PHOTOLYSIS OF PBDES IN SOLVENTS BY EXPOSURE TO DAYLIGHT IN A ROUTINE LABORATORY

Thomas Herrmann, Bernd Schilling and Olaf Päpke
ERGO Forschungsgesellschaft mbH, Geierstraße 1, D-22305 Hamburg, Germany

Introduction

Polybrominated Diphenyl Ethers (PBDEs) are used as flame retardants for textiles, furniture, insulation of wires and electrical appliances including television sets, computers, computer printers, fax machines and printed circuit boards. In the last years increasing scientific attention was focused on PBDEs and analytical methods for their detection in environmental and biological matrices were developed[1]. In general it is known, that PBDEs show a certain sensitivity to light exposure[2,3,4]. For this reason e.g. brown glass equipment is used in ERGO laboratories for storage of final sample extracts. In 2003 we analysed larger sample numbers of human milk for PBDEs initiated by federal German and US authorities and institutes. Within the frame of quality control procedure the potential degradation of PBDEs in solvent extracts due to daylight exposure was taken into account, in order to obtain and document more detailed information about the phenomenon of light sensitivity.

Material and Methods

Native PBDE 17; 28; 47; 66; 77; 85; 99; 100; 138; 153; 154; 183 and 209 were matter of investigation. The concentration of each compound in the toluene test solution was 500 ng/ml (for PBDE 47 and 209: 2500 ng/ml). Five white glass respectively 5 brown glass vials, each containing 0.03 ml of the test solution, were placed on an office windowsill. The vials were exposed to natural daylight (including sunlight). One white glass and one brown glass were taken at specified time intervals (2, 5, 7 respectively 14 days). In addition two control samples without exposure were stored (control sample). After the individual exposure time described, ^{13}C-labeled PBDE 28; 47; 99; 153; 154; 183 and 209 were added to the solutions, which were stored in darkness at - 18 °C. After the final exposure time of 14 days all sample solutions were analysed in series using ^{13}C-labeled PBDE 139 as syringe standard. The measurements were performed using high-resolution gas chromatography /high resolution mass spectrometry (HRGC /HRMS, HP 5890 coupled with VG Autospec) at RP=10,000 using a DB 5 column (30 m, 0,25 mm ID, 0,1 µm film) for gas chromatographic separation.

Results and Discussion

The results are presented in Table 1 (brown glass storage) and in Table 2 (white glass storage) respectively. For reasons of clarity, data is shown as percent of individual PBDE congener compared to the control sample (no exposure to light). Figures 1 and 2 present the data of PBDE 47 and PBDE 209 for both storage methods and for each time interval. In Figure 3 all PBDEs investigated are shown after total exposure time of 14 days.

No significant changes were observed for any of the compounds after 14 days of storage in brown glass vials. Storage in white glass vials did not significantly influence PBDE 17; 28; 47; 66; 77; 85; 99; 100; 138; 153; 154 and 183 (lowest data in this group was found for PBDE 138 (79 %)). In strong contrast to these PBDEs, PBDE 209 was significantly degradated. Only 6 % of PBDE 209 were found after 5 days of storage. After 14 days the remaining quantity was 1 % of the initial concentration.
Our results are in good agreement with the data of Tysklind[2] and Eriksson[3] who also found a remarkable high degradation for PBDE 209 and only minor changes for other PBDEs due to photolysis when investigating PBDEs in solutions and environmental matrices like soil.
Taking into account our results the following procedures are essential for PBDE (especially PBDE 209) analysis: Final sample extracts have to be stored in brown glass vials. Light exposure should be reduced to a minimum within the whole sample preparation (extraction, clean-up), e.g. by wrapping flasks in aluminium foil. PBDE 209 should not be analysed without use of ^{13}C-labeled PBDE 209. The comparison of analytical data from different laboratories is difficult to explain when these basic procedures are not performed.

