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Title:	Analysis of Minor and Trace Elements in Plutonium Using Polarized Energy Dispersive X-Ray Fluorescence
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ANALYSIS OF MINOR AND TRACE ELEMENTS IN PLUTONIUM USING POLARIZED ENERGY DISPERSIVE X-RAY FLUORESCENCE

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Wavelength dispersive X-ray fluorescence (WDXRF) has been used for many years in our laboratories for quantifying gallium in plutonium metal. Polarized energy dispersive X-ray fluorescence (EDXRF) was evaluated here for gallium and trace elemental analysis in plutonium. This instrument has fewer facility interface requirements than a high power WDXRF instrument (eg. no facility chilled water system is needed). Secondary targets are used to irradiate the specimen, and a target material with a K line energy above but near the analyte line absorption edge is used to induce efficient analyte fluorescence. The secondary target polarizing geometry also minimizes spectral background. Thus, some trace elements such as uranium can potentially be detected. A disadvantage of using EDXRF is contending with the presence of X-ray and gamma peaks that originate from the inherent sample radioactivity; these peaks are not normally observed with WDXRF due to instrumental geometry. Examples will be discussed.

The WDXRF sample preparation method currently used for gallium quantification entails dissolving the plutonium metal, removing the plutonium with ion exchange solid phase extraction, and analyzing the eluted solution. To eliminate the possibility of radioactive solution leaking out of the specimen cups, an evaporation technique will be explored for use with polarized EDXRF which has the additional benefit of pre-concentrating the solution. Thus, detection limits for trace elements such as uranium are greatly improved. Preliminary assessment of this pre-concentration approach will be discussed for uranium trace analysis.

Zinc is currently used as an internal standard for gallium, but germanium is a less common impurity and will be studied for use as the internal standard. The efficacy of using the secondary target scatter peak will also be compared with using an internal standard. Once the optimal sample preparation and analysis parameters are determined, the gallium method uncertainty will be examined.

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Outline

- Introduction
  - Gallium and Uranium in Plutonium
  - Polarized EDXRF
- Experimental
- Results
- Summary
- Future Directions

Introduction

- Plutonium metals and oxides
  - Gallium
    - Common plutonium metal alloy for machining purposes
    - Present in raw feed for making Pu/U mixed oxide nuclear fuel
  - Uranium – Pu radioactive alpha decay daughter product
- Quantification of Ga and U needed
- WDXRF
  - Currently used for gallium quantification
  - Uranium possible with adequate sample preparation

Introduction

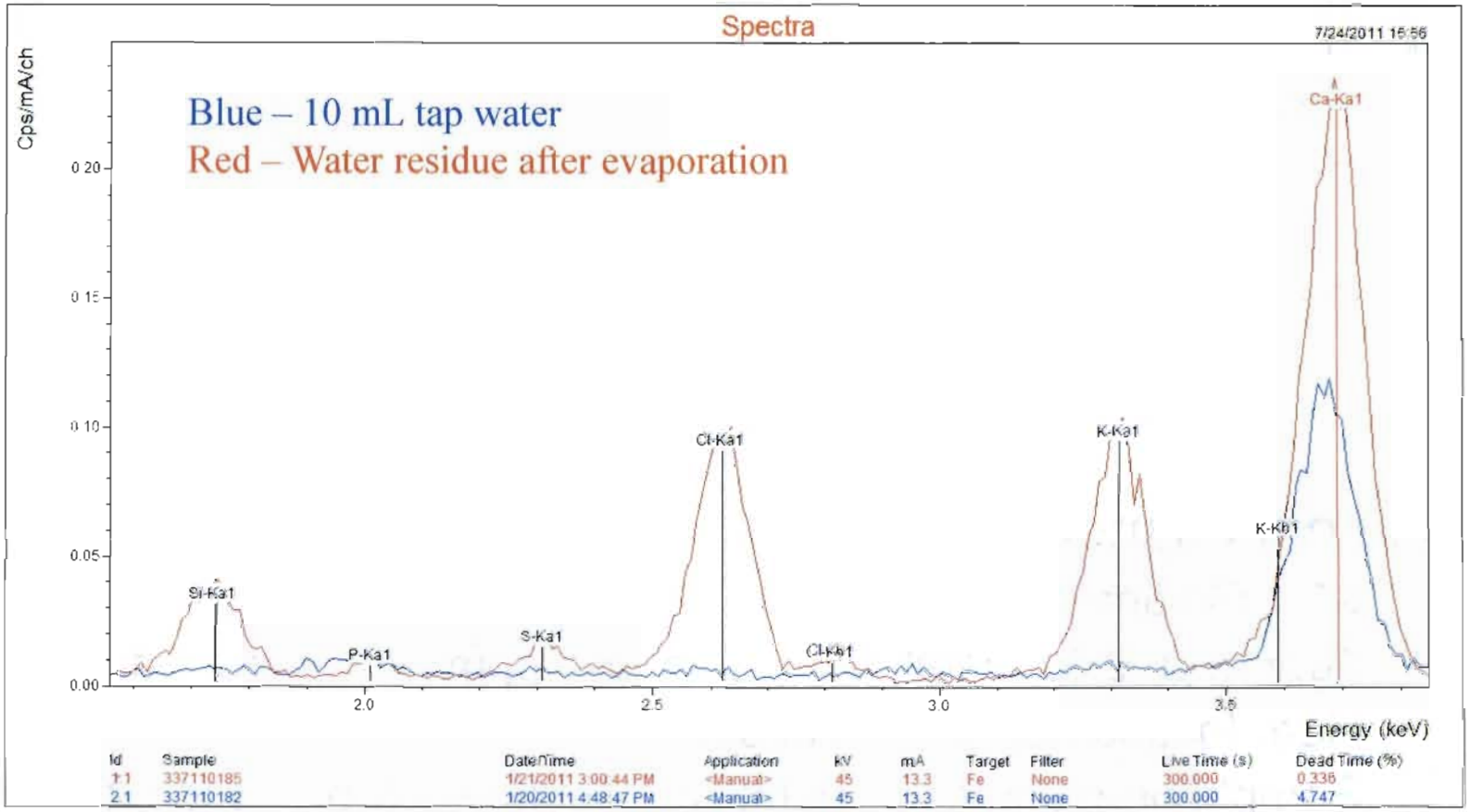
- Old WDXRF instrument used for Gallium in Plutonium
- Polarized EDXRF – Quantify Ga & U in Plutonium
  - Easier / cheaper installation in nuclear facility vs. WDXRF
  - Trace elemental capabilities
    - Polarization geometry - Low background
    - Secondary targets - Optimal analyte excitation
  - Specimen polymer film will not break from X-ray exposure
    - Best LLDs – Very long count times possible
  - 100 kV source – Excitation of higher energy K lines
- Sample alpha radioactive decay
  - Detector dead time can be problematic with EDXRF
  - Peak overlaps – Software peak deconvolution helps
  - Remove Pu, Am, Np with ion exchange chromatography

Introduction

- Plutonium mixed oxide fuel feed (MOX)
  - 1000-10,000 ppm Ga
  - 1000-1500 ppm U
  - Currently Ga by ICP-MS
    - Many serial dilutions introducing error
  - Currently U by IDMS
    - Time consuming and overkill
  - Development - Both Ga and U by Polarized XRF
- Plutonium metals
  - ≤1% Ga and 10-100 ppm U
  - 10ppm U, 0.5g metal, 5 mL soln → 1 ppm → **Pre-concentrate**
  - Here focused on MOX samples
  - Sample prep same for metals except dissol & preconcentration

Introduction – Sample Pre-concentration

- Tap water example



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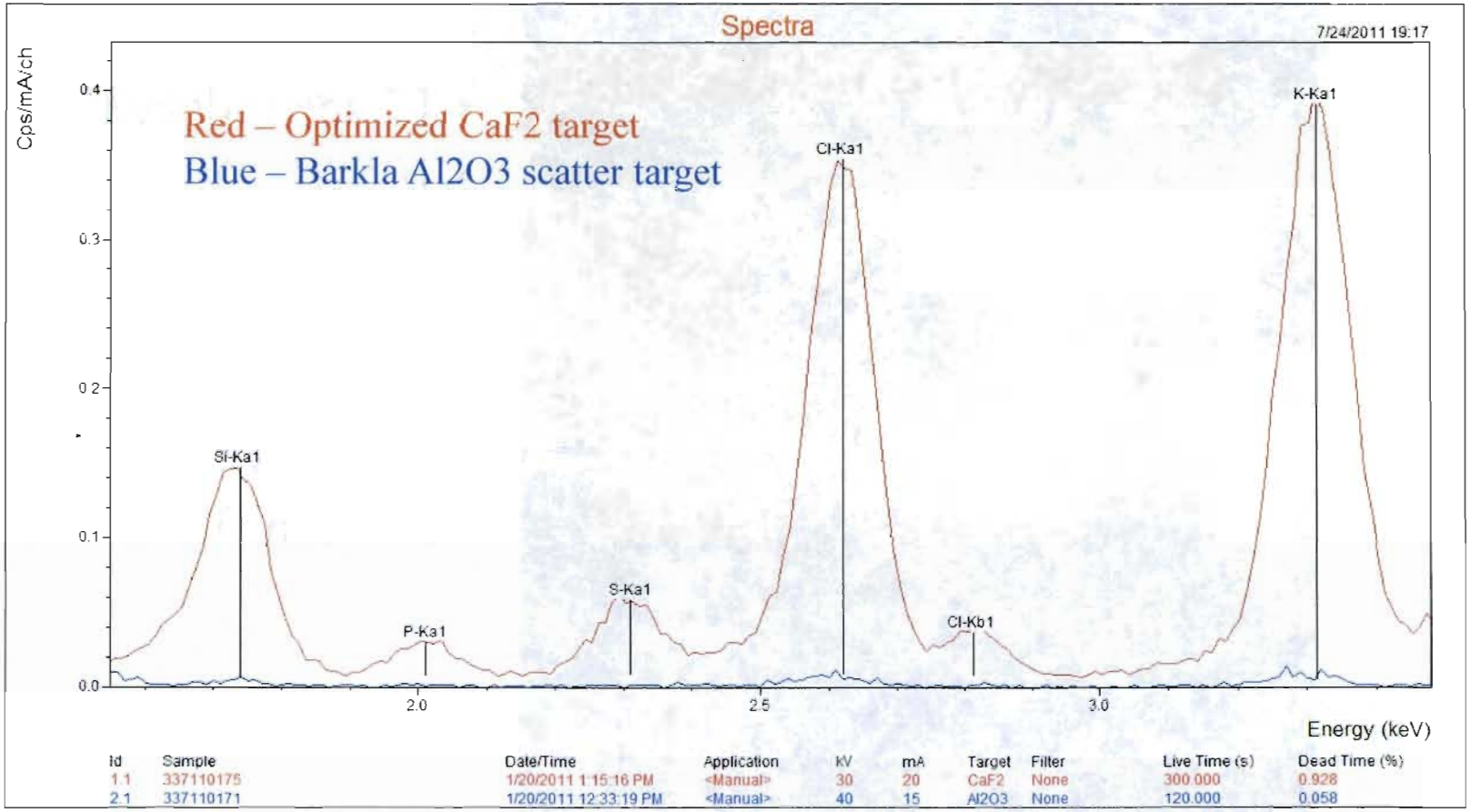
Experimental - Instrumentation

