Fast evaluation of complex high-resolution mass spectra of chlorinated paraffins (CPs) and chlorinated olefins (COs) in plastic consumer products

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Chlorinated paraffins (CPs) are high production volume chemicals with production rates of about 1 million t/y. CPs are widely used in plastic materials both as plasticizers and flame-retardants.[1] Technical CPs are produced in non-selective processes through radical chlorination of n-alkanes. This results in complex mixtures of millions of constitutional isomers and stereoisomers. CPs are produced with carbon-chain lengths of C_9-C_{30} (C-homologues) and with chlorination degrees of Cl_3-Cl_{20} (Cl-homologues). In other words, such a technical CP-mixture applied in plastic material can contain up to 400 C-Cl-homologue classes. Mass spectra of such CP-mixtures can contain up to 20'000 ions of ^{12}C-/^{13}C- and ^{35}Cl-/^{37}Clisotopologues.

Furthermore, such spectra are interfered with ions of chlorinated olefins (COs), which are an important family of CP transformation products. The formation of COs and chlorinated di-olefins (CdiOs) was observed during thermal exposure of CPs[2] and during exposure of CPs on reactive metal surfaces formed during metalwork.[3]

We have developed an LC-APCI-Orbitrap-MS method that is able to resolve such complex mass spectra. As will be demonstrated here, the newly developed R-based automatic spectra evaluation routine (RASER) has been used to identify and extract specific ions of the various isotope clusters of different CP- and CO-homologues. The applied soft-ionization technique, which supports the formation of chloride-adduct $[M+Cl]^-$ ions, together with the high resolution of the Orbitrap-MS of 140'000 are crucial to solve the conundrum.

We will demonstrate the potential of our new approach on four CP-containing plastic materials from widely used consumer products. The combination of a soft-ionization technique, a mass spectrometer with high resolution and the automatic data evaluation with RASER allowed us to distinguish about 660 different CP- and CO-homologues, which corresponds to mass spectra with about 11'000 ions. The new RASER method will be presented in a separate contribution. Its potential will be demonstrated on plastic materials commonly found in Swiss households (this work) as well as on Swiss sewage sludge samples.

[1] J. Glüge et al., *Sci. Total Environ.* **89** (2016) 1123-1146.
[2] L. Schinkel et al., *Anal. Chem.* **287** (2017) 5923-5931.
[3] L. Schinkel et al., *Chemosphere* **194** (2018) 803-811.