DETERMINATION OF PCDD/PCDF AND DL-PCB IN CHICKEN FEED USING GC-MS/MS AND HRGC/HRMS: A COMPARATIVE STUDY

XÁC ĐỊNH PCDD/PCDF VÀ DL-PCB TRONG THỨC ĂN NUÔI GÀ BẰNG GC-MS/MS VÀ HRGC/HRMS: MỘT NGHIÊN CỨU SO SÁNH

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ABSTRACT

There are persistent environmental contaminants that pose major concerns to food safety. These contaminants include polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs). There is a comparison made in this study between the performance of gas chromatography-tandem mass spectrometry (GC-MS/MS) and high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) in terms of determining the amounts of PCDD/PCDF and dl-PCB in chicken feed samples. According to the findings, CDD has the highest concentration, which ranges from 4.002 to 10.015pg/g. On the other hand, OCDF shows at substantially lower levels (0.012 - 0.014pg/g), which would imply that dioxins are more prevalent than furans. There is a presence of tetrachlorinated chemicals, such as 2,3,7,8-TCDF and 2,3,7,8-TCDD, at trace levels (less than 0.3pg/g). Additionally, pentachlorinated (PeCDF, PeCDD) and hexachlorinated (HxCDF, HxCDD) congeners have been discovered at low concentrations. In terms of animal feed, the toxic equivalency (TEQ) values that have been determined vary from 0.092 to 0.243pg TEQ/g, which is far lower than the regulation limit set by the EU, which is 0.75pg TEQ/g. According to the findings of this study, GC-MS/MS is capable of producing results that are comparable to those obtained by HRGC/HRMS. This demonstrates that GC-MS/MS has the potential to be a more cost-effective alternative for routine screening. However, HRGC/HRMS continues to be necessary for confirmatory analysis and regulatory compliance.

Keywords: *PCDD/PCDF, dl-PCB, animal feed contamination, GC-MS/MS, HRGC/HRMS.*

TÓM TẮT

Có những chất gây ô nhiễm môi trường dai dẳng gây ra những lo ngại lớn đối với an toàn thực phẩm. Những chất gây ô nhiễm này bao gồm polychlorinated dibenzo-p-dioxin (PCDD), polychlorinated dibenzofurans (PCDF) và polychlorinated biphenyls giống dioxin (dl-PCB). Nghiên cứu này có sự so sánh giữa hiệu suất của sắc ký khí - phổ khối song song (GC-MS/MS) và sắc ký khí độ phân giải cao/phổ khối độ phân giải cao (HRGC/HRMS) về mặt xác định lượng PCDD/PCDF và dl-PCB trong các mẫu thức ăn cho gà. Theo các phát hiện, CDD có nồng độ cao nhất, dao động từ 4,002 đến 10,015pg/g. Mặt khác, OCDF cho thấy ở mức thấp hơn đáng kể (0,012 - 0,014pg/g), điều này cho thấy rằng dioxin phổ biến hơn furan. Có sự hiện diện của các hóa chất tetrachlorinated, chẳng hạn như 2,3,7,8-TCDF và 2,3,7,8-TCDD, ở mức vết (ít hơn 0,3pg/g). Ngoài ra, các đồng loại pentachlorinated (PeCDF, PeCDD) và hexachlorinated (HxCDF, HxCDD) đã được phát hiện ở nồng độ thấp. Về thức ăn chăn nuôi, các giá trị tương đương độc hại (TEQ) đã được xác định dao động từ 0,092 đến 0,243pg TEQ/g, thấp hơn nhiều so với giới hạn quy định do EU đặt ra là 0,75pg TEQ/g. Theo các phát hiện của nghiên cứu này, GC-MS/MS có khả năng tạo ra các kết quả tương đương với các kết quả thu được bằng HRGC/HRMS. Điều này chứng tỏ rằng GC-MS/MS có tiềm năng trở thành một giải pháp thay thế hiệu quả hơn về mặt chi phí cho sàng lọc thường quy. Tuy nhiên, HRGC/HRMS vẫn cần thiết cho phân tích xác nhận và tuân thủ quy định.

