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Polychlorinated biphenyl mixtures have previously been used as additives to improve the chemical and physical resistance of plastics and surface coatings and have been used in electrical equipment and as hydraulic and heat transfer fluids. Polychlorinated biphenyls are now widespread in our environment. The presence of contaminants in commercial chlorinated biphenyl preparations which are potentially more toxic than chlorinated biphenyls is therefore of considerable concern.

Rec'd Dec 30, 1974 (STPM)

We reported at last year's AOAC meeting the presence of chlorinated dibenzofurans in Kanechlor 400, a commercial chlorinated biphenyl mixture of Japanese origin. This finding raised the question of whether chlorinated dibenzofurans in Kanechlor 400 may have contributed to the observed toxic effects when rice oil contaminated with Kanechlor 400 was ingested by several hundred Japanese in the Yusho incident as reported by Kuratsune. Chlorinated dibenzofurans were reported by Vos and co-workers in two commercial chlorinated biphenyl mixtures of European origin that had shown high mortality, liver necrosis and chick edema-like lesions in chicks. Vos failed to detect chlorinated dibenzofurans in Aroclor 1260.

In this paper, we report the finding of chlorinated dibenzofurans in production lots of Aroclor 1254, 1242 and 1016 that were manufactured in 1973. No evidence was obtained for chlorinated dibenzofurans in a production lot of Aroclor 1221 manufactured during the same period.

DSW 338651

The procedure used in the current work was a considerably modified version of that applied earlier to the analysis of Kanechlor 400. The current procedure used three types of adsorbent columns for sample preparation.

Call for Slide 1. (Flow chart of sample preparation)

The alumina column was 50 g of WOELM W-200 alumina which was eluted with 400 ml of 1% methylene chloride/hexane followed by 400 ml of 20% methylene chloride/hexane. The 20% eluate containing the material of interest was then concentrated to less than one ml prior to addition to an alumina micro column.

The micro columns were disposable pipets of roughly 5 mm bore into which a small wad of glass wool had been inserted to retain the aluminum oxide. WOELM W-200 alumina was poured into the columns to a depth of 2.5 cm. The micro columns were eluted with 10 ml of 1% methylene chloride/hexane and 6 ml of 20% methylene chloride/hexane.

Prior to the Florisil column, eluates from two, 100 mg Aroclor portions, each being less than one ml, were combined. The Florisil column was 8 g of 60/100 mesh PR grade Florisil which was eluted with 150 ml of hexane and 100 ml of 5% ethyl ether/hexane. The latter eluate was concentrated to less than 20 microliters and was never permitted to go to dryness.

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All for Slide 1.

The concentrated eluates were analyzed by combined gas chromatography/mass spectrometry using a Finnigan 1015 quadrupole mass spectrometer interfaced thru a Gohlke all-glass jet separator to a six-foot by two millimeter bore 3% OV-101 column at 200°C with a helium carrier gas flow of twenty milliliters per minute. Mass spectra of authentic chlorinated dibenzofurans were obtained under identical operating conditions using a mixture of mono-, di-, tri-, and tetra- chlorodibenzofurans kindly provided by Dr. Albert Pohland of FDA. A summary of the results for each Aroclor sample analyzed is given in the following slides. In each case, the mass spectral data obtained for the chlorinated dibenzofurans included the parent ion and fragment ions derived from losses of CO + Cl. Taken together, these data are considered characteristic for the chlorinated dibenzofurans. Each analyzed extract also gave evidence of some chlorinated biphenyls indicating the column separation procedure used did not completely separate Cl-DBF from the chlorinated biphenyls.

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In each Aroclor found to contain Cl-DBF, the level of contamination was estimated to be in the ppm range. Studies are now under way to obtain more meaningful quantitative data on the level of Cl-DBF contamination.

Call for Slide 2.

Six, 200 mg replicates of an Aroclor 1254 sample were analyzed along with a reagent blank. Tetra- and pentachlorodibenzofurans were found in all six extracts. Hexa- and heptachlornaphthalene were also found. None of these compounds was found in a reagent blank equivalent in size to a 200 mg sample.

Call for Slide 3.

Two 600 mg replicates of an Aroclor 1242 sample were analyzed. Di, tri and tetrachlorodibenzofurans were detected in both. In addition, tetra-, penta- and hexachloronaphthalene, a trichloroterphenyl, and three unidentified halogenated compounds were detected. The unidentified halogenated compounds may form a homologous series differing from one another only in their degree of chlorination. The tentative molecular weights of these unidentified components were 278 (possible 4 chlorines), 312 (5 chlorines) and 346 (possible 6 chlorines).

These may have been methylchloronaphthalenes or chlorophenyl cyclopentadienes. However, their only observed fragmentation was a loss of one chlorine atom. The data for these unidentified compounds was therefore too sparse to permit identification.

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Call for Slide 4.

