Soft ionization GC-HRMS of Polychlorinated Biphenyls (PCBs)

Summary

In this study we demonstrate, how SICRIT® expands the range of analytes addressable with LC-MS instruments on example of PCB analysis via SICRIT® GC coupling.

Introduction

Polychlorinated biphenyls (PCBs) are derivatives from biphenyl. There are 209 PCB components (congeners) which are characterized by different replacements patterns. PCBs were widely deployed as coolant fluids and in electrical equipment, and were commonly used as compound mixtures. Thus, a broad variety of PCBs can be found in PCB products. Since the toxicity and cancerogenity of PCBs has been discovered in the 1970s, their production has declined and was completely banned in 2001 by the Stockholm Convention on Persistent Organic Pollutants. Due to the longevity of the compounds, PCBs remain for long periods cycling between air, water and soil.

As a consequence, they can be found ubiquitious in all environmental matrices. For this reason, the EU set maximum residue limits for PCB components in food (EU No 1259/2011).

For quantification of PCBs, GC is a prerequisite to separate the components and high-resolved detection is needed to assign the congeners. Thus, specially tailored GC-HRMS methods based on expensive magnetic sector instruments were established in the 1970s, which are still used for sensitive analysis of dioxin and PCB compounds.

However, modern LC-MS instruments could present an alternative, if they could be combined with GC. The SICRIT® Ion source allows for this coupling of GC instruments with any API (atomspheric pressure inlet)-MS system and therefore opens up the possibility to analyze PCBs and other non-polar components on triple quad, time-of-flight (TOF) or orbitrap LC-MS systems. The soft ionization mechanism of the DBD-based plasma source ensures substance identification based on molecular ions in full scan mode, which is dedicated for non-target analysis of environmental samples on HRMS instruments.

Experimental Setup

In the experimental setup, a GC was coupled to a Thermo LTQ Orbitrap high-resolution MS by SICRIT® Ion source. As GC carrier gas, Helium was used, the plasma source was operated with dry nitrogen. MS detection was performed in full-scan positive mode with a resolution of 30,000 FWHM (mass range 75-750 m/z).

Table 1 - Experimental setup for PCB analysis.

Samples	PCB mix, 10 µg/mL in isooctane (36906, Sigma-Aldrich)
Solvent	MS-grade Hexane (Sigma-Aldrich)
Mass spectrometer	LTQ Orbitrap XL (Thermo Fisher)
SICRIT Plasma	1.5 kV, 15 kHz
GC	Trace GC Ultra (Thermo Fisher)
Column	RXI-5ms, 30 m, 0.25 mm ID, 0.25 µm stationary phase (Restek)
Liner	5 mm Splitless Borosilicate glass, deactivated, 105 mm (Restek)
Inject volume	2 µL
Split ratio	Splitless
Carrier gas	Helium
Flow rate	1.2 mL/min
Injector temperature	280°C
Start temperature	40°C
Temperature ramp	20°C/min (40-230°C), 5°C/min (230-260°C), 20°C/min (260-310°C)
Final temperature	310°C, hold for 2 min
Transferline temperature	280°C

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Results

Table 2- Investigated PCB components.

Compound	Congener	Exact Mass M_{theo} (m/z)
2,4,5-Trichlorobiphenyl	PCB-28	255.9608
2,2‘,4,4‘-Tetrachlorobiphenyl	PCB-52	289.9218
2,2‘,3,4,6-Pentachlorobiphenyl	PCB-101	323.8828
2,2‘,4,4‘,5,6‘-Hexachlorobiphenyl	PCB-138	357.8439
2,2‘,4,4‘,5,6‘-Hexachlorobiphenyl	PCB-153	357.8439
2,2‘,3,3‘,4,4‘,6-Heptachlorobiphenyl	PCB-180	391.8052

All compounds of the PCB mix could be separated and their identities were confirmed by HRMS data using a 5 ppm window (see Fig. 1).

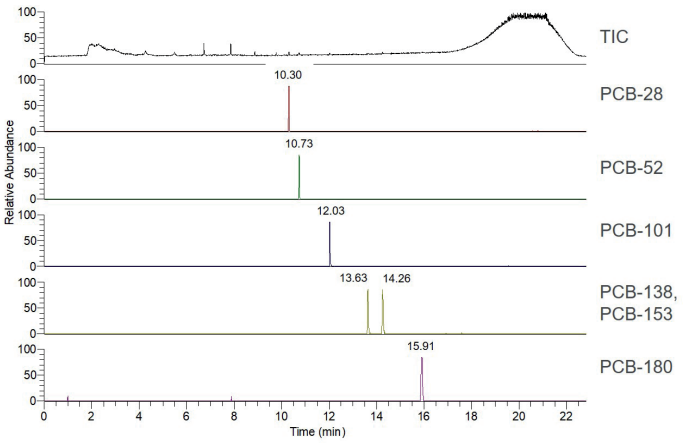

Figure 1 - Extracted ion chromatogram (EIC) of investigated PCB components.

