

REDUCTION IN THE FORMATION OF PCDD, PCDF AND OTHER CHLORINATED ORGANICS FROM MUNICIPAL WASTE INCINERATION BY THE INTRODUCTION OF AN INHIBITOR

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ABSTRACT

Two samples of fly ash obtained from a municipal waste incinerator were compared for levels of PCDD, PCDF and other chlorinated species. One of the fly ash samples was obtained during normal operating conditions and the other during the introduction of an aqueous solution of triethanol amine prior to the electrostatic precipitator sector. It was found that this treatment significantly inhibited the production of all chlorinated organic compounds.

INTRODUCTION

After the first report by Olie *et. al.* [1] on the presence of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) found in the fly ash sampled from Dutch municipal solid waste (MSW) incinerators, many other studies were undertaken which eventually established the fact that PCDD and PCDF formation arises as a result of refuse incineration [2-5].

The mechanism leading to the formation of these compounds is not yet fully understood and is a question that is currently under investigation. In a model study conducted in this laboratory, it was found that dioxins were formed from a variety of precursors, including non-chlorinated chemically dissimilar compounds as a result of the catalytic activity of MSW incinerator fly ash [6]. Recently the production of PCDD and PCDF from pentachlorophenol on a lab scale was observed to give significantly lower yields when the fly ash used was coated with various catalytic inhibitors [7,8]. We now report the successful industrial scale application of one such compound.

EXPERIMENTAL

1. Sources and Treatments of Fly Ash Samples

Results presented are for two samples of fly ash obtained from a MSW incinerator with an operating capacity of 900 tons of refuse per day. One fly ash sample was obtained during a normal incineration process while the other was sampled during the application of an inhibitor treatment process. For the latter, a

solution of 42% triethanol amine and 58% water was introduced prior to the electrostatic precipitator sector of the incinerator at a rate of 0.4 gallons per minute (calculated as 1-2% to fly ash). The fly ash sample was taken 3 hours after the onset of the inhibitor treatment.

2. Extration of Fly Ash Samples

Each sample was sieved ($<180\mu\text{m}$) and two 50.00 g portions from each sample were Soxhlet extracted with 350 mL of Toluene (BDH, glass distilled grade). The extracts were concentrated to 1 mL by rotoevaporation, and the 2 extracts for each sample were then combined. The extracts were further concentrated under a nitrogen stream, to a final volume of 1 mL.

3. GC-ECD Analysis

GC-ECD analyses of the extracts of the fly ash samples were performed on a Hewlett Packard 5880A series Gas Chromatograph, equipped with a 5880A series GC terminal (Level Four). Conditions used were as follows:

Injector: cold (on-column)
Detector: 320°C (ECD)
Column: DB-5 fused silica 30m x 0.32 mm i.d.
Carrier Gas: He, 16 psi
Temperature Program: 80°C for 1 min., ramped at 6°C/min. to 300°C, held for 20 min.

In the case of both extracts, 1.0 μL was introduced into the GC column and the terminal set with area count threshold of 2 and peak width of 0.02 to insure that all signals would be included in the integration.

4. GC-MSD Analysis

Quantitative analysis of PCDD and PCDF in the fly ash extracts was performed by GC-MS. The system used was a Hewlett Packard 5890 GC/5970 MSD. Conditions were as follows:

Carrier Gas: He, 9 psi
Injector: Cold, on-column
Column: DB-5 fused silica, 30m x 0.25 mm i.d.
Temperature Program: 100°C(1 min.), 15°C/min. to 230°C, 3°C/min. to 300°C, held 18 min.
Ion source temperature: 230°C
MS mode: EISIM (70 eV, 2 characteristic ions monitored for each congener group)

For quantitations, signal responses were compared against that of an external reference standard containing all isomers of PCDD and PCDF.

RESULTS AND DISCUSSION

Figure 1 illustrates the chromatograms resulting from the GC-ECD analyses of both fly ash extracts. The GC-ECD tracings may be directly compared, since the amounts of fly ash extracted, final volumes of the extracts and amounts of extract injected were the same throughout for both samples, as well as the sensitivity settings of the integrator. As indicated by this illustration, the effect of the inhibitor is pronounced. The extract from the fly ash sampled during the inhibitor treatment process yields notably smaller peaks, which corresponds to a reduction in the production of chlorinated compounds, including PCDD and PCDF.

Table 1 lists the summed area counts for these two chromatograms. The retention window for PCDD/F was determined in a separate analysis of the reference standard. The area counts of all peaks within this window were summed and assumed to represent PCDD/F. All areas for peaks outside of this window were summed separately and represent other chlorinated compounds. The total area counts for all the peaks are also given. These total peak areas reflect a 71% overall reduction in the production of all chlorinated compounds while operating with the inhibitor treatment process. A 77% reduction of PCDD/F was observed, while that of compounds outside this class of chemicals was 67%.

