



# Nuclear magnetic resonance as a tool to determine chlorine percentage of chlorinated paraffin mixtures

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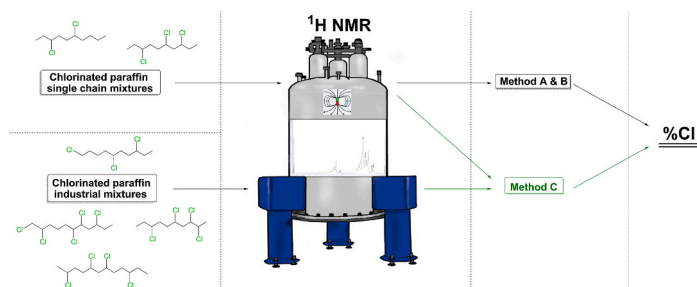
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## HIGHLIGHTS

- Synthesis of 10 single-chain chlorinated paraffin mixtures.
- Indicative NMR analysis of single polychlorinated alkanes and mixtures of diastereomers.
- Chlorine percentage calculations of industrial and single chain chlorinated paraffin mixtures using <sup>1</sup>H NMR spectroscopy.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A new simple method for chlorine percentage calculations (method C), from proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy, has been established and applied to an industrial chlorinated paraffin (CP) mixture and 13 single-chain CPs of known carbon chain lengths. Two modified methods (method A and B), originating from the work of Sprengel et al., have been utilized on the same single-chain mixtures. All samples were analysed by <sup>1</sup>H NMR and two-dimensional heteronuclear quantum coherence (HSQC) for this purpose. All three methods worked well for medium chlorinated (45–55% Cl) single-chain mixtures of known carbon chain lengths. Method A yielded the best result for mixtures of lower chlorine content (<45% Cl), method C gave better estimations for higher chlorine contents (>55% Cl). Compared to Mohr's titration, method A showed a deviation of 0.7–7.8% (3.6% average), method B 4.1–11.3% (7.0% average) and method C 0.6–11.6% (5.2% average), for all 13 single-chain mixtures. The new method C is the only method that could be applied for determining the chlorine percentage of industrial mixtures of multiple, unknown chain lengths.

## 1. Introduction

Chlorinated paraffins (CPs) are a class of industrial chemicals used as

plasticisers and flame-retardant additives in plastics and rubbers, as high-temperature, high-pressure lubricants in metalworking machinery and several other applications (Glüge et al., 2016; Tomy et al., 1998).

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Produced since early 20th century, technical CPs are described as complex mixtures of polychlorinated *n*-alkanes (i.e.,  $C_nH_{2n+2-y}Cl_y$ ), typically with a chlorination degree of 30–70% and chain lengths ranging from 10 to 36 carbons. Their high production volumes (Glüge et al., 2016), resistance to degradation and potential for bioaccumulation and toxicity make CPs of environmental concern. Analysis of CPs has been conducted for decades but, due to the complexity of the mixtures, chromatographic resolution of the constituents remains elusive (van Mourik et al., 2020). The complexity arises from the number of compounds present in the mixtures, with potentially several hundred thousand isomers (Yuan et al., 2020). Due to the challenging analysis, variations in quantitation results have been observed between laboratories, especially if they have insufficient matching of standards and sample (Fernandes, 2022). The variation accentuates the need for representative standards that matches the occurrence profile of the sample. To produce well-defined standards, reliable analysis techniques are of essence.

Nuclear magnetic resonance (NMR) spectroscopy occupies an important role for structural elucidation of molecules (Friebolin, 1998). More recently, NMR spectroscopy has been increasingly applied to the analysis of CP mixtures. Examples include GC-fractionation to attempt to elucidate the composition of enriched samples (van Mourik et al., 2021), or studying two-dimensional spectra of CPs to indicate structural motifs present in mixtures (Sprenkel et al., 2019, 2020; Yuan et al., 2020; Fernandes, 2022). Additionally, NMR spectroscopy has been used to estimate the positional selectivity of chlorines in the top one hundred isomers present in a complex mixture, using neural networks from databases of predicted one- and two-dimensional NMR spectra. (Yuan et al., 2020). Furthermore, a chlorine percentage calculation model using  $^1H$  NMR spectroscopy has recently been reported for single-chain CP mixtures (Sprenkel et al., 2019).

The aim of this study is to investigate  $^1H$  NMR as a tool for determination of chlorine percentage in CP mixtures, for both single-chain and industrial mixtures. Thirteen synthesized single-chain CP mixtures ( $C_9$ – $C_{15}$ ), one industrial mixture with multiple and unknown chain lengths, and five binary/ternary mixtures of CPs were analysed on one- and two-dimensional NMR. Stereoisomeric mixtures of CPs were also synthesized and analysed, and their analysis were used to indicate structural motifs present in complex mixtures of CPs. The data received from  $^1H$  NMR was used for calculation of chlorine percentage by three different calculation models. Two of the models A and B are modified versions of a previous calculation model (Sprenkel et al., 2019), and the third C is a new calculation model that also allows chlorine percentage estimation of industrial mixtures of multiple and unknown chain lengths. These were compared against reference values obtained by Mohr's titration for chloride content after dechlorination and in some cases chlorine specific elemental analysis.

