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Elemental Analysis of Wines from Various Regions Around the World - prep*FAST* IC

Introduction

Wine is a popular beverage of choice throughout the world and can range in quality, cost, taste, and flavor. The perception of wine quality is generally characterized by the overall score received from a wine critic or the popularity among consumers. However, analytical testing is an important aspect for determining the quality of the wine from the perspective of food safety. The testing can be broken into a few categories: molecular or organic content and elemental or inorganic content. The elemental content can affect various properties of wine; some inorganics (e.g. S, P, Fe, Mg, or Ca) can affect the flavor, color, aroma, and rate of precipitation, whereas elements such as As, Cd, Hg, and Pb are considered toxic and pose great risk for the consumer.

The most common method for elemental analysis is inductively coupled plasma-optical emission spectroscopy or -mass spectrometry (ICP or ICPMS). ICPMS is normally the preferred choice of instruments since it offers superior detection limits. For certain elements (e.g. As) detecting the total amount in the wine does not provide all relevant information when trying to assess levels of toxic species present. For example, arsenic has various forms that exist as both organic and inorganic species. Inorganic arsenic (As III or As V) is more bioavailable, thus is more dangerous as compared to organic arsenic species (AsB, AsC, DMA, or MMA).

This work will present an automated method for measuring total elemental content and elemental speciation in wine using a single sample introduction platform (prep*FAST* IC, Elemental Scientific, Inc.) in combination with an ICP-MS. The total elemental measurements will include both essential and toxic elements in the panel. Various types of wine (red, white, sweet, and port) from France, United States, Chile, Italy, Australia, South Africa, Spain, Portugal, and Argentina were included in this study (Table 1).

Table 1. List of wines analyzed in this study based on wine type and region of the world.

	Sweet	White	Red	Other
USA	Moscato	Pinot Grigio	Merlot	
Italy	Moscato, Stella Peach	Pinot Grigio	Toscano	
Australia		Pinot Grigio	Shiraz	
Argentina	Torrontes-Sweet	Torrontes	Cabernet Sauvignon, Malbec	
Chile			Carmenere	Rosé
South Africa			Cabernet Sauvignon	
France	Sauternes	White Burgundy	Red Bordeaux	
Spain		Macabeo	Tempranillo	
Portugal		Vinho Verde		Late Vintage, 10 year Tawny

Instrumentation

A NexION 2000 ICPMS in combination with the prep*FAST* IC was used for the analysis of wine from various regions around the world. The elements and species measured for each method can be found in Table 2. Undiluted wine samples were vacuum loaded (syringe loading can also be used) into a 500 µL loop (sample loop) followed by subsequent dilution into a second 500 µL loop (dilution loop). In total metals mode the sample is introduced directly to the ICPMS by bypassing the column, whereas in speciation mode, the sample is injected onto the column prior to introduction to the ICPMS. The total metals method utilized 2% HNO_3 as the carrier and diluent, internal standards (Rh and Ir) were spiked into the sample during the dilution step, and wine samples were analyzed using a 10X dilution factor. The arsenic speciation method utilizes ammonium carbonate as the eluent and wine samples were analyzed using a 10X dilution factor.

