Rapid Actinide Analysis for Soil
New Developments

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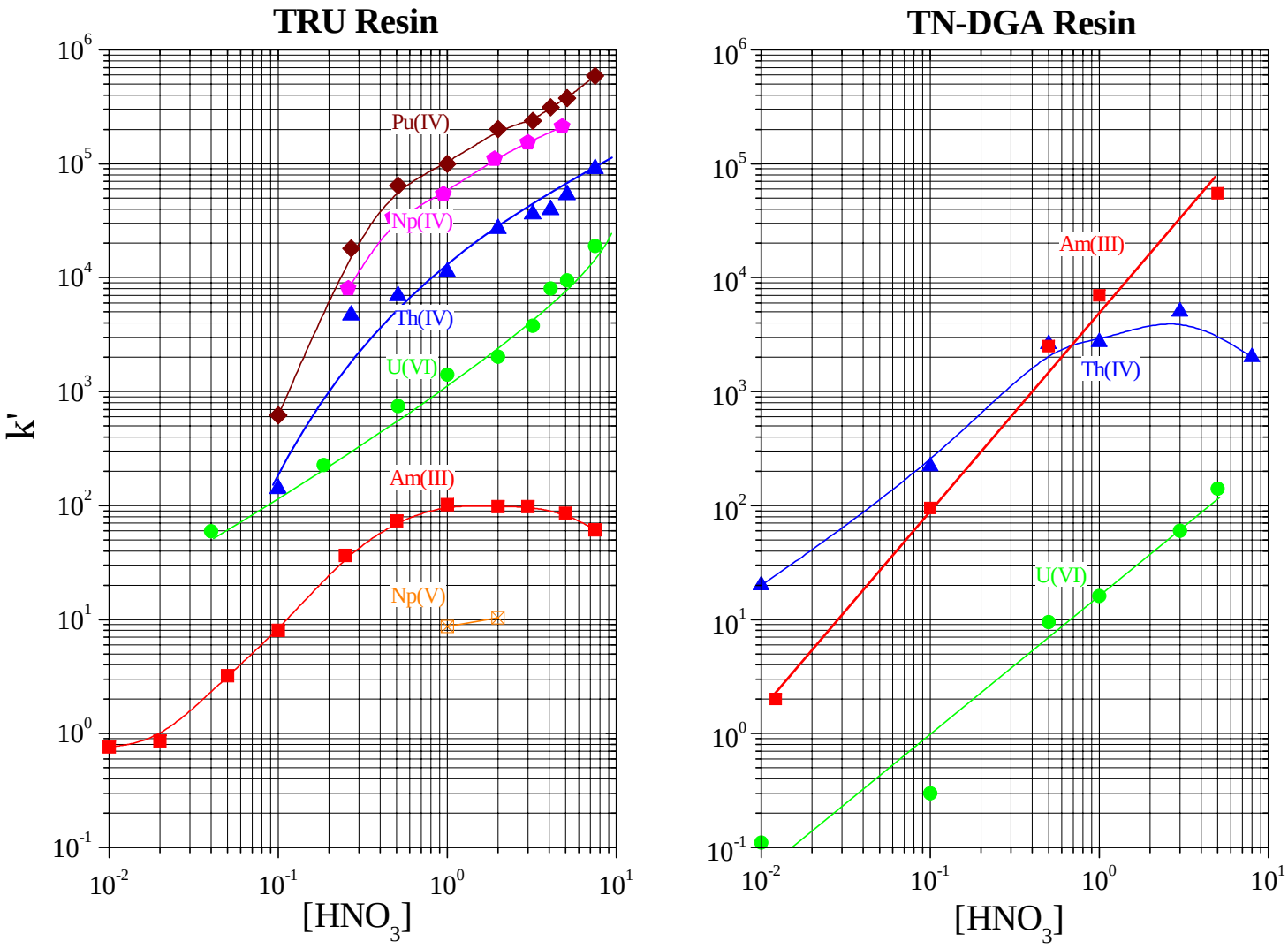
Needs

- Total dissolution-refractory particles
- Rapid sample preparation
  - Removal of interferences
  - Consistent recoveries
- Emergency methods-even faster
- Very large sample analysis-100+grams

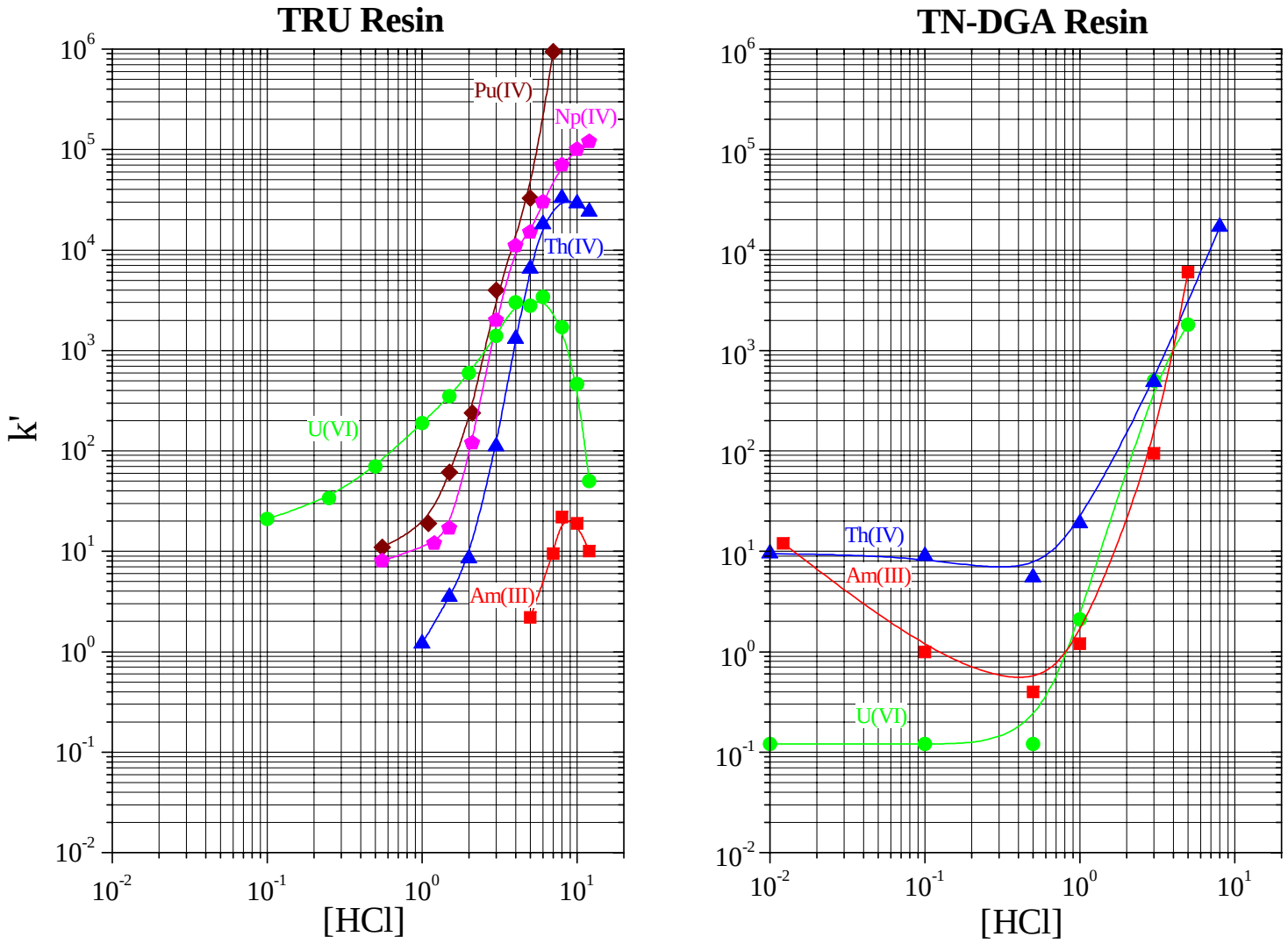
New Developments

- Routine method- total dissolution
  - Shorter sample preparation
- Emergency method-total dissolution
  - 1 day sample preparation
- 100+ gram soil method-leach
- Common features
  - Cerium fluoride precipitation for soil matrix removal
  - Column separation using TEVA+TRU+DGA

Comparison of TRU and DGA Resins



Comparison of TRU and DGA Resins



Routine Method

- 5-10 g sample size
- Fusion with 15 g sodium hydroxide (no sodium peroxide)
  - Less oxidizing than sodium peroxide (U reduction)
- Iron hydroxide precipitation in 225 ml centrifuge tube, not large 1 L beaker
- No additional rinse of CeF3 ppt.
- Simpler, faster sample preparation

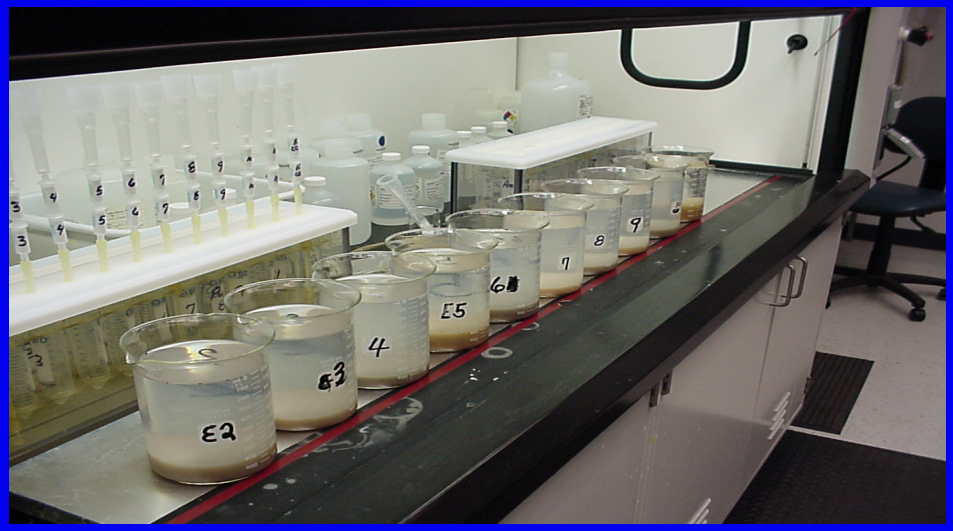
After adding tracers and heating at 550C for 4 hours,

Ash with HNO3/HCl/HF, then HNO3/HF, then HNO3 only to remove silicates

Transfer to Zr crucible and evaporate

Add 15 grams sodium hydroxide

Furnace at 600C for 20 min.



