UNIVERSITÀ DI TORINO

100 + 1 year anniversary of SCG!
November the 28th, 2022

SOCIÉTÉ CHIMIQUE DE GENÈVE

From *Sensomics* to AI smelling and Computer Vision: Exploring the chemical sensory code of premium chocolate

Chiara Cordero

Dipartimento di Scienza e Tecnologia del Farmaco, Università degli Studi di Torino
Via P. Giuria 9, I-10125 Turin, Italy
email: chiara.cordero@unito.it

UNIVERSITÀ DI TORINO

SOCIÉTÉ CHIMIQUE DE GENÈVE

Foreword

...the boundaries between chemistry and biology are vanishing[1]...

Food-omics domains and strategies of investigation

The role of multidimensional (gas) chromatography

Artificial Intelligence Smelling and *Computer vision*

Premium cocoa origin *identitation*
and aroma blueprint

- ✓ *Computer vision* a change of perspective
- ✓ *Artificial Intelligence smelling* for large screenings

Conclusive remarks

From *Sensomics* to AI smelling and Computer Vision:
Exploring the chemical sensory code of premium chocolate

Prof. Irene Chetschik

1. Prof. Thomas Hofmann J. Agric. Food Chem. 2015, 63, 32, 7095–7096

UNIVERSITÀ DI TORINO

...the boundaries between chemistry and biology are vanishing...

Prof. Thomas Hofmann
J. Agric. Food Chem. 2015, 63, 32, 7095–7096

REVIEW ARTICLE

JOURNAL OF SEPARATION SCIENCE

Comprehensive two-dimensional gas chromatography as a boosting technology in food-omic investigations

Federico Stilo[1] | Carlo Bicchi[1] | Stephen E. Reichenbach[2,3] | Chiara Cordero[1]

Food metabolomics
Chemical composition of food *vs.*

- ✓crop botanical origin
- ✓harvesting area
- ✓climate impact
- ✓post-harvest
- ✓storage conditions

Nutrimetabolomics
Human metabolome by

- ✓dietary patterns
- ✓specific foods
- ✓nutrients
- ✓micro-organisms
- ✓bioactives

Sensomics
Food hedonic profile

- ✓ potent odorants
- ✓ chemical odor code
- ✓ volatiles patterns
- ✓ odor activity value
- ✓ olfactometry

Food safety

- ✓ Xenobiotics
- ✓ Non-intentionally added substances
- ✓ Contaminants
- ✓ MOSH/MOAH

Higher level information Understanding

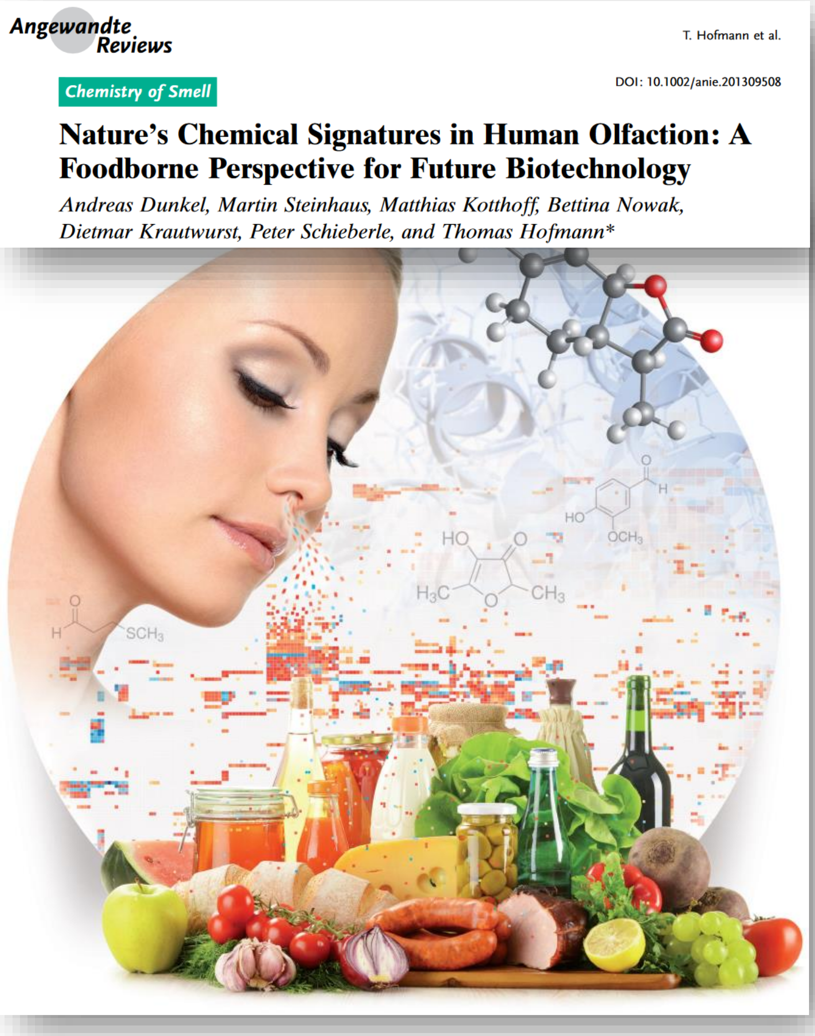
Data mining
machine learning
unsupervised/supervised

Data processing
targeted/untargeted
profiling/fingerprinting

Multidimensional Analytical platforms

1D/2D Chromatography
Detection:

- (HR)-Mass Spectrometry
- Olfactometry
- Parallel detection


Angewandte Reviews

T. Hofmann et al.

Chemistry of Smell

DOI: 10.1002/anie.201309508

Nature’s Chemical Signatures in Human Olfaction: A Foodborne Perspective for Future Biotechnology

*Andreas Dunkel, Martin Steinhaus, Matthias Kotthoff, Bettina Nowak, Dietmar Krautwurst, Peter Schieberle, and Thomas Hofmann**

UNIVERSITÀ DI TORINO

Artificial Intelligence smelling machine

Context: *Sensomics*[1]

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

Methods: extract, isolate, quantify potent odorants by reliable and robust methodologies

Outcome: **Sensomics-Based Expert System[2] (SEBES)** that predicts key-aroma signatures of food without using human olfaction.

Computer Vision

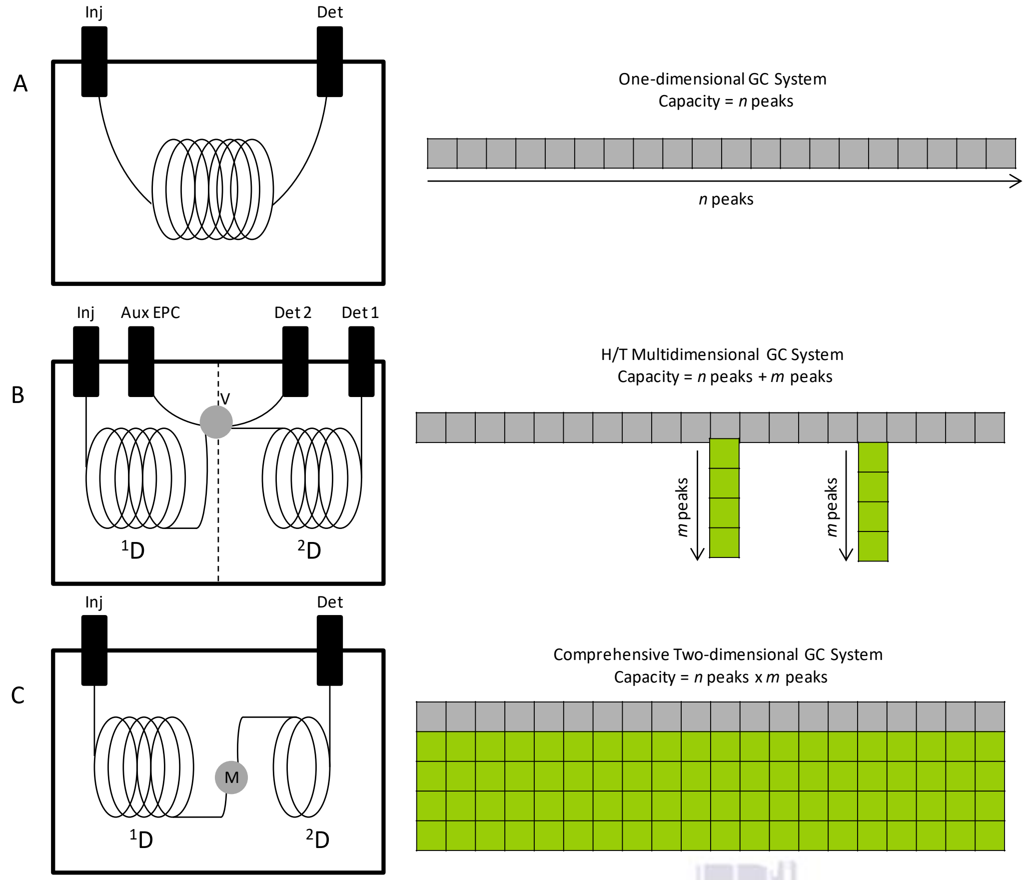
"... is a field of artificial intelligence (AI) that enables computers and systems to derive meaningful information from digital images....— and take actions or make recommendations based on that information.
If AI enables computers to think, computer vision enables them to see, observe and understand."[3]

https://www.viatech.com/en/2018/05/history-of-artificial-intelligence/

1. Dunkel, A.; Steinhaus, M.; Kotthoff, M.; Nowak, B.; Krautwurst, D.; Schieberle, P.; Hofmann, T. Angew. Chemie - Int. Ed. 53 (28) (2014) 7124–7143.
2. Nicolotti, L.; Mall, V.; Schieberle, P. J. Agric. Food Chem., 67 (2019) 4011–4022
3. https://www.ibm.com/topics/computer-vision

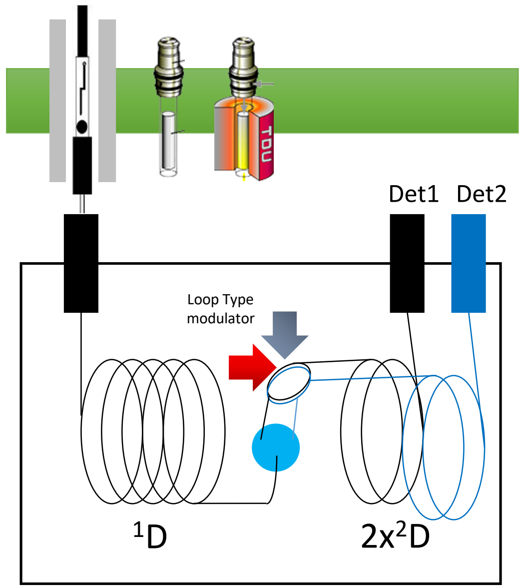
Comprehensive 2D GC

PLATFORMS

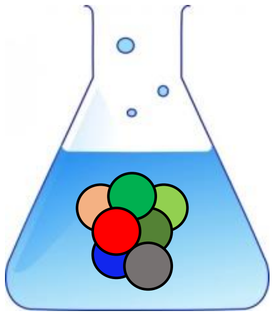


- ✓ Separation power (peak capacity) is given by the product of the two chromatographic dimensions (GC×GC)[1]
- ✓ Independent (almost) displacement in both dimensions produces rational retention patterns for homologue series[1]
- ✓ Band compression (in space - for thermal modulators) produces signal-to-noise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

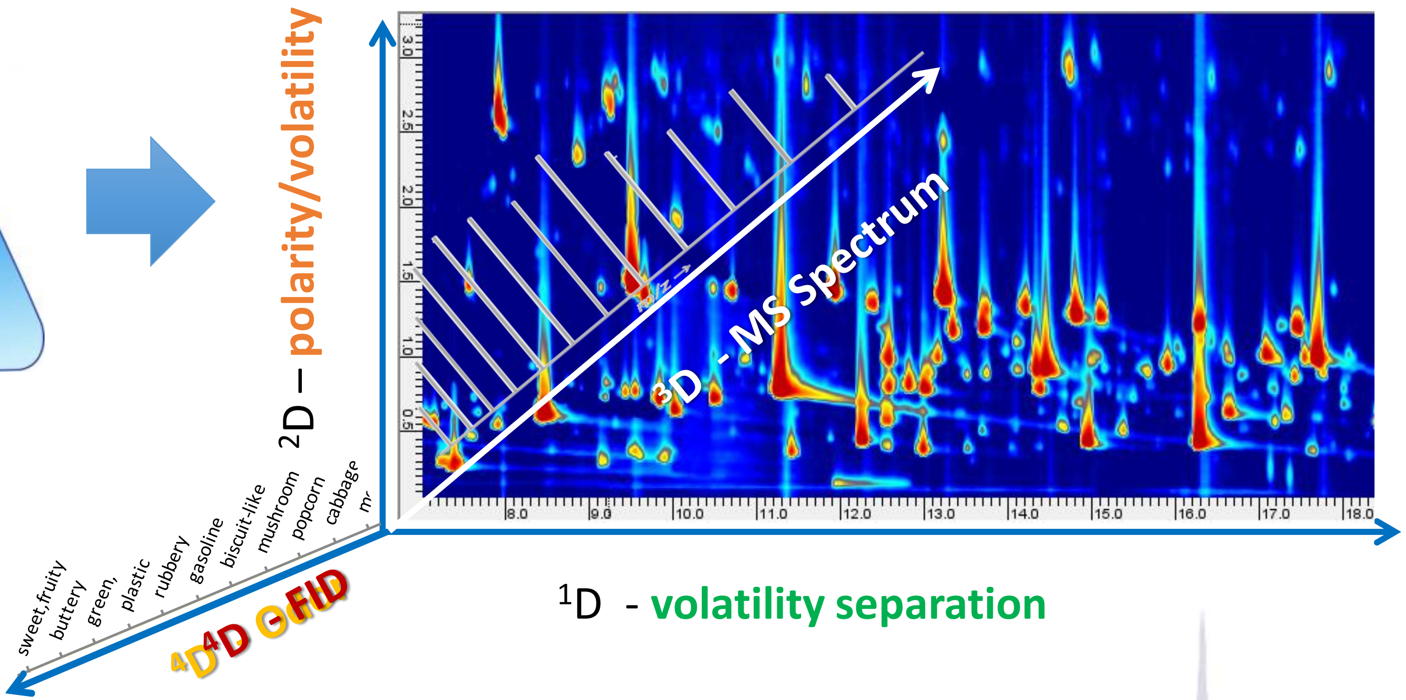
[1] Giddings, J.C. (1987), Concepts and comparisons in multidimensional separation. J. High Resol. Chromatogr., 10: 319-323.



