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Pesticide Residues

Sidney Williams and J. William Cook, Division of Food Chemistry, Food and Drug Administration, U. S. Department of Health, Education, and Welfare, Washington, D. C.

RESEARCH IN THE FIELD of methodology for residue analysis has received much attention during the two-year review period from November 1964 through October 1966. In preparing this review, no attempt has been made to include all articles dealing with residue analyses but, rather, the authors have tried to select those which, in their opinion, will be most useful to the worker in this field.

Much of the literature refers to the "multidetection" methods in which many chemicals can be determined during one analysis. The possible inclusion of so many compounds in one analysis is a tremendous step forward but it does increase the problem of interpreting the responses properly so that one has adequate assurance of the identity of the compounds reported. This problem is basically no different from interpreting the response of the older methods such as a color reaction of the "wet chemical" or "specific" methods; for example the "specific" colorimetric method for parathion also responds to paraoxon, methyl parathion, EPN, Chlorthion, etc. The GLC methods generally give separate response for each of these; thus the possible misinterpretation is more obvious. This problem has been given a great deal of study and considerable progress has been made as indicated in numerous places throughout the review.

Closely associated with the field of methodology, particularly with the multidetection methods, is that of the "nature of the terminal residues." A pesticide chemical may be altered by its environment after application to yield terminal residues sufficiently close to the parent chemical to appear as a response to the detection system of a multidetection method. Developments in this field should be closely watched and taken into consideration as aids in the interpretation of responses in many of the methods now available.

There is no single uniform system of nomenclature used in the literature for pesticide chemicals, so for many pesticides there is no single generally recognized name. Both the coined patent names and the common names vary with the country and worker; thus there may be a number of names to describe the same compound. On the other hand, some names have recognition by all workers in the field. Because of these problems and because the authors believe that the use of chemical nomenclature exclusively would make the review difficult to follow, we have arbitrarily adopted a mixed system. In Frear's "Pesticide Index" (*111*), probably the most comprehensive listing of pesticides, common names, trade and chemical names are listed and cross-indexed. We have tried to use the name which we believe will be most meaningful to the reader and, where possible, to use a name which may be found in Frear's Index. Common names which appear in the United States Food and Drug Administration tolerance regulations have been used where possible. Common names of other compounds have been used whenever they exist and are considered to be well known. For those compounds best known by a single trade name we have used the trade name in capitalized form. In those instances where the common or trade name may be confusing or is not well known, we have tried to include the chemical name as well. Thus the reader should, with the help of Frear's Index, be able to

identify almost every compound referred to in this paper.

The literature on pesticide residues has maintained its rapid growth in the two years since the previous biannual review (*75*). Gunther (*133*) has continued his excellent series of "Residue Reviews" and 15 volumes have now been published. These volumes contain articles on many aspects of pesticide residues written by experts in the specific fields. Volume 1 of the Food and Drug Administration's "Pesticide Analytical Manual" (*19*), probably the most widely used manual of methods for pesticide residue analysis, has undergone continuous revision and updating. The methods in this volume have been studied in FDA laboratories and are known to be useful combinations of extraction, cleanup, and determinative steps which yield quite satisfactory qualitative and quantitative results for many compounds.

The U. S. Public Health Service has published a 2-volume "Guide to the Analysis of Pesticide Residues" (*55*) which includes methods for the analysis of water and soil as well as foods. However, this is primarily a compilation of methods recommended by a variety of laboratories and which have not necessarily been used or tested by the U. S. Public Health Service.

Several new periodicals of interest have appeared in the period covered by this review. The "Bulletin of Environmental Contamination and Toxicology" (*53*) is a bimonthly journal designed to provide a rapid publication in fields including pesticide residue methodology. The first issue was dated January-February 1966.

The U. S. Department of Agriculture began the publication of "Pesticides Documentation Bulletin" (*243*) on March 19, 1965. This biweekly is a ". . . computer produced permuted title index in three parts: Keyword Index, Bibliography, and Author Index." This is excellent as a general reference for those interested in many aspects of pesticides but is of little value to the residue analytical chemist as a specific reference because only those words which appear in the title of an article will appear as entries. There is no grouping of subjects such as "methods of analysis" or "chemical methods of analysis" unless those words appear in the titles of the original article.

More recent and potentially most valuable to the pesticide residue chemist is the "Health Aspects of Pesticides—Literature Bulletin" (*146*). This is an experimental monthly publication of the Office of Pesticides of the U. S. Public Health Service. The first issue, dated September 1966, contained 117 abstracts including 23 of recent articles dealing with analysis. In addition to author and subject indexes, the contents are also divided into sections dealing with pollution, toxicity and toxicological factors, analysis, etc.

This two-year period has also seen the beginnings of attempts to automate pesticide residue analysis. Gunther *et al.* (*136*) designed a system for the determination of total chlorine. They combined an automatic combustion apparatus with a continuous flow chloride ion detector. It was capable of handling as much as 2-gram equivalents of plant extractives and had a useful range of 0.01 to 500 ppm. The burning cycle of 7 minutes was automatic and the chloride ion measured and recorded. Ott and Gunther (*233*) reported an automated colorimetric phosphorus determination which had a sensitivity well below 0.1 μg phosphorus per milliliter of final solution. Samples were cleaned up and burned in a Schöniger flask and the solution was transferred to an *Auto*Analyzer which carried out the analysis and recorded the result. Several procedures were reported for the automatic determination of cholinesterase inhibition using the *Auto*Analyzer. Voss (*283*) described a procedure in which acetylthiocholine was used as the substrate. The liberated thiocholine acted on 5,5-dithiobis-2-nitrobenzoic acid producing a color which was measured at 420 mμ. Ott and Gunther (*231*, *232*) used acetylcholine as the substrate and measured the transmittance at 555 mμ as affected by change in color of phenol red.

All of the above procedures required prior extraction and cleanup before the sample solution could be placed in the *Auto*Analyzer. The first fully automated analysis was reported by Gunther and Ott (*137*) for the determination of biphenyl in citrus fruit rind. The sample was automatically homogenized in water and the biphenyl steam distilled. Oils and waxes were removed with H_2SO_4 and a cyclohexane solution of the biphenyl was passed through the cell of a recording UV spectrophotometer with readings taken at 246 mμ and recorded. The useful range was said to be from 1 to 150 ppm on a whole fruit basis with a reproducibility of about 3%.

GAS CHROMATOGRAPHY

Another area which received considerable attention was detectors for gas chromatography. As the need for detectors capable of selective specificity for compounds containing halogens, phosphorus, sulfur, and nitrogen became greater, several new approaches were taken. McCormack, Tong, and Cooke (*204*) developed a detector based on selective monitoring of the emission spectra of the eluted organic compound. Using argon as the carrier gas, the spectra are excited in the plasma of a 2450-Mc electrodeless discharge. By measuring the intensity of selected atomic lines and molecular bands, the system can be made quantitative and highly specific for the halogens, phosphorus, and sulfur. Bache and Lisk (*13*) used this emission spectrometer detector to analyze a number of foods for such organophosphorus pesticides as diazinon, dimethoate, disulfoton (Di-Syston), ethion, parathion, and ronnel by measuring the intensity of the 2535.65 Å. line. Recoveries of 72–115% were obtained at levels ranging from 0.03 to 0.60 ppm.

Brody and Chaney (*50*) developed a flame photometric detector for determining sulfur- and phosphorus-containing compounds. The flame emission spectra were generated in a hydrogen–air flame and narrow bandpass interference filters used for isolation of the phosphorus and sulfur emission at 526 mμ and 394 mμ, respectively. The sensitivity was said to be 0.25 ng for malathion or parathion and in the submicrogram range for sulfur-containing compounds.

Coulson (*77*) introduced an electrolytic conductivity detector for gas chromatography. The effluent from the GLC column was passed through a combustion tube where the compounds were oxidized to CO_2, SO_2–SO_3 and HCl. The gases were passed into a stream of deionized water and into an electrolytic conductivity cell where the conductivity was measured by a simple Wheatstone bridge. The detector was 10,000 times as sensitive for halogen or sulfur compounds as for carbon or nitrogen.

Coulson (*78*) later modified this system to determine nitrogen-containing compounds. The effluent from the GLC, instead of being oxidized, was reduced with hydrogen in the presence of a catalyst to change any nitrogen to NH_3. Any acids formed were removed with $Sr(OH)_2$ and the NH_3 was passed through to the electrolytic conductivity detector. The apparatus was used for the determination of such nitrogen-containing compounds as simazine, parathion, amitrole, etc.

Martin (*198*) reported a method for the determination of nitrogen-containing compounds which also reduced the effluent from the GLC column with hydrogen to produce NH_3. The NH_3 was then passed into a titration cell where it was automatically titrated with coulometrically generated hydrogen ion. However, with some compounds, some of the nitrogen atoms were converted to elemental nitrogen which would not be converted to NH_3. Guthion, for example, gave only 39% recovery. Although the method was developed for petroleum industry use, it was said to be applicable to pesticide analysis.

A number of papers were published

on the thermionic detector, all of which gave strong support to the validity of the detector. Beckman and Gauer (*26*) reviewed the literature and development of the sodium thermionic detector. They described the construction and operation of a detector based on Giuffrida's design. Hartmann (*145*) reported a thermionic detector for phosphorus in which cesium bromide was used as the alkali metal source. The cesium bromide plus a suitable filler was pressed under high pressure to form a ceramic-like pellet which was then shaped to serve as the tip of the burner. Coahran (*71*) described a modified detector in which a ceramic tube filled with granular anhydrous Na_2SO_4 was placed around the jet.

Giuffrida and Ives (*123*) used dual detectors in an investigation of cleanup procedures for organophosphorus pesticide residues. The effluent from the GLC column was passed through a stream splitter and into two detectors. The response of a regular flame ionization detector was indicative of the amount of plant extractives present and thus of the cleanup efficiency. The response of the thermionic detector showed the amount of pesticides recovered.

Giuffrida, Ives, and Bostwick (*124*) described and explained the operating parameters for electron capture and the thermionic detectors. Specific details were given on how to adjust each detector and GLC system for most suitable operation for residue analyses. This paper should be required reading for residue analysts using gas chromatography.

Karmen (*173*) described a stacked flame ionization detector for phosphorus and chlorine. He indicated that the detector worked because phosphorus and halides increased the vapor pressure of the alkali metal and thus made more of it available for ionization. Abel, Lanneau, and Stevens (*5*) reported a modified stacked flame detector, claiming a controlled specificity for phosphates and halides in the order of 100,000–200,000 to 1 over other organic species.

Burchfield *et al.* (*54*) discussed various types of GLC detectors, pointing out the advantages of each. Burchfield and Wheeler (*57*) described the use of the microcoulometric detector in both the oxidative and reductive modes. Burchfield *et al.* (*56*) also reported the use of the microcoulometric detector for the determination of phosphorus, sulfur, and chlorine. The effluent from the GLC was carried through a reducing oven with H_2, forming PH_3, H_2S, and HCl. All three products were measured by a microcoulometric titration cell with silver electrodes. By inserting subtraction columns before the cell, HCl (by silica gel) or both H_2S and HCl (by Al_2O_3) could be removed, thus giving the system a high specificity.

