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Arsenic Speciation Analysis of Wine for the Characterization of Carcinogenic Metalloid Compounds

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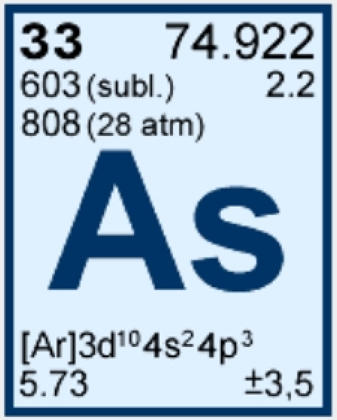
Presentation Outline:

- Why we care about Arsenic and Arsenic Speciation
- Arsenic Sources
- Applied Analytical Methods
- Analytical Findings
- Holding Time Results
- Unknown Arsenic Species



Why we care about Arsenic and Arsenic Speciation

inorganic As species are much more toxic than organic species (LC_{50} = 10 mg/kg vs. 700 mg/kg)

As(III) and As(V) are equally toxic, since As(V) is quickly reduced inside organisms

but: As(III) and As(V) have different uptake rates and pathways, so they may not have the same effects

symptoms:

"heavy metal poisoning": deactivation of enzyme systems with –SH groups

decoupling of cellular energy cycle; cell necrosis

deactivation of glutathione

Sources of Arsenic – Naturally Occurring

Volcanic – Minimal atmospheric emissions unless eruption occurs, mobility limited to runoff

Soil/Sediment – The concentration of arsenic in soil and sediment is highly dependent on the parent material (rock and decomposed organic matter). Typically soils/sediment rich in series 4 transition metals contain elevated concentrations of As. The mobility of As in soil/sediment depends on the complexation of As, pH, redox, soluble cations and anions, temperature, and presence of microbial organisms.

Sources of Arsenic – Naturally Occurring

Rock – The concentration and molecular form of As in rock and other minerals is highly dependent on the variables associated with the formation of the solid.

- Volcanic rock typically contains lower concentrations of As due to the relatively fast formation from homogenous magma.
- Sedimentary rock can contain significant higher concentration of As due to the slow formation over centuries allowing for aggregation of Fe, Mn, Al, and other elements which have greater capacities for As retention.

Conclusions: The molecular form, concentration, fate, and transport of arsenic in solid substrates cannot be assumed.

Arsenic concentrations in the lithosphere is quite heterogeneous resulting in different forms and concentrations in raw food materials.

Sources of Arsenic – Naturally Occurring

River Water – Arsenic concentrations in river water are highly dependent on the source of the water (snow melt or rainfall), runoff, and effluents from industrial complexes. Natural runoff from rocks and soil are heavily impacted by the pH of the rainfall, arsenic concentration in the solid substrate, molecular form of As, and capacity of the substrate to retain As.

Groundwater: The fate and transport of As in groundwater is typically dictated by the mineralogy of the soil, pH, redox conditions, dissolved oxygen, and presence of series 4 transition metals (Fe, Mn, Pb, Cu, etc).

Sources of Arsenic – Naturally Occurring

Lakes – Inflows from tributaries, industrial discharge, runoff, and wet and dry deposition have the greatest impact on the arsenic concentrations in lake and ponds. The molecular form and stratification of As in lakes and ponds is typically dictated by the depth (affecting light penetration), size, shape, aquatic foliage, microbial activity in the sediment, and seasonal temperature differences which can induce mixing.

Rain – The most significant impact on the As concentration in rain is the atmospheric loading from coal fired power plants, volcanic activity, and incinerators.

Conclusion: Oxidized forms of As are thermodynamically favored in most aquatic systems. Arsenate is most prevalent in oxygenated waters; however, speciation becomes significantly more complex in reducing conditions. **Bioaccumulation and metabolism is species (plant and animal) specific**.

