SHIMADZU

Determination of Dioxin in Food by GC-MS/MS Coupled with Boosted Efficiency Ion Source (BEIS)

Yin Ge¹, Tian Feifei², Fan Jun¹, Takakura Masato³, Tanaka Koki³, Kuhn Eberhardt⁴ Luo Dan⁴, Huang Taohong¹ 1 Shimadzu (China) Corporation. 1, No. 180 Yizhou Road, Xuhui District, Shanghai, China, P/C: 200233.

1. Overview

A boosted efficiency ion source (BEIS) with optimized method was applied for determination the trace level of PCDD/Fs in food by GCMS-TQ8050 NX. The TEQs from GCMS-TQ8050 NX are in good agreement with those consensus values.

2. Introduction

Dioxin contains 75 congeners of polychlorinated dibenzo-*p*-dioxins (PCDD, and 135 congeners of polychlorinated dibenzofurans (PCDFs). Due to persistency, bioaccumulation, and adverse effect to biotas, PCDD/Fs have attracted widespread concern. Determination of PCDD/Fs in food is challenging due to high demand of sensitivity and selective of the instrument. For a long time, gas chromatography coupled with magnetic mass spectrometry (GC-HRMS) has been used as the gold standard for dioxin analysis. In 2014, GC-MS/MS has also been included as confirmatory method for dioxin analysis by EU committee. In the present study, we applied GCMS-TQ8050 NX coupled with boosted efficiency ion source (BEIS) for dioxin analyses. The performance of the instrument was evaluated by low standard solutions and food samples.



Figure 1 Structure of PCDDs and PCDFs

3. Methods

PCDD/Fs standards and ¹³C-labeled isotope internal standards were purchased from Wellington Laboratories. The CSL level was diluted 10-fold and 5-fold by nnonane, respectively, to prepare CSLQ (0.01 pg/µL for TCDD/F) and CSLQx2. In parallel, CSL-CS3 (20µL) were transferred to the vial to set up the calibration points.

The food samples were pretreated according to EPA-1613B. In brief, pre-weighted fresh sample was extracted after spiking surrogate standard. The lipid content was determined gravimetrically. Further clean-up was performed on multi-layer silica gel column, basic alumina column and carbon column, respectively. The PCDD/Fs fraction was eluted with toluene to separate from other legacy POPs. Prior to instrumental analysis, the samples were evaporated till dryness and spiked with volumetric standard.

Instrument

GCMS-TQ8050 NX triple quadruple gas chromatography mass spectrometer coupled with BEIS (Shimadzu, Japan)



Figure 2 GCMS-TQ8050 NX equipped with BEIS

Instrumental parameters Column: DB-5 MS (60m x 0.25mm x 0.25µm) Column oven program: 120°C(1min) 43°C/min 220°C (15min) Flow control mode: Constant flow Column flow: 1.5 mL/min Sampling time: 4 min Injection volume: 2 µL Ionization mode: EI (70 eV)Ion source Temp: 230°C Interface Temp: 300°C CID pressure: 150 kPa Solvent cut time: 17 min Detector voltage: 1.8kV (A Tuning mode: High sensit Acq. mode: MRM, inform Loop time: 1.4 s

4. Results

The TIC diagram of the standard solution is shown in Figure 1, and the information on retention time and transition ions of each compound is shown in Table 1.





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2.3°C/min 250°C 0.9°C/min 260°C 20°C/min 310°C(9 min)
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Absolute)	
ivity	
mation on transition ions was shown in 7	Table 1

4-1. Total ion current (TIC) of PCDD/Fs

Figure 3. Mass chromatogram of PCDD / Fs (EPA 1613-CS3). The peak number corresponds to the compound number in Table 1.

