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Simultaneous determination of 28 polychlorinated biphenyls in cereal grains by rapid multi-plug filtration cleanup and gas chromatography-mass spectrometry: Method development, validation and greenness assessment

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ABSTRACT: Polychlorinated biphenyls (PCBs) are highly persistent and toxic chemicals that pose severe health risks, making their detection in food products such as cereal grains critical for food safety. However, the accurate quantification of PCBs in cereal grains remains challenging owing to complex matrix interferences. This work presents a novel method based on multi-plug filtration cleanup (m-PFC) coupled with gas chromatography-mass spectrometry (GC-MS) for the simultaneous determination of 28 PCBs in cereal grains, including maize, wheat, and rice. The m-PFC procedure utilized a mixed sorbent composed of carboxylated multi-walled carbon nanotubes (CMWCNTs) and primary secondary amine (PSA), which significantly enhanced cleanup efficiency. Weak matrix effects (within $\pm 20\%$) were observed for all target analytes, allowing the use of solvent-based standards for quantification. Method validation demonstrated satisfactory analytical performance: linearity (correlation coefficients > 0.998), accuracy (recoveries of 73.1%–118.8%), precision (relative standard deviations $< 14.3\%$), and sensitivity (limits of detection: 0.01–0.06 $\mu\text{g/kg}$ and limits of quantification: 0.02–0.18 $\mu\text{g/kg}$). The validated method was applied to analyze real cereal samples, and no target PCBs were detected above the method's limits of quantification. Furthermore, greenness assessment using the Analytical Eco-Scale (AES) and Green Analytical Procedure Index (GAPI) confirmed the method's acceptable environmental profile, while highlighting key areas for future improvement. The proposed protocol offers a simple, reliable, and highly practical tool for the routine surveillance of PCBs in cereal grains.

Keywords: Cereal grain; Polychlorinated biphenyls; M-PFC; GC-MS; Greenness receptor

1. Introduction

As a dietary staple, cereal grains are primary contributors to daily nutrient intake, providing carbohydrates and fiber, as well as a range of vitamins and minerals^[1]. Among cereal crops, wheat (*Triticum aestivum*), rice (*Oryza sativa*), and maize (*Zea mays*) rank as the three most widely consumed globally^[2]. A significant concern, however, is that during field growth, these crops absorb persistent pollutants, such as polychlorinated biphenyls (PCBs), leading to the presence of these chemicals in grain products^[3–7]. Since diet

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accounts for over 90% of total PCB intake in humans, food contamination by PCBs poses a significant public health threat^[8-9]. Therefore, developing robust analytical techniques to monitor PCBs in cereal samples is deemed imperative, as it serves as a critical safeguard for public health.

Current methods for determining PCBs in cereals most commonly employ gas chromatography (GC) coupled with diverse detection systems, including mass spectrometry (MS)^[3-5], tandem MS (MS/MS)^[6, 7], and electron capture detector (ECD)^[10-11]. Among these, GC-MS is often the preferred choice owing to its superior sensitivity, selectivity, and identification capability compared to ECD, while being more cost-effective and convenient than MS/MS. However, accurate quantification of PCBs in cereals remains challenging due to the complexity of cereal matrices, which can induce significant matrix effects. Consequently, sample pretreatment is indispensable prior to instrumental analysis with purification being the critical step for effective removal of matrix interferences. Traditional pretreatment approaches, such as Soxhlet extraction (SE)^[3-5], accelerated solvent extraction (ASE)^[11], solid-phase extraction (SPE)^[7, 12], and column chromatography^[5, 13], are widely utilized but often suffer from specialized instrumentation, high solvent consumption, and tedious operations. Highly popular technologies, such as QuEChERS (quick, easy, cheap, effective, rugged, and safe)^[6] and dispersive SPE (d-SPE)^[14], have been successfully applied to detect PCBs in cereals because of their simplicity, low solvent consumption, and enhanced operability. To further streamline sample pretreatment, filtration-based cleanup strategies have attracted increasing interest. The continued relevance of this design concept is highlighted by recent innovations, such as automatic pressure filtration^[15] and filter-press cleanup^[16], which validate the efficiency of this format for complex food matrices. As a pioneering technique in this domain, the multi-plug filtration cleanup (m-PFC) was initially proposed by Zhao et al.^[17] for pesticide analysis in fruits and vegetables. This method employs a syringe tube where sorbent materials are immobilized between two sieve plates. Efficient matrix cleanup is achieved by manipulating the syringe plunger to pass the sample solution through the sorbents^[18-19], a process that can be completed within seconds and eliminates traditional pretreatment steps such as vortexing and centrifugation^[20]. To date, m-PFC has found extensive application in food safety surveillance for the accurate measurement of diverse chemical hazards, such as pesticide residues, veterinary drugs, mycotoxins and *p*-phenylenediamines^[21-27], demonstrating significant improvements in both cleanup efficiency and operational simplicity. Sorbent selection represents a critical determinant of m-PFC performance. Currently employed sorbents mainly include multi-walled carbon nanotubes (MWCNTs) and primary-secondary amine (PSA)^[18, 20, 23, 28]. Among them, MWCNTs are well-studied nanocarbon-based sorbents distinguished by their hollow cylindrical structure and high specific surface area. Functionalization with chemical moieties, such as carboxyl groups, can further enhance their properties by providing increased surface area and improved dispersion^[29]. These properties establish them as effective sorbents in m-PFC for isolating pesticides and other contaminants from food matrices^[30, 31]. Nevertheless, the application of m-PFC utilizing functionalized MWCNTs for the detection of PCBs in cereal samples has not yet been documented.

In this work, a rapid technique combining m-PFC with GC-MS was introduced to quantify 28 PCBs in cereal grains (maize, wheat, and rice). The analyte list (Table 1) includes the indicator PCBs, all WHO-defined dioxin-like PCBs, and some other congeners frequently reported in food and environmental samples^[32–35]. The method employed carboxylated MWCNTs (CMWCNTs) and PSA as the m-PFC sorbents for sample cleanup. Key parameters in the instrumentation, extraction, and cleanup steps were optimized to maximize analytical performance. The validated protocol was subsequently applied to real grain samples, and its greenness was systematically evaluated. To our knowledge, this study is the first to develop and validate a CMWCNTs/PSA-based m-PFC method coupled with GC-MS for determining PCBs in cereal grains.

2. Materials and methods

2.1. Chemicals and reagents

The standard solution mix of 28 PCBs at 100 mg/L in *n*-hexane was supplied by Tanmo Quality Testing Co, Ltd. (Beijing, China). Chromatography grade acetonitrile, *n*-hexane, and acetone were procured from Thermo Fisher Scientific (Shanghai, China). Analytical grade toluene was supplied by Shanghai Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Graphitized carbon black (GCB, 120–400 mesh) and PSA (40–60 µm) were bought from Agela Technologies Co., Ltd. (Tianjin, China). MWCNTs (10–20 nm outer diameter, 10–30 µm length) and CMWCNTs (10–20 nm outer diameter, 10–30 µm length) were supplied by XFNANO Materials Tech Co., Ltd. (Nanjing, China).

2.2 Instruments

The ultrasonic cleaner (KQ-500DE, Supmile, Kunshan, China), the high-speed centrifuge (16R, CenLee, Hunan, China), and the nitrogen blowing instrument (HSC-24B, HengAo, Tianjin, China) were used in sample preparation. The analytes were determined using an Agilent 8890 GC system interfaced to a 5977B single-quadrupole mass spectrometer featuring an Xtr electron impact ionization source (Santa Clara, CA, USA).