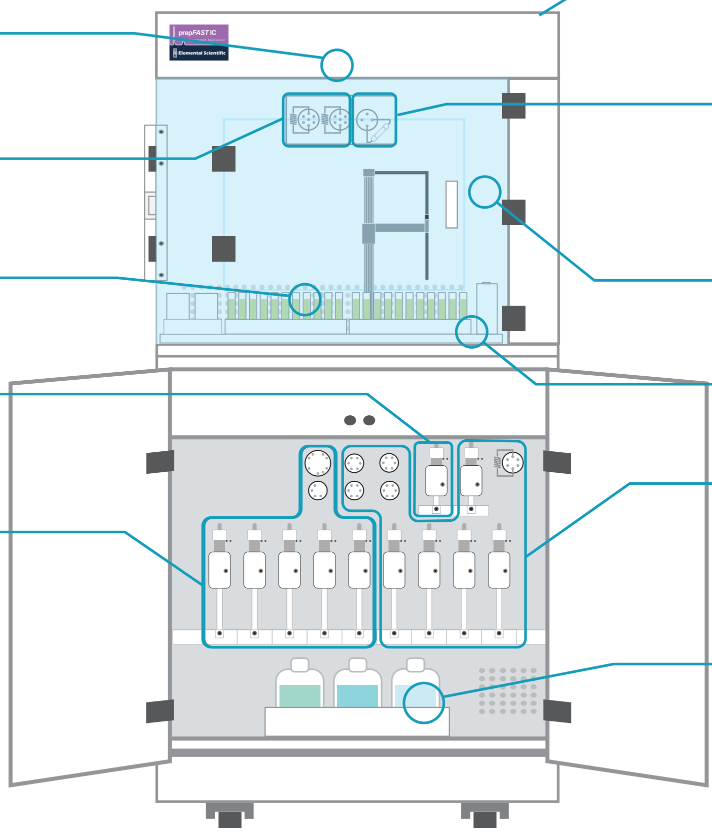

Figure 1. prep*FAST* IC features diagram.

Table 2. Elements included in each method.

	Elements Included
Total Metals	Na, Mg, Si, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Sn, Sb, Cs, Ba, Tl, Pb, and U
Arsenic Speciation	Arsenobetaine (AsB), Arsenite (As III), Dimethylarsinic Acid (DMA), Arsenocholine (AsC), Monomethylarsonic Acid (MMA), and Arsenate (As V)

Results

Total Metals

The total metals method for wine measured for 20 elements per sample, all in KED mode. All elements were measured in KED mode to simplify and speed up the overall time of the ICPMS measurement. Figure 2a and 2b displays typical calibration curves for Cu, As, and Pb. The calibration curves showed good linearity across all elements analyzed. Mn, Fe, Cu, Zn, As, Cs, Ba, and Pb had the most variation from sample-to-sample, whereas the other elements had a more consistent trend in the measured value across the different types of wine. Na, Mg, Si, Mn, Fe, and Zn were measured in the mg/L (ppm) range for these 24 wine samples. All other elements were detected in the µg/L (ppb) range. Arsenic was detected in all wine samples and ranged from 2.1 - 56 µg/L. Chromium was detected in all but two wine samples (both ports) and ranged from 2.0 - 59 µg/L.

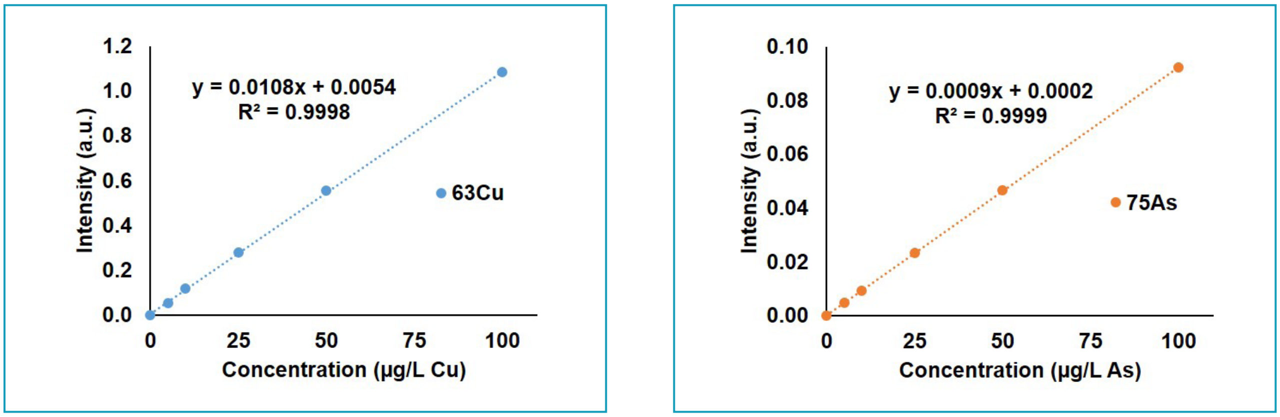

Figure 2a. Typical calibration curves from the total metals method for Cu and As.

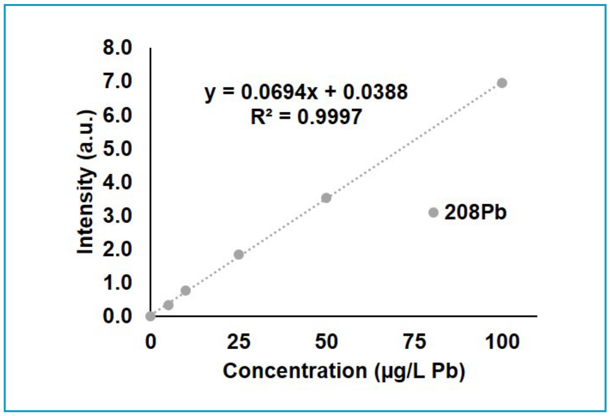

Figure 2b. Typical calibration curve from the total metals method for Pb.

