High Temperature Static Headspace Analysis of Polymers using Comprehensive GCXGC with a Mass Selective Detector

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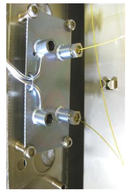
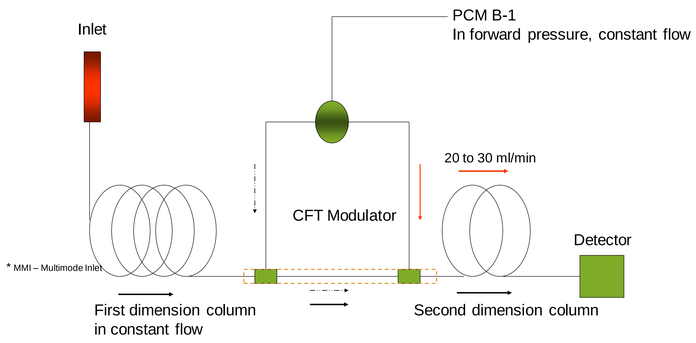
Introduction

Headspace analysis of polymer breakdown at 300 C yields a complex emissions profile. Pulsed Flow Modulation (PFM) GCXGC coupled to a static headspace sampler capable of sample equilibration at high temperatures can yield a great deal of information when used with a mass selective detector. Simultaneous signal acquisition of FID and MSD is possible by splitting the high second column flow at the MSD interface using a Capillary Flow Technology (CFT) device. High speed data acquisition make the narrow peaks associated with GCXGC compatible with an MSD. In this system, GCXGC gives a simple easy to interpret fingerprint of polymeric material.



Pulsed Flow Modulator
with fixed collection channel

Modulator Operation



➢Hydrogen carrier gas used for all experiments

System Flow and Pressure Characteristics

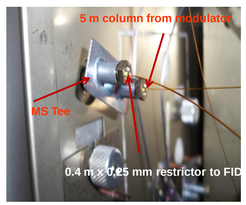
Oven Temp	Vacuum (x 10^-4)	Total Flow @ PCM	FID Flow	Pressure at MS Tee *	MSD Flow *
40	1.01	25.5	23.5	2.4	2.3
80	1.11	25.0	22.8	2.9	2.5
120	1.14	24.9	22.5	3.2	2.6
160	1.18	24.4	22.0	3.6	2.7
200	1.21	24.1	21.6	4.1	2.8
240	1.24	24.0	21.4	4.6	2.9
260	1.25	23.9	21.0	4.8	3.0

> Since modulated peaks are approximately 120ms to 150ms wide, the scan range must be carefully chosen to ensure 3 or more scans/peak

> Approximately a 6:1 split occurs at the MS Tee

> Performance turbo works well up to 3.5 ml/min hydrogen flow

> System is generally not suitable for trace analysis



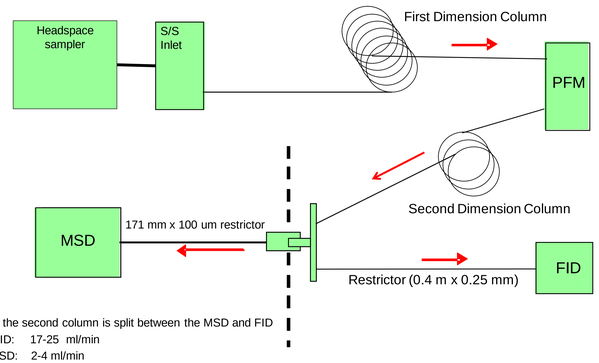
Typical scan range: 30 – 275 amu

Scan rate: 12,500 amu/sec

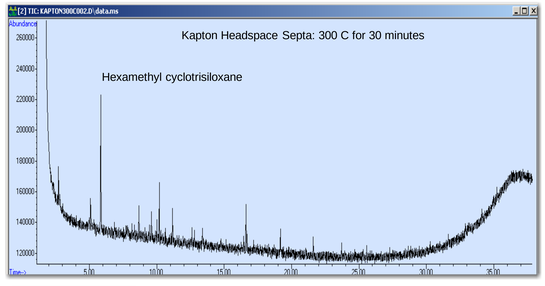
Scans/sec: 26

* Calculated value

PFM- GCXGC Configuration with a MSD



Flow from the second column is split between the MSD and FID
Flow to FID: 17-25 ml/min
Flow to MSD: 2-4 ml/min



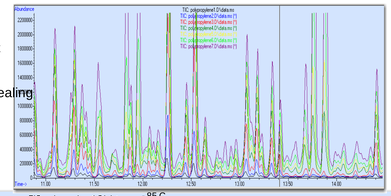
High Temperature static headspace analysis requires a septa capable of operation at 300°C without degradation and bleed. In this study, kapton lined septa are used. These show very low bleed with only one minor trisiloxane peak present in a blank run.

