Journal of Chromatography, 641 (1993) 309–317
Elsevier Science Publishers B.V., Amsterdam

CHROM. 25 118

High-resolution gas chromatographic–mass spectrometric determination of neutral chlorinated aromatic sulphur compounds in stack gas samples

S. Sinkkonen*, E. Kolehmainen, J. Koistinen and M. Lahtiperä

Department of Chemistry, University of Jyväskylä, P.O, Box 35, SF-40 351 Jyväskylä (Finland)

(First received January 8th, 1993; revised manuscript received March 25th, 1993)

ABSTRACT

Four stack gas samples from waste incineration were analysed by high-resolution GC–MS for neutral chlorinated aromatic sulphur compounds such as polychlorinated dibenzothiophenes, thianthrenes and diphenyl sulphides. Samples were analysed tentatively also for some methylated derivatives of these compounds. The stack gas samples had earlier been found to contain some tri- and tetrachlorodiphenyl sulphides. Two of the stack gas samples contained tetra- and pentachlorodibenzothiophenes. One sample was strongly suspected to contain some tri- and tetrachlorothianthrenes in low concentrations. No methylated derivatives of these compounds could be found. Polychlorothianthrenes, some polychlorodibenzothiophenes and some methylated model compounds were prepared; some of the model compounds used in the analysis had been prepared previously. The model compounds were purified by reversed-phase HPLC and their structures were determined by GC–MS and ^{1}H NMR spectroscopy.

INTRODUCTION

Polychlorinated dibenzothiophenes (PCDBTs) have attracted interest along owing to the availability of model compounds and the discovery of these compounds in incineration gases, bleached pulp mill effluents and some aquatic organisms [1–4]. In the combustion of chlorine-containing materials many kinds of persistent chlorinated aromatic compounds, such as polychlorinated dibenzo-*p*-dioxins, dibenzofurans, diphenylethers and chlorophenols [5,6] are formed. Sulphur compounds are generally found in raw materials and chemicals and during the combustion process can react with chlorinated materials in the waste or fuels used in combustion. Hence it is possible that many kinds of chlorinated sulphur-containing compounds are formed. PCDBTs, polychlorinated thianthrenes (PCTAs) and polychlorinated diphenyl sulphides (PCDPSs) are three groups of compounds which in theory can possibly be formed in this way.

Reference materials and model compounds for the high-resolution gas chromatography–mass spectrometry (HRGC–HRMS) determination of PCDBTs and PCDPSs have been prepared previously [7–10]. In this study, mixtures of chlorinated derivatives were prepared by direct chlorination of the parent compounds dibenzothiophene (DBT) and thianthrene (TA) with sulphuryl chloride and some methylated derivatives from polychloropolymethylbenzenes and sulphur using $AlCl_3$ as catalyst. Pure isomers were obtained by RP-HPLC fractionation of the chlorination mixtures.

Four stack gas samples from waste incineration were analysed by HRGC–HRMS with a resolution of 20 000 for the occurrence of these compounds. Tetra (Te)- to hexa (He)CDBTs, tri

* Corresponding author.

0021-9673/93/$06.00

(Tri)- to penta (Pe)CTAs and Tri- to HeCDPSs were analysed by GC–selected ion monitoring (SIM) MS using the exact values of the M^+ and $(M+2)^+$ ions. However, a resolution of near 40 000 is needed for the unique separation of some of these compounds and the fragments of these based exclusively on MS. Additionally, some methylated derivatives of these compounds were tentatively screened in a similar way.

Several Te- and PeCDBTs and Tri- and TeCDPSs were found in the samples. One stack gas sample which was not found to contain any Te- and PeCDBTs was strongly suspected to contain Tri- and TeCTAs in low concentrations. The detailed analyses of these samples for PCDPSs have been reported previously [10]. Methylated derivatives of these compounds were not found.

EXPERIMENTAL

Model compounds

Preparation and purification. Model compound mixtures were prepared by direct chlorination of the parent compounds DBT, TA and DPS. Sulphuryl chloride was used as the chlorination agent in a mixture of *o*- and *p*-chlorotoluene (50:50). Buckholtz *et al.* [11] have used this mixture in the chlorination of thianthrene. Sulphuryl chloride was added stepwise during 4 h at 60°C until the GC–photoionization detection (PID) analysis showed that no parent compound was present any longer and that the degree of chlorination was three to four.

The chlorination of TA produced one TriCTA and one TeCTA as the main products. Additionally, two TriCTAs, four TeCTAs and some PeCTAs were observed in minor concentrations. Fig. 1 shows the SIM chromatograms of the chlorination mixture with exact m/z values of $(M+2)^+$ ions of (a) TriCTAs (m/z 319.8869), (b) TeCTAs (m/z 353.8479) and (c) PeCTAs (m/z 387.8089).