## 2. Materials and methods

### 2.1. Chemicals

Single chain mixtures of CPs  $C_9$  to  $C_{14B}$  has been produced and donated by Chiron AS and single chain mixtures  $C_{14c}$  and  $C_{15}$  has been synthesized by Quimica del Cinca and donated by the Chlorinated Paraffin Industry Association (CPIA). Technical CP mixture ( $C_{tech}$ ) has been purchased from FUJIFILM Wako. All single-chain mixtures of CPs have been prepared synthetically and purified by flash column chromatography, excluding any inorganic material, before they were analysed by NMR spectroscopy. The consistency between the analytical results of chlorine percentage additionally indicated that potential halogen contaminants were not present or negligible.

Different mixtures of  $C_{10-12}$  and  $C_{tech}$  were weighed out accurately and mixed for chlorine percentage estimation of multicomponent mixtures by NMR method C.

Three stereoisomeric mixtures of 1,2,5,6,9,10-hexachlorododecane

(1), 1,2,6,7,10,11-hexachlorotridecane (2) and 3,4,6,7,10,11-hexachlorotetradecane (3) were also prepared by synthetic procedures that are to be published on a later date. Each CP contains compounds of different stereochemistry.

### 2.2. NMR analysis

Deuterated chloroform with 0.03 v/v% TMS was dried by shaking it with  $Na_2SO_4$  and NaOH, followed by filtration. Compounds 1, 2 and 3 (15–20 mg) and CP single-chain mixtures (100–150 mg) were dissolved in the deuterated chloroform (0.65 mL) for NMR analysis.

NMR-analysis were performed with either a Bruker 400 MHz Avance III HD equipped with a 5 mm SmartProbe z-gradient probe, or a Bruker 600 MHz Avance III HD equipped with a 5 mm cryogenic CP-TCI z-gradient probe. The resulting data were analysed in ACD/Spectrum processor 2019.2.2 (software). TMS was used as a reference peak ( $\delta$  0.00). Data for calculation of chlorine percentage are shown in SI.

### 2.3. Titration

A detailed procedure for the titrations of chlorinated compounds is described in SI (Section 1). The method was tested up against a control sample of a single CP (1,2,7,8-tetrachlorooctane) with known atomic composition and purity. The control sample was used for method validation of titration, giving a value of  $56.9 \pm 0.4\%$  Cl (theoretical 56.3% Cl) and 1.1% accuracy through 9 measurements (see SI, Section 1.3).

The general procedure involved converting organic chlorine to inorganic chloride ions by means of sodium in isopropanol followed by a standard Mohr's titration of a known volume of the analyte solution and  $K_2CrO_4$  as indicator (Asinger, 1968; Sezey and Audun, 2019). Silver nitrate was titrated into the chloride solution until formation of a dark red silver chromate precipitate appear (see SI, Section 1.1). The amount of chloride ions in solution was assumed to be equimolar to the number of chlorines in the CP mixture.

### 2.4. Chlorine percentage calculations from NMR spectroscopy

Three  $^1H$  NMR models for chlorine percentage estimations have been applied and investigated in this study, where A and B are modified literature models (Sprenkel et al., 2019). The third model C is a new calculation model with expanded opportunities for determining chlorine percentage of industrial mixtures of multiple and unknown chain lengths. The strengths and limitations of each method, when applied to various CP mixtures, will be discussed in the following section.

#### Method A

Following the  $^1H$  NMR literature method (Sprenkel et al., 2019), the  $CH_2$  and  $CH_3$  regions are integrated as a joint cluster region (see Fig. 1 (a)) and adjusted by using a stochastic probability model. See Equation (2.1) and Equation (2.2).

$$X_{CH_3/CH_2} = \frac{A_{CH_3/CH_2}}{B} \quad (2.1)$$

Where  $X_{CH_3/CH_2}$  is the adjusted area and  $A_{CH_3/CH_2}$  is the total area of  $CH_2$  and  $CH_3$ . The  $B$  describes the stochastic probability of  $CH_2$  versus  $CH_3$  occurrence in a straight-chain alkane and is given in Equation (2.2), where  $n$  denotes number of carbons (chain length) (Sprenkel et al., 2019).

$$B = 2 \cdot \frac{n-2}{n} + 3 \cdot \frac{2}{n} \quad (2.2)$$

This model assumes that all terminal positions in the alkane chains are completely occupied by protons and that chlorination at the end of the chain is negligible. Previous research has shown that terminal chlorination is negligible in CP mixtures of lower chlorine content (Yuan et al., 2020), and method A is therefore expected to give more accurate

