Evaluation of sample preparation methods for elemental profiling of wine by ICP-MS: comparison of direct dilution, microwave digestion, and filtration

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Introduction

Wine elemental composition is known to vary with respect to origin, grape variety, environment, and winemaking practices. Elemental analysis of wines is usually performed employing inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS analysis of wine is challenging as the variable level of organic matrix components requires special operating conditions and matrix-matching. Additionally, organic matrix components and suspended particulates can build up in the sample introduction system. Sample preparation prior to analysis offers the opportunity to eliminate or minimize these interferences. However, the absence of a universal pretreatment for wine ICP-MS analysis has contributed to conflicting recommendations of best practices.

Purpose

To compare sample preparation methods in the elemental analysis of wine by ICP-MS:

- Direct analysis after dilution (DD)
- Acidification prior to filtration (AF)
- Filtration prior to acidification (FA)
- Microwave assisted acid digestion (MW)

Experimental

Experimental Design

- Samples: prepared in triplicate by each method
  - Unfiltered nor fined wine samples of Chardonnay (C), Pinot Noir (PN), Syrah (S), and Tempranillo (T) with 12-15% ethanol content (UC-Davis winery)
  - Method blanks (BL) were a 12% ethanol solution prepared via all four methods
  - All wines were centrifuged at 4°C and 5000 x g for 10 minutes prior to preparation to reduce suspended particulates in unrefined wine samples
- Calibration
  - 43 isotopes were quantified via a 6 point external calibration ranging from 0.1 to 500 µg/L
  - Cu in wine was also quantified using isotope dilution after spiking with 100 µg/L ^{65}Cu
- Spikes
  - 100 µg/L ^{65}Cu and 5 µg/L ^{206}Pb stable isotope standards were chosen to represent typical wine levels
- Quality Control
  - Instrument performance was continuously monitored using an internal standard (ISTD) mix containing 1 µg/L ^{6}Li, ^{45}Sc, ^{72}Ge, ^{89}Y, ^{115}In, ^{159}Tb, ^{209}Bi in 1% HNO_3
  - Repeat analysis of 10 µg/L calibration standards of each calibration series approximately every 15 samples accurate and precise within 20% of value and <20% RSD per analytical run
- Statistical Analysis ($P \leq 0.05$)
  - Analysis of Variance (ANOVA)
  - Multivariate Analysis of Variance (MANOVA)
  - Principal Component Analysis (PCA)
  - Tukey's Honestly Significant Differences (HSD)

Instrumental Parameters

Agilent Technologies 8800x ICP-MS

Parameter	Value
RF power:	1550 W
RF matching:	1.8 V
Nebulizer pump speed:	0.1 rps
Replicates:	3
Sweeps per replicate:	100
Carrier Gas (Ar):	1.05 L/min
Collision Gas (He):	5 mL/min (He mode) 10 mL/min (HEHe mode)

Table 1. ICP-MS operating conditions

Experimental

Direct Dilution (DD)	Acidification Prior to Filtration (AF)	Filtration prior to Acidification (FA)	Microwave Digestion (MW)
Samples diluted 1:3 with 5% HNO_3 (v/v)	Samples diluted 1:3 with 5% HNO_3 (v/v)	Sample filtered using Agilent Captiva Premium syringe filter (PTFE, 15 mm, 0.45 µm)	2 x 1mL concentrated HNO_3 added to 2 mL sample in PTFE microwave tube
	Diluted sample filtered using Agilent Captiva Premium syringe filter (PTFE, 15 mm, 0.45 µm)	Filtered samples diluted 1:3 with 5% HNO_3 (v/v)	Capped sample tubes digested using Milestone UltraWAVE according to manufacturer's recommendations (**Table 2**)
			2mL aliquot of digested sample diluted 1:5 with Ultrapure water

Milestone UltraWAVE

Parameter	Value
Power:	1500 W
Pressure:	150 bar
Temperature:	240°C
Temperature ramp time:	20 minutes
Hold time:	10 minutes

Table 2. Milestone UltrWAVE microwave digestion settings.

