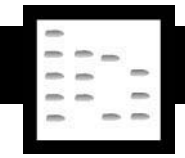
INORGANIC EXTRACTION: MOLECULAR RECOGNITION TECHNOLOGY

See III / MOLECULAR RECOGNITION TECHNOLOGY IN INORGANIC EXTRACTION

INSECTICIDES



Gas Chromatography

P. Brown, Central Science Laboratory, York, UK

Developments in insecticide analysis have been closely linked to developments in gas chromatography (GC). Indeed, the invention of the electron-capture detector led to the discovery of residues of the persistent organochlorine insecticides in dead birds and this in turn raised concerns regarding pesticide residues in food and the environment. The range of applications of GC to insecticide analysis is very wide and the choice of technique must be appropriate for the intended purpose. The first requirement is to detect the compounds of interest; most GC detectors have some use in insecticide analysis. Different types of column are needed for different applications and the choice of injection technique is related to the analyte and the type of column. The ability to obtain a chromatogram from a solution of insecticides is just a starting point. The insecticides have to be extracted from a variety of samples and separated from many other co-extracted compounds which can interfere with the separation or degrade the column. There are four major classes of insecticides, each of which has its particular analytical requirements.

Applications of GC in Insecticide Analysis

Insecticides are biologically active compounds used principally in agriculture but also in public health applications. There is public concern over their production and use, their presence in food and their persistence in the environment. The requirement for insecticide analysis is wide-ranging. GC is better suited to residue analysis than measuring the high concentrations encountered in formulations. For GC analysis, the insecticides must be sufficiently volatile and thermally stable.

A manufacturer may be interested in a particular compound together with its metabolites and degradation products in biological systems and the environment. In cases of animal poisoning by an insecticide, the identification of the poison is the main task. Foods are monitored for many different insecticides and some degradation products; small residues around statutory limits must be identified and measured accurately in a wide variety of foods, each of which poses particular analytical challenges. Residues in water and air are even smaller and must be trapped and concentrated prior to measurement.

With such a variety of applications, it is essential that the analytical method is fit for its purpose.

Detectors for GC of Insecticides

A list of detectors and their application to insecticide analysis is shown in **Table 1**.

Columns and Injection Ports for GC of Insecticides

Packed Columns

GC of insecticides began with packed columns that gave low resolution and were limited by the temperature at which the nonbonded stationary phase began to bleed. To achieve sufficient resolution for identification and to obtain good peak shapes, a wide range of stationary phases was needed. Packed columns are not well suited to temperature programming and the sample is usually introduced by vaporization of a solution in a heated injection port. This is unsuitable for the thermally labile carbamates which have to be converted to more stable derivatives.

Capillary Columns

The introduction of fused silica capillary columns and bonded stationary phases brought higher resolution GC to routine analysis of insecticides. Higher

Table 1 Detectors used in the gas chromatography of insecticides

Detector	*Species detected*	*Insecticide classes*	*Comments*
FID (flame ionization) PID (photoionization)	Carbon compounds	All	With these detectors, difficult to identify the insecticides amongst the peaks from co-extracted compounds in residue analysis
ECD (electron capture)	Halogens and other electron-capturing species	Organochlorines, most pyrethroids, some OPs	Sensitive but not highly selective. Responds to some nonhalogenated compounds. Response affected by co-extractives
Electrolytic conductivity	Chlorine or sulfur or others	Organochlorines	More selective than ECD but less sensitive. Less robust. Requires more maintenance
NPD (nitrogen phosphorus)	Nitrogen and phosphorus	Organophosphates, carbamates	Responds to both elements. Slightly 'tunable'. Response changes slowly as salt bead ages. Response affected by co-extractives
Chemiluminescence	Nitrogen	Carbamates	Rarely used to date
FPD (flame photometric)	Phosphorus (with 526 nm filter)	Organophosphates some have phosphorus and sulfur	Very selective for phosphorus but large amounts of sulfur compounds may interfere
	Sulfur (394 nm)	Others with sulfur	Nonlinear response. Affected by bleed
AED (atomic emission)	Carbon, chlorine, nitrogen, sulfur, phosphorus, oxygen (not all at once)	All (but selective for chosen elements)	Versatile selective multielement detector but not as sensitive as some and costs more to buy and run
FTIR (Fourier transform infrared)	Functional groups that absorb infrared	Various, but only at high levels	Not sensitive enough for residue analysis
MS (mass spectrometry)			
Total ion chromatogram	All that ionize in MS	All	Same disadvantages as FID (above), but other modes are selective (below)
Selected ion(s)	Selected ions	All chosen compounds	Selective for compounds producing the chosen ions
Full spectrum	Mass spectrum	Identification of peak	Good identification if sufficiently sensitive
Negative-ion CI	Halogens (as ECD)	OCs, pyrethroids	Limited application
MS-MS	Fragmentation of ion	Co-eluting compounds or sparse spectrum	Aids identification in these difficult situations

