

Forensic Radiochemistry

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There has long been a thriving black market in “nuclear materials”



Most of these items have been scams of one sort or another

Samples of red mercury, ^{187}Os , medical isotopes, depleted uranium and smoke-detector sources have all been offered for sale as materials essential for the production of nuclear weapons

The widespread use of radioactive isotopes in industry and medicine provides the opportunity for these materials to be diverted

Fortunately, even though these materials can be dangerous, they are not important from the perspective of non-proliferation

There is an emerging black market in weapons-usable nuclear materials



Most of the concern about a true nuclear black market has been focused on the former Soviet republics

October 1992	Seizure of 3 lb of highly-enriched uranium (HEU) near Moscow
Late '92-early '93	4.5 lb HEU seized in Lithuania
March 1994	6 lb HEU seized in St. Petersburg
August 1994	1 lb plutonium seized at the Munich airport
December 1994	6 lb HEU seized in Prague

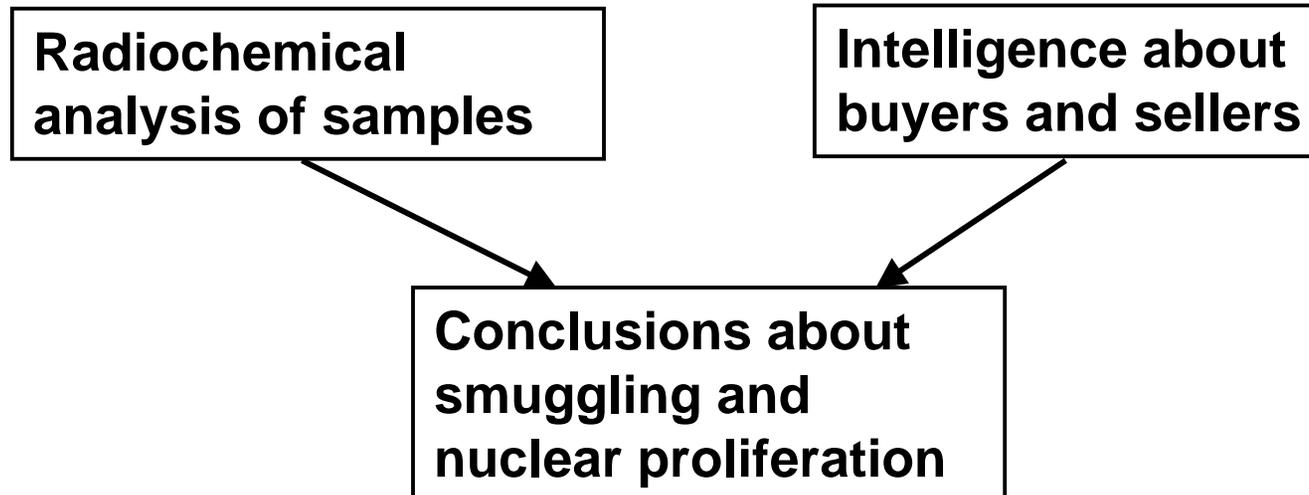
After 1994, seizures of bomb-grade heavy elements have continued, but on a much smaller scale

- - - *Until recently*

We are developing techniques to link (attribute) plutonium and uranium samples to their producer



The goal is to determine who produced the material and how they did it



The benefit is an enhanced understanding of the “leaks” that introduce these samples into the black market

Route attribution is a more formidable challenge



Identification of the origin of a particular sample defines where the sample stopped being “legitimate”, if it ever was

This is of most interest to policy makers

The way it got from its legitimate owner to the place that it was interdicted (the route) is also important

This is more important to law enforcement personnel

Since the route is usually through the non-nuclear world, the nuclear clues are of less interest

Conventional forensic science (fingerprints, fibers, hair, pollen, etc.) becomes critical

Determination of both the origin and the route require the intersection of radiochemistry with traditional forensic science

Nuclear forensic measurements on plutonium



Through the analysis of a small sample of plutonium (0.1g to 1g) we can determine:

Time (date) of last chemical purification

Time (date) of casting as metal (if appropriate)

Details about the reactor irradiation resulting in the material

- Type of reactor used (including neutron spectrum and flux)

- Enrichment of uranium starting material

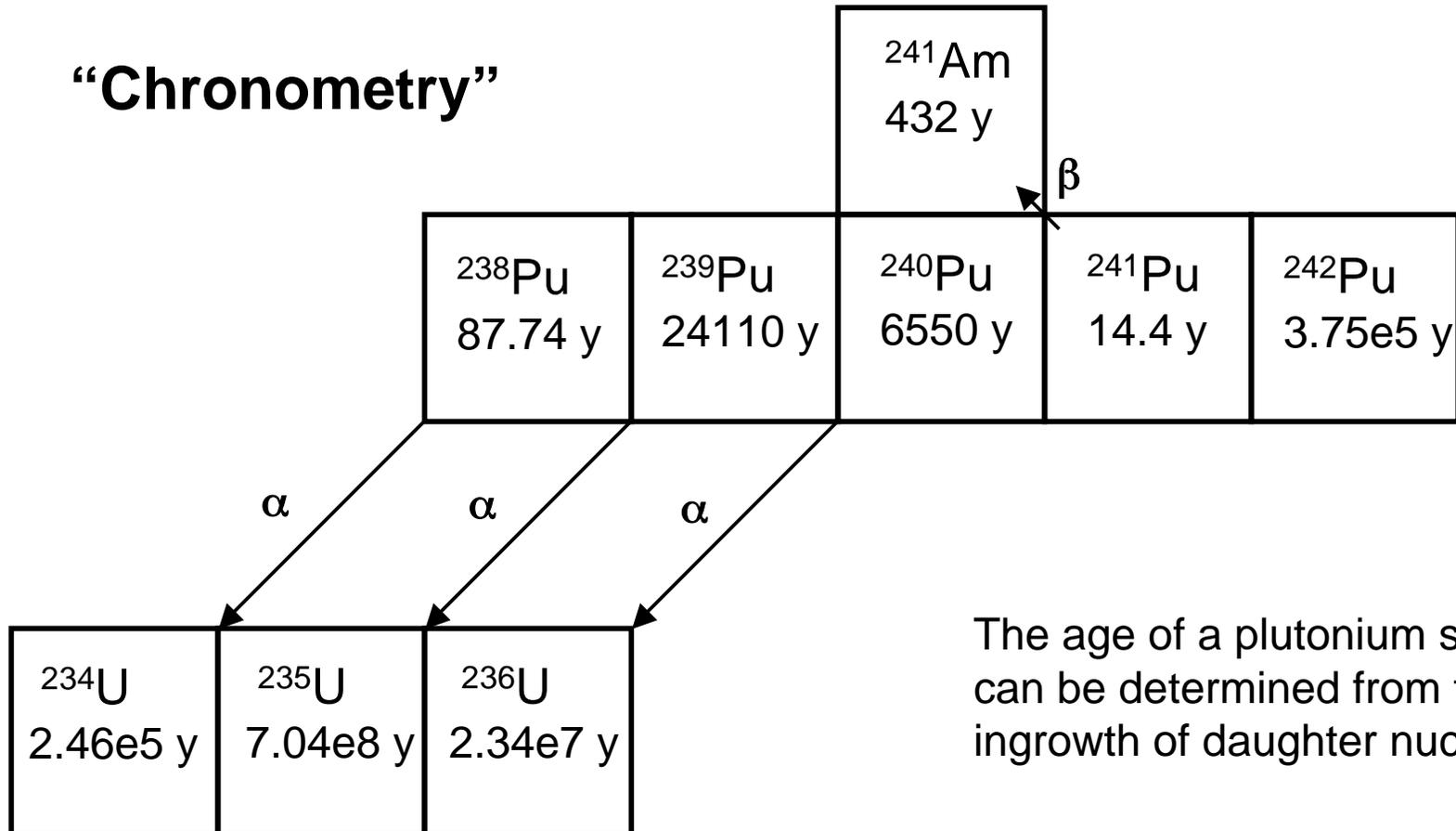
- Length of irradiation

The plutonium reprocessing technique

The age of the material and the dates of processing are very important for identifying the producer



