Sicrit technology

Application Note

Soft ionization GC-HRMS of Polycyclic Aromatic Hydrocarbons (PAHs)

Summary

We show the feasibilty of GC-SICRIT®-HRMS for trace analysis of poylcyclic aromatic hydrocarbons.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are neutral, nonpolar organic molecules that comprise two or more benzene rings arranged in various configurations that form from incomplete combustion. PAHs are of environmental concern because they are toxic to aquatic life and human carcinogens. For this reason, the U.S. Environmental Protection Agency (EPA) has included 16 PAHs on its list of priority pollutants to be monitored in water and waste and can be also found in various matrices, eg. food.
For detection, common methods following to EPA methods 610/8100 are high performance liquid chromatography (HPLC) with fluorescence detection and gas chromatography with flame ionization detector (FID) or coupled to mass spectrometry (GC/MS).
In recent years, LC-MS/MS methods and their respective ionization efficiencies are gaining interest. Beside electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and atmospheric pressure photoionization (APPI), also dieelectric barrier discharge ionization (DBDI) could present a new approach in PAH detection.
The SICRIT® Ion source features DBD-based cold plasma ionization and allows for easy coupling of GC to any LC-MS instrument, resulting in a GC-soft ionization-MS hyphenation. In this study we demonstrate qualification and quantification of PAH compounds using GC-SICRIT®-high resolution MS with a special focus on obtained ion species.

Experimental Setup

Experiments were conducted in the lab of Plasmion and also in the lab of Prof. Zenobi at ETH Zurich. Results of the experiments were published. [1]

Table 1 - Experimental setup and GC parameters (ETH Zurich).

Samples	PAH mix CRM47930 in DCM (Sigma- Aldrich)
Solvent	MS-grade Acetonitrile (Fisher Scientific)
Mass spectrometer	LTQ Orbitrap XL (Thermo Fisher)
SICRIT Plasma	1.6 kV, 10 kHz / 15 kHz
GC	GC-2014 (Shimadzu)
Column	SLB-5ms, 20 m, 0.18 mm ID, 0.18 µm stationary phase (Supelco)
Liner	4 mm ID
Inject volume	2 µL
Split ratio	Splitless
Carrier gas	Helium
Flow rate	Constant flow 30 cm/s
Start temperature	55°C, hold for 1.2 min
Temperature ramp	25°C/min (-270°C), 35°C/min (-320°C)
Final temperature	320°C, hold for 3 min
Transferline temperature	280°C

In both cases, 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 or humidfied nitrogen (90% R.H.) using a gas bubbler system. MS detection was performed in full-scan positive mode with a resolution of 30,000 FWHM (mass range 50-500 m/z).

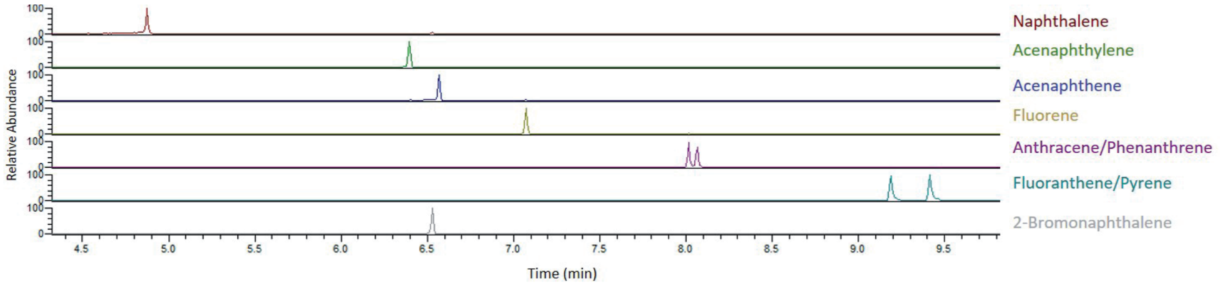

Figure 1 - Reconstructed GC-MS chromatogram of PAH compounds showing respective XICs of $[M+H]^+$ species.

Table 2- Investigated PAH components.

Compound	Molecular Formula	Exact Mass M_{theo} (m/z)
Napthalene	$C_{10}H_8$	128.0621
Acenaphthylene	$C_{12}H_8$	152.0621
Acenaphthene	$C_{12}H_{10}$	154.0777
Fluorene	$C_{13}H_{10}$	166.0777
Phenanthrene	$C_{14}H_{10}$	178.0777
Anthracene	$C_{14}H_{10}$	178.0777
Fluoranthene	$C_{16}H_{10}$	202.0777
Pyrene	$C_{16}H_{10}$	202.0777
2-Bromonaphthalene	$C_{10}H_7Br$	205.9726
Benz[a]anthracene	$C_{18}H_{12}$	228.0934
Chrysene	$C_{18}H_{12}$	228.0934
Benzo[b]fluoranthene	$C_{20}H_{12}$	252.0934
Benzo[a]pyrene	$C_{20}H_{12}$	252.0934
Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276.0934
Benzo[g,h.i]perylene	$C_{22}H_{12}$	276.0934
Dibenz[a,h]anthracene	$C_{22}H_{14}$	278.1090

Results

All compounds of the PAH mix could be separated (see Figure 1), and their identities were confirmed by HRMS data. Exact masses of the PAH mix are listed in Table 2.