OPs, organophosphates; OCs, organochlorines; CI, chemical ionization.

resolution, less active sites, temperature programming, cool on-column injection and the development of sensitive mass spectrometric detectors enabled many insecticides, including some that are thermally labile, to be analysed on a low polarity stationary phase (dimethyl polysiloxane, DB-1 or methylphenyl polysiloxane, DB-5, DB-17, etc.)

For fast analyses or for thermally labile compounds, a short wide-bore column (10 m × 0.53 mm i.d. with a 1 μm stationary phase thickness) works well in combination with semi-selective detectors (electron-capture, nitrogen-phosphorus and flame photometric detectors). If the analyte is sufficiently stable, a packed column injector can be converted for direct injection into a 0.53 mm capillary column by the addition of a liner with a volume of about 1 mL and an appropriate reducing adapter. For cool on-column injection, a purpose-built port is necessary. A carrier gas (nitrogen or preferably helium or hydrogen) flow of about 5 mL min^{-1} and a temperature gradient from 50 or 100°C at 5°C min^{-1} to 250°C will be suitable for the analysis of most insecticides.

For higher resolution, a smaller bore (e.g. 0.25 mm internal diameter) and/or longer column is needed. Also, if the detector is a mass spectrometer, a low carrier flow around 1 mL min^{-1} is preferred. Concentrated sample solutions are best analysed with a split injection technique where only a small proportion of the injected extract goes on to the column. For most insecticide analysis, splitless injection is used together with an initial column temperature low enough to

cold-trap the analytes and to condense the solvent if the solvent effect is to be employed.

Cool on-column injection is ideal for compounds that start to decompose in a hot injection port, but nonvolatile co-extracted solutes remaining in sample extracts will rapidly contaminate the column. A wide-bore retention gap will trap nonvolatiles and allow injection with a conventional syringe needle (instead of needing a fragile thin needle to inject directly into a small-bore column). Some carbamate insecticides can be analysed without derivatization on a nonpolar column with on-column injection.

Large volume injection is becoming popular for the analysis of low concentrations of insecticides in water samples. Volumes in excess of 100 μL of extract are injected into packing in an injection port liner from which the solvent is evaporated. The solutes are thermally desorbed on to the column where they are cold-trapped prior to the start of temperature-programmed GC analysis.

A thermal desorption and cold-trapping technique is also used for analysis of air samples from which contaminants have been trapped by passage through a tube of adsorbent.

Volatile insecticides used as fumigants in grain and other stored commodities may be analysed by headspace analysis; the volatile compounds are sampled from the air above the samples and passed in a gas stream to be trapped on the top of the GC column.

Analysis for Insecticides in Biological and Environmental Samples

Before insecticide residues can be analysed by GC, they have to be extracted from the samples containing them. These extracts contain many other co-extractives in addition to the insecticides and require a clean-up.

Extraction

The simple – and usual – way to check whether an analytical procedure will extract compounds of interest is to add a solution of the compounds to the exposed surfaces of sample (whole, chopped up or finely ground), allow the solvent to evaporate fully, then apply the analytical procedure. Residues that have been acquired by a plant or animal by systemic processes (transport via a plant's vascular system or the processes through gut and internal organs following ingestion by an animal) may be more difficult to extract than surface residues. Studies using radiolabelled compounds may be needed to determine whether such residues are extractable or bound.

Extracts are usually obtained by cutting the sample very finely (blending, homogenizing, milling, grinding, etc.) and extracting with an organic solvent. Extraction may be a one- or two-stage process aided by agitation (shaking, ultrasonicating, homogenizing) followed by filtration or centrifugation (to separate solid and liquid). It may be continuous as in liquid–liquid extraction (for liquid samples) or in Soxhlet extraction, accelerated solvent extraction or supercritical fluid extraction (for solid samples).

Clean-up

The effects of co-extractives on GC include:

1. visible additional peaks on the chromatogram, perhaps unresolved from the analyte peak;
2. volatile substances that, although not themselves showing a detector response, elute with the analyte and affect the chromatography or the response of the detector to the analyte;
3. nonvolatile solutes deposited on injection, coating the injection liner and top of the column, changing the characteristics of the stationary phase in that region.

