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Berylliant
Beryllium
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Extraction and Fluorescence Method for the Determination of Trace Beryllium in Soils

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Overview

Investigations of ammonium bifluoride (ABF) extraction and fluorescence measurement of [Be]:

1) Beryllium measurements in occupational hygiene samples (re-cap)
   A. Agrawal et al., *J. Environ. Monit.* [2006] **40**: 619-624.
   K. Ashley et al., *Anal. Chim. Acta* [2007] **584**: 281-286.

2) Beryllium determination in CRM soils
   A. Agrawal et al., *Environ. Sci. Technol.* [2008] **42**: 2066-2071.

3) Interlaboratory study of BeO-spiked soils
   J. P. Cronin et al., *J. Environ. Monit.* [2008] **10**: 955-960.

4) Beryllium speciation in soils – preliminary experiments

Recovery of beryllium compounds from various media

(*JEM*, 2006; *ACA*, 2007)

Sample / media	temperature	% recovery ± std dev (n ≥ 3)
• Be sulfate	room temp.	100 ± 4
• Be metal	room temp.	96 ± 3
• BeO	room temp.	86 ± 3
• BeO	~85 °C	97 ± 7
• Be sulfate / MCE filters	room temp.	99 ± 2
• Be metal / MCE filters	room temp.	93 ± 7
• BeO / MCE filters	room temp.	86 ± 6
• BeO/MCE filters	~85 °C	99 ± 8
• Be sulfate / Whatman 541 filters	room temp.	98 ± 3
• Be metal / Whatman 541 filters	room temp.	95 ± 4
• BeO / Whatman 541 filters	room temp.	86 ± 8
• BeO / Whatman 541 filters	~85 °C	96 ± 6

5 or 10 ml 1% ABF, mechanical agitation or heating for ≥ ½ hour;

5-10 mg of material per sample

Dissolution of High Fired BeO (UOX) on Whatman 541 Filter

Summary of results in μg Be/filter

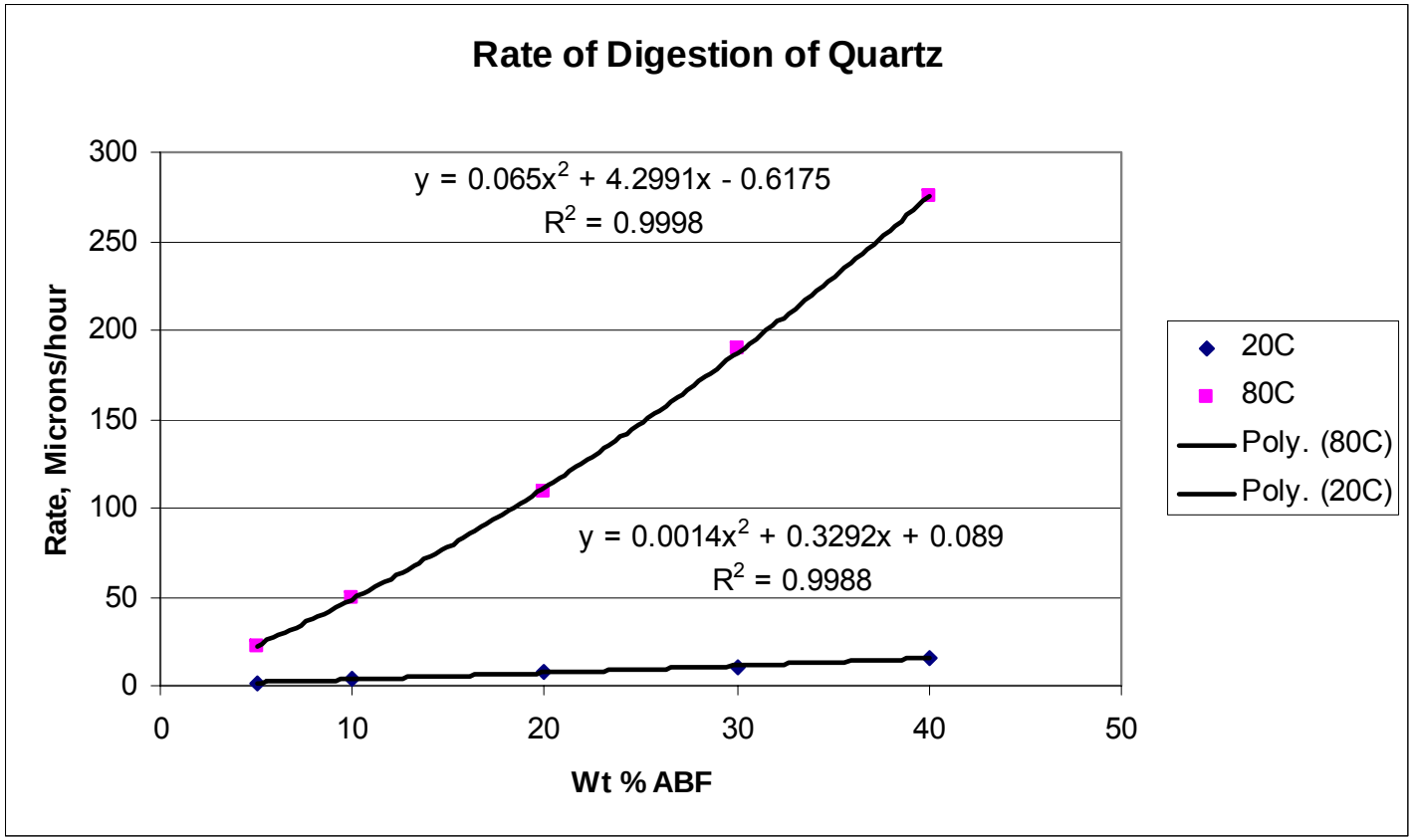
BeO, μl	expected	Rotated Room Temp	75 °C	90 °C
3	0.2	0.19	0.23	0.21
15	1 to 1.2	0.65	1.11	1.20
60	4 to 5	2.68	4.54	4.20

