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

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1. 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 PCBs congeners that meets performance outlined in EPA 8082A while utilizing the latest advancements in GC technology.

2. Experimental

A Shimadzu GC-2030 with split/splitless injector (SPL), electron capture detector (ECD-exceed) and AOC-30i autosampler were used for this analysis. Analytical conditions are outlined in Table 1.

PCB-free transformer oil spiked with PCBs was diluted and cleaned up based on EPA method 3580A [2] and 3665A [3], then used for GC analysis.

Internal standards were automatically added by AOC-30i autosampler just before GC injections.

Shimadzu LabSolutions software was used for data acquisition and processing.

Table 1: Instrument Configuration and Analysis Conditions

GC system	Shimadzu Nexis GC-2030 with SPL, ECD-exceed, AOC-30i autosampler
Column	SH-1, 15 m x 0.25 mm x 0.25 µm
Column Temp	100 °C ramp to 200°C at 40 °C/min, hold 2min, then ramp to 290 °C at 20 °C/min, hold 2 min
Injection	0.5 µL sample + 0.5 µL internal standard
Injection mode	Split at 1:5 ratio
Carrier Gas	He
Flow mode	Constant linear velocity of 40 cm/sec
ECD Detector	320 °C, 2 nA, N_2 makeup at 45 mL/min

3. Results and Discussion

3.1. 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 GC and 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 be queued up and run without human intervention. Furthermore, the use of internal standard (IS) is highly recommended for congener analysis and can be added automatically to samples right before injection by the autosampler.

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. To minimize potential carryover, three different solvents with varying polarities (acetone, toluene, and hexane) were used to rinse the syringe post-injection in this analysis.

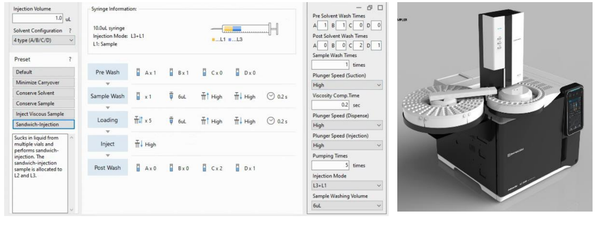

Figure 1: AOC-30i autosampler with AOC-20s U sampler tray and Sampler Navigator window of autosampler AOC-30i in LabSolutions.

3.2. Chromatographic runs

Faster GC runs enables laboratories to process more samples in the same amount of time. A shorter column coupled with faster oven ramping method was utilized to elute all 19 PCB congeners listed in EPA 8082A method along with the internal standard 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 (Figure 2). 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 IS. The IS (PCB209, decachlorobiphenyl) was added by the autosampler AOC-30i when drawing samples, prior to analysis (Figure 1). The relative standard deviation (RSD) of IS peak area was < 5% (n = 14). Inset in Figure 2 demonstrates the excellent reproducibility of the IS peak area.

Calibration curves were fitted quadratically with 1/A weighting. Table 2 shows the coefficient of determination (r^2) from six-point calibration (10 - 500 µg/L) for each congener with IS quantification method. The RSE calculated for all target compounds in each calibration standard ranged between -12.7% and 12.4%.

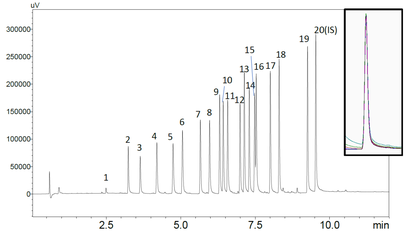

Figure 2. Chromatogram of PCB congener mix. Inset: overlay of IS peaks in 10 - 500 µg/L standard. See right for peak IDs.

Peak #	Compounds	r^2
1	PCB1	0.998
2	PCB5	1.000
3	PCB18	0.999
4	PCB31	0.999
5	PCB52	0.998
6	PCB44	0.999
7	PCB66	0.999
8	PCB101	0.999
9	PCB87	0.999
10	PCB110	0.999
11	PCB151	0.999
12	PCB153	0.999
13	PCB141	0.999
14	PCB138	0.999
15	PCB187	0.998
16	PCB183	0.999
17	PCB180	0.999
18	PCB170	0.999
19	PCB206	0.999
20	PICB209(IS)	n. a.

Table 2. Peak ID and r^2 of calibration for each congener.

3.3. Recovery of spiked oil sample

The recovery of PCB-free transformer oil spiked with PCB congeners was evaluated (Figure 3). Triplicated injections of oil extracted sample were run, and the concentration of each PCB congener was determined. A peak from oil coeluted with PCB1; hence, quantification of PCB1 was not feasible. Recovery ranged from 70% to 94% with repeatability under 6% for all other congeners. The recovery of matrix spiked samples is within the acceptable range outlined in EPA 8000D [4] (70-130%).

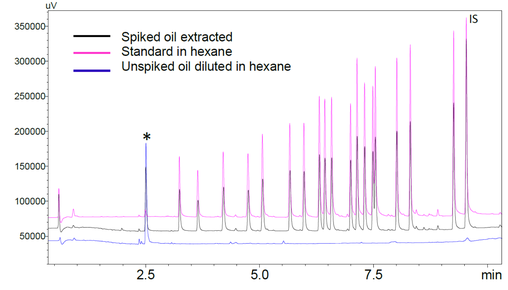

Figure 3. Chromatograms of PCB congener mix (pink) and spiked oil standard (black) at equivalent concentrations. IS was automatically added to both injections. (*) peak present in oil, which coelutes with PCB1.

4. 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, achieved by minimizing human error and potential solvent loses while samples are in the autosampler rack waiting for analysis. Additionally, the automatic addition of internal standard may help in decreasing standards' use and waste. The autosampler also has flexible solvent wash settings that can help minimize carryover issues.

In this work, the GC run time was shortened by three-fold with 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 down time, and increasing throughput.

5. Reference

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. *SW-846 Test Method 8000D, Determinative Chromatographic Separations, EPA (2018).*