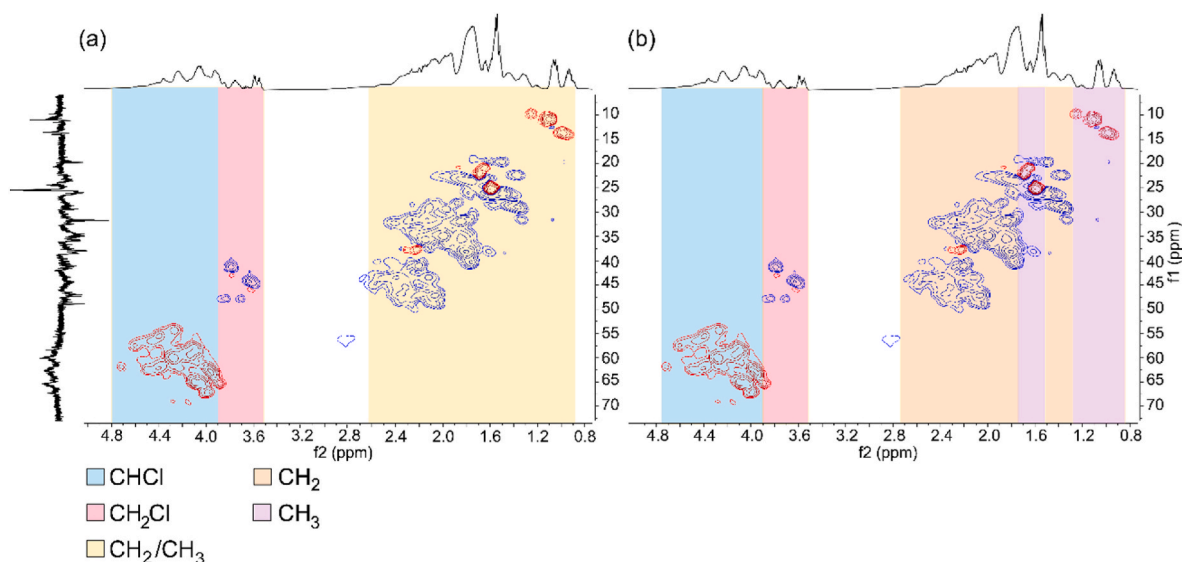


Fig. 1. Separation of the integrated areas used in (a) method A and (b) method B and C, in a  $^1\text{H}$  NMR spectrum projected onto a 2D HSQC spectrum (600 MHz,  $\text{CDCl}_3$ ).

results with lower chlorine content.

One way of minimizing the error caused by a high presence of terminal chlorines is to adjust the CHCl and  $\text{CH}_2\text{Cl}$  region individually (see Fig. 1 (a)). The individual proton integration area ( $A_{\text{CH}_x\text{Cl}_y}$ ) must be adjusted by the positional number of protons ( $x$ ), as described in Equation (2.3) to give the individual adjusted area ( $X_{\text{CH}_x\text{Cl}_y}$ ).

$$X_{\text{CH}_x\text{Cl}_y} = \frac{A_{\text{CH}_x\text{Cl}_y}}{x} \quad (2.3)$$

The remaining part of calculation A follows the reported model (Sprenkel et al., 2019). The relative area ( $A_{\text{rel},\text{CH}_x\text{Cl}_y}$ ) can hence be calculated from the general formula in Equation (2.4).

$$A_{\text{rel},\text{CH}_x\text{Cl}_y} = \frac{X_{\text{CH}_x\text{Cl}_y}}{\sum X_{\text{CH}_x\text{Cl}_y}} \quad (2.4)$$

An estimation of the number of chlorines ( $y$ ) present in an average molecule is derived from the general formula of an alkane chain ( $\text{C}_n\text{H}_{2n+2}$ ) and is described in Equation (2.5).

$$y = 2n + 2 - n \left( \left( 2 \frac{n-2}{n} + 3 \frac{2}{n} \right) A_{\text{rel},\text{CH}_3/\text{CH}_2} + 2A_{\text{rel},\text{CH}_2\text{Cl}} + A_{\text{rel},\text{CHCl}} \right) \quad (2.5)$$

The number of hydrogens can be expressed from the formula of an alkane chain when the average number of chlorines are known, and together with the chain length of the single-chain mixture, the chlorine percentage (% Cl) can be approximated by the general formula in Equation (2.6), with the atomic weights of carbon (12.011 g/mol), hydrogen (1.078 g/mol) and chlorine (35.453 g/mol) (Meija et al., 2016).

$$\% \text{Cl} = \frac{y * M_{\text{Cl}}}{n * M_{\text{C}} + (2n + 2 - y) * M_{\text{H}} + y * M_{\text{Cl}}} \times 100\% \quad (2.6)$$

#### Method B

This  $^1\text{H}$  NMR method relies upon the ability to separate all the different constitutional regions of the chlorinated alkanes ( $\text{CH}_3$ ,  $\text{CH}_2$ , CHCl, and  $\text{CH}_2\text{Cl}$ ) by chemical shifts (Sprenkel et al., 2019). The identity of these regions can be deduced from the  $^1\text{H}$  NMR spectrum and by assistance from the corresponding 2D-HSQC spectrum, see Fig. 1 (b).

The calculations are essentially the same as in method A, but all constitutional regions are integrated individually and are adjusted by a factor that represents their chemical environment, as described in Equation (2.3). These values are inserted in the equation for relative

areas (Equation (2.4)).