Old method:
Used to dilute to 1 L in large beakers

Now ppt. directly in 225 ml centrifuge tube/ice 5 to 10 minutes
(125 mg Fe, 5 mL $TiCl_3$, 1 mL 10% $Ba(NO_3)_2$, ~5-10 mg Ce)

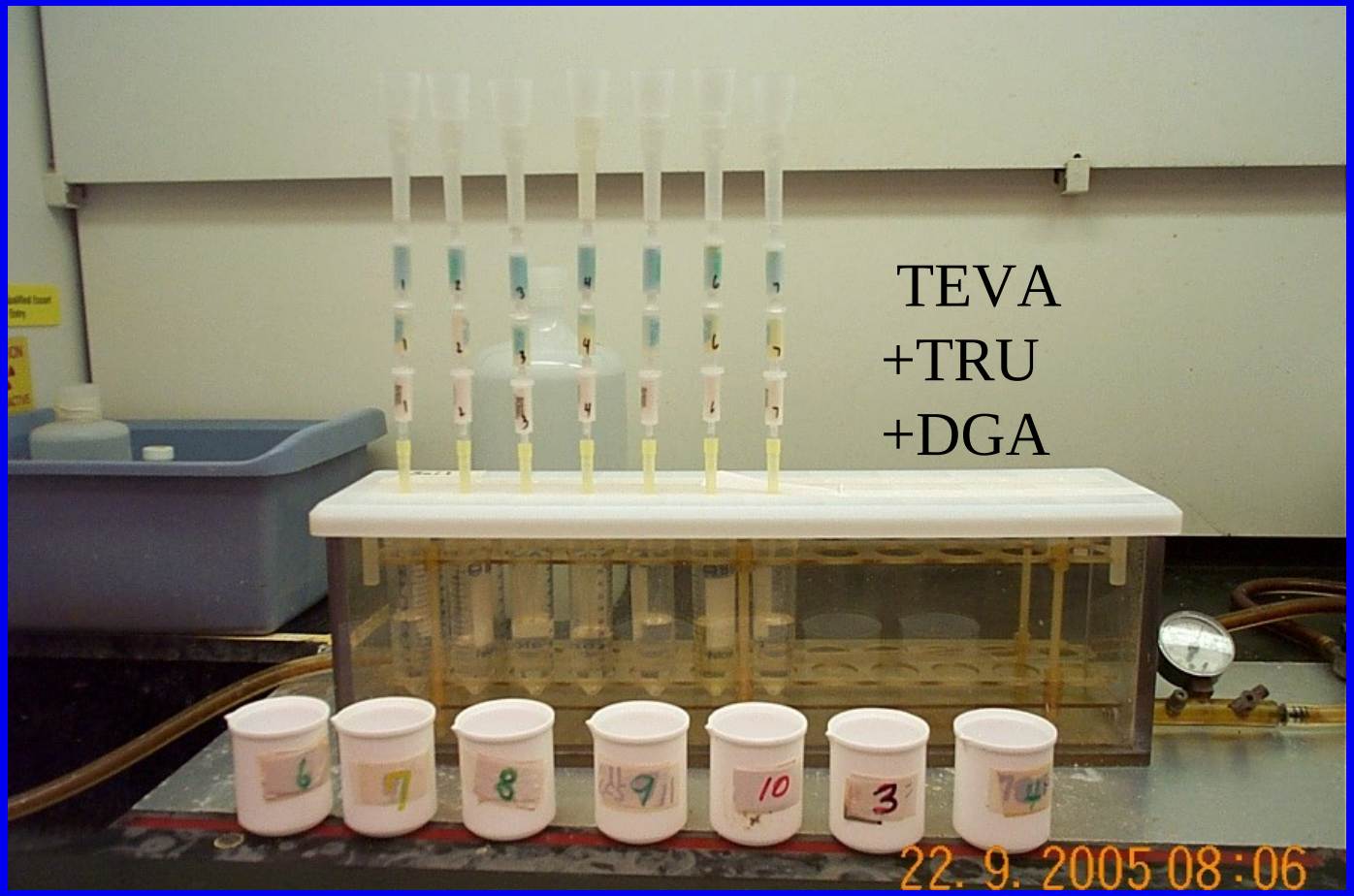
Ice to room temp.

Centrifuge 5 minutes.

Redissolve to 60 mL volume with 1.5M HCl. Dilute to 170 mL with 0.01M HCl.

Add 10 mL TiCl3, 2 mg Ce and 20 mL con. HF). Ice 10 minutes and centrifuge 20 minutes.

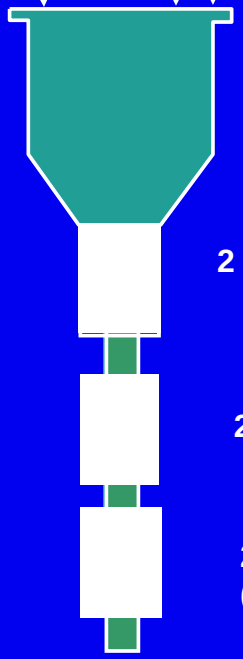
Redissolve in 5 mL warm 3M HNO3-0.25M boric acid, add 6 mL 7M HNO3 and then 7.5 mL of 2M Al(NO3)3


TEVA
+TRU
+DGA
22. 9. 2005 08 : 06

Actinides in Soil

1) Redissolve in 5 mL warm 3M $HN0_3$ - 0.25M boric acid, add 6mL 7M HNO3 and 7.5 mL 2M $Al(N0_3)_3$
2) Add 0.5 mL 1.5M Sulfamic Acid + 1.25 mL 1.5M Ascorbic Acid
3) Add 1 mL 3.5 M Sodium Nitrite

Rinse
Beaker rinse: 3mL 6M$HN0_3$
Separate cartridges:
TEVA: 7 mL 3M$HN0_3$ Collect/acidify - with 3 mL16M $HN0_3$ then to TRU
TEVA:10 mL 5M HNO_{3-}
8 mL 3M $HN0_3$



Th Elution
20mL 9MHCl

Pu (and/or Np) Elution
20mL
0.10MHC1 - 0.05MHF - 0.03M TiCl3

Add 0.5 mL 30 wt% H2O2

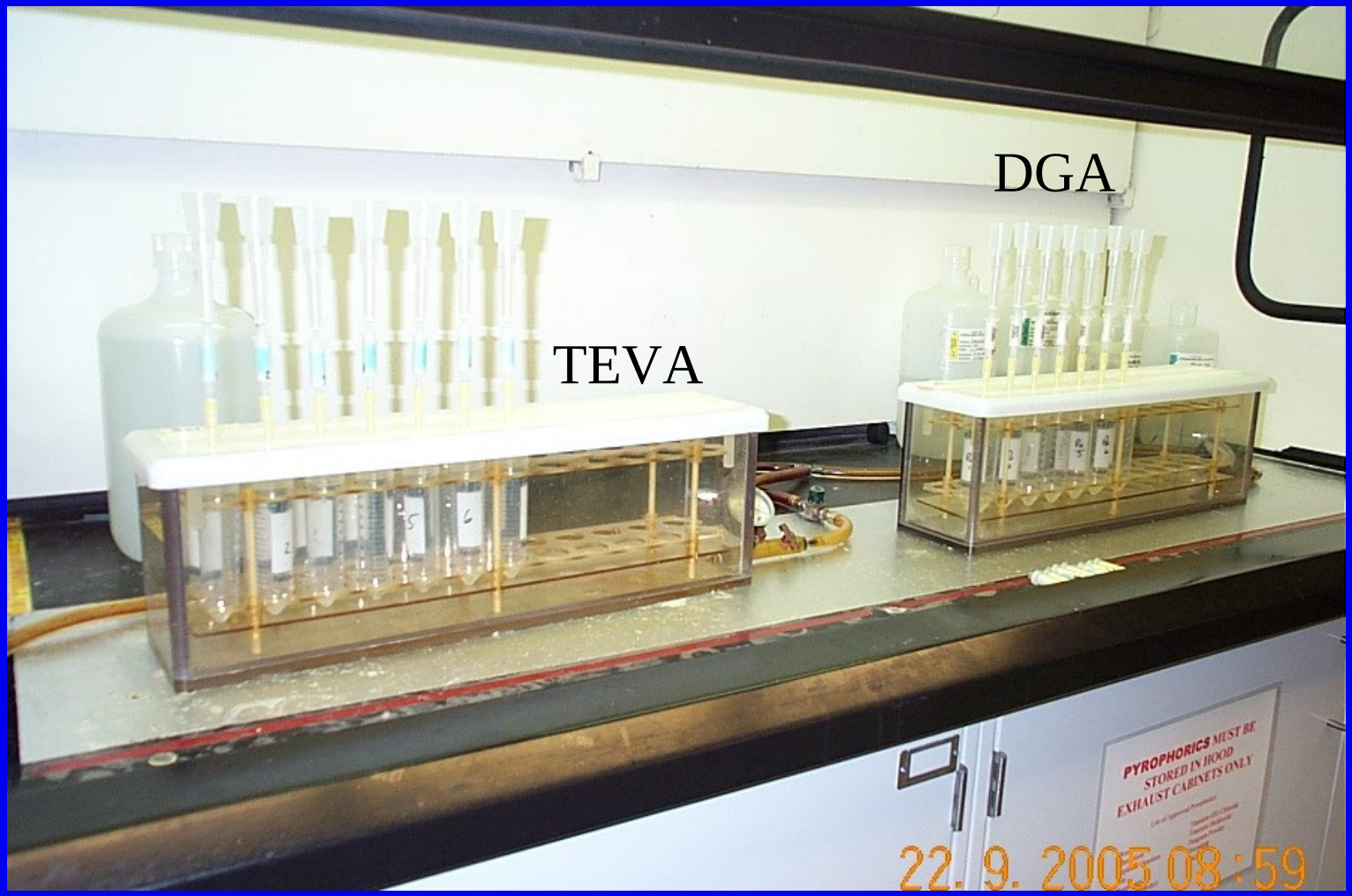
2 mL TEVA Resin
(50-100 um)

Cerium fluoride

Alpha spectrometry

2 mL TRU-Resin
(50-100 um)

2 mL DGA-Resin
(50-100 um)


DGA
TEVA
PYROPHORICS MUST BE
STORED IN HOOD
EXHAUST CABINETS ONLY
22. 9. 2005 08 : 59

Elute any U from DGA only with 5 mL of 0.25M HNO3 (then add 4 mL con. HNO3 to adjust acid).

