A COMPARATIVE STUDY OF PCDD/PCDF DETERMINATION IN FISH FEED USING GC-MS/MS AND HRGC/HRMS

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Nguyen Thi Thu Ly[1], Nguyen Thi Thu[1], Nguyen Duc Thang[1], Vu Trung Hieu[1], Tran Dinh Phien[1], Nguyen Thanh Tuan[1], Nguyen Thi Hoai Phuong[1,*]

[1]*Department of Chemistry and Environment, Joint Vietnam-Russia Tropical Science and Technology Research Center*

**E-mail: hoaiphuong1978@gmail.com*

TÓM TẮT

NGHIÊN CỨU SO SÁNH XÁC ĐỊNH PCDD/PCDF TRONG THỨC ĂN CHO CÁ BẰNG GC-MS/MS VÀ HRGC/HRMS

Ô nhiễm môi trường dai dẳng gây ra những vấn đề đáng kể liên quan đến an toàn thực phẩm. Các chất gây ô nhiễm bao gồm polychlorinated dibenzo-p-dioxin (PCDD) và polychlorinated dibenzofuran (PCDF). Nghiên cứu này trình bày đánh giá so sánh hai kỹ thuật phân tích, GC-MS/MS và HRGC/HRMS, để xác định polychlorinated dibenzo-p-dioxin (PCDD) và polychlorinated dibenzofuran (PCDF) trong các mẫu thức ăn cho cá. Một loạt các mẫu đã được phân tích và kết quả cho từng đồng loại và giá trị tổng lượng chất độc tương đương (TEQ) đã được so sánh. Hầu hết các đồng loại thể hiện sự khác biệt phần trăm tương đối (RPD) dưới 10%, chứng tỏ sự phù hợp tốt giữa hai phương pháp. Mặc dù một số hợp chất, chẳng hạn như 1,2,3,7,8-PeCDF và 2,3,7,8-TCDF, cho thấy RPD cao hơn tới 18,2%, nhưng các giá trị TEQ tổng thể được tính toán từ cả hai phương pháp vẫn nhất quán, với sự khác biệt trong khoảng từ 0,9% đến 5,1%. Những phát hiện này chỉ ra rằng GC-MS/MS có thể đóng vai trò là giải pháp thay thế đáng tin cậy và tiết kiệm chi phí cho HRGC/HRMS để theo dõi thường xuyên tình trạng ô nhiễm PCDD/PCDF trong thức ăn cho cá. Nghiên cứu này nhấn mạnh tính ứng dụng thực tế của GC-MS/MS trong phân tích an toàn thực phẩm và môi trường, đưa ra giải pháp khả thi cho các phòng thí nghiệm có khả năng tiếp cận hạn chế với thiết bị đo độ phân giải cao.

Từ khóa: *PCDD/PCDF, ô nhiễm thức ăn chăn nuôi, GC-MS/MS, HRGC/HRMS.*

1. INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are highly toxic persistent organic pollutants (POPs) that pose considerable environmental and health risks [1-3]. These chemicals were unintended byproducts of industrial processes such as waste incineration, metal refining, and chemical manufacturing [4]. Upon environmental release, they persisted for prolonged periods due to their considerable chemical stability and lipophilicity, leading to bioaccumulation in animal adipose tissue and biomagnification along the food chain. Humans mostly encountered these contaminants through the consumption of animal-derived products, such as meat, dairy, fish, and eggs [5]. Regulatory authorities worldwide have established stringent limitations on their concentrations in food and animal feed due to their potential to cause carcinogenic, immunotoxic, neurotoxic, and endocrine-disrupting effects [6, 7]. Animal feed is a crucial control measure

in reducing dioxin and PCB contamination in the food supply chain. Contaminated feed components, such as fish meal, animal fats, clay-based binders, and plant-derived compounds exposed to atmospheric pollution, could significantly increase the overall toxic load in livestock and poultry [8]. Fish feed might get contaminated with PCDDs and PCDFs due to the utilization of polluted raw materials. Moreover, insufficient processing and storage methods could exacerbate contamination during feed production. When ingested by animals, these compounds accumulated in adipose tissues and were then transferred to human consumers. To mitigate this risk, reliable monitoring and analytical detection methods were essential for the accurate quantification of PCBs in feed samples. The complex formulation of animal feed, often containing several organic and inorganic components, necessitated highly efficient sample preparation and analytical methods to achieve the required detection limits and quantification accuracy [9, 10].