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

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1. INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (DL-PCBs) are extremely hazardous persistent organic pollutants (POPs) that provide significant environmental and health hazards [1-3]. These substances are inadvertent results of industrial activities such trash incineration, metal refining, and chemical production [4, 5]. Upon environmental discharge, they last for extended durations owing to their significant chemical stability and lipophilicity, resulting in bioaccumulation in animal adipose tissue and biomagnification within the food web. Humans predominantly encounter these pollutants via the ingestion of animal-derived goods, including meat, dairy, fish, and eggs [6]. Due to their capacity to induce carcinogenic, immunotoxic, neurotoxic, and endocrine-disrupting effects, regulatory bodies globally have implemented rigorous restrictions on their levels in food and animal feed [7, 8]. Animal feed serves as a pivotal control point in mitigating dioxin and PCB contamination throughout the food supply chain. Contaminated feed components, including fish meal, animal fats, clay-based binders, and plant-derived materials subjected to atmospheric pollution, can substantially augment the overall toxic burden in livestock and poultry [9-11]. Upon ingestion by animals, these chemicals accumulate in adipose tissues, subsequently transferring to human consumers. To alleviate this risk, dependable monitoring and analytical detection techniques are crucial for the precise quantification of dioxins and PCBs in feed samples. Due to the intricate composition of animal feed, which frequently comprises many organic and inorganic elements, highly effective sample preparation and analytical techniques are essential to attain the needed detection thresholds and quantification precision [12, 13].

Dioxin and PCB analysis is standardised using high-resolution gas chromatography and mass spectrometry [14, 15]. This method is preferred for regulatory compliance testing because to its superior sensitivity, specificity, and selectivity. HRGC/HRMS quantifies harmful congeners at femtogram (fg) levels for accurate toxic equivalency (TEQ) calculations. However, the process is costly, time-consuming, and requires trained instrument operators and maintainers. Due to HRGC/HRMS analysis's complexity and high operational expenses, new analytical methods with equivalent performance and increased efficiency and accessibility have been investigated. In recent years, gas chromatography combined with tandem mass spectrometry (GC-MS/MS) has shown promise for PCDD/PCDF and DL-PCB analysis [16, 17]. Triple quadrupole MS systems can identify ultra-trace quantities of these pollutants thanks to greater sensitivity [18]. Compared to HRGC/HRMS, GC-MS/MS is cheaper, easier to maintain, and faster to analyze. The EU has approved GC-MS/MS as an official confirmatory method for dioxin and PCB analysis in food and feed, supporting its use in routine monitoring programs.

This study compares GC-MS/MS and HRGC/HRMS for chicken feed PCDD/PCDFs and DL-PCBs in detail. The main goal is to compare GC-MS/MS sensitivity, selectivity, and accuracy to HRGC/HRMS. To determine their suitability for regular analysis, the study evaluates sample preparation, extraction, and cleanup efficiency for both methods. The quantification limits and precision of each method in real feed samples are examined to see if GC-MS/MS can replace HRGC/HRMS in regulatory compliance testing. This research compares these two analytical methods to get insight into their pros and cons and help build more efficient and accessible dioxin and PCB analysis methods. This study impacts food safety monitoring, regulatory decision-making, and laboratory efficiency. If GC-MS/MS performs similarly to HRGC/HRMS, it could be a cost-effective and widely used alternative for dioxin and PCB determination, improving chicken feed and food supply chain monitoring and control.

2. MATERIALS AND METHODS

2.1. Chemicals

All solvents and compounds must be Merck or Aldrich Sigma analytical purity: Concentrated Sulfuric Acid (H_2SO_4) with a density of 1.83g/mL, Granulated Sodium Sulfate (Na_2SO_4), Granulated Potassium Hydroxide (KOH), Sodium Chloride (NaCl), Neutral Aluminum Oxide (Al_2O_3), AX Cambridge Isotope Laboratory (CIL-USA) supplied the $^{12}C12$ standard solutions (for method accuracy and repeatability), $^{13}C12$ isotope-labeled standard solutions (companion standards for recovery efficiency), and PCDD/PCDF and dl-PCB calibration curve standard solutions.

