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Evaluation of four mass spectrometric methods for the gas chromatographic analysis of polychlorinated *n*-alkanes

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Abstract

The suitability of four mass spectrometric methods for the gas chromatographic analysis of polychlorinated *n*-alkanes (PCAs, also called chlorinated paraffins) was evaluated and compared using spiked and fish liver samples. Electron ionization tandem mass spectrometry (EI–MS/MS) as well as electron capture negative ionization (ECNI) combined with low and high resolution mass spectrometry and CH_4/CH_2Cl_2-negative ion chemical ionization (NICI) low resolution mass spectrometry were investigated. All methods showed an accuracy of <21% for the analysis of spiked fish samples. However, the analysis of real samples showed deviations of up to 46% between the four mass spectrometric methods. The influence of the selected reference standard on quantification was also evaluated. The use of a quantification standard with a degree of chlorination deviating from that of the sample can result in differences of >100% for the ECNI methods. EI–MS/MS and CH_4/CH_2Cl_2-NICI led to errors of maximum 17% and 33%, respectively, independent from the degree of chlorination of the used reference standard.
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1. Introduction

Polychlorinated *n*-alkanes (PCAs) are highly complex technical mixtures, which are also known as chlorinated paraffins. These mixtures have a chlorination degree between 30% and 70% and a linear chain length of C_{10}–C_{13} (short chain PCAs or sPCAs, also called short chain chlorinated paraffins (SCCPs)), C_{14}–C_{17} (medium chain PCAs or mPCAs, also called medium chain chlorinated paraffins (MCCPs)) or $C_{>17}$ (long chain PCAs) [1]. PCAs are of concern due to their toxicological properties and their capability to bioaccumulate. As consequence of their widespread and unrestricted use and the properties mentioned above, PCAs are present in aquatic and terrestrial food webs in rural and remote areas [2–5].

Little attention has been paid to the analysis of these compounds in the past. Therefore, analytical methods and information about environmental levels are limited. However, recently sPCAs, have been included in the list of substances for priority action of the Convention for the Protection of the Marine Environment of the North-East Atlantic (The "OSPAR Convention") [6], in the list of priority dangerous substances of the European water framework directive [7,8] and in that of selected substances for immediate priority action of the Helsinki Commission (HELCOM) [9]. Consequently, environmental levels of PCAs should be monitored more extensively in the near future, which will require reliable analytical methods. Nowadays PCA analysis is mainly performed by electron capture negative ionization (ECNI) combined with high resolution (HRMS) [10] or low resolution mass spectrometry (LRMS) [11,12]. However, ECNI has some disadvantages: The use of different technical mixtures as quantification standards can lead to considerable deviations in the results [13,14]. Additionally, lower chlorinated PCAs ($Cl_{<5}$) are hardly detectable, and the data processing is quite time consuming.

Recently, alternative approaches for the mass spectrometric analysis of these compounds have been reported. A CH_4/CH_2Cl_2 gas mixture has been used as reagent for

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negative ion chemical ionization (NICI) in combination with LRMS [15]. The addition of dichloromethane to the reagent gas favored the formation of chlorine adduct ions and reduced the dependence of the response factors from the degree of chlorination. Similar results could also be achieved by Moore et al. using metastable atom bombardment as ionization technique [16]. Electron ionization tandem mass spectrometry (EI–MS/MS) was proposed for the simultaneous detection of all short and medium chain PCA congeners [17]. This approach is based on fragment ions with low mass-to-charge ratios, which are common to all (or most) PCAs and has the advantage, that the response factors of different PCA mixtures are not dependent on their degree of chlorination. Additionally, the use of ECNI–LRMS monitoring the $[HCl_2]^-$ and $[Cl_2]^-$ ions has been reported [18]. Similarly to EI–MS/MS this technique allows the determination of the total PCA concentration, but congener and homologue specific analysis is not possible. Moreover, liquid chromatography combined with chloride enhanced atmospheric pressure chemical ionization mass spectrometry was used for the analysis of PCAs [19]. However, the suitability of this technique for environmental samples was not proven yet.

The aim of this work was to investigate the comparability of results obtained by high resolution gas chromatography coupled to ECNI–HRMS, ECNI–LRMS, CH_4/CH_2Cl_2-NICI–LRMS and EI–MS/MS and to point out advantages and limitations of these techniques. The comparison was carried out with both spiked fish tissue and fish liver samples from the North Sea and Baltic Sea.

