Research Article

Modified QuEChERS Based on Mixed Adsorbent Cleanup of Mycotoxins in Corn

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In order to analyze the mycotoxins in corn, the modified QuEChERS high-performance liquid chromatography was applied to extract, clean up, and detect mycotoxins in a nonpolar system. The impurities such as fat and protein were removed from the corn sample, and the impurities in the sample solution have almost no effect on extraction efficiency. The proposed method leads to a greater choice of mycotoxin-extraction solvents in high-fat-solid samples. An appropriate extraction solvent was selected, the pretreatment conditions were optimized, and the extraction and cleanup of mycotoxins in high-fat solids were enhanced. By changing the experiment parameters, this method can be further used for the extraction and analysis of mycotoxins in complex samples (nonfat, low-fat, or high-fat). This method achieves good linearity in the range of 2.5–1000 µg/kg with the correlation coefficients for all analytes in the range of 0.9975 to 0.9989. The acceptable standard deviations for intraday and interday precision were 1.8–4.3% and 3.2–5.2%, respectively, with recoveries from 89.7 to 105.9%.

1. Introduction

In 1960, about 100,000 turkeys died from acute aflatoxin poisoning in the United Kingdom. After aflatoxin was confirmed to be seriously carcinogenic in the following year, mycotoxins began attracting widespread attention [1, 2]. Mycotoxins are a series of toxic secondary metabolites produced by some molds (mainly *aspergillus*, *penicillium*, and *fusarium*) after they mature [3–5]. They can be divided into field toxins and storage toxins, depending on where they grow [6, 7]. The identification and classification of molds have traditionally been based on morphological and cultural characteristics, but the morphological characteristics of molds are complex, and morphological studies of them are often questioned on the basis of lack of standards and excessive subjectivity. The common mycotoxin is aflatoxins (AFs, including AFB₁, AFB₂, AFG₁, and AFG₂), zearalenone (ZEN), deoxynivalenol (DON), sterigmatocystin (ST),

citreoviridin (CIT), ochratoxin A (OTA), and so on [8]. Mycotoxins seriously endanger the health of livestock and poultry [9, 10] and, thereby, indirectly endanger human health, leading to severe economic losses to the companies producing them [11, 12]. The WHO and the FAO have identified mycotoxins as the main cause of foodborne illness. Globally, mycotoxins contaminate 25 percent of food according to the FAO. Therefore, rapid and effective detection of mycotoxins can prevent their occurrence and improve the quality and safety of animal products.

Various regions have established maximum residue limit (MRL) of mycotoxin standards to regulate it. China's national standards stipulate that the MRLs of AFB₁, DON, ZEN, and OTA in corn are 20, 1000, 60, and 5 µg/kg, respectively (GB 2761-2017). In the European Union, the MRLs of AFB₁, DON, ZEN, and OTA in corn are 2.0, 1750, 350, and 5 µg/kg, respectively. In the U.S., the MRLs of AFB₁, DON, ZEN, and OTA in corn are 5.0, 4000, 350, and 5 µg/kg,

respectively. However, the MRLs of AFB₂, ST, and CIT in corn are not specified. And the classification of standard is still not specific enough to effectively distinguish the limit value of raw grain and finished grain [13–15]. Therefore, it is necessary to continuously improve the relevant analysis methods, which will help to come up with a more reasonable limit standard to ensure the corn food security.

At present, commonly used pretreatment methods are liquid-phase microextraction [16–18], liquid-liquid microextraction [19], dispersive liquid-liquid microextraction [20–22], QuEChERS [23–25], SPE [26], and DSPE [27]. Most of these methods are used for the extraction of a single mycotoxin. There are few reports on the analysis of several mycotoxins. Compared with other methods, QuEChERS is more and more widely used due to its advantages of quick, easy, cheap, effective, rugged, and safe. The association of official analytical chemists (AOAC) and European committee for standardization (EN) have released the method standard based on this technology (AOAC 2007.01 and EN 15662:2008) [28, 29]. In order to expand the use of the QuEChERS method, this work improved it.

In this work, the modified QuEChERS procedure was developed to extract, separate, and clean up mycotoxins in corn samples. A mixture of ethyl acetate and n-hexane was used as an extraction solvent. The extraction and cleanup can be completed in one step, and analysis speed can be greatly improved.