Results and Discussion

Limits of Detection (LOD) and Method Blank Concentrations

		Instrumental LOD (µg/L)		Mean Method Blank Concentrations (µg/L)			
Isotope	**Mode**	**AF-FA-DD**	**MW**	**AF**	**DD**	**FA**	**MW**
^{7}Li	NG	0.096	0.030	1.23	1.77	1.50	0.962
^{27}Al	He	0.748	1.035	<LOD	1.84	<LOD	13.72
^{47}Ti	He	0.220	0.182	0.611	<LOD	<LOD	2.27
^{51}V	He	0.009	0.009	0.013	0.020	0.015	0.029
^{52}Cr	He	0.205	0.052	<LOD	1.04	<LOD	5.07
^{55}Mn	He	0.063	0.042	<LOD	0.772	<LOD	20.08
^{59}Co	He	0.004	0.003	<LOD	0.026	<LOD	1.36
^{60}Ni	He	0.080	0.044	<LOD	0.600	<LOD	5.22
^{63}Cu	He	0.046	0.044	<LOD	<LOD	<LOD	0.248
^{65}Cu	He	0.017	0.011	<LOD	<LOD	<LOD	0.045
^{66}Zn	He	0.261	0.192	<LOD	<LOD	<LOD	1.16
^{71}Ga	He	0.004	0.004	0.007	0.006	0.010	<LOD
^{75}As	HEHe	0.012	0.012	0.056	0.154	0.116	0.106
^{78}Se	HEHe	0.074	0.019	<LOD	<LOD	<LOD	0.280
^{85}Rb	He	0.040	0.068	0.467	0.558	0.279	0.130
^{88}Sr	He	0.019	0.021	0.065	<LOD	<LOD	0.050
^{93}Nb	He	0.007	0.007	<LOD	0.018	<LOD	0.525
^{98}Mo	NG	0.070	0.018	<LOD	0.072	0.099	1.95
^{101}Ru	He	0.008	0.010	0.009	<LOD	<LOD	<LOD
^{103}Rh	He	0.002	0.001	<LOD	<LOD	<LOD	0.034
^{107}Ag	He	0.014	0.002	<LOD	<LOD	<LOD	0.138
^{111}Cd	He	0.007	0.009	0.040	<LOD	0.040	<LOD
^{123}Sb	He	0.040	0.013	<LOD	0.060	<LOD	0.732
^{125}Te	NG	0.003	0.003	<LOD	0.007	0.004	0.005
^{133}Cs	He	0.017	0.015	0.029	0.033	0.074	0.033
^{137}Ba	He	0.038	0.043	<LOD	<LOD	<LOD	0.124
^{140}Ce	He	0.002	0.004	0.003	0.002	<LOD	<LOD
^{141}Pr	He	0.000	0.003	<LOD	0.003	<LOD	<LOD
^{146}Nd	He	0.002	0.003	0.005	0.002	0.002	<LOD
^{147}Sm	He	0.002	0.002	0.002	0.004	<LOD	<LOD
^{153}Eu	He	0.000	0.003	<LOD	0.001	<LOD	<LOD
^{157}Gd	He	0.001	0.004	<LOD	0.004	<LOD	<LOD
^{163}Dy	He	0.001	0.005	<LOD	<LOD	<LOD	<LOD
^{165}Ho	He	0.000	0.003	0.001	0.000	<LOD	<LOD
^{166}Er	He	0.001	0.003	<LOD	0.003	<LOD	<LOD
^{169}Tm	He	0.001	0.002	<LOD	0.001	<LOD	<LOD
^{172}Yb	He	0.001	0.003	0.008	0.004	0.005	0.005
^{181}Ta	He	0.020	0.035	<LOD	0.032	<LOD	1.94
^{182}W	He	0.109	0.013	<LOD	0.189	0.122	1.27
^{205}Tl	He	0.002	0.003	0.005	0.007	0.008	<LOD
^{206}Pb	He	0.009	0.003	<LOD	0.140	<LOD	0.030
^{208}Pb	He	0.006	0.004	0.017	0.130	<LOD	0.043
^{238}U	He	0.004	0.001	0.009	<LOD	0.009	<LOD

