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# Kinetics of As reduction for analysis using hydride-generation

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# Why Use HG-OES

- Detection Limit of HG-OES is comparable with MS
- Elements that form Hydrides: As, Se, Hg, Sb, Bi

Example of As:

Drinking water quality limit (WHO) for As reduced from 50  $\mu\text{g/L}$  to 10  $\mu\text{g/L}$

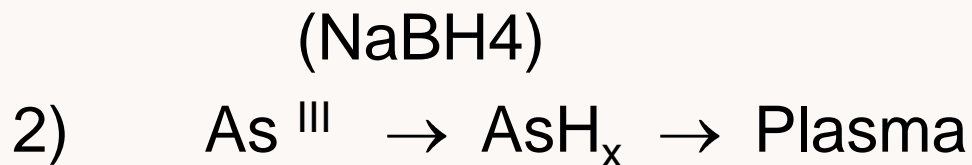
OES	HG-OES	MS
53 <sup>a</sup>	0.5	0.5

Units are in  $\mu\text{g/L}$ ,  $3\sigma$  instrumental DL, <sup>a</sup> USEPA



# Basics of As hydride generation

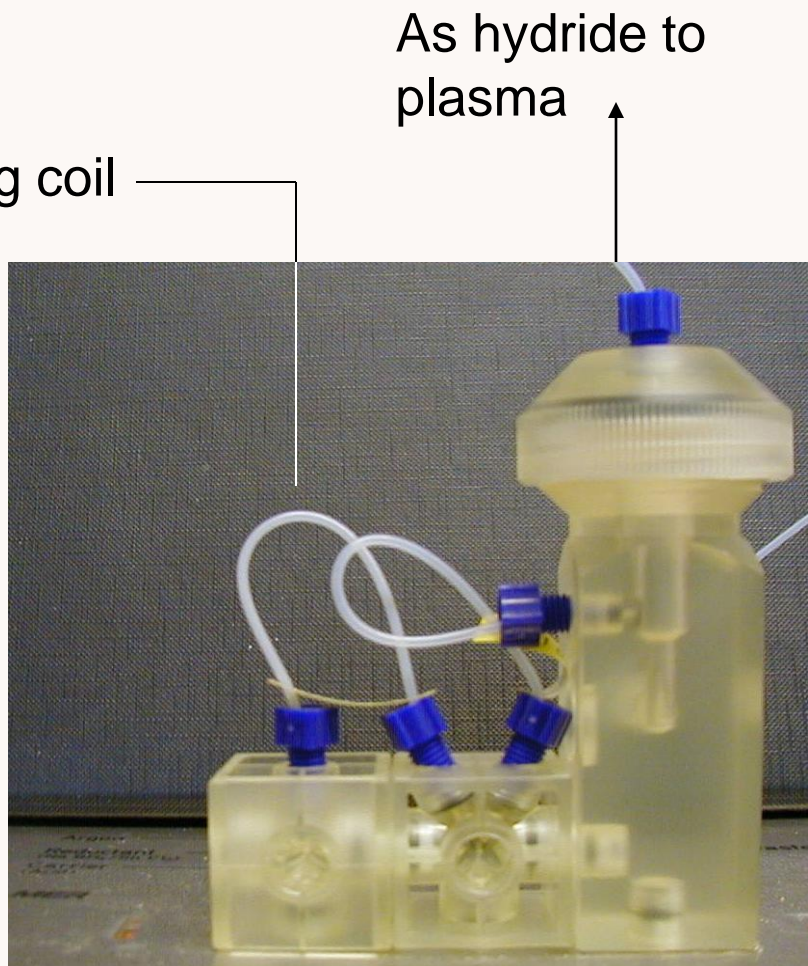
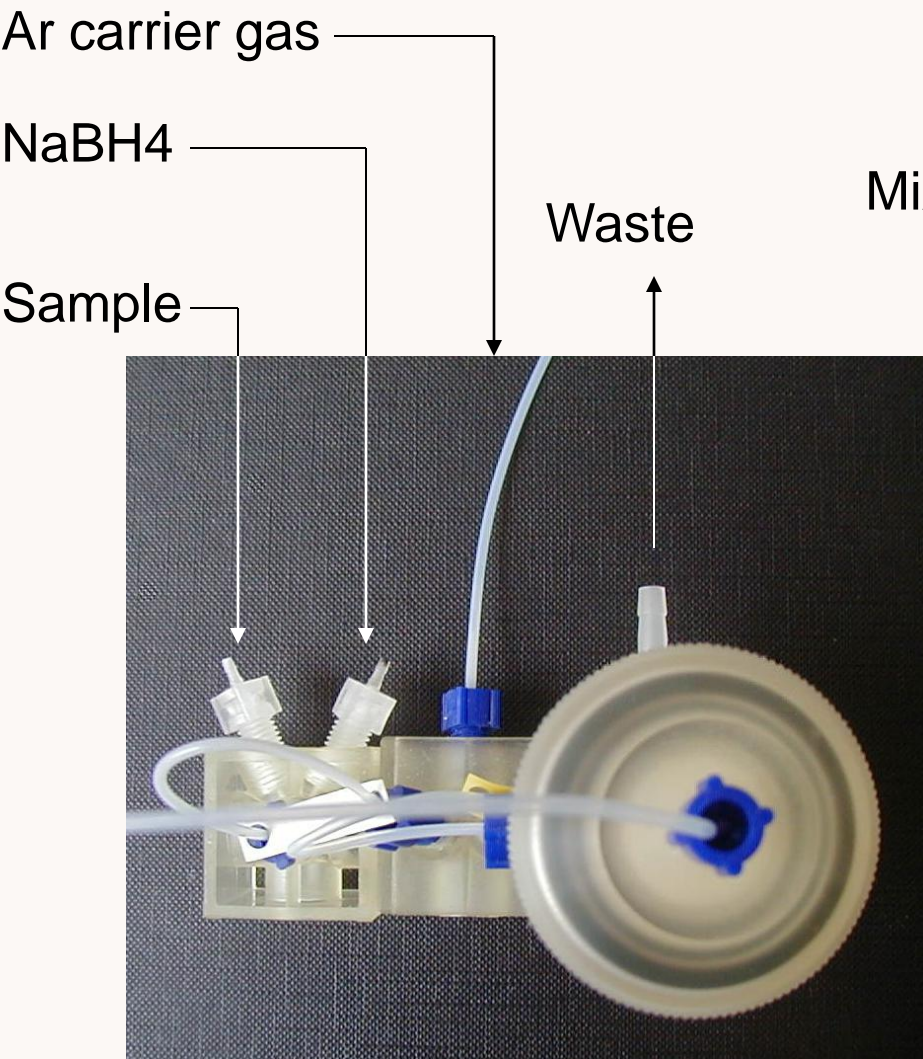
- As III, As V and Organic arsenic species are all hydride forming depending on conditions used
- For total As analysis all As species are reduced to +III oxidation state using KI and then reacted with NaBH<sub>4</sub> to produce a hydride







