

# Determination of Selected Polychlorinated Biphenyls in Soil Using a QuEChERS-based Method and Gas Chromatography Tandem Mass Spectrometry

## Application Note

Environmental

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### Abstract

Soil is an important object in pollution assessment, environmental behavior, and toxicity studies for polychlorinated biphenyls (PCBs). Accelerated solvent extraction and solid phase extraction are generally required for extraction and cleanup of PCBs in soil. These are tedious and time-consuming procedures. In this research, a modified QuEChERS procedure combined with gas chromatography-triple quadrupole mass spectrometry was developed for the determination of 20 selected PCB congeners in soil. The average recoveries from spiked soils ranged between 70 and 120 %, with satisfactory relative standard deviations for all the PCBs. The limits of quantitation (LOQs) were in the range of 0.01 and 0.05 ng/g. The method was successfully applied to the analysis of 66 agricultural soils. The procedure proved to be simple, sensitive, efficient, and environmentally friendly.



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## Introduction

Polychlorinated biphenyls (PCBs) are one of the most widespread and persistent pollutants in the world [1]. There are 209 individual PCB components, known as congeners, and, because of their persistence and hydrophobicity, they accumulate in soils where they are likely to be retained for many years. Consequently, soils are a primary reservoir for PCBs [2]. Because of their global contamination and adverse effects on environmental and human health [3], the production of PCBs has been banned worldwide since the early 1970s. Although PCBs have been banned for decades, they are still found in soils, surface waters, sediments, and air, since they are transported far from their sources [4]. Due to the increasing concern about chemical contamination of soil, there is growing interest in the scientific community and international agencies for soil pollution monitoring and assessment. To study environmental behavior in soil, it is critical to develop simple, sensitive, and reliable analytical methods.

The Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method, originally developed for extracting pesticides in fruit and vegetables in 2003 by Anastassiades *et al.* [5], has extended its application to many other matrices and pollutants. The QuEChERS multiresidue procedure omits or replaces many complicated analytical steps commonly used in traditional methods, making the sample preparation simple and efficient.

The aim of this research was to develop a simple, robust, and effective multiresidue method based on the QuEChERS procedure for the determination of 20 selected PCBs in soil. Different extract solvents, extract times, and cleanup adsorbents were tested and optimized. The optimum method provided a new chemical analysis method for PCB monitoring and environmental behavior studies in soil. This application note describes a recently published study of selected polychlorinated biphenyls in soil and earthworm using a QuEChERS-based method and gas chromatography tandem mass spectrometry [6]. It is a rapid multiresidue method based on a QuEChERS sample preparation, combined with GC/MS/MS detection, aiming to determine selected PCBs in soil.

## Reagents and standards

Acetonitrile, hexane, and cyclohexane were HPLC grade. Water was purified by a Milli-Q system. PCB congeners (IUPAC numbers 28, 52, 77, 91, 95, 101, 105, 114, 118, 136, 138, 149, 153, 157, 167, 169, 176, 180, 183, and 189 in isooctane all at 100 µg/mL), surrogate ( $^{13}\text{C}_{12}$ -PCB 52, 40 µg/mL in isooctane), and internal standard (PCB 202, 100 mg/L in isooctane) were purchased from Accustandard (New Haven, CT, USA). Stock standard solution (20 PCB mixtures) and surrogate solution of 1 µg/mL were prepared in cyclohexane, respectively. A 0.1 µg/mL internal standard solution was prepared in cyclohexane. Ceramic homogenizers and dispersive solid phase extraction adsorbent (PSA, C18,  $\text{MgSO}_4$ ) were purchased from Agilent Technologies (CA, USA). Certified reference material of seven PCBs in soil was obtained from Agro-Environmental Quality Supervision & Testing Center, MOA (Tianjin, China).

