TRACEABILITY CONTROL OF WINE PURCHASES USING PROTON NMR

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ESTACIÓN ENOLÓGICA DE HARO (EEH)

6 de junio de 2023

44th OIV Congress, Spain 2023

La Rioja
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Territorio y Población

PRESENT-DAY

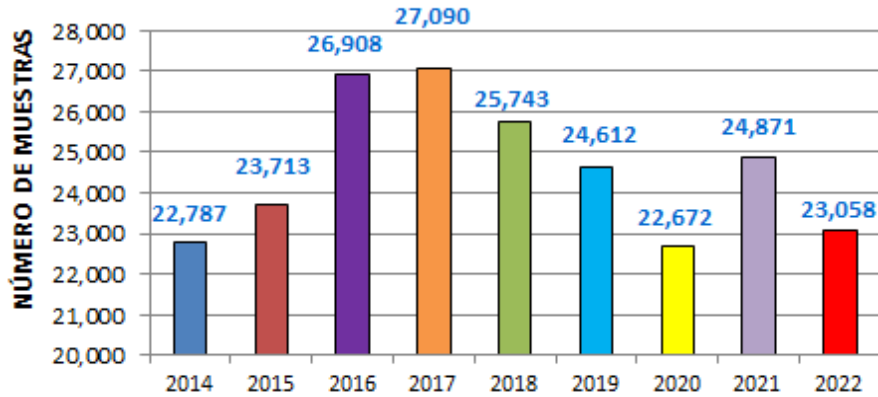| DEPARMENT OF AGRICULTURE, LEVESTOCK, RURAL AREAS, TERRITORY AND POPULATION | DIRECTORATE-GENERAL FOR AGRICULTURE, LEVESTOCK | AGRICULTURAL AND VEGETABLE HEALTH RESEARCH SERVICE | ESTACIÓN ENOLÓGICA DE HARO |

Instituto de Ciencias de la Vid y del Vino
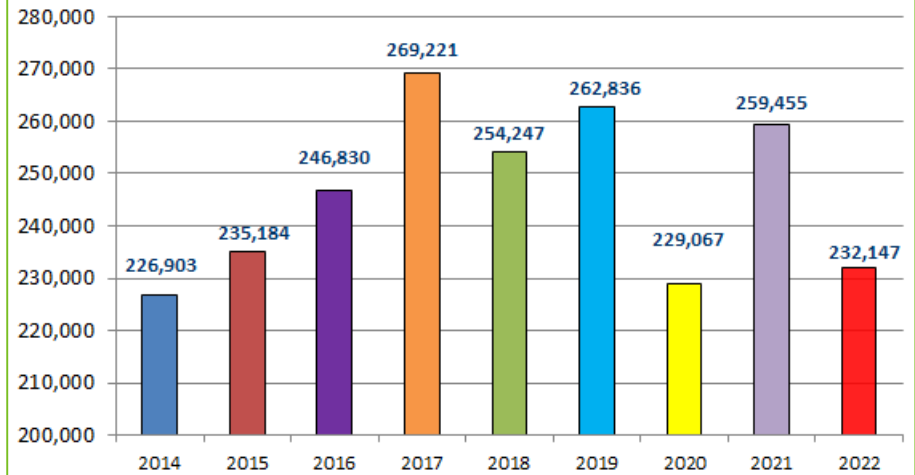
PRESENT-DAY

