Rapid Method for Po-210 in Urban Matrices

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Recent News- Potential RDD Plans

- **"Brussels attacks: Belgium fears Isis seeking to make 'dirty' nuclear bomb" March-2016**
  - http://www.independent.co.uk/news/world/europe/brussels-attacks-belgium-fears-isis-seeking-to-make-dirty-nuclear-bomb-a6951661.html

- **"An official at Belgium's Federal Agency for Nuclear Control told *The Times*: "When you start filming someone in the way they did, the logical conclusion is that they wanted to abduct that person and to obtain radioactive material.""**

Need for Rapid Methods

- **1998: Chechen authorities foiled a possible terrorist act when they found and defused a mine attached to a container "full of radioactive substances" near Grozny,**
  - terrorists stole radioactive waste from Russian RADON storage facility

- ***"Mexico Finds Stolen Radioactive Material Amid Dirty Bomb Fears"*** **http://www.voanews.com/content/nuclear-materia-stolen-in-mexico/1803195.html,12/4/13**
  "A dirty bomb detonated in a major city could cause mass panic, as well as serious economic and environmental consequences"

- **Are we ready??**

List of Threat Radionuclides

Alpha Emitters			Beta/Gamma Emitters		
Radionuclide	**Half-Life**	**Emission Type**	**Radionuclide**	**Half-Life**	**Emission Type**
^{241}Am	432.6 y	α, γ	Ac-227†	21.77 y	β, γ
^{252}Cf	2.64 y	α, γ			
^{242}Cm	163 d	α	Ce-141*	32.51 d	β, γ
^{243}Cm	29.1 y	α, γ	Ce-144‡	284.9 d	β, γ
^{244}Cm	18.10 y	α	Co-57*	271.7 d	ε, γ, x-ray
^{237}Np	2.14×10^{6} y	α, γ, x-ray	Co-60*	5.271 y	β, γ
^{210}Po *	138.4 d	α	Cs-134*	2.065 y	β, γ
^{238}Pu	87.7 y	α	Cs-137§	30.07 y	β, γ
^{239}Pu	2.41×10^{4} y	α	H-3*	12.32 y	β only
^{240}Pu	6.56×10^{3} y	α	I-125*	59.40 d	ε, γ, x-ray
^{226}Ra†	1.60×10^{3} y	α, γ	I-129†	1.57×10^{7} y	β, γ, x-ray
^{228}Th	1.912 y	α, γ	I-131*	8.021 d	β, γ
^{230}Th	7.538×10^{4} y	α, γ	Ir-192*	73.83 d	β, γ
^{232}Th	1.405×10^{10} y	α	Mo-99†	65.94 h	β, γ
^{234}U	2.455×10^{5} y	α	P-32*	14.26 d	β only
^{235}U	7.038×10^{8} y	α, γ	Pd-103*	16.99 d	β, γ
^{238}U	4.468×10^{9} y	α	Pu-241	14.29 y	α, β
U-Nat	—	α	Ra-228†	5.75 y	β only
			Ru-103†	39.26 d	β, γ
			Ru-106†	373.6 d	β only
			Se-75*	119.8 d	ε, γ
			Sr-89*	50.53 d	β only
			Sr-90†	28.79 y	β only
			Tc-99*	2.11×10^{5} y	β only

The half-lives of the nuclides are given in years (y), days (d) or hours (h)
* No radioactive progeny or progeny not analytically useful.
† Radioactive progeny with short half-lives, and the progeny may be used as part of the detection method for the parent.
‡ Radioactive progeny not used for quantification, only screening.
§ Radioactive progeny used for quantification only, not screening.

Po-210

- **^{210}Po ($T_{1/2}$=138.38 days)**
  - naturally-occurring alpha emitting radionuclide used in industrial applications
    - **static elimination**
  - ^{210}Po is present in the environment as a result of the ^{238}U decay chain
  - one of the most toxic naturally-occurring radionuclides
    - *an ingestion intake as small as 1 µg of Po-210 may be lethal for the most radiosensitive members of the population*

Risk of Po-210 Attack

- **Former Russian intelligence officer Alexander Litvinenko died in a London hospital on November 23, 2006**
  - *Deliberately poisoned with ^{210}Po*
  - *Police discovered those involved in this crime had spread ^{210}Po over many locations in London*
  - *Incident caused widespread psychological concern and a heightened political and public health response*

– **Naturally-occurring radionuclides such as ^{226}Ra and ^{210}Po can also be used in a radiological dispersive device (RDD) as part of a terrorist attack**

From a Tea Pot….

