

Arsenic Speciation

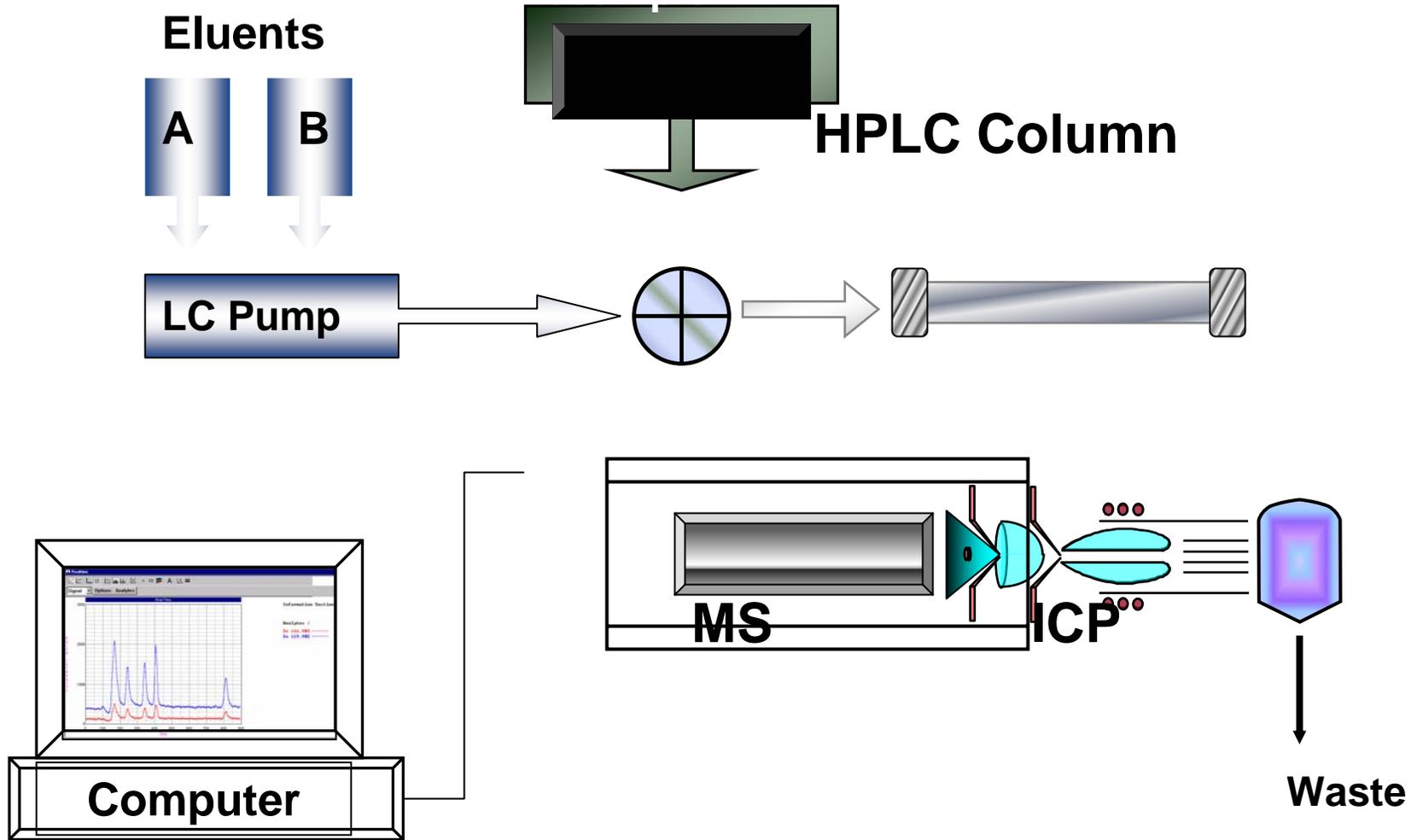
- **Methods for analysis of MMA^{III} and DMA^{III}**
- **Problems of instability**
- **Uncharacterized arsenic species**
- **Binding of trivalent arsenic metabolites (e.g., with Hb) and arsenic in blood**

