Advances in Flow Modulated comprehensive GCXGC-MS at full sensitivity applied to profiling complex indoor&outdoor air samples.

Eligio Sebastiani[1], Fabio Villanelli [1], Luca Calamai [2]
[1]SRA Instruments Italia SpA, Via alla Castellana 3, 20063 Cernusco sul Naviglio (MI), Italy -e-mail: sebastiani@srainstruments.com
[2]Dipartimento di Scienza del Suolo e Nutrizione della Pianta – Università degli Studi di Firenze

Agilent Technologies
Premier Solution Partner

Introduction

Comprehensive two-dimensional gas chromatography (GCxGC) is a separation method receiving increased attention in recent years due to its superior peak capacity and separation power in the analysis of complex mixtures such as those found in the petrochemical, environmental, and fragrance industries.
Today, the most popular commercially available systems employ thermal modulators which require liquid N_2 for trapping analyte after 1 D column and hydrogen as carrier gas.
The **TotalFlowModulated_ GC × GC_MS methodology uses two capillary columns in series** coupled by a flow modulator (Figure 1).
These columns are usually of very different polarities.
Within the flow modulator[1], analyte bands from the first column are collected in a fixed-volume loop which is successively quickly and periodically injected into a short second column, by a larger flow. The 2D column is maintained under vacuum conditions, such to obtain very narrow bands at high flow rates.
At these conditions, any separation achieved on the first column is preserved during transfer to the second column and hydrogen as carrier gas is not required

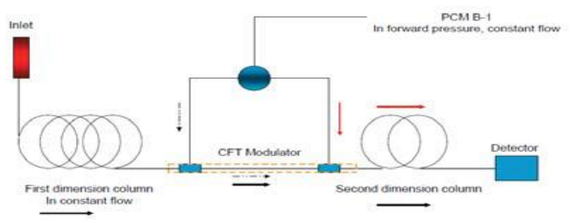
Materials and Methods

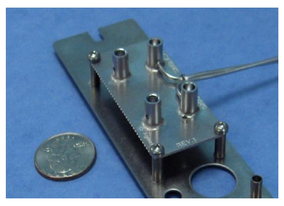
Agilent Technologies GC mod. 7890B
Inlet:Gerstel CIS 4 PTV mode, solvent vent
Column1D: HP-5, 30 m x 0.25 mm ID df: 0.25 µm
Column2D: HP-Innowax, 5 m x 0.32 mm ID
Oven: 37 °C for 3 min
then 8 °C/min to 80 degrees C for 1 min
then 20 °C/min to 260 degrees C for 3 min
Agilent Technologies GC-MS/MS mod. 7000B
Transfer line temp.: 260°C
Source temp.: 270°C
Acquisition mode: full scan
Software: Agilent Mass Hunter, Zoex Image
On-line air sampling and thermal desorption: Markes Unity with tube desorber and Air Server

Experimental

Schematic Diagram of PTFM_GCXGC-MSD

Fig.1





After tube desorption, the sample undergo separation in the first dimension (1D) column. At regular time intervals, a sample loop inside the Flow Modulator device collects fraction from the 1D column. Here, using an high flow rate the sample loop is completely flushed by a larger flow into a second column directly connected to the MS.
Flow rates in 1D and 2D columns are adjusted such to have complete compatibility with MS system, with no needs of split flow, and the sample eluted from the second column flows entirely in the MS source without signal loss.
GCxGC affords the coeluting compounds in the first column (fig. 2, *), to be separated in the second dimension thanks to the orthogonal polarity of the chromatographic phases, resulting in different signals at same retention time in the first dimension (x-axis), but separated with different retention times in the second dimension (y-axis) (blobs) .
The chromatographic run in second dimension has to be completed in the same time used to fill again the sample loop: in this way all the collected fractions in the sample loop are analyzed, obtaining a comprehensive result, and the chromatogram is a series of slices every few seconds.
A 2D Zoex Image software reconstructs the chromatographic run turning every slice in the orthogonal direction, and building a two-dimensional map.
The figures 2,3 and 4 show the capability of the proposed system to magnify the separation of a complex mixture, occupying a lot of the space available, and pushing some compounds until the upper limit of the 2D chromatographic space.
The baseline is easily recognized because of the air presence, not retained in the second column and giving the starting point of the second dimension chromatographic run.
The peak intensity is easily recognizable thank to the colours used, but if necessary, it is possible to build, via-software, a three-dimensional map, with a conical peak shape: every signal is integrated as peak volume, because the reconstructed peak is like a solid.
Each peak is identified using a standard NIST Library, and inserted in a peak table helpful to identify the unknown samples. As example of complexity of real sample, 3L of air were collected with the standard procedure, close to a land fill and trapped in a proprietary tube packed with carbograph and tenax (Fig. 4). **TotalFlowModulated_ GC × GC_MS** analysis is reported.

