

Actinide Mass Spectrometry for Nuclear Forensics and Safeguards

Ross Williams
Chemical Sciences Division
Physical and Life Sciences Directorate
Lawrence Livermore National Laboratory

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Photograph from *Preparing for the Worst*, Nature **433**, 26-Oct-2006, p. 907
Commentary by Michael May, Jay Davis and Raymond Jeanloz.

Actinides

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| | | | | | | | | | |
|-----------------------|---|---------------------------------------|--|--|---|--|---|---|--|
| Cm235 E 3.3 | Cm236 α ? ϵ ? E 1.7 236.0514 | Cm237 ϵ ? E 2.7 | Cm238 2.4 h ϵ α 6.52 E 1.0 238.05302 | Cm239 (7/-) ~3 h ϵ γ 187, ... E 1.8 | Cm240 27 d α 6.291, 6.248, ... γ 44.6 ω SF $\nu\nu\omega$ 240.055519 | Cm241 1/+ 32.8 d ϵ , γ 471.8, ... α 5.939 (ω), 5.929, 5.884, ... γ 145.6D (ω), ... E 7.67 | Cm242 162.8 d α 6.1127, 6.0694, ... γ 44.1 ω (e^-), ... SF $\nu\nu\omega$ α 2E1, 12E1 α < 5 242.058829 | Cm243 5/+ 29.1 a α 5.785, 5.742, ... γ 277.6, 228.2, ... SF $\nu\nu\omega$ α 13E1, 22E1 α 61E1, 16E2 243.061382 | Cm244 18.1 a α 5.8048, 5.7627, ... γ 42.8 ω (e^-), ... SF $\nu\nu\omega$ α 15, ~65E1 α 1.0, 11 244.062746 |
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|---|---|--|--|---|---|---|---|---|--|
| Am234 2.3 m ϵ α 6.46 ? E 4.2 | Am235 15 m ϵ ? E 2.6 | Am236 4 m ϵ E 3.3 | Am237 5/(-) 1.22 h ϵ γ 280.2, ... α 6.04 ω E 1.5 | Am238 1+ 1.63 h ϵ β^+ , ω γ 962.8, 918.7, 561.0, ... α 5.94 $\nu\omega$ E 2.3 | Am239 5/(-) 11.9 h ϵ γ 277.6, 228.2, ... α 5.774 (ω), 5.734, ... γ 49.3 ω E 8.03 | Am240 3(-) 2.12 d ϵ γ 987.7, 888.8, ... α 5.378 $\nu\omega$, ... E 1.38 | Am241 5/(-) 432.7 a α 5.4857, 5.4430, ... γ 59.5, 26.3-955 SF $\nu\nu\omega$ α (6E1+5E1), (19E1+13E2) α 3.2, 14 241.056823 | Am242 1- 141 a 16 02 h α 5.4857, 5.4430, ... β^- 83, 67 α 5.207 ω , ... γ 42.2 e^- γ 49.2 ω , ... SF $\nu\nu\omega$ α 17E2, 2E2 α 70E2, 18E2 E + 751 | Am243 5/(-) 7.37E3 a α 5.276, 5.234, ... γ 44.8 ω , 311-832.2 SF $\nu\nu\omega$ α (74+), (17E2+11E1) α -0.074, 0.06 243.061373 |
|---|---|--|--|---|---|---|---|---|--|

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|---|--|--|---|---|---|--|---|--|---|
| Pu233 20.9 m ϵ γ 235.3, 534.7, ... α 6.30 ω E 2.1 | Pu234 8.8 h ϵ α 6.200, 6.149, ... E 3.9 | Pu235 5/ (+) 25.3 m ϵ γ 49.2, 756.4, ... α 5.85 ω E 1.14 | Pu236 2.87 a α 5.7675, 5.7209, ... γ 47.6-643.7 ω SF $\nu\nu\omega$ α 16E1, 1E3 236.046048 | Pu237 7/- 45.2 d ϵ , γ 59.5, ... α 5.344 (ω), ... γ 280.4 (ω), 289.9, 320.8, ... α 24E2 E 22 | Pu238 87.7 a α 5.4992, 5.4565, ... γ 43.5 ω (e^-), ... γ 99.9 (e^-), ... SF $\nu\nu\omega$ α 54E1, 20E1 α 19, ~33 238.049553 | Pu239 1/+ 2.410E4 a α 5.156, 5.144, 5.105, ... γ 51.6 e^- , 30.1-1057.3 ω SF $\nu\nu\omega$ α 271, 20E1 α 750, 30E1 α < 0.4 mb 239.052157 | Pu240 6.56E3 a α 5.1683, 5.1237, ... γ 45.2 ω (e^-), ... γ 104.2 (e^-), ... SF $\nu\nu\omega$ α 290, 81E2 α 0.05, 2.4 240.053807 | Pu241 5/+ 14.4 a β^- 0208 γ 4.897 ω , 4.853, ... γ 148.5 (ω), 103.7, ... α 361, 16E1 α 101E1, 57E1 α < 0.2 mb E 0208 | Pu242 3.75E5 a α 4.901, 4.856, ... γ 44.9 ω (e^-), ... SF $\nu\nu\omega$ α 19, 11E2 α < 0.2, 0.23 242.058737 |
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|---|--|--|---|--|---|---|---|---|---|
| Np232 (4+) 14.7 m ϵ γ 326.8, 819.2, 866.8, 864.3, ... E 2.8 | Np233 5/ (+) 36.2 m ϵ γ 312.0, 298.9, 546.5, ... α 5.53 ? ω E 1.0 | Np234 (0+) 4.4 d ϵ β^+ 79 ω γ 1558.7, 1527.2, 1602.2, ... α 9E2 E 1.81 | Np235 5/+ 1.085 a ϵ α 5.021 ($\nu\omega$), 5.004, ... γ 25.6-188.8 $\nu\omega$ α (15E1+7) E 124 | Np236 6(-) 22.5 h 1.55E5 a ϵ , β^- , γ 160.3, ... γ 54, ... γ 62.3, ... γ 687.6, ... α 2.7E3, 7E2 E + 9, E - 0.5 | Np237 5/+ 2.14E6 a α 4.788, 4.771, ... γ 29.4, 86.5, ... α 15E1, 66E1 α 0.02, 7 237.048167 | Np238 2+ 2.117 d β^- 263, 1.248, ... γ 984.5, 1028.5, ... α 21E2, 9E2 E 1.292 | Np239 5/+ 2.355 d β^- 438, 341, ... γ 106.1, 277.6, 228.2, ... α (3E1+3E1) α < 1 E 722 | Np240 5 (+) 7.22 m 1.032 h β^- 2.18, β^- 89 1.60, ... γ 554.6, 973.9, 597.4, 600.6 E 2.20 | Np241 5/+ 13.9 m β^- 1.3, ... γ 174.9, 133.0 (e^-), 518.8, ... E 1.3 |
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| U231 5/(-) 4.2 d ϵ γ 25.65, 84.2, ... α 5.456 ω , ... γ 68.33, 53.23, ... α 3E2 E 382 | U232 69.8 a α 5.3203, 5.2635, ... γ 57.8 ω (e^-), ... 129.1, ... SF $\nu\nu\omega$ α 46, 14E1 α 73, 28E1 α 75, 38E1 232.037146 | U233 5/+ 1.592E5 a α 4.824, 4.783, ... γ 42.5 ω , 97.1, 54.7, ... SF $\nu\nu\omega$ α 46, 14E1 α 531, 76E1 α < 0.3 mb 233.039628 | U234 U11 0.0055 2.46E5 a α 4.776, 4.725, ... γ 53.2 (e^-), 120.9, ... α 4.398, 4.366, ... γ 185.72, 143.76, ... SF $\nu\nu\omega$ α 99, 14E1 α 585-275 α < 1 mb 234.040946 | U235 7/- 26 m U2 76.8 eV ω (e^-), ω 0.7200 7.04E8 a α 4.398, 4.366, ... γ 185.72, 143.76, ... SF $\nu\nu\omega$ α 99, 14E1 α 585-275 α < 1 mb 235.043923 | U236 2.342E7 a α 4.494, 4.445, ... γ 49.4 ω (e^-), 112.8, ... SF $\nu\nu\omega$ α 5, 1, 36E1 α 0.04, 4 236.045562 | U237 1/+ 6.75 d β^- 24, 25, ... γ 59.5, 208.0, ... α 4E2, 12E2 α < 0.35 E 519 | U238 UI 99.2745 4.47E9 a α 4.197, 4.147, ... γ 49.6 ω (e^-), ... SF $\nu\nu\omega$ α 258, 277 α < 9 mb 1.3 mb 238.050783 | U239 5/+ 23.47 m β^- 1.21, 1.28, ... γ 74.7, 43.5, ... α 22 α 15 E 1.263 | U240 14.1 h β^- 36 γ 44.1 (e^-), ... E 3.9 |
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|--|--|---|--|---|---|--|---|---|
| Pa230 2- 17.4 d ϵ , γ 952.0, ... β^- 51, ... γ 314.8 ω , ... α 4.766 - 5.345 $\nu\omega$ α 15E2 E + 1.3010 E - 564 | Pa231 3/- Pa 100 3.28E4 a α 5.013, 4.950, 5.029, ... γ 27.4, 300.1, ... α 20E1, 5E2 α 0.020, 0.05 231.035879 | Pa232 (2-) 1.31 d β^- 31, 29, ... γ 969.3, 894.3, ... ϵ ? α 5E2, 3E2 α 7E2 E 1.34 | Pa233 3/- 26.967 d β^- 256, 15, ... γ 312.0, ... α (21+20), (46E1+44E1) α < 0.1 E 570 | Pa234 4+ UX2 1.17 m UX 6.69 h β^- 2.29, β^- 48, 65, 1001.0, ... 766.4, ... γ 131.3, 34-1938 IT < 10 γ 73.9 ω , e^- E 2.195 | Pa235 3/(-) 24.4 m β^- 1.41, ... γ 30.1 - 658.9 E 1.4 | Pa236 1- 9.1 m β^- 2.0, 3.1, ... γ 642.3, 687.5, 1762.7, ... SF $\nu\nu\omega$ E 2.9 | Pa237 (1/+) 8.7 m β^- 1.2, 1.5, 2.25, ... γ 853.6, 865.0, 529.3, 540.7, ... E 2.3 | Pa238 3- 2.3 m β^- 1.7, 1.2, 2.2, ... γ 1015, 635, 448, 680, ... E 3.5 |
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| Th229 5/+ 7.3E3 a α 4.845, 4.901, 4.814, ... γ 193.6, 86.4, 210.9, 31.5, ... α 6E1, 1.0E3 α 31, 5E2 229.031755 | Th230 Io 7.54E4 a α 4.688, 4.621, ... γ 67.7 e^- , 110.0-620. α 23.0, 101E1 α < 0.5 mb 230.033127 | Th231 5/ (+) UY 1.063 d β^- 305, ... γ 25.64, 84.21, ... E 3.90 | Th232 Th 140 1.40E10 a α 4.012, 3.947, ... γ 63.81 ω (e^-), 140.88 SF ($\nu\nu\omega$) α 7.37, 85 α < 1 μ b 232.038050 | Th233 (1/+) 21.83 m β^- 1.245, ... γ 86.5, 29.4, 459.3, ... α 15E2, 4E2 α 15 E 1.245 | Th234 UX1 24.10 d β^- 198, ... γ 63.3, 92.4, 92.8, ... α 2 α < 0.01 E .273 |
|---|--|---|---|---|---|

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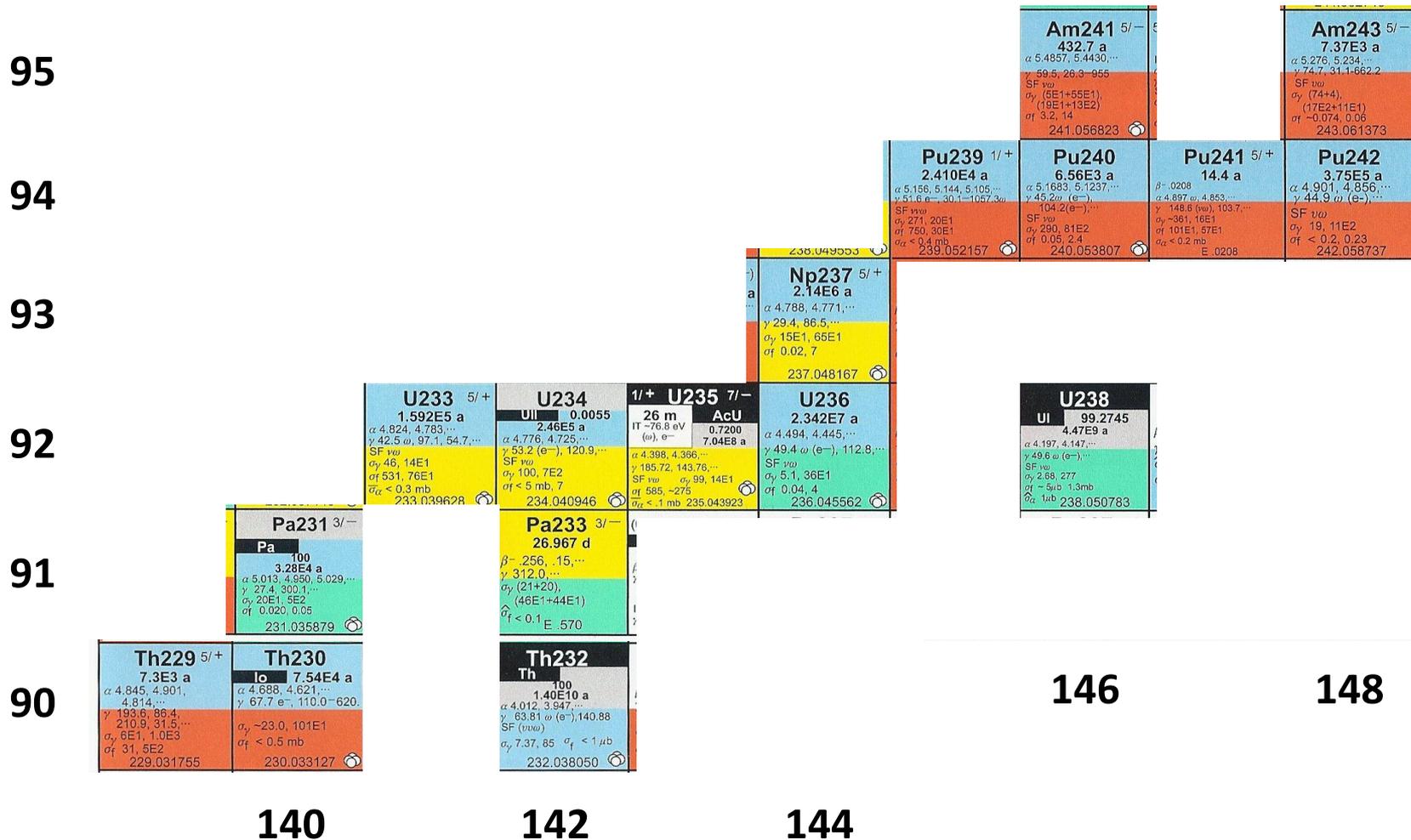
140