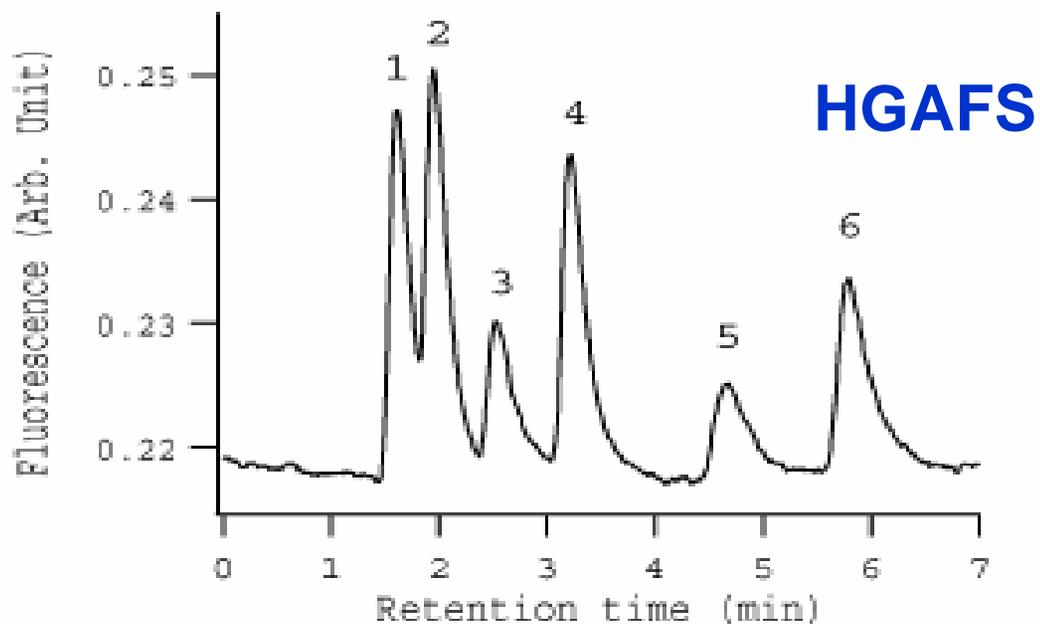
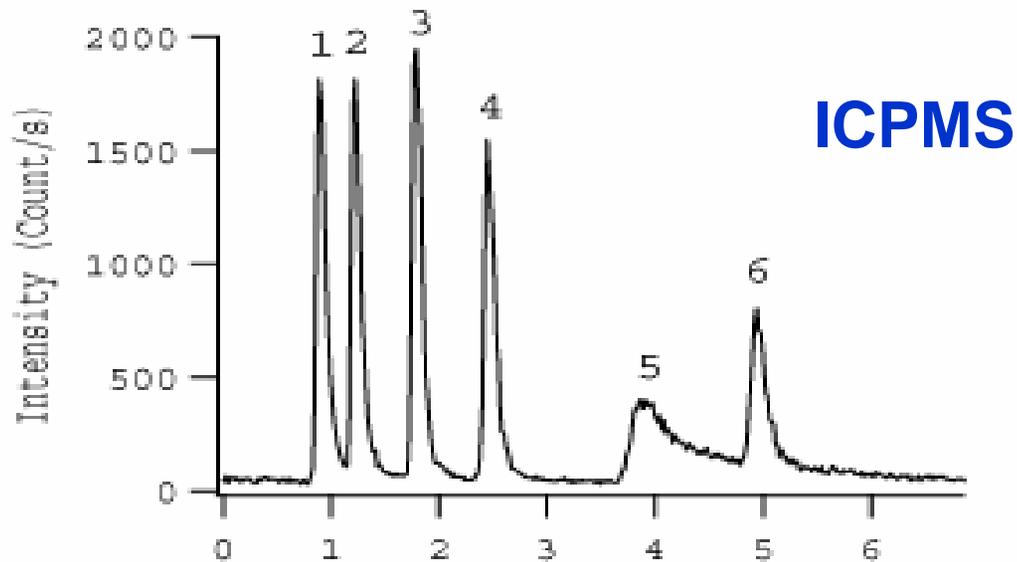
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HPLC-ICPMS

