

Dioxins analysis by New JMS-TQ4000GC and software "TQ-DioK"

Product used : Mass spectrometer(MS)

Dioxins are a general term for polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). Their structures consist of two chlorinated rings. Many congeners differ in terms of number of chlorine atoms and binding sites (Fig. 1). These substances 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 because they are regulated (7 PCDDs and 10 PCDFs). 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 (EU644/2017). Especially, GC-triple quadrupole MS is interesting in terms of handling, instrument size and operating costs. Recently, JEOL has developed a new GC-triple quadrupole MS (JMS-TQ4000GC) and a new dedicated dioxins analysis software called TQ-DioK. In this study, we evaluated JMS-TQ4000GC with TQ-DioK using dioxins standard samples.

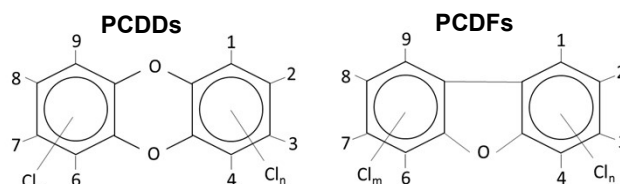


Fig 1. The structures of PCDDs(Left) and PCDFs(Right)

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/ μ L (OCDD and OCDF: 0.05 - 2 pg/ μ L) (Table 1).

Table 1. Concentrations of each calibration point

PCDD/Fs	Concentration ¹² C (pg/ μ L)	Concentration ¹³ C (pg/ μ L)
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:	2 μ L
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 μ m)
Oven temp.:	120 °C (3 min) \rightarrow 50 °C/min \rightarrow 200 °C (0 min) \rightarrow 4 °C/min \rightarrow 300 °C (5 min) \rightarrow 40 °C/min \rightarrow 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	30
6	13C-12378-PeCDF	13C-P5CDF	351.9	287.9	353.9	289.9	
7	12378-PeCDF	P5CDF	339.9	276.9	341.9	278.9	30
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	25
10	13C-12378-PeCDD	13C-P5CDD	367.9	303.9	369.9	305.9	
11	12378-PeCDD	P5CDD	355.9	292.9	357.9	294.9	30
12	13C-123478-HxCDF	13C-H6CDF	385.9	321.9	387.9	323.9	
13	123478-HxCDF	H6CDF	373.8	310.9	375.8	312.9	30
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	25
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	30
18	13C-123478-HxCDD	13C-H6CDD	401.9	337.9	403.9	339.9	
19	123478-HxCDD	H6CDD	389.8	326.9	391.8	328.9	30
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	25
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	30
24	13C-123789-HxCDF	13C-H6CDF	385.9	321.9	387.9	323.9	
25	123789-HxCDF	H6CDF	373.8	310.9	375.8	312.9	30
26	13C-1234678-HpCDF	13C-H7CDF	419.8	355.9	421.8	357.9	
27	1234678-HeCDF	H7CDF	407.8	344.8	409.8	346.8	30
28	13C-1234678-HpCDD	13C-H7CDD	435.8	371.9	437.8	373.9	
29	1234678-HpCDD	H7CDD	423.8	360.8	425.8	362.8	30
30	13C-1234789-HpCDF	13C-H7CDF	419.8	355.9	421.8	357.9	
31	1234789-HpCDF	H7CDF	407.8	344.8	409.8	346.8	30
32	13C-12346789-OCDD	13C-O8CDD	471.8	407.8	469.8	405.8	
33	12346789-OCDD	O8CDD	459.7	396.8	457.7	394.8	30
34	13C-12346789-OCDF	13C-OCDF	455.8	391.8	453.8	389.8	
35	12346789-OCDF	OCDF	443.8	380.8	441.8	378.8	30

Result

The GC-MS/MS method was validated in terms of chromatographic separation, sensitivity and RRF. Some criteria, especially separation and RRF have to comply with EU commission regulation(EU2017/644).

