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

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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.

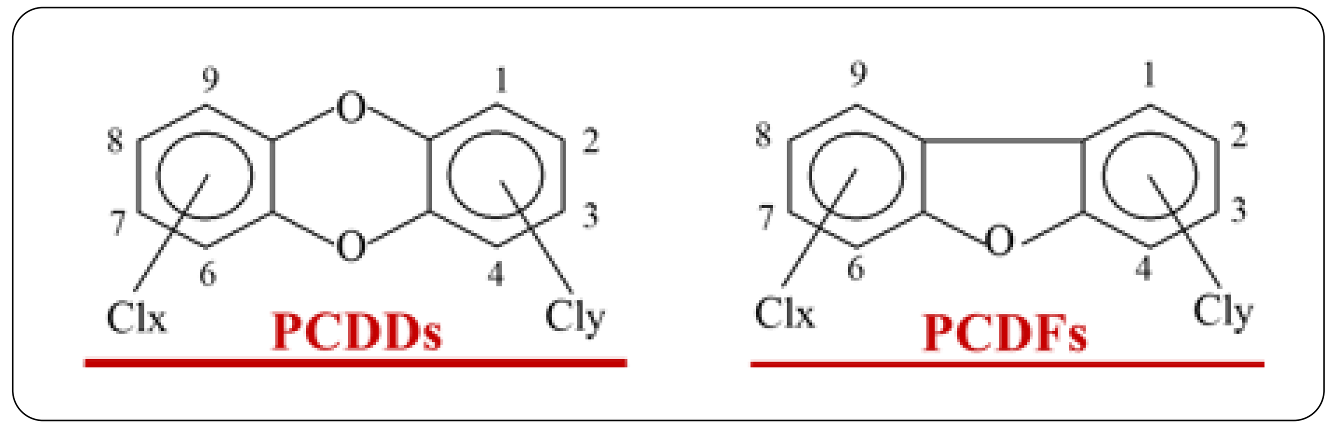

Figure 1 Structure of PCDDs and PCDFs

3. Methods

PCDD/Fs standards and ^{13}C-labeled isotope internal standards were purchased from Wellington Laboratories. The CSL level was diluted 10-fold and 5-fold by *n*-nonane, 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)

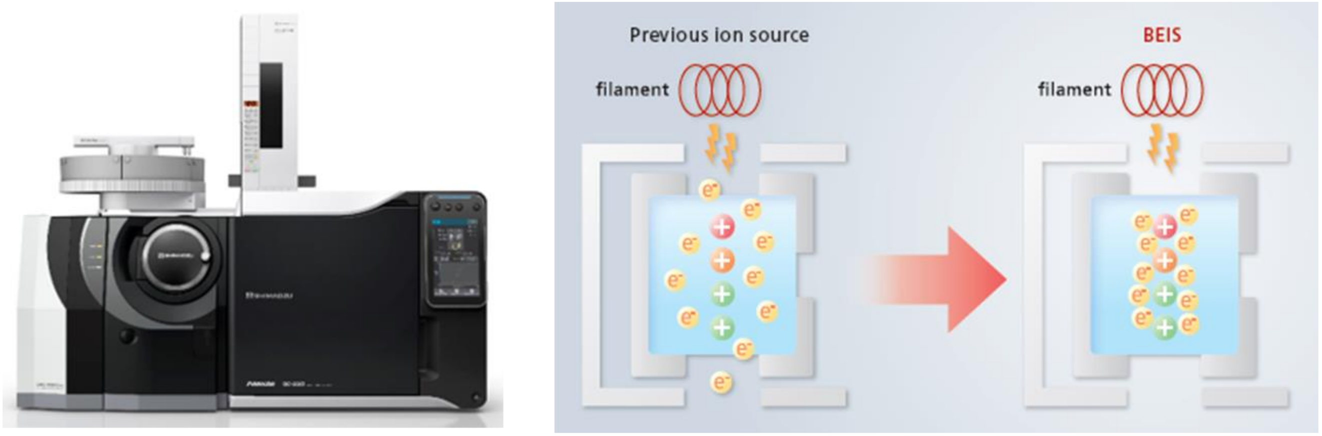

Figure 2 GCMS-TQ8050 NX equipped with BEIS

Instrumental parameters

Column: DB-5 MS (60m x 0.25mm x 0.25μm)
Column oven program：
120℃(1min)_43℃/min_220℃（15min）_2.3℃/min_250℃_0.9℃/min_260℃_20℃/min_310℃(9 min)
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℃
Interface Temp：300℃
CID pressure：150 kPa
Solvent cut time：17 min
Detector voltage：1.8kV (Absolute)
Tuning mode：High sensitivity
Acq. mode：MRM，information on transition ions was shown in Table 1
Loop time: 1.4 s

