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# Modern methods of pesticide residue analysis

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## *Summary*

This report describes a study on modern methods of pesticide residue analysis in the United Kingdom. In part 2 a general idea is given of the way in which pesticide residue control in the United Kingdom is effectuated. In the following parts several methods of analysis in use at the particular divisions of the institutes visited are discussed, as well as the problems encountered within this field. An insight was gained in the modern set-up of pesticides laboratories in the United Kingdom and several methods for pesticide residue analysis were extensively studied. It was possible to get acquainted with modern equipment in this field by witnessing demonstrations and performing practical work.

## *1. Introduction*

The purpose of this study was to acquire additional knowledge in matters of pesticide residue analysis, principally with respect to methods suitable for screening for various classes of pesticidal compounds, with a view to incorporate this knowledge in the existing system of methods of analysis as used at the pesticides laboratory of the Food Inspection Service for the district of Haarlem.

During the course of the fellowship special attention was paid to modern instrumentation techniques, as applied to the analysis of organochlorine and organophosphorus compounds, as well as to unambiguous confirmation techniques in this regard.

The study was completed at the following institutes:

Laboratory of the Government Chemist. London.

Huntingdon Research Centre, Huntingdon.

## *2. Pesticide control in the United Kingdom*

Food control in general in the United Kingdom is based on the Food and Drugs Act. In this Act the special liability of additives to render food injurious to health is recognised and therefore extended powers are given for the making of regulations requiring, prohibiting or regulating the addition of any specified substance to any food for sale for human consumption. Manufactures introducing a new additive may be called upon to supply satisfactory information

and evidence as to the absence of toxic effects, both acute and chronic, from the quantities of the material under conditions of its proper use.

Additives used of express intent are more or less amenable to control by regulation, but with the type of additive which may be present as an unavoidable contamination or residue the case is different. Risks to health from this type of additive could arise for example from pesticide residues on agricultural products, and in foods prepared from them.

In the Netherlands an Act was passed which makes possible the regulation of the sale and use of pesticides and the sale of food that may be contaminated by pesticides. Under this act tolerances have been established for pesticide residues on agricultural products. In contrast to this development pesticide control in the United Kingdom is based entirely on voluntary schemes.

Manufacturers, importers and distributors of pesticides notify the government of new toxic chemicals and formulations which they propose to introduce for agricultural purposes, with full information on the product. After due investigation, recommendations are issued for conditions of use which should entail no risk of a treated crop becoming injurious to consumers. The product further should comply with certain standards of composition and performance. Labels and directions for use also require approval and through this there is a certain safe guard against excessive dosage.

An approved list is published by the Ministry of Agriculture, Fisheries and Food which includes cautionary notes on the safe use of products, on minimum safety intervals, and on prevention of feeding injury to animals, poultry and bees.

On the whole this co-operation between government and industry appears to be working well. An unassessable factor of course is the extent to which the ultimate user of a product can be relied upon to conform to the instructions given with it. Another serious problem concerns imported foods. Obviously there are practical difficulties in knowing what chemical treatments may have been applied to crops or food before importation. Even after the presence of a certain residue has been established it is difficult to take action against the importer. Under the Food and Drugs Act it would be necessary to prove that this particular residue presents a health risk to the consumer.

The enforcing of the Food and Drugs Act is entrusted to local «food and drugs» authorities. These are: the councils of larger cities and urban districts and sometimes the county councils. Each authority should appoint a qualified analyst; some analysts act for more than one authority. Sampling officers are also appointed by the authority and are empowered to purchase samples of any food or drug and to submit them to the public analyst for analysis.

As mentioned before no regulations have been made specifying tolerances for pesticide residues in food. Control at present rests on the principle of preventing as far as possible their presence on agricultural products. Pesticide residue analysis is mainly being done in a national survey by different laboratories. Within the scope of this program samples of different origins are being analysed, like agricultural products, wildlife, soil and water, and parts of human bodies.

In this way the government tries to form a clear picture on the extent of the contamination of the environment by pesticides.

