E T A D

Analytical Sub-committee

Minutes of the 10th Meeting held at Ludwigshafen/Rh.
on 23rd and 24th November, 1977

MONS 200070

3.3. Supplements to ETAD Analysis Method 212
(Amines in pigments and solvent-soluble dyestuffs)
Remarks on various items of Method 212 in regard to the weighed portion, amount and concentration of extraction agent, the solvents used, detection limits, blank values, etc. have been prepared by Dr. Trautner and Dr. Rosenthal (both from Bayer) and copies of these papers will be sent to ASC members by Dr. Steuerle.

ACTION

The suggestions for improvement are to be taken into account should any urgent reason for revising Method 212 arise.

4. PCB's in pigments Nov 23, 1977

4.1. Results of round-robin test to determine PCB's in ®Heliogen Blue

4.2. Discussion and decision on further action

Items 4.1. and 4.2. were discussed together.

The results of the agreed ring test were summarized in a list (Appendix ASC 10.2.). This contained the results, listed according to specimen preparation and final determination. The Hoechst findings were presented at the meeting and are to be found in Appendix ASC 10.2. The results differ very greatly (extreme values 16 and 139 ppm), and no dependency was observed either on specimen preparation or the type of final determination. At all events a large group of results, 80-140 ppm with the accent on 110, was considered to be apparently correct as it appeared possible that losses could occur in preparation of the specimens whereas, in contrast, simultaneous detection of constituents other than PCB did not appear very probable, for a variety of reasons. One of these resulted from conformity of the

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values found at BASF using another chlorine-specific detector, a further reason was conformity of the Hoechst values as ascertained by measuring with UV, a third reason being that the clean-up does not really influence the results. ICI and BASF found that the PCB's present in the specimens consist mainly of an isomer blend of biphenyls chlorinated six times and small quantities of biphenyls chlorinated five times. Bayer had claimed that there was a larger proportion of the latter.

The existence of oxygen-containing compounds mentioned by Bayer was confirmed in principle by BASF. The concentration of these compounds was comparatively low and had practically no influence on the determination of PCB's. According to BASF, chlorinated dibenzofuranes as mentioned by Bayer are not present, but chlorinated biphenylethers (Cl_5-Cl_7) are present.

In view of the multiplicity of PCB isomers and homologues, which would be practically impossible to deal with individually, it was suggested that (at least temporarily) a screening method be developed such as would involve no undue precleaning and little effort.

TION In this connection, the question is put to the Technical Committee as to whether a method covering a range of a few ppm and yet having an error limit of $\pm$ 30 %, satisfies the requirements. More exact methods involve very much more effort.

The following methods were suggested: Determination following reduction with $LiAlH_4$ using FID as biphenyl;

direct gas chromatographic determination using ECD. Both to follow separation of the PCB's with n-hexane from sulphuric acid solution in accordance with the BASF method*. Direct perchlorination by the ICI method. It was pointed out that the methods which involve reduction or perchlorination of the PCB's do not in principle indicate which compounds were originally present. This means that wrong conclusions could possibly be drawn if the results are used without caution. On the other hand, there is the advantage that constituents which would otherwise be detected together with the PCB's are almost certainly excluded.

By offering several methods, it is possible for laboratories having varying apparatus to carry out PCB determination.

ACTION

All ASC member companies at the meeting declared their willingness to carry out five tests with each of the three methods and using the sample of copper phthalocyanine sent previously to them by BASF. Farbwerke Hoechst will concentrate on the problem of the low chlorinated biphenyls possibly formed from dichlorobenzidine.

The question as to which stages of chlorination of biphenyl need to be determined (on which no guidance has been received from the toxicologists) was provisionally dealt with by stating that, initially, the high-chlorinated stages from $C_{12}H_6Cl_4$ should be determined in view of greater tendency to accumulate in fatty tissue.

*The methods of determining PCB's via biphenyl or decachlorobiphenyl had already been passed on by ACNA and ICI to ASC members at previous meetings.
At the 10th Meeting, BASF passed on their method of direct determination of PCB's in copper phthalocyanine to ASC members.