2.2. Separation, extraction, and enrichment of PCDD/PCDF and dl-PCB

A 20 g chicken feed sample was spiked with EDF-8999 and EC-4937 standards and extracted using Soxhlet with toluene for 5 hours, followed by a second extraction with a 9:1 toluene–ethanol mixture for 16 hours. Solvents were evaporated using a rotary evaporator and replaced with 80mL of n-hexane. The extract underwent cleanup with acid (H_2SO_4), base (KOH), and salt (NaCl) washes, followed by dehydration with Na_2SO_4. Further purification was performed using a multilayer silica column (neutral, acid, and alkali-impregnated silica gels) and an activated carbon column, where PCDD/PCDF and dl-PCBs were eluted with toluene at 118°C. After toluene evaporation, 30 mL of n-hexane was added, and the extract was separated on an alumina column. dl-PCBs were eluted with a 95:5 n-hexane mixture and PCDD/PCDF with a 1:1 mixture. After solvent evaporation, the concentrated extract was dried under nitrogen gas. Isotope-labeled $^{13}C_{12}$-PCDD standards were used to assess recovery. Final volumes were adjusted to 10µL (PCDD/PCDF) and 20µL (dl-PCB) for GC-MS/MS analysis.

2.3. Analysis of samples using GC-MS/MS

Gas chromatography was performed using a TR-DIOXIN capillary column (60m × 0.25mm ID, 0.25µm film thickness; ThermoFisher Scientific). Injection was splitless, with volumes of 2µL for PCDD/PCDFs and 1µL for dl-PCBs. For PCDD/PCDFs, the oven temperature started at 140°C (2 min), ramped to 220°C at 20°C/min (held 16 min), then to 320°C at 5°C/min (held 6.6 min), for a total run time of 48.6 min. For dl-PCBs, the oven started at 150°C (2 min), increased to 220°C at 20°C/min (held 16 min), then to 300°C at 5°C/min (held 1.5 min), totaling 39 min. Helium was used as the carrier gas at 1.2mL/min. The interface and ion source temperatures were 290°C and 280°C, respectively, with electron ionization at 70eV and an emission current of 250µA. Analysis targeted 17 toxic congeners of PCDD/PCDFs and 12 of dl-PCBs, using specific retention times and mass transitions based on precursor and product ions for accurate identification and quantification.

Two studies were conducted to ascertain the amounts of PCDD/PCDF and dl-PCB in three chicken feed samples: triple quadrupole mass spectrometry (GC-MS/MS) and high-resolution gas chromatography mass spectrometry (HRGC/HRMS). RPD (%) and result bias were two metrics employed to assess the two analytical techniques for the research samples.

3. RESULTS AND DISCUSSION

3.1. PCDD/PCDF analytical capability evaluation

The analytical capability for PCDD/PCDF using GC-MS/MS was assessed according to the criteria established for PCDD/PCDF analysis by HRGC/HRMS in accordance with US EPA Method 1613B. The criteria stipulate that the relative retention time (RRT), defined as the ratio of the retention time of 12C-PCDD/PCDF to that of the corresponding 13C-PCDD/PCDF isotope in the standard, must fall within the permissible range, as the time ratio between the companion standard and the primary standard dictates the recovery efficiency. Recovery efficiency of congeners (Rec, %); The overlap between 2,3,7,8-TCDD and other TCDD isomers must not surpass 25%. The analytical findings of the EDF-4141 standard are displayed in Table 1, while the separation capacity of TCDD isomers is depicted in Figure 1.

The analytical findings in Table 1 indicate that the capacity to analyze PCDD/PCDF using GC-MS/MS is excellent, with all metrics conforming to the standards of the US EPA 1613B analytical method. The RRT coefficient is within the permissible range established by the method, and the recovery efficiency for all 17 harmful PCDD/PCDF congeners, along with their related standards, remains within the acceptable limits. Figure 1 illustrates that the overlap between 2,3,7,8-TCDD and other TCDD isomers is 30%, which is relatively favorable. Consequently, the GC-MS/MS method effectively separates PCDD/PCDF isomers.