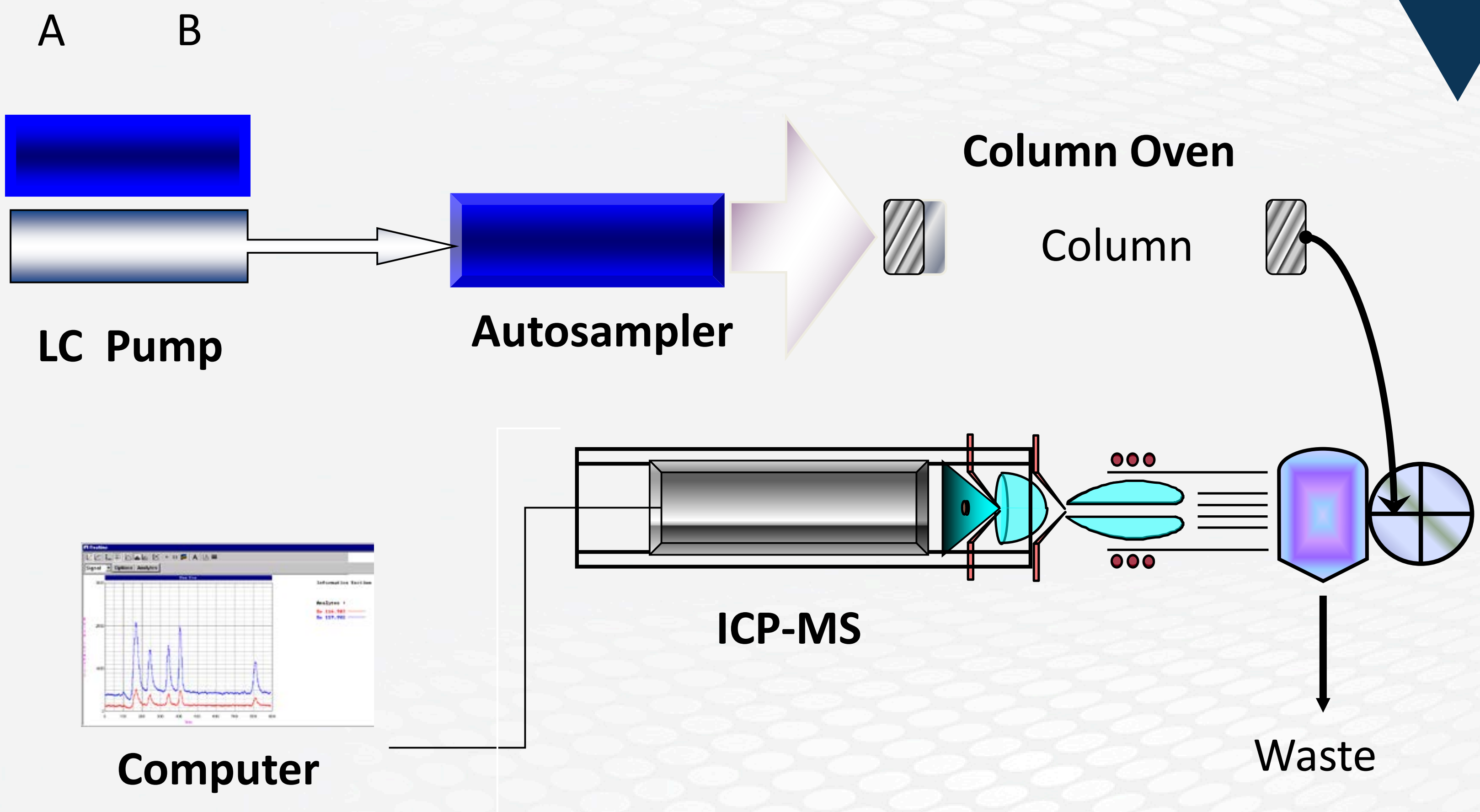
Sources of Arsenic – Anthropogenic

mining and smelting (Au, Cu)
semiconductor production (Ga doping)
biocides
wood preservation (CCA)
defoliation (DMAs)
herbidices (MMAs, DMAs, As_2O_3)
beetle control (MMAs)
orchards (Pb-arsenate)
feed additives for livestock (phenyl-As compounds)
stainless steel
coal combustion (fly ash)
phosphate detergents
phosphate fertilizers