- PANalytical Epsilon 5 Polarized EDXRF

- 15 secondary targets
- 100 kV W/Sc anode
- 600 W anode
- Ge solid state detector (LN2 cooled)
- <140 eV res @ Mn Kα
- Helium flush system

Experimental – Instrumentation

- Signal improvements with optimized secondary target



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Experimental - Sample Preparation

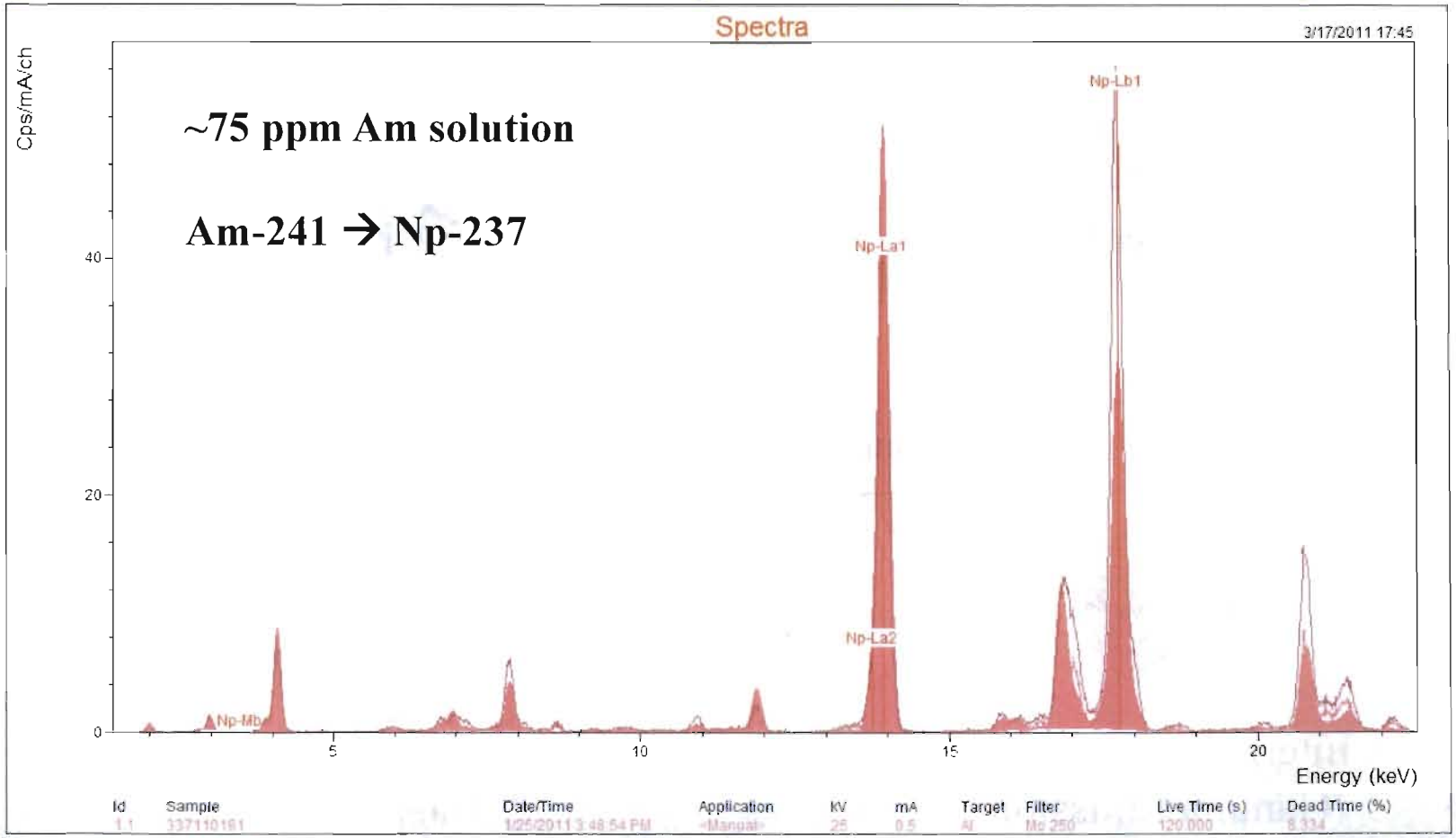
- Dissolve Pu oxide in 12 M HCl / trace HF and HNO_3
- Duplicate 50 mg sample cuts
- Add 6 M HCl
- Air exposure – Wait for Uranium to oxidize to U+6
- Add 100 mg ascorbic acid
  - Reduce all plutonium to Pu+3 state

Experimental – Sample Preparation

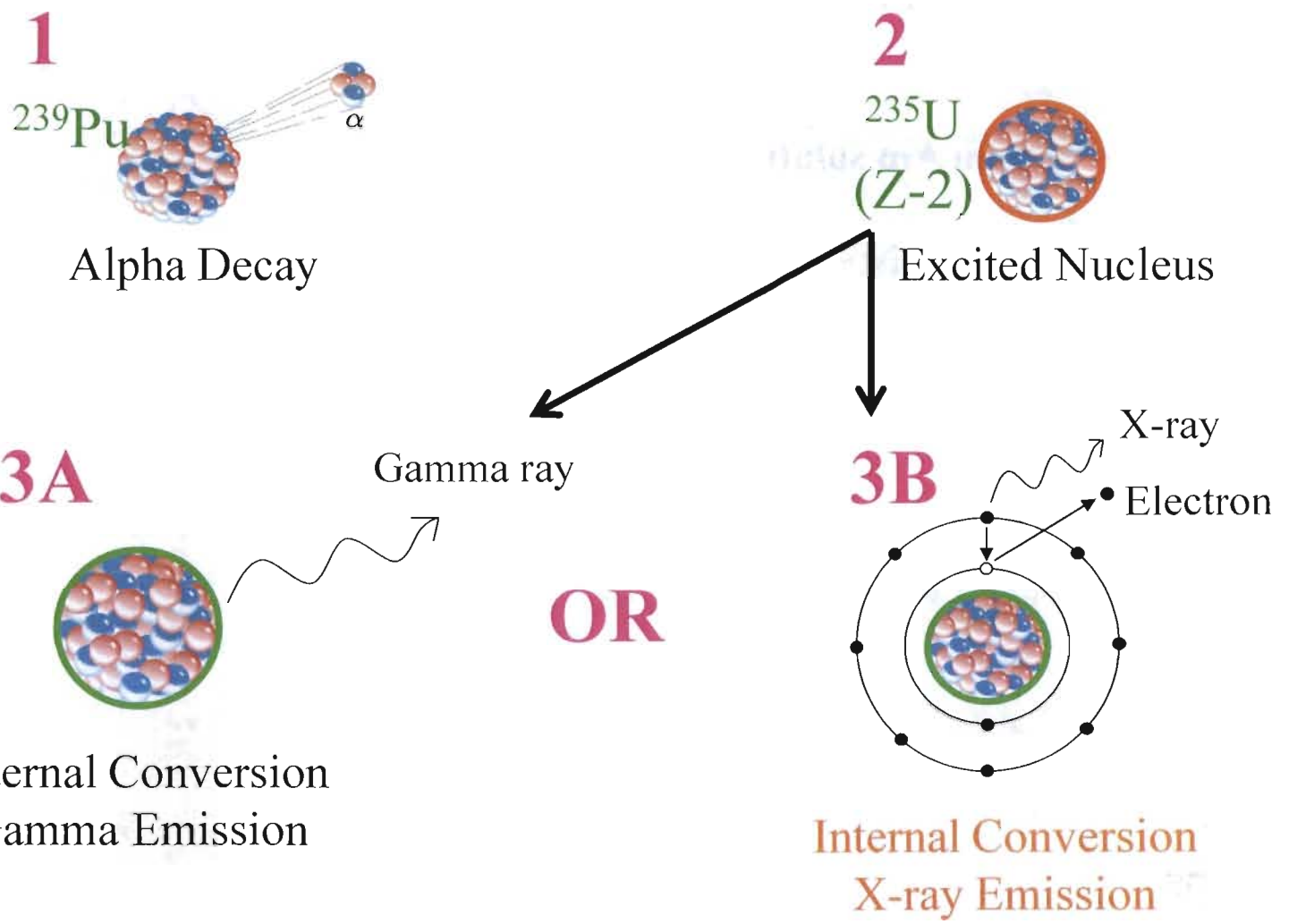
- Ion exchange with BioRad AG1-X4 chloride form resin
  - 6 M HCl for ion exchange separation
  - Ga and U retained; Pu, Am, trace Np eluted
  - Elute Ga and U with 0.1 M HCl
  - Ge and Y internal standards for Ga and U respectively
- Reduce volume to 4 mL with heat lamp
- Transfer 3.5 mL to specimen cup
- Seal in cup with Kapton
  - Apply parafilm over Kapton to prevent any leaks

