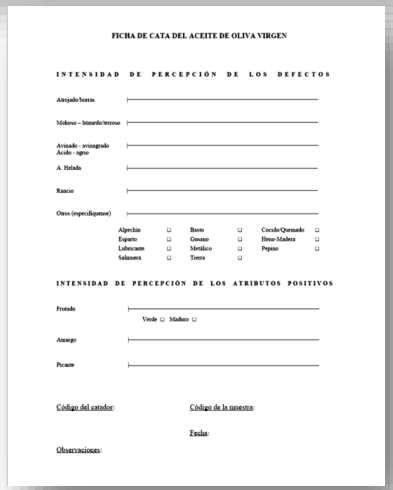
Analytical Solutions Addressing Olive Oil Quality Issues

Diego Luis García González

*Instituto de la Grasa-CSIC (dlgarcia@ig.csic.es)

Standard Method (IOC/EU) of Sensory Assessment



FICHA DE CATA DEL ACEITE DE OLIVA VIRGEN

INTENSIDAD DE PERCEPCIÓN DE LOS DEFECTOS

Atrojado/borras

Mohoso – húmedo/terroso

Avinado – avinagrado
Ácido – agrio

A. Helada

Rancio

Otros (especifíquese)

Alperchín	☐	Basto	☐	Cocido/Quemado	☐
Esparto	☐	Graso	☐	Heno-Madera	☐
Lubricante	☐	Metálico	☐	Pepino	☐
Salmuera	☐	Tierra	☐		

INTENSIDAD DE PERCEPCIÓN DE LOS ATRIBUTOS POSITIVOS

Frutado

Verde ☐ Maduro ☐

Amargo

Picante

Código del catador:

Código de la muestra:

Fecha:

Observaciones:

Standard Method (IOC/EU) of Sensory Assessment

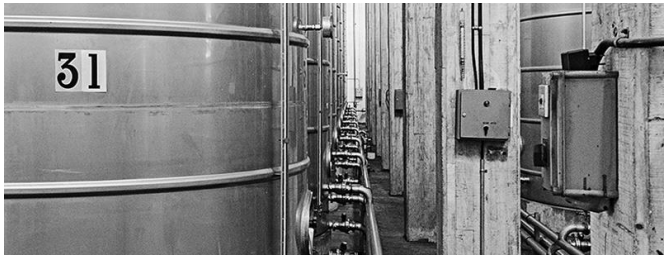
COI/T.20/DOC. 4/REV.1 - 2007 Sensory analysis: general basic vocabulary

COI/T.20/DOC. 5/REV.1 - 2007 Glass for oil tasting

COI/T.20/DOC. 6/REV.1 - 2007 Guide for the installation of a test room

COI/T.20/DOC.14/2013 - Guide for the selection, training and monitoring of skilled virgin olive oil tasters

COI/T.20/DOC.15/Rev. 7 - 2015 - Sensory analysis of olive oil - method for the organoleptic assessment of virgin olive oil (February 2015)



80s

Quality Improvement

2017

Standard Method (IOC/EU) of Sensory Assessment

IMPROVEMENTS

COI/T.20/DOC. 4/REV.1 - 2007 Sensory analysis: general basic vocabulary

COI/T.20/DOC. 5/REV.1 - 2007 Glass for oil tasting

COI/T.20/DOC. 6/REV.1 - 2007 Guide for the installation of a test room

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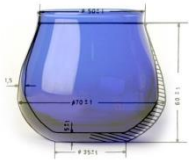
COI/T.20/DOC.15/Rev. 7 - 2015 - Sensory analysis of olive oil - method for the organoleptic assessment of virgin olive oil (February 2015)

Panelist training

Reference Materials

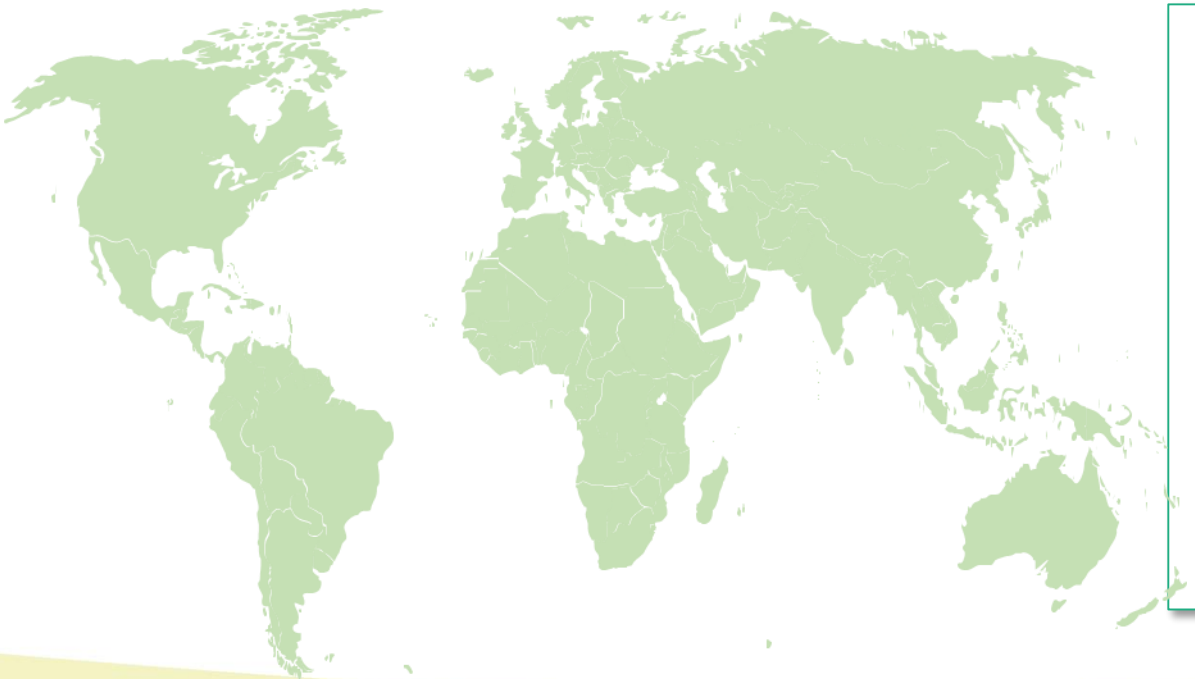


Statistics

Accreditation and Harmonization

A standardized instrumental method to support panel test work

Shelf life and freshness control



Shlef-Life

↓

Quality decay

↓

Needs of analytical support

Health claim and phenol analysis

http://ec.europa.eu/nuhclaims/?event=search#

efsa European Food Safety Authority

EFSA Journal 2011;9(4):2033

SCIENTIFIC OPINION

Scientific Opinion on the substantiation of health claims related to polyphenols in olive and protection of LDL particles from oxidative damage (ID 1333, 1638, 1639, 1696, 2865), maintenance of normal blood HDL-cholesterol concentrations (ID 1639), maintenance of normal blood pressure (ID 3781), "anti-inflammatory properties" (ID 1882), "contributes to the upper respiratory tract health" (ID 3468), "can help to maintain a normal function of gastrointestinal tract" (3779), and "contributes to body defences against external agents" (ID 3467) pursuant to Article 13(1) of Regulation (EC) No 1924/2006[1]

EFSA Panel on Dietetic Products, Nutrition and Allergies (NDA)[2, 3]

European Food Safety Authority (EFSA), Parma, Italy

SUMMARY

Following a request from the European Commission, the Panel on Dietetic Products, Nutrition and Allergies was asked to provide a scientific opinion on a list of health claims pursuant to Article 13 of Regulation (EC) No 1924/2006. This opinion addresses the scientific substantiation of health claims in relation to polyphenols in olive and protection of LDL particles from oxidative damage, maintenance of normal blood HDL-cholesterol concentrations, maintenance of normal blood pressure, "anti-inflammatory properties", "contributes to the upper respiratory tract health", "can help to maintain a normal function of gastrointestinal tract", and "contributes to body defences against external agents". The scientific substantiation is based on the information provided by the Member States in the consolidated list of Article 13 health claims and references that EFSA has received from Member States or directly from stakeholders.

