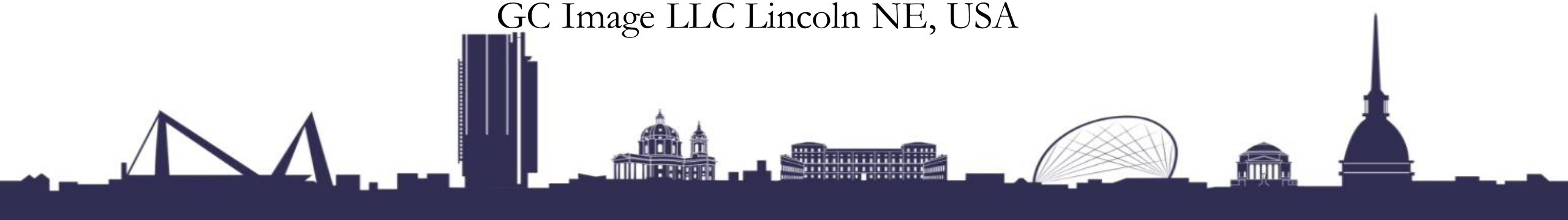
Progress in hazelnut quality assessment via artificial intelligence (AI) smelling based on GC×GC

Simone Squara[1], Andrea Caratti[1], Erica Liberto[1], Carlo Bicchi[1],
Stephen E. Reichenbach[2,3], and Chiara Cordero[1]
Università degli Studi di Torino, Turin Italy
University of Nebraska, Lincoln NE, USA
GC Image LLC Lincoln NE, USA



AI smelling approach

Context: Sensomics

Principle: key-odorants and patterns evoke specific smell/aroma

Methods: identification and quantification of potent odorants

Results: Sensomics based expert system (SEBES[1]) capable to predict key-aroma signatures without the human smell

1. L. Nicolotti, V. Mall, P. Schieberle, J. Agric. Food Chem. 67 (2019) 4011–4022. doi:10.1021/acs.jafc.9b00708

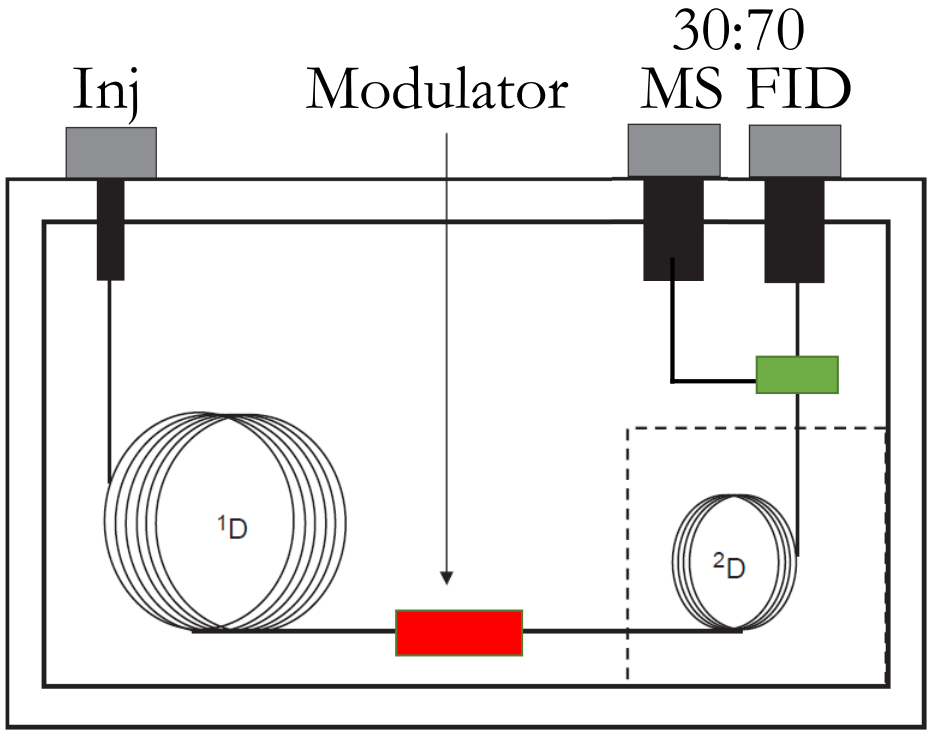
Comprehensive 2D Gas Chromatography

Comprehensive Multidimensional separation technique – two separation dimensions in series

