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Separation of Polychlorinated Biphenyls from DDT and Its Analogs Using Chromic Acid and Silica Gel

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The following method allows the pesticide residue chemist to separate and determine Polychlorinated Biphenyls (PCB's) in the presence of DDT and its analogs. P,P' DDE is treated with chromic acid to convert it to p,p' dichlorobenzophenone (MILES 1972) prior to separation on a silica gel column. Since other pesticides and/or industrial chemicals are usually present in residues containing DDT's, twenty-nine pesticides were eluted from the silica gel column to determine their elution pattern.

MATERIALS AND METHODS

Preparation of Reagents:

1. Silica Gel for absorption activation Grade I-ICN Pharmaceuticals, Inc. activate at 135°C for a minimum of 12 h.
2. Chromic Acid-dissolve 10 g in 6 mL water with heat, cool and add 120 mL glacial acetic acid.
3. Anhydrous Sodium Sulfate-heat in a muffle at 475°C for a minimum of 4 h and store in a glass container.

Apparatus:

1. Glass micro column with stop-cock, 10 mm I.D. 300 mm length.
2. 250 mL Kuderna Danish (K-D) concentrator Kontes ₹ 24/40 inner joint and ₹ 19/22 outer joint.
3. Snyder condenser Kontes ₹ 19/22.
4. 5 mL tip Kontes ₹ 19/22.
5. Tracor 222 gas chromatograph or equivalent with an electron capture detector.

Procedure: #1 Chromic Acid Conversion of p,p' DDE

P,P' DDE must be calculated before conversion. Transfer eluate (petroleum ether or hexane) from florisil column cleanup (HORWITZ 1975) containing PCB's and the DDT's to a 125 mL separator (total volume of eluate and rinse not to exceed 3 mL). Add 5 mL of chromic acid reagent, shake separator 2 min for each ug of p,p' DDE present in the separator.

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Add 20 mL water, shake 30 seconds, let separate, drain chromic acid-water into a 2nd 125 mL separator containing 20 mL hexane, shake 1 min and discard chromic acid-water layer. To the 1st separator, again add 5 mL chromic acid reagent, shake 2 min, add 20 mL water, shake 10 seconds, add 20 mL hexane and shake 1 min. Transfer chromic acid-water layer to the 2nd separator and shake 1 min, discard chromic acid-water layer. Add 20 mL water to the 1st separator, shake 10 seconds, let separate, drain water into 2nd separator, shake 10 seconds, let separate and discard water. Add 20 mL water to the 1st separator and repeat above step. Combine hexane in 2nd separator with hexane in 1st separator.

Prepare a funnel by placing a glass wool plug in the stem and adding 30 g of anhydrous sodium sulfate, rinsing sodium sulfate with 25 mL hexane. Drain the combined hexane from the separator through the sodium sulfate into a K-D equipped with a 5 mL tip, rinse separator with two separate 25 mL portions of hexane, draining each through the sodium sulfate. Evaporate hexane to appropriate volume and inject on GLC. The peak with the same retention time as p,p' DDE must be calculated as p,p' DDE and subtracted from the original calculation. The remainder will be the amount of p,p' DDE present in the eluate. Set aside for silica gel separation.

Procedure #2 Silica Gel Separation

Prepare a column by placing a glass wool plug in the bottom of the column to hold the silica gel. Remove the silica gel from the oven and weigh 4 g and transfer it to the column, pack by tapping. Place ca 5 mm of sodium sulfate on top of the silica gel, let cool for 15 min, pre-wet with 15 mL hexane. Place a 250 mL K-D equipped with a 5 mL tip under the column to receive the first fraction. Transfer the hexane containing the converted p,p' DDE to the column letting all of the hexane enter the silica gel. Wash the tip with two 5 mL portions of 0.5% benzene/hexane v/v, letting each wash enter the silica gel before adding next wash, then elute with 35 mL 0.5% benzene/hexane. Remove the K-D and replace with a 2nd K-D similarly equipped and elute the 2nd fraction with 55 mL 0.5% benzene/hexane. Remove the K-D and replace with a 3rd K-D similarly equipped and elute the 3rd fraction with 25 mL 4% ethyl acetate/benzene v/v. Evaporate the eluates to the desired volume for injection on GLC.