[1] On request from the European Commission, Question No EFSA-Q-2008-2070, EFSA-Q-2008-2374, EFSA-Q-2008-2375, EFSA-Q-2008-2432, EFSA-Q-2008-2615, EFSA-Q-2008-3598, EFSA-Q-2008-4195, EFSA-Q-2008-4196, EFSA-Q-2008-4498, EFSA-Q-2008-4500, adopted on 12 November 2010.

[2] Panel members: Carlo Agostoni, Jean-Louis Bresson, Susan Fairweather-Tait, Albert Flynn, Ines Golly, Hannu Korhonen, Pagona Lagiou, Martinus Løvik, Rosangela Marchelli, Ambroise Martin, Bevan Moseley, Monika Neuhäuser-Berthold, Hildegard Przyrembel, Seppo Salminen, Yolanda Sanz, Sean (J.J.) Strain, Stephan Strobel, Inge Tetens, Daniel Tomé, Hendrik van Loveren and Hans Verhagen. Correspondence: nda@efsa.europa.eu

[3] Acknowledgement: The Panel wishes to thank for the preparatory work on this scientific opinion: The members of the Working Group on Claims: Carlo Agostoni, Jean-Louis Bresson, Susan Fairweather-Tait, Albert Flynn, Ines Golly, Marina Heinonen, Hannu Korhonen, Martinus Løvik, Ambroise Martin, Hildegard Przyrembel, Seppo Salminen, Yolanda Sanz, Sean (J.J.) Strain, Inge Tetens, Hendrik van Loveren and Hans Verhagen. The members of the Claims Sub-Working Group on Cardiovascular Health/Oxidative Stress: Antti Aro, Marianne Geleijnse, Marina Heinonen, Ambroise Martin, Wilhelm Stahl and Henk van den Berg.

Suggested citation: EFSA Panel on Dietetic Products, Nutrition and Allergies (NDA); Scientific Opinion on the substantiation of health claims related to polyphenols in olive and protection of LDL particles from oxidative damage (ID 1333, 1638, 1639, 1696, 2865), maintenance of normal blood HDL-cholesterol concentrations (ID 1639), maintenance of normal blood pressure (ID 3781), "anti-inflammatory properties" (ID 1882), "contributes to the upper respiratory tract health" (ID 3468), "can help to maintain a normal function of gastrointestinal tract" (3779), and "contributes to body defences against external agents" (ID 3467) pursuant to Article 13(1) of Regulation (EC) No 1924/2006. EFSA Journal 2011;9(4):2033 [25 pp.]. doi:10.2903/j.efsa.2011.2033. Available online: www.efsa.europa.eu/efsajournal

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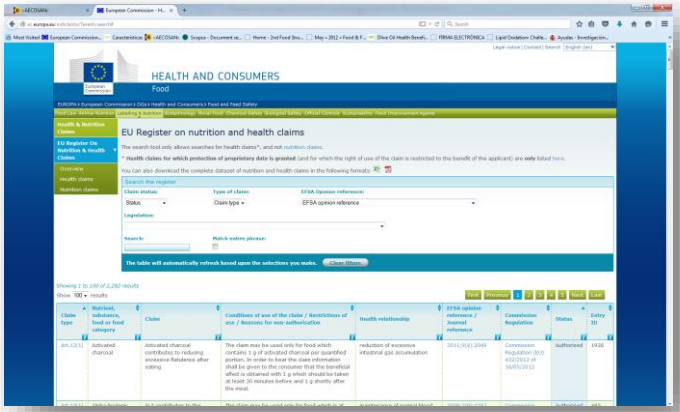

(Only 11% of submitted health claims are authorized)

efsa European Food Safety Authority
Committed to ensuring that Europe's food is safe

"Polyphenols in olive and olive oil"

Protection of LDL particles from oxidative damage

"containing at least **5 mg** of hydroxytyrosol and its derivatives (e.g. oleuropein complex and tyrosol) per **20 g of olive oil**"

How to "translate" this in analytical terms (Analytical method)

Objectives

Panel test improvement (quantitative panel test)

Volatile analysis to support panel tests

Analytical tolos for Shelf life control

Health claim and

Standard Method (IOC/EU) of Sensory Assessment

IMPROVEMENTS

COI/T.20/DOC. 4/REV.1 - 2007 Sensory analysis: general basic vocabulary

COI/T.20/DOC. 5/REV.1 - 2007 Glass for oil tasting

COI/T.20/DOC. 6/REV.1 - 2007 Guide for the installation of a test room

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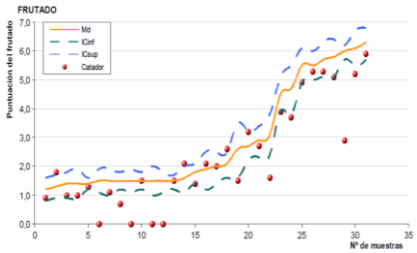
COI/T.20/DOC.15/Rev. 7 - 2015 - Sensory analysis of olive oil - method for the organoleptic assessment of virgin olive oil (February 2015)

European Commission

Reference Materials

Natural (VOO)



- Highly representative
- Not homogeneus year after year
- Insufficient amount for a continuous monitoring

Synthetic (volatile compounds + estable matrix)

CHARACTERIZATION BY VOLATILE COMPOUNDS

- Selection of volatile markers
- Chemical characterization of sensory defects

Sampling strategy

6 Sensory panels

P1	36 samples
P2	32 samples
P3	14 samples
P4	41 samples
P5	30 samples
P6	27 samples

→ 180 samples → 60 samples

- 12 EVOO
- 30 VOO
- 18 LVOO

26	Fusty
11	Rancid
6	Musty
4	Winey-vinegary
1	Frostbitten
2	Others (brine)

SPME-GC-FID

SPME-GC-MS

TDU-GC-MS

GC-Olfactometry

FGC-E-Nose

Distillation-NMR

UNIFIED PROTOCOL FOR SAMPLING, SHIPPING AND STORING







Participants.

Tullia Gallina Toschi (tullia.gallinatoschi@unibo.it)
Alessandra Bendini (alessandra.bendini@unibo.it)
Enrico Valli (enrico.valli4@unibo.it)

Diego L. García González (dlgarcia@ig.csic.es)
Ramón Aparicio-Ruiz (aparicioruiz@cica.es)
Noelia Tena (tena@ig.csic.es)

Paul Brereton (paul.brereton@fera.co.uk)
James Donarski (james.donarski@fera.co.uk)
Victoria Bailey-Horne (victoria.bailey-horne@fera.co.uk)

Ole Winkelmann (olewinkelmann@eurofins.de)

Stefania Vichi (stefaniavichi@ub.edu)

Maurizio Servili (maurizio.servili@unipg.it)

