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Journal of Chromatography A, 1081 (2005) 225–231
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

New quantification procedure for the analysis of chlorinated paraffins using electron capture negative ionization mass spectrometry

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Received 11 March 2005; received in revised form 10 May 2005; accepted 24 May 2005

Abstract

An improved quantification procedure for the analysis of chlorinated paraffins (CPs) is presented based on electron capture negative ionization mass spectrometry. It compensates differences in response factors between reference CP mixtures and the CP pattern present in environmental samples. The use of a CP standard with a matching degree of chlorination is no longer necessary. It could be shown that the response factors of C_{10}-, C_{11}-, C_{12}- and C_{13}-CP mixtures of both 50 and 60% chlorine content were only slightly influenced by the carbon chain length. A linear correlation ($R^2 = 0.965$) between the total response factor of a CP mixture and its chlorine content was obtained for seven short chain chlorinated paraffin mixtures (SCCP, C_{10}–C_{13}) with different composition and chlorine content (51–69%). Maximum single deviations were <7% for this reference set. It allowed to determine the correct total response factor of the CP composition present in a sample. The deviations were not more than 7–33% for five independent SCCP control samples compared to up to 373% for the conventional procedure. The procedure was tested by quantifying the SCCP and MCCP levels in 10 fish liver samples. The proposed method allowed to compensate the influence of the degree of chlorination of the applied reference standard on the total response factor.

Keywords: Polychlorinated *n*-alkanes; PCAs; CPs; Quantification; ECNI mass spectrometry

1. Introduction

The environmental analysis of polychlorinated compounds applied as technical mixtures such as polychlorinated biphenyls, toxaphenes or chlorinated paraffins (CPs) is very demanding due to their complex composition, changes in the congener patterns in the environment and the lack of suitable reference standards. The presence of thousands of different isomers, enantiomers and diastereomers in CP mixtures makes them the real challenge of all.

CPs contain polychlorinated *n*-alkanes and are subdivided according to their carbon chain length into short chain CPs (SCCPs, C_{10}–C_{13}), medium chain CPs (MCCPs, C_{14}–C_{17}) and long chain CPs (LCCPs, $C_{>17}$). Furthermore, the degree of chlorination can vary between 30 and 70% depending on the field of application [1].

Currently, worldwide only a few laboratories analyse CPs [2], though these compounds are classified as persistent, bioaccumulate and are toxic to aquatic organisms [3]. The demonstrated presence of CPs in air, sediments, fish and marine mammals underlines the necessity for a more permanent monitoring [4–7]. CPs are listed in the priority substance list of the European water framework directive. Consequently, environmental levels of CPs should be monitored in Europe in 2006, which will require reliable analytical methods and quantification procedures [8,9]. The current standard analysis technique is high-resolution gas chromatography (HRGC) combined with high-(HRMS) or low-resolution mass spectrometry (LRMS) in the electron capture negative ion (ECNI) mode [4,10,11]. Quantification is usually performed with technical or synthetically adapted CP mixtures as well as CP compositions of defined carbon

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0021-9673/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.chroma.2005.05.061

chain lengths [4,10,12]. Congener groups with 5–10 chlorine atoms are usually quantified in environmental samples [4,10].

The high selectivity and sensitivity of ECNI-MS is well documented [13]. However, its main limitation is the strong dependence of the response factors of congeners on their degree of chlorination [14]. The use of well-defined single references compounds is not possible, since environmental samples still contain thousands of congeners of variable composition, which cannot be separated by HRGC. Therefore, only quantification of single congener groups with many unresolved isomers is possible [10].

The quantification procedure described by Tomy et al. is mainly applied [10]. However, the results are strongly influenced by the degree of chlorination of the selected technical standard [15]. Moreover, technical mixtures can contain interfering additives such as stabilizers [10]. Even mixtures from tailored synthesis do not match well with the composition of CPs in environmental samples leading to differences in response factors [4]. Tomy et al. and Coelhan et al. already reported that quantification differences of 100% and more are possible, if the chlorine content of the standard mixture is changed or does not fit to the sample [10,12]. Later, Zencak et al. quantified three SCCP mixtures with different degree of chlorination against each other and showed that errors of 65–940% can occur, when ECNI-MS is applied [15]. The quantified amount was lower, if the employed standard had a higher chlorine content and vice versa. Congeners with a higher degree of chlorination have higher response factors due to a higher electron affinity [13]. Consequently, quantification has to be carried out with a standard composition similar to that of the sample. Coelhan et al. tried to compensate this with mixtures of homologues of different chlorine contents and by selecting standards for each chain length with mass spectra as similar as possible to those of the respective homologue groups in the sample [12]. However, this also requires a large number of standard mixtures and the interpretation of the data is time-consuming. Moreover, it may be difficult to define “similar”.

