Fragrance Analysis by Using Selectable $^{1}D^{2}D$-SBSE-GCMS Technique

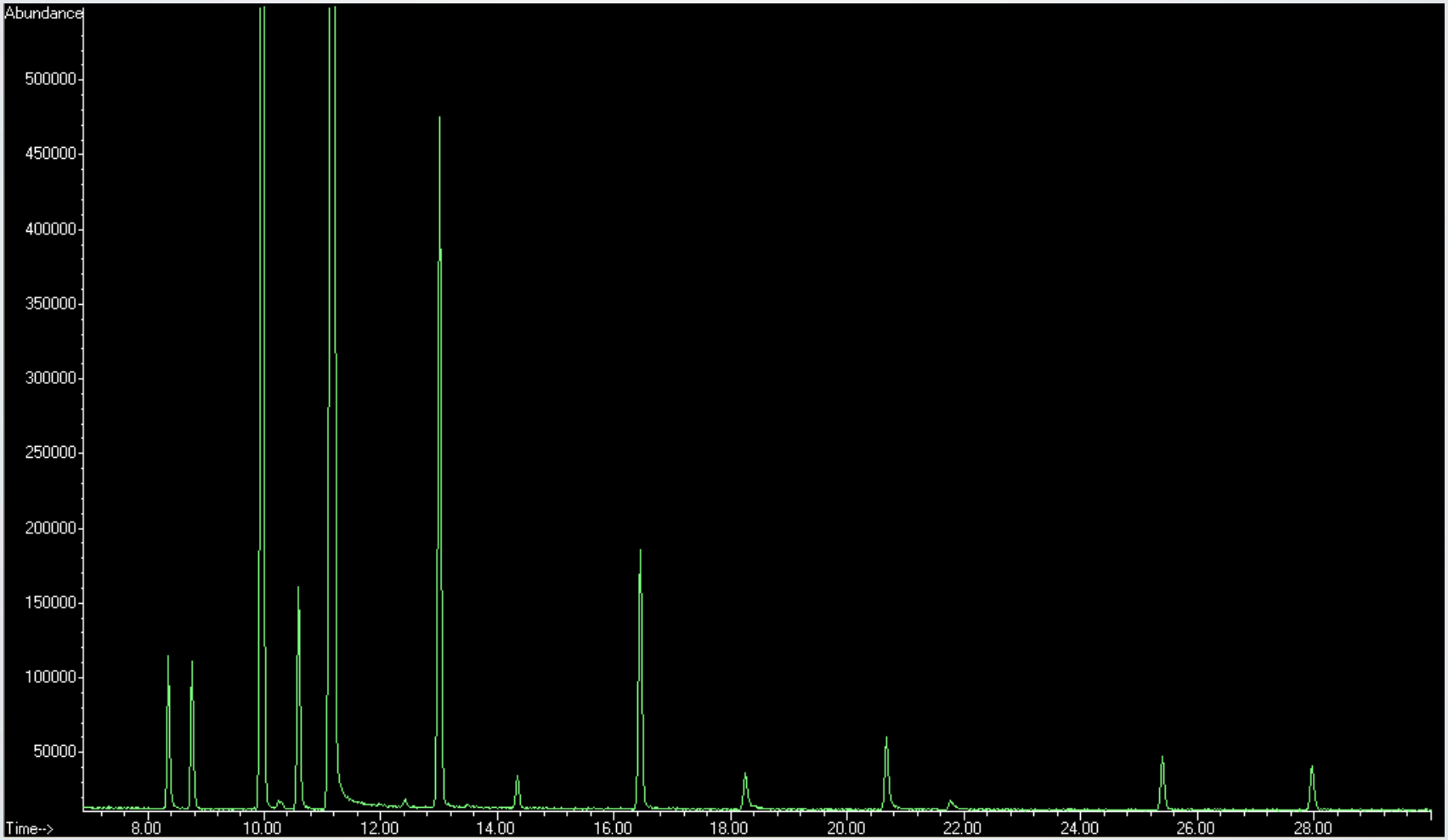
Khim-hui NG, PhD
Senior Manager – Analytical Services

01 Introduction

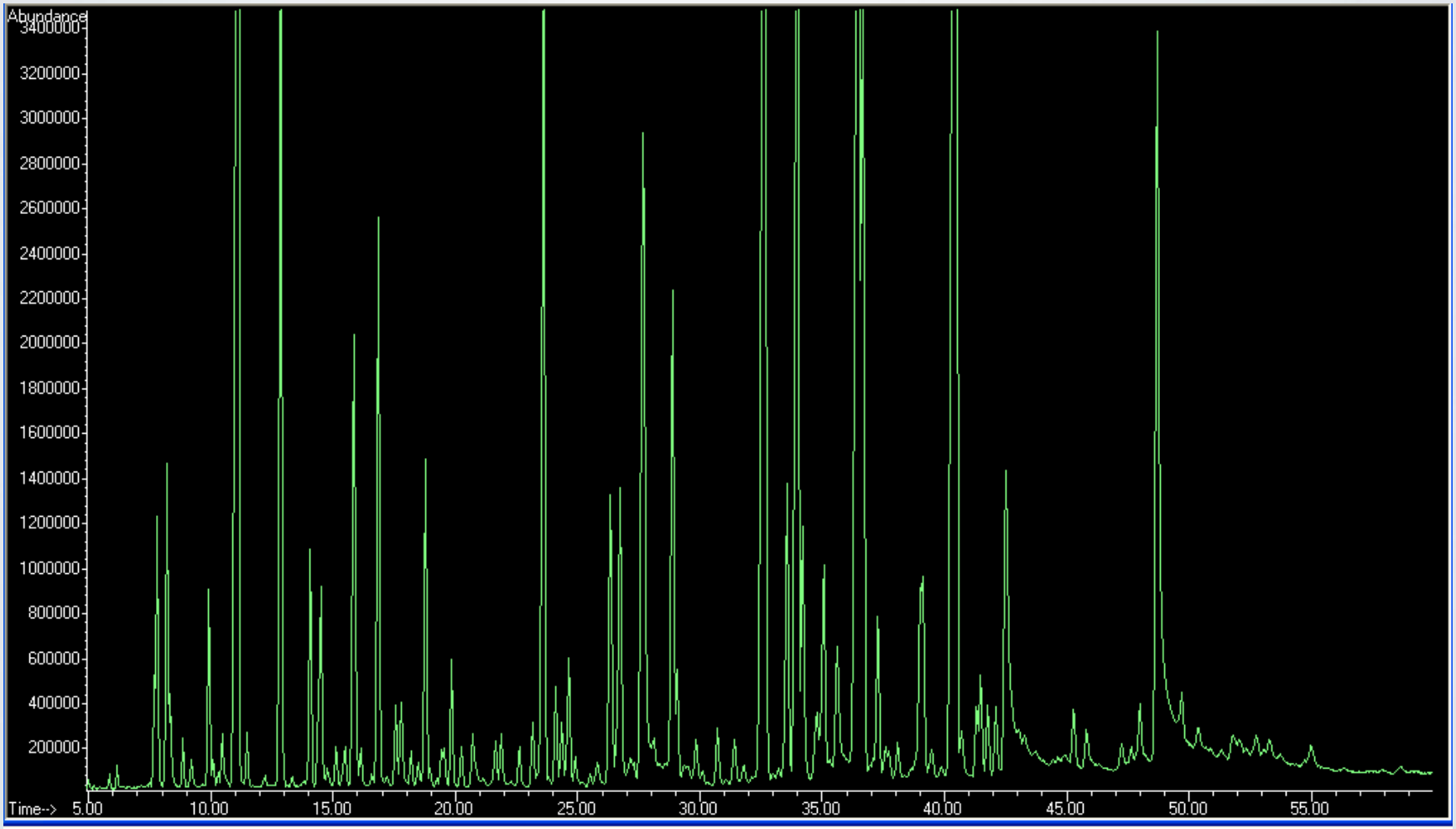
INTRODUCTION

- GC-MS is a widely used technique in fragrance analysis – volatiles
- Challenges in the analyses of perfumes and essential oils
  - Separation of co-elution compounds
- Enhancement in separation of compounds is needed – Multi-dimensional GC-MS
  - ^{2}D comprehensive GC (GC X GC) – total profiling
  - Conventional heart-cutting ^{2}D GC – target analysis

INTRODUCTION



INTRODUCTION



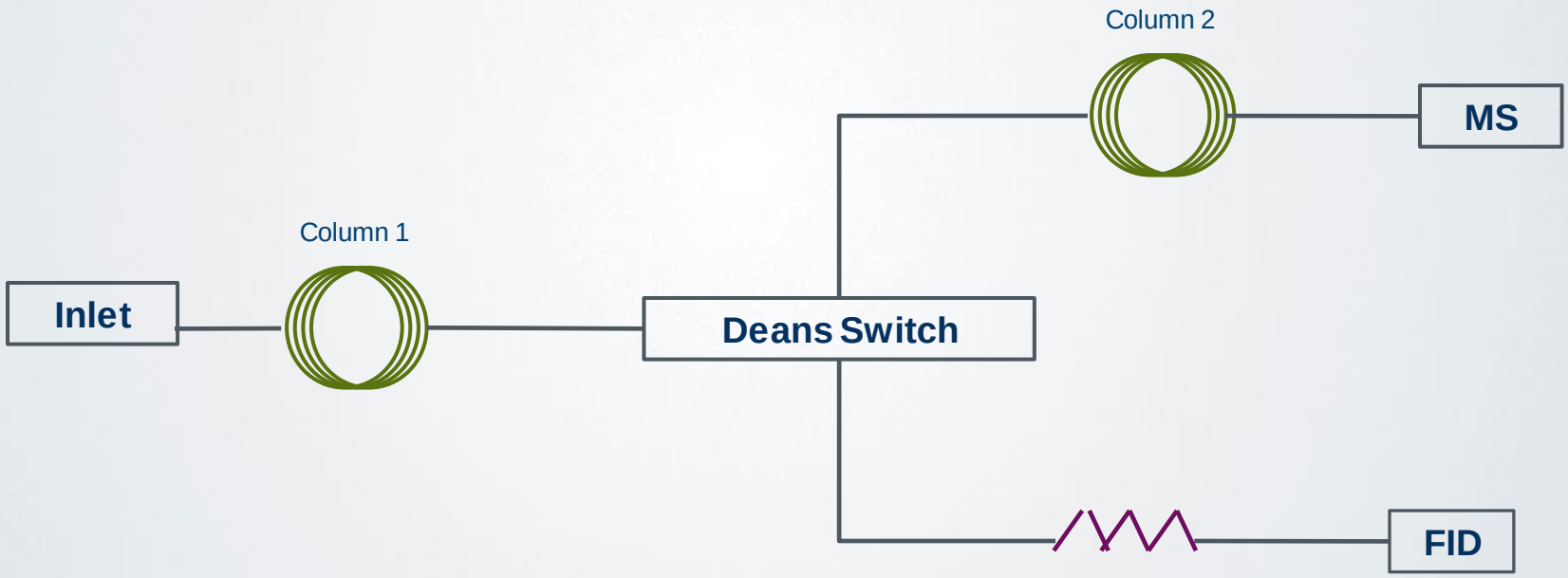
Firmenich

Heart-cutting ^{2}D GC technique

- Separation of co-elution compounds in ^{1}D analysis
  - Complexity in identification
  - Perplexity in olfactive detection
- Conventional heart-cutting ^{2}D GC configuration
  - Two individual GC for independent oven programming
  - Two capillary columns with different polarity
  - 1st GC – coupled with monitoring detector (FID)
  - 2nd GC – coupled with confirmation detector (MS)
  - Unable to perform routine ^{1}D confirmation analysis of unknowns