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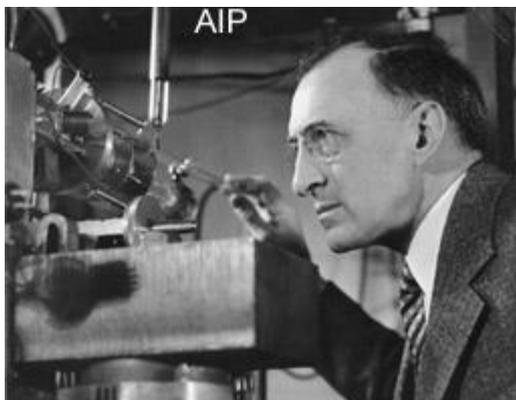
144



Actinides commonly measured by mass spectrometry



Science and instrument development



Arthur Jeffrey Dempster
Discoverer of ^{235}U



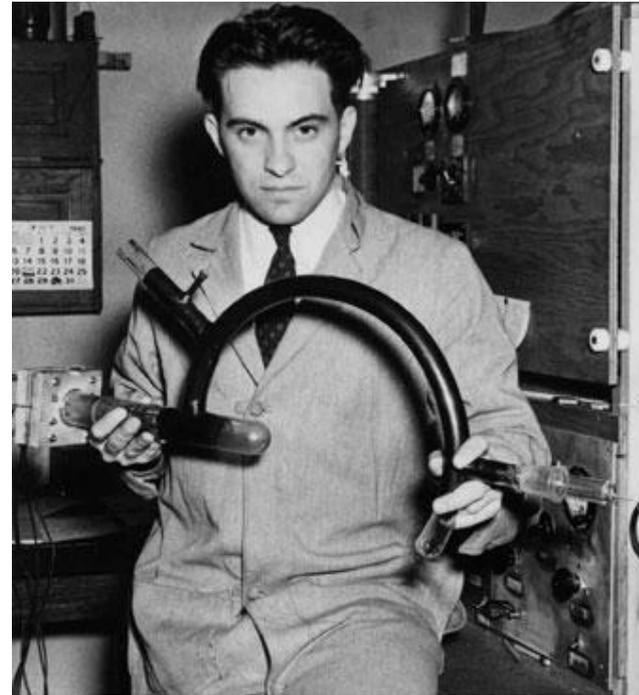
Alfred Otto Carl Nier
Inventor of the modern
mass spectrometer

| | | | |
|---------------------------------|----------|-----------------|---------------------------|
| | Dempster | Nier | Cowan and Adler |
| | (1935) | (1939) | Garner (1975) |
| $^{238}\text{U}/^{235}\text{U}$ | > 100 | $138.9 \pm 1\%$ | $137.9 \pm 0.3 \text{ ‰}$ |



Nier: the father of modern mass spectrometry

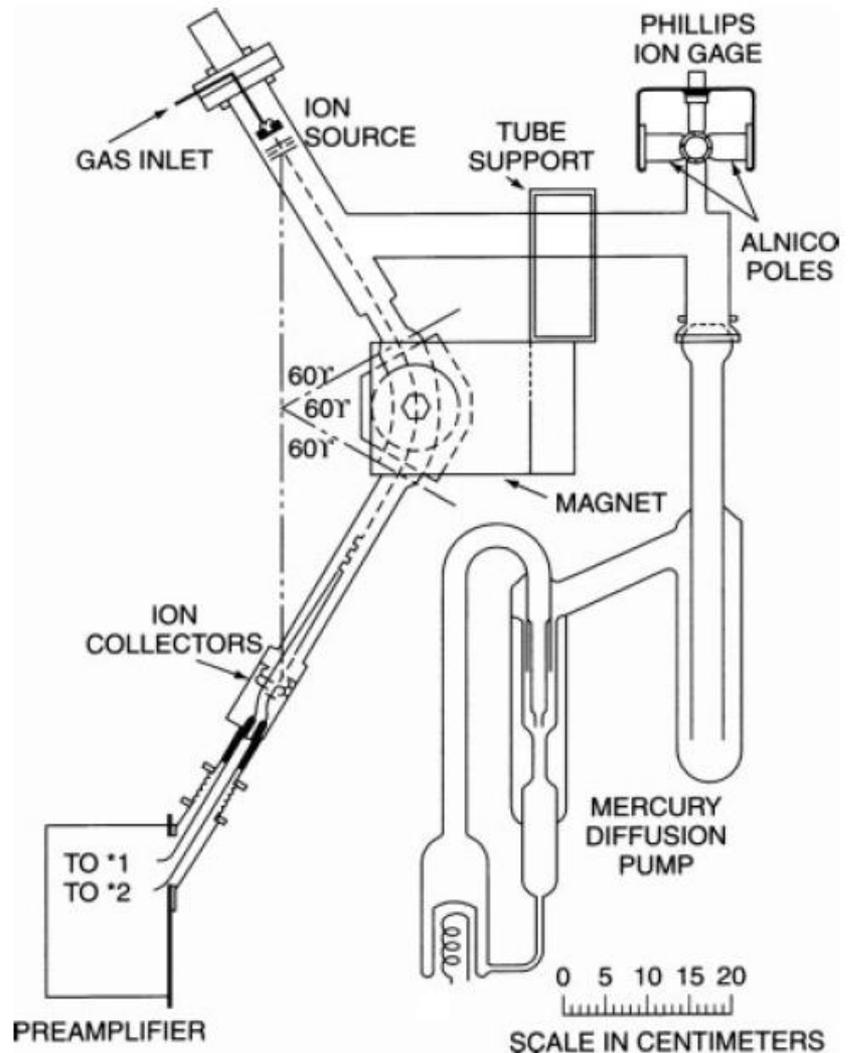
- Built sector field mass spectrometer
- Separated ^{235}U for Manhattan Project experiments
- Measured isotopic composition of U
- Determined atomic weight for U and Pb



Alfred Otto Carl Nier, 1911-1994

Nier mass spectrometer - 1940

- Parts of mass spectrometer
 - Ion source
 - Mass analyzer
 - Detector
- 60° sector field magnet
 - Smaller, lighter, lower power consumption
 - Ion source and detector out of influence of magnetic field
- Electronic measurement of ion beam



Measurement of $^{238}\text{U}/^{235}\text{U}$

JANUARY 15, 1939

PHYSICAL REVIEW

VOLUME 55

The Isotopic Constitution of Uranium and the Half-Lives of the Uranium Isotopes. I†

ALFRED O. NIER*

Research Laboratory of Physics, Harvard University, Cambridge, Massachusetts

(Received November 3, 1938)

uranium. Allowing for systematic errors such as errors in calibration, discrimination of apparatus against different mass numbers, etc., one can probably safely assume that the best value for the ratio is 138.9 or 139, with a limit of error of one percent.

A.O. Nier, *Phys. Rev.* 1939, 55:150-153

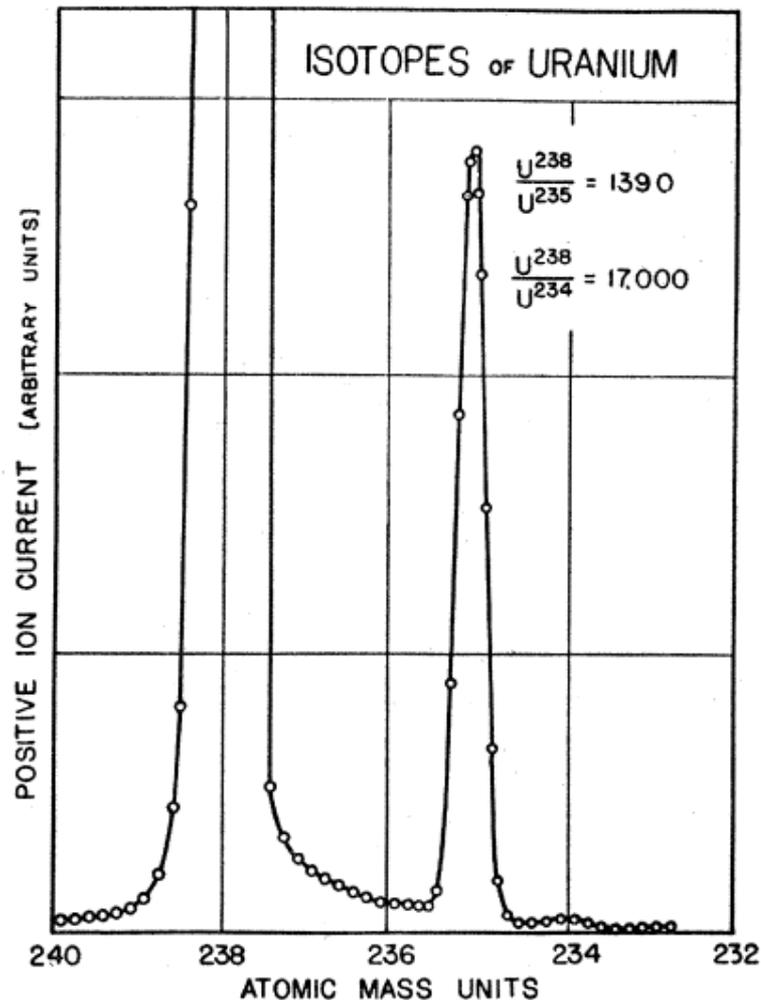
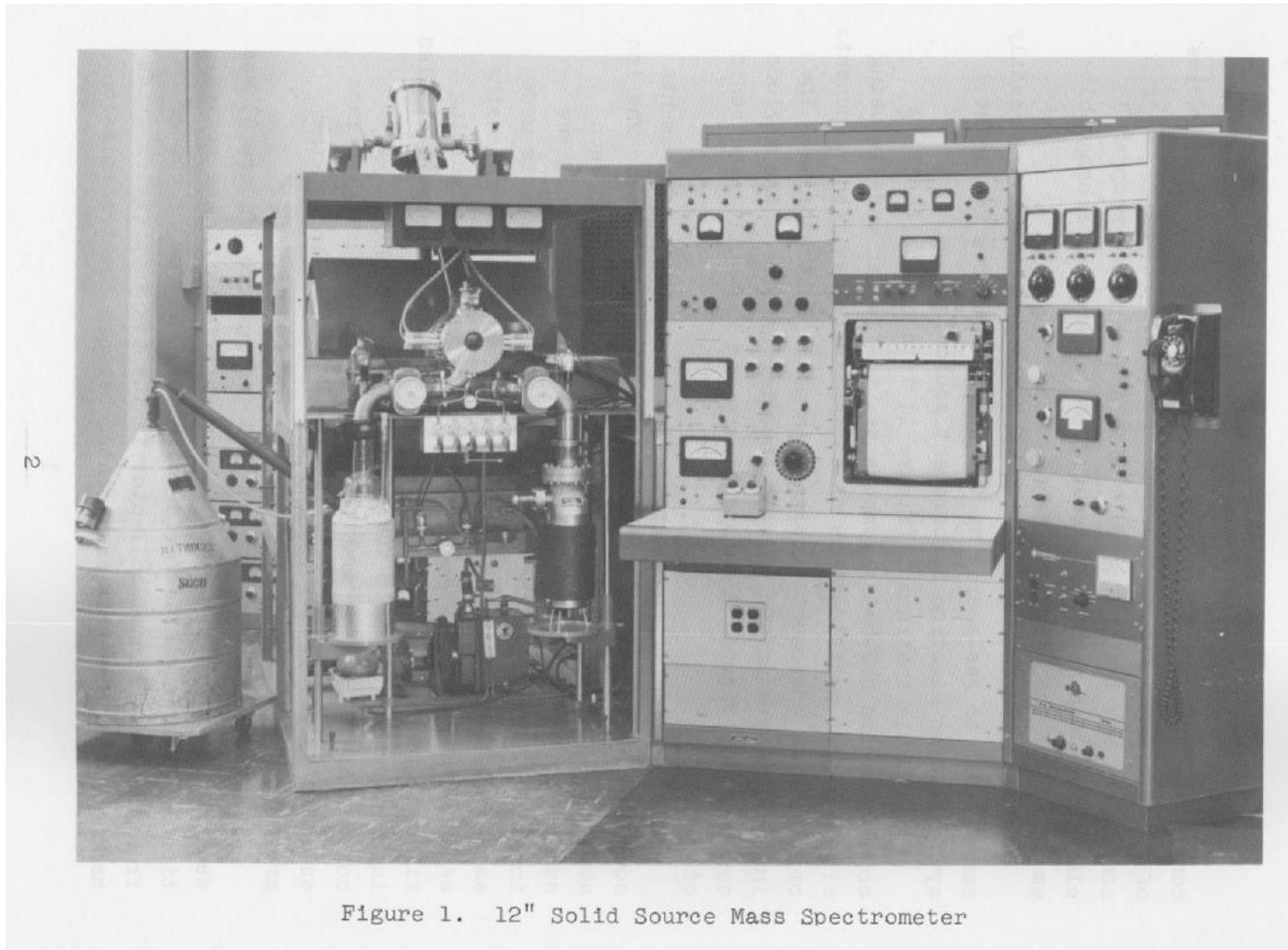


FIG. 1. Mass spectrum showing isotopes of uranium. The experimental points are obtained by plotting positive ion current passing through the exit slit of the analyzer as a function of the energy of the ions while the magnetic field is held constant. As there is a definite relation between the energy and the mass of the ions collected, namely, $\text{energy} \times \text{mass} = \text{a constant}$, the voltage scale can be readily changed to a mass scale, as was done in the figure. The width of the peaks is, of course, caused by the finite width of the slits used and the imperfections in focusing.



