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STANDARDIZATION OF AROCLOR LOTS FOR INDIVIDUAL-PEAK GAS CHROMATOGRAPHIC CALIBRATION

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SUMMARY

Commercially available Aroclors were compared to characterized lots of Aroclors to estimate their weight-percent composition, and thus expand the availability of characterized Aroclors required for individual peak calibration. Individual peak calibration is recommended for the gas chromatographic electron capture determination of polychlorinated biphenyls which result from partially degraded Aroclors. An application is described where polychlorinated biphenyls are determined in chemically dehalogenated oil using response factors derived from characterized Aroclor standards. Rapid clean-up using disposable silica cartridges was used to prepare oil samples prior to gas chromatographic analysis.

INTRODUCTION

The concern for widespread polychlorinated biphenyl (PCB) contamination in the environment has resulted in an increasing need for PCB determinations in a variety of samples. The most common and the most sensitive instrumental technique has been gas chromatography with electron-capture detection (GC–ECD). The analysis is complicated since the "PCB concentration" represents the sum of the individual concentrations of mono- through decachlorobiphenyl and their isomers. This amounts to a total of 209 theoretically possible compounds, many of which have different sensitivities at the electron-capture detector.

The ultimate method would provide the separate quantitation of each PCB compound. The rigorous analytical calibration of all 209 compounds has not been reported; however, this capability may eventually be realized since capillary GC provides resolution superior to that obtained using packed GC columns, and *ca.* 80 PCB compounds are commercially available for calibration [Ultra Scientific Inc. (formerly RFR Corp.), Hope, RI, U.S.A.]. In practice, as this goal is approached, the analysis becomes cumbersome and one that would not usually be appropriate for routine use. The analysis can be simplified by making varying levels of approximations, and so the reliability of the PCB analyses depends upon the validity of these assumptions. The limitations of such approximations must be recognized and justi-

fied according to the type of PCB contamination encountered.

Aroclors® are complex mixtures of PCB compounds which were used in a variety of applications such as product additives, coolants and insulating fluids. Aroclors are identified by the type of molecule (12 = biphenyl) and the total weight-percent of chlorine, e.g. Aroclor 1232 is a biphenyl containing 32% chlorine.

Aroclor 1016 is an exception; it is a biphenyl containing 41% chlorine. Aroclors with the prefixes 54, 25, and 44 are chlorinated terphenyls and blends of PCBs with chlorinated terphenyls. The Aroclors 1242, 1254 and 1260 were produced in the largest amounts and are generally considered the most prevalent in the environment.

The GC–ECD analysis is simplified when contamination is due to a single Aroclor and the relative peak intensities in the chromatogram match those of an available Aroclor standard. In this case, quantitation has been accomplished by comparing selected peak heights or total peak areas for the samples to those in Aroclor standards[1–3]. This simplistic approach, however, is not suitable for quantitating PCB contamination arising from: (i) Aroclors which have partially decomposed through biological or chemical action; (ii) PCBs not originating from an Aroclor; (iii) mixtures of Aroclors[4,5].

A GC calibration technique was proposed by Webb and McCall[6] which employed individual-peak response factors. A table was provided for each Aroclor where the weight-percent composition of each peak was listed and the peaks were identified by whole numbers representing their relative retention times versus a reference compound, p,p'-DDE (1,1-dichloro-2,2'-bis-p-(chlorophenyl)ethylene), defined as 100. The weight-percent compositions of Aroclors were determined using GC–mass spectroscopy and a Coulson conductivity (or Hall-type) detector. These tables were used for the individual calibration of each peak, with the precaution that the tables are valid only for these specific lots of Aroclors.

Sawyer[7] characterized a set of Aroclors in the same manner as Webb and McCall and used these Aroclors in an interlaboratory comparison of analytical methods. This study concluded that individual peak calibration is the most reliable approach for samples containing a non-Aroclor PCB residue[5].

We have made a peak-by-peak comparison of other lots of Aroclors (available commercially for GC calibration) to characterized lots of Aroclors in order to provide an estimate of their weight-percent compositions. This expands the availability of characterized Aroclor standards required for individual-peak calibration of PCBs, and also provides some insight as to the variation which might be expected from different lots of the same type of Aroclor.

Application of the individual-peak calibration technique was made to monitor a plant-scale process for the economical removal of PCBs from oil (to less than 5 ppm) by chemical dehalogenation with sodium naphthalide reagent[8] (see Fig. 2). Recommendations are made for establishing appropriate response factors required for this determination. Consideration is given to the possibility of variations in the ratio of co-eluting isomers for an individual peak occurring during chemical treatment.

