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Capillary gas chromatography combined with atomic emission detection for the analysis of polychlorinated biphenyls

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Abstract

Capillary gas chromatography with atomic emission detection (GC–AED) was evaluated for the analysis of polychlorinated biphenyls (PCBs). Since Cl-responses were almost independent of the PCB structure, individual PCBs were quantitated with an accuracy better than 10% utilizing a Cl-calibration plot based on a single randomly selected congener (universal calibration). In addition, within a 5–10% accuracy, GC–AED enabled estimation of total PCB residue levels and calculation of the percentage by weight of chlorine in contaminating PCB mixtures. Thus, although PCB detection limits were higher with GC–AED than with GC–ECD, the former technique was very attractive for PCB investigations and enabled significant simplification of PCB quantitation.

Keywords: Atomic emission detector; Polychlorinated biphenyls

1. Introduction

The unique physical and chemical properties of mixtures of polychlorinated biphenyls (PCBs), such as remarkable thermal stability, low flammability, high electrical resistivity, and suitable viscosity–temperature relationships, have since 1929 stimulated an extensive use of this type of mixtures for many industrial applications [1]. Although utilization of PCBs has been banned in many countries since the late 1970s, they are still major environmental pollutants owing to careless waste disposal and their high stability and bio-accumulation potential [2]. Several publications have demonstrated that the non-*ortho* substituted PCBs (IUPAC No. 77, 81, 126, and 169) belong to the most toxic group, the mono-*ortho* substituted PCBs 60, 105, 110, 114, 118, 156, 157, and 167 are moderately toxic, whereas the remaining 197 congeners are expected to be relatively non-toxic [3–5]. Because of this, environmental risk assessment for PCBs should not only take into account "total PCB" residue levels, but also include separation and quantitation of the individual congeners.

PCB analysis normally includes extensive sample clean up and preconcentration followed by high-resolution capillary gas chromatography (GC) either with electron-capture (ECD) or mass-selective detection (MSD) [6,7]. GC–ECD is the most popular technique owing to the relatively low costs, whereas the high selectivity of GC–MSD is superior in the presence of abundant electron-capturing coextractives. Although both techniques provide the high

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sensitivity required for PCB investigations, quantitative analysis is complicated by structural variations of ECD- and MSD-response factors [6,8,9]. Thus, pure references for all the PCB congeners of interest are required for accurate calibration. Even if all 209 congeners have been synthesized [10], this type of calibration is rather cumbersome in cases where several individual PCBs are of interest. Alternatively, quantitation may be carried out by capillary gas chromatography with flame ionization detection (GC–FID) [9]. Because the molar response of PCBs obtained by GC–FID are nearly constant, individual PCBs may be determined without all the actual congeners available as pure references (universal calibration). Unfortunately, without very sophisticated and time-consuming sample preparation, GC–FID is not suitable for PCB determinations in real samples owing to the lack of specificity and to the low sensitivity.

Besides GC–FID, universal calibration has been reported with capillary gas chromatography combined with atomic emission detection (GC–AED) [11–22]. Although GC–AED provides excellent elemental selectivity, also this technique suffers from a relatively low sensitivity. Therefore, GC–AED has only been briefly discussed for PCB analysis [23–25], and quantitative data have been presented only utilizing packed columns [26]. However, because several recent publications have demonstrated that detection limits of GC–AED may be improved substantially by minor technical modifications [25,27–30], the interest of this technique for PCB analysis is expected to increase considerably within the near future.

In the present work, therefore, the quantitative aspects of GC–AED were extensively evaluated for the analysis of PCBs in technical mixtures and in environmental samples. Special attention was focused on the quantitation by universal calibration of individual congeners, the estimation of total PCB, and on calculation of the percentage by weight of chlorine in PCB residues. These experiments were carried out with a commercial GC–AED system to report data of general interest. In addition, a laboratory-built instrument providing improved detection limits was utilized to investigate the sensitivity aspects of GC–AED for PCB analysis.