Table 1. Retention time and transition ions for PCDD /	/ Fs h
labeled isotope internal standar	ds

Peak no (#) Compound time (min) Target transition CE (V) ions Reference transition ions (V) 1 2,3,7,8-TCDD 25.25 319.90>256.90 25 321.90>258.90 25 2 1,2,3,7,8-HeCDD 40.29 389.80>326.90 25 391.80>328.90 25 3 1,2,3,6,7,8-HxCDD 40.53 389.80>326.90 25 391.80>328.90 25 5 1,2,3,4,6,7,8-HxCDD 41.15 389.80>326.90 25 391.80>328.90 25 6 1,2,3,4,6,7,8-HxCDD 41.15 389.80>326.90 25 450.5362.80 25 7 OCDD 49.28 457.70>394.70 25 459.70>396.70 25 8 2,3,7,8-TCDF 24.18 303.90>276.90 34 307.90>274.90 34 10 2,3,4,7,8-HxCDF 38.08 373.80>310.90 34 375.80>312.90 34 12 1,2,3,6,7,8-HxCDF 38.88 373.80>310.90 34 375.80>312.90 34 13 2,3,4,6,7,8-HxCDF 38.80 373.80>							
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12.3,7,8-PeCDD22.25319,90-256,9025321,30-250,902521,2,3,4,7,8-HxCDD32.72355,90-229,9025391,80-328,902531,2,3,4,7,8-HxCDD40.29389,80-326,9025391,80-328,902541,2,3,6,7,8-HxCDD41.15389,80-326,9025391,80-328,902551,2,3,4,6,7,8-HpCDD45.85423,80-360,8025425,80-362,802561,2,3,4,6,7,8-HpCDD45.85423,80-360,8025459,70-396,702582,3,7,8-TCDF24.18303,90-276,9034305,90-242,903491,2,3,7,8-PeCDF30,46339,90-276,9034337,90-274,9034102,3,4,7,8-PeCDF38,08373,80-310,9034375,80-312,9034121,2,3,6,7,8-HxCDF38,38373,80-310,9034375,80-312,9034132,3,4,6,7,8-HpCDF41.85373,80-341,9034375,80-341,29034141,2,3,7,8,9-HxCDF41.85373,80-341,9034375,80-341,29034151,2,3,4,6,7,8-HpCDF46.36407,80-344,8034409,80-346,8034161,2,3,4,7,8,9-HpCDF46.36407,80-344,8034409,80-346,8034161,2,3,4,7,8,9-HpCDF40.51401,80-337,9025333,90-270,0025201,2,3,7,8,7-HCDD- ¹³ C1225,23331,90-268,0025333,90-270,0025211,2,	no (#)	2 2 7 0 TODD	time (min)		05	transition ions	(V) 25
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41,2,3,0,7,8-TACDD40.53389.80>326.9025391.80>328.902551,2,3,7,8,9-HxCDD41.15389.80>326.9025391.80>328.902561,2,3,4,6,7,8-HpCDD49.28457.70>394.7025459.70>396.70257OCDD49.28457.70>394.7025459.70>396.702582,3,7,8-TCDF30.46339.90>276.9034337.90>274.9034102,3,4,7,8-PeCDF32.12339.90>276.9034337.90>274.9034111,2,3,4,7,8-HxCDF38.08373.80>310.9034375.80>312.9034121,2,3,6,7,8-HxCDF38.08373.80>310.9034375.80>312.9034132,3,4,6,7,8-HxCDF39.80373.80>310.9034375.80>312.9034141,2,3,7,8,9-HxCDF41.85373.80>310.9034375.80>312.9034151,2,3,4,6,7,8-HpCDF46.36407.80>344.8034409.80>346.8034161,2,3,4,7,8,9-HpCDF46.36407.80>344.8034409.80>346.803417OCDF49.45441.80>378.8034433.90>270.0025201,2,3,7,8-PeCDD- ¹³ C1222.23331.90>268.0025333.90>270.0025211,2,3,4,7,8-HxCDD- ¹³ C1232.71367.90>337.9025399.90>335.9025221,2,3,7,8,78-HxCDD- ¹³ C1240.26401.80>337.9025399.90>335.9025231,2,3,4,6,7	3	1,2,3,4,7,8-HXCDD	40.29	389.80>326.90	25	391.80>328.90	25