A clean-up from which a wide range of insecticides can be recovered will also recover many other co-extracted compounds. Some analysts use extracts with little or no clean-up, and selective detection such as GC-mass spectrometry (GC-MS). They compensate for chromatographic effects from co-extractives by the use of carefully chosen internal standards or prepare matrix-matched external standards in extracts of analyte-free sample material. An instrument used in this way will require frequent maintenance, but the overall result may be cost-effective.

Clean-up is a source of potential loss of analyte and adds extra time to analyses (but in recent years equipment for partial automation of this process has been introduced).

Gel permeation chromatography (GPC) is a technique that delays small molecules such as insecticides as they flow in and out of pores in the gel while larger molecules flow past in the solvent stream. The large molecules mainly form the nonvolatile material deposited at the GC injection port, so GPC is potentially a useful clean-up for insecticides in a wide range of sample matrices. The disadvantage of traditional GPC is that it uses large quantities of solvents (hundreds of millilitres) which have to be removed by evaporation. High performance GPC works on a smaller scale and can be automated, but the columns are expensive compared to analytical high performance liquid chromatography columns.

Column adsorption chromatography using quantities of between 1 g and 50 g of materials such as alumina, silica gel and Florisil was the traditional method for clean-up of extracts containing insecticides. These traditional columns have been largely superseded by small particle size materials in quantities from 100 mg to 1 g in cartridges, usually requiring a small pressure or vacuum to give a suitable flow rate. Cartridges of this type, including those with reversed-phase (C_{18}) and ion exchange packings, are now known as solid-phase extraction (SPE) cartridges. Equipment for automated operation of these cartridges is widely available.

Partition between two immiscible solvents, such as water and hexane, may be used to separate polar co-extractives from insecticides that are generally of low polarity. Originally separating funnels were used, but there are now cartridges of inert material that will absorb an aqueous solution but still allow efficient partition of insecticides into a water-immiscible solvent poured through the cartridge. A partition mechanism also operates with SPE cartridges containing bonded C_{18} packing material. Insecticides in aqueous solution are extracted by a partition process into the C_{18} and then eluted selectively from the cartridge by organic solvent mixtures of appropriate polarity.

There are other clean-up techniques developed for specific purposes. Sweep co-distillation is a process analogous to steam distillation, in which insecticides and other volatile materials are distilled out of heated liquid fat samples. Some of the organochlorine insecticides are resistant to chemical attack, so reaction of interfering compounds with strong acids or oxidizing agents has been used as a clean-up for these compounds.

The extraction and clean-up methods to be employed depend on the insecticide(s) to be analysed and the nature of the sample material. The analyst should consult the literature for a particular application, but if no suitable technique is described, some experimentation will be necessary.

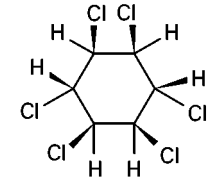
Determination of Insecticides by GC

The requirements for GC determination depend on the purpose of the analysis. Generally, GC determination with a semi-selective detector or a single ion on a mass spectrometer requires additional confirmation, by an alternative technique or by measurement of other ions.

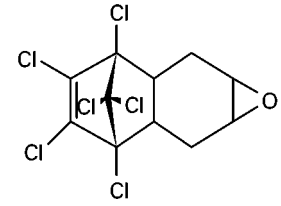
Organochlorines

Most of the insecticides of this type have been withdrawn from use in many countries, but residues persist in the environment. Organochlorine insecticides are of several different chemical types but all contain chlorine atoms and are fat-soluble (non-polar). Lindane (hexachlorocyclohexane (gamma isomer), γ-HCH), dichlorodiphenyltrichloroethane (DDT) and dieldrin are examples (**Figure 1**). They are very slightly soluble in water, but are readily extractable into hexane from water or homogenized water-containing samples. Diethyl ether or ethyl acetate will also extract them from dry materials on which they are adsorbed. An alternative is to use a water-miscible solvent such as acetone to extract from water-containing samples; this is followed by partition between water and hexane. Supercritical fluid extraction with carbon dioxide as solvent and a C_{18} trap has also been used to extract organochlorine insecticides from relatively dry commodities. For clean-up of hexane extracts of fatty samples, chromatography on deactivated alumina or Florisil with further hexane elution recovers most of the organochlorines while leaving most co-extractives behind. GPC and sweep co-distillation are sometimes used to clean up extracts containing organochlorines. Although these insecticides are solids, care must be taken when evaporating extracts as, for example, γ-HCH is easily lost if a solution is evaporated to dryness.