Figure 2 shows the TIC tracings obtained during the GC-MS analysis and Table 2 summarizes the data obtained for the quantitation of PCDD and PCDF. A 65% reduction in the production of total PCDD and PCDF was observed. A breakdown of the data by congener groups is given in Table 3 for PCDD, and Table 4 for PCDF. The inhibitor treatment appears to be more effective for the higher chlorinated compounds, a trend which is especially pronounced in the PCDF series, for which the lowest reduction was observed to be 42% for T4CDF, while the highest value of 87% was seen for OCDF.

This data clearly supports the fact that there was a substantial overall reduction in the amounts of chlorinated compounds produced during the municipal solid waste incineration while the inhibitor treatment process was implemented. It should be noted that there were no unusual peaks detected in the GC-ECD tracing of the fly ash extract which was subjected to the inhibitor treatment, thus no by-products of this treatment are evident. A more detailed report on the fate of the inhibitor is currently being prepared for publication.

Acknowledgment

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Figure 1 GC-ECD Tracings of Fly Ash Extracts

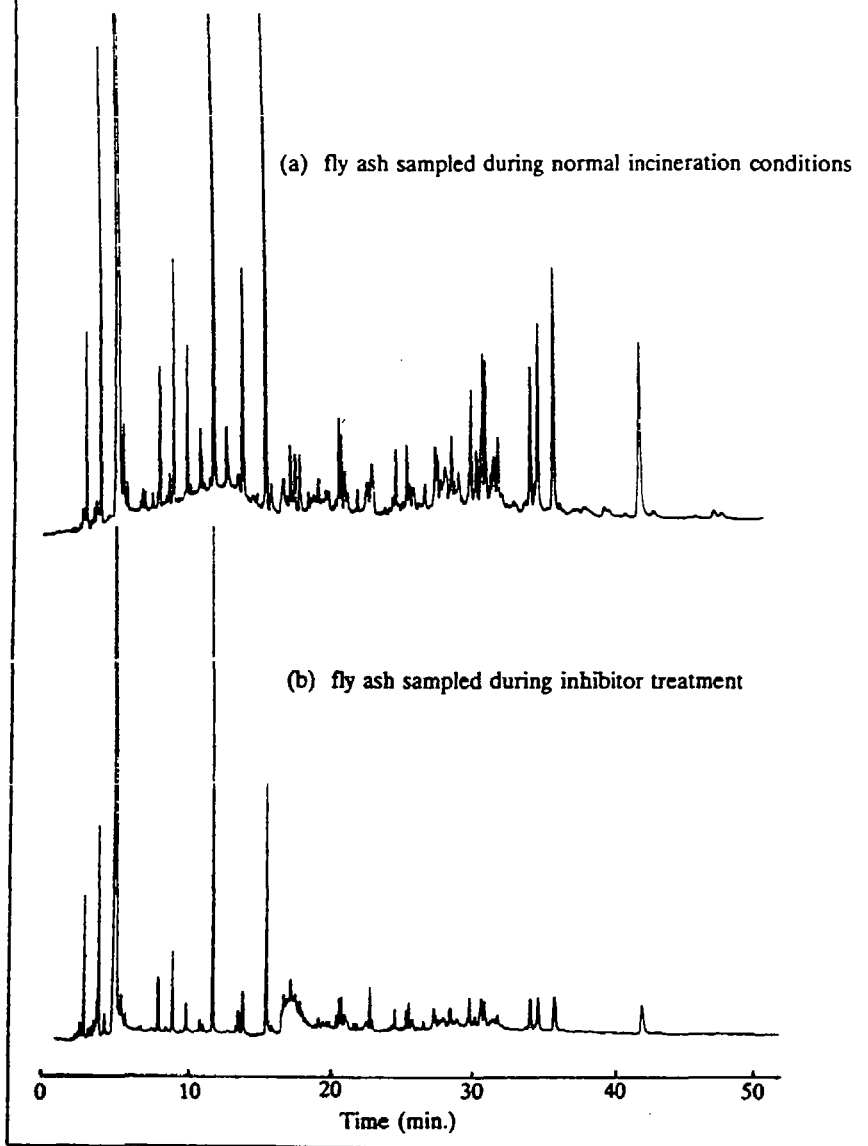


Figure 2 TIC Tracings of Fly Ash Extracts

(a) fly ash sampled during normal incineration conditions

(b) fly ash sampled during inhibitor treatment

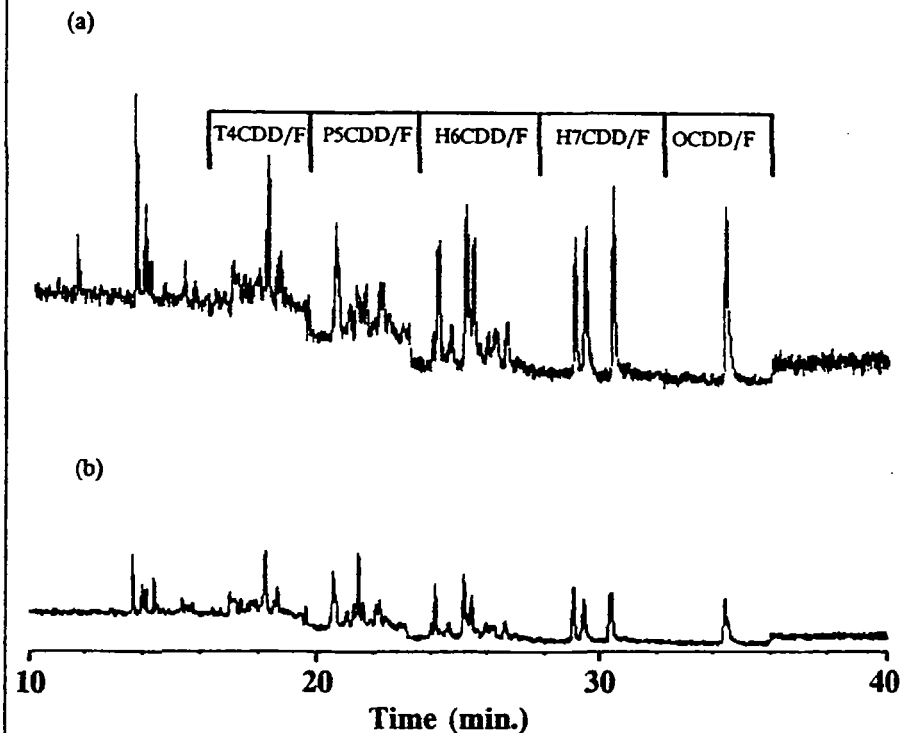