ACNA suggests in an additional letter (22.12.77):
"If possible, it would be better to aim at an extraction method useful both for the high chlorinated biphenyls in Cu phthalocyanine and for low chlorinated biphenyls (3.3-dichlorobiphenyl) in dichlorobenzidine pigments. According to our experience, this is possible following ACNA method where PCB's are in contact with the conc. sulphuric acid only for five minutes in an ice-bath, whereas applying BASF extraction method the contact time is about 2 hours at room temperature; during this long period, about 30 % 3.3'-dichlorobiphenyl could be sulphonated (see ACNA letter to Members of ASC-ETAD 5.9.77)."

5. Accumulation of dyes in fish

Dr. Steuerle reported on the efforts of BASF to obtain authorization from MITI for two disperse dyes. The results obtained in the first test series were reported on at the 9th Meeting of the ASC. Following submission of the results of a second test series to MITI, more details were objected to than was the case with the first series, i.e.:

1. The use of commercial dye instead of pure substance which would then have had to be dispersed in accordance with the MITI rules.

2. Maintenance of the fish, in which the water-containing test substance was renewed daily and not continuously.

3. The analysis, as mackerel and not carp were used to determine the recovery factor.

Comments: Dr. Rüttner referred to the remarks made during the visit to Japan in 1977 regarding the results of tests with water-insoluble substances.
All member companies who had previously submitted results of tests with disperse dyes considered

BASF AG-Ludwigshafen
Untersuchungslaboratorium

15.11.1977

Für die Sitzung ASC der ETAD am 23./24.11.77

Bestimmung von PCB's in Kupferphthalocyanin

Probe: Heliogenblau Cu-Phthalocyanin ex BASF 15.08.1977

Firma	Methode	gefunden Biphenyl ppm	gefunden PCB $(Cl)_{5-6}$ ppm	gefunden DCB ppm	berechnet PCB $(Cl)_{1-6}$ ppm
ACNA	1) H_2SO_4/Kieselgur// Kieselgelsäule/n-Hexan// $LiAlH_4$//GC-FID	47/40/47/45 41			87
	2) Soxhlet-Extraktion//GC	39/39			83
BASF	1) H_2SO_4/n-Hexan 2 h// GC-ECD		106/113 118/116 113/102 [65/61] 107/170 108/110 111 ± 5 (ohne Ausreißer)		111
Bayer	1) wie ACNA 1)	12			25
	2) Wie ICI 3)			140	92
	3) Bayer 2077/0001775/01 DMF/CH_3CN/H_2O/n-Hexan// DC-Kieselgel///$(C_2H_5)_2O$// n-Hexan//GC-Kapillare		80/37		80/37
Ciba-Geigy	Isolierung nach Bayer 3)// Reinigung 1 n/KOH// 1 n/H_2SO_4// Perchlorierung nach ACAC// GC-ECD			75	16
ICI			a)	b) *)	a) b)
	1) n-Hexan Soxhlet 3 h		30	41	30 30
	2) n-Hexan Soxhlet 6 h		30	48	30 35
	3) H_2SO_4/n-Hexan 12 h a) Direkt GC-ECD b) Perchlorierung//GC-ECD		35	55	35 40
Sandoz	1) Soxhlet Toluol 9 h Soxhlet Toluol 13 h Soxhlet Hexan Soxhlet Aceton Perchlorierung//GC-FID			212 182 157 161	179 119 103 105
	2) Quellen DMF / Extr. Toluol// Quellen DMF / Extr. Toluol// Perchlorierung//GC-FID			94 101	62 60
	3) H_2SO_4/Kieselgur//Kieselgel/ n-Hexan//Perchlorierung//			191/???	17?

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Fortsetzung:

Hoechst	1) H_2SO_4, n-Pentan// GC (OV)		75 64 75		75 64 75
	2) Clean up wie // Bayer 3) GC		99 63 102 73 102		99 63 102 73 102