Determination of ultra-trace elements in wine samples by means ETV-ICP-MS

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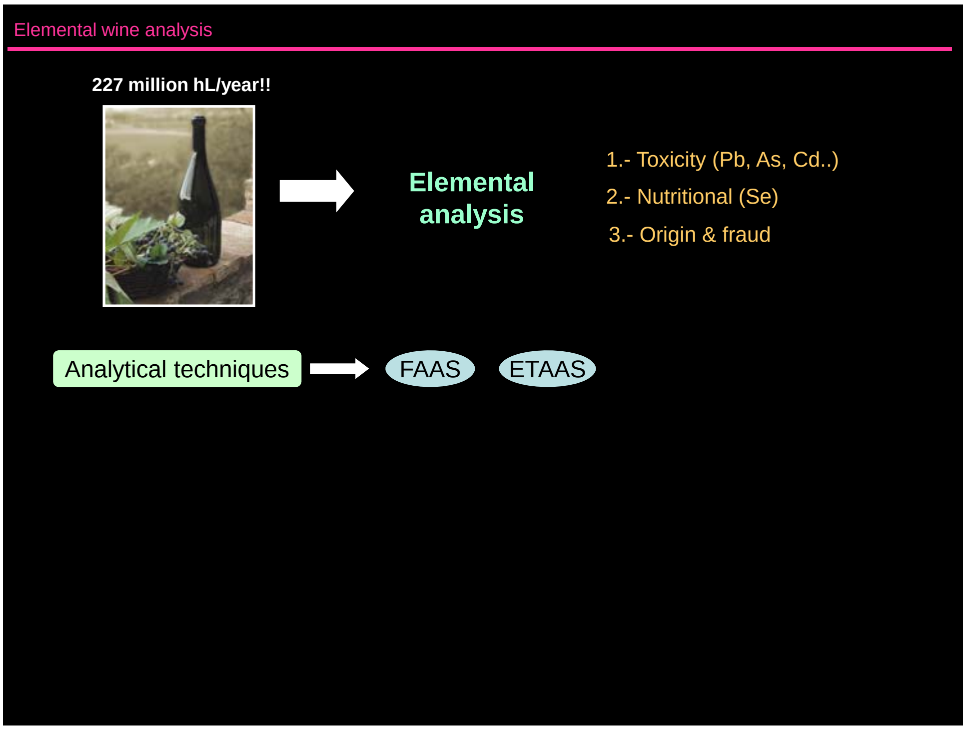
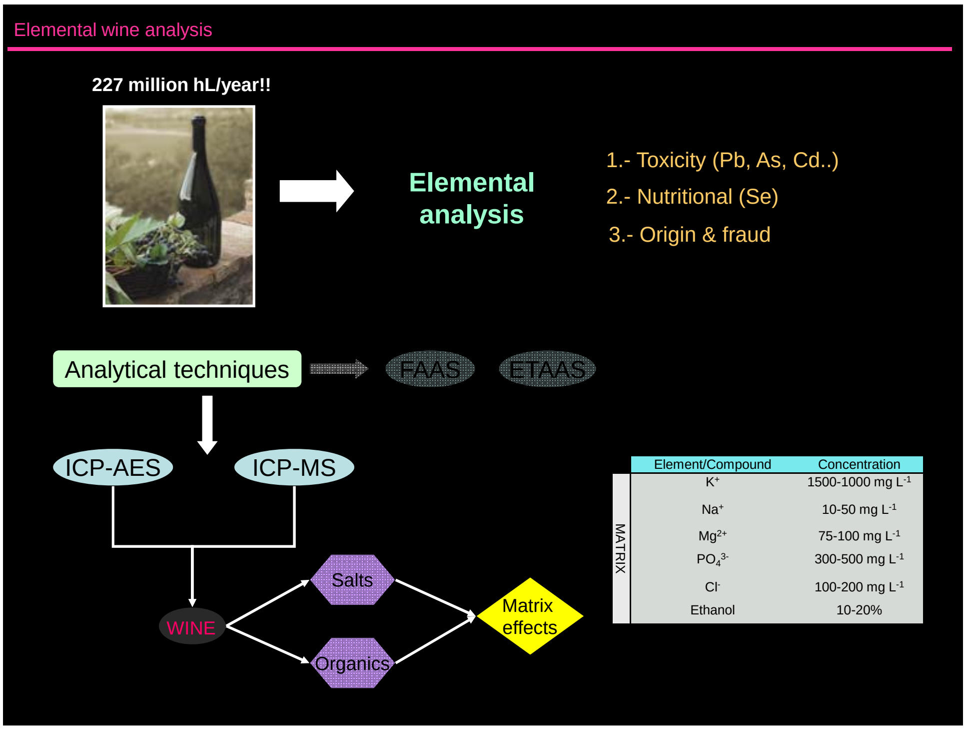
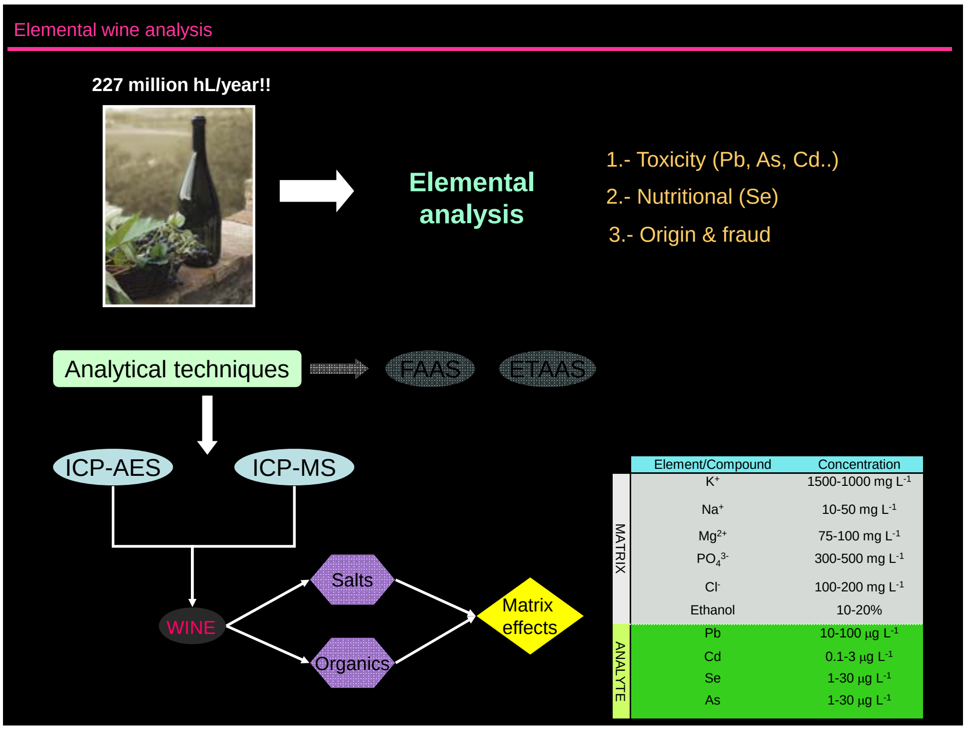
Introduction





