WASHINGTON STATE UNIVERSITY

Development of a novel CE-XRF instrument for elemental speciation of contaminants in complex water systems

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Goal

- *To set up a low power XRF-detection system as an elemental sensitive non-invasive detector for liquid-based separation techniques in complex aqueous matrices.*

- *Once optimized:*
  - *Allow for sensitive & accurate probing of elements in liquid phase separation*
  - *Provide excellent conditions for determining elemental contaminants and their speciation (e.g. Cr, Hg, As, Pb)*
  - *Study of dynamic change in oxidation state during elemental migration*

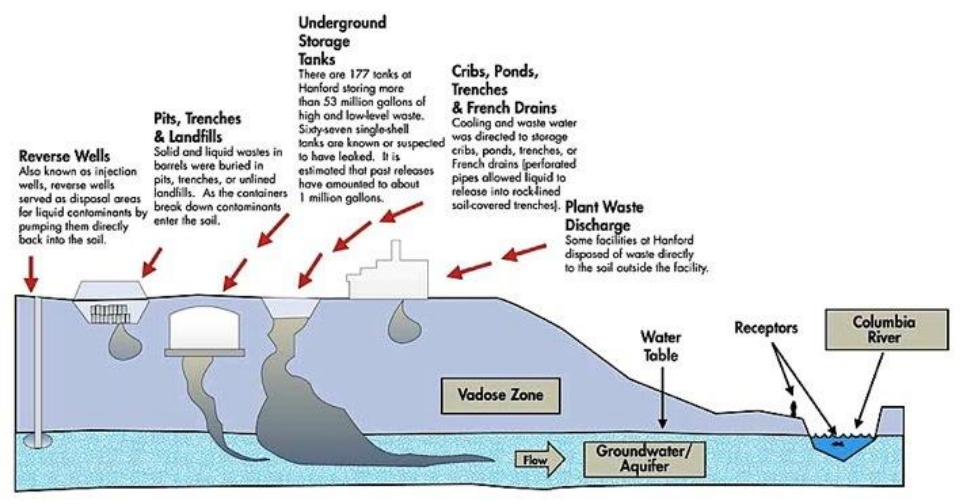
Inspiration

- *Hanford, Washington, USA*
  - *Enriched plutonium*

https://en.wikipedia.org/wiki/Hanford_Site

Problem

- *Contaminated water*
  - *1.7 trillion liters*
  - *320 km downstream*
- *Hg*
- *Cr*
- *U*
- *TC*
- *Sr*
- *As*
- *Cl*
- *F*
- *Nitrates*
- *Sulfates*



http://groundwater.pnl.gov/images/conditions_figure.jpg

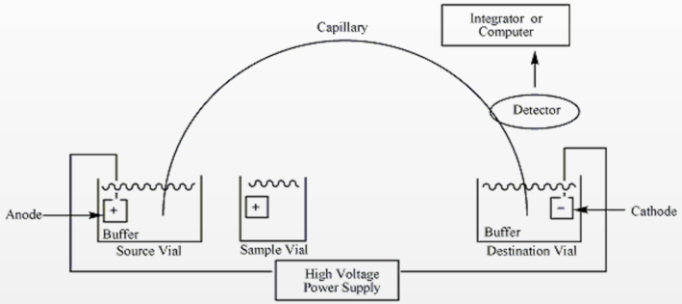
Problem

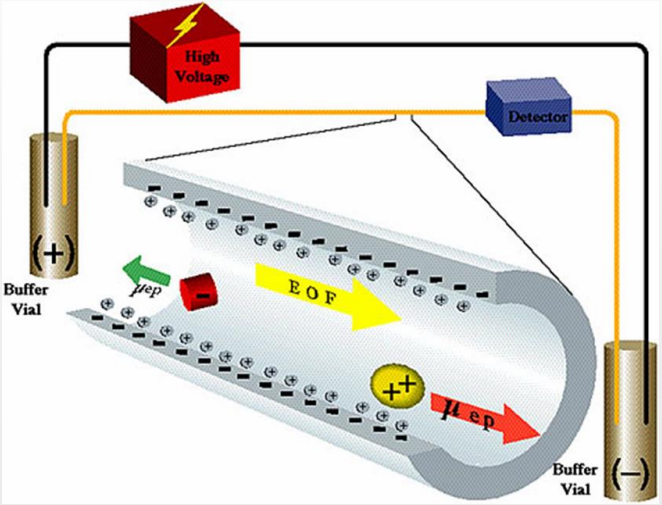
- *The mobilization of an element, as well as its bioavailability and toxicity in the biosphere depends on its chemical form.*