NBS 12-64 Mass Spec



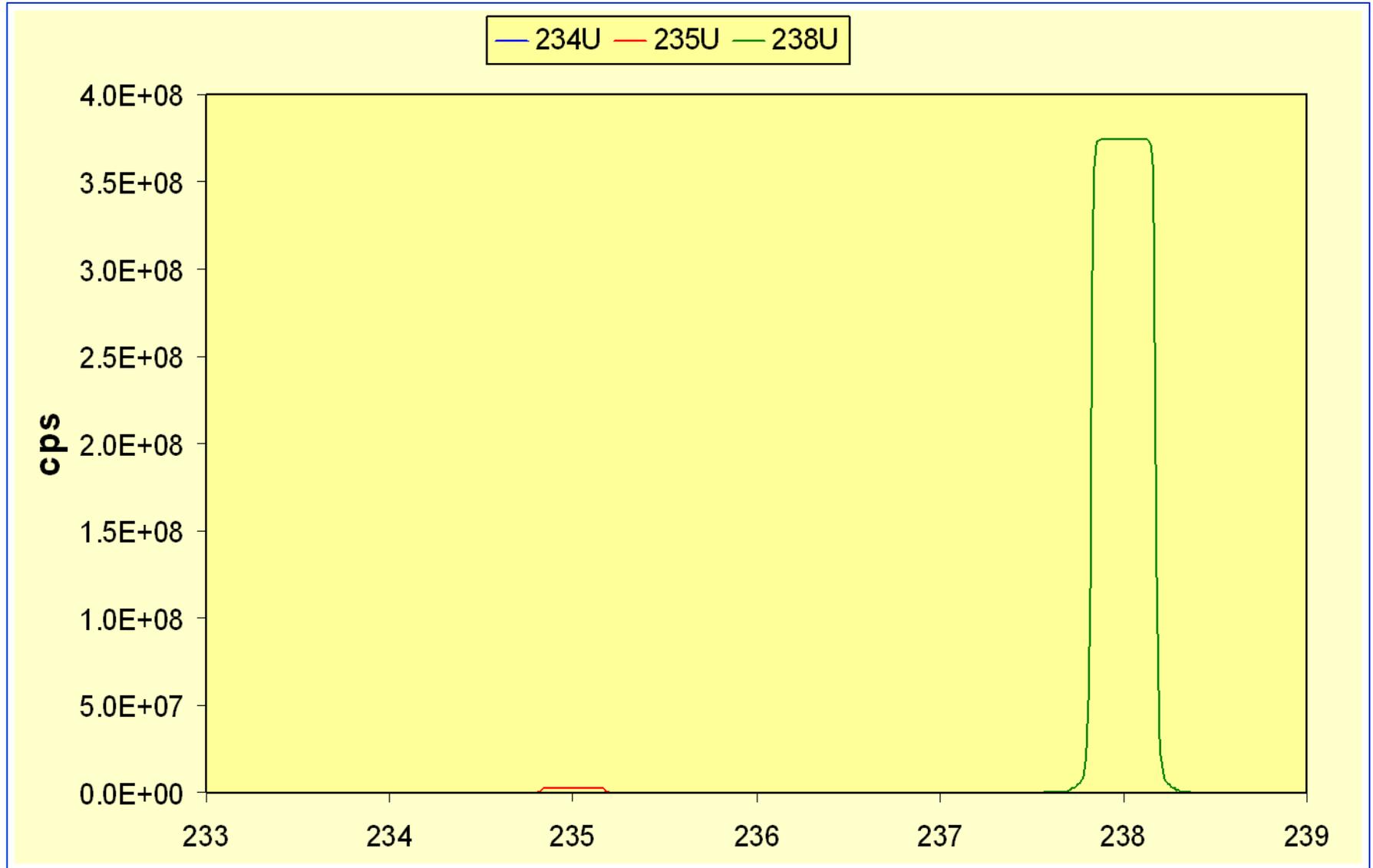
IsoProbe Multi-Collector ICP Mass Spectrometer

