Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Measurement of Trace Alpha-Emitting Actinide Contaminants in Molybdenum-99

CHUCK SODERQUIST, LORI DARNELL, JAMIE WEAVER

Pacific Northwest National Laboratory

2016 Topical Meeting on Molybdenum-99 Technological Development

Measurement of Trace Alpha-Emitting Actinides in Mo-99

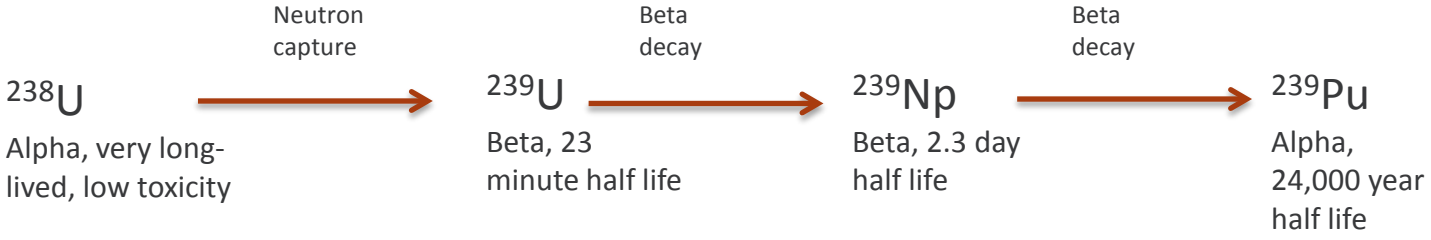
Introduction and Background

- ^{99}Mo is made by fission of ^{235}U, accompanied by a much larger amount of other fission products. A target of ^{235}U is placed in a reactor and irradiated with neutrons to fission some of the ^{235}U. About 6% of the fissions make ^{99}Mo. After irradiation, the target is removed from the reactor and chemically processed to recover the ^{99}Mo alone, without any other fission products. Process has been in use for decades.

- The ^{99}Mo must be quite pure to be used as a pharmaceutical. Extensive chemical separations are used to make a very pure product.

Measurement of Trace Alpha-Emitting Actinides in Mo-99

- Highly enriched ^{235}U makes an excellent target, but ^{235}U constitutes a proliferation risk.
- Lower enrichment uranium also works well. 20% ^{235}U, 80% ^{238}U makes ^{99}Mo, but will not work in a weapon. Avoids proliferation risk.
- The much larger amount of ^{238}U in the target produces new contaminants. Neutron capture in ^{238}U makes ^{239}Pu, which has high radiotoxicity.



Measurement of Trace Alpha-Emitting Actinides in Mo-99

- The switch from high- to low-enriched U carries new risk that plutonium could get into the product.
- ^{99}Mo product needs to be analyzed to prove the absence of ^{239}Pu.
- Specification for maximum allowable alpha contamination is 1 part alpha in 10^9 parts ^{99}Mo, eight days after production.
- Extremely high beta-gamma activity of ^{99}Mo precludes direct measurement of alpha emitters by alpha spectrometry.
- Need a method for measuring and identifying the alpha emitters in the ^{99}Mo.

Analytes are ^{239}Pu, ^{234}U and ^{235}U (from the target), and ^{241}Am (from neutron activation of ^{239}Pu). No other alpha emitters have credible chance being in the ^{99}Mo.

Measurement of Trace Alpha-Emitting Actinides in Mo-99

- Can't measure U, Pu, Am by alpha spectrometry in the presence of high-activity ^{99}Mo. High beta activity distorts the alpha spectra.
- Must chemically separate U, Pu, Am from the ^{99}Mo before measurement.

- Chemical forms of ^{99}Mo and ^{99m}Tc are MoO_4^{2-} and TcO_4^-. Stable and **soluble under basic conditions**. ^{99}Mo is less soluble under acidic conditions.
- U, Pu, and Am are quite **insoluble under basic conditions**. Soluble in acidic solution.
- This makes possible a fast, simple separation of actinide elements (U, Pu, Am) from ^{99}Mo solution.

Measurement of Trace Alpha-Emitting Actinides in Mo-99

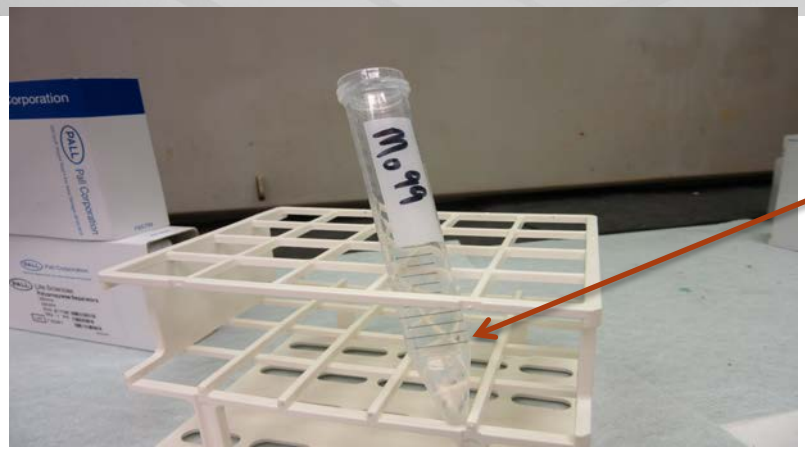
Analytical Procedure for Measurement of Alpha-Emitting Actinides

