determinations.

SUMMARY

Residues of dinoseb have been determined in many substrates to a lower limit of sensitivity of 0.05 ppm. Recovery experiments have been performed validating the method in nearly every crop for which there is an established EPA tolerance. An average percent recovery in the high 80's can be expected from the method when performed by a qualified analyst. Utilizing adsorption onto alumina and the selectivity and sensitivity of the electron-capture detector, quantities of 20 pg of dinoseb methyl ether and less have been quantitated in the presence of substrate extract.

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Routine Determination of Mirex and Photomirex in Fish Tissue in the Presence of Polychlorinated Biphenyls

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A procedure for the routine determination of mirex and photomirex in fish tissue is described which provides rapid analysis and confirmation using conventional gas chromatographic/electron capture detection (GC/ECD) methods. Coeluting intereferences (i.e., polychlorobiphenyls, PCB's) are nitrated allowing for simple separation from mirex analogue by column chromatography. In chinook salmon tissue (*Oncorhynchus tshawytscha*), PCB removal averaged 78% and mirex and photomirex recoveries were 91 and 86%, respectively. The method has been used successfully for trace analysis of mirex levels as low as 100 pg.

The pesticide chemical mirex was first discovered in fishes from Lake Ontario by Kaiser (1974). His discovery of mirex (dodecachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalene) was based on computerized mass spectral analysis indicating the presence of a *m/e* 272 $[C_5Cl_6]^+$ ion, an ion not seen in polychlorobiphenyl (PCB) mass spectral fragmentation patterns. Kaiser's work indicated that conventional gas chromatographic/electron capture detection (GC/ECD) analysis of fish samples gave misleading results with respect to trace contaminants because PCB's and mirex have overlapping retention times. Many laboratories had probably been misinterpreting mirex as a part of a PCB isomer peak. Similar situations had occurred previously with PCB interference in GC/ECD analyses of dichlorodiphenyltrichloroethane (DDT) and other related chlorinated pesticides (Reynolds, 1969; Bonelli, 1971; Gustafson, 1970).

The discovery of mirex in Lake Ontario stimulated research by various academic groups and regulatory agencies. Several analytical methologies for GC/ECD analysis of mirex were developed; many were modeled on PCB/chlorinated pesticide column chromatographic separation techniques (Reynolds, 1969; Armour and Burke, 1970; Holden and Marsden, 1969). Although high yields and separation efficiencies were reported for these methods, the procedures were not entirely satisfactory. Reproducibility was difficult to maintain in both adsorbent and solvent systems (Berg et al., 1972; Holdrinet, 1974; Task Force on Mirex, 1977).

Further analytical complications arose with the discovery in fish tissue of a new group of degradation products of mirex (Hallett et al., 1976). Photomirex (8-monohydromirex), with concentrations as high as 50% of the reported mirex values (TFM 1977), also coelutes with PCB's, making analysis by conventional GC/ECD techniques difficult.

A simple analytical procedure for separating mirex and photomirex from PCB's is needed for rapid routine assessment of the environmental impact of these persistent pesticides. Initially, our objective was to determine the concentrations of mirex in Lake Ontario fish and to determine where mirex accumulates within the fish. To accomplish this, we developed and report on a routine analytical procedure for mirex and photomirex. Also, our preliminary results on pesticide distribution within fish are presented.

One general approach to the problem of separating mirex and photomirex from PCB's is to chemically alter the PCB's by perchlorination or nitration and change their chromatographic behavior. Perchlorination converts all PCB isomers to the decachlorobiphenyl isomer by means of antimony pentachloride. In routine GC analyses, decachlorobiphenyl elutes sufficiently beyond mirex, thereby yielding adequate separation. The second type, nitration,

