Analysis of dioxins in food and feed by using New JMS-TQ4000GC and software "TQ-DioK"

Product used：Mass spectrometer(MS)

Dioxins are considered as persistent organic pollutants (POPS) due to their presence in the environment and the health risks associated. A World Health Organization (WHO) study has demonstrated the health risks (carcinogenic and immunotoxic) when population are exposed to them. In addition, dioxins have been regulated by the Stockholm convention on POPs in May 2001. In particular, 17 substances have to be monitored. The highest toxic compound is the 2378-TeCDD. Currently, dioxins analysis can be done not only using GC-HRMS but also with GC-MS/MS according to European commission regulation (EU589/2014). Recently, JEOL has developed a new GC-triple quadrupole MS (JMS-TQ4000GC) and a new dedicated dioxins analysis software called TQ-DioK. In addition, we have already introduced dioxins analysis result by using standard sample（MSTips338）. In this study, we evaluated JMS-TQ4000GC with TQ-DioK using food samples.

Experimental

Standard Sample

The standard PCDDs and PCDFs(PCDD/Fs) solutions (DF-IS-A, DF-ST-A and DF-LCS-C from *WELLINGTON Laboratories* (CANADA)) were used for the measurement. Then, the range of concentrations for calibration curve was prepared from 0.025 to 1 pg/μL (OCDD and OCDF: 0.05 - 2 pg/μL) (Table 1).

Table 1) Concentrations of each calibration point

PCDD/Fs	Concentration ^{12}C (pg/μL)	Concentration ^{13}C (pg/μL)
Cal. 1	0.025(OCDD and OCDF 0.05)	1.25(OCDD and OCDF 2.5)
Cal. 2	0.05(OCDD and OCDF 0.1)	1.25(OCDD and OCDF 2.5)
Cal. 3	0.1(OCDD and OCDF 0.2)	1.25(OCDD and OCDF 2.5)
Cal. 4	0.25(OCDD and OCDF 0.5)	1.25(OCDD and OCDF 2.5)
Cal. 5	0.5(OCDD and OCDF 1.0)	1.25(OCDD and OCDF 2.5)
Cal. 6	1.0(OCDD and OCDF 2.0)	1.25(OCDD and OCDF 2.5)

GC-MS/MS measurement conditions

Table 2 shows the GC-MS/MS measurement conditions. A split/splitless inlet was used, and nitrogen gas was applied as collision gas. Table 3 shows the precursor ion, product ion and collision energy (CE). Two specific precursor ions from each non-labeled compound and labeled compound were set.

Table 2) GC-MS/MS measurement conditions

[GC]	
Inj. volume:	2μL
Inlet type:	Split/Splitless
Inj. mode:	Splitless
	(Purge time 1 min, Purge flow 20 mL/min)
Inlet temp.:	280 °C
Column flow:	1 mL/min (Constant flow)
GC column:	DB- 5MS (60 m x 0.25 mm, 0.25 μm)
Oven temp.:	120 °C (3 min) → 50 °C/min → 200 °C (0 min) → 4 °C/min → 300 °C (5 min) → 40 °C/min → 325 °C (5 min)

[MS]	
MS:	JMS-TQ4000GC
Ionization:	EI+
Acquisition mode:	High sensitivity mode
IS temp.:	280 °C
ITF temp:	280 °C