A rapid sample preparation scheme is proposed as an alternative to a more tedious Florisil clean-up, recommended by the U.S. Environmental Protection Agency (EPA).

EXPERIMENTAL

Apparatus

A Hewlett-Packard Model 5840A gas chromatograph equipped with a ^{63}Ni electron-capture detector (15 mCi) and automatic liquid sampler, Model 7671A, was used.

Sep-Pak® silica cartridges, used for sample clean-up, were obtained from Waters Assoc. (Milford, MA, U.S.A.) part No. 51900.

GC conditions

GC conditions were maintained similar to those reported elsewhere[6,7,9] to retain the order of elution of PCB compounds as listed in the weight-percent composition tables being referenced.

A glass column (183 cm × 2 mm I.D.) was packed with 3 % OV-1 on Supelcoport, 100–120 mesh. The carrier gas was methane–argon (5:95) at a flow-rate of 20 ml/min. The column and detector temperatures were maintained at 180°C and 250°C, respectively. The injection volume was 5 μl and the attenuation range was 2^4 to 2^6 (or 16 to 64 ×).

Chemicals

Solvent. Pesticide-grade hexane (Burdick & Jackson, Muskegon, MI, U.S.A.), was used in the preparation of all samples and standards, and as a final rinse for all glassware.

Aroclor standards. The source and lot numbers for each series of Aroclors used in this study are given in Table I. Commercial suppliers, viz. Applied Science, Analabs and Ultra Scientific, have indicated through personal communication that they are

TABLE I

LOT NUMBERS FOR AROCLORS USED IN THIS STUDY

Aroclor	Source*				
	Applied Science	Analabs	Ultra Sci.	Sawyer[7]	Webb/McCall[6]
1016	721	F-216A	NA**	77029	NA
1221	101	K-099F	NA	NA	—***
1232	17	NA	—	NA	—
1242	KA-478	J-147C	—	71696	AK55
1248	07771	L-279	NA	71697	—
1254	610	J-147A	NA	71698	AK38
1260	07771	NA	—	71699	—
1268	NA	G-266M	—	NA	NA

* Applied Science Products, State College, PA, Cat. No. 19589; Analabs, North Haven, CT, Cat. No. RCS-066; Ultra Scientific Inc., RI, Cat. No. RPCK-1; Sawyer, these are the same Aroclor lots as characterized in ref. 7, obtained from the Food and Drug Administration, Washington, DC; Webb/McCall, these are the same Aroclor lots as characterized in ref. 6, obtained from Radian Corporation, Austin, TX.
** Not available from this source.
*** No lot number listed on Aroclor sample.

dispensing from single lots of each Aroclor and, as a lot of Aroclor is exhausted, they will discontinue supplying that Aroclor. These Aroclors were produced by Monsanto (St. Louis, MO, U.S.A.), however, no identification such as batch number or time of production is available.

Preparation of Aroclor solutions

Separate solutions of the following Aroclors were accurately prepared to contain *ca.* 1 mg/ml: Aroclors 1016, 1221, 1232, 1242, 1248, 1254 and 1260. These solutions are stable indefinitely provided they are properly sealed, refrigerated and protected from ultraviolet light.

Working standards were prepared daily by diluting 30 μl of the above solutions to 50 ml with hexane. These solutions will contain *ca.* 600 ng/ml or 3 ng/5 μl injection aliquot.

Procedure for comparison of Aroclor lots

The comparison of different lots (or sources) of the same type of Aroclor was made as follows. A single GC run was made for solutions prepared with each available lot, then this sequence was repeated a minimum of nine times. The relative standard deviation of individual peak areas, determined from the repetitive injections of a single Aroclor lot, was generally *ca.* 1–2% for the major Aroclor components. This GC precision was usually well within the precision reported by Sawyer[7] for the weight-percent determinations of these peaks using a Hall detector.

Individual-peak calibration with Aroclors

To calibrate for sample analyses, chromatograms with integrated peak areas were obtained for known injected weights of each of the Aroclors, 1221 through 1260. Each peak in the chromatograms was identified by a whole-number relative retention time (R_{DDE}) *versus p.p'*-DDE, whose retention time is defined as 100 (*ca.* 17 min). This format, which was originally used by Webb and McCall[6], is also used throughout this article. Labeled chromatograms (Fig. 1) show the R_{DDE} and resolution for some of the Aroclor peaks. The response factor for each peak is calculated as follows:

$$R_{F(n)} = \frac{W_{tot} \cdot \%_{on}}{A_n \cdot 100}$$

where $R_{F(n)}$ is the external response factor for a peak with a relative retention time (R_{DDE}) of n; W_{tot} is the total weight of Aroclor injected; $\%_{on}$ is the weight-percent of peak "n" in the Aroclor; A_n is the integrated area for peak "n".

