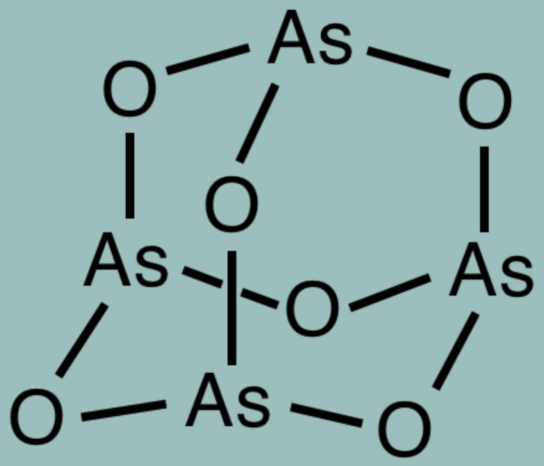
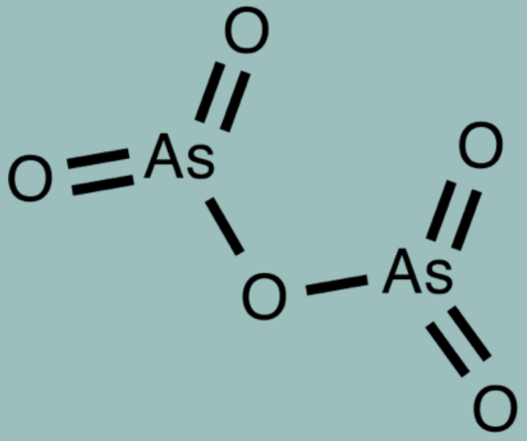
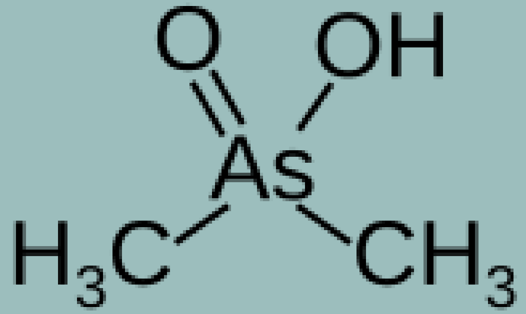
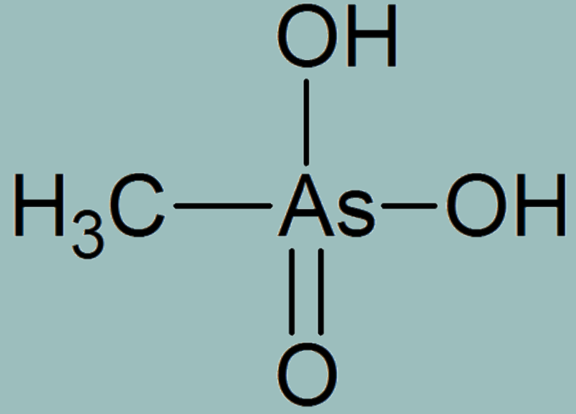






