PCBS IN COLOURING AGENTS – CONTAMINATION AND PATTERNS IN SELECTED SAMPLES

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Introduction

Polychlorinated Biphenyls (PCBs) are known for long as being toxic with different toxicological modes of action, comprising dioxin-like (dl-) and non-dioxin-like (ndl-) effects, depending on the congener specific chlorination pattern. Derived from these facts, Californian government issued a "safe harbour level" for PCBs[1], describing a maximum daily intake of "Total PCBs" considered as not being harmful to human health. Furthermore, PCBs in general have been recognised as being carcinogenic to humans by the IARC[2]. These regulations imply the demand of precisely analysing the Total PCB content in terms of determining all 209 possible congeners. Besides of that, the discussion on POPs in general is still ongoing. We have to acknowledge that persistent compounds are still – decades after their ban – released into the environment in different ways, among them unspecific release from inhabited areas, remobilization from glaciers, or – perhaps more important as by-products from chemical production. Especially dyes and organic colourants can contain trace amounts of PCBs originating from the basic chemicals of their production or formed during chemical reactions[3,4] .
Among the broad variety of colouring agents, there is a steady monitoring for undesired or banned colouring agents within the EU, e.g. of the Sudan Red type. Besides of being banned due to their toxicity, the question arose in how far they might contain PCBs themselves. This study presents some results starting from an analytical method which has been specifically developed and evaluated in our laboratory.

Materials and methods

In total, 19 samples of 14 colouring agents have been analysed for 209 PCBs, including calculation of the congener group totals, at the Eurofins GfA Lab Service in Hamburg. The samples consist of commercially available colourants (mainly technical grade purity), with one exception all being azo dyes (see table 1).

Sudan Red I	*(842-07-9)*	*Para Red*	*(6410-10-2)*
Sudan Red II	*(3118-97-6)*	*Ponceau 2R = Ponceau Xylidine*	*(3761-53-3)*
Sudan Red IV	*(85-83-6)*	*Rhodamine B#*	*(81-88-9)*
Sudan orange G	*(2051-85-6)*	*Xylene Fast Yellow 2G*	*(6359-98-4)*
Sudan black B	*(4197-25-5)*	*Sunset Yellow FCF**	*(2783-94-0)*
Acid Red 1	*(3734-67-6)*	*Chromotrope FB = Azorubine**	*(3567-69-9)*
Acid Red 88	*(1658-56-6)*		
Acid Orange = Orange II	*(633-96-5)*		

Table 1: list of the examined colouring agent samples (CAS-nr. in brackets)

#Rhodamine B is a xanthene dye. The major part of the analysed colourants are not allowed in food within the EU, with certain exceptions for the substances marked with * (Sunset Yellow FCF and Chromotrope FB)[6].

The analytical method consisted of an essentially improved protocol based on existing methods for determination of PCBs in colouring agents as well as EPA1668C[3], modified for comprehensive analysis of all 209 PCB-congeners, where the sample intake has been reduced in order to adapt to possibly high findings. The samples have essentially been dissolved and cleaned with n-hexane and conc. sulphuric acid under ultrasonication. The following HRGC separation was performed on an HT8-PCB 60m * 0.25 mm * 0.25 µm GC-column using a Waters Autospec Premier HRMS at mass resolution R ≥ 10.000. Quantification was performed using the isotope dilution method, accepting ca. 170 separations for reasons of constant data quality. Afterwards results of the individual congeners were added to form congener group totals from Monochlorobiphenyls to Decachlorobiphenyl. Though the method has not been optimized for dioxin-like PCB to reach the lowest feasible LOQ, a TEQ calculation has been made within the designed frame, reaching upperbound LOQs in the range of ca. 20 ng $TEQ_{WHO2005}$/kg.
All analytical data are reported in µg/kg product, all TEQ values are given using WHO-TEFs (2005).

QA/QC measures consisted e.g. in monitoring the quantification standard recovery rates (criterion range 40-130%; acceptable for >95% of all values), as well as batch blanks and control samples. The limit of quantification was established based on an approach according to EN1948-4 using averaged blank values plus 5-fold standard deviation. For calibration, an initial multipoint calibration curve was established for reference purposes, and daily single-point calibrations were used with the initial calibration as criterion. This has been performed individually for all reported congeners/peak groups. Further details of the method and quality criteria are described elsewhere[7].

