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Review

Capillary gas chromatography for the determination of halogenated micro-contaminants

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Abstract

Capillary gas chromatography (GC) is a very useful technique for the determination of complex mixtures of halogenated contaminants. Initially, this technique has shown its merits for the determination of polychlorinated biphenyls and organochlorine pesticides. In addition, it has also broken new grounds towards the identification and quantification of relatively unknown halogenated compounds, often complex mixtures, such as toxaphene, polychlorinated naphthalenes and paraffins and brominated flame retardants. Capillary GC is, however, not the final solution for the determination of all these mixtures. For some of them, with a relatively simple constitution or with only a few major components, such as chlordanes and brominated diphenylethers, a reliable congener-specific analysis may be carried out by single-column capillary GC. For others more advanced techniques will be required. Multi-dimensional (MD) GC techniques, such as heart-cut MDGC or comprehensive MDGC, are still under development or have only been applied for non-routine analyses. Given the importance of some of these complex mixtures, such as several brominated flame retardants, which are still produced and used daily and world-wide, it may be expected that next to the use of GC–MS, these more advanced GC techniques will be used more frequently in the near future. The current state-of-the-art of capillary GC with regard to the different compounds classes indicated below is described. Also, attention is given to the sample preparation. The following groups of contaminants are being discussed: polychlorinated dibenzo-*p*-dioxins and dibenzofurans, chlorinated bornanes (toxaphene), chlordane, polychlorinated terphenyls, polychlorinated diphenylethers, polychlorinated naphthalenes, polychlorinated alkanes, polybrominated biphenyls and polybrominated diphenylethers.

Keywords: Reviews; Sample preparation; Polychlorinated dibenzodioxins; Polychlorinated dibenzofurans; Toxaphene; Chlordane; Polychlorinated terphenyls; Polychlorinated diphenylethers; Polychlorinated naphthalenes; Chlorinated paraffins; Polybrominated biphenyls; Polybrominated diphenylethers

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1. Introduction

Polychlorinated biphenyls (PCBs) and organochlorine pesticides such as 1,1,1-trichloro-2,2-bis(*p*-chloro-phenyl)ethane (DDT) have been found in the environment since the 1960s [1]. After their discovery much attention has been paid to the development of analytical methods for these micro-contaminants. Gas chromatography (GC) has always been the method of choice for the determination of these compounds. The main reasons for this choice are the volatility of the PCBs and pesticides and the availability of electron-capture detection (ECD) which is very sensitive for halogens. Initially, the use of packed GC columns offered only a very limited resolution. Consequently, PCBs could only be determined as total-PCB based on a comparison of an environmental sample with a technical PCB mixture which resulted in considerable errors [2]. The introduction of (fused silica) capillary columns was a real breakthrough in this field and enabled a congener-specific determination of PCBs [3]. This development provoked the commercial production of individual chlorobiphenyls as analytical standards. In addition, the availability of the capillary column paved the way to the analysis of other complex mixtures of halogenated micro-contaminants. A higher sensitivity, partly caused by the use of capillary GC, and more focused studies resulted in the discovery in the environment of several other halogenated contaminants, often complex mixtures of industrial compounds, such as polychlorinated naphthalenes (PCNs), chlorinated alkanes (PCAs), polybrominated biphenyls (PBBs) and diphenylethers (PBDEs) and others. In Table 1 an overview is presented of the most important complex mixtures of halogenated micro-contaminants together with their degree of complexity.

The use of capillary GC for the determination of these contaminants will be discussed here. PCBs will not be included in this discussion because attention is given to them elsewhere in this issue [4]. The same is true for organochlorine pesticides, with the exception of toxaphene and chlordane [5].

Table 1
Complex mixtures of halogenated micro-contaminants

Name	Abbreviation	No. of congeners[a]
Polychlorinated biphenyls	PCBs	209
Polychlorinated dibenzodioxins	PCDDs	135
Polychlorinated dibenzofurans	PCDFs	75
Chlorinated bornanes	CHBs, PCCs[b]	32 768
Chlordanes	–	ca. 150
Polychlorinated terphenyls	PCTs	8149
Polychlorinated diphenylethers	PCDEs	209
Polychlorinated naphthalenes	PCNs	75
Polychlorinated alkanes	PCAs	Unknown
Polybrominated biphenyls	PBBs	209
Polybrominated diphenylethers	PBDEs	209

[a] Possible enantiomers are not included.
[b] None of the abbreviations chlorobornanes, polychlorinated camphenes, cover the complete mixture.

The goal of this overview is to show the application of capillary GC for the determination of various halogenated micro-contaminants, highlighting the different requirements of the different types of contaminants, particularly due to the degree of complexity. Prior to the discussion of the various types of contaminants, sample preparation techniques are discussed. The differences in sample preparation for the different types of contaminants are relatively small. The following sections focus on nine different groups of halogenated micro-contaminants and discuss mainly the use of capillary GC in general, possibilities of congener-specific analysis, types of columns used, the need for multi-dimensional GC techniques and available detection techniques and their limitations. Finally, several less known groups of halogenated micro-contaminants are discussed in a miscellaneous section.

2. Sample preparation

Although for some contaminants such as polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) more complicated sample preparation techniques are required, the techniques used for most types of halogenated micro-contaminants have many similarities. However, the sample preparation is dependent of the nature of the matrix sampled. In general analysis of halogenated contaminants in water does not occur very often because, due the hydrophobic character of these contaminants, the concentrations of the contaminants in water are always much lower than those in sediments or biota. If water samples are being analysed, an extraction with a non-polar solvent is recommended immediately after sampling [6]. Extracts of water samples may be stored for longer periods in pre-cleaned glass containers sealed with PTFE-faced caps [6].

Sediment and biota samples can be kept in glass jars in the freezer (−20°C) [6]. The jars for the sediment samples should be wide-mouthed and they should not be overfilled to avoid breakage of the glass due to the expansion of the water during freezing [6]. Plastic materials should be avoided during storage, extraction and clean-up because they contain plasticisers such as phthalates which can heavily interfere with the target compounds in the chromatograms, particularly when using GC–ECD. Fat decomposition may take place during storage of biota samples in the freezer, but the effects on the final analytical result are negligible [7].

Extraction and clean-up are the two stages in the entire method for halogenated contaminants prior to GC analysis. Extracts of water analysis may be injected directly after drying and concentration. Amberlite XAD-2 resin columns were used by Tanabe et al. [8] and Schulz-Bull et al. [9] for the extraction of PCBs from sea water. Other solid sorbents that have been used are Tenax [10] and polyurethane foam [11]. Because the extremely low concentrations in sea water background contamination is the most serious problem in this type of analysis [6].

Overviews of extraction methods for sediments and biota have been published [12,13]. Soxhlet extraction is the most frequently used technique, but saponification, ultrasonic extraction, liquid–liquid extraction, supercritical extraction (SFE), accelerated solvent extraction (ASE) and microwave extraction can be used as well. Saponification may affect some of the compounds discussed here. It has been shown that it can dechlorinate higher chlorinated PCBs [14]. Dichloromethane is often used in Soxhlet extraction, alone or in combination with non-polar solvents such as pentane. Obviously, dichloromethane should completely be removed before analysis by GC–ECD. This can easily be carried out by rotary evaporation using a higher boiling solvent such as isooctane as a keeper [13]. The use of SFE is promising for sediment analysis [6]. However, also for biota samples, SFE techniques are being developed and seem to become more reliable [15]. The great advantage of this technique is the combination of extraction and clean-up which means that expensive time is gained.