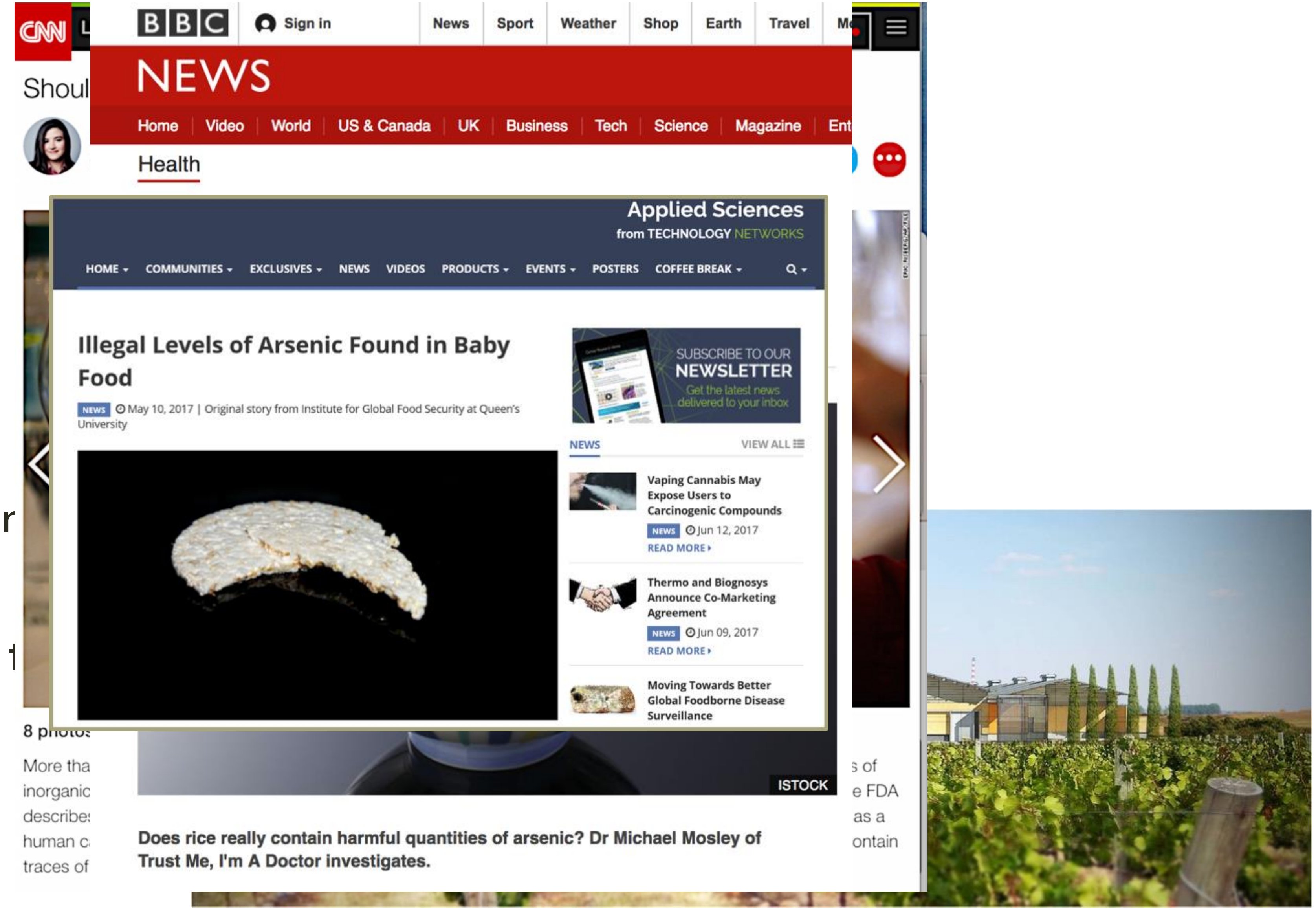


FAST ARSENIC SPECIATION ANALYSIS OF WINES AND RICE WITH LC-ICP-QQQ

Courtney Tanabe
UC Davis

THE INTEREST

- Public interest
- UCD Arsenic Workshop
- Sources of Arsenic i wine
- Regulations around t world



REGULATIONS

Wine

No US regulations

VQA Ontario: 100 ppb total As

Organisation of Vine and Wine (OIV) 200 ppb total As

No regulations for individual As species

Rice

FDA proposed action level for iAs in infant rice ceral: 100 ppb

China: 200 ppb rice grains

EU:

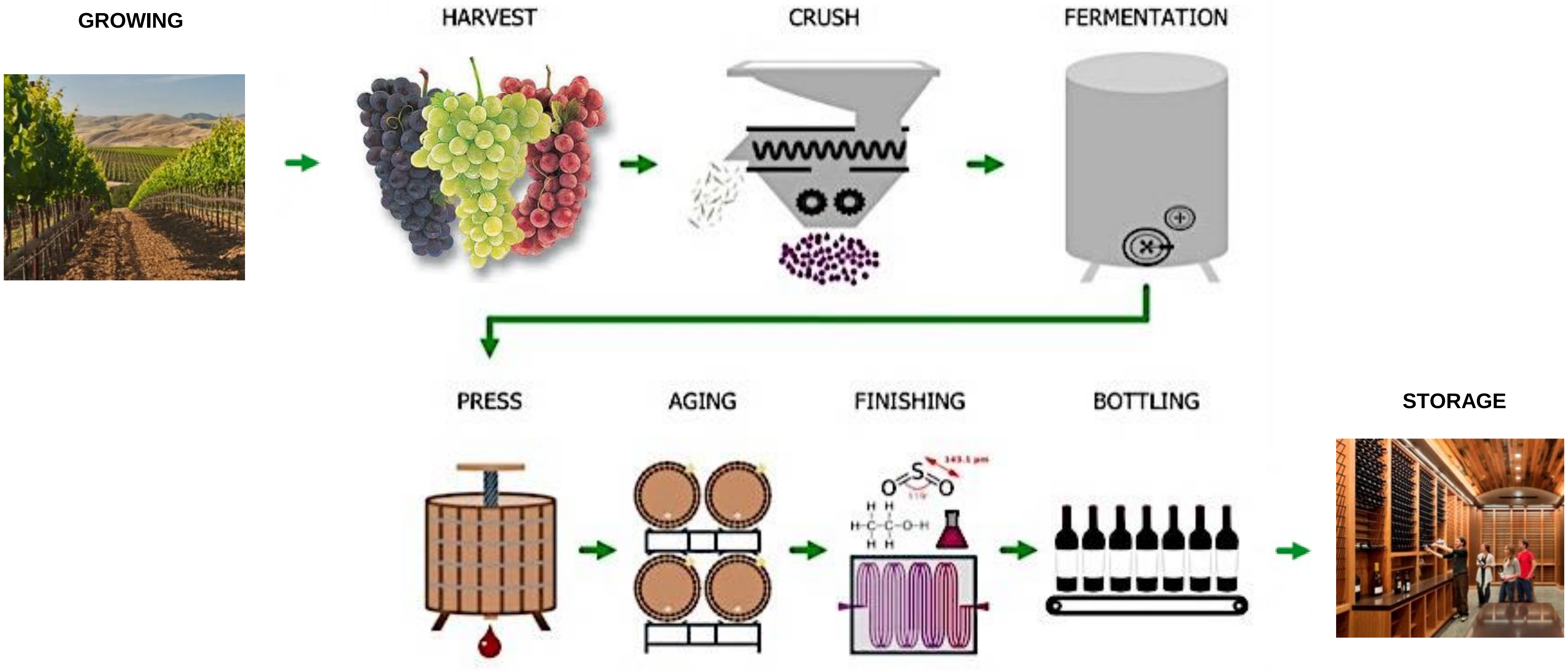
- 100 ppb iAs maximum level in rice for infants/childre
- 200 ppb iAs maximum level in non-parboiled rice

  250 ppb iAs maximum level in parboiled rice

  300 ppb iAs maximum level in rice cakes, crackers, wafers, waffles

http://www.oiv.int/oiv/cms/index?lang=en;
http://www.vqaontario.ca/Resources/Library

ORIGIN OF ARSENIC IN WINE?



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JAAS

ROYAL SOCIETY OF CHEMISTRY

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A fast and fit-for-purpose arsenic speciation method for wine and rice†

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This fit-for-purpose method was designed in response to recent and proposed food standards, both international and national, that limit inorganic arsenic rather than total, organic, or individual arsenic species such as arsenite (As^{III}) and arsenate (As^{V}). In this method, As^{III} is intentionally oxidized to As^{V} with H_2O_2 during sample preparation, converting all inorganic arsenic (the sum of As^{III} and As^{V}) to the As^{V} form. Arsenic species were separated in less than 2 minutes using a short, narrow bore, 5 µm chromatography column. This analysis time is 10× faster than the current FDA regulatory method. The use of O_2 reaction gas with inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ with MS/MS capability) avoided spectral interferences and dramatically increased sensitivity, allowing for low volume injections. The small injection volume and modified mobile phase composition mitigate non-spectral interferences such as carbon enhanced ionization. Furthermore, the shortened analysis time significantly increases sample throughput. Validation data from two laboratories demonstrate the method's accuracy and reproducibility of both wine and rice matrices in a single analytical batch.

