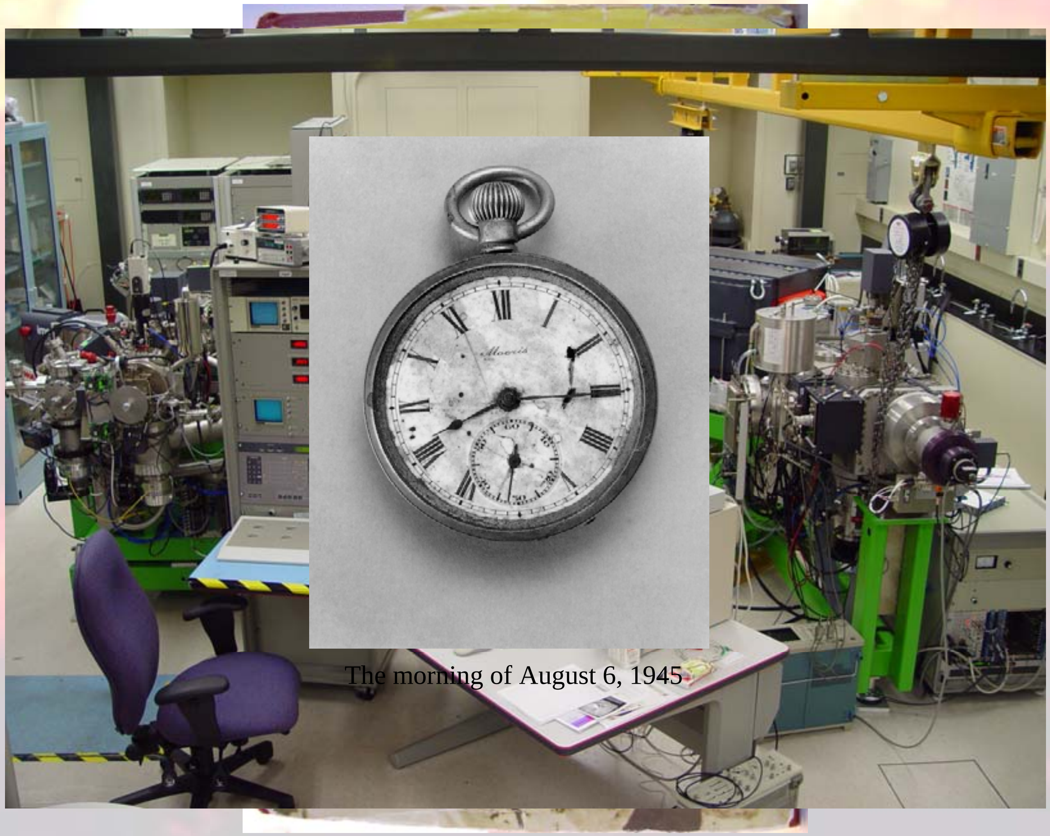
Precision Isotopic Measurements of Anthropogenic Uranium with the CAMECA ims-1270



The morning of August 6, 1945

Albert J. Fahey

National Institute of Standards and Technology
Gaithersburg, MD 20899

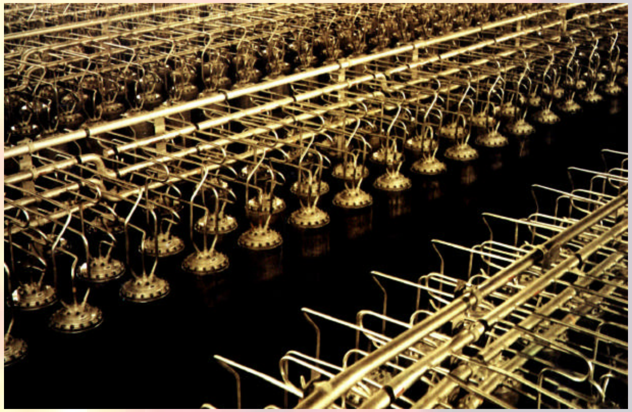
Purpose of Precision Isotopic Measurements of Uranium

- The determination of the isotopic composition of uranium has always been a key component of nuclear non-proliferation efforts, especially for organizations such as the International Atomic Energy Agency (IAEA).
- NIST has played an important supporting role with respect to the IAEA.
- Assisting in the development of searching capabilities.
- The development of precision isotopic measurements of uranium particles of anthropogenic origin by SIMS.