Comprehensive: every portion of the ^{1}D eluate undergoes a further separation in the ^{2}D

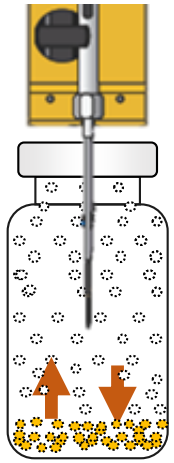
The **modulator** ensures the full transfer of the sample from the ^{1}D to the ^{2}D, preserving ^{1}D resolution.

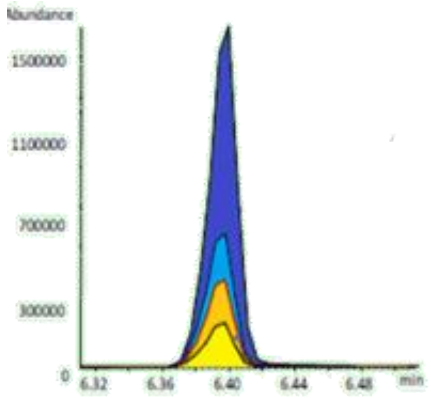
The **splitter** after the ^{2}D allows parallel detection and data acquisition from two detectors providing complementary information



Quantification approach

Solid phase microextraction (SPME)





EXTR 1
EXTR 2
EXTR 3
EXTR 4

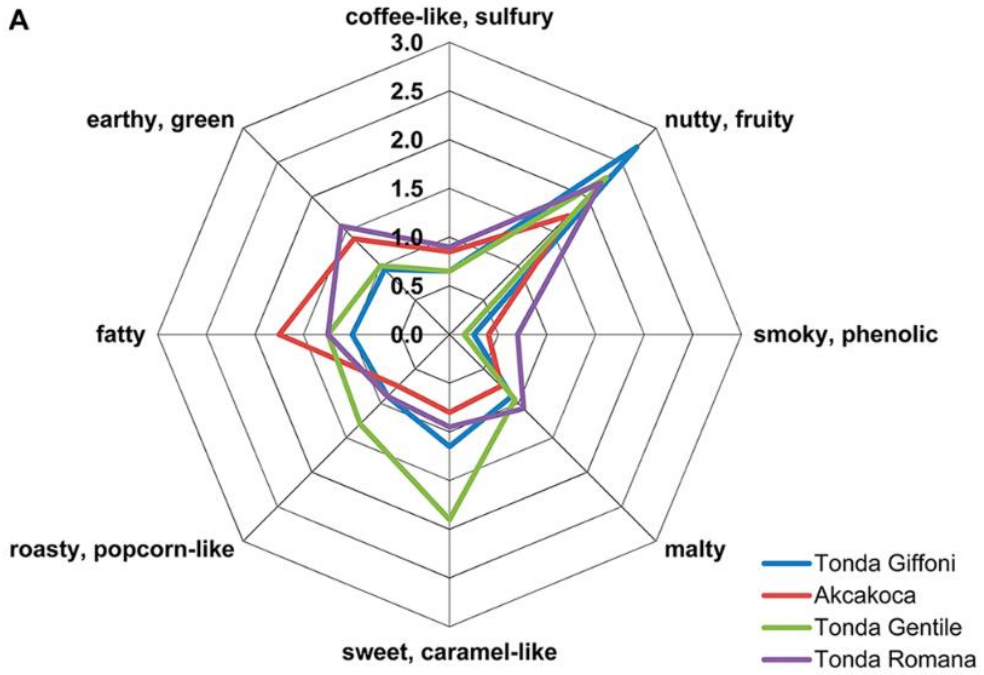
External calibration
Multiple headspace extraction (MHE[1])

$$A_T = \sum_{i=1}^{=\infty} A_i = A_1 \frac{1}{(1-e^{-q})} = \frac{A_1}{(1-\beta)}$$

