Fenton's Reagent Digestion of Urine for Polonium Analysis

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Radiobioassay & Radiochemical Measurements Conference

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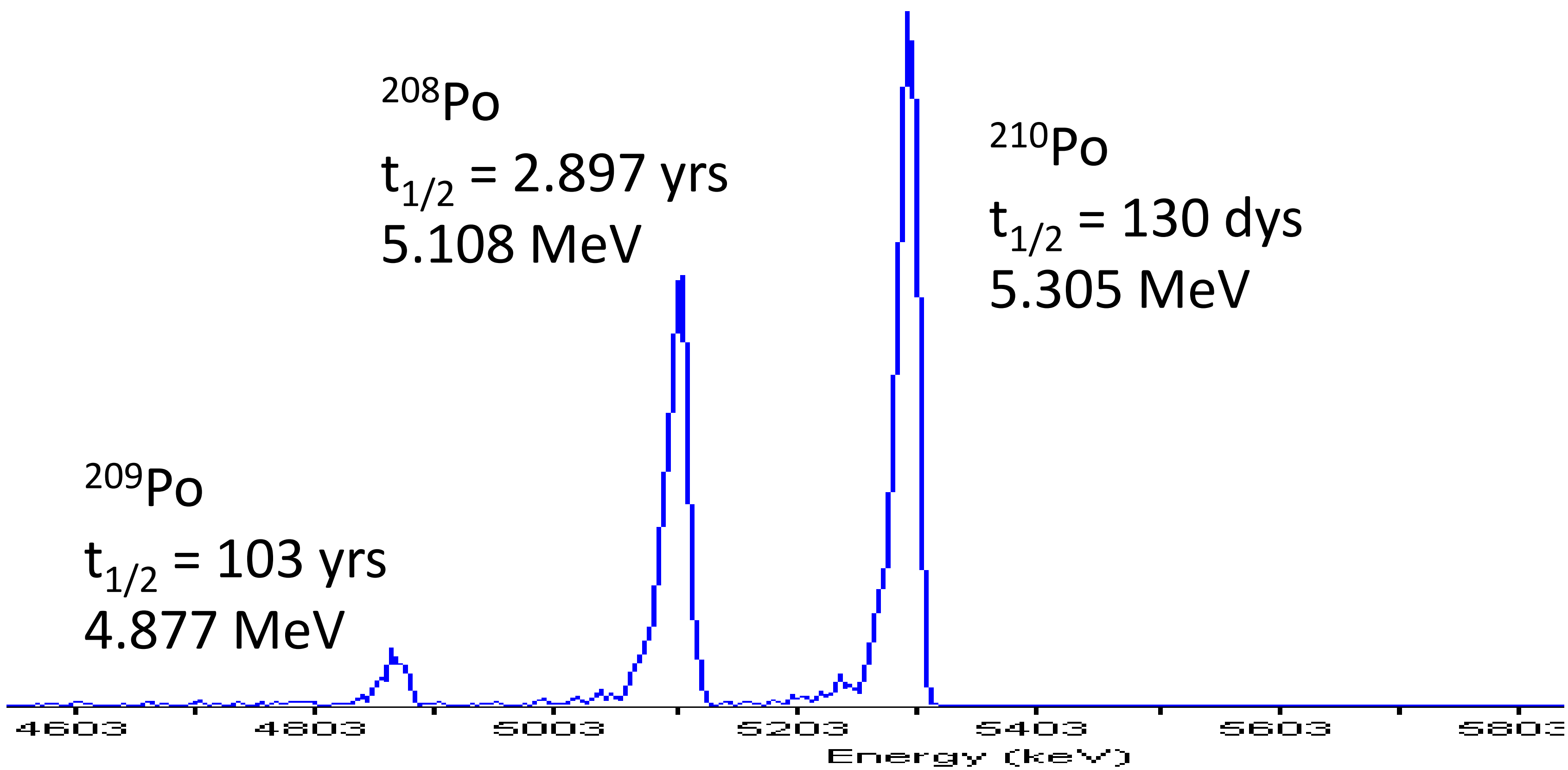
Honolulu, Hawaii

Polonium

Element 84

Po-210 from U-238/Ra-226 Decay

Relatively volatile ($PoCl_4$ sublimes at 200°C)



Biological Studies with Polonium, Radium and Plutonium," R. M. Fink, McGraw-Hill Book Company, New York, 1950

Early Analysis Methods

Lacassagne studied biological distribution of ^{210}Po in rabbits (1924-1938)

Urine boiled with HCl, and Po deposited onto silver foil.

Tissues digested with KClO3 and HCl, and Po deposited onto silver foil.

Only 12% activity balance in excrement and tissues.

Initially concluded that significant losses must occur through respiration of volatile Po species.

Later studies showed that low activity balance due to incomplete recovery of Po. Digestion procedures inadequate.

Better recoveries from urine/tissue digested with HNO3/HClO4 in Kjeldahl flask.

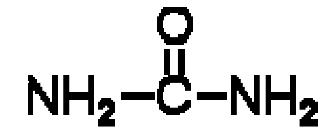
"Only six of 5000 samples caught fire"

Biological Studies with Polonium, Radium and Plutonium," R. M. Fink, McGraw-Hill Book Company, New York, 1950.
A. Lacassagne, J. Lattes, J. Lavedan, *J. Radiol. Electrol*, 9:1, 67 (1925).

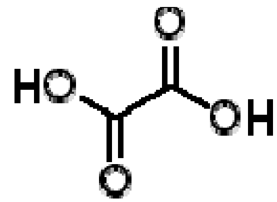
Challenging Matrix

1) Volume: 600- 2500 ml/24 hrs. Average: 1,200 ml.
2) Specific gravity: 1.003 - 1.030
3) (pH: 4.7 - 7.5) Average pH: 6.0
4) Total solids: 30 - 70 g/liter.

