INSTABILITY OF OCTACHLORO DIBENZOFURAN DURING ANALYSIS

Hans Wagenaar, Evert Boelhouwers and Hans Olthof
Solvay Duphar B.V., P.O. Box 900, 1380 DA Weesp, The Netherlands
Hans de Kok
TAUW Milieu B.V. PO Box 133, 7400 AC Deventer
Harry Govers and Kees Olie
University of Amsterdam, The Netherlands

INTRODUCTION

Polychlorinated dibenzo-p-dioxins and dibenzofurans are generally recognised as very stable compounds. However, photolysis and, under extreme conditions, chemical destruction are known to be possible. Although subject to rigid conditions during analysis, such as contact with very reactive adsorbents and high temperatures during the gas chromatographic process, dioxins and furans are assumed to be unaffected. Low recovery of labelled internal standards is usually not attributed to degradation but, for instance, to losses by adsorption.
In analysing a number of samples with relatively high concentrations of OCDF, we noticed that the results were not always consistent. It was therefore postulated that OCDF degrades during analysis. As in many laboratories, we did not use $^{13}C_{12}$-labelled OCDF as an internal standard for analyses of native OCDF. Instead, we used $^{13}C_{12}$-labelled OCDD. As a consequence, losses of native OCDF specifically may have remained unnoticed.
A number of experiments were done to establish whether OCDF is sensitive to degradation and in which part of the analysis: drying, solid/liquid extraction, clean-up and GCMS analysis. We also checked whether lower chlorinated dibenzofurans would be formed. $^{13}C_{12}$-labelled OCDD and native OCDF were used as test compounds to evaluate differences in stability. Native OCDD and $^{13}C_{12}$-labelled OCDF were used as internal standard for the quantification.

EXPERIMENTAL

Drying of solids at room - and elevated temperatures

Nominal 50 ng $^{13}C_{12}$-labelled OCDD and 50 ng OCDF were applied on to 1 g silica gel (about 60 µm) or on to alumina (neutral, about 50µm) by preparing a slurry in dichloromethane. The solvent was then removed under reduced pressure. The spiked materials were stored at room temperature (RT) or heated at 50, 100 or 150°C, in the dark, *for 22 hours.*

Extraction of solids with toluene according to Soxhlet; a simulation of the refluxing stage
Experiment I: for 120 hours, 24 hours per day, a solution containing nominal 220 ng $^{13}C_{12}$-labelled OCDD and 230 ng OCDF in 50 ml toluene was refluxed in normal daylight. An equivalent solution was stored at room temperature in normal daylight.
Experiment II: for 92 hours, 24 hours per day, solutions containing nominal 240 ng $^{13}C_{12}$-labelled OCDD and 250 ng OCDF in 50 ml toluene were refluxed, in normal daylight and protected from light.

Contact with adsorbents during clean-up
For 5 hours, a solution containing nominal 50 ng $^{13}C_{12}$-labelled OCDD and 50 ng OCDF in 50 ml hexane was recirculated continuously through 15 cm x 1.5 cm columns, at a flow rate of 5 ml/min. For experiments in the dark (D), all parts of the experiments were protected from light; for experiments in daylight (L), only the column was exposed to daylight.

Sensitivity to photolysis during handling of extracts after isolation, in between clean-up steps and before gas chromatography-mass spectrometry
In a foregoing study (1) we exposed solutions of OCDF and OCDD in hexane, methanol and 1,4-dioxane to artificial daylight (Xenon lamp).

Gas chromatography
To study possible degradation of OCDF, we used a GC-MS system (HP5890-HP5971) equipped with a PTV injector (CIS II,Gerstel) and DB-5 CB column. We studied two type of injections: normal injections of 1 µl using glass insert liners with swirlholes and large volume injections of 10 µl using glass insert liners filled with non deactivated glass wool.

RESULTS AND DISCUSSION

Drying
Experiments with silica gel showed no significant loss of OCDF or OCDD, see table 1. Experiments with alumina showed loss of OCDF which was only substantial at 150°C, while no lower chlorinated dibenzofurans were found. A second test with alumina confirmed the results.

