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Comprehensive two-dimensional gas chromatography a gestalt in separation science

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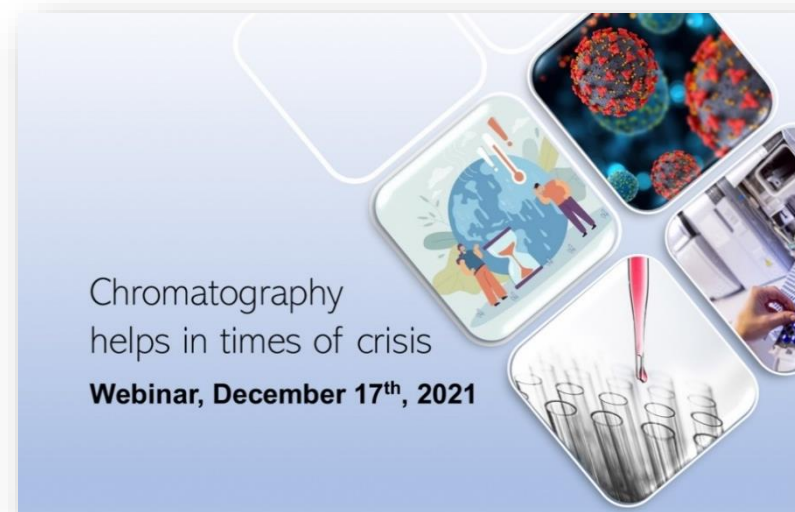
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(Article begins on next page)



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Chromatography helps in times of crisis

.... Comprehensive two-dimensional gas chromatography
a *gestalt* in separation science”

Chiara Cordero;¹ Simone Squara;¹ Andrea Caratti;¹ Carlo Bicchi;¹ Nicola Spigolon;² and Stephen E. Reichenbach ^{3,4}

1: Dept. of Drug Science and Technology, University of Turin, Turin, Italy

2: Soremartec Italia, Ferrero Group, Alba-CN, Italy

3: GC Image LLC (Lincoln NE, USA)

4: Dept. of Computer Science and Engineering, University of Nebraska, (Lincoln NE, USA)





Foreword

Is comprehensive two-dimensional gas chromatography worthy to be adopted in food chemical characterization?

Opinions...

Gestalt: *a configuration or pattern of elements so unified as a whole that it cannot be described merely as a sum of its parts*

Platforms: dimensions, information space, configurations, instrumentation

Data processing: new perspectives for fingerprinting

- ✓ Challenge 1: Cocoa origins *identification* - thermal vs. flow modulation
- ✓ Challenge 2: Hazelnuts volatiles and spoilage patterns - Computer vision
- ✓ Challenge 3: Extra-virgin olive oil aroma blueprint - *AI Smelling machines*

Combine challenges in a single step analytical process

Conclusive remarks



GC: The State of the Art

Chairperson: Pat Sandra
 Participants: Steven Lehotay
 Hans-Gerd Janssen
 Chiara Cordero
 Frank David
 John Hinshaw

GC: The State of the Art

November 01, 2017

By Chiara Cordero, Pat Sandra, John Hinshaw, Hans-Gerd Janssen, Frank David, Steven Lehotay

Pat Sandra: Comprehensive GC×GC has gained prominence at international meetings and in the literature in recent years. Do you expect a breakthrough in the coming years for routine analyses? Will modulation by temperature or by flow be mostly applied? Is the data handling sufficiently developed in terms of accuracy and speed for routine applications?

Steven Lehotay: GC×GC provides greater selectivity in separations, but as it is commonly used now, it adds too much time to the analysis. Another major problem is that a microbore second-dimension column is easily overwhelmed by high concentration matrix components, which is nearly always the case in real-world samples. GC×GC is overkill in common applications and fails in many difficult ones, thus, it needs to be used in a different way to provide faster separations with more sample capacity. I think a breakthrough in GC×GC would have been possible many years ago if the drivers of the technology had decided to overcome its practical limitations, including excessive liquid nitrogen usage for cryogenic modulation, rather than demonstrate niche applications.



Frank David: GC×GC will definitely find its way to routine application, mainly in petrochemical analysis. All types of modulators can be used, but easier, user-friendly, intuitive software and data handling are needed. Moreover, the application potential of GC×GC should not be overestimated. One-dimensional GC and GC-MS are able to cover most GC-amenable applications.



Hans-Gerd Janssen: GC×GC is already routinely used in the mineral oil area and in the flavour and fragrance industry, simply because one-dimensional GC cannot do the job. For many other applications we are forced, by government policies or for company-internal reasons, to stick with one dimensional GC. I do not expect a dramatic breakthrough for GC×GC, but it could evolve to 10–15% of the GC market.





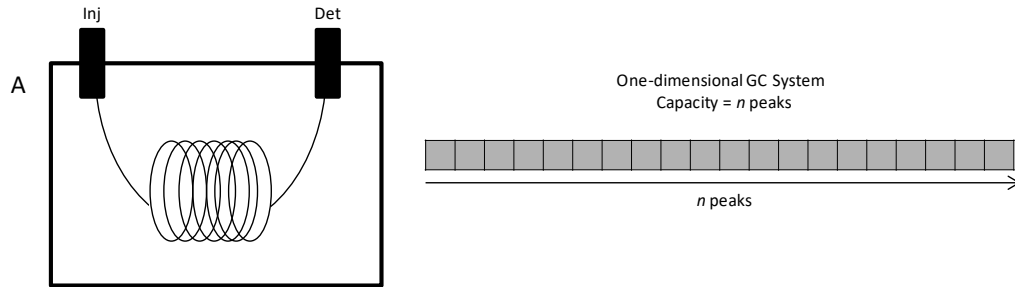
GESTALT

noun \ gə-'stält

understanding the whole,
not merely the sum of
its parts.

...a configuration or pattern of elements so unified as a whole that it cannot be described merely as a sum of its parts...

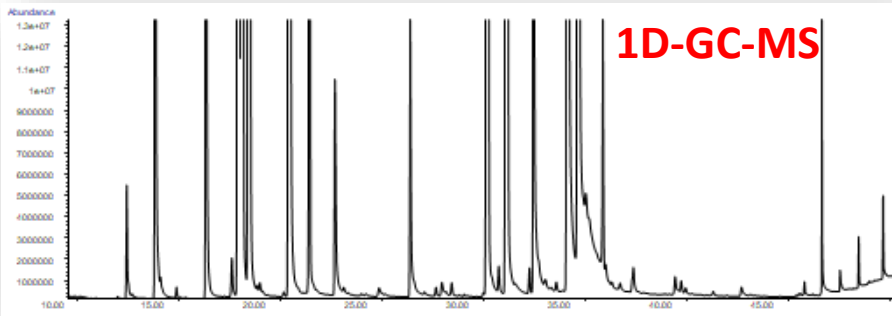




- ✓ Separation power (peak capacity) is given by the product of the two chromatographic dimensions (GC×GC);
- ✓ Independent (almost) displacement in both dimensions produces rational retention patterns for homologue series
- ✓ Band compression (in space - for thermal modulators) produces Signal-to-Noise ratio enhancement - sensitivity
- ✓ Bi-dimensional peak patterns exploits a 3D space where fingerprinting could be more accurate than in a 2D space (as for 1D-GC profiles)



Gestalt



Profiling¹

detailed analysis of the chemical pattern

Targeted - Untargeted profiling²

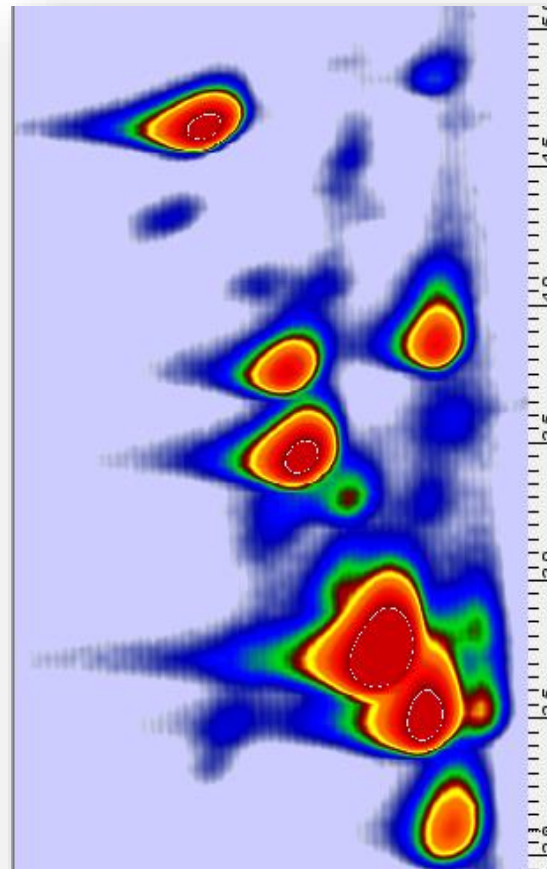
multidimensional platforms provide data on analytes identity (MS signatures) and amount in the sample

Fingerprinting¹

general and rapid high-throughput screening

-> discriminate and classify samples

Comprehensive 2D GC unified multi-dimensional platform



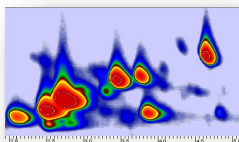
Chromatographic fingerprinting²
pattern recognition
extends samples comparison to all detectable analytes

“High resolution” profiling
GC×GC separation power enables accurate quantitative profiling in complex samples

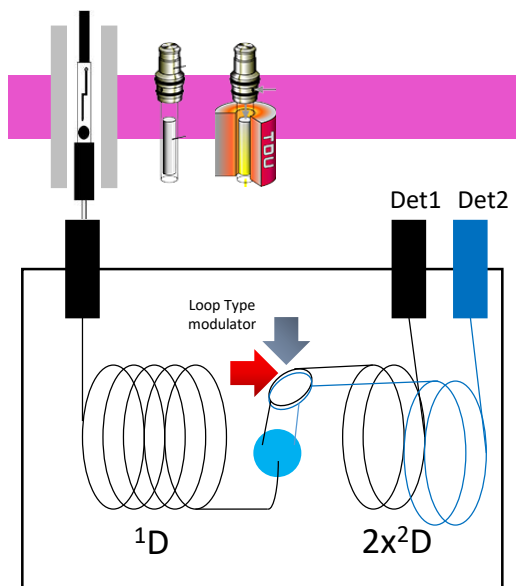
Rationalized patterns of chemical classes
Group-Type Analysis
Ordered elution patterns for chemically correlated analytes

[1] Harrigan G., Goodacre R. (2003) Metabolic profiling: its role in biomarker discovery and gene function analysis. Kluwer Academic Publishers: Boston

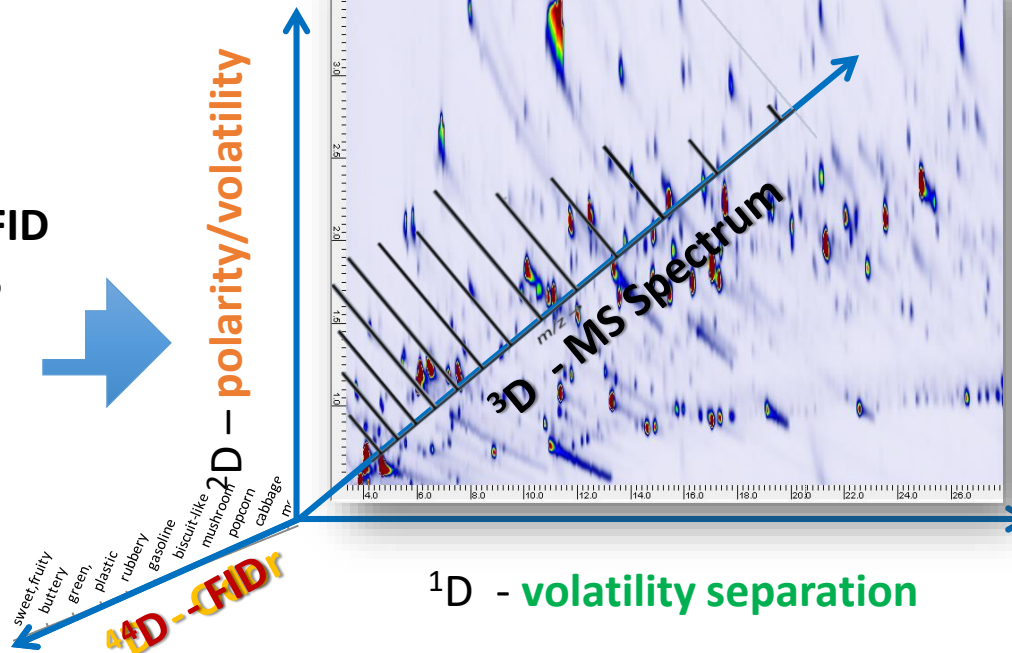
[2] S.E. Reichenbach et al. J. Chromatogr. A 1226 (2012) 140–148



Platforms



Sample prep - GCx2GC-MS/FID
 Sample prep - GC(O)xGC-MS



Information dimensions
 spectral signature (identity)
 volatility/polarity
 sensory descriptor (bio-assay)



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[1] J.C. Giddings, Sample dimensionality: a predictor of order-disorder in component peak distribution in multidimensional separation, J. Chromatogr. A 703(1995) 3-15.



Rational information space

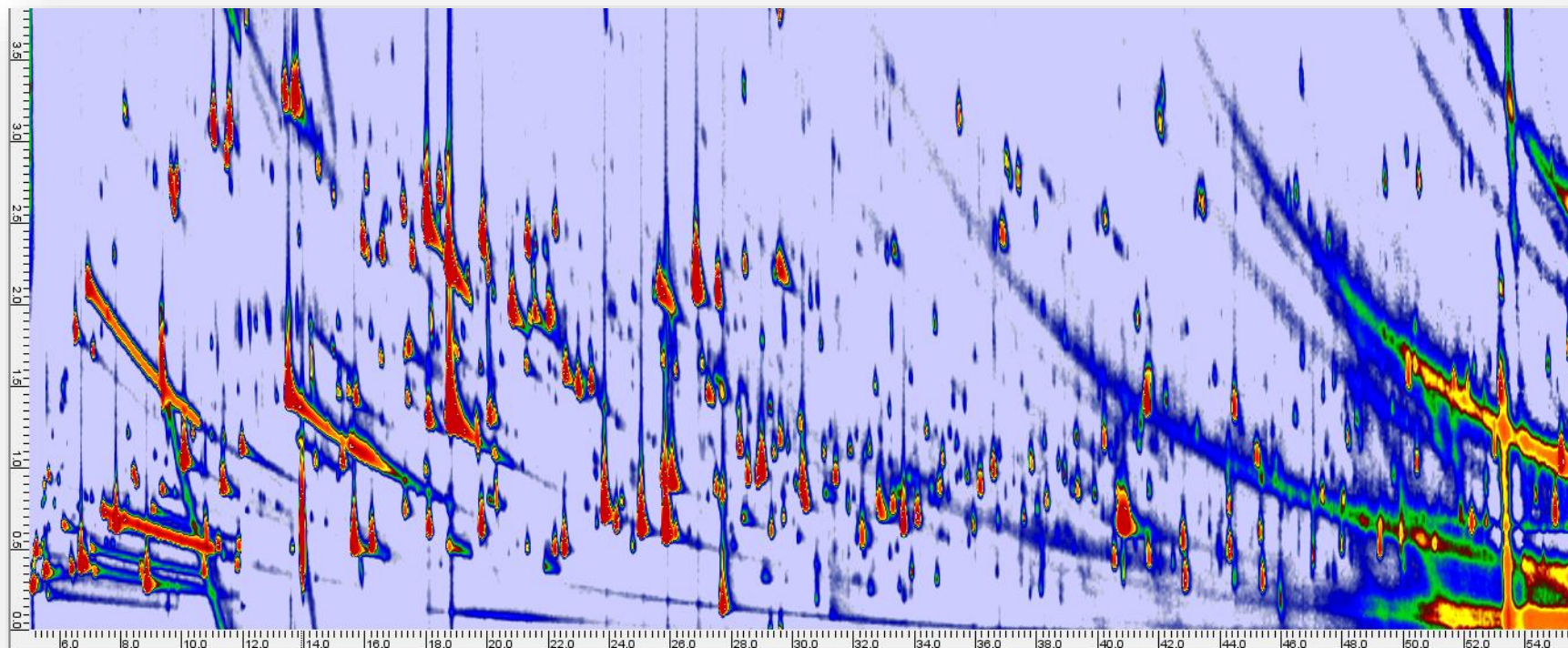


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Extra Virgin Olive oil **volatiles** - Italian origin
HS-SPME (CAR/PDMS/DVB) - 500 mg - 50°C/50 min

