactory results were obtained with 1.0 mL of acetonitrile: acetic acid (95:5, v/v). Thus, this volume was regarded as the volume of back

extraction solvent in future experimentation.

3.2.7. Extraction solvent volume effect

The FPSE media was in contact with different volumes (2.0-10.0 mL) of the standard OTA solution containing 10 ng of analyte. As presented in Fig. 4c, when the sample volume increased from 2.0 to 10.0 mL, the extraction efficiency was improved. High volume of extraction solution can help the analyte diffusion and mass transfer through the matrix of the sample to the extraction media. It decreases the time needed for creating extraction equilibrium, and makes the extraction more efficient. It can be concluded that the solution in high volume can lead to greater extraction values [25].

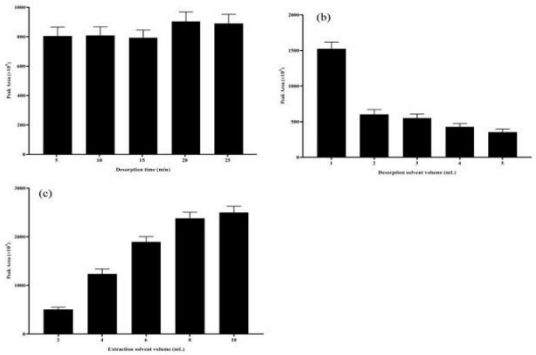

Fig. 4. Optimization of experimental conditions: (a) desorption time effect; (b) desorption solvent volume; (c) extraction solvent volume

3.3. Method Validation and analysis of real samples

The calibration curve was constructed using the optimized conditions. The method showed a linear range of 2-17.5 ng/mL with a correlation coefficient greater than 0.97 (Table 1). The limit of quantification (LOQ) and the limit of detection (LOD) was defined as the signal-to-noise ratio of 10:1 and 3:1, respectively. The method accuracy was determined based on the recovery of ochratoxin A and the results showed recoveries in an acceptable range (Table 2). The relative standard deviation for within the laboratory repeatability (RSDr) was 3.29%.

Also, OTA was quantified in real samples including wheat and chickpea, spiked at different levels of OTA (Table 2). The results indicate the effectiveness of the presented method. No interfering peak was observed at the retention time corresponding to ochratoxin A. Acceptable recoveries were obtained for wheat (97.7-104.0%) and chickpea (73.0–100.4%), which were in the range recommended by AOAC (Feizy et al. 2011). The percentage recoveries were different for each sample at various concentrations, which is probably due to unpredictable matrix behaviour. Reinforce graphene FPSE-HPLC-FLD typical chromatograms of samples spiked at 5 ng/g are depicted in Fig. 5a and Fig. 5b for wheat and chickpea, respectively.

4. CONCLUSION

In the current study, a novel graphene-reinforced FPSE-HPLC-FLD method was developed and validated for the extraction/pre-concentration of ochratoxin A in food samples. The results showed the fabric phase sorptive extraction technique can be effective in reducing solvent volume and analysis time. These advantages make this technique more economic, green, and environmentally friendly. The method validation parameters yielded good results and included linearity, precision, and accuracy. Therefore, this study demonstrates the FPSE method is rapid, precise, reproducible, and sensitive for the determination of ochratoxin A in different food samples.

Table 1. Graphene reinforce FPSE-HPLC-FLD characteristics of ochratoxin A.

Parameter	Ochratoxin A
Correlation coefficient (R^2)	0.9786
Linear calibration range (ng/mL)	2.5-17.5
RSD (%)	3.29
LOD (ng/g)	0.49
LOQ (ng/g)	1.49

Table 2. Mean recoveries of ochratoxin A in wheat and chickpea samples.

Analyte	Sample	Spiked level (ng/g)	Recovery (%)	(RSD; %) (n=3)
Ochratoxin A	Wheat	5	67.7	13.0
		10	104.0	4.1
	Chickpea	20	73.0	2.9
		40	100.4	2.8