Table 3. Limits of detection (LOD) and average method blank (n=3) concentration of 43 isotopes monitored by ICP-MS without a collision gas (NG), in helium mode (He), and high energy helium mode (HEHe). Limits of detection are expressed as 3.14 times the standard deviation (n=6 for direct methods or n=8 for MW) of matrix matched calibration blanks per analytical run. LODs for direct methods shown are the average of two analytical runs.

Results and Discussion

Principal Component Analysis

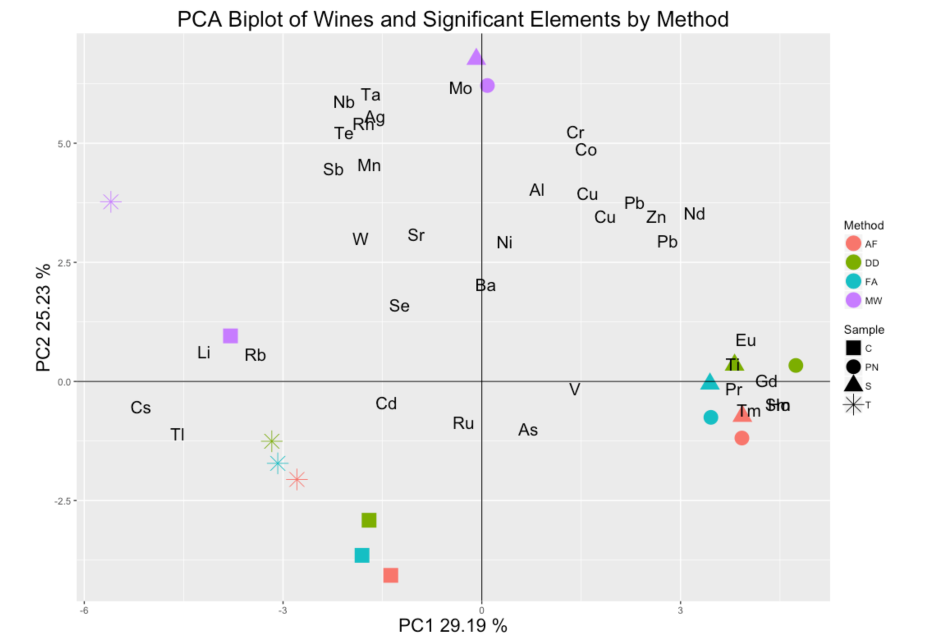


Figure 1. PCA biplot of scores of wine means and loadings of significant elements by ANOVA in first two principal components (54.42 % total variance).

