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An analytical method for environmental pollutants using GC×GC-MS/MS with ultra-fast MRM switching mode

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1. Introduction

Generally, gas chromatograph mass spectrometer (GC-MS) is used for the analysis of environmental pollutants. The number of environmental pollutants dramatically increases these days, the number of analysis methods together with sample pretreatment methods largely increases. These methods require specialized experience and advanced technique for sample pretreatment and data analysis for environmental analysis.

To resolve such complexity and difficulty, the analysis system for multitarget analysis with high separation ability and highly sensitive/selective detection has been developed. Comprehensive two dimensional gas chromatograph (GC×GC) and triple quadrupole mass spectrometer (MS/MS) were coupled, and the analysis of PCBs in environmental samples by the system has been investigated.

2. Experimental

Materials

STD : 19 types of PCBs (0.1 – 100 pg), 14 types of ^{13}C-PCBs (ISTD, 100 pg)

2-Chlorobiphenyl (PCB1)
4-Chlorobiphenyl (PCB3)
2,6-Dichlorobiphenyl (PCB10)
4,4'-Dichlorobiphenyl (PCB15)
2,2',6-Trichlorobiphenyl (PCB19)
3,4,4'-Trichlorobiphenyl (PCB37)
2,2',6,6'-Tetrachlorobiphenyl (PCB54)
3,3',4,4'-Tetrachlorobiphenyl (PCB77)
2,2',4,6,6'-Pentachlorobiphenyl (PCB104)
3,3',4,4',5-Pentachlorobiphenyl (PCB126)
2,2',4,4',6,6'-Hexachlorobiphenyl (PCB155)
3,3',4,4',5,5'-Hexachlorobiphenyl (PCB169)
2,2',3,4',5,6,6'-Heptachlorobiphenyl (PCB188)
2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB189)
2,2',3,3',5,5',6,6'-Octachlorobiphenyl (PCB202)
2,3,3',4,4',5,5',6-Octachlorobiphenyl (PCB205)
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (PCB206)
2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl (PCB208)
Decachlorobiphenyl (PCB209)

^{13}C-3,4,4',5-Tetrachlorobiphenyl (PCB81-L)
^{13}C-3,3',4,4'-Tetrachlorobiphenyl (PCB77-L)
^{13}C-2,3,3',4,4'-Pentachlorobiphenyl (PCB105-L)
^{13}C-2,3,4,4',5-Pentachlorobiphenyl (PCB114-L)
^{13}C-2,3',4,4',5-Pentachlorobiphenyl (PCB118-L)
^{13}C-2',3,4,4',5-Pentachlorobiphenyl (PCB123-L)
^{13}C-3,3',4,4',5'-Pentachlorobiphenyl (PCB126-L)
^{13}C-2,3,3',4,4',5-Hexachlorobiphenyl (PCB156-L)
^{13}C-2,3,3',4,4',5'-Hexachlorobiphenyl (PCB157-L)
^{13}C-2,3',4,4',5,5'-Hexachlorobiphenyl (PCB167-L)
^{13}C-3,3',4,4',5,5'-Hexachlorobiphenyl (PCB169-L)
^{13}C-2,2',3,3',4,4',5-Heptachlorobiphenyl (PCB170-L)
^{13}C-2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB180-L)
^{13}C-2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB189-L)

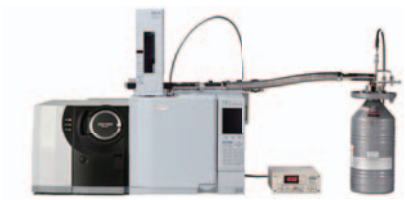
Sample : Fly ash (NIES CRM No.17) - Rough extracted solution

Analytical Condition

GC-MS : GCMS-TQ8030
Column : 1st Rxi-5MS (30 m length, 0.25 mm I.D., df = 0.25 µm)
2nd BPX-50 (2.5m length, 0.1 mm I.D., df = 0.1 µm)

[GC]
Injection Temp. : 250°C
Column Oven Temp. : 80°C - (1 min) - (4°C/min) - 310°C (10 min)
Injection Mode : Splitless
Flow Control Mode : Pressure (270 kPa (1 min) - (3.4 kPa/min) - 465.5 kPa (10 min))
Injection Volume : 1 µL
Modulation Period : 4 sec (320°C, 0.3 sec)

[MS]
Interface Temp. : 250°C
Ion Source Temp. : 200°C
Acquition Mode : MRM
Sampling Rate : 70 Hz
MRM monitoring *m/z* :



