Advanced GC/MS Techniques for Enhanced Analysis of Trace Compounds in Complex Matrices

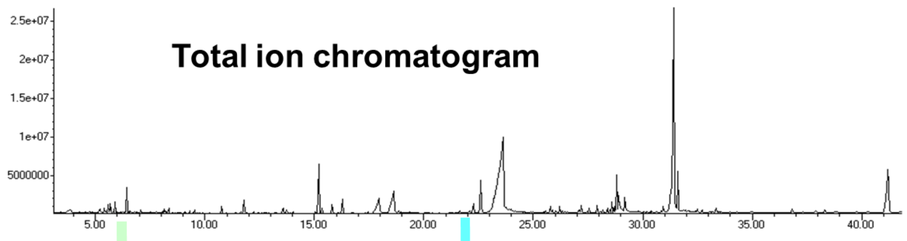
Moritz Hebestreit, Agilent Technologies, Waldbronn, Germany

Abstract

With the regulatory changes that are coming in the EU, pressure onto testing laboratories is increasing. Tools like Deconvolution Reporting Software (DRS) and Capillary Flow Technology (CFT) can help a lot to increase productivity.
E.g. selectivity of GC/MS-analyses is very often limited due to varying matrices. Either the results may be uncertain or long lasting chromatographic developments can be the consequences. DRS combines the MSD Chemstation with mass spectral deconvolution from AMDIS and a NIST search with retention times as further qualifier. DRS will report fewest false positive and negative results in the shortest time.

CFT-devices allow for easy to use column connections inside the GC oven. This technique opens up many capabilities like detector splitting, twodimensional gas chromatography, column change without venting the MS or backflush (reversing the carrier gas flow). Backflush avoids long bakeout procedures at the end of a GC-run. It therefore enhances column lifetime and reduces source maintenance, as high boiling matrix compounds are backflushed through the split line at lower temperatures.

DRS – Automated Report from three Integrated Processes



Targets are identified by comparison to locked R.T.s and 3 qualifier ion ratios, then quantified using target ion area vs ISTD cal table

AMDIS deconvolutes component spectra and searches target MS database using locked RT as a qualifier

Deconvoluted Target spectra confirmed by AMDIS, searched against NIST08 MS database

Confirmed AMDIS hits

AMDIS Quant Result

Quant Results

Confirmed NIST08 hits

Combined quantitative and qualitative HTML summary report

MSD Deconvolution Report
Sample Name: + 400 ppb ISTDs, 25 µL PTV
Data File: C:\msdchem\1\DATA\SPINACH.D
Date/Time: 10:15 AM Tuesday, Nov 11 2008
The NIST library was searched for the components that were found

NIST 08 Match and Hit number of the top 100 hits from 191,000+ compounds

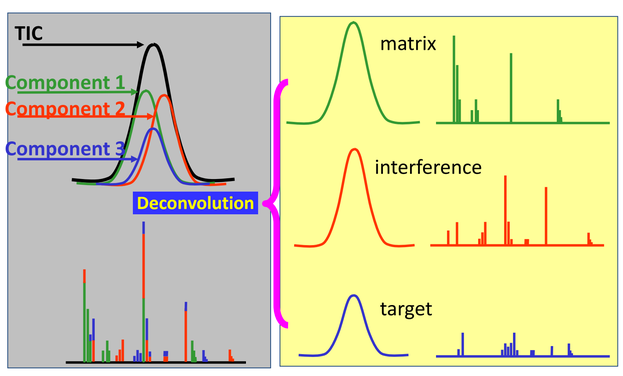
			Amount (ppm)		AMDIS		NIST	
R.T.	Cas #	Compound Name	Chem station	AMDIS	Match	R.T. Diff sec.	Reverse Match	Hit Num
18.4431	84742	Di-n-butylphthalate	7.04		95	1.7	91	2
23.9754	80057	Bisphenol A			97	8.7	91	1
24.0705	72559	p,p'-DDE			74	3.0	82	1
25.7154	72548	p,p'-DDD			52	1.8	65	2
26.9932	50293	p,p'-DDT			53	0.7	43	6
27.0103	85687	Butyl benzyl phthalate			54	0.2	57	25
27.9265	51036	Piperonyl butoxide	37.79		96	1.6	94	1
29.6685	117817	Bis(2-ethylhexyl)phthalate			93	1.2	85	3
31.6131	52645531	Permethrin II			90	3.8	91	3
13.718		Phenanthrene-d10	10					

