POLYBROMINATED DIBENZO-P-DIOXIN AND POLYBROMINATED DIBENZOFURAN EMISSIONS FROM INCINERATION OF FLAME-RETARDED RESINS IN A SIMULATED MUNICIPAL WASTE INCINERATOR

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ABSTRACT

Protocols for the incineration of flame-retarded resins in a simulated municipal waste incinerator and analysis of polybrominated dibenzo-p-dioxins and polybrominated dibenzofurans (PBDD/PBDF) in incinerator emissions were developed and demonstrated. Preliminary data with a single flame-retarded resin indicate that significant levels of PBDF are generated from incineration of flame-retarded resins under municipal waste incineration conditions.

INTRODUCTION

The purpose of this research effort was to develop and demonstrate two testing protocols: one for the incineration of flame-retarded resins and one for the analysis of polybrominated dibenzo-p-dioxins and polybrominated dibenzofurans (PBDD/PBDF) in incineration emissions generated from flame-retarded resins.

Incineration Protocol

The incineration protocol includes the following specifications: description of the incineration system, conditions for incineration, sampling system to be used to collect samples, sampling procedures, and data collection. The incineration system and conditions used for this effort, simulate, as closely as possible, those of a municipal incinerator, as follows:

- Precombustion temperatures: 100-650 F,
- Peak combustion temperatures: 2500-2700 F,
- Furnace exit temperatures: 600-1800 F,
- Residence times: 1-5 seconds,
- O_2 concentrations: 2-12%,
- CO_2 concentrations: 4-18%,
- H_2O concentrations: 3-50%,
- CO concentrations: 10-100 ppm, and
- NO_x concentrations: 100-1500 ppm.

Many of these general performance conditions are achievable when municipal incinerators are operated under guidelines known as "good combustion practices" for minimizing trace organic emissions.[1]

A conventional horizontal batch-tube furnace was selected to simulate a municipal waste incineration system. Precedence for the use of horizontal batch-tube furnaces for incineration simulation and plastics combustion is available in the technical literature.[2,3] Sampling of emissions from this laboratory incinerator is conducted with an EPA Modified Method 5 (MM5) sampling train.[4] Proven sampling procedures for the MM5 sampling train were included as an addendum to the incineration protocol.

Analytical Protocol

The analytical protocol was developed to closely simulate current standard methods for determination of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) in incinerator emissions.[5,6] These standard PCDD/PCDF methods have been successively applied to determination of PBDD/PBDF in incinerator ash.[7] The analytical protocol involves solvent extraction of MM5 sample components; silica, alumina, and carbon column cleanup of sample extracts; and PBDD/PBDF determination by high resolution gas chromatography/mass spectrometry.

The analytical protocol was developed for determination of total PBDD/PBDF by congener class (tetra- through octa-PBDD/PBDF). The basis of the determination is the use of $^{13}C_{12}$-labelled PBDD/PBDF internal standards for quantification. Only tetra-, penta-, and hexa-BDD/BDF $^{13}C_{12}$-labelled internal standards were commercially available at the time of this study, consequently, only tetra- through hexa-BDD/BDF were determined in the protocol demonstration. In addition, lack of most unlabelled PBDD/PBDF standards restricts typical methods of identification. Consequently, to determine gas chromatographic (GC) retention times for use in identification, the protocol relies on the use of GC retention indices previously published for PBDD/PBDF.[8,9,10]

Protocol Demonstration

A series of test burns was conducted according to the procedures described in the incineration protocol. The flame-retarded resin used for the test burns was a glass fiber reinforced polybutyleneterephthalate resin, flame retarded with decabromodiphenylether and antimony oxide synergist. Run 1 was a field blank. In Run 2, approximately 480 g of resin was incinerated. As discussed below, this amount of resin produced copious amounts of incineration emissions which impeded flow of combustion air through the MM5 sampling train. Consequently, the amount of resin incinerated was reduced in the Runs 3 and 4. MM5 emission samples collected in the test burns were analyzed for PBDD/PBDF according to the analytical protocol. Some modifications to the protocol were necessary based on the large amount of particulate matter collected in the samples.