The estimation of number of chlorines is described in Equation (2.7).

$$y = 2n + 2 - n(3A_{\text{rel}(\text{CH}_3)} + 2A_{\text{rel}(\text{CH}_2)} + 2A_{\text{rel}(\text{CH}_2\text{Cl})} + A_{\text{rel}(\text{CHCl})}) \quad (2.7)$$

The chlorine percentage is then estimated as before, from Equation (2.6).

#### Method C

Method C is a new and simple method for chlorine percentage calculation. Unlike the two previous methods, it is also possible to perform a chlorine percentage estimation for mixtures where the chain length or average chain length is not known (industrial/technical mixtures). The constitutional regions ( $\text{CH}_3$ ,  $\text{CH}_2$ , CHCl, and  $\text{CH}_2\text{Cl}$ ) are divided in the same fashion as in method B, see Fig. 1 (b), and the individual adjusted areas are calculated as in Equation (2.3) for all regions.

The number of hydrogens present in the mixture ( $A_{\text{H}}$ ) is expressed as the sum of integrals of all constitutional regions ( $A_{\text{CH}_x\text{Cl}_y}$ ) in the  $^1\text{H}$  NMR spectrum, described in Equation (2.8).

$$A_{\text{H}} = \sum A_{\text{CH}_x\text{Cl}_y} \quad (2.8)$$

The amount of chlorines present ( $A_{\text{Cl}}$ ) correlate to the CHCl and  $\text{CH}_2\text{Cl}$  regions and can be calculated by Equation (2.9).

$$A_{\text{Cl}} = A_{\text{CHCl}} + \frac{A_{\text{CH}_2\text{Cl}}}{2} \quad (2.9)$$

An estimation of the average chain length can be derived from the general equation for straight chain alkanes, as shown in Equation (2.10).

$$n = \frac{A_{\text{H}} + A_{\text{Cl}} - 2 * SF}{2} \quad (2.10)$$

Where  $SF$  is a scaling factor to account for incorrect scaling of the integral, much like what is done for a single compound, where a peak corresponding to a known number of protons is set as a reference for the rest of the peaks.  $SF$  is derived from the possible end positions for an alkane, equal to 6, and the peak clusters that corresponds to end positions. For each  $\text{CH}_2\text{Cl}$ , there must be a Cl population that is half the size of the proton population. The expression for the  $SF$  is presented in Equation (2.11).

$$SF = \frac{6}{A_{\text{CH}_3} + A_{\text{CH}_2\text{Cl}} + 0.5A_{\text{CH}_2\text{Cl}}} \quad (2.11)$$

Now that all atoms are 'counted', the chlorine percentage can be calculated from Equation (2.12).

$$\%Cl = \frac{M_{Cl} * A_{Cl}}{M_H * A_H + M_{Cl} * A_{Cl} + M_C * n} \quad (2.12)$$

### 3. Results and discussion

#### 3.1. Indicative NMR analysis

Proton NMR of single chlorinated alkanes can provide some indicative results for proton NMR spectra of complex mixtures (Sprengelet al., 2019; Yuan et al., 2020). Which shifts that are expected to belong to certain motifs can be elucidated by their presence in either the NMR spectra of known single compounds or stereoisomeric mixtures of CPs.

Published NMR data of single isomer CPs or stereoisomeric mixtures are sparse, but a few compounds has been briefly discussed and elucidated in the literature (Beaume, 2005; Coelhan, 2003). There are also NMR data available for short, chlorinated alkanes (chlorobutanes, etc.) in databases (SDBSWeb, 2021). By combining these data, some general trends for the CH<sub>3</sub> shifts become apparent (see Table 1).

Methyl groups with two geminal chlorines in  $\alpha$ -position (CH<sub>3</sub>-CCl<sub>2</sub>-) give proton shifts around 2.2 ppm, protons with one vicinal chlorine in  $\alpha$ -position (CH<sub>3</sub>-CHCl-) give a shift in the range of 1.5 ppm and isolated CH<sub>3</sub> groups (chlorine in  $\beta$ -position or further) give shifts near 1.0–0.9 ppm. The exact shifts will vary slightly around these generalizations, depending on other specific structural motifs present in complex mixtures. A visualization of this is shown in Figure 17.1 in SI, which also shows how complex the separation of integrals in the CH<sub>2</sub>/CH<sub>3</sub> region can be.

A comparison of the CHCl/CH<sub>2</sub>Cl region of the three polychlorinated alkanes in Fig. 2 shows a general trend for compounds with vicinal chlorines.