2. Experimental

2.1. Chemicals and solvents

Technical sPCA (chlorine contents of 51.5%, 55.5% and 63.0%) and mPCA mixtures (chlorine contents of 42.0%, 52.0% and 57.0%) at concentrations of 100 ng/μl in cyclohexane were purchased from Ehrenstorfer (Augsburg, Germany). $^{13}C_{10}$-*trans*-chlordane (99%) at a concentration of 100 ± 10 ng/μl in nonane was obtained from Cambridge Isotope Laboratories (Andover, USA). Cyclohexane, dichloromethane and *n*-hexane for pesticide residue analysis were purchased from Scharlau (Barcelona, Spain). Florisil®PR (60–100 mesh) and sodium sulfate (Pestanal®) were obtained from Fluka (Buchs, Switzerland) and silica gel (200–400 mesh, 0.035–0.070 mm) from CU Chemie Uetikon AG (Uetikon, Switzerland). Before use, all three chemicals were treated at 600 °C overnight and afterwards kept for 6 h at 130 °C.

2.2. Environmental samples

Fish samples were collected in August and September 2002 by the German Federal Research Center for Fisheries (liver samples 1–3: cod (*Gadus morhua*) captured at 54°51′N and 14°01′E; liver samples 4 and 5: North Sea dab (*Limanda limanda*) captured at 54°31′N and 10°39′E and 55°30′N and 4°40′E, respectively). Spiked samples were prepared adding 1500 ng of a technical sPCA mixture (55.5% Cl content), or 1500 ng of each of sPCAs (55.5% Cl content) and mPCAs (52% Cl content) to 8–10 g of homogenized mackerel muscle. The clean-up method is described in brief, since more details have been published elsewhere [12,20]. Samples were homogenized with a tenfold excess of Na_2SO_4. $^{13}C_{10}$-*trans*-chlordane (10 ng, internal standard) in 10 μl of cyclohexane were added and the sample column-extracted with 250 ml of *n*-hexane/CH_2Cl_2 (1 + 1, v/v). The clean-up of the extracts included removal of lipids by column chromatography on 40 g of silica gel impregnated with 44% H_2SO_4. The lipid-free sample was eluted with 120 ml of *n*-hexane/CH_2Cl_2 (1 + 1, v/v). Then, adsorption chromatography on 16 g of Florisil® (1.5% H_2O water content) was carried out with 60 ml of *n*-hexane (fraction 1), with 7 ml of CH_2Cl_2 (fraction 2) and with 60 ml of CH_2Cl_2 (fraction 3). The last one contained all PCAs.

2.3. Instrumentation

ECNI–HRMS analysis was performed on a VG AutoSpec (Micromass, Manchester, UK) coupled to a HP 5890II (Hewlett-Packard, Palo Alto, USA) gas chromatograph equipped with a split/splitless injector and a fused silica capillary column (25 m length, 0.20 mm i.d.) coated with a 0.33 μm thick film of HP-1 (dimethylpolysiloxane, J&W Scientific, Folsom, USA) and 1 μl was injected in the splitless mode. The injector temperature was 260 °C. Helium (99.999%) was used as carrier gas at an inlet pressure of 137.8 kPa (20 psi). The temperature program was as follows: 150 °C isothermal for 2 min, then 7 °C/min to 260 °C, isothermal for 8 min, increased to 280 °C at 10 °C/min and then isothermal for 13 min. The mass spectrometer was operated in the ECNI mode using argon as reagent gas at a source housing pressure of 2×10^{-5} mbar. A resolution of 12,000 at an acceleration voltage of 6 kV was employed. The temperature of the ion source was set to 170 °C, the filament emission current was set to 0.3–1 mA and the electron energy was in the range 25–40 eV. Perfluorokerosene was used as calibration compound. The most abundant isotopes of the $[M - Cl]^-$ ions of PCAs and of the $[M]^-$ and $[M - 4Cl - 2H]^-$ ions of $^{13}C_{10}$-*trans*-chlordane were detected in the selected ion monitoring (SIM) mode with dwell times of 50 ms each [10].

