The CP/CO problem: Limitations of conventional GC-ECNI-MS when analyzing mixtures of chlorinated paraffins (CPs) and chlorinated olefins (COs)

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Introduction

Chlorinated paraffins (CPs) are high production volume chemicals (>1 Mio t a^{-1}) widely used as plasticizers, flame retardants and additives in metal working fluids.[1] They are of environmental concern and information about their fate, in particular their transformation, is of urgent need. The analysis of CPs is demanding due to mixtures of thousands of isomers, limited chromatographic resolution, complex isotopic patterns and unknown compositions of standard materials. Analytical challenges further increase in presence of CP transformation products such as chlorinated olefins (COs). COs can form from CPs via HCl elimination under thermal stress. Thermal exposure of CPs during various applications is likely. For example, in polymer processing, CPs can be exposed to temperatures of up to 200°C. Recently, we showed, that COs also form when CPs are used in metal work applications, e.g. as cutting fluids.[2] Further, COs can be found in technical CP products and have been identified in the environment.[3] COs and CPs of the same carbon chain length and chlorination degree show severe mass interferences that require mass resolutions >20'000 for short-chain CPs or even more for longer chain lengths.[4]

Previously, we presented three novel methods based on liquid chromatography mass spectrometry (LC-MS) that are able to solve this CP/CO problem applying soft ionization techniques.[5] CP/CO mass interferences were either resolved by sufficient mass resolution or by mathematical deconvolution of full scan mass spectra.[5,6] Even though an increasing number of CP studies now apply LC-MS methods, most laboratories continue to use gas chromatography electron capture negative ionization mass spectrometry (GC-ECNI-MS).[7,8]

In here, we investigate conventional GC-ECNI-MS for its suitability to analyze CP/CO mixtures. We demonstrate analytical limitations regarding mass resolution, mass accuracy and in-source fragmentation that lead to additional interferences.

Materials and methods

This study was conducted using a polychlorinated tridecane mixture (60 wt%Cl). Thermal exposure and sample preparation was done according to Schinkel et al. (2017).[4] Samples were exposed to 200 °C for 0, 1, 2, 4 and 8 h. After exposure, samples were spiked with internal standard (β-hexabromocyclododecane) and extracted with methanol. GC-ECNI-MS was applied on a Thermo Scientific Q Exactive Orbitrap at resolution modes of R=120'000 and R=15'000 (FWHM at m/z 200). The GC-MS conditions were adopted from Diefenbacher et al. (2015)[9] and applied in full scan mode. The two most intense ions of the [M-Cl]$^-$ cluster were monitored. Raw data was processed using Thermo Xcalibur 4.0.27.19 Qual Browser.

Results and discussion
In-source fragmentation of CPs to COs

Even though ECNI is considered a soft ionization method for CPs, additional fragment ions can be observed besides the commonly monitored [M-Cl]$^-$ ions. Those fragment ions can cause severe interferences when mass resolution is insufficient.[10] **Figure 1a** and **Figure 1b** show that $C_{13}H_{20}Cl_8$-CPs ionized by [M-HCl-Cl]$^-$ and $C_{13}H_{19}Cl_7$-COs ionized by [M-Cl]$^-$, both result in ions with exactly the same mass of [$C_{13}H_{19}Cl_6$]$^-$. Thus, with GC-ECNI-MS, we observed a formation of COs by in-source fragmentation of CPs. Extracted ion chromatograms (EIC) were derived for the non-exposed polychlorinated tridecane mixture (R~120'000, mass accuracy 5 ppm). **Figure 1c** shows EICs of $C_{13}H_{20}Cl_8$-CPs (gray) and $C_{13}H_{19}Cl_7$-COs (orange) for [M-Cl]$^-$ ions. It demonstrates that this irresolvable mass interference can also not be resolved by chromatography because CPs and COs co-eluted (red area). Due to this in-source formation of COs, conventional GC-ECNI-MS cannot be used to investigate chlorinated olefins, even if infinite instrumental mass resolution is applied. As seen in **Figure 1c** (orange, lower panel), the early eluting and some of the late eluting part of $C_{13}H_{19}Cl_7$-COs cannot be explained by interfering fragments of $C_{13}H_{20}Cl_8$-CPs (red area). This indicates that COs are already present in non-exposed CP mixtures or are formed in the hot GC injector or column.