Table 1:The effects of drying of solids at room temperature (RT) and elevated temperatures: contents relative to spiked amount (%)

substance	silica gel			alumina			
	RT	50°C	150°C	RT	50°C	100°C	150°C
OCDD	104	108	92	100	94	98	98
OCDF	104	108	96	101	94	96	35*

* Lower chlorinated dibenzofurans or dibenzo-p-dioxins were not found, limit of quantification was 0.5 ng/g.

These results for alumina are similar to those reported by Schoonenboom and Olie (2). However, since samples are dried well below 150°C, we may assume that drying of samples containing alumina does normally not lead to an artefact

Soxhlet extraction

From experiment I and II we concluded (see table 2) that:
At room temperature, in daylight, no degradation of OCDD occured in contrast to OCDF, for which significant degradation was found. The main conversion product for reductive dechlorination of OCDF was 1234678-HpCDF by preferential loss of either the 1 or 9 position chlorine atoms.
Under reflux conditions, in daylight, degradation of some OCDD and minor formation of 1234679-HpCDD, by loss of either the 2, 3, 7 or 8 position chlorine atoms, were found. The decrease in OCDF was much larger. The main degradation product for reductive dechlorination pathway was again 1234678-HpCDF, whilst lower chlorinated PnCDFs and HxCDFs were also detected at low levels.

The refluxing solutions protected from light performed in experiment II gave little to no degradation of OCDF and OCDD.

Table 2: Effects of refluxing with toluene under light conditions: contents relative to spiked amount of OCDD and OCDF(%)

Substance	room temperature	reflux (111°C) under daylight conditions	
	-	experiment I	experiment II
1234679-HpCDD	-	1.0	1.2
OCDD	100	89	98
1234678-HpCDF	5.3	13	43
OCDF	82	1.0	42

Walraven et al (3) found also photodegradation of PnCDF internal standards during Soxhlet-extraction with toluene. In their paper they described that almost complete photodegradation of OCDF occured with formation of lower chlorinated furans (1234678-HpCDF was found to be the main conversion product).

Clean up

No measurable loss of OCDF or OCDD occurred as a result of contact with the adsorbents used in clean-up procedures. Exposure of the columns to daylight (L) did not affect this finding; see table 3.

Table 3: Effects of contact with adsorbents during clean-up. contents relative to spiked amount IN %

substance	glass wool control sample		SiO_2/44% H_2SO_4		SiO_2/33% 1M NaOH		SiO_2/10% $AgNO_3$		basic Al_2O_3	
	D	L	D	L	D	L	D	L	D	L
OCDD	102	102	100	100	102	100	100	102	98	98
OCDF	102	102	104	100	104	102	102	102	100	102

Gas chromatography

For the 1 µl injection we did not found significant degradation of OCDF. The maximum ratio HpCDF/OCDF was 0.02. However, the large volume injection with the glass wool insert liner showed major degradation of OCDF. The maximum ratio of HpCDF/OCDF was 0.33, all four HpCDF isomers were found with 1234678-HpCDF as most dominant . We also found HxCDF, PnCDF and minor formation of TeCDF.
Olie et al. (7) also described degradation of OCDF during gas chromatography. All four hepta chlorinated dibenzofurans were reported as degradation products, of which 1234678-HpCDF was dominant.

Sensitivity to photolysis during handling of extracts after isolation, in between clean-up steps and before gas chromatography-mass spectrometry

Above, we have already shown that OCDF photolytically degrades in toluene, at room temperature by daylight, while OCDD is not affected. In other solvents like hexane using a Xenon lamp, degradation of OCDF was about twice as fast as for OCDD. In methanol and 1,4-dioxane, OCDF degraded within minutes, while no decrease in OCDD concentration could be detected during the photolysis time.

