United States
Environmental Protection
Agency

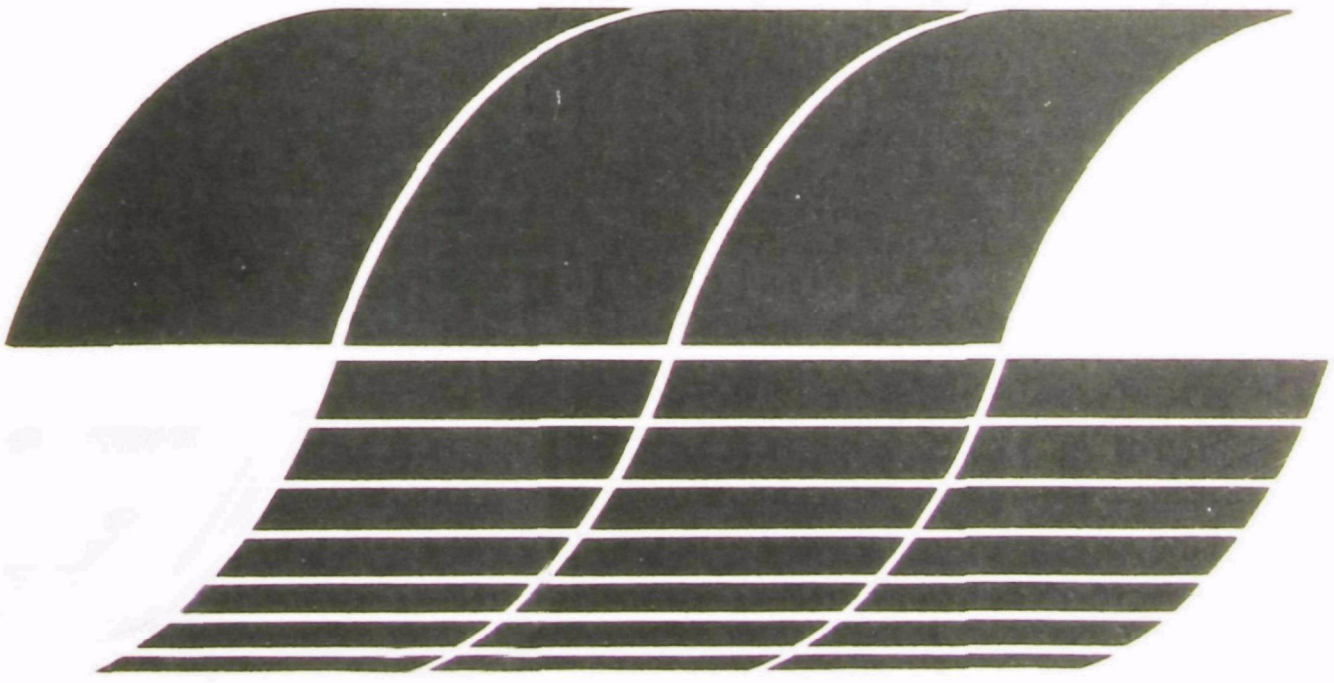
Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/7-79-047
February 1979

EPA

Measurement of PCB Emissions from Combustion Sources

Interagency Energy/Environment R&D Program Report



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Measurement of PCB Emissions from Combustion Sources

by

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Contract No. 68-02-2150
T.D. 10102
Program Element No. INE624

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

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I. INTRODUCTION

The purpose of the contract award to Arthur D. Little, Inc., (EPA Contract No. 68-02-2150) by the Process Measurements Branch of IERL/RTP is to provide advanced organic sampling and analysis capabilities and method development. The effort covered by the contract has been divided into several areas, including the development of procedures for more complete organic analyses which will be required in Level 2 (Technical Directive 10202). As part of the effort in this category, EPA requested an examination of the methods used for polychlorinated biphenyl (PCB) analysis that would provide reliable data when applied to emissions from combustion sources. Verification of a recommended PCB procedure was part of the request.

In preparation of this report, three areas of effort have been defined. 1) Pertinent publications have been reviewed to allow drafting of a tentative PCB analysis procedure. 2) Laboratory experiments have been conducted to test the tentative procedure using well characterized reference materials. 3) Verification of the PCB analysis procedure has been made using complex organic samples, representative of the types of samples expected in environmental assessment studies. The recommended procedure for PCB analysis is described in detail in Appendix A.

II. BACKGROUND

The analysis and measurement of PCB emissions from combustion sources encounters problems not dealt with in most reported PCB analysis methods. Many reviews[1-4] have been published which present different analytical methodologies developed for PCB analysis and present a good understanding of the PCB analysis problem. Of the methods typically utilized for PCB analyses, gas chromatography has been widely implemented as a low cost, yet sensitive analytical technique.

Gas chromatographic analyses for PCB can be classified as using either a pattern recognition approach or the measurement of individual PCB peaks. The EPA Federal Register Method for PCB analysis in industrial effluents[5] (Vol. 38, No. 78, pt. II) uses the pattern recognition approach utilizing conventional GC techniques with an electron capture detector. In this method the gas chromatogram of the sample is examined for similarity to one of the known Aroclors, after a series of clean-up steps, as appropriate for each sample. If a match is made, the PCB content is reported as the suspected Aroclor. The several difficulties associated with the pattern recognition approach have been recognized by researchers conducting this type of analysis. In particular, interferences introduced by co-eluting pesticides are especially common for water and sediment samples. Elemental sulfur and other common species such as phthalates are common interferences.

The quantitative method proposed by Webb and McCall [6] was partially incorporated into the Federal Register method as being recommended for use only if the pattern recognition method seems to be nonapplicable. The method of Webb and McCall measures each individual PCB peak, obviating the need for prior assessment of which PCB is present to determine the proper calibration material. Even if there are interferences in the chromatograms, use of individual peaks minimizes the errors caused by non-PCB species.

Most of the EPA work on PCBs to date, has been on water and sediment samples. As these methods have been applied to samples from combustion sources, a variety of problems have been encountered. Samples from coal-fired power plants and incinerators have been difficult to analyze for PCBs. One of the problems is that the PCBs exposed to a combustion process have a substantially different pattern than the known Aroclor PCBs. Most of these samples show a loss of the low end PCBs (mono-, di, and trichloro) with a residual of the higher molecular weight PCBs (tetra-, penta-, and hexachloro)[7]. In addition, the nature of the GC interferences is different in these combustion effluent samples than in the water and sediment samples.

To simplify the GC/ECD measurement procedure and increase the detection limit sensitivity for PCB', Haile[7a] and Armour [8] have proposed perchlorination of the PCBs using antimony pentachloride. This procedure converts all of the individual PCB species to a single species, decachlorobiphenyl (DCB). Measurement of a single species can be a

great improvement over the analysis of a complex mixture. However, Armour cautions that the perchlorination method is only for confirmatory purposes and to enhance the sensitivity of the analysis. In the Armour procedure, the conventional pattern recognition approach must be used to establish the identity of the sample prior to DCB formation. Since different amounts of DCB are produced from the individual PCBs, adjustment factors ranging from 0.4 to 0.8 are required to convert DCB values to quantities of specific Aroclor mixtures, and ultimately the accuracy of the PCB measurement depends upon correct identification of the PCB present.

Application of the perchlorination procedure for source measurement of PCBs has been made to incinerator emissions [7a-9], with the procedures described in detail in EPA document EPA-600/4-77-048[7a]. After perchchlorination, DCB was detected indicating the presence of PCBs. However careful examination by GC/MS of aliquots of the original samples, blanks, and incinerator fuels [10] showed that no PCBs were present.

Because of the false positives problem and the difficulties in accurate quantitative calibration, the perchlorination (DCB) procedure is not sufficiently reliable to warrant use in measuring PCB emissions from combustion sources. The Federal Register procedure for PCB measurement in industrial effluent is not applicable because of the changes in relative composition during combustion. Thus a new procedure was needed for combustion sources.

III. DEVELOPMENT OF AN ALTERNATIVE PCB ANALYSIS METHOD

A. Discussion of GC/MS Method

Automated gas chromatography/mass spectrometry (GC/MS) appeared to offer the greatest potential for a sensitive quantitative analysis method that would provide reliable PCB concentration data from the complete range of environmental samples, including those from combustion sources.

Since chlorine in natural abundance exists as approximately a 3/1 ratio of $^{35}Cl/^{37}Cl$, the isotope clusters produced in the mass spectra of PCBs provides a unique opportunity to both confirm identity and make quantitative concentration measurements. The GC/MS method developed by Dudenbostel[12] and used in the EPA Region II laboratories makes use of these factors. In their method, GC/MS data are collected in narrow mass ranges corresponding to the molecular ion clusters of the mono-, di, etc., chlorobiphenyls. Selected spectra throughout the chromatogram are examined to verify that the data collected do correspond to PCBs according to the isotope patterns expected in each mass range. The reconstructed chromatogram is then pattern-matched to one of the Aroclors. Quantitative measurement is based upon the ratio of the most intense peaks in the sample and standard. The work by others, and in this report, is concentrated on the Aroclor PCBs, because they are the only PCB's that are found with regularity in environmental studies in the United States.

While the Dudenbostel method[11] has many of the desirable specificity features inherent in GC/MS, it still relies upon pattern recognition and analysis of PCB as one of the Aroclors. This approach would not be acceptable for combustion source samples.

The paper by Eichelberger, Harris and Budde[12] lays the groundwork for an alternate approach using GC/MS. The essence of their method is to use PCB subset mass scanning with a particular mass chosen for each of the monochloro.....heptachlorobiphenyl groups. They selected particular masses for each chlorobiphenyl so that there would be minimum overlap between chloro groups. The approaches to using the method quantitatively were only lightly touched upon in that paper. Quantitative analysis was by pattern recognition and measurements as one of the Aroclors. Interference by pesticides, etc., was minimized by selection of the subset masses. Although not stated explicitly in the paper, this method clearly leads to the possibility of reporting PCBs in terms of the amount of each chlorobiphenyl group (mono-, di-, etc.) present. This kind of approach would overcome the difficulties found in combustion source samples where the original Aroclor distribution patterns are altered.

The approach developed in this study is based upon the excellent groundwork developed by Webb and McCall[6], Dudenbostel[11] Eichelberger, Harris and Budde[12]. The essence of the analysis method is as follows:

1) Acquire GC/MS data in PCB subset mass windows large enough to encompass all of the isotope cluster(s).

2) Examine selected mass spectra to verify PCBs by their chlorine isotope abundance patterns.

3) Generate mass chromatograms from a single mass chosen to represent each chlorobiphenyl.

4) Integrate the areas of each mass chromatogram only in the relative retention time (RRT) region corresponding to the mono-, di, etc., chlorobiphenyls.

5) Quantify either from selected peaks in Aroclor reference standards or with pure chlorobiphenyl isomers. The details of the quantitative calibration are the subject of follow-on studies, discussed in section IV. A complete description of the analytical procedure is found in Appendix A.

B. Selection of MS Data Acquisition Masses

The previous EPA work[11,12] has clearly shown the increased sensitivity to be gained for PCB analysis by using a selected subset masses for each GC/MS scan. The question then becomes one of how to select the correct mass or mass range for each chlorobiphenyl. We feel that one must collect data over the full isotope cluster range in order to be able to verify the PCB composition by means of the isotope abundance pattern. The book by Safe and Hutzinger[13] provides a great deal of information on the mass spectra of PCBs. Significant (> 5%) ^{37}Cl isotope peaks are found as follows for the various PCB groups.

PCB Group	Significant Ions
Cl_1	M, +2
Cl_2	M, +2, +4
Cl_3	M, +2, +4
Cl_4	M, +2, +4
Cl_5	M, +2, +4, +6
Cl_6	M, +2, +4, +6
Cl_7	M, +2, +4, +6, +8
Cl_8	M, +2, +4, +6, +8
Cl_9	M, +2, +4, +6, +8
Cl_{10}	M, +2, +4, +6, +8, +10

The initial data acquisition subset then should at least include most of these ions. The mass spectrum of a chlorobiphenyl is dominated by mass clusters at regions corresponding to the molecular ion (M^+) and M^+-Cl, M^+-HCl, M^+-Cl_2. The M^+-Cl and M^+-HCl clusters usually have only about 10% relative intensity, whereas the M^+ and M^+-Cl_2 ions are of about equal intensity. The M^+-Cl ion will be offset one mass lower than the corresponding PCB isomer, while the M^+-HCl and M^+-Cl_2 ions will be offset by two mass units from their corresponding PCB isomer. Simplified

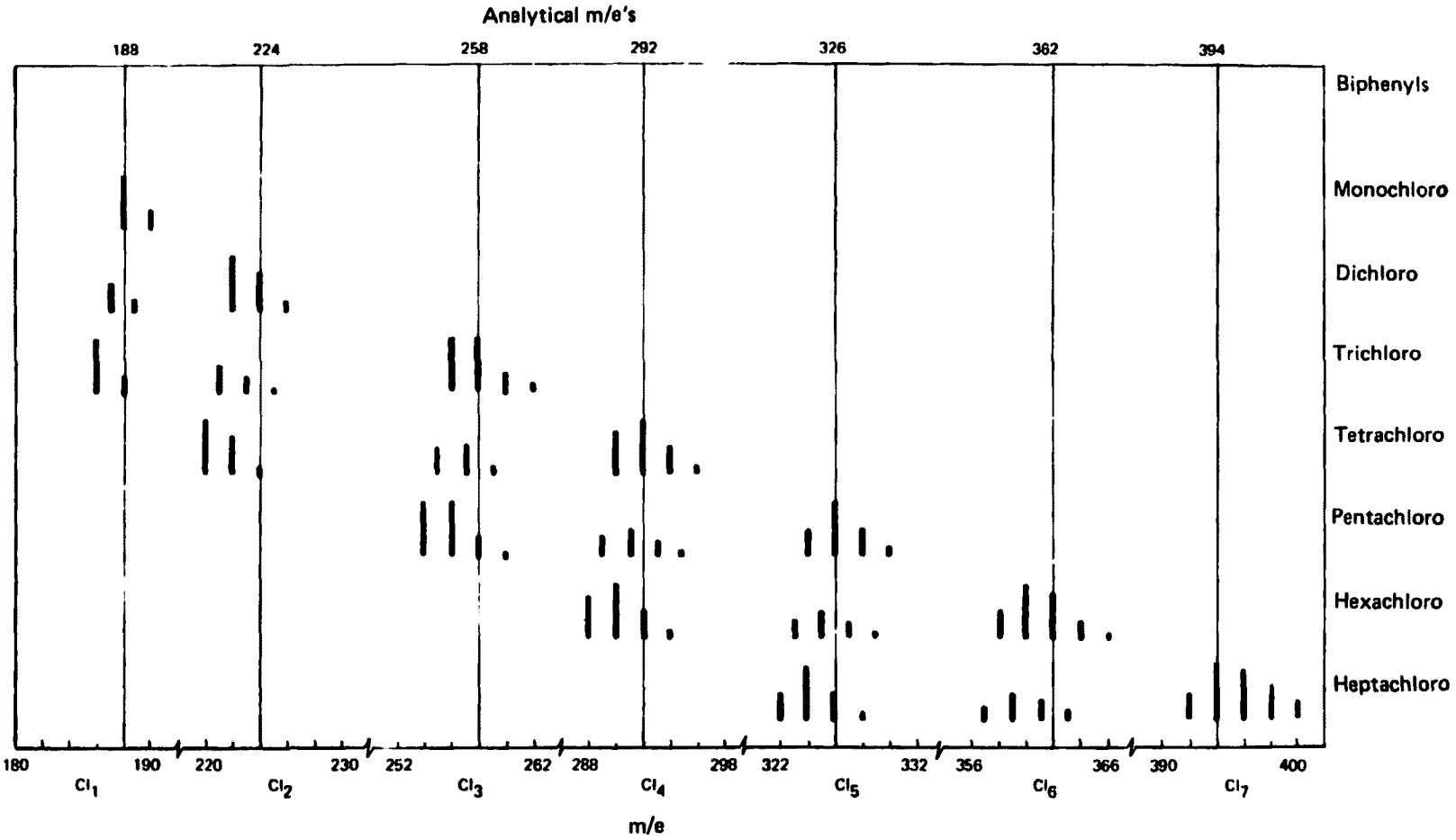

FIGURE 1 HYPOTHETICAL MASS SPECTRA OF PCB's

spectra of the PCB groups containing one to seven chlorines are shown in Figure 1. In each case only the ion clusters due to M^+, M^+-Cl and M^+-Cl_2 are shown. M^+ and M^+-Cl_2 are shown as equal intensity and M^+-Cl is shown at 50% intensity. From an examination of these data, a subset mass range was chosen for each PCB group as shown in Table 1. The ranges were chosen to include the fragment ions from higher PCBs and enough of the isotope cluster to allow unambiguous identification of the PCB.

The analytic method described in this report is applicable to PCBs containing from one to ten chlorines. The samples analyzed during the verification phase of this project were spiked with PCBs containing no more than 8 chlorines. In the test samples, PCBs with higher chlorine content were not found and, therefore, are not discussed in the following sections.

Once the PCB identity has been confirmed, there are a variety of ways of treating the data to obtain a quantitative measure of the PCB groups. A single mass has been chosen which represents the most intense mass in the molecular ion cluster with the minimum fragment ion interference. When the GC retention window criteria are superimposed, as discussed in the next section, it is only necessary to eliminate (or minimize) the interferences from the one higher chloro group (i.e., M^+-Cl. The analytical masses felt to represent the best choices are shown in Figure 1 and are listed in the last column of Table 1.

C. GC Retention Time Criteria

The M^+-Cl_2 fragment ion in the mass spectra of chlorinated biphenyls could represent a difficult problem in the quantitative analysis of PCB groups. The results of the careful work by Webb and McCall[6,14], however, present a means for overcoming this problem. A careful examination of their data reveals that there is no GC overlap between chlorinated biphenyls differing by two chlorines and only slight overlap by biphenyls differing by one chlorine. The single chlorine overlap does not present a serious problem for the GC/MS analysis, because the M^+-Cl or -HCl peaks are generally of only 10% relative intensity, and the analytical masses can be chosen to minimize this problem.

From the Aroclor composition and GC data given by Webb and McCall[6], a tentative set of relative retention time (RRT) windows have been chosen for each PCB group as shown in Table 2.

The PCB analysis procedure would then be to obtain the GC/MS data in the subset mass ranges for the entire chromatogram. After PCB identities are confirmed by isotope ratio checking, mass chromatograms would be obtained for each analytical mass. The area in the proper RRT window would then be integrated for a measure of each PCB chloro group.

An example of this procedure can be seen from some preliminary work conducted in the ADL laboratories. Figure 2 shows the reconstructed chromatogram obtained from a GC/MS run using the subset mass ranges

TABLE 1

Mass Spectrometry Data Acquisition Subsets

PCB Cluster	M^+	m/e Range	Total m/e	Analytical* m/e
Cl_1	188	186 - 190	5	188
Cl_2	222	220 - 226	7	224
Cl_3	256	254 - 260	7	258
Cl_4	290	288 - 294	7	292
p,p'-DDE	316	316 - 321**	6	318
Cl_5	324	322 - 328**	7	326
Cl_6	358	356 - 364	9	362
Cl_7	392	392 - 400	9	394
Cl_8	426	426 - 434	9	428
Cl_9	460	460 - 468	9	464
Cl_{10}	494	494 - 504	11	498

*40 m sec integration time per m/e.

**p,p'-DDE (1,1-di[p-chlorophenyl] dichloroethylene) is used as internal standard and its mass range may be combined with that for pentachlorobiphenyl to meet the constraints of the data system.

TABLE 2

Gas Chromatography RRT Windows Relative to p,p'-DDE* = 100

PCH Cluster	Relative Retention Time (RRT) Window	Analytical m/e
Cl_1	0(5) - 20	188
Cl_2	15 35	224
Cl_3	25 - 55	258
Cl_4	40 - 100	292
Cl_5	70 - 150	326
Cl_6	125 - 250	362
Cl_7	160 - 350	394
Cl_8	275 - 600	428
Cl_9	400 - 1000	464
Cl_{10}	650 - 1200	498

*p,p'-DDE (1,1-di-[p-chlorophenyl[dichloroethylene) is used as internal standard.

