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Application News

No. GC-2201

Gas Chromatography

Enhanced GC Analysis of Polychlorinated Biphenyl Congeners with Nexis GC-2030 Equipped with AOC-30i Autosampler

■ Abstract

In this study, we demonstrated the performance of the AOC-30i in combination with the Nexis GC-2030 for the analysis of polychlorinated biphenyl (PCB) congeners. Superior repeatability and minimal carryover were achieved by the automatic internal standard addition and flexible solvent wash capabilities of the AOC-30i. A method with a run time of 11 min was developed. Results showed excellent accuracy and resolution. Demonstrated method performance together with the user-friendly features and tool-free maintenance of the Nexis GC-2030 enabled higher throughput for analyzing PCBs in environmental samples.

■ Introduction

Polychlorinated biphenyls (PCBs) are a group of highly toxic compounds that were widely used in electrical equipment and plasticizers for decades until they were banned by the Environmental Protection Agency (EPA) in 1979. Because of PCBs' high persistence, clean-up efforts to mitigate their contamination are still on-going. A common monitoring method is EPA 8082A, in which PCBs can be determined in the form of individual congeners or Aroclors [1]. When determined as congeners, internal standard quantification is recommended. In this work, we aimed to develop an enhanced method for the analysis of PCB congeners that meets performance outlined in EPA 8082A while utilizing the latest advancements in GC technology.

■ Materials and Methods

Reagents

ECD grade hexane was purchased from Sigma (Cat. No. 1043711000). The internal standard (IS) stock solution (PCB209/decachlorobiphenyl, Cat. No. 32289) and PCB congener mix (32416) were purchased from Restek. The standards were then diluted in hexane to required working concentrations. PCB-free transformer oil was purchased from Fluids Inc. (HYVOLT II inhibited).

Sample Preparation

Sample dilution and clean up were carried out based on EPA methods 3580A [2] and 3665A [3]. PCB-free transformer oil spiked with PCBs was placed in a glass vial with a Teflon-lined cap, 5 mL hexane were added to the vial and mixed with the oil. Then approximately 1 mL of concentrated sulfuric acid was added to the vial. The vial was capped and vortexed to aid digestion of the oil. The acid layer and hexane layer were then allowed to separate, and the hexane layer was carefully removed and transferred to a clean vial to be used for GC analysis.

Instrumentation

A Shimadzu Nexis GC-2030 with split/splitless injector, ECD Exceed detector and AOC-30i autosampler was used for analysis of PCBs according to EPA method 8082A using helium carrier gas. Analytical conditions are outlined in Table 1. Shimadzu LabSolutions software was used for data acquisition and processing.

Table 1: Instrument Configuration and Analytical Conditions

GC system	Shimadzu GC-2030 with SPL, ECD-2030 Exceed and AOC-30i autosampler
Column	SH-Rxi-5ms, 15 m x 0.25 mm x 0.25 µm
Injector Mode	Split at 1:5 ratio
Injection Volume	0.5 µL sample + 0.5 µL internal standard
Carrier Gas	Helium
Flow mode	Constant initial linear velocity of 40 cm/sec
Column Temp	100 °C, 0min – 40 °C/min – 200 °C, 2min – 20 °C/min – 290 °C, 2min
Injection Port Temp	250 °C
Detector Temp and Current	320 °C, 2nA
Detector Gases	N_2 45 mL/min

■ Results and Discussion

Using the GC-2030, a mixture of PCB congeners was analyzed using helium carrier gas. EPA method 8082A provided example analysis conditions of 19 congeners along with internal standard (IS) PCB 209 (decachlorobiphenyl), but the elution of the last compound (PCB 209) took more than 32 min [1]. In this study, we modified analysis conditions to allow all compounds to elute in under 10 min. Results discussed in the subsequent sections demonstrate the system suitability of the Shimadzu Nexis GC-2030 equipped with an AOC-30i and ECD Exceed in accordance with the quality assurance and quality control criteria outlined in EPA method 8082A.

