Fingerprinting of Chlorinated Paraffins and their Transformation Products in Plastic Consumer Products

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Chlorinated paraffins (CPs) are high production volume chemicals (1 million t/y) commonly used as plasticizers and flame retardants in plastic materials and as coolant fluids in metalwork [1]. Technical CP mixtures can contain a broad range of carbon (C, n_C=9–30) and chlorine (Cl, n_{Cl}=2–20) homologues with millions of constitutional isomers and stereoisomers. Therefore, CP-containing plastics used in our daily life can contain up to 400 C-Cl-homologues and a detailed mass spectrometric analysis provides complete homologue distributions and with it, fingerprints of such materials.

Exposing CPs to heat leads to the formation of unsaturated compounds such as chlorinated mono- (COs), di (CdiOs) and tri-olefins (CtriOs) [2]. These transformations can occur at different stages of plastic manipulations altering homologue distributions of initial CP mixtures providing new patterns. These patterns can be interpreted as specific fingerprints, motifs that can be distinguished and tracked. Such fingerprints may lead to manufacturers, production processes or specific applications of CP-containing materials. Therefore, CP fingerprinting can develop to a promising tool for future source apportionment studies to identify polluting sources and with it, to reduce environmental burden of CPs and hazards to humans.

We have developed an LC-APCI-Orbitrap-MS method to analyze plastic consumer products. The formation of $[M+Cl]^-$ ions by a soft-ionization technique and the high resolution of the Orbitrap-MS are required in the analysis of CPs and their transformation products. Moreover, an R-based automatic spectra evaluation routine (RASER) was used to evaluate thousands of ions of the various isotope clusters corresponding to 1600 homologues of CPs, COs, CdiOs and CtriOs [3].

We will demonstrate the potential of the new method on several CP-containing plastic materials. Five unique patterns were deduced per item from C- and Cl-homologue distributions, carbon and chlorine numbers, and saturation degrees, which collectively created the fingerprint of each plastic material.

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[2] Schinkel, L. et al., Chemosphere, 194 (**2018**) 803–811.

[3] Knobloch, M. et al., Anal. Chem., 94 (**2022**) 13777–13784.