Chemical dimensions

²D - volatility separation



¹D - polarity/volatility separation

Targeted peaks over more than 800 detectable analytes

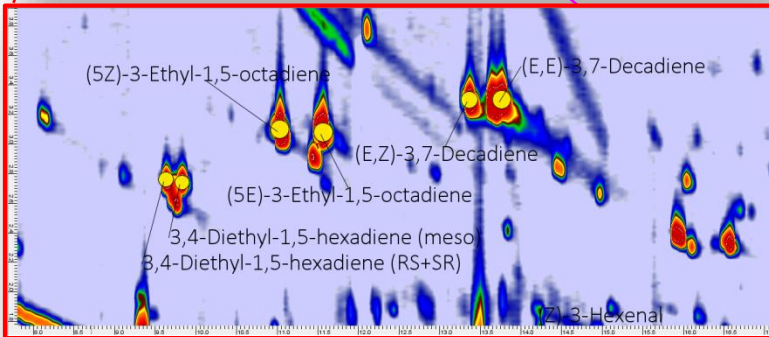
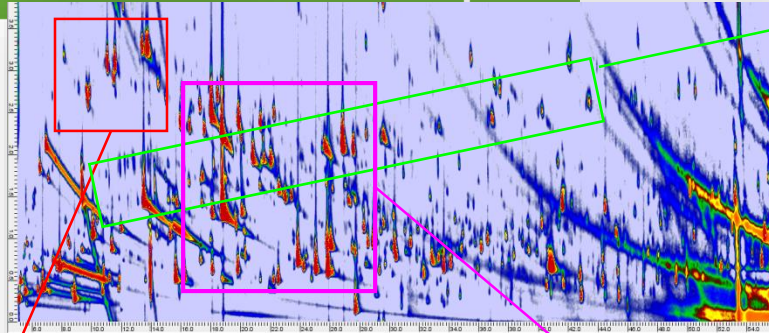
255 reliably identified by 70 eV spectrum and I^T coherence

Various chemical classes highly correlated with autoxidation processes, enzymatic peroxidation, aroma compounds and potent odorants

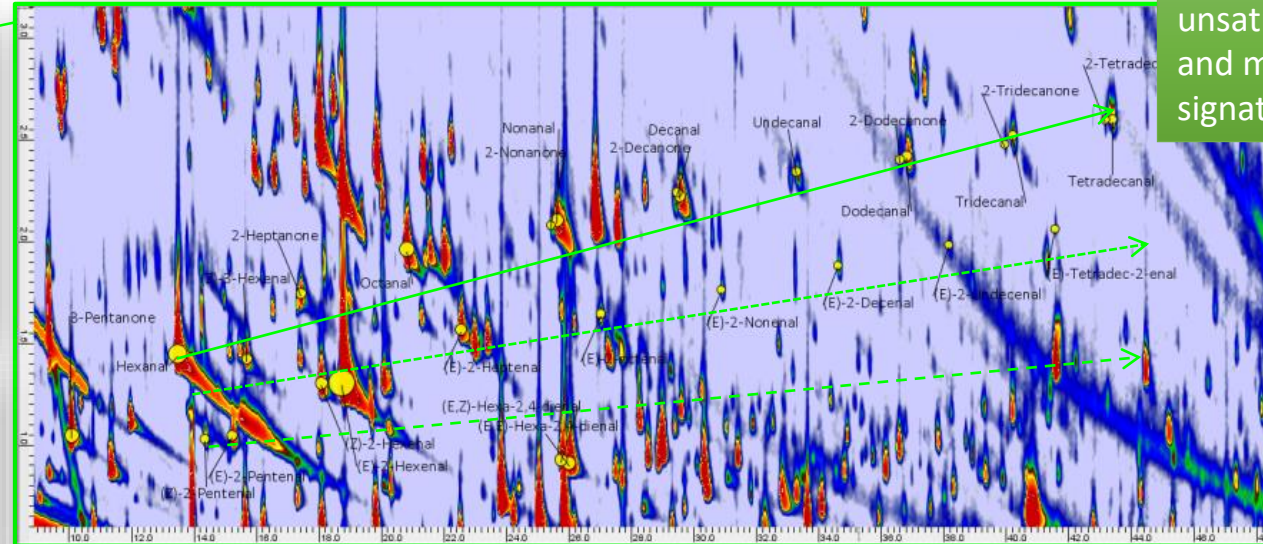


Rational information space

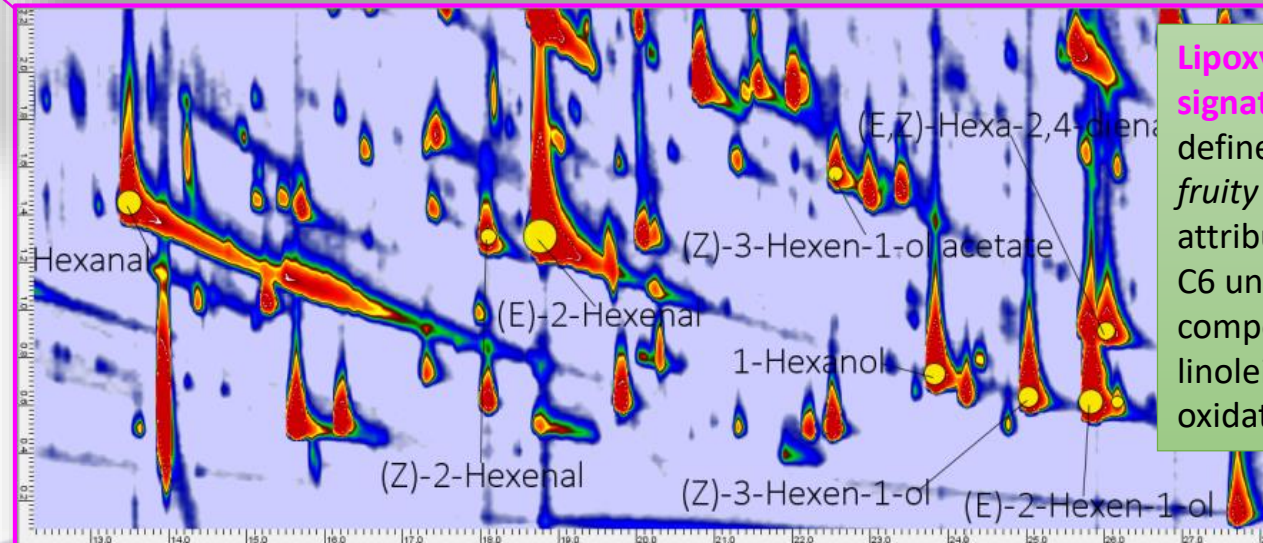
Chemical dimensions



Unsaturated hydrocarbons: distinctive for earlier harvest stages: 3,4-diethyl-1,5-hexadiene (*RS* p *SR*), 3,4-diethyl-1,5-hexadiene (*meso*), (5*Z*)-3-Ethyl-1,5-octadiene, (5*E*)-3-Ethyl-1,5-octadiene, (*E,Z*)-3,7-decadiene, (*E,E*)-3,7-decadiene, and (*E*)-4,8-Dimethyl-1,3,7-nonatriene



Linear saturated and unsaturated aldehydes and methyl-ketones signatures

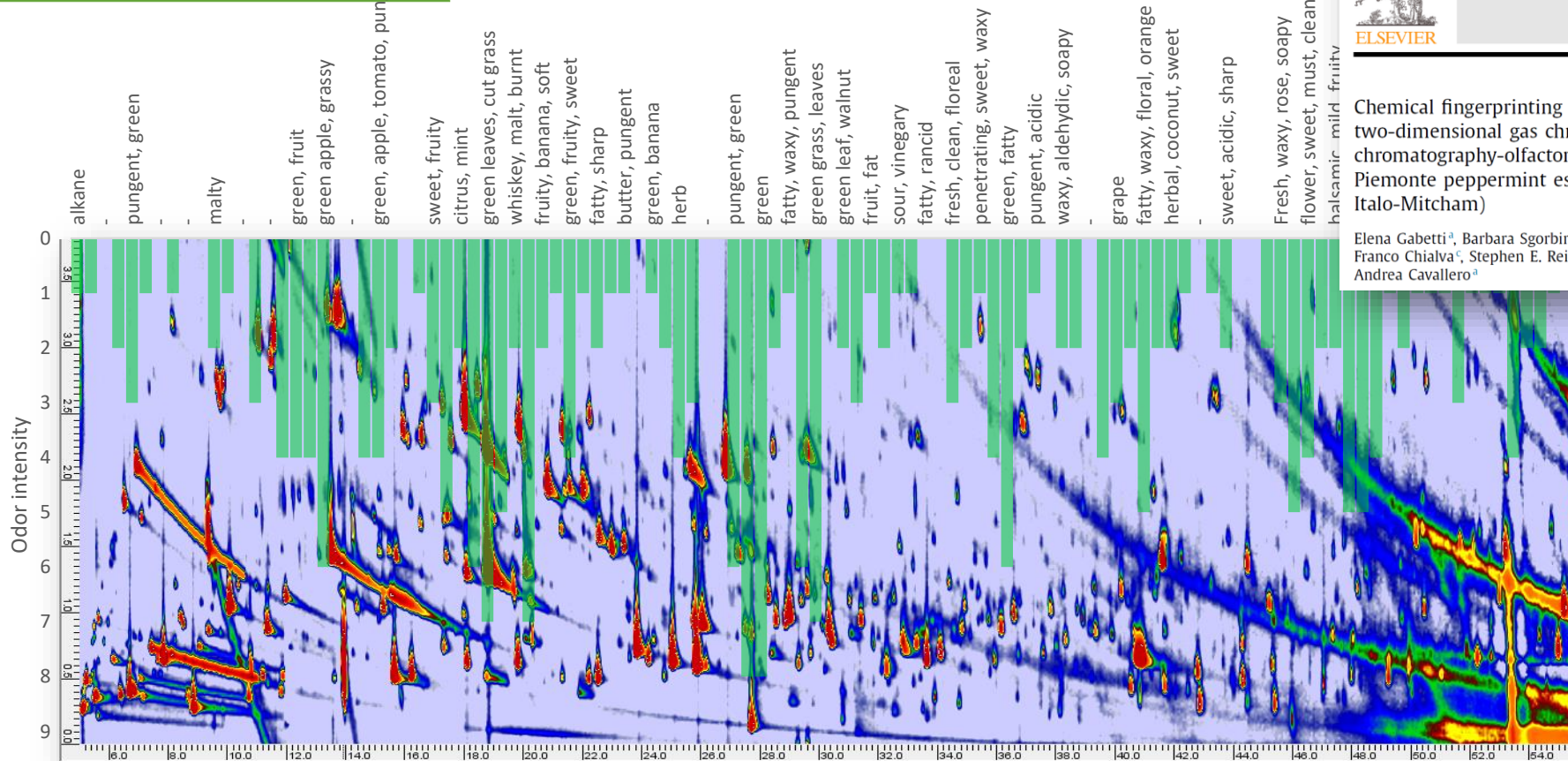


Lipoxygenase (LOX) signature: fundamental to define *fresh-green* and *fruity* notes (positive attributes) -> biogenesis of C6 unsaturated compounds derived from linoleic and linolenic acids oxidative cleavage.



Orthogonal information space

2D - volatility separation



1D - polarity/volatility separation

alkane
pungent, green
malty
green, fruit
green apple, grassy
green, apple, tomato, pungent
sweet, fruity
citrus, mint
green leaves, cut grass
whiskey, malt, burnt
fruity, banana, soft
green, fruity, sweet
fatty, sharp
butter, pungent
green, banana
herb
pungent, green
green
fatty, waxy, pungent
green grass, leaves
green leaf, walnut
fruit, fat
sour, vinegary
fatty, rancid
fresh, clean, floreal
penetrating, sweet, waxy
green, fatty
pungent, acidic
waxy, aldehydic, soapy
grape
fatty, waxy, floral, orange
herbal, coconut, sweet
sweet, acidic, sharp
Fresh, waxy, rose, soapy
flower, sweet, must, clean
balsamic mild fruity



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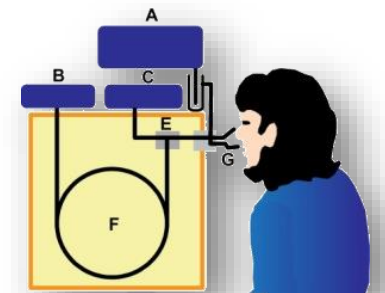
Contents lists available at ScienceDirect

Journal of Chromatography A

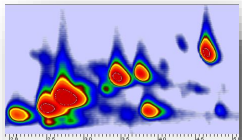
journal homepage: www.elsevier.com/locate/chroma

Chemical fingerprinting strategies based on comprehensive two-dimensional gas chromatography combined with gas chromatography-olfactometry to capture the unique signature of Piemonte peppermint essential oil (*Mentha x piperita* var Italo-Mitcham)

Elena Gabetti^a, Barbara Sgorbini^b, Federico Stilo^b, Carlo Bicchi^b, Patrizia Rubiolo^b, Franco Chialva^c, Stephen E. Reichenbach^{d,e}, Valentina Bongiovanni^a, Chiara Cordero^{b,*}, Andrea Cavallero^a

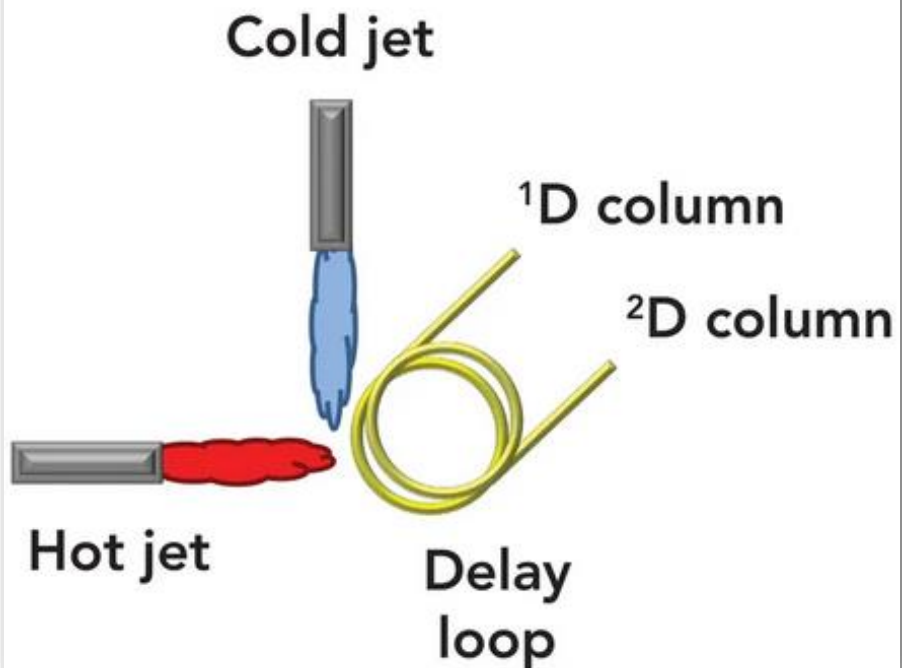


Picture from:
TrAC (2011) 30(11) :1756–1770



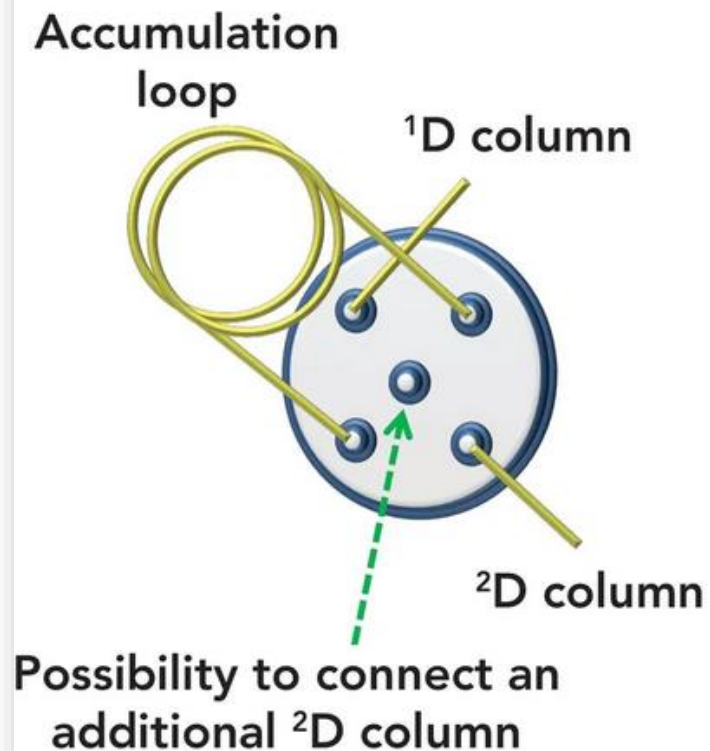
Thermal/cryogenic modulation

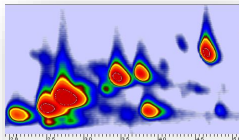
Cryogenic modulator



Differential-flow modulation

Flow modulator

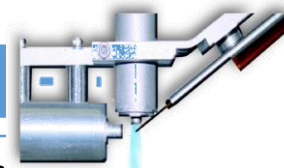




Platforms



Thermal/cryogenic modulation



Successful "**high resolution**" investigations

- ✓ in-depth sample characterization
- ✓ adulterations - origin
- ✓ classification based on chemical signatures

- *food metabolomics*
- *sensomics*
- *food safety*
- *emerging issues (MOH)*



Careful tuning of experimental conditions
Expert analysts (separation science)
Data processing - new concepts

Rather high instrumental costs
High **operational costs** (cryogenics)
Trained analyst

Differential-flow modulation

Careful tuning of experimental conditions
Expert analysts (separation science)
Data processing - new concepts

Moderate instrumental costs
No additional costs for operation

Trained analyst

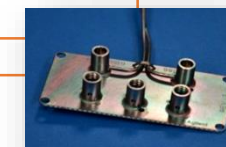


Method Translation^{1,2}

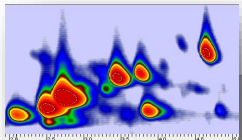
Context of Fast GC - speed - capacity - resolution
Carrier gas conditions (p_i , p_0 and F), temp. programming