- “Pinpoint Homicide”
- ~1000 people requested follow-up (urine analysis)
- 137 people contaminated (above background)
- 19 Environmental Teams, 24/7 for weeks
- 47 sites evaluated for contamination
- Many locations “sealed” for ~ 5 years
- Some people view this event as a “Micro-Terrorist” event

- **Can we imagine the impact of a Po-210 RDD?**
  - A non-explosive dispersive attack is also a serious concern

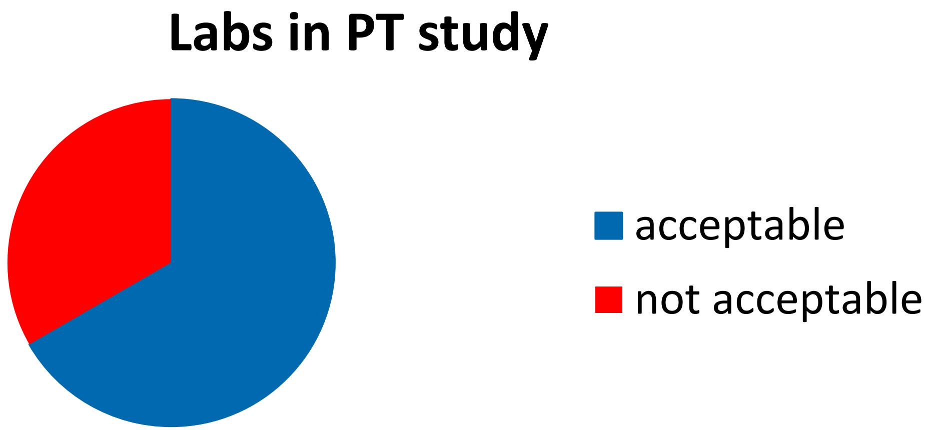
Current Analytical Method Challenges

- What are the challenges with Po-210 assay?
  - Acid digestion of solid samples- Po volatilization
- Methods typically involve spontaneous auto-deposition of ^{210}Po onto silver or other metal disks followed by alpha spectrometry
  - auto-deposition times range from 90 minutes to 24 hours or more, at times with yields that may be less than desirable
  - If sample interferences are present, decreased yields and degraded alpha spectra can occur, due to an unpredictable increase in thickness in the deposited layer
- Problematic, especially during a radiological emergency,
  - where rapid detection of ^{210}Po is critical and the safety of the public is at stake
  - method rigor and minimizing rework are extremely important

IAEA ALMERA PT Study

- International Atomic Energy Agency (IAEA) ALMERA (Analytical Laboratories for the Measurement of Environmental Radioactivity) network
  - *administered proficiency testing for the rapid analysis of ^{210}Po in water after the Litvinenko event.*
  - *ALMERA network, established by the IAEA in 1995, is a technical collaboration of existing institutions and makes available to Member States …..*
    - *a worldwide network of analytical laboratories capable of providing reliable and timely analysis of environmental samples in the event of an accidental or intentional release of radioactivity.*

ALMERA Network PT Study: How did they do?



- ***Only 70 % of the results reported by the 33 labs met the IAEA requirements***
- *Only 19 of the 33 labs met the one week target*
- *22 of 33 participants reported results which "fit the purpose of rapid detection of Po-210 in water"*
- ***Reporting times were usually about 10 days for most labs, but some labs took over 20 days and still did not report acceptable results***

Challenge: Polonium Volatilization

"Polonium is often lost in the initial digestion because it has a relatively low volatilization temperature, 180 C"

Martin A, Blanchard RL (1969) The thermal volatilisation of caesium-137, Po-210 and lead-210 from in vivo labelled samples. Analyst 94(1119):441–446. doi:10.1039/AN9699400441

Mabuchi H (1963) The volatility of some Po compounds. J Inorg Nucl Chem 25:657–660. doi:10.1016/0022-1902(63)80154-2

What can we do??

Savannah River Environmental Laboratory Approach

- **Alkaline fusion**
  - Fast, rugged, inhibits Po volatilization
  - Quick preconcentration –$Fe(OH)_3$
- **DGA Resin- k' in HCl for Po ~100,000**
- **Po-210 on Sr Resin**
  - eluted with 6M HNO_3, autodeposition, 50-70% yields,
  - k' in HCl using DGA Resin much higher
  - Vajda, N., La Rosa, J., Zeisler, R., Danesi, P., Kis-Benedek, G.Y., (1997) A Novel technique for the simultaneous determination of ^{210}Pb and ^{210}Po using a crown ether, J. Environ. Radioactive. 37: 355-372
- ***Use fast microprecipitation instead of autodeposition***
  - Can be eluted from DGA Resin and collected quickly ($BiPO_4$)
  - Optimized in this work

Use of DGA Resin and $BiPO_4$ Microprecipitation

J Radioanal Nucl Chem
DOI 10.1007/s10967-013-2644-2

Rapid determination of ^{210}Po in water samples

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Calcium phosphate ppt. and DGA Resin +$BiPO_4$ microprecipitation

Received: 22 May 2013

Challenges

- **SRS solid sample fusion methods**
  - Preconcentration of actinides with Fe/Ti hydroxide
  - Fe/Ti/silicates removal with LaF_3
  - Fe can interfere with some resin methods
    - *Fe (III) has synergistic effect that may cause Ca(II) ions to be retained more than normal*
  - Colloidal Si can be a nightmare

