Optimization of the Zoex Thermal Modulator in GC×GC

Introduction

Dual-stage thermal modulation is considered the golden standard in GC×GC thanks to its high efficiency in producing very sharp modulated peaks and therefore excellent two-dimensional resolution. Thermal modulation is driven by hot and cold gaseous jets that trap and periodically re-mobilize portions of eluting peaks from the primary column into the secondary column. The process typically uses a constant cold jet and carefully timed hot pulse. A high gaseous nitrogen consumption is requested for operation, as well as liquid nitrogen for the capability to successfully modulate very volatile compounds. Fine-tuning of cold jet flow and hot jet pulse duration during the GC run can help achieving ideal refocusing/re-mobilization dynamic and optimal modulation ratio also for applications covering a wide volatility range. This is key to fully exploit the potential of the operation principle and maximize performance. The optimized combination of thesetwo aspects in fact determines operation: the efficiency of the modulation in terms of preventing break-through of the high volatility compounds and avoid exessive trapping for heavy semi-volatile compounds. SRA Instruments' Optimode is an independent programmable device that offers extended control on the Zoex Loop Thermal Modulator. A precise mass flow controller allows reducing the cold flow during the run to avoid un-efficient re-injection for high boilers as well as implementing a stand-by mode to save nitrogen consumption. An additional feature enables programming the hot pulse valve activity to obtain carefully controlled and variable hot pulse duration and modulation period.

Experimental

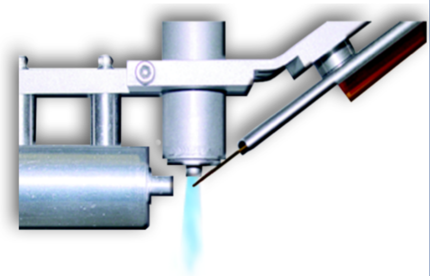
An hydrocarbons mixture with wide range of boiling compounds was used to demonstrate how an optimized combination of cold flow and hot pulse time jet can significantly enhance modulation.

Zoex Loop Thermal Modulator with liquid nitrogen cooling
GC Image Software package (Zoex).

Cold Jet conditions and their effect on the modulation

STAND-BY-FLOW: a minimum N_2 flow is set in between runs to lower consumption during idle times while avoiding ice formation in the cold jet line. Gas flow is reduced from operation rate (flow 20-15 L/min) to about 1.5 L/min,

PROGRAMMABLE N_2 COLD FLOW controlled by MFC, highly reproducible, allows ideal trapping across a wide range of volatility components.



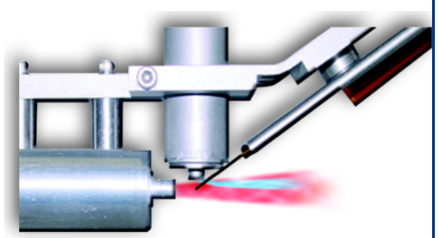
Cold Jet: immobilizes and traps the compounds by rapid cooling

Hot Jet conditions and their effect on the modulation

VALVE PULSE timing controlled externally from the GC.

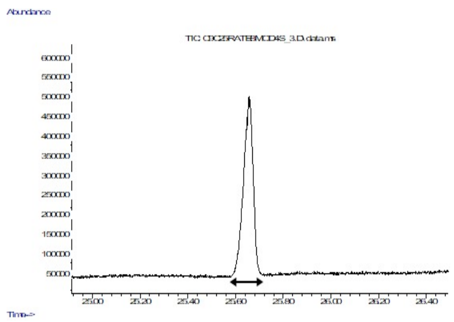
PROGRAMMABLE HOT PULSE TIME within a run to avoid carryover of heavy compounds.

TWO MODULATION PERIOD TIME programmable within a run to optimize modulation ratio.



Hot Jet: flash heating to re-mobilize the trapped compounds into the gas phase

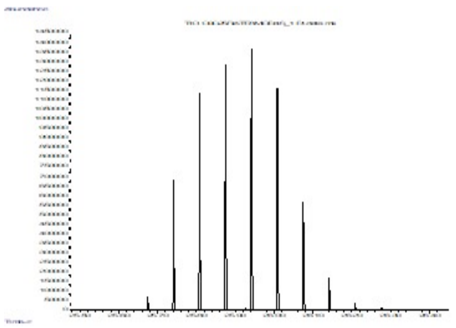
Un-modulated n-C25



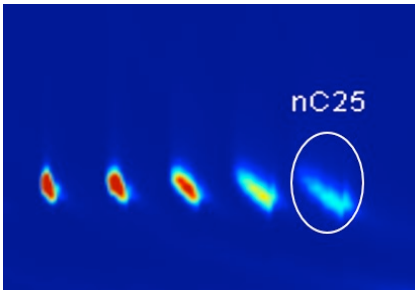
Peak width at baseline: 9.12 s

With 4 sec modulation = <u>2.28 theorical modulated peaks</u>

Modulated n-C25



2-D view



Cold jet flow = 6 L/min

Hot jet pulse Time = 250 ms

Inefficient re-mobilization:

