# Minimizing mass spectral interferences during analysis of short- and medium-chain chlorinated paraffins by GC-ECNI-LRMS

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## Introduction

**Overview**

- Chlorinated paraffins (CPs) are a complex mixture of thousands of individual compounds.
- Widely used as plasticizers and flame retardants.[1]
- Global production exceeding 1 million t/y in 2016.
- Human exposure via indoor dust and food.[2]
- SCCPs Stockholm Convention POPs since 2017.

**Analysis**

- SCCPs and MCCPs commonly analysed by gas chromatography (GC) - low resolution mass spectrometry (LRMS) operated in electron capture negative ionization mode (ECNI).
- Interferences due to GC coelution and mass overlaps between CP homologues and other halogenated contaminants.
- Isotope ratio's used to identify coeluting SCCP and MCCP congeners of the same mass.

**Objectives**

- Minimize mass spectral interferences using a simple sample preparation procedure and an improved selection of SIM parameters.

## Materials and Methods

**Dispersive SPE**

- 0.3 g lyophilized salmon tissue (~30% w/w lipids)
- 4 g acid silica (44% w/w)
- Hexane/DCM 3:1

**Fractionation**

- 500 mg/ 3 mL Silica cartridge

**6 mL Hexane**

- PCBs, PBDEs, DPs and most OCPs

**12 mL DCM**

- SCCPs, MCCPs, MeO-BDEs, HCHs

**Analysis**

- Agilent 6890 GC – 5973 MS
- ECNI mode
- 15 m DB5-MS column
- 24 SCCPs: $C_{10\text{-}13}$ $Cl_{5\text{-}10}$
- 24 MCCPs: $C_{14\text{-}17}$ $Cl_{5\text{-}10}$
- SIM of [M-Cl]- and [M-HCl] ions

**Assessment of SIM Parameters**

- Mass overlaps between coeluting homologues were identified by analysing technical standards of SCCPs and MCCPs and comparing the measured ratio between major isotopes of each congener group with those of theoretical ratios.
- Visual inspection of extracted ion chromatograms was also used to identify impacts of mass overlaps by comparing peak shapes of m/z values of isotopes from the same ion cluster.

## Results

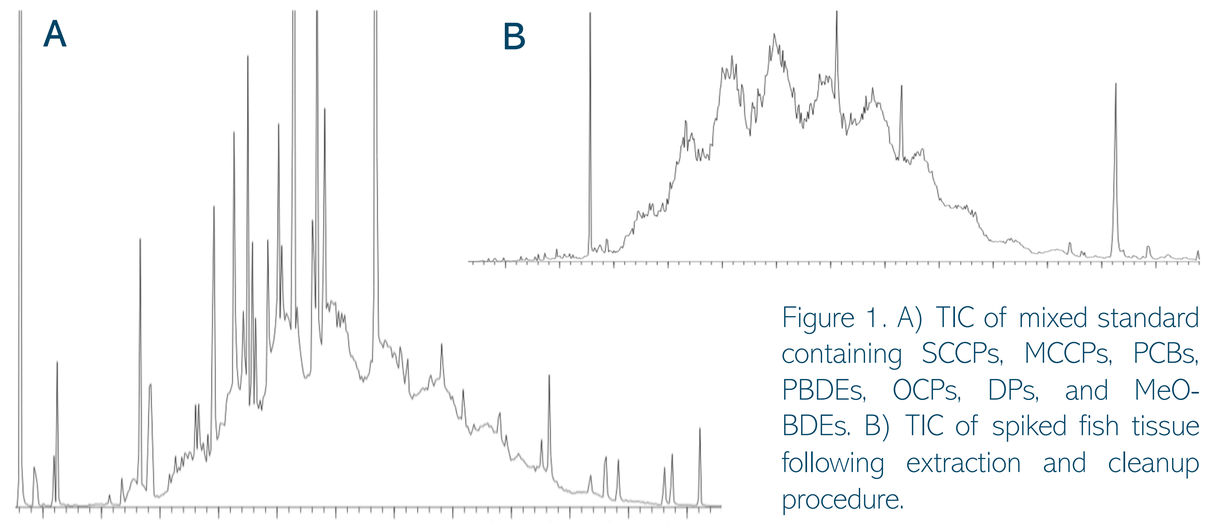


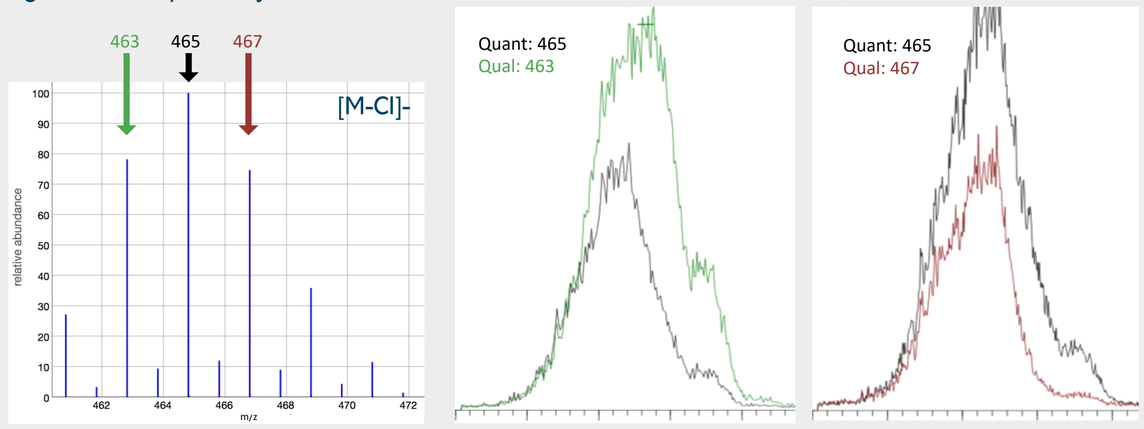

Figure 1. A) TIC of mixed standard containing SCCPs, MCCPs, PCBs, PBDEs, OCPs, DPs, and MeO-BDEs. B) TIC of spiked fish tissue following extraction and cleanup procedure.