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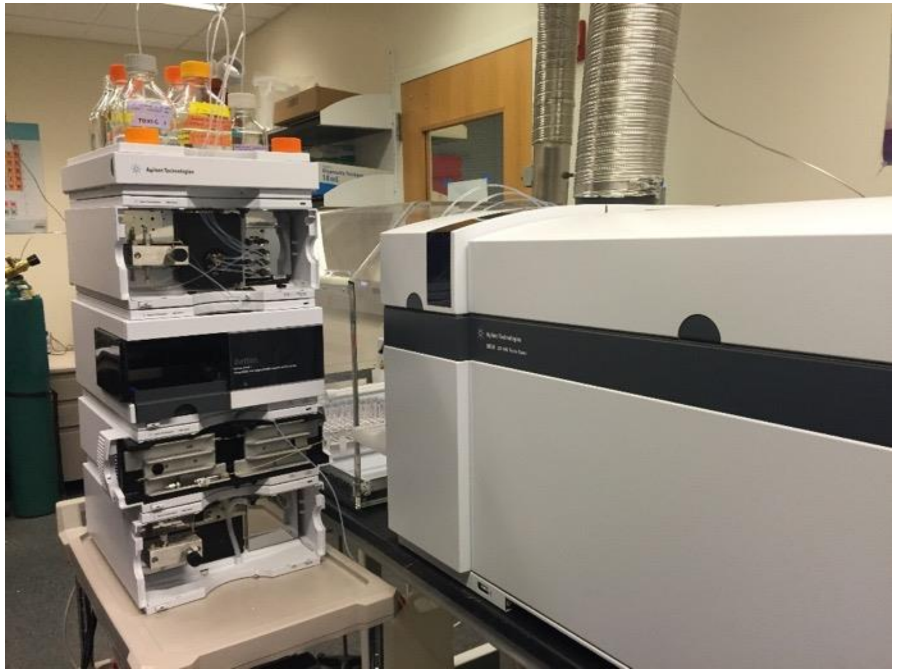
rsc.li/jaas

METHOD PARAMETERS



3 species analyzed: MMA, DMA, and iAs

- H_2O_2 addition

Column: PRP-X100 50x2.1 mm 5µm Hamilton

Mobile Phase: 40 mM ammonium carbonate, 3% methanol, pH 9.0

Detection of AsO^+ at m/z 91

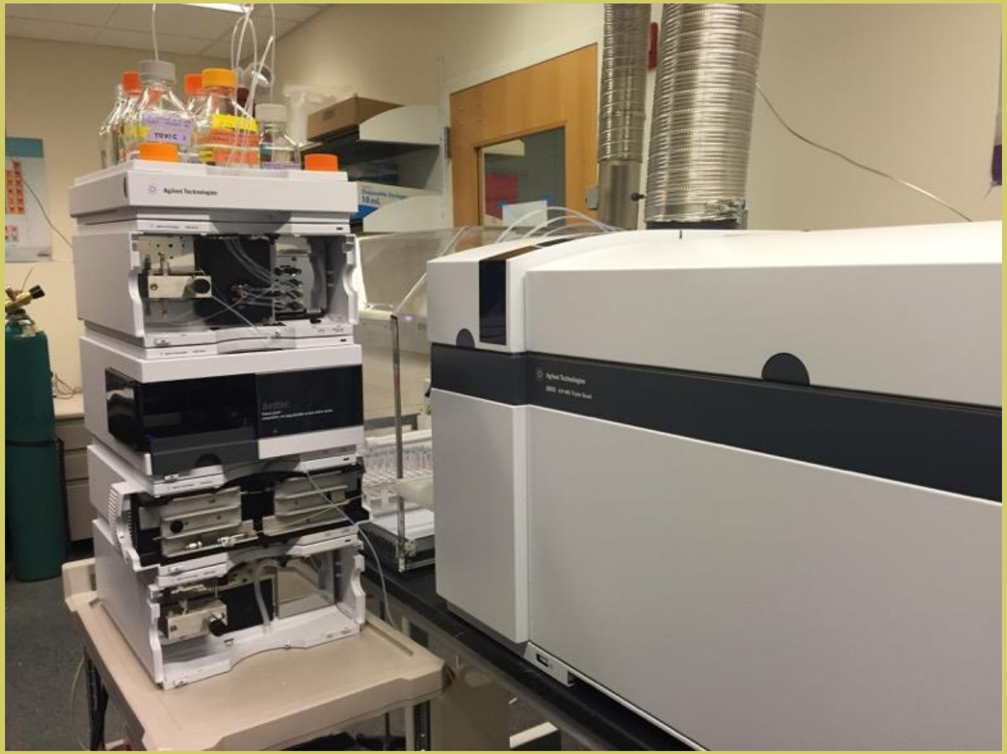
- Agilent 8800 ICP-QQQ
- Agilent 1260 HPLC