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111,2,3,4,7,8-HxCDF38.08373.80>310.9034375.80>312.9034121,2,3,6,7,8-HxCDF38.38373.80>310.9034375.80>312.9034132,3,4,6,7,8-HxCDF39.80373.80>310.9034375.80>312.9034141,2,3,7,8,9-HxCDF41.85373.80>310.9034375.80>312.9034151,2,3,4,6,7,8-HpCDF44.61407.80>344.8034409.80>346.8034161,2,3,4,7,8,9-HpCDF46.36407.80>344.8034409.80>346.803417OCDF49.45441.80>378.8034443.80>380.8034181,2,3,4-TCDD- ¹³ C1225.23331.90>268.0025333.90>270.0025201,2,3,7,8-PeCDD- ¹³ C1222.71367.90>303.9025365.90>301.9025211,2,3,4,7,8-HxCDD- ¹³ C1240.26401.80>337.9025399.90>335.9025221,2,3,6,7,8-HxCDD- ¹³ C1240.51401.80>337.9025399.90>335.9025231,2,3,7,8,9-HxCDD- ¹³ C1241.14401.80>37.9025399.90>335.9025241,2,3,4,6,7,8-HxCDD- ¹³ C1245.85435.80>371.8025437.80>373.802525OCDD- ¹³ C1249.28469.80>405.8025471.80>407.8025262,3,7,8-FeCDF- ¹³ C1230.46351.90>287.9034349.90>285.9034271,2,3,7,8-PeCDF- ¹³ C1234.06351.90>287.9034349.90>285.90 <td>10</td> <td>2,3,4,7,8-PeCDF</td> <td>32.12</td> <td>339.90>276.90</td> <td>34</td> <td>337.90>274.90</td> <td>34</td>	10	2,3,4,7,8-PeCDF	32.12	339.90>276.90	34	337.90>274.90	34
121,2,3,6,7,8+RCDF38.38373.80>310.9034375.80>312.9034132,3,4,6,7,8+RCDF39.80373.80>310.9034375.80>312.9034141,2,3,7,8,9-HxCDF41.85373.80>310.9034375.80>312.9034151,2,3,4,6,7,8-HpCDF44.61407.80>344.8034409.80>346.8034161,2,3,4,7,8,9-HpCDF46.36407.80>344.8034409.80>346.803417OCDF49.45441.80>378.8034443.80>380.8034181,2,3,4-TCDD- ¹³ C1225.23331.90>268.0025333.90>270.0025201,2,3,7,8-PeCDD- ¹³ C1232.71367.90>303.9025365.90>301.9025211,2,3,4,7,8-HxCDD- ¹³ C1240.26401.80>337.9025399.90>335.9025221,2,3,6,7,8-HxCDD- ¹³ C1240.51401.80>337.9025399.90>335.9025231,2,3,7,8,9-HxCDD- ¹³ C1241.14401.80>337.9025399.90>335.9025241,2,3,4,6,7,8-HpCDD- ¹³ C1241.14401.80>337.9025399.90>335.902525OCDD- ¹³ C1249.28469.80>405.8025471.80>407.8025262,3,7,8-PeCDF- ¹³ C1244.17315.90>287.9034349.90>285.9034271,2,3,4,7,8-HxCDF- ¹³ C1232.11351.90>287.9034349.90>285.9034282,3,4,7,8-HxCDF- ¹³ C1238.87385.80>321.9034387.80>323	11	1,2,3,4,7,8-HxCDF	38.08	373.80>310.90	34	375.80>312.90	34
13 $2,3,4,6,7,8$ -HxCDF $39,80$ $373,80>310.90$ 34 $375,80>312.90$ 34 14 $1,2,3,7,8,9$ -HxCDF 41.85 $373,80>310.90$ 34 $375,80>312.90$ 34 15 $1,2,3,4,6,7,8$ -HpCDF 44.61 $407,80>344.80$ 34 $409,80>346.80$ 34 16 $1,2,3,4,7,8,9$ -HpCDF 46.36 $407,80>344.80$ 34 $409,80>346.80$ 34 17OCDF 49.45 $441.80>378.80$ 34 $443.80>380.808$ 34 18 $1,2,3,4$ -TCDD- $^{13}C12$ 25.23 $331.90>268.00$ 25 $333.90>270.00$ 25 20 $1,2,3,7,8$ -PeCDD- $^{13}C12$ 32.71 $367.90>303.90$ 25 $365.90>301.90$ 25 21 $1,2,3,4,7,8$ -HxCDD- $^{13}C12$ 40.26 $401.80>337.90$ 25 $399.90>335.90$ 25 22 $1,2,3,7,8,9$ -HxCDD- $^{13}C12$ 40.51 $401.80>337.90$ 25 $399.90>335.90$ 25 23 $1,2,3,7,8,9$ -HxCDD- $^{13}C12$ 41.14 $401.80>337.90$ 25 $399.90>335.90$ 25 24 $1,2,3,4,6,7,8$ -HpCDD- $^{13}C12$ 45.85 $435.80>371.80$ 25 $437.80>373.80$ 25 25OCDD- $^{13}C12$ 49.28 $469.80>405.80$ 25 $471.80>407.80$ 25 26 $2,3,7,8$ -TCDF- $^{13}C12$ 24.17 $315.90>287.90$ 34 $349.90>285.90$ 34 27 $1,2,3,7,8$ -PeCDF- $^{13}C12$ 32.11 $351.90>287.90$ 34 $349.90>285.90$ 34 28 $2,3,4,7,8$ -HxCDF- 13	12	1,2,3,6,7,8-HxCDF	38.38	373.80>310.90	34	375.80>312.90	34
14 $1,2,3,7,8,9$ -HxCDF 41.85 $373.80>310.90$ 34 $375.80>312.90$ 34 15 $1,2,3,4,6,7,8$ -HpCDF 44.61 $407.80>344.80$ 34 $409.80>346.80$ 34 16 $1,2,3,4,7,8,9$ -HpCDF 46.36 $407.80>344.80$ 34 $409.80>346.80$ 34 17OCDF 49.45 $441.80>378.80$ 34 $443.80>380.80$ 34 18 $1,2,3,4$ -TCDD- $^{13}C12$ 24.49 $331.90>268.00$ 25 $333.90>270.00$ 25 19 $2,3,7,8$ -TCDD- $^{13}C12$ 25.23 $331.90>268.00$ 25 $333.90>270.00$ 25 20 $1,2,3,7,8$ -PeCDD- $^{13}C12$ 25.23 $331.90>268.00$ 25 $339.90>270.00$ 25 21 $1,2,3,4,7,8$ -PeCDD- $^{13}C12$ 40.26 $401.80>337.90$ 25 $399.90>335.90$ 25 22 $1,2,3,7,8,9$ -HxCDD- $^{13}C12$ 40.51 $401.80>337.90$ 25 $399.90>335.90$ 25 23 $1,2,3,7,8,9$ -HxCDD- $^{13}C12$ 41.14 $401.80>337.90$ 25 $399.90>335.90$ 25 24 $1,2,3,4,6,7,8$ -HpCDD- $^{13}C12$ 45.85 $435.80>371.80$ 25 $471.80>407.80$ 25 25OCDD- $^{13}C12$ 49.28 $469.80>405.80$ 25 $471.80>407.80$ 25 26 $2,3,7,8-PeCDF-^{13}C12$ 30.46 $351.90>287.90$ 34 $349.90>285.90$ 34 27 $1,2,3,7,8-PeCDF-^{13}C12$ 30.46 $351.90>287.90$ 34 $349.90>285.90$ 34 28 $2,3,4,7,8-PeCDF-^{13}$	13	2,3,4,6,7,8-HxCDF	39.80	373.80>310.90	34	375.80>312.90	34
15 $1,2,3,4,6,7,8-HpCDF$ 44.61 $407.80>344.80$ 34 $409.80>346.80$ 34 16 $1,2,3,4,7,8,9-HpCDF$ 46.36 $407.80>344.80$ 34 $409.80>346.80$ 34 17OCDF 49.45 $441.80>378.80$ 34 $443.80>380.80$ 34 18 $1,2,3,4-TCDD-{}^{13}C12$ 24.49 $331.90>268.00$ 25 $333.90>270.00$ 25 19 $2,3,7,8-TCDD-{}^{13}C12$ 25.23 $331.90>268.00$ 25 $333.90>270.00$ 25 20 $1,2,3,7,8-PeCDD-{}^{13}C12$ 32.71 $367.90>303.90$ 25 $365.90>301.90$ 25 21 $1,2,3,4,7,8-HxCDD-{}^{13}C12$ 40.26 $401.80>337.90$ 25 $399.90>335.90$ 25 22 $1,2,3,7,8-HxCDD-{}^{13}C12$ 40.51 $401.80>337.90$ 25 $399.90>335.90$ 25 23 $1,2,3,7,8-HxCDD-{}^{13}C12$ 41.14 $401.80>337.90$ 25 $399.90>335.90$ 25 24 $1,2,3,4,6,7,8-HpCDD-{}^{13}C12$ 45.85 $435.80>371.80$ 25 $471.80>407.80$ 25 25OCDD-{}^{13}C12 24.17 $315.90>251.90$ 34 $349.90>285.90$ 34 26 $2,3,7,8-PeCDF-{}^{13}C12$ 30.46 $351.90>287.90$ 34 $349.90>285.90$ 34 27 $1,2,3,7,8-PeCDF-{}^{13}C12$ 30.46 $351.90>287.90$ 34 $349.90>285.90$ 34 28 $2,3,4,7,8-HxCDF-{}^{13}C12$ 38.08 $385.80>321.90$ 34 $387.80>323.90$ 34 30 $1,2,3,6,7,8$	14	1,2,3,7,8,9-HxCDF	41.85	373.80>310.90	34	375.80>312.90	34