These peak response factors, determined with several Aroclors, are shown in Table II along with a calculated overall (or average) factor. Considerations related to the calculation of these factors are discussed in the text.

Preparation and clean-up of oil samples

An accurately weighed portion of oil sample (*ca.* 1–10 g) was dissolved in 50 ml of hexane. A Sep-Pak silica cartridge was attached to a 5-ml glass syringe and pre-eluted with 5 ml of hexane. An aliquot of the sample solution (1–5 ml) was passed through the cartridge. The PCBs were eluted from the cartridge with three 3-ml portions of hexane while the unwanted constituents were retained on the Sep-Pak. All eluent was collected in a 25-ml volumetric flask and diluted to the mark with hexane.
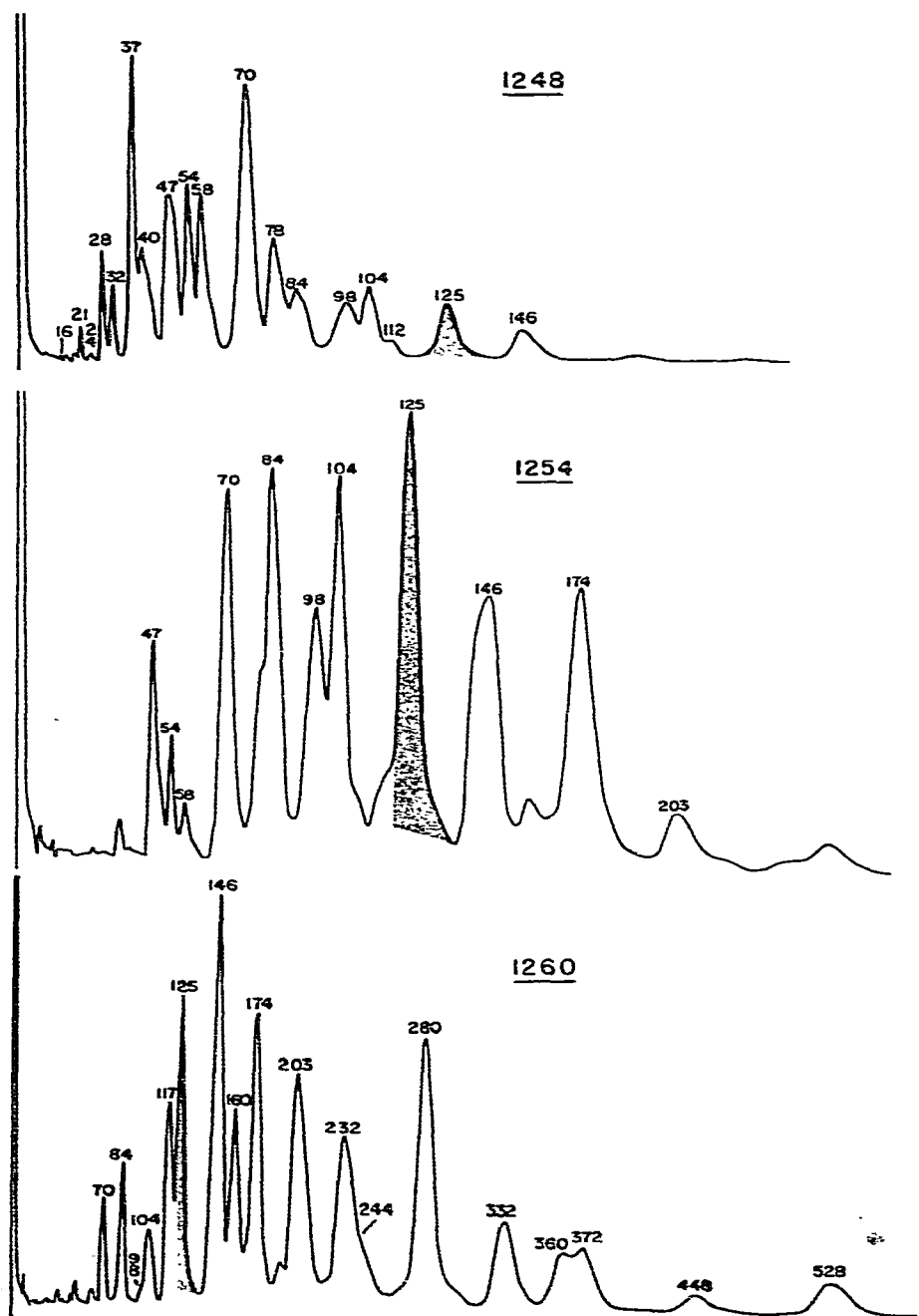
Fig. 1. Chromatograms for selected Aroclors. Peaks are identified by retention times relative to p,p'-DDE = 100.