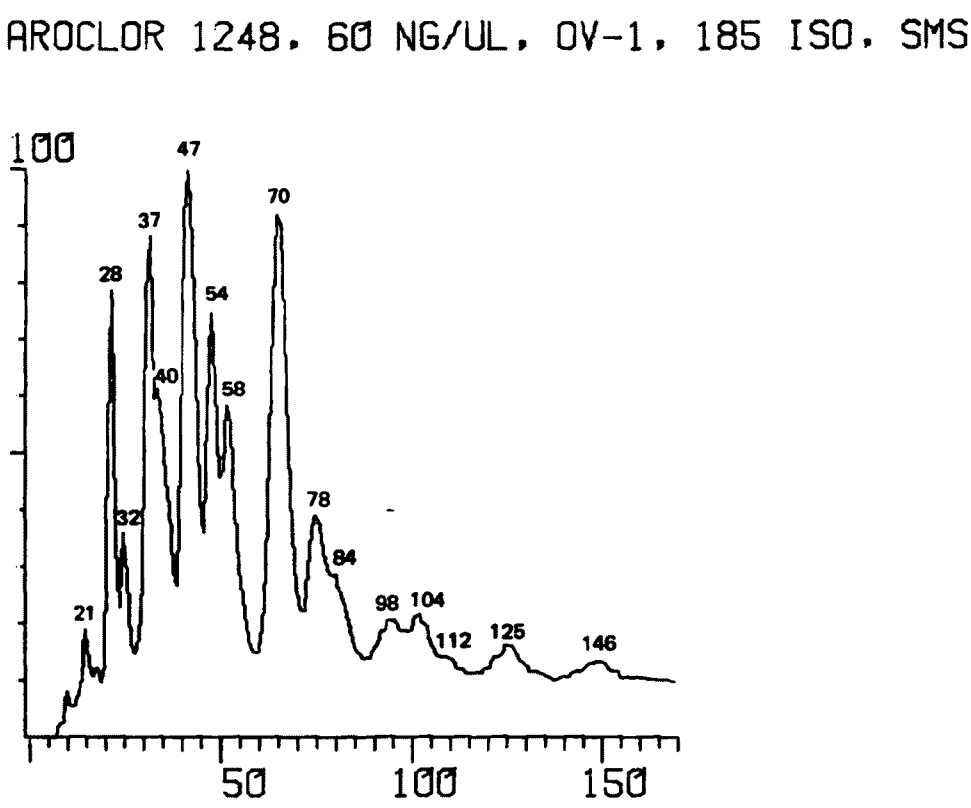

FIGURE 2: GC/MS Subset Mass Chromatogram of Aroclor 1248

RRTs for specific peaks labeled above peak

chromatogram obtained from a GC/MS using the subset mass ranges given in Table 1. The RRT's were assigned by comparison of this chromatogram to that published by Webb and McCall[6]. The chromatogram represents a 60 ng injection analyzed on a 2 m OV-1 column operated isothermally at 185°C. The mass chromatograms constructed from each of the analytical masses are shown in Figure 3. Each chromatogram is self-normalized to 100.

The appropriate RRT windows for each chlorobiphenyl group are shown on their respective mass chromatograms. One can see that using this procedure eliminates the overlap problem from fragment ions appearing in a particular mass chromatogram, due to another chlorobiphenyl. For instance, the $M-Cl_2$ peaks due to trichloro and tetrachlorobiphenyl, respectively, are seen in the 188 and 224 mass chromatograms, but the RRT window criteria eliminate these interferences.

These windows may have to be adjusted alightly for some samples in order to properly integrate the GC areas. The PCB isotope pattern criteria should be used in making these adjustments.

The chromatographic peak area found for each PCB group of this Aroclor 1248 sample within the designated relative retention time window are listed in Table 3. Comparison of the area % data found for this test sample with the weight % data of Webb and McCall[6] for a different Aroclor 1248 sample shows excellent agreement, using the assumption that each PCB cluster has the same weight/response sensitivity. The close agreement shown in Table 3 may be a fortuitous concidence in view of the fact that two different samples of Aroclor 1242 are being compared. However, the closeness of the data suggests that relatively simple calibration procedures may yield accurate quantitative determinations.

D. Quantitative Calibration

Several approaches are possible for quantitative calibration of the different PCB groups. For the simplest case, if one assumes that each of the different PCB clusters has the same weight/response sensitivity, then a single PCB species would allow calibration of all of the PCB isomers found in a sample. A slightly more complex method would involve preparation of a calibration mixture containing a single isomer for each PCB group. This method assumes that all of the isomers within a single PCB group have identical weight/response sensitivities. A third, readily available method would be to use previously calibrated Aroclor reference standards, such as those evaluated by Webb and McCall for the GC/ECD analysis method, under conditions identical to those used with samples.

Since the PCBs are always found as complex isomer mixtures and the various Aroclors have similar complexity, the third method offers self-correcting advantages not available with the other two methods. Selection of either one or two isomer peaks for each chlorobiphenyl group which are well defined by GC, have no other chlorobiphenyl overlap and

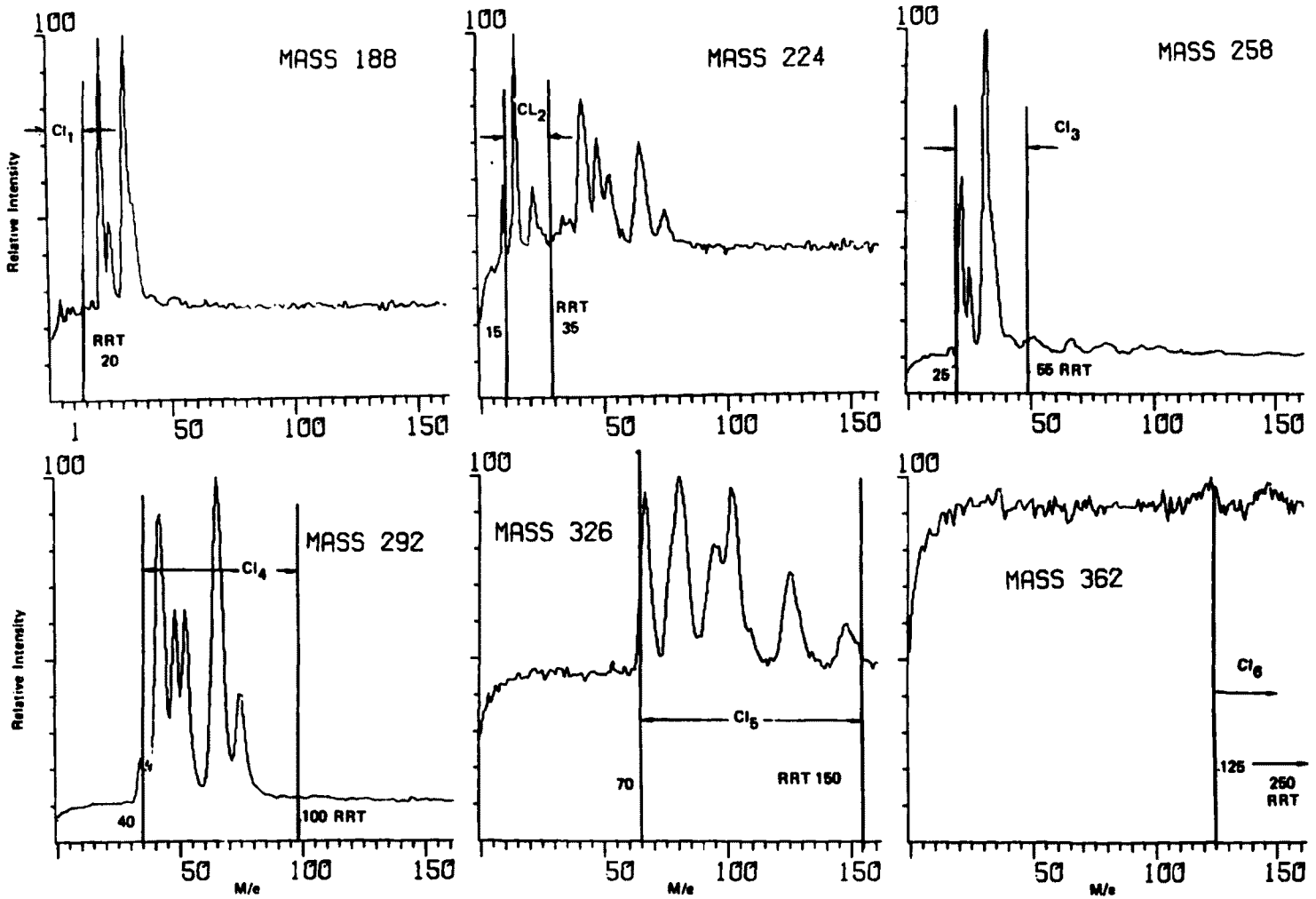

FIGURE 3 ANALYTICAL MASS CHROMATOGRAMS FOR AN AROCLOR 1248 SAMPLE

TABLE 3

Aroclor 1248 Composition Analysis

PCB Group	m/e	RRT Window	Area	%[b]	Known %[c]
Cl_1	188	1-20	—	(0)	0
Cl_2	224	15-35	1452	2	1.2
Cl_3	258	25-55	17423	26	24.7
Cl_4	292	40-100	36896	55	57.8
Cl_5	326	70-150	11629	17	19.8
Cl_6	362	125-180[a]	0	0	0.4

a. Limit of chromatogram

b. Percentage each group was off the sum of the individual group areas assuming that each PCB group has the same sensitivity.

c. Webb and McCall (reference 6, Table 4).

TABLE 4

Possible Aroclor Calibration Standards

PCB Cluster	Aroclor	RRT Peak[a]	% RRT peak is of Aroclor[b]
Cl_1	CBP*	11	100
Cl_2	1242	20, 21	11.3
Cl_3	1242	37, 40	22.6
Cl_4	1254	47	6.2
Cl_5	1254	84	17.3
Cl_6	1254	174	8.4
Cl_7	1260	280	11.0
Cl_8	c	--	--
Cl_9	d	--	--
Cl_{10}	DCB**	1,100	100

[a] Relative to p,p'-DDE = 100

[b] Webb and McCall (Ref. 6) (Appendix B)

[c] Octachlorobiphenyl may be calibrated from Aroclor 1260 although it is present at about 1% by weight. As an alternate method, calibration against a pure octachlorobiphenyl is recommended.

[d] Nonachlorobiphenyl is not found in common Aroclors; calibration against pure nonachlorobiphenyl is recommended. If nonachlorobiphenyl is unavailable, assume equal sensitivity between octachloro and nonachlorobiphenyl.

** Decachlorobiphenyl

whose abundance is reasonably high, or by using the entire envelope of each PCB group, allows calibration under conditions of sample complexity similar to that expected in actual analyses, as well as allowing routine monitoring of all experimental equipment.

Table 4 lists a set of peaks abstracted from the work of Webb and McCall[6] which could be used for PCB calibration. Other sets of peaks could be chosen for calibration purposes, or even the entire RRT window for each PCB group, as noted previously. Use of the entire RRT window affords optimum self-correction by averaging the individual chlorobiphenyl isomer sensitivities, which may be of significance if the individual isomer sensitivities show large variations. The other previously proposed methods make the tacit assumption that the individual isomer sensitivities do not vary too greatly. Use of a calibration based upon the complete RRT window for any chlorobiphenyl group gives directly an ensemble averaged calibration factor which should accurately describe the average GC/MS system response to each chlorobiphenyl group.

Preliminary study of some individual chlorinated biphenyl isomers have been conducted to evaluate the validity in GC/MS response between isomers. A selection of pure compounds was obtained from RFR Corporation (1 Main Street, Hope, Rhode Island 02831). Certain of these were selected on a random basis within PCB groups for initial study. Solutions were prepared in benzene containing 5-15 μg/mL. A 2-μL aliquot of each solution was analyzed by GC/MS using a Finnigan 4000 with their 6100 data system. An OV-1 glass column was used and operated isothermally at either 185°C or 200°C depending on the isomer groups. A single injection of each solution was made, and the data for each compound were tabulated for comparison. A set of subset masses slightly different from that recommended in the proposed method was used with an integration time of 20 msec/mass. The PCBs have a significant mass defect (exact masses less than nominal mass) and the spectrometer was not tuned to compensate for this fact. Thus, the data obtained are in some cases from the sides of mass peaks and are not the optimum achievable.

The GC area response obtained for each of the isomers studied is shown in Table 5. For this small set of data, standard deviations between 12% and 37% were found. Also, the average area/ng responses for the different chloro groups vary by up to a factor of 2. As an extreme case, consider the comparison of the tetrachlorobiphenyls. The area/ng sensitivities for these species vary by a factor of 3. Therefore any method which is based upon a single calibrating isomer is potentially subject to sizeable error. Of the alternatives presented for calibration, a calibration based upon the complete envelope of peaks for each chloro-containing group seems to be the most attractive. The procedure is essentially the same as that recommended by Webb and McCall for the GC/ECD analysis of PCBs. Since the complexity of the calibration samples approximates that found in environmental samples, the error due to sensitivity differences between isomers is minimized.

Table 5

PCB GC/MS Sensitivity Data: GC Areas

Sample	Compound	Quantity (ng)	GC Area	Area/ng
RPC-19	2,3,5-trichlorobiphenyl	27.7	206991	7470
RPC-21	2,2′,5-trichlorobiphenyl	29.5	261941	8880
RPC-23	2,4,5-trichlorobiphenyl	28.0	191635	6840
				avg. 7730
				± 1040 (13%)
RPC-27	2,3,4,5-tetrachlorobiphenyl	28.4	268218	9400
RPC-30	2,2′,4,5-tetrachlorobiphenyl	24.0	284449	11900
RPC-33	2,3′,4′,5-tetrachlorobiphenyl	8.32	158440	19000
				avg. 13400
				± 5000 (37%)
RPC-38	2,2′,3,4′,5-pentachlorobiphenyl	9.40	135933	14500
RPC-41	2,2′,3′,4,6-pentachlorobiphenyl	12.06	208174	17300
				avg. 15900
				± 2000 (12%)
RPC-47	2,2′,4,4′,5,5′-hexachlorobiphenyl	19.26	167214	8700
RPC-51	2,2′,3,5,5′,6-hexachlorobiphenyl	18.20	112066	6200
				avg. 7400
				± 1800 (24%)

IV. EVALUATION OF THE PCB ANALYSIS PROCEDURE

In the previous section, calibration of the different chlorobiphenyl groups using the entire RRT window for that group from a well defined Aroclor reference material was recommended as the method of choice. That procedure was evaluated in terms of its ability to give consistent results over a period of time.

A. Calibration Procedure Evaluation

To evaluate the calibration procedure, samples of three Aroclor reference materials, Aroclor 1242, Aroclor 1254, and Aroclor 1260, were obtained from the batches analyzed by Webb[6]. The solutions were obtained at a concentration of 1 mg Aroclor per 1 mL of solution in isooctane. Aliquots of each of the three Aroclor reference materials were diluted to 20 µg/mL and p,p'-DDE was added to each to a level of 1 µg/mL. Each Aroclor was then analyzed a minimum of six times over a period of one week by the recommended GC/MS procedure using the conditions listed in Table 6. After the completion of a run, the ion chromatograms for each of the analytical ions and the internal standard were obtained.

Overlapping the ion chromatograms of PCBs differing by two chlorines (e.g., M and M+2Cl) serves to clearly delineate the retention time windows. For cases where the PCB group containing one more chlorine (M+Cl) is at a much higher concentration than M, the mass spectra of the peaks in the ion chromatogram is used to pinpoint the location of RRT window for M. The total ion chromatograms for the different Aroclors, Figures 4-6, show a pattern for these three Aroclors similar to those found by GC/ECD methods. The results for the different Aroclors are shown in Table 7 for Aroclor 1242, Table 8 for Aroclor 1254, and Table 9 for Aroclor 1260.

The relative standard deviations for the analysis of each of the Aroclor reference materials show excellent agreement. A majority of the deviations are less than 3% and all are below 8%.

One may assess the validity of the equal weight/response sensitivity method of calibration discussed in the previous section from Tables 7, 8, and 9.

For some of the PCB chloro group, typically the major component(s), the agreement between the known and found results was very good. However, the chloro groups present at less than 20% by weight can show considerable error. Thus, using one group of chloro-containing PCBs, such as the tetrachloro biphenyls, for calibration of the different chlorobiphenyls may give acceptable results.

The method detailed in Appendix A, which uses calibration of the specific chloro groups against a well characterized reference standard will not be subject to the errors observed when the equal sensitivity assumption is used. With this recommended analysis method more

accurate concentration data can be obtained for a small increase in analysis time. For the remaining sections, the recommended PCB procedure was used exclusively.