Separation

123478-HxCDF and 123678-HxCDF peaks were perfectly separated by using GC-MS/MS method (Fig.2). Indeed, EU commission regulation in force, allows a 25% valley between these 2 peaks.

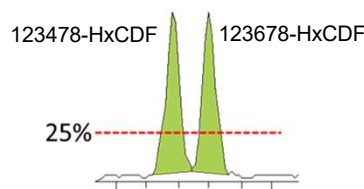
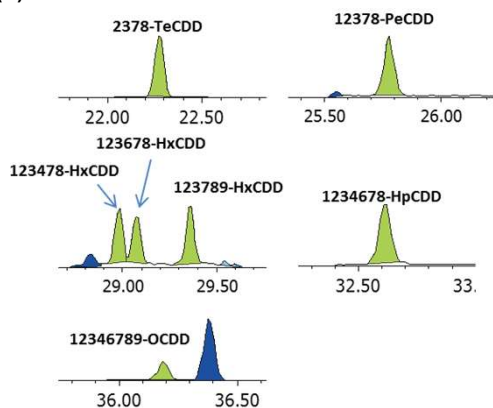


Fig. 2 Separation of 123478-HxCDF and 123678 HxCDF.

Sensitivity

All target compounds in the lowest calibration point were detected (Fig.3). In addition, the lowest calibration point was measured 8 times for the instrument detection limit (IDL) determination. Then, IDL was calculated using 2378-TeCDD. As a result, IDL value was equal to 4 fg (Fig.4).

(A) PCDDs



(B) PCDFs

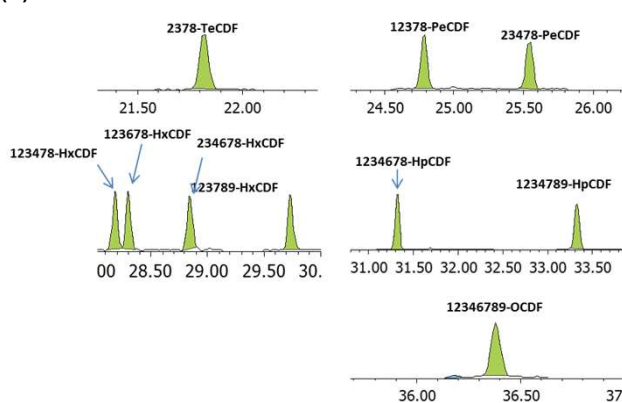
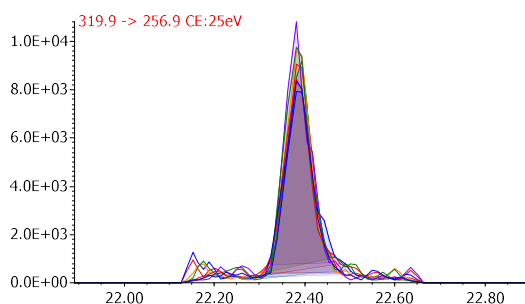


Fig. 3 Average SRM chromatograms of PCDDs(A) and PCDFs(B) in calibration point 1.



Average	Standard deviation	CV%	IDL [fg]
69077.5	1847.6	2.7	4.0

Fig. 4 IDL data by 2378-TeCDD

RRF

Fig. 5 shows calibration curves of 2378-TeCDD and 2378-TeCDF. Table 4 shows the result of relative standard deviation (RSD) of relative response factor (RRF) for the lowest calibration point, average of RRF, RSD of RRF and limit of quantification (LOQ). RSD of RRF obtained with the lowest calibration point was between 2.2 and 12.9 %. Average of RRF value was between 0.94 and 1.14. According to EU regulation, RSD for RRF has to be under 15% . Here, RSD of RRF from the average of all calibration points was within 9.1 % . Regarding LOQ, its value was calculated by signal-to-noise (S/N = 3) of the lowest calibration point. As a result, obtained LOQ value was between 0.08 and 1.69 fg/ μ L.