# The Chemifold



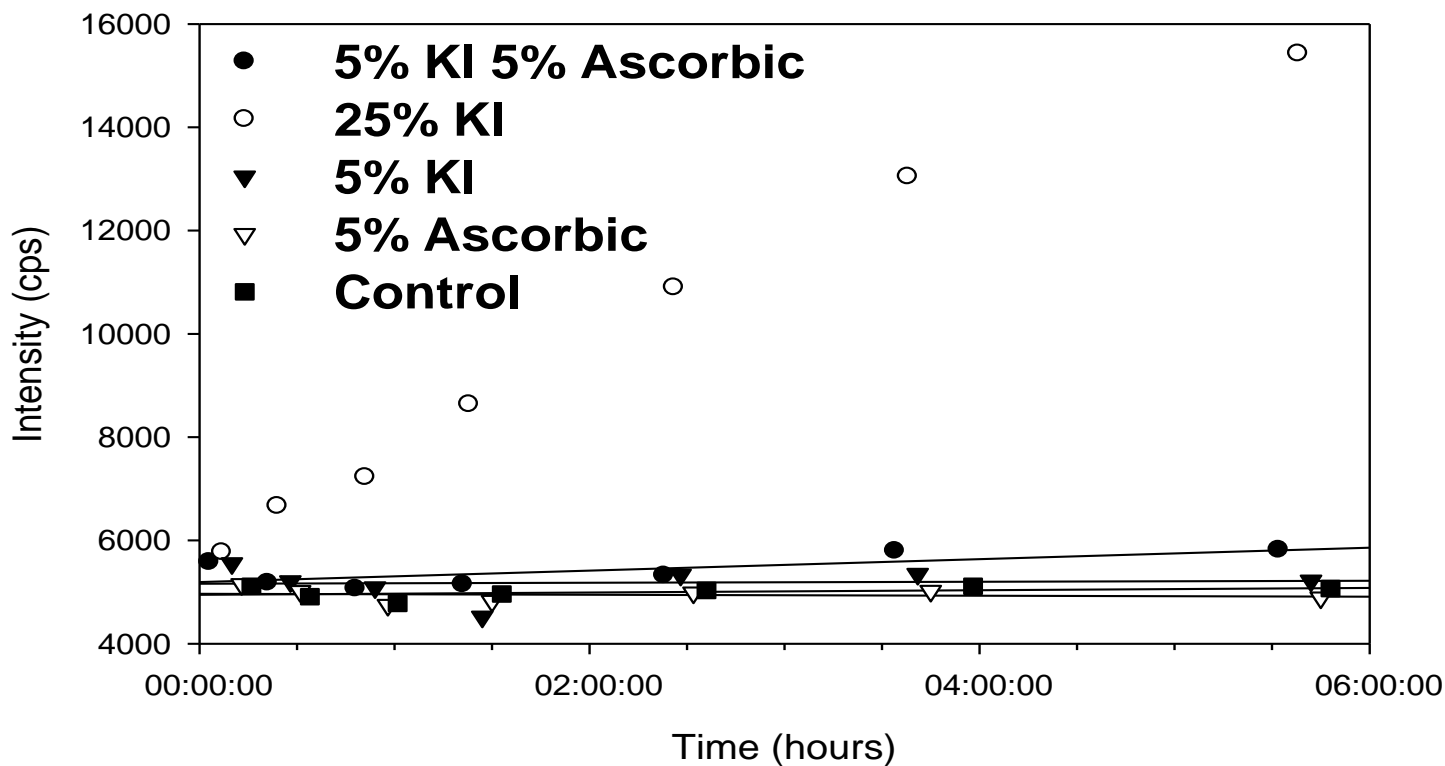


# As Reduction Conditions

Method	KI and Asc (%)	HCl (%)	Reaction time (hours)	Complete (?)
1) PE	0.2 KI 0.2 Asc	0.5	0.25	?
2) PSA	1.0 KI 0.2 Asc	30	0.5	Yes
3) BGS-KW	0.3 KI 0.033 Asc	10	2.0	Yes
4) Other	5.0 KI	2.0	12.0	?
<b>5) Kinetics</b>	<b>0.2 KI</b> <b>0.2 Asc</b>	<b>10</b>	<b>?</b>	<b>?</b>