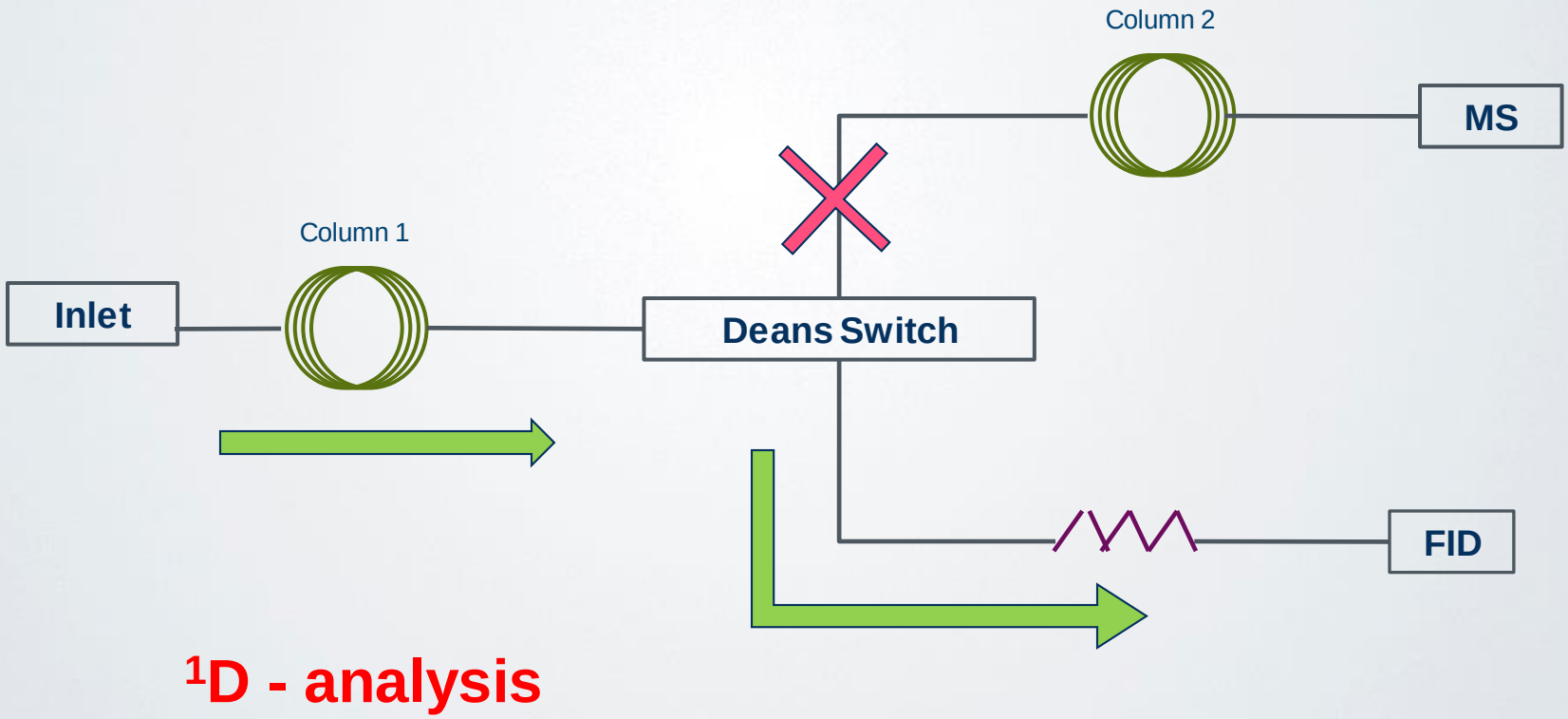
Heart-cutting ^{2}D GC technique

- Conventional heart-cutting ^{2}D GC configuration



Heart-cutting ^{2}D GC technique

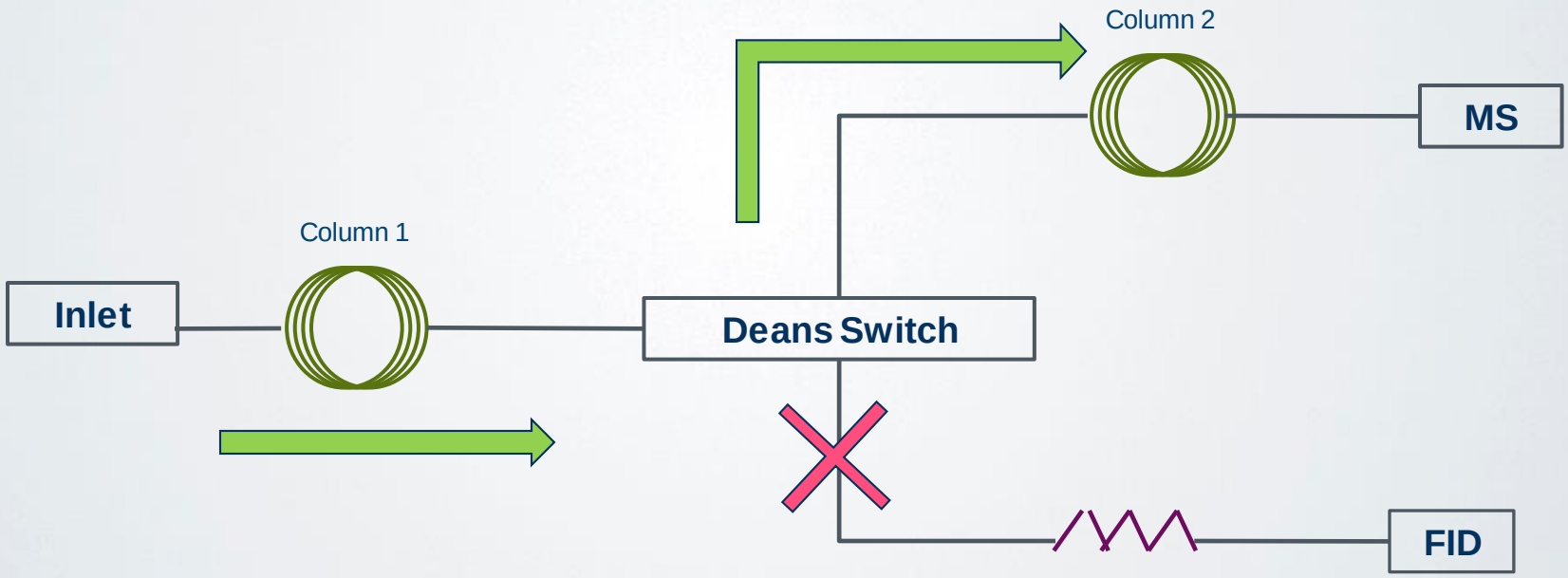
- Conventional heart-cutting ^{2}D GC configuration



Firmenich

Heart-cutting ^{2}D GC technique

- Conventional heart-cutting ^{2}D GC configuration



^{2}D - analysis

Firmenich

02

Selectable $^{1}D^{2}D$ GC-MS Technique

Firmenich

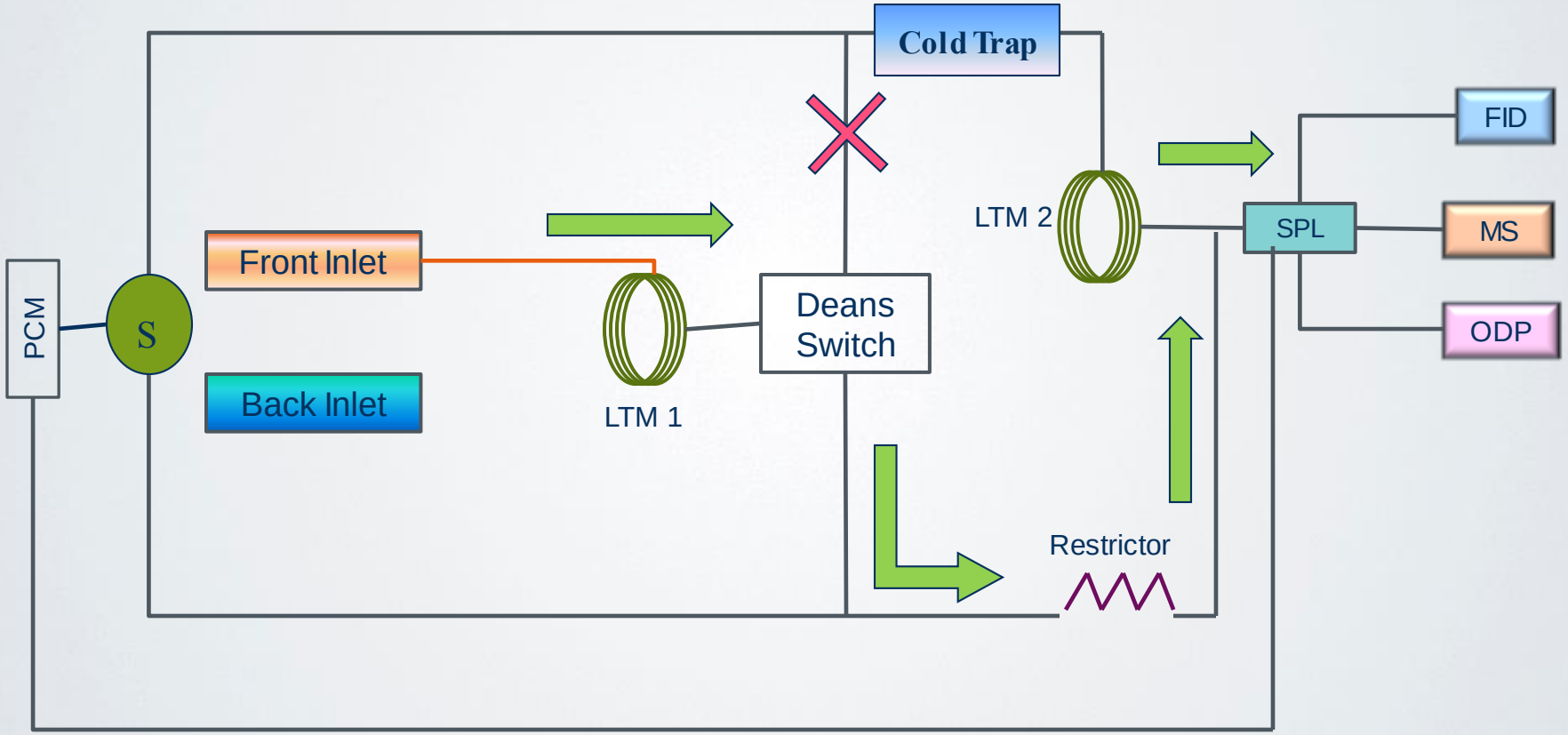
New approach of ^{2}D GC-MS technique

- New generation of Deans Switch
- Capillary flow technology
- Low thermal mass GC (LTM-GC)
- Advantages
  - Rapid heating and cooling
  - Independent temperature control
  - Low dead volume of Deans Switch
  - Inert
  - Electronic pressure control
- Developed by K. Sasamoto & N. Ochiai (Gerstel K.K.) in 2010

Selectable $^{1}D/^{2}D$ GC-MS-ODP System

Firmenich

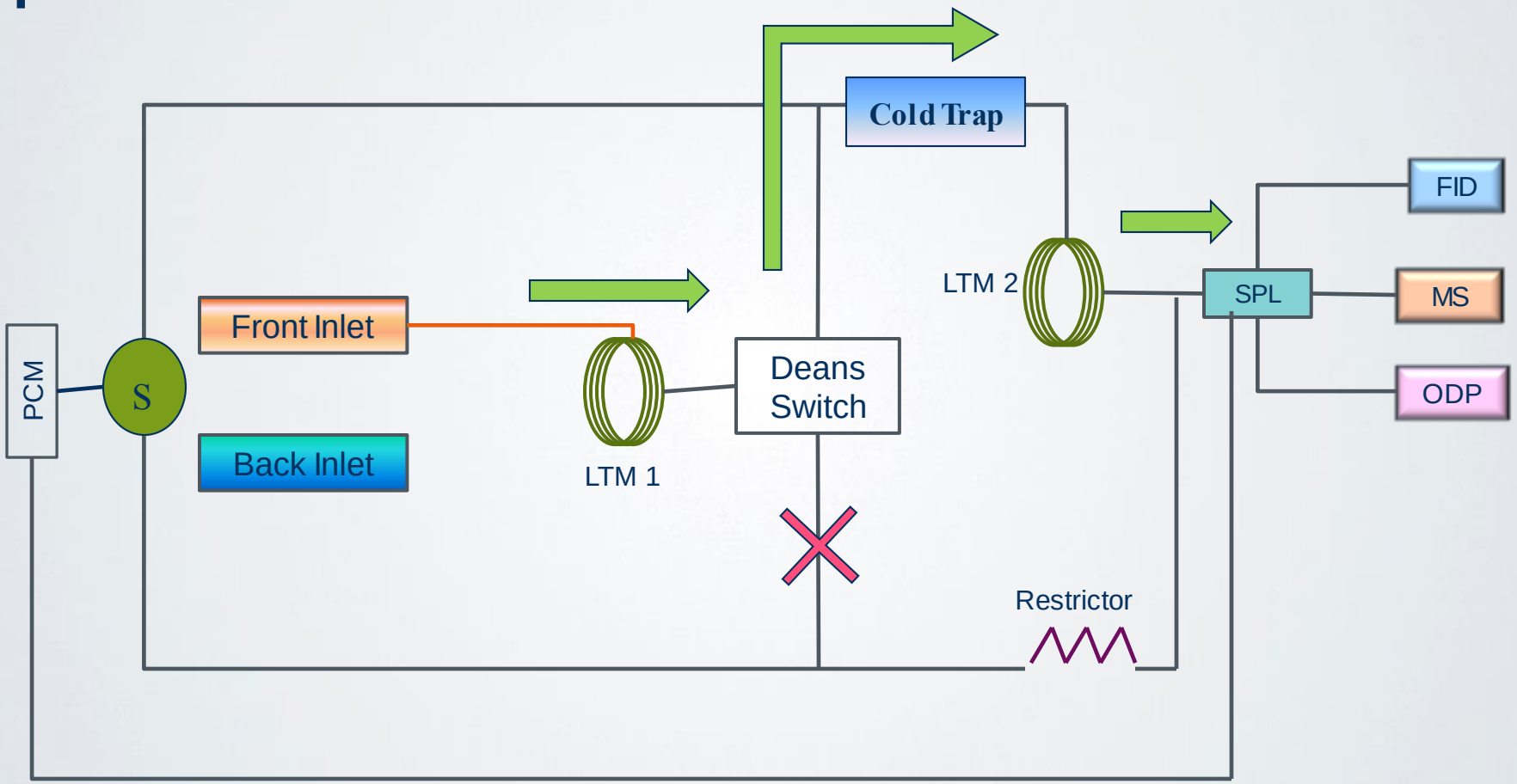
Selectable $^{1}D/^{2}D$ GC-MS-ODP System