Compound Name	Quantitative Transition Precursor > Product	CE (V)	Qualitativve Transition Precursor > Product	CE (V)
Chlorobiphenyl	188.0>152.0	24	190.0>152.0	24
Dichlorobiphenyl	222.0>152.0	24	224.0>152.0	24
Trichlorobiphenyl	256.0>186.0	24	258.0>186.0	24
Tetrachlorobiphenyl	289.9>219.9	24	291.9>221.9	24
Pentachlorobiphenyl	323.9>253.9	24	325.9>255.9	24
Hexachlorobiphenyl	357.9>287.9	27	359.9>289.9	27
Heptachlorobiphenyl	391.9>321.9	30	393.9>323.9	30
Octachlorobiphenyl	427.8>355.8	30	429.8>357.8	30
Nonachlorobiphenyl	461.8>391.8	30	463.8>393.8	30
Decachlorobiphenyl	495.7>425.7	30	497.7>427.7	30
^{13}C-Tetrachlorobiphenyl	301.9>231.9	24	303.9>233.9	24
^{13}C-Pentachlorobiphenyl	335.9>265.9	24	337.9>267.9	24
^{13}C-Hexachlorobiphenyl	369.9>299.9	27	371.9>301.9	27
^{13}C-Heptachlorobiphenyl	403.9>333.9	30	405.9>335.9	30

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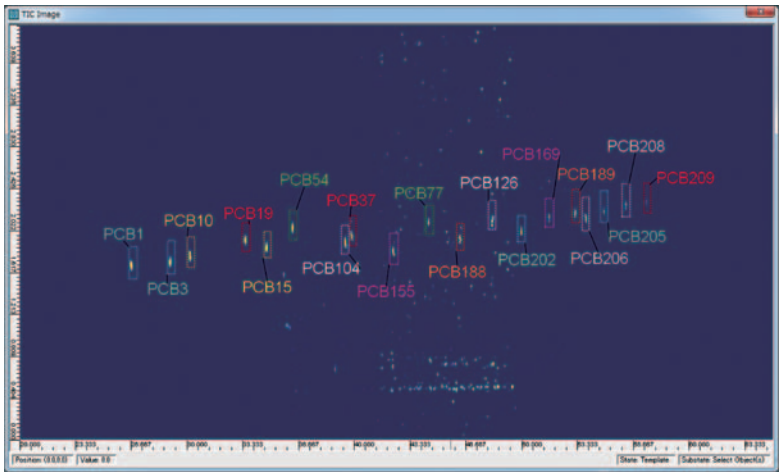
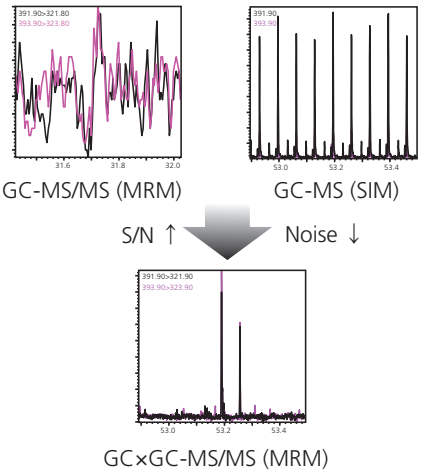
3. Results

