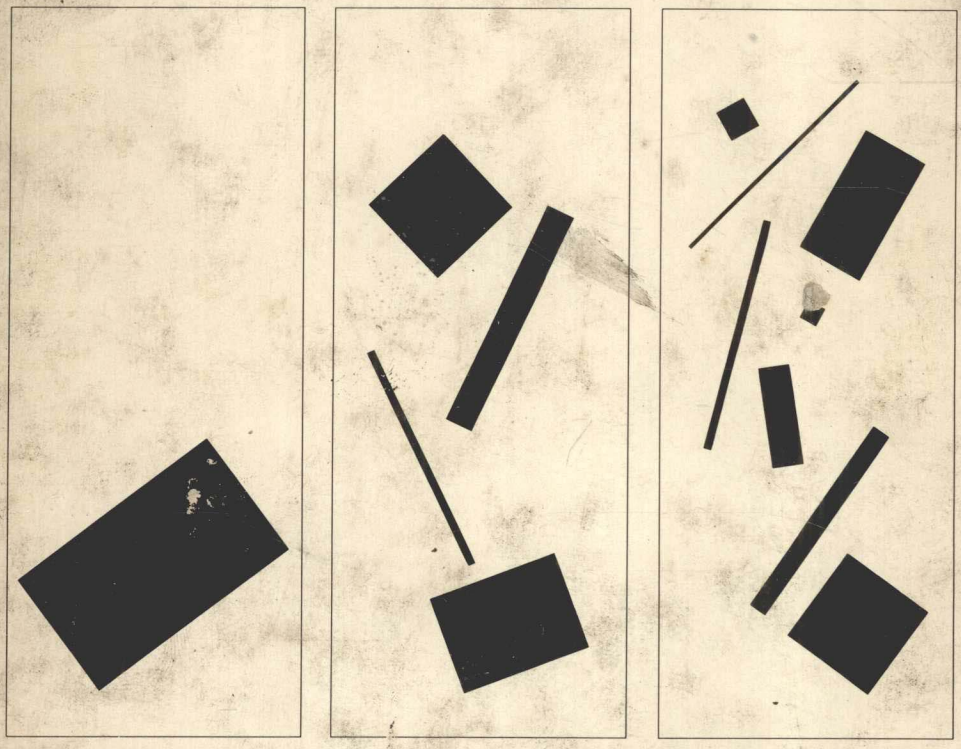
Chemical Derivatization in Analytical Chemistry

Volume 1: Chromatography



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Chemical Derivatization in Analytical Chemistry

Volume 1: Chromatography

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Chemical Derivatization in Analytical Chemistry

Volume 1: Chromatography

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Edited by R. W. Frei and J. F. Lawrence

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Preface

The first volume in this series is devoted to derivatization techniques in chromatography, for very obvious reasons. In gas chromatography (GC) chemical derivatization as an aid to expand the usefulness of the technique has been known for more than a decade and has become an established approach.

The first chapter deals to a great extent with derivatization for the purpose of making compounds amenable to GC. Although the discussion concentrates on pesticides, some generally valid conclusions can be drawn from this chapter. Chemistry will not be limited to the separation—it can also have a pronounced impact on the sample cleanup, another topic covered in Chapter 1.

Since the introduction of coupled GC–mass spectroscopy (GC–MS), a very powerful tool, derivatization techniques have taken still another direction—taking into consideration chromatographic as well as mass spectrometric improvement of the compounds of interest. Cyclic boronates are discussed as derivatization reagents for this purpose in the second chapter.

Chemical derivatization in liquid chromatography (LC) is a somewhat younger branch. In principle, one differentiates between prechromatographic and postchromatographic (precolumn and postcolumn) techniques. The former has now gained a status comparable to derivatization in GC. The third chapter deals with this aspect. The various possibilities for reacting different groups of compounds are critically discussed and a few examples are given, usually from the pharmaceutical area; but the chapter is by no means restricted to pharmaceuticals. The treatment of the subject in Chapter 3 permits extrapolation into any analytical area in need of derivatization procedures. Also discussed are optical isomers and ion pair formation.

The fourth and final chapter deals with postcolumn reaction detectors in LC. This is no doubt one of the newest lines in the field of derivatization, but it is currently undergoing very rapid development. This chapter gives a comprehensive survey of the state-of-the-art of reaction detectors, including theoretical aspects, a discussion of tubular reactors with segmented and nonsegmented streams, and bed reactors. The technical aspects are grouped according to detection modes (fluorescence, uv–visible) and information on application possibilities are given. Finally, a critical assessment of development potential and trends (i.e., coupling to other detection modes, column switching, automation, etc.) is presented.

