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Detection and Measurement of Pesticide Residues

Gas chromatographs with selective detectors have streamlined analysis.

Donald J. Lisk

The term "pesticide residue" refers to deposits of one or more pesticides, and possibly their metabolites, on or below the surface of a biological and often edible substance. A metabolite is an altered pesticide molecule which may be more or less toxic than the original compound that was applied for pest control. Metabolites may result from metabolic reactions in the plant or animal (oxidation, reduction, hydrolysis, esterification) or weathering (ultraviolet light, atmospheric oxidation) which the parent compound undergoes as it comes in contact with a living organism (plant, fungus, insect, or other).

Pesticides can be divided into three categories. (i) Insecticides—to control injurious insects affecting plants, animals, and humans. (ii) Fungicides—to prevent or cure plant diseases caused by fungi. (iii) Herbicides and plant growth regulators—to kill weeds and to make plants grow faster or slower or to alter them in order to increase their benefit to man. Rodenticides, antibiotics, defoliants, and desiccants could also be included.

Pesticides become residues directly or indirectly: (i) by direct application on crops or animals, (ii) plant uptake from treated soil, (iii) drift or runoff from adjacently treated areas, and (iv) by-product contamination, such as residues in meat, milk, and eggs picked up from feeding forage which contained residues. Pesticide molecules are designed to be toxic for effective pest control. Owing to the state of the art of control, and to biochemical similarities in many species, the selectivity of the toxicant is sometimes too broad. Potency occasionally spills over to affect organisms other than the target. Concern for humans and valuable domestic and wildlife species, which may suffer ill effects from long-term exposure, necessitates accurate analysis of toxic residues.

A decade ago the number of pesticides was still comparatively small. Most residue measurements involved either spectrophotometry, combustion analysis, enzymatic methods, or biological assay. However, synthesis of new compounds steadily increased and now we have a veritable arsenal of effective chemicals, with thousands of new compounds being tested each year.

For the kinds of analyses discussed here, the molecular structures of these compounds may be conveniently placed in three broad groups: halogenated compounds, organophosphorus insecticides, and others containing carbon, hydrogen, oxygen, and possibly sulfur or nitrogen. In addition, there are compounds which would fit into two or all of these groups. Prominent classes of compounds include: chlorinated hydrocarbons, organophosphorus esters, phenyl-substituted carbamates and ureas, halogenated phenoxy and benzoic acids, triazines, benzonitriles, nitrophenols, miscellaneous hydrocarbons containing sulfur, and heterocyclic, polynuclear, and organo-metallic compounds.

Residue Sampling, Extraction, and Isolation

A sampling procedure in residue analysis must be designed to minimize not only the errors from biological variability and unevenly distributed spray deposits, but also the extreme dilution errors which are inherent in the procedure. The final measurement is only as valid as the sample is representative.

For example, 1.0 kilogram of an herbicide may be applied to a hectare of soil (the plow layer is estimated to weigh about 0.4 million kilograms) and cultivated in for weed control. When this plot is sampled some time later for residue analysis, 10 to 50 samples may be collected at various stations and depths throughout the field. These samples are sieved, mixed, and subsampled for extraction and analysis. If the final isolated herbicide is contained in 10 milliliters of solvent, and 10 microliters are injected for gas chromatographic analysis, then the fraction of the equivalent total treated soil (0.4×10^6 kilograms) which is represented in the injection is about one part in 10^{11}.

There are numerous problems of residue extraction. Because of the diverse

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chemical structures of pesticides, many reactions occur when these compounds enter biological systems. In a few cases, the compound may remain intact on the surface of the sample. Simply tumbling the sample with an appropriate solvent to dissolve and extract the residue usually suffices. Fat-soluble compounds, notably chlorinated hydrocarbons such as DDT, may require digestion with perchloric and acetic acids (*1*) to release the fat containing the residue. Compounds having free amino groups or those metabolically capable of yielding amines (hydrolysis of substituted ureas, reduction of nitro compounds, or *N*-dealkylation of tertiary amines) may form protein complexes in biological systems. Compounds having carboxyl groups by structure or as a result of metabolism (oxidation of nitriles or beta-oxidation of phenoxyalkanoic acids) may form sugar esters (*2*). Phenolic pesticides or phenolic metabolites (as from hydrolysis of phenylcarbamates or phenoxyacids, or aromatic ring hydroxylation) may form water-soluble ester conjugates (glucurondes, and the like) in animal systems (*3*). Before extraction, the pesticide moiety must be freed by acid or alkaline hydrolysis.

