

Rapid analysis of polychlorinated biphenyls (PCBs) in vegetables by QuEChERS-based extraction and GPC–GCMS

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Overview

7 kinds of PCBs in two complicated matrix—carrot and ginger were analyzed by gel permeation chromatography coupled with gas chromatography-mass spectrometry (GPC–GCMS), which could remove majority of macromolecules such as oil and pigment.

Introduction

Polychlorinated biphenyls (PCBs), one of the most famous “dirtydozen” persistent organic pollutants (POPs) with carcinogenicity, teratogenicity and mutagenicity, are used to be produced and commercially used as mixtures. Because of their specific properties such as good stability, low volatility, insulativity and non-flammability, PCBs have been applied in a series of industrial applications such as coating, links, flame retardants, paints, electronic appliances, heat-transfer systems and hydraulic fluids.

Even PCBs were banned by most countries as early as 1970s, they can still be detected in air, soil, water, sediment and biota at a global scale, even in remote areas such as the polar regions, deep seas and high mountains. In this research, carrot and ginger were selected as representative samples analyzed by on-line GPC-GCMS system characterized by remove macromolecules for further purification.

Methods

Sample Preparation

The purification procedure was referenced to the QuEChERS method: 10g crushed sample, vortex in 10 mL acetonitrile, add 4 g of $MgSO_4$ and 1 g of NaCl; vortex mixed for 1 min and centrifuged for 10 min at 3000 rpm;

2 mL of the upper layer was transferred into a 5 mL centrifuge tube containing 150 mg of $MgSO_4$ and 25 mg of PSA, after vortex mixing for 1 min, centrifuged for 10 min at 3000 rpm and was ready for injection.

GPC-GCMS Analysis

Instrument	: GPC-GCMS (Shimadzu Corporation, Japan)
GPC system condition	
Column	: Shodex CLNpak EV-200 (2.1mm x 150mm)
Mobile phase	: acetone/ cyclohexane (3/7, v/v)
Flow rate	: 0.1 mL/min
Sample volume	: 10 μ L

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GCMS system	
Retention gap	: 5 m x 0.53 mm
Pre-column	: Rtx-5 MS, 5 m x 0.25 mm x 0.25 µm
Analytical column	: Rtx-5 MS, 25m x 0.25mm x 0.25µm
Temp. program	: 82 °C (5 min)_8 °C/min_300 °C (7.75 min)
PTV injection temperature program	: 120 °C (5 min)_100 °C/min_250 °C (33.7min)
Injection pressure program	: 120 kPa (0 min)_100 kPa/min _180 kPa (4.4 min)_ (-49.8 kPa/min)_120 kPa (33.8 min)
Purge program	: 5.0 mL/min_(-10 mL/min)_ 0 mL/min (6 min)_ 10 mL/min_5 mL/min (5 min)
Sampling time	: 7 min
Solvent cut time	: 9.7 min
Interface temperature	: 300 °C
Ion source temperature	: 200 °C
Acquisition mode	: SIM

Table 1 GCMS parameters for PCBs

No.	Compound	CAS	Retention time	Quantitation ions	Qualification ions 1	Qualification ions 2
1	PCB28 (2,4,4'-Trichlorobiphenyl)	7012-37-5	20.74	256	258	186
2	PCB52 (2,2',5,5'-Tetrachlorobiphenyl)	35693-99-3	21.65	292	220	290
3	PCB101 (2,2',4,5,5'-Pentachlorobiphenyl)	37680-73-2	23.88	326	254	328
4	PCB118 (2,3',4,4',5-Pentachlorobiphenyl)	31508-00-6	25.42	326	328	324
5	PCB138 (2,2',3,4,4',5'-Hexachlorobiphenyl)	35065-28-2	25.96	360	362	290
6	PCB153 (2,2',4,4',5,5'-Hexachlorobiphenyl)	35065-27-1	26.63	360	362	290
7	PCB180 (2,2',3,4,4',5,5'-Heptachlorobiphenyl)	35065-29-3	28.23	396	394	324