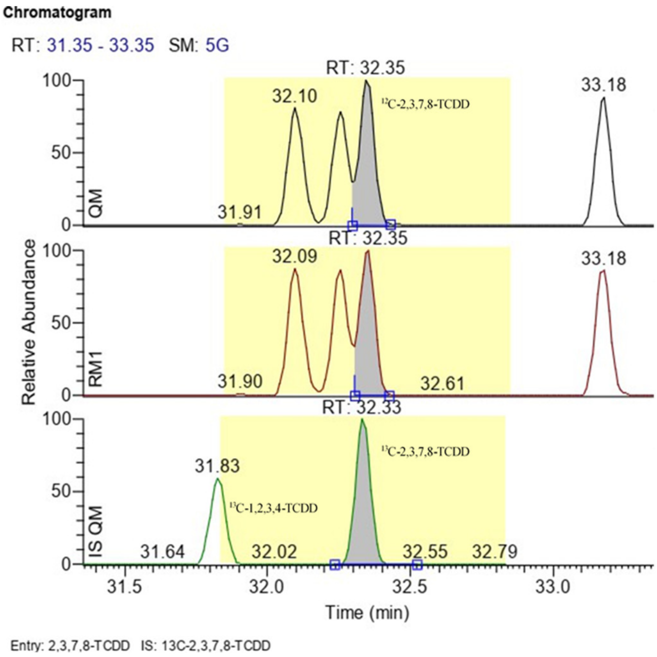

Figure 1. Chromatogram of TCDD isomers analyzed on GC-MS/MS system

3.2. PCDD/PCDF analytical in chicken feed

Analysis was performed to ascertain the concentrations of PCDD/PCDF and dl-PCB in three chicken feed samples utilizing a triple quadrupole mass

Table 1. Cal/Win/Res EDF-4141 daily standard analysis results

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

spectrometry (GC-MS/MS) system and a high-resolution gas chromatography mass spectrometry (HRGC/HRMS) system. The analytical results indicated that certain congeners of PCDD/PCDF and dl-PCB were identified using the HRGC/HRMS device, whereas they were not detected by the GC-MS/MS device. The analytical results (RPD, %) for the majority of toxic congeners of PCDD/PCDF and dl-PCB across the two devices showed deviations not exceeding 20%. This suggests that the GC-MS/MS system is capable of effectively analyzing PCDD/PCDF and dl-PCB within the chicken feed sample matrix. All toxic congeners of PCDF, dl-PCB, HpCDD, and OCDD were identified in the C1 chicken feed sample. In the C2 and C3 chicken feed samples, only certain low-chlorine toxic congeners of PCDF (TeCDF, PeCDF), high-chlorine toxic congeners of PCDD (HpCDD and OCDD), and low-chlorine toxic congeners of dl-PCB (TeCB, PeCB, and HxCB) were identified. The total toxicity TEQ of PCDD/PCDF in all three chicken feed samples ranged from 0.092 to 0.237pg TEQ/g, while the total TEQ of dl-PCB varied from 0.050 to 0.062pg TEQ/g.

The quantities of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) fluctuate among various congeners in the chicken feed samples. The findings are articulated by MS/MS and HRMS analysis, accompanied by relative percent differences (RPD) to evaluate technique consistency. OCDD exhibits the highest recorded concentration among all samples, with values spanning from 4.002 to 10.015pg/g. OCDF is identified at significantly lower concentrations (0.012 - 0.014pg/g), suggesting a higher prevalence of dioxins relative to furans in the meal. Tetrachlorinated chemicals, including 2,3,7,8-TCDF and 2,3,7,8-TCDD, are present at trace concentrations (< 0.3pg/g). Likewise, pentachlorinated congeners (PeCDF, PeCDD) and hexachlorinated dioxins/furans (HxCDF, HxCDD) exhibit comparatively low amounts. The TEQ values, derived from the toxic equivalency factors (TEFs) of each congener, vary from 0.092 to 0.243pg TEQ/g in the samples. These values must be evaluated against the regulatory threshold for dioxins in animal feed (EU limit for dioxins in feed: 0.75pg TEQ/g). Most compounds exhibit a low Relative Percent Difference (RPD) of less than 10%, indicating strong concordance between MS/MS and HRMS methodologies. Nevertheless, some congeners (2,3,4,7,8-PeCDF in C2, OCDD in C1, 1,2,3,7,8,9-HxCDF in C1) demonstrate elevated RPD values (> 10%), suggesting possible analytical variability. Matrix effects,

Table 2. Results of analysis to determine PCDD/PCDF and dl-PCB concentrations in chicken feed samples

