APPLICATION NOTE

Determination of Polychlorinated Biphenyls (PCBs) in water using GC-SQMS

AN177 v2; SCION Instruments

Introduction

Polychlorinated biphenyls (PCBs) were produced in large quantities between 1930 and 1980, typically used in electrical devices and coolant fluids. They were identified as environmental toxic and were banned in the US in 1979, and in 1986, an international agreement banned most uses of PCB's due to environmental concerns. PCBs persist in the environment for long periods of time and can travel over distances through air, water and soil. PCBs are associated with a range of health issues, including skin problems, liver effects and have potential carcinogenic effects on both humans and animals.

PCBs are formed by attaching one or more chlorine atoms to a pair of connected benzene rings, shown in figure 1[1]. Depending on the number and position of the chlorine atoms attached to the biphenyl structure, 209 different PCBs can be formed.

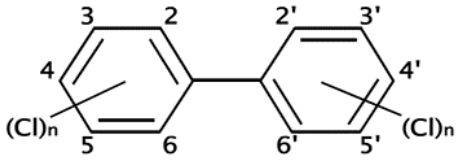

Figure 1 Polychlorinated Biphenyls chemical structure

Different countries have regulations[2] for controlling the usage of PCBs, due to concerns about the environment and health effects. Regulations aim to prevent and protect people from adverse effects, minimize releases and ensuring cleaner ecosystems. Regulations accelerate the removal of PCBs by strict controls on their use, storage and disposal.

Testing PCBs is very important because it ensures compliance with disposal and cleaning requirements. This can contribute in preventing leakages into the environment. Regular testing gives information about the PCB levels in air, water and soil. Monitoring PCBs determines which actions could be taken to control the contamination.

This application can be performed on either the SCION Instruments 8300 GC & 8500 GC (Figure 2) platform with an 8700 SQMS and the SCION 8400PRO Autosampler. A SCION-5MS column is used for obtaining the best separation of the PCB components.

MS-SQ is used for the identification of the components, using the built in NIST library search tool.

Experimental

For this application a PCB standard and an Internal standard was purchased for the qualification and the quantification of the unknown samples. The PCB standard contains 15 PCB compounds with a concentration of 10 µg/mL. The internal standard contains 2 components of 1000 µg/mL: Decachlorobiphenyl and Tetrachloro-m-xylene (TCMX), the used internal standard is decachlorobiphenyl.

Table 1: Instrumentation operating conditions GC and SQMS

GC Part	Settings
Injector	240°C Split program, Initial: 50:1, 0.01 min: off, 0.50 min: 50:1 Pressure pulse: 20 psi, 0.5 min
Injection Volume	2.0 µL
Column	SCION-5MS 30m x 0.25mm x 0.25µm
Carrier Gas	Helium 1 mL/min
Oven Program	80°C (hold 2.0 min), 20°C/min to 325°C (hold 1.25 min)
Run Time	15.50 min
Software	MSWS
MS Part	**Settings**
MS transfer line temp	275°C
Ion source temp	300°C
MS mode	Electron Ionization
Delay collection time	8.5min
Scan mode	SIM mode

Figure 2 SCION Instruments 8300 & 8500-GC and 8700 SQMS and 8400PRO Autosampler.

Sample preparation

A calibration set from the PCB standard (Table 2) diluted with iso-octane is prepared at 6 levels ranging from 0.0005 µg/mL up to 0.005 µg/mL for the linearity. For the repeatability calibration standard 4 is used with a concentration of 0.0025 µg/mL. Decachlorobiphenyl (0.003 µg/mL) is used as an internal standard (IS) and added to all the standards and samples.

Table 2: Components and CAS numbers of the PCB-standard.

No.	Compound	CAS Number	Quantifier Ion and Qualifier Ions
1	2,2',5-Trichlorobiphenyl	37680-65-2	186/256/258
2	2,3,3'-Trichlorobiphenyl	38444-84-7	186/258/265
3	2,4,4'-Trichlorobiphenyl	7012-37-5	186/256/258
4	2,4',5-Trichlorobiphenyl	16606-02-3	186/256/258
5	2,2',3,5'-Tetrachlorobiphenyl	41464-39-5	220/290/292
6	2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	220/290/292
7	2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	324/326/328
8	2,3,3',4,4'-Pentachlorobiphenyl	32598-14-4	324/326/328
9	2,3',4,4',5-Pentachlorobiphenyl	31508-00-6	324/326/328
10	2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	358/360/362
11	2,2',3,4',5',6-Hexachlorobiphenyl	38380-04-0	290/360/362
12	2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	145/360/362
13	2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6	324/394/396
14	2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	394/396/398
15	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	35694-08-7	179/358/428

Tap water samples were prepared in triplicate by an extraction of 50 mL tap water with 10 mL iso-octane containing 0.003 µg/mL IS. The solution was stirred for 15 minutes with a magnetic stirrer two layers appeared. The top (organic) layer is transferred into a sample container and afterwards concentrated under N_2-gas until approximately 1 mL is left. The extract is inserted into an injection vial and ready for analysis.