- *On-line species separation and detection is an essential way to elucidate elemental mobilization parameters.*

http://groundwater.pnl.gov/images/conditions_figure.jpg

Capillary Electrophoresis (CE)

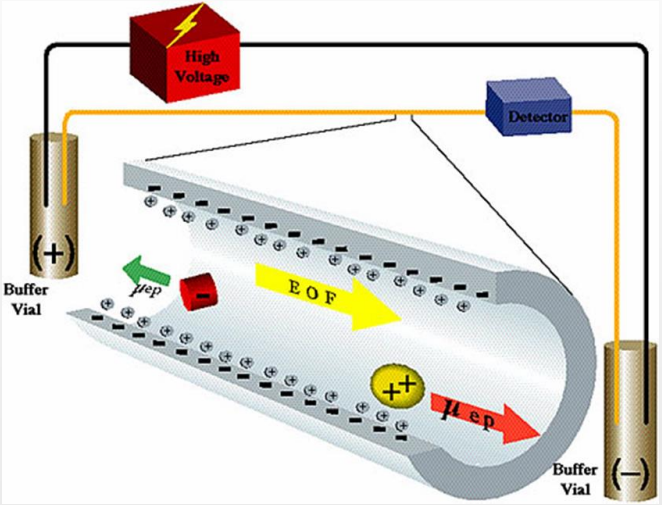




- *High cost-efficiency*
  - *Small volumes*
- *Separates based on electrophoretic mobility*

CE

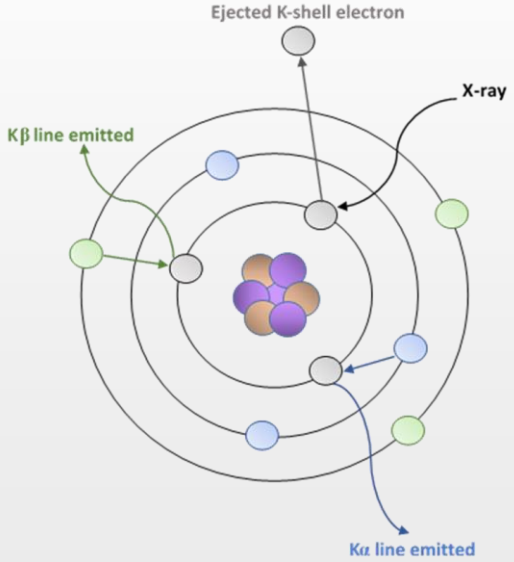
- *No stationary phase*
  - *Short analysis times*
  - *High efficiency*
  - *High N*
  - *Small bandwidths*
  - *Metal-ligand bonds*



CE as an analytical tool for liquids

- *UV-visible*
  - *incapable of detecting inorganic ions or metal complexes due to low absorbance*
- *Inductively coupled plasma mass spectrometry*
  - *Bulky*
  - *Expensive*
  - *Destructive*
  - *Requires physical access to the mobile phase*
  - *Complex interface*

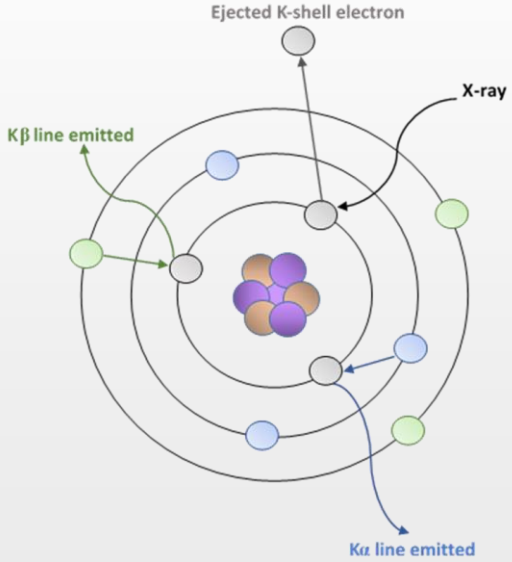
X-Ray Fluorescence (XRF)