Results – Radioactive sample self fluorescence

Np L series from Americium alpha decay (Mo filter, low power)

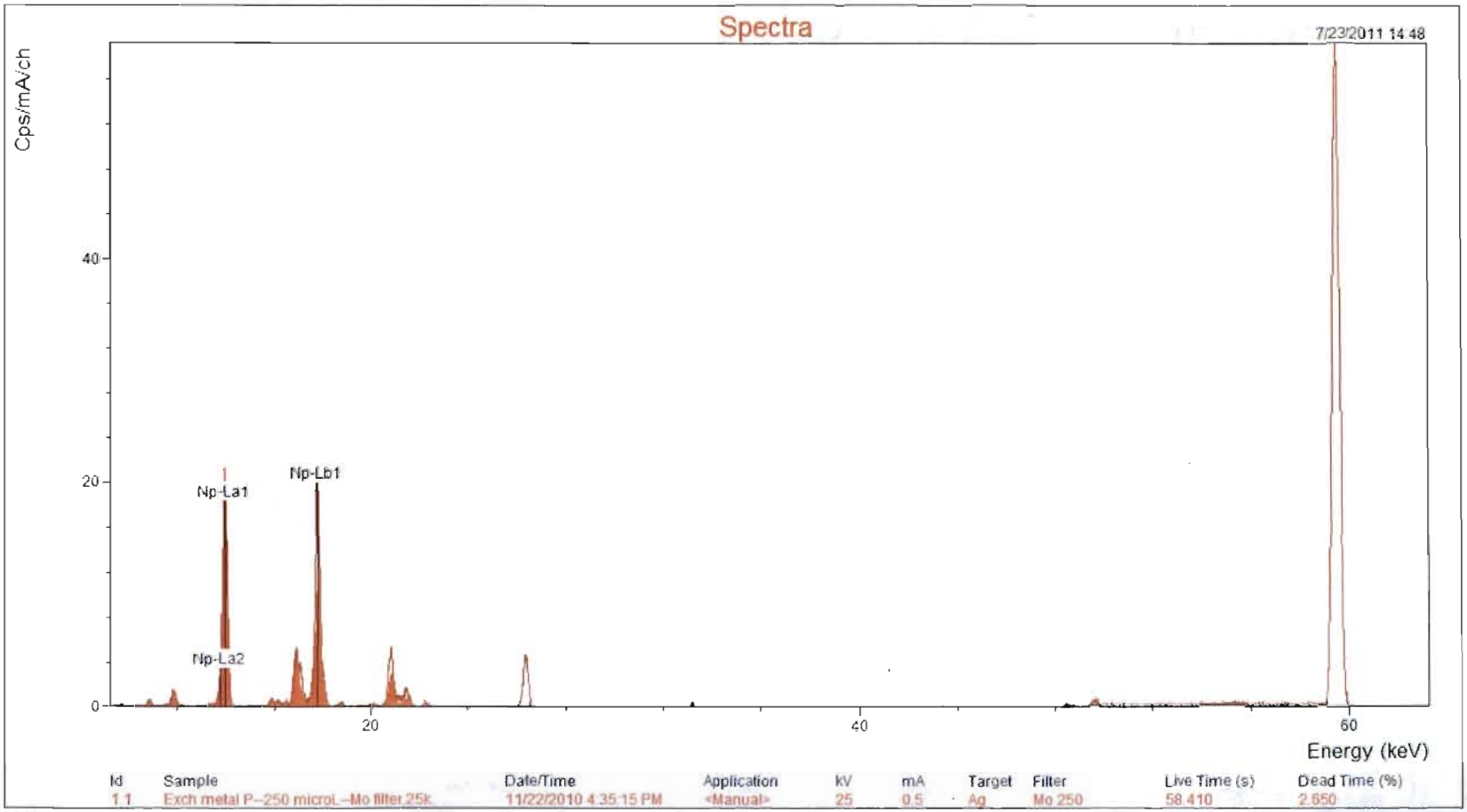


Results – Internal Conversion



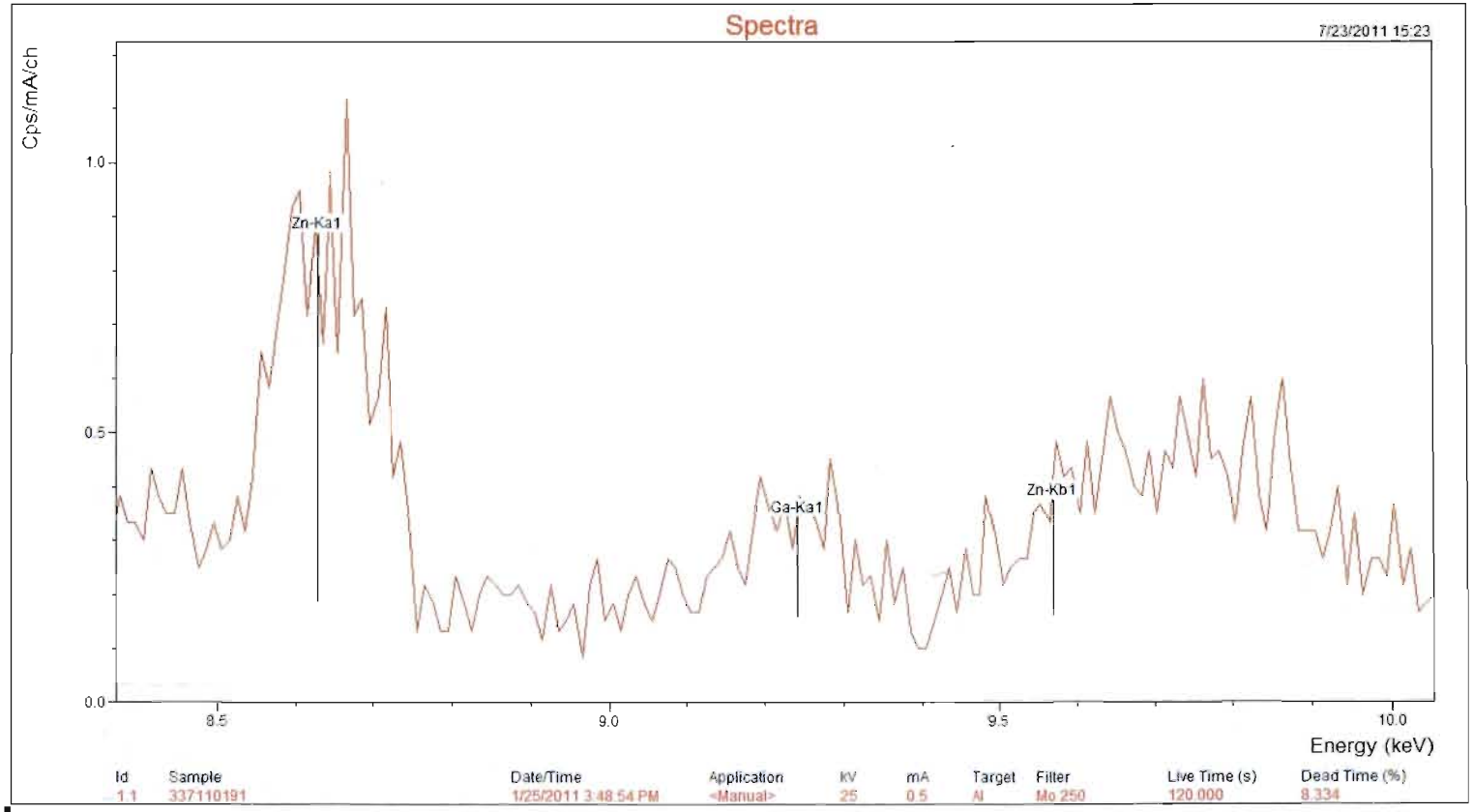
Results – Americium increases dead time

- Np L series and Am 26 and 59.5 keV gammas (increase dead time)



Results – Alpha radiation-induced analyte fluorescence

- 1000 ppm Zn, 75 ppm Ga solution
- X-ray source "off" (low power with Mo filter/beam stop)