RESULTS AND DISCUSSION

Monitoring data on the laboratory incinerator collected during test burns are presented in Table 1. In general, these data met the target incinerator conditions listed in the incineration protocol. Pertinent observations on the incineration process made during the test burns included the following:

- The bulk of the copious quantity of volatile incineration by-products generated was done so within 2 to 3 minutes of exposing the flame-retarded resin to the high temperature environment.
- Following this initial release of volatile incineration by-products, flow of combustion air through the chamber became impeded by the coalescence of residual solid incineration by-products in the bed, which typically amounted to about 50 percent of the initial mass.

Information was sought from the technical literature that would rationalize the performance of the laboratory incinerator when incinerating resin containing brominated flame retardants. The following information was discovered [11,12,13]:

- Smoke production from the combustion of plastics fire-retarded with bromine (and antimony) maximizes at early stages of combustion.
- The typical yield of volatile products from the combustion of plastics containing brominated flame-retardants is about 50 percent on an initial mass basis.
- Upon combustion, the bromine used to fire-retard plastic resins quantitatively appears as a volatile by-product.

These literature data corroborate that the laboratory incinerator operated as described in the incineration protocol generates the same combustion by-products from incineration of resin containing brominated flame retardants as would a full-scale municipal waste incinerator.

Initial and routine calibration data generated in the PBDD/PBDF analyses included native and recovery response factors used in quantification of PBDD/PBDF and internal standard recoveries, respectively. These data met the criteria for acceptable calibration listed in the analytical protocol which include percent relative standard deviations less than 30 percent; signal-to-noise ratios for GC signals greater than 2.5, and isotopic ratios within specified control limits. Retention time windows were calculated each day from analysis of a single calibration solution and corresponding published retention index values prior to analysis of samples as described in the analytical protocol.

Results from the analysis of MM5 emission samples collected in the test burns are presented in Table 2. As shown, trace quantities of TBDF, PeBDF, and HxBDF were detected in the field blank (Run 1) and laboratory method blank. PBDD were not detected in these two blanks. The

source of this trace PBDF contamination is unknown. Recoveries for the field and method blanks were generally greater than 50 percent.

In the initial analysis of MM5 emission samples, high responses were obtained in PBDF windows. Responses were not detected at the expected retention times for any of the internal standards although peaks were detected in the internal standard windows. Brominated diphenylether interferences were not detected. The apparent high levels of PBDD/PBDF in these samples were suspected to have overloaded cleanup columns in sample preparation thus leading to loss of internal standards and/or inefficient removal of analytical interferences. Additional sample preparation on a portion of the remaining sample extract was conducted to eliminate suspected column overload and associated loss of internal standards. Results for the reanalysis of Run 3 are also presented in Table 2 along with associated method blank results. Very high levels of PBDF were detected in this reanalysis which is consistent with qualitative results in the original analyses. A trace level of HxBDD was also detected. These data are presented with the following qualifications:

- Since the original internal standard spiked into these samples could not be detected due to loss in sample preparation or analytical interferences, a similar loss in native PBDD/PBDF from the original sample is suspected. Therefore, the concentrations reported are probably significantly lower than the total amount of PBDD/PBDF generated in the test burn.
- Identification of internal standards was difficult due to interferences in the internal standard mass windows. The tentative identifications made for internal standards in this analysis may contribute some error in quantification of PBDD/PBDF concentrations.

CONCLUSIONS

Based on the data and discussion presented above, the following conclusions were derived from this research effort:

1. The laboratory incinerator used for the test burns successfully simulates municipal waste incineration conditions.
2. Incineration of a lower load of resin would eliminate sampling and analytical difficulties encountered in collecting and analyzing PBDD/PBDF emissions from the laboratory incinerator. Alternatively, only a portion of the combustion effluent could be collected which would also minimize these difficulties.
3. The analytical protocol can be used to accurately quantify PBDD/PBDF in incinerator emissions provided a lower load of resin is incinerated. The protocol removes possible diphenylether interferences, generates acceptable internal standard recoveries in the absence of overwhelming matrix effects, and provides part-per-trillion detection limits.
4. Nondisposable glassware exposed to high PBDD/PBDF levels used in sample preparation should be checked for contamination prior to reuse for PBDD/PBDF sample preparation.
5. Incineration of resin containing brominated flame retardants may produce significant levels of PBDF emissions. Trace PBDD levels may also be produced.

