Bull. Environ. Contam. Toxicol. (1986) 37:10–17

Bulletin of Environmental Contamination and Toxicology

Effect of Oil Matrix on PCB Quantification

Kay W. Turman,[1] Mitchell D. Erickson,[1]* Phyllis J. Boone,[1] Jairus D. Flora, Jr.,[1] and Daniel T. Heggem[2]

[1]Midwest Research Institute, 425 Volker Boulevard, Kansas City, MO 64110 and [2]Field Studies Branch (TS 798), Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, 401 M Street SW, Washington, DC 20460

Because of its extreme sensitivity and selectivity toward halogenated compounds, the electron capture detector (ECD) has been the most common method for gas chromatographic analysis of polychlorinated biphenyls (PCBs) (ASTM 1983; AOAC 1980a; DCMA 1982; EPA 1982, 1984a; FDA 1977; Erickson 1985). While it is considered a selective detector, ECD can detect many non-PCB compounds (halogenated pesticides, polychlorinated naphthalenes (PCNs), chloroaromatics, phthalate and adipate esters, and other compounds) which may be differentiated from PCBs only on the basis of retention time. In addition, there are other interferences which do not give discrete peaks. Elemental sulfur can interfere with PCB analysis in sediment and other samples which have been subjected to anaerobic conditions. Another non-specific interference is mineral oil (ASTM 1983), a complex mixture of hydrocarbons, which is used as a dielectric fluid. Mineral oil in transformers often contains PCBs as a result of cross-contamination of transformer oils. A typical analysis of mineral oil for PCBs entails simple dilution with hexane to reduce the viscosity and also achieve a concentration in the linear range of ECD (Sonchik et al. 1984). The mineral oil in the diluted sample reduces the ECD response (ASTM 1983). In order to minimize the effects of the mineral oil interference on the quantitation, ASTM (1983) recommends that the sample and standard contain the same amount of mineral oil.

This study reports the effect of the oil concentration in sample extracts on the ECD and the accuracy and precision of this homolog method of analysis. The study was conducted using the Dry Color Manufacturers Association (DCMA) homolog mix, a homolog mix prepared at Midwest Research Institute, and Aroclor 1260 as standard spiking solutions.

MATERIALS AND METHODS

Three standard spiking solutions (Table 1) were prepared in hexane for use in the study: (a) a DCMA congener mix obtained from Supelco, Inc., Bellefonte, PA, (b) an MRI congener mix prepared

* Correspondence and reprint requests.

Table 1. Composition and Retention Time Ranges of Standard Solutions.

Solution Designation	Congener[a] no.	Congener	Spiking amount (µg)	Final concentration (µg/mL)	Retention time range (min)[b]
DCMA	1	2-Mono	5.0	0.50	1.23-1.33
	11	3,3'-Di	5.0	0.50	3.45-3.55
	29	2,4,5-Tri	0.50	0.050	4.25-4.35
	47	2,2',4,4'-Tetra	0.50	0.050	5.85-5.95
	121	2,3',4,5',6-Penta	0.50	0.050	7.40-7.50
	136	2,2',3,3',6,6'-Hexa	0.50	0.050	9.80-9.90
	185	2,2',3,4,5,5',6-Hepta	0.25	0.025	13.25-13.35
	194	2,2',3,3',4,4',5,5'-Octa	0.25	0.025	17.70-17.80
	206	2,2',3,3',4,4',5,5',6-Nona	0.25	0.025	18.85-18.95
	209	Decachlorobiphenyl	0.25	0.025	19.65-19.75
MRI	1	2-Mono	6.4	0.64	1.23-1.33
	3	4-Mono	24.00	2.40	1.70-1.80
	7	2,4-Di	0.60	0.060	2.33-2.43
	30	2,4,6-Tri	0.55	0.055	3.10-3.20
	50	2,2',4,6-Tetra	0.75	0.075	4.65-4.75
	97	2,2',3',4,5-Penta	0.75	0.075	9.25-9.35
	143	2,2',3,4,5,6'-Hexa	0.70	0.070	10.80-10.90
	183	2,2',3,4,4',5',6-Hepta	0.21	0.021	12.80-12.90
	202	2,2',3,3',5,5',6,6'-Octa	0.20	0.020	13.60-13.70
	207	2,2',3,3',4,4',5,6,6'-Nona	0.21	0.021	17.00-17.10
	209	Decachlorobiphenyl	0.11	0.011	19.65-19.75
Aroclor 1260	-	-	250	0.25	9.00-20.00

a Ballschmiter and Zell (1980).
b Measurement windows were determined by manually inspecting a chromatogram for baseline resolution between peaks.

from neat compounds obtained from Ultra Scientific, Inc., Hope, RI, and (c) an Aroclor 1260 solution prepared from neat commercial mixture obtained from the U.S. Environmental Protection Agency, Las Vegas, NV. Mineral oil used in the study was purchased locally (Squibb Control No. 4A825).