- ***Cannot* precipitate Po as a fluoride to remove Fe/silicates!**

- **How do we overcome this problem??**

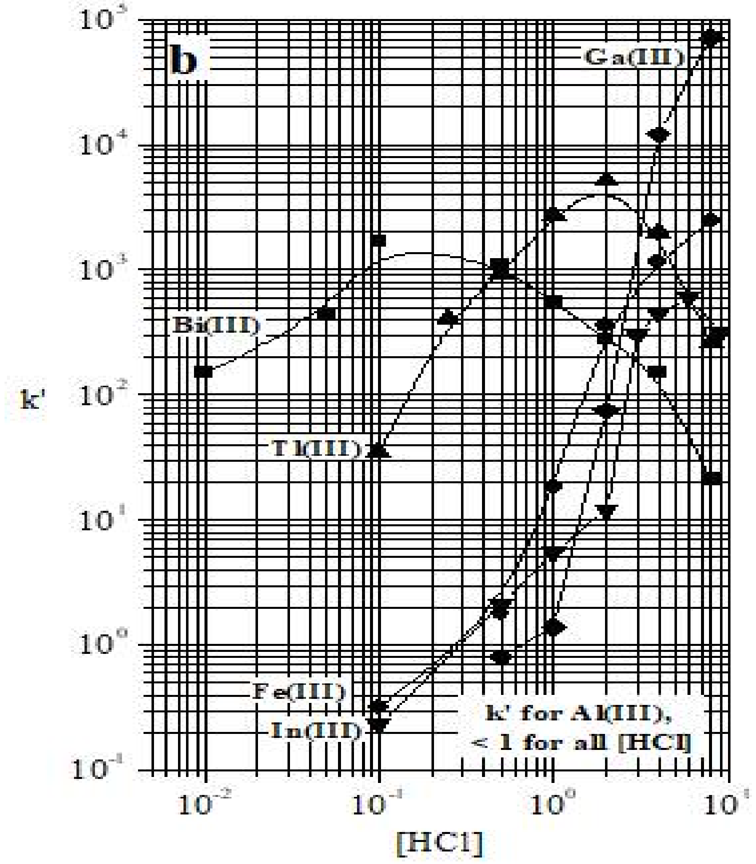
Potential Solution

- **Fluoride can stabilize silicates in solution**
- **Can we add fluoride to the sample load solution**
  - to keep Si in solution and eliminate Si gel/colloids and clogging
  - *and still retain Po on DGA?*
- **Test a dilute HCl-HF solution to load Po^{+4} onto DGA Resin**
  - *Po (IV) retention is very high even in low HCl*
  - *If Po complexing is stronger with chloride…may be ok*

Success!

- ***F^- does not interfere significantly with Po^{+4} retention on DGA***
- **Silicates pass through column without colloidal solids/gel formation!**
- ***Fe has minimal retention on DGA Resin in low HCl***
  - *$Fe(OH)_3$ can be employed*
  - *Does not interfere*

Fe on DGA Resin in HCl



D.R. McAlister and E.P. Horwitz, "Synergistic enhancement of the extraction of trivalent lanthanides and actinides by tetra(n-octyl)diglycolamide from chloride media," *Solv. Extr. Ion Exch.*, 26(1), 12-24 (2008).

