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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 $\mu\text{g/L}$

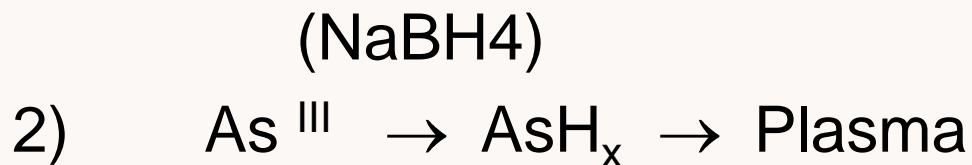
OES	HG-OES	MS
53 ^a	0.5	0.5

Units are in $\mu\text{g/L}$, 3σ instrumental DL, ^a USEPA



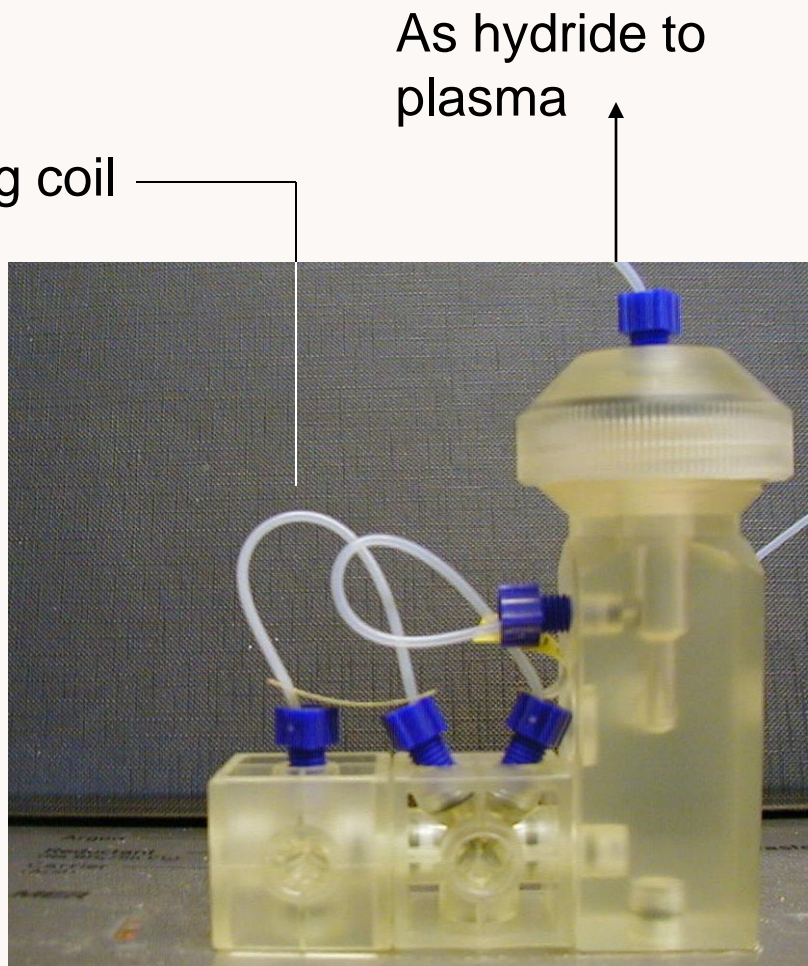
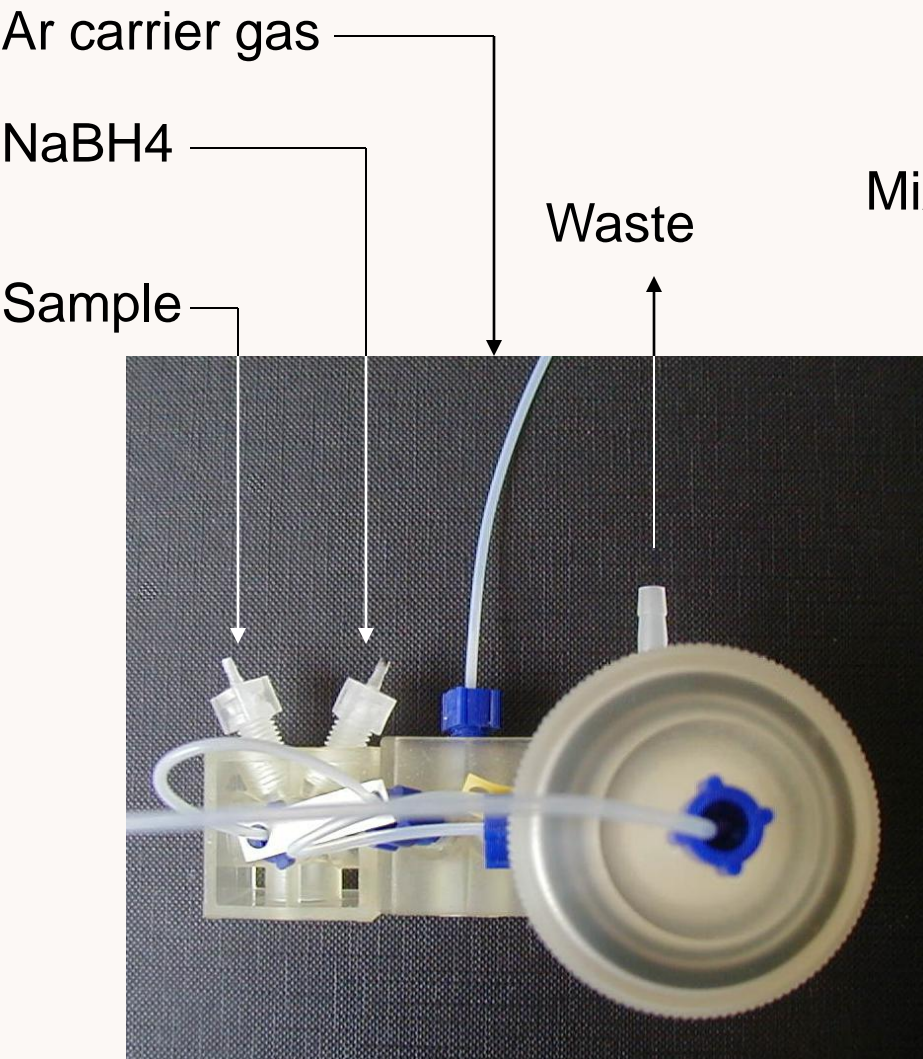
Basics of As hydride generation