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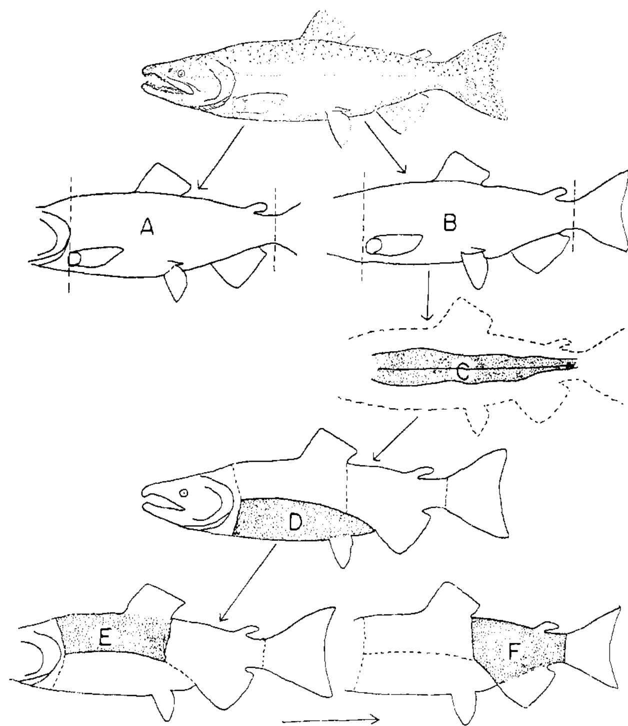

Figure 1. Tissue sections analyzed for mirex and photomirex: (A) the whole fillet, (B) the skin only, (C) the "red muscle" (*Muscle lateralis superficialis*), (D) the belly flap, (E) the anterior dorsal loin, and (F) the caudal peduncle.

converts PCB's to nitrated PCB's (hydrogen replacements) with fuming nitric acid. The nitrated PCB's are then separated from mirex by means of column chromatography.

The perchlorination method was developed by Armour (1973) from work originally presented by Berg et al. (1972). Hallett et al. (1976) has used a perchlorination technique for the analysis of tissue samples. It is claimed that this method has the strong advantage of PCB removal for mirex analysis and total PCB quantitation with high recoveries for both (99 ± 0.5% at ppm levels). However, the results of perchlorinating mixtures known to contain photomirex have not yet been reported. If photomirex is perchlorinated under the conditions reported, the amounts of mirex using this method may be misleadingly high.

A nitration procedure for use with tissue samples has been developed by Norstrom et al. (1978). Unlike perchlorination, total PCB's can not be quantitated. However, no confusion concerning chlorination of photomirex surrounds this method. We have modified Norstrom's (1978) procedures for our use.

EXPERIMENTAL SECTION

Chinook salmon (*Oncorhynchus tshawytscha*) collected from Lake Ontario were filleted into six predefined tissue sections based on the types and amounts of fat present in the fish. The tissue sections were (A) the whole fillet, (B) the skin, (c) the "red muscle" (*Muscle lateralis superficialis*), (D) the belly flap, (E) the anterior dorsal loin, and (F) the caudal peduncle (Figure 1). A total of 18 tissue samples were analyzed (three samples per tissue section).

Each tissue section was ground and mixed throughly in an Intedge food processor. A 5-g aliquot was mixed with 20 g of anhydrous sodium sulfate and ground to a homogeneous mixture using a Virtis "45" tissue homogenizer. The contents were packed into an extraction thimble and extracted overnight (a minimum of 200 Soxhlet cycles) in a Soxhlet extraction apparatus with 75 mL of a solvent mixture containing 20% methylene chloride and 80% hexane (20:80 solvent mixture). The 20:80 solvent mixture was used because it gave partitioning coefficients of ~1.0 (Calway, 1977) as opposed to 0.87 for hexane and 0.89 for benzene (Norstrom 1977).

A 15-mL aliquot of the extraction solvent was concentrated to ~1 mL in a 50-mL graduated centrifuge tube under nitrogen. The tube walls were then washed with 5 mL of the 20:80 solvent mixture and again concentrated to ~1 mL. The 1-mL sample and two subsequent 1-mL rinses of the tube with the 20:80 solvent mixture were placed on a Florisil column for cleanup.

Florisil columns were constructed using 1-cm (i.d.) burets cut to ~25 cm in length. Columns were plugged initially with glass wool and topped with a thin layer of sand. Five grams of Florisil (60–100 mesh, ranging from 1.5–2.5% water by weight) was slurried in 100 mL of 20:80 solvent mixture inside a 500-mL dropping funnel before column packing. This procedure made column packing convenient and hastened adsorbent/solvent equilibration. The slurry was added to a partially filled solvent column (stopcock open) and tapped gently to promote even packing. The column was topped with ~1.5 cm of anhydrous sodium sulfate. This procedure routinely gave a uniform packing.

The 20:80 solvent mixture was used to elute the sample into 50-mL graduated centrifuge tubes. With an elution rate of ~4 mL/min, a total of 50 mL was collected. Depending on the elution rate, the final volume collected should be adjusted for maximum recovery of the pesticide of interest (i.e., mirex, photomirex, or mirex and photomirex together). More information on this is presented in the Results section. The eluate was slowly evaporated to dryness under nitrogen, the tube walls washed with 5 mL of the 20:80 solvent mixture, and again evaporated to dryness.