1) Benefits from improved system configuration

Shimadzu Nexis GC-2030 with autosampler AOC-30i was chosen for this analysis to maximize automation of the assay. Both the GC and the autosampler can be fully controlled by LabSolutions software.

AOC-30i can hold up to 30 samples by itself, and up to 150 samples with the expandable tray (Figure 1), and up to twelve 4-mL vials for solvents. Therefore, a large number of samples can queue up and run without human intervention. Furthermore, the use of IS is highly recommended for congener analysis and can be added automatically to samples right before injection by the autosampler.

To minimize potential carryover, three different solvents with varying polarities (acetone, toluene, and hexane) were used to rinse the syringe post-injection. AOC-30i can accommodate up to four different solvents and the order and number of washes are highly customizable (Figure 1). There are also preset injection and wash programs to simplify method development.

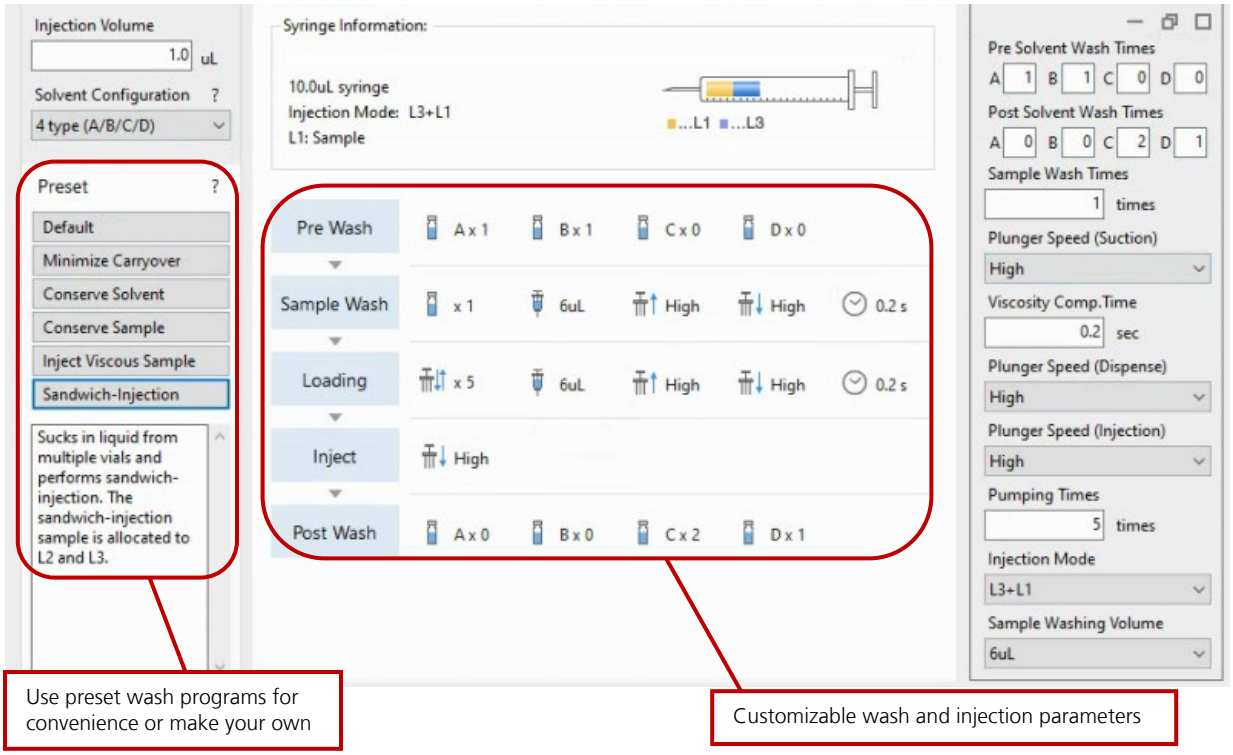

Figure 1: AOC-30i autosampler with AOC-20s U sampler tray and Sampler Navigator window of autosampler AOC-30i in LabSolutions.