16 $1,2,3,4,7,8,9-HpCDF$ 46.36 $407.80>344.80$ 34 $409.80>346.80$ 3417OCDF 49.45 $441.80>378.80$ 34 $443.80>380.80$ 3418 $1,2,3,4-TCDD^{-13}C12$ 24.49 $331.90>268.00$ 25 $333.90>270.00$ 25 19 $2,3,7,8-TCDD^{-13}C12$ 25.23 $331.90>268.00$ 25 $333.90>270.00$ 25 20 $1,2,3,7,8-PeCDD^{-13}C12$ 32.71 $367.90>303.90$ 25 $365.90>301.90$ 25 21 $1,2,3,4,7,8-HxCDD^{-13}C12$ 40.26 $401.80>337.90$ 25 $399.90>335.90$ 25 22 $1,2,3,6,7,8-HxCDD^{-13}C12$ 40.51 $401.80>337.90$ 25 $399.90>335.90$ 25 23 $1,2,3,7,8,9-HxCDD^{-13}C12$ 41.14 $401.80>337.90$ 25 $399.90>335.90$ 25 24 $1,2,3,4,6,7,8-HpCDD^{-13}C12$ 45.85 $435.80>371.80$ 25 $437.80>373.80$ 25 25OCDD^{-13}C12 49.28 $469.80>405.80$ 25 $471.80>407.80$ 25 26 $2,3,7,8-PeCDF^{-13}C12$ 24.17 $315.90>251.90$ 34 $349.90>285.90$ 34 27 $1,2,3,7,8-PeCDF^{-13}C12$ 32.11 $351.90>287.90$ 34 $349.90>285.90$ 34 28 $2,3,4,7,8-PeCDF^{-13}C12$ 38.08 $385.80>321.90$ 34 $387.80>323.90$ 34 30 $1,2,3,6,7,8-HxCDF^{-13}C12$ 38.37 $385.80>321.90$ 34 $387.80>323.90$ 34 31 $2,3,4,6,7,8-HxCDF^{-13}C12$ <	15	1,2,3,4,6,7,8-HpCDF	44.61	407.80>344.80	34	409.80>346.80	34
17OCDF49.45441.80>378.8034443.80>380.803418 $1,2,3,4$ -TCDD- 13 C1224.49 $331.90>268.00$ 25 $333.90>270.00$ 2519 $2,3,7,8$ -TCDD- 13 C1225.23 $331.90>268.00$ 25 $333.90>270.00$ 2520 $1,2,3,7,8$ -PeCDD- 13 C1232.71 $367.90>303.90$ 25 $365.90>301.90$ 2521 $1,2,3,4,7,8$ -HxCDD- 13 C1240.26 $401.80>337.90$ 25 $399.90>335.90$ 2522 $1,2,3,6,7,8$ -HxCDD- 13 C1240.51 $401.80>337.90$ 25 $399.90>335.90$ 2523 $1,2,3,7,8,9$ -HxCDD- 13 C1241.14 $401.80>337.90$ 25 $399.90>335.90$ 2524 $1,2,3,4,6,7,8$ -HpCDD- 13 C1245.85 $435.80>371.80$ 25 $437.80>373.80$ 2525OCDD- 13 C1249.28 $469.80>405.80$ 25 $471.80>407.80$ 2526 $2,3,7,8$ -TCDF- 13 C1230.46351.90>287.9034349.90>285.903427 $1,2,3,7,8$ -PeCDF- 13 C1230.46351.90>287.9034349.90>285.903428 $2,3,4,7,8$ -HxCDF- 13 C1238.08385.80>321.9034387.80>323.903430 $1,2,3,6,7,8$ -HxCDF- 13 C1239.78385.80>321.9034387.80>323.903431 $2,3,4,6,7,8$ -HxCDF- 13 C1239.78385.80>321.9034387.80>323.903432 $1,2,3,7,8,9$ -HxCDF- 13 C1241.83385.80>321.9034387.80>323.90<	16	1,2,3,4,7,8,9-HpCDF	46.36	407.80>344.80	34	409.80>346.80	34
18 $1,2,3,4$ -TCDD- 13 C12 24.49 $331.90>268.00$ 25 $333.90>270.00$ 2519 $2,3,7,8$ -TCDD- 13 C12 25.23 $331.90>268.00$ 25 $333.90>270.00$ 2520 $1,2,3,7,8$ -PeCDD- 13 C12 32.71 $367.90>303.90$ 25 $365.90>301.90$ 2521 $1,2,3,4,7,8$ -HxCDD- 13 C12 40.26 $401.80>337.90$ 25 $399.90>335.90$ 2522 $1,2,3,6,7,8$ -HxCDD- 13 C12 40.51 $401.80>337.90$ 25 $399.90>335.90$ 2523 $1,2,3,7,8,9$ -HxCDD- 13 C12 41.14 $401.80>337.90$ 25 $399.90>335.90$ 2524 $1,2,3,4,6,7,8$ -HpCDD- 13 C12 45.85 $435.80>371.80$ 25 $437.80>373.80$ 2525OCDD- 13 C12 49.28 $469.80>405.80$ 25 $471.80>407.80$ 2526 $2,3,7,8$ -TCDF- 13 C12 24.17 $315.90>251.90$ 34 $317.90>253.90$ 34 27 $1,2,3,7,8$ -PeCDF- 13 C12 30.46 $351.90>287.90$ 