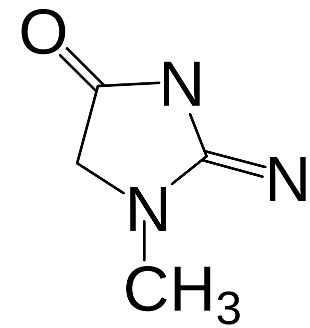
Na^{+} (3-6g)
K^{+} (1-3g)
Ca^{2+} (0.1-0.3g)
PO_4^{3-} (1-2g)
SO_4^{2-} (1-4g)
Mg (40-200mg)
NH_4^{+} (0.3-1g)
I (50-250mg)
Cl^{-} (9-16g)



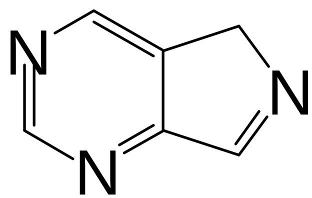
Urea (25-30g)



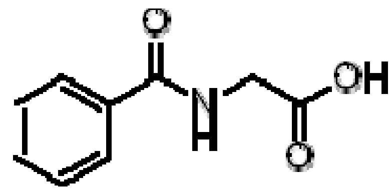
Oxalic acid (15-20mg)



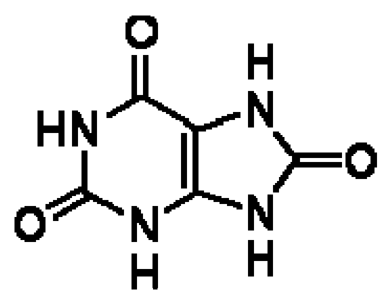
Creatinine (0.5-2g)



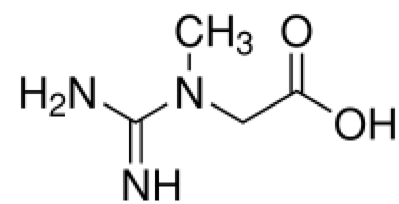
Purine Bases (7-10mg)



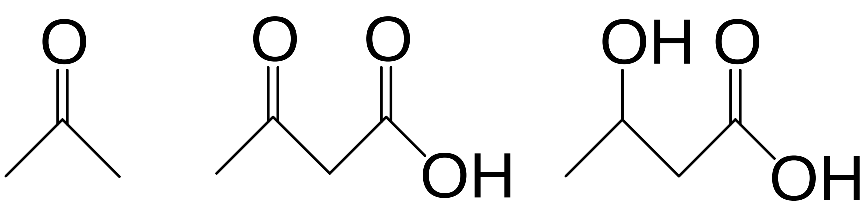
Hippuric acid (0.1-1g)



Uric acid (0.3-1g)



Creatine (0.5-2g)



Ketone Bodies (3-15mg)

Fenton's Reagent

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO\cdot$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\cdot + H^+$$

$$HO\cdot\ R\text{-}H \rightarrow R\cdot + H_2O + \Delta$$

$$\rightarrow COOH \rightarrow CO_2$$

$$\rightarrow NO_3^-$$

$$\rightarrow SO_4^{2-}$$

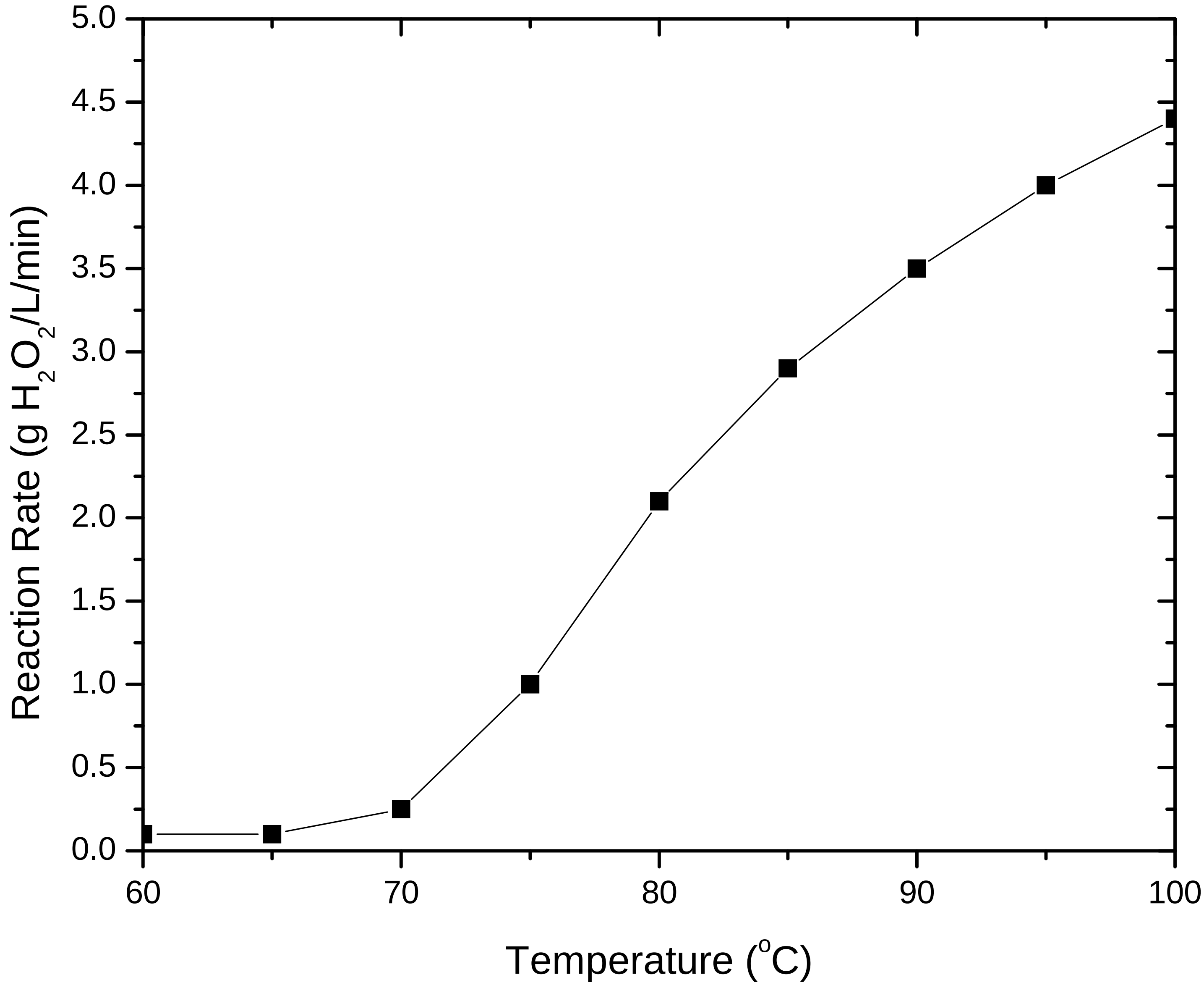
$$2HO\cdot\ H_2O_2 \rightarrow 2H_2O + O_2$$

Fenton's Reagent Revisited, C. Walling, *Accounts of Chemical Research*, 8, 125-131(1975).