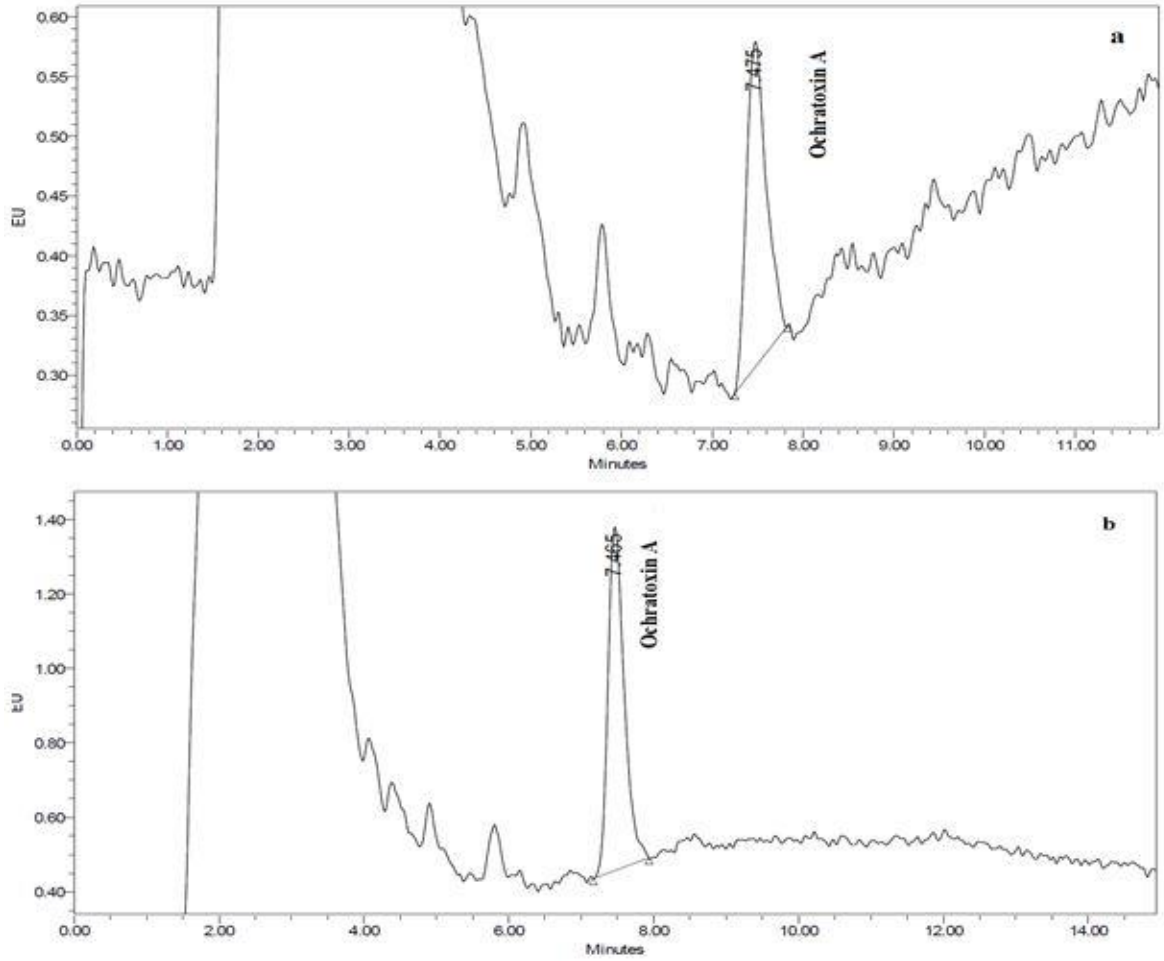

Fig. 5. Typical graphene reinforce FPSE-HPLC-FLD chromatograms of spiked samples at the level of 5 ng/g for (a) wheat and (b) chickpea.

Abbreviations: OTA: Ochratoxin A; FPSE: Fabric phase sorptive extraction; HPLC-FLD: High-performance liquid chromatography-fluorescence detection; MeOH: Methanol; HOAC: Acetic acid; ACN: Acetonitrile; MTMS: Methyl-tri-methoxysilane; PTHF: Polytetrahydrofuran; SEM: Scanning electron microscopy; LOQ: Limit of quantification; LOD: Limit of detection; RSD: Relative standard deviation; DLLME: Dispersive liquid-liquid microextraction; SPE: Solid phase extraction; SPME: Solid phase microextraction; LPME: Liquid phase micro extraction.

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REFERENCES

[1] J. Feizy, H.R. Beheshti, S.S. Fakoor Janati and N. Khoshbakht Fahim, Survey of ochratoxin A in rice from Iran using affinity column cleanup and HPLC with fluorescence detection, *Food Addit. Contam. Part B.* 4 (2011) 67-70.

[2] S.S. Fakoor Janati, H.R. Beheshti, M. Asadi, S. Mihanparast and J. Feizy, Preliminary Survey of Aflatoxins and Ochratoxin A in Dried Fruits from Iran, *Bull. Environ. Contam. Toxicol.* 88 (2012) 391-395.

