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→ WB Papageorge — StL

D.W.H. CASEY

5th October, 1970.

P.C.B's.

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A.F. REGAN.

A meeting concerning polychlorbiphenyls in connection with GLC Analytical Methods and Wildlife was held at the Tunstall Laboratories of Shell Research Limited at Sittingbourne, Kent on 29th September 1970. The meeting was arranged by the Ministry of Agriculture, Fisheries and Food, and followed a similar meeting held in 1969. Approximately forty people attended, mainly from various branches of the Ministry and related Research Associations. Several Universities were represented. Industrial representation was limited to Unilever, Shell and Monsanto. The proceedings were conducted informally, although presentations on various topics were made in brief lecture form. Some notes are presented.

S. Bailey [Min.of. Ag.etc] gave a brief account of the previous meeting which had been held to discuss various aspects of PCB determination. The interest had arisen from work carried out on determination of various chlorinated pesticide residues in animal and agricultural samples where the PCB's first appeared as unknown contaminating peaks.

A. Richardson [Shell] discussed some aspects of DDT and PCB analysis. He mentioned Burg [Canada] who had evolved a technique of catalytic reduction/hydrogenation converting PCB's to dicyclohexyl type hydrocarbons for FID determination. This was generally thought to be of little use if the analyst had access to EC detection. Clean-up techniques were briefly mentioned.

Telling & Siscone [Unilever] outlined their methods emphasizing an oxidative clean-up procedure. Total recoveries were good, in the 90-95% range with the main losses occurring during solvent removal. Their main research-type development was a shift to high-resolution [eg. capillary] chromatography with use of coupled physical methods e.g. NMR or MS in order to establish peak identity. This showed that some ordinary GC peaks were actually multiplets.

Cleaning up procedures were mentioned, stressing their need where other residue peaks overlay PCB peaks. A new GC stationary phase poly-m-phenoxylene had been tried and was one of the few phases found to elute DDE [a chlorinated pesticide] in an area free from large PCB peaks. The phase had a good upper temperature limit of about work.

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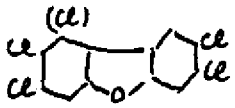
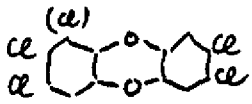
R.A. Lidgett [MCL Res.Burban]. R.A.L. briefly outlined the MCL position as far as analytical methods were concerned mentioning that the MC "methodology package" had been made available. The present research investigations into high-resolution GC with other physical methods being used to establish peak identity were also indicated.

The writer, asked to comment briefly from a plant producing Aroclors, outlined the equipment available at Newport and mentioned our monitoring of effluent discharge and advisory service to customers, or any other interested parties.

Professor van Genderen [Utrecht, Holland] described some of the work on PCB's at Utrecht. Three commercial chlorinated diphenyls were being looked at in one particular investigation. These were, Aroclor 1260, Clophen [of German origin? Bayer] and Phenachlor [French origin - ? Prodelec], both of the latter being in the same range as 1260. These three appeared to be of different toxicity levels with Aroclor 1260 being the least harmful from the studies with controlled diet feeding to rats. Analytical investigation showed that the Clophen and Phenachlor contained compounds of the following types:



tetra chlor dibenzofuran
[penta]



Tetra chlor dibenzo dioxadiene
[penta]

which from other work are known to be quite toxic; in particular they can set up skin conditions of the chlor-acne type. Measurement and identification were made by a combination of gas chromatography and mass spectrometry. Aroclor 1260 was found to have none of these compounds, Clophen could have up to 5 ppm and Phenachlor up to 20 ppm.

Holden [Fishery Research, Pitlochry], spoke about possible modes of entry of PCB's into the animal environment [especially the marine environment]. One apparent source that they had uncovered was from the dumping of sewage sludges. Sewage farms in the Glasgow area periodically dumped sludges well down the Clyde and some, but not all of those farms had sludges with PCB contents giving a total dump of about 1 ton of PCB per year. Similar checks in the London area had shown the same state of affairs. The Bristol region, however, had not shown any worthwhile dump rate. The speaker wondered whether land dumps also presented a possible route via the animal feeding chain i.e. for small creatures to pick up PCB's in their diet, ending up perhaps with the large animals such as birds and various marine animals. He mentioned that as yet no PCB's had been found in fresh water fish

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Franklin [Chelsea College]. Speaking on enzyme induction effects of PCB's described experiments in progress on rats where rather large [25mg/kg bodyweight] injections of Aroclor 1242 were given. In tests lasting up to 20 days no ill-effects were observed in that the rats did not die and remained visibly healthy. PM examination showed the expected increase in fatty tissue around the liver which is not peculiar to PCB's, but is caused by many other compounds as well. Various in vivo and in vitro tests were described to demonstrate that the PCB effect seemed to be causing an increased production of various enzymes.

General Discussion.

Considerable general discussion took place and some points are noted below:

1. The Monsanto attitude to the PCB question was warmly welcomed in that the Company was taking part in the present discussions, in that it made information on methods readily available and provided samples of Aroclors, and was plainly seen to be co-operative.

2. Many speakers deprecated the Press presentation on PCB's which tended to imply that this was the major reason for toxic effects particularly on sea birds and other marine animals. As one speaker succintly put it "why blame PCB's?". It was hoped that the present accent on PCB's was not drawing off unnecessarily a large amount of technical effort. Here the MCL people could only point out that Aroclors had been made in this country for 20 years, and in the U.S. for about 20 years before that and that one might have expected toxic effects to have shown up earlier.

3. The Bristol Channel area was mentioned as having been surveyed for evidence of PCB's and some surprise was felt at virtually none being found, although the Newport Plant was in that area. We stressed that our works effluent was monitored and the PCB discharge was at a very low figure, [no figure was mentioned, nor was reference made to estuarine mud examination].

4. One speaker questioned the normal variation in chlorine content of an Aroclor. The answer of about $\pm$ 0.5% on the nominal value with no effect on the interpretation of a PCB chromatograph was satisfactory. This question seemed to indicate that many people working in this field did not have all the technical information available to them. The impression was formed that some people without a chemical background felt that e.g. Aroclor 1242 was a distinct chemical entity, different from e.g. Aroclor 1254, and did not fully appreciate that both were mixtures of similar chloro compounds in differing ratios.

5. Mention was made of the fact that some toxicity work was being done on Aroclor 1260, some on 1242 and so on. This led to questions on the quantities produced of the various grades and also on the use-pattern by area and perhaps by industry.

   None of these questions was answered directly, but it was pointed out that certain information might be made available to workers in the field if a written request was presented.

This might enable interest to be concentrated on some PCB's more widely used than others. It was further pointed out that MC was not the only producer of PCB's and thus North Sea pollution might be arising not from MC material. In this respect some of Professor van Genderen's remarks were quite relevant.

6. The trend to high-resolution GC and indentification of peaks promted several people to point out that there could be considerable differences in toxicity between the various components of a PCB. Although the size of the task of identifying all the peaks in a chromatogram was large enough, that of attempting toxicity studies on individual components was very much larger.

Summary.

The meeting served to keep Newport in touch with possible analytical developments in the PCB field, and also outlined the wider complications.

It was also fairly obvious that although the Company has made much information available, we might still have more to do in the educative line even if only to ensure that people do not make erroneous assumptions about PCB's.

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