Results and discussion:

The main data are given in *table 2* and *figure 1*. The presented method gives a first insight into the PCB impurities or contamination of a number of colourants, mainly azo dyes from a group of additives not allowed for human consumption. The method enables us to get an insight into the characteristics of their PCB distributions. The results are mainly relatively low, coming from the point of view of by-products as well as classical residue analysis or acceptable residue levels for regulated PCB single congeners (e.g. marker PCBs, dl-PCBs). This could also be expected since the examined colouring agents do not contain chlorine atoms. This finds only one interesting exception in Sudan Orange G, a non-chlorinated azo colourant (see below), whereas the only analysed colouring agent containing chlorine in their molecule, Xylene Fast Yellow 2G, does not have especially high PCB contents.

	Sunset Yellow FCF	Acid Red 1	Acid Red 88	Chromotrope FB	Orange II (Acid Orange)	Para red	Ponceau Xylidin	Rhodamine B	Sudan I	Sudan II[#a]	Sudan II[#b]	Sudan IV	Sudan Orange G[#1]	Sudan Orange G[#2]	Sudan black B[#x]	Sudan black B[#y]	Xylene Fast Yellow 2G
	avg. (n=2)	avg. (n=2)	n=1	n=1	n=1	n=1	n=1	n=1	n=1	n=1	n=1	n=1	n=1	n=1	n=1	n=1	n=1
									µg/kg								
Total MonoCB	n.d.	2	11	0	2	9	1	n.d.	130	4	4	2	15000	29000	10	50	1
Total DiCB	n.d.	n.d.	2	n.d.	n.d.	11	n.d.	1	60	3	n.d.	0	3	190	n.d.	46	5
Total TriCB	n.d.	n.d.	3	n.d.	n.d.	9	14	17	160	23	n.d.	0	6	11	1	42	15
Total TetraCB	n.d.	6	4	4	n.d.	8	16	16	100	15	n.d.	1	1	1	n.d.	34	210
Total PentaCB	n.d.	20	26	22	18	15	23	8	17	8	6	0	1	4	n.d.	27	20
Total HexaCB	n.d.	30	41	33	31	21	31	10	47	6	0	0	0	0	n.d.	46	11
Total HeptaCB	n.d.	8	10	8	8	5	8	2	8	0	n.d.	n.d.	n.d.	n.d.	n.d.	9	2
Total OctaCB	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total NonaCB	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DecaPCB	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total PCB	n.d.	67	97	67	58	77	93	54	520	58	11	4	15000	29000	11	250	260
									ng/kg								
$TEQ_{WHO2005}$ (upper)	n.d.	20	22	18	26	22	22	22	64	22	22	22	22	26	26	26	22
$TEQ_{WHO2005}$ (lower)	n.d.	0,048	0,068	0,05	0,034	0,039	0,083	0,043	56	0,005	n.d.	0,03	n.d.	n.d.	n.d.	0,18	0,13

Table 2: PCB homologue groups in colouring agent samples (n.d. = not detected)

The most interesting facts are some general observations like:

1. Colouring agents show a broad variety of concentrations as well as single compound distribution (here displayed in form of congener group totals and some examples). The concentrations range from n.d. (LOQ usually around 0.2-0.4 µg/kg per single compound) up to 35,000 µg/kg (= 35 mg/kg) in single cases.
2. Several of the analysed colouring agents display a pattern similar to technical PCB patterns of the higher chlorinated Aroclor types indicating that nonspecific background contamination should have taken place in connection with synthesis, manufacturing or storage of the respective compounds. These patterns are especially rich in congeners usually found in connection with the radicalic chlorination used for manufacturing of the technical Aroclor PCB mixtures.

The highest concentrations of PCBs have been found in the two samples of Sudan Orange G, with predominantly the Monochlorobiphenyls present (table 1) and other, higher chlorinated biphenyls only to a minor extent. Here it is interesting that Sudan Orange G does not possess any chlorine atoms in its molecule. Therefore, it has to be concluded that the PCB contamination originates here from carried-over impurities of the raw materials from the colourant synthesis.

Another special case is Xylene Fast Yellow 2G, where a p-dichlorobenzene unit is present within the molecule. It is obvious to assume that a reaction of two units of p-dichlorobenzene form a PCB molecule with 2,2',5,5'-substitution pattern. Hence it is fitting to see this configuration present as main compound for the detected congener pattern profile with PCB #52 (2,2',5,5'-TetraCB) being the most prominent compound. In a similar way, the next frequent congeners might be formed, being, PCB #101 (2,2',4,5,5'-PentaCB), PCB #95 (2,2',3,5',6-PentaCB) and PCB #70 (2,3',4',5-TetraCB).

