Soft ionization GC-HRMS of n-Alkanes C_8 - C_{20} (Thermo LTQ Orbitrap XL)

Summary

We introduce a versatile new method for trace analysis of non-polar short-chain n-alkanes C_8-C_{20} using GC-SICRIT®-HRMS.

Introduction

Mineral oils and their residues play an important role in environmental and food analytics. Saturated hydrocarbons (MOSH) or alkanes form the main compound species in mineral oil. Due to the complexity of the MOSH (alkane) fraction, analysis is a demanding and still not standardized task in analytical chemistry.

To date, GC-FID is the most common MOSH detection method, however, clear sample differentiation is difficult. Thus, more comprehensive methods are needed, and mass spectrometry could be a suitable technique. But, in view of the molecular structure of alkanes, GC-EI-MS is also linked to challenges: As the EI ionization process often leads to identical fragments, the product ions do not allow for verification and quantification of the molecular alkane isomers.[1] To overcome this problem of unresolved complex mixture (UCM), soft ionization as provided by LC-MS instruments would be a possible answer. Unfortunately, LC-MS is not capable of separating and ionizing alkanes, since they have no functional and thus ionizable groups.

In this study we demonstrate the first GC-soft ionization-MS hyphenation allowing for qualification and quantification of n-alkanes C_8-C_{20}. In our approach, we investigate n-alkanes by "Soft Ionization by Chemical Reaction In Transfer" (SICRIT®)-GC high resolution MS.

With Plasmion's Plug & Play SICRIT® soft ionization source it is fast and easy to combine any standard LC-MS to GC instruments creating the unique possibility of powerful GC-MS couplings.[2]

The main advantages of GC-SICRIT®-HRMS are
• Soft ionization and less fragmentation
• High-sensitive flow-through ionization
• Extension of analyte range to low polarity
• High-resolution MS data for identification

Experimental Setup

Figure 1 - SICRIT® cold-plasma ion source features soft ionization GC-HRMS coupling (Thermo LTQ Orbitrap XL).

Table 1 - Experimental setup and GC parameters.

Samples	Alkane standard solution C_8-C_{20} (40 mg/L) in Hexane (04070, Sigma Aldrich)
Solvent	MS-grade Hexane (103701, Merck)
Mass spectrometer	LTQ Orbitrap XL (Thermo Fisher)
SICRIT Plasma	1.5 kV, 15 kHz
GC	Trace GC (Thermo Finnigan)
Liner	5 mm Spitless liner with Borosilicate glass, deactivated, 105 mm (23325, Restek)
Column	RXI-5ms, 30 m, 0.25 mm ID, 0.25 µm stationary phase (13423, Restek)
Inject volume	1 µL
Split ratio	Splitless
Carrier gas	Helium
Flow rate	Constant flow 1 mL/min
Start temperature	40°C, hold for 2 min
Temperature ramp	20°C/min
Final temperature	280°C, hold for 6 min
Transferline temperature	280°C

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Results

Successful GC separation of the n-alkane C_8-C_{20} standard is detected by Orbitrap-HRMS.

All 13 compounds could be separated, and their identities were confirmed by HRMS data.

Figure 2 shows the extracted ion chromatogram (XIC) of the n-alkanes, represented by the most abundant [M+O-3H]+ and [M+2O-H]+ species. Thanks to the high-resolution mass spectra, these literature-known characteristic product ions can be clearly assigned to the respective alkane (see Table 2).[3]
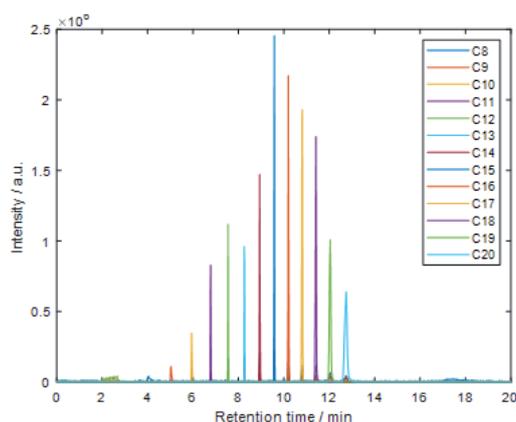
Figure 2 - Reconstructed GC-MS chromatogram of n-alkane mix (C_8-C_{20}) showing respective XICs.