Changes in polarity of a molecule must also be considered in devising an efficient method of extraction. Metabolic epoxidation reactions, such as the conversion of heptachlor to its epoxide or aldrin to dieldrin, increase the polarity, and therefore the persistence, of the insecticides. The oxidation of thiophosphorus insecticides to their respective oxygen analogs and oxidative conversion of their thioether linkages to sulfoxides and sulfones similarly increase the polarity and persistence of the insecticides. The sample must be blended with polar extracting solvents, such as acetone or isopropanol, to promote effective extraction.

After extraction, the residue must be isolated from coextracted sample interferences by various separation procedures. The more rigorous the extraction procedure, the greater the separation problem will be, because many solubilized and extraneous sample substances will have been released. The extent of separation is determined by the desired sensitivity and the degree of selectivity of the final measuring device. The source of the sample also affects the degree of isolation. If the sample is part of a planned residue field experiment in which accurate spray records and representative unsprayed control samples are available, the results will be easier to interpret since the analyst knows what pesticide and possible metabolites to expect. Conversely, if a similar sample of unknown history is taken on the open market, elaborate separations may be required to identify and measure several unknown compounds and metabolites. Apple trees, for instance, may be treated with as many as 15 different compounds for pest control during one growing season.

With the exception of those pesticides which are stable enough to tolerate selected wet-ashing procedures (DDT) and ignition methods (compounds containing metals) for destruction of interferences, most isolation schemes involve a number of sequential separations. A *p*H adjustment followed by solvent extraction is commonly used to isolate phenols, aromatic amines, and acids. Acetonitrile (*4*) is widely used for selective extraction of many pesticides from hydrocarbon solvents containing fats, waxes, and other similar materials. Waxes and fats can be removed by precipitating them at low temperatures. Steam distillation is also routinely used for separating phenols and amines from extraneous sample constituents prior to their determination.

Column chromatography on adsorbents such as florisil, alumina, charcoal, and silicic acid effectively isolates and separates many pesticides on the basis of their respective adsorbabilities and solubilities. Paper, and more recently, thin-layer chromatography with silicic acid or alumina, are used on a preparative scale for separation of compounds or, in the analytical mode, for on-plate detection of residues. Ion exchange is used to isolate and concentrate water-soluble anionic and cationic residues.

Even partial isolation of a few micrograms of a pesticide from milligram or gram quantities of other substances is a formidable task. The accuracy of the method is regularly checked by including a recovery with each set of analyses. The pesticide or metabolite is added to the control sample prior to extraction, and this fortified sample is run through the same procedure used for analysis of other samples. The level of pesticide added should correspond roughly to that expected in the unknown. The percent of added compound recovered is a measure of the accuracy of the method and thus of the suitability of the separation procedure. Finding the particular step in which pesticide losses may be occurring is accomplished by fortifying separate control samples at various stages of the procedure and noting that sample which results in low recovery. Recoveries in the range of 75 to 100 percent are considered normal in residue analysis.

Spectrophotometric Methods

Spectrophotometry is one of the major methods for the final detection and measurement of residues. Colorimetric methods are sensitive (often to 0.01 part per million) and are highly specific when used in conjunction with appropriate isolation procedures. For numerous pesticides, they are the only satisfactory methods available, but they have serious limitations. The time required to isolate the compound prior to color development is lengthy and results in pesticide losses. Also, it is difficult to determine more than one compound in a multi-component residue.

Other methods include analysis of aromatic and condensed ring pesticides by ultraviolet absorption and determination of compounds containing various absorbing groups of infrared spectrophotometry. The need for adequate separation of the desired constituent is usually more critical with these methods than with the colorimetric method, since the practical sensitivity is lower, and a larger sample size may be required. Many sample substances which occur naturally absorb strongly throughout the ultraviolet and infrared spectral regions. Although infrared analysis has great potential for determining several components simultaneously in a residue mixture, its use is limited by the difficulty and the time required to separate and eliminate interferences. The development of elaborate infrared spectrophotometers with scale expanders, beam condensers, cells for micro samples, and multiple internal reflectance attachments to improve sensitivity increases the need for purification prior to absorption measurement. Blinn and Gunther (*5*) have prepared an excellent account of infrared analysis as well as the ultraviolet method.

