

CHIRON  
CHIRON  
CHIRON

Catalogue No.: S-4513-K-T  
No. Compounds: 16  
**CHIRON CHIRON CHIRON** Deuterated IS All-in-1  
1000 µg/mL in toluene  
For research and analytical purposes  
Chiron AS Stiklestadveien 1  
www.chiron.no

Your  
**Quality**  
is our  
**Business**



Your **quality**  
is our **business**

A close-up photograph of a single drop of golden-brown liquid, likely petroleum, falling and creating ripples on a surface. The background is a soft, out-of-focus gradient of brown and orange.

Petroleum

A photograph of a laboratory setting with a blue tint. It shows various pieces of glassware, including beakers and test tubes, some containing liquids. The lighting is dramatic, highlighting the textures of the glass and the colors of the liquids.

Toxicology

A photograph of fresh produce including a halved orange, an apple, and several bowls of different types of grains or powders. The lighting is warm and focused on the food items.

Food safety

A photograph of a globe of the Earth resting on a green grassy field. The globe is the central focus, showing the continents and oceans. The background is a soft, hazy landscape.

Environment



# New generation of reference standards for chlorinated paraffins

The Eurostars CHLOFFIN, the EU GreenREF and REVAMP projects

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## About CPs - What are they?

Complex mixtures of polychlorinated paraffins (CPs)

CPs are subdivided according to their carbon chain length:

- Short chain CPs (SCCPs, C10–13)
- Medium chain CPs (MCCPs, C14–17)
- Long chain CPs (LCCPs, C>17)

Degree of chlorination CPs can vary between 30 and 70 wt%

**SCCP**  
12425.10  
2,3,4,5-Tetrachlorododecane

**MCCP**  
141331.15  
3,4,7,8,14,15-Hexachloropentadecane

**LCCPs**  
14701.18  
3,4,6,7,9,10,15,17,18-Octachlorooctadecane



## Why are they important?

- ☠ Emerging environmental concern
- ☠ High volume of production  
(*>2 million tonnes per yr*)
- ☠ Long-range transport
- ☠ Persistence in the environment
- ☠ Bio-accumulation
- ☠ Toxicity (Carcinogenic)



SCCPs were classified as POPs under the UN Stockholm Convention in 2017.

Placed on several monitoring lists, such as the 2000/60/EC Water Framework Directive.

Toxicity and transformation studies on MCCP and LCCP is scarce.

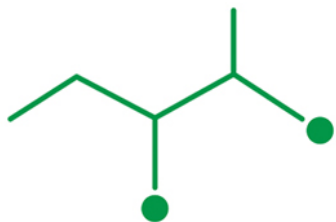
## Current challenges

- No suitable and generally accepted **reference standards** are commercially available yet.
- Currently available standards differ significantly in chain length and Cl distribution from those seen in technical mixes and the environment.
- CP mixtures used today for quantification are not well characterised nor purity assessed.
- Only semi-quantitative (sum of SCCP, MCCP and LCCP)

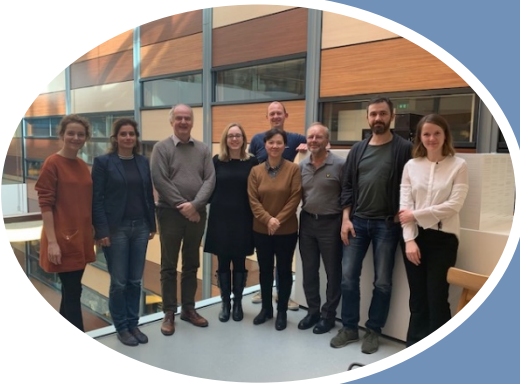




# Chloffin



The **EUROSTARS CHLOFFIN** Project,  
new standards for the analysis of  
chlorinated paraffins



VRIJE  
UNIVERSITEIT  
AMSTERDAM



**CHLOFFIN consortium**

[www.chloffin.eu](http://www.chloffin.eu)





## CHLOFFIN aims

To develop **CP standards with defined composition** and **response factors**, which are similar to industrial mixtures.

These standards will enable **accurate quantification** of CPs as well as helping in **distinguishing the various congener groups** according to carbon chain length and chlorine content.

