Flow Modulated GC×GC in Combination with Atmospheric Pressure Mass Spectrometry using the SICRIT Ionization Source

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Introduction

Comprehensive two-dimensional gas chromatography (GC×GC) has the major advantage of being able to separate complex mixtures from the combination of two orthogonal stationary phases. Additionally, this creates an ordered chromatogram that can provide some structural elucidation of the mixture. With the addition of a mass spectrometer (MS), these individual compounds can be identified, allowing for a more complete characterization of complicated mixtures.

Typically, time of flight (TOF) MSs are used as these have high data acquisition rates that can handle the fast peaks of the GC×GC chromatogram. Additionally, these MSs can also handle slightly higher flow rates (1-2 mL/min) that are used in the second dimension separation with thermal modulation. However, flow modulated GC×GC has greater second dimension flow rates (20 mL/min), and flow is typically split to waste or a second detector, such as a flame ionization detector (FID).

SICRIT Technology

Figure 1: Schematic diagrams of the SICRIT source with plasma-based core (left) and attached to an atmospheric pressure MS (right)

The SICRIT (Soft Ionization by Chemical Reaction in Transfer) ionization source is interfaced with the atmospheric pressure inlet of the MS. Gaseous samples enter the MS inlet and are ionized by a dielectric barrier discharge, which produces a soft form of ionization.

Advantages of this source include an enhanced range of analytes: from non-polar to polar compounds and minimal fragmentation of parent ions.

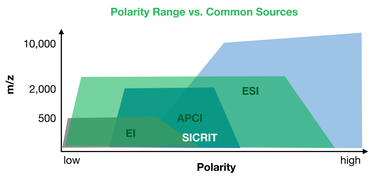


Figure 2: Typical m/z and polarity ranges for analytes using common sources as well as SICRIT. SICRIT covers a large portion of the analyte range of EI, APCI, and ESI.

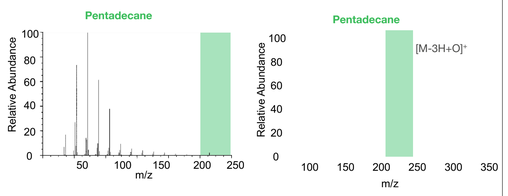


Figure 3: (Left) EI spectra of pentadecane showing common fragmentation. (Right) SICRIT spectra of pentadecane showing parent ion in the form of $[M-3H+O]^+$.

These advantages of the SICRIT source makes for a potential source to combine flow modulated GC×GC to atmospheric MSs. Further, as these MSs have higher vacuum capabilities, hydrogen can be used as a carrier gas at these higher flow rates, while maintaining sensitivity.

Experimental Conditions and Instrument Setup

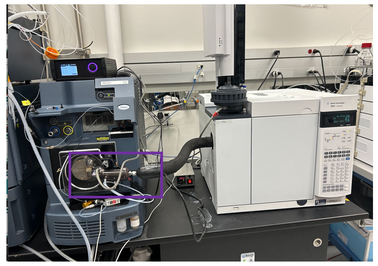
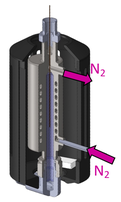


Figure 4: Instruments include an Agilent 7890B and Waters Xevo TQD which are connected with the SICRIT source and a 0.5m heated transfer line

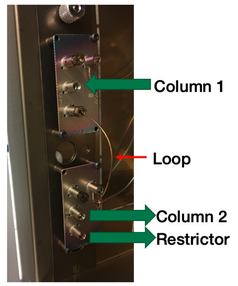
GC/SPME Module

Heated transfer line connects to GC/SPME module, which connects to the SICRIT source on the triple quadrupole MS.



GC column is inserted into the heated module, at ambient pressure.

Dry N_2 (or humidified N_2) from the MS can be used as a make up gas to constantly flush the module and ensure a clean background.



RFF Flow Modulator

A home-made flow modulator, based on the reversed-fill/flush design was used for this set up with hydrogen as the carrier gas.

Polar x Non-Polar Column Set

D1: HP-50: 25 m × 0.250 mm × 0.25 µm;
flow: 0.5 mL/min H_2
D2: DB-1HT: 5 m × 0.250 mm × 0.10 µm;
flow: 22 mL/min H_2
Restrictor: 3 m × 0.100 mm

Table 1: Instrument setup and conditions

GC Conditions Agilent 7890B GC	GC×GC Flow modulator	SICRIT Source	Triple Quadrupole Mass Spectrometer Waters Xevo TQD
Inlet: S/SL; split mode at 100:1 Temp: 275°C Agilent 7693 Autosampler injection Oven: 40°C (2min) – 280°C @5°C/min (10 min) FID (dual detection): 300°C H_2: 20 mL/min Air: 350 mL/min N_2 Makeup: 10 mL/min CDS: OpenLab Chemstation	D1: HP-50 25m × 0.250mm × 0.25µm film; 0.500 mL/min D2: DB-1HT 5m × 0.250mm × 0.10um film; 22 mL/min Restrictor: 3m × 0.100mm Modulation: 3s (130ms flush) For dual detection: 3-way CFT splitter to FID and MS (5:1 split) ChromSpace used for data analysis. Raw chromatograms were first converted to .cdf or .csv files	Transfer line: 0.5m Temp: 290°C GC/SPME Module: Temp: 300°C Dry N_2: 2.0 L/min (controlled by needle valve) Voltage: 1800V Frequency: 50 kHz	Nanospray Settings Cone Voltage: 20V Purge Gas: 2.0 L/min Source Temp: 70°C MS Scan Mode Mass Range: 50 – 500 Acquisition Rate: 20Hz CDS: MassLynx

Hydrocarbon Analysis

Hydrocarbon and fuel samples were used as example samples to determine efficacy of setup. The SICRIT source has been used previously with alkanes and aromatics as a soft ionization source, demonstrating the applicability to these compound classes.