### *3. Laboratory of the government chemist*

This laboratory is one of the research stations in the Ministry of Technology. Its functions are principally:

- to provide a comprehensive analytical service to all government departments requiring this; for example much work is being done for Customs and Excise; on quality control of foods for the armed forces; on forensic chemistry and in water and effluent analysis.
- to give direct scientific advice based on analytical and other chemical considerations for government departments; e. g. the government chemist is referee analyst under several Acts of Parliament: Food and Drugs Act, Fertilizers and Feeding Stuffs Act, Public Health Act. etc.
- to carry out research in analytical chemistry where the development of methods of analysis is of public importance; for example development of modern instrumental techniques and automation of methods for routine analysis.

#### *3.1 Methods, research, information*

The division «Pesticides and toxic gases» is especially concerned with certain aspects of environmental contamination with toxic compounds. It undertakes research into the development of selective and sensitive methods for the detection and determination of residues of pesticidal compounds in food, water, animal tissue etc. It also provides a pesticide residue information service.

One of the problems in conducting a survey for pesticide residues in samples of all kinds is the fact that usually it is impossible to know what pesticides will be present. An experienced analyst may be able to make reasonable good guesses to what groups of pesticides could be present, however, it would still leave him with the problem of testing for every pesticide in those groups. Thus it is easy to see that a great need exists for analytical methods able to detect the presence of pesticides of a particular class and, possibly, simultaneously to identify and to determine individual members of this class. Many methods have been published in the last decade which accomplish one or all of these goals, mainly by chromatographic techniques. The division too has contributed several interesting methods in this field; of some a short description will be given.

##### *a) Organophosphorus-pesticides (1)*

The organophosphorus pesticides including their oxidation products are hydrolyzed to produce dialkylphosphates or O,O-dialkylphosphorothionates. The compounds are methylated by the diazomethane technique and then yield products that can be separated and detected by gaschromatography. As most organosphates



contain 0,0-dimethyl or 0,0-diethyl groupings the following four compounds can be expected principally:

Trimethylphosphate, diethylmethylphosphate, trimethylphosphorothionate and diethylmethylphosphorothionate.

As a very good method for organophosphates is available in thin layer chromatography with *enzymatic detection* (2), the method could easily find application as an additional confirmatory technique for the presence of organophosphates, especially with samples that give rise to severe interference with the *enzymatic technique* (onions, radish etc). Unfortunately the method has its weak points too. In the first place it is rather cumbersome as it asks for several partitionings, a hydrolyzing and a methylating procedure, but worse is that natural phosphorus containing compounds can give rise to phosphoric acid after hydrolyzation, which on methylating yields trimethylphosphate. Thus an important part of the organophosphorus pesticides is excluded from detection.

#### *b) Urea and carbamate pesticides (3)*

The method considered here makes use of the fact that many of these herbicides yield an aromatic amine on hydrolysis. In the case of clean samples, like water, the herbicides are extracted and separated by thin layer chromatography. Hydrolysis is effected during the thin layer procedure on the plate by spraying with hydrochloric acid and the resulting amines are coupled to 1-fluoro-2,4-dinitrobenzene. These compounds are eluted from the plate and determined by gas-chromatography with electron-capture detection. Extracts from plant materials have to be subjected to a clean-up procedure. The sensitivity of the method lies in the 0,02—0,05 ppm range.

Apart from the fact that it will not always be possible to distinguish between herbicides that produce the same amine, this method certainly will be useful in the analysis of these important compounds.

### *3.2 Pesticide residue surveys*

Routinary pesticides residue surveys are being carried out with regard to environmental contamination control. Among the samples examined are food-stuffs, parts of human beings and wildlife and other tissues.

#### *a) Chlorinated pesticides*

The problem of determining residues of chlorinated pesticides in animal samples was extensively discussed. The method used for these samples is a modification of Wood's method (4).