Table 1 Photolysis of PBDEs in toluene solution after exposure to daylight, storage in brown glass

		Relative amounts (% remaining compared to control sample)			
	Exposure time (days)				
	0*	***2***	***5***	***7***	***14***
PBDE 17	100	99	97	98	96
PBDE 28	100	101	99	101	98
PBDE 47	100	100	99	101	99
PBDE 66	100	102	102	106	106
PBDE 77	100	102	100	104	104
PBDE 85	100	105	94	101	99
PBDE 99	100	102	100	102	102
PBDE 100	100	103	96	99	99
PBDE 138	100	97	99	95	100
PBDE 153	100	99	97	97	99
PBDE 154	100	97	99	102	100
PBDE 183	100	98	102	105	103
PBDE 209	100	100	94	98	104

***control sample without light exposure

Figure 1 Storage of PBDE solution in brown glass , daylight exposure over 14 days

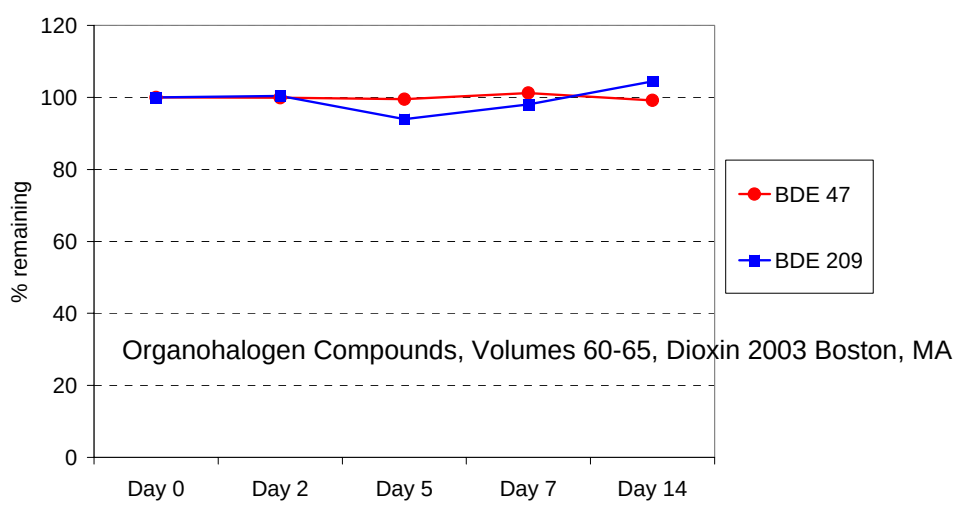


Table 2 Photolysis of PBDEs in toluene solution after exposure to daylight, storage in white glass

		Relative amounts (% remaining compared to control sample)			
	Exposure time (days)				
	0*	***2***	***5***	***7***	***14***
PBDE 17	100	101	96	98	98
PBDE 28	100	99	99	97	98
PBDE 47	100	102	106	104	101
PBDE 66	100	97	97	93	96
PBDE 77	100	99	97	98	100
PBDE 85	100	101	97	93	88
PBDE 99	100	100	96	94	94
PBDE 100	100	102	97	98	105
PBDE 138	100	94	87	90	79
PBDE 153	100	96	94	91	82
PBDE 154	100	98	94	90	87
PBDE 183	100	104	97	96	92
PBDE 209	100	31	6	4	1

***control sample without light exposure

Figure 2 Storage of PBDE solution in white glass , daylight exposure over 14 days