2. Experimental

2.1. Commercial GC–AED equipment

All samples in this work were analyzed with an HP 5921A atomic emission detector from Hewlett-Packard (Avondale, PA, USA). The element-specific chromatograms for carbon (2nd order of 247.9 nm), hydrogen (486.1 nm), and chlorine (479.5 nm) were recorded by an HP 35920A GC–AED ChemStation. Helium (99.9999%; AGA, Oslo, Norway) at 30 and 40 ml/min was utilized as make-up and window purge gases, respectively, and oxygen (99.999%; AGA) was selected as dopant gas for the plasma. The spectrometer was continuously purged with 2 l/min of nitrogen (99.996%; AGA). Both the cavity and the transfer line temperatures were kept at 290°C. The atomic emission detector was interfaced with an HP 5890 Series II Plus gas chromatograph. The GC system was equipped with an HP 7673A automatic sampler and a split/splitless capillary injection port with electronic pressure control. Sample volumes of 1 μl were injected in the splitless mode (2.0 min, 280°C). The GC system was supplied with a 30 m×0.25 mm I.D., 0.1 μm Rtx-35 (65% dimethyl–35% diphenyl polysiloxane) fused-silica capillary column from Restek (Bellefonte, PA, USA). The oven temperature was maintained at 80°C for 2 min following injection, and was then programmed at 2°C/min to 280°C. Helium (99.9999%; AGA) at 25 cm/s was used as carrier gas.

2.2. Laboratory-built GC–AED equipment

For comparison of sensitivity, one sample was analyzed also on a laboratory-built GC–AED system based on a 350 kHz on-column RF-plasma. This system, which has been described in detail elsewhere [28–30], utilized emission at 837.6 nm for chlorine-selective detection. Helium at 10 ml/min (99.9999%; Hydro, Oslo, Norway) was used as make-up gas, and oxygen (99.998%; AGA) was selected as plasma dopant. The detector, which was operated at 350°C, was interfaced with a Model 4200 gas chromatograph from Carlo Erba (Milan, Italy) equipped with a capillary split/splitless injection port

and a 25 m×0.32 mm I.D., 0.17 μm HP-5 (95% dimethyl–5% diphenyl polysiloxane) fused-silica capillary column from Hewlett-Packard. The GC conditions were identical as those used on the commercial GC–AED system (Section 2.1).

2.3. GC–ECD equipment

GC–ECD was performed with an HP 5890 Series II gas chromatograph equipped with an electron-capture detector from Hewlett-Packard. Nitrogen (99.99%; AGA) at 50 ml/min was utilized as make-up gas, and the detector temperature was 285°C. The GC system was equipped with an HP 7673 automatic sampler and a split/splitless capillary injection port. Sample volumes of 1 μl were injected in the splitless mode (1.25 min, 255°C). The GC system was supplied with a 60 m×0.25 mm I.D., 0.25 μm Rtx-35 (65% dimethyl–35% diphenyl polysiloxane) fused-silica capillary column from Restek. The oven temperature was maintained at 120°C for 2 min following injection, and was then programmed at 30°C/min to 180°C and at 3°C/min to 280°C. Hydrogen (99.9997%; AGA) at 30 cm/s was used as carrier gas.

2.4. Sample workup for sediment analysis

Following addition of internal standard (PCB 53), 15 g of dry sediment was extracted twice with 35 ml cyclohexane–acetone (20:15) for 10 min forced by a 475 W Virsonic ultrasonification probe (Virtis, New York, NY, USA). The extracts were combined and extracted twice with water (20 and 35 ml), 100 μl of iso-octane was added, and solvent was gently evaporated to give a final volume of 0.5 ml [31]. This was diluted to 3 ml by dichloromethane and followed by injection onto the system for high-performance size-exclusion chromatography (HP-SEC). A 100-μl volume of iso-octane was added to the PCB fraction collected from the HP-SEC clean up, and the solvent was evaporated to give a volume of 0.5 ml. Cyclohexane was added to give a final volume of 2 ml, which was treated with 5 ml of concentrated suprapure sulfuric acid [32].

