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## FORMATION OF POLYCHLORINATED DIBENZO-*p*-DIOXINS UPON COMBUSTION OF COMMERCIAL TEXTILE PRODUCTS CONTAINING 2,4,4'-TRICHLORO-2'-HYDROXYDIPHENYL ETHER (IRGASAN® DP300)

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### SUMMARY

Commercial textile products containing 2,4,4'-trichloro-2'-hydroxydiphenyl ether (Irgasan DP300) as an antimicrobial agent gave dichlorodibenzo-*p*-dioxin(s) (di-CDD) upon combustion. The extent of conversion of Irgasan DP300 into di-CDD(s) reached 19–43% at 600°C. Upon bleaching the textile products with sodium hypochlorite, Irgasan DP300 was chlorinated to 2',3,4,4'-tetrachloro-2-hydroxydiphenyl ether, 2',4,4',5-tetrachloro-2-hydroxydiphenyl ether and 2',3,4,4',5-pentachloro-2-hydroxydiphenyl ether. These chlorinated derivatives were converted into trichlorodibenzo-*p*-dioxins and tetrachlorodibenzo-*p*-dioxin upon combustion, which are more toxic than di-CDD(s). These results suggest that the bleaching and incineration of textile products containing Irgasan DP300 result in environmental pollution by PCDDs.

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### INTRODUCTION

The formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) upon the incineration of municipal refuse has recently become a serious problem<sup>1–3</sup>. Thus, it is of environmental and toxicological importance to investigate their mechanism of formation and precursors<sup>4</sup>.

2,4,4'-Trichloro-2'-hydroxydiphenyl ether (Irgasan DP300) (I) is widely used as an antimicrobial agent for textile products and as a bacteriostat for shampoo and toilet soap<sup>5–7</sup>. We have reported previously<sup>8</sup> that Irgasan DP300 was detected in commercial textile products more often than were other bacteriostatic agents. The average amount was estimated to be 1483 µg/g with the range being 251–5890 µg/g. Furthermore, Irgasan DP300 was easily chlorinated with sodium hypochlorite to give 2',3,4,4'-tetrachloro-2-hydroxydiphenyl ether (II), 2',4,4',5-tetrachloro-2-hydroxydiphenyl ether (III) and 2',3,4,4',5-pentachloro-2-hydroxydiphenyl ether (IV)<sup>9</sup>. Onodera *et al.*<sup>10</sup> have also demonstrated that derivatives II–IV were formed upon disin-

fection and deodorization with sodium hypochlorite of water containing Irgasan DP300. Though Irgasan DP300 is regarded as a compound of low toxicity<sup>11-14</sup>, there are few reports on the toxicity of the three chlorinated derivatives. Furthermore, Irgasan DP300 and its chlorinated derivatives were shown to be converted into various PCDDs by heating or UV irradiation<sup>9</sup>.

These results prompted us to examine whether or not PCDDs were formed from commercial textile products containing Irgasan DP300 by bleaching with sodium hypochlorite followed by combustion.

## EXPERIMENTAL

### *Reagents*

Irgasan DP300 was obtained from Ciba-Geigy (Basle, Switzerland), 1,2,4-trichlorodibenzo-*p*-dioxin (1,2,4-tri-CDD) and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-tetra-CDD) from Gasukuro Kogyo (Tokyo, Japan). The three chlorinated derivatives II-IV and dichlorodibenzo-*p*-dioxin (di-CDD, a mixture of 2,7- and 2,8-di-CDD) were synthesized as reported previously<sup>9</sup>. Other reagents were of analytical reagent grade.

### *Fabrics*

Of the commercial textile products treated with antimicrobial agents, fabrics in which Irgasan DP300 was detected<sup>8</sup> were used as samples.

### *Capillary gas chromatography-mass spectrometry (GC-MS)*

A Shimadzu DF2000 GC-MS system equipped with a GC-MSPAC 1100 data-processing system was used with a Shimadzu CBP5-50-05 capillary column (50 m × 0.35 mm I.D.). The column temperature was programmed from 140 to 260°C at 4°C/min. The injector temperature was 260°C and the separator temperature was 280°C. The carrier gas was helium (1.3 kg/cm<sup>2</sup>).