## Instrument conditions

### GC Conditions

GC system	Agilent 7890A, coupled with an Agilent 7693 autosampler
Column	Agilent HP-5 MS UI (30 m × 0.25 mm, 0.25 µm) (p/n 19091S-433 UI)
Oven temperature	60 °C hold 1 minute, at 40 °C/min to 120 °C, at 5 °C/min to 275 °C
Carrier gas	Helium
Flow rate	1.0 mL/min
Injection port temperature	280 °C
Injection volume	1.0 µL
Injection mode	Splitless, purge on after 1.5 minutes

### MS Conditions

MS system	Agilent 7000C Triple Quadrupole GC/MS System
Ion source	EI
Ionization voltage	70 eV
Ion source temperature	280 °C
Quadrupole temperature	Q1 150 °C Q2 150 °C
Interface temperature	280 °C
Solvent delay	10.0 minutes

Table 1 gives the retention time and MRM transition parameters for the selected PCB congeners.

### Sample preparation

Soil used in the recovery experiment was collected from an agriculture field in Tianjin, China. The soil was air-dried at room temperature, ground, and sieved through a 2-mm mesh. The physicochemical properties of the soil were as follows: pH 7.53, 1.53 % organic matter, 16.72 % clay, 43.25 % sand, and 39.71 % silt.

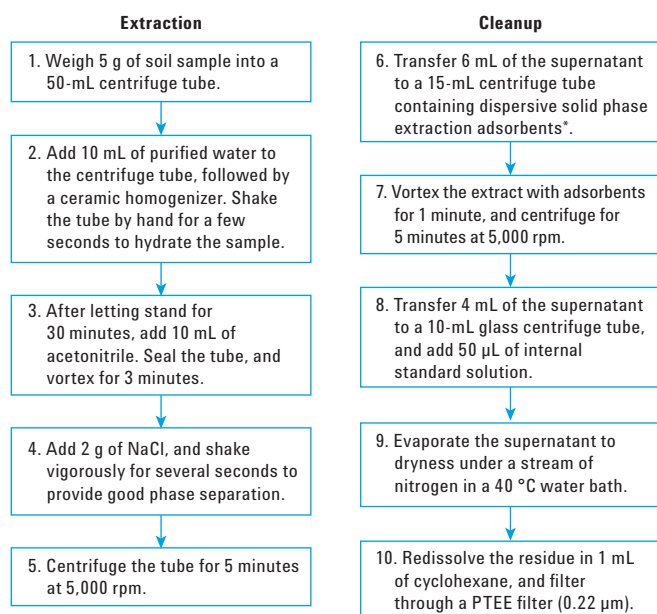
Table 1. Retention Time and MRM Transition Parameters for the Selected PCB Congeners

Compound	$t_R$ (min)	MRM1	CE	MRM2	CE	MRM3	CE
PCB28	17.75	256 → 186	25	258 → 188	25	258 → 186	25
<sup>13</sup> C <sub>12</sub> -PCB52 <sup>a</sup>	19.05	232 → 162	40	232 → 197	30	304 → 269	15
PCB52	19.06	290 → 220	25	292 → 222	25	292 → 220	25
PCB95	21.46	326 → 256	25	328 → 256	30	326 → 291	15
PCB91	21.69	326 → 256	25	328 → 256	25	326 → 291	15
PCB101	22.31	326 → 256	30	328 → 256	30	326 → 254	30
PCB136	23.53	360 → 290	30	362 → 290	30	360 → 288	30
PCB77	23.63	290 → 220	25	292 → 222	25	220 → 150	35
PCB149	24.51	360 → 290	30	362 → 290	30	360 → 325	15
PCB118	24.57	326 → 256	30	328 → 256	30	326 → 254	30
PCB114	24.97	326 → 256	25	328 → 256	25	326 → 254	25
PCB153	25.39	360 → 290	25	362 → 290	25	360 → 288	25
PCB105	25.52	326 → 256	30	328 → 256	30	326 → 254	30
PCB176	26.16	394 → 324	25	396 → 324	25	396 → 326	25
PCB138	26.37	360 → 290	30	360 → 325	15	362 → 290	30
PCB183	27.14	394 → 324	30	396 → 326	30	396 → 324	30
PCB167	27.36	360 → 290	25	362 → 290	25	360 → 288	30
PCB202 <sup>b</sup>	28.10	428 → 358	30	430 → 360	30	430 → 358	30
PCB157	28.35	360 → 290	30	362 → 290	30	360 → 288	30
PCB180	28.74	394 → 324	30	394 → 359	15	396 → 326	30
PCB169	29.45	360 → 290	30	362 → 290	30	360 → 288	30
PCB189	30.72	396 → 324	30	396 → 326	30	394 → 324	30