TABLE II

RELATIVE RESPONSE FACTORS* DETERMINED USING CHARACTERIZED AROCLORS

No. of chlorines	Peak R_{DDE}***	Overall R_F[1]	Aroclors**						
			1221	1232	1016	1242	1248	1254	1260
1	11	23	27	18					
	14	38	45	30					
	16	13	16	12	12	(152)	(1.3)		
	19	2.0	2.0	3.5	—	—	—		
2	21	3.8	4.7		2.8	—	—		
	24	2.9	—	—	2.9	(0.42)	(0.26)		
	28	3.7	4.4	3.5	3.8	4.0	2.6		
	32	2.4	3.6	2.2	2.3	2.5	1.5		
3	37	1.4	1.2	1.3	1.7	1.7	1.0		
	40	1.5		1.5	1.7	1.7	1.4		
	47	1.6		1.2	1.7	1.7	1.8	1.7	
	54	1.5		1.4	1.5	1.6	1.5	1.3	
	58	1.0		1.1	1.2	1.0	1.1	0.77	
4	70	1.0		0.88	0.77	0.86	1.1	1.3	1.1
	78	0.72		0.88		0.46	0.83	—	—
	84	0.96					0.76	1.2	0.88
	98	0.68					0.55	0.83	0.66
5	104	0.74					0.48	1.0	
	112	0.87					0.87	—	—
	117	0.60					—	—	0.60
	125	0.62					0.29	0.65	0.93
	146	0.47					0.23	0.50	0.68
	160	0.63							0.63
	174	0.51						0.39	0.62
6	203	0.42						0.23	0.61
	232	0.55							0.55
	244	0.55							
7	280	0.47							0.47
	332	0.42							0.42
	360	0.41							0.41
	372	0.41							
	448	0.24							0.24
	528	0.28							0.28
	900	0.44	(decachlorobiphenyl)						

* These are relative values, provided to compare peak factors obtained using different Aroclors. Actual response factors must be determined by each analyst.

** Aroclor 1221 and 1232 were portions of the same lots characterized by Webb and McCall[6]. The remaining Aroclors were from lots characterized by Sawyer[7].

*** Relative retention time for Aroclor peaks versus p,p'-DDE (assumed to be 100).

[1] Overall response factors represent the average of values obtained using different Aroclors. Factors were excluded from the average when judged to be inaccurate due to a low abundance of these isomers in the Aroclor.

RESULTS AND DISCUSSION

Commercial and characterized Aroclor lots

Individual-peak calibration using Aroclors is a widely recommended approach for the determination of PCB residues, especially those arising from the degradation of Aroclors. Webb & McCall[6] and Sawyer[7] determined the weight-percent distribution of PCBs in different types of Aroclors according to the resolved peaks in their GC–ECD chromatograms. These lots of Aroclors were then used to calibrate individual peaks. It was emphasized that the distribution of PCBs may vary for different lots of the same Aroclor type, and so these characterizations are valid only for their specific Aroclor lots. The U.S. Food and Drug Administration is currently using Sawyer's lots of Aroclors as standards for their PCB analyses.

Characterized Aroclors for this type of calibration are not commercially available. Such characterization requires an effort and equipment which are beyond the capability of many analytical laboratories. Aroclors generally marketed for GC calibration (Table I) have not been characterized in this manner. These commercial suppliers have indicated that their Aroclors are from single, but randomly obtained, lots originally produced by Monsanto for industrial applications.

When calibrating with non-characterized lots of Aroclors, the assumption is implied in the analysis that Aroclors of the same type have identical compositions. To test this assumption, we have made direct, statistical comparisons of Aroclors from several GC supply houses to the same lots of Aroclors characterized by Sawyer[7] and by Webb and McCall[6]. The peak compositions (weight-percent) were calculated for the commercial Aroclors and are given in Tables III-IX. Sawyer's Aroclor standards were used as the reference in most comparisons. Since Aroclors 1221 and 1232 were not characterized by Sawyer, Webb and McCall's values were used for them.