Element/Compound	Concentration
K^+	1500-1000 mg L^{-1}
Na^+	10-50 mg L^{-1}
Mg^{2+}	75-100 mg L^{-1}
PO_4^{3-}	300-500 mg L^{-1}
Cl^-	100-200 mg L^{-1}
Ethanol	10-20%



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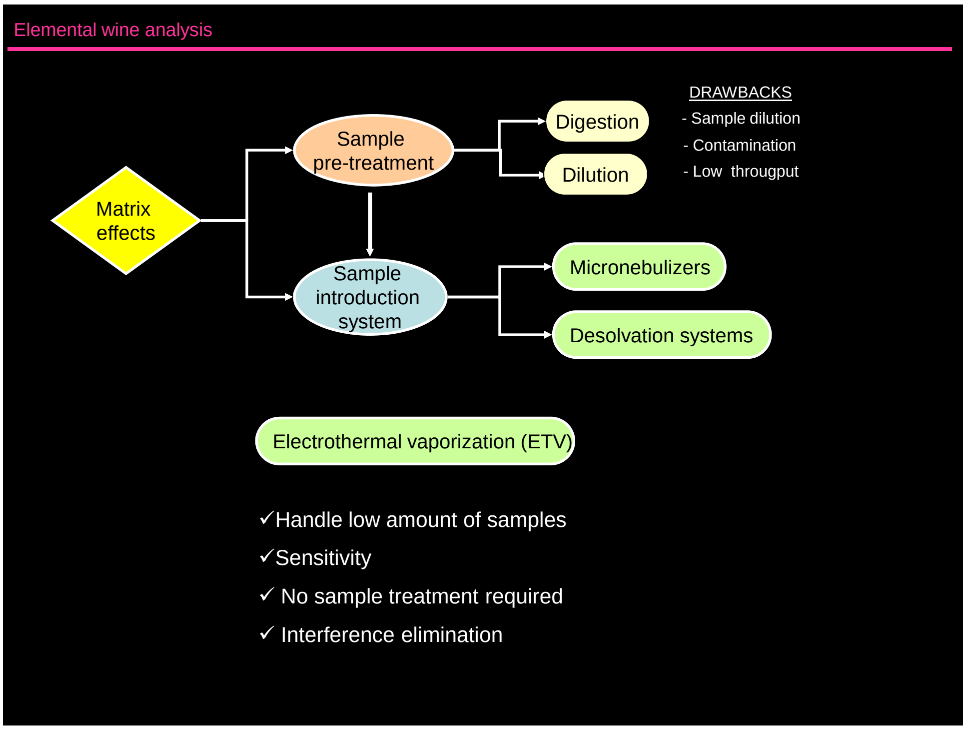
PO_4^{3-}	300-500 mg L^{-1}
Cl^-	100-200 mg L^{-1}
Ethanol	10-20%
Pb	10-100 μg L^{-1}
Cd	0.1-3 μg L^{-1}
Se	1-30 μg L^{-1}
As	1-30 μg L^{-1}



Objective

ETV performance for elemental wine analysis in ICP-MS

1. Optimization of ETV experimental conditions:
   a. sample amount
   b. pyrolysis and vaporization temperature
   c. modifier

2. Calibration methodology

3. Analysis of wine:
   a. toxic elements (Pb, Cd, As)
   b. micronutrients (Se)

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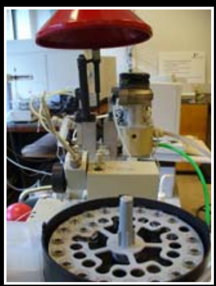
Experimental

ICP-MS instrument and ETV unit

Perkin-Elmer Elan 5000



HGA-600 MS
Autosampler AS-60

Plasma forward power (W)	1000
Argon flow rate (L min^{-1})	
Plasma	15
Auxiliary	0.8
Carrier	1.5

Step	*Temperature (ºC)*	*Ramp time (s)*	*Hold time (s)*
Drying	90	10	10
Pyrolysis	Variable	10	15
Vaporization	Variable	0.7	10
Cleaning	2650	1.0	5
Cooling	20	1.0	20

Analytes and modifier

Analyte(isotope): Pb (208) Cd (114) Se (82) As (75)

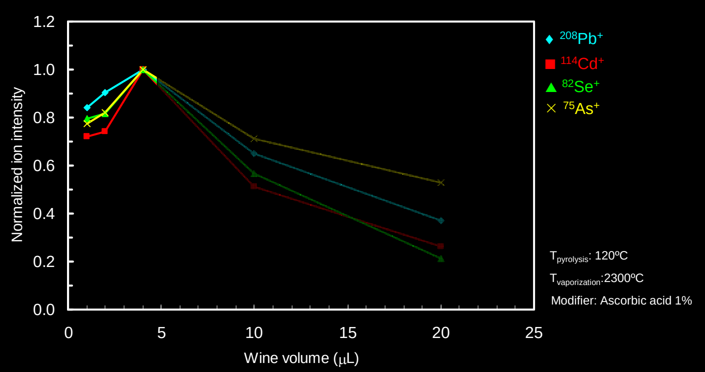
Modifier: Pd, ascorbic acid, citric acid

Results

Optimization of ETV experimental conditions

Influence of the sample amount

$I_{(wine+20\ ppb)} - I_{wine} = 20\ \mu g\ L^{-1}$ net analyte intensity



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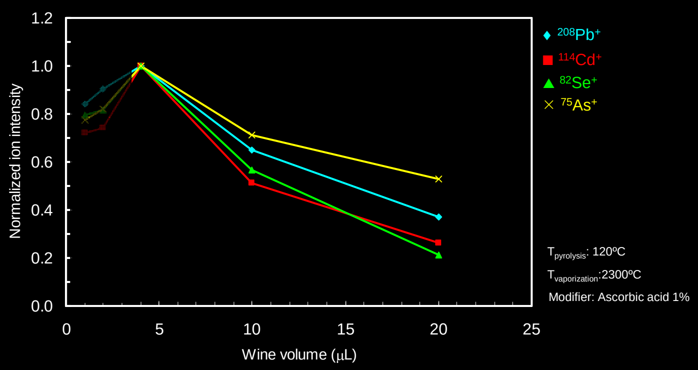