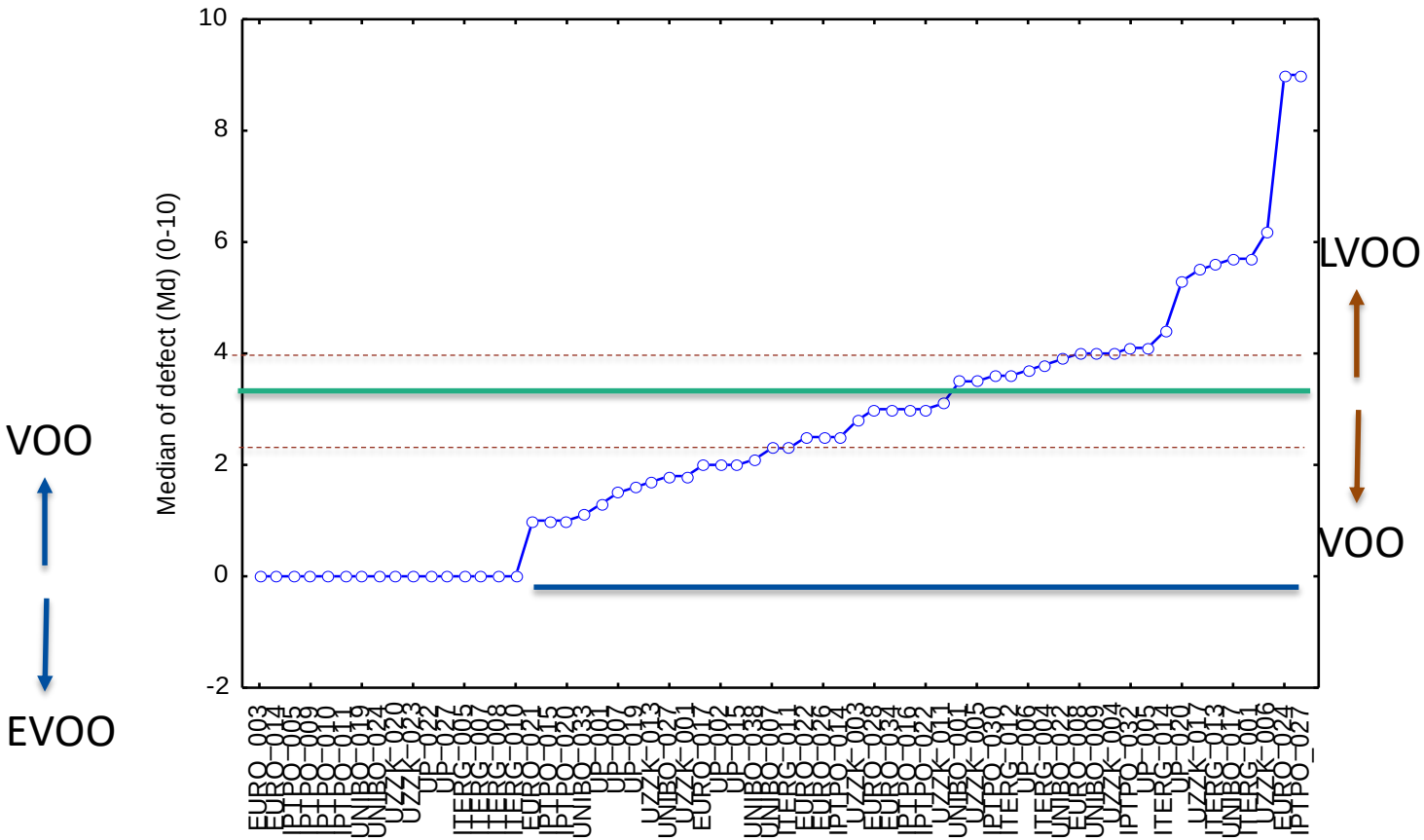
Florence Lacoste (f.lacoste@iterg.com)

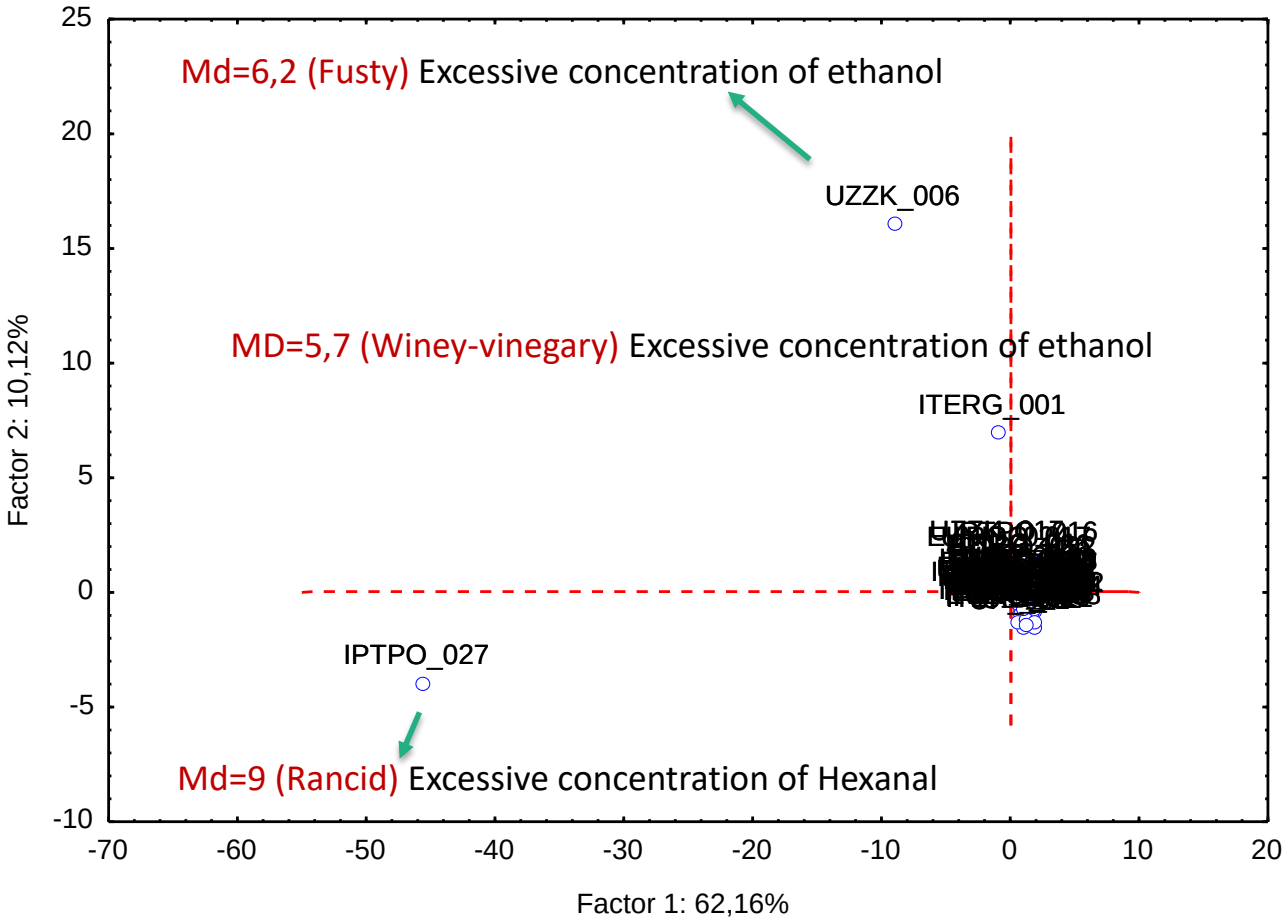
Lanfranco Conte (lanfranco.conte@uniud.it)

Pierre-Alain Golay (*pierre-alain.golay*@rdls.*nestle*.com)

