9 Feb 2022

Applications on My Journey Towards Super-High Resolution Gas Chromatography-Mass Spectrometry & Initiatives at Monash

Philip Marriott

School of Chemistry, Monash University

home page:

http://www.monash.edu/science/research-groups/chemistry/marriott-group

(MDGC and GCxGC Tutorial / 19 page)

History & Studies

PhD LaTrobe Uni	MECA Spectroscopy & GC / FID / FPD (Ni, Pd, Pt) Metal DTP Complexes
PDF Bristol Uni	GC-MS of metalloporphyrins; Porphyrin geochemistry
Lect/Snr Lect NUS	GC reactor studies; Cyclophanes (Prof YH Lai; NUS) & oximes
Lect/Prof RMIT	Capillary electrophoresis Gas chromatography;. Multidimensional GC (MDGC) Comprehensive two-dimensional gas chromatography (GC×GC) & GC reactor oximes (extractions; fundamentals; applications)
Prof Monash	MDGC; GC×GC & GC reactor oximes HPLC-MS Phase developments Simulations

All research collaborators ~ co-authors:

A
cock, J.; Ades, P.; Ahad, J.; Allen, M.; Althakafy, J.T.; Amador-Muñoz, O.; Amaral, M.S.S.; Amberg, A.; Amer, M.; Amiet, R.G.;
s, T.; Aragón-Piña, A.; Araújo, R.C.S.; Armstrong, D.W.; Aryasuk, K.; Ashdown, R. P.; Augustini, R.; Auh, J.H.; Bano, A.; Barrett, D.; Barros,
D.; Batten, S. R.; Beale, M. H.; Beardall, J.; Beens, J.; Beger, R.; Begnaud, F.; Belt, S. T.; Bieri, S.; Bizzo, H.R.; Bjerregaard, P.;
Blinet, P.; Boer, S.; Bonaccorsi, I.; Bonnet, B.; Bourke, M.; Boysen, R.I.; Brady, P.; Brenna, T.; Brennecke, S.P.; Cacciola, F.; Canty, A. J.;
.; Caradoc-Davies, T.; Caramão, E. B.; Cardeal, Z. L.; Cardwell, T. J.; Caridi, D.; Carpenter, P.; Carslaw, N.; Casagrande, M.; Casili, A.;
Chaffee, A.; Chai, S. Y.; Chaintreau, A.; Chan, W. H.; Chifuntwe, C.; Chin, S. T.; Cho, S. M.; Choi, H.K.; Choy, A. L.; Choy, C.K.L.; Choy, K.H.C.; Clarke, B.;
Coimbra, M. A.; Colton, R.; Conte, L. S.; Cook, P.; Cornwell, C.; Cotroneo, A.; Cumbers, M.; Curtis, N. E.; Danielsson, C.; Davies, N. W.; Daykin, C.; De
Silva, S.; Debonville, C.; Di, X.; Drevermann, B.; Drummer, O.; Dufour, J. P.; Dugo, G.; Dugo, P.; Dummett, C. J.; Dunn, M. S.; Duong, M.; Eglinton, G.;
Elgar, M. A.; Elis Engel, E.; Evans, D.; Evenhuis, C. J.; Evershed, R. P.; Eyres, G. T.; Fan, T. W. M.; Fergeus, J.; Fermas, S.; Fiehn, O.; Fievez, V.; Frank, R.
A.; Galbally, I.E.; Gao, H.; Gao, X.; Gardiner, M.G.; Gas, B.; Gill, J.P.; Glud, R.; Gomes da Silva, M.D.R.; Goodacre, R.; Gor, M.C.; Grace, M.R.; Grant, J.;
Griffin, J.L.; Griffiths, A.; Grosjean, E.; Guasca, A.O.; Gude, N.M.; Guijt, R M.; Gunes, G.; Guo, B.; Haddad, P.R.; Haglund, P.; Hallifax, G.; Hargreaves, C.;
Harju, M.; Hartmann, C.; Harynuk, J.; Hasler-Sheetal, H.; Hatvani, T.; Hau Fung Cheung, R.; Hawes, C.S.; Hearn, M.T.W.; Hein, C.S.; Henry, T. B.; Hewitt,
L. M.; Higashi, R.; Hruska, V.; Hugel, H.; Hughes, J.G.; Huie, C. W.; Hussain, I.; Hyun, S.H.; Izgorodina, E. I.; Jackson, W. R.; James, D.; Jayasinghe, L. Y.;
Jiang, M.; Johansson, M.; Jones, O. A. H.; Jones, R. C.; Junge, M.; Jytka Zrostlı´kova Kamalanathan, M.; Kawila, N.; Keast, R.; Kee, C. L.; Keyani, R.;
Khummueng, W.; Kim, D. Y.; Kim, H.; Kim, J. H.; Kim, L.; Kim, S. H.; Kim, Y.; King, R. G.; Kinghorn, R. M.; Kirkin, C.; Knowles, D. J.; Knowles, G. P.; Kondo,
E.; Kopka, J.; Korkiasaari, K.; Kotsos, A.; Kouremenos, K.; Koutoulis, A.; Krisnangkura, K.; Kroger, S.; Kruaysawat, J.; Kueh, A. J.; Kulsing, C.; Kwong, A.
H.; Lai, Y. H.; Lambropoulos, N.; Lane, A.N.; Larkman, T.; Lau, S. S. G.; Lee, A.L.; Lee, A.W.M.; Lee, H.K.; Lee, J.; Lee, L.M.; Lee, S.Y.; Leeming, R.;
Lengger, S. K.; Leus, M.; Lewis, A. C.; Li, C.G.; Li, D.; Li, H.; Li, J.; Lin, J.M.; Lindholst, C.; Lindon, J.C.; Lingham, A.R.; Liu, C.; Liu, J.; Liu, X.; Liu, X.; Logan,
G.A.; Lopes, E.S.O.; Low, M.Y.; Lundstedt, S.; Lu, R.; Luong, J.; Lupton, D.; Macfarlane, D.R.; Macka, M.; Maikhunthod, B.; Mantri, N.; Manzin, V.; Massil,
T.; Mastello, R. B.; Mateus, E. P.; Matyska, M. T.; Maxwell, J. R.; May, B.; Mayadunne, R.; McCormick, L.; McCormick, M.; McDonough, P. S.; McGuire,
E.; McQuaid, J. B.; Meng, Z.; Mete, J. B.; Millington, K.; Min, W.; Mitrevski, B.; Mok, C.Y.; Mokhtar, S.; U. Mondello, L.; Monteiro, M.; Moret, S.; Morris, E.;
Morris, V.M.; Morrison, P.; Murillo-Tovar, M. A.; Naz, R.; Neto, F.R.d.A.; Nguyen, A. M.; Nguyen, T. T.; Nicholls, A. W.; Nichols, P. D.; Nicolazzo, J.A.;
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Palmeri, G.; Pan, Y.J.; Pang, E.; Park, H. E.; Park, S. J.; Parker, R. M.; Pasa, V. M. D.; Patricio, P.; de Souza P. A.; Pedersen, S. N.; Peng, Z.; Perera,
R.M.M.; Perlmutter, P.; Pesek, J. J.; Peters, S.; Pitt, J.; Piatnicki, C.M.S.; Pojjanapornpun, S.; Porter, C. J. H.; Porter, N.; Poynter, S. D. H.; Pripdeevech, P.;
Probost, J. P.; Purcaro, G.; Pye, T. C.; Qian, H.; Ranganathan, V.; Rasdell, S.; Ratel, J.; Rawson, P.; Reily, M. D.; Rezende, C.R.; Ribeiro, A. B.; Riga, S.;
Rocha, S. M.; Rook, T.J.; Rose, G.; Rowland, S. J.; Rühle, C.; Russell, I.; Ryan, D.; Samykanno, K.; Sari, E.; Scanlon, M.J.; Scarlett, A.G.; Schmarr, H.- G.;
Schoenmakers, P.; Schurig, V.; Sciarrone, D.; Shao, Y. J.; Sharif, K. M.; Shellie, R.; Sheng, S. J.; Sherrard, B. K.; Shi, H.; Short, J. L.; Sidisky, L. M.; Silva, I.;
da Silva Junior, A.I.; Simpson, N.; Small, D. M.; Smith, G. C.; Smith, J.; Song, S. M.; Sotheeswaran, S.; Stevenson, G.; Story, D.; Sumner, L. W.; Sun, K.;
Symons, R.; Tahir, A.T.; Tan, B. C. D.; Tan, C. Y.; Tan, Y. S.; Tian, S. J.; Tiyapongpattana, W.; Tolhurst, V. A.; Traeger, J.; Tran, T. C.; Tranchida, P.; Trapp,
O.; Trenerry, C.; Truong, T.; Tuck, K.; Turchini, G.; Turner, D. R.; Urban, S.; van Wilgenburg, E.; Veleska, B.; Viant, M.; Villalobos-Pietrini, R.; Villarosa, L.;
Vine, J. H.; Vivó-Truyols, G.; Vlaeminck, B.; von Mühlen, C.; Vulic, N.; Wakt kins, P.; Webster, R.; West, C. E .; West, R.; Western, R. J.;
Whitehead, S.; Whittock, S.P.; Wickramanayake, P. U.; Wilairat, P.; Wilde, M A.; Winniford, W.; Wong, Y. F.; Wongpornchai, S.; Wu, G. Z.; Wu,
Z. Y.; Wynne, P. M.; Xie, L. L.; Xue, C. C. L.;Yan, D.D.; Yang, M. Y.; Yang, S ; Yang, Z.; Yasmin, H.; Yeo, G.N.; Yi, F.; Zaher, P.; Zappia, G.;
Zeng, A. X.; Zeng, Z.; Zhang, Y.; Zhou, S.; Zhou, W.; Zhu, F.; Zini, C.; A.;
Z

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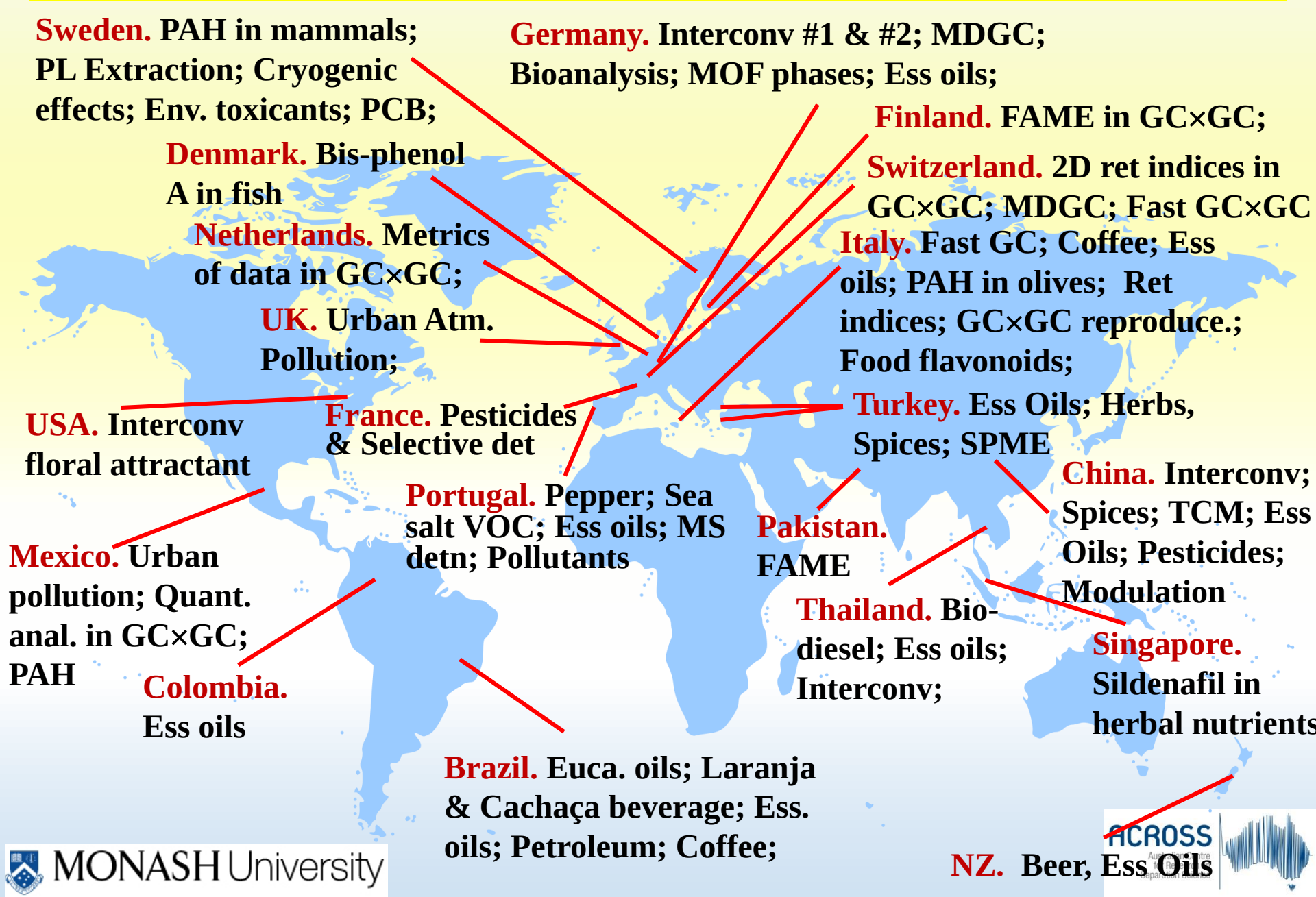
Visitors to my lab since 2004:

Dr Ally Lewis, **UK**; Prof. Peter Haglund, **Sweden**; Mr Graham Eyres, **New Zealand**; Prof Jean-Pierre Dufour, **New Zealand**; Prof Elena Stashenko, **Columbia**; Ms Carin von Muhlen, **Brazil**; Ms Patcharee Pripdeevech, **Thailand**; Prof Zenilda de Lourdes Cardeal, **Brazil**; Dr Fabian Kuhn, **Switzerland**; Dr Stefan Bieri, **Switzerland**; Prof Allen Goldstein, **USA**; Prof Marco Diogo Richter, **Portugal**; Ms Sonja Peters, **The Netherlands**; Mr Bruno Vlaeminck, **Belgium**; Ms Kornkanok Aryasuk, **Thailand**; Ms Kati Korkiasaari, **Finland**; Ms Rebekka Oelze, **Germany**; Ms Giorgia Purcaro, **Italy**; Mr Omar Amador Munoz, **Mexico**; Mr Marc Brulet, **France**; Ms Jacqui Hamilton, **UK**, Mr Warawut Tiyapongpattana, **Thailand**; Ms Anne Baumann, **Germany**; Mr Patterson de Souza, **Brazil**; Mr Christian Ruehle, **Germany**; Dr Kok Chin NG, **Singapore**; Prof Hyung Kyoon CHOI, **South Korea**; Assoc Prof Zhu FENG, **China**, Ms Isabel Silva, **Portugal**; Ms Grace Gao, **China**; Dr Erwan Engel, **France**; Dr Humberto Bizzo, **Brazil**; Dr Malgorzata Kowalczyk, **Poland**; Dr JinYoung Kim, **South Korea**; Prof Alexandra Ribeiro, **Portugal**; Dr Eduardo Mateus, **Portugal**; Ms Izabel Cardeal, **Brazil**; Dr XiangPing Liu, **China**; Ms Asia Nosheen, **Pakistan**; Ms Celale Kirkin, **Turkey**; Dr Charles West, **UK**; Ms Lyn May Lee; **Singapore**; Ms Xiao Ying Wong, **Singapore**; Mr ZhiHong Tay, **Singapore**; Dr Ming Jiang, **China**; Ms Michely Capobiango, **Brazil**; Ms Raissa Mastello, **Brazil**; Ms Constanze Hartmann, **Germany**; Ms Rachel West, **UK**; Ms Sabrina Kroger, **Germany**; Ms Marcella Casagrande, **Brazil**; Ms Laura Kreig, **Germany**; Prof Melek Merdivan, **Turkey**; Ms Dandan Yang, **China**; Mr Sebastian Weber, **Germany**; Dr Emily Goh, **Malaysia**; Mr Kakming Wong, **Malaysia**; Prof Danilo Sciarrone, **Italy**; Mr Fabio Novaes, **Brazil**; Prof Ademario da Silva, **Brazil**; Prof Song Shen, **China**; Mr Federico Floris, **UK**; Ms Siriluck Pojjanaponpun, **Thailand**; Prof Francesco Cacciola, **Italy**; Mr Calvin Goh, **Malaysia**; Ms Katorzyna Owczarek, **Poland**; Ms Anna Lipphardt, **Germany**; Ms Luisa Seyerlein; **Germany;** Mr Kenny Choo, **Malaysia**; Mr Dwi Ramadhan, **Indonesia**; Mr Aji Sarosa, **Indonesia**; Dr Elvina Iftitah, **Indonesia**;Prof Chandrawati Cahyani, **Indonesia**;

International Visitors ~ Collaboration Studies:



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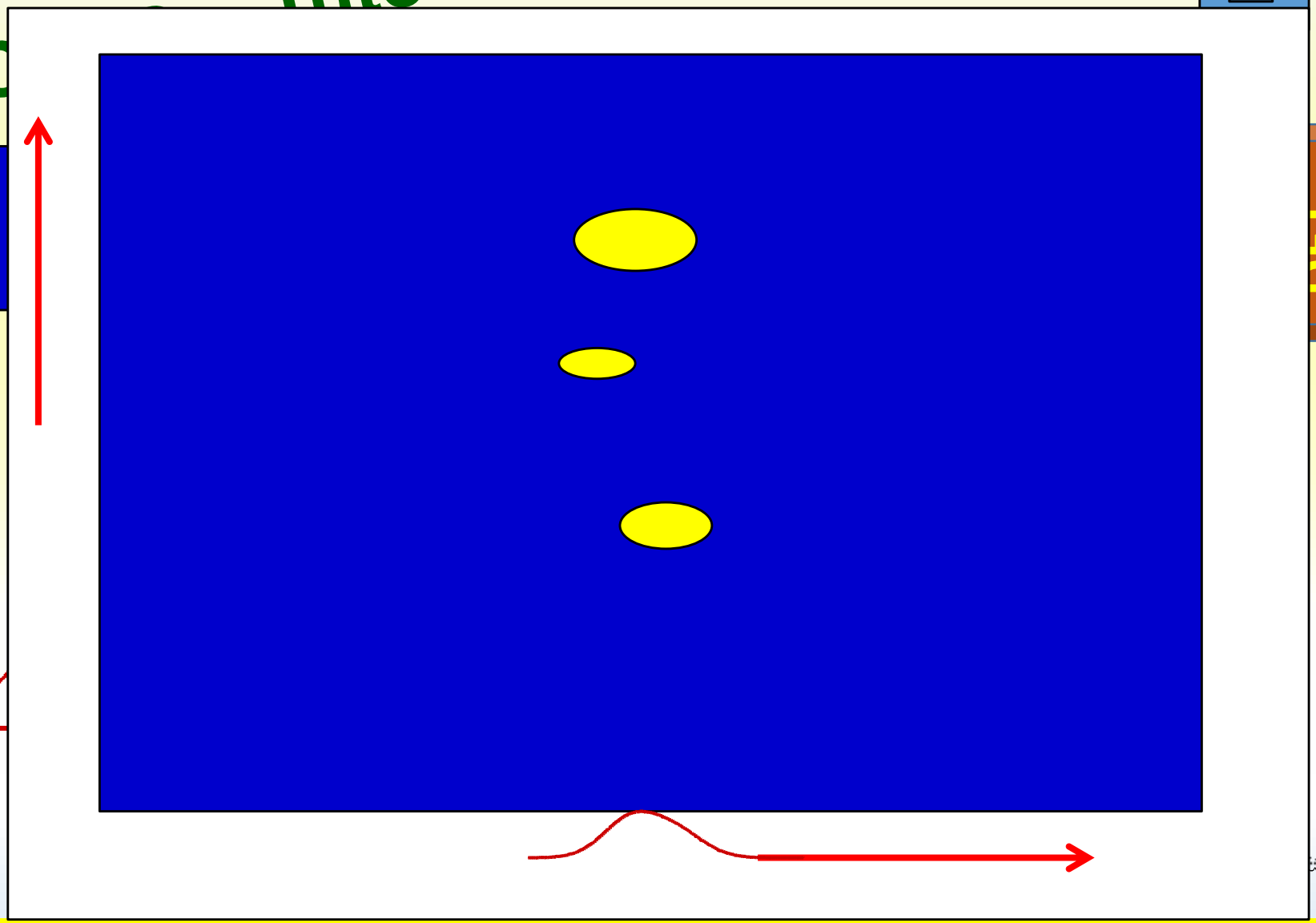
Arabica Coffee

SPME-GC×GC/TOFMS: 1 fee bean

GC×GC is a gas chromatographic technique

- We SHOULD expect it to **possess all the attributes** of GC
  - Can all GC principles be applied to GC×GC?
  - Was GC×GC designed to obey the features of 1D GC analysis?
  - Will researchers be able to apply known GC parameters to the GC×GC environment?
  - Can we deconvolve GC×GC chemical selectivity of homologues (^{1}D), and chemical classes (^{2}D) into a 2D 'chemical property' map

We decided to examine GC×GC with respect to established GC parameters



Peaks are sliced (modulated); each slice is introduced into a short ^{2}D column to provide further separation. Data presented as a 2D plot.

Advantages & Attributes of GC×GC

- GC×GC Uses 2 columns; 1st = long, 2nd = short
- GC×GC Has a modulator
- GC×GC Samples narr… …er to 2D
- GC×GC 2D p…
- GC×GC Gene… …n space
- GC×GC Peak … …ion e.g. 5 s → 0.2 s
- GC×GC Better detection sensitivity – improved LOD
- GC×GC Improves MS detection – reduces chemical background

A Disruptive GC Technology


GCXGC
VICTORIA
Mercedes-Benz Brighton

The Genesis of my Cryogenic modulator for MDGC & GC×GC..

Longitudinally Modulated Cryogenic System

@ ISCC Riva del Garda Conference Italy

(Hans-Gerd Janssen Lecture)

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Attending a conference??

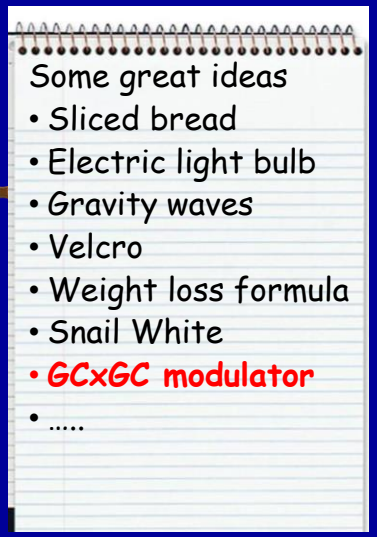
You SHOULD have an INNOVATIVE IDEA (at least ONE)!!

All you need is …

pen

+ paper

+ idea / inspiration



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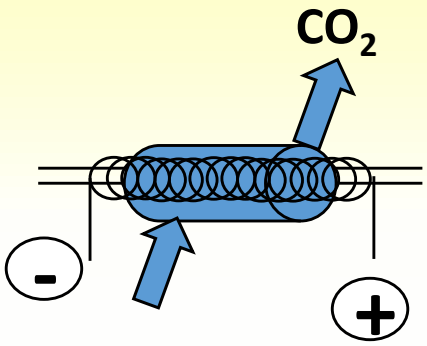
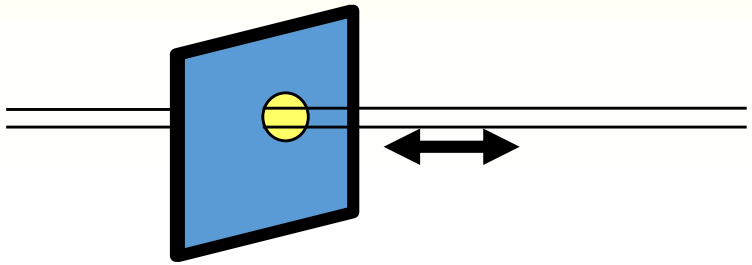
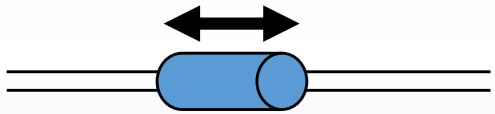
My thoughts / idea ….

- Large volume injection – needs a focussing approach…. GOOD IDEA!
- How do we do this??
- Apply Cryofluid, then rapidly heat the cold zone
- OR … MOVE the COLUMN/CRYOFOCUS ZONE!!



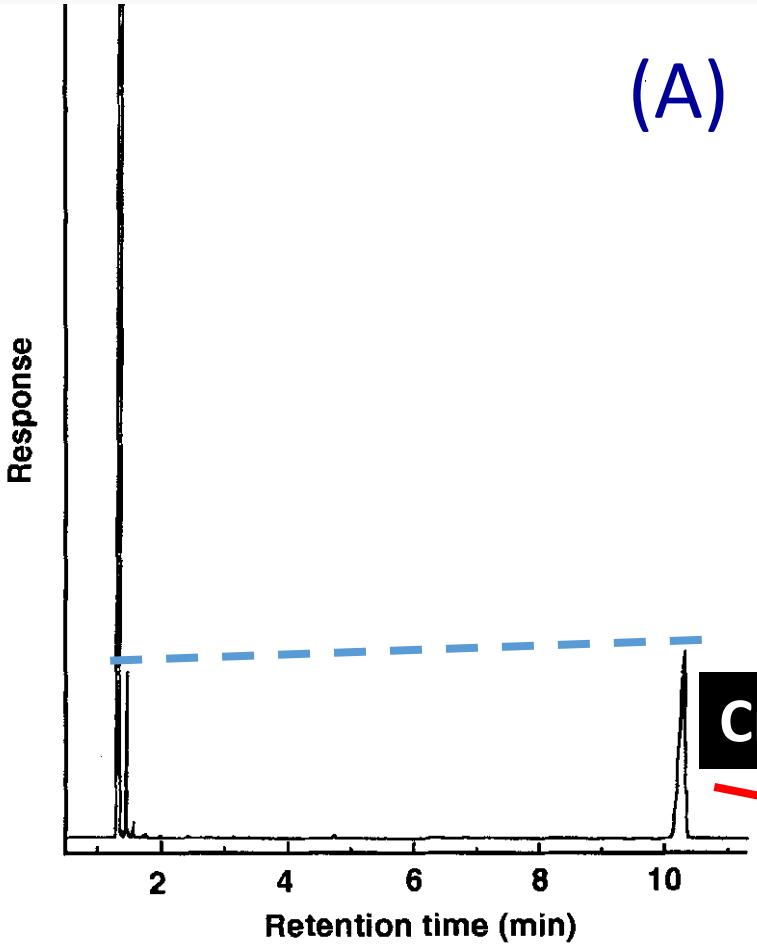




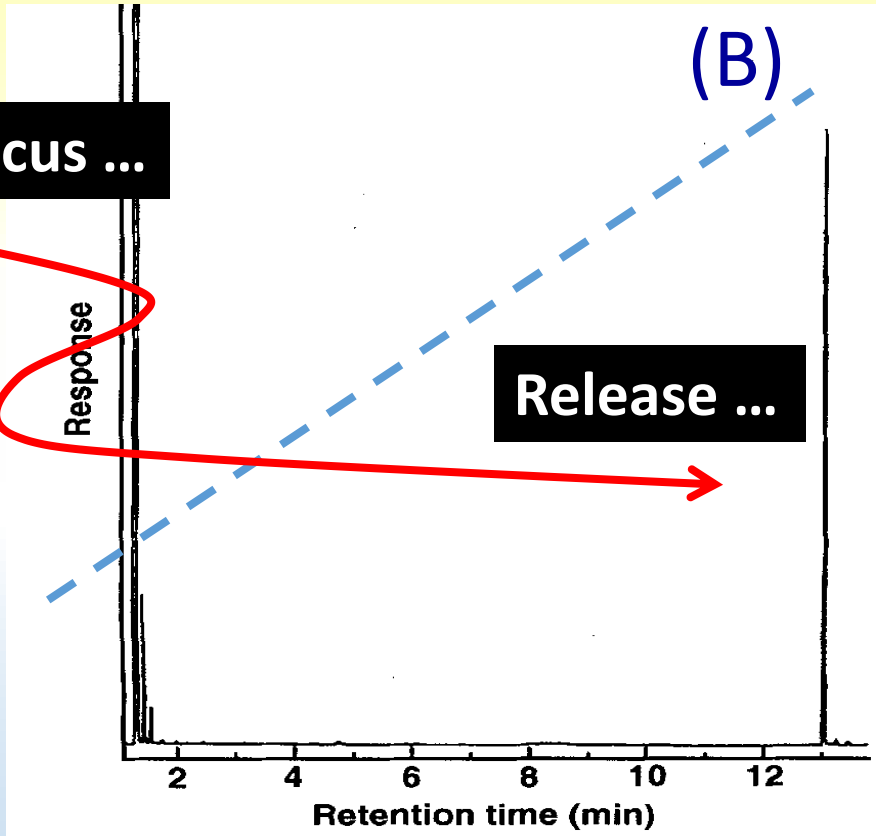
- Return home – and do something about it!!