The selection of areas and the manner and level of treatment of fundamental and applied aspects should render this book of interest to analytical chemists and investigators in many fields where chromatography is used, e.g., in pharmaceutical, environmental, medicinal, agricultural, and biochemical disciplines.

R.W. Frei
J.F. Lawrence

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Chapter 1

Chemical Derivatization in Pesticide Analysis

W. P. Cochrane

1. INTRODUCTION

Many approaches have been used in the identification and determination of pesticides at both the macro- (formulations) and micro- (residues) levels in various substrates. A number of the more commonly used methods of analysis are shown in Table 1 and the range of techniques used gives an indication of the difficulties encountered by the pesticide analyst. Traditionally, chemical derivatization has played an integral part in the analysis of pesticides since the widespread use of the organochlorine (OC) insecticides and herbicides in the 1940s. In 1955 Gunther and Blinn published *Analysis of Insecticides and Acaracides*, which gave detailed formulation and residue procedures for about 90 inorganic and organic compounds used in current pest control practices.[1] Of the 15 or so organochlorine insecticides discussed, many of the formulation procedures employed a total chlorine method while others utilized specific reactions to produce colored compounds. While DDT formulations could be determined via total chlorine, DDT residues were analyzed by the Schechter–Haller method involving nitration to a tetranitro derivative which produced a colored compound on

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TABLE 1. Methods Used in the Identification of Pesticides

1. Instrumental methods
   - Spectral techniques — infrared, uv, visible, mass, NMR
   - Paper and thin-layer chromatography
   - Gas–liquid chromatography — multiple column and detector systems
   - Neutron activation analysis
2. Microchemical methods
   - Chemical and photochemical conversion of pesticides into derivatives
3. Biological assay methods
   - Enzymatic
   - Immunological
   - Phytotoxicity, etc.
4. Partition methods
   - Liquid–liquid — p values
   - Liquid–solid — column chromatography

treatment with alcoholic sodium methoxide. An alternate method was the dehydrochlorination of DDT to DDE and uv quantitation which was similar to the recommended residue method for methoxychlor. Again for the 15 organophosphorus (OP) insecticides included, colorimetry or spectrophotometry was generally the method of choice although enzymatic methods were also recommended. Diazinon, described at that time as a promising new insecticide, was hydrolyzed with alcoholic KOH to 2-isopropyl-4-methyl-6-hydroxypyrimidone which was quantitated by uv at 272 nm. No carbamate or herbicidal compounds were covered in this early book; these pesticides together with plant growth regulators and food additives were subsequently included in the multivolume series started by Zweig in 1964.[2] Again different chemical reactions were used for formulation and residue analysis. For example, the recommended formulation method for carbaryl was alkaline hydrolysis to 1-naphthol and methylamine with volumetric determination of the methylamine. For carbaryl residues the 1-naphthol produced was coupled with p-nitrobenzenediazonium fluoroborate then quantitated at 590 nm. By today's standards these methods appear rather crude. However, with the introduction of gas chromatography (GC) in the 1950s many organic compounds were qualitatively and quantitatively analyzed intact by this procedure without further alteration. The application of GC to pesticide formulation and residue analysis was not successfully

used before 1960 primarily due to the lack of the selectivity of the then available detection systems. The microcoulometric[3] and ^{3}H-electron capture detectors[4] were both reported in 1960–1961 and became commercially available within the following few years. These detectors were quickly followed by the alkali flame ionization (1964), electrolytic conductivity (1965), and flame photometric (1966) detectors which displayed varying degrees of selectivity and sensitivity to N-, P-, S-, or halogen-containing compounds. They were immediately utilized in the pharmaceutical and pesticide fields of residue analysis and to verify product integrity. By 1967, the GC operating parameters for approximately 50 pesticides had been established.[5] In addition, derivatization procedures to enhance sensitivity or impart selectivity were incorporated into many methods for pesticide analysis. Since GC is a "multiple-detection" end method for quantitative analysis the limitations of the EC (electron capture) and other detectors quickly became apparent. Even after the application of the more common cleanup techniques, EC–GC interferences occurred not only from peak overlap of the various pesticides themselves (Figure 1) but also from interferring coextractives which originate from the sample being analyzed, as well as extraneous contamination from solvents or other materials used in the method. With the increased use of capillary column GC in pesticide analysis in the 1970s earlier separation problems were easily solved. For example, in the chlordane field it

