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Determination of PCDD/Fs and dioxin-like PCBs in food and feed using gas chromatography-triple quadrupole mass spectrometry

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A method was developed on a gas chromatograph coupled to a triple quadrupole mass spectrometer (GC-MS/MS) for trace level determination of polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in food and feed. The results demonstrated good sensitivity and repeatability for PCDD/Fs and DL-PCBs at an extremely low level (10 pg mL^{-1} for 2,3,7,8-TCDD/F), as well as wide linear response of over 3 or 4 orders of magnitude in concentration ranges; 0.5–200 ng mL^{-1} for PeCDD/F and 0.2–2000 ng mL^{-1} for DL-PCBs. The method detection limits for PCDD/Fs and DL-PCBs were in the range from 0.018–0.17 pg g^{-1} to 0.13–0.36 pg g^{-1}, respectively. The performance of the GC-MS/MS for food and feed sample analysis showed high precision and accuracy compared to the high resolution gas chromatograph/high resolution mass spectrometer. The results indicated the feasibility of GC-MS/MS as a confirmatory method for the measurement of PCDD/Fs and DL-PCBs in food and feed as required by European Union legislation.

PCDD/Fs, DL-PCBs, food, feed, GC-MS/MS

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1 Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs or dioxins) and polychlorinated biphenyls (PCBs) are ubiquitous environmental organic contaminants which were listed in the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2001. PCDD/Fs are unintentionally produced as by-products during chlorinated intermediates' production and incomplete combustion of chlorinated materials [1]. Conversely, PCBs are artificial chemical products which were widely used in various industrial applications, especially in electrical equipment [2,3]. Even though the commercial production of PCBs has been banned, PCBs have been continuously detected in different environmental matrices all over the globe [4,5]. These compounds have aroused a special concern related to their harmful health effects. Among more than 200 individual congeners of both PCDD/Fs and PCBs, seventeen 2,3,7,8-substituted PCDD/Fs as well as twelve non- and mono-*ortho* PCBs (which have characteristics similar to dioxins and defined as dioxin-like PCBs or DL-PCBs) were found with high toxicity [6]. Because of the properties of lipophilicity and high chemical stability, PCDD/Fs and PCBs can persist in the environment, enter the food chain from environmental media and accumulate in adipose tissues of higher trophic level organisms including humans [1].

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Dietary intake of food contaminated with dioxins and DL-PCBs is a major route of human exposure to these toxic organic pollutants [7]. For the general population, dietary exposure to dioxins is from contaminated animal origin food including fish, meat, dairy products, etc. [8]. Hence dioxins contamination events involving food and feed generally attracted great public attention in the world, e.g., Germany's dioxin-tainted food scandal in 2011 led to the shutdown of more than 4700 farms, thousands of chickens were killed and hundreds of thousands of eggs were destroyed [9]. In the past decades, dioxin contamination incidents of feed and foodstuffs not only brought great hazards to the environment and human health, but also caused tremendous economic losses. Therefore, many countries and international organizations have issued a series of regulations and policy measures for monitoring the levels of dioxins and dioxin-like substances in the environment, food and feed supply.

High resolution gas chromatography coupled to high resolution mass spectrometry (HRGC/HRMS) is recognized as the confirmatory method for PCDD/Fs analysis. Excellent sensitivity and selectivity of HRGC/HRMS method can meet the demand of ultra-trace level contaminants determination in complex matrices. However, besides the expensive instrument, the operating and maintenance cost of HRGC/HRMS is relatively high. Therefore, increasing studies have focused on the development of alternative approaches in order to reduce dioxin analysis costs. Historically, gas chromatography coupled to quadrupole ion storage tandem mass spectrometry (GC-QISTMS), gas chromatography-triple quadrupole mass spectrometry (GC-MS/MS), atmospheric-pressure chemical ionization source for gas chromatography coupled with tandem quadrupole mass spectrometry (APGC-MS/MS), fast GC or comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (FGC-TOFMS or GC×GC-TOFMS) are promising as the preliminary screening methods [10–14].

