PCB NEWSLETTER

August 20, 1970

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ANALYTICAL

Richard A. Schoettger, Ph. D., Fish-Pesticide Research Laboratory, Columbia, Missouri

The FDA procedure published by Burke et al. in JOAC for separation of PCB's and pesticides prior to GC analysis was found to be satisfactory. Further evaluation and development of this technique is under way.

The response of two chlorine specific GC detectors, the electrolytic conductivity or microcoulometric, can be calibrated in µg or ng of chlorine. This allows calculation of µg or ng of compound when the molecular weight of the component is known. Thus, the concentration of a PCB component can be calculated when no standards are available, using the following equation:

$$\mu g \text{ comp.} = \frac{MW}{\text{No. of Cl}} \cdot \frac{\mu g \text{ Cl}}{35.5}$$

Determination of the amounts of Aroclor^{R} 1248, 1254, and 1260 in residue extracts is possible since each PCB mixture contains two major components which are not present in the next higher eluting mixture of PCB's. This technique requires cleaned-up extracts. Pesticides should not be present in these extracts unless mass spectrometry is employed to confirm GC peak identity.

An attempt is under way to prepare ^{36}Cl-labelled PCB's by exposing Aroclors to a flux of thermal neutrons. The radio labelled PCB's are destined for use in uptake and metabolism studies and to evaluate analytical methods.

James J. Lichtenberg, Analytical Quality Control Laboratory, Cincinnati, Ohio

The carbon adsorption method (CAM) is being evaluated as a technique for sampling and concentrating polychlorinated biphenyls from water. Duplicate samples are obtained in the laboratory by dosing 1500 liters of water with 2 µg/l of the PCB being studied into tap water (adequate supply of raw river water not presently available). The following Aroclors are being studied: 1221, 1232, 1242, 1248, 1254, 1260, 1262, 1268 and 4465.

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James J. Lichtenberg (Continued)

The underlined compounds are first priority. Simultaneously the stability of these compounds in water is being observed over the sampling period. An effort will be made to correlate the CAM recovery efficiencies with stability.

Results to date indicate that the Aroclors are stable, at least, over the five day CAM sampling period. Assay of the effluent from the carbon cartridges indicate that the adsorption efficiency was 100%. However, recovery of the individual Aroclors by extraction with chloroform was variable and poor (25-30% for the higher boiling range Aroclors). The gas chromatographic elution patterns of the CAM extracts of the lower boiling range Aroclors were significantly different than those of the original standards. Both loss of original constituents and addition of new constituents were noted. The latter may have resulted from the dosing water. These low and variable results were not expected and a significant amount of additional work will be required to accurately define the applicability of the CAM for this purpose.

National Water Quality Laboratory, Duluth, Minnesota

Gas chromatograms of all PCB's except those of the 4400 and 5400 series have been taken and the retention times compiled. Ultraviolet and fluorescent spectroscopy have been investigated, especially with the 4400 and 5400 series, as possible methods of measuring PCB's. Direct measurement with ultraviolet seems promising. Solubility of these compounds and appropriate emulsifiers are being investigated.

A. W. Garrison, FWQA, Southeast Water Laboratory, Athens, Georgia

A general information paper entitled, "PCB's--A Class of Ubiquitous Pollutants," has been prepared by Dr. Carl Gustafson for submission to Environmental Science and Technology.

Several PCB isomers, separated by Dr. Fred Lee's group at the University of Wisconsin, are being used to develop analytical methods for the Aroclors. Mass spectrometry, using the gas chromatographic inlet mode for separation of components, will be used to determine the number of chlorine atoms in each PCB of the Aroclor (as well as the molecular weight). The Coulson detector gas chromatograph will then be used to give

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A. W. Garrison (Continued)

a peak area for each PCB from which, knowing the molecular weight and number of chlorine atoms in the compound, the quantity of each major PCB present in the Aroclor can be calculated.

A modest program of isolation and chemical identification of the major PCB isomers from commercial Aroclor mixtures has begun. Preparative gas chromatography of 1221 and 1242 into their major fractions has been completed. SE-30 gave better separation than DC-200 or a mixture of 5% QF-1 and 5% DC-200. OV-17 has been useful in further separation of some of the major fractions. A survey of 1221, 1232, 1242, 1248, 1254, and 1260 revealed that many of the same GC peaks are found in several of the mixtures. In all, there appear to be about 22 major peaks in this series. Undoubtedly some of these represent more than one compound. Using an 8% SE-30 column at 200° and a Coulson detector, one peak was found to be common to Aroclors 1232 through 1262. In our samples this is the largest peak in 1248. This peak was assigned a retention time of 1.00 and all other peaks are identified by retention times relative to it. Thus in 1221 the major peaks are 0.18, 0.22, 0.25, 0.32, and 0.41. By comparison of retention times and the IR and NMR spectra of the purified fractions with known compounds the peaks have been identified as 2-chlorobiphenyl (0.18); 4-chlorobiphenyl (0.22); 2,2'-dichlorobiphenyl (0.25); and 4,4'-dichlorobiphenyl (0.41). Peak 0.32 is probably 2,4'-dichlorobiphenyl.