Data obtained with the system showed in the materials and methods picture. The system is installed in a mobile lab of Bari University, dr. De Gennaro

VOCSODOR
VALUTAZIONE DELLE EMISSIONI DI COMPOSTI ORGANICI VOLATILI E DEGLI IMPATTI ODORIGENI PRODOTTI DAI NUOVI MATERIALI E DALLE NUOVE TECNOLOGIE PER I SISTEMI PRODUTTIVI
"Intervento cofinanziato dall'Accordo di Programma Quadro in materia di Ricerca Scientifica Il Atto Integrativo - PO Puglia FESR 2007-2013, Asse I, Linea 1.2 – PO Puglia FSE 2007-2013 Asse IV" Intervento "Reti di Laboratori Pubblici di Ricerca"
CODICE PROGETTO 52
Realizzatore dell'intervento: Università degli Studi di Bari "A. Moro"
"Investiamo nel vostro futuro"

Results and Conclusions

Fig.2 VOC Standard solution , trapped in a packed tube with carbograph and tenax

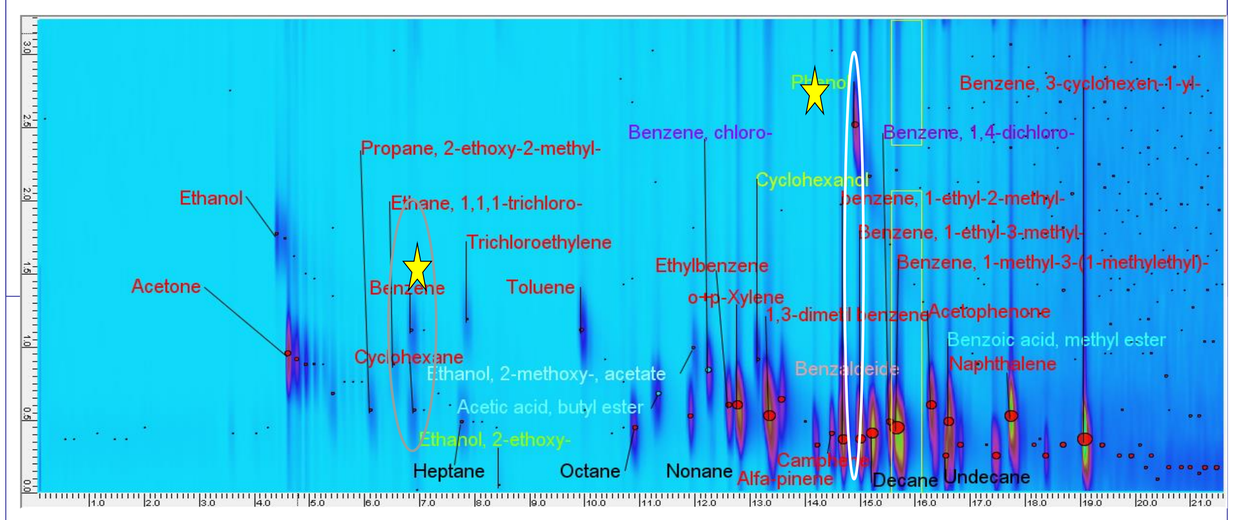


Fig.3 Air sample, 3L, collected in an office close to the university chemical lab and trapped in a Markes tube packed with Carbograph and Tenax

