Journal of Chromatography, 270 (1983) 227–234
Elsevier Science Publishers B V, Amsterdam — Printed in The Netherlands

CHROM 16,142

GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC STUDY ON THE FORMATION OF POLYCHLORINATED DIBENZO-*p*-DIOXINS AND POLYCHLOROBENZENES FROM POLYVINYL CHLORIDE IN A MUNICIPAL INCINERATOR

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(Received July 13th, 1983)

SUMMARY

Laboratory-scale experiments have indicated that the presence of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorobenzenes (BPCs) on fly ash from municipal incinerators may be the result of combustion of polyvinyl chloride (PVC). Data shown here are the result of addition of 300% the usual level of PVC to a municipal incinerator. The concentrations of PCDDs and BPCs are compared before and after addition of PVC. No significant differences in the concentrations of these substances on the fly ash were found.

INTRODUCTION

Municipal incineration of waste coupled with energy recovery is a practice which promises to increase in the near future. However, chlorinated compounds are known to be adsorbed on fly ash from incineration of municipal waste. These include polychlorobenzenes (BPCs), polychlorobiphenyls (PCBs), and the toxic polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs)[1]. Understanding the origin and formation mechanisms of these compounds is necessary if reduction of their levels is to be accomplished, making municipal incineration a safe method of waste reduction near urban centres.

Pyrolysis studies have shown that PCDDs and PCDFs are formed from BPCs and PCBs[2,3]. Some pilot-scale experiments have not found any PCDDs from combustion of pentachlorophenol but have tentatively identified BPCs from combustion of polyvinylchloride (PVC)[4,5].

It has been postulated that PCDDs and PCDFs are formed from precursors such as BPCs, PCBs and PVC[6,7]. This concept arises more from intuitive means than

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from experimental data. There seems to be little emphasis on the catalytic surface reactions which can occur on fly ash and the resulting chlorination of organic products including PCDDs[8-11].

In this study, a 300% addition of PVC was made to the normal feed of a large energy-recovering municipal incinerator furnace. This was part of a series of planned experiments in which a study of operating conditions for minimization of dioxin formation was sought. The organic compounds formed on the fly ash are compared before and after addition of PVC Particular attention is given to the comparative levels of PCDDs and BPCs, which may give some insight into the formation mechanisms of PCDDs and other chlorinated compounds.

EXPERIMENTAL

Sampling.

An energy recovering incinerator of the Martin design located in Paris (France) was used for sampling under the direction of Electricité de France —Traitement Industriel des Résidus Urbains (EDF-TIRU) Two sets of three samples were collected. one set was collected during incineration of regular garbage, the other after spiking the same garbage of a statistically steady composition with PVC

Electrostatic precipitators for removal of fly ash had two on-line hoppers. Preliminary work had shown that PCDDs were more concentrated on the fly ash collected in the second hopper. This appears to be related to smaller particle sizes as indicated by previous results[12]. Samples were then taken from this second hopper.

The same furnace was used for both assays, so that all operating conditions, such as the amount of waste incinerated and excess air, which controls the flame temperatures could be kept constant for both sample sets. The garbage feed rate was set at 16 tons/h which corresponds to a steam generation rate of 30 tons/h. Primary air flow was regulated to obtain 12% more oxygen than that required for combustion.

Each sampling program lasted 4 h which included a 2-h equilibration time followed by collection every 30 min for a total of three samples. The fly-ash samples were taken directly from the hopper into glass flasks which were filled to the top and immediately sealed The glassware was cleaned as in a previously described procedure[1].

A second sampling program was performed after spiking the waste with PVC in the feeding hopper. The transit time of waste in this hopper to the combustion grate was 30 min. Unspiked garbage was found to contain 1% PVC of the total feed by laboratory analysis. Bags of 25 kg, each of shredded PVC were added to the waste every 5 min to give a total addition of 300 kg/h. Sample collection was started 30 min after initial spiking and samples collected at 30-min intervals for a total of 3 samples. This constitutes a 300% increase in the amount of PVC normally incinerated in the furnace. The transit time of ashes and steam from the flame to the electrostatic precipitator was determined to be 10 sec.

Sample extraction and concentration.

The samples were extracted using procedures which have been described in an earlier study[1]. These procedures include. 16-h Soxhlet extraction of a 30–45-g sample with 400 ml of distilled-in-glass benzene, concentration to 30 μl by rotary evaporation

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under aspirator vacuum and analysis by gas chromatography-mass spectrometry (GC-MS) with no additional sample treatment. This method has been reported to extract 90% of PCDDs on fly ash[13].