Optimization of ETV experimental conditions

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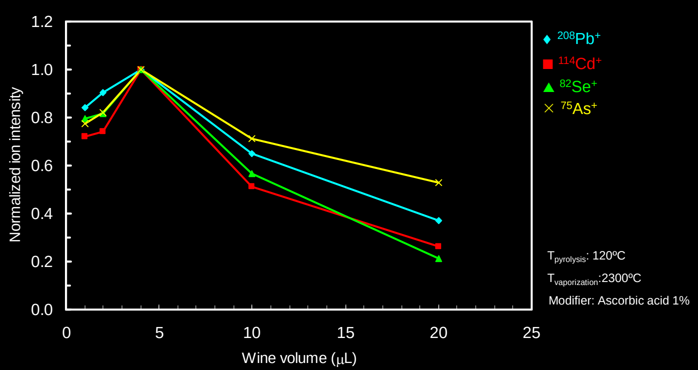
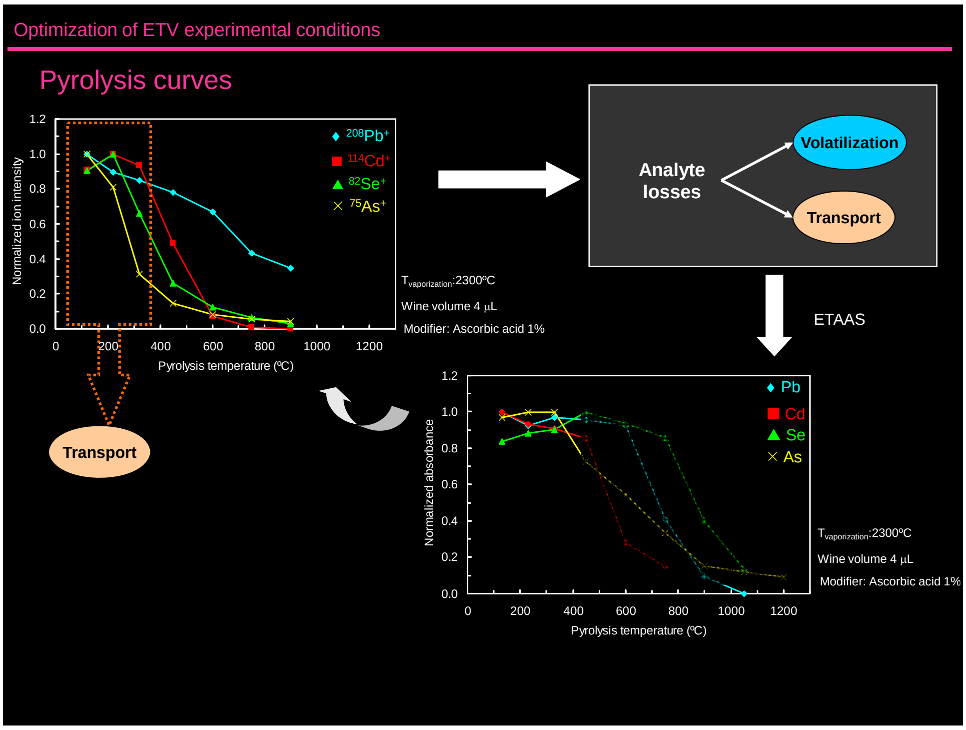
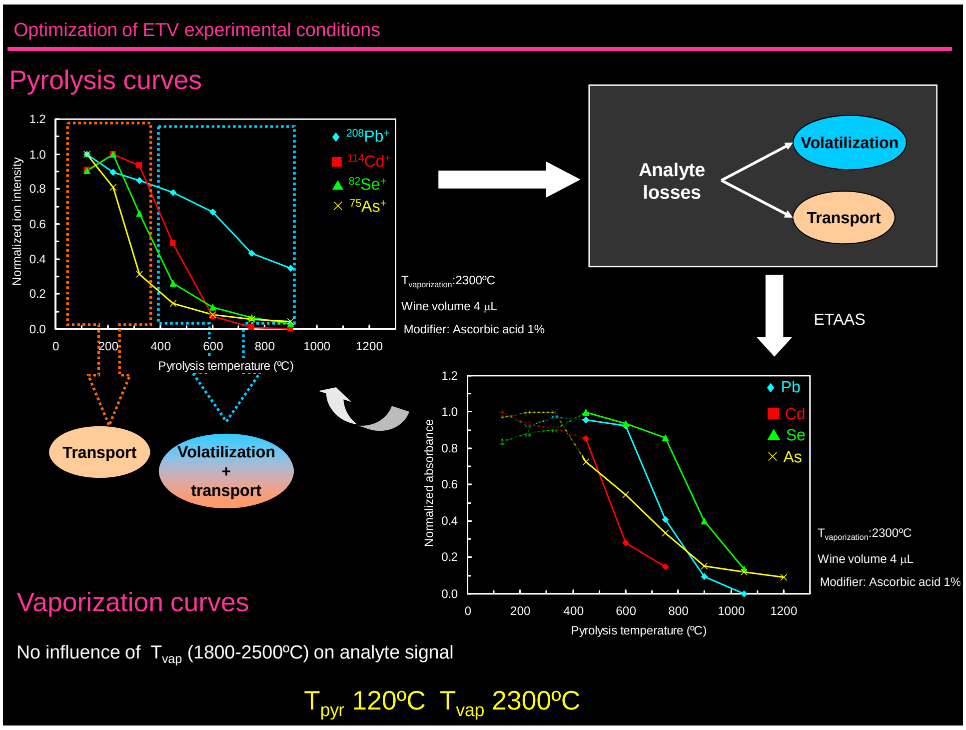


