RESOLUTION OIV-OENO 662K-2024

DETERMINATION OF MINERAL ELEMENTS IN GRAPE JUICES, RECONSTITUTED GRAPE JUICE, CONCENTRATED GRAPE JUICES, AND GRAPE NECTARS USING ICP-AES (INDUCTIVELY COUPLED PLASMA / ATOMIC EMISSION SPECTROMETRY)

Type IV method

THE GENERAL ASSEMBLY,

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

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

CONSIDERING the application of the Method OIV-MA-AS322-13 of the Compendium of International Methods of Wine and Must Analysis,

CONSIDERING that for concentrated grape juice the dilution of the sample should be taken into account on the calculation,

DECIDES to add the following method:

Determination of mineral elements in grape juices, reconstituted grape juice, concentrated grape juices, and grape nectars using ICP-AES (inductively coupled plasma / atomic emission spectrometry)

Type IV method

1. Warning

SAFETY PRECAUTIONS - When handling acids, operators should protect their hands and eyes. Acids must be handled under a suitable hood.

2. Scope

This method specifies an inductively coupled plasma atomic emission spectroscopy (ICP-AES) method to determine the concentration of the following elements in grape juice, reconstituted grape juice, concentrated grape juice and grape nectar:

Major mineral elements:

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- Potassium (up to 3000 mg/L)
- Calcium (up to 800 mg/L)
- Magnesium (up to 1080 mg/L)
- Sodium (up to 40 mg/L)

Minor mineral elements:

- Iron (0.2 mg/L to 10.0 mg/L)
- Copper (0.1 mg/L to 5.0 mg/L)
- Zinc (0.5 mg/L to 10.0 mg/L)
- Strontium (0.1 mg/L to 3.0 mg/L
- Aluminium (0.2 mg/L to 5 mg/L)
- Barium (0.1 mg/L to 5.0 mg/L)

3. Principle

3.1. Simultaneous analysis of major and minor elements

A 1:5 dilution factor is suggested to prepare the samples in this method in order to be able to analyse both the major and minor elements.

The calibration range contains nitric acid (HNO_3 - 1% v/v) which is used to stabilize the solutions. In this method, to minimize the impact of other non-spectral interferences, the use of the lines Sc 335.372 (scandium at 5 mg/l) and Cs 697.327 (caesium at 1% m/v $CsNO_3$) is recommended as internal standard.

Other internal standards, chosen wisely, may also be used in order to optimize the method, such as $Y_{371.029}$.

Caesium, in the form of $CsNO_3$, also serves as an ionic buffer when used as an internal standard. The presence of this buffer therefore sets the ionization balances of the other components. Caesium chloride, CsCl, can also be used as an ionic buffer.

The internal standards and ionic buffer are prepared in the same flask and then introduced into the sample through the addition of a third channel in the peristaltic pump before entering the nebuliser as a homogenous mixture.

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3.2. Analysis of the major elements only

The analysis of the major elements only can also be performed by carrying out a 1:50 dilution of the sample. Nitric acid (HNO_3 - 1% v/v) is added into the standards and the samples in order to stabilize the solutions.

Given the dilution performed, the matrix effects are considered negligible. The use of internal standards will not be necessary.

4. Reagents and materials

Unless otherwise specified, all the reagents used must be of a recognized analytical quality.

4.1. Ultra-pure water or equivalent quality in accordance with ISO 3696 standard.

4.2. Certified mono-element solution(s) (to 1000 mg/L or 10000 mg/L) for the mineral elements and the internal standard (scandium for example).

4.3. Internal control: certified reference material (grape juice, reconstituted grape juice, concentrated grape juice and grape nectar) or sample from a proficiency testing scheme, comprising the elements analyzed.

4.4. Nitric acid of a concentration greater than 60% (for trace analysis) (CAS No. 7697-37-2).

4.5. A solution of 1 % v/v nitric acid.

Prepare a 1% nitric acid solution by placing water (4.1) in the volumetric flask, adding 10 mL of nitric acid (4.4) into a 1000 mL flask (5.3) and completing with water (4.1).

To prepare a 1% nitric acid solution, water (4.1) is placed in the volumetric flask

4.6 A solution of 10 % nitric acid.

Prepare a 10 % v/v nitric acid solution by placing water (4.1) in the volumetric flask, adding 100 mL of nitric acid (4.4) into a 1000 mL flask (5.3) and completing with water (4.1).

4.7 Argon, minimum purity of 99.999%.

5. Apparatus

5.1. Optical emission spectrometer with excitation by induced argon plasma and dispersive system (for wavelength analysis, see table in section 7) with axial, radial or dual configuration and preferably sequential PM, CCD, CID or SCCD type detector.

Note 1: When an internal standard is used in the method, it is highly recommended to

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perform the multi-elemental analysis using a simultaneous type spectrometer.

Note 2: Other systems for introducing the sample may be used in order to increase the sensitivity and robustness of the method (continuous flow injection system, microwave desolution system (MWDS, etc.).

5.2. Calibrated micropipettes making it possible to take volumes from 200 µL to 5 mL and/or 1.5 and 10 mL volumetric pipettes.

5.3. Volumetric flasks.

Note 3: All the material to be used in the determination should be immersed in a nitric solution (4.6) for 12 hours and then be rinsed several times with the water (4.1). Appropriate precautions should be taken to avoid contamination.

In order to assess the robustness of the method on the instrument used, it is recommended that the Mg 279.800/Mg 285.213 intensity ratio is calculated; Mg 285.213 being an atomic line and Mg 279.800 being an ionic line.

6. Preparation of the sample

6.1. Preparing the calibration range

The number of calibration solutions depends on the reliability required. At least five calibration solutions are needed. The accuracy of the results can be verified by analysing a reference material.

The range will be chosen according to the sample dilution performed. It should cover the scope of the various elements. It is important that the nitric acid concentration is the same in the standards and samples.

6.1.1. Preparing a standard solution for simultaneous analysis of major and minor elements (1:5 dilution):

Using a micropipette (5.2), introduce the volume of standard required to achieve the intended concentration in the final solution and 1 mL of nitric acid (4.4) into a 100 mL flask (5.3). Make up to 100 mL with water (4.1) and mix.

6.1.2. Preparing a standard solution for analysing major elements only (1:50 dilution):

Using a micropipette (5.2), introduce the desired volume of standard required to achieve the intended concentration in the final solution into a 100 mL flask (5.3), make up to 100 mL with nitric acid solution (4.5) and mix.

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6.2. Preparing the test samples

6.2.1. Preparing test samples for simultaneous analysis of major and minor elements (1:5 dilution):

Using a volumetric pipette or micropipette (5.2), introduce 10 mL of sample and 1 mL of nitric acid (4.4) into a 50 mL flask (5.3). Make up to 50 mL with water (4.1) and mix.

Mineralization, for example by microwave digestion in nitric acid, allows the destruction of organic compounds. If the concentration of some elements is too high (higher than the highest concentration standard in the calibration), a higher dilution may be required.

Note 4: Depending on the robustness of the instrument used and given the use of the ionic buffer and internal standards, it is possible to work with a 1:2 dilution factor in order to improve the sensitivity of the method for trace elements. As a result, the calibration ranges and possibly the experimental parameters (power) must be modified.

6.2.2. Preparing test samples for analyzing major elements only (1:50 dilution)

Using a volumetric pipette or micropipette (5.2), introduce 1 mL of the sample and 0.5 mL of nitric acid (4.4) into a 50 mL flask (5.3). Make up to 100 mL with water (4.1) and mix.

Note: For the concentrated grape juice, dilute the juice five times (m/m) with water, before initiate the item 6.2.1 or 6.2.2 above. Consider this dilution in the final calculation (item 8).

7. Procedure

7.1. Experimental parameters

The instrument parameters are presented here as an example and may be modified depending on the instrument used.

- Power: 1.3 Kw
- Plasma gas flow: 15 L/min
- Auxiliary gas flow: 1.5 L/min
- Nebulizer pressure: 200 kPa
- Stabilization period: 20 s

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- Measurement time per replicate: 5 s
- Pump speed: 15 rpm
- Rinsing time: 30 s
- Internal standard inlet internal diameter: 0.51 mm
- Sample inlet internal diameter: 0.8 mm
- Turn the unit on (pump operational and plasma switched on) and clean the system for at least 20 minutes with 1% nitric acid (4.5).

Analyze a blank followed by the series of standards in increasing order of concentration. A reference sample can be used as internal quality control (4.3) to verify the calibration. Next, analyze the blank again to ensure the absence of memory effect. Next, conduct the analysis of the samples by inserting a quality control every 10 samples and at the end of the analysis series (as an example).

A control chart can be drawn up from the results obtained in relation to the control sample in order to define the acceptance criteria and actions to be performed in the event of drift. The analyses will be performed for each element with a minimum of 3 replicates. In table I are described the lines that can be used for the various elements as example (other lines may be used depending on the equipment).

Table I – Mineral elements and their respective main line, secondary line and associated internal standard

Elements	Main line ($E_{sum} = E_{exc} + E_{ion}$)	Associated internal standard	Secondary line ($E_{sum} = E_{exc} + E_{ion}$)	Associated internal standard
K	769.897 (I) *(1.6 eV)*	Cs 697.327	766.491 (I) *(1.6 eV)*	Cs 697.327
Ca	317.933 (II) *(10 eV)*	Sc 335.372	315.887 (II) *(10.1 eV)*	Sc 335.372
Mg	285.213 (I) *(4.3 eV)*	Cs 697.327	279.800 (II) *(10.6 eV)*	Sc 335.372

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Elements	Main line ($E_{sum} = E_{exc} + E_{ion}$)	Associated internal standard	Secondary line ($E_{sum} = E_{exc} + E_{ion}$)	Associated internal standard
Na	589.592 (I) *(2.1 eV)*	Cs 697.327		
Fe	259.940 (II) *(12.7 eV)*	Sc 335.372	239.563 (II) *(11.4 eV)*	Sc 335.372
Cu	327.395 (I) *(3.8 eV)*	Cs 697.327	324.754 (I) (3.8 eV)	Cs 697.327
Zn	213.857 (I) *(5.8 eV)*	Cs 697.327	206.200 (II) *(12.2 eV)*	Sc 335.372
Mn	257.61 (II) *(12.3 eV)*	Sc 335.372	260.568 (II) *(11 eV)*	Sc 335.372
Sr	421.552 (II) *(8.6 eV)*	Sc 335.372	407.771 (II) *(8.7 eV)*	Sc 335.372
Al	396.152 (I) *(3.1 eV)*	Cs 697.327	167.019 (I) *(7.4 eV)*	Cs 697.327
Rb	780.026 (I) *(1.6 eV)*	Cs 697.327		
Li	670.783 (I) *(1.9 eV)*	Cs 697.327		
Ba	455.403 (II) *(7.9 eV)*	Sc 335.372		
Sc	335.372 (II) *(10.3 eV)*			
Cs	697.327 (I) *(1.8 eV)*			

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8. Calculation and results expression

Calculate the concentration of the elements in the sample using the following equation:

$$C = \frac{Cm \times Vt}{Vm}$$

Where:

C: concentration of the element in the sample (mg/L)

Cm: concentration of the element in the diluted solution (mg/L)

Vt: volume of the dilution flask (mL) (here V=50 mL)

Vm: volume of the sample taken for dilution (mL) (here V=1 or 10 mL)

The results are expressed in mg/L, in one decimal place.

9. Characteristics of the method

A validation study was carried out for the purpose of assessing the suitability of the method for grape juice, taking into account the accuracy of the method, determined by defining the levels of precision and trueness of the method.

For the data acquisition, reference materials of each mineral element (synthetic solutions and spiked samples) distributed across the range covering the scope of application of the methods in terms of concentration were used. Each of the n=5 materials was analyzed, in duplicate, under conditions of reproducibility and within the temporal limits of stability of each material for the parameter considered.

9.1. Precision results

The precision results of each mineral element are shown below in the Table's II, III, IV, V, VI, VII, VIII, IX, X and XI. Where Sr is the repeatability standard deviation, r is the repeatability, SI the intermediate precision standard deviation and %CVr the precision coefficient of variation.

Table II – Precision data for Potassium 766.4 nm (mg/L)

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Precision	**Material 1** (synthetic solution)	**Material 2** (grape juice)	**Material 3** (grape juice)	**Material 4** (grape juice)	**Material 5** (grape juice)
Target value	100.00	750.00	1500.00	2250.00	3000.00
Mean	104.97	800.80	1600.30	2345.90	3146.00
Sr	1.58	17.67	22.25	68.14	51.49
r	4.44	49.44	62.31	190.81	144.19
SI	5.55	46.74	88.32	148.47	201.42
$\%CV_r$ (k=2)	10.58	11.67	11.04	12.66	12.80

Table III – Precision data for Calcium 317.9 nm (mg/L)

Precision	**Material 1** (synthetic solution)	**Material 2** (grape juice)	**Material 3** (grape juice)	**Material 4** (grape juice)	**Material 5** (grape juice)
Target value	2.00	200.00	400.00	600.00	800.00
Mean	2.10	201.25	402.40	590.10	770.10
Sr	0.16	3.82	5.60	7.19	12.21
r	0.46	10.70	15.93	20.13	34.18
SI	0.20	3.08	8.92	11.5	17.85
$\%CV_r$ (k=2)	19.30	3.06	4.43	3.90	4.64

Table IV – Precision data for Magnesium 279.0 nm (mg/L)

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Precision	**Material 1** (synthetic solution)	**Material 2** (grape juice)	**Material 3** (grape juice)	**Material 4** (grape juice)	**Material 5** (grape juice)
Target value	5.00	270.00	540.00	810.00	1080.00
Mean	5.34	279.90	540.20	779.40	997.80
Sr	0.34	4.50	4.63	7.45	14.37
r	0.95	12.61	12.95	20.87	40.24
SI	0.63	6.58	11.60	20.52	37.84
$\%CV_r$ (k=2)	23.79	4.70	4.29	5.27	7.59

Table V – Precision data for Sodium 588.9 nm (mg/L)

Precision	**Material 1** (synthetic solution)	**Material 2** (grape juice)	**Material 3** (grape juice)	**Material 4** (grape juice)	**Material 5** (grape juice)
Target value	6.00	10.00	20.00	30.00	40.00
Mean	5.99	10.08	17.35	27.47	40.92
Sr	0.04	0.13	0.29	0.63	0.22
r	0.12	0.37	0.82	1.78	0.64
SI	0.29	0.48	0.82	1.54	2.16
$\%CV_r$ (k=2)	9.87	9.51	9.49	11.27	10.56

Table VI – Precision data for Iron 238.2 nm (mg/L)

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Precision	**Material 1** (synthetic solution)	**Material 2** (grape juice)	**Material 3** (grape juice)	**Material 4** (grape juice)
Target value	0.25	2.50	7.50	10.00
Mean	0.23	2.56	7.63	9.81
Sr	0.01	0.08	0.33	0.14
r	0.03	0.23	0.93	0.40
SI	0.05	0.17	0.43	0.74
$\%CV_r$ (k=2)	46.70	13.78	11.51	15.19

Table VII – Precision data for Copper 224.7 nm (mg/L)

Precision	**Material 1** (synthetic solution)	**Material 2** (grape juice)	**Material 3** (grape juice)	**Material 4** (grape juice)	**Material 5** (grape juice)
Target value	0.10	1.25	2.50	3.75	5.00
Mean	0.10	1.28	2.61	3.83	5.01
Sr	0.01	0.05	0.03	0.04	0.06
r	0.02	0.15	0.07	0.11	0.17
SI	0.01	0.08	0.12	0.13	0.23
$\%CV_r$ (k=2)	23.38	13.75	9.20	6.82	9.55

Table VIII – Precision data for Zinc 213.8 nm (mg/L)

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Precision	**Material 1** (synthetic solution)	**Material 2** (grape juice)	**Material 3** (grape juice)	**Material 4** (grape juice)	**Material 5** (grape juice)
Target value	0.08	2.50	5.00	7.50	10.00
Mean	0.07	2.44	4.91	7.28	9.55
Sr	0.01	0.04	0.05	0.10	0.11
r	0.01	0.12	0.15	0.28	0.32
SI	0.01	0.05	0.13	0.24	0.24
$\%CV_r$ (k=2)	20.90	4.29	5.62	6.51	4.94

Table IX – Precision data for Strontium 407.7 nm (mg/L)

Precision	**Material 1** (synthetic solution)	**Material 2** (grape juice)	**Material 3** (grape juice)	**Material 4** (grape juice)
Target value	0.07	1.50	2.25	3.00
Mean	0.07	1.50	2.25	3.02
Sr	0.01	0.06	0.04	0.03
r	0.01	0.19	0.13	0.11
SI	0.01	0.12	0.17	0.25
$\%CV_r$ (k=2)	35.98	16.10	15.35	16.96

Table X – Precision data for Aluminum 396.0 nm (mg/L)

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Precision	**Material 1** (synthetic solution)	**Material 2** (grape juice)	**Material 3** (grape juice)	**Material 4** (grape juice)	**Material 5** (grape juice)
Target value	0.20	1.25	2.50	3.75	5.00
Mean	0.26	1.29	2.43	3.58	4.91
Sr	0.01	0.06	0.04	0.10	0.04
r	0.04	0.16	0.11	0.28	0.12
SI	0.02	0.09	0.11	0.10	0.28
$\%CV_r$ (k=2)	16.80	14.68	9.64	6.08	11.62

Table XI – Precision data for Barium 455.4 nm (mg/L)

Precision	**Material 1** (synthetic solution)	**Material 2** (grape juice)	**Material 3** (grape juice)	**Material 4** (grape juice)	**Material 5** (grape juice)
Target value	0.12	1.25	2.50	3.75	5.00
Mean	0.15	1.28	2.52	3.74	4.83
Sr	0.01	0.02	0.055	0.05	0.05
r	0.01	0.04	0.12	0.13	0.13
SI	0.01	0.02	0.05	0.06	0.07
$\%CV_r$ (k=2)	8.87	2.44	4.15	3.00	2.98

10. Bibliography

1. OIV. Compendium of International Methods of Analysis of Wines and Musts. Method OIV-MA-AS322-13:R2013.

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2. ISO 3696. Water for analytical laboratory use - Specification and test methods.

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