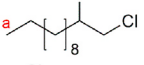


The effect of chlorine on the chemical proton shift in -(CHCl) <sub>$\alpha$</sub> -CHCl-(CH<sub>2</sub>) <sub>$\alpha$</sub> -C <sub>$\beta$</sub> -C <sub>$\gamma$</sub> - either at  $\beta$ - or  $\gamma$ -position is demonstrated in Fig. 2. Position H-4 and H-6 in compound 3 has a shift of 4.50–4.20 ppm from chlorines in  $\alpha'$  and  $\beta$ -position, whereas H-7 and H-10 has a shift of 4.10–4.07 ppm due to chlorines in  $\alpha'$  and  $\gamma$ -position. Having only a chlorine in  $\alpha'$ , as in position H-3 and H-11 in compound 3, gives a shift around 4.01–3.97 ppm. Compounds 1 and 2 shows similar proton shifts.

The order of the NMR signals follows the expected inductive substituent effect of an alkane, where the effects are more prominent when the substituents are in closer proximity of the observed proton (Friebolin, 1998). The nearby chlorines cause deshielding of the proton nucleus which experiences an increased magnetic field.

#### 3.2. Chlorine percentage calculations

The results of the <sup>1</sup>H NMR chlorine percentage calculations of fourteen different chlorinated paraffin mixtures are listed in Table 2, and

**Table 1**  
<sup>1</sup>H and <sup>13</sup>C NMR (CDCl<sub>3</sub>) spectral data for CH<sub>3</sub>-groups with different methylene chlorine neighbor substitution pattern. Includes 2-chlorobutane (SDBSWeb, 2021), 2,3-dichlorobutane (SDBSWeb, 2021), 2,2-dichloropropane (SDBSWeb, 2021), and 1,2-dichlorododecane (this work).

Name	Structure	Position	<sup>1</sup> H NMR shift [ppm]	<sup>13</sup> C NMR shift [ppm]
2-Chlorobutane		a b	~1.5 ~1.0	~25 ~11
1,2-Dichlorododecane		a	~0.9	~14
2,3-Dichlorobutane		a	~1.6	~20–22
2,2-Dichloropropane		a	~2.2	~39

values obtained from Mohr titration are displayed as a reference.

Elemental analysis was conducted for C<sub>12</sub>A and C<sub>tech</sub>, giving values of 53.2% Cl and 41.5% Cl, respectively, for direct measurements of the Cl-atom. Chlorine percentages was also calculated from elemental analysis of the C-, H-, (S-), and N-atoms, assuming no other elements were present, where for C<sub>12</sub>A was found 56.2% Cl and for C<sub>tech</sub>, 41.3% Cl.

Measurement uncertainty of the NMR methods A, B and C is mainly attributed by operator error (integration error) or sample error (such as inhomogeneity). Impact of integrational error is described below and summarized in Fig. 4, whereas total measurement uncertainty was calculated for one single-chain mixture. The chlorine percentage was estimated by all three methods by four individual samples of the C<sub>12</sub>A mixture (for data see SI, Section 7.1) and measurement uncertainty was determined to be 0.4% Cl for method A, 0.2% Cl for method B and 0.7% Cl for method C.

Fig. 3 shows a graphical representation of the experimental results, from Table 2, of the mixtures that were titrated.

The <sup>1</sup>H NMR methods A, B and C give similar estimated values, slightly on the lower side of the titration curve. This is expected as <sup>1</sup>H NMR will neither account for the carbons with full chlorine occupancy nor potential inorganic chloride contamination.

Compared to the titration approach, the NMR methods are much quicker and easier to perform. There is also a higher probability of user error with titration. Among these, not obtaining full conversion for the dechlorination, inaccurate measurements or equipment, inappropriate conditions, and difference in perception of endpoint. The cost of reagents used for titration may also surpass the cost of an NMR experiment. Finally, whereas NMR analysis is non-destructive, the titration will consume the sample in the dechlorination step.

#### 3.3. Chlorine percentage of binary and ternary CP mixtures

Unlike the two other methods, method C can estimate chlorine percentages for mixtures of different and unknown chain lengths. In Table 3 we present our <sup>1</sup>H NMR results with a binary mixture of a low (ca 40% Cl) and high-chlorinated (ca 60% Cl) CPs (Entry 1), a binary mixture of a medium (ca 50% Cl) and high-chlorinated CPs (Entry 2), and three ternary mixtures of CPs (Entries 3–5). Calculations are described in SI, Section 16.

Comparable chlorine percentages were obtained between the sum of individual single-chain CPs (method C<sup>1</sup>) and <sup>1</sup>H NMR estimations of the mixture (method C). Highest deviation of 1% Cl was observed for the low- and high-chlorinated CP mixture (Entry 1) due to extended overlap in the CH<sub>2</sub>/CH<sub>3</sub> region (observed by <sup>1</sup>H NMR and HSQC) and less accurate integration.