### *Quantitation of PCDDs*

Di-CDD was quantified on the basis of the intensity at *m/z* 252 (base peak) in the mass spectrum of the mixture of 2,7- and 2,8-di-CDD used as standard. Under the conditions employed, the two isomers were not separated. Similarly, the amounts of tri-CDD and tetra-CDD were determined from the intensity at *m/z* 286 and 320 in the mass spectra of 1,2,4-tri-CDD and 2,3,7,8-tetra-CDD used as the standards, respectively.

### *Bleaching of fabrics with sodium hypochlorite*

The available chlorine concentration in the sodium hypochlorite solution was determined, to be 0.02% by iodometric titration<sup>15</sup>. A 1.0-g amount of fabric was placed in a 50-ml test-tube equipped with a cap, and then 20 ml of sodium hypochlorite solution were added. After the tube was heated at 45°C for 30 min, the fabric was washed well with distilled water and dried. Irgasan DP300 and its chlorinated derivatives in the fabrics were quantified by high-performance liquid chromatography (HPLC) as previously reported<sup>9</sup>.

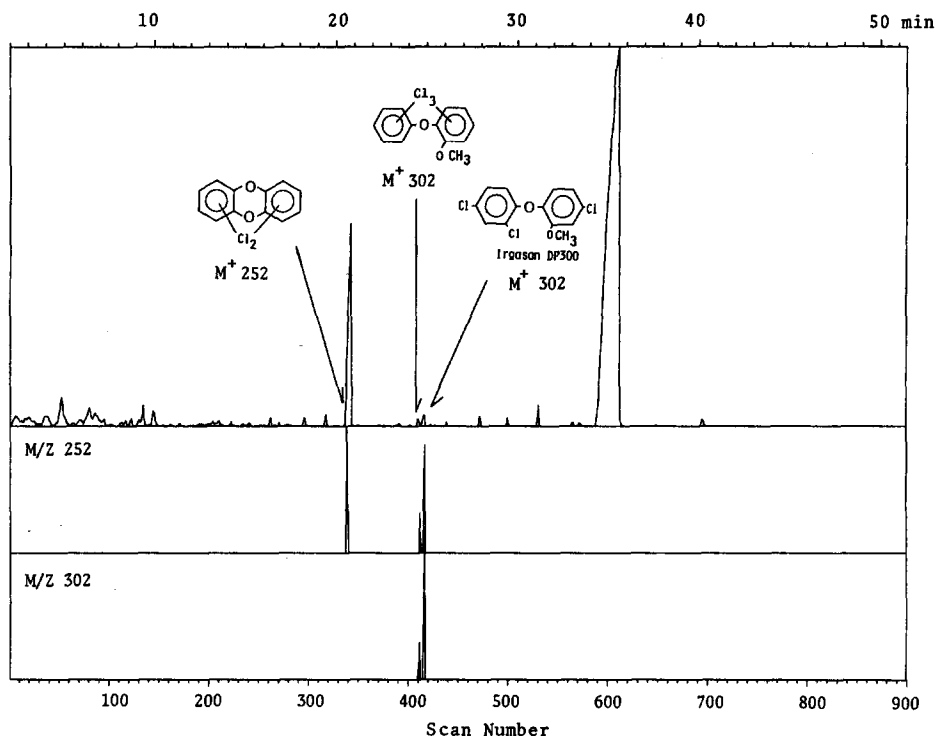


Fig. 1. TIM chromatogram of the combustion products of a commercial textile product (bath mat) containing Irgasan DP300 after separation by Florisil column chromatography and methylation with diazomethane.

#### Combustion of fabrics and detection of PCDDs

A 1.0-g amount of fabric containing Irgasan DP300 was placed on a quartz glass boat (90 mm × 15 mm width, 15 mm depth) and combusted at 400, 600 and 800°C in a quartz glass tube (720 mm × 40 mm I.D.) with a tubular furnace (300 mm × 50 mm I.D.). The unheated part (350 mm) of the quartz glass tube was utilized as an air cooler. Air was passed through the tube at a flow-rate of 2 l/min in order to transport the gases formed by combustion into a series of trapping bottles containing successively water, benzene and ethanol (each 20 ml). These solvents were then pooled in a separating funnel and shaken with two 50-ml portions of ethyl acetate after addition of 100 ml of water. The apparatus used for the combustion was washed well with 300 ml of ethyl acetate. The ethyl acetate layers were pooled, dried over anhydrous sodium sulphate, filtered and concentrated. The concentrate was placed on a Florisil column (170 mm × 12 mm I.D., packed with 10 g of Florisil PR, Floridin) and eluted with 200 ml of ethyl acetate-*n*-hexane (1:1). The eluate was evaporated to dryness. The residue was dissolved in 1 ml of ethyl acetate and placed on a silica gel column (160 mm × 12 mm I.D., packed with 10 g of Kieselgel 60, Merck). The dioxins were eluted with 200 ml of *n*-hexane. The eluate was evaporated to dryness and dissolved in an adequate volume of *n*-hexane for repeated clean-up by silica gel column chromatography as above. The dioxin fraction was analyzed by