- *Elemental sensitive detection*
- *Characteristic X-rays*
- *P to U*
  - *(Ca to U)*

http://wiki.utep.edu/display/~dmarrufo/X-Ray+Fluorescence

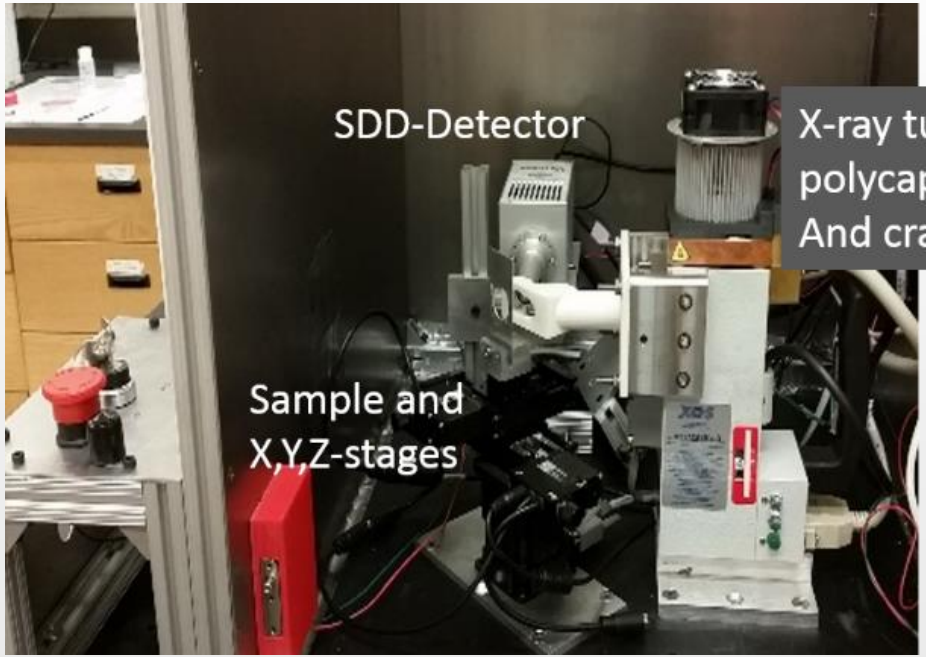
XRF

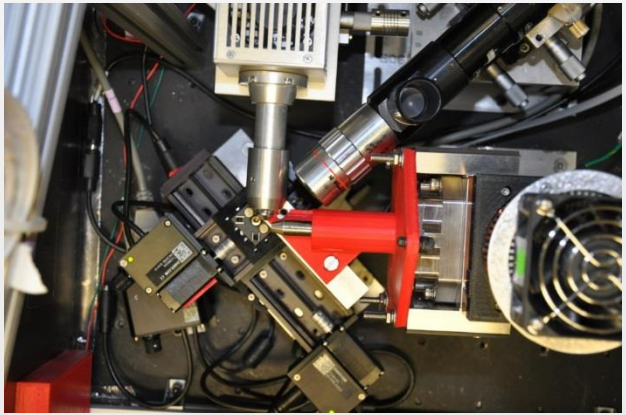


- *High information depth*
- *Small sample amounts*
- *In-situ elemental imaging*
- *Trace elemental analysis*
- *Low cost of sample prep*
- *Quasi nondestructive*