Determination of Hg in Water and Urine by Gold Film Sensor Following Fenton's Reagent Digestion, L. Ping, P.K. Dasgupta, *Anal. Chem.*, 61, 1230-1235 (1989).

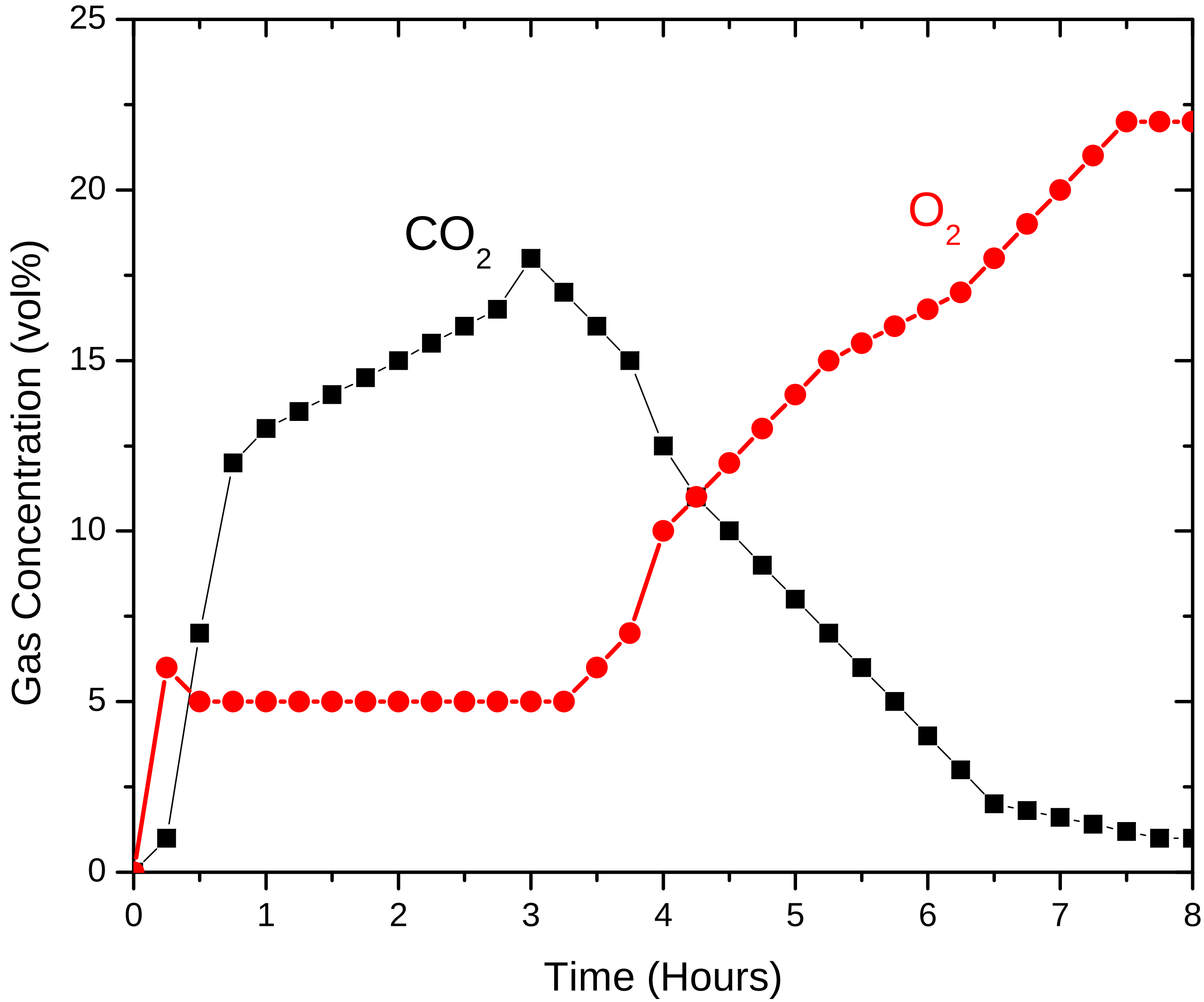
Fenton Digestion of Milk for Iodinalysis, C.P. Shelor, et al., *Anal. Chem.*, 83, 8300-8307 (2011).

Peroxide Consumption vs Temperature



"Destruction of Ion-Exchange Resin in Waste from the HFIR, T1, and T2 Tanks Using Fenton's Reagent," P.A. Taylor, ORNL/TM-2002/197.

Gas Evolution vs Time



"Destruction of Ion-Exchange Resin in Waste from the HFIR, T1, and T2 Tanks Using Fenton's Reagent," P.A. Taylor, ORNL/TM-2002/197.

Application to Urine Digestion

25mL Urine sample in 50 mL polypropylene centrifuge tube

25mg Fe as $Fe(NH_4)_2(SO_4)_2$ → 2mL 0.25M Fe(II) in 2M H_2SO_4

0.25mL conc. H_2SO_4 →

100uL 1-octanol (anti-foam)

5mL cold 30% H_2O_2

Ramp to 65^{o}C over 1hr

Ramp to 85^{o}C over 1hr (Destroy Residual H_2O_2)

Chemical separation or direction autodeposition on copper

Note: For safety, loosely cap vials to allow off-gassing. Digest in well vented area/hood.