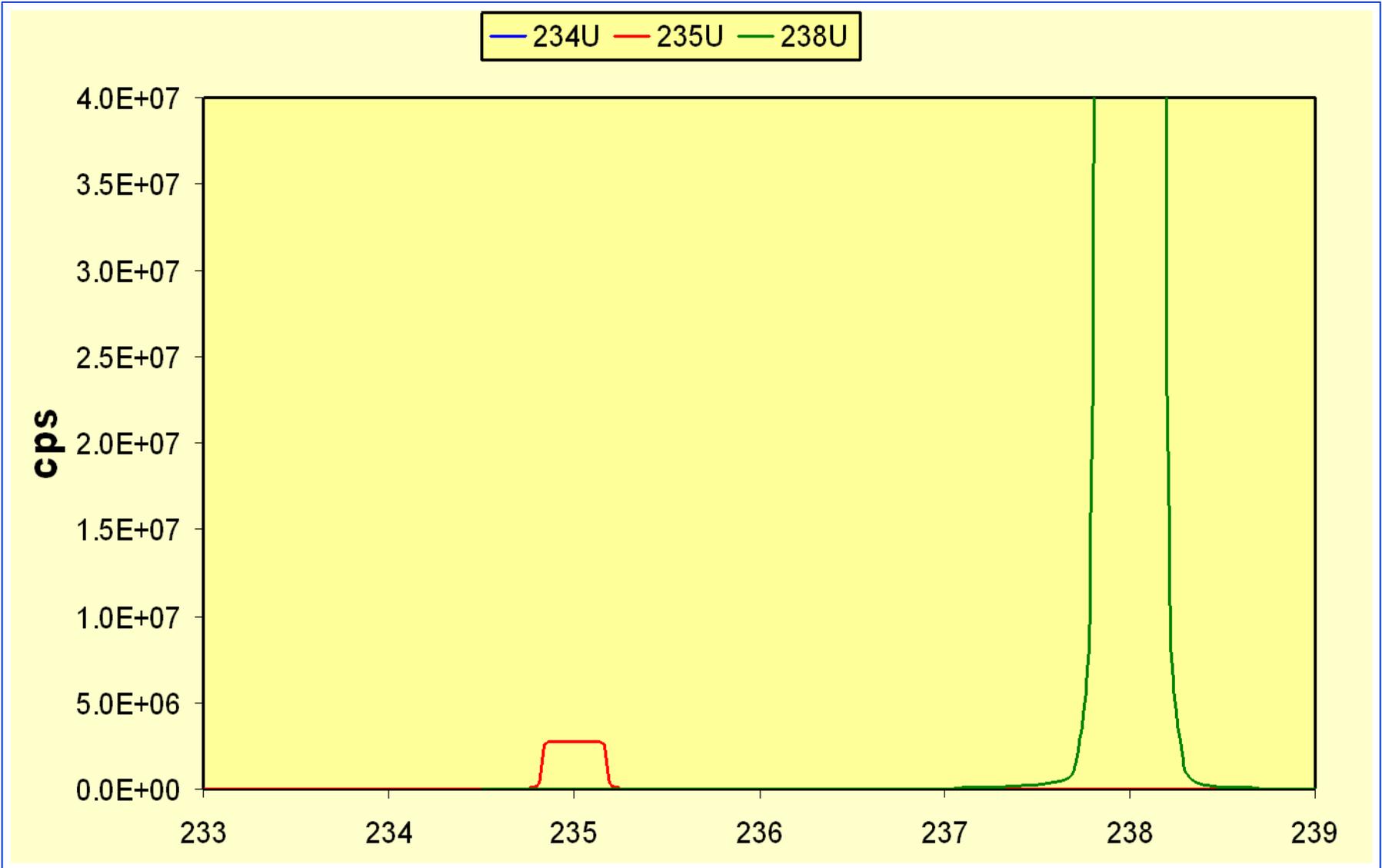


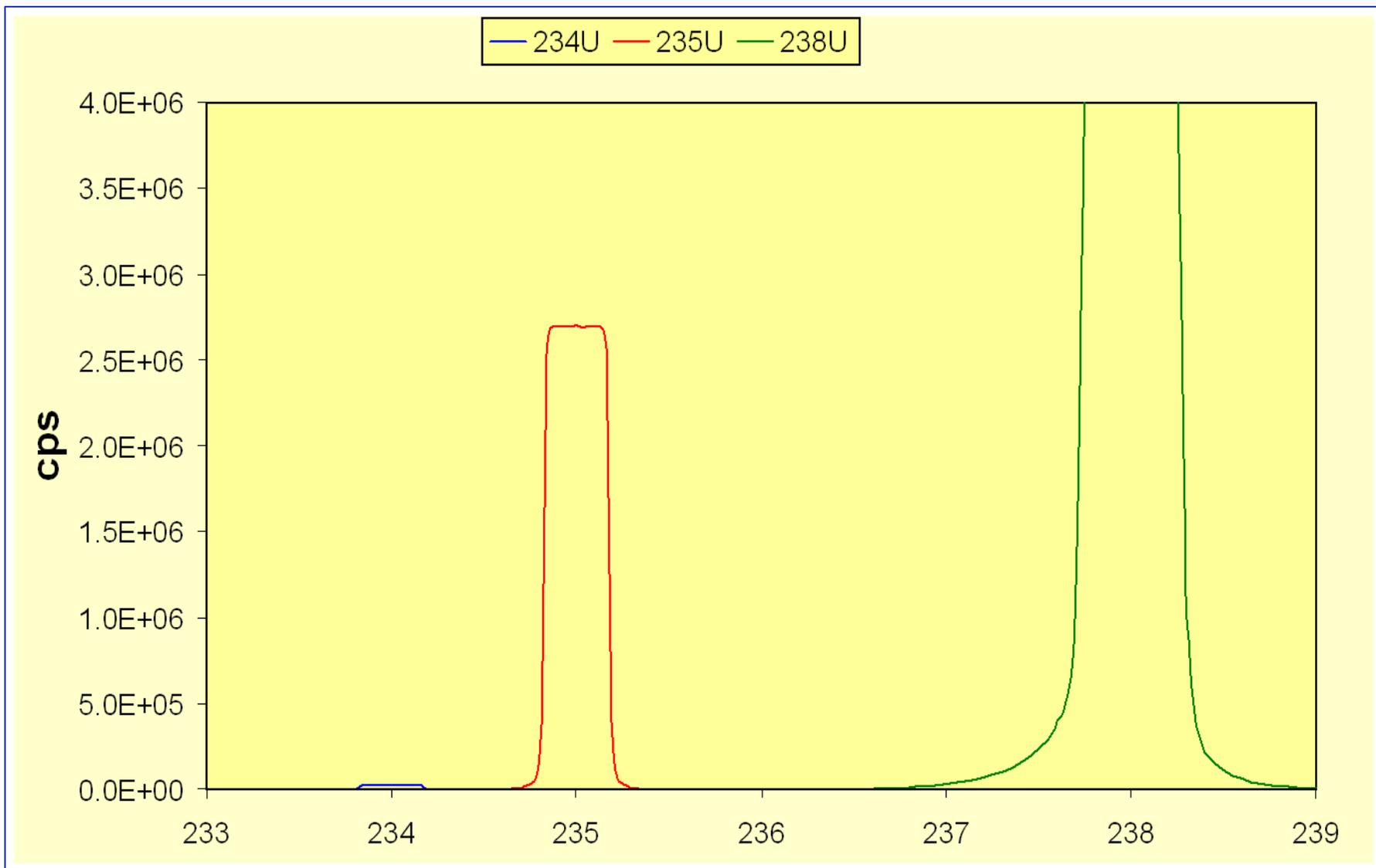
NuPlasma HR

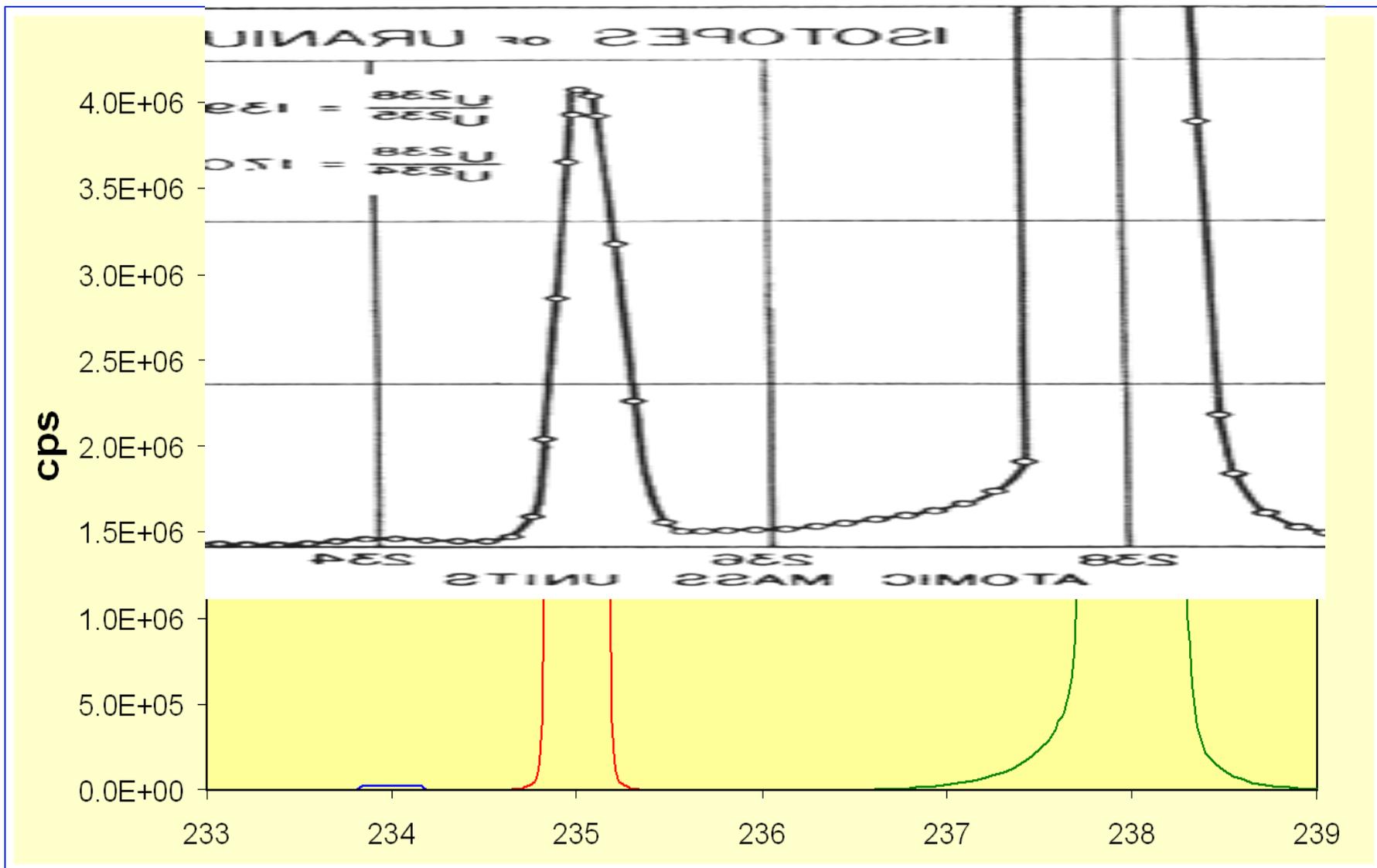


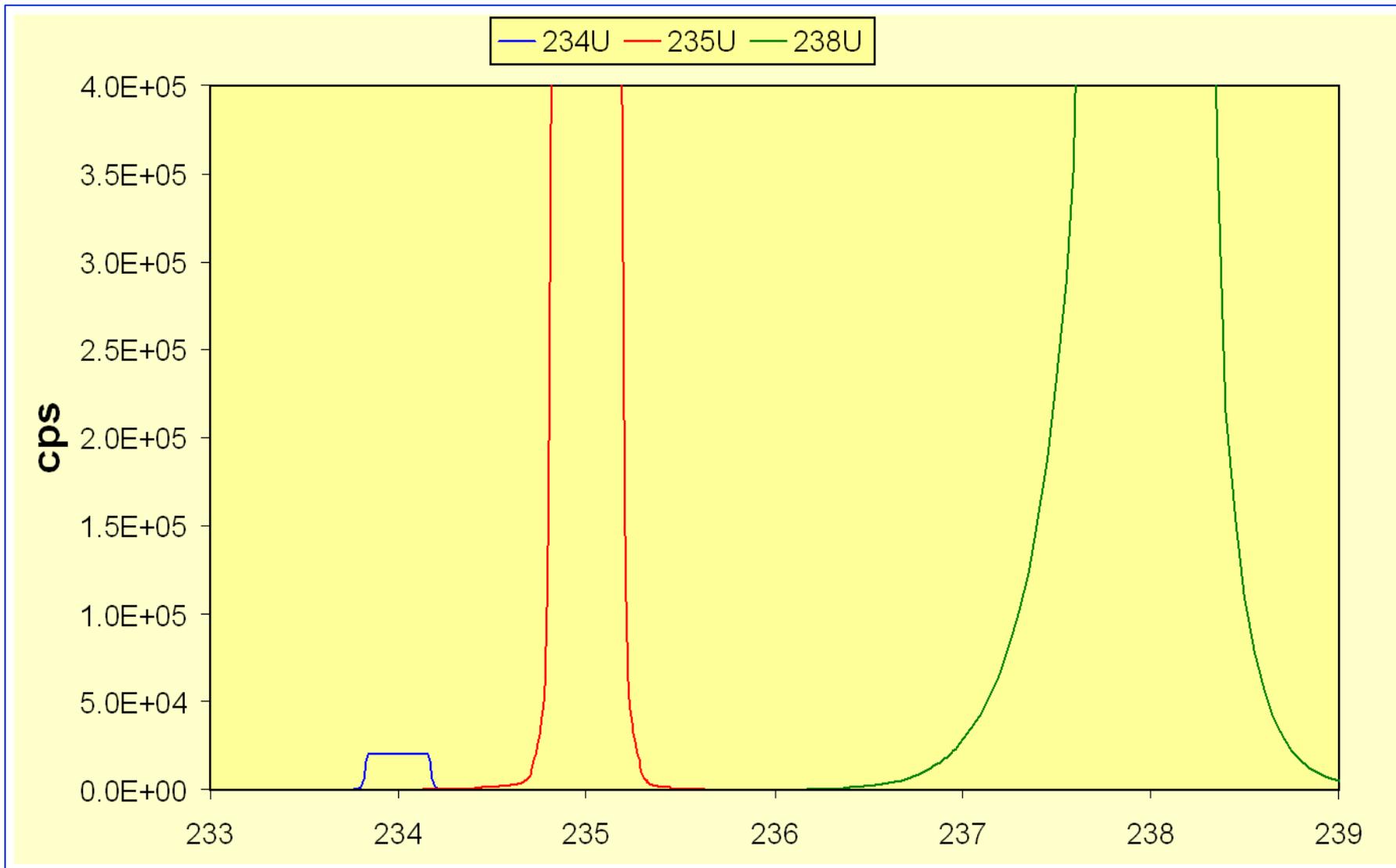
Normal Uranium -- ^{238}U signal = 6 volts