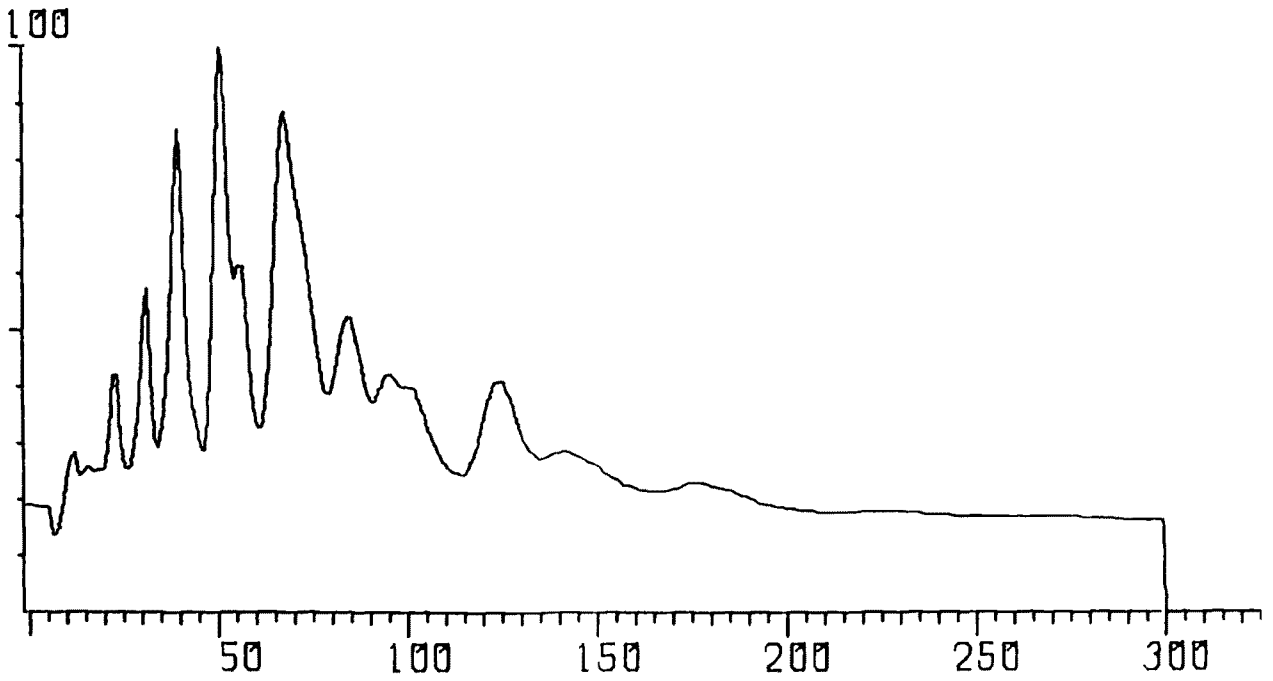

FIGURE 4 GC/MS SUBSET MASS CHROMATOGRAM OF AROCLOR 1242 STANDARD

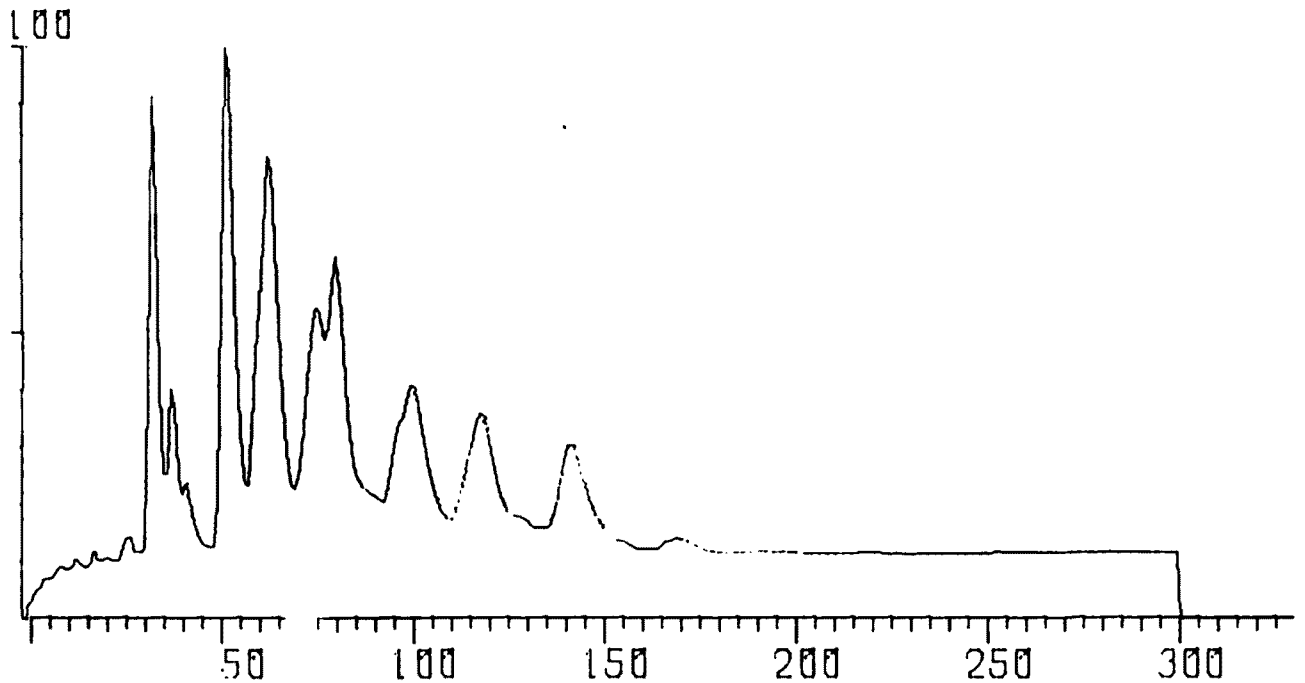

FIGURE 5 GC/MS SUBSET MASS CHROMATOGRAM FOR AROCLOR 1254 STANDARD

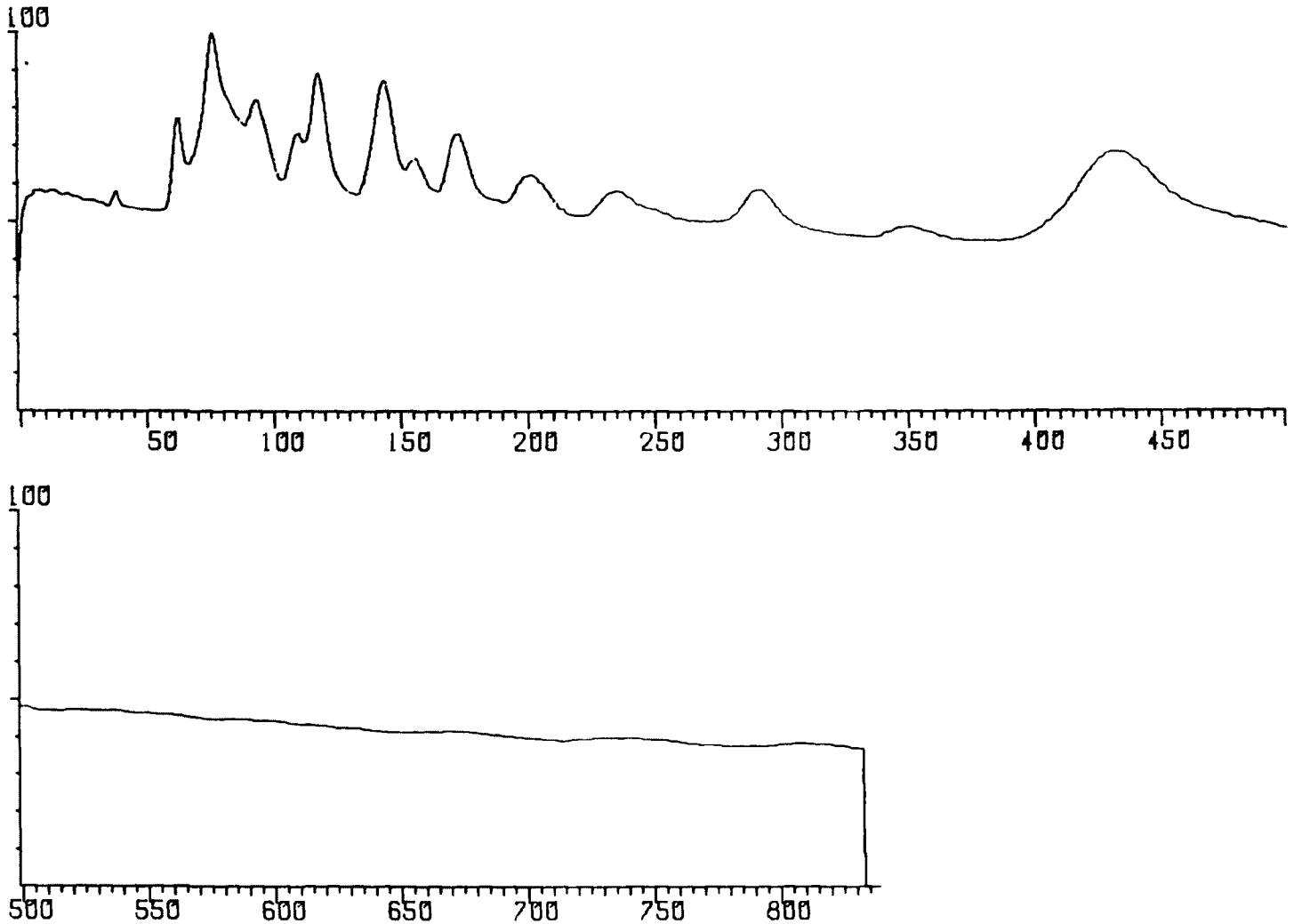

FIGURE 6 GC/MS SUBSET MASS CHROMATOGRAM FOR AROCLOR 1260 STANDARD

TABLE 6

GC/MS Conditions

I. Gas Chromatographic Conditions

a) Finnigan Model 9610 GC

b) 6-ft glass column packed with OV-1 coated Supelcoport 100/120.

c) Multilinear temperature program

1) isothermal program at 185°C for 30 min.

2) linear program from 185°-300° at 25°C/min.

3) isothermal program at 300°C for 25 min.

d) 2-3 µL injections

II. Mass Spectrometric Condition

a) Finnigan Model 4000 mass spectrometer

b) mass range - 186-190, 220-226, 254-260, 288-294, 316-328, 356-364, 392-400, 426-434

c) integration time - 50 msec/amu

d) electron multiplier - -1800V

e) electron energy - 50 eV

f) filament emission - 30 ma

g) scan rate - 3 sec/spectrum

TABLE 7

Analysis of Aroclor 1242

PCB Cluster	m/e	Known[1] Results	% By Weight[2] Found	Rel. Std. Deviation
Cl_1	188	1.1	4.74	.0217
Cl_2	224	16.95	9.16	.0330
Cl_3	258	39.19	45.67	.0101
Cl_4	292	31.83	32.17	.0319
Cl_5	326	9.64	7.62	.0016
Cl_6	362	.49	.63	.0120

[1] Webb & McCall, Ref. 6

[2] Weight percent found by normalizing raw area ratio (PCB cluster area/internal standard area) by the isotopic abundance of the analytical ion and the molecular weight for the chloro group.

TABLE 8

Analysis of Aroclor 1254

PCB Cluster	m/e	Known[1] Results	% By[2] Weight Found	Rel. Std. Deviation
Cl_2	224	--[3]	.17	.003
Cl_3	258	—[3]	1.03	.0056
Cl_4	292	13.80	21.68	.0106
Cl_5	326	61.92	56.88	.0204
Cl_6	362	23.28	19.08	.0019
Cl_7	394	1.00	1.17	.0071

[1] See Table 7

[2] See Table 8

[3] Webb reported components only >1%

TABLE 9

Analysis of Aroclor 1260

PCB Cluster	m/e	Known[1] Results	% By Weight[2] Found	Rel. Std. Deviation
Cl_2	224	--[3]	.20	.0009
Cl_3	258	--[3]	.34	.0029
Cl_4	292	--[3]	1.52	.0032
Cl_5	326	11.52	17.85	.0776
Cl_6	362	46.14	47.39	.0152
Cl_7	394	34.84	28.24	.0619
Cl_8	428	6.10	4.46	.0102

[1] see Table 7

[2] see Table 7

[3] Webb reported only components >1%

V. VERIFICATION OF METHOD

A. Evaluation of Test Samples

In order to demonstrate the application of the PCB procedure to actual samples, two test mixtures were obtained, dosed with different Aroclor materials and analyzed by the proposed procedure. One of the test mixtures was a complex combination of several wastes and waste extracts (see Table 10 for the mixture composition) while the other mixture was the extract of a sample collected from a ferroalloy smelter. Both samples had a wide variety of organic compounds ranging from low mass to above mass 400.

The wastes and waste extracts comprising the first test sample are listed in Table 10. These represent a complex system with numerous potential interferences. The perchloroethylene waste did, in fact, have some PCB content which added to the complexity of that sample. Aliquots of the waste solution were dosed with either Aroclor 1242 or Aroclor 1260 to a level of 10 µg per mL, and the internal standard p,p'-DDE added to a level of 1 µg per mL prior to analysis. The amount of dissolved material in this solution was about 0.28 g per mL, greatly in excess of the amount of PCBs present. Figure 7 shows the reconstructed gas chromatogram (RGC) of the waste sample obtained from the intensities of the ions in the mass ranges listed in Table 1 for each of the PCB groups.

This sample contained no added Aroclor. With no preliminary separation of the sample as is the case with the first sample, the normal GC/ECD pattern recognition approach would have been unable to even indicate the presence of PCBs in the sample. The presence of PCBs would be even further obscured if ions had been acquired over the entire mass range of interest, the normal GC/MS data acquisition mode.

Figure 8a shows the RGC for this mixture dosed with Aroclor 1260. Since this sample consisted of primarily low molecular weight species, the higher mass PCBs show relatively little interference from background species. The RRT windows used for each species are shown in Figures 8b-d, which is an RGC constructed from only the ions of analytical interest. Table 11a lists the recovery data for the Aroclor 1260 dosed sample. For the major Aroclor containing components (Cl_6 and Cl_7 biphenyls) the recoveries are within $\pm$5% and the relative standard deviations are less than 3%. The other large component (Cl_5) has a higher error (+10%) than for the two major components but it still represents a reasonably accurate measurement. The minor Cl_8 biphenyl group shows large error (22%) and standard deviations (35%), but the absolute level of this component was quite low (about 600 pg injected or 1.4×10^{-12} mole), approaching the instrumental detection limit. Measurement at such levels will show large errors for replicate runs due to instrumental fluctuations.

TABLE 10

Organic Mixture Composition

Styrene waste	- mixture of aromatic hydrocarbons
API waste extract	- mixture of aliphatic unsaturated hydrocarbons and aromatic hydrocarbons
Lucidol waste	- mixture of α-methylstyrene, cumene, cumyl alcohol and acetophenone
Perchloroethylene waste	- hexachlorobutadiene, hexachlorobenzene and a mixture of other chlorinated hydrocarbons
Simulated coke waste extract	- mixture of phenol, cresol, amines and benzoic acid
p-Toluene sulfonic acid	

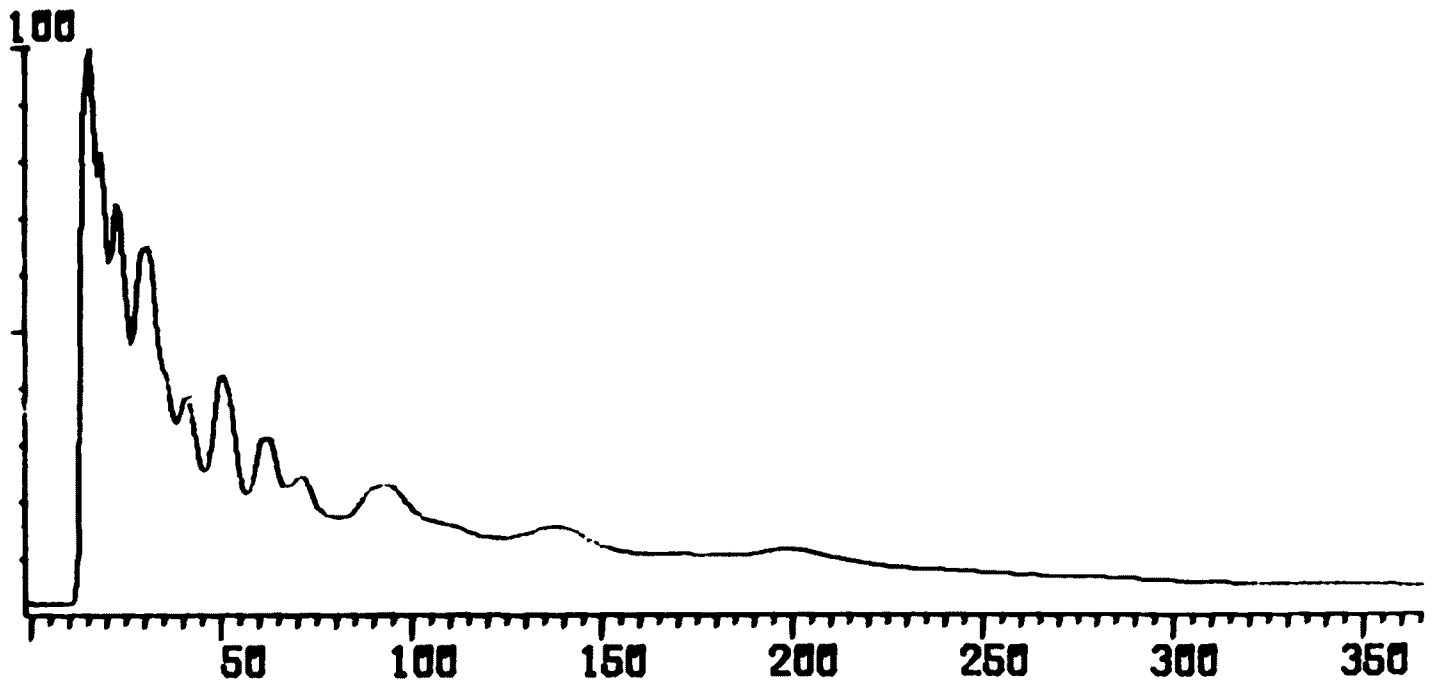

FIGURE 7 GC/MS SUBSET MASS CHROMATOGRAM FOR WASTE EXTRACT MIXTURE

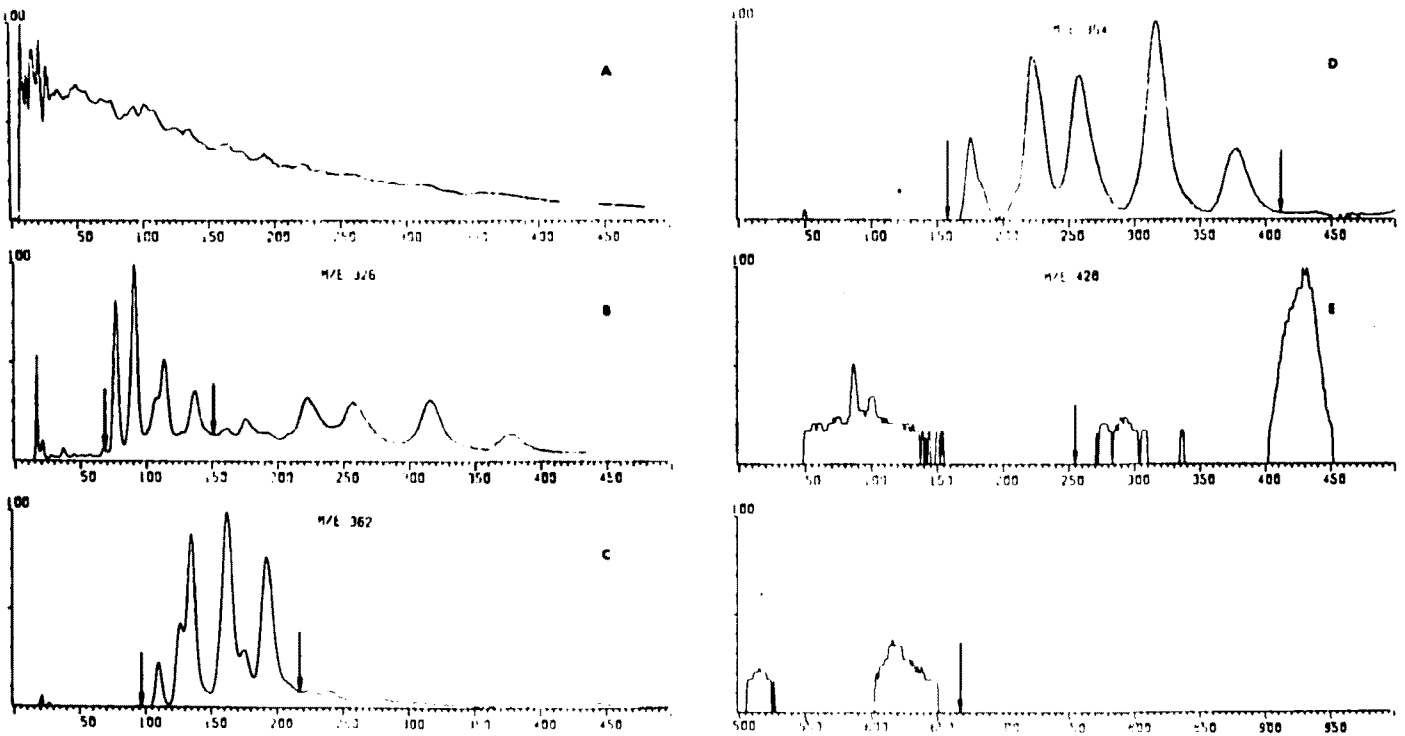

FIGURE 8 a) GC/MS SUBSET MASS CHROMATOGRAM, b–e) SINGLE ION CHROMATOGRAMS FOR ANALYTICAL IONS OF AROCLOR 1260 (326, 362, 394 AND 428) FOR WASTE EXTRACT MIXTURE DOSED WITH AROCLOR 1260. SOLID LINES DELINEATE RELATIVE RETENTION TIME WINDOWS USED

When the above sample was dosed with Aroclor 1242 instead of Aroclor 1260, the interference due to the lower weight species became more important. Figure 9 shows the RGC for the dosed sample using the set of selective scanned masses (Figure 9a) and the chromatograms obtained for each of the analytically important masses (Figures 9 b-g). The interference at mass 188 (Cl_1 biphenyl) swamps out the signal for that chlorog group making it impossible to quantitate the level of monochlorobiphenyl present. The other chloro groups from the added Aroclor 1242 show a decreasing amount of interference as the mass of the chloro group increases. The results are tabulated in Table 11b.

The second test mixture collected from a ferroalloy smelter represented a substantially different test for the PCB analysis procedure than the previous mixture. This mixture contained aromatic hydrocarbons and various oxygenated compounds ranging in mass to above 500, with major components found in the 220-300 mass range. This range covers the Cl_2-Cl_4 PCBs, and the high levels of high mass species present a challenge for the determination of Cl_5 and higher PCBs not encountered with the previous sample.

Examination of the ferroalloy extract prior to any Aroclor dosing showed no detectable quantity of any PCBs. An aliquot of the extract was then dosed with Aroclor 1254 to a level of 10 µg/mL, and repetitively analyzed for PCBs. Figures 10 a-d show the various chromatograms obtained for the ferroalloy sample extract dosed with Aroclor 1254. The large variety of high mass species caused a nearly uniform total signal during the elution of the PCBs, in contrast to the decreasing total signal during the course of the PCB elution seen in the previous samples. The recoveries for the various PCB groups are listed in Table 12.

The low recovery observed for the Cl_8 biphenyl is in part due to the high background observed for that ion throughout the chromatographic run. Fluctuations in the background level near the RRT window for the hexachloro group will cause error in the estimation of the background level, with overestimation of the background level leading to low recoveries. However the recoveries found are acceptable for these low level analyses, particularly since no pretreatment or separation procedures were used.

B. Recovery from Flyash

As a final test of the recommended PCB procedure, a sample of flyash was thoroughly extracted with methylene chloride, dosed with Aroclor 1254 and re-extracted with methylene chloride to ascertain the recovery of PCB from a flyash sample. To 2 g of the pre-extracted flyash, 10 µg of Aroclor 1254 in 50 mL of methylene chloride was added and the mixture evaporated to dryness. The sample was then re-extracted with ten 10 mL portions of methylene chloride. The ten portions were combined and evaporated to 1 mL. The concentrated extract was dosed with 1 µg of the internal standard material, p,p'-DDE, and analyzed via the recommended procedure.

TABLE 11

Analysis of Mixture of Wastes and Waste Extract

a) Mixture dosed with Aroclor 1260:

PCB Cluster	Mixture Background (µg)	Mixture + Aroclor 1260 (µg)	Aroclor 1260 Found (µg)	Aroclor 1260 Added (µg)	Recovered (%)	Relative Standard Deviation
Cl_5	.234	1.497	1.263	1.152	109.6	.037
Cl_6	.351	4.919	4.568	4.614	99.0	.015
Cl_7	1.059	4.739	3.680	3.484	105.6	.029
Cl_8	.066	.813	.747	.610	122.5	.353

b) Mixture dosed with Aroclor 1242

PCB Cluster	Mixture Background (µg)	Mixture + Aroclor 1242 (µg)	Aroclor 1242 Found (µg)	Aroclor 1242 Added (µg)	Recovered (%)	Relative Standard Deviation
Cl_1	--	--	--	.11	--	--
Cl_2	--	--	5.85	1.70	34.4*	.090
Cl_3	--	3.83	3.83	3.92	97.7	.099
Cl_4	.013	2.68	2.67	3.18	84.0	.050
Cl_5	.234	.905	.671	.96	69.9	.051
Cl_6	.351	.372	.021	.05	42.0	.255

* From reference 15, test sample was a mixture of each of the waste ans waste extracts listed.