A near-infrared method of analysis (*6*) for residues of *N*-methyl-carbamate insecticides (with a sensitivity of 0.2 part per million) has been used

to determine several of these compounds in crops. It depends on absorption measurement of the $N-H$ stretching vibration at 2.88 microns after acetone extraction of the sample, a phosphoric acid precipitation of interferences, and chromatographic separation on alumina. It is only one of the generally applicable and satisfactory methods available for quantitative determination of this important class of compounds.

Spectrophotofluorometry has been used to a limited extent in residue research. Many aromatic and particularly polynuclear molecules, when maintained in an excited electronic state through absorption of radiation for about 10^{-8} to 10^{-9} second, will fluoresce, that is, emit radiation of longer wavelength. The presence of amino and hydroxyl groups on aromatic rings increases fluorescence, whereas carboxyl, nitro, and halogen substituents tend to decrease fluorescence. Measurement of fluorescent radiation for analysis potentially permits the determination of quantities 10 to 1000 times smaller than those determined by colorimetric methods. The principal disadvantage is the need for very efficient separation procedures to remove interfering fluorescent substances. This requirement is crucial when residues are located within the tissues being analyzed and extraction consequently releases many extraneous internal constituents. Conversely, a strongly fluorescent substance present mainly as an external residue can sometimes be extracted from the surface with an appropriate solvent and rapidly determined directly in the solution. The nature of the solvent (some oxygen-containing solvents repress fluorescence), its purity, and *p*H must be carefully controlled to maximize the practical sensitivity of fluorescent methods. The need for preliminary purification is particularly critical in the fluorescent method. MacDougall (*7*) has summarized the subject of residue analysis with fluorescence procedures.

Other Methods

Neutron activation analysis has been used to a limited extent for residue analysis. This method involves neutron bombardment of the sample to induce radioactivity in a specific element or elements of the pesticide residue. Subsequent measurement of the radioactive emanations indicates the concentration of the elements. Chlorine, bromine, iodine, and mercury have been determined as elemental fractions of pesticide residues in various samples. The method has sensitivity in the part-per-billion range and is often quite rapid. Samples may be nondestructively activated and measured directly without extraction. However, the method will not distinguish between an element in inorganic or organic combination, and the equipment is expensive. Analysis can be time-consuming and fairly complex if the desired element is not easily activated, or if other induced interfering radioactivity requires properly timed activation, precise measurement, or the filtering out of interfering emanations. Guinn and Schmitt (*8*) provide a detailed account of this method.

Polarography has been used for analysis of certain chloro-, nitro-, and organophosphorus compounds, as well as such metals as copper, lead, and zinc. This method records the current at the surface of a dropping mercury electrode caused by oxidation or reduction of desired ions or organic compounds in solution. The current measured is a function of the potential applied to the electrode. The results are both qualitative and quantitative. Its sensitivity has been increased about tenfold with instruments in which the entire changing applied potential is swept during the life of one mercury drop, and current is recorded on an oscilloscope. Also, analysis time is shortened and resolution of mixed compounds or ions to be discriminated on the basis of their redox potential is improved. As with other methods, the sensitivity of polarography depends on the degree of preliminary residue purification. Detection of compounds at the 0.1 part per million level is not uncommon. Polarography is being replaced by more rapid and sensitive gas chromatographic methods. A discussion of polarography and a review of its application to residue analysis has been prepared (*9*).

In the isotope technique, the pesticide under study is synthesized to contain a radioactive atom or atoms. The radiations of these atoms may be quantitatively measured after appropriate separations. Labeled atoms, such as C^{14}, H^3, Cl^{36}, and P^{32}, are typical in residue studies. These methods of high specificity and sensitivity are most commonly employed in laboratory studies of the metabolism of pesticides in plants, animals, and soil. Pesticides which are isotopically labeled are only sparsely used in field studies, because they must be rigidly confined and later accounted for.

Gas Chromatographic Procedures

The application of gas chromatography to residue problems has revolutionized the field with its advantages of speed, accuracy, sensitivity, and versatility for separation and analysis of many compounds. The basic principal of operation may be briefly reviewed.