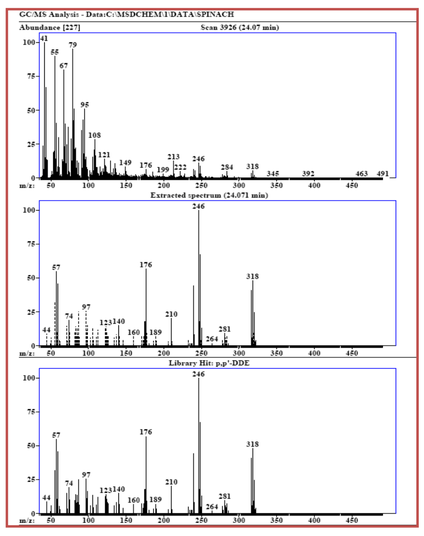
ISTD, used for targets amount

Match against AMDIS library

RT diff in sec. vs expected locked RT

DRS – AMDIS

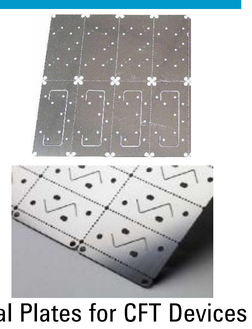




By combining MSD Chemstation results with mass spectral deconvolution from AMDIS and a NIST search with retention times as further qualifier, DRS will report fewest false positive and negative results in the shortest time.

CFT – Technique and Devices

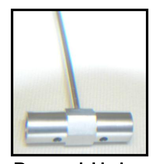
- Photolithographic chemical milling for low dead volume
- Diffusion bond two halves to form a single flow plate
- Small, thin profile provides fast thermal response
- Projection welded connections for leak tight fittings
- Deactivation of all internal surfaces for inertness
- The metal ferrule does not loosen (leak) even with thousands of runs to 350 °C



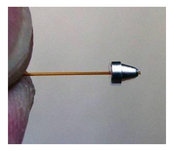
Metal Plates for CFT Devices

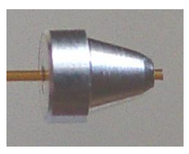
Threeway Splitter inside GC oven

Deans Switch



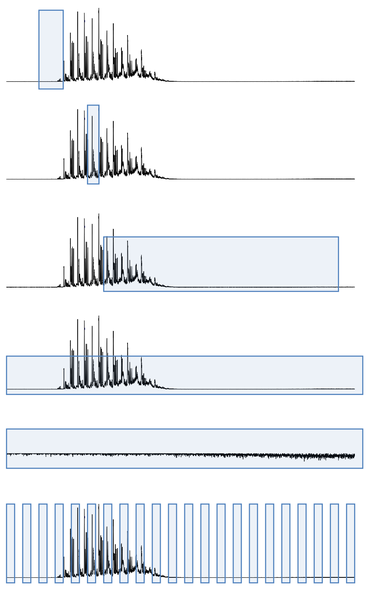
Purged Union





Metal Ferrule

CFT – New (and old) Capabilities



Solvent Bypass

Heart Cutting (Deans Switch)