The analysis of PCBs was standardized by high-resolution gas chromatography and mass spectrometry [11]. This method was favored for regulatory compliance testing because to its enhanced sensitivity, specificity, and selectivity. HRGC/HRMS measured deleterious congeners at femtogram (fg) levels for precise toxic equivalency (TEQ) assessments. Nevertheless, the procedure was expensive, labor-intensive, and necessitated skilled instrument operators and maintenance personnel. In light of the complexity and substantial operational costs associated with HRGC/HRMS analysis, other analytical approaches exhibiting comparable performance alongside enhanced efficiency and accessibility have been explored. In recent years, gas chromatography coupled with tandem mass spectrometry (GC-MS/MS) has demonstrated potential for the analysis of PCDD/PCDF [12]. Triple quadrupole mass spectrometry devices might detect ultra-trace levels of these contaminants due to enhanced sensitivity. In comparison to HRGC/HRMS, GC-MS/MS was more cost-effective, simpler to maintain, and quicker in analysis [13]. The EU sanctioned GC-MS/MS as an official confirmatory technique for the analysis of PCBs in food and feed, endorsing its application in routine monitoring programs.

This work conducted a detailed comparison of GC-MS/MS and HRGC/HRMS for the analysis of PCDD/PCDFs in fish feed. The primary objective was to evaluate the sensitivity, selectivity, and accuracy of GC-MS/MS in comparison to HRGC/HRMS. The study assessed the sample preparation, extraction, and cleanup efficiency of both procedures to ascertain their appropriateness for routine analysis. The limits of quantification and precision of each method in actual feed samples were assessed to determine whether GC-MS/MS could substitute HRGC/HRMS in regulatory compliance testing. This study evaluated these two analytical techniques to elucidate their advantages and disadvantages, thereby facilitating the development of more efficient and accessible methods for PCB analysis. This research influenced with food safety surveillance, regulatory determinations, and laboratory efficacy. If GC-MS/MS exhibited comparable performance to HRGC/HRMS, it might serve as a cost-effective and broadly applicable option for the determination of PCBs, thereby enhancing the monitoring and management of fish feed and the food supply chain.

2. EXPERIMENT

2.1. Chemicals

Every component and solvent were at analytically pure according to Merck or Aldrich Sigma standards. AX Cambridge Isotope Laboratory (CIL-USA) provided the ^{12}C12 standard solutions (for method accuracy and repeatability), ^{13}C12 isotope-labeled standard solutions (companion standards for recovery efficiency), PCDD/PCDF calibration curve standard solutions, and concentrated sulfuric acid (H_2SO_4) with a density of 1.83 g/mL, granulated sodium sulfate (Na_2SO_4), granulated potassium hydroxide (KOH), sodium chloride (NaCl), and neutral aluminum oxide (Al_2O_3).

2.2. PCDD/PCDF separation, extraction, and enrichment

A 20 g fish feed sample was spiked with EDF-8999 and EC-4937 standards and extracted using Soxhlet with toluene for 5 h, followed by 16 h with a 9:1 toluene–ethanol mixture. After rotary evaporation, the residue was redissolved in 80 mL n-hexane and cleaned using acid, base, and salt washes, then dried with Na_2SO_4. The extract was purified via multilayer silica and activated carbon columns, where PCDD/PCDF were eluted with toluene at 118 °C. After evaporation, 30 mL n-hexane was added and fractionated on an alumina column using a 1:1 eluent. The final extract was dried under nitrogen, spiked with $^{13}C_{12}$-PCDD standards for recovery evaluation, and concentrated to 10 µL for GC-MS/MS analysis.

2.3. Examination of specimens utilizing GC-MS/MS

Gas chromatography was performed using a TR-DIOXIN capillary column (60 m × 0.25 mm ID, 0.25 µm film; ThermoFisher Scientific) with 2 µL splitless injection for PCDD/PCDFs. The oven program started at 140 °C for 2 min, ramped to 220 °C at 20 °C/min (held for 16 min), then to 320 °C at 5 °C/min (held for 6.6 min), totaling 48.6 min. Helium was the carrier gas at 1.2 mL/min. Interface and ion source temperatures were 290 °C and 280 °C, respectively, with 70 eV electron ionization and a 250 µA emission current. Seventeen toxic PCDD/PCDF congeners were identified using specific retention times and mass transitions. Two methods, GC-MS/MS and HRGC/HRMS, were applied to determine PCDD/PCDF concentrations in three fish feed samples. Relative percent difference (RPD) and result bias were used to compare the analytical performance of the two techniques.