http://wiki.utep.edu/display/~dmarrufo/X-Ray+Fluorescence

Confocal micro-XRF

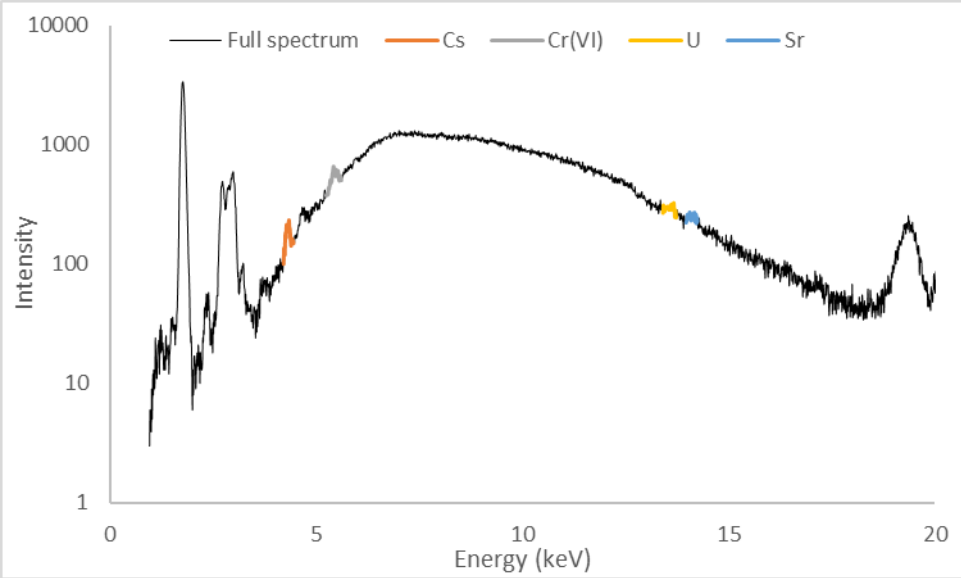




XRF

$$LLD = \frac{3 \times C \times \sqrt{N_{BG}}}{N_i}$$

- *Spectrum of mixture*
  - *Cr(VI)* $K\alpha = 5.412$
  - *Sr* $K\alpha = 14.142$
  - *Cs* $L\alpha = 4.284$
  - *U* $L\alpha = 13.596$



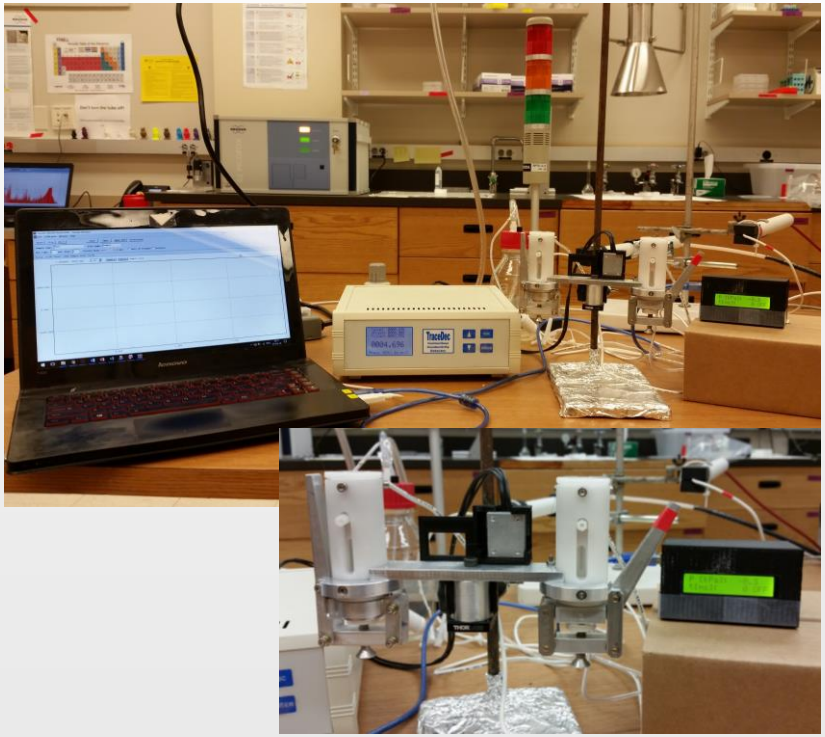
Why CE-XRF?