The electron capture detector continues in wide use but only a few papers suggested modifications. Yauger *et al.* (*287*) reported the use of Ni^{63} as the radioactivity source, the big advantage being that such a detector can be operated at temperatures up to 300° C. Abbott and de Faubert Maunder (*3*) described a simple electron capture detector that could be constructed from a standard 75-ohm co-axial cable plug and a strip of tritiated copper foil at a total cost of material of less than $10.

Gas chromatography has become so accepted in pesticide residue analysis that its use in procedures is now taken for granted much like the analytical balance or a spectrophotometer. However, several papers have appeared which treat gas chromatography as a general topic. Gudzinowicz (*125*) compiled a vast amount of data on the use of electron capture gas chromatography in pesticide residue analysis. He listed the R_f and sensitivities for a large number of the pesticides on a variety of columns. Burke and Holswade (*58*) tested 17 liquid phases in the search for a GLC column which would elute the common pesticides in a different order than the widely used DC-200 column. They recommended a column prepared by mixing equal portions of Gas Chrom Q coated with 15% QF-1 and Gas Chrom Q coated with 10% DC-200. They listed retention times and response data on the column for over 85 pesticide chemicals using both the electron capture and the microcoulometric detector.

Berck (*29*) listed retention times, both absolute and relative to *n*-pentane, for 34 fumigants on a column packed with 10% SE-30 on Diatoport-S. Kanazawa (*171*) evaluated and compared columns with two liquid phases, 5% Dow Silicone 11 and 2% polyethylene glycol, for the separation of chlorinated and phosphorus pesticides and herbicides. Linear ranges, sensitivities, and separation efficiencies are reported. Gaul (*114*) compared five methods of measuring GLC peaks and discussed the problems with toxaphene, chlordane, and BHC. She suggested ways of measuring the peak areas when the pesticides were separate and in mixture. It was also pointed out that in determining BHC the analyst should bear in mind that the electron capture response to the β-isomer is about 50% of the response to the other isomers.

Giuffrida (*121*) described a GLC system for the collection of fractions for infrared analysis. The fractions were collected individually directly on KBr and then pressed into micro disks. About 10 mg of KBr was used and good spectra were obtained with as little as 3 μg of pesticide.

CHLORINATED PESTICIDES

General Procedures. Chlorinated pesticides continue to be the most widely used group and it is natural that methodology for these compounds received a great deal of attention. Beynon and Elgar (*36*) prepared an excellent review of work published up to May 1965. They list 324 references and cover all aspects of residue analysis from the collection and storage of samples through extraction and cleanup to the numerous means of quantitation and identification.

Mumma and coworkers (*218*) investigated the effectiveness of a commonly used extraction procedure in removing pesticide residues which had been picked up by growing crops. Using crops grown in soil containing dieldrin, they found that the widely used hexane–isopropanol (2:1) extraction procedure removed only about 64% of the dieldrin present. When this was followed by a 12-hourextraction with a 1:1 mixture of chloroform and methanol complete extraction of the dieldrin was obtained.

In the past two years, several collaborative studies were made of widely used analytical procedures. Johnson (*167*) reported on a study of the Mills' procedure involving the determination of heptachlor epoxide and dieldrin in evaporated milk and in butterfat. The results for 20 laboratories showed a standard deviation of ±0.039 ppm for heptachlor epoxide at the 0.29-ppm level and a standard deviation of ±0.052 ppm for dieldrin at the 0.26-ppm level. Several collaborative studies of the Mills, Onley, Gaither procedure were also reported. Krause (*187*) studied the recovery of aldrin, DDE, and methoxychlor from potatoes. Gaul (*115*) investigated the recovery of lindane, heptachlor, and TDE from endive and cauliflower, and Davidson (*87*) reported on the determination of BHC, *p,p'*-DDT and endrin in apricots and strawberries. Each study demonstrated the validity of the procedure.

A large number of articles describe general procedures for the determination of chlorinated pesticide residues. Many of these are modifications of previously reported methods. Gunther and Barkley (*134*) modified a microcoulometeric gas chromatograph so that, when desired, the GLC column could be bypassed with the sample going directly to the combustion furnace. This permitted easy determination of "total chlorides." Advantages of the arrangement include a more accurate measurement of toxaphene since the entire residue registered as one peak.

Robertson and Tyo (*246*) determined chlorinated pesticides in oysters using a continuous perforated basket centrifuge for extraction of sample with aceto-

nitrile. After partitioning of the residues into petroleum ether, the determination was made by electron capture GLC. Recoveries for heptachlor, heptachlor epoxide, DDE, and DDT ranged from 97 to 115% at the 0.16-ppm level. Kadis and Jonasson (*170*) used a modification of the method of Langlois *et al.* [*Milk and Food Technol.* **27**, 202 (1964)] to determine chlorinated pesticides in blood. The sample was ground with Florisil, transferred to a Florisil column, and eluted with 30% methylene chloride in petroleum ether. After evaporation and solution in hexane, analysis was by electron capture GLC. Jain and coworkers (*161*) used a simplified procedure to determine 23 pesticides including chlorinated, organophosphorus, and a nitro compound in blood. The sample was extracted with an acetone-ether mixture (1:1), evaporated, taken up in hexane, and injected into an electron capture GLC. There was no interference from the blood but the sensitivity was limited by the size of sample that could be chromatographed (equivalent to 1 mg blood).

Radomski and Fiserova-Bergerova (*245*) described the determination of chlorinated pesticides in tissues using electron capture GLC. They blended the sample with petroleum ether, added anhydrous Na_2SO_4, made to volume with petroleum ether, and injected an aliquot into the GLC without any cleanup. Sensitivities were reported in the range from 0.001 to 0.06 ppm. Hamence and coworkers (*142*) analyzed animal tissue by extracting with acetone, partitioning the residues into petroleum ether, extracting with acetonitrile, and again partitioning into petroleum ether. Final cleanup was on an alumina column. Determination was by electron capture GLC. To confirm identity and separate compounds with similar retention times, aliquots were reacted with HBr, alcoholic KOH, and chlorine, and gas chromatography was repeated. Data are given for 12 compounds.

Stanley and LeFavoure (*263*) used a perchloric–acetic acid mixture to digest samples of animal tissues. The fat and pesticides were extracted with *n*-hexane and cleaned up on a sulfuric acid–Celite column before determination by electron capture GLC. Aldrin, dieldrin, and endrin are destroyed by the procedure. Parker *et al.* (*238*) combined portions of previously reported methods for the determination of chlorinated pesticide residues in animal and human tissues. Frozen samples were blended with Dry Ice to a powder and extracted with hexane. Acetonitrile extraction and a column containing Florisil, Celite, attapulgus clay, and charcoal were used for cleanup before determination by electron capture GLC. Onley and Bertuzzi (*229*) reported a rapid procedure for the analysis of fish, meat, and fat by electron capture GLC. The method combined the use of a mixture of acetone, methyl Cellosolve, and formamide to extract the pesticide residues with the use of calcium stearate to coagulate and hold fatty constituents. Recoveries ranged from 76–108% at levels of 0.002–1.0 ppm. Kotula and Moats (*183*) used TLC to analyze eggs or poultry fat samples in less than 2 hours. Extraction was with ethyl ether with cleanup on a carbon–Celite 545 column. As an alternative, fat could be dissolved in petroleum ether and cleaned up on a Florisil column. In each case, suction was used to speed up the elution from the column. Eight chlorinated compounds were determined with a sensitivity of about 0.1 ppm. Sawyer (*254*) used acetone to extract chlorinated pesticides from eggs. After partitioning into petroleum ether, the residues were cleaned up on a Florisil column for determination by microcoulometric or electron capture GLC. In addition to being fast, it was claimed that this procedure eliminated interferences sometimes found in other procedures. Cummings and coworkers (*83*) combined features of the method of Stemp *et al.* [*Poultry Sci.* **43**, 273 (1964)] with those of Mills *et al.* [*JAOAC* **46**, 186 (1963)] for the analysis of eggs. The sample was ground with Florisil and anhydrous Na_2SO_4 and the mixture transferred to the top of a Florisil column. The pesticides were eluted in two fractions and concentrated for analysis by electron capture GLC. The sensitivity was reported as 0.001 ppm, and recoveries for lindane, heptachlor epoxide, DDT, dieldrin, and endrin ranged from 78 to 109%.

Moats (*214*) used TLC to determine chlorinated pesticides in dairy products with a sensitivity of about 0.125 ppm on a fat basis. Stemp and Liska (*265*) reported a simplified and shortened procedure for the analysis of milk. A 10-ml sample of milk was mixed with deactivated Florisil, slurried with 20% CH_2Cl_2 in petroleum ether, and decanted through a column of deactivated Florisil. The eluate was evaporated; the residue was taken up in hexane and injected into an electron capture GLC. Recoveries were over 90% at levels of 0.1 to 10 ppm whole milk basis. It was stated that 40–50 samples could be cleaned up by one technician in a day.

Giuffrida *et al.* (*122*) described a procedure for milk, fats, and oils. Milk was extracted with acetone and the residues were partitioned into petroleum ether. Fats and oils were dissolved in petroleum ether. The samples were transferred to a column of deactivated Florisil, and after removal of solvent pesticides were eluted with acetonitrile containing 10% H_2O. After partitioning into petroleum ether, the extracts were further cleaned up on an activated Florisil column and determined by electron capture GLC. Tolbert (*276*) used a column of sand, magnesium oxide, and Celite 545 to replace the Florisil column in the analysis of oils by electron capture GLC. Saha (*249*) determined aldrin, heptachlor, endrin, and dieldrin in wheat using electron capture GLC. The ground samples were extracted with acetonitrile in a Soxhlet; residues were partitioned into petroleum ether and cleaned up on a magnesia–Celite column.

Several procedures have been reported for the determination of chlorinated pesticide residues in water. Lamar and coworkers (*190*) extracted large (up to 4 liters) samples of water with hexane and used electron capture GLC for the determinative step. Smith and Eichelberger (*260*) described a thin layer chromatographic cleanup of the carbon chloroform extract (of water) resulting in a solution suitable for electron capture GLC. Lerenard and Simon (*194*) used an automatic liquid–liquid extractor which they found capable of extracting 80–90% of lindane and dieldrin from water at concentrations of 1 ppb. Sanderson and Ceresia (*253*) reported on a continuous liquid–liquid extraction apparatus. With a sample flow rate of 1 liter/hour, recoveries of about 90% at the 1-ppb level were obtained. Teasley and Cox (*271*) compared extraction procedures for removing endrin and DDT from soils. They reported that the Immerex extraction method was the best. The procedure involved a 16-hour extraction with *n*-hexane–acetone (9 + 1) in an Immerex tester, an apparatus designed for the analysis of bituminous paving mixture which uses an extraction basket for the sample container.

Samuel (*252*) reported a screening procedure for chlorinated and thiophosphorus pesticides in dairy products, fruits, vegetables, and animal tissue. After sample extraction, a combination of 1 or more of 3 cleanup procedures prepared the sample for final analysis by electron capture or microcoulometric GLC. Recoveries of 75–100% were reported at levels of 0.05–2 ppm. Water soluble organothiophosphorus compounds do not come through the procedure.

