Optimization of the thermal modulation in comprehensive two-dimensional gas-chromatography

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Introduction

The two-stage thermal modulator is one of the most efficient device to produce sharp modulated peaks in GCXGC [1][2][3]. The thermal modulation uses hot and cold jets of gaseus nitrogen to continuously and efficiently trap and inject portions of eluting peaks from the primary column into the secondary column. The thermal processes are determined by the nitrogen cold flow and the temperature/time of the hot pulse, furthemore a high gas and liquid nitrogen cosumption is requested for operation. In order to obtain an optimal modulation ratio of 3-4 [4], the cold jet flow [5] and the activity time of the hot jet pulse must change during the GC run for such application that requires the simultaneous determination of either very volatile compounds and high boiling compounds. The optimized combination of these two parameters improve the modulator operation: the efficiecy of the modulation in terms of preventing break-through of the high volatility compounds and avoid the trapping for semi-volatile compounds causing increase contribution on the modulation ratio and peak tailing.
In this experiment an independent programmable device is used as accessory for the thermal modulator to control, with a mass flow controller, the cold flow during and after the GC run. An additional feature controls and programs the hot pulse valve activity.
An hydrocarbons mixture with wide range of boiling compounds was used to demostrate the contribution of the modulator on the modulated-peaks and how an optimized combination of cold flow and hot pulse time jet can allow a proper modulation.

Experimental

GC Agilent Technologies mod. 6890N
Inlet: Split/Splitless with EPC, Pressure: 205KPa He const flow
Column 1: HP-1, 30 mt x 0.32 mm ID df: 0.25 µm
Column 2: BPX-50, 2.5 mt x 0.1 mm ID df: 0.1 µm
Oven: 45°C (5min) to 320°C, rate 2.5°C
2nd Oven: 60°C (5min) to 340°C, rate 2.5°C
Software MSD Agilent Chemstation

Zoex KT-2005 GCXGC Dual Stage Thermal Modulator
Zoex GC-Image Software

Hot Jet temp.: 145°C (5min) to 320°C, rate 2.5°C
Modulation Period: 4 sec and 8 sec
Modulation tube: 2 mt X 0.18 mm ID uncoated fused silica
Liquid Nitrogen cooling system
Bronkhorst Hi-Tech Mass Flow Controller 0-30 Nlt/min Nitrogen
Programmable Logic Controller Horner

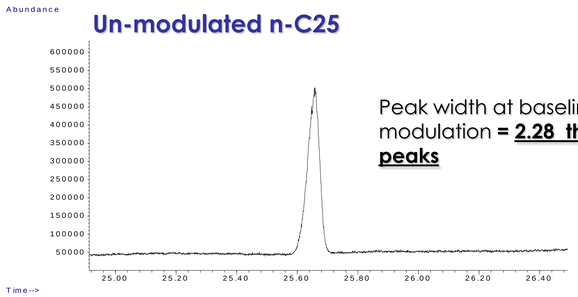
qMSD 5975B Inert Agilent Techonologies
Fast Scan 45-420 amu
Sample: nC5-nC28 p/n 25950.200 Analytical-Controls BV, NL

Cold Jet conditions tested and their effect on the modulation

- ***STAND-BY-FLOW:*** a minimum N2 flow is maintained between each run or after the modulation time within an analysis. It reduces the N2 gas flow from operation rate (flow 30-15 lt/min) to about 3 lt/min, without transfer-line iceing. Reduced use of gas & liquid N2.
- ***N2 COLD FLOW*** controlled by MFC, reproducible run by run
- ***PROGRAMMABLE N2 COLD FLOW*** allows proper trapping of a wide range of volatility components in a sample: high rate for very volatile and low rate for heavy compounds within a run.

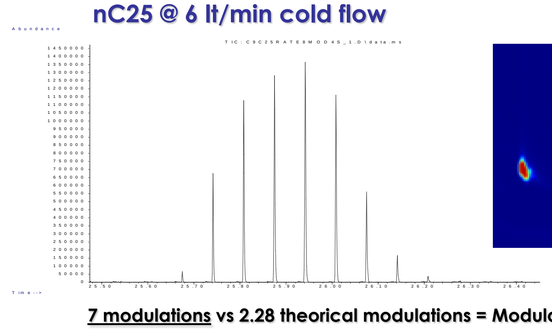
***Cold Jet: immobilize and trap the compounds by rapid cooling**