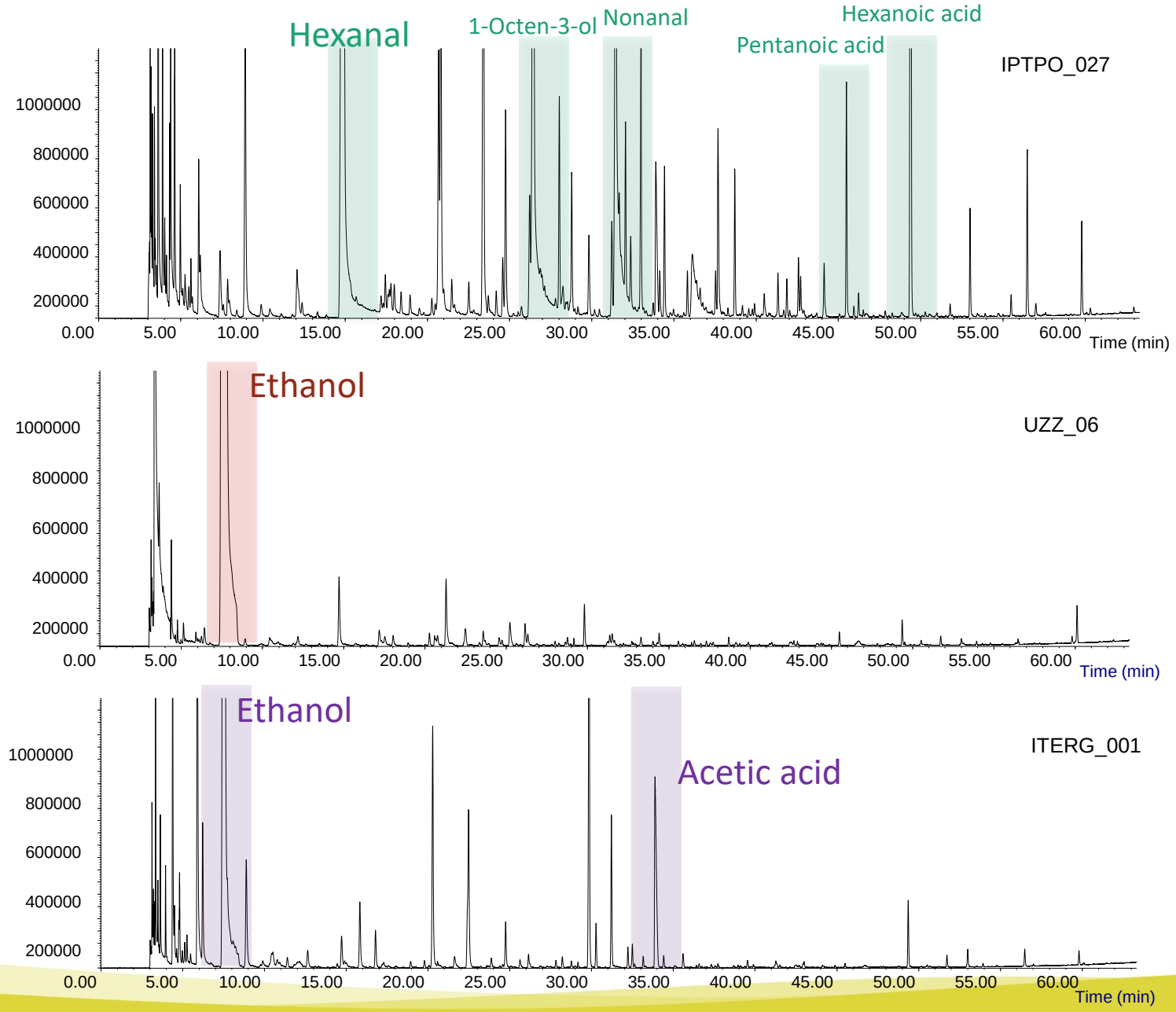
Alain Maquet (Alain.MAQUET@ec.europa.eu)

DO WE STUDY ALL THE RANGE? YES

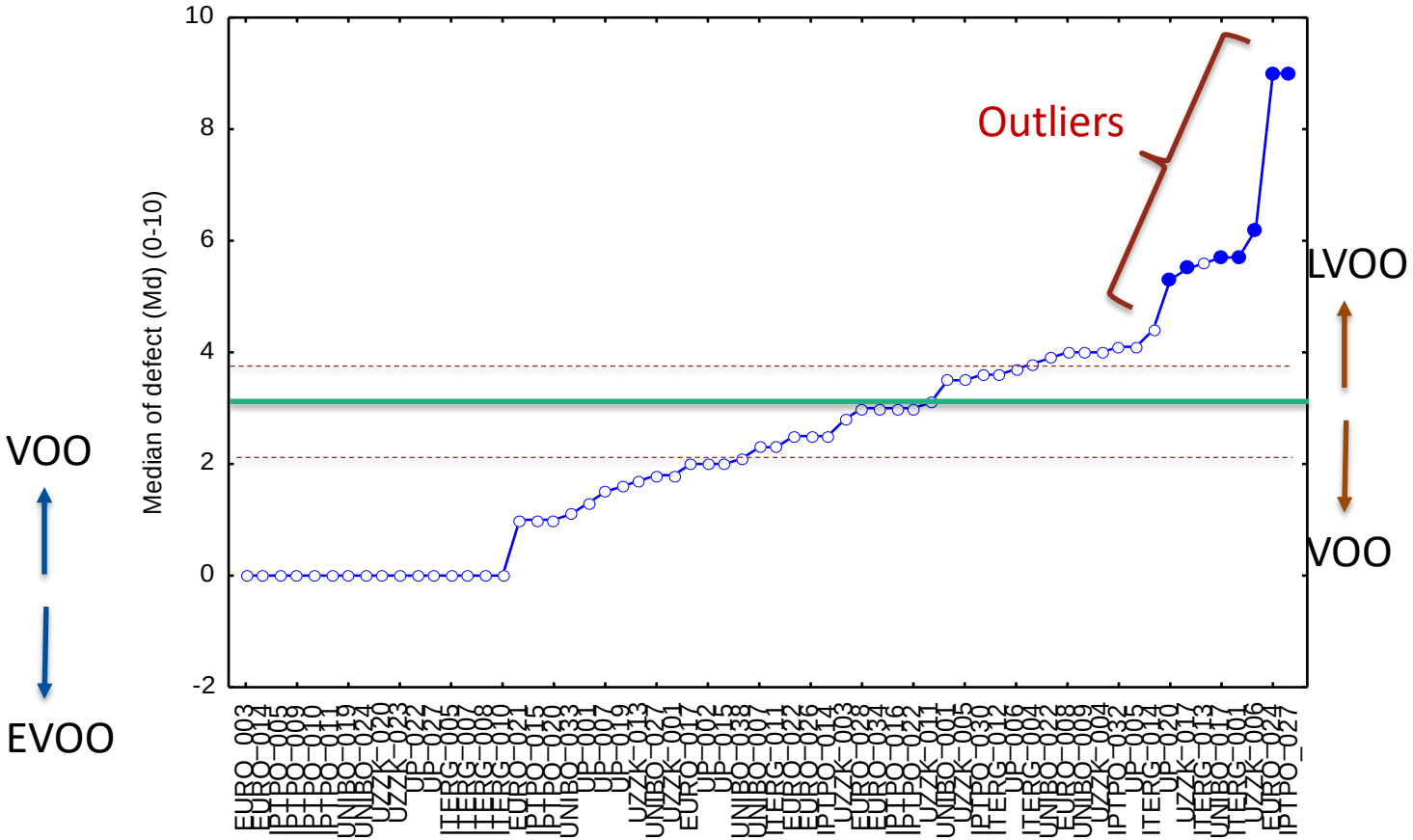



Md=6,2 (Fusty) Excessive concentration of ethanol
UZZK_006
MD=5,7 (Winey-vinegary) Excessive concentration of ethanol
ITERG_001
IPTPO_027
Md=9 (Rancid) Excessive concentration of Hexanal
Factor 2: 10,12%
Factor 1: 62,16%
25
20
15
10
5
0
-5
-10
-70
-60
-50
-40
-30
-20
-10
0
10
20