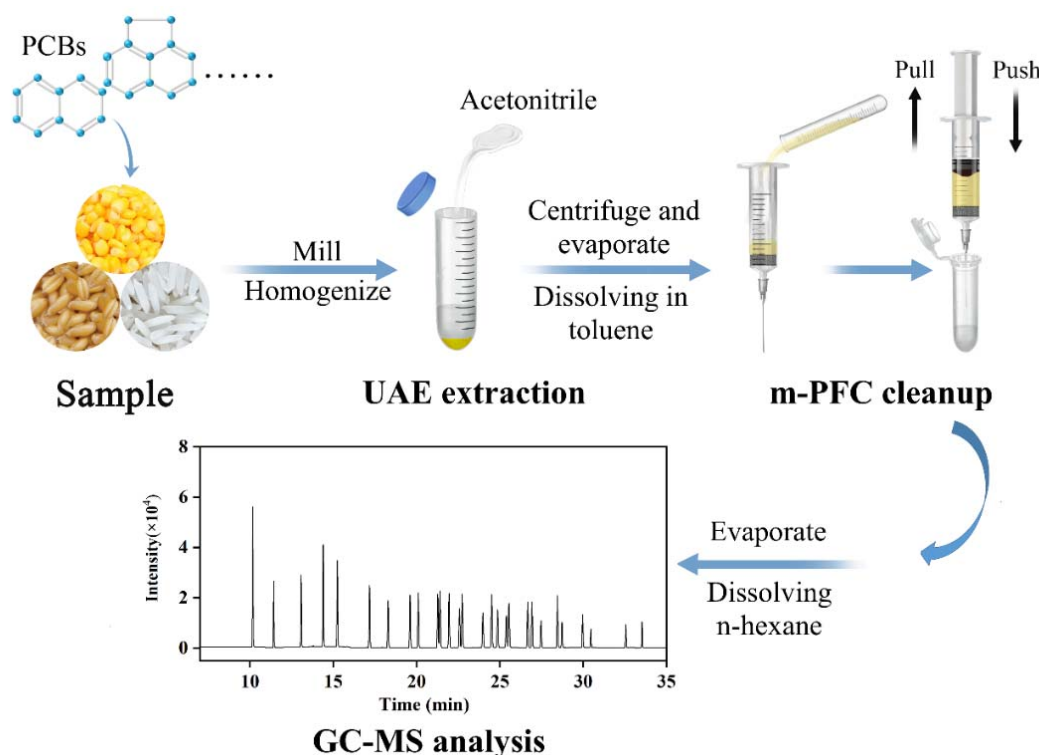
2.3 Sample treatment and extraction

Three cereal grain samples comprising rice, wheat and maize were obtained from agricultural bases and local farmers in Suzhou, China. Samples are dry grains with moisture contents below 14.3%, measured gravimetrically by drying the samples at 105 °C to constant weight. Prior to analysis, they were milled and homogenized.

A 2.0 g portion of the homogenized sample was accurately weighed into a 50 mL centrifuge tube. To this, 10 mL of acetonitrile was added, and the mixture was ultrasonicated for 5 min, followed by centrifugation at 9000 r/min for 3 min. A 5 mL aliquot of the supernatant was transferred to a 10 mL centrifuge tube and evaporated to nearly dry under nitrogen at 80 °C. The remaining residue was then reconstituted in 4 mL of toluene for subsequent cleanup.

2.4 m-PFC cleanup procedure

Sample cleanup was performed using a laboratory-made m-PFC column packed within a 5-mL syringe. First, a polyethylene (PE) sieve plate was positioned at the bottom. A homogeneous mixture of 0.01 g of CMWCNTs and 0.12 g of PSA was then added. The syringe was gently tapped to settle the powder, and the sorbent was compacted with a flat-tipped rod to form a uniform bed. The packing was subsequently secured with a second PE sieve plate on top. For purification, the entire 4 mL of toluene extract was loaded onto the column. As illustrated in Scheme 1, the extract was slowly filtered through the sorbent bed via 1 cycle of pulling and pushing the syringe plunger. The collected eluate was evaporated to near-dryness under nitrogen at 80 °C. Finally, the resulting residue was reconstituted in 1 mL of *n*-hexane, filtered through a 0.22 µm nylon membrane filter, and transferred to a vial for GC-MS analysis.



Scheme 1. Schematic diagram of the main steps of the developed analysis technique.

2.5 GC-MS conditions

An HP-5MS capillary column (30 m×0.25 mm×0.25 µm) was employed for chromatographic separation. High-purity helium (99.999%) served as the carrier gas at a flow rate of 1.2 mL/min. The column temperature was set as follows: an initial hold at 50 °C for 1 min, followed by a ramp of 25 °C/min to 180 °C (hold for 2 min), then increased at 3 °C/min to 232 °C, and a subsequent increase of 6 °C/min to a final temperature of 280 °C (hold for 2 min). The sample (1 µL) was injected into the injection port in splitless mode at 280 °C.

The mass spectrometer was operated in electron ionization mode at 70 eV, and data acquisition was performed in selected ion monitoring mode. Key operational parameters were set as follows: the ion source was maintained at 250 °C, while the quadrupole and transfer line were kept at 150 °C and 280 °C, respectively. A 5-minute solvent delay was implemented. The retention times and selective ions monitored for all analytes are detailed in Table 1.

Table 1 Intestinal microorganisms producing indole derivatives and their functional properties

Peak No.	PCB congener	Formula	Retention time (min)	Qualifier ion (m/z)	Quantifier ion (m/z)
1	8	C ₁₂ H ₈ Cl ₂	10.24	224, 152	222
2	18	C ₁₂ H ₇ Cl ₃	11.51	258, 186	256
3	28	C ₁₂ H ₇ Cl ₃	13.17	258, 186	256
4	52	C ₁₂ H ₆ Cl ₄	14.51	220, 290	292
5	44	C ₁₂ H ₆ Cl ₄	15.36	220, 290	292
6	66	C ₁₂ H ₆ Cl ₄	17.31	290, 220	292
7	101	C ₁₂ H ₅ Cl ₅	18.42	254, 328	326
8	81	C ₁₂ H ₆ Cl ₄	19.77	289, 294	292
9	77	C ₁₂ H ₆ Cl ₄	20.26	289, 294	292
10	123	C ₁₂ H ₅ Cl ₅	21.43	328, 324	326
11	118	C ₁₂ H ₅ Cl ₅	21.58	328, 324	326
12	114	C ₁₂ H ₅ Cl ₅	22.11	328, 324	326
13	153	C ₁₂ H ₄ Cl ₆	22.74	362, 290	360
14	105	C ₁₂ H ₅ Cl ₅	22.90	328, 324	326
15	138	C ₁₂ H ₄ Cl ₆	24.15	362, 290	360
16	126	C ₁₂ H ₅ Cl ₅	24.70	328, 324	326
17	187	C ₁₂ H ₃ Cl ₇	25.03	396, 324	394
18	167	C ₁₂ H ₄ Cl ₆	25.55	362, 290	360
19	128	C ₁₂ H ₄ Cl ₆	25.73	362, 358	360
20	156	C ₁₂ H ₄ Cl ₆	26.84	362, 358	360
21	157	C ₁₂ H ₄ Cl ₆	27.10	362, 290	360
22	180	C ₁₂ H ₃ Cl ₇	27.63	396, 323	394
23	169	C ₁₂ H ₄ Cl ₆	28.62	362, 358	360
24	170	C ₁₂ H ₅ Cl ₅	28.88	396, 324	394
25	189	C ₁₂ H ₃ Cl ₇	30.13	396, 324	394
26	195	C ₁₂ H ₂ Cl ₈	30.60	428, 358	430
27	206	C ₁₂ HCl ₉	32.69	466, 462	464
28	209	C ₁₂ Cl ₁₀	33.66	500, 496	498