#### 3.4. Limitation of the models

The three proposed <sup>1</sup>H NMR methods all suffer from some

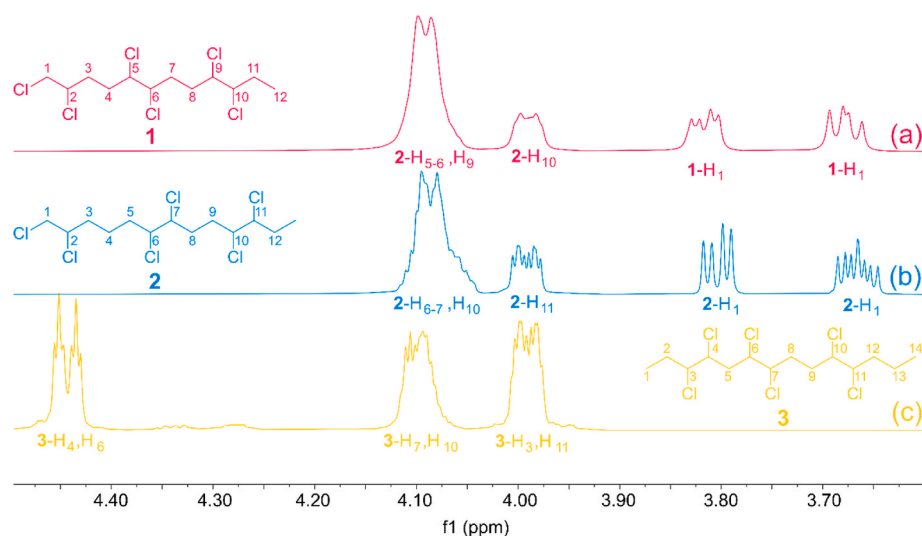


Fig. 2. The chlorinated regions in the  $^1\text{H}$  NMR spectra (600 MHz,  $\text{CDCl}_3$ ) for stereoisomeric mixtures of (a) 1,2,5,6,9,10-hexachlorododecane (1), (b) 1,2,6,7,10,11-hexachlorotridecane (2) and (c) 3,4,6,7,10,11-hexachlorotetradecane (3).

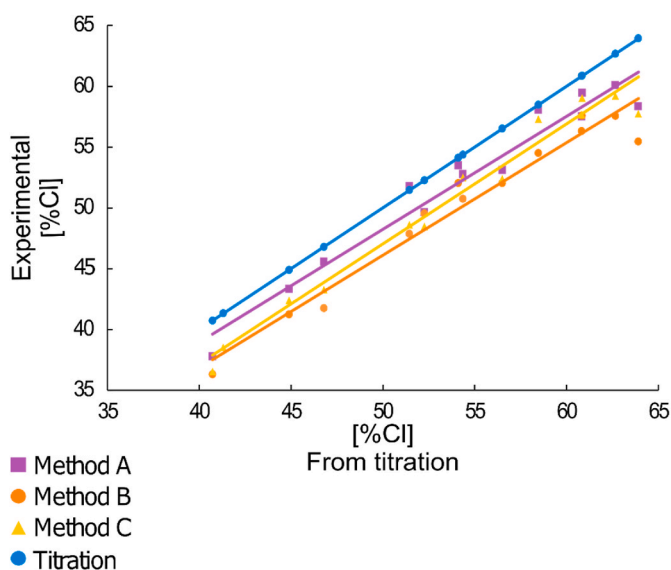


Fig. 3. Graphical representation of the chlorine percentage data for the NMR methods A, B and C compared to the values from titration.

limitations. They are all based upon the assumption that full chlorination of a single carbon ( $-\text{CCl}_2-$ ,  $-\text{CCl}_3$ ) does not take place, as they rely upon integration of the  $^1\text{H}$  NMR spectra (Sprenkel et al., 2019). Hence, all the mixtures are likely to give an underestimation for the chlorine percentages since they do not take constituents that are fully chlorinated into account. This is expected to be more problematic for highly chlorinated mixtures, as they are expected to contain more of fully chlorinated single carbons (Yuan et al., 2020).

Method A gives the highest general chlorine percentage of the three methods (see Fig. 3), which is likely due to the assumption that all ends are populated by hydrogens. The advantage using a stochastic model for the  $\text{CH}_3/\text{CH}_2$  region is still valid, as the amount of  $\text{CH}_3$  with a shift around  $\delta$  2.2 ppm increases and is in complete overlap with the  $\text{CH}_2$  region. However, the number of terminal chlorines will increase with a higher chlorination degree and the validity of the assumption of full terminal proton occupancy becomes debatable. A higher estimation of the degree of chlorination may look desirable as all methods give an underestimation when  $-\text{CCl}_2-$  and  $-\text{CCl}_3$  is present, nevertheless the

Table 2

Chlorination percentage calculation of thirteen single-chain and one technical mixture of CP using the  $^1\text{H}$  NMR methods A, B and C, and Mohr titration. Standard error of titration is given with a 99% confidence interval.