Gases, liquids, and solids capable of being vaporized are introduced into a column which is heated at a constant temperature. The column is usually packed with a solid inert support such as powdered firebrick coated with silicone grease. The mixture is kept moving through the column in an inert gas stream (carrier gas) and separation of the components takes place according to their boiling points and solubilities in the silicone grease. The higher solubilities and boiling points, the slower the movement. A sensing device detects the separated fractions as they emerge from the column, and transmits a signal to an amplifier and then to a strip chart recorder. The signal is traced on moving paper and appears ideally as a series of discrete symmetrical peaks. The record is called a gas chromatogram, in which signal intensity is plotted against time. The time, known as retention time, refers to the time each component is retained in the column. Since retention time is characteristic of the component, it qualitatively identifies it. With constant column temperature, gas flow rate, and solvent, the retention time can be reproduced. The height of the peak indicates the quantitative measure.

Although gas chromatography is about 15 years old, it was not used earlier in residue problems because of the more recent development of specific detectors with high sensitivity. A single column, usually about 1.8 meters long, would not completely separate several hundred compounds in an injected sample extract. Detectors available only 5 years ago were nonspecific, and therefore were useless in solving these residue problems. A detector was needed which would respond selectively to the desired compound or compounds in spite of other miscellaneous constituents present in the de-

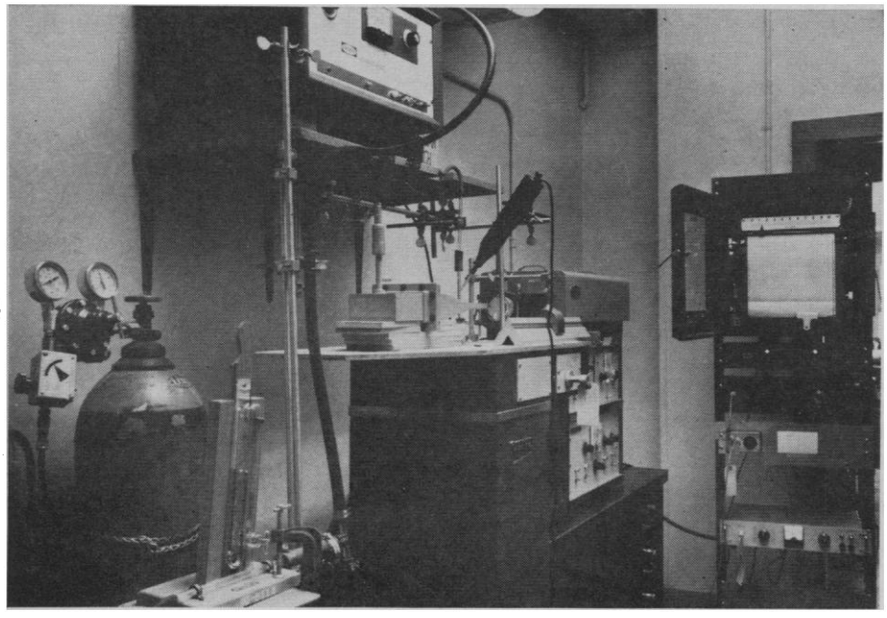

Fig. 1. A sensitive emission spectrometric detector.

tector. Most pesticide molecules possess atoms or structures not commonly found in organic compounds occurring naturally, a factor which enables the development of selective detectors.

One of the first detectors used in the gas chromatographic analysis of residues was the microcoulometric detector developed by Coulson (*10*). In its present design, this detection system specifically responds to pesticides containing halogen or sulfur. The separated compounds, after emerging from the column, are combusted in an oxygen stream to yield hydrogen halide or sulfur dioxide. These gases are swept into the detector cell, in which silver ion or triiodide are electrically and automatically generated, to yield precipitated silver halide or sulfur trioxide, respectively. The coulombs of electricity flowing to generate the necessary titrant stoichiometrically determine the quantity of the gas, and therefore the quantity of the pesticide.

This system has been used to determine amounts of residues of halogenated and organophosphorus insecticides less than 0.1 part per million. Since the amount of equivalent sample represented in one injection may range from 10 to 25 grams, the preliminary isolation of pesticide from the sample extractives must be thorough. A specific microcoulometric detection system for phosphorus compounds based on reduction to phosphine (*11*) has recently been marketed. Another titration system for nitrogen compounds is under development.