Table 3) Precursor ion, product ion and CE

No.	Compound name	Group name	Precursor ion	Product ion	Precursor ion	Product ion	CE(V)
1	13C-2378-TeCDF	13C-T4CDF	315.9	252	317.9	254	25
2	2378-TeCDF	T4CDF	303.9	240.9	305.9	242.9	
3	13C-1234-TeCDD	13C-T4CDD	333.9	270	331.9	268	25
4	13C-2378-TeCDD	13C-T4CDD	331.9	268	333.9	270	
5	2378-TeCDD	T4CDD	321.9	258.9	319.9	256.9	
6	13C-12378-PeCDF	13C-P5CDF	351.9	287.9	353.9	289.9	30
7	12378-PeCDF	P5CDF	339.9	276.9	341.9	278.9	
8	13C-23478-PeCDF	13C-P5CDF	351.9	287.9	353.9	289.9	
9	23478-PeCDF	P5CDF	339.9	276.9	341.9	278.9	
10	13C-12378-PeCDD	13C-P5CDD	367.9	303.9	369.9	305.9	25
11	12378-PeCDD	P5CDD	355.9	292.9	357.9	294.9	
12	13C-123478-HxCDF	13C-H6CDF	385.9	321.9	387.9	323.9	30
13	123478-HxCDF	H6CDF	373.8	310.9	375.8	312.9	
14	13C-123678-HxCDF	13C-H6CDF	385.9	321.9	387.9	323.9	
15	123678-HxCDF	H6CDF	373.8	310.9	375.8	312.9	
16	13C-234678-HxCDF	13C-H6CDF	385.9	321.9	387.9	323.9	
17	234678-HxCDF	H6CDF	373.8	310.9	375.8	312.9	
18	13C-123478-HxCDD	13C-H6CDD	401.9	337.9	403.9	339.9	25
19	123478-HxCDD	H6CDD	389.8	326.9	391.8	328.9	
20	13C-123678-HxCDD	13C-H6CDD	401.9	337.9	403.9	339.9	
21	123678-HxCDD	H6CDD	389.8	326.9	391.8	328.9	
22	13C-123789-HxCDD	13C-H6CDD	401.9	337.9	403.9	339.9	
23	123789-HxCDD	H6CDD	389.8	326.9	391.8	328.9	
24	13C-123789-HxCDF	13C-H6CDF	385.9	321.9	387.9	323.9	30
25	123789-HxCDF	H6CDF	373.8	310.9	375.8	312.9	
26	13C-1234678-HpCDF	13C-H7CDF	419.8	355.9	421.8	357.9	30
27	1234678-HeCDF	H7CDF	407.8	344.8	409.8	346.8	
28	13C-1234678-HpCDD	13C-H7CDD	435.8	371.9	437.8	373.9	30
29	1234678-HpCDD	H7CDD	423.8	360.8	425.8	362.8	
30	13C-1234789-HpCDF	13C-H7CDF	419.8	355.9	421.8	357.9	30
31	1234789-HpCDF	H7CDF	407.8	344.8	409.8	346.8	
32	13C-12346789-OCDD	13C-O8CDD	471.8	407.8	469.8	405.8	30
33	12346789-OCDD	O8CDD	459.7	396.8	457.7	394.8	
34	13C-12346789-OCDF	13C-OCDF	455.8	391.8	453.8	389.8	30
35	12346789-OCDF	OCDF	443.8	380.8	441.8	378.8	

Result

Dioxins in “Grass”, “Egg” and “Pork fat” samples were extracted and purified using the Büchi “SpeedExtractor E-914” and the MIURA "GO-4 HT". After then, samples were measured by both GC-HRMS and GC-MS/MS, and the obtained results were compared. Also, ratio of the selected two transition product ions was confirmed before calculation of quantitative value.

Ratio of selected two transition product ion

The tolerance of ratio of the selected two transitions product ions for average value or calculated value should be < ±15% according EU regulation(EU2017/644). Average value of each compound was calculated using all calibration points. Those ratios for each compound were within ±15% of average value(Fig. 1).