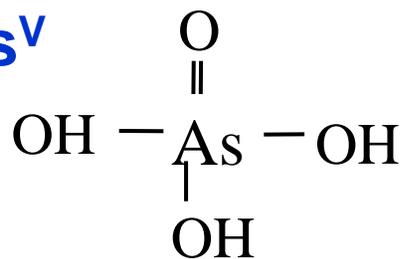




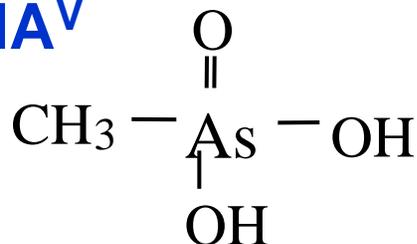
- 1, iAs^{III}**
- 2, MMA^{III}**
- 3, DMA^V**
- 4, MMA^V**
- 5, DMA^{III}**
- 6, iAs^V**

Hydride Generation

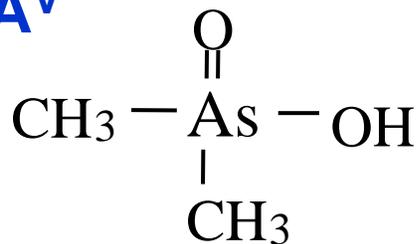
iAs^V



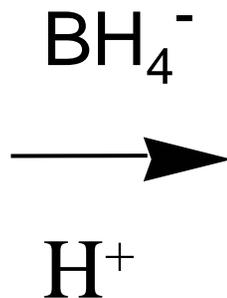
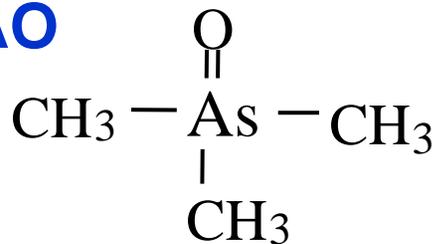
MMA^V



DMA^V

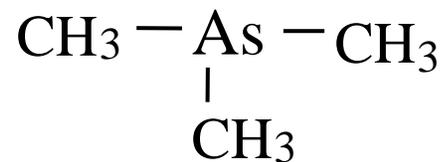
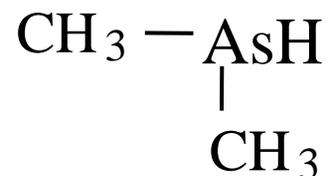
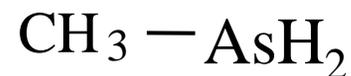


TMAO



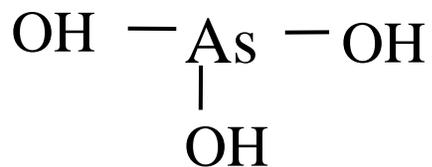
pH 1

Volatile arsines

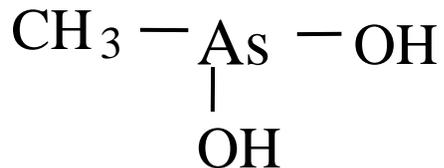


Hydride Generation

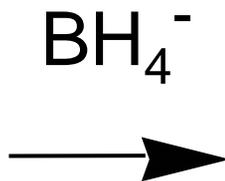
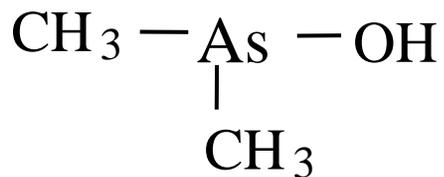
iAs^{III}



MMA^{III}

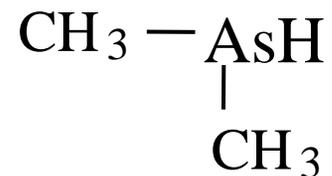
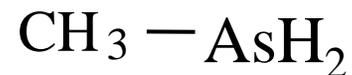