Sample prep - GC×2GC-MS/FID
Sample prep - GC(O)×GC-MS



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



UNIVERSITÀ DI TORINO

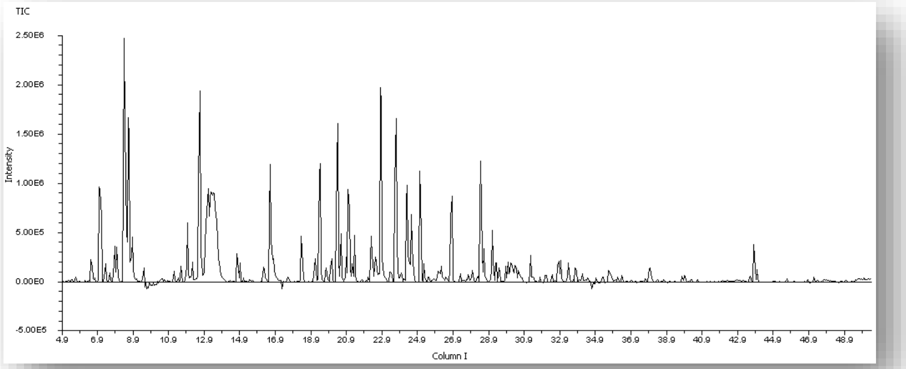
PLATFORMS

[1] J.C. Giddings J. Chromatogr. A 703(1995) 3–15.

UNIVERSITÀ DI TORINO

DATA PROCESSING

Conventional 1D GC



Profiling[1]
detailed analysis of the chemical pattern

Target(ed) analysis[2]
GC-MS metadata (retention and spectra)
analytes identity and amount

Chromatographic fingerprinting[1,3]
general and rapid high-throughput screening -> discriminate/classify samples

Limits
high chemical dimensionality[4]
complexity of food samples

isomers/isobars might co-elute and analytes discrimination becomes challenging

Need of multiple dimensions (separation / detection) to explore compositional complexity[4]

Prof. Philip Marriott
“If you are not using GC×GC, you will never know what you are missing!”

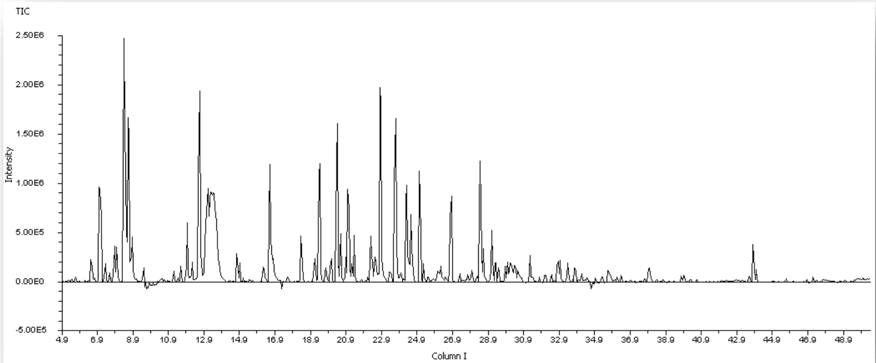
J. Agric. Food Chem. 69, 11535–11537 (2021)

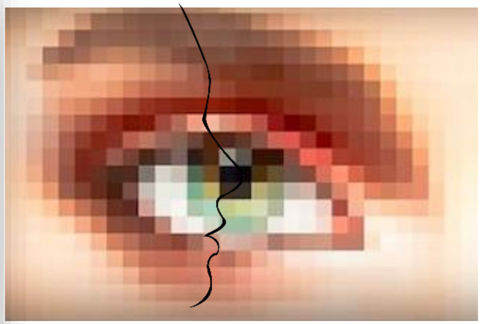
[1] Harrigan G., Goodacre R. (2003) Metabolic profiling: its role in biomarker discovery and gene function analysis. Kluwer Academic Publishers: Boston
[2] S.E. Reichenbach et al. J. Chromatogr. A 1226 (2012) 140– 148
[3] Stilo, F., Bicchi, C., Jimenez-Carvelo, A.M., Cuadros-Rodriguez, L., Reichenbach, S.E., Cordero, C. TrAC Trends Anal. Chem. 134 (2021) 116133
[4] Giddings, J. C. (1995) J. Chromatogr. A. 703, 3–15.

UNIVERSITÀ DI TORINO

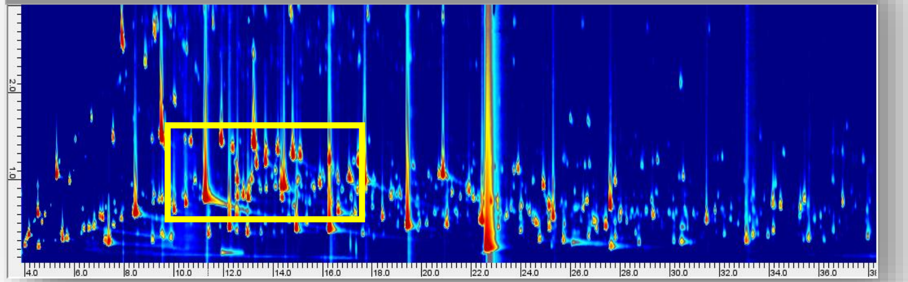
DATA PROCESSING

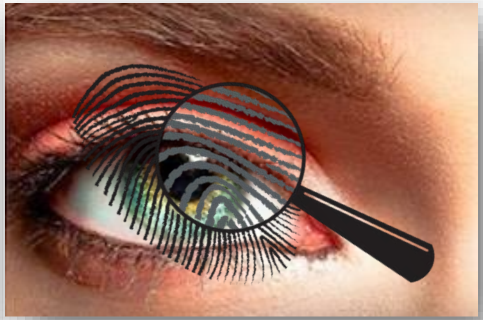
Conventional 1D GC

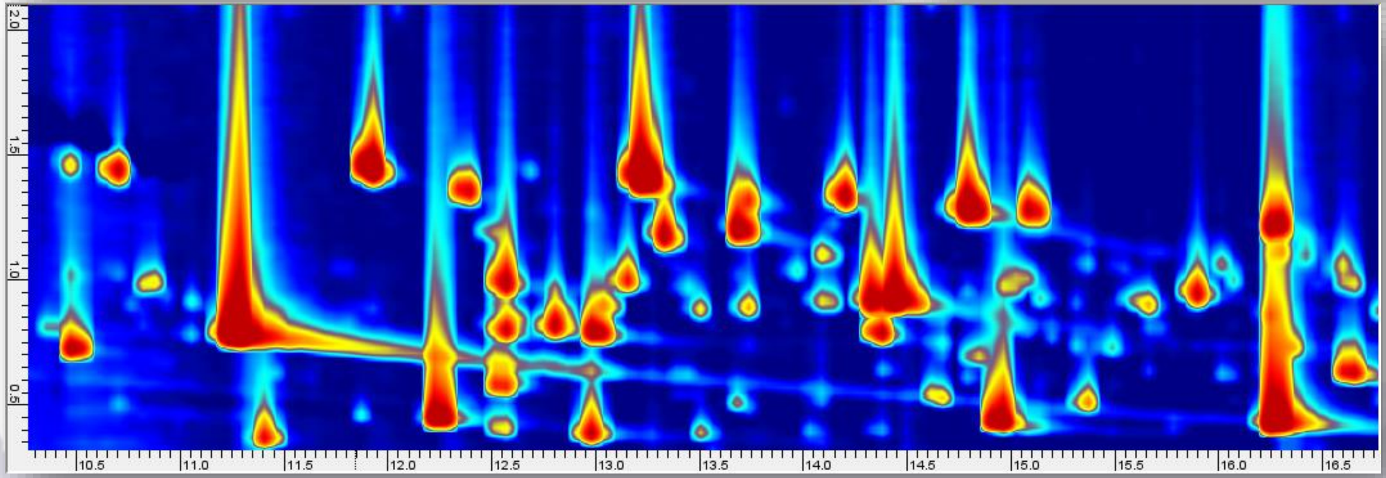




Comprehensive 2D GC







Prof. Philip Marriott
“If you are not using GC×GC, you will never know what you are missing!”

J. Agric. Food Chem. 69, 11535–11537 (2021)

“High resolution” profiling
GC×GC <u>separation power</u>
accurate quantitative profiling

***2D/3D Chromatographic fingerprinting*[1]**
<u>pattern recognition (forensics)</u>
comprehensive sample comparison

Group-Type Analysis
Rational retention logic
Ordered elution patterns

[1] Stilo, F., Bicchi, C., Jimenez-Carvelo, A. M., Cuadros-Rodriguez, L., Reichenbach, S. E., & Cordero, C. (2021). TrAC Trends in Analytical Chemistry, 134, 116133.

UNIVERSITÀ DI TORINO

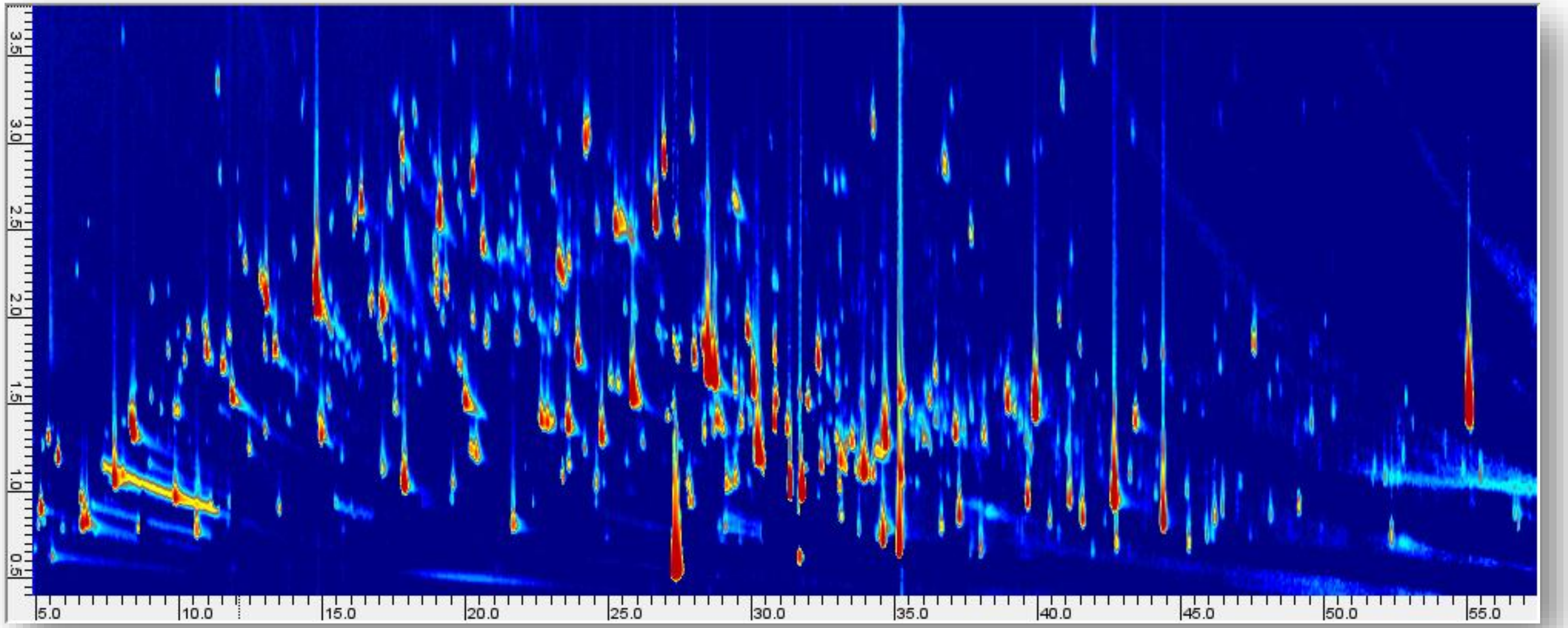
DATA PROCESSING

Roasted cocoa from Sao Tomé volatiles

HS-SPME (CAR/PDMS/DVB) - 500 mg - 50°C/50 min

Chemical dimensions

^{2}D - volatility separation (DB1701)



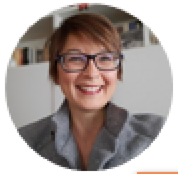
^{1}D - polarity/volatility separation (PEG / Carbowax)

About 700 detectable features (2D peaks) over 20 S/N

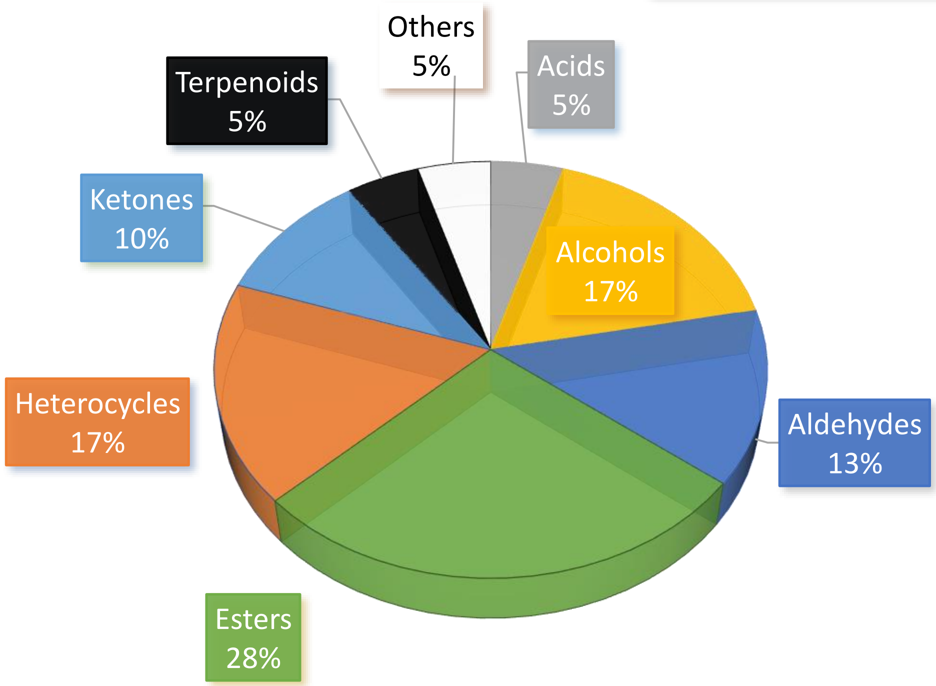
Of them 220 reliably identified by 70 eV spectrum and I^T coherence

Various chemical classes highly correlated with **post-harvesting** practices, **fermentation** processes, **technological** impact, **aroma compounds** and **potent odorants**