After the use of more conventional extraction methods such as Soxhlet extraction a clean-up of the samples is necessary because those extraction methods are not sufficiently selective and the presence of lipids in the extracts can cause a deterioration of the GC column and a contamination of the injector and detector [6]. Alumina columns are often used to remove the lipids from the biota extracts or to further clean the sediment extracts. Other columns are Florisil and silica columns, but these are often used in combination with alumina columns to create a

pre-separation of different compound classes such as PCBs and organochlorine pesticides. Sulphuric acid treatment is an alternative but some compounds may not be resistant to such a treatment. A non-aggressive alternative is gel permeation chromatography (GPC) which is based on molecular size. By using GPC sulphur can be removed from sediment extracts which is essential to obtain a good GC–ECD chromatogram [6]. In case GPC is not used, alternative methods such as stirring the extracts with copper powder [16] or with tetrabutylammoniumsulphite can be used [17]. Because of the possible presence of many different mixtures of contaminants in environmental samples it may be recommended to perform a pre-fractionation prior to the final GC analysis. High-performance liquid chromatography (HPLC) is a useful technique for creating such pre-separations. It is often used for the pre-fractionation of PCDDs and PCDFs, for which porous graphitic carbon columns [18] and 2-(1-pyrenyl) ethyldimethylsilylated silica (PYE) columns are often used [19]. However, for some compound classes such chlordanes and chlorinated bornanes pre-fractionation has not been successful until now. Because mass fragments of these compound groups are in many cases identical, mass spectrometry (MS) is not always able to distinguish these compounds and an identification on the basis of retention times is the only possibility left.

3. Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)

A complete picture of the state-of-the-art of the PCDD and PCDF analysis was recently given by Liem and Theelen [20]. PCDDs and PCDFs are not produced by industry but can be formed during several processes during which halogenated compounds are exposed to higher temperatures. An example is the formation of PCDDs and PCDFs in municipal waste incinerators. PCDDs and PCDFs belong to the most toxic compounds for humans and animals. Therefore, much research effort has been devoted to this group of contaminants. Although there are theoretically 75 PCDFs and 135 PCDDs, 17 of them (seven PCDDs and ten PCDFs) are regularly analysed and found in food, environmental and human samples. Twelve of them (five PCDDs and seven PCDFs) are considered to be more toxic than the others. Capillary GC is used by most laboratories to determine PCDDs and PCDFs. Table 2 shows the separation characteristics of nine capillary GC columns for the 12 more toxic PCDDs and PCDFs [20]. The five less toxic PCDDs and PCDFs not included are 1,2,3,4,6,7,8-heptaCDD, octaCDD, 1,2,3,4,6,7,8-heptaCDF, 1,2,3,4,7,8,9,-heptaCDF and octaCDF. For most of the compounds mentioned in Table 1, including PCDDs and PCDFs, the column dimensions, temperature programmes and injection techniques used are rather similar. The column length is generally around 50 m and the internal diameter around 0.15–0.25 mm. A film thickness of 0.1–0.2 μm is generally used. Longer columns would result in longer analysis times and broadening of peaks and the use of more narrow columns is restricted due to maximum inlet pressures and leakages at the column connections due to higher pressures required. A thicker film thickness may provide a better resolution in the beginning of the chromatogram, but also causes longer analysis times. Temperature programmes are normally applied with temperatures varying between 100 and 280°C, depending on the stationary phase used. Both splitless injection and on-column injection techniques can be used. When using splitless injection attention should be given to possible discrimination effects. On-column injection techniques can be used to avoid this problem, but the installation of the column to the injector, although nowadays easier than before, is more critical and the technique is sensitive for the accumulation of non-volatile compounds at the column-inlet [20].

Table 2 shows that a complete separation of the 12 PCDDs and PCDFs studied from each other and from other PCDDs and PCDFs cannot be obtained [20]. Apolar columns enable a separation between homologous groups and between the 2,3,7,8-congeners. However, they cannot provide a separation between the 2,3,7,8-congeners and the less toxic congeners. The resolution improves on more polar stationary phases such as the CP Sil 88 and SP 2331, but the separation of 2,3,7,8-TCDD, 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF remains incomplete. TCDF is most difficult to resolve and requires a medium-polar column such as DB 17 (Table 2). Ballschmiter et al. [23] suggested coupling of a Smectic column and a 100% cyanopropyl column to

Table 2
Separation of toxic congeners of PCDDs and PCDFs on capillary gas chromatographic columns of different polarity [20–22][a]

Congener	DB-1	DB-5	DB-17	DB-210	DB-225	CPS-1	SP-2331	SIL 88	Smectic
PCDDs									
2,3,7,8	QNT	CE2	CE1	CE1	QNT	CE4	BS	QNT	BS
1,2,3,7,8	QNT	BS	QNT	CE1	CE1	BS	BS	BS	BS
1,2,3,4,7,8	QTT	QTT	BS	NBS	NBS	BS	NBS	NBS	QTT
1,2,3,6,7,8	QTT	QTT	BS	NBS	NBS	BS	NBS	NBS	QTT
1,2,3,7,8,9	CE1	CE1	BS	BS	BS	BS	BS	BS	BS
PCDFs									
2,3,7,8	CE5	CE5	BS	QNT	CE1	CE1	QNT	QNT	CE1
1,2,3,7,8	QT	QNT	CE1	CE2	CE1	CE1	CE1	CE1	BS
2,3,4,7,8	CE1	CE3	BS	BS	BS	QNT	BS	BS	CE1
1,2,3,4,7,8	CE1	CE1	QNT	CE1	QNT	CE1	CE1	CE1	NBS
1,2,3,6,7,8	NBS	QNT	CE1	CE1	CE2	NBS	QTT	QTT	NBS
1,2,3,7,8,9	NBS	NBS	BS	CE1	BS	BS	BS	BS	BS
2,3,4,6,7,8	CE1	QNT	QNT	BS	CE1	BS	BS	BS	CE1

[a] Abbreviations: BS=no overlap with others; NBS=almost no overlap; QTT=quantifiable, but may overlap with congener with same toxicity; QNT=quantifiable, but may overlap with non-toxic congener; CE*n*=co-elution (100% overlap) with *n* non-toxic congeners. Stationary phases: DB-1: 100% methylpolysiloxane, DB-5: 5% phenyl–95% methylpolysiloxane, DB-17: 50% phenyl–50% polysiloxane, DB-210: 50% trifluorpropyl–50% methylpolysiloxane DB-225: 25% cyanopropyl–25% phenyl–50% dimethylpolysiloxane, CPS-1: 100% dimethylpolysiloxane, SP-2331 and SIL-88: 100% cyanopropylpolysiloxane, Smectic: liquid crystalline polysiloxane with a biphenylcarboxylate ester side-chain.

obtain a better separation of the TCDF. In addition they obtained a successful separation of all 2,3,7,8 dioxin and furan congeners on a DB-Dioxin column (44% methyl–28% phenyl–20% cyanopropylpolysiloxane). Apolar columns can be used for the determination of PCDDs and PCDFs in human samples, as those samples only contain 2,3,7,8-substituted congeners [20]. Apolar columns have generally longer lifetimes and do not cause decomposition of highly chlorinated PCDDs and PCDFs as can occur on polar phases [24,25]. Other samples such as environmental samples, fly ash, air and aquatic biota samples require polar columns because they may contain non-laterally substituted congeners [20]. An example of the difference in complexity between abiotic and human samples is shown in Fig. 1. An alternative stationary phase, Rtx-2330 (cross-bound) was used by de Jong et al. [26] and de Jong and Liem [21]. This polar column can withstand temperatures up to 275°C, while decomposition of higher chlorinated congeners is not observed. In addition, analysis times are shorter than of other polar columns. Until now more advanced GC systems such as multidimensional (MD) GC or comprehensive MDGC [27–32] have hardly been applied for PCDD/PCDF analysis. A combination of such advanced GC systems with mass spectrometric detection is, however, expected to solve the current separation problems in PCDD/PCDF analysis.