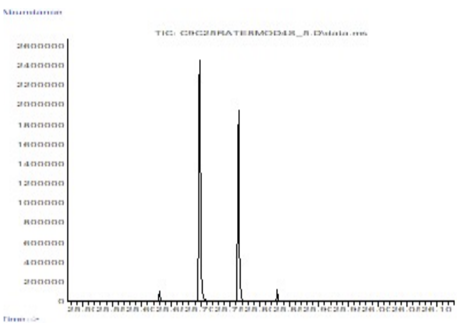
7 modulations, poor 2D peak shape

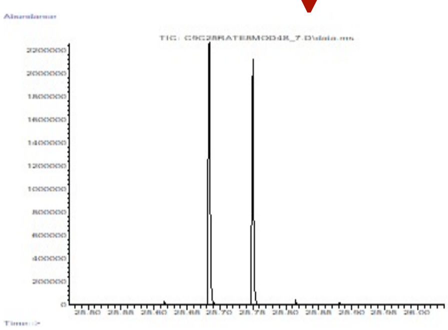
Reduce cryogenic trapping

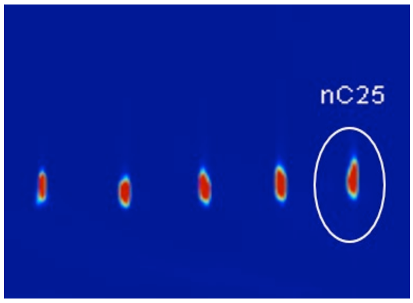
Cold jet flow = 3.6 L/min

Enhance re-mobilization

Hot Pulse = 500 ms

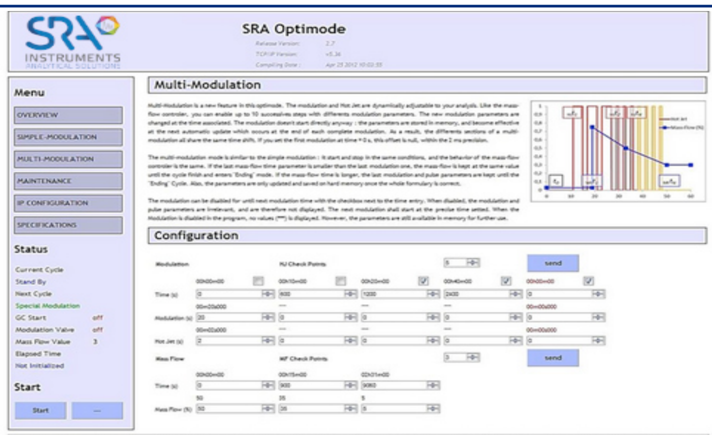






☑ 2+ modulations

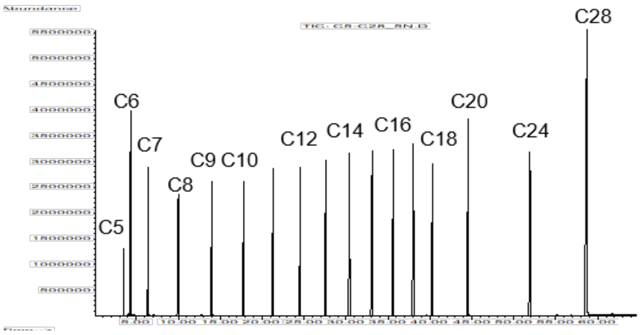
☑ Excellent 2D peak shape



OPTIMODE Control Interface

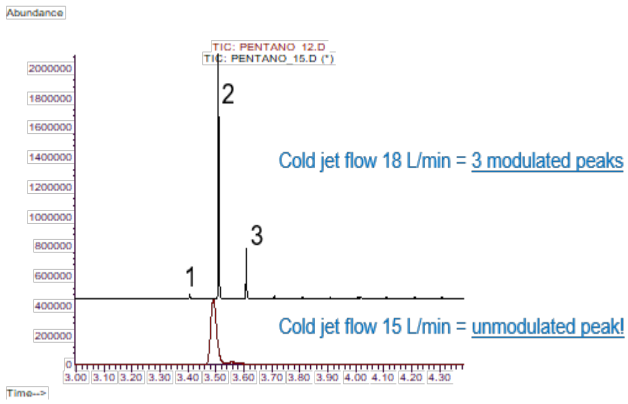
Modulation optimization across a wide boiling point range sample (36°C-431°C)

