Recent Advances in 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]. The thermal modulation uses hot and cold jets of gaseous 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. In order to obtain an optimal modulation ratio of 3-4 [2], the cold jet flow [3] 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 improves the modulation efficiency in the prevention of the high-volatility compounds breakthrough and trapping of semi-volatile compounds, thus making an important contribution on modulation ratio and peak tailing.

An independent programmable device named Optimode is presented, used as accessory for the thermal modulator to manage, with a mass flow controller, the cold flow during and after the GC run. Additional features allow programmation of the hot pulse valve activity with a very high precision and modification of the modulation period during the run.

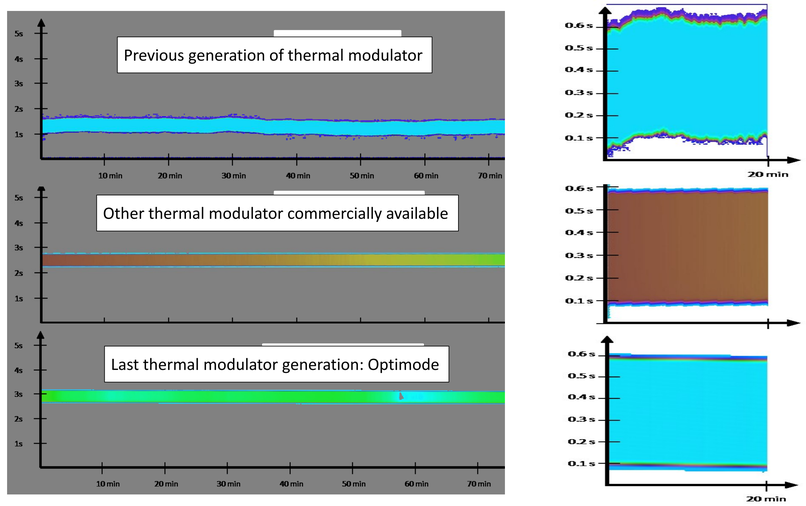
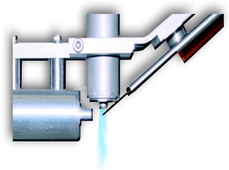


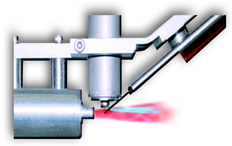
Fig. 1 **: Two hot jet modulation (unsuitable and irregular) compared to one more stable from Optimode device (bottom)**

OPTIMODE FEATURES



Cold jet: immobilizes and traps the compounds by rapid cooling

- **Programmable N_2 cold flow:** allows proper trapping of a wide range of boiling points over the chromatographic run.
- **Stand-by flow:** a minimum N_2 flow is maintained between each run or after the modulation time within an analysis. It reduces the N_2 gas flow from operation rate (flow 15-30 *SLPM*) to about 3 *SLPM*, without transfer-line iceing. Reduced consumption of gas & liquid N_2.
- **N_2 cold flow:** reliable and precise, controlled by a digital MFC
- **Valve pulse & power:** independent from the GC
- **Hot jet pulse time:** programmable within a run for proper re-mobilization of heavy compounds
- **Modulation period:** programmable and multi-steps capability within a run



Hot jet: flash heating to deviate cold flow and release trapped compounds

Optimode detailled specifications:

Hot jet modulation			
Modulation resolution	0.1 µs	**Modulation step**	1 ms
Hot jet resolution	0.1 µs	**Hot jet step**	1 ms
Modulation repeatability	12.5 ns	**Modulation length**	from 2 ms
Hot jet repeatability	12.5 ns	**Multi-modulation steps**	up to 10
Mass flow controller			
Mass flow resolution	0.39 %	**Mass flow steps**	up to 10

Multi-modulation is an interesting feature available with Optimode. Modulation and Hot Jet duration are dynamically adjustable to analysis needs. Like with the mass-flow controller, it is possible to set up to 10 successive steps with different modulation parameters.

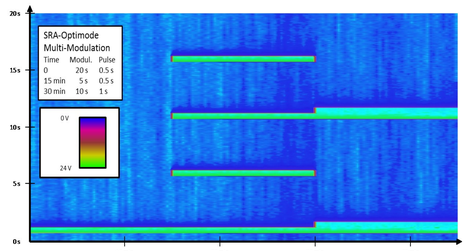


Fig. 2 **: illustration of the multi-modulation mode**

Multi-modulation mode is similar to the classic one step mode: modulation starts and stops in the same conditions, and behavior of the mass-flow controller is the same. If the last mass-flow time parameter is smaller than the last modulation one, the mass-flow is kept at the same value until the cycle is over. If mass-flow time is longer, last modulation and pulse parameters are kept until end of the cycle. Each new modulation step shall start at the precise time set.

OPTIMODE WEB INTERFACE

A dedicated interface allows Optimode configuration through an ethernet communication. At any time status of the system is displayed. Once the time of the modulation or the various steps of modulation are set, analysis can be started directly from the interface. A maintenance function allows operator to apply a correction if a drift of the modulation is observed over the time.

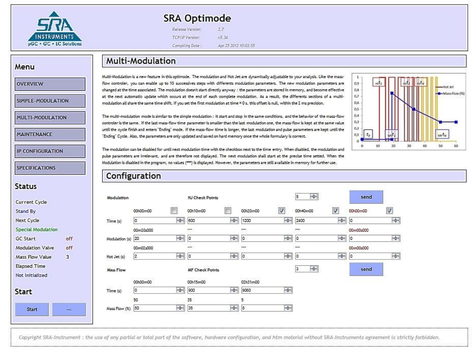
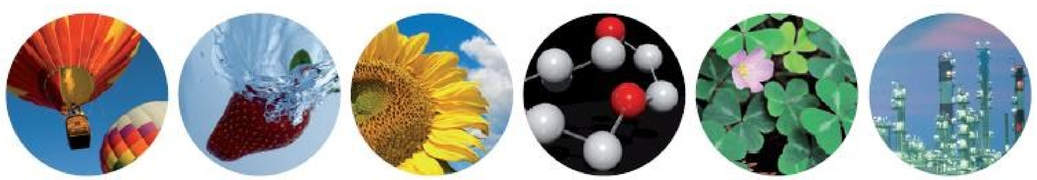


Fig. 3 **: Optimode web interface**

Using Optimode, an accurate optimization of the thermal conditions can be reach in order to obtain a proper modulation ratio along the entire run, especially for wide range of boiling point samples. Otherwise, quantitative remobilization of material into the secondary column is improved thanks to Optimode.

References:

[1] E. B. Ledford *et al.* HRC J. High Res. Chrom **23** (2000) 205
[2] W. Khummueng *et al.* Anal. Chem. **78** (2006) 4578
[3] R. B. Gaines *et al.* J. Sep. Science **27** (2004) 380



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