New Po-210 Fusion Method

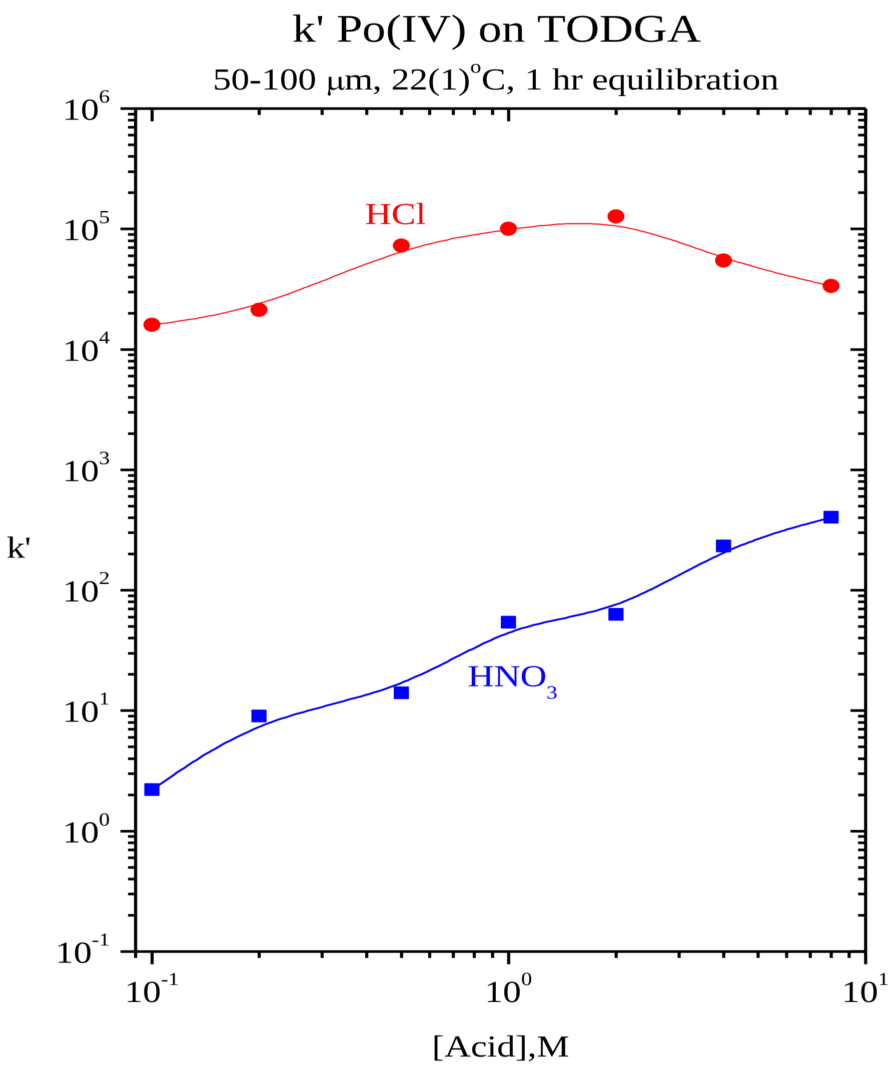
1. Add Po-209 tracer to 1g solid matrix in Zr crucible containing 3 mL 14.5M NH4OH
2. Add 15g NaOH pellets. Place crucible in furnace at 200°C and ramp to 300 °C and hold for ~10-15 min. Ramp temperature to 500°C and fuse sample for 20-25 minutes.
3. Transfer fusion matrix to 225 mL centrifuge tube with water. Add 125 mg Fe, Dilute to 180-200 mL with water. Mix. Cool with ice for ~10 minutes.
4. Centrifuge each tube 6 minutes and discard supernate.
5. Add 5 to 7mL 4M HCl-0.2M HF and 5 mL 0.5M HCl-0.02M HF to each tube to dissolve solids. Transfer solids to a 50 mL tube. Rinse 225 mL tube with 10 mL 0.5M HCl-0.02M HF, then 5 ml 0.5M HCl-0.02M HF and transfer rinse to 50 mL tube. Vortex tube to mix well. Centrifuge 4 minutes and transfer sample solution to a new 50 ml tube. Discard any traces of solids.
6. Column Load Solution for DGA Resin

