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METHODOLOGY FOR MEASUREMENT OF POLYCHLORINATED BIPHENYLS IN AMBIENT AIR AND STATIONARY SOURCES: A Review

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METHODOLOGY FOR MEASUREMENT OF POLYCHLORINATED BIPHENYLS IN AMBIENT AIR AND STATIONARY SOURCES - A REVIEW

by

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ABSTRACT

The state of development of methodology for measurement of polychlorinated biphenyls (PCBs) in ambient air and stationary sources was reviewed.

The most promising method for ambient air measurements involves collection of PCBs on polyurethane foam, extraction with an organic solvent, removal of interferences by column chromatography, and confirmation and analysis by electron-capture gas chromatography. Quantitation by perchlorination of PCBs to decachlorobiphenyl (DCB) is the most promising quantitation technique, but the procedure has not yet been perfected to the point where all PCBs are quantitatively converted to DCB. Perfection of this technique should allow for significant improvement in the quality of ambient PCB data being generated.

Source and ambient methods differ mainly in sampling. Work on methodology for stationary sources is in the early stages of development and further investigations are needed.

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ACKNOWLEDGMENTS

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SECTION 1

INTRODUCTION

Polychlorinated biphenyls (PCBs) were first introduced into the environment in 1929.[1] Interest in PCBs accelerated in 1966 with the discovery of their widespread occurrence in Sweden.[4] This discovery led to the recognition that in many cases, environmental damage previously blamed on organochlorine pesticides (e.g., DDT) were actually due to PCBs. PCBs are released to the environment by a number of pathways, including: incomplete combustion in incinerators; vaporization from paints, plasticizers, and coatings; and evaporation and distillation from bodies of water. In the ambient air, PCBs exist in the vapor state as liquid aerosols and adsorbed onto particulate matter.

The toxicity of PCBs is of particular concern because they are persistent in the environment.[1] PCBs, which are lipophilic, have been found in the remains of wildlife[1] and in human adipose tissue,[2] and have been implicated as carcinogens in laboratory studies in mammals.[3]

PCBs are manufactured in many countries. In the United States the sole producer, the Monsanto Company, markets them under the trade name Aroclor. Monsanto sold 73,100,000 pounds of Aroclor in the United States in 1970,[3] but in December of that year, the company voluntarily restricted sales to closed-system applications.

Ambient concentrations are generally in the nanogram-per-cubic-meter range; a concentration of 9.4 ng/m^3 was measured in Providence, R. I.[5]

Measurement of PCBs emitted from stationary sources is just beginning; therefore, the state of the art in this area is changing rapidly.

Recognizing the potentially harmful effects of PCBs on humans, the American Conference of Government Industrial Hygienists has set standards for workplace exposure.[6] Since PCBs released into the environment remain there for a considerable length of time and have a high potential for being introduced into the food chain, reliable methodology must be developed to identify sources that release PCBs and to measure and control the amounts to which humans are exposed. Methodology for measurement of ambient and stationary source concentrations of PCBs must include the capability to quantitatively sample particulate and vaporous forms at the nanogram- and microgram-per-cubic-meter levels, respectively. Attention must be paid to removal of interferents from samples taken from the ambient air and from stationary sources.

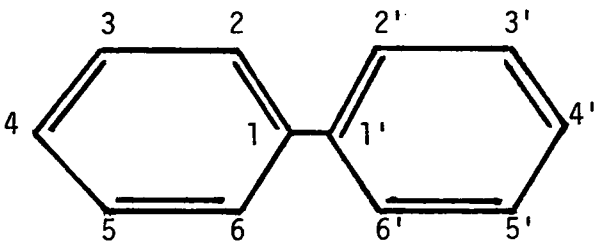
Analytical sensitivity obtained by use of electron-capture detection with gas chromatography has been more than adequate. This technique has been used for analysis of trace amounts of pesticides in soil and water.[7] Improvements in the quantitation technique are needed, however.

This report reviews the state of the art of methodology for measuring PCBs in ambient air and from stationary sources (with emphasis on the former). Four main areas are covered: (1) physical and chemical properties of PCBs, (2) sample preparation by extraction of PCBs from the collected sample and removal of interferents, (3) analysis, and (4) quantitation.

SECTION 2

PHYSICAL AND CHEMICAL PROPERTIES

Aroclors are prepared by catalytic chlorination of biphenyl with anhydrous chlorine.[8] This process produces a complex mixture of substitution products ranging in composition from one to ten chlorine atoms per biphenyl molecule. 209 compounds are theoretically possible.[8] The compounds are named as derivatives of biphenyl:



The Aroclors are characterized by a four-digit number. The first two digits represent the type of molecule, 12 = chlorinated biphenyl (54 = chlorinated terphenyl), and the last two digits represent the average weight percent of chlorine in the mixture.[8] Thus, Aroclor 1242 is a mixture of chlorinated biphenyls with an average of 42 % chlorine. (Aroclor 1016, a chlorinated biphenyl with 42 % chlorine, deviates from this nomenclature.)