# Reduction kinetics in dilute HCl matrix

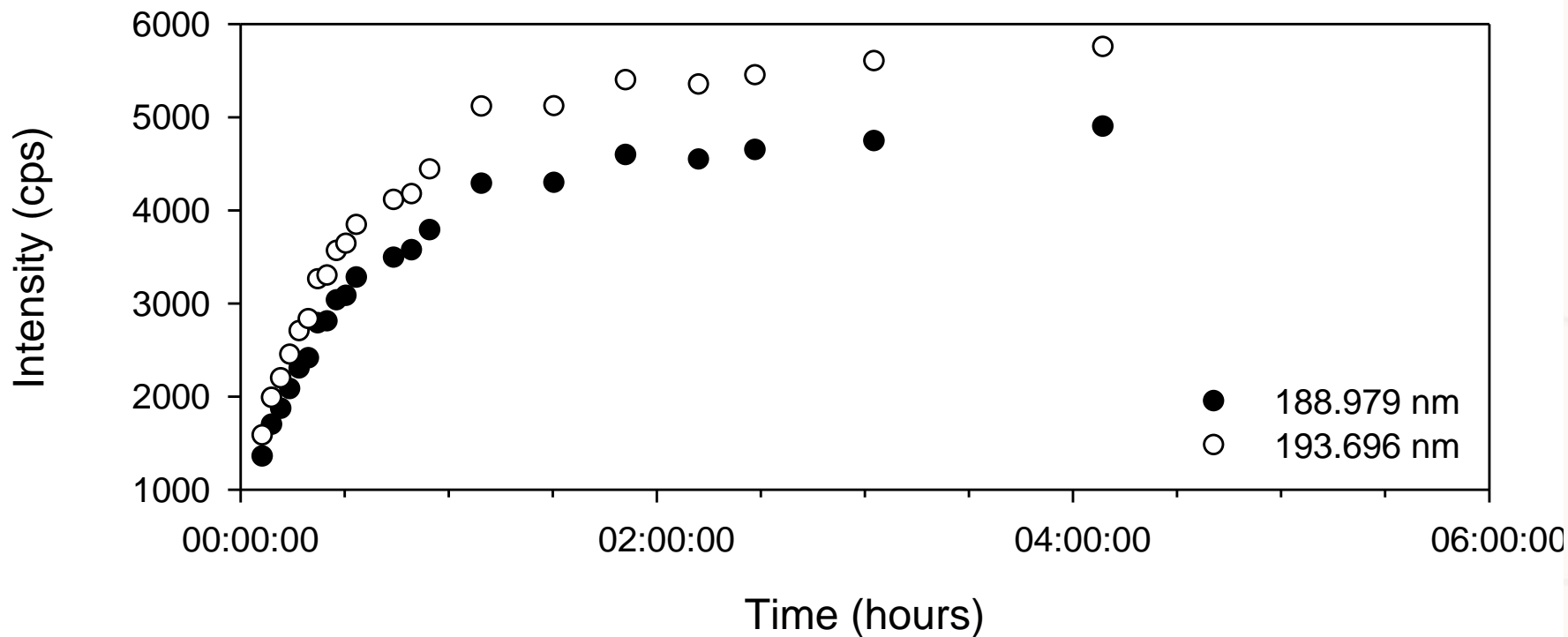


Batch reactions in 2% HCl, using 