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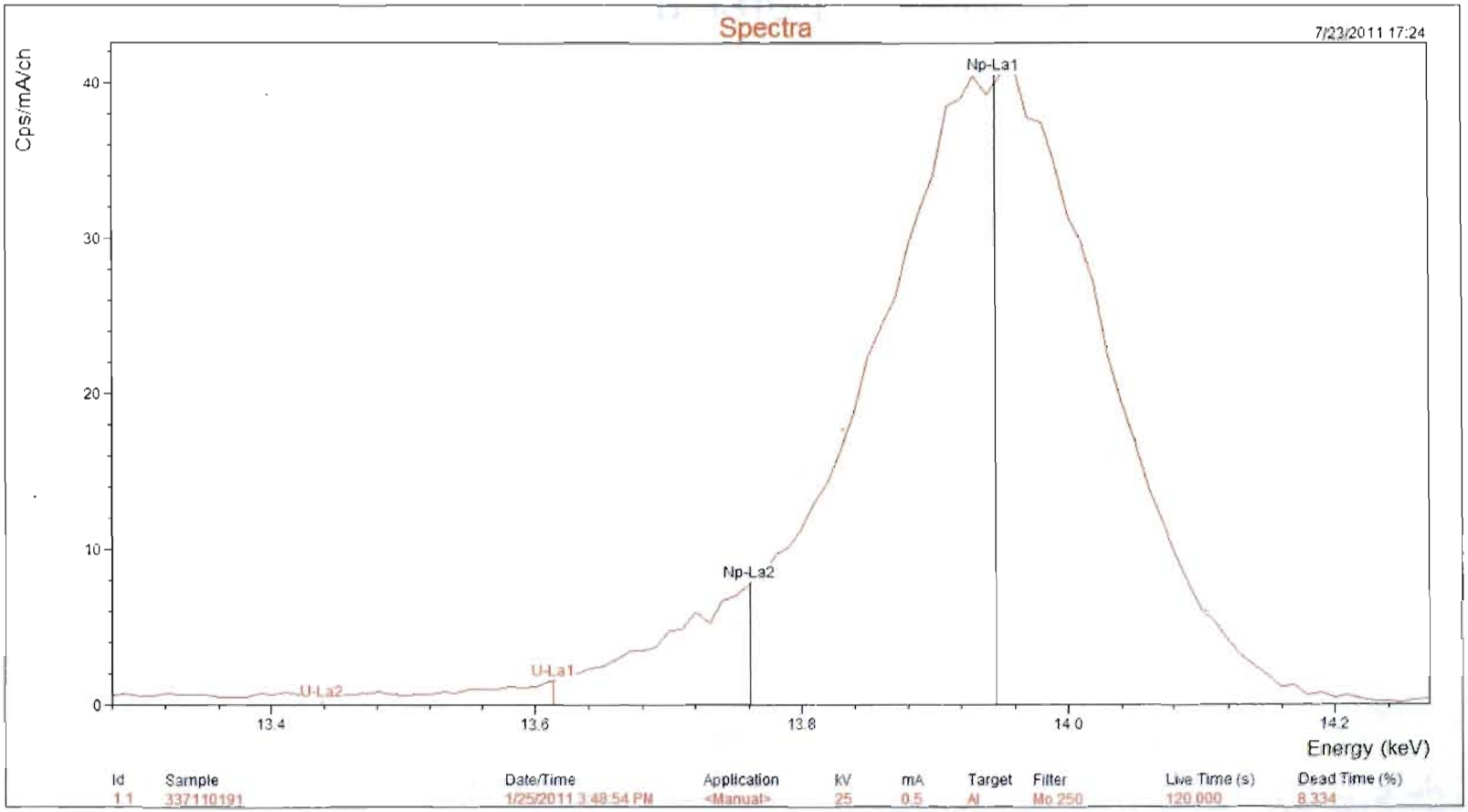
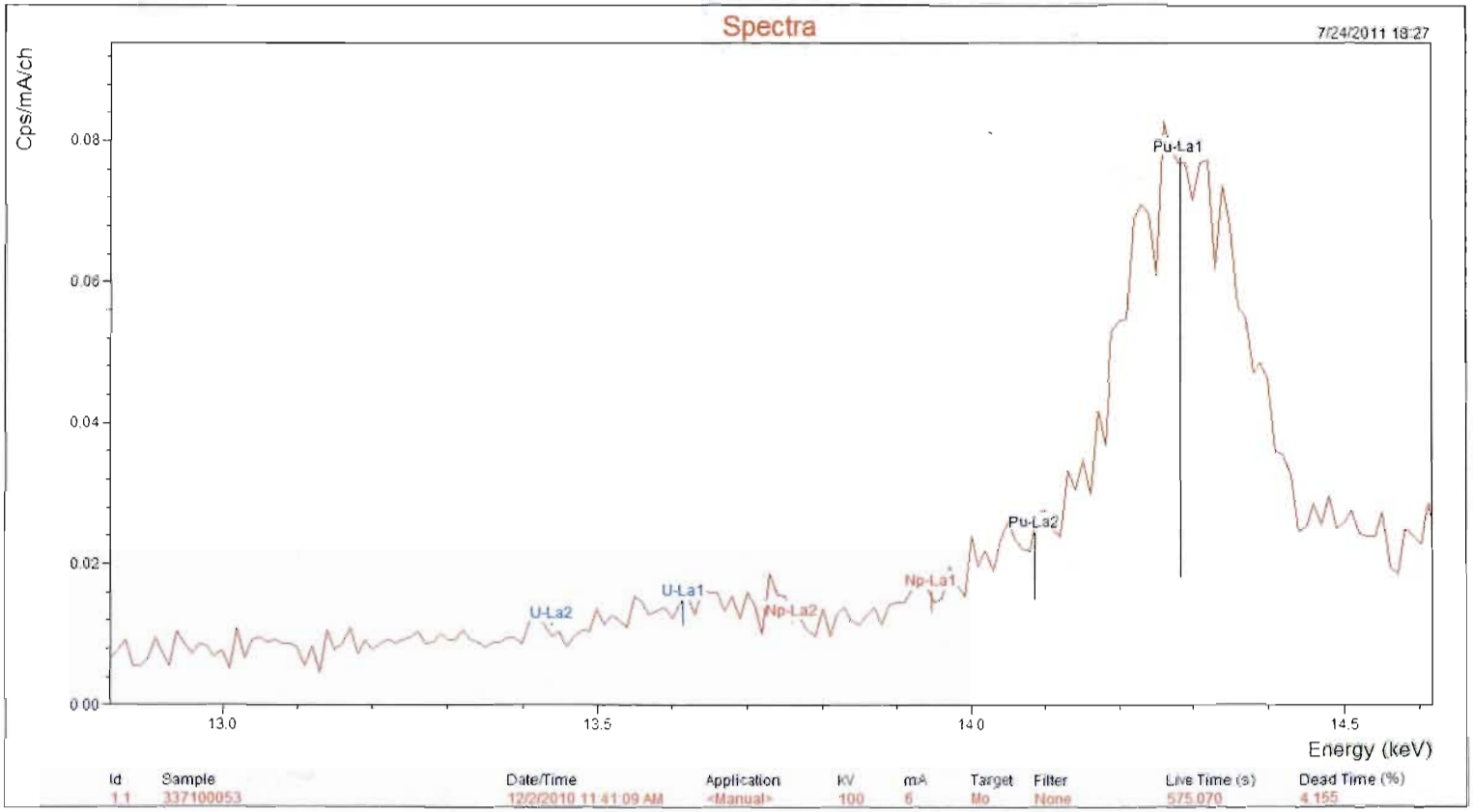
Results – Americium decay Np L fluorescence

- Difficult to analyze trace uranium without removing Am



Results – Trace Americium sample

- 850 ppb Am specimen - No Neptunium L present
  - Much better for low level Uranium



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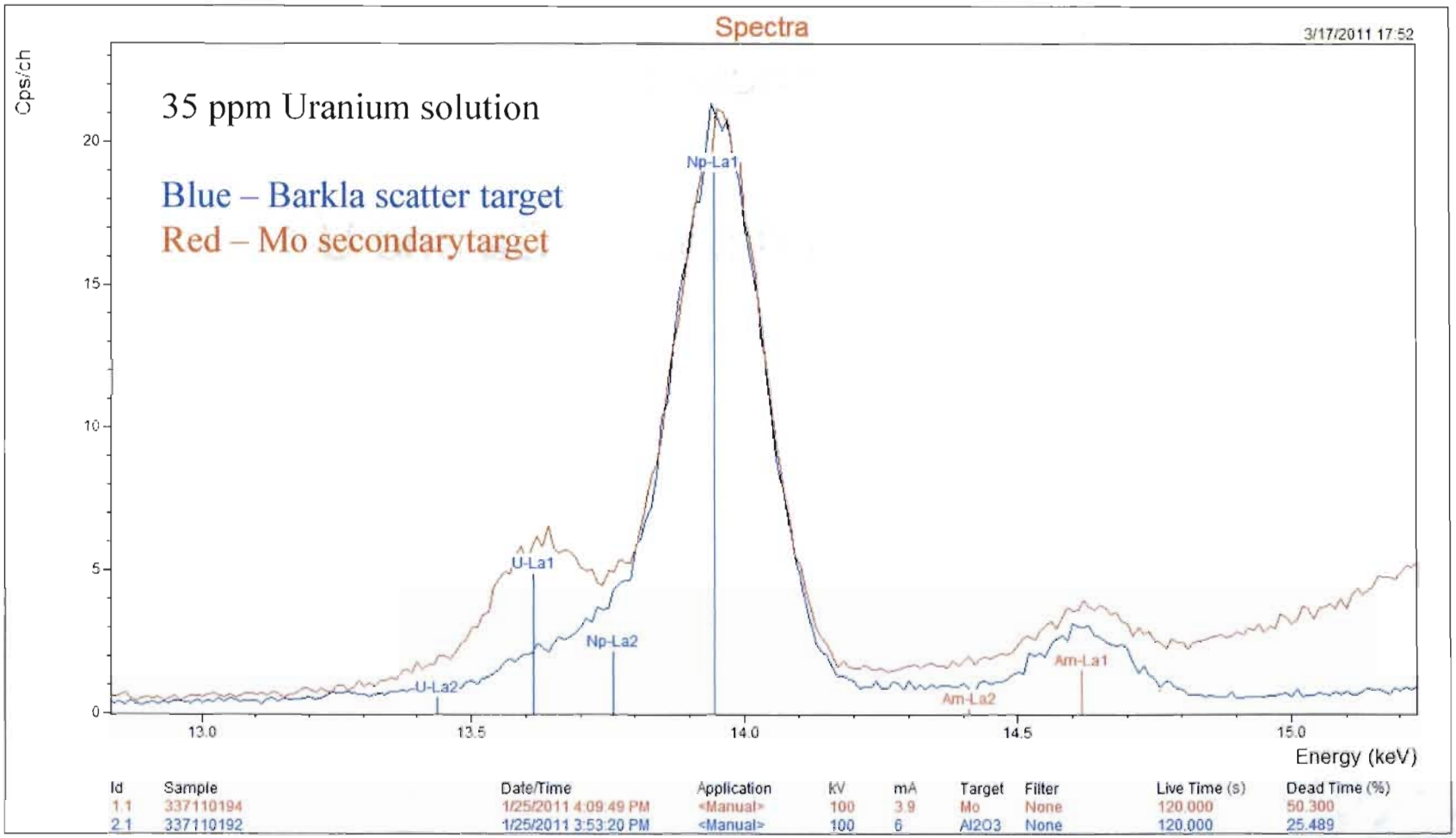
Results – Optimized secondary target for Uranium