Timeline

Qualitative Cold Tests (Color/Smell/Residue)

Spike Fresh/Aged Urine (High Level Po-210 by LSC)

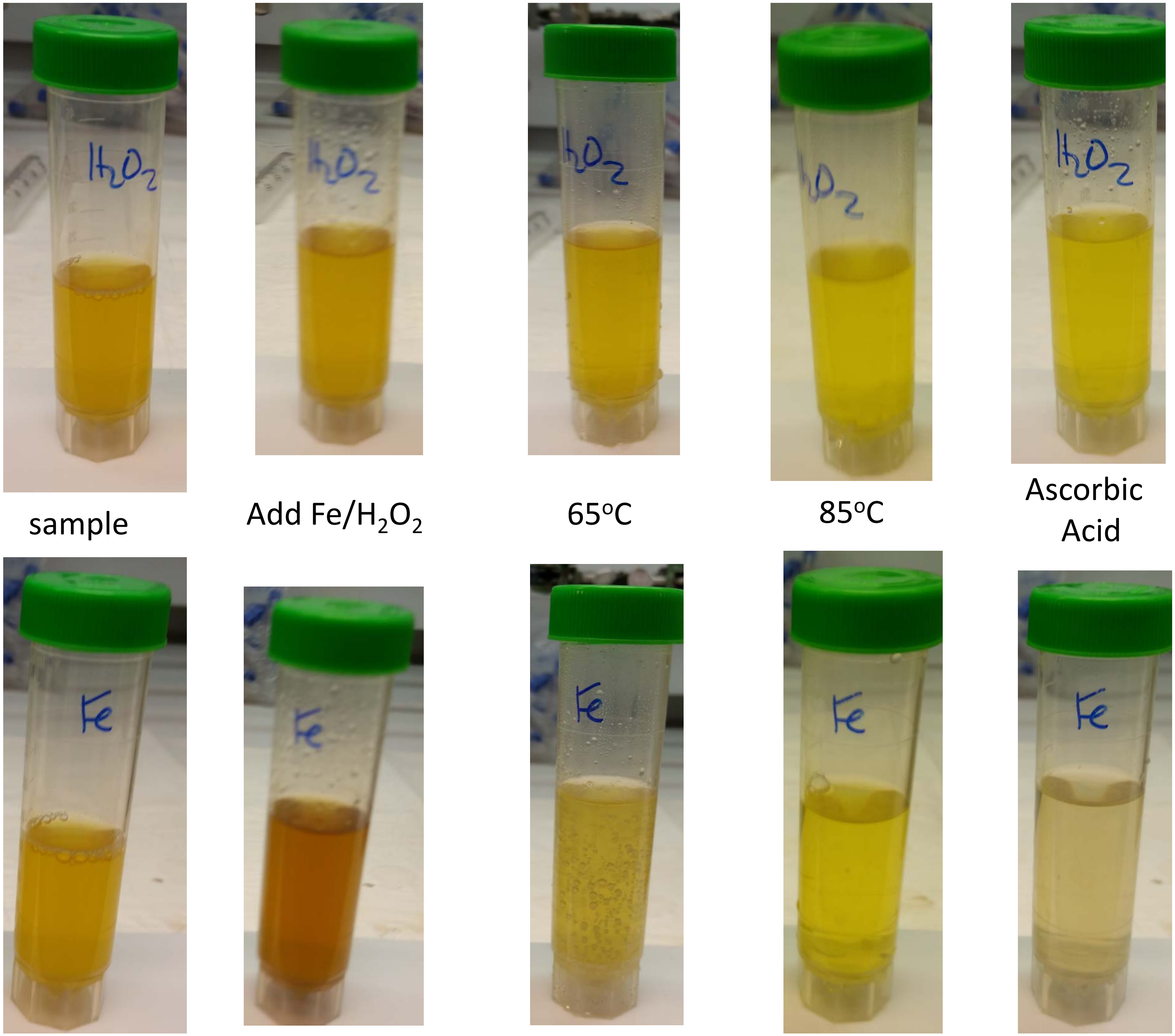
Po-210 Spiked/Aged-Difficult Urine (3 months)

Add Po-208/209, Digest, Analyze

Troubleshoot Repeat

D. R. McAlister and E. P. Horwitz, “Chromatographic radionuclide generator systems for the Actinides and Natural Decay Series Elements,” *Radiochimica Acta*, 99, 151-159 (2011).

J. Harvey, J. A. Nolen, T. Kroc, I. Gomes, E. P. Horwitz, D. R. McAlister, “Production of Ac-225 via high energy proton induced spallation of Th-232,” Proceedings of Application of high energy proton accelerators, Fermilab, Chicago, IL, October 19-21, eds. Rajendran Raja and Shekhar Mishra, pp. 321-326 (2009).