1. Measure ^{99}Mo sample into centrifuge tube.
2. Acidify the sample with nitric acid to assure that actinides are in solution.
3. Add 50 µg Gd to serve as carrier.
4. Add large excess of ammonium hydroxide. Precipitate of $Gd(OH)_3$ forms, and carries with it any actinides that might be present. ^{99}Mo and ^{99m}Tc stay in solution.

$$Gd^{3+}_{(aq)} + NH_4OH \rightarrow Gd(OH)_{3(s)}\downarrow$$

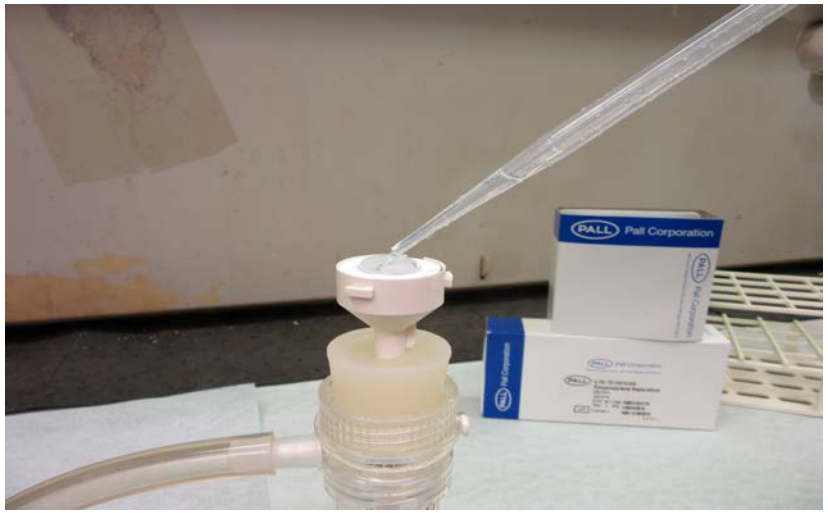
(All oxidation states of plutonium are insoluble under these conditions. Oxidation state does not need to be controlled.)

Analytical procedure, continued



Colorless suspension of $Gd(OH)_3$ in NH_4OH. 50 µg of Gd is nearly impossible to see.

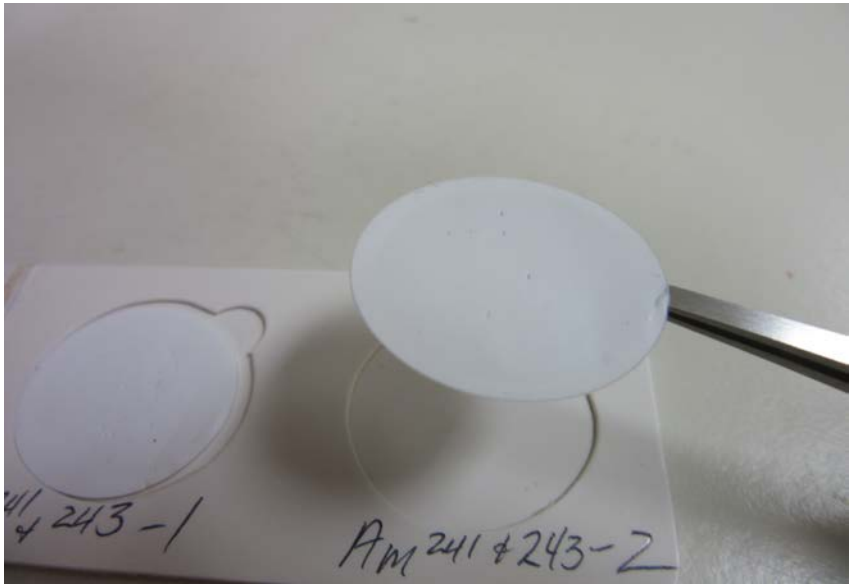
5. Pass the suspension of $Gd(OH)_3$ in ^{99}Mo solution through a membrane filter. The $Gd(OH)_3$ stops at the filter, but the high-activity ^{99}Mo passes through.



Suspension of $Gd(OH)_3$ is passed through a membrane filter. Actual ^{99}Mo sample has high dose rate. Shielding is not shown.

Analysis of Alpha Emitters in Mo-99

50 µg of Gd precipitated as hydroxide and loaded onto a 2.5-cm membrane filter makes a suitable source for alpha spectrometry. Spectral resolution is adequate to resolve the alpha emitters.