“Chronometry”

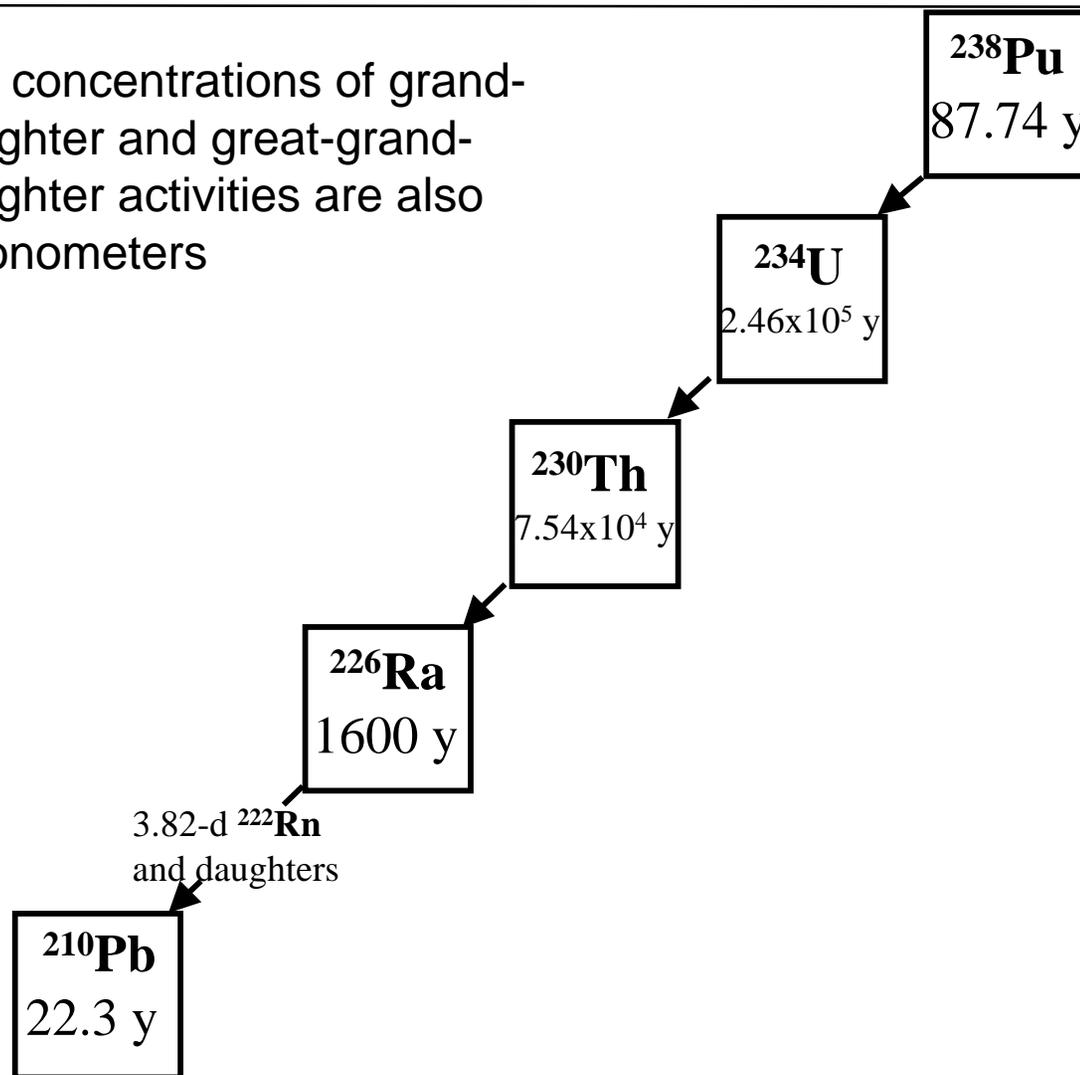


The age of a plutonium sample can be determined from the ingrowth of daughter nuclides

Measurements of high-order progeny make it almost impossible to “spooF” a chronometric determination



The concentrations of grand-daughter and great-grand-daughter activities are also chronometers



The time since the final metallurgical procedure is determined by the Kr and Xe present in the sample



From the mass-yield distribution for the spontaneous fission of ^{240}Pu , we can calculate the amount of fission-product isotopes that will grow into a sample of plutonium

We can perform chronometry with these fission products

1 gram of weapons-grade plutonium undergoes 1500 spontaneous fissions per minute, ~1% of which result in Kr

Metallurgy retains many of the contaminants, but Kr is purged

In one year, a 1-gram sample of w.g. plutonium will grow in

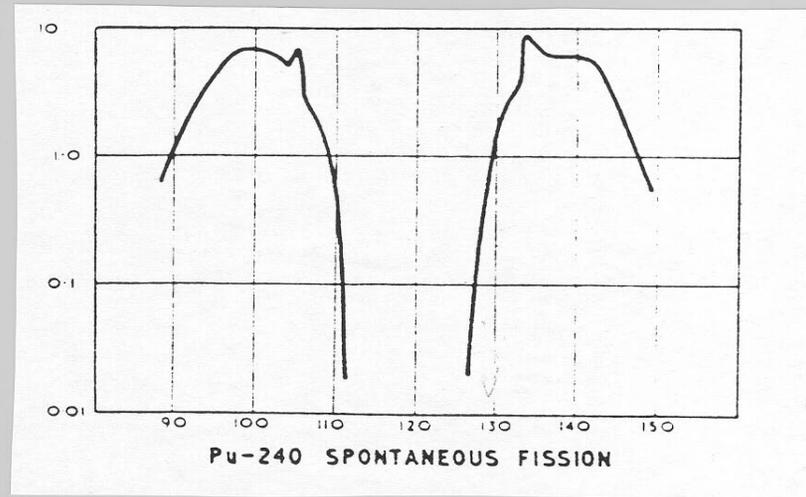
4.3×10^6 atoms of ^{84}Kr (stable)

1.2×10^6 atoms of ^{85}Kr ($t_{1/2} = 10.7$ y)