Results

The results of this research indicated that the relative coefficients of the 7 kinds of PCBs ranged from 1 to 500 µg/L were above 0.998. Precision (n=6) of this method was measured by analyzing the sample at 1 µg/L. The overall RSDs of analysis were below 5%. The limit of detection (LOD; S/N=3) of most compounds were below 0.05 µg/L. Commercially available carrot and ginger

were used for recovery test, spiked concentration was 10 µg/kg and the recoveries of carrot were between 97% and 125% and those of ginger were between 85% and 104%. The developed method in this study was proved to be reliable and accurate, and permits rapid determination of PCBs can be easily applied for quality control of vegetables.

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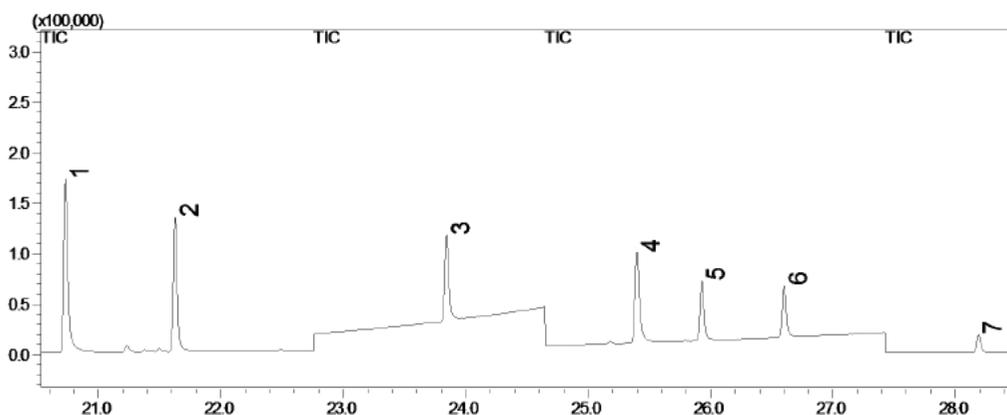


Figure 1 SIM chromatograms of PCBs (10 ng/mL)