3. RESULTS AND DISCUSSION

3.1. Assessment of PCDD/PCDF analytical proficiency

The analytical proficiency for PCDD/PCDF utilizing GC-MS/MS was evaluated based on the standards set for PCDD/PCDF analysis by HRGC/HRMS, in compliance with US EPA Method 1613B. The criteria specified that the relative retention time (RRT), which was the ratio of the retention time of 12C-PCDD/PCDF to that of the corresponding 13C-PCDD/PCDF isotope in the standard, had to remain within the acceptable range, as the time ratio between the companion standard and the primary standard determines the recovery efficiency. The recovery efficiency of congeners (Rec, %) should not exceed 25% overlap between 2,3,7,8-TCDD and other TCDD isomers. The analytical results of the EDF-4141 standard were presented in Table 1, and the separation capability of TCDD isomers was illustrated in Figure 1.

Table 1. Cal/Win/Res EDF-4141 daily standard analytical outcomes.

No.	Compounds	RRT	Rec, %
1	2,3,7,8-TCDF	1.0005	96.0
2	1,2,3,7,8-PeCDF	1.0003	103.6
3	2,3,4,7,8-PeCDF	1.0003	93.8
4	1,2,3,4,7,8-HxCDF	1.0001	100.3
5	1,2,3,6,7,8-HxCDF	1.0001	96.6
6	1,2,3,7,8,9-HxCDF	1.0004	99.9
7	2,3,4,6,7,8-HxCDF	1.0007	104.8
8	1,2,3,4,6,7,8-HpCDF	1.0001	104.0
9	1,2,3,4,7,8,9-HpCDF	1.0002	95.2
10	OCDF	1.0083	99.0
11	2,3,7,8-TCDD	1.0004	91.2
12	1,2,3,7,8-PeCDD	1.0004	92.6
13	1,2,3,4,7,8-HxCDD	1.0002	98.9
14	1,2,3,6,7,8-HxCDD	1.0002	108.2
15	1,2,3,7,8,9-HxCDD	1.0000	112.2
16	1,2,3,4,7,8,9-HpCDD	1.0003	99.7
17	OCDD	1.0002	101.6
18	^{13}C -2378-TCDF	0.9978	103.7
19	^{13}C -12378-PeCDF	1.1181	108.3
20	^{13}C -23478-PeCDF	1.1482	108.8
21	^{13}C -123478-HxCDF	0.9706	108.3
22	^{13}C -123678-HxCDF	0.9738	113.5
23	^{13}C -234678-HxCDF	0.988	112.3
24	^{13}C -123789-HxCDF	1.0112	108.6
25	^{13}C -1234678-HpCDF	1.0448	105.3
26	^{13}C -1234789-HpCDF	1.0916	104.5
27	^{13}C -2378-TCDD	1.0159	97,8
28	^{13}C -12378-PeCDD	1.1548	102,2
29	^{13}C -123478-HxCDD	0.9904	101.3
30	^{13}C -123678-HxCDD	0.9928	93.3
31	^{13}C-1234678-HpCDD	1.0731	106.2
32	^{13}C-OCDD	1.1633	114.7
33	^{37}Cl-2378-TCDD	1.0164	94.4

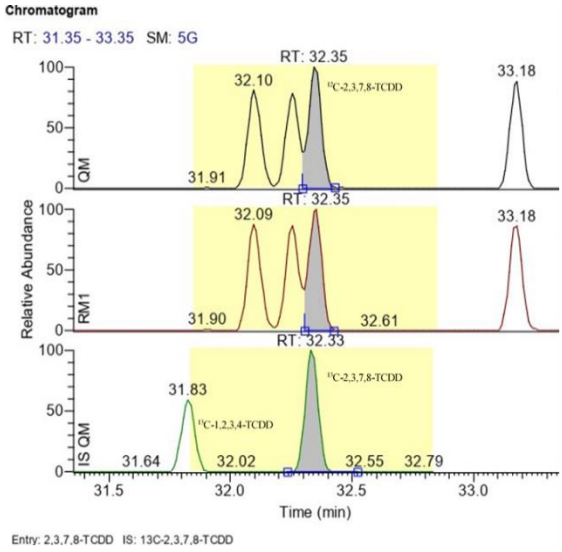

Figure 1. Chromatogram of TCDD isomers examined using a GC-MS/MS system.