Maintain alkalinity on heat ramp to avoid Po loss

Keep HCl low

Use F^- to keep Si ‘happy’ in solution

Po Retention on DGA Resin

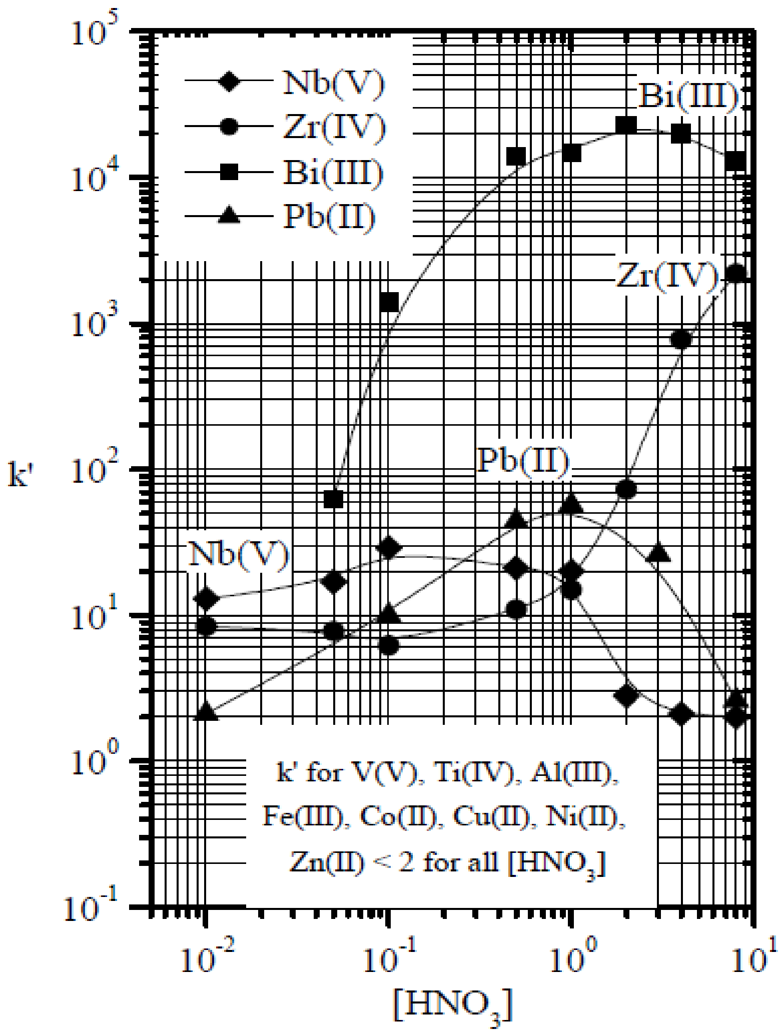


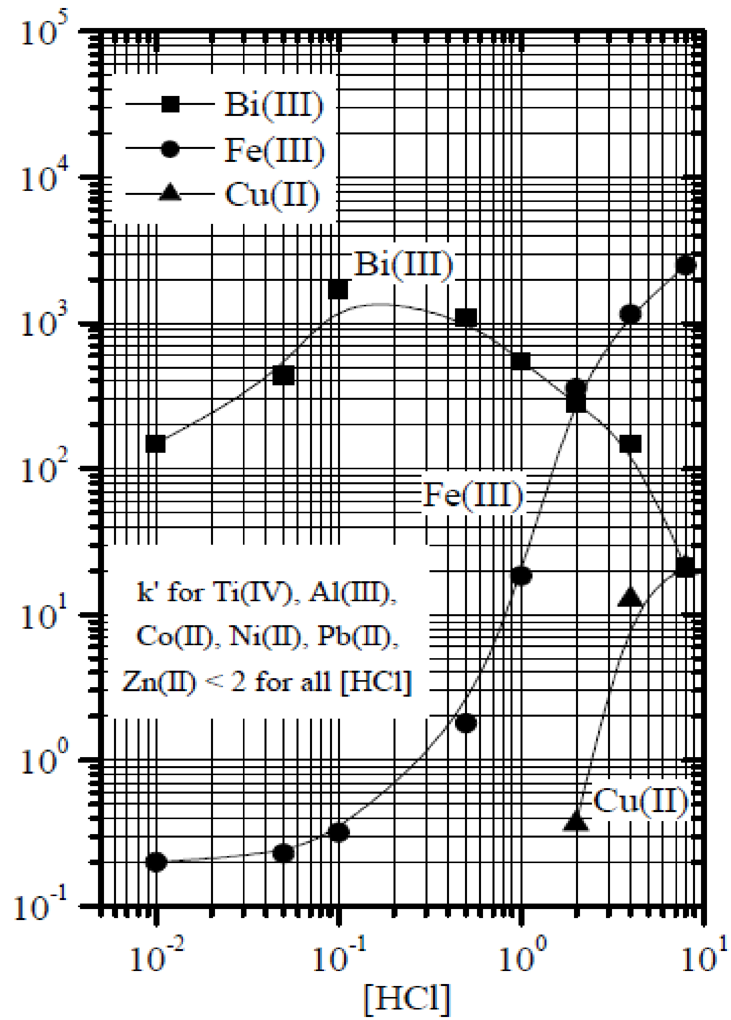
We can elute Po with 0.05M HNO_3 however 10-15% would stay on resin

How to optimize?

Add trace oxalate to 0.05M HNO_3

Bi Retention on DGA Resin





Fast Po-210 Purification using DGA Resin

Column Load Solution

Add 50 µL 30 wt% H_2O_2 to ensure Po^{+4}

↓

Load to 2 mL DGA Resin cartridge @1 drop/sec

↓

Rinse DGA cartridge

-10mL 1M HCl-0.25M boric acid tube rinse @1 drop/sec

-20 mL 0.25M HCl @~1-2 drops/sec (actinides)

-10 mL 0.5M HCl-0.2M HF @~1-2 drops/sec (any residual Th)

-10 mL 8M HNO3 @~1 drop/sec (turn up vacuum to remove residual acid)