Table 1. Retention time and transition ions for PCDD / Fs homologues and 13C-labeled isotope internal standards

Peak no（#）	Compound	Retention time（min）	Target transition ions	CE（V）	Reference transition ions	CE（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-PeCDD	32.72	355.90>292.90	25	353.90>290.90	25
3	1,2,3,4,7,8-HxCDD	40.29	389.80>326.90	25	391.80>328.90	25
4	1,2,3,6,7,8-HxCDD	40.53	389.80>326.90	25	391.80>328.90	25
5	1,2,3,7,8,9- HxCDD	41.15	389.80>326.90	25	391.80>328.90	25
6	1,2,3,4,6,7,8-HpCDD	45.85	423.80>360.80	25	425.80>362.80	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>240.90	34	305.90>242.90	34
9	1,2,3,7,8-PeCDF	30.46	339.90>276.90	34	337.90>274.90	34
10	2,3,4,7,8-PeCDF	32.12	339.90>276.90	34	337.90>274.90	34
11	1,2,3,4,7,8-HxCDF	38.08	373.80>310.90	34	375.80>312.90	34
12	1,2,3,6,7,8-HxCDF	38.38	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
17	OCDF	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	1,2,3,6,7,8-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
25	OCDD-^{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	30.46	351.90>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	38.08	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	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

4. Results

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

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.

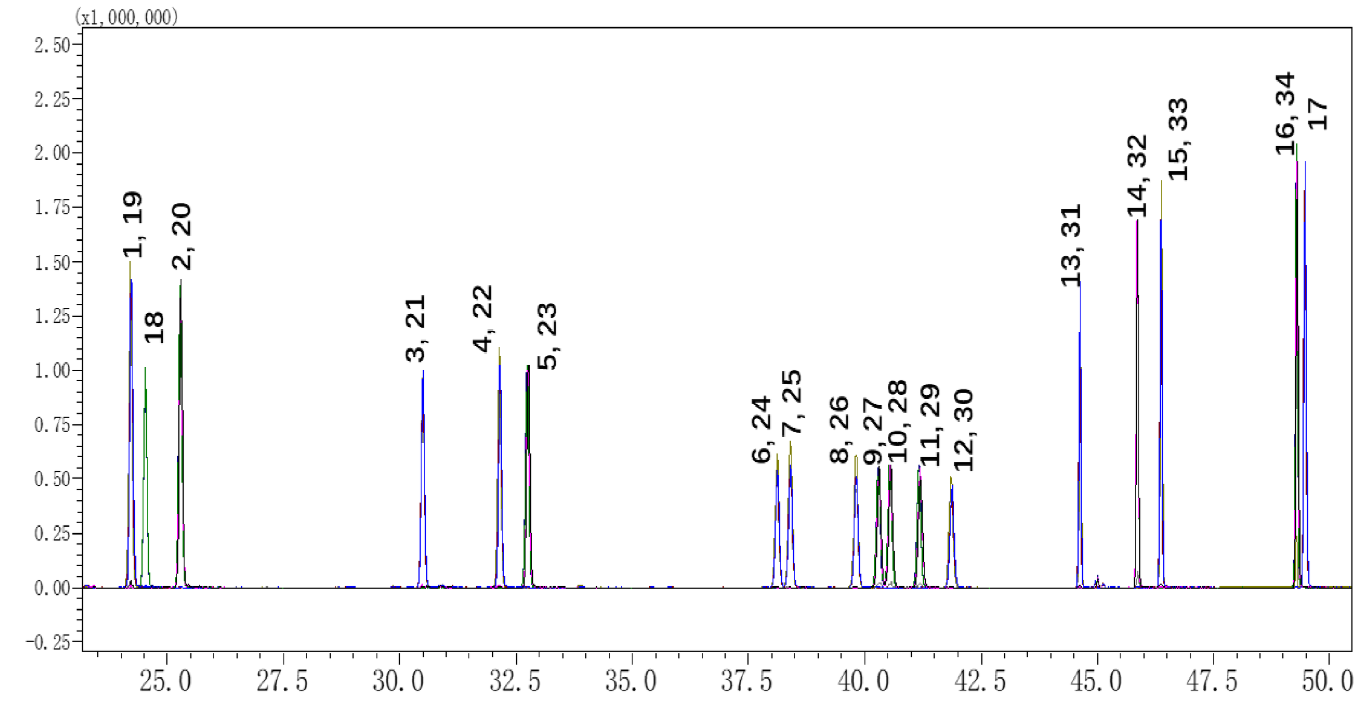

Figure 3. Mass chromatogram of PCDD / Fs (EPA 1613-CS3). The peak number corresponds to the compound number in Table 1.