ROLES

OFFICIAL

ACCREDITATION

THE
INDUSTRY

TRAINING

REGULATORY
BODIES DOCS

RESEARCH

estaenol@larioja.org

SAMPLES/YEAR

ANALYSIS/YEAR

% Clients 2022

OTRAS PROVINCIAS — RIOJA

42,2%   57,8%
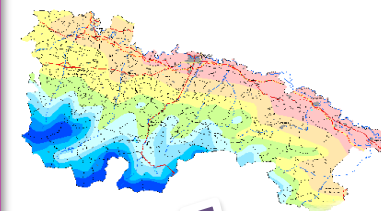
NMR LABORATORY

OFFICE

MICROBIOLOGY LABORATORY

INSTRUMENTAL ANALYSIS AND QUALITY CONTROL LABORATORY

NMR LABORATORY
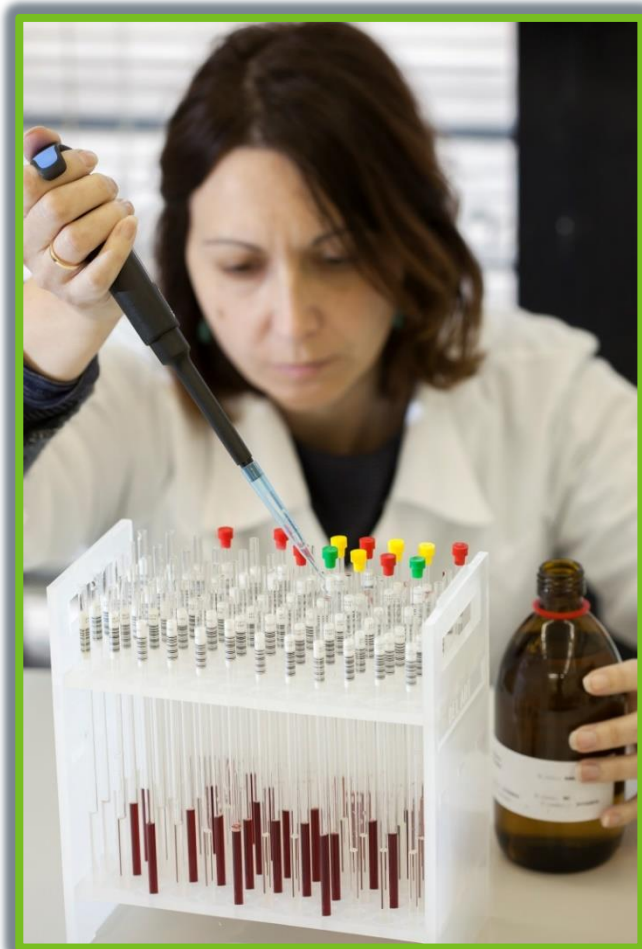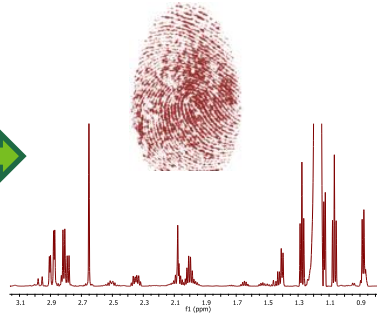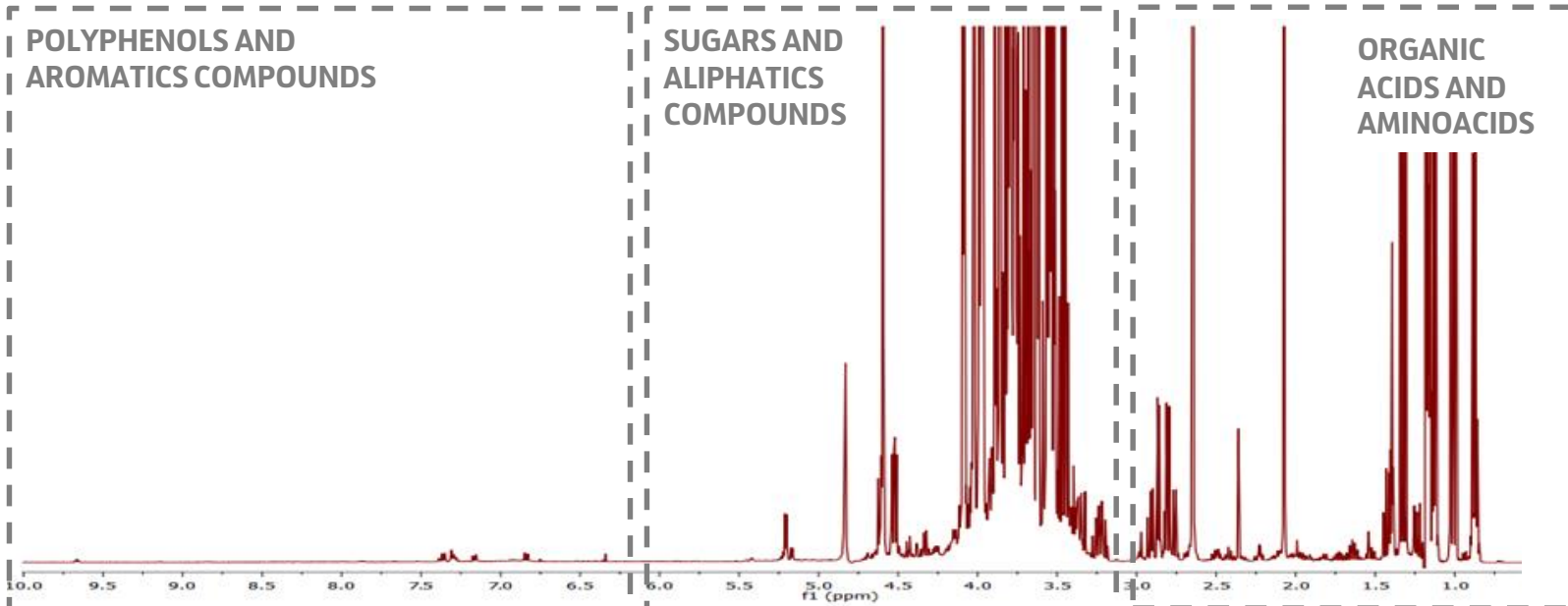
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ESTACIÓN
ENOLÓGICA
DE HARO

BRUKER **WINE-PROFILING**

Wine sample

Preparation and aquisition of the spectrum

"Fingerprint"

POLYPHENOLS AND AROMATICS COMPOUNDS

SUGARS AND ALIPHATICS COMPOUNDS

ORGANIC ACIDS AND AMINOACIDS

11

Wine sample

Preparation and aquisition of the spectrum
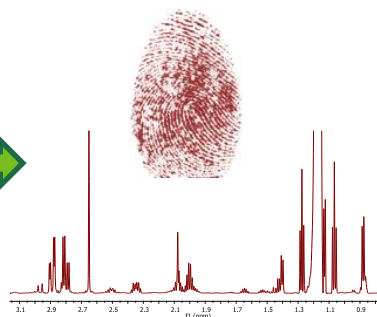
"Fingerprint"

QUANTITATION

OIV-MA-AS316-01

COMPENDIUM OF INTERNATIONAL ANALYSIS OF METHODS – OIV
Quantitation of glucose, malic acid, acetic acid, fumaric acid, shikimic acid and sorbic acid in wine using quantitative nuclear magnetic resonance spectrometry (1H NMR)

Method OIV-MA-AS316-01   Type IV method

Quantitation of glucose, malic acid, acetic acid, fumaric acid, shikimic acid and sorbic acid in wine using quantitative nuclear magnetic resonance spectrometry (^{1}H NMR)
OIV-OENO 618-2020

Wine sample → Preparation and aquisition of the spectrum → "Fingerprint"

QUANTITATION

OIV-MA-AS316-01

Compound	LOQ
2-PHENYLETHANOL	25 mg/L
3-METYL-BUTANOL	100 mg/L
ISOBUTANOL	70 mg/L
ETHYLLACTATE	150 mg/L
METHANOL	30 mg/L
ETHYLACETATE	50 mg/L
ETHANAL	10 mg/L
TARTARIC ACID	0.5 g/L
MALIC ACID	0.2 g/L
CITRIC ACID	200 mg/L
GLUCONIC ACID	400 mg/L
ACETIC ACID	100 mg/L
SHIKIMIC ACID	20 mg/L
GLYCEROL	0.5 g/L
GLUCOSE	0.5 g/L
FRUCTOSE	0.5 g/L
SORBIC ACID	10 mg/L
pH	upH
ALCOHOLIC DEGREE	% vol