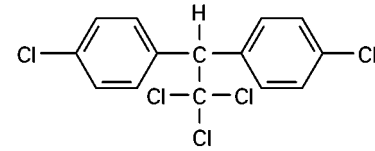
All the organochlorine insecticides chromatograph well on dimethyl silicone stationary phases (DB-1, OV-1, etc.). Endrin and 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (*p*,*p*′-DDT) may break down or



γ-HCH or lindane (hexachlorocyclohexane)



Dieldrin (HEOD)



p,*p*′-DDT

Figure 1 Organochlorine insecticides.

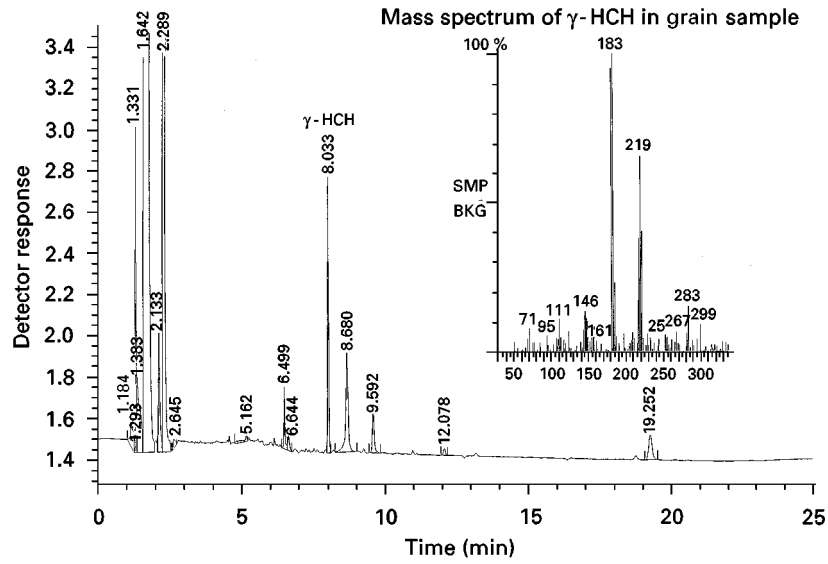


Figure 2 Chromatogram of extract of grain sample containing γ-HCH. Chromatogram of a cleaned-up extract of grain showing a residue of γ-HCH (0.7 mg kg^{-1}). 1 μL direct injection at 150°C on to 30 m × 0.53 mm i.d., DB-1 column (1.5 μm film thickness). Gradient from 100°C (1.0 min) at 25°C min^{-1} to 225°C then at 2.5°C min^{-1} to 265°C (3 min). Helium carrier gas. Hewlett Packard 5890 GC with ECD. GC-MS confirmation on 30 m × 0.25 mm i.d. BPX5 column (0.25 μm film thickness) in Finnigan GCQ instrument.

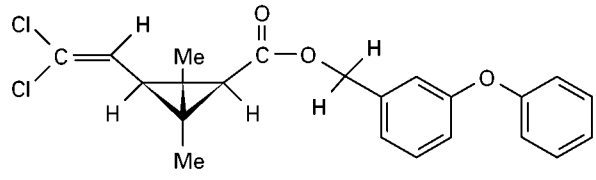
adsorb strongly if the injection liner and top of column become dirty or active. Splitless injection is usually used for residue analysis. A 20 m long, 0.53 mm i.d. column gives satisfactory resolution with a temperature programme from 100°C to 225°C. A chlorine-selective detector such as the very sensitive electron-capture detector or the less sensitive but more selective atomic emission detector may be used. For certainty of identification, a bench-top mass spectrometer is used to obtain a full mass spectrum; the chromatogram is monitored for selected ions at particular retention times to locate any organochlorine peaks (**Figure 2**). A capillary column has to be used to suit the maximum gas flow requirements of the mass spectrometer. For some of the organochlorines, negative-ion chemical ionization mass spectrometry is a successful detection technique.

Synthetic Pyrethroids

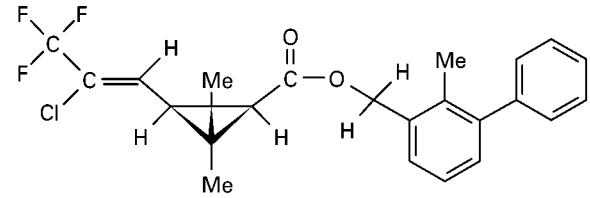
Synthetic pyrethroid insecticides have certain structural features in common. Permethrin, bifenthrin and fenvalerate are typical examples (**Figure 3**). They are only slightly more polar than the organochlorines and may be extracted in a similar way. Mixtures of, for example, hexane and ether will elute pyrethroids from Florisil clean-up columns or cartridges. Those synthetic pyrethroids that do not contain chlorine atoms contain other halogens or chemical groups that are electron-capturing. Retention times are longer than for the organochlorine compounds, so the temperature programme has to rise to 275°C (**Figure 4**). However, resolution of the isomers of some pyrethroids (e.g. cypermethrin) requires a higher resolution column (e.g. 30 m × 0.25 mm i.d.).