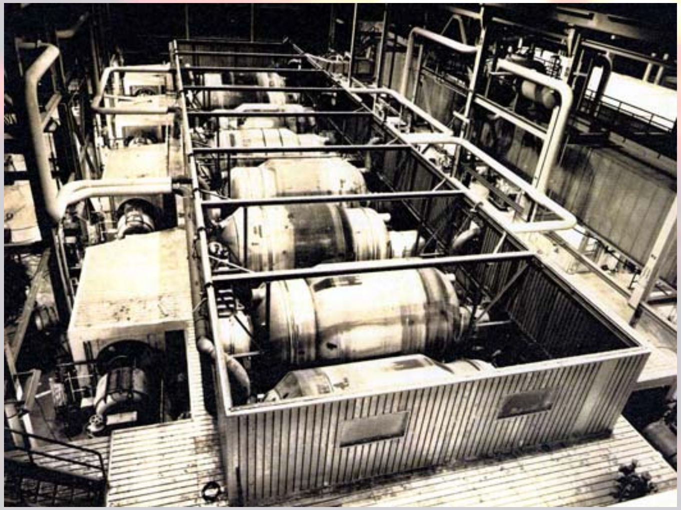
Example Enrichment Facilities

Oak Ridge Calutrons

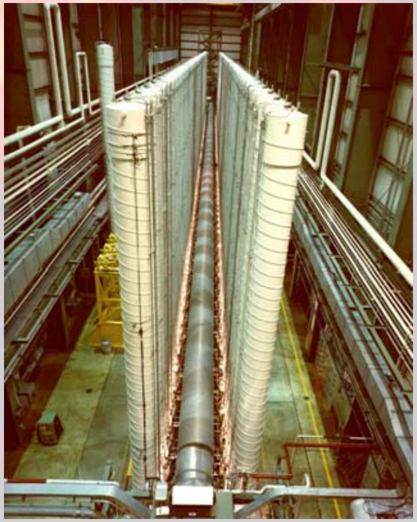
Almelo, NL Urenco Centrifuge operations.