$0.4 < \beta < 0.95$

1. R. Costa, L. Tedone, S. De Grazia, P. Dugo, L. Mondello, Anal. Chim. Acta. 770 (2013) 1–6. doi:10.1016/j.aca.2013.01.041.

Raw Hazelnuts



Ashes (~3%)

Aroma profile of raw hazelnuts from different cultivar/origin[1]

Volatiles (<0.01%)

List of raw hazelnuts **key food odorants** [2]:

Volatiles encrypt data regarding:

Geographical origin

Harvest year

Post-harvest practices

Storage time and conditions

Hexanal
3-methyl-4-heptanone
5-methyl-(E)-2-heptен-4-one
2-acetyl-1-pyrraline
dimethyl trisulfide
2-propionyl-1-pyrraline
2-furfurylmercaptan
3-(methylthio)propionaldehyde
3,5-dimethyl-2-ethylpyrazine
2,3-diethyl-5-methylpyrazine
3,7-dimethylocta-1,6-dien-3-ol
2-acetyl-1,4,5,6tetrahydropyridine
2-acetyl-3,4,5,6-tetrahydropridine
3-methylbutanoic acid
(E,E)-2,4-nonadienal

Spoilage markers[2]:

Hexanoic, Heptanoic and Octanoic acid, γ-nonalactone, γ-hexalactone, Acetone

Lipid oxidation markers:

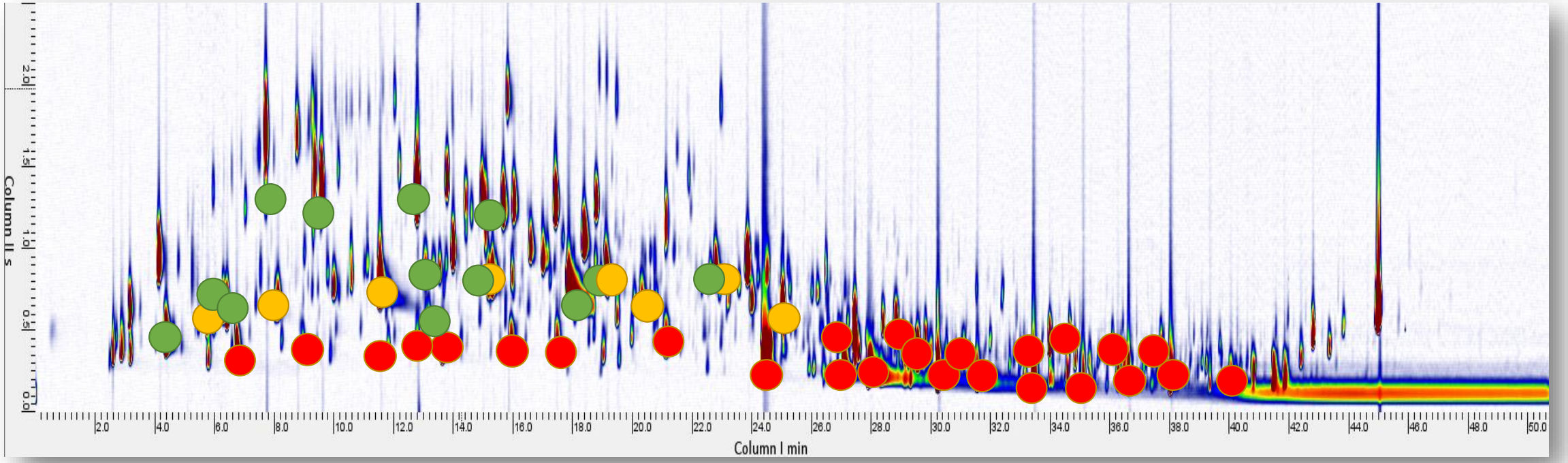
Heptanal, Octanal, Nonanal, (E)-2-heptanal, (E)-2-hexanal, 1-octen-3-ol