In recent years, GC-MS/MS and APGC-MS/MS instruments have been used in dioxin analysis in varying matrices, which showed the similar sensitivity and accuracy of these instruments compared with HRGC/HRMS [12,15,16]. In 2014, the European Commission laid down the latest amendment methods of sampling and analysis for the official control of the levels of PCDD/Fs and PCBs in food and feed (No. 589/2014 [17] and 709/2014 [18]), in which GC-MS/MS was recognized as an appropriate confirmatory method for checking compliance with the maximum levels of PCDD/Fs and PCBs in food and feed control. GC-MS/MS has been validated to meet the analytical criteria and satisfy the requirements set by the EU regulations [16,19]. It can be anticipated that the applications of GC-MS/MS in the analysis of POPs and other contaminants in food safety field will further increase in the following years. However, to our best knowledge, there is no research work that has been reported before on using GC-MS/MS for determination of PCDD/Fs and DL-PCBs in food and feedstuffs in China.

In this study therefore, a method for PCDD/Fs and DL-PCBs analysis in food and feedstuffs was developed on a GC-MS/MS system and the performance was evaluated. The method was applied to selected food and feed samples and the feasibility of GC-MS/MS as a confirmatory method for the analysis of PCDD/Fs and DL-PCBs was discussed.

2 Experimental

2.1 Chemicals

All solvents and reagents were of pesticide, chromatographic or analytical grade. Toluene, *n*-hexane and dichloromethane (DCM) were from J. T. Baker Chemical Company (USA). Nonane was purchased from Sigma-Aldrich Corporation (USA). Celite (545 coarse, Fluka 22140) and carbon (Carbopak C, Supelco 10258) were purchased from Supelco (USA). Anhydrous sodium sulfate, sulfuric acid and sodium hydroxide were supplied by Beijing Chemical Factory (China). Silica gel 60 (70–230 mesh) was obtained from Merck (Germany). The activation of column sorbents and the preparation of the carbon mixture, acidic and basic silica gels were described in our previous work [20]. Native and $^{13}C_{12}$-isotope labeled standard solutions of PCDD/Fs and PCBs were obtained from Wellington Laboratories (Canada). The standard solutions for PCDD/Fs were EPA-1613PAR, EPA-1613CSL, EPA-1613CS0.5, EPA-1613CVS (EPA-1613CS1-CS4), EPA-1613LCS and EPA-1613ISS. The standard solutions for PCBs were 68C-CVS (68C-CS0.2 and 68C-CS1-CS5), 68C-PAR, 68C-LCS and 68C-IS.

2.2 Sample preparation

Food (fish, beef) and feed (corn silage) samples were analyzed for PCDD/Fs and DL-PCBs to verify the GC-MS/MS instrument performance. A fish sample was acquired from Interlaboratory Comparison on POPs in Food 2015 (16th Round) organized by Norwegian Institute of Public Health [21]. Beef and corn silage samples were purchased from the local market. The sample preparation primarily followed the U.S. Environmental Protection Agency (EPA) Method 1613B [22] and Method 1668B [23] with proper modifications. The detailed description of the sample preparation procedures referred to our previous studies [24–26]. In brief, the samples were freeze-dried and homogenized. 10 μL EPA-1613LCS (100–200 ng mL^{-1}) and 10 μL dilute 68C-LCS (100 ng mL^{-1}) were spiked into the homogenized samples as $^{13}C_{12}$-isotope labeled surrogate standards before extraction. The spiked samples were extracted using accelerated solvent extraction (ASE) with DCM:*n*-hexane (1:1, *v*/*v*). Before the purification procedure, the extract of the

beef sample was concentrated to dryness for the gravimetric determination of the lipid weight and then dissolved into *n*-hexane. The acidic silica gel (44% sulfuric acid) was added to the extract as the initial purification step to remove fat and polar interfering substances. Multilayer silica gel column and activated carbon column were used for further clean-up procedures. The final eluate was transferred into a vial and concentrated to 20 μL. 5 μL EPA-1613ISS (200 ng mL^{-1}) and 5 μL 68C-IS (200 ng mL^{-1}) were spiked into the vial as $^{13}C_{12}$-isotope labeled injection standards prior to instrumental analysis.