2.5. Sample workup for cod liver analysis

An amount of 2 g of cod liver was extracted with 35 ml cyclohexane–acetone (20:15) for 10 min forced by a 475 W Virsonic ultrasonification probe (Virtis). The organic phase was extracted with 10 ml of a 0.5% NaCl solution, and the water phase was extracted with a new portion of 35 ml cyclohexane–acetone (20:15) [31]. The combined organic extracts were evaporated to dryness, and 0.2 g of the residue was dissolved in dichloromethane. Internal standard (PCB 53) was added, followed by injection onto the HP-SEC system. A 100-μl volume of iso-octane was added to the PCB fraction from the HP-SEC clean up, and solvent was evaporated to give a volume of 0.5 ml. Cyclohexane was added to give a final volume of 2 ml, which was treated with 5 ml of concentrated suprapure sulfuric acid.

2.6. Size-exclusion chromatography

The SEC equipment consisted of a Model 510 HPLC pump from Waters (Milford, MA, USA), a Model SPD-6AV UV–Vis detector (254 nm) from Shimadzu (Kyoto, Japan), a Waters Fraction Collector, and a Model SP 4270 integrator from Spectra-Physics (San Jose, CA, USA). Two Waters Envirogel TM GPC columns (150×19 mm I.D. and 300×19 mm I.D.) were connected in series to accomplish the required separation. The system was operated with dichloromethane as the mobile phase at a flow-rate of 5.0 ml/min (500 p.s.i.), and the PCBs were collected in the 80–105 ml fraction.

2.7. References materials

PCB Nos. 28, 31, 52, 53, 101, 105, 110, 114, 118, 126, 128, 138, 141, 149, 153, 154, 157, 169, 180, 185, 187, 188, 194, and 209 were all obtained as 10 ng/μl solutions in iso-octane from Labor Dr. Ehrenstorfer (Augsburg, Germany). Arochlor 1232 and 1260 (1000 ng/μl in iso-octane) were purchased from Supelco (Bellefonte, PA, USA), whereas the dilution of Aroclor 1254 (to 931 ng/μl in iso-octane) was performed in-house.

3. Results and discussion

For several years, polychlorinated biphenyls (PCBs) have been monitored in sediments collected along the Norwegian coast by the Norwegian Institute for Water Research. Although extensive sample clean-up has been applied (as described in Section 2), PCB analysis by capillary gas chromatography with electron-capture detection (GC–ECD) has been problematic in several cases owing to high levels of GC–ECD-sensitive coextractives. For PCB investigations in such highly contaminated samples, preliminary research has demonstrated a high potential of capillary gas chromatography combined with atomic emission detection (GC–AED). Based on this experience, the quantitative aspects of GC–AED for PCB analysis were extensively investigated as reported below.

3.1. Quantitation of individual congeners

Because both the biologic and toxic effects of PCBs are highly structure-dependent [3–5], PCB analysis normally includes quantitation of selected individual congeners. Capillary gas chromatography (GC) with electron-capture (ECD) or mass-selective detection (MSD) are traditionally applied for this purpose, but the applicability of both detection systems is complicated by major structure-related variations of analyte responses [6,8,9]. Thus, calibration curves for each of the congeners of interest have to be established for accurate quantitation. Below follows an investigation whether this cumbersome quantitation procedure may be simplified utilizing capillary gas chromatography coupled with atomic emission detection (GC–AED).

Initially, Cl-, C-, and H-response factors (area counts per ng element) were calculated for a number of selected PCB congeners available as pure standards. The results for Cl and C varied by less than 10%, and the response factors were almost unaffected both by the position (Table 1) and by the number of chlorine atoms (Table 2) within the biphenyl moiety. Consequently, it was possible to accurately quantitate individual PCBs (<10%) based on a single Cl- or C-calibration plot (area counts versus ng element) obtained from one or a few randomly selected congeners (universal calibration). This attractive feature was further supported by the results summarized in Table 3 and Table 4, where some representative PCB congeners were quantitated both in marine sediment (Fig. 1) and in cod liver (Fig. 2). Thus, with the exception of PCB 28, values calculated from GC–AED (universal calibration) deviated by less than 15% from GC–ECD results. The major deviation for PCB 28 was probably due to incomplete separation from PCB 31 because the GC–AED experiments were carried out with a relatively short column (30 m). Whereas the GC–ECD procedure required individual calibration plots for each of the seven congeners, calibration with GC–AED was based only on the response factor for PCB 53 added