Our first early attempt at on-line ‘cryogenic operation’ circa 1996

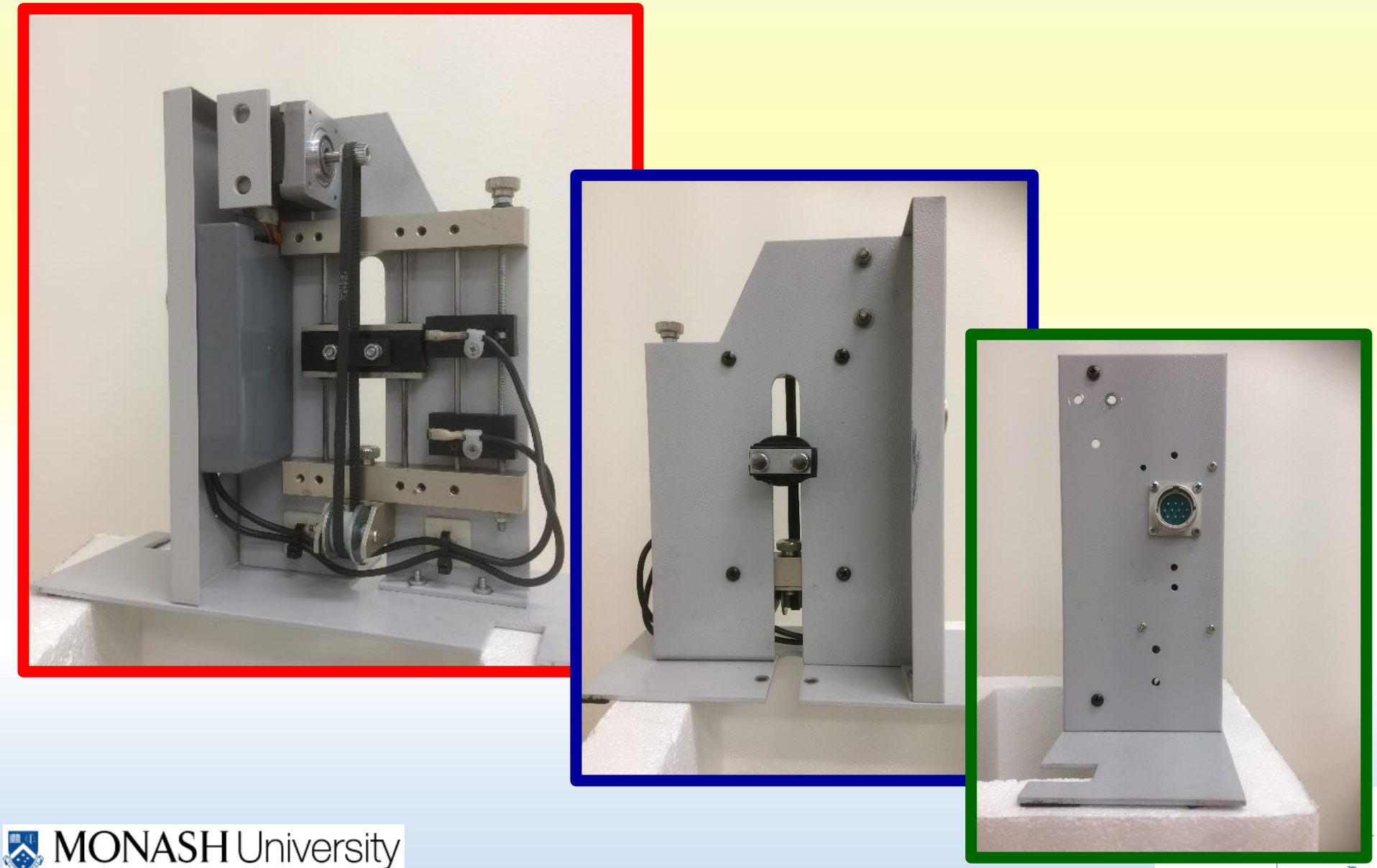
The broader peak in (A) is made considerably sharper in (B); and taller …



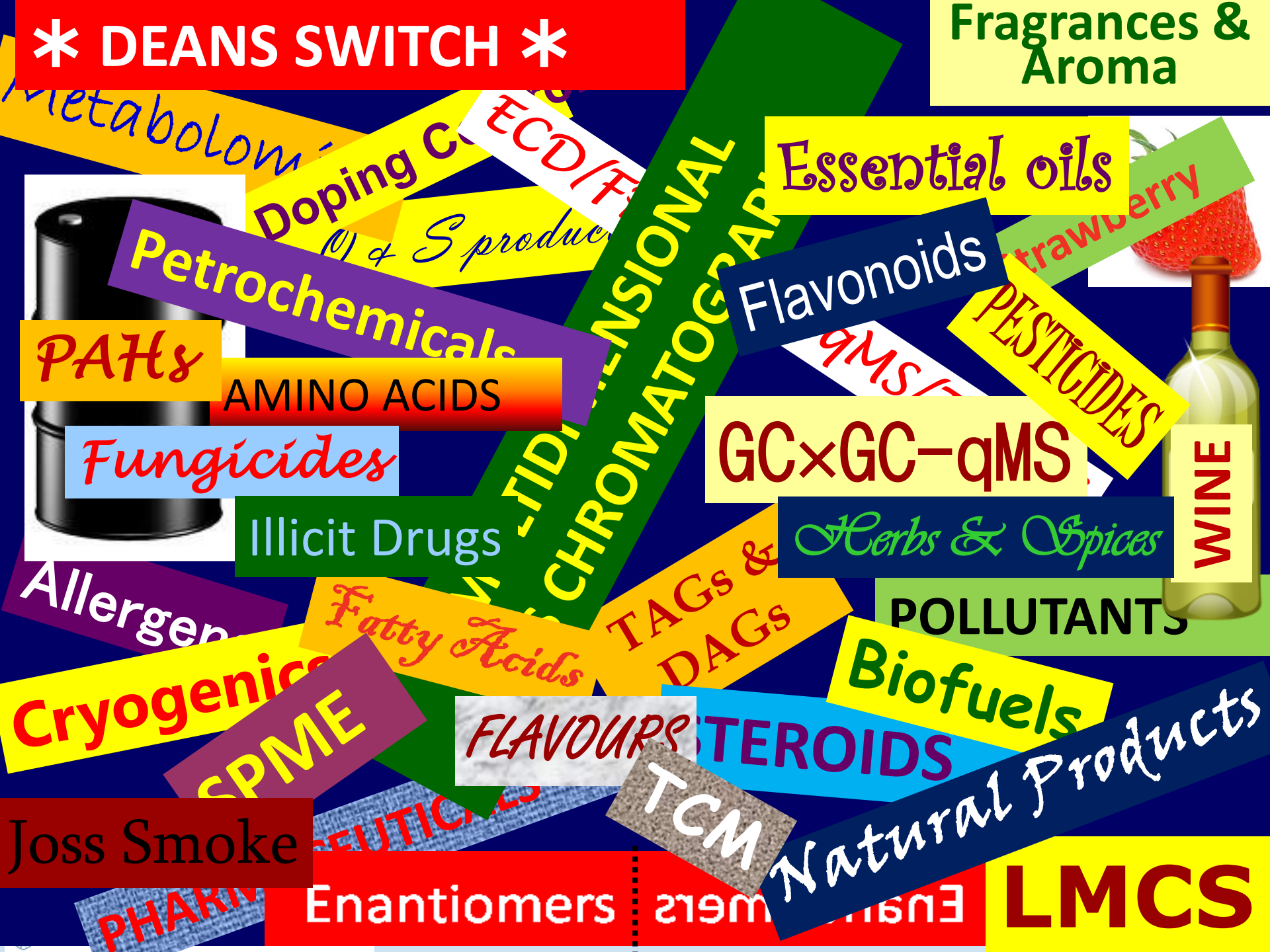
Cryofocus …



The Modulator Hardware



The NEW electronic controller


* DEANS SWITCH *
Fragrances & Aroma
Metabolom
Doping C
ECD/F
Essential oils
Petrochemicals
Flavonoids
PESTICIDES
PAHs
AMINO ACIDS
GC×GC-qMS
Fungicides
Illicit Drugs
Herbs & Spices
WINE
Allerge
Fatty Acids
TAGs & DAGs
POLLUTANTS
Cryogenic
SPME
FLAVOURS
Biofuels
STEROIDS
Joss Smoke
TCM
Natural Products
Enantiomers
LMCS

The GC×GC / MDGC ‘Systems’ Team

Russell Kinghorn

Then

Robert Shellie

Ruby Ong

Danielle Ryan

Michael Dunne

Tin Tran

James Harynuk

Weeraya Khummueng

Graham Eyres

Stefan Bieri

Shin-Miin Song

Yada Nolvachai

Blagoj Mitrevski

Yong-Foo Wong

Sung-Tong Chin

Sharif Khan

Chadin Kulsing

Now

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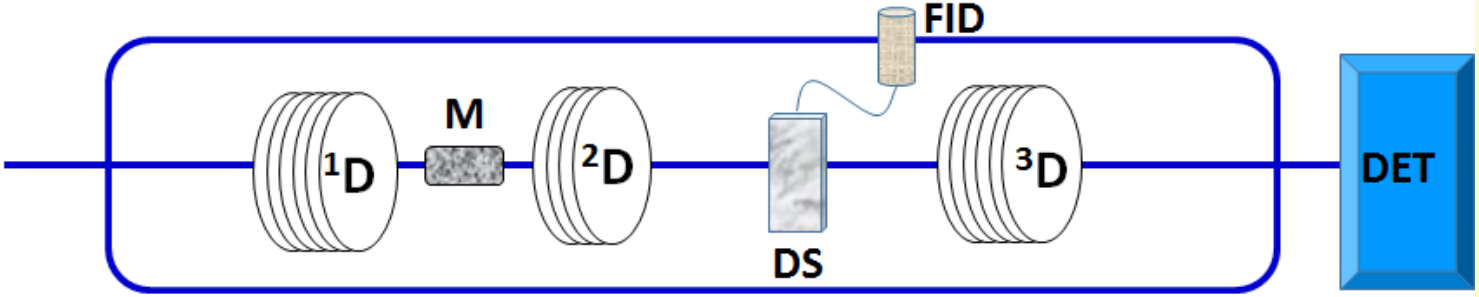
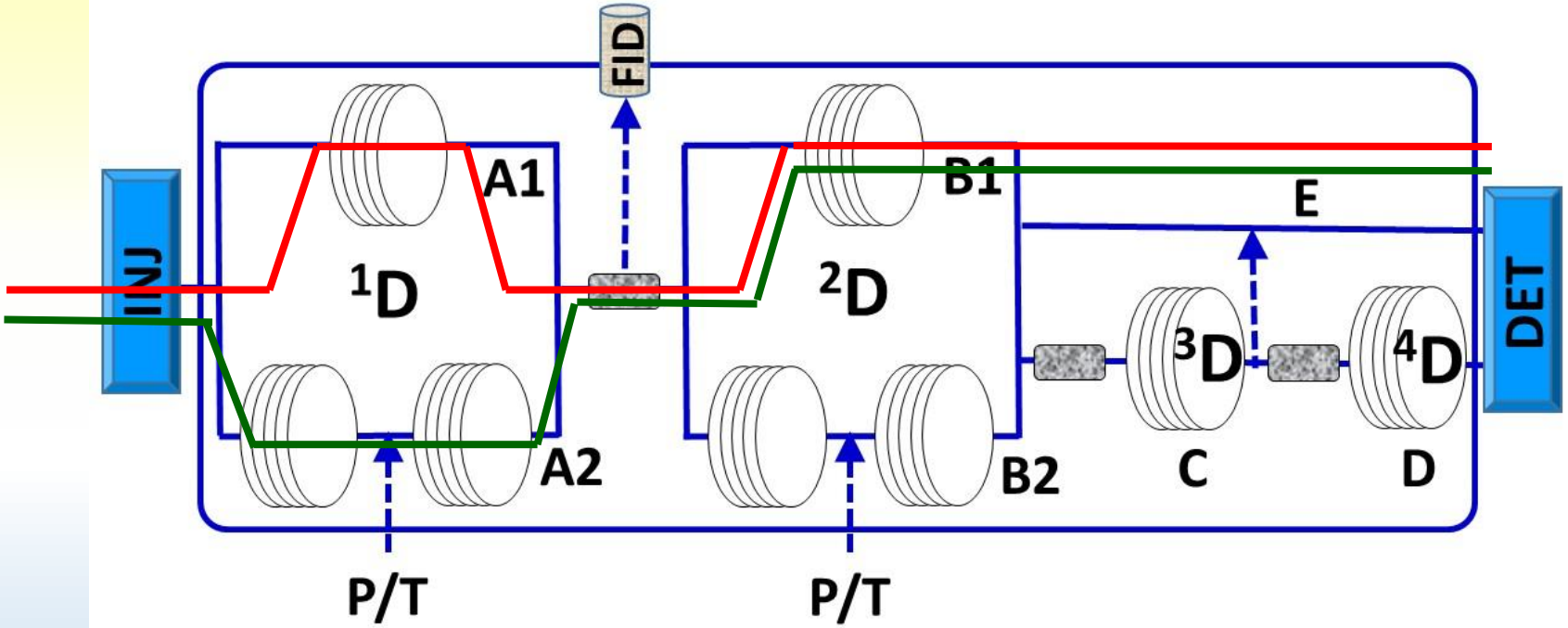
hybrid GC×GC-MDGC



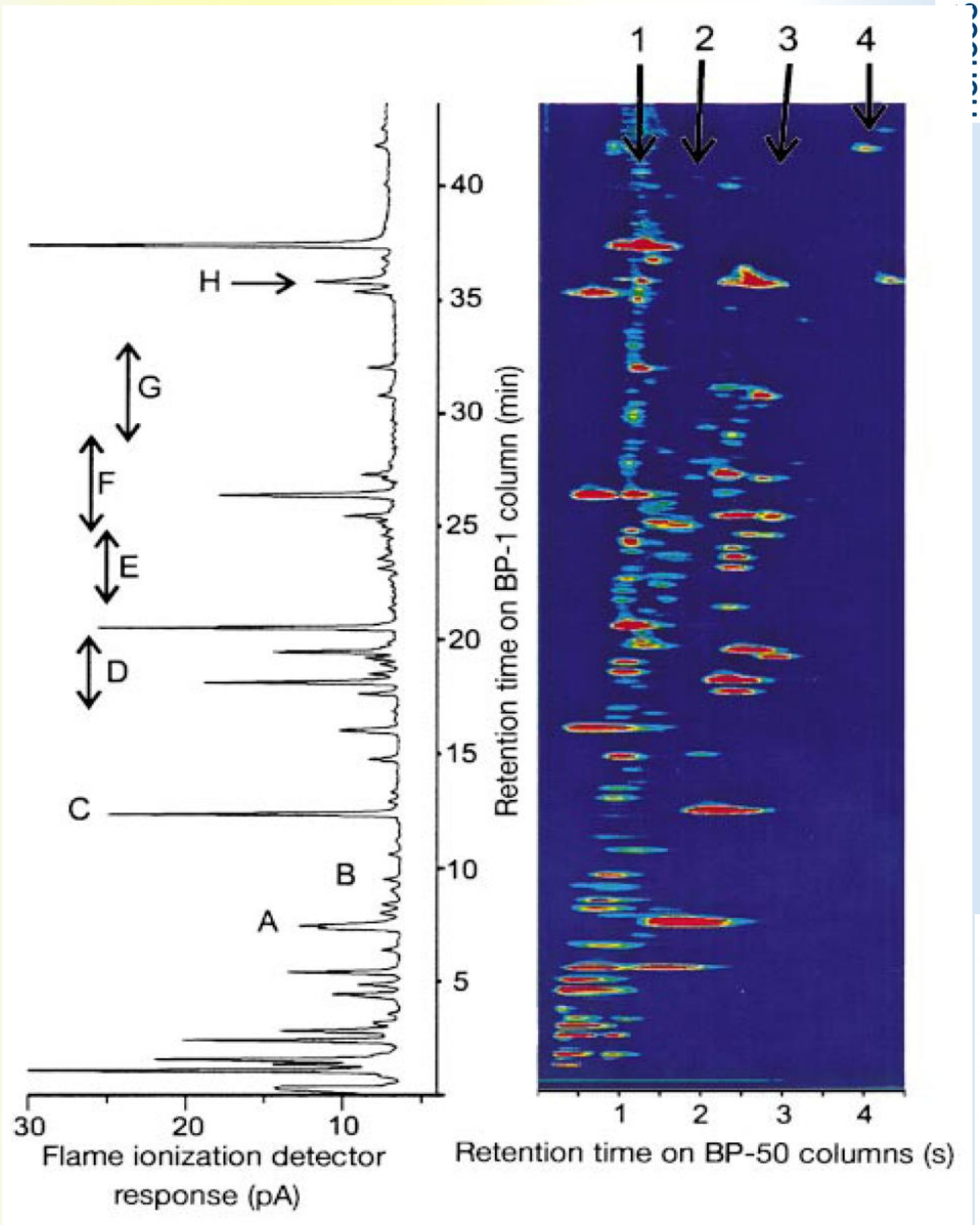
GCxGC PT-GCxGC



Nolvachai et al. *Trends Anal. Chem.* 106 (2018) 11-20

Russell Kinghorn - started own analytical consulting company; now sold (for a good profit!)

Started our GC×GC research; Pneumatic modulator, then the LMCS.
2000 paper in Nature on urban atmospheric pollution
MDGC of PCBs
Studies on various modes of cryogenic modulation
General studies expounding GC×GC with cryomodulation



Robert Shellie - postdoc Germany (Oliver Fiehn); University of Tasmania; SGE/Trajan; now Professor Deakin University, Melbourne, Australia

Amazing undergraduate success (5 publications) & 16 more in PhD

Vetiver; sandalwood; tea tree; lavender

Chiral GC×GC: *e*GC×GC & GC×*e*GC

Fast GC×GC

GC×GC-ToFMS

Vacuum ^{2}D operation

Translation of GC×GC-FID to GC×GC-qMS

Non-linear chromatography peaks in GC×GC

Isomer interconversion processes in GC×GC

Retention time reproducibility in GC×GC – Interlab study

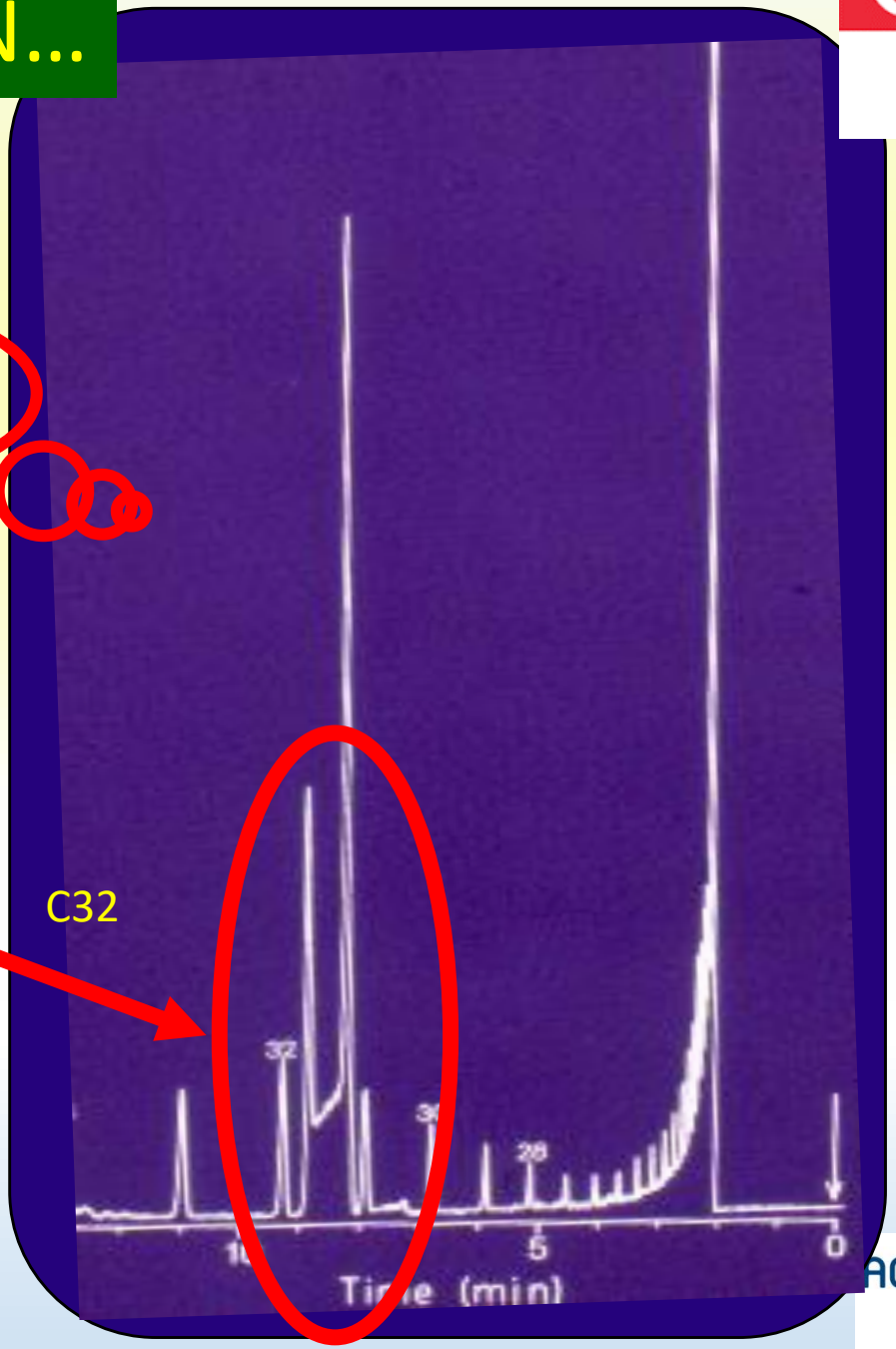
Isomer interconversion processes

- NUS: Cyclophanes & oximes; $Cr(CO)_3$MeNaphth; $Cr(trifluoroacac)_3$
- RMIT: Shellie, GC×GC oximes
- Kornkanok Aryusuk, Interconversion in GC×GC
- Monash: Chewe Chifuntwe, Interconversion of chiral oximes in GC×GC
- Sabrina Kroger: Interconversion of chiral oximes with ^{1}D and ^{2}D chiral columns in GC×GC
- Wong Yong Foo: Chiral 3D and 4D GC×GC on-column interconversion dynamics

INTERCONVERSION…

First Observation
Capillary GC
NU SINGAPORE
with Prof YH Lai

What is This???



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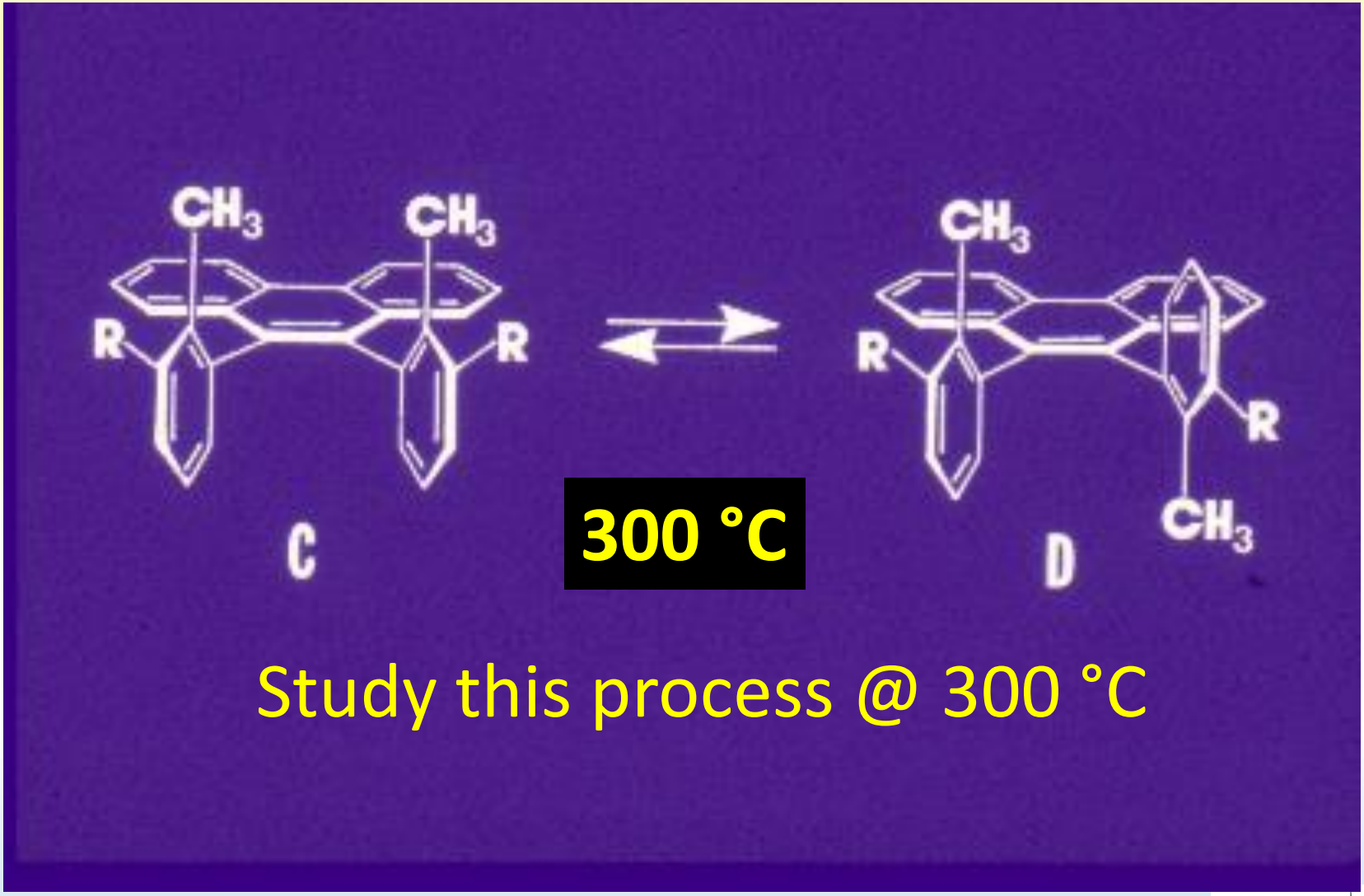
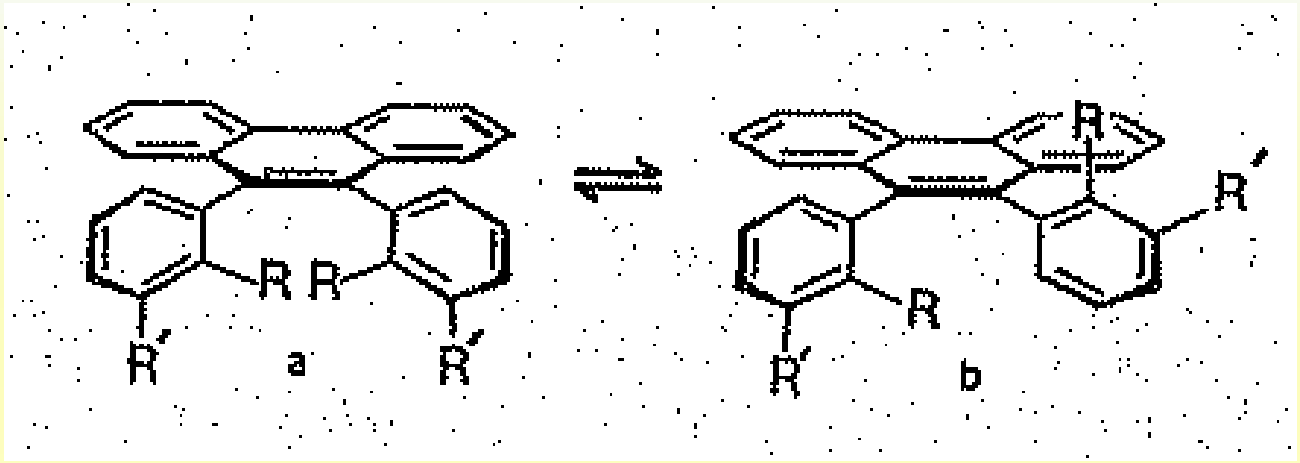
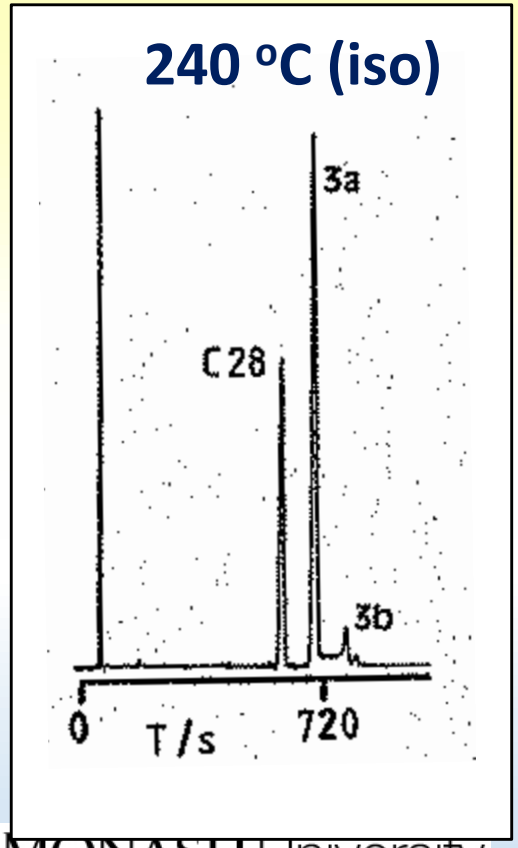
The Rationale