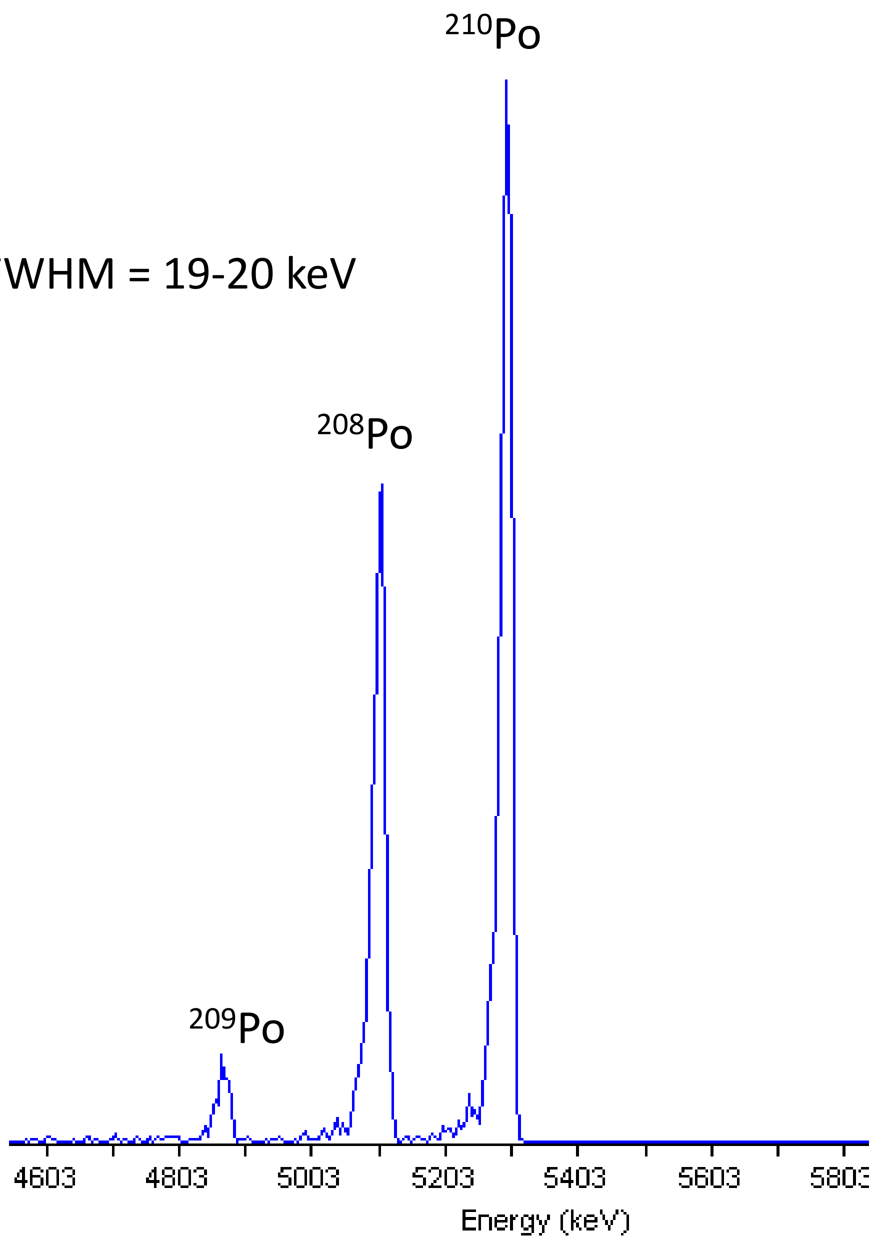

sample
Add Fe/H_2O_2
65°C
85°C
Ascorbic Acid
H_2O_2
Fe

Cleaned c er)

Inverted 5

Remove s

FWHM = 19-20 keV



Autodeposition Po recoveries
from raw spiked urine samples

Fresh Sample	Aged Sample
2-13 %	20-36 %

Recovery By Autodeposition (Fenton's Digest)

Replicate	% Rec. Po-208	% Rec. Po-210	% Po-210 % corr
1	71	72	101
2	72	77	108
3	73	73	101
4	63	67	107
5	72	70	97
6	69	71	103
average	70	72	103
SD	4	3	4

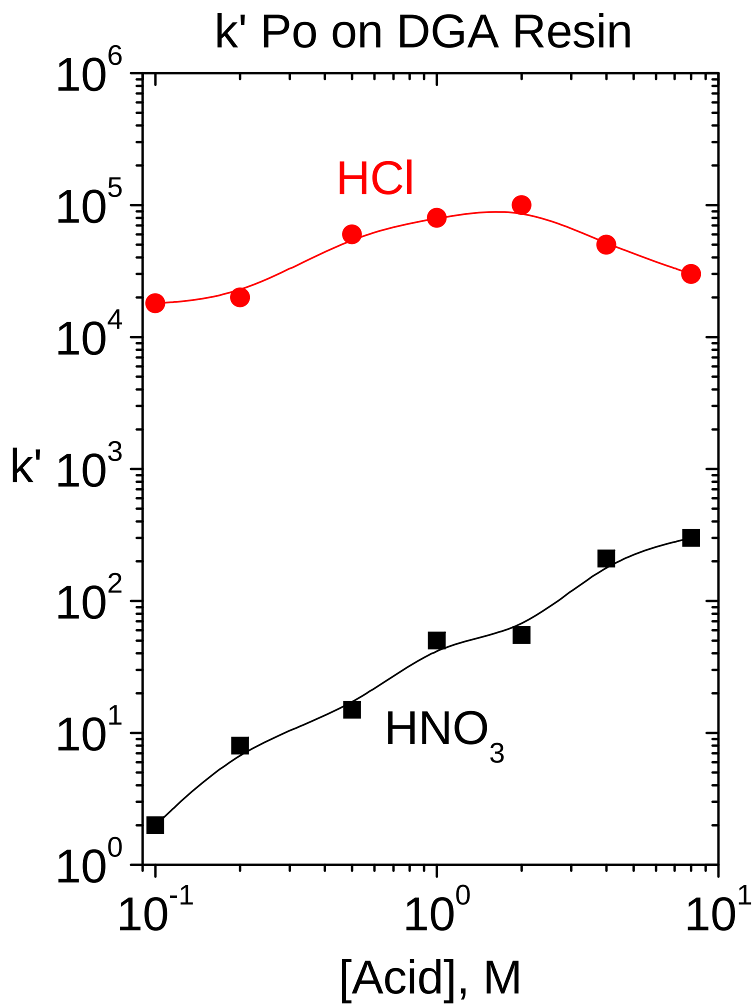
25mL urine sample (aged/difficult)		
Fenton's digest 25mg Fe		
2mL 1M Ascorbic acid quench		
cleaned/polished copper		
3hr at 85C		
0.66Bq Po-208		
0.99Bq Po-210		
4 hour count time		

Recovery By Autodeposition (DI Water)

Replicate	% Po-209	%Po-208
1	76	89
2	89	85
3	93	80
4	93	89
5	76	81
6	83	84
average	85	85
SD	8	4

25mL DI Water	
Direct Spike	
2mL 1M Ascorbic acid quench	
cleaned/polished copper	
3hr at 85C	
0.66Bq Po-208	
0.99Bq Po-210	
4 hour count time	