Considerable use has been made of thin layer chromatography in the analysis for chlorinated pesticides. Matherne and Bathalter (*200*) described a cleanup procedure making use of 8- × 8-inch plates with channels 10 mm wide by 2 mm deep which were filled with Al_2O_3–G coating. Sample extracts were spotted on individual channels and the plates developed twice with two different solvents. This separated the

pesticide residues from the plant extracts and after elution from the scraped off adsorbent, the residues were in suitable form for electron capture GLC.

Kovacs (*186*) used $3^1/_2 \times 4$-inch microplates for TLC and reported that as many as 26 chlorinated pesticides could be resolved in 5–10 minutes and identified. The lower limit of detection for many of the commonly used chlorinated pesticides was 0.005 μg. Crabtree (*79*) used microscope slides coated with Al_2O_3 and developed in hexane in $3^1/_2$ minutes for rapid confirmation of identity. Beckman and Winterlin (*27*) described what they called "thin-strip thin layer chromatography." They used a tool to scrape coated 8 × 8-inch plates in such a manner that individual TLC strips or channels 4 mm wide were formed. As many as 20 channels could be used on one plate. The advantages claimed were that, since the spots could not spread, sensitivity was increased and that it was easier to remove separated spots for GLC and IR. Engst *et al.* (*99*) used silica acid gel plates and reported the detection of 6 chlorinated pesticides with a sensitivity of 0.05 μg. Abbott and coworkers (*4*) studied the effect of temperature on R_f values. R_f values for 16 chlorinated pesticides in 16 solvent/adsorbent systems were given. Ballschmiter and Toelg (*16*) investigated fluorescence indicators for TLC. Twenty-four substances were studied. Fluorescence or quenching of spots at levels of 0.02–5 μg were noted with six reagents. Adamovic (*7*), investigating spray reagents for TLC, reported that the chlorinated pesticides under ultraviolet light reacted with aromatic amines to form characteristically colored spots even without zinc chloride or iodine. A total of 18 aromatic amines were tested with the 6 most promising showing sensitivities down to 0.5 μg.

There have been several papers on chlorinated pesticides which are of general interest to the residue chemist. Gunther, Hylin, and Spenger (*135*) investigated the nature of the organic chlorine interferences in the total halogen methods for organic chlorine pesticides. Using Cl^{36} tracer, they have tentatively identified the interferences as quaternary chloride salts of lecithins. Burke *et al.* (*59*) studied the losses of pesticides in various methods of concentrating solutions down to volumes of 0.5 ml or less. They found that large losses occurred when the solutions were evaporated by a stream of air. Losses increased as the residual volume approached dryness and the percentage losses were greater when smaller amounts of pesticides were present. They found that by using a micro Snyder column, solutions could be rapidly concentrated to 0.1–0.3 ml on the steam bath without loss of pesticide. Moats and Kotula (*215*) speeded up the elution from cleanup columns by using suction. They reported that elution rates of 250 ml/min from Florisil columns and 100 ml/min from carbon–Celite columns gave good recoveries without adversely affecting the cleanup.

Mumma and Kantner (*217*) made use of the mass spectrometer for more positive identification of pesticides. They determined the mass spectra of several chlorinated pesticides and found that each gave easily recognizable molecular ion peaks and characteristic ion fragments. Their procedure was to collect the GLC peaks in medicine droppers containing GLC column packing material. The pesticide was washed out, concentrated, and injected into the mass spectrometer. The procedure has been run on dieldrin, DDT, and DDE from wheat and alfalfa. The sensitivity was 0.1 ppm, and 0.1 μg has given a good mass spectrum. Payne and Cox (*239*) used infrared for the identification of chlorinated pesticide residues in sludge, soils, industrial effluents, and fish and other aquatic fauna. Column and thin layer chromatography were used for the cleanup and separation of the individual pesticides. Minyard and Jackson (*213*) attempted to make identification by electron capture GLC more certain through the use of flash heater inserts packed with various salts to modify the pesticides. A number of salts were investigated, and the authors suggested the possible use of several modifiers in parallel ahead of a single column and detector. Sequential injection of an extract into the various modifiers would produce normal and modified chromatograms which were characteristic of the pesticide. Lee and coworkers (*193*) encountered a contaminant which had the same R_f on a silicone elastomer/Celite GLC column as aldrin, and on a column of Apiezon L had the same R_f as β-BHC. By means of infrared they identified the contaminant as dibutyl phthalate which they thought came from plastic containers and plastic-based paints used in the laboratory.

Specific Procedures. Shuman and Cieri (*257*) reported a method for determining residues of chlorbenside including its sulfoxide and sulfone oxidation products. Samples were extracted according to the Mills, Onley, Gaither procedure and all forms of chlorbenside residue converted to the sulfone by oxidation with chromic–acetic acid solution. After cleanup on an Al_2O_3 column, determination was made by electron capture GLC. Thruston (*275*) compared the electron capture gas chromatogram of a chlordane standard with that of a weathered chlordane residue found on squash. He noted that in the weathered residue, the first 4 major peaks of chlordane were small or had disappeared, while the last 3 peaks were not changed significantly. Gajan and Link (*113*) used oscilloscopic polarography for the determination of DDT. They reported that with an electrolyte of 0.1*M* tetramethyl ammonium bromide in 50% aqueous acetone–ethanol, only DDT and those analogs such as methoxychlor containing the trichloroethane group gave responses in the −0.3 to −1.7-volt range. The regular wave showed a peak indicating the total *o,p'*- and *p,p'*-DDT whereas the derivative showed two peaks whose ratios was equal to the ratio of the two isomers.

Several papers dealt with the determination of DDT. Dingle (*90*) modified Davidow's sulfuric acid cleanup for fat [*JAOAC* **33,** 130 (1950)] and obtained solutions suitable for PC, GLC, IR, or colorimetric determination. Recoveries were said to be better than 98%. Stempkovskaya and Vekshtein (*266*) reported a modification of the Schecter-Haller technique using KNO_3 or NH_4NO_3 with H_2SO_4 in place of fuming HNO_3. They also described a stable artificial color standard consisting of a solution of $CuCl_2$, crystal violet, and $K_2Cr_2O_7$ which was said to correspond to the color produced by 100 μg of DDT. Crosby and Archer (*80*) determined the DDT group in milk, blood, and tissue as their dehydrohalogenated compounds after treatment with KOH. Extraction was with pentane and determination by electron capture GLC. The first foot of the GLC column was packed with calcium carbide to remove traces of water and ethanol. Beckman and coworkers (*24*), after showing that the pesticides were present only in the yolk of eggs, determined DDT and DDE by extracting the yolks with acetone. The extract was evaporated; the residue was taken up in hexane and cleaned up on a Florisil column before determination by electron capture GLC. Recoveries at 0.05–1.0-ppm levels averaged 94%. The time required for analysis was less than 1 hour per sample. Schuntner and Schnitzerling (*256*) used gradient elution from a cooled, water-jacketed, silicic acid column to separate DDT and its metabolites into individual components. Compounds separated included *o,p'*- and *p,p'*-DDT, DDE, *p,p'*-DDD, Kelthane, *p,p'*-dichlorobenzophenone, and *p,p'*-DDA.

Hansen (*143*) reported that the colorimetric method of Jones and Riddick [ANAL. CHEM. **23,** 349 (1951)] for the determination of Dilan could be made about 10 times more sensitive by decreasing the total volume of the final solution while keeping the same ratios of reagents.

Harrison (*144*) was able to determine endrin in wildlife in the presence of

large amounts (100–500-fold) of DDE and dieldrin by making a preliminary separation on TLC before using GLC. Although recoveries were slightly better on silica gel plates, alumina gave better separation of endrin from dieldrin. Engel *et al.* (*97*) determined heptachlor and heptachlor epoxide in alfalfa hay by blending the sample with water and ethanol and then extracting with hexane. They used the procedures of Samuel (*252*) for cleanup. Ott *et al.* (*235*) used thin layer chromatography and oscillopolarography to determine *p,p'*-Kelthane and *p,p'*-dichlorobenzophenone. They suggested that in analyzing crop extracts, TLC be used for cleanup before polarographing the sample. Mestres and Chave (*209*) determined lindane in flour by extracting with acetonitrile, cleaning the extract on a Na_2SO_4 and Florisil column, and then using electron capture GLC. Recovery of 0.25 ng of lindane was 95 ± 3%. To determine toxaphene in milk, fat, blood, and hay, Archer and Crosby (*12*) used KOH to dehydrohalogenate the toxaphene before injection into the electron capture GLC. Advantages claimed for the procedure were very rapid and effective cleanup, a higher and more compact peak which eluted before the DDT group, and a two-fold increase in sensitivity. Recoveries ranged from 74–95% at 0.1 and 0.5-ppm levels. Faucheux (*103*) investigated the use of diphenylamine–$ZnCl_2$ as a chromogenic reagent for toxaphene, DDT, and chlordane on alumina TLC plates. Characteristic colors were obtained from these pesticides. Five μg each of toxaphene and chlordane could be detected in mixture. DDT and TDE could be estimated semiquantitatively when all forms were present. Color reactions of 34 pesticides at the 20-μg level were reported.

ORGANOPHOSPHORUS PESTICIDES

General Procedures. Storherr and coworkers (*268*) reported a procedure they used for the determination of five organophosphorus pesticides (malathion, parathion, methyl parathion, diazinon, and carbophenothion) in a number of vegetables and fruits. The sample was blended with acetonitrile and filtered. The extract was concentrated under vacuum to remove the acetonitrile and was then extracted with ethyl acetate. After cleanup on a column of carbon and Celite, the pesticides were determined by GLC using the thermionic detector. Other aliquots were examined by the colorimetric *p*-nitrobenzyl pyridine method (*118*), a total phosphorus procedure (*117*), and by paper chromatography. Watts and Storherr (*285*) described a rapid extraction procedure in which the crop sample was extracted by blending with ethyl acetate. Storherr and Watts (*269*) developed a rapid cleanup procedure for organophosphate pesticides which also shows promise of being useful as a general cleanup method for many other types of compounds. The procedure, called sweep codistillation, makes use of a heated short glass column packed with glass wool. An ethyl acetate extract of the sample was injected into the tube, and pesticides and solvent were swept through into a receiver by a stream of N_2. Repeated injections of small amounts of ethyl acetate resulted in nearly complete recovery of the pesticides while crop material remained in the tube. The effluent was clean enough for gas chromatography using the thermionic detector. Recoveries from five crops fortified with a mixture of carbophenothion (Trithion), diazinon, malathion, parathion, and methyl parathion ranged from 89 to 101%, and only 20 minutes was required to clean up each sample.

Getz and Watts (*118*) reported a colorimetric procedure which had a sensitivity of 2 μg of organophosphorus compound. A cleaned up residue was heated with 4-(*p*-nitrobenzyl) pyridine and cyclohexylamine for 2 minutes, diluted, and the absorbance was read at 520 mμ. The procedure worked for all 24 organophosphorus pesticides tested. Getz (*117*) described a procedure in which the organophosphorus compounds were quantitatively converted to orthophosphates by ammonium persulfate and then measured as molybdenum blue with an absorbance at 660 mμ. Residues were separated on paper chromatograms, the spots were cut out, and the determination was run directly with the piece of paper. Sensitivity was 0.1 μg P, equivalent to about 1 μg pesticide. Irudayasamy and Natarajan (*159*) used paper chromatography for the determination of thiophosphorus pesticides. After development, the dried chromatogram was exposed to bromine vapors, air dried, and sprayed with a solution of Congo red. The pesticides appeared as blue spots on a red background and were stable for 10 days if protected from light. The test was sensitive to 0.5 μg of pesticide. Zadrozinska (*290*) used paper chromatography in the determination of organophosphorus pesticides in various food crops. He extracted the sample with carbon tetrachloride and after separation by paper chromatography used enzymatic and fluorescein methods for making the spots visible. Bates (*20*) also used paper chromatography but extracted the food samples with acetone, cooled the extracts to −80°C. and filtered them to remove fats and waxes and used a MgO column for further cleanup. The pesticides were separated and identified by 2-dimensional paper chromatography. For quantitiation, the spots were cut out and phosphorus was determined by the molybdenum blue reaction after wet digestion or Schöniger flask combustion. R_f's are listed for 20 compounds.

