SOLID PHASE EXTRACTION COLUMNS FOR ANALYSIS OF POLYBROMINATED DIBENZOFURANS AND DIBENZODIOXINS (PBDF/PBDD)

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1. Introduction

The procedures for separation and detection of various congeners of poychlorinated dibenzofurans and dibenzo-p-dioxins (PCDF/PCDD) are now well-developed[1-3]. These procedures have been found to afford believable results at different laboratories, and now are routinely used by analytical laboratories. The results obtained by using these procedures under Good Laboratory Practices (GLP) are accepted by Environmental Regulatory Agencies. In contrast, little information is available on analytical procedures for polybrominated dibenzofuran and dibenzo-p-dioxin (PBDF/PBDD) analysis[4,5]. We have found that the same procedures used for PCDF/PCDD analysis can be used for PBDF/PBDD analysis with some minor modifications.

Germany has recently amended the 'German Dioxin Ordinance' (GDO) to include eight 2,3,7,8-substituted brominated furans and dioxins. This action has accelerated the activities in PBDF/PBDD analysis area. Manufacturers of various plastic components for consumer and commercial appliances such as TV cabinets, office equipments etc. are now required to be certain that their materials satisfy the GDO requirements. Their concerns arise from the fact that brominated flame retardants are widely used as additives in plastics used for fabrication of such equipments. The PBDF/PBDD analysis is time consuming and costly. In this paper, we describe the use of disposable, pre-packed solid phase extraction (SPE) columns for PBDF/PBDD analysis. Use of these readily available columns can greatly reduce total analysis time and eventually cost of analysis since more samples can be run within the same time limits.

2. Experimental

All native and C-13 labelled PBDF and PBDD standards were obtained from Cambridge Isoptope Laboratories, Woburn, MA. Silica Gel (60A), mesh size 230-400, was obtained from Baxter, IL. Basic Alumina (Brockman Activity grade I for chromatography) was obtained from J.T. Baker Co, Phillipsburg, NJ and was activated at 650^0 C for six hours. Acidic silica and basic silica were prepared as described by other workers[1].

Disposable silica and basic alumina columns were purchased from Waters Chromatography, Milford, MA as Sep-Pak™ 20 cc (5 g) columns. A Supelco Visiprep™ sample preparation apparatus was used with the solid phase extraction columns to manipulate several samples at a time.

Solvents were removed after column operations under mild heating and a gentle flow of nitrogen. Residues were redissolved in minimum volume of toluene (10 uL) containing HexaCDD and OctaCDD as recovery standards. These solutions were analyzed by GC/MS using selected ion recording (SIR) techniques. One microliter of sample was injected on-column (typically a DB-5 0.25 mm 0.d. 30 meter - J&W) using an autosampler (HP-7673A & HP-5890 Series II GC). Three ions were monitored for each native congener and two ions were monitored for each labelled and recovery standard (VG Trio-1 MS). Software programs have been written for automated peak detection and quantitation (including recovery calculations) using isotopic ratio determination and retention time window criteria.

Standard solution containing C-13 labelled 2,3,7,8-TetraBDF; 2,3,7,8-TetraBDD; 2,3,4,7,8-PentaBDF; and 1,2,3,7,8-PentaBDD at 100 ppb of each congener was prepared and passed through silica Sep-Pak™ (pre-wetted with 5 mL heptane). Another 75 mL heptane was passed and collected. The heptane solution was passed through basic alumina Sep-Pak™ and was followed with 50 mL 10:90 chloroform and heptane mixture. The PBDF/PBDD congeners were then eluted from the alumina with 50 mL 50:50 methylene chloride and heptane mixture. This fraction was analyzed for recoveries.

Another standard solution containing native 2,3,7,8-TetraBDF; 2,3,7,8-TetraBDD; 2,3,4,7,8-PentaBDF; 1,2,3,7,8-PentaBDF; 1,2,3,7,8-PentaBDD; 1,2,3,4,7,8-HexaBDF; 1,2,3,4,7,8-HexaBDD; 1,2,3,6,7,8/1,2,3,7,8,9-HexaBDD; and 1,2,3,4,6,7,8-HeptaBDF was also treated in the same way as described earlier and recoveries of the congeners were determined.

For comparison to gravity columns, these standards were also passed through multi-phase silica columns. The multi-phase silica columns were then eluted with 90 mL heptane. The heptane solutions were passed through activated basic alumina columns and followed by 70 mL 18:82 chloroform and heptane mixture wash. The PBDF/PBDDs were then eluted in a fraction with 50 mL 50:50 methylene chloride and heptane mixture. These fractions were analyzed for recoveries.

3. Results and Discussion

The procedures as described in the experimental section for PBDF/PBDD analysis are very similar to the PCDF/PCDD procedures which utilize gravity columns. We have used these procedures succesfully with actual samples. We have extensive experience with gravity column procedures. The main drawback of these gravity columns is the time required for preparation of the packings and columns for each sample. Also these columns operate very slowly and need constant operator attention. We also found that recoveries of C-13 labelled internal standards to be somewhat low (40-60%) with gravity columns.

The use of solid phase extraction columns with vacuum operated sample preparation apparatus greatly reduces analysis times. The solid phase extraction column procedures are very fast. These columns are commercially available already prepacked at reasonable cost. We tested these columns with known PBDF/PBDD mixtures (both native and C-13 labelled) to validate their use in PBDF/PBDD analysis. The following tables give the recoveries of the labelled standards and the native congeners.

Table I

Per Cent Recoveries of C-13 labelled PBDF/PBDD

C-13 Labelled Congeners	Run #1	Run #2
2,3,7,8-tetraBDF	74.1	65.0
2,3,7,8-tetraBDD	63.6	52.1
2,3,4,7,8-pentaBDF	65.6	53.6
1,2,3,7,8-pentaBDD	75.7	59.0

Table II

Per Cent Recoveries of Native PBDF/PBDD with SPE columns

PBDF/PBDD Congeners	Run #1	Run #2	Run #3
2,3,7,8-Tetra BDF	101	137	124
2,3,7,8-Tetra BDD	110	127	125
2,3,4,7,8-Penta BDF	51	56	57
1,2,3,7,8-Penta BDF	78	78	75
1,2,3,7,8-Penta BDD	54	59	63
1,2,3,4,7,8-Hexa BDF	86	70	72
1,2,3,4,7,8-Hexa BDD	77	95	89
1,2,3,6,7,8/ 1,2,3,7,8,9-Hexa BDD	86	130	119
1,2,3,4,6,7,8-Hepta BDF	52	71	67

As can be seen from Tables I and II, the SPE columns can be substituted for gravity columns without any loss in accuracy. The recoveries of C-13 labelled congeners were between 50 and 75 % and this compares well with 40 to 60 % found with gravity columns. Typically 50 to 150 % recoveries are acceptable for such complex analysis procedures. The per cent recoveries of the native congeners were very good (Table II), and the reproducibility of the results from three different runs is acceptable for such multistep analytical procedures.

4. Conclusion

Pre-packed commercially available disposable solid phase extraction columns can be safely substituted for gravity columns in PBDF/PBDD analysis procedures. Our work with standard mixtures prove that improved results can be obtained in less time and with lower cost. Other advantages of using SPE columns are:

- no handling of strong acid/base reagents to prepare packings.
- less chance of contamination because the SPE columns are used only once and then disposed off.
- higher productivity as more samples can be analyzed in less time.

5. References

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