Chemical Separation



Fenton's Digestion

Oxidative quench of H_2O_2

Concentrate with $Fe(OH)_3$

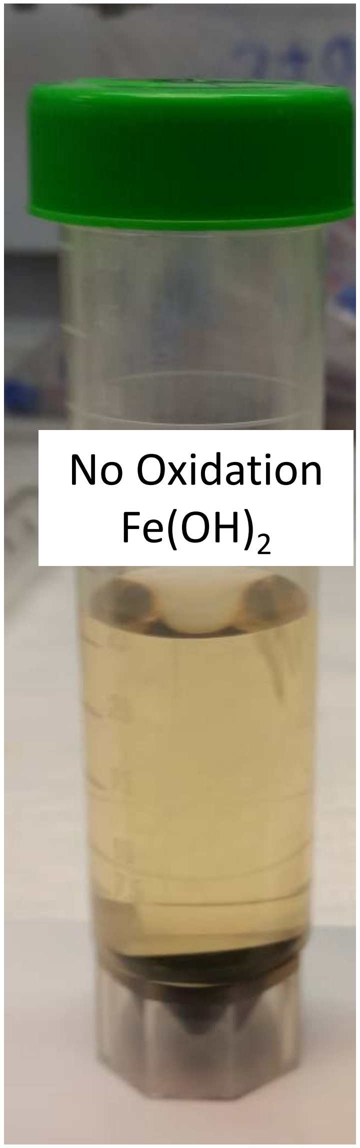
Acidify (HNO_3) or HCl

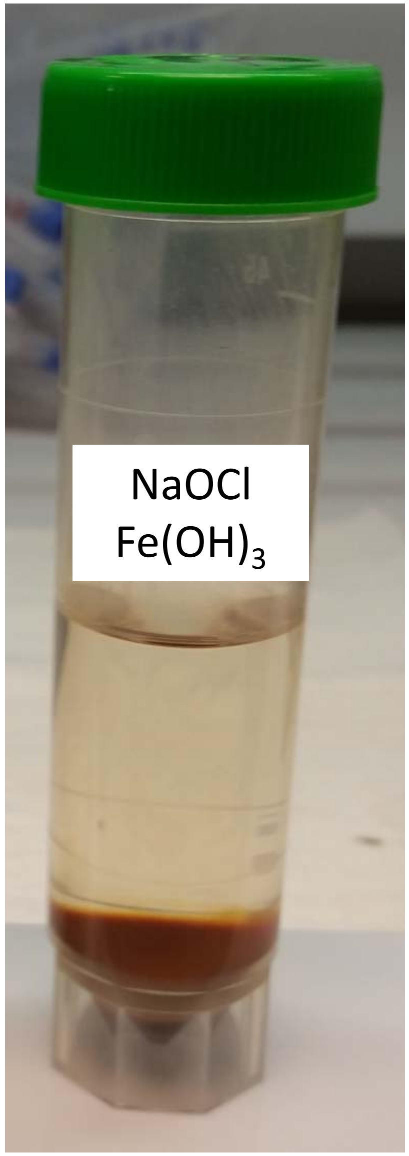
(TRU) DGA Separation

$BiPO_4$ microprecipitation

S.L. Maxwell, B.K. Culligan, J.B. Hutchison, R.C. Utsey, D.R. McAlister, "Rapid Determination of ^{210}Po in Water Samples," *Radioanalytical and Nuclear Chemistry*, 298(3), 1977-1989, (2013).

