

Highlights of Analytical Sciences in Switzerland

Division of Analytical Sciences

A Division of the Swiss Chemical Society

RASER – A Tool for Rapid Mass Spectra Analysis of Chlorinated Paraffins

Marco C. Knobloch^{ab}, Jules Hutter^{ac}, Adriana Tell^{ac}, Oscar Mendo Diaz^{ab}, Flurin Mathis^{ac}, Urs Stalder^b, Laurent Bigler^b, Susanne Kern^c, Norbert V. Heeb^{a*}, and Davide Bleiner^{ab}

*Correspondence: Dr. N. Heeb^a, E-Mail: norbert.heeb@empa.ch

^aEmpa, Laboratory for Advanced Analytical Technologies, Überlandstrasse 129, CH-8600 Dübendorf; ^bUniversity of Zürich, Department of Chemistry, Winterthurerstrasse 190, CH-8057 Zürich; ^cZürich University of Applied Sciences ZHAW, Institute of Chemistry and Biotechnology, Einsiedlerstrasse 31, CH-8820 Wädenswil

Keywords: Automatic spectra evaluation · Chlorinated paraffins · High-resolution mass spectrometry · Persistent organic pollutants

Chlorinated paraffins (CPs) are complex mixtures of polychlorinated alkanes with carbon chain-length n_c between 10 to 30 (C-homologues) and chlorine numbers n_{Cl} between 2 to 14 (Cl-homologues). CP materials are widely used in metalworking fluids and in plastic. Short-chain CPs (SCCPs, C_{10-13}) are restricted and classified as persistent organic pollutants (POPs) under the Stockholm Convention. Medium-chain CPs (MCCPs, C_{14-17}) are under evaluation for legal restrictions as well, while information about environmental hazards of long-chain (LCCPs, $C_{\geq 18}$) is scarce. Technical CP mixtures can contain hundreds of homologues and millions of constitutional isomers and stereoisomers. This analytical complexity increases even more when CP transformation products, such as chlorinated olefins (COs), are present.

We developed a method based on liquid chromatography coupled to atmospheric pressure chemical ionization and Orbitrap mass spectrometry (LC-APCI-Orbitrap-MS) with mass resolution of $\geq 100,000$ that allows to study complex CP mixtures. Respective mass spectra can contain up to 7'300 ions from 384 homologues. Manual data processing of this vast number of ions consumes several weeks.

Therefore, we developed an R-based automatic spectra evaluation routine (RASER) to identify and read-out MS-signals and report here data from a plastic insulation. The algorithm identifies signals by comparing simulated isotope clusters with measured ones. With RASER, CP-distributions of such materials were obtained within hours only. The workload to evaluate such mass spectra was reduced by a factor of 75. In total, 2'225 signals from 163 CP-homologues were identified in the spectrum of the plastic material. The distribution is bimodal with respect to the C-homologues and unimodal with respect to the Cl-homologues. MCCPs (52%) were the major CP-class, with relevant contributions of SCCPs (23%) and LCCPs (25%). **Therefore, LC-APCI-Orbitrap-MS in combination with RASER is a selective and time-efficient method to study complex CP mixtures from plastic materials and environmental samples.**

Received: December 5, 2022

Acknowledgement

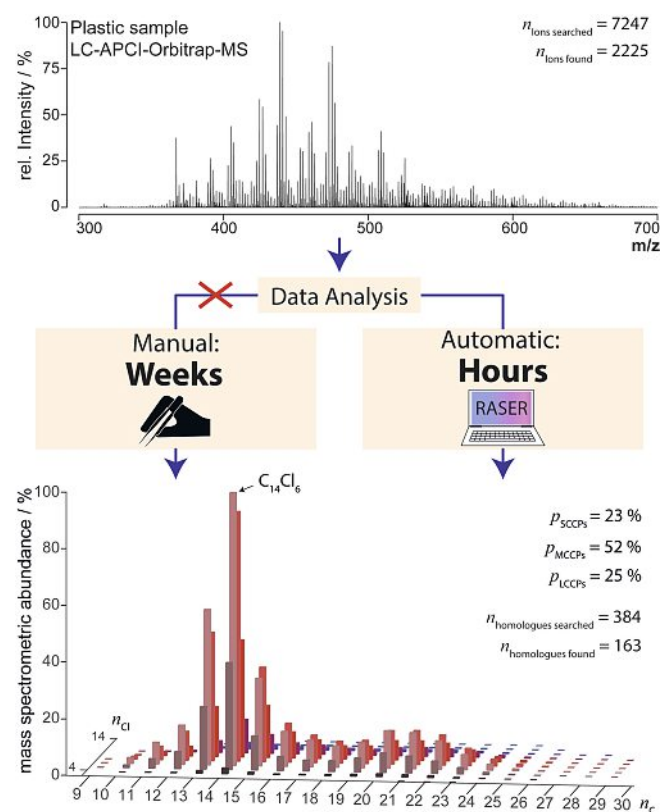
We thank the Federal Office for the Environment (FOEN) for the financial support (Grant 19.0011.PJ/S113-1600).

Reference

M. Knobloch, F. Mathis, O. Mendo Diaz, U. Stalder, L. Bigler, S. Kern, D. Bleiner, N. Heeb, *Anal. Chem.* **2022**, *94*, 13777, <https://doi.org/10.1021/acs.analchem.2c02240>



Technical CP mixtures are applied in plastic materials as plasticizers and flame-retardants. Photo by Marco C. Knobloch.



Evaluation of complex CP mass spectra from LC-APCI-Orbitrap-MS can take weeks when done manually. RASER reduces the workload to hours and provides C- ($n_c = 9$ to 30) and Cl- ($n_{Cl} = 4$ to 14) homologue distributions of CPs as found in the plastic coating of various electric cables.

Can you show us your analytical highlight?

Please contact: Dr. Veronika R. Meyer, Unterstrasse 58, CH-9000 St. Gallen
Tel.: +41 71 222 16 81, E-mail: analytical_highlights@chimia.ch