Carbamates

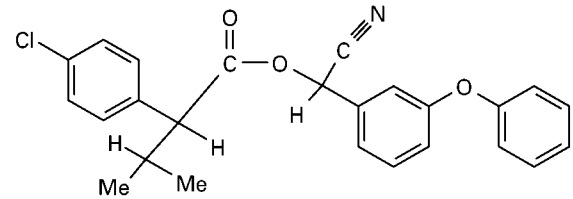
The carbamate insecticides are of two types, esters of *N*-methyl (or *N*,*N*-dimethyl) carbamic acid with



Permethrin



Bifenthrin



Fenvalerate

Figure 3 Synthetic pyrethroid insecticides.

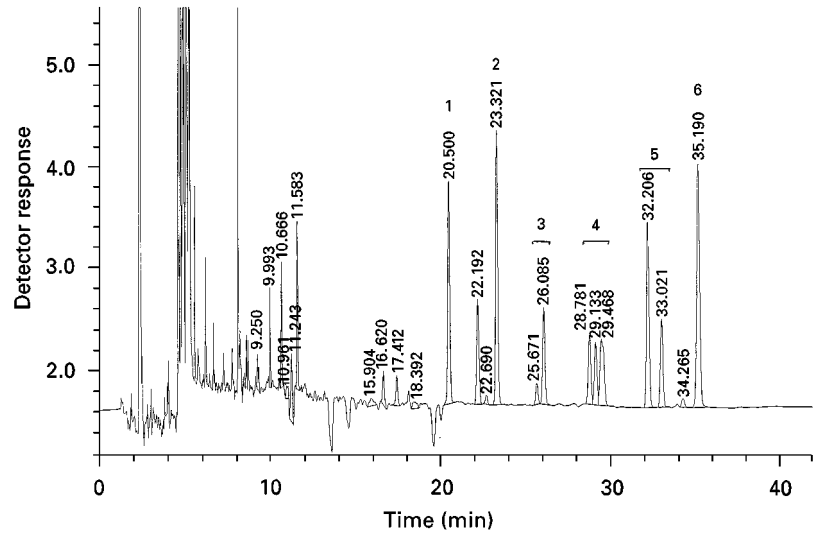
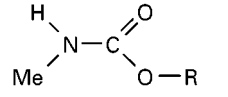


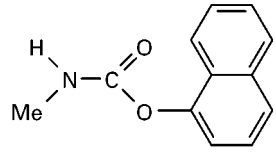
Figure 4 Chromatogram of six synthetic pyrethroids in honey bee extract. Chromatogram of cleaned-up supercritical fluid extract of honey bees spiked before extraction with six pyrethroids, each at 0.1 mg kg^{-1}. 1, Bifenthrin; 2, λ-cyhalothrin; 3, permethrin; 4, cypermethrin; 5, fenvalerate; 6, deltamethrin. 1 μL direct injection at 175°C on to 30 m × 0.53 mm i.d., DB-1 column (1.5 μm film thickness). Gradient from 50°C (1.0 min) at 25°C min^{-1} to 225°C then at 2°C min^{-1} to 275°C (9 min). Helium carrier gas. Hewlett Packard 5890 GC with ECD.

either a phenol or an oxime. Carbaryl and pirimicarb are examples of the phenolic type. Aldicarb and methomyl are examples of the oxime type (**Figure 5**). They are extractable with diethyl ether, dichloromethane, ethyl acetate or acetone. Supercritical fluid extraction with carbon dioxide as extractant and a C_{18} trap is effective for dry or easily dried samples. Extracts containing carbamates may be cleaned up on columns or cartridges of silica gel, Florisil or very deactivated alumina eluted with hexane–diethyl ether mixtures or hexane with small additions of acetone. Gel permeation is an alternative clean-up technique that is useful for multiclass analyses.

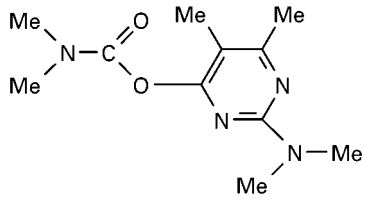


R is PhR′ or N=CR′

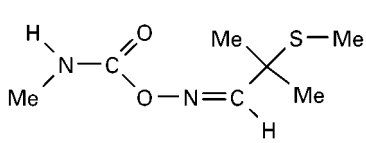
Carbamate insecticide: general structure



Carbaryl



Pirimicarb (an *N,N*-dimethyl carbamate)



Aldicarb (an *N*-methyl oxime carbamate)

Figure 5 Carbamate insecticides.