a) Un-modulated nC5-nC28 analysis

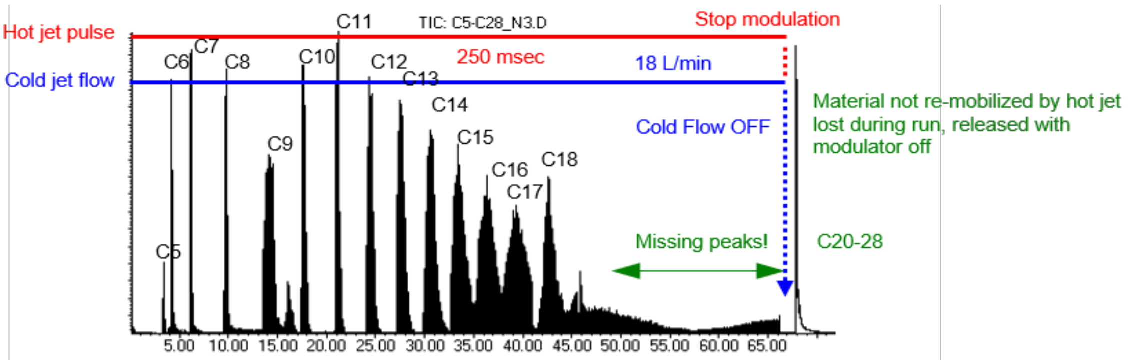


	nC5	nC8	nC15	nC20	nC28
Peak width (s)	14.4	22.8	24	30	34.2
Modulation ratio (modulation period 8s)	1.8	2.85	3	3.75	4.3

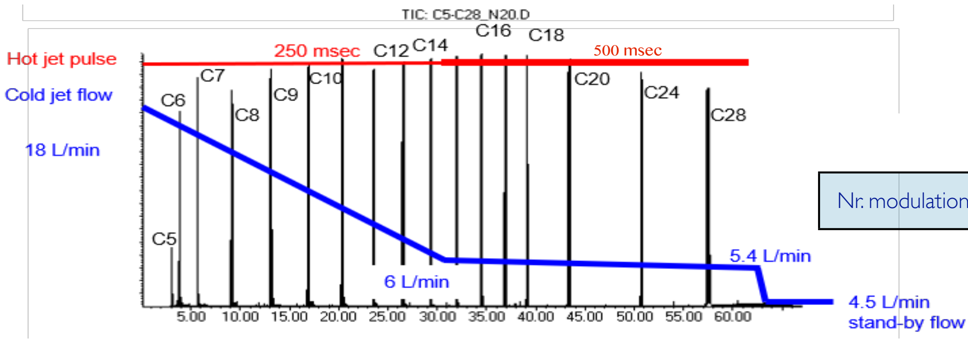
b) Determination of the minimum cold jet flow necessary to modulate nC5 (b.p.36°C)



c) Modulated nC5-nC28 analysis at constant cold flow (at minimum value to modulate nC5)

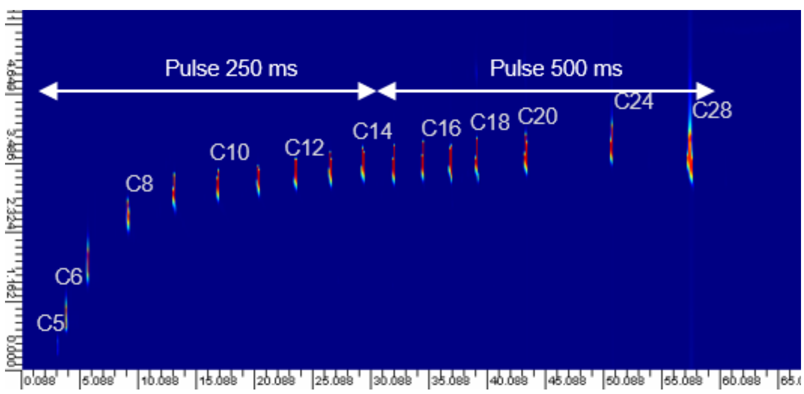


d) Modulated nC5-nC28 analysis with optimized cold flow rate and hot pulse time to obtain correct modulation ratio



	nC5	nC8	nC15	nC20	nC28
Nr. modulations*	2	3	3	4	5

* with 8 seconds modulation period



2D view

8 sec modulation period, 2 cycle events
Cycle 1: 0-30 min cold jet from 18 L/min to 6 L/min with 250 ms pulse
Cycle 2: 30'-67 min cold jet from 6 L/min to 5.4 L/min with 500 ms pulse

Conclusions

- Thermal modulation requires accurate optimization of temperatures and timing to achieve correct operation and optimal performance, especially for samples characterized by a wide boiling point range.
- Proper modulator operation ensures efficient trapping as well as quick and quantitative remobilization of the components into the secondary column.
- With SRA Instruments' Optimode cold jet flow and hot jet pulse duration can be optimized to ensure an accurate process and obtain the expected modulation ratio.
- Programming the cold jet flow during and after runs allows a significant reduction of gas and liquid nitrogen consumption, making operation more cost-effective and environmentally friendly.

Aknowledgements

Thanks to:

Prof. Chiara Emilia Cordero and Prof. Carlo Bicchi at the Dipartimento di Scienza e Tecnologia del Farmaco, University of Turin - Italy.

SRA Instruments S.p.A
20063 Cernusco S/N (MI)
Tel +39 02 9214 3258
www.srainstruments.com
info@srainstruments.com

SRA Instruments SAS
69280 Marcy l'Etoile Lyon
Tel +33 04 7844 2947
www.srainstruments.com
info@sra-instruments.com

SRA INSTRUMENTS ANALYTICAL SOLUTIONS
Agilent Premier Solutions Partner