H_2O_2 Quench/Precipitation

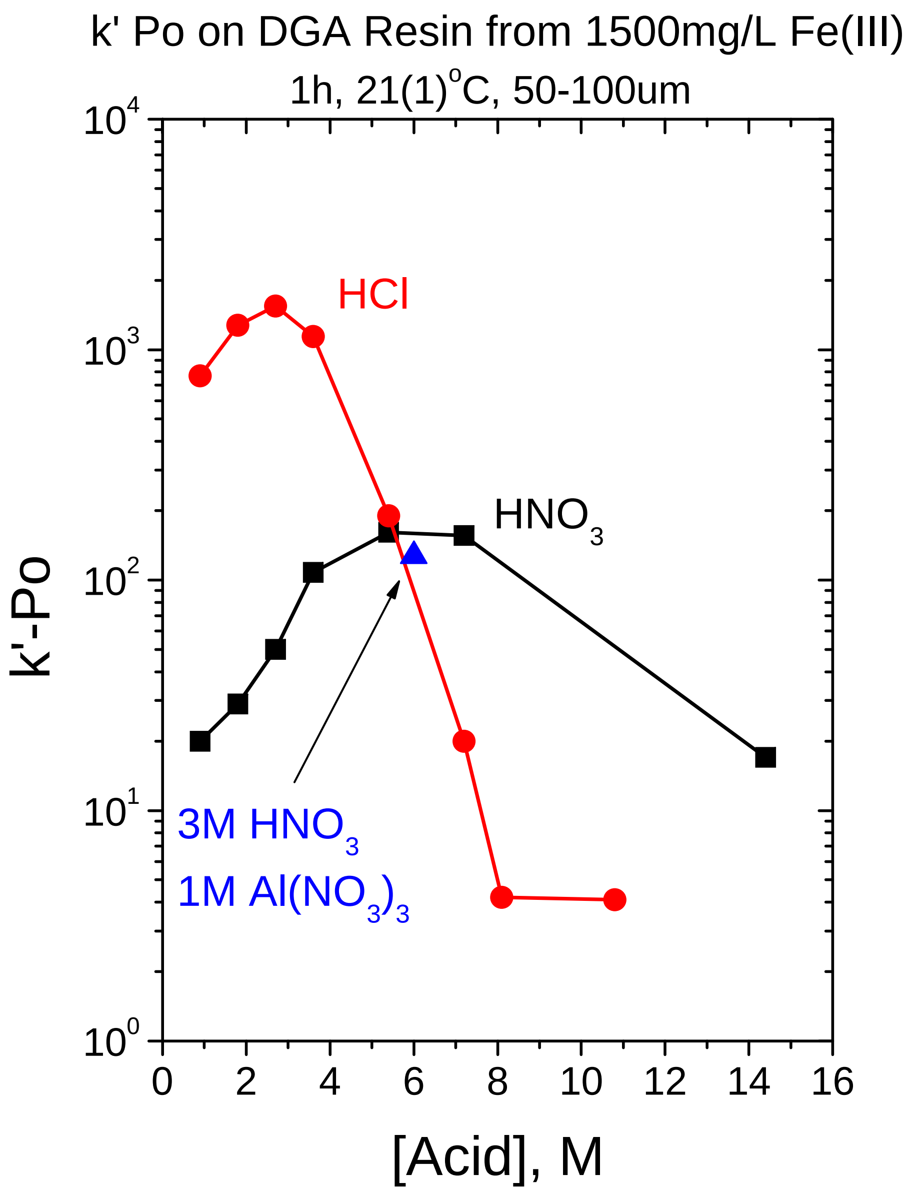


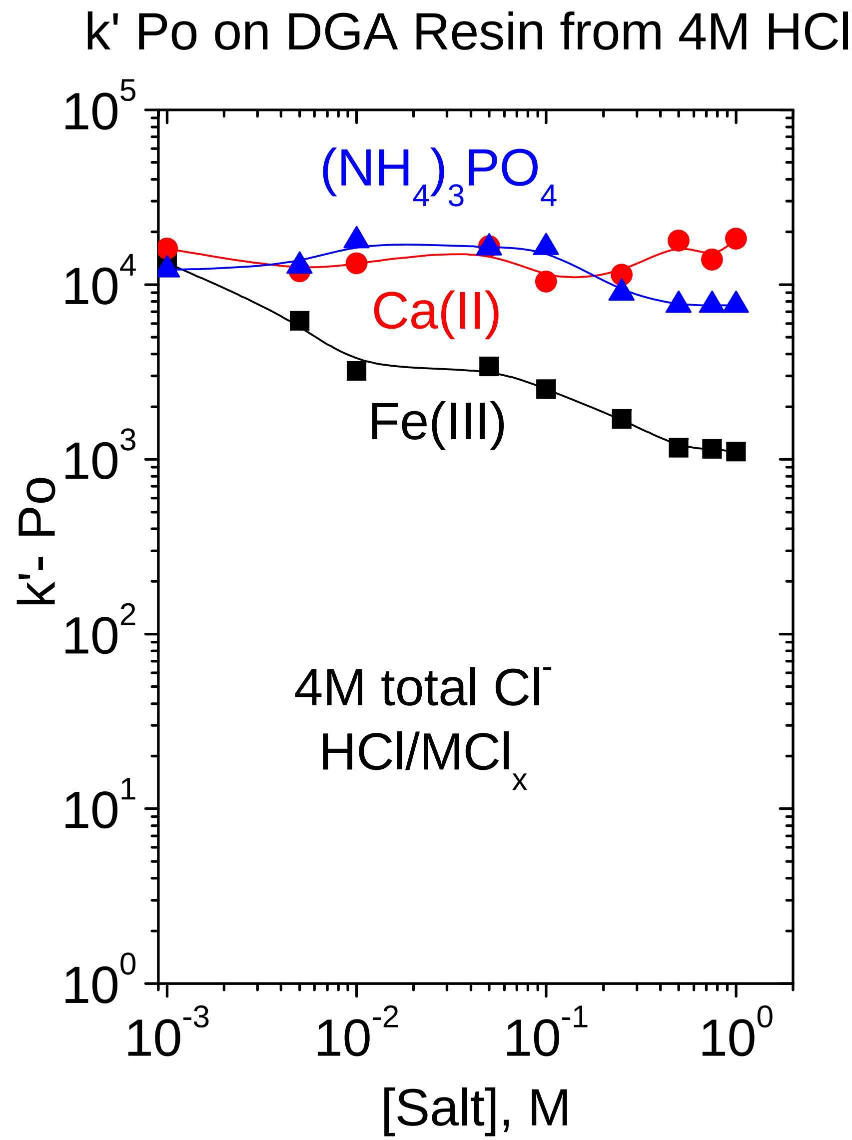


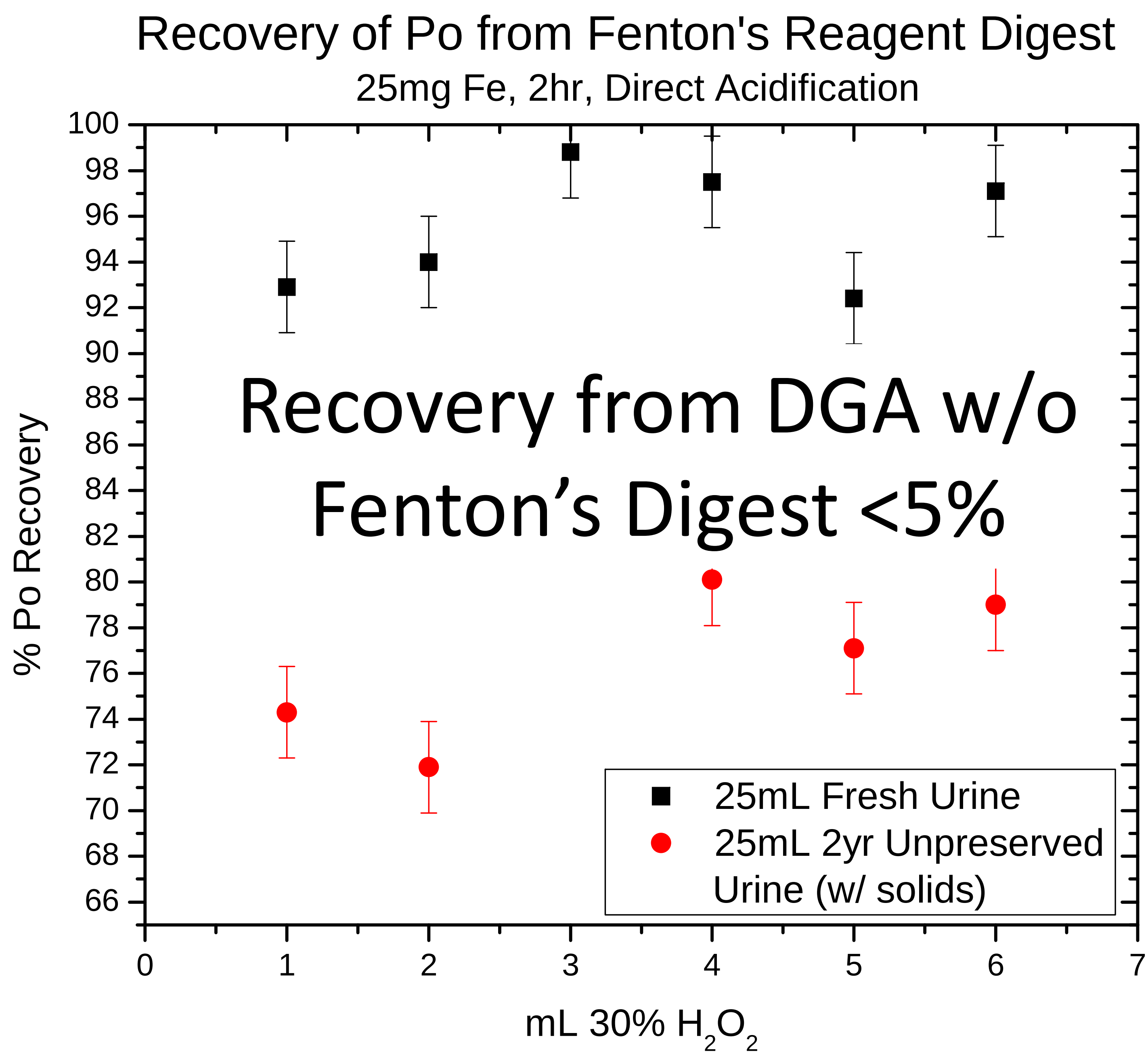
Precipitate	Oxidizing	Reducing
Fe(OH)x	75 ± 6	66 ± 2
Phosphate*	97 ± 1	23 ± 5