[3] S.S. Fakoor Janati, H.R. Beheshti, N. Khoshbakht Fahim and J. Feizy, Aflatoxins and Ochratoxinin A in Bean from Iran. Bull. Environ. Contam, *Toxicol.* 87 (2011) 194-197.

[4] Z. Ráduly, L. Szabó, A. Madar, I. Pócsi and L. Csernoch, Toxicological and medical aspects of Aspergillus-derived Mycotoxins entering the feed and food chain, *Front. Microbiol.* 10 (2020) 2908.

[5] X. Shi, X. Zhu, Y. Chai, Y. Zhou and R. Yuan, Non-enzymatic electrochemiluminescence biosensor for ultrasensitive detection of ochratoxin A based on efficient DNA walker, *Food Chem.* 407 (2023) 135113.

[6] Y. Guan, P.-B. Si, T. Yang, Y. Wu, Y.-H. Yang and R. Hu, A novel method for detection of ochratoxin A in foods—Co-MOFs based dual signal ratiometric electrochemical aptamer

sensor coupled with DNA walker, *Food Chem.* 403 (2023) 134316.
[7] S. Rahi, V. Lanjekar and V. Ghormade, Development of a rapid dot-blot assay for ochratoxin A (OTA) detection using peptide conjugated gold nanoparticles for bio-recognition and detection, *Food Control.* 136 (2022) 108842.
[8] A.M. Al-Dhahebi, R. Jose, M. Mustapha and M.S.M. Saheed, Ultrasensitive aptasensor using electrospun MXene/polyvinylidene fluoride nanofiber composite for Ochratoxin A detection, *Food Chem.* 390 (2022) 133105.
[9] F.S. Jahed, S. Hamidi, S. Ghaffary and B. Nejati, Dispersive micro solid phase extraction of busulfan from plasma samples using novel mesoporous sorbent prior to determination by HPLC-MS/MS, *J. Chromatogr. B.* (2020) 122091.
[10] M.J. Trujillo-Rodríguez and J.L. Anderson, Silver-based polymeric ionic liquid sorbent coatings for solid-phase microextraction: materials for the selective extraction of unsaturated compounds, *Anal. Chim. Acta*. 1047 (2019) 52-61.
[11] A. Shishov, A. Gerasimov, D. Nechaeva, N. Volodina, E. Bessonova and A. Bulatov, An effervescence-assisted dispersive liquid-liquid microextraction based on deep eutectic solvent decomposition: determination of ketoprofen and diclofenac in liver, *Microchem. J.* (2020) 104837.
[12] Z.N. Khoshkbar, Z. Talebpour, S.N. Ghamat and F. Farzaneh, Fabrication, characterization, and application of zeolitic imidazolate framework-8/acrylate monolithic polymer as a composite phase for stir bar sorptive extraction, *Microchem. J.* (2020) 105060.
[13] M. Nisoa, A. Plodkaew, C. Sirisathitkul, K. Wattanasit, B. Somjit, P. Pacdeepin and Y. Sirisathitkul, Simulation and experimentation on parameters influencing microwave-assisted extraction of bioactive compounds from Kaempferia parviflora rhizomes, *Alex. Eng. J.* 65 (2022) 357-366.
[14] A.T. Khanyile, J.E. Andrew, V.Paul and B.B. Sithole, A comparative study of supercritical fluid extraction and accelerated solvent extraction of lipophilic compounds from lignocellulosic biomass, *Sustain. Chem. Pharm*. 26 (2022) 100608.
[15] F. Zhou, L. Zhang, A. Liu, Y. Shen, J. Yuan, X. Yu, X. Feng, Q. Xu and C. Cheng, Measurement of phenolic environmental estrogens in human urine samples by HPLC–MS/MS and primary discussion the possible linkage with uterine leiomyoma, *J. Chromatogr. B.* 938 (2013) 80-85.
[16] A. Kabir, K.G. Furton and A. Malik, Innovations in sol-gel microextraction phases for solvent-free sample preparation in analytical chemistry, *Trac-Trends Anal. Chem.* 45 (2013) 197-218.
[17] C. Nerín, J. Salafranca, M. Aznar and R. Batlle, Critical review on recent developments in solventless techniques for extraction of analytes, *Anal. Bioanal. Chem*. 393 (2009) 809.
[18] A. Kabir and K.G. Furton, Fabric phase sorptive extraction: a new genration, green sample preparation approach, in: Solid-Phase Extraction, *Elsevier*, 2020, pp. 355-386.
[19] Z. Es'haghi, H.R. Beheshti and J. Feizy, Extraction of aflatoxins from food samples using graphene-based magnetic nanosorbents followed by high-performance liquid chromatography: a simple solution to overcome the problems of immunoaffinity columns, *J. Sep. Sci*. 37 (2014) 2566-2573.
[20] H. Noori, J. Feizy and Z. Eshaghi, Development of a Nanoparticle-Assisted Fabric Phase Sorptive Extraction Technique Coupled with High-Performance Liquid Chromatography for Sensitive Determination of Aflatoxins in Food Samples, *Anal. Bioanal. Chem. Res.* 10 (2023) 121-134.
[21] R. Kumar, A.K. Malik, A. Kabir and K.G. Furton, Efficient analysis of selected estrogens using fabric phase sorptive extraction and high performance liquid chromatography-fluorescence detection, *J. Chromatogr. A.* 1359 (2014) 16-25.
[22] M. Celeiro, R. Acerbi, A. Kabir, K.G. Furton and M. Llompart, Development of an analytical methodology based on fabric phase sorptive extraction followed by gas chromatography-tandem mass spectrometry to determine UV filters in environmental and recreational waters, *Anal. Chim. Acta: X*. 4 (2020) 100038.
[23] A. Montarsolo, M. Periolatto, M. Zerbola, R. Mossotti and F. Ferrero, Hydrophobic sol-gel finishing for textiles: Improvement by plasma pre-treatment, *Text. Res. J*. 83 (2013) 1190-1200.
[24] E. Zilfidou, A. Kabir, K.G. Furton and V. Samanidou, An improved fabric phase sorptive extraction method for the determination of five selected antidepressant drug residues in human blood serum prior to high performance liquid chromatography with diode array detection, *J. Chromatogr. B.* 1125 (2019) 121720.
[25] V. Alampanos, A. Kabir, K.G. Furton, V. Samanidou and I. Papadoyannis, Fabric phase sorptive extraction for simultaneous observation of four penicillin antibiotics from human blood serum prior to high performance