The extracted fat is mixed with Celite 545 until a dry powder remains. A chromatographic column is filled with the powder. The pesticides are eluted with a small volume of dimethylsulfoxide and the eluate is received on a second chromatographic column consisting of a layer of prepared florisil upon a layer of prepared alumina. Then the pesticides are eluted from this second column with hexane. After concentration of the eluate to a suitable volume the extract can

be used for gas-liquid chromatography. Detection is by electron-capture. The sensitivity of this method is in the range of 0,02—0,05 parts per million, depending on the pesticide concerned.

Before concluding to the presence of a certain pesticide care should be taken of an additional identification of the compound.

This can be done in several ways:

1. Routinary all extracts are chromatographed on three gaschromatography columns of different polarity. When the retention times of a compound on these columns are identical to the retention times of a certain pesticide standard, one can be reasonably sure that the pesticide concerned is present in the sample.

2. More conclusive evidence can be attained by using thin layer chromatography. The extract that has been used for gaschromatography is concentrated to a small volume and spotted entirely in a streak on a thin layer silicagel plate. To the right and left of the streak 10  $\mu$ l amounts of a 0,1 % of the suspected pesticide(s) are spotted and the plate is developed in a suitable solvent. After development the part of the plate where the sample extract has been spotted is covered and the plate is sprayed with a suitable detection agent. Spots of the pesticide standards should become visible. The unsprayed part of the thin layer plate with the same  $R_f$ -value as the pesticide standard is now scraped off and eluted with a suitable solvent, like benzene. After concentration to the original volume gaschromatograms are run again. On all columns the peak with a retention time identical to that of the suspected pesticide should appear again.

3. For the identification of several important chlorinated compounds chemical reactions exist.

The extract is evaporated cautiously to dryness and the reaction is carried out. After completion of the reaction the reaction mixture is extracted with hexane and the extract injected into the gaschromatograph again. The original peak should have disappeared from the gaschromatogram and a new peak should appear. Of course one should carry out the procedure with a standard solution of the pesticide to determine the exact retention times of the reaction products on the different columns.

Thus p,p'-DDT(dichlorodiphenyltrichloroethane) and p,p'-TDE(dichlorodiphenyldichloroethane), a metabolite of DDT, can be converted to respectively p,p'-DDE(dichlorodiphenyldichloroethylene) and p,p'-DME(dichlorodiphenylmonochloroethylene) by heating the residue of the extract for 5 minutes with an alcoholic potassiumhydroxyde solution. Another metabolite of p,p'-DDT, p,p'-DDE can be oxidized by chromiumtrioxide in glacial acetic acid to dichlorobenzophenone. By a reaction with a chlorine solution aldrin can be oxidized.

Dieldrin, endrin and heptachlorepoxyde can be converted by heating with concentrated HBr or HCl in glacial acetic acid to reaction products in which the epoxide ring is split open.

4. Identification by Infrared-spectrometry is also very reliable but the equipment is rather expensive and the technique is rather complicated.

5. The determination of the *p*-value of a compound also can be used as a means for identification (5). This value is a partition coefficient of a compound between two immiscible liquids, e. g. hexane and acetonitril, though somewhat differently defined.

An important drawback is that for compounds of equal polarity *p*-values lay close together and an identification cannot be made.

A further complication in the analysis of animal fat samples is the occurrence of polychlorinated biphenyls (PCB's). These compounds which have several important uses in industry, are met regularly in samples of human, wildlife and water, and thus seem to have contaminated the environment to quite an extent (6). PCB's differ among each other in number of chlorine atoms per molecule (mostly 3—7); moreover for every number a multiple of isomers is possible. Furthermore it is highly possible that these compounds are partly metabolized in the living body, so it is understandable that their presence can give rise to complicated gaschromatograms which are easily misinterpreted.

At the moment it is not clearly understood how PCB's get into the fat of humans and animals, nor what effect, if any, they have on the body in the amounts found. Anyhow they present a problem to the analyst looking for pesticide residues, who should always bear in mind that these compounds may be present in fat samples.

By column chromatography it is possible to separate PCB's partly from chlorinated pesticides. The sample extract is brought onto a column of silicagel (3% w/w of water) in hexane and eluted with hexane. The eluate should contain all PCB's plus *p,p'*-DDE and hexachlorobenzene. The chlorinated pesticides can be eluted with hexane-diethylether (9+1).