2.6 Evaluation of matrix effect

Two types of calibration curves were prepared: a solvent-based curve and a matrix-matched curve, both at levels of 0.5, 1, 5, 10, 20, 100 and 500 µg/L (corresponding to 0.5, 1, 5, 10, 20, 100 and 500 µg/kg of PCBs in the studied matrices). Matrix effect (ME) was determined according to Eq. (1), which is based on the ratio of the slopes of the matrix-matched and solvent-based calibration curves. ME values within ±20% were categorized as a weak matrix effect, which permits the use of solvent-based calibration. Those exceeding this range were considered to indicate either a medium (20% < |ME| < 50%) or strong (|ME| ≥ 50%) matrix effect, both of which necessitate the use of matrix-matched calibration for reliable quantification^[36-38].

$$ME = \left[\left(\frac{\text{Slope of matrix-matched calibration}}{\text{Slope of solvent-based calibration}} \right) - 1 \right] \times 100\% \dots \dots \dots (1)$$

2.7 Method validation and greenness assessment

Validation of method performance was conducted by determining its linearity, accuracy, precision, and sensitivity^[39]. Linearity was established via the construction of seven-point calibration curves, utilizing solvent-based standard solutions at concentrations of 0.5–500 µg/L. Method accuracy was estimated through recovery experiments by spiking representative real-world cereal samples with the analytes at 0.5, 2 and 10

μg/kg. Precision was evaluated by analyzing six replicate extractions for each matrix. Accuracy was expressed as recovery rate (%) and precision as relative standard deviation (RSD, %). Mean recovery rates (70%–120%) and RSDs (< 20%) were deemed acceptable. The limits of detection (LODs) and quantification (LOQs) were used to evaluate method sensitivity. They were defined as the lowest analyte concentrations that could produce signal-to-noise (S/N) ratios of 3 and 10, respectively. The method's greenness was assessed by applying two established metrics: the Analytical Eco-Scale (AES)^[40] and the Green Analytical Procedure Index (GAPI)^[41].

2.8 Quality control and analyte identification

For reliable identification and accurate quantification, a quality control protocol was implemented throughout the analysis process^[42–45]. Solvent and procedural blanks were analyzed to monitor instrumental background and potential contamination from sample preparation. Periodic washing runs and solvent blanks were incorporated within the analytical sequences among calibration standards and real samples to check for instrumental carryover. To verify the stability of the GC-MS, a standard mixture of 28 PCBs was injected every 20 samples; deviations of less than 20% between the quantitative results and the standard concentrations indicated acceptable instrumentation performance. For each batch of samples, duplicate analyses and matrix spike recovery tests were performed on randomly selected real samples, with acceptance criteria of 70–120% recovery and RSDs < 20%.

The identity of target analytes was confirmed according to the SANTE/11312/2021 guideline^[39]. Positive identification required the simultaneous fulfillment of three criteria: retention time matching that of authentic standards within ± 0.1 min, detectable signals ($S/N \geq 3$) for one quantifier and two qualifier ions, and ion abundance ratios within $\pm 30\%$ relative to those observed in the calibration standards from the same analytical sequence.

3. Results and discussion

3.1 Optimization of GC-MS

To enhance chromatographic performance, key GC parameters, including the oven temperature, injector temperature, and carrier gas (helium) flow rate, were optimized. Under the optimized conditions (details in Section 2.5), satisfactory separation and response for target compounds were achieved on a non-polar HP-5MS column, as shown in Fig. 1.

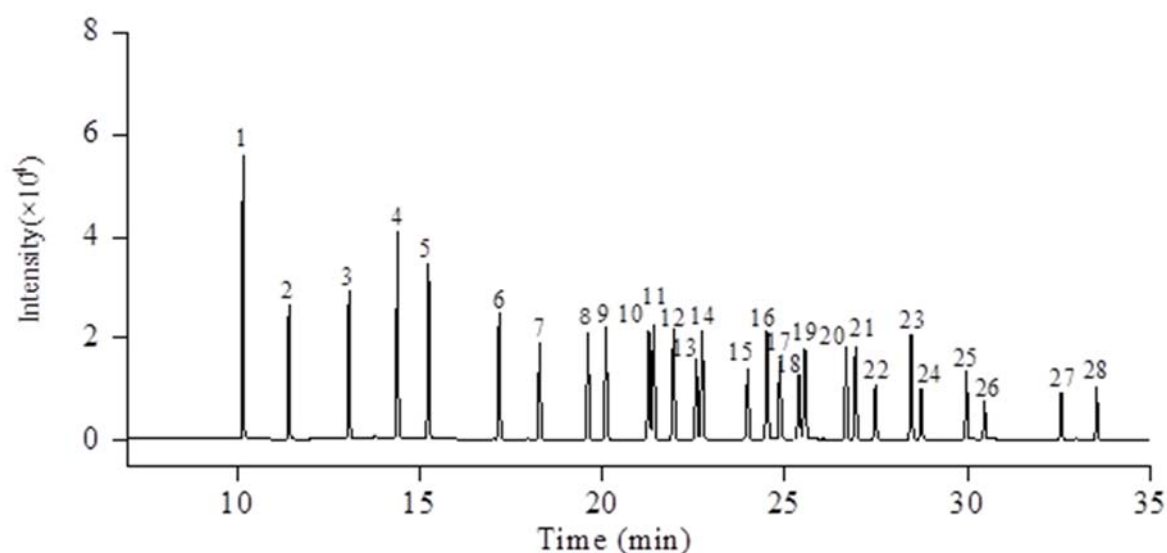


Fig. 1. GC-MS chromatograms of 28 PCBs standard solution at 100 µg/L. The number denoted was the same as that denoted in Table 1.

The MS conditions were optimized to enhance the method's sensitivity and selectivity. Since the signal strengths of the analytes varied with different ion source temperature, this parameter was optimized and fixed at 280 °C to achieve the maximum response. A working standard solution (100 µg/L in *n*-hexane) was analyzed in full-scan mode to acquire mass spectra. From the acquired spectra, fragment ions with high-abundance and low interference were chosen as the monitored ions for the 28 PCBs. After establishing retention times from the total ion chromatogram (TIC) data, the analytes were grouped within the MS acquisition method to maximize dwell time and thereby further improve detection sensitivity. For confirmation and quantification, one quantifier ion and two qualifier ions were monitored per analyte, as listed in Table 1.

3.2 Optimization of extraction and cleanup procedures

To optimize the extraction and cleanup procedures, maize was chosen as the representative cereal matrix because its composition is more complex than that of wheat and rice. The recovery of the 28 PCBs from samples spiked at 10 µg/kg served as the primary evaluation index. For the extraction step, a range of variables was tested, including the volume of water added (0, 1, 2 and 3 mL), the extraction solvent type (acetonitrile, *n*-hexane, ethylacetate and mixtures of acetone and *n*-hexane (1:1 and 1:2, V/V)) and volume (5, 8, 10 and 15 mL), the extraction time (5, 10, 15 and 20 min), and the toluene volume (2, 3, 4 and 5 mL). The optimization of the m-PFC procedure focused on the mass of two sorbents, CMWCNTs (0.01, 0.02, 0.03 and 0.04 g) and PSA (0.10, 0.11, 0.12, 0.13 and 0.14 g), and the number of cleanup cycles (1, 2, 3 and 4).