- **40 individual CP standards** – focus on new generation of CPs
- **8 <sup>13</sup>C-labelled individual CPs**
- **10 congener mixtures**
- **1 matrix CRM**



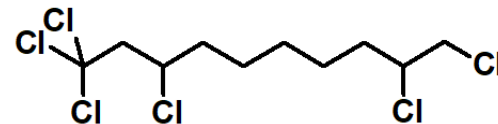
## THREE GENERATIONS INDIVIDUAL CPs DEVELOPED

### 1<sup>st</sup> Generation – CPs with terminal and geminal chlorines

Three or more chlorines at the end of the chain

Will elute differently and are useful internal standards

Not present in commercial mixes



ICS > 13 > 13.060 > 13.060.50

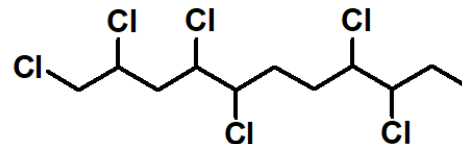
#### ISO 12010:2019

Water quality — Determination of short-chain polychlorinated alkanes (SCCP) in water — Method using gas chromatography-mass spectrometry (GC-MS) and negative-ion chemical ionization (NCI)

### 2<sup>nd</sup> Generation – CPs with 1 or 2 terminal chlorine(s)

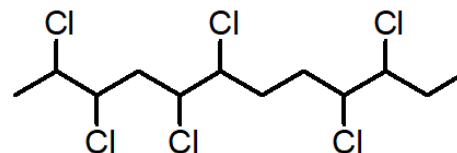
One or two chlorines at the end of the chain

Minor quantities in commercial mixes



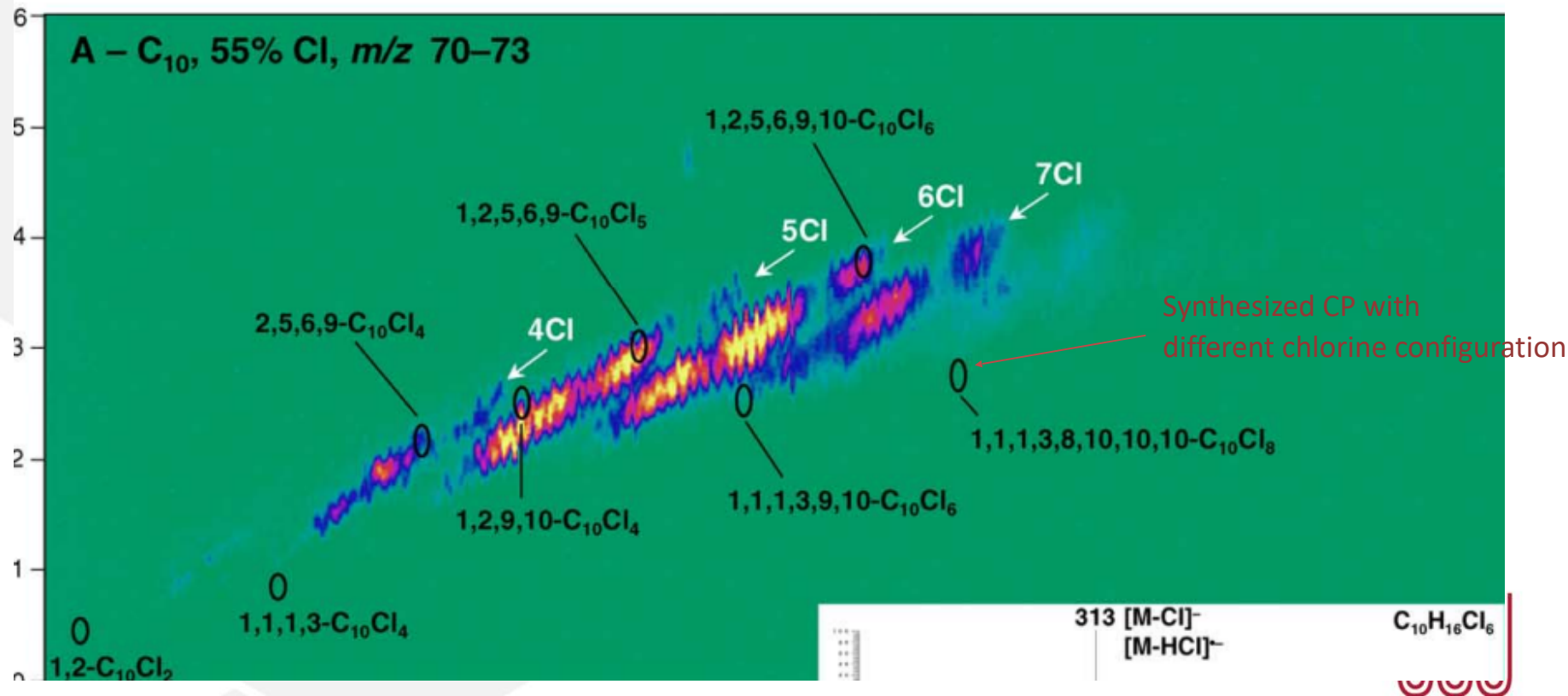
### 3<sup>rd</sup> Generation – CPs with all chlorines on the chain

