Determination and Elimination of Polyhalogenated Dioxins and Furans in Analytical Laboratory Wastes

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Introduction

In research laboratories investigating polybrominated and polychlorinated dibenzo-*p*-dioxins and -furans (PXDD/F) a lot of wastes contaminated with these substances may arise. These wastes have to be disposed of as hazardous waste. Thus, the analysis of PXDD/F may contribute to the occurrence of these substances in the environment if the laboratory waste is not decontaminated on the spot.
It was aimed to quantify the load of the wastes of our dioxin laboratory occurring during the residue analytical procedures. Within this the wastes of the GC/MS system (i.e., pump oil) should be considered, too, since the not-ionizated PXDD/F could accumulate in the mass spectrometer.
Furthermore, it should be investigated whether these wastes could be decontaminated by UV-photolysis. It is known that the PXDD/F decompose in organic solution if they are irradiated by UV-light of the 250-315 nm region[1]. In the environment photolysis is also one of the main degradation pathways for dioxins. In contrast to the predominantly particle-bound occurrence of the PXDD/F in the environment, in the laboratory wastes they usually are already in solution or could be easily converted into the liquid phase by extraction.

Methods

From the GC/MS-system the waste oils of the turbomolecular pump and rough pump, and used insertliners of the programmable temperature vaporizer injector (KAS II, Gerstel) were investigated. From the laboratory the solvent wastes from the cleaning of glass instruments, pasteur pipettes, adsorbents from the column chromatography, old samples and overlaid standards in vials and separatly their caps were investigated for their content of PXDD/F.
The solid wastes were extracted by soxhlet extraction with toluene for 16 hours, the further clean up procedures followed the method of Hagenmaier et al[2].
The determination of the tetra- to octachlorodibenzo-*p*-dioxins and -furans (PCDD/F) and mono- to hexabromodibenzo-*p*-dioxins and -furans (PBDD/F) was done by means of GC/MS with selected ion monitoring (HP 5970, Hewlett-Packard). As capillary columns a CP Sil 88 (single congeners; 50 m, 0.24 mm ID, 0.22 µm film thickness) and a DB-5 (sum of isomers;

30 m, 0.25 mm ID, 0.25 µm film thickness) was used. The PXDD/F were quantified by external calibration, since the usually applied ^{13}C-PXDD/F internal standards were part of the sample matrix itself.
For the investigation of the UV-degradation of the PXDD/F in the waste samples or their extracts, resp., a Hg high pressure lamp (Heraeus TQ 150, 150 W, emission maxima at 254 and 313 nm) was applied, as reaction vessel a 100-ml reactor was used. The effectiveness of the photolysis apparature was proved with a hexane solution of PXDD/F-standards (all 2,3,7,8-tetra- to octaCDD/F and one mono- to octaBDD/F-isomer each). Then the solvent waste, the extract of the vial caps (extract 1) and the extract of the pasteur pipettes (extract 2) were irradiated for one hour. After 15 minutes a 5 ml sample was taken. The clean up procedure of the samples and UV-irradiated solutions was carried out in analogous to the waste samples.