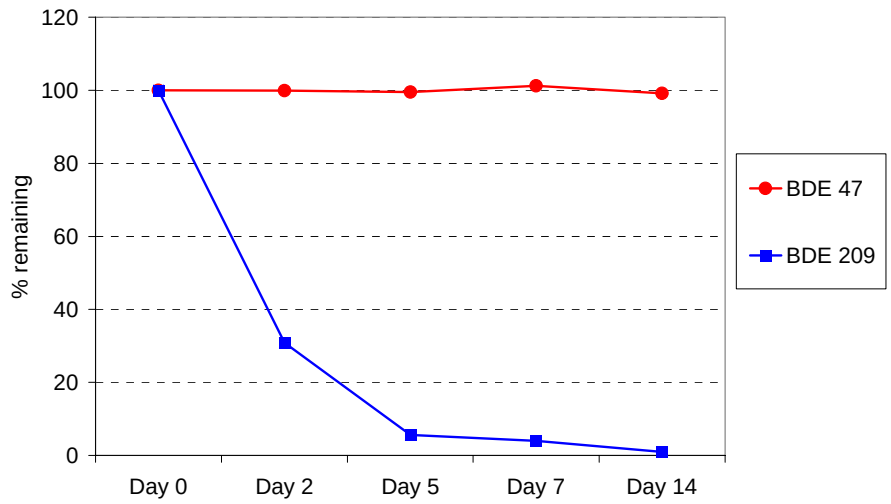
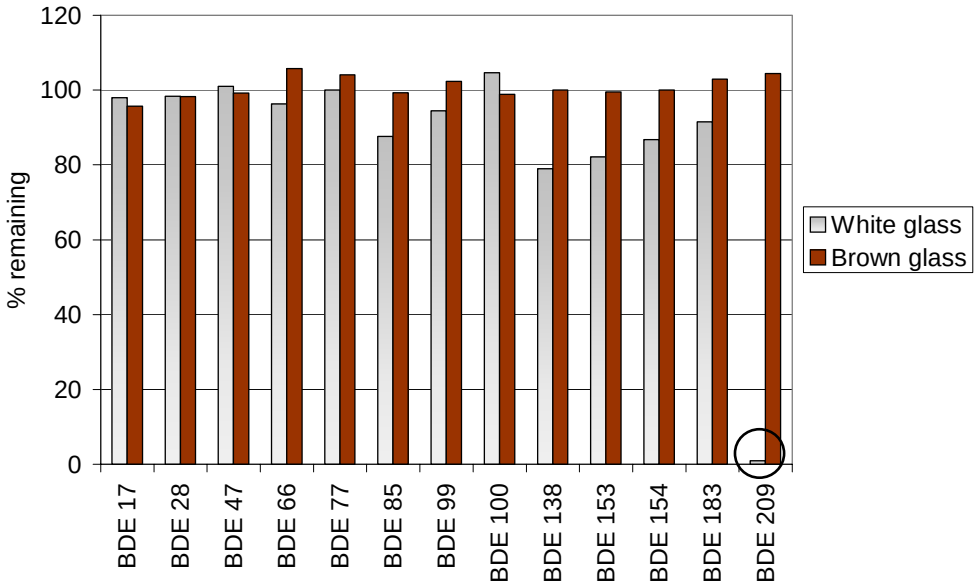


Figure 3 Storage of PBDE solutions in white and brown glass vials after 14 days of exposure to daylight



References

1. Schröter-Kermani C., Helm D., Herrmann T., Päpke O., *The German Environmental Specimen Bank – Application In Trend Monitoring Of Polybrominated Diphenyl Ethers In Human Blood.*,Organohalogen Compounds, Vol. 47, 49 – 52, 2000

2. Tysklind M., Sellström U., Söderström G., de Wit C., *Abiotic transformation of polybrominated diphenylethers (PBDEs): Photolytic debromination of decabromo diphenylether*, The Second International Workshop on Brominated Flame Retardants, Abstracts, 51 – 54, Stockholm, 2001

3. Eriksson J., Jakobsson E., Marsh G., Bergman Å., *Photo decomposition of brominated diphenylethers in methanol/water*, The Second International Workshop on Brominated Flame Retardants, Abstracts, 203 – 206 , Stockholm, 2001

4. Watanabe I., Kawano M., Tatsukawa R., *The Photolysis of Halogenated Dibenzofurans in Hexane Solution and on Airborne Dust by Sunlight*, Organohalogen Compounds, Vol. 19, 235 – 238, 1994