Table 3. Total metals results for the 24 wine samples analyzed in direct mode using the prep*FAST* IC.

		^{23}Na	^{24}Mg	^{28}Si	^{52}Cr	^{55}Mn	^{57}Fe	^{59}Co	^{60}Ni	^{63}Cu	^{66}Zn	^{75}As	^{98}Mo	^{114}Cd	^{118}Sn	^{121}Sb	^{133}Cs	^{138}Ba	^{205}Tl	^{208}Pb	^{238}U
Country	**Wine Type**	**mg/L**			**µg/L**																
France	White Bourgogne	15	35	62	30	678	578	2.9	16	64	669	7.9	1.6	0.38	1.8	0.51	6.9	48	0.60	9.9	0.33
France	Red Bordeaux	15	40	65	30	1589	3411	4.1	33	113	1010	12	5.8	0.32	1.9	0.35	2.4	182	0.11	16.9	0.08
France	Sauternes	34	47	70	22	1838	591	3.9	21	85	915	12	7.2	0.31	2.6	1.1	1.7	231	0.36	22.5	0.27
USA	Merlot	14	57	92	34	2046	3040	6.4	30	218	1274	15	3.7	1.5	6.4	2.1	9.9	336	1.27	4.2	1.1
USA	Pinot Grigio	33	38	66	59	1210	1658	3.4	25	154	846	56	25	0.77	12	2.5	4.4	94	0.38	14.6	2.7
USA	Moscato	25	40	40	12	1034	527	3.5	16	122	918	7.3	4.2	0.85	4.7	0.34	4.0	119	0.23	8.7	0.21
Chile	Rosé	19	47	61	42	1184	965	4.0	15	5.9	1192	40	15	0.29	4.9	0.73	11	55	0.11	4.3	0.12
Chile	Carmenere	15	50	67	30	1376	2498	3.2	12	174	784	11	1.1	0.19	1.2	0.12	16	135	0.14	4.6	0.07
Italy	Toscana	16	54	67	30	1671	2595	4.3	32	117	833	4.4	1.2	0.17	1.0	0.16	106	175	0.81	8.9	0.01
Italy	Stella Peach	16	34	31	2	308	945	1.0	4.9	292	*	4.8	2.6	0.20	3.5	0.31	0.9	39	0.09	5.1	0.11
Italy	Moscato	23	49	22	7	489	256	1.2	12	82	201	2.1	1.1	0.34	19	0.23	4.2	34	0.21	2.6	0.13
Italy	Pinot Grigio	27	52	61	32	751	1002	1.2	14	95	319	6.5	2.1	0.10	2.7	0.36	1.5	111	0.07	4.9	0.16
Australia	Shiraz	52	73	71	27	1505	1334	4.1	11	69	831	5.2	3.1	0.21	1.4	0.05	0.9	176	0.09	2.2	0.01
Australia	Pinot Grigio	20	39	56	21	1544	340	4.4	13	36	881	5.1	5.4	0.20	5.9	0.19	1.3	101	0.09	7.7	0.18
South Africa	Cabernet Sauvignon	28	73	71	25	2178	3386	2.6	12	36	546	6.6	1.9	0.05	2.0	0.18	10	295	0.68	5.9	0.16
Spain	Viura	20	37	61	28	469	555	1.9	7.9	57	283	6.1	0.7	0.16	2.7	0.22	2.6	46	0.15	5.4	0.19
Spain	Crianza	30	54	64	31	566	1095	1.9	10	31	676	4.8	1.7	0.07	0.4	0.09	3.8	54	0.10	2.3	0.10
Portugal	Vinho Verde	20	51	39	12	989	1765	3.3	13	28	407	4.8	1.2	0.28	4.6	0.34	8.1	106	0.41	9.6	0.15
Portugal	Tawny Port	23	46	101	*	2304	1356	8.1	29	221	547	22	7.4	0.30	2.0	1.0	73	47	0.49	39.4	1.4
Portugal	Vintage Port	9	66	101	*	3165	642	8.8	75	34	440	6.0	0.5	0.24	3.7	0.33	13	70	0.56	8.2	0.14
Argentina	Cabernet Sauvignon	21	54	74	18	1121	1501	1.8	10	42	582	30	5.0	0.16	0.8	0.51	1.2	113	0.15	5.8	1.2
Argentina	Malbec	85	32	65	29	710	1504	1.9	7.5	251	194	39	7.9	0.24	8.3	0.75	1.5	32	0.17	19.0	2.0
Argentina	Torrontes-Sweet	56	33	34	43	549	1118	1.8	8.1	281	183	13	5.8	0.26	4.6	0.44	1.0	28	0.07	17.6	0.50
Argentina	Torrontes	28	50	73	18	1291	1845	2.0	11	253	530	18	2.2	0.20	3.4	0.15	1.4	77	0.09	5.2	0.49