TABLE 1. INCINERATOR CONDITIONS

Condition	Run 2	Run 3	Run 4
Resin Load (g)	480	130	80
Sampling Volume (ft^3)	3.7	2.4	2.1
O_2 (%)	6	7	8
CO_2 (%)	11	12	11.5
CO (ppm)	<150	<150	<150

TABLE 2. PBDD/PBDF CONCENTRATIONS IN MODIFIED METHOD 5 SAMPLES[a]

Sample	Concentration (ng/ft^3) TBDF	TBDD	PeBDF	PeBDD	HxBDF	HxBDD
Field Blank (Run 1)	0.64	(0.0066)	0.49	(0.012)	0.11	(0.052)
Method Blank	1.68	(0.011)	1.95	(0.031)	(0.28)	(0.26)
Run 2	NA[b]	NA	NA	NA	NA	NA
Run 3 (ug/ft^3)[c]	680	(0.72)	903	(1.1)	4663	1.2
Run 4	NQ[d]	NQ	NQ	NQ	NQ	NQ
Method Blank (ug/ft^3)[c]	0.037	(0.00002)	0.043	(0.000057)	0.133	(0.000047)

a. Parentheses indicate analyte not detected; value within parentheses represents analytical detection limit.
b. NA = Not analyzed.
c. Concentrations are in ug/ft^3; data generated from reanalysis of dilute sample extract.
d. NQ = Not quantified since analytical interferences prevented identification of internal standards.

REFERENCES

1. Kilgroe, J., Seeker, W., and Lanier, W., "Good Combustion Practice and Emission Regulations for Municipal Waste Incineration", International Symposium on Incineration of Hazardous, Municipal, and Other Wastes, American Flame Research Foundation (1987).

2. Taylor, P., Dellinger, B., and Lee, C., "Development of a Thermal Stability Based Ranking of Hazardous Organic Compound Incinerability", *Environmental Science and Technology* 24, 316-328 (1990).

3. Morimoto, T., Takeyama, K.-I., and Konishi, F., "Composition of Gaseous Combustion Products of Polymers", Journal of Applied Polymer Science 20, 1967-1976 (1976).

4. Method 0010: Modified Method 5 Sampling Train, Test Methods for Evaluating Solid Waste, SW-846, U.S. Environmental Protection Agency, November, 1986.

5. U.S. EPA Resource Conservation and Recovery Act (RCRA) Method 8280, Revised.

6. Method 8290, "Analytical Procedures and Quality Assurance for Multimedia Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans by High-Resolution Gas Chromatography/High Resolution Mass Spectrometry (Exhibits D and E)", Environmental Monitoring Systems Laboratory, Las Vegas, Nevada (1987).

7. Donnelly, J. R., Grange, A. H., Nunn, N. J., Sovocool, G. W. J. Brumley, W. C., Mitchum, R.K.; "Analysis of Thermoplastic Resins for Brominated Dibenzofurans", Biomed. Environ. Mass Spec., 18, (10), 884 (1989).

8. Donnelly, J. R., Munslow, W. D., Vonnehme, T.L., Nunn, N.J., Hedin, C. M., Sovocool, G. W., Mitchum, R. K.; "The Chemistry and Mass Spectrometry of Brominated Dibenzo-p-dioxins and Dibenzofurans", Biomed. Environ. Mass Spec., 14, 465-472 (1987).

9. Van Den Dool, H., Gratz, P.D.; "Generation of the Retention Index System Including *Linear Temperature Programmed* Gas-Liquid Partition Chromatography", J. Chromatogr., I, 463 (1963).

10. Hale, M. D., Hileman, F. D., Mazer, T., Shell, T. L., Noble, R. W., Brooks, J. J.;"Mathematical Modeling of Temperature Programmed Capillary Gas Chromatographic Retention Indexes for Polychlorinated Dibenzofurans", Anal. Chem., 57, 640 (1985).

11. DiPietro, J. and Stepniczka, H., "A Study of Smoke Density and Oxygen Index of Polystyrene, ABS, and Polyester Systems", Flammability of Solid Plastics, 7, pp. 23-40 (1974).

12. Day, M., Suprunchuk, T., and Wiles, D. M., "Influence of Flame-Retarded Chemicals on the Gas-Phase Combustion of Poly (Ethylene Terephthalate)", Behavior of Polymeric Materials in Fire, ASTM Special Technical Publication 816 (1983).

13. Fenimore, C. and Jones, G., "Modes of Inhibiting Polymer Flammability", Combustion and Flame 10, 295-301 (1966).