- 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 NaBH₄ to produce a hydride





The Chemifold



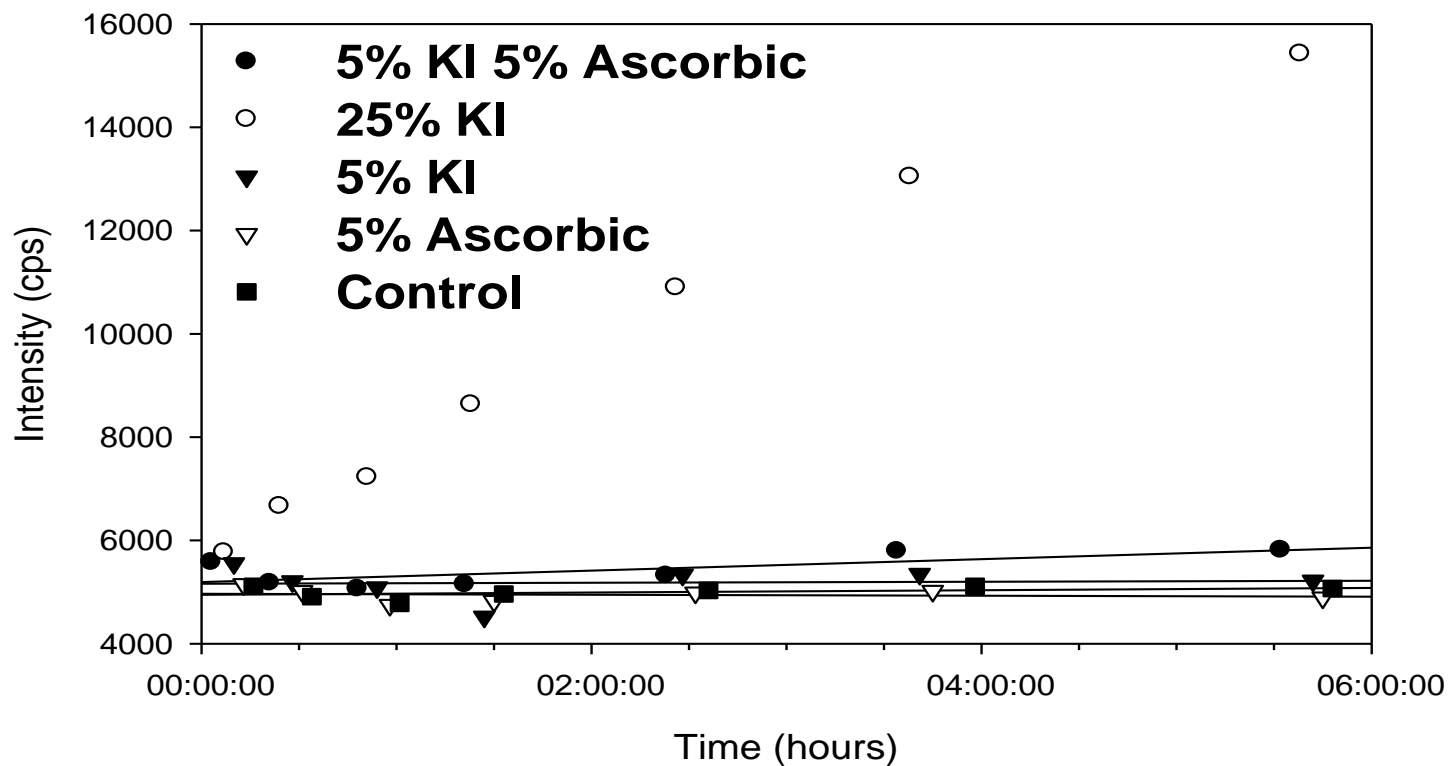


As Reduction Conditions

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	?
5) Kinetics	0.2 KI 0.2 Asc	10	?	?