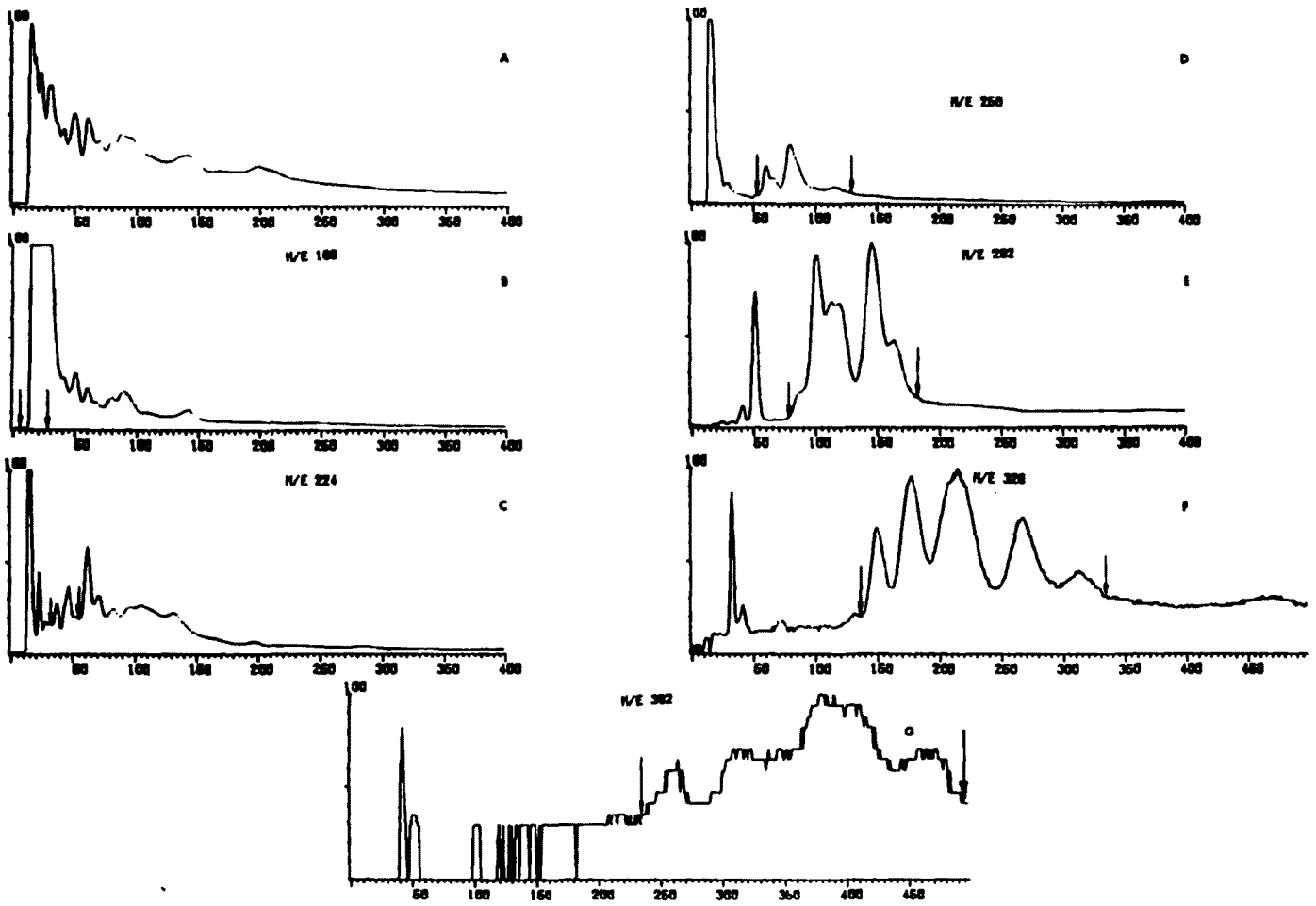

FIGURE 9 a) GC/MS SUBSET MASS CHROMATOGRAM, b–g) SINGLE ION CHROMATOGRAMS FOR THE ANALYTICAL IONS OF AROCLOR 1242 (188, 224, 258, 292, 326) FOR WASTE EXTRACT MIXTURE DOSED WITH AROCLOR 1242. ARROWS DELINEATE THE RELATIVE RETENTION TIME WINDOWS USED

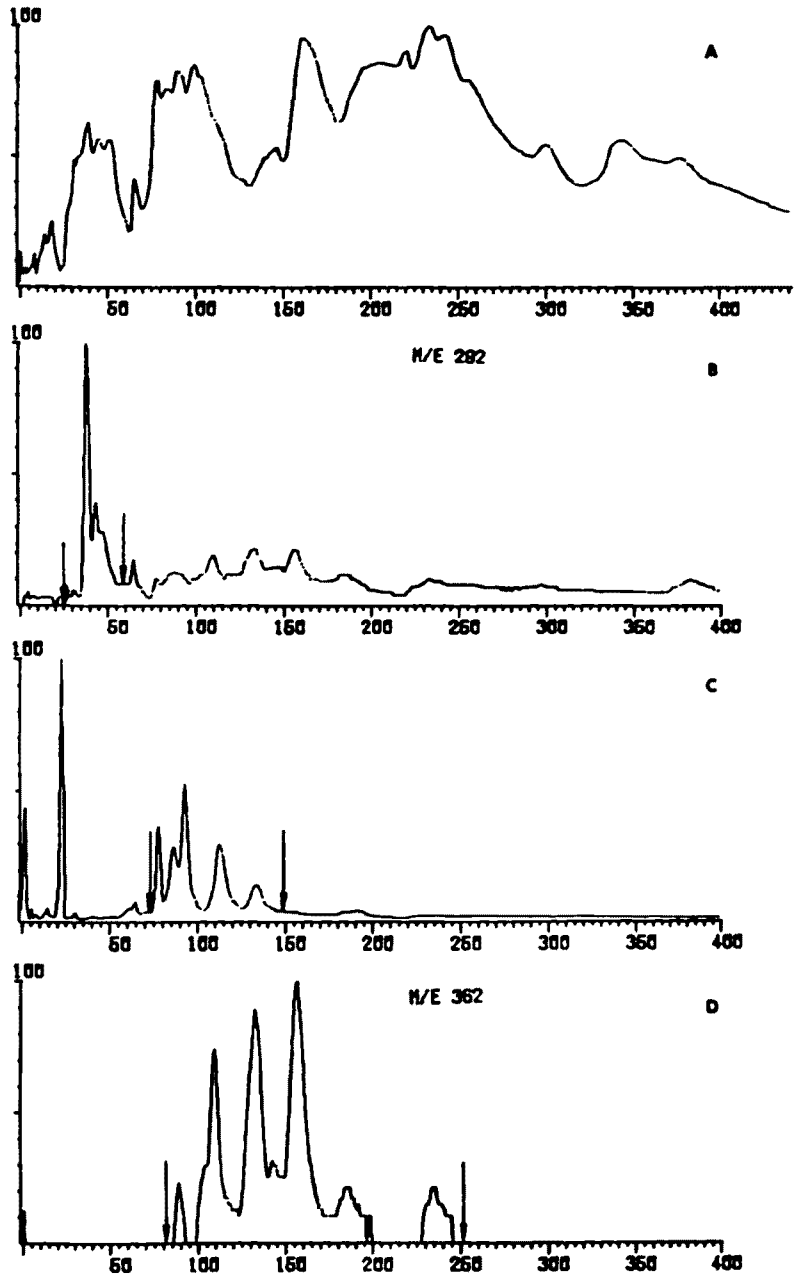

FIGURE 10 a) GC/MS SUBSET MASS CHROMATOGRAM, b–d) PROMINENT ION CHROMATOGRAMS FOR ANALYTICAL IONS 292, 326, 362 OF FERRO-ALLOY SMELTER SAMPLE DOSED WITH AROCLOR 1254. ARROWS DELINEATE RELATIVE RETENTION TIME WINDOWS USED

TABLE 12

PCB Analysis of Ferroalloy Sample[1]

PCB Cluster[2]	PCB Found (µg)	Aroclor 1254 Added (µg)	Recovered (%)
Cl_4	1.35	1.38	97.8
Cl_5	4.98	6.19	80.5
Cl_6	1.61	2.33	69.1
Cl_7	—	.10	—

[1] Values reported are for 1 mL of sample volume.

[2] Cl_3 cluster was observed in reference material but interferences in the RRT window from other species prevent measurement.

The RGC obtained from the extracted flyash sample was virtually identical to the RGC obtained for the Aroclor 1254 reference material. Figure 11 allows comparison of the Aroclor 1254 reference sample with the re-extracted flyash sample. The recoveries were quite good, at least 80% for the major PCB components (see Table 13). The Cl_3 biphenyl was seen in both the reference material and the dosed flyash sample and the relative responses agreed within 5% for the reference standard and the extracted flyash.

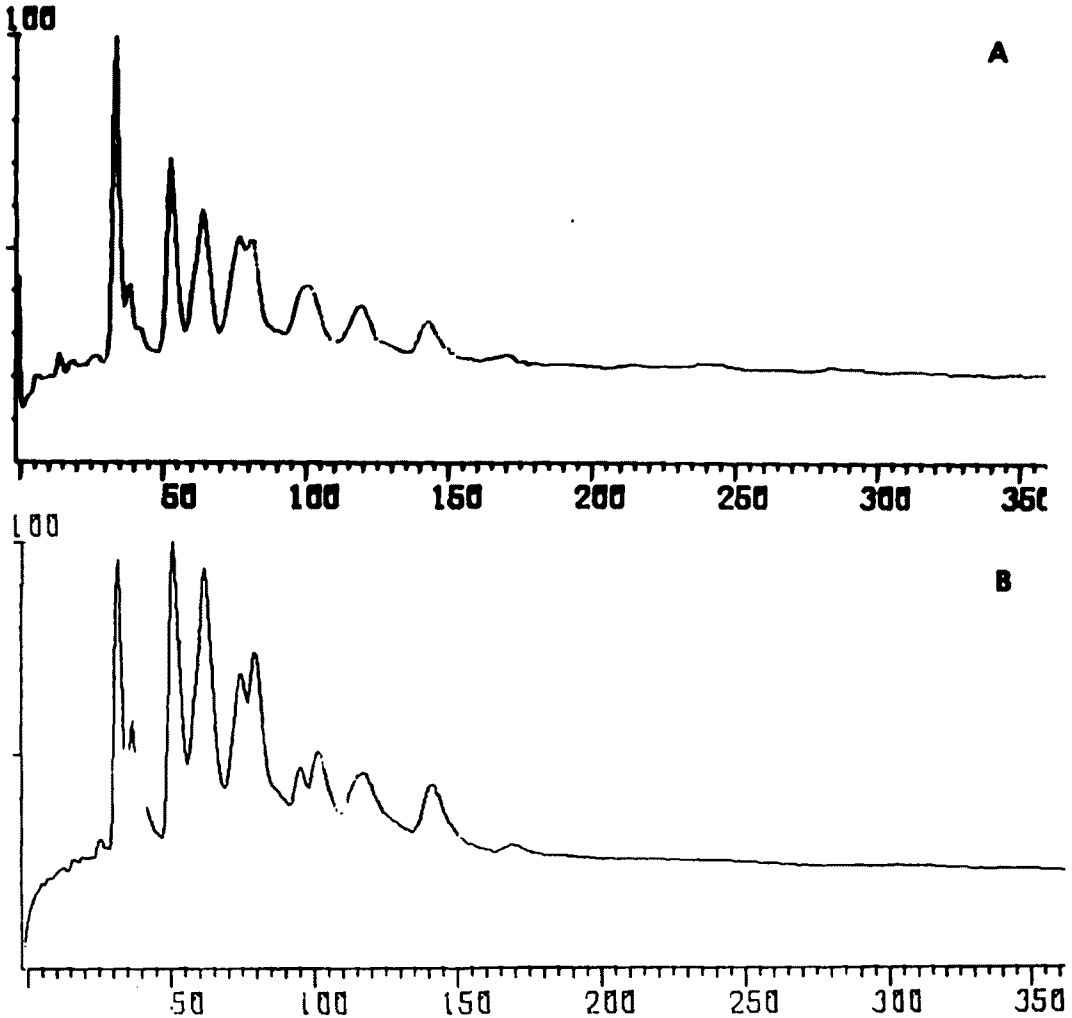

FIGURE 11 GC/MS SUBSET MASS CHROMATOGRAM FOR EXTRACTED FLYASH SAMPLE DOSED WITH AROCLOR 1254 (a) AND AROCLOR 1254 STANDARD (b)

TABLE 13

PCB Analysis for Recovery of Aroclor 1254 in Dosed Flyash[1]

PCB Cluster[2]	PCB Found (µg)	Aroclor 1254 Added (µg)	Recovered (%)
Cl_4	1.17	1.38	84.8
Cl_5	5.11	6.19	82.6
Cl_6	2.47	2.33	106.0
Cl_7	—	.16	—

Notes: See notes for this table on following page.

[1] Values reported are for 1 mL of sample volume.

[2] Cl_3 cluster observed in both reference material and sample. Agreement between the Cl_3 cluster to internal standard ratio for the reference and the standard is within 5%.

VI. CONCLUSION

The analysis procedure for the measurement of PCB emissions from combustion sources, Appendix A, has been tested for several representative samples. The recoveries found were quite good without any form of extraction or sample cleanup. For complex samples, use of a preliminary separation scheme should improve the quantitative measurement of PCBs by eliminating low mass interferences which can be quite sizeable. Standard separation procedures such as those described in the Federal Register Method for PCBs may be used for pretreatment of samples prior to analysis of PCBs.

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APPENDIX A

Proposed Method
(Abbreviated)

Measurement of Polychlorinated Biphenyls (PCBs) in Combustion Sources

1. Abstract of the Method

The method is designed primarily to address the problem of measurement of PCB emissions from combustion sources, but should be applicable to PCB measurements from any source.

The method uses an automated gas chromatograph/mass spectrometer. Data are acquired in a select subset of masses and integrated according to gas chromatographic retention time criteria. Data are reported as quantity of monochloro-, dichloro- .....decachlorobiphenyl.

2. Interferences

Interferences in the PCB analysis are minimized with this procedure. Isotope abundance patterns are used to verify the composition as a PCB. Selected mass chromatograms and retention time windows provide a high degree of specificity in the analysis of a specie as a PCB.

3. Sample Extraction

Sample extractions should be done using distilled-in-glass pentane or methylene chloride (Burdick and Jackson). Samples should be concentrated to 1.0 µl using a Kuderna-Danish evaporator. If necessary to achieve sensitivity samples may be further concentrated to 0.1 ml using a gentle stream of nitrogen.

4. Sample Cleanup

It may be possible to analyze the extracted samples directly without further cleanup. The analysis itself should be the criteria for determining the need for further cleanup as described for the Standard EPA method for PCBs in industrial effluents.[5] If cleanup is required, use the florisil/silica gel procedures described in the EPA method.

5. Analysis

A. GC Conditions

Use a 2 m x 2 mm I.D., glass column containing any of several phases. OV-1, OV-101, OV-17, Dexsil 300 and Dexsil 400 at 3% on 80/100 Chromosorb have all been used successfully for the PCB analysis. Temperature programming from about 150°-280°C has been used, but the chromatograms are more reproducible when run in the isothermal mode. A temperature of 185°C on OV-1 is good for the Aroclors through 1248. A temperature of 200°C is used for the higher Aroclors. A 2-5 µl sample size injection is made dependent on the concentration in the sample. Use of less than 2 µl will lead to poor reproducibility. The GC gas stream is diverted for the first 30 sec allowing the solvent to elute and be vented and then the diverter is closed and data acquisition initiated.

B. MS Conditions

Extract Conditions will depend on spectrometer type and condition. Care should be taken to calibrate the mass scale to accommodate the significant mass defect of the PCBs. It is recommended that an Aroclor mixture be used in place of PC-43 (or other PFKs) to construct an alternate mass calibration scale for the PCB analysis. Set the mass ranges for data acquisition as follows:

PCB Group	Range	Analytical m/e
Cl_1	186 - 190	188
Cl_2	200 - 226	224
Cl_3	254 - 260	258
Cl_4	288 - 294	292
Cl_5	322 - 328	326
Cl_6	356 - 364	362
Cl_7	392 - 400	394
Cl_8	426 - 434	428
Cl_9	460 - 468	464
Cl_{10}	494 - 504	498

Integration times will vary with instruments. A setting of 50-64 msec/amu is recommended.

6. Qualitative Identification of PCBs

A total chromatogram is constructed from the sum of all the mass used in data acquisition. Individual mass spectra are obtained at GC peak maxima. These spectra are examined to determine whether the proper isotope abundance patterns are present for the given chlorobiphenyl group.

7. Quantitative Measurement of PCB Groups

When the species have been confirmed as PCB's, individual mass chromatograms are obtained for the analytical masses corresponding to the PCB groups, 188, 224, --- 498. An Aroclor sample such as Aroclor 1232 and Aroclor 1254 is used to establish a relative retention time (RRT) scale using the data given by Webb and McCall[6]. The area for each PCB group is integrated over the RRT regions indicated below:

PCB Group	Analytical m/e	RRT Region
Cl_1	188	0(5) - 20
Cl_2	224	15 - 35
Cl_3	258	25 - 55
Cl_4	292	40 - 100
Cl_5	326	70 - 150
Cl_6	363	125 - 250
Cl_7	394	160 - 350
Cl_8	428	275 - 600
Cl_9	464	400 -1000
Cl_{10}	498	650 -1200

The RRT windows may need to be adjusted slightly for proper measurement of total areas. Use of these windows minimized interferences from other PCBs.

Complete details of the quantitative calibration have not been worked out at this time. It is tentatively recommended that calibration be based upon specific GC peaks in Aroclor reference.

8. Sensitivity

The sensitivity of this method has not been established, but is expected to be at least 0.1 ng/injected sample.

Quantitative PCB Standards for Electron Capture Gas Chromatography

by **Ronald G. Webb** and **Ann C. McCall**, Southeast Environmental Research Laboratory, National Environmental Research Center—Corvallis Environmental Protection Agency, Athens, Georgia 30601

Abstract

The weight of PCB represented by each electron capture gas chromatographic (EC-GC) peak in solutions of Aroclors 1221-1260 has been determined. The Aroclor samples from which these solutions were prepared are proposed as quantitative PCB standards. Their compositions were determined by elemental analysis, GC with a Coulson conductivity detector, and combined GC/MS. Retention times relative to p,p'-DDE are recommended to designate individual GC peaks of PCB's. A table is given for each Aroclor showing the weight percent of each EC-GC peak in the mixture. A procedure using Aroclors 1242, 1254, and 1260 is recommended for analyzing environmental samples containing more than one Aroclor mixture. Stock solutions of the Aroclors in isooctane are stable except when directly exposed to sunlight. Ampoules of the Aroclor solutions are offered.

Introduction

Quantitation of polychlorinated biphenyls (PCB's) from electron capture (EC) chromatograms is complicated because the EC detector responds differently to each PCB isomer (1,2). Quantitation by direct comparison of an unknown EC chromatogram with those of Aroclor standards is difficult because individual peaks in environmental samples are sometimes obscured by pesticide residues, are completely missing, or have considerably different relative intensities.

To avoid these difficulties, Berg and co-workers (3) have proposed that the PCB's in a sample be converted to decachlorobiphenyl, and the EC signal from this derivative be compared with that from conversion of a known amount of Aroclor 1254 to decachlorobiphenyl. This method appears to be ideally suited to a monitoring program designed for rapid and sensitive measurement of the total quantity of PCB's without regard to composition. In many cases, this derivative approach is undesirable because an extra analytical step is required and because any evidence of metabolism or degradation of the sample is destroyed. The disadvantages of both the direct comparison method and the derivative method can be largely overcome by using Aroclor standards in which the quantitative composition of each EC-GC peak is known. We have prepared these standards and recommend procedures for their use.