- *Small footprint*
- *Low cost*
- *Easy to use*
- *Small volumes*
- *Quantitative results*
- *Non-invasive on-line measurements*
- *Simultaneous multi-element detection*

Goals

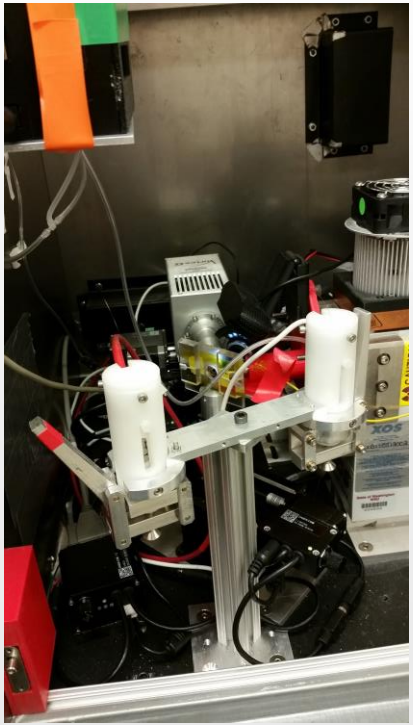
- *Custom-made CE*
- *XRF as detection for CE?*
- *Couple CE and XRF*
  - *Separation*
  - *On-line detection*

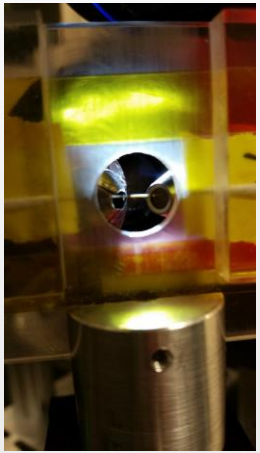
CE-XRF – Initial Setup



- *Hydrodynamic injection*
- *HVPS (0-6 kV)*
- *Capacitively Coupled Contactless Conductivity Detector (C^4D)*