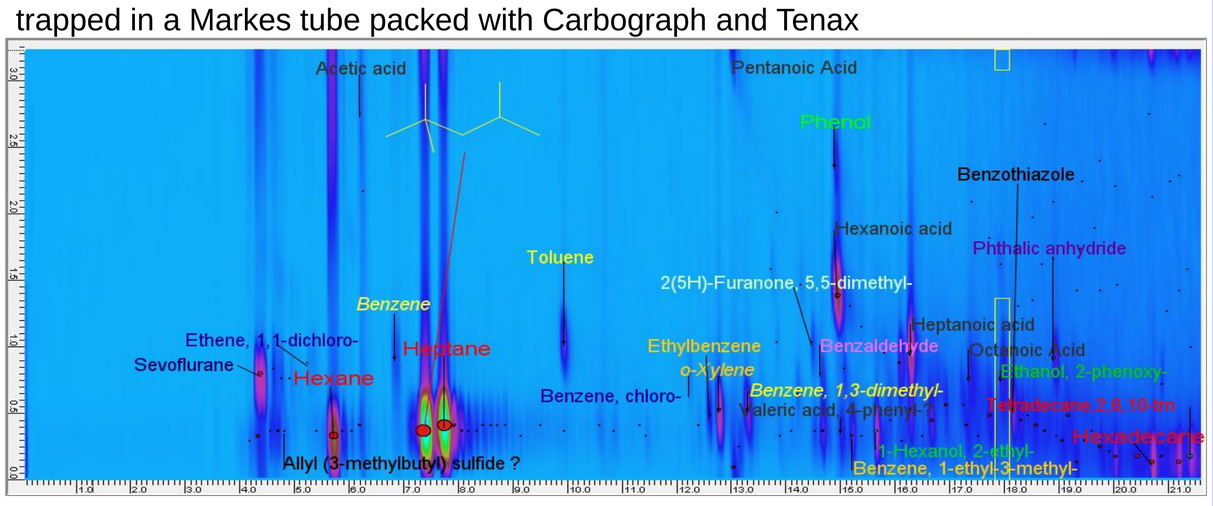
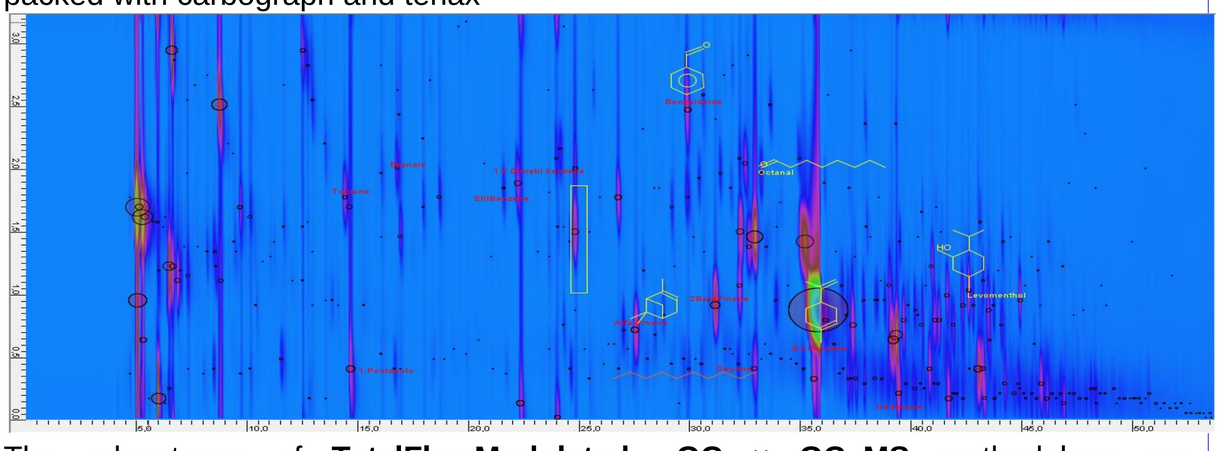


Fig.4 Air sample, 3L, collected close to a land fill and trapped in a Markes tube packed with carbograph and tenax



The advantages of **TotalFlowModulated_ GC × GC_MS** methodology are undoubtedly related to the ease of use and robustness of Agilent micro fluidics plates and pneumatics (PCM and solenoid valves) compared to thermal modulation with cryogenics. Accurate electronic pneumatic controlling ensure good repeatability and linearity.
The information potential and the higher level of separation achievable by GC×GC-MS could be easily extended to the routine screening analysis labs.

Reference:

[1] Seeley J.V., Micyus N.J., McCurry J.D., Seeley S.K., Comprehensive two-dimensional gas chromatography with a simple fluidic modulator, American Laboratory, 2006, 38, 9, 24-26.