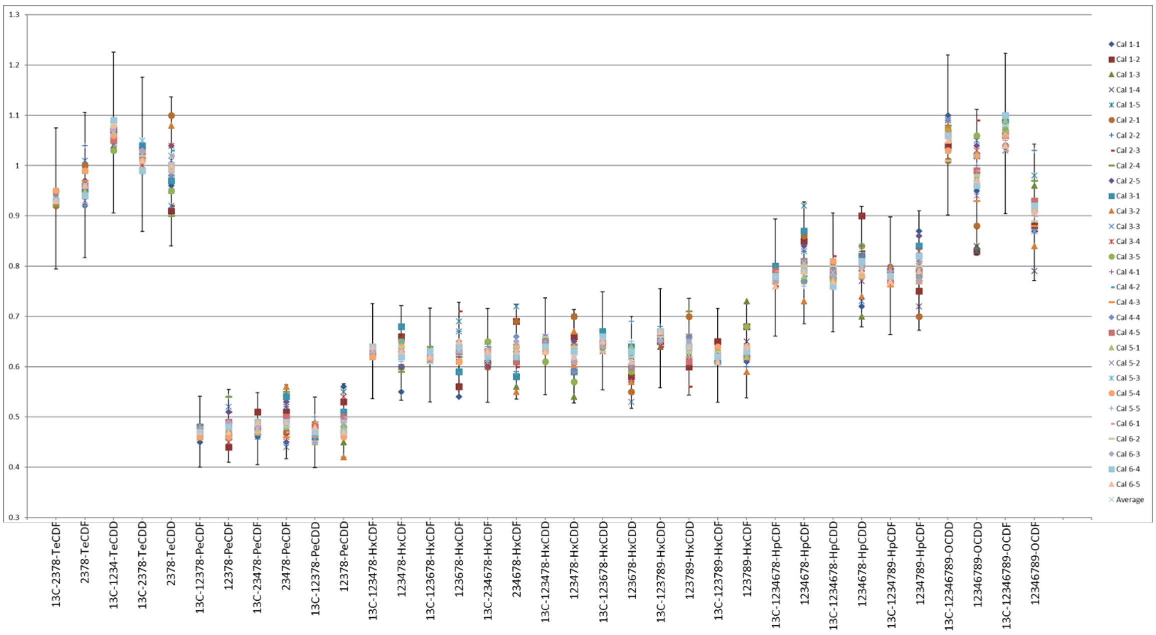


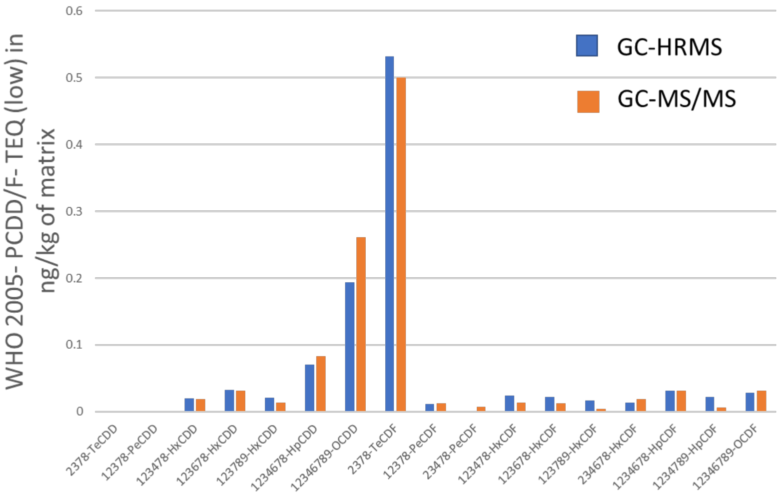
Fig. 1 Ratios of selected two transition product ions

Comparison of GC-HRMS and GC-MS/MS systems

Grass, Egg and Pork fat were measured by both GC-HRMS and GC-MS/MS systems. Toxic Equivalent Quantity (TEQ) was calculated using Toxic Equivalency Factors (TEF) based on WHO 2005. Fig. 2 shows the comparison data of Grass, Egg and Pork fat. The TEQ calculated for each compound by GC-MS/MS was similar to GC-HRMS result. By consequence the difference between the Dioxin OMS-TEQ in ng/kg of matrix calculated by GC-HRMS and the GC-MS/MS TEQ(dioxins) was within 20%.

