PCB DESTRUCTION BY CATALYTIC HYDRODECHLORINATION (CHD) AND t-BuOK METHOD: COMBINATORIAL BIO/CHEMICAL ANALYSIS

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Introduction

Several non-incineration PCB destruction technologies (such as base catalysed decomposition, molten salt treatment, solvated electron technology, supercritical water oxidation, steam detoxification, *in situ* vitrification, sodium, high temperature hydrogenation, plasma arc) are currently under critical evaluation[1,2,3]. The presently described method uses a catalytic hydrodechlorination (CHD) with 5% Pd/C (5 hrs; 180 °C under 1.1 atm H_2), and an additional reaction with potassium tert-butyloxide (t-BuOK) at 250 °C for the complete destruction (>99.9999%) of the remaining PCBs[4,5].

Using this PCB destruction, Ohno et al. (1997)[4] showed that PCB- and PCDD/F-TEQ values in PCB insulating oils are decreased from 260 µg-PCB-TEQ/kg and 5.2 ng PCDD/F-TEQ/kg to less than the detection limit (<0.5 ppb Co-PCBs; <0.0002 ng PCDD/F-TEQ/kg).

Advantages of the present combination of 2 dechlorination methods is (1) almost complete dechlorination of high concentrations of PCBs (such as 10% solutions), (2) closed system, (3) no unwanted by-products such as PCDD/Fs, (4) easy recovery of solvent, catalyst and products; (5) economically treatment of also lower volumes of waste material.

The aim of the present study was to confirm the decrease of PCBs and other unwanted by-products such as PCDD/Fs by chemical analysis (sum of PCBs, Co-PCB-TEQ and PCDD/F-TEQ) and additionally by Micro-EROD[6-7] and DR-CALUX®-bioassays[8-10].(EROD-TEQ/DR-CALUX®-TEQ). These bioassays offer the possibility for a toxicological risk assessment of the PCB destruction flow by measuring the total sum of dioxin-like activity on each treatment step.

Materials and Methods

1. PCB CHD/t-BuOK-treatment

PCB capacitor oil 2 (from 4 condensers) was treated (2 kg) according to Ohno and Hirata (1997)[3].

2. PCB capacitor oil sampling, clean-up and analysis

Sampling for bio/chemical analysis (0.1 g PCB capacitor oil). Clean up methods: (A): liquid/liquid exchange from paraffin oil to DMSO; (B) additional clean-up by a silicagel (1g)/silicagel-H_2SO_4 (22%) column (4 g) and 50 ml n-hexane elution. Analysis of PCBs/PCDD/Fs in treated and untreated samples were carried out according to previous publications[4,5].

3. DR-CALUX®- and Micro-EROD-bioassay

a.) DR-CALUX®-bioassay (BioDetection Systems, BDS): The validation samples and one treated/untreated capacitor oil were analysed according to the guidelines from BDS (www.biodetectionsystems.com) and recently published studies[9,10].
b.) DR-CALUX®-bioassay (Kaneka Corporation, KC): The samples at KC were also analysed according to a.), but the luciferase activity was measured using LucLite™ (Packard) and the TopCount NXT® Microplate Scintillation & Luminescence Counter (Packard)[8].
c.) The Micro-EROD bioassay was performed as already published[6-8].

Results and Discussion

As **cross-validation** study for the DR-CALUX® technology, PCB-126, one untreated and one treated capacitor oil (a/b/c; in ng TEQ/g) were analysed at BDS and KC. These samples were additional analysed by chemical analysis and Micro-EROD bioassay : ·

1.) **PCB-126:** DR-CALUX®-relative potency (REP): a.) BDS: REP= 0.073; n=3; CV=22%; b.) KC: REP= 0.073, n=6, CV=19%]. Compared to Micro-EROD-REP: 0.050 ; n=6, CV=36%.

2.) **PCB standard mixtures** analysed by DR-CALUX®: (1) Mixture of non-(#77, 81, 126, 169), mono- (#118) and di-ortho- PCBs (#28, 52, 101, 138, 153, 180) (BDS: 140, n=2; KC: 98, n=3; CV=21%; chemical origin: 160) and (2) a mixture of coplanar PCBs (#77, 81, 126, 169) (BDS: 330, n=2; KC: 270, n=11; CV=22%; chemical origin: 240) [all data in pg TEQ/ml].