For the quantification of PCDDs and PCDFs high-resolution (HR) MS is currently the only technique able to provide the required sensitivity and selectivity [20]. Quantification is generally performed by using stable isotope-labelled $^{13}C_{12}$ analogues of the PCDDs and PCDFs to be determined as internal standards (isotope dilution method). Electron impact (EI) is the most widely used ionisation method. Selected ion monitoring (SIM) provides the highest sensitivity. EI mass spectral properties have been described by Buser [33]. Negative chemical ionisation (NCI) may be used as an alternative technique for improved molecular mass determination and/or increased sensitivity. Methane is most commonly used as reagent gas. Characteristics of the NCI mass spectra of PCDDs and PCDFs have been given by Oehme and Kirschner [34], Buser et al. [35], and Rappe et al. [36]. NCI is less sensitive for the determination of 2,3,7,8-TCDD as for the other TCDDs [35] and more sensitive for PCDFs than for PCDDs [20]. The detection limits for GC–EI-HRMS

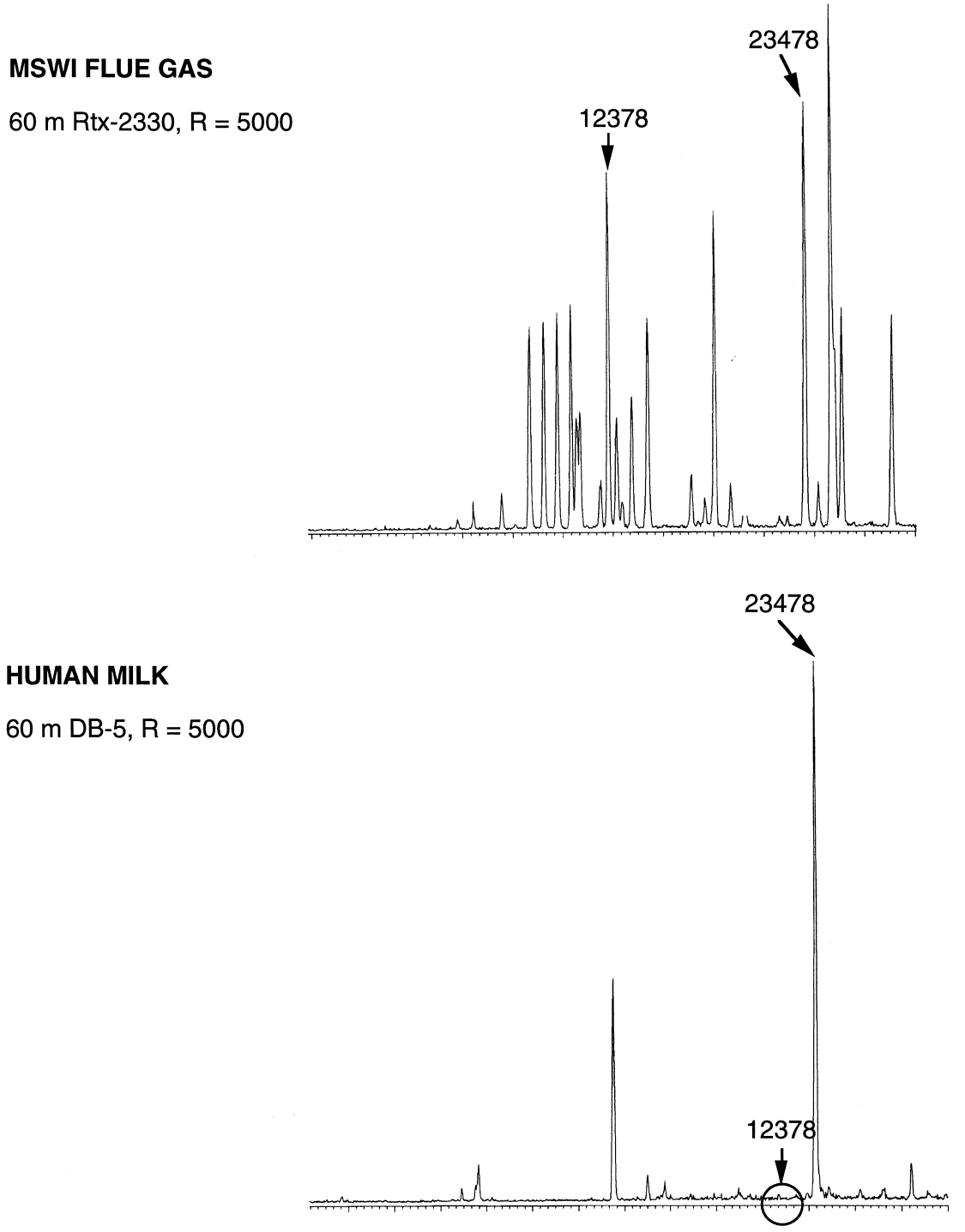

Fig. 1. GC–HRMS analysis of pentachlorodibenzofurans in a sample extract of flue gas from a municipal solid waste incinerator, and in a human milk extract. Traces are normalised molecular ions. GC–MS analyses have been accomplished on Rtx-2330 (flue gas) and DB-5 (human milk) columns at a mass resolution of 5000 [20].

are between 1 and 10 pg for the tetra- to hepta-chlorinated PCDDs and PCDFs and between 10 and 50 pg for the octa- to deca-PCDDs and PCDFs. The newest HRMS systems with a resolution of 5000–10 000 may be capable of reducing these detection limits down to 10–200 fg. Low-resolution (LR) NCI-MS usually shows detection limits in the order of 10–100 fg, but considerably higher for 2,3,7,8-TCDD [20]. ECD would have detection limits of 0.1–2 pg, but due to the lack of selectivity, ECD is not considered as a useful detection method for the determination of PCDDs and PCDFs.

4. Chlorinated bornanes (toxaphene)

Toxaphene is a very complex mixture primarily consisting of chlorobornanes, together with chlorobornenes, chlorinated bornadienes, chlorinated camphenes and chlorinated dihydrocamphenes [37]. Toxaphene has been used as an insecticide in cotton growing in the USA since 1945, and for the same purpose in many other countries [38]. Due to aerial transportation toxaphene has been found in relatively high concentrations in northern areas such as the Great Lakes [39]. Toxaphene was found in North Sea fish around 1990 [40]. Before that time toxaphene was incidentally reported as an interference in PCB analysis [41]. However, due to the aliphatic character of the toxaphene compounds, the ECD response is much lower than for PCBs. For that reason the toxaphene concentrations have been overlooked or underestimated. There are theoretically 32 768 congeners (Table 1) of which a large number is chiral [42]. However, a considerable number of these are not present in the technical mixture. Nevertheless the technical mixture is very complex and until now the exact number of congeners is unknown. Jansson and Wideqvist [43] reported the separation of 670 individual components in technical toxaphene whereas Zhu et al. [44] separated more than 300 penta- to decachlorobornanes and bornene/camphene isomers after pre-separation into five fractions by HPLC on silica gel followed by GC with NCI-MS while they found 76 partially resolved peaks with possible co-elution in a total ion chromatogram (150–500 amu) when the mixture was not pre-separated.

Initially, toxaphene concentrations have been measured as total-toxaphene using a technical toxaphene mixture as a standard [45]. However, due to considerable differences between the technical toxaphene mixtures [46] and the toxaphene patterns in sediments and biota, which is due to a relatively high sensitivity of toxaphene compounds to biotic and abiotic transformation processes, considerable errors are being made when carrying out such a total-toxaphene determination. In addition, differences between different technical toxaphene mixtures contribute to that error [45]. This rather unsatisfactory situation has initiated a trend towards a congener-specific chlorobornane analysis as soon as individual chlorobornane standards were introduced by Parlar et al. [47].