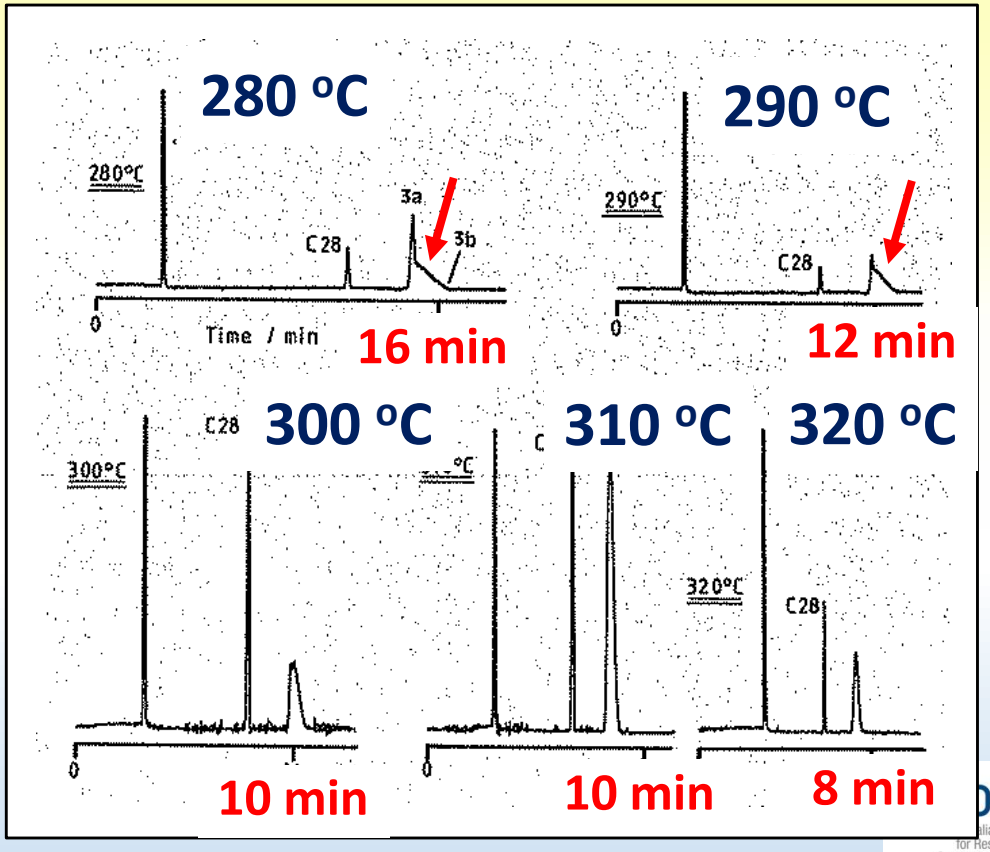


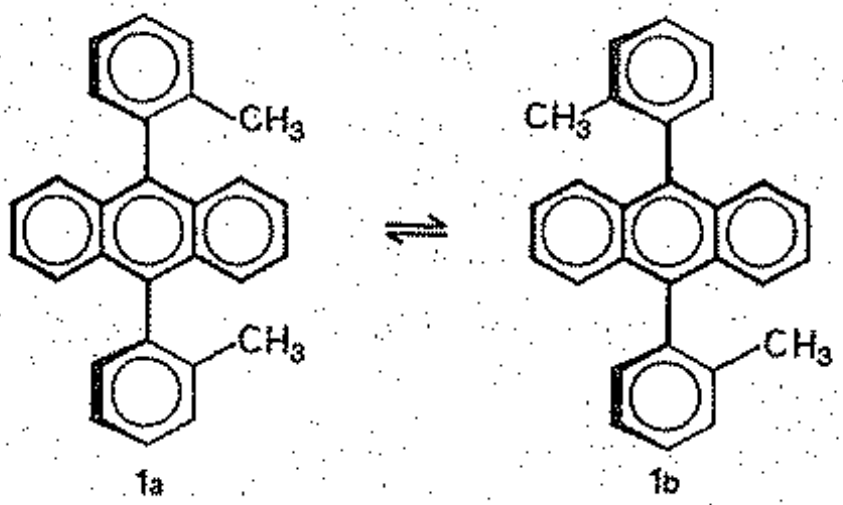
Study this process @ 300 °C

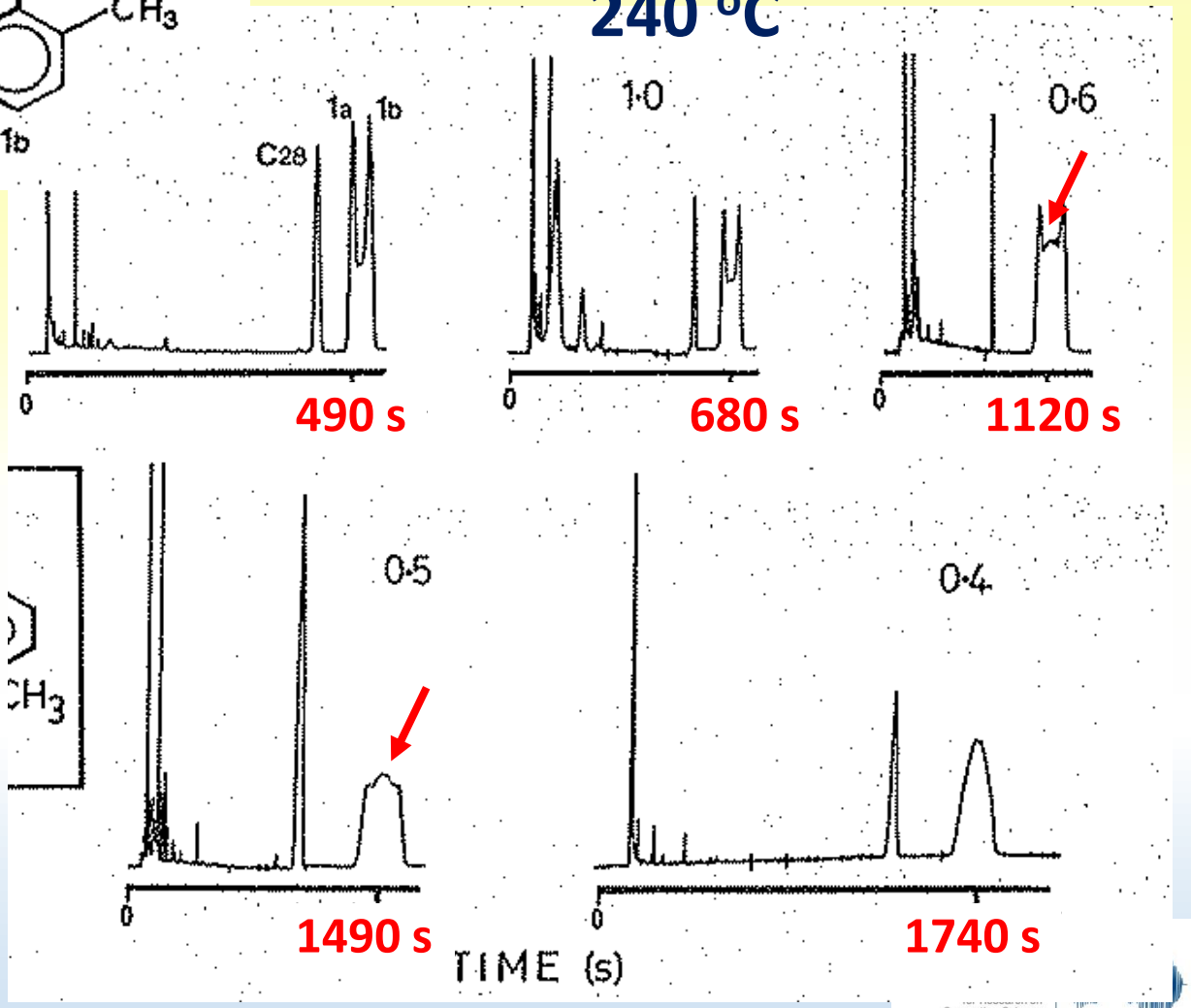


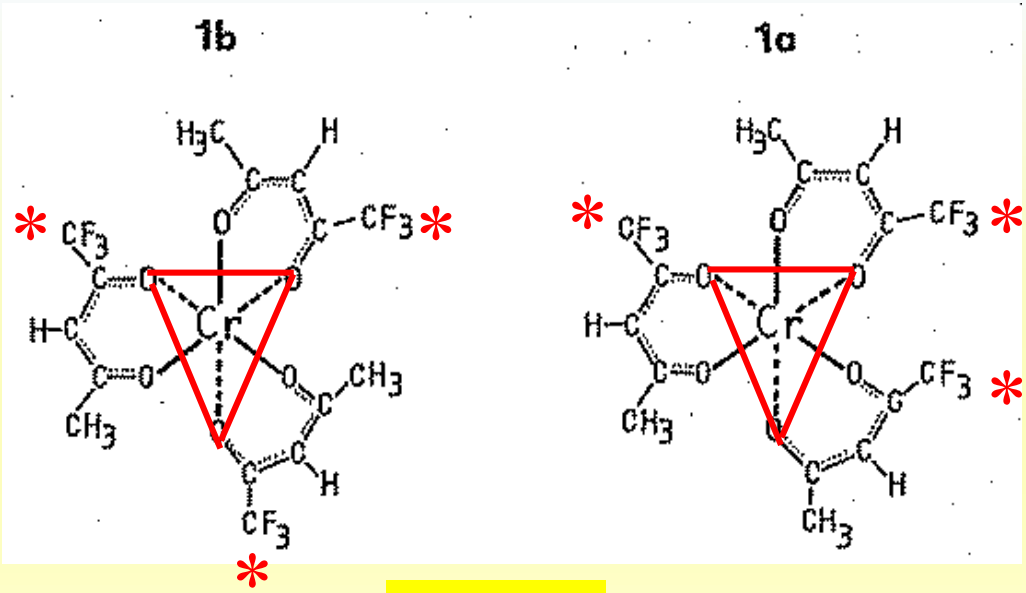
2a, 2b; R = R' = CH_3
3a, 3b; R = CH_3; R' =H
4a, 4b; R = CH_3; R' = Cl
5a, 5b; R = H; R' = CH_3






CH3
CH3
CH3
CH3
1a
1b

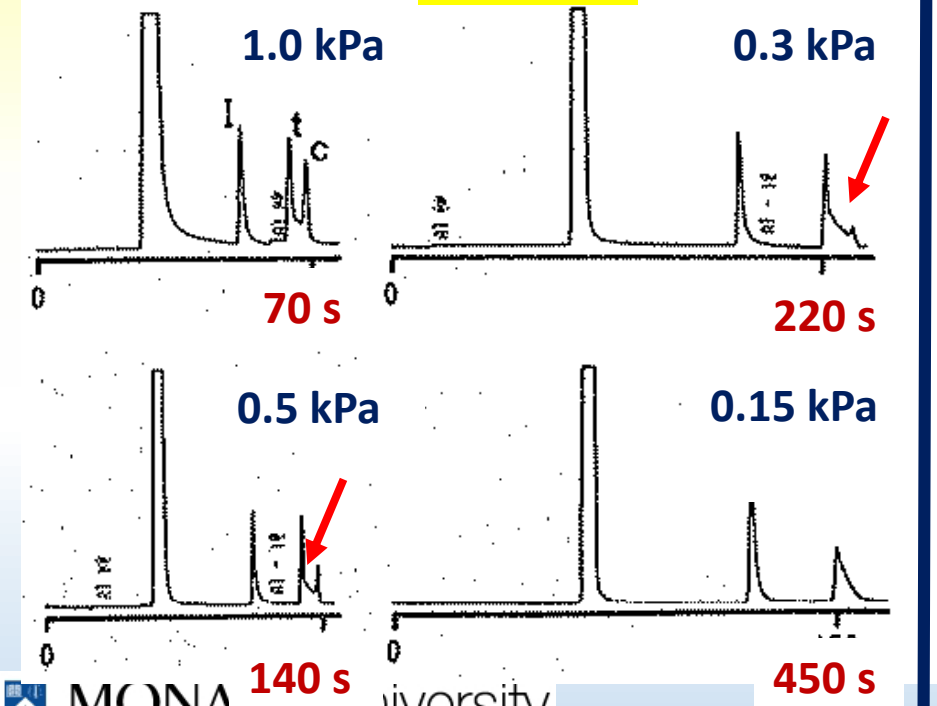

240 °C
C28
1a
1b
1·0
0·6
0·5
0·4
0
490 s
680 s
1120 s
1490 s
1740 s
TIME (s)



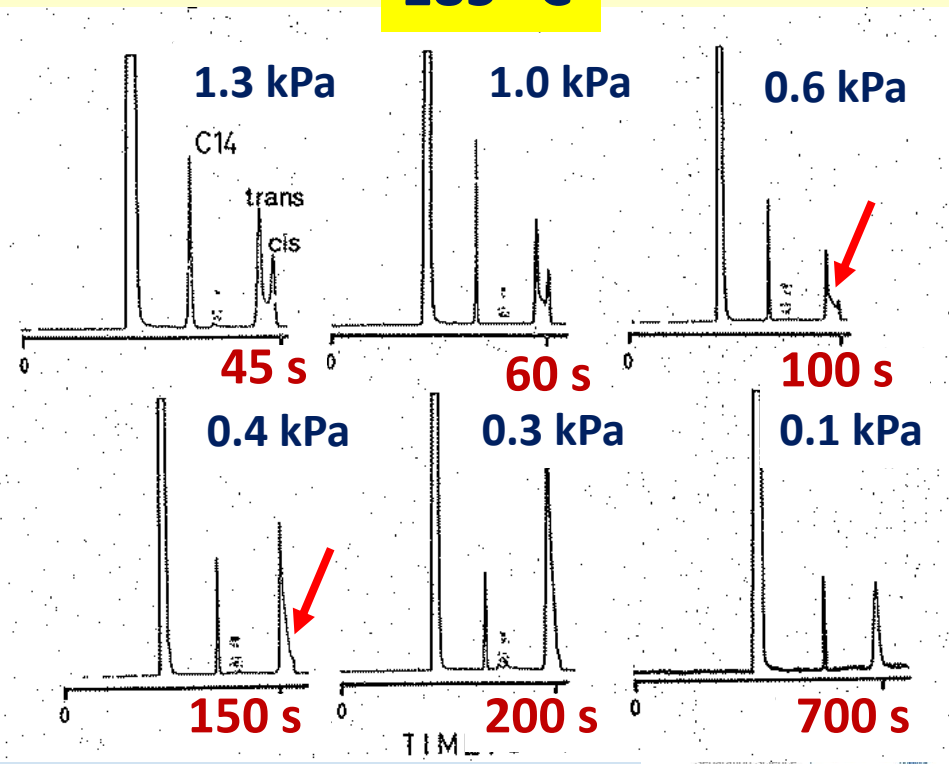
Marriott PJ & Lai YH, Isomerization Processes observed for Chromium Compounds by Using the Gas Chromatography Reactor Inorg. Chem. 25 (1986) 3680-3

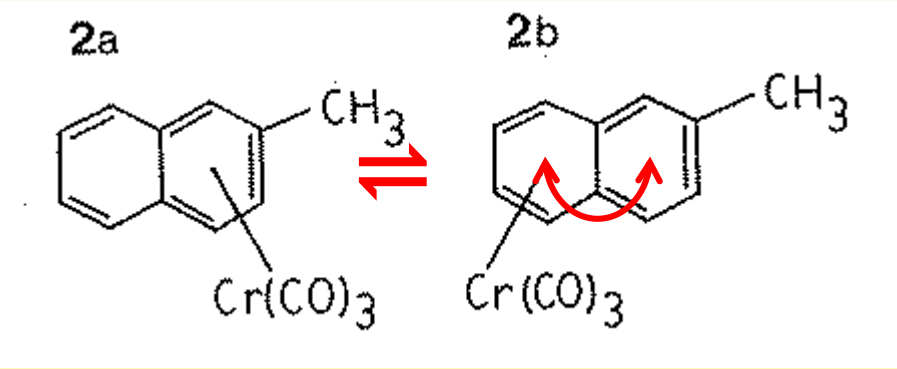
25 m x 0.32 mm ID non-polar phase

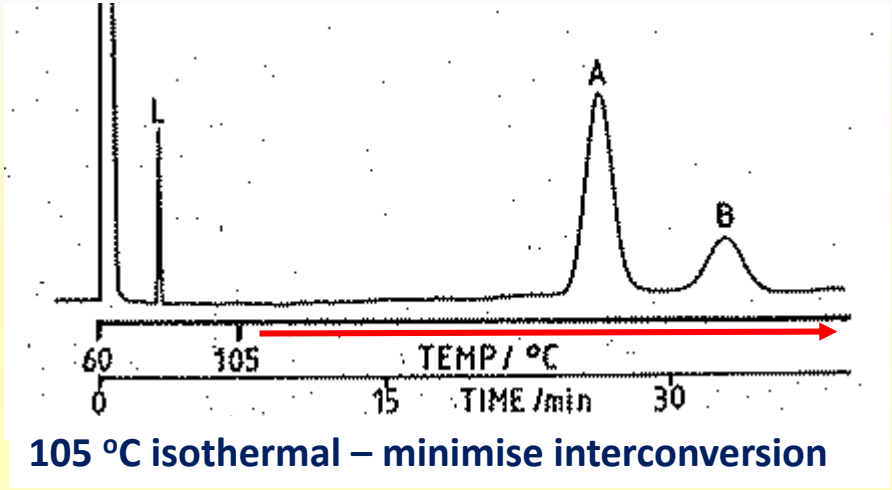
175 °C



185 °C

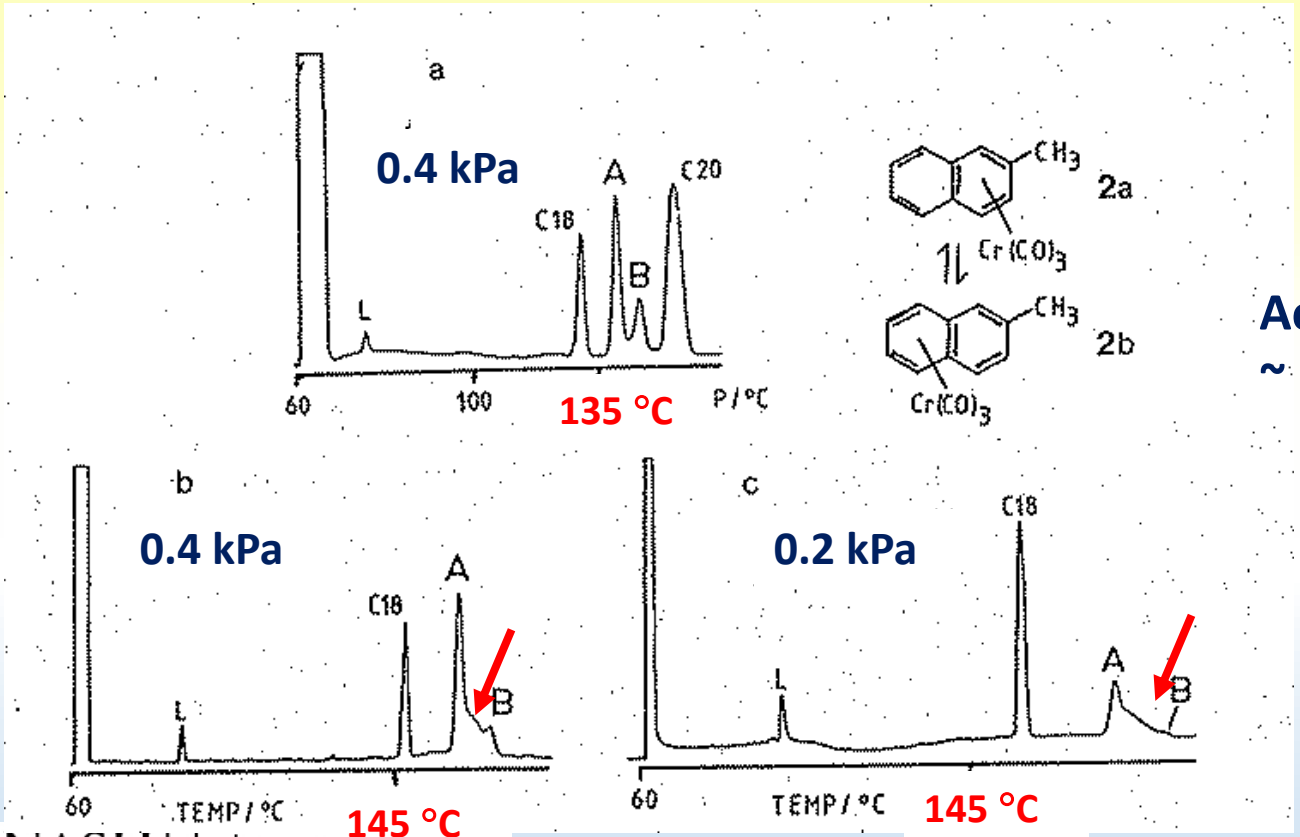






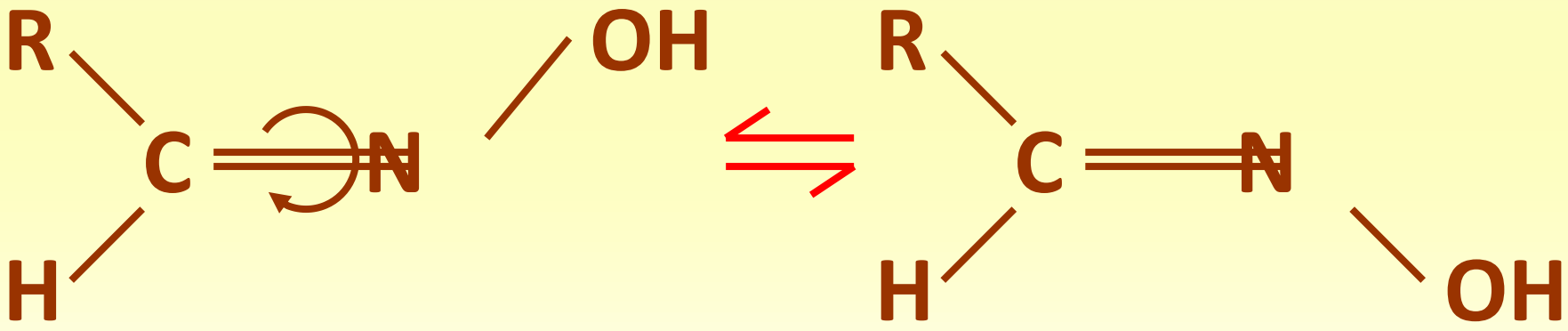
5 m x 0.54 mm ID non-polar phase

105 °C isothermal – minimise interconversion



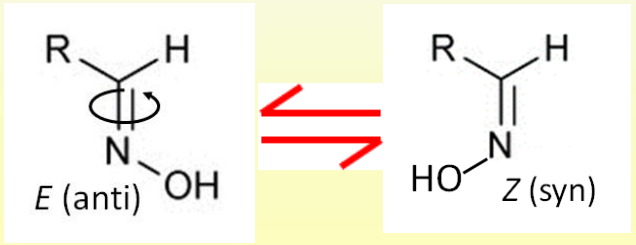
Activation energy
~ 100 ± 10 kJ mol^{-1}

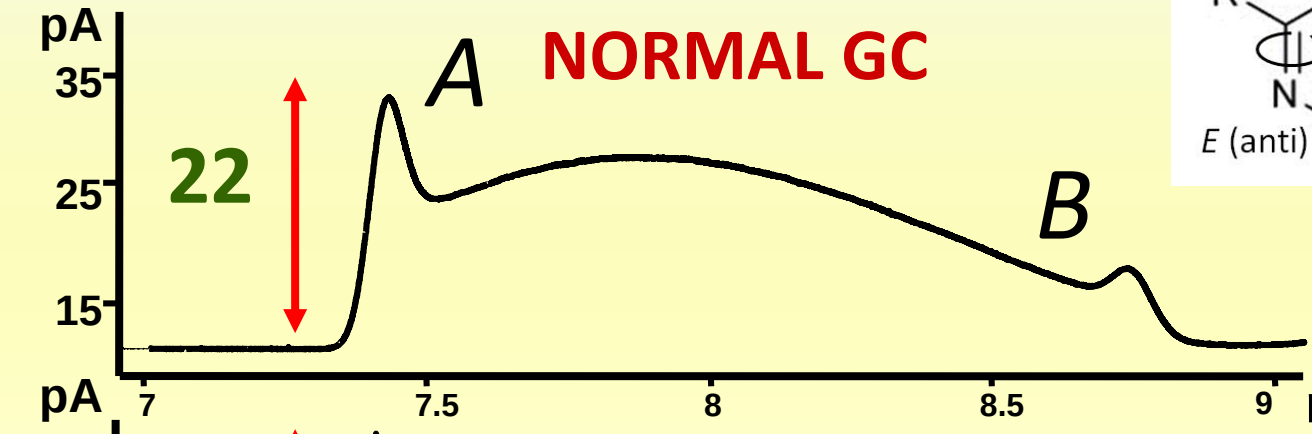
Dynamic Molecular Interconversion in OXIMES; *E-Z* isomers

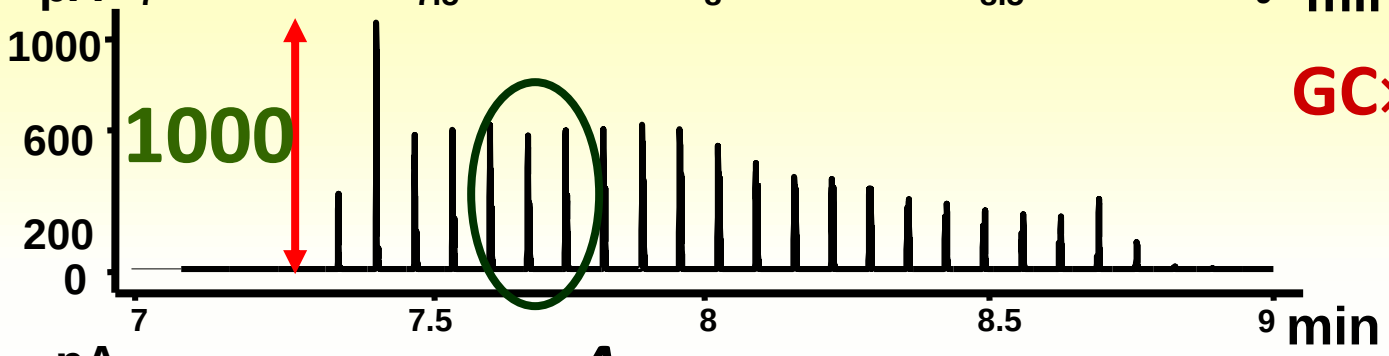


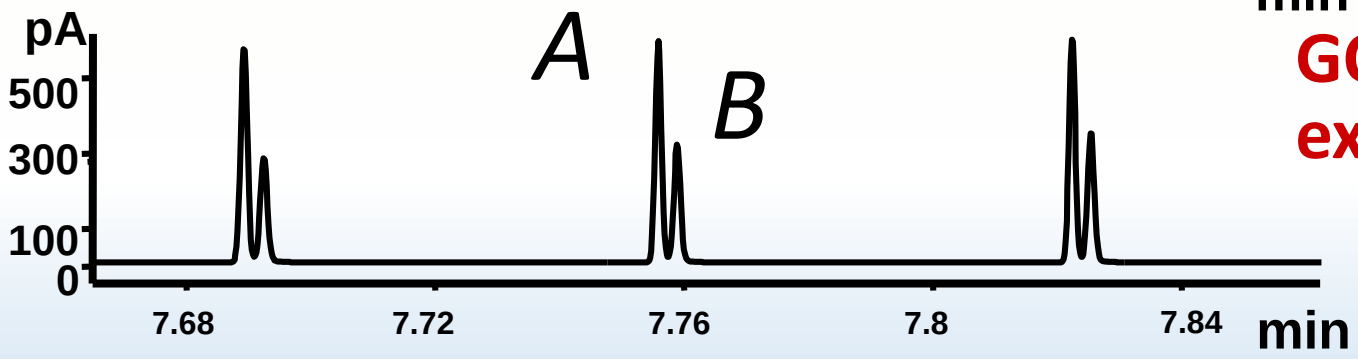
- Resolvable by GC using polar column
- Energy barrier 'suitable' for temp of GC analysis
- Calculate thermodynamic parameters by both
  ⇒ conventional means ⇒ modelling the GC trace

EXAMPLE - ACETALDOXIME @ 80°C









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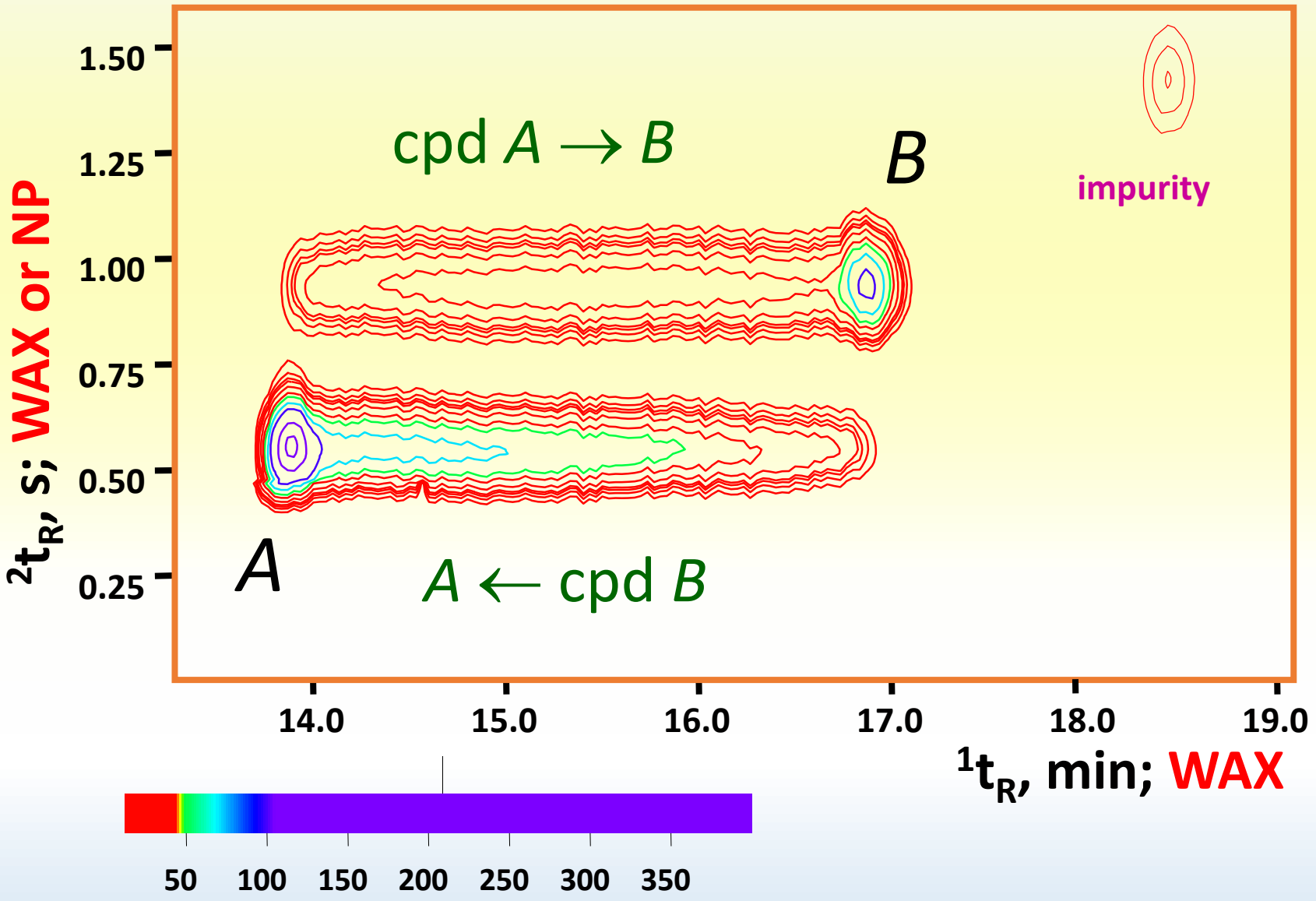
Acetaldoxime @ 80°C; 5psi