This indexing of commercially available lots of Aroclors to characterized Aroclor standards expands the availability of standards suitable for individual-peak calibration and provides some insight as to how different lots of the same Aroclor compare.

Comparison of Aroclor lots

Variations in the calculated peak compositions are noted for different lots of the same Aroclor type. These differences were tested for significance using the "t-test" at an 80% confidence level[10]. An Aroclor lot could be considered to be the same as the reference Aroclor (Sawyer or Webb and McCall) if the majority of the prominent peaks passed the "t-test". This did occur for some lots of Aroclors 1248 and 1016.

Although most Aroclor lots were not statistically identical by this criterion, the differences in the peak compositions between many lots were relatively small. In several cases, this difference was within the precision reported in the original weight-percent characterizations of the reference Aroclors.

From this limited survey, it appears that application of Sawyer's or Webb and McCall's weight-percent composition tables to other lots of Aroclors would not always result in gross errors in the response factor calibration. The best analytical practice, however, would dictate that the calibration be done with Aroclor lots where the weight-percent composition of each peak has been established. The weight-percent composition data for commercially available Aroclor standards are provided in Tables III–IX.

TABLE III

COMPOSITION OF AROCLOR 1016 LOTS, CALCULATED BY COMPARISON TO A CHARAC-
TERIZED AROCLOR 1016 STANDARD

Peak R_{DDE}**	Wt.% reported for standard		Wt.%, calculated*	
	Sawyer[7]	HECD Precision***	Applied Science[8]	Analabs[9]
11	0.2	(±0.05)	0.2	0.2
16	3.8	(0.3)	3.5	3.8
21	8.1	(0.6)	7.5	7.8
24	1.2	(0.1)	1.2	1.2
28	16.8	(1.1)	16.8	16.8
32	7.6	(0.6)	7.5	7.5
37	18.5	(1.3)	18.4	18.2
40	14.6	(1.0)	14.3	14.1
47	11.6	(0.9)	11.6	11.7
54	7.7	(0.5)	7.1	7.4
58	6.4	(0.5)	5.6	6.2
70	3.4	(0.4)	1.7	2.3

* Weight-percent composition for each peak was calculated relative to that in a characterized Aroclor standard. The weight-percent reported for the characterized Aroclor (Wt. $\%_{oStd}$) and the relative peak areas (A_{Std}, A_x) for equal amounts of the two Aroclors injected were used.

$$\text{relative wt.} \% = \frac{A_x}{A_{Std}} \cdot \text{Wt.} \%_{oStd}$$

Aroclor lot numbers are given in Table I. Each value represents the average of nine runs.

** Relative retention times for Aroclor peaks *versus* p,p'-DDE (assumed to be 100).

*** Absolute precision for the weight-percents reported[6,7] for the characterized Aroclor standard using a Hall electrolytic conductivity detector (HECD). This is included to show the uncertainty of the standard weight percent values and does not reflect precision for the comparison of Aroclor lots by GC–ECD.

[8] Application of the "*t*-test"[10] indicates that the weight-percents for the major Aroclor peaks are statistically equivalent to those of the characterized Aroclor standard, *i.e.* the existence of a difference was not proved with a confidence limit of 80%.

TABLE IV

COMPOSITION OF AROCLOR 1221 LOTS, CALCULATED BY COMPARISON TO A CHARAC-
TERIZED AROCLOR 1221 STANDARD

Peak R_{DDE}*	Wt.% reported for standard		Wt.%, calculated*	
	Webb and McCall[6]	HECD Precision***	Applied Science	Analabs[9]
11	31.8	(±5.0)	32.5	31.7
14	19.3	(1.8)	17.9	19.7
16	10.1	(1.0)	9.4	9.7
19	2.8	(0.3)	2.4	2.7
21	20.8	(1.9)	17.2	20.1
28	5.4	(0.8)	5.7	6.3
32	1.4	(0.4)	2.5	2.1
37 and 40	1.7	(0.8)	3.7	2.9

*,***,*** [8] See footnotes to Table III.