...by translating

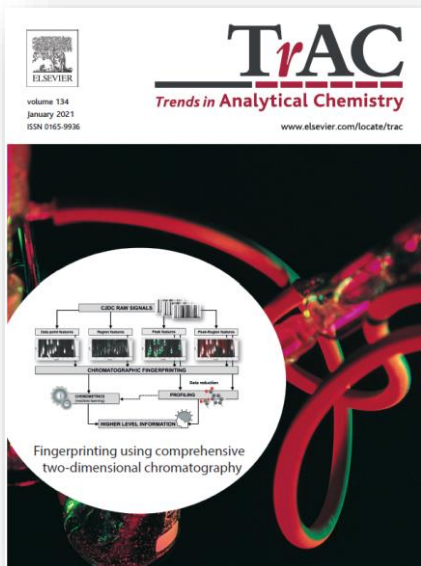
Preserve the elution order
Keep **coherent elution pattern, and resolution**
Exploit all **information dimensions**
Speed-up the analysis



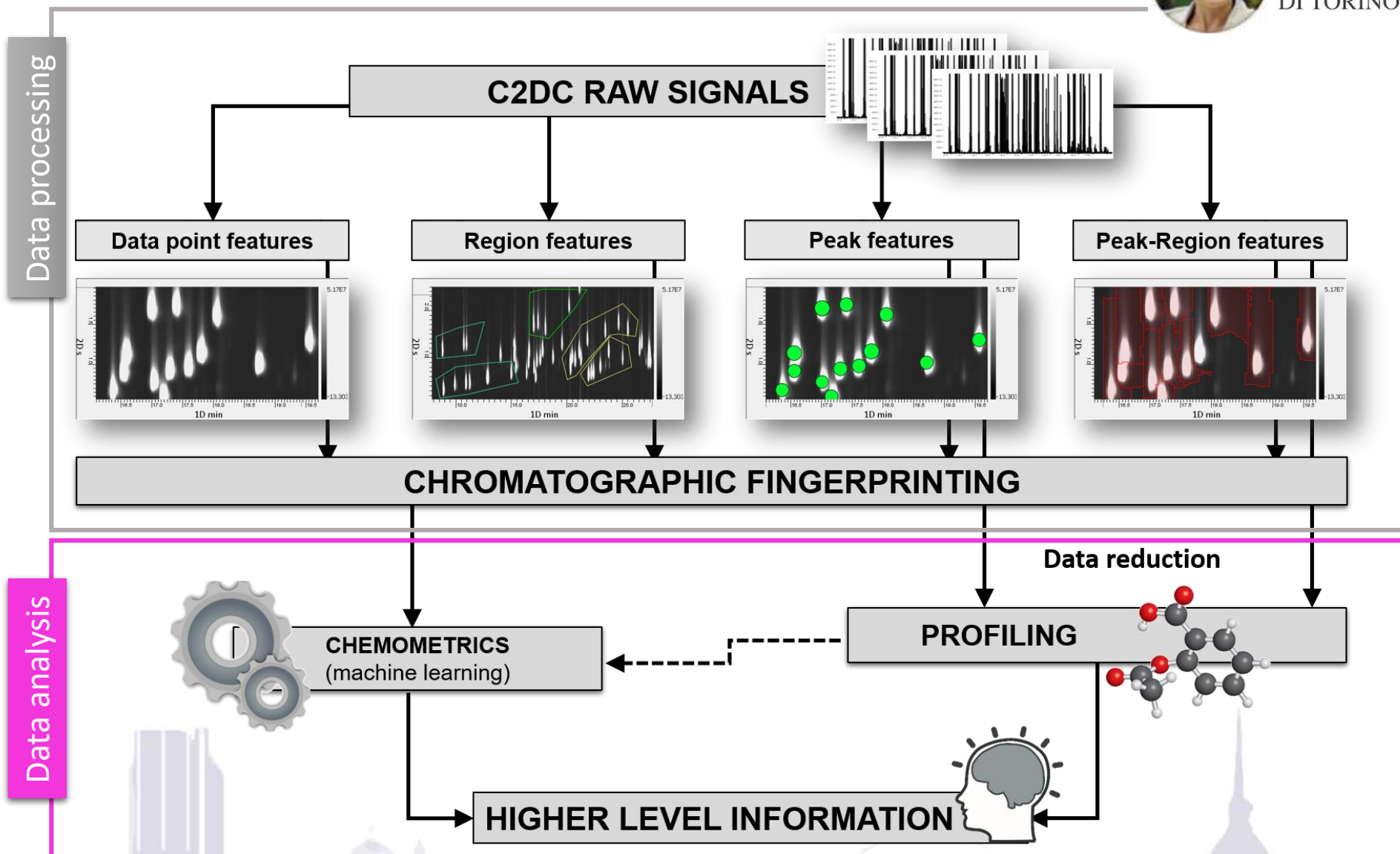
1. L. Blumberg and M. Klee Anal Chem 1998 70: 3828-3829
2. M. Klee and L. Blumberg J. Chrom Sci 2002 40: 234-247

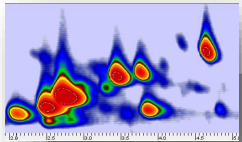


Data processing



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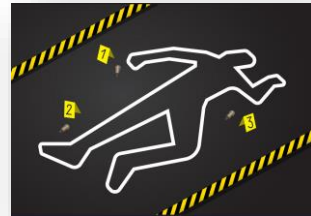


Data processing

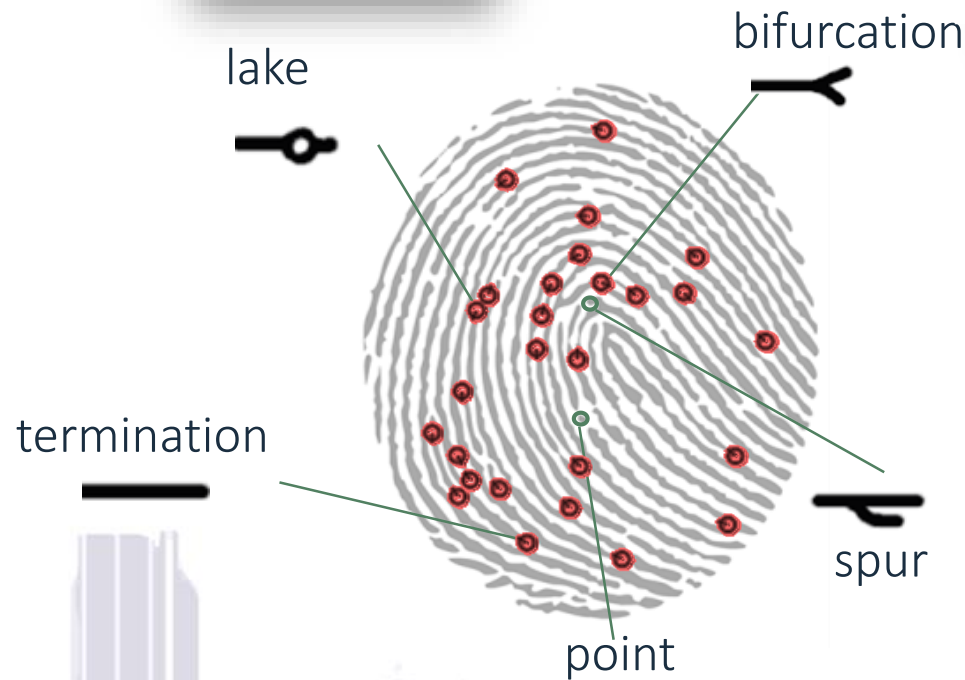
A **fingerprint** is the pattern of ridges and valleys on the surface of a fingertip
-> Everyone has unique fingerprints

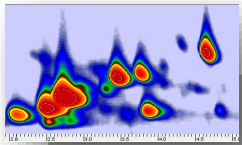


Crime scene fingerprint



Database fingerprints





Data processing

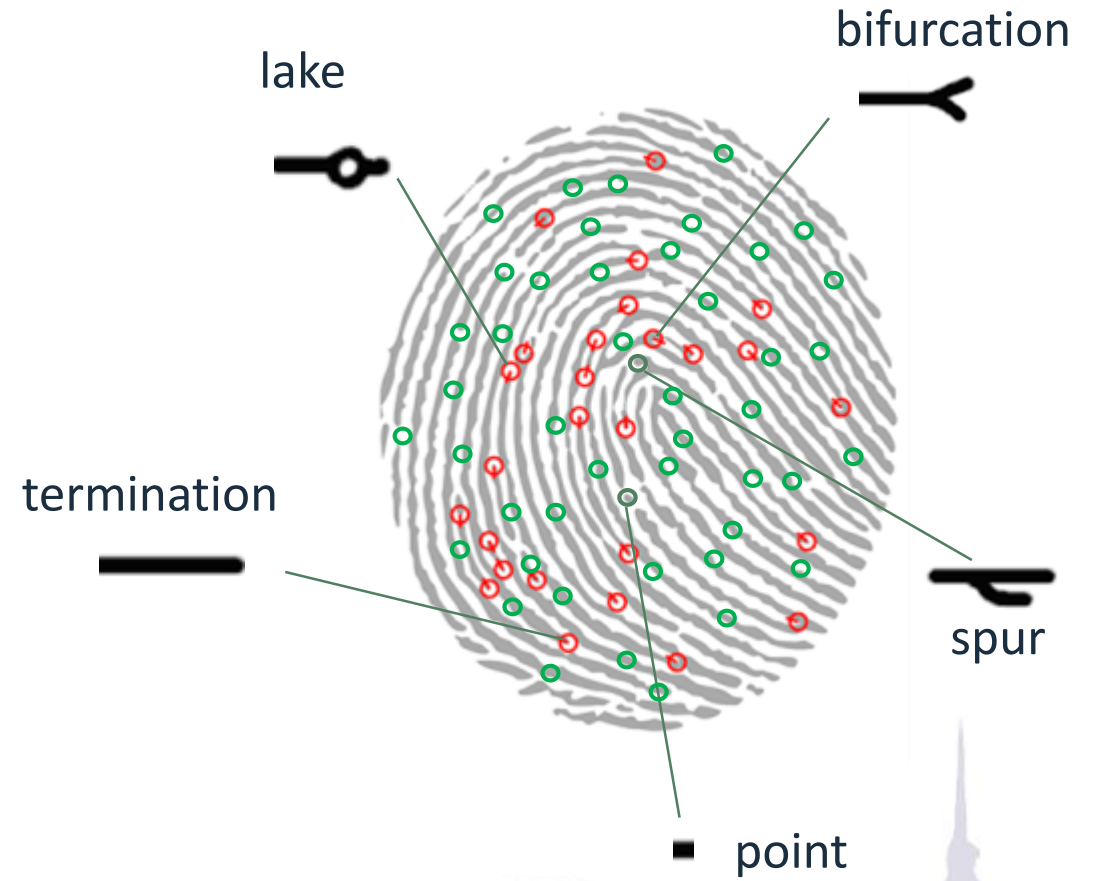
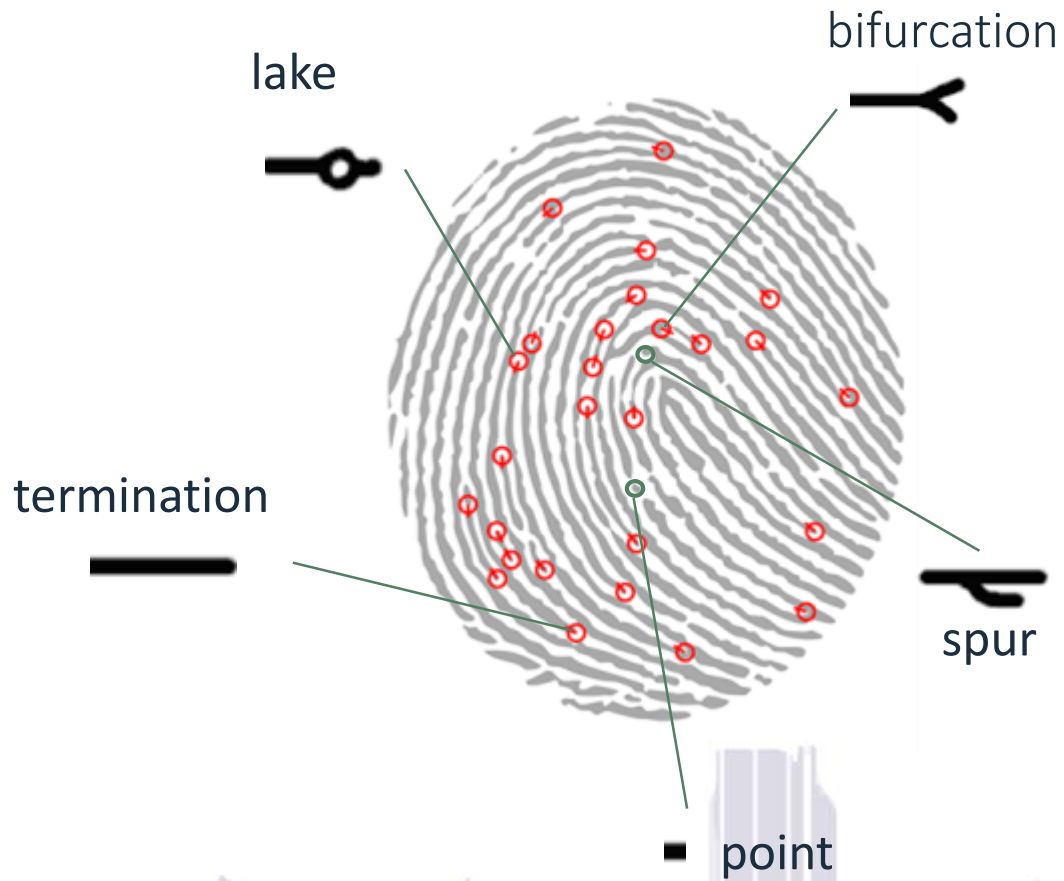


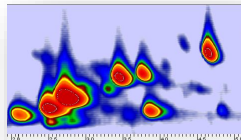
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Targeted - minutiae

Untargeted - Targeted

UT - extended investigation





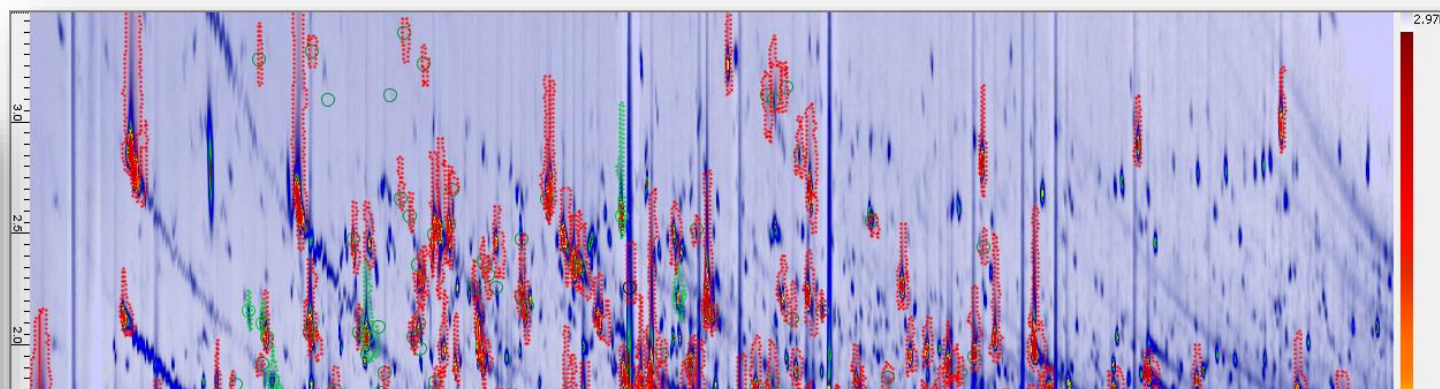
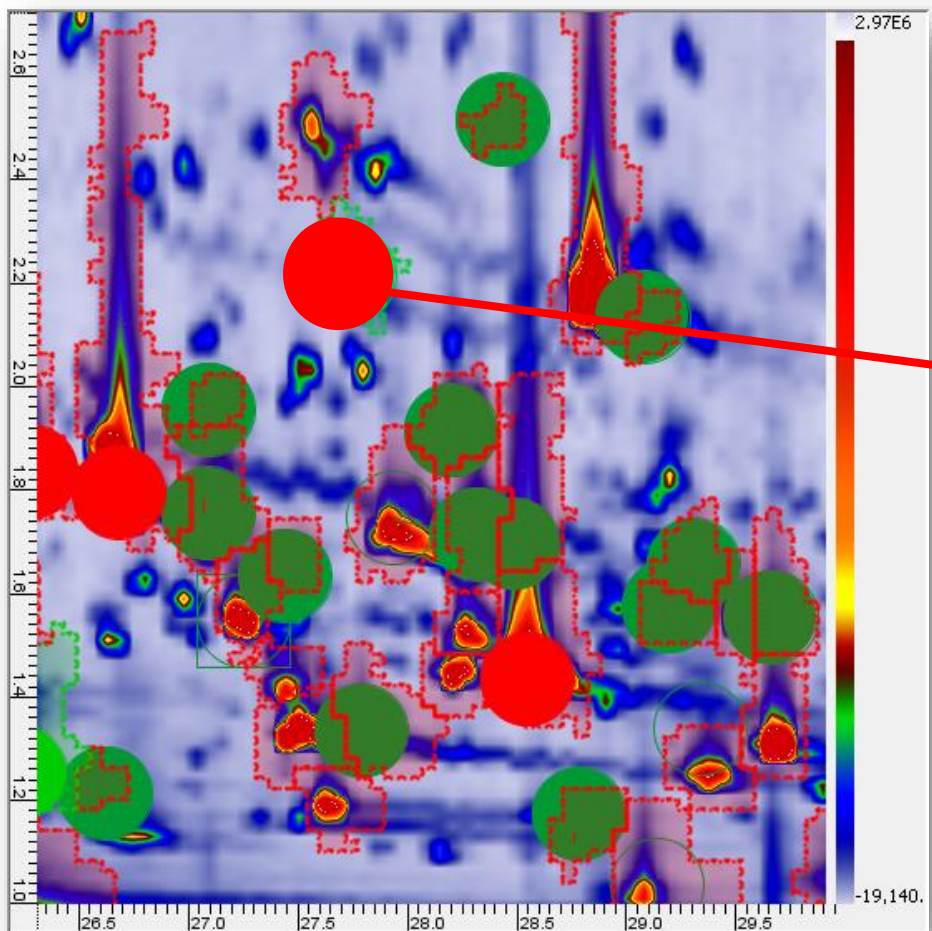
STEP 1