The number of congeners which is finally found in environmental samples is relatively small. Nevertheless it is higher than the number of PCB congeners in environmental samples. Depending on the level in the food chain, the number of toxaphene congeners present in organisms may be estimated at several hundreds. This means that single-column capillary column GC is insufficient for the separation of all these congeners. De Boer et al. found 246 compound peaks in technical toxaphene using two-dimensional heart-cut GC using ECD while only 107 peaks were found using a single column GC–ECD set-up [48]. The number of chlorobornanes regularly analysed is slowly increasing. Recently, Parlar [49] reported that the following group of six congeners would be the most persistent ones: B[12012]-(202) (Parlar No. 26), B[12012]-(212) (Parlar No. 50), B[12012]-(112) (Parlar No. 40), B[21020]-(122) (Parlar No. 41), B[20030]-(122) (Parlar No. 44) and B[30030]-(122) (Parlar No. 62). Until now most analyses have focused on B[12012]-(202), B[12012]-(212) and B[30030]-(122) (nomenclature of Wester et al. [37]), but it may be assumed that the other three chlorobornanes mentioned above will be added soon to various toxaphene research and monitoring programmes.

4.1. Gas chromatographic separation

In most cases the toxaphene compounds are separated on a relative non-polar stationary phase [DB-5, Sil-8, Ultra-2 (5% phenyl–95% di-

methylpolysiloxane)] with lengths of 30 to 60 m and inner diameters of 0.15 to 0.32 mm. However, more polar columns are sometimes used to validate the results, e.g., DB-1701 (14% cyanopropyl phenyl–86% dimethylpolysiloxane) [50], or DB-1301 (6% cyanopropylphenyl–94% dimethylpolysiloxane) [51]. Krock et al. obtained a relatively good separation using a very non-polar Sil-2 stationary phase (comparable to squalene) [52]. On the CP-Sil 2 column the same elution order as on the slightly more polar DB-5 column was found [53]. The authors used this phase successfully up to a temperature of 290°C, although the supplier advised a maximum temperature of 200°C [54]. An improved separation is obtained by heart-cut MDGC [29]. De Boer et al. [48] used heart-cut MDGC and tested several column combinations. A DB-5 type column was combined with a 15% dimethylsilicone–85% polyethylene glycol (DX-4), a polyethylene glycol–terephthalic acid ester (FFAP) and a 10% cyanopropyl–90% biscyanopropyl–polysiloxane (Rtx-2330) column. A large number of peaks were found in the second dimension separation indicating that the resolution offered by one single column is insufficient and can easily lead to false-positive results, especially when the non-selective ECD is used for quantification. There were no large differences between the column combinations but the DB-5–Rtx-2330 combination was preferred because of a slightly better separation and its low bleed. However, Baycan-Keller and Oehme [55] found degradation of several chlorobornanes on the Rtx-2330 phase. Re-evaluation of the multidimensional heart-cut data of de Boer et al. [48] showed that the standard of B[12012]-(212) had the same profile (a broad heap eluting together with the actual peak) as described by Baycan-Keller and Oehme [55], and indeed this could have been caused by decomposition on the stationary phase. For B[12012]-(202), B[30012]-(111) and B[30030]-(122) normal peak shapes were obtained. Karlsson and Oehme also mention that there is a possibility that the low response of B[30030]-(122) is due to losses on the polar Rtx-2330 phase [50].

Alder et al. found that B[12012]-(202) and B[30030]-(122) were decomposed to a great extent on the highly polar DX-4 phase [56]. In the study of de Boer et al. [48] no degradation effects were observed on this phase, also not after re-evaluation of the data and recent new experiments with this stationary phase. This can, at least partly, be due to the fact that a shorter column was used (15 m instead of 30 m) which limits the exposure time of the components to a high temperature, which was only 220°C.

Two inter laboratory studies organised by Health Canada showed relative standard deviations (RSDs) of 50–100% for total toxaphene and individual chlorobornanes [57,58]. Although these high RSD values could partly be explained by losses during the clean-up of biological samples, errors in separation and quantification seemed also to contribute significantly to the final RSD value.

Because of the high complexity of toxaphene, an advanced technique as comprehensive MDGC is expected to be a valuable technique for a complete separation of toxaphene compounds [27–29]. Until now such a technique has not been applied for this type of analysis.

4.2. Injection

Alder et al. state that the injector temperature should not exceed 240°C because severe decomposition of compounds may take place [56]. Bartha et al. [54] recommend an injector temperature below 250°C. Alawi et al. [59] showed that the response factors after splitless injection are lower than after on-column injection. Vetter et al. [60] reported the use of pressure pulse injection (PPI) at 225°C, which resulted in up to four-times higher response factors compared with the widely used conventional splitless injection. Especially for compounds with a low vapour pressure and long elution times {e.g., B[30030]-(122)} this increase was significant [54]. Using this technique, the residence time of the compounds in the detector is short, and, therefore, the chance of degradation is smaller.

4.3. Detection

EI-LRMS is a selective method for residual toxaphene analysis [61]. NCI-MS shows a completely different peak profile, which is probably caused by a higher variation in response factors for individual congeners [62]. Andrews et al. [63] used HRMS-SIM at m/z 158.8768 and 160.9739 in the EI mode

to obtain a single bornane result without interference from 69 other organochlorine compounds used in a screening study of fish extracts. However, this approach is less sensitive than NCI-MS and it does not distinguish between homologue groups. NCI offers both selectivity and sensitivity for bornane congeners [64], but does not offer the possibility of structure elucidation. NCI is most widely used for MS detection of toxaphene. NCI-MS is more sensitive than ECD for toxaphene, but is considerably less sensitive for the lower chlorinated congeners. EI-MS is more sensitive for lower chlorinated congeners [65]. Often the M^- and $(M-Cl)^-$ ions are monitored [47,57]. During GC–MS analysis of toxaphene in the SIM mode (NCI) interference from oxygen adducts of PCBs have been observed [43,45,66]. Krock et al. [52] demonstrated that the oxygen adducts were formed in the GC–MS system due to air leakage. Fragments of higher chlorinated bornane congeners can also interfere with toxaphene determination. Good linearity over four-orders of magnitude for five chlorinated bornane congeners was obtained using NCI-MS [59]. It was tentatively found that a 2,2,5,5-substitution of chlorobornane congeners ([30030]) had a negative effect on the NCI-MS response [67,68].

Buser and Müller used tandem EI-MS–MS to identify B[12012]-(202) and B[12012]-(212) in penguin and harbour seal samples [69]. Chan et al. [70] used ion trap MS–MS and reported a superior selectivity compared to NCI-MS or ECD, which enabled a very good separation of toxaphene congeners from interferences of other organochlorines. When using the ECD, removal of interfering compounds is a prerequisite. Moreover, ECD is less sensitive. Alder and Vieth [62] determined the toxaphene concentration in a standard reference sample (SRM 1588) on the basis of three indicator congeners and using GC–ECD. They found a total toxaphene concentration of about 1600 μg/kg. In the same sample Fowler et al. [71] had determined a value of 5410 μg/kg using GC–NCI-MS. Alder and Vieth [62] reanalysed the sample then using NCI-MS and found a value of 5210 μg/kg, which is close to the value reported by Fowler et al. They concluded that this large difference is caused by the large difference in response factors between congeners with NCI which gives a positive bias to the results when compared with ECD which has a smaller difference between response factors. Differences between NCI-MS and ECD determinations of toxaphene were also reported by Rantio et al. [72]. However, Xu et al. [73] found that GC–ECD gave identical results as GC–NCI-MS for the quantification of individual chlorobornanes in fish samples. The NCI-MS results may possibly be dependent of the type of MS used. Further study is required to solve this problem.

4.4. Enantiomers

Most of the compounds in toxaphene are chiral. Since bioaccumulation and metabolism in biota are often different for enantiomers, a change in the enantiomer ratio can be expected during disposition in the food chain. Furthermore, enantiomers often have different toxic properties. The determination of enantiomer ratios of chlorinated bornane congeners in biota gives an indication whether a specific biological mechanism changes the ratio in the course of disposition in the body. If a significant deviation is found, this suggests that one enantiomer is subject to a specific metabolic transformation [74]. The comparison of the enantiomer ratios of different congeners in combination with their molecular structures can help understand the metabolism of these compounds.