34 $349.90>285.90$ 34 28 $2,3,4,7,8$ -HxCDF- 13 C12 38.08 $385.80>321.90$ 34 $387.80>323.90$ 34 30 $1,2,3,6,7,8$ -HxCDF- 13 C12 39.78 $385.80>321.90$ 34 $387.80>323.90$ 34 31 $2,3,4,6,7,8$ -HxCDF- 13 C12 39.78 $385.80>321.90$ 34 $387.80>323.90$ 34 31 $2,3,4,6,7,8$ -HxCDF- 13 C12 41.83 $385.80>321.90$ 34 $387.80>323.90$ 34 32 <t< td=""><td>17</td><td>OCDF</td><td>49.45</td><td>441.80>378.80</td><td>34</td><td>443.80>380.80</td><td>34</td></t<>	17	OCDF	49.45	441.80>378.80	34	443.80>380.80	34
19 $2,3,7,8$ -TCDD- 13 C12 25.23 $331.90>268.00$ 25 $333.90>270.00$ 25 20 $1,2,3,7,8$ -PeCDD- 13 C12 32.71 $367.90>303.90$ 25 $365.90>301.90$ 25 21 $1,2,3,4,7,8$ -HxCDD- 13 C12 40.26 $401.80>337.90$ 25 $399.90>335.90$ 25 22 $1,2,3,6,7,8$ -HxCDD- 13 C12 40.51 $401.80>337.90$ 25 $399.90>335.90$ 25 23 $1,2,3,7,8,9$ -HxCDD- 13 C12 41.14 $401.80>337.90$ 25 $399.90>335.90$ 25 24 $1,2,3,4,6,7,8$ -HpCDD- 13 C12 45.85 $435.80>371.80$ 25 $437.80>373.80$ 25 25OCDD- 13 C12 49.28 $469.80>405.80$ 25 $471.80>407.80$ 25 26 $2,3,7,8$ -TCDF- 13 C12 24.17 $315.90>251.90$ 34 $317.90>253.90$ 34 27 $1,2,3,7,8$ -PeCDF- 13 C12 24.17 $315.90>287.90$ 34 $349.90>285.90$ 34 28 $2,3,4,7,8$ -PeCDF- 13 C12 32.11 $351.90>287.90$ 34 $349.90>285.90$ 34 29 $1,2,3,4,7,8$ -HxCDF- 13 C12 38.37 $385.80>321.90$ 34 $387.80>323.90$ 34 30 $1,2,3,6,7,8$ -HxCDF- 13 C12 39.78 $385.80>321.90$ 34 $387.80>323.90$ 34 31 $2,3,4,6,7,8$ -HxCDF- 13 C12 39.78 $385.80>321.90$ 34 $387.80>323.90$ 34 31 $2,3,4,6,7,8$ -HxCDF- 13 C12 41.83 $385.80>321.90$ 34 $387.80>323.90$ <td>18</td> <td>1,2,3,4-TCDD-¹³C12</td> <td>24.49</td> <td>331.90>268.00</td> <td>25</td> <td>333.90>270.00</td> <td>25</td>	18	1,2,3,4-TCDD- ¹³ C12	24.49	331.90>268.00	25	333.90>270.00	25
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	19	2,3,7,8-TCDD- ¹³ C12	25.23	331.90>268.00	25	333.90>270.00	25
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	20	1,2,3,7,8-PeCDD- ¹³ C12	32.71	367.90>303.90	25	365.90>301.90	25
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	21	1,2,3,4,7,8-HxCDD- ¹³ C12	40.26	401.80>337.90	25	399.90>335.90	25
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	22	1,2,3,6,7,8-HxCDD- ¹³ C12	40.51	401.80>337.90	25	399.90>335.90	25
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	23	1,2,3,7,8,9-HxCDD- ¹³ C12	41.14	401.80>337.90	25	399.90>335.90	25
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	24	1,2,3,4,6,7,8-HpCDD- ¹³ C12	45.85	435.80>371.80	25	437.80>373.80	25
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	25	OCDD-13C12	49.28	469.80>405.80	25	471.80>407.80	25