Data processing

Untargeted/Targeted Fingerprinting - comprehensive mapping



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Blob Properties

Labels

Compound Name:

Compound Library:

Group Name:

Constellation Name:

Compound Description

`saturated aldehydes`
`LRI (WAX) 1277±7`

Auto Fill

Flags

Include Add Text Object

Internal Standard Add Chemical Structure

Exclude Set Color Custom Color

Statistics Analysis Qualifier/Quantifier Ions

Analysis CLIC (aCLIC)

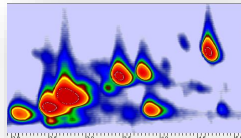
Qualifier CLIC (qCLIC)

Reference MS

Reference Peak

Hit List

OK and View Spectrum OK Cancel



STEP 2

Data processing

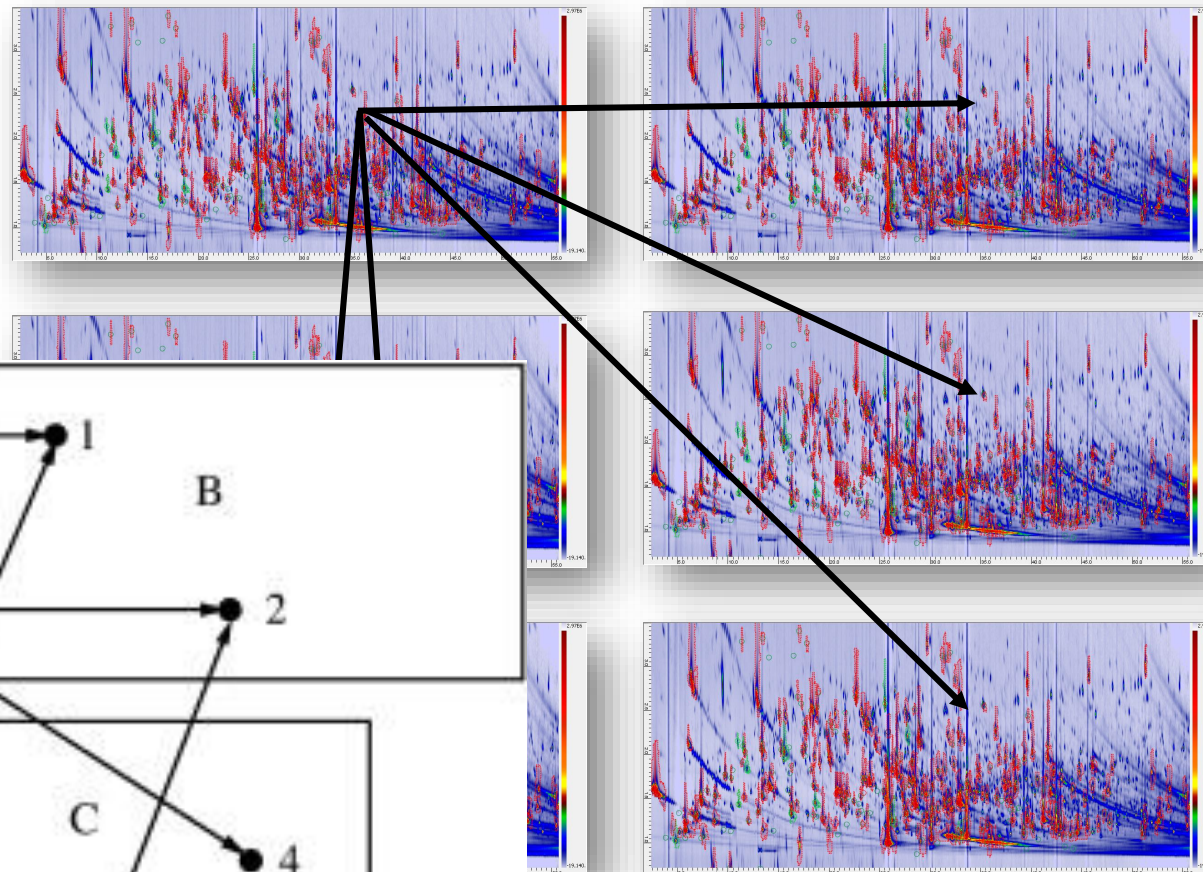
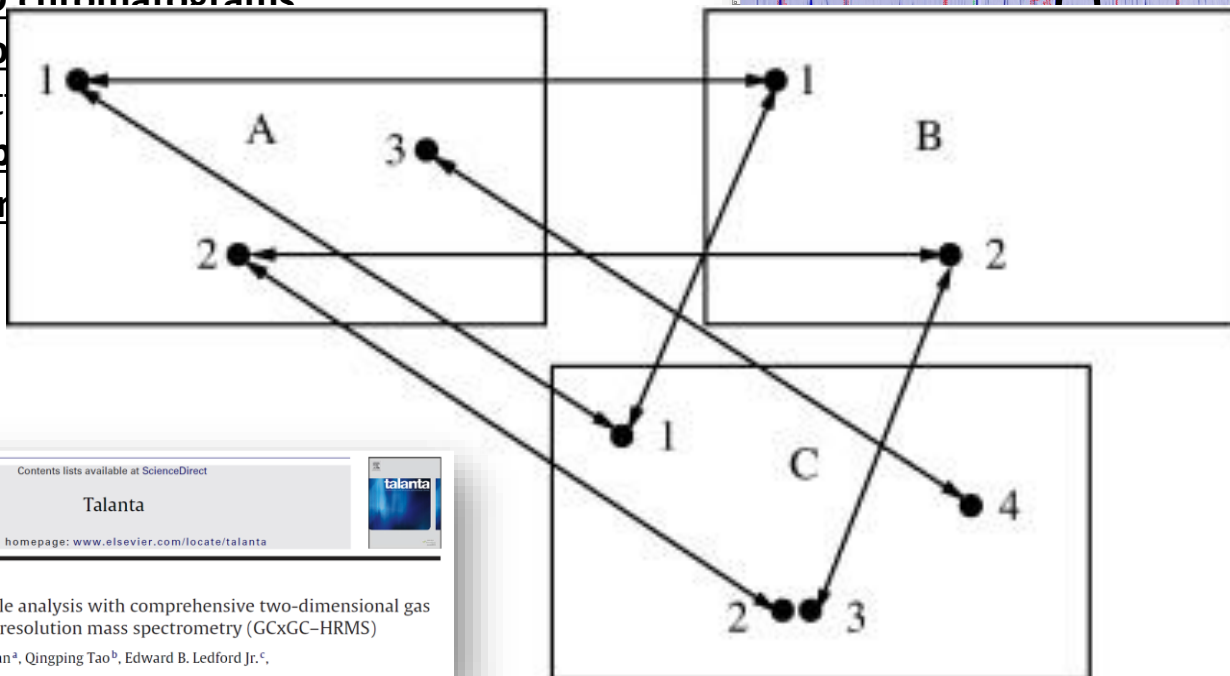
Untargeted/Targeted Fingerprinting - comprehensive mapping



Untargeted Template Construction (GC Investigator™)

Beginning with pre-targeted chromatograms:

- comprehensive pair-wise peak matching
- determination of **reliable registration peaks**
- **alignment of 2D chromatograms**
- generation of **co**
- definition of pat
- building of **temp**
- **and peak-region**

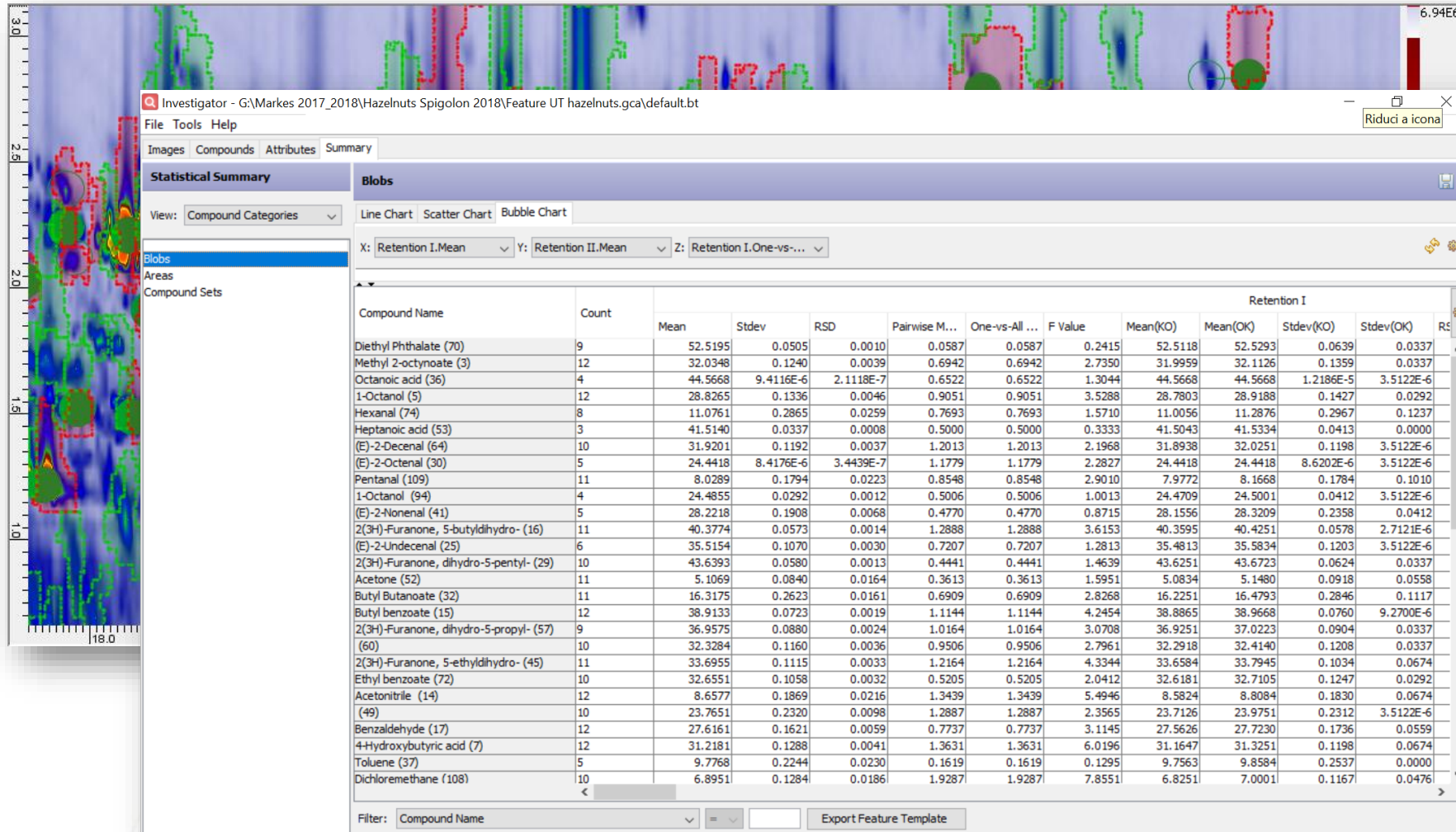


Informatics for cross-sample analysis with comprehensive two-dimensional gas chromatography and high-resolution mass spectrometry (GCxGC-HRMS)

Stephen E. Reichenbach^{a,*}, Xue Tian^a, Qingping Tao^b, Edward B. Ledford Jr.^c, Zhanpin Wu^c, Oliver Fiehn^d

STEP 2

Data processing



Targeted and **untargeted** peak(-region) features are cross-aligned between all samples and metadata collected for further processing



Challenge 1

Cocoa identification



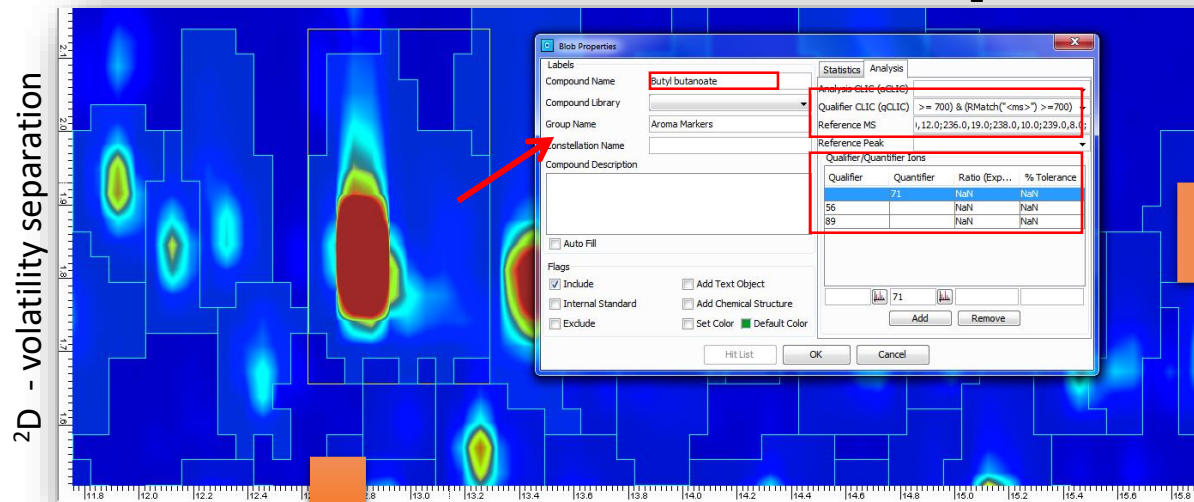
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Cocoa roasted stage **volatiles** - Mexico Chontalpa origin
HS-SPME (CAR/PDMS/DVB) - 500 mg - 50°C/50 min
¹D CW 20 m × ²D OV1701 - thermal modulation LN₂



Theobroma cacao
volatiles encrypt
information on
quality - origin -
processing impact

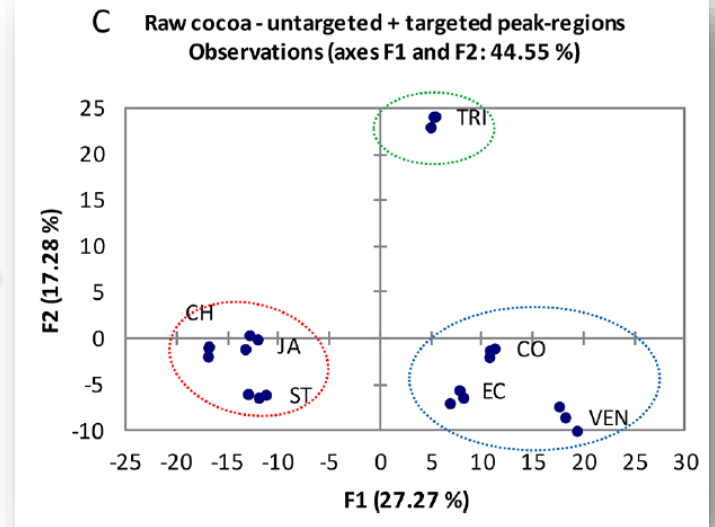
Study on seven
origins from South
America, Africa,
Sao Tomè
and Java



²D - volatility separation

¹D - polarity/volatility separation

A **template** consisting of **all detected peak-regions**
595 peak-regions including **130 targeted analytes** and
17 key-odorants eliciting characteristic cocoa notes



JOURNAL OF
AGRICULTURAL AND
FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Comprehensive Chemical Fingerprinting of High-Quality Cocoa at Early Stages of Processing: Effectiveness of Combined Untargeted and Targeted Approaches for Classification and Discrimination

Federico Magagna,[‡] Alessandro Guglielmetti,[‡] Erica Liberto,[‡] Stephen E. Reichenbach,[‡] Elena Allegrucci,[§] Guido Gobino,[§] Carlo Bichi,[‡] and Chiara Cordero^{*†}

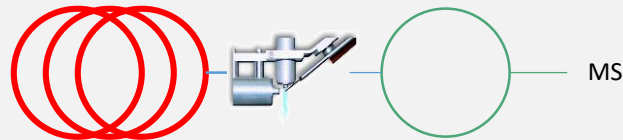


Challenge 1

Cocoa identification

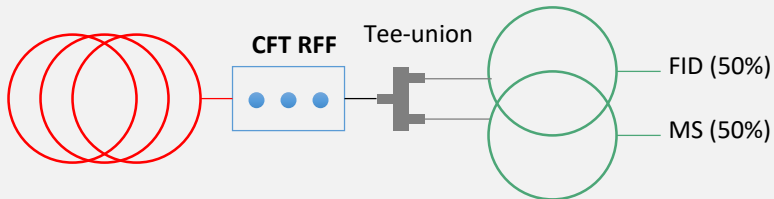


Thermal Modulation Agilent 7890-5975C with Zoex KT 2004 loop-type thermal modulator Optimode v2.0 - Cryogenic liquid nitrogen