TABLE V

COMPOSITION OF AROCLOR 1232 LOTS, CALCULATED BY COMPARISON TO A CHARAC-
TERIZED AROCLOR 1232 STANDARD

Peak R_{DDE}**	Wt.% reported for standard		Wt.%, calculated*	
	Webb and McCall[6]	HECD Precision***	Applied Science	Ultra Sci[‡]
11	16.2	(±0.6)	15.1	16.8
14	9.9	(0.3)	9.6	10.5
16	7.1	(0.5)	6.0	7.4
20 and 21	17.8	(0.4)	15.7	20.1
28	9.6	(0.3)	9.9	11.1
32	3.9	(0.2)	4.7	4.5
37	6.8	(0.2)	7.4	8.0
40	6.4	(0.2)	7.0	7.6
47	4.2	(0.2)	4.3	4.7
54	3.4	(0.1)	3.6	4.0
58	2.6	(0.1)	2.8	3.1
70	4.6	(0.1)	4.9	5.8
78	1.7	(0.1)	2.0	2.3

*,**,***,‡ See footnotes to Table III.

Choice of Aroclor for peak calibration

Individual-peak calibration is required when the distribution of PCBs in the sample does not match that for a specific Aroclor since the electron–capture response for PCB compounds may vary as much as 100-fold.

TABLE VI

COMPOSITION OF AROCLOR 1242 LOTS, CALCULATED BY COMPARISON TO A CHARAC-
TERIZED AROCLOR 1242 STANDARD

Peak R_{DDE}**	Wt.% reported for standard		Wt.%, calculated*			
	Sawyer[7]	HECD Precision***	Applied Science[‡]	Analabs[‡]	Ultra Sci[‡]	Webb and McCall[6,‡]
16	3.4%	(±0.1)	3.9	3.9	3.0	5.4
21	10.3	(0.3)	10.6	10.0	10.0	10.6
24	1.1	(0.2)	1.1	1.1	1.1	1.1
28	15.8	(0.4)	15.2	15.8	16.7	15.6
32	7.3	(0.2)	6.9	7.2	7.8	7.2
37	17.0	(0.4)	15.3	15.9	16.7	15.9
40	13.0	(0.3)	12.4	12.8	13.5	12.8
47	9.9	(0.2)	10.1	10.7	10.0	10.2
54	7.1	(0.2)	7.0	7.2	7.0	7.1
58	4.4	(0.1)	4.4	4.5	4.3	4.4
70	8.7	(0.2)	8.9	8.7	8.0	8.6
78	1.9	(0.5)	2.0	1.9	1.7	1.9

*,**,***,‡ See footnotes to Table III.

TABLE VII

COMPOSITION OF AROCLOR 1248 LOTS, CALCULATED BY COMPARISON TO A CHARAC-
TERIZED AROCLOR 1248 STANDARD

Peak R_{DDE}**	Wt.% reported for standard		Wt.%, calculated*		
	Sawyer[7]	HECD Precision***	Applied Science[3]	Analabs[1]	Webb and McCall[6, 1]
16	0.3	($\pm$0.06)	0.1	0.3	0.2
21	1.1	(0.1)	0.2	1.0	0.8
24	0.2	(0.02)	0.05	0.2	0.2
28	6.0	(0.3)	5.4	5.8	6.3
32	2.6	(0.1)	2.3	2.6	2.7
37	8.7	(0.5)	9.0	9.7	8.6
40	7.4	(0.3)	7.4	7.7	7.4
47	15.7	(0.6)	15.5	14.9	15.6
54	9.3	(0.5)	8.9	8.6	9.2
58	8.3	(0.5)	8.2	7.9	8.2
70	18.2	(0.8)	19.7	18.7	18.2
78	6.4	(0.4)	6.7	6.4	6.3
84	4.6	(0.2)	3.8	3.8	4.5
98	3.4	(0.2)	2.5	2.7	3.3
104	3.3	(0.2)	2.8	2.8	3.0
112	1.0	(0.1)	0.9	1.0	1.0
125	2.3	(0.1)	1.9	1.8	2.1
146	1.2	(0.1)	1.1	1.0	1.2

*,**,***, 1 See footnotes to Table III.

TABLE VIII

COMPOSITION OF AROCLOR 1254 LOTS, CALCULATED BY COMPARISON TO A CHARAC-
TERIZED AROCLOR 1254 STANDARD

Peak R_{DDE}**	Wt.% reported for standard		Wt.%, calculated*		
	Sawyer[7]	HECD Precision***	Applied Science[3]	Analabs[1]	Webb and McCall[6, 1]
47	7.1	($\pm$0.3)	4.0	6.0	6.6
54	2.7	(0.1)	1.9	2.2	2.5
58	1.2	(0.1)	1.1	0.8	1.0
70	14.7	(0.5)	13.9	12.8	13.9
84	18.6	(0.5)	12.2	18.1	18.1
98	8.3	(0.3)	7.3	7.9	7.9
104	14.1	(0.5)	12.5	13.4	13.4
125	15.6	(0.4)	17.2	15.1	14.9
146	9.0	(0.3)	10.5	8.7	8.5
174	7.4	(0.3)	8.0	7.2	6.7
203	1.3	(0.1)	1.4	1.2	1.2

*,**,***, 1 See footnotes to Table III.