DMA^{III}

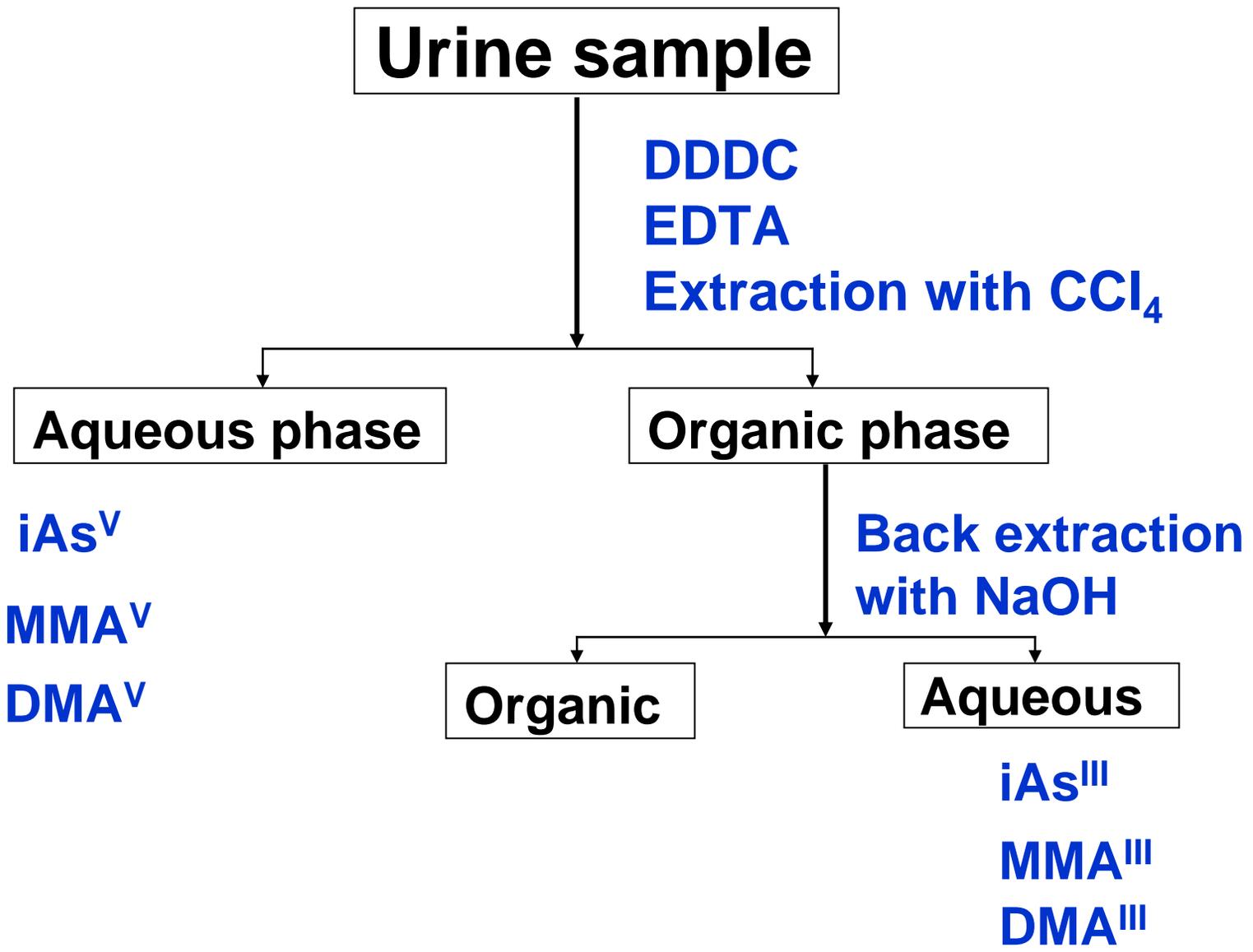


pH 6

Volatile arsines



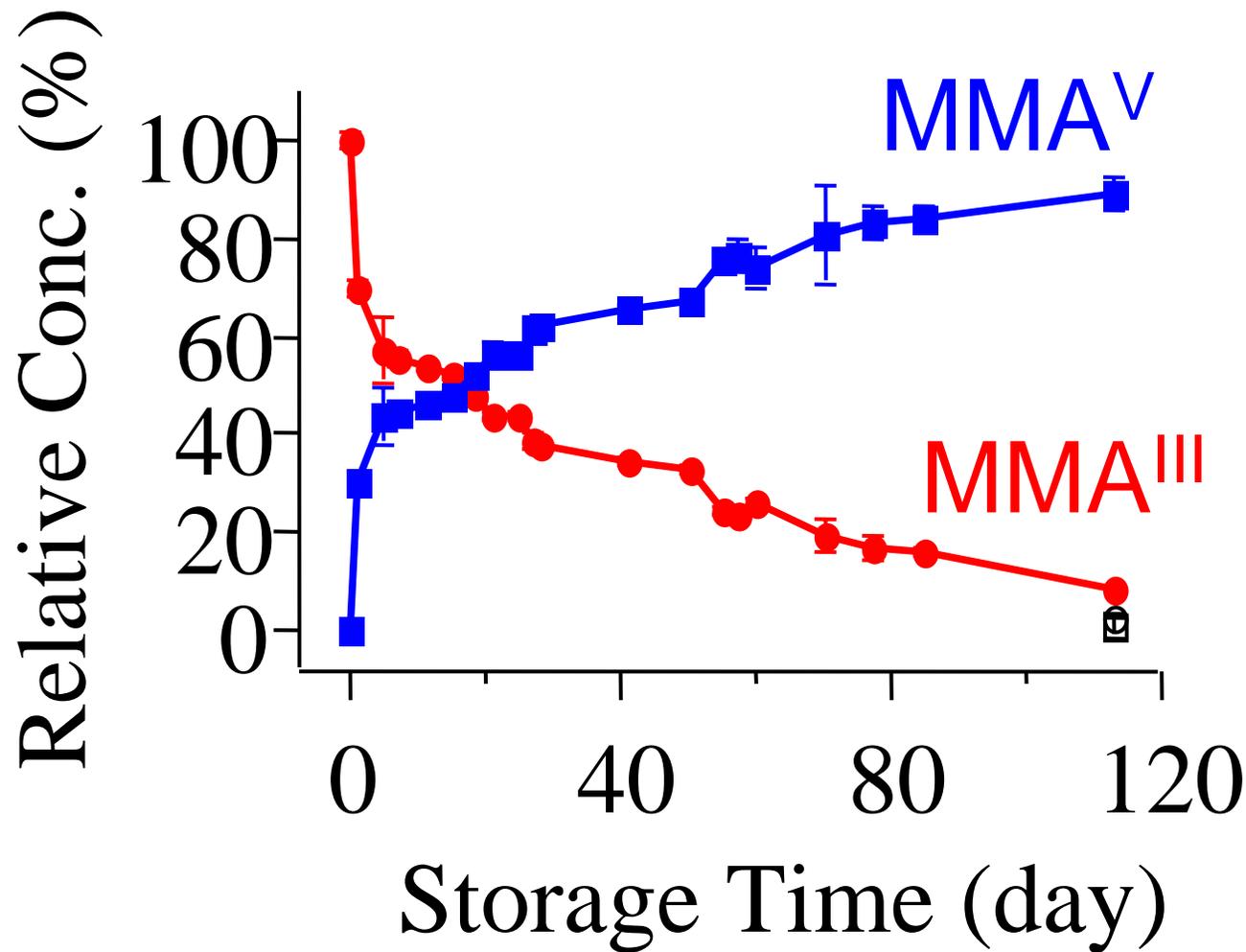
Solvent Extraction



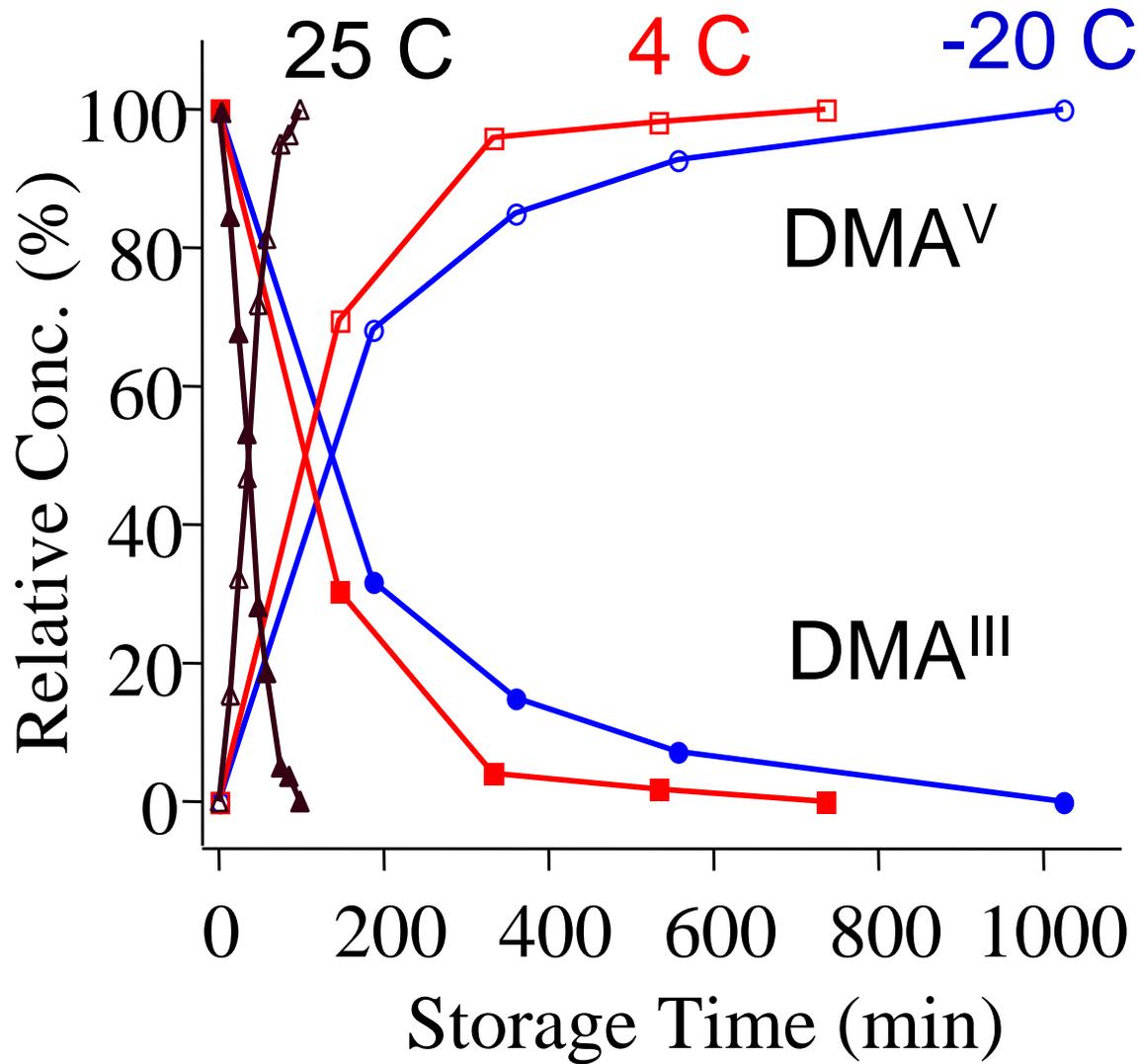
Methods of arsenic speciation analysis

- 1. Direct HPLC separation with ICPMS or HGAFS detection**
 - Least alteration to the sample
 - Ability to analyze new arsenic species
- 2. Selective hydride generation and GC-AAS**
- 3. Selective solvent extraction followed by HPLC-ICPMS**
- 4. Other methods based on chromatography and mass spectrometry**

2. Change of MMA^{III} to MMA^V in spiked urine, stored at -20 °C



Change of DMA^{III} to DMA^V in urine



Valenzuela et al. *Environ. Health Perspect.* 113, 250-254 (2005).