The environmentally important physical and chemical properties of the Aroclors warrant discussion. All Aroclors are characterized by low water solubility, the solubility decreasing with increasing chlorine content. Aroclor 1242 has a reported water solubility of 200 ppb.[8] Other workers

have found considerably lower values for Aroclor 1254.[52] (Aroclors are soluble in a number of organic solvents.) Vapor pressures of the more volatile (those with lower degree of substitution) Aroclors are of the order of 10^{-3} to 10^{-5} mm of Hg over the range 20-40°C (68-104°F).[8] The rate of vaporization of PCBs from solid surfaces decreases as the extent of halogenation increases.[53] The densities of Aroclors are much greater than that of water.

Chemically the Aroclors are quite stable. They are resistant to oxidation and change on exposure to acid or alkaline conditions at ambient temperatures. The Aroclors do undergo reductive dechlorination in the atmosphere from exposure to ultraviolet radiation. This property is important in analyzing environmental samples for PCBs and is discussed below.

SECTION 3

AMBIENT AIR METHODOLOGY

SAMPLING. The sampling procedures that have been used fall into three general categories: (1) liquid absorption, (2) liquids on solid supports, and (3) solid adsorbents.

Liquid Absorption

Liquid absorption methods usually involve the use of some type of impinger or fritted-glass gas bubbler in conjunction with a vacuum pump. One procedure utilizing a Greenburg-Smith Impinger, consists of drawing air by vacuum pump through a trapping medium of ethylene glycol at a rate of up to 30 liters per minute.[9] A collection efficiency of 75 to 83 % has been reported.[10] Toluene,[11] hexane,[12] and hexylene glycol[13] (for chlorinated pesticides only), have also been used to collect PCBs.

EPA has used the ethylene glycol procedure to collect pesticides and PCBs.[7] The procedure consists of four Greenberg-Smith impingers each containing 100 milliliters of ethylene glycol. A glass fiber filter is used ahead of the impingers to trap particulate matter. Two impingers are operated in series for 12 hours and the other two for an additional 12 hours. A column of activated alumina has been used after the second impinger to trap pesticides not retained by the ethylene glycol,[14] and it would presumably aid in collecting PCBs.

Fritted glass bubblers with toluene as the solvent have been used to collect PCBs.[3] This method is recommended by the American National

Standards Institute.[11]

Because of the ubiquitous nature of PCBs, glassware, solvents and other equipment must be scrupuously cleaned.[7,21]

Several limitations are inherent in liquid absorption systems. The most important of these is the collection of a sufficient volume of air. The highest airflow rate used is about 30 liters per minute; therefore, a 24-hour sampling period results in the collection of PCBs from a total of only 43 cubic meters of air.[9] The detection limit of electron capture detectors is about 50 picograms per microliter.[15] Assuming a sample volume (for analysis) of about 10 ml and a 50 cubic meter air volume, this works out to a lower limit of detection (LDL) of 10 ng/m^3 - if collection efficiency for PCBs is 100%. Presumably, the LDL could be lowered by extending the sampling time; however, the more volatile and or less soluble PCBs may be lost from the impinger.

Liquid absorption methods appear suitable for sampling at sites where relatively high concentrations are expected, such as near capacitor manufacturing plants and low temperature incinerator stacks.

Liquid Phases on Solid Supports.

These sampling procedures fall into two categories: (1) those that are used in conjunction with a vacuum pump that include measurement of the air volume sampled and therefore the concentration of PCB sampled and (2) those employing static samplers where there is no measurement of air volume.

Static samplers, such as Nylon nets coated with a silicone oil,[16] are useful for qualitative determination of PCBs, but are not useful for monitoring PCB concentrations.

In the other category of samplers, ceramic saddles coated with a silicone oil[17] and Florisil - 5% glycerine[18] have been used to sample

PCBs. These systems allow higher airflow rates than do the liquid - impinger samplers because of the porosity of the solid support. A lower limit of detection of 2 ng/m^3, using electron capture gas chromatography, is claimed for the latter procedure.[18] With the ceramic saddle - silicone oil system a glass fiber filter was inserted in front of the coated saddles to trap suspended particulate matter; a flow rate of 0.6 m^3/min and a collection efficiency of 70% (for Aroclor 1254) were reported. It was expected that PCBs in the vapor and liquid aerosol phase would easily pass through the filter and be trapped in the silicone oil, while those PCBs adsorbed onto solid particles would be retained by the filter. It was observed, however, that less than 1% of the total PCB collected was on the filter.[17] In maintaining their equilibrium vapor pressure with the surrounding air at the high flow rates used, the particulate-bound PCBs were most likely entrained in the airflow. Thus, no conclusion as to the relative concentration of PCBs in the particulate and aerosol-vapor phase was possible. Other workers[5] have suggested that PCBs adsorbed onto particulate matter are not retained on glass fiber filters during sampling.

Cottonseed-oil-coated glass beads[14] and paraffin-coated Chromosorb A[14] have both been tested for collection of a variety of pesticides and may have utility for collecting PCBs. While the former system appears promising, prolonged sampling of air can result in oxidation and polymerization of the cottonseed oil making extraction of the oil difficult.[29] More work is needed on liquid phase-solid support systems to define the collection efficiency for the more volatile components of Aroclors, mono- and dichloro-biphenyls. Higher collection efficiences than 70% are also desirable.