In general, ECNI mass spectra of CPs can vary between different instruments and are influenced by the chosen source parameters. In here, we further observe that CP fragmentation patterns can also depend on the chlorination degree of CPs and possibly on their chain length.
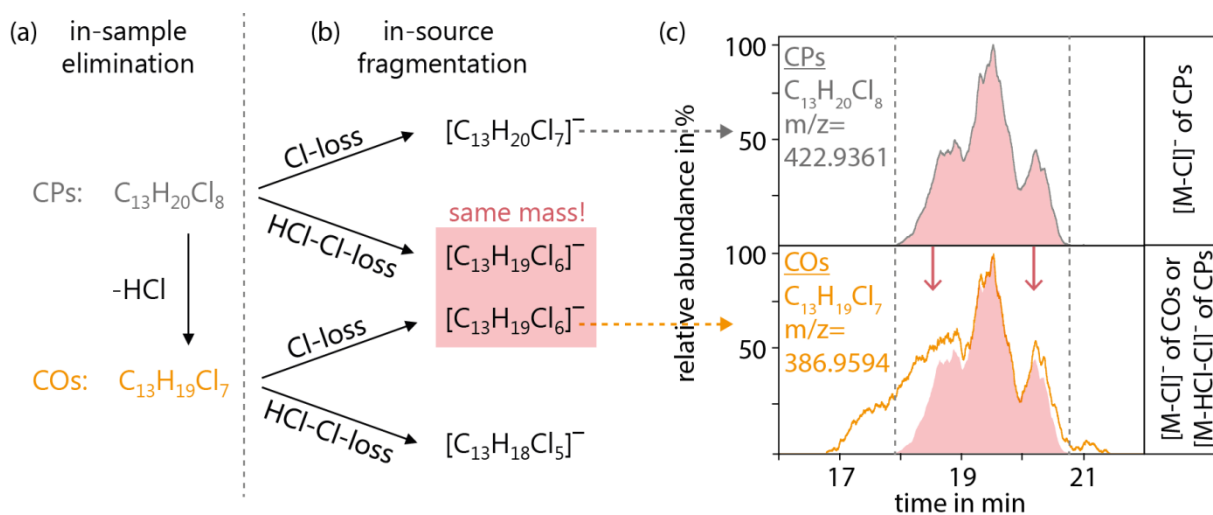
Figure 1. Interfering chlorinated paraffin (CP) and chlorinated olefin (CO) fragment ions in ECNI-MS. HCl elimination can occur in samples (a) or in the ion source of the MS (b), leading to identical ions of CPs and COs that co-elute (c).

Influence of mass resolution and mass accuracy

CPs and COs of the same chain length and chlorination degree show severe mass interferences that require mass resolutions of R>20'000.[4] **Figure 2** shows the influence of mass resolution and mass accuracy on the EIC of $C_{13}H_{21}Cl_7$-CPs for monitored [M-Cl]¯ ions (in non-exposed chlorotridecane mixture). With highest mass resolution and high mass accuracy (**Figure 2a**), CP target ions can be extracted without mass interferences. When applying insufficient mass resolution (15'000), target masses get shifted due to underlying interferences. **Figure 2b** indicates that insufficient mass resolution (15'000) but application of high mass accuracy (5 ppm) can lead to an underestimation of CPs (red arrow). On the other hand, application of low mass accuracy (50 ppm, **Figure 2c**) can lead to an overestimation of CPs, since underlying mass interferences are now included (red arrow). Here, these interferences are mainly caused by [M-HCl-Cl]¯ ions of $C_{13}H_{20}Cl_8$-CPs but could also be caused by [M-Cl]¯ ions of corresponding $C_{13}H_{19}Cl_7$-COs. Both result in interfering ions of *m/z* 388.9566.
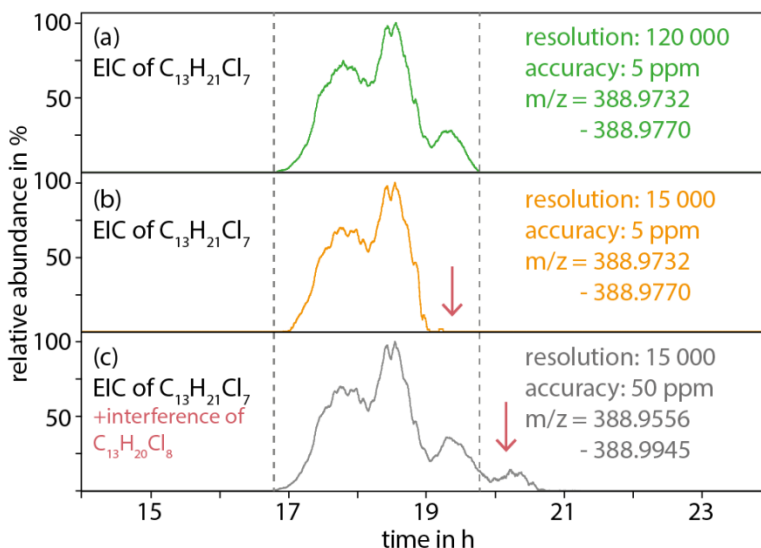
Figure 2. Influence of mass resolution and mass accuracy on the extracted ion chromatogram (EIC) of $C_{13}H_{21}Cl_7$-CP ions [M-Cl]¯. If mass resolution is insufficient (15'000), underlying mass interferences of COs can lead to (b) false negative or (c) false positive quantification of CPs (indicated by red arrows).