Place TRU on top of DGA cartridges.
Elute Am from TRU onto DGA with 15 mL 4M HCl.

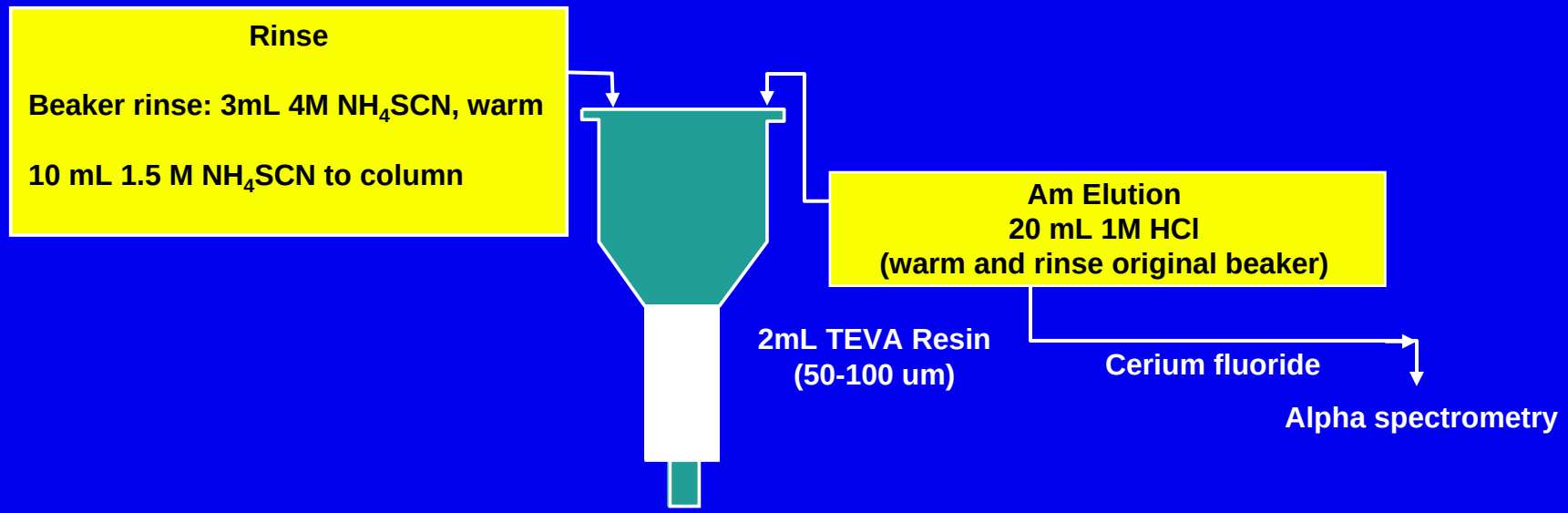
Strip Am from DGA with 10 mL 0.25M HCL.

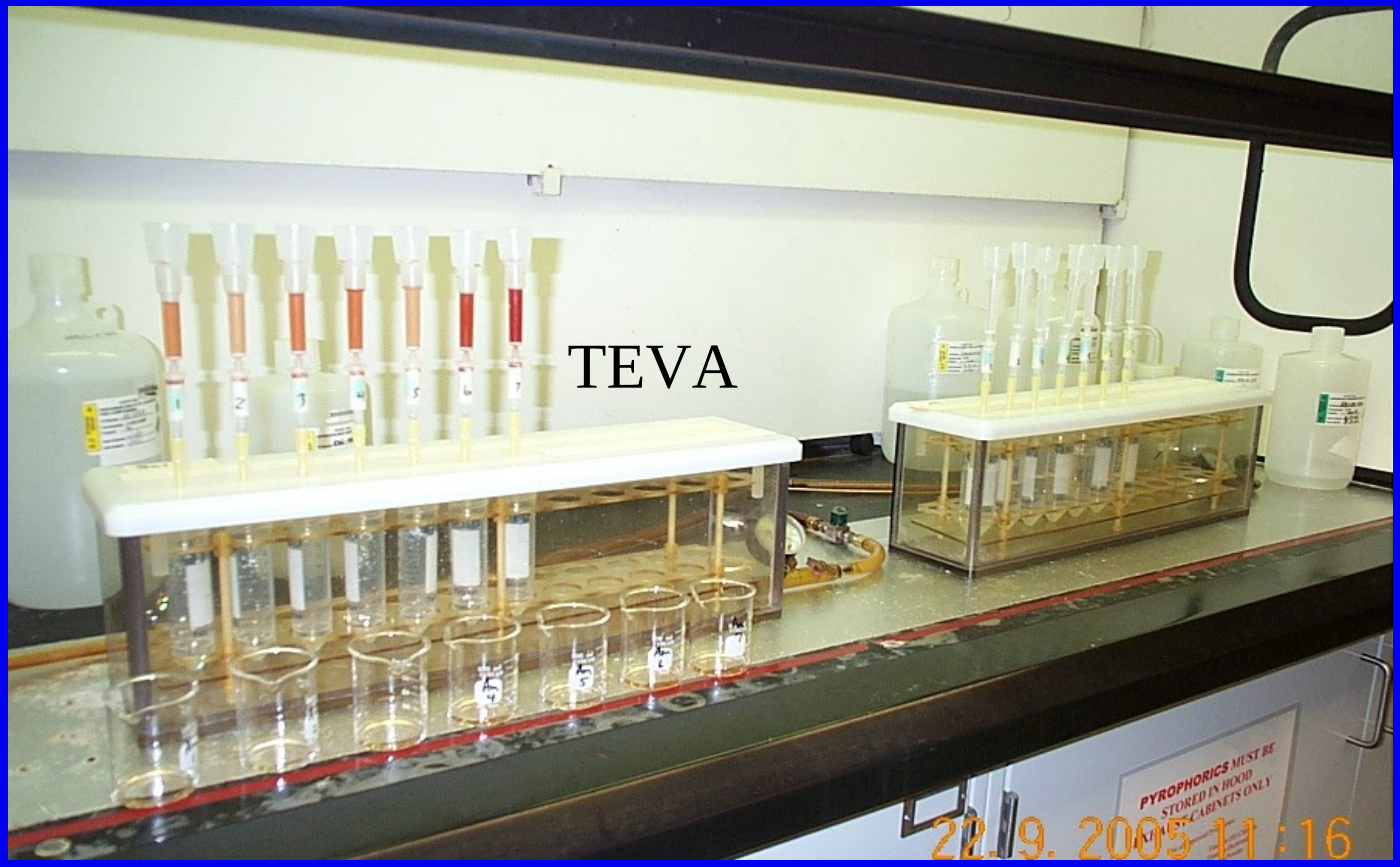
Add 50 uL 1.8M H_2SO_4 and 2mL con. HNO_3, evaporate. Ash once with 2 mL con. HNO_3 and 2 mL 30 wt% H_2O_2

Add 3M HNO3 rinse (then adj. ~7M HNO3) from TEVA to load to TRU only
Add U fraction from DGA adjusted to ~ 7M HNO3 to add any U from DGA to TRU and remove any Po-210. 7 mL 7 M HNO3 rinse (Po removal)
Add 18 mL 4M HCl-0.2M HF to TRU to remove Th
U strip with 15 mL 0.1M ammonium bioxalate

Am/RE Removal on TEVA

1) Evaporate 0.25 M HCl with 2mL con.HNO3, 50 uL of 1.8M H2SO4, then ash with nitric acid and hydrogen peroxide 1 time
2) Redissolve in 5 mL of 4M NH_4SCN, warm gently.





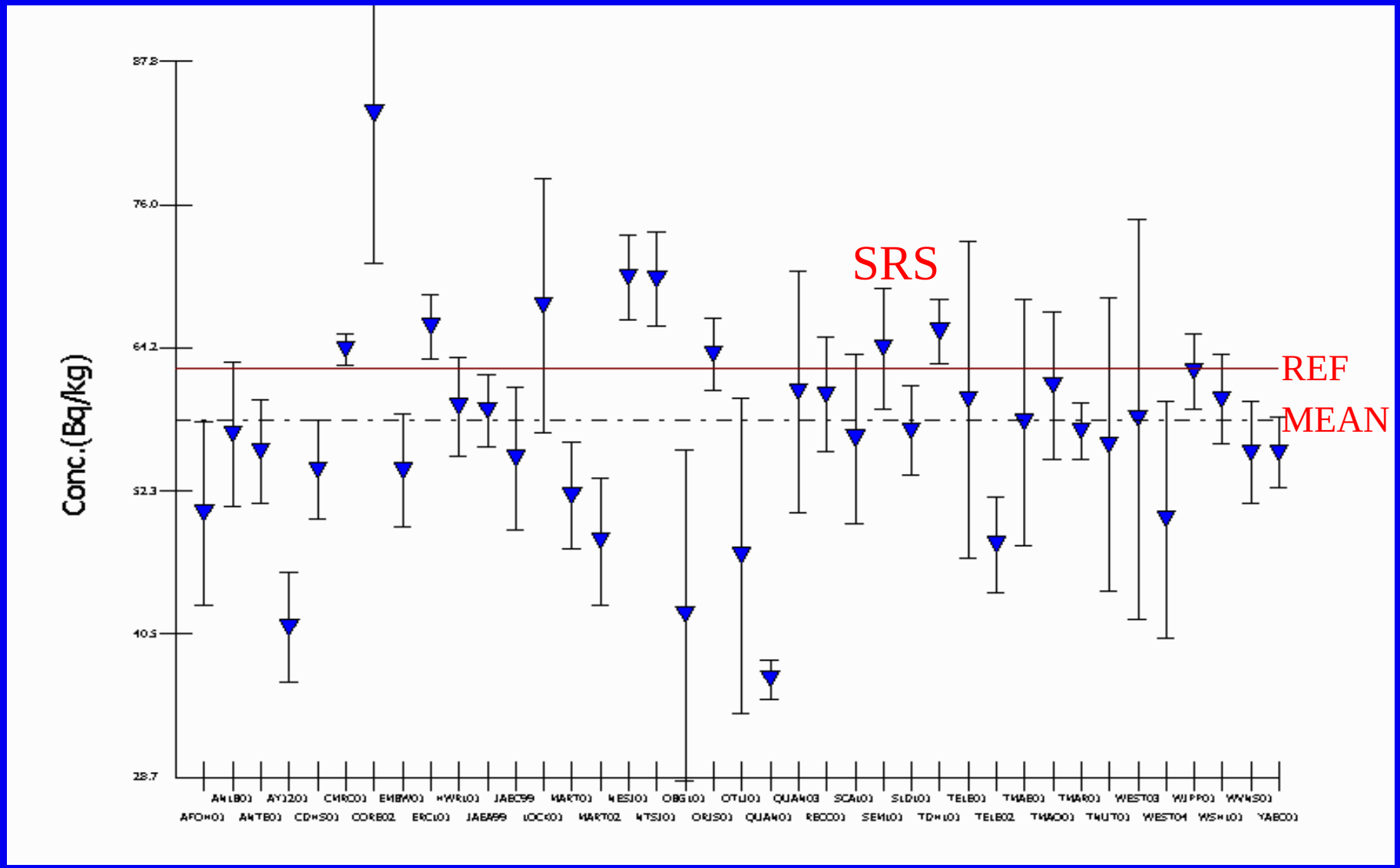
Am/Cm separation from rare earths using TEVA-SCN