¹D - Polar PEG (Sol-gel WAX)
30 m × 0.25 mm × 0.25 μm
He carrier @ **1.5 mL/min**

²D - Medium polarity OV1701
1.0 m × 0.10 mm × 0.10 μm
He carrier @ **1.5 mL/min**



¹D - Polar PEG (Sol-gel WAX)
10m×0.10mm×0.10μm
He carrier @ **0.30 mL/min**

²D - Medium polarity OV1701
two parallel 1.5m×0.10mm×0.10μm
He carrier @ **4 mL/min**



Differential Flow Modulation with Reverse Inject Agilent 7890-5977B HES with CFT plate for RFF DFM

Speed gain: 2.1424

Original Method Parameters

Parameter	Value
Length (m)	30 m
Inner Diameter (μm)	250 μm
Film Thickness (μm)	0.25 μm
Phase Ratio	249.25
Inlet Pressure (gauge)	251.35 kPa
Outlet Flow (mL/min)	1.5 mL/min
Average Velocity (cm/s)	16.615 cm/sec
p_{mid} Pressure (abs)	301 kPa
Holdup Time	3.0093 min
Outlet Velocity (cm/s)	18.007 cm/sec

Calculated Method Parameters

Parameter	Value
Length (m)	10 m
Inner Diameter (μm)	100 μm
Film Thickness (μm)	0.10 μm
Phase Ratio	249.25
Inlet Pressure (gauge)	509.52 kPa
Outlet Flow (mL/min)	0.3 mL/min
Average Velocity (cm/s)	11.865 cm/sec
p_{mid} Pressure (abs)	534 kPa
Holdup Time	1.4046 min
Outlet Velocity (cm/s)	12.687 cm/sec

#	Ramp Rate (°C/min)	Final Temp (°C)	Final Time (min)
Init		40	1.00
1	3.0000	260	10.00

Total Run Time: 84.33 min

#	Ramp Rate (°C/min)	Final Temp (°C)	Final Time (min)
Init		40	0.47
1	6.4272	260	4.67

Total Run Time: 39.37 min



Challenge 1

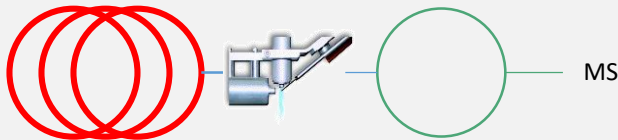
Cocoa identification



Agilent 7890-5975C with Zoex KT 2004 loop-type thermal modulator
Optimode v2.0 - Cryogenic liquid nitrogen



Thermal Modulation



¹D - Polar PEG (Sol-gel WAX)

30 m × 0.25 mm × 0.25 μm

He carrier @ 1.5 mL/min

²D - Medium polarity OV1701

1.0 m × 0.10 mm × 0.10 μm

He carrier @ 1.5 mL/min

GC Oven programming: 40°C (1') to 260°C (10') @ 3°/min

S/SL injector: 270°C, split mode, split ratio 1:20

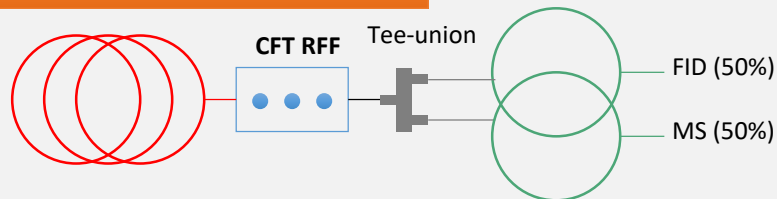
MS Transfer line: 270°C MS in EI mode, 70 eV Full Scan acquisition

Loop dimensions: 1.0 m × 0.10 mm deactivated silica

MS Tune: Atune option; Scan range 40-240 m/z; scan rate 12,500 amu/s

Optimode settings: modulation period 3s, hot-jet pulse time 250 ms
cold jet stream MFC from 35% to 5% in 60 min

Translated conditions



¹D - Polar PEG (Sol-gel WAX)

10m×0.10mm×0.10μm

He carrier @ 0.30 mL/min

²D - Medium polarity OV1701

two parallel 1.5m×0.10mm×0.10μm

He carrier @ 4 mL/min

GC Oven programming: 40°C (0.47') to 260°C (4.67') @ 6.4272°/min

S/SL injector: 260°C, split mode, split ratio 1:20

MS Transfer line: 260°C MS in EI mode, 70 eV Full Scan acquisition

MS Tune: HES Etune; Scan range 40-240 m/z; scan rate 12,500 amu/s

FID: 150 Hz acquisition frequency

Modulation valve settings: modulation delay: 0.2 s, modulation period 2s
injection time 200 ms



Differential Flow Modulation with Reverse Inject
Agilent 7890-5977B HES with CFT plate for RFF DFM

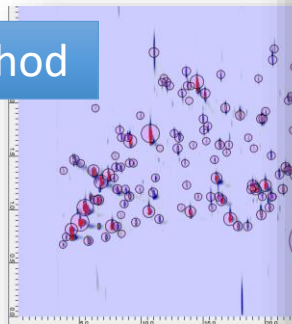


Challenge 1

Cocoa identification



Original method

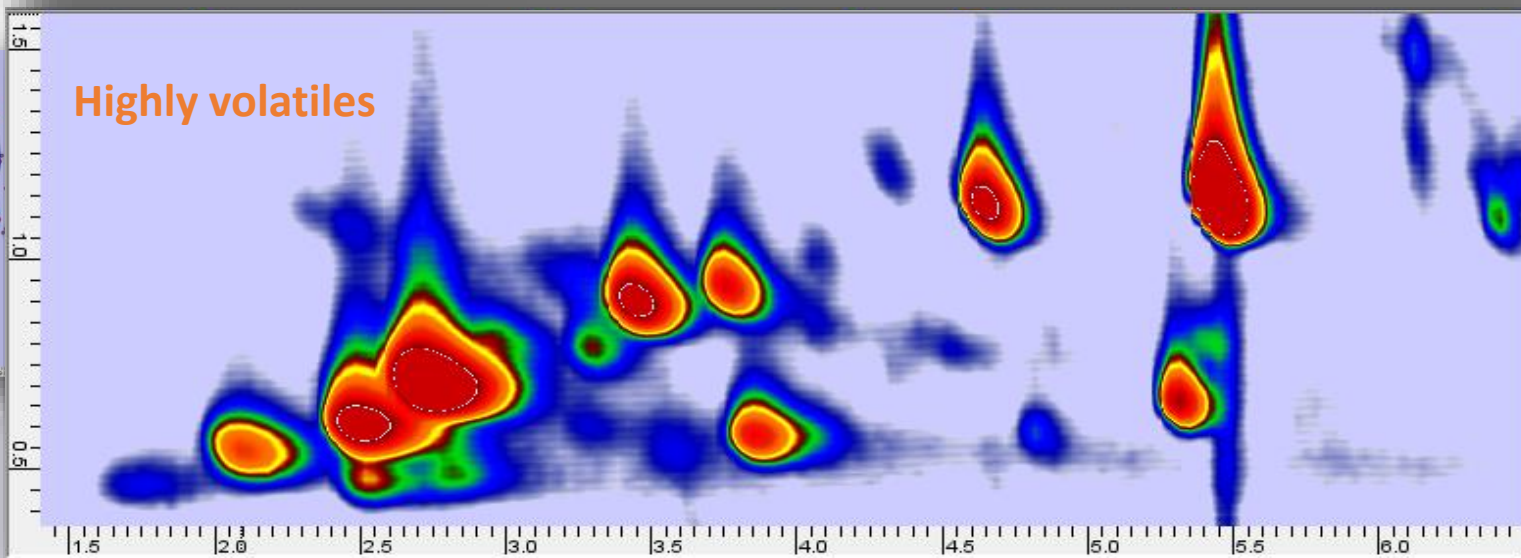
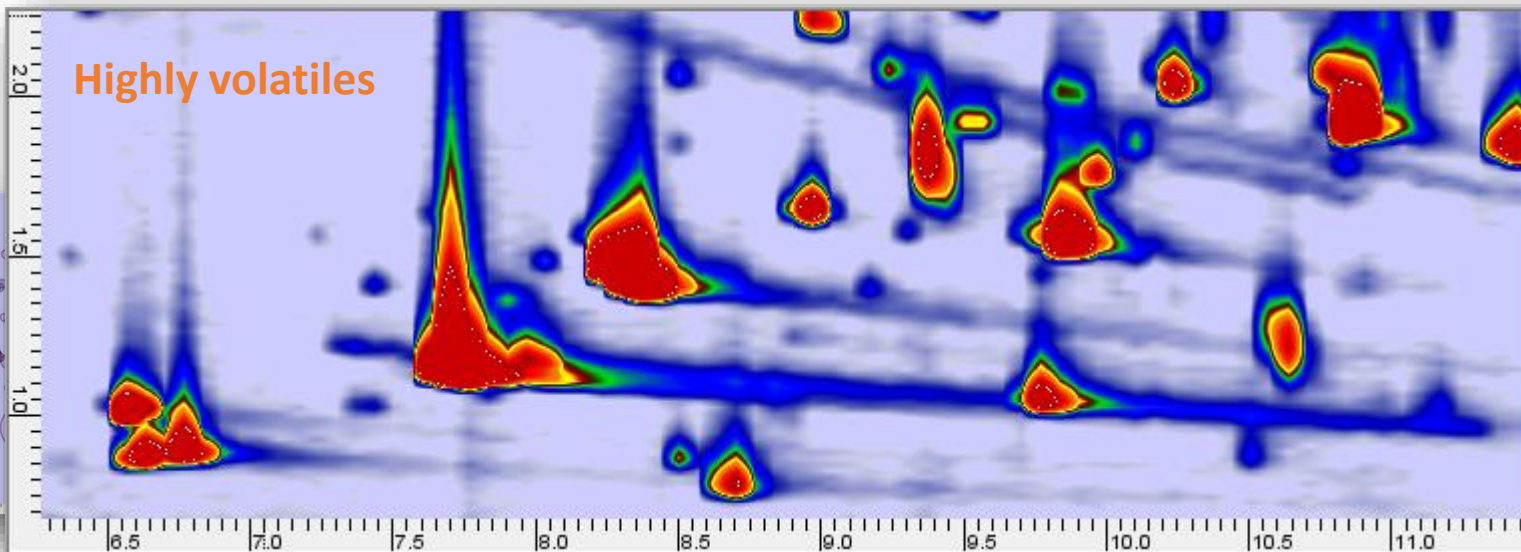
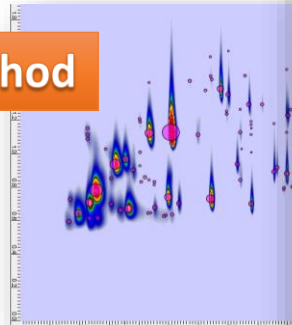


Cocoa roasted stage **volatiles** - Mexico Chontalpa origin
HS-SPME (CAR/PDMS/DVB) - 500 mg - 50°C/50 min
¹D CW 20 m × ²D OV1701 - method translation



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Translated method





Challenge 1

Cocoa identification

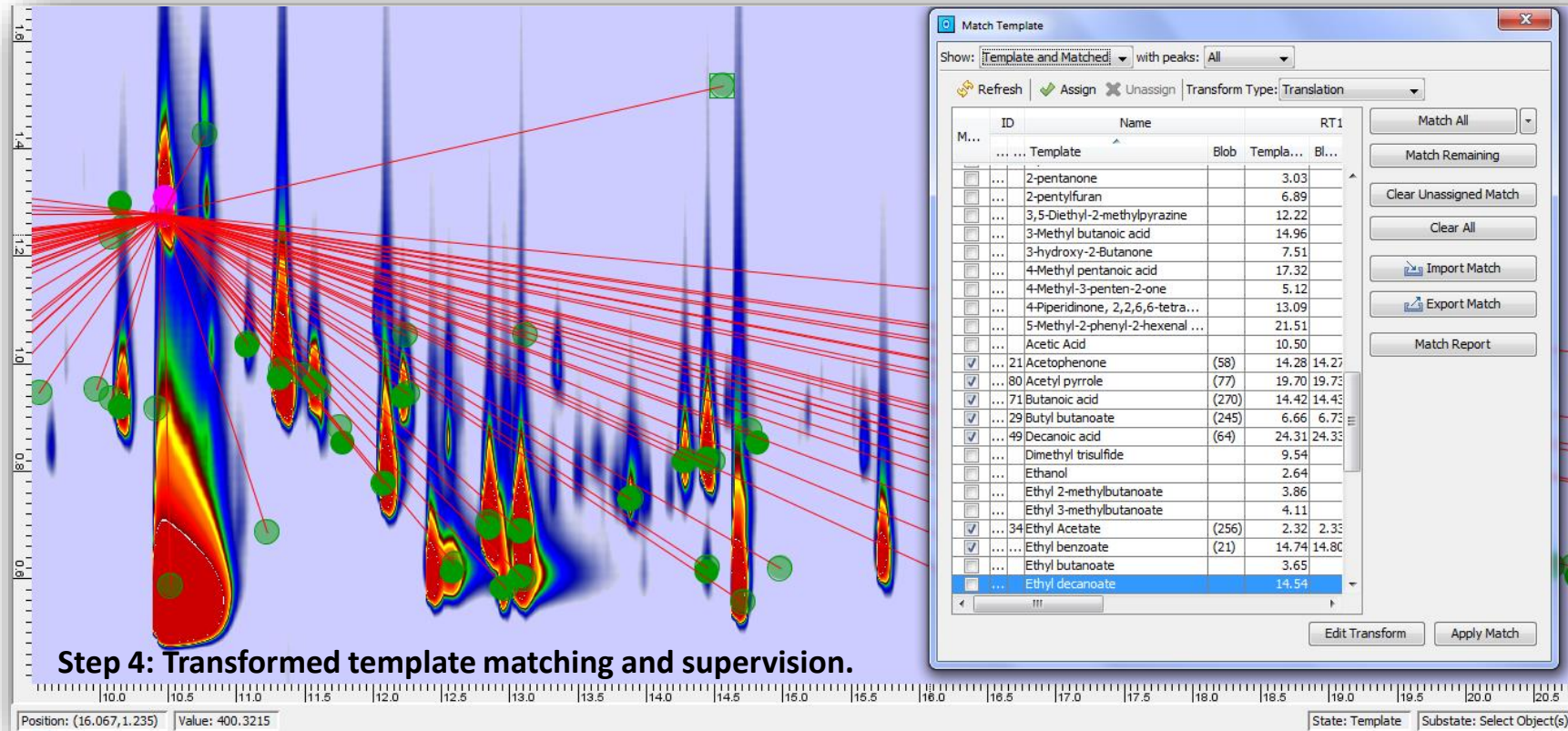


Target analysis

Adaptation of peaks pattern

Template transformation

Second-degree polynomial global transformation algorithms^{1,2}



Cocoa roasted stage

volatiles - Mexico

Chontalpa origin

HS-SPME

(CAR/PDMS/DVB) - 500 mg

- 50°C/50 min

1. S.E. Reichenbach et al. Anal. Chem. 87 (2015) 10056–10063
2. D.W. Rempe et al. Anal. Chem. 88 (2016) 10028–10035



Challenge 1

Cocoa identification



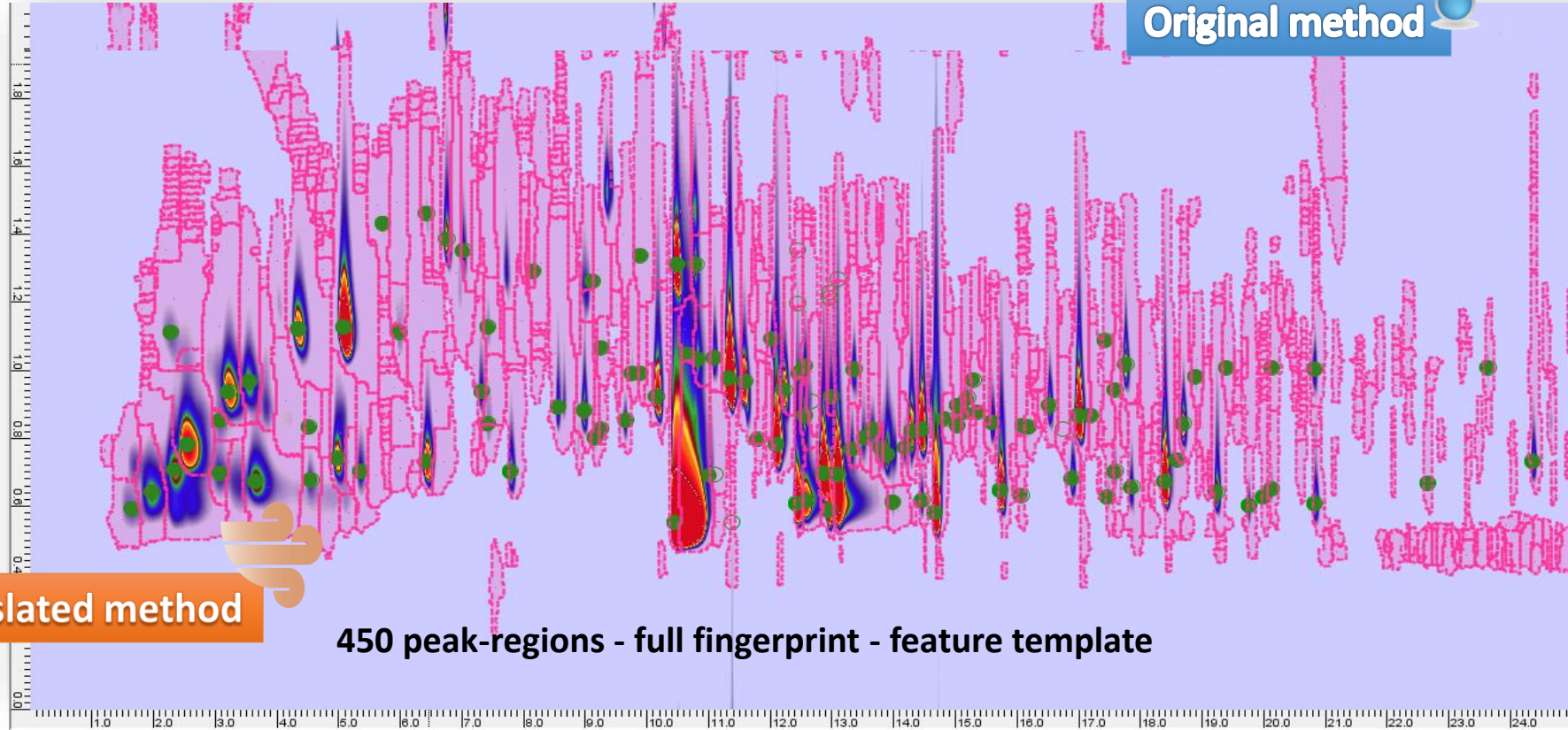
UT fingerprinting

Peak-regions (targeted and untargeted)