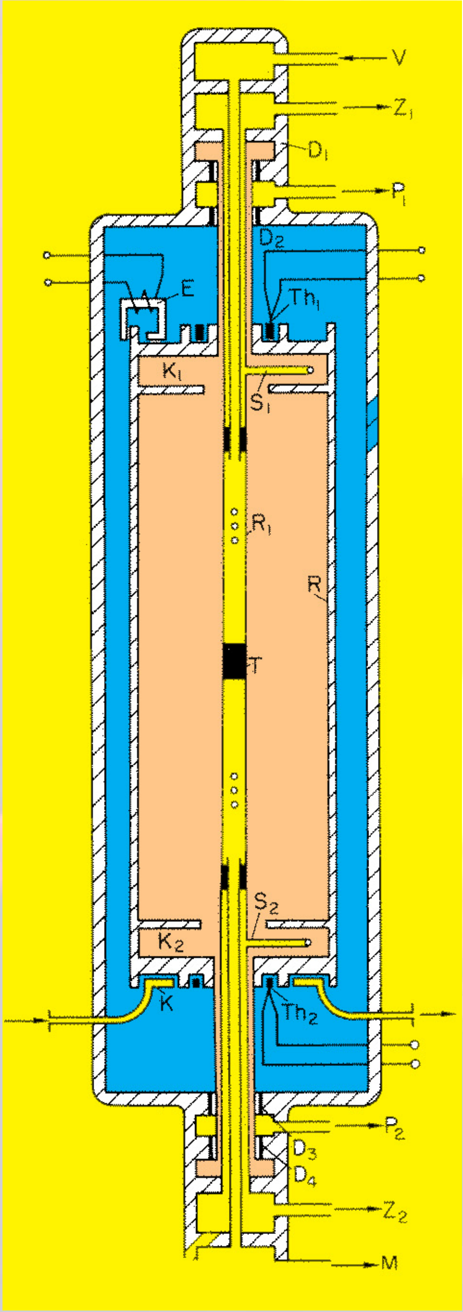
Oak Ridge K25 Diffusion Operations



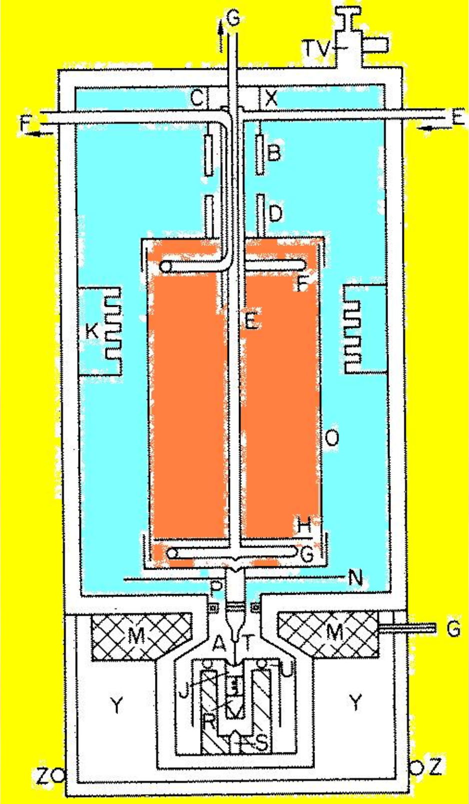
Oak Ridge Experimental Centrifuge plant.



Groth ZG5 Centrifuge

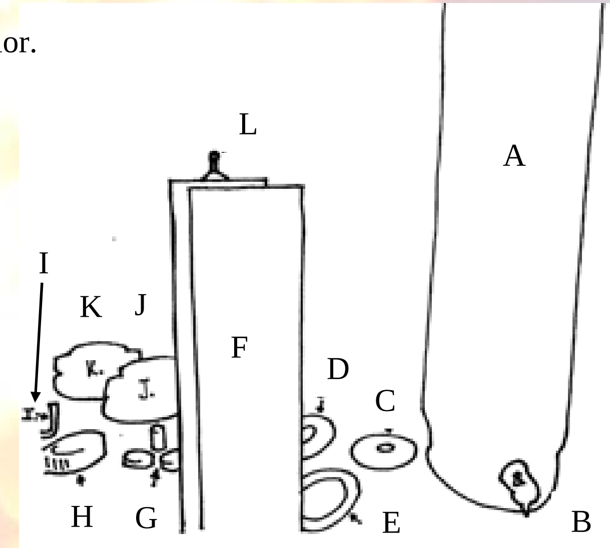


Zippe Centrifuge



- Low power requirements compared to other methods.
- Smaller than other methods.
- Fewer “materials” constraints.

A. Vacuum casing, with cooling coils wrapped around exterior.
B. Electrical connection for Motor.
C. Lower end cap of rotor and armature plate.
D. Upper end-cap, with hole for feed pipes.
E. Weir baffle.
F. Carbon-fiber rotor, 62 cm long.
G. Magnetic bearing components.
H. Motor winding and stator.
I. Cooling loop for motor.
J. Base.
K. Base with motor.
L. Spiral groove pivot bearing.