DOE MAPEP -05-MaS13-SOIL

	SRS		REF.	Ratio
Pu-238	0.51	(0.48)	0.48	1.062
Pu-239	85.3	(84.1)	89.5	0.953
Am-241	100	(101)	109	0.917
U-234	64.1	(64.9)	62.5	1.026
U-238	242	(252)	249	0.972

Results in Bq/kg
5 gram sample analyzed
Streamlined method results

U-233/234 in MAPEP SOIL



QAP Results

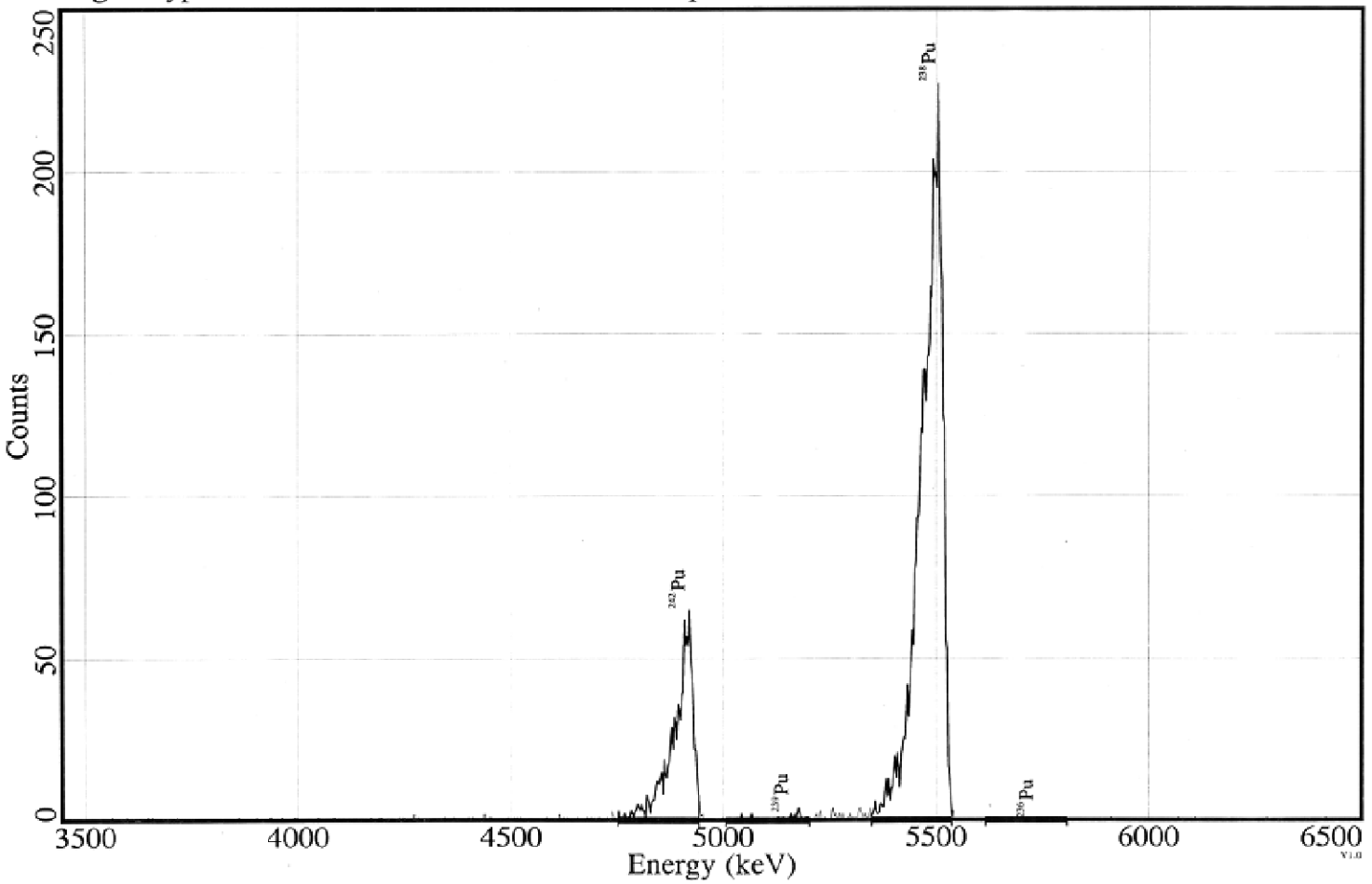
	SRS	REF.	Ratio
Pu-238	31.2	30.4	1.02
Pu-239	15.0	14.6	1.03
Am-241	17.5	18.4	0.95
U-234	125	127.3	0.98
U-238	126.4	127.1	0.99

Results in Bq/kg
5 gram sample analyzed
QAP 03-09

Environmental & Bioassay Laboratories

Filename: S_500001234$300093094_PU Detector: 7
Acquisition Start: 15-SEP-2005 16:43:23
Region type: STANDARD Tracer ID: pu242-444

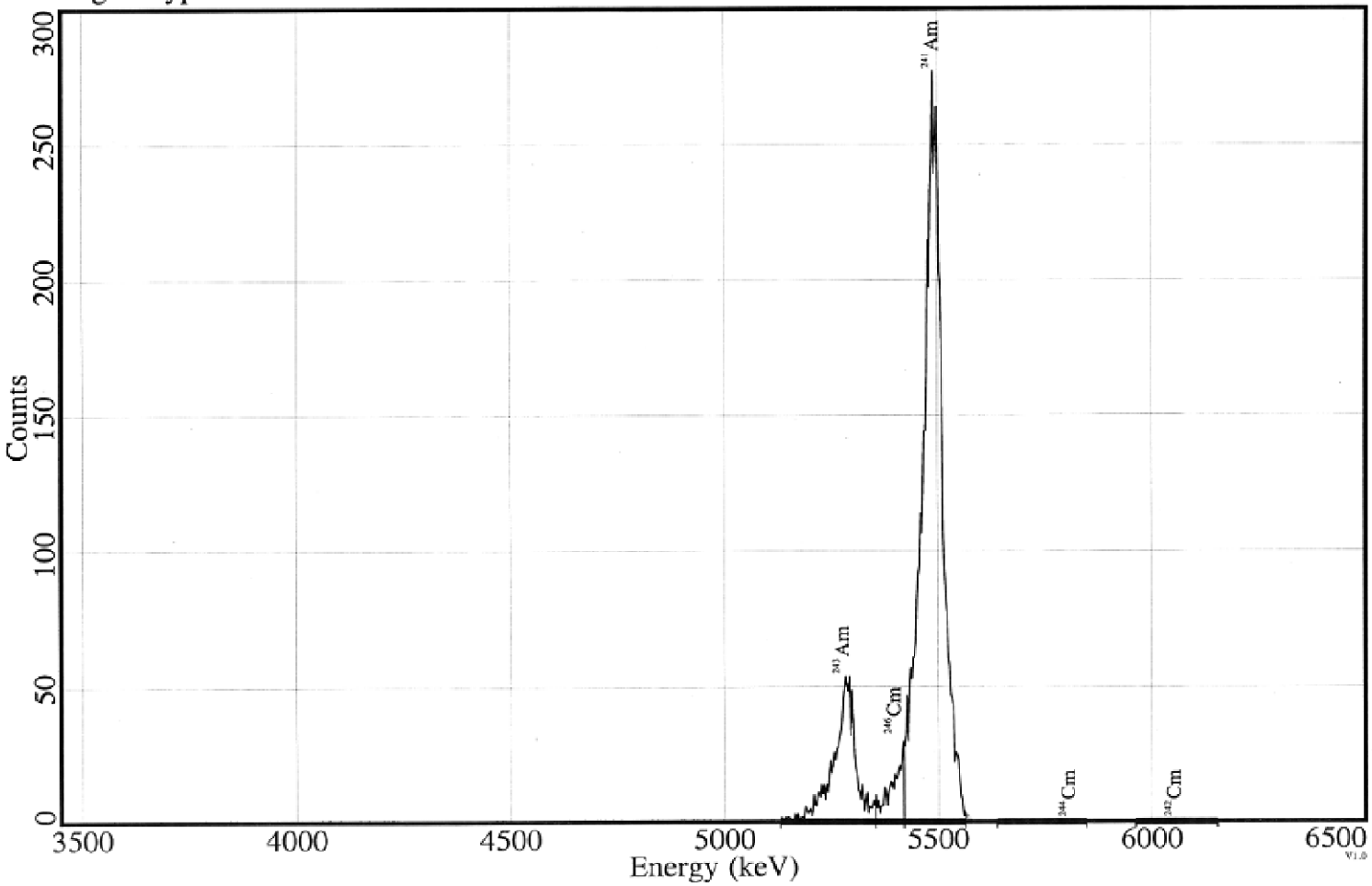
Chemical Yield: 95.989%
Count Time: 0 16:00:01
Tracer FWHM: 39.812