595 peak-regions - full fingerprint - feature template

Original method



Translated method

450 peak-regions - full fingerprint - feature template

Independent processing - UT fingerprinting
2D peaks have different σ in both dimensions
tailored peak-regions



Cocoa roasted stage

volatiles - Mexico

Chontalpa origin

HS-SPME

(CAR/PDMS/DVB) - 500 mg

- 50°C/50 min



Challenge 1

Cocoa identification



Original method



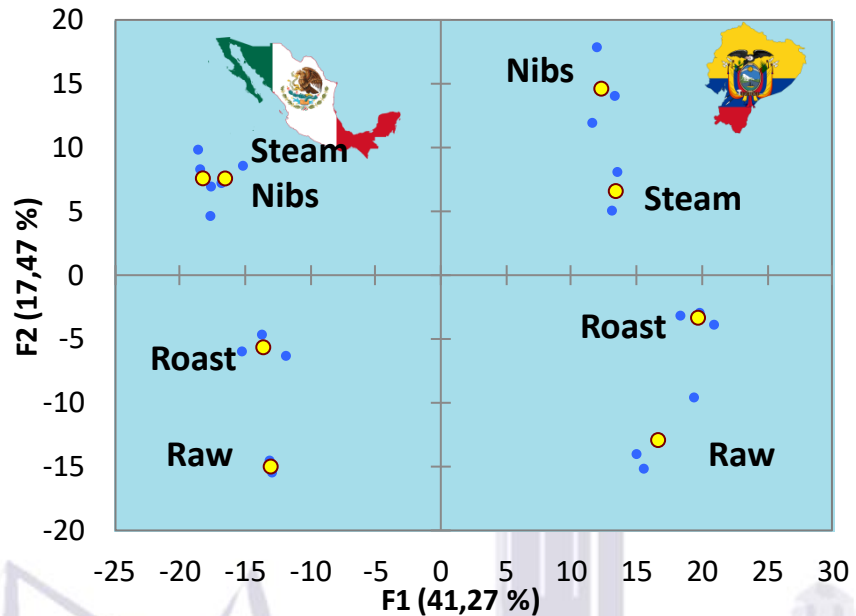
HS-SPME - GC×GC-MS
Loop-type Thermal Modulation

Translated method

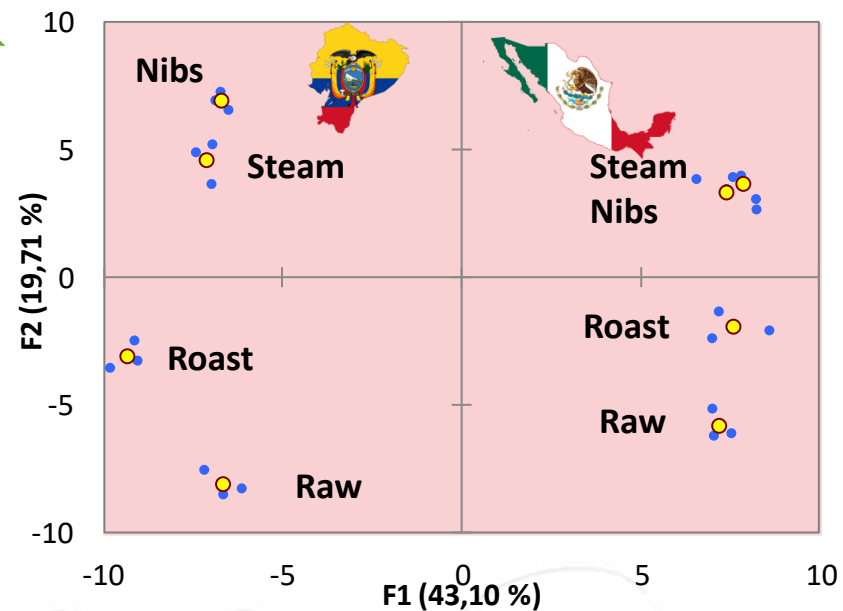


HS-SPME - GC×2GC-MS/FID
Differential Flow Modulation with Reverse Inject

Observations (axes F1 and F2: 58,74 %)



Observations (axes F1 and F2: 62,81 %)





Challenge 1

Cocoa identification



UT fingerprint Peak-regions (targeted and untargeted)



Original method

HS-SPME - GC×GC-MS
Loop-type Thermal Modulation



Translated method

HS-SPME - GC×2GC-MS/FID
Differential Flow Modulation

Multiple factor analysis Targeted 2D peaks Chontalpa Mexico



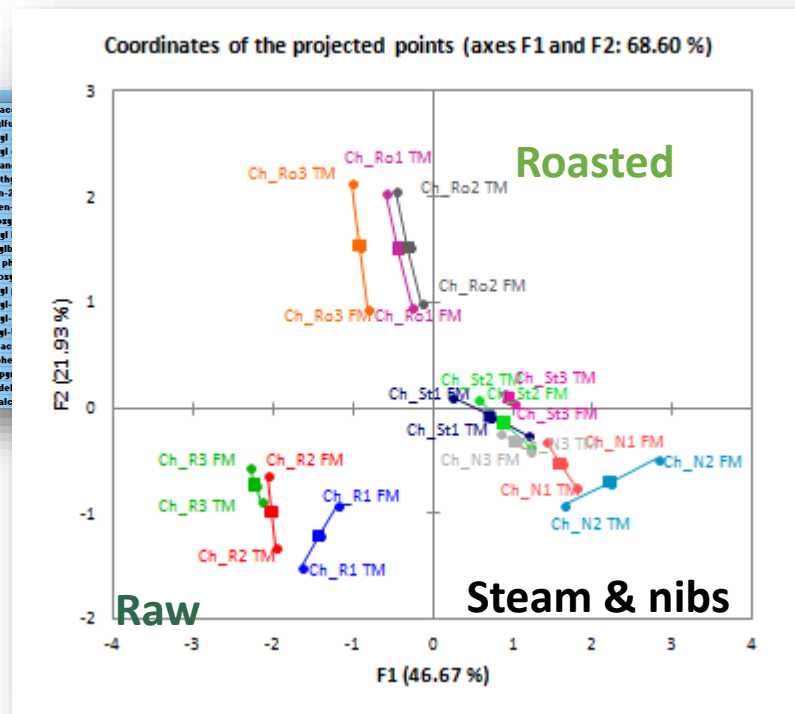
Loss of sensitivity

130 vs. 75 reliably identified targets
595 vs. 450 reliable peak-regions
17 vs. 14 key-aroma compounds

- ✓²D two parallel columns
- ✓ higher outlet flows toward MS

Fingerprint informative role is preserved

55	Pentyl ac
56	2-pentylf
57	2-Phenyl
58	2-Phenyl
59	2-Propan
60	3,5-Dieth
61	3-Ethen-2
62	3-Hepten
63	3-Hydroxy
64	3-Methyl
65	3-methyl
66	4-Ethyl p
67	4-Hydroxy
68	4-Methyl
69	4-Methyl
70	5-Methyl
71	6-methyl
72	Acetic ac
73	Acetophe
74	Acetyl pp
75	Benzalde
76	benzyl ac



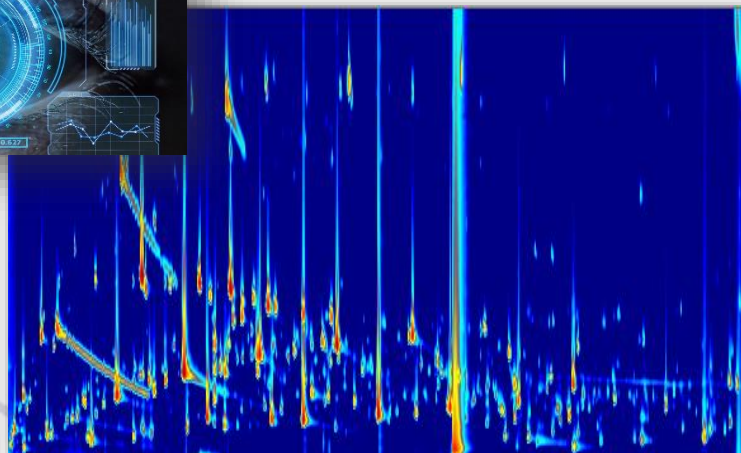


Challenge 2

Computer vision



Quality assessment at industrial level focuses on morphological aspects, presence of damaged kernels, perceivable sensory defects (mould, rancid, *cimiciato*, stale etc..)



Step-ahead in quality assessment *molecular resolution* probes:



1. Cuadros-Rodríguez, L.; Ruiz-Samblás, C.; Valverde-Som, L.; Pérez-Castaño, E.; González-Casado, A. *Anal. Chim. Acta* **2016**, *909*, 9–23.
2. Cialìè Rosso, M.; Mazzucotelli, M.; Bicchi, C.; Charron, M.; Manini, F.; Menta, R.; Fontana, M.; Reichenbach, S. E.; Cordero, C. J. *Chromatogr. A* **2020**, *1614* (460739)



Challenge 2

Computer vision



Computer Vision strategy Classification trees

Volatiles patterns
diagnostic of spoilage

Computer Vision tools
Prompt identification of
non-conform samples
and confident rejection



Good (OK)


Rancid (KO)

Spoiled (KO)

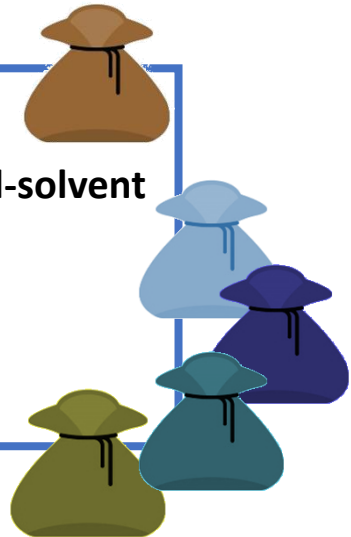
Collection of defected hazelnuts

- ✓ harvest years
- ✓ origin
- ✓ shelf-life stage

Flash profiling



Mould
Mould-rancid-solvent
Rancid
Rancid-stale
Solvent
Uncoded KO



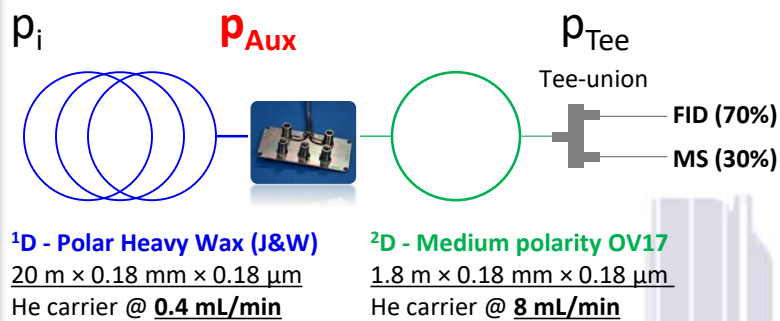


Challenge 2

Computer vision



Platform



Headspace SPME



Tools

ISTDs Pre-loading

α and β-Thujone
100 mg/L (5.0 μL)

Methyl-2-octynoate
100 mg/L (5.0 μL)



5 min
50°C



Hazelnuts
powder
0.100 g



50 min
50°C

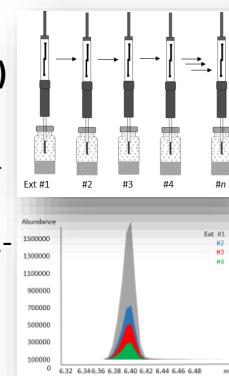
Multiple Headspace SPME - quantitation

MHS-SPME enables **accurate quantitation** of **several markers (ESTD and response factors)**

secondary products of lipid oxidation (hexanal, heptanal, octanal, nonanal, (E)-2-octenal, (E)-2-nonenal);

key-aroma compounds (3-methylbutanal, ethyl 2-methylbutanoate, (E)-β-damascenone, 2-nonanone, heptanoic acid etc);

markers of defected hz (nonanoic acid, butyric acid, 4-heptanol, 1-pentanol, propanoic acid, 2-heptanol, pentanoic acid etc)



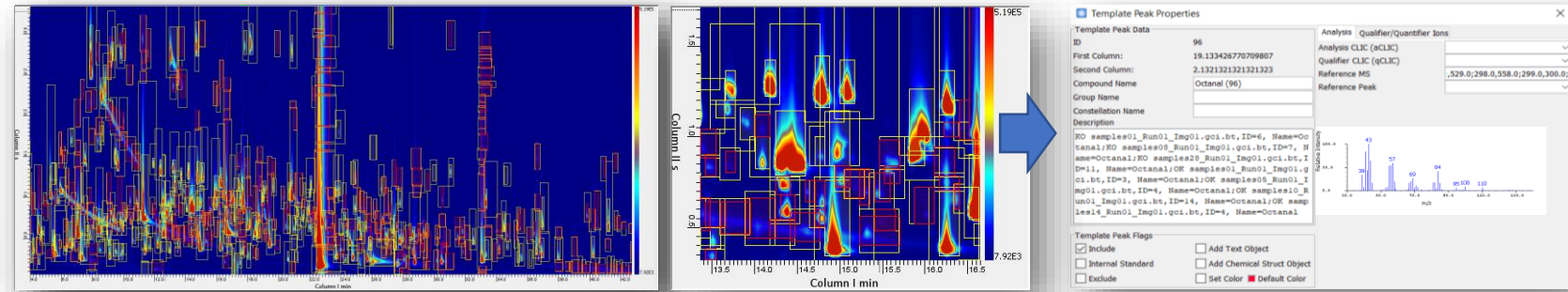


Challenge 2

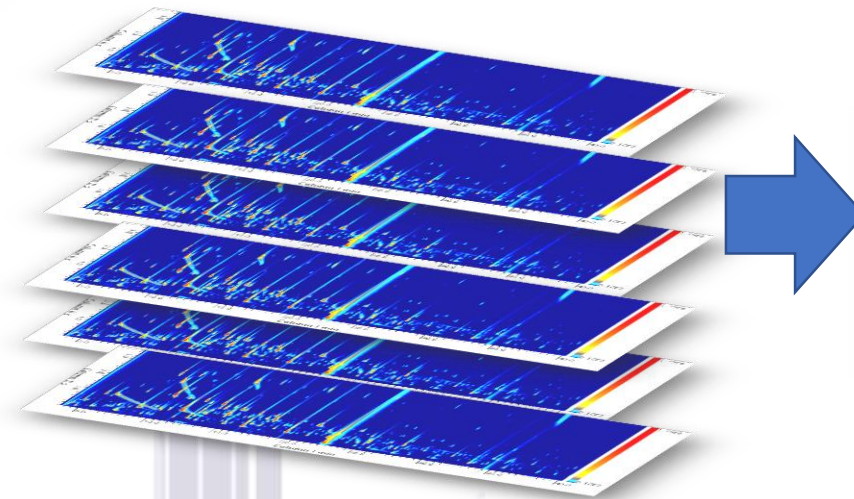
Computer vision



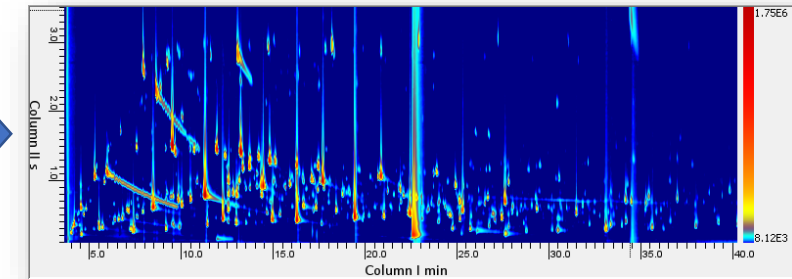
Untargeted/Targeted (UT) fingerprinting on single chromatograms