Spiking experiments of PCDD/Fs and DL-PCBs were conducted to test the method detection limits (MDLs) for food and feed analysis. Chicken is one of the commonest foodstuffs and thus was selected as the blank matrix. The samples were extracted with DCM:*n*-hexane (1:1, *v*/*v*) before the spiking procedure. 10 μL EPA-1613LCS (100–200 ng mL^{-1}), 10 μL dilute 68C-LCS (100 ng mL^{-1}), 10 μL dilute EPA-1613PAR (100–1000 pg mL^{-1}) and 50 μL dilute 68C-PAR (200 pg mL^{-1}) were added into each of three parallel blank samples (15 g for each). The extraction and purification procedures were the same as for the actual samples. Prior to instrumental analysis, 5 μL EPA-1613ISS (200 ng mL^{-1}) and 68C-IS (200 ng mL^{-1}) were spiked in the final concentrates as injection standards.

2.3 Instrumental analysis

The sample analyses were performed on both gas chromatograph-triple quadrupole mass spectrometer (GCMS-TQ8040, Shimadzu, Japan) and gas chromatograph (Agilent 6890N, USA) coupled to a high-resolution mass spectrometer (AutoSpec Ultima, Waters, USA).

2.3.1 GC-MS/MS conditions

The GC system was equipped with a 60 m DB-5MS column (0.25 mm id, film thickness of 0.25 μm, J & W Scientific, USA). The injection mode was splitless and the injection volume was 1 μL (or 2 μL for the sensitivity check and repeatability test). The oven temperature programming for PCDD/Fs was as follow: the initial column temperature was set at 150 °C for 3 min, then ramped to 230 °C at a rate of 20 °C min^{-1} and maintained for 18 min, subsequently ramped to 235 °C at 5 °C min^{-1} and held for 10 min, finally ramped to 330 °C at 4 °C min^{-1} and held for 3 min. For DL-PCBs, the temperature was set at 120 °C initially for 1 min, then ramped to 150 °C at 30 °C min^{-1}, and finally ramped to 300 °C at 2.5 °C min^{-1} where it was held for 1 min. Helium was the carrier gas with a constant column flow rate of 1.0 mL min^{-1}. The measurements were carried out in electron impact (EI) ion source with multiple reaction monitoring (MRM) acquisition mode. The interface temperature was 270 °C, while the ion source temperatures were 250 °C for PCDD/Fs or 270 °C for DL-PCBs. The electron emission energy was 70 eV and emission current was set at 250 μA. Two MRM transitions were selected as the quantitative and qualitative transitions. For 2,3,7,8-substituted PCDD/Fs compounds, the molecular ions [$M^{\bullet+}$] (native and $^{13}C_{12}$-labeled congeners) were chosen as the precursor ions and ions formed by the loss of $[COCl]^-$ (native congeners) or $[^{13}COCl]^-$ (isotope labeled congeners) were selected as product ions. For DL-PCBs (native and $^{13}C_{12}$-labeled congeners), the precursor and product ions were the molecular ion [$M^{\bullet+}$] and the fragment ions formed by the loss of 2$[Cl]^-$, respectively. The collision induced dissociation (CID) gas pressure changed from 200 kPa to 150 kPa to improve the intensities of the product ions. The voltages of collision energy were tested from 20 V to 40 V for each compound to optimize ionization conditions. The retention time and MS parameters of MRM acquisition mode for PCDD/F and DL-PCB congeners are given in Table S1 and Table S2 (Supporting Information online). In order to increase peak intensities and improve the peak shapes of the analytes at low concentration levels (e.g., 10 pg mL^{-1} 2,3,7,8-TCDD/F), the event time of MS acquisition for 2,3,7,8-TCDD/F was manually extended to 2 or 3 times longer than the labeled congeners.