2. Materials and Methods

2.1. Sample. Three kinds of corn in the grain storehouse were randomly selected and simulated in a container transportation environment. The samples were divided into sample 1, sample 2, and sample 3, and the samples were crushed to ensure that 75% of the corn samples passed through an 80-mesh sieve. All samples were sealed and stored at –20°C for testing.

2.2. Reagents and Equipment. The main apparatus are listed in Supplementary Table 1. Acetonitrile and methanol (chromatographical pure) were purchased from Thermo-Fisher, USA. The formic acid and ammonium formate were purchased from Sigma-Aldrich, USA. All other reagents (analytical grade) were purchased from the Beijing Chemical Factory (Beijing, China). The water used in the experiment was Milli-Q ultrapure water.

Mycotoxin standards, including aflatoxin B₁ (AFB₁), aflatoxin B₂ (AFB₂), sterigmatocystin (ST), and citreoviridin (CIT), were prepared in acetonitrile at a concentration of 100 µg/mL as a standard stock solution. All standard stock solutions were stored in a refrigerator at 4°C. A standard working solution (10 µg/mL) was prepared by diluting the standard stock solution with acetonitrile weekly.

As mycotoxins are extremely toxic, endangering health and polluting the environment, it is necessary to take good care during the experiment to avoid contact between mycotoxins and the skin. The containers, consoles, and items that have been exposed to mycotoxins must be disinfected

with a 5% sodium hypochlorite-acetone solution. The containers should be immersed in a closed disinfectant for at least 30 minutes and then washed with water.

2.3. Chromatographic Conditions. The analytical column was Eclipse XDB-C18 column (150 mm × 4.6 mm i.d., 3.5 µm, Agilent, USA), the column temperature was 35°C, mobile phase A had 0.1% formic acid aqueous solution, mobile phase B had methanol, gradient elution procedure was carried out: 0.0 min → 2.0 min, 5% B; 2.0 min → 10.0 min, 5% B → 50% B; 10.0 min → 12.0 min, 50% B → 60% B; and 12.0 min → 25.0 min, 60% B → 90% B, the flow rate was 0.5 mL/min, and injection volume was 10 µL. The DAD detection was carried out at a wavelength of 225 nm. The reference wavelength and bandwidth were 360 and 4 nm, respectively.

2.4. Modified QuEChERS Procedure. The 5.000 g (to within 0.001 g) corn-powder samples were accurately weighed and added into a 50 mL centrifuge tube with a lid, and 16 mL 0.5% (volume concentration) formic-acid aqueous solution was added. Then, the mixed sample solution was homogenized in a high-speed homogenizer. After 30 s, the tube was vigorously shaken for 5 min and the 6 mL extraction solvent (ethyl acetate: n-hexane = 1: 1) and 0.3 g NaCl were added into the tube. The ultrasonic extraction was carried out for 5 min, the mixed solution was centrifuged at 0°C and 15,000 rpm for 5 min, and the supernatant was transferred into another centrifuge tube containing 80 mg of adsorbent (40 mg of diatomaceous earth + 40 mg PSA); after shaking, the mixture was centrifuged at 15,000 rpm for 5 min, then the supernatant was transferred to a glass flask and evaporated to dryness at 35°C in a vacuum rotary evaporator, and the residue was redissolved with 100 µL of solvent (acetonitrile). Finally, the analytical solution was filtered with a PTFE filter and analyzed.

2.5. Method Evaluation

2.5.1. Linear Range. A standard curve was prepared from the peak area versus the analyte concentration. The linearity of the data was evaluated using a linear correlation coefficient.

2.5.2. Precision and Recovery. For the same sample, analyze it 5 times a day to find the intraday precision. For the same sample, analyze it once a day for five days to get the interday precision. The intraday and interday precisions are expressed as relative standard deviations (RSDs). Then, the average extraction recoveries were obtained.

2.5.3. Limit of Detection and Limit of Quantitation. The detection limit (LOD) and the lower limit of quantification (LOQ) are the lowest concentration values when the signal-to-noise ratio is 3 and 10 times, respectively.

TABLE 1: Analytical performance.