220 targeted compounds



UNIVERSITÀ DI TORINO



Ketones

Acetone
2-Butanone
2,3-Butanedione
2,3-Pentanedione
3-Penten-2-one
4-Methyl-3-penten-2-one
2-Heptanone
3-Hydroxy-2-butanone
2-Octanone
1-Hydroxy-2-propanone
3-Hepten-2-one
2,3-Octanedione
6-Methyl-5-hepten-2-one
4-Hydroxy-4-methyl-2-pentanone
2-Nonanone
1-Acetyloxy-2-propanone
2-Undecanone
Acetophenone
Geranyl acetone

Acids

Acetic acid
Propanoic acid
3-hydroxy-Butanoic acid
2-Methyl propanoic acid
Butanoic acid
3-Methyl butanoic acid
Hexanoic acid
Octanoic acid
Nonanoic acid

Heterocycles

2-Methyl-tetrahydrofuran
2,4,5-Trimethyl-1,3-dioxolane
2,4,5-trimethyl-oxazole
2-Pentylfuran
2,5-Dimethylpyrazine
2,6-Dimethylpyrazine
2,3-Dimethyl pyrazine
2,4,6-trimethyl-Pyridine
2-Ethyl-6-methylpyrazine
2-Ethyl-5-methylpyrazine
2,3,5-Trimethylpyrazine
2-ethyl-3,6-dimethyl-pyrazine
Tetramethylpyrazine
2-ethyl-3,5-dimethyl-pyrazine
6-Methyl-2-vinylpyrazine
2,3-diethyl-5-Methylpyrazine
3,4,5,6-Tetramethyl-2-pyridone
3,5,6-Trimethyl-2-ethylpyrazine
2,2,6,6-Tetramethyl-4-piperidone
Dihydro-5-methyl-2(3H)-furanone
Dihydro-2(3H)-furanone
Dihydro-5-ethyl-2(3H)-furanone
2-Acetyl-3,5-dimethylpyrazine
6-Methyltetrahydro-2H-pyran-2-one
4-Hydroxy-2,5-dimethyl-3(2H)-furanone
1(3H)-Isobenzofuranone
Pyridine
Methyl pyrazine
Ethylpyrazine

Aldehydes

Acetaldehyde
2-Methylpropanal
2-Methyl-butanal
3-Methyl-butanal
Pentanal
Hexanal
2-Methyl-2-butenal
Heptanal
Octanal
2-Ethyl-2-hexenal
5-Methyl-isopropyl-2-hexenal
Nonanal
Furfural
Decanal
Benzaldehyde
2-Nonenal
Undecanal
Phenyl acetaldehyde
Dodecanal
Benzyl acetate
Tridecanal
3-Phenylpropenal
3-Phenyl-2-propenal
Tetradecanal
2-Phenyl-2-butenal
1H-Pyrrole-2-carboxaldehyde

Alcohols

Ethanol
2-Methyl-3-buten-2-ol
2-Methyl-1-propanol
1-Methoxy-2-propanol
1-Penten-3-ol
2-Methyl-1-butanol
1-Pentanol
2-Heptanol
Hept-4-en-2-ol
1-Hexanol
2,4-Dimethyl-3-pentanol
Hexen-1-ol
3-Ethoxy-1-propanol
2-Butoxyethanol
2-Ethyl-1-hexanol
1-Octanol
4-Isopropoxybutanol
2-Furan methanol
4-Butoxy-1-butanol
5-Methyl-2-Furan methanol
1-Phenyl ethanol
Geraniol
Benzyl alcohol
Phenylethyl Alcohol
1,4-Butanediol
Phenol
2-phenoxy-ethanol
2-Pentanol
1-Butanol
2-Hexanol

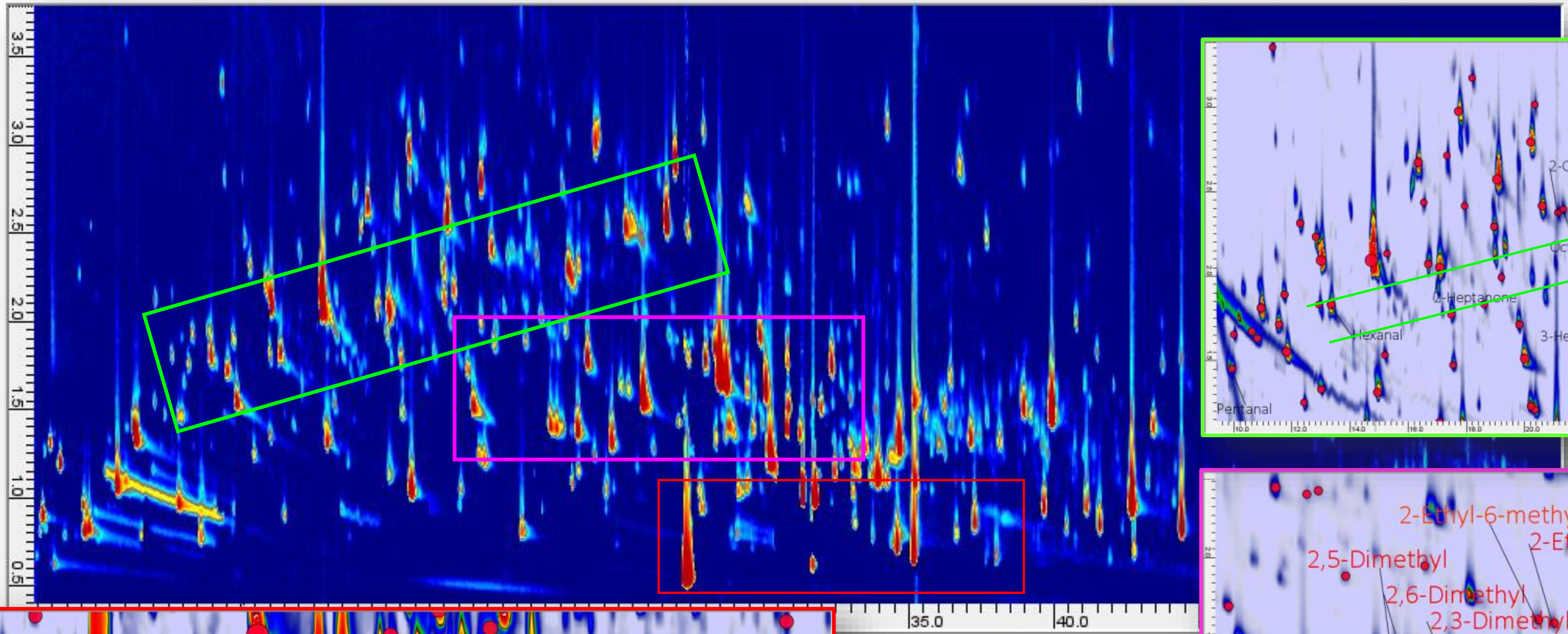
Esters

Methyl acetate
Ethyl Acetate
Ethyl propanoate
1 - Methyl propyl acetate
2-Methylpropyl acetate
Ethyl butanoate
Ethyl 2-methylbutanoate
Ethyl 3-methylbutanoate
Butyl acetate
2-Pentyl acetate
1-Butanol, 3-methyl-, acetate
Ethyl pentanoate
Butyl 2-methyl propanoate
4-Methyl-2-pentyl acetate
Ethyl 4-methylpentanoate
4-Pentenyl acetate
Butyl butanoate
2-Pentenyl acetate
Ethyl hexanoate
Ethyl tiglate
Prenyl acetate
2-Heptyl acetate
Hexyl acetate
Methyl 2-hydroxypropanoate
Ethyl heptanoate
Ethyl 2-hydroxypropanoate
2-Propenyl hexanoate
1,1-Ethanediol-diacetate
Ethyl 2-hydroxy-3-methylbutanoate
Ethyl octanoate
Octyl acetate
2,3-Butanedioldiacetate
2,3-Butanedioldiacetate
Ethyl 2-hydroxy-4-methylpentanoate
Linalyl acetate
Menthyl acetate
1-Methoxy-2-propyl acetate
Isobornyl acetate
Ethyl isobutyrate
Tetrahydrofurfuryl acetate
Ethyl 2-methylpropanoate
Ethyl decanoate
Ethyl benzoate
Linalyl propionate
2-Phenyl ethyl acetate
Ethyl dodecanoate
2- Methyl propyl benzoate
Ethyl 3-phenylpropionate
γ-.octalactone
delta-2-decenolactone
γ-nonalactone
Pentyl acetate
Triacetin

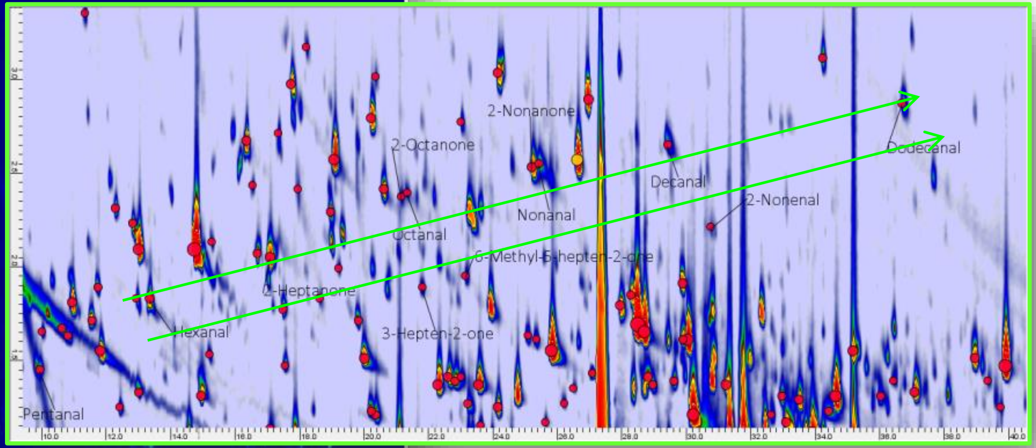
Terpenoids

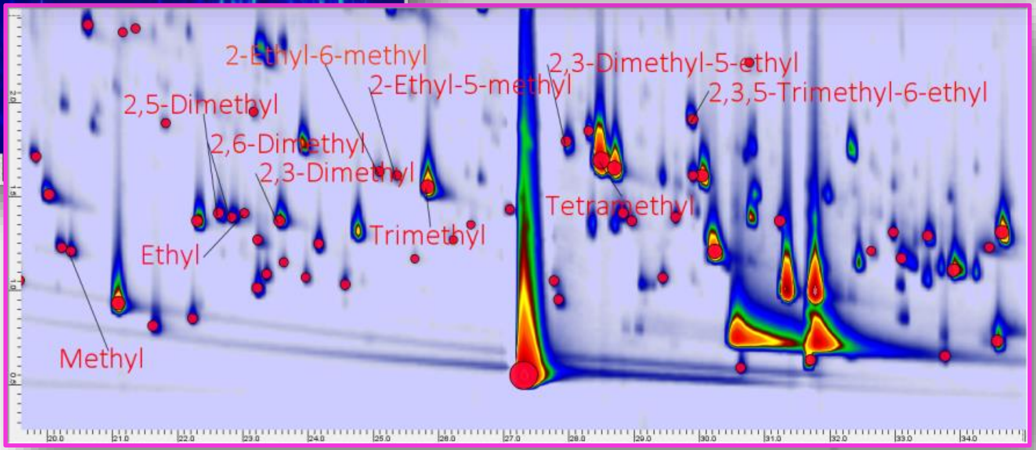
α-pinene
Myrcene
Limonene
Eucalyptol
Terpinene
Trans-linalool oxide

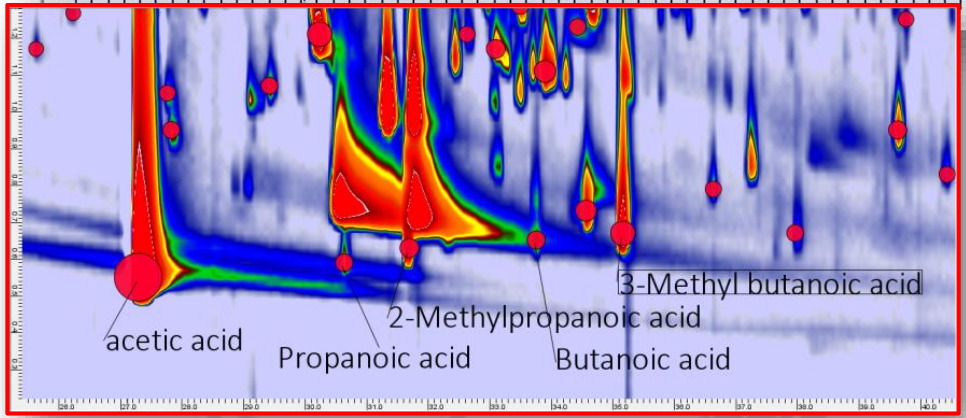
Roasted cocoa from Sao Tomé volatiles HS-SPME (CAR/PDMS/DVB) - 500 mg - 50°C/50 min



Linear saturated aldehydes and ketones signature







Pyrazines signature: this chemical group of volatiles, formed through Maillard reaction of di-carbonyls and amino acids, is informative about geographical origin of cocoa.