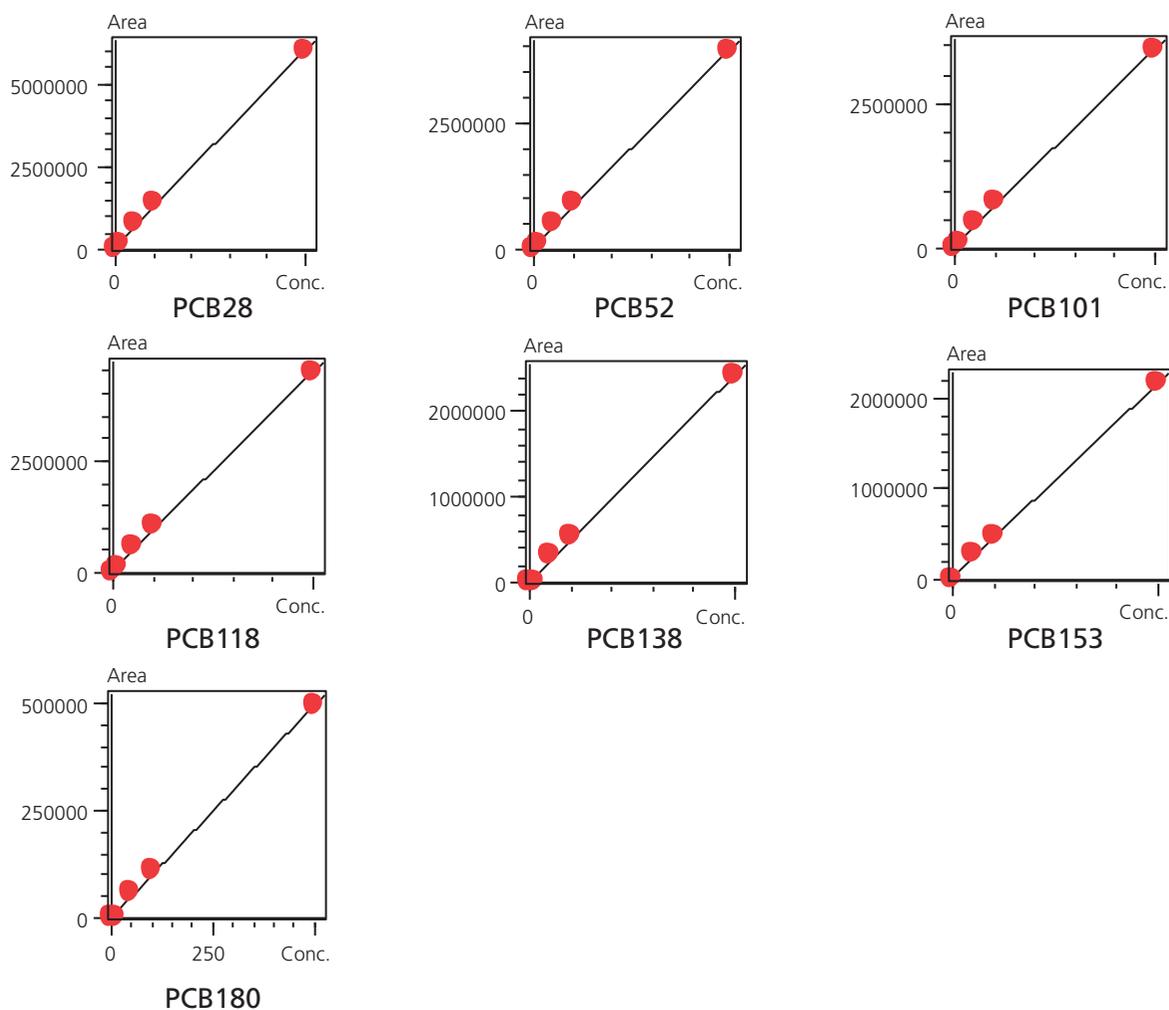


Figure 2 Calibration curve

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Table 2 Relative coefficients, limit of detection (LOD, S/N=3) and recovery of the 7 kinds of PCBs

No.	Compound	Relative coefficients	LOD (µg/L)	Recovery	
				Carrot	Ginger
1	PCB28	0.9990	0.02	100.54	104.39
2	PCB52	0.9991	0.01	97.76	101.63
3	PCB101	0.9991	0.02	98.01	84.13
4	PCB118	0.9991	0.05	99.22	95.70
5	PCB138	0.9989	0.02	108.86	87.79
6	PCB153	0.9996	0.02	116.63	92.21
7	PCB180	0.9994	0.07	125.67	84.94

Table 3 Precision of PCBs (1 ng/mL each, n=6)

No.	Compound	Area						RSD (%)
		1	2	3	4	5	6	
1	PCB28	20882	21137	21076	21016	20311	21474	1.83
2	PCB52	13494	13944	13702	13926	13942	13706	1.33
3	PCB101	11428	11678	11653	11397	11349	11558	1.21
4	PCB118	13891	14251	13501	13602	14160	14300	2.45
5	PCB138	5965	5993	5557	5777	5800	5861	2.70
6	PCB153	5469	5470	5063	5148	5364	5091	3.58
7	PCB180	1141	1082	1044	1061	1109	1100	3.20

Table 4 Sample test result

No.	Compound	Carrot	Ginger
1	PCB28	N.D	N.D
2	PCB52	N.D	N.D
3	PCB101	N.D	N.D
4	PCB118	N.D	N.D
5	PCB138	N.D	N.D
6	PCB153	N.D	N.D
7	PCB180	N.D	N.D

N.D.: Not detected

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Conclusions

Using the online GPC-GC/MS to analyse 7 kinds of PCBs in carrot and ginger, the method has the advantages of simple operation, high sensitivity and excellent precision.