100 $\mu$ g/L As V





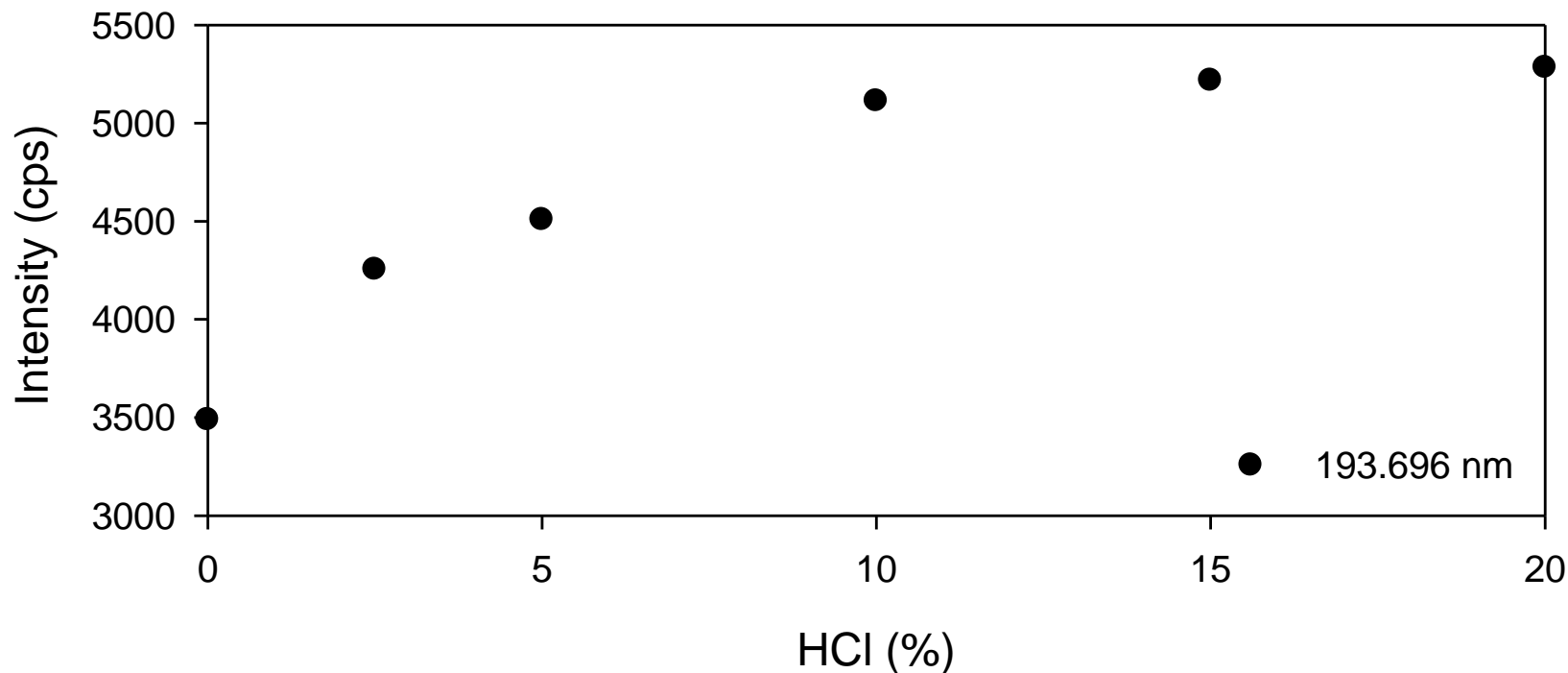
# Reduction kinetics in strong HCl matrix