GENERAL DISCUSSION

As shown, there are three parts of the analytical procedure which can lead to an analytical artefact: Soxhlet extraction using toluene in daylight, photolysis of extracts and GC-MS analysis. Soxhlet extraction using toluene in daylight is probably of major concern. Photolysis during Soxhlet is enhanced by the higher temperature.
To obtain an indication about the effect of photolysis during handling of extracts after isolation, in between clean-up steps and before instrumental analysis under normal light conditions, we calculated photolytic half-lifes for midday and midseason at 40°N latitude of OCDF in 1,4-dioxane. Table 4 presents half-life's as calculated by Koshioka et al (4) and half-life's calculated from quantum yields given by Wagenaar et al (1).

Table 4: photolytic half-life's of OCDF

Season	**Half-lifes [Min]**	
	Koshioka	Wagenaar
spring	12	164
summer	10.3	141
fall	18.2	249
winter	29.7	407

These photolytic half-life's show that OCDF can degrade within minutes to a few hours under normal light conditions in 1,4-dioxaan. For methanol and hexane half-lifes in the same order of magnitude can be expected.

The half-lifes of OCDF are very short compared to those of OCDD. Choudry (5) reported half-lifes of OCDD at 40°N ranging from 18 days in summer to 50 days in winter. Tysklind and Rappe (6) showed that the half-life of OCDF in n-tetradecane exposed to UV light (Mercury lamp, 300-400 nm) is eighteen times less than OCDD (half-life of 2.1 and 37.3 hours, respectively).

Under certain conditions like large volume injections using insert liners filled with glass wool with decreased deactivation, OCDF can degrade during GC-MS analysis with formation of lower chlorinated PCDF. In our experiments the injection part of the GC-MS was the main cause (thermal degradation), this was also found by Olie et al. They also showed that OCDF can degrade during the chromatographic process using very polar columns (7).
Concerning degradation pathways, in all experiments, we only looked for products formed via reductive dechlorination. We did not determine a total mass balance. Other pathways are possible as well, e.g. with the photolysis experiments we could only explain a part (less than 50%) of the loss of OCDF with reductive dechlorination.

CONCLUSION AND RECOMMENDATIONS

For accurate quantification of OCDF extra precautions must be taken compared to standard PCDD and PCDF analysis, such as drying of samples at moderate temperatures, protection of extracts and solutions from light; GCMS conditions must be compatible with the stability of OCDF. The use of $^{13}C_{12}$ labelled OCDF for analyses of OCDF is highly recommended.

REFERENCES

1 Wagenaar WJ, Boelhouwers EJ, de Kok HAM, Groen CP, Govers HAJ Olie K, de Gerlache J, de Rooij CG
A comparative study of the photolytic degradation of octachlorodibenzofuran and octachlorodibenzo-p-dioxin
Chemosphere (1995), 2983-2992
2. Schoonenboom MH, Olie K
The dechlorination of OCDD and OCDF on alumina support
12th International Symposium on Dioxins and Related Compounds
24-28 August, Tampere, Finland
3 Walraven SACM, Langelaan, FCGM, de Weerd H, Fransen NCMI, Boers JP and Hafkenscheid Th.L
Photodegradation of polychlorinated dibenzofuran internal standards during Soxhlet-extraction with toluene.
13th International Symposiumon dioxins and related compounds
September 1993, Vienna, Austria.
4 Koshioka M, Ishizaka M, Yamada T. Kanazawa J.and Murai T
Quantum yields of chlorinated aromatic compounds and their half-life periods in photodegradation
J. Pesticide Sci. 15 (1990), 439-443
5 Choudhry GG and Webster GRB
Environmetal photochemistry of PCDDs. 2 quantum yields of the direct phototransformation of 1237-Tetra-,1368-Tetra-,1234678-Hepta and Octachlorodibenzo-p-dioxin in Aqueous Acetonitrile and their sunlight half-lives.
J.Agric.food Chem. 37 (1989), 254-261
6 Tysklind M, Rappe C
Photolytic transformation of polychlorinated dioxins and dibenzofurans in fly ash
Chemosphere 23 (1991), 1365-1375
7. Olie K, Slot PC, Wever H
Decomposition of octachlorodibenzofuran and formation of the hepta congeners during GLC analysis
Chemosphere 19 (1989), 103-108