2.3.2 HRGC/HRMS conditions

GC-MS/MS and HRGC/HRMS shared the same chromatographic column and GC conditions, such as injection mode, injection volume, oven temperature programming and column flow rate. The EI ionization was selected for the analysis of target compounds. The electron emission energy was 35 eV and the ion source temperature was set at 270 °C for both 2,3,7,8-substituted PCDD/Fs and DL-PCBs. The MS system was operated in selected ion monitoring (SIM) mode. The selection of monitoring ions followed the U.S. EPA Method 1613B and Method 1668B. The mass resolution of HRGC/HRMS was above 10000.

2.3.3 Qualitative and quantitative analyses

The analysis method followed the U.S. EPA Method 1613B and Method 1668B. The qualitative and quantitative analyses were performed using ^{13}C-isotope dilution and internal standard methods. Averaged response factors (RF) were used to calculate the concentrations of the target compounds on both GC-MS/MS and HRGC/HRMS.

3 Results and discussion

3.1 Chromatograms

The mass chromatograms of PCDD/Fs and DL-PCBs are shown in Figure S1 (Supporting Information online). The medium-concentration calibration verification solutions (EPA-1613CS3 and 68C-CS3) were selected to evaluate the chromatographic separation of the analytes. The mass chromatograms showed the sufficient gas-chromatographic

separation of the seventeen 2,3,7,8-substituted PCDD/F isomers and twelve DL-PCB isomers.

3.2 Sensitivity

A low-concentration dilute PCDD/Fs solution (1:50 dilution of EPA-1613CS1) was analyzed to check the performance of GC-MS/MS system. In the dilution, the concentrations of TCDD/F, PeCDD/Fs-HpCDD/Fs and OCDD/F were 10, 50 and 100 pg mL^{-1}, respectively. Taking into account the injection volume (2 μL), the amount of 2,3,7,8-TCDD/F on the column was as low as 20 fg. The mass chromatograms of the native PCDD/Fs in the low-concentration dilute solution are shown in Figure S2. The signal to noise ratio (*S*/*N*) values of all PCDD/F congeners were higher than 40. The detection results suggested that the GC-MS/MS system had the ability to detect trace amounts of dioxins.

3.3 Repeatability

The repeatabilities of PCDD/Fs and DL-PCBs determination were evaluated by intra- and inter-day variances. A total of 12 injections (2 μL, 4 injections per day×3 days) and 9 injections (1 μL, 3 injections per day×3 days) were measured with 1:50 diluted EPA-1613CS1 and 68C-CS0.2, respectively. The results exhibited good repeatabilities of the peak areas of PCDD/F and PCB congeners of which the relative standard deviations (RSDs) were lower than 15% (Figure S3).

3.4 Linearity range

Six-level calibration solutions for PCDD/Fs (EPA-1613CSL, EPA-1613CS0.5 and EPA-1613CS1-CS4) and DL-PCBs (68C-CS0.2 and 68C-CS1-CS5) were analyzed to test the linearity range in the GC-MS/MS instrument. The correlation coefficient (R^2) and average of relative response factor (RRF) for each congener are given in Table 1. Wide linear range calibration curves were observed for both PCDD/Fs (0.1–40 ng mL^{-1} for TCDD/F, 0.5–200 ng mL^{-1} for PeCDD/Fs-HpCDD/Fs and 1.0–400 ng mL^{-1} for OCDD/F) and DL-PCBs (0.2–2000 ng mL^{-1}). The R^2 values were higher than 0.999 and the RSDs of RRFs for PCDD/F and DL-PCB congeners were lower than 15%. The excellent linearity of the method meets the requirement of EPA's methods.