A nitration procedure was used to reduce interfering PCB's. The method is similar to that described by Norstrom (1977) but differs in sample/reagent amounts and the type of adsorbent used for separation. These changes facilitated handling and resulted in increased recoveries. Nitration reagent was prepared from 90% red fuming nitric acid and concentrated sulfuric acid as a 1:1 mixture. Five milliliters of the nitration reagent was added to the sample tube and the tube was stoppered. After swirling to thoroughly coat the tube walls, the sample tube was placed in a water bath at 70 °C for 30 min. The tube was then removed and cooled in ice. *Carefully*, 10 mL of high-purity distilled water was added and the sample vortexed to insure homogeneity. This deliberate reverse order of adding water to an acid reduces sample loss by transfer and is safe *if* the sample is iced and water is added slowly. The tube was allowed to come to room temperature, and 10 mL of the 20:80 mixture was added. After vortexing for a minimum of 30 s, the emulsion was allowed to separate, and exactly 5 mL of the solvent layer was removed into a 15-mL graduated centrifuge tube. The solvent was *completely* evaporated under nitrogen, and the tube was washed with 5 mL of hexane only. The sample was concentrated to ~1 mL under nitrogen. It is important that all the methylene chloride from the 20:80 solvent mixture be removed prior to Florisil separation. We have found that small amounts of methylene chloride will cause the nitrated PCB's to elute prematurely from the column with the mirex analogues. A similar situation also occurs with the alumina column separation (Norstrom, 1977).

Florisil "micro" columns were prepared to separate the nitrated PCB's from the mirex analogues. Short-barrelled

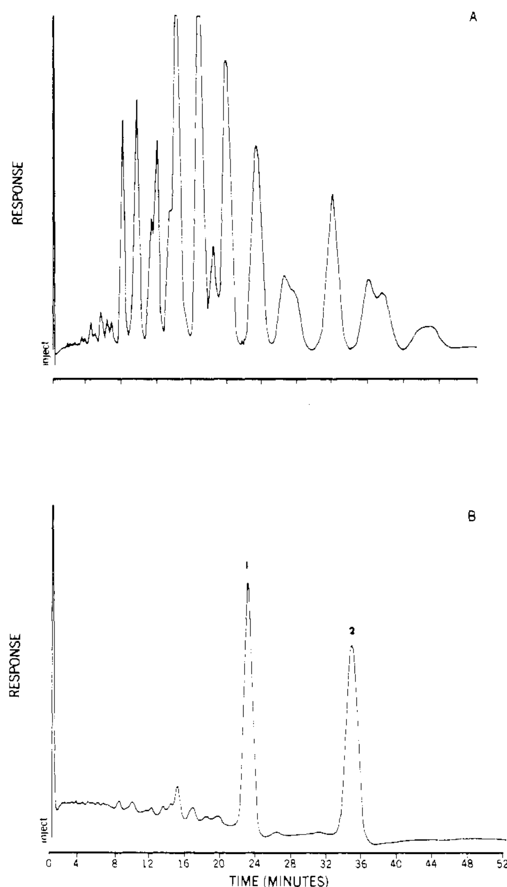

Figure 2. Gas chromatograms of standard test mixture (group II) before (A, 2-μL injection) and after (B, 10-μL injection) nitration. 1 and 2 indicate the photomirex and mirex peaks, respectively.

Pasteur pipets were plugged with glass wool and packed with an unactivated Florisil/hexane slurry to a length of ~5 cm. To insure uniformity we used a 1-mL syringe to pack the Florisil slurry (60–100 mesh). Microcolumns were topped with ~1 cm of anhydrous sodium sulfate and stored in hexane until used.

The 1-mL hexane sample was added to the column, followed by two 1-mL hexane "washes" of the tube. A total of 15–20 mL of the hexane eluate was collected in a 50-mL graduated centrifuge tube. Again the volume eluted should be adjusted for maximum recovery of the pesticide of interest (i.e., mirex, photomirex, or mirex and photomirex together). Beyond 20 mL, there is a strong tendency for the nitrated PCB's to elute from the column. The sample was concentrated under nitrogen to a final volume of exactly 1 mL and is ready for GC analysis. With columns prepared in advance, sample processing time can be shortened to ~4–6 h after extraction.