For the determination of enantiomer ratios (ERs) the separation should be enantioselective as well as isomer-specific. Unfortunately, this doubles the number of peaks that have to be separated. Therefore, even with a reduced number of compounds in biota compared with technical mixtures, co-elutions either with other toxaphene compounds or sample constituents will easily occur when using single-column GC. This makes quantification quite challenging [75], particularly when ECD is used, as proposed by Alder et al. [56].

A *tert.*-butyldimethylsilylated β-cyclodextrin phase [75] has been shown to give a good enantiomer separation of toxaphene compounds [45,64,69,73,74,76–79]. However, the enantiomer separation of bornane congeners is still a rather empirical task and the selection of a convenient stationary phase is primarily determined by trial and error [78]. It has been shown that columns based on

heptakis(2,3,6-*O*-*tert*.-butyldimethylsilyl)-β-cyclodextrins (TBDM-CDs) are particularly suitable for the separation of polychlorinated bornane enantiomers [69,72,80,81]. Unfortunately, this stationary phase is not very well defined and batch-to-batch differences have been observed [82].

The obtainable enantiomer resolution is dependent on the column temperature. It was found that this phase can be used up to a temperature of 265°C in a programmed run, however, at lower temperatures the obtained resolution is much higher [78]. Baycan-Keller and Oehme [77] showed that a temperature ramp of 1°C resulted in much better separations compared to 10°C/min. This was confirmed by De Geus et al. [78]. Unfortunately, slow temperature programmes lead to very long run and a lower sensitivity.

5. Chlordane

Chlordane is a chlorinated cyclodiene which was introduced in the 1940s as an insecticide [83]. It was widely used in the USA in agricultural and household applications and in termite control in buildings [84]. During the period 1950–1970 the formulation consisted of 43–75% *cis*- and *trans*-chlordane and lesser amounts of heptachlor, nonachlor and chlordenes. Later a more concentrated formulation (HCS 3260) containing over 95% chlordane was used. Oxychlordane, a metabolite of chlordane, has also been detected in the technical mixture. Chlordane was banned by the US Environmental Protection Agency (EPA) and in most other countries around 1990 [85,86] because of its persistency, known toxicity and potential carcinogenicity [87]. Chlordane residues have been found in environmental samples from all over the world, although the use in other parts of the world seems to be limited compared to that in the USA. Dearth and Hites [87] resolved more than 120 components in technical chlordane, using capillary GC–NCI-MS. The most abundant congeners are *cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor, heptachlor, and, to a minor extent, α- and β-chlordene. *Cis*- and *trans*-chlordane, *trans*-nonachlor and the two metabolites β-heptachlorepoxide and oxychlordane are the most frequent occurring components in environmental samples [88]. Because the other chlordane components only occur in minor quantities, most studies on environmental chlordane contamination focus on these five compounds, sometimes together with *cis*-nonachlor and α- and β-chlordene [89,90]. Incidentally more chlordane compounds were identified such as U 82, MC-2, MC-5 and U-4 [87,91,92]. In humans and seals U 82 and MC 5 are the most abundant octachloro chlordane congeners. Because of the commercial availability of some chlordane compounds and the errors made in a total-chlordane determination (cf. Section 4), a total-chlordane determination is rarely carried out.

Traditional methods for PCB and organochlorine pesticide clean-up result in two fractions after elution over silica columns, one PCB fraction and one pesticide fraction in which most chlordanes are present. However, a part of the *trans*-nonachlor and, dependent of the type of silica column used, parts of *cis*- and *trans*-chlordane may be found among the PCBs in the first fraction as well [93]. Capillary column GC normally provides sufficient resolution for a separation of the chlordanes from each other and from the chlorinated pesticides. If a silica fractionation is not applied, separation problems may occur between PCBs and chlordanes. Suitable stationary phases are apolar or semi-polar phases such as HP 1 (100% methylpolysiloxane), DB 5, SE 54, CP Sil 8 (all 5% phenyl–95% dimethylpolysiloxane), DB 17 (50% phenyl–50% dimethylpolysiloxane) and CP Sil 19 (14% cyanopropyl–86% dimethylpolysiloxane). Karl et al. [90] used GC–ECD with SE-54 columns (50 m×0.32 mm) for the determination of *cis*- and *trans*-chlordane, oxychlordane and *trans*-nonachlor, and OV 1701 columns (50 m×0.32 mm) for confirmation. Further confirmation was carried out with GC–EI-MS with 60 m×0.25 mm DB 5 columns.

All chlordanes except *cis*- and *trans*-nonachlor are chiral compounds and exist in two enantiomeric forms [94]. First reports on the separation of chiral chlordane compounds were presented by König et al. [95] and Buser and Müller [96]. Oehme et al. [94] separated enantiomeric pairs of 10 chlordane compounds on a tandem glass capillary column consisting of a 30 m×0.25 mm 90% biscyanopropanol–10% Rtx 2330 (0.1 μm) column and a 18 m×0.3 mm 2.5% PS-086–0.25% dimethyl-*tert*.-

butylsilylated β-cyclodextrin (BSCD) (0.14 μm) column. Buser and Müller [96] also separated these enantiomers of chlordanes using different columns based on permethylated β-cyclodextrin [heptakis (2,3,6-tri-*O*-methyl)-β-cyclodextrin (PMCD)], perethylated α-cyclodextrin [hexakis(2,3,6-tri-*O*-ethyl)-α-cyclodextrin (PECD)] and *tert.*-butyldimethylsilyl-β-cyclodextrin (BSCD).

Chlordanes can be detected by ECD [83,88,97] and by MS [92]. MS techniques obviously offer a higher selectivity. Karl et al. [89] used GC–EI-MS and used the mass fragments *m/z* 373/375 for the quantification of *cis*- and *trans*-chlordane, *m/z* 408, 409 for the quantification of *trans*-nonachlor and *m/z* 115, 386 for the quantification of oxychlordane. Most relevant chlordane compounds contain five or more chlorine atoms which makes NCI-MS an attractive detection method [87]. Buser and Müller [96] used both NCI-MS and EI-MS for the detection of chlordane compounds. Most of the chlordane compounds showed extensive fragmentation under EI as well as under NCI. The extent of these fragmentations differed significantly between isomers. The relative response between isomers and the isomer profiles observed for a particular sample are therefore dependent of the ionisation technique used [95]. Typically, M^- (NCI) and $(M-Cl)^+$ ions (EI), and sometimes additional (e.g., retro-Diels–Alder) fragment ions were monitored for several compounds, e.g., photoheptachlor and the photo-*cis*-chlordanes yielded intense $(M-Cl)^+$ fragment ions in EI, but no M^- ions under the NCI conditions used. The photo compounds could be monitored with NCI using the $(M-2HCl)^-$ and $(M-3HCl)^-$ fragment ions ($C_{10}H_3Cl_5$, *m/z* 298), respectively, although these ions are less characteristic and may also be formed by other chlorinated hydrocarbons [96].

6. Polychlorinated terphenyls (PCTs)

Although PCTs have a relatively low volatility, GC is the preferred analytical method for the determination of PCTs. The retention times are evidently longer for PCTs than for PCBs. Often higher oven temperatures, up to 300°C, are necessary. Therefore, elution from columns with a lower maximum allowable oven temperature is not complete. PCTs belong to the most complex types of mixtures of halogenated micro-contaminants. The theoretical number of over 8000 congeners [41] is reduced in environmental samples to some extent, but the sensitivity to biotransformation or abiotic degradation is much lower than for example for toxaphene, which means that several hundreds to thousands of congeners may still be present in environmental samples. In the 1970s and 1980s many PCT determinations were carried out on packed GC columns, measuring the total area under all the peaks of the PCT pattern in an environmental sample and comparing that to a technical PCT mixture. This resulted in considerable errors, due to differences between the PCT patterns in the technical mixtures and the environmental samples and the different response factors of the PCTs [98]. Perchlorination was tried as an alternative technique, but this method included a considerable risk on false positive results [99–103]. In addition, information on PCT patterns, possibly containing information on the distribution in the environment and on the chlorine degree are lost and information on individual PCT congeners, of which some will be more toxic than others could not be obtained.