Most similar to the majority of compounds in the commercial mixes



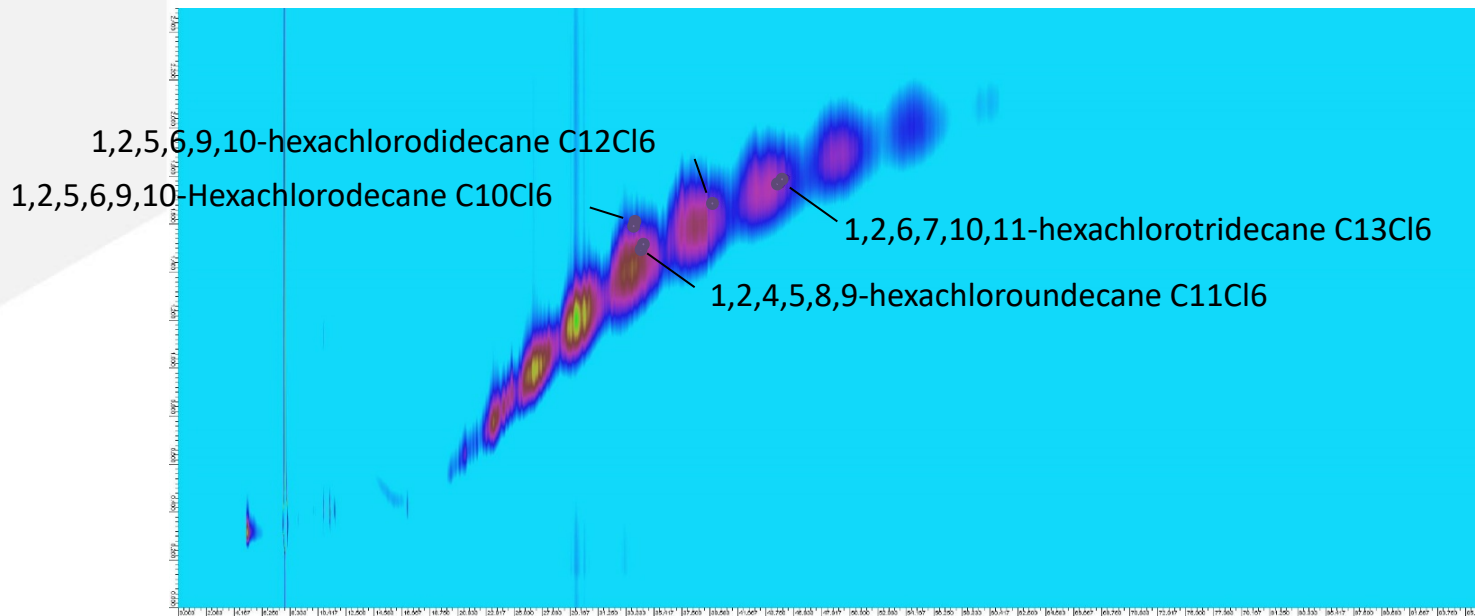
# 2005 Jacob de Boer, Pim Leonards & Peter Korytar: Start using GCxGC for CP analysis

*P. Korytár et al. / J. Chromatogr. A 1086 (2005) 71–82*



GCxGC chromatogram with technical mixture SCCP C10 55% Cl and synthesized single congener standards