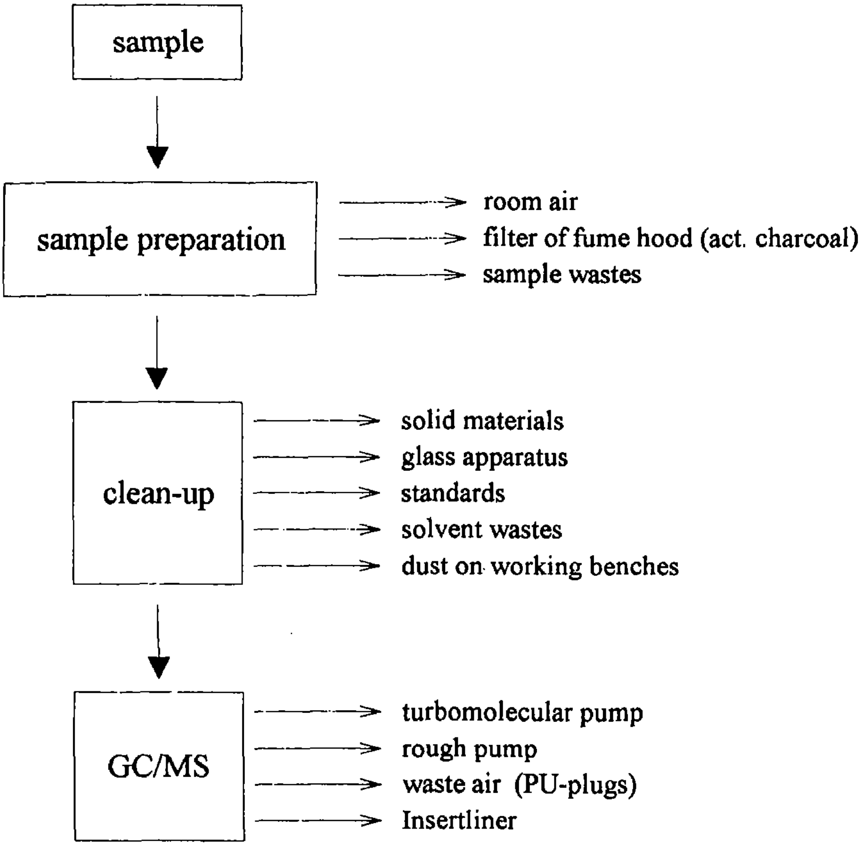

Fig. 1. Course of Dioxin Analysis and possible contamination pathways

Table 1. Sum of PCDD/F- and PBDD/F-contents and toxicity equivalents (TEQ) of the investigated wastes

waste type	*Σ PCDD/F* [ng/kg]	*Σ PBDD/F* [ng/kg]	*TEQ (BGA* [ng TEQ/kg]	*TEQ (I-TEF)* [ng TEQ/kg]
KAS-Insertliner	1 190	< 150	2	1
waste oil of the MS-turbomolecularpump	13 600	14 000	271	233
waste oil of the MS-rough-pump	< 200	< 250	< 150	< 150
*solvent waste**	5 280	1 500	97	104
used pasteur pipettes	3 200	175	16	14
used adsorbents	189	96	8	8
sample wastes	9 310	20 400	511	392
old vial caps	6 610	9 200	115	40
overlaid standards	10 700	6 010	723	1 000

*contents and TEQ in ng/L

Results and discussion

In table 1 the contents of PXDD/F in the investigated wastes are listed as sums of PCDD/F and PBDD/F, and as toxicity equivalents (TEQ), calculated with the BGA- and the NATO-CCMS-method (I-TEF). On account of the comparable toxicological mechanisms the TEQ-factors of the PCDD/F were also used for the PBDD/F. Thus, the TEQs were summarized over all PXDD/F[3]. The concentration of PXDD/F in the individual waste matrices shows a strong variation, but could yield substantial amounts. The high value of the waste oil of the MS-turbomolecular pump, which is located directly under the quadrupole rods shows that a significant amount of PXDD/F entering the mass spectrometer is not destructed and then accumulated in the pump oil. Thus, during services at the mass spectrometers and handling the waste oil, the same security standards as for all contacts with dioxins should be applied.

The content of PXDD/F in the laboratory wastes is comparable with the concentrations found in accidental fire residues[3] (500 ng TEQ/kg mean value). A special declaration and treatment of the wastes of a dioxin laboratory seems to be justified from our results, since a mixing with other laboratory wastes would considerably increase the amount of dioxin containing waste. Furthermore, investigating the pathways of PXDD/F residues during sample preparation, clean up and detection is necessary to optimize safety standards for "dioxin laboratories" as well as its waste management.

The results of the experiments for decontamination of the wastes by means of UV-photolysis are shown in table 2. As can be seen, after one hour of irradiation in all investigated solutions a degradation of more than 99% was achieved. Even after 15 minutes the highly toxic 2,3,7,8-PCDD/F are decomposed to more than 75%.

Table 2. Results of the UV-irradiation of the waste solutions, extracts and standards

		Σ PCDD/F [ng/l]	*Σ 2,3,7,8-PCDD/F* [ng/l]	*Σ PBDD/F* [ng/l]
solvent waste	0min	15 800	30 400	13 100
	15 min	5 020	7 540	223
	60 min	92	58	< 2.0
degradation after 60 min		99.41 %	99.81 %	> 99.98 %
extract 1	0 min	327	297	882
	15 min	55	< 40	< 400
	60 min	< 0.5	< 1.0	< 2.0
degradation after 60 min		> 99.85 %	> 99.66 %	> 99.77 %
extract 2	0 min	7 040	742	426
	15 min	1 475	10	< 200
	60 min	8	< 2.0	< 2.0
degradation after 60 min		99.89 %	> 99.73 %	> 99.53 %
standards	0 min	145 000	67 700	20 200
	15 min	1 785	73	< 250
	60 min	< 2.5	< 5	< 50
degradation after 60 min		> 99.99 %	> 99.99 %	> 99.75 %

The efficiency of degradation differs little between the solutions of the pure PXDD/F-standards and the wastes. This indicates that the waste solutions may contain some substances, which influence the photochemical behaviour negatively, e.g. by quenching. The degradation of the 2,3,7,8-isomers of PCDD/F occures faster than of the other PCDD/F-isomers. The photolysis of PBDD/F is the fastest at all.

Because of these results we regard the photolysis of the wastes or their extracts, resp., as a powerful tool for reduction of the PXDD/F-contents in laboratory wastes.

Literature

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