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%.

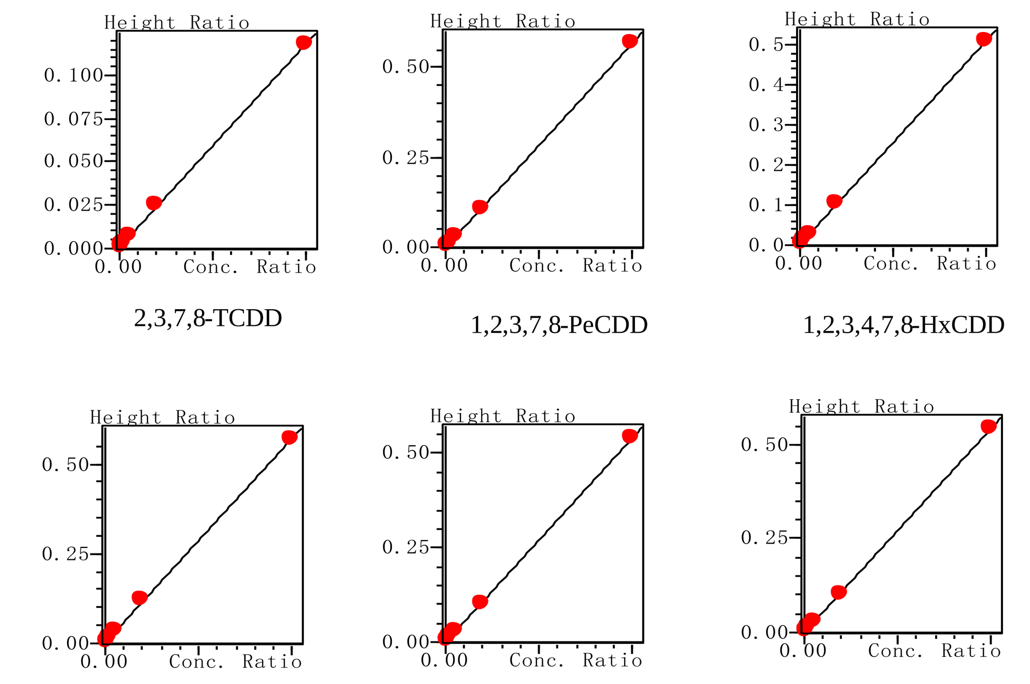

Figure 4 Representative calibration curve of PCDD/Fs

4-3. Accuracy

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.