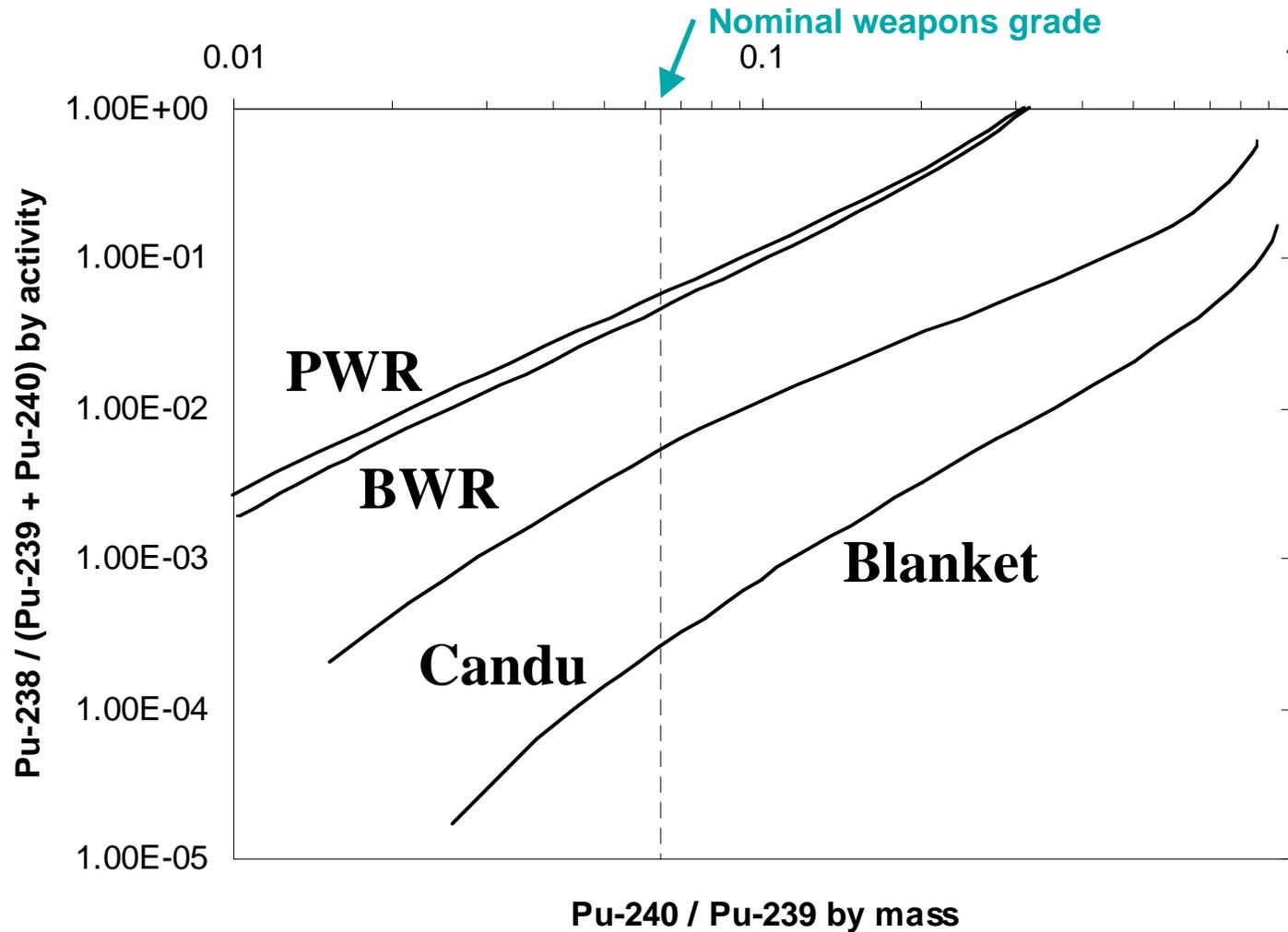
7.1×10^6 atoms of ^{86}Kr (stable)

Krypton is released on dissolution and can be analyzed by mass spectrometry

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Plutonium isotopic ratios are determined by the reactor type and the hardness of the neutron spectrum



Incomplete decontamination of Pu from fission products and actinides gives clues to the chemical methods used in reprocessing



For every gram of ^{239}Pu produced in a short (<1 year) reactor irradiation, also formed are:

<u>Nuclide</u>	<u>half life (yr)</u>	<u>amount (mg)</u>	<u>activity (dpm)</u>
^{90}Sr	29	36	1.1×10^{13}
^{93}Zr	1.5×10^6	42	2.4×10^8
^{99}Tc	2.1×10^5	43	1.6×10^9
^{106}Ru	1.02	3	1.0×10^{13}
^{129}I	1.6×10^7	7	2.7×10^6
^{137}Cs	30	59	1.1×10^{13}

After appropriate chemical separations are performed, we can measure these nuclides at the level of 1 dpm

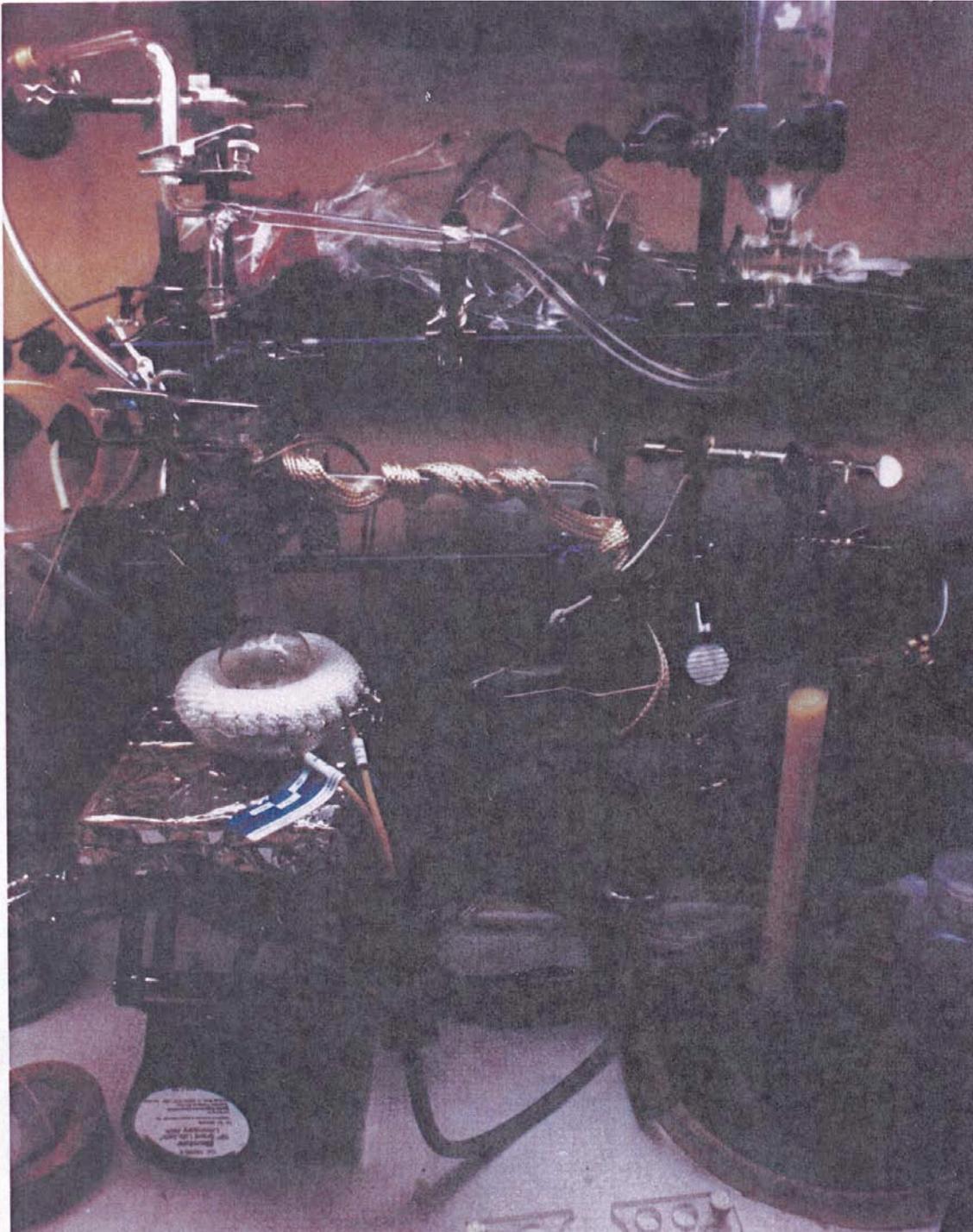
The various reprocessing chemistries have distinct contaminant signatures:

Redox (old Hanford)	^{93}Zr
Butex (old Windscale)	^{106}Ru
Purex (modern)	Am and low-level rare earths