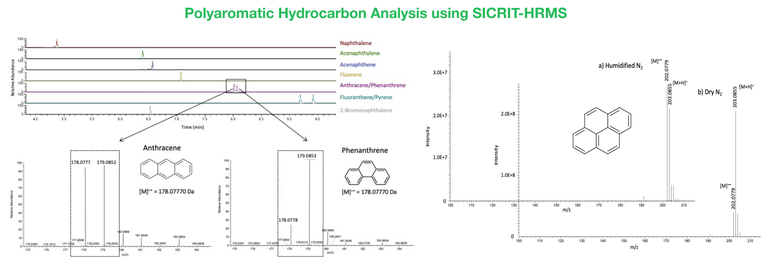


Figure 5: GC-SICRIT-HRMS analysis of PAHs demonstrating the ionization under humidified conditions as $[M]^{+\bullet}$ (left) as well as a comparison to dry conditions, which promote $[M+H]^+$ ionization (right).

Results and Discussion

Response Time & Points Per Peak

It is important to ensure that the modulation produces good cuts of the peaks as well as the MS having a fast enough response time to provide enough points per peak.

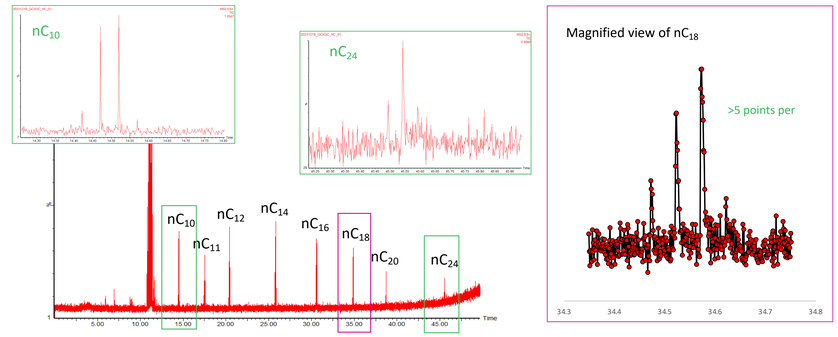


Figure 6: (Left) Raw chromatogram of GC×GC-SICRIT-MS analysis of n-alkanes with at 3 - 4 cuts per peak with a 3s modulation period. (Right) Extracted data plotted with each data point, demonstrating more than 5 points across each peak.

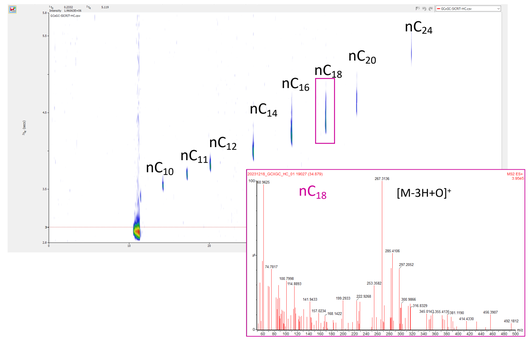


Figure 7: GC×GC-SICRIT-MS analysis of hydrocarbons as a contour plot with MS spectra of C_{18} showing parent peak ionized as $[M-3H+O]^+$

Table 2: Hydrocarbons C_{10} – C_{24} and their measured masses

Compound	Measured Mass as $[M-3H+O]^+$
nC10	155.08
nC11	169.18
nC12	183.04
nC14	211.19
nC16	239.25
nC18	267.26
nC20	295.21
nC24	337.42

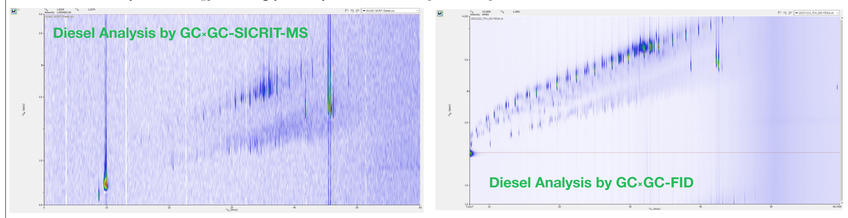


Figure 8: (Left) GC×GC-SICRIT-MS analysis of diesel diluted in cyclohexane and a Comparison of the same mixture split to an FID (Right)

Conclusions

Preliminary results demonstrate this source to be a viable connection between flow modulated GC×GC with LCMS instruments. These MSs can handle the high flow rate of flow modulation, fast peaks, as well as the use of hydrogen as a carrier gas.

References

J.F. Griffith, W.L. Winniford, K. Sun, R. Edam, J.C. Luong, J. Chromatogr. A. 1226 (2012) 116-123
SICRIT App Notes can be found at: www.plasmion.com

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