Batch reaction in 10% HCl, 0.2% KI using 25  $\mu\text{g/L}$  As V



# Acidity: effect on signal intensity



25 $\mu$ g/L As III



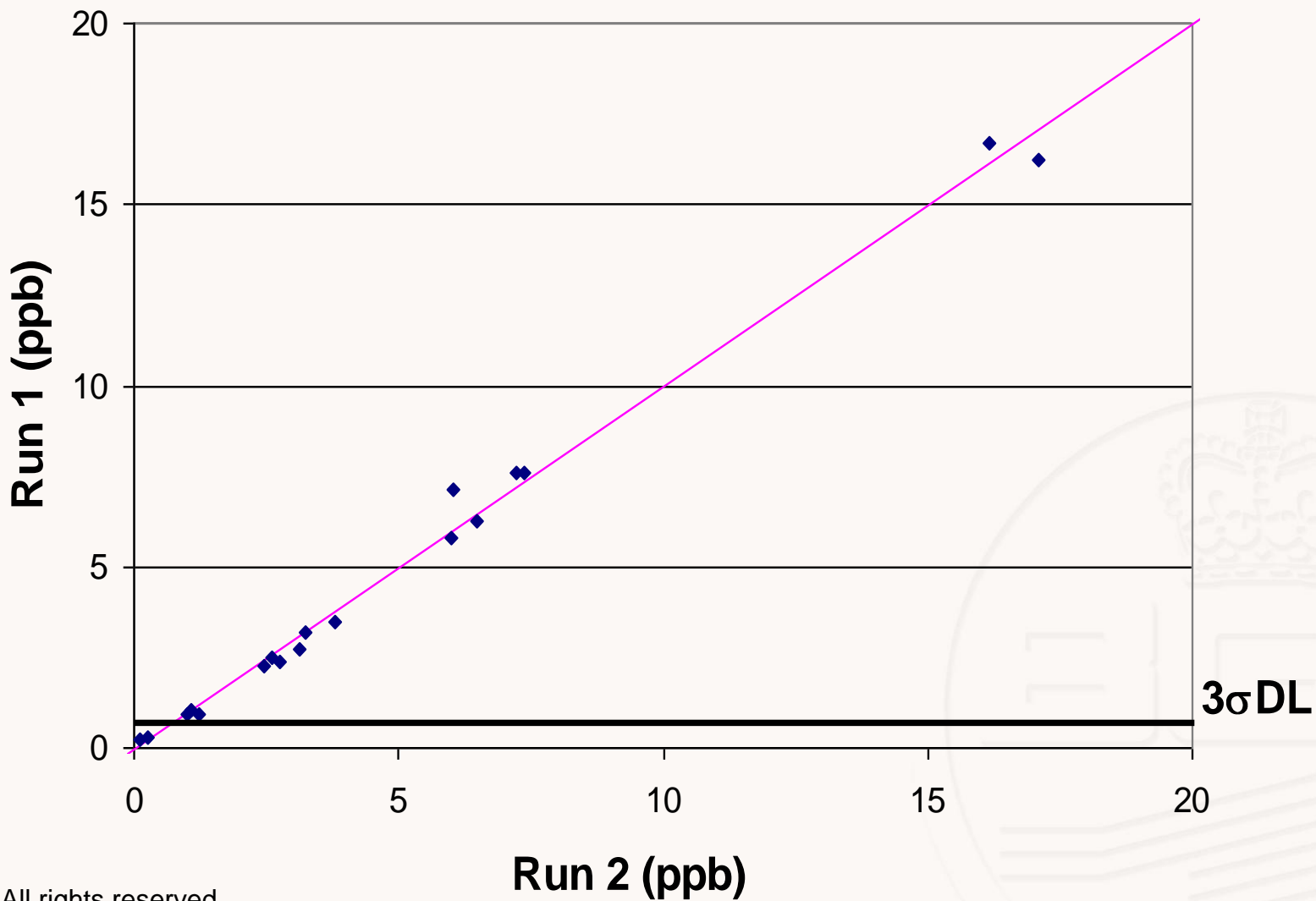


# Optimal Conditions for reduction kinetics

- 10% HCl
  - 1) Fast enough reduction kinetics to carry out on the same day as analysis
  - 2) Optimal signal intensity
  - 3) More economic on HCl use
- Chemifold allows low sample volume, important for some applications e.g. porewater analysis



