

Photodegradation of polychlorinated dibenzofuran internal standards during Soxhlet-extraction with toluene

S.A.C.M. Walraven, F.C.G.M. Langeleen, H. de Weerd, N.C.M.I. Fransen, J.P. Boers and Th.L. Hafkenscheid

TNO Institute of Environmental Sciences, Department of Analytical Chemistry
Delft, The Netherlands

Introduction

Photochemical degradation of polychlorodibenzofurans (PCDF) is one of the few topics in dioxin research that has attracted relatively minor attention. Recently, Dung and O'Keefe have reported on the photolysis of 2378- and 1278-tetrachlorodibenzofuran in n-hexane and in aqueous solutions under artificial and natural lighting, using a mercury lamp and direct sunlight, respectively¹. Relatively rapid photodegradation was observed under these conditions. Further information on similar experiments performed under artificial conditions has been published in literature reviews by Choudhry et al.^{2,3}.

Here, we report the inadvertent occurrence of photodegradation of ¹³C₁₂-labeled PCDF internal standards with numbers of Cl-atoms ≥ 6 during Soxhlet-extraction of samples of electrofilter ash with toluene.

Materials and methods

Materials

Glass-fibre extraction thimbles were obtained from Schleicher & Schuell (Den Bosch, NL). n-Hexane (HPLC-grade) and toluene (glass-distilled grade) were purchased from Rathburn (Walkerburn, UK).

¹²C₁₂- and ¹³C₁₂-polychlorodibenzodioxin and -dibenzofurans were obtained from Cambridge Instruments Laboratories (Woburn, MS, USA) and Chemsyn Science Laboratories (Kansas, KA, USA).

Gas chromatography was performed on a Varian 3400 gas chromatograph (Varian, Houten, NL). The column used was a 60m x 0.25 mm ID SP-2331 fused-silica capillary column (Supelco, Leusden, NL).

Mass-spectrometric detection was performed on a Finnegan MAT 95 mass spectrometer (Finnegan MAT, Bremen, G) using 70 eV electron impact ionization and selected-ion monitoring.

Methods

PCDD/F were determined according to the following experimental procedure. An accurately weighed amount of about 5 g of sample was placed in a pre-extracted glass fibre extraction thimble.

After addition of a mixture of $^{13}\text{C}_{12}$ -labeled PCDD/F, consisting of all congeners except 123678-H6CDD, 12378-P5CDF, 123478-H6CDF and 234678-H6CDF, the sample was treated with 3% (v/v) hydrochloric acid for 2 hours and allowed to dry.

The dried sample was extracted for ≈ 20 hours in a Soxhlet apparatus using toluene. After evaporation of the toluene, the sample was submitted to a clean-up involving active carbon, 'multi-layer' silica gel and activated aluminum oxide. After evaporation of excess solvent the cleaned extract was taken up in n-nonane, to which a known amount of $^{13}\text{C}_{12}$ -1234-T4CDD was added as a syringe standard.

Analysis was performed using high-resolution gas chromatography (HRGC) on an SP-2331 capillary column with high-resolution mass-spectrometric (HRMS) detection. Identification of the PCDD/F was based on a combination of agreement of retention times and mass-abundance ratios of both $^{12}\text{C}_{12}$ and $^{13}\text{C}_{12}$ congeners with an external standard. Quantification of the PCDD/F was based on comparison of responses with those of the internal standards added, correcting for relative responses of ^{12}C and ^{13}C compounds.

Recoveries were determined for all internal standards except the octachlorodibenzofuran which is assumed to partly degrade when chromatographed on an SP-2331 stationary phase.

Results and discussion

Analysis for PCDD/F of a sample of electrofilter ash using the above experimental procedure revealed a highly unlikely pattern of recoveries of the added $^{13}\text{C}_{12}$ -hexachloro- and heptachloro-DF internal standards.

While recoveries for 123678-H6CDF and 1234678-H7CDF were higher than those expected on the basis of the recoveries of the other PCDD/F, recoveries of 123789-H6CDF and 1234789-H7CDF were significantly lower.

Analyses of the original sample extract using high-resolution gas chromatography on a DB-5 column in combination with low-resolution mass spectrometry as well as on a second HRGC-HRMS combination gave results similar to those originally found.

Based upon examination and subsequent elimination of the consecutive steps in the analytical procedure it was concluded, that the cause of the problems was located somewhere in the sample treatment or the extraction procedure used.