Solid Adsorbents

Several solid adsorbents have been used to collect PCBs. Even though low flow rates of 2 to 3 l/min were used, Florisil showed no breakthrough of PCBs from the first Florisil column after 5 days sampling.[19] Low analytical blanks for the Florisil - 0.1 ng - using electron-capture gas chromatogrpahy were obtained. This collection system warrants further investigation at higher flow rates.

A highly promising sampling system is the polyurethane foam system of Bidleman and Olney[5,10] which has been tested for PCBs. In this system, an 8-by-10-inch glass-fiber filter for particulate collection is placed on top of a container holding the solid trapping medium. The medium consists of a porous polyurethane foam plug, pre-cleaned by washing with water and extraction with acetone and petroleum ether. The entire apparatus is fitted to a high volume sampler. Such an apparatus, developed under an EPA contract with Environmental Sciences and Engineering, Inc.,[20] is shown in Figure 1. High airflow rates of 0.4 to 0.8 m^3/min have been obtained[5,10,20] allowing the collection of large air volumes.

The efficiency of this system for collection of tri-, tetra-, and pentachloro- biphenyl vapors was found to be 99 to 96 %; 1 % or less of the total PCB was formed on a backup plug.[10] Similar quantitative recovery of Aroclor 1221, which is 51 and 32 % mono- and dichloro- biphenyl, respectively, has been obtained by other workers.[20] Ambient PCB concentrations of 4 ng/m^3 have been measured in a 4-hour sampling time.[20] Refrigerated storage of collected samples prior to analysis is recommended.

The ability to sample large volumes of air with quantitative retention of PCBs indicates that the polyurethane foam sampling system is the most pro-

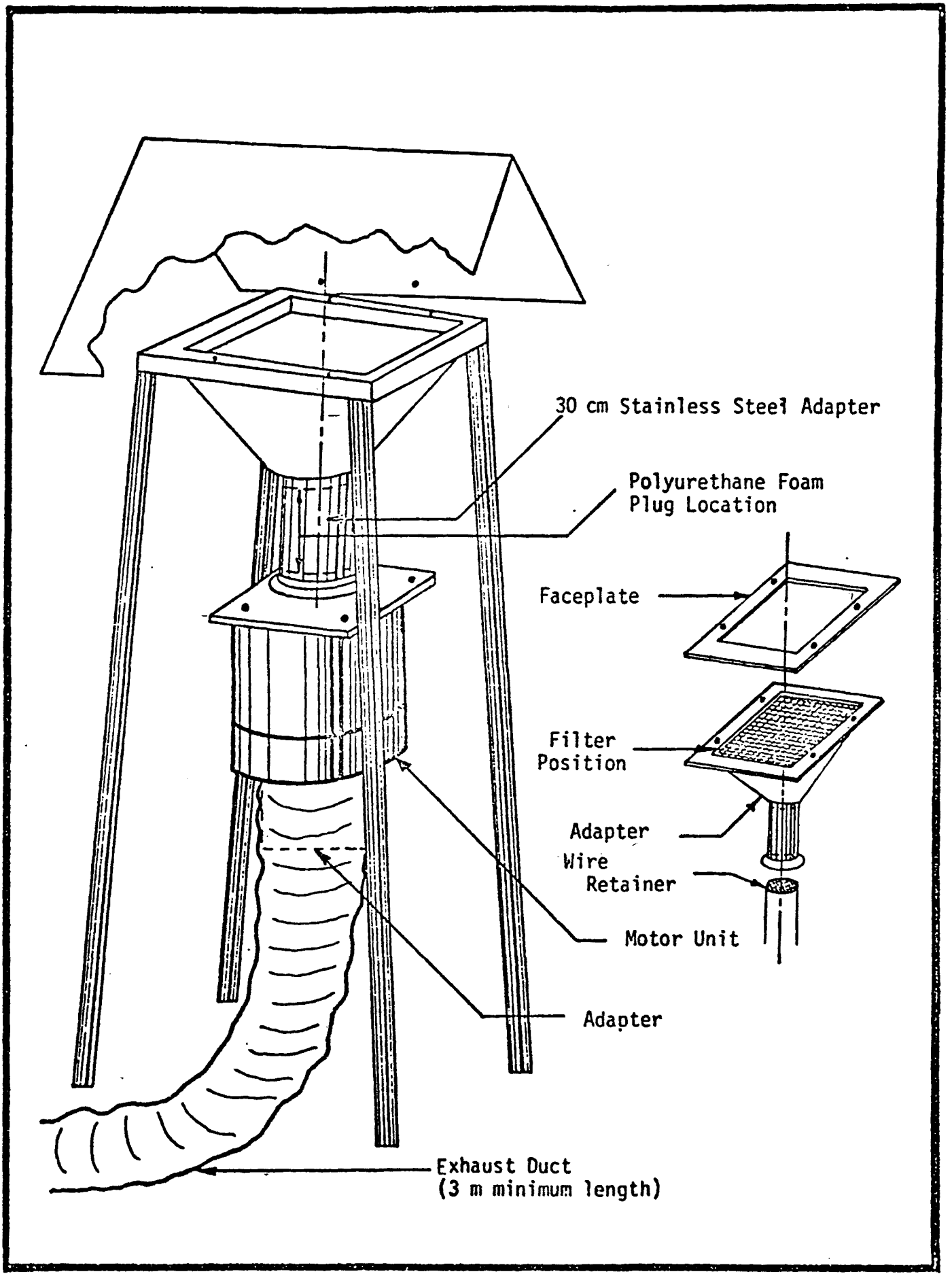


Figure 1. Assembled sampler and shelter with exploded view of the filter holder.

mising sampling system available at this time. In addition to quantitative recovery, this system has the advantage, over liquid-phase solid support sampling systems, of not requiring separation of a liquid sampling phase prior to analysis. Additionally, the operating requirements of the sampler, which are similar to the high volume sampler for measurement of suspended particulate matter,[22] make it adaptable to routine sampling.