Finished alpha spectrometry counting mounts

Alpha spectrometry counting system

Analytical method, continued

A few important details previously left out for clarity:

- Special equipment is required. The work area needs lead shielding to cut exposure to the analyst. The ^{99}Mo is too hot to directly handle.
- Actinide elements are typically measured using a tracer. The tracer is added at the start of the analysis and shows up in the alpha spectrum as a second peak.
- The precipitation needs to be repeated once in order to reduce the ^{99}Mo activity sufficiently. Dissolve the first precipitate in dilute nitric acid, then re-precipitate it with fresh ammonium hydroxide as before. Pass the suspension though a clean membrane filter.

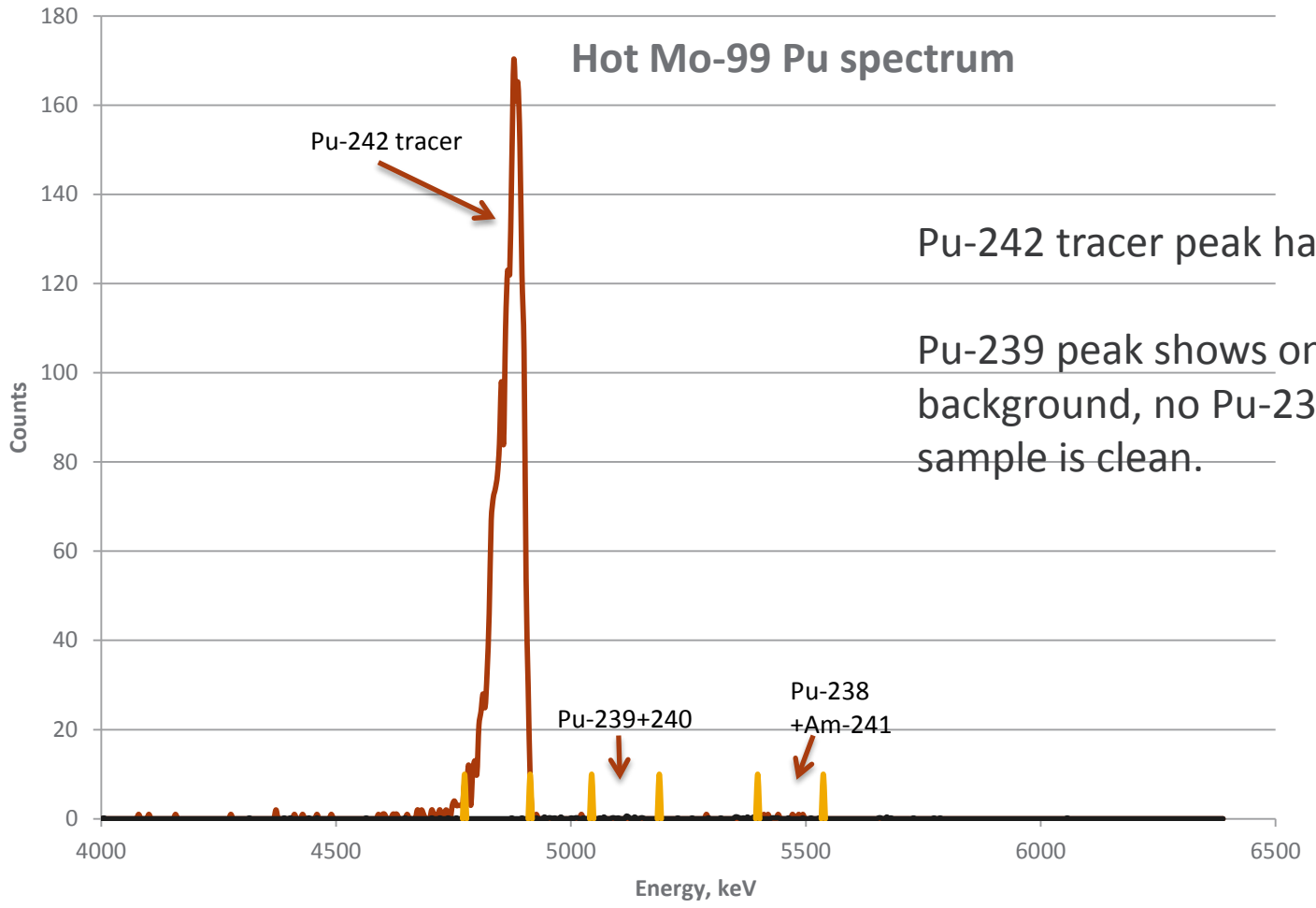
Analytical Results

In the alpha spectra shown in the next several slides, some used high-activity ^{99}Mo and others used a chemically identical solution, but without actual ^{99}Mo. The alpha spectra are indistinguishable with or without ^{99}Mo.