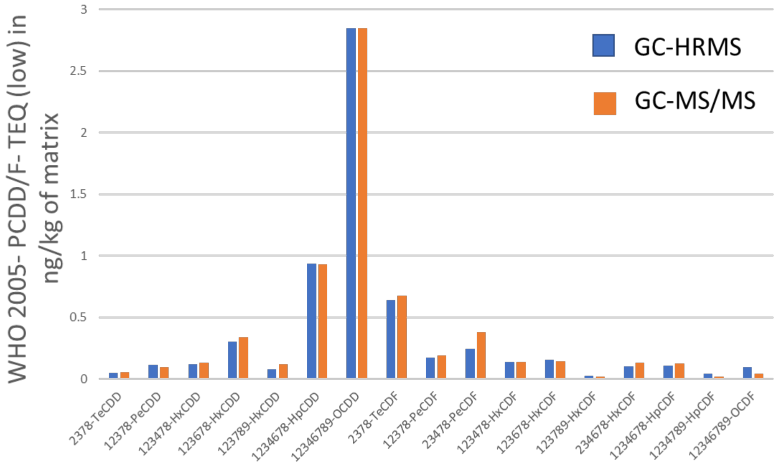
(A) Grass

	GC-HRMS	GC-MS/MS
2378-TeCDD	-	-
12378-PeCDD	-	-
123478-HxCDD	0.020	0.019
123678-HxCDD	0.033	0.032
123789-HxCDD	0.021	0.013
1234678-HpCDD	0.070	0.083
12346789-OCDD	0.193	0.262
2378-TeCDF	0.532	0.500
12378-PeCDF	0.012	0.012
23478-PeCDF	-	0.008
123478-HxCDF	0.025	0.013
123678-HxCDF	0.022	0.013
123789-HxCDF	0.017	0.004
234678-HxCDF	0.014	0.019
1234678-HpCDF	0.031	0.032
1234789-HpCDF	0.022	0.007
12346789-OCDF	0.028	0.032
OMS2005-Dioxin- TEQ (low) in ng/kg of matrix	0.070	0.065



(B) Egg

	GC-HRMS	GC-MS/MS
2378-TeCDD	0.045	0.051
12378-PeCDD	0.112	0.097
123478-HxCDD	0.121	0.133
123678-HxCDD	0.300	0.340
123789-HxCDD	0.079	0.117
1234678-HpCDD	0.936	0.931
12346789-OCDD	2.845	2.848
2378-TeCDF	0.641	0.673
12378-PeCDF	0.173	0.191
23478-PeCDF	0.245	0.381
123478-HxCDF	0.135	0.135
123678-HxCDF	0.156	0.141
123789-HxCDF	0.026	0.021
234678-HxCDF	0.103	0.131
1234678-HpCDF	0.108	0.125
1234789-HpCDF	0.045	0.019
12346789-OCDF	0.093	0.040
OMS2005-Dioxin- TEQ (low) in ng/kg of matrix	0.404	0.449



(C) Pork fat

	GC-HRMS	GC-MS/MS
2378-TeCDD	-	0.001
12378-PeCDD	0.042	0.032
123478-HxCDD	0.041	0.020
123678-HxCDD	0.048	0.038
123789-HxCDD	0.030	0.040
1234678-HpCDD	0.368	0.442
12346789-OCDD	2.216	2.406
2378-TeCDF	0.000	0.009
12378-PeCDF	0.014	0.016
23478-PeCDF	0.036	0.022
123478-HxCDF	0.037	0.036
123678-HxCDF	0.042	0.028
123789-HxCDF	0.026	0.019
234678-HxCDF	0.031	0.042
1234678-HpCDF	0.157	0.119
1234789-HpCDF	0.033	0.004
12346789-OCDF	0.091	0.050
OMS2005-Dioxin- TEQ (low) in ng/kg of matrix	0.084	0.069

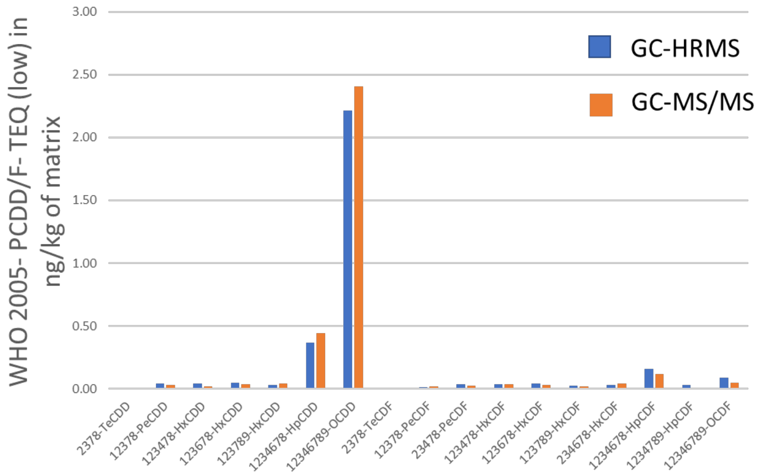


Fig. 2 Comparison data by GC-HRMS and GC-MS/MS of Grass(A), Egg(B) and Pork fat(C).

Conclusion

The JMS-TQ4000GC was evaluated for analysis of dioxins in food and feed. The results have shown that the obtained TEQ(dioxins) of JMS-TQ4000GC was similar to GC-HRMS. This result shows that the JMS-TQ4000GC is a powerful tool for analyzing dioxins.

Acknowledgement

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