For the ECNI–LRMS and the CH_4/CH_2Cl_2-NICI–LRMS analysis, gas chromatographic separations were performed on a HP 5890II (Hewlett-Packard, Palo Alto, USA) gas chromatograph equipped with a split/splitless injector and a fused silica capillary column (15 m length, 0.25 mm i.d.) coated with a 0.25 μm thick film of DB5-MS (5% crosslinked phenyl-methylpolysiloxane, J&W Scientific, Folsom, USA) and 1.5 μl were injected in the splitless mode. The injector temperature was 275 °C. Helium (99.999%, Carbagas, Basel,

Switzerland) was used as carrier gas at an inlet pressure of 68.9 kPa (10 psi). The temperature program was as follows: 100 °C isothermal for 2 min, then 10 °C/min to 260 °C and isothermal for 10 min. A MS Engine HP 5989B (Hewlett-Packard, Palo Alto, USA) was employed in the negative ion mode. The transfer line temperature was kept at 275 °C, the ion source temperature at 200 °C and the quadrupole temperature at 100 °C. Methane (99.995%, Carbagas, Basel, Switzerland) was used at a reagent gas pressure of 1.0–1.6 mbar (0.8–1.2 Torr) in ECNI. The most abundant isotopes of the $[M-Cl]^-$ ions of PCAs and of the $[M]^-$ ion of $^{13}C_{10}$-*trans*-chlordane were detected in the SIM mode with dwell times of 75 ms each [11]. For the CH_4/CH_2Cl_2-NICI–LRMS analysis, dichloromethane was introduced through a modified transfer line. The reagent gas pressure was 2.0 mbar (1.5 Torr) and the CH_4/CH_2Cl_2 ratio was 80 + 20. The $[M+Cl]^-$ ions of PCAs and of the $[M]^-$ ion of $^{13}C_{10}$-*trans*-chlordane were detected in the SIM mode with dwell times of 75 ms each using the most abundant isotope signals[15].

For EI–MS/MS analysis, a 1200 triple quadrupole MS (Varian, Wallnut Creek, USA) was employed. Gas chromatographic separations were performed on a CP-3800 (Varian, Wallnut Creek, USA) gas chromatograph equipped with a fused silica capillary column (15 m length, 0.25 mm i.d.) coated with 0.25 μm of DB-5MS (5% crosslinked phenyl-methylpolysiloxane, J&W Scientific, Folsom, USA). The injector temperature was set to 275 °C. Helium was used as carrier gas at a constant flow of 2 ml/min (linear flow velocity of 74 cm/s). The temperature program was as follows: 100 °C isothermal for 1 min, then 50 °C/min to 300 °C and isothermal for 4 min. Splitless injections (splitless time, 1.5 min) of 2.5 μl volume were carried out with a Combi Pal autosampler (CTC Analytics, Zwingen, Switzerland). The transfer line temperature was set to 275 °C, the ion source temperature to 200 °C and the manifold temperature to 40 °C. Conditions for EI–MS/MS were as follows: 70 eV electron energy; emission current, 300 μA; dwell time, 50 ms; resolution of Q1 at 0.8 and of Q3 at 1.2; and argon as CID gas at 0.12–0.15 Pa (0.9–1.1 mTorr). PCAs were detected using the *m/z* 102 → 67 (collision energy, −10 V), 102 → 65 (collision energy, −18 V) and 91 → 53 (collision energy, −10 V) fragmentation reactions. The precursor ion *m/z* 383 $[M-Cl]^+$ and the product ion *m/z* 276 $[M-4Cl]^+$ were chosen for $^{13}C_{10}$-*trans*-chlordane (collision energy, −21 V).

2.4. Quantification

PCA quantification was performed with a technical sPCA mixture (55.5% Cl content) and a technical mPCA mixture (52% Cl content) for all four methods. The detailed procedure for ECNI–MS has been previously described by Tomy et al. [10]. This quantification method was also applied for CH_4/CH_2Cl_2-NICI–LRMS. Additionally, the problems due to mass overlap were reduced for LRMS as described by Reth and Oehme [11]. The technical sPCA mixture with 55.5% chlorine content was used as reference for the determination of the total s + mPCA concentration by EI–MS/MS.