^{1}D - analysis

Firmenich

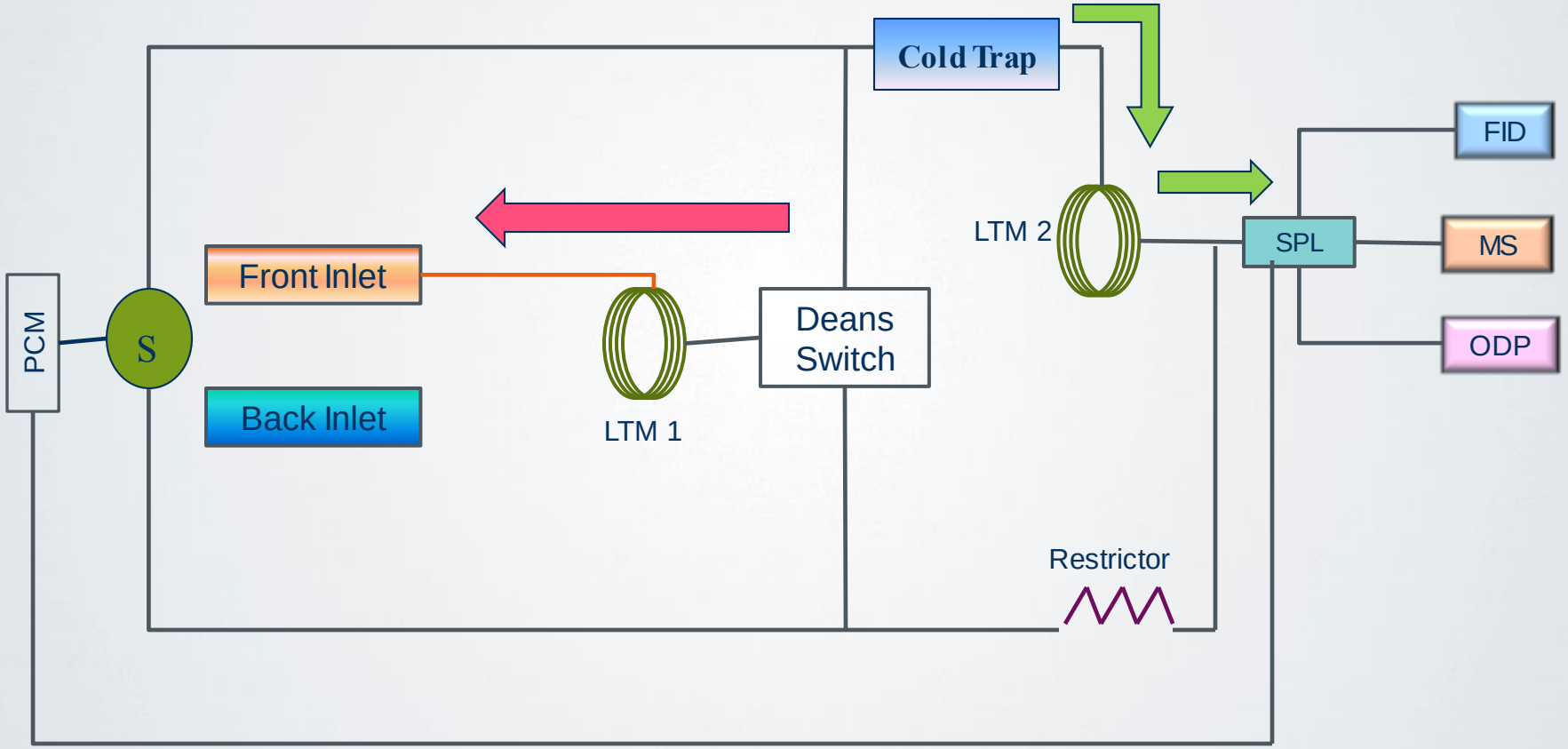
Selectable $^{1}D/^{2}D$ GC-MS-ODP System



Heart-cutting

Firmenich

Selectable $^{1}D/^{2}D$ GC-MS-ODP System



^{2}D - analysis

Firmenich

Selectable $^{1}D/^{2}D$ GC-MS-ODP System

03

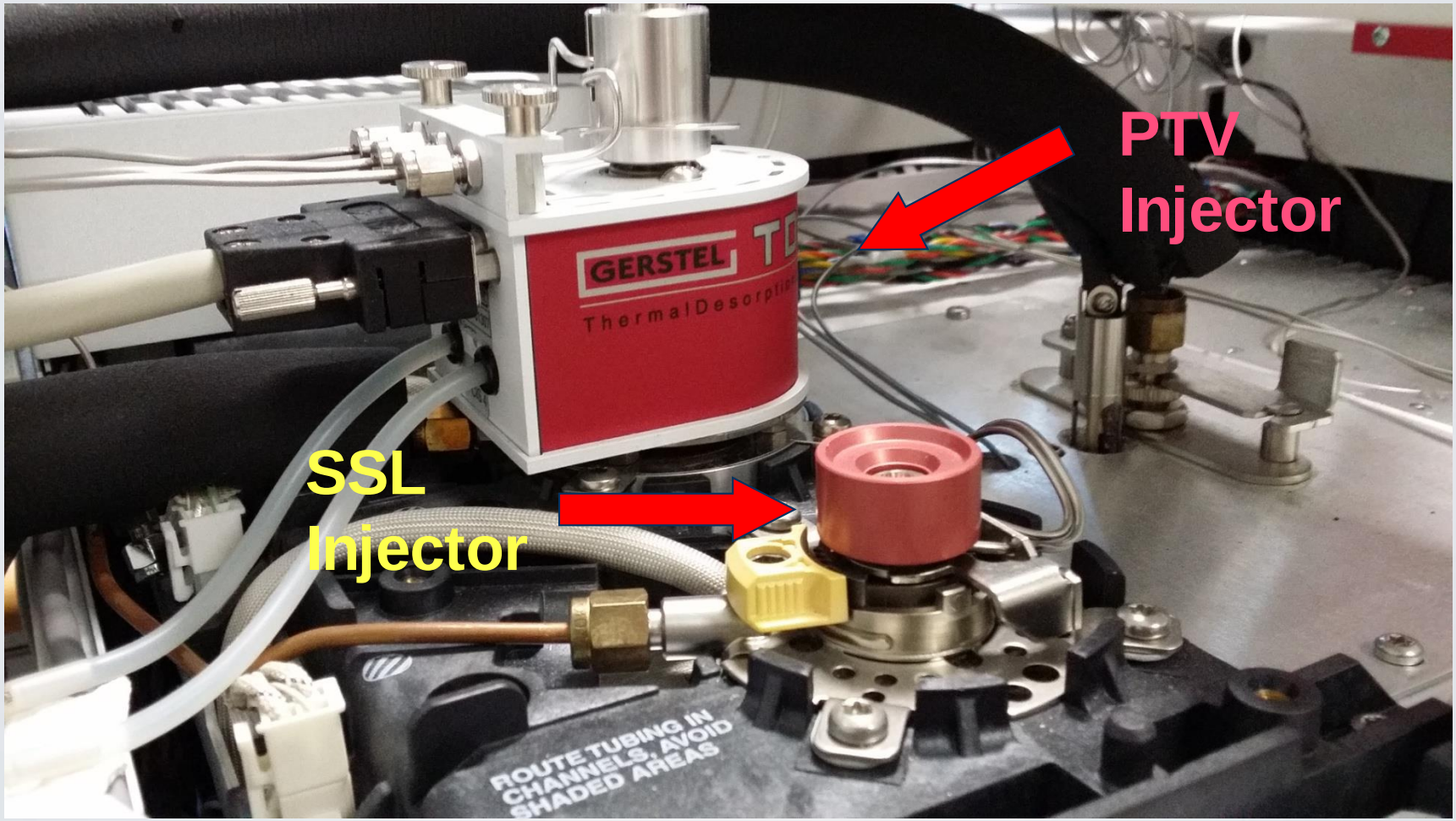
Dual-linked Injectors Set-up

Firmenich

Dual-linked Injectors Setup

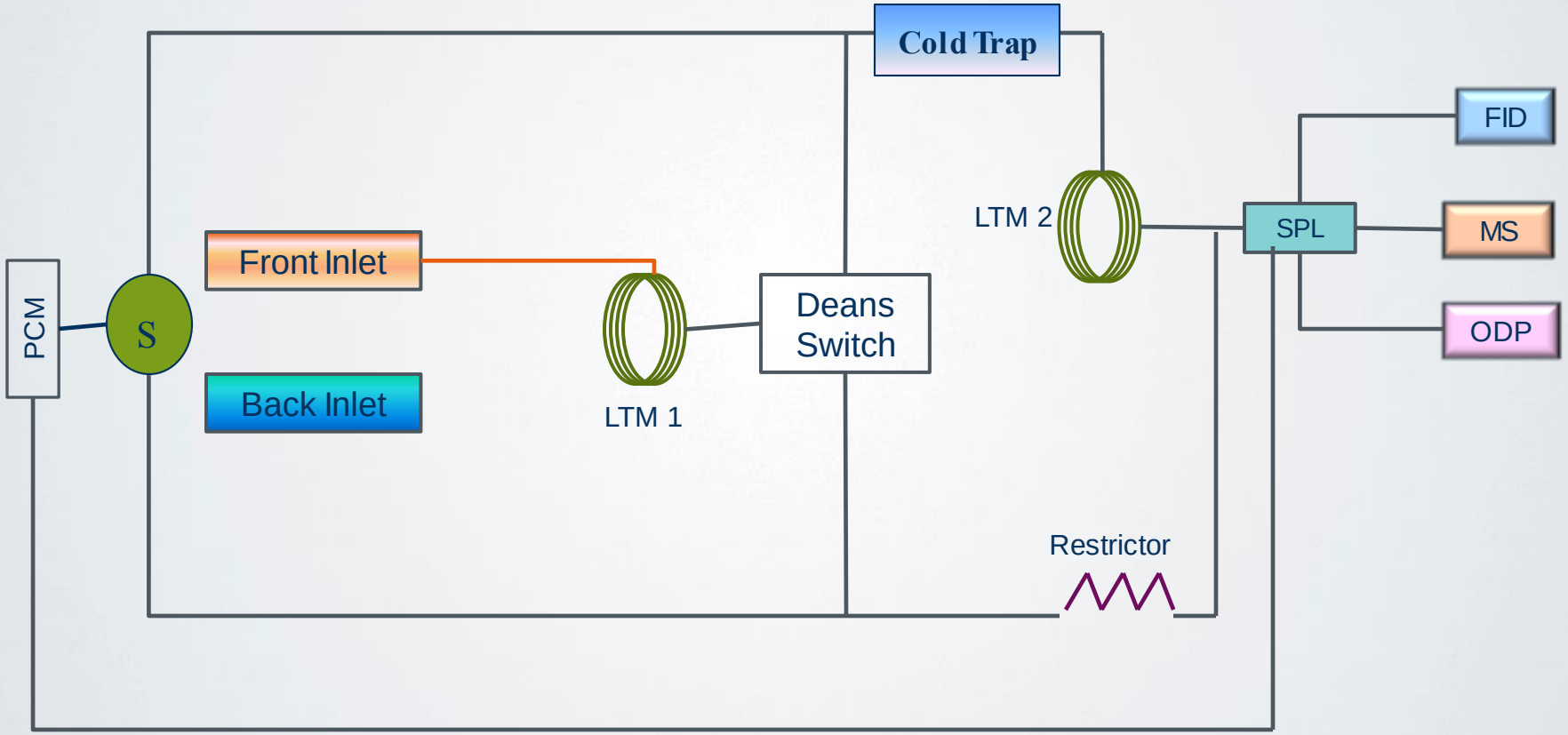
- Multiple sample extraction techniques are required in consumer products analysis for fragrance
  - Liquid extraction
  - Stir bar sorptive extraction (SBSE)
  - Solid phase microextraction (SPME)
  - Headspace sorptive extraction (HSSE)
  - Direct thermal desorption (DTE)
  - Dynamic Headspace (DHS)
- Different injector ports are needed
  - Split/Splitless injector – liquid injection
  - PTV injector – thermal desorption