Recently, three new mass spectrometric methods have been developed to minimize the quantification problem. The first one is based on electron ionization tandem mass spectrometry (EI-MS/MS) and allows a fast determination of the total CP amount, but cannot distinguish between SCCPs, MCCPs and LCCPs [16]. The second one applies negative ion chemical ionization (NICI) MS with CH_4/CH_2Cl_2 as reagent gas. This leads to equal response factors for congeners of different degree of chlorination and enables the precise determination of CP congener patterns [14]. However, it is not suitable for a high sample throughput due to a rapid contamination of the ion source [14]. The third technique uses metastable atom bombardment combined with high-resolution MS [17]. A recently published comparison showed that ECNI-LRMS, ECNI-HRMS, EI-MS/MS and NICI-MS give comparable results for standards and spiked samples. However, a difference in the CP chlorine content between sample and standard can result in deviations of >100% for ECNI-MS due to changed response factors [15].

Therefore, this study developed a compensation technique, which minimized the influence of the degree of chlorination on the response factors of different CP mixtures, when ECNI is employed. On this basis a procedure was developed, which allows quantification even when the chlorine content of reference standard and sample does not match well. Details of the approach and its performance are described and discussed.

2. Experimental

2.1. Standards

Three tailor-made SCCP mixtures ($C_{10–13}$, 51, 55.5 and 63% chlorine, 100 ng/μl, solutions in cyclohexane) and four MCCP mixtures ($C_{14–17}$, 52 and 57% chlorine, 100 ng/μl, solutions in cyclohexane) were obtained from Ehrenstorfer (Augsburg, Germany). Additionally, a 1 + 1 solution was prepared from the SCCP mixtures with 51 and 55.5% (53% Cl) as well as from the SCCP mixtures with 55.5 and 63% (59% Cl). The SCCP mixture Hordalub 80 (56% Cl) from Hoechst (Frankfurt, Germany) was diluted to 100 ng/μl in cyclohexane. The SCCP mixtures Cereclor 60 L (59% Cl) and Cerechlor 70 L (69% Cl), both from Imperial Chemical Industries (ICI, London, UK), were diluted to 107 ng/μl in cyclohexane. A 1 + 1 mixture of them (64% Cl) was used as linearity control. Four pure MCCP mixtures from ICI and of different chlorine content were diluted to 100 ng/μl in cyclohexane. The MCCP mixtures Hordalub 80 EM (49% Cl) and Hordaflex SP (56% Cl) from Hoechst (Frankfurt, Germany) and the MCCP mixture Cloparin 50 from Caffaro (Cesano Maderno, Italy) were diluted to 100 ng/μl in cyclohexane. Synthesized C_{10}-, C_{11}-, C_{12}- and C_{13}-CP mixtures of both 50% and 60% chlorine content (20 μg/μl, solution in cyclohexane) were provided by Dr. Mehmet Coelhan from the Technical University of Munich (Germany) and diluted to 100 ng/μl in cyclohexane. [$^{13}C_{10}$] *trans*-Chlordane (100 ng/μl, solution in nonane, purity 99%) was purchased from Cambridge Isotope Labs. (Andover, USA) and employed as internal standard (ISTD). ε-Hexachlorocyclohexane (ε-HCH) was obtained from Ehrenstorfer and used as recovery standard. Reference solutions for quantification of the fish liver samples contained 1500 ng of CPs, 10 ng of ε-HCH and 10 ng of [$^{13}C_{10}$] *trans*-chlordane in ca. 150 μl of cyclohexane.