Valor central
Z-score 2.00
Z-score
Z-score -2.00
Z-score 3.00
Z-score -3.00
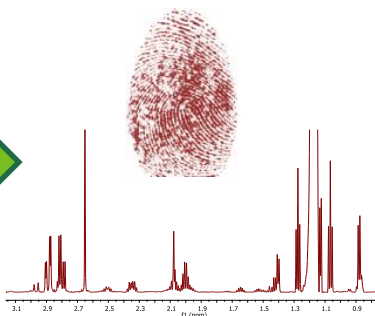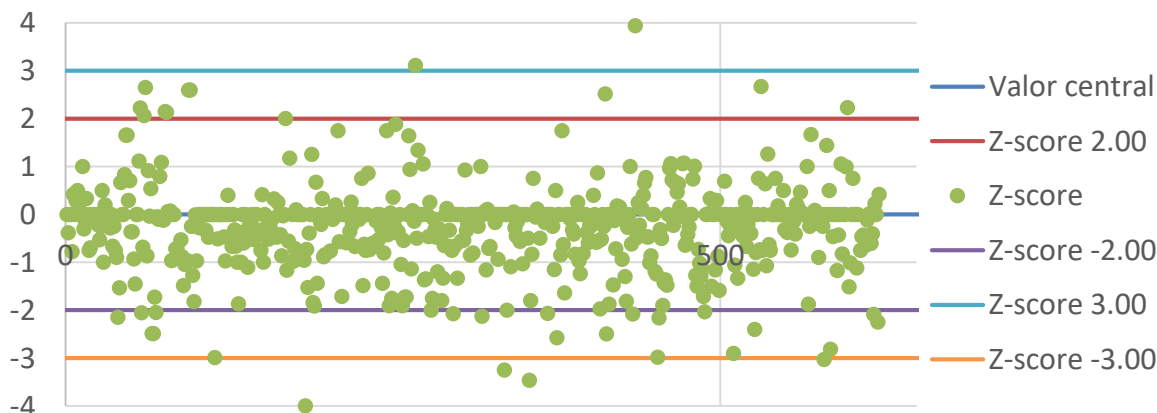
RING-TESTS RESULTS FROM 2019
(BIPEA AND OFFICIAL SPANISH LABORATORIES)

13

Wine sample

Preparation and aquisition of the spectrum

"Fingerprint"

QUANTITATION
OIV-MA-AS316-01

VERIFICATION OF CONSISTENCY OF ORIGIN AND VARIETIES
PÓSTER 2023-3244
44th OIV Congress, Spain 2023

AUTENTHIC WINES
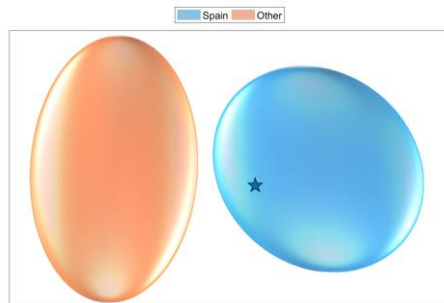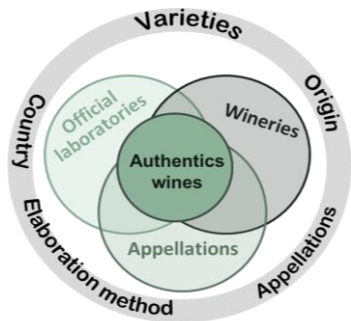
	RED WINE	sensitivity	WHITE WINE	sensitivity	ROSÉ WINE	sensitivity
ORIGIN	España	99.0	España	99.0	España	99.0
	DOCa. Rioja	99.0	DOCa. Rioja	99.0	DOCa. Rioja	99.1
	DO. Navarra	98.8	DO. Rías Baixas	99.1		
	DO. Ribera del Duero	98.9	DO. Rueda	99.0		
	DO. Ribera de Guadiana	97.6	DO. Valencia	99.3		
	DO. Valencia	99.1				
	DO. Bierzo	99.3				
VARIETY	Tempranillo	98.8	Albariño	98.9	Tempranillo	99.1
	Garnacha T.	98.8	Viura	98.5		
	Monastrell	96.1	Verdejo	98.9		
	Cabernet Sauvignon	98.9	Chardonnay B.	98.0		
	Merlot Noir	98.8	Sauvignon B.	99.0		
	Pinot Noir	99.0	Moscatel	99.0		
	Syrah	97.8	Riesling	99.0		
	Mencía	98.7				

TO BUILD MODELS OF ORIGIN AND VARIETIES

Wine sample

Preparation and aquisition of the spectrum
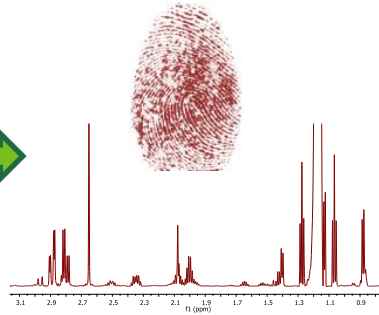
"Fingerprint"

QUANTITATION
OIV-MA-AS316-01

VERIFICATION OF CONSISTENCY OF ORIGIN AND VARIETIES
PÓSTER 2023-3244
*44th OIV Congress, Spain 2023*

STATISTIC STUDIES:
IDENTITY CHECK ANALYSIS

PURCHASE OF BULK WINE
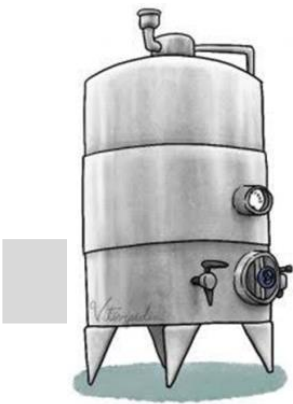
INITIALLY CHOSEN WINES
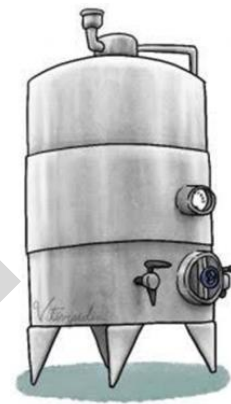
RECEIVED WINE