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Ruby Ong - SGE then returned to Singapore to Agilent, now with Thermo

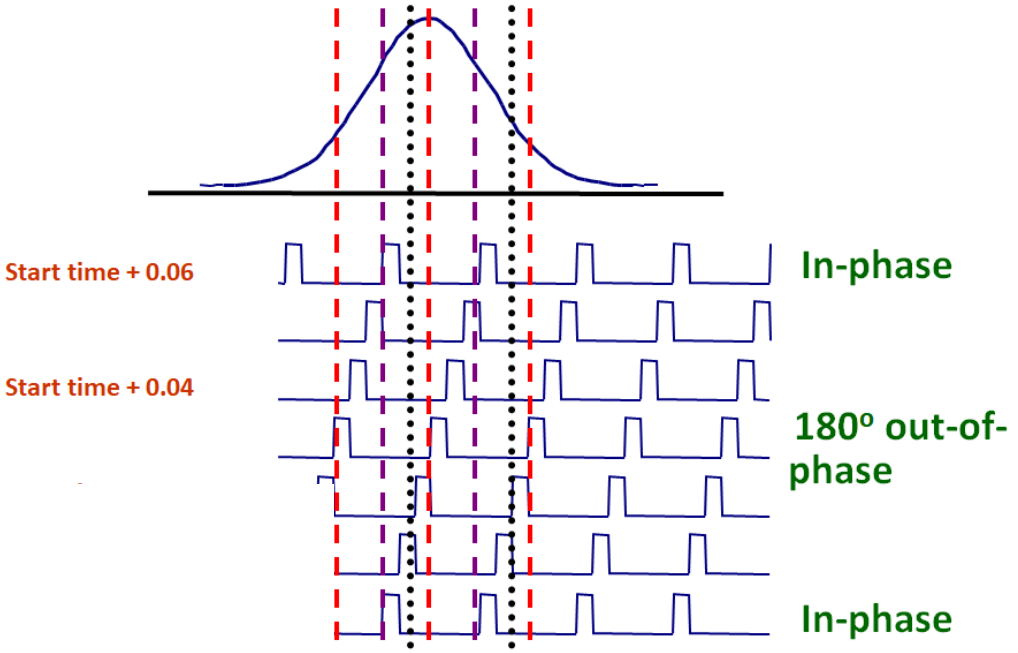
Phase & frequency of modulation & peak patterns in GC×GC

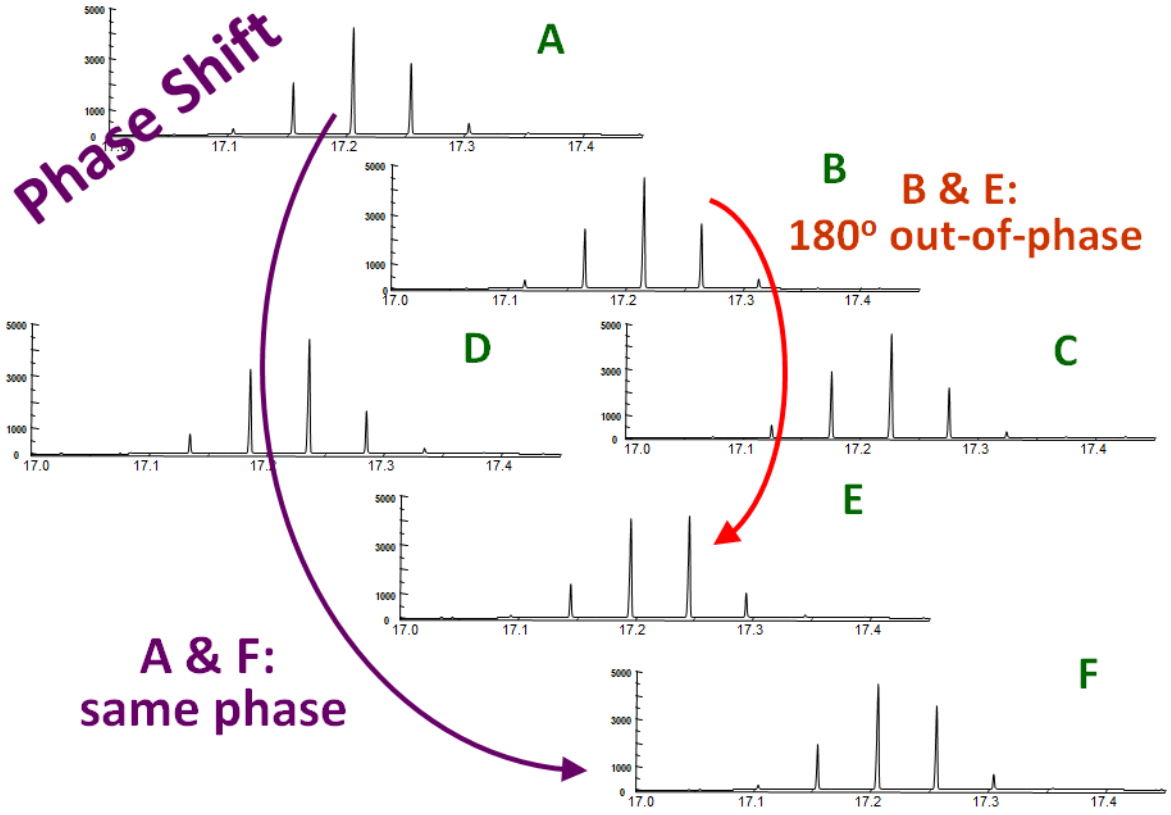
Planer PCBs in GC×GC

Shape selectivity of PCBs

Effect of chromatographic conditions on GC×GC

Modulation Phase and Frequency in GCxGC





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Danielle Ryan – Professor, Charles Sturt University

Orthogonality studies in GC×GC
Molecular interconversion in GC×GC
Coffee analysis
Strawberry volatiles analysis
Methoxypyrazines, labelled IS, SPME for wine analysis
TCD detection studies
Unresolved complex mixture petrochemical studies

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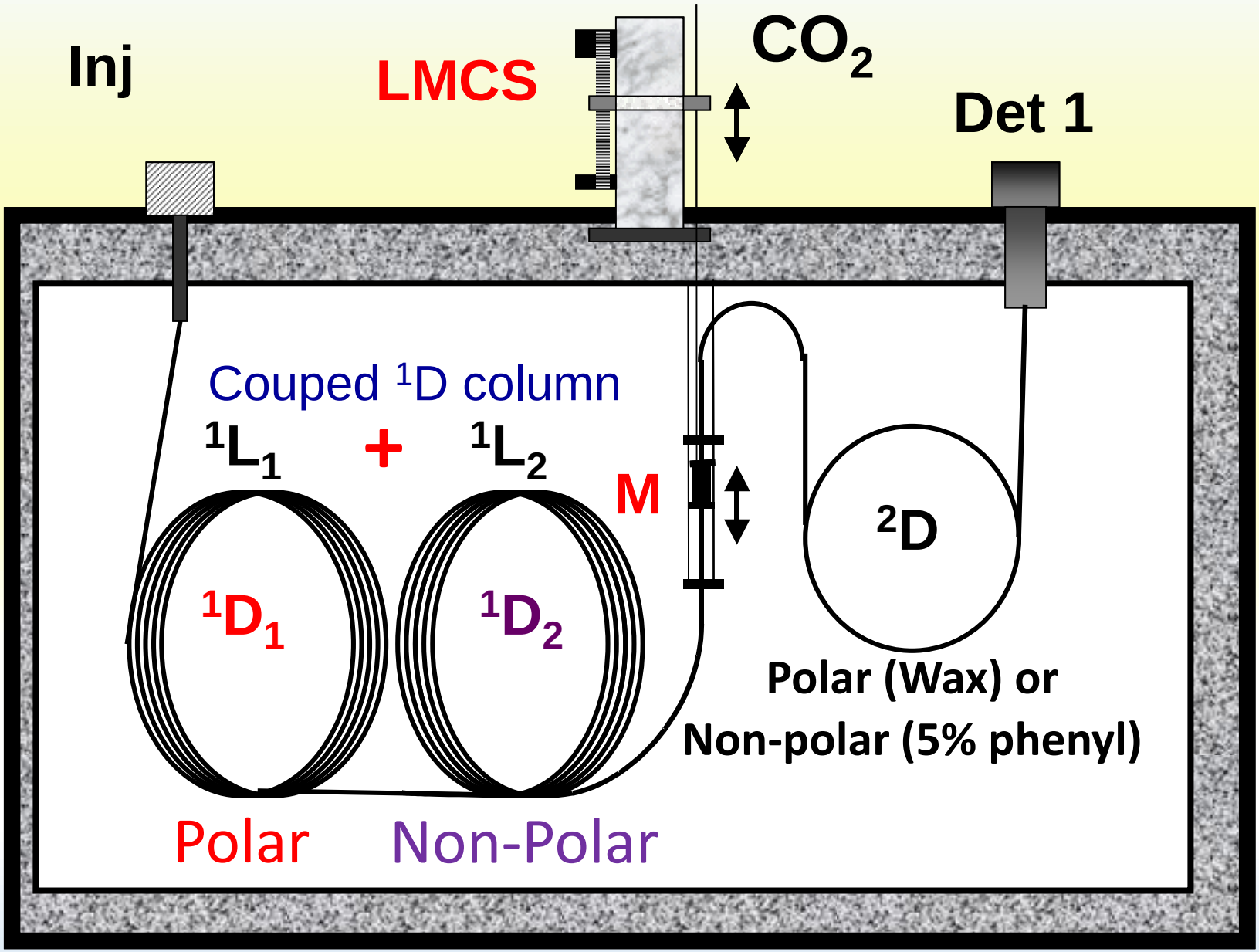

Inj
LMCS
CO_2
Det 1
Couped ^{1}D column
$^1L_1$ + $^1L_2$
M
^2D
$^1D_1$
$^1D_2$
Polar (Wax) or
Non-polar (5% phenyl)
Polar
Non-Polar

The BRAZIL "Orthogonality Experiment"

Orthogonal Non-Polar x Polar

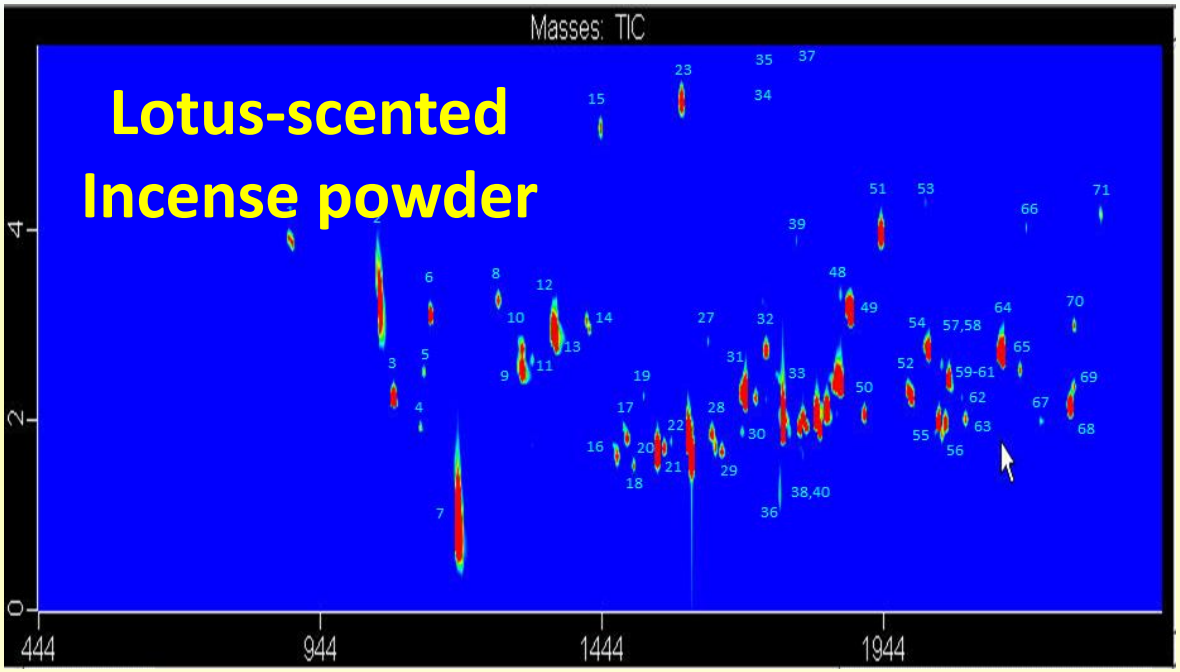
Tin Tran - Australian Botanical Products

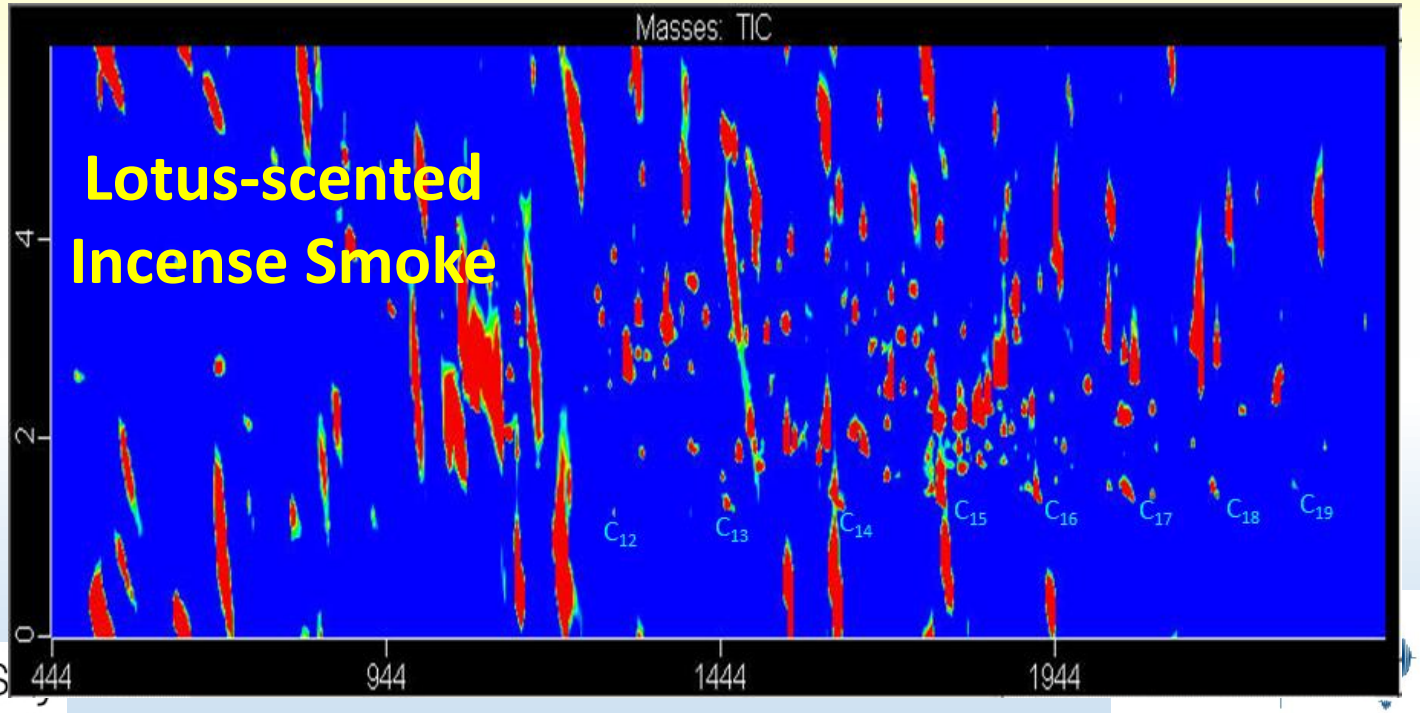
Incense and incense smoke analysis studies in GC×GC – ECD; NPD, MS

Choice of column phase geometries for petrochemical analysis

Characterisation of petroleum UCM

GC×GC-TOFMS of Incense





Weeraya Khummueng –
Professor Prince of Songkhla University, Thailand

Development of concepts of modulation ratio in GC×GC
Detector technologies for GC×GC
Fungicide residues in vegetables using GC×GC-NPD/ECD

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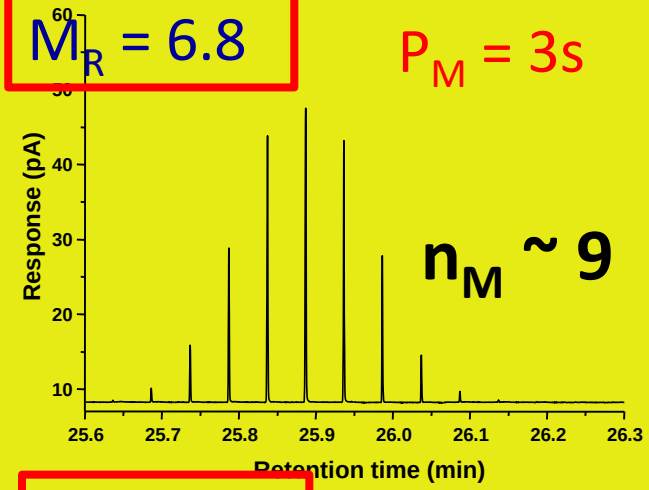
M_R = 6.8

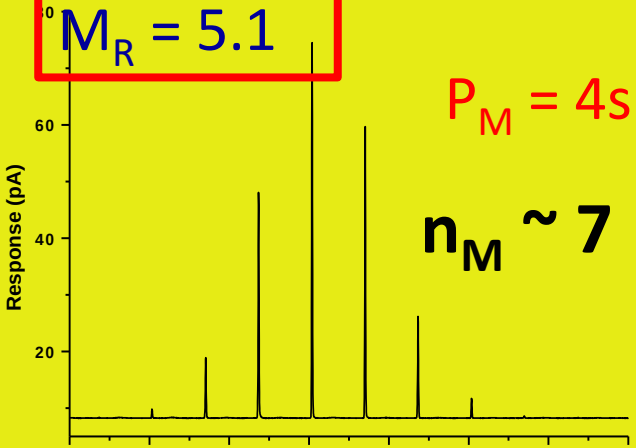
P_M = 3s



n_M ~ 9

M_R = 5.1

P_M = 4s



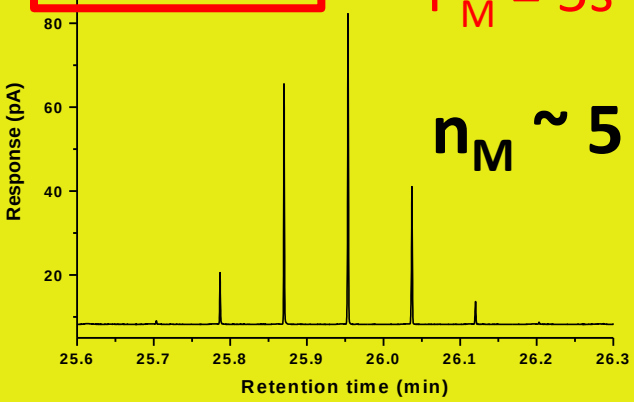
n_M ~ 7

… Alter P_M

$M_R = {}^1w_b/P_M$

M_R = 4.1

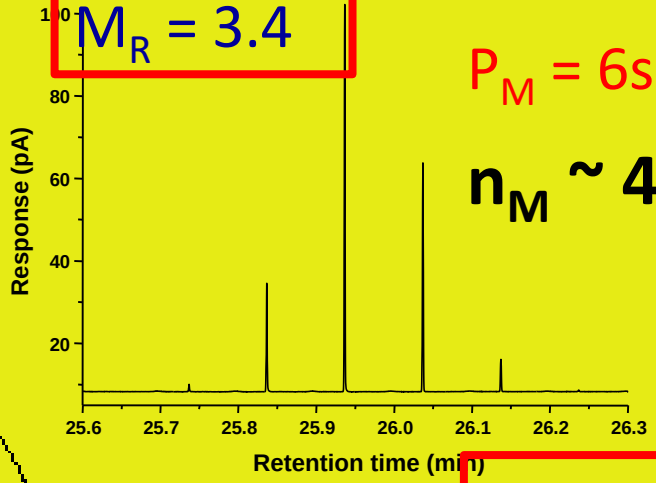
P_M = 5s



n_M ~ 5

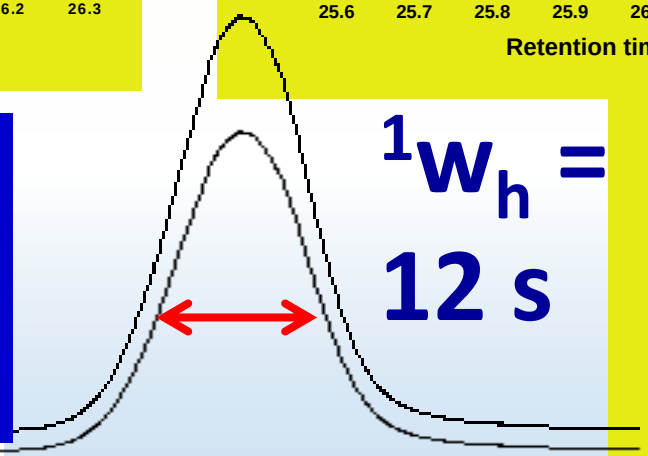
M_R = 3.4

P_M = 6s



n_M ~ 4

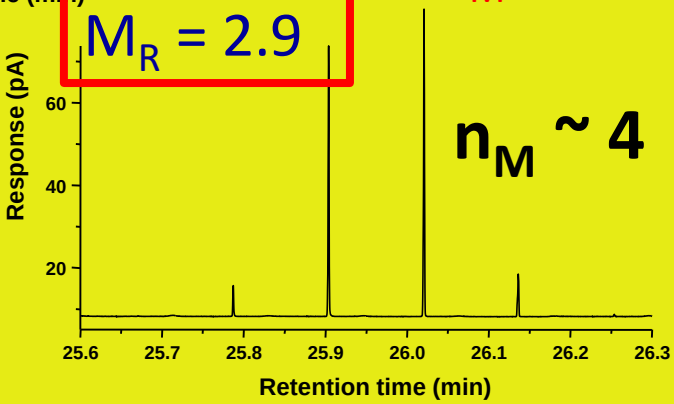
HOW MANY modulations do we want??



^1w_h = 12 s

P_M = 7s

M_R = 2.9



n_M ~ 4

Stefan Bieri - Switzerland Food control Lab, (similar to Koni Grob).

**** Received Swiss Chem Soc award for his work o retention indices in GC×GC; visited Kováts to discuss his work**

Development of approaches for retention index concepts ^{1}I and ^{2}I in GC×GC

Dual injection system for ^{1}I and ^{2}I in GC×GC

Fast enantioseparation for allergens analysis (ca. 4 min)

Michael Dunne -

Development of approaches for targeted multidimensional gas chromatography.
Rapid analysis supported by cryogenic modulation.
Allergens; peppermint

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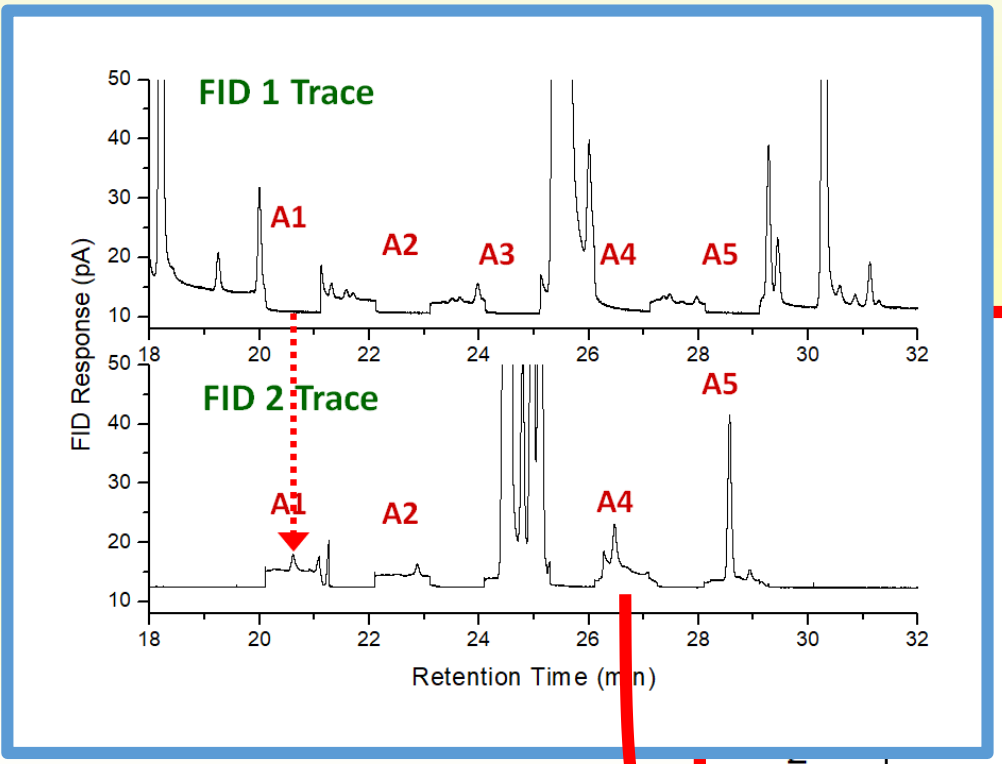

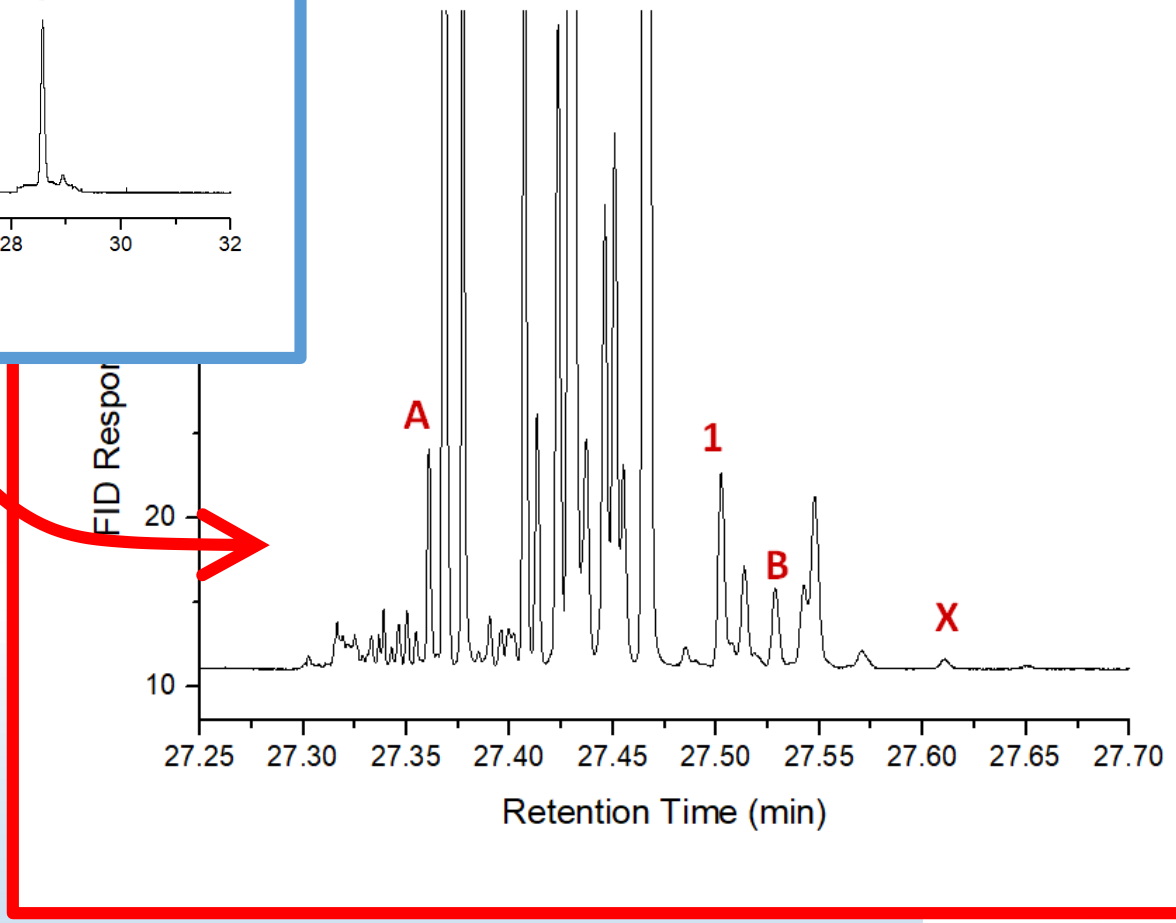

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James Harynuk – Professor University of Alberta – Canada

Analysis of thermally-labile compounds in GC and GC×GC
Modulation ratio concepts in GC×GC
Fatty acids and selective FAME columns GC×GC
Fast GC×GC with short primary columns
Sample dimensionality and structured retention patterns in GC×GC
Microwave derivatization for metabolomics in GC×GC