Experimental

The Monsanto Company* provided the Aroclor samples, which were not marked with lot numbers. Elemental analysis by Galbraith Laboratories, Knoxville, Tennessee, showed the following percent compositions (average of triplicate analyses):

Aroclor 1221	C, 72.94; H, 4.45; Cl, 22.74
1232	C, 64.44; H, 3.46; Cl, 31.96
1242	C, 54.64; H, 2.70; Cl, 42.85
1248	C, 49.50; H, 2.17; Cl, 48.54
1254	C, 44.10; H, 1.61; Cl, 54.33
1260	C, 38.18; H, 0.94; Cl, 60.97

The Food and Drug Administration provided the primary standard p,p'-DDE, which was used as a retention time standard and calibration standard for the conductivity detector.

A Microtek 220 gas chromatograph was equipped with a Coulson conductivity detector. The column was a 6 ft x ¼ in., o.d., glass U-shaped tube packed with 3% SE-30 on 80/100 Gas Chrom Q. The carrier gas was helium at a flow rate of 60 ml/min. All Aroclors were chromatographed isothermally; Aroclors 1221 and 1232 at 175°C; 1242, 1248 and 1254 at 185°C; and 1260 at 190°C. The chromatograms were quantitated by measuring peak areas with either a planimeter or disc integrator.

A Microtek 220 gas chromatograph with Ni-63 EC detector was operated at 15-30 V (DC) and 275°C. The column was a 6 ft x ¼ in., o.d., glass U-shaped tube packed with 3% SE-30 on 80/100 mesh Gas Chrom Q. The carrier gas was nitrogen at 90 ml/min. Aroclors 1221 through 1254 were chromatographed isothermally at 200°C and Aroclor 1260 at 215°C.

An F&M 700 gas chromatograph with tritium EC detector at 205°C was operated at a pulse interval of 15 microseconds. The coiled glass column was 8 ft x ¼ in., o.d., packed with 3% SE-30 on 80/100 Gas Chrom Q. The carrier gas was 95% argon and 5% methane at 80-100 ml/min. All samples were chromatographed isothermally at 195°C.

Mass spectra (70 eV) were obtained on a Finnigan 1015-C quadrupole mass spectrometer interfaced with a Gohlke separator to a modiifed Varian 1400 GC. GC conditions were set to produce chromatograms equivalent to those from EC-GC. The spectrometer was controlled by a DEC PDP-8 computer, and spectra were collected on magnetic tape and printed or plotted under computer control.

**Mention of products or companies does not imply endorsement by the Environmental Protection Agency.*

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Results and Discussion

The weight of PCB present in each GC peak of a given Aroclor can be calculated from two pieces of information:

1) the empirical formula of the compound represented by the peak, and
2) the absolute amount of chlorine represented by the peak.

Combined GC/MS determines the first, and a GC equipped with an electrolytic conductivity detector can determine the second.

GC/MS examination of Aroclors showed that several peaks were mixtures of PCB's with different numbers of chlorines. To estimate the composition of a GC peak containing PCB's with different numbers of chlorines, the following observation was used: equal weights of two PCB's that differ only by one chlorine give the same sum, within 25%, when the intensities of all the signals from the molecular ion, or parent, cluster, the parent-minus-one-chlorine cluster and parent-minus-two-chlorine cluster of each PCB are added. This rule was derived from a limited study of quadrupole mass spectra of a series of synthetic PCB's (4) and may not hold for other types of spectrometers.

Figure 1 is the mass spectrum from an Aroclor 1242 GC peak that is a mixture of one or more trichlorobiphenyls and one or more tetrachlorobiphenyls. The molecular ion pattern at m/e 290-298 is typical of four-chlorine molecules. These molecules lose one chlorine, producing a three-chlorine fragment pattern (parent-minus-one-chlorine) at m/e 255, 257, 259, and 261. However, between these signals, there is also a strong three-chlorine pattern at m/e 256, 258, 260, and 262; this is the parent ion cluster of the trichlorobiphenyl(s). The signals at m/e 220-224 are seen after loss of two chlorines from the tetrachlorobiphenyl (the trichlorobiphenyl(s) does not show a significant signal for loss of one chlorine), and the signals at m/e 186 and 188 are seen after loss of two chlorines from trichlorobiphenyl.

In Figure 1, the tetrachlorobiphenyl intensities (peak heights) totaled 612 mm and the trichlorobiphenyl 304 mm. Tetrachlorobiphenyl is thus about two-

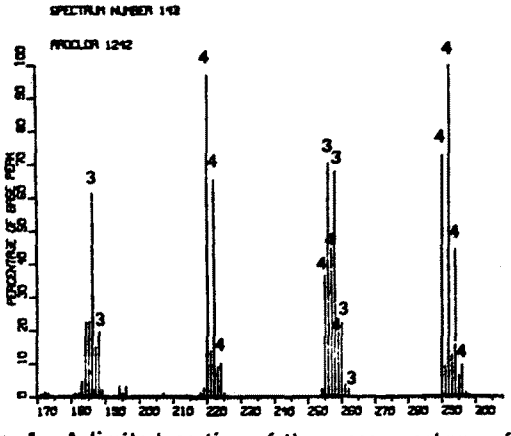

Figure 1. A limited portion of the mass spectrum of a mixture of tetrachlorobiphenyl(s) and trichlorobiphenyl(s) from RRT peak 54 of Aroclor 1242 (See Figure 5). The abcissa is marked in atomic mass units (m/e).

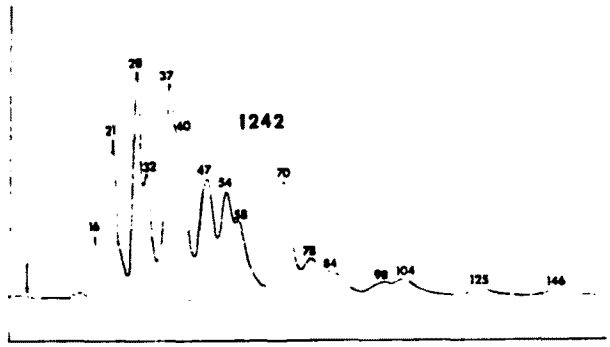

Figure 2. Gas chromatogram of Aroclor 1242 on SE-30 with an electrolytic conductivity detector. The peak identification numbers correspond to the retention time relative to p,p'-DDE=100. From injection, at the arrow, to peak 146 was about 20 min.

thirds of the mixture. These data were used to calculate the average molecular weight of the material in the GC peak.

The Coulson conductivity detector responds linearly to chlorine. Linear response to PCB's was shown with individual PCB isomers (4) containing one to six chlorines, and the detector response was checked for reproducibility several times each day with p,p'-DDE. A typical Coulson chromatogram for 1242 is shown in Figure 2. Peak resolution was not completely optimized here or in the GC-MS work so that these separations would be typical of those in the pesticide literature (5-10). Other studies (4, 11, 12) have show that the Aroclors are much more complicated than shown here, but this resolution is adequate for routine analysis.

The area of each Aroclor peak was determined and the weights (nanograms) of chlorine and PCB present were calculated using the response of p,p'-DDE as follows:

$$\frac{\text{ng DDE injected}}{\text{DDE peak area (cm}^2\text{)}} \times \frac{4 \times \text{at. wt. Cl}}{\text{mol. wt. DDE}} = \frac{\text{ng Cl}}{\text{cm}^2}$$

$$\frac{\text{ng Cl}}{\text{cm}^2} \times \text{PCB peak area (cm}^2\text{)} = \text{ng Cl}$$

$$\text{ng Cl} \times \frac{\text{Gram molecular weight}}{\text{No. of chlorines in molecule} \times 35.46\ \text{g}} = \text{ng PCB}$$

Tables I-VI present these results as the percent of

4. Webb, R. G., and McCall, Ann C., J. Assoc. Offic. Anal. Chemists 55, 746 (1972).
5. Zitco, V., Bull. Environ. Contam. Toxicol. 6, 464 (1971).
6. Biros, F. J., Walker, A. C., and Medberry, A., Bull Environ. Contam. Toxicol. 5, 317 (1970).
7. Grant, D. L., Phillips. W. E. J., and Villeneuve, A.. Bull. Environ. Contam. Toxicol. 5, 317 (1970).
8. Holmes, D. C., Simmons, J. H., and Tatton, J. O'G.. Nature 216, 227 (1967).
9. Bagley, G. E., Reichel, W. L., and Cromartie, E.. J. Assoc. Offic. Anal. Chemists 53, 251 (1970).
10. Rote, J. W.. Murphy, P. G.. Bull. Environ. Contam. Toxicol. 6, 377 (1971).
11. Stalling, D. L., and Huckins, J. N.. J. Assoc. Offic. Anal. Chemists 54, 801 (1971).
12. Sissons, D., and Welti, D., J. Chromatog. 60, 15 (1971).

Table I. Composition of Aroclor 1221

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	No. of Chlorines[c]
11	31.8	15.8	1
14	19.3	9.1	1
16	10.1	9.7	2
19	2.8	9.7	2
21	20.8	9.3	2
28	5.4	13.9	2 ┐ 85%
			3 ┘ 15%
32	1.4	30.1	2 ┐ 10%
			3 ┘ 90%
37	1.7	48.8	3
40			3
Total	93.3		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of seventeen results as a percentage of the mean of the results.

[c]From GC/MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table II. Composition of Aroclor 1232

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	No. of Chlorines[c]
11	16.2	3.4	1
14	9.9	2.5	1
16	7.1	6.8	2
20	17.8	2.4	2
21			2
28	9.6	3.4	2 ┐ 40%
			3 ┘ 60%
32	3.9	4.7	3
37	6.8	2.5	3
40	6.4	2.7	3
47	4.2	4.1	4
54	3.4	3.4	3 ┐ 33%
			4 ┘ 67%
58	2.6	3.7	4
70	4.6	3.1	4 ┐ 90%
			5 ┘ 10%
78	1.7	7.5	4
Total	94.2		

Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quanti[illegible].ted as one peak are bracketed.

Standard d[illegible]ation of four results as a means of the results.

From GC/MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

total Aroclor weight represented by each GC peak. The peaks are identified by their retention times relative to p,p'-DDE. We recommend that this be adopted as a standard method for designating individual PCB GC peaks. The separate percentages given for overlapping peaks were obtained by dividing the area with a perpendicular to the baseline from the minimum point between the two peaks. The accuracy of the Coulson determinations was checked by comparing each Aroclor's calculated percent chlorine with its elemental analysis. The amount found by Coulson GC was 98-102% of the elemental analyses except for Aroclor 1221.

Seventeen analyses with 1221 were performed and the average of the data was used to prepare Table I. Willis and Addison (13) have recently reported semiquantitative values for the composition of Aroclor 1221. Their analysis was based on EC-GC and flame ionization GC. They found 12.7% biphenyl present and about the same amounts of other materials as in Table I. Willis and Addison accounted for 92.3% of the weight of materials in 1221. If their 12.7% biphenyl

Table III. Composition of Aroclor 1242

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	No. of Chlorines[c]
11	1.1	35.7	1
16	2.9	4.2	2
21	11.3	3.0	2
28	11.0	5.0	2 ┐ 25%
			3 ┘ 75%
32	6.1	4.7	3
37	11.5	5.7	3
40	11.1	6.2	3
47	8.8	4.3	4
54	6.8	2.9	3 ┐ 33%
			4 ┘ 67%
58	5.6	3.3	4
70	10.3	2.8	4 ┐ 90%
			5 ┘ 10%
78	3.6	4.2	4
84	2.7	9.7	5
98	1.5	9.4	5
104	2.3	16.4	5
125	1.6	20.4	5 ┐ 85%
			6 ┘ 15%
146	1.0	19.9	5 ┐ 75%
			6 ┘ 25%
Total	98.5		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[b]Standard deviation of six results as a percentage of the mean of the results.

[c]From GC/MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

13. Willis, D. E., and Addison, R. F., J. Fisheries Res. Board Can. 29, 592 (1972).

is added to the PCB values in Table I, the weight percent Aroclor is 106.0 A mixture composed of the PCB's that Willis and Addison quantitated would contain 19.6% by weight chlorine; the Coulson determinations gave 22.9%; elemental analysis gave 22.7%.

When the data in Tables I-VI are compared to Aroclor chromatograms from an EC detector operated in the DC mode (Figures 3-8), peak size obviously is not a valid indication of concentration. For example, in Aroclor 1242 (Figure 5a) peaks 21, 28, 37, and 40 each represent about 11% of the mixture (See Table III), but their areas differ by as much as 65%. There are also major differences in peak ratios when the Aroclors are measured with a detector operated in the pulsed mode as shown in Figure 5b.

A Technique to Quantitate PCB's in Environmental Samples

The chromatograms of PCB's from environmental samples usually show some evidence of degradation or metabolism. A sample may contain a single partially degraded Aroclor or a combination of Aroclors. Such samples can be quantitated by using the standard Aroclors, the data in Tables I-VI, and some simple computation rules. The key principle is that the total amount of PCB present is *the sum of the amounts from all the individual peaks.*

To quantitate PCB's, chromatograph known amounts of the standards. Measure the area for each peak. Using the tables, determine the response factor

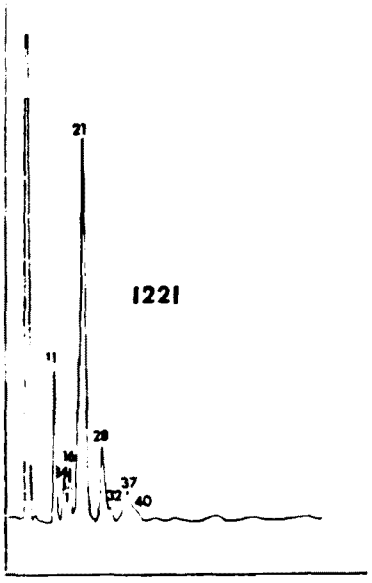

Figure 3. EC chromatogram of Aroclor 1221 chromatographed on SE-30 with a Ni-63 detector operated in the DC mode. The peak identification numbers correspond to the retention time relative to p,p'-DDE=100.

Table IV. Composition of Aroclor 1248

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	No. of Chlorines[c]
21	1.2	23.9	2
28	5.2	3.3	3
32	3.2	3.8	3
37	8.3	3.6	3
40	8.3	3.9	3] 85%
			4] 15%
47	15.6	1.1	4
54	9.7	6.0	3] 10%
			4] 90%
58	9.3	5.8	4
70	19.0	1.4	4] 80%
			5] 20%
78	6.6	2.7	4
84	4.9	2.6	5
98	3.2	3.2	5
104	3.3	3.6	4] 10%
			5] 90%
112	1.2	6.6	5
125	2.6	5.9	5] 90%
			6] 10%
146	1.5	10.0	5] 85%
			6] 15%
Total	103.1		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[b]Standard deviation of six results as a percentage of the mean of the results.

[c]From GC MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table V. Composition of Aroclor 1254

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	No. of Chlorines[c]
47	6.2	3.7	4
54	2.9	2.6	4
58	1.4	2.8	4
70	13.2	2.7	4] 25%
			5] 75%
84	17.3	1.9	5
98	7.5	5.3	5
104	13.6	3.8	5
125	15.0	2.4	5] 70%
			6] 30%
146	10.4	2.7	5] 30%
			6] 70%
160	1.3	8.4	6
174	8.4	5.5	6
203	1.8	18.6	6
232	1.0	26.1	7
Total	100.0		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[b]Standard deviation of six results as a percentage of the mean of the results.

[c]From GC, MS data. Peaks containing mixtures of isomers are bracketed.

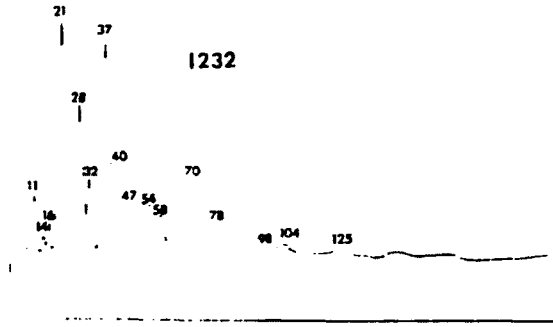

Figure 4. EC chromatogram of Aroclor 1232 chromatographed on SE-30 with a Ni-63 detector operated in the DC mode. The peak identification numbers correspond to the retention time relative to p,p'-DDE=100.

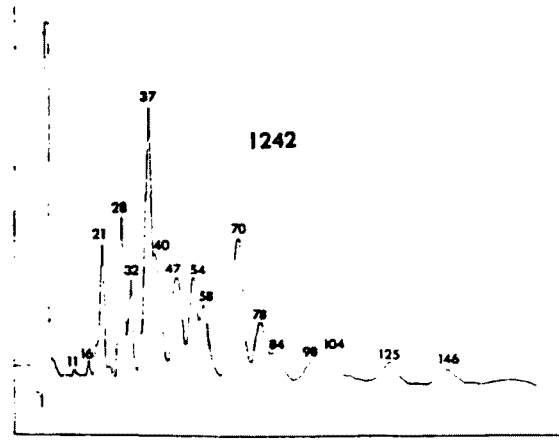

Figure 5a. EC chromatogram of 0.3 ng Aroclor 1242 chromatographed on SE-30 with a Ni-63 detector operated in the DC mode. The peak identification numbers correspond to the retention time relative to p,p'-DDE=100.

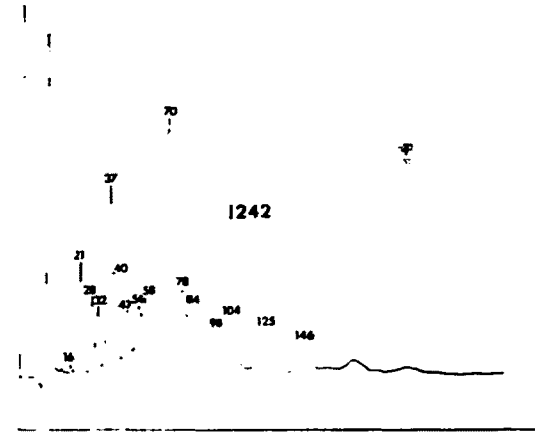

Figure 5b. Pulsed mode EC chromatogram of Aroclor 1242 chromatographed on SE-30 with a tritium foil detector. The peak identification numbers correspond to the retention time relative to p,p'-DDE=100.

Table VI. Composition of Aroclor 1260

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	No. of Chlorines[c]
70	2.7	6.3	5
84	4.7	1.6	5
98	3.8	3.5	[d]
104			5 60%
			6 40%
117	3.3	6.7	6
125	12.3	3.3	5 15%
			6 85%
146	14.1	3.6	6
160	4.9	2.2	6 50%
			7 50%
174	12.4	2.7	6
203	9.3	4.0	6 10%
			7 90%
232			[e]
244	9.8	3.4	6 10%
			7 90%
280	11.0	2.4	7
332	4.2	5.0	7
372	4.0	8.6	8
448	.6	25.3	8
528	1.5	10.2	8
Total	98.6		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of six results as a mean of the results.

[c]From GC MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

[d]Composition determined at the center of peak 104.

[e]Composition determined at the center of peak 232.

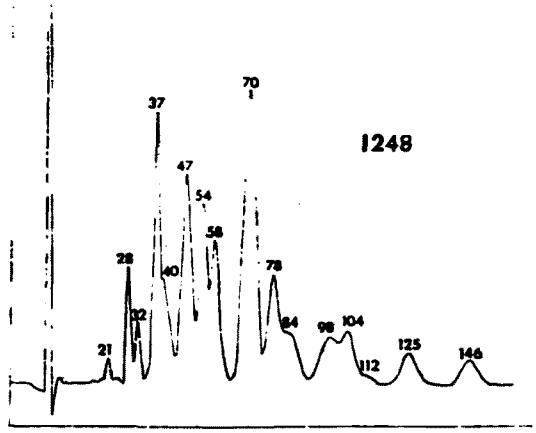

Figure 6. EC chromatogram of Aroclor 1248 chromatographed on SE-30 with a Ni-63 detector operated in the DC mode. The peak identification numbers correspond to the retention time relative to p,p'-DDE=100.

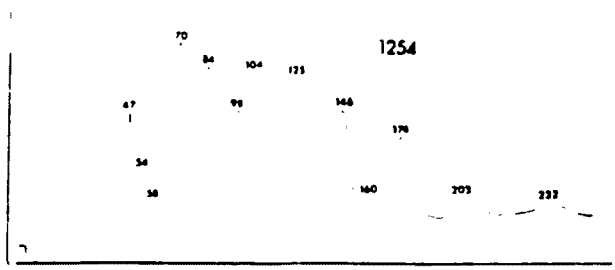

Figure 7. EC chromatogram of Aroclor 1254 chromatographed on SE-30 with a Ni-63 detector operated in the DC mode. The peak identification numbers correspond to the retention time relative to p,p'-DDE=100.