The most widely used and most sensitive detector for analysis of halogenated, nitro, and certain other pesticide compounds is the electron-affinity detector (*12*). It consists of a chamber containing a cathode, anode, and a radioactive source emitting beta rays. Nitrogen is usually the carrier gas; after it enters the detector it interacts with the beta rays to produce a loosely associated "negative molecular ion" (a nitrogen molecule with one extra attached electron). These negative ions are attracted to the anode, to which a low positive voltage is applied, and the resulting current produced is recorded as the baseline current. Compounds containing halogens, nitro groups, and other electrophilic substituents have a high affinity for electrons. These compounds, when reaching the detector, capture a portion of the electrons (those loosely held by nitrogen) and cause a corresponding decrease in baseline current. This current drop is amplified and represents detector response.

The response is very selective since halogenated pesticides possess a much higher electron affinity than that of sample constituents. Often only preliminary separation procedures are required. This is particularly true when the past pesticide history of a sample is known and representative control samples are available. The detector is sensitive to only a few organophosphorus insecticides. Many pesticides with low electron affinity have been converted to sensitive electron-capturing derivatives by bromination (*13*) and nitration (*14*) of the molecules before their residues are analyzed by gas chromatography.

The electron-affinity detector, more than any other analytical device, has proved the ubiquitous presence of stable, persistent, chlorinated pesticides in the general environment. The public concern aroused by these findings is probably due, in no small way, to the striking manner in which gas chromatographic data presents itself. Recorded data of amounts of a toxicant in food as low as 10 parts per billion can be represented by full scale peaks, obscuring the fact that in that specific case the residue concentration may be toxicologically insignificant. This is in sharp contrast with older colorimetric procedures in which the chemist recorded an optical density representing 10 parts per billion of the same toxicant, a level which may well have approached the sensitivity limit of the method. Furthermore, the faintly colored solution often faded before it could be exhibited or photographed.

A sensitive, specific detector for organophosphorus insecticides was reported in 1964 by Giuffrida (*15, 16*). Called the sodium thermionic detector, it is a modification of the well-known flame-ionization detector, in which compounds emerging from a gas chromatographic column are burned in a hydrogen flame. The resultant increased conductivity of the flame is measured as detector response by a collector electrode. As little as 0.01 microgram of an organic compound containing ten carbon atoms can be detected. The flame-ionization detector is not specific, but it has been used in a few instances for residue determinations.

Giuffrida modified this detector by placing a thin platinum spiral, coated with sodium sulfate, in the upper portion of the flame. The detector responds very selectively to organophosphorus compounds with sensitivities up to 600 times that of the flame-ionization detector. The presence of sodium ions in the flame increases the response of phosphorus, but the exact mechanism is not understood. The sodium thermionic detector is also selective for chlorinated compounds, but it is more sensitive for phosphorus compounds. This

device is now being used to analyze organophosphorus insecticide residues in several laboratories. It could be used on a wider scale simply by converting the flame-ionization detectors.

A novel and rapid isolation procedure for organophosphorus compounds was recently developed (*17*) for use before they are detected as residues with the sodium thermionic method. Raw sample extracts are injected into a heated (175°C) tube filled with glass wool. The insecticide passes through freely, while many extraneous materials are deposited on the glass wool. The insecticide condenses in a Teflon tube coiled in an ice bath. The purified compound is removed from the tube with solvent, and the solution is chromatographed. Good recoveries of several compounds from fruits and vegetables are reported. A version of the sodium thermionic detector with dual stacked flame-ionization detectors was developed by Karmen (*16*) and is being marketed.

Cooke (*18*) reported the development of a sensitive emission spectrometric detector (Fig. 1) with specific responses for phosphorus, sulfur, and halogens in organic compounds eluting from a gas chromatograph. Separated compounds emerge from the column in argon carrier gas. The gas stream passes through a quartz capillary tube positioned in the cavity of a 2450-megacycle microwave generator. A spark coil is used to initiate an intense plasma in the tube; the plasma is sustained by the coupled microwave field. Organic compounds entering this plasma are torn apart by bombardment of electrons (and the intense heat of the discharge) and are excited by the production of atomic emission lines and molecular bands. This emitted radiation is focused into a grating spectrometer with the wavelength adjusted to pass only the emission of the desired element. A photomultiplier tube measures intensity of emission, and the signal is amplified and recorded. The emission spectrum of a compound is developed by vaporizing the pure compound directly into the plasma with argon, the wavelength scale is spectrometrically scanned, and the results are recorded. Emission lines are chosen for analysis on the basis of line intensity and location with respect to nearby interfering lines.