**2020 Jacob de Boer, Louise van Mourik, (Sicco Brandsma), Chiron & EC JRC Geel:**  
**First results of the CHLOFFIN project: 4 SCCP single congener standards –**  
**with comparable Chlorine configuration**



**Figure:** GCxGC chromatogram with technical mixture SCCP C10-13 55% Cl and first 4 SCCP single congener standards from CHLOFFIN project



# Results – CHLOFFIN and greenREF

- A total of 96 single CP congeners are made available, both SCCPs, MCCPs and LCCPs

[sales@chiron.no](mailto:sales@chiron.no)

- Totally 22 single chain mixtures are prepared, %Cl: 50-60%
- Totally 8 <sup>13</sup>C SCCPs, MCCPs and LCCPs were synthesized
- 2 common calibration mixtures for Fish matrix material certification by EU (JRC)

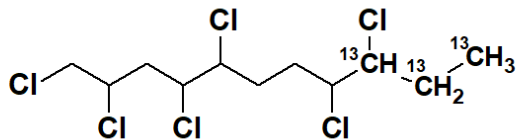


## 22 Single chain mixtures made

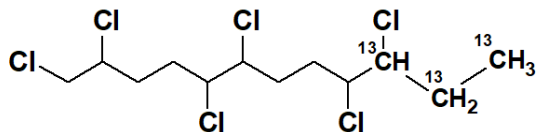
Chain length	Low Chlorine	High Chlorine
	%Cl (NMR )	%Cl (NMR )
<b>SCCPs</b>		
C9 (vSCCP)	48.5 %	N/A
C10	52.5 %	58.4 %
C11	52.3 %	57.6 %
C12	53.8 %	57.3 %
C13	45.9%	60.0 %
<b>MCCPs</b>		
C14	49.2%	58.7 %
C15	47.7%	59.3%
C16	51.5%	58.4%
C17	56.3%	60.3%
<b>LCCPs</b>		
C18	56.9%	58.4%
C19	N/A	N/A
C20	38.0%	59.0%



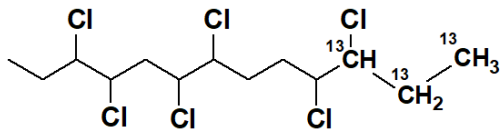
# $^{13}\text{C}$ -labelled SCCPs synthesized: $\text{C}_{11-13}\text{Cl}_6\text{-}^{13}\text{C}_3$



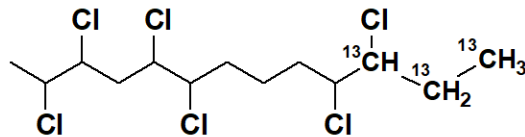
CLF15135.11



CLF15213.12

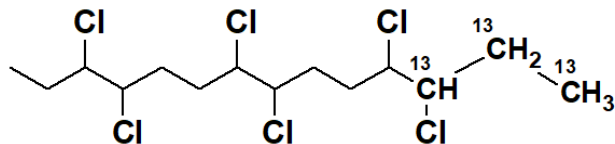


CLF15223.13

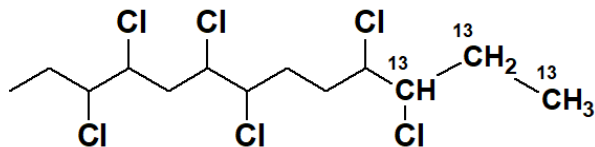


CLF15357.13

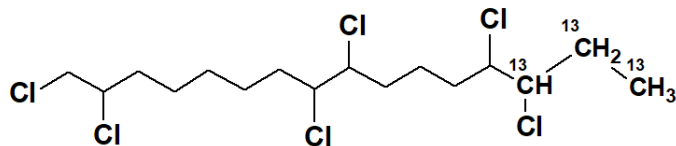
# $^{13}\text{C}$ -labelled MCCPs synthesized: $\text{C}_{14-16}\text{Cl}_6\text{-}^{13}\text{C}_3$