2.2. Chemicals and solvents

Cyclohexane, dichloromethane and *n*-hexane for pesticide residue analysis were obtained from Scharlau (Barcelona, Spain). Florisil PR (60–100 mesh) and sodium sulphate (Pestanal grade) were purchased from Fluka (Buchs, Switzerland), and silica gel (200–400 mesh, 0.035–0.070 mm) from

CU Chemie Uetikon (Uetikon, Switzerland). All three chemicals were dried overnight at 600 °C and kept for another 6 h at 130 °C before usage.

2.3. Fish samples and clean-up

Seven cod samples (G*adus morhua*) and a dab sample (*Limanda limanda*) were collected at two different locations in the Baltic Sea (54°33.36N/10°42.13E and 54°51.76N/14°01.51E) by the Federal Research Centre for Fisheries (Hamburg, Germany) in August 2002 and August 2003. Furthermore, a flunder (*Platychtus flesus*) and five North Sea dabs (*Limanda limanda*) were caught in the North Sea in August 2003. Single livers as well as one pooled liver sample ($n = 5$) were analysed. The clean-up method is published elsewhere and therefore only briefly described [4]. 2–8 g of fish liver was homogenized with a 10-fold excess of anhydrous sodium sulphate. Ten nanograms of [$^{13}C_{10}$] *trans*-chlordane (internal standard) in 10 μl of cyclohexane was added and the sample was extracted with 250 ml of *n*-hexane/CH_2Cl_2 (1 + 1, v/v) in a glass column. After concentration, lipids were removed by column chromatography on 40 g of silica gel impregnated with 44% (w/w) of conc. H_2SO_4. The lipid-free sample was eluted with 120 ml of *n*-hexane/CH_2Cl_2 (1 + 1, v/v). A further fractionation was carried out on 16 g of Florisil (1.5% water content) with 85 ml of *n*-hexane (fraction 1), 5 ml of CH_2Cl_2 (fraction 2) and 60 ml of CH_2Cl_2 (fraction 3). The last fraction contained all CPs. Ten nanograms of ε-HCH in 10 μl of cyclohexane was added as a recovery standard to the concentrated CP fraction before analysis. This clean-up allows elimination of the interferences caused by other chlorinated compounds (e.g. toxaphenes) so that ECNI-LRMS can be applied successfully [4].

2.4. Instrumentation

Chromatographic separations were performed on an HP 5890II (Hewlett-Packard, Palo Alto, CA, USA) gas chromatograph equipped with a split/splitless injector and a fused silica capillary column (15 m, 0.25 mm i.d.) coated with a 0.25 μm thick film of DB5-MS (5% phenylmethylpolysiloxane, J&W Scientific, Folsom, CA, USA). Sample volumes of 1.5 μl were injected in the splitless mode (2 min) at an injector temperature of 275 °C. Helium (99.999%, Carbagas, Basel, Switzerland) was used as carrier gas at a column inlet pressure of 68.9 kPa (10 psi). The temperature programme was as follows: 100 °C, isothermal for 2 min, then 15 °C/min to 280 °C and isothermal for 8 min.

An HP 5989B (Hewlett-Packard) mass spectrometer was employed in the ECNI mode using methane (99.995%, Carbagas, Basel, Switzerland) as reagent gas at a pressure of 127 Pa (0.95 Torr). The electron energy was 100 eV. The ion source temperature was kept at 200 °C, the quadrupole temperature at 100 °C and the transfer line temperature at 280 °C. The most abundant isotopes of the $[M - Cl]^-$ ions of CPs and of the $[M]^-$ ion of [$^{13}C_{10}$] *trans*-chlordane were detected in the selected ion monitoring (SIM) mode with dwell times of 75 ms for each ion as described in detail elsewhere [18].

3. Results and discussion

3.1. Influence of the chlorine content

CP homologues with different chlorine contents were compared to investigate the influence of the chlorine content on the response factor. The total response factors of the CP mixtures were calculated as follows. First, the relative total CP area is needed (see Eq. (1)):

$$\text{Relative total CP area} = \sum_i \frac{\text{area } i \text{ (congener group)}}{\text{area } i \text{ (ISTD)}} \quad (1)$$

where "*i*" assigns the CP congener group. The amount of internal standard in the sample and in the standard solutions was the same in this study and could therefore be eliminated from the equations. The total response factor can then be expressed as:

$$\text{Total response factor (CP mixture)} = \frac{\text{rel. total CP area (Std.)}}{\text{amount CPs (Std.)}} \quad (2)$$

The total response factors of C_{10}-, C_{11}-, C_{12}- and C_{13}-CPs with two different degrees of chlorination are shown in Fig. 1. They increased by a factor of 2.5–5.7 from 50 to 60% Cl.