2) Chromatographic runs

Faster GC runs enable laboratories to process more samples in the same amount of time. A shorter column coupled with a faster oven ramping method was utilized to elute all 19 PCB congeners listed in EPA method 8082A along with the internal standard in under 10 min. Despite the fast run (approximately three times faster than the original EPA 8082A [1]), only two congeners (PCB 187 and PCB 183) out of the 19 targets partially co-eluted. Partial overlap did not affect the quantification of these two congeners in accordance with EPA quantification guidelines.

Figure 2 shows the chromatogram of PCB congeners at 100 µg/L of each with the IS. The IS (PCB209, decachlorobiphenyl) was added by the AOC-30i when drawing samples, prior to analysis (Figure 1). The relative standard deviation (RSD) of the internal standard peak area was less than 5% (n = 14).

Insert in Figure 2 demonstrates the excellent reproducibility of the IS peak area, achieved by minimizing human error and potential solvent loses while samples are in the autosampler rack waiting for analysis. Additionally, the automatic addition of the internal standard may help in decreasing standards' use and waste.

A resolution requirement is not specified in EPA method 8082A. Since the GC run was shortened significantly compared to the original EPA method, the peak resolution was examined. All peaks are well separated (resolution > 2) except for PCB 187 and 183 (resolution = 1.0) which can be seen in Table 2. Despite the lack of baseline resolution for this congener pair, quantification was not affected, as shown by the calibration.

3) Calibration Curve

Six-point calibration curves in solvent were constructed for each PCB congener in the mix using the internal standard quantification method. The data were fitted quadratically with 1/A weighting. Coefficients of determination were calculated for all target analytes. As shown in the results in Table 2, fittings with r^2> 0.998 were obtained for all analytes. With this calibration, all concentrations presented a relative error of within ±13% of expected values (Table 3). Although EPA 8082A does not include specific criteria for assessing the quality of the calibration curve, the approach outlined in the TNI Guidance on Instrument Calibration was followed in this work [4]. Accuracy with weighting exceeded that of concentrations calculated with a curve without weighting (difference with expected concentration of up to 40%; data not shown).