Mycotoxin	Regression equation	Correlation coefficient	Linear range ($\mu\text{g/kg}$)	LOD ($\mu\text{g/kg}$)	LOQ ($\mu\text{g/kg}$)
AFB ₁	$A = 138.54c + 19.04$	0.9981	2.5–1000	3.5	10.4
AFB ₂	$A = 102.56c + 16.03$	0.9989	2.5–1000	4.8	16.3
ST	$A = 54.82c + 5.63$	0.9975	2.5–1000	7.2	35.1
CIT	$A = 39.53c + 7.21$	0.9987	2.5–1000	6.3	20.6

TABLE 2: Analytical results of samples.

Sample	Mycotoxin	Added level ($\mu\text{g/kg}$)	Recovery (%)	Intra-RSD (%)	Inter-RSD (%)
1	AFB ₁	10.0	104.2	1.8	3.4
		100.0	103.1	1.7	3.6
	AFB ₂	10.0	101.8	2.0	4.1
		100.0	102.9	1.8	3.2
	ST	10.0	95.0	2.2	4.5
		100.0	98.3	1.9	3.6
	CIT	10.0	89.7	1.9	3.9
		100.0	92.1	2.4	5.2
	AFB ₁	10.0	102.6	1.9	3.7
		100.0	103.5	1.8	3.6
2	AFB ₂	10.0	100.6	2.0	4.3
		100.0	103.0	2.1	4.2
	ST	10.0	93.4	2.3	4.2
		100.0	95.5	2.1	4.8
	CIT	10.0	96.5	2.4	5.0
		100.0	94.8	2.5	5.1
	AFB ₁	10.0	102.9	2.0	4.7
		100.0	104.5	2.2	4.3
	AFB ₂	10.0	99.8	2.1	4.1
		100.0	102.7	1.9	3.6
3	ST	10.0	97.4	1.7	3.2
		100.0	95.3	2.1	3.6
	CIT	10.0	90.2	1.9	4.1
		100.0	91.4	1.8	3.2

3. Results and Discussion

3.1. Optimization of Extraction Conditions

3.1.1. Effects of Type and Volume of Extraction Solvent. The experiments examined the effects of acetonitrile (ACN), acetone (AO), ethyl acetate (EA), n-hexane (HA), and ethyl acetate/ n-hexane (EA/HA, V: V = 1: 1) on mycotoxin extraction. As shown in Supplementary Figure 1, due to the strong polarity of acetonitrile, it cannot effectively penetrate high-fat samples and is not conducive to the extraction of analytes. N-hexane is nonpolar, but although it can effectively penetrate the sample, its ability to dissolve the more polar mycotoxin is limited, resulting in lower recovery of target analytes. The ethyl acetate is cheap, has low toxicity, evaporates easily, and has medium polarity. Ethyl acetate has a more suitable polarity and is more conducive to the extraction of target analytes with similar polarity. Compared with other extraction solvents, the interference peaks of the chromatogram obtained by ethyl acetate/n-hexane extraction were less and the baseline noise was lower. After extraction of ethyl acetate/n-hexane, the target analytes are adsorbed and the fat remains in the solution, thereby eliminating its effects on the extraction of the analytes.

Therefore, ethyl acetate and n-hexane (EA/HA, V: V = 1: 1) were selected as the extraction solvents in this experiment.

The effect of volume of the extraction solvent in the range of 2.00 to 8.00 mL on extraction of the analytes was also investigated. As the volume of the extraction solvent increases, the recoveries of the analytes increase first and then remain constant. At 6.00 mL, maximum recoveries of analytes are achieved, and therefore 6.00 mL of ethyl acetate and n-hexane (1:1) was used in this experiment.

3.1.2. Effects of Ultrasonic Extraction Time. Ultrasonic extraction is an equilibrium extraction, and the optimal extraction efficiency is established by equilibrium. The effects of the ultrasonic extraction time on recoveries of mycotoxins were evaluated by performing a single factor experiment taking 2–6 min. The results are shown in Supplementary Figure 2. When the extraction time increased from 2 to 5 min, the peak quantity of analytes increased significantly, but the recoveries did not change as the extraction time continued to increase. This may be because the surface area of extraction solvent and aqueous solution is large, the target analytes transfer quickly between the two phases, the extraction equilibrium can be reached in a very short time, and

FIGURE 1: HPLC chromatograms. (a) Standard solution, (b) blank sample, and (c) spiked sample ($10 \mu\text{g/kg}$). 1 AFB1, 2 AFB2, 3 ST, and 4 CIT.