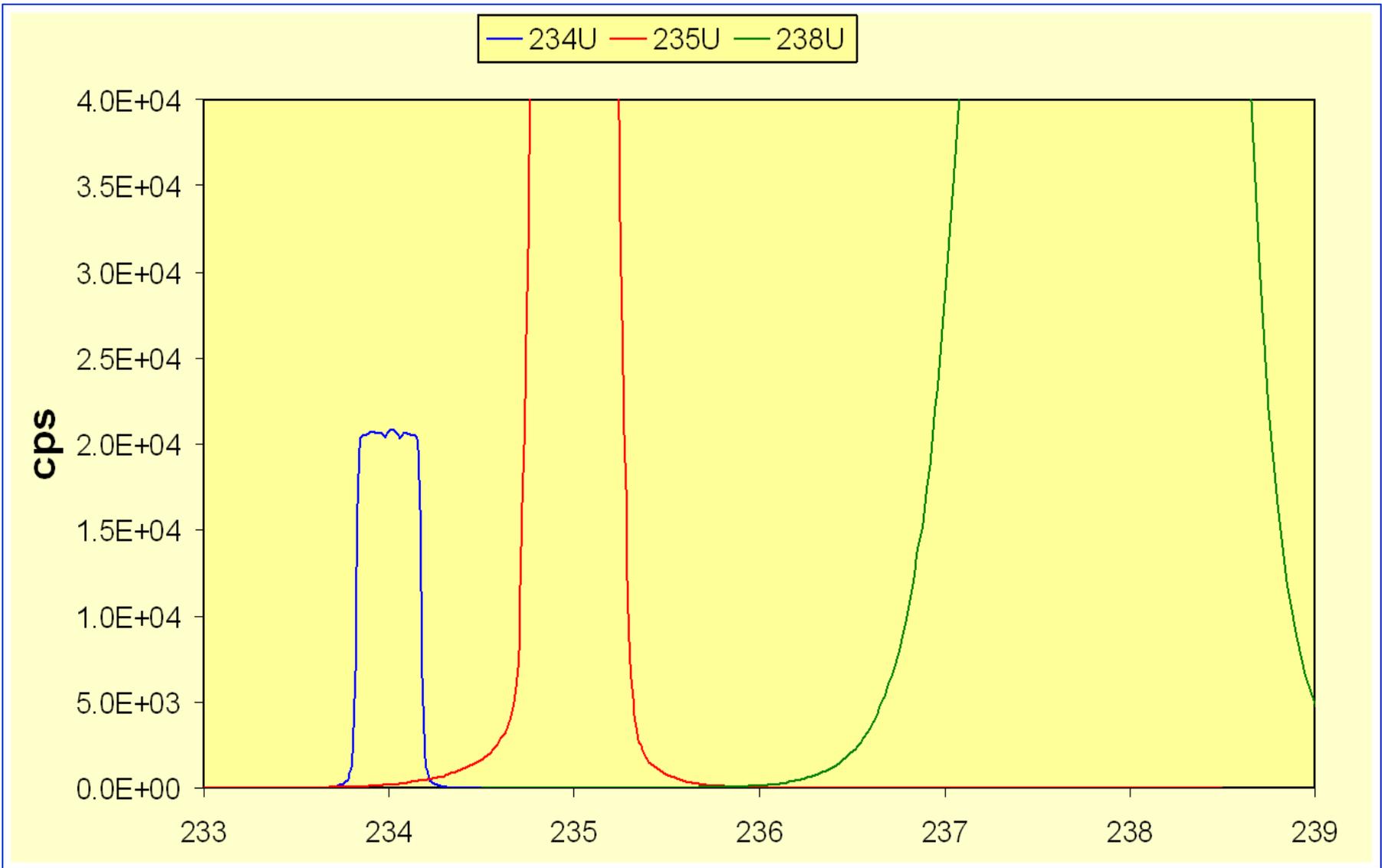




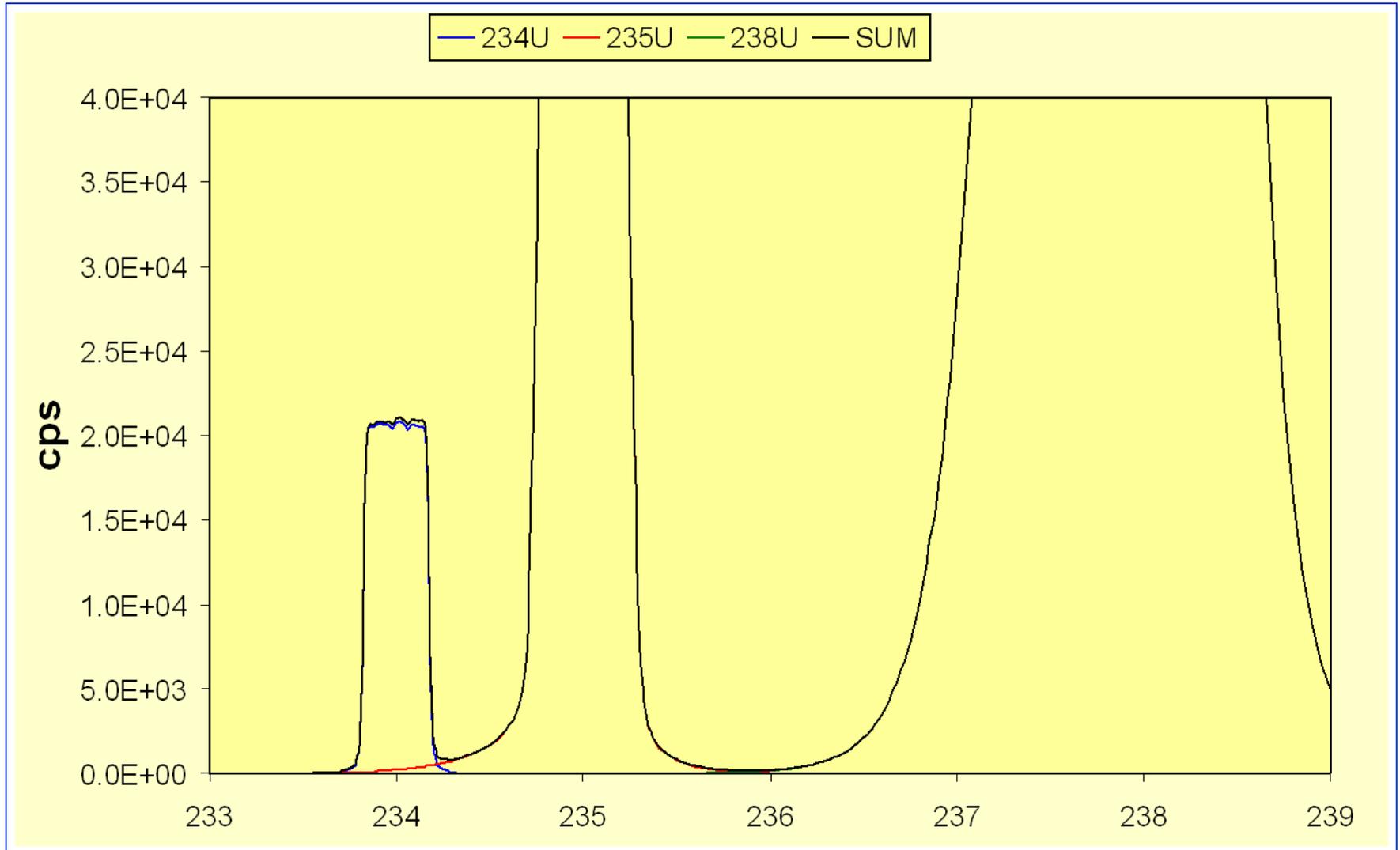




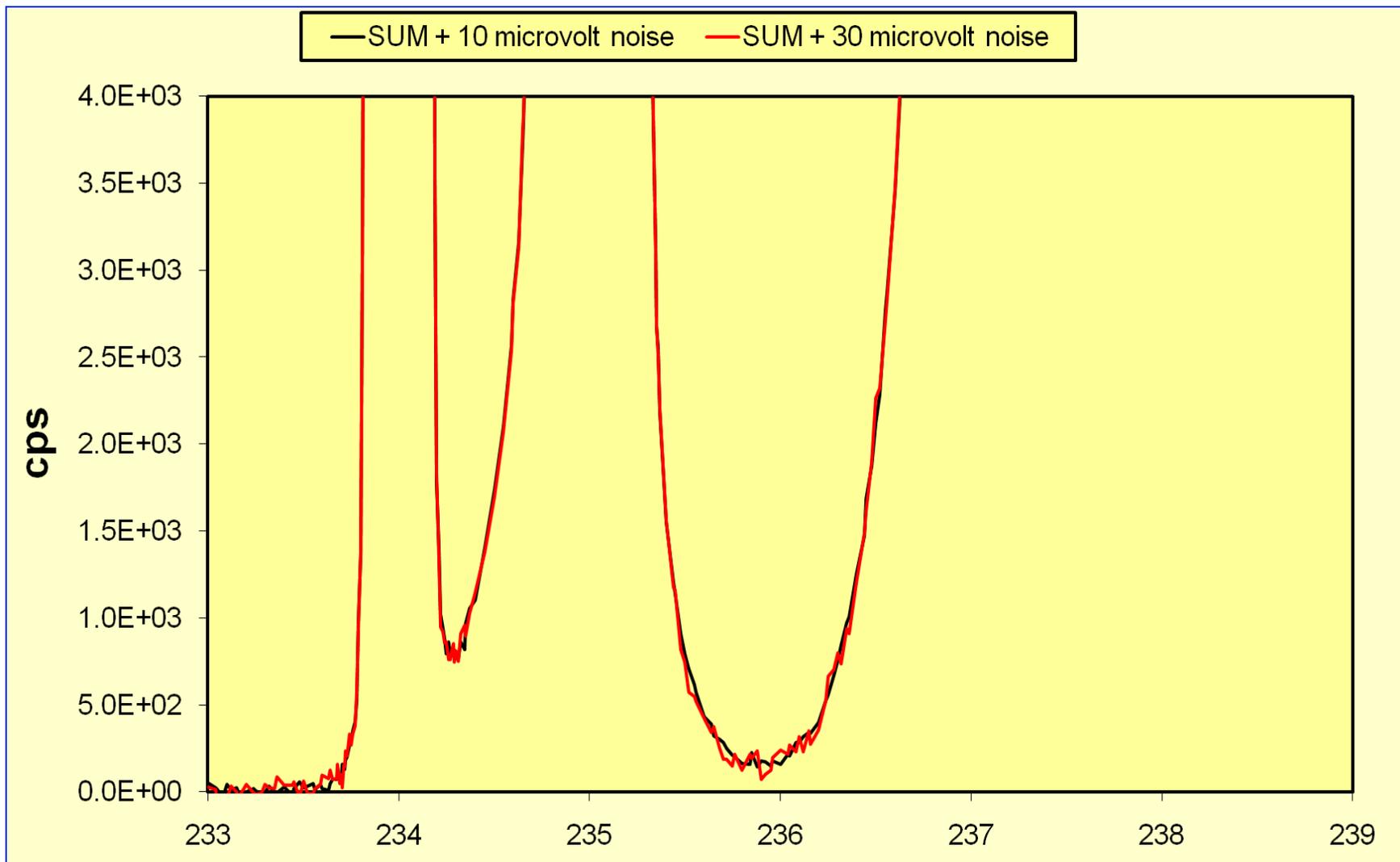




Abundance sensitivity at mass 237 w/r/t 238 is 76 ppm

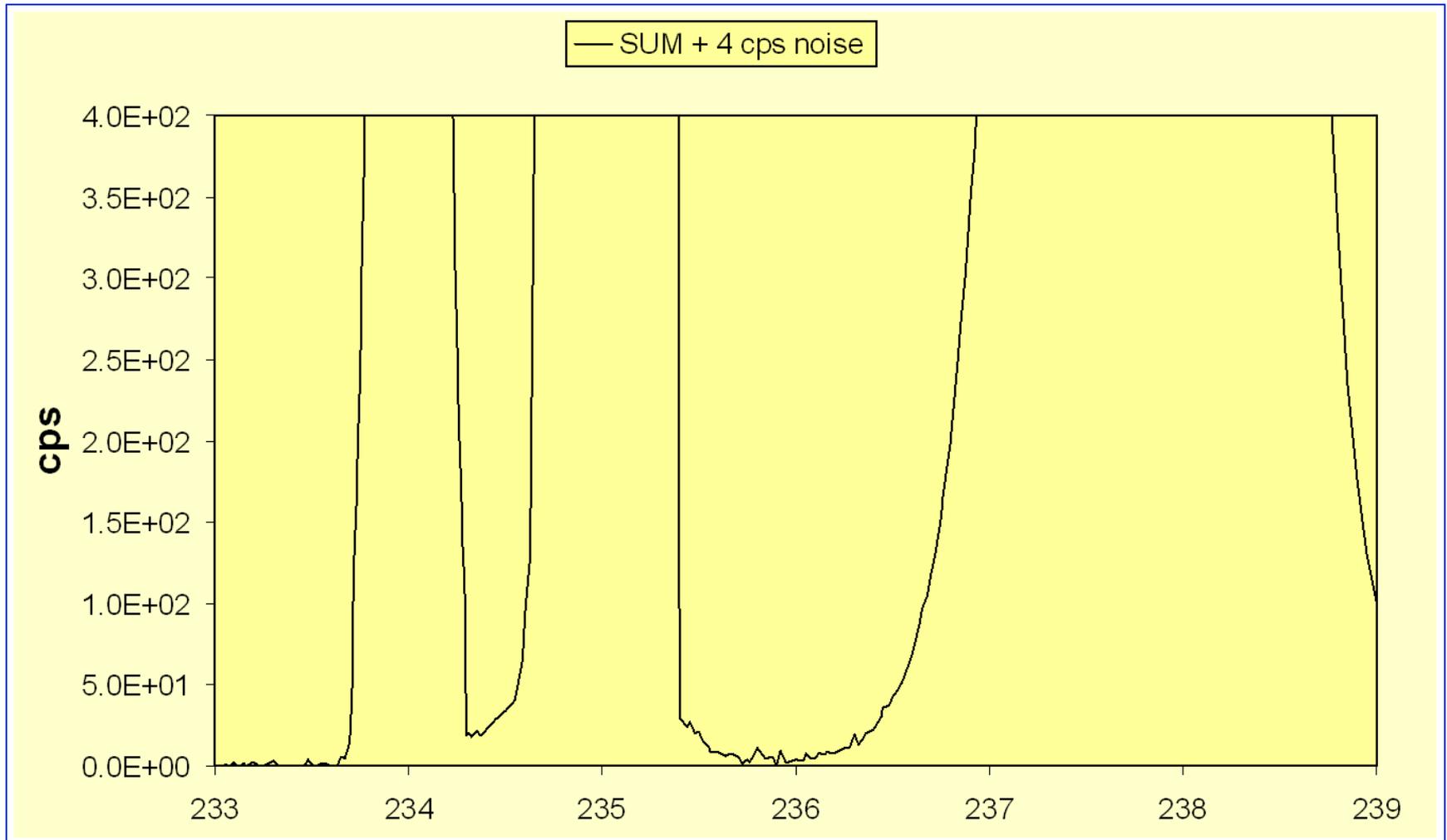


Abundance Sensitivity at mass 236 w/r/t 238 is 0.5 ppm

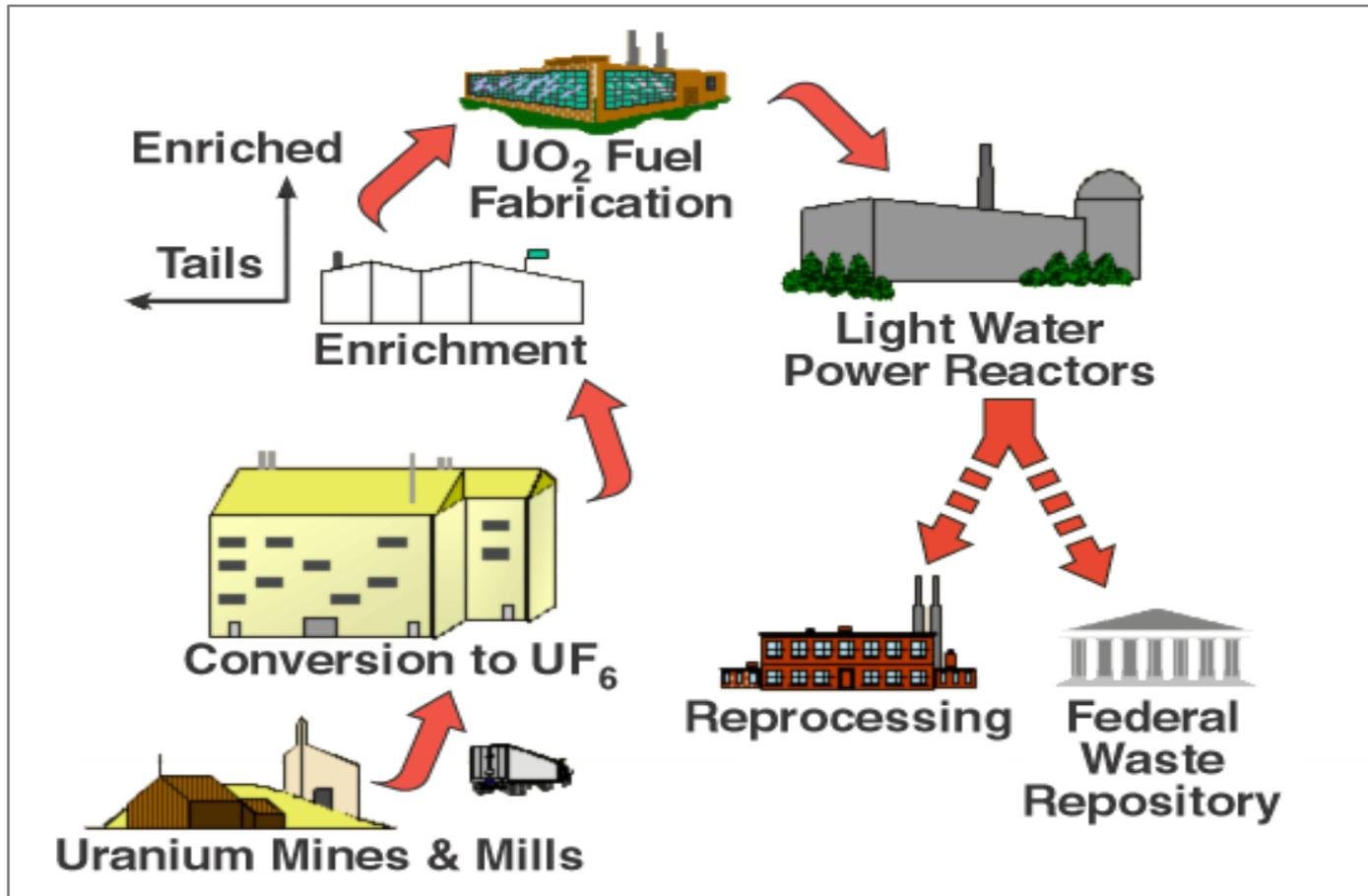


^{234}U and ^{236}U through energy filter

Abundance sensitivity at mass 236 w/r/t 238 is 10 ppb

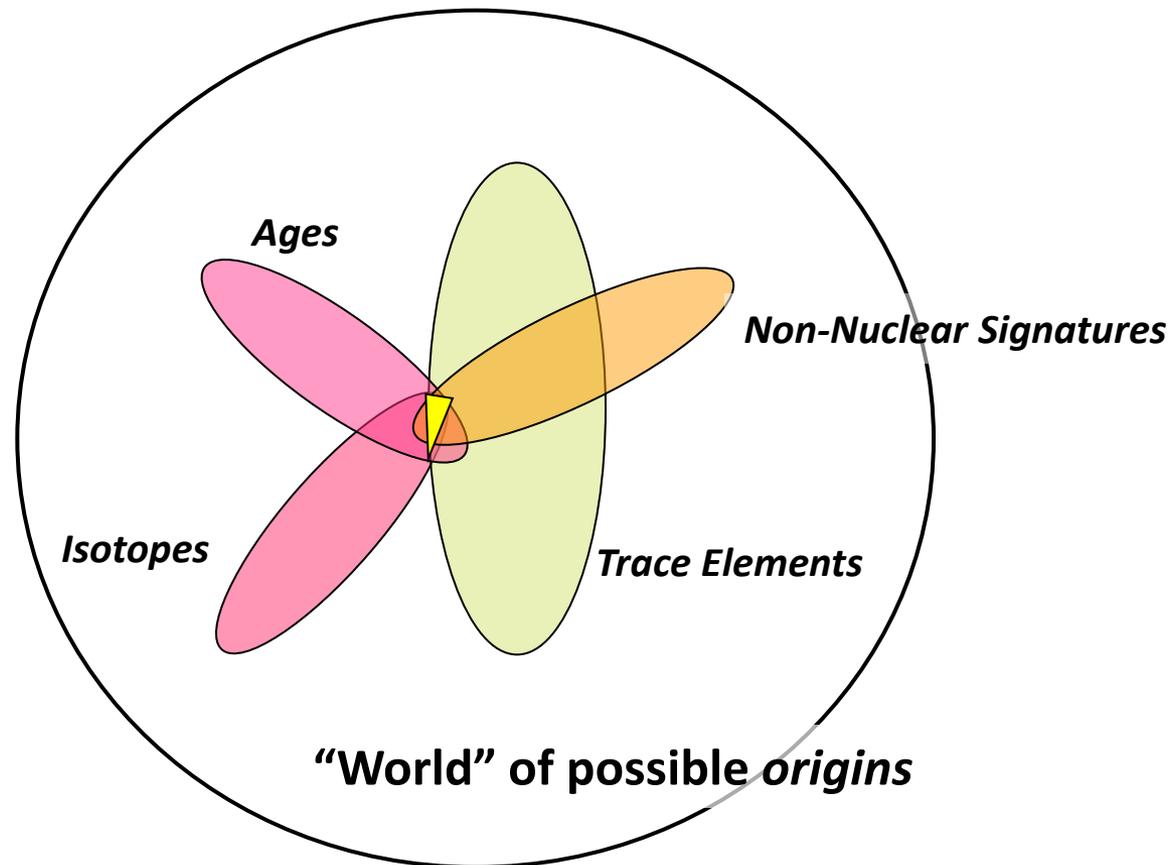


Signatures are created and erased throughout the life cycle of nuclear materials



Environmental sampling collects signatures across the complete life cycle of nuclear materials

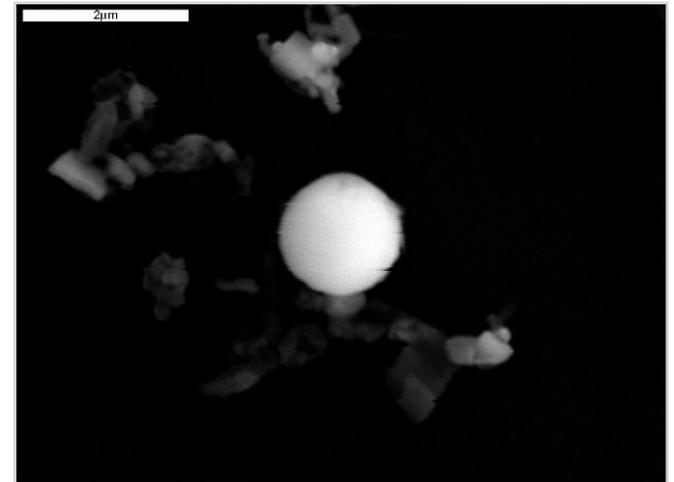
No single signature provides a “silver bullet”



The intersection of multiple signatures provides information on sample provenance and history

The technical basis for environmental sampling

- Nuclear processes emit trace amounts of material to the environment
- This material can settle on equipment and surfaces within buildings and can be transported outside to deposit on vegetation and soil or reach water systems
- Modern analytical techniques can detect and characterize these extremely low levels of nuclear material

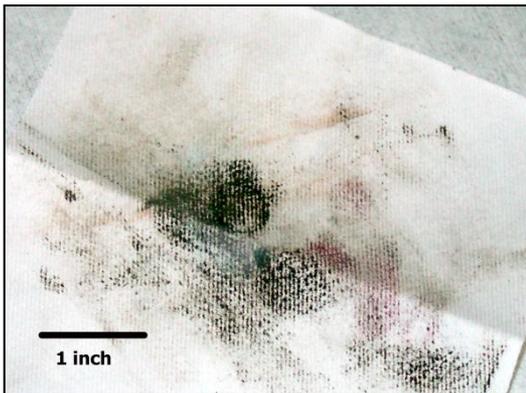


A one-micron-diameter uranium particle
(Photo: V. Stebelkov, Laboratory for Microparticle Analysis, Moscow, Russian Federation)

Source: IAEA STR-348, *Environmental Sampling for Safeguards*, September 2005

Environmental sampling

Photo: IAEA



- Extremely powerful technique for detecting **undeclared** nuclear material and activities
- *Ad hoc* use in early 1990s cases illustrated potential
- 93+2 field trials established feasibility as an IAEA tool
- IAEA has an “in-house” lab (*SAL*) and a network of analytical laboratories in Member States (*NWAL*)
- More than 5,000 samples collected and analyzed

Early examples of *ad hoc* IAEA use of environmental sampling

Photo: IAEA



Iraq



Photo: IAEA



CNN

DPRK



Program 93+2 field trials

- Swipe sampling was determined to be a viable, cost-effective technique
 - Use at declared sites authorized in 1995
 - Use at other locations authorized in 1997 for AP States
- Wide-area monitoring seen as useful but too expensive
 - AP provides for wide-area environmental sampling only after Board of Governors approves its use