3.2.1 Optimization of extraction procedure

Cereal grains usually present as dry samples; hence, water addition is often employed to soak the samples before extraction to improve efficiency. However, this practice may increase co-extraction of matrix interferences, potentially hindering the extraction of target analytes. In this study, we investigated the extraction efficiency of PCBs under different volumes of water addition (0–3 mL). As illustrated in Fig. 2A, the optimal extraction efficiency was achieved when no water was added, yielding recovery rates of 84%–95% that were

higher than those obtained with water addition. As a result, all subsequent sample extractions were performed without the addition of water.

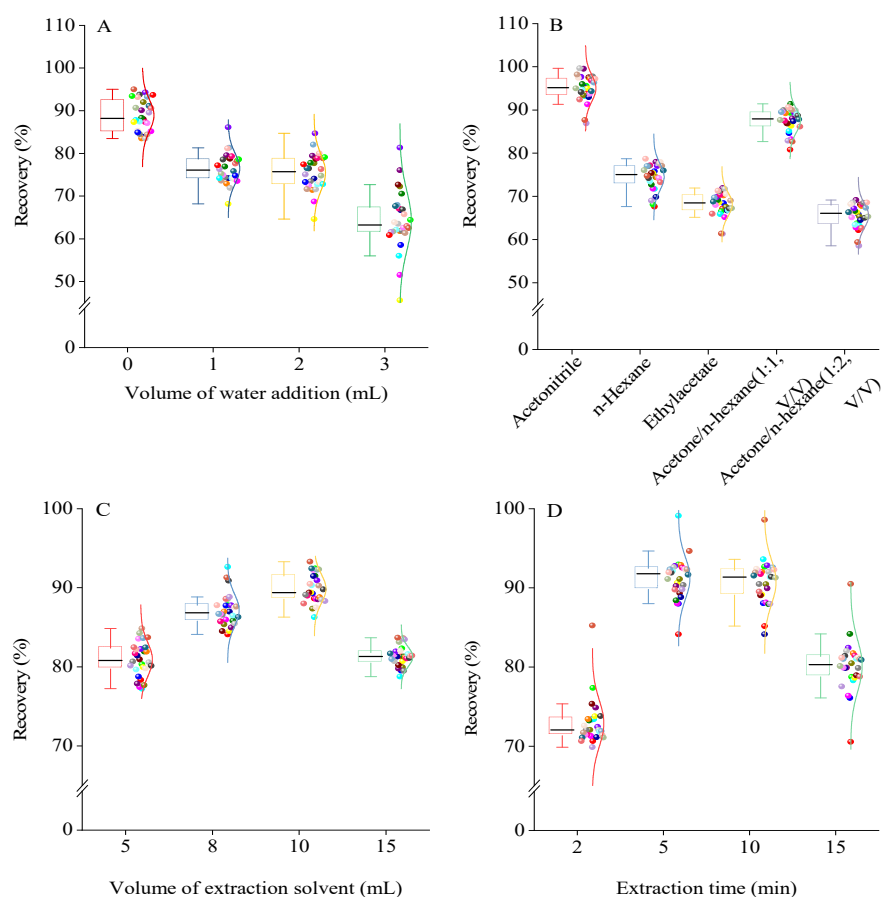


Fig. 2. Effects of (A) volume of water addition, (B) extraction solvent, (C) volume of extraction solvent, and (D) extraction time on extraction efficiency ($n=3$).

The type and volume of the extraction solvent critically influence the recovery of PCBs. Frequently used solvents for this purpose include acetonitrile^[46–48], *n*-hexane^[49–50], ethylacetate^[51–52] and acetone/*n*-hexane mixtures (1:1 and 1:2, V/V)^[53, 54]. To select an optimal solvent for the current methodology, these five options were evaluated. As Fig. 2B showed, the recoveries of PCBs varied among the solvents: acetonitrile yielded 87%–100%, *n*-hexane 68%–79%, ethyl acetate 61%–72%, while acetone/*n*-hexane (1:1 and 1:2, V/V) resulted in 81%–91% and 59%–69%, respectively. The results suggested that acetonitrile was a more effective solvent for the extraction process than the other tested solvents. Consequently, acetonitrile was used for further optimization, and its volume was examined over a range of 5 to 15 mL. Fig. 2C showed that the recoveries of PCBs improved when the solvent volume was raised from 5 mL to 10 mL, but decreased with a further increase beyond this volume. This may be attributed to the fact that a larger solvent volume reduces the thermodynamic driving force for the mass transfer of PCBs into the extraction solution, which subsequently decreases extraction efficiency. Therefore, 10 mL of acetonitrile was adopted in subsequent experiments.

Ultrasound-assisted extraction (UAE) was adopted in our analytical protocol owing to its simplicity, batch-processing capability and compatibility with automated systems^[55]. Extraction time was a critical parameter in UAE, as it affected the mass transfer of analytes from the sample matrix to the solvent, thereby determining the extraction efficiency. To achieve optimal recovery of PCBs, we examined an extraction time

range of 2 to 15 min. As Fig. 2D showed, the recoveries of PCBs rose from 2 to 5 min and then declined. Consequently, a 5-min extraction time was chosen as optimal and used for all further work.

3.2.2 Optimization of *m*-PFC procedure

Crude cereal extracts typically contain complex co-extractives, such as organic acids and pigments, which can induce matrix effects and contaminate analytical instrumentation. Consequently, effective purification prior to GC-MS detection is essential. In this study, the *m*-PFC method was employed to eliminate these interferences. For this approach, selecting an optimal sorbent is critical to maximize impurity removal while minimizing analyte loss. Preliminary experiments showed that the crude maize extract was turbid and visibly colored (Fig. 3A), indicating significant pigment contamination that hindered accurate PCB analysis. To mitigate this interference, three carbon-based sorbents with high affinity for pigments (MWCNTs, CMWCNTs, and GCB) were evaluated. Each sorbent (0.01 g) was tested using recovery experiments spiked at 10 µg/kg ($n = 3$). As illustrated in Fig. S1, the pigment removal efficiency followed the order: CMWCNTs > MWCNTs > GCB. Notably, the extract treated with CMWCNTs appeared nearly clear and colorless. For analyte recovery, all three sorbents exhibited strong adsorption towards planar PCBs, resulting in suboptimal recoveries for these specific congeners; in particular, PCBs 81, 77, 126, and 169 were completely adsorbed and not recovered. However, CMWCNTs demonstrated the best overall performance among the tested materials. The total number of PCBs with recoveries between 70% and 120% was 16 for CMWCNTs, compared to 14 for both MWCNTs and GCB. Furthermore, the average recovery of the 28 PCBs reached 75% for CMWCNTs, whereas MWCNTs and GCB averaged only 58% and 62%, respectively. Consequently, CMWCNTs were selected as the primary sorbent for further purification.