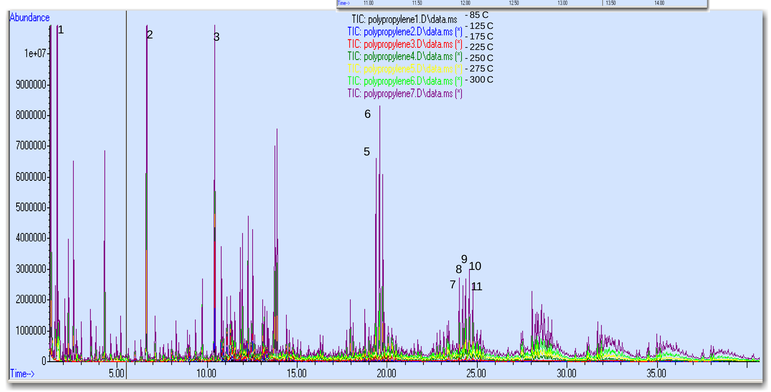
One Dimensional GC Temperature Study of Polypropylene Resin from 85°C to 300°C

10ml headspace vials purged with nitrogen before sealing

Column: 30 m x 0.25 mm x 0.25 um DB-5ms

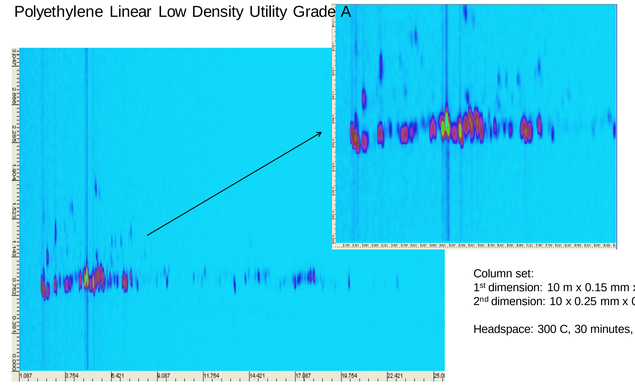
Overlay 1D TIC's of Polypropylene Resin





2D Plots of Polymer Headspace at 300°C

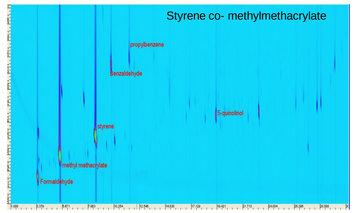
Polyethylene Linear Low Density Utility Grade A

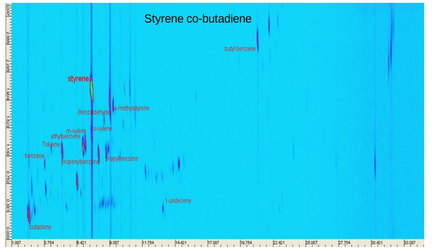


Column set:
1st dimension: 10 m x 0.15 mm x 0.15 um DB-5ms
2nd dimension: 10 x 0.25 mm x 0.10 um DB-Wax

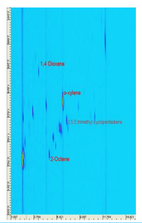
Headspace: 300 C, 30 minutes, 10 ml vial, 1.7 grams polymer

Styrene co-Polymers

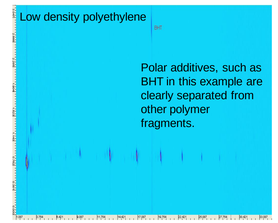




Poly(ethylene terephthalate) PET



Other Examples



Summary

High temperature static headspace can be employed to characterize polymers. Heating at 300°C may provide valuable information about the chemical structure, thermal stability, and degradation pathways of polymers. Operating the headspace sampler at high temperatures is made possible by the use of kapton lined headspace vial caps that do not degrade or outgas at 300°C. A combination of one dimensional and comprehensive GCXGC techniques have been employed to investigate evolved gases of various polymeric materials. GCxGC can give a unique visualization and separation of degradation compounds (especially at 300°C) while a traditional one dimensional separation with an MSD is useful for identification of individual compounds in less complex headspace. The approach to polymer characterization described in this work is complimentary to pyrolysis techniques operating in the 400-600°C range.

Reference: Shin, T., Hajime, O., Chuichi, W.,(2011). Pyrolysis-GC/MS Data Book of Synthetic Polymers, Oxford, UK: Elsevier.