271,2,3,7,8-PeCDF-13C1230.46351.90>287.9034349.90>285.9034282,3,4,7,8-PeCDF-13C1232.11351.90>287.9034349.90>285.9034291,2,3,4,7,8-HxCDF-13C1238.08385.80>321.9034387.80>323.9034301,2,3,6,7,8-HxCDF-13C1238.37385.80>321.9034387.80>323.9034312,3,4,6,7,8-HxCDF-13C1239.78385.80>321.9034387.80>323.9034321,2,3,7,8,9-HxCDF-13C1241.83385.80>321.9034387.80>323.9034331,2,3,4,6,7,8-HpCDF-13C1241.62419.80>355.9034421.80>357.9034341,2,3,4,7,8,9-HpCDF-13C1246.36419.80>355.9034421.80>357.9034	26	2,3,7,8-TCDF- ¹³ C12	24.17	315.90>251.90	34	317.90>253.90	34
282,3,4,7,8-PeCDF-13C1232.11351.90>287.9034349.90>285.9034291,2,3,4,7,8-HxCDF-13C1238.08385.80>321.9034387.80>323.9034301,2,3,6,7,8-HxCDF-13C1238.37385.80>321.9034387.80>323.9034312,3,4,6,7,8-HxCDF-13C1239.78385.80>321.9034387.80>323.9034321,2,3,7,8,9-HxCDF-13C1241.83385.80>321.9034387.80>323.9034331,2,3,4,6,7,8-HpCDF-13C1244.62419.80>355.9034421.80>357.9034341,2,3,4,7,8,9-HpCDF-13C1246.36419.80>355.9034421.80>357.9034	27	1,2,3,7,8-PeCDF- ¹³ C12	30.46	351.90>287.90	34	349.90>285.90	34
291,2,3,4,7,8-HxCDF-13C1238.08385.80>321.9034387.80>323.9034301,2,3,6,7,8-HxCDF-13C1238.37385.80>321.9034387.80>323.9034312,3,4,6,7,8-HxCDF-13C1239.78385.80>321.9034387.80>323.9034321,2,3,7,8,9-HxCDF-13C1241.83385.80>321.9034387.80>323.9034331,2,3,4,6,7,8-HpCDF-13C1244.62419.80>355.9034421.80>357.9034341,2,3,4,7,8,9-HpCDF-13C1246.36419.80>355.9034421.80>357.9034	28	2,3,4,7,8-PeCDF- ¹³ C12	32.11	351.90>287.90	34	349.90>285.90	34
30 1,2,3,6,7,8-HxCDF- ¹³ C12 38.37 385.80>321.90 34 387.80>323.90 34 31 2,3,4,6,7,8-HxCDF- ¹³ C12 39.78 385.80>321.90 34 387.80>323.90 34 32 1,2,3,7,8,9-HxCDF- ¹³ C12 41.83 385.80>321.90 34 387.80>323.90 34 33 1,2,3,4,6,7,8-HpCDF- ¹³ C12 44.62 419.80>355.90 34 421.80>357.90 34 34 1,2,3,4,7,8,9-HpCDF- ¹³ C12 46.36 419.80>355.90 34 421.80>357.90 34	29	1,2,3,4,7,8-HxCDF- ¹³ C12	38.08	385.80>321.90	34	387.80>323.90	34
31 2,3,4,6,7,8-HxCDF- ¹³ C12 39.78 385.80>321.90 34 387.80>323.90 34 32 1,2,3,7,8,9-HxCDF- ¹³ C12 41.83 385.80>321.90 34 387.80>323.90 34 33 1,2,3,4,6,7,8-HpCDF- ¹³ C12 44.62 419.80>355.90 34 421.80>357.90 34 34 1,2,3,4,7,8,9-HpCDF- ¹³ C12 46.36 419.80>355.90 34 421.80>357.90 34	30	1,2,3,6,7,8-HxCDF- ¹³ C12	38.37	385.80>321.90	34	387.80>323.90	34
32 1,2,3,7,8,9-HxCDF- ¹³ C12 41.83 385.80>321.90 34 387.80>323.90 34 33 1,2,3,4,6,7,8-HpCDF- ¹³ C12 44.62 419.80>355.90 34 421.80>357.90 34 34 1,2,3,4,7,8,9-HpCDF- ¹³ C12 46.36 419.80>355.90 34 421.80>357.90 34	31	2,3,4,6,7,8-HxCDF- ¹³ C12	39.78	385.80>321.90	34	387.80>323.90	34
331,2,3,4,6,7,8-HpCDF-13C1244.62419.80>355.9034421.80>357.9034341,2,3,4,7,8,9-HpCDF-13C1246.36419.80>355.9034421.80>357.9034	32	1,2,3,7,8,9-HxCDF- ¹³ C12	41.83	385.80>321.90	34	387.80>323.90	34
34 1,2,3,4,7,8,9-HpCDF- ¹³ C12 46.36 419.80>355.90 34 421.80>357.90 34	33	1,2,3,4,6,7,8-HpCDF- ¹³ C12	44.62	419.80>355.90	34	421.80>357.90	34
	34	1,2,3,4,7,8,9-HpCDF- ¹³ C12	46.36	419.80>355.90	34	421.80>357.90	34