Pyrazines are also key-odorants imparting *earthy* and *roasty* notes

Short chain fatty acids signature: linear and branched chain FAs derived from beans fermentation during post-harvest

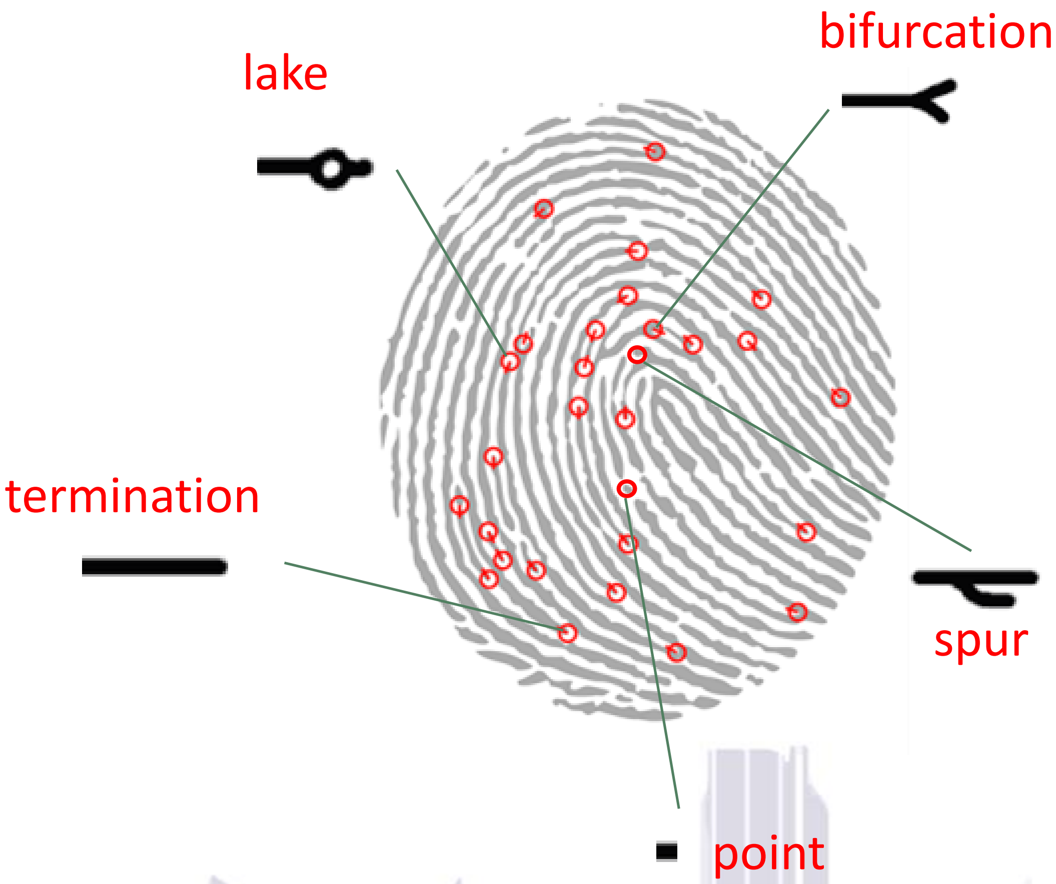
"... *Computer vision* ***enables them to see, observe and understand...***"[1]

How can we see compositional differences? -> Comprehensive Chromatographic Fingerprinting

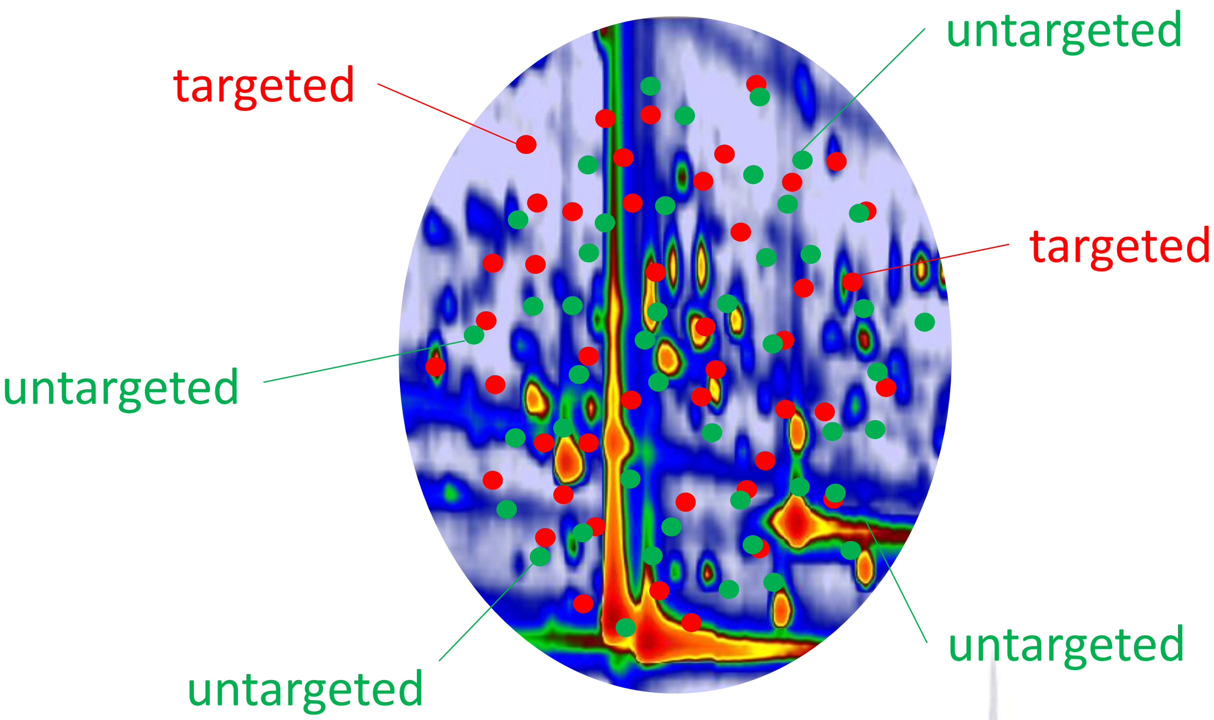
UNIVERSITÀ DI TORINO

DATA PROCESSING

Targeted - fingerprinting



Untargeted Targeted[2] - fingerprinting

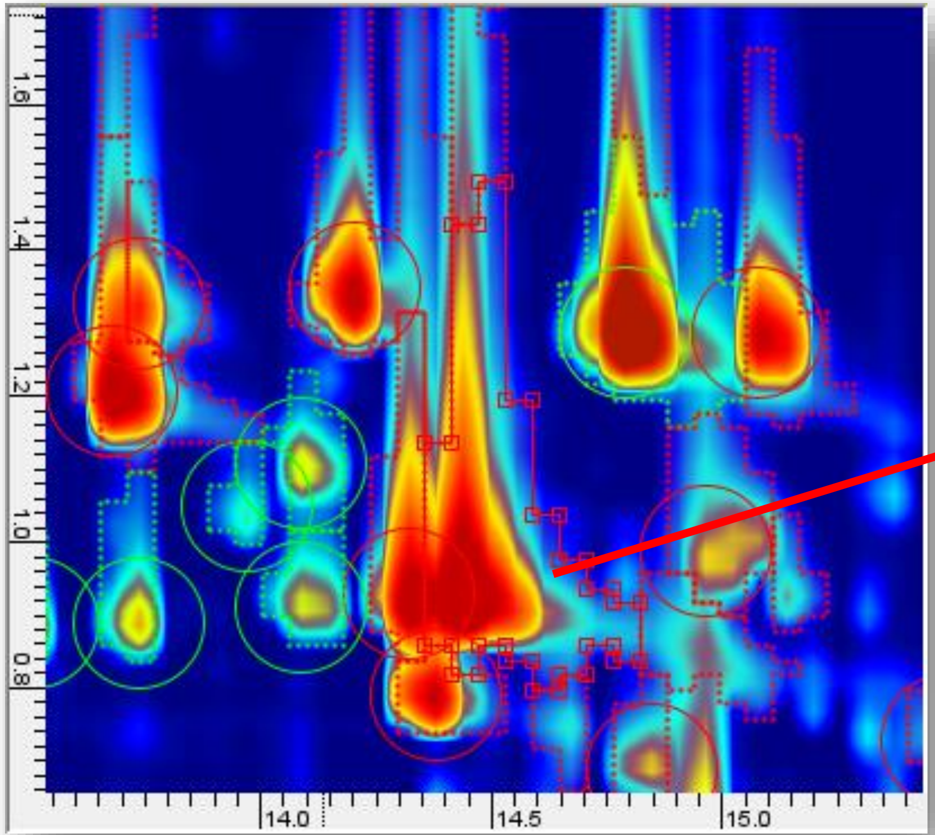


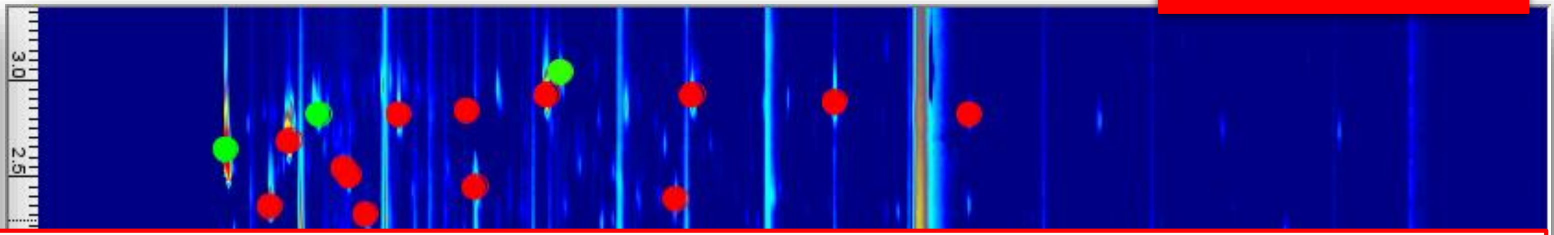
1. https://www.ibm.com/topics/computer-vision
2. 1. Stilo, F., Bicchi, C., Jimenez-Carvelo, A.M., Cuadros-Rodriguez, L., Reichenbach, S.E., Cordero, C., 2021. TrAC Trends Anal. Chem. 134, 116133

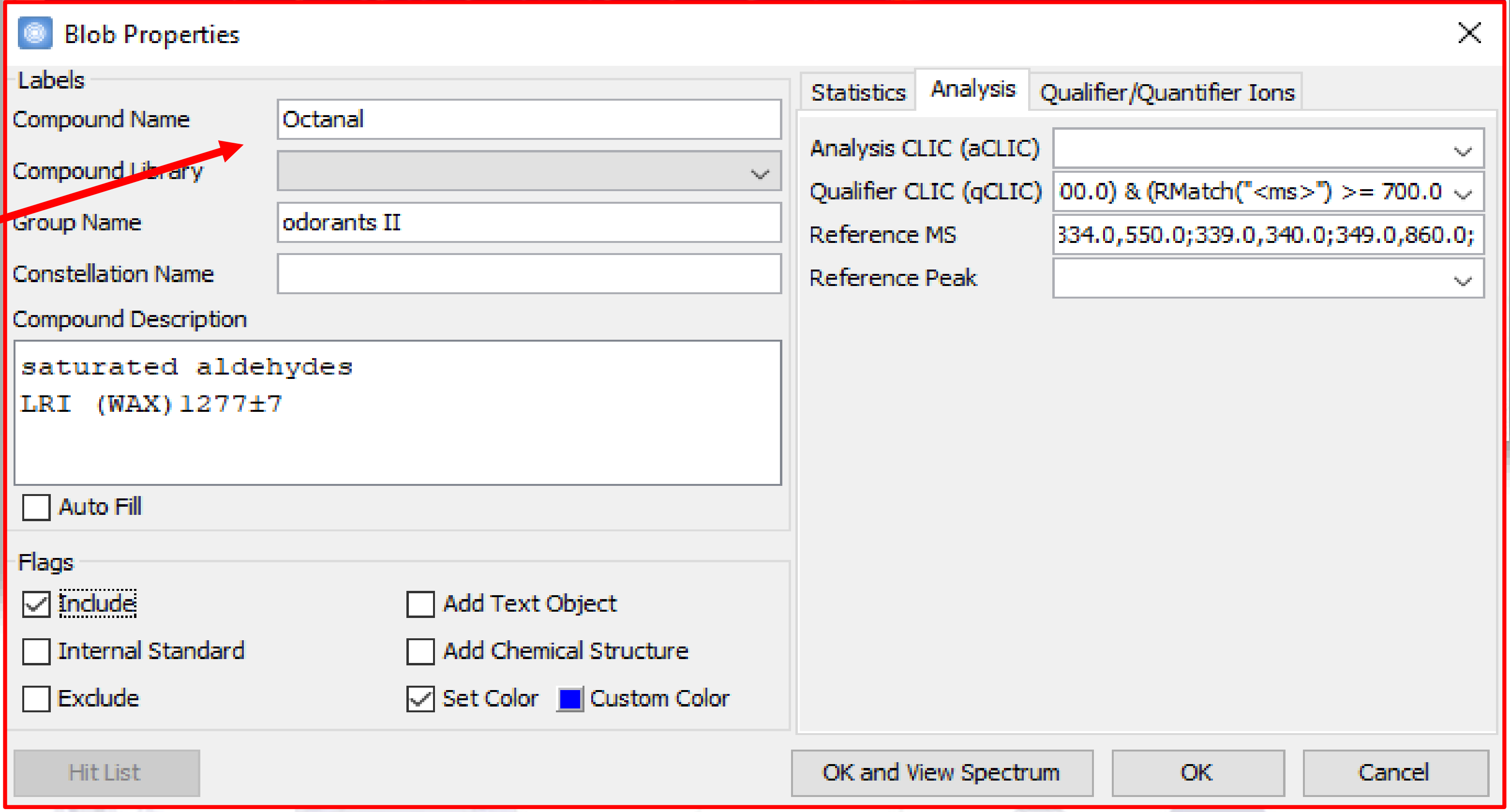
"... *Computer vision* *enables them to see, observe and understand...*"[1]

How can we see compositional differences? -> Comprehensive Chromatographic Fingerprinting