3.) **Untreated capacitor oil 1 and treated capacitor oil 2 (Pd/C and t-BuOK)** a.) DR-CALUX®-TEQ {at BDS: untreated oil 1: 2500; n=2/ treated oil 2: 0.30; n=2}; DR-CALUX®-TEQ {at KC: untreated oil 1: 2330; SD 360; n=10; CV=16%/ treated oil 2: 0.36; n=6; SD 0.05; CV: 15%} b.) Micro-EROD bioassay {analysed at KC untreated oil 1/treated oil 2: 1510/0.08} and c.) TEQ {chemical analysis: untreated oil 1/treated oil 2: 1150/0.114}[all data in ng-TEQ/g oil].

The resulted DR-CALUX® TEQ values for both laboratories have a good agreement and were comparable to chemical analysis in a certain ratio.

After the cross-validation study with BDS, one more untreated and 2 more treated PCB oils were analysed at KC (see Table 1):

- The TEQ/EROD-TEQ (72 h kinetic)/DR-CALUX®-TEQ (24 h kinetic) values of the untreated PCB capacitor oil 1 are 1150/1540/2330 ng TEQ/g .
- PCB capacitor oil 2 could be efficiently reduced from 2500 (TEQ)/4100 (EROD-TEQ)/5140 (DR-CALUX®-TEQ) ng/g to finally <0.11/0.08/0.4 [all data in ng TEQ/g].
- This resulted in a treatment efficiency for PCB capacitor oil 2 around 99.99% in TEQs; DR-CALUX®-TEQs and in EROD-TEQs. Sum of PCBs were reduced from 960000 to 0.13 mg/kg) with a resulting treatment efficiency of > 99.99999%.
- The Ratio between bioassay-derived TEQ and TEQ values for untreated PCB capacitor oil (Micro-EROD: 1.3/1.8 and DR-CALUX®: 2.0/2.1) were maximal doubled.
- Dose-response curves of the DR-CALUX® activity are shown in Graph 1 (24 h kinetic; curves were fitted using a one-ligand curve-fit; three independent measurements; EROD dose-response curves were similar).

Recently, the authors have reviewed several studies reporting about the dioxin-like toxicity of coplanar PCB-congeners and technical PCB-mixtures by bioassays and chemical analysis (Behnisch et al. 2001). Similar ratios of TEQ values between bioassay (EROD) and chemical analysis for Arochlor 1254 (1.4) and Clophen A 50 (0.89) have been reported (Schmitz et al. 1996). PCB-126 contributed most to the EROD activity (64/40%) and TEQ (95/90%). Nevertheless, several studies showed that di-ortho-PCBs have antagonistic effects resulting in alterations in slope of the dose-response curves[12,13,14]. The slope of dose-response curves of the here presented PCB capacitor oils are similar to already reported studies from several technical PCB-mixtures[13,14].

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References

1. United Nations Environment Programme (2000). Survey of Currently Available Non-Incineration PCB Destruction Technologies.
2. Costner, P (1998). Technical Criteria for the Destruction of Stockpiled Persistent Organic Pollutants. Greenpeace, ISBN 90-73361-47-8.
3. Environment Australia (1997). Appropriate Technologies for the Treatment of Scheduled Wastes.
4. Ohno M., Hirata K. (1997) Organohalogen Compounds 31,405
5. Ohno M., Kaneda H., Hirata K. (1997) Organohalogen Compounds 31,415
6. Behnisch P. A., Hosoe K., Shiozaki K., Sakai S. (2000) Organohalogen Compounds 45,220
7. Behnisch P. A., Hosoe K., Shiozaki K., Sakai S. ESPR-Environ.Sci. & Pollut. Res. (submitted).
8. Behnisch P. A., Hosoe K., Brouwer A., Sakai S. (2001) Organohalogen Compounds (in press).
9. Bovee T.F.H., Hoogenboom L.A., Hamers A.R., Traag W.A., Zuidema T., Aarts J.M., Brouwer A., Kuiper H.A. (1998) Food Add. Contam. 15, 863
10. Hamers T., van Schaardenburg M.D., Felzel E.C., Murk A.J., Koeman J.H. (2000) Sci. Tot. Environ. 262, 159
11. Behnisch P.A., Hosoe K., Sakai S. (2001). Environ Int. (in press).
12. Schmitz H. J., Behnisch P., Hagenmaier A., Hagenmaier H., Bock K. W. and Schrenk D. (1996). Environmental Toxicology and Pharmacology. 1, 73-79.
13. Van der Plas S., Sundberg H. van den Berg H., Scheu G., Wester P., Jensen S., Bergman A., de Boer J., Koeman J. and Brouwer A. (2000) Toxicology and Applied Pharmacology. 169, 255-268.
14. Garrison P.M., Tullis K., Aarts J.M.M.J.G., Brouwer A., Giesy J.P. and Denison M.S. (1996) Fund Appl. Tox. 30, 194-203