No.	Compounds	C1			C2			C3		
		MS/MS	HRMS	RPD, %	MS/MS	HRMS	RPD, %	MS/MS	HRMS	RPD, %
I	**PCDD/PCDF**									
1	2,3,7,8-TCDF	0.007	0.008	9.2	0.121	0.103	16.1	0.299	0.255	15.8
2	1,2,3,7,8-PeCDF	0.725	0.694	4.4	0.089	0.103	15.1	0.173	0.152	12.7
3	2,3,4,7,8-PeCDF	0.174	0.179	2.7	0.06	0.073	19.4	0.071	0.062	13.7
4	1,2,3,4,7,8-HxCDF	0.773	0.803	3.8				0.083	0.092	9.9
5	1,2,3,6,7,8-HxCDF	0.225	0.223	0.7						
6	1,2,3,7,8,9-HxCDF	0.018	0.02	11.1						
7	2,3,4,6,7,8-HxCDF	0.403	0.424	5.1						
8	1,2,3,4,6,7,8-HpCDF	0.088	0.092	4.9	0.117	0.125	6.7	0.144	0.145	0.8
9	1,2,3,4,7,8,9-HpCDF	0.009	0.01	11.6						
10	OCDF	0.012	0.014	13.7						
11	2,3,7,8-TCDD				0.031	0.032	1.9			
12	1,2,3,7,8-PeCDD					0		0.032	0.032	0.9
13	1,2,3,4,7,8-HxCDD				0.035	0.038	7.1			
14	1,2,3,6,7,8-HxCDD									
15	1,2,3,7,8,9-HxCDD									
16	1,2,3,4,7,8,9-HpCDD	0.024	0.026	8.8	0.218	0.236	7.9	0.753	0.903	18.1
17	OCDD	4.691	5.043	7.2	4.002	4.068	1.6	9.865	10.015	1.5
	TEQ, pg TEQ/g	**0.237**	**0.243**	**2.5**	**0.092**	**0.096**	**4.3**	**0.119**	**0.113**	**5.2**
II	**dl-PCB**									
1	PCB#81	0.522	0.563	7.6	0.914	0.929	1.6	0.746	0.741	0.7
2	PCB#77	20.744	21.192	2.1	5.039	4.48	11.7	5.221	4.91	6.1
3	PCB#123	0.183	0.187	2.2				3.233	3.09	4.5
4	PCB#118	7.467	6.582	12.6	11.301	10.738	5.1	26.869	30.23	11.8
5	PCB#114	0.522	0.452	14.4				0.577	0.564	2.3
6	PCB#105	4.255	3.946	7.5	3.897	4.44	13	9.312	9.073	2.6
7	PCB#126	0.461	0.482	4.5	0.489	0.449	8.4	0.596	0.584	2.1
8	PCB#167	0.246	0.275	11.1	1.151	1.259	8.9	1.887	2.241	17.2
9	PCB#156	0.507	0.464	8.9	0.516	0.521	1	1.174	1.29	9.4
10	PCB#157	0.138	0.16	15						
11	PCB#169	0.057	0.048	17						
12	PCB#189	0.15	0.149	0.9						
	Total TEQ dl-PCB	**0.05**	**0.052**	**3.9**	**0.051**	**0.046**	**10.3**	**0.062**	**0.061**	**1.6**
	Total TEQ PCDD/PCDF+dl-PCB	**0.287**	**0.295**	**2.7**	**0.143**	**0.142**	**0.3**	**0.181**	**0.174**	**3.9**

equipment sensitivity, and calibration errors may contribute to inconsistencies. The presence of PCDD/PCDFs in chicken feed raises concerns about bioaccumulation in po ultry, potentially resulting in contamination of eggs and meat. The discovered amounts are quite modest relative to legal thresholds; yet, ongoing monitoring is important to guarantee food safety.

3.3. Comparison of GC-MS/MS and HRMS methods in chicken feed analysis

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are extremely toxic pollutants capable of bioaccumulating within the food chain. Their presence in chicken feed is a considerable worry as it may result in the contamination of poultry products (meat, eggs), hence creating possible health risks to consumers. To guarantee precise, dependable, and regulatory-compliant measurement of these pollutants, analytical techniques must exhibit high sensitivity, specificity, and repeatability. Assessing these methods is essential for establishing their suitability in routine monitoring, maintaining result consistency, and validating innovative approaches against established gold-standard methodologies.