Thin layer chromatography was used by a number of workers. Kovacs (*185*) separated thiophosphorus compounds on Al_2O_3–G plates and located the pesticides with a tetrabromophenolphthalein–$AgNO_3$ spray. R_f's were given for 19 compounds and 11 of these were detectable at the 0.05-μg level. Barney (*18*) investigated previously reported chromogenic reagents for organophosphorus compounds and developed 2 new tests. The developed plates were sprayed with HI solution, heated, sprayed with ammonium persulfate solution, heated again, and sprayed with ammonium molybdate followed by buffered benzidine solution. The procedure determined all compounds tested except for one phosphonium compound. Omitting the ammonium persulfate resulted in a test which detected organophosphates but only some of the organophosphonic acids. The lower limit of detection was less than 1 μg. Watts (*284*) adapted the *p*-nitrobenzyl pyridine reagent (*118*) for use as a chromogenic spray in paper and thin layer chromatography. Twenty organophosphorus pesticides tested gave distinct and persistent spots. The test was sensitive to about 0.5 μg for both the thio and nonthio organophosphorus pesticides. Klisenko (*180*) used Al_2O_3 plates and 3 chromogenic sprays for detecting organophosphorus residues. Zadrozinska (*291*) used silica gel and talc adsorbents with 16 mobile phases. El-Refai and Hopkins (*96*) described the use of plates coated with cellulose powder containing 10% $CaSO_4$ as binder, for the separation of organophosphorus pesticides and their oxons. Two solvent systems were used, each including an immobile solvent phase. Four spray reagents were used including one based on cholinesterase inhibition directly on the plate which was sensitive to 0.001–2 ng of the various pesticides. The authors discussed the choice of systems for specific separations and listed R_f values. Melchiorri *et al.* (*206*) used Silica Gel GF 254 plates for the separation and identification of 13 organophosphorus pesticides in vegetable oils. Various solvent systems are described. Salamé (*250*) studied the chromatography of 10 organophosphorus compounds on silica gel using 16 solvent systems and reported R_f values. He used two chromogenic reagents, one (Br_2, $FeCl_3$ and sulfosalicylic acid) had a sensitivity of about 5 μg and the other (palladium chloride) a sensitivity of about 2 μg. Stanley (*262*) used 3 × 1-inch microscope slides coated with silica gel-G. He listed R_f values for 31 organophosphorus compounds in 6 solvent systems and described 7 spray reagents.

A number of workers have used GLC for the separation and identification of organophosphorus pesticides. Horiguchi *et al.* (*155*) separated 9 compounds on three different GLC columns using an electron capture detector. Kanazawa and coworkers (*172*) were able to separate any combination of 19 organophosphorus pesticides by the use of three GLC columns, although no one column gave complete separation of all 19 compounds. Hrivnak and Pastorek (*157*) reported the successful separation of 11 *O,O*-dialkyl-*O*-(4-nitrophenyl)thiophosphates describing the columns and operating conditions used. Nelson (*223*) used microcoulometric GLC for the determination of 16 thiophosphates in 25 crops at levels as low as 0.1 ppm. Samples were extracted by the Mills, Onley, Gaither procedure [*JAOAC* **46,** 181 (1963)] and the residues partitioned into petroleum ether before the gas chromatography. Recoveries of over 70% were obtained for all compounds except Guthion (16%), demeton (46%), and dimethoate (0%). Later modifications (*224*) increased the recovery of dimethoate and Guthion to 70–98%. Cook and coworkers (*74*) studied the electron capture response of 7 organophosphorus pesticides in an attempt to correlate structure to response. They found that in general the electron affinity changed in the manner:

$$\underset{\text{P—O}}{\overset{\text{O}}{\overset{\|}{}}} < \underset{\text{P—O}}{\overset{\text{S}}{\overset{\|}{}}} < \underset{\text{P—S}}{\overset{\text{O}}{\overset{\|}{}}} < \underset{\text{P—S}}{\overset{\text{S}}{\overset{\|}{}}}$$

and that the methoxy group bonded to the central phosphorus atom resulted in lower electron affinity than did the ethoxy group.

McCaulley (*203*) used a combination of GLC with infrared for the determination of organophosphorus residues from fruits and vegetables. The sample was extracted by blending with acetonitrile, water salted out and the acetonitrile extract evaporated. The residue was subjected to distillation under a vacuum of about 0.5 micron with the pesticide residues being collected on a cold finger cooled with liquid nitrogen. The residues were rinsed off, adjusted to volume, and injected into a GLC. For identification, the peaks of interest were collected and their infrared spectra obtained. Hermann (*151*) used frustrated multiple internal reflection (FMIR) infrared for the identification of trace amounts of organophosphorus pesticides eluted from column, paper, and thin layer chromatograms.

Nangniot (*221*) determined 22 phosphoric acid ester pesticides by oscillographic polarography. Operating conditions for each are listed.

Damico (*85*) determined the mass spectra of 23 organophosphorus pesticides. In addition to giving the spectra, rearrangement and fragmentation patterns are discussed.

Specific Procedures. Blinn and Pasarela (*41*) used a colorimetric procedure to determine Abate, (*O,O, O',O'* - tetramethyl - *O,O'* - thiodi - *p* - phenylene phosphorothioate) in water, mud, and oysters. After extraction and cleanup, the Abate was hydrolyzed to 4,4'-thiodiphenol and reacted with 4-aminoantipyrine under oxidizing conditions. The color formed was extracted into butanol and read at 510 mμ. Recoveries from water at 0.025–0.045 ppm levels ranged from 79 to 88% and from mud and oysters at 0.1–0.66 ppm levels, 60 to 82%.

Katague and Anderson (*174*) used electron capture GLC for the determination of Bay 37289 (*O*-ethyl-*O*-2,4,5 - trichlorophenyl - ethylphosphonothioate), its oxygen analog, and 2,4,5-trichlorophenol, in a number of crops including alfalfa, beans, carrots, and potatoes. After extraction of the sample with acetone/benzene, the 2,4,5-trichlorophenol was removed with 0.1*N* NaOH for separate determination. Bay 37289 and its oxygen analog were then hydrolyzed to 2,4,5-trichlorophenol, acetylated, and injected into the GLC. The sensitivity of the method was about 0.1 ppm with recoveries ranging from 75 to 104%.

Several procedures have been reported for the determination of Bidrin (dimethyl phosphate of 3-hydroxy-*N,N*-dimethyl-*cis*-crotonamide). Sun *et al.* (*270*) described a fly bioassay said to be specific for Bidrin in the presence of 1 or more of 46 insecticides. It was sensitive to 0.05 ppm. Stevens and Van Middelem (*267*) used electron capture GLC to determine Bidrin in cabbage with a sensitivity of 0.01 ppm. After extraction and cleanup, the Bidrin was reacted with NaOH and iodine–KI solution to form iodoform which was extracted and injected into the GLC. The method, which is specific for methyl vinyl phosphates will thus also detect Phosdrin and phosphamidon. Murphey *et al.* (*219*) described a procedure in which Bidrin was hydrolyzed with NaOH and the resulting dimethylamine distilled and determined colorimetrically as dimethyl dithiocarbamate following addition of Cu^{+2} and CS_2. Recoveries from alfalfa, lettuce, orange peel, string beans, etc. at levels of 0.2–10 ppm ranged from 80 to 108%. The color reaction is specific for dialkylamines. Thus, *N,N*-dimethylcarbamates such as Dimetilan isolan, and Pyrolan would interfere and could be determined by this reaction. Lau (*192*) used cholinesterase inhibition for the determination of both Bidrin and the closely related Azodrin (dimethyl phosphate of 3-hydroxy-*N*-methyl-*cis*-crotonamide) in crops with a sensitivity of 0.1 ppm. The two compounds could be separated from each other and from other insecticides through procedures that are described.

The insecticide, diethyl-1-(2,4-dichlorophenyl)-2-chlorovinyl phosphate, or compound 4072, is known in England as chlorfenvinphos or by the trade name Birlane. Claborn and Ivey (*70*) described a procedure for its determination in milk and tissue in which compound 4072 is hydrolyzed to 2,2',4'-trichloroacetophenone and determined as such by electron capture GLC. Beynon and coworkers (*34*) reported the analysis for compound 4072 in soil and crops. After extraction of the sample and cleanup on a Florisil column, the insecticide was determined either by cholinesterase inhibition or by electron capture GLC. Compound 4072 consists of 6% cis isomer and 90% trans. When these isomers were gas chromatographed as the intact compounds, they had different retention times. Sensitivity of the two determinative procedures was about equal, 0.01 ppm. Robinson *et al.* (*247*) determined compound 4072 in sheep fat, liver, and other tissues. The parent compound and its metabolite, trichloracetophenone, were separated from chlorinated pesticides and from each other on a column of unactivated Florisil. Each was then determined by electron capture GLC. The sensitivity for compound 4072 was 0.003 ppm and for the trichloroacetophenone 0.001 ppm. Bazzi and Fabbrini (*22*) determined Cidial (ethyl mercaptophenylacetate, *O,O*-dimethyl phosphorodithioate) in oil by extracting a hexane solution of the oil with acetonitrile and after cleanup determining phosphorus as molybdenum blue.

Irudayasamy and Natarajan (*160*) reported a colorimetric method for the determination of carbophenothion (Trithion). The pesticide was hydrolyzed with alkali to *p*-chlorothiophenol which was then reacted with diazotized *o*-dianisidine to give a yellow color with maximum absorbance at 375 mμ.

Boone (*43*) used microcoulometric GLC to determine DDVP and naled (Dibrom) in apples, cabbages, and carrots. A silicic acid column was used for cleanup. Buechler *et al.* (*51*) modified and improved the resorcinol method for the determination of DDVP.