Environmental & Bioassay Laboratories

Filename: S_500001217$300093090_AM Detector: 30
Acquisition Start: 15-SEP-2005 14:54:50
Region type: STANDARD Tracer ID: am243-444

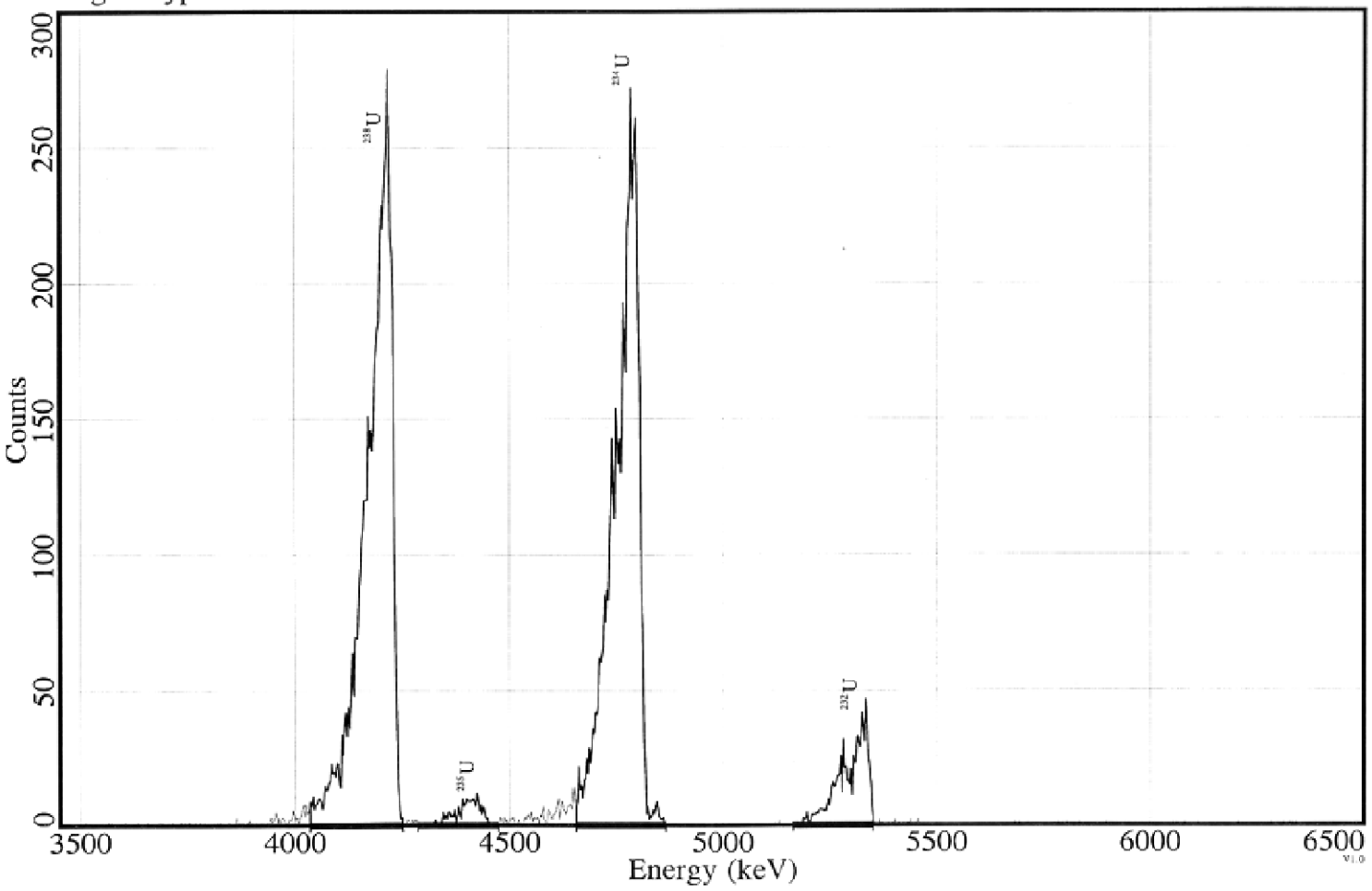
Chemical Yield: 91.123%
Count Time: 0 16:00:01
Tracer FWHM: 43.593



Environmental & Bioassay Laboratories

Filename: S_500001235$300093258_TU Detector: 68
Acquisition Start: 15-SEP-2005 16:31:02
Region type: STANDARD Tracer ID: u232-109

Chemical Yield: 66.431%
Count Time: 0 16:00:03
Tracer FWHM: 71.950



Emergency Method

- Radiological Preparedness Exercise (NRIP'04)
  - Kenneth Inn, NIST
  - spoke at RRMC-2004 of "need to improve efficiency and effectiveness of radioanalytical capabilities"
- Need for faster radiological analyses for Homeland Security reasons

Emergency Method

- 3-5 g sample size
- Rapid preparation
- No drying and hour furnace at 550C
  - Add H2O2 during HNO3/HF ashing steps
- Fusion with 15 g sodium hydroxide
- 4-5 hours sample preparation to remove matrix/load solution
- 4-5 hours column separation-TEVA+TRU+DGA
- Testing rare earth removal on DGA instead of TEVA-SCN

Timeline

- 7 am –weigh aliquots/add tracers
- 9:00 am ashing complete/transferred to crucibles
- 11:00 am-fusion plus cerium fluoride precipitation complete
- 11:30 sample loading
- 4:30 samples to count room
- Count as needed

QAP Results

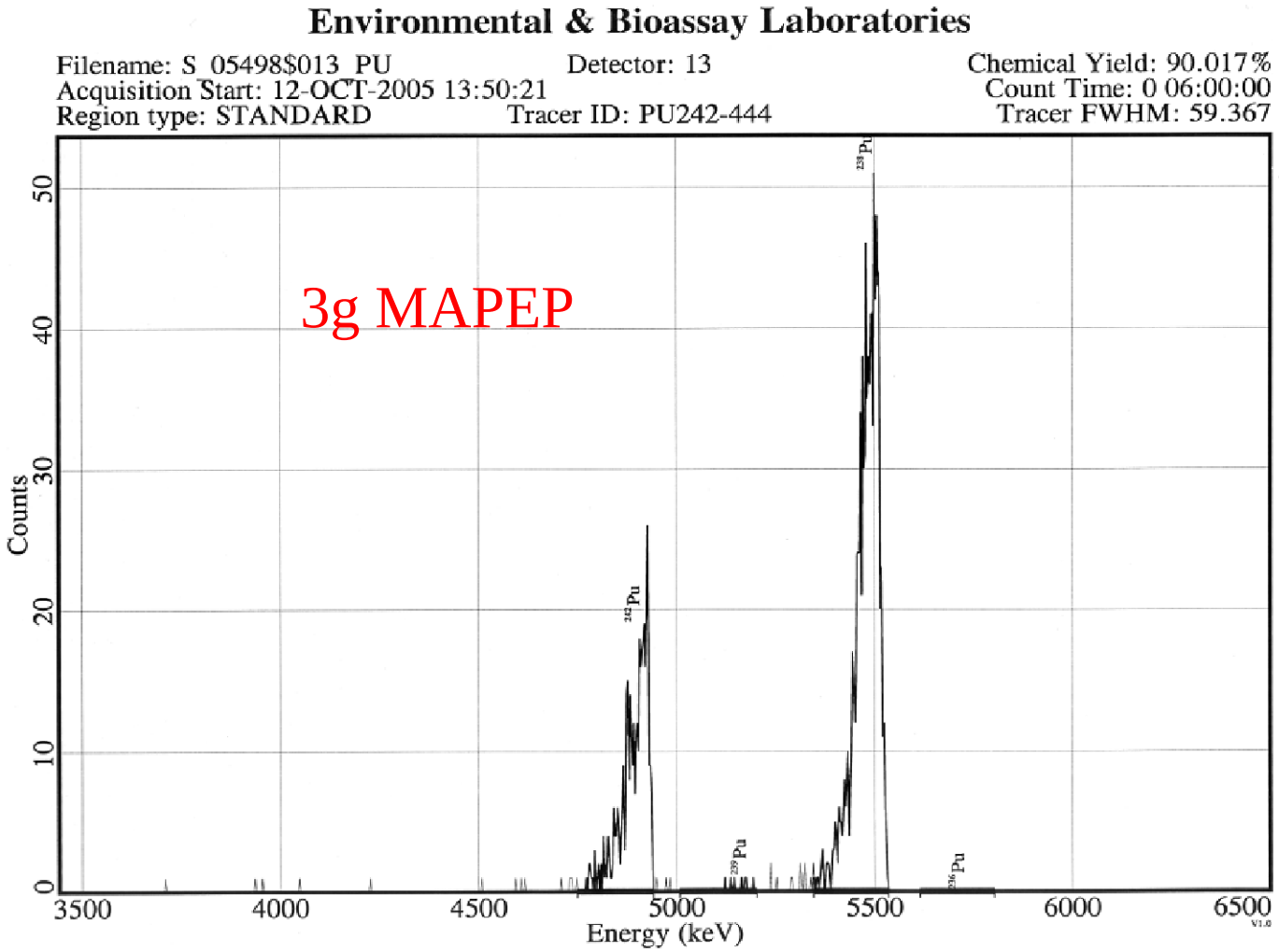
	% Pu-242 Recovery	Pu-239 pCi/g
	97.1	0.185
	93.0	0.241
	67.9	0.219
	87.1	0.225
Avg.	87.7	0.225
		8.32 Bq/kg
	Ref.	8.11 Bq/kg
QAP 99-03	% Diff.	2.6