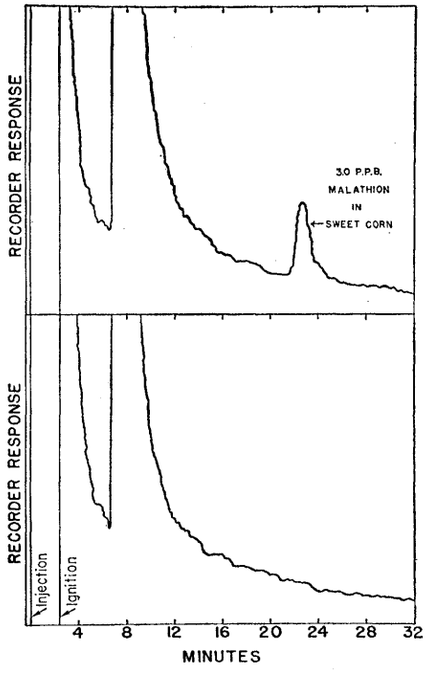

Fig. 2. Chromatograms of malathion (3 ppb) in sweet corn, and the control.

The method has been used to analyze organophosphorus insecticide residues (*19*) and to oxidize metabolites of these compounds in soil (*20*). It has also been successfully used as a specific detector for organic compounds containing iodine and to determine an iodinated herbicide and its possible metabolites in grain and soil (*21*). Figure 2 shows 3.0 parts of malathion [*S*-(1,2-dicarbethoxyethyl)-*O,O*-dimethyl phosphorodithioate] per billion in sweet corn and the control corn. Figure 3 shows chromatograms of 0.1 part per million each of ioxynil-(3,5-diiodo-4-hydroxybenzonitrile) herbicide and a possible metabolite, IBA (3,5-diiodo-4-hydroxybenzoic acid), added to wheat grain, and the control. The grain was extracted with benzene, the compounds were partitioned in sodium bicarbonate, and after acidification, they were extracted into chloroform. This solution was concentrated, an injection was made representing 1.5 grams of grain, and the 2062-Å atomic iodine emission was monitored.

This detection system is sensitive to 0.1 nanogram of phosphorus or iodine. Its sensitivity to phosphorus is in the same range as the sodium thermionic detector. Analysis of these elements is made by monitoring the intensity of atomic emission of the 2535.6-Å phosphorus or the 2062-Å iodine line. The system is highly specific, with selectivity ratios (as compared to hexane) for compounds containing iodine or phosphorus of 1000 and 10,000 to one, respectively. This degree of specificity is possible because there is little hydrocarbon emission in the deep ultraviolet region and because a high resolution spectrometer (0.2 Å) is used. The sensitivity and selectivity of the detector for other halogens and sulfur is lower. The potential for positive identification of compounds is obvious since one may rely not only on retention time, but also on response at one or more wavelength settings depending on elemental composition and concentration. Phosphorus shows several atomic- and band-emission lines, any of which could be selected for identification. A less sensitive line could be chosen purposely if residues are high and dilution is undesirable. The detector has a wide linear dynamic range. This equipment may be used for routine operations. Samples are commonly injected repeatedly and the daily reproducibility of standard curves is remarkable. A quartz

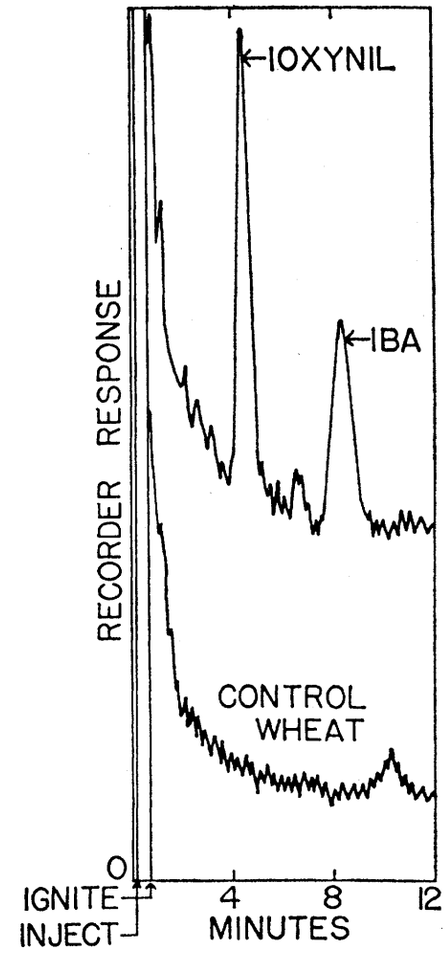

Fig. 3. Chromatograms of ioxynil and IBA (0.1 ppm each) in wheat, and the control.

capillary tube in continuous use lasts for 6 months. No carbon is deposited in the tube, and therefore dismantling and cleaning is unnecessary. Almost any solvent may be used for injection of samples.