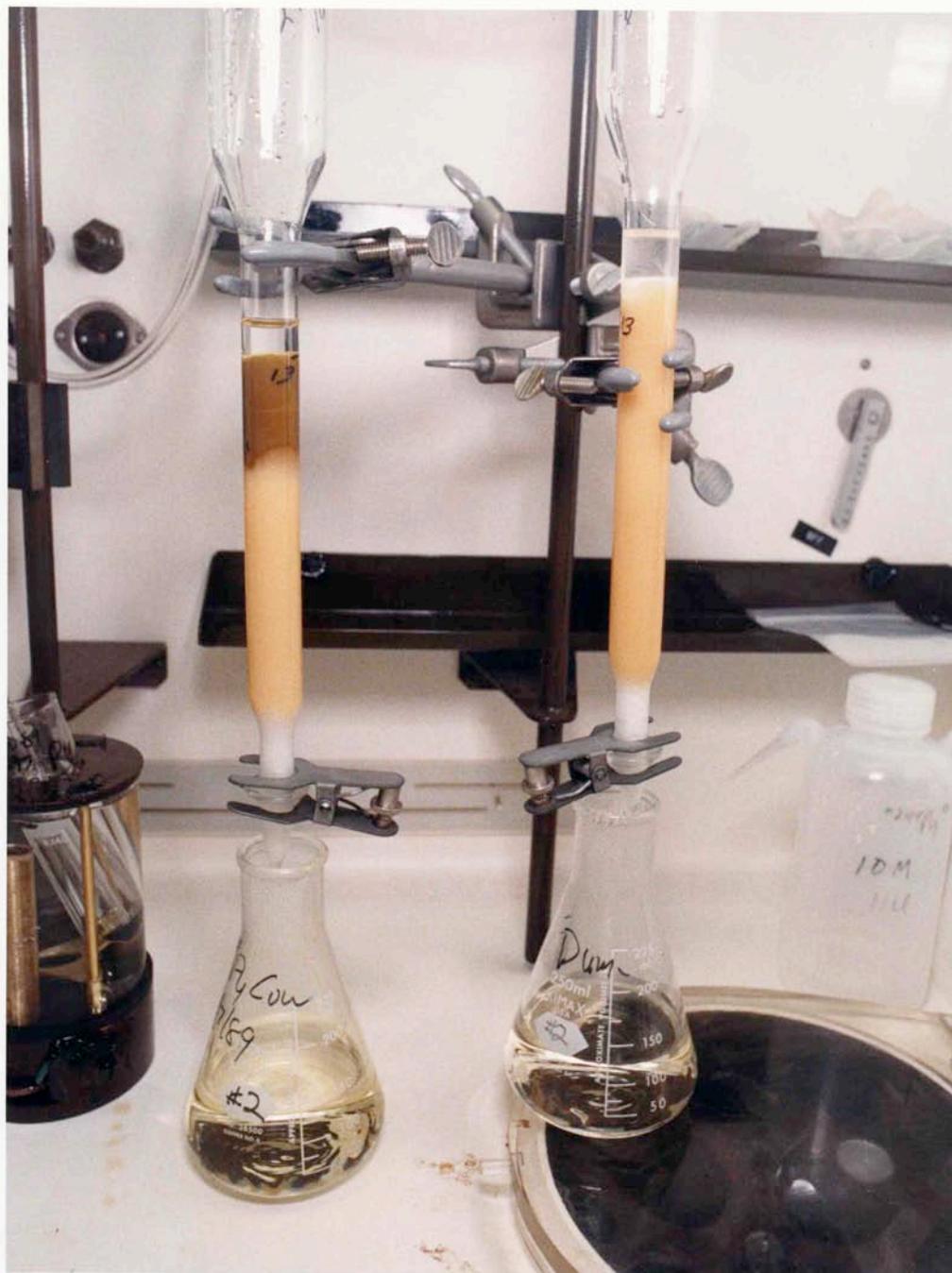
OK, so prove it

- Analyses are performed using a variety of radioanalytical techniques
- Non-destructive analysis using gamma-spec, X-ray fluorescence, neutron counting
- A portion of the sample is quantitatively dissolved, and aliquots are processed for various information
 - Gamma-spec and alpha-spec on unseparated material for grams/gram analysis
 - Chemical separations (based on ion exchange) to quantify minor sample constituents
 - Fractions for each element from Ra to Cm and the fission products are generated
 - Analysis via gamma-spec, alpha-spec, beta counting, ICP-MS, and TIMS
- Portions of the original sample are subjected to particle analysis, light-inorganic analysis, and organic analysis as necessary



**A lab-scale apparatus
for the analysis of 1
gram of plutonium,
mounted in a glove box**

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One gram of plutonium
on an anion-exchange
column (chloride)

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Results from our first blind test



Radionuclide content, sample BG522-3, 850 mg Pu metal, corrected to day 67, 1993

<u>Nuclide</u>	<u>Atoms</u>	<u>Nuclide</u>	<u>Atoms</u>
^{227}Ac	$(1.21 \pm 0.18) \times 10^8$	^{236}Pu	$(2.64 \pm 0.22) \times 10^{10}$
^{228}Th	$(5.02 \pm 0.68) \times 10^8$	^{238}Pu	$(3.09 \pm 0.05) \times 10^{17}$
^{229}Th	$(3.51 \pm 2.12) \times 10^8$	^{239}Pu	$(2.01 \pm 0.03) \times 10^{21}$
^{230}Th	$(3.38 \pm 0.51) \times 10^{11}$	^{240}Pu	$(1.28 \pm 0.02) \times 10^{20}$
^{232}Th	$(2.7 \pm 2.5) \times 10^{15}$	^{241}Pu	$(4.97 \pm 0.07) \times 10^{18}$
^{231}Pa	$(3.80 \pm 0.35) \times 10^{13}$	^{242}Pu	$(1.13 \pm 0.02) \times 10^{18}$
^{232}U	$(3.96 \pm 0.41) \times 10^{10}$	^{244}Pu	$\leq 9 \times 10^{15}$
^{233}U	$(1.49 \pm 0.07) \times 10^{13}$	^{241}Am	$(1.09 \pm 0.02) \times 10^{18}$
^{234}U	$(9.16 \pm 0.37) \times 10^{15}$	$^{242\text{m}}\text{Am}$	$\leq 1 \times 10^8$
^{235}U	$(2.22 \pm 0.09) \times 10^{17}$	^{243}Am	$(2.54 \pm 0.42) \times 10^{13}$
^{236}U	$(4.99 \pm 0.20) \times 10^{16}$	^{242}Cm	$(2.10 \pm 0.27) \times 10^5$
^{238}U	$(4.64 \pm 0.20) \times 10^{16}$	^{244}Cm	$(3.71 \pm 0.08) \times 10^{10}$
^{237}Np	$(5.75 \pm 0.39) \times 10^{15}$		

No Zr, Ru, I or Cs isotopes observed in excess of spontaneous fission
Kr isotopes lost to an air leak

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The analytical data is almost always more easily interpreted when expressed as chronometers



Time of chemical separation, sample BG522-3, relative to day 67, 1993

<u>Nuclide pair</u>	<u>Time of separation, years</u>
$^{241}\text{Am}/^{241}\text{Pu}$	(4.12 ± 0.09)
$^{237}\text{Np}/^{241}\text{Am}$	(6.22 ± 0.42)
$^{234}\text{U}/^{238}\text{Pu}$	(3.70 ± 0.16)
$^{235}\text{U}/^{239}\text{Pu}$	(3.85 ± 0.17)
$^{236}\text{U}/^{240}\text{Pu}$	(3.69 ± 0.16)
$^{238}\text{U}/^{242}\text{Pu}$	$\gg 1000$
$^{228}\text{Th}/^{232}\text{U}$	(3.30 ± 0.75)
$^{230}\text{Th}/^{234}\text{U}$	26

Data are consistent with a final separation time of (3.736 ± 0.093) years before the analysis time, or **June 12, 1989 \pm 34 days**

At separation, small amounts of Am and Np, and relatively large amounts of Th were left in the sample – this is characteristic of the Purex process

The two Th chronometers require two separation times – neither separation was very effective at removing Th

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The history of plutonium sample BG522-2



The material was produced from near-natural uranium fuel in a graphite-moderated reactor

From the decay of the $^{242}\text{Cm}/^{244}\text{Cm}$ ratio, the reactor irradiation ended in 1983 (± 1 year)

Chemical purification took place at two distinct times (Th, Am, U):

First separation was shortly after reactor discharge

Second separation was in June, 1989

The reprocessing chemistry was based on the Purex process (extraction of nitrates into TBP in kerosene)

When we checked the answers, we found that we were almost completely correct

Nuclear forensic measurements on Oralloy (Highly Enriched Uranium, or HEU)



The analysis of a 1-gram sample of Oralloy (or a somewhat larger sample of other mixtures of uranium isotopes) can result in the determination of:

Time (date) of last chemical separation

Reactor irradiation of feed materials

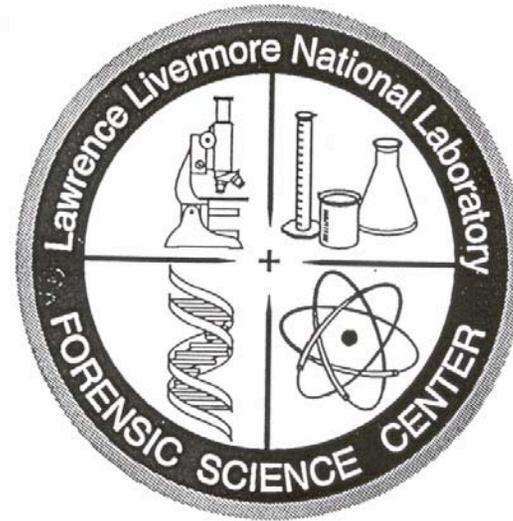
Presence of other heavy elements in the plant

Chemical steps used in purification or casting

An application of nuclear forensics in a field study



UCRL-ID-118814



Project PUBLIC: Counter-Forensic Investigation of U. S. Gaseous Diffusion Plants (U)

The LLNL Forensic Science Team*
Forensic Science Center, L-371
Lawrence Livermore National Laboratory
Livermore, CA 94550

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The “counter-forensic investigation” of the Portsmouth and Paducah enrichment plants took place in July, 1994



Since the plants were no longer enriching uranium for the purpose of weapon production, the IAEA argued that they should be allowed to inspect the plants

Could the forensic analysis of environmental debris from the sites be used to reverse-engineer the gaseous-diffusion barrier?

Details of construction of the barrier are closely held classified information

We collected approximately 20 samples at each site, and returned them to Livermore

We not only reverse engineered the barrier, we extracted information about the weapons complex in the 1960s and 1970s

To the best of our knowledge, the IAEA has not been allowed to visit the buildings we sampled

Some samples were collected magnetically



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Other samples were collected more conventionally



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The weapons complex, from Paducah floor sweepings



The Gaseous Diffusion Plant feed stock was previously irradiated for the production of plutonium

The production reactor was graphite-moderated, near-natural U fuel
Plutonium was weapons grade

Recovery of Pu and purification of U through the PUREX process

UF_6 was produced through the action of F_2 on UF_4

Cascade losses of uranium were about 1%

The cascade was counter-current, not simple

Site contamination was through mechanical dispersion rather than gas release

Enrichment took place as early as the mid 1950s



Real world sample #0
Drug Enforcement Agency

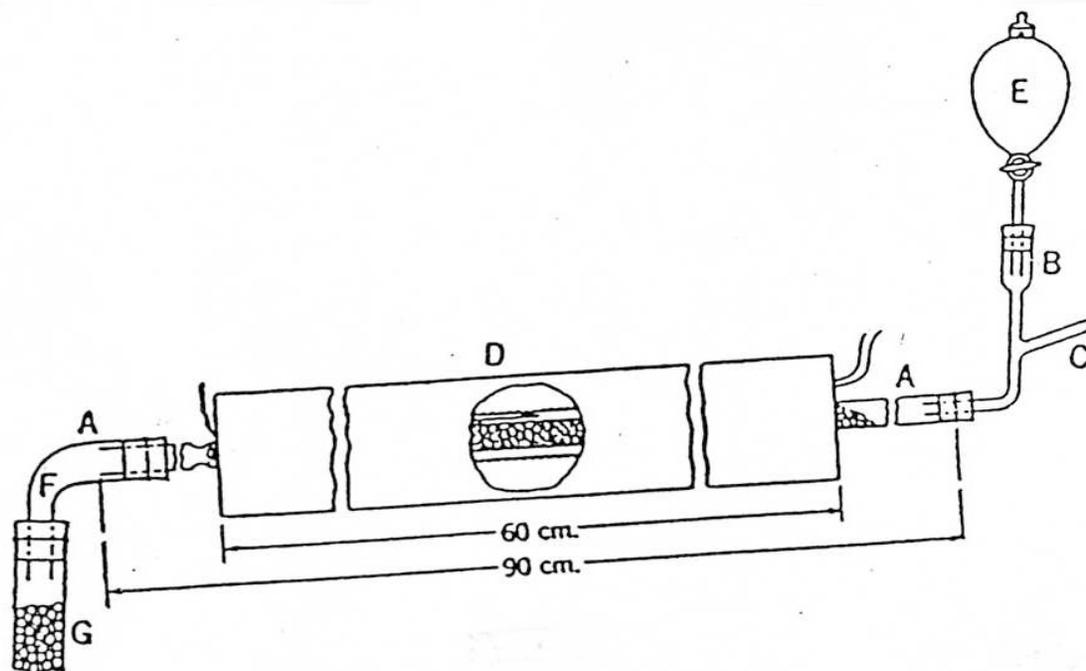
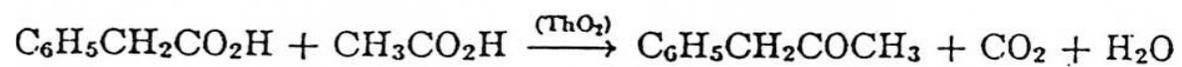


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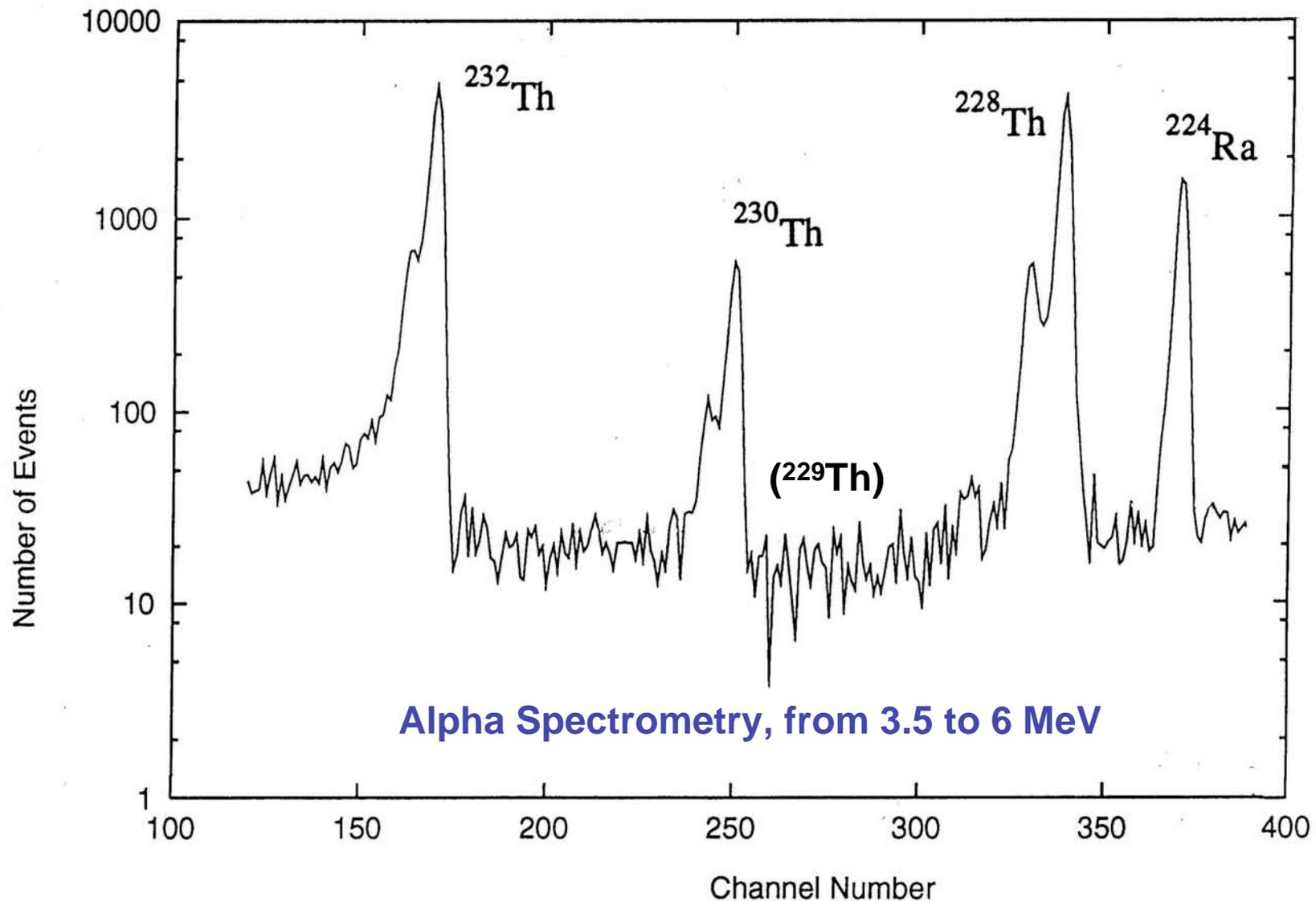
Methyl benzyl ketone