WINE SAMPLES

- Small problem…
  - Alcohol content in wine ranges from 7-24% in US
  - Plasma interference
- Added 3% EtOH to all calibration standards, CCVs, CRMs
- 2 lab validation study
  - 5 samples for validation study
  - 5 additional samples for market basket study
- Commercial wines purchased in Davis, CA

RICE SAMPLES

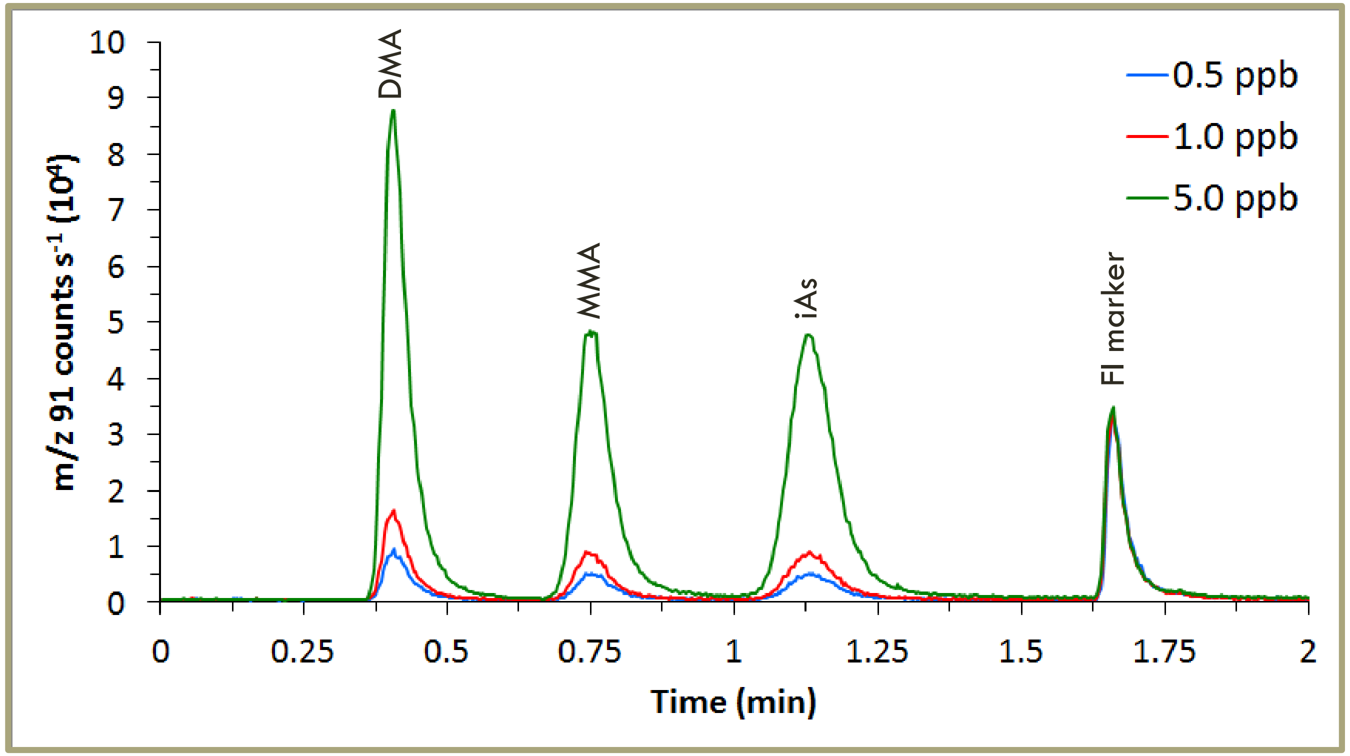
- Reference samples
  - NIST 1568b
  - NMIJ 7503a
  - NMIJ 7532a
  - ERM BC-211
- Rice samples only analyzed at FDA