- Morning urine samples
- Immediately frozen on dry ice
- Analyzed within 6 h after collection
- Hydride generation GC-AAS method
- **The highest %DMA^{III} in urine ever reported**

- DMA^{III} 49% DMA^V 23.7% **Sum 72.7%**
- MMA^{III} 7.4% MMA^V 2.8% **Sum 10.2%**
- iAs^{III} 8.5% iAs^V 8.6% **Sum 17.1%**

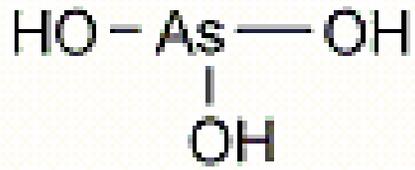
Reasons for the very high concentrations of DMA^{III} in human urine of this Mexico population

- Minimal oxidation of DMA^{III} to DMA^V?
- Stability of DMA^{III} in these urine samples?
- Anything else special about this study population (e.g., diet)?

3. Arsenic species in blood and biological tissues

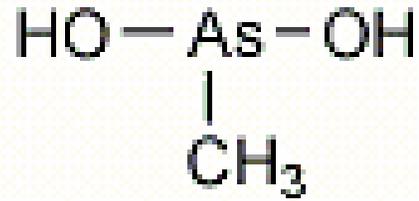
- **Urinary arsenic is a good marker of exposure**
- **Arsenic speciation in other biological samples is useful for studying metabolism and toxicity**
- **Protein interaction with trivalent arsenic metabolites**