*DGA Resin - removes Th, U, Ra, Pu, Am isotopes

1M HCl-Boric Acid rinse to eliminate any traces of ThF_4 on Resin

↓

Elute Po from DGA Resin with 20 mL 0.05M HNO_3 -0.005M oxalate @~1 drop/sec

↓

Add 125µg Bi

+ 50 µL 30 wt % H_2O_2

+ 0.75 mL 3.2M $(NH_4)_2HPO_4$

+ 1000 µL 14.5M NH_4OH or as needed to medium pink phenolphthalein indicator

Cap and vortex, wait 20 minutes,

Collect $BiPO_4$ on 0.1 µm polypropylene filter

↓

Alpha spectrometry

Now using HNO_3-oxalate to enhance Po elution from DGA

Added indicator to ensure optimal pH

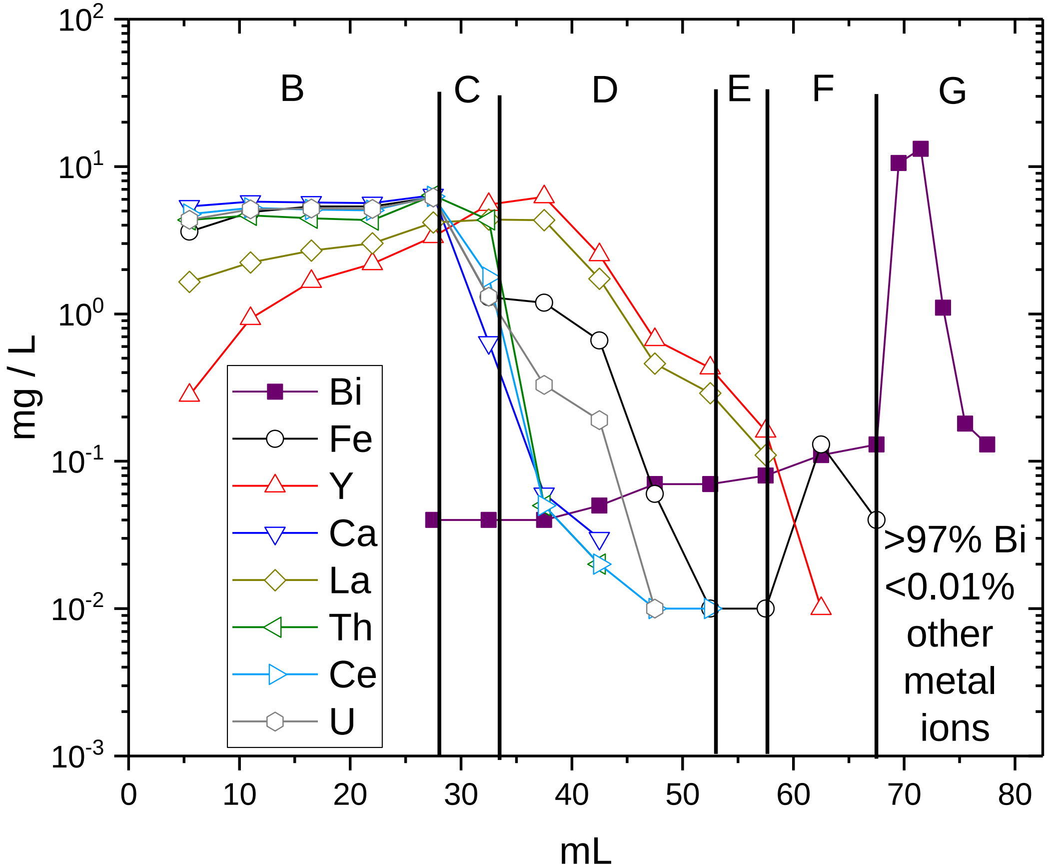
....Bi elutes as well

Po Elution- DGA Resin

Elution of Po-210 on 2 mL TODGA Cartridge				
		Po-210 LSC		
Fraction	total mL	%		
Load*	25	0.47		
Rinse 1M HCl - 0.25M Boric Acid	5	0.05		
Rinse 0.25M HCl	20	0.14		
Rinse 0.5M HCl - 0.01M HF	10	0.14		
Rinse 8M HNO3	10	0.02		
Strip 0.05M HNO3 - 0.005M Bioxalate	5	96.0	total 20 mL strip	
Strip 0.05M HNO3 - 0.005M Bioxalate	5	0.3	96.7	
Strip 0.05M HNO3 - 0.005M Bioxalate	5	0.2		
Strip 0.05M HNO3 - 0.005M Bioxalate	5	0.2		
cartridge	2	2.4		
Precondition cartridge 10 mL 1M HCl				
*Load = 5 mL 4M HCl-0.2M HF + 20 mL 0.5M HCl - 0.02M HF				
DGA lot DNSR16A				

85-94% recovery with 0.05M HNO_3 only

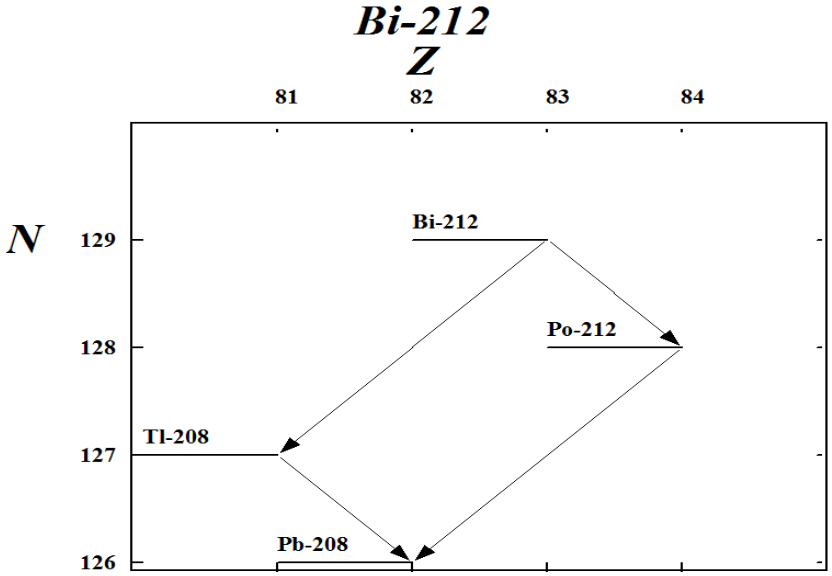
Po Elution Curve on DGA Resin



A = Precondition 10 mL 1M HCl. B = Load 5 mL 4M HCl – 0.2M HF + 23 mL 0.5M HCl – 0.02M HF. C = 5 mL 1M HCl. D = 20 mL 0.25M HCl. E = 5 mL 0.5M HCl – 0.02M HF. F = 10 mL 8M HNO3. G = 20 mL 0.05M HNO3 – 0.005M ammonium bioxalate.