Generation of composite class-images from samples groups - one for each sensory defect
 ✓ patterns re-alignment by reliable 2D peaks and raw data summation (composite image)



Cumulative class-image "Mould"



The effect of dominant variables (origin, harvest year, cultivar, shelf-life etc..) is minimized while the "signature" of *mold* sensory defect emphasized - easier detection

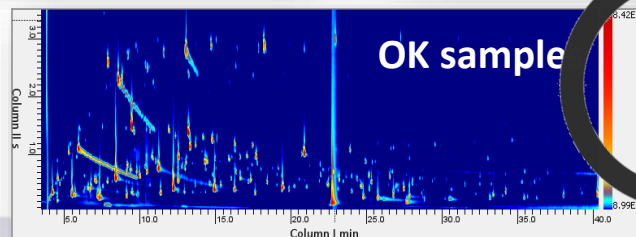
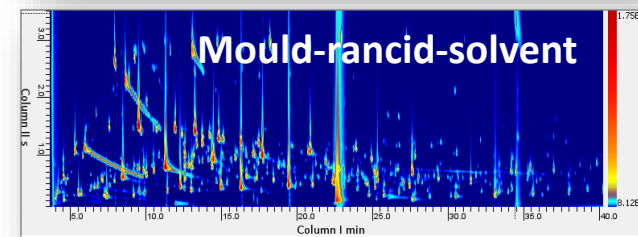
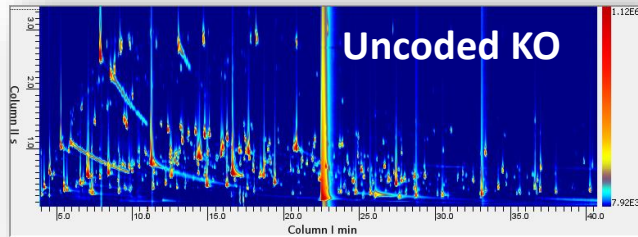
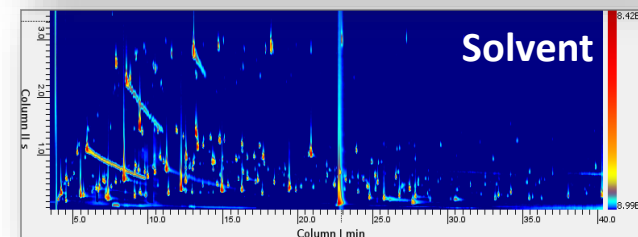
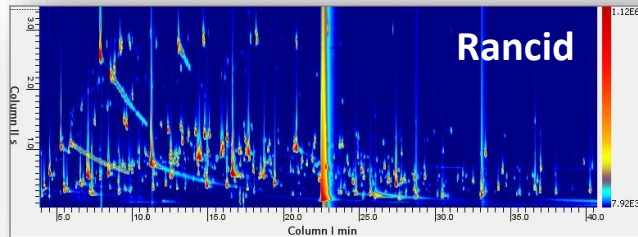
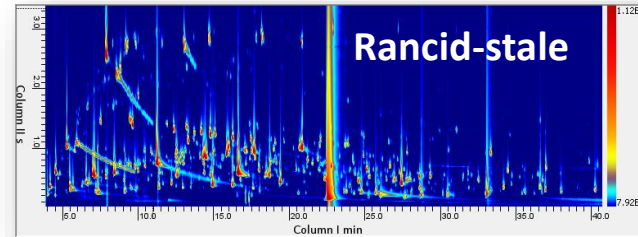
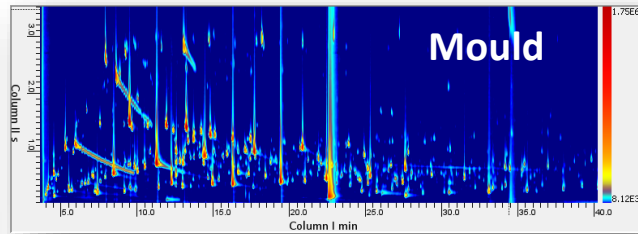


Challenge 2

Computer vision



Composite class-images from samples groups - one for each sensory defect



- Mould
- Mould-rancid-solvent
- Rancid
- Rancid-stale
- Solvent
- Uncoded KO



Reference OK samples

Contents lists available at ScienceDirect

Food Chemistry

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

An effective chromatographic fingerprinting workflow based on comprehensive two-dimensional gas chromatography – Mass spectrometry to establish volatiles patterns discriminative of spoiled hazelnuts (*Corylus avellana* L.)

Federico Stilo^a, Erica Liberto^a, Nicola Spigolon^a, Giuseppe Genova^a, Ginevra Rosso^a, Mauro Fontana^a, Stephen E. Reichenbach^{b,c}, Carlo Bicchi^a, Chiara Cordero^a

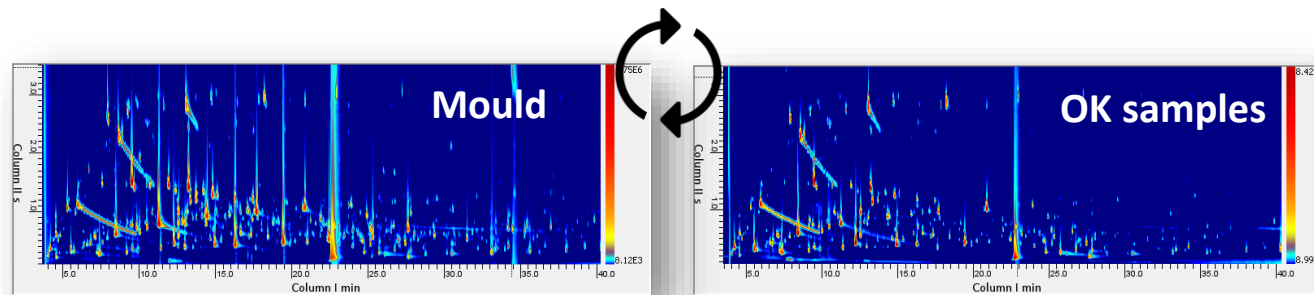


Challenge 2

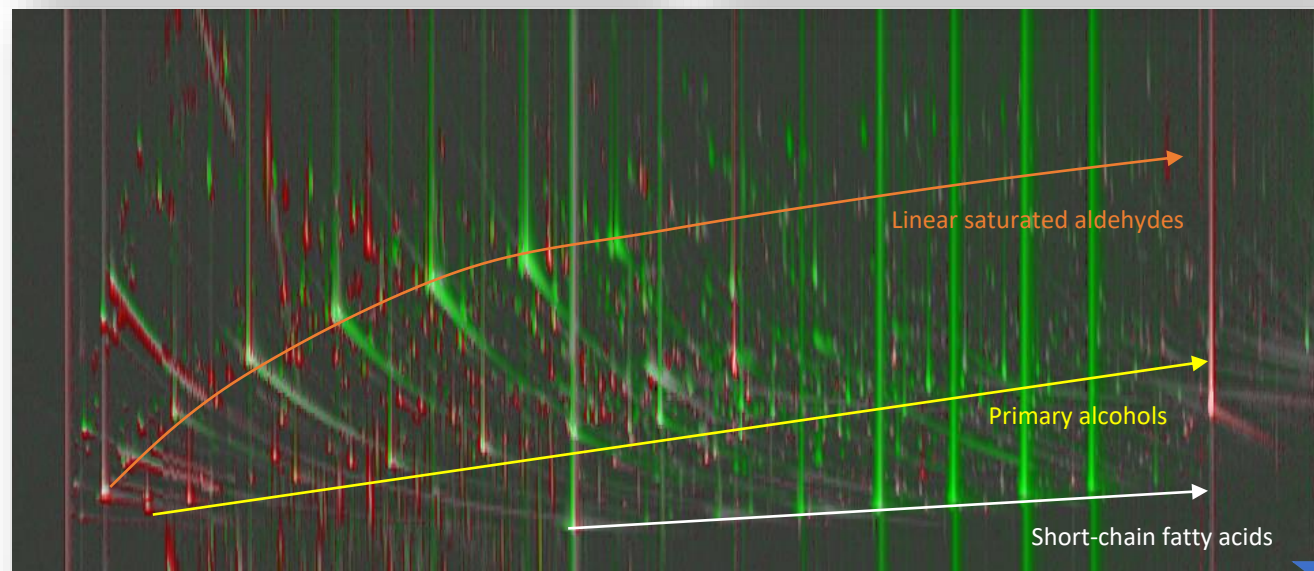
Computer vision



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**Datapoint features
fingerprinting combined
to peak-regions UT
fingerprinting**



**Computer vision and
chemical patterns**

First Image

BlobID	Compound ...	Retention I	Retention II	Peak Value
9	Heptanoic acid	41.417	0.661	1027913.00
10		10.908	1.351	2002502.00
11		14.642	1.562	1919573.00
12	Nonanoic acid	47.367	0.721	1150889.00
13		21.000	0.931	1722252.00

Second Image

BlobID	Compound ...	Retention I	Retention II	Peak Value
97	Heptanoic acid	41.533	0.631	165949.000
98	1-Decene	10.208	2.883	165851.000
99	3-Penten-2-...	12.658	1.021	163385.000
100	Oxirane, pe...	13.592	1.682	162084.000
101	1-Nonene	7.467	2.132	161864.000



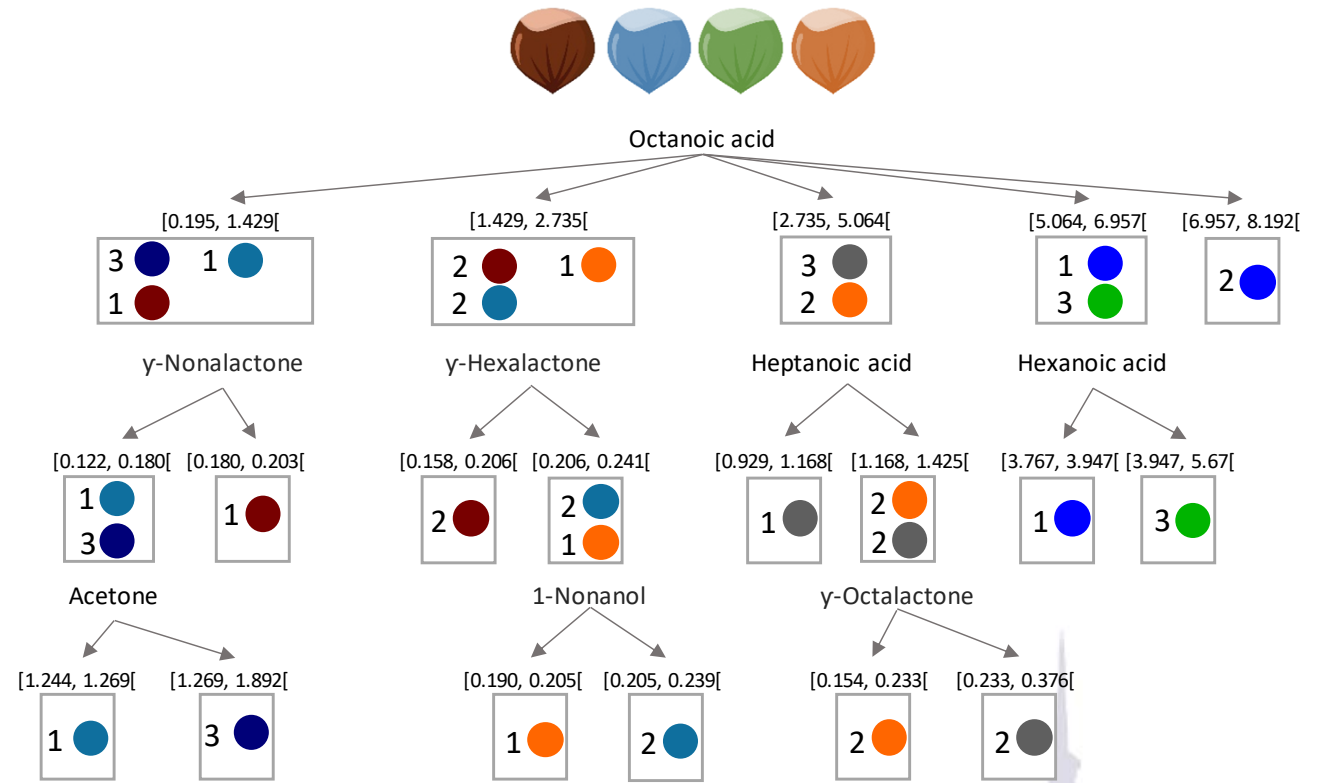
Challenge 2

Computer vision



VOCs patterns distinctive of spoiled hazelnuts guide effective classification into seven classes.

- ✓ **Octanoic acid** guides the classification tree being positively correlated to **mould**;
- ✓ **γ-nonalactone, γ-hexalactone, acetone, and 1-nonanol** are decisive to classify OK and rancid samples;
- ✓ **heptanoic and hexanoic acids and γ-octalactone** are present in high relative abundance in rancid-solvent and rancid-stale samples





Challenge 3

AI smelling



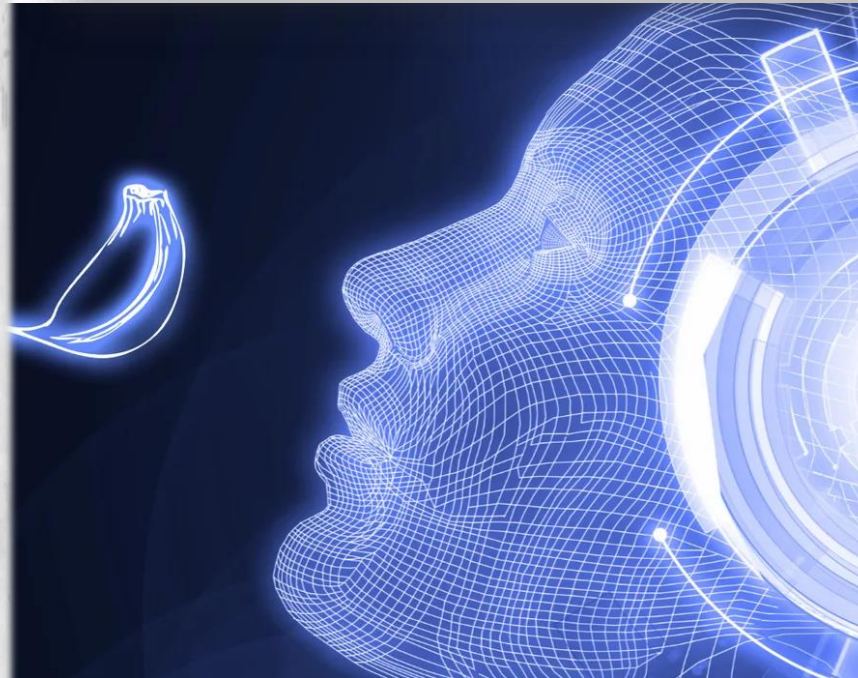
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Our noses are busy beasts. At any given moment, multiple smells are competing for our attention, and somehow the brain can tell when it's smelling an orange even against a backdrop of other scents, say perfume or soap.

The brain's olfactory bulb has hundreds of receptors tracking odors all the time, and yet somehow keeps everything straight. Scientists at Cornell University working with researchers at Intel have just created an AI algorithm trained to recognize 10 scents by mimicking the mammalian olfactory bulb (MOB).

Give the algorithm a computer chip to run on and it can learn to identify new odors.¹

[1] <https://bigthink.com/>



Artificial Intelligence Smelling²

Context: *Sensomics*³

Principle: key-odorants and odorants patterns evoke specific smells/aroma qualities while contributing to define the overall flavor perception of a food

Methods: extract, isolate, quantify potent odorants by reliable methods

Outcome: *Sensomics*-based expert system (SEBES)² capable to predict key-aroma signatures of food without using human olfaction

2. Dunkel, A.; Steinhaus, M.; Kotthoff, M.; Nowak, B.; Krautwurst, D.; Schieberle, P.; Hofmann, T. *Angew. Chemie - Int. Ed.* 53 (28) (2014) 7124–7143.