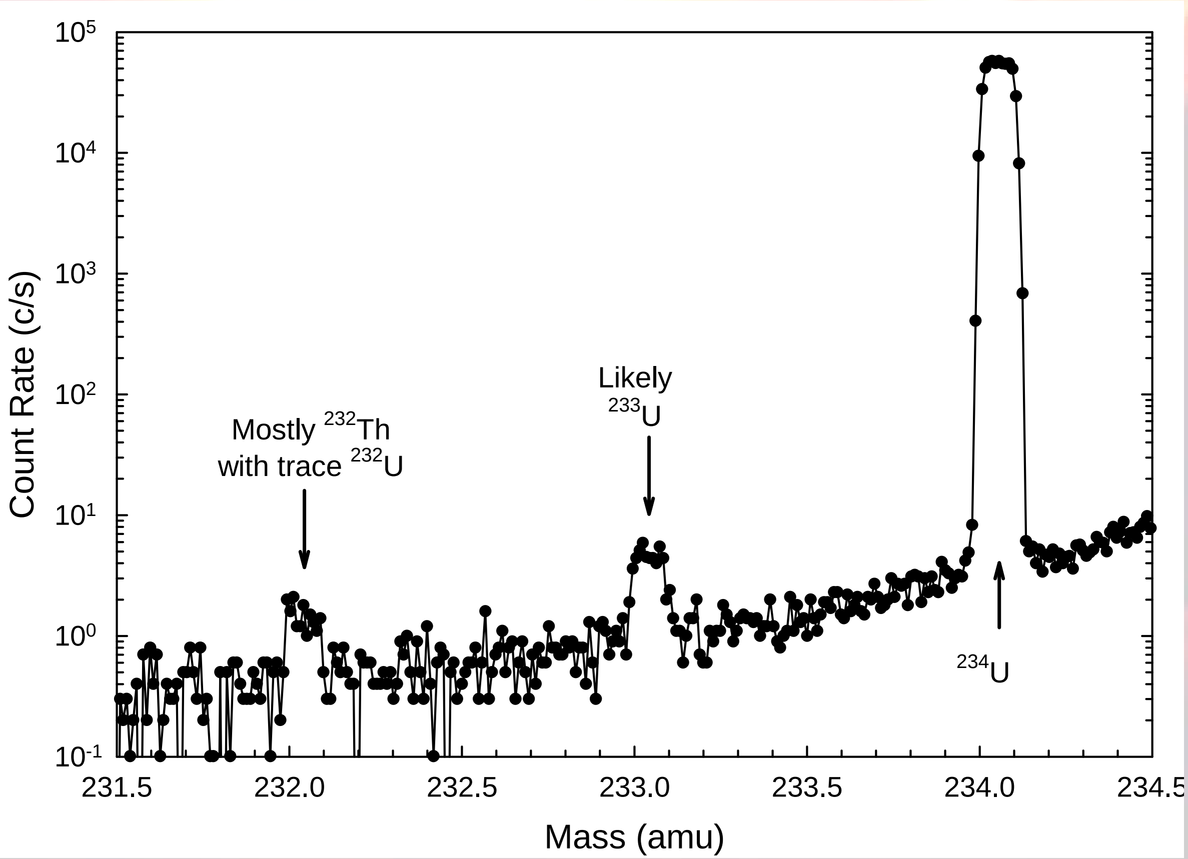


Lybian A.Q. Khan-style Centrifuges.

Some Characteristics of Anthropogenic Uranium

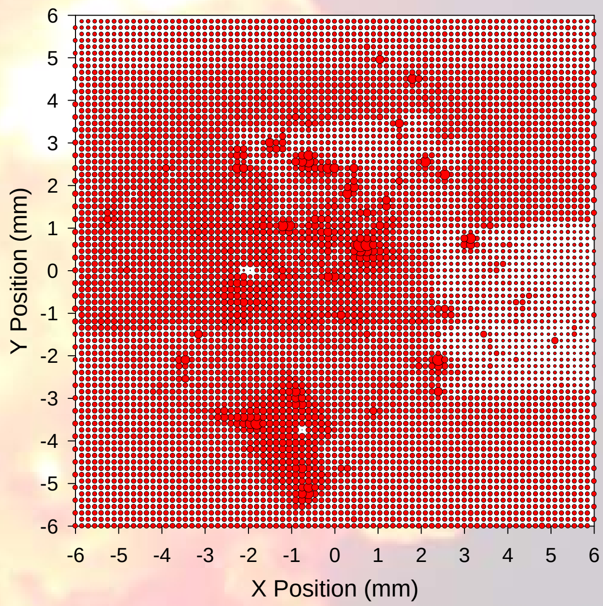
- ^{235}U is the sought-after isotope for nuclear reactions. During enrichment:
  - All abundances change if enriched or depleted by centrifuge or diffusion.
  - ^{235}U abundance is disproportionately perturbed by EMIS or AVLIS.
- Some anthropogenic uranium contains ^{236}U from the use of recycled irradiated fuel rods.
- Other radio isotopes of uranium, or other elements, may also be present at trace levels.