Will Bi Isotopes Interfere?

- Bi-210 ($T_{1/2}$ = 5.1 days) 100% beta emission abundance
- Bi-214 ($T_{1/2}$ = 19.9 min) 0.02% alpha emission abundance
- Po-214 ($T_{1/2}$ = 136.6 µsec) 99.99% alpha abundance, 7.69 MeV
- Bi-212 ($T_{1/2}$ = 60.55 min) 35.94% alpha abundance, ~6.05 MeV
- Po-212 ($T_{1/2}$ = 2.98E-7s) 100% alpha abundance, ~8.78 MeV



Results for Po-210 Spiked in Concrete Samples

Sample ID	^{209}Po Yield (%)	^{210}Po Reference Value (mBq g^{-1})	^{210}Po Measured Value (mBq g^{-1})	^{210}Po Native Value (mBq g^{-1})	^{210}Po Corrected Value (mBq g^{-1})	Difference (%)
1	99.6	366.7	486.9	110.9	376.0	2.5
2	99.8	366.7	491.0	110.9	380.1	3.7
3	86.4	366.7	485.1	110.9	374.2	2.0
4	91.8	366.7	494.7	110.9	383.8	4.7
5	81.3	366.7	495.8	110.9	384.9	5.0
6	78.9	366.7	476.2	110.9	365.3	-0.4
7	88.8	366.7	529.1	110.9	418.2	14.0
8	79.8	366.7	495.8	110.9	384.9	5.0
9	94.0	366.7	484.7	110.9	373.8	1.9
10	88.8	366.7	481.0	110.9	370.1	0.9
11	83.6	366.7	462.1	110.9	351.2	-4.2
12	96.6	366.7	465.1	110.9	354.2	-3.4
13	90.4	366.7	465.1	110.9	354.2	-3.4
14	82.8	366.7	439.9	110.9	329.0	-10.3
15	86.5	366.7	460.7	110.9	349.8	-4.6
Avg	88.6		480.9			0.89
SD	6.8		20.9			5.69
% RSD	7.8		4.3			

Results for Po-210 Spiked in Granite Samples

Sample ID	^{209}Po Yield (%)	^{210}Po Reference Value (mBq g^{-1})	^{210}Po Measured Value (mBq g^{-1})	^{210}Po Native Value (mBq g^{-1})	^{210}Po Corrected Value (mBq g^{-1})	Difference (%)
1	96.4	366.7	460.7	97.49	363.2	-1.0
2	92.2	366.7	478.0	97.49	380.5	3.8
3	104.7	366.7	464.4	97.49	366.9	0.1
4	92.8	366.7	494.3	97.49	396.8	8.2
5	98.8	366.7	480.0	97.49	382.5	4.3
6	88.5	366.7	462.1	97.49	364.6	-0.6
Avg	95.6		473.3			2.47
SD	5.7		13.2			3.60