Dual-linked Injectors Setup



Firmenich

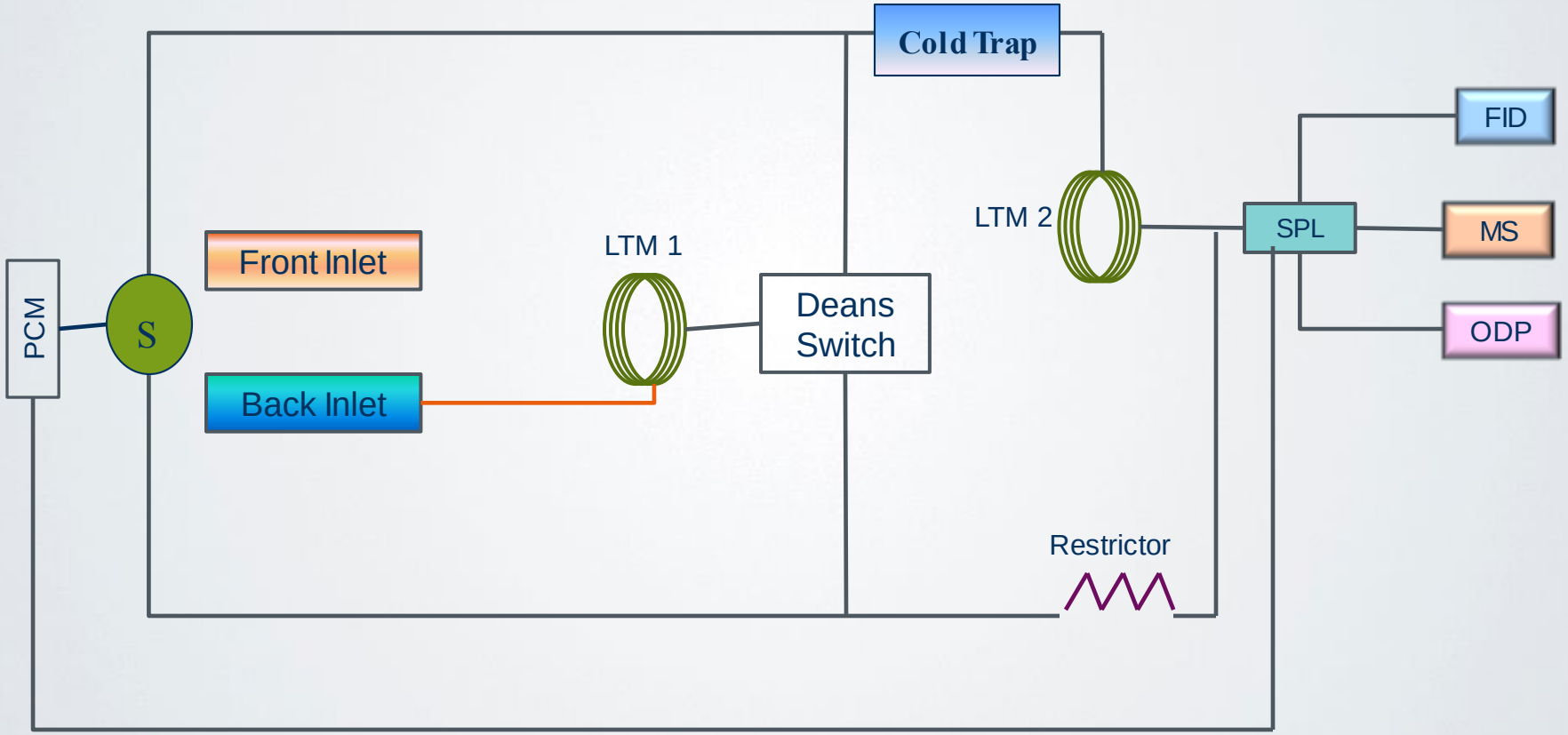
Dual-linked Injectors Setup



Injection via front inlet – Split/Splitless injector

Firmenich

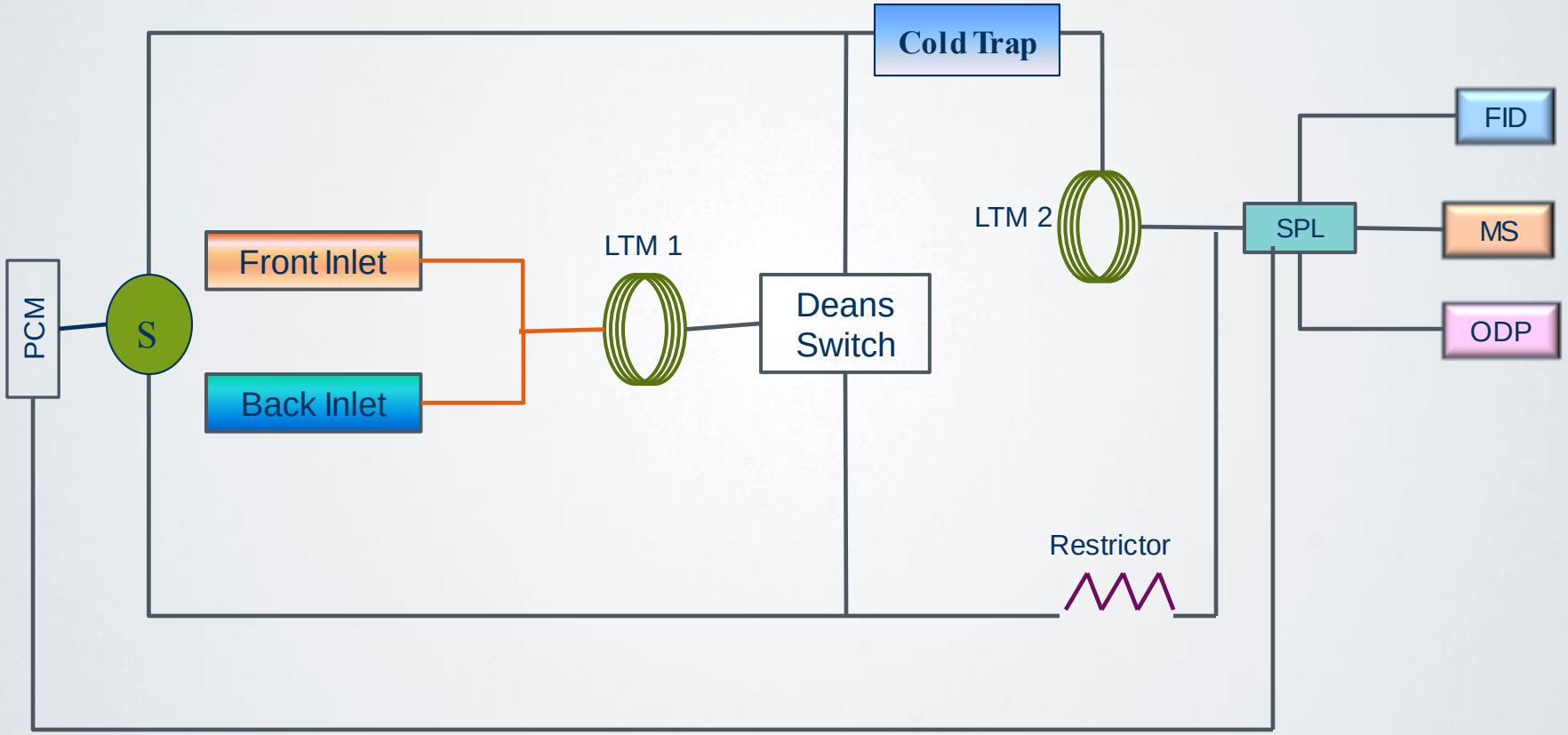
Dual-linked Injectors Setup



Injection via back inlet – TDU/CIS4

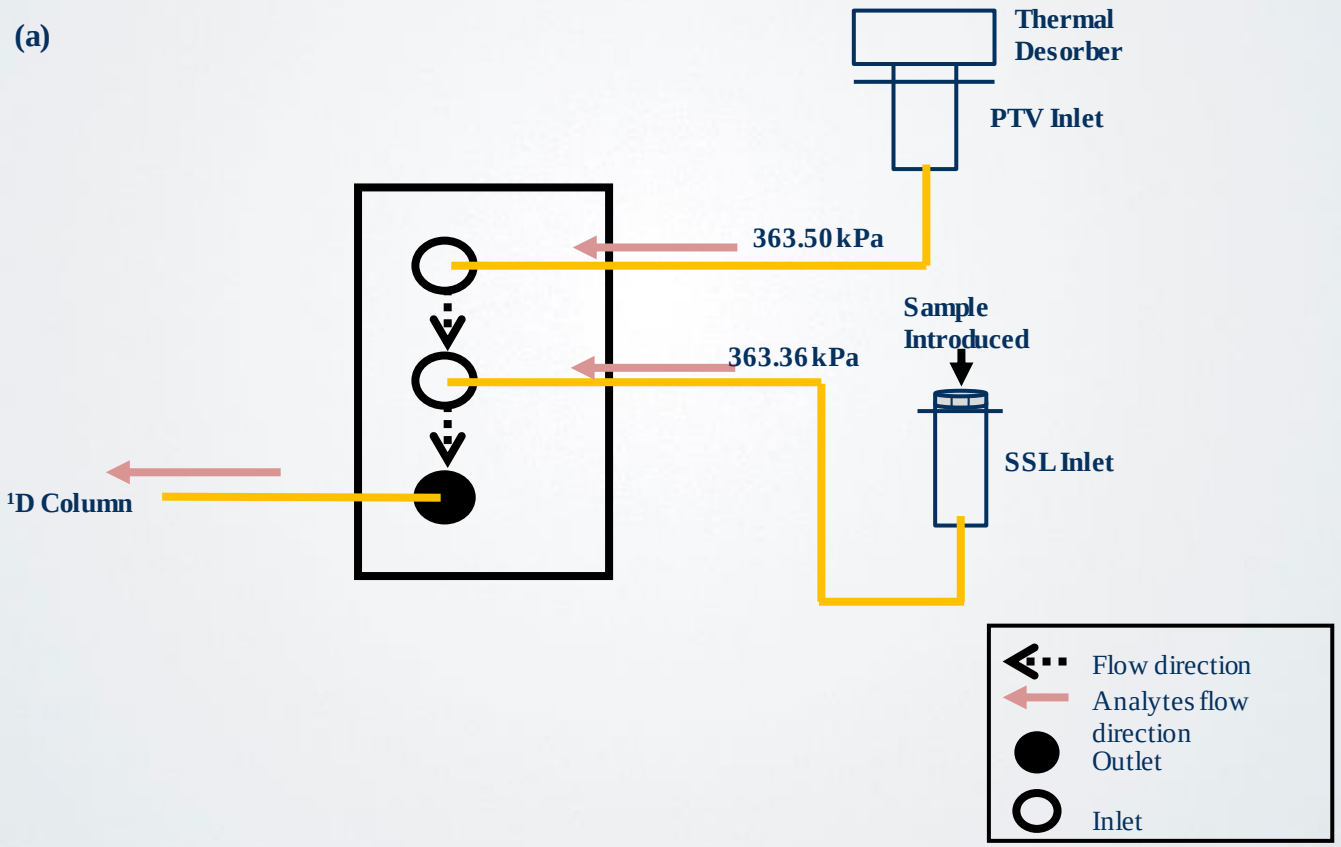
Firmenich

Dual-linked Injectors Setup



Selectable injection via front or back inlet

Dual-linked Injectors Setup

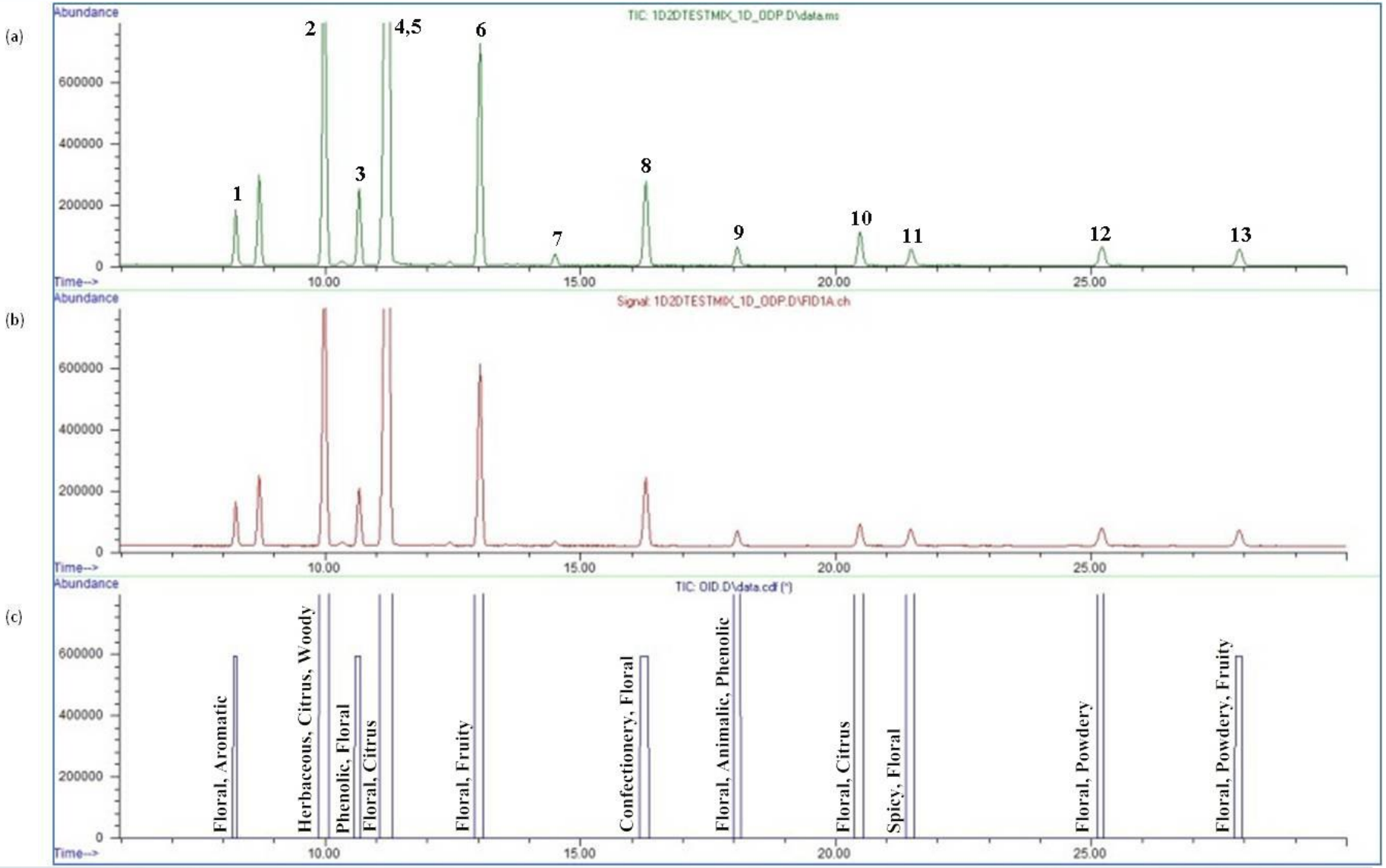


Firmenich

03

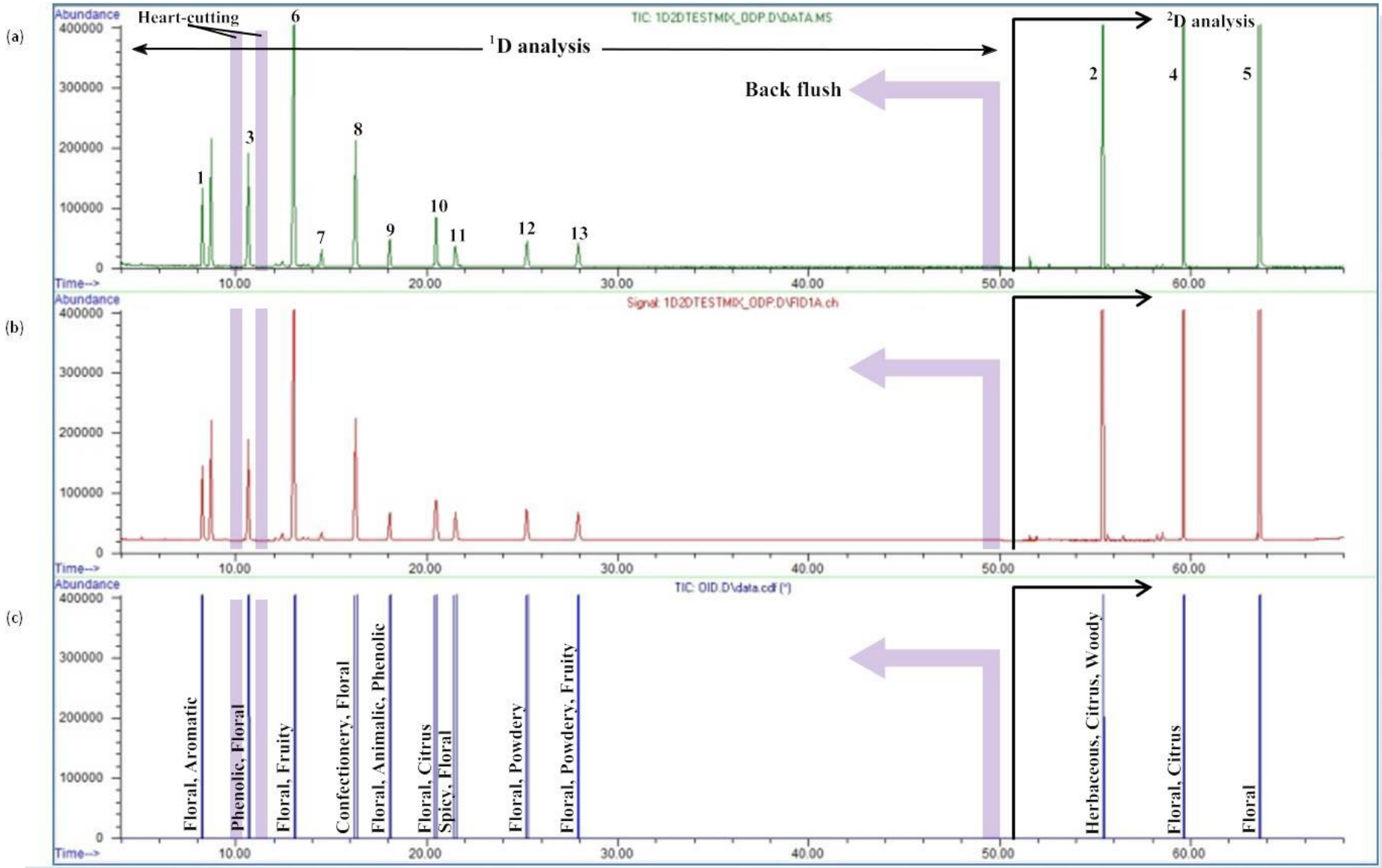
$^{1}D/^{2}D$ Analysis of Fragrance with Simultaneous MS-FID-ODP Detection

Firmenich