Dissolution: 30 minutes in 5 ml of 1% ABF aqueous solution

Dissolution Protocol - Soils

- ABF reacts with silicates, which may reduce its ability to dissolve anthropogenic beryllium.
- Experiments were done to evaluate:
  - Dissolution conditions to determine natural levels of beryllium in soils
  - Dissolution conditions for determining anthropogenic beryllium in soils.

Dissolution of SiO_2 using Ammonium Bifluoride*



$$SiO_2 + 4\,NH_4HF_2 \rightarrow (NH_4)_2\,SiF_6 + 2\,NH_4F + 2\,H_2O;$$

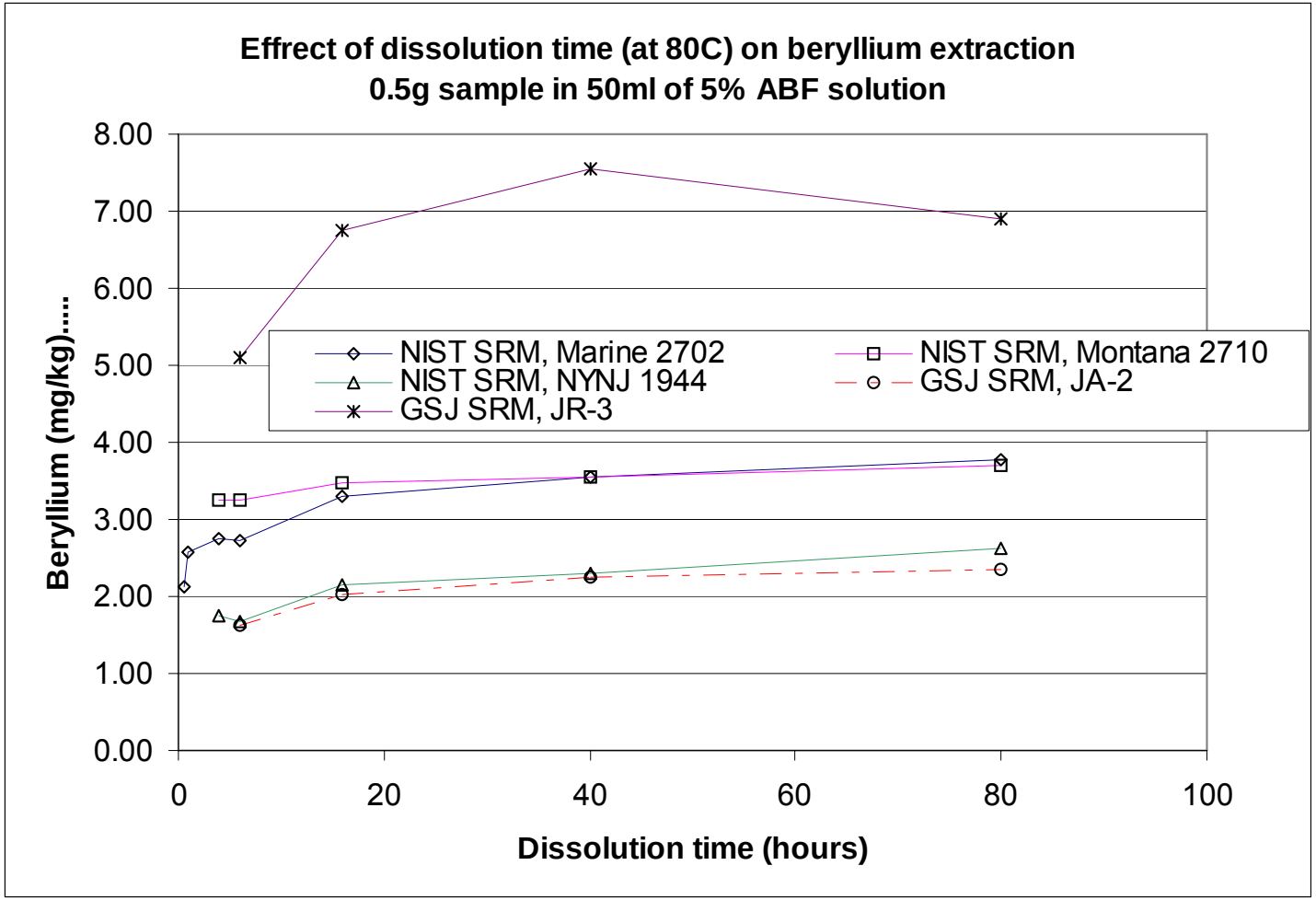
0.5 g pure silica would require 38 ml of 5% ABF