3.2. Influence of the carbon chain length

Total response factors were compared to different SCCP homologues with the same chlorine content but different chain lengths. Data were normalized to the C_{10} mixtures and are given in Fig. 2. The total response factors were hardly influenced for CPs with a degree of chlorination of 50%.

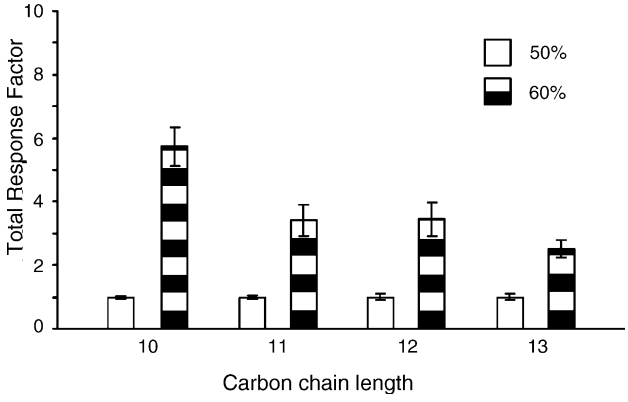

Fig. 1. Total response factors (average of three measurements) of C_{10}-, C_{11}-, C_{12}- and C_{13}-CPs determined by HRGC-ECNI-LRMS. Results were normalized to the mixtures with a chlorine content of 50%. Error bars indicate the standard deviation.

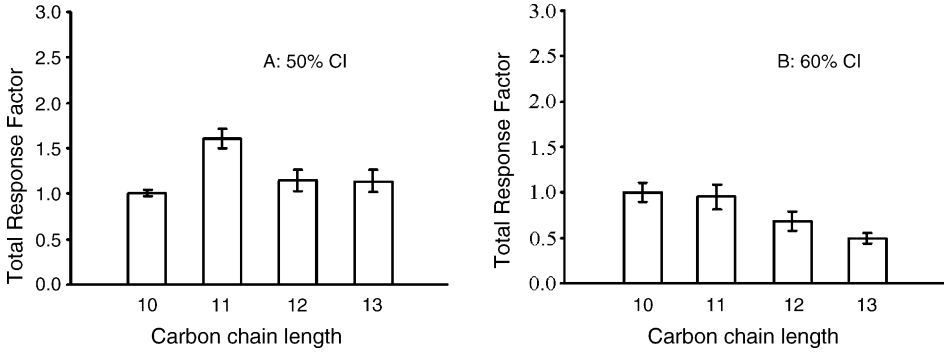

Fig. 2. Total response factors (average of three measurements) of SCCP homologues with a degree of chlorination of 50% (A) and 60% (B) determined by HRGC-ECNI-LRMS. Results were normalized to the mixtures of C_{10}-homologues. Error bars indicate the standard deviation.

They decreased slightly with increasing the chain length for 60% Cl. However, compared to the chlorine content, the differences were much lower (factor of 0.5–1.6).

3.3. Total response factors of CP mixtures

The correlation between response factor and chlorine content was investigated using SCCP mixtures. The chlorine content of a CP mixture can be calculated as shown in Eq. (3).

$$\text{Chlorine content (CP mixt.)} = \sum_i \frac{\text{rel. area (cong. group } i\text{)chlorine content (cong. group } i\text{)}}{\text{rel. total CP area}} \quad (3)$$

The relative area is the area of the congener group divided by the area of the internal standard ([$^{13}C_{10}$] *trans*-chlordane). The calculation of the chlorine content is similar to that of the average molar mass as described by Tomy et al. [10].