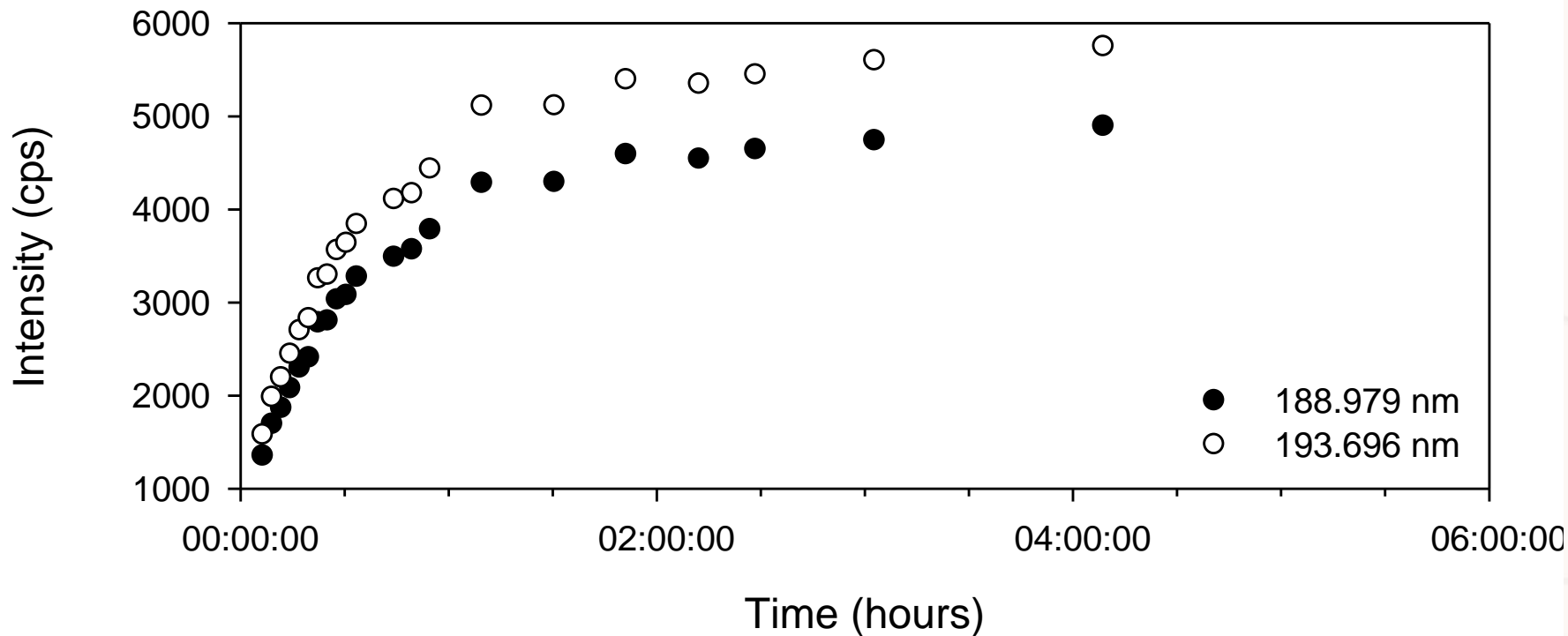
Reduction kinetics in dilute HCl matrix



Batch reactions in 2% HCl, using 100 μ g/L As V



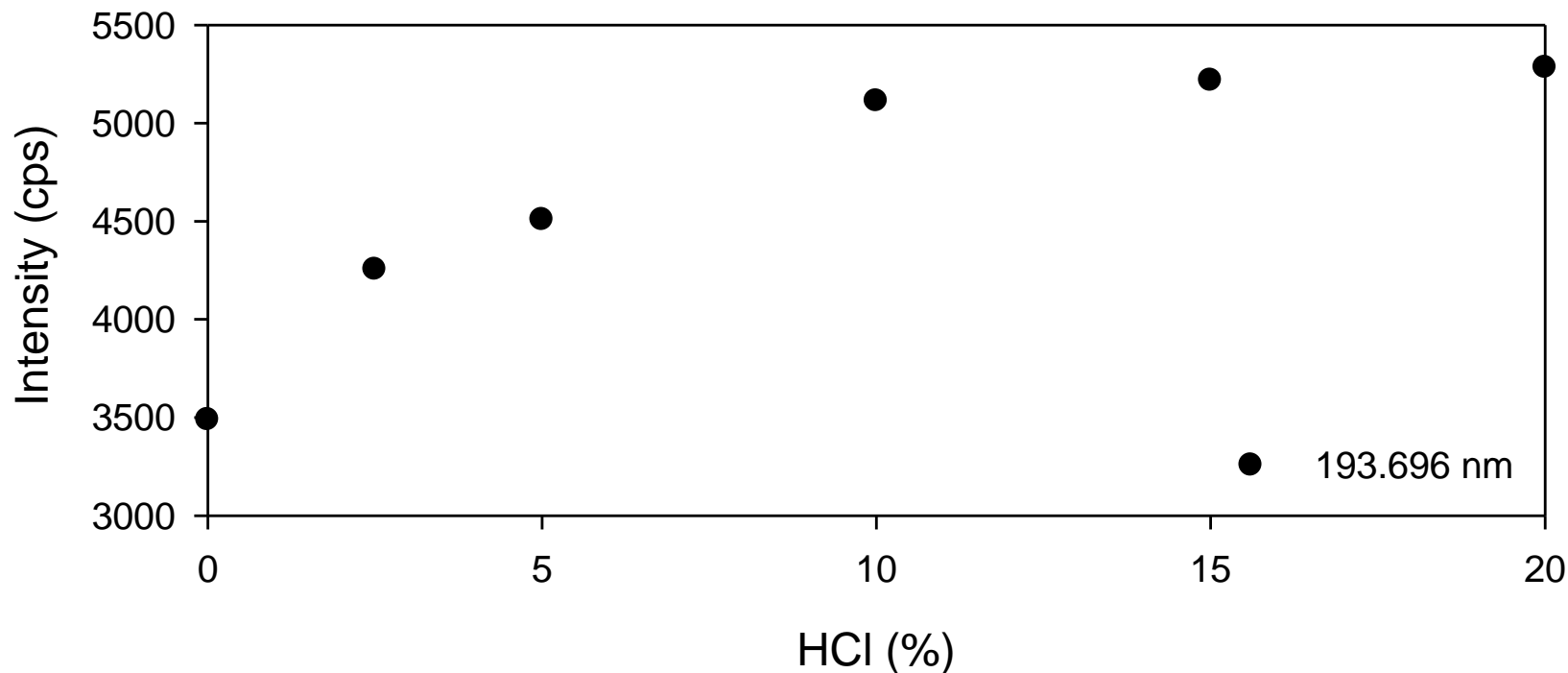
Reduction kinetics in strong HCl matrix