3.5 Ion abundance ratio

Two MRM transitions were selected as quantitation and qualification transitions. The qualification/quantitation transition ratio was an indispensable parameter for checking the accuracy of peak integration. The theoretical and measured (average values of calibration standards) ion abundance ratios of qualification/quantitation transitions are listed in Table S3. In the EU regulations, the relative ion intensities need to be within maximum permitted tolerance (±15%) [17,18]. Table S3 also shows the upper and lower limits of theoretical ion ratios of individual congeners. In actual sample analysis, tolerable limits of ion abundance ratios were referred to, to guarantee accurate determination of PCDD/Fs and DL-PCBs.

3.6 Method detection limits

In HRGC/HRMS system, *S*/*N* values were used to calculate

Table 1 Linearity of calibration curves and the mean relative response factors (RRF) of PCDD/F and DL-PCB congeners

	Congener	Concentration range (ng mL^{-1})	R^2	Mean RRF	RRF RSD (%)
PCDD/Fs	2,3,7,8-TCDD	0.1–40	0.9999	1.24	8
	1,2,3,7,8-PeCDD	0.5–200	0.9999	1.04	2
	1,2,3,4,7,8-HxCDD	0.5–200	0.9999	1.10	4
	1,2,3,6,7,8-HxCDD	0.5–200	0.9999	1.08	5
	1,2,3,7,8,9-HxCDD	0.5–200	0.9999	1.00	14
	1,2,3,4,6,7,8-HpCDD	0.5–200	0.9999	1.05	6
	OCDD	1.0–400	0.9999	1.13	5
	2,3,7,8-TCDF	0.1–40	0.9998	1.19	4
	1,2,3,7,8-PeCDF	0.5–200	0.9999	1.09	8
	2,3,4,7,8-PeCDF	0.5–200	0.9999	1.04	5
	1,2,3,4,7,8-HxCDF	0.5–200	0.9999	1.11	5
	1,2,3,6,7,8-HxCDF	0.5–200	0.9999	1.09	6
	2,3,4,6,7,8-HxCDF	0.5–200	0.9998	1.02	5
	1,2,3,7,8,9-HxCDF	0.5–200	0.9997	1.05	10
	1,2,3,4,6,7,8-HpCDF	0.5–200	0.9999	1.10	3
	1,2,3,4,7,8,9-HpCDF	0.5–200	0.9999	1.08	3
	OCDF	1.0–400	0.9999	1.51	9

(To be continued on the next page)

(Continued)

	Congener	Concentration range (ng mL^{-1})	R^2	Mean RRF	RRF RSD (%)
DL-PCBs	PCB-77	0.2–2000	0.9997	1.11	5
	PCB-81	0.2–2000	0.9998	1.10	4
	PCB-105	0.2–2000	0.9999	1.03	3
	PCB-114	0.2–2000	0.9999	1.04	8
	PCB-118	0.2–2000	1.00	1.06	2
	PCB-123	0.2–2000	1.00	1.03	5
	PCB-126	0.2–2000	0.9999	1.11	3
	PCB-156	0.2–2000	0.9999	1.01	8
	PCB-157	0.2–2000	0.9999	1.02	6
	PCB-167	0.2–2000	0.9999	1.04	9
	PCB-169	0.2–2000	0.9999	1.01	6
	PCB-189	0.2–2000	0.9999	0.89	7

the limits of detection (LOD) and limits of quantification (LOQ). However, due to the good filtering capacity of triple quadrupole mass spectrometry, the background noises in standards and actual samples reduce tremendously [16,19]. The low-noise baseline would result in unrealistic *S*/*N* values that cannot reflect the real performance of GC-MS/MS in sample analysis. Therefore, MDLs of GC-MS/MS system in this study were evaluated based on the results of spiking experiments instead of *S*/*N* values.