For determining the recovery, six water samples were prepared the same way as the water sample above and spiked with 0.0005 µg/mL PCB standard prior to extraction. These spiked samples are used to determine the LOQ of the method accordance with EPA regulations[2].

Blank injections of iso-octane are performed in between samples, to ensure that the system is not contaminated after sample injections.

Results

Because there are so many components present in this standard and method, not all components will be mentioned in the Results section.

If necessary, the full validation report is accessible by request. Selected compounds for showing results are PCB compounds that were found in the sample. 2,2',5-Trichlorobiphenyl (#1), 2,3,3'-Trichlorobiphenyl (#2), 2,2',4,5,5'-Pentachlorobipheny l(#7), 2,3,3',4,4'-Pentachlorobiphenyl (#8), 2,2',3,4,4',5'-Hexachlorobiphenyl (#10),

The calibration curves for the PCB standards were prepared at 6 levels from 0.0005 µg/mL up to 0.005 µg/mL.

The system precision of the method was obtained by nine consecutive injections of PCB standard (#4) (0.0025 µg/mL).

The results of the precision of the selected PCB compounds can be found in Table 3, along with the linearity results (R^2) obtained from the calibration curves.

Table 3: Summary of Results – Linearity and repeatability

No.	Component	R^2	Repeatability (%RSD)
1	2,2',5-Trichlorobiphenyl	0.995	2.20
2	2,3,3'-Trichlorobiphenyl	0.996	1.94
7	2,2',4,5,5'-Pentachlorobiphenyl	0.996	2.59
8	2,3,3',4,4'-Pentachlorobiphenyl	0.993	2.94
10	2,2',3,4,4',5'-Hexachlorobiphenyl	0.986	3.16

For all PCB components an R^2 of 0.986 or higher was achieved, which is an excellent result, with many regulations requiring an R^2 value of ≥0.98.

Repeatability results show that for most PCB components the relative standard deviations (RSD%) are below 4%. This is a good precision for the method, since most acceptance criteria for PCB method validation require an RSD ≤15%[3].

2,2′,5-Trichlorobiphenyl

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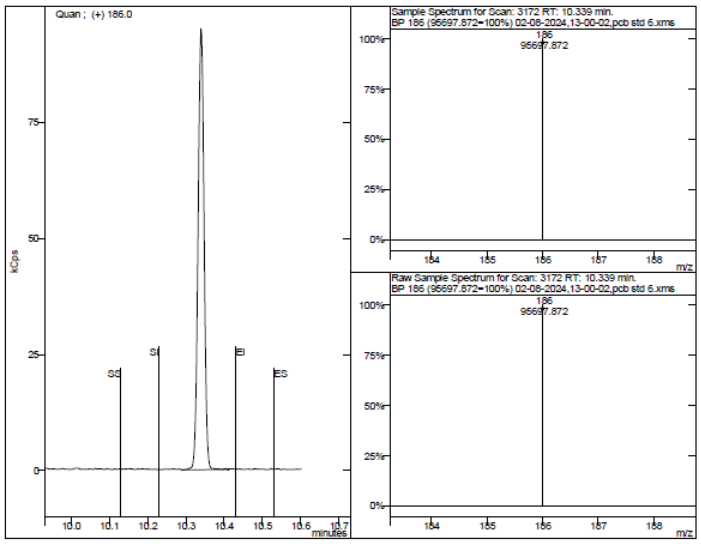
Sample ID:	PCB std 6	Operator:	LR
Instrument ID:	GC-MS	Last Calibration:	13/08/2024 14:30
Measurement Type:	Area	Calibration Type:	Internal Standard
Acquisition Date:	02/08/2024 13:01	Data File:	...-00-02,pcb std 6.xms
Calculation Date:	13/08/2024 14:30	Method:	...ity calc with is.mth
Sample Type:	Calibration		
Inj. Sample Notes:	None		

Compound Information

Peak Name: 1,1'-Biphenyl, 2,2',5-trichloro-
Result Index: 3 Compound Number: 2 CAS Number: 37680-65-2 Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	10.330 +/- 0.200	10.340 min.	Pass
Match Result		N/A	
Qual. Ion Ratio (2 ions)	m/z 258.0:62.6%	42.6%- 82.6% 47.6%	Pass
	m/z 256.0:64.5%	44.5%- 84.5% 50.5%	Pass