Peaks 0.18, 0.25, 0.32, and 0.41 have also been isolated from 1242. In addition we have isolated from 1242 enough of fractions 0.46, 0.54, 0.58, 0.82, 1.00, 1.10, and 1.19 to obtain their IR and NMR spectra. We plan to separate 1254 and obtain spectra of the individual isomers. Since no other pure PCB isomers are available commercially further identification will be slow. We plan to synthesize known compounds by reasonably unambiguous routes and compare their spectra with the isolated unknowns.

John H. Neil, Ontario Water Resources Commission, Toronto, Ontario

Identification and Quantitation of Polychlorinated Biphenyls by Catalytic Dechlorination. A Preliminary Note.

The possible presence of PCB residues in wildlife samples, and the difficulties encountered in their analysis and the analysis of chlorinated hydrocarbon pesticides in their presence, has for some time been of

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considerable concern to residue analysts. Direct confirmation of the presence of PCB is a difficult matter for the average laboratory. In general, a combination of mass spectrometery gas chromatograph is required. Various chemical approaches have been tried, for example, saponification, nitration, but these have been basically aimed at removal of other chlorinated pesticides from the mixtures. These approaches, coupled with chromatographic behaviour, have been used for the identification of PCB inference.

We have attempted to devise a simple confirmatory technique for the direct identification of PCB. The technique which we have developed is quite simple, and does not require highly sophisticated equipment; in fact the determinative step is done with a gas chromatograph equipped with FI detector.

The method we are using and developing further at present involves catalytic dechlorination of PCB to the corresponding fully reduced hydrocarbon. Thus, all PCB are reduced to bicyclohexyl. Other chlorinated pesticides respond as well, although the reaction products are not as well defined. However, the gas chromatographic behaviour of bicyclohexane is such that it can be recognized easily amongst other reaction products. We have found that our approach has several advantages:

1. The multiplicity of peaks normally associated with PCB is converted to a single peak, which represents uniquely the concentration of PCB present. This has been isolated and identified by infrared spectroscopy as bicyclohexyl. (It might be added parenthetically that bicyclohexyl is commercially available*). Similarly, under favorable conditions, all DDT type compounds should yield one peak.

2. Only compounds of the chlorine substituted biphenyl type will give the bicyclohexyl product. Thus, removal of all typical peaks in the EC chromatograph of the reaction product, coupled with the production of bicyclohexyl peak on FI chromatograph gives an indirect confirmation of the presence of PCB.

The main disadvantage of this procedure is that the reaction products, hydrocarbons, produce little response on the EC detector. Analysis, must, therefore, be carried out with other types of detectors. This of course cuts down on sensitivity, in our case about 1/1000 of that of EC. This is

*Eastman Kodak.

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John H. Neil (Continued)
partially compensated by the conversion of all PCB components to one peak.

The reductive dechlorination is carried out on noble metal catalyst (1-5 percent Pt or Pd deposited on 60-80 mesh porous glass beads**), at moderate temperatures, 150-250° C, and under atmospheric pressure of hydrogen. The reactor is of a very simple design, a 12-inch, 1/4-inch diameter stainless steel tube attached to a modified Swagelok tee. As a matter of convenience, we are using a Konte's sweep codistillation as the oven. It has an oven of suitable geometry and is provided with a good temperature controller.

The reaction products are trapped in a coiled 2-ft. length of 1/8-inch Teflon spaghetti tubing; cooled in an ice bath. The tubing is connected to the reactor outlet and then led into a 15 ml centrifuge tube to collect the condensate.

To date the basic lines of investigation have been the following:

1. Batch reaction of PCB and DDT group of compounds. This will provide sufficient product for large-scale separation and IR examination for checking identity.

2. A semi-micro scale, 20 mg and down, flow reactor system, involving catalytic dechlorination of PCB and DDT type of compounds. Conversions of up to 100% of both PCB and DDT to the saturated hydrocarbons have been achieved. Promising results have been obtained with mixtures of DDT and PCB, giving two major peaks. Work is on hand to establish optimum reaction conditions, catalyst compositions. (It appears that Pd catalyst is more suitable than Pt - fewer side reactions). Good (95%) conversions of PCB have been achieved with quantities as low as 10 µg. It may be noted here that we found it necessary when using this reactor to flush the system with 5-6 0.5 ml injections of solvent hexane after sample injection to recover all the bicyclohexyl produced. This is presumably due to the rather high boiling point of the PCB.

