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PO-CON1371E

GC-MS/MS determination of PCBs and screening of environmental pollutants using simultaneous scan and MRM modes

Dioxin 2013 P-0007

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1. Introduction

An analytical method was developed for a determination of PCBs and organochlorine pesticides, and a screening of environmental pollutants using a tandem quadrupole mass spectrometer (GC-MS/MS). The GC-MS/MS was operated in simultaneous scan and MRM measuring (scan/ MRM) to reduce an analysis time.
For the determination of PCBs and organochlorine pesticides, the conventional method (isotope dilution method) was applied to the MRM data in order to obtain precise quantitation results. On the other hand, Automated Identification and Quantification System with a Database (AIQS-DB) was applied to the scan data for the screening of environmental pollutants.
AIQS-DB allows an automatic identification and semi-quantitation of targets compounds without standard sample analysis. It was developed by Kadokami et al. [1] for 1000 pollutants. The database includes retention indices, mass spectra, and internal calibration curves for pollutants. The pollutants are identified using the mass spectrum and retention time predicted by retention index and retention times of n-alkanes. Semi-quantitation is performed using an internal calibration curve.
The developed method was applied to river water samples. PCBs were selectively detected and determined from the MRM data and 84 compounds were semi-quantitated from the scan data. The results demonstrated that the developed method is effective for the target analysis of PCBs and organochlorine pesticides, and the screening of environmental pollutants by only one analysis.

2. Experimental

Sample River water in Vietnam

Sample Preparation

Sample, 1 L (in separating funnel)
← Phosphate buffer (1 mol/L, pH 7.0, 1 mL)
← NaCl (50 g)
Extraction
10 min shaking with 50 mL of DCM (2 times)
Dehydration (Sodium sulfate)
Concentration (Rotary Evaporator, 5 mL)
← 1 mL of hexane
Concentration (under gentle N_2, 1 mL)
← IS mixture (10 µg/mL, 100 µL)
GCMS analysis

Analytical Condition

GC-MS : GCMS-TQ8030
Column : DB-5MS (30 m length, 0.25 mm I.D., df = 0.25 µm)

[GC]
Injection Temp. : 250°C
Column Oven Temp. : 40°C (2 min) - (8°C/min) - 310°C (5 min)
Injection Mode : Splitless
Flow Control Mode : Linear velocity (40.0 cm/sec)
Injection Volume : 1 µL

[MS]
Interface Temp. : 200°C
Ion Source Temp. : 300°C
Acquition Mode : Scan/MRM, SIM
Scan Speed : 5000 u/sec

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Precise determination using MRM data of Scan/MRM

Internal standards (5 compounds)

	Quantitative Transition Precurser > Product	CE (V)	Qualitative Transition Precurcer > Product	CE (V)
Acenaphthene-D10	164.10>162.10	31	164.10>164.10	25
Phenanthrene-D10	188.10>186.10	28	188.10>160.10	31
Fluoranthene-d10	212.20>210.20	37	212.20>208.20	46
Chrysene-D12	240.20>238.20	26	240.20>236.20	41
Perylene-D12	264.20>260.20	47	264.20>262.20	44

PCBs (70 compounds)

Chlorobiphenyl	188.00>152.00	24	190.00>152.00	24
Dichlorobiphenyl	222.00>152.00	24	224.00>152.00	24
Trichlorobiphenyl	256.00>186.00	24	258.00>186.00	24
Tetrachlorobiphenyl	289.90>219.90	24	291.90>221.90	24
Pentachlorobiphenyl	323.90>253.90	24	325.90>255.90	24
Hexachlorobiphenyl	357.90>287.90	27	359.90>289.90	27
Heptachlorobiphenyl	391.90>321.80	30	393.90>323.80	30
Octachlorobiphenyl	427.80>355.80	30	429.80>357.80	30
Nonachlorobiphenyl	461.80>391.80	30	463.80>393.80	30
Decachlorobiphenyl	495.70>425.70	30	497.70>427.70	30

Organochlorine pesticides (22 Compounds)