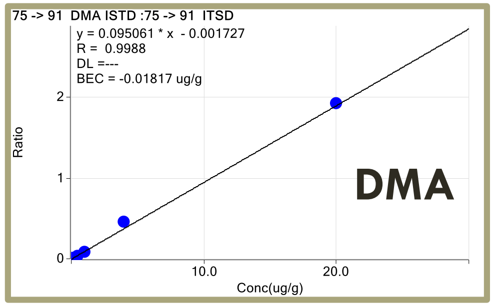


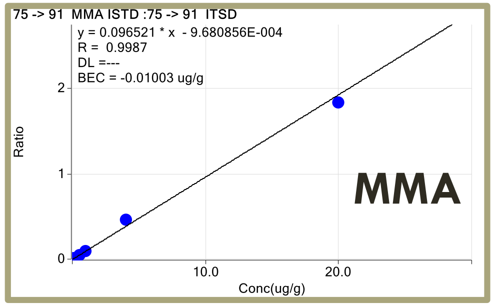
SHORT COLUMN STUDY

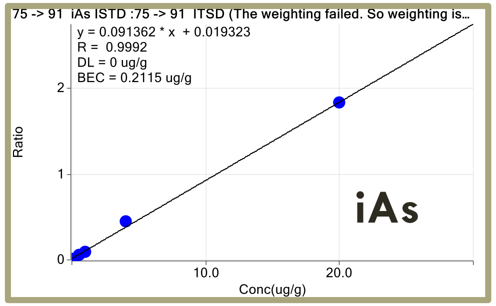
RESULTS

- Separation of 3 arsenic species
- Overlay: 0.5 ppb, 1 ppb, and 5 ppb









RESULTS – FORTIFICATION RECOVERY

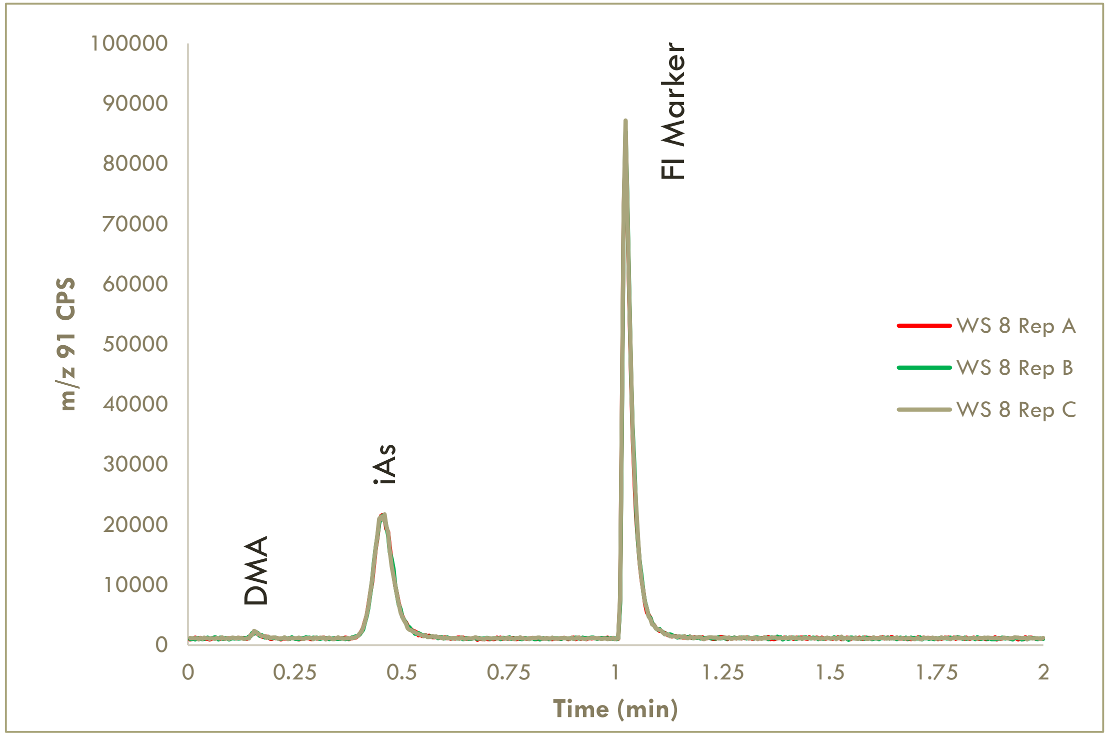
UCD Average Fortification Recovery for duplicates at 5, 10, and 30 ppb