The carbamate insecticides in general, and the oxime carbamates in particular, break down when heated. Before fused silica capillary GC columns and cool on-column injection became available, the carbamates were usually chromatographed as derivatives. A widely used derivatization procedure involved hydrolysis with hot aqueous sodium hydroxide solution, reaction of the phenol with 1-fluro-2, 4-dinitrobenzene and analysis on a dimethyl silicone packed column with electron-capture detection. Another procedure formed derivatives from intact carbamates and trifluroacetic anhydride prior to GC analysis. Aldicarb, an oxime carbamate, and its toxic breakdown products may all be oxidized to aldicarb sulfone using peracetic acid or potassium permanganate. Aldicarb sulfone is chromatographed on a nonpolar column with a nitrogen-phosphorus detector (NPD), but with an injection port packed with glass wool at a temperature of 300°C where the carbamate breaks down and forms a nitrile from the oxime part of the molecule.

Carbamates of the phenolic type may be analysed successfully by using a nonpolar column of moderate length (10–15 m × 0.53 mm i.d.) together with cool

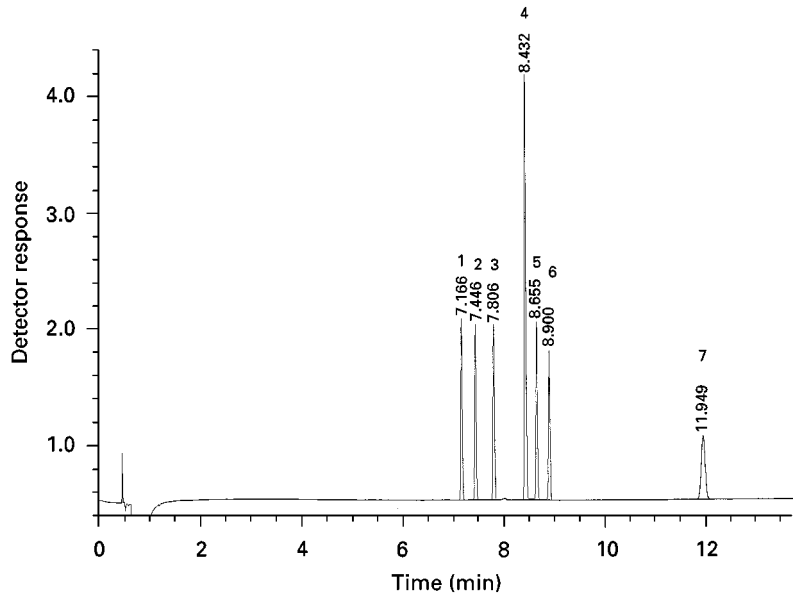


Figure 6 Chromatogram of seven *N*-methyl carbamates. 1, Propoxur; 2, bendiocarb; 3, carbofuran; 4, pirimicarb; 5, carbaryl; 6, methiocarb; 7, carbosulfan, 2 μg mL^{-1} solution of each, 1 μL cool on-column injection at 50°C on to 15 m × 0.53 mm i.d., DB-1 column (1.5 μm film thickness). Gradient from 50°C (0.5 min) at 20°C min^{-1} to 235°C (4 min). Helium carrier gas. Hewlett Packard 5890 GC with NPD. Note: Pirimicarb has four nitrogen atoms, so gives a larger response than the others.

on-column injection, a gentle temperature gradient and NPD (**Figure 6**). For analysis by GC-MS, small bore capillaries are used, coupled with a 0.53 mm i.d. retention gap. GC of most oxime carbamates is unsuccessful unless they are converted to derivatives. For oxime carbamates, and perhaps for many phenol carbamates, the preferred method of analysis is by liquid chromatography-MS (LC-MS) or by liquid chromatography with post-column conversion to a fluorescent derivative.