Five replicate samples for each of three oil levels were prepared for each standard spiking solution. All replicates were spiked at the same level for each standard spiking solution. Table 1 lists spiking and final concentrations for all compounds. The spiking was performed by adding aliquots of standard spiking solution to containers holding either 5, 0.5, or 0.05 mL oil. As mentioned above, five replicate spikes were prepared at each oil level. Hexane was then added to each sample to achieve a total volume of 10.0 mL. One milliliter concentrated sulfuric acid was added to each sample and the sample was agitated to mix the two phases. The acid was allowed to separate, and 1.0 mL of the hexane layer was removed to a clean vial. To this aliquot, approximately 100 mg Florisil was added and the mixture shaken. A 3.0 µL aliquot was then withdrawn for analysis.

All samples were analyzed by GC/ECD using a Varian Model 3700 equipped with a ^{63}Ni electron capture detector. A glass column, 180 x 0.2 cm (ID), packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) was used for separation. Operating

conditions were 250°C injector temperature, 300°C detector temperature, and nitrogen flow rate of 30 mL/min. The column temperature was held at 150°C for 1.0 min, then programmed at 5°/min to 250°C, then held for 4.0 min. Chromatograms were recorded using both a Nelson Analytical Model 4400 Data System and a Heath Model SR-204 analog strip chart recorder. Calibration curves for the three standard spiking solutions were constructed and used to calculate analyte concentrations in the samples. The samples were quantitated against the corresponding standard solutions at three concentrations using linear regression. The Aroclor 1260 amounts were quantitated using the summed areas of all peaks eluting from 9 to 20 min. The summed areas were compared to total areas for Aroclor 1260 standard solutions within the same measurement window. The levels of individual PCB congeners in the DCMA and MRI standard solutions were determined by comparing total areas in designated retention time ranges to the areas of the congener peak in that retention time range. The congeners' retention time ranges for the DCMA and MRI congener solutions are listed in Table 1.

RESULTS AND DISCUSSION

As reported by ASTM (1983), the mineral oil content of the sample matrix can depress the ECD response and thus yield erroneously low readings. In an attempt to quantitate this phenomenon, samples were prepared as described with different amounts of oil. As shown in Tables 2 and 3, the amounts of the individual congeners found was not dependent on the oil content. Similarly, for the Aroclor 1260, no trend of response depression was found (Table 4).

Analysis of variance was performed to compare the observed concentrations of each isomer of PCB under the four different levels of oil. The results are summarized in Tables 2 and 3. Each table presents the mean observed concentration for each level of oil (0, 0.50, 5.0, and 50%) for each PCB isomer. (Even though only two significant figures are given, all statistical work was performed using four to five significant figures.) The F statistic for testing equality of these means is also presented. The F statistics indicate that there are statistically significant (at the 5% level) differences among the oil levels for most isomers. The p-values presented in the last column indicate the significance of the differences in the values. Unless noted by "NS," all sets contained at least one oil level which was significantly (at the 0.05 level; i.e., 95% confidence) different from the others.

While differences in means exist, they did not correlate with the amount of oil. The pattern of response observed was for the 0% oil level to show the highest concentration, followed by the 5.0% level, followed by the 50% level, with the 0.50% level showing the lowest. The two lowest are reversed in penta through hepta for MRI and in hexa through octa in DCMA. Other differences, for example which congeners exhibit non-significant p-values, are not readily explainable, but did not appear to affect the overall conclusion.