Gas chromatographic analysis

A Hewlett-Packard 5830A GC was used with a 2 m × 2 mm I D Aue packed column and flame ionization detection, as used in previous work[1] Temperature programming was 70°C held for 1 min then to 250°C at 4°C/min, held for 15 min. Chlorobenzenes were quantitated using 1,2,3,4-tetrachlorobenzene (BT4C), pentachlorobenzene (BP5C), and hexachlorobenzene (BHC) standard solutions using the external standard technique and GC generated areas. Total organic content was estimated using GC area peaks and an average response factor from previous work.

GC-MS analysis

A Hewlett packard 5992A GC-MS-Calculator was used in the selected-ion monitoring (SIM) mode for PCDD determination. This instrument was equipped with a cool on-column injection port, 30-m × 0 32-mm I D. fused-silica capillary columns with cross-linked DB-5 stationary phase, capillary glass restrictor inlet, *x-y* plotter and dual floppy disk system. The carrier gas flow-rate was 3 ml/min.

The ions monitored for tetrachlorodibenzo-*p*-dioxin (TCDD) were 319.9 and 321 9 The ions selected for penta-(P5CDD), hexa-(H6CDD), hepta(H7CDD) and octa-(OCDD)-chlorodibenzo-*p*-dioxin were 355 9, 389.8, 425 8 and 459 7, respectively A dwell-time of 50 msec was used for each ion.

SIM areas generated by the GC-MS data system were used for quantification. A standard mixture of 1,2,3,4-TCDD, 1,2,3,4,7,8-H6CDD, 1,2,3,4,6,7,8-H7CDD and OCDD was prepared in benzene for quantitation P5CDD was quantified using a response factor intermediate to that of TCDD and H6CDD standards.

Chromatographic conditions were: initial oven temperature, 180°C, to 300°C final temperature at 4°C/min. Injection port temperature was 70°C. Each sample was

TABLE I

CONCENTRATIONS OF PCDD ON FLY ASH (ng/g)

	French incinerator — TIRU								*Canadian[14] mean***
	Normal operation				*+ PVC*				
	1	*2*	*3*	*Mean ± S.D.*	*1*	*2*	*3*	*Mean ± S.D*	
TCDD	ND	ND*	ND	–	ND	ND	ND	–	330
P5CDD	1	10	10	8 ± 6	5	7	6	7 ± 3	400
	t	8	18		4	13	8		
H6CDD	6	28	43	28 ± 18	t4	29	33	25 ± 9	600
	8	30	51		t4	30	31		
H7CDD	10	72	99	75 ± 30	49	64	96	74 ± 19	450
	50	76	120		66	74	97		
OCDD	70	170	240	180 ± 90	111	85	180	140 ± 50	470
	110	180	330		140	100	220		

* Not detected at instrumental detection limit 0 1 ng/μl

** Mean of six analyses

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TABLE II

CONCENTRATIONS OF CHLOROBENZENES ON FLY ASH (ng/g)

	Normal operation				+ PVC			
	1	2	3	Mean ± S.D.	1	2	3	Mean ± S.D.
Tetrachlorobenzene	49	6	12	12 ± 6	5	7	6	6 ± 1
Pentachlorobenzene	200	100	160	150 ± 50	83	120	100	100 ± 18
Hexachlorobenzene	130	63	130	110 ± 40	91	96	90	92 ± 3

run in duplicate and the mean and standard deviation for each sample are reported in Tables I and II.

Before operating in SIM mode, the mass spectrometer was tuned daily by the manufacturer supplied program AUTOTUNE using a perfluorotributylamine calibration standard.

RESULTS AND DISCUSSION

The waste feed used for incineration was collected from a large metropolitan area and consequently was remarkably constant in composition. The sample extracts were run on the GC-MS system to produce the total ion current (TIC) seen in Fig. 1. Comparing the chromatogram of the extract obtained during normal operation to that after the PVC addition, there appears to be little difference between the two in the components present. This is confirmed by the GC-MS results since all the compounds identified from both sets of samples are the same, as seen by the compounds listed in Table III. Only peak 11, a pentachlorobiphenyl, is missing in the sample from normal operation. It is striking that there is a distinctive lack of hydrocarbons and polycyclic aromatic hydrocarbons, which is characteristic of more complex mixtures generated by incinerators of other types. These latter compounds are still present on the fly ash from high temperature incinerators[12,14]. The samples contained an estimated total organic content (TOC) of 1100 ng/g of fly ash. This value did not change considerably for either sample set as seen in Table IV. The data also indicate that this incinerator produces less TOC than a Canadian counterpart but a comparable amount to a high-temperature incinerator[14].