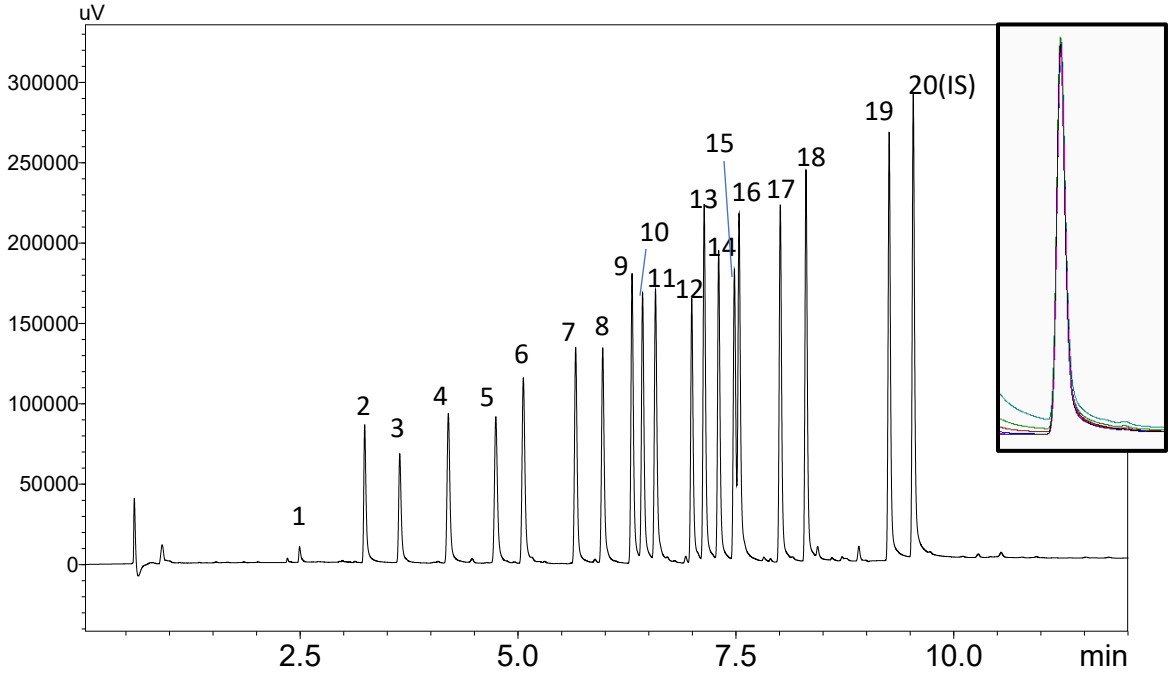

Figure 2: Chromatograms of 100 µg/L PCB congener mix. Inset: overlay of IS peaks in 10 -500 µg/L standard.

Table 2: Retention time, peak resolution, and coefficient of determination (r^2) of the calibration curves.

Peak No.	Compounds	RT (min)	Resolution (100 µg/L)	r^2
1	PCB1	2.495	n.a.	0.998
2	PCB5	3.242	17.427	1.000
3	PCB18	3.646	8.258	0.999
4	PCB31	4.203	10.107	0.999
5	PCB52	4.748	9.054	0.998
6	PCB44	5.065	5.171	0.999
7	PCB66	5.665	10.474	0.999
8	PCB101	5.974	5.699	0.999
9	PCB87	6.311	6.351	0.999
10	PCB110	6.433	2.337	0.999
11	PCB151	6.580	2.795	0.999
12	PCB153	6.996	8.053	0.999
13	PCB141	7.141	2.867	0.999
14	PCB138	7.307	3.300	0.999
15	PCB187	7.487	3.547	0.998
16	PCB183	7.540	1.012	0.999
17	PCB180	8.013	9.358	0.999
18	PCB170	8.308	6.011	0.999
19	PCB206	9.277	7.403	0.999
20	PlCB209(IS)	9.604	5.684	n. a.

Table 3: Calibration curve accuracy: % recovery of measured concentrations from expected concentrations.

Expected conc.	10 ppb	20 ppb	50 ppb	100 ppb	200 ppb	500 ppb
PCB1	95.2%	98.2%	112.4%	103.0%	94.3%	101.5%
PCB5	96.6%	100.0%	103.2%	100.7%	98.5%	100.2%
PCB18	87.3%	106.6%	106.3%	102.8%	95.9%	100.8%
PCB31	92.9%	100.7%	105.0%	104.0%	96.0%	100.7%
PCB52	90.9%	99.7%	107.5%	105.0%	94.8%	101.0%
PCB44	97.0%	98.3%	102.4%	105.1%	96.2%	100.6%
PCB66	95.2%	95.9%	107.7%	104.2%	95.5%	100.8%
PCB101	93.0%	98.9%	106.4%	103.9%	95.8%	100.7%
PCB87	92.3%	99.9%	105.8%	104.5%	95.5%	100.8%
PCB110	92.2%	100.8%	105.5%	104.0%	95.8%	100.7%
PCB151	89.9%	102.3%	106.4%	104.2%	95.4%	100.8%
PCB153	91.0%	100.7%	106.2%	104.3%	95.5%	100.9%
PCB141	96.7%	99.0%	101.8%	105.1%	96.4%	100.5%
PCB138	92.1%	100.6%	105.8%	103.7%	96.0%	100.7%
PCB187	88.9%	101.6%	107.3%	104.5%	95.1%	101.0%
PCB183	93.1%	101.8%	104.3%	102.5%	97.0%	100.5%
PCB180	91.6%	102.3%	104.9%	103.4%	96.3%	100.6%
PCB170	95.4%	98.7%	104.4%	103.7%	96.5%	100.5%
PCB206	92.3%	97.7%	107.4%	104.7%	95.3%	100.7%

4) Recovery of spiked oil sample

The recovery of PCB-free transformer oil spiked with PCB congeners was evaluated. Sample was diluted and cleaned up per EPA method 3580A [2] and 3665A [3] as described in the Materials and Methods section. Same as for the preparation of the calibration curve, the IS (PCB209, decachlorobiphenyl) was added automatically by the autosampler (AOC-30i) prior to sample analysis.

