5) Possible Interference by Chlorinated Biphenyls—by G. Widmark (Institute of Analytical Chemistry, University of Stockholm, Roslagsvagën 90, Stockholm 50, Sweden)

A large number of unknown but chlorine-containing compounds have been detected in addition to the ordinary pesticides in the analysis of samples, using both the electron capture and the microcoulometric detector. The spectra of some of these compounds obtained with a combined gas-chromatograph-mass spectrometer (LKB-9000) indicated that most of the unknown compounds are polychlorinated biphenyls, potentiated somewhat in nature towards those of higher degree of chlorination. A large number of samples have been examined. Polychlorinated biphenyls are found especially in fish and in birds, but also in conifer needles and in some samples of human depot fat. Two hundred samples of soil and water and twenty samples of terrestrial mammals contained no detectable amounts of chlorinated biphenyls. Typical GLC traces are given by Jensen and Widmark (1). By using a nitration method, most of the ordinary pesticides can be removed from extracts and the polychlorinated biphenyl will be unaffected. In this way, it has been shown that two of the major chlorinated biphenyl peaks overlap the peaks of *p,p'*-DDT and *o,p'*-DDT, respectively. This overlap is found with SF-96 columns, most frequently used for the quantitative residue analyses reported in literature, but not with QF-1 columns.

(c) Confirmation of Identity—by K. E. Elgar (Shell Research Ltd., Woodstock Agriculture Research Centre, Sittingbourne, Kent, England)

Multidetection methods would seem to be essential for the analysis of organochlorine residues because of the number of chlorinated components which can be present in any one sample. However, there are problems of interpretation even when techniques are used with the resolution and sensitivity of electron capture GLC. For example, the resolution of the GLC column may not be sharp enough to separate components; or impurities present in the technical pesticide or other natural products present in the extract may complicate the analysis; or some insecticides may thermally or catalytically decompose during the analysis.

For these reasons, residues of organochlorine compounds should be confirmed by other analytical methods. If enough material can be isolated, infrared spectroscopy or mass spectroscopy can give powerful evidence of identity. However, with other methods in common use the physical basis underlying separation is very similar. Robinson *et al.* (2) reported a highly significant concordance between the "p-values" for pesticides in the various partition systems described by Beroza and Bowman (3). Similarly, retention times on different GLC stationary phases and R_f of pesticides in various TLC or paper chromatographic systems are highly correlated. Furthermore, R_f values in paper chromatography are closely correlated with R_f values in TLC and with p-values. It is possible to do a great deal of work with the intention of establishing the identity of a compound, but very little additional evidence will be gained because the results from the methods used were not independent. GLC retention time, an R_f value from TLC or paper chromatography (or a p-value), a GLC retention time of a derivative formed by chemical reaction, and pesticidal activity against a susceptible organism are considered to be independent parameters giving significant evidence of identity.

5. Organophosphorus Insecticide Residue Analysis

The Commission concluded that while the regulatory methods were adequate for parathion and malathion, clarification of the terminal residue situation would be welcome in some instances. However, more work on the cleanup stage for malathion residues in eggs, milk, and dried fruit was indicated.

6. Dichlorvos Residue Analysis

By R. A. E. Galley (Shell Research Ltd., Woodstock Agricultural Research Centre, Sittingbourne, Kent, England)

Five different approaches have been developed for the determination of traces of dichlorvos: total phosphorus (4, 5), colorim-

DSW 201196

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etry using dinitrophenylhydrazine (6), alkaline resorcinol (7, 8), specific bioassay (9), cholinesterase inhibition (10–12), and gas-liquid chromatography with the thermionic detector (13) and the microcoulometric detector (14).

On the basis of sensitivity, selectivity, speed, and possibility of multidetection, the most suitable technique is GLC. Its sensitivity (in the nanogram range with the more sensitive detectors) is approached only by the cholinesterase inhibition procedure, and it is unmatched on the other counts. However, there are two aspects in the analysis of traces of dichlorvos by GLC in which improvements are needed. These are the suppression of decomposition of dichlorvos on the GLC column, and the selection of the best detector from (*a*) electron capture, (*b*) thermionic, (*c*) microcoulometric, and (*d*) flame photometric.

The other sensitive method which is in widespread use (and which, together with GLC, offers additional evidence of identity) is the cholinesterase inhibition procedure. This is a general method for anticholinesterases; to analyze mixtures of inhibitors, separation before the analysis is required. However, the volatility of dichlorvos is such that it can be steam distilled from extracts even when they contain a high proportion of fatty material. It is possible, therefore, to obtain a degree of specificity in the analysis for dichlorvos by cholinesterase inhibition by incorporating a steam distillation step before the determination.

Procedures for the collection of dichlorvos vapor from the air, extraction of residues from crops and tissues, and cleanup are available. Dichlorvos may be quantitatively removed from air by bubbling through distilled water. Chloroform, methylene chloride, and benzene have been used to extract dichlorvos residues. Partitioning from an organic solvent into water, column chromatography on silica gel, and steam distillation provide adequate cleanup from fatty and nonfatty materials.

7. Piperonyl Butoxide Residue Analysis

The Commission recognized the need for reliable methods for residues of piperonyl butoxide and certain allied materials such as allethrin and MGK 245.

8. Radioactivation Methods of Analysis

The Commission was informed that the International Atomic Energy Agency (IAEA) had indicated that it would be prepared to (*a*) provide facilities for co-ordinating collaborative studies of existing radioactivation methods, (*b*) assist organizations in the use of activation techniques for the evaluation of analytical methods in general, and to help laboratories wishing to establish radiochemical techniques (15). It was agreed that while radiochemical methods of analysis were useful for mercury and for bromine residue determinations, they were very expensive and not necessarily more sensitive or more specific than some other methods. Moreover, although they were often useful in metabolic or field residue trial studies, radiochemical methods were in general inappropriate to regulatory methods of analysis; the development of various other methods of regulatory residue analysis was far more suitable.

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DSW 201197

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