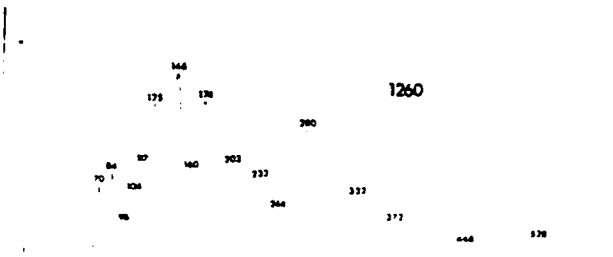

Figure 8. EC chromatogram of Aroclor 1260 chromatographed on SE-30 with a Ni-63 detector operated in the DC mode. The peak identification numbers correspond to the retention time relative to p,p'-DDE=100.

(ng PCB/cm²) for each peak. Chromatograph the sample and measure the area of each peak. Multiply the area of each peak by the response factor for that peak. Add the nanograms of PCB found in each peak to obtain the total nanograms of PCB present.

Environmental Samples Containing Only One Aroclor

An example of a sample containing a single Aroclor that is partially metabolized or degraded is seen in Figure 9a. This is a chromatogram of fat extract from a turkey that had been fed fishmeal contaminated with Aroclor 1242. Figure 9b is standard Aroclor 1242 run at the same conditions.

Several peaks present in the standard are completely missing in the sample, *e.g.*, those at relative retention times (RRT) 28 and 54. Some quantitation methods do not make an adjustment when a peak is missing from the sample. For example, one method used to quantitate this sample compared the sum of all the major sample peak heights with the sum of all the peak heights in the standard. This approach assumes that all the peaks present in the standard are also present in the sample and that all PCB peaks have the same electron capture response. Neither assumption is valid. Quantitation by calculating the amount of PCB present in each individual peak is the solution of this missing peak problem. Calculation by the sum-of-heights method indicates 0.28 ng of PCB is present; the individual peak method gives 0.18 ng.

The standard Aroclor (Figure 9b) shows the peak at RRT 84 separated only as a barely discernible shoulder on peak 78; in the sample their proportions

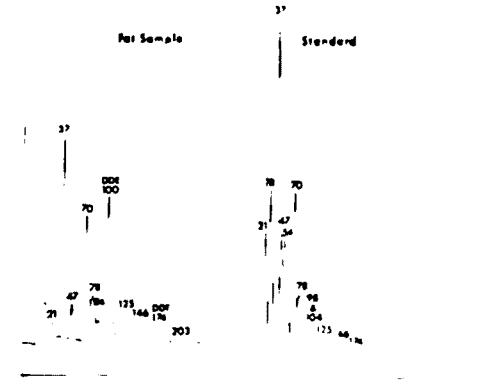

Figure 9a. DC mode EC chromatogram of a fat sample from a turkey that had been fed fishmeal contaminated with Aroclor 1242. The peak identification numbers correspond to the retention time relative to p,p'-DDE=100.

Figure 9b. Standard Aroclor 1242 run under the same conditions as Figure 9a.

are different and they elute as two separate peaks. Since individual values are given for these peaks in Table III, their individual values can be calculated. In Figure 9, peaks 37 and 40 elute as a single peak for both the sample and the standard. They are quantitated by combining the values in Table III. The sample peak at RRT 203 was not quantitated because no accurate comparison from the standard was available. Here, fortunately, the peak is only a small portion of the total and can be ignored without seriously biasing the results.

Peaks arising from pesticides can be mistaken for PCB's; DDE and DDT were present in this sample. The PCB peaks eluting in these RRT regions are only about 4% of Aroclor 1242 and can be omitted from the total without causing major error. If there is any question about the presence of DDT, chlorinated naphthalenes, chlorinated terphenyls, or other interferences, then the total PCB residues computed by this method can be confirmed by the derivative technique [3, 14]. Methods are also available to separate DDT-type pesticides from PCB's if these results are necessary [3, 15-17].

Environmental Samples Containing More Than One Aroclor

Most PCB contaminated samples of fish, water, and sediment contain residues of several Aroclors. Usually the sample chromatogram can simply be divided into three separate areas and peaks in each area quantitated by using the appropriate Aroclor. Peaks with RRT 11-70 are compared individually to cor-

14. Hutzinger, O., Safe, S., and Zitco, V., Intern. J. Environ. Anal. Chem. 2, 95 (1972).
15. Armour, Judith, and Burke, J., J. Assoc. Offic. Anal. Chemists 53, 761 (1970).
16. Burke, J. A., J. Assoc. Offic. Anal. Chemists 53, 2[illegible] (1972).
17. Leoni, V., J. Chromatog. 62, 63 (1971).

responding peaks in Aroclor 1242, peaks 84-174 with Aroclor 1254, and peaks with larger RRT with Aroclor 1260. These three Aroclors have been chosen for routine use as standards because they are the PCB's most often found in environmental samples, they were sold in largest quantities (particularly 1242 and 1254), and their chromatograms include all the EC peaks normally found in other Aroclor mixtures. In addition, this system of dividing the chromatograms generally matches the changes in chlorine numbers; i.e., the peaks used from the 1242 standard are the mono-through-tetra chlorobiphenyls, the peaks calculated with 1254 are penta- and hexachlorobiphenyls, and the peaks from the 1260 standard are used to measure the hepta- and octachlorobiphenyls.

Figure 10 is the chromatogram of a composite liver extract of three bluegills from a PCB-contaminated river. This sample obviously contains residues of several Aroclors and was quantitated as described above. However, some sample chromatograms require a more rigorous division. A schematic of this division procedure is shown in Figure 11.

The logic of this division is based on several key facts. Since Aroclor 1254 shows no appreciable peaks (see Figure 7) before RRT 47, any peaks with a lower RRT indicate the presence of some Aroclor of less chlorine content. The most likely compound, from experience and commercial usage, is 1242. Ideally, all peaks through RRT 78 would be calculated against 1242 (though many of them are present in 1254 as well), because peak 78 is unique to 1242 and not ordinarily discernible in 1254 (compare Figures 5 and 6). However, when chromatographic resolution is not optimum, mixtures of the two Aroclors may show peak 78 as only a shoulder on peak 84. Experiments with known mixtures, described below, show that in this case better results are obtained by making the division at RRT 70 and treating peak 78 + 84 as though it were all peak 84 from 1254.

A peak with RRT 117 is present in Aroclor 1260, but absent from 1254. The presence or absence of this peak in the sample chromatogram determines the standard used to quantitate the remaining peaks. Since some columns do not resolve peak 117, the investigator will not always know that 1260 is present. Experiments with mixtures show that calculations based on 1254 are adequate in this case.

All peaks of RRT larger than 174 are calculated with Aroclor 1260 because the relative standard deviations for these peaks are much lower in 1260 (Table VI) than in 1254 (Table V). These rules were tested with known-weight-ratio Aroclor mixtures that were chromatographed through a low resolution column with the GC detector operated in the pulsed mode. Table VII gives the amount of PCB measured as a percentage

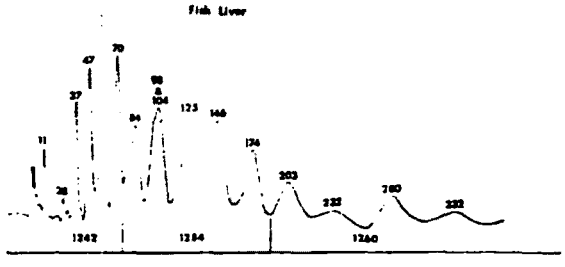

Figure 10. Division for quantitation of a DC mode EC chromatogram of PCB's from bluegill liver extract. The column substrate was SE-30. The large peak at RRT 58 is an artifact.

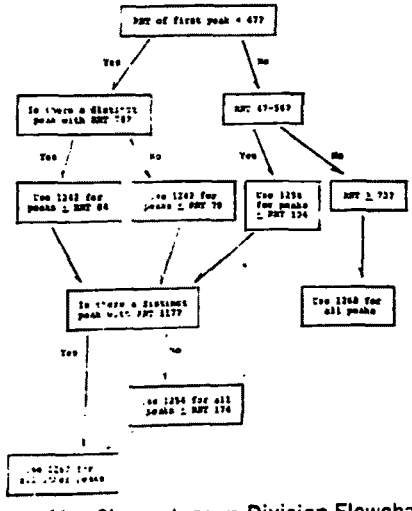

Figure 11. Chromatogram Division Flowchart.

Table VII. Percent Recoveries of Aroclor Mixtures Using Chromatogram Division Rules

Mixture	Weight Ratio	% Recovery 1242[a]	% Recovery 1242[b]	% Recovery 1254[c]	% Recovery 1254[d]
1242	1	98	103		
1254	1				
1242	3	96	100		
1254	1				
1242	4	96	100		
1254	1				
1242	5	99	102		
1254	1				
1242	2	103[e]	107[e]		
1260	1	102[d,e]	104[d,e]		
1254	1.5			109	101
1260	1				
1254	1			103	94
1260	1.5				
1254	1			105	96
1260	4				
1242	4			99[a]	99[a]
1254	1			105[b]	103[b]
1260	2				

[a]Peaks through RRT 70 calculated as 1242 (Table III).
[b]Peaks through RRT 84 calculated as 1242 (Table III).
[c]Peaks through RRT 104 calculated as 1254 (Table V).
[d]Peaks through RRT 174 calculated as 1254 (Table V).
[e]All other peaks calculated as 1260 (Table VI).

of that injected. These results were calculated using peak heights from the chromatograms, Tables III, V, and VI, and the rules given above.

These computation rules and Tables I-VI should also apply to chromatogram run on DC-200, OV-17 and OV-101 columns. However, QF-1 and OV-225 elute PCB's in a different order and the tables do not apply.

Standard Solution Stability

To test the stability to UV light of Aroclor solutions in concentrations typically used in GC analyses (18), several sealed glass ampoules of Aroclors 1242 and 1254 (10 ng/μl isooctane) were prepared. Some samples were stored in the dark, some were continuously exposed two feet from a fluorescent light fixture fitted with a decorative clear plastic shield, and several were stored in a window that received several hours of sunshine each day. No measurable changes in peak ratios were observed by EC-GC in five observations over two months' time. However, after identical samples were exposed to direct sunlight for nine days, some peak ratios changed significantly. For example, in 1254 the apparent weight of material in RRT peak 125 decreased by 50% and RRT peak 104 increased by 15%. Therefore, direct exposure to sunlight should be avoided.

Limited supplies of Aroclors 1242, 1254, and 1260 as dilute isooctane solutions in glass ampoules are available from the authors as reference Aroclor kits. Aroclors 1221, 1232, and 1248 are also available if there is a special need.

Acknowledgment

The authors wish to thank Alfred Thruston for the use of the turkey fat chromatograms and William Loy for the fish liver chromatogram. ■

Manuscript received October 2, 1972

18. Safe, S., and Hutzinger, O., Nature 232, 641 (1971).

Appendix C. Determination of Total PCB Emissions from Stationary Sources (Draft Method)*

PART A. INDUSTRIAL, SEWAGE SLUDGE, AND MUNICIPAL REFUSE INCINERATORS

1. Principle and Applicability

1.1 Principle. Gaseous and particulate PCBs are withdrawn isokinetically from the source using a sampling train. The PCBs are collected in the Florisil adsorbent tube and in the impingers in front of the adsorbent. The total PCBs in the train are determined by perchlorination to decachlorobiphenyl (DCB) and gas chromatographic determination of the DCB.

1.2 Applicability. This method is applicable for the determination of PCB emissions (both vaporous and particulate) from industrial, sewage sludge, and municipal refuse incinerators.

2. Range and Sensitivity

The range of the analytical method may be expanded considerably through concentration and/or dilution. The total method sensitivity is also highly dependent on the volume of gases sampled. However, the sensitivity of the total method as described here is about 10 ng DCB for each analytical replicate.

3. Interferences

Excessive quantities of acid-resistant organics may cause significant interferences obscuring the analysis of DCB in the perchlorinated extracts. Biphenyl, although unlikely to be present in samples from combustion sources, can form DCB in the perchlorination processes.

Throughout all stages of sample handling and analysis, care should be taken to avoid contact of samples and extracts with synthetic organic materials other than TFE® (polytetrafluoroethylene). Adhesives must not be used to hold TFE® liners on lids, and lubricating and sealing greases must not be used on any sample exposed portions of the sampling train.

4. Precision and Accuracy

From sampling with identical and paired sampling trains, the precision of the method has been determined to be 10 to 15% of the PCB concentration measured. Recovery efficiencies on source samples spiked with PCB compounds ranged from 85 to 95%.

(*) Method found in reference 7a

5. Apparatus

5.1 Sampling Train. See Figure A-1; a series of four impingers with a solid adsorbent trap between the third and fourth impingers. The train may be constructed by adaptation from a Method 5 train. Descriptions of the train components are contained in the following subsections.

5.1.1 Probe nozzle--Stainless steel (316) with sharp, tapered leading edge. The angle of taper shall be ≤ 30 degrees and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. The wall thickness of the nozzle shall be less than or equal to that of 20 gauge tubing, i.e., 0.165 cm (0.065 in.) and the distance from the tip of the nozzle to the first bend or point of disturbance shall be at least two times the outside nozzle diameter. The nozzle shall be constructed from seamless stainless steel tubing. Other configurations and construction material may be used with approval from the Administrator.

5.1.2 Probe liner--Borosilicate or quartz glass equipped with a connecting fitting that is capable of forming a leak-free, vacuum tight connection without sealing greases; such as Kontes Glass Company "O" ring spherical ground ball joints (model K-671300) or University Research Glassware SVL teflon screw fittings.

A stainless steel (316) or water-cooled probe may be used for sampling high temperature gases with approval from the Administrator. A probe heating system may be used to prevent moisture condensation in the probe.

5.1.3 Pitot tube--Type S, or equivalent, attached to probe to allow constant monitoring of the stack gas velocity. The face openings of the pitot tube and the probe nozzle shall be adjacent and parallel to each other but not necessarily on the same plane, during sampling. The free space between the nozzle and pitot tube shall be at least 1.9 cm (0.75 in.). The free space shall be set based on a 1.3 cm (0.5 in.) ID nozzle, which is the largest size nozzle used.

The pitot tube must also meet the criteria specified in Method 2 and be calibrated according to the procedure in the calibration section of that method.

5.1.4 Differential pressure gauge--Inclined manometer capable of measuring velocity head to within 10% of the minimum measured value. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However,

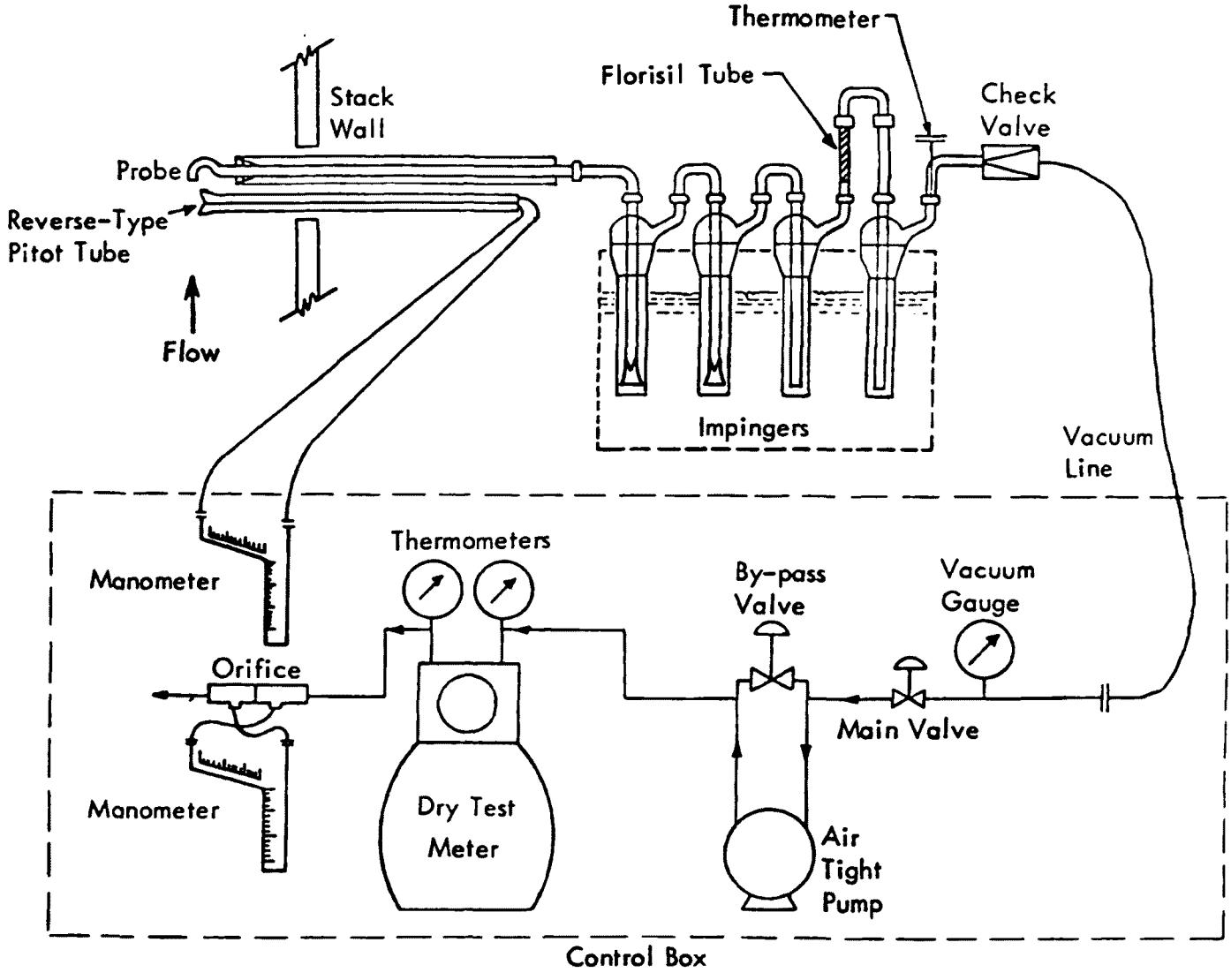

Figure A-1. PCB Sampling Train for Incinerators

micromanometers are not easily adaptable to field conditions and are not easy to use with pulsating flow. Thus, other methods or devices acceptable to the Administrator may be used when conditions warrant.

5.1.5 Impingers--Four impingers with connecting fittings able to form leak-free, vacuum tight seals without sealant greases when connected together as shown in Figure A-1. The first and second impingers are of the Greenburg-Smith design. The final two impingers are of the Greenburg-Smith design modified by replacing the tip with a 1.3 cm (1/2 in.) ID glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flask.

5.1.6 Solid adsorbent tube--Glass with connecting fittings able to form leak-free, vacuum tight seals without sealant greases (Figure A-2). Exclusive of connectors, the tube has a 2.2 cm inner diameter, is at least 10 cm long, and has four deep indentations on the inlet end to aid in retaining the adsorbent. Ground glass caps (or equivalent) must be provided to seal the adsorbent-filled tube both prior to and following sampling.

5.1.7 Metering system--Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (~ 5°F), dry gas meter with 2% accuracy at the required sampling rate, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

5.1.8 Barometer--Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value shall be requested and an adjustment for elevation differences shall be applied at a rate of -2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase.

5.2 Sample Recovery

5.2.1 Ground glass caps--To cap off adsorbent tube and the other sample exposed portions of the train.

5.2.2 Teflon FEP® wash bottle--Two, 500 ml, Nalgene No. 0023A59 or equivalent.

5.2.3 Sample storage containers--Glass bottles, 1 liter, with TFE®-lined screw caps.

5.2.4 Balance--Triple beam, Ohaus Model 7505 or equivalent.

5.2.5 Aluminum foil--Heavy duty.

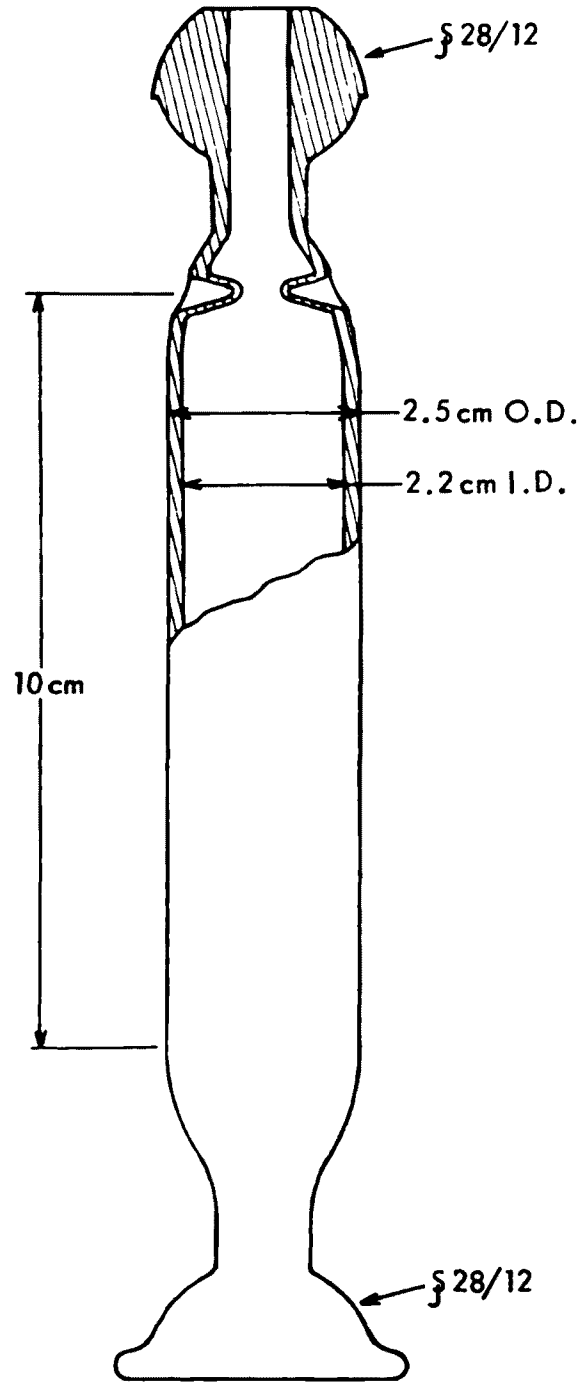

Figure A-2. Florisil Adsorbent Tube

5.2.6 Metal can--To recover used silica gel.

5.3 Analysis

5.3.1 Glass Soxhlet extractors--40 mm ID complete with 45/50 ℥ condenser, 24/40 ℥ 250 ml round bottom flask, heating mantle for 250 ml flask, and power transformer.

