RESOLUTION OIV-OENO 666-2023

MULTIELEMENTAL ANALYSIS IN WINE USING INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY (ICP-MS)

WARNING: this resolution withdraws the following resolution:
- *OIV/OENO 344/2010*

THE GENERAL ASSEMBLY,

IN VIEW OF ARTICLE 2, paragraph 2 iv of the Agreement of 3rd April 2001 establishing the International Organisation of Vine and Wine,

CONSIDERING Resolution OIV/OENO 344/2010 “Multielemental analysis using ICP-MS” adopted in 2010,

CONSIDERING the analytical method OIV-MA-AS323-07 “Multielemental analysis using ICP-MS”,

AT THE PROPOSAL of the “Methods of Analysis" Sub-Commission,

DECIDES to withdraw Resolution OIV/OENO 344/2010 “Multielemental analysis using ICP-MS” and adopt the following resolution,

DECIDES to modifythe analytical method OIV-MA-AS323-07 as a result with the following:

MULTIELEMENTAL ANALYSIS IN WINE USING INDUCTIVELY COUPLED PLASMA- MASS SPECTROMETRY (ICP-MS)

Type II method[1]

1. SCOPE OF APPLICATION

This method can be applied to the analysis of the elements present in wines within the range of concentrations indicated and featured in the following list:

- Aluminium between 0.25 and 5.0 mg/L
- Arsenic between 0.010 and 10 mg/L
- Boron between 10 and 40 mg/L

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- Bromine between 0.20 and 2.5 mg/L
- Cadmium between 0.001 and 0.040 mg/L
- Cobalt between 0.002 and 0.050 mg/L
- Copper between 0.10 and 2.0 mg/L
- Strontium between 0.30 and 1.0 mg/L
- Iron between 0.80 and 5.0 mg/L
- Lithium between 0.010 and 0.050 mg/L
- Magnesium between 50 and 300 mg/L
- Manganese between 0.50 and 1.5 mg/L
- Nickel between 0.010 and 0.20 mg/L
- Lead between 0.010 and 0.20 mg/L
- Rubidium between 0.50 and 1.2 mg/L
- Sodium between 5 and 30 mg/L
- Vanadium between 0.003 and 0.20 mg/L
- Zinc between 0.30 and 1.0 mg/L

The ICP-MS technique can also be used to analyze other elements in wine.

Optionally, in some samples, such as, for example, of wines with more than 100 g/L of sugars, prior mineralization may be beneficial. In this case, it is recommended to perform a digestion with nitric acid in a closed microwave system.

The method can also be applied to musts, after mineralization.

2. BASIS

Multielemental quantitative determination using Inductively Coupled Plasma Mass Spectometry (ICP-MS).

Injection and nebulization of the sample in high-frequency plasma. The plasma causes the desolvation, atomization and ionization of the elements in the sample. The ions are extracted using a vacuum system fitted with ionic lenses. The ions are separated according to the mass-to-charge ratio in a mass spectrometer, for example, a quadrupole. Detection and quantification of ions is performed using an electron

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multiplier system.

3. REAGENTS AND SOLUTIONS

3.1. Grade 1 water, in accordance with ISO 3696.

3.2. Certified solution(s) (for example, 100 mg/L) containing the metals to be analyzed. Multielemental or monoelemental solutions can be used.

3.3. Internal standard solutions (normally 1 g/L). Some examples of internal standards that can be used in this method are indium, scandium, tellurium, rhodium, yttrium, iridium and germanium (tellurium, yttrium and germanium are specifically recommended for As determination).

3.4. Nitric acid (HNO3) ≥ 60 % V/V (metal impurities $\leq$ 0.1 µg/L). CAS 7697-37-2

3.5. Argon, minimum purity of 99.999%. CAS 7440-37-1

3.6. Nitrogen (maximum impurity content: $H_2O \leq$ 3 mg/L, $O_2 \leq$ 2 mg/L and CnHm $\leq$ 0.5 mg/L). CAS 7727-37-9.

3.7. Isopropyl alcohol, minimum purity of 99.8%. CAS 67-63-0

NOTE: the laboratory will demonstrate through the study of the reagent blanks the absence of contamination of the elements that being analyzed, for the volumes of additions specified in the method.

Solution concentration and internal standards are given by way of reference.

Preparation of standard solutions:

The concentration of nitric acid in the standards and in the final dilution of the wine samples must be the same. The concentration of nitric acid that can be used will depends on the ICP-MS device tolerance (usually between 1 to 5% (V/V)). The following is an example.

3.8. Stock solution (5 mg/L).

Place 5 mL of water (3.1) and 500 µL of solution (3.2) in a 10 mL (4.4) tube and add 100 µL of HNO3 (3.4). Level off to 10 mL with water (3.1) and homogenize.

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3.9. Internal standard solution (1 mg/L).

Using micropipettes (4.3), place 25 mL of water, 50 µL of indium or rhodium solution (3.3) and 500 µL of HNO3 (3.4) in a 50 mL tube (4.5). Level off to 50 mL with water (3.1) and homogenize.

3.10. Internal standard solution (for on-line addition of the internal standard).

The internal standard solution can be inserted via a separate channel of the tubing pump, mixed with the sample and calibration solution using a Y-piece.

Prepare this solution diluting solution 3.9, according to the internal diameter (ID) of the inlet tubes so that, in the final mixture, the concentration of the internal standard is, for example, 10 µg/L.

3.11. Standard solutions of the calibration curve.

Will be prepared by diluting the stock solution (3.8). Adapt the range of the series of standards according to the dilution on the sample or the equipment used.

Use 1000 µL and 100 µL pipettes (4.3).

Add internal standard so that its final concentration in the dilution is equal in the standards and in the samples (10 µg/L in this example). When the internal standard is added on-line, as explained in section 3. 10, the internal standard is not added to the calibration solution.

These standard solutions can also be prepared gravimetrically.

4. MATERIAL AND EQUIPMENT

4.1. Inductively coupled plasma mass spectrometer with/without collision/reaction cell.

4.2. Autosampler (optional).

4.3. 1000 µL, 500 µL and 100 µL micropipettes.

4.4. 10 mL plastic, graduated test tubes with stopper.

4.5. 50 mL plastic, graduated test tubes with stopper.

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4.6. Teflon coated block digestion system or water bath, for applications up to 90°C.

5. SAMPLE PREPARATION

Degas samples containing CO2 by nitrogen bubbling (3.6), ultrasonic or other appropriate methods.

Using a micropipette (4.3), pour 5 mL of water (3.1), 500 µL of wine, 100 to 500 µL of HNO3 (3.4) and 100 µL of internal standard solution (3.9) (except for on-line, addition of the internal standard, as explained in point 3.10), into a 10 mL tube (4.4). Level off with water (3.1) and homogenize.

When the standards are prepared gravimetrically, the final dilution of the sample must also be obtained gravimetrically.

For certain elements a higher dilution may be necessary owing to their high natural content in the sample.

Special cases

A. Bromine

Br has high ionization potential and its ionization in plasma may be incomplete because of the presence of high concentrations of other elements in wines with low ionization potential. This may result in the incorrect quantification of Br and therefore a 1/50 dilution is recommended to avoid this effect (in the event of another dilution being used, confirm the results by checking recovery after an addition).

B. Arsenic

In the determination of arsenic by ICP-MS, the ethanol in the sample increases the ionization of arsenic in the plasma, resulting in an overestimation of its concentration. There are different alternatives to counteract this effect, by way of examples, the 3 following examples are given:

B.1. Using tellurium (Te) as internal standard:

Having a high ionisation energy, Te corrects the matrix effect in the determination of arsenic. Te is added to standards and samples either on-line, as explained in 3.10, or during the preparation of standards and samples, as explained in 3.11 and 5

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respectively.

B.2. Addition of isopropyl alcohol to the standards and samples:

To mask the matrix effect of the wine ethanol on the ionisation of As, when preparing the sample solutions, add 200 µL of isopropyl alcohol (3.7) before bringing it to level.

Isopropyl alcohol (3.7) must also be added to the standard solutions (3.11) to achieve the same concentration as in the sample solutions.

Alternatively, when the internal standard is added on-line using a Y-piece, the isopropyl alcohol (3.7) can be added to the internal standard solution (3.10) instead of adding it when preparing the standard and sample solutions. To calculate the concentration of isopropyl alcohol (3.7) in the final mixture, the internal diameter of the sample and the internal standard inlet tubes must be taken into account. It is recommended that the concentration of isopropyl alcohol in the final mixture is approximately 2% (v/v). The concentration of isopropyl alcohol (3.7) in the final mixture can be calculated using the following expression:

$$Cf = Co \times F$$

Where:

- Cf: Concentration of isopropyl alcohol (3.7) in the final mixture
- Co: Concentration of isopropyl alcohol (3.7) added to the internal standard solution (3.10)
- F: Dilution factor obtained with the following equation:

$$F = \frac{(\frac{DI_1}{2})^2}{\left[(\frac{DI_2}{2})^2 + (\frac{DI_2}{2})^2\right]}$$

Where:

DI_1: Internal diameter of the internal solution inlet tube

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DI_2: Internal diameter of the sample inlet tube

B.1. Mineralization of the sample

The following conditions are given as an example:

Sample preparation: remove the stopper carefully to ensure that the wine is not contaminated with cork debris. Wine samples are pipetted directly from the bottle without transfer to an intermediate container. Use a micropipette (4.3) to transfer 2.5 mL of wine, 2.5 mL of concentrated HNO3 (3.4), 2 mL of water (3.1) and 500 µL of internal standard solution (3.9) into a 50 mL tube (4.4).

Wait a few minutes because an exothermic reaction can cause overflows.

The tubes are hermetically sealed or fitted with a system allowing reflux. The solutions are placed in a heating system (4.6) thermostated at 90 °C during 180 min.

Once digestion is complete, allow samples to cool to room temperature.

Bring the volume to 50 mL with water (3.1) and homogenize.

6. PROCEDURE

This procedure is given as an example.

Following the Instrument Manufacturer's instructions, switch on the device (pump working and plasma on).

Clean the system for 20 minutes using 2% (V/V) HNO_3(3.4).

Check that the device is functioning correctly. Analyze a blank and the series of standard solutions in increasing concentrations, and the internal quality controls established by each laboratory.

Element	m/z*
Aluminium	27
Arsenic	75 / 91 (for AsO in reaction with oxygen)
Boron	11
Bromine	79
Cadmium	114

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Cobalt	59
Copper	63
Strontium	88
Iron	56/57
Lithium	7
Magnesium	24
Manganese	55
Nickel	60
Lead	average of 206, 207 and 208
Rubidium	85
Sodium	23
Vanadium	51
Zinc	64

*The above table is given by way of example. Other isotopes may be required, depending on the equipment.

In the event of using equipment with no collision/reaction cell, correction equations may be necessary for some elements.

NOTE:

Spectral interferences can interfere with the quantification of certain elements. It could be:

- isobaric interference (2 elements of similar mass; ex: 115 In and 115Sn). In this case, the choice of the isotope studied must be adapted;
- interference from double charges and interference from oxides: the levels of oxides and double charges can be checked before analysis by means of control

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solutions, the optimization of the parameters of the apparatus (flow rate of nebulization, settings lenses, position of the torch, of the nebulizer, etc. makes it possible to reduce these interferences;

- polyatomic interferences which can be corrected through the use of correction equations or even collision/reaction cells.

7. RESULTS

The software can calculate the results directly.

The results should be expressed in the same units as the maximum limits set in the regulations.

Obtain, by interpolating in the calibration curve, the concentration of the elements in the diluted samples. Use the following equation to calculate the concentration of the elements in the sample:

$$C = \frac{C_m x V_t}{V_m}$$

Where:

- C = Concentration of the element in the sample
- Cm = Concentration of the elements in the diluted sample
- V_t = Final volume of the measurement solution, in mL
- V_m = Aliquot volume of wine, in mL.

8. PRECISION

The results of the statistical parameters of the collaborative trial are shown in Appendix A.

Table 1 represents the % of the relative standard deviation of Repeatability and Reproducibility (RSDr% y RSDR%) of the method. (*) C = Concentration

Table 1: relative standard deviation of Repeatability and Reproducibility

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Element	Concentration	RSDr %	RSDR %
Aluminium	0.25 – 5.0 mg/L	4	10
Boron	10 - 40 mg/L	3.8	6.3
Bromine	0.20– 1.0 mg/L	4.1	16.3
	≥ 1.0 – 2.5 mg/L	2.1	8.0
Cadmium	0.001 – 0.020 mg/L	0,06 C*+0,18	10
	≥ 0.020 – 0.040 mg/L	1.5	10
Cobalt	0.002 – 0.050 mg/L	3.2	13.2
Copper	0.10 – 0.50 mg/L	3.8	11.4
	≥ 0.50 – 2.0 mg/L	2.0	11.4
Strontium	0.30 – 1.,0 mg/L	2.5	7.5
Iron	0.80– 1.0 mg/L	4.2	15.7
	≥ 1.0-5.0 mg/L	4.2	7.8
Lithium	0.010 – 0.050 mg/L	7	12
Magnesium	50 - 300 mg/L	2	6
Manganese	0.50-1.5 mg/L	3	7
Nickel	0.010 – 0.20 mg/L	5	8
Lead	0.010 – 0.050 mg/L	8	7
	≥ 0.050 – 0.20 mg/L	2	7

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Rubidium	0.50 – 1.2 mg/L	3	6
Sodium	5 - 10 mg/L	2	10
	≥ 10 - 30 mg/L	0.3 C*-2.5	10
Vanadium	0.003 – 0.010 mg/L	8	10
	≥ 0.010 – 0.20 mg/L	3	10
Zinc	0.30 – 1.0 mg/L	5	12

The results of the statistical parameters of an internal validation for arsenic are shown in Appendix B.

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APPENDIX A RESULTS OF THE COLLABORATIVE TRIALS

The method has been checked with two collaborative trials, by evaluating precision in accordance with ISO 5725.The trueness of the method has been obtained through recovery studies.

1st Collaborative Trial

8 samples (A, B, C, D, E, F, MH1 and MH2) were used from the following origins:

- Three samples of red wine, with and without addition.
- Three samples of white wine, with and without addition.
- Two samples of synthetic hydroalcoholic mixture, prepared with ethanol and water.

Hydroalcoholic sample MH1 presented problems of instability during the trial and the results have not been taken into account.

	MH2	A	B	C	D	E	F
Metal (mg/L)	Hydroalcoholic mixture	RW2	RW3	WW2	WW3	red wine	white wine
Aluminium	5	0.5	2	2	1	No addition	No addition
Cadmium	0.001	0.005	0.02	0.05	0.01	No addition	No addition

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Strontium	0.300	No addition	No addition	No addition	No addition	No addition	No addition
Lithium	0.020	0.01	0.02	0.04	0.01	No addition	No addition
Magnesium	50	100	200	50	25	No addition	No addition
Manganese	0.500	0.5	1	1	0.5	No addition	No addition
Nickel	0.070	0.025	0.2	0.1	0.1	No addition	No addition
Lead	0.010	0.05	0.1	0.15	0.05	No addition	No addition
Rubidium	1.0	No addition	No addition	No addition	No addition	No addition	No addition
Sodium	20	10	10	20	5	No addition	No addition
Vanadium	0.070	0.025	0.2	0.1	0.1	No addition	No addition
Zinc	0.010	0.05	0.1	0.15	0.05	No addition	No addition

2nd Collaborative Trial

Sixteen samples (A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, P) from the following origins were used:

- Four samples of red wine, with and without addition.
- Four samples of Port wine, with and without addition.
- Six samples of white wine, with and without addition.
- Two samples of champagne.

Amounts added to the samples

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Samples	Code	Addition	B	Br	Co	Cu	Fe
			mg/L	mg/L	µg/L	mg/L	mg/L
White wine	F-N	No addition	0.0	0.0	0.0	0.0	0.0
	C-I	Addition 1	5.0	0.5	5.0	5.0	1.0
	A-O	Addition 2	10.0	1.0	10.0	1.0	2.0
Liqueur wine	B-K	No addition	0.0	0.0	0.0	0.0	0.0
	E-L	Addition 3	15.0	1.5	20.0	1.5	3.0
Red wine	D-M	No addition	0.0	0.0	0.0	0.0	0.0
	H-J	Addition 4	20.0	2.0	50.0	2.0	5.0
Sparkling wine	G-P	No addition	0.0	0.0	0.0	0.0	0.0

PRECISION PARAMETERS (Tables 1 to 17):

The values of Horratr and HorratR have been obtained by using the Horwitz equation taking into account Thompson's modification for the concentration below 120 µg/L.

Table 1: Aluminium (mg/L)

SAMPLE	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	Horwitz R RSDR (%)	HorratR
A	11	10	0.68	0.020	0.06	2.9	11	0.26	0.077	0.22	11	17	0.66
B	11	9	2.1	0.043	0.12	2.0	9.4	0.22	0.21	0.61	10	14	0.71
C	11	9	2.1	0.032	0.09	1.5	9.5	0.16	0.21	0.59	10	14	0.69
D	11	10	1.2	0.041	0.12	3.4	10	0.34	0.10	0.29	8.3	16	0.56
E	11	10	0.34	0.014	0.04	4.1	12	0.34	0.029	0.08	8.5	19	0.46
F	11	10	0.27	0.006	0.02	2.2	13	0.17	0.028	0.08	10	20	0.52
MH2	11	8	5.2	0.26	0.73	5.0	8.2	0.60	0.56	1.6	11	13	0.86

Table 2: Boron (mg/L)

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SAMPLE:	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A-O	8	6	18	0.77	2.2	4.3	6.8	0.62	0.94	2.69	5.2	10	0.50
B-K	8	4	4.5	0.27	0.76	6.0	8.4	0.72	0.40	1.14	8.9	13	0.70
C-I	8	4	13	0.31	0.89	2.4	7.2	0.33	0.33	0.94	2.5	11	0.24
D-M	8	7	11	0.26	0.74	2.4	7.4	0.31	1.1	3.11	10	11	0.90
E-L	8	5	21	0.47	1.3	2.2	6.7	0.33	0.85	2.43	4.0	10	0.40
F-N	8	5	8.3	0.43	1.2	5.2	7.7	0.68	0.47	1.34	5.7	12	0.48
G-P	7	4	3.1	0.094	0.27	3.0	8.9	0.34	0.18	0.51	5.8	14	0.43
H-J	8	5	31	1.0	3.0	3.2	6.3	0.54	1.6	4.43	5.2	9.6	0.52

Table 3: Bromine (mg/L)

SAMPLE:	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A-O	6	2	1.21	0.028	0.08	2.3	10.3	0.22	0.041	0.12	3.4	15.6	0.22
B-K	5	2	0.19	0.006	0.02	2.9	13.6	0.21	0.0043	0.012	2.3	20.5	0.11
C-I	6	3	0.81	0.017	0.05	2.1	10.9	0.19	0.062	0.18	7.7	16.5	0.47
D-M	6	4	0.38	0.017	0.05	4.5	12.2	0.37	0.066	0.19	17.4	18.5	0.94
E-L	6	3	1.72	0.030	0.09	1.7	9.7	0.17	0.22	0.62	12.8	14.8	0.86
F-N	6	3	0.22	0.014	0.04	6.4	13.3	0.48	0.046	0.13	20.9	20.1	1
H-J	6	2	2.30	0.061	0.17	2.7	9.3	0.28	0.092	0.26	4	14.1	0.28

Table 4: Cadmium (µg/L)

SAMPLE:	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A	12	11	6	0.2	0.6	3.3	15	0.22	1	3	17	22	0.77
B	12	11	16	0.4	1	2.5	15	0.17	2	6	13	22	0.59
C	12	9	40	0.4	1	1.0	15	0.07	3	8	7.5	22	0.34
D	12	10	10	0.3	0.8	3.0	15	0.20	0.9	3	9.0	22	0.41
E	8	7	0.3	0.20	0.6	67	15	4.47	0.20	0.67	67	22	3.05
F	8	6	0.3	0.04	0.1	13	15	0.87	0.20	0.45	67	22	3.05

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MH2	9	5	0.9	0.08	0.2	8.9	15	0.59	0.10	0.29	11	22	0.50

Table 5: Cobalt (µg/L)

SAMPLE:	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A-O	10	6	22	0.5	1	2.3	15	0.15	2	6	9.1	22	0.41
B-K	10	6	8	0.3	0.9	3.8	15	0.25	1	4	13	22	0.59
C-I	10	8	19	0.4	1	2.1	15	0.14	3	7	16	22	0.73
D-M	10	3	3	0.07	0.2	2.3	15	0.15	0.1	0.3	3.3	22	0.15
E-L	10	8	27	1	3	3.7	15	0.25	3	9	11	22	0.50
F-N	10	7	12	0.5	2	4.2	15	0.28	1	4	8.3	22	0.38
G-P	9	5	2	0.2	0.5	10	15	0.67	0.3	0.8	15	22	0.68
H-J	10	6	49	0.5	1	2.3	15	0.15	6	18	12	22	0.55

Table 6: Copper (mg/L)

SAMPLE	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A-O	10	8	1.1	0.013	0.040	1.2	10	0.12	0.11	0.32	10	16	0.63
B-K	10	8	0.21	0.006	0.020	2.9	13	0.22	0.021	0.060	10	20	0.50
C-I	10	7	0.74	0.009	0.030	1.2	10	0.12	0.046	0.13	6.2	17	0.36
D-M	10	8	0.14	0.007	0.020	5.0	14	0.36	0.015	0.043	11	22	0.50
E-L	10	9	1.7	0.061	0.17	3.6	7.8	0.5	0.16	0.46	9.0	15	0.60
F-N	10	7	0.16	0.006	0.020	3.8	14	0.27	0.029	0.083	18	21	0.86
G-P	9	4	0.042	0.004	0.010	9.5	15	0.63	0.006	0.017	14	22	0.64

Table 7: Strontium (µg/L)

SAMPLE	LAB. N°	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSD R (%)	Horwitz R RSDR (%)	HorratR
A	12	11	1091	33	93	3.0	10	0.30	78	222	7.2	16	0.45
B	12	8	1139	66	188	5.8	10	0.58	69	195	6.1	16	0.38
C	12	9	328	6	18	1.8	13	0.14	19	54	5.8	19	0.31

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D	12	10	313	7	20	2.2	13	0.17	22	61	7.0	19	0.37
E	12	10	1176	28	80	2.4	10	0.24	86	243	7.3	16	0.46
F	12	10	293	3	9	1.0	13	0.08	22	62	7.5	19	0.39
MH2	12	9	352	7	19	2.0	12	0.17	24	69	6.8	19	0.36

Table 8: Iron (mg/L)

SAMPLE	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A-O	10	6	3.2	0.017	0.05	0.53	8.9	0.06	0.23	0.66	7.2	13	0.55
B-K	10	6	1.5	0.085	0.24	5.7	9.9	0.58	0.11	0.31	7.3	15	0.49
C-I	10	5	2.1	0.036	0.10	1.7	9.4	0.18	0.18	0.51	8.6	14	0.61
D-M	10	5	3.1	0.033	0.094	1.1	8.9	0.12	0.29	0.83	9.4	14	0.67
E-L	10	5	4.3	0.120	0.34	2.8	8.5	0.33	0.29	0.83	6.7	13	0.52
F-N	10	6	1.1	0.051	0.15	4.6	10	0.46	0.16	0.46	15	16	0.94
G-P	9	6	0.83	0.024	0.07	2.9	11	0.26	0.14	0.40	17	16	1.06
H-J	10	7	7.8	0.180	0.52	2.3	7.8	0.29	1.2	3.52	15	12	1.25

Table 9: Lithium (µg/l)

SAMPLE	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A	11	10	34	2	5	5.9	15	0.39	4	11	11	22	0.50
B	11	11	42	3	8	7.1	15	0.47	4	12	10	22	0.45
C	11	11	47	1	4	2.1	15	0.14	5	13	9.8	22	0.45
D	11	11	18	1	4	5.6	15	0.37	2	7	14	22	0.64
E	11	11	25	1	3	4.0	15	0.27	3	9	12	22	0,55
F	11	9	9	0,3	1	3.8	15	0.25	0.6	2	7.2	22	0.33
MH2	11	7	22	1	3	4.6	15	0.31	1	3	5.3	22	0.24

Table 10: Magnesium (mg/L)

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SAMPLE:	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A	10	7	182	2.9	8.1	1.6	4.3	0.37	9.3	26	5.1	7.3	0.70
B	10	6	280	3.9	11	1.4	4.5	0.31	6.0	17	2.1	6.9	0.30
C	10	7	104	2.4	6.9	2.3	5.3	0.43	6.8	19.25	6.5	8.0	0.81
D	10	6	85	1.4	4.0	1.7	5.4	0.31	2.2	6.1	2.6	8.2	0.32
E	10	7	94	2.2	6.2	2.3	5.3	0.43	5.5	16	5.9	8.1	0.73
F	10	7	65	0.95	2.7	1.5	5.6	0.27	3.8	11	5.9	8.5	0.69
MH2	10	7	51	0.90	2.5	1.8	5.8	0.31	2.4	6.9	4.7	8.9	0.53

Table 11: Manganese (mg/L)

SAMPLE	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A	11	10	1.3	0.014	0.040	1.1	10	0.11	0.13	0.37	10	15	0.67
B	11	9	1.8	0.14	0.40	7.8	9.7	0.80	0.20	0.56	11	15	0.73
C	11	8	1.5	0.028	0.080	1.9	9.9	0.19	0.084	0.24	5.6	15	0.37
D	11	8	1.0	0.035	0.10	3.5	11	0.32	0.049	0.14	4.9	16	0.31
E	11	9	0.84	0.019	0.050	2.3	11	0.21	0.057	0.16	6.8	16	0.43
F	11	9	0.59	0.015	0.040	2.5	11	0.23	0.031	0.090	5.3	17	0.31
MH2	11	8	0.52	0.029	0.080	5.6	12	0.47	0.037	0.10	7.1	18	0.39

Table 12: Nickel (µg/L)

SAMPLE	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A	11	10	40	2	6	5,0	15	0.33	5	13.90	13	22	0.59
B	12	10	194	7	20	3.6	14	0.26	17	48.96	8.8	21	0.42
C	12	8	148	4	10	2.7	14	0.19	5	15.12	3.4	21	0.16
D	12	8	157	4	12	2.6	14	0.19	8	23.10	5.1	21	0.24
E	11	8	15	0.6	2	4.0	15	0.27	1	3.33	6.7	22	0.30
F	12	9	66	1	4	1.5	15	0.10	4	10.58	6.1	22	0.28

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MH2	11	7	71	5	14	7.0	15	0.47	4	11.41	5.6	22	0.25

Table 13: Lead (µg/L)

SAMPLE	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A	12	9	59	1	4	1.7	15	0.11	3	9	5.1	22	0.23
B	12	10	109	2	6	1.8	15	0.12	8	23	7.3	22	0.33
C	12	9	136	3	9	2.2	14	0.16	13	37	9.6	22	0.44
D	12	9	119	2	6	1.7	15	0.11	5	13	4.2	22	0.19
E	12	10	13	1	3	7.7	15	0.51	1	4	7.7	22	0.35
F	12	9	92	1	4	1.1	15	0.07	4	11	4.4	22	0.20
MH2	12	10	13	1	3	7.7	15	0.51	1	3	7.7	22	0.35

Table 14: Rubidium (µg/L)

SAMPLE	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A	11	6	717	14	41	2.0	11	0.18	13	36	1.8	17	0.11
B	11	7	799	25	70	3.1	11	0.28	30	86	3.8	17	0.22
C	11	8	677	10	27	1.5	11	0.14	34	96	5.0	17	0.29
D	11	7	612	18	51	2.9	11	0.26	18	50	2.9	17	0.17
E	11	9	741	19	53	2.6	11	0.24	66	187	8.9	17	0.52
F	11	9	617	10	28	1.6	11	0.15	43	123	7.0	17	0.41
MH2	11	7	1128	10	28	0.89	10	0.09	64	181	5.7	16	0.36

Table 15: Sodium (mg/L)

SAMPLE	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A	10	9	19	0.59	1.7	3.1	6.8	0.46	2.2	5.7	12	10	1.20
B	10	9	20	1.3	3.6	6.5	6.7	0.97	2.2	6.3	11	10	1.10

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C	10	7	28	0.33	0.93	1.2	6.4	0.19	1.9	5.4	6.8	9.7	0.70
D	10	8	11	0.24	0.68	2.2	7.4	0.30	1.1	3.0	10	11	0.91
E	10	8	9.8	0.19	0.53	1.9	7.5	0.25	0.89	2.5	9.1	11	0.83
F	10	8	6.1	0.093	0.26	1.5	8.1	0.19	0.74	2.1	12	12	1.00
MH2	10	8	24	1.8	5.0	7.5	6.6	1.14	2.6	7.2	11	9.9	1.11

Table 16: Vanadium (µg/L)

SAMPLE	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A	12	11	46	1	3	2.2	15	0.15	5	13	11	22	0.50
B	12	11	167	5	15	3.0	14	0.21	19	54	11	21	0.52
C	12	11	93	3	8	3.2	15	0.21	12	33	13	22	0.59
D	12	9	96	3	8	3.1	15	0.21	8	22	8.3	22	0.38
E	10	7	3	0.2	0.7	6.7	15	0.45	0.3	0.9	10	22	0.45
F	10	8	3	0.2	0.6	6.7	15	0.45	0.2	0.7	6.7	22	0.30
MH2	12	9	11	0.3	1	2.7	15	0.18	0.9	3	8.2	22	0.37

Table 17: Zinc (µg/L)

SAMPLE	LAB. No.	Accepted	Assigned value	Sr	r	RSD r (%)	Horwitz RSDr (%)	Horratr	SR	R	RSDR (%)	HorwitzR RSDR (%)	HorratR
A	11	8	405	22	61	5.4	12	0.45	45	128	11	18	0.61
B	11	9	1327	49	138	3.7	10	0.37	152	429	11	15	0.73
C	11	9	990	14	41	1.4	11	0.13	86	243	8.7	16	0.54
D	11	9	1002	28	79	2.8	11	0.25	110	310	11	16	0.69
E	11	9	328	13	37	4.0	13	0.31	79	224	24	19	1.26
F	11	9	539	15	42	2.8	12	0.23	61	172	11	18	0.61
MH2	11	8	604	72	204	12	11	1.09	89	251	15	17	0.88

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APPENDIX B RESULTS OF AN INTERNAL VALIDATION FOR ARSENIC

DETERMINATION OF ARSENIC IN WINE BY ICP-MS ACCORDING TO METHOD OIV/OENO 344/2010 USING TELLURIUM AS INTERNAL STANDARD

The samples were prepared and analyzed in duplicate in 5 non consecutive days. The quantitation was performed using 2 different ICP-MS.

The samples were prepared according to method OIV/OENO 344/2010, diluting 1 mL of wine in 20 mL of 3% HNO3, without using prior mineralization in any of the samples.

Internal standard: Te, added on-line.

Results of the validation:

Product	Reference value µg/l	Result µg/l	spike µg/l	Recovery %	RSDr%	RSDR%
Red wine		<5	10	101	3.27	8.1
			200	100	0.98	3.1
			1000	102	3.1	5.8
White wine		<5	10	99	1.8	5.1
			200	102	2.8	4.7
			1000	101	2.2	5.8
Liqueur wine		<5	10	102	0.9	5.4
			200	104	1.4	5.2
			1000	103	1.1	4.4

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Sparkling wine		<5	10	101	3.2	6.8
			200	101	0.8	4.3
			1000	103	4.1	5.8
*CRM red wine MAPA 2021	39.0 ± 2,17	39.77	NA	102	3.8	1.1
*[1]CRM white wine MAPA 2021	59.5 ± 3,7	58.16	NA	98	2.0	1.9

*Certified Reference Material (CRM) of red wine produced by an intercomparison test by the Spanish Ministry of Agriculture, Fisheries and Food (Ministerio de Agricultura, Pesca y Alimentación – MAPA) in 2021.

*[1]Certified Reference Material (CRM) of white wine produced by an intercomparison test by the Spanish Ministry of Agriculture, Fisheries and Food (Ministerio de Agricultura, Pesca y Alimentación – MAPA) in 2021.

[1] Type II for the listed elements except arsenic. Type IV for arsenic.

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