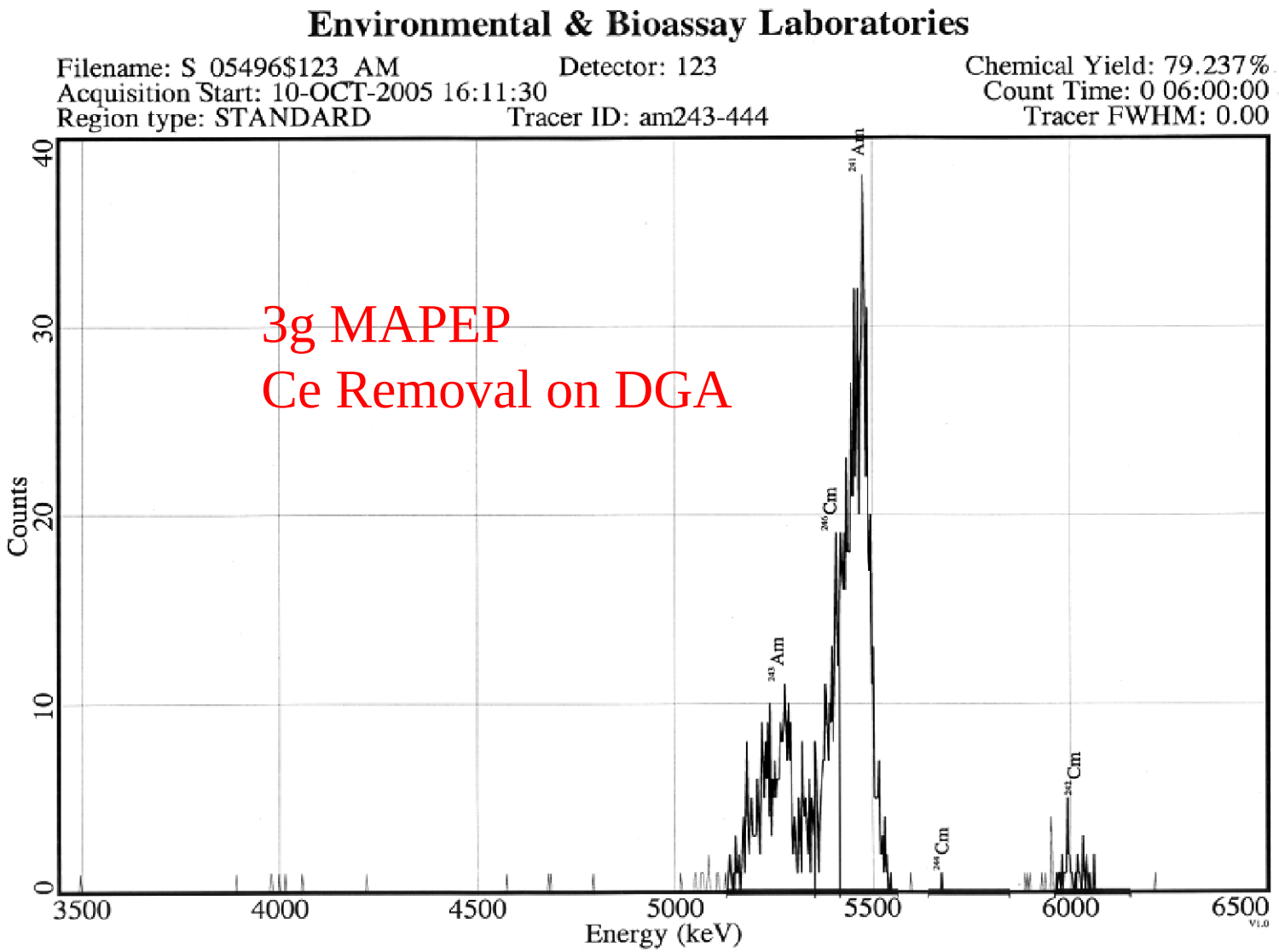
QAP Results

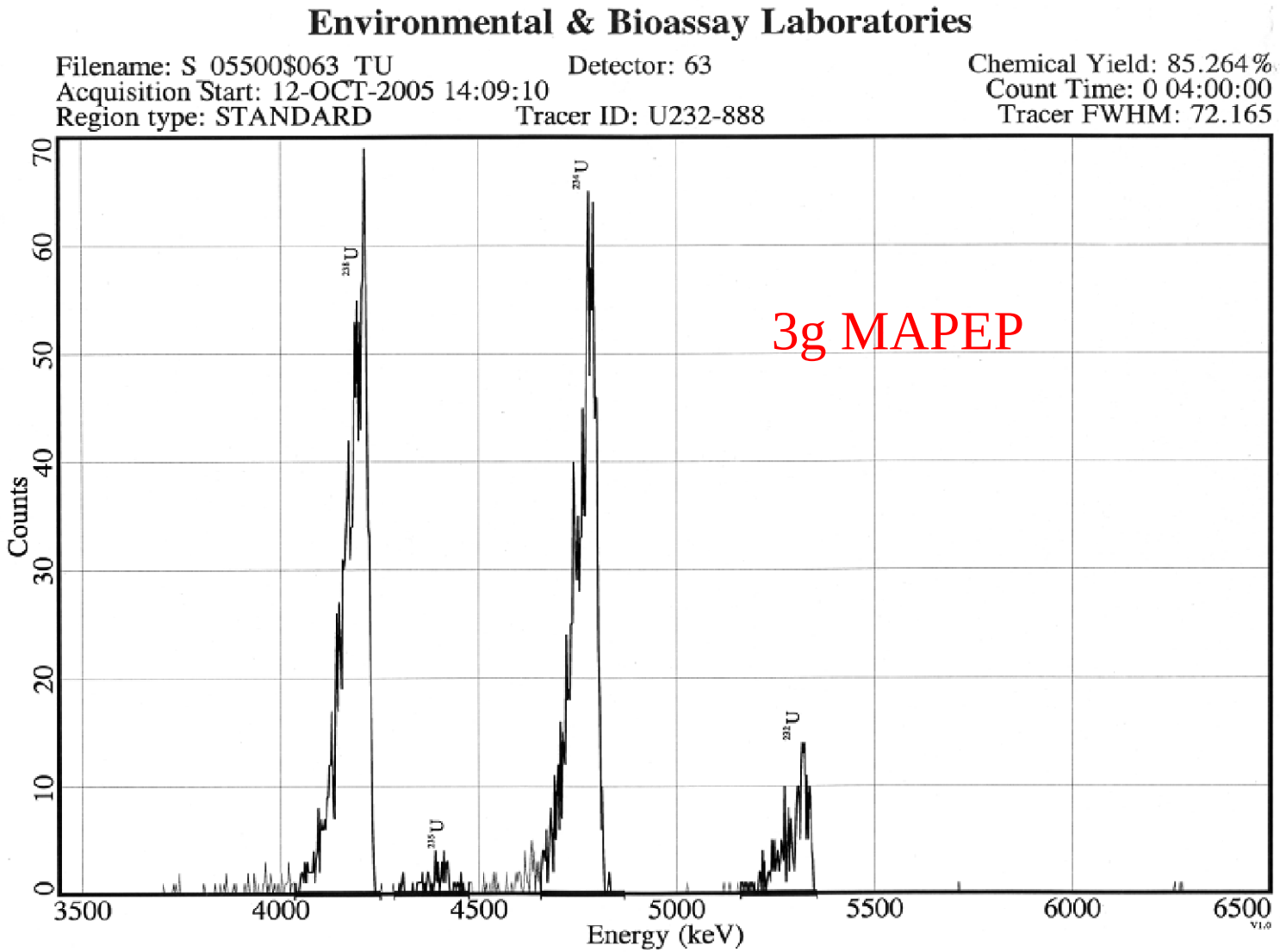
		% U-232 Recovery	U-234 pCi/g	U-238 pCi/g
		76.4	3.85	4.09
		75.5	3.94	4.18
		80.2	3.59	3.94
		72.0	3.90	4.26
Avg.		76.0	3.82	4.12
			141.5 Bq/kg	152.5 Bq/kg
QAP 99-03	Ref.		140.7 Bq/kg	145 Bq/kg
	% Diff.		0.56	5.2

QAP Results

		% Am-243 Recovery	Am-241 pCi/g
		78.7	0.0924
		93.1	0.0944
		88.6	0.0755
		90.4	0.0859
Avg.		87.7	0.087
			3.224 Bq/kg
	Ref.		3.220 Bq/kg
QAP 00-03	% Diff.		0.13


Environmental & Bioassay Laboratories
Filename: S_05498$013_PU
Detector: 13
Chemical Yield: 90.017%
Acquisition Start: 12-OCT-2005 13:50:21
Count Time: 0 06:00:00
Region type: STANDARD
Tracer ID: PU242-444
Tracer FWHM: 59.367
3g MAPEP
Counts
0
10
20
30
40
50
3500
4000
4500
5000
5500
6000
6500
Energy (keV)
V1.0

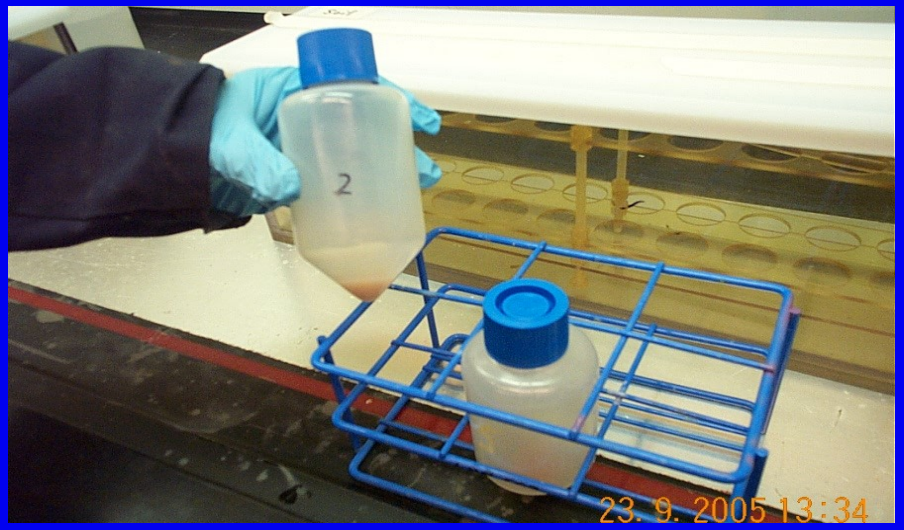

Environmental & Bioassay Laboratories
Filename: S 05496$123 AM
Detector: 123
Chemical Yield: 79.237%
Acquisition Start: 10-OCT-2005 16:11:30
Count Time: 0 06:00:00
Region type: STANDARD
Tracer ID: am243-444
Tracer FWHM: 0.00
3g MAPEP
Ce Removal on DGA
Counts
Energy (keV)
241Am
246Cm
243Am
244Cm
243Cm
0
10
20
30
40
3500
4000
4500
5000
5500
6000
6500