Despite the effective pigment removal, full-scan GC-MS analysis of the CMWCNTs-purified extract revealed persistent interference from two prominent peaks (Fig. 3B). These were identified as palmitic acid (*n*-hexadecanoic acid) and linoleic acid (9,12-octadecadienoic acid) based on spectral comparison with the NIST 11 library (Figs. S2 and S3). Since these compounds severely compromised the qualitative and quantitative analysis of PCBs, PSA was incorporated into the *m*-PFC protocol. Although PSA exhibits limited pigment removal capacity^[52-53], it was selected due to its high affinity for fatty acids and other organic acids^[56]. As depicted in Fig. 3, the combination of CMWCNTs and PSA significantly attenuated the interfering fatty acid peaks and yielded a lower chromatographic baseline compared to CMWCNTs alone, confirming the efficacy of PSA for fatty acid removal in the maize matrix. Accordingly, a composite sorbent composed of CMWCNTs and PSA was ultimately adopted for the *m*-PFC column.

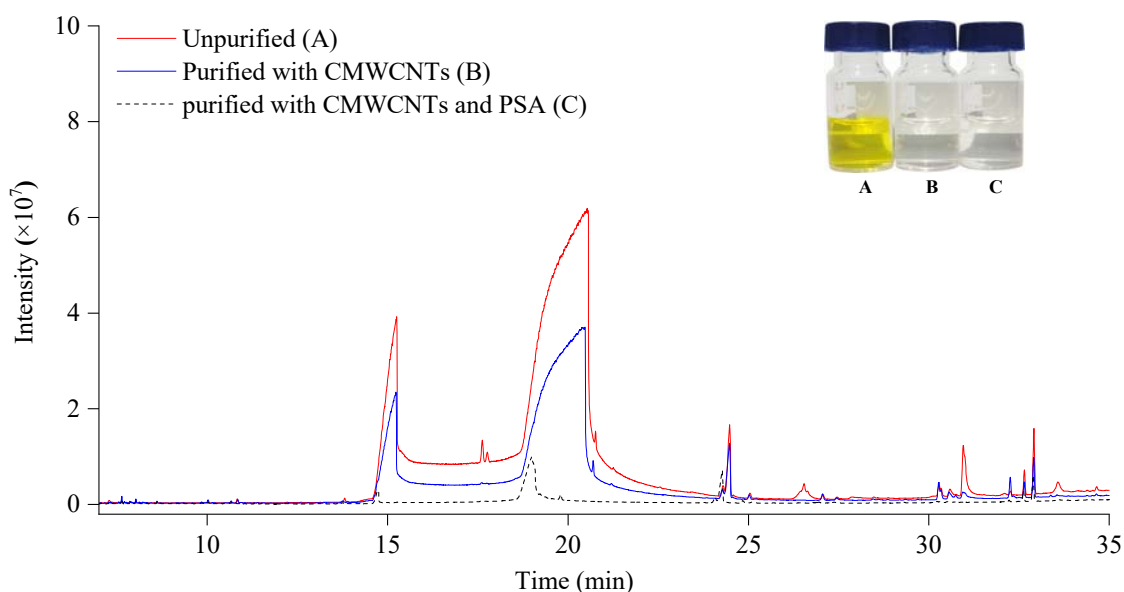


Fig. 3. Chromatogram of maize extracts processed by different sorbents. (A) unpurified, (B) purified with CMWCNTs, and (C) purified with CMWCNTs and PSA.

While the combination of CMWCNTs and PSA effectively removed matrix components, their application conditions required optimization to prevent analyte loss^[53]. As noted above, applying CMWCNTs directly to the initial acetonitrile extract led to substantial depletion of planar PCBs, particularly congeners 81, 77, 126 and 169. This phenomenon was attributed to strong π - π stacking interactions between CMWCNTs and these PCB congeners. To address this, a solvent exchange step using toluene was introduced to implement a selective elution strategy. This selectivity is achieved by leveraging competitive adsorption, wherein the aromatic rings of toluene preferentially occupy the strong π - π binding sites on CMWCNTs. This prevents the co-adsorption of target PCBs, ensuring high recoveries without compromising the removal of matrix interferences, primarily pigments. The volume of toluene used to reconstitute the extract was first optimized. Specifically, volumes ranging from 2 to 5 mL were evaluated. As displayed in Fig. 4A, the recovery of PCBs increased with the toluene volume from 2 to 4 mL, beyond which no further improvement was observed. Hence, 4 mL was chosen for subsequent experiments. Following this, the optimal dosages of the two sorbents were investigated. For this purpose, the toluene extracts were treated with varying amounts of CMWCNTs (0.01–0.04 g) and PSA (0.10–0.14 g). Fig. 4B shows that elevated CMWCNTs dosages reduced PCB recovery; a dosage of 0.01 g provided the optimal recovery (93%–102%) and effective matrix removal (Fig. 3B). According to Fig. 4C, recovery improved with increasing PSA dosage up to 0.12 g, beyond which it declined. This decrease is likely due to solvent retention and the resulting difficulty in phase separation, as well as potential non-specific adsorption at higher sorbent masses. Moreover, Fig. 3C demonstrates that PSA effectively minimized matrix interferences in the final extracts. Based on these findings, to ensure high analyte recovery while achieving effective matrix purification, 0.01 g of CMWCNTs and 0.12 g of PSA were selected for the m-PFC column and subsequent tests.

To achieve optimal recovery, another critical factor to be considered in the m-PFC procedure is the cleanup cycle, which refers to the number of times the sample extract is passed through the optimized sorbents

by pulling and pushing the syringe plunger. Our evaluation of different cleanup cycles (1, 2, 3 and 4) revealed that the highest analyte recoveries (87%–94%) were achieved with 1 cycle, beyond which yields progressively decreased (Fig. 4D). We hypothesize that repeated passages increase the contact probability between target PCBs and the sorbent's active sites, thereby promoting irreversible adsorption. promote adsorption of target PCBs onto the sorbent's active sites. Consequently, 1 cycle of m-PFC cleanup was adopted for the final protocol.

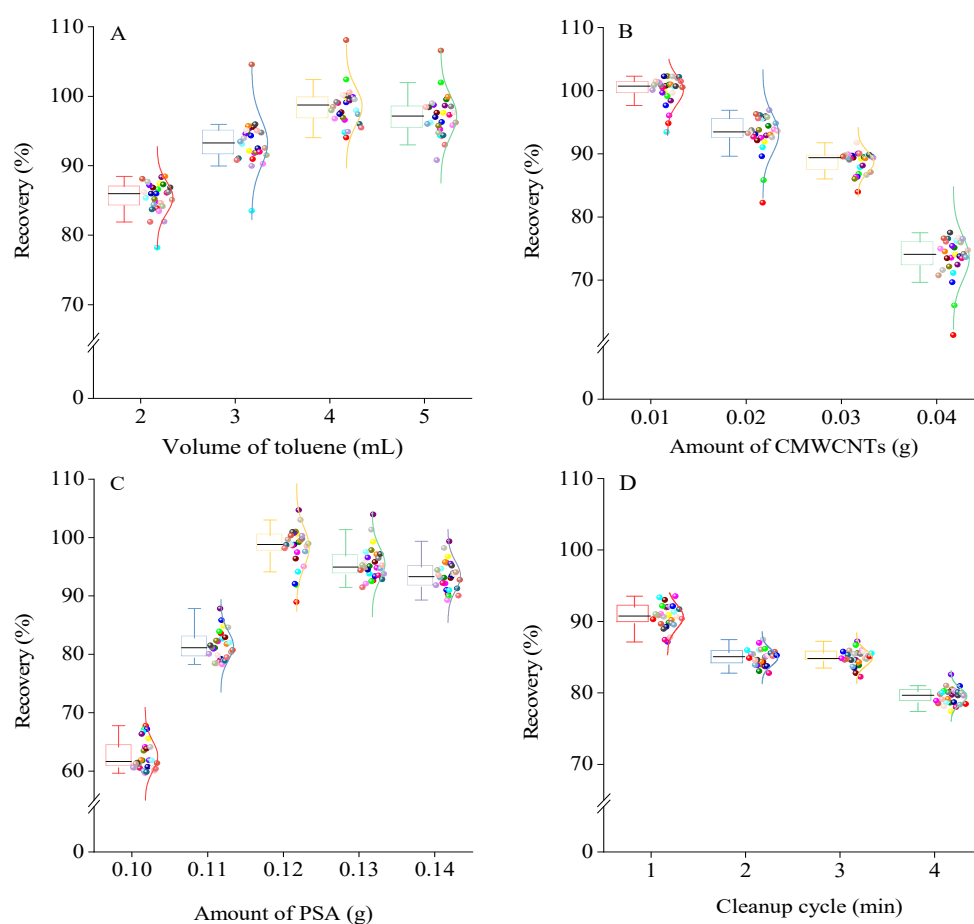


Fig. 4. Effects of (A) volume of toluene, (B) amount of CMWCNTs, (C) amount of PSA, and (D) cleanup cycle on purification performance (n=3).