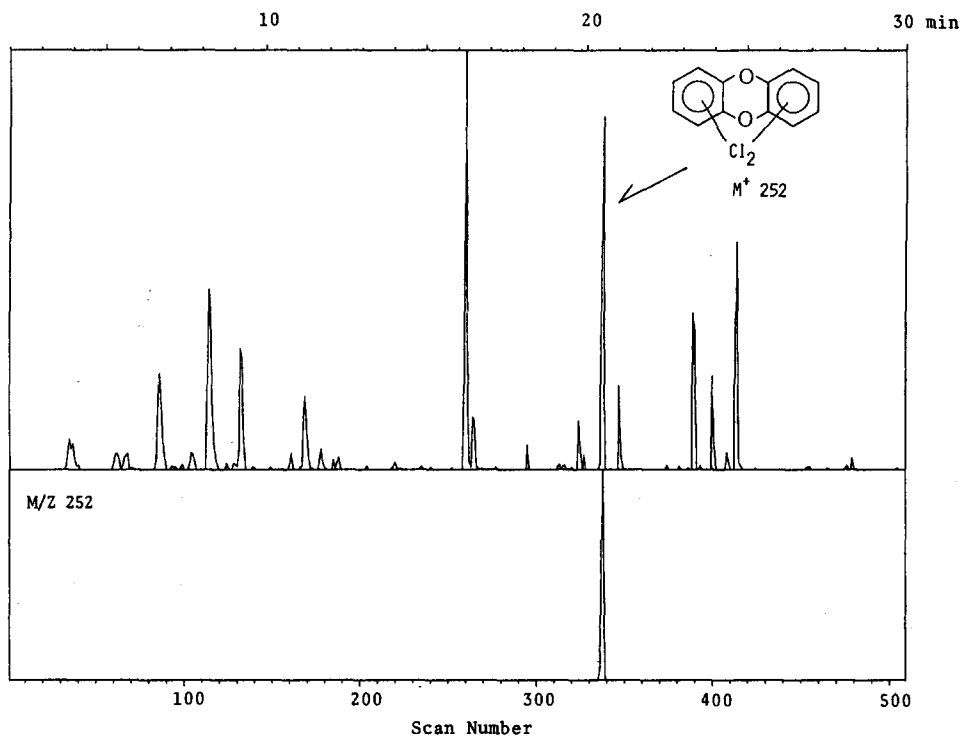


Fig. 2. TIM chromatogram of the dioxin fraction from the combustion products of a commercial textile product (bath mat) containing Irgasan DP300.

capillary GC-MS. When another trapping bottle containing benzene was directly connected to the trapping system, no PCDD was found in the additional trap. Therefore, PCDDs formed upon combustion should be completely trapped by the system. The recoveries of PCDDs in the preparation of the dioxin fraction were 102 and 103% (averages from two experiments) in the cases of di-CDD(s) and tri-CDD, respectively.

For the preparation of cotton gauze containing each of the chlorinated derivatives of Irgasan DP300, a 1.0-mg amount of each chlorinated derivative was dissolved in 1.0 ml of acetone and added to 1.0 g of cotton gauze. The gauze was air-dried at room temperature. The combustion of the gauze and analysis of the products were carried out as described above.