CLF15214.14



CLF15224.15

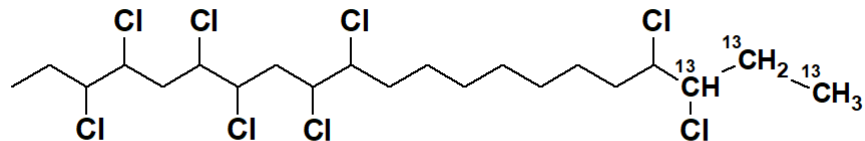


CLF15215.16





## 13C-labelled LCCPs synthesized: C<sub>21</sub>Cl<sub>8</sub>-<sup>13</sup>C<sub>3</sub>

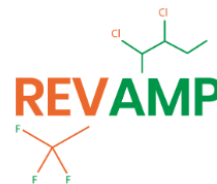


CLF15338.21

## 13C-labelled CPs synthesis: next steps

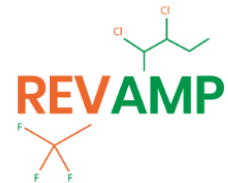
More labelled CPs

More numbers of 13C labelling?

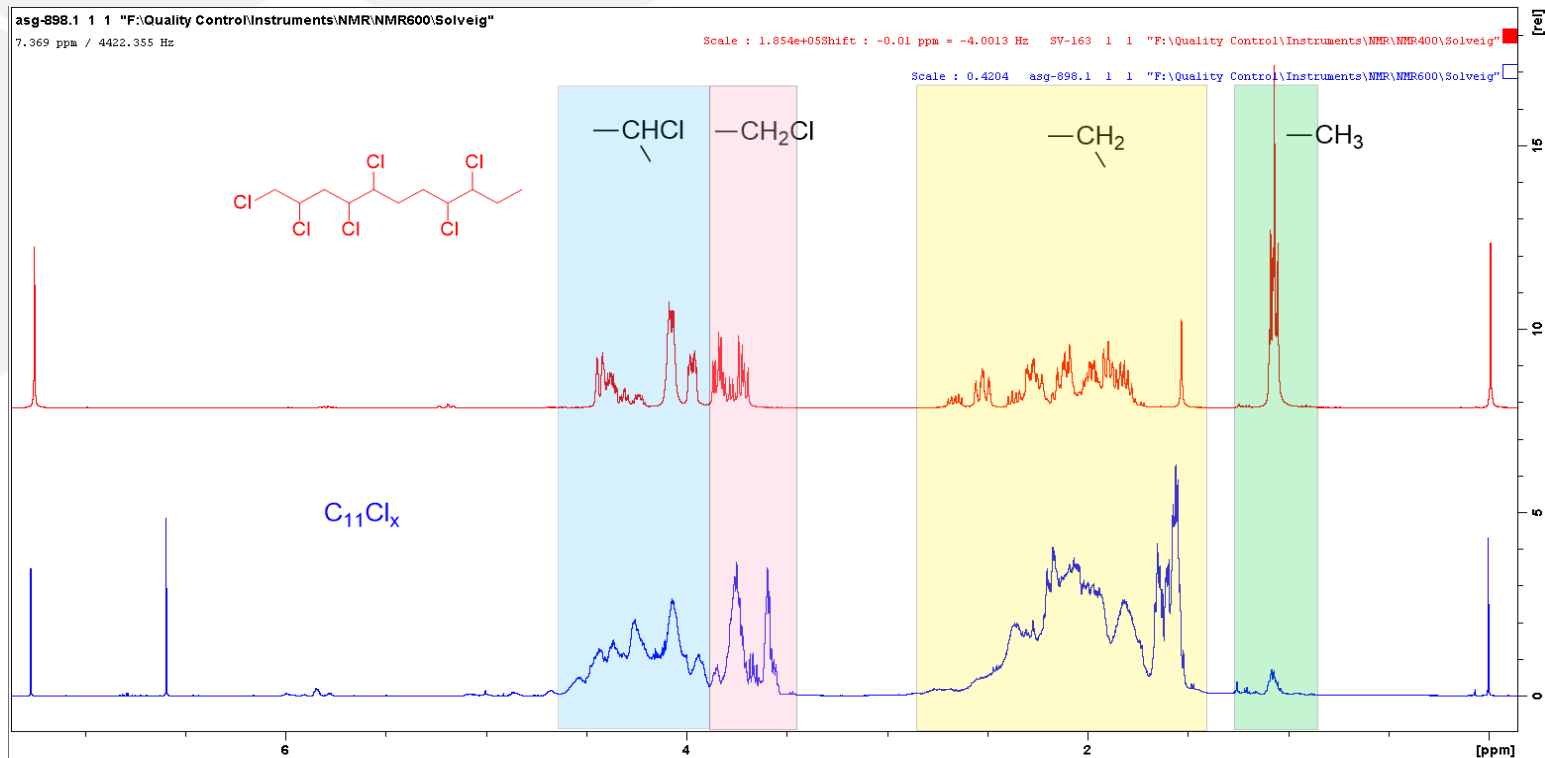


# ANALYTICAL METHODS USED

- GC-MS, GC-FID
- High res GC-MS
- LC-MS
- NMR
- TGA (Water, ash, and solvents)
- Chlorine content
  - by titration
  - by elemental analysis
  - By NMR methods
- X-ray



# Chlorine content by NMR



# Chlorine content by NMR



%Cl Calculation by NMR area

$$X_{[CH_3^-, -CH_2]} = \frac{A_{[CH_3^-, -CH_2]}}{2 \frac{x-2}{x} + 3 \frac{2}{x}}$$

$$A_{sum} = A_{[-CHCl-]} + X_{[CH_3^-, -CH_2]}$$