Fig. 1 shows that OCDD is the highest peak in both chromatograms. It has been determined that OCDD is also the most concentrated component of all the PCDD as listed in Table I. The data seem to indicate that there is some direct relationship between concentration and degree of chlorination of PCDD. Perhaps it is that OCDD is the most stable PCDD formed in the combustion chamber, resulting from the temperature and mass action of HCl present in sufficient quantities to affect the degree of chlorination. This distribution between the PCDD congeners is consistent with that observed in high temperature incinerators. Also, it can be seen from the data in Table I that in incinerators of older design like the Canadian one which was built without energy recovery facilities, the quantities of all dioxins are much higher and the distribution is shifted toward the lower chlorinated species[12,14].

Quantitation results for BPC are shown in Table II. The data shows that BT4C

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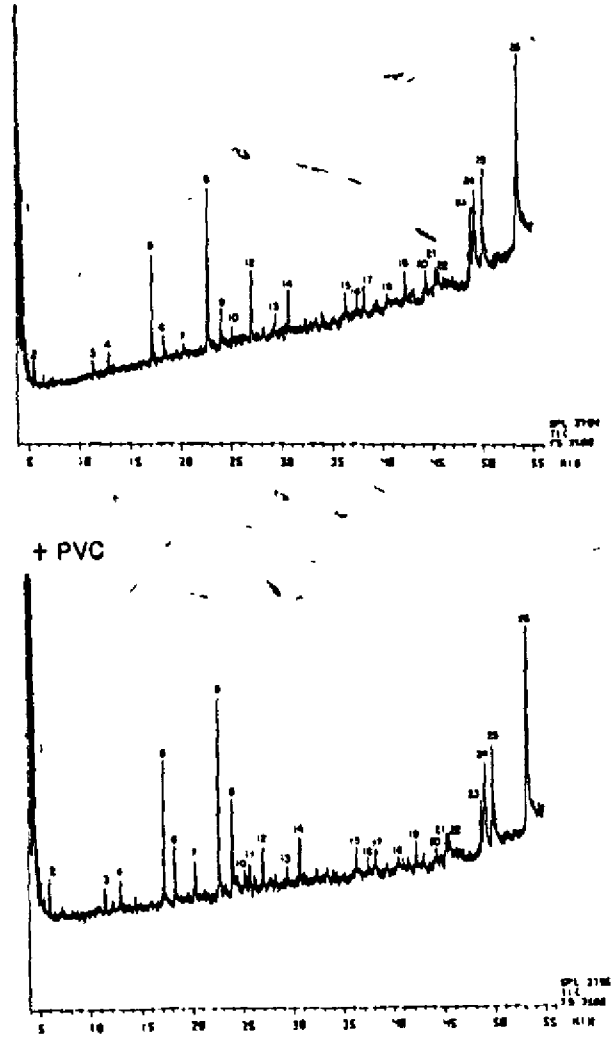

Fig 1 Comparison of TIC for extracts of fly ash obtained from a municipal incinerator operated under normal conditions and with 300% increase in PVC concentration, peak numbers correspond to the compounds listed in Table I

is present at lower levels than BP5C and BHC, which are present at almost the same concentrations within experimental error Furthermore, comparing the values obtained for the normal operation and the PVC added experiments, no great difference is observed between the two sample sets. This can also be seen in Fig 1.

Since the composition of all the samples are very similar to that seen in Fig

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TABLE III

IDENTIFICATION OF COMPOUNDS ADSORBED ON THE FLY-ASH SAMPLES FROM THE MUNICIPAL INCINERATOR SHOWN IN FIG 1 UNDER NORMAL OPERATION AND WITH ADDITION OF PVC

Compound	*Retention time (min)*	*Peak No*	*Compound*	*Retention time (min)*	*Peak No*
Alkylbenzenes	4 5	1	Pentachlorobiphenyl	30.8	14
Alkylphenol	5 6	2	Pentachlorodibenzofuran	36 4	15
Tetrachlorobenzene	11 4	3	Bis(*p*-chlorophenyl)-1,4-dithun	37 6	16
Tetrachlorobenzene	12 9	4	Butylbenzylphthalate	38 3	17
Pentachlorobenzene	17 3	5	Pentachlorodibenzofuran	40 5	18
Tetrachlorophenol	18 4	6	Dioctylphthalate	42.3	19
Tetrachlorobiphenyl	20 3	7	Hexachlorodibenzofuran	44 3	20
Hexachlorobenzene	22 8	8	Hexachlorodibenzofuran	45 3	21
Pentachlorophenol	24 1	9	Hexachlorodibenzo-*p*-dioxin	45 6	22
Tetrachlorobiphenyl	25 3	10	Heptachlorodibenzofuran	48 8	23
Pentachlorobiphenyl	25 8	11	Heptachlorodibenzo-*p*-dioxin	49 1	24
Bibutylphthalate	27 1	12	Heptachlorodibenzo-*p*-dioxin	49 9	25
Dihexylphthalate	29 5	13	Octachlorodibenzo-*p*-dioxin	53 4	26