DATA PROCESSING





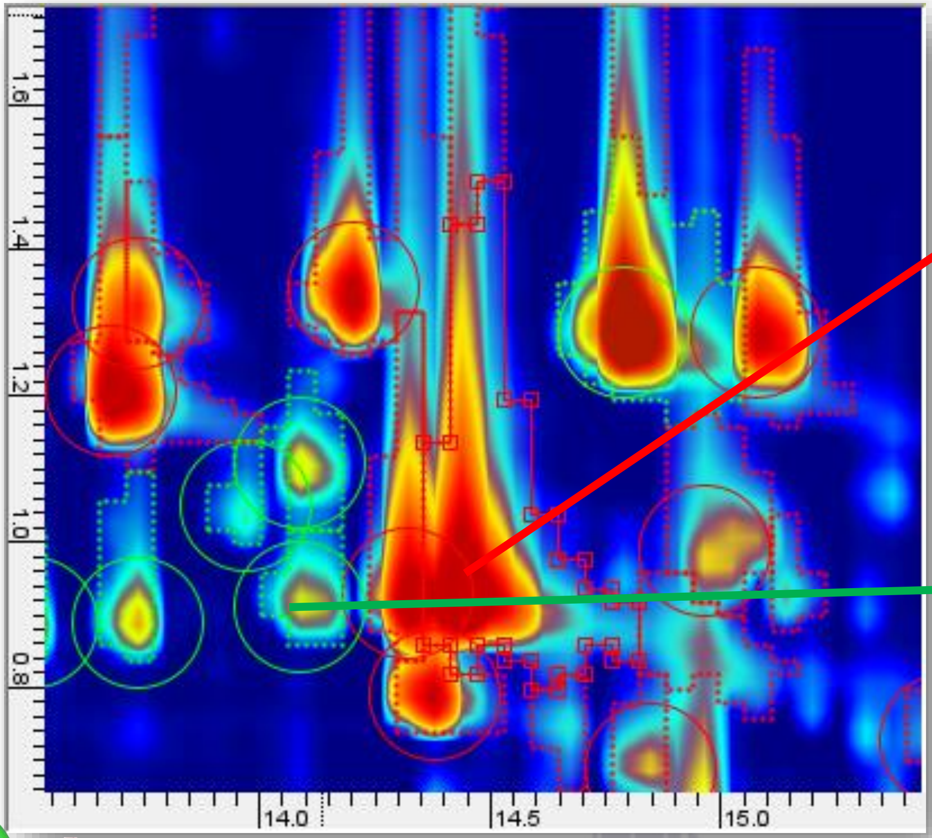


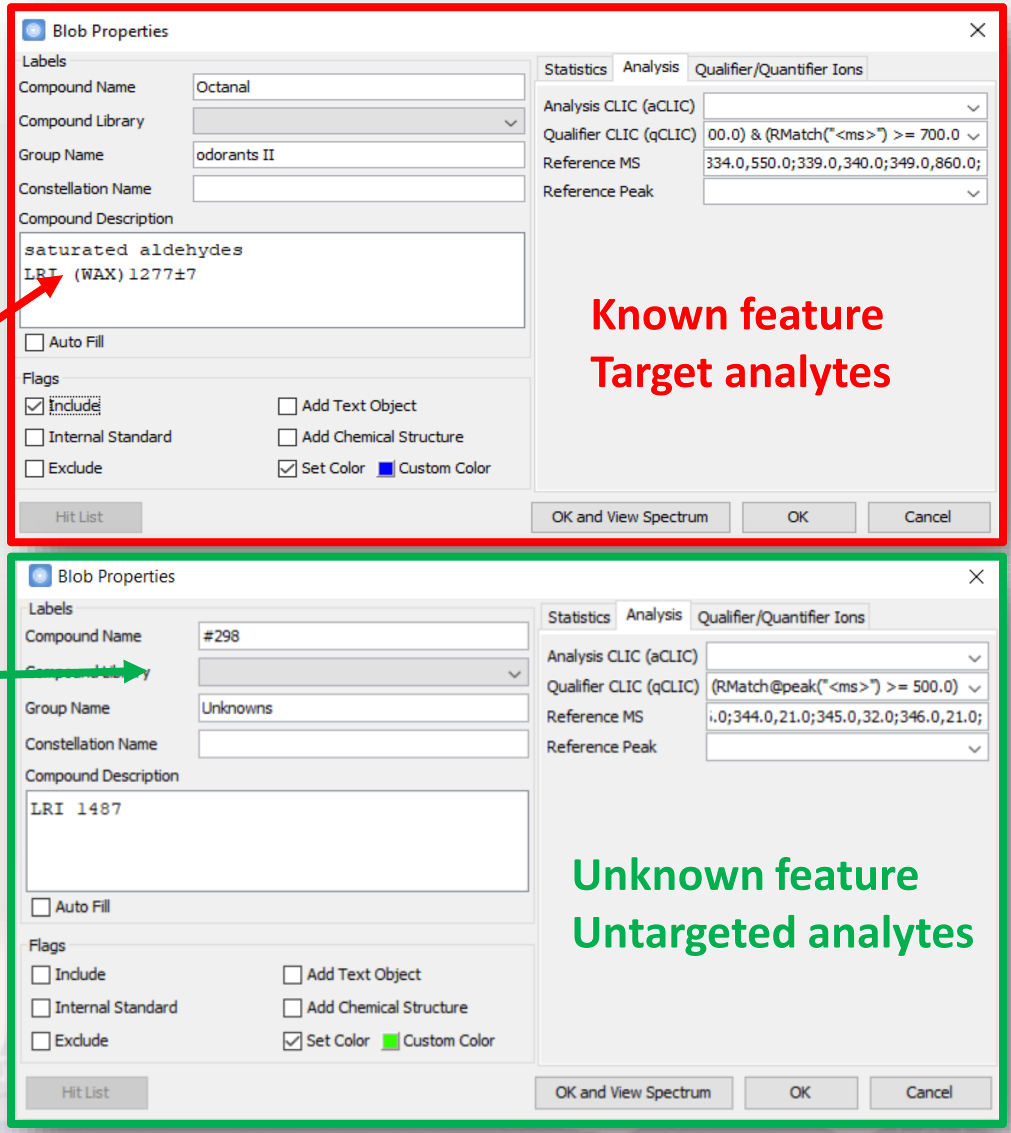
"... *Computer vision enables them to see, observe and understand...*"[1]

How can we see compositional differences? -> Comprehensive Chromatographic Fingerprinting

UNIVERSITÀ DI TORINO

DATA PROCESSING

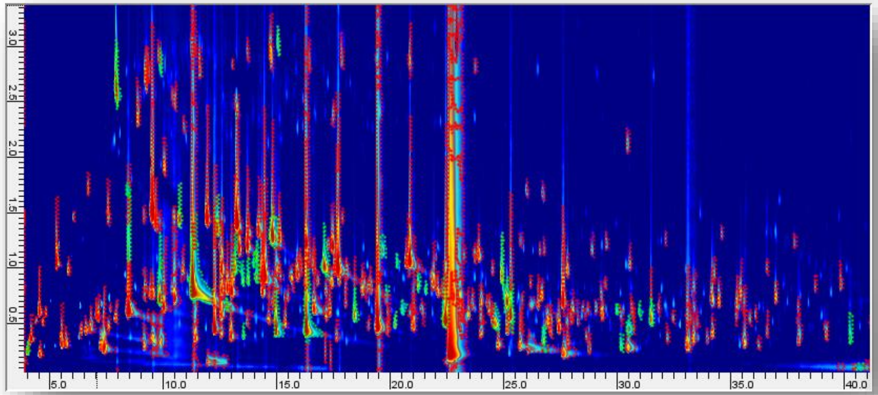


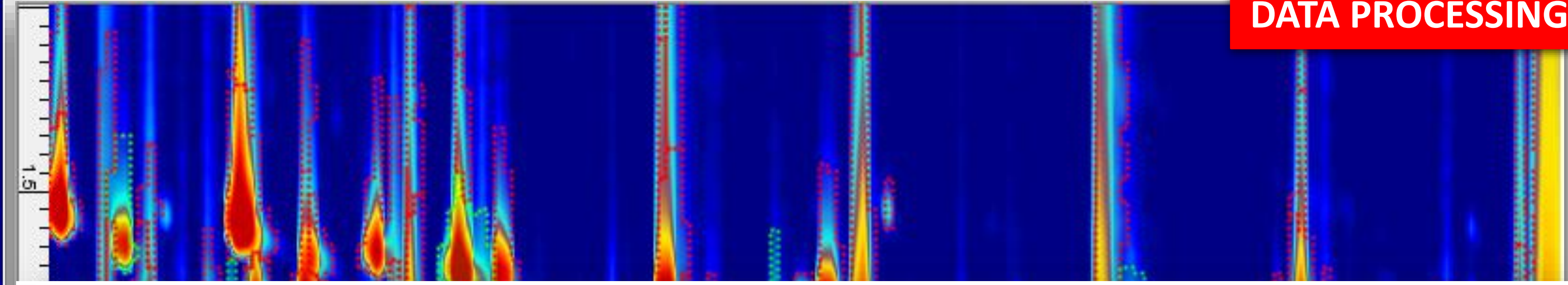


"... *Computer vision enables them to see, observe and understand*..."[1]

How can we see compositional differences? -> Comprehensive Chromatographic Fingerprinting

DATA PROCESSING





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

Investigator - G:\Markes 2017_2018\Hazelnuts Spigolon 2018\Feature UT hazelnuts.gca\default.bt

File Tools Help

Images Compounds Attributes Summary

Statistical Summary

View: Compound Categories

Blobs
Areas
Compound Sets

Blobs

Line Chart Scatter Chart Bubble Chart

X: Retention I.Mean Y: Retention II.Mean Z: Retention I.One-vs-...

Compound Name	Count	Retention I Mean	Stdev	RSD	Pairwise M...	One-vs-All ...	F Value	Mean(KO)	Mean(OK)	Stdev(KO)	Stdev(OK)
Diethyl Phthalate (70)	9	52.5195	0.0505	0.0010	0.0587	0.0587	0.2415	52.5118	52.5293	0.0639	0.0337
Methyl 2-octynoate (3)	12	32.0348	0.1240	0.0039	0.6942	0.6942	2.7350	31.9959	32.1126	0.1359	0.0337
Octanoic acid (36)	4	44.5668	9.4116E-6	2.1118E-7	0.6522	0.6522	1.3044	44.5668	44.5668	1.2186E-5	3.5122E-6
1-Octanol (5)	12	28.8265	0.1336	0.0046	0.9051	0.9051	3.5288	28.7803	28.9188	0.1427	0.0292
Hexanal (74)	8	11.0761	0.2865	0.0259	0.7693	0.7693	1.5710	11.0056	11.2876	0.2967	0.1237
Heptanoic acid (53)	3	41.5140	0.0337	0.0008	0.5000	0.5000	0.3333	41.5043	41.5334	0.0413	0.0000
(E)-2-Decenal (64)	10	31.9201	0.1192	0.0037	1.2013	1.2013	2.1968	31.8938	32.0251	0.1198	3.5122E-6
(E)-2-Octenal (30)	5	24.4418	8.4176E-6	3.4439E-7	1.1779	1.1779	2.2827	24.4418	24.4418	8.6202E-6	3.5122E-6
Pentanal (109)	11	8.0289	0.1794	0.0223	0.8548	0.8548	2.9010	7.9772	8.1668	0.1784	0.1010
1-Octanol (94)	4	24.4855	0.0292	0.0012	0.5006	0.5006	1.0013	24.4709	24.5001	0.0412	3.5122E-6
(E)-2-Nonenal (41)	5	28.2218	0.1908	0.0068	0.4770	0.4770	0.8715	28.1556	28.3209	0.2358	0.0412
2(3H)-Furanone, 5-butyldihydro- (16)	11	40.3774	0.0573	0.0014	1.2888	1.2888	3.6153	40.3595	40.4251	0.0578	2.7121E-6
(E)-2-Undecenal (25)	6	35.5154	0.1070	0.0030	0.7207	0.7207	1.2813	35.4813	35.5834	0.1203	3.5122E-6
2(3H)-Furanone, dihydro-5-pentyl- (29)	10	43.6393	0.0580	0.0013	0.4441	0.4441	1.4639	43.6251	43.6723	0.0624	0.0337
Acetone (52)	11	5.1069	0.0840	0.0164	0.3613	0.3613	1.5951	5.0834	5.1480	0.0918	0.0558
Butyl Butanoate (32)	11	16.3175	0.2623	0.0161	0.6909	0.6909	2.8268	16.2251	16.4793	0.2846	0.1117
Butyl benzoate (15)	12	38.9133	0.0723	0.0019	1.1144	1.1144	4.2454	38.8865	38.9668	0.0760	9.2700E-6
2(3H)-Furanone, dihydro-5-propyl- (57)	9	36.9575	0.0880	0.0024	1.0164	1.0164	3.0708	36.9251	37.0223	0.0904	0.0337
(60)	10	32.3284	0.1160	0.0036	0.9506	0.9506	2.7961	32.2918	32.4140	0.1208	0.0337
2(3H)-Furanone, 5-ethyldihydro- (45)	11	33.6955	0.1115	0.0033	1.2164	1.2164	4.3344	33.6584	33.7945	0.1034	0.0674
Ethyl benzoate (72)	10	32.6551	0.1058	0.0032	0.5205	0.5205	2.0412	32.6181	32.7105	0.1247	0.0292
Acetonitrile (14)	12	8.6577	0.1869	0.0216	1.3439	1.3439	5.4946	8.5824	8.8084	0.1830	0.0674
(49)	10	23.7651	0.2320	0.0098	1.2887	1.2887	2.3565	23.7126	23.9751	0.2312	3.5122E-6
Benzaldehyde (17)	12	27.6161	0.1621	0.0059	0.7737	0.7737	3.1145	27.5626	27.7230	0.1736	0.0559
4-Hydroxybutyric acid (7)	12	31.2181	0.1288	0.0041	1.3631	1.3631	6.0196	31.1647	31.3251	0.1198	0.0674
Toluene (37)	5	9.7768	0.2244	0.0230	0.1619	0.1619	0.1295	9.7563	9.8584	0.2537	0.0000
Dichloremethane (108)	10	6.8951	0.1284	0.0186	1.9287	1.9287	7.8551	6.8251	7.0001	0.1167	0.0476

Filter: Compound Name = Export Feature Template

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

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 Bicchi,[†] and Chiara Cordero*[†]

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Comprehensive two-dimensional gas chromatography coupled with time of flight mass spectrometry featuring tandem ionization: Challenges and opportunities for accurate fingerprinting studies☆

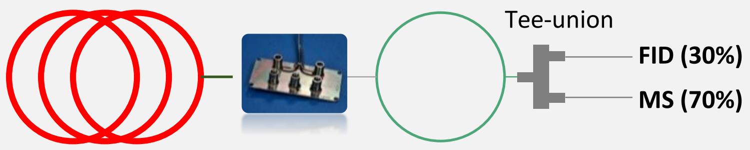
Chiara Cordero[a,*], Alessandro Guglielmetti[a], Carlo Bicchi[a], Erica Liberto[a], Lucie Baroux[b], Philippe Merle[b], Qingping Tao[c], Stephen E. Reichenbach[c,d]

Cocoa origins *identitation*[1] by Computer Vision

UNIVERSITÀ DI TORINO

Platform

Columns set-up and qMS acquisition



^{1}D - Polar PEG (Heavy-Wax)
20 m × 0.18 mm × 0.18µm
He carrier @ **0.4 mL/min**

^{2}D - Medium polarity OV1701
1.8 m × 0.18 mm × 0.18µm
He carrier @ **8 mL/min**

GC Oven programming: 40°C(2.02’) to 270°C (10.08’) @ 3.47°/min
S/SL injector: 250°C, split mode, split ratio 1:20
MS Transfer line: 280°C qMS at 70 eV
MS Aquisition: Mass range 40-350 m/z; acquisition frequency 25 Hz,
FID Acquisition: frequency 200 Hz
Modulation period: 3.0s, modulation pulse 200 ms
Bleeding capillary: 3.12 m, d_c 0,10 mm

Contents lists available at ScienceDirect

Journal of Chromatography A

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

ELSEVIER

CrossMark

Advanced fingerprinting of high-quality cocoa: Challenges in transferring methods from thermal to differential-flow modulated comprehensive two dimensional gas chromatography

Federico Magagna[a], Erica Liberto[a], Stephen E. Reichenbach[b], Qingping Tao[c], Andrea Carretta[d], Luigi Cobelli[d], Matthew Giardina[e], Carlo Bicchi[a], Chiara Cordero[a,*]

SAMPLES

South America
CO Colombia;
EC Ecuador;
VEN Venezuela

Trinidad - TRI (Africa)

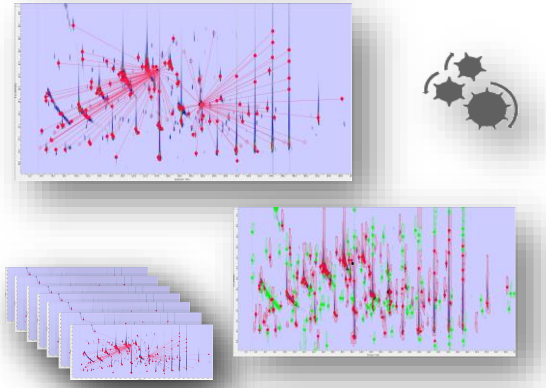
CH Mexico
JA Java
ST Sao Tomè

1. Cuadros-Rodríguez, L.; Ruiz-Samblás, C.; Valverde-Som, L.; Pérez-Castaño, E.; González-Casado, A. Chromatographic fingerprinting: An innovative approach for food “identitation” and food authentication – A tutorial. Anal. Chim. Acta 2016, 909, 9–23

Can we easily SEE pattern differences even if chemical dimensionality is high?