#### *b) Organophosphorus-pesticides*

Organophosphorus compounds are another group of pesticides which is regularly analysed in the division. These compounds more and more tend to replace the organochlorine compounds in view of their much lesser persistency. The method chosen here is gaschromatography too, but detection is by the thermionic detector (7). This detector is a modification of the well-known flame-ionisation detector which makes it selectively sensitive to phosphorus-containing compounds. This is effected by bringing salt of an alkalimetal in the flame which enhances the response to organophosphates up to 600 times. The theory of this effect is not quite clear.

Several designs of the detector are possible.

One consists of a platinum wire on which the alkali salt is deposited by dipping in the molten salt and cooling off. The wire which had been coiled before the dipping, is situated around and above the flame.

Another is made of a pressed tablet, bored through and put on top of the flame tip. This is the design used in the division. The alkali salt chosen is caesium-bromide and tablets are pressed by the technical division of the laboratory. Much time was devoted to establish optimum working conditions for the detector.



As is generally known it is very sensitive to changes in flowrate of the burning gases, especially the hydrogen flowrate. But the response can be influenced too by the geometry of the salt tablet. After several trials it was decided that a salt tip with a slight depression in the top gave best results.

#### *4. Huntingdon research centre*

The Huntingdon Research Centre was formed in 1952 as a private consultant and research practice. Since then the organization has been expanding fast and now is one of the largest organizations for sponsored research in the world. Though originally specializing in nutrition, the organization now does research work on medical, biological, biochemical and chemical problems. The largest part of its resources are devoted to toxicological problems rising in the manufacture and release of new drugs, food additives, cosmetics, pesticides, packing materials etc. For this purpose a wide selection of animal species is maintained, supported by all necessary laboratory facilities, so that it is possible to take a candidate drug or pesticide through the complete range of laboratory and clinical studies designed to establish efficacy and safety prior to marketing.

#### *Organophosphorus and organosulphur pesticides*

For phosphorus-containing compounds use of the recently developed flame-photometric detector is often possible, providing the pesticide in question is sufficiently volatile to be gaschromatographed. The detector was described in 1966 by Brody and Chaney (8) and produces a very specific and sensitive response for organophosphates or organosulphur compounds. The response of the detector is based on the strong hydrogen flame emission at 526 nm for phosphorus and at 394 nm for sulphur compounds. The geometry of the flame housing allows a photomultiplier tube to view only the tip of the flame, and narrow band interference filters allow only the desired wavelength emissions to pass into the tube.

With this detector some practical work was done. The carrier gas was nitrogen, and hydrogen and oxygen were used as the burning gas mixture. The hydrogen flowrate is held normally at 150 ml/min and the oxygen flow at 25 ml/min.

These burning gas flowrates were varied in a wide range but no significant change in response could be detected. In this the flamephotometric detector compares very favourably to the thermionic detector. After every injection of 1  $\mu$ l or more the flame, will extinguish, therefore the hydrogen flow was shut off until the solvent cleared the column. This normally takes about 15–30 seconds. The hydrogen flow was then reset while current was passed through the igniter coil.

Conventional gaschromatographic procedures require extensive sample clean-up and even these clean-up procedures may fail to remove substances which interfere with the determination. Since compounds other than organophosphates or -sulphates have virtually no photometric response as long as the concentration of the contaminant in the sample injected does not exceed about  $10^4$  ng it is to be expected that fewer sample clean-up steps are required. In addition, the detector



can distinguish between phosphorus and sulphurous compounds by just changing the filter and running the sample again (a detector is now commercially available which has both modes of operation simultaneously).

For quantitation purposes it is best to use the 526 nm optical filter since response to phosphorus containing compounds is linear over four decades of concentration. Response to sulphurous compounds is non-linear and about one order of magnitude less sensitive than the corresponding phosphate variety.

As an extra the detector can function as a conventional flame-ionisation detector simultaneously with its photometric mode of operation.

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