Just a few "**key-food odorants**" play a role in delineating the aroma

1. Kiefl, J.; Schieberle, P. J. Agric. Food Chem. 2013, 61 (22), 5236–5244.
2. Stilo, F. *et al.* Food Chemistry. 2021, 340. doi:10.1016/j.foodchem.2020.128135

Volatilome analysis

HS-SPME-GC×GC-MS/FID of a raw hazelnut (0.10 g) from Italy. Colum set-up: Heavy-Wax × OV17. MS:FID 30/70 - here represented the contour plot of the FID channel. Detectable features: 442. Untargeted features - 350 / Targeted features - 92.



Key aroma compounds Oxidation markers Spoilage markers

Aroma blueprint and potent odorants

42 Quantified analytes

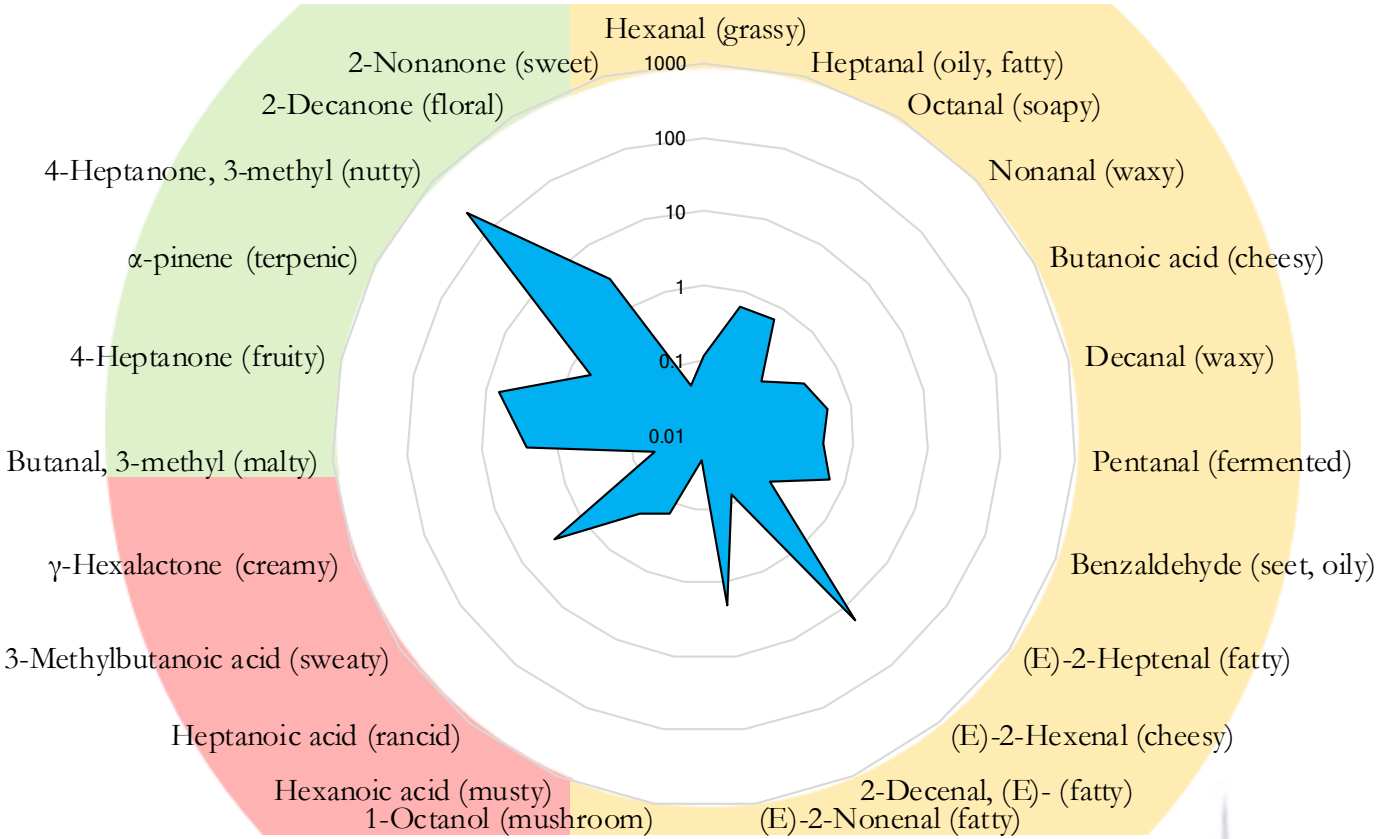
ODOUR ACTIVITY VALUE

$$OAV = \frac{[\text{Analyte ng/g}]}{\text{OT ng/g}}$$

OAV>1 highlight volatiles that likely have an **impact** on the overall aroma

Odour threshold (OT): lowest concentration of a certain odorant that is perceivable by the human sense of smell