Organophosphates

The organophosphorus insecticides are esters of phosphoric acid (or its sulfur analogues) and are therefore often referred to as organophosphates to distinguish them from compounds with a C–P bond. There are several groups of chemically related organophosphates. Dichlorvos, malathion and parathion are examples (**Figure 7**). Organophosphates cover a wide polarity range from persistent and fat-soluble compounds such as carbophenothion to water-soluble and easily hydrolysed compounds such as mevinphos. Most are extractable from dried samples with dichloromethane, diethyl ether or ethyl acetate. As with carbamates, supercritical fluid extraction with carbon dioxide and a C_{18} trap will extract most of them from dry samples (or from samples that can be dried with sufficient drying agent). Clean-up depends on the compounds being analysed and the nature of the sample material. Silica

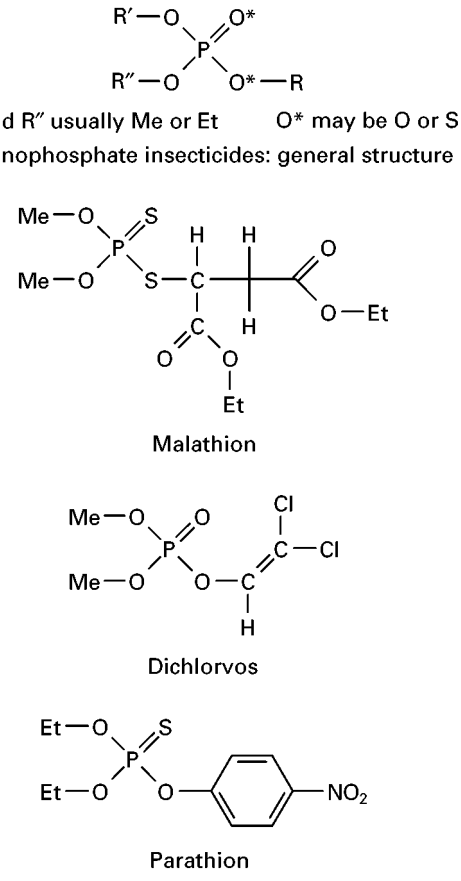


Figure 7 Organphosphate insecticides.

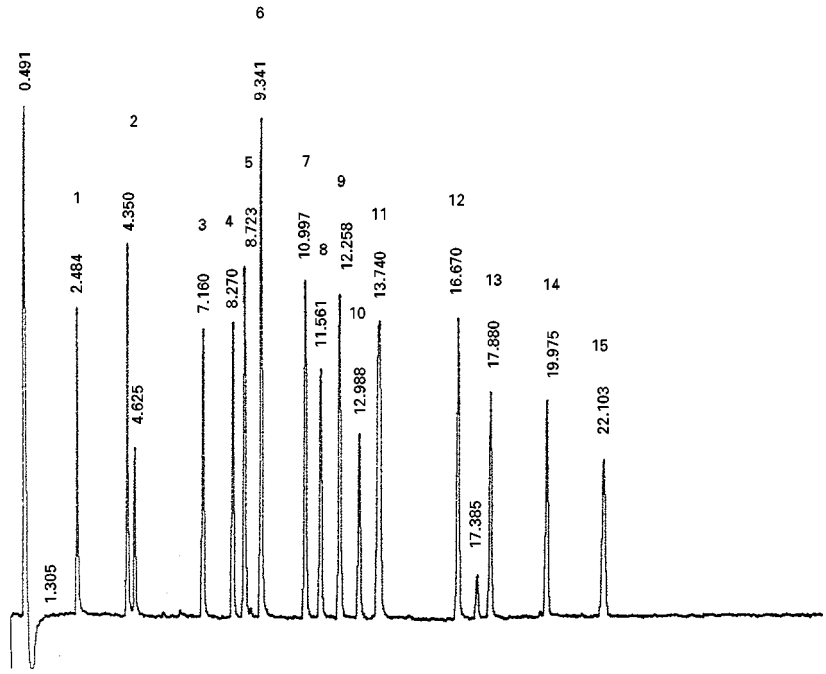


Figure 8 Chromatogram of 15 organophosphates in pheasant gizzard. Chromatogram of diethyl ether Soxhlet extract of pheasant gizzard contents, spiked before extraction with a mixture of 15 organophosphates, each at approximately 4 mg kg^{-1}. 2 μL direct injection at 225°C on to 15 m × 0.53 mm i.d., DB-17 column (1.0 μm film thickness). 1, Dichlorvos; 2, mevinphos (E + Z); 3, phorate; 4, diazinon; 5, fonofos; 6, dimethoate; 7, pirimiphos-methyl; 8, malathion; 9, fenthion; 10, chlorfenvinphos; 11, fosthiazate; 12, carbophenothion; 13, triazophos, 14, phosalone; 15, azinphos-methyl. Gradient from 140°C (0.5 min) at 10°C min^{-1} to 180°C then at 6°C min^{-1} to 270°C (10.5 min). Helium carrier gas. AI Cambridge Ai93 GC with Tracor FPD.

gel does not give a very effective multiresidue clean-up from fatty materials as many organophosphates are eluted with co-extractives. Active alumina will break down some organophosphates. Gel permeation is probably the best choice when analysing organophosphates covering a wide range of polarities.