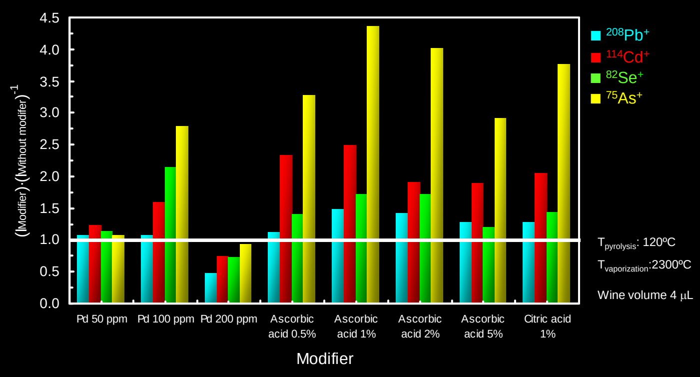
Optimum wine volume 4 μL


Optimization of ETV experimental conditions
Pyrolysis curves
208Pb+
114Cd+
82Se+
75As+
Normalized ion intensity
Pyrolysis temperature (ºC)
Tvaporization:2300ºC
Wine volume 4 µL
Modifier: Ascorbic acid 1%
Transport
Analyte losses
Volatilization
Transport
ETAAS
Pb
Cd
Se
As
Normalized absorbance
Pyrolysis temperature (ºC)
Tvaporization:2300ºC
Wine volume 4 µL
Modifier: Ascorbic acid 1%


Optimization of ETV experimental conditions
Pyrolysis curves
208Pb+
114Cd+
82Se+
75As+
Normalized ion intensity
Pyrolysis temperature (ºC)
Tvaporization:2300ºC
Wine volume 4 µL
Modifier: Ascorbic acid 1%
Transport
Volatilization + transport
Analyte losses
Volatilization
Transport
ETAAS
Pb
Cd
Se
As
Normalized absorbance
Pyrolysis temperature (ºC)
Tvaporization:2300ºC
Wine volume 4 µL
Modifier: Ascorbic acid 1%
Vaporization curves
No influence of Tvap (1800-2500ºC) on analyte signal
Tpyr 120ºC Tvap 2300ºC

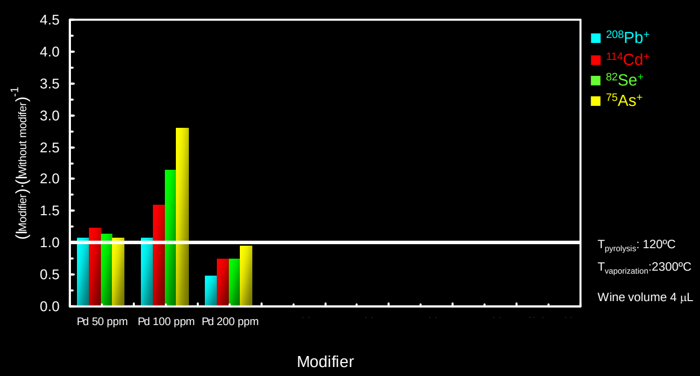
Optimization of ETV experimental conditions