IDENTITY CHECK ANALYSIS

FOUR STATISTICAL PARAMETERS

Parameter for Identity-Test	Result	Reference	Flag
Number of selected features	218		–
Average relative deviation [%]	2.9	max 4.0	🟢
95%-quantile of deviations [%]	9.7	max 12.5	🟢
Deviations less than 5% [%]	84	min 75	🟢
Correlation Index	0.93	min 0.85	🟢
Overall Result		**Identical**	
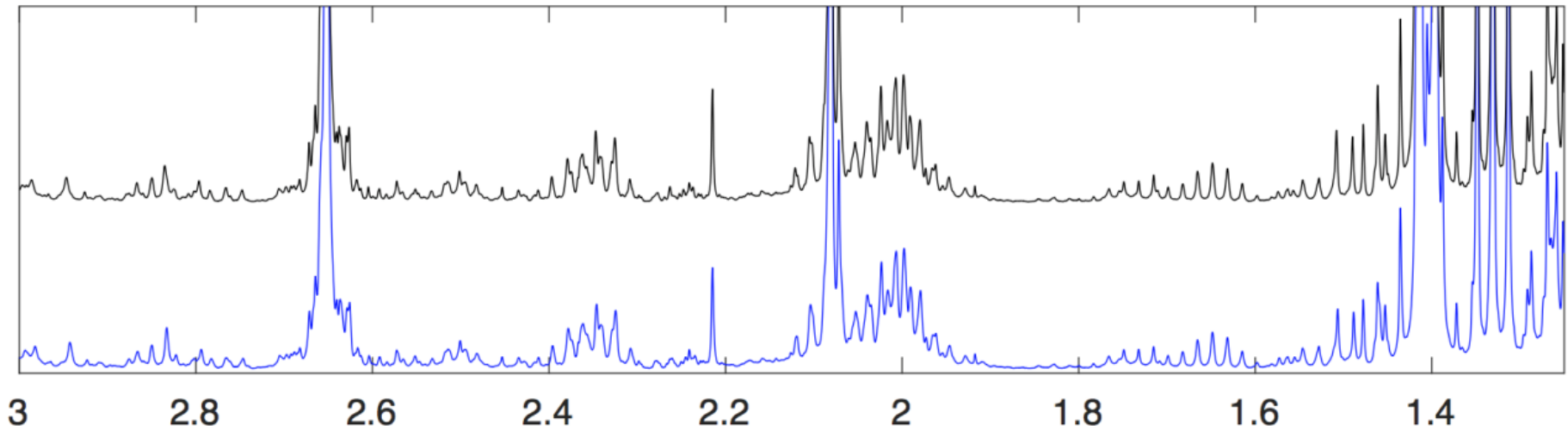
IDENTITY CHECK ANALYSIS

Parameter for Identity-Test	Result	Reference	Flag
Number of selected features	214		–
Average relative deviation [%]	10.7	max 4.0	🔴
95%-quantile of deviations [%]	31.4	max 12.5	🔴
Deviations less than 5% [%]	32	min 75	🔴
Correlation Index	0.33	min 0.85	🔴
Overall Result	**Not Identical**		
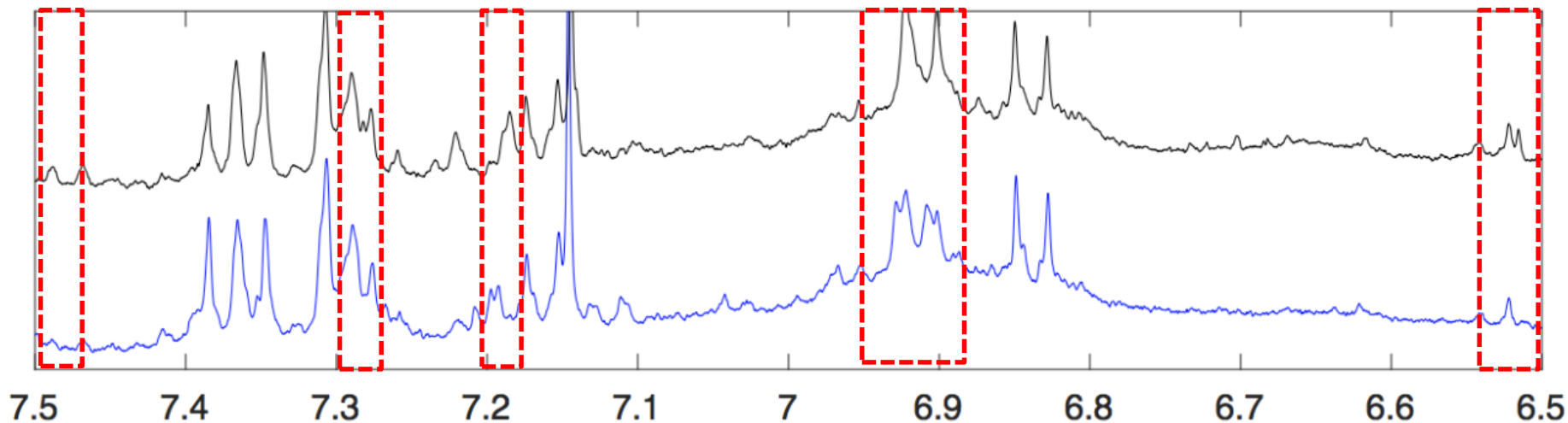
MATERIALS AND METHODS

OFFICIAL WINERY OF GOVERNMENT
OF LA RIOJA (La Grajera)

	2022	
Part 1	**Part 2**	**Final**
January to May 2022	May to november 2022	February 2023
17 WEEKS / 18 TANKS	18 WEEKS / 10 TANKS	7 TANKS

	VARIABLES
External variables	Sampling Storage Common winemaking practice (sulfur correction, blended)
Internal variables	pH Spectra acquisition
Time evolution	

Tanks	volume (L)	Color	Type of wine
4	5500	red	young
6	5500	red	young
15	20500	red	young
17	20500	red	young
18	20500	red	young
19	20500	red	young
20	3300	red	young
24	5000	red	young
25	5000	white	young
27	3300	white	young
28	3300	white	aged in a oak barrel
29	2000	red	aged in a oak barrel
30	1000	white	young
31	2000	red	aged in a oak barrel
34	3300	red	Barrel tank
35	900	red	during oak barrel aging
36	2000	red	young
39	1500	red	aged in a oak barrel

EXTERNAL VARIABLES: *SAMPLING*

TOP OF THE TANK
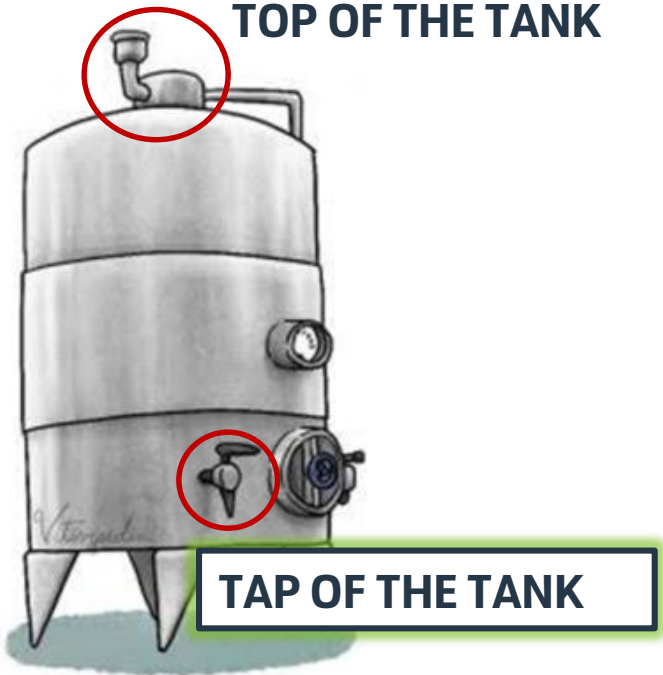
TAP OF THE TANK

THE TAP OF THE STEEL TANKS IS VERY NARROW AND DIFFICULT
TO CLEAN AND DISINFECT.