## RESULTS AND DISCUSSION

### *Formation of di-CDD(s) upon combustion of commercial textile products containing Irgasan DP300*

2,4,4'-Trichloro-2'-hydroxydiphenyl ether (Irgasan DP300) has been demonstrated to give di-CDD(s) upon heating<sup>9,16</sup>. Thus, di-CDD(s) may be also formed upon combustion of commercial textile products containing Irgasan DP300. Fig. 1

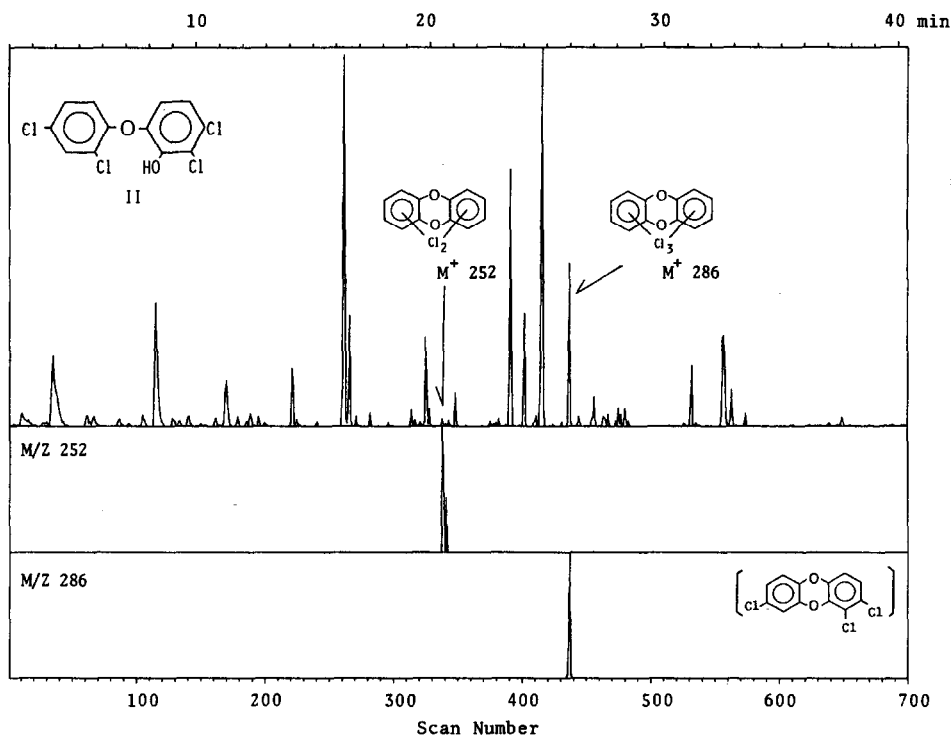


Fig. 3. TIM chromatogram of the dioxin fraction from the combustion products of a cotton gauze containing 2',3,4,4'-tetrachloro-2-hydroxydiphenyl ether (II).

shows the total ion monitoring (TIM) chromatogram of the combustion products of a commercial textile product (bath mat), which were separated by Florisil column chromatography and methylated with diazomethane. Di-CDD(s) was detected at 20.6 min with small amounts of Irgasan DP300 and its isomer, probably formed by thermal rearrangement involving a chlorine atom, at 24.7 and 24.3 min, respectively. Though the peak(s) due to di-CDD(s) was overlapped with that of interfering substance(s), further purification of the combustion product(s) by silica gel chromatography gave a sharp single peak due to di-CDD(s) at 20.6 min without any interfering substances as shown in Fig. 2. The extents of conversion of Irgasan DP300 into di-CDD(s) were determined, using the textile product containing 515 ppm Irgasan DP300, to be 26 (20–32), 43 (38–48) and 24 (21–26)% (averages from two experiments, with the ranges as given) at combustion temperatures of 400, 600 and 800°C respectively. Therefore, subsequent combustion experiments were carried out at 600°C. Table I shows the conversions of Irgasan DP300 into di-CDD(s) upon combustion of four commercial textile products. The values were 19–43%, in good agreement with the results obtained in the pyrolysis of Irgasan DP300<sup>9</sup>.

*Formation of PCDDs upon bleaching with sodium hypochlorite followed by combustion of commercial textile products containing Irgasan DP300*

Our previous paper<sup>9</sup> showed that Irgasan DP300 (I) is readily converted into its chlorinated derivatives (II–IV) with sodium hypochlorite and the chlorinated de-

TABLE I  
 FORMATION OF Di-CDD(s) FROM 2,4,4'-TRICHLORO-2'-HYDROXYDIPHENYL ETHER (IRGASAN DP300) IN COMMERCIAL TEXTILE PRODUCTS BY COMBUSTION AT 600°C

Values are averages from two experiments, with the ranges of the data in parentheses.