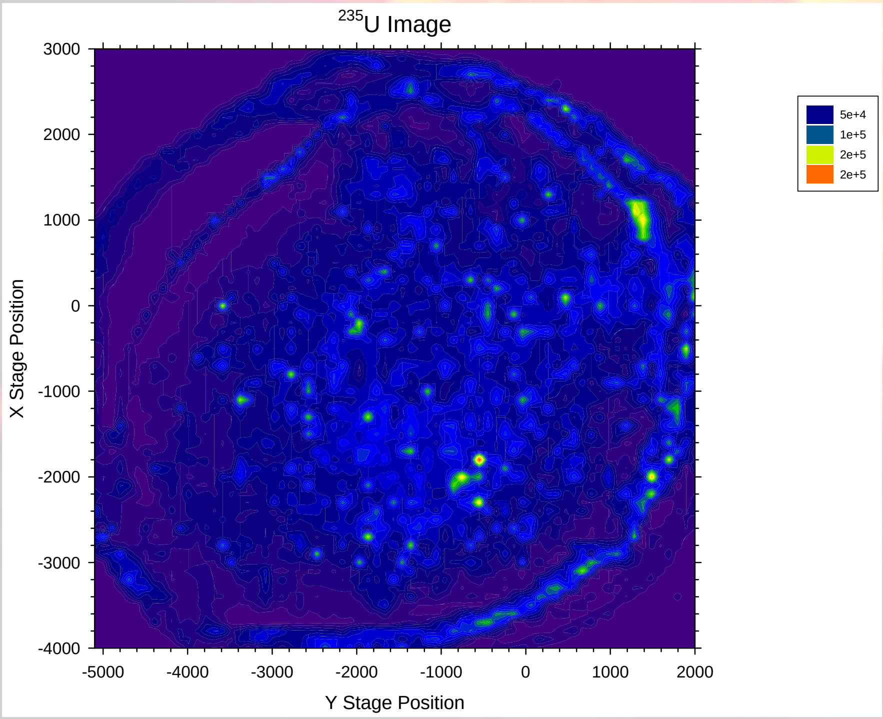
Example of Trace Component Measurements in Uranium (U_3O_8) Powder.