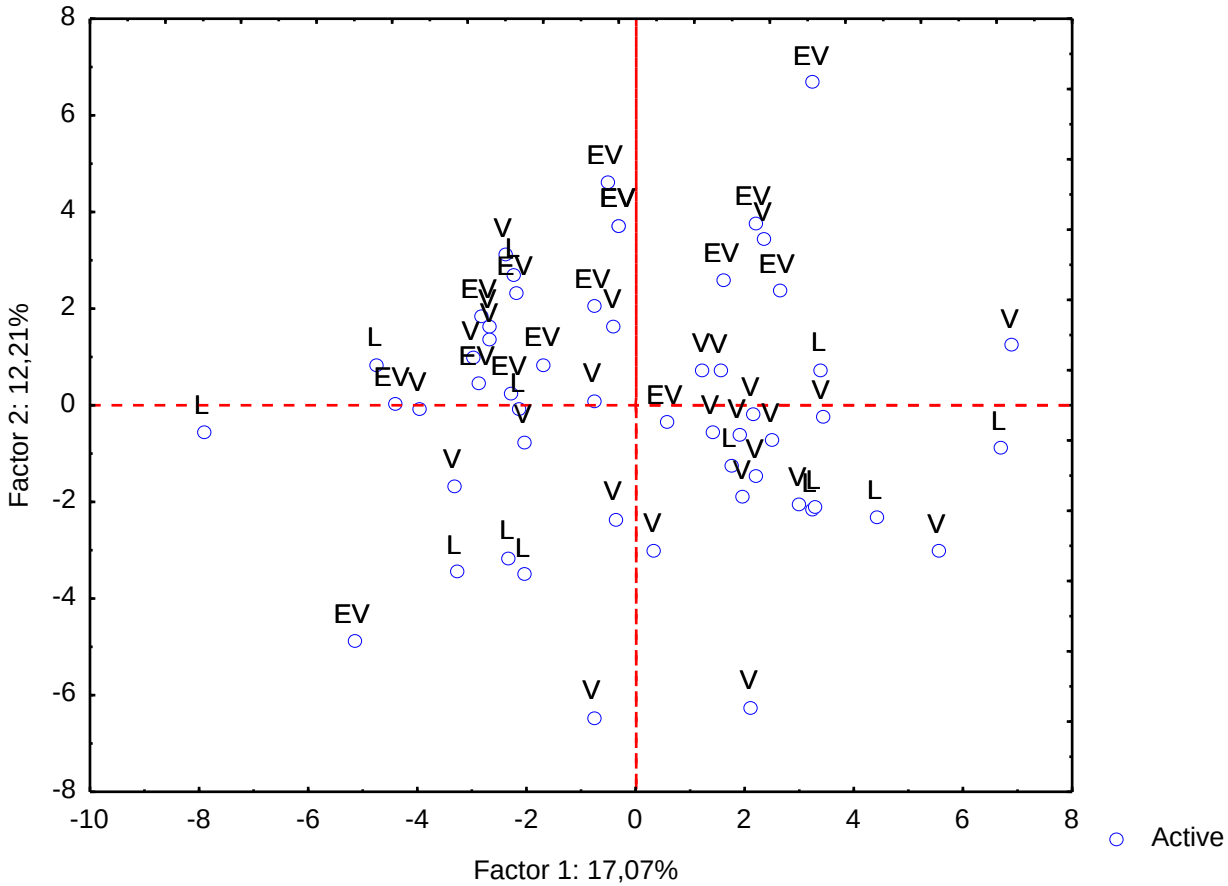
Oleum


Hexanal
1-Octen-3-ol
Nonanal
Pentanoic acid
Hexanoic acid
IPTPO_027
Ethanol
UZZ_06
Ethanol
Acetic acid
ITERG_001
1000000
800000
600000
400000
200000
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
60.00
Time (min)

Median of defect



Analysis with all volatile compounds (82)

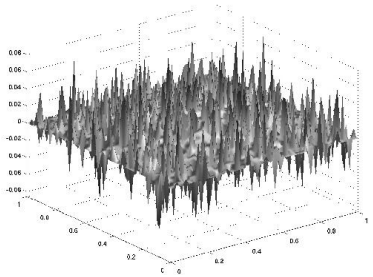


All variables (82)

Noise

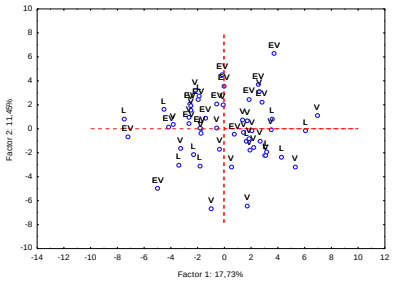
+

Informative data



Oleum

All volatile compounds (82)



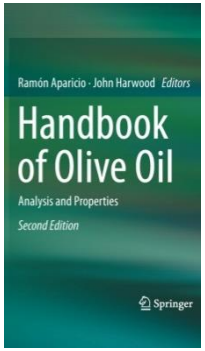
Selection by ANOVA+Brown-Forsythe ($p<0.05$)

- EVOO vs. the rest
- EVOO vs. VOO
- VOO vs. LVOO
- EVOO vs. LVOO

Octane	Pentanal	Pentan-3-ol
2-Methyl-1-propanol	3-Methyl-1-butanol	Isobutiric acid
E-2-pentenal	Propanoic acid	Pentanoic acid
6-Methyl-5-hepten-2-one	2-Butanol	Ethanol
E-2-Decenal	Ethyl acetate	Butanoic acid (SLDA)
Ethyl butanoate	Hexanal	Acetic acid (SLDA)
Nonanal	Hexanoic acid	Octanal (SLDA)

Oleum

Checking with previous works



Morales et al. Handbook of Olive Oil. Analysis and Properties, Aparicio, R., Harwood, J. (Eds.). 2013, pp. 261-309.

García-González et al., Handbook of Fruit and Vegetable Flavors, Hui, Y.H. (Ed.), 2010, pp. 821-847.

Morales et al. (2005). Food Chem. 91, 293-301.

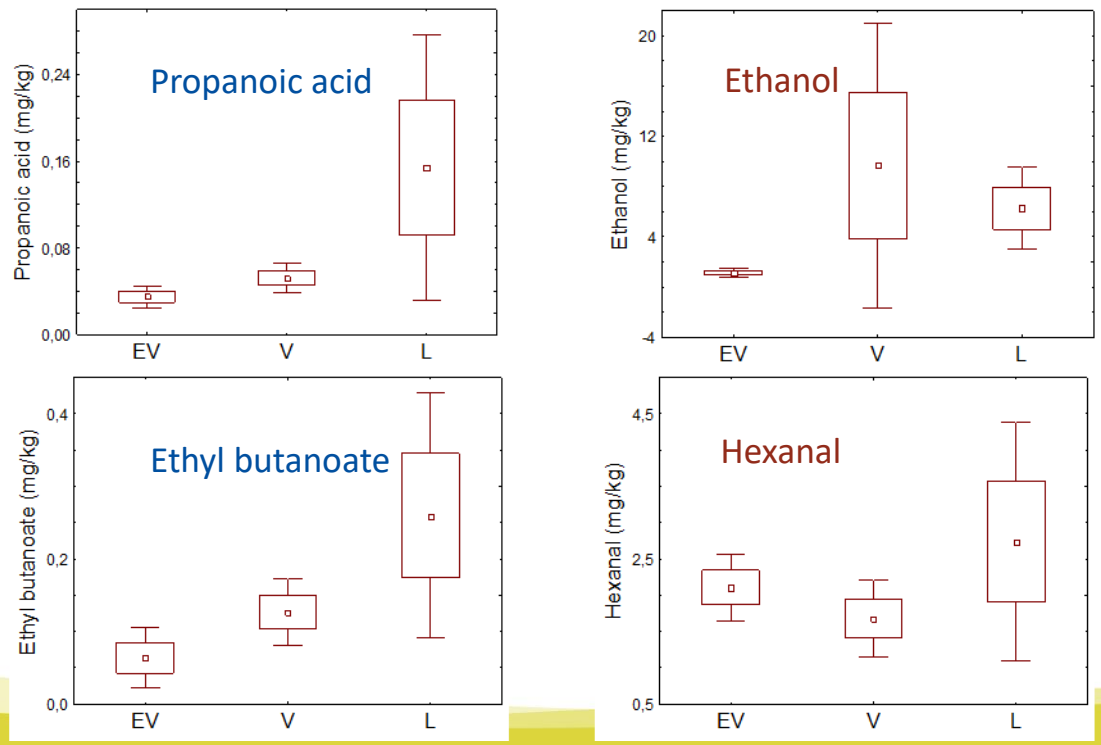
Sensory defect	Chemical compound	OT (mg/kg)	Sensory descriptor
Fusty	Octane	0.94	Alcane
	Ethyl butanoate	0.03	Fruity
	Butanoic acid	0.65	Fusty
	Propanoic acid	0.72	Sour, mould
	3-Methyl-1-butanol	0.10	Vinegary
	2-Methyl-1-propanol	1.00	Irritant
Muddy-sediment	Heptan-2-ol	0.01	Earth
	6-Methyl-5-hepten-2-one	1.00	Oily
	1-Penten-3-one	0.004	Mustard
	2-Butanol	0.15	Vinegary
Mustiness-humidity	1-Octen-3-ol	0.05	Musty, Earth
	1-Octen-3-one	0.01	Mushroom, mould
	Ethyl acetate	0.94	Intense
	Heptan-2-ol	0.01	Earth
	Acetic acid	0.50	Vinegary, sour
	Heptan-2-ol	0.01	Earth
	E-2-Heptenal	0.042	Fatty, oxidized
	Propanoic acid	0.72	Sour, mould
Winey-vinegary	Acetic acid	0.50	Vinegary, sour
	Ethyl acetate	0.94	Intense
	Ethanol	30.0	Alcohol
	3-Methyl-butan-1-ol	0.10	Whisky
Rancid	Pentanal	0.24	Oily
	Hexanal	0.08	Oily, fatty
	Heptanal	0.50	Oily, fatty
	E-2-Heptenal	0.042	Fatty, oxidized
	Octanal	0.32	Fatty
	Nonanal	0.15	Wax, fatty
	E-2-Decenal	0.01	Fatty
	Hexanoic acid	0.70	Rancid
Metallic	1-Octen-3-one	0.01	Mushroom, mould
	1-Penten-3-one	1×10^{-3}	Mustard
	1,5-Octadien-3-one	5×10^{-4}	Metallic, geranium
Burnt, Heated	(E)-2-Hexenol	5.00	Strong green
	1-Hexanol	0.40	Astringent
	Pentanal	0.24	Oily
	Nonanal	0.15	Waxy, fatty
	Hexanal	0.08	Oily, fatty
Bottled	2,6-Nonadienal	0.09	Cucumber