3. Results and discussion

3.1. Limits of detection

The technical details of all detection methods applied in this work are described in detail elsewhere [10,11,15,17]. Therefore, only a description of their performance is given here. PCA quantification by ECNI–HRMS has been extensively described by Tomy et al. [10]. The authors reported limits of detection (LODs) of 60 pg/μl of technical sPCA mixture (70% Cl content) for their instrumentation. This sensitivity could not be achieved on the high resolution mass spectrometer used in this work, which showed an LOD of 1 ng/μl of sPCA mixture with a degree of chlorination of 55.5%. The explanation for this deviation is the lower degree of chlorination of the sPCA standard used in this work. It is well known, that the congener response increases with the degree of chlorination under ECNI conditions. Consequently, a higher chlorinated PCA mixture leads to a higher response for the main congeners. The LODs for ECNI–LRMS and for CH_4/CH_2Cl_2-NICI–LRMS were 1 ng/μl of sPCA mixture with a chlorination degree of 55.5% (detection of the most abundant congeners). EI–MS/MS showed lower LODs in the range of 0.15–0.3 ng/μl of sPCA mixture (55.5% Cl content) depending on the selected fragmentation.

3.2. Analysis of standards and spiked samples

Two standards were used to evaluate the quantification of PCAs and a possible interference by mPCAs. Standard one contained 1500 ng of a sPCA mixture (55.5% Cl content) and standard two 1500 ng of the sPCA and 1500 ng of the mPCA mixture (52% Cl content). The results are summarized in Table 1. Interday reproducibility (five measurements over several months) was 8% or less for all techniques. For standard 1, all four techniques led to an acceptable result (bias < 10%). For standard 2, ECNI–LRMS did not allow to eliminate completely the interferences from mPCAs with similar mass-to-charge ratios to sPCAs. Therefore, the deviation from the expected amount was higher (14%). However, also the bias of ECNI–HRMS increased (24%) despite the higher resolution. The reason of this deviation is not clear. In contrast, the determined mPCA amount was lower than expected for both ECNI techniques, leading to a good accuracy for the overall content. CH_4/CH_2Cl_2-NICI–LRMS allowed to determine both sPCAs and mPCAs with good accuracy in the two standards. Also EI–MS/MS showed errors below 10%.

To evaluate the interference of matrix, three mackerel muscle samples (s + mPCAs < 1 ng/g) were spiked with PCAs (samples 1 and 2 with 1500 ng sPCAs and sample 3 with 1500 ng of sPCAs and mPCAs each). The results

Table 1
Quantification of s- and mPCAs in standard solutions using the four mass spectrometric methods (single measurement)

Compound	Expected (ng)	ECNI–HRMS (ng, %)	ECNI–LRMS (ng, %)	CH_4/CH_2Cl_2-NICI–LRMS (ng, %)	EI–MS/MS (ng, %)
Standard 1					
sPCAs	1500	1350 (10)	1590 (6)	1590 (6)	1420 (5)
Standard 2					
sPCAs	1500	1870 (24)	1710 (14)	1590 (6)	n.p.
mPCAs	1500	1140 (24)	1370 (9)	1510 (1)	n.p.
s + mPCAs	3000	3010 (1)	3080 (3)	3100 (3)	2760 (8)

n.p., not practicable. Standard 1 contained 1500 ng of sPCAs with 55.5% Cl content and standard 2 contained 1500 ng of sPCAs and mPCAs each with Cl contents of 55.5% and 52%, respectively. The relative deviations (%) from the expected values are given in parenthesis.

obtained with the different techniques are summarized in Table 2. Interday reproducibility (five measurements over several months) of ECNI–LRMS for these samples was <6% for sPCAs and <9% for mPCAs. CH_4/CH_2Cl_2-NICI–LRMS had an interday reproducibility of <13% for sPCAs and <12% for mPCAs whereas EI–MS/MS had an interday reproducibility <10%. Most results showed errors of 15% or less. Only for CH_4/CH_2Cl_2-NICI–LRMS and sample 1 as well as ECNI–HRMS and sample 2, the deviation was ca. 20%. The analysis of sample 3 containing both sPCAs and mPCAs showed similar results for all three s/m-PCA specific techniques (errors of ca. 15% for the determination of sPCAs and of ca 10% for mPCAs). The total PCA concentration determined by EI–MS/MS was in good agreement with the results obtained with the other techniques.

3.3. Analysis of fish samples

Since the results obtained for spiked samples showed good accuracy and repeatability with all detection methods, five fish liver samples were cleaned-up and analyzed. The results are summarized in Table 3. Usually, total PCA concentration in fish liver from the North and Baltic Sea is between 20 and 600 ng/g wet weight [20].