Commonly, CPs are analyzed in the selected ion monitoring mode (SIM). Two ions of a CP isotope cluster are extracted and their ratio is used to identify the respective CP homologue. In here, we tested whether this ratio can be used to detect underlying mass interferences caused by COs. For this, we used a thermally degraded chlorinated tridecane mixture that contains high levels of COs. When applying sufficient mass resolution (120'000) and high mass accuracy (5ppm), ion ratios of $C_{13}H_{21}Cl_7$-CPs were determined correctly with small deviations (0-3%) from the theoretical ratio. In case of low mass resolution (15'000) and low mass accuracy (50 ppm), measured ion ratios deviated from the theoretical ratio by 10-21%. When applying a common tolerance level of 15-20%, CPs would be falsely quantified even though they are interfered by 27-42% COs, in this example. Here, COs are present in

samples as thermal transformation products and are also formed by CP fragmentation in the ion source. SIM is therefore not well suited to detect underlying CO mass interferences, when resolution is insufficient (<20'000). We recommend the use of full scan measurement to detect potential mass interferences. Furthermore, full scan spectra would allow the application of deconvolution methods to mathematically separate CP and CO mass interferences.[4] As discussed, GC-ECNI-MS cannot be used to determine levels of chlorinated olefins due to in-source fragmentation of CPs to COs. To circumvent in-source fragmentation, we recommend the use of softer ionization methods like chlorine-enhanced atmospheric pressure chemical ionization.[4,5,11]

Data on CP transformation and fate is urgently needed, but respective studies are demanding. As shown in here, interfering transformation products and in-source fragmentation ions can impede the analysis of CPs and COs. Thus, when investigating the fate of CPs, it is essential to fully assess the used analytical method for its applicability.

References

1. Glüge J, Wang Z, Bogdal C, et al. (2016). *Sci Total Environ*, 573: 1132-1146
2. Schinkel L, Lehner S, Knobloch M, et al. (2018), *Chemosphere*, 194: 803-811
3. Li T, Gao S, Ben Y, et al. (2018), *Environ Sci Technol*, 52(4): 1862-1870
4. Schinkel L, Lehner S, Heeb N, et al. (2017), *Anal Chem*, 89(11): 5923-5931
5. Schinkel L, Lehner S, Heeb N, et al. (2017), *Organohalogen Compounds Database*: 9634
6. Schinkel L, Lehner S, Heeb N, et al. (submitted), „*Dealing with strong mass interferences of chlorinated paraffins and their transformation products: An analytical guide*"
7. van Mourik LM, van der Veen I, Crum S, et al. (2018), *TrAC-Trend Anal Chem*, 102: 32-40
8. Krätschmer K, Cojocariu C, Schächtele A, et al. (2018), *J Chromatogr A*, 1539: 53-61
9. Diefenbacher P, Bogdal C, Gerecke AC, et al. (2015), *Environ Sci Technol*, 49(16): 9778-9786
10. Yuan B, Alsberg T, Bogdal C, et al. (2016), *Anal Chem*, 18(88): 8980-8988
11. Bogdal C, Alsberg T, Diefenbacher P, et al. (2015), *Anal Chem*, 87(5): 2852-2860