Photo: IAEA

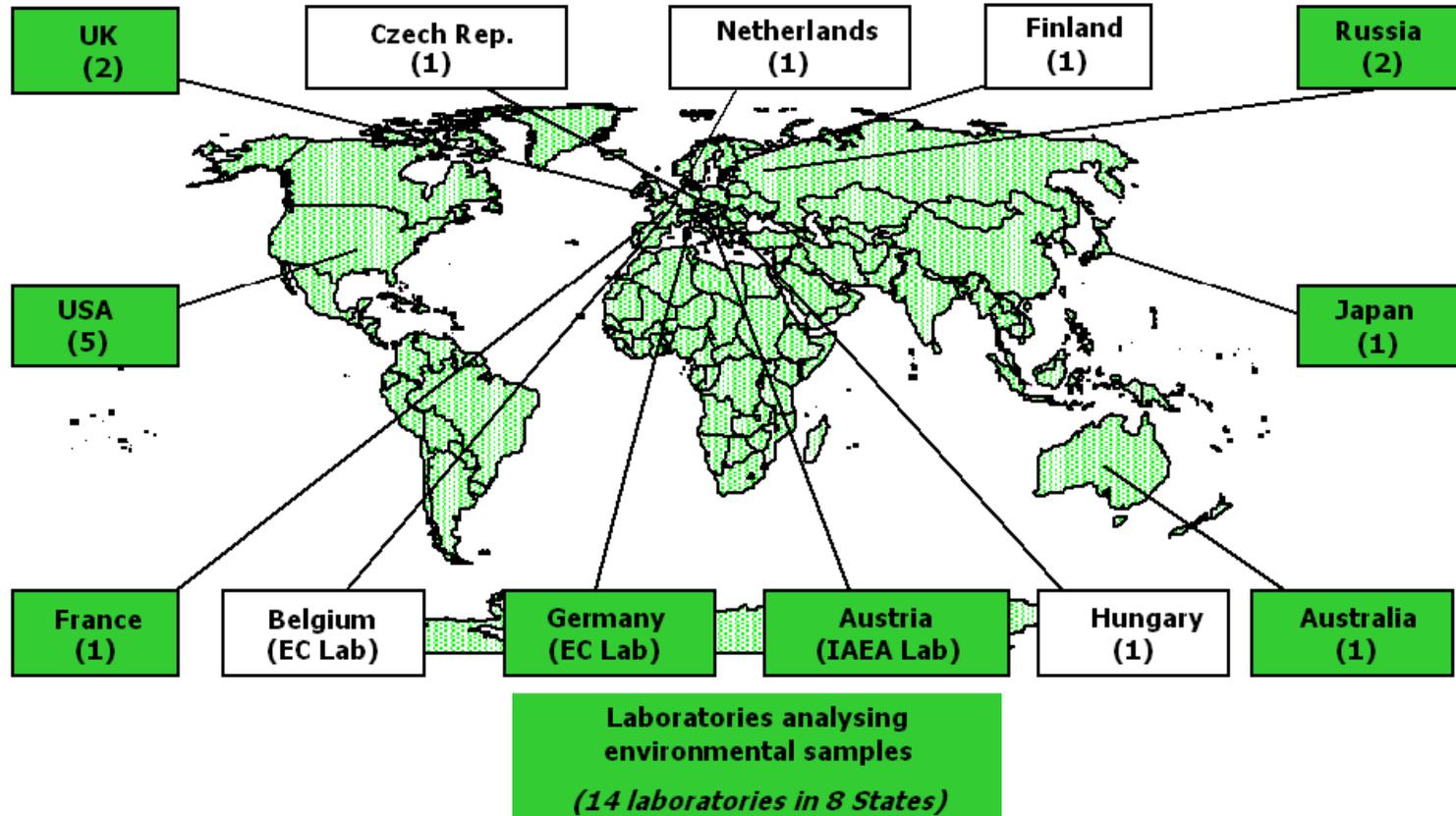


Photo: IAEA



IAEA Network of Analytical Laboratories (NWAL)

(Number of laboratories in the State)



(As of Fall 2006)



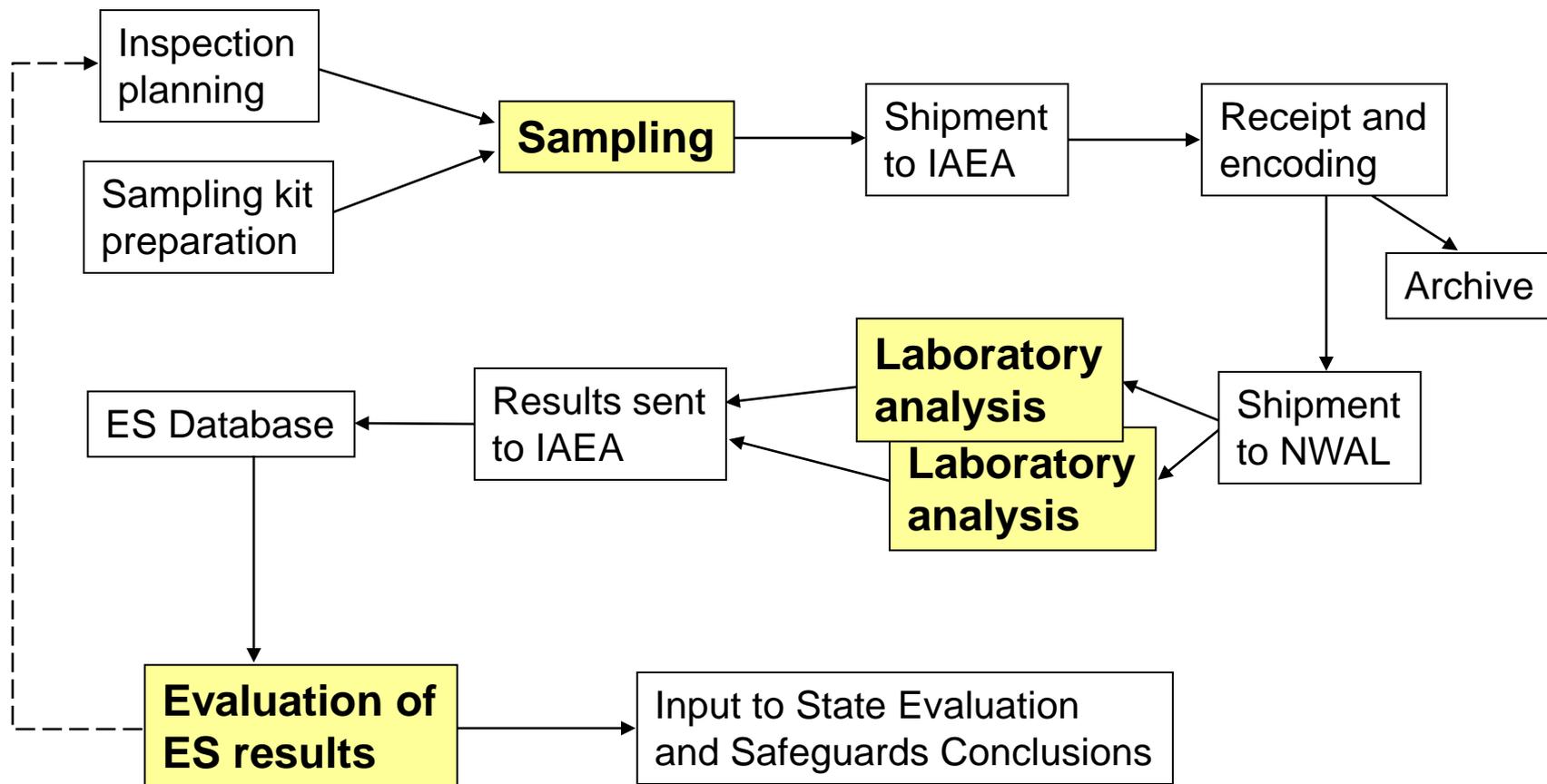
What is measured and what is inferred?

- Uranium isotope ratios that differ from natural composition indicate enrichment activity
- Minor isotope ratios can indicate additional detail about enrichment processes and feed materials
- Presence of fission products can indicate processing of spent fuel
- Plutonium isotope ratios ($^{240}\text{Pu}/^{239}\text{Pu}$) indicate fuel burn-up
- Radioactive parent-daughter ratios (e.g., $^{241}\text{Am}/^{241}\text{Pu}$) can serve as “chronometers” to indicate time since last chemical separation

Source: IAEA STR-348, *Environmental Sampling for Safeguards*, September 2005



Major steps in the IAEA's process



Sampling

- The most common method involves wiping surfaces with a specially prepared cloth
- Specific procedures are followed to avoid cross-contamination and ensure audit trail
- Other methods:
 - Vegetation
 - Soil
 - Water sampling



- 1 large outer bag (30×30 cm), with a CL identification number and security seal
- 6 cotton swipes (10×10 cm Texwipes[®]) bagged in a small mini-grip bag (15×15 cm)
- 6 small mini-grip bags (15×15 cm) to bag the swipes in individual bags
- 6 medium mini-grip bags (20×20 cm) for double-bagging the swipes
- Peel-off labels for samples that are stored in the facility or given to the Facility/State Authorities
- 2 pairs of latex or plastic clean-room gloves (medium size)
- 1 blank working paper *WP EMI* (see Annex 2)
- 1 pen



Photo: IAEA

Laboratory analysis

- Two main types of analysis
 - **Bulk** analysis looks at a whole sample
 - **Particle** analysis looks at individual microscopic particles (more sensitive, more expensive)
- Analytical instruments include
 - Radiation detectors
 - Mass spectrometers
 - Scanning electron microscope, electron microprobe
- Isotopic ratios, age, chemical form, morphology, all can provide clues

Sources:

--IAEA STR-348, *Environmental Sampling for Safeguards*, September 2005;

--*Safeguards Techniques and Equipment, 2003 Edition* (IAEA Nuclear Verification Series)

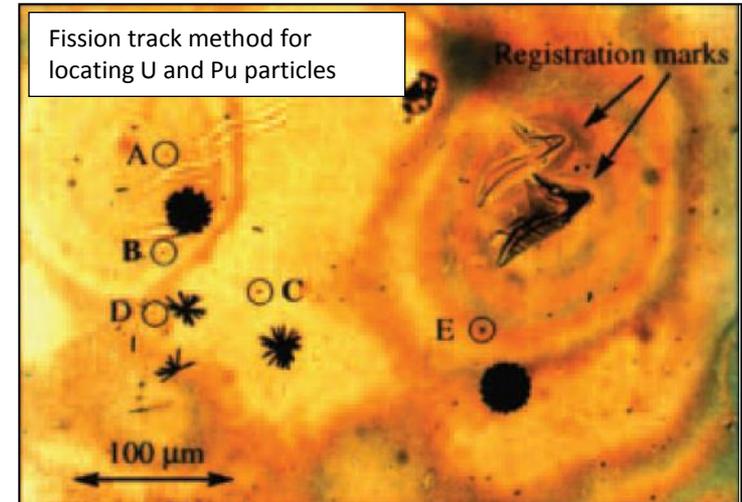
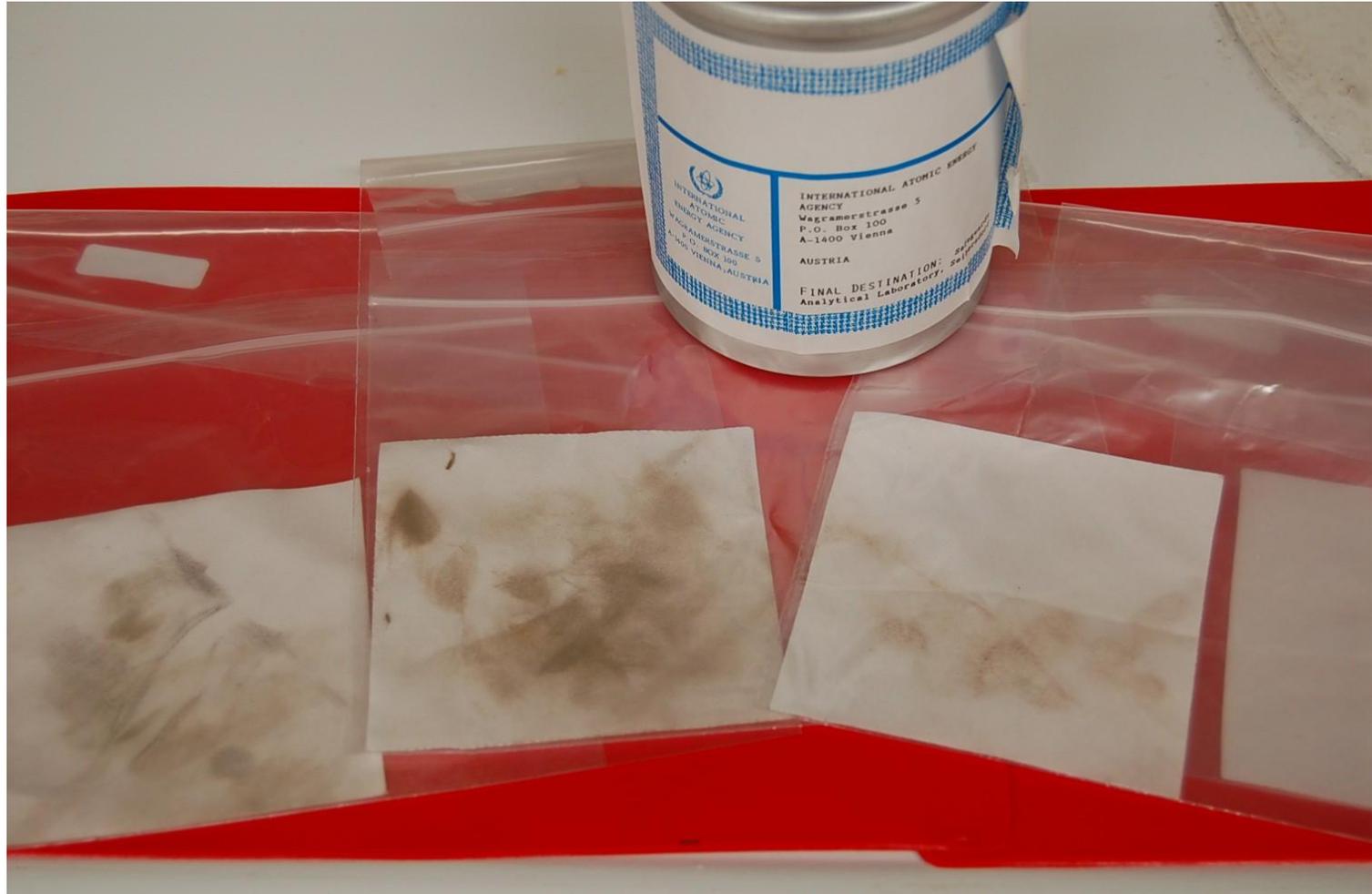