The chlorination mixture was fractionated by reversed-phase HPLC with an Elsico C_8 column. Acetonitrile–water (65:35) at a flow rate of 1 ml/min was used as the eluent. UV detection at 254 nm was applied. The fractions obtained from HPLC were analysed by GC–MS and their

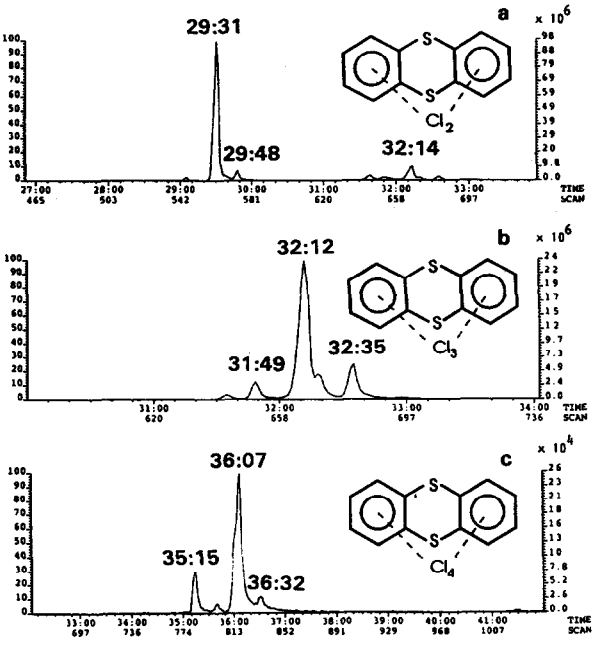

Fig. 1. SIM chromatograms of the chlorination mixture of TA with exact m/z values of $(M+2)^+$ ions of (a) TriCTAs (m/z 319.8869), (b) TeCTAs (m/z 353.8479) and (c) PeCTAs (m/z 387.8089). Time in min.

structures were determined by ^{1}H NMR spectroscopy. The main TriCTA isomer was obtained in >90% purity and ^{1}H NMR analysis showed it to be 2,3,7-TriCTA; the ^{1}H NMR spectrum of 2,3,7-TriCTA and its interpretation are given in

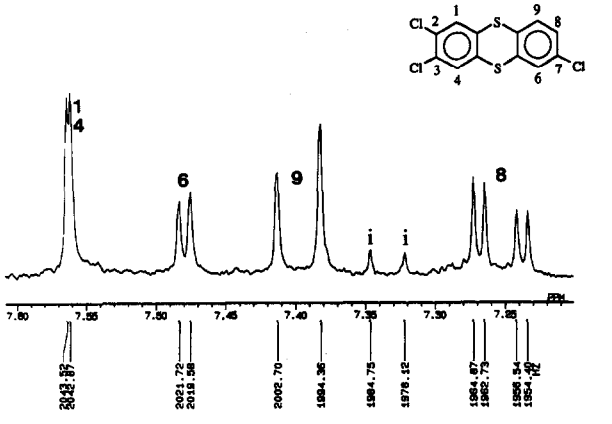

Fig. 2. ^{1}H NMR spectrum of 2,3,7-trichlorothianthrene and its interpretation. Chemical shifts, δ (ppm): 7.57 and 7.56 (H-1 and H-4, assignment is ambiguous), 7.48 (H-6), 7.40 (H-9), 7.26 (H-8). Coupling constants (Hz): 2.14, ^4J(H-6, H-8); 8.34, ^3J(H-8,H-9). Impurity signals are denoted by i.

Fig. 2. The purification of the main component of TeCTAs partially failed; the fraction obtained was calculated to consist of about 80% of this TeCTA isomer. The ^{1}H NMR spectrum of this TeCTA contained only one peak at δ 7.57 ppm (from TMS), which is very close to the values of protons 1 and 4 at δ 7.56 and 7.57 (assignment is ambiguous) of 2,3,7-TriCTA (see Fig. 2). Therefore, it can be concluded that the tetrachloro isomer obtained is 2,3,7,8-TeCTA (thio analogue of 2,3,7,8-TCDD). This finding is in agreement with the general knowledge of the *ortho*- and *para*-directing properties of sulphur in electrophilic aromatic substitution reactions.

The mixture of PCDBTs obtained from the chlorination of DBT with sulphuryl chloride in similar way to that of TA was more complex, containing at least 20–30 different chlorinated compounds. The GC–MS total ion chromatogram (*m/z* 50–500) of the chlorination mixture of DBT and electron impact (EI) mass spectra of one Di-, one Tri- and one TeCDBT isomer are presented in Fig. 3.