The total PCA concentration obtained by the different techniques showed a relative standard deviation of 30% or less for all fish liver samples. This error is acceptable taking into account that the interday reproducibility (five measurements) for these samples was <12% for sPCAs and <18% for mPCAs (ECNI–LRMS), <28% for sPCAs and <10% for mPCAs (CH_4/CH_2Cl_2-NICI–LRMS) and <20% for s + mPCAs (EI–MS/MS).

The differences between the results of ECNI–LRMS and ECNI–HRMS were in the range of the interday reproducibility. The determination of mPCAs showed good agreement between low and high resolution ECNI–MS for samples 2 and 3. For sample 1, a slightly higher mPCA concentration was obtained by ECNI–LRMS. This might be explained by possible interferences by other compounds not resolved by LRMS. The analysis of sPCAs by ECNI–LRMS was not possible for sample 3, since it contained too much lipid (>6 g), which overloaded the clean-up method. Therefore, the extract contained a considerable amount of polychlorinated compounds like PCBs, toxaphenes and chlordanes interfering the ECNI–LRMS analysis. The detection of mPCAs in sample 3 was possible even by ECNI–LRMS, since the medium chained PCA congeners form ions with mass-to-charge ratios different from those of the interfering compounds. Samples 4 and 5 were not analyzed by ECNI–HRMS, which was not available in-house.

Most PCA concentrations determined by CH_4/CH_2Cl_2-NICI–LRMS were lower than those determined by the ECNI methods. Only in sample 5, the sPCA concentration obtained by CH_4/CH_2Cl_2-NICI–LRMS was higher. This technique considerably suppresses the ionization of other compounds, so that sPCA analysis was possible for sample 3. Also EI–MS/MS was not disturbed by interfering compounds in the extract. Fig. 1 shows the mass chromatograms for the sPCA congener $C_{12}H_{14}Cl_7$ in sample 3 obtained by the different detection methods.

Table 2
Quantification of s- and mPCAs in spiked fish samples using the four mass spectrometric methods (single measurement)

Compound	Expected (ng)	ECNI–HRMS (ng, %)	ECNI–LRMS (ng, %)	CH_4/CH_2Cl_2-NICI–LRMS (ng, %)	EI–MS/MS (ng, %)
Sample 1					
sPCAs	1500	1720 (14)	1560 (5.7)	1810 (20)	1610 (7)
Sample 2					
sPCAs	1500	1190 (21)	1610 (7.2)	1300 (13)	1580 (5)
Sample 3					
sPCAs	1500	1730 (15)	1750 (17)	1290 (14)	n.p.
mPCAs	1500	1360 (9)	1510 (1)	1450 (3)	n.p.
s + mPCAs	3000	3090 (3)	3260 (9)	2740 (9)	2950 (2)

n.p., not practicable. Samples 1 and 2 contained 1500 ng of sPCA with 55.5% Cl content and sample 3 contained 1500 ng of sPCAs and mPCAs each with Cl contents of 55.5% and 52%, respectively. The relative deviations (%) from the expected values are given in parenthesis.

Table 3
Quantification of s- and mPCAs in fish samples using the four mass spectrometric methods

Compound	ECNI–HRMS (ng/g)	ECNI–LRMS (ng/g)	CH_4/CH_2Cl_2-NICI–LRMS (ng/g)	EI–MS/MS (ng/g)	Mean (ng/g)	Relative standard deviation (%)
Sample 1						
sPCAs	57	43	21	n.p.	40	
mPCAs	52	75	40	n.p.	56	
s + mPCAs	109	118	61	84	93	28
Sample 2						
sPCAs	30	19	23	n.p.	21	
mPCAs	21	25	25	n.p.	24	
s + mPCAs	51	44	48	59	48	18
Sample 3						
sPCAs	13	[a]	20	n.p.	24	
mPCAs	77	76	37	n.p.	82	
s + mPCAs	90	n.p.	57	66	94	27
Sample 4						
sPCAs	n.a.	48	42	n.p.	45	
mPCAs	n.a.	130	61	n.p.	96	
s + mPCAs	n.a.	178	103	117	133	30
Sample 5						
sPCAs	n.a.	37	141	n.p.	89	
mPCAs	n.a.	221	112	n.p.	167	
s + mPCAs	n.a.	258	253	298	270	9

n.a., not analysed; n.p., not practicable.
[a] ECNI–LRMS determination of sPCAs in this sample was not possible due to an overloaded clean-up.