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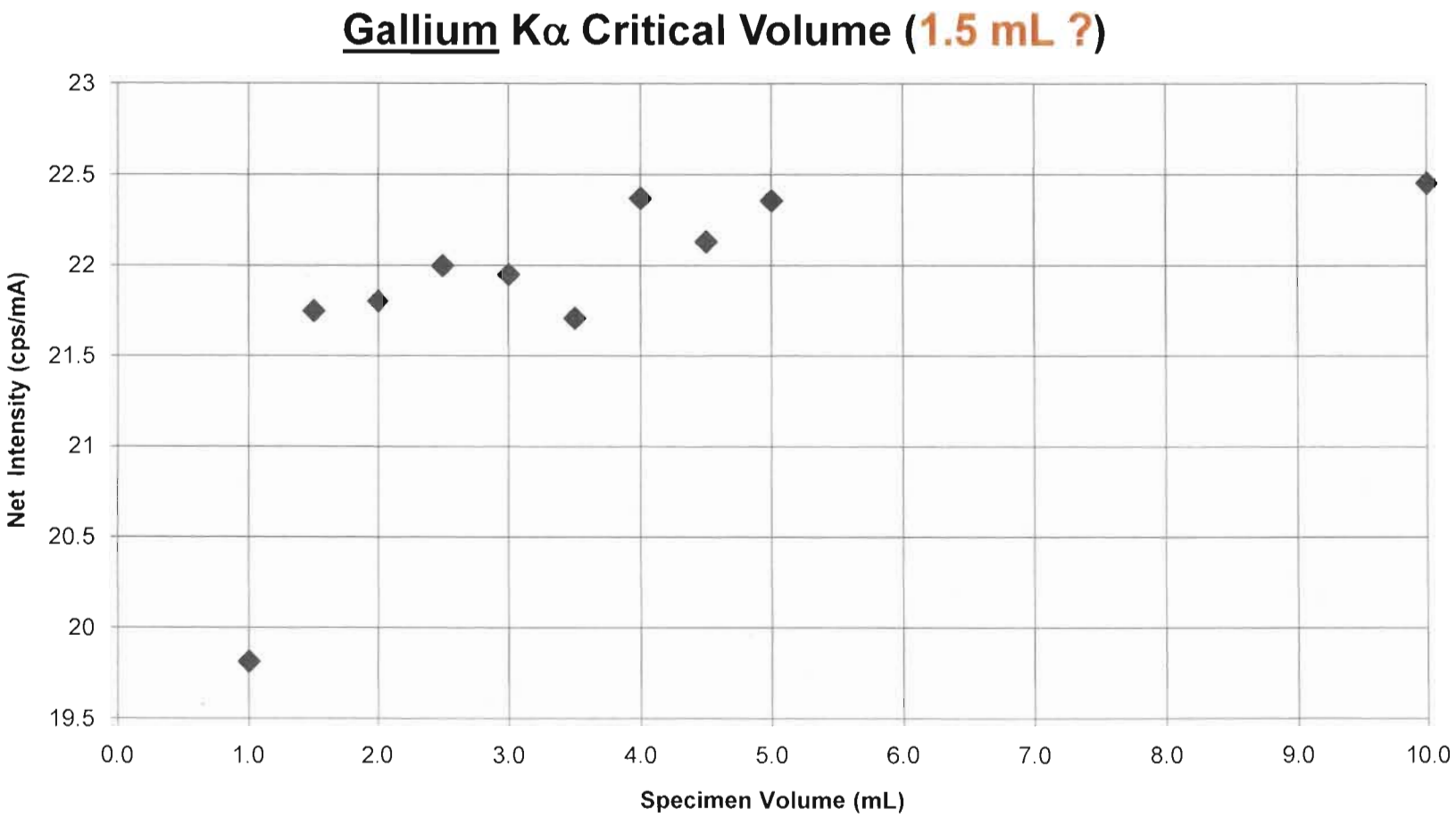
Results – Specimen infinite thickness/volume

- Ga/U standard with concentration of average Pu oxide sample
- Ge and Y internal standards for Ga and U
- Filled specimen cups with different volumes
- Compared net intensities to determine intensity plateaus

Results – Determining infinite thickness/volume



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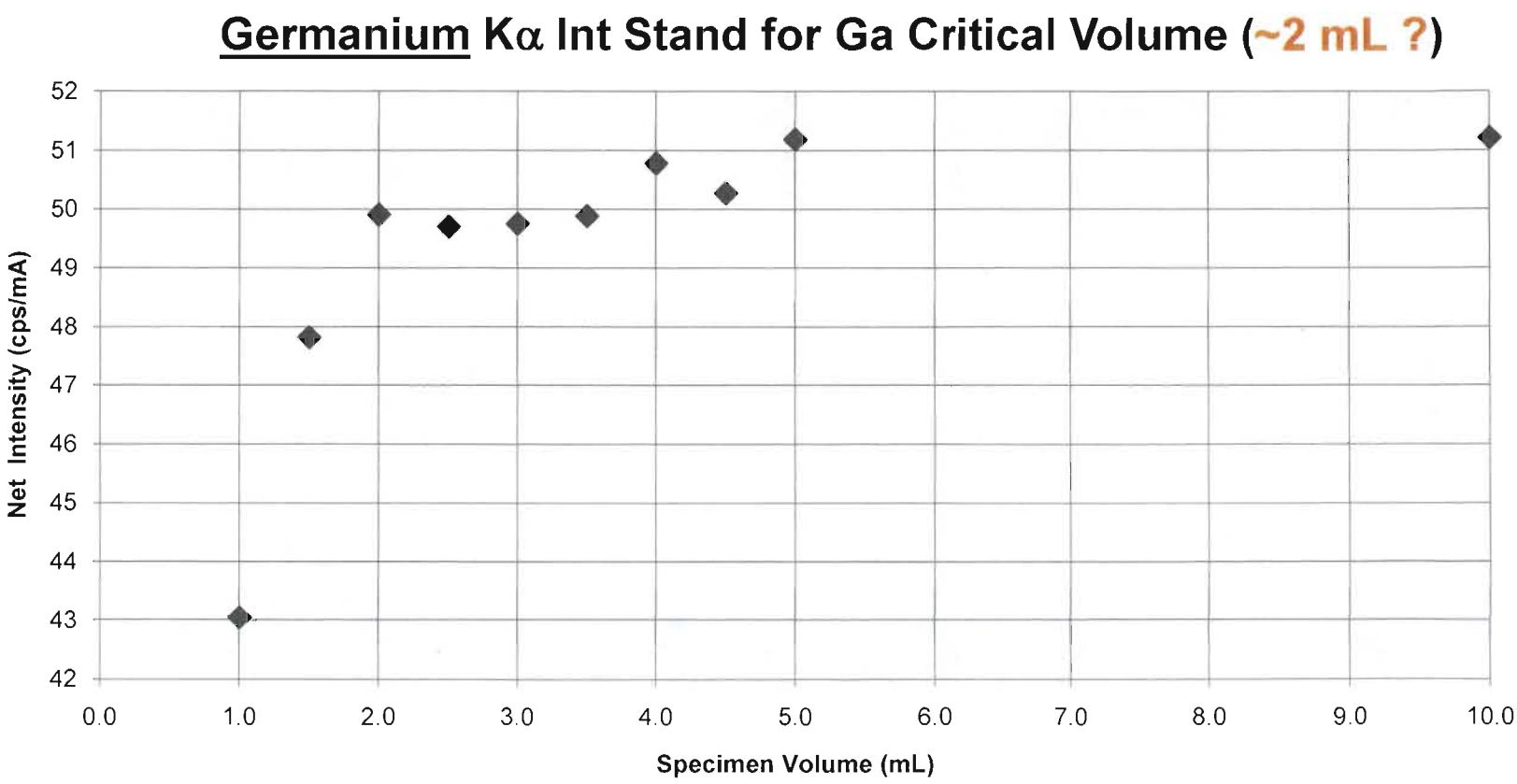
Results – Determining infinite thickness/volume