Graph 1: Dose- sponse curves of DR-CALUX® activity (24 h kinetic) for untreated (n=2) and treated (n=6) PCB capacitor oils by PCB-CHD/t-BuOK-treatment

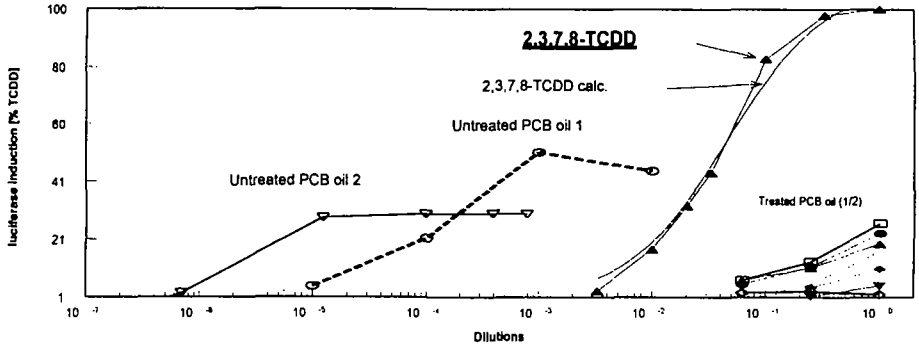

Table 1 : DR-CALUX®-TEQ^A, EROD-TEQ^B and TEQs (Co-PCBs and PCDD/Fs)- values for treated and untreated PCB capacitor oil. [Clean up methods: (A): liquid/liquid exchange from paraffin oil to DMSO; (B) additional clean-up by a silicagel (1g)/silicagel-H_2SO_4 (22%) column (4 g) and 50 ml n-hexane elution]

	[Unit]	Oil 1	Oil 2	Pd/C treatment (run 1) of oil 2	Pd/C treatment (run 2) of oil 2	t-BuOK (5 min) of Pd/C (run 2)	t-BuOK (20 min) of Pd/C (run 2)
Chemical	**Analysis**						
PCB	mg/kg	900000	960000	≤ 0.5	5.2	0.13	0.16
PCB-TEQ (WHO-TEF_{1997})	ng-TEQ/g	1100	2400	≤ 0.004	0.004		
PCDD/F-TEQ (WHO-TEF_{1997})	ng-TEQ/g	52	100	≤0.11	0.11		
Sum-TEQ	ng-TEQ/g	1150	2500		0.114		
Bioassay	**Analysis**						
EROD-TEQ	ng-TEQ/g	1540	4100	(A) 0.04 (B) 0.34	(A) 0.07 (B) 0.24	(A) 0.08 (B) <0.07	(A) 0.07 (B) 0.07
DR-CALUX-TEQ (24h)	ng-TEQ/g	2330	5140	(A) 0.78 (B) 0.36	(A) 0.35 (B) 0.45	(A) 0.36 (B) 0.06	(A) 0.41 (B) 0.18
DR-CALUX-TEQ (48h)	ng-TEQ/g	1440	4180	(A) 0.44 (B) 0.14	(A) 0.14 (B) 0.33	(A) 0.082 (B) 0.02	(A) 0.17 (B) 0.12