*Timokhin et al., *Glass and Ceramics* **44** (1987) 240.

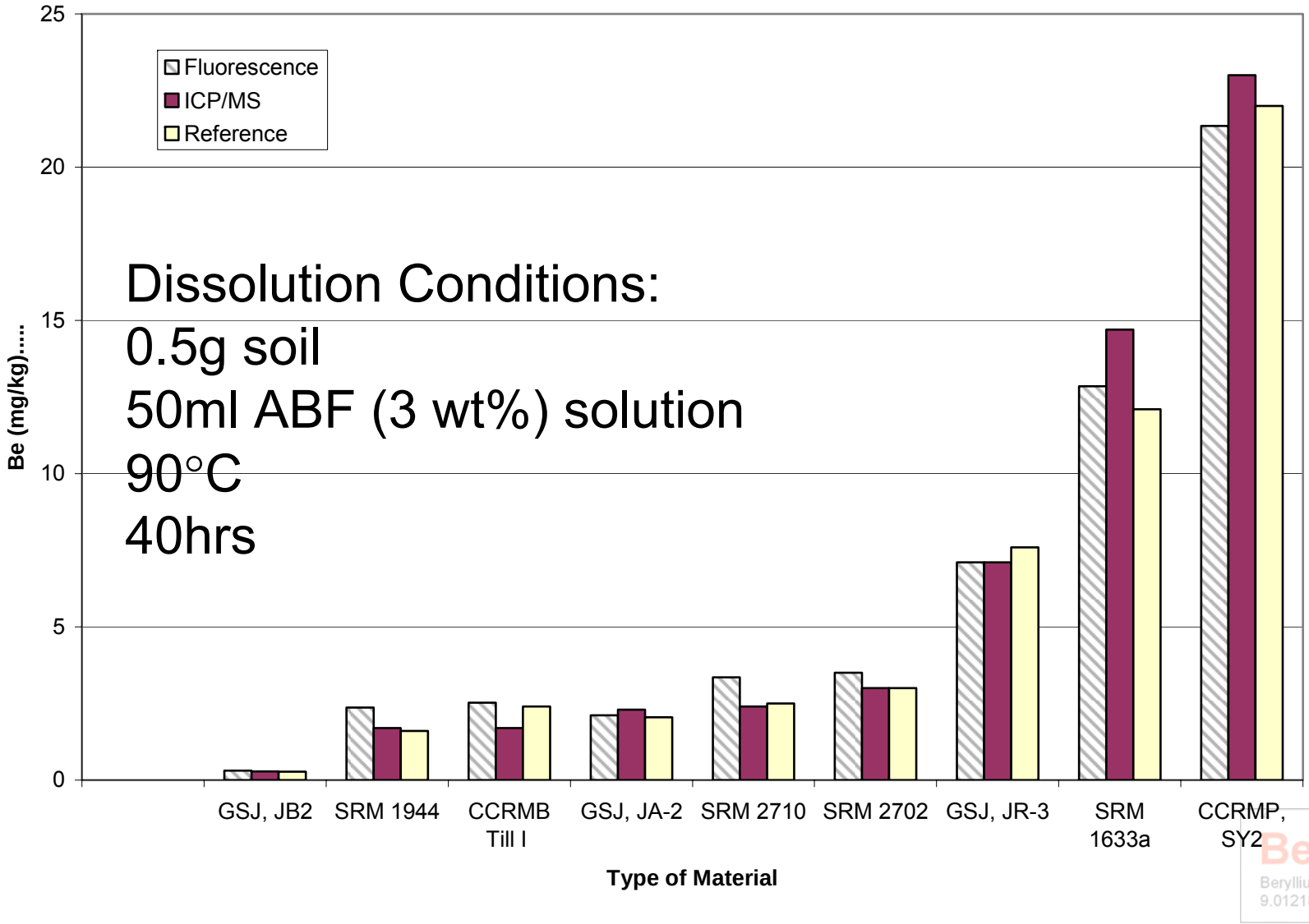
CRMs used in the *ES&T* (2008) study

Reference Material	Particle Size Information	Beryllium content,		Iron content,	Silicon content, %
		mg/kg	Uncertainty	%	
NIST SRM 2702, Marine Sediment	Passed through 70 µm screen	3[#]	Not known	7.91*	Not known
NIST SRM 2710, Montana Soil	Passed through 74 µm screen	2.5 [Ref 1]	±0.07	3.38*	28.97*
NIST SRM 1944, NY/NJ Waterway Sediment	Passed through 250 to 61 µm screens	1.6[γ]	± 0.3	3.53*	31[γ]
NIST SRM 1633a, Coal Fly Ash	Less than 88 µm	12.1[#]	Not known	0.0*	22.8*
GSJ JA-2, Andesite	Median 6.06 µm	2.05[γ]	±0.44	4.34[γ]	26.4[γ]
GSJ JR-3, Rhyolite	Median 4.57 µm	7.6[γ]	±0.831	3.3[γ]	34[γ]
GSJ JB-2, Basalt volcanic rock	Median 5.41 µm	0.27[β]	±0.043	9.97[γ]	53.2[γ]
CCRMP SY2 Syenite	Passed through 74 µm screen	22[β]	Not known	4.42[γ]	28.1[γ]
CCRMP Till-1 Soil	Passed through 74 µm screen	2.4[#]	Not Known	4.81[β]	28.5[β]

Effect of Dissolution Time



Method Effectiveness for Soil Dissolution



Inter-Laboratory Comparison

(*JEM*, 2008)

CCRMP Till-1 Spiked with BeO (UOX 125)

Unspiked ($2.4\ \mu g\ g^{-1}$)	**Low [Be] (4.36 µg g-1)**	**Medium [Be] (11.5 µg g-1)**	**High [Be] (124 µg g-1)**	**Very high [Be] (246 µg g-1)**
2.43 ± 0.215	**5.13 ± 0.528**	**12.4 ± 0.59**	**126 ± 9.0**	**234 ± 16.1**

Analysis by fluorescence, data from six participating labs

Dissolution Conditions:

- 0.5g soil
- 50ml ABF (3 wt%) solution
- 90°C
- 40hrs

New ASTM International Standard

- ASTM D7458: *Determination of Beryllium in Soil, Rock, Sediment, and Fly Ash using Ammonium Bifluoride Extraction and Fluorescence Detection*

- Use to determine [Be] in native soils and in (suspected) anthropogenically contaminated dust & soil
- Available from www.astm.org