Hot ^{99}Mo measurements used equipment with shielding. Hot ^{99}Mo sample must be handled with extension tools. No direct handling is possible.

Any actinide element present in the sample will appear in the alpha spectrum. If a uranium-contaminated sample is analyzed for plutonium, uranium will appear in the plutonium spectrum.

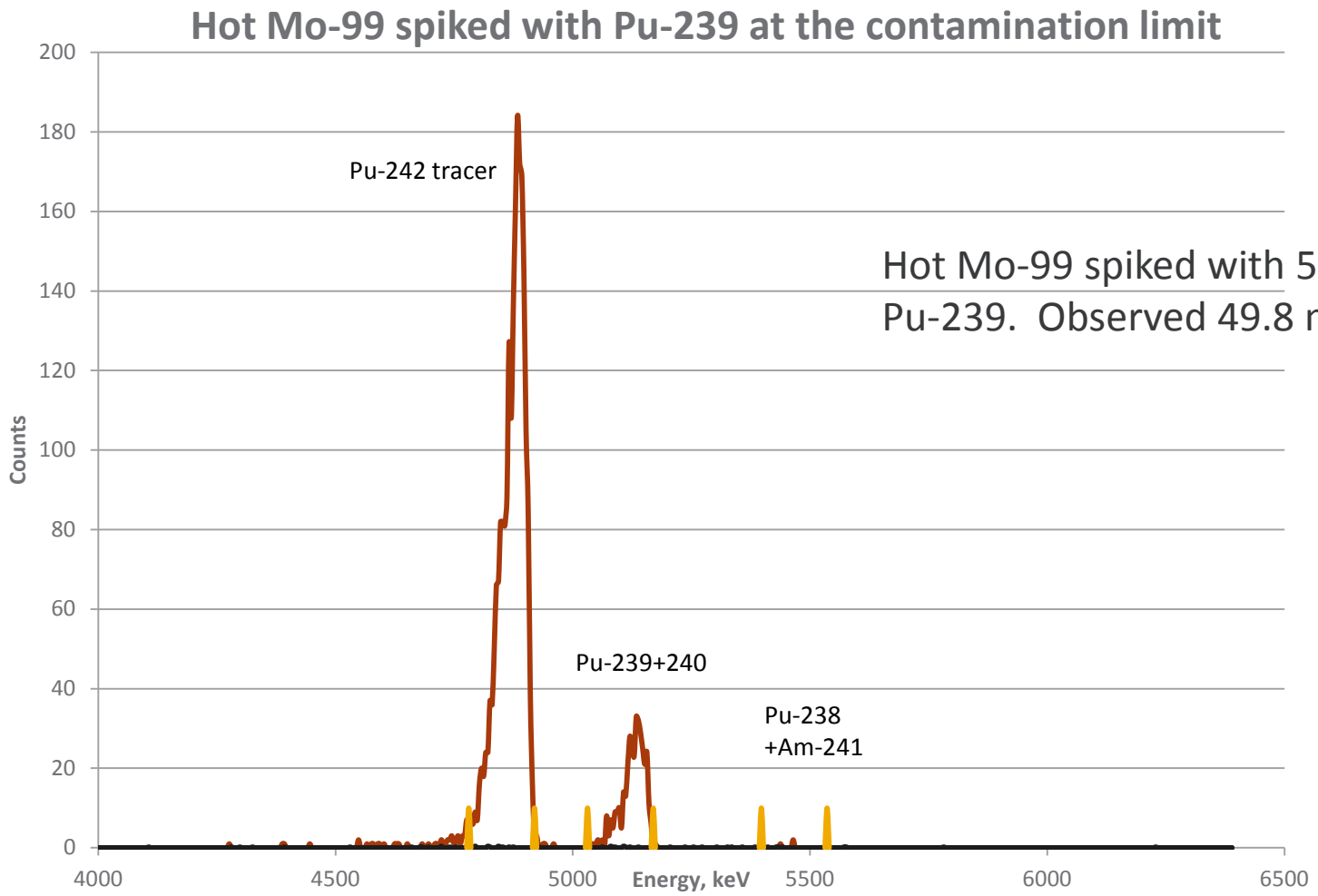
Plutonium Alpha Spectrum



Pu-242 tracer peak has 280 mBq.