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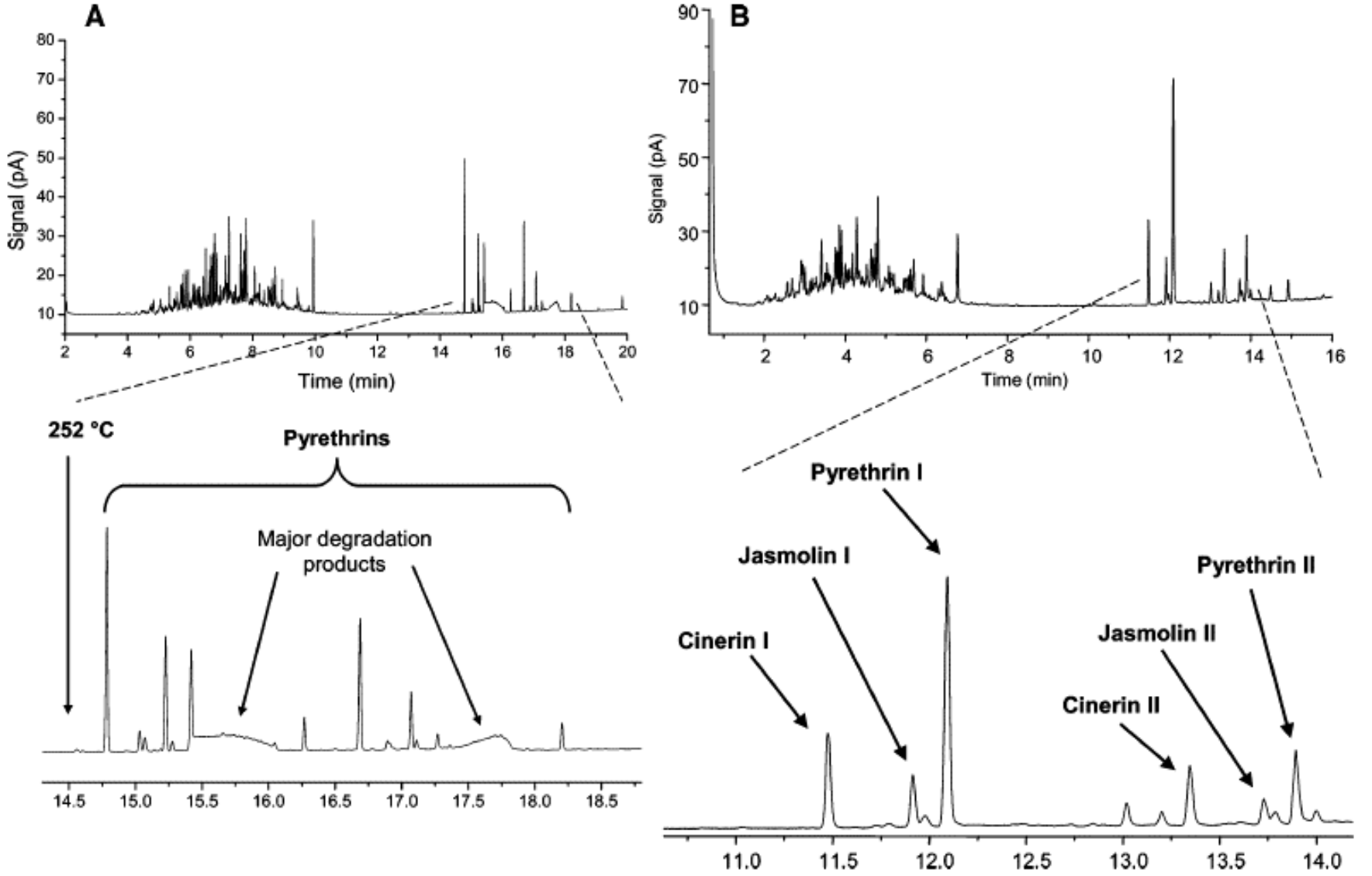
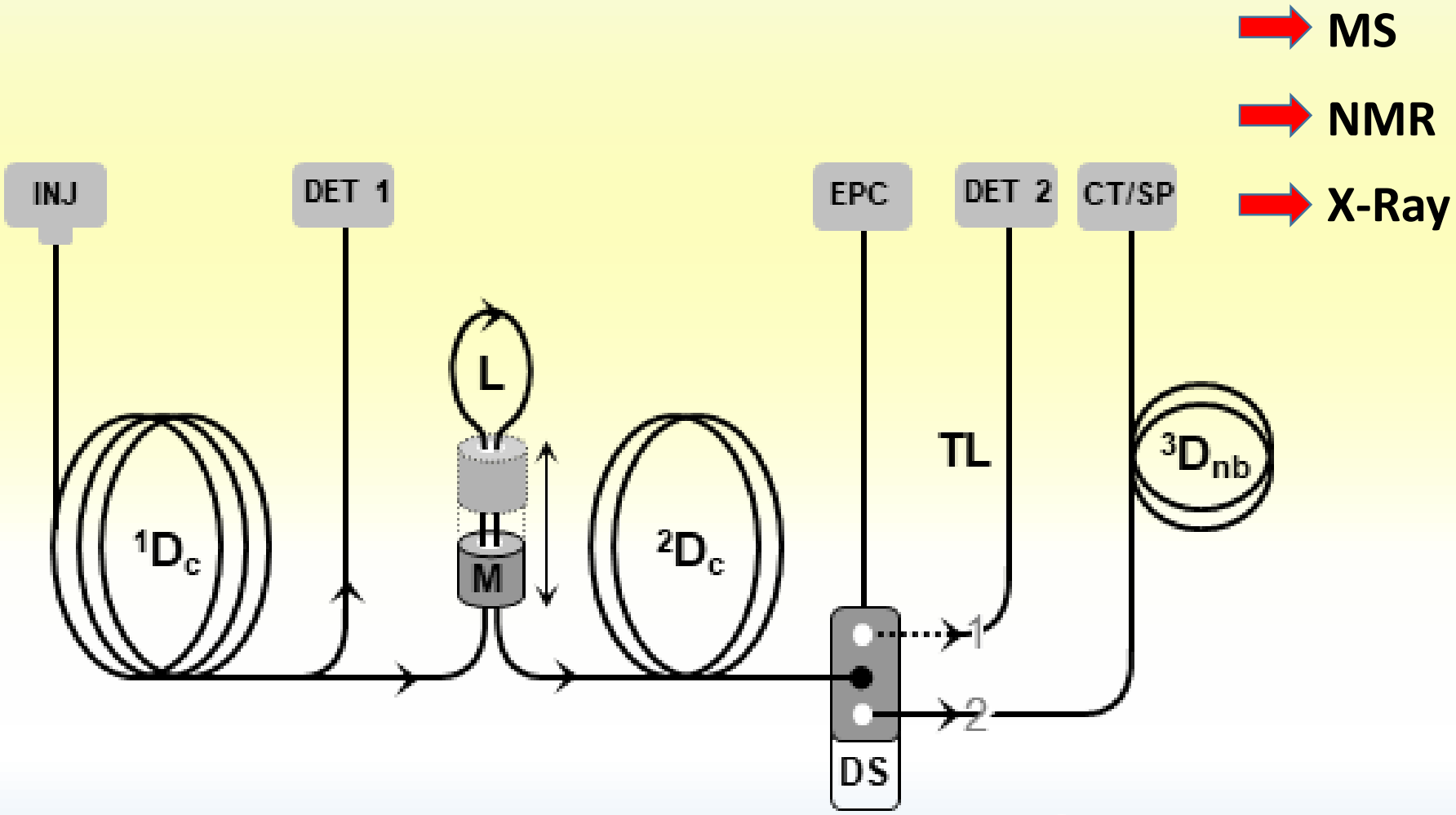
Fast GC×GC with Short Primary Columns

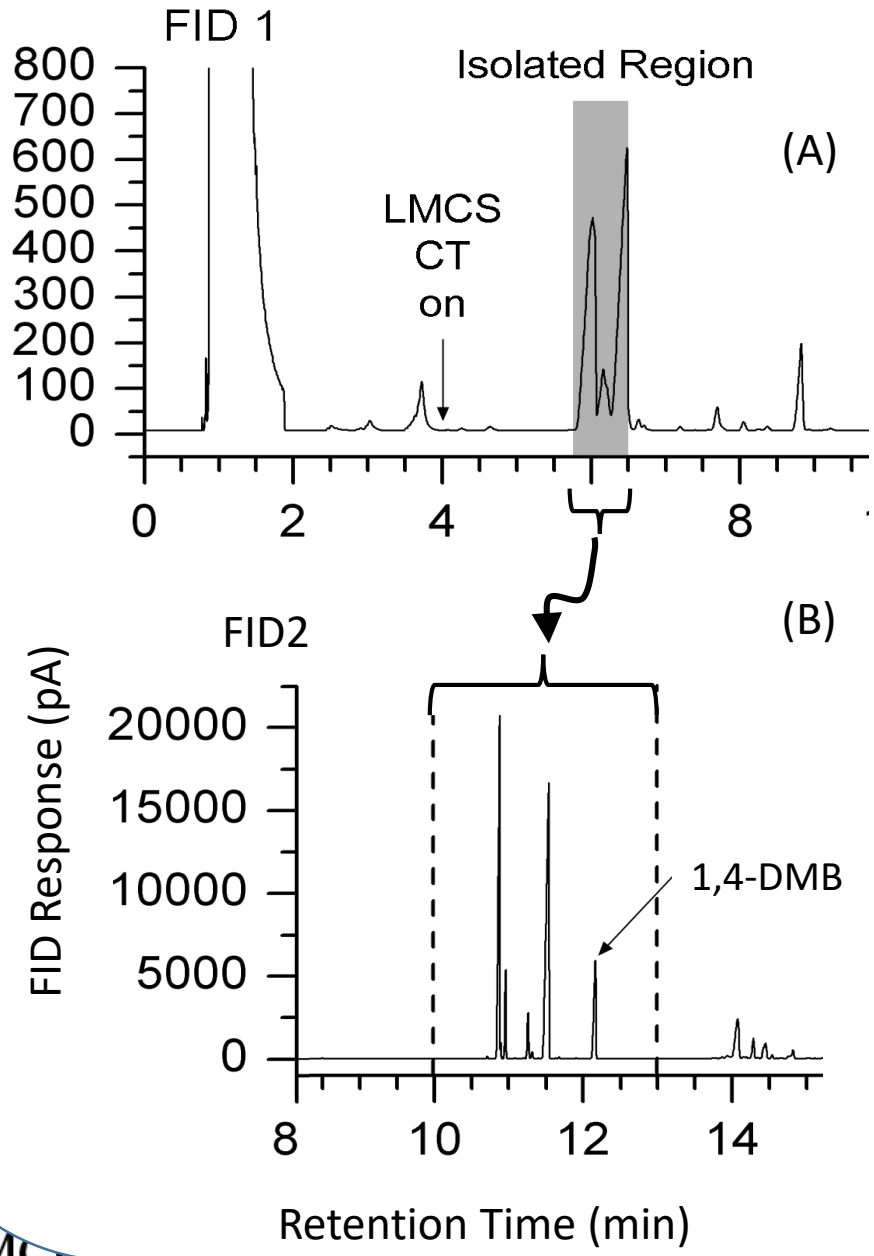
Prevent thermal degradation of natural pyrethrums …

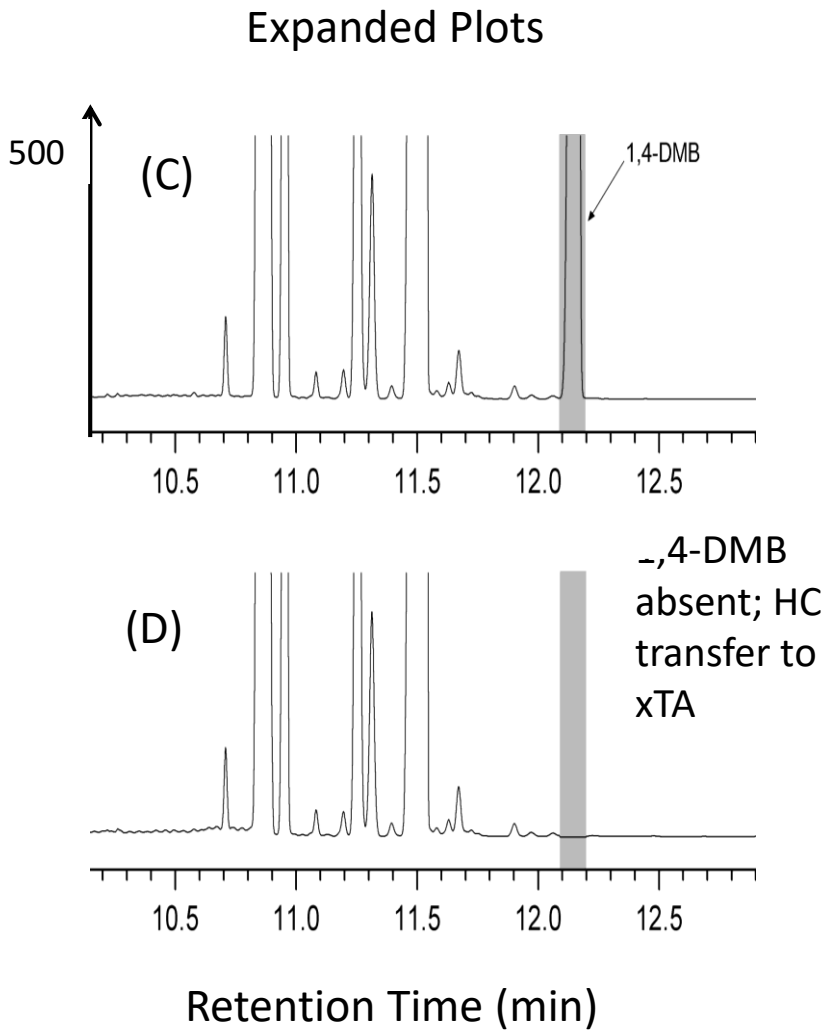


Graham Eyres – Professor Otago University Food Science, New Zealand

Spicy fractions in Hop analysis by GC×GC
Character-impact odorants in coriander and wild coriander, with olfactometry and GC×GC
Potent odorants in wine and brewed coffee, with with olfactometry and GC×GC
MDGC for micro-preparative scale identification of target compounds with MS and NMR
Flavour analysis with GC×GC


MS
NMR
X-Ray
INJ
DET 1
EPC
DET 2
CT/SP
L
TL
$^{3}D_{nb}$
$^{1}D_{c}$
M
$^{2}D_{c}$
1
2
DS


FID 1
Isolated Region
(A)
LMCS
CT
on
800
700
600
500
400
300
200
100
0
0
2
4
8
FID2
(B)
FID Response (pA)
20000
15000
10000
5000
0
1,4-DMB
8
10
12
14
Retention Time (min)


Expanded Plots
500
(C)
1,4-DMB
10.5
11.0
11.5
12.0
12.5
(D)
_,4-DMB
absent; HC
transfer to
xTA
10.5
11.0
11.5
12.0
12.5
Retention Time (min)

Shin-Miin Song - Health Science Authority Singapore, then A-Star Singapore; award for best forensic science paper

GC×GC-TOFMS for drug screening and confirmation
GC×GC-qMS for drug profiling
Chemical fingerprinting of illicit drug seizures with GC×GC

Blagoj Mitrevski - CSIRO Oceans & Atmosphere, Melbourne

Development of novel hybrid comprehensive 2D - multidimensional gas chromatography

Dual ionic liquid columns for GC×GC of fatty acid methyl esters

Steroid analysis by using GC×GC

Chemical signature of ecstasy volatiles by GC×GC

Identification of anabolic agents in doping control with GC×GC

WADA criteria for anabolic agents examined by GC×GC

Oxidative degradation products in algal-derived fuel oil by GC×GC

GC×GC-FPD of organophosphorus pesticides in foods

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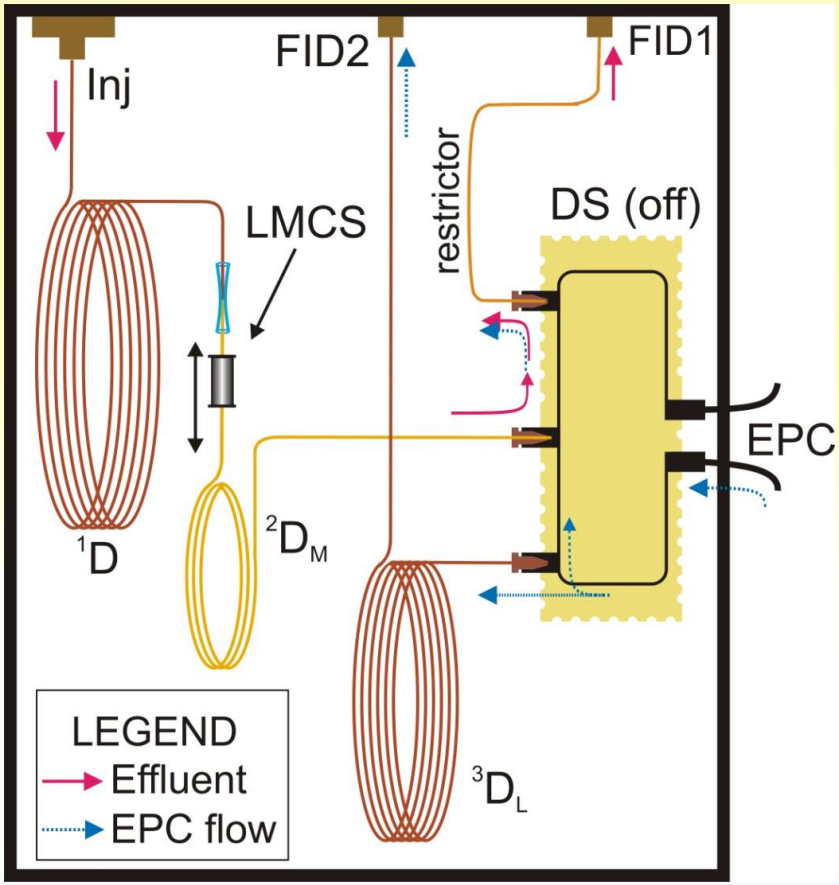
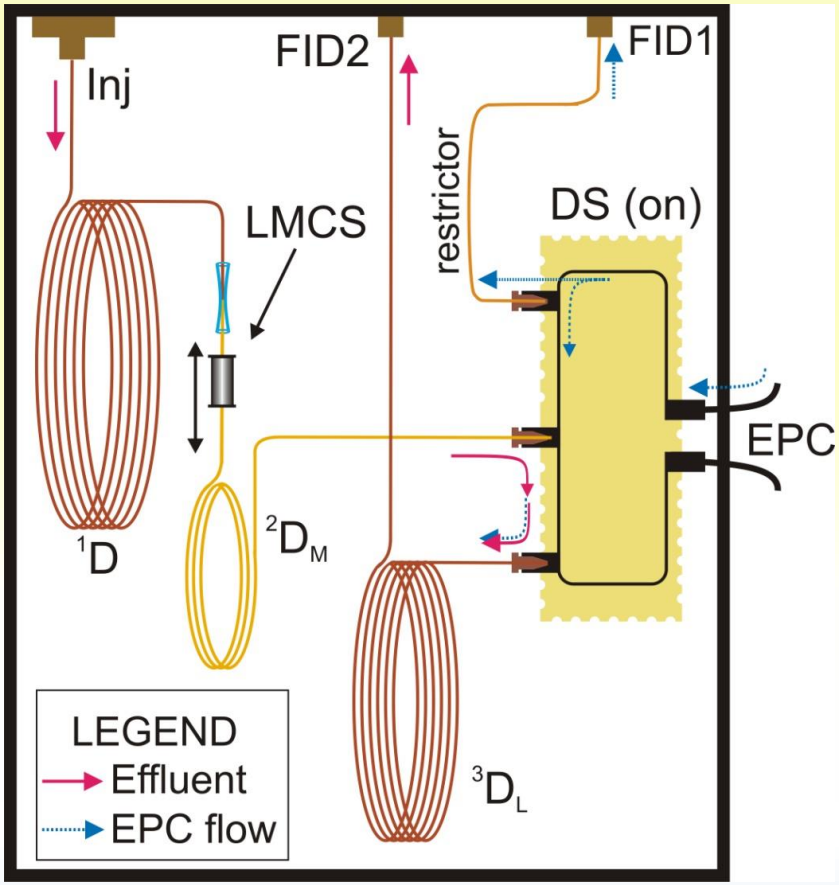
DS OFF: (GC×GC)



DS ON: (GC×GC-MDGC)



^{1}D column: SolgelWax (30m x 0.32mm x 0.5µm)

^{2}D$_M$ column: VF5 (5m x 0.15mm x 0.15µm)

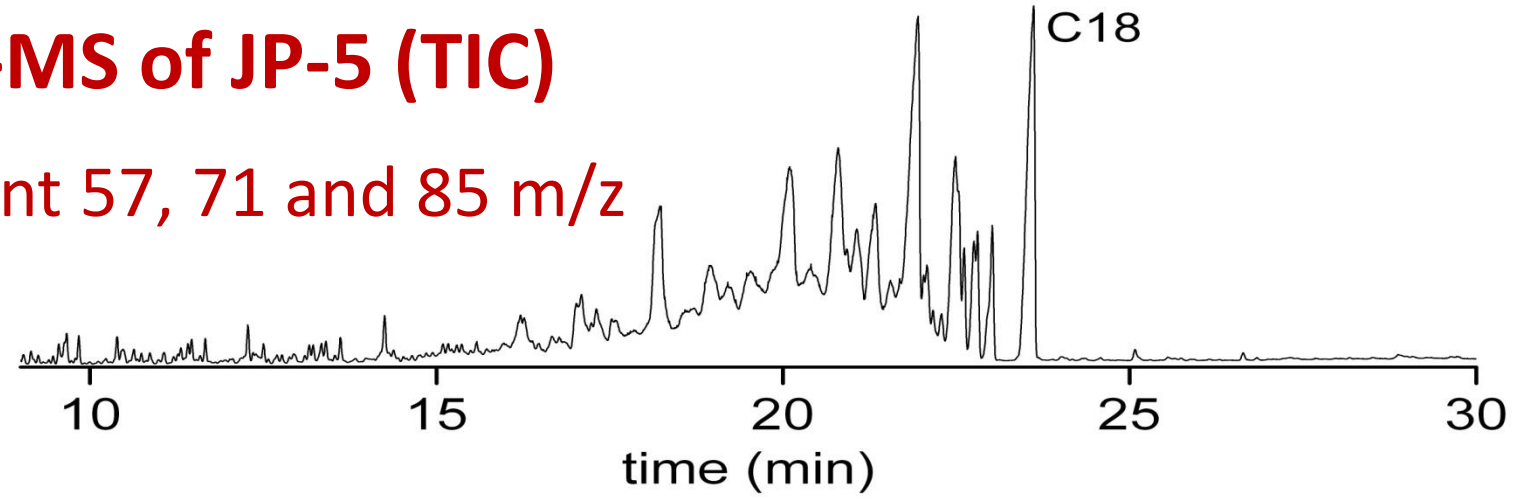
^{3}D$_L$ column: Rxi 17Sil (20m x 0.18mm x 0.18µm)

Results

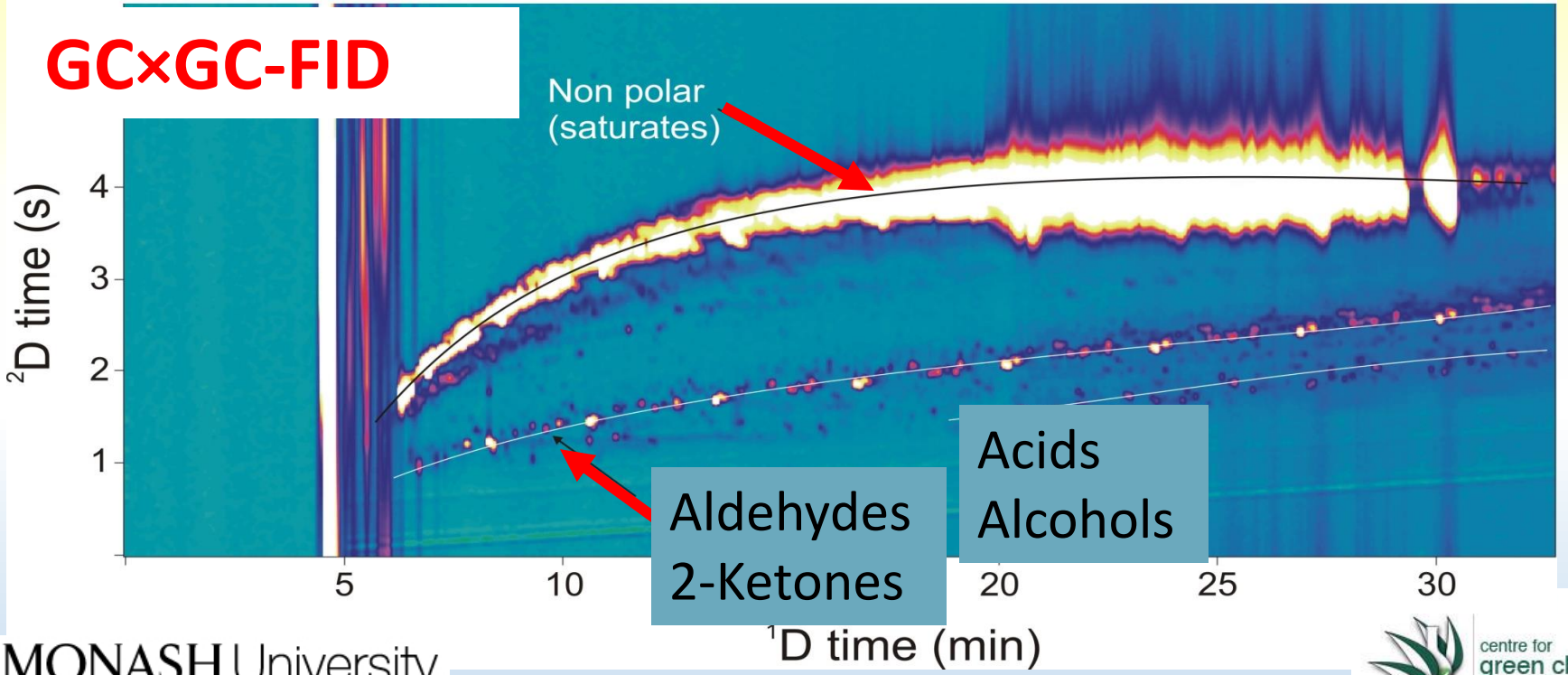
S-compounds

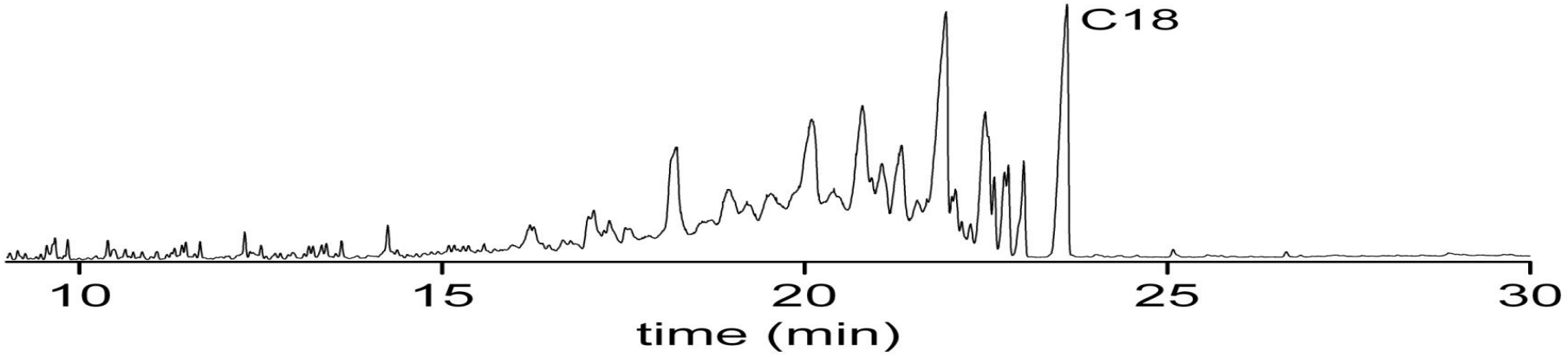
1D GC-MS of JP-5 (TIC)