Comparison of BeO and Soil Dissolution

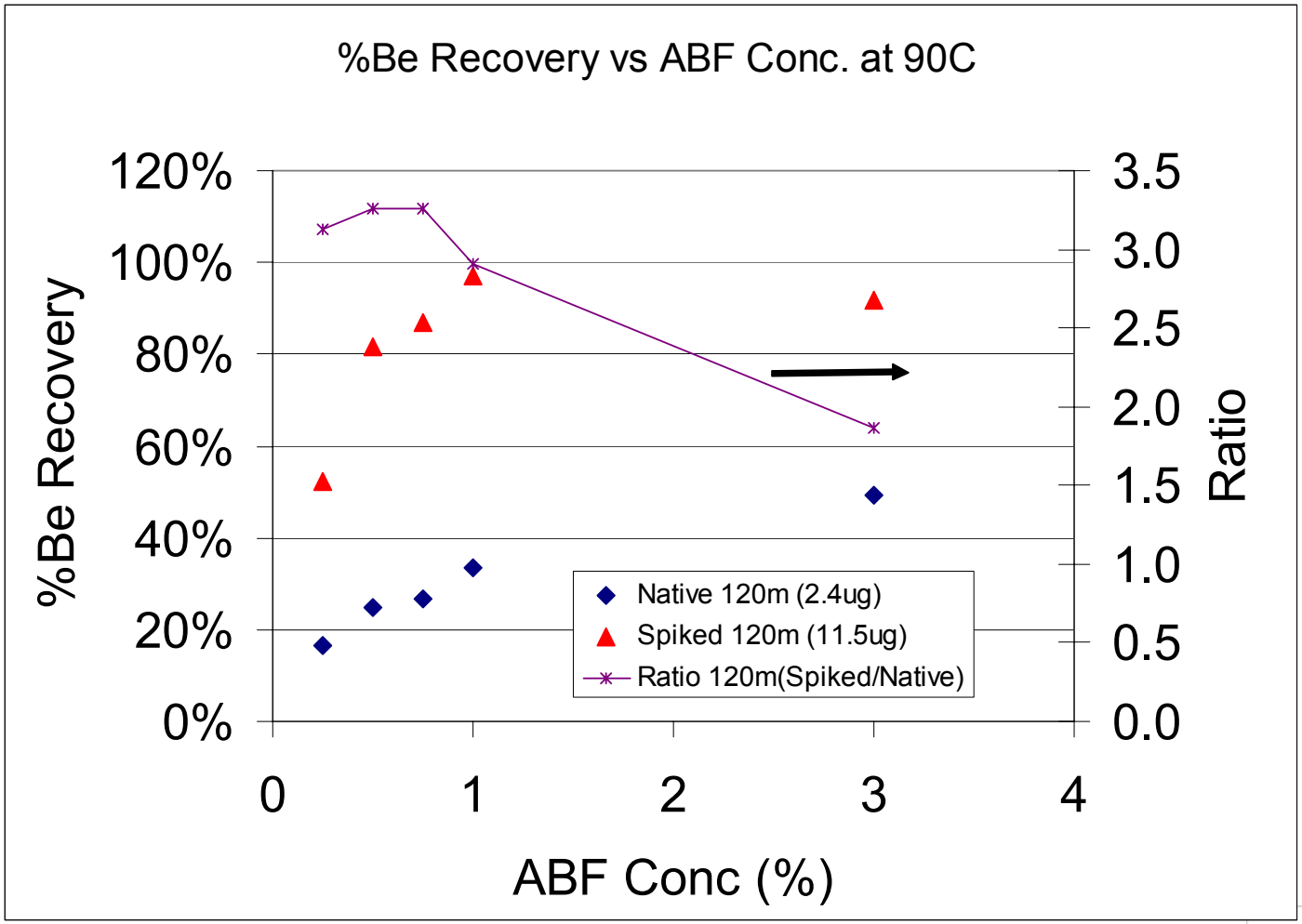
	High Fired BeO (UOX125)	Soils (for native beryllium)
Dissolution time	30 minutes	40 hours
Temperature of dissolution	75-90C	90C
Conc. Of ABF solution	1%	3-5%

Does this mean that anthropogenic beryllium in soils could dissolve differentially, thus leading to speciation?