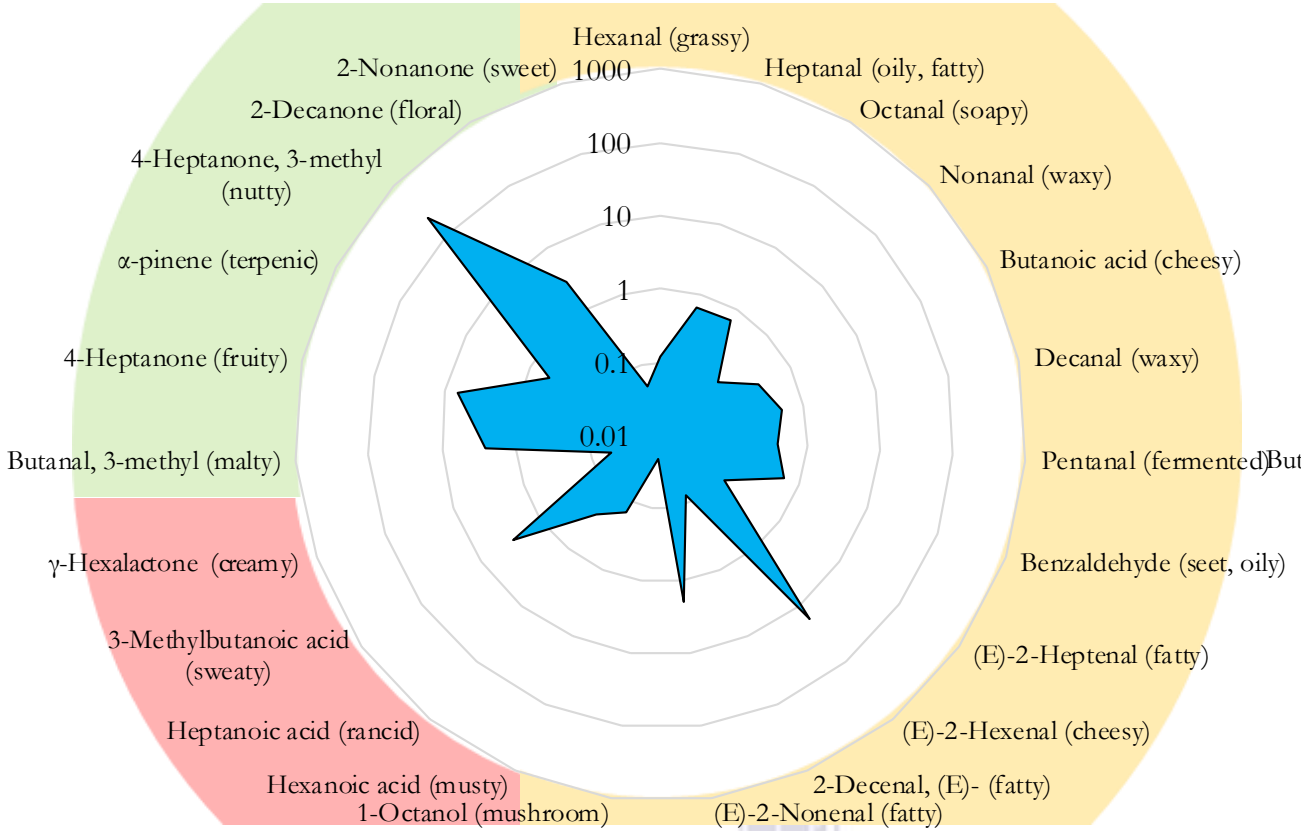
Raw hazelnuts from Italy - harvest 2020