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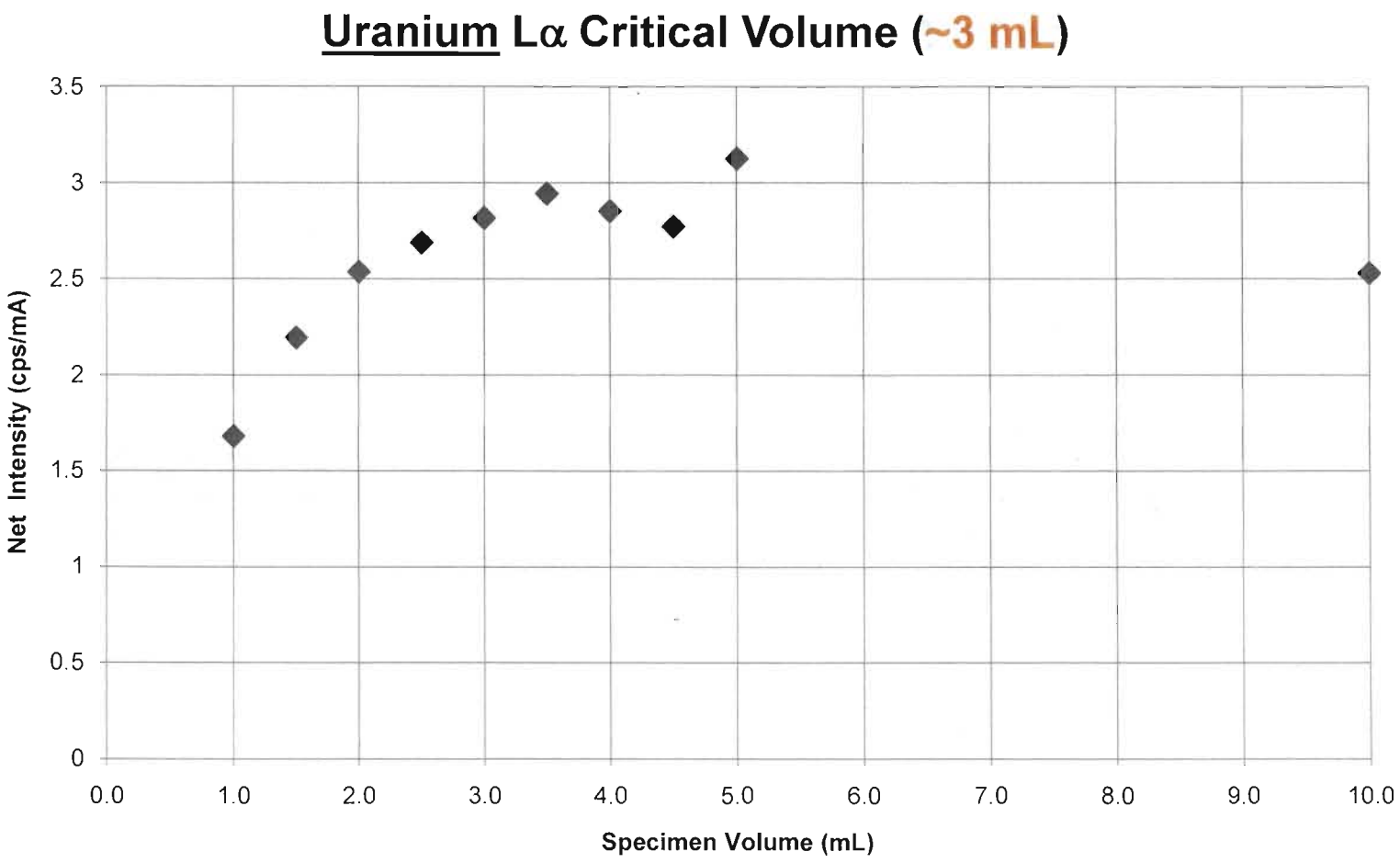
Results – Determining infinite thickness/volume



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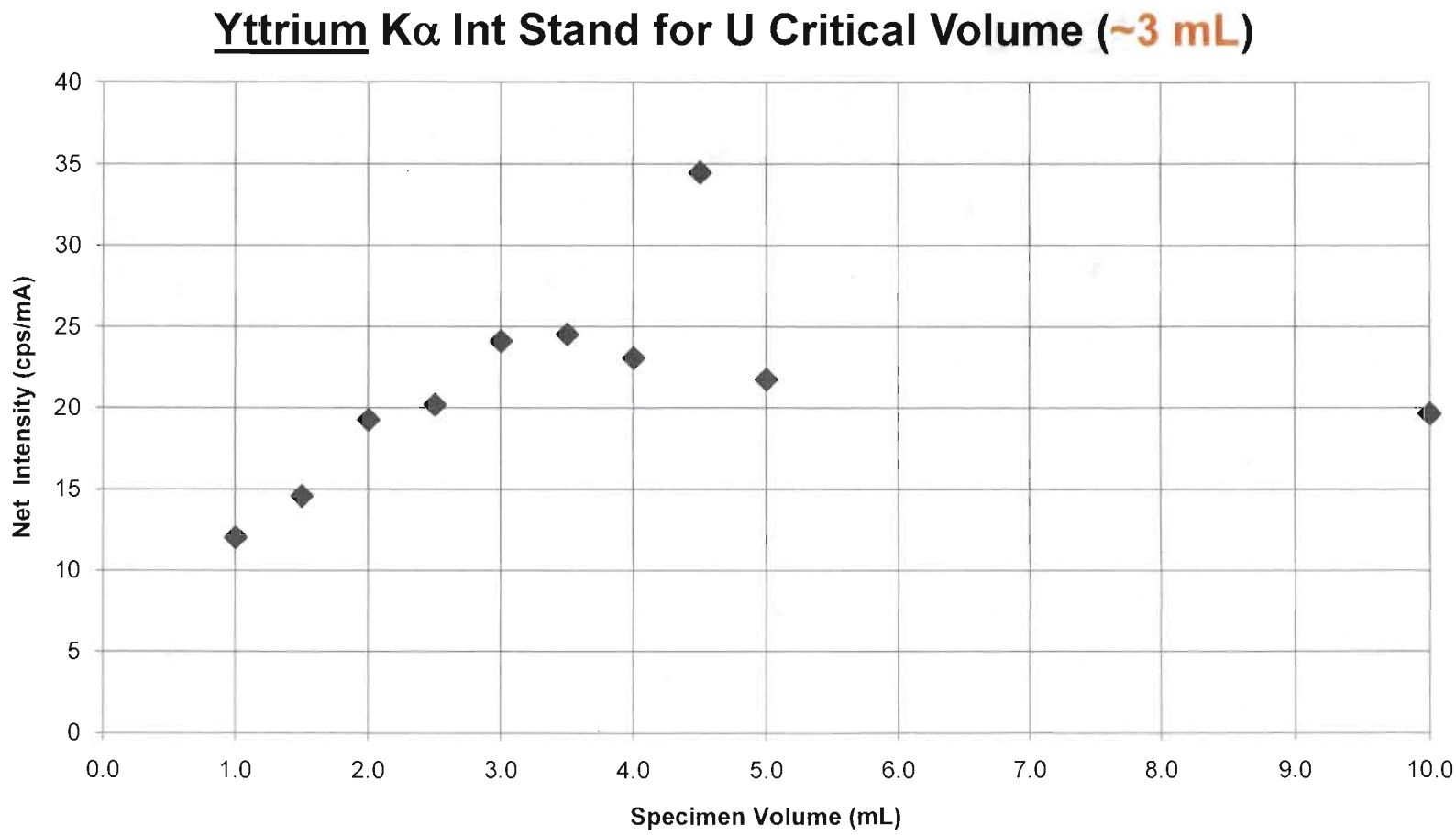
Results – Determining infinite thickness/volume



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Results – Infinite thickness/volume

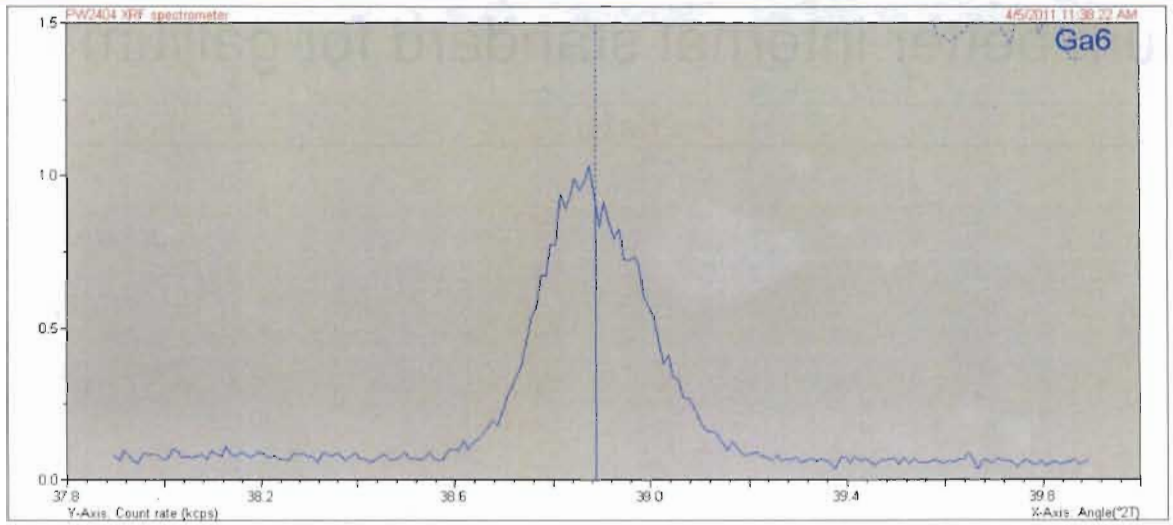
- ~3 mL volume infinitely thick for Ga, U, Ge, & Y
- Reduce ion exchange eluate volume to 4 mL with heat
  - Maximizes solution concentration
  - Possible could reduce further since more concentrated and infinte thickness will decrease some
- 3.5 mL aliquot currently analyzed