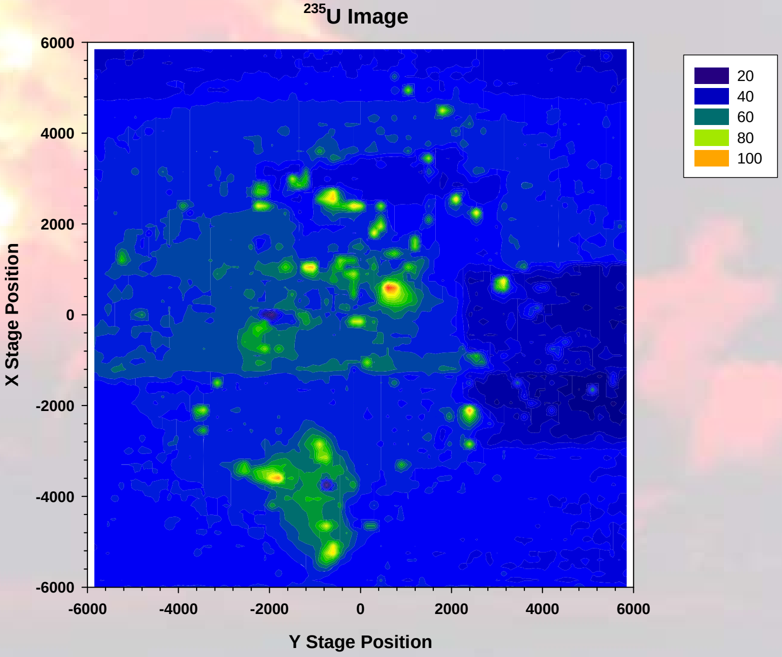


Particle Location and Large Area Surveys

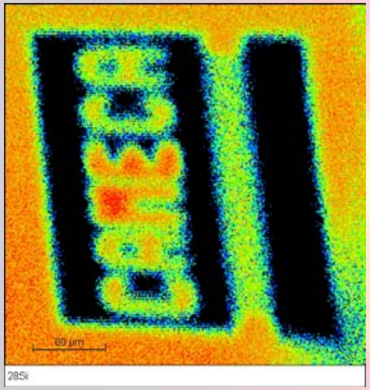
- High-Speed Particle Searching with SIMS.
  - Uses EM to record counts.
  - Augment the RAE-based particle searching.
  - Possibly use the multi-collector on the ims-1270.