Two, 200 mg replicates of an Aroclor 1016 sample were analyzed. Dichlorodibenzofuran was found in each of the samples.

Call for Slide 5.

Initially, 2, 200 mg replicates of an Aroclor 1221 sample and a reagent blank were analyzed. No Cl-DBF were detected. Sensitivity of the instrument for the molecular ions of lower Cl-DBF was then enhanced by limiting the mass scan to roughly 170 to 290 a.m.u. and a third 200 mg sample was analyzed. The results were again negative for Cl-DBF. Mono-, di- and trichlorobiphenyls were the only halogenated species detected in the sample extracts. The reagent blank analyzed with this lot contained a barely detectable trace of dichlorobiphenyl. Another reagent blank was then prepared and was found to be free of halogenated materials.

Call for Slide 6. (flow chart of recycle experiment)

To investigate the possibility that the observed chlorinated dibenzofurans may be artifacts produced in the sample analytical

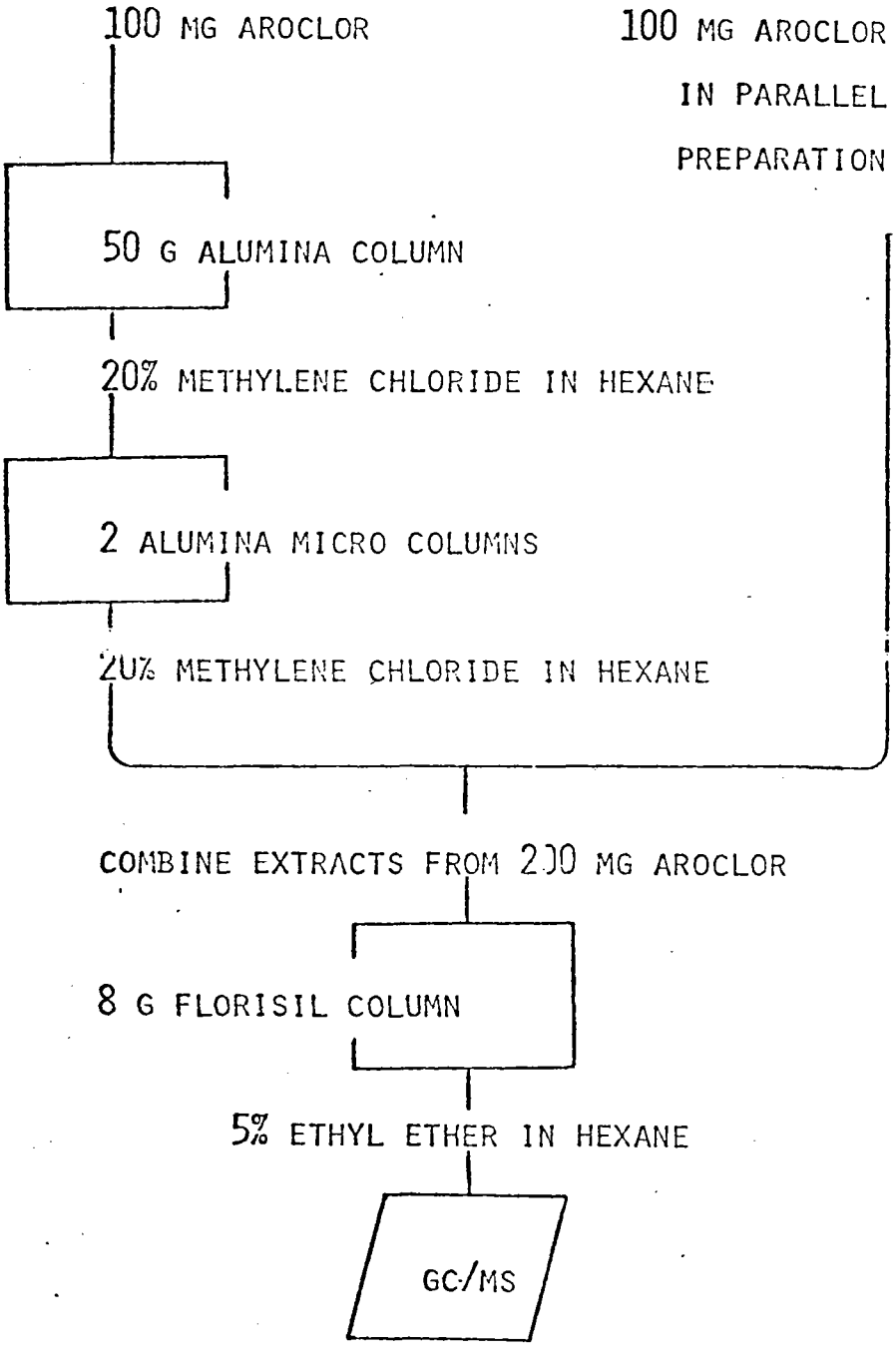
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procedure, duplicate experiments with Aroclor 1254 were carried out in which all eluates normally discarded in the procedure were retained and pooled. The pooled sample eluates were then concentrated and re-subjected to the sample preparation procedure. The original samples and the samples prepared from the pooled eluates were examined by combined gas chromatography/mass spectrometry on the same day under identical operating conditions. No chlorinated dibenzofurans were detected in the samples resulting from the pooled eluates that had been resubjected to the sample preparation procedure. If we had found a significant level of chlorinated dibenzofurans in the pooled samples, this would have suggested that the procedure itself was capable of making chlorinated dibenzofurans from one or more constituents of the sample.