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



Acidity: effect on signal intensity



25 μ g/L As III

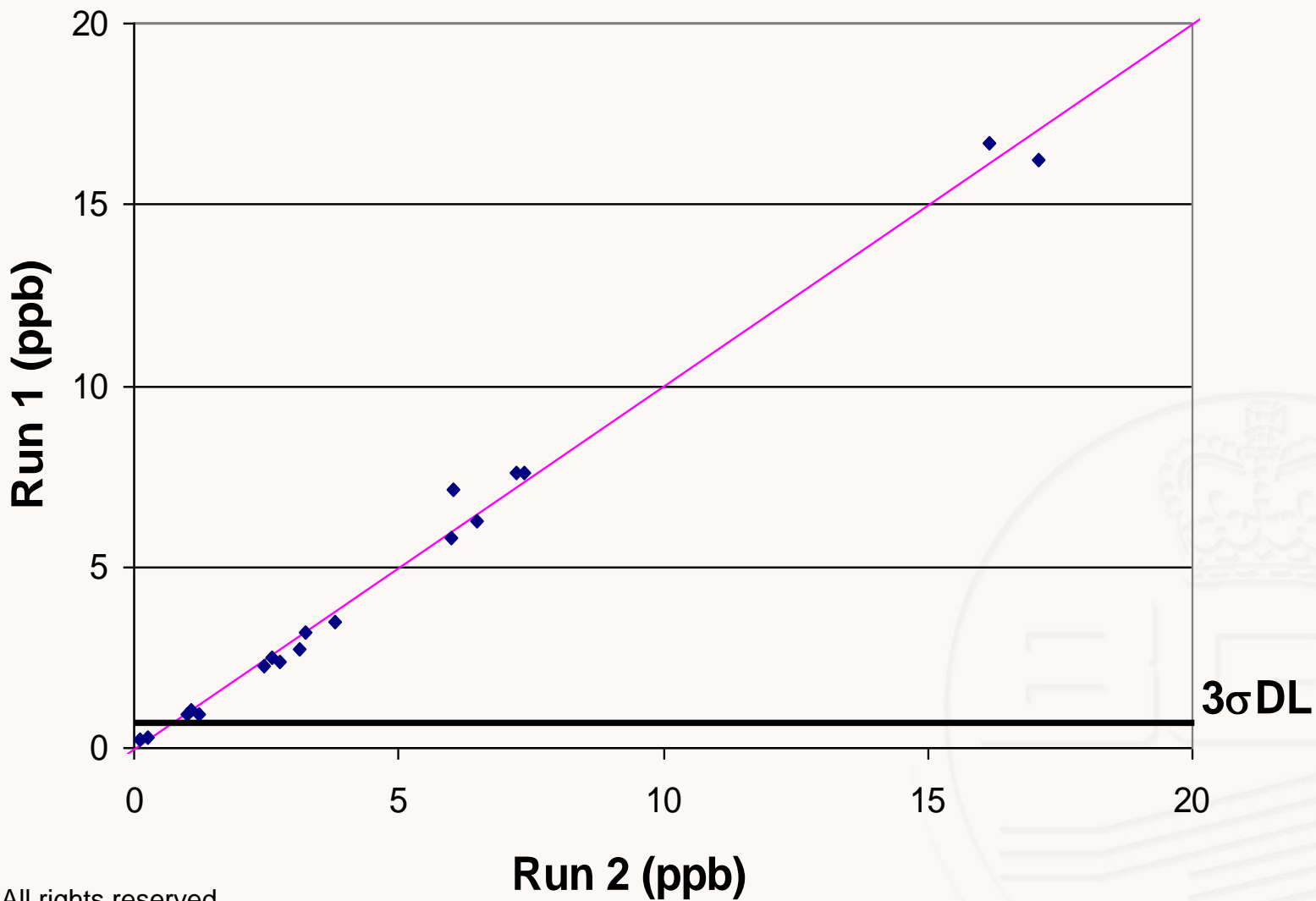


Optimal Conditions for reduction kinetics

- 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