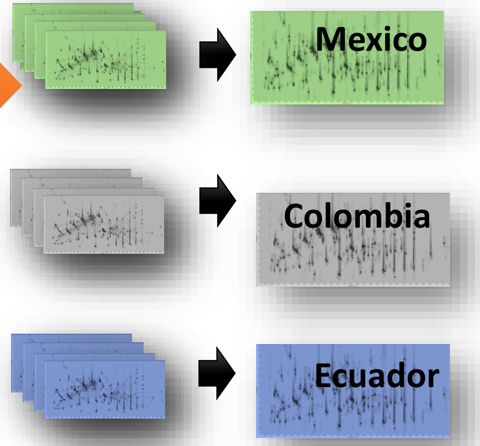
UNIVERSITÀ DI TORINO

Step 1 - *UT fingerprinting* - all samples



Construction of a untargeted and targeted peaks *UT* template

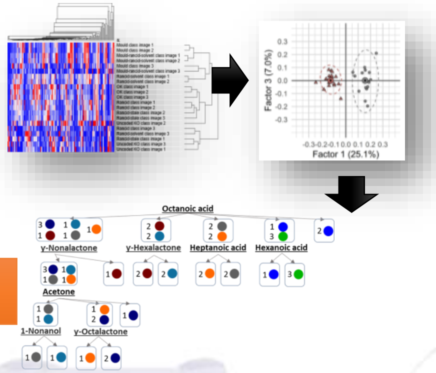
Step 2 - Composite Class-images



Construction of **Composite-class images** for each group

UT template matching to **composite class images**

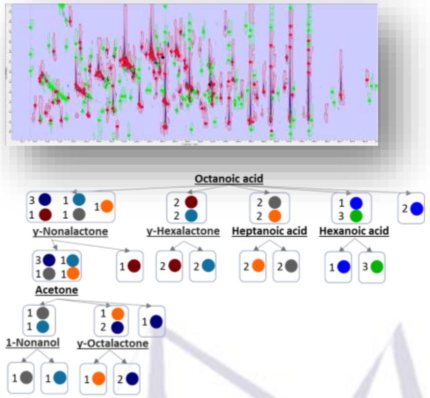
Step 3 - Machine Learning - Chemometrics



Unsupervised statistics (HC and PCA)

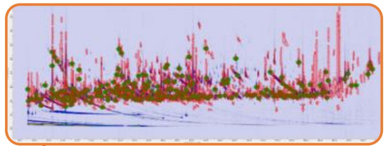
Supervised statistics (PLS-DA and Classification tree)

Step 4 - Validation



Confirmation of the discriminant role of markers using classic fingerprinting based on single chromatograms

UNIVERSITÀ DI TORINO



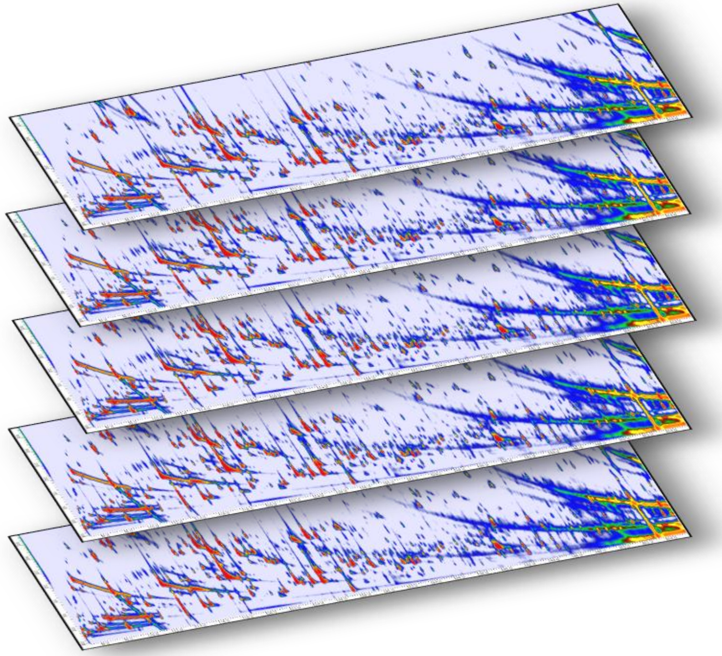
Processed 2D chromatograms - *UT template* already applied

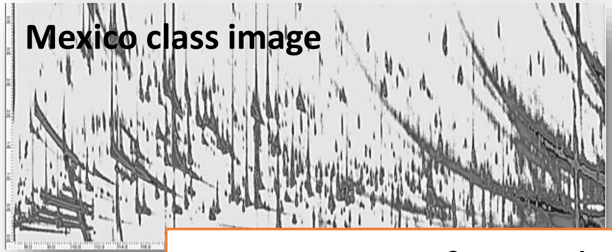
Alignment of 2D chromatograms and generation of a composite chromatogram for each sample group

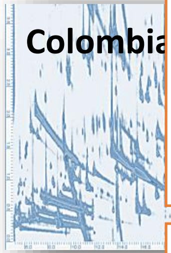
Definition of pattern of peak-regions for all detected 2D peaks

Building of *feature* templates with *reliable* peaks and peak-regions

Computer vision



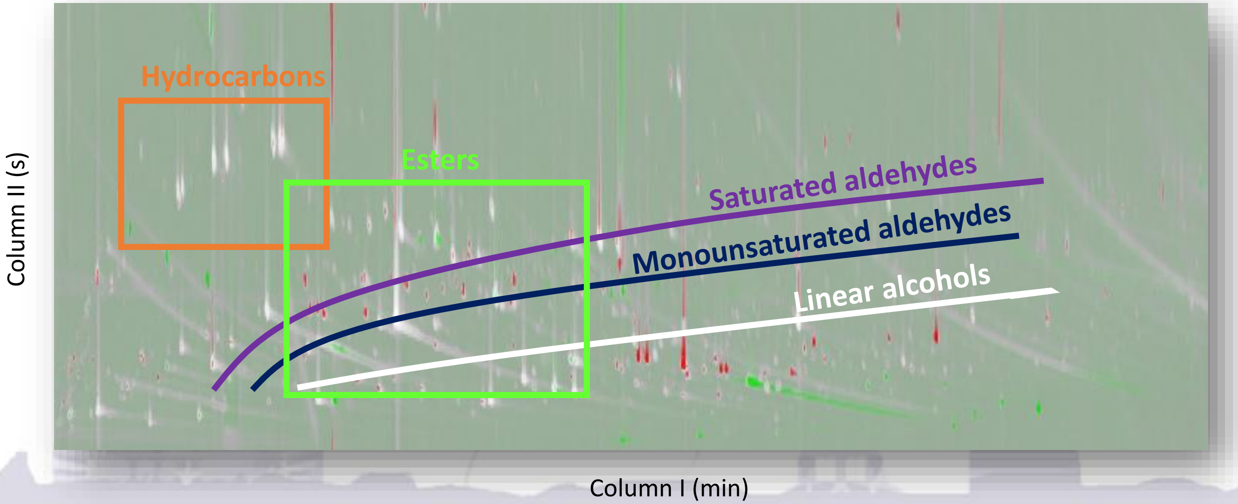




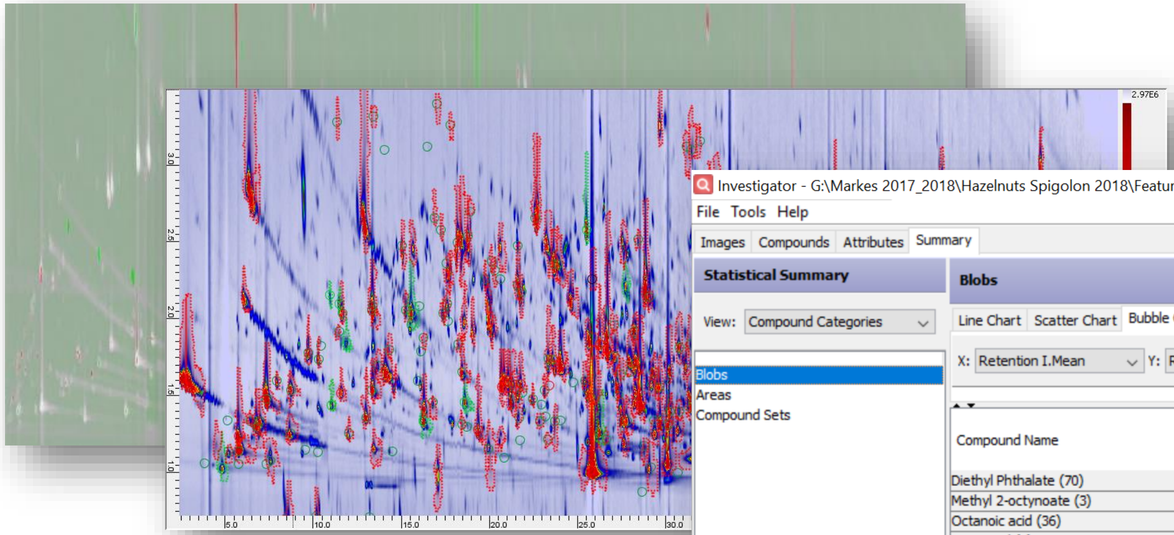
Generation of cumulative class-images by re-aligned images and datapoints fusion. Cocoa origins have distinctive "class-images"

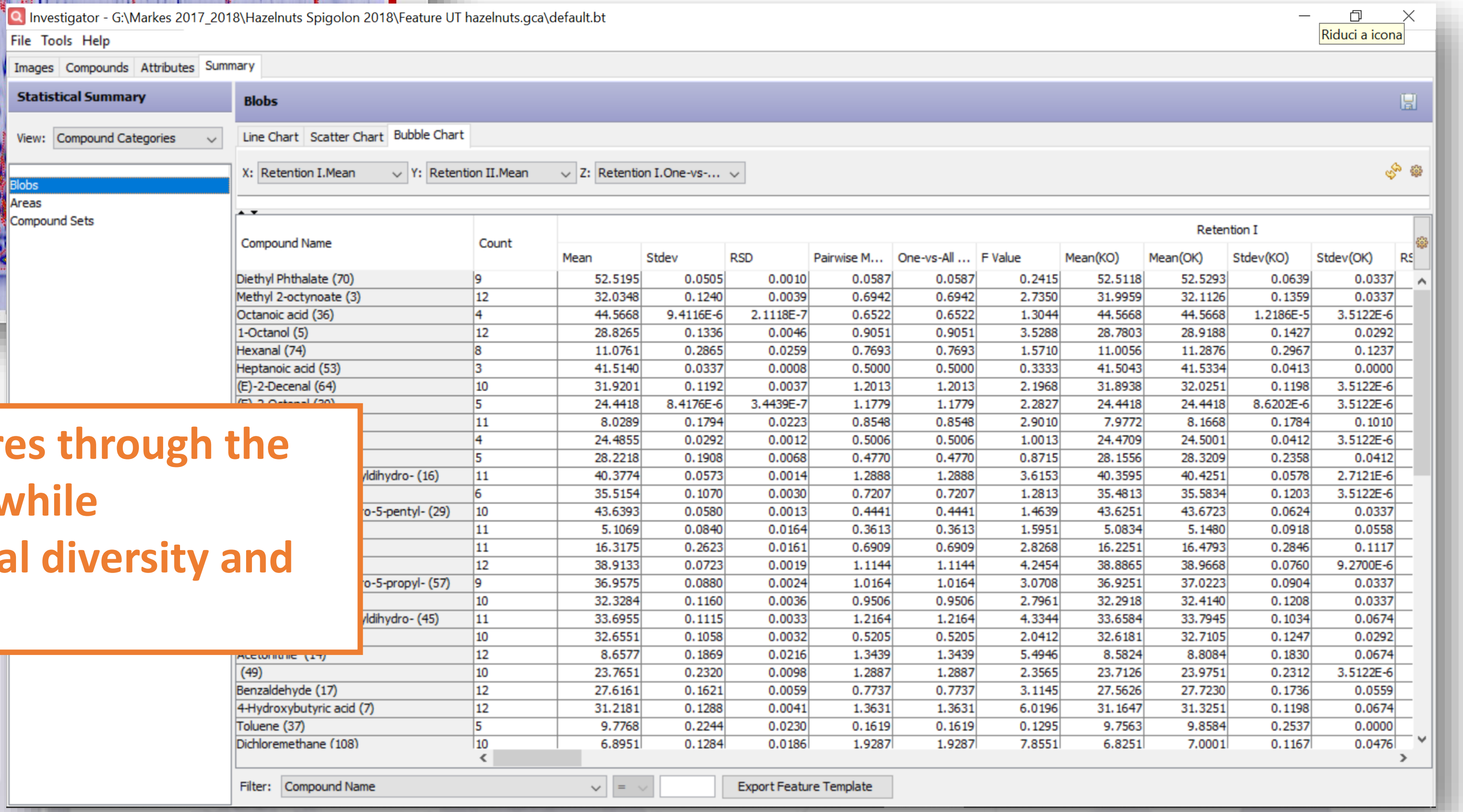
Class-images can be "pair-wise" compared to delineate diagnostic chemical patterns

Pair-wise comparison datapoint features UT *peak-regions* mapped



UNIVERSITÀ DI TORINO





We can SEE chemical signatures through the chromatographic fingerprint while investigating samples chemical diversity and peculiar aroma properties