Arsenic Speciation

The arsenic speciation method measured for six arsenic species in wine (AsB, DMA, MMA, AsC, As III, and As V). The arsenic measurements were carried out in KED mode (helium gas), the corresponding chromatograms were exported and reprocessed in ESI's data processing software (Xceleri). Figure 3a and 3b displays typical calibration curves for DMA, AsC, and As III. Figure 4 displays the chromatograms of the USA merlot wine unspiked and spiked with each arsenic species. It is typical to see matrix effects for samples such as urine or seawater due to the high salt content; in these cases an inline dilution is applied to reduce/eliminate these effects. Figure 5 displays the spiked merlot wine chromatograms for 10X, 25X, 50X, and 100X dilution factors. Good recovery for all dilution factors (Table 4) and no shifting of peaks (elution times) were detected for the different dilution factors, therefore a 10X dilution factor was applied for the sample analyses.

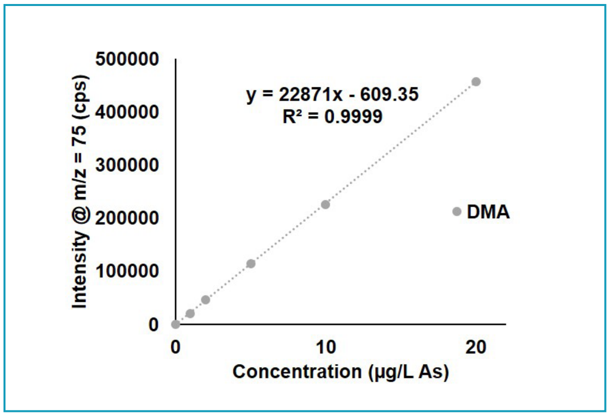

Figure 3a. Typical calibration curve from the arsenic speciation method for DMA.

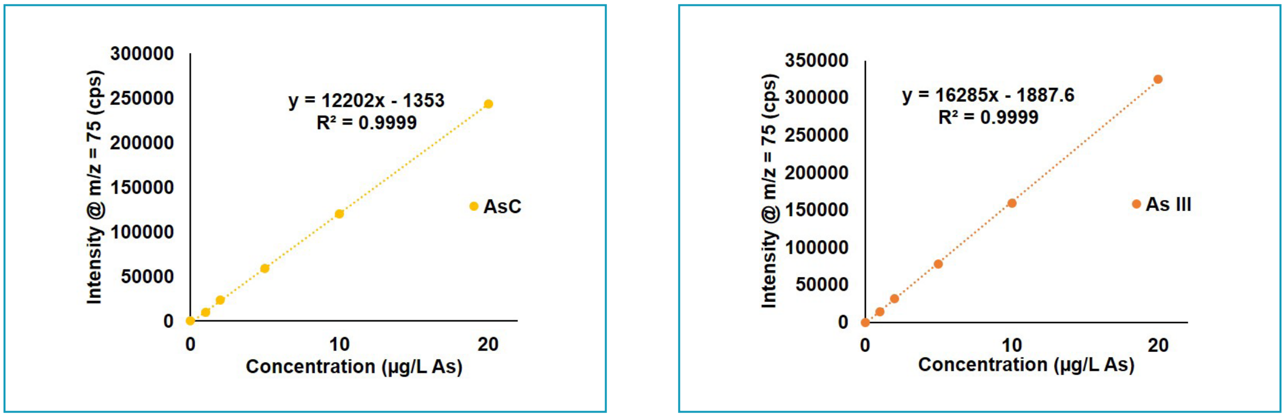

Figure 3b. Typical calibration curves from the arsenic speciation method for AsC and As III.