When DPS was chlorinated in similar way, 2,4,4'-TriCDPS and 2,2',4,4'-TeCDPS were the main products obtained, as was expected from the *ortho*- and *para*-directing properties of sulphur. Additionally, three DiCDPSs and five PeCDPSs in small concentrations were formed [10]. Fig. 4 presents the SIM chromatograms of the chlorination mixture of DPS with the exact *m/z* values of the $(M+2)^+$ ions of (a) DiCDPSs (*m/z* 253.9724), (b) TriCDPSs (*m/z* 289.9305), (c) TeCDPSs (*m/z* 323.8915) and (d) PeCDPSs

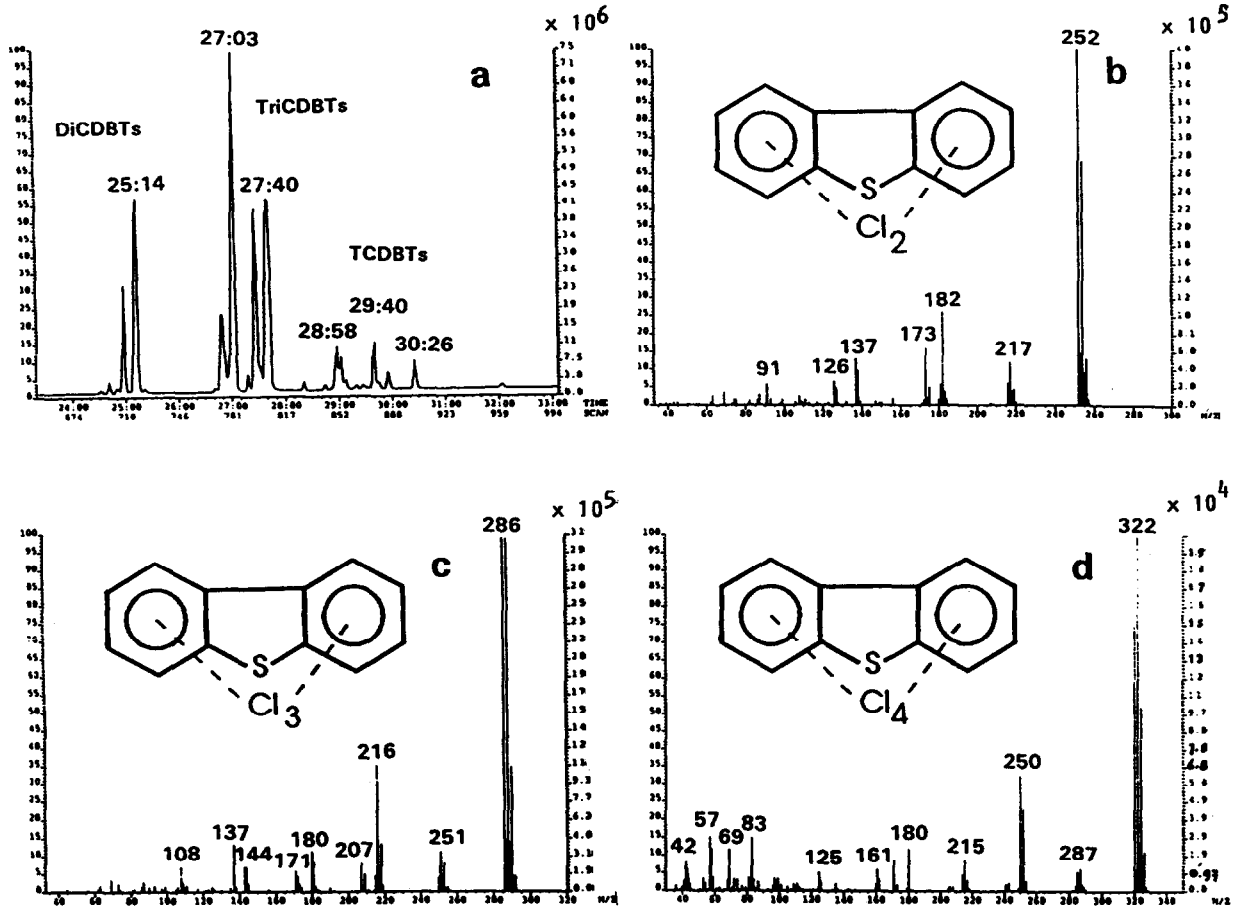

Fig. 3. (a) GC–MS total ion chromatogram (*m/z* 50–500) of the chlorination mixture of DBT, and EI mass spectra of (b) one DiCDBT, (c) one TriCDBT and (d) one TeCDBT isomer.