If determined by ECNI the chlorine content of low chlorinated CP mixtures is systematically too high, since congeners with 3 and 4 chlorine atoms are not detected and the relative abundances of higher chlorinated congeners are overestimated due to much higher response factors. Therefore, the chlorine content determined in this way always differs from the value specified by the manufacturer of the CP mixture [14]. In contrast to low chlorinated CPs, the chlorine content of highly chlorinated CPs (>65%) is slightly underestimated.

Already Tomy et al. assumed that the signal area of a congener group is proportional to the number of chlorine atoms as well as to its molar concentration. Therefore, they proposed to divide the signal area of each congener group by the number of their chlorine atoms as a quantification correction [10]. This relation was investigated in detail with seven SCCP mixtures of different composition and chlorine content (51–69%). A reasonably linear correlation was found between chlorine content and total response factor (see Fig. 3A). Slopes and intercepts deviated not more than 12% for five repetitions on five different days. Correlation coefficients (R^2) were always >0.9. The same was found for MCCPs as shown in Fig. 3B. Slopes and intercepts deviated not more than 8% for three repetitions on three different days. Correlation coefficients (R^2) were always >0.8. As can be seen in Fig. 3, a slight variation of the measured chlorine content can lead to a considerable variation in the response factor. Therefore, an accurate determination of the chlorine content is very important.

The chlorine content of technical SCCP mixtures can vary between 30 and 70%. However, the working range of ECNI-MS methods is limited. In mixtures with a chlorine content lower than 50%, many congener groups are not detected since they contain congeners with 1–4 chlorine atoms. Therefore, a mixture of a chlorine content of 51% was set as lowest point of the linearity. A mixture of 69% was chosen to cover the whole range up to highly chlorinated mixtures, although CPs with such high chlorine contents could not be detected in environmental samples. As can be seen in Fig. 3A, the

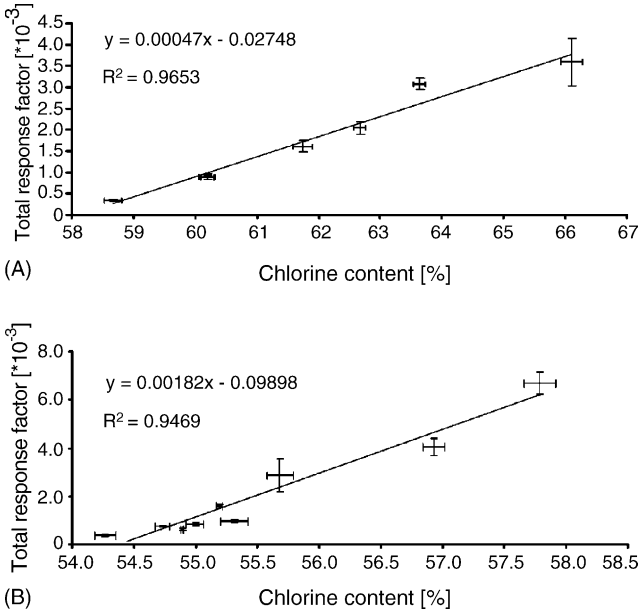

Fig. 3. Dependence of the total response factor on the degree of chlorination for seven different SCCP mixtures ((A) 51–69% chlorine, average of five interday measurements) and nine different MCCP mixtures (B) average of three interday measurements). Error bars indicate the standard deviation.

Table 1
CP quantification of different SCCP mixtures (51–69% Cl) based on chlorine content corrected total response factors: the expected amount, the measured amount and the relative error are given

SCCP mixture (% chlorine content)	Expected amount (ng)	Measured amount (ng)	Relative error (%)
Standards used for establishment of linear function ($R^2 = 0.9730$, $y = 0.00041x - 0.02391$)			
51 (58.7% Cl)	1500	1600	7
55[a] (60.2% Cl)	1500	1600	7
59 (61.7% Cl)	1600	1600	0
64 (64.5% Cl)	1100	1000	7
69 (66.1% Cl)	1600	1700	6
Control standards			
55[a] (60.2% Cl)	1500	1600	7
53 (59.8% Cl)	1500	1400	7
59 (62.7% Cl)	1500	1700	13
63 (63.6% Cl)	1500	2000	33
Hordalub 80 (56% Cl) (60.3% Cl)	1500	1900	27

The chlorine contents calculated from the ECNI-LRMS measurements are given in brackets.
[a] The CP mixture with a chlorine content of 55% was analyzed twice.

response factor varied more for this highly chlorinated mixture. The ionization might be influenced by different chemical and physical properties of highly chlorinated mixtures which have for example two chlorine atoms bound to one carbon atom (e.g. $C_{10}H_{11}Cl_{11}$).