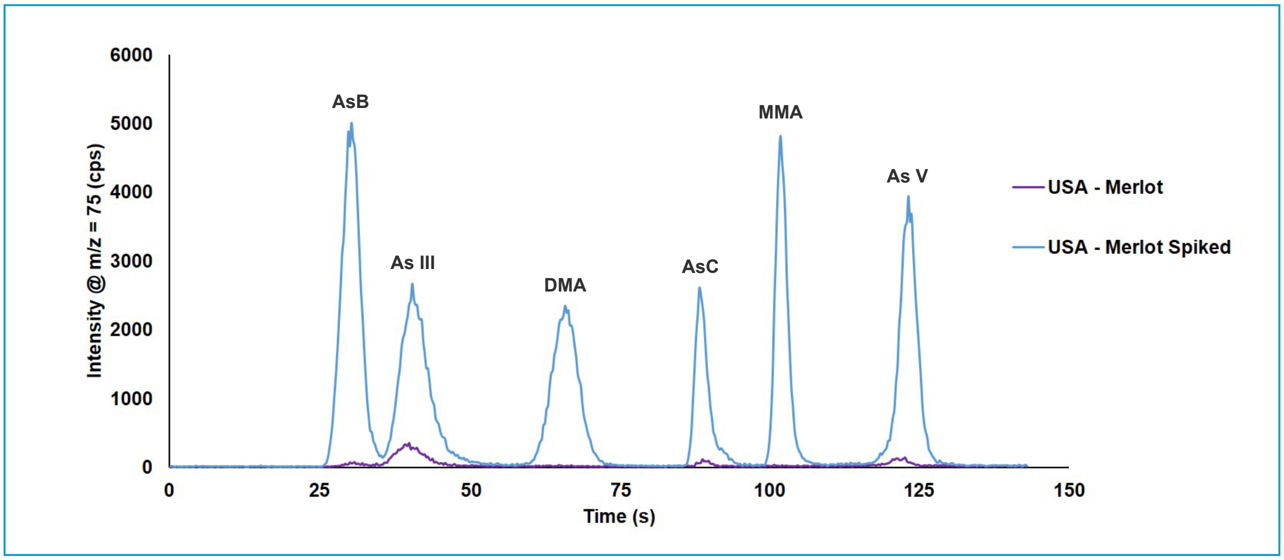

Figure 4. Overlay of USA merlot spiked chromatograms measured with different dilution factors. The USA merlot was spiked with 10 µg/L of each arsenic species.

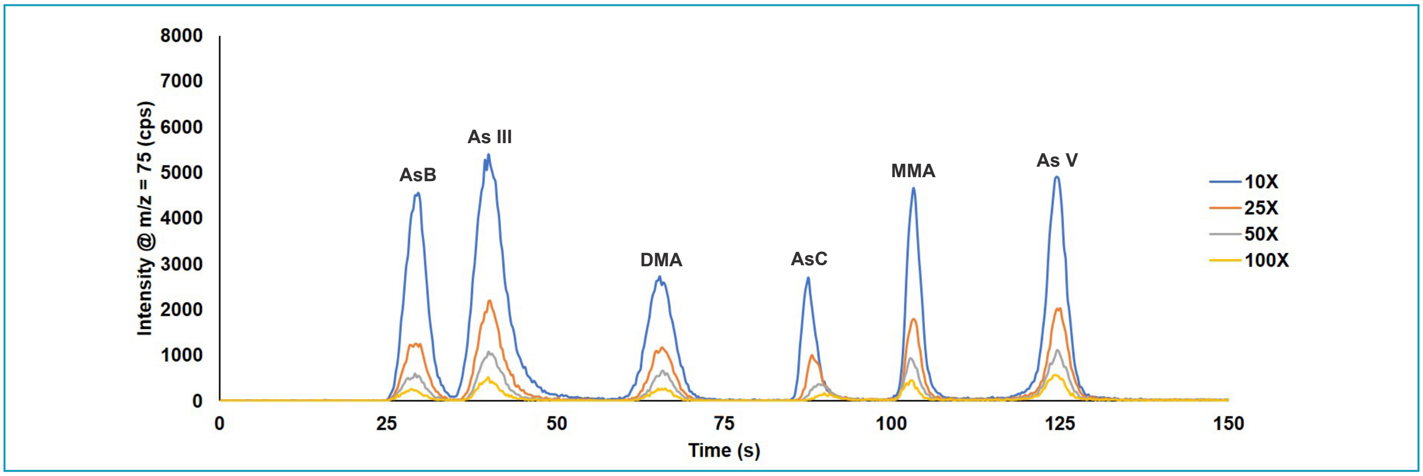

Figure 5. Overlay of USA merlot spiked chromatograms measured with different dilution factors. The USA merlot was spiked with 10 µg/L of each arsenic species.