1: Methylparacresol; 2: Terpinene Gamma; 3: Methyl Benzoate; 4: Linalool; 5: Phenethylol; 6: Benzyl Acetate; 7: 1, 4-Dibromobenzene; 8: Ethyl Phenylacetate; 9: Indol; 10: Methyl Anthranilate; 11: Eugenol; 12: Ionone Alpha; 13: Ionone Beta

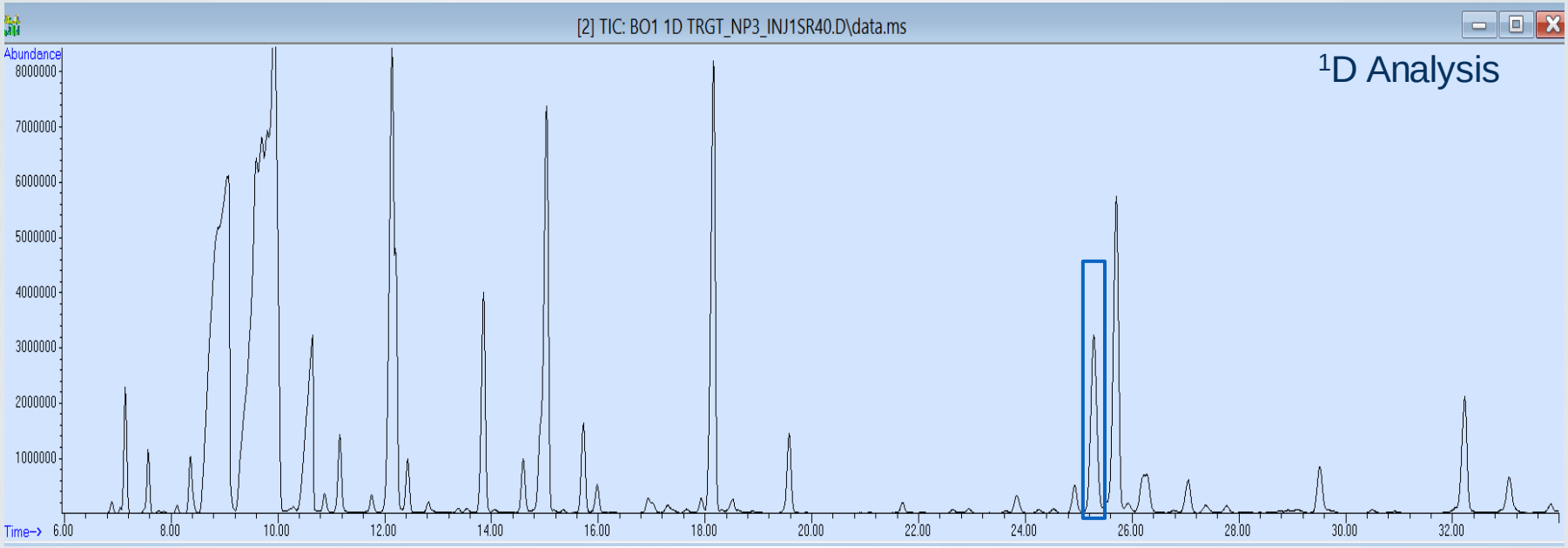
Firmenich

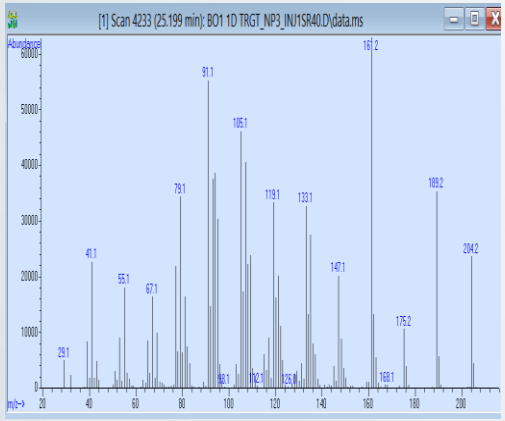


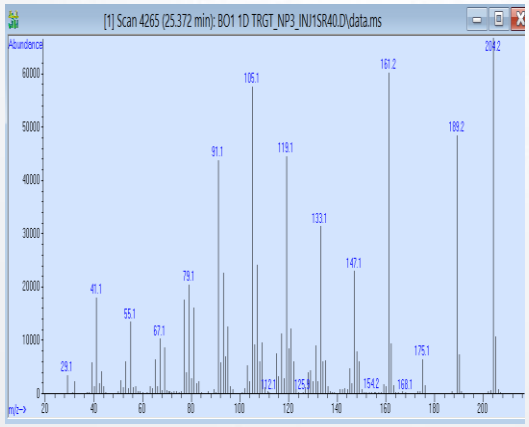
1: Methylparacresol; 2: Terpinene Gamma; 3: Methyl Benzoate; 4: Linalool; 5: Phenethylol; 6: Benzyl Acetate; 7: 1, 4-Dibromobenzene; 8: Ethyl Phenylacetate; 9: Indol; 10: Methyl Anthranilate; 11: Eugenol; 12: Ionone Alpha; 13: Ionone Beta

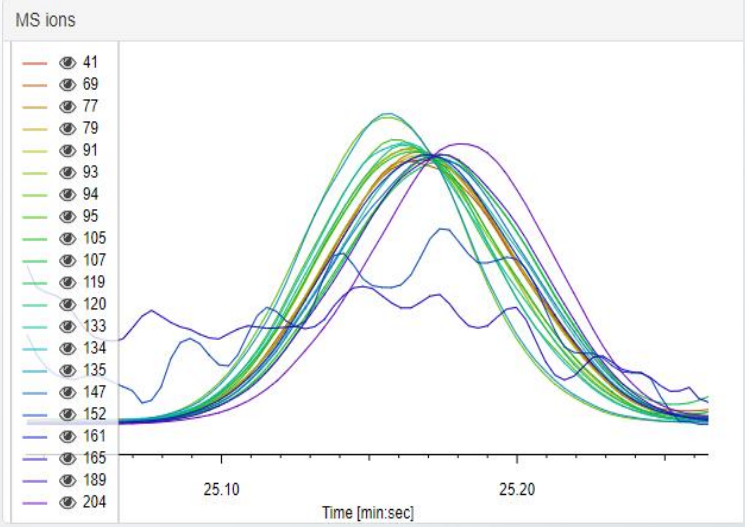
Firmenich

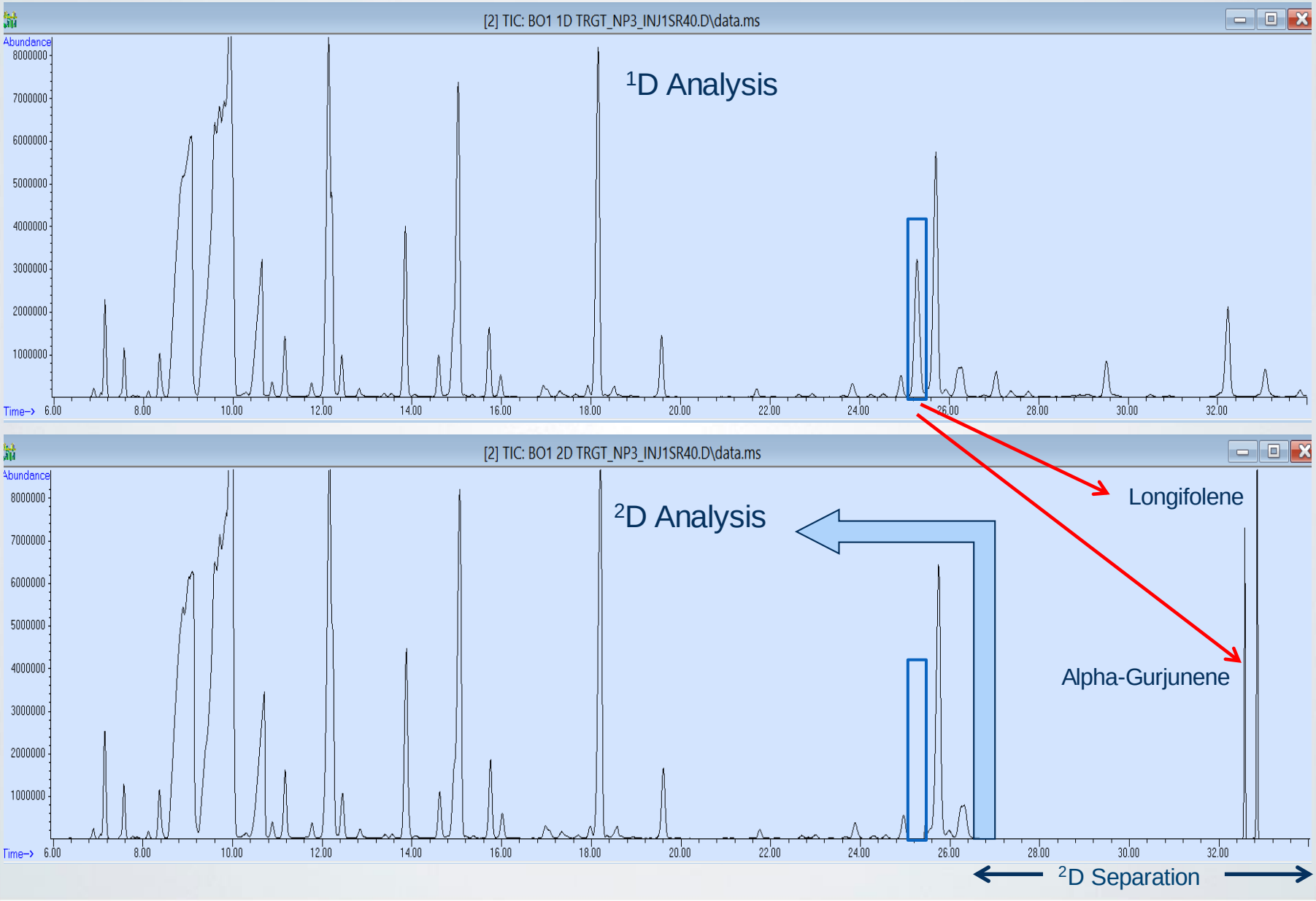
^{1}D Analysis


[2] TIC: BO1 1D TRGT_NP3_INJ1SR40.D\data.ms
Abundance
Time→
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
32.00