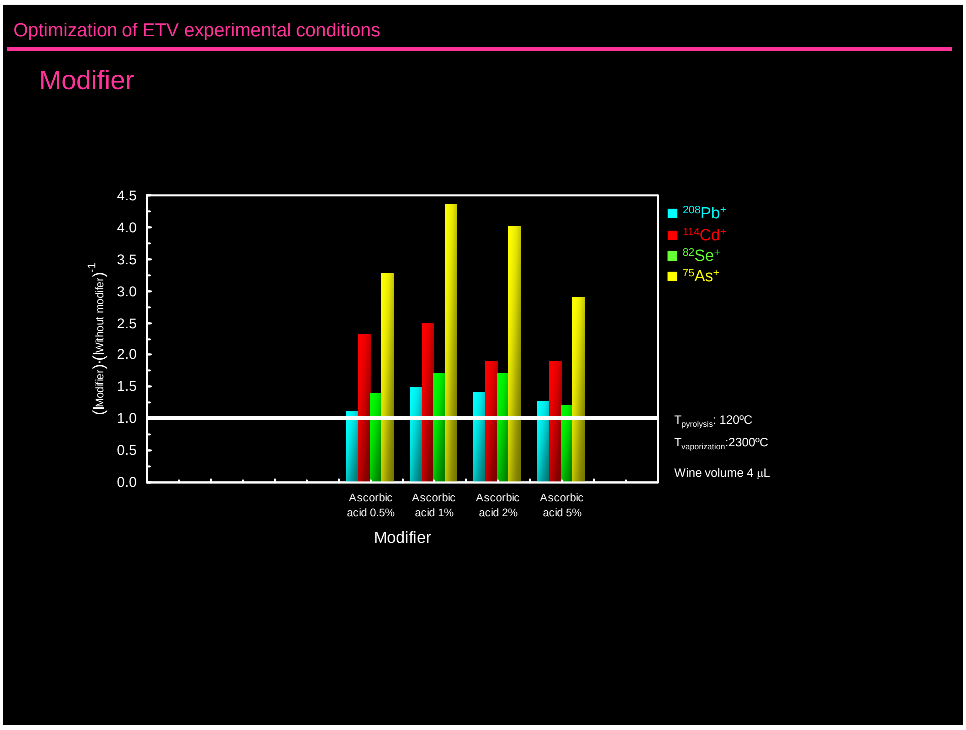
Modifier

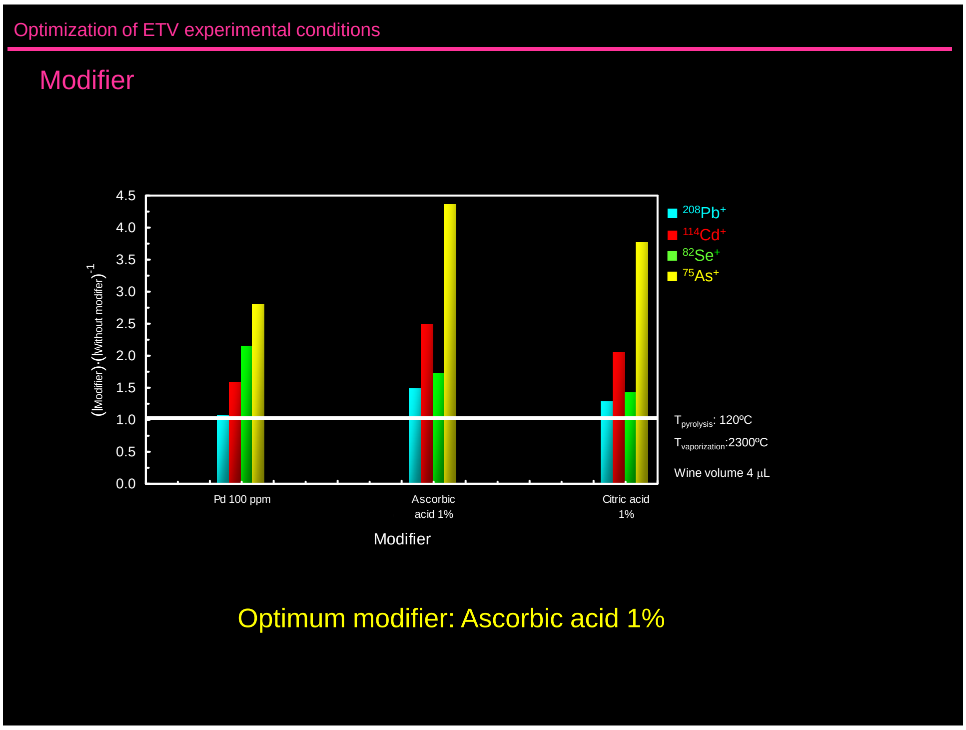


Optimization of ETV experimental conditions

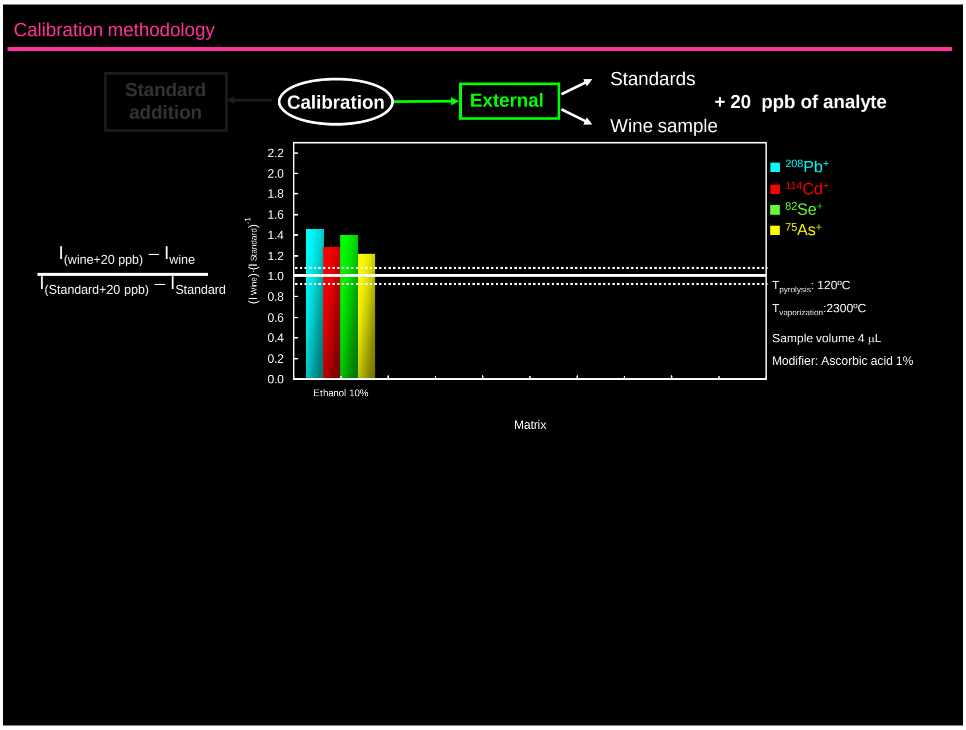
Modifier

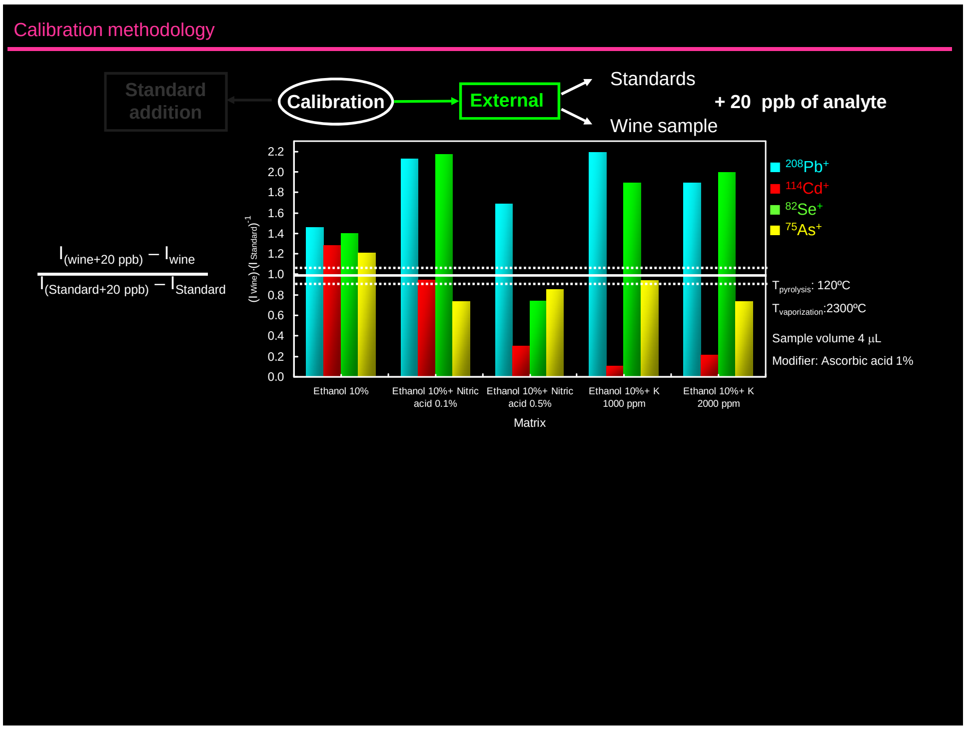


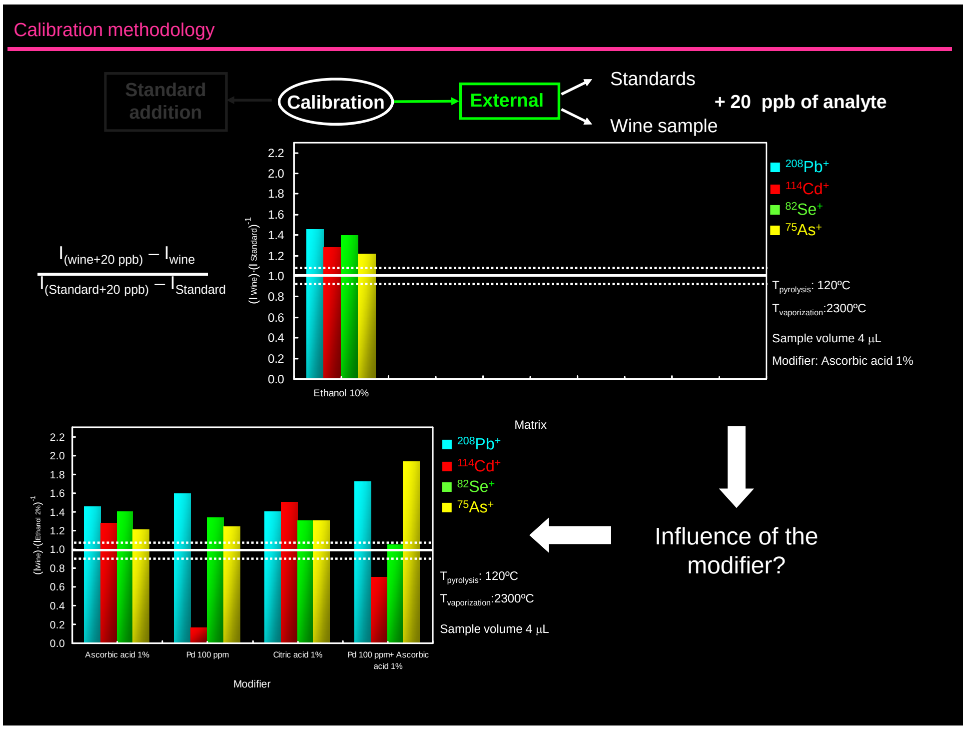

Optimization of ETV experimental conditions
Modifier
(IModifier)·(IWithout modifier)-1
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
208Pb+
114Cd+
82Se+
75As+
Tpyrolysis: 120ºC
Tvaporization:2300ºC
Wine volume 4 µL
Ascorbic acid 0.5%
Ascorbic acid 1%
Ascorbic acid 2%
Ascorbic acid 5%
Modifier

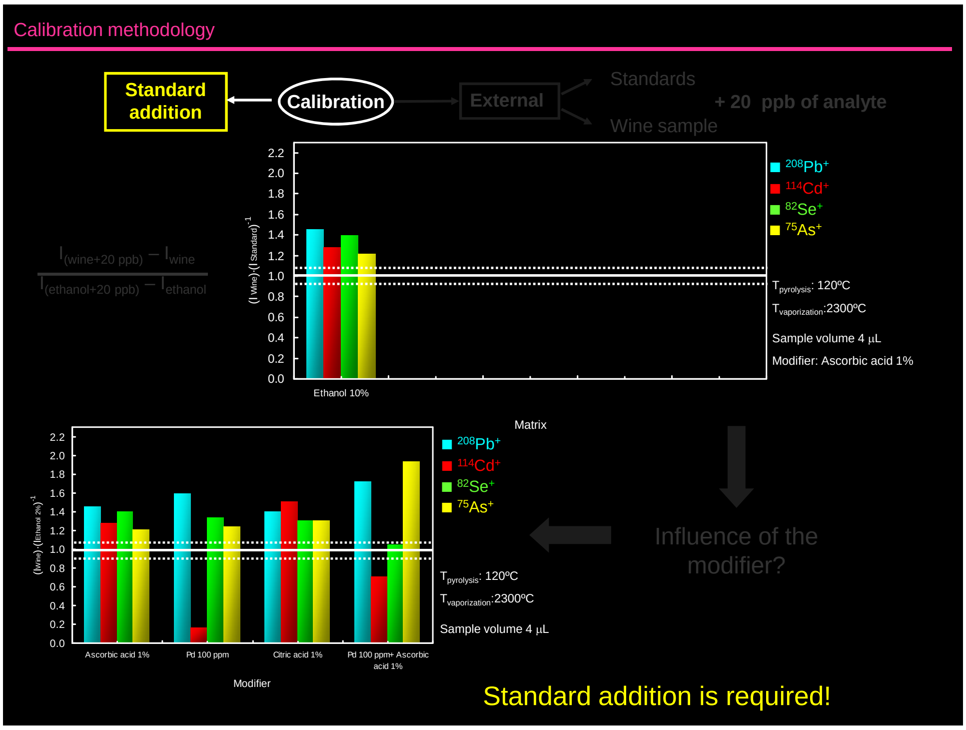

Optimization of ETV experimental conditions
Modifier
(IModifier)·(IWithout modifier)-1