2D chromatograph of STD 0.1 pg



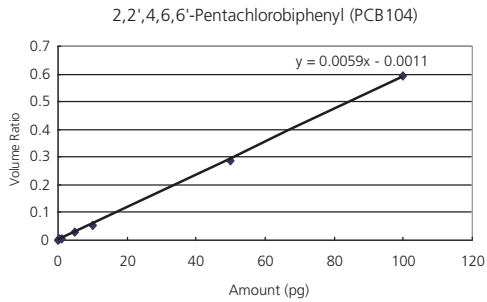
PCB208 0.1 pg

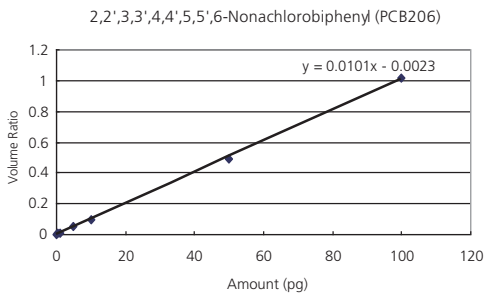


Instrument Detection Limit (IDL) & Calibration Curve

Compound Name	IDL (pg)	R
2-Chlorobiphenyl (PCB1)	0.014	0.9990
4-Chlorobiphenyl (PCB3)	0.012	0.9999
2,6-Dichlorobiphenyl (PCB10)	0.015	1.0000
4,4'-Dichlorobiphenyl (PCB15)	0.020	0.9999
2,2',6-Trichlorobiphenyl (PCB19)	0.012	0.9999
3,4,4'-Trichlorobiphenyl (PCB37)	0.040	0.9997
2,2',6,6'-Tetrachlorobiphenyl (PCB54)	0.035	1.0000
3,3',4,4'-Tetrachlorobiphenyl (PCB77)	0.036	0.9990
2,2',4,6,6'-Pentachlorobiphenyl (PCB104)	0.032	0.9999
3,3',4,4',5-Pentachlorobiphenyl (PCB126)	0.028	0.9996
2,2',4,4',6,6'-Hexachlorobiphenyl (PCB155)	0.034	0.9993
3,3',4,4',5,5'-Hexachlorobiphenyl (PCB169)	0.091	0.9992
2,2',3,4',5,6,6'-Heptachlorobiphenyl (PCB188)	0.041	0.9998
2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB189)	0.056	0.9999
2,2',3,3',5,5',6,6'-Octachlorobiphenyl (PCB202)	0.071	0.9996
2,3,3',4,4',5,5',6-Octachlorobiphenyl (PCB205)	0.039	0.9996
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (PCB206)	0.073	0.9999
2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl (PCB208)	0.073	0.9990
Decachlorobiphenyl (PCB209)	0.032	0.9992

IDLs were calculated by CV% (0.1 pg, n=5).





High sensitivity and good accuracy were achieved by ultra fast MRM switching (min. Dwell time < 1 msec).

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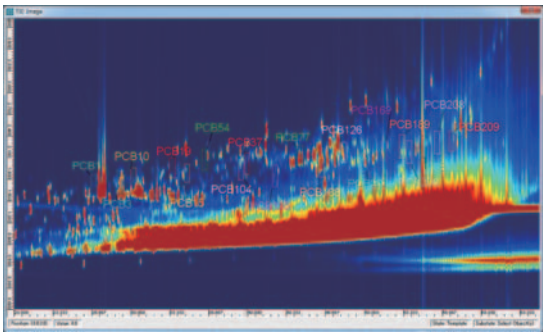
Result of Fly ash

GC×GC-MS (Scan)



GC×GC-MS/MS (SIM)

Matrices were remaining and would cause miss detecting blobs.

GC×GC-MS/MS (MRM)

GC×GC-MS/MS system enabled to separate and remove almost matrices.

Quantification Result

Compound Name	Amount (pg)	Compound Name	Amount (pg)
2-Chlorobiphenyl (PCB1)	2.139	2,2',4,4',6,6'-Hexachlorobiphenyl (PCB155)	0.509
4-Chlorobiphenyl (PCB3)	25.386	3,3',4,4',5,5'-Hexachlorobiphenyl (PCB169)	6.671
2,6-Dichlorobiphenyl (PCB10)	0.482	2,2',3,4',5,6,6'-Heptachlorobiphenyl (PCB188)	0.653
4,4'-Dichlorobiphenyl (PCB15)	5.223	2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB189)	6.593
2,2',6-Trichlorobiphenyl (PCB19)	0.273	2,2',3,3',5,5',6,6'-Octachlorobiphenyl (PCB202)	1.088
3,4,4'-Trichlorobiphenyl (PCB37)	16.231	2,3,3',4,4',5,5',6-Octachlorobiphenyl (PCB205)	5.654
2,2',6,6'-Tetrachlorobiphenyl (PCB54)	N.D.	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (PCB206)	4.978
3,3',4,4'-Tetrachlorobiphenyl (PCB77)	20.530	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl (PCB208)	14.820
2,2',4,6,6'-Pentachlorobiphenyl (PCB104)	0.325	Decachlorobiphenyl (PCB209)	14.154
3,3',4,4',5-Pentachlorobiphenyl (PCB126)	18.254		

※Reference Value

4. Summary

- GC×GC-Ultra fast switching MRM analysis achieved high sensitivity and good quantitative performance.
- Sample pretreatment is expected to be easier because almost matrices could be separated and removed by high separation capacity and high selectivity.
- Although target compounds were only PCBs in this study, another pollutants (ex. Dioxins, Cl-PAHs) will be added and validated in the future plan.
- This GC×GC-MS/MS system can accept sharp peaks of GC×GC without lacking of sampling rate in case of increasing target compounds because GCMS-TQ8030 has ultrafast switching ability (Max. 600 trans/sec).

⇒Quick and high sensitive multi-target analysis will be enabled using this GC×GC-MS/MS system.

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