[1] Scan 4233 (25.199 min): BO1 1D TRGT_NP3_INJ1SR40.D\data.ms


[1] Scan 4265 (25.372 min): BO1 1D TRGT_NP3_INJ1SR40.D\data.ms


MS ions
41
69
77
79
91
93
94
95
105
107
119
120
133
134
135
147
152
161
165
189
204
25.10
25.20
Time [min:sec]


[2] TIC: BO1 1D TRGT_NP3_INJ1SR40.D\data.ms
Abundance
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
32.00
1D Analysis
[2] TIC: BO1 2D TRGT_NP3_INJ1SR40.D\data.ms
Abundance
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
32.00
2D Analysis
Longifolene
Alpha-Gurjunene
2D Separation

Journal of Chromatography A, 1333 (2014) 106–115

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Quantitative analysis of fragrance in selectable one dimensional or two dimensional gas chromatography–mass spectrometry with simultaneous detection of multiple detectors in single injection

Hui Peng Tan, Tow Shi Wan, Christina Liew Shu Min, Murray Osborne, Khim Hui Ng*

Firmenich Asia Pte Ltd, 10 Tuas West Road, 638377 Singapore

ARTICLE INFO

Article history:
Received 27 November 2013
Received in revised form 24 January 2014
Accepted 27 January 2014
Available online 1 February 2014

Keywords:
Perfume
Selectable $^{1}D/^{2}D$ GC–MS/FID/ODP system
Multidimensional gas chromatography–mass spectrometry
Stir-bar sorptive extraction
Thermal desorption
Dual-linked injectors

ABSTRACT

A selectable one-dimensional (^{1}D) or two-dimensional (^{2}D) gas chromatography–mass spectrometry (GC–MS) system coupled with flame ionization detector (FID) and olfactory detection port (ODP) was employed in this study to analyze perfume oil and fragrance in shower gel. A split/splitless (SSL) injector and a programmable temperature vaporization (PTV) injector are connected via a 2-way splitter of capillary flow technology (CFT) in this selectable $^{1}D/^{2}D$ GC–MS/FID/ODP system to facilitate liquid sample injections and thermal desorption (TD) for stir bar sorptive extraction (SBSE) technique, respectively. The dual-linked injectors set-up enable the use of two different injector ports (one at a time) in single sequence run without having to relocate the ^{1}D capillary column from one inlet to another. Target analytes were separated in ^{1}D GC–MS/FID/ODP and followed by further separation of co-elution mixture from ^{1}D in ^{2}D GC–MS/FID/ODP in single injection without any instrumental reconfiguration. A $^{1}D/^{2}D$ quantitative analysis method was developed and validated for its repeatability – t_R; calculated linear retention indices (LRI); response ratio in both MS and FID signal, limit of detection (LOD), limit of quantitation (LOQ), as well as linearity over a concentration range. The method was successfully applied in quantitative analysis of perfume solution at different concentration level (RSD $\leq$ 0.01%, n = 5) and shower gel spiked with perfume at different dosages (RSD $\leq$ 0.04%, n = 5) with good recovery (96–103% for SSL injection; 94–107% for stir bar sorptive extraction-thermal desorption (SBSE-TD).

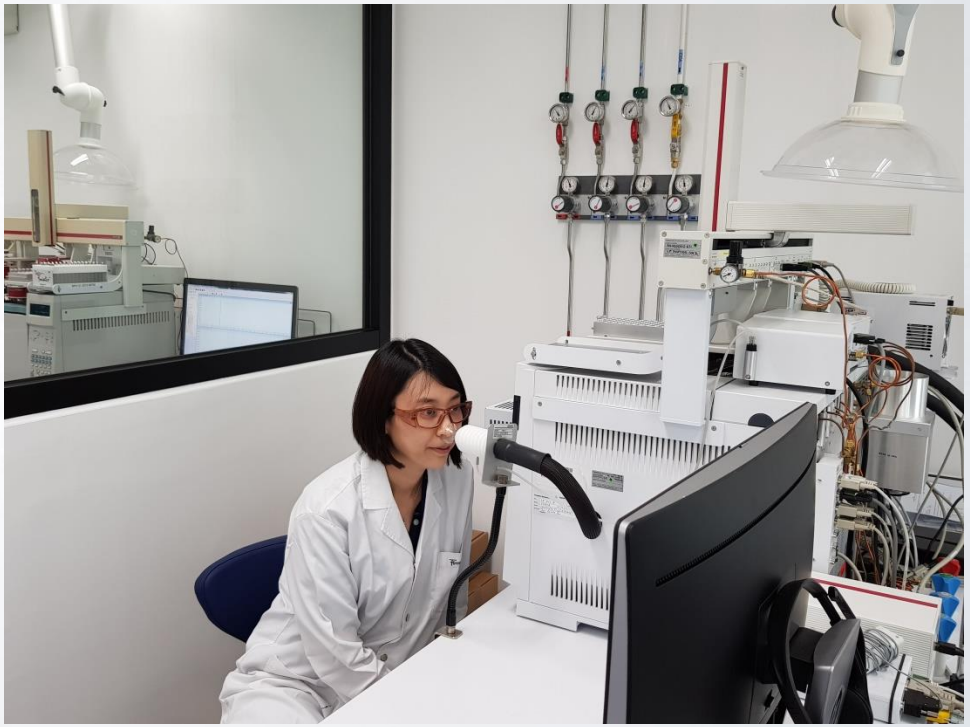
04

Aroma compound trapping by $^{1}D/^{2}D$ SBSE-GCMS Technique

Firmenich

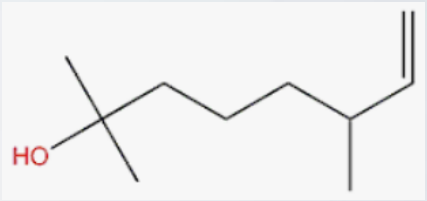
Fragrance Reconstitution Analysis

- Sample extraction
- Intrumental analysis
- Data interpretation
- Olfactive evaluation
- Fragrance Reconstruct



Can we keep the aroma for later ??

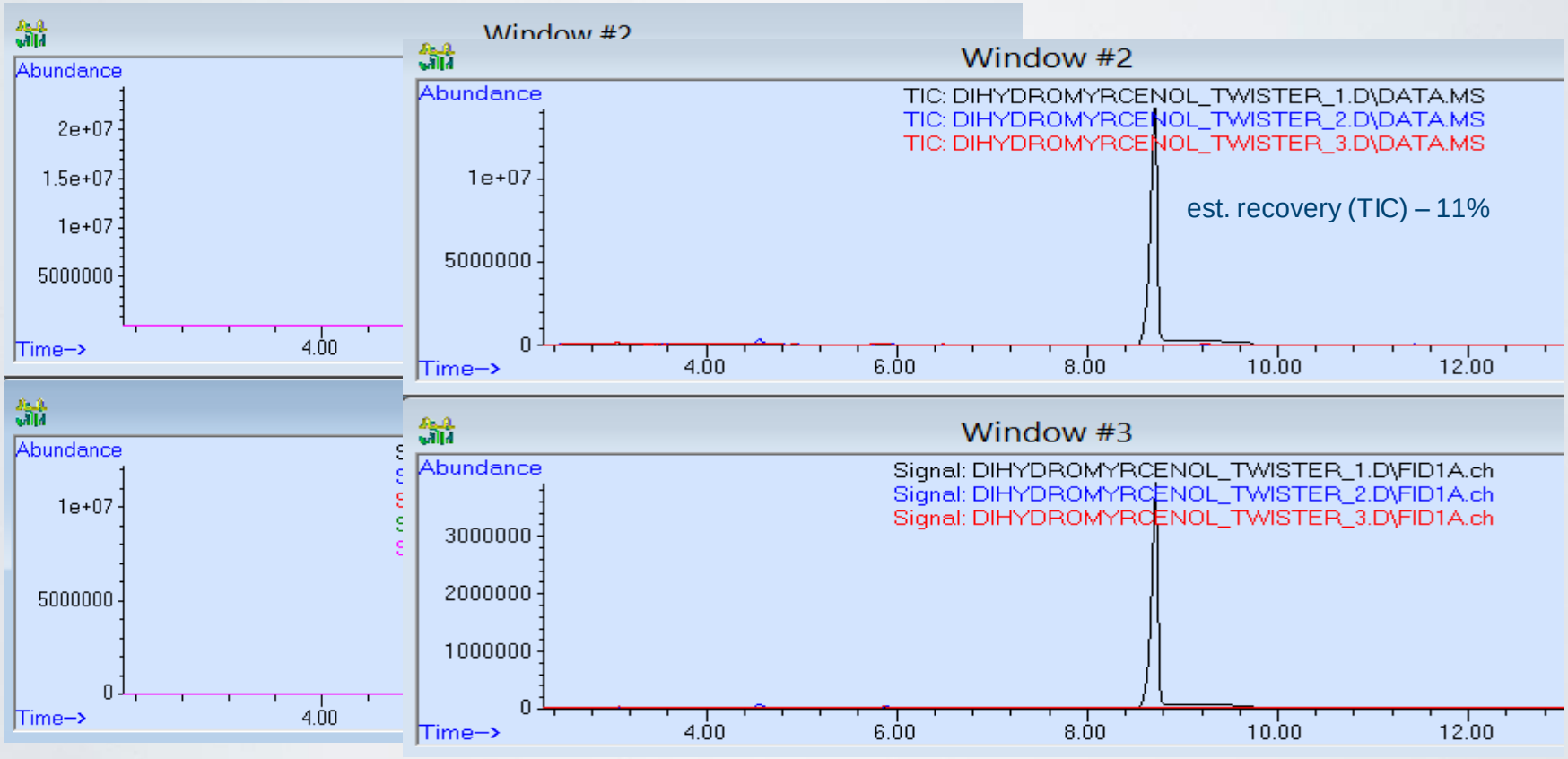
Trapping of Dihydromyrcenol



- Reference standard in lab
- $LogP_{(o/w)}$ – 2.99
- 10% in EtOH
- Inj. vol. 1µL
- Split ratio – 1:50
- 5x manual trapping via ODP
- 3 Twister Bars
  - 1mm x 10mm length

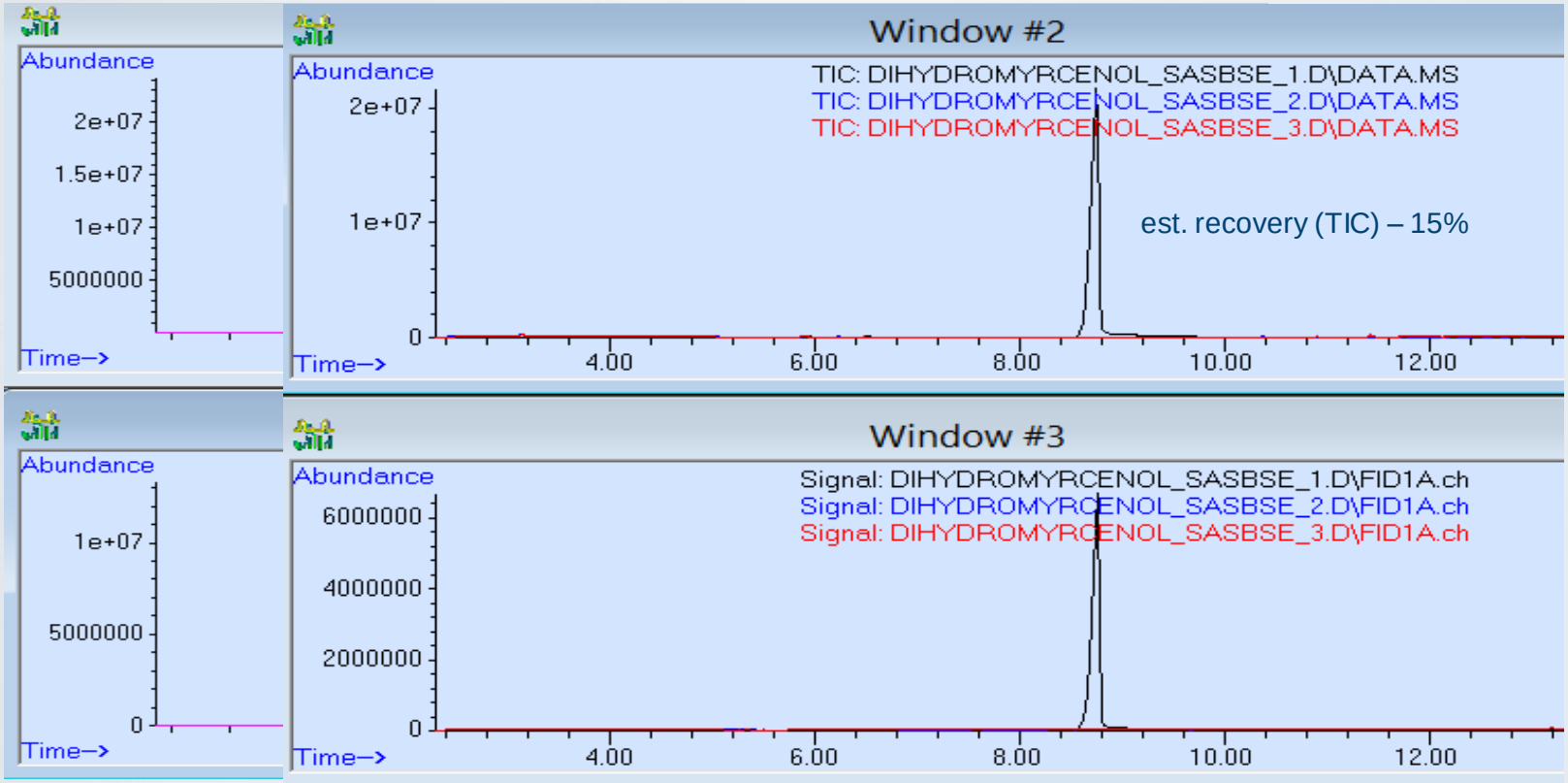
Firmenich

Trapping of Dihydromyrcenol by SBSE



- TDU: 25°C, delay 0.50 min, int. 0.50 min; ramp 100°C/min, end temp. 230°C, hold 1.00 min; splitless desorption
- CIS4: Int. temp. -100°C, equilb time 0.05 min; ramp 12°C/s, end temp. 230°C, hold 5.00 min