El-Refai and Giuffrida (*95*) used GLC with the thermionic detector to determine DDVP and trichlorfon (Dipterex) in water and in formulations. They also studied the hydrolysis rates of each pesticide and the rate of conversion of trichlorfon to DDVP. Anderson and coworkers (*10*) reported a method for the determination of trichlorfon and its metabolites, chloral hydrate, and trichloroethanol, in plant and animal tissue using electron capture GLC. After extraction and cleanup,

trichlorfon and chloral hydrate were injected into the GLC with trichlorfon breaking down and both compounds registering as chloral. To determine the trichlorethanol, a separate aliquot was acetylated to form trichloroethyl-acetate and then chromatographed. Mustafa *et al.* (*220*) used a colorimetric procedure for determining trichlorfon. The sample was spotted on a filter paper impregnated with 3,5-dintrobenzoic acid and heated at 70°C. for 2 minutes. Trichlorfon gave a blue spot, which was measured in a densitometer with a 550 mμ filter. The reaction, based on the cleavage of the P — C bond and reaction of the phosphite esters with the 3,5-dinitrobenzoic acid, distinguished between trichlorfon and DDVP, which did not react. Szyszko (*298*) reported an oscillopolarographic method for trichlorfon in which lindane and DDT did not interfere. However, maneb and zineb did interfere. Szyszko (*297*) also reported an oscillopolarographic method for demeton-*S*-methyl in foods where maneb and zineb did not interfere. Giang and Schechter (*119*) described a method for the determination of demeton and its metabolites in fruits and vegetables. After extraction and cleanup, the parent compounds and metabolites were all converted to the sulfones by oxidation with *m*-chloroperbenzoic acid. After additional cleanup on a cellulose column, the residue was dissolved in CS_2 and read in a 5-mm infrared cavity cell using 5× scale expansion. The absorption at 7.55 microns was used for calculation. Recoveries at 0.6 ppm levels ranged from 76 to 102%.

Gilmore and Cortes (*120*) used dual band TLC as cleanup for the determination of diazinon. By means of a divider in the applicator, the plates were coated with a mixture of Darco G60 and Solka-Floc on the lower 4 cm and with silica gel H on the remaining 16 cm. The crude extract along with a standard were applied to the charcoal–cellulose band, and after development, the sample spots, located by comparison with the standard R_f's, were removed for analysis. Fifty grams of spinach was purified by the above procedure and recoveries as followed by S^{35} labeled diazinon, averaged 95%. Abbott and coworkers (*2*) reported the use of multiband chromatoplates for the TLC determination of dimethoate. They prepared plates having 3 bands of different adsorbents and spotted cleaned up sample extracts. Development separated the dimethoate from the remaining plant materials and most other organophosphorus compounds. The dimethoate spots were made visible by spraying with Brilliant green and exposure to bromine vapor. The square root of the spot areas plotted against the log. of amount of dimethoate gave a straight line. Recoveries from fruits and vegetables at 0.1–0.5 ppm levels ranged from 80 to 108%. George *et al.* (*116*) described a colorimetric method for dimethoate in plants and milk. After extraction and cleanup, the residue was treated with methanolic NaOH and 1-chloro-2,4-dinitrobenzene to form a color which was read at 505 mμ. Although the oxygen analog would react, it did not come through the cleanup. The authors tested 33 insecticides, 3 herbicides, and 1 fungicide and found that they did not interfere with the analysis. Smart (*259*) compared three colorimetric procedures for the determination of dimethoate in fruits and vegetables, and reported that the procedure of Chilwell and Beecham worked best. Bache and Lisk (*15*) reported the use of GLC with the emission spectra detector (*204*) for the determination of dimethoate and phorate in soil.

Blinn and Boyd (*40*) reported a colorimetric as well as a thin layer procedure for the determination of the dithiolane insecticides, 2-diethoxyphosphinothioylimino-1,3-dithiolane, and its oxygen analog. After extraction and cleanup, the insecticides could be determined on TLC plates made with equal parts of silica gel-G and silica gel-HF. Under ultraviolet light, the compounds appeared as dark areas on a fluorescent background. In the colorimetric procedure, the cleaned up residue was treated first with acid and then with alkali to form thiocyanate which was converted to cyanogen bromide and reacted with benzidine in pyridine to form an intense red solution with an absorption maximum at 530 mμ.

Adams and Anderson (*8*) reported a spectrophotofluorometric procedure for the determination of Guthion [*O,O*-dimethyl - *S* - 4 - oxo - 1,2,3 - benzotriazin-3(4*H*)-ylmethyl phosphorodithioate] in milk and meat. After extraction and cleanup by liquid–liquid partitioning and the use of an alumina column, the pesticide was hydrolyzed to anthranilic acid, and divided into 2 equal aliquots; standard hydrolyzed Guthion was added to one. The fluorescence of both solutions was measured at 400 mμ using an activation wavelength of 340 mμ. The oxygen analog was measured as well as the parent compound. Sensitivity of the procedure was reported as 0.005 ppm in milk, 0.02 ppm in tissue, and 0.03 ppm in fat.

Anderson and coworkers (*11*) used a somewhat similar procedure for the determination of the anthelmintic, *N*-hydroxynaphthalimide diethyl phosphate. Based on the procedure of P. A. Giang [*J. Agr. Food Chem.* **9**, 42 (1961)] for the sulfur analog, Bayer 22,408, the fluorescence was measured at 480 mμ using an activation wavelength of 372 mμ.

Szyszko (*296*) used oscillographic polarography for the determination of Guthion. A most characteristic curve was obtained using a pH 4.0 acetate buffer as electrolyte.

Bowman and Beroza (*44*) reported two procedures for the determination of Imidan [*O,O*-dimethyl-*S*-phthalimidomethyl phosphorodithioate] in milk and corn plants. After extraction and cleanup, electron capture GLC was used for the determination step using a column which was preconditioned by injection of Imidan just prior to use. A colorimetric method, based on the hydrolytic cleavage to liberate formaldehyde which was then reacted with chromotropic acid, was also described although it was not so good as the GLC procedure.

Gutenmann and coworkers (*138*) also used electron capture GLC for the determination of Imidan. They reported that Imidan, its oxygen analog, folpet, and phthalic acid all had the same retention time. It was therefore believed that all broke down to phthalic anhydride on GLC.

Gudzinowicz (*126*) described some of the GLC properties of fenthion (*O,O*-dimethyl - *O* - [4 - (methylthio)-*m*-tolyl]-phosphorothioate) also known as Lebaycid. He used both electron capture and flame ionization detectors and reported that as little as 22 ng was easily detected.

Koivistoinen *et al.* (*182*) studied procedures for the extraction of malathion from fruits using a colorimetric procedure for the determinative step. They reported that for samples analyzed 2–3 days after pesticide application, tumbling the unmacerated fruit with benzene gave the highest values. However, for samples with longer periods between application and analysis, procedures which called for blending of sample with polar or mixed solvents gave higher values. Mestres and Chave (*210*) described a procedure for the determination of malathion in flour which involved extraction with acetonitrile and petroleum ether and Florisil column cleanup. Determination was by GLC using paired thermionic and flame ionization detectors. Sensitivity was reported as 0.1 ppm.

A number of workers reported procedures for the determination of parathion. Lodi (*195*) used electron capture GLC for its determination in wine and biological materials. With wine, a preliminary cleanup by paper or thin layer chromatography was needed. Ott *et al.* (*234*) described a rapid thin layer procedure having a sensitivity of 0.5 ppm by which they were able to obtain qualitative and semiquantitative results on canned peaches in one hour. Szyszko (*295*) used oscillopolarography in which zineb did not interfere but maneb did. Beckman and coworkers (*25*) analyzed for parathion in cole crops,

using a Florisil column to remove crop interferences and chlorinated pesticides before the final determination by either electron capture GLC or the Averill-Norris colorimetric method.

Moye and Winefordner (*216*) reported a rapid method for the determination of *p*-nitrophenol in urine, using phosphorimetry. The method could determine as little as 0.01 μg in 5 ml of urine in 40 minutes with an average recovery of 88%. Skuric (*258*) described a fluorometric method for the determination of methyl paraoxon based on the oxidation of indole in the presence of methyl paraoxon.

Winnett and Katz (*286*) described a colorimetric procedure for phorate (Thimet) in vegetables in which the cleaned up phorate residue was hydrolyzed with HBr and the released H_2S determined as methylene blue. Claborn and Ivey (*69*) determined ronnel in milk and in animal tissues, using electron capture GLC after cleanup on a Florisil column. As little as 0.001 ppm could be determined in milk and 0.005 ppm in tissues. Sulfotepp was measured by oscillopolarography by Szyszko (*299*).

Sumithion [*O,O* - dimethyl - *O* - (3 - methyl - 4 - nitrophenyl)phosphorothioate] has been determined colorimetrically by alkaline hydrolysis to sodium 3-methyl-4-nitrophenolate with the absorbance at 400 mμ being measured for quantitation. Kovac and Sohler (*184*) used this procedure following extraction and cleanup on Al_2O_3 thin layer plates to determine Sumithion in fruits and vegetables at levels as low as 0.1 ppm, while Franz and Kovac (*110*) reported a similar determination in milk. Oi and Umeda (*227*) used infrared for the simultaneous determination of Sumithion and methyl parathion in spinach and lettuce at about 1 ppm. The absorption peak at 10.3 microns was used to measure the Sumithion and the peak at 10.8 microns for methyl parathion. Coahran (*72*) reported the use of GLC with the thermionic detector for the determination of Zinophos (*O,O*-diethyl-*O*-2-pyrazinyl phosphorothioate) in soil following overnight extraction in a Soxhlet.

CARBAMATES

General Procedure. Eberle and Gunther (*94*) conducted an extensive investigation of 5 carbamates—carbaryl, Dimetilan, isolan, Pyrolan and Zectran. They studied the effect of natural sunlight and ultraviolet light on these compounds and presented useful basic information concerning their analytical behavior with GLC, TLC, oscillographic polarography, and fluorescence spectrometry. Henkel (*149*) described the TLC behavior of herbicidal carbamates and presented methods for their determination in soil, water, and potato extract. Adsorbents, solvent systems, and spray reagents were discussed. In a later publication, Henkel (*150*) reported on 3 thin layer chromatographic systems and 5 chromogenic color development systems for a number of *N*-methyl and *N,N*-dimethyl carbamates. Limits of detections for these carbamates ranged from 0.05 to 0.15 μg. Hylin (*158*) used thin layer chromatography to determine the dithiocarbamates on leaves. R_f values were given for ziram, thiram, zineb, maneb, and others. Sensitivity was approximately 2.5 μg.

Zielinski and Fishbein (*293*) presented data on the GLC behavior of *N*-substituted carbamates on 3 different columns while Fishbein and Zielinski (*107*) described the GLC behavior of the trimethylsilyl derivatives of a number of carbamates and ureas. Damico and Benson (*86*) developed and tabulated the mass spectra of 14 carbamate pesticides. The significant fragmentation ions were noted and ions were postulated for 8 *N*-methylcarbamate rearrangements. Chen and Benson (*63*) reported the infrared spectra of 32 carbamate pesticides and model compounds. The characteristic absorption frequencies and associated structures were tabulated in a summary and presented in a correlation chart. Broderick *et al.* (*49*) reported that methyl anthranilate, because of its absorption bands at 2.86 and 2.95 microns, interfered in the infrared determination of methylcarbamates. They described a method for removing methyl anthranilate in the analysis of Concord grapes for carbamate residues.

Specific Procedures. Johnson and Stansbury (*162*) reviewed the various methods for determination of carbaryl in a variety of products and in water, and described extraction and cleanup procedures.