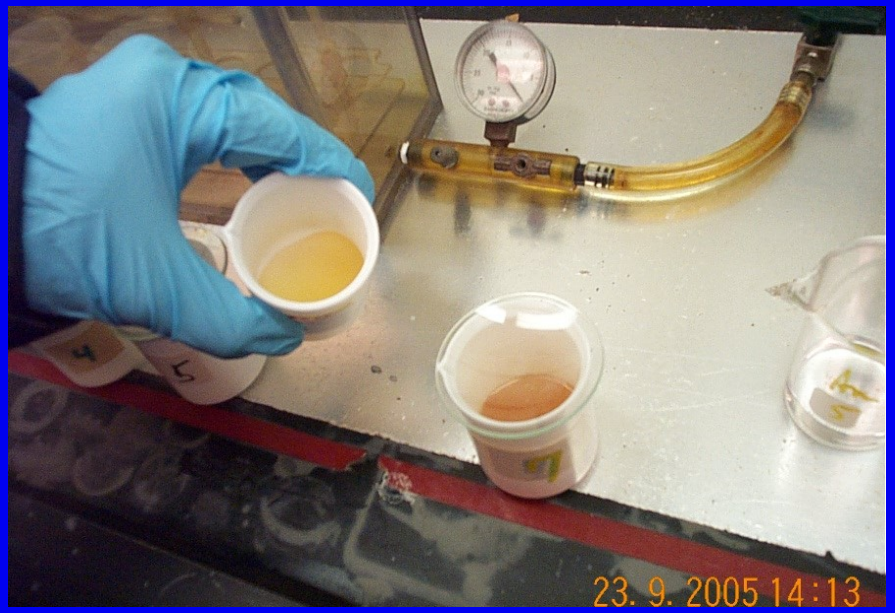

Environmental & Bioassay Laboratories
Filename: S_05500$063_TU
Acquisition Start: 12-OCT-2005 14:09:10
Region type: STANDARD
Detector: 63
Tracer ID: U232-888
Chemical Yield: 85.264%
Count Time: 0 04:00:00
Tracer FWHM: 72.165
3g MAPEP
Counts
Energy (keV)
0
10
20
30
40
50
60
70
3500
4000
4500
5000
5500
6000
6500

Sample Leach-100+grams

- Testing with 100-200 g soil
- Testing with HNO3/HCl leach with and without HF
- Am recoveries 100 g+- 60-80%
- Pu recoveries 100 g+ - 60-80%