A Hewlett-Packard 5750-B Research gas chromatograph, equipped with a high-temperature ^{63}Ni pulsed electron-capture detector, was used to analyze samples. The primary column used was a 4 ft × $^1/_8$ in. glass packed with 3.8% UCW-982 on 80/100 Chromosorb W.H.P. An alternate column consisting of 6 ft × $^1/_8$ in. stainless steel packed with 4% SE-30 on 60/80 Chromosorb W-AW was also used. Operating parameters were as follows: pulse interval, 50 μs; carrier gas and purge gas, 95% argon–5% methane at 25 and 50 mL/min, respectively; injection port temperature, 210 °C; column temperature, 200 °C; and detector temperature, 230 °C. Retention times for photomirex and mirex were 23 and 35 min, respectively. GC peak areas were determined by polar planimetry. Mirex, arochlor 1254, and arochlor 1260 standards were obtained from Chem Services. Photomirex standard was prepared by the Mississippi State Chemical Laboratory, Mississippi State, MS.

Table I. Effects of Heating Duration on Nitration and Recovery Efficiencies for Mirex and Photomirex (Combined) between Test Groups I and II (Three Determinations (n = 3) Were Made for Each Treatment)

	x ± SE		
	heating duration		
	30 min	8 h	16 h
nitration efficiency, %			
group I	96 ± 0	97 ± 0	98 ± 0
group II	96 ± 0	97 ± 0	98 ± 0
	97 ± 0.4% ($\bar{x}$ ± SE)		
recovery efficiency, %			
group I	95 ± 1.0	95 ± 2.1	95 ± 0.6
group II	94 ± 2.0	95 ± 0.6	95 ± 1.5
	95 ± 0.2% ($\bar{x}$ ± SE)		

Table II. Initial and Improved Nitration Efficiencies from Different Tissue Samples (Three Determinations (n = 3) Were Made for Each Treatment)

	$\bar{x}$ ± SE, %	
tissue section	initial	improved
whole fillet	59 ± 0.9	77 ± 0.3
skin	47 ± 0.7	73 ± 1.2
red muscle (*Muscle lateralis superficialis*)	55 ± 2.2	74 ± 0.3
belly flap	53 ± 1.7	78 ± 0.6
anterior dorsal loin	75 ± 1.5	86 ± 0.7
caudal peduncle	71 ± 0.3	82 ± 0.6
($\bar{x}$ ± SE)	60 ± 4.4	78 ± 2.0

RESULTS

We define nitration efficiency as the reduction in PCB peak size of a sample after nitration expressed as percent of the PCB peak size before nitration. To evaluate the removal of interfering PCB peaks by the nitration procedure, we analyzed salmon tissue and a series of test mixtures containing mirex, photomirex, and PCB standards. The two test mixtures established were as follows: group I (25 μg of arochlor 1254, 25 μg of arochlor 1260, 2 μg of photomirex, and 2 μg of mirex) and group II (50 μg, 50 μg, 4 μg, and 4 μg). For test mixtures I and II, the nitration efficiency averaged 97 ± 0.4% ($\bar{x}$ ± SE), indicating a 97% reduction in PCB peak size (Figure 2).

The effect of the length of the heating period during nitration on the text mixtures was evaluated by adjusting the duration of heating time from 30 min to 8 h and later to 16 h. No significant changes in peak resolution, retention time, nitration efficiencies, or recoveries of mirex or photomirex were evident between test mixtures I and II (Table I). With the 8- and 16-h heating times, no nitration of photomirex occurred. Photomirex is apparently treated as an alkane and does not undergo electrophilic aromatic substitution.

In the salmon tissue, nitration efficiency decreased with samples of high oil content (i.e., skin > belly flap > red muscle). To alleviate this problem, larger amounts of Florisil were initially used for column chromatography. However, the larger amounts of Florisil caused handling problems.