In sum, the refined parameters for the extraction and cleanup procedures were no water addition to the sample, 10 mL of acetonitrile as extraction solvent, UAE time of 5 min, 0.01 g of CMWCNTs and 0.12 g of PSA as m-PFC sorbents, and 1 cycle for m-PFC cleanup.

3.4 Evaluation of matrix effect

MEs are prevalent issues encountered during GC-MS analysis, and they compromise the reliability of analytical results by either enhancing or suppressing the response of target analytes^[57]. Multiple factors contribute to MEs, such as the properties of analytes, the composition of sample matrices, and sample preparation protocols employed^[58-59]. Fig. 5 presents the calculated MEs in this study. The ME values for the studied PCBs in maize, wheat, and rice matrices ranged from -12.9% to +18.0%, indicating that matrix effects

were weak (within $\pm 20\%$) under the current methodology. Consequently, solvent-based standard calibration curves were applied for quantification.

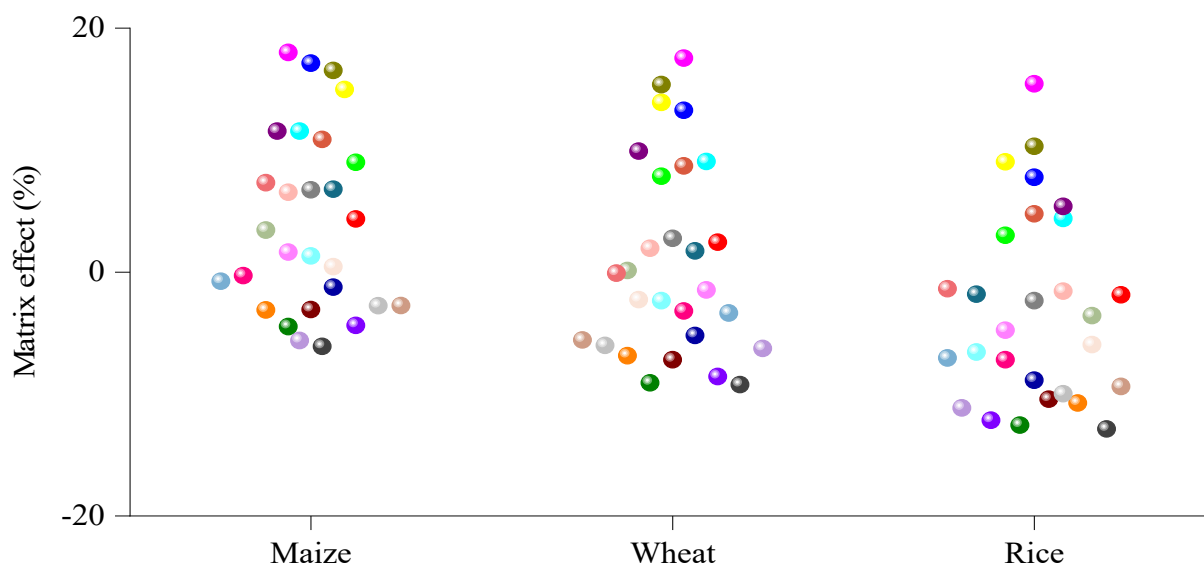


Fig. 5. The matrix effects of 28 PCBs in maize, wheat, and rice.

3.5 Method validation

Tables 2 and 3 summarized the method validation data for all the studied compounds. Calibration curves exhibited linearity over the range of 0.5–500 $\mu\text{g/L}$, and all correlation coefficients (r) exceeded 0.998. The method showed high sensitivity, with LODs and LOQs ranging from 0.01 to 0.06 $\mu\text{g/kg}$ and 0.02 to 0.18 $\mu\text{g/kg}$, respectively. The mean recoveries of PCBs from spiked maize, wheat, and rice matrices ranged from 73.1% to 118.8%, with RSDs between 0.8% and 14.3%. These results confirmed the reliability of the method for quantifying PCBs in cereal samples.

Table 2 Analytical figures of merit of the developed method

PCB congener	Linear range ($\mu\text{g/L}$)	Regression equation	r	LODs ($\mu\text{g/kg}$)			LOQs ($\mu\text{g/kg}$)		
				Mazie	Wheat	Rice	Maize	Wheat	Rice
8	0.5-500	$y=1662.03x-3061.04$	0.9998	0.01	0.01	0.01	0.02	0.02	0.03
18	0.5-500	$y=792.43x-1765.52$	0.9998	0.02	0.02	0.03	0.04	0.05	0.08
28	0.5-500	$y=1341.69x-4176.08$	0.9996	0.01	0.01	0.02	0.03	0.04	0.05
52	0.5-500	$y=655.11x-2013.43$	0.9996	0.01	0.01	0.01	0.03	0.03	0.04
44	0.5-500	$y=802.03x-2741.20$	0.9995	0.01	0.01	0.02	0.03	0.03	0.04
66	0.5-500	$y=1274.45x-5382.21$	0.9993	0.02	0.02	0.02	0.04	0.04	0.07
101	0.5-500	$y=855.59x-3436.22$	0.9994	0.02	0.04	0.03	0.06	0.11	0.09
81	0.5-500	$y=1243.03x-5981.07$	0.9991	0.02	0.02	0.02	0.05	0.04	0.04
77	0.5-500	$y=1396.19x-7486.99$	0.9990	0.02	0.02	0.02	0.04	0.05	0.06
123	0.5-500	$y=1078.44x-6004.76$	0.9988	0.02	0.02	0.03	0.06	0.07	0.09
118	0.5-500	$y=1192.32x-6691.15$	0.9989	0.02	0.02	0.03	0.06	0.07	0.08
114	0.5-500	$y=1107.62x-6230.99$	0.9989	0.02	0.02	0.02	0.06	0.07	0.07
153	0.5-500	$y=802.27x-4162.27$	0.9990	0.03	0.03	0.04	0.08	0.09	0.11
105	0.5-500	$y=1153.16x-6761.94$	0.9988	0.02	0.02	0.02	0.06	0.06	0.07
138	0.5-500	$y=685.01x-3706.15$	0.9989	0.02	0.02	0.02	0.07	0.06	0.07
126	0.5-500	$y=1140.41x-7243.29$	0.9985	0.02	0.02	0.02	0.06	0.06	0.06
87	0.5-500	$y=590.50x-3064.38$	0.9990	0.02	0.02	0.02	0.06	0.06	0.07
167	0.5-500	$y=602.58x-3175.74$	0.9990	0.03	0.02	0.01	0.1	0.07	0.03
128	0.5-500	$y=982.65x-6451.44$	0.9985	0.02	0.02	0.03	0.06	0.07	0.09
156	0.5-500	$y=828.15x-5281.38$	0.9985	0.02	0.03	0.03	0.07	0.08	0.07
157	0.5-500	$y=868.73x-5707.94$	0.9985	0.03	0.02	0.03	0.08	0.07	0.08
180	0.5-500	$y=554.29x-3393.90$	0.9986	0.03	0.02	0.03	0.09	0.07	0.09
169	0.5-500	$y=878.45x-6186.61$	0.9982	0.02	0.02	0.02	0.07	0.05	0.05
170	0.5-500	$y=495.26x-3178.90$	0.9985	0.03	0.03	0.03	0.08	0.09	0.08
189	0.5-500	$y=619.52x-4333.42$	0.9982	0.02	0.02	0.03	0.04	0.05	0.07
195	0.5-500	$y=442.86x-2804.49$	0.9985	0.03	0.03	0.04	0.1	0.1	0.11
206	0.5-500	$y=232.17x-1487.23$	0.9985	0.03	0.03	0.04	0.09	0.09	0.12
209	0.5-500	$y=268.53x-1529.85$	0.9988	0.03	0.04	0.06	0.08	0.13	0.18