Other excitation sources were studied (*22*), including the hydrogen flame and various electrical discharges, but the intensity of emission and signal-to-noise ratio of the 2450-megacycle microwave-powered argon source was highest. This detector system has been modified to increase its sensitivity to organophosphorus insecticides by a factor of 10 to 15. Its use for determining these compounds as residues at concentrations down to about 2 parts per billion with a minimum of preliminary isolation will soon be reported. Research is underway to extend the application of this detector to other compounds. Brody (*23*) developed an emission detector for phosphorus compounds using a flame source and a filter to isolate the 5260-Å phosphorus emission.

Gas chromatography is also used on raw sample extracts with minimum prior purification. In many residue studies, the precise structures of possible metabolites are unknown. It is therefore impossible to devise preliminary isolation procedures which are applicable and which will not result in the possible loss of the metabolites by vaporization, adsorption, or unintentional discard. By direct injection of the initial extract into a gas chromatographic system, the analyst has at least provided that their metabolites might get through the column (barring thermal decomposition or irreversible adsorption) and be detected.

These same considerations apply to the direct analysis of sample extracts for known pesticides. A gas chromatograph is expensive, but it does separate desired and extraneous compounds and permits rapid analysis. If the desired compound appears in an area of the control chromatogram in which other peaks are absent, and if the accuracy of the procedure is acceptable as judged by recovery studies, the appearance of peaks at other times in the chromatogram is insignificant. Direct injection of samples therefore permits maximum utilization of the separation capabilities and speed of the instrument. Losses of pesticides during preliminary isolation steps are obviated. If the life of the column is shortened, a new column is easily prepared with commercial packings which do not require long periods of conditioning before use.

Other gas chromatographic detectors are being developed. The use of mass spectrometry, especially time-of-flight instruments for use in tandem with gas chromatography, is increasing. More sensitive magnetic deflection instruments and high-resolving double-focusing models have been applied to residue and metabolite studies. Their entrance into the pesticide field is very recent, and their true usefulness cannot yet be properly evaluated. The sensitivity of mass spectrometry and its ability to provide structural information make it a very enticing tool for pesticide research.

The incorporation of rapidly scanning infrared spectrometers with gas chromatography to obtain the infrared spectra of compounds as they are being eluted is a very new procedure. The emerging compound condenses on a thin, cooled plate which is transparent to infrared radiation. Infrared frequencies normally pass into the end of the plate at such an angle (less than the critical angle) that they undergo multiple internal reflections which pass endwise through the plate and emerge undistorted from the opposite end. The condensed compound on the plate surface reduces the reflected beam at those frequencies which the compound absorbs. These absorptions are measured to yield the infrared spectrum of the compound. Provision is made for alternately cooling and heating the plate between peaks so that the measured compound may be vaporized off and the plate again cooled for condensation and measurement of the next eluted compound. These internal reflections simulate a longer sample light path for absorption and increased sensitivity. The infrared spectra of a few micrograms of several pesticides have been measured as they emerge from a chromatograph. Again, the utility of the method for residue analysis remains to be proved, and will depend on thorough initial purification and concentration procedures.

Specific detectors based on the use of Geiger and scintillating counters can be used for selective measurement during the elution of isotopically-labeled compounds. This system could be very useful for identifying pesticide metabolites. Geiger counters do not possess the high sensitivity of scintillating systems but, on the other hand, they can function at elevated temperatures to yield a true flow-through system for rapid identification of succeeding compounds. The scintillating anthracene crystal cannot be maintained at high temperatures and the eluted compounds must be successively deposited on the same crystal for counting, with a resulting progressive increase in background radiation and lowered sensitivity. This problem may be obviated by combustion of eluted compounds to yield a labeled gas which will flow through the scintillating system at room temperature.

In the future, instruments which will be even more sensitive and specific for residue analysis will certainly be developed. The skill and persistence of the analyst will, however, remain essential for their successful application.

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