TABLE IX

COMPOSITION OF AROCLOR 1260 LOTS, CALCULATED BY COMPARISON TO A CHARAC-
TERIZED AROCLOR 1260 STANDARD

Peak R_{DDE}**	Wt.% reported for standard		Wt.%, calculated*		
	Sawyer[7]	HECD Precision***	Applied Science [§]	Ultra Sci [§]	Webb and McCall[6, §]
70	2.4	(±0.1)	2.6	2.6	3.0
84	3.6	(0.4)	3.9	4.1	4.8
98 and 104	2.8	(0.2)	3.0	3.2	3.3
117	4.4	(0.3)	4.3	4.4	4.4
125	11.0	(0.7)	11.2	11.7	12.4
146	13.3	(0.7)	13.8	13.8	14.5
160	5.5	(0.4)	5.2	5.4	5.3
174	10.0	(0.5)	10.8	11.2	12.2
203	10.9 -	(0.7)	9.6	10.1	10.1
232 and 244	11.2	(0.7)	10.4	10.7	10.5
280	12.5	(1.0)	11.1	11.6	11.3
332	4.2	(0.5)	4.1	4.4	4.4
360 and 372	5.4	(0.5)	4.3	4.6	4.6
448	0.8	(0.1)	0.7	0.7	0.7
528	2.0	(0.2)	1.6	1.6	1.6

*,**,***, [§] See footnotes to Table III.

Since individual peak response factors often vary when determined with dif-
ferent Aroclor types, it is important to consider the approximations which are implied
in this mode of calibration. Peaks in an Aroclor chromatogram usually represent the
co-elution of two or more PCB compounds. Peaks having the same relative retention
times (R_{DDE}) occur in different Aroclor types. If co-eluting compounds have different
electron-capture responses and their relative concentrations vary in the different Ar-
oclors, peak response factors will vary accordingly. For example, the relative re-
sponse factors determined for peak R_{DDE} 125 were 0.29, 0.65 and 0.93 when calibrat-
ing with Aroclors 1248, 1254 and 1260, respectively. Peak 125 comprises the co-
elution of penta- and hexachlorobiphenyl in the ratios 9:1, 7:3 and 2:9 for these
respective Aroclors. Thus, the selection of the type of Aroclor for peak calibration
will affect the quantitation of PCBs.

Webb and McCall[6] proposed a flow-chart scheme to identify residues of Ar-
oclors 1242, 1254 and 1260 in mixtures by the presence (or absence) of certain peaks.
This scheme is incorporated in the EPA method for PCBs in oil as a guide to de-
termine which of these Aroclors to use for individual peak calibration[11]. The ef-
fectiveness of this procedure was tested, when contamination was not due to the
above Aroclors, by analyzing a known amount of Aroclor 1248. The scheme dictated
calibration of the first group of peaks ($\leqslant R_{DDE}$ 84) with Aroclor 1242 and the remain-
ing peaks with Aroclor 1254. The recovery of Aroclor 1248 was 116%.

If Aroclors are partially decomposed, the peak compositions may be different
from those for Aroclor peaks with the same retention time. To determine PCBs
arising from the decomposition of Aroclors, we recommend that individual peaks be

calibrated by averaging peak factors determined from a series of Aroclors. This series includes the original Aroclor (before decomposition) and Aroclors of less chlorination. Aroclor standards with chlorine contents higher than that of the original Aroclor are not used in the calibration. For example, in the analysis of PCBs from decomposed Aroclor 1248, the response factor used for peak R_{DDE} 28 would be the average of the factors for this peak calculated from Aroclors 1221, 1232, 1016, 1242 and 1248.

It is assumed that the peak compositions of the Aroclors reflect a favored distribution of PCB compounds over a wide range of total chlorination. Thus, averaging peak factors from several Aroclors appear to be preferable to using factors from a single Aroclor when degradation has occurred. The improvement in accuracy would vary depending on the distribution of PCBs in the sample; however, the recovery of a known amount of Aroclor 1248 was 102% by this method, whereas Webb and McCall's scheme yielded 116% recovery. A disadvantage in this approach is that more effort is required to calculate and average peak response factors for several Aroclor types rather than using peak factors from a single Aroclor. The decision of which calibration approach to apply must be made by a qualified analyst after considering the type of PCB contamination.