3. Nicolotti, L.; Mall, V.; Schieberle, P. *J. Agric. Food Chem.*, 67 (2019) 4011–4022



Challenge 3

AI smelling

Characterization of the Key Odorants in High-Quality Extra Virgin Olive Oils and Certified Off-Flavor Oils to Elucidate Aroma Compounds Causing a Rancid Off-Flavor

Anja Neugebauer, Michael Granvogel, and Peter Schieberle*

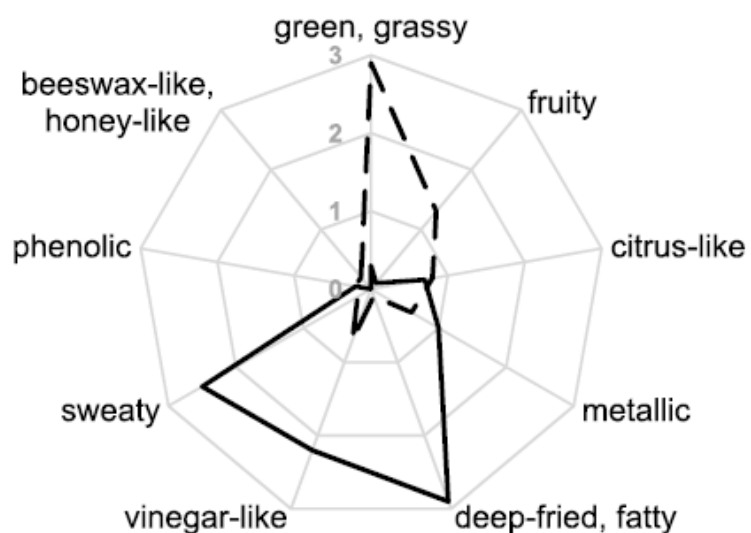


Figure 1. Aroma profile analysis of the rancid olive oil (*RanOO1*, solid line) and the premium extra virgin olive oil (*PreOO1*, dashed line).

aroma compound	OT _{oil} ^a (μg/kg)	OAV ^b	
		PreOO1	RanOO1
(<i>E,Z</i>)-2,4-decadienal	4 ^c	<1	3480
hexanoic acid	460	<1	3070
octanal	140	<1	2590
hexanal	300	4	1090
(<i>E</i>)-2-octenal	120 ^d	<1	1000
(<i>E,E</i>)-2,4-decadienal	66	<1	971
butanoic acid	34	<1	821
acetic acid	350	10	614
3-ethylphenol	8 ^d	<1 ⁱ	516
pentanoic acid	400	<1	480
(<i>E</i>)-2-nonenal	140	<1	385
(<i>E,E</i>)-2,4-nonadienal	30	<1	325
(<i>Z</i>)-2-nonenal	4	<1	144
heptanal	500	<1	89
<i>trans</i> -4,5-epoxy-(<i>E</i>)-2-decenal	13	23	78
(<i>E</i>)-2-heptenal	1200	<1	66
(<i>E</i>)-2-decenal	2200 ^d	n.c. ^k	33
(<i>E,Z</i>)-2,4-nonadienal	30 ^e	n.c. ^k	33
nonanal	610 ^d	<1	27
3-methylbutanoic acid	11	<1	20
(<i>E,Z</i>)-2,6-nonadienal	65	<1	8
(<i>E</i>)-2-undecenal	7700 ^d	<1	8
(<i>E,Z</i>)-2,4-heptadienal	55 ^f	<1 ⁱ	5



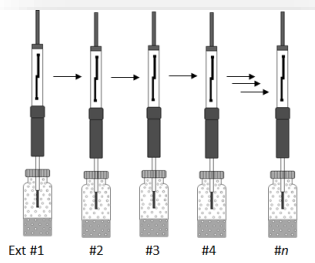
Challenge 3

AI smelling



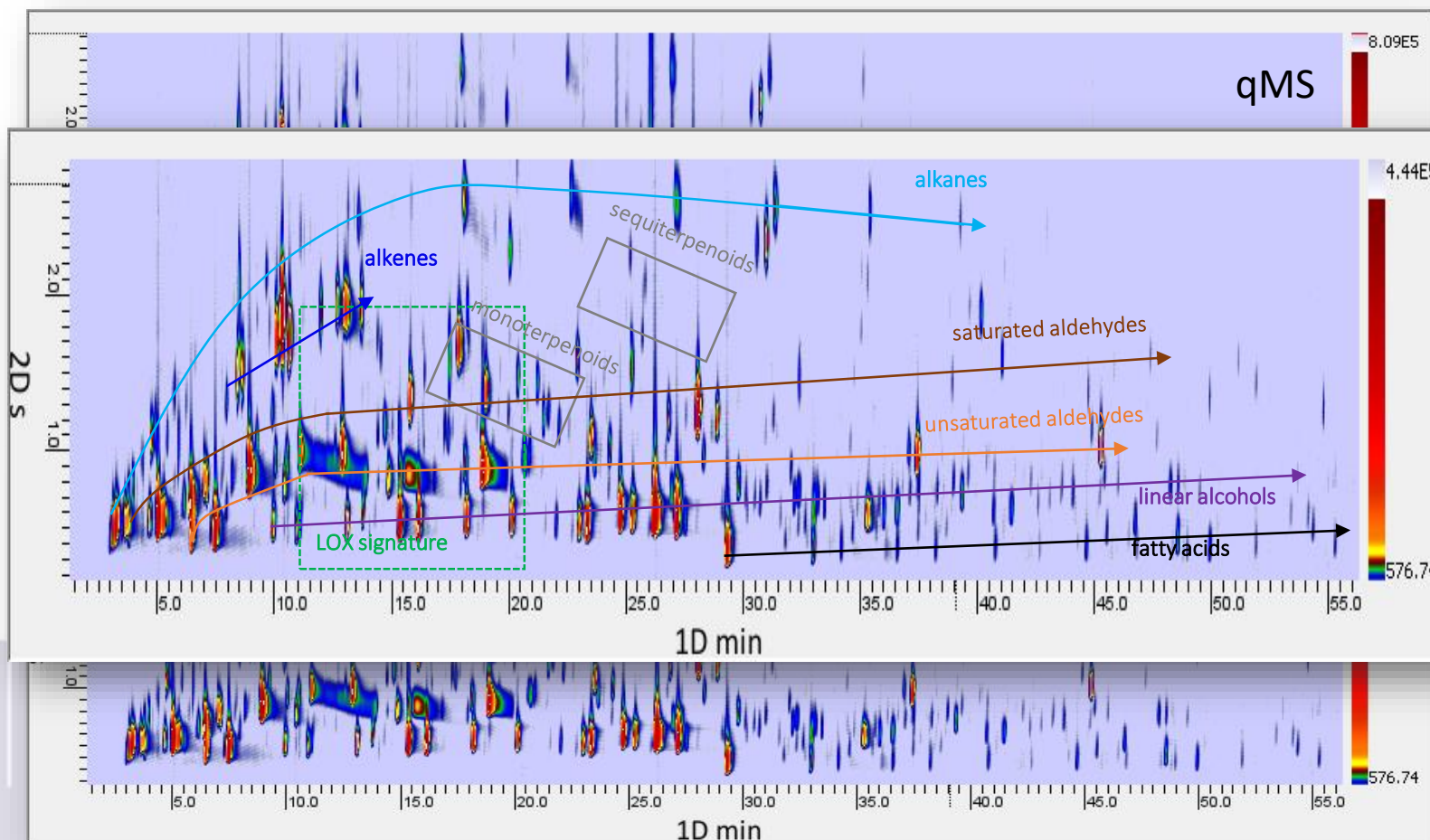
Develop a sensomics-based expert system acting as AI smelling machine

Multiple Headspace SPME
Accurate quantification / ESTD and RF



42 analytes
key-aromas
markers

Differential-flow modulator
parallel detection qMS/FID





Challenge 3

AI smelling

Extra virgin olive oil - EVOO

Identification of markers of origin and of sensory quality (i.e., positive attributes and defects)
AI smelling



Italy - Regional discrimination



Italy vs. Brazil

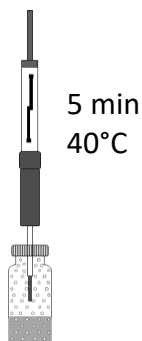


HS SPME - HS linearity conditions

ISTDs Pre-loading

α and β -Thujone
100 mg/L (5.0 μ L)

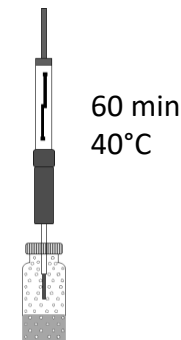
Methyl-2-octynoate
1000 mg/L (5.0 μ L)



Sampling

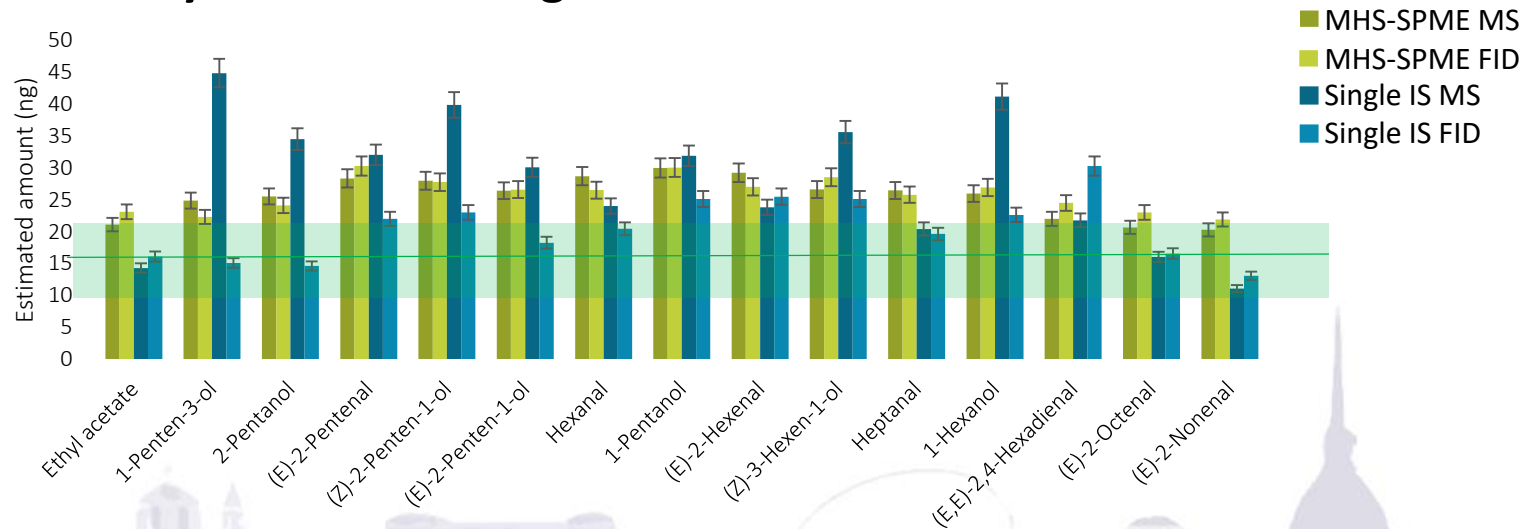
EVOO

0.100 g



Predicted Relative Response Factors (RRFs) based on combustion enthalpies and molecular structure - FID quantification without ESTD

Accuracy results on 25 ng calibration solution





Challenge 3

AI smelling

JOURNAL OF
**AGRICULTURAL AND
FOOD CHEMISTRY**

pubs.acs.org/JAFC



Article

Chromatographic Fingerprinting Enables Effective Discrimination and Identification of High-Quality Italian Extra-Virgin Olive Oils

Federico Stilo, Ana M. Jiménez-Carvelo,* Erica Liberto, Carlo Bicchi, Stephen E. Reichenbach, Luis Cuadros-Rodríguez, and Chiara Cordero*

1-Penten-3-one -

Contents lists available at [ScienceDirect](https://www.sciencedirect.com)

Journal of Chromatography A

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



Delineating the extra-virgin olive oil aroma blueprint by multiple headspace solid phase microextraction and differential-flow modulated comprehensive two-dimensional gas chromatography

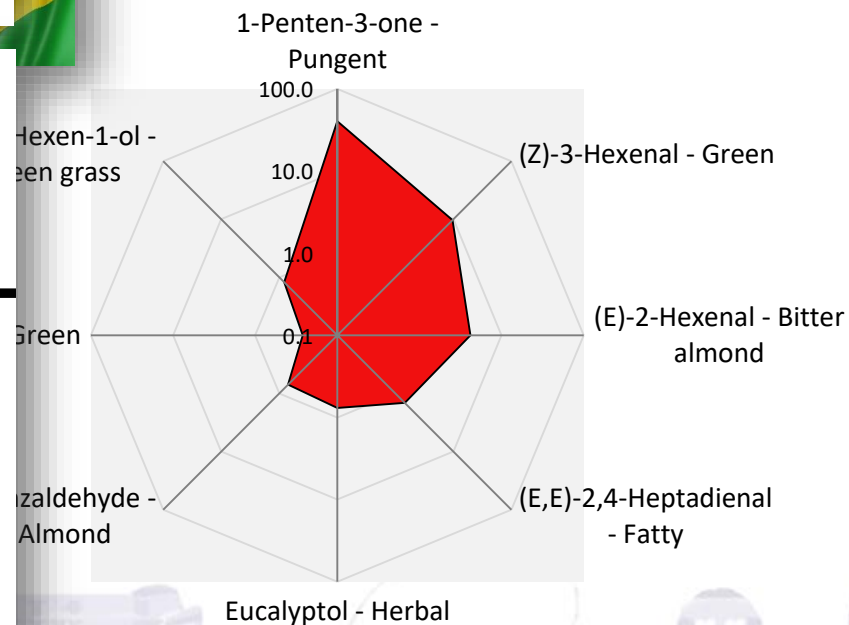
Federico STILO^a, Maria del Pilar SEGURA BORREGO^b, Carlo BICCHI^a, Sonia BATTAGLINO^b, Raquel Maria CALLEJÓN FERNANDEZ^b, Maria Lourdes MORALES^b, Stephen E. REICHENBACH^{c,d}, James MCCURRY^e, Daniela PERONI^f, Chiara CORDERO^{a,*}



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Brazil blueperint





Gestalt



...a configuration or pattern of elements so unified as a whole that it cannot be described merely as a sum of its parts...

Chromatographic Fingerprinting and Computer vision



Accurate quantitative fingerprinting/profiling

**Artificial Intelligence smelling machine
molecular resolution tool**



G=STALT

noun \ gə-ˈstält

understanding the whole,
not merely the sum of
its parts.

Chiara Cordero: GC-GC cannot be an alternative to GC×GC! They are both capable of expanding the potentials of 1D-GC where a single dimension is not sufficient or selective enough to solve an analytical challenge. However, one is still a multiple 1D-GC approach (that is, GC-GC) and does not require a change of mindset or skills for new users while, as already mentioned, GC×GC requires a "jump" towards new measurement concepts. Once we overcome this gap, we cannot turn back!



GC: The State of the Art

Chairperson: Pat Sandra
Participants: Steven Lehotay
Hans-Gerd Janssen
Chiara Cordero
Frank David
John Hinshaw

GC: The State of the Art

November 01, 2017

By Chiara Cordero, Pat Sandra, John Hinshaw, Hans-Gerd Janssen, Frank David, Steven Lehotay



Chiara Cordero: I see GC×GC growing in core application areas, including petrochemical, environmental, food and flavours, natural products, and metabolomic studies, and in my research activity I've met new users approaching this technique with curiosity but also with many prejudices and false convictions. My feeling is that we still are in the "induction period".

The possibility of applying dedicated pattern recognition approaches to the analysis of 2D chromatographic data opens new perspectives for fingerprinting studies. This last aspect is a key feature of the technique and it will soon trigger the widespread use of GC×GC in many fields. As experts and passionate chromatographers we have to continue research in the direction of making this technique more intuitive and easy to use with new data analysis tools and approaches to create a "toolbox" for various applications.

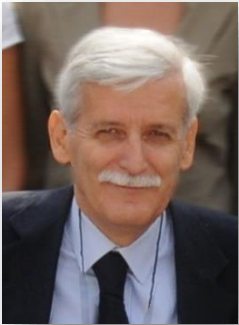


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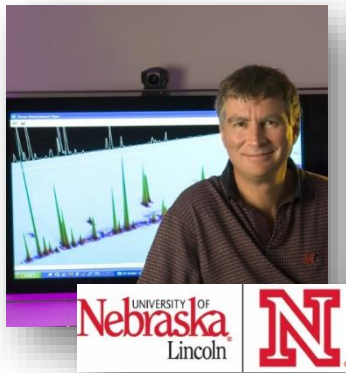
Thank you for your attention

Acknowledgments

Prof. Carlo Bicchi



Prof. Stephen E Reichenbach



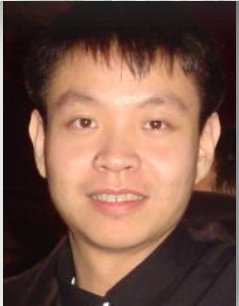
Dr. Andrea Caratti



Dr. Simone Squara



Applications and Core
Technology University
Research (ACT-UR)
Project #4294



Dr. Qingping Tao

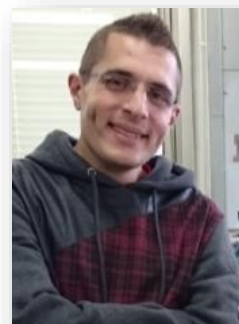
Dr. Marta Cialìe Rosso PhD



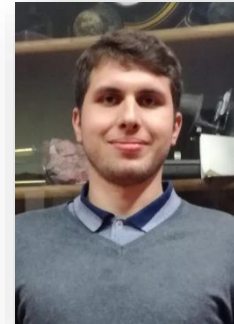
Dr. Federico Stilo PhD



Dr. Alessandro Guglielmetti PhD



Dr. Federico Magagna PhD



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Firmenich



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<https://www.gcxgc-symposium.com/>



19th International GCxGC Symposium

May 29 – June 2, 2022

Canmore, Alberta

Home

Symposium Information

GCxGC Awards

WELCOME

On behalf of the GCxGC committee, I am excited to welcome everyone to the 19th International GCxGC Symposium to be held in beautiful Canmore, Alberta.

We are planning this as a hybrid event so that we can include as many people as possible.

Prof. James Harynuk
University of Alberta
Symposium Chair



PROGRAM

The preliminary outline of our scientific and social program is now available!

New this year, we will be holding an advanced course as well as our familiar introductory course.

[Click here to visit the program page](#)

COVID-19 INFO

We are committed to providing a safe in-person meeting experience and facilitating the navigation of travel requirements for our attendees as much as we can. [Please check our Covid-19 Page for current travel](#)

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