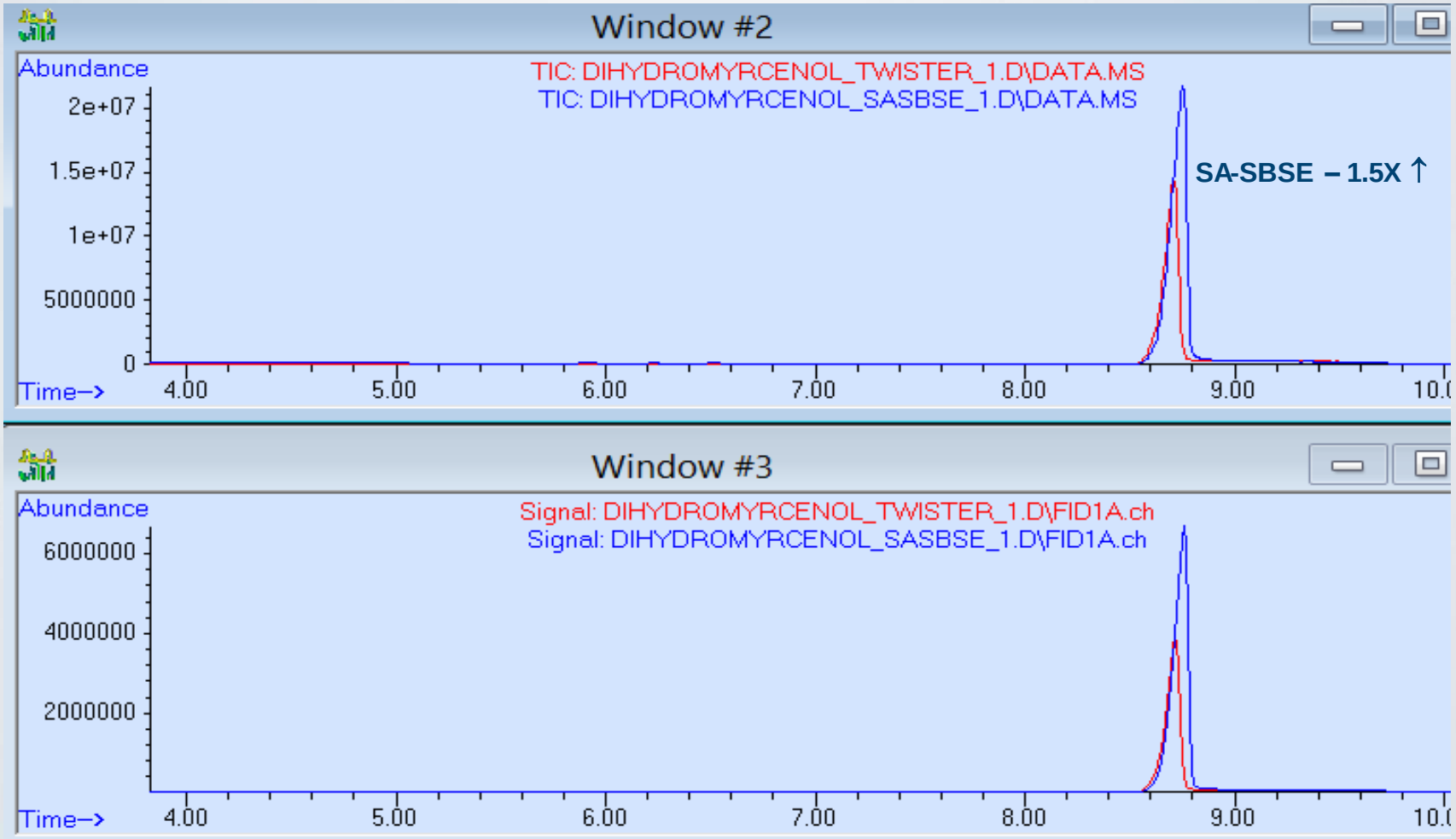
Trapping of Dihydromyrcenol by SA-SBSE*



- TDU: 25^{O}C, delay 0.50 min, int. 0.50 min; ramp1: 10^{O}C/min, end temp. 60^{O}C, hold 5.00 min; ramp2: 35^{O}C/min, end temp. 230^{O}C, hold 3.00 min; splitless desorption
- CIS4: Int. temp. -100^{O}C, equilb time 0.05 min; ramp 12^{O}C/s, end temp. 230^{O}C, hold 5.00 min

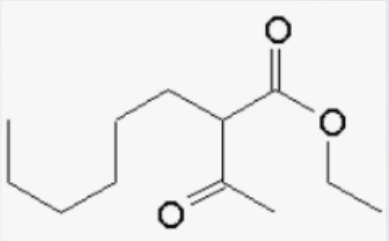
* N. Ochiai, K. Sasamoto, F. David, P. Sandra, Journal of Chromatography A, 1455 (2016) 45–56

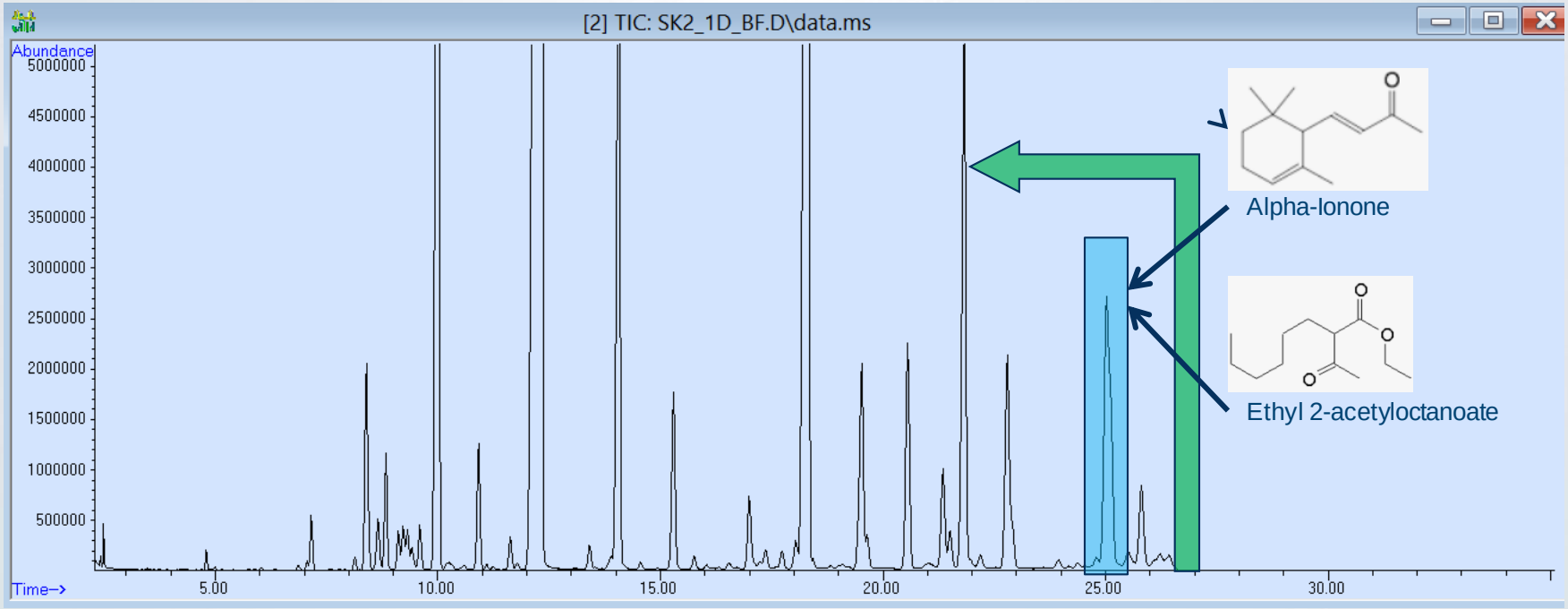
Trapping of Dihydromyrcenol – SBSE vs SA-SBSE



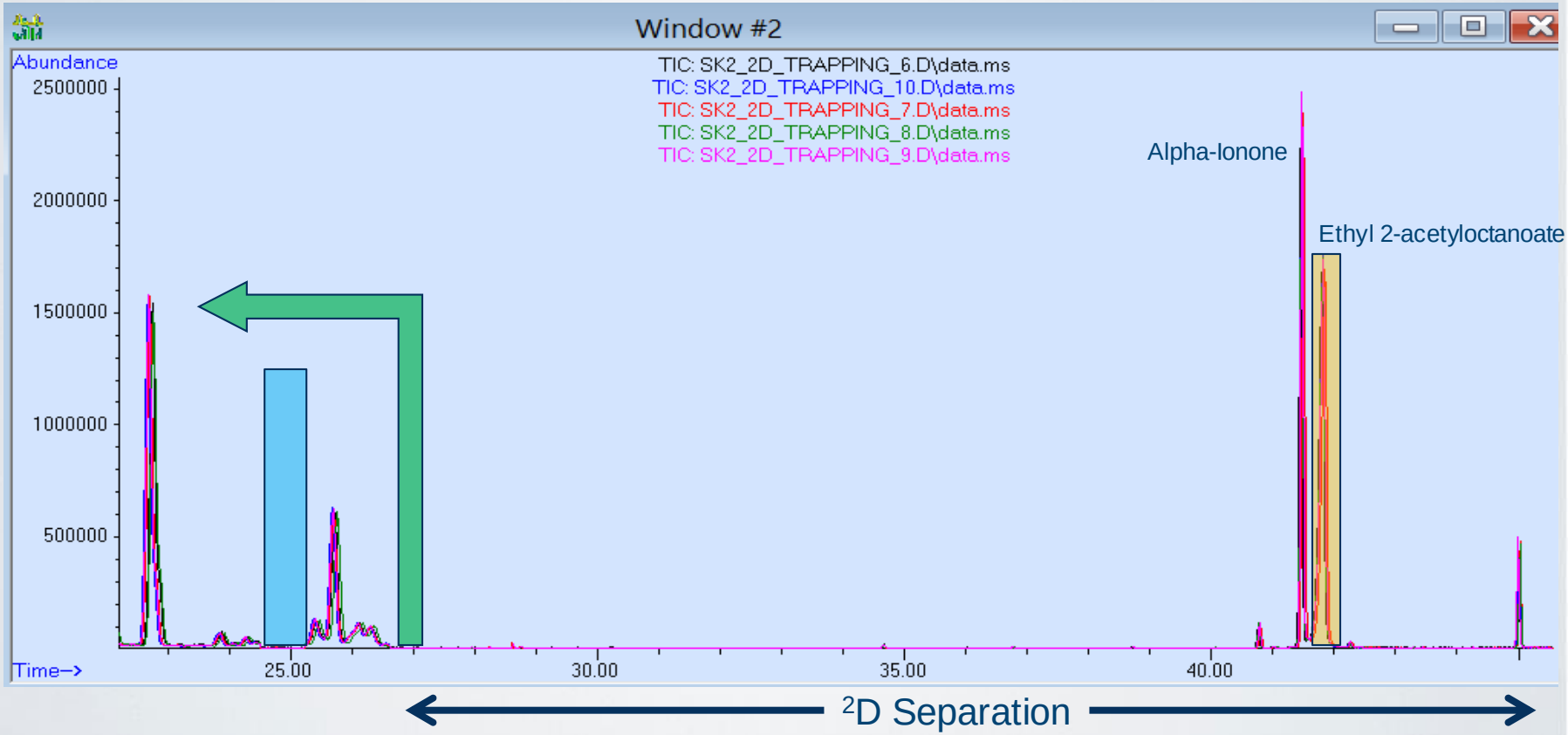
Trapping of Ethyl 2-acetyloctanoate by $^{1}D/^{2}D$ SBSE