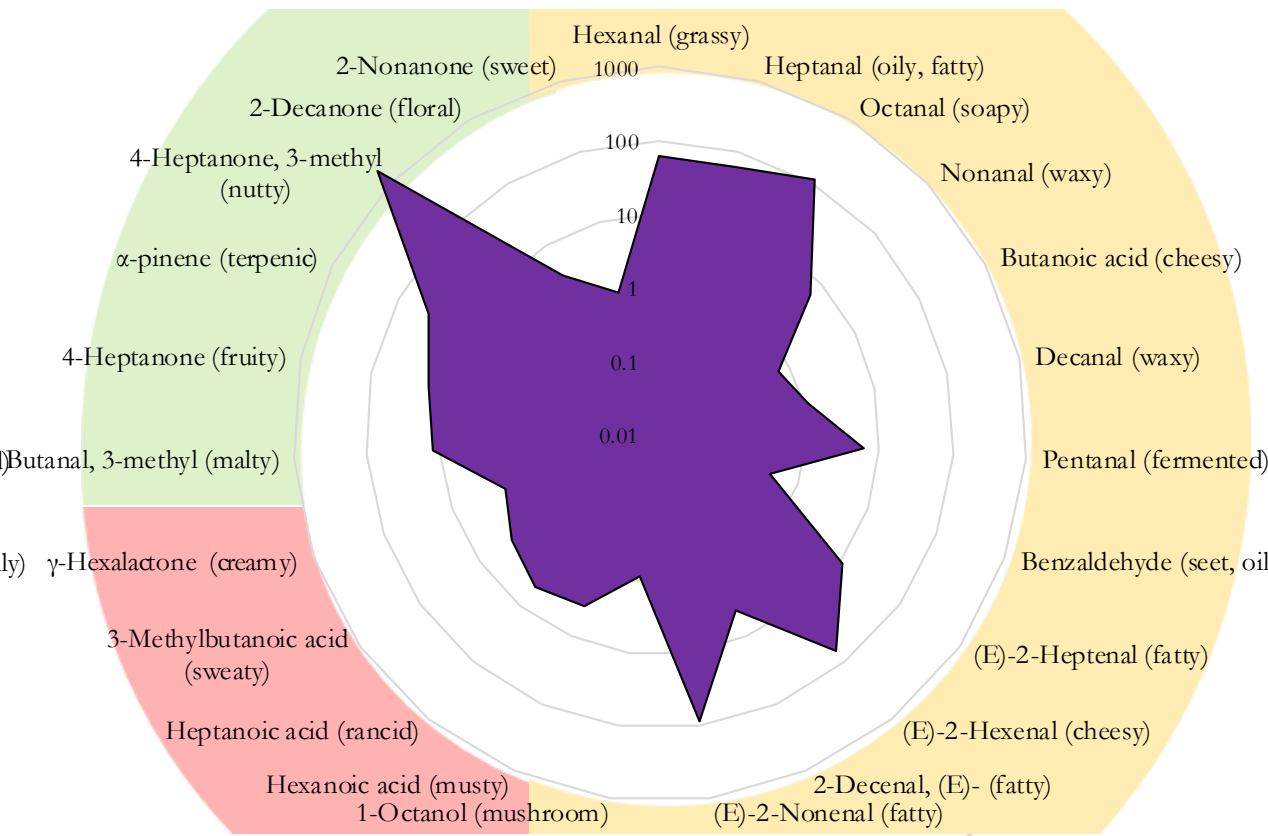
Sensory maps based on OAV values and visualized in log(10) scale