Kates (1972) notes that solvent elution rate is critical for proper column performance. By reducing the amount of Florisil back to the initial 5 g and maintaining the elution rate at ~4 mL/min, improved precision and increased nitration efficiencies (70 ± 2.0%) for these oily

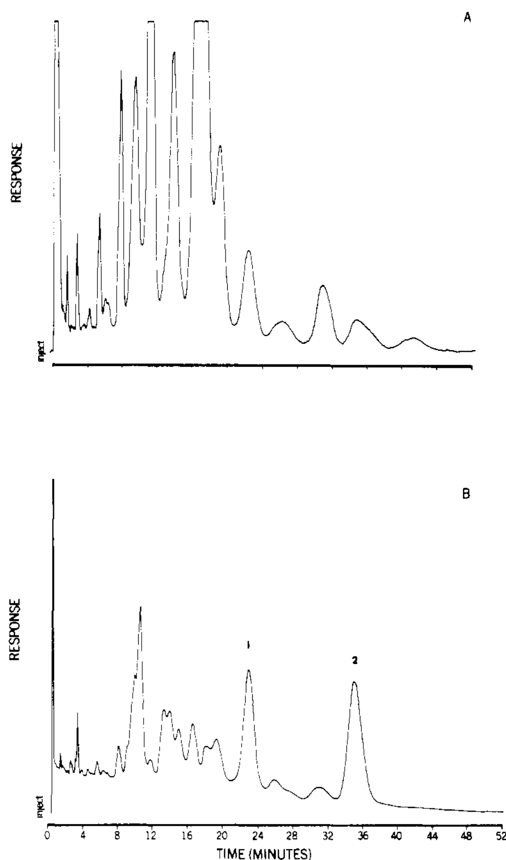

Figure 3. Gas chromatograms of salmon tissue (1 g) with Florisil split (A, 2-μL injection) and with Florisil split plus nitration (B, 15-μL injection). 1 and 2 indicate the photomirex and mirex peaks, respectively.

samples were achieved (Table II). Although the nitration was not as efficient as in the test standards, the procedure allowed for more than adequate removal of PCB's in the tissue samples (Figure 3).

Recovery efficiencies were calculated for the standard test mixture and fish tissue by spiking in the following manner. Standard test mixtures were concentrated under nitrogen in the reaction tubes. These mixtures were nitrated and analyzed as described in the Methods section. Using a microsyringe, we spiked the fish tissues by injecting a standard directly into the tissue sample while the tissue was in the homogenizer cup. After 5 min, the sample was ground and analyzed by the procedure described in the Methods section. Rinse blanks of the empty homogenizer cup after grinding indicated that no detectable amounts of the spike were present. The recovery of mirex and photomirex added before the initial Florisil column cleanup was 95 ± 0.2% ($\bar{x}$ ± SE); n = 9 for group I and group II, total of 18.

Recovery efficiencies for "spiked" tuna fish (packed in oil) in tissue samples were lower than those for standard test mixtures. Mirex averaged 91 ± 0.8% as compared to 95 ± 0.2% for the test mixtures. Photomirex recoveries were initially low, 62 ± 1.3%. This low recovery rate appears to be associated again with the Florisil lipid cleanup. During column cleanup, mirex repeatedly eluted completely within the first 20–30 mL. Photomirex would begin to elute in the 30–40-mL fraction and would sometimes require up to 100 mL of solvent to elute completely. When the elution rate was optimized at 4 mL/min, photomirex recoveries were increased to 85 ± 3.1% and both mirex and photomirex were completely eluted within 50 mL (Table III). In the Experimental Section, we recommend an elution rate of ~4 mL/min.

Table III. Initial Photomirex and Improved Photomirex and Mirex Recovery Efficiencies for Different Tissue Samples (Three Determinations (n = 3) Were Made for Each Treatment)

	$\bar{x}$ ± SE, %		
tissue section	initial photomirex	improved photomirex	improved mirex
whole fillet	59 ± 1.4	85 ± 1.2	91 ± 0.3
skin	66 ± 1.7	86 ± 2.3	88 ± 0.9
red muscle (*Muscle lateralis superficialis*)	59 ± 3.3	85 ± 1.8	93 ± 1.2
belly flap	64 ± 2.3	84 ± 1.2	94 ± 1.4
anterior dorsal loin	59 ± 0.9	86 ± 0.3	91 ± 1.5
caudal peduncle	64 ± 1.7	85 ± 0.6	91 ± 0.6
($\bar{x}$ ± SE)	62 ± 1.3	85 ± 3.1	91 ± 0.8

Table IV. Preliminary Tissue Distribution Data of Mirex and Photomirex in Chinook Salmon [Three Samples Were Analyzed (Two Females, One Male; All Immature)][a]

	corrected concn, mg/kg	
	mirex ($\bar{x}$ ± SE)	photomirex ($\bar{x}$ ± SE)
whole fillet	0.22 ± 0.03	0.13 ± 0.01
skin	0.23 ± 0.04	0.14 ± 0.02
red muscle (*Muscle lateralis superficialis*)	0.17 ± 0.01	0.05 ± 0.00
belly flap	0.22 ± 0.02	0.14 ± 0.03
anterior dorsal loin	0.10 ± 0.01	0.05 ± 0.00
caudal peduncle	0.09 ± 0.00	0.05 ± 0.00
($\bar{x}$ ± SE)	0.17 ± 0.02	0.09 ± 0.02

[a] Length, 47.5 ± 0.5 cm ($\bar{x}$ ± SD); weight, 1.231 ± 0.08 kg ($\bar{x}$ ± SD).