TABLE 3: Comparison of the proposed method with other methods.

Matrix	Method*	Sample amount (g)	Organic solvent (mL)	The linear range	Extraction time (min)	Spiked level	Recovery (%)	RSD (%)	Reference
Corn	Modified QuEChERS-HPLC	5.0	6.1	2.5~1000 ($\mu\text{g/kg}$)	2	10, 100 ($\mu\text{g/kg}$)	89.7~105.9	1.8~4.3	This work
Juice	AS-DLLME-LC-MS	5.0	2.6	1~500 ($\mu\text{g/L}$)	20	0.2, 1, 10 ($\mu\text{g/kg}$)	75.6~110.0	1.4~15.5	[22]
Feed	QuEChERS-UHPLC-MS/MS	2.0	10.5	1~500 ($\mu\text{g/L}$)	21	5, 20, 100 ($\mu\text{g/kg}$)	89.3~112.6	0.9~6.1	[23]
Cereal	QuEChERS-HPLC	2.0	10.1	0.66~150 ($\mu\text{g/kg}$)	5	2, 20 ($\mu\text{g/kg}$)	60~98	7.2~12.1	[24]
Notoginseng	QuEChERS--UHPLC-MS/MS	2.0	11	0.25~125 ($\mu\text{g/L}$)	102	20 ($\mu\text{g/L}$)	80.1~116.2	0.2~5.7	[25]
Oil	SPE-HPLC	5.0	26	0.5~50 ($\mu\text{g/L}$)	60	0.5, 1, 2 ($\mu\text{g/kg}$)	81.4~105.3	1.3~8.6	[26]
Oil	DSPE-HPLC	2.0	10.5	50~40000 ($\mu\text{g/L}$)	32	0.2~8 ($\mu\text{g/kg}$)	60~120	4.16~25.2	[27]

the extraction efficiency will not be affected by the increase of extraction time. Therefore, the time we selected was 5 min.

3.1.3. Effects of Type of Cleanup Adsorbent. The effects of different cleanup adsorbents, including C18, diatomite, PSA, neutral alumina Al_2O_3 , and diatomaceous earth + PSA (1 : 1), on recoveries of target analytes were surveyed. As shown in Supplementary Figure 3, the recoveries of mycotoxins are the highest when the mixed adsorbent of diatomaceous earth and PSA was used as clean-up adsorbent. There are two possible reasons. On one hand, mycotoxins are polar molecular substances, which are a molecule with strong anode polarity. When selecting a cleanup adsorbent, it is necessary to have a molecular structure with polarity and the capacity for ion exchange. Different cleanup adsorbents have different capacities for absorbing mycotoxins. The zeolite and bentonite are unipolar and swell in water. They can adsorb both aflatoxins and water-soluble nutrients. On the other hand, the mixed cleanup adsorbent of diatomaceous earth and PSA, which is bipolar, has the best cation exchange balance, does not swell in water, has a strong ability to adsorb toxins, and has a wide range. It can adsorb not only aflatoxin, but also vomiting toxin, zearalenone, and T-2 toxin. However, it does not absorb nutrients. Therefore, when diatomaceous earth and PSA were mixed, the four mycotoxins had the highest recoveries. Hence, the diatomaceous earth + PSA (1 : 1) was selected as a cleanup adsorbent in further work.

3.1.4. Effects of Amount of Mixed Cleanup Adsorbent. The experiment also examined the effect on the recoveries when the amount of the mixed adsorbent was changed from 40 mg to 250 mg. The results (Supplementary Figure 4) showed that the amount of adsorbent was too small to be sufficiently purified, and the recoveries of the mycotoxin analytes increased with the increase in the amount of the mixed adsorbent. When the mixed adsorbent amounted to 80 mg, the recoveries reached its highest point. This is

because when the amount of adsorbent is greater than 80 mg, the cleanup adsorbent will have a stronger adsorption on the mycotoxin, which is not easy to be eluted, and on the contrary, the recoveries will be reduced. So, 80 mg was the amount of the cleanup adsorbent in further work.