3.4. Problems of quantification

The PCA concentrations in fish liver obtained with the different methods varied more than for the spiked samples (ca. 30% compared to 15%). One possible reason could be, that the same PCA mixture was added to the spiked samples and used for quantification. It has already been shown that the congener composition strongly varies between different technical products and, in addition, in the environment. Tomy et al. [13] and later Coelhan et al. [14] showed that the use of PCA mixtures with a different degree of chlorination as quantification standard for ECNI may give deviations of up to 100%. Table 4 summarizes the data of the analysis of three standards of sPCAs with a different degree of chlorination against different PCAs mixtures used as reference. As can be seen, ECNI causes huge errors (>100%), due to the difference in the degree of chlorination between sample and standard material. CH_4/CH_2Cl_2-NICI–LRMS showed a lower dependency reducing the errors to <32%. This is a considerable advantage, since a perfect match between the chlorine content of standard and sample is less important. Finally, the best results were obtained by EI–MS/MS. This technique is not influenced by the degree of chlorination of the quantification standard, and errors were <17% even when extremely different PCA mixtures were selected as standard. This makes EI–MS/MS, originally developed for screening, very attractive for the quantitative determination of total PCA concentrations, although it cannot be applied for the study of congener patterns and is unable to differentiate between short and medium chained PCAs.

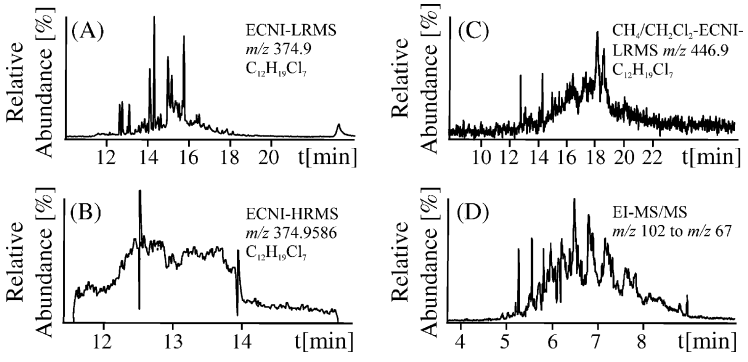

Fig. 1. Mass chromatograms for the congener $C_{12}H_{19}Cl_7$ in sample 3. Quantification of sPCAs was not possible by ECNI–LRMS due to an overloaded clean-up (A). ECNI–HRMS (B); CH_4/CH_2Cl_2-NICI–LRMS (C) and EI–MS/MS for the fragmentation *m/z* 102–67 (D) had a sufficient selectivity for quantification. The chromatograms were obtained with different chromatographic conditions.

Table 4
Quantification of three sPCA solutions using different sPCAs as reference standard

Standard	51[a]		55[a]		63[a]	
Sample	55[b]	63[b]	51[b]	63[b]	51[b]	55[b]
ECNI–LRMS	4300 (190)	15600 (940)	522 (65)	5440 (260)	143 (90)	413 (72)
CH_4/CH_2Cl_2-NICI–LRMS	1770 (18)	1210 (19)	1270 (15)	1030 (31)	1860 (24)	1980 (32)
EI–MS/MS	1590 (6)	1450 (3)	1430 (5)	1323 (12)	1700 (14)	1750 (17)

The spiked amount was 1500 ng for all solutions. The relative errors (%) from the expected result are given in parenthesis.
[a] Sample: sPCA, %Cl.
[b] Standard: sPCA, %Cl.

3.5. Congener patterns

One important step of the quantification of PCAs as described by Tomy et al. is the determination of the congener and homologue composition, which also gives important information about differences in environmental samples [10]. EI–MS/MS does not provide this kind of information, but all other techniques do. Fig. 2 shows the congener pattern of a sPCA mixture (55.5% Cl content) obtained with ECNI–HRMS, ECNI–LRMS and CH_4/CH_2Cl_2-NICI–LRMS. The correction factors described by Tomy et al. were applied for the ECNI methods. They were not used the CH_4/CH_2Cl_2-NICI–LRMS, since the response of different congeners is not dependent on the number of chlorine atoms.