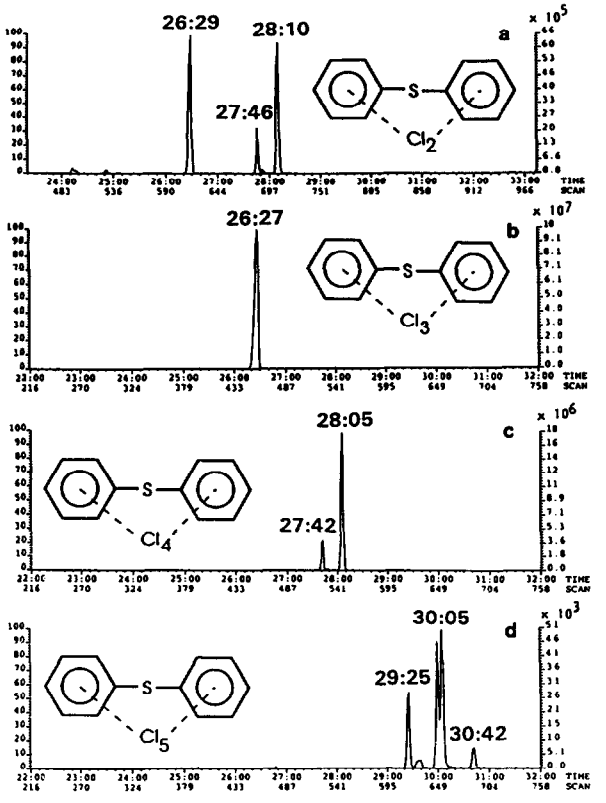

Fig. 4. SIM chromatograms of the chlorination mixture of DPS with the exact m/z values of the $(M+2)^+$ ions of (a) DiCDPSs (m/z 253.9724), (b) TriCDPSs (m/z 289.9305), (c) TeCDPSs (m/z 323.8915) and (d) PeCDPSs (m/z 357.8525).

(m/z 357.8525). The scales of the ion intensities in the chromatograms are different so the concentrations of the compounds cannot be directly compared using the heights or areas of the peaks.

PCDBTs have also been prepared by reactions of PCBs with sulphur [7–9]. Some PCDPSs have been prepared from chlorobenzenes and sulphur with $AlCl_3$ as catalyst [10]. Some dichlorodimethyldiphenyl sulphides have been prepared similarly from chlorotoluenes. For example, 2-chlorotoluene produced a mixture containing four dichlorodimethyldiphenyl sulphides as the main products and two dichlorodimethyldiphenylsulphides as minor products. Several dichloromethyl sulphides were also found to be formed in small amounts. Additionally, relatively large amounts of some dichlorodimethylthianthrenes and dichlorodimethyldiphenyl disulphides were formed. Fig. 5 presents (a) the total ion chromatogram of the synthesis mixture, and EI mass spectra of (b) a dichlorodimethyl diphenylsulfide, (c) a dichlorodimethyldiphenyl disulfide and (d) a dichlorodimethylthianthrene isomer. The mixture could not be fractionated by RP-HPLC with Elsico or Spherisorb columns and acetonitrile–water eluents.

GC–MS. A VG AutoSpec high-resolution mass spectrometer connected to an HP 5890 Series II gas chromatograph was used for GC–full-scan (m/z 50–500) EI–MS of the model compounds. The column was 25 m × 0.2 mm I.D. HP-5 (0.11 μm). Helium was used as carrier gas. The temperature program was 100°C (held for 1 min), increased at 20°C/min to 180°C then at 5°C/min to 280°C (held for 15 min). The temperatures were injector 260°C, transfer line 280°C and ion source 260°C. The EI potential was 36 eV.

The EI mass spectra of PCDBTs, PCTAs and PCDPSs all have an intense molecular ion (M^+). The molecular ion and the fragment ions show the typical expected clustering due to chlorine isotopes. The EI mass spectra of PCDBTs show a relatively small M^+- 2Cl fragment and a smaller M^+- Cl fragment. Tri- and TeCTAs show strong fragments due to the formation of M^+- Cl and M^+- 2Cl ions. PCDPSs show a very strong fragment due to M^+- 2Cl and a small fragment due to M^+- Cl.

NMR spectroscopy. High-resolution ^1H NMR spectroscopy combined with HRMS provides an excellent tool for isomer-specific structure elucidation of substituted aromatics such as DPSs, DBTs and TA [8–10]. Using these methods, three isomeric TriCDPSs, 2,2',4-TriCDPS, 2,4,4'-TriCDPS and 2,4',6-TriCDPS, and two isomeric TeCDPSs, bis(2,4-dichlorophenyl) and bis(3,4-dichlorophenyl) sulphide, have been determined [10]. Further, two isomeric DBTs, 2,3,7,8- and 2,3,6,7-tetramethyl derivatives, and three PCDBTs, 3-chloro-, 1,3-dichloro- and 1,3,4-trichloro derivatives, have been verified in the reaction mixtures. The existence of a thio analogue of the highly toxic 2,3,7,8-tetrachlorodibenzodioxin (TCDD), *viz.*, 2,3,7,8-TeCTA, has also been proposed.