SICRIT® ionization results in spectra with PCB radical cation species $[M]^{\bullet+}$ confirmed by the expected chlorine isotope pattern as illustrated in Figure 2 on example of PCB-28. The softness of the plasma ionization can be illustrated by full spectra showing barely fragmentation in comparison with EI ionization (see Fig. 3). As a result, qualification and quantification can be realized in a non-target manner by exact mass traces in full scan mode based on $[M]^{\bullet+}$ species. In our tests we observed, that the use of dry nitrogen led to a significant enhancement of the ionization efficiency compared to humidified nitrogen. Therefore, calibration experiments were conducted using dry nitrogen as ion source carrier gas.

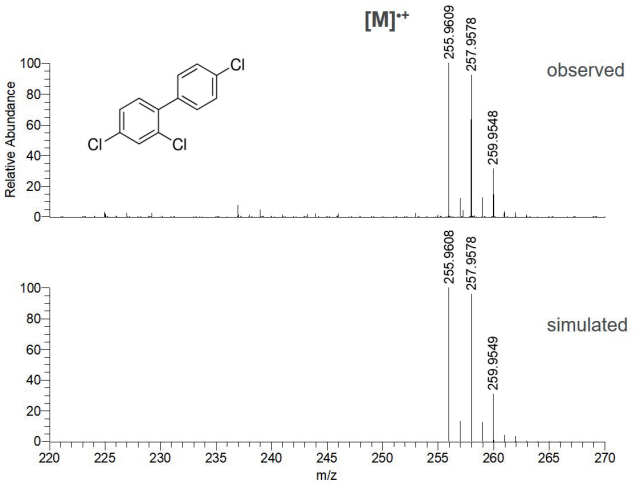

Figure 2 - Full scan mass spectrum of PCB-28 in positive mode, showing $[M]^{\bullet+}$ species with specific chorine isotope pattern.

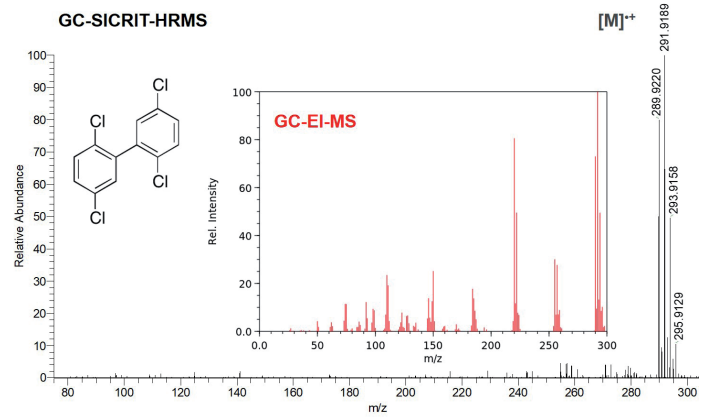

Figure 3 - Full scan spectrum of PCB-52 achieved with SICRIT soft ionization in comparison with GC-EI-MS NIST spectrum (insertion).

The measurement of PCB mix dilutions showed high linearity of the method between 20-1000 ng/mL and instrumental LODs < 10 ng/mL for all six investigated PCB components.

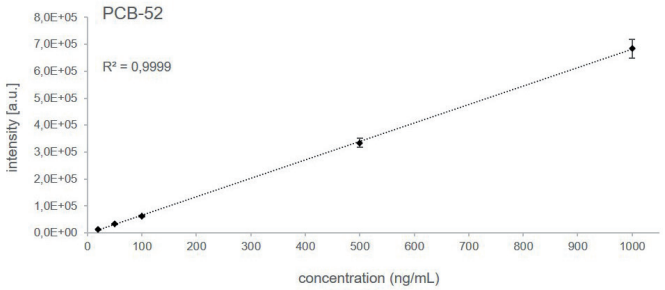

Figure 4 - Calibration of PCB-52 based on $[M]^{\bullet+}$, obtained on LTQ Orbitrap XL in full scan mode.

Conclusions

The presented data show efficient soft ionization of PCB compounds. Dry nitrogen as ion source gas was found to be favourable for PCBs and other chlorinated analytes. Calibration curves for the investigated PCBs show instrumental limits of detection in the low ppb range. Thus, combination with powerful LC-MS instrumentation and further method optimization may prove SICRIT® beeing an valuable and cost-effective alternative to magnetic sector HRMS systems. This would expand the user‘s view towards low polarity compounds on an universal MS platform and bridging the gap between LC-MS and GC-MS.

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