The polyurethane foam sampling system is being evaluated further under the EPA contract with Environmental Science and Engineering cited above. The effect of sampling time and temperature on retention of PCBs are being studied.

The present extraction procedure for cleaning the polyurethane foam plugs prior to sampling is lengthy: water wash, extraction for 12-hours with acetone, followed by 2 hours with petroleum ether or hexane.[20] Blank values giving an electron-capture response of 500 ng/plug after extraction have been obtained.[20] It is not known whether this reponse is due to PCBs or electron-accepting impurities from foam processing. Moderately high blank values can be tolerated without seriously affecting the LDL, however. For example, a blank value of 560 ng/plug means that to measure an ambient concentration of 10 ng/m^3 of PCB (as decachlorobiphenyl) requires a sampling time of 125 minutes at a sampling rate of 0.8 m^3/min.[20]

Since it is desirable to have a blank value that is reproducible from plug to plug and obtainable with a shorter extraction time than above, development of foam specifications were included in the above work.[20]

SECTION 4

SAMPLE PREPARATION

Preparing a sample for analysis usually involves two procedures, (1) removal of PCBs from the sampling medium by extraction with an organic solvent and (2) treatment of the extract to remove interferences.

The solvents most frequently used to extract PCBs are petroleum ether[5,10,20] and hexane.[17,9] Before use the solvent must be analyzed to determine the PCB content; some pretreatment of the solvent is usually required to reduce the PCB content to an analytically acceptable value.[7] Pesticide grade solvents are commercially available. Sample extraction times of 2 and 3 hours, and shaking the solvent-sample[10,20] mixture in a separatory funnel[17] have been reported. Since removal of PCBs from the polyurethane foam sampling medium[10,20] appears to require considerably less time than preparation of the foam for sampling, the blank response may indeed be caused by electron-accepting compounds other than PCBs as was observed earlier.

Since the sampling procedures for PCBs are not selective, they may collect some interfering compounds along with PCBs; therefore, some treatment of the extract prior to analysis may be required. Chlorinated and other pesticides present a serious interference problem in analyzing residue samples[23] and are also the main interferents in air samples. Procedures developed for removal of these interferents in residue analysis[7] can be

applied to air samples.

Figure 2 shows a chromatogram of an Aroclor 1254 - pesticide mixture; the similarity of retention times for the Aroclor components and the pesticides is striking and demonstrates the non-specificity of the electron capture detector and the need for careful confirmation of the presence of PCBs by use of at least two columns.[23]

Two separate procedures are used to remove all of the interferring pesticides prior to analysis: column chromatography using Florisil[7] (magnesia-silicate) — silicic acid and silica gel - Celite.[24,25] The Association of Analytical Chemists has a standard method for the Florisil procedure.[21] Both columns must be activated (heated)[21] to obtain optimum separation; a water content of 3%[24] in the silica gel - Celite procedure is recommended for optimum separation. Florisil can be used to separate PCBs from some pesticides (e.g., dieldrin and endrin), but the eluate retains DDT and its metabolites.[7] Silicic acid - Celite can be used to separate PCBs from the latter compounds.[24,25]

The stability of PCBs to alkali and acid permits removal of some pesticides by chemical treatment. Treatment with alkali permits removal of DDT.[21,23] Treatment with H_2SO_4 destroys dieldrin and organophosphate pesticides.[21,26]

Removal of interferences can require a significant amount of laboratory work by the analyst. Sampling history and the identification of compounds in a sample chromatogram can be used to reduce this work. For example, sampling in the area of a known source of PCBs should produce a high ratio of PCBs to interferents. If this is confirmed by a sample chromatogram, interference removal is probably not necessary. Removal of interferences is more likely

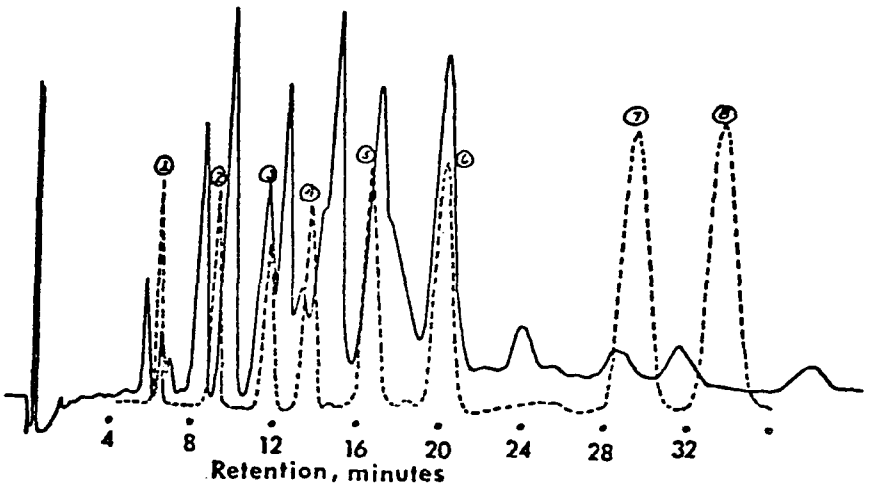


Figure 2. Gas Chromatogram of:

Aroclor 1254 (solid line)

and pesticide mixture

(dotted line). Column

4% SE-30/6% QF-1, 200°C

carrier flow 70 ml/min.[23]

1. Aldrin
2. Hept. Epoxide
3. p,p'-DDE
4. Dieldrin
5. p,p'-DDD
6. p,p'-DDT
7. Dilan I and Methoxychlor
8. Dilan II

to be necessary when sampling in areas removed from PCB sources where interferents would be more predominate. Interference from DDT and its metabolites cannot be discounted; nanogram quantities of DDT and p,p'-DDE resulting from aerial fallout have been measured in southern California.[27]

SECTION 5

QUALITATIVE AND QUANTITATIVE ANALYSES

PCBs are usually determined by gas-liquid chromatography using electron capture detectors.[7] Microcoulometric detectors have been used, but lack the sensitivity required for analysis of PCB's in ambient air.[29] Electron capture detectors are specific only to electron-accepting molecules.[54] Because of their high sensitivity, electron-capture detectors are preferred for analysis of the low concentrations of PCBs present in ambient air.

A number of different liquid-solid support columns have been used to separate PCBs. Liquid phases include: OV-17, SE-30 and QF-1;[7,20,30] OV-210 and OV-101; DC-200, and SF-96.[30] Solid supports include: chromosorb W, Gas Chrom P, and Gas Chrom Q.[30] Selection of the proper column and optimization of chromatographic conditions is important to obtaining good resolution of the Aroclor components and interferents.

During analysis it is very important to confirm the presence of PCBs, because of the numerous interferents that can be present. Of the procedures used for confirmation, perchlorination of the sample to convert PCBs to decachlorobiphenyl[31] and mass spectrometry coupled with gas chromatography[32] are the most absolute procedures. Qualitative identification of PCBs can be made by comparing retention times of chromatographic peaks with those produced by individual chlorinated biphenyls[33,35] or Aroclors. Standard Aroclor formulations are available from EPA.[34] All retention times should be relative

to some arbitrary standard such as aldrin or p,p'-DDE. Gas - liquid chromatographic retention times - relative to p,p'-DDE - for individual compounds in the Aroclors are given in reference eight and twenty-eight and may be useful to workers in the field of PCB methodology.

The various Aroclors exhibit different chromatograms, which can be useful in distinguishing between them. The electron-capture chromatograms for five different Aroclors are shown in Figure 3. The numbers on peaks refer to individual compounds. Identification by the retention time procedure should be confirmed by use of two columns of different polarity.[30] Confirmation of the existence of PCBs may also be obtained by thin layer chromatography.[30]

Once the identification of PCBs has been confirmed, quantitation may be achieved by (1) comparing properties of the sample chromatogram with those produced by Aroclor standards (2) using analyzed Aroclor standards, and (3) perchlorinating the PCBs to decachlorobiphenyl. Accurate analysis of PCBs is difficult at the present time. Each of the above procedures is discussed below:

Comparison. Techniques based on comparison include subjectively matching the chromatogram of the sample to that of the Aroclor it most closely resembles.[7] Quantitation is obtained by integrating the area under all of the peaks in the sample and comparing the total area to that obtained, under the same chromatographic conditions, from a known weight of the Aroclor standard.[7] If the presence of more than one Aroclor is indicated, the sample is quantitated using Aroclor standards judged appropriate for different portions of the chromatogram.[7,23] This "fingerprinting" technique is the most widely used approach to quantitation because of its practicality.[23]