Table 1. Selected alternative SIM qualifier parameters.

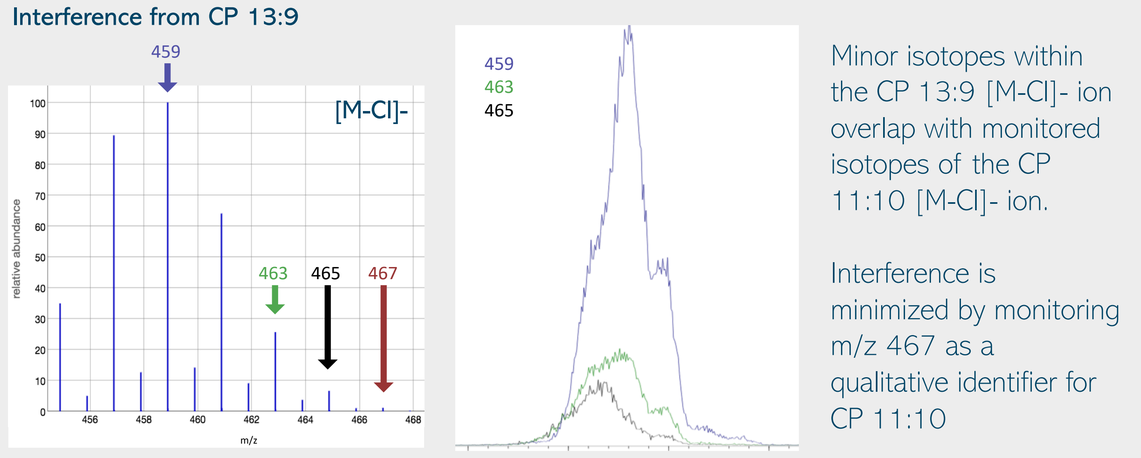
| Compound | | Most Abundant (Quant) | | 2nd Abundant (Common Qual) | | | Alternative Qualifier | | |
|---|---|---|---|---|---|---|---|---|---|
| Congener Group | Ion | m/z | Isotope | m/z | Isotope | M/T Ratio % | m/z | Isotope | M/T Ratio % |
| CP 10:5 | [M-HCl]- | 278 | X+2 | 276 | X | 196 | 280 | X+4 | 121 |
| CP 11:5 | [M-HCl]- | 292 | X+2 | 290 | X | 221 | 294 | X+4 | 92 |
| CP 11:10 | [M-Cl]- | 465 | X+4 | 463 | X+2 | 225 | 467 | X+6 | 69 |
| CP 12:10 | [M-Cl]- | 479 | X+4 | 477 | X+2 | 102 | 481 | X+6 | 101 |
| CP 14:5 | [M-Cl]- | 335 | X+2 | 333 | X | 225 | 337 | X+4 | 79 |
| CP 16:6 | [M-Cl]- | 397 | X+2 | 399 | X+4 | 817 | 395 | X | 140 |
| CP 16:7 | [M-Cl]- | 431 | X+2 | 433 | X+4 | 322 | 429 | X | 146 |

M/T Ratio % = measured qual ratio /theoretical qual ratio

Figure 2. Example analysis of CP 11:10




Interference from CP 13:9




Minor isotopes within the CP 13:9 [M-Cl]- ion overlap with monitored isotopes of the CP 11:10 [M-Cl]- ion.

Interference is minimized by monitoring m/z 467 as a qualitative identifier for CP 11:10

## Discussion and Conclusion

**Sample Preparation**

- The d-SPE method was able to adequately remove lipids from the samples with 4 g of acid silica per sample.
- The optimal solvent composition was 3:1 hexane/DCM (v/v) with respect to recovery of CP analytes and retention of lipids.
- PCBs, PBDEs, DPs, and most OCPs were separated completely from the SCCPs and MCCPs during fractionation (Figure 1).
- MeO-BDEs and HCHs remained within the same fraction as CPs but were found not to interfere significantly with quantification.

**Selection of SIM Parameters**

- Response ratios between the commonly monitored 1st and 2nd most abundant isotopes of [M-Cl]- and [M-HCl]- ions were impacted by m/z overlaps within and between SCCPs and MCCPs for 13 congener groups.
- Alternative confirmation m/z values were selected within monitored ion clusters to reduce the degree of mass overlap for 7 of the 13 congener groups (Table 1, Figure 2).
- For the remaining 6 congener groups, no confirmation isotope could be identified within the monitored ion cluster which was not heavily impacted by mass overlap from other CP groups. In these instances, alternative confirmation measures may be required, such as the monitoring of an m/z value from a separate representative ion.

**Conclusion**

- This work presents a simple and fast method for the extraction and cleanup of SCCPs and MCCPs from lipid-rich foods to remove interfering halogenated contaminants and offers alternative SIM parameters to enhance differentiation of CP homologues during ECNI-LRMS analysis.

**References**

1. Glüge J, et al. 2016. Science of the Total Environment 573:1132-46
2. Gao W, et al. 2018. Environmental Science and Technology 52:32-9

Financial support was provided by Federal Public Service (FPS) Health, Food Chain Safety and Environment, project RT 19/8 PARCLINTA, and by the University of Antwerp.

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