Table 1 demonstrated that GC-MS/MS effectively quantifies PCDD/PCDF, meeting all criteria of US EPA Method 1613B. The RRT coefficients and recovery efficiencies for all 17 toxic congeners fell within acceptable limits. The RRT values complied with the method's specified range, ensuring analytical reliability. Figure 1 showed a 30% overlap between 2,3,7,8-TCDD and other TCDD isomers, which remained within a desirable threshold. These results confirmed that the GC-MS/MS method provides accurate identification and effective separation of PCDD and PCDF isomers.

3.2. Determine the linear range of the calibration curve, detection limit, quantification limit, repeatability, and reproducibility

The linearity range of the PCDD/PCDF (and dl-PCB) calibration curves was established by creating 8-point (and 6-point) calibration curves using the EDF-9999 calibration set from CS0.1 to CS5 (and EC-5396 from CS1 to CS6). The analytical outcomes of the PCDD/PCDF and dl-PCB calibration points are displayed in Table 2.

Table 2. Results of determining the linear range of the standard curve.

No	Compounds	C (pg/□L)	R^2	RF average	RSD (%)
1	2378-TCDD	0.05-40	0.999863	1.09	5.98
2	12378-PeCDD	0.25-200	0.999958	0.98	9.69
3	123478-HxCDD	0.25-200	0.999975	1.03	6.80
4	123678-HxCDD	0.25-200	0.999889	0.99	8.97
5	123789-HxCDD	0.25-200	0.999996	1.09	4.03
6	1234678-HpCDD	0.25-200	0.999998	0.98	7.35
7	OCDD	0.50-400	0.999981	1.18	9.22
8	2378-TCDF	0.05-40	0.999578	1.04	4.10
9	12378-PeCDF	0.25-200	0.999954	1.05	4.06
10	23478-PeCDF	0.25-200	0.999626	1.08	8.78
11	123478-HxCDF	0.25-200	0.999983	1.11	5.36
12	123678-HxCDF	0.25-200	0.999998	1.06	7.26
13	234678-HxCDF	0.25-200	0.999996	1.03	2.92
14	123789-HxCDF	0.25-200	0.999965	1.04	8.71
15	1234678-HpCDF	0.25-200	0.999998	1.19	4.38
16	1234789-HpCDF	0.25-200	0.999979	1.15	9.07
17	OCDF	0.50-400	0.999869	1.38	6.20
	Total TEQ (pg/g)				
	Compounds	**LOD, pg/g**	**LOQ, pg/g**	**SD**	
1	2378-TCDD	0.006	0.025	0.25	
2	12378-PeCDD	0.019	0.125	2.25	
3	123478-HxCDD	0.023	0.125	0.91	
4	123678-HxCDD	0.031	0.125	2.94	
5	123789-HxCDD	0.011	0.125	1.50	
6	1234678-HpCDD	0.029	0.125	2.56	
7	OCDD	0.052	0.250	2.29	
8	2378-TCDF	0.005	0.025	1.31	
9	12378-PeCDF	0.013	0.125	3.05	
10	23478-PeCDF	0.016	0.125	2.61	
11	123478-HxCDF	0.006	0.125	0.62	
12	123678-HxCDF	0.006	0.125	2.63	
13	234678-HxCDF	0.025	0.125	3.02	
14	123789-HxCDF	0.030	0.125	5.51	
15	1234678-HpCDF	0.017	0.125	2.70	
16	1234789-HpCDF	0.020	0.125	4.87	
17	OCDF	0.056	0.250	10.67	
	Total TEQ (pg/g)	**0.045**	**0.285**	**0.25**	
	Compounds	**RSD**	**R%**	**b%**	
1	2378-TCDD	1.42	88.2	-11.8	
2	12378-PeCDD	2.42	92.9	-7.1	
3	123478-HxCDD	1.03	88.0	-12.0	
4	123678-HxCDD	3.42	85.9	-14.1	
5	123789-HxCDD	1.64	91.8	-8.2	
6	1234678-HpCDD	2.78	92.1	-7.9	
7	OCDD	2.36	97.3	-2.7	
8	2378-TCDF	1.45	90.5	-9.5	
9	12378-PeCDF	3.37	90.4	-9.6	
10	23478-PeCDF	1.31	99.9	-0.1	
11	123478-HxCDF	3.39	91.5	-8.5	
12	123678-HxCDF	2.87	91.7	-8.3	
13	234678-HxCDF	3.02	100.0	0.0	
14	123789-HxCDF	5.97	92.2	-7.8	
15	1234678-HpCDF	2.68	100.7	0.7	
16	1234789-HpCDF	5.22	93.3	-6.7	
17	OCDF	5.92	90.1	-9.9	
	Total TEQ (pg/g)	**1.42**	**88.2**	**-11.8**	