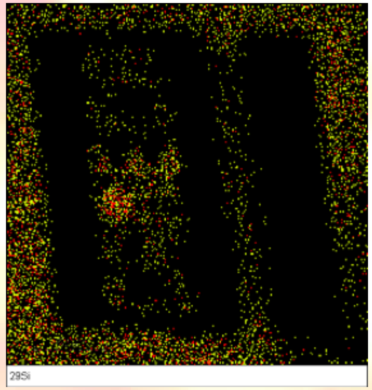




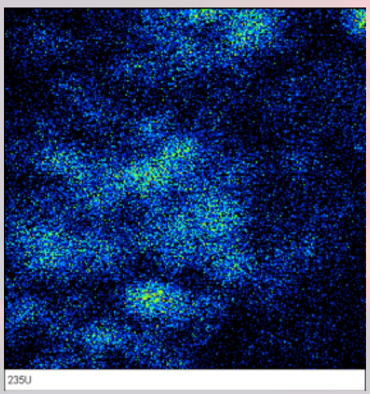
^{28}Si



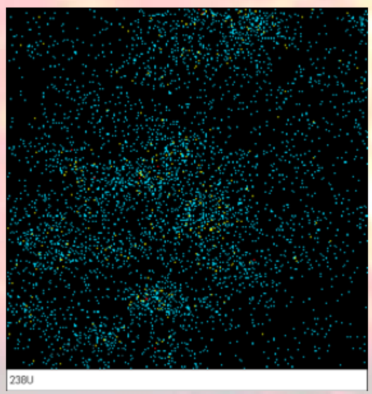
^{29}Si



^{235}U



^{238}U



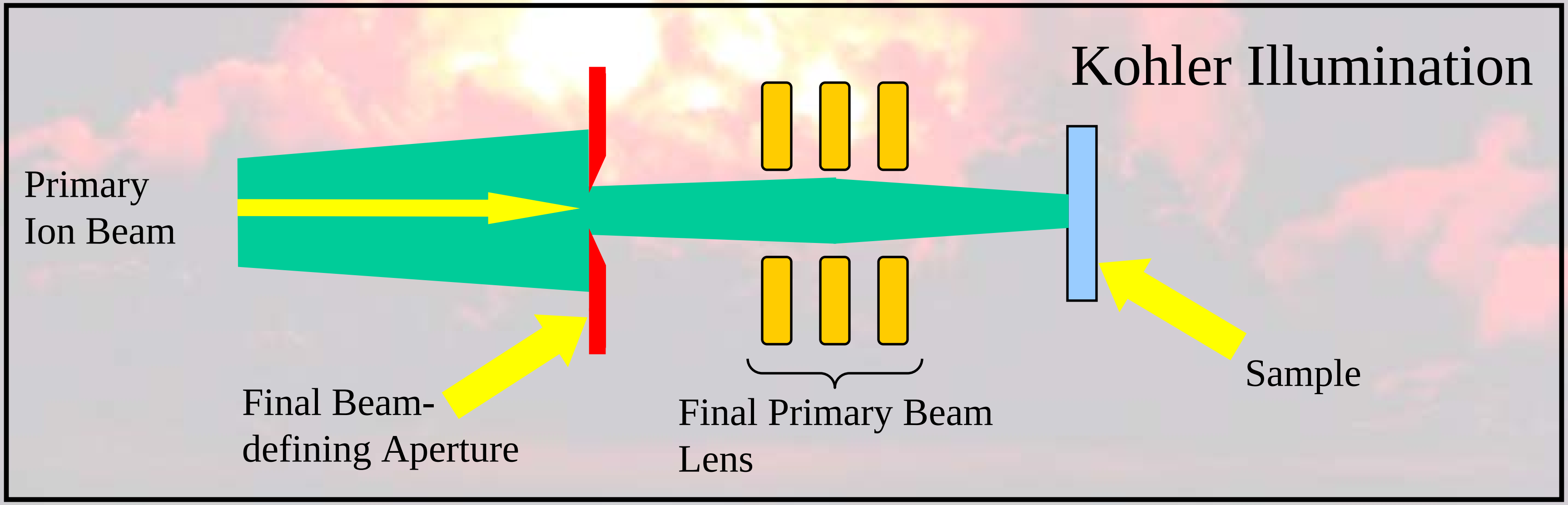
Multi-collector Imaging.

- Can get up to 5 masses on the collectors.Scanning ion imaging
  - Spatial resolution limited for higher primary currents.
  - Could do real-time analysis and re-focus to analyze a single particle found.
- New software needs to be written for this application.
  - Higher speed scanning.
  - Precision isotopic analysis.
  - Re-focusing on individually located particles.

Precision Isotopic Abundance Measurements

Measurement Conditions

- Kohler illumination with primary O^- at 12-13 keV (~35 μm spot).
- Typically 1-3 nA current.
- Particles are never completely consumed (most of nearly all the particles remain after the measurement).
- 20-30 cycles through the masses.



Measurement Method

- Cycle of masses includes (1 second settling between peaks):
  - 233.5 (low mass to allow for magnet settling)
  - ^{234}U
  - ^{235}U
  - $^{236}U + {}^{235}UH$
  - ^{238}U
  - ^{238}UH
- ^{236}U is computed from:

$$^{236}U = {}^{236}I - \frac{^{238}UH}{^{238}U} \times {}^{235}U$$

- This works well in all cases except:
  - When ^{239}Pu is present.
  - Then the ^{235}U enrichments is very high (>90%).

Isotope Ratios and Abundances

Computation of Atomic Abundance:

$$ {}^{i}U = \frac{{}^{i}U}{{}^{234}U + {}^{235}U + {}^{236}U + {}^{238}U} $$

${}^{i}U$ - Can be a count rate or a ratio.

Isotopic abundances can be computed on a cycle-to-cycle basis and the observed variation used as the uncertainty.