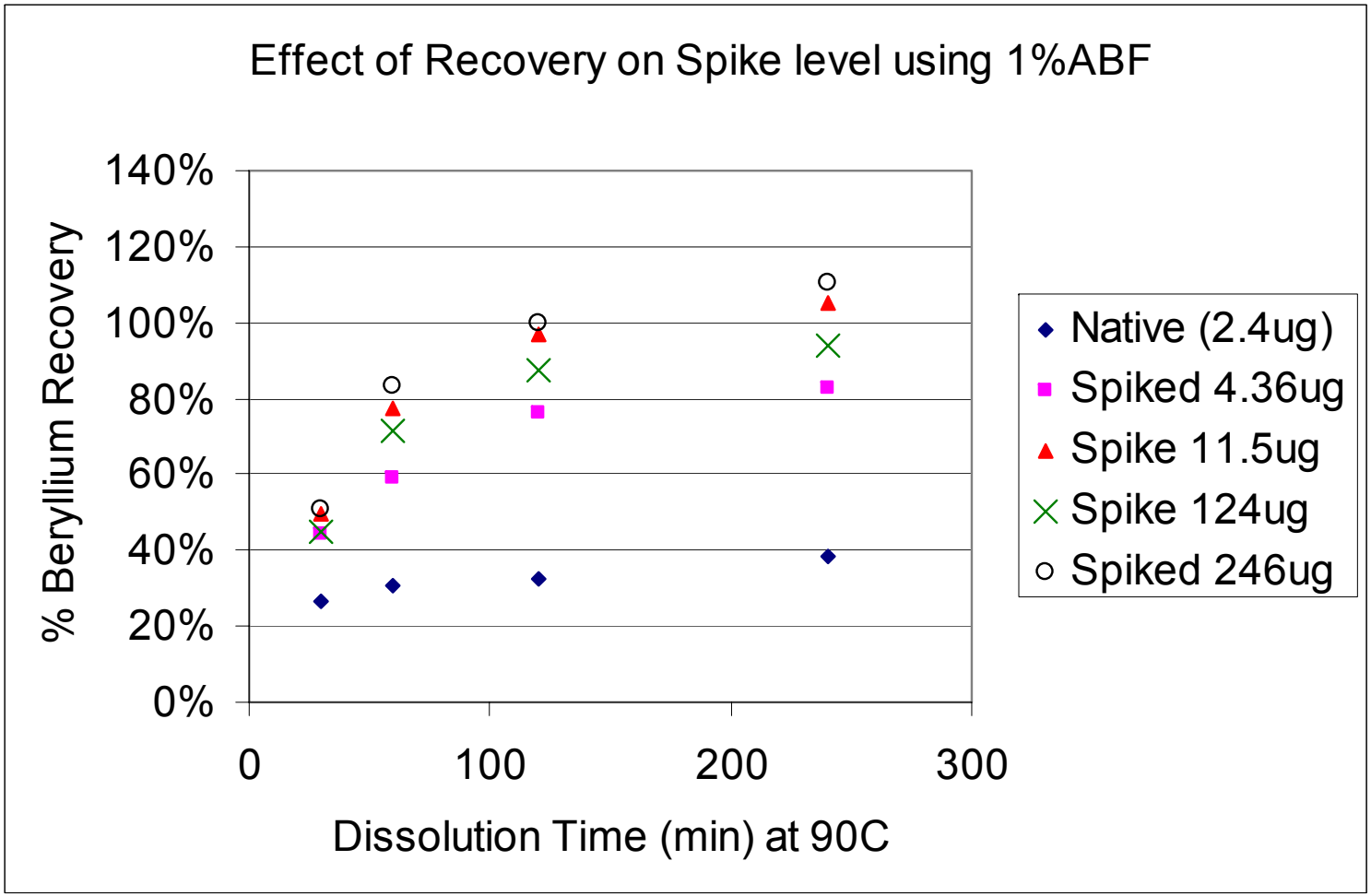
Preliminary Results

- All results using Canadian Till-1 soil CRM (2.4μg of beryllium/g of soil)
- Soil spiked with UOX BeO
- Dissolution using 50ml of ABF
- Sample size 0.5g
- Dissolution temperature 90°C

Effect of ABF Concentration on Beryllium Recovery of Spiked and Native Canadian Till-1 Soil



Effect of Spike Level on Beryllium Recovery



Conclusions

- ABF is a highly effective dissolution medium for both high-fired BeO and Be in soils (including silicates)
- Dissolution conditions can be optimized by changing the ABF concentration, time and temperature of dissolution.
- Dissolution kinetics may make it possible to assess whether the measured beryllium is anthropogenic or native to the soils.

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High-Purity Standards