Table 4. Results from the dilution study for USA merlot spiked wine analyzed at 10, 25, 50, and 100X dilution factors (spike = 10 µg/L of each As species)

	AsB	As III	DMA	AsC	MMA	As V
Dilution Factor	µg/L					
10X	10.3	10.2	10.2	10.3	10.3	10.2
25X	10.1	9.9	10.4	10.7	10.1	10.6
50X	10.3	10.0	10.1	10.0	10.1	10.3
100X	9.6	10.0	9.8	10.4	9.8	10.0

Figure 6 displays the arsenic speciation chromatograms from the Chile Rosé, Argentina Malbec, USA pinot grigio, and USA merlot wines. These 4 wines were found to have the highest levels of arsenic in this study. Table 5 displays the arsenic species results for the 24 wines analyzed. The results show that 11 of the wines exceeded 10 ppb As total arsenic and 8 of these were due to inorganic arsenic (As III and As V) which is the most harmful of the arsenic species. Figure 7 displays a linear regression plot for the comparison of the total arsenic values with the sum of all 6 arsenic species. The data points fall along the target line (slope = 1) suggesting a linear regression and no bias between the two detection methods.

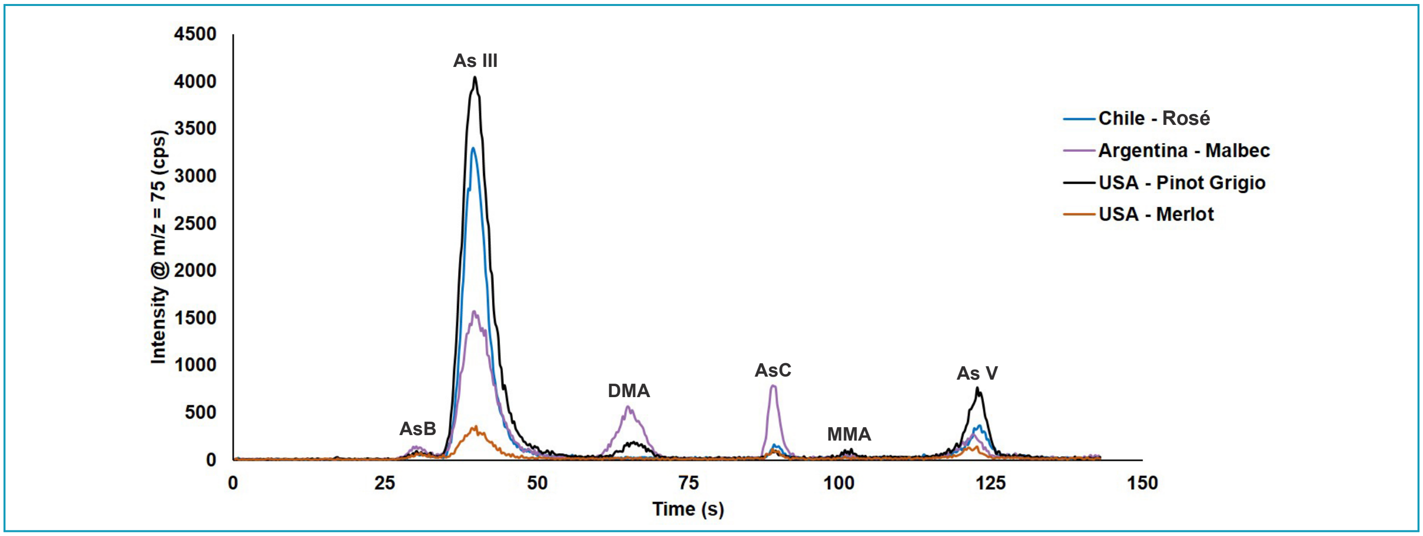

Figure 6. Overlay of chromatograms from a few of the wine samples measured in this study.