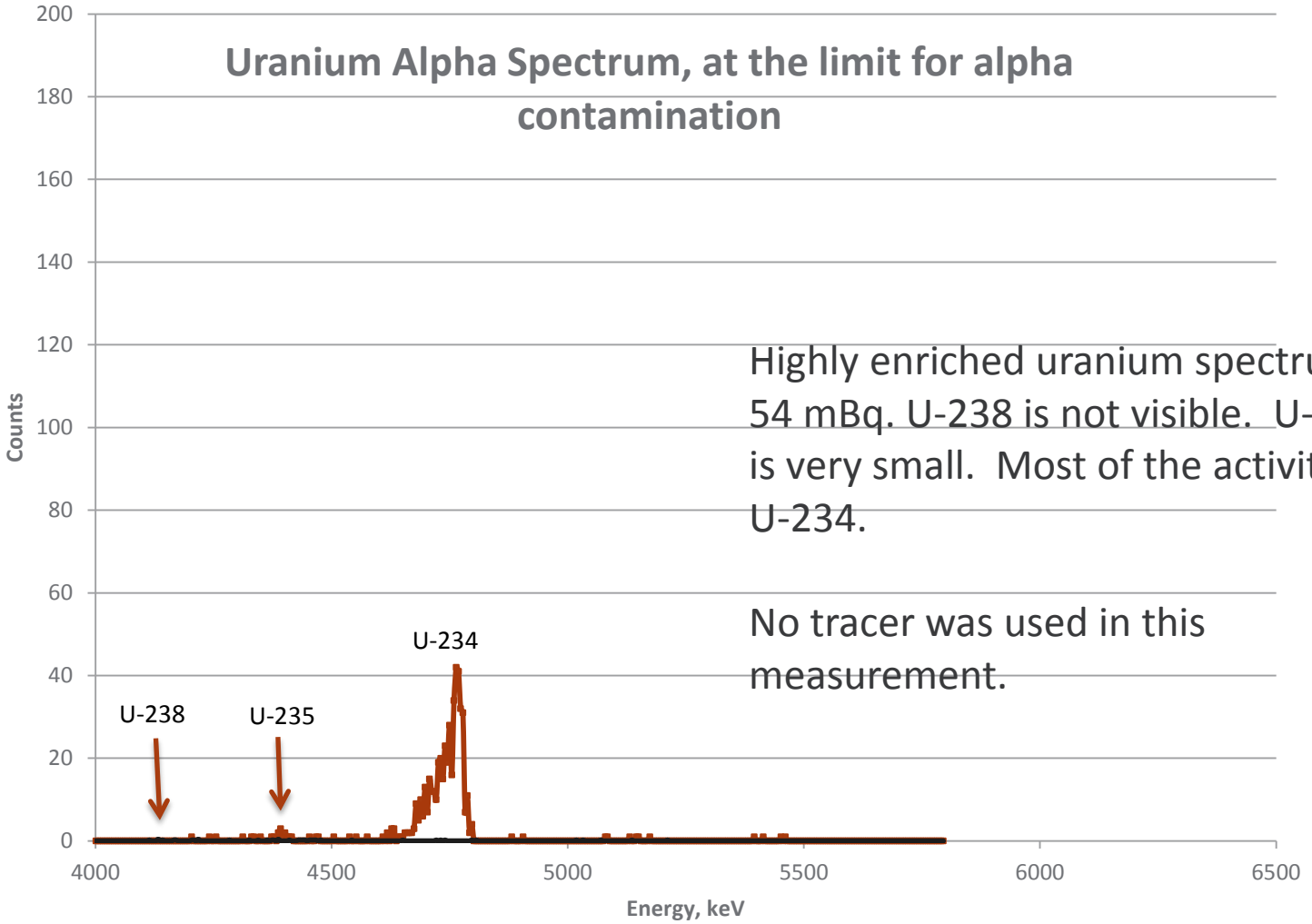
Pu-239 peak shows only detector background, no Pu-239. Mo-99 sample is clean.