iAs^{III}



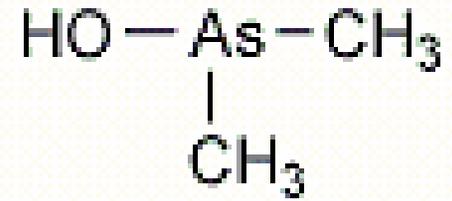
**Inorganic
arsenite**

MMA^{III}

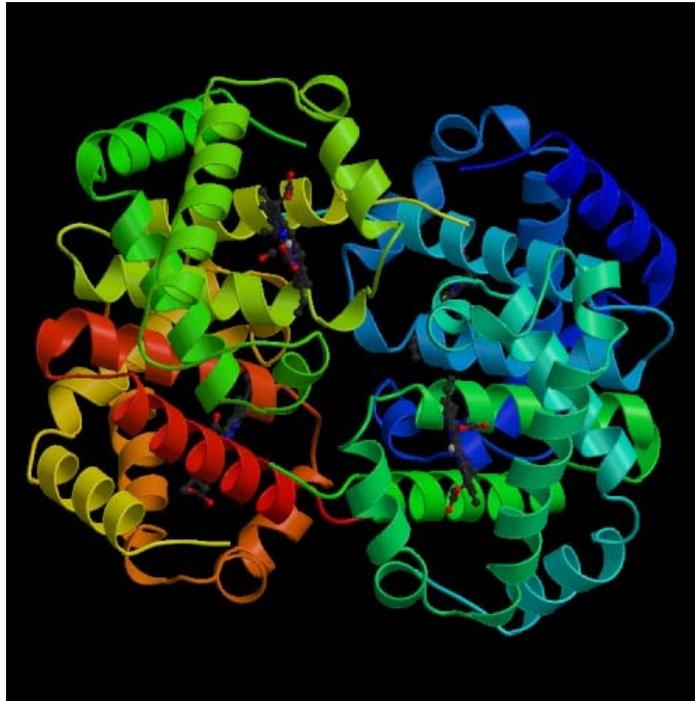


**Monomethylarsonous
acid**

DMA^{III}

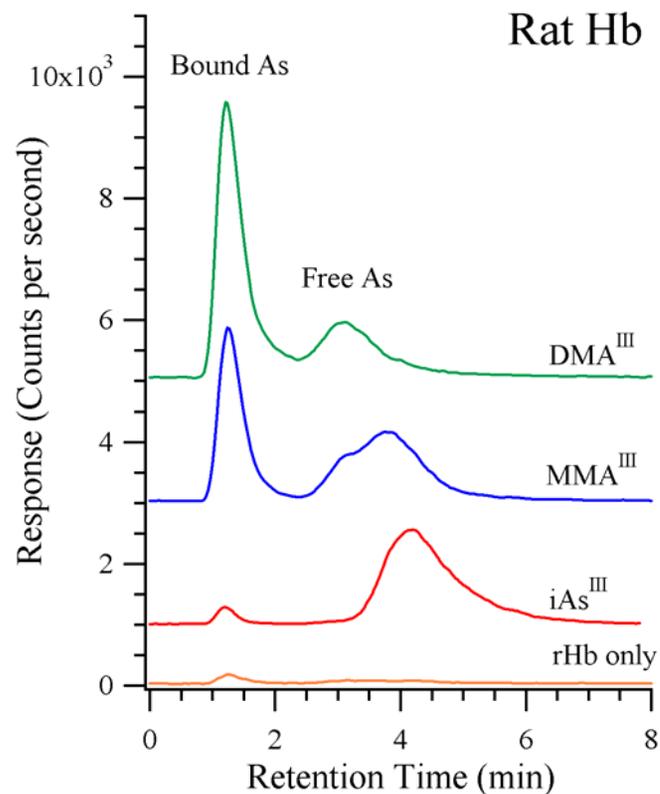
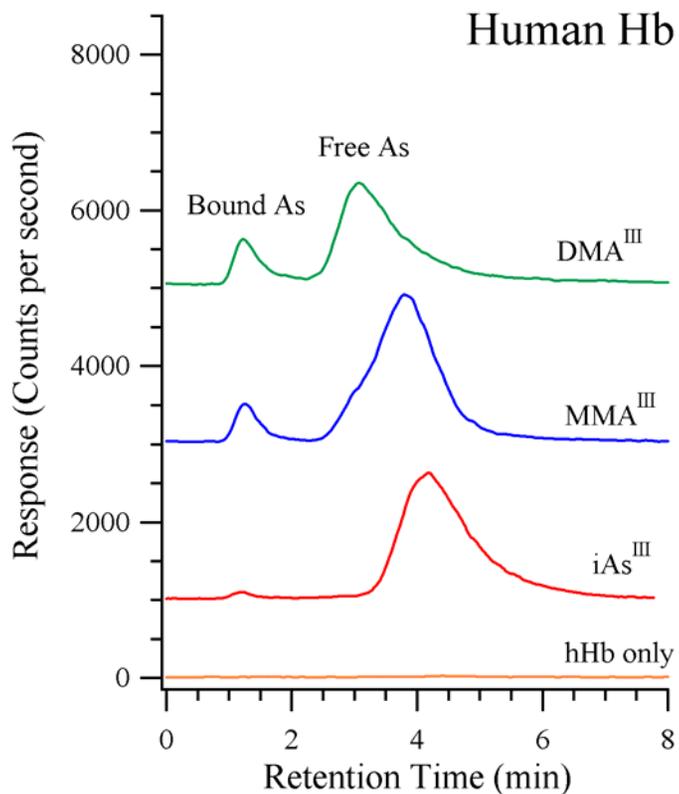


**Dimethylarsinous
acid**



Protein

LC-ICPMS analysis of protein-bound As



4. Unidentified Arsenic Species

- **We can only study what we can measure**
- **Metabolic processes are complex and they produce various metabolites**
 - Human
 - Animal models
 - Bacteria
- **Some metabolites have not been identified and their toxicity is unknown**

Arsenic Speciation Analysis

- 1. Methods for arsenic speciation analysis**
- 2. Problems of species instability**
- 3. Binding of trivalent arsenic metabolites and arsenic in blood**
- 4. Uncharacterized arsenic species**

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