CE-XRF – Initial Setup

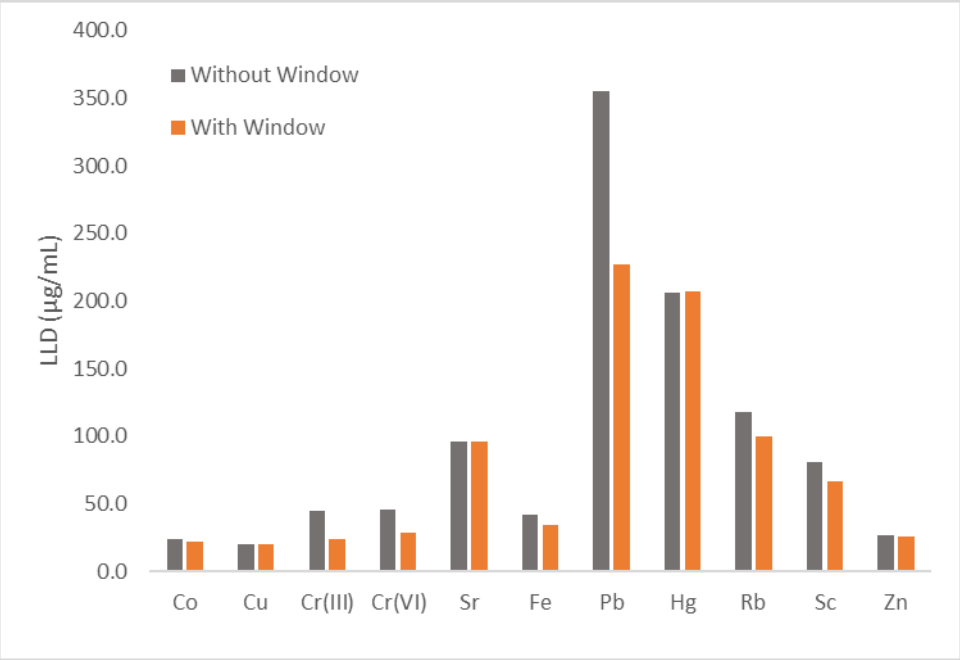




- *Hydrodynamic injection*
- *HVPS (0-30 kV)*
- *CMXRF*

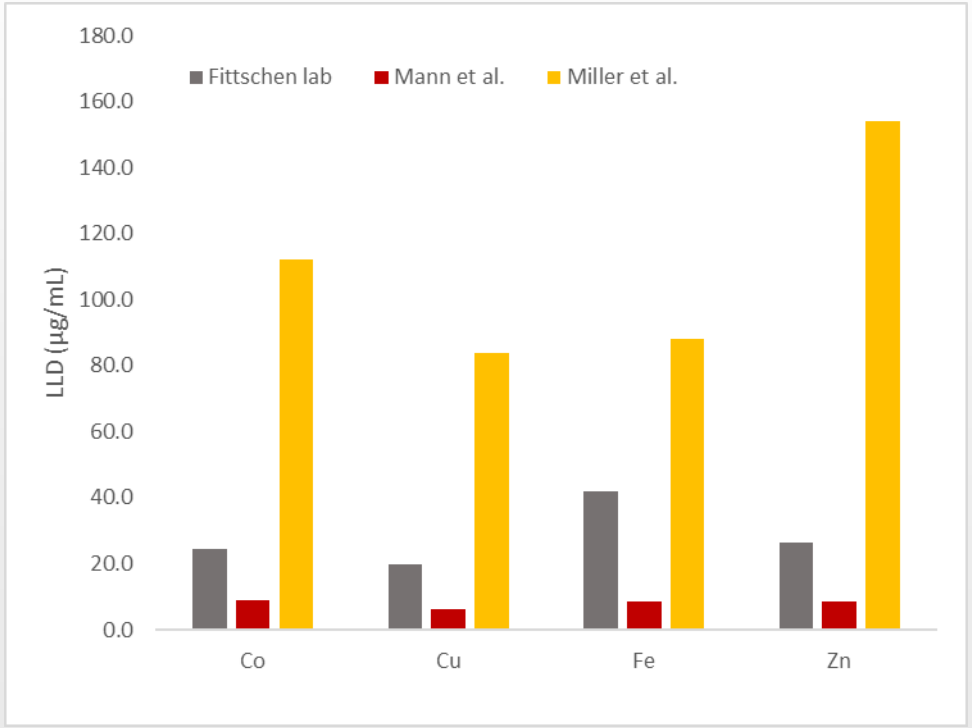
Detection Windows

$$LLD = \frac{3 \times C \times \sqrt{N_{BG}}}{N_i}$$



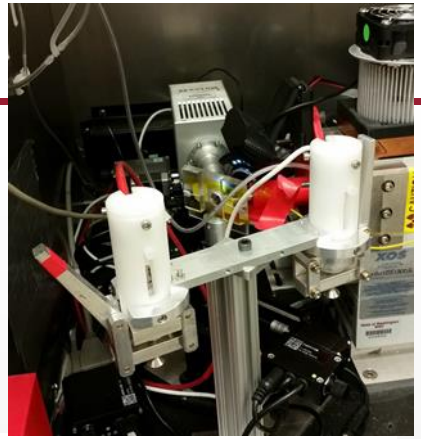
Detection Windows

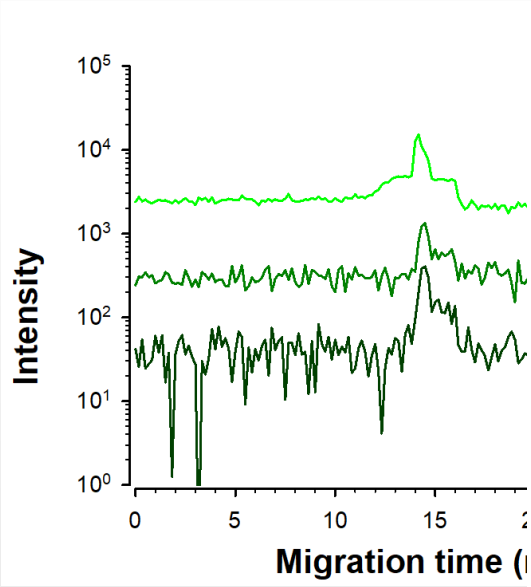
$$LLD = \frac{3 \times C \times \sqrt{N_{BG}}}{N_i}$$