Mixture	Chemical formula	Method A [%]	Method B [%]	Method C [%]	Titration <sup>a</sup> [%]
C <sub>9</sub>	C <sub>9</sub> H <sub>20-y</sub> Cl <sub>y</sub>	51.8	47.9	48.6	50.2 ± 0.1
C <sub>10A</sub>	C <sub>10</sub> H <sub>22-y</sub> Cl <sub>y</sub>	52.8	50.7	52.5	54.4 ± 0.1
C <sub>10B</sub>	C <sub>10</sub> H <sub>22-y</sub> Cl <sub>y</sub>	60.1	57.6	59.2	62.7 ± 0.3
C <sub>11A</sub>	C <sub>11</sub> H <sub>24-y</sub> Cl <sub>y</sub>	53.1	52.0	52.1	56.5 ± 0.1
C <sub>11B</sub>	C <sub>11</sub> H <sub>24-y</sub> Cl <sub>y</sub>	58.3	55.5	57.7	63.9 ± 0.2
C <sub>12A</sub>	C <sub>12</sub> H <sub>26-y</sub> Cl <sub>y</sub>	53.5	52.0	53.8	54.1 ± 0.7 <sup>b</sup>
C <sub>12B</sub>	C <sub>12</sub> H <sub>26-y</sub> Cl <sub>y</sub>	58.1	54.5	57.3	58.5 ± 0.2 <sup>c</sup>
C <sub>13A</sub>	C <sub>13</sub> H <sub>28-y</sub> Cl <sub>y</sub>	45.6	41.8	43.3	46.8 ± 0.1
C <sub>13B</sub>	C <sub>13</sub> H <sub>28-y</sub> Cl <sub>y</sub>	57.5	56.3	57.7	60.8 ± 0.1
C <sub>14A</sub>	C <sub>14</sub> H <sub>30-y</sub> Cl <sub>y</sub>	37.8	36.3	36.5	40.7 ± 0.1
C <sub>14B</sub>	C <sub>14</sub> H <sub>30-y</sub> Cl <sub>y</sub>	43.3	41.2	42.4	44.9 ± 0.1
C <sub>14C</sub>	C <sub>14</sub> H <sub>30-y</sub> Cl <sub>y</sub>	59.5	57.6	59.0	60.9 ± 0.1
C <sub>15</sub>	C <sub>15</sub> H <sub>32-y</sub> Cl <sub>y</sub>	49.6	49.5	48.5	52.3 ± 0.2
C <sub>tech.</sub>	C <sub>n</sub> H <sub>2n+2-y</sub> Cl <sub>y</sub>	–	–	38.5	40.3 ± 0.7

<sup>a</sup> Average value of three titrations.

<sup>b</sup> Average value of nine titrations.

<sup>c</sup> Average value of six titrations.

results may be “right for the wrong reasons”.

Model B and C rely on individual integration of the  $\text{CH}_2$  and  $\text{CH}_3$  region, which in most cases can be readily distinguished. It becomes more complex at the extremities of lower and higher chlorination degrees for the individual single-chain CPs and mixtures of these. For mixtures with lower chlorination percentages the  $\text{CH}_2$  region will experience less deshielding from nearby chlorines and move upfield towards the  $\text{CH}_3$  region. Conversely, as the chlorination degree becomes higher, the mixtures will contain more  $\text{CH}_3$  groups that will overlap with the  $\text{CH}_2$  region, see Fig. 17.1 (SD). As a result, mixtures of single-chain and technical CPs of low and high-chlorination degree will give a less accurate integration due to overlap.

Fig. 4 shows a model of how the chlorine percent will vary if the  $\text{CH}_3$  area is 0–20% over- and underestimated for the three single-chain mixtures C<sub>10B</sub> (ca 60% Cl), C<sub>12A</sub> (ca 55% Cl) and C<sub>14A</sub> (ca 40%).

Method C is relatively robust in terms of integrational error, while a higher variation can be seen for method B, especially at lower chlorine percentages (Fig. 4 (a)).