3. A micro-flow reactor, consisting of a catalyst-packed precolumn for a gas chromatograph. Hydrogen is used as the carrier gas and temperature control for the reactor is achieved, using the injector block control on the gas chromatograph. Glass systems are being investigated to replace stainless steel in both above applications.

**Applied Science Laboratories, State College, P.A.

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John H. Neil (Continued)

It is hoped to work with a closed reactor loop, provided with a gas sampling valve, so that the products may be flushed directly into the chromatograph.

Work will soon be commenced on the application of this technique to other halogenated pesticides and aromatic compounds.

OCCURRENCE

Gilman D. Veith and G. Fred Lee, University of Wisconsin, Madison

A study of the occurrences of the chlorinated biphenyls in fish and water of the Milwaukee River system has shown that, unlike the more remote areas of Wisconsin, no area of the river from West Bend to Lake Michigan is free of the contamination of chlorinated biphenyls. Confirmatory evidence in the form of mass and infrared spectra and retention volumes in multiple GLC systems has verified the presence of the more highly chlorinated isomers. The degree of chlorination varied from 42 to 60 percent chlorine, depending somewhat upon the distance from major sources.

Based on estimates from commercial mixtures which produce similar chromatograms, the concentrations in fish ranged from 2.3 µg/gm (60 percent Cl) near Grafton to 405 µg/gm (42 percent CL) near Estabrook Park, with Lake Michigan fish ranging from 15 to 25 µg/gm (54 percent Cl).

The effluent from sewage treatment facilities of all municipalities examined contained chlorinated biphenyls at concentrations as high as 0.52 µg/l (60 percent Cl). The concentrations in the river water ranged from 0.02 µg/l (54 percent Cl) in the Milwaukee Harbor to 2.8 µg/l (42 percent Cl) near East Riverside Park. This area of most significant contamination receives untreated sewage from the combined sewer overflows in the City of Milwaukee.

TOXICITY

Richard A. Schoettger, Fish Pesticide Research Laboratory, Columbia, Missouri

Due to the limited solubility of PCB's (ca. 100 µg/l) acute, static bioassays were essentially terminated. Constant flow bioassays were

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Richard A. Schoettger (Continued)

essentially terminated. Constant flow bioassays were initiated with channel catfish and bluegills. The 8-day TL_{50} values for Aroclor^R 1254 at 20° C are about 250 ppb, but we expect even greater toxicity as the study progresses. Three other studies in progress involve exposure of lake trout, channel catfish and bluegills to Aroclor^R 1232, 1248, 1254, or 1260 in their diets at concentrations of 1.2 to 12 ppm. We will examine PCB accumulations and degradation, growth, calcium metabolism, steroidogenesis, thyroid activity, liver enzyme induction, response to thermal shock, and energy utilization. Later this year we will initiate research on effects of PCB's on channel catfish reproduction, interactions between PCB's and cyclodiene pesticides, and biodegradation of PCB's by microorganisms.

National Water Quality Laboratory, Duluth, Minnesota

Research is now being conducted using fish and fish food organisms to determine their tolerance to PCB on survival and reproduction. Fathead minnows, rainbow trout, freshwater shrimp (scuds), aquatic insect larvae, and Daphnia, will be tested to establish safe levels of PCB's in the aquatic environment. Preliminary testing with Daphnia agrees with the limited amount of literature on relative toxicities; the lower chlorine compounds are more toxic to them than the higher chlorine compounds. An exception is the solid 5442 which is very toxic.

J. J. Hickey, University of Wisconsin, Madison

During May and June, the Department of Wildlife Ecology at the University of Wisconsin has been collecting eggs of herons and mergansers in Wisconsin to get at DDE/PCB ratios and possible changes in eggshell thickness. The field work is being carried out by research assistant R. A. Faber under J. J. Hickey's direction.

Herring gull eggs were also collected by D. W. Anderson of this department in Green Bay for DDE/PCB ratios that we now have annually worked out since 1966. This biological material is quite variable in residue level, and no trends of DDE in it have been evident in annual collections that started in 1963.

In June, Anderson and Hickey hope to complete a paper on the build-up and seasonal variation of DDE and PCB's in (a) wild herring gulls and (b) captive gulls exposed for 1 year to a diet of Lake Michigan alewives and small

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J. J. Hickey (Continued)
amounts of beef heart. The PCB estimates are based on those methods described by Anderson et al. 1969. Saponification of the extracts is included in the analyses, but confirmation of the identity of the PCB's by mass spectrometer has not yet been attempted. This study, like others in this department, is financed by a contractual arrangement with the Patuxent Wildlife Research Center of the Bureau of Sport Fisheries and Wildlife.

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