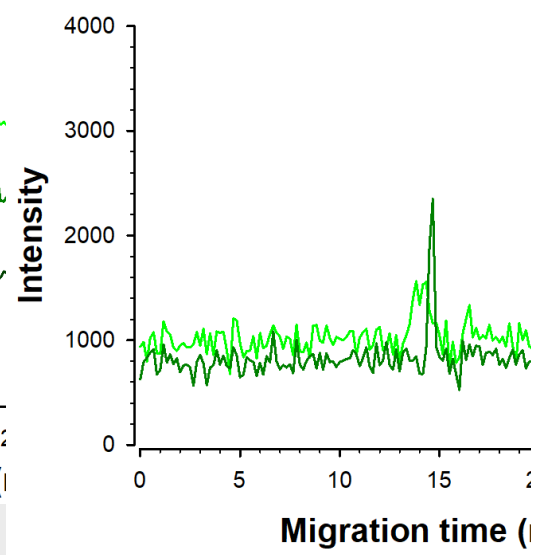


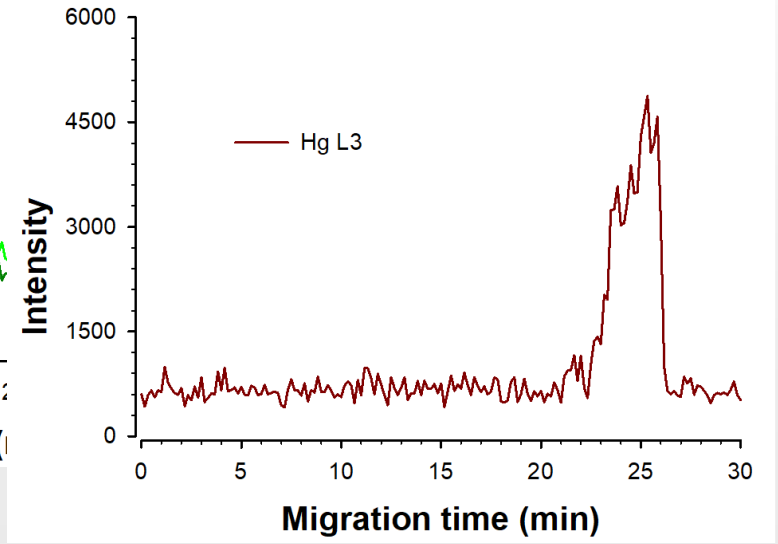
Mann et al. 2000. Anal Chem 72(8):1754-1758.
Miller et al. 2003. Anal Chem 75(9): 2048-2053.