A disadvantage of ^1H and even more of ^{13}C

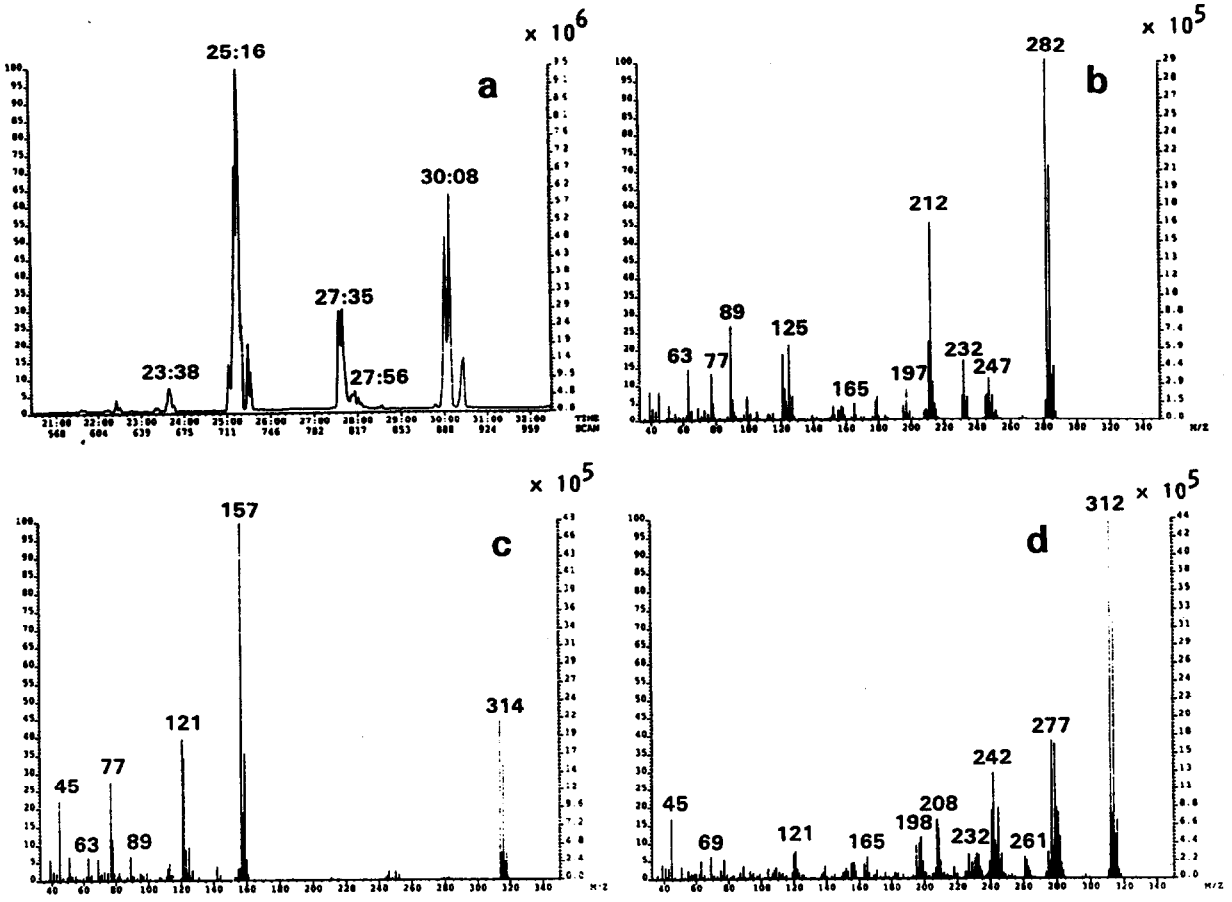

Fig. 5. (a) Total ion chromatogram of the synthesis mixture, and EI mass spectra of (b) a dichlorodimethyldiphenyl sulfide, (c) a dichlorodimethyldiphenyl disulfide and (d) a dichlorodimethylthianthrene isomer.

NMR spectroscopy is their insensitivity in comparison with, *e.g.*, MS or FT-IR spectroscopic methods. This insensitivity can be problematic, because the synthetic scale and concentrations of these potentially harmful compounds should be maintained as low as possible. In addition, interferences to NMR resonances from solvent and/or impurity signals may strongly disturb the reliable detection and analysis of the NMR spectra. Therefore, the selection of the measuring conditions and especially choosing a suitable solvent and minimizing its amount are of extreme importance.

The method developed for terpenoid type off-flavour compounds [12] was used. By this means, a ^{1}H NMR spectrum of *ca.* 5 μg of monoterpenoid compound collected directly in the NMR solvent by preparative GC could be measured reliably. In order to decrease the solvent volume from 700 μl (a recommended amount in a standard 5 mm O.D. NMR tube) to 100 μl, a thick-wall (5 mm O.D., 2 mm I.D.) sample tube was selected for these measurements. By using special spherically shaped ampoules the volume of the solvent can be further decreased. A special ^{1}H high-sensitivity probe head available for the JEOL GSX-270 FT-NMR spectrometer was used. In some instances subtraction of the solvent signal also gave good results.

For the aromatic sulphur compounds studied, $C^2H_2Cl_2$ was found to be a suitable medium, because its ^{1}H NMR signal is located at 5.30 ppm from tetramethylsilane (TMS). Consequently, it does not overlap with either the ^{1}H NMR lines of aromatic protons, which resonate characteristically at δ 6.9–8.9 ppm [1–3], or with

the aryl-bound methyl signals, which resonate at δ 2.3–2.5 ppm [2] from TMS. Similarly, $C^2H_2Cl_2$ can be used in ^{13}C NMR spectroscopy, hence its resonance pattern does not interfere with the signals of aromatic carbons and aryl-bound methyls under any conditions or in any neutral derivative concerned.