Since the Soxhlet-extraction was performed in a newly equipped room relatively unprotected from entering indirect daylight, it was decided to run side-by-side extraction experiments in extractors both protected and unprotected from indirect daylight.

For these experiments, which were conducted two-by-two in order to establish the repeatability of the procedure, samples of the original E-filter ash were used.

The recoveries found for the added $^{13}\text{C}_{12}$ -PCDD/F are given in Table 1 together with the values calculated for the ^{12}C -PCDD/F present in the samples. These results show that marked differences occur between 'light' and 'dark' extractions for all hexachlorodibenzofurans and 1234678-heptachlorodibenzofuran.

The contents found for 123478- and 123678-H6CDF are considerably lower when extraction has been performed under light, while the opposite occurs for 123789- and 234678-H6CDF. The contents found for 1234678-H7CDF are somewhat lower upon extraction under light, the contents of OCDF are similar. The net results of these differences are higher TTEQ-value for the samples extracted under light.

Table 1: results of side-by-side extraction experiments

Congener	Extractions in 'light'				Extractions in dark			
	TEQ (ng/kg)	Rec. (%)	TEQ (ng/kg)	Rec. (%)	TEQ (ng/kg)	Rec. (%)	TEQ (ng/kg)	Rec. (%)
2378 T4CDD	44	69	42	74	37	99	43	90
12378 P5CDD	97	93	91	93	94	91	99	94
123478 H6CDD	22	99	21	93	22	101	22	101
123678 H6CDD	38		34		37		39	
123789 H6CDD	40	91	39	92	47	95	48	94
1234678 H7CDD	56	85	52	95	50	87	57	93
08CDD	25	85	23	101	22	113	27	105
2378 T4CDF	17	97	18	91	17	107	16	117
12378 P5CDF	46		51		40		45	
23478 P5CDF	431	74	430	66	381	94	411	93
123478 H6CDF	31		31		158		130	
123678 H6CDF	64	353	64	334	176	119	133	143
123789 H6CDF	140	25	130	25	46	102	55	82
234678 H6CDF	1190		1240		337		434	
1234678 H7CDF	87	148	87	155	139	99	134	101
1234789 H7CDF	20	5	18	6	16	99	16	89
08CDF	15	ND	15	ND	12	ND	13	ND
TTEQ (ng/kg)	2363		2386		1631		1721	

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The explanation for the differences observed can be found upon examination of the recoveries of the corresponding internal standards: recoveries 'under light' are >300% for 123678-H6CDF but only 25% for 123789-H6CDF, recoveries of 1234678-H7CDF are ≈150%, recoveries for 1234789-H7CDF are ≈5%. These anomalous recoveries suggest the occurrence of degradation/formation of the respective ¹³C₁₂-PCDF: while 123789-H6CDF and 1234789-H7CDF apparently degrade, 123678-H6CDF and 1234678-H7CDF are formed during the extraction proces. Formation of the latter may be due to degradation of the ¹³C₁₂-O8CDF for which no recoveries have been calculated. The occurrence of such conversions has been confirmed by model extraction experiments under light.

It has been found, that:

- 123789-H6CDF is converted for ≈80% to 12378-P5CDF and 2378-T4CDF
- 1234789-H7CDF is converted for ≈85%, 123678-H6CDF, 123478-H6CDF and 23478-P5CDF being the main conversion products.

Also, almost complete photodegradation of O8CDF has been found, its main conversion products being 1234678-H7CDF, 234678-H6CDF and possibly 124678-H6CDF and 23489-P5CDF.

Lastly, it should be noticed that the recoveries of 1234789-H7CDF (5%) upon extraction under light of the E-filter ash subsamples hardly affect its TEQ-values, while the opposite is true for the TEQ-values for the H6CDF and the 1234678-H7CDF (Table 1).

Apparently for the latter congeners unlabeled PCDF present in the samples behave differently from the labeled PCDF added before extraction.

This observation implies that under the specific extraction conditions the internal standards for some of the PCDF do not behave as 'true' internal standards.

An explanation may be that, while the internal standards are present in solution and readily available for possible reactions the unlabeled PCDF are slowly liberated from the matrix and, hence, not or to a lesser extent, subject to degradation.

Literature

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2 Choudhry, G.H. and Hutzinger, O. Residue Reviews, 84, 113 (1982)

3 Choudhry, G.H. and Webster, G.R.. Toxicol. Environ. Chem., 14, 43 (1987)