Plutonium Alpha Spectrum



Hot Mo-99 spiked with 50.3 mBq Pu-239. Observed 49.8 mBq

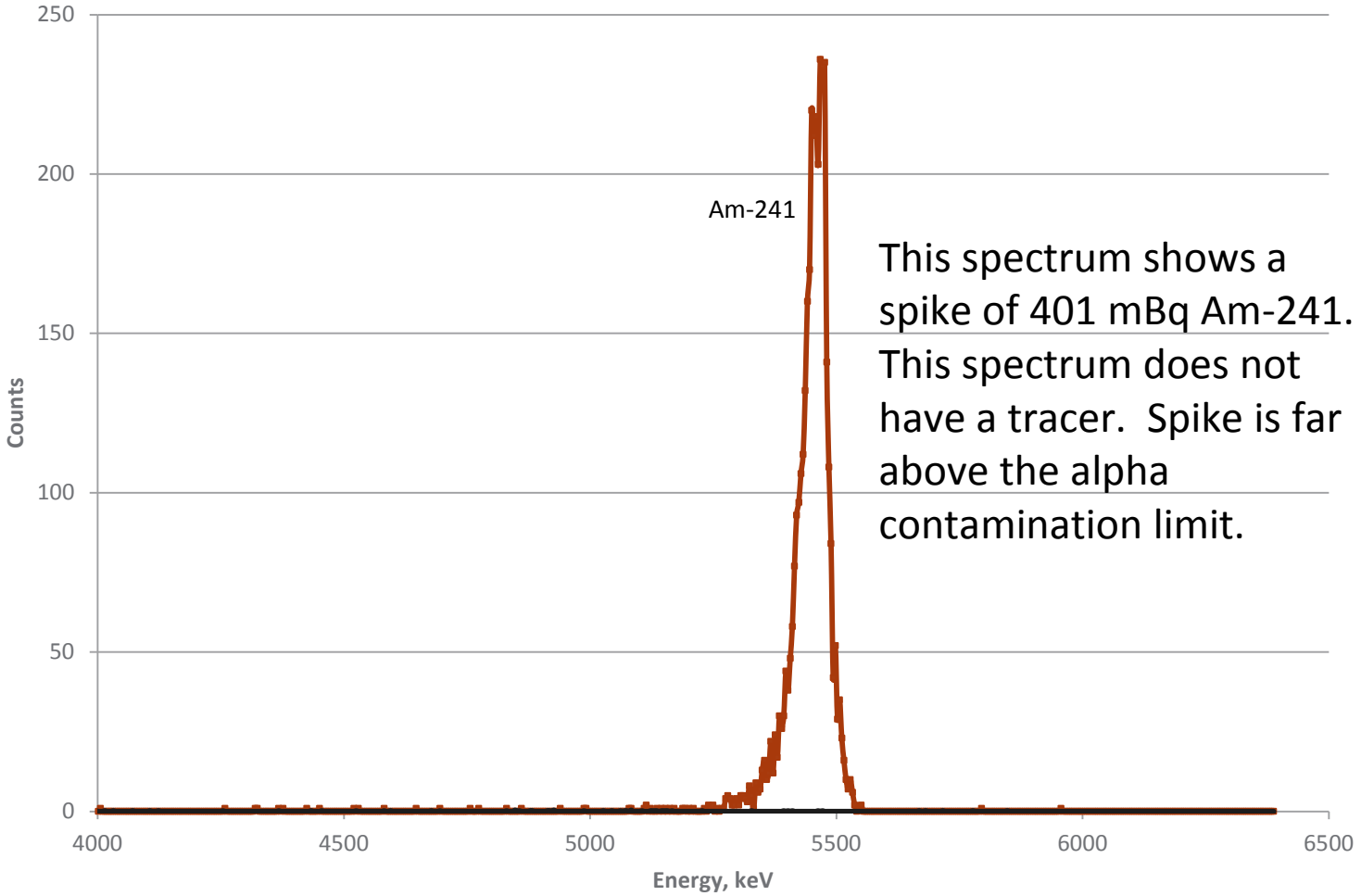
Uranium Alpha Spectrum using this method