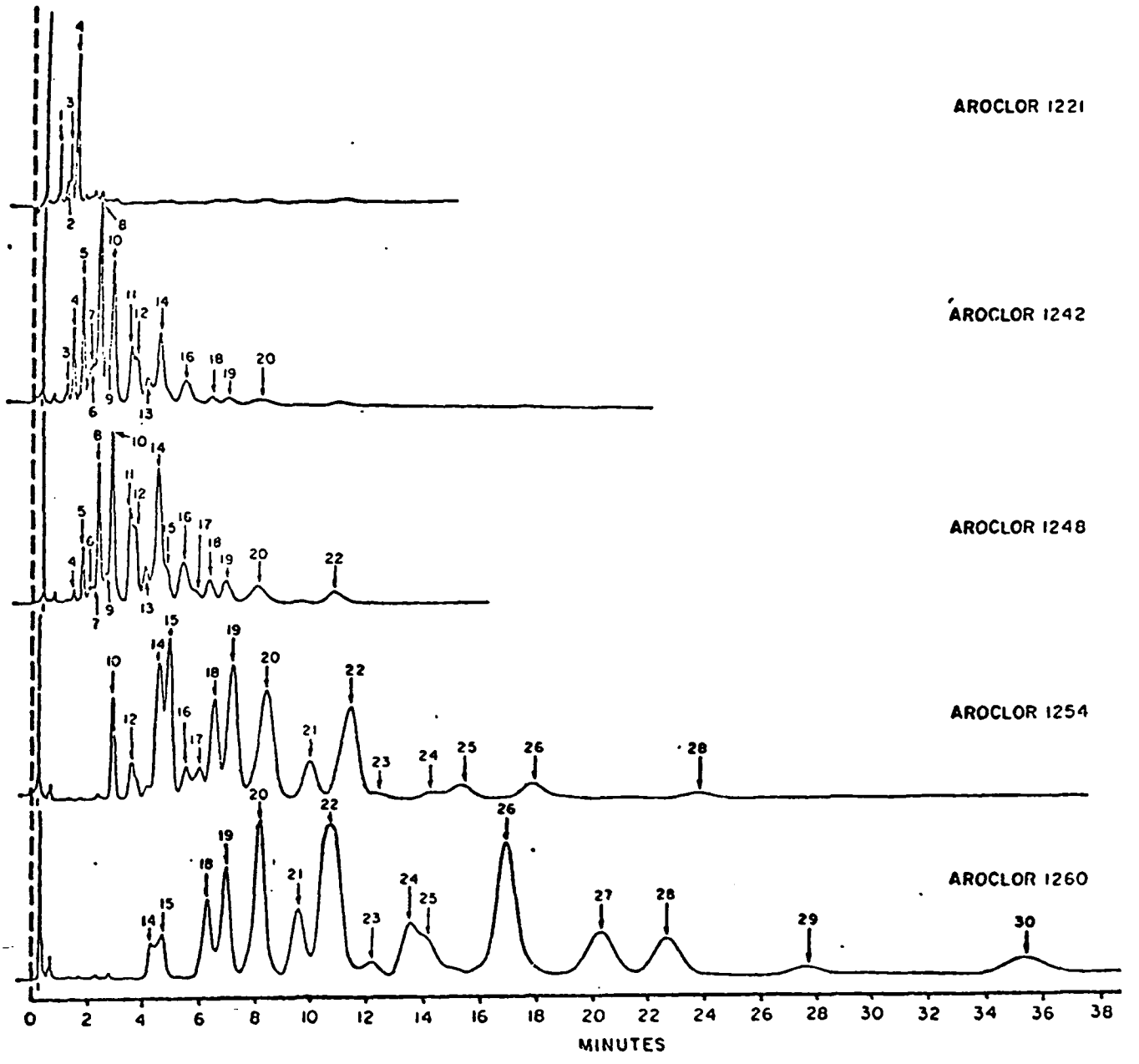


Figure 3. Comparison of electron capture chromatograms for Aroclor 1221, 1242, 1248, 1254, and 1260.

Source: Reference 11. Reprinted with permission from American National Standards Institute, 1430 Broadway, New York, N. Y. 10018. Publication C-107.1 - 1974, Copyrighted by ANSI.

Other techniques are based on determining the ratio of peak heights or areas between sample and Aroclor standard chromatograms for selected peaks.[30,33]

The adequacy of all comparison procedures depends on the similarity of sample and standard chromatograms.[33] Because of photochemical breakdown in the atmosphere and non-representative sampling of Aroclor components (due to different vapor pressures of the components) the chromatogram obtained from an environmental sample is hardly ever identical to that of the original Aroclor. Samples may also be composites of several Aroclors. Also the electron-capture response of different chlorinated biphenyls can vary as much as 10,000 fold.[23,35] The weakness of comparative procedures, therefore, lies in the impossibility[23] of matching the sample and standard chromatograms. Comparison techniques should be considered as semi-quantitative procedures.

Analyzed Aroclor Standards. By use of GC-mass spectrometry and a GC with an electrolytic conductivity detector (to measure chlorine) the weight percent of PCB in each peak of a given Aroclor has been determined.[36] This information and the analyzed standards can be used to determine response factors for corresponding peaks in an environmental PCB sample.[36] The total amount of PCB then becomes the amounts from all the individual peaks. The authors in their paper have offered limited quantities of these standards to interested parties.

Other workers[37,38] have used the above procedure to analyze environmental samples for PCBs. This technique is an accurate means of analyzing PCBs provided all peaks in the environmental samples are identified. The technique, although accurate, is tedious. The obvious limitation of this technique is the availability of the standards.

Perchlorination. This technique of quantitation eliminates errors inherent in the subjective nature of the comparison - "fingerprinting" techniques, if the perchlorination itself is quantitative.

The reported procedure[39] involves reacting the sample, after removal of interferences, with $SbCl_5$ in chloroform solvent in a closed system at 165-175°C overnight. This chlorination converts the chlorinated biphenyls, with different degrees of chlorination, to decachlorbiphenyl (DCB). Average conversions of 93 to 100% were obtained with six different Aroclors.[39] (The chloroform, of course, must be removed prior to analysis because it responds to electron capture detectors.)