Application to chemically dehalogenated oil

The efficient destruction of PCBs in oil has been accomplished by chemical dehalogenation with sodium naphthalide reagent[8]. Supporting analyses require the determination of non-Aroclor PCB mixtures. It is apparent in Fig. 2 that, as the dehalogenation of Aroclor 1242 proceeds, the higher chlorinated PCBs diminish more rapidly than the lower chlorinated compounds. The calibration and analyses of these samples were performed using average (or overall) peak factors, as described previously.

Sample clean-up prior to GC analysis was accomplished using disposable silica cartridges, as outlined in the Experimental section. This procedure was accomplished in less than 5 min and was effective in removing miscellaneous GC-interfering contaminants and filtering insoluble residues which would accumulate on the GC column. PCBs were quantitatively recovered from the silica cartridge in the first 5 ml of hexane eluent.

If a significant amount of alcohol or tetrahydrofuran (used in the dehalogenation treatment) was present in the oil, the silica failed to remove the soluble impurities. Alcohol and tetrahydrofuran were removed from the oil by warming on a Roto-Vap to 60°C at reduced pressure (25 mmHg) for 60 min. Anhydrous sodium sulfate was added during this process to remove traces of water. This step was required only when poor GC resolution or extraneous peaks were observed in the chromatogram.

The silica cartridge is favored over the Florisil column clean-up because of the shorter preparation time and the smaller amounts of solvents required.

CONCLUSIONS

The compositions of several Aroclor lots marketed for GC calibration are similar to characterized Aroclors previously reported in the literature; however,
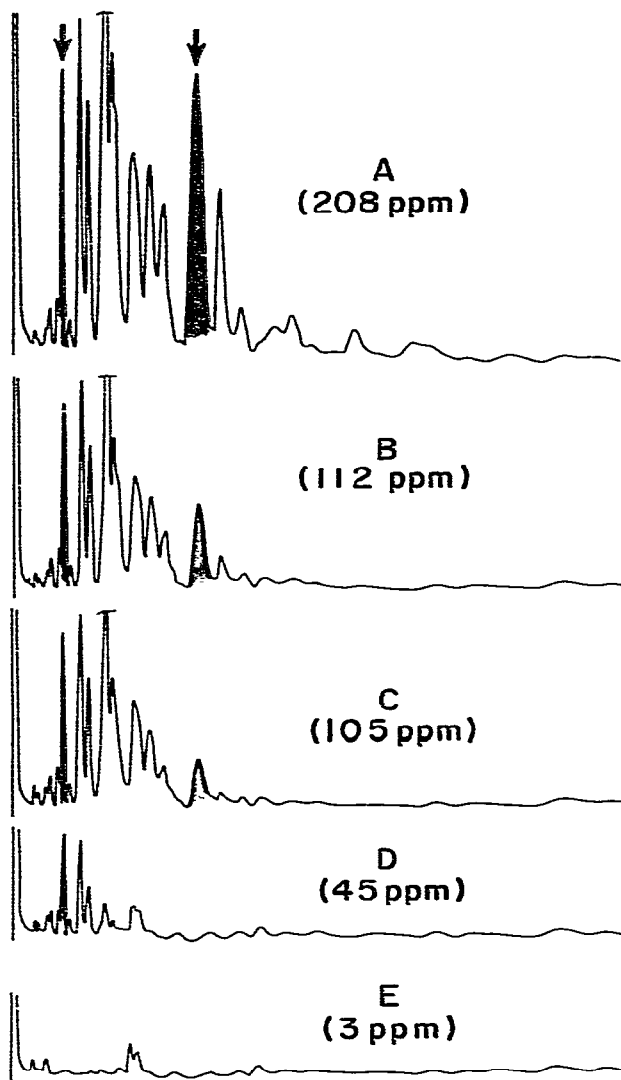
Fig. 2. Chromatograms for oil samples taken during the dehalogenation of PCBs with sodium naphthalide reagent. A, Oil sample before treatment, 208 ppm Aroclor 1242; E, oil sample after treatment, 3 ppm.

characterized materials are preferable for PCB calibration. The weight-percent distribution of PCBs in commercial Aroclors was obtained by direct comparison to characterized Aroclor lots, thus expanding the availability of standards suitable for individual-peak calibration.

Averaging of peak response factors calculated from different Aroclor types is recommended when individual-peak calibration is required.

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