Gutenmann and Lisk (*139*) used electron capture GLC for the determination of carbaryl in various crops. After extraction and cleanup, the carbaryl was hydrolyzed to α-naphthol, which was then brominated with I and Br_2 in glacial acetic acid. The brominated residue was taken up in benzene and injected into the GLC, which actually determined brominated 1-naphthyl acetate. Van Middelem and coworkers (*278*) reported a somewhat similar technique in which the α-naphthol formed by hydrolysis was brominated with bromine and the electron capture GLC determination made of brominated α-naphthol. Results were reported for levels as low as 0.1 ppm. Benson and Finocchiaro (*28*) modified the official AOAC colorimetric method for carbaryl [Johnson, D. P., *JAOAC* **47**, 283 (1964)] to eliminate the need for special equipment and to shorten the time of analysis. Johnson and Stansbury (*164*) modified the official AOAC method to determine carbaryl in bees, using a Florisil column for additional cleanup.

Gajan *et al.* (*112*) reported an oscillographic polarographic procedure whereby carbaryl could be determined in the presence of α-naphthol. Using a modified cleanup, recoveries of carbaryl from fortified crops averaged 95% at levels from 0.2 to 10.0 ppm. Among a number of pesticides tested, only *o*-phenylphenol interfered. Engst and coworkers (*100*) formed nitro derivatives of carbaryl by treatment with HNO_3. These derivatives were then determined quantitatively by both d.c. and pulsed polarography with a sensitivity of 0.5 and 0.005 ppm of carbaryl, respectively.

Finocchiaro and Benson (*105*) used thin layer chromatography for the determination of carbaryl. After the samples were spotted and the plates developed, the carbaryl was hydrolyzed by spraying with KOH and then coupled with *p*-nitrobenzenediazonium fluoborate to produce blue spots. The procedure was sensitive to about 0.05 ppm and distinguished carbaryl from α-naphthol, which had a lower R_f. Dingle (*91*) determined carbaryl in cattle dipping solutions by simple dilution with ethanol and measuring the absorbance at 280 mμ. Correction for α-naphthol was based on its absorbance at 324 mμ.

Johnson and Stansbury reported similar colorimetric procedures for the determination of Temik, 2-methyl-2(methylthio) propionaldehyde *O*-(methylcarbamoyl) oxime (*165*) and for Tranid, 3-exo-chloro-6-endocyano-2 - norbornanone - *O* - (methylcarbamoyl)-oxime (*166*). The oxime carbamates were hydrolyzed with NaOH to form the oxime which was then hydrolyzed with HCl to release hydroxylamine. The hydroxylamine was oxidized with iodine to nitrous acid which diazotized sulfanilic acid. The latter was coupled with 1-naphthylamine to form a color which was read at 530 mμ. The sensitivity of these methods was reported to be about 0.03 ppm. Niessen and Frehse (*225*) described a colorimetric procedure for the determination of Bayer 39,007 (Baygon, Unden) (*o*-isopropoxyphenyl methylcarbamate) in leafy vegetables. After extraction and cleanup, the pesticide was saponified, neutralized, and treated with triethanolamine, aminoantipyrine, and $K_3Fe(CN)_6$ to form a color read at 490 mμ.

CHOLINESTERASE INHIBITION

Enzyme inhibition continues to be a useful tool in pesticide residue work. Its lack of specificity, objectionable as it may be in many uses, actually enhances its value as a screening tool,

since dangerous amounts of inhibitor may be detected no matter of what nature. Beynon and Stoydin (*37*) reported such a rapid screening test for cholinesterase inhibition making use of agar-agar plates. As little as 0.001 μg of DDVP and other inhibitors could be detected.

Ortloff and Franz (*230*) conducted the test for detection of organophosphorus pesticides on TLC plates, using either 2-azobenzene-1-naphthylacetate (yielding white spots on a red background) or indoxyl acetate (white spots on blue) as substrate. Ackermann (*6*) used silica gel TLC plates for the semiquantitative estimation of organophosphorus and carbamate pesticides. Beam and Hankinson (*23*) reported a procedure for the determination of organophosphorus compounds and carbaryl in milk based on cholinesterase inhibition.

Several workers described the automation of cholinesterase inhibition determinations using the Technicon *Auto*Analyzer. Among these are Voss (*283*) and Ott and Gunther (*231*) whose procedures required prior extraction and cleanup. In a later publication, Ott and Gunther (*232*) used the spots scraped off a TLC plate as input sample for the *Auto*Analyzer.

Guilbault and Kramer (*128*) reported 2 new fluorogenic substrates, resorufin butyrate and indoxyl acetate. Both are nonfluorescent compounds which are hydrolyzed by cholinesterase to highly fluorescent materials. As little as 0.0003 units/ml of horse serum cholinesterase could be determined. However, in addition to cholinesterase, such enzymes as acylase, acid phosphatase, and chymotrypsin also hydrolyzed the substrates to varying degrees. Bauman *et al.* (*21*) reported an immobilized enzyme system which could be used for continuous monitoring of substrate concentration and thus for the detection of cholinesterase inhibitors. A urethane foam pad was impregnated with starch-immobilized cholinesterase and a solution of the substrate, butyrylthiocholine, passed through it. Any inhibition acting on the enzyme reduced the hydrolysis to easily oxidized thiocholine iodide. This caused a change in current flowing through 2 platinum electrodes placed on opposite sides of the pad and thus signaled the presence of an inhibitor. Guilbault and Kramer (*131*) used a similar immobilized enzyme pad in a continuous fluorometric system for determining anticholinesterase compounds in air and water. The substrates, the acetyl and butyl esters of 1- and 2-naphthol, which do not fluoresce, were continuously passed through the pad and were hydrolyzed to the fluorescent phenols. Upon inhibition, the fluorescence dropped.

HERBICIDES

Faust and Hunter (*104*) have reviewed the chemical methods for the detection of aquatic herbicides including diquat, paraquat, and the phenoxy alkyl acids. They discussed various cleanup and determinative procedures. Henkel (*148*) reported on the TLC behavior of the phenoxyalkyl acid herbicides. Adsorbents and pretreatment, liquid phases, R_f's and reagents for detection were discussed. Hosogai and Kawashiro (*156*) separated 16 herbicides in mixtures by TLC, using various nonpolar and polar solvents. Johnson (*168*) described a colorimetric method for the determination of *N*-1-naphthylphthalamic acid in cabbage, asparagus, and alfalfa meal. The sample was heated with zinc and NaOH and the released 1-naphthylamine steam distilled. After cleanup, the 1-naphthylamine was coupled with diazotized sulfanilic acid and the absorbance read at 535 mμ.

Olney and coworkers (*228*) used a modified procedure for the electron capture GLC determination of amiben in vegetables. The sample was digested with alkali to release amiben from any complexes. After extraction and cleanup, it was methylated and further cleaned up on a Florisil column before being injected into the GLC. Sensitivity of 0.01 ppm was reported.

Hilton and Uyehara (*152*) modified the colorimetric procedure of Storherr and Burke [*JAOAC* **44,** 196 (1961)] to determine amitrole in sugar cane. Recoveries ranged from 71 to 125% at levels of 0.0025 to 0.5 ppm. Pease (*240*) used temperature programmed, microcoulometric GLC for the determination of bromacil in tissue, plants, and soil. Recoveries averaged 98% at levels of 0.04 to 5.6 ppm.

A number of methods have been reported for the determination of 2,4-D and other chlorophenoxy alkyl acid herbicides. Hagin and Linscott (*141*) described a procedure for the determination of 2,4-D and 2,4-DB in forage plants which made use of quick freezing and blanching of the plant material before extraction. Determination was by electron capture GLC after esterification with diazomethane.

Meagher (*205*) reported a procedure for 2,4-D and 2,4,5-T in citrus. The peel was extracted by blending with hot acetone, and the bound, the free acid, and the ester forms were separated, and each was hydrolyzed to the free acid. The free acids were esterified with 2-butoxyethanol saturated with HCl gas and cleaned up on a Florisil column before determination by electron capture GLC. Chromatographing the compounds as their butoxyethyl esters had the advantage that the long retention times separated the peaks from interferences present near the solvent front. Recoveries ranged from 89 to 93% at 0.0002–0.4 ppm levels. Crosby and Bowers (*81*) reported a method for the determination of 2,4-D in milk and other high protein samples where the 2,4-D may be bound to the sample. They refluxed the sample with NaOH and methanol to release the 2,4-D which was methylated for electron capture GLC determination. Yip (*288*) used programmed temperature microcoulometric GLC to determining a number of the chlorinated herbicides in oils. Recoveries ranged from 87 to 113% at 0.02–0.08 ppm levels. Yip and Ney (*289*) determined free 2,4-D and its esters in milk and forage. After extraction, cleanup, and methylation, determination was made by both microcoulometric GLC and paper chromatography.

Flanagan *et al.* (*108*) reported a paper chromatographic procedure for dalapon, using $AgNO_3$ and phenoxyethanol as chromogenic reagent. Smith and coworkers (*261*) described a method for dicamba in milk and a number of crops, using electron capture GLC after methylation. Meulemans and Upton (*211*) determined dichlobenil and its metabolite 2,6-dichlorobenzoic acid in fruits, soil, water, and fish. The two were separated and determined by electron capture GLC after cleanup. The dichlobenil was chromatographed as such but the metabolite was first methylated. Beynon and coworkers (*35*) reported an electron capture GLC method for the determination of dichlobenil and Chlorthiamid (2,6-dichlorothiobenzamide) in crops, soils, and water. Several extraction and cleanup procedures and 3 GLC columns are described. Recoveries ranged from 80 to 100% at levels of 0.03–5.0 ppm. Boyack *et al.* (*48*) used GLC with a flame ionization detector to determine diphenamid in vegetables and peanuts, with a sensitivity of 0.05 ppm.

Engelhardt and McKinley (*98*) studied the polarographic behavior of diquat. Using previously published extraction and cleanup procedures, they were able to determine diquat polarographically at levels as low as 0.01 ppm with recoveries of 84–97%.

Calderbank and Yuen (*61*) described an improved ultraviolet method for diquat in potatoes. After extraction and cleanup on a cation exchange column, the diquat was reduced to a free radical with sodium dithionite and its absorbance read at 379 mμ. Earlier, they had reported a similar method for paraquat (*60*). Katz (*175*) reported both colorimetric and TLC procedures for five substituted urea herbicides in water. After extraction with chloroform, diuron, monuron, linuron, neburon, and fenuron were hydrolyzed, diazotized, and coupled with *N*-(1-naphthyl)ethylenediamine dihydrochloride to form magenta dyes which were extracted with *n*-butanol and read at

555 mμ. TLC with ninhydrin spray reagent was used for identification of the specific herbicide.

Gutenmann and Lisk (*140*) used electron capture GLC to determine DNOC, DNOSBP, ioxynil, and bromoxynil in milk, apples, and grains. They noted that reacting the phenolic pesticides with diazomethane to form the methyl ethers eliminated trailing on the GLC. Boggs (*42*) also reported the superior chromatographic behavior of the methyl ethers of the dinitrophenols. Bache and Lisk (*14*) reported a similar GLC procedure for ioxynil but used the emission spectrometric detector of McCormack, Tong, and Cooke (*204*) to measure the atomic iodine line at 2062 Å. Ford and coworkers (*109*) described a colorimetric procedure for the determination of norea (Herban) in vegetables, grains, and oil seeds with a sensitivity of 0.1 ppm. The herbicide was hydrolyzed by caustic to dimethyl amine and the primary bicyclic amine which were both steam distilled. After reaction with 1-fluoro-2,4-dinitrobenzene, the complex with the bicyclic amine was separated out on an alumina column and the absorbance in alkaline dimethylformamide read at 443 mμ. Koivistoinen and Karinpää (*181*) reported a modified procedure for IPC and CIPC on fruits and vegetables. Samples were extracted by tumbling with benzene and the herbicides hydrolyzed. The amines were steam distilled, diazotized, and coupled with *N*-(1-naphthyl)ethylenediamine; the absorbance was read at 555 mμ. Recoveries from spinach, cabbage, tomatoes, and strawberries ranged from 86 to 113% at 0.5–200 ppm levels.