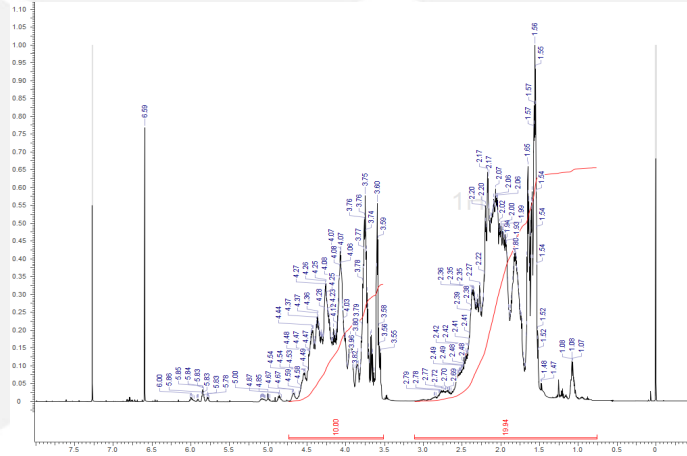
$$A_{rel[-CHCl-]} = \frac{A_{[-CHCl-]}}{A_{sum}}$$

$$A_{rel[CH_3^-, -CH_2]} = \frac{X_{[CH_3^-, -CH_2]}}{A_{sum}}$$

$$y = 2x + 2 - x(A_{rel[-CHCl-]} + A_{rel[CH_3^-, -CH_2]} * 2 * \frac{x-2}{x} + 3 * \frac{2}{x})$$

$$Cl\% = \frac{y * M_{Cl}}{x * M_c + (2x + 2 - y) * M_H + y * M_{Cl}}$$

# Chlorine content by NMR



## C11 Mix

### By NMR area

A (CH3-/CH2-)	19,57
A (-CHCl-)	10
X (CH3-/CH2-)	8,96958333
Asum	18,9695833
Arel (-CHCl-)	0,47284029
Arel (CH3-/CH2-)	0,47284029
y	4,28763152
Cl%	0,50002709

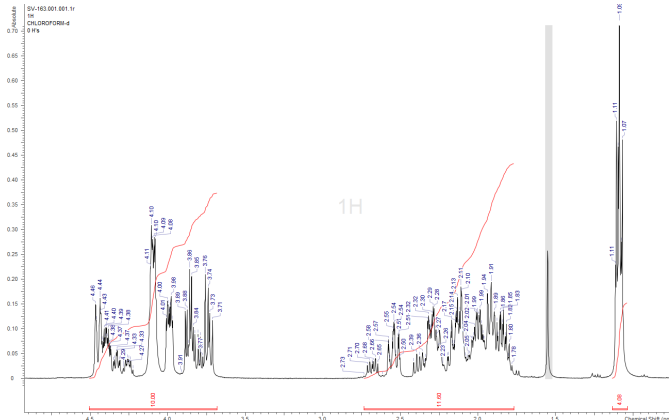
## 1,2,4,5,8,9-Hexachloroundecane

### By NMR area

A (CH3-/CH2-)	15,69
A (-CHCl-)	10
X (CH3-/CH2-)	7,19125
Asum	17,19125
Arel (-CHCl-)	0,41830873
Arel (CH3-/CH2-)	0,41830873
y	5,86904675
Cl%	0,58044737