liquid chromatography and photo-diode array detection, *Microchem. J.* 149 (2019) 103964.

روش استخراج فاز پارچه تقویت شده با گرافن جهت تعیین اکراتوکسین در مواد غذایی

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چکیده

در این مطالعه یک روش جدید میکرواستخراج بر پایه جاذب، جهت استخراج سریع اکراتوکسین از نمونه‌های غذایی توسعه پیدا کرد. این روش بر پایه استخراج فاز پارچه تقویت شده با گرافن، سپس اندازه‌گیری اکراتوکسین با کروماتوگرافی مایع با کارایی بالا مجهز به آشکارساز فلورسانس بود. جداسازی کروماتوگرافی روی ستون C18 با فاز متحرک آب: استونیتریل: استیک اسید (۲:۴۹:۴۹ حجمی/حجمی/حجمی) با سرعت جریان یک میلی‌لیتر در دقیقه و طول موج تحریک ۳۳۳ نانومتر و نشر ۴۴۷ نانومتر بود. به منظور بهینه‌سازی روش و به دست آوردن حداکثر کارایی استخراج، پارامترهای pH، مقدار گرافن در محلول سل، زمان استخراج، قدرت یونی محیط، حجم حلال استخراج، نوع و حجم حلال واجذب و زمان واجذب مورد ارزیابی قرار گرفت. نتایج به دست آمده برای شرایط بهینه شامل pH برابر ۷، ۴۰ میلی‌گرم گرافن به ازای ۱۰ میلی‌لیتر محلول سل، زمان استخراج ۴۰ دقیقه و زمان واجذب ۲۰ دقیقه، حجم حلال استخراج ۱۰ میلی‌لیتر و بهترین حلال واجذب یک میلی‌لیتر استونیتریل: استیک اسید (۵:۹۵ حجمی/حجمی) بود. رنج خطی روش با ضریب همبستگی بیشتر از ۰/۹۷ برابر ۱۷/۵-۲ نانوگرم بر میلی‌لیتر بود. حد تشخیص و حد اندازه‌گیری کمی به ترتیب برابر ۰/۴۹ و ۱/۴۹ نانوگرم بر گرم و درصد بازیافت (۶۷/۷ تا ۱۰۴ درصد) با درصد انحراف استاندارد نسبی خوب بدست آمد. علاوه بر این روش توسعه یافته در نمونه‌های گندم و نخود ارزیابی و موثر بودن روش اثبات شد.

واژه‌های کلیدی

مایکوتوکسین، نخود، پیش تغلیط، استخراج جذبی