Dominant 57, 71 and 85 m/z

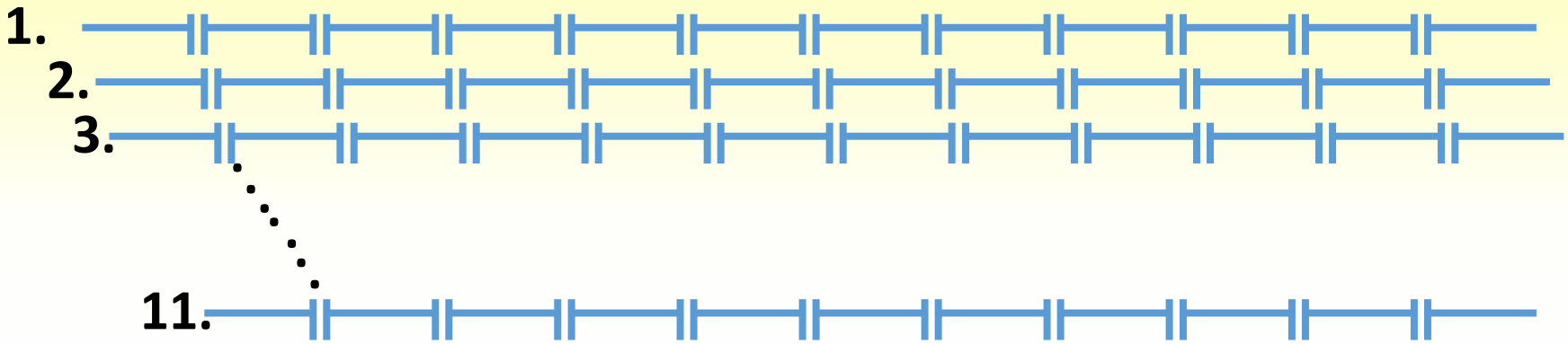


GC×GC-FID



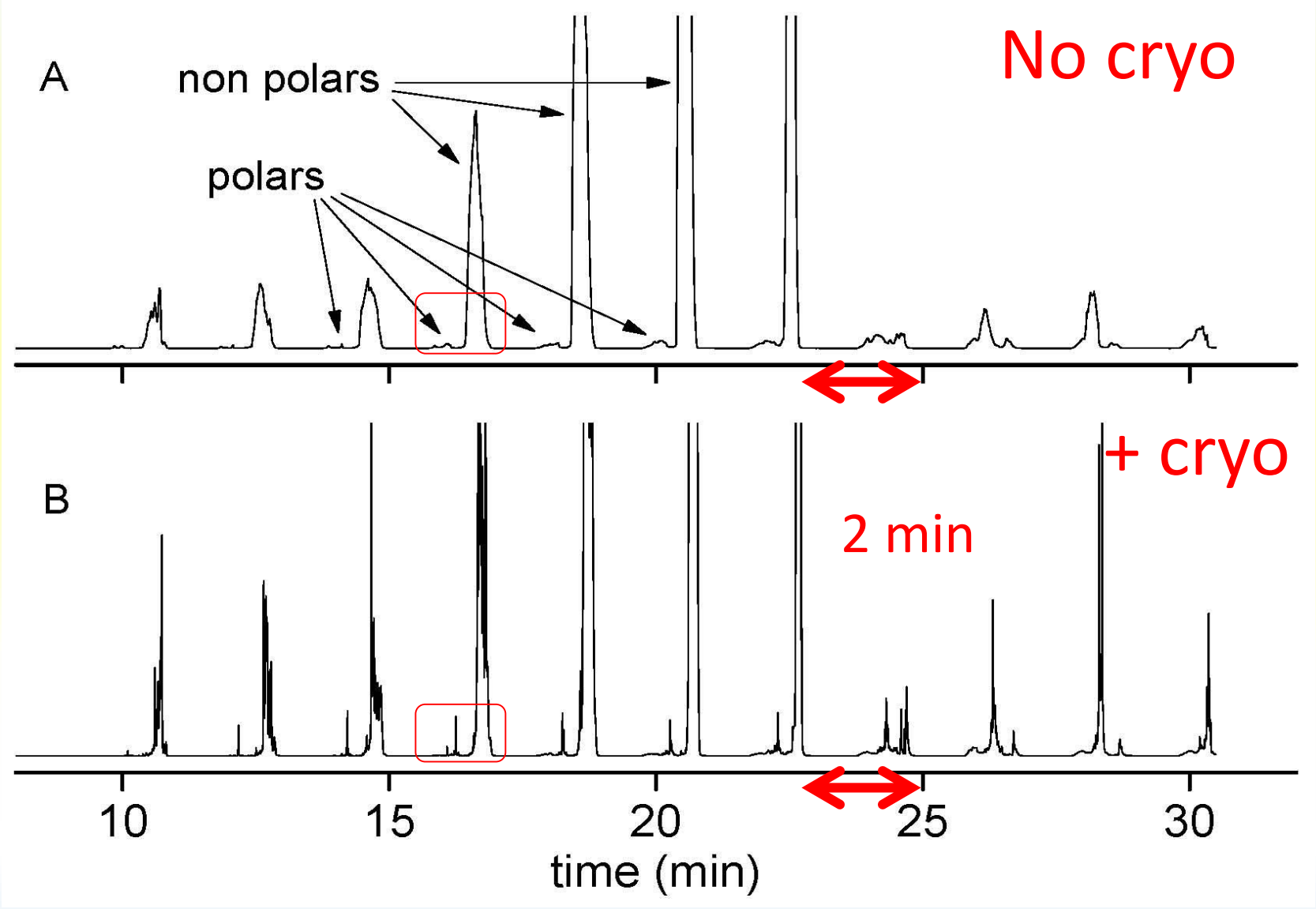


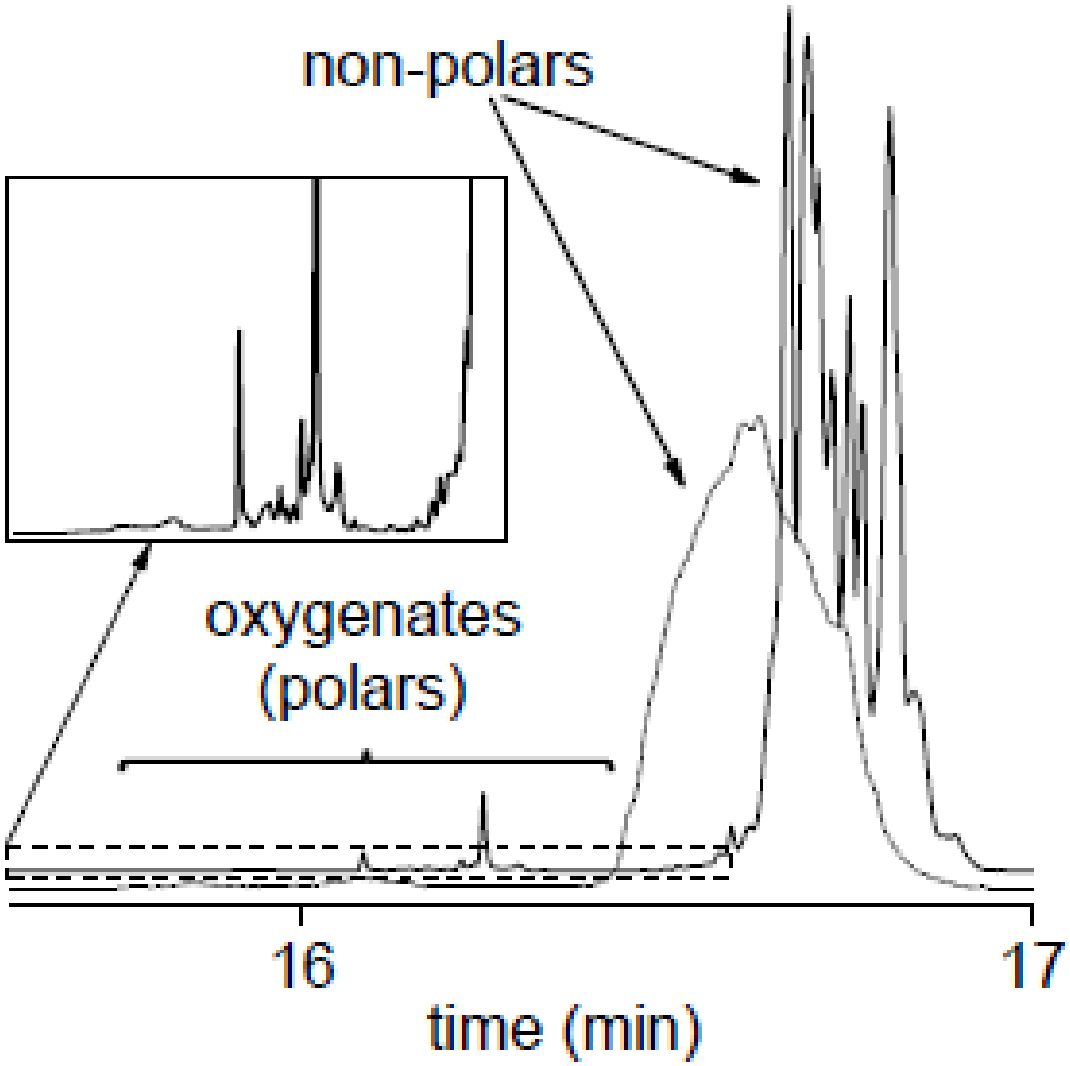
Multidimensional sampling strategy



Sample 0.2 min, 2 min apart
= 10 analyses to cover a full sample

& complete each heartcut in 2 min

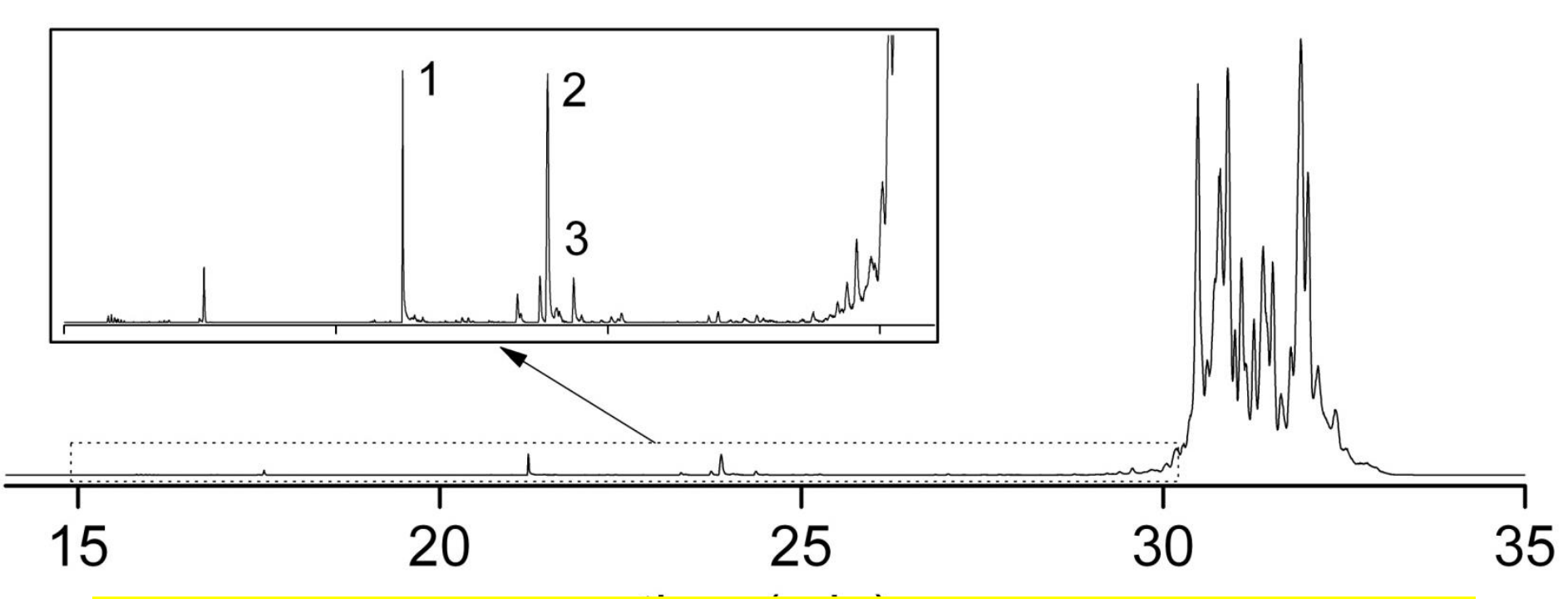

A
non polars
polars
No cryo
B
+ cryo
2 min
10
15
20
25
30
time (min)



Single (12 s) heart-cut; with (——) & without (·····) cryotrapping. Without: can hardly recognize oxygenates: With: easy to recognize oxygenates

Another approach:

- Single heart-cut, cryotrap, reduce oven temp., release...
  - Very high peak capacity (~600)
  - Cut a 0.2 min section from the 1D GC run … GC



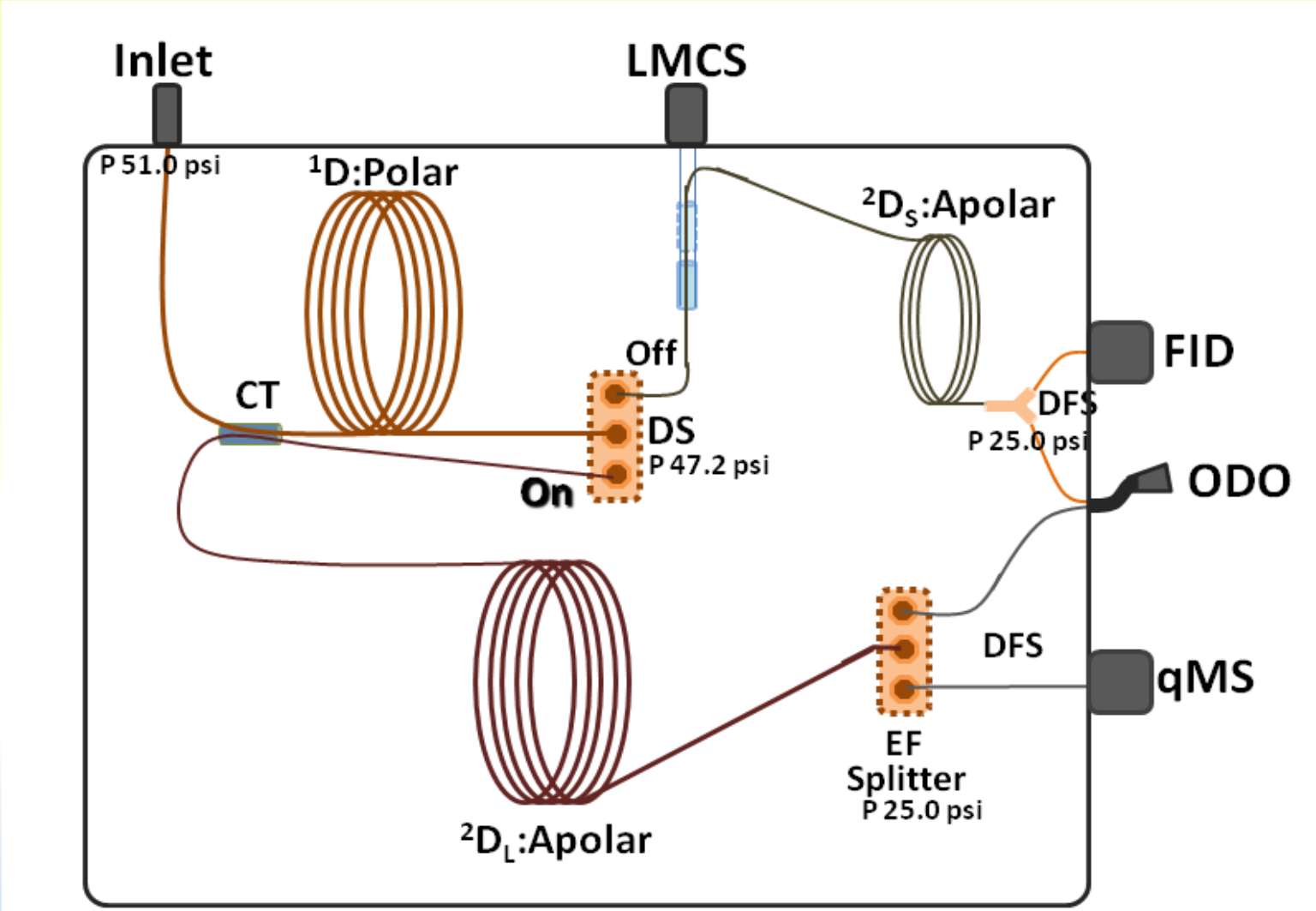
Single (12 s) heart-cut (see previous slide)
PROCESS: (1) cryotrap; (2) cool the oven; (3) then elute on the long ^{2}D column

Sung-Tong Chin - Imperial College (UK) and metabolomics, Murdoch University

S- and P- compound analysis with GC×GC-FPD
On-line concentration of target compounds with in-oven cryotrapping
Cumulative SPME gas chromatography-olfactometry of Shiraz
Integrated GC×GC & MDGC with mass spectrometry and olfactometry
Profiling of soil fatty acids using GC×GC-MS
Enantiomeric separation in GC×GC with accurate mass MS

Integrated GC×GC & MDGC with mass spectrometry and olfactometry

GC-FID/O
GC×GC-FID
MDGC-MS/O



Chadin Kulsing – Professor Chulalongkorn University, Thailand

Two-dimensional retention indices and GC×GC of saffron improves component identification

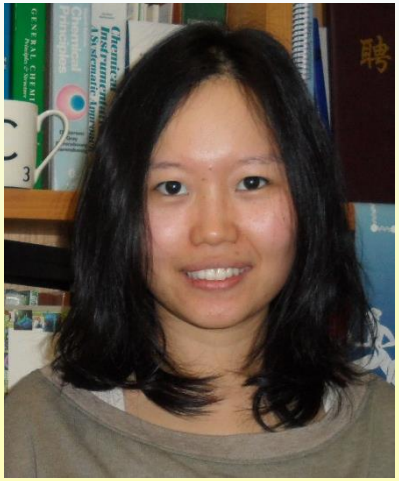
Molecular structures of ionic liquids to predict retention of fatty acid methyl esters in GC×GC

Continuum in MDGC technology; MDGC to GC×GC

GC×GC group type analysis of compounds in thermally stressed jet fuel

Multiple heart-cutting comprehensive MDGC

Yada Nolvachai – Postdoc Monash University



Thermally sensitivity of ionic liquid columns explains unusual orthogonality in GC×GC

In silico modeling of 100,000 experiments for optimisation in GC×GC

GC×GC-MS modelling – a super-resolved separation technique

Olive oil triacylglycerol analysis with MDGC-MS

Molecular modelling of FTIR to improve identification in GC-FTIR/MS

Ionic liquid phases for GC×GC of FAME

Winner of the inaugural Kováts Award, of the Hungarian Society for Separation Sciences

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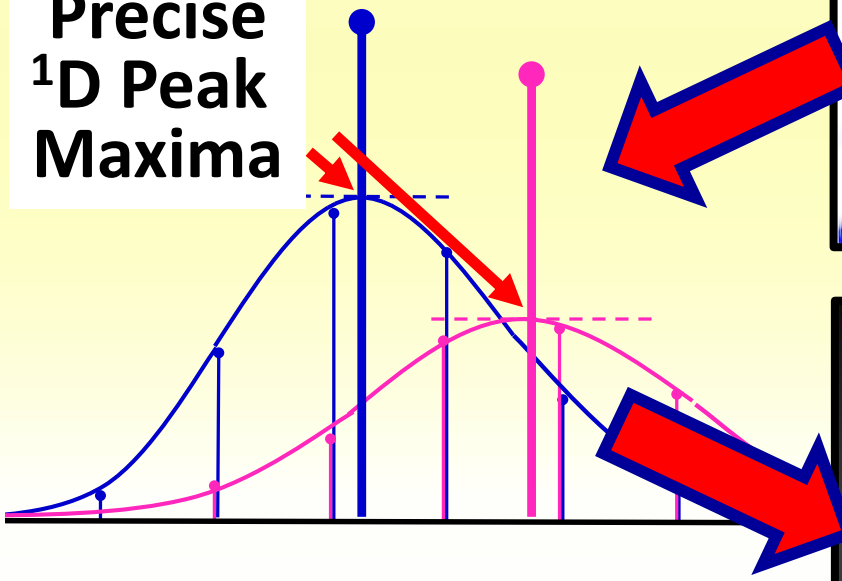
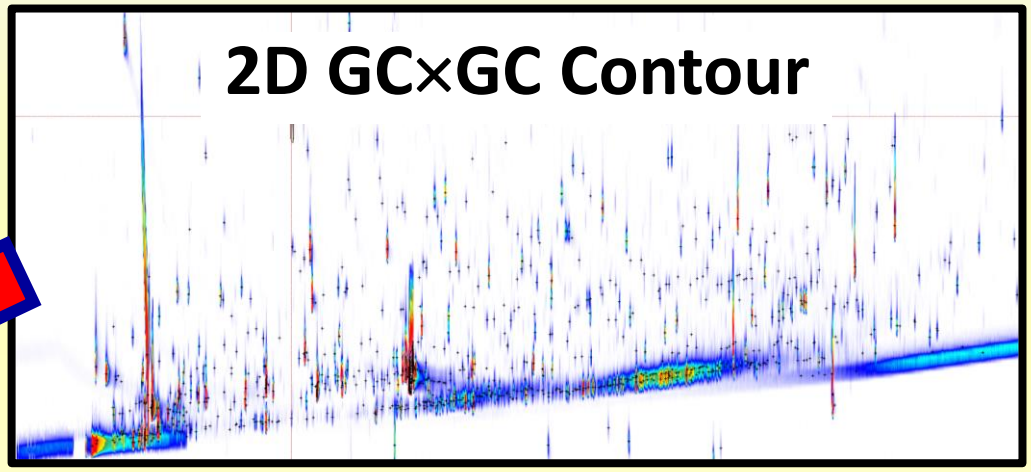
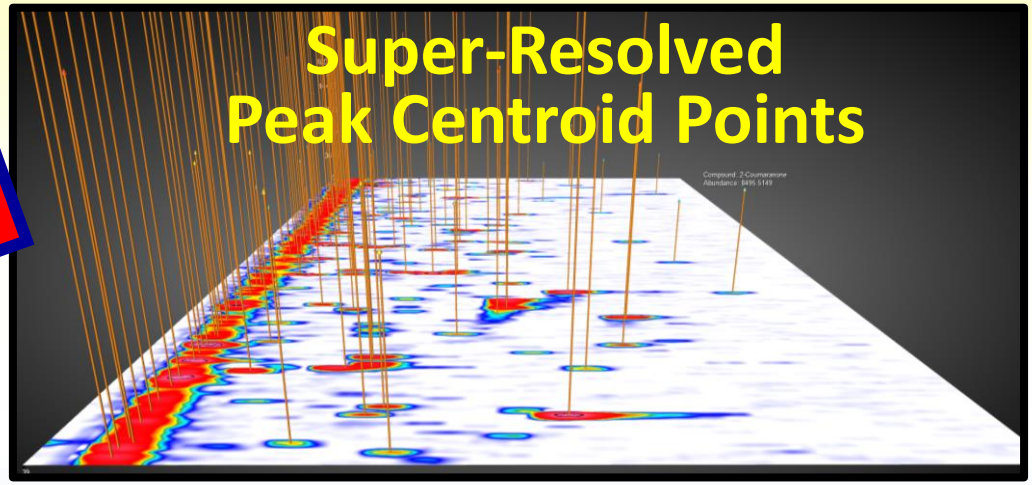
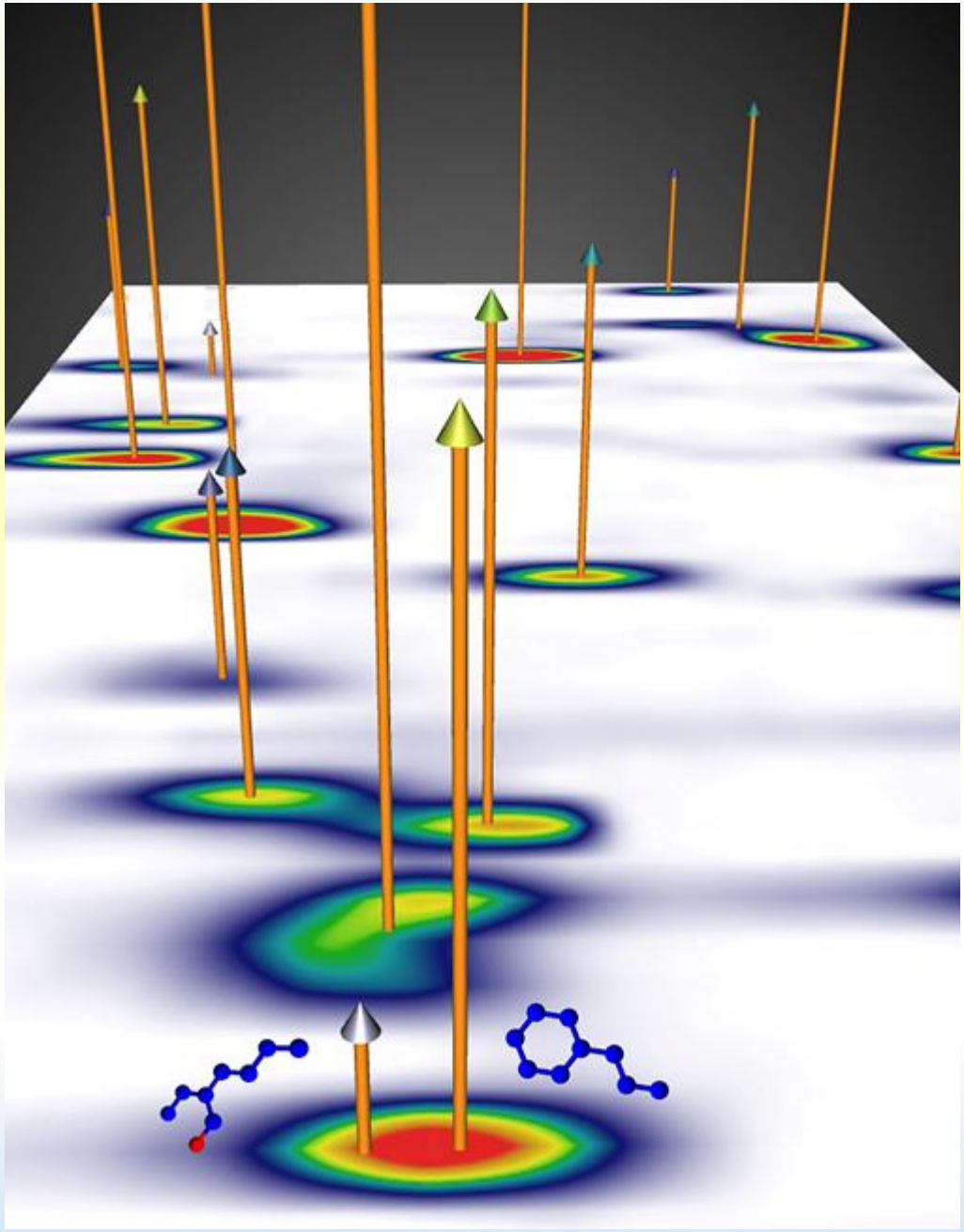
Locate Precise ^{1}D Peak Maxima









Monash & Markes / SepSolve.

GC×GC–MS: toward a super-resolved separation technique.
Anal. Chem. **92 (18) (2020) 12572.**

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Yong-Foo Wong – Professor Science University (Univesiti Sains), Penang, Malaysia

Metabolic profiling of plant-fungus interaction by use of GC×GC-MS

Enantiomers interconversion GC×GC with enantioselective columns in both ^{1}D and ^{2}D

Enantioselective MDGC of monoterpenes for authenticity control of tea tree oil

Analysis of copaifera oleoresin using GC×GC and gas chromatography with soft and cold electron ionisation

Sequential hybrid 3D GC×GC-MDGC with accurate MS

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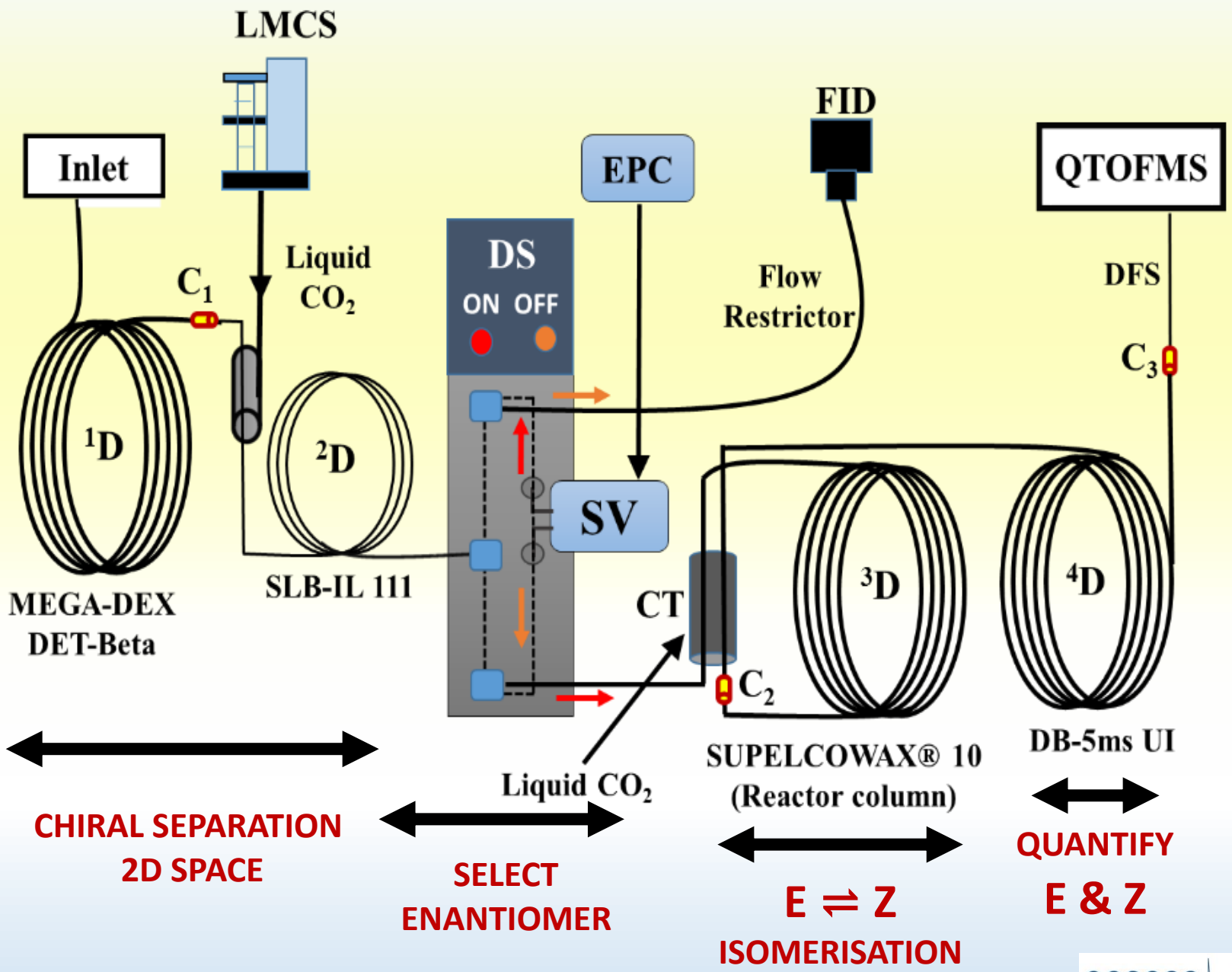