Sample	Material	Amount of Irgasan DP300* (µg/g)	Di-CDD(s) formed (µg/g)	Conversion rate (%)**
Bath mat	Acrylic	515	194 (172-216)	43
Men's socks	Cotton	5890	999 (627-1370)	19
Men's shirt	Nylon	747	182 (109-255)	28
Slip	Cotton	463	132 (129-135)	33
	Acrylic			

\* The data were reported previously<sup>8</sup>.

\*\* Calculated from the initial amounts of Irgasan DP300.

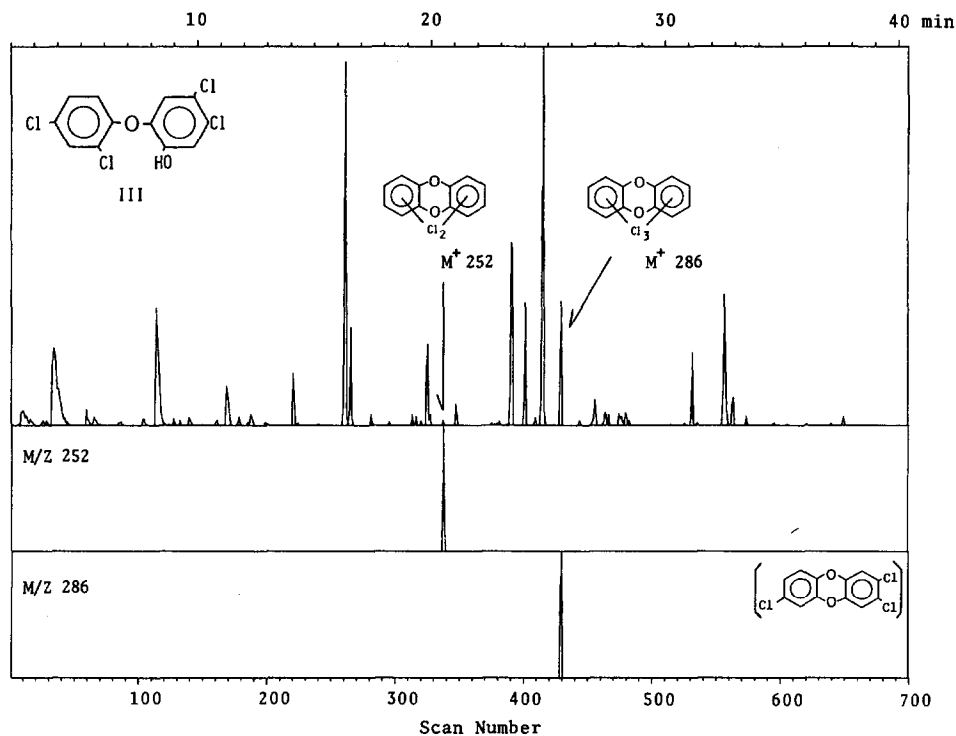


Fig. 4. TIM chromatogram of the dioxin fraction from the combustion products of a cotton gauze containing 2',4,4',5-tetrachloro-2-hydroxydiphenyl ether (III).

derivatives give various PCDDs upon heating. Since commercial textile products containing Irgasan DP300 would probably be bleached with sodium hypochlorite, a domestic bleaching agent, they may give not only di-CDD(s) but also more toxic PCDDs<sup>17</sup> upon bleaching followed by combustion. Thus, preliminary combustion experiments were carried out using a cotton gauze treated with each of the chlorinated derivatives II–IV as samples. Fig. 3–5 show the TIM chromatograms of dioxin fractions separated from combustion products of the samples containing derivatives II, III and IV, respectively. A tri-CDD was found at 25.9 min with a small amount of di-CDD(s) at 20.6 min in Fig. 3. A small amount of di-CDD(s) and a tri-CDD were observed at 20.6 and 25.5 min in Fig. 4. A tetra-CDD appeared at 30.1 min as a major product with a small amount of di-CDD(s) at 20.6 min and three tri-CDDs at 24.5, 25.5 and 25.9 min in Fig. 5. Table II summarizes the amounts of PCDDs formed upon combustion of the gauze containing derivatives II–IV. Though all the chlorinated derivatives gave PCDDs, tri-CDDs were formed as major products from II and III, tetra-CDD from IV.