Table 3 Recoveries and RSDs of the proposed method

PCB congener	Recovery and RSDs (% , n=6)								
	Corn (µg/kg)			Wheat (µg/kg)			Rice (µg/kg)		
	0.5	2	10	0.5	2	10	0.5	2	10
8	77.2±5.6	77.1±4.2	113.3±4.8	88.6±4.3	80.8±3.8	79.4±2.8	91.2±5.3	81.9±2.4	84.0±2.2
18	114.9±7.5	108.0±3.7	106.0±4.4	103.0±5.9	106.9±4.4	86.0±2.7	107.4±3.9	107.0±4.0	89.7±2.5
28	87.5±5.8	87.0±2.7	107.8±5.9	88.6±5.6	85.8±3.6	85.0±2.4	83.8±7.1	86.2±1.3	90.5±2.4
52	73.1±14.3	97.6±5.7	105.7±2.9	93.3±6.7	85.4±5.0	84.0±3.2	79.4±9.8	80.2±2.9	87.6±2.5
44	78.4±6.4	84.1±3.1	106.5±4.0	87.5±5.2	81.5±3.8	83.0±2.4	73.7±8.5	79.5±2.4	87.4±3.2
66	91.4±6.1	88.7±3.2	94.7±4.9	87.7±3.4	86.8±5.9	87.6±2.5	83.2±7.3	87.2±1.2	94.3±3.9
101	77.3±11.9	83.7±4.0	107.0±4.7	89.9±4.6	87.7±5.5	88.3±3.0	82.3±8.8	86.8±2.5	93.4±3.3
81	94.6±4.6	95.1±2.9	98.7±5.7	92.0±5.1	93.5±5.1	91.5±2.5	118.8±7.8	94.9±0.8	97.0±2.1
77	94.2±6.5	92.5±2.5	96.2±4.9	86.7±3.3	88.0±2.7	89.7±2.3	85.8±9.7	90.7±1.9	95.7±2.8
123	106.0±4.9	96.4±3.1	107.0±6.0	112.8±3.7	98.5±4.1	92.6±2.4	90.8±8.8	94.8±3.2	99.4±4.0
118	98.5±5.6	91.9±2.7	93.1±5.0	90.8±3.7	91.4±4.1	90.0±2.4	89.1±8.0	92.3±2.0	97.1±3.8
114	101.4±7.9	92.6±3.1	105.7±5.3	88.2±2.7	91.5±3.9	93.8±2.4	85.3±9.8	92.7±1.6	98.8±2.6
153	99.6±6.2	93.6±2.9	95.6±5.3	92.8±4.0	92.0±5.3	93.3±2.8	89.7±7.7	92.9±1.4	98.1±1.9
105	95.1±6.0	89.7±2.5	106.2±5.5	88.2±3.7	88.9±2.1	91.1±2.6	87.5±4.8	91.8±1.6	96.4±1.9
138	103.1±5.7	95.1±2.8	110.1±4.7	120.7±6.1	103.4±3.7	94.3±2.5	96.8±5.0	94.6±1.2	97.0±3.1
126	100.4±4.9	91.6±1.4	99.1±5.2	87.8±3.2	92.5±4.7	91.5±2.2	92.0±6.3	94.7±1.7	98.0±3.2
87	96.3±5.2	93.3±2.4	106.1±5.0	93.1±2.5	92.1±3.8	91.3±2.8	97.9±5.1	92.9±1.1	98.4±3.0
167	107.2±7.2	89.7±3.3	92.1±4.8	89.7±6.1	86.0±1.8	88.2±3.3	93.0±11.1	87.2±2.3	97.3±3.0
128	107.4±6.2	98.9±3.5	93.6±5.4	90.4±6.9	94.2±3.7	60.4±3.3	97.2±6.0	99.0±2.0	97.7±2.8
156	111.7±5.9	95.7±3.2	103.5±4.9	87.5±3.6	93.5±2.8	93.6±2.8	93.5±8.0	96.5±2.3	101.7±2.8
157	112.5±6.9	95.0±2.1	106.2±3.4	93.6±2.2	95.5±3.8	95.9±2.5	93.4±7.2	96.4±2.3	101.7±3.2
180	110.6±5.0	95.0±3.9	97.7±4.4	98.7±4.0	95.2±3.2	95.9±2.6	96.7±5.9	97.7±1.3	101.5±2.6
169	110.4±7.7	95.5±1.9	105.7±1.3	112.1±2.6	95.1±1.6	94.6±2.6	107.8±6.4	103.5±1.4	100.9±1.6
170	116.7±7.4	91.7±2.9	107.1±3.9	90.2±5.6	92.8±3.3	92.0±2.3	92.7±10.8	93.5±1.8	98.3±2.2
189	103.2±9.7	90.6±3.2	95.5±5.4	92.3±5.4	95.9±2.7	91.8±2.6	84.9±6.2	93.6±2.2	99.5±2.8
195	117.4±8.8	94.2±2.9	109.4±4.9	111.7±6.6	99.7±1.8	93.5±2.6	104.2±9.6	90.8±1.5	95.1±3.4
206	106.1±8.4	80.2±4.1	101.1±4.6	90.4±6.6	94.7±4.2	86.7±3.0	92.6±11.0	87.3±2.1	90.3±4.4
209	109.6±10.0	77.1±2.4	103.9±4.8	109.7±5.1	92.2±3.9	86.9±1.3	86.6±7.7	85.2±2.1	90.1±4.2

3.6 Comparison to other reported methods

Table 4 compares the proposed method against existing protocols for PCB quantification in cereals and related matrices, focusing on key parameters such as analytical method, pretreatment approach, sample matrix type, number of PCB congeners analyzed, solvent usage, linear range, and LODs. These results show that our methodology exhibits significant advantages, including shorter pretreatment time, wider linear range, and lower LODs, demonstrating its superior speed, sensitivity, and quantitative capability. Operationally, the approach reduces solvent usage and obviates the need for bulky or expensive apparatus (e.g., Soxhlet extractor, accelerated solvent extractor, or GPC instrumentation), thereby simplifying the pretreatment process and reducing analytical costs. Crucially, the workflow is designed to maximize efficiency. The major preparation steps, including extraction, centrifugation, and solvent evaporation, can be conducted in parallel, significantly reducing the effective time per sample. Furthermore, the m-PFC purification step itself is rapid (typically <1 min). The syringe-based design allows multiple pre-packed columns to be processed simultaneously, ensuring high throughput for routine laboratory analysis.