A

Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	223			–
Average relative deviation [%]	4.0	max	4.0	🟡
95%-quantile of deviations [%]	11.3	max	12.5	🟢
Deviations less than 5% [%]	69	min	75	🔴
Correlation Index	0.90	min	0.85	🟢
Overall Result		**Not Identical**		

B

TANK 20 — ACETIC ACID
- WEEK 1
- WEEK 17

19
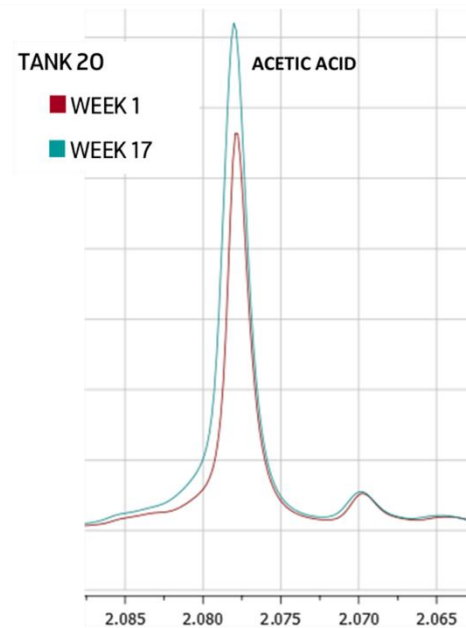
EXTERNAL VARIABLES: *STORAGE UNTIL ANALYSIS*

STORAGE AT ROOM TEMPERATURE
WITHOUT TEMPERATURE CONTROL

A

Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	216			-
Average relative deviation [%]	9.9	max	4.0	🔴
95%-quantile of deviations [%]	28.5	max	12.5	🔴
Deviations less than 5% [%]	46	min	75	🔴
Correlation Index	0.20	min	0.85	🔴
Overall Result		**Not Identical**		

B

ACETIC ACID

ACETALDEHYDE

ACETALDEHYDE

ACETATES

ACETALDEHYDE

- PRESENCE OF ACETIC BACTERIAS AND
  FLOWER VEIL YEASTS
- TEMPERATURE AND OXYGEN
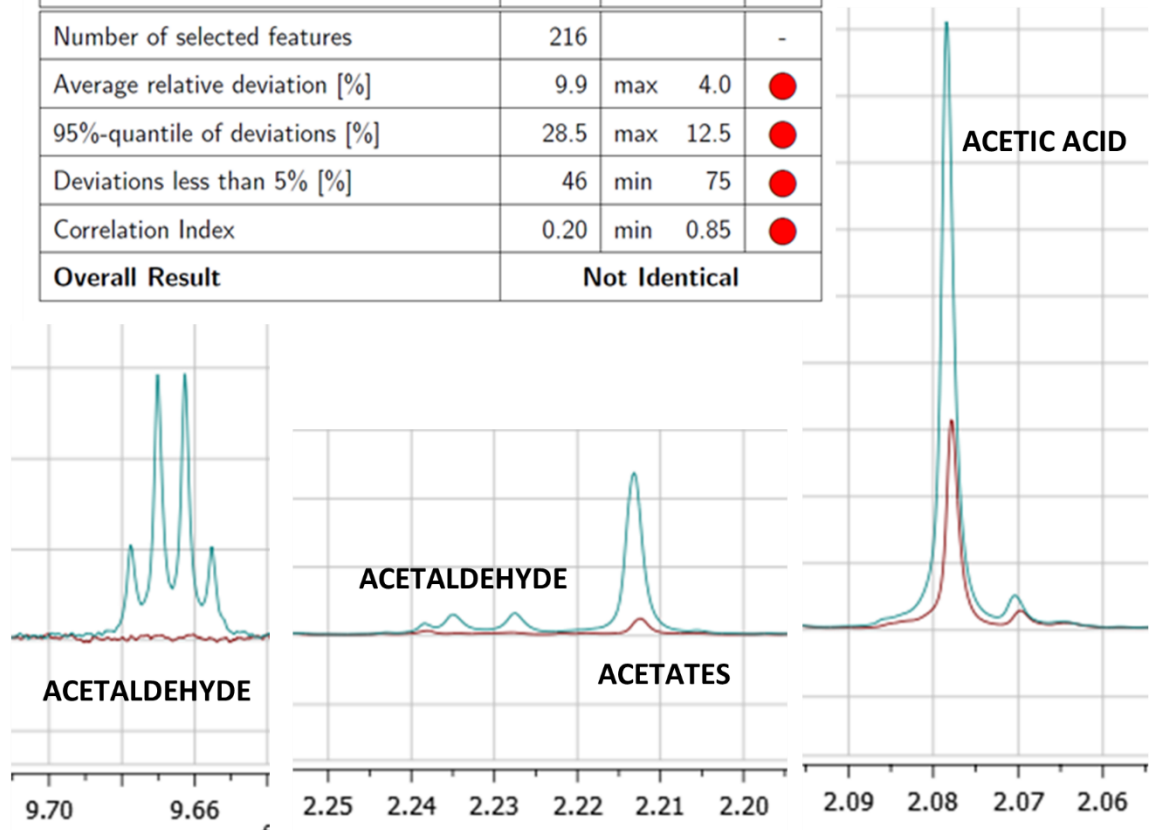
EXTERNAL VARIABLES: *SULPHUR DIOXIDE CORRECTION*

TWO SULPHUR DIOXIDE CORRECTIONS

LACTIC ACID

SUCCINIC ACID
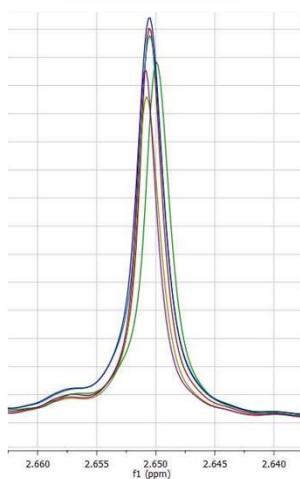
WEEK 12

Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	212			-
Average relative deviation [%]	2.6	max	4.0	🟢
95%-quantile of deviations [%]	7.1	max	12.5	🟢
Deviations less than 5% [%]	86	min	75	🟢
Correlation Index	0.94	min	0.85	🟢
Overall Result		Identical		