Cocoa origins *identitation*[1] by Computer Vision -> AI smelling

UNIVERSITÀ DI TORINO


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 Bicchi,[†] and Chiara Cordero[*,†]


Contents lists available at ScienceDirect

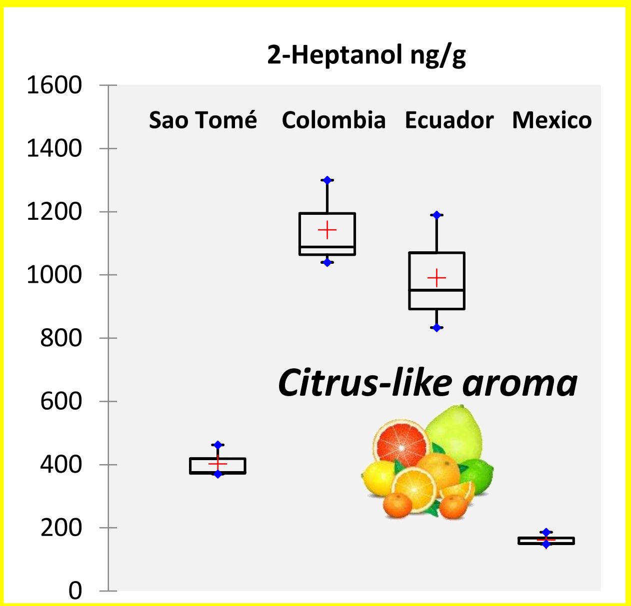
Journal of Chromatography A

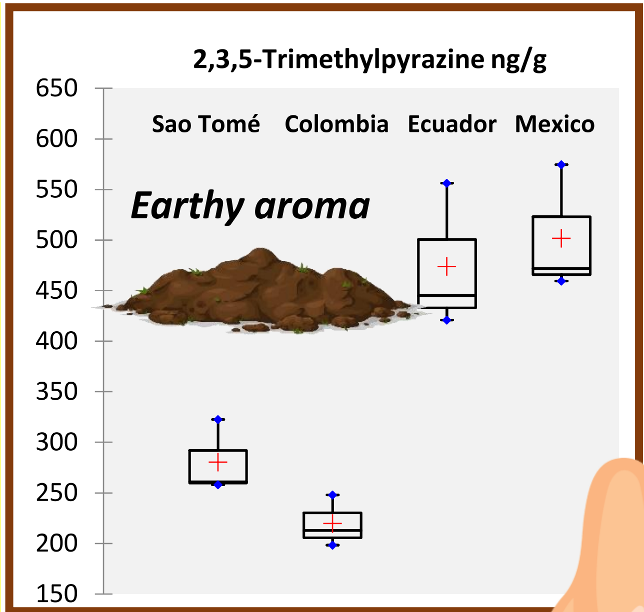
journal homepage: www.elsevier.com/locate/chroma

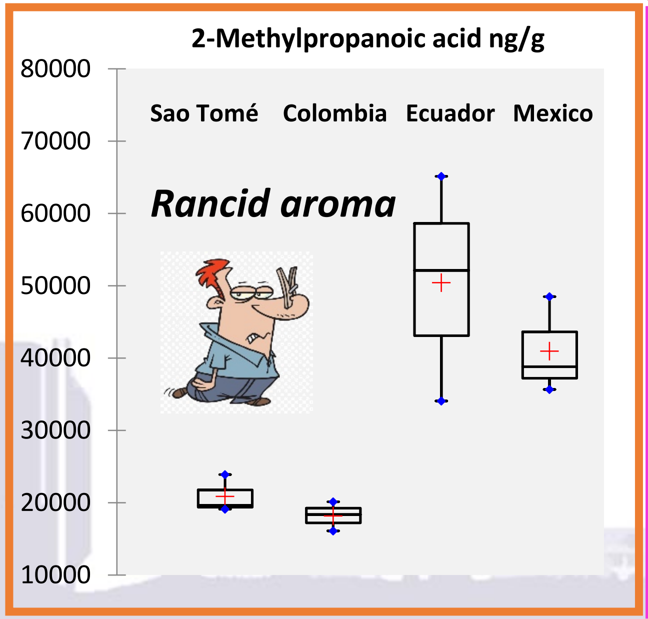
ELSEVIER

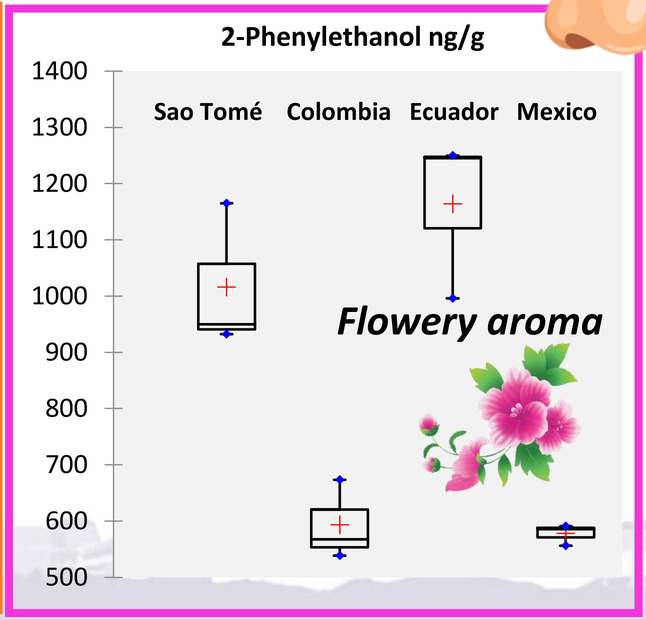
Advanced fingerprinting of high-quality cocoa: Challenges in transferring methods from thermal to differential-flow modulated comprehensive two dimensional gas chromatography

Federico Magagna[a], Erica Liberto[a], Stephen E. Reichenbach[b], Qingping Tao[c], Andrea Carretta[d], Luigi Cobelli[d], Matthew Giardina[e], Carlo Bicchi[a], Chiara Cordero[a,*]





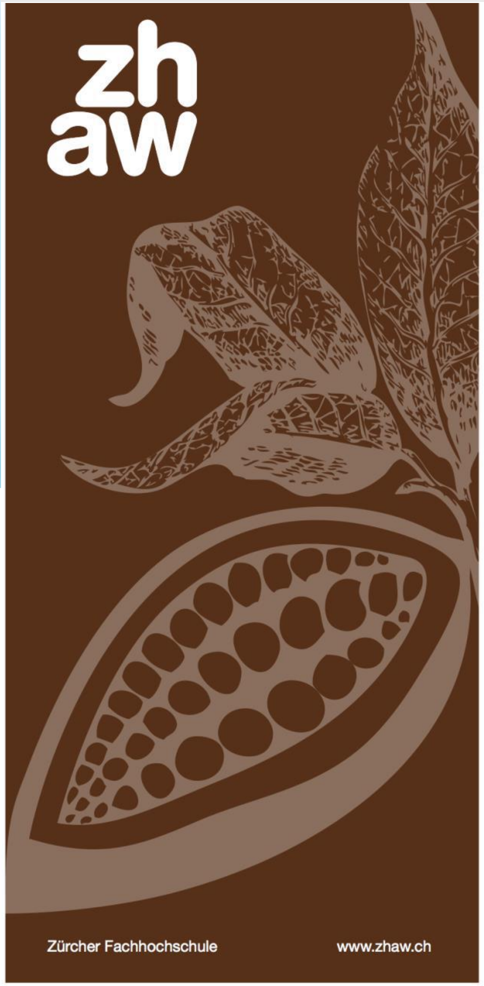




By quantitative fingerprinting, the *identitation* achieves high robustness and transferability over time and over analytical platforms

AI smelling machine -> Sensomic-based expert system acting as ...

Prof. Irene Chetschik



ILTURAL AND
CHEMISTRY

coa

ke

like

like

rancid,

Figure 1. Orth... and roasted
(—■—) Criollo

Odor Acti...

OAV= con... d

Table 4. Odor Thresholds and OAVs of Important Aroma Compounds in Unroasted and Roasted Cocoa Beans

odorant	odor threshold[a] (μg/kg)	OAV[b] unroasted beans	OAV[b] roasted beans
acetic acid	124[c]	8870	2660
3-methylbutanoic acid	22[c]	424	440
ethyl 2-methylbutanoate	0.26[c]	138	135
3-methylbutanal	13[c]	123	2610
methylpropanoic acid	190[d]	51	73
3-hydroxy-4,5-dimethyl-2(5*H*)-furanone	0.2[c]	43	65
ethyl 2-methylpropanoate	1.24[c]	25	21
2-methylbutanoic acid	203[e]	17	17
2-phenylethanol	211[c]	17	36
2-phenylacetic acid	360[c]	14	16
2-methoxyphenol	16[c]	6.9	14
2-heptanol	263	4.4	4.1
butanoic acid	135[c]	4.2	4.2
2-methylbutanal	140[c]	4.0	32
2-phenylethyl acetate	233[e]	4.0	4.0
dimethyl trisulfide	2.5[c]	3.6	21
linalool	37	3.2	3.5
phenylacetaldehyde	22[c]	3.0	250
2,3-diethyl-5-methylpyrazine	0.5[c]	2.4	6.6
δ-octenolactone	4730[e]	2.3	2.4
2-ethyl-3,5-dimethylpyrazine	2.2[c]	2.3	7.6
2-isobutyl-3-methoxypyrazine	0.8[c]	1.3	1.2
4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	25[c]	<1	48
4-methylphenol	68[d]	<1	<1
2-ethyl-3,6-dimethylpyrazine	57[c]	<1	1.0
2-methyl-3-(methyldithio)furan	0.4[c]	<1	1.5
δ-octalactone	2490[e]	<1	<1
2,3,5-trimethylpyrazine	290[d]	<1	3.2
1-octen-3-one	10[c]	<1	<1

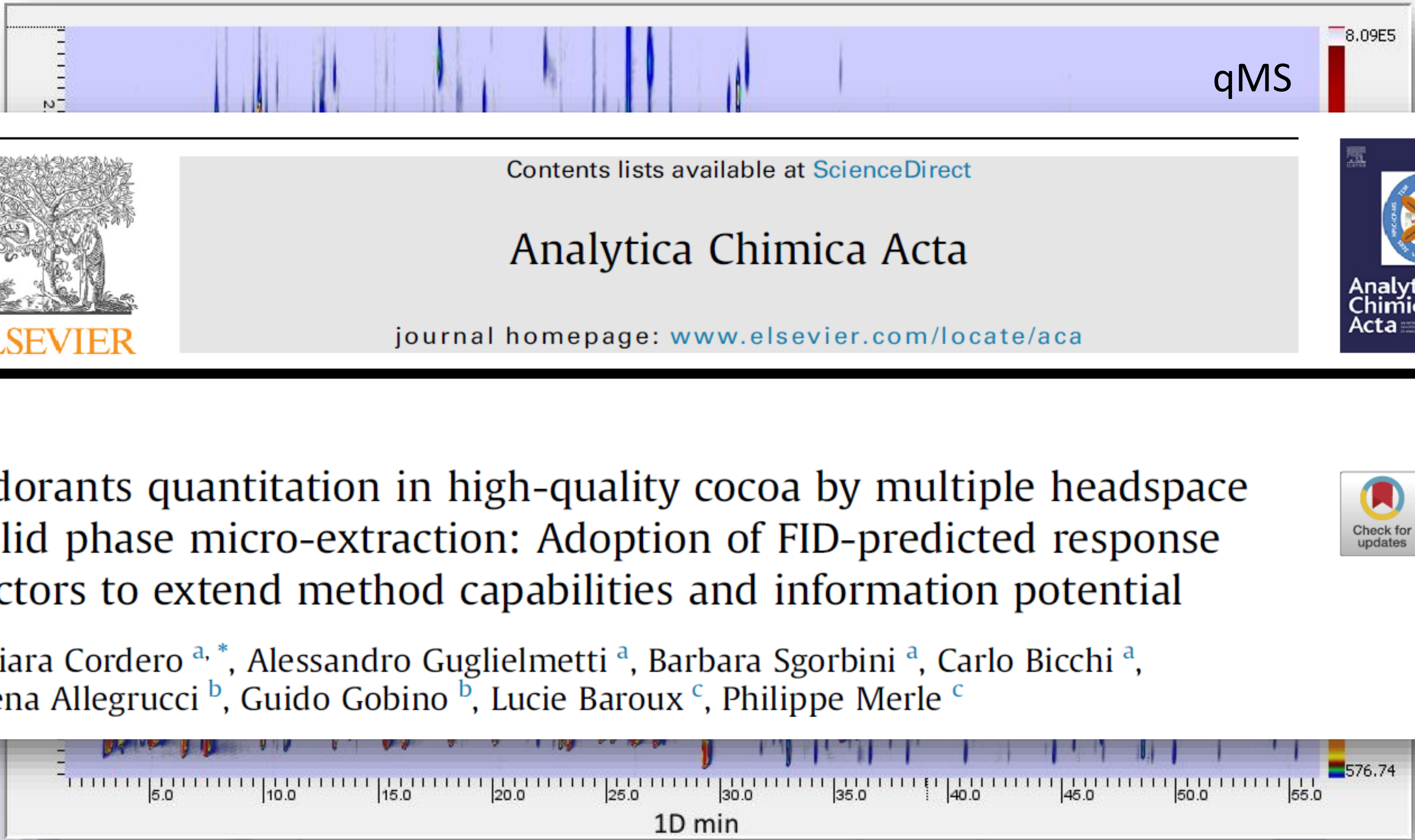
UNIVERSITÀ DI TORINO

AI smelling machine potentials

UNIVERSITÀ DI TORINO

Sensomics-based expert system[1] acting as AI *smelling machine*

Isoamyl acetate
2-Heptanone
Heptanal
3-Hydroxy-2-butanone
2-Heptanol
2-Ethyl-5-methylpyrazine
2-Nonanone
2,3,5-Trimethylpyrazine (REF)
3-Ethyl-2,5-dimethylpyrazine
Ethyl octanoate
2-Ethyl-3,6-dimethylpyrazine
Benzaldehyde
2-Methylpropanoic acid
γ-Butyrolactone
3-Methylbutanoic acid
Ethyl phenyl acetate
2-Phenylethyl acetate
Guaiacol
2-Phenylethanol
(E)-2-Phenyl-2-butenal
2-Acetyl pyrrole
Phenol
Octanoic acid
DDMP
Phenylacetic acid



Contents lists available at ScienceDirect
Analytica Chimica Acta
journal homepage: www.elsevier.com/locate/aca
ELSEVIER