Highly enriched uranium spectrum, 54 mBq. U-238 is not visible. U-235 is very small. Most of the activity is U-234.

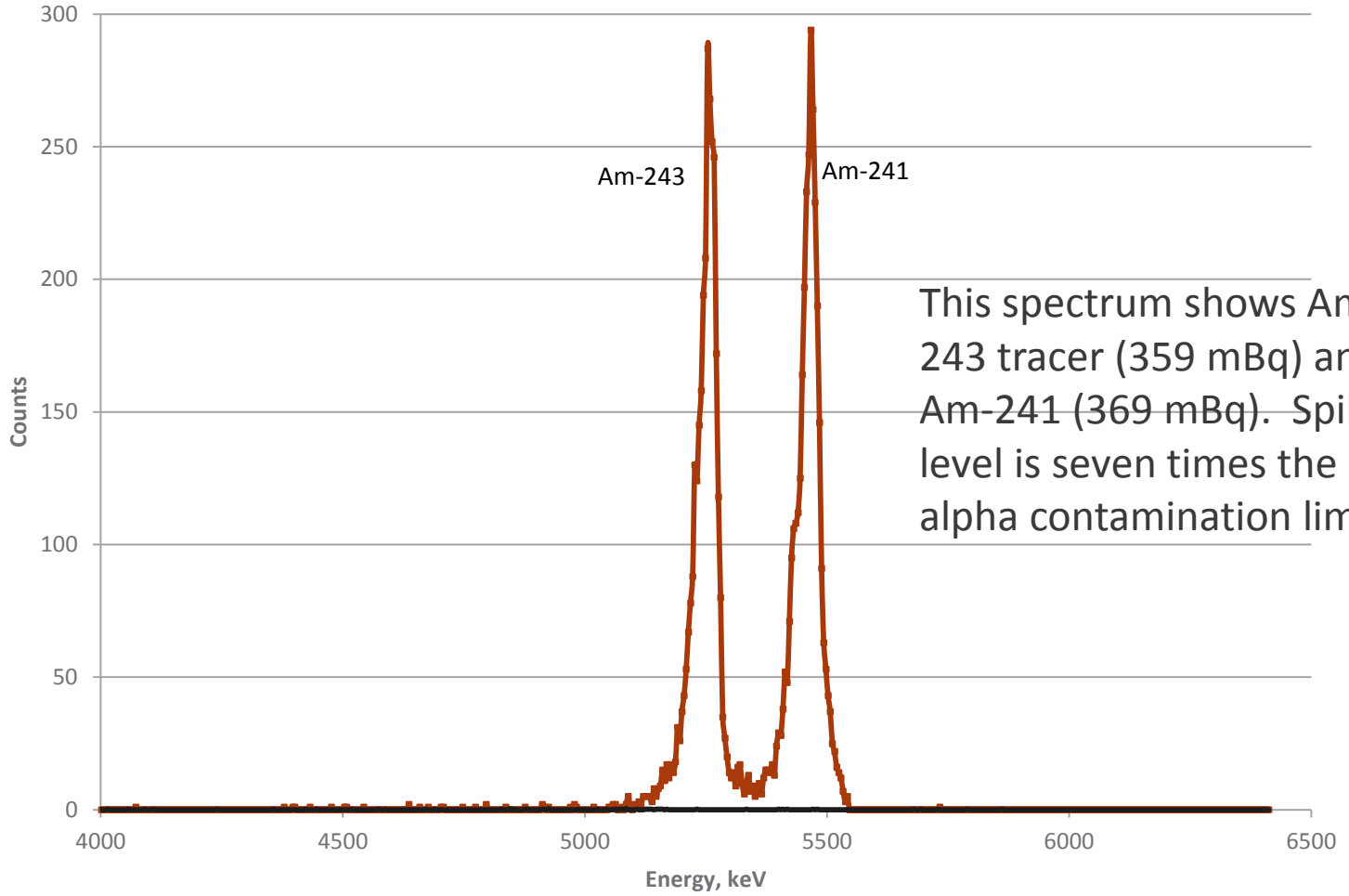
No tracer was used in this measurement.