(2-Propanone, 1-phenyl-)

(A) (From Phenylacetic and Acetic Acids)



Most of the forensic information in a Thorium sample is in the purified Th fraction





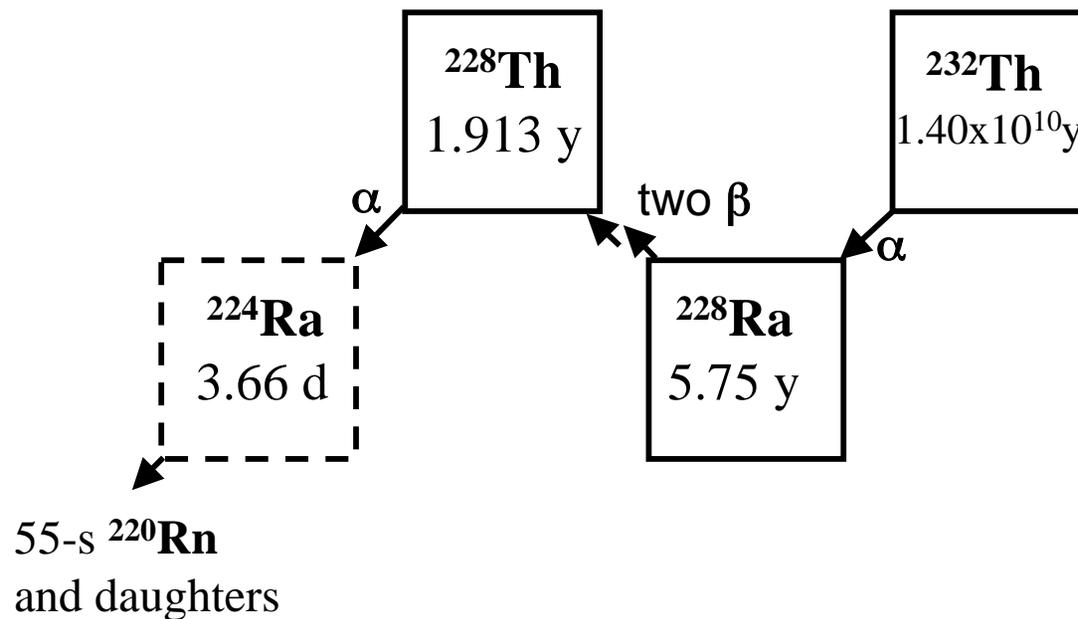
Chronometry with the thorium isotopes

In Nature, ^{228}Th , ^{228}Ra and ^{232}Th all have equal activities (radiochemical equilibrium)

Following a chemical purification, ^{228}Th begins to decay relative to ^{232}Th

At some point, ^{228}Ra grows back in to the sample to the point that the ^{228}Th concentration stops decreasing and begins increasing, until equilibrium is re-established

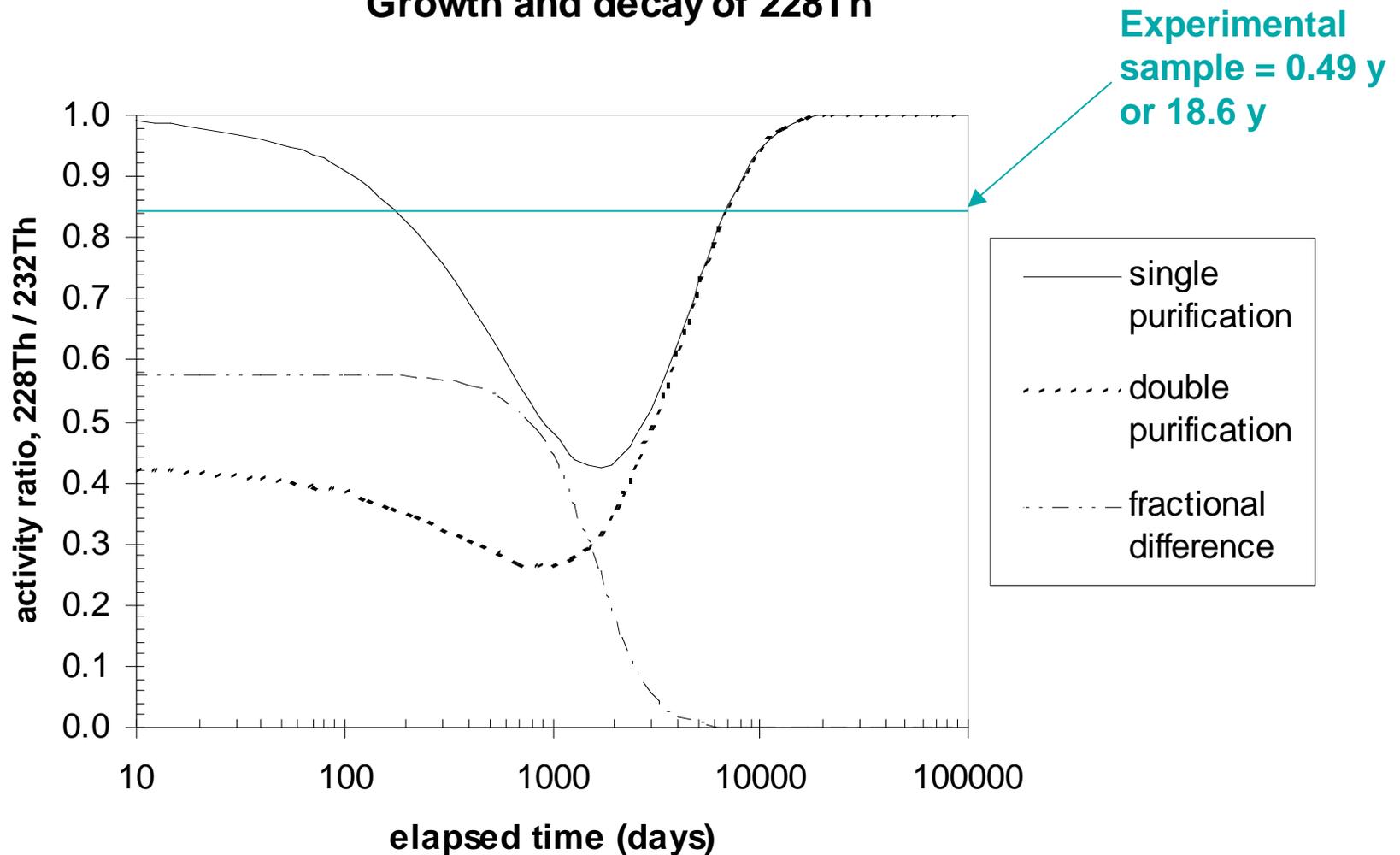
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The $^{228}\text{Th}/^{232}\text{Th}$ activity ratio is two-valued with respect to time



Growth and decay of ^{228}Th



Thorium nitrate sample from the Drug Enforcement Agency, Conclusions



Derived from ore in which U/Th = 0.414

Consistent with Monazite, too low for Uranite or Uranothorite

Thorium recovered from acid leach process

From residual $^{226}\text{Ra}/^{228}\text{Ra}$

No prior use in reactor applications

Last purification of the sample was May 1, 1978 \pm 110 days

Real-world sample #1 : South-east asia



- Through contacts in law enforcement, we received a large, radioactive sample.
 - Offered for sale as a “nuclear weapon component” to a federal agent on overseas assignment in south-east Asia
- Sample weighs 9 Kg. It is metal, in a complicated shape. Arc-shaped scratches imply that it was a moving part.
- Gross density is 16.9 g/cc, more than that of Pb (11.4) but less than that of pure α -phase uranium (19.0).
- Xray fluorescence of the surface indicates a nickel coating.
- Gamma-ray spectroscopy of the whole sample is consistent with depleted uranium.
- An alpha survey of the surface indicates that the nickel layer is not intact.