^1H NMR spectral assignment was mainly based on the synthetic procedure used, symmetry considerations of possible products and characteristic intra-aromatic couplings. The ^1H NMR parameters refined by computer-assisted iterations [13]. In ^{13}C NMR spectral assignment, the substituent chemical shifts were generally utilized.

Preparation of stack gas samples

The four stack gas samples from waste incineration were originally prepared for the determination of polychlorinated dibenzo-*p*-dioxins and dibenzofurans at the Institute for Environmental Research in Jyväskylä and were kindly given to us for the determination of the chlorinated sulphur compounds. These compounds have been found to enter the dioxin fraction in the analysis process [3,4,10].

Two of the samples contained gas phase and particles (samples 2 and 4) and two only particles (samples 1 and 3). The volume of the gas phase was 3.5 N m^3 (0°C, 101.3 kPa). The particle phase was extracted with toluene for 48 h and treated with sulphuric acid and the dioxin fraction was isolated by column chromatography with basic alumina and activated carbon [14]. $^{13}C_{12}$-labelled 2,3,7,8-TeCDD (12.5 ng/per sample), which was used as an internal standard in the dioxin analysis, was added to all samples before extraction.

HRGC–HRMS of the samples

The same VG AutoSpec high resolution mass spectrometer that was used to measure full-scan EI mass spectra was used in the HRGC–HRMS analysis of the stack gas samples. The same GC and MS conditions were utilized.

Because of the complexity of the fractions analysed, the resolution was normally kept at 20 000 (5% valley) to eliminate interfering compounds or fragments of compounds with higher molecular mass. For example, the exact mass of the $(M+2)^+$ ion of TeCTA is 353.8479 and that of the M^+ ion of pentachlorodioxin 353.8398, so a resolution near 44 000 is needed for the separation of these two ions. The TeCTAs and PeCDDs had close retention times under the GC–MS conditions used.

TABLE I

EXACT *m/z* VALUES OF M^+ AND $(M+2)^+$ IONS USED IN THE HRGC–SIM-HRMS ANALYSIS

Compound	Formula	M^+	$(M+2)^+$
TeCDD	$C_{12}H_4O_2Cl_4$	319.8965	321.8937
PeCDD	$C_{12}H_3O_2Cl_5$	353.8576	355.8547
TriCDBT	$C_{12}H_5SCl_3$	285.9178	287.9148
TeCDBT	$C_{12}H_4SCl_4$	319.8788	321.8758
PeCDBT	$C_{12}H_3SCl_5$	353.8398	355.8369
TriCTA	$C_{12}H_5S_2Cl_3$	317.8898	319.8869
TeCTA	$C_{12}H_4S_2Cl_4$	351.8509	353.8479
PeCTA	$C_{12}H_3S_2Cl_5$	385.8119	387.8089
TriCDPS	$C_{12}H_7SCl_3$	287.9334	289.9305
TeCDPS	$C_{12}H_6SCl_4$	321.8944	323.8915
PeCDPS	$C_{12}H_5SCl_5$	355.8555	357.8525

Selected ion monitoring was done with the *m/z* values of M^+ and $(M+2)^+$ ions for TeCDDs, PeCDDs, TeCDBTs, PeCDBTs, TriCTAs, TeCTAs, PeCTAs, TriCDPSs, TeDPSs and PeCDPSs. The exact values for the M^+ and $(M+2)^+$ ions of tri-, tetra- and pentachlorinated compounds used in the HRGC–SIM-HRMS analysis were calculated by the Opus Version I.6 isotope program of the Fisons Instruments V6 Analytical Autospec mass spectrometer. The values are given in Table I.

RESULTS AND DISCUSSION

The results from the HRGC–SIM-HRMS analyses are given in Table II. Rough quantitative estimations were made by comparing the peak heights of the compounds under investigation with that of the $^{13}C_{12}$-labelled 2,3,7,8-TeCDD. The knowledge of the MS fragmentation of PCDPSs and PCTAs was applied in their quantification.

TABLE II

RESULTS OF DETERMINATION OF THE COMPOUNDS IN THE SAMPLES

Concentrations of individual isomers (ng per sample) with number of isomers in parentheses.

Compound	Sample 1	Sample 2	Sample 3	Sample 4
TeCDBT	14 (1)	7–69 (10–15)	n.d.[a]	5–63 (15–20)
PeCDBT	n.d.	1–5 (10–15)	n.d.	1–5 (15–20)
TriCDPS	0.1–0.3 (3)		n.d.	n.d.
TeCDPS	1.6, 0.5 (2)		n.d.	n.d.
TriCTA	n.d.	n.d.	2.1, 0.9 (2)	n.d.
TeCTA	n.d.	n.d.	1.8, 1.5 (2)	n.d.