Table 1 Comparison of Peak Area Counts in the GC-ECD Tracings of the Fly Ash Extracts

FLY ASH SAMPLE	SUMMED PEAK AREAS		
	PCDD+PCDF	OTHER CI CONTAINING SPECIES	TOTAL
NO INHIBITOR	11709100	20267000	31976100
WITH INHIBITOR	2642570	6733490	9376060
% REDUCTION:	77	67	71

Table 2 Amounts of PCDD and PCDF Detected by GC-MS Analysis

FLY ASH SAMPLE	PCDD (ng/g)	PCDF (ng/g)	TOTAL PCDD + PCDF (ng/g)
NO INHIBITOR	832	485	1317
WITH INHIBITOR	269	187	456
% REDUCTION:	68	61	65

Table 3 Amounts Detected (ng/g) From Each Congener Group of PCDD

CONGENER GROUP	FLY ASH SAMPLE		% REDUCTION
	NO INHIBITOR	WITH INHIBITOR	
T4CDD	50	18	64
P5CDD	108	48	56
H6CDD	210	81	61
H7CDD	295	76	74
OCDD	169	46	73
TOTAL	832	269	68

Table 4 Amounts Detected (ng/g) From Each Congener Group of PCDF

CONGENER GROUP	FLY ASH SAMPLE		% REDUCTION
	NO INHIBITOR	WITH INHIBITOR	
T4CDF	55	32	42
P5CDF	101	45	55
H6CDF	168	61	64
H7CDF	131	45	66
OCDF	30	4	87
TOTAL	485	187	61

REFERENCES

1. K. Olie, P.L. Vermeulen, O. Hutzinger *Chemosphere* 6, 455 (1977)
2. H.R. Buser, H.P. Bossart, C. Rappe *Chemosphere* 7, 165 (1978)
3. G.A. Eiceman, R.E. Clement, F.W. Karasek *Anal. Chem.* 51, 2343 (1979)
4. L.L. Lamparski, T.J. Nestruck *Anal. Chem.* 52, 2045 (1980)
5. A.C. Viau, S.M. Studak, F.W. Karasek *Can. J. Chem.* 62, 2140 (1984)
6. F.W. Karasek, L.C. Dickson *Science* 237, 754 (1987)
7. K.P. Naikwadi, F.W. Karasek *Chemosphere* 19(1-6), 299 (1989)
8. L.C. Dickson, D. Lenoir, O. Hutzinger, K.P. Naikwadi and F.W. Karasek *Chemosphere* 19(8/9), 1435 (1989)