Blueprint comparison

Raw hazelnut from Italy 0 months



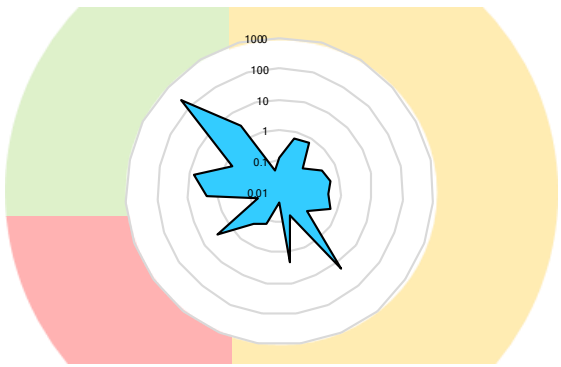
Raw hazelnut from Turkey 24 months - Air



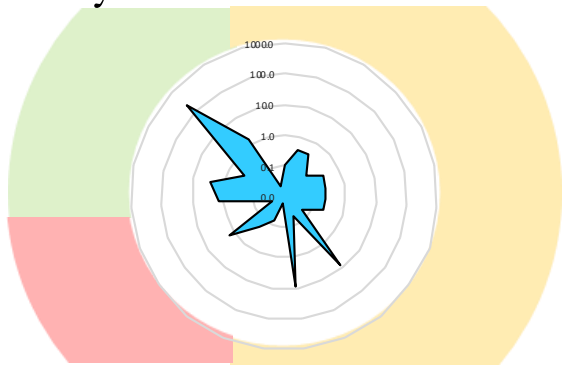
Sensory maps created from OAV values and visualized in log(10) scale

Blueprint evolution

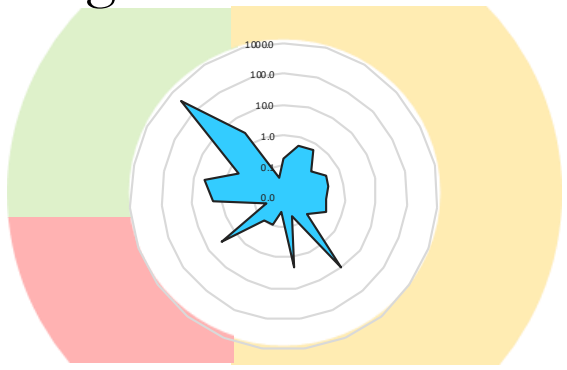
Raw hazelnuts from Italy – under vacuum storage