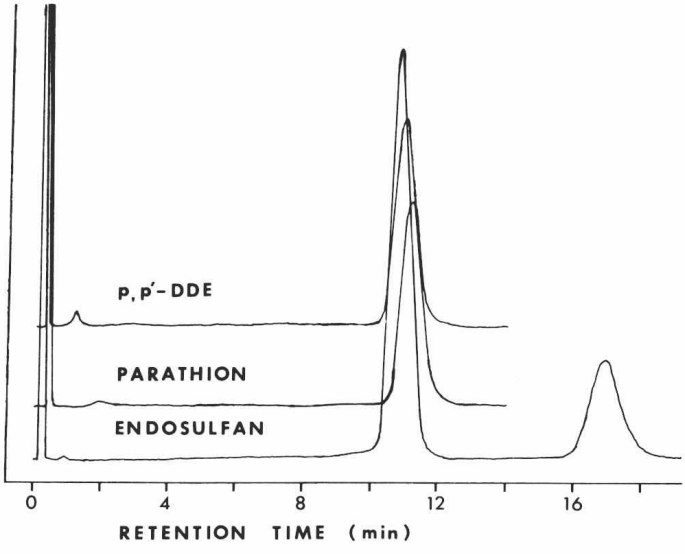

Fig. 1. Chromatograms of *p,p'*-DDE, parathion, and endosulfan I on 4% SE-30/6% QF-1 on chromosorb W at 190°C with electron-capture detection showing potential for misidentification.

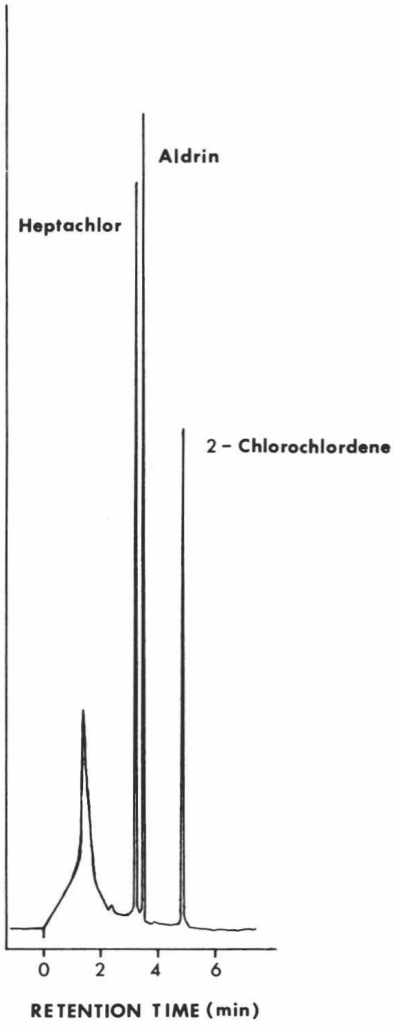

Fig. 2. Separation of heptachlor and 2-chlorochlordene on a 25 m × 0.25 mm i.d. OV-17 WCOT at 175°C with electron capture detection; injection time 25 sec; solvent effect with purified dodecane.

had been previously stated in 1971 that "no suitable GLC column had been obtained that will successfully separate the two compounds" heptachlor and its isomer 2-chlorochlordene.[6] However, as seen in Figure 2, a capillary OV-101 column will resolve these two isomeric compounds.

The identity of one large area of "interfering coextractives" observed by residue chemists involved in multiresidue analysis was solved by the late 1960s. The interfering compounds were shown to be the polychlorinated biphenyl (PCB) class of industrial chemicals.[7] Also implicated have been the polychlorinated terphenyls (PCT), naphthalenes, terpenes, and chlorinated paraffins. Even in the late 1960s there was ample evidence that a sig-

nificant proportion of the then-current residue data was not based on adequate analytical information since cases of "mistaken identity" were not infrequent. This, of course, led to much research into ways and means of either separating the PCBs and other interferences from the organochlorine residues or chemically altering one or other to eliminate coelution on GC and improve quantitation. Therefore, chemical derivatization techniques for confirmation of residue identity of all classes of pesticides has received considerable attention from the late 1960s to the present.[6,8,9]