WEEK 13   **SULPHUR DIOXIDE CORRECTION**

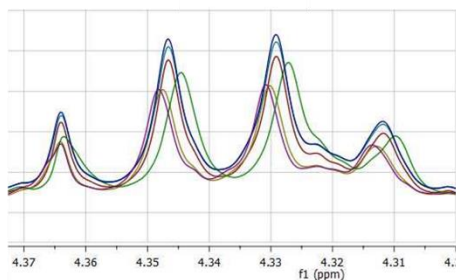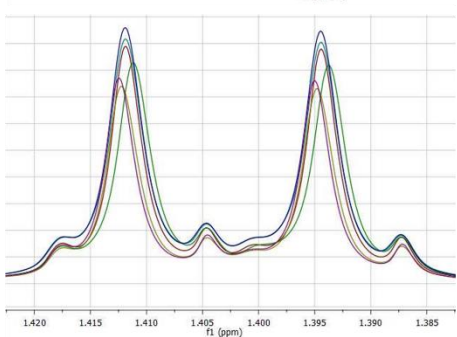| Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	220			-
Average relative deviation [%]	4.5	max	4.0	🟡
95%-quantile of deviations [%]	14.4	max	12.5	🟡
Deviations less than 5% [%]	75	min	75	🟢
Correlation Index	0.74	min	0.85	🔴
Overall Result		Not Identical		

WEEK 14

Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	222			-
Average relative deviation [%]	4.1	max	4.0	🟡
95%-quantile of deviations [%]	13.0	max	12.5	🟡
Deviations less than 5% [%]	78	min	75	🟢
Correlation Index	0.82	min	0.85	🟡
Overall Result		Questionable		

WEEK 15

Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	222			-
Average relative deviation [%]	3.0	max	4.0	🟢
95%-quantile of deviations [%]	10.4	max	12.5	🟢
Deviations less than 5% [%]	86	min	75	🟢
Correlation Index	0.87	min	0.85	🟢
Overall Result		Identical		

PRESENCE OF FREE SULPHUR DIOXIDE SIGNALS OF THE SPECTRA WERE SHIFTED TO A DIFFERENT PPM

AFTER THESE TWO WEEKS, MODIFICATION WAS REVERSIBLE

EXTERNAL VARIABLES: *SULPHUR DIOXIDE CORRECTION*

TWO SULPHUR DIOXIDE CORRECTIONS
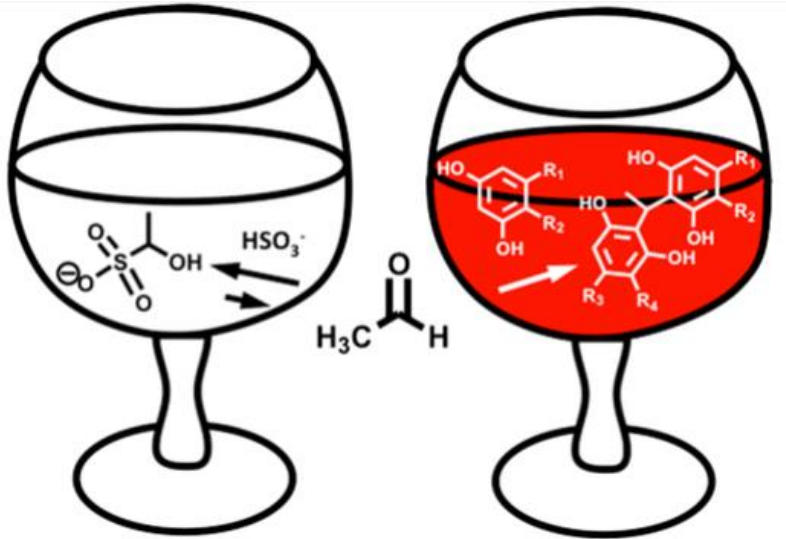
J. Agric. Food Chem., **64**, 8615–8624. (2016)

Tank 35	acetaldehyde (mg/L)
week 13	66
week 14	66
week 15 (sulfur correction)	<10
week 16	<10
week 17	<10

EFFECTIVENESS OF THE SULPHUR DIOXIDE DECREASES IN WINE DUE TO THE COMBINATION WITH DIFFERENT COMPOUNDS

ACETALDEHYDE

EXTERNAL VARIABLES: *SULPHUR DIOXIDE CORRECTION*

TWO SULPHUR DIOXIDE CORRECTIONS

PRESENCE OF ACETALDEHYDE

AFTER THESE TWO WEEKS, MODIFICATION WAS IRREVERSIBLE

WEEK 12

Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	230			-
Average relative deviation [%]	3.2	max	4.0	🟢
95%-quantile of deviations [%]	9.5	max	12.5	🟢
Deviations less than 5% [%]	82	min	75	🟢
Correlation Index	0.86	min	0.85	🟢
Overall Result		**Identical**		

WEEK 13   ETHANAL

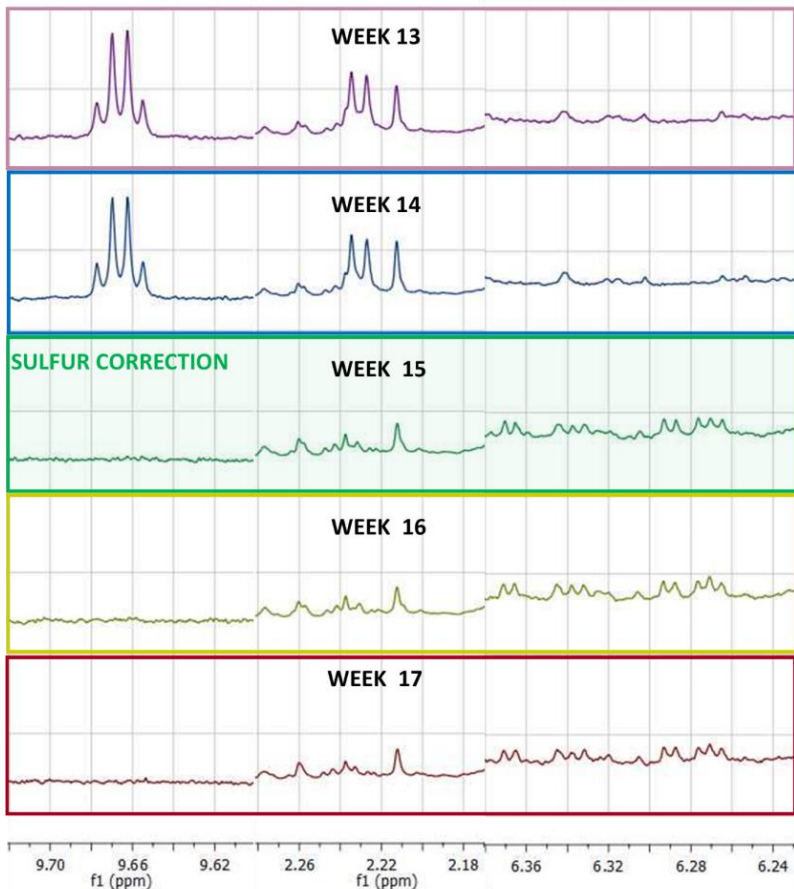| Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	229			-
Average relative deviation [%]	4.6	max	4.0	🟡
95%-quantile of deviations [%]	11.5	max	12.5	🟢
Deviations less than 5% [%]	65	min	75	🔴
Correlation Index	0.79	min	0.85	🔴
Overall Result		**Not Identical**		