[a] n.d. = Not detected.

Samples 2 and 4 were found to contain TeCDBTs in relatively high concentrations. The isomer profiles of the TeCDBTs in these two samples were identical. About twenty resolved isomers could be seen. The real number of isomers in the samples may be greater owing to unresolved peaks. The number of possible TeCDBT isomers is 38. The total concentration of all TeCDBTs seems to be nearly equal to the total concentration of all TeCDDs, even though the concentrations of individual TeCDBT isomers is about one tenth of the concentration of the most abundant TeCDD isomer.

Fig. 6 shows the SIM chromatograms of sample 2 with the values for the $(M+2)^+$ ions of (a) TeCDBTs (321.8758) and (b) TeCDDs (321.8937). With the ions used to analyse PeCDBTs there were many interferring peaks in sample 2. There were some peaks with the correct $M^+/(M+2)^+$ peak ratios in the retention window of the PeCDBTs, but these peaks could not be unambiguously ascertained to be pure PeCDBT isomers. The situation was the same with HeCDBTs. Sample 1 contained one TeCDBT isomer but no PeCDBTs. Neither TeCDDs nor PeCDDs could be found this sample. Sample 3 did not contain any TeCDBTs or PeCDBTs. TeCDDs could be found in very low concentrations, but no PeCDDs were detected.

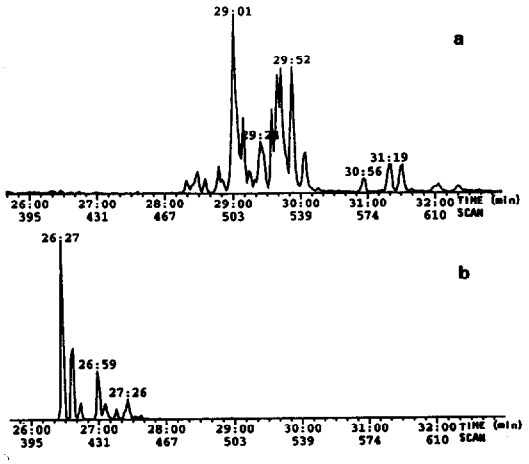

Fig. 6. SIM chromatograms of sample 2 with the values for $(M+2)^+$ ions of (a) TeCDBTs (321.8758) and (b) TeCDDs (321.8937).

The PCDPSs have been determined previously in the same stack gas samples [10]. Some Tri- and TeCDPSs were found.

With the m/z values of 317.8898 and 319.8869 for TriCTAs, 351.8509 and 353.8479 for TeCTAs and 385.8119 and 387.8089 for PeCTAs, the interpretation of the chromatograms was difficult because of many interfering peaks in the same retention time range as for the compounds studied. Relatively large interfering peaks with these ions appeared in the retention time range 30–36 min. The origin of these peaks could not be elucidated. It is possible that they originate as fragment ions from some kind of larger chlorinated compounds. For example, when samples, that contain PCDBTs are analysed it must be taken into account that for the separation of the $(M+2)^+$ ion for TriCTA (319.8869) from the M^+ ion for TeCDBT (319.8788) a resolution near 40 000 (39 500) in MS is needed. Some isomers of the TriCTAs and TeCDBTs were