It should be stressed that by far the best method of confirmation of pesticide identity is by mass spectrometry (MS). The GC–MS system has become the single most powerful tool for analysis of trace organic contaminants in biological and environmental samples, primarily owing to the development of the computerized measurement of mass spectra.[10] With the use of an interactive data system it is possible to get a complete spectrum on 100 pg of 2,4,5-T methylester depending upon type of system used. Increased sensitivity is possible, e.g., 20 pg of 2,4,5-T methyl ester can be identified by multiple ion monitoring of the six most intense peaks in the spectrum. However, the use of a GC–MS data system is often limited by availability, cost, or sample type (with or without cleanup and residue level). Once the nature or identity of a particular interference is known, the residue analyst is then in a much better position to deal with it—for example, chemical derivatization to alter its retention time or by proper choice of cleanup procedure.

From the above introduction it can be seen that two different types of chemical derivatization techniques have been mentioned. There is the chemical derivatization of a pesticide as a prerequisite of the method of analysis, for example, the esterification of chlorophenoxy acid herbicides prior to EC–GC analysis. Since this derivatization step is part of the actual method it must meet all the requirements associated with a practical, viable analytical procedure, namely, reproducibility, good recovery, freedom from interferences, and accuracy. In the case of a confirmatory test the demands are less severe in that the main criteria are speed, ease of operation, and acceptable yields. In addition, there are two other uses of chemical and photochemical reactions in pesticide analysis. On-column derivatization occurs in the heated injection port or column of the GC. The most commonly used conversion to date has been the alkylation of pesticides or their derivatives which contain acidic NH or OH functional groups. When an OP insecticide in alcohol is injected onto a precolumn containing NaOH-coated glass beads, the P–O–C bond is cleaved with formation of the appropriate ester, e.g., the methyl ester if methanol is used. Although good yields are

obtained, the method characterizes only the P-containing portion of the molecule and as such this type of derivatization technique is better suited as a screening method. Similarly, on-column transesterification of the *N*-methyl carbamates results in the formation of methyl-*N*-methyl carbamate, which indicates the original compound was a carbamate but not the identity of the pesticide. Finally, there is that class of chemical reactions that are used to clean up or remove specific interferences rather than form identifiable derivatives. This type of chemical cleanup approach has a long history of use in pesticide analysis. For example, treatment of a wildlife sample extract containing cointerfering mirex and PCB residues can be treated with a 1:1 mixture of concd H_2SO_4–fuming HNO_3 to "eliminate" PCB interference in the quantative analysis of mirex and its derivatives (Figure 3). Essentially, nitration of the PCBs occurs and their GC retention times are sufficiently long to effect a separation between them and the mirex constituents.

The aim of this review is to survey the application of chemical and photochemical derivatization techniques that have been used in the analysis of pesticides. This includes a survey of the four general areas discussed above, namely, chemical derivatization as used in (a) the analytical method, (b) confirmation of identity, (c) screening procedures, and (d) cleanup reactions.

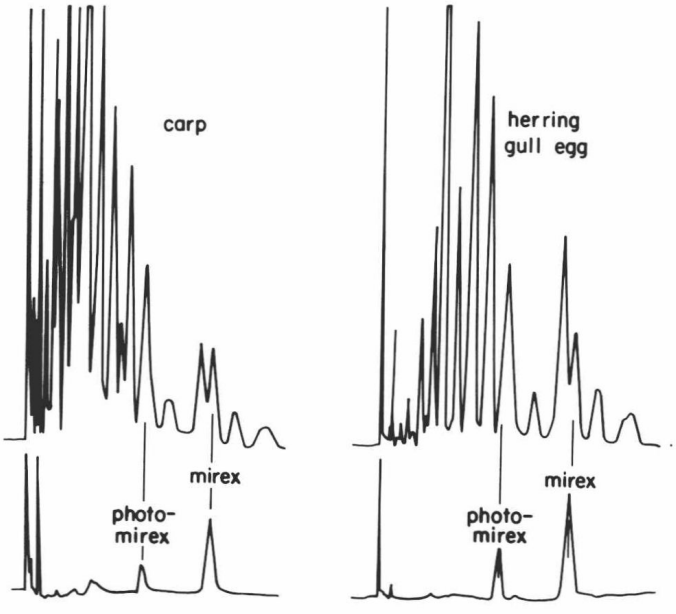

Fig. 3. Chromatograms of carp and herring gull egg extracts, from Lake Ontario, before (top) and after (bottom) nitration. Column 180 cm × 2 mm i.d., 1% SP-2100 on 80-100 mesh Supelcoport at 180°C.

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