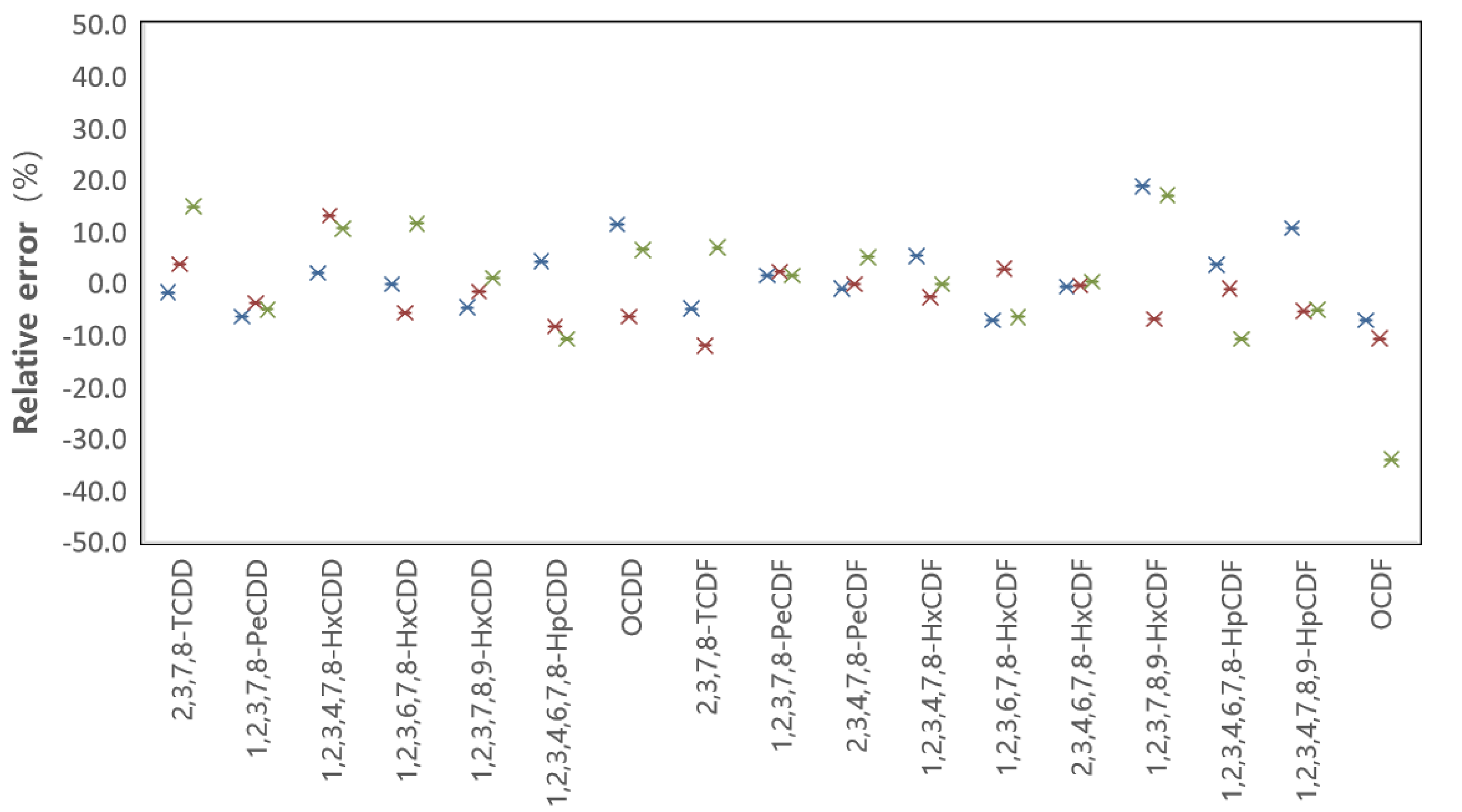

Figure 5 relative error of quantitation CSLQx2 level

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 TEQs from GCMS-TQ8050 NX are in good agreement with those consensus value published by NIPH (Figure 6).

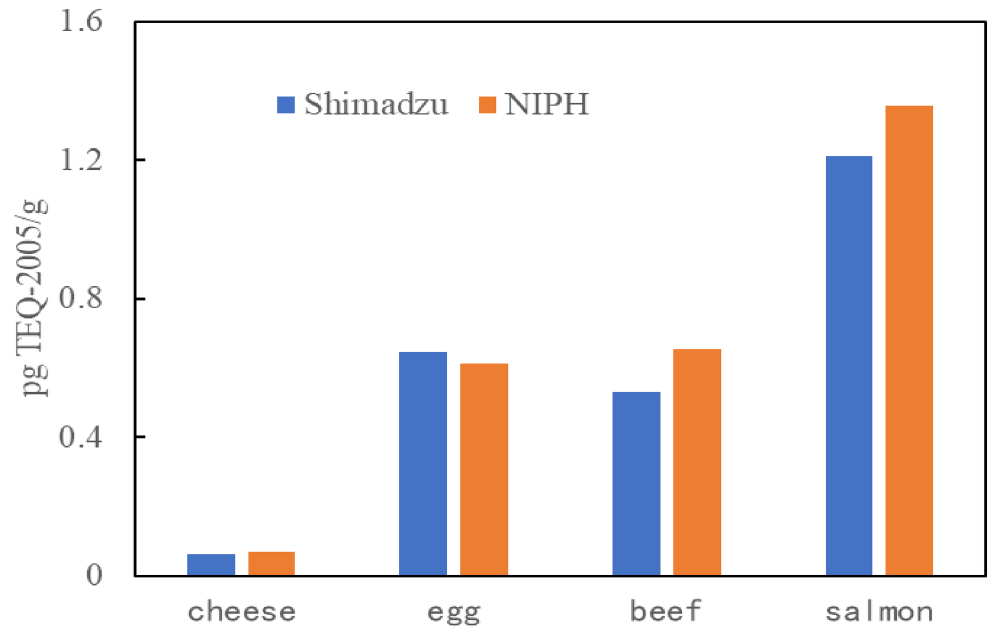

Figure 6 Comparison of TEQ between GCMS-TQ8050 NX and consensus value from NIPH

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.