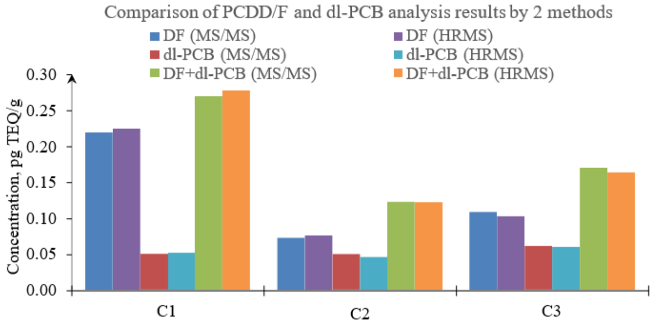

Figure 2. Comparison of analytical results for determining PCDD/PCDF and dl-PCB concentrations in chicken feed samples using two methods

The Bland-Altman plot (Figure 3) demonstrates a strong agreement between GC-MS/MS and HRGC/HRMS methods for determining PCDD/PCDF and DL-PCB in chicken feed samples. Most data points lie close to the mean difference line and within the 95% limits of agreement, indicating minimal bias and good consistency across concentrations. There is no clear proportional bias, and the very high Pearson correlation coefficient (r = 0.997) further supports the similarity between the two methods. These results suggest that GC-MS/MS provides comparable performance to HRGC/HRMS and can be reliably used for routine analysis. The Pearson correlation coefficient (r) of 0.997 indicates a very great connection between the two methodologies, signifying that their results are nearly identical.

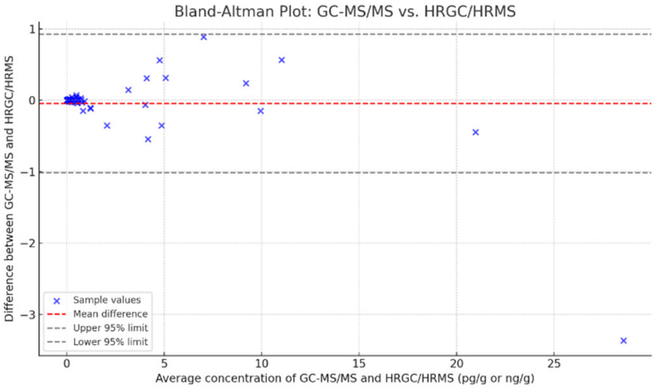

Figure 3. Bland-Altman plots of two GC-MS/MS and HRGC/HRMS analyses for determination of PCDD/PCDF and DL-PCB for three chicken feed samples

HRMS is the pinnacle of dioxin and furan analysis, offering unparalleled sensitivity, accuracy, and resolution. Nonetheless, GC-MS/MS is becoming a feasible option owing to its reduced cost and expedited processing time; yet, it may not consistently achieve the sensitivity of HRMS in detecting ultra-trace levels.

Table 3. Comparison of GC-MS/MS and HRMS in chicken feed analysis

Parameter	GC-MS/MS	HRMS
Sensitivity	High, but may struggle with ultra-trace levels	Extremely high, capable of detecting ultra-trace contaminants
Selectivity	High, but may have interferences in complex matrices	Excellent due to ultra-high mass resolution
Regulatory Acceptance	Emerging as an alternative method	Gold standard for dioxin analysis
Quantification Accuracy	Good, but susceptible to matrix effects	Highly accurate and precise
Instrument Cost & Complexity	Lower cost, easier to operate	Expensive, requires highly trained personnel

The comparison between GC-MS/MS and HRMS showed strong agreement, with most congeners exhibiting low relative percent differences (RPD < 10%). A few compounds, such as 2,3,4,7,8-PeCDF (C2: 19.4%) and OCDD (C1: 7.2%), showed higher RPDs, indicating minor methodological discrepancies. TEQ values from both methods remained within an acceptable RPD range (2.5 - 5.2%), supporting the reliability of GC-MS/MS for regulatory screening. While HRMS remains the preferred choice for confirmatory analysis and ultra-trace detection, GC-MS/MS offers a cost-effective alternative for routine monitoring. Method refinement may be needed if significant differences arise.

4. CONCLUSION

This study evaluated the quantification of PCDDs, PCDFs, and dl-PCBs in chicken feed using GC-MS/MS and HRGC/HRMS, focusing on analytical performance and comparability. Results showed strong agreement between methods, with most congeners having low relative percent differences (RPD < 10%) and TEQ values differing by only 2.5 - 5.2%, supporting GC-MS/MS as a reliable alternative for routine screening. Although some higher RPDs (> 10%) suggest minor variability due to matrix effects or sensitivity differences, the Bland-Altman plot confirmed high agreement (r = 0.997) with negligible bias. GC-MS/MS is well-suited for rapid, cost-effective screening, while HRGC/HRMS remains essential for confirmatory and regulatory analysis requiring greater sensitivity and legal defensibility. Future work should focus on refining GC-MS/MS calibration and expanding data to strengthen its role in dioxin and dl-PCB monitoring.

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