2,2′,3,4′,5′,6-Hexachlorobiphenyl

Print Date: 13 Aug 2024 14:48:53 — Target Compound Report for #9 from ...2024,13-00-02,pcb std 6.xms - Page 9

Sample ID:	PCB std 6	Operator:	LR
Instrument ID:	GC-MS	Last Calibration:	13/08/2024 14:30
Measurement Type:	Area	Calibration Type:	Internal Standard
Acquisition Date:	02/08/2024 13:01	Data File:	...-00-02,pcb std 6.xms
Calculation Date:	13/08/2024 14:30	Method:	...ity calc with is.mth
Sample Type:	Calibration		
Inj. Sample Notes:	None		

Compound Information

Peak Name: 2,2',3,4',5',6-Hexachlorobiphenyl
Result Index: 9 Compound Number: 8 CAS Number: 38380-04-0 Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	12.610 +/- 0.200	12.607 min.	Pass
Match Result		N/A	
Qual. Ion Ratio (2 ions)	m/z 362.0:77.6%	57.6%- 97.6% 79.3%	Pass
	m/z 290.0:88.8%	68.8%- 108.8% 101.6%	Pass

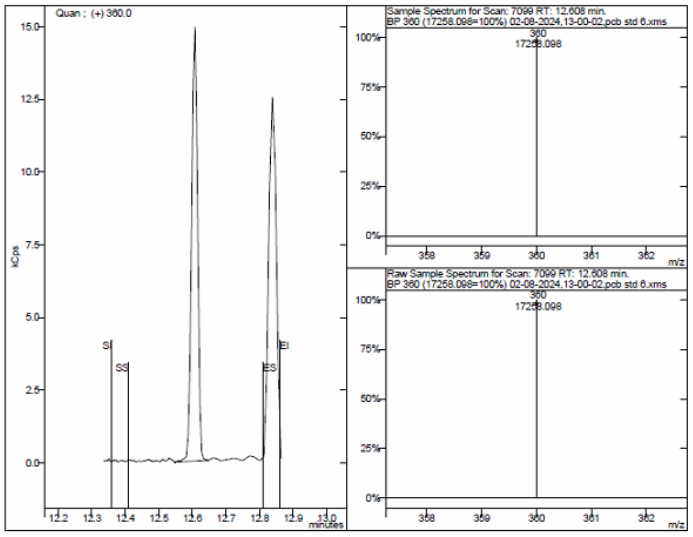


Figure 3: Example report spectra showing SIM mode of selected peaks from PCB standard