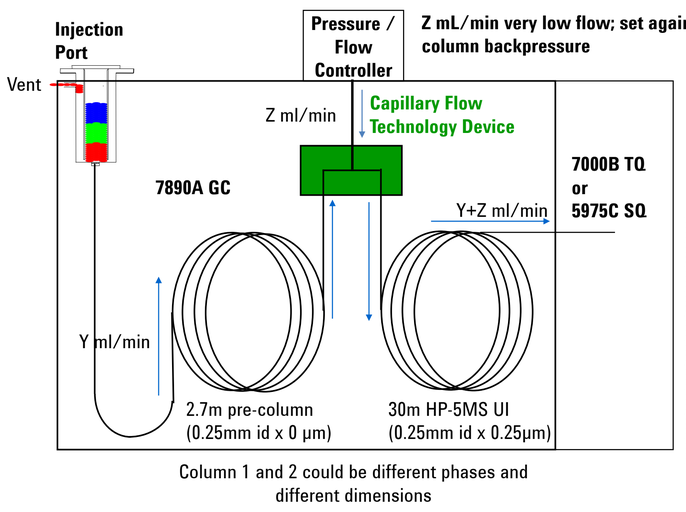
Backflush

Detector Splitting

Column Change without Vent

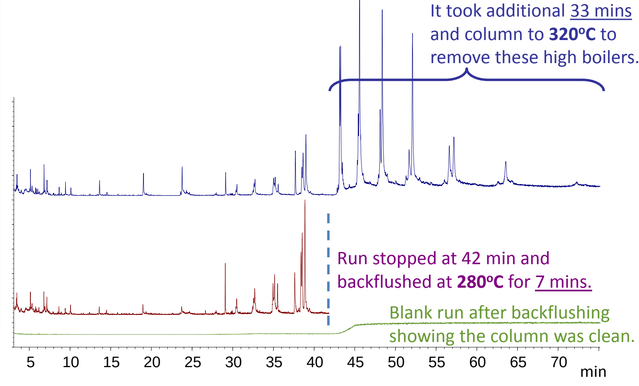
Modulation (GCXGC)

CFT – Backflush



Column 1 and 2 could be different phases and different dimensions

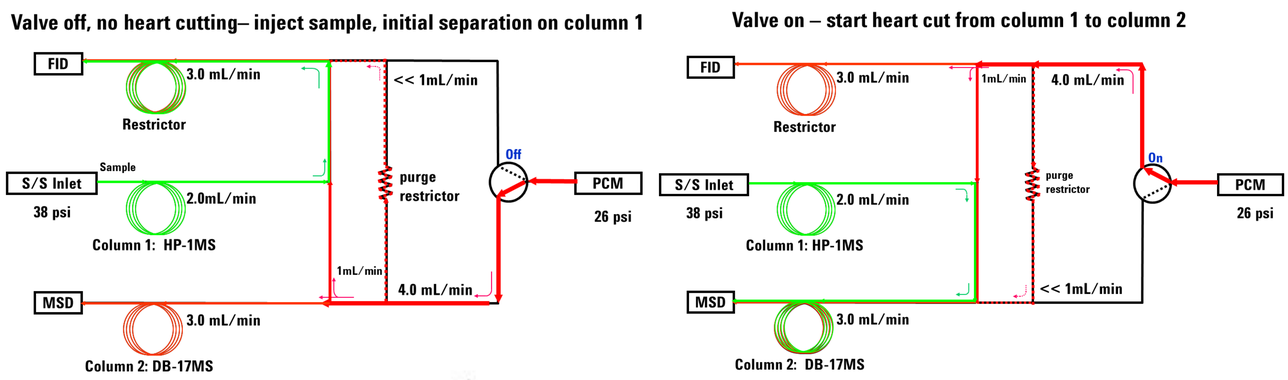
Typical Backflush Configuration



Applying Backflush to the Analysis of a Milk Extract

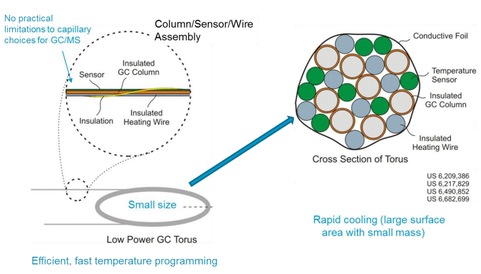
In backflush mode, the inlet pressure is reduced to 1 psi, after the last compound of interest has passed the CFT device. The carrier gas flow is reversed on the first column and high boiling compounds are eliminated quicker at lower temperatures.

CFT – Heartcutting: Twodimeninal GC for Demanding Chromatography



- Modules outside isothermal GC oven for fast heating/cooling
- Use same GC injectors, detectors, autosamplers, software, ...
- Independent and simultaneous temperature programming

7890A GC Equipped with LTM 1



Setup of Low Thermal Mass Modules

RT-windows from a first (usually nonpolar) column with coeluting compounds are transferred (cut) on a second (usually polar) analytical column for superior chromatographic resolution. When using LTM-modules, two independent oven programs can be applied simultaneously.