Octane	Pentanal	Pentan-3-ol
2-Methyl-1-propanol	3-Methyl-1-butanol	Isobutiric acid
E-2-pentenal	Propanoic acid	Pentanoic acid
6-Methyl-5-hepten-2-one	2-Butanol	Ethanol
E-2-Decenal	Ethyl acetate	Butanoic acid (SLDA)
Ethyl butanoate	Hexanal	Acetic acid (SLDA)
Nonanal	Hexanoic acid	Octanal (SLDA)

Mean

Mean±SE

Mean±1,96*SE



Breakdown analysis between designations

Box & Whisker plots

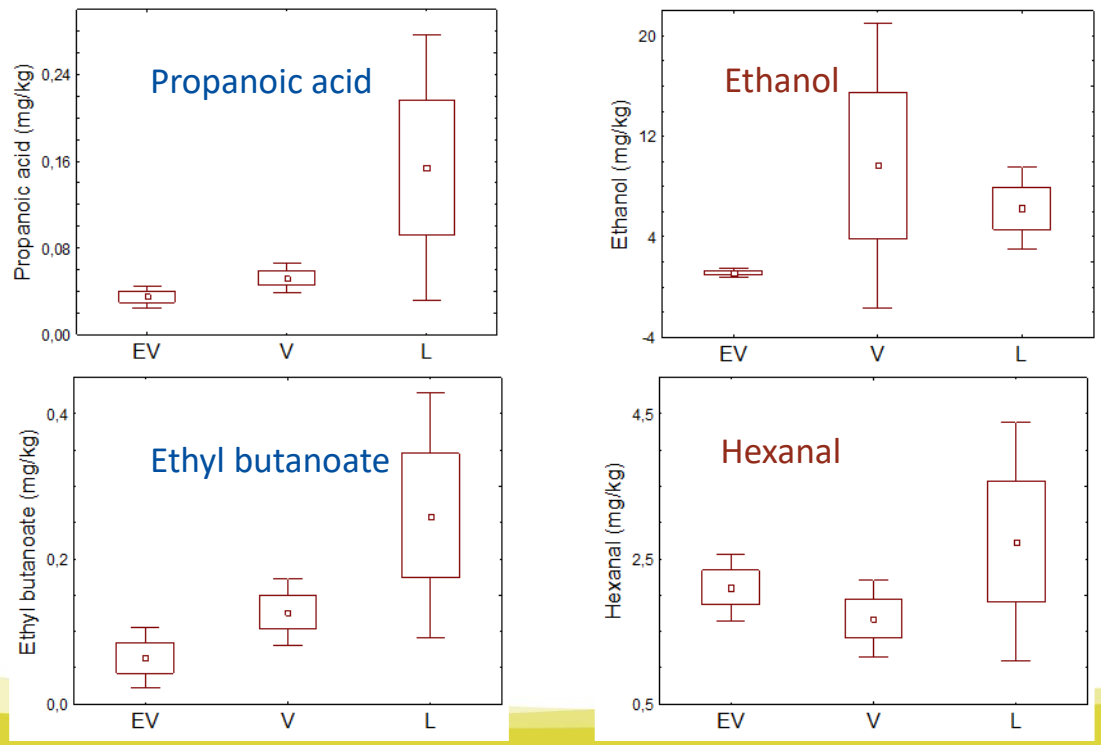
Oleum

Octane	Pentanal	Pentan-3-ol
2-Methyl-1-propanol	3-Methyl-1-butanol	Isobutiric acid
E-2-pentenal	Propanoic acid	Pentanoic acid
6-Methyl-5-hepten-2-one	2-Butanol	Ethanol
E-2-Decenal	Ethyl acetate	Butanoic acid (SLDA)
Ethyl butanoate	Hexanal	Acetic acid (SLDA)
Nonanal	Hexanoic acid	Octanal (SLDA)

Mean

Mean±SE

Mean±1,96*SE



Breakdown analysis between designations

Box & Whisker plots

Samples with winey-vinegary defect

EURO28 Md=3

UNIBO7 Md=2.3

Main defect, agreement in panel tests

Other samples where winey-vinegary has been mentioned:

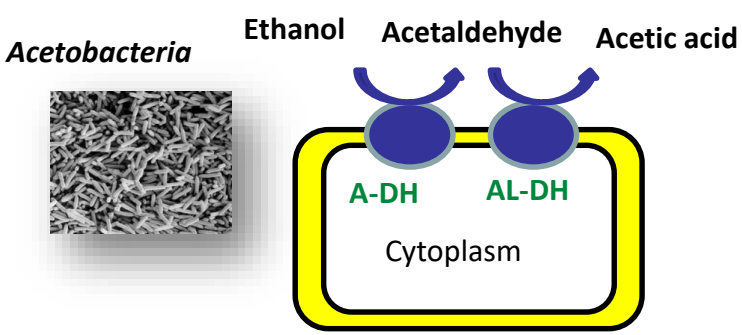
UP6, ITERG1, EURO26, EURO34, EURO21, UZZK6