WEEK 14   ETHANAL

Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	230			-
Average relative deviation [%]	4.3	max	4.0	🟡
95%-quantile of deviations [%]	13.2	max	12.5	🟡
Deviations less than 5% [%]	72	min	75	🟡
Correlation Index	0.76	min	0.85	🔴
Overall Result		**Not Identical**		

WEEK 15   SULPHUR CORRECTION

Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	231			-
Average relative deviation [%]	2.6	max	4.0	🟢
95%-quantile of deviations [%]	9.0	max	12.5	🟢
Deviations less than 5% [%]	87	min	75	🟢
Correlation Index	0.92	min	0.85	🟢
Overall Result		**Identical**		

WEEK 16

Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	229			-
Average relative deviation [%]	3.5	max	4.0	🟢
95%-quantile of deviations [%]	9.9	max	12.5	🟢
Deviations less than 5% [%]	73	min	75	🟡
Correlation Index	0.92	min	0.85	🟢
Overall Result		**Questionable**		

WEEK 17

Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	227			-
Average relative deviation [%]	4.3	max	4.0	🟡
95%-quantile of deviations [%]	12.9	max	12.5	🟡
Deviations less than 5% [%]	72	min	75	🟡
Correlation Index	0.82	min	0.85	🟡
Overall Result		**Questionable**		

EXTERNAL VARIABLES: *BLENDING OF WINES*
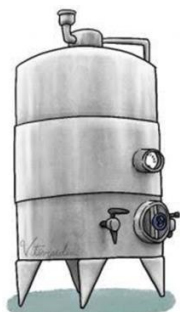
TANK 6
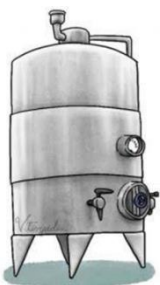
TANK 20
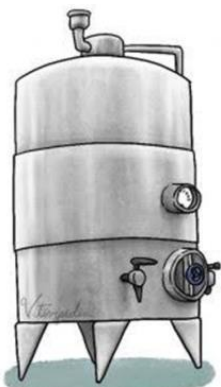
TANK 21
62,5% TANK 6
37,5% TANK 20

TANK 6 (WEEK1) WITH TANK 21 (BLENDED TANKS 6 AND 20)

Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	210			-
Average relative deviation [%]	6.2	max	4.0	●
95%-quantile of deviations [%]	15.4	max	12.5	●
Deviations less than 5% [%]	56	min	75	●
Correlation Index	0.65	min	0.85	●
Overall Result		Not Identical		

TANK 20 (WEEK1) WITH TANK 21 (BLENDED TANKS 6 AND 20)

Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	212			-
Average relative deviation [%]	7.8	max	4.0	●
95%-quantile of deviations [%]	20.4	max	12.5	●
Deviations less than 5% [%]	42	min	75	●
Correlation Index	0.66	min	0.85	●
Overall Result		Not Identical		

Tanks	volume (L)	Color	Type of wine
6	5500	red	young
20	3300	red	young

VERY INTERESTING TO KNOW THE PERCENTAGES OF THE BLENDS, BUT THIS WOULD REQUIRE A DEEPER STUDY ON THE SUBJECT

INTERNAL VARIABLES: *PREPARATION OF THE SAMPLES (pH)*

BTPH UNIT ADJUSTS PH TO WINE PH REFERENCE (3.10 ± 0.02 PH UNITS) WITH 1 M NAOH OR 1 M HCL.
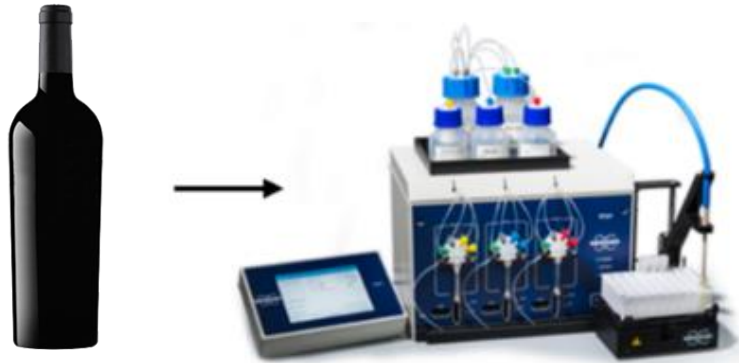
-900 µL WINE
-100 µl BUFFER (D$_2$O+NaN$_3$+TSP)

■ EXPIRED PH REFERENCE

Parameter for Identity-Test	Result	Reference		Flag
Number of selected features	212			-
Average relative deviation [%]	4.1	max	4.0	🟡
95%-quantile of deviations [%]	11.7	max	12.5	🟢
Deviations less than 5% [%]	73	min	75	🟡
Correlation Index	0.78	min	0.85	🔴
Overall Result		**Not Identical**		