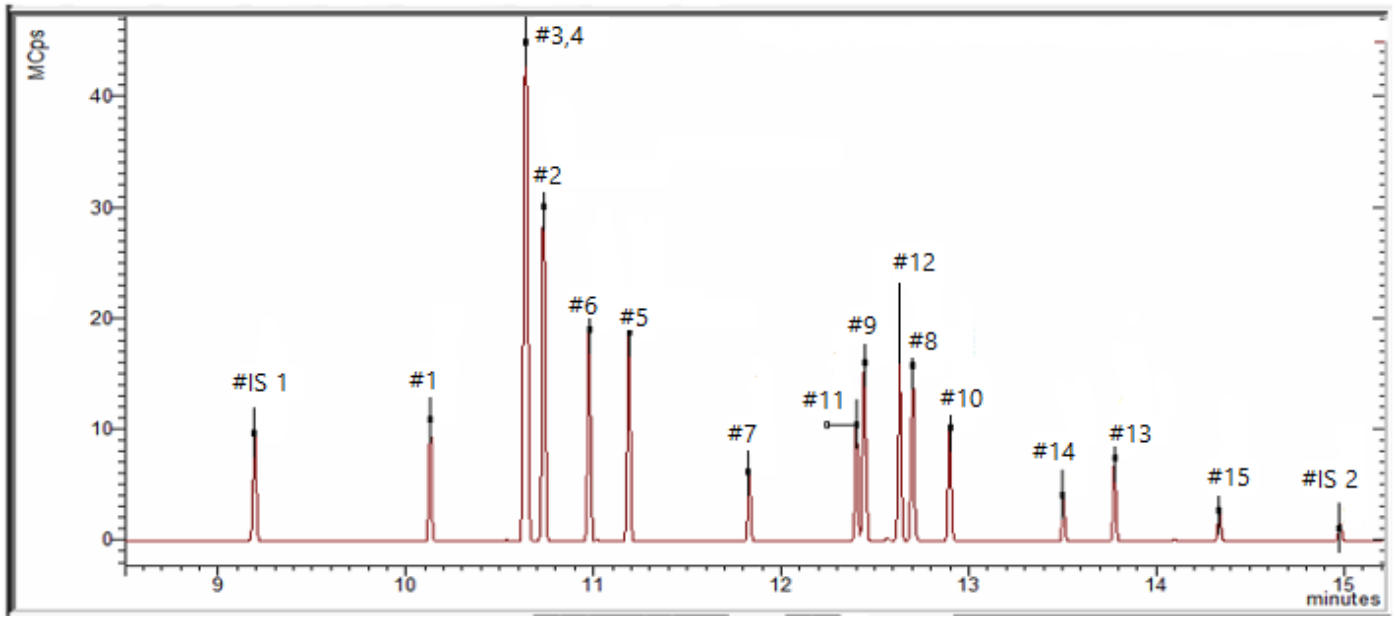


Figure 4: Example Total Ion Chromatogram (TIC) of PCB standard + Internal Standard

The TIC shown in figure 4 shows good separation of the PCBs + IS in MSWS. Except for peak 2,4',5-Trichlorobiphenyl and peak 2,4,4'-Trichlorobiphenyl are not separated and identified as a mixture of 2.

Figure 3 shows an example chromatogram from MSWS of the peaks 2,2',5-Trichlorobiphenyl and 2,2',3,4',5',6-Hexachlorobiphenyl and their corresponding mass spectra.

Table 4: Summary of Results – Recovery

No.	Component	Water sample (µg/mL)	Spiked water sample (µg/mL)	Recovery (%)	RSD (%)
1	2,2',5-Trichlorobiphenyl	n.d.	0.00046	92	4.45
2	2,3,3'-Trichlorobiphenyl	n.d.	0.00049	97	4.15
7	2,2',4,5,5'-Pentachlorobiphenyl	n.d.	0.00050	113	7.37
8	2,3,3',4,4'-Pentachlorobiphenyl	n.d.	0.00050	87	3.83
10	2,2',3,4,4',5'-Hexachlorobiphenyl	n.d.	0.00050	115	6.80

n.d. = not detected

The water sample was prepared with (n=6) and without (n=3) spiked PCB standard to determine the recovery. The results (table 4) indicate that none of the PCB components were detected in the water sample. The recovery percentages for the spiked samples ranged from 87% to 131%, with repeatability (RSD) values between 3.83% and 7.47% demonstrating good method efficiency and reliability.

Conclusion

The SCION 8500 GC platform equipped with a split/spitless injector, SCION 5MS column and 8700 SQMS and 8400PRO sampler is a perfect solution for analysing PCBs in water for qualitative and quantitative analysis. Good system precision, linearity, results and recovery results are achieved for this application. The LOQ of 0.0005 ppm according to EPA regulations[2] was achieved with the spiked recovery sample, confirming good working of the method.

The results were achieved with the SCION Instruments GC-MS set up and MS-Work Station software. The SCION-5MS column shows good separation between the PCBs.

The analysed water sample is, according to multiple results obtained by this application, most likely water that has not been exposed to PCBs.

References

1. Polychlorinated Biphenyls (PCBs) | Biomonitoring California https://biomonitoring.ca.gov/chemicals/polychlorinated-biphenyls-pcbs (Accessed 13-08-2024)

2. National Primary Drinking Water Regulations | US EPA https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations (Accessed 13-08-2024)

3. HJ 743-2015 English PDF (chinesestandard.net) https://www.chinesestandard.net/PDF/English.aspx/HJ743-2015 (Accessed 16-08-2024)

Order Information

Ordering Information for the 8300 GC	
Part	**Part Number**
8300 GC with 8700-MS-SQ EI Select, with S/SL inlet (120V)	SCIONSQ83SEL311
8300 GC with 8700-MS-SQ EI Select, with S/SL inlet (230V)	SCIONSQ83SEL312
8400 PRO Autosampler for 8300 GC and 8500 GC	840000001
MS WorkStation Software	394195791
NIST 20 MS Library and Search Program for MSWS	4121057

Suggested Consumables	
Part	**Part number**
15% Graphite/85% Vespel Ferrule 1/16" with 0.4 mm hole pk/10	41312148
BTO Septa 9 mm, pk/50	CR298713
10µL fixed needle syringe, 5 cm, 0.47 mm OD, 26 g conical needle	41312133
SCION-5MS column 30m x 0,25mm x 0,25 µm	SC32223
1177 4mm SPLT LINER / FRT-SILTEK PK/5EA	RT210462145

SCION offers other MS options such as the 8700 SQ Premium and 8900 TQ, as well as additional spectral libraries such as Designer Drugs and Wiley, please contact your local SCION sales representative to discuss your needs.

For more information, please contact:

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W: www.scioninstruments.com