Table 2. Mean Concentrations Found in DCMA Congener Mixture Samples.[a]

Congener No.	Homolog	Prepared Concentration (µg/mL)	Analyzed Concentration (µg/mL)					
			0% Oil	0.50% Oil	5.0% Oil	50% Oil	F-Statistic	p-Value
1	Mono	0.50	0.50	0.45	0.46	0.45	6.53	0.0063
11	Di	0.50	0.49	0.48	0.49	0.48	3.40	0.0504 NS[b]
29	Tri	0.050	0.050	0.047	0.048	0.048	7.98	0.0029
47	Tetra	0.050	0.049	0.047	0.048	0.047	5.28	0.0134
121	Penta	0.050	0.048	0.047	0.048	0.047	6.66	0.0058
136	Hexa	0.050	0.050	0.048	0.049	0.048	5.90	0.0091
185	Hepta	0.025	0.023	0.023	0.023	0.022	8.75	0.0019
194	Octa	0.025	0.023	0.018	0.016	0.020	2.56	0.0998 NS
206	Nona	0.025	0.025	0.023	0.024	0.025	5.14	0.0146
209	Deca	0.025	0.024	0.023	0.024	0.025	11.06	0.0007

a Five replicates for each sample, except two replicates for each 0% oil sample.
b Not significant at the 0.05 level.

Table 3. Mean Concentrations Found in MRI Congener Mixture Samples.[a]

Congener No.	Homolog	Prepared Concentration (µg/mL)	Analyzed Concentration (µg/mL)					
			0% Oil	0.50% Oil	5.0% Oil	50% Oil	F-Statistic	p-Value
1	2-Mono	0.64	0.60	0.52	0.54	0.53	36.38	0.0001
3	4-Mono	2.40	2.24	2.13	2.17	2.16	1.45	0.2748 NS[b]
7	Di	0.060	0.058	0.051	0.053	0.053	31.92	0.0001
30	Tri	0.060	0.057	0.053	0.054	0.053	11.66	0.0005
50	Tetra	0.080	0.077	0.081	0.081	0.079	1.95	0.1710 NS
97	Penta	0.080	0.077	0.074	0.076	0.073	9.36	0.0015
143	Hexa	0.070	0.063	0.061	0.063	0.061	6.02	0.0084
183	Hepta	0.020	0.020	0.019	0.020	0.019	7.85	0.0030
202	Octa	0.020	0.020	0.019	0.020	0.019	2.49	0.1067 NS
207	Nona	0.020	0.020	0.016	0.014	0.012	4.71	0.0195
209	Deca	0.010	0.010	0.0088	0.0097	0.0091	2.25	0.1312 NS

a Five replicates for each sample, except two replicates for each 0% oil sample.
b Not significant at the 0.05 level.

The data (Table 4) from the Aroclor 1260 were also statistically analyzed. There were significant (at the 0.05 level) differences among the mean concentrations found at the four levels of mineral oil. In contrast to the other preparation, in the Aroclor, the control (0% oil) had the lowest mean found PCB concentration. Group means are presented in Table 4. Little difference is found among the three levels (0.50%, 5.0 and 50%), although the middle level happened to have a slightly lower value than the other two. At the joint 5% level, using Dunnet's T, the 0.50% oil and the 5.0% oil values were significantly higher than the control, while the 5.0% oil level did not quite reach significance. As with the individual congeners, despite the significant differences in the amounts found, there was no correlation between the amount of PCB found and the amount of oil.

Table 4. Mean Concentrations Found in Aroclor 1260 Sample.[c]

% Oil	Number of Samples	Analyzed Concentration (µg/mL)
0	2	0.248
0.5	5	0.254
5.0	5	0.250
50	4	0.254
F Statistic	5.49	
p-Value	0.0132	

c Prepared Concentration = 0.250 µg/mL

While there are some differences among the oil levels which are statistically significant, there is no trend in any of the three PCB solutions with the amount of oil. Therefore, we conclude that, under the conditions of this experiment, there is no observable effect on PCB determination with mineral oil levels up to 50%. Thus, the recommendation (ASTM 1983) that samples and standards contain the same amount of mineral oil does not appear to be necessary.

Since there were no observable trends with the amount of oil, the samples were judged to be equivalent and were therefore pooled to assess the accuracy and precision. The results of the accuracy determinations for all samples are given in Table 5. Mean recoveries are given both by homolog and overall for each spiking solution. The results of the precision determinations are given in Table 5. Relative standard deviations are given by homolog and overall for each spiking solution.