In summary, we have shown the presence of chlorinated dibenzofurans as trace contaminants in recent production lots of Aroclor 1254, 1242, and 1016 but not in Aroclor 1221 when samples of comparable size were analyzed. No dibenzofurans were detected in reagent and equipment blanks run with the samples. The procedure itself does not appear to produce chlorinated dibenzofurans as an artifact of analysis.

The authors wish to acknowledge the technical assistance of Tom Lyon and Linda Laderach in the preparation of these samples for analysis.

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100 MG AROCLOR
100 MG AROCLOR IN PARALLEL PREPARATION
50 G ALUMINA COLUMN
20% METHYLENE CHLORIDE IN HEXANE
2 ALUMINA MICRO COLUMNS
20% METHYLENE CHLORIDE IN HEXANE
COMBINE EXTRACTS FROM 200 MG AROCLOR
8 G FLORISIL COLUMN
5% ETHYL ETHER IN HEXANE
GC/MS

DSW 338657

AROCLOR 1254 PRODUCTION DATE 10/73

SAMPLES ANALYZED: 6

SAMPLE SIZE: 200 MG

FOUND: TETRA- AND PENTACHLORODIBENZOFURANS

CHLORINATED NAPHTHALENES

DSW 338658

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AROCLOR 1242 PRODUCTION DATE 9/73

SAMPLES ANALYZED: 2

SAMPLE SIZE: 60.0 MG

FOUND: DI-, TRI-, AND TETRACHLORODIBENZO-FURANS

CHLORINATED NAPHTHALENES
TRICHLOROTERPHENYL
UNIDENTIFIED HALOGENATED COMPOUNDS

DSW 338659

STLCOPCB4082398

AROCLOR 1016 PRODUCTION DATE 10/73

SAMPLES ANALYZED: 2

SAMPLE SIZE: 200 M3

FOUND: DICHLORODIBENZOFURAN

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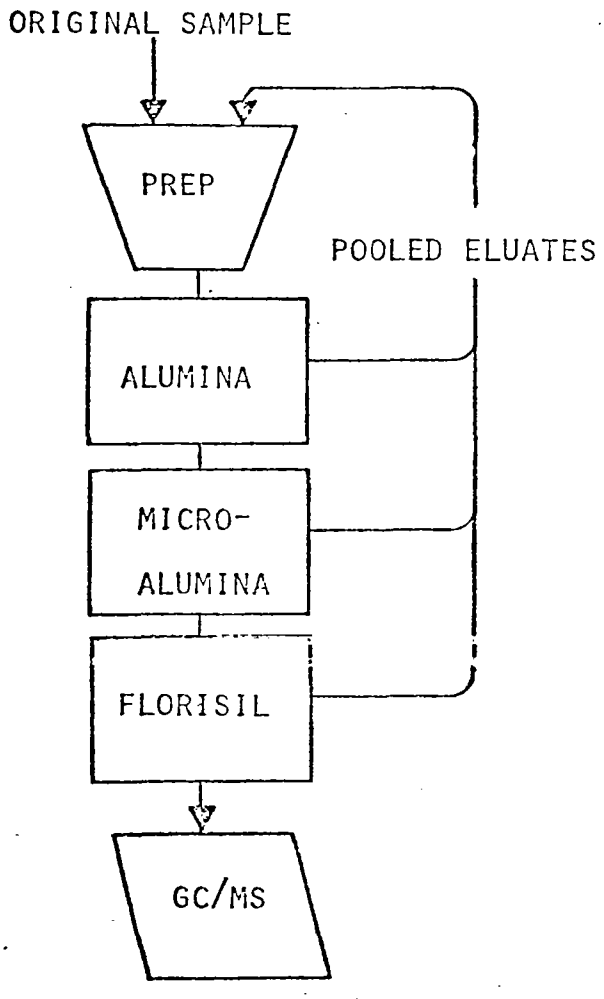
DSW 338661

AROCLOR 1221 PRODUCTION DATE 6/73

SAMPLES ANALYZED: 3

SAMPLE SIZE: 20.0 MG

NO CHLORINATED DIBENZOFURANS DETECTED


ORIGINAL SAMPLE
PREP
POOLED ELUATES
ALUMINA
MICRO-
ALUMINA
FLORISIL
GC/MS

DSW 338662