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MONSANTO CHEMICALS LIMITED
RESEARCH AND DEVELOPMENT DEPARTMENT
RUABON

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MEETING REPORT

Meeting: Informal discussion on Analytical Problems caused in Pesticide Analysis by Interference of Polychlorinated Biphenyls. Organised by The Ministry of Agriculture, Fisheries and Food (Biochemistry Section).

Held at: Ministry of Agriculture, Fisheries and Food,
Whitehall Place East,
London, S.W.1.

On: September 17th 1969.

Attended by: E. Parry
R.A. Lidgett.

INTRODUCTION AND SUMMARY:

The meeting was arranged as a very informal discussion between approximately 15 representatives from industry, government and conservation authorities on the problems introduced in the analysis of pesticides by the discovery of interfering polychlorinated biphenyls. An active chairman kept discussion almost wholly on the analytical problem; toxicity of p.c.b.s was generally avoided - no major analytical developments were announced, but the strength and weakness of various methods was discussed at length. The meeting was of most value in enabling an appreciation of the attitudes of the various participants to be assessed.

As the meeting was both informal and had no fixed programme, questions and answers were spontaneous and covered a wide range of problems in P.C.B. and pesticide analysis and the interpretation and use of results. The Chairman kept the discussion centred on the analytical problems and although questions on toxicity, source of P.C.B.s etc. were raised, these constituted only a small proportion of the discussion. For convenience, the points of interest to

Monsanto which were raised at the meeting have been divided ihto two sections:-

1. Analytical

It is evident that there are two schools of thought on the analytical difficulties which arise in the unambiguous confirmation of P.C.B.s in biological and other extracts. The industrial and government representatives are showing greater concern about absolute identification, e.g. by the use of combined gas chromatography-mass spectrometry, while a number of the representatives from the conservation authorities tended to be less well informed about the complexity of P.C.B.'s, e.g. the use of two or three columns of different polarity to confirm identity of a possible P.C.B. was frequently quoted - the ten or so peaks usually obtained on a packed column being taken as representing the same number of isomers and homologues. It was also suggested that the higher boiling components of many industrial P.C.B.'s are not considered in quantitative analysis since they are generally not detected on the chromatogram. One case was quoted where a chromatograph left running for 18 hours produced a large number of small peaks of long retention time and these were "identified" as P.C.B.'s. However, it was not explained why industrial P.C.B. mixtures should produce chromatograms with large gaps between the major components and those of higher R.T. and it was agreed that although some small late peaks could arise from P.C.B.'s, these were negligable compared with the major components.

1.2 Sources of Non-Biological Contamination

Contamination of specimens prior to analysis was discussed in some detail and a number of interesting examples were given :-

(a) Salmon from the Coho river in Canada have been under examination because of suspected contamination with chlorinated hydrocarbons (P.C.B.'s chlorinated naphthalenes etc.). It has now been found that contamination has been caused by extraction of additives from the polyethylene sample bags, the contaminants being identified as phthalates used as plasticisers and such contamination often occurs if the samples are of a fatty nature, e.g. seal blubber. In this respect a question was raised on the possibility of P.C.B.'s being used as plasticisers or in conjunction with plasticisers but this was not pursued.

Phthalates have also been found in other biological samples and although the source is unknown, contamination was thought to arise from sample handling (one laboratory consistently found phthalates after repainting!).

1.3 Separation of P.C.B.'s from D.D.T. residues

It was generally agreed that the most fruitful analytical methods for mixtures of P.C.B.'s and pesticide residues involve prior liquid chromatographic separation of the P.C.B.'s either from the D.D.T. residues directly or by oxidation of the D.D.T. residues with chromic acid/glacial acetic acid or perchlorobenzoic acid to ketonic derivatives followed by column chromatographic separation. The most suitable columns used for such separation have been

found to be of thin diameter packed with dry silica gel of small particle size. These are far easier to prepare reproducibly than Florasil columns.

It was reported that a method for the single stage clean up of D.D.T. residues has been accepted for publication (author A.V. Holden, Freshwater Fisheries, Pitlochry) by the Journal of Chromatography.

In the course of the discussion on liquid/solid chromatography separations one example was quoted by D.C. Abbott (Laboratory of the Government Chemist) where a single P.C.B. isomer (not identified, but a Cl_6 isomer) has been isolated from an alumina column separation. This was isolated from a heron egg extract (believed to have been obtained from S. Lincolnshire) with a quoted total P.C.B. content of 900 ppm.

1.4 Quantitation of P.C.B.'s.

It was accepted that because of the absence of reliable standard P.C.B.'s absolute quantitative determination is at present impossible for biological extracts. Abbot et al have calculated an "average electron capturing power" for certain P.C.B.'s (mainly Aroclors) and this is applied to unknown P.C.B. peaks in residue analysis. The estimated difference between isomers with low and high electron capturing properties is considered to be an order of magnitude.

The view taken by Shell Research is that quantitation of P.C.B. chromatograms in residues presents such a problem that an approach using the measurement of total chlorine content coupled with gas chromatographic measurement of the pesticide residues may well have to be used. Alternatively, measurement of the total biphenyl moiety is being tentatively examined, this is along the same lines as the use of the Beroza unit in Applied Sciences Section.

2. General

A number of interesting comments were made at the meeting which were not directly concerned with the analytical problems. These are given below:

(a) Jensen is intending to publish in J.A.O.A.C. methods for the absolute identification and quantitation of P.C.B.'s in residues. Emphasis was placed on the fact that it is intended to publish as there seems to be some disagreement between various Swedish workers in this field and the paper has been in preparation for some time.

(b) Professor Widmark has agreed to address the Pesticides Group in London in approximately one month. This meeting will be attended if possible.

(c) Moore and Jeffries of The Nature Conservancy at Monkswood have carried out a survey of P.C.B. distribution in the United Kingdom. It was not determined whether this would be published or not.

(d) After the recent outbreak of foot and mouth disease in the United Kingdom an apparent increase in "P.C.B." contamination has been found in biological specimens. This was made as an observation rather than a statement of fact based on statistics, and was included with a question as to whether P.C.B.'s are used in agricultural disinfectants. An alternative interpretation (not made at the meeting) can be made that this may be an example of the biological change of non P.C.B. materials into components producing P.C.B. like chromatograms.

(e) It was also noted that samples taken from terrestial birds show the higher chlorinated P.C.B. homologues at relatively low levels while fish specimens show lower chlorinated P.C.B. homologues at high levels. This was interpreted as being a function of the different metabolisms of cold and hot blooded species.

(f) In a private discussion after the meeting Dr. C. Franklin (Dept. of Pharmacology, Chelsea College) requested samples of Monsanto Aroclors for a project being carried out by him on the effect of chlorine residues on liver enzymes. He has agreed to keep Monsanto informed of results and thought that initial effects, if present, would be observable between 4 - 6 weeks after initial dosing.

The meeting, although short, was very useful for making contact with people working in the pesticide/P.C.B. field.

R A Liggett

R.A. LIDGETT

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