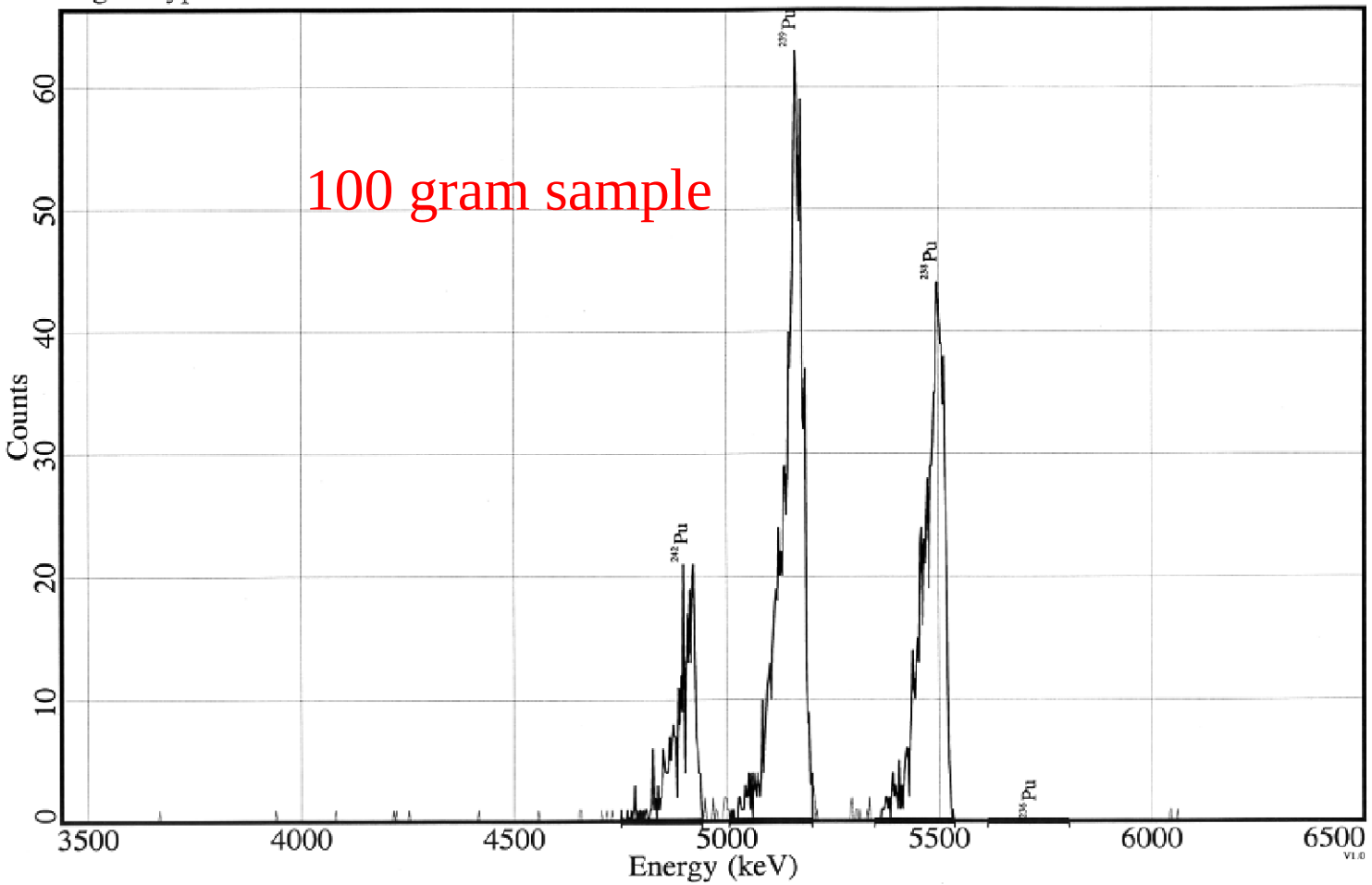

LINDBERG/BLUE
1000 mL PYREX
614 100g
614 100g
614 200g
3
HOT
22. 9. 2005 08:08

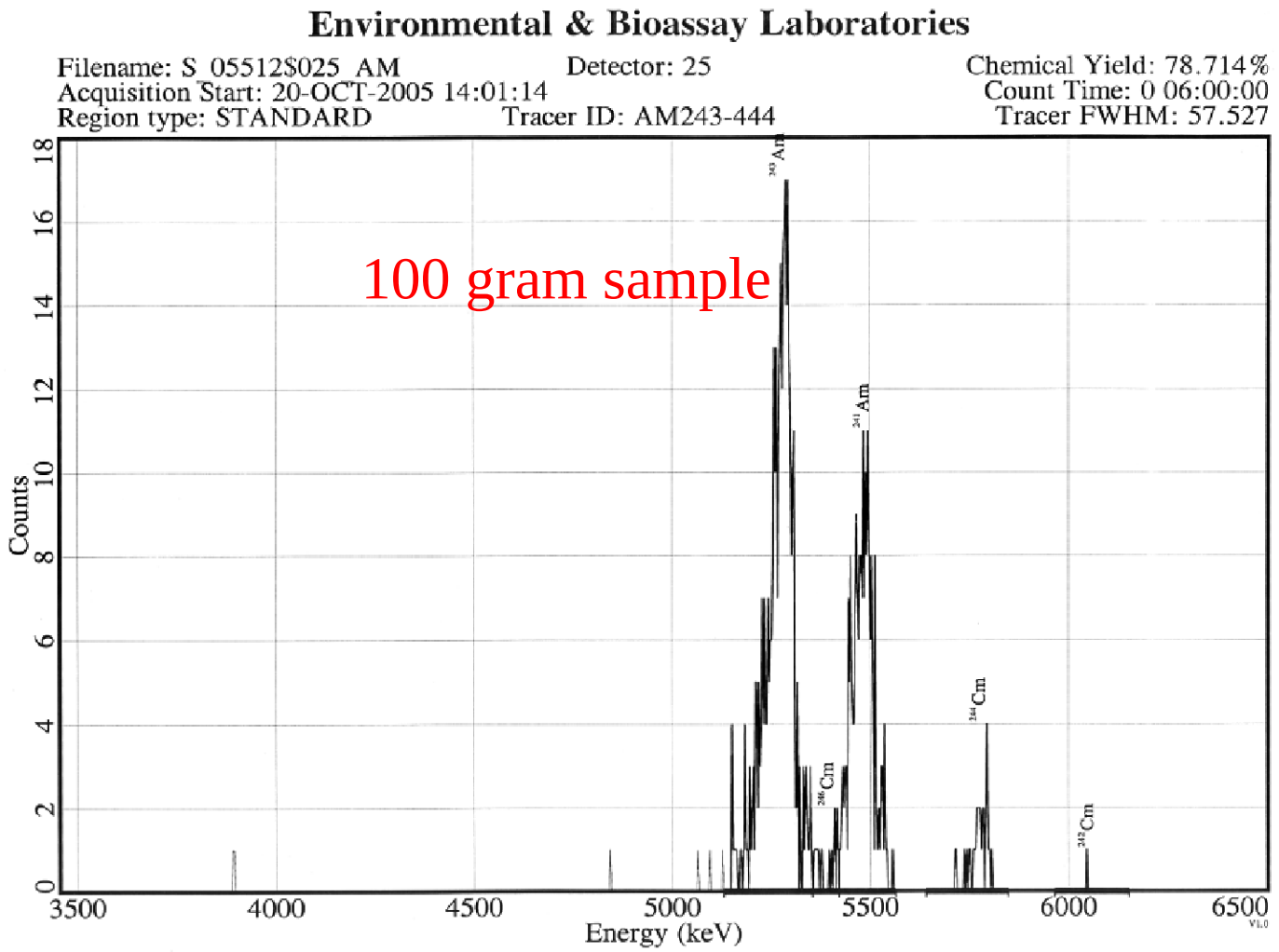

2
23. 9. 2005 13:34

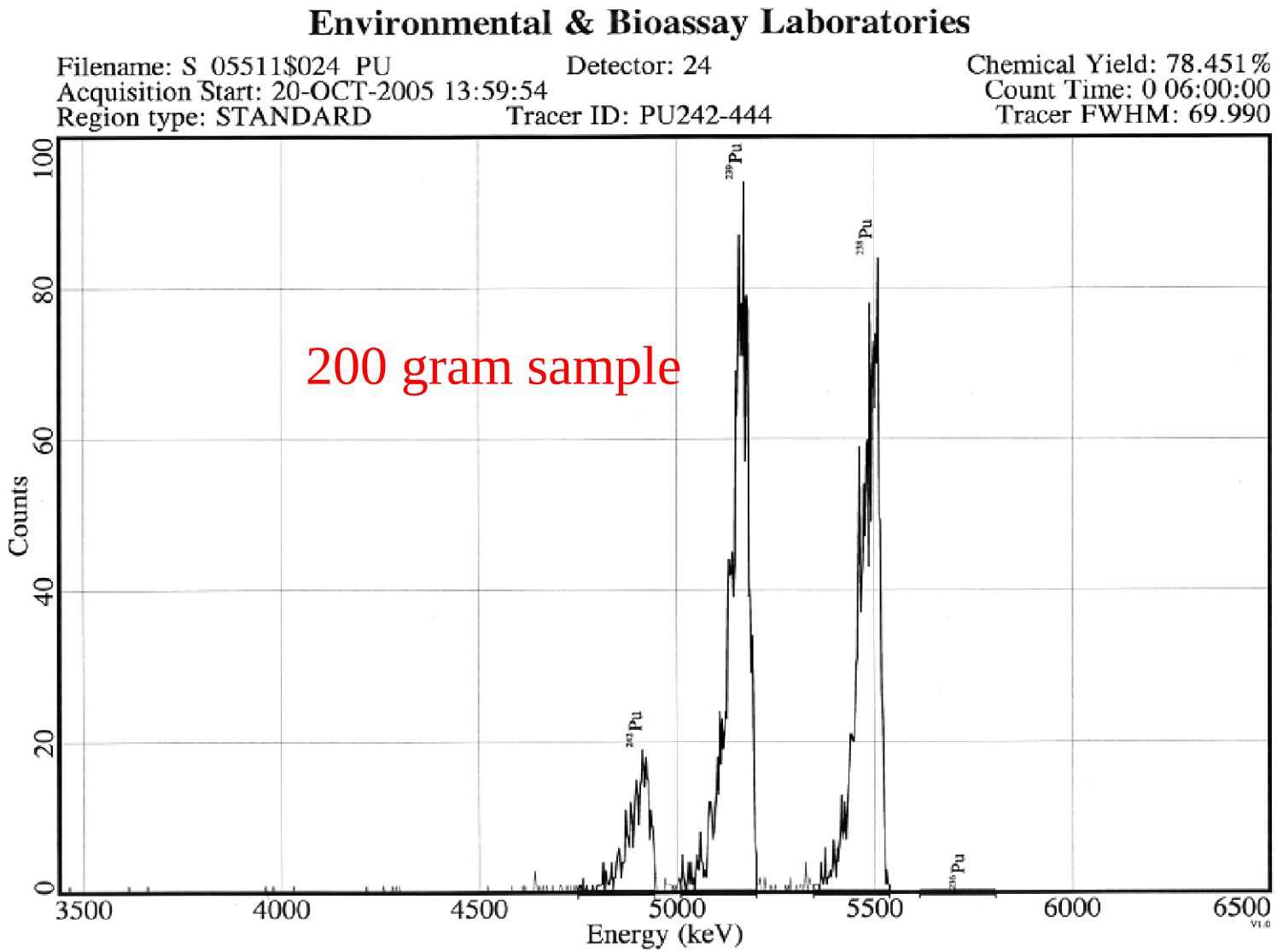

23. 9. 2005 14:13

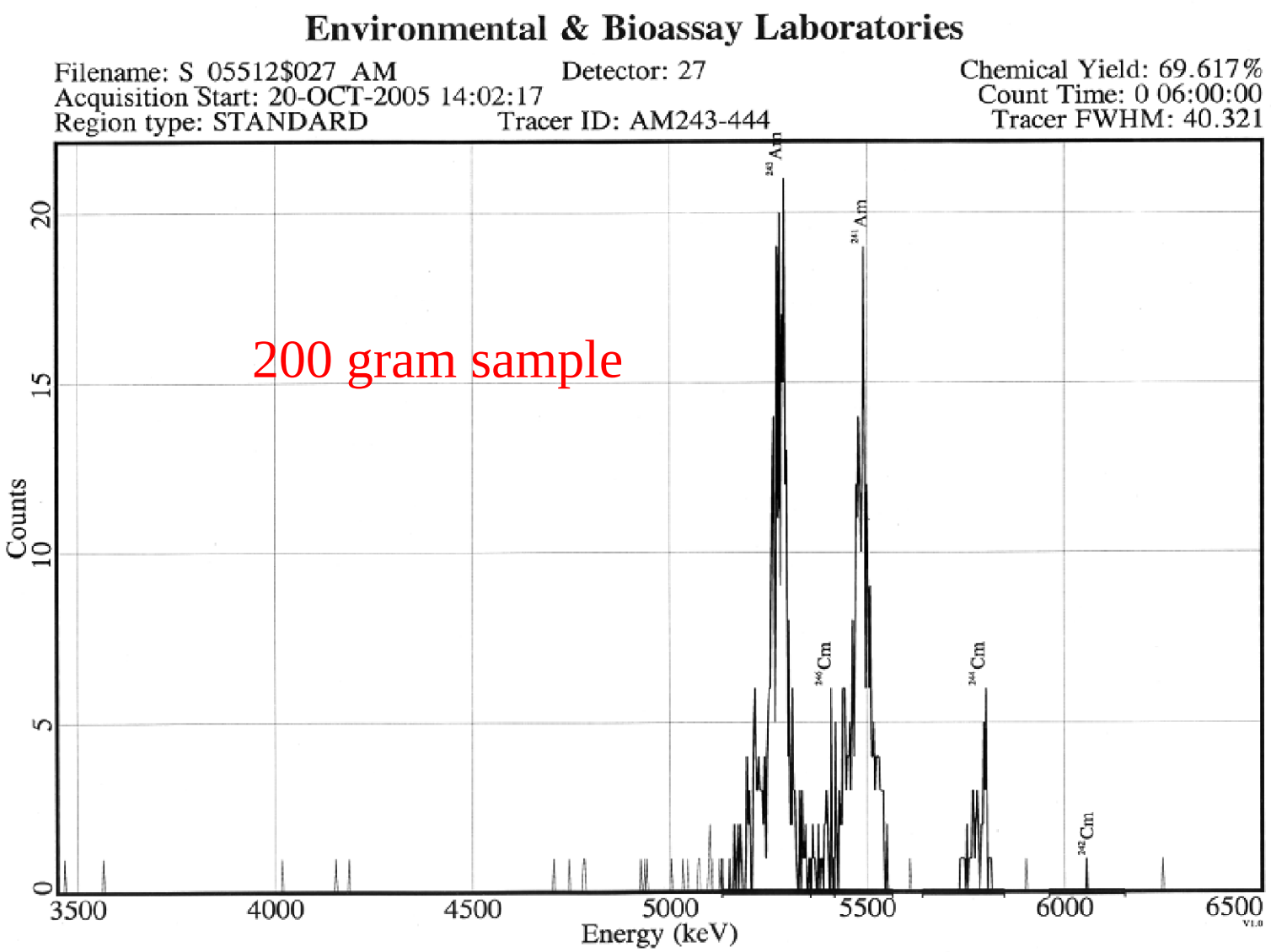
Environmental & Bioassay Laboratories

Filename: S_05511$019_PU
Acquisition Start: 20-OCT-2005 13:58:21
Region type: STANDARD
Detector: 19
Tracer ID: PU242-444
Chemical Yield: 74.801%
Count Time: 0 06:00:00
Tracer FWHM: 43.068




Environmental & Bioassay Laboratories
Filename: S_05512$025_AM
Acquisition Start: 20-OCT-2005 14:01:14
Region type: STANDARD
Detector: 25
Tracer ID: AM243-444
Chemical Yield: 78.714%
Count Time: 0 06:00:00
Tracer FWHM: 57.527
100 gram sample
Counts
Energy (keV)
243Am
241Am
244Cm
242Cm
238Cm
0
2
4
6
8
10
12
14
16
18
3500
4000
4500
5000
5500
6000
6500


Environmental & Bioassay Laboratories
Filename: S_05511$024_PU
Detector: 24
Chemical Yield: 78.451%
Acquisition Start: 20-OCT-2005 13:59:54
Count Time: 0 06:00:00
Region type: STANDARD
Tracer ID: PU242-444
Tracer FWHM: 69.990
200 gram sample
Counts
Energy (keV)
239Pu
238Pu
236Pu
0
20
40
60
80
100
3500
4000
4500
5000
5500
6000
6500


Environmental & Bioassay Laboratories
Filename: S_05512$027_AM
Acquisition Start: 20-OCT-2005 14:02:17
Region type: STANDARD
Detector: 27
Tracer ID: AM243-444
Chemical Yield: 69.617%
Count Time: 0 06:00:00
Tracer FWHM: 40.321
200 gram sample
243Am
241Am
240Cm
244Cm
242Cm
Counts
0
5
10
15
20
3500
4000
4500
5000
5500
6000
6500
Energy (keV)

Summary

- Streamlined routine actinides in soil method
  - Faster, simpler
- Emergency method
  - Homeland Security
- Progress on very large samples (100g+)
- Cerium fluoride plus TEVA, TRU and DGA
  - DGA has made Am separation much easier and more effective