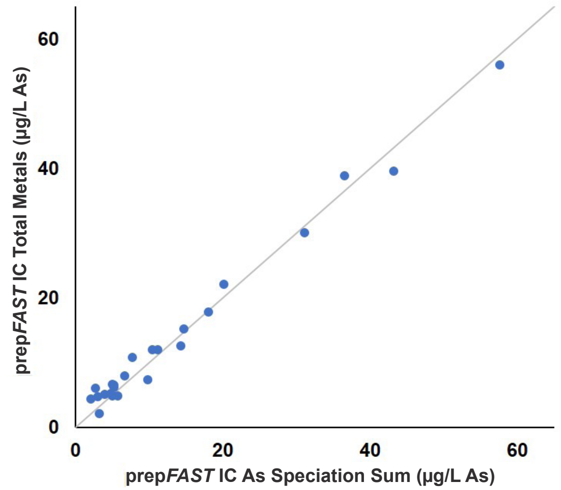

Figure 7. Comparison of arsenic results from the total metals and arsenic speciation (sum of all arsenic species) measurements.

Table 5. Arsenic speciation results for the 24 wines analyzed in this study. Sum column represents the total sum of the 6 arsenic species and Total As column represents the measured values from the total metals measurements.

		µg/L							
Country	**Type**	**AsB**	**As III**	**DMA**	**AsC**	**MMA**	**AsV**	**Sum**	**Total As**
France	White Bourgogne	0.8	3.7	0.2	0.1	0.3	1.6	6.7	7.9
France	Red Bordeaux	0.9	7.4	0.2	0.3	0.3	1.3	10.5	11.9
France	Sauternes	0.8	3.5	0.7	4.9	0.2	1.0	11.1	12.0
USA	Merlot	0.7	10.9	0.2	0.8	0.3	1.9	14.7	15.2
USA	Pinot Grigio	0.5	54.2	0.9	0.2	0.2	1.8	57.6	56.1
USA	Moscato	0.8	7.7	0.5	0.0	0.2	0.7	9.8	7.3
Chile	Rosé	0.6	39.6	0.5	1.0	0.0	1.6	43.2	39.6
Chile	Carmenere	0.7	5.0	0.2	1.3	0.1	0.3	7.7	10.8
Italy	Toscana	0.5	1.4	0.1	0.0	0.0	0.0	2.1	4.4
Italy	Stella Peach	0.1	3.9	0.5	0.0	0.1	0.3	5.0	4.8
Italy	Moscato	0.3	2.5	0.2	0.0	0.0	0.2	3.2	2.1
Italy	Pinot Grigio	0.5	3.8	0.7	0.3	0.0	0.0	5.2	6.5
Australia	Shiraz	0.9	3.3	0.2	0.4	0.0	0.1	4.8	5.2
Australia	Pinot Grigio	0.5	3.2	0.2	0.1	0.0	0.0	3.9	5.1
South Africa	Cabernet Sauvignon	0.7	3.2	0.2	0.9	0.0	0.0	5.0	6.6
Spain	Viura	0.3	4.0	0.9	0.0	0.0	0.0	5.2	6.1
Spain	Crianza	0.6	1.9	0.1	0.5	0.0	0.0	3.1	4.8
Portugal	Vinho Verde	0.3	5.4	0.0	0.0	0.0	0.0	5.7	4.8
Portugal	Tawny Port	0.6	12.5	1.1	0.2	0.2	5.5	20.1	22.1
Portugal	Vintage Port	0.4	1.7	0.5	0.0	0.0	0.0	2.6	6.0
Argentina	Cabernet Sauvignon	1.2	20.7	0.7	6.8	0.2	1.4	31.1	30.0
Argentina	Malbec	1.1	24.3	4.8	5.5	0.0	0.7	36.5	38.9
Argentina	Torrontes-Sweet	0.3	11.3	0.8	1.5	0.0	0.3	14.2	12.5
Argentina	Torrontes	1.0	10.5	1.7	4.8	0.0	0.0	18.0	17.8

Summary

The results were summarized into categories (country or wine type) for total metals (Table 6) and arsenic speciation (Table 7). Red wine showed statistically higher levels for Fe, Zn, Ba. Sweet wine showed statically higher levels for Cu, whereas, white wine had no statistically higher levels. Port showed the highest levels for Si, Mn, Ni, Cs, and Pb. The wine tested from USA, Chile, and Argentina displayed the highest levels of inorganic As.

Table 6. Average total metals results sorted by country and wine type, for the 24 wine samples analyzed in direct mode using the prep*FAST* IC.