MADE IN U.S.A.

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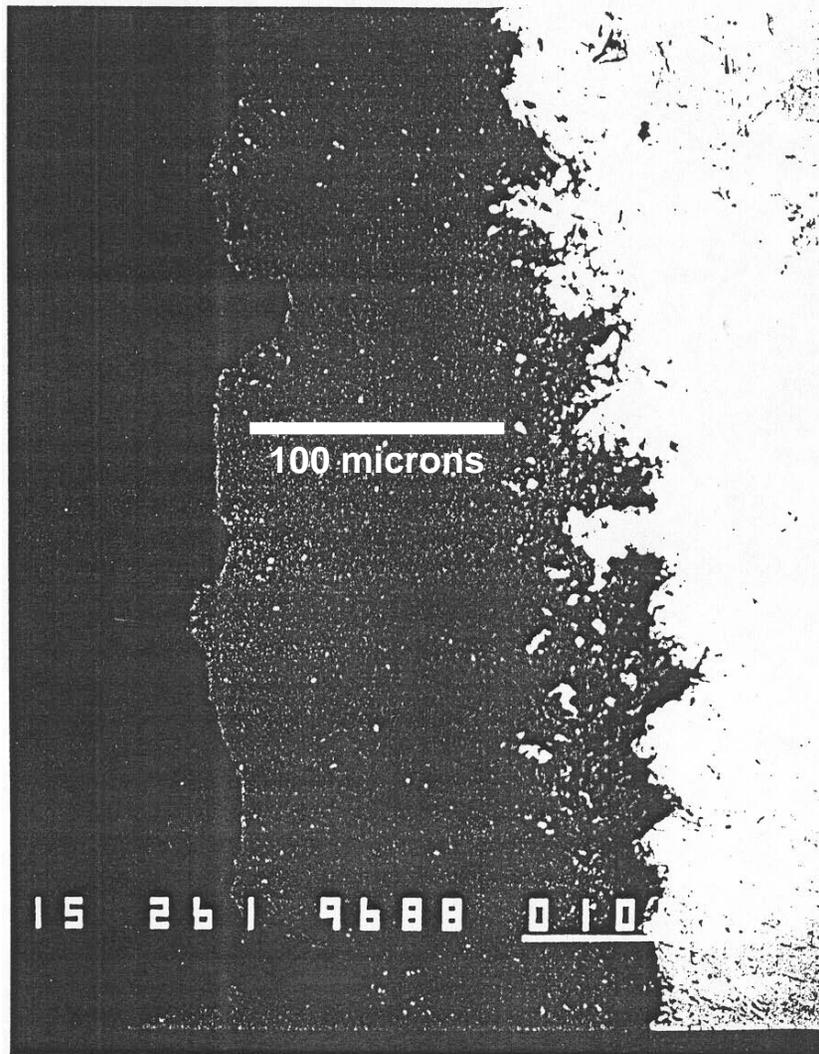
3818448-1B
CAUTION – RADIOACTIVE MATERIAL
URANIUM – HIGH SALVAGE VALUE
3683-3

We performed radiochemical and inorganic analyses on several components of the sample



- Four sub-samples:
 - dilute-nitric surface wash of whole sample
 - more concentrated nitric wash of a limited surface area
 - a piece of “nickel” peeled from the edge of a scratch
 - a 0.3-g piece hacksawed from one corner of the sample
- Analysis of samples characteristic of the surface showed:
 - nickel coating is 99+% pure, ~90 μm thick, electroplated
 - the surface was coated with Cd (containing trace Pb)
 - Cd is often used as a lubricant on screws or machine parts
 - the surface around the scratches was contaminated with Fe, Co, Mn, and Cr in the proportions found in 200-series steels
- No evidence of use involving other radionuclides

SEM photograph of the edge of the region of a polished uranium sample



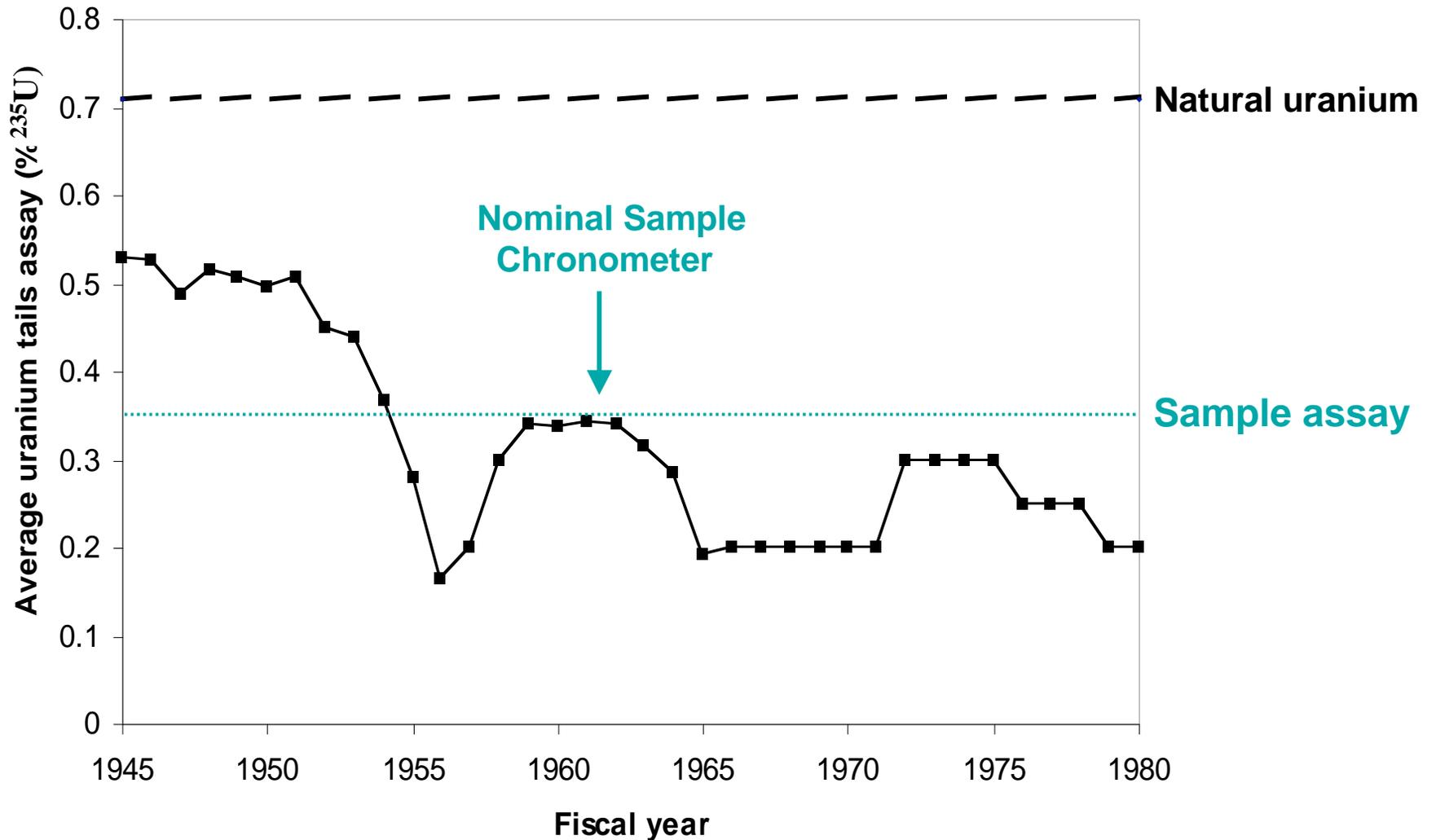
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Analysis of the bulk material provided the clues to identify the sample