<sup>a</sup> surrogate standard

<sup>b</sup> internal standard

## Optimized extraction and cleanup procedure



\*The Dispersive solid phase extraction adsorbents kits for soil (p/n 5982-5156)

## Results and Discussion

### Method validation

The analytical parameters including linearity, limit of quantitation (LOQ), repeatability, and recoveries were studied under the optimized extraction and cleanup conditions. To determine the method accuracy, a recovery study was carried out, comparing the concentration of each PCB measured by performing the complete procedure with the known concentration fortified to blank soil samples at 0.1, 1, and 10 ng/g in replicates (n = 5). Blank soil samples were preanalyzed to verify the absence of selected PCBs. The matrix-dependent LOQ of the method were determined using spiked blank samples, and defined as the lowest fortified concentrations that produce a signal-to-noise (S/N) ratio above 10. Calibration curves were calculated with standards in solvent at concentrations of 0.1, 1, 5, 10, and 50 ng/mL for each PCB.

Good linearity was obtained for all the PCB congeners within the concentration range of 0.1 to 50 ng/mL, with a coefficient of detection ( $R^2$ ) higher than 0.999. Table 2 shows the results of the recovery experiments for soil under optimized extraction and cleanup conditions.

Table 2. LOQs, Recoveries, and Relative Standard Deviation (RSDs) of Selected PCBs for Soil Spiked at 0.1 ng/g, 1 ng/g, and 10 ng/g

	0.1 (ng/g)		1 (ng/g)		10 (ng/g)		LOQ (ng/g)
	Rec (%)	RSD (%)	Rec (%)	RSD (%)	Rec (%)	RSD (%)	
PCB28	112.9	20.1	108.0	2.0	102.6	5.7	0.02
<sup>13</sup> C <sub>12</sub> -PCB52	105.1	3.7	98.7	2.4	105.5	3.2	0.01
PCB52	115.0	9.0	105.7	1.8	107.8	3.9	0.01
PCB95	108.9	7.9	100.9	1.4	109.6	2.7	0.01
PCB91	108.9	6.0	98.5	2.3	107.7	3.3	0.02
PCB101	116.5	6.7	96.9	1.7	102.3	3.8	0.02
PCB136	114.9	5.2	99.4	0.4	108.9	2.4	0.01
PCB77	94.8	8.7	93.7	1.4	100.7	5.5	0.02
PCB149	105.8	10.2	98.1	0.9	100.1	4.2	0.01
PCB118	95.0	7.3	90.6	0.8	95.3	4.6	0.02
PCB114	93.3	3.4	88.8	1.5	95.9	4.5	0.02
PCB153	99.8	1.9	83.2	3.0	87.1	5.0	0.02
PCB105	115.5	9.8	91.0	5.0	99.9	3.6	0.02
PCB176	110.9	11.5	85.0	2.8	94.7	5.0	0.01
PCB138	117.7	6.1	90.1	5.0	96.1	3.1	0.01
PCB183	96.7	13.6	79.3	2.2	84.1	6.6	0.02
PCB167	80.3	10.7	80.8	5.5	84.6	4.4	0.02
PCB157	98.9	8.7	84.5	2.1	89.2	5.1	0.05
PCB180	89.5	15.8	79.0	2.6	83.0	5.8	0.05
PCB169	92.2	12.2	72.4	3.5	70.1	6.2	0.05
PCB189	83.6	13.1	70.0	2.5	76.2	5.3	0.02