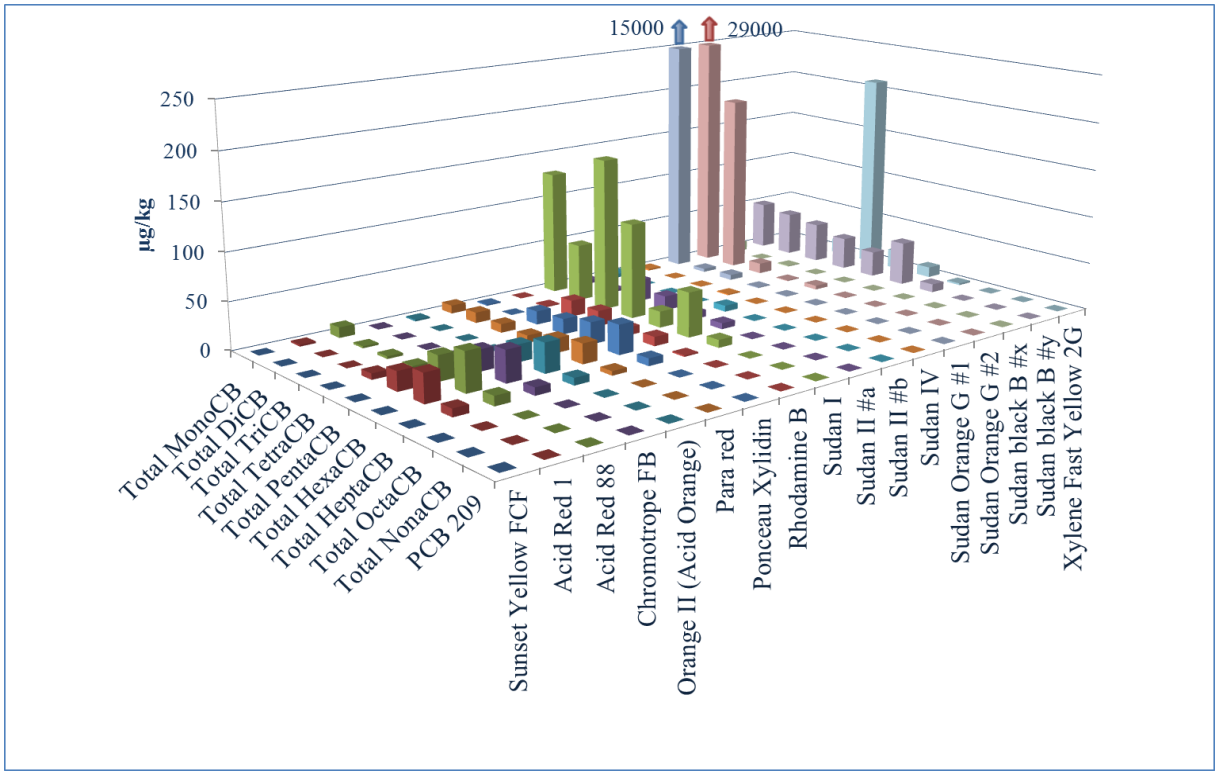

Figure 1: PCB homologue group pattern for colouring agent samples (magnified)

Xylene Fast Yellow 2G			Sudan Orange G	
congener	% of total		congener	% of total
PCB 52 / 69	71,0%		PCB 1	60,8%
PCB 101	3,2%		PCB 3	19,8%
PCB 70	2,7%		PCB 2	19,1%
PCB 93 / 95 / 98 / 102	1,5%		PCB 5 / 8	0,2%
PCB 44	1,5%		PCB 15	0,05%
PCB 92	1,3%		PCB 12 / 13	0,02%
PCB 18	1,2%		PCB 18	0,01%
PCB 153	1,1%		PCB 6	0,01%
PCB 139 / 149	1,0%		PCB 20 / 33	0,01%
PCB 31	1,0%		PCB 9	0,01%
contribution to Total PCB	85,4%		contribution to Total PCB	100,0%

Figure 2: The ten most abundant PCB congeners in selected colourants

Figure 3: PCB Single congener distribution pattern for Xylene Fast Yellow 2G

The task of examining colourants has been undertaken not only to counter-check for possible trace levels of PCBs in industrial chemicals used – or possibly in food colourants – but also to point towards the discussion of all PCB congeners as a whole since their general recognition as human carcinogens and respective legislation.

Conclusion: The present findings underline the necessity to further evaluate the occurrence of PCBs in colourants and dyes. Even with concentrations mainly in the ppb- to ppt-range, there remains the fact that as well concentrations as congener distribution are not only driven by the question of chlorine being part of the molecule structure of the colourant.

References:

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