Results - LLDs

- Lower Limit of Detection – Ga and U
  - Gallium – Ample signal with short count times
  - Uranium
    - 3 min count time insufficient for acceptable reproducibility
    - Even 20 min not ideal for best reproducibility
    - However, customer does not have a specific precision requirement

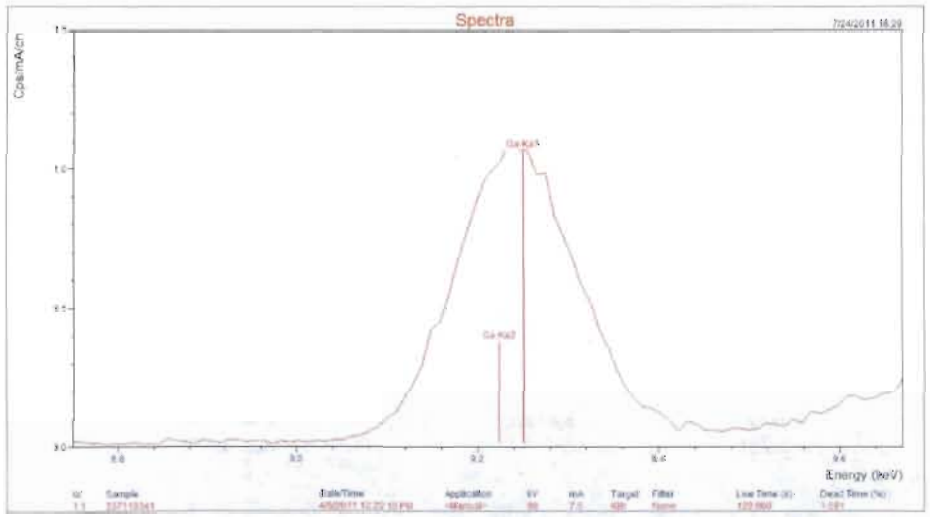
Element	Short count time (min)	Long count time (min)	Specimen LLD (μg)	Oxide LLD (ppm)	Nominal concentr in Pu oxide (ppm)	X greater than LLD
Ga	3	---	5.44	218	6000	28
U	3	---	11.43	457	1200	3
U	---	20	4.43	177	1200	7

Results – Ga Kα WDXRF vs. Epsilon



WDXRF

4000 W
LiF 200
150 µm collimator
750 µm Al filter



Epsilon 5

KBr target
600 W

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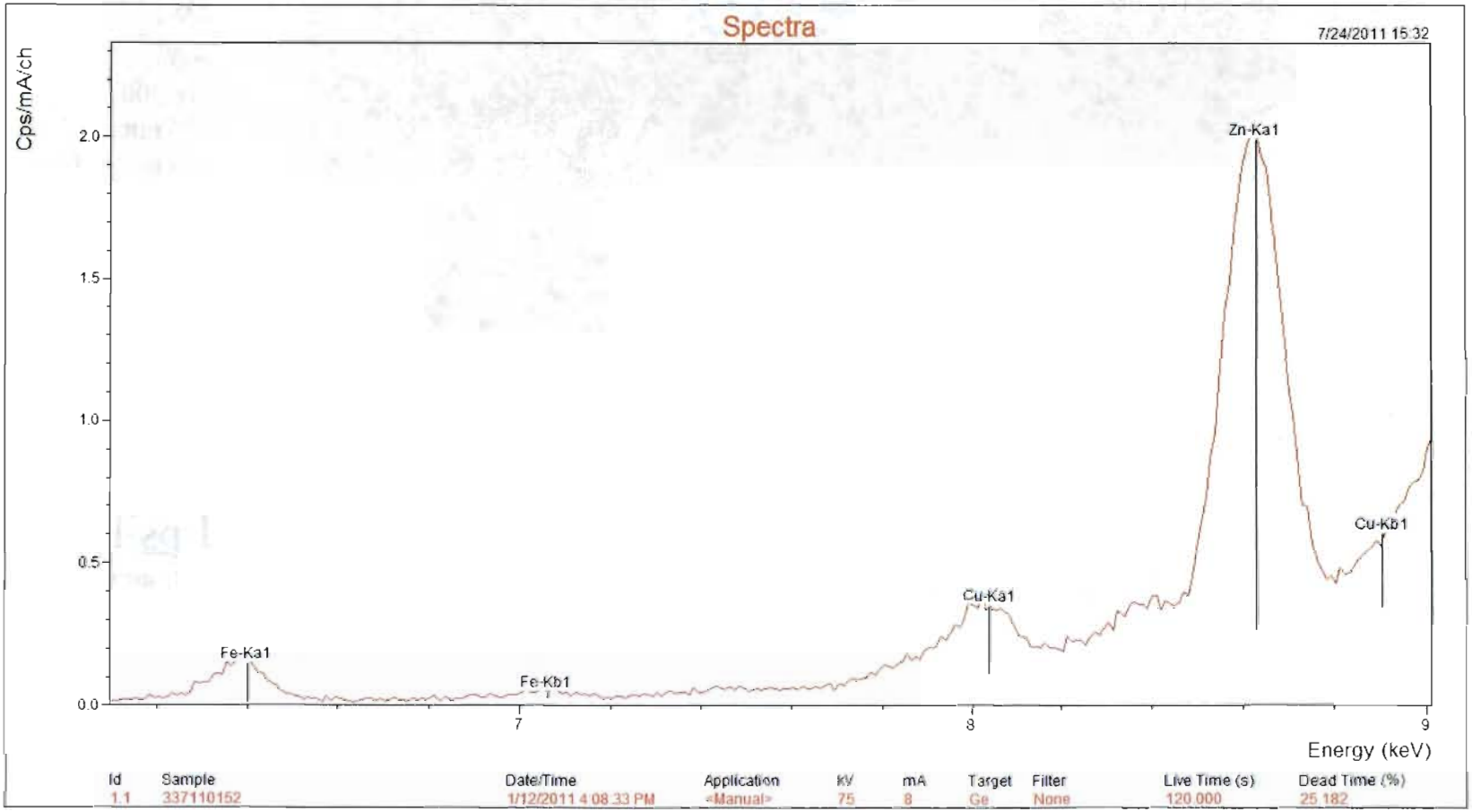
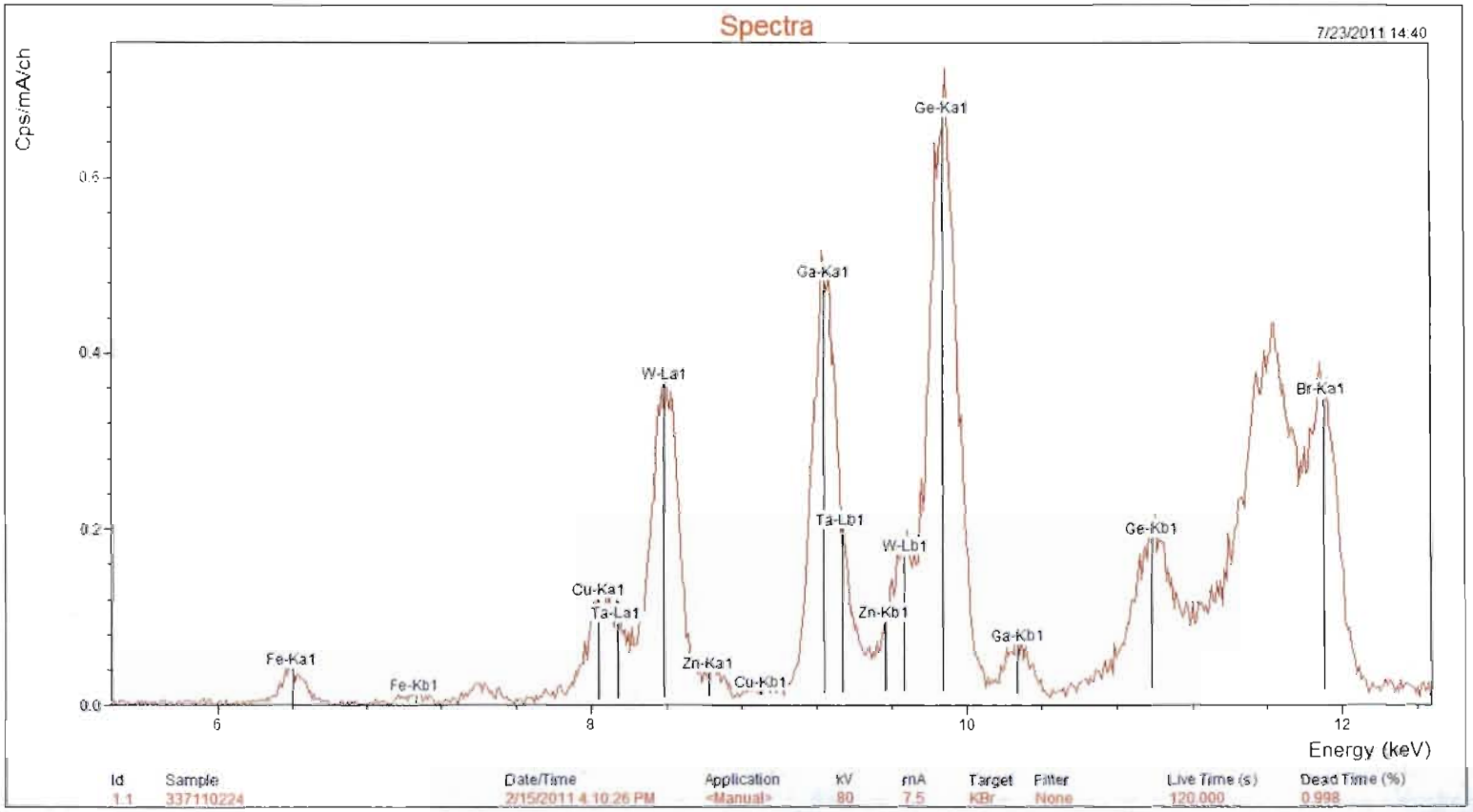
Results – Zinc impurity in specimen cups