Ethyl acetate

Ethanol

Acetic acid

Alcoholic fermentation



A-DH= Alcohol dehydrogenase
AL-DH= Aldehyde dehydrogenase

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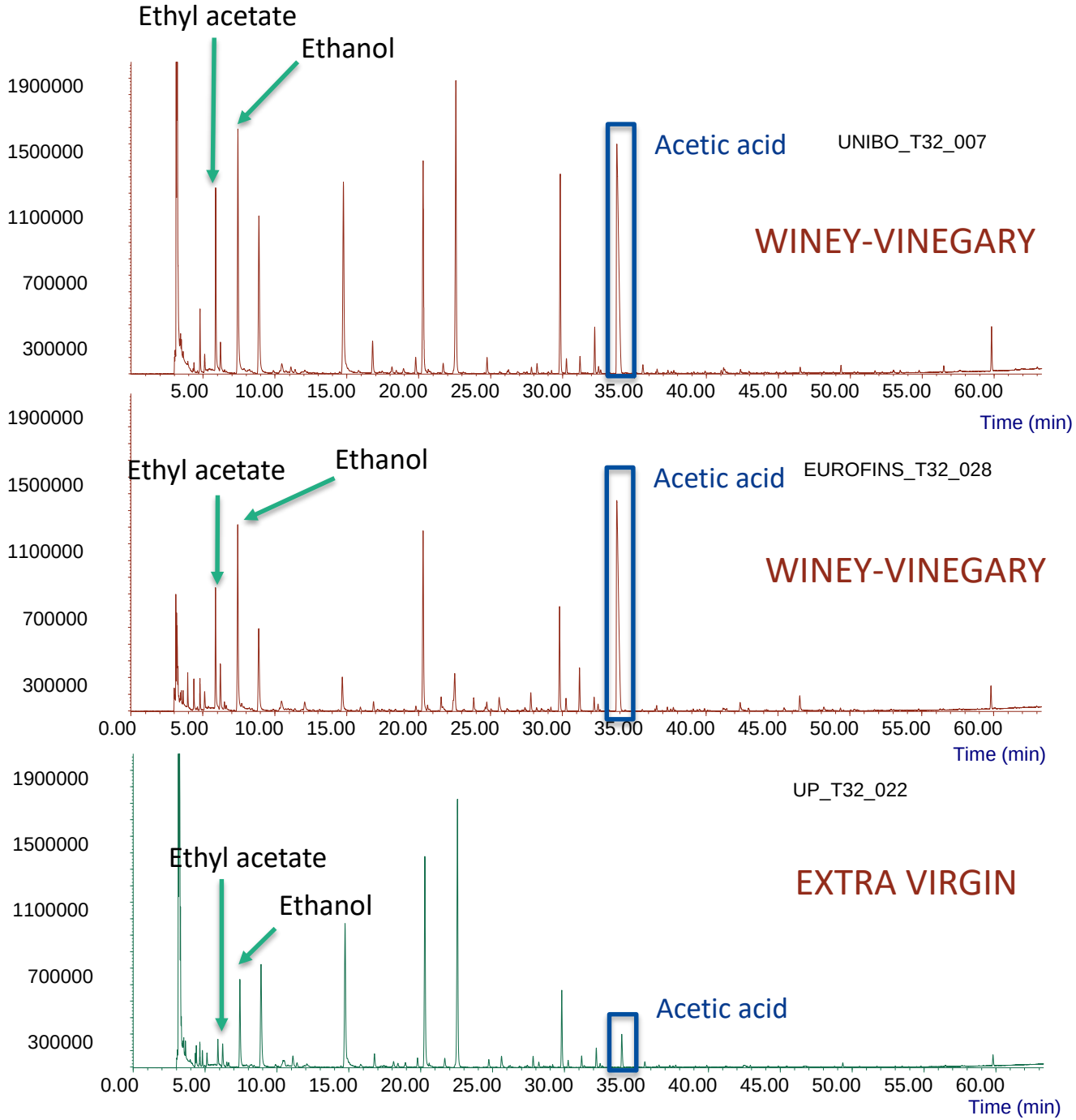
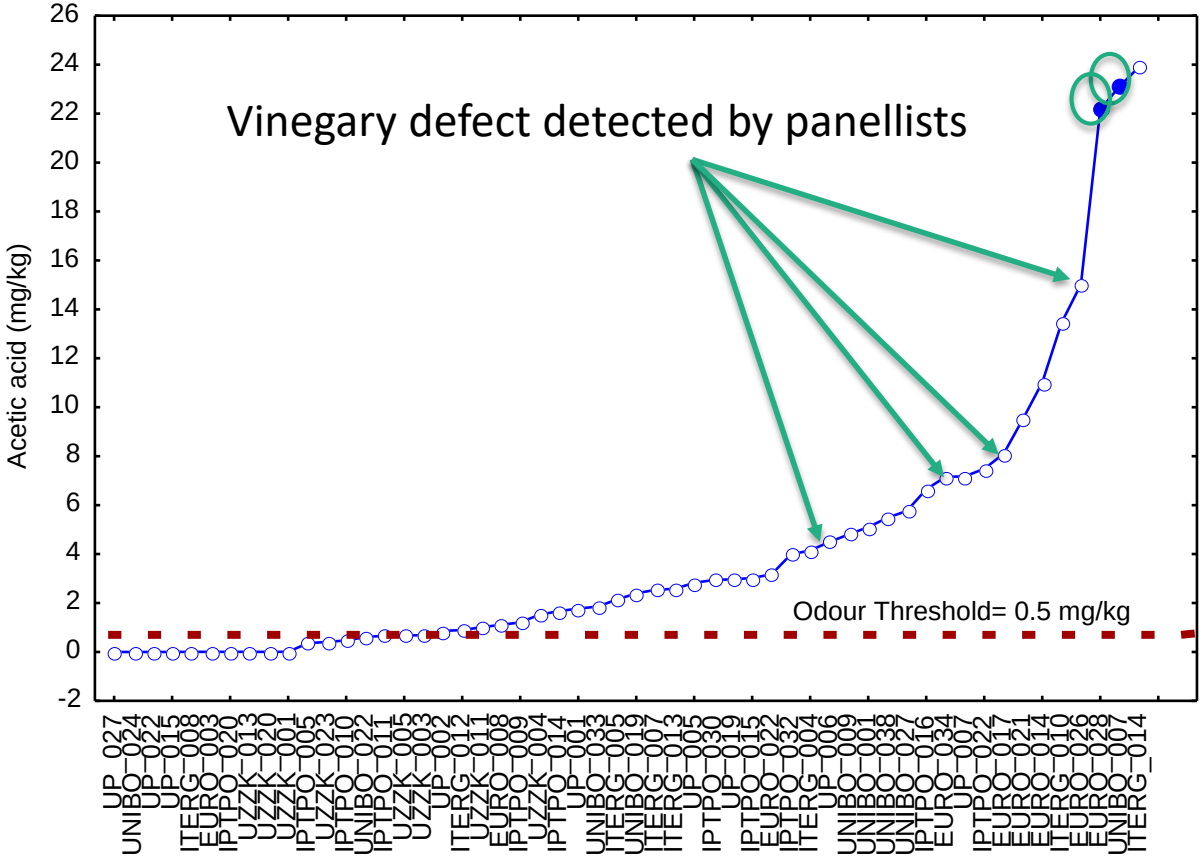

Ethyl acetate
Ethanol
Acetic acid
UNIBO_T32_007
WINEY-VINEGARY
1900000
1500000
1100000
700000
300000
5.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 45.00 50.00 55.00 60.00
Time (min)
Ethyl acetate
Ethanol
Acetic acid
EUROFINS_T32_028
WINEY-VINEGARY
0.00 5.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 45.00 50.00 55.00 60.00
Time (min)
UP_T32_022
Ethyl acetate
Ethanol
EXTRA VIRGIN
Acetic acid
Time (min)