Pease (*242*) described a gas chromatographic method for the determination of the herbicide 3-cyclohexyl-5,6-trimethyleneuracil in sugar beets and soil. Using the flame ionization detector, crop blanks ran as high as 0.04 ppm. Merkle *et al.* (*207*) used electron capture GLC after methylation to determine picloram (4-amino-3,5,6-trichloropicolinic acid) in soil. They noted that the acidity of the extracting solvent (acidified acetone) was very important. It had to be acid enough to convert the picloram to the free acid but not so acid as to convert the amino group to a quaternary salt.

Kerr and Olney (*176*) determined trifluralin in vegetables by electron capture GLC and prometryne by hydrolysis to hydroxypropazine which was measured spectrophotometrically. Drescher (*92*) described 2 methods for determining pyrazon. In one procedure which can be used for detection on paper or thin layer chromatograms, the pyrazon was diazotized, losing its chlorine atom, and was then coupled with 2-naphthol to form a dye. In the second procedure, pyrazon was treated with NaOH-methanol to split off aniline which was steam distilled, diazotized and coupled with *N*-(1-naphthyl)ethylenediamine. The absorbance, measured at 530 mμ, permitted detection as low as 0.05 ppm.

Several workers have reported methods for the determination of the *s*-triazines. Mattson *et al.* (*201*) described a procedure for the determination of both chloro and methylmercaptyl *s*-triazines, using microcoulometric GLC with the chlorine and sulfur cells, respectively. A sensitivity of 0.05 ppm was attainable for most crops and recoveries ranged from 75 to 107%. Abbott and coworkers (*1*) used thin layer chromatography to determine 8 *s*-triazines in soil and water. Using silica gel G as the adsorbent the developed chromatograms were sprayed with an 0.5% solution of Brilliant green and exposed to Br_2 fumes. The triazines appeared as deep green spots on an off white background and were immediately marked in outline. For quantitation, the square root of the area of the spots plotted against the log of weight triazine gave a straight line. Manner (*197*) also used TLC to detect 8 *s*-triazines on silica gel GF254. Ninety-one mobile solvent systems and R_f's for each are listed. Plates were examined under ultraviolet light (254 mμ) with the *s*-triazines appearing as dark brown spots on a yellowish green, fluorescing background. The spots could be eluted for additional determinations. Radke *et al.* (*244*) evaluated the pyridine–alkali colorimetric method for the determination of atrazine. They showed that the color intensity increased with acidity of the system and that 20° ± 2° C was a suitable temperature for color development. Chiba and Morley (*66*) reported a microcoulometric GLC method for trichloroacetic acid in wheat sensitive to 0.1 ppm. Compounds such as Kelthane, which could break down to give $CHCl_3$, interfered.

FUNGICIDES

Gunther and Ott (*137*) described a fully automated procedure for the determination of biphenyl in citrus fruit rind. The sample was automatically homogenized and steam distilled; waxes and oils were removed from distillate and the biphenyl in cyclohexane was fed through a cell of a recording ultraviolet spectrophotometer. Chioffi (*67*) used TLC on silica gel to determine biphenyl and *o*-phenylphenol in lemons. Norman and coworkers (*226*) used TLC for cleanup in the determination of biphenyl in citrus fruit and wrappers. Sample extracts were spotted on Eastman silica gel chromagrams and, after development, the spots were located under ultraviolet light. The spots were then cut out, extracted with ethanol, and the absorbance of the biphenyl was measured at 248 mμ. Sensitivity was reported as 5 ppm in citrus fruit and 5 mg/wrapper. McCarthy and Winefordner (*202*) combined a TLC cleanup with phosphorimetric determination for biphenyl in oranges. For the phosphorimetry they used an excitation wavelength of 275 mμ and emission of 470 mμ. Vogel and Deshusses (*281*) reported a GLC procedure for biphenyl in citrus fruit and wrappers. The biphenyl was distilled and absorbed in cyclohexane, which was injected into a GLC with an ionization detector. Sensitivity was reported as 0.5 ppm. Viel (*279*) reported a colorimetric method for the determination of captan and folpet in grapes and strawberries. After extraction and cleanup, the dried residue was treated with pyridine and then with KOH and the absorbance read at 435 mμ. Fishbein *et al.* (*106*) used thin layer chromatography on silica gel for the determination of captan and Captax (2-mercaptobenzothiazole). As chromogenic reagents, they used resorcinol in glacial acetic acid for captan and cupric chloride–hydroxylamine for Captex. Cheng and Kilgore (*64*) described an electron capture GLC method for the determination of Botran (2,6-dichloro-4-nitroaniline) in stored fruits. A sensitivity of 0.01 ppm was attained by tumbling the macerated sample with benzene, drying the benzene with Na_2SO_4, filtering, and injecting into the GLC. Vogel and Deshusses (*280*) reported a polarographic procedure for 2,6-dichloro-4-nitroaniline which had an accuracy of ±3% at levels of 2–7 ppm.

Hoffman and coworkers (*154*) reported both a colorimetric and thin layer method for the determination of dichlone in tobacco. For the colorimetric determination, the residues were extracted by blending with benzene, cleaned up on a Florisil column, evaporated, dissolved in absolute alcohol, triethylamine added, and absorbance read at 640 mμ. In the TLC method, the developed plates were sprayed with diethylamine and the spots compared with standards. Miller (*212*) investigated 4 colorimetric methods for dichlone and combined parts of 2 for collaborative study. The sample was stripped with benzene and cleaned up on a Florisil column, and color was developed with dimethylamine for reading at 495 mμ. Ten collaborators analyzed samples containing 0.5–4.0 ppm dichlone and obtained recoveries with an overall range of 78–112%. Sensitivity of the method was 0.25 ppm.

Thornton and Anderson (*273*) used electron capture GLC for the determination of Chemagro 2635, a mixture of 1,2,4-trichloro-3,5-dinitrobenzene and 1,2,3-trichloro-4,6-dinitrobenzene. The sensitivity of the method was 0.1 ppm and recoveries from cucumbers, potatoes, spinach, cottonseed, etc. were over 85%. Lyalikov and Solonar (*196*) described the polarographic determination

of hexachlorobutadiene and stated that other chlororganic compounds did not interfere.

Cullen and Stanovick (*82*) used electron capture GLC for the determination of korax, 1-chloro-2-nitropropane, in vegetables. The sample was blended with benzene and methanol and after washing and drying the benzene solution was injected into the GLC. Recoveries averaged 80–102% at 0.005–0.1 ppm levels. Voloshchenko and Klisenko (*282*) described a colorimetric method for the determination of Mylone, (3,5-dimethyl - 1,3,5,2*H* - tetrahydrothiadiazine-2-thione). The compound was hydrolyzed with acid to release CS_2 which was reacted with diethylamine and cupric acetate to form copper dithiocarbamate. The sensitivity of the method was reported as 0.02 ppm and recoveries from vegetables ranged from 93 to 120%. Cotta-Ramusino and Stacchini (*76*) reported a spectrofluorometric method for the determination of *o*-phenylphenol on citrus fruit. The extract was diluted with 0.1*N* NaOH and the fluorescence measured at 425 mμ, using an excitation wavelength of 325 mμ.

MISCELLANEOUS PESTICIDES

Kroeller (*188*) used the colorimetric method for arsenic in food based on the reaction of AsH_3 with silver diethyldithiocarbamate after wet digestion and preliminary separation by distillation from HCl. Kirchmann and Roderbourg (*179*) used radioactivation for the determination of arsenic in plant matter. After irradiation the arsenic was separated by wet ashing and precipitation as As_2S_5 before measurement of As^{76}. The limit of detection was 2×10^{-8} gram. Banderis (*17*) reported a colorimetric method for the determination of chlorates in plants and soil. It was based on the reaction of chlorates with HCl to release chlorine. The chlorine was reacted with *o*-tolidine to form a yellow color which was read at 448 mμ.

Several methods have been reported for the determination of cyanide. Kroeller (*189*) used a specially designed still to distill cyanide from foods under nitrogen. The distilled HCN was converted to cyanobromide which reacted with pyridine–benzidine to form a red color which was measured. Guilbault and Kramer (*129*) reported a fluorometric method in which the cyanide was reacted with quinone monoxime benzene sulfonate ester in dimethylsulfoxide to give a green fluorescence. With an excitation wavelength of 440 mμ and emission of 500 mμ as little as 0.5 μg of cyanide was easily detected and no other ions were found to interfere. These authors (*130*) investigated this reaction and those of various other quinone derivatives with cyanide, studying the effect of substituents, solvents, pH, and interferences. They found that the fluorescence produced with *p*-benzoquinone was proportional to the cyanide concentration over the range of 0.2–50 μg. They later reported (*132*) an ultra-sensitive specific qualitative test for cyanide, using *p*-nitrobenzaldehyde and *o*-dinitrobenzene to form a highly colored blue complex by which as little as 3 nanograms total cyanide could be detected.

Steller *et al.* (*264*) described a colorimetric method for cyanimide on cottonseeds. The seeds were extracted by tumbling with water followed by cleanup with activated charcoal. The cyanimide was then reacted with a solution of trisodium pentacyanoammine ferroate to give a red color which was read at 530 mμ. The sensitivity of the method was 0.03 ppm and recoveries at levels of 0.03–0.20 ppm averaged about 85%.

Cottonseed has been analyzed for DEF (*S,S,S*-tributyl phosphorotrithioate), using gas chromatography after Florisil column cleanup. Thomas and Harris (*272*) used the microcoulometric detector while Thornton and Anderson (*274*) used electron capture detection in their procedure. Bielorai and Alumot (*38*) reported a procedure for the determination of ethylene dibromide in foods and feeds, using GLC with a flame ionization detector. Benzene was added to the sample and distilled. The distilled benzene was dried and then injected into the GLC. Results by this method were in good agreement with the chemical titrimetric method at 15–1500 ppm levels. Kimura and Miller (*178*) reported a thin layer chromatographic procedure for the determination of gibberellic acid in rhubarb having a sensitivity of 3 ppb. The gibberellic acid spots were located on the acidified silica gel plate by their fluorescence under ultraviolet light. Zielinski and Fishbein (*292*) reported that they could gas chromatograph maleic hydrazide after reacting it in pyridine with hexamethyldisilazane in the presence of trimethylchlorosilane. Hoffman *et al.* (*153*) discussed possible interferences in the colorimetric method for maleic hydrazide and described a Norit-A cleanup to eliminate interferences. Lane (*191*) conducted a collaborative study of the colorimetric method for maleic hydrazide [J. R. Lane, *JAOAC* **46,** 211 (1963)]. Five collaborators obtained average recoveries of 70–92% from samples of cranberries, potatoes, onions, etc. fortified at 1.3- to 85-ppm levels.