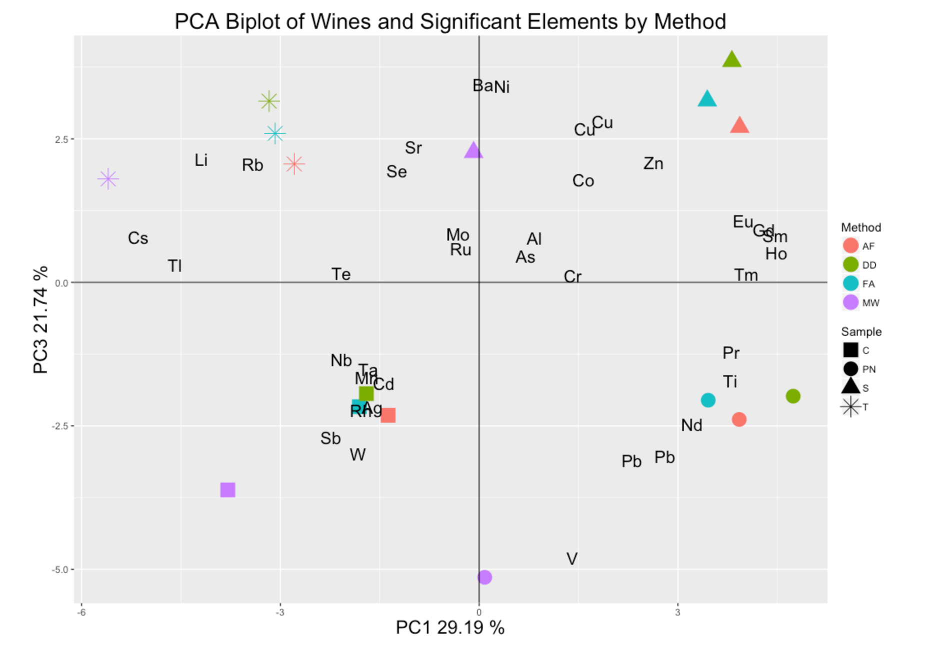


Figure 2. PCA biplot of scores of wine means and loadings of significant elements by ANOVA in first and third dimensions (54.42 % total variance).

Spike Recovery

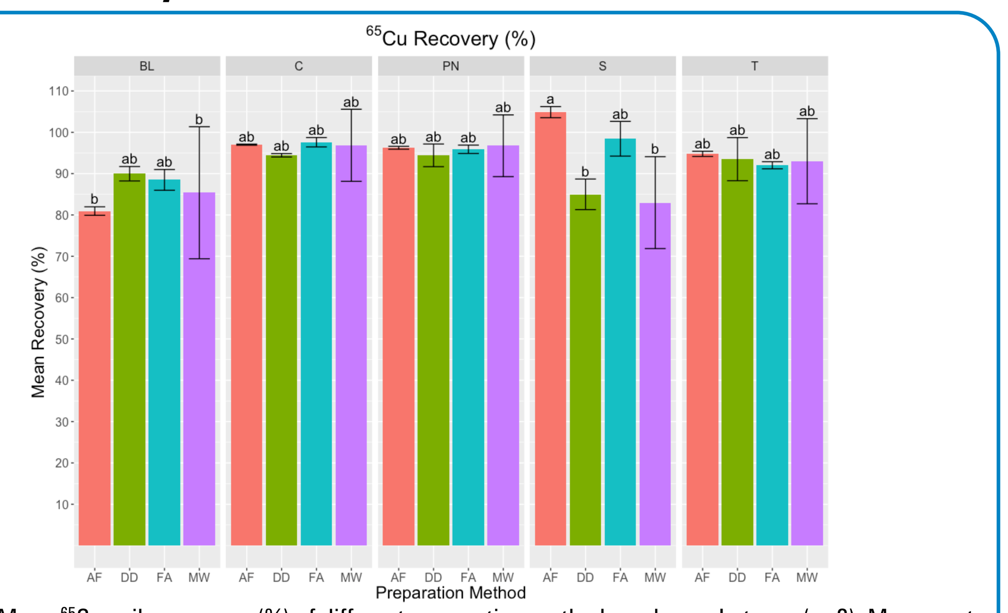


Figure 3. Mean ^{65}Cu spike recovery (%) of different preparation methods and sample types (n=3). Means not sharing a letter are statistically significantly different by Tukey's HSD.