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
208Pb+
114Cd+
82Se+
75As+
Tpyrolysis: 120ºC
Tvaporization:2300ºC
Wine volume 4 µL
Pd 100 ppm
Ascorbic acid 1%
Citric acid 1%
Modifier
Optimum modifier: Ascorbic acid 1%

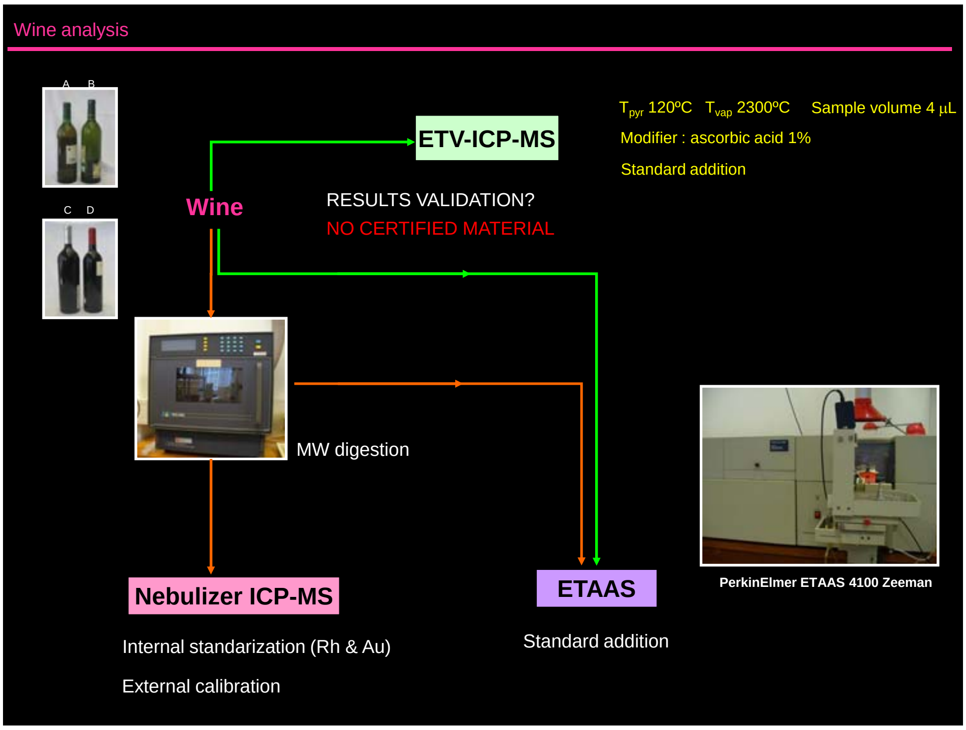

Calibration methodology
Standard addition
Calibration
External


Calibration methodology
Standard addition
Calibration
External
Standards
+ 20 ppb of analyte
Wine sample
I(wine+20 ppb) − Iwine
I(Standard+20 ppb) − IStandard
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Ethanol 10%
Matrix
208Pb+
114Cd+
82Se+
75As+
Tpyrolysis: 120ºC
Tvaporization:2300ºC
Sample volume 4 µL
Modifier: Ascorbic acid 1%