RESULTS

TABLE 1

Recovery Data and Elution Pattern of Twenty-Nine Pesticides Using Procedure #2

Pesticides	Fract. 1	Fract. 2	Fract. 3	Total Recovery
CIPC	-	-	82%	82%
Lindane	-	-	74%	74%
Heptachlor	78%	-	-	78%
Aldrin	88%	-	-	88%
Hept. Epox.	-	-	90%	90%
Dieldrin	-	--	96%	96%
Endrin	-	-	-	Zero
Diazinon	-	-	-	Zero
Parathion	-	-	72%	72%
Ethion	-	-	62%	62%
TCNB	12%	80%	-	92%
PCNB	86%	-	-	86%
Dicofol	-	-	62%	62%
p,p' DDT	-	102%	-	102%
Methoxychlor	-	-	105%	105%
Malathion	-	-	60%	60%
alpha BHC	-	-	97%	97%
p,p' DDE	100%	-	-	100%
p,p' TDE	-	-	103%	103%
Methyl Parathion	-	-	68%	68%
Carbophenothion	-	-	-	Zero
Dichloran	-	-	80%	80%
Dacthal	-	-	82%	82%
Endosulfan I	-	-	95%	95%
Endosulfan II	-	-	83%	83%
O,P DDT	19%	55%	-	74%
Endosulfan Sulfate	-	-	102%	102%
Tetradifon	-	-	86%	86%
Mirex	92%	-	-	92%

TABLE 2

Recovery Data Using Procedure #1 & 2

Pesticide	Recovered	Added	% Recovered
Aroclor 1248	2.72 ug	3.0 ug	91
p,p' DDE	2.84 ug	3.0 ug	95
O,P DDT	0.94 ug	1.0 ug	94
p,p' DDT	0.91 ug	1.0 ug	91
p,p' TDE	1.07 ug	1.0 ug	107

A trace of O,P DDT eluted in the aroclor fraction.

DISCUSSION

The conversion of p,p' DDE to p,p' dichlorobenzophenone will be incomplete if fat or oil is present in the eluate. An excellent cleanup for extracts containing fats or oils is Gel Permeation Chromatography (GPC) (GRIFFITT 1974), followed by florisil (HORWITZ 1975). Extracts containing fats or oils cleaned up on GPC will have a minimum amount of fat or oil in the eluate, and will cause little if any interference in the conversion of p,p' DDE.

Heat was tried to facilitate the conversion of p,p' DDE (MILES 1972) and it was found that chromic acid acted upon PCB and diminished its recovery. The conversion carried out as outlined in this paper gave excellent results.

Fraction #1 from the silica gel separation will contain the PCB's. Fraction #2 will contain p,p' DDT, and O,P DDT. Fraction #3 will contain p,p' dichlorobenzephenone and p,p' TDE. The conversion of p,p' DDE to p,p' dichlorobenzophenone is not quantitative, therefore DDE present in the eluate cannot be calculated from the conversion product. Any PCB peaks which fall under p,p' DDE on the GLC chromatogram must be calculated as DDE and subtracted from the original DDE calculation.

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REFERENCES

MILES, J.R.W.: J. Assoc. Offic. Anal. Chem. 55, 1039 (1972).

HORWITZ, W. (Ed.) Offic. Methods of Analysis, 12th Ed., Assoc. of Off. Anal. Chem. Wash., D.C. 29.015 (1975).

GRIFFITT, K.R. and CRAUN, J.C.: J. Assoc. Off. Anal. Chem. 57, 168 (1974).