### By Mw

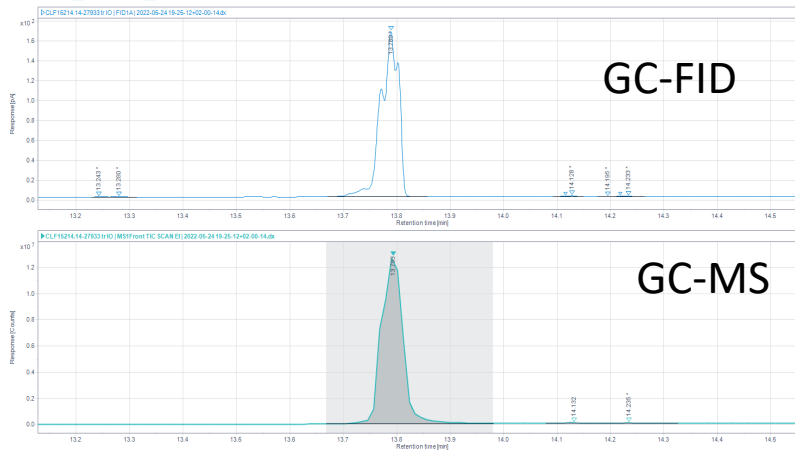
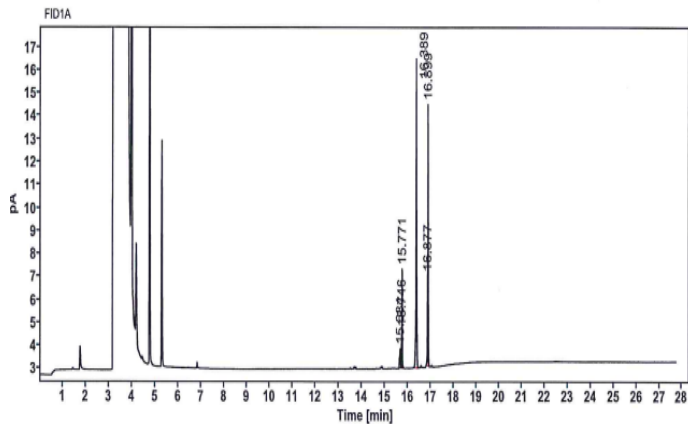
Mw	362,97
Cl%	0,58599884



## CLF-5248 Common Calibrant mix of SCCP single congeners

Cat. No	Component	Chromat. Purity (%)	Loss on Drying (%)	Residue on Ignition (%)	Concentration ( $\mu\text{g mL}^{-1}$ )
CLF12284.10	1,2,5,6,9,10-Hexachlorodecane	99.4	0.2	2.6	4
CLF14069.11	1,2,4,5,8,9-Hexachloroundecane	95.9	<0.1	0.8	13
CLF14072.12	1,2,5,6,9,10-Hexachlorododecane	99.4	0.2	0.5	13
CLF14131.13	1,2,6,7,10,11-Hexachlorotridecane	95.1	0.1	1.7	35
CLF14496.13	2,3,6,7,10,11-Hexachlorotridecane	94.2	0.2	0.5	35