DISCUSSION

The method described in this paper provides for the routine tissue analysis of mirex and photomirex in the presence of high levels of PCB's. The relative ease of analysis, simplistic design, and quantitation of mirex and photomirex without sophisticated instrumentation make this procedure attractive. Although quantitation of PCB's is not possible, the method does offer high sensitivity for mirex and photomirex. In our laboratory, the procedure has been capable of quantitating mirex at levels as low as 100 pg.

Our preliminary results of mirex and photomirex distribution in various tissues of salmon are given in Table IV. Mirex levels are similar in the whole fillet, skin, red muscle, and belly flap. Mirex levels in the anterior dorsal loin and caudal peduncle are comparable but are half the levels seen in the other tissue sections.

Photomirex levels mimic the mirex distribution in that photomirex concentrations in the whole fillet, skin, and belly flaps are similar. However, concentrations in the red muscle are low, with levels similar to those seen in the anterior dorsal loin and caudal peduncle. The significance of this result is not fully understood at this time.

Our results suggest that the recommendation made by state and federal agencies (N.Y.S. Department of Environmental Conservation 1978; Duttweiler and Voiland, 1979) on dressing of salmonids to reduce mirex intake in humans consuming fish is correct. However, our results represent only spring fish and are of a preliminary nature.

Much is already known about mirex's entry and accumulation in the lake, toxicity, and persistency. The occurrence of photomirex in high concentrations (Hallett et al., 1976; TFM 1977, Table IV) within lake biota is of interest, especially since it is more toxic than mirex (Hallett

et al., 1978; Villeneuve et al., 1979). Since mirex is known to photolyze to photomirex in the environment (Carlson et al., 1976; Ivie et al., 1974), it is possible that photomirex levels may be increasing in the environment. However, no data are currently available to dismiss or substantiate this hypothesis. Furthermore, the chemical pathway and site of conversion of mirex into photomirex into the lake ecosystem is poorly understood. Trophic level studies of mirex and photomirex in the Lake Ontario ecosystem could provide valuable additional insight into organochlorine pesticide kinetics.

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Potential Interference by Free Fatty Acids in the Gas–Liquid Chromatographic Analysis of Rice Bran for Pesticide Residues Using Electron Capture, Potassium Chloride Thermionic, and Hall Electrolytic Conductivity Detectors

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Free fatty acids were found to be potential interferences in the gas–liquid chromatographic (GLC) determinative step when rice bran was analyzed for pesticide residues using the multiresidue analytical procedure for fatty food in the Food and Drug Administration Pesticide Analytical Manual. Oil was extracted from the rice bran and cleaned up by petroleum ether–acetonitrile partitioning and Florisil column chromatography. The residues were determined by GLC. Chromatographic peaks encountered with electron capture, potassium chloride thermionic, and Hall electrolytic conductivity detectors were identified as palmitic acid, oleic acid, and linoleic acid. The oil extracted from the rice bran contained an unusually high quantity of free fatty acids, 54.4% as oleic acid. Cleanup of rice bran oil using petroleum ether–acetonitrile partitioning and Florisil column chromatography failed to separate the fatty acids from possible pesticide residues. The GLC response factor for several free fatty acids and their methyl esters was determined using electron capture, potassium chloride thermionic, and Hall electrolytic conductivity detectors.

The development of sensitive, selective detectors promoted the application of gas–liquid chromatography (GLC) to the determination of pesticide residues. The electron capture detector (ECD) (Lovelock, 1957) has been widely used for the measurement of trace amounts of organochlorine pesticide residues in complex environmental samples. The potassium chloride thermionic detector (KCl-TD) was introduced as a sensitive and selective detector for the determination of organophosphorus pesticide residues by Giuffrida (1964). The Hall electrolytic conductivity detector (HECD) is highly selective for either chlorine, bromine, iodine, sulfur, or nitrogen, depending upon the detector's mode of operation (Hall, 1976).

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