Stability of Polybrominated Dibenzo-p-dioxin and Dibenzofuran Standard Solutions

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1. Introduction

Accurate and reliable analytical standards are essential in the analysis of Polybrominated Dibenzo-p-dioxins (PBrDDs) and Dibenzofurans (PBrDFs). Methods for the accurate preparation and quality control of Polyhalogenated Dibenzo-p-dioxin and Dibenzofuran analytical standards have been described.[1)] To maintain the integrity of prepared standards, long-term stability testing of standard solutions has been undertaken. Results from stability testing of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans indicated no appreciable degradation of standard solutions over a minimum of two years.[2)] A similar study is underway to determine long-term stability of PBrDDs and PBrDFs in n-Nonane.

The objectives of the study were to:

- Determine chemical degradation of PBrDD/DF standard solutions,
- Determine chemical degradation of crystalline PBrDD/DFs, and
- Establish shelf-life data to determine reasonable expiration dates for PBrDD/DF standard solutions.

2. Materials and Methods

The study included six PBrDDs and five PBrDFS (See Table 1). Each compound was synthesized and purified by well established isomer-specific methods. Original compounds were purified to 96-99% chemical purity. Initial chemical purities for crystalline materials were established using a gas chromatograph equipped with a flame ionization detector (GC-FID) Standard solutions of each compound were prepared in n-Nonane at 5 μg/mL, filled into ampules and flame sealed. Ampules were then stored at ambient temperature and protected from light. Original crystalline materials were stored in Teflon®-

lined, screw-cap vials at ambient temperature and protected from light. After storage for a minimum of three years, crystalline materials were analyzed for chemical purity and random ampules were assayed for analyte concentration. Chemical purity assays of neat materials were determined by GC-FID. To determine analytical concentration, original solutions were compared to new standard solutions. New solutions were prepared from crystalline materials. Comparison analyses were performed using HPLC analysis prepared in n-Nonane at 5 μg/mL.

3. Results

Analytical results of chemical purity assays of neat materials are illustrated in Table 1. There were no significant changes in purity of any of the isomers tested. Original synthesis lots of neat materials for three of the isomers were not available for testing.

Results of analysis of solution concentrations are illustrated in Table 2. Direct comparisons of responses of existing and new solutions were done and percent differences were calculated for each isomer. The percent differences had a range of 0.6% to 9.7%. Octabromodibenzo-p-dioxin (OBrDD) had the highest percent difference at 9.7%. Studies are currently underway to determine whether the difference is due to preparation error in the original solution or if degradation is occurring. The minimum time period in the stability study was three years.

4. Conclusions

- Appreciable (>1%) chemical degradation of crystalline PBrDDs and PBrDFs did not occur.
- No significant changes in solution concentration of PBrDDs and PBRDFs were observed over time with the exception of OBrDD.
- Conditions of ambient temperature and protected from light are adequate for long-term storage of neat materials and standard solutions.

5. References

1) Re, M.A., Bradley, J.C., Nichols, A.W., Organohalogen Compounds, Vol 2:Dioxin '90 EPRI Seminar, 1990, 289.

2) Re, M.A., Armstrong, E.M., Bradley, J.C., Lewis, D.L., Nichols, A.W., Chemosphere, 1992, 25, 1355.

Table 1
Summary of Isomers Studies and GC-FID Purity Data of Neat Materials

Isomer	Lot No.	Time Period of Stability Study (years)	Initial Purity (%)	Stability Analysis Purity (%)
Dibenzo-p-dioxins				
2,3,7,8-TBrDD	MLB-706-79	6.5	98	98
1,2,3,7,8-PBrDD	MLB-13648-3	6.5	98	98
1,2,3,4,7,8-HxBrDD	MB-13106-78	NA[a]	98	NA[a]
1,2,3,6,7,8-HxBrDD	MLB-13106-6	6.5	99	99
1,2,3,7,8,9-HxBrDD	MLB-22308-13	3	98	98
OBrDD	MB-13106-86	NA[a]	98	NA[a]
Dibenzofurans				
2,3,7,8-TBrDF	MB-13106-77	6	98	98
1,2,3,7,8-PBrDF	MB-13106-82	6	98	98
2,3,4,7,8-PBrDF	MAR-20386-61	6	98	NA[a]
1,2,3,4,7,8-HxBrDF	MB-13106-85	NA[a]	98	NA[a]
1,2,3,4,6,7,8-HpBrDF	CJG-22438-77	NA[a]	96	NA[a]

[a] Crystalline material not available for stability analysis.

Table 2
Comparison of Existing Solutions to New Solutions by HPLC

Isomer	Time Period of Stability Study (years)	Response of Existing Solution[a]	Response of New Solution[a]	% Difference
Dibenzo-p-dioxins				
2,3,7,8-TBrDD	6.5	1491050	152210	2.0
1,2,3,7,8-PBrDD	6.5	616017	629283	2.1
1,2,3,4,7,8-HxBrDD	7	573413	606337	5.4
1,2,3,6,7,8-HxBrDD	6.5	226407	225017	0.6
1,2,3,7,8,9-HxBrDD	3	510170	531733	4.1
OBrDD	5.5	216143	239480	9.7
Dibenzofurans				
2,3,7,8-TBrDF	6	698743	714907	2.3
1,2,3,7,8-PBrDF	7	571310	603917	5.4
2,3,4,7,8-PBrDF	5	752377	741247	1.5
1,2,3,4,7,8-HxBrDF[b]	--	--	--	--
1,2,3,4,6,7,8-HpBrDF	3.5	463917	474330	2.2

[a] Area count mean of triplicate injections.
[b] Stability data not available.