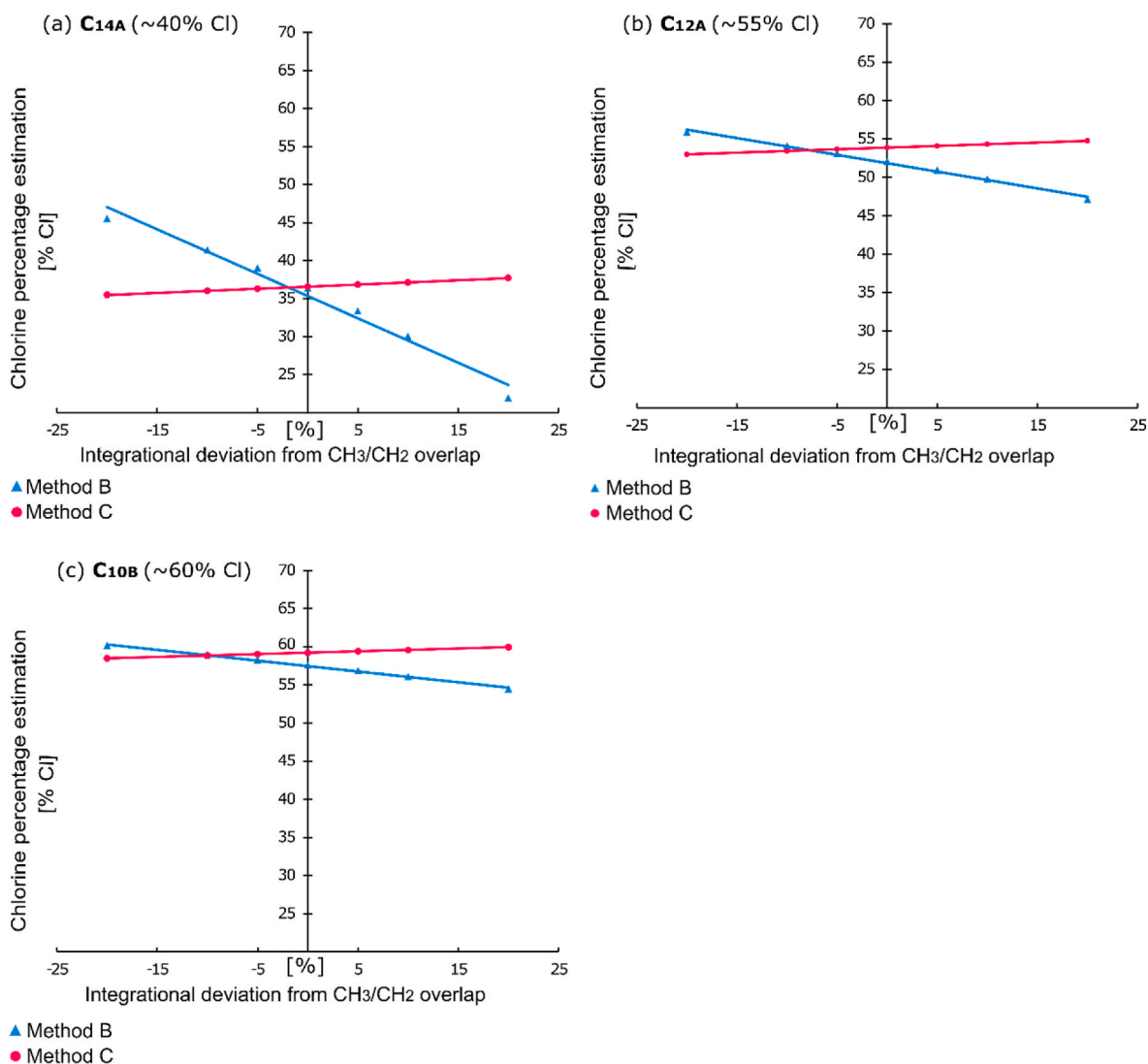


Fig. 4. Variation in the chlorine percentage calculation of NMR method B and C when over- and underestimating the area integration of CH<sub>3</sub> versus the CH<sub>2</sub> of (a) C<sub>14A</sub>, (b) C<sub>12A</sub> and (c) C<sub>10B</sub>.

Table 3

Chlorination percentage estimation of binary and ternary single-chain CP mixtures from 1H NMR spectroscopy using method C. Sum method C<sub>i</sub> (%Cl<sub>mix</sub>) was calculated using values for the individual single-chain mixtures in Table 2.

Entry	Components	Wt. Fraction	Sum method C <sup>a</sup> [%]	Method C [%]
1	C <sub>tech</sub>	0.50	49.0	48.0
	C <sub>10B</sub>	0.50		
2	C <sub>10A</sub>	0.49	55.9	55.1
	C <sub>10B</sub>	0.51		
3	C <sub>10B</sub>	0.41	55.5	54.4
	C <sub>11A</sub>	0.28		
	C <sub>12A</sub>	0.31		
4	C <sub>10A</sub>	0.36	53.8	53.9
	C <sub>11A</sub>	0.33		
	C <sub>12B</sub>	0.30		
5	C <sub>10A</sub>	0.44	56.8	56.1
	C <sub>10B</sub>	0.30		
	C <sub>11B</sub>	0.44		

<sup>a</sup> Calculated from the formula:  $\%Cl_{mix} = \sum_n X_n \%Cl_n$ , where  $X_n$  is the weight fraction and  $\%Cl_n$  is the chlorine percentage for individual single-chain mixture  $n$ .

#### 4. Conclusion

A new calculation method from <sup>1</sup>H NMR, and two modifications of a previous model, was used to determine the chlorine weight percentage of CP mixtures. Accurate and simple methods for analysis and assessment of mixtures is helpful in the process towards more available standards for CP analysis. The newly developed calculation model (model C) provides an easy and accessible way to determine the chlorine percentages of both single-chain mixtures, as well as technical CP mixtures of multiple, unknown chain lengths. The possible complication of this method, due to overlap between the CH<sub>2</sub> and CH<sub>3</sub> region in the <sup>1</sup>H NMR spectrum, was shown to have only a limited effect on the results.

#### Credit authorship contribution statement

Solveig Valderhaug: Conceptualization, Investigation; Data curation; Formal analysis; Investigation; Methodology; Visualization; Writing – Original Draft. Huiling Liu: Conceptualization, Project administration; Supervision; Validation; Writing – review & editing. Alexey Gorovoy: Investigation. Jon Eigill Johansen: Funding acquisition; Project administration; Validation. Louise van Mourik: Writing – review & editing. Jacob de Boer: Writing – review & editing. Odd Reidar Gautun: Conceptualization, Supervision; Validation; Writing – review & editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2022.136312>.

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