Multi-detector Configurations and Applications of Differential Flow Modulation GCXGC (K.29)

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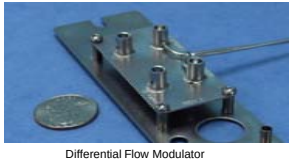
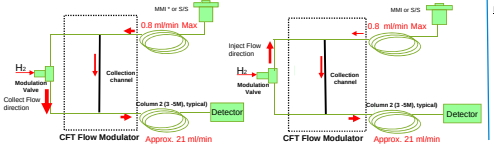
Introduction

The enhanced separation power of GC x GC can be combined with selective and non-selective detectors to provide enhanced sample information and confirmation that would otherwise not be possible in a single run. Simultaneous multi-detector signal acquisition is possible with constant flow-modulated GCXGC when various Capillary Flow Technology (CFT) devices, and carefully sized restrictors are coupled to the second column flow from the modulator. Recent advances in high speed data acquisition now make it possible to use quadrupole MSD's for many applications. Due to the high second column flow associated with flow modulation, CFT splitting devices are used to control and limit flow.

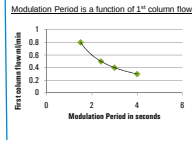


Differential Flow Modulator

Modulator Operation



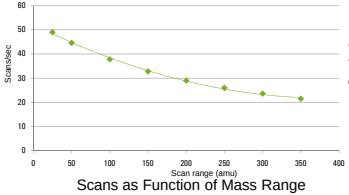
* MMI – Multimode Inlet



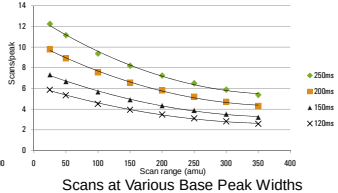
- Hydrogen carrier gas used for all experiments
- S/S Inlet in constant flow mode, column 1 flow rate 0.8 ml/min maximum
- PCM in pressure control mode, column 2 in constant flow at 22 ml/min

- Scan ranges must be carefully considered to achieve sufficient data points across a peak

MSD Scan Characteristics for Modulated GC x GC Peaks



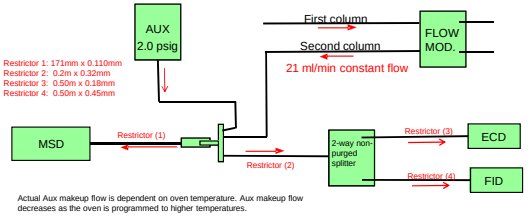
Scans as Function of Mass Range



Scans at Various Base Peak Widths

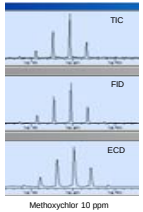
Multi-Detector Configurations using CFT Technology

MSD-FID-ECD System Pneumatics



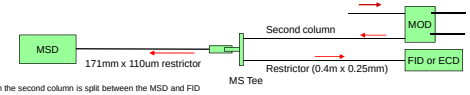
Actual Aux makeup flow is dependent on oven temperature. Aux makeup flow decreases as the oven is programmed to higher temperatures.

Modulated Chromatogram



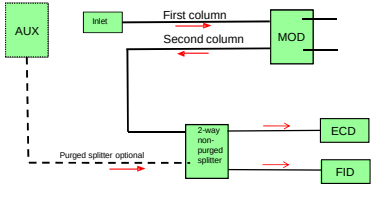
Methoxychlor 10 ppm

MSD-FID // MSD-ECD System Pneumatics



Flow from the second column is split between the MSD and FID
Flow to FID: 17 ml/min
Flow to MSD: 4 ml/min

FID-ECD System Pneumatics



Typical Conditions for the Three-detector System

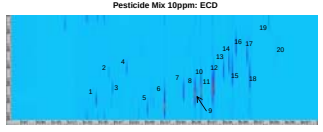
Inlet: Split/splitless with double taper helix deactivated line
Injection: Pulsed splitless
Column 1: 20M x 0.18mm x 0.18um DB-5ms
Column 2: 5M x 0.25mm x 0.15um DB-17HT
Micro ECD, 275C, 140ml/min Nitrogen makeup
FID, 275C
5975 MSD, scan 50-450 amu
Modulation Period: 2.42 seconds, load 2.31 seconds

Oven Program: 120 C (1 min) @ 5 C/min to 160 C (1 min) @ 3 C/min to 289 C (3 min)

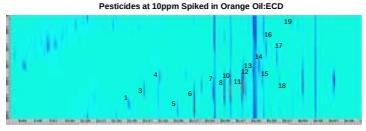
2D Data Processing: GC Image, GC Image LLC, Lincoln, NE, USA

ECD-FID-MSD System Performance

Pesticide Mix 10ppm: ECD

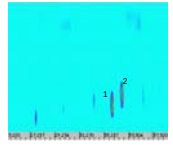


Pesticides at 10ppm Spiked in Orange Oil:ECD



1. alpha-BHC
2. beta-BHC
3. gamma-BHC
4. delta-BHC
5. Heptachlor
6. Aldrin
7. Heptachlor Epoxide
8. gamma-chlorodane
9. Endosulfan I
10. alpha-chlorodane
11. p p DDE
12. Dieldrin
13. Endrin
14. Endosulfan II
15. p p' DDD
16. Endrin aldehyde
17. Endosulfan sulfate
18. p p' DDT
19. Endrin Ketone
20. Methoxychlor

Column 1 Flow: 0.5 ml/min,
Column 2 Flow: 22 ml/min



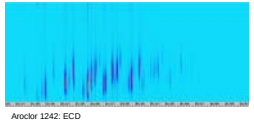
1 ppm chloronated pestisides in orange oil

SIM: ions 375, 372, 237

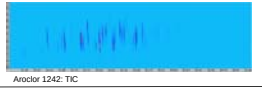
1. gamma-Chlorodane
2. alpha-Chlorodane

Column 1 flow: 0.4 ml/min
Column 2 flow: 23 ml/min

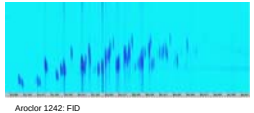
Aroclors



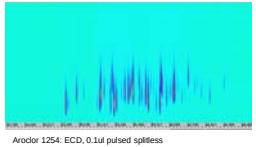
Aroclor 1242: ECD



Aroclor 1242: TIC



Aroclor 1242: FID



Aroclor 1254: ECD, 0.1ul pulsed splitless

2D images of Aroclor 1242 all produced from one injection

Summary

This work has shown the feasibility of coupling flow modulated GC x GC with two or three detectors collecting data simultaneously. Detector combinations can provide complimentary information, combining sensitivity, specificity, and general detection. Several capillary flow technology (CFT) devices can be configured in series with appropriate restrictors to provide appropriate flow. Use of the MSD as one of the detectors is possible though a CFT splitting device to simultaneously collect TIC, and SIM mode signals. Overall sensitivity is reduced due to flow splitting and use of makeup gas for purged splitters. Also, some peak broadening occurs due to multi-restrictor flow paths.

With proof-of-concept shown, these configurations offer the possibility of separating target analytes in complex interfering matrices by combining selective and non-selective detection. The system can serve as a useful screening tool with the MSD providing confirmation in many applications, however, GC x GC-MSD is not generally suitable for trace analysis in most cases due to second column effluent splitting, although SIM offers enhanced selectivity and sensitivity. For chlorinated compounds the ECD achieves ppb sensitivity with these configurations.