Table 1
Effect of chlorine position on Cl-, C-, and H-response factors for selected PCB congeners

IUPAC No.	Number of Cl	Responses normalized against PCB	Cl-response factor[a]	C-response factor[a]	H-response factor[a]
105	5	105	1.000±0.025	1.000±0.019	1.000±0.094
110	5	105	1.044±0.013	1.061±0.010	0.971±0.054
114	5	105	1.011±0.023	1.017±0.014	0.935±0.134
128	6	128	1.000±0.021	1.000±0.015	1.000±0.032
149	6	128	1.061±0.024	1.037±0.017	1.012±0.097
154	6	128	1.039±0.005	1.026±0.012	0.973±0.074
157	6	128	1.011±0.007	0.985±0.006	0.902±0.089
169	6	128	0.986±0.013	0.979±0.009	0.820±0.014
185	7	185	1.000±0.015	1.000±0.013	1.000±0.094
187	7	185	1.009±0.009	1.027±0.021	1.286±0.048
188	7	185	1.022±0.003	1.060±0.008	1.453±0.148

[a] Based on five repetitive injections.

Table 2
Effect of chlorine number on Cl-, C-, and H-response factors for selected PCB congeners

Number of chlorine	IUPAC No.	Cl-response factor[a]	C-response factor[a]	H-response factor[a]
3	31	0.974±0.016	0.950±0.002	1.001±0.016
4	53	1.049±0.016	1.021±0.007	1.082±0.070
5	105, 110, 114,	1.000±0.011[b]	1.000±0.027[b]	1.000±0.049[b]
6	128, 141, 149, 154, 157, 169	0.966±0.011	0.958±0.010	1.065±0.067
7	185, 187, 188	1.018±0.009	0.998±0.013	1.191±0.092
8	194	1.050±0.011	1.041±0.018	1.411±0.253
10	209	1.059±0.013	1.070±0.008	–

[a] Based on five repetitive injections.
[b] Response defined as 1.000.

Table 3
Quantitation of PCBs in a marine sediment (dry weight) collected close to Bergen (Norway)

PCB No.	GC–AED (μg/kg)	GC–ECD (μg/kg)	Deviation (%)
28	53	34	+55.8
52	64	71	−9.9
101	38	41	−7.3
118	44	42	+4.8
138	13	15	−13.3
153	10	11	−9.0
180	4	4	–

as internal standard. Thus, congener-specific quantitation was significantly simplified by GC–AED. The two environmental applications also demonstrated the superiority of the highly selective Cl-chromatogram for quantitation, and the difficulties of utilizing the C- and H-traces owing to coextractives in the PCB fraction. The value of H-chromatograms for PCB quantitation was further reduced by major structure-related effects for the H-response (Table 1 and Table 2). The elevation of the hydrogen signals for the hepta- and octa-chlorinated biphenyls probably arose owing to chemical reactions in the plasma, and supported results observed previously [33].

Table 4
Quantitation of PCBs in liver from cods (fat weight) collected in the Oslo harbor (Norway)

PCB No.	GC–AED (μg/kg)	GC–ECD (μg/kg)	Deviation (%)
28	n.d.	36	–
52	212	248	−14.5
101	1179	1143	+3.1
118	1555	1834	−15.2
138	2815	2649	+6.3
153	4103	3983	+3.0
180	1368	1387	−1.4

3.2. Estimation of total PCB

Although an environmental risk assessment should include the analysis of individual PCB congeners as discussed above, the total PCB residue level remains an important parameter in many PCB investigations. Owing to the above-mentioned structure-related variations of response factors for GC–ECD and GC–MSD, accurate determinations of the total PCB level are rather difficult with these techniques [6]. Thus, total levels of PCB are often estimated from a quantitative analysis of a few representative congeners (e.g. PCB 28, 52, 101, 118, 138, 153, and 180), which are compared with technical mixtures of known composition. Owing to compositional changes following biological or nonbiological degradation, however, this procedure may result in considerable inaccuracies [8]. Alternatively, PCBs may be perchlorinated with $SbCl_5$ to decachlorobiphenyl [34,35] or reduced with $LiAlH_4$ to biphenyl [36,37], whereby total PCB may be determined by quantitation of a single peak. With these latter procedures, however, the information on congener composition is lost.