Odorants quantitation in high-quality cocoa by multiple headspace solid phase micro-extraction: Adoption of FID-predicted response factors to extend method capabilities and information potential

Chiara Cordero [a,*], Alessandro Guglielmetti [a], Barbara Sgorbini [a], Carlo Bicchi [a], Elena Allegrucci [b], Guido Gobino [b], Lucie Baroux [c], Philippe Merle [c]

AI smelling machine potentials

UNIVERSITÀ DI TORINO

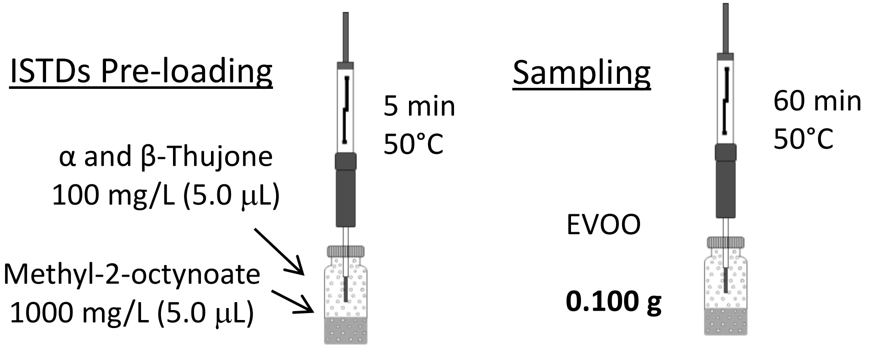
Cocoa samples at different processing stages

Accurate quantification of potent odorants responsible of **sensory quality** (*i.e.*, positive attributes and defects)
AI *smelling SEBES principle*

Comprehensive mapping of all detectable analytes - origin *identitation*

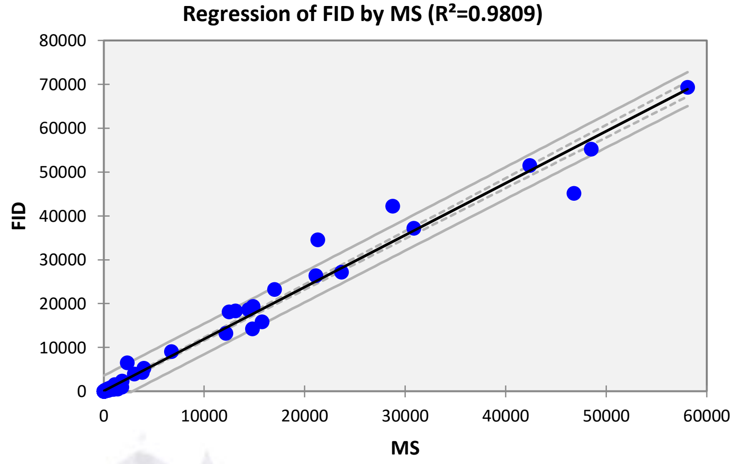


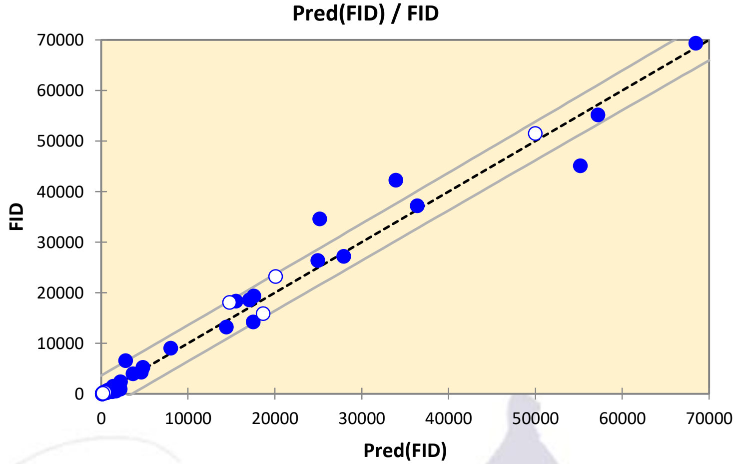
HS SPME - HS linearity conditions



Predicted Relative Response Factors (RRFs) based on combustion enthalpies and molecular structure[1] - FID quantification without ESTD

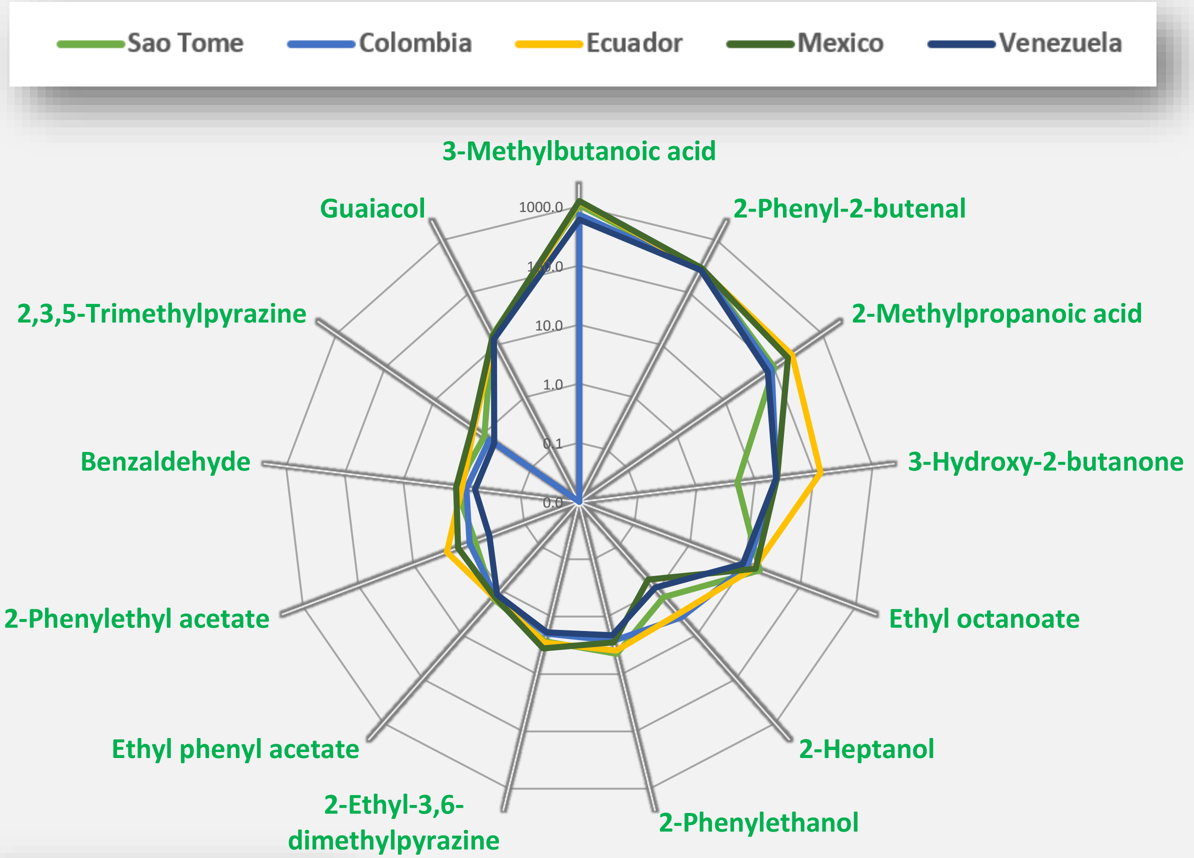
Accuracy results - MS *vs.* FID and FID *vs.* predicted RRFs

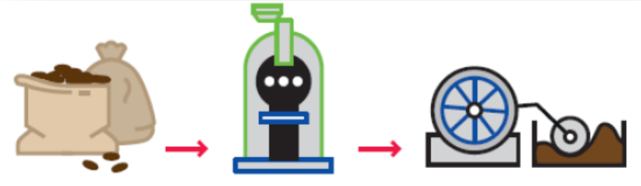




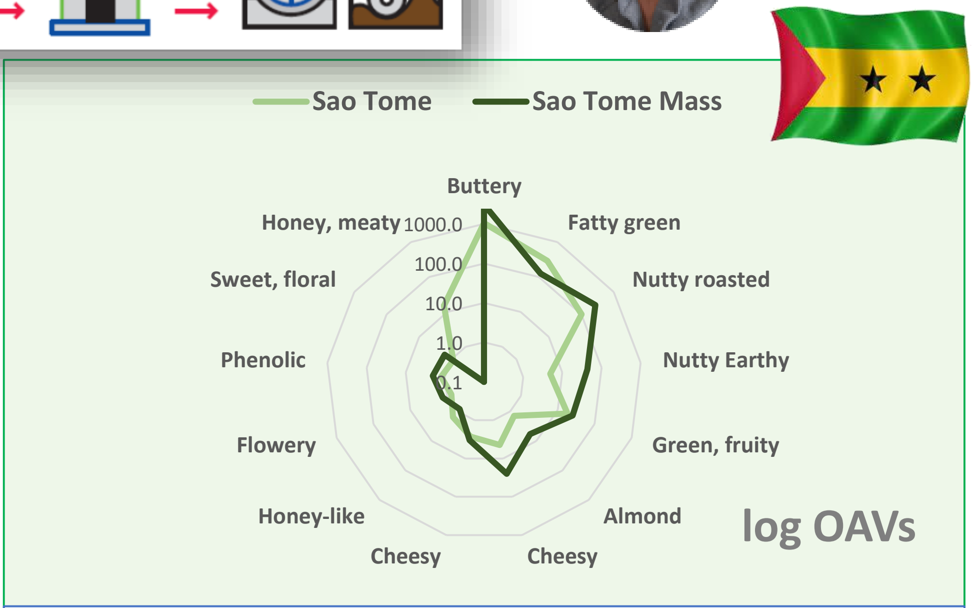
[1] J.Y. De Saint Laumer, E. Cicchetti, P. Merle, J. Egger, A. Chaintreau, Anal. Chem. 82 (2010) 6457–6462. doi:10.1021/ac1006574.

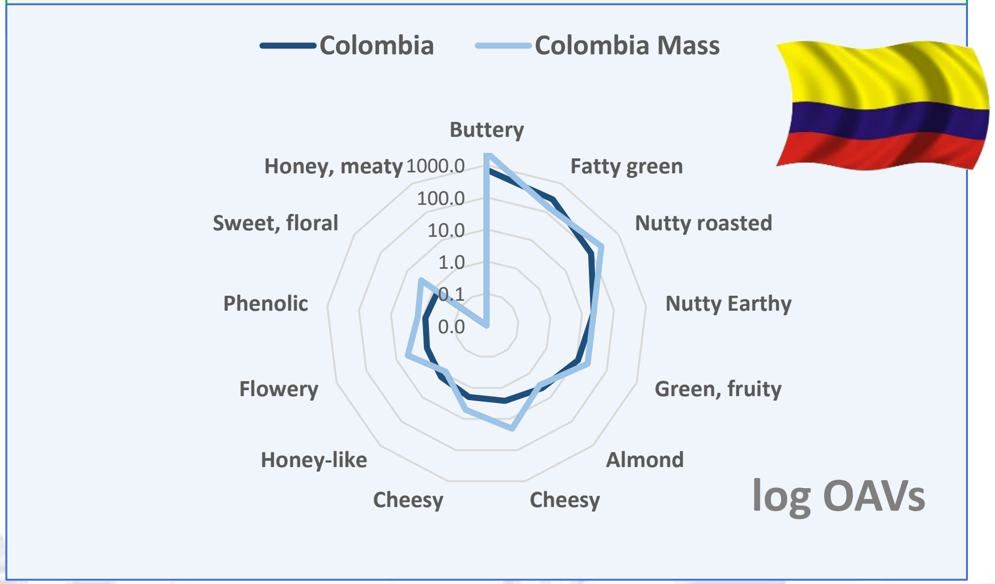
AI smelling machine potentials

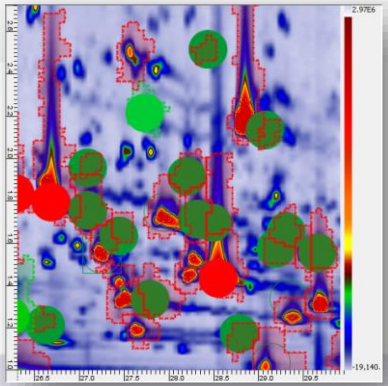




UNIVERSITÀ DI TORINO







UNIVERSITÀ DI TORINO

HIGHER LEVEL INFORMATION

...the boundaries between chemistry and biology are vanishing[1]...

Fingerprinting/profiling to unreveal marker patterns

Chromatographic Fingerprinting and Computer vision *Identitation*

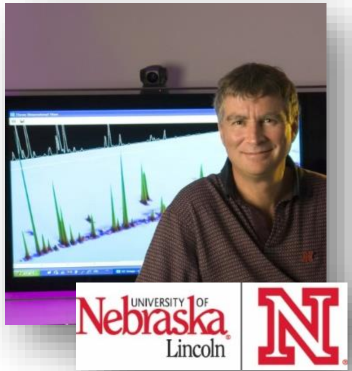
Artificial Intelligence smelling machine molecular resolution tool

1. Prof. Thomas Hofmann J. Agric. Food Chem. 2015, 63, 32, 7095–7096

Thank you for your attention

Prof. Carlo Bicchi

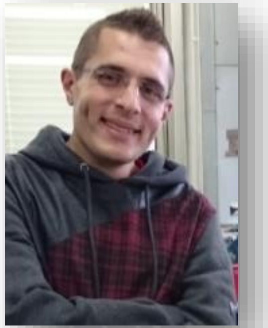
Prof. Stephen E Reichenbach



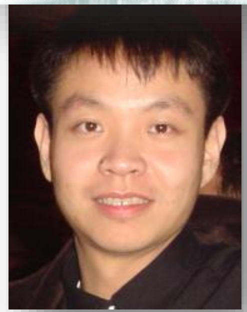
Dr. Andrea Caratti

Dr. Simone Squara

GC IMAGE
Software for Multidimensional Chromatography

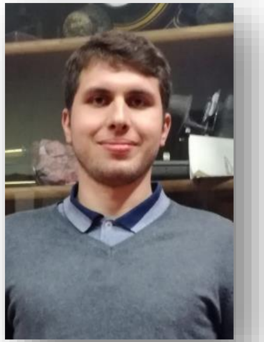


Dr. Qingping Tao



Dr. Federico Magagna PhD

Dr. Alessandro Guglielmettti PhD



Acknowledgments

Agilent

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

Firmenich

SRA INSTRUMENTS ANALYTICAL SOLUTIONS

GUIDO GOBINO

SOREMARTEC
Gruppo FERRERO