3.4. Quantification approach

The total response factor of the CPs in the sample can be determined from the chlorine content using the linear correlation:

$$\text{Total response factor (CPs in the sample)} = ax + b \quad (4)$$

where a is the slope of the linear regression, x the chlorine content calculated from the ECNI analysis and b the axis intercept. Once, the total response factor is determined, the total CP amount in the sample can be calculated as follows:

$$\text{CP amount (sample)} = \frac{\text{relative total area (sample)}}{\text{total response factor(calculated for the sample)}} \quad (5)$$

Compared to the conventional quantification procedure, this modified quantification procedure is independent from the chlorine content of the CP standard and requires only the establishment of the correlation by determining the total response factors for a set of CP standards prior to the analysis of a series of samples.

3.5. Quantification of different SCCP mixtures

The procedure was first checked with different SCCP mixtures. Five mixtures were used to establish the linear function, and another five SCCP mixtures of different chlorine content were quantified as controls. The expected and determined amounts and deviations are listed in Table 1.

Deviations were <7% for CP mixtures being part of the correction function. Control samples with chlorine contents of 53, 55, 59 and 63% showed relative errors between 7 and 33%. This is one order of magnitude less than the systematic errors observed by Coelhan et al. [12] and Zencak et al. [15] (65–940%) and acceptable for a quantification of such complex mixtures with thousands of isomers. The conventional quantification of the SCCP mixture of 55% based on the single members of the linear function led to errors of 61, 7, 93, 113 and 373%, respectively.

3.6. Quantification of biota

Ten fish liver samples from the North and Baltic Sea were quantified by both the conventional [10] and the modified quantification procedure described above. The composition of CPs in fish can be quite different. This can be seen from the chlorine content or the average molar mass as demonstrated by other research groups [10,11]. In general, the average molar mass increases with higher chlorine content. The chlorine contents of SCCPs varied between 59 and 62% (388–422 g/mol) in fish from the North and Baltic Sea [4]. Borgen et al. reported average molar masses from 378 to 456 g/mol in freshwater fishes from different locations in Norway (chlorine contents were not specified) [11].

First, the chlorine contents of the SCCPs in the fish samples were determined by HRGC-ECNI-LRMS. The degree of chlorination varied between 59.2–62.9% (392–426 g/mol). For routine analysis of the samples only three SCCP standard were used for the establishment of the linear function (51, 55.5 and 63%, according to the manufacturer). The limited number of standard mixtures was chosen to reduce the overall time of the nevertheless long analysis procedure and to avoid the use of technical CP mixtures with additives. Therefore, the only three commercially available CP standards of 100% purity were used. Their measured chlorine contents were 58.5, 60.1 and 63.6% (389, 403, 437 g/mol, average of three measurements, relative standard deviations of less than 1%). The deviation to the manufacturer declaration is due to the reasons given before. The chlorine contents of the samples

Table 2
SCCP concentrations (ng/g wet weight) of 10 fish liver samples obtained with the described method and based on three commercial SCCP standards with different chlorine content (51, 55.5 and 63%)

	Quantification			
	According to Tomy et al. [10]			Via total response factor[a]
	Standard 51 (58.7% Cl)	Standard 55 (60.3% Cl)	Standard 63 (64.0% Cl)	
Sample 1 (61.9% Cl)	790	140	43	73
Sample 2 (62.9% Cl)	1060	180	58	82
	Standard 51 (58.2% Cl)	Standard 55 (59.9% Cl)	Standard 63 (63.4% Cl)	
Sample 3 (62.2% Cl)	210	94	21	29
Sample 4 (61.7% Cl)	360	160	37	57
	Standard 51 (58.6% Cl)	Standard 55 (60.2% Cl)	Standard 63 (63.5% Cl)	
Sample 5 (61.1% Cl)	170	81	17	34
Sample 6 (62.0% Cl)	160	76	16	24
Sample 7 (60.6% Cl)	180	88	18	47
Sample 8 (61.8% Cl)	2500	1200	250	410
Sample 9 (59.2% Cl)	730	350	73	520
Sample 10 (59.9% Cl)	56	27	6	21