In contrast to GC–ECD and GC–MS, total PCB levels were readily calculated from GC–AED results. Thus, in dilutions of three technical PCB mixtures (Fig. 3), Cl-, C-, and H-peak areas for all the individual PCBs were summed electronically and divided by average Cl-, C-, and H-response factors

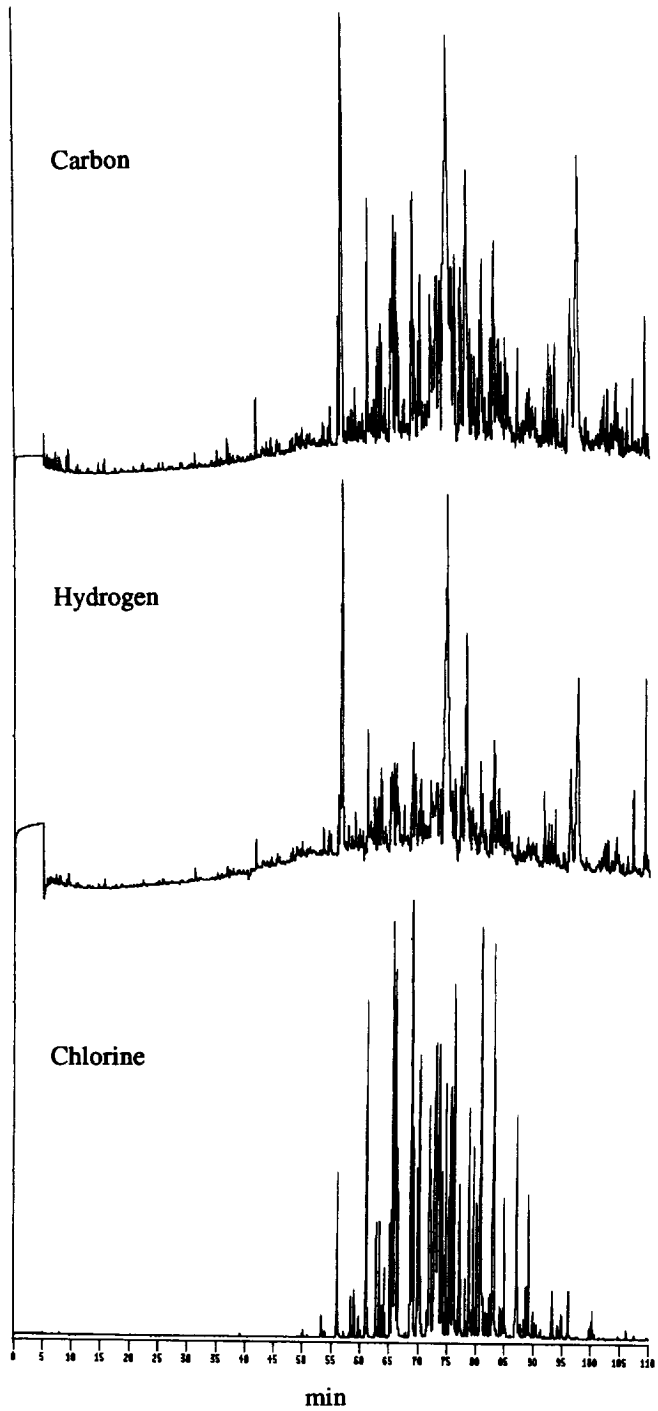

Fig. 1. C-, H-, and Cl-specific chromatograms from an extract of marine sediments collected close to Bergen (Norway).