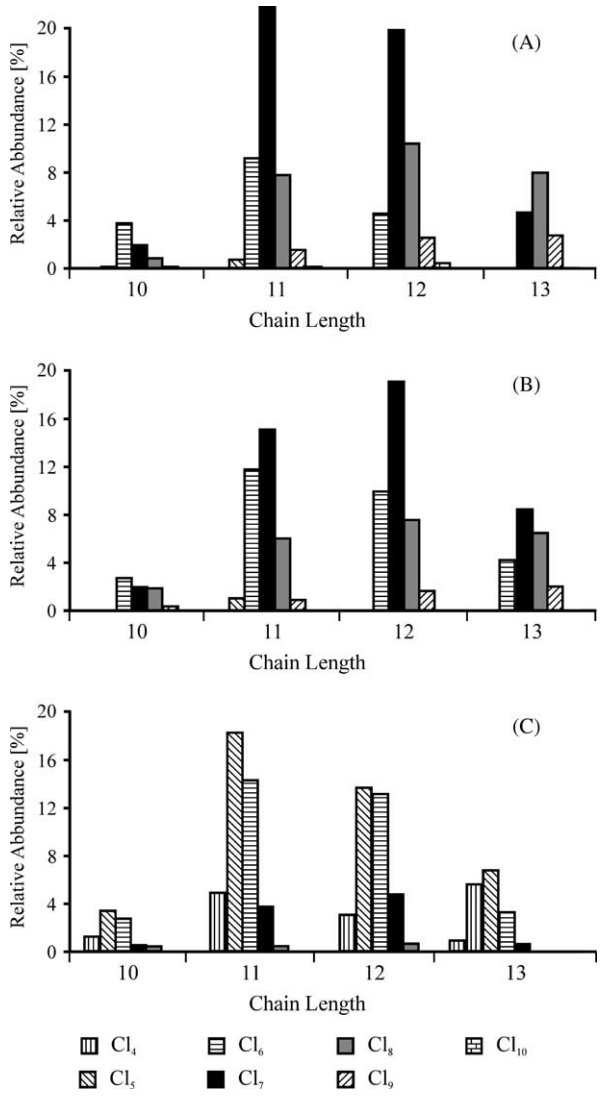

Fig. 2. sPCA congener and homologue patterns of a technical sPCA mixture with a degree of chlorination of 55.5% determined by ECNI–HRMS (A); ECNI–LRMS (B) and CH_4/CH_2Cl_2-NICI–LRMS (C).

As can be seen from Fig. 2, C_{12} was the main homologue group for ECNI–LRMS and C_{11} for ECNI–HRMS. Additionally, some differences were observed in the pattern of the same homologue group. It is not possible to say which technique gave the true composition. However, both methods allow to chose a quantification standard with a pattern close to the sample, which is important to reduce the error of the quantification. The use of the CH_4/CH_2Cl_2 reagent gas mixture allowed also the detection of lower chlorinated compounds ($Cl_{4–5}$). Therefore, and since there is no increase in the response factors for higher chlorinated congeners, the congener distribution is shifted to lower chlorinated congeners. Since the real composition of PCA mixtures is unknown, it is not possible to say which technique gives the true composition. Moreover, a direct comparison of the congener patterns obtained by conventional ECNI and by CH_4/CH_2Cl_2-NICI may lead to erroneous conclusions.

4. Conclusions

All mass spectrometric methods were comparable for the analysis of standards and spiked samples giving results with satisfying accuracy. Variability of the results was reduced to the instrumental methods, since the same solutions were analyzed and used for quantification. However, for the analysis of fish liver some differences in the results were observed. Main reasons are probably a “not perfect” matching of the PCA composition of the sample and the reference material as well as the variable influence of the degree of chlorination on the response factors. This problem can have a strong influence on the results obtained by ECNI–MS. Consequently, a careful selection of the quantification standard is necessary when ECNI is applied. EI–MS/MS and CH_4/CH_2Cl_2-NICI–MS showed little dependency on the degree of chlorination of the standard used for quantification, which is a

considerable advantage for these methods. Moreover, comparable results were obtained by HRMS and LRMS. This confirms that interferences between PCAs forming ions with the same *m*/*z* can be reduced even if LRMS is applied. Finally, ECNI–LRMS requires more thorough sample clean up than the other methods.

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