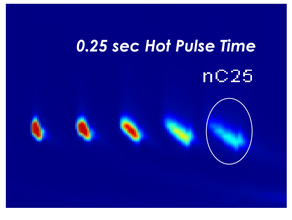
Un-modulated n-C25



Peak width at baseline 9.12s with 4 sec modulation = **2.28 theorical modulated peaks**

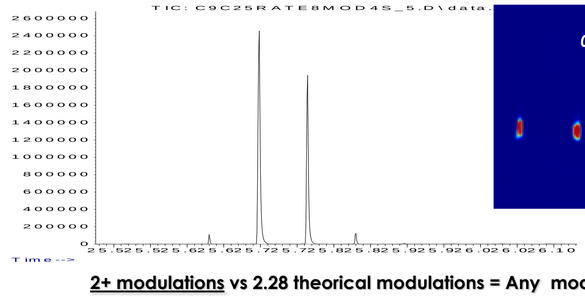
nC25 @ 6 lt/min cold flow — **2-D view**

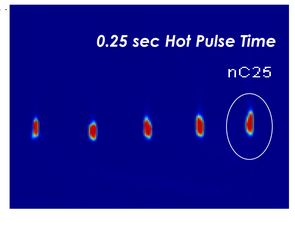




7 modulations vs 2.28 theorical modulations = Modulator trapping effect

nC25 @ 3.6 lt/min cold flow — **2-D view**

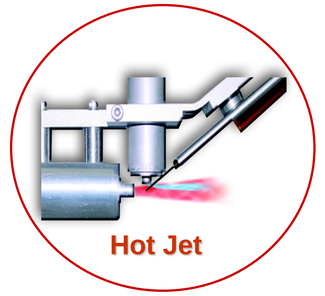




2+ modulations vs 2.28 theorical modulations = Any modulator contribution

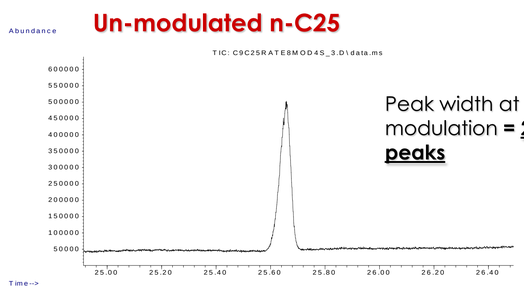
Hot Jet conditions tested and their effect on the modulation

- ***VALVE PULSE & POWER*** controlled externally from the GC
- ***HOT PULSE TIME PROGRAMMABLE*** for proper carryover of heavy compounds
- ***TWO PULSE TIME*** programmable within a run
- ***TWO MODULATION PERIOD TIME*** programmable within a run



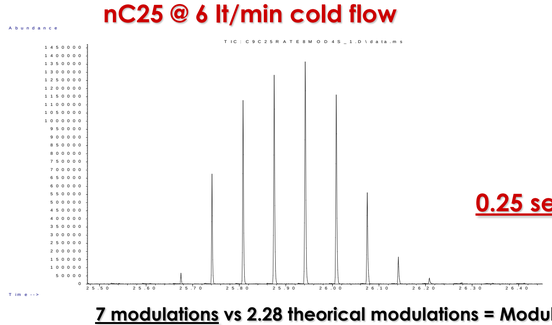
***Hot Jet: flash heating to launch the trapped compounds**

Un-modulated n-C25



Peak width at baseline 9.12s with 4 sec modulation = **2.28 theorical modulated peaks**

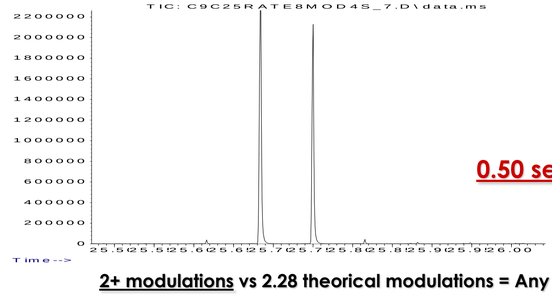
nC25 @ 6 lt/min cold flow



0.25 sec Hot Pulse Time

7 modulations vs 2.28 theorical modulations = Modulator trapping effect

nC25 @ 6 lt/min cold flow



0.50 sec Hot Pulse Time

2+ modulations vs 2.28 theorical modulations = Any Modulator contribution