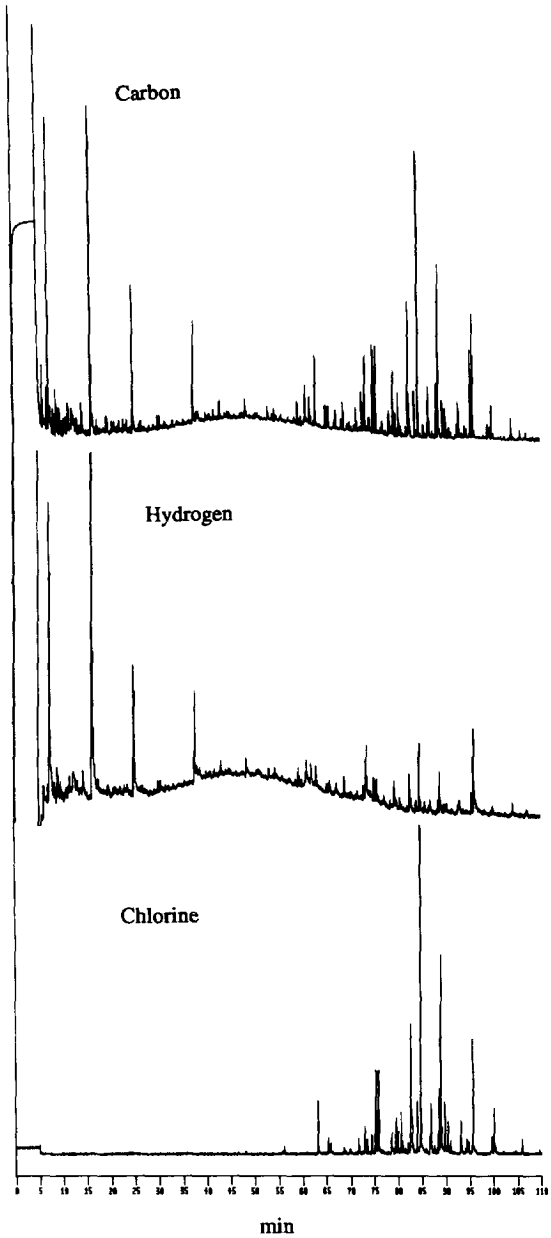

Fig. 2. C-, H-, and Cl-specific chromatograms from an extract of cod liver collected in the Oslo harbor (Norway).

(area counts per ng element) to calculate the total PCB level. As illustrated in Table 5, the results on total PCB were accurate to within 8%. The experiments were proceeded to PCBs present in two environmental samples, where total residue levels of 1138 and 20048 μg/kg were estimated in a marine sediment (Fig. 1) and in cod liver (Fig. 2), respec-

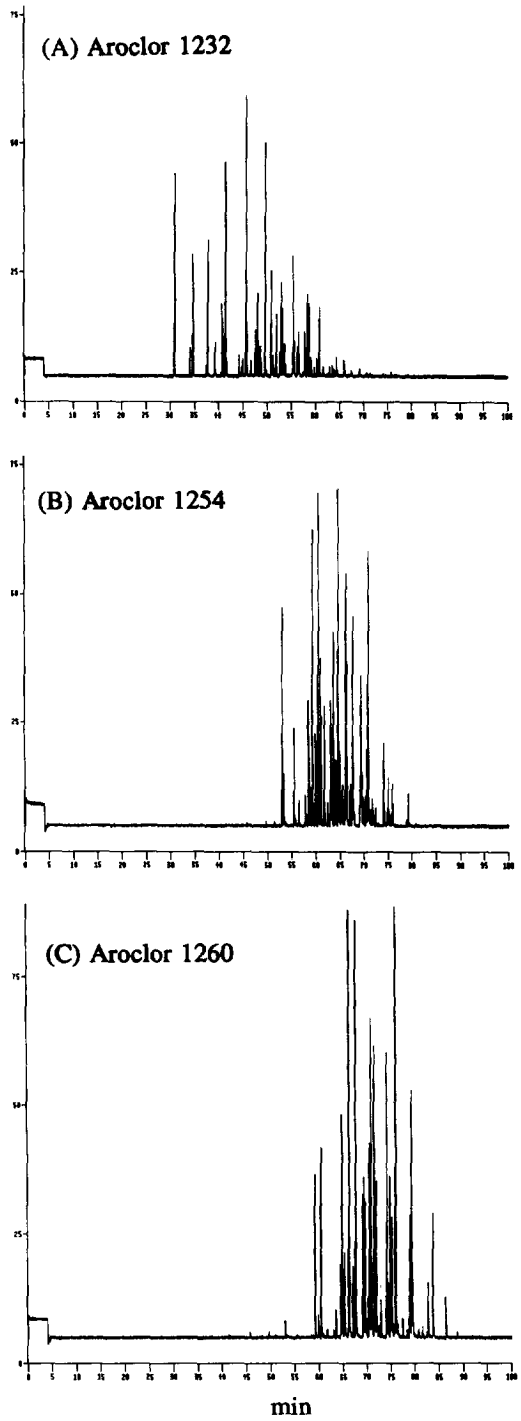

Fig. 3. Chlorine-specific chromatograms of (A) Aroclor 1232 (1000 ng/μl), (B) Aroclor 1254 (931 ng/μl), and (C) Aroclor 1260 (1000 ng/μl).

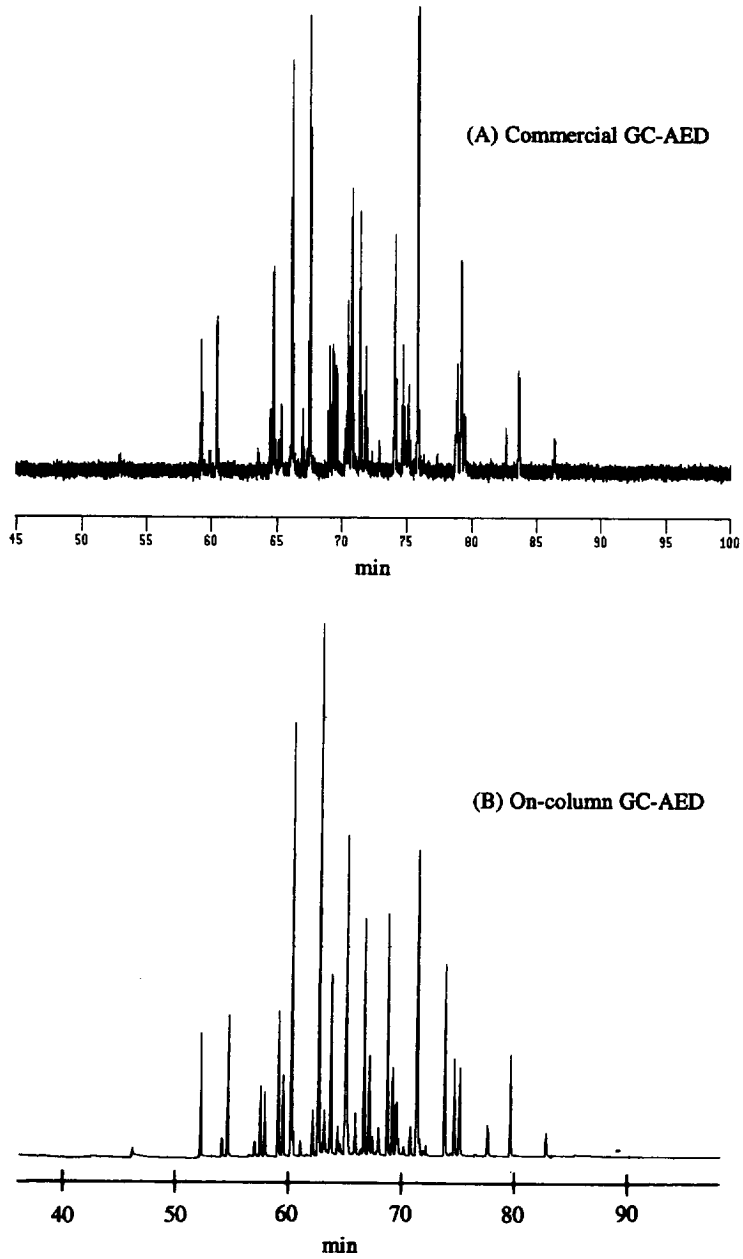

Fig. 4. Comparison of PCB detectability with (A) a commercial GC–AED equipment and (B) a laboratory-built on-column GC–AED system.

tively. In both cases, the calculations were slightly complicated by an increased complexity of C- and H-chromatograms from the sample matrices. Thus, prior to the area summation, manual inspection of the peak-integration report was necessary to extract the C- and H-peaks with corresponding Cl-signals. A few samples of even higher complexity (hydrocarbon matrices) were also analyzed, but the summation of total C, H, and Cl present as PCBs was impossible since the PCBs disappeared among coextractives in

Table 5
Estimation of total PCB in dilutions of Aroclor 1232, 1254, and 1260

Aroclor	Actual concentration (ng/μl)	Determined concentration (ng/μl)	Deviation (%)
1232	1000	922	−7.8%
1254	931	866	−7.5%
1260	1000	1006	+0.6%

Table 6
Estimation of chlorine content in 1 μg/μl dilutions of Aroclor 1232, 1254, and 1260

Aroclor	Expected Cl-content (%)	Determined Cl-content (%)
1232	32	31
1254	54	57
1260	60	60

the C- and H-specific chromatograms. Because the percentage by weight of chlorine was unknown for these samples, estimation of total PCB levels only from Cl-specific chromatograms was impossible as well. In addition to hydrocarbons present as matrix components, PCB fractions may also contain other chlorinated compounds eluting within the PCB retention window. In such cases, they obviously have to be identified and excluded from calculations of total PCB.

3.3. Estimation of the percentage by weight of chlorine

Frequently, PCB profiles obtained from the analysis of environmental samples are compared with the composition of technical PCB mixtures in order to estimate the percentage by weight of chlorine and to investigate the type of PCB mixture responsible for the contamination. As for the determination of total PCB (Section 3.2), estimations of the percentage by weight of chlorine from GC–ECD or GC–MSD are based on comparison with mixtures of known composition. In cases with no compositional changes, this type of classification is effectively carried out through the application of chemometrics [38,39]. However, PCB mixtures in the environment may be exposed to compositional changes, complicating comparison with laboratory standards.

In Section 3.2, the total levels of Cl, C, and H present as PCBs were determined and summed to give the total level of PCB in dilutions of Aroclor 1232, 1254, and 1260 (Fig. 3). From these data, the percentage by weight of chlorine was readily calculated as the weight ratio of chlorine versus total PCB. As illustrated in Table 6, these data from GC–AED based on universal calibration agreed with expected values to within 5%. In two further experiments, the same procedure was utilized to estimate chlorine contents of 41 and 58% in PCB-contaminated sediment (Fig. 1) and cod liver (Fig. 2), respectively. Also in this case, the calculations were somewhat complicated by coextractives present in the C- and H-specific chromatograms.

3.4. Detection limit considerations

With the commercial atomic emission detector, standard solutions of PCBs were detected down to the 250–400 pg level (Table 7), whereas detection limits with GC–ECD were in the range 0.02–0.04 pg. Even close to the detection limit, the baseline stability was excellent with GC–AED, whereas significant baseline fluctuations were observed with GC–ECD. Therefore, the difference in AED and ECD detection limits was smaller for practical work than reported above with pure standard solutions. Nevertheless, the present version of the commercial GC–AED system was useable only for relatively concentrated PCB extracts, and followingly demanded for preparation of large sample amounts in cases of low PCB levels. Recent instrumental development, however, has demonstrated that GC–AED detectability may be significantly improved by sustaining the plasma inside the end of the capillary GC column [28–30]. Owing to the small volume of the plasma cell, introduction of make-up gas may be reduced providing improved detection limits. Thus, when PCBs were monitored from a laboratory-built on-column plasma system, GC–AED detection limits were improved by a factor of approximately 30 (Table 7), and the applicability of GC–AED for trace analysis was substantially enhanced (Fig. 4). Improvement of the optical part of this on-column GC–AED system is currently in progress, and is expected to further improve the Cl-detectability. This in combination with the attractive quantitative as-

Table 7
Comparison of detection limits for PCB 31, 110, and 185

PCB No.	Number of Cl	Detection limit (pg)		
		Commercial GC–AED	On-column GC–AED	GC–ECD
31	3	400	12	0.04
110	5	263	9	0.03
185	7	248	8	0.02

pects found in the present work suggests GC–AED to be a very attractive technique for PCB analysis within the near future.

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