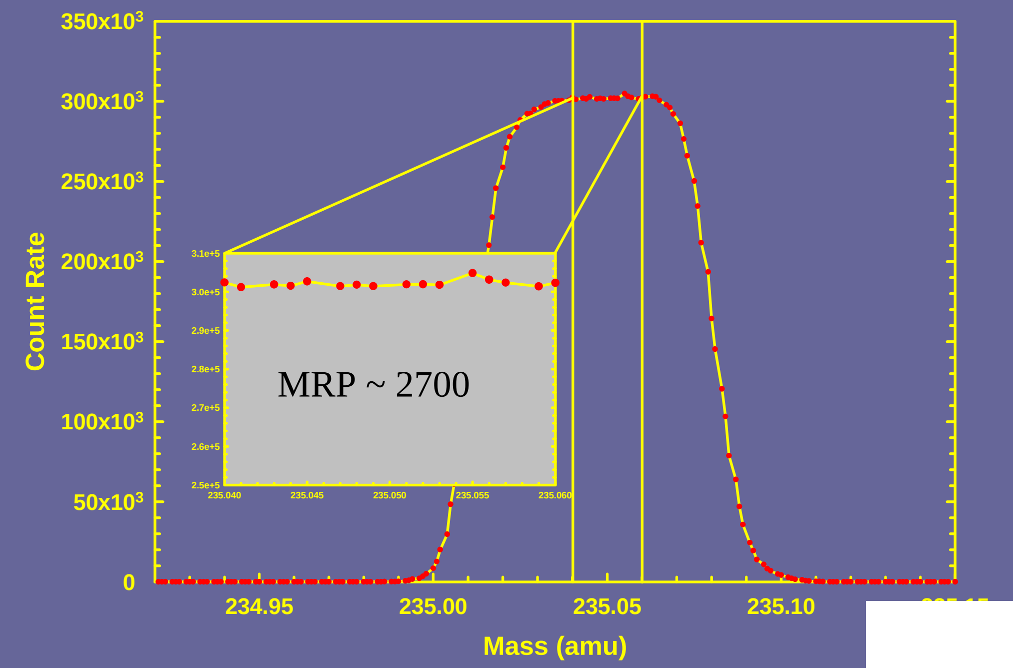
This allows ratios to be computed and then corrected for mass fractionation without having to propagate correlated uncertainties from the computation of Atomic Abundance.

Analysis of Data

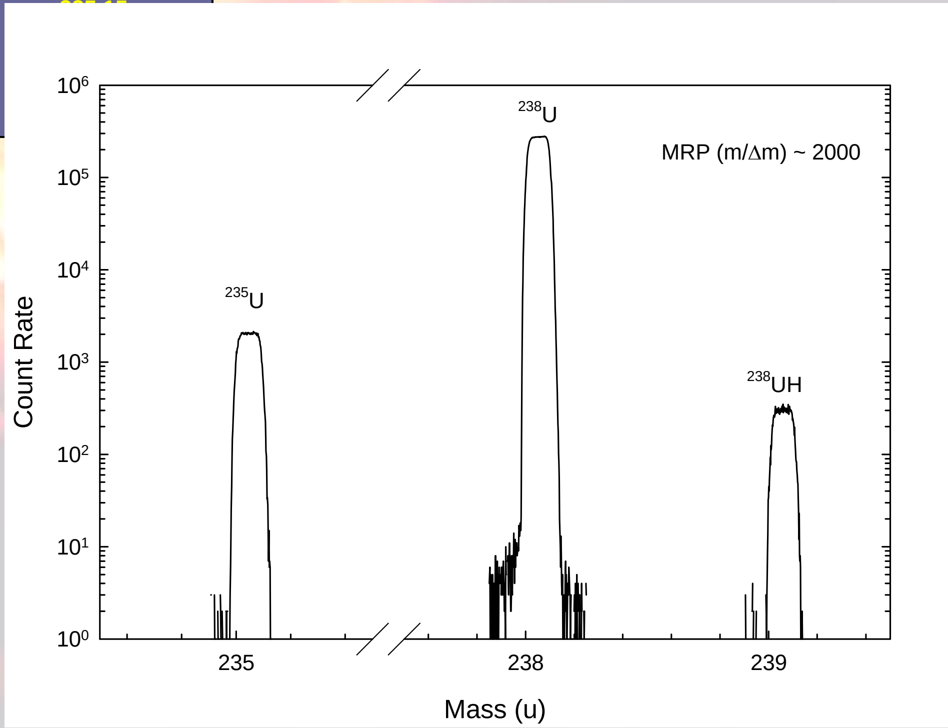
- Count rates are corrected for dead time.
- Count rates are interpolated to compensate for time variations.
- The ^{236}U is computed for each cycