OIV-MA-AS322-12 Analysis of mineral elements in wines using ICP-AES inductively coupled plasma/atomic emission spectrometry)

Type III 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 wines:
-Major mineral elements:

- Potassium (up to 1500 mg/L)
- Calcium (up to 250 mg/L)
- Magnesium (up to 150 mg/L)
- Sodium (up to 100 mg/L)

Minor mineral elements:

- Iron (1 to 10 mg/L)
- Copper (0.1 to 5 mg/L)
- Zinc (0.5 to 5 mg/L)
- Manganese (0.5 to 5 mg/L)
- Strontium (0.1 to 3 mg/L)
- Aluminium (0.75 to 7.5 mg/L)
- Barium (0.1 to 5 mg/L)

3. Principle

3.1. Simultaneous analysis of major and minor elements

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

The calibration range contains ethanol (2.5%) to take into account the matrix effects related to its presence during nebulisation and at the plasma temperature, along with nitric acid (HNO_3 - 1%) which is used to stabilise the solutions.

The lines $Sc_{335.372}$ (scandium at 5 mg/L) and $Cs_{697.327}$ (caesium as 1% in $CsNO_3$) proposed in this method can be used as an internal standard in order to minimise the impact of other non-spectral interferences.

Other internal standards, chosen wisely, may also be used in order to optimise 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 ionisation 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.

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%) is added into the standards and the samples in order to stabilise the solutions.

Given the dilution performed, the matrix effects are considered negligible. The use of internal standards will not be necessary. Likewise, there will be no need to add ethanol to the calibration range.

4. Reagents and solutions

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

4.1. Ultra-pure, demineralised water with a resistivity (greater than 18 MΩ), in accordance with the ISO 3696 standard.

4.2. Certified mono-element solution(s) (to 1000 or 10,000 mg/L) for the mineral elements analysed and the internal standard (scandium for example).

4.3. Internal control: certified reference material (wine) or sample from an intercomparison programme between laboratories, comprising the elements analysed.

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

4.5. Ethanol of a concentration greater than 95% (for trace analysis) (CAS No. 64-17-5).

4.6. A solution of 1% nitric acid

Prepare a 1% nitric acid solution by adding 10 mL of nitric acid (4.4) into a 1000 mL flask.

5. Apparatus and equipment

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: *Multi-element analysis using a simultaneous type spectrometer is strongly advised if an internal standard is used in the method.*

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 desolvation system (MWDS, etc.).*

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

5.3. Class A volumetric flasks

Note 3: *The equipment in contact with the sample must remain in the nitric acid solution (4.4) at a concentration of 10% for 12 hours and then be rinsed several times with the demineralised water (4.1).*

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. Sample preparation

6.1. Preparing the calibration range

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

The range will be chosen according to the 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 desired volume of standard, 2.5 mL of ethanol (4.5) and 1 mL of nitric acid (4.4) into a 100 mL flask (5.3). Make up to 100 mL with demineralised 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 into a 100 mL flask (5.3), make up to 100 mL with nitric acid solution (4.6) and mix.

6.2. <u>Preparing the test samples</u>

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

Using a graduated 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 demineralised water (4.1) and mix.

Sparkling wine samples must be subjected to degassing using an ultrasound bath for example, for at least 10 minutes.

Particularly for samples rich in sugar, mineralisation by microwave digestion in nitric acid is used to destroy organic compounds. Finally, a higher dilution may need to be considered due to a concentration which is too high for certain elements. In this case, the ethanol content may be adjusted accordingly in the solutions and standards.

<u>Note 4</u>*: 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, ethanol content and possibly the experimental parameters (power) must be modified.*

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

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

7. **Procedu**re

7.1. Experimental parameters

The optimal instrument parameters that have enabled us to achieve the specificity for this method in terms of repeatability and reproducibility are described below. They 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

Nebuliser pressure: 200 kPa

Stabilisation period: 20 s

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 (4.6).

Analyse a blank following the series of standards in increasing order of concentration. A reference sample (4.3) can be used as internal quality control to verify that the calibration is satisfactory. Next, analyse 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.

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.

Lines that can be used for the various elements (other lines may be used depending on the equipment).

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
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)*			

8. Calculation

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 wine 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)

9. Precision

Elements	Repeatability (RSD %)	Reproducibility (RSD %)	LD (mg/L)	LQ (mg/L)	Recovery rate
K	2.3	5.5	major	major	Between 80% and 120%
Ca	3.5	11.3	major	major	
Mg	2.4	8.9	major	major	
Na	2.6	9.1	major	major	
Fe	2.2	6.9	0.08	0.25	
Cu	13.4	15.8	0.03	0.10	
Zn	3.6	6.5	0.03	0.10	
Mn	4.7	7.0	0.03	0.10	
Al	5.6	17.0	0.03	0.10	
Sr	2.1	9.9	0.03	0.10	
Ba	8.2	20.8	0.03	0.10	

APPENDIX:

Validation study – Results of the collaborative trials

A validation study was performed in November 2011 (pre-study) and in February 2012 (validation study) in accordance with ISO 5725 and resolution OENO 6/2000.

Pre-study:

3 samples (dry white wine, red wine and sweet white wine), spiked with Al, Fe, Cu, Sr, Ba, Mn and Zn.

	Samples		
Element (mg/L)	Red wine	Dry white wine	Sweet wine
K	1258	725	841
Ca	50	75	81
Na	20	28	24
Mg	78	70	66
Al	1.29	1.33	1.97
Fe	8.12	6.91	9.29
Cu	0.86	0.86	0.94
Sr	1.07	1.08	1.07
Ba	0.77	0.72	0.63
Mn	1.6	2.01	1.77
Zn	1.51	2.53	1.69