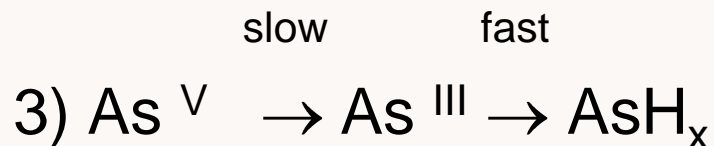
# Cross plot for real samples





# Selectivity for As III

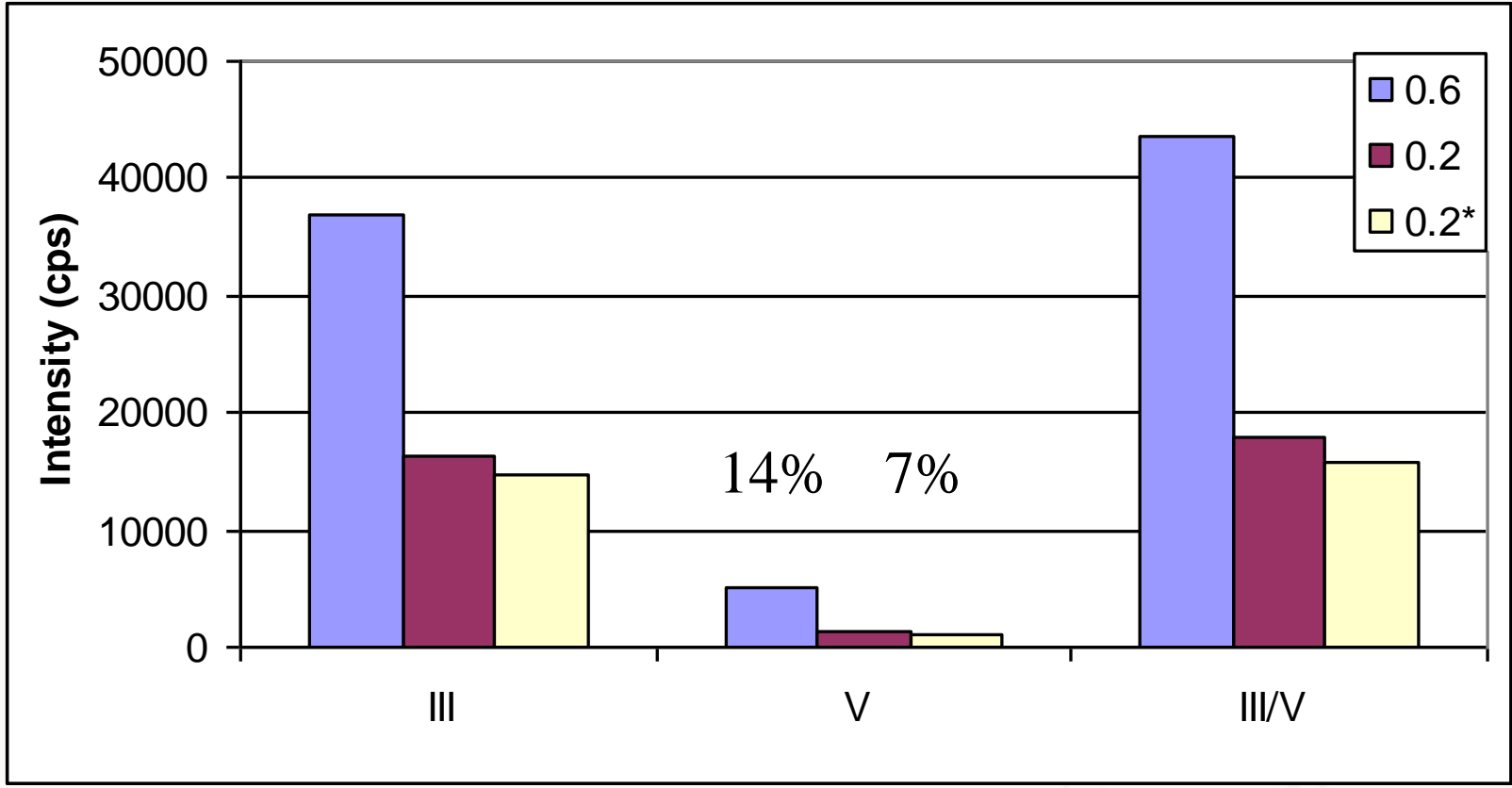
- Difference method employed by labs for calculation of As species
- Acetic acid and citric acid buffers have been reportedly used for the selective reduction of As III by NaBH<sub>4</sub> (assuming that only fully protonated species form hydrides), however As V can still be reduced to As III by NaBH<sub>4</sub>.



- Selectivity using acetic acid was investigated at pH ~6



# Selectivity for As III: acetate buffer



Even using a buffer reduction was still not fully selective





# Final Remarks

- Good method for total As
  - As V reduction by KI is highly dependant on acidity
  - As hydride formation is dependant on acidity and is not selective for As III, therefore calculating As V by difference is not an option
- HG-OES gives a DL for total As comparable with that of MS, ~ 0.5µg/L, with good reproducibility at concentrations close to the detection limit
- Recently started looking at IC-AFS for speciation (does have the limitation of being single element method)
- Speciation could be done using IC-HG-OES if time-resolved integration was possible in the Winlab software



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# Questions