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TABLE IV

ESTIMATED CONCENTRATIONS OF TOTAL ORGANIC CONTENT (ng/g) ON FLY ASH FROM DIFFERENT INCINERATORS

French — TIRU			*Canadian*[1,17]
Sample	*Normal operation*	*+ PVC*	
1	1300	1100	80,000
2	1100	1800	60,000
3	800	800	65,000
Mean ± S D	1100 ± 250	1200 ± 500	68,000 ± 10 000

1 and listed in the tables, it is evident that in these experiments the addition of PVC to the feedstock had no observable effect on the levels of PCDD, and other compounds generated in the incineration process. If PVC and the other compounds are precursors of PCDDs, one would expect a significant increase in BPCs and PCDDs[6,7].

It could be argued that increased amounts of PVC could result in the enrichment of one or more of the several isomers in a class rather than a change in total concentration. This would be observed by a change in the usual isomeric pattern from that seen in the fly ash from normal operation This possibility was investigated and the results are shown in Fig. 2. For all samples in both sets, the isomeric patterns remained constant. No pattern alteration could be found between the organic com-

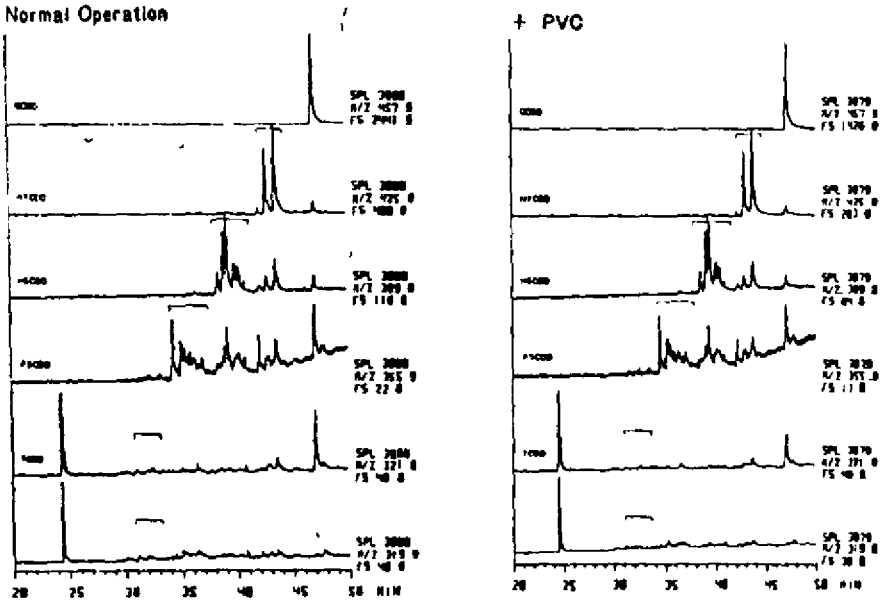

Fig 2 Comparison of SIM traces showing differences in isomeric patterns for PCDDs from normal operation and from PVC-added fly-ash extracts

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pounds generated on the fly ash for the PVC added and normal operation experiments. The data do not indicate that enrichment occurs as a result of addition of PVC to the incinerator feed.

The above results do not support the hypothesis that PVC is a primary source of chlorobenzenes and consequently PCDDs are end-products of waste incineration An addition of 300% the amount of PVC above the normal levels found in waste could be expected to result in an observable increase in both BPCs and PCDDs. This was not observed. This does not preclude the existence of this mechanism, but if it does occur it can not contribute significantly to the final composition of organic compounds. Perhaps this is due to the design of the Martin incinerator Synthesis of the adsorbed PCDDs on fly ash may be more dependent on incinerator conditions, in which case, control of emissions could be accomplished by a very detailed, systematic study of the incinerator conditions and other variables[15].

ACKNOWLEDGEMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada and Electricité de France — Traitement Industriel des Résidus Urbains.

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