The main advantage of this technique over other techniques is that the chromatogram of the sample has only one peak, DCB. Quantitation is obtained by comparing the peak height or area of the DCB peak with that of a known weight of DCB of known purity. Comparison of the perchlorination technique with the finger-printing technique gave good agreement when the DCB analysis was reported in terms of the particular Aroclor.[39] Since the response of electron capture detectors depends on the number of chlorine atoms in the biphenyl molecule, the perchlorination technique also increases the sensitivity over that obtained with other quantitation techniques.

Some workers have been unsuccessful in obtaining quantitative conversion of PCBs to DCB;[20] typical results are shown in Figure 4.[56] These chromatograms were obtained using a starting mixture containing seven different mono- di- and trichlorobiphenyls. One of the problems appears to be trying to perchlorinate PCBs with varying degrees of chlorination - and consequently varying susceptibilities to electophillic substitution - with one set of reaction conditions.[40] The use of milder perchlorination conditions is indicated.[40] In addition to optimizing the conditions of

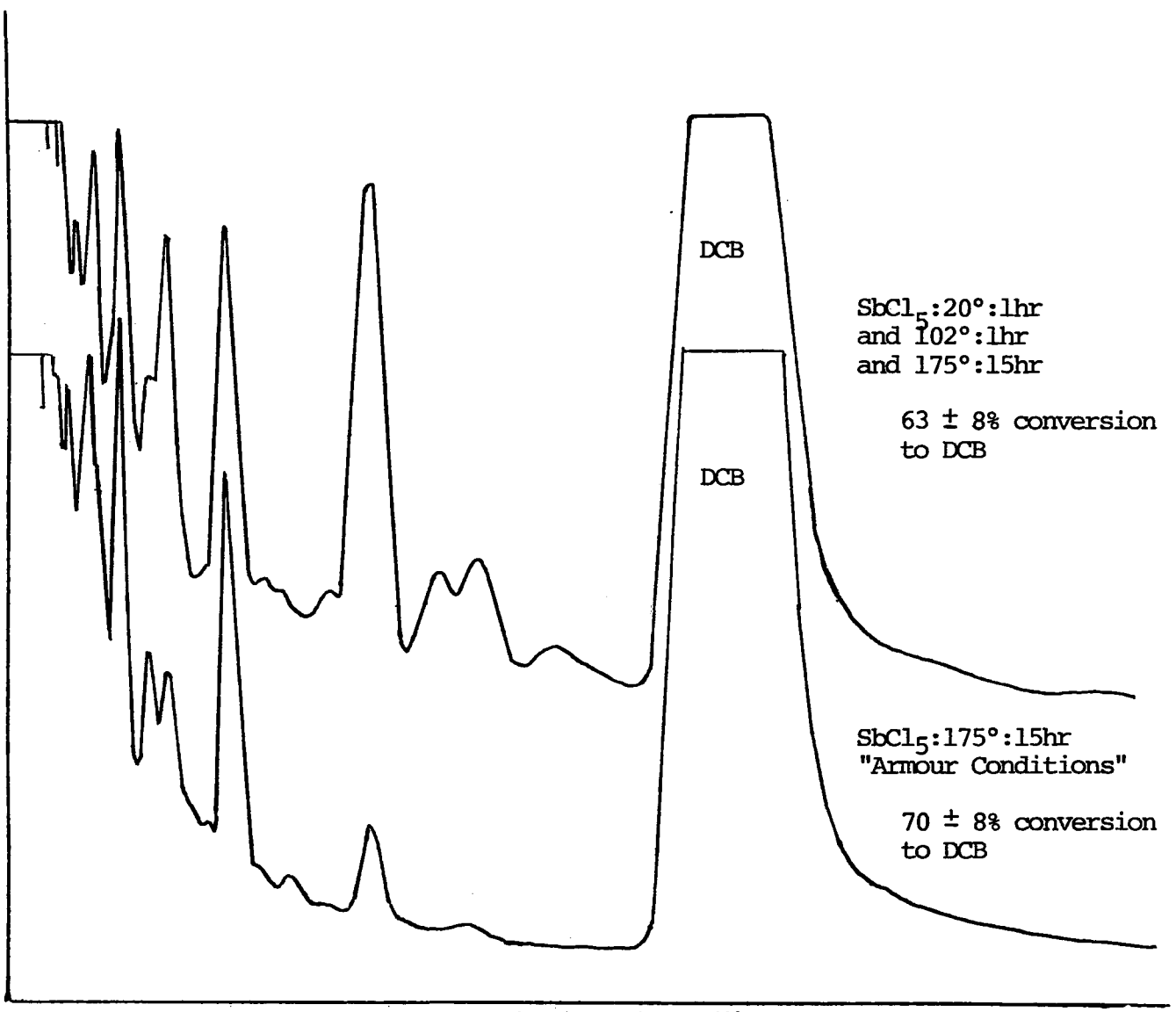


Figure 4. Chromatogram of Perchlorinated PCB Mixture.
column: glass 6', OV-17/QF-1 on chromosorb w at ~200°C

perchlorination, any significant amounts of biphenyl in samples will, of course, have to be removed prior to perchlorination.

Impurities, $SbCl_4Br$ and DCB, have been found in $SbCl_5$.[41] The former compound produces bromononachlorobiphenyl and, of course, affects conversion of PCBs[41] to DCB. Varying amounts of DCB have been found in different commercial sources of $SbCl_5$, but in general, the amount of DCB impurity is not significant because of the small amount of $SbCl_5$ required in the perchlorination reaction.