Vinegary defect detected by panellists
Acetic acid (mg/kg)
26
24
22
20
18
16
14
12
10
8
6
4
2
0
-2
Odour Threshold= 0.5 mg/kg
UP_027
UNIBO_024
UP_022
UP_015
ITERG_008
EURO_003
IPTPO_020
UZZK_013
UZZK_020
UZZK_001
IPTPO_005
UZZK_023
IPTPO_010
UNIBO_022
IPTPO_011
UZZK_005
UZZK_003
UP_002
ITERG_012
UZZK_011
EURO_008
IPTPO_009
UZZK_004
IPTPO_014
UP_001
UNIBO_033
ITERG_005
UNIBO_019
ITERG_007
ITERG_013
UP_005
IPTPO_030
UP_019
IPTPO_015
EURO_022
IPTPO_032
ITERG_004
UP_009
UNIBO_001
UNIBO_038
UNIBO_027
IPTPO_016
EURO_034
UP_007
IPTPO_022
EURO_017
EURO_021
EURO_014
ITERG_010
EURO_026
EURO_028
UNIBO_007
ITERG_014

Winey-vinegary defect: ongoing work

Chemical characterization of defects

Selection of markers

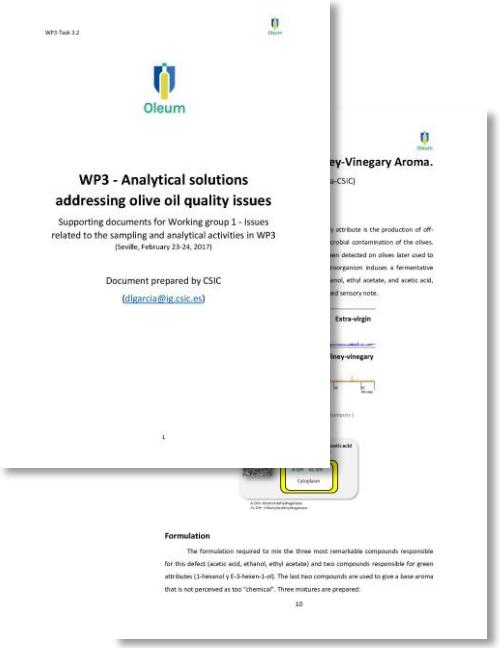
Design of formulations

ISO Characteristics

Representative?
Stable?
Homogeneous?

No

Yes



Oleum

Concluding remarks

- Developing RMs can be applied for training panels, continuous evaluation of panellists, and harmonization activities without the problem of having limited quantities.

- The analysis of volatile can support the work of a panel test in different aspects, overall when doubts between categories (e.g. EVOO-VOO).

- Adressing VOO quality from diferent perspectives (volatiles, shelf life, phenols) allows incorporating recent analytical advances into quality control.

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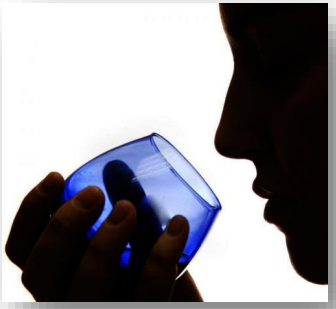
Thank you for your attention

Diego L. García González (dlgarcia@ig.csic.es)

Instituto de la Grasa (CSIC)



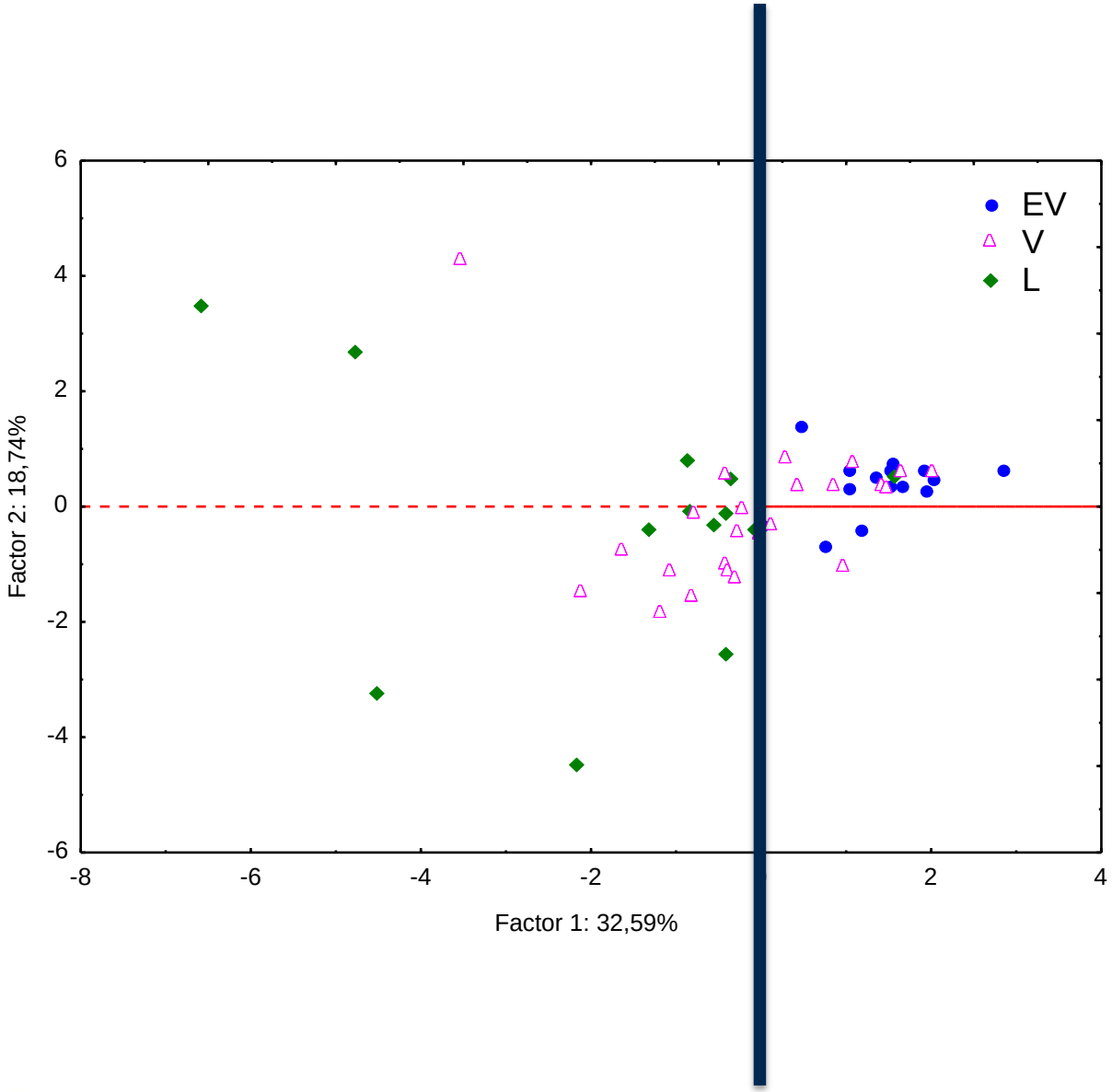
Needs for a Rerence Materials

- Natural (VOO)
  - Highly representative
  - Non homogeneous between years
  - Insufficient amount for a continuous monitoring

- Emuled with volatile compounds + stable matrix
  - Aroma that resembles this of sensory defects.
  - Homogeneus year after year (closer to ISO definition of RM).
  - Sufficient amount for a continuous monitoring.

CHARACTERIZATION OF VOLATILE COMPOUNDS

- Selection of volatile markers
- Chemical characterization of sensory defects


EV
V
L
6
4
2
0
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-6
-4
-2
2
4
Factor 2: 18,74%
Factor 1: 32,59%

Oleum

Volatile compounds

Calibration of Sensory Panels

REVISION of “Guide for the selection….” COI/T.20/DOC.14/2013

Guarantee Health Claim

Better reliability

Hydroxytyrosol and derivatives

RM

Objectives

Freshness assessment

Method + validated software

Method to detect/quantify volatile compounds

Non volatile volatile compounds

Develop/Validate

Strategy

Formulations

Statistical Sensory Wheel/Update of literature
List of descriptors for voatile compounds
Previous experiences

Open debate (free-choice sensory description)

GC analysis

Adjustment of concentration balance