We have previously reported that penta- and hexa-CDDs were produced upon pyrolysis of derivative IV at 400°C for 10 min in a small glass bulb fitted with an air cooler<sup>9</sup>. Such conditions may allow the intermolecular shift of chlorine atoms (disproportionation) to give higher chlorinated PCDD(s). In the present study, however,

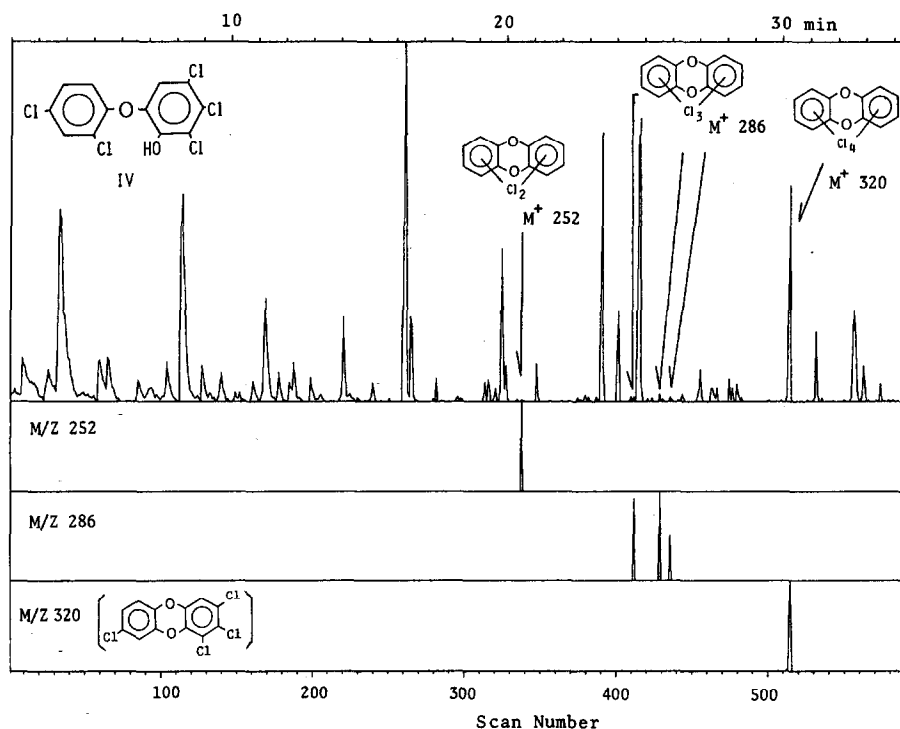


Fig. 5. TIM chromatogram of the dioxin fraction from the combustion products of a cotton gauze containing 2',3,4,4',5-pentachloro-2-hydroxydiphenyl ether (IV).

TABLE II

FORMATION OF PCDDs FROM 2',3,4,4'-TETRACHLORO-2-HYDROXYDIPHENYL ETHER (II), 2',4,4',5-TETRACHLORO-2-HYDROXYDIPHENYL ETHER (III) AND 2',3,4,4',5-PENTACHLORO-2-HYDROXYDIPHENYL ETHER (IV) CONTAINED IN COTTON GAUZE UPON COMBUSTION AT 600°C

Values are averages from two experiments, with the ranges of the data in parentheses. N.D. = Not detected (<0.5 µg).

Compound	Amount of PCDD formed (µg)			Total amount of PCDDs formed (%) <sup>*</sup>
	di-CDD	tri-CDD	tetra-CDD	
II	9 (6.4-11)	61 (57-64)	N.D.	8
III	19 (18-19)	102 (80-124)	N.D.	14
IV	6 (3-8)	18[3]** (11-25)	70 (48-92)	11

<sup>\*</sup> Calculated from the initial amounts of II, III and IV.

<sup>\*\*</sup> The value in brackets is the number of isomers detected.



TABLE III  
FORMATION OF PCDDs FROM COMMERCIAL MEN'S SOCKS CONTAINING IRGASAN DP300 AFTER BLEACHING WITH SODIUM HYPOCHLORITE AND COMBUSTION

Values are averages from two experiments, with the ranges of the data in parentheses.

Sample	Amounts formed after bleaching ( $\mu\text{g/g}$ )*				Amounts formed after combustion ( $\mu\text{g/g}$ )**			
	Irgasan DP300	II	III	IV	di-CDD(s)	tri-CDD	tetra-CDD	
Untreated	5890**	N.D.	N.D.	N.D.	999 (627-1370)	N.D.	N.D.	N.D.
Treated with 0.02% available chlorine	2580 (2380-2780)	458 (421-494)	215 (194-236)	1180 (1080-1280)	268 (254-282)	132[3]§ (121-142)	93 (81-104)	

\* N.D. = Not detected ( $< 1 \mu\text{g/g}$ ).