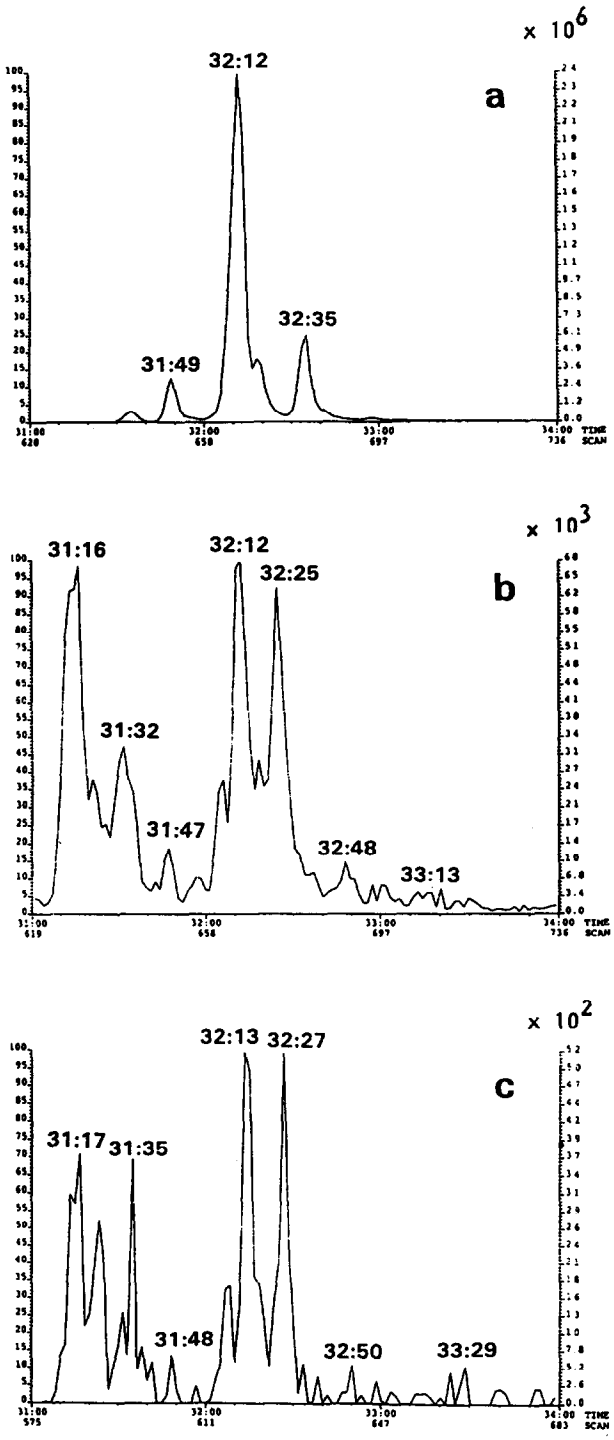

Fig. 7. SIM chromatograms of (a) the chlorination mixture of TA, (b) sample 4 with the value of the $(M+2)^+$ ion of TeCTAs (353.8479) and (c) sample 4 with the value of the M^+ ion of PeCDBTs (353.8398).

eluted simultaneously in GC under these conditions. The situation was the same with PeCDBTs and TeCTAs and probably also with the corresponding higher chlorinated isomers. Fig. 7 presents the SIM chromatograms of (a) the chlorination mixture of TA, (b) sample 4 with the value of the $(M+2)^+$ ion of TeCTAs (353.8479) and (c) sample 4 with the value of the M^+ ion of PeCDBTs (353.8398). This makes it impossible to use the ratios $M^+/(M+2)^+$ for the unambiguous identification of these compounds. However, the $M^+/(M+2)^+$ ratios for the TeCDBTs and PeCDBTs were so close to the theoretically correct values that it can be concluded that if there are any Tri-, Te- or PeCTAs in the samples their concentrations are very low compared with the concentrations of the PCDBTs. However, sample 3, which did not contain any TeCDBTs or PeCDBTs, is suspected to contain at least two TriCTA isomers with the correct retention times and the correct $M^+/(M+2)^+$ ratio for trichlorinated compounds. In sample 3 there could also be seen small peaks with the m/z values of the M^+ and $(M+2)^+$ ions of TeCTAs with a retention time very close to that of 2,3,7,8-TeCTA. The $M^+/(M+2)^+$ ratio was also typical for tetrachlorinated compounds. For a more reliable analysis of PCTAs from this kind of sample, however, more purification is needed even if an MS resolution of more than 20 000 is used.

REFERENCES

1 H.-R. Buser and C. Rappe, *Anal. Chem.*, 63 (1991) 1210–1217.
2 H.-R. Buser, I.S. Dolezar, M. Wolfensberger and C. Rappe, *Environ. Sci. Technol.*, 25 (1991) 1637–1643.
3 S. Sinkkonen, J. Paasivirta, J. Koistinen and J. Tarhanen, *Chemosphere*, 23 (1991) 583–587.
4 S. Sinkkonen, J. Paasivirta, J. Koistinen, M. Lahtiperä and R. Lammi, *Chemosphere*, 24 (1992) 1755–1763.
5 B. Ahling and A. Lindskog, in O. Hutzinger, R.W. Frei, E. Merian and F. Pocchiari (Editors), *Chlorinated Dioxins and Related Compounds*, Pergamon Press, New York, 1982, 215–225.
6 K. Olie, P.L. Vermeulen and O. Hutzinger, *Chemosphere*, 6 (1977) 455–459.
7 S. Sinkkonen and J. Koistinen, *Chemosphere*, 21 (1990) 1161–1171.
8 S. Sinkkonen, E. Kolehmainen and J. Koistinen, *Int. J. Environ. Anal. Chem.*, 47 (1992) 7–20.

9 S. Sinkkonen, E. Kolehmainen, K. Laihia and J. Koistinen, *Int. J. Environ. Anal. Chem.* in press.
10 S. Sinkkonen, E. Kolehmainen, K. Laihia, J. Koistinen and T. Rantio, *Environ. Sci. Technol.*, in press.
11 H.E. Buckholtz, *U.S. Pat.*, 3 989 715 (1976).
12 A. Veijanen, E. Kolehmainen, R. Kauppinen, M. Lahtiperä and J. Paasivirta, *Water Sci. Technol.*, 25 (1992) 165–170.
13 R. Laatikainen, *J. Magn. Reson.*, 27 (1977) 169–180.
14 J. Tarhanen, J. Koistinen, J. Paasivirta, P.J. Vuorinen, J. Koivusaari, I. Nuuja, N. Kannan and R. Tatsukawa, *Chemosphere*, 18 (1989) 1067–1077.