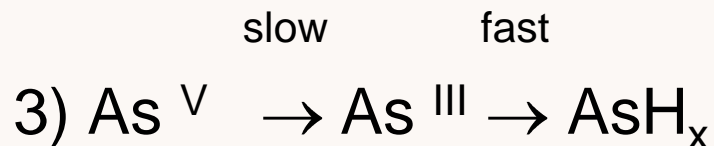
Cross plot for real samples





Selectivity for As III

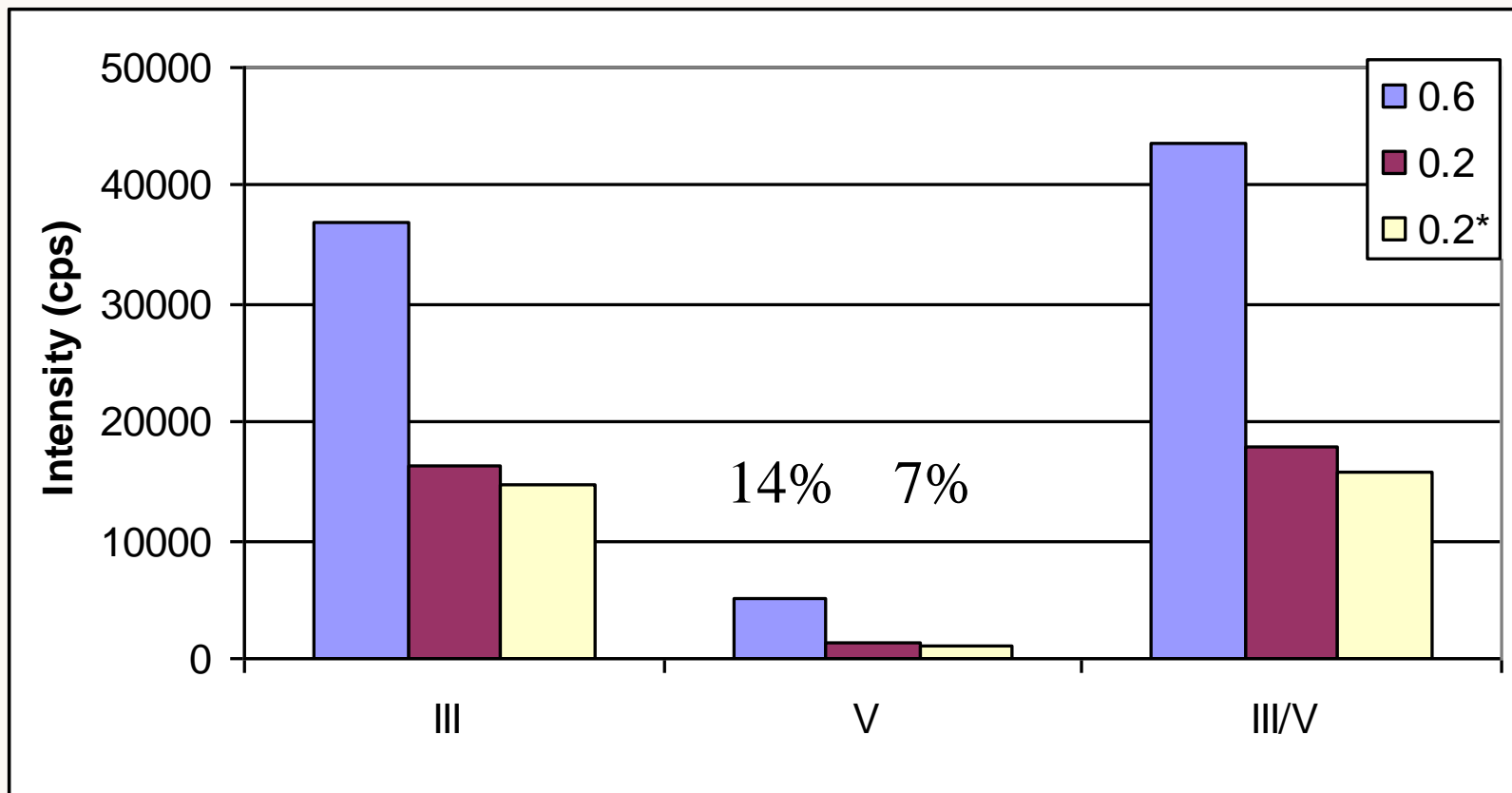
- Difference method employed by labs for calculation of As species
- Acetic acid and citric acid buffers have been reportedly used for the selective reduction of As III by NaBH₄ (assuming that only fully protonated species form hydrides), however As V can still be reduced to As III by NaBH₄.



- 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