When compared to a recent d-SPE method using CMWCNTs and PSA for PCB analysis in cereals^[14], our m-PFC technique demonstrates superior operational efficiency and analytical performance, primarily through its streamlined syringe-based format. This design consolidates purification into a single pass-through step, effectively eliminating the labor-intensive vortexing and centrifugation required in d-SPE, thus substantially enhancing operational simplicity and speed. It is also highly compatible with automated multi-port apparatus, facilitating high-throughput analysis as validated in previous studies^[28, 30, 60, 61]. Analytically, m-PFC enables effective cleanup for a broader spectrum of congeners, yielding extended linearity and enhanced sensitivity (Table 4). Overall, these comparisons confirm the proposed method as a simple, reliable, and highly practical solution for the routine monitoring of PCBs in cereal samples.

Table 4 Comparison of the developed method with previously reported methods for the determination of PCBs

Analytical method	Pretreatment method		Sample matrix	Number of tested PCBs	Solvent usage (mL)	Linear range (µg/L)	LODs (µg/kg)	Ref.
	Method	Time (min)						
GC-MS/MS	QuEChERS	>130	Wheat and barley	40	10	0.5-200	0.12-0.40	[6]
GC-ECD	ASE-GPC-SPE	>46	Rice, wheat, corn and soybean	8	>20	1.38-138	0.07–0.3	[11]
GC-MS	SE-column chromatography	>1441	Rice and wheat	33	>50	5-200	0.03–0.1	[13]
GC-MS	UAE-d-SPE	≈50	Rice, wheat and corn	18	15	0.5-50	0.04–0.1	[14]
GC-MS/MS	UAE-d-SPE	≈45	Pu-erh tea	18	10	0.5-200	0.3-1.0	[62]
GC-MS	QuEChERS	>40	Canned foods	12	21	0.1-40	0.06-0.32	[63]
GC-MS	UAE-m-PFC	≈43	Maize, rice and wheat	28	15	0.5-500	0.01-0.06	This work

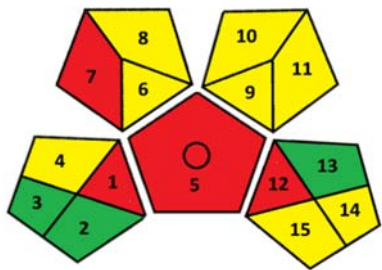
3.7 Method application

To further evaluate the method's practical performance, we analyzed 31 real grain samples (11 rice, 10 maize and 10 wheat). No target PCBs were detected above the method's LOQs in the samples, but significant peaks emerged after spiking, indicating that the cereal matrix does not interfere with the detection. Spike-recovery studies at 0.5, 2.0 and 10.0 $\mu\text{g/kg}$ ($n = 6$) were performed to evaluate method accuracy. As listed in Table 3, the recovery rates were 73.1%–118.8% with RSDs less than 14.3%, affirming the method's applicability for real grain sample analysis.

3.8 Assessment of method greenness

The greenness profile was assessed using the AES^[40] and the GAPI^[41]. The AES employs a numerical scoring system to assess environmental impact, where the final score is calculated by subtracting total penalty points (PPs) from 100. These PPs are assigned based on reagent hazard and amount, energy consumption, occupational exposure risk, and waste generation. A higher score reflects a greener analytical procedure, with scores categorized as excellent (> 75), acceptable (50–75), or inadequate (< 50). As shown in Table 5, the developed method achieved a score of 72, indicating that it is an acceptable green procedure.

Table 5 Greenness Assessment of the Proposed Method by AES and GAPI

AES		GAPI	
Reagents and solvents	PPs		
Acetonitrile (10 mL)	8		
Toluene (4 mL)	6		
<i>n</i> -hexane (1 mL)	8		
CMWCNTs (0.01 g)	0		
PSA (0.12 g)	0		
Instruments	PPs		
GC-MS	2		
Ultrasonic cleaner	0		
Nitrogen evaporator	0		
Centrifuge	0		
Occupational hazard	PPs		
Hermetization of analytical process	0		
Waste	PPs		
5.99 mL/g	3		
Degradation	1		
Total PPs	28	6-Scale of extraction (microextraction); 7-Solvents/reagents used (Non-green reagents used); 8-Additional treatments (simple treatments) Reagents and solvents 9-Amount (10–100 mL/g); 10- Health hazard (moderately toxic); 11- Safety hazard (NFPA Flamambility score 3) Instrumentation 12- Energy (>1.5 kWh per sample); 13-Occupational hazard (Hermetic sealing of analytical process); 14-Waste (1–10 mL/g); 15-Waste treatment (degradation)	
Score	72		

The GAPI evaluates method greenness through a pictogram composed of five pentagons, where green, yellow, and red denote low, medium, and high environmental impact, respectively. As shown in Table 5, the GAPI profile for the developed method displays three green, eight yellow, and four red ratings. These red fields are primarily attributed to offline sampling, extraction, the use of non-green solvents, and energy consumption exceeding 1.5 kWh per sample. While these factors are currently dictated by the requirement for

desired analytical performance, they significantly contribute to the method's environmental impact and thus represent critical areas requiring focused attention. Specifically regarding solvent usage, although acetonitrile was selected as the extraction solvent due to its optimal recovery (Fig. 2B) and toluene is currently employed for effective sample reconstitution in the current protocol, the toxicity associated with both solvents constitutes a significant environmental drawback within the greenness profile. This reflects a necessary trade-off made during method development, where the analytical requirement of achieving high-efficiency, quantitative extraction of trace PCBs was prioritized over strict adherence to green chemistry principles for these specific steps. Accordingly, the use of toluene (a hazardous solvent) and the high energy consumption of GC-MS analysis are identified as the most critical limitations. Future work will therefore prioritize mitigating these issues, aiming to reconcile analytical performance with environmental sustainability. For instance, subsequent studies could explore substituting toluene with less hazardous alternatives (e.g., less toxic aromatic analogues) and optimize instrument parameters (e.g., column temperature programs) to reduce energy consumption, all without compromising the method's analytical performance. These efforts are expected to achieve an enhanced greenness profile.

4. Conclusion

Herein, a straightforward and rapid method based on m-PFC and GC-MS was established to quantify 28 PCBs in cereal grains, including maize, wheat, and rice. The m-PFC procedure utilized a mixed sorbent of CMWCNTs and PSA to effectively remove matrix interferences from these complex samples, resulting in weak matrix effects (within $\pm 20\%$). Notably, the entire purification was completed within tens of seconds in a single syringe, eliminating the need for vortexing and centrifugation. The validated method demonstrated satisfactory performance in terms of linearity, accuracy, precision, and sensitivity. The AES and GAPI assessments confirmed its acceptable environmental profile and identified key areas prioritized for future improvement. Collectively, our proposed approach is simple, reliable, and highly practical for the routine monitoring of PCBs in cereal grains. Moreover, the developed m-PFC protocol holds potential for extension to the multi-residue analysis of other persistent organic pollutants in grains, particularly non-polar and aromatic compounds such as organochlorine pesticides (e.g., DDT and HCB) and polybrominated diphenyl ethers (PBDEs), upon further optimization and validation.

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Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as

potential competing interests:

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