Five samples for a total of n=30

Matrix		DMA	MMA	iAs
Wine	Average	102%	97%	99%
	Range	97-107%	91-102%	95-103%

RESULTS –ADDITIONAL SAMPLES

Wine Sample	% EtOH (v/v)	DMA	MMA	iAs	Sum of Species	Total As	% Mass Balance
WS-6	13.5	<LOD	<LOD	32.9 ± 0.8	32.9 ± 0.8	34.4 ± 0.4	96%
WS-7	13.8	<LOD	<LOD	9.1 ± 0.4	9.1 ± 0.4	9.1 ± 0.3	100%
WS-8	13.5	1.1 ± 0.0	<LOD	27.6 ± 0.7	28.6 ± 0.7	28.9 ± 0.3	99%
WS-9	10.5	1.0 ± 0.1	<LOD	27.5 ± 0.9	28.5 ± 0.9	27.9 ± 0.9	102%
WS-10	13.5	<LOD	<LOD	4.5 ± 0.1	4.5 ± 0.1	4.7 ± 0.1	94%
Average ± 1σ, n=3 for the individual species							
Average ± 1σ, n=3 for the Total As concentration							



Overlay of sample WS-8 triplicate chromatograms

RESULTS – LONG METHOD (EAM §4.10) VS. FAST AND FIT-FOR-PURPOSE METHOD

- Comparison of the FDA §4.10 Extension results (Long) with the Fast and Fit-for-purpose results (Fast)
- Percent difference in parentheses

Style	Cultivar	% ethanol	DMA		iAs		Total As	
			Long	Fast	Long	Fast	EAM §4.7	Sum Species
Rosé	Zinfandel	9.5	0.81 ± 0.1	0.72 ± 0.04 (89%)	14.4 ± 1.0	16.0 ± 0.5 (111%)	16.5 ± 0.02	16.7 ± 0.5 (101%)
White	Sauvignon blanc	13	0.74 ± 0.04	0.72 ± 0.06 (98%)	10.7 ± 0.2	11.4 ± 0.4 (107%)	12.6 ± 0.16	12.1 ± 0.3 (96%)
Sparkling	Sparkling white blend	12	0.75 ± 0.1	0.83 ± 0.04 (111%)	9.2 ± 0.4	9.5 ± 0.6 (103%)	10.4 ± 0.11	10.3 ± 0.5 (99%)
Dessert	Petite Sirah	20	1.7 ± 0.1	1.86 ± 0.06 (109%)	2.1 ± 0.3	2.3 ± 0.4 (109%)	4.5 ± 0.01	4.1 ± 0.4 (92%)
Red	Cabernet Sauvignon	14.5	0.45 ± 0.01	0.47 ± 0.04 (105%)	1.5 ± 0.3	1.7 ± 0.3 (113%)	2.4 ± 0.03	2.2 ± 0.3 (90%)

RESULTS – FAST AND FIT-FOR-PURPOSE RICE REFERENCE SAMPLES

- Analyses of rice reference materials
- Uncertainty shown as 1 standard deviation (n = 3)
- % recovery shown in parentheses

Rice	DMA		MMA		iAs		Sum	
	Reference	Measured	Reference	Measured	Reference	Measured	Reference	Measured
NIST 1568b	180 ± 12	195 ± 4 (109%)	11.6 ± 3.5	14.9 ± 0.9 (128%)	92 ± 10	105 ± 1 (114%)	285 ± 14	315 ± 3 (110%)
NMIJ 7503a	13.3 ± 0.9	15.4 ± 0.1 (116%)	None reported	< LOD	84.1 ± 3*	79 ± 4 (94%)	98 ± 7	94 ± 4 (96%)
NMIJ 7532a	18.6 ± 0.8	18.7 ± 1.3 (101%)	None reported	2.2 ± 1.9	298 ± 8	277 ± 12 (93%)	320 ± 10	297 ± 12 (93%)
ERM BC-211	119 ± 13	146 ± 3 (123%)	None reported	19.9 ± 0.6	124 ± 11	124 ± 2 (100%)	260 ± 13	290 ± 5 (112%)

* NMIJ 7503a iAs uncertainty estimated as the square root of the sum of squares of the AsIII and AsV uncertainties.

CONCLUSIONS

- Validation of Fast and Fit for purpose method for wine analysis
  - Shorter run time compared to FDA 4.10 extension method for wine analysis
  - Results show separation of all analyzed arsenic species
  - Good results between the labs in validation study
  - Can analyze various wine types
- Fast and Fit for purpose method for rice analysis
  - Shorter run time compared to FDA 4.11 method for rice analysis
  - Improved sensitivity and limits of detection

ACKNOWLEDGMENTS

FDA

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