

## R-based Automatic high-resolution mass Spectra Evaluation Routine (RASER) for the rapid analysis of chlorinated paraffins and olefins

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Technical chlorinated paraffins (tCPs) are produced in large scales of 1 million t/y and are used in various applications as plasticizers and flame-retardants in plastic and as metalwork fluids.<sup>1</sup> They are complex mixtures with millions of constitutional and stereo-isomers of poly-chlorinated *n*-alkanes with carbon-chain lengths of C<sub>10</sub>-C<sub>30</sub> (C-homologues) and variable chlorination degrees of Cl<sub>3</sub>-Cl<sub>20</sub> (Cl-homologues). Technical CP mixtures can contain up to 10<sup>8</sup> isomers.<sup>1</sup> Because of their toxicity and environmental risks, the use of short-chain CPs (C<sub>10</sub>-C<sub>13</sub>) has been restricted and SCCPs are regulated as persistent organic pollutants (POPs) under the Stockholm Convention.<sup>2</sup> This forced a shift to a production and use of medium-(C<sub>14</sub>-C<sub>17</sub>), long- (C<sub>18</sub>-C<sub>21</sub>), and very long- chain (C<sub>>21</sub>) CPs. The analysis of CPs is challenging because of mass spectrometric interferences of the numerous isomers, the absence of suitable reference materials and the presence of side-products or transformation products such as chlorinated olefins (COs).

We applied liquid-chromatography coupled to an atmospheric pressure chemical ionisation method with a high resolution mass selective detector (LC-APCI-Orbitrap-MS) to study complex mixtures of up to 1320 homologues of CPs and olefinic transformation products. Such spectra are indeed complex, containing up to 30'000 relevant signals. An R-based Automatic Spectra Evaluation Routine (RASER) was self-developed and used to read-out defined CP and CO signals of specific homologues. With it, C- and Cl-homologue distributions of CPs and COs are obtained. The procedure reduced the workload required for the spectra evaluation from weeks to hours. Visual validation of measured and expected isotope clusters and the reconstruction of full scan mass spectra showed the presence of hundreds of CP- and CO-homologues. Mass spectrometric abundances were highest for medium-chain CPs and COs. CO-homologues were detected in abundances up to 10 % with respect to CP-homologues

The soft ionization technique applied favours the formation of quasi-molecular chloride-adduct without formation of fragment ions. The high mass resolution allowed to distinguish CPs and olefinic materials. RASER provide the possibility evaluate complex spectra of technical CP-mixtures containing up to 30'000 ions. This procedure can be applied to CP containing materials of different origin such as environmental samples or plastic from consumer products. The potential of the method was evaluated on sewage sludge (this contribution) and plastic materials we are exposed to in daily live.

[1] W. Vetter, J. Sprengel, K. Krätschmer *Chemosphere* **2022**, 287, 132032

[2] UNEP. Decision SC-8 / 11 (2017) 14