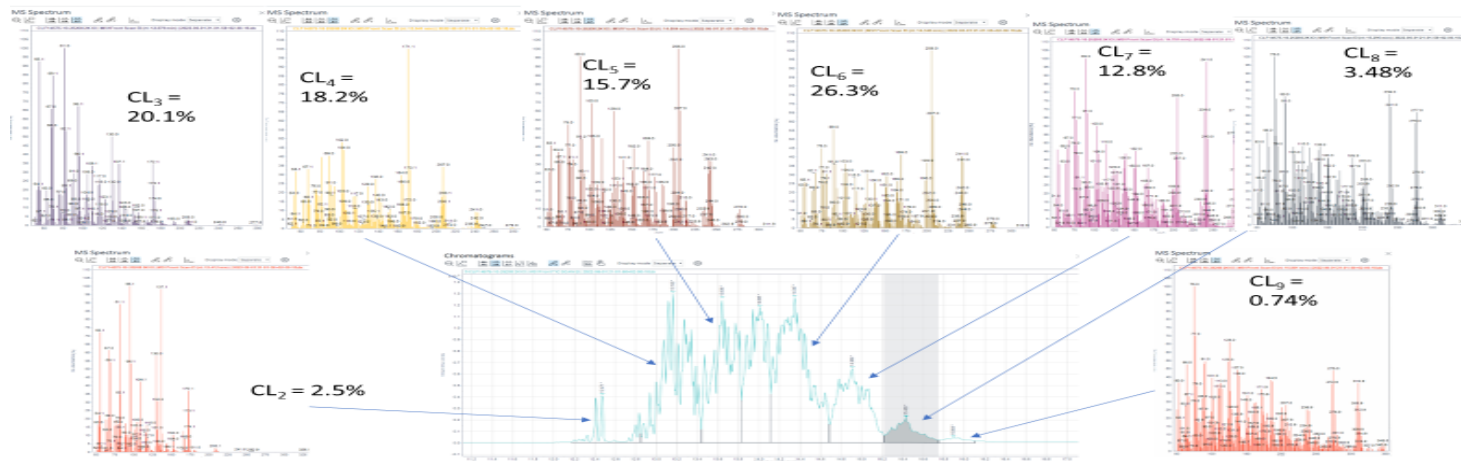
GC FID resultater



# CLF5371 Common Calibrant mixture of single chain mixtures

Cat. No	Compound	% Cl NMR	% Cl Mohr's Titration	Estimated Cl distribution GC-MS (extracted ion chromatography)	Chromat. Purity (%)	Loss on Drying (%)	Residue on Ignition (%)	Conc. ( $\mu\text{g mL}^{-1}$ )
CLF14575.10	Chloroparaffin single chain mixture $\text{C}_{10}\text{Cl}_2\text{-Cl}_6$	52.5	54.4	<Cl4 (2.5%) Cl4 (20.1%), Cl5 (34.0%) +Cl6 (39.2%), Cl7 (4.1%)	99.7 +/- 0.1	0.6	0.6	0.7
CLF14576.11	Chloroparaffin single chain mixture $\text{C}_{11}\text{Cl}_2\text{-Cl}_6$	52.3	56.5	<Cl4 (0.3%) Cl4 (7.8%), Cl5 (22.8%) +Cl6 (29.0%), Cl7 (25.3%), Cl8 (11.1%), Cl9 (3.0%), Cl10 (0.6%)	99.8 +/- 0.1	1.8	1.8	1.6
CLF15318.12	Chloroparaffin single chain mixture $\text{C}_{12}\text{Cl}_2\text{-Cl}_6$	53.8	n/a	<Cl4 (0.8%) Cl4 (6.7%), Cl5 (22.1%) +Cl6 (54.6%), Cl7 (11.9%), Cl8 (3.0%)	99.9 +/- 0.1	0.8	0.8	1.2
CLF14577.13	Chloroparaffin single chain mixture $\text{C}_{13}\text{Cl}_2\text{-Cl}_6$	45.9	46.8	<Cl4 (0.3%) Cl4 (12.3%), Cl5 (69.4%) +Cl6 (14.5%), Cl7 (3.5%)	99.8 +/- 0.1	0.4	0.4	2.0
CLF14687.13	Chloroparaffin single chain mixture $\text{C}_{13}\text{Cl}_5\text{-Cl}_8$	60.0	60.8	<Cl4 (0%), Cl4 (0.4%), Cl5+Cl6 (5.8%), Cl7 (41.1%), Cl8 (43.4%), Cl9 (7.5%), Cl10 (1.9%)	99.9 +/- 0.1	0.2	0.4	4.5

## GC-MS evaluation of single chain CP mixtures



# Future work after CHLOFFIN

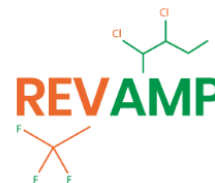
**LCCPs**

**More <sup>13</sup>C-labelled CPs**

More labelled CPs

More numbers (>3 ) <sup>13</sup>C labelling?

**More mixtures**





**Any further questions?**

***Thank you for your attention!***



**Your quality is our business**

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