Table 2: Investigated MOSH components.

Compound		Measured mass for [M+O-3H]+ product ion (m/z)	Difference to calculated mass (ppm)
n-Octane	C8	127.1116	-0.8
n-Nonane	C9	141.1273	-0.9
n-Decane	C10	155.1429	-0.7
n-Undecane	C11	169.1587	0.0
n-Dodecane	C12	183.1742	-0.8
n-Tridecane	C13	197.1898	-0.9
n-Tetradecane	C14	211.2056	-0.3
n-Pentadecane	C15	225.2214	0.3
n-Hexadecane	C16	239.2371	0.6
n-Heptadecane	C17	253.2527	0.5
n-Octadecane	C18	267.2692	0.1
n-Nonadecane	C19	281.2839	0.2
n-Eicosane	C20	295.2996	0.3

The soft character of the ionization can be confirmed by MS full scans of the alkane GC peaks as exemplarily shown in Figure 3 for n-pentadecane (nominal mass 212).

The mass spectrum is dominated by the oxidized species signals (m/z 225.2, m/z 243.2), whereas fragment ions as known from EI-MS are barely formed. This allows for confident identification of the C_n alkane based on its exact mass.
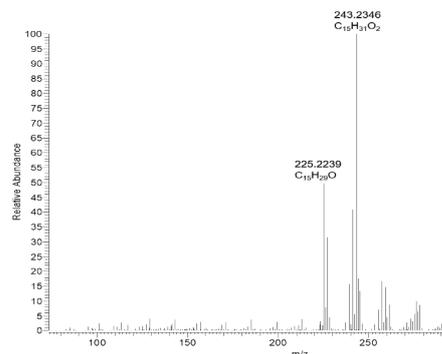
Figure 3 - Soft ionization mass spectrum of C_{15} n-Alkane, most abundant ions [M+O-3H]+, [M+2O-H]+ at m/z 225.2 and m/z 243.2, respectively.

Furthermore, quantification of the n-alkanes was evaluated (see Figure 4). The calibration curves show low RSD, a linear dynamic range of 3 orders of magnitudes, and LODs in the low ppb range.
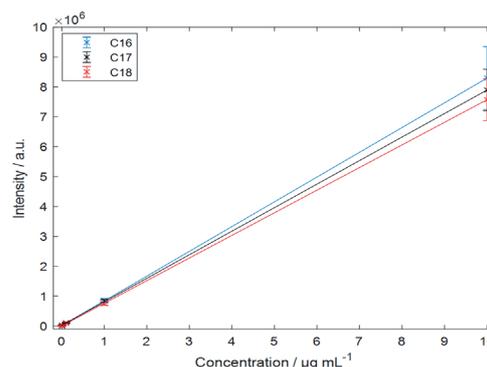
Figure 4 - Calibration curve of n-alkanes (C_{16}, C_{17}, C_{18}) with 10 ng, 1 ng, 100 pg, 10 pg and 0 pg standard mixture on column ($R^2 > 0.999$).

Conclusions

The presented data show that GC-SICRIT®-HRMS can be used for easy, fast and reliable identification and quantification of n-alkanes. This proves Plasmion's SICRIT® ion source being a promising new technology for MOSH analysis on any LC-MS instrument.

References

[1] M.S. Alam, C. Stark, R.M. Harrison, Anal. Chem. 2016, 88, 8, 4211-4220.
[2] M.F. Mirabelli, J.-C.Wolf, R. Zenobi, Analyst 2017, 142, 1909-1915.
[3] Y. Nunome, K. Kodama, Y. Ueki et al., Talanta 2019, 204, 310-319.

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