Applied Analytical Methods

- **HG-CT-GC-AFS (hydride generation cryogenic trapping gas chromatography atomic fluorescence spectroscopy)**
- IC-HG-AFS (ion chromatography hydride generation atomic fluorescence spectroscopy)
- **IC-ICP-MS (ion chromatography inductively coupled plasma mass spectrometry) with and without DRC and CRC technology**
- RP-ICP-MS (reverse phase chromatography inductively coupled plasma mass spectrometry)
- NP-ICP-MS (normal phase chromatography inductively coupled plasma mass spectrometry)
- SEC-ICP-MS (size exclusion chromatography inductively coupled plasma mass spectrometry)

Arsenic Speciation Analysis by IC-ICP-MS



Scope of Investigation

- 48 different wines were purchased at grocery and convenient stores in western Washington
- Sample collection included: white wines, red wines, mixtures, and fortified wines
- What did we find…?

Arsenic Speciation Analysis Results

	As(III)	DMA	MMA	Unk 7.5 minutes	As(V)	TIAs
1514002-01 A	8.40	0.30	0.00	0.16	2.63	11.03
1514002-02 A	3.20	0.60	0.10	0.07	0.69	3.88
1514002-03 A	3.35	0.15	0.00	0.00	0.96	4.31
1514002-04 A	25.94	0.87	0.00	0.32	0.00	**25.94**
1514002-05 A	1.78	0.20	0.00	0.20	0.48	2.26
1514002-06 A	1.50	0.25	0.00	0.15	0.65	2.15
1514002-07 A	9.17	0.74	0.09	0.24	0.35	9.52
1514002-08 A	1.04	0.36	0.00	0.31	0.57	1.62
1514002-09 A	6.83	0.00	0.00	0.18	0.00	6.83
1514002-10 A	4.08	0.47	0.00	0.21	0.21	4.29
1514002-11 A	9.04	0.18	0.09	0.00	0.00	9.04
1514002-12 A	14.50	2.22	0.20	0.23	12.84	**27.34**
1514002-13 A	4.22	0.98	0.00	1.07	1.84	6.06
1514002-14 A	0.53	0.05	0.00	0.00	0.33	0.86
1514002-15 A	0.84	0.08	0.00	0.11	0.00	0.84
1514002-16 A	3.17	0.32	0.00	0.00	2.38	5.55
1514002-17 A	5.33	0.39	0.00	0.60	4.82	10.15
1514002-18 A	9.71	1.03	0.00	0.61	1.45	11.15
1514002-19 A	5.03	0.39	0.13	0.00	0.38	5.41
1514002-20 A	5.53	0.29	0.00	0.18	2.48	8.01
1514002-21 A	2.18	0.34	0.00	0.09	0.91	3.09
1514002-22 A	2.51	0.22	0.00	0.00	0.00	2.51
1514002-23 A A	0.51	0.10	0.00	0.16	0.00	0.51
1514002-24 A	1.89	0.14	0.00	0.00	1.14	3.03

Reporting Limit for all analyses and all species is 0.8ug/L

Arsenic Speciation Analysis Results

	As(III)	DMA	MMA	Unk 7.5 minutes	As(V)	TIAs
1514002-25 A	0.82	0.12	0.00	0.08	0.11	0.93
1514002-26 A	0.80	0.23	0.00	0.32	0.09	0.89
1514002-27	7.04	0.29	0.00	0.17	0.00	7.04
1514002-28	1.02	1.03	0.00	0.19	1.59	2.61
1514002-29	5.31	0.39	0.00	0.27	6.49	11.80
1514002-30	6.41	2.06	0.00	2.55	3.89	10.30
1514002-31	13.17	0.80	0.00	0.07	1.98	15.15
1514002-32	3.30	0.33	0.00	0.31	1.05	4.35
1514013-01 A	4.10	0.93	0.00	2.91	1.22	5.33
1514013-02 A	4.95	0.72	0.00	2.02	1.39	6.35
1514013-03 A	7.83	0.41	0.00	0.20	0.41	8.24
1514013-04 A	4.06	0.49	0.00	0.16	3.25	7.31
1514013-05 A	23.44	1.08	0.20	0.00	0.91	**24.35**
1514013-06 A	18.94	0.46	0.00	0.00	0.54	**19.48**
1514013-07 A	7.38	0.49	0.18	0.21	0.16	7.54
1514013-08 A	5.58	0.19	0.00	0.00	0.00	5.58
1514013-09 A	26.41	1.09	0.15	0.23	0.28	**26.70**
1514013-10 A	19.92	0.61	0.00	0.09	0.15	**20.07**
1514013-11 A A	5.37	0.74	0.10	0.00	2.59	7.96
1514013-12 A	4.29	0.53	0.00	0.00	1.94	6.23
1514013-13 A	16.11	0.81	0.13	0.98	0.00	16.11
1514013-14 A	29.13	1.28	0.00	0.19	7.05	**36.18**
1514013-15 A	8.81	2.38	0.00	2.57	0.86	9.67
1514013-16 A	0.22	0.21	0.00	0.00	0.26	0.48