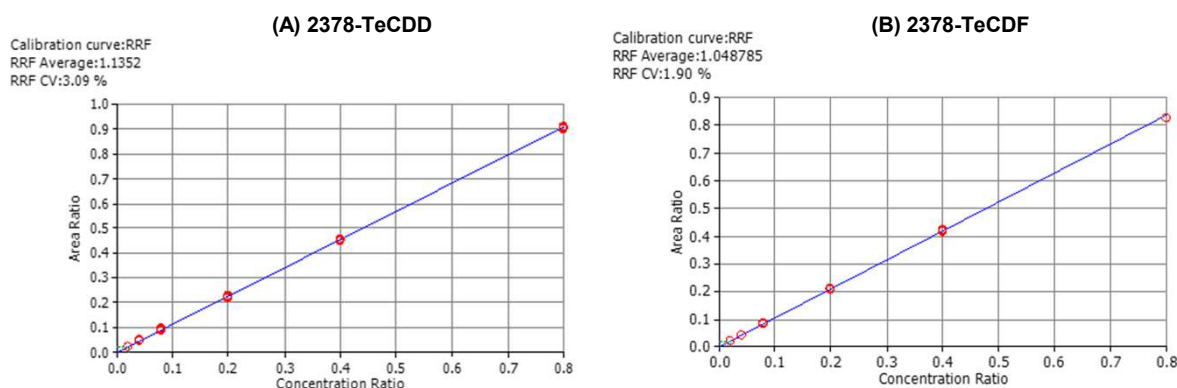


Fig. 5 Calibration curve of 2378-TeCDD(A) and 2378-TeCDF(B)

Table 4. Results of RSD of RRF for the lowest calibration point, average of RRF, RSD of RRF and LOQ

Compound	Lowest calibration point (pg/ μ L)	RSD of RRF by the lowest calibration point (%)	Average of RRF	RSD of RRF (%)	LOQ (fg/ μ L)
PCDFs					
2378-TeCDF	0.025	2.2	1.04	1.8	0.13
12378-PeCDF	0.025	2.3	1.04	2.4	0.45
23478-PeCDF	0.025	4.0	1.05	3.9	0.68
123478-HxCDF	0.025	3.7	1.00	2.9	0.40
123678-HxCDF	0.025	12.9	1.00	6.1	0.36
234678-HxCDF	0.025	8.7	1.03	5.6	0.42
123789-HxCDF	0.025	5.3	1.01	3.5	0.35
1234678-HeCDF	0.025	4.2	1.07	4.0	0.08
1234789-HpCDF	0.025	5.5	1.04	4.0	0.08
12346789-OCDF	0.050	4.1	0.95	9.1	1.19
PCDDs					
2378-TeCDD	0.025	3.6	1.14	3.1	0.41
12378-PeCDD	0.025	5.4	1.00	4.1	0.21
123478-HxCDD	0.025	12.5	1.00	6.4	1.46
123678-HxCDD	0.025	12.5	0.94	8.6	1.69
123789-HxCDD	0.025	5.9	1.03	4.5	1.11
1234678-HpCDD	0.025	8.9	1.10	5.8	0.22
12346789-OCDD	0.050	8.3	1.03	9.0	0.90

Conclusion

The JMS-TQ4000GC was evaluated for dioxins quantification. The results have shown that the JMS-TQ4000GC instrument complies with the EU commission regulation. These results show that the JMS-TQ4000GC system associated with TQ-DioK software are a powerful tool for analyzing dioxins.

Acknowledgement

All measurements and evaluation about the basic performances of JMS-TQ4000GC were organized and tested by the 'Laboratoire d'Etude des Résidus et Contaminants dans les Aliments (LABERCA), Nantes, France.

Copyright © 2021 JEOL Ltd.

Certain products in this brochure are controlled under the "Foreign Exchange and Foreign Trade Law" of Japan in compliance with international security export control. JEOL Ltd. must provide the Japanese Government with "End-user's Statement of Assurance" and "End-use Certificate" in order to obtain the export license needed for export from Japan. If the product to be exported is in this category, the end user will be asked to fill in these certificate forms.