The MDLs were defined as 3 times standard deviations of nine injections (3 injections per sample×3 blank matrix samples). Table 2 describes the MDLs measured in the blank matrix samples for PCDD/F and DL-PCB congeners. The MDLs of target congeners were in the range of 0.018–0.17 pg g^{-1} (PCDDs), 0.025–0.13 pg g^{-1} (PCDFs) and 0.13–0.36 pg g^{-1} (DL-PCBs). The sum of MDLs were 0.144 pg WHO_{2005}-TEQ g^{-1} (PCDD/Fs) and 0.185 pg WHO_{2005}-TEQ g^{-1} (PCDD/Fs and DL-PCBs) which were lower than one fifth of the maximum level (ML) in food and feed [27,28]. The results indicated that the method is in accordance with analytical criteria of the EU regulations.

3.7 Actual sample analysis

The analyses of food and feed samples were performed in parallel on GC-MS/MS and HRGC/HRMS. The results obta-

Table 2 Method detection limits of PCDD/Fs and DL-PCBs

Compound (PCDD/Fs)	MDL (pg g^{-1})	WHO_{2005}-TEQ (pg g^{-1})	Compound (DL-PCBs)	MDL (pg g^{-1})	WHO_{2005}-TEQ (pg g^{-1})
2,3,7,8-TCDF	0.025	0.0025	PCB-77	0.168	0.00002
1,2,3,7,8-PeCDF	0.055	0.0017	PCB-81	0.174	0.00005
2,3,4,7,8-PeCDF	0.073	0.0220	PCB-105	0.219	0.00001
1,2,3,4,7,8-HxCDF	0.065	0.0065	PCB-114	0.214	0.00001
1,2,3,6,7,8-HxCDF	0.101	0.0101	PCB-118	0.361	0.00001
2,3,4,6,7,8-HxCDF	0.089	0.0089	PCB-123	0.274	0.00001
1,2,3,7,8,9-HxCDF	0.080	0.0080	PCB-126	0.360	0.03605
1,2,3,4,6,7,8-HpCDF	0.097	0.0010	PCB-156	0.223	0.00001
1,2,3,4,7,8,9-HpCDF	0.081	0.0008	PCB-157	0.134	0.00000
OCDF	0.130	0.00004	PCB-167	0.213	0.00001
2,3,7,8-TCDD	0.018	0.0179	PCB-169	0.132	0.00395
1,2,3,7,8-PeCDD	0.029	0.0292	PCB-189	0.319	0.00001
1,2,3,4,7,8-HxCDD	0.101	0.0101	Sum		0.041
1,2,3,6,7,8-HxCDD	0.124	0.0124			
1,2,3,7,8,9-HxCDD	0.121	0.0121			
1,2,3,4,6,7,8-HpCDD	0.081	0.0008			
OCDD	0.171	0.00005			
Sum		0.144			

ined by HRGC/HRMS were used as reference values to validate the accuracy measurement of GC-MS/MS. Each sample was repeatedly injected (6 injections for PCDD/Fs and 3 injections for DL-PCBs) on GC-MS/MS to test method reproducibility. LOD (corresponding to *S*/*N* of 3) and MDLs (based on spiking experiments) were used as detection limits in the respective HRGC/HRMS and GC-MS/MS instruments.

Concentrations and profiles of PCDD/F and DL-PCB congeners in fish, beef and corn silage samples are shown in Figure 1. In this study, if the isomer concentration was lower than the detection limit, the result was reported as LOD or MDL. In the fish sample (Figure 1(a)), 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF contributed nearly 75% of sum concentration of PCDD/Fs. OCDD was the predominant congener in the beef sample (Figure 1(c)), followed by 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF and OCDF. In the corn silage sample (Figure 1(e)), the content of 1,2,3,4,6,7,8-HpCDF and OCDD were higher than other congeners while higher concentrations of HxCDFs and HpCDFs were determined than those in the fish and beef samples. All the twelve DL-PCB congeners were detected in the three samples. PCB-105 and PCB-118 accounted for more than 70% of sum concentration of DL-