Reporting Limit for all analyses and all species is 0.8ug/L

Arsenic Speciation Analysis Results

	As(III)	DMA	MMA	Unk 7.5 minutes	As(V)	TIAs
Average of 48 Wines	7.39	0.59	0.03	0.38	1.49	8.88
Standard Deviation	7.41	0.53	0.06	0.70	2.34	8.22
Red Wine Average	4.88	0.57	0.01	0.62	1.37	6.25
White wine Average	10.43	0.62	0.05	0.12	1.63	12.06

Statistical significance

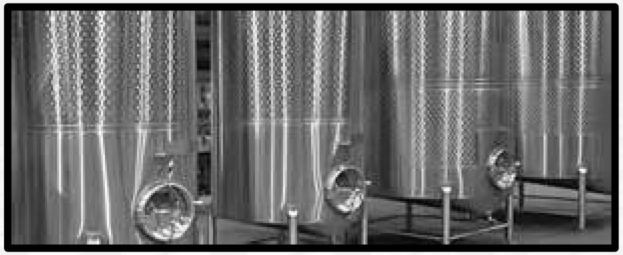
Statistical significance

Statistical significance

Arsenic Speciation Analysis Results

- Where does the arsenic come from?

- Grapes
  - Different Varieties
  - Soil
  - Pesticides/Herbicides
  - Water (Irrigation)
- Processing
  - Stainless Steel
  - Refining (filtration)
    - Fine Clay (kieselguhr)
    - Diatomaceous Earth
    - Perlite
- Various other chemicals used in production



Stability of Arsenic Species in Wine

- Subset of red and white wine samples were analyzed ten days after opening the bottle for the initial analysis
- Wine samples were stored in both refrigerated and ambient conditions

Stability of Arsenic Species in Wine

Relative Standard Deviations Between Initial Analysis and Reanalyses
10 Days After Storage Under Refrigerated and Ambient Conditions

Sample ID	As(III)	DMA	MMA	Unk 7.5 minutes	As(V)
1514002-04 A - 4C	3%	13%	173%	12%	92%
1514002-12 A - 4C	4%	4%	96%	38%	5%
1514002-17 A - 4C A	5%	15%	173%	6%	4%
1514002-18 A - 4C	4%	5%	< DL	10%	3%
1514002-26 A - 4C	8%	1%	< DL	7%	173%
1514002-30 - 4C	4%	4%	< DL	7%	2%

Indicates concentrations were within 10x the eMDL

What we Know About Unknown Arsenic Compound

- Unknown arsenic species is anionic
- Greater anionic interaction than arsenite, MMAs, and DMAs
- Extremely stable (does not degrade after heated HNO_3 digestion)
- No inferences can be made with regards to the toxicological significance of the unknown arsenic species.
- Lower concentration does not necessary mean it is insignificant

Conclusions

From the micro-scale investigation we pursued:

- White wine, overall, contains higher concentrations of inorganic arsenic
- The presence of the unknown arsenic compound is independent of the grape variety
- Arsenic species are stable in wine for up to ten days independent of refrigeration or storage under ambient conditions
- Identification of the unknown arsenic species is of paramount importance to better understand the toxicological significance

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