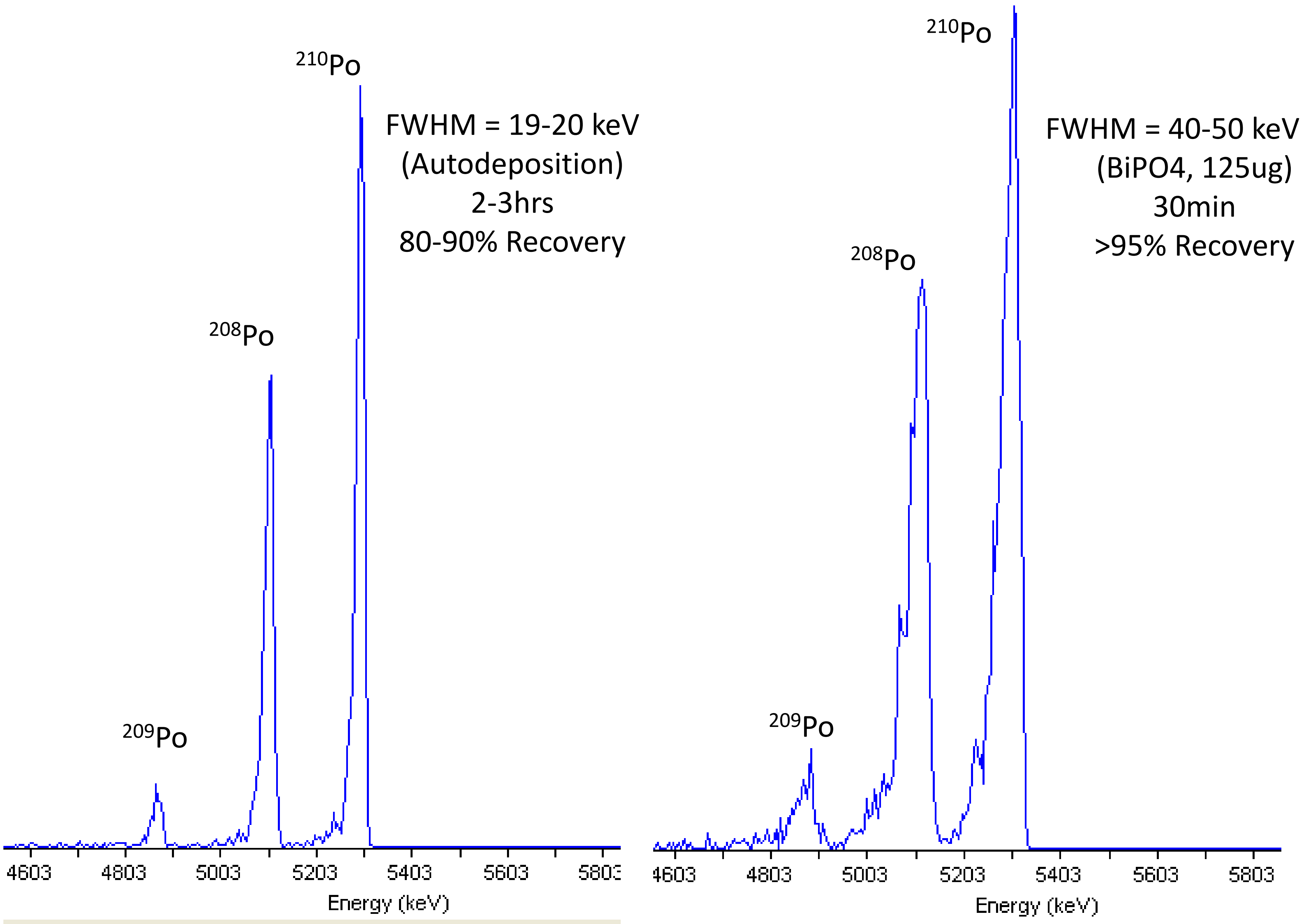
*25mg Fe/25mg Ca

W. Liu, et al., “Optimal Methods for Quenching Residual H_2O_2 Prior to UFC Testing,” *Water Research*, 37, 3697-3703 (2007).


k' Po on DGA Resin from 1500mg/L Fe(III)
1h, 21(1)°C, 50-100um
k'-Po
[Acid], M
HCl
HNO3
3M HNO3
1M Al(NO3)3


k' Po on DGA Resin from 4M HCl
k'- Po
[Salt], M
(NH4)3PO4
Ca(II)
Fe(III)
4M total Cl-
HCl/MClx


Recovery of Po from Fenton's Reagent Digest
25mg Fe, 2hr, Direct Acidification
% Po Recovery
mL 30% H2O2
Recovery from DGA w/o Fenton’s Digest <5%
25mL Fresh Urine
25mL 2yr Unpreserved Urine (w/ solids)
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
0
1
2
3
4
5
6
7



^{210}Po
FWHM = 19-20 keV
(Autodeposition)
2-3hrs
80-90% Recovery
^{208}Po
^{209}Po
4603
4803
5003
5203
5403
5603
5803
Energy (keV)
^{210}Po
FWHM = 40-50 keV
(BiPO4, 125ug)
30min
>95% Recovery
^{208}Po
^{209}Po
4603
4803
5003
5203
5403
5603
5803
Energy (keV)

Recovery By DGA/BiPO4 (Fenton's Digest)

	% Rec.	% Rec.	% Po-210
Replicate	**Po-208**	**Po-210**	**% corr**
1	57	54	95
2	79	72	92
3	69	64	93
4	64	59	92
5	67	63	93
6	63	61	96
average	67	62	94
SD	7	6	2

25mL urine sample (aged/difficult)		
Fenton's digest 25mg Fe		
2mL 10% NaOCl quench/ Fe(OH)3 ppt		
Load 25mL 8M HNO3 onto DGA resin		
BiPO4 ppt onto filter		
0.66Bq Po-208		
0.99Bq Po-210		
4 hour count time		

Additional Matrices

Aqueous samples and IX Resins have been demonstrated.

EXC Resins more challenging. (Hydrophobic)

Cellulose filters need H_2SO_4 contact.

Vegetation and Tissue, possible.

- Need physical decomposition first.
- How to solubilize fat? (Basic pH/Different Metal Ion?).
- Fe, Cu, Mn, Ni
- Lyophilization?

Larger Urine Samples/Additional Analytes.

Thank you !!!