Figure 3 shows the chromatograms of mineral oil spiked with 5 µg/g of each PCB congener. This is equivalent to a 100 µg/L concentration in hexane, assuming 100% recovery. Smaller area peaks in the oil sample suggest matrix suppression or limited extraction efficiency.

Triplicated injections of the oil extracted sample were run and the concentration of each PCB congener was determined. A contamination peak from oil coeluted with PCB1; hence, quantification of PCB1 was not feasible. Recovery, calculated based on the concentration spiked (5 µg/g), ranges from 70% to 94% with repeatability under 6%, as shown in Table 4. EPA method 8082A refers to EPA method 8000D [5] for quality control criteria. Despite the lack of surrogate or use of matrix matched calibration, the recovery of matrix spiked samples is within the acceptable range outlined in EPA 8000D (70-130%).

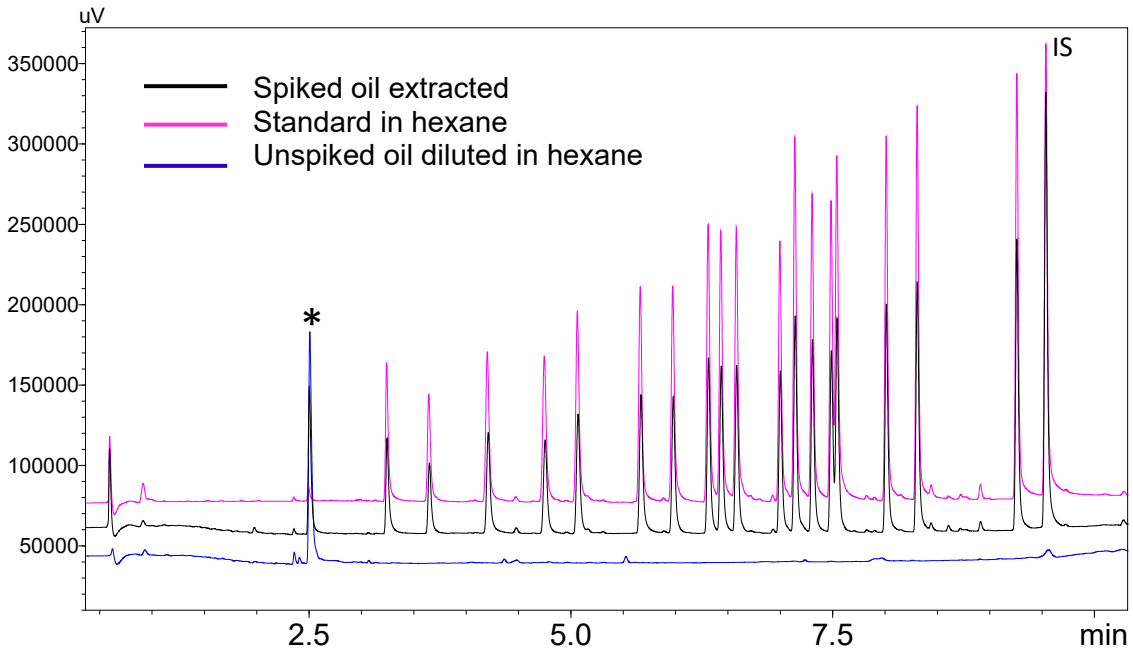

Figure 3: Chromatograms of 100 µg/L PCB congener mix in hexane (pink) and spiked oil standard (black). IS was automatically added to both injections. (*)peak present in oil, which coelutes with PCB1.

Table 4: Recovery of PCB congeners from oil sample spiked with a 5 µg/g standard mix.