The chlorine contents calculated from the ECNI-LRMS measurements are given in brackets.
[a] Linearity determined with three SCCP mixtures (51, 55.5 and 63% Cl, $R^2 = 0.999$ for samples 1 and 2, $R^2 = 0.969$ for sample 3 and 4, $R^2 = 0.964$ for samples 5–10).

were between those of the standards and none of them would therefore be ideal.

The results obtained by the correction mode and the conventional quantification procedure are listed in Table 2. Considerable differences were found, when the standards 55 and 63 were used (for example sample 8: 1200 and 250 ng/g). The corrected results were mainly between the results of the standards 55 and 63 (Table 3).

The correction was also applied to the quantification of MCCPs. The degree of chlorination of the sample CPs varied between 53.5 and 57.0% (426–456 g/mol). Only two suitable MCCP standard mixtures could be found (52 and 57%, according to the manufacturer). Their measured chlorine contents were 55.4 and 57.8% (442 g/mol, 460 g/mol, average of three measurements, relative standard deviations of 2 and 1.5%). The interday reproducibility of MCCPs was not as good as that for SCCPs. Especially low chlorinated MCCPs, such as $C_{15}H_{26}Cl_6$ had a retention time range of six minutes, which increases the possibilities of integration errors. The calculated chlorine contents of the MCCPs in samples 1, 3 and 4 were coincidentally close to one of the MCCP standards. Therefore, both calculation methods gave similar results. Sample 9 contained a high amount of lower chlorinated MCCPs. Therefore, its chlorine content was far below that of the standard mixtures, and it had to be excluded from quantification. The calculated chlorine

Table 3
MCCP concentrations (ng/g wet weight) of 10 fish liver samples obtained with the described method and based on two commercial MCCP standards with 52 and 57% chlorine content

	Quantification		
	According to Tomy et al. [10]		Via total response factor
	Standard 52 (56.3% Cl)	Standard 57 (58.0%)	
Sample 1 (56.5% Cl)	74	64	72
Sample 2 (55.7% Cl)	110	92	120
	Standard 52 (55.4% Cl)	Standard 57 (57.3%)	
Sample 3 (56.8% Cl)	62	36	39
Sample 4 (57.0% Cl)	97	56	58
	Standard 52 (55.4% Cl)	Standard 57 (57.3%)	
Sample 5 (55.0% Cl)	480	33	210
Sample 6 (56.2% Cl)	320	22	47
Sample 7 (56.7% Cl)	630	44	71
Sample 8 (55.1% Cl)	3120	220	1270
Sample 9 (53.5% Cl)	890	63	n.d.
Sample 10 (56.0% Cl)	240	17	40

The chlorine contents calculated from the ECNI-LRMS measurements are given in brackets. n.d. not determined.

content of sample 2 was slightly below that of the available standards. Consequently, the procedure by Tomy et al. led to an underestimation of the MCCP concentration.

4. Conclusions

The determination of the CP chlorine content requires the quantification of all CP congener groups in a sample. Moreover, only a limited number of CP standard mixtures with different composition and different chlorine content are commercially available. However, it is important to use a standard mixture with chlorine content similar to that of the sample to avoid systematic errors of 100% or more. The presented quantification procedure makes benefit from the linear relation between response factors and chlorine contents and allows a quantification of SCCPs and MCCPs independent from the chlorine content of the used standard mixtures. The correction mode was only tested on quadrupole MS. Therefore, it is important to check it also on other types of mass spectrometers.

Acknowledgements

We like to thank the German Environmental Protection Agency (contract no. FKZ 20025224) and the Swiss National Science Foundation (project no. 200020-109098) for financial support. We also thank Dr. Mehmet Coelhan from the Technical University of Munich and Dr. Markus Niederer from Kantonales Laboratorium Basel-Stadt for providing several CP mixtures. Special thanks go to Dr. Michael Haarich from the German Federal Institute for Fisheries for the fish samples.

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