The data in Table 2 indicated that the correlation coefficient R^2 exceeds 0.999, and the relative standard deviation was

below 15.0%. The results achieved align with the evaluation criteria ($R^2 > 0.99$ and %RSD < 15%). The linear range of the standard curve was as follows: TCDD/TCDF: 0.05 - 200 ng/mL (pg/µL); Pe- to Hp-CDD/CDF: 0.25 - 1,000 ng/mL (pg/µL); OCDD/OCDF: 0.5 - 2,000 ng/mL (pg/µL).

The outcomes of assessing the recovery efficiency (R%) of the corresponding standards for each sample matrix from all 15 samples (5 blank samples, 5 LOQ samples, and 5 mid samples) were formed. The findings indicated that the recovery efficiency of the associated standards of PCDD/PCDFs fell within the range of 75-105%, hence meeting the criteria established by the US EPA Method 1613B. The outcomes of the standard curve development, together with the analytical results for the Blank, LOQ, and Mid samples, were comprehensively detailed in the report validating the method for measuring PCDD/PCDFs in fish feed samples utilizing a triple quadrupole gas chromatography mass spectrometer.

3.3. Analytical assessment of PCDD/PCDF in fish feed and comparison of GC-MS/MS & HRMS methods

The research team quantified PCDD/PCDF levels in three fish feed samples using both GC-MS/MS and HRGC/HRMS systems. Results were shown in Table 3 and Figure 2. Some congeners were detected only by HRGC/HRMS; however, the relative percent difference (RPD) for most toxic congeners between the two methods was under 20%, confirming GC-MS/MS's suitability for feed analysis. Toxic PCDF congeners were present in most samples, while hazardous PCDD congeners appeared in only a few. The total TEQ toxicity from all PCDD/PCDF congeners remained approximately 2–3 times below the European Commission limit of 1.25 pg TEQ/g.

Table 3. Analysis results for PCDD/PCDF concentrations in fish feed samples

No	Analytical compounds	MSMS	HRMS	RPD, %
F1				
1	2,3,7,8-TCDF	1.345	1.256	6.8
2	1,2,3,7,8-PeCDF	0.025	0.030	18.2
3	2,3,4,7,8-PeCDF	0.019	0.016	11.8
4	1,2,3,4,7,8-HxCDF	0.064	0.063	1.6
5	1,2,3,6,7,8-HxCDF	0.051	0.053	3.8
6	1,2,3,7,8,9-HxCDF	0.063	0.069	9.1
7	2,3,4,6,7,8-HxCDF	0.046	0.050	8.3
8	1,2,3,4,6,7,8-HpCDF	0.026	0.025	3.9
9	1,2,3,4,7,8,9-HpCDF	0.121	0.144	17.4
10	OCDF	0.043	0.047	8.9
11	2,3,7,8-TCDD	0.279	0.302	7.9
12	1,2,3,7,8-PeCDD	0.139	0.121	13.8
13	OCDD	0.038	0.042	10.0
	TEQ, pg TEQ/g	**0.585**	**0.580**	**0.9**
F2				
1	1,2,3,7,8-PeCDF	0.054	0.045	18.2
2	2,3,4,7,8-PeCDF	0.040	0.048	17.4
3	OCDD	0.926	0.912	1.5
	TEQ, pg TEQ/g	**0.038**	**0.040**	**5.1**
		F3		
1	2,3,7,8-TCDF	0.135	0.161	17.9
2	1,2,3,4,7,8-HxCDF	0.074	0.072	2.7
3	1,2,3,7,8,9-HxCDF	0.046	0.04	14.6
4	2,3,4,6,7,8-HxCDF	0.025	0.023	6.7
5	1,2,3,4,6,7,8-HpCDF	0.103	0.105	2.3
6	2,3,7,8-TCDD	0.030	0.031	4.3
7	OCDD	0.897	0.83	7.8
	TEQ, pg/g	**0.081**	**0.083**	**2.4**