Capillary GC has been used more recently [98,104,105]. The stationary phases used for the determination of PCTs are generally non-polar and semi-polar. Care should be taken to avoid co-elution with other contaminants. Peak-overlap is possible between higher chlorinated PCBs and lower chlorinated PCTs (≤5 chlorine atoms) [98]. The resolution obtained by normal capillary columns (ca. 50 m×0.2 mm) is insufficient to offer a congener-specific PCT determination. Consequently, a semi-quantitative total-PCT determination is still the most frequently used method [98,104,105]. MDGC techniques [27–29] have not been applied to the analysis of PCT until now. It may be expected that heart-cut techniques would be able to provide a better resolution, which would enable at least the complete separation of some congeners. Comprehensive two-dimensional GC is expected to offer a final solution, but this technique is still under development [106].

Both ECD and MS have been used for the detection of PCTs. The determination of total PCT by MS is difficult [98]. Chemical transformations in the environment, biological availability, uptake

kinetics, metabolism and elimination from organisms will influence the PCT pattern in samples and make it rather different from the profile in the technical PCT mixtures. Combined with the lack of commercial availability of most individual PCT congeners, this makes accurate quantification of PCTs virtually impossible. Both EI and NCI techniques can be used for MS detection of PCTs. The use of EI results in a more fragmented spectrum, which may provide more structural information [105]. NCI provides a higher sensitivity [98]. Lower chlorinated congeners ($\leq$4 chlorine atoms) show a lower sensitivity with NCI. However, lower chlorinated PCTs are hardly present in Aroclor 5442, and even less so in Aroclor 5460. Caixach describes the need for HREI-MS for a reliable determination of PCTs [105]. Due to the interference of $[M-2Cl]^+$ fragments from higher chlorinated PCTs with $[M]^+$ fragments of lower chlorinated PCTs substantial errors can be made in the quantification of homologues in technical PCT mixtures. An MS resolution of 35 000 is recommended to avoid calculation errors due to interfering fragments [105]. Wester et al. [98] calculated total PCT concentrations using GC–NCI-MS with different technical PCT mixtures as a standard and different selected ions. Deviations up to 30% for biota samples and up to 80% for sediment samples were noted when the peak pattern of the technical PCT mixture used as a standard differed substantially from that of the environmental sample.

7. Polychlorinated diphenylethers (PCDEs)

Polychlorinated diphenylethers (PCDEs) – sometimes called chlorinated diphenyloxides – have a structure that resembles that of PCBs. The difference is an oxygen atom that connects the two phenyl rings, which is absent in the PCB structure. Their widespread occurrence in the environment is mainly due to their presence as impurities in chlorophenol preparations which are widely used as wood-preservations [107]. High concentrations of PCDEs have particularly been found in Finland, near local sources of pentachlorophenol [108,109]. Paasivirta et al. [110] and Kurz and Ballschmiter [111] also mentioned the formation of hexa- and hepta-CDEs in municipal waste incinerators.

The presence of PCDEs often interferes with the PCDD and PCDF analysis [111]. An example of a combined method for the determination of PCDDs, PCDFs and PCDEs is that used by Koistinen et al. [112]. The final PCDE determination was carried out with GC–LRMS. HRMS (resolution 10,000) was used for the verification of the PCDEs. The GC column used was a 25 m$\times$0.2 mm, 0.33 μm HP5 column. The carrier gas was helium. Temperatures: injector 250°C, transferline 260°C (HRMS) or 300°C (LRMS), oven 1 min 100°C, 20°C/min to 180°C, 5°C/min to 280°C or 290°C. A splitless injection of 1 μl was used. Fifty CDEs were determined. Internal standards, added before extraction, included one $^2H_5$-penta CDE. The same method was used by Koistinen et al. [113] for the determination of PCDEs in sediments. Birkholz et al. [114] used $^{13}C_{12}$-CDEs as internal standards. GC–HRMS (resolution 10 000) in the SIM mode was used for identification and quantification of the PCDEs.

Huestis and Sergeant [115] developed a method for the removal of PCDEs as interferences during the PCDD/PCDF analysis. This method was used by Niimi et al. [116] for the determination of PCDEs in biota. HRMS (resolution 10 000) was used for the identification and quantification of the PCDEs. The oven temperature programme was used as applied by Koistinen et al. [114]. An Rtx-5 column (60 m$\times$0.25 mm, 0.25 μm) was used, with helium as a carrier gas. Seventeen CDE congeners were determined. The detection limits reported are 0.4 ng/g.

Nevalainen and Koistinen [117] synthesised 54 CDEs. Their structures were confirmed by MS and proton magnetic resonance spectroscopy. Retention times on SE-54 and OV-1701 capillary GC columns were determined relative to ^{13}C-CB77. The retention times for PCDEs increased with the increasing number of vicinal chlorines within a series of isomers.

ECD is in theory also suitable for the detection of PCDEs. ECD is considered to be sufficiently sensitive for the analysis of PCDEs with three or more chlorine atoms. Detection limits are in the order of 1–10 ng/g wet mass [118]. The limited selectivity may, however, lead to ambiguous results [118]. Chlorobornanes, e.g., elute in the same retention time window as tetra- to hepta-CDEs on a DB-5 column [119].

8. Polychlorinated naphthalenes (PCNs)

PCNs have mainly been used as dielectric fluids, flame retardants and fungicides [120,121]. They are also by-products of human activities such as copper-rasting, degradation of polychlorinated alkenes and combustion processes [121]. They are found in environmental samples [121,122] and humans [123] and are particularly known for their toxicity [124]. Because of their planar structure there is a close resemblance in behaviour with PCDDs [122]. The technical mixtures are called Halowaxes.

Capillary GC is a suitable method for the analysis of PCNs. Other methods such as HPLC with UV detection and thin-layer chromatography [125,126] and dechlorination [127] or perchlorination techniques [128] have been used in the past as well, but all suffered from either a lack of sensitivity (HPLC and dechlorination) or a risk on false positive or false negative results (de- and perchlorination). The advantage of capillary GC is the resolution. Nowadays most of the 75 possible individual PCN congeners are available. Most of them can be separated on apolar or semi-polar capillary GC columns, although a separation of 1,2,3,5,6,7-hexa CN and 1,2,3,4,6,7-hexa CN has not been achieved until now [124,129]. Falandysz et al. [130,131] used an Rtx-5 column (60 m×0.32 mm, film thickness 0.25 μm) and identified 44 higher chlorinated CNs, but a considerable number of these were not separated. Imagawa and Yamashita [132] separated the two pairs 1,2,3,4,5,7- and 1,2,3,4,6,8-hexa CN and 1,2,4,5,6,8- and 1,2,4,5,7,8-hexa CN on α- and β-cyclodextrin columns. They also separated 1,2,3,4,5,7- and 1,2,4,5,6,7-hexa CN on a SB-Smectic column, but could not separate 1,2,3,5,6,8- and 1,2,4,5,7,8-hexa CN on that column. Some authors only used four reference compounds for quantification, assuming that molar response factors in GC–EI-MS increase with the increasing degree of chlorination [121,130,133,134]. Järnberg and co-workers [122,135] quantified the PCNs using EI-MS against the first eluting congener of a substitution level (except for a hexa CN), assuming the same response for all congeners from one substitution level. Although the number of CN congeners (75) is relatively low, it seems to be difficult to separate all PCNs on a single capillary column. The use of multi-dimensional GC techniques has not been reported for PCNs until now, but both heart-cut techniques [48,136] and comprehensive MDGC [27–29,106] may be able to offer a more complete separation of CN congeners.