Compounds	Average concentration (ppm)	% RSD (n = 3)	Recovery
PCB1	n. a.	n. a.	n. a.
PCB5	4.70	5.67%	94%
PCB18	4.14	4.27%	83%
PCB31	4.44	3.35%	89%
PCB52	3.97	3.42%	79%
PCB44	3.89	3.59%	78%
PCB66	4.34	4.88%	87%
PCB101	3.84	3.43%	77%
PCB87	3.85	2.08%	77%
PCB110	3.81	1.78%	76%
PCB151	3.51	0.98%	70%
PCB153	4.01	1.92%	80%
PCB141	3.74	1.42%	75%
PCB138	3.88	1.75%	78%
PCB187	3.83	1.61%	77%
PCB183	3.48	1.16%	70%
PCB180	3.85	0.88%	77%
PCB170	3.91	0.83%	78%
PCB206	4.03	1.25%	81%

■ Conclusion

Shimadzu Nexis GC-2030 with AOC-30i autosampler was employed to analyze PCB congeners. The results obtained demonstrated the excellent performance and robustness of the system. AOC-30i is capable of automatically adding internal standards to samples during injection with excellent repeatability. The autosampler also has flexible solvent wash settings that can help minimize carryover issues. Furthermore, the footprint of AOC-30i is much smaller compared to other advanced autosamplers with these functions. In addition, two AOC-30i with or without an expanded sampler tray can be installed on one GC. Therefore, it's possible to double the throughput by simultaneously analyzing two samples at the same time. Up to 30 samples can be injected by each AOC-30i without the sampler tray and up to 150 samples can be queued with the expanded sampler tray. With outstanding repeatability, large and expandable sample capacity, flexible washing cycles and internal standard addition automation, AOC-30i is an ideal autosampler for complex analyses such as PCBs. Analysis of PCBs as Aroclors is demonstrated in a separate application note [6].

In this work, the GC run time was shortened by three-fold with a modified column and oven program, while maintaining excellent accuracy and resolution. Up to 8 samples could be analyzed per hour with a dual-line setup. And with Shimadzu's Xtra life inlet septum, up to 1000 injections could be made without stopping to perform maintenance, further decreasing downtime, and increasing throughput.

Other features of the GC-2030, such as its user-friendly interface and tool-free inlet maintenance, allow analysts, even inexperienced ones, to quickly implement robust workflows. Nexis GC-2030 with AOC-30i is the perfect workhorse for routine analysis, not just analysis of PCBs, in environmental labs.

■ References

1. *SW-846 Test Method 8082A, Polychlorinated Biphenyls (PCBs) by Gas Chromatography, EPA (2007).*
2. *SW-846 Test Method 3580A, Waste Dilution, EPA (July 1992).*
3. *SW-846 Test Method 3665A, Sulfuric Acid/Permanganate Cleanup, EPA (December 1996).*
4. *TNI Guidance on Instrument Calibration, GUID-3-110-Rev0, NELAC Institute, (December 2018).*
5. *SW-846 Test Method 8000D, Determinative Chromatographic Separations, EPA (2018).*
6. *Fast Analysis of Polychlorinated Biphenyls (PCBs) as Aroclors in Transformer Oil with Nexis GC-2030 Equipped with Autosampler AOC-30i. Shimadzu Scientific Instruments Application News (2022)*

■ Consumables

Part Number	Description	Unit	Instrument
227-35511-01	Xtra life inlet septa, red	Pk of 25	GC-2030
227-35007-01	Split Liner with Wool, GC-2030	Pk of 5	
221-32126-05	Graphite ferrules, for 0.25mm-0.32mm ID columns	Pk of 10	
221-34618-00	Syringe, 10 µL, fixed needle	each	AOC-30i
220-97331-31	Sample Vials, 1.5 mL Amber Glass with Caps & Septa	Pk of 100	
220-97331-47	Sample Vials, 1.5 mL Amber Glass with Caps & Septa	Pk of 1000	
220-97331-62	200 µL Glass Inserts for 1.5mL Vials	Pk of 100	
REST-23096	Rinse/Waste Vials with Diffusion Caps	Pk of 12	
221-75940-15	SH-I-5MS Capillary Column, 15 x 0.25 x 0.25	each	Column

First Edition: April 2022

SHIMADZU Corporation
www.shimadzu.com/an/

SHIMADZU SCIENTIFIC INSTRUMENTS
7102 Riverwood Drive, Columbia, MD 21046, USA
Phone: 800-477-1227/410-381-1227, Fax: 410-381-1222
URL: www.ssi.shimadzu.com