- Germanium better internal standard for gallium than zinc



Results – Instrument tungsten issue

- Tungsten X-ray beam restrictor
  - Some overlap with gallium and germanium



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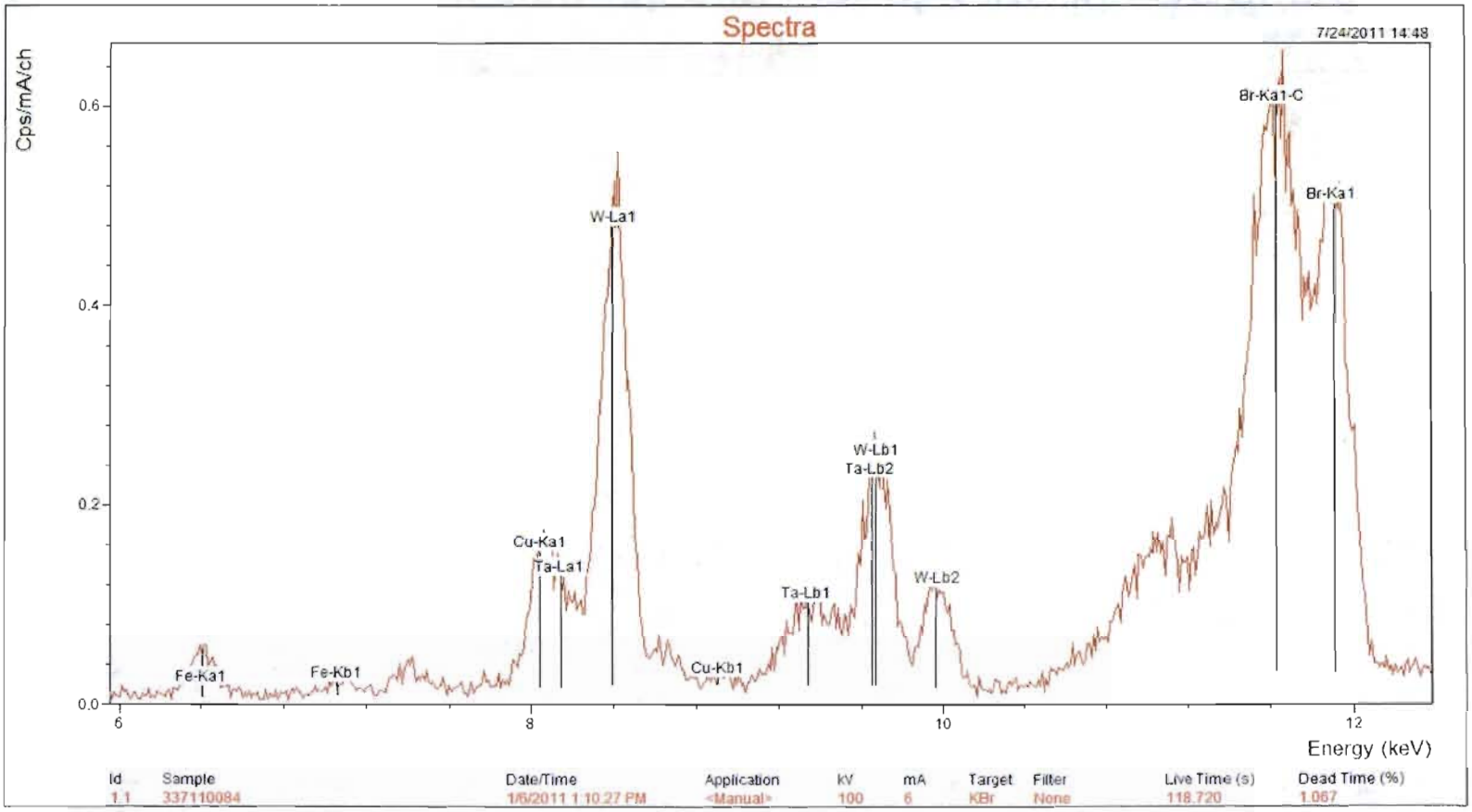
Results - Instrument tungsten issue

- Empty specimen cup – W, Ta?, Cu, Fe interferences
  - Problematic for thin film trace analysis of these elements or Gallium



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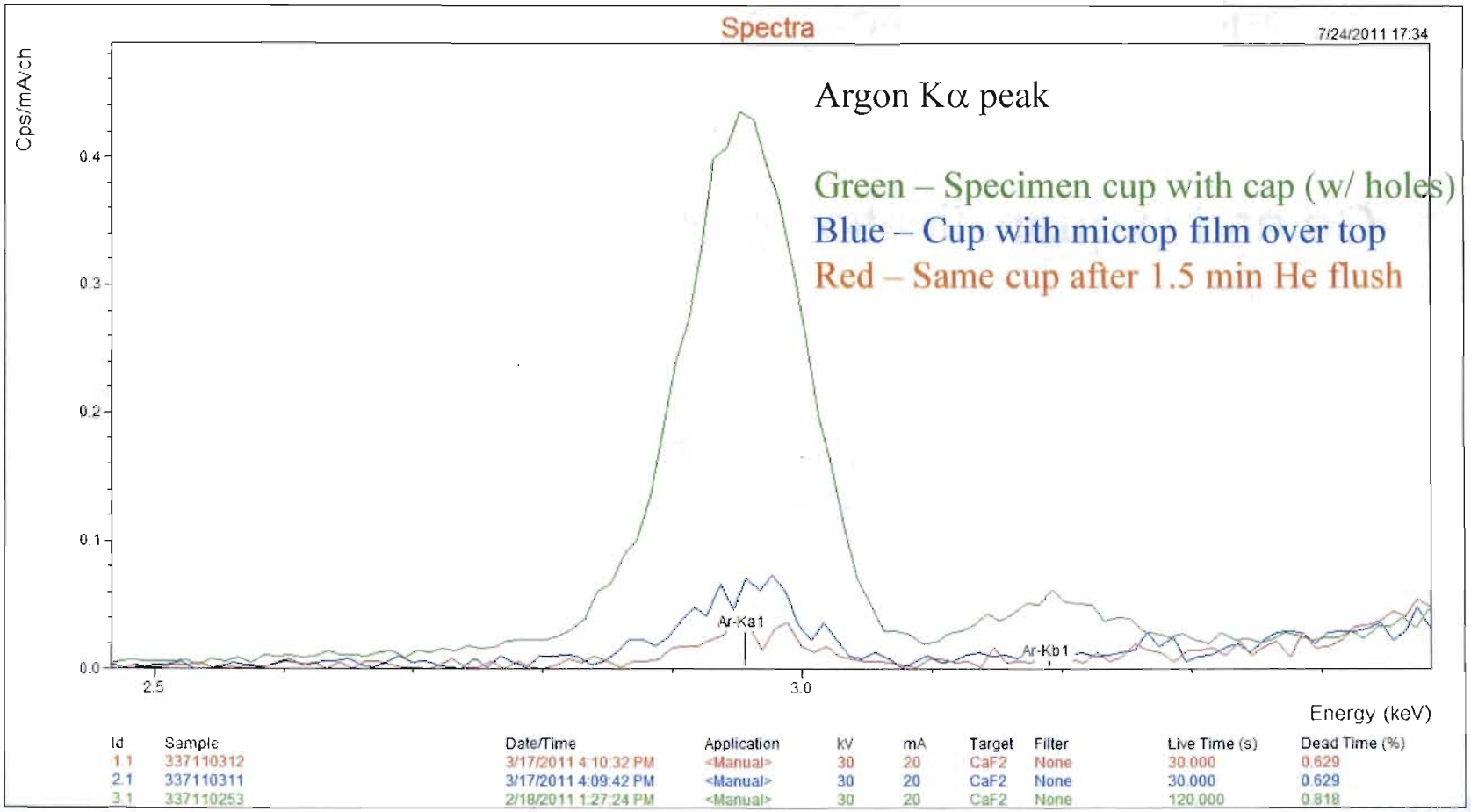
Results – Argon in liquid cup spectra

- He flush time important for light element analysis in liquid cups



Id	Sample	Date/Time	Application	kV	mA	Target	Filter	Live Time (s)	Dead Time (%)
1.1	337110312	3/17/2011 4:10:32 PM	<Manual>	30	20	CaF2	None	30.000	0.629
2.1	337110311	3/17/2011 4:09:42 PM	<Manual>	30	20	CaF2	None	30.000	0.629
3.1	337110253	2/18/2011 1:27:24 PM	<Manual>	30	20	CaF2	None	120.000	0.818

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Summary

- Americium alpha decay a challenge for EDXRF
- Ion exchange (hopefully) will eliminate Americium
- Ga and U quantification promising
  - Sample prep and instrumental parameters determined
  - Ion exchange effectiveness needs to be proven
- Instrumental interferences (mainly tungsten) not an issue for higher levels of gallium

Future Directions

- Prepare and analyze Pu oxide sample duplicates
- Spike one with Ga and U to determine ion exchange % recoveries
- Determine method uncertainty
- Develop pre-concentration method for trace U in metals

Acknowledgements

- DOE Plutonium Sustainment Program
- Elmer Lujan
- Frank Dixon