3.2. Method Evaluation

3.2.1. Linear. A series of standard solution of mycotoxins was prepared, respectively. The above standard solution of 20 μL was injected into the high-performance liquid chromatograph. The standard curves were drawn with the concentration of analytes in the standard solution as the abscissa, and the peak areas of chromatogram were as the ordinate. The recoveries of the analytes were calculated according to the standard curve. All concentrations were tested in quintuplicate. The formula for calculating the recovery is

$$\text{recovery} = \frac{\text{change in the amount of measured analyte}}{\text{amount of analyte spiked into the sample}} \times 100\%. \quad (1)$$

The linear regression equations and correlation coefficients are listed in Table 1. This method achieves good linearity with correlation coefficients for all analytes in the range of 0.9975 to 0.9989.

3.2.2. Precision and Recovery. The precision of the method was assessed by measuring intraday and interday precision. Intraday precision is measured of corn samples with a concentration of 10 and 100 $\mu\text{g/kg}$ five times in one day. Interday precision is measured of corn samples with a concentration of 10 and 100 $\mu\text{g/kg}$ once a day for five consecutive days. Table 2 lists the relative standard deviations and recoveries. The results showed that the acceptable standard deviations for intraday and interday precision were 1.8~4.3% and 3.2~5.2%, respectively, with recoveries from 89.7 to 105.9%.

3.2.3. Limit of Detection and Limit of Quantitation. The limits of detection (LOD) and the limit of quantitation (LOQ) are the concentration values of the analytes when the signal of the measured object is 3 times and 10 times of the noise signal, respectively. As shown in Table 1, the limits of detection (LOD, S/N ratio = 3) for all analytes range from 3.5 to 7.2 $\mu\text{g/kg}$. The limit of quantitation (LOQ, S/N ratio = 10) for all analytes is below 10 $\mu\text{g/kg}$, which is below the MRL stipulated by the European Union.

3.2.4. Sample Analysis. The analysis of the actual sample can get good recoveries (89.7–105.9%) and precision ($\leq 5.2\%$). The chromatograms are shown in Figures 1(a)–1(c). Table 2 shows the actual results. The AFB₁, AFB₂, ST, and CIT in three kinds of corn were undetectable.

3.3. Comparison of the Proposed Method with Other Methods. The proposed method was compared with [22–27]. As shown in Table 3, the proposed method has four advantages. Firstly, the proposed method uses simpler instruments and equipment, such as centrifuge and oscillator. Secondly, the method has lower technical difficulty and simpler pretreatment steps. Thirdly, it takes less time. The whole extraction process does not exceed 7 min. Finally, the simultaneous extraction and cleanup of four mycotoxins can be realized by designing the proportion of extraction solution, the types of salt, and purifying agents.

4. Conclusion

According to the characteristics of QuEChERS, a modified QuEChERS method for extraction and cleanup of mycotoxins in corn was established and developed. The effects of type and volume of extraction solvents, ultrasonic extraction time, and cleanup adsorbent on recovery of mycotoxins during the pretreatment of mycotoxins by the modified QuEChERS method were discussed. Compared with other methods, this method is simpler to operate, the detection time is shortened to less than 7 minutes, and the amount of organic reagent is less, which is suitable for the detection of large amount of samples. The proposed method can effectively overcome the errors caused by sample pretreatment and matrix effect. It expands the choice of mycotoxin extraction solvents in high-fat-solid samples. Choosing a suitable solvent and optimizing the mixed adsorbent was a promising approach to improving the efficiency of extraction and purification of the mycotoxin in the high-fat-solid samples. By changing the experiment parameters, the method could be further used for extraction and analysis of mycotoxins in complex samples.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

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

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Supplementary Materials

Supplementary Table 1: the list of apparatus. Supplementary Figure 1: effect of the type of extract solvents on the recoveries of the analytes. Supplementary Figure 2: effect of ultrasonic extraction time on the recoveries of the analytes. Supplementary Figure 3: effect of the type of adsorbents on recoveries of analytes. Supplementary Figure 4: effect of the amount of adsorbents on the recoveries of the analytes. (*Supplementary Materials*)

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