5.3.2 Teflon FEP wash bottle--Two, 500 ml, Nalgene No. 0023A59 or equivalent.

5.3.3 Separatory funnel--1,000 ml with TFE® stopcock.

5.3.4 Kuderna-Danish concentrators--500 ml.

5.3.5 Steam bath.

5.3.6 Separatory funnel--50 ml with TFE® stopcock.

5.3.7 Volumetric flask--25.0 ml, glass.

5.3.8 Volumetric flask--5.0 ml, glass.

5.3.9 Culture tubes--13 x 100 mm, glass with TFE®-lined screw caps.

5.3.10 Pipette--5.0 ml glass.

5.3.11 Aluminum block--Drilled to support culture tubes while heating.

5.3.12 Hot plate--Capable of heating to 200°C.

5.3.13 Teflon®-glass syringe--1 ml, Hamilton 1001 TLL or equivalent with Teflon® needle.

5.3.14 Syringe--10 µl, Hamilton 701N or equivalent.

5.3.15 Gas chromatograph--Fitted with electron capture detector capable of operation at 300°C and with 2 mm ID x 1.8 mm glass column packed with 3% OV-210 on 100/120 mesh inert support (e.g., Supelcoport®).

5.3.16 Electric muffle furnace--Capable of heating to 650°C.

5.3.17 Electric oven--Capable of heating to 150°C.

5.3.18 Disposable glass pipettes with bulbs--To aid transfer of the extracts.

5.3.19 Porcelain casserole--Capable of withstanding temperatures as high as 650°C.

6. Reagents

6.1 Sampling

6.1.1 Florisil--Floridin Co., 30/60 mesh, Grade A. The Florisil is cleaned by 8 hr Soxhlet extraction with hexane and then by drying for 8 hr in an oven at 110°C and is activated by heating to 650°C for 2 hr (not to exceed 3 hr) in a muffle furnace. After allowing to cool to near 110°C transfer the clean, active Florisil to a clean, hexane-washed glass jar and seal with a TFE®-lined lid. The Florisil should be stored at 110°C until taken to the field for use. Florisil that has been stored more than 1 month must be reactivated before use.

6.1.2 Glass wool--Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-washed glass jar with TFE®-lined screw cap.

6.1.3 Water--Deionized, then glass-distilled, and stored in hexane-rinsed glass containers with TFE®-lined screw caps.

6.1.4 Silica gel--Indicating type, 6-16 mesh. If previously used, dry at 175°C for 2 hr. New silica gel may be used as received.

6.1.5 Crushed ice.

6.2 Sample Recovery

6.2.1 Acetone--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.2.2 Hexane--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.3 Analysis

6.3.1 Hexane--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.3.2 Acetone--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.3.3 Water--Deionized and then glass-distilled, stored in hexane-rinsed glass containers with TFE®-lined screw caps.

6.3.4 Sodium sulfate (Na_2SO_4)--Anhydrous, granular. Clean by overnight Soxhlet extraction with hexane, drying in a 110°C oven, and then heating to 650°C for 2 hr. Store in 110°C oven or in glass jar closed with TFE®-lined screw cap.

6.3.5 Sulfuric acid (H_2SO_4)--Concentrated, ACS reagent grade or equivalent.

6.3.6 Antimony pentachloride ($SbCl_5$)--Baker Analyzed Reagent or equivalent.

6.3.7 Hydrochloric acid (HCl) solution--ACS reagent grade or equivalent, 50% in water.

6.3.8 Glass wool--Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-rinsed glass jar with TFE®-lined cap.

6.3.9 Decachlorobiphenyl--RFP Corp., No. RPC-60, or equivalent.

6.3.10 Compressed nitrogen--Prepurified.

6.3.11 Carborundum boiling stones--Hengar Co. No. 133-B or equivalent, rinsed with hexane.

7. Procedure

Caution: Section 7.1.1 should be done in the laboratory.

7.1 Sampling. The sampling shall be conducted by competent personnel experienced with this test procedure and cognizant of the constraints of the analytical techniques for PCBs, particularily contamination problems.

7.1.1 Pretest preparation. All train components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.

7.1.1.1 Cleaning glassware. All glass parts of the train upstream of and including the adsorbent tube, should be cleaned as described in Section 3A of the 1974 issue of "Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples." Special care should be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. These grease residues should be removed by soaking several hours in a chromic acid cleaning solution prior to routine cleaning as described above.

7.1.1.2 Solid adsorbent tube. Weigh 7.5 g of Florisil, activated within the last 30 days and still warm from storage in a 110°C oven, into the adsorbent tube (pre-rinsed with hexane) with a glass wool plug in the downstream end. Place a second glass wool plug in the tube to hold the sorbent in the tube. Cap both ends of the tube with ground glass caps. These caps should not be removed until the tube is fitted to the train immediately prior to sampling.

7.1.2 Preliminary determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2 and moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate calculations. Estimates may be used. However, final results will be based on actual measurements made during the test.

Determine the molecular weight of the stack gases using Method 3.

Select a nozzle size based on the maximum velocity head so that isokinetic sampling can be maintained at a rate less than 0.75 cfm. It is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size.

Select a suitable probe length such that all traverse points can be sampled. Consider sampling from opposite sides for large stacks to reduce the length of probes.

Select a sampling time appropriate for total method sensitivity and the PCB concentration anticipated. Sampling times should generally fall within a range of 2 to 4 hr.

It is recommended that a buzzer-timer be incorporated in the control box (see Figure 1) to alarm the operator to move the probe to the next sampling point.

In some circumstances, e.g., short batch processes, it may be necessary to sample through two or more batches to obtain sufficient sample volume. In these cases, sampling should cease during loading/unloading of the furnace.

7.1.3 Preparation of collection train. During preparation and assembly of the sampling train, keep all train openings where contamination can enter covered until just prior to assembly or until sampling is about to begin. Immediately prior to assembly, rinse all parts of the train upstream of the adsorbent tube with hexane.

Mark the probe with heat resistant tape or by some other method at points indicating the proper distance into the stack or duct for each sampling point.

Place 200 ml of water in each of the first two impingers, and leave the third impinger empty. CAUTION: do not use sealant greases in assembling the train. If the preliminary moisture determination shows that the stack gases are saturated or supersaturated, one or two additional empty impingers should be added to the train between the third impinger and the Florisil tube. See Section 10.1. Place approximately 200 to 300 g or more, if necessary, of silica gel in the last impinger. Weigh each impinger (stem included) and record the weights on the impingers and on the data sheet.

Unless otherwise specified by the Administrator, attach a temperature probe to the metal sheath of the sampling probe so that the sensor is at least 2.5 cm behind the nozzle and pitot tube and does not touch any metal.

Assemble the train as shown in Figure A-1. Through all parts of this method use of sealant greases such as stopcock grease to seal ground glass joints must be avoided.

Place crushed ice around the impingers.

7.1.4 Leak check procedure--After the sampling train has been assembled, turn on and set (if applicable) the probe heating system(s) to reach a temperature sufficient to avoid condensation in the probe. Allow time for the temperature to stabilize. Leak check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum. A leakage rate in excess of 4% of the average sampling rate of 0.0057 m^3/min (0.02 cfm) whichever is less, is unacceptable.

The following leak check instruction for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until 380 mm Hg (15 in. Hg) vacuum is reached. Do not reverse direction of bypass valve. This will cause water to back up into the probe. If 380 mm Hg (15 in. Hg) is exceeded, either leak check at this higher vacuum or end the leak check as described below and start over.

When the leak check is completed, first slowly remove the plug from the inlet to the probe and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the probe.

Leak checks shall be conducted as described above prior to each test run and at the completion of each test run. If leaks are found to be in excess of the acceptable rate, the test will be considered invalid. To reduce lost time due to leakage occurrences, it is recommended that leak checks be conducted between port changes.

7.1.5 Train operation--During the sampling run, an isokinetic sampling rate within 10%, or as specified by the Administrator, of true isokinetic shall be maintained. During the run, do not change the nozzle or any other part of the train in front of and including the Florisil tube.

For each run, record the data required on the data sheets. An example is shown in Figure A-3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, and when sampling is halted. Take other data point readings at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity head readings) necessitate additional adjustments in flow rate. Be sure to level and zero the manometer.

Clean the portholes prior to the test run to minimize chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify (if applicable) that the probe heater is working and up to temperature, and that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available for sampling trains using type S pitot tubes with 0.85 ± 0.02 coefficients (C_p), and when sampling in air or a stack gas with equivalent density (molecular weight, M_d, equal to 29 ± 4), which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. APTD-0576 details the procedure for using these nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomograph unless appropriate steps are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to avoid water backing into the probe. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross section, as required by Method 1 or as specified by the Administrator. To minimize chance of extracting deposited material, be careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes.

FIELD DATA

PLANT _____
DATE _____
SAMPLING LOCATION _____
SAMPLE TYPE _____
RUN NUMBER _____
OPERATOR _____
AMBIENT TEMPERATURE _____
BAROMETRIC PRESSURE _____
STATIC PRESSURE, (P_s) _____
FILTER NUMBER (s) _____

PROBE LENGTH AND TYPE _____
NOZZLE I.D. _____
ASSUMED MOISTURE, % _____
SAMPLE BOX NUMBER _____
METER BOX NUMBER _____
METER $\Delta H_@$ _____
C FACTOR _____
PROBE HEATER SETTING _____
HEATER BOX SETTING _____
REFERENCE Δp _____

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY _____ MINUTES

TRAVERSE POINT NUMBER	SAMPLING TIME, min / CLOCK TIME (24 hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
				DESIRED	ACTUAL		INLET ($T_{m\,in}$), °F	OUTLET ($T_{m\,out}$), °F			

COMMENTS:

Figure A-3. Field Data Sheet

EPA (Dur) 235
4 72

During the test run, make periodic adjustments to keep the probe temperature at the proper value. Add more ice and, if necessary, salt to the ice bath, to maintain a temperature of less than 20°C (68°F) at the impinger/silica gel outlet, to avoid excessive moisture losses. Also, periodically check the level and zero of the manometer.

If the pressure drop across the train becomes high enough to make isokinetic sampling difficult to maintain, the test run should be terminated. Under no circumstances should the train be disassembled during a test run to determine and correct causes of excessive pressure drops.

At the end of the sample run, turn off the pump, remove the probe and nozzle from the stack, and record the final dry gas meter reading. Perform a leak check.* Calculate percent isokinetic (see calculation section) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

7.1.6 Blank train--For each series of test runs, set up a blank train in a manner identical to that described above, but with the nozzle capped with aluminum foil and the exit end of the last impinger capped with a ground glass cap. Allow the train to remain assembled for a period equivalent to one test run. Recover the blank sample as described in Section 7.2.

7.2 Sample recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle. Remove the probe from the train and close off both ends with aluminum foil. Cap off the inlet to the train with a ground glass cap.

Transfer the probe and impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

7.2.1 Adsorbent tube--Remove the Florisil tube from the train and cap it off with ground glass caps.

---

* With acceptability of the test run to be based on the same criterion as in 7.1.4.

7.2.2 Sample container No. 1--Remove the first three impingers. Wipe off the outside of each impinger to remove excessive water and other debris, weigh (stem included), and record the weight on data sheet. Pour the contents directly into container No. 1 and seal.

7.2.3 Sample container No. 2--Rinse each of the first three impingers sequentially first with 30 ml acetone and then with 30 ml hexane, and put the rinses into container No. 2. Quantitatively recover material deposited in the probe using 100 ml acetone and then 100 ml hexane and add these rinses to container No. 2 and seal.

7.2.4 Silica gel container--Remove the last impinger, wipe the outside to remove excessive water and other debris, weigh (stem included), and record weight on data sheet. Transfer the contents to the used silica gel can.

7.3 Analysis. The analysis of the PCB samples should be conducted by chemical personnel experienced in determinations of trace organics utilizing sophisticated, instrumental techniques. All extract transfers should be made quantitatively by rinsing the apparatus at least three times with hexane and adding the rinses to the receiving container. A boiling stone should be used in all evaporative steps to control "bumping."

7.3.1 Extraction

7.3.1.1 Adsorbent tube. Expel the entire contents of the adsorbent tube directly onto a glass wool plug in the sample holder of a Soxhlet extractor. Although no extraction thimble is required, a glass thimble with a coarse-fritted bottom may be used.

Rinse the tube with 5 ml acetone and then with 15 ml hexane and put these rinses into the extractor. Assemble the extraction apparatus and extract the adsorbent with 170 ml hexane for at least 4 hr. The extractor should cycle 10 to 14 times per hour. After allowing the extraction apparatus to cool to ambient temperature, transfer the extract into a Kuderna-Danish evaporator.

Evaporate the extract to about 5 ml on a steam bath and allow the evaporator to cool to ambient temperature before disassembly. Transfer the extract to a 50-ml separatory funnel and set the funnel aside.

7.3.1.2 Sample container No. 1. Transfer the aqueous sample to a 1,000-ml separatory funnel. Rinse the container with 20 ml acetone and then with two 20-ml portions of hexane, adding the rinses to the separatory funnel.

Extract the sample with three 100 ml portions of hexane, transferring the sequential extracts to a Kuderna-Danish evaporator.

Evaporate the extract to about 5 ml and allow the evaporator to cool to ambient temperature before disassembly. Filter the extract through a micro column of anhydrous sodium sulfate into the 50 ml separatory funnel containing the corresponding Florisil extract. The micro column is prepared by placing a small plug of glass wool in the bottom of the large portion of a disposable pipette and then adding anhydrous sodium sulfate until the tube is about half full.

7.3.1.3 Sample container No. 2. Transfer the organic solution into a 1,000 ml separatory funnel. Rinse the container with two 20 ml portions of hexane and add the rinses to the separatory funnel. Wash the sample with three 100 ml portions of water. Discard the aqueous layer and transfer the organic layer to a Kuderna-Danish evaporator.

Evaporate the extract to about 5 ml and allow the evaporator to cool to ambient temperature before disassembly. Filter the extract through a micro column of anhydrous sodium sulfate into the 50 ml separatory funnel containing the corresponding Florisil and impinger extracts.

7.3.2 Extract cleanup--Clean the combined extracts (in 50 ml separatory funnel) by shaking with 5 ml concentrated sulfuric acid. Allow the acid layer to separate and drain it off.

Transfer the hexane layer to a Kuderna-Danish evaporator and evaporate to about 5 ml. Allow the evaporator to cool to ambient temperature before disassembly.

The extract should be essentially colorless. If it still shows significant color, additional cleanup may be required before assaying for PCBs. In this event, further clean the extract by liquid chromatography on Florisil according to procedures described in Section 5A of the 1974 issue of "Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples" Reduce the Florisil eluant to about 10 ml by Kuderna-Danish evaporation techniques described above.

Transfer the cleaned extract to a 25 ml volumetric flask and dilute to volume with hexane. Pipette three 5.0 ml aliquots into culture tubes for perchlorination. Retain the remaining 10 ml for later verification, if required (see Section 10.2).

7.3.3 Extract perchlorination--Evaporate the aliquots in the culture tubes just to dryness with a gentle stream of dry nitrogen. If the aliquots will not evaporate to dryness, refer to Section 10.3 concerning special cases. Add 0.2 ml antimony pentachloride with a 1 ml glass-TFE® syringe and

seal the tube with a TFE®-lined screw cap. Heat the reaction mixture to 160°C for 2 hr by placing the tube in a hole in an aluminum block on a hot plate.

Allow the tube to cool to ambient room temperature before adding about 2 ml of 50% HCl in water to destroy residual antimony pentachloride. This is a convenient "stopping point" in the perchlorination procedure.

Extract the reaction mixture by adding about 1 ml hexane to the tube, shake, and allow layers to separate. Remove the upper hexane layer with a disposable pipette and filter through a micro column of anhydrous sodium sulfate directly into a 5 ml volumetric flask. Repeat the extraction three times for a total of four extractions. Dilute the extract to volume with hexane.

7.3.4 PCB determination--Assay the perchlorinated extracts for decachlorobiphenyl (DCB) by gas chromatographic comparison with DCB standard solutions and correct this result for the DCB concentration determined for the blank train. (Column temperature and carrier gas flow parameters of 240°C and 30 ml/min, are typically appropriate. The concentrations of the standard solutions should allow fairly close comparison with DCB in the sample extracts. Standards near 25 to 50 picograms/microliter may be appropriate.)

8. Calibration

Maintain a laboratory log of all calibrations.

8.1 Sampling Train

8.1.1 Probe nozzle--Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.).

When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use.

Each nozzle shall be permanently and uniquely identified.

8.1.2 Pitot tube--The pitot tube shall be calibrated according to the procedure outlined in Method 2.

8.1.3 Dry gas meter and orifice meter--Both meters shall be calibrated according to the procedure outlined in APTD-0576. When diaphragm

pumps with bypass valves are used, check for proper metering system design by calibrating the dry gas meter at an additional flow rate of 0.0057 m^3/min (0.2 cfm) with the bypass valve fully opened and then with it fully closed. If there is more than ± 2% difference in flow rates when compared to the fully closed position of the bypass valve, the system is not designed properly and must be corrected.

8.1.4 Probe heater calibration--The probe heating system shall be calibrated according to the procedure contained in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

8.1.5 Temperature gauges--Calibrate dial and liquid filled bulb thermometers against mercury-in-glass thermometers. Thermocouples should be calibrated in constant temperature baths.

8.2 Analytical Apparatus

8.2.1 Gas chromatograph--Prepare a working curve from at least five standard injections of different volumes of the DCB standard.

9. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

9.1 Nomenclature

G_n = Corrected weight of DCB in nth perchlorinated aliquot (n = 1, 2, 3), µg.

G_s = Total weight of PCBs (as DCB) in sample, µg.

C_s = Concentration of PCBs in stack gas, µg/m^3, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

I = Percent of isokinetic sampling.

M_w = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole (21.83 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry gas meter temperature °K (°R).

T_s = Absolute average stack gas temperature °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_{lc} = Total volume of liquid collected in impingers and silica gel, ml. volume of water collected equals the weight increase in grams times 1 ml/gram

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample corrected to standard conditions, scm (scf).

V_t = Total volume of sample, ml.

V_s = Stack gas velocity, calculated by EPA Method 2, m/sec (ft/sec).

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

ρ_w = Density of water, 1 g/ml (0.00220 lb/ml).

θ = Total Sampling time, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

9.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure A-3).

9.3 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions [20°C, 760 mm Hg (68°F, 29.92 in. Hg)] by using Equation A-1).

$$V_{m(std)} = V_m \frac{T_{std}}{T_m} \left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} \right] = K V_m \frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m}$$

Equation A-1

where $K = 0.3855$ °K/mm Hg for metric units

$= 17.65$ °R/in. Hg for English units

9.4 Volume of water vapor

$$V_{w(std)} = V_{lc} \frac{\rho_w}{M_w} \frac{RT_{std}}{P_{std}} = K V_{lc}$$

Equation A-2

where $K = 0.00134$ m^3/ml for metric units

$= 0.0472$ ft^3/ml for English units

9.5 Moisture content

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}}$$

Equation A-3

If the liquid droplets are present in the gas stream assume the stream to be saturated and use a psychrometric chart to obtain an approximation of the moisture percentage.