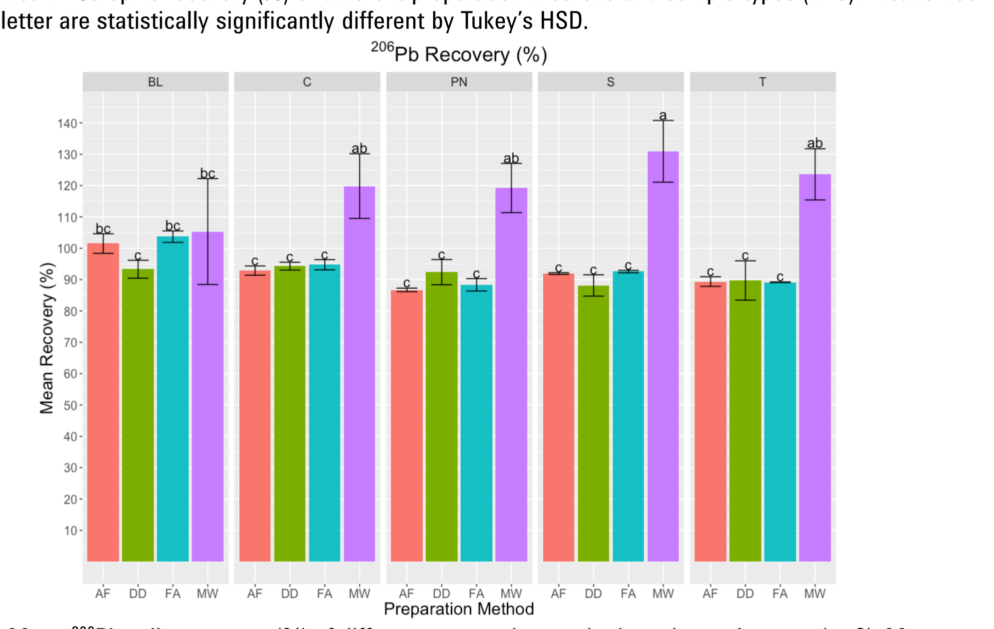
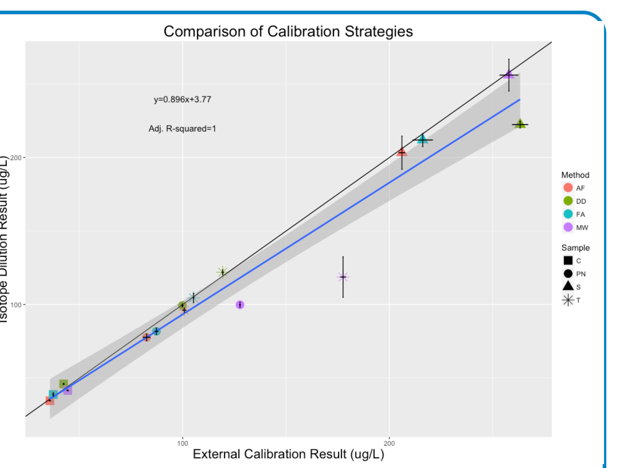


Figure 4. Mean ^{206}Pb spike recovery (%) of different preparation methods and sample types (n=3). Means not sharing a letter are statistically significantly different by Tukey's HSD.

Cu Isotope Dilution

Figure 5. Comparison of isotope dilution and external calibration results for ^{63}Cu shown averaged by sample and method. Black line represents identical results (slope=1), blue line is the best fit linear approximation of the data.



$$[^{63}Cu] = [^{65}Cu_{Spike}]x\left(\frac{m_{spike}}{m_{sample}}\right)x\left(\frac{W_{spike}}{W_{sample}}\right)x\left(\frac{R\times A_{65}-A_{63}}{B_{63}-R\times B_{65}}\right)$$

- **R**: instrument response ratio of ^{63}Cu:^{65}Cu
- **m_{spike}**: mass of spike solution added to sample
- **m_{sample}**: mass of sample
- **W_{spike}**: atomic weight of Cu in spike
- **W_{sample}**: atomic weight of Cu in sample
- **A_{63} and A_{65}**: abundances of ^{63}Cu and ^{65}Cu in spike solution
- **B_{63} and B_{65}**: natural abundances of ^{63}Cu and ^{65}Cu in sample

Conclusions

- Significant effect of preparation method observed
  - 37 isotopes in wine significantly differed by method
- MW is most variable preparation treatment in wine analysis and significantly differed from all other methods for 21 isotopes measured when averaged over the wines
  - Number of steps present risk for contamination
- Statistical significance may not mean scientific significance
  - All methods tested adequately separated the different wine samples (Figure 2), although extreme care must be taken if using MW for absolute quantitation