One of the problems in capillary GC of PCNs is the separation of PCBs and PCNs. These two compound classes normally elute together on most stationary phases. Therefore, a pre-separation of these two groups is required. Several column chromatographic and HPLC techniques have been used for the pre-separation of PCBs and PCNs, such as activated carbon column chromatography [120,137] and HPLC with PYE [2-(1-pyrenyl)ethyl dimethyl silylated silica] columns [122,129,135]. The most promising results were obtained with the PYE columns.

PCNs can be detected by ECD and MS. MS techniques are preferred because of the better selectivity. In addition NCI is very sensitive for CN congeners with more than four chlorine atoms [120,138]. GC–EI-MS was used by Falandysz and Rappe [121].

9. Polychlorinated alkanes (PCAs)

PCAs, often called chlorinated paraffins (CPs) are mainly polychlorinated *n*-alkanes with chain lengths between 10 and 30 and a chlorination degree between 30 and 70% [139]. They are used as additives in plastics, paints and cutting oil additives and as flame retardants [140]. The world production of PCAs has shown a slow growth over the last decades from ca. 230 000 tons per year in 1977–1979 [141,142] to ca. 300 000 tons per year in 1997 [139]. PCA mixtures are the most complex ones of all halogenated contaminant mixtures. The total number of possible congeners is unknown, but by far exceeds 10 000. PCAs are classified according to chain length and chlorine percentage (Table 3). PCAs have been found in relatively high concentrations in environmental samples, up to 3 mg/kg wet mass in mussels from the UK [139]. PCA concentrations in sediments from the rivers Seine (France) and Mersey (UK) were 10 μg/kg on a dry mass basis (<63 mm fraction) [143]. In contrast with PCBs their con-

Table 3
Classification of CPs [139]

% Cl	Chain length		
	C_{10}–C_{13} (short)	C_{14}–C_{17} (medium)	C_{18}–C_{30} (long)
30–50 (low)	CP-SL	CP-ML	CP-LL
50–70 (high)	CP-SH	CP-MH	CP-LH

centrations in terrestrial animals are higher than in aquatic organisms.

The analysis of PCAs is difficult and until now only semi-quantitative analyses have been carried out. Single-capillary column GC is by far insufficient as regards resolution to separate the different congeners. PCA chromatograms normally show a big hump with less individual peaks than for example in PCB chromatograms produced by packed columns (Fig. 2). Stationary phases used in capillary GC determinations of PCAs are normally non-polar such as SE-54 [144,145], CP Sil 5 [146], DB 1 [147] and DB 5 [148]. Until now co-elution of PCAs with other halogenated compounds is only studied to a limited extent. Bergström and Jansson [147] used a pre-separation based on four serial-coupled GPC columns (PL-gel, 5 μm, 50 Å, 300 mm×7.5 mm, Polymer Labs.). Only comprehensive MDGC would possibly provide the required resolution for a separation of congeners [27–29,106]. If such a congener-specific PCA analysis would be possible at all, this would result in an enormous dataset. Data reduction or a strict selection of relevant congeners would be essential to avoid an extremely laborious data interpretation. In addition to capillary GC other methods have been used as well, such as thin-layer chromatography [141], HPLC [142] and GC–flame ionisation detection (FID) with packed columns after dechlorination. Obviously the sensitivity and precision of these methods is lower than of capillary GC. Sistovaris and Donges [149] determined PCAs with capillary GC–FID after dechlorination on 1% palladium chloride and 12 mg/g sodium hydroxide catalyst on Chromosorb P a in a 2 cm insert in the injector. The dechlorinated PCAs could be separated from other dechlorinated contaminants such as PCBs and DDT. Brominated compounds and *para*-PCTs were less efficiently dehalogenated. Possibly present dechlorinated compounds can interfere and cause

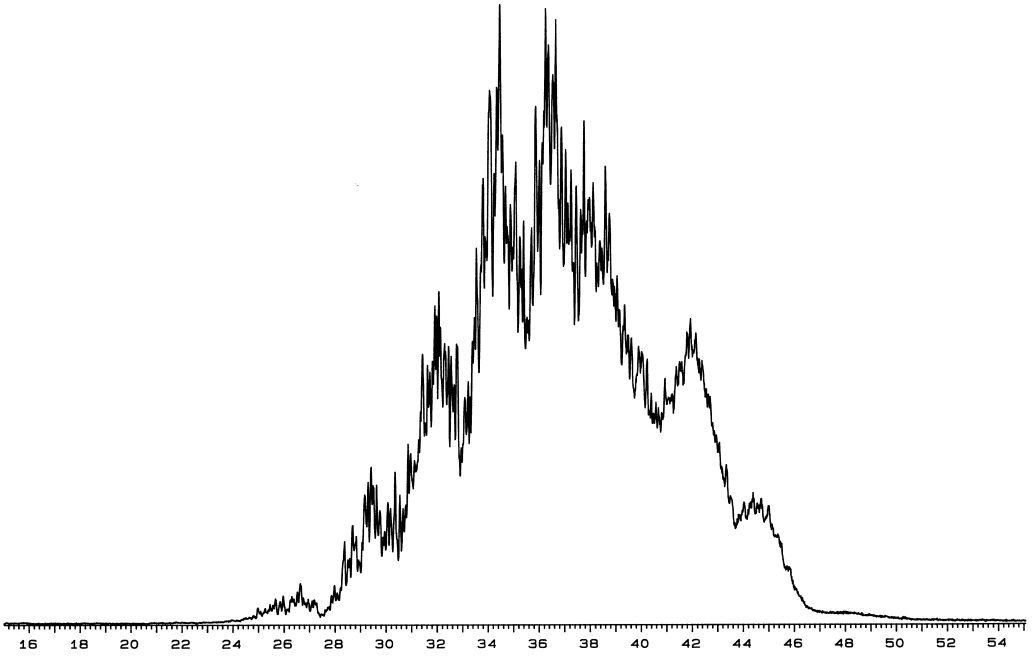

Fig. 2. Total-ion chromatogram (m/z 277, 279, 311, 313, 345, 347, 379, 381, 415, 417, 449, 451) of a chlorinated paraffin mixture (PCA-70) on a 50 m×0.20 mm CPSil 8 column (x-axis: t_R in min) (21).

false positive results. Dechlorination on a palladium catalyst in the GC, followed by packed column or capillary column GC was also used by Roberts et al. [150], who used a platinum catalyst in combination with hydrogen as well.

PCAs have been quantified by ECD [120] and NCI-MS [151,152]. Gjøs and Gustavsen [153] used NCI-MS with a direct sample introduction, without a GC separation. Zitko [140] used GC–EI-MS for the identification of C_{12} PCAs. Muir et al. [154] used GC–HRNCI-MS (resolution ca. 12 000) for the determination of C_{10}–C_{13} PCAs in Canadian and Arctic lake sediments. In a detailed report on the method used in that study, Tomy et al. [155] concluded that the advantages were a determination of individual formula groups, allowing a correction for differences in patterns between analyte and standard, and avoidance of interferences from other PCAs and other organochlorine compounds. Coelhan et al. [156] also used GC–NCI-MS, but were the first to use pure C_{10} PCAs with different degrees of chlorination as individual standards. Tomy [157] found a decrease in the abundance of both the adduct ion, $[M+Cl]^-$ and the $[M\text{-}Cl]^-$ ion with increasing source temperature, while the abundance of structurally non-characteristic ions, HCl_2 and $Cl_2^{-\cdot}$ increased. An increase of the PCA concentrations led to an increase of the $[M+Cl]^-$ concentrations, the most notable increase occurring for congeners containing chlorine atoms at terminal positions. For non-terminal chlorine compounds this ion was not significant. In EI spectra Tomy [157] found an abundant m/z 139 ion, $C_5H_9Cl_2^+$, for compounds containing vicinal chlorine atoms located at terminal positions. Tomy [158] organised a first international inter-laboratory study on the determination of PCAs. Seven laboratories participated using GC–ECD, GC–NCI-MS or GC–HRNCI-MS. The ranges of results were for two PCA solutions: 75–267 ng/μl (target 73.6), 163–477 ng/μl (target 117.8), and for two extracts: 32–80 ng/μl and 24–58 ng/μl.