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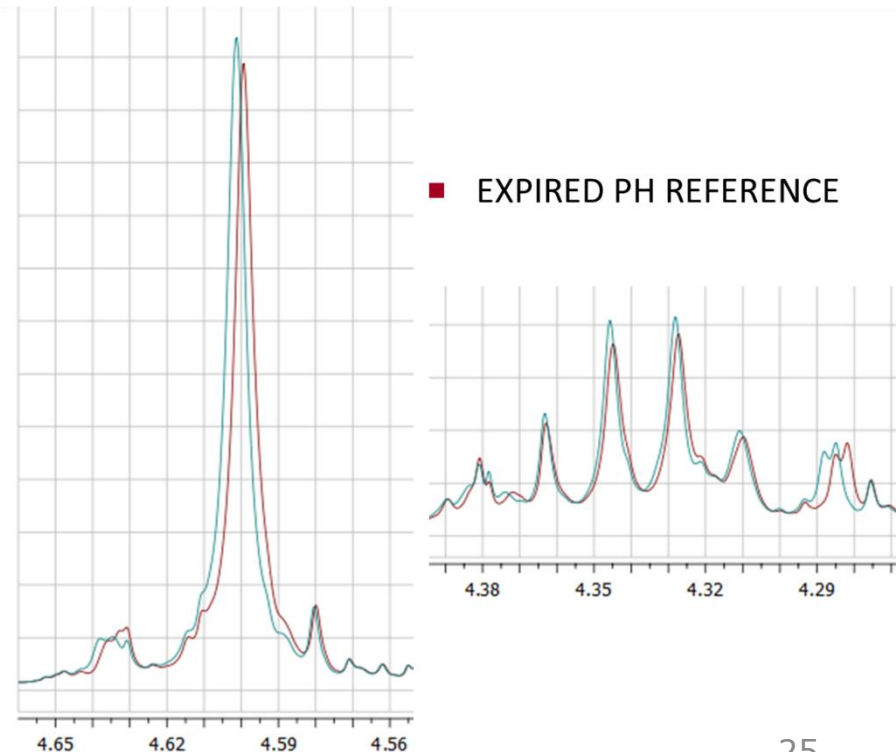
INTERNAL VARIABLES: *ACQUISITION OF THE SPECTRA*

BRUKER'S AUTOMATED METHODS IN THE WINE-SCREENER

COMPENDIUM OF INTERNATIONAL ANALYSIS OF METHODS – OIV
Quantitation of glucose, malic acid, acetic acid, fumaric acid, shikimic acid and sorbic acid in wine using quantitative nuclear magnetic resonance spectrometry (1H NMR)

Method OIV-MA-AS316-01   Type IV method

Quantitation of glucose, malic acid, acetic acid, fumaric acid, shikimic acid and sorbic acid in wine using quantitative nuclear magnetic resonance spectrometry (^1H NMR)
OIV-OENO 618-2020

BRUKER

DAkkS
Deutsche Akkreditierungsstelle

Deutsche Akkreditierungsstelle GmbH

Appendix to accreditation certificate D-PL-19229-01-00 according to DIN EN ISO/IEC 17025:2018

Valid from: 18.09.2020
Date of issue: 18.09.2020

AA-72-02-05   Wine profiling
2020-09   Wine analysis by NMR for ingredients, authenticity and quality, as well as NMR-based quantification, statistics and chemometrics

CHECKED DAILY:
- TEMPERATURE
- THE SIGNAL-TO-NOISE RATIO
- QUALITY OF THE SUPPRESSION OF THE WATER SIGNAL
- OTHERS PARAMETERS...

METHODOLOGY ROBUST AND REPETITIVE

NO INFLUENCE OF THE ACQUISITION OF THE SPECTRA OF THE IDENTITY CHECK ANALYSIS WAS FOUND.

TIME EVOLUTION

2022		
Part 1	**Part 2**	**Final**
January to May 2022	May to november 2022	February 2023
17 WEEKS / 18 TANKS	18 WEEKS / 10 TANKS	7 TANKS

53 WEEKS

Tanks	volume (L)	Color	Type of wine
4	5500	red	young
6	5500	red	young
15	20500	red	young
17	20500	red	young
18	20500	red	young
19	20500	red	young
20	3300	red	young
24	5000	red	young
25	5000	white	young
27	3300	white	young
28	3300	white	aged in a oak barrel
29	2000	red	aged in a oak barrel
30	1000	white	young
31	2000	red	aged in a oak barrel
34	3300	red	Barrel tank
35	900	Tinto	during oak barrel aging
36	2000	Tinto	young
39	1500	Tinto	aged in a oak barrel

TIME BETWEEN ANALYSIS				
Tanks	31 WEEKS	32 WEEKS	41 WEEKS	53 WEEKS
4	I	I	I	
15	I	I	N	N
17	I	I	Q	N
18	I	I	I	Q
19	Q	Q	N	
24	I	I	I	N
29	I	I	I	I
34	I	I	N	
35	I	Q	I	N
39	I	I	I	I
Total identical (%)	90 %	80 %	60 %	29 %

I IDENTICAL   **N** NOT IDENTICAL

Q QUESTIONABLE

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- IDENTITY CHECK ANALYSIS IS A HIGHLY SENSITIVE METHOD, CAPABLE OF DETECTING MINOR CHANGES IN THE WINE. PERFECT TO CONTROL THE PURCHASE OF BULK WINE.

- THE STORAGE OF THE SAMPLES UNTIL THE MOMENT OF THE ANALYSIS MUST BE DONE AT A CONTROLLED TEMPERATURE TO AVOID ANY EVOLUTION OF THE WINE.

- THE MOST COMMON WINEMAKING PRACTICES CAN INFLUENCE THE RESULT, SO IT IS NECESSARY TO PROVIDE THIS INFORMATION IN THE ANALYSIS REQUEST TO ENSURE A CORRECT INTERPRETATION OF THIS ANALYSIS

- WITH A QUALITY CONTROL OF THE SAMPLING, BTPH UNIT AND THE ACQUISITION OF THE SPECTRA ARE ENOUGH TO ENSURE THE RESULT.

- TIME EVOLUTION OF WINE DEPENDS ON THE KIND OF WINE. IF THE WINE IS YOUNG OR NOT STABLE THE COMPARISON WITH THIS ANALYSIS CAN BE DONE UNTIL WEEK 32. ON THE OTHER HAND, WINE AGED IN AN OAK BARREL (STABLE) CAN BE COMPARED, AT LEAST, UNTIL WEEK 53.

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RMN (RESONANCIA MAGNÉTICA NUCLEAR) EN VINO "HUELLA DACTILAR"

Determinaciones incluidas	Precio (€)
Informe completo de confirmación de consistencia de vinos por RMN (*)	200 €
Informe análisis cuantitativa de vinos por RMN	100 €
Confirmación de identidad por RMN (2 vinos)	150 €
Nota: Cantidad mínima de muestra 100 ml.	

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THANKS FOR YOUR ATTENTION !!!