Results for Po-210 Spiked in Soil Samples

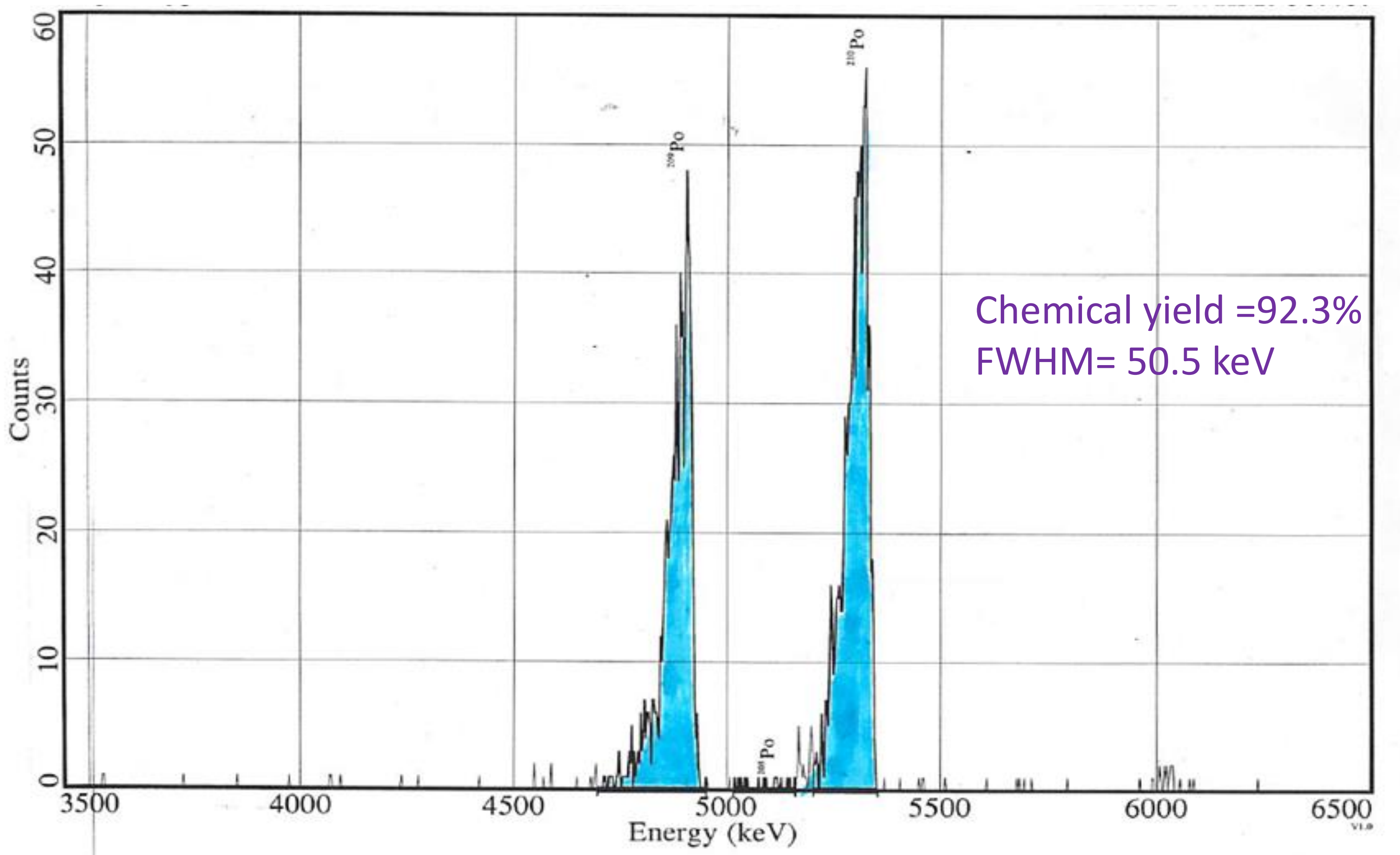
Sample ID	^{209}Po Yield (%)	^{210}Po Reference Value (mBq g^{-1})	^{210}Po Measured Value (mBq g^{-1})	^{210}Po Native Value (mBq g^{-1})	^{210}Po Corrected Value (mBq g^{-1})	Difference (%)
1	84.2	366.7	417.7	64.57	353.1	-3.7
2	99.3	366.7	432.2	64.57	367.6	0.3
3	74.0	366.7	442.9	64.57	378.3	3.2
4	78.0	366.7	433.6	64.57	369.0	0.6
5	78.2	366.7	461.0	64.57	396.4	8.1
Avg	82.7		437.5			1.69
SD	10.0		15.9			4.35

Po-210 Spiked In Soil-Enhanced Precipitation

Sample ID	^{210}Po Yield (%)	^{210}Po Reference Value ($mBq\ g^{-1}$)	^{210}Po Measured Value ($mBq\ g^{-1}$)	^{210}Po Native Value ($mBq\ g^{-1}$)	^{210}Po Corrected Value ($mBq\ g^{-1}$)	Difference (%)
1	88.5	366.7	441.0	64.57	376.4	2.7
2	98.7	366.7	410.7	58.46	352.2	-3.9
3	90.0	366.7	431.8	58.46	373.3	1.8
4	94.0	366.7	414.4	58.46	355.9	-2.9
Avg	92.8		424.5			-0.60
SD	4.6		14.4			3.32

Added 25 mg Ca at $Fe(OH)_3$ precipitation step....

Po-210 Alpha Spectra Granite Samples



Analytical Method Timeline

• Spiking and Alkaline Fusion	45 minutes
• Preconcentration as $Fe(OH)_3$	45 minutes
• DGA Resin Separation	90 minutes
• $BiPO_4$ microprecipitation	30 minutes
• Sample preparation time	3 hr. 30 minutes
• Alpha Spectrometry counting	60-1000 minutes

Summary

- **New fast method for Po-210 in urban matrices**
  - Rugged alkaline fusion to minimize Po volatilization
    - *Concrete*
    - *Granite*
    - *Soil*
  - Fast alpha source preparation
    - *Eliminates potential autodeposition issues, can save time, improve yields, spectra*
    - *$BiPO_4$ microprecipitation*
    - *Potential to stack Sr Resin and DGA Resin for Pb-210*
- **Future work**
  - Limestone, Marble
  - Glass fiber air filters