Based on the data presented above, the accuracy of the PCB determination using this method is estimated to be between 90 and 105% of the true value and the single laboratory precision of an analysis can be expected to be less than ± 5%. These values apply only for the concentrations studied and do not take into account effects of other matrix interferences. More significantly, the ECD response factors vary widely among the congeners, as reviewed by Erickson (1985). Thus, differences in the PCB composition of the sample and the calibration solution will markedly affect both the accuracy and precision, although the extent of these effects cannot be reliably assessed. These differences can occur from mixing two or more Aroclors or other commercial PCB products. They can also be caused by selective degradation of the PCBs via chemical or biological action, or "weathering." In addition, PCBs may be present as by-products of other chemical manufacture (EPA 1984b).

Table 5. Accuracy and Precision of PCB Homolog Method for All Samples.[a]

Standard Spiking Solution	Congener No.	Homolog	Accuracy (% Recovery)	Precision (Relative Standard Deviation)
DCMA	1	Mono	91.8	3.25
	11	Di	97.0	1.93
	29	Tri	95.6	1.77
	47	Tetra	95.0	1.89
	121	Penta	94.6	1.55
	136	Hexa	97.2	1.90
	185	Hepta	90.4	1.73
	194	Octa	89.9	7.17
	206	Nona	96.8	2.19
	209	Deca	96.0	2.02
		Overall	94.4 ± 2.74	2.54
MRI	1	2-Mono	84.1	1.57
	3	4-Mono	90.2	2.86
	7	Di	88.3	1.48
	30	Tri	90.0	1.49
	50	Tetra	100	3.46
	97	Penta	93.8	1.47
	143	Hexa	88.6	1.34
	183	Hepta	95.5	1.78
	202	Octa	97.0	1.97
	207	Nona	97.0	11.64
	209	Deca	93.0	8.29
		Overall	92.5 ± 4.72	3.40
Aroclor			99.9 ± 2.37	0.84

a Total number of samples was 17 each for the DCMA and MRI solutions and 16 for the Aroclor solution.

Acknowledgments. This work was performed pursuant to Work Assignment No. 6 of Contract No. 68-02-3938 with the U.S. EPA.

REFERENCES

American Society for Testing and Materials (1983) Standard method for analysis of polychlorinated biphenyls in mineral insulating oils by gas chromatography ANSI/ASTM D 4059-83. In: Annual book of ASTM standards Part 40. Philadelphia, Pennsylvania.

Araki Y, Tanaka K (1974) Simple screening method for [hepatic] enzyme-inducing agents of polychlorinated biphenyl (PCB) type. Fukuoka-Igaku-Zasshi 65(1):47-52; Chem Abst 81:146433n.

Association of Official Analytical Chemists (1980a) General method for organochlorine and organophosphorus pesticides, method 29.001. In: Horwitz W (ed) Official methods of analysis of the association of offical analytical chemists. Washington, DC, pp. 466-474.

Ballschmiter K, Zell M (1980) Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. Composition of technical Aroclor- and Clophen-PCB mixtures. Fresenius' Z Anal Chem 302:20-31.

Dry Color Manufacturers Association (1982) An analytical procedure for the determination of polychlorinated biphenyls in dry phthalocyanine blue, phthalocyanine green, and diarylide yellow pigments. Arlington, VA.

Erickson MD (1985) The analytical chemistry of PCBs. Butterworths Press, Boston, Massachusetts.

Longbottom JE, Lichtenberg JJ (eds) (1982) Methods for organic chemical analysis of municipal and industrial wastewater. U.S. Environmental Protection Agency Report No. EPA-600/4-82-057.

Sonchik S, Madeleine D, Macek P, Longbottom J (1984) Evaluation of sample preparation techniques for the analysis of PCBs in oil. J Chromatogr Sci 22:265-271.

U.S. EPA (1982) Test methods for evaluating solid waste-physical/chemical methods, SW-846, 2nd edition. Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA (1984a) Organochlorine pesticides and PCBs--Method 608. Fed Reg 49(209):89-104.

U.S. EPA (1984b) 40 CFR Part 761, polychlorinated biphenyls (PCBs); manufacturing, processing, distribution commerce and use prohibitions; response to individual and class petitions for exemptions; exclusions, exemptions, and use authorizations, final rule. Fed Reg 49:28154-28209.

U.S. FDA (August 1, 1977) Pesticide analytical manual. Vol. I.

Received August 16, 1985; accepted September 16, 1985.