Americium Alpha Spectrum



This spectrum shows a spike of 401 mBq Am-241. This spectrum does not have a tracer. Spike is far above the alpha contamination limit.

Americium spectrum with tracer

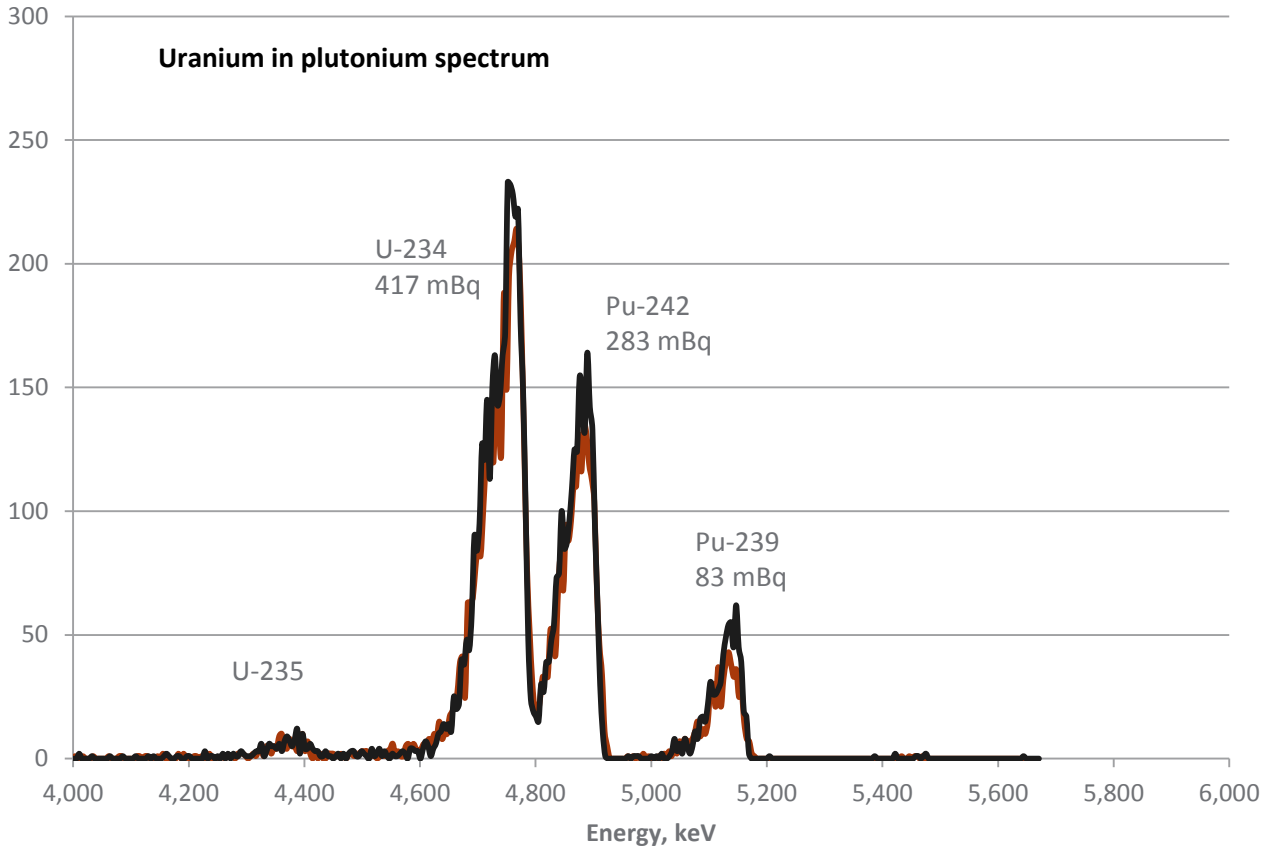


This spectrum shows Am-243 tracer (359 mBq) and Am-241 (369 mBq). Spike level is seven times the alpha contamination limit.

Summary

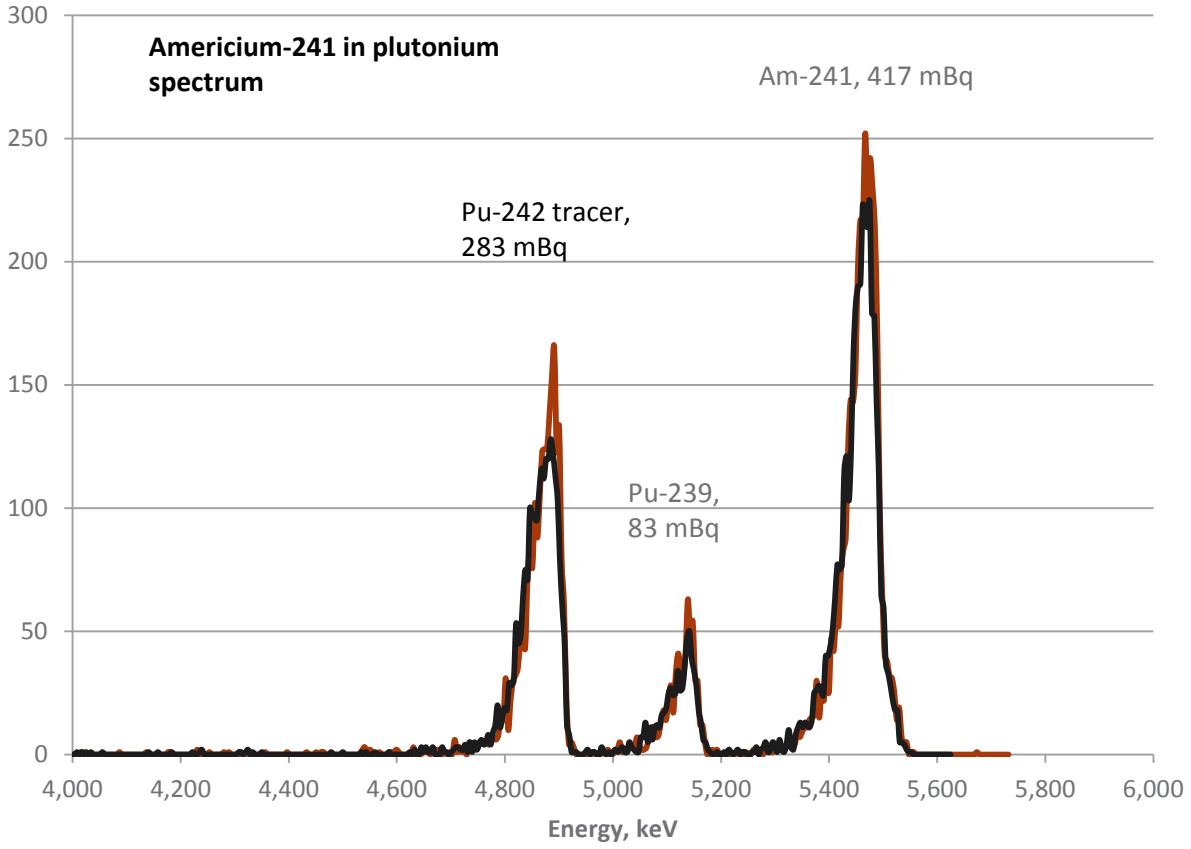
- Method is fast. Sample set consists of
  - Sample
  - Duplicate sample
  - Spiked sample (for quality control)
  - Blank sample (for quality control)
- Requires 2-3 hours lab time
- Requires 12 hours counting time
- 24-hour turnaround easily obtained
- Sensitivity easily measures 1 part alpha in 10^9 parts ^{99}Mo
- Method identifies the alpha emitters in the sample
- Alpha spectrum looks the same with or without actual ^{99}Mo. High beta-gamma activity does not measurably affect the final alpha result.

More Alpha Spectra



Heavy uranium contamination spiked into a plutonium measurement. Spectrum shows duplicate analyses superimposed.

More Alpha Spectra



Heavy ^{241}Am contamination spiked into plutonium measurement. Duplicate analyses shown superimposed.