- $LogP_{(o/w)}$ – 3.268; 40% in EtOH
- Fatty, jasmone, fruity
- Inj. vol. 1µL; split ratio – 1:25
- 5x manual trapping; 1 Twister Bar (1mm x 10mm length)



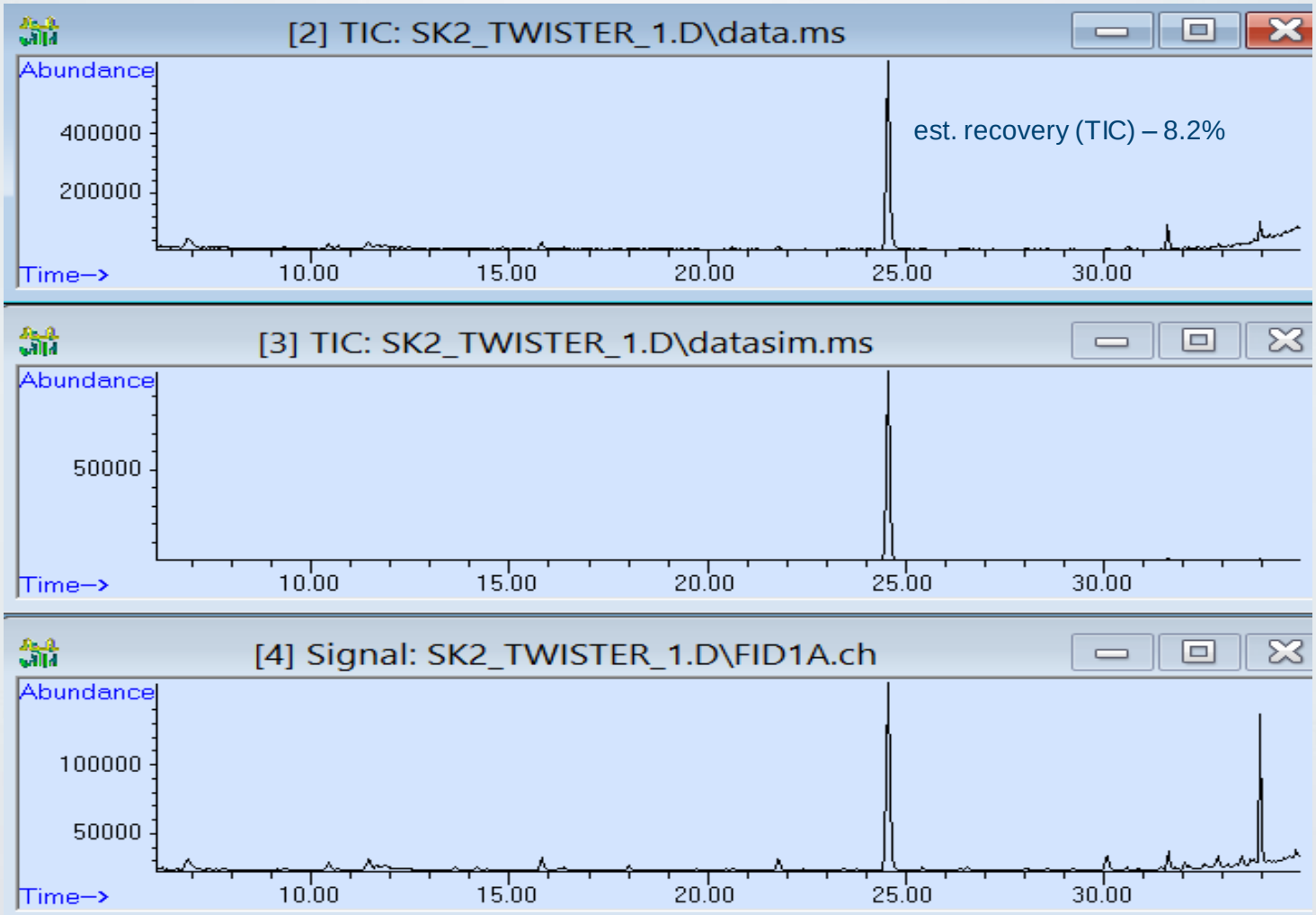


Trapping of Ethyl 2-acetyloctanoate by $^{1}D/^{2}D$ SBSE

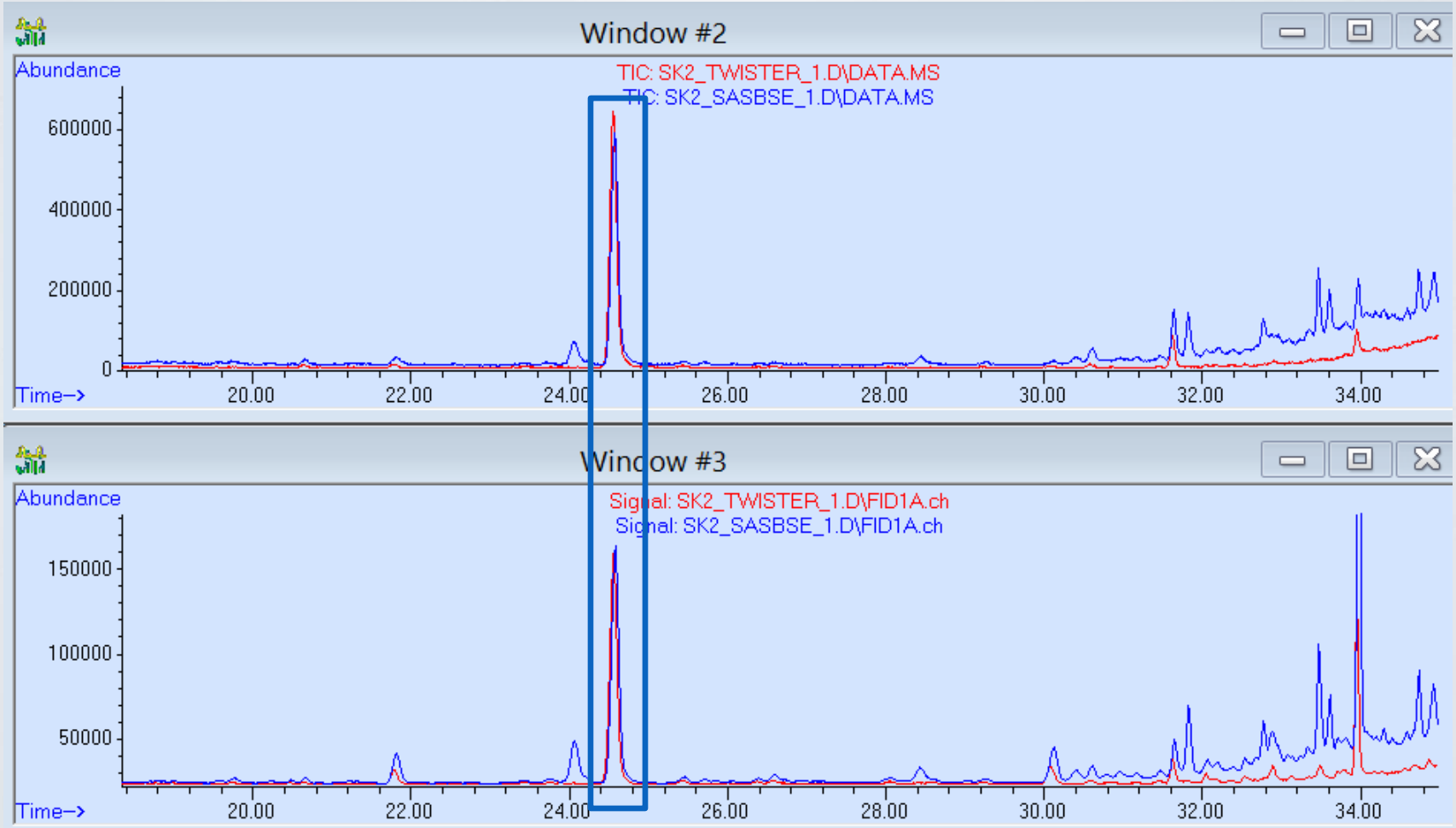


- Valve1: 24.5 min ON, 25.22 min OFF
- FR.Inlet: 400 kPa hold 26.46 min, ramp 999 kPa/min > 50 kPa hold 23.19; BK.Inlet: 380 kPa hold 26.46 min, ramp 999 kPa/min > 50 kPa hold 23.19 splitless desorption
- CTS2: Int. temp. 250°C, Int. time 20.00 min; ramp1: 20°C/s, end temp. -100°C, hold 7.00 min; ramp2: 20°C/s, end temp. 250°C, hold 1.00 min

Thermal Desorption of Ethyl 2-acetyloctanoate from SBSE



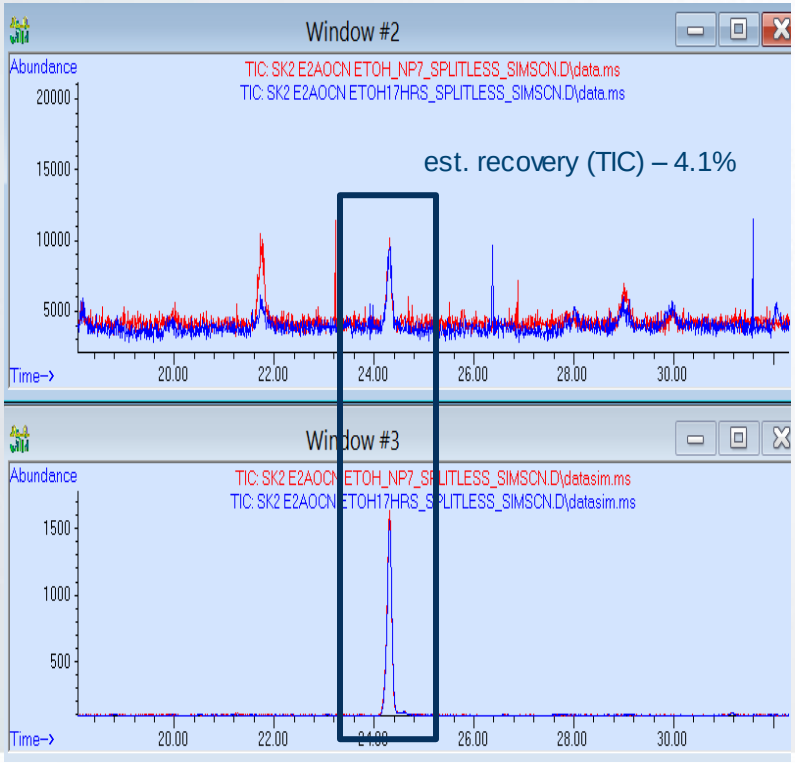
Desorption of Ethyl 2-acetyloctanoate (SBSE vs SA-SBSE)



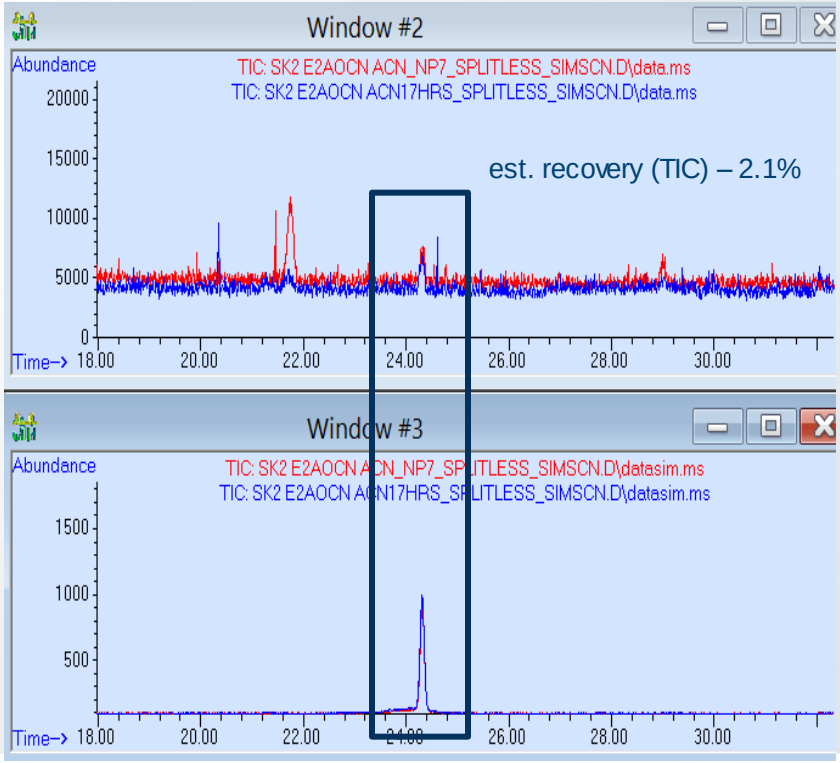
Back Extraction of Ethyl 2-acetyloctanoate from SBSE

- Inj. vol. 1µL; split ratio – 1:5; 3x manual trapping; 1 Twister Bar (1mm x 10mm length)
- 0.5 mL of solvent (ethanol, acetonitrile)
- 1 hr (stirring at 800rpm); 17 hrs + 1hr (stirring at 800rpm)

Extracted by Ethanol



Extracted by Acetonitile



Acknowledgement

Dr Kikuo Sasamoto, Gerstel K.K. Japan
Dr Christina Liew, Gerstel LLP Singapore

Firmenich

inspiring!

INNOVATIVE CRAFTSMANSHIP IN FRAGRANCES AND FLAVORS SINCE 1895