Photo: IAEA

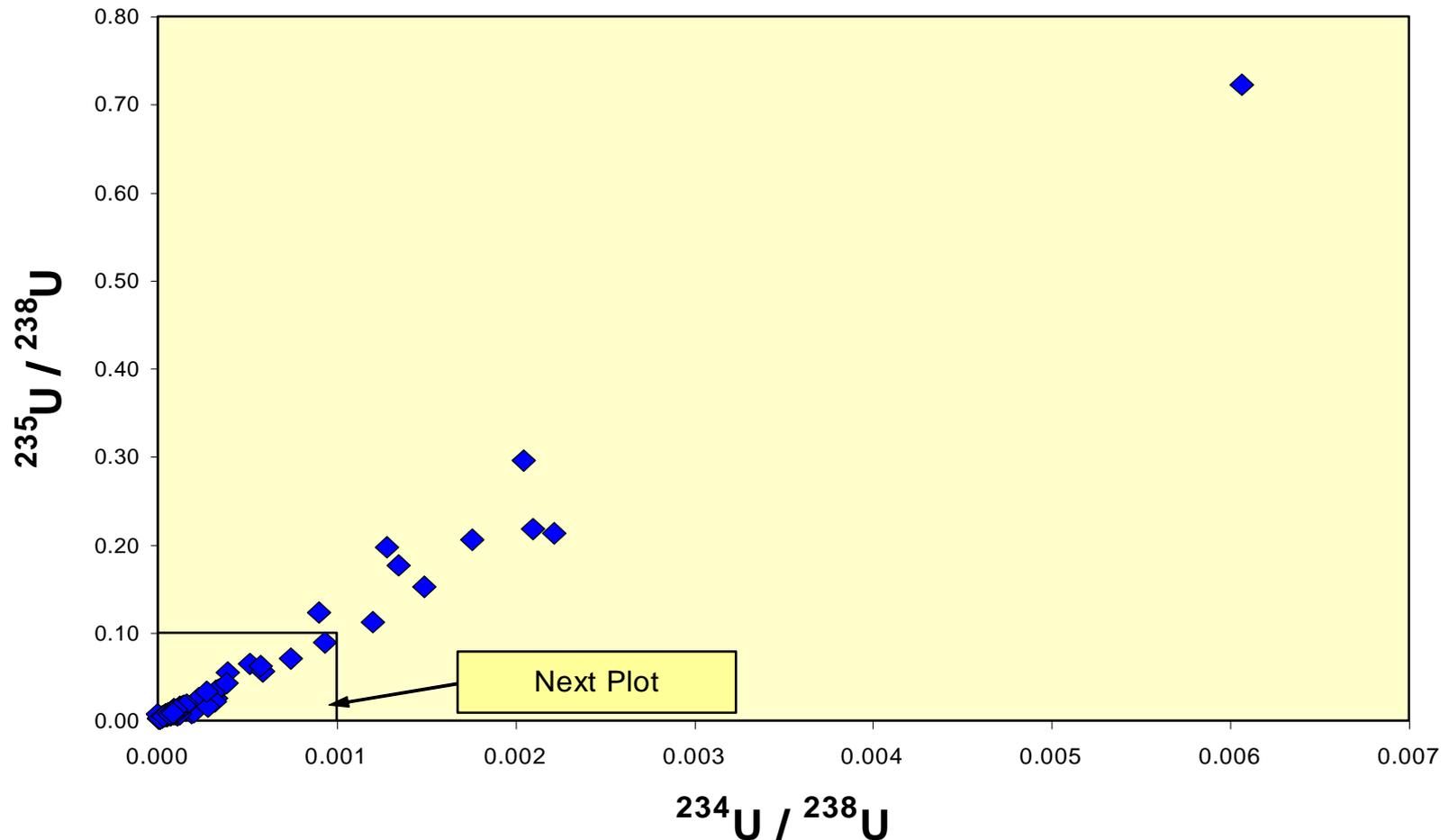


Photo: IAEA

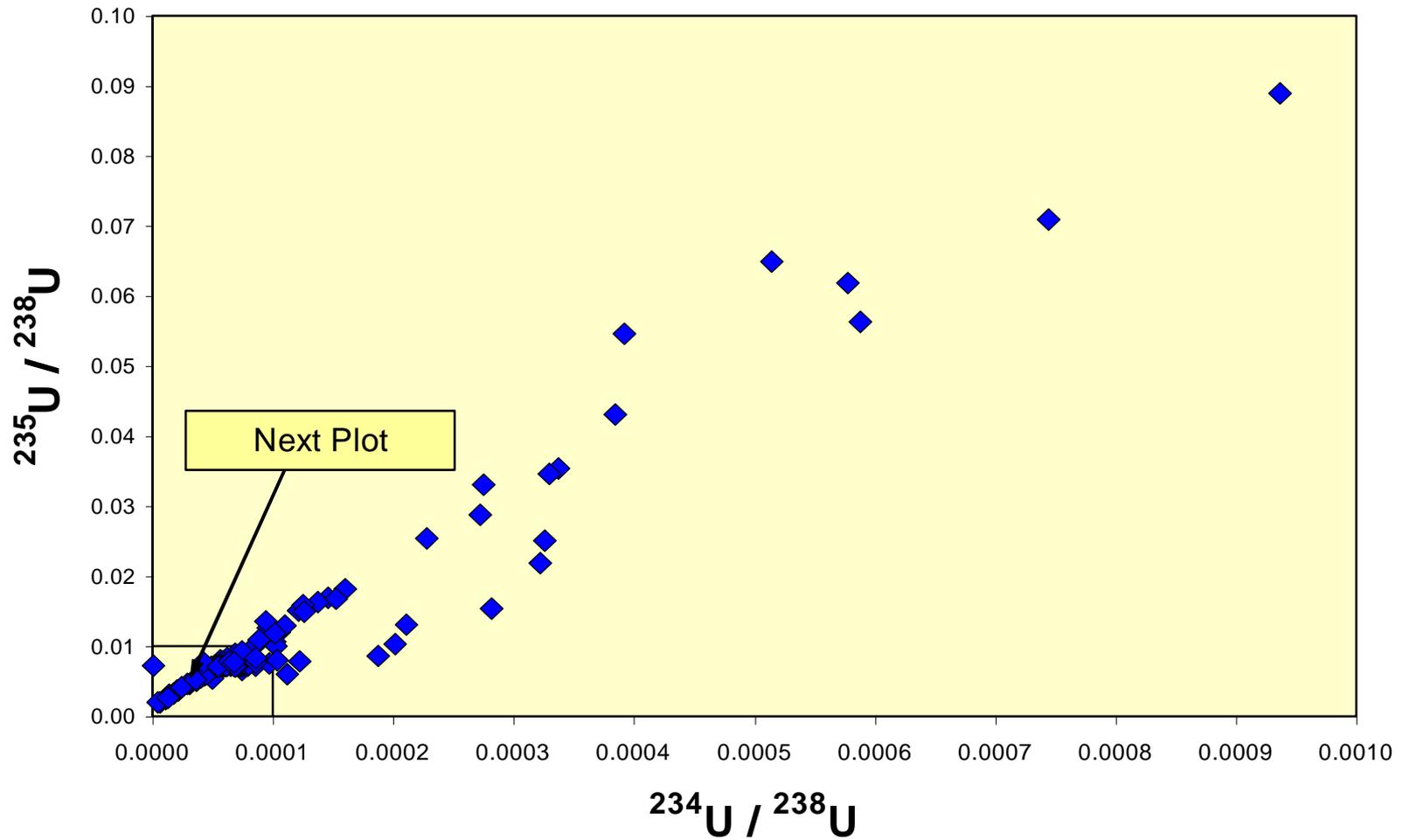
Bulk environmental samples for analysis



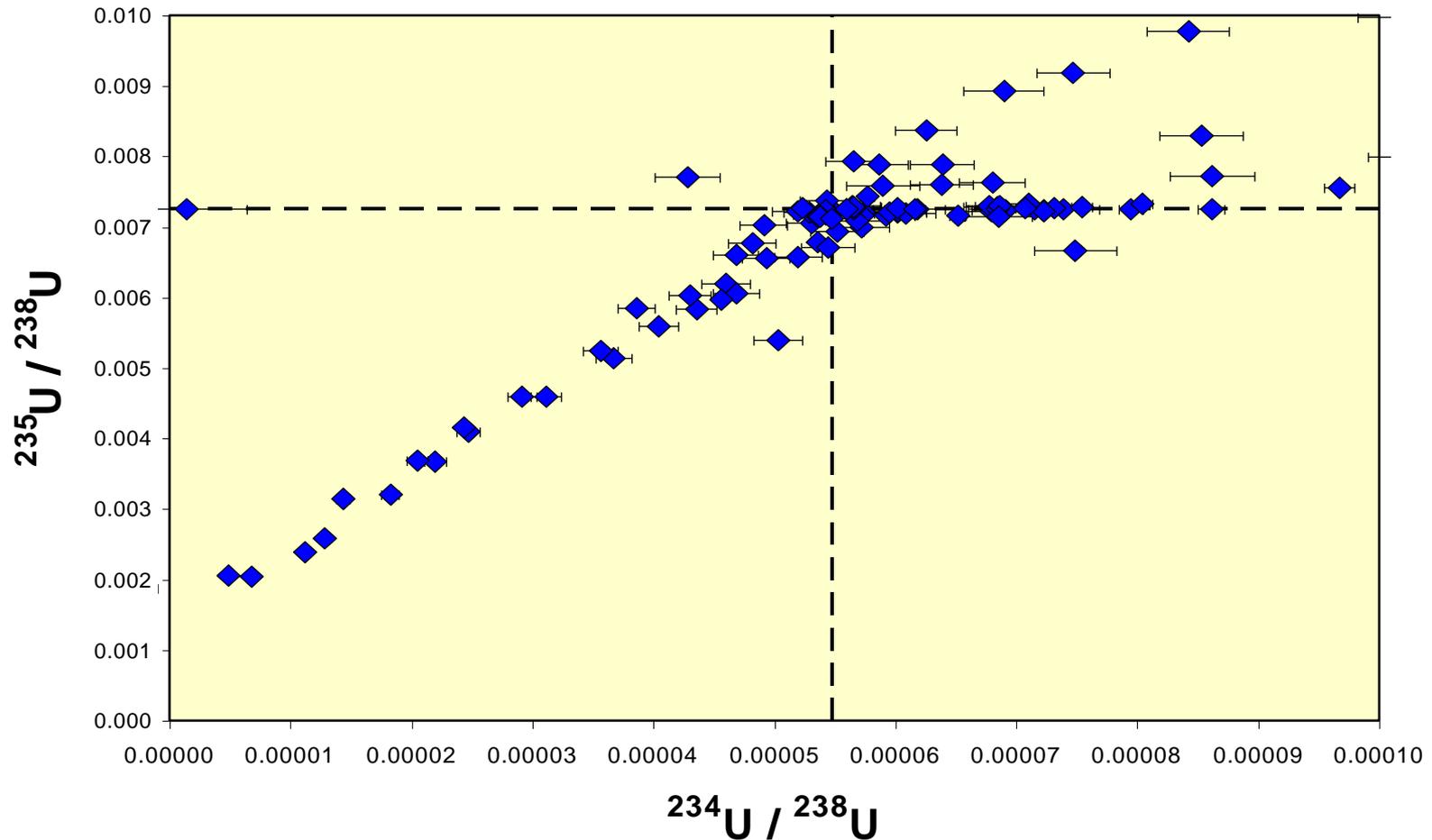
Environmental samples show correlated variations in uranium isotope ratios



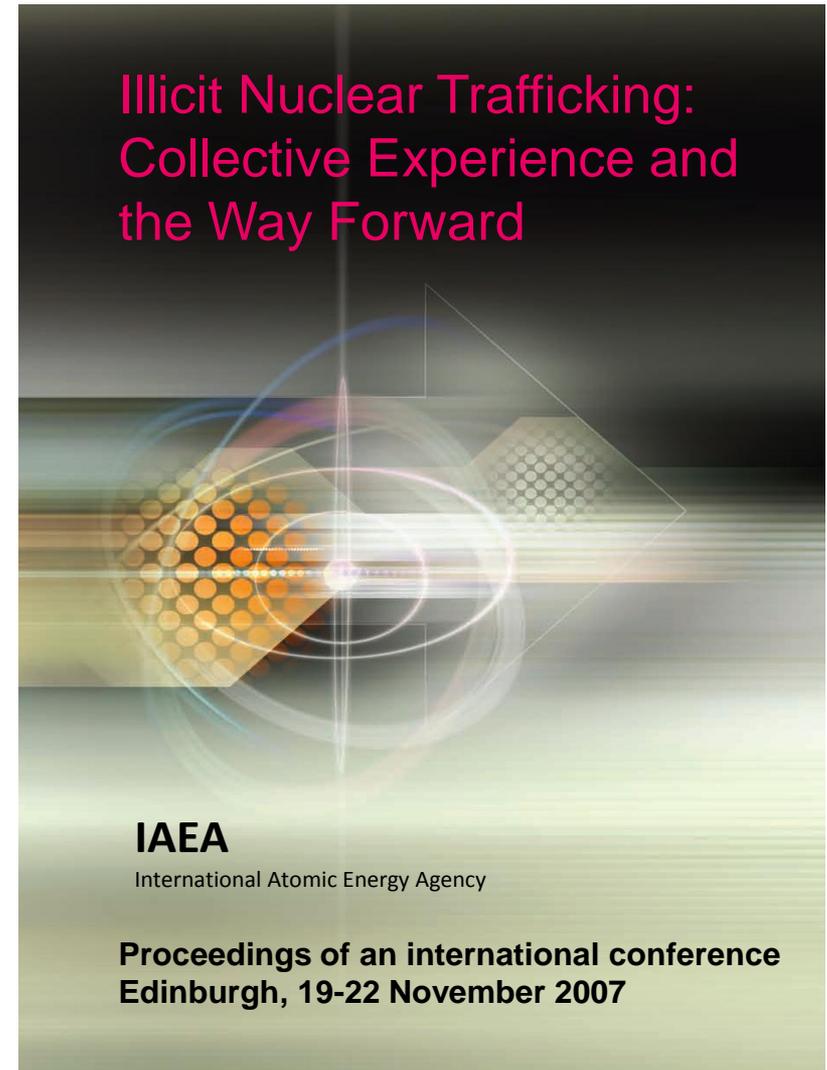
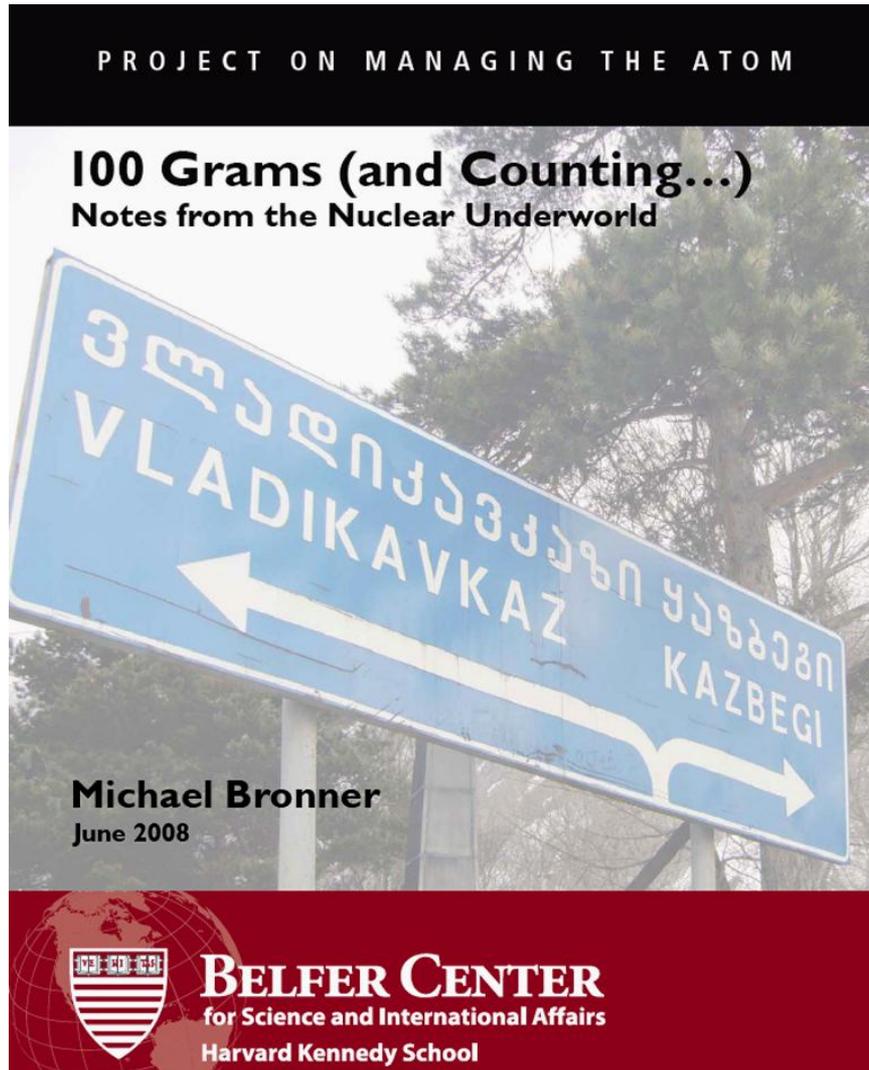
Compositions reflect processes and starting materials