Country	^{23}Na	^{24}Mg	^{28}Si	^{55}Mn	^{57}Fe	^{59}Co	^{60}Ni	^{63}Cu	^{66}Zn	^{75}As	^{98}Mo	^{114}Cd	^{118}Sn	^{121}Sb	^{133}Cs	^{138}Ba	^{205}Tl	^{208}Pb	^{238}U
	mg/L																		
France	21	41	66	1368	1527	3.7	23	87	865	11	5	0.3	2.1	0.7	3.7	154	0.4	16	0.2
USA	24	45	66	1430	1741	4.4	24	165	1013	26	11	1.0	7.6	1.6	6.1	183	0.6	9.2	1.3
Chile	17	49	64	1280	1732	3.6	14	90	988	25	8.2	0.2	3.0	0.4	14	95	0.1	4.5	0.1
Italy	21	47	45	805	1199	1.9	15	147	451	4.5	1.8	0.2	6.5	0.3	28	90	0.3	5.4	0.1
Australia	36	56	64	1524	837	4.2	12	52	856	5.1	4.3	0.2	3.7	0.1	1.1	139	0.1	4.9	0.1
S. Africa	28	73	71	2178	3386	2.6	12	36	546	6.6	1.9	0.1	2.0	0.2	10	295	0.7	5.9	0.2
Spain	25	46	63	517	825	1.9	8.9	44	479	5.4	1.2	0.1	1.6	0.2	3.2	50	0.1	3.9	0.1
Portugal	17	54	80	2153	1254	6.7	39	94	465	11	3.0	0.3	3.4	0.6	32	75	0.5	19	0.6
Argentina	47	42	62	918	1492	1.9	9.2	207	372	25	5.2	0.2	4.3	0.5	1.3	63	0.1	12	1.1
Wine Type	^{23}Na	^{24}Mg	^{28}Si	^{55}Mn	^{57}Fe	^{59}Co	^{60}Ni	^{63}Cu	^{66}Zn	^{75}As	^{98}Mo	^{114}Cd	^{118}Sn	^{121}Sb	^{133}Cs	^{138}Ba	^{205}Tl	^{208}Pb	^{238}U
	mg/L																		
White	23	43	60	990	1106	2.7	14	98	562	15	5.5	0.3	4.7	0.6	3.8	83	0.3	8.2	0.6
Red	31	54	70	1397	2092	3.5	18	98	793	17	5.1	0.3	3.0	0.5	16	158	0.4	7.7	0.5
Sweet	31	41	40	843	687	2.3	12	172	554	8	4.2	0.4	6.9	0.5	2.4	90	0.2	11	0.2
Port	16	56	101	2735	999	8.5	52	128	494	14	3.9	0.3	2.8	0.7	43	59	0.5	24	0.7

Table 7. Average arsenic speciation results sorted by country and wine type, for the 24 wine samples analyzed in speciation mode using the prep*FAST* IC. Sum column represents the sum of the arsenic species and the i-As column represents the sum of As III and As V.

	µg/L							
Country	**AsB**	**As III**	**DMA**	**AsC**	**MMA**	**AsV**	**i-As**	**Sum**
France	0.8	4.9	0.4	1.8	0.3	1.3	6.2	9.4
USA	0.6	24	0.5	0.3	0.2	1.4	26	27
Chile	0.6	22	0.3	1.2	0.1	1.0	23	25
Italy	0.3	2.9	0.4	0.1	0.0	0.1	3.1	3.9
Australia	0.7	3.2	0.2	0.2	0.0	0.1	3.3	4.4
South Africa	0.7	3.2	0.2	0.9	0.0	0.0	3.2	5.0
Spain	0.5	3.0	0.5	0.2	0.0	0.0	3.0	4.1
Portugal	0.4	6.5	0.5	0.1	0.1	1.8	8.4	9.5
Argentina	0.9	17	2.0	4.7	0.1	0.6	17	25
	µg/L							
Wine Type	**AsB**	**As III**	**DMA**	**AsC**	**MMA**	**AsV**	**i-As**	**Sum**
White	0.6	12.1	0.6	0.8	0.1	0.5	13	15
Red	0.8	11.8	0.7	1.7	0.1	0.7	13	16
Sweet	0.5	5.8	0.5	1.3	0.1	0.5	6.3	8.7
Port	0.5	7.1	0.8	0.1	0.1	2.8	9.9	11