Residue-level GC may be carried out using splitless or cool on-column injection with detection by mass spectrometry, flame photometric or atomic emission detector or NPD (of these, NPD is the least selective). Medium polarity columns (such as 50% phenyl) give good separation and peak shapes, but a more polar phase such as cyanopropyl is sometimes useful (avoid using it with an NPD). As for column length and diameter, although a 15 m × 0.53 mm i.d. column will separate many organophosphates over a long slow temperature gradient, there are so many compounds of this type that some are bound to co-elute whatever the resolving power of the column (**Figure 8**).

Future Trends in the Analysis of Insecticides by GC

Capillary columns have largely replaced packed columns and precise electronic control of temperatures and gas pressures are standard features of modern gas chromatographs. The bench-top mass spectrometer is now firmly established as the detector of choice for most applications. As computers increase in power, software for interpreting chromatograms and spectra and selecting results of interest will continue to develop and will become integrated with laboratory information management systems. The atomic emission detector may gradually displace the well-established element-selective detectors in a role complementary to GC-MS-MS in the larger analytical laboratories. The move away from GC for the thermally less stable compounds will continue as LC-MS is now sufficiently sensitive and robust for routine residue analysis. Large volume injection is becoming established as a standard technique in water analysis. The slow trend towards the analysis of smaller and smaller residues in food and environmental samples may take a step forward when large volume injection is used together with improved cartridge clean-up methods. For some sample types, solid-phase microextraction will routinely provide rapid transfer of analyte to the GC.

Automation of extraction and clean-up operations has been predicted as a major area of advance for the past 15 years. The laboratory robot has not taken over all laboratory work and the trend is towards laboratory instruments with added versatility and capacity for automation.

Supercritical fluid extraction is making slow progress, probably because of its high cost compared to traditional extraction methods, Perhaps eventually the gas chromatograph will control the extraction and clean-up of its own samples, recording all steps with a thorough audit trail. Trends in insecticide analysis will also depend on what new classes of compounds are approaching commercial use. Element-selective detectors may not be suitable, but GC-MS-MS and LC-MS-MS should be able to cope with just about anything.

See also: **III/Herbicides:** Gas Chromatography; Solid-Phase Extraction; Thin-Layer (Planar) Chromatography. **Insecticides:** Solid-Phase Extraction.

Further Reading

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Solid-Phase Extraction

A. Przyjazny, Kettering University, Flint, MI, USA

Introduction

Synthetic insecticides represent an almost universal environmental pollutant. Chemical structures of insecticides are very diverse, but major groups include organochlorine and organophosphorus compounds, methylcarbamates, and synthetic pyrethroids.

Organochlorine insecticides have been largely phased out of general use because of their toxicities and especially their persistence and accumulation in food chains. The structures of several common organochlorine insecticides are shown in **Figure 1**.

Organophosphorus insecticides have largely replaced organochlorine insecticides, because organophosphorus compounds readily undergo biodegradation and do not bioaccumulate. The structural formulas of some common organophosphorus insecticides are shown in **Figure 2**.

Carbamate insecticides are widely used for crop protection. Methylcarbamates are of environmental concern because of their high acute toxicity. **Figure 3** depicts the structures of several common carbamate insecticides.

Synthetic pyrethroids have been widely produced as insecticides during recent years. They have several advantages over organochlorine and organophosphorus insecticides, including greater photostability, enhanced insecticidal activity, and relatively low toxicity. The structures of common pyrethroids are shown in **Figure 4**.

As a result of their toxicity and carcinogenicity, insecticides are hazardous to human health and life. The major route of human exposure to insecticides is the gastrointestinal system. Besides regular use of polluted water, humans eat large amounts of food in which these pollutants have been accumulated, e.g., milk and dairy products, fish, poultry and meat, and fruits and vegetables.

Prior to 1960, an individual analytical procedure was used for almost every insecticide. As the number of insecticides in use increased, it became impractical to apply a large number of individual methods for all the insecticides that may be present. This has led to the development of multiresidue methods for the analysis of environmental samples. Ideally, multiresidue methods should provide rapid identification and quantification of as many different insecticides as possible at the required detection level.

The concentrations of insecticides in the environment are very low, typically in the parts-per-trillion to the parts-per-billion range. Furthermore, the sample matrices in which insecticides are usually determined are very complex in most cases. Consequently, extensive sample extraction, clean-up, and preconcentration are often required prior to the analysis.