All recoveries at 0.1, 1, and 10 ng/g ranged between 70 and 120 %, with the majority of recoveries greater than 90 % at all concentrations. The precision was satisfactory, with the majority of RSDs below 10 %, which complies with SANCO/12471/2013 [7]. In general, the PCBs with seven chlorine atoms had relatively lower recoveries than those with six or fewer chlorine atoms. The LOQs of these 20 PCB congeners in soil ranged between 0.01 and 0.05 ng/g, which were lower than those previously reported by other authors [8-10]. Table 2 gives the resulting LOQs.

As described above, the performance of the present method was satisfactory, with low LOQs as well as good recovery and precision. Compared with traditional methods such as Soxhlet extraction and accelerated solvent extraction, the proposed method used less organic solvent (only 10 mL of acetonitrile was needed), a shorter extraction time (3 minutes of vortexing), and no special equipment, which made the method simple and environmentally friendly.

### Analysis of certified reference material

Metrological traceability is essential to ensure that measurement results are comparable in time and space [11]. The use of certified reference material (CRM) provides quality assurance in environmental analysis, and makes reliable and tractable analytical results possible. To further test the QuEChERS-based method, we analyzed CRM BW 3714, seven PCBs in soil. The results for the PCB-containing CRM is listed in Table 3. The results obtained by the QuEChERS-based method were in good agreement with the certified value of the CRM. All the results were within the uncertainty range given in the CRM, and good repeatability was obtained.

Table 3. Results from the Analysis of CRM Using the QuEChERS-based Method

PCBs	BW3714		Analysis results	
	Certified value (ng/g)	Uncertainty range (ng/g)	Analyzed value (ng/g)	SD (n = 3)
PCB28	7.36	6.63–8.09	6.80	0.03
PCB52	1.40	1.23–1.57	1.33	0.04
PCB101	1.45	1.32–1.58	1.57	0.07
PCB118	4.56	4.20–4.92	4.79	0.10
PCB153	0.64	0.60–0.68	0.64	0.04
PCB138	0.89	0.78–1.00	0.81	0.04
PCB180	0.23	0.18–0.28	0.23	0.03

### Analysis of real samples

The method was used to analyze 66 soil samples collected from agricultural fields located in different cities in Shandong Province, China. Soil samples 1–16 were collected from rice fields, vineyards, and apple orchards. Samples 17–66 were collected in greenhouses from Shouguang, the largest vegetable base in China, located in east Shandong province. Soil was sampled from the upper layer (0–30 cm), and transported to the laboratory where it was air-dried and sieved through a 2-mm mesh. The soil samples were weighed into a 50-mL centrifuge tube, and 0.5 mL of surrogate (25 ng/mL) was added. The samples were allowed to stand for 24 hours in room temperature before extraction. Nine of the 20 PCB congeners were identified in 16 soil samples, with four of them being marker PCBs (PCB 28, 52, 138, and 153). The detection rates and concentrations of the PCBs were typically low. Only seven samples were found to contain PCB congeners with concentrations higher than the corresponding LOQs. Most of the detected PCBs were at concentrations lower than the LOQs. Compared to the low concentrations of PCBs in agricultural fields, the detection rate and concentrations in the E-Waste site soil were much higher [12-13].

### Conclusions

This application note demonstrates the applicability of the QuEChERS-based procedure, combined with GC/MS/MS for the determination of 20 selected PCBs in soil. Satisfactory validation parameters including linearity, LOQ, and RSD were obtained, demonstrating the feasibility of the method. The method was applied for 66 agricultural soils, and nine of the 20 PCBs were detected at low concentrations. This simple and sensitive method is expected to provide a new chemical analysis method for PCB monitoring and environmental behavior studies in soil.

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