10. Polybrominated biphenyls (PBBs)

PBBs are brominated flame retardants which are today still being produced and used (mainly decaBB) in many applications in modern life, such as in electronics and housing of television sets and computers, in clothing and car seats. Although the properties of PBBs are very similar to those of PCBs, surprisingly little action has been taken to ban these chemicals and substitute them by alternatives. PBBs are comparable to PCTs in terms of volatility. This means that for a gas chromatographic PBB analysis oven temperatures of up to 300°C are required and stationary phases used should be stable at those temperatures. Although PBBs have exactly the same number of congeners as PCBs (the only difference is the replacement of Cl atoms by Br atoms), there is hardly any information on congener-specific PBB analyses. Most PBB analyses have been carried out as semi-quantitative total-PBB analyses, both at packed columns and at capillary columns, with similar disadvantages as described for the PCTs. The limited availability of individual PBB standards may have been one of the reasons. Only recently results of congener-specific PBB analysis in aquatic organisms have been reported [159,160]. The detection of PBBs in sperm whales showed that these compounds can be considered as global pollutants [160].

The analysis of PBBs is more difficult than that of PCBs. PBBs adsorb to glass more tenaciously than PCBs [161]. Higher brominated PBBs may also be less stable than their PCB equivalents, which may cause decomposition during the analysis at higher temperatures. Most technical PBB mixtures consists of mainly hexabrominated biphenyls, 2,4,5,2′,4′,5′-hexa BB in particular, such as in the mixture BP-6 (Michigan Chemicals) [162]. The number of congeners found in environmental samples is even smaller. This means that single-capillary column GC normally offers sufficient resolution for a congener-specific PBB determination. The use of narrow bore (0.15–0.20 mm I.D.) capillary columns is recommended to obtain the required resolution [163]. De Boer et al. [160] reported concentrations in marine mammals of the congener Nos. 49 (2,4,2′,5-tetra), 52 (2,5,2′,5′-tetra), 101 (2,4,5,2′,5′-penta) and 153 (2,4,5,2′,4′,5′-hexa) with concentrations of the congener Nos. 15 (4,4′-di), 169 (3,4,5,3′,4′,5′-hexa and 209 (2,3,4,5,6,2′,3′,4′,5′,6′-deca) below detection limits. Higher chlorinated PCBs and PCTs may interfere with lower brominated PBBs during the GC analysis [98,163]. Therefore, MS is the most advan-

tageous technique for detection of PBBs [163]. Apart from the recent reports of de Boer et al. [160] and Hendriks et al. [159], there is only one earlier report on the use of PBB congeners (2- and 4-bromobiphenyl) as standards [164].

De Boer et al. used NCI as their ionisation technique [160]. This method is advantageous because it offers a high sensitivity for compounds with four or more bromine atoms. The sensitivity of NCI for these compounds is approximately 10-times higher than with the use of ECD [163]. EI is less sensitive than NCI and ECD.

11. Polybrominated diphenylethers (PBDEs)

PBDEs are also used as flame retardants. The production volumes are higher than those of PBBs [165]. PBDEs were detected in freshwater fish by Wolf and Rimkus [166]. Relatively high concentrations of the decabrominated diphenylether, up to 1.7 mg/kg on a dry mass basis ($\leq$63 μm fraction) were found in sediment of the Mersey estuary (UK) [143]. PBDEs were also found in sperm whales, in higher concentrations than the PBBs [160], which shows that also this group of compounds can be considered as a global pollutant. Nevertheless the production is ongoing. Applications are similar to those mentioned for PBBs. PBDEs are identical to PCDEs, apart from the chlorine atoms which have been replaced by bromine atoms. This means that as with PCBs 209 congeners can occur. The number of PBDE congeners found in environmental samples is, however, much less. A few congeners, 2,4,2′,4′-tetra BDE and 2,4,5,2′4′-penta BDE are the most frequently detected PBDE congeners although deca-BDE is the main compound produced nowadays. This means that single-capillary column GC offers sufficient resolution for a congener-specific PBDE determination. In traditional analytical methods for the determination of PCBs and organochlorine pesticides PBDEs normally elute in the second (pesticide) fraction after elution over silica gel columns [88]. The PBDEs can relatively easily be determined at the end of the chromatograms on Apolar or semipolar columns such as SE-30, SE 54, CP Sil 8, DB 5 or CP Sil 19 [87,163]. In case a fractionation between PCBs and pesticides is not applied, coelution of PCB Nos. 180 and 2,4,2′,4′-tetra BDE may occur. A multi-residue method was developed by Jansson et al. [137]. This method includes a multi-step separation enabling the determination of several polychlorinated an polybrominated pollutants in biological samples.

Both ECD and MS with EI or NCI may be used for the final analysis of PBDEs [167]. NCI-MS is a very sensitive method for many halogenated compounds. Using GC–MS, the type of reaction gas can influence the data. A study of PBDE residues in Guillemot eggs showed an increase in levels of 2,2′,4,4′-TeBDE, an unidentified PeBDE, and 2,2′,4,4′,5-PeBDE of, respectively, 10–35%, 25–80% and 0–20% after re-analysis using ammonia as reaction gas instead of methane [167].

Loganathan et al. [168] and Takasuga et al. [169] investigated the analysis of PBDE residues in environmental samples with GC–HRMS. The mass spectrometer was operated in the SIM mode. Additionally mass peak profile monitoring acquisition at high-resolution and low-resolution scanning were performed to identify the interferences. With this method the identification of PBDEs as interferences to heptachlorinated dibenzofurans in the analysis of routine environmental samples can be quantified [169].

In most studies the technical mixture Bromkal 70-5 DE is used as external standard. The percentage of PBDE congeners of Bromkal 70-5 DE is ca. 40% 2,2′,4,4′-TeBDE, ca. 40% 2,2′,4,4′,5-PeBDE and ca. 8% of an unknown PeBDE [163,167,170]. Synthesised pure standards of 2,2′,4,4′-TeBDE, 2,2′,4,4′,5-PeBDE, 2,2′,4,4′,5,5′-HxBDE [166,167] and several other BDEs are now available.

12. Miscellaneous

Together with the PCBs the mixtures of halogenated compounds discussed above are currently considered to be most important mixtures of halogenated contaminants in terms of occurrence and toxicity. There are numerous other halogenated compounds, either as mixtures or as single compounds, which have been produced for industrial purposes or as insecticides, or are released during industrial processes. Some of them occur in rela-

tively high concentrations in the environment, but have not been discussed here because they are single compounds. Examples are the brominated flame retardants tetrabromobisphenol-A (BBP-A) and hexabromocyclododecane (HBCD) [171,172], octachlorostyrene (OCS) [173], tris(4-chlorophenyl)-methanol, tris(4-chlorophenyl)methane [174,175], bis(4-chlorophenyl) sulphone [176], 3,3′-dichlorobenzidine [177], and bromocyclen [178]. Others occur less frequently, or in lower concentrations, or have only been found locally. Examples are halogenated/nitrated diphenylethers [179], different organofluorine compounds [180,181], and polychlorinated diphenylsulfides [182].

For most of these compounds capillary GC with ECD or MS is the most important analytical method. This confirms the essential role of capillary GC for the determination of halogenated contaminants. Given the ongoing production of several halogenated compounds such as CPs and brominated flame retardants and the detection of several ''new'' halogenated contaminants, it may be expected that at least for the coming decade and presumably for a longer period, halogenated contaminants may continue to draw the attention of policy makers and, consequently, of environmental laboratories. This will result in a more intensive use of capillary GC. Given the high degree of complexity of most mixtures, it is very likely that more advanced techniques such as MDGC will become more important and will be more commonly used in this type of analysis.

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