- Alloy is standard “U-10Moly”, 9.9 wt% molybdenum, density 16.9 g/cc
 - This is not an alloy that is common in the nuclear industry
- Uranium isotopics are not consistent with modern standard depleted uranium, having too much of the minor isotopes
 - The concentrations of ^{233}U and ^{236}U preclude the possibility that the material is blended from depleted and natural materials
- The bulk material was very clean of other actinides, containing less than 2 ppb ^{237}Np and 2 ppt $^{\text{mix}}\text{Pu}$
- The average of ages measured from four chronographic pairs indicates that the material was last purified in May of 1961 \pm 2.8 years
- The isotopic ratio of $^{235}\text{U}/^{238}\text{U} = 0.003516$ is consistent with the “tails” uranium assays from U.S. enrichment plants in 1959-1962

The average ^{235}U assay of U.S. enrichment-plant “tails” changed from year to year



In combination with more conventional forensics, we learned:



- The sample is part of an aircraft counterweight assembly. It is high-density ballast whose position can be changed to adjust the trim of a plane in flight
 - The density of uranium is so high that it finds commercial uses as shielding and ballast, and a military use in ammunition
- The part number stamped on the sample is similar to those found on Lockheed components, but we were unable to match it with any commercial aircraft
- Coupled with the age of the sample and where it was obtained, we believe that we have identified an artifact of the Vietnam conflict

Real-world sample #2 : Bulgaria



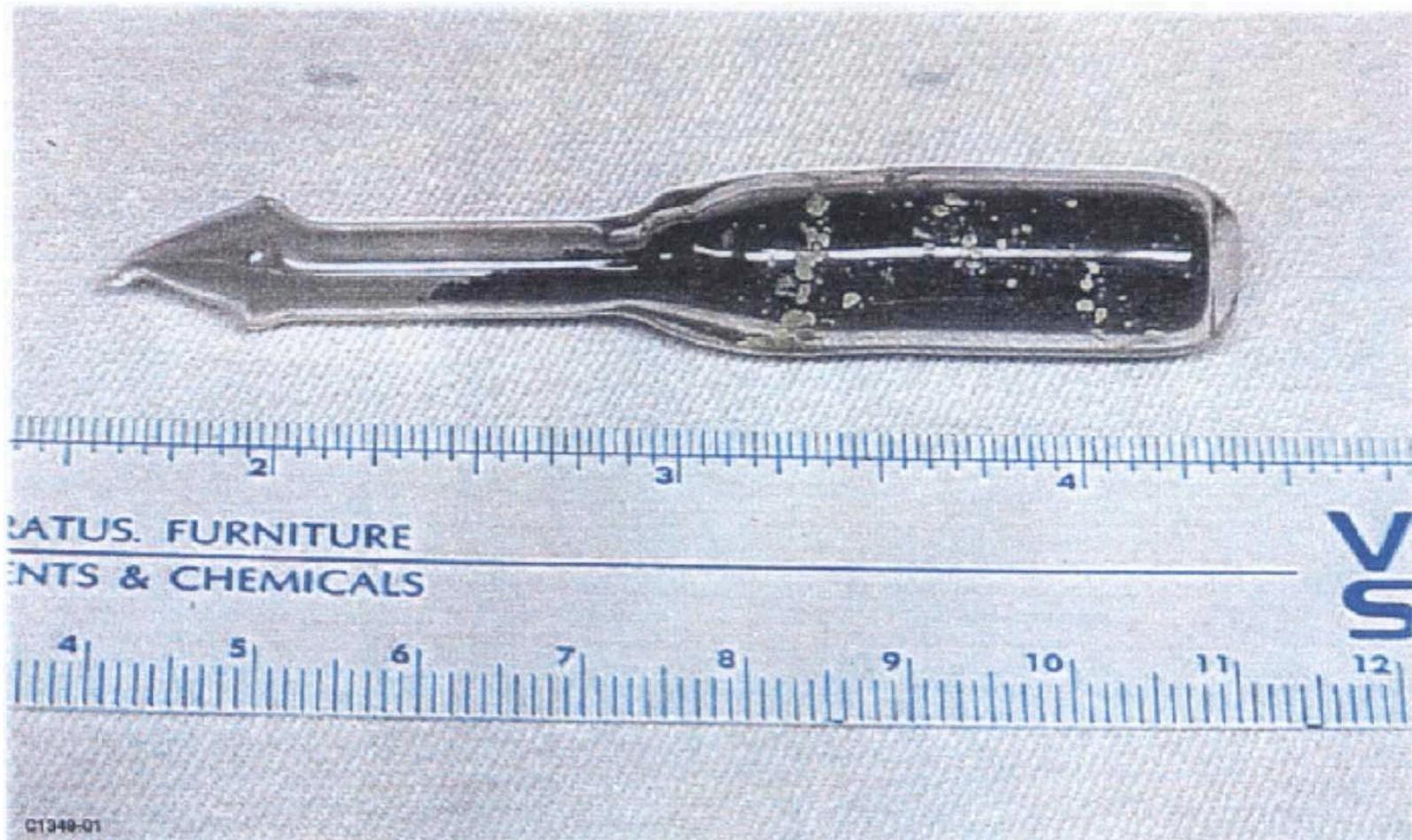
- The sample consisted of a fine black powder, sealed in a glass ampoule. The ampoule was packed into a lead “pig”, cushioned with a layer of paper and a waxy substance
- On-scene analysis by gamma-spec convinced local authorities that the material was a mixture of highly-enriched uranium and natural thorium
 - Thorium result was incorrect. Gamma-spec analysis was confused by several ppb of ^{232}U in the material, which gives similar gamma-rays.
- On receipt, the ampoule was opened and an aliquot of the material was dissolved
 - Total sample weight was 7 grams
 - XRF detected no inorganic contaminants
 - Quantitative dilution measurement resulted in 81.5 wt% uranium

The pig provided several conventional forensic clues



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Glass ampoule containing the uranium sample



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Radiochemical analysis of the material indicates that it was recovered from used reactor fuel



Uranium isotopics:

^{238}U	(13.996 ± 0.015) at%
^{236}U	(12.133 ± 0.010) at%
^{235}U	(72.693 ± 0.013) at%
^{234}U	(1.177 ± 0.001) at%
^{233}U	(299 ± 7) ppb
^{232}U	(10.8 ± 0.2) ppb

Material is 2.8 ppb **Pu** and 7.7 ppb ^{237}Np .

The ^{238}Pu content of the plutonium fraction is very high, consistent with the burn of light-mass uranium in a reactor

^{134}Cs , ^{137}Cs , and ^{125}Sb fission products were observed in the sample
Absence of other fission products gives clues to the reprocessing chemistry used

The radionuclide content of the sample is consistent with reactor irradiation of HEU



- Reconstructing the isotopics of the starting material, assuming a simple cross section model:
 - » ^{238}U 12%
 - » ^{235}U 87%
 - » ^{234}U 1%
- Reactor type is research or propulsion
- The enrichment of the material, the size of the sample, and the action of fuel reprocessing limits the possibilities for the source of the material
- More sophisticated reactor calculations and studies of potential reprocessing chemistries are being performed

Beware of friends and allies



Sample processing in a glove bag



100 grams of HEU oxide in nested European-style zip-lock baggies



To close ...



“If you give me six lines written by the hand of the most honest of men, I will find something in them which will hang him.”

- Cardinal Richelieu 1586 - 1642