Correlation between ^{234}U and ^{235}U persists in depleted uranium



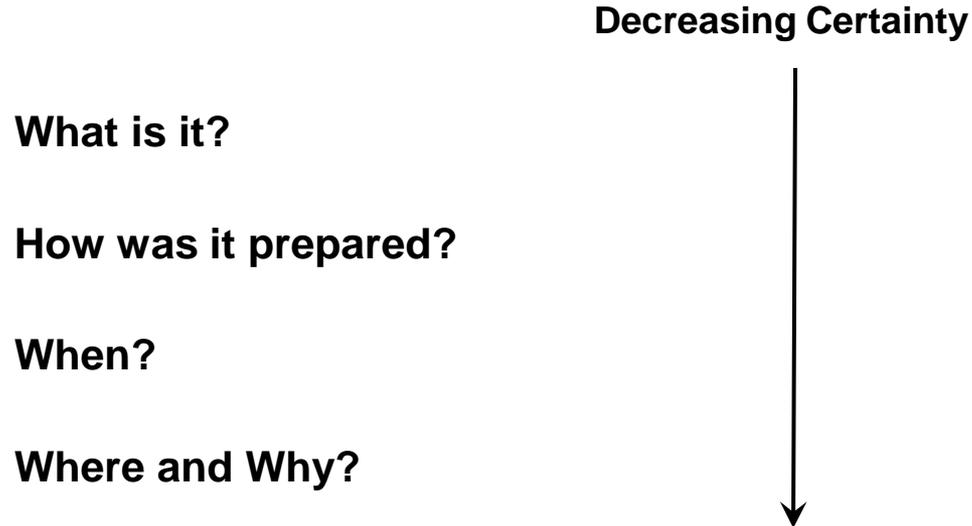
Threats & Risks



Nuclear Forensics

Characterization of nuclear materials seized by law enforcement

Physical – Chemical – Radiological and Isotopic



LLNL led a multi-lab investigation of HEU seized in Rousse, Bulgaria

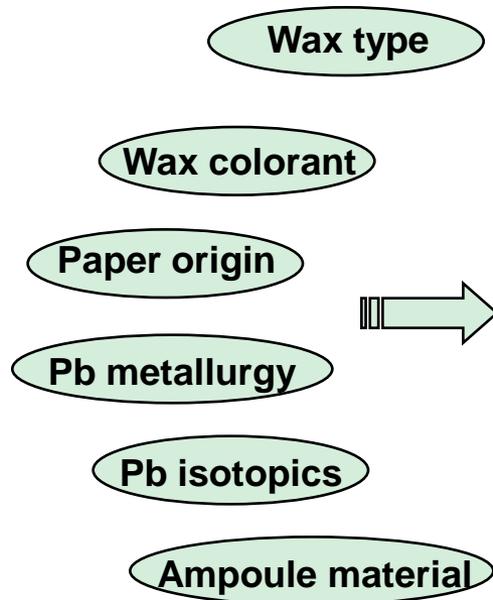


- Interdicted May 29, 1999 at a border crossing between Bulgaria & Romania
- Pb canister hidden in car trunk inside portable air compressor; Turkish national carrying a Cyrillic bill of lading
- U.S. State Dept. arranged for DOE to take possession in Feb. 2000
- LLNL led a 6-laboratory nuclear forensics working group to execute the investigation
- Borosilicate glass ampoule; a common container for archiving samples

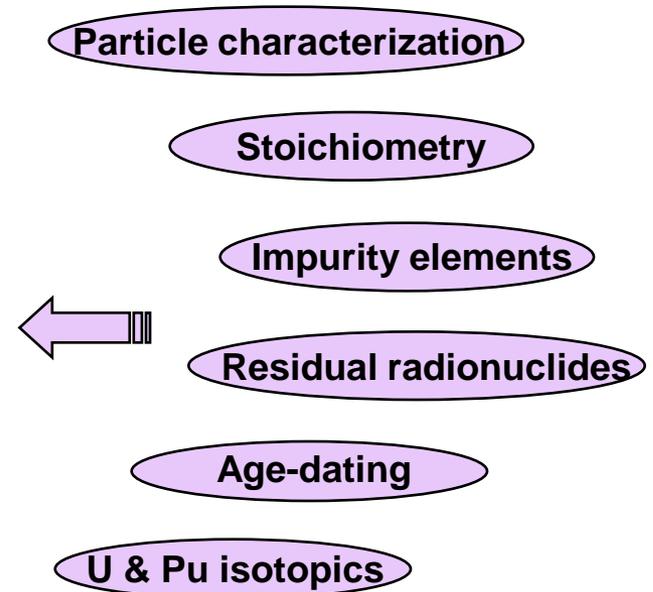


The model action plan calls for a broad scrutiny of nuclear and non-nuclear materials

Non-nuclear forensics



Nuclear material forensics



- **Highly-enriched uranium (73%, ~4 grams)**
- **Trace plutonium (2.8 parts per billion)**

Highly Enriched Uranium ~4 grams



- **U isotopes (atom %)**
 - 232 = 1.08×10^{-6}
 - 233 = 2.98×10^{-5}
 - 234 = 1.18
 - 235 = 72.7
 - 236 = 12.1
 - 238 = 14.0
- **Modeling indicates about 50% burnup of initial U-235**
- **Trace plutonium (2.8 ppb)**

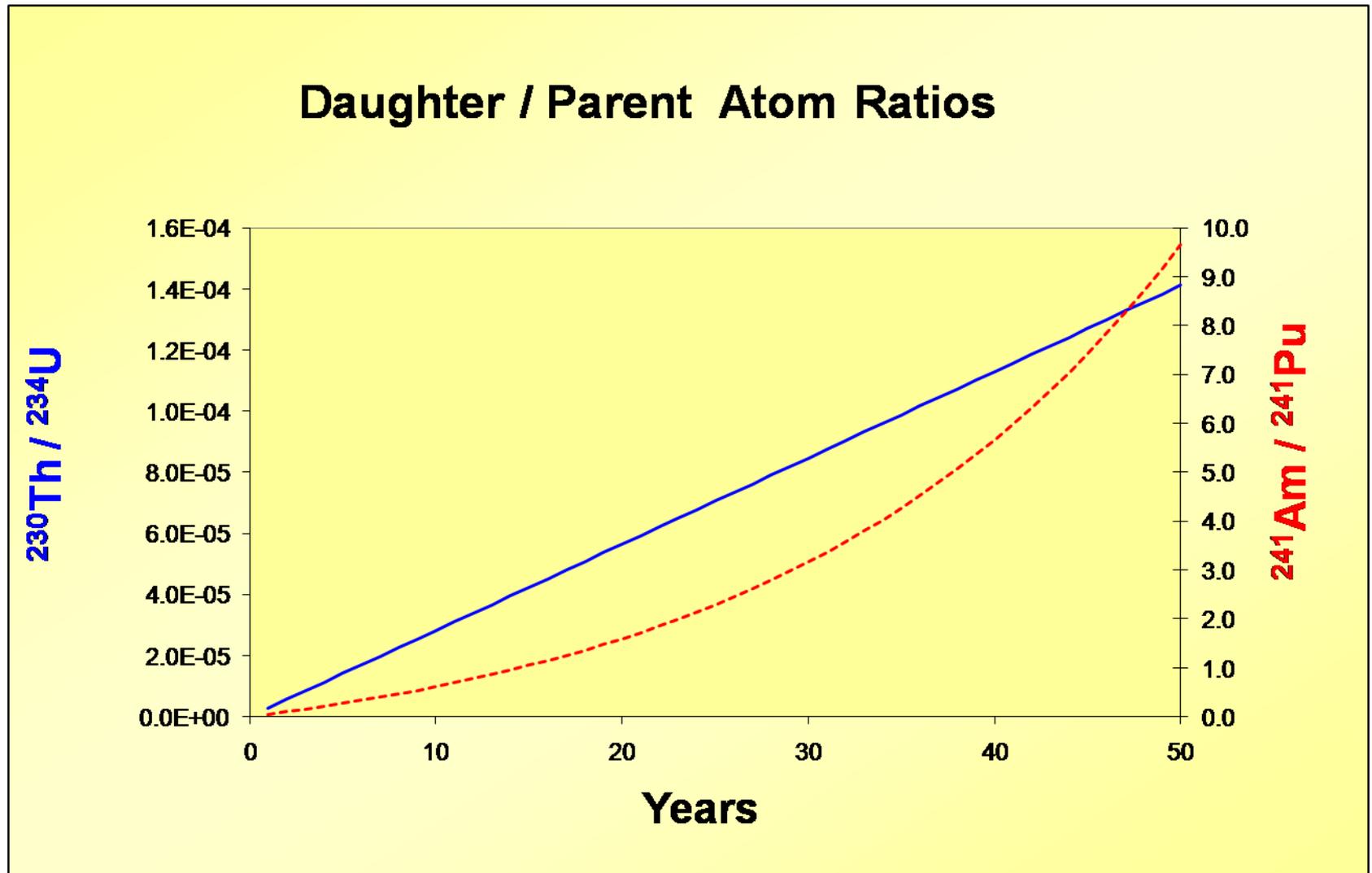
Science, v. 298, 1-Nov-02, p. 952

Non-nuclear forensics suggest East European packaging

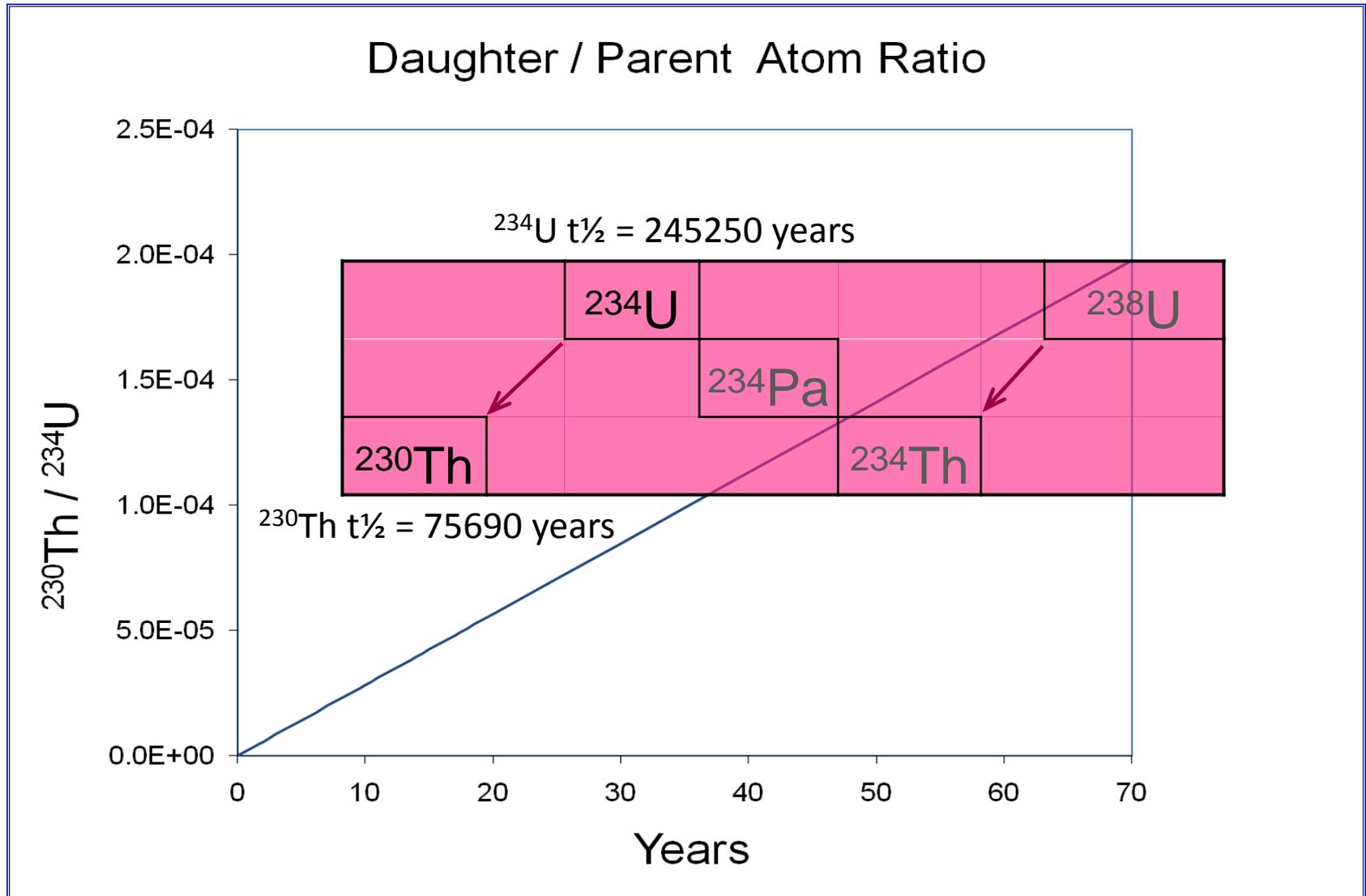


- Wax is an uncommon type of paraffin
- Yellow colorant is BaCrO_4 (carcinogenic)
 - Rare in western countries but prevalent in Brazil, China, India, and Eastern Europe
- Paper label and liner are wood pulp not found in North America or Western Europe
- Pb is hardened with 5 wt% Sb
- Pb isotope composition excludes U.S. ores; consistent with European & Asian mines

Some Nuclear Chronometers



^{230}Th - ^{234}U age-dating of uranium



Age Dating Uranium Standards