To investigate the effect of carrier gas composition on plasma ionization of PAHs, ion species and signal intensities were compared for dry and humidfied nitrogen.

As illustrated in Figure 2 on example of pyrene, the spectrum comparison shows clear differences depending on carrier gas conditions. Using humified nitrogen, radical cation and protonated ion species are both formed in similar ratio, and also some oxidation products are observed. In contrast, under dry carrier gas conditions the PAH molecule protonation reaction is the clearly preferred pathway over formation of radical cation. Thus spectra are dominated by $[M+H]^+$ and, additionally, oxidized species are minimized (see Figure 3).

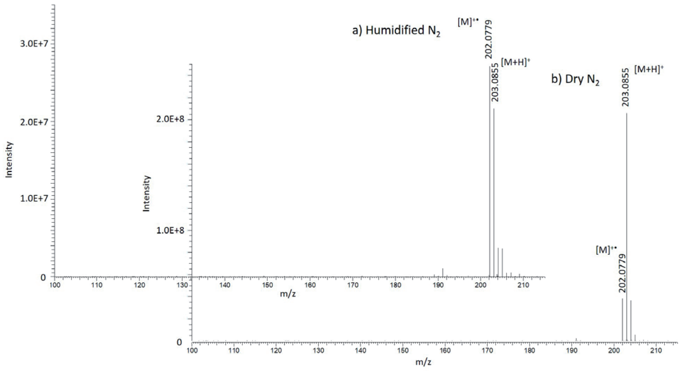

Figure 2 - Effect of plasma conditions on observed ion species, exemplarily shown for pyrene, Humidifid nitrogen (a), dry nitrogen (b), respectively.

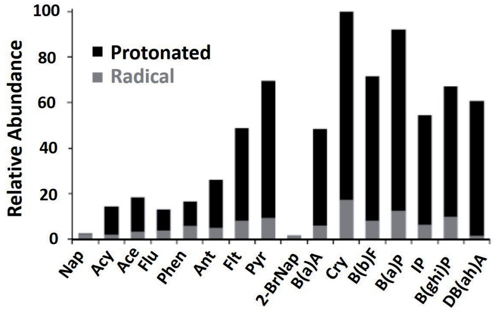

Figure 3 - Distribution of protonated and radical PAH ion species. [1]

In conclusion, we recommend dry nitrogen as plasma carrier gas to ensure best results in terms of S/N ratios and sensitivity for PAH trace analysis.

However, further investigation will be focussed on addition of dopants and carrier gas composition to further enhance ionization effiencies. [1]

Using dry nitrogen as carrier gas, sensitivity of the SICRIT® approach was estimated based on PAH mix dilution down to 10 ppb, analyzed in positive full scan mode on the Thermo LTQ Orbitrap (see Figure 4). All compounds could be detected based on their $[M+H]^+$ species at 10 ppb in full scan mode, suggesting sensitivities in the ppt range under optimized MRM conditions on triplequad systems.

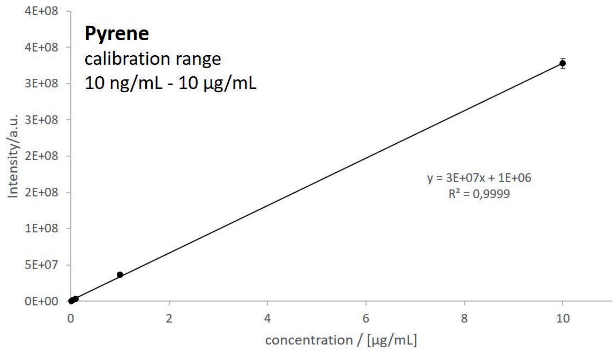

Figure 4 - Calibration of pyrene based on $[M+H]^+$, obtained on LTQ Orbitrap XL.

Conclusions

The presented data show the importance of plasma carrier gas conditions on obtained product ion species. For PAH compounds, we recommdend dry nitrogen achieving best results for qualification and quantification based on $[M+H]^+$ species. Calibration curves for the investigated PAHs suggest limits of detection down to ppt levels under optimized conditions, which is competitive to state of the art-methods.

References

[1] A.K. Huba, M.F. Mirabelli, R. Zenobi, Anal. Chem. 2019, 91. 10694-10701.