Calibration methodology
Standard addition
Calibration
External
Standards
+ 20 ppb of analyte
Wine sample
I(wine+20 ppb) − Iwine
I(Standard+20 ppb) − IStandard
208Pb+
114Cd+
82Se+
75As+
Tpyrolysis: 120ºC
Tvaporization:2300ºC
Sample volume 4 µL
Modifier: Ascorbic acid 1%
Ethanol 10%
Ethanol 10%+ Nitric acid 0.1%
Ethanol 10%+ Nitric acid 0.5%
Ethanol 10%+ K 1000 ppm
Ethanol 10%+ K 2000 ppm
Matrix


Calibration methodology
Standard addition
Calibration
External
Standards
+ 20 ppb of analyte
Wine sample
I(wine+20 ppb) − Iwine
I(Standard+20 ppb) − IStandard
208Pb+
114Cd+
82Se+
75As+
Tpyrolysis: 120ºC
Tvaporization:2300ºC
Sample volume 4 µL
Modifier: Ascorbic acid 1%
Ethanol 10%
Matrix
Ascorbic acid 1%
Pd 100 ppm
Citric acid 1%
Pd 100 ppm+ Ascorbic acid 1%
Modifier
Influence of the modifier?


Calibration methodology
Standard addition
Calibration
External
Standards
+ 20 ppb of analyte
Wine sample
I(wine+20 ppb) − Iwine
I(ethanol+20 ppb) − Iethanol
(I Wine)·(I Standard)-1
208Pb+
114Cd+
82Se+
75As+
Tpyrolysis: 120ºC
Tvaporization:2300ºC
Sample volume 4 µL
Modifier: Ascorbic acid 1%
Ethanol 10%
Matrix
(Iwine)·(Iethanol 2%)-1
Ascorbic acid 1%
Pd 100 ppm
Citric acid 1%
Pd 100 ppm+ Ascorbic acid 1%
Modifier
Influence of the modifier?
Standard addition is required!


Wine analysis
A B
C D
ETV-ICP-MS
Wine
RESULTS VALIDATION?
NO CERTIFIED MATERIAL
Tpyr 120ºC Tvap 2300ºC Sample volume 4 µL
Modifier : ascorbic acid 1%
Standard addition
MW digestion
PerkinElmer ETAAS 4100 Zeeman
Nebulizer ICP-MS
ETAAS
Internal standarization (Rh & Au)
External calibration
Standard addition

Wine analysis

Pb Cd Se As

Technique	Sample introduction system	Sample preparation	Concentration (μg L-1)			
			A	B	C	D
ICP-MS	Nebulizer	Wine digestion$	10.0±0.4	7.9±0.4	15.1±0.7	8.9±0.6
	ETV	Untreated wine	8.5±0.8	7.4±0.7	13±2	7.7±0.6

$ Internal standard Rh

P (3, 0.95)

Wine analysis

Pb Cd Se As

Technique	Sample introduction system	Sample preparation	Concentration (μg L-1)			
			A	B	C	D
ICP-MS	Nebulizer	Wine digestion$	10.0±0.4	7.9±0.4	15.1±0.7	8.9±0.6
	ETV	Untreated wine	8.5±0.8	7.4±0.7	13±2	7.7±0.6
ETAAS	—	Wine digestion	9.4±0.7	9.0±0.6	14±2	9.5±0.7
	—	Untreated wine	11±3	9±3	16±2	10±3

$ Internal standard Rh

P (3, 0.95)

Wine analysis

Pb **Cd** Se As

Technique	Sample introduction system	Sample preparation	Concentration (µg L^{-1})			
			A	B	C	D
ICP-MS	Nebulizer	Wine digestion	—	—	—	—
	ETV	Untreated wine	—	—	—	—
ETAAS	—	Wine digestion	0.39±0.05	0.47±0.06	0.59±0.07	0.42±0.06
	—	Untreated wine	0.29±0.06	0.30±0.07	0.49±0.08	0.32±0.06

P (3, 0.95)

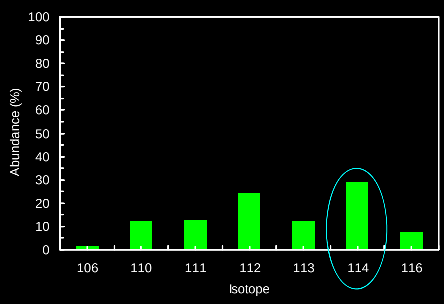
Wine analysis

Pb **Cd** Se As

Technique	Sample introduction system	Sample preparation	Concentration (µg L^{-1})			
			A	B	C	D
ICP-MS	Nebulizer	Wine digestion	—	—	—	—
	ETV	Untreated wine	—	—	—	—

Origin

- Low isotope abundance
- High ionization potencial (9 eV)



Wine analysis

Pb Cd **Se** As

Technique	Sample introduction system	Sample preparation	Concentration (μg L^{-1})			
			A	B	C	D
ICP-MS	Nebulizer	Wine digestion$	2.8±0.4	2.3±0.3	3.2±0.5	3.5±0.3
	ETV	Untreated wine	1.9±0.3	1.7±0.4	2.7±0.5	2.5±0.5
ETAAS	—	Wine digestion	—	—	—	—
	—	Untreated wine	—	—	—	—

$ Internal standard Au

P (3, 0.95)

Wine analysis

Pb Cd Se **As**

Technique	Sample introduction system	Sample preparation	Concentration (μg L^{-1})			
			A	B	C	D
ICP-MS	Nebulizer	Wine digestion$	8.7±0.2	7.5±0.5	9.5±0.4	6.3±0.3
	ETV	Untreated wine	3.4±0.5	2.5±0.3	2.6±0.6	3.8±0.4
ETAAS	—	Wine digestion	—	—	—	—
	—	Untreated wine	—	—	—	—

$ Internal standard Au

P (3, 0.95)