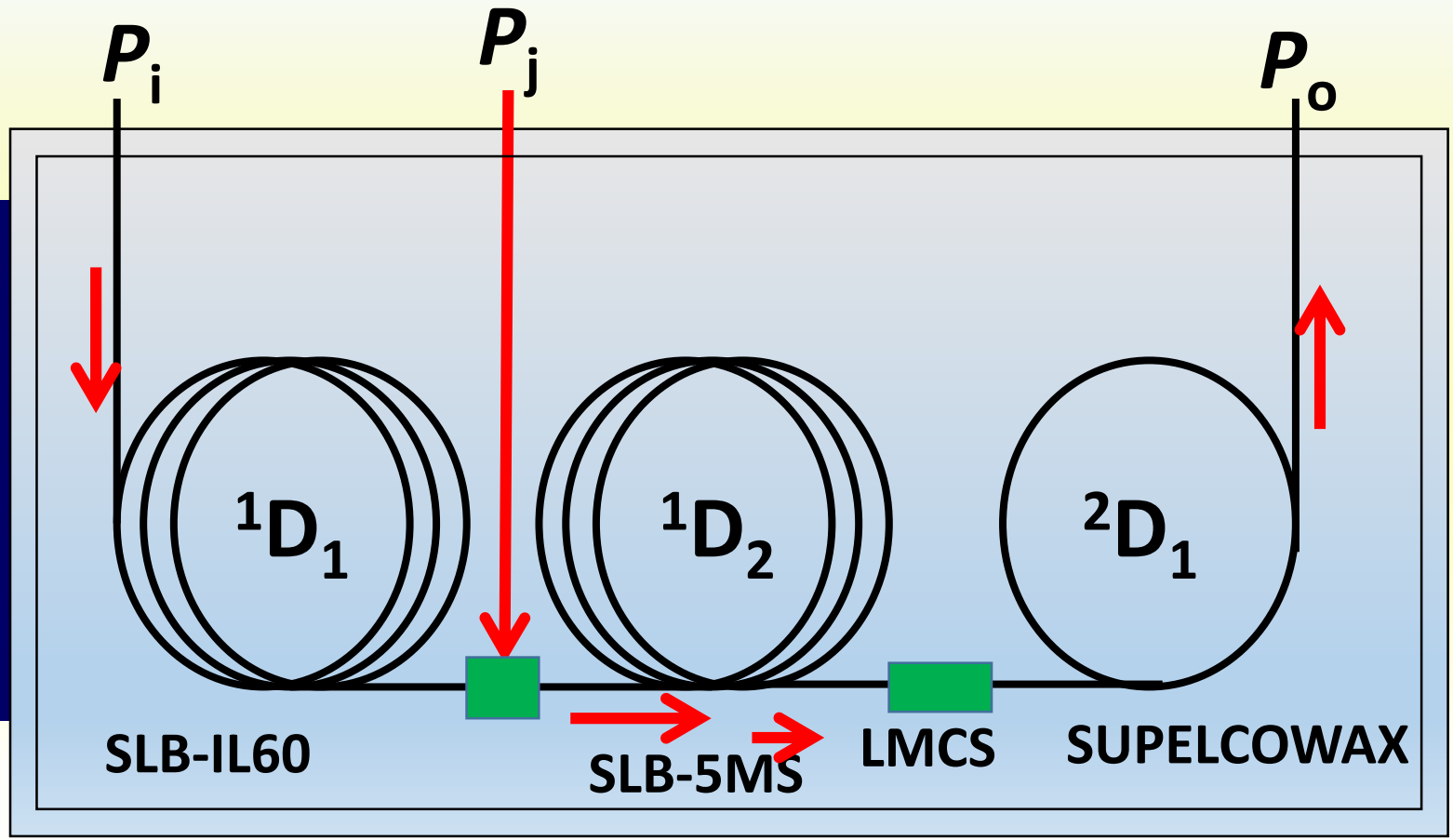
Wong et al. *Anal. Chem.* **89 (2017) 5620−5628**

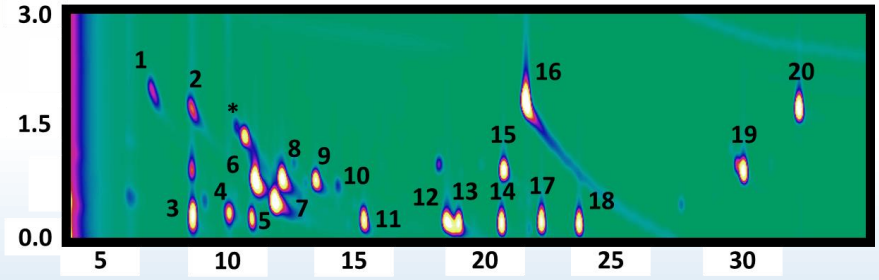
Sharif Khan - Dartmouth College, New Hampshire,
Then Wake-Forest University, North Carolina, USA.
Now, Cargill Inc. Minneapolis

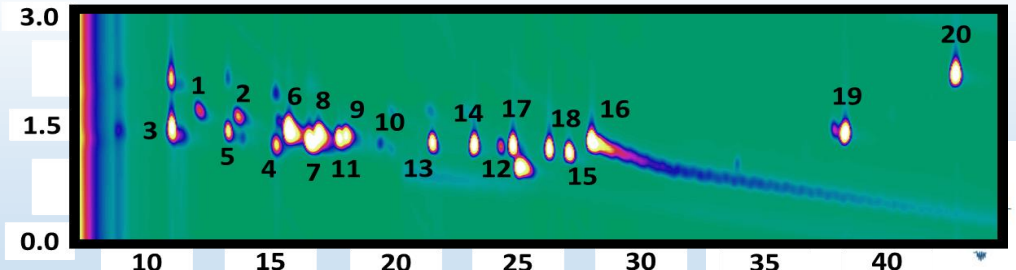
Pressure–tuning of ^{1}D and ^{2}D columns in GC×GC & Retention Indies in P/T - GC×GC

Pressure Tuned ^1D.

.. alters selectivity of the ^1D separation







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Study of
SEPARATION OF 27 STEROIDS BY 1D GC AND GC×GC with FID & MASS SPECTROMETRY

Mitrevski & Marriott

^{1}D: BPX5, 30m, 0.25mm, 0.25um

Inj.: 320 °C

H_2 Flow: 1.2 ml/min

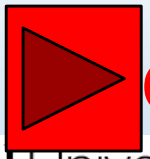
^{2}D: BPX50, 1 m, 0.1 mm, 0.1um

Det.: 330 °C

FID Sampling Rate:100 Hz

Modulation Period: 5 s

Oven: 240 °C, 2 °C/min to 270 °C, 4 °C/min to 320 °C, hold 10 min



Compound Proof of Identity

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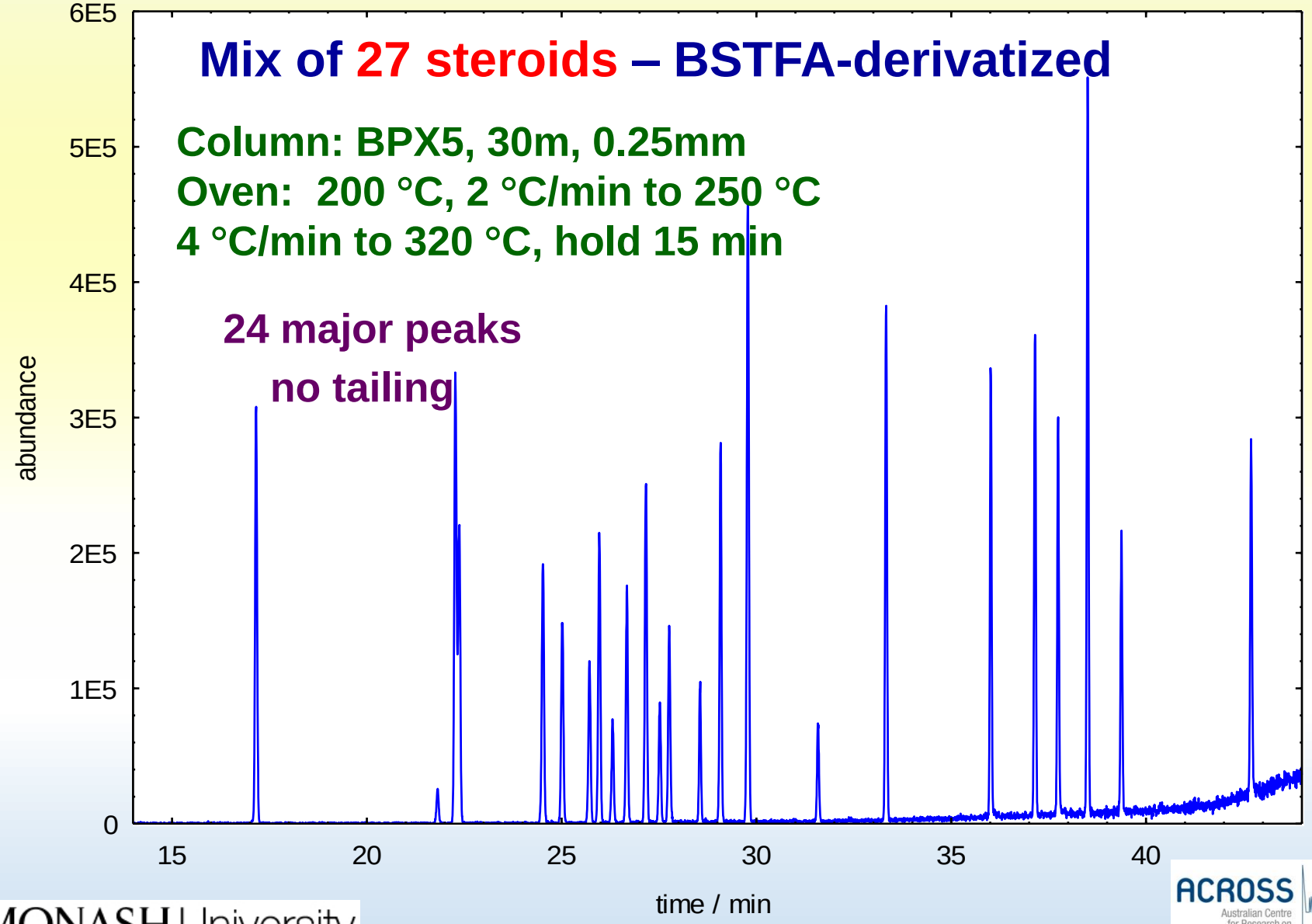
BSTFA-DERIVATIZED STEROIDS ON 1D GC/MS



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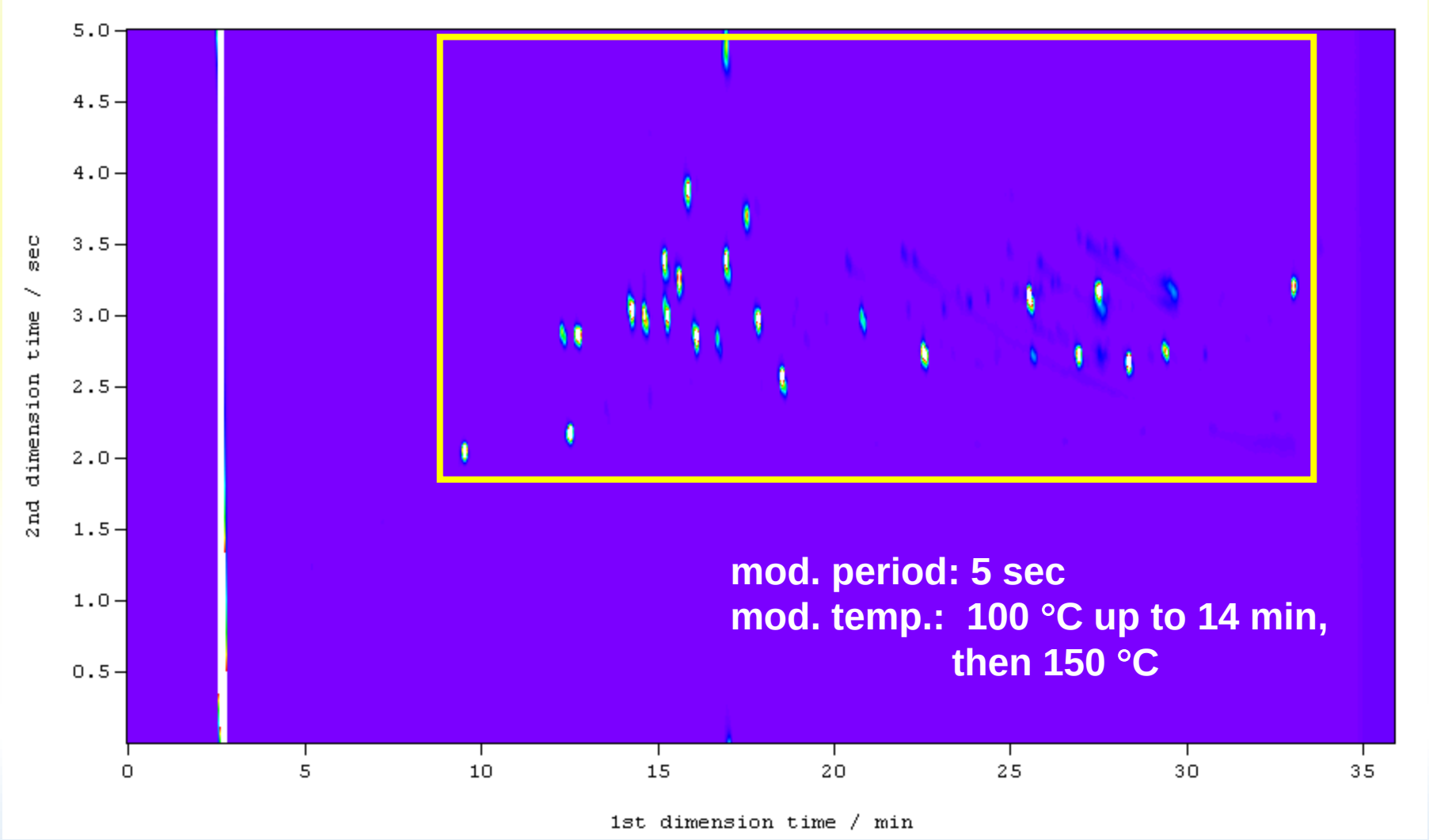
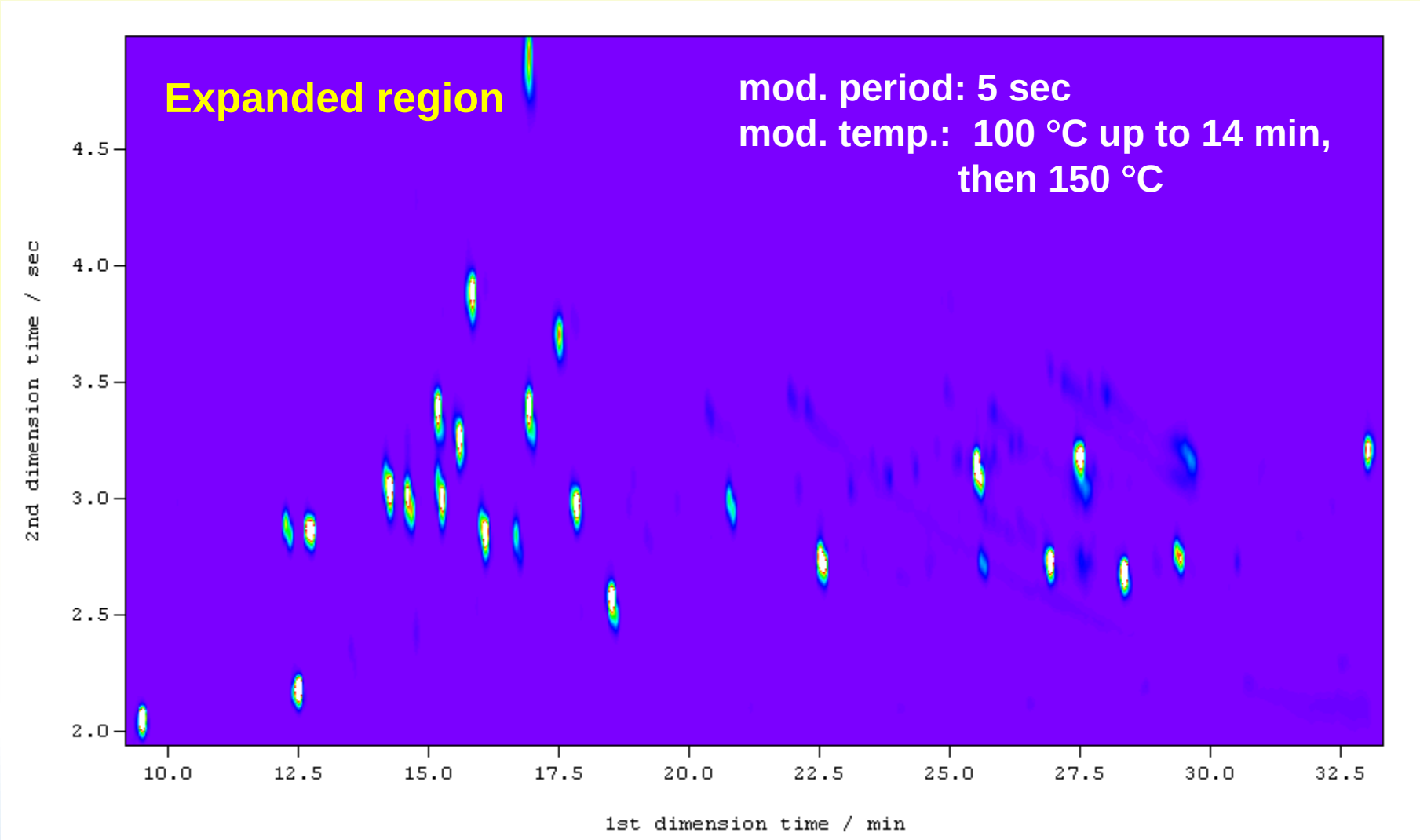
BSTFA-DERIVATIZED STEROIDS: GCxGC/FID



BSTFA-DERIVATIZED STEROIDS: GCxGC/FID



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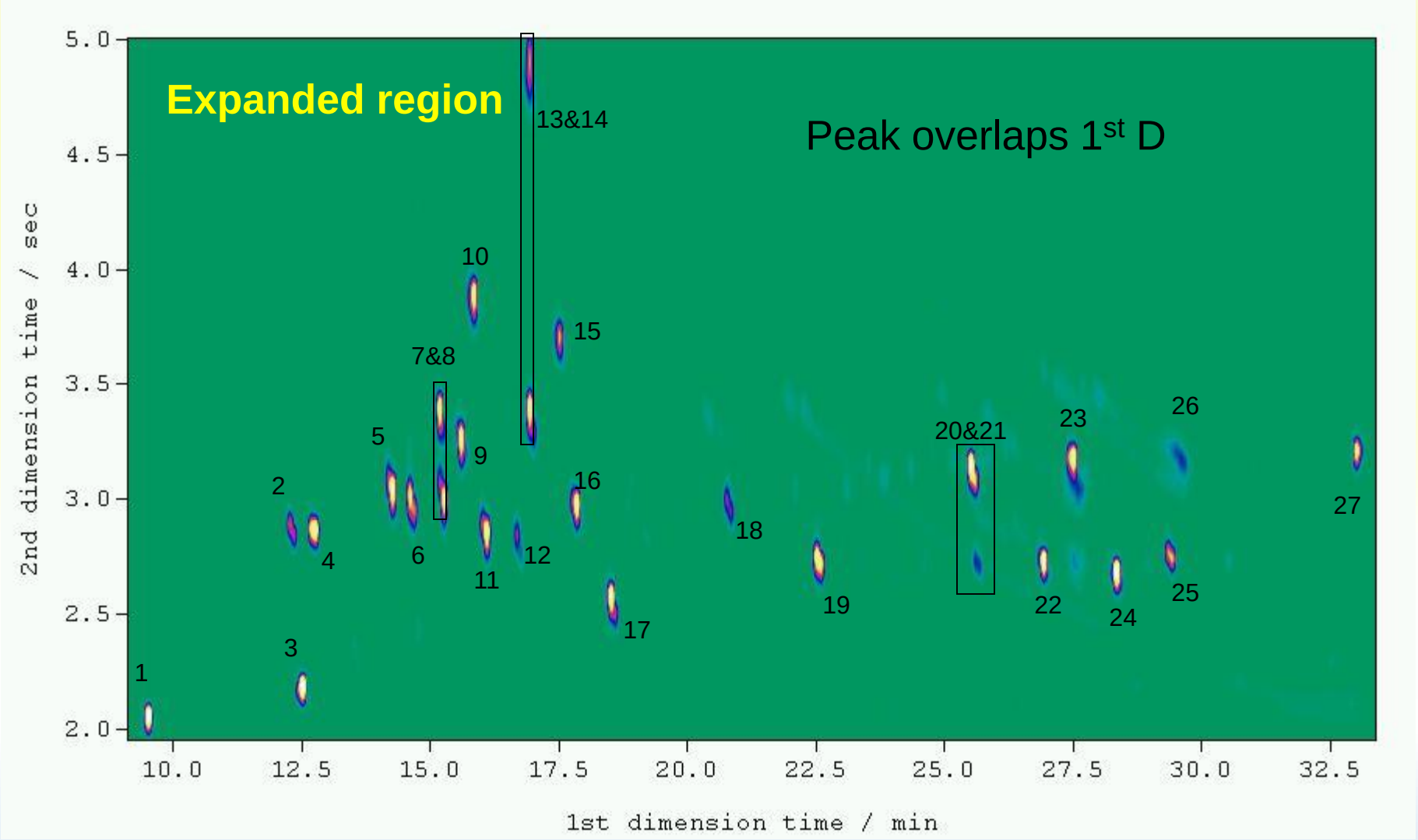
BSTFA-DERIVATIZED STEROIDS: GCxGC/FID



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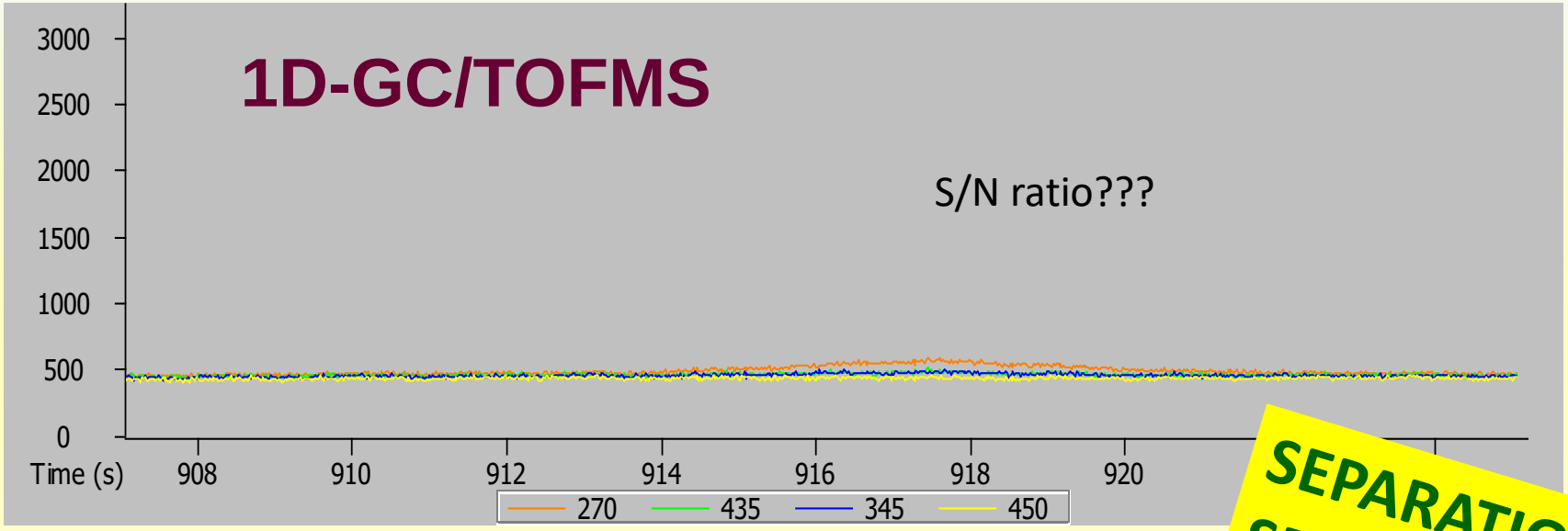

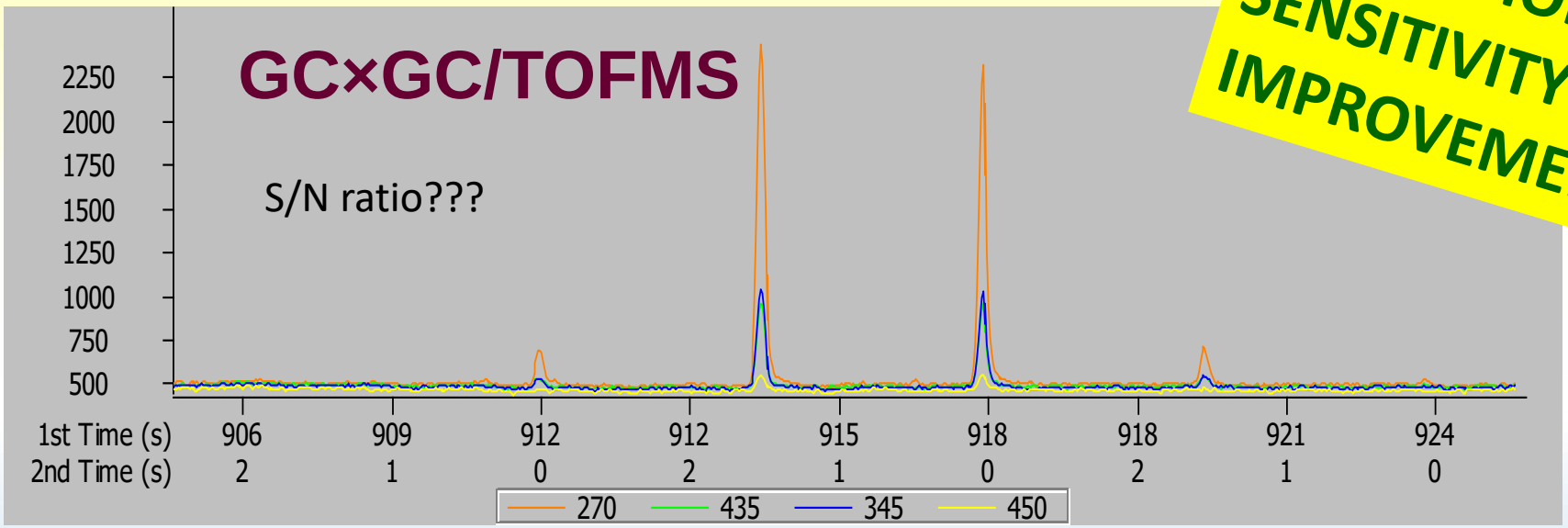

SEPARATION & SENSITIVITY IMPROVEMENT!