	Quantitative Transition Precurser > Product	CE (V)	Qualitative Transition Precurcer > Product	CE (V)
BHC (alpha, beta, gamma, delta)	218.90>182.90	8	218.90>145.00	20
Hexachlorobenzene	283.90>248.80	24	283.90>213.90	28
Heptachlor	271.80>236.80	20	271.80>117.00	32
Aldrin	262.90>192.90	28	262.90>202.90	26
Heptachlor-exo-epoxide	352.90>262.90	14	352.90>281.90	12
Oxychlordane	386.90>286.90	26	386.90>322.90	18
Heptachlor-endo-epoxide	352.90>288.90	6	352.90>252.90	26
Chlordane (cis, trans)	372.90>336.90	10	372.90>265.90	22
DDE (o,p'-, p,p'-)	246.00>176.00	30	246.00>211.00	22
Nonachlor (cis, trans)	408.90>373.90	16	408.90>145.00	24
Dieldrin	276.90>240.90	8	276.90>170.00	38
DDD (o,p'-, p,p'-)	235.00>165.00	24	235.00>199.00	14
Endrin	262.90>190.90	30	262.90>227.90	22
DDT(o,p'-, p,p'-)	235.00>165.00	24	235.00>199.00	16

Screening and semi-quantitation using scan data of Scan/MRM and AIQS-DB

- 942 environmental pollutants were registered in the Compound Composer database.
- Qualitative and semi-quantitative analysis are possible without the use of standards.

Category 1	Num.	Category 2	Num.	Category 1	Num.	Category 2	Num.
Internal Standard	8		8	Compounds consisting of CHN(O)	113	Aromatic amines	43
Compounds consisting of CH	194	Aliphatic Compounds	31			Quinoline	3
		Benzenes	14			Nitro compounds	42
		Polycyclic compounds	79			Nitrosoamines	5
		PCB's	62			Others	20
		Others	8	CHS(NO)	12		12
Compounds consisting of CHO	150	Ethers	11	CHP(NOS)	8	Phosphoric esters	8
		Ketones	6	*PPCP's	14		14
		Phenols	50	Pesticides	451	Insecticides	184
		Phthalates	11			Herbicides	118
		Fatty acid esters	34			Fungicides	116
		Others	38			Others	33
				Total			942

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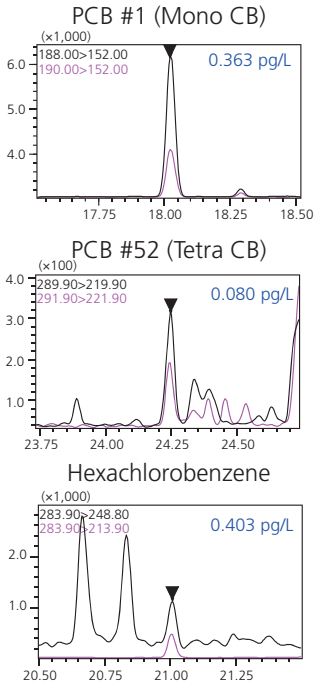
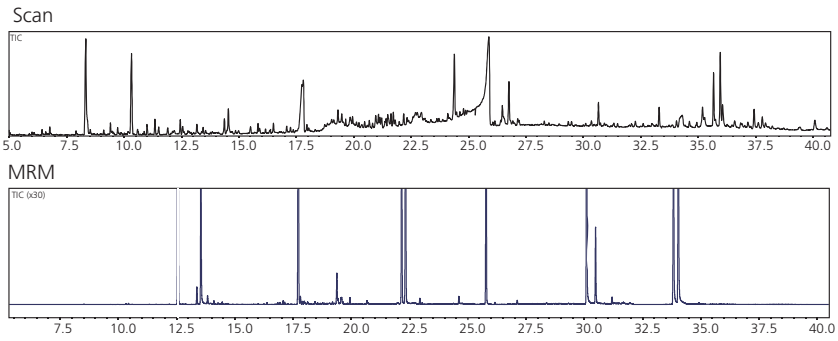
3. Results