4-2. Relative response factors (RRFs) and calibration curve

The calibration curves and RRFs of represented PCDD/Fs are shown in Figure 4. The curve was composed of seven points, ranging from CSLQ to CS3 (e.g. for TCDD, the concentration ranges 0.01-10 ng/mL). The average RRFs were in the range of 0.91-1.39, and the relative standard deviations of the RRF of each component in the linear range were basically within 12%.



Figure 4 Representative calibration curve of PCDD/Fs

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4-3. Accuracy

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By using the average RRF obtained from the curve, we quantified CSLQx2 level, and further compared with the real concentration to evaluate the accuracy. The relative error is shown in Figure 5. In general, the relative error of each component was below 20%, indicating GCMS-TQ8050 NX have good accuracy at such low level.



Figure 5 relative error of quantitation CSLQx2 level

4-4. Real sample analysis

Several food samples covering various of food type provided by Norwegian Institute of Public Health (NIPH) was utilized for method validation. It was shown that the TEOs from GCMS-TQ8050 NX are in good agreement with those consensus value published by NIPH (Figure 6).



Figure 6 Comparison of TEQ between GCMS-TQ8050 NX and consensus value from NIPH

5. Conclusions

By using GCMS-TQ8050 NX coupled with an advanced ion source, a MRM method was established for determination of PCDD/Fs in food. The linearity, resolution, accuracy of standard is satisfied. The developed method was successful applied to real samples, and it was indicated that TEQ level by GCMS-TQ8050 NX has good consistency with the consensus value provided by NIPH.