\*\* The data were reported previously<sup>8</sup>.

\*\*\* N.D. = Not detected ( $< 0.5 \mu\text{g/g}$ ).

§ The value in brackets is the number of isomers detected.

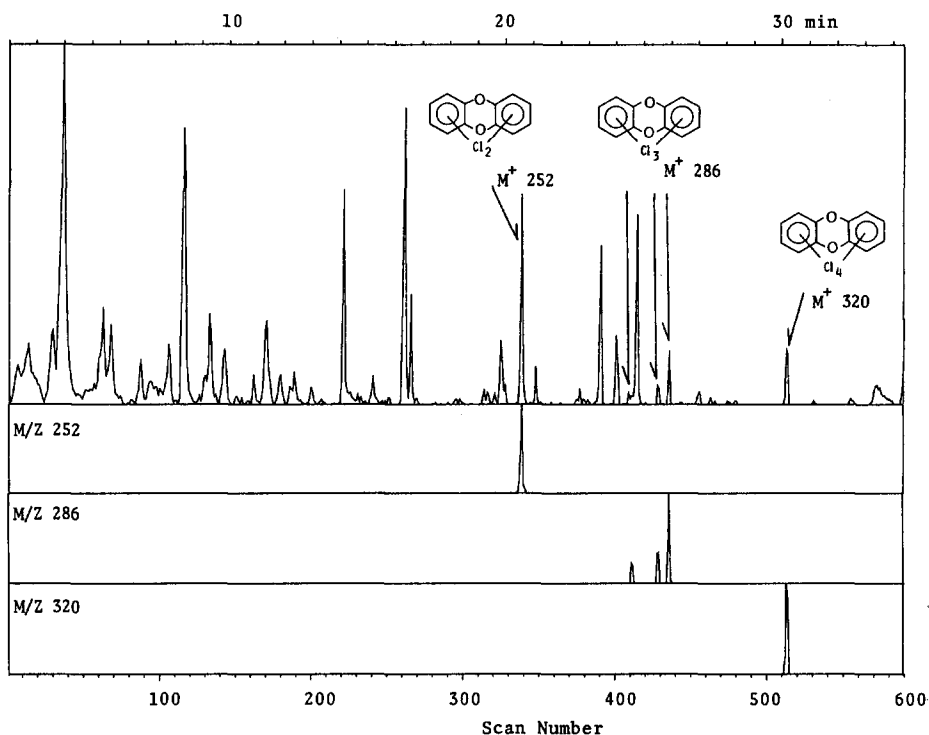


Fig. 6. TIM chromatogram of the dioxin fraction from the combustion products of commercial men's socks containing Irgasan DP300 after bleaching with sodium hypochlorite.

the combustion was carried out under a stream of air where the intermolecular reaction is less favoured. Therefore, the formation of higher chlorinated PCDDs was not observed upon combustion of the gauze containing derivatives II–IV.

Fig. 6 shows the TIM chromatogram of the dioxin fraction obtained from socks containing Irgasan DP300 after bleaching with sodium hypochlorite at 45°C for 30 min, followed by combustion at 600°C. In the chromatogram, three tri-CDDs and one tetra-CDD were detected at 24.5, 25.5, 25.9 and 30.1 min, respectively, in addition to di-CDD(s) at 20.6 min. The tri-CDDs at 25.5 and 25.9 min and tetra-CDD at 30.1 min were identified as 2,3,7-tri-CDD formed from III, 1,2,8-tri-CDD from II and 1,2,3,8-tetra-CDD from IV, respectively, by comparison of their retention times and mass fragmentation patterns with those of PCDDs obtained by heating of derivatives II–IV<sup>9</sup>.

The amounts of PCDDs formed from the socks upon combustion are shown in Table III, together with those of the chlorinated derivatives of Irgasan DP300 (II–IV) formed upon bleaching. These results revealed that Irgasan DP300 itself in fabrics was the precursor for di-CDD(s) but not for more toxic tri-CDDs and tetra-CDD. However, Irgasan DP300 in fabrics gave tri-CDDs and tetra-CDD upon combustion once it had been chlorinated by bleaching with sodium hypochlorite.

From the results obtained, it is suggested that the bleaching and incineration of textile products containing Irgasan DP300 result in environmental pollution by PCDDs.

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