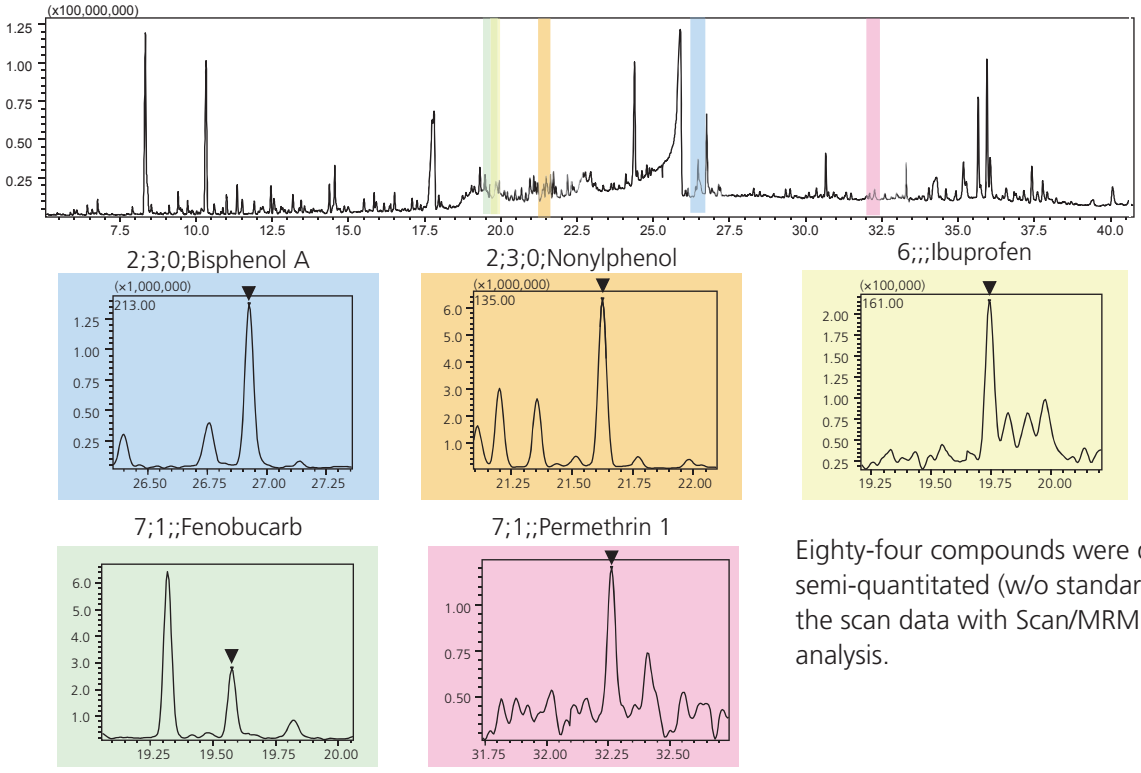
Precise determination using MRM data of Scan/MRM





Detected Compounds	Conc. (ng/L in water)	Detected Compounds	Conc. (ng/L in water)
PCB #1 (Mono CB)	0.363	PCB #70 (Tetra CB)	0.159
PCB #3 (Mono CB)	0.401	PCB #66 (Tetra CB)	0.144
PCB #4 & #10 (Di CB)	0.194	PCB #101 + PCB #90 (Penta CB)	0.063
alpha-BHC	0.032	PCB #99 (Penta CB)	0.079
Hexachlorobenzene	0.403	PCB #119 (Penta CB)	0.028
PCB #8 (Di CB)	0.244	p,p'-DDE	0.306
PCB #19 (Tri CB)	0.026	PCB #110 (Penta CB)	0.381
PCB #18 (Tri CB)	0.111	PCB #149 (Hexa CB)	0.013
PCB #15 (Di CB)	0.116	PCB #153 & PCB #168 (Hexa CB)	0.081
delta-BHC	2.820	PCB #105 (Penta CB)	0.255
PCB #52 (Tetra CB)	0.080	PCB #138 & PCB #129 (Hexa CB)	0.057
PCB #49 (Tetra CB)	0.039	PCB #187 (Hepta CB)	0.006
PCB #44 (Tetra CB)	0.092	PCB #183 (Hepta CB)	0.007
PCB #41 (Tetra CB)	0.108	PCB #180 (Hepta CB)	0.011
PCB #74 (Tetra CB)	0.169	PCB #169 (Hexa CB)	0.026

Screening and semi-quantitation using scan data of Scan/MRM and AIQS-DB



Eighty-four compounds were detected and semi-quantitated (w/o standard sample) from the scan data with Scan/MRM simultaneous analysis.

4. Summary

- A novel analytical method was developed for a determination of PCBs and organochlorine pesticides, and a screening of environmental pollutants using a tandem quadrupole mass spectrometer (GC-MS/MS).
- The data were acquired using simultaneous scan and MRM measuring of GC-MS/MS (Scan/MRM mode).
- MRM data was used for the precise determination of PCBs and organochlorine pesticides and scan data was used for the screening and semi-quantitation.
- Using this method, 30 of PCBs and organochlorine pesticides were determined, and 84 compounds were detected and semi-quantitated in the river water sample obtained in Vietnam.
- These results demonstrated the effectiveness of the developed method.

First Edition: August, 2013

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