While further investigations are needed to optimize the perchlorination procedure, the technique has considerably more potential for accurately quantitating PCBs than either comparison or analyzed standard techniques. Further development of the perchlorination procedure is in progress under an EPA contract.[20]

It should be noted that PCB values reported as ppm DCB will be higher than values based on an individual Aroclor. The DCB analysis value can be reliably converted to an individual Aroclor value[39] only if a positive identification of the Aroclor - in the collected sample - is achieved. As discussed earlier, this identification is not an easy task.

Other Techniques. Computer controlled high resolution mass spectrometry,[42] polarography,[44] and plasma chromatography,[43,55] have been used to analyze PCBs.

SECTION 6

SUMMARY AND CONCLUSIONS

The most promising methodology for analyzing PCBs in ambient air at the present time involves: (1) collecting the sample on polyurethane foam, (2) extracting PCBs with an organic solvent, (3) removing interferents - as necessary - by column chromatography, (4) confirming the presence of PCBs by perchlorination in conjunction with electron capture - gas chromatography or by mass spectrometry - gas chromatography, and (5) analysis with electron capture - gas chromatography. A reliable and widely applicable quantitation procedure has not yet been developed. However, perchlorination offers considerable promise for fulfilling these requirements. Until such a procedure is developed, most workers will be forced to use subjective techniques for quantitation.

Work on this method is still in the development stage and a number of areas, as discussed in this review, need further investigation and improvement before the method should be considered capable of producing reliable data. Quantitation is the main area in need of improvement. A standard source of high-purity decachlorobiphenyl would be useful if the perchlorination technique can be successfully developed. Quality control samples, e.g., PCBs on polyurethane foam, are needed to aid the analyst in obtaining reliable data.

Methodology for measuring PCBs in ambient air is technically demanding and requires considerable operator skill; however, the sampling procedure

appears potentially suitable for routine use by technician-level personnel. In operating a monitoring network, e.g., around a source of PCBs, collected samples could be returned to a central laboratory that possessed the skills required to carry out the analysis and quantitation.

SECTION 7

STATIONARY SOURCES

As mentioned earlier, work on methodology for measurement of PCBs in stationary sources appears to be in the early stages of development.

A common source of PCBs is incinerators which seldom maintain the temperature of 2000°F required to obtain complete combustion.

The main difference between source and ambient methodology is in sampling. In stationary sources, gases at varying elevated temperatures (e.g., 150 to 800°F, depending on the particular source)[45] need to be sampled isokinetically. These gases contain varying amounts of water vapor and sometimes liquid water.[45] These properties of stationary source emissions impose some additional requirements on sampling over those required for ambient sampling. Namely, the absorbing medium, especially for liquids, must be cooled to retain PCBs, and water must be removed before the gases reach the absorption medium.

Liquids, liquids on solid supports, and solids have been used to collect PCBs. In laboratory studies, hexane, in impingers maintained at -78°C, quantitatively recovered PCBs; continued bubbling of air through a hexane - PCB solution containing 8 ppm PCBs showed no loss of PCBs.[46] The system has been used for sampling a waste treatment plant.[46] Other workers[47] have used cooled hexane to sample incinerator stack emissions for PCBs. Aqueous 10 % glycerine solutions contained in 2 absorption bottles showed 98 % recovery of PCBs; the system has been used to sample incinerator gases.[48] Toluene[49]

has been recommended for collecting PCBs in source emissions.

Glycerine on Florisil[47] has been used to sample incinerator gases. Two solid sampling materials, Tenax, poly(2,6-diphenyl-p-phenyleneoxide), and Florisil have produced quantitative recovery of PCBs at elevated temperatures.[45] Florisil is especially promising because of its low cost and low blank values.

Interferences from stationary source emissions vary with the incineration process and the materials being burned.

Electron capture - GC[47,49] and GC coupled with mass spectrometry[50] have been used to analyze source samples. Quantitation by perchlorination has been used in source analysis on at least two occasions,[47,51] but neither group of workers obtained quantitative conversion of PCBs to DCB. Bi- tri-, and tetrachlorobiphenyls gave lower conversions than the more highly chlorinated components of PCBs.[51]

Further investigations, especially in the area of sampling, are needed to develop reliable methods for measuring PCBs in stationary sources. The work being carried out to develop the perchlorination technique of quantitation should be of mutual benefit to investigators interested in ambient and source methodology.

SECTION 7

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16. ABSTRACT

The state of development of methodology for measurement of polychlorinated biphenyls (PCBs) in ambient air and stationary sources was reviewed.

The most promising method for ambient air measurements involves collection of PCBs on polyurethane foam, extraction with an organic solvent, removal of interferences by column chromatography, and confirmation and analysis by electron-capture gas chromatography. Quantitation by perchlorination of PCBs to decachlorobiphenyl (DCB) is the most promising quantitation technique, but the procedure has not yet been perfected to the point where all PCBs are quantitatively converted to DCB. Perfection of this technique should allow for significant improvement in the quality of ambient PCB data being generated.

Source and ambient methods differ mainly in sampling. Work on methodology for stationary sources is in the early stages of development and further investigations are needed.

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