Error sources

1.- Reagents contamination <0.3 μg L^{-1}

Wine analysis

Pb Cd Se **As**

Technique	Sample introduction system	Sample preparation	Concentration (μg L^{-1})			
			A	B	C	D
ICP-MS	Nebulizer	Wine digestion$	8.7±0.2	7.5±0.5	9.5±0.4	6.3±0.3
	ETV	Untreated wine	3.4±0.5	2.5±0.3	2.6±0.6	3.8±0.4
ETAAS	—	Wine digestion	—	—	—	—
	—	Untreated wine	—	—	—	—

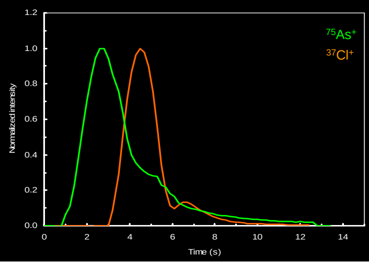
$ Internal standard Au

P (3, 0.95)

Error sources

1.- Reagents contamination <0.3 μg L^{-1}

2.- Isobaric $ArCl^+$ interference



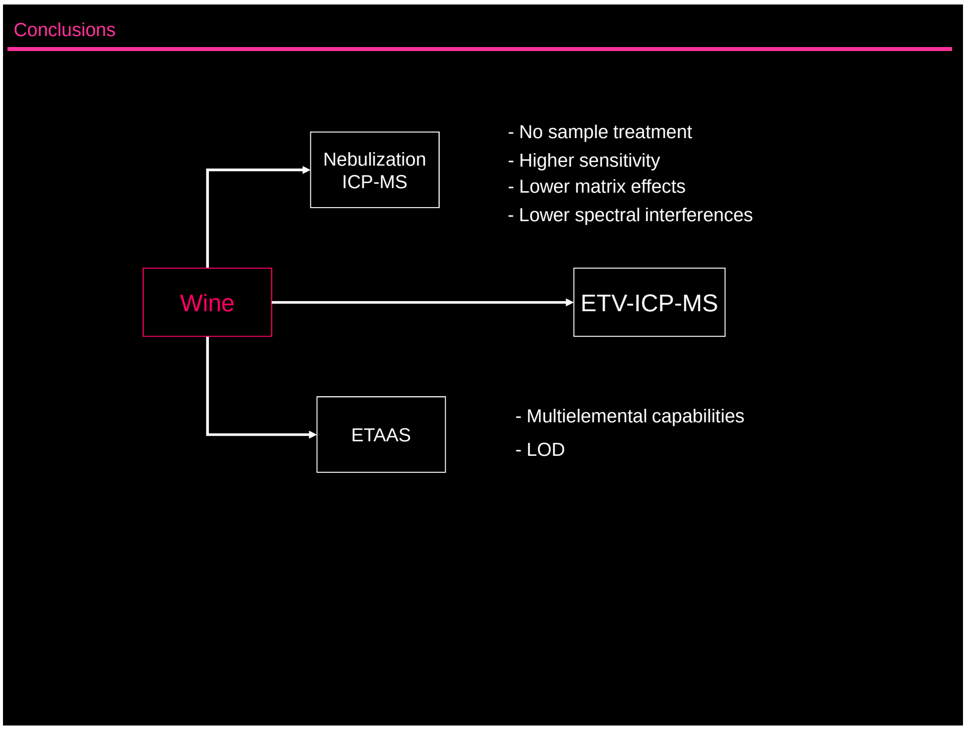
$T_{pyrolysis}$: 120ºC

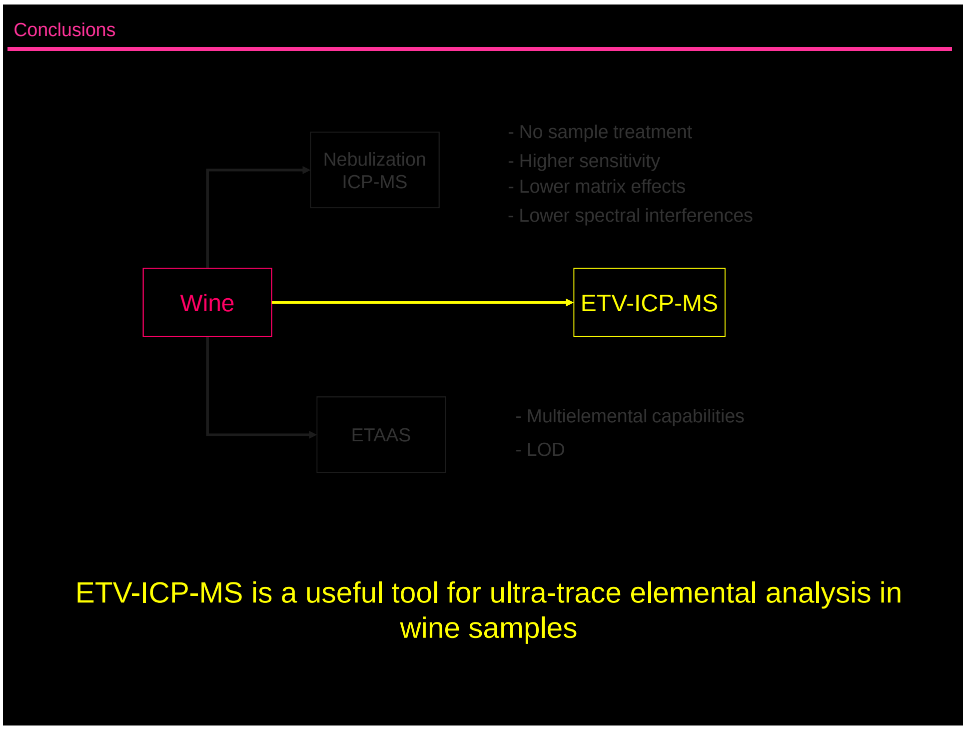
$T_{vaporization}$: 2300ºC

Wine amount 4 μL

Modifier: Ascorbic acid 1%

Conclusions


Conclusions
Nebulization ICP-MS
- No sample treatment
- Higher sensitivity
- Lower matrix effects
- Lower spectral interferences
Wine
ETV-ICP-MS
ETAAS
- Multielemental capabilities
- LOD


Conclusions
Nebulization ICP-MS
- No sample treatment
- Higher sensitivity
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Wine
ETV-ICP-MS
ETAAS
- Multielemental capabilities
- LOD
ETV-ICP-MS is a useful tool for ultra-trace elemental analysis in wine samples

ACKNOWLEDGMENTS

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