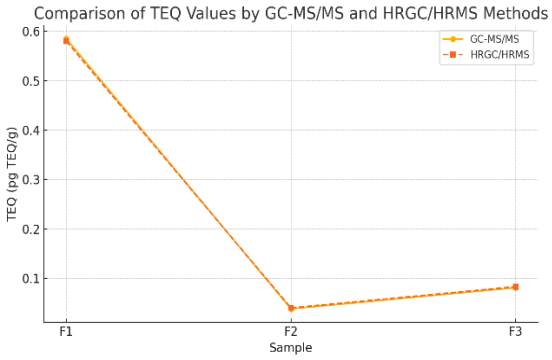

Figure 2. graph comparing the TEQ values (pg TEQ/g) for the 3 samples (F1, F2, F3) using GC-MS/MS and HRGC/HRMS methods.

The graph compared total toxic equivalent (TEQ) values of PCDD/PCDFs in three fish feed samples (F1, F2, F3) using GC-MS/MS and HRGC/HRMS. Both methods showed strong agreement. For F1, TEQ values were 0.585 pg TEQ/g (GC-MS/MS) and 0.580 pg TEQ/g (HRGC/HRMS), differing by less than 1%. In F2, the values were 0.038 and 0.040 pg TEQ/g, with a 5.1% RPD. F3 showed 0.081 and 0.083 pg TEQ/g, with a 2.4% RPD. These minor differences confirmed the reliability of GC-MS/MS for TEQ quantification. All samples contained harmful PCB congeners, with total TEQ levels ranging from 0.038 to 0.585 pg TEQ/g. F1 had the highest toxicity (0.585 pg TEQ/g), containing all toxic PCDF, TCDD, and PeCDD congeners. F2 had the lowest TEQ (0.038 pg TEQ/g), with only PeCDF and OCDD detected. F3 contained toxic PCDF congeners, yielding an intermediate TEQ value. Overall, both methods provided consistent results, and GC-MS/MS proved suitable for routine monitoring of dioxin contamination in fish feed.

The comparison of GC-MS/MS and HRMS methods for analyzing PCDD/F congeners in fish feed samples (F1, F2, F3) showed good overall agreement, with most relative percent differences (RPD) below 10%. In F1, compounds like 1,2,3,4,7,8-HxCDF (1.6% RPD) and 1,2,3,6,7,8-HxCDF (3.8%) showed strong concordance, though 1,2,3,7,8-PeCDF (18.2%) and 1,2,3,4,7,8,9-HpCDF (17.4%) had higher variation. F2 had limited data, but OCDD showed a low RPD of 1.5%. In F3, compounds such as 1,2,3,4,6,7,8-HpCDF (2.3%) and 2,3,7,8-TCDD (4.3%) matched well, while 2,3,7,8-TCDF showed a higher RPD (17.9%). TEQ values across samples showed strong consistency, with RPDs from 0.9% to 5.1%, supporting the reliability of both methods. Despite minor differences, GC-MS/MS proved to be a reliable alternative to HRMS for TEQ-based PCDD/F analysis in fish feed.

4. CONCLUSION

This study demonstrated that GC-MS/MS and HRGC/HRMS methods offered comparable performance for the determination of PCDDs and PCDFs in fish feed samples. Most analytes exhibited relative percent differences (RPD) below 10%, indicating good agreement between the two techniques. Although some individual congeners showed higher RPDs, the calculated TEQ values remained consistent, with differences generally within 5%. These findings suggested that GC-MS/MS, with its advantages of greater accessibility, lower cost, and faster analysis time, could serve as a reliable alternative to HRGC/HRMS for routine monitoring of PCDD/PCDF contamination in fish feed. The results supported broader application of GC-MS/MS for environmental and food safety assessments where high precision and regulatory compliance are required.

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