A cold vapor atomic absorption apparatus was designed by Schachter (*255*) to measure submicrogram quantities of mercury in the vapor phase at room temperature. Using this apparatus, Pappas and Rosenberg developed procedures for the determination of mercury in wheat (*236*) and in fish and eggs (*237*) at levels as low as 0.01 ppm. Epps (*101*) used the colorimetric dithizone method for determining mercury in rice following digestion with nitric and perchloric acids. An excellent and thorough study of the dithizone method for mercury in foods was recently reported (*169*). Each step in the procedure was evaluated and the resulting method studied collaboratively. Recoveries at 0.1 ppm were excellent and the sensitivity was thought to be 0.05 ppm (dried sample). Neutron activation has also been used for the determination of mercury. Kim and Silverman (*177*) used it for the analysis of wheat and tobacco, making a chemical separation after irradiation before measuring activity of ^{197}Hg. Tomizawa and coworkers (*277*) used neutron activation to determine mercury in rice. Again, a chemical separation was made after irradiation but these workers measured ^{203}Hg.

Hearth *et al.* (*147*) reported an oscillopolarographic method for the determination of Morestan (6-methyl-2,3-quinoxalinedithiol cyclic carbonate) in orange rind. The hexane stripping solution was concentrated and cleaned up on silica gel TLC plates. The spots were located by their fluorescence under ultraviolet light, scraped off, and eluted with ethanol for the polarographic determination. Martin and Schwartzman (*199*) reported that the ultraviolet spectrophotometric method for nicotine, at times, could not distinguish between crop interference from mustard greens and nicotine; they described a TLC procedure which did make the distinction.

Narahu and coworkers (*222*) used the gas chromatograph with a thermal conductivity detector to determine pentachlorophenol in soy sauce. They chromatographed the PCP as the phenol, using dehydroacetic acid as an internal standard. Cheng and Kilgore (*65*) in determining pentachlorophenol and its sodium salt in fruits, first methylated these compounds with diazomethane before using electron capture GLC for the determinative step. Akisada (*9*) described a colorimetric method for pentachlorophenol and tetrachlorophenol in urine and in air. The phenols were distilled off from the acidified urine while the air was passed through an absorbing solution containing a borate buffer at pH 7.13. They were then reacted with 4-aminoantipyrine and $K_3Fe(CN)_6$ and the colors extracted into xylene. The absorbance was measured at 470 mμ for tetrachlorophenol and at 570 mμ for pentachlorophenol. Zielinski and Fishbein (*294*) gas chromatographed piperonyl butoxide and a number of 3,4-methylenedioxyphenyl derivatives, both as the compounds themselves and as the methyl and trimethylsilyl derivatives of these compounds. Mestres and Barrios (*208*) used gas chromatography to determine propylene oxide and propylene glycol in fruit. By means of a system in which 1–20 mg samples were

introduced directly into the injection chamber, they demonstrated that propylene oxide was rapidly absorbed by prunes in which it was hydrolyzed to propylene glycol.

Delfel (*88*) described the use of HI as a color reagent for the detection of rotenone on paper chromatograms. Rotenone gave a characteristic blue color with the reagent while elliptone gave a pink or violet color. None of the other materials present in crude extracts of *Derris elliptica* or *Tephrosia vogelii* gave any color with the reagent. Delfel (*89*) also studied the TLC behavior of rotenone and related compounds and described a number of solvent systems and chromogenic agents to give desired separations. Johnson and Stansbury (*163*) reported a colorimetric method for the defoliant, sodium cis-3-chloroacrylate (Prep), in cottonseeds. The sample was acidified and the free acid extracted by blending with 1-butanol. After cleanup, it was reacted with pyridine and NaOH to produce a colored solution which was passed through an alumina column and then read at 395 mμ. Toxaphene, chlordane, DDT, and TDE did not interfere. Christian and coworkers (*68*) described a polarographic method for selenium in biological materials while Cummings *et al.* (*84*) used a colorimetric procedure measuring the absorbance of a complex of selenium with 3,3′-diaminobenzidine. Pease (*241*) determined sulfamates in apples and pears by removing all the sulfates and then reducing the sulfamates to H_2S which was reacted with *p*-dimethylaminoaniline to form methylene blue. Bowman and Beroza (*47*) reported a gas chromatographic procedure for the determination of tepa, apholate, hempa, and several other chemosterilants. Using the flame photometric detector of Brody and Chaney (*50*) they could detect as little as 0.1 ng of the sterilants. Bullard (*52*) used GLC with flame ionization detector to determine tetramine (tetramethylenedisulfotetramine), a systemic toxicant used to keep animals from feeding on seed and young seedlings. Recoveries from a variety of foliages consistently averaged above 80%. Billy and coworkers (*39*) reported a spectrophotometric procedure for the determination of the lampricide, 3-trifluoromethyl-4-nitrophenol (TFM), in water and in fish tissue. After cleanup by liquid–liquid partitioning and ion exchange column the determination was made by measuring the absorbance at 395 mμ.

MISCELLANY

Duggan (*93*) described the procedures used by the Food and Drug Administration to validate multiple residue methods on the varieties of foods. To illustrate the magnitude of the problem, he pointed out that with the 12 major food classes and the 50 chemicals most commonly found, there were 1.35×10^{16} possible different combinations that the residue chemist could encounter.

In exploring methods for the determination of organo-metallic fungicides on crops, Gudzinowicz and Luciano (*127*) showed that atomic absorption could be used to determine zinc, manganese, and iron. However, the amounts of these metals found in untreated plants were so high that their measurement did not seem a promising means of detecting fungicide residues.

Beroza and Bowman (*30*) introduced the concept of *p*-values—based on the distribution ratios between 2 immiscible solvents—as the basis for identification of pesticide residues and other compounds. In its simplest form, a solution of the residue was analyzed by GLC and then after shaking with an equal volume of immiscible solvent it was again analyzed by GLC. The ratio of the 2nd result to the first is the *p*-value. The authors refined the procedure by the use of a 5-plate Craig counter current distribution apparatus (*31*); they listed *p*-values for 131 pesticides in 6 binary systems (*45*); they designed an apparatus for rapid extraction (*32*) and a device as well as an equation for obtaining *p*-values using nonequilibrated solvents (*46*). They (*33*) also studied the extraction of added pesticides from milk with hexane–diethyl ether with and without prior mixing of sample with ethanol. They found that without ethanol, the extraction efficiencies paralleled the polarities as judged by *p*-values.

Farrow *et al.* (*102*) reported a cleanup procedure for both chlorinated and organophosphate pesticides based on vacuum sublimation. The dried sample extract was subjected to vacuum sublimation at 85°C. for 15 minutes and the pesticide residues were collected on a cold finger cooled with Dry Ice–acetone. The residues were rinsed from the cold finger, made to volume, and injected into the electron capture GLC. The procedure was tested on 35 pesticides in spinach and recoveries for 25 of these exceeded 80%. Most of the others were recovered in the 60–80% range except for a few low values from waxy plant extractives.

Rybakov (*248*) reviewed the use of polarography and discussed methods for the analysis of pesticides containing sulfur, phosphorus, chlorine, and nitrogen.

Coffin (*73*) reviewed the use of paper chromatography in pesticide residue analysis, discussing its advantages and disadvantages as well as various detection systems.

Salo and Salminen (*251*) tabulated TLC data for 29 common pesticides under a number of solvent systems.

Chen (*62*) described a micro technique for infrared by which good spectra could be obtained from as little as 1 μg of pesticide. The procedure, which has been used to identify pesticides separated by GLC, consisted of incorporating the sample into 4 mg of KBr in a micropellet formed in a 2-mm diameter hole in folded aluminum foil. It was pointed out that it was essential to compare sample spectra with standard spectra obtained in the same manner since weak bands are missing at microgram levels.

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Petroleum

F. D. Tuemmler, Shell Development Co., Emeryville, Calif.

Introduction

THIS IS THE EIGHTH in a series of Reviews of Analytical Chemistry in the Petroleum Industry (*11A*, *12A*, *22–26A*) sponsored by the Petroleum Division of the American Chemical Society. It covers essentially the years of 1964 and 1965, or rather the papers abstracted in the ACS *Chemical Abstracts* (Sections 2 and 27), in the *American Petroleum Institute Refining Literature Abstracts*, in the *Journal of the Institute of Petroleum* and in the *Analytical Abstracts* (*London*) from the period July 1964 to July 1966. Because of the time interval between original publication and abstracting, some papers published prior to 1964, but not referenced in the earlier reviews, have been included. Generally, those published in 1966 and abstracted, have been set aside for the next issue in this series of Reviews.

Several persons (E. T. Seafe, Mobil Oil Corp., J. F. Hickerson, Humble Oil and Refining Co., and the writer) were involved in the searching of the several abstract journals mentioned above for a collection of abstracts of appropriate papers. These abstracts were further intensely screened (by R. L. LeTourneau, Chevron Research Corp. and the writer) and organized by various subjects that seemed to possess a community of interest. These were further screened by the sixteen Reviewers of the twelve subject classifications which follow. The success of this review is due to the generous assistance of these dedicated people.

In organizing the papers into subject classifications, it was the basic pattern to accommodate papers dealing with a class of products. Since many analyses by a given technique or by competitive techniques would be scattered throughout the Review, classifications by component or by property measured were set up to simplify location of the more closely related material. Thus, it became necessary to decide under which catagory a given paper belonged. Some readers will undoubtedly prefer that we should have classified many papers differently and in these cases we ask their tolerance.

While nearly all of the papers included in this review concern a specific subject, there are a few which deal with reviews of analysis of material types, or of specific analytical processes. On the side of products, there is the three-volume work on bituminous materials including their analysis by Hoiberg (*14A*, *15A*). Advances in general gas analysis have been reviewed by Pavlenko (*37A*) and in fuel gas analysis by Raschke (*38A*). Il'ina (*18A*) describes the use of spectrographic analysis for measurement of impurities in fuels and lubricants. A detailed description of the analysis of catalytic feed streams, petroleum products and catalysts for the more common elements in the parts per million and parts per billion range appeared in a book by Milner (*34A*).

An interesting historical paper by Kurtz (*20A*) reviewed the development of hydrocarbon analysis during the past 100 years. Dawson (*7A*) discussed the role of hydrocarbon analysis in refinery quality control operations. Application of gas chromatography in this area is discussed by Dietz (*8A*), Mayor (*33A*), Martin (*31A*), and Andrezijak and Gilewiz (*1A*). Aspects of linear elution adsorption chromatography for extraneous material was reviewed by Snyder (*40A*).

Applications of neuclear magnetic resonance in analytical chemistry has been described by Flockhart and Pink (*10A*), Flanagan *et al.* (*9A*), Chamberlain (*5A*). Zimmerman (*42A*), Oelert and Luther (*35A*), Mair (*30A*) and Louis (*28A*). The large number of review papers indicate the rapidly growing use of this newer technic.

Another analytical process that is rapidly expanding its usefulness is neutron activation analysis; papers by Braier and Mott (*3A*), Iddings (*17A*), Hull (*16A*), and Guinn *et al.* (*13A*) have indicated its usefulness. The utility of x-ray fluorescence analysis has been described by Louis (*27A*) and by Okamoto (*36A*). Some applications of the mass spectrometer have been described by Reed (*39A*). The use of an electron probe microanalysis in a