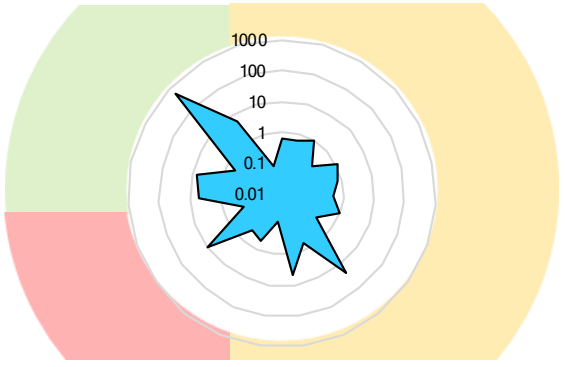
0 months



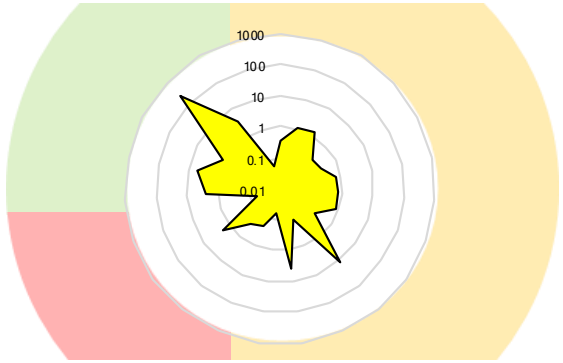
6 months

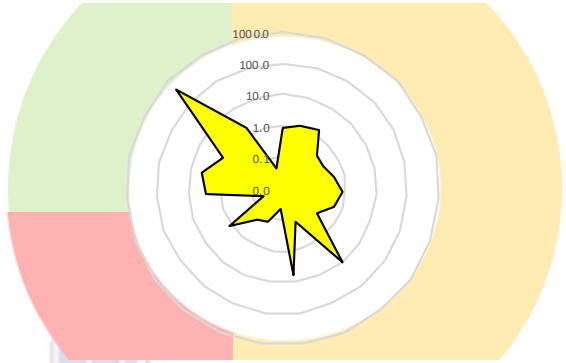


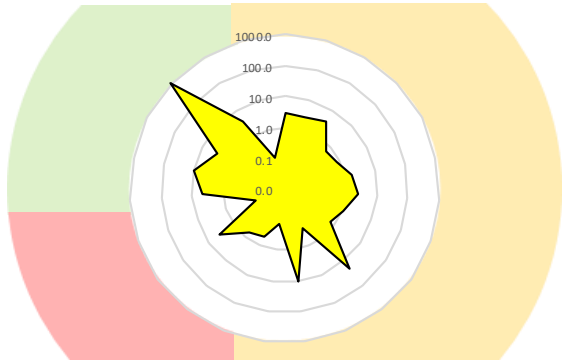
9 months

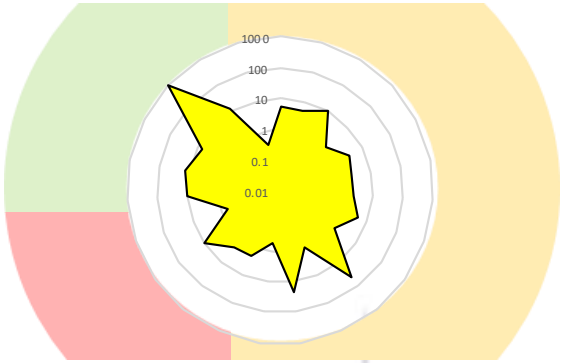


12 months





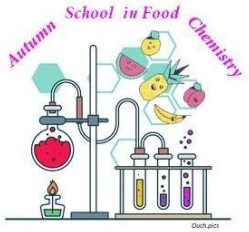




Raw hazelnuts from Turkey – std. atmosphere storage

Sensory maps created from OAV values and visualized in log(10) scale

Conclusions



One analytical run can provide many answers, such as assessing the global hazelnut quality by using the Fingerprinting approach, and digitalizing the aroma quality with AI sensory maps thanks to the accurate quantification of key odorants

GC×GC offers the suitable resolution for the AI smelling approach and is highly stable with differential-flow modulation, thus suitable for routine based analyses

MHE-SPME is a valid approach for volatile quantification purposes on solid matrices and a valid/greener alternative to solvent extraction

Thank you!

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Prof. Chiara E. Cordero