CE-XRF separation

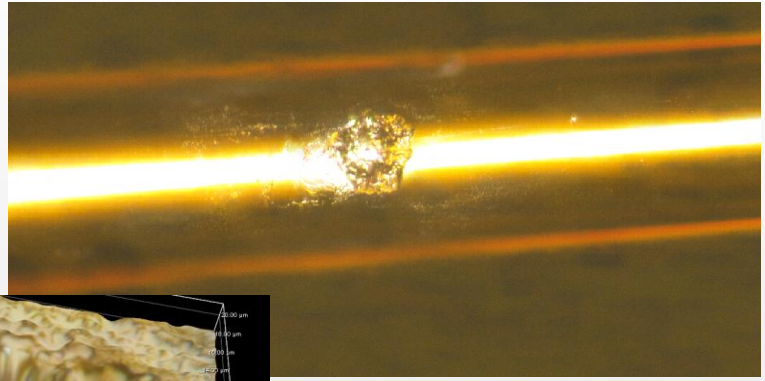


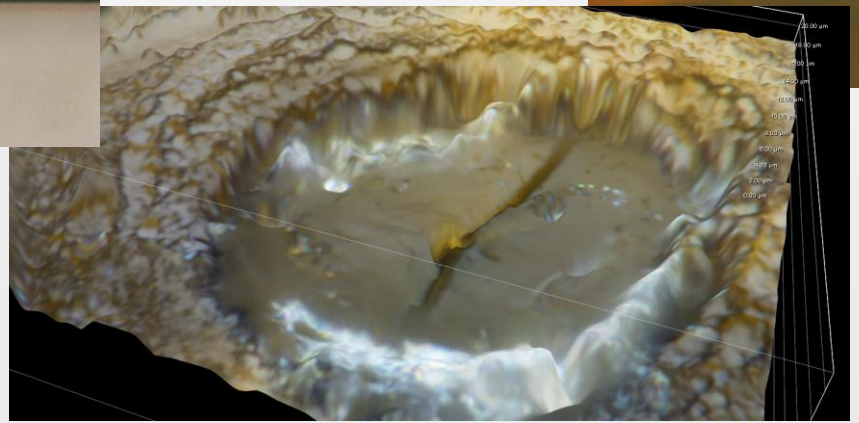






CapEx

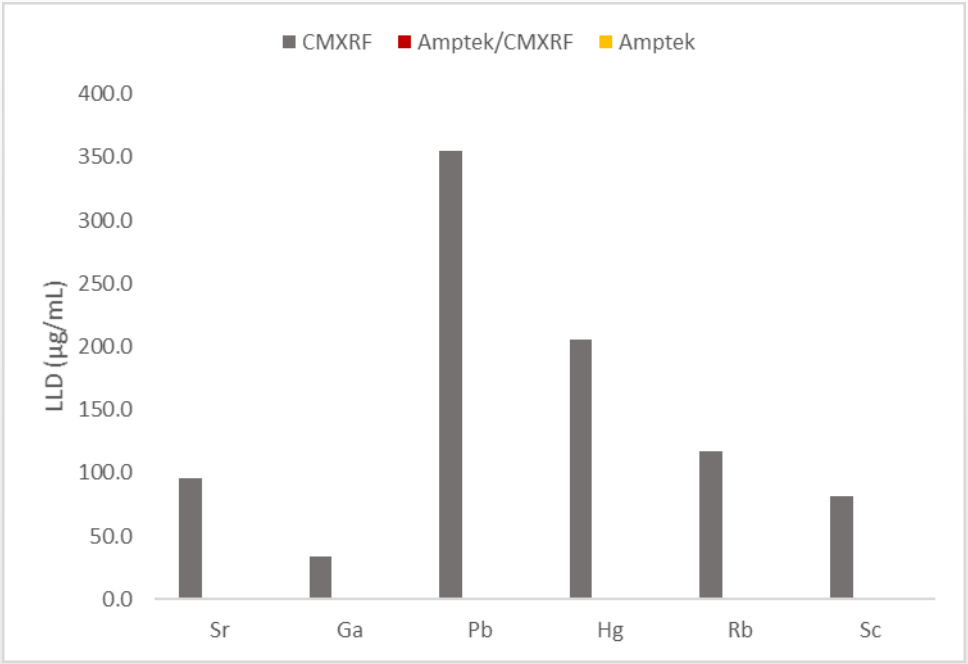




- *Radiolysis?*

X-Ray Sources & Detectors

$$LLD = \frac{3 \times C \times \sqrt{N_{BG}}}{N_i}$$



http://amptek.com/products/mini-x-ray-tube/

Summary

1) *XRF as elemental detection on CE*
   a. *Improved LLD compared to literature*
   b. *Separation and detection feasible*

2) *Feasible to use low cost source and detector*

Future Directions

- *Increase sensitivity*
- *Build an XRF detector for CE and LC*
  - *Low cost*
  - *Small footprint*
  - *Easy to use*
- *High-efficiency detection cell*
- *Method validation*
- *Further applications?*

Acknowledgements

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Lab moving to

TU Clausthal

Clausthal University of Technology