9.6 Concentration

9.6.1 Calculate the total PCB residue (as DCB) in the sample from the weights of DCB in the perchlorinated aliquots according to Equation A-4.

$$G_s = \frac{5(G_1 + G_2 + G_3)}{3}$$ Equation A-4

9.6.2 Concentration of PCBs (as DCB) in stack gas. Determine the concentration of PCBs in the stack gas according to Equation A-5.

$$C_s = K \frac{G_s}{V_{m(std)}}$$ Equation A-5

where $K = 35.31\ ft^3/m^3$

9.7 Isokinetic variation

9.7.1 Calculations from raw data.

$$I = \frac{100\ T_s\ [K\ V_{lc} + (V_m/T_m)\ (P_{bar}) + \Delta H/13.6)]}{60\ \theta\ v_s\ P_s\ A_n}$$

Equation A-6

where $K = 0.00346$ mm Hg-m^3/ml-°K for metric units

$= 0.00267$ in. Hg-ft^3/ml-°R for English units

9.7.2 Calculations from intermediate values.

$$I = \frac{T_s\ V_{m(std)}\ P_{std}\ 100}{T_{std}\ v_s\ \theta\ A_n\ P_s\ 60\ (1-B_{ws})}$$

$$= K \frac{T_s\ V_{m(std)}}{P_s\ v_s\ A_n\ \theta\ (1-B_{ws})}$$ Equation A-7

where $K = 4.323$ for metric units

$= 0.0944$ for English units

9.8 Acceptable results. The following range sets the limit on acceptable isokinetic sampling results:

If 90% < I < 110%, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may option to accept the results.

10. Special Cases

10.1 Sampling moisture saturated or supersaturated stack gases. One or two additional modified Greenburg-Smith impingers may be added to the train between the third impinger and the Florisil tube to accommodate additional water collection when sampling high moisture gases. Throughout the preparation, operation, and sample recovery from the train, these additional impingers should be treated exactly like the third impinger.

10.2 PCB verification. It is recommended that an unperchlorinated aliquot from at least one sample be subjected to GC/MS examination to verify that PCB isomers are present.

To accomplish this, the unperchlorinated portion of each extract is first screened by GC with the same chromatographic system used for DCB determination except for a cooler column temperature, typically 165 to 200°C. The elution patterns are compared with those of commercial PCB mixtures (in hexane solution) to determine the most similar mixture.

After determining what PCB isomers are possible present, the sample is examined by GC/MS using multiple ion selection techniques for ions characteristic of the molecular clusters of the PCBs possibly present.

10.3 Evaporation of extracts for perchlorination. For cases where the extract will not evaporate to dryness or excessive PCB loss by volatilization is suspected, the hexane may be removed by azeotrophic evaporation from the hexane/chloroform mixture.

Add 3 ml of chloroform to the aliquot in the culture tube. Add a boiling chip and concentrate by slow boiling in a water bath to 1 ml. Repeat the chloroform addition and evaporation three times in order to remove all residual hexane. Then further concentrate (slowly) to a volume of approximately 0.1 ml. Under no circumstances should the water bath temperature be permitted to exceed 76°C or the solvent be evaporated to dryness. The final volume (0.1 ml) may be determined with sufficient accuracy by comparison of solvent level with another reaction vial containing 0.1 ml of chloroform. When a volume of 0.1 ml is achieved, cap the reaction vial immediately and allow to cool. Proceed with the perchlorination as described in Section 7.3.3.

11. References

Martin, Robert M., "Construction Details of Isokinetic Source Sampling Equipment," Environmental Protection Agency, Air Pollution Control Office Publication No. APTD-0581.

1973 Annual Book of ASTM Standards, Part 23, Designation: D 1179-72.

Thompson, J. F., Ed., "Analysis of Pesticide Residues in Human and Environmental Samples," Environmental Protection Agency, Research Triangle Park, N.C., 1974.

PART B. CAPACITOR- AND TRANSFORMER-FILLING PLANTS

1. Principle and Applicability

1.1 Principle. Gaseous and particulate PCBs are withdrawn isokinetically from the source. The PCBs are collected on Florisil and determined by gas chromatography against an Aroclor® standard.

1.2 Applicability. This method is applicable for the determination of PCB emissions from the room air, room air exhaust and process point exhausts at capacitor- and transformer-filling plants.

2. Range and Sensitivity

The range of the analytical method may be expanded considerably through concentration and/or dilution of the extract. The total method sensitivity is also highly dependent on the volume of gases sampled. However, sensitivity of the total method is near 1 µg per test or near 10 ng per test where the perchlorination assay method is used.

3. Interferences

Throughout all stages of sample handling and analysis, care should be taken to avoid contact of samples and extracts with synthetic organic materials other than TFE® (polytetrafluoroethylene). Lubricating and sealing greases should not be used on the sample exposed portions of the sampling train.

4. Precision and Accuracy

Sampling with identical and paired sampling trains, the precision of the method should be 10 to 15% of the PCB concentration measured. Recovery efficiencies on source samples spiked with PCB compounds ranged from 85 to 95% of the spike.

5. Apparatus

5.1 Sampling Train. The sampling train, see Figure B-1, consists of a glass-lined probe, an adsorbent tube containing Florisil, and the appropriate valving and flow meter controls for isokinetic sampling as described in Part A of the procedure. The sampling apparatus in Figure B-1 is the same as that in Figure A-1 and Section 5.1 of Part A, except that the Smith-Greenburg impingers and heated probe are not used. If condensation of significant quantities of moisture prior to the solid adsorbent is expected, Part A of the method should be used. Since probes and adsorbent tubes are not cleaned up in the field, a sufficient number must be provided for sampling and allowance for breakage.

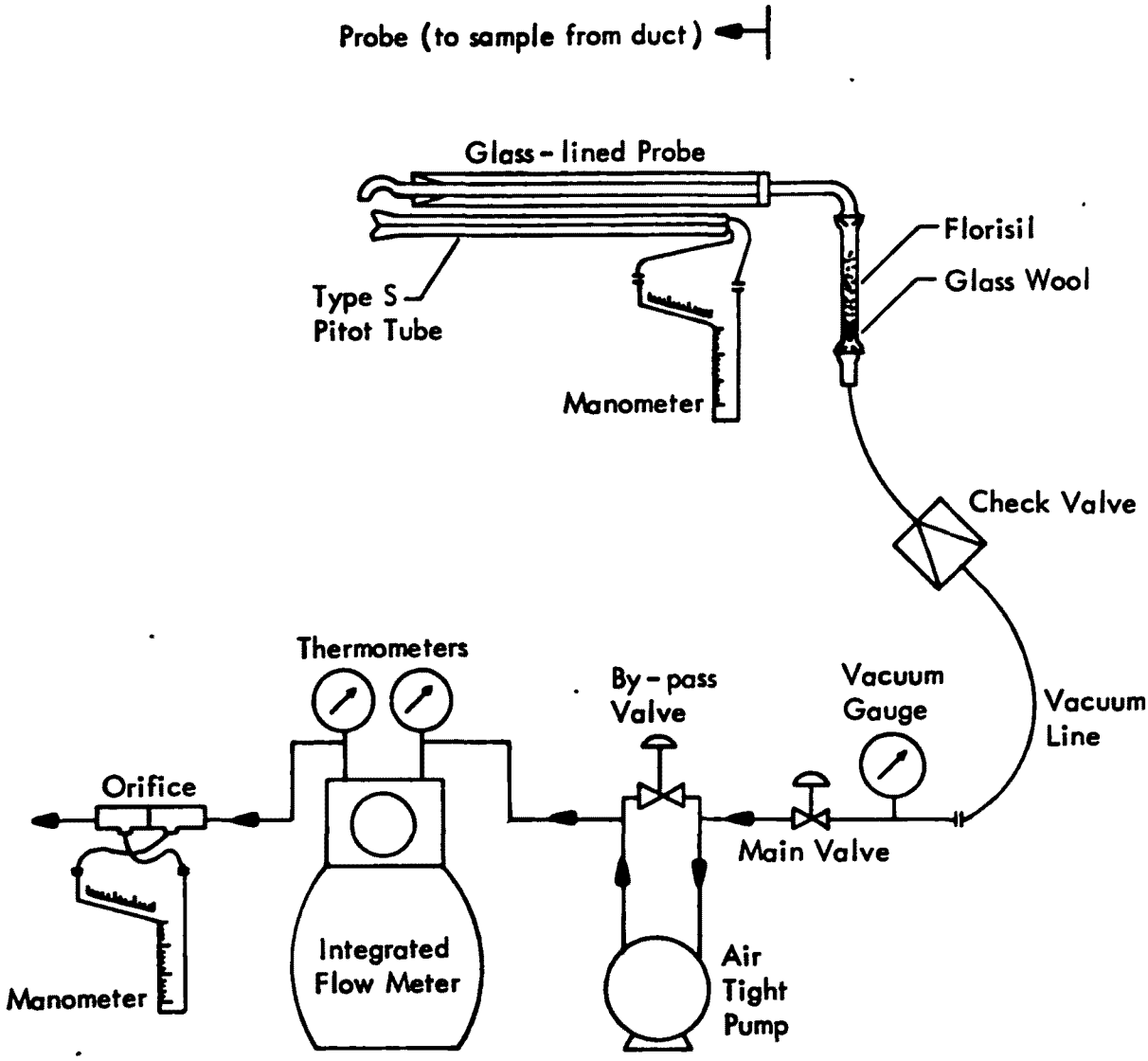

Figure B-1. PCB Sampling Train for Capacitor- and Transformer-Filling Plants

5.2 Sample Recovery. Heavy duty aluminum foil must be provided to cap off the probe prior to shipment.

5.3 Analysis. The equipment required for the analysis is identical to that specified in Part A except that the equipment necessary for perchlorination of the PCBs collected to the decachlorobiphenyl form is not required. (Perchlorination of the sample here is optional and should be employed only if the GC fingerprint technique of this procedure is not applicable.)

6. Reagents

6.1 Sampling

6.1.1 Florisil--Floridin Company, 30/60 mesh, Grade A. The Florisil is cleaned by overnight Soxhlet extraction with hexane and then drying overnight at 110°C and is activated by heating to 650°C for 2 hr (not to exceed 3 hr) in a muffle furnace. After allowing to cool to near 110°C, transfer the clean, active Florisil to a clean, hexane-washed glass jar and seal with a TFE®-lined lid. The Florisil should be stored at 110°C until taken to the field for use. Florisil that has been stored more than 1 month must be reactivated.

6.1.2 Glass wool--Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-washed glass jar with TFE®-lined screw cap.

6.2 Analysis

6.2.1 Hexane--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.2.2 Acetone--Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.2.3 Sodium sulfate (Na_2SO_4)--Anhydrous, granular. Clean by overnight Soxhlet extraction with hexane, drying in a 110°C oven, and then heating to 650°C for 2 hr. Store in 110°C oven or in glass jar closed with TFE®-lined screw cap.

6.2.4 Sulfuric acid (H_2SO_4)--Concentrated, ACS reagent grade or equivalent.

6.2.5 Glass wool--Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-rinsed glass jar with TFE®-lined cap.

6.2.6 Carborundum boiling stones--Hengar Company No. 133-B or equivalent, rinsed with hexane.

6.2.7 Standard Aroclor PCB mixtures--Aroclors® 1016, 1221, 1232, 1242, 1248, 1254, 1260, and 1262 may be obtained from the Pesticide Repository, EPA/HERL/ETD, Research Triangle Park, North Carolina.

7. Procedure

7.1 Sampling. The sampling shall be conducted by competent personnel knowledgeable with this test procedure and cognizant of the constraints of the analytical techniques for PCBs, particularly contamination problems.

The sampling procedure for capacitor and transformer plants is identical to that described in Part A with the following exceptions: (a) impingers and a heatable probe are not required prior to the adsorbent tube; and (b) the PCB concentrations may be considerably higher for capacitor and transformer plants, compared to most incinerators, thus the sampling time can be less than the 2 hr specified in Part A.

The selection of sampling time and rate should be based on the approximate levels of PCB residues expected in the sample. The sampling rate should not exceed 14 liters/min and may typically fall in the range of 5 to 10 liters/min. Sampling times should be more than 20 min but should not exceed 4 hr.

Because the processes for filling the capacitors and transformers can vary significantly between plants, isokinetic sampling is required in the procedure. However, if it can be shown to the satisfaction of the Administrator that isokinetic sampling is not necessary, then sampling at a proportional rate is an acceptable alternative. Proportional or constant flow rate sampling may also be necessary in cases where the standard pitot/nozzle assembly physically blocks a significant portion of the stack or where the flow rate is too low (less than 10 ft/min) for the pitot tube.

7.2 Sample Recovery

7.2.1 Adsorbent tube--Remove the Florisil tube from the collection system and cap it off with ground glass caps for shipment to the analytical laboratory.

7.2.2 Probe (where applicable)--Remove the probe from the collection system and cap it off with aluminum foil.

7.3 Analysis. The analysis of the PCB samples should be conducted by chemical personnel experienced in determinations of trace organics utilizing sophisticated instrumental techniques. All extract transfers should be made quantitatively by rinsing the apparatus at least three times with hexane and adding the rinses to the receiving container. A boiling stone should be used in all evaporative steps to control "bumping."

7.3.1 Extraction

7.3.1.1 Adsorbent tube. Expel the entire contents of the adsorbent tube directly onto a glass wool plug in the sample holder of a Soxhlet extractor. Although no extraction thimble is required, a glass thimble with a coarse-fritted bottom may be used.

Rinse the tube with about 5 ml acetone and then about 15 ml hexane into the extractor. Assemble the extraction apparatus and extract the adsorbent with 170 ml hexane for at least 4 hr. The extractor should cycle 10 to 14 times per hour. After allowing the extraction apparatus to cool to ambient temperature, transfer the extract into a Kuderna-Danish evaporator.

Evaporate the extract on a steam bath to about 5 ml and allow the evaporator to cool to ambient temperature before disassembly. Transfer the extract to a 50 ml separatory funnel and set the funnel aside.

7.3.1.2 Probe (where applicable). Rinse the probe with hexane into a Kuderna-Danish evaporator. Evaporate the extract to about 5 ml and allow the evaporator to cool to ambient temperature before disassembly. Add the concentrated extract to the 50-ml separatory funnel containing the corresponding Florisil extract.

7.3.2 Extract cleanup--Clean the combined extracts (in 50-ml separatory funnel) by shaking with 5 ml concentrated sulfuric acid. Allow the acid layer to separate and drain it off.

Transfer the hexane layer to a Kuderna-Danish evaporator and evaporate to about 5 ml. Allow the evaporator to cool to ambient temperature before disassembly.

The extract should be essentially colorless. If it still shows significant color, additional cleanup may be required before assaying for PCBs. In this event, further clean the extract by liquid chromatography on Florisil according to procedures described in Section 5A of the 1974 issue of "Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples." Reduce the Florisil eluant to about 10 ml by Kuderna-Danish evaporation techniques described above.

Transfer the cleaned extract to a 25-ml volumetric flask and dilute to volume with hexane for gas chromatographic analysis.

7.3.3 PCB determination--Assay the cleaned extracts by gas chromatographic comparison with standard solutions of a similar commercial PCB mixture (A column temperature between 165 and 200°C at a flow rate of 30 ml/min may be appropriate. Aroclor® standard solutions at concentrations near 10 ng/µl should be appropriate for calibration of the gas chromatograph.) If PCB mixtures were being used at the sampling site, a standard solution of that mixture, e.g., Aroclor® 1016, will likely be appropriate. Quantitation should be based on the summed areas of at least five major peaks coincident in the chromatograms of the sample extracts and standards. The range and sensitivity of the method may be extended somewhat by diluting concentrated extracts with hexane or concentrating dilute extracts by evaporation under a gentle stream of dry nitrogen. If the sample chromatograms do not closely resemble a particular PCB standard, e.g., in the case of emissions from more than one Aroclor® product, refer to Section 10.1 concerning Special Cases. Correct the PCB assays for PCBs determined in the blank train.

8. Calibration

Maintain a laboratory log of all calibrations.

8.1 Sampling Train

8.1.1 Probe nozzle--Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.).

When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use.

Each nozzle shall be permanently and uniquely identified.

8.1.2 Pitot tube--The pitot tube shall be calibrated according to the procedure outlined in Method 2.

8.1.3 Dry gas meter and orifice meter--Both meters shall be calibrated according to the procedure outlined in APTD-0576. When diaphragm pumps with bypass valves are used, check for proper metering system design by calibrating the dry gas meter at an additional flow rate of 0.0057 m^3/min (0.2 cfm) with the bypass valve fully opened and then with it fully closed. If there is more than ± 2% difference in flow rates when compared to the fully closed position of the bypass valve, the system is not designed properly and must be corrected.

8.1.4 Temperature gauges--Calibrate dial and liquid filled bulb thermometers against mercury-in-glass thermometers. Thermocouples need not be calibrated. For other devices, check with the Administrator.

8.2 Analytical Apparatus

8.2.1 Gas chromatograph--Prepare a working curve from at least five standard injections of different volumes of the Aroclor® standard in hexane solution.

9. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

9.1 Nomenclature

G_s = Total weight of Aroclor® in sample, µg.

C_s = Concentration of Aroclor® in stack gas, $\mu g/m^3$, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg).

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

I = Percent of isokinetic sampling.

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole (21.83 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry gas meter temperature °K (°R).

T_s = Absolute average stack gas temperature °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).

V_s = Stack gas velocity, calculated by Method 2, Equation 2 to 7, m/sec (ft/sec).

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

9.2 Average dry gas meter temperature and average orifice pressure drop.

9.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions [20°C, 760 mm Hg (68°F, 29.92 in. Hg)] by using Equation B-1.

$$V_{m(std)} = V_m \frac{T_{std}}{T_m} \left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} \right] = KV_m \frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m}$$

Equation B-1

where K = 0.3855 °K/mm Hg for metric units
= 17.65 °R/in. Hg for English units

9.4 Concentration

9.4.1 Concentration of Aroclor® in stack gas. Determine the concentration of Aroclor® in the stack gas according to Equation B-2.

$$C_s = \frac{G_s}{V_{m(std)}}$$

Equation B-2

10. Special Cases

10.1 Quantitation of PCB Residues Not Similar to a Commercial Mixture. In cases where the composition of the PCB residue does not closely resemble an available commercial PCB mixture, i.e., from comparison of EC-GC chromatograms, direct quantitation against available standard mixtures may be difficult and inaccurate. These extracts should be split, perchlorinated, and total PCBs quantitated by procedures described in Part A, Sections 7.3.2, 7.3.3, and 7.3.4, and the total PCB residue of the sample calculated from Equation A-4.

10.2 PCB Verification. It is recommended that an unperchlorinated aliquot from at least one sample be subjected to GC/MS examination to verify that PCB isomers are present.

After determining what PCB isomers are possibly present by the quantitation procedures in Section 7.3.3, the sample is examined by GC/MS using multiple ion selection techniques for ions characteristic of the molecular clusters of the PCBs possibly present.

11. Reference

Martin, Robert M., "Construction Details of Isokinetic Source Sampling Equipment," Environmental Protection Agency, Air Pollution Control Office of Publication No. APTD-0581.

1973 Annual Book of ASTM Standards, Part 23, Designation: D 1179-72

Thompson, J. F., Ed., "Analysis of Pesticide Residues in Human and Environmental Samples," Environmental Protection Agency, Research Triangle Park, N.C., 1974.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/7-79-047		

4. TITLE AND SUBTITLE	5. REPORT DATE
Measurement of PCB Emissions from Combustion Sources	February 1979
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
P. L. Levins, C. E. Rechsteiner, and J. L. Stauffer	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Arthur D. Little, Inc. Acorn Park Cambridge, Massachusetts 02140	INE624
	11. CONTRACT/GRANT NO.
	68-02-2150, T.D. 10102

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711	Task Final; 12/76 - 12/78
	14. SPONSORING AGENCY CODE
	EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Larry D. Johnson, MD-62, 919/541-2557.

16. ABSTRACT

The report describes a gas chromatographic/mass spectrometric (GC/MS) procedure that overcomes problems encountered when using GC procedures (previously used to determine polychlorinated biphenyls (PCBs) in solids and water) on emissions from combustion sources. The GC/MS procedure, which relies on selected mass scanning in restricted regions of the chromatograms, was developed because in the combustion process the distribution pattern of the individual PCBs changes, rendering invalid the pattern matching approach used with the gas chromatographic/electron capture detection (GC/ECD) method.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Chlorine Aromatic Compounds	Stationary Sources	07C
Biphenyl Mass Spectroscopy	Polychlorinated Biphenyls	21B
Combustion		14B
Measurement		07D
Gas Chromatography		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Unlimited	Unclassified	88
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)