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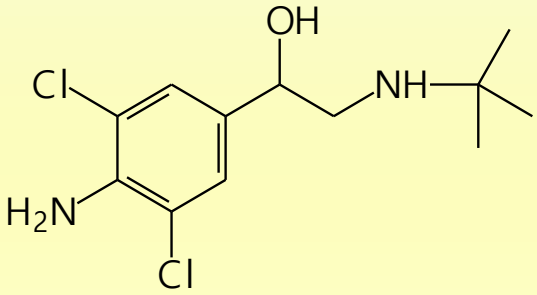
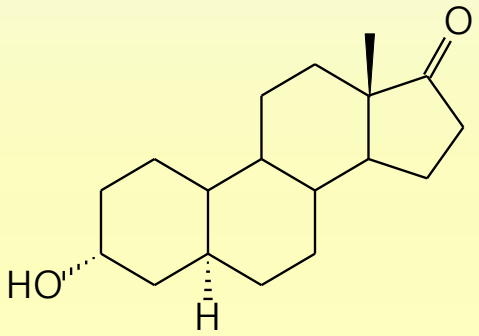
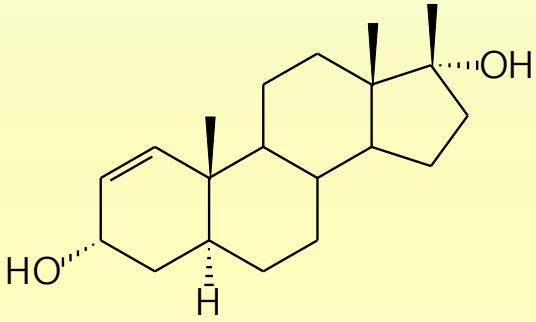
The substances: WADA (World Anti-Doping Agency) key anabolic agents



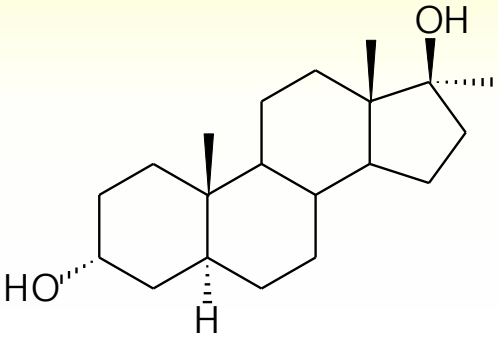
1. Clenbuterol



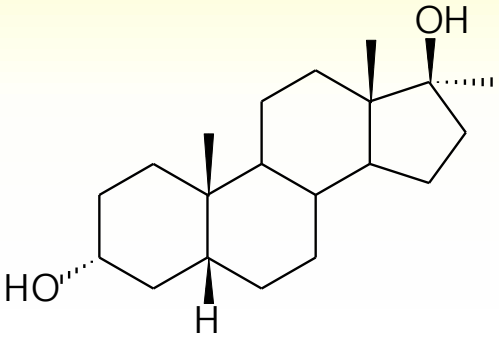
2. 19-norandrosterone



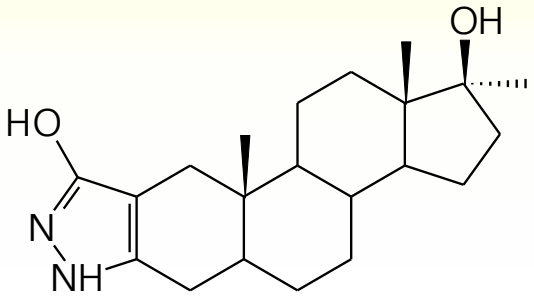
3. Epimethendiol



4. Methyltestosterone metabolite M1



5. Methyltestosterone metabolite M2



6. 3'hydroxystanozolol

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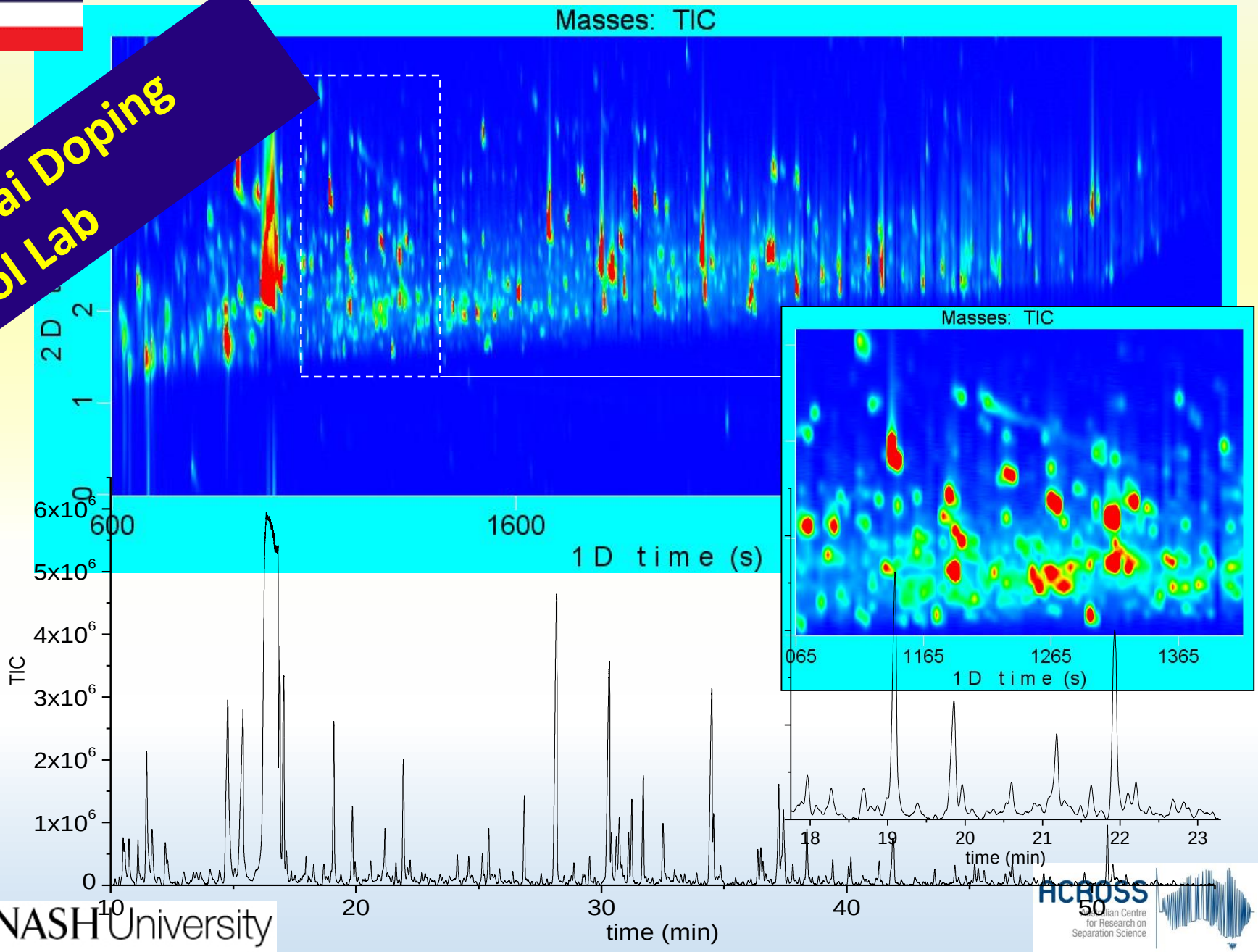
WADA Urine Positive Control (UPC), spike 5 ng/mL

With Thai Doping Control Lab



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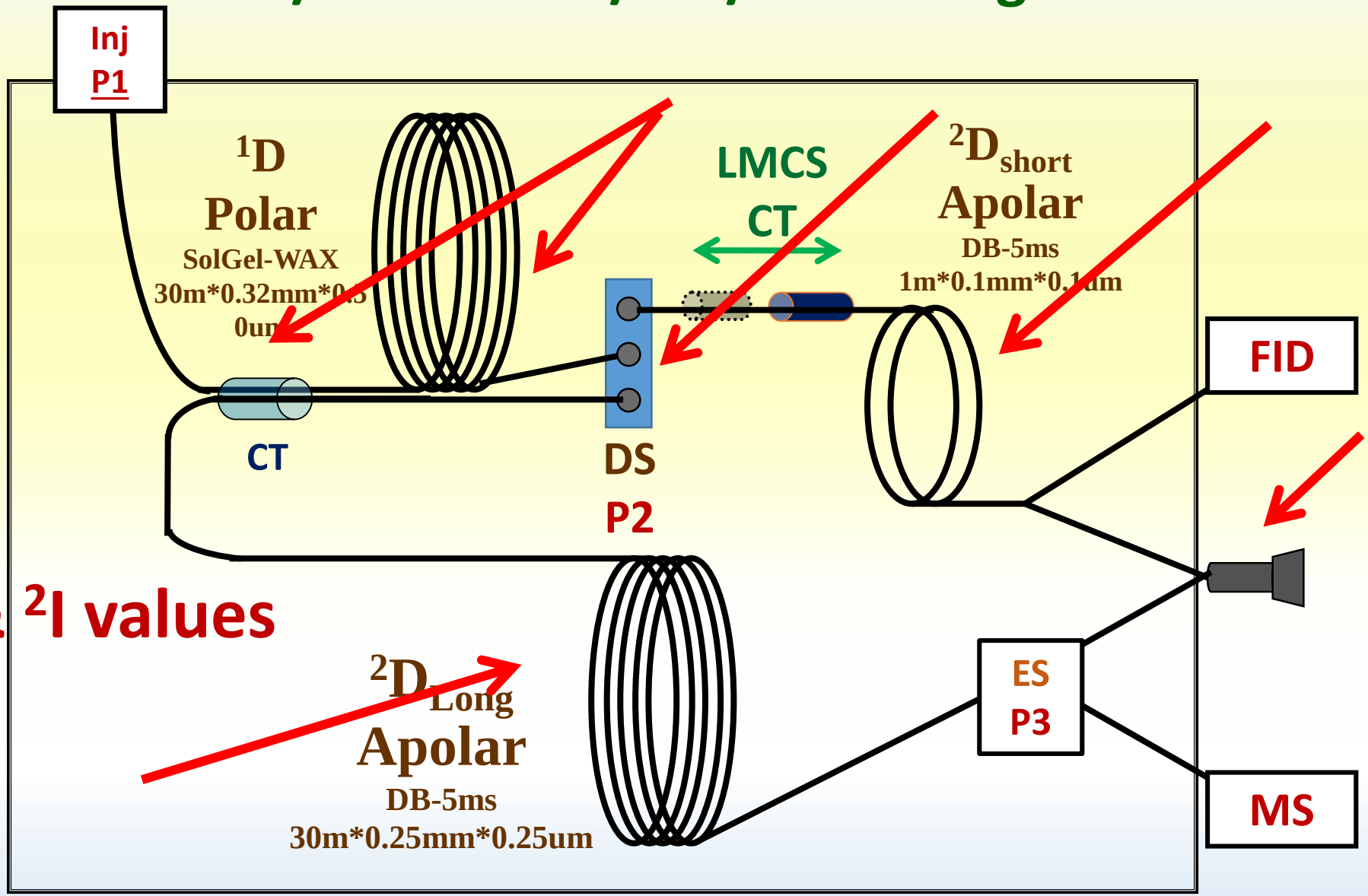
MDGC/GC×GC – O/FID/MS Configuration

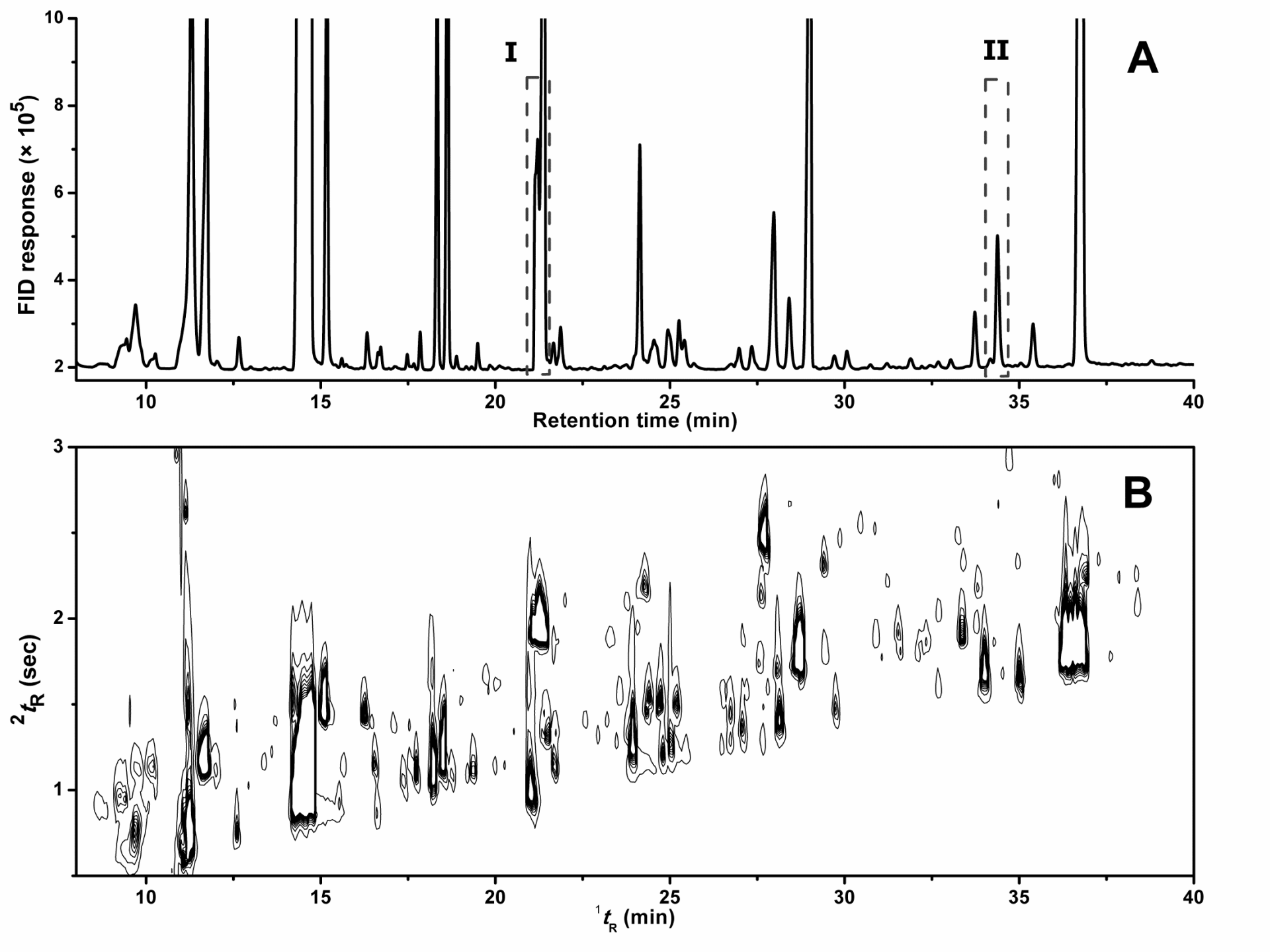


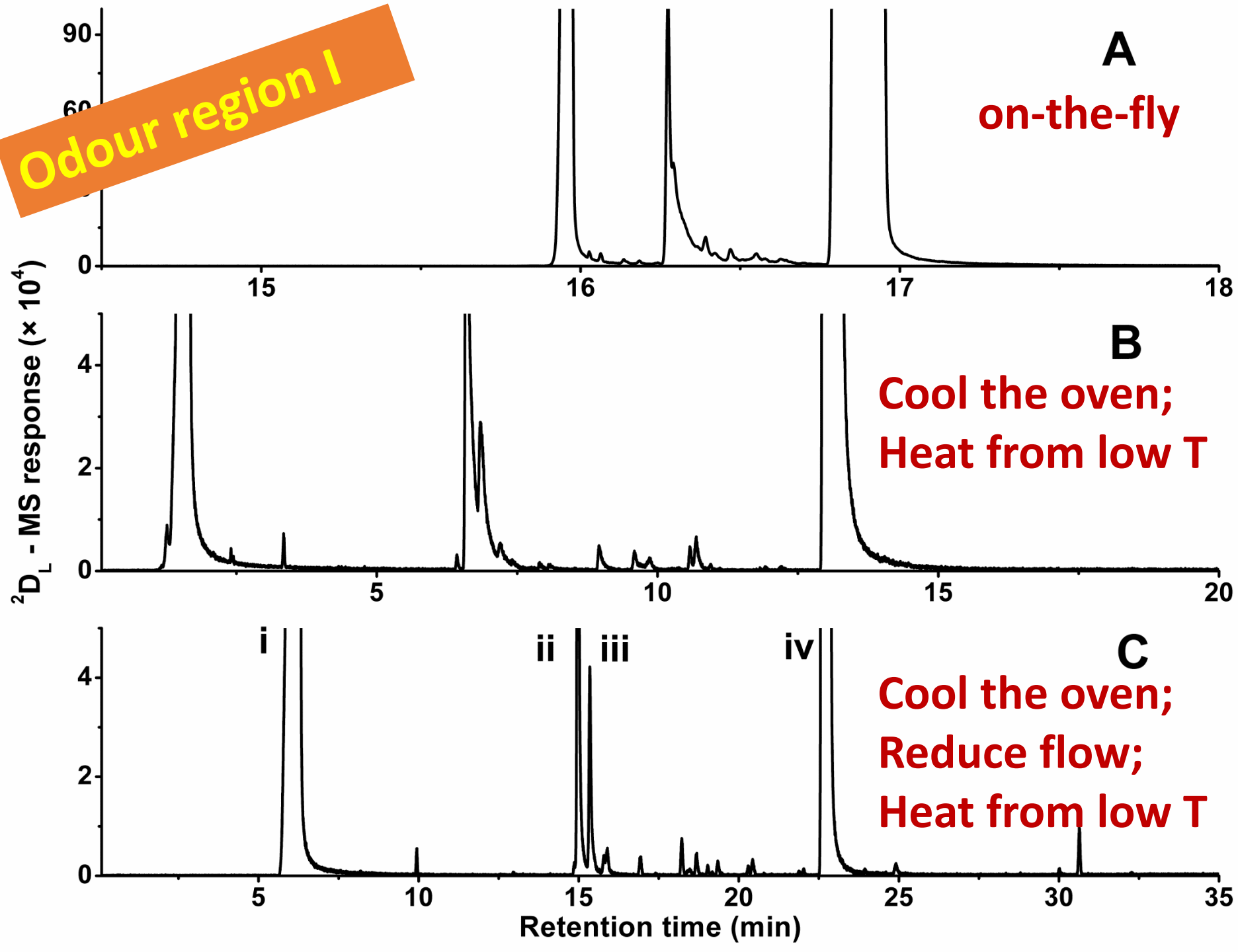
S-T Chin et al. *Anal. Chem.* 84 (21) (2012) 9154

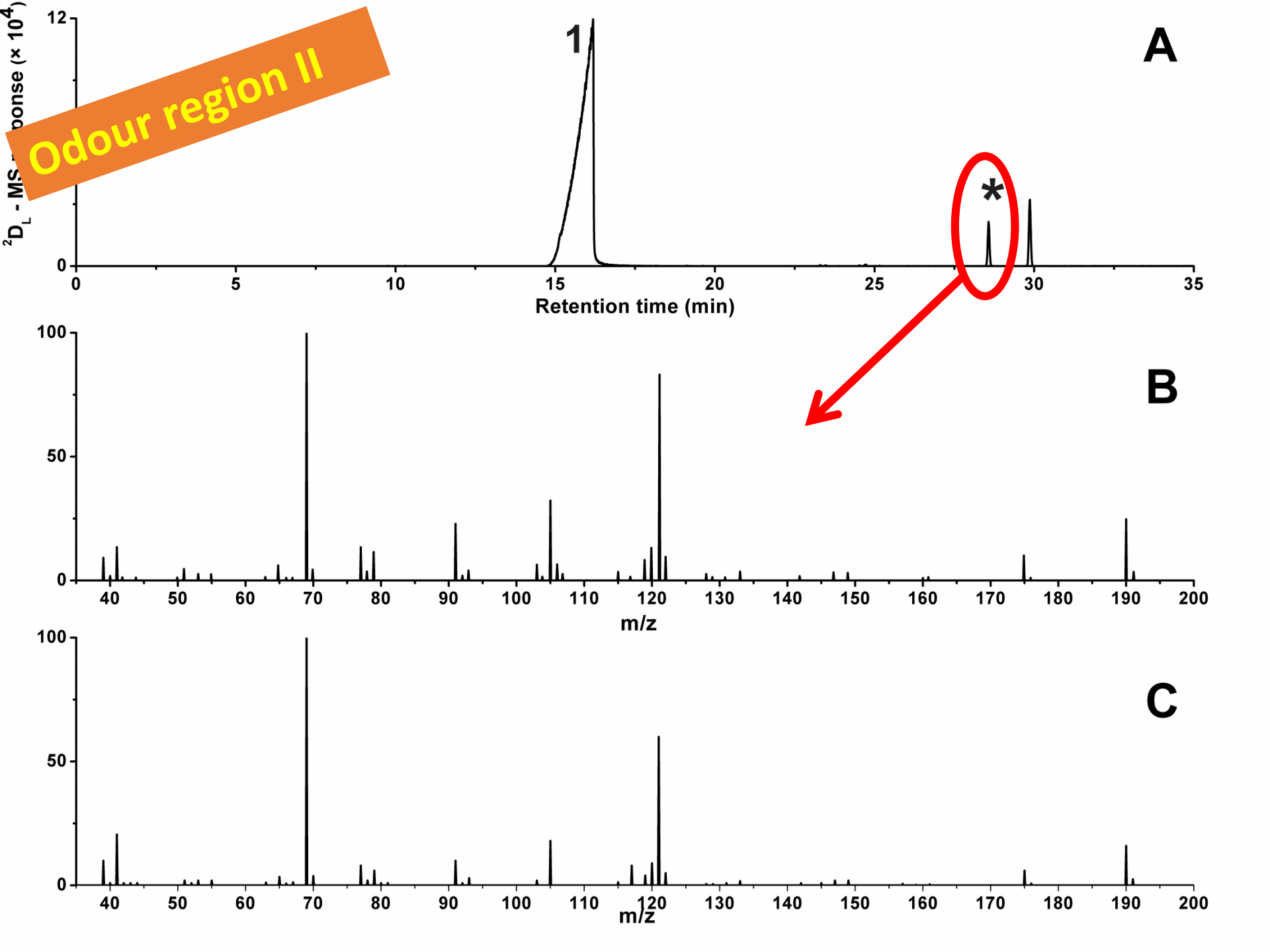
Method protocol:

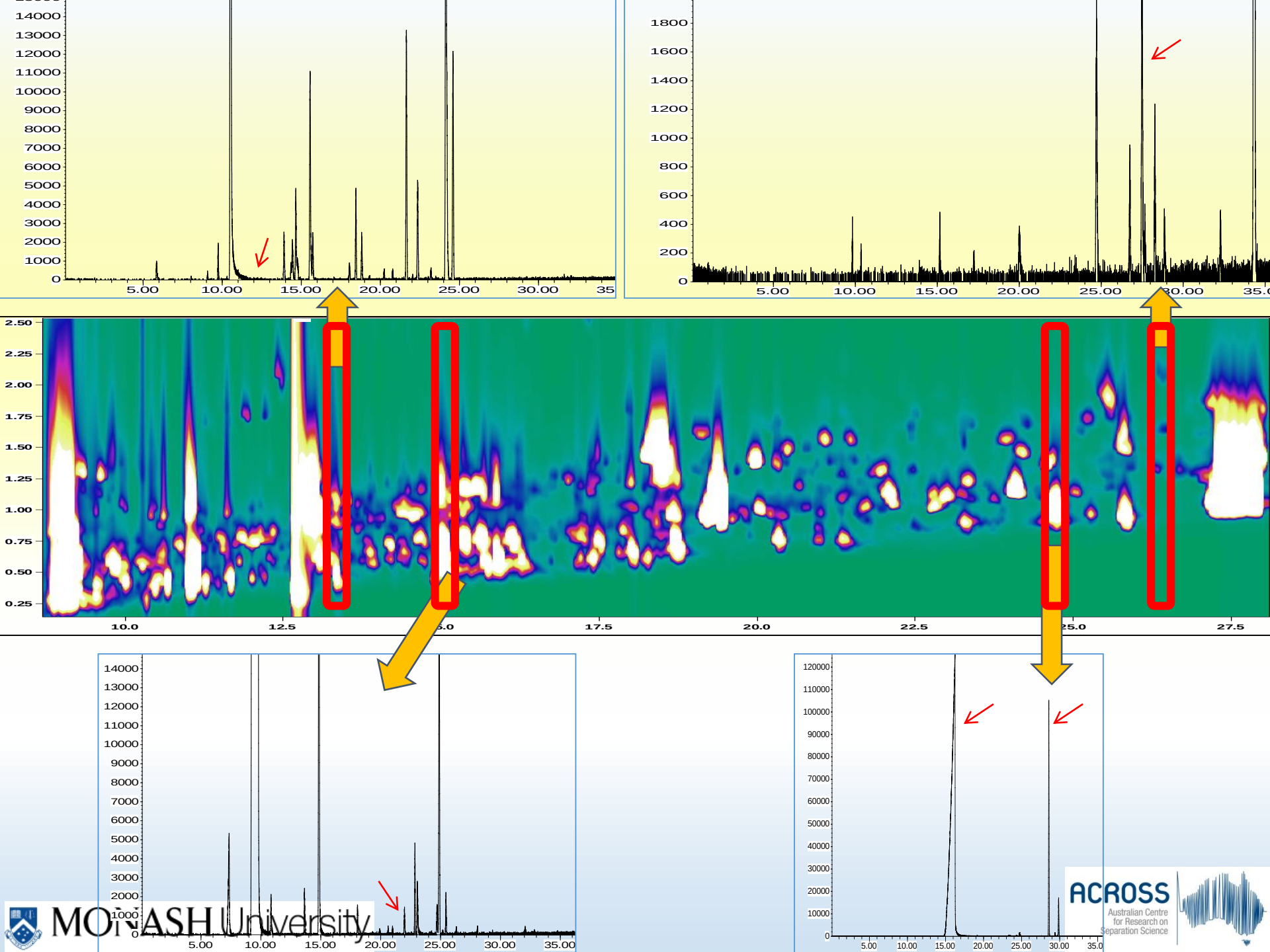
- SPME of Wine / Herbs / Spices / Coffee
- Multiple SPME extraction; cryofocus at ^{1}D
- GC-O to define total odour regions
- GC×GC-FID using $^{2}D_{S}$ to profile all compounds
- Heart-cut target regions to $^{2}D_{L}$ and cryofocus
- Cool oven; reduce carrier flow velocity
- Release target compounds
- Obtain parallel O – MS data


RYMILL
COONAWARRA
E= mc²
A classic alliance of Cabernet Sauvignon, Merlot and Cabernet
Vintage 2001
750ML
Wine – an Energy Drink!
MOUNT PLEASANT
PHILIP
HUNTER VALLEY SHIRAZ
WINE OF AUSTRALIA
CELLAR 2003 RELEASE
VINTAGE


A
I
II
FID response (× 10^5)
Retention time (min)
B
2t_R (sec)
1t_R (min)


Odour region I
A
on-the-fly
B
Cool the oven;
Heat from low T
C
Cool the oven;
Reduce flow;
Heat from low T
i
ii
iii
iv
^2D_L - MS response (× 10^4)
Retention time (min)


Odour region II
A
1
*
Retention time (min)
B
m/z
C
m/z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We have travelled towards s… resolut… chromat…

Are we there yet?

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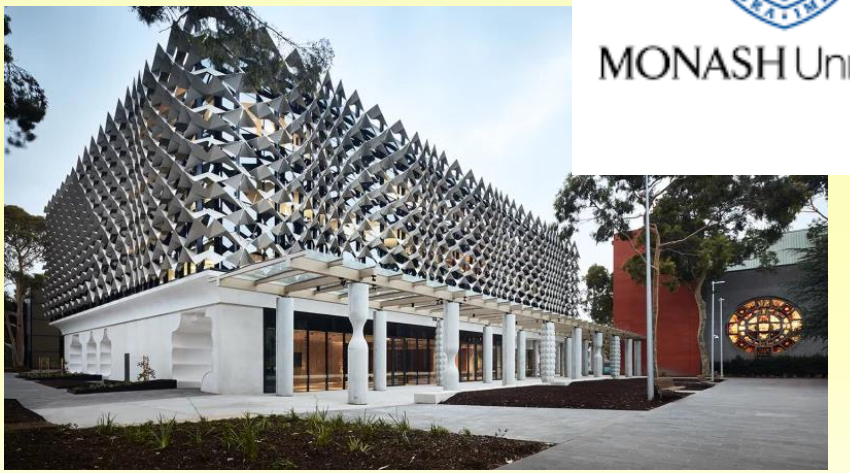

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University

Campuses:
Clayton
Caulfield
Parkville
Peninsula
Malaysia
SEU – Monash, China
Prato Centre, Italy
Indonesia
IITB Monash Academy

Faculty of Science & School of Chemistry @ Monash

Dean of Science:

Prof Jordan Nash. High energy / particle physics

1700 publications; h-index 132

(Chemistry; Physics & Astronomy; Mathematics; Biological Sciences; Earth, Atmosphere & Environment; School of Science (Malaysia)

Head of Chemistry:

Prof Phil Andrews. Inorganic Chemist

180 publications; h-index 31

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Recent Initiatives in Chemistry @ Monash

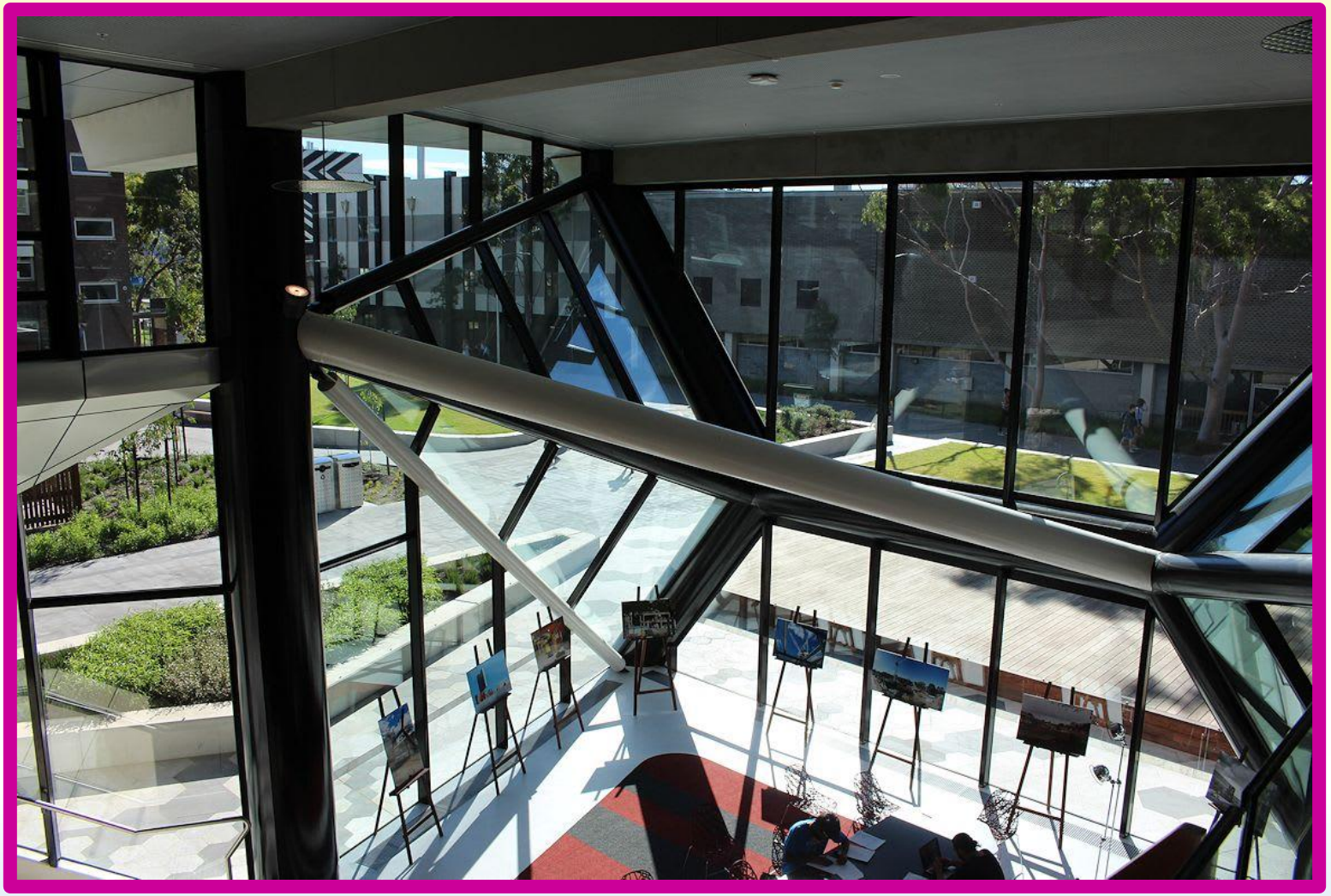
School of Chemistry …

- Very early Australian Research Council (ARC) Centre of Excellence funding for
  Centre for Green Chemistry ~ 15 years ago.
  Prof W Jackson & Prof C Raston,
  Then Prof M Hearn Director. Major application for a dedicated Green Chemical Futures
- Established credentials in Green Chemistry
- Prof Paul Anastas; Prof Martyn Poliakoff collaborators

Recent Initiatives in Chemistry @ Monash

School of Chemistry …

- Ranked #1 Chemistry Department in Australia
- International ranking top 30
- New Green Chemical Futures funding building – Chemistry and Chemical Engineering
- Strong success in ARC Competitive Discovery funding over the years; now increased interest in ARC Linkage (Industry) funding.



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Involvement in a range of recent funding initiatives:

- Monash Food Innovations
- ARC-Funded Industrial Training Centre in Green Chemistry & Sustainability, with local & International Businesses
- ARC-Funded Training Centre in Food, with local & International
- ARC-Funded Industrial Transformation Training Centre for Green Chemistry in Manufacturing
- ARC Centre of Excellence for Electromaterials Science


Where is
Your Flag??

GC×GC & MDGC still Rocks

END

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.. when you take the Road to Paradise, there is No Exit!