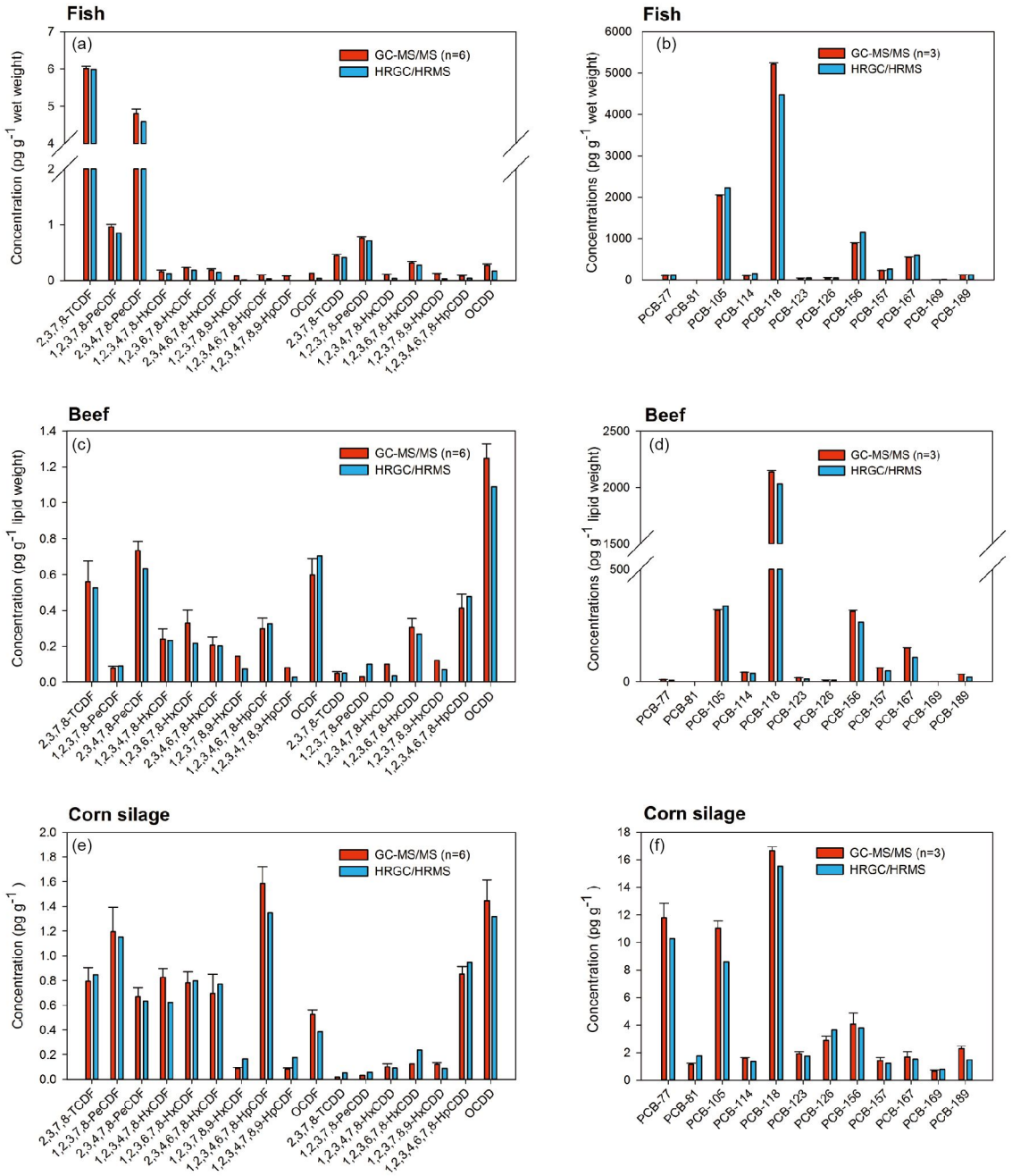

Figure 1 Concentrations and congener profiles of PCDD/Fs and DL-PCBs in actual samples. (a, b) Fish; (c, d) beef; (e, f) corn silage (color online).

PCBs in the fish sample (Figure 1(b)). PCB-118 was the most abundant congener in the beef sample (Figure 1(d)) of which the concentration was approximately 6 times higher than the other congeners. In the corn silage sample (Figure 1(f)), PCB-105 and PCB-118 were also the predominant congeners as well as PCB-77. The concentration and homologue profiles of food and feed samples measured in GC-MS/MS were in agreement with those derived from HRGC/HRMS.

Table 3 shows the TEQ values and the deviations between two instruments. The deviation between two methods were calculated as [12]:

$$\text{Deviation}\,(\%) = \frac{\text{TEQ}_{\text{MS/MS}} - \text{TEQ}_{\text{HRMS}}}{\text{TEQ}_{\text{HRMS}}} \times 100\,\%$$

The total TEQ values (PCDD/Fs and DL-PCBs) in the fish, beef and corn silage samples were 8.9 pg WHO_{2005}-TEQ g^{-1} wet weight (ww), 1.39 pg WHO_{2005}-TEQ g^{-1} lipid weight (lw) and 1.06 pg WHO_{2005}-TEQ g^{-1}, respectively. The TEQ values calculated by GC-MS/MS were within ±15% deviations of HRGC/HRMS values (ranged from −14% to 5.9%). The consensus TEQ concentrations for PCDD/Fs, DL-PCBs and PCDD/Fs+DL-PCBs measured in the fish sample on Interlaboratory Comparison were 3.1, 5.5 and 8.6 pg WHO_{2005}-TEQ g^{-1} ww, respectively [21]. The deviations of TEQ values (PCDD/Fs, DL-PCBs and PCDD/Fs+DL-PCBs) between GC-MS/MS and consensus values were below 10%, indicating good accuracy of GC-MS/MS system for the analyses of PCDD/Fs and DL-PCBs in food matrix.

In the actual sample analyses, the congener concentrations, homologue profiles as well as TEQ values obtained by GC-MS/MS were consistent with those obtained by HRGC/HRMS. The results indicated that GC-MS/MS has the comparable sensitivity and selectivity of trace-level PCDD/Fs and DL-PCBs to HRGC/HRMS in the food and feed sample analysis.

Table 3 The WHO_{2005}-TEQ values of food and feed samples calculated by HRGC/HRMS and GC-MS/MS system

Sample	Compound	WHO_{2005}-TEQ		Deviation(%)
		MS/MS	HRMS	
Fish (pg g^{-1} ww)	PCDD/Fs	3.4	3.2	5.9
	DL-PCBs	5.6	5.7	−0.7
	Sum	9.0	8.9	1.7
Beef (pg g^{-1} lw)	PCDD/Fs	0.51	0.58	−12
	DL-PCBs	0.82	0.81	1.2
	Sum	1.33	1.39	−4.3
Corn Silage (pg g^{-1})[a)]	PCDD/Fs	0.66	0.72	−8.3
	DL-PCBs	0.29	0.34	−14
	Sum	0.95	1.06	−10

a) Relative to corn silage with a moisture content of 12%.

4 Conclusions

In this study, we developed a high sensitivity and selectivity method for food and feed sample analysis using GC-MS/MS. The method showed good sensitivity and repeatability in analysing ultra-trace levels of PCDD/Fs and DL-PCBs. The analytical results of actual samples of GC-MS/MS were comparable to those obtained from HRGC/HRMS. This suggests that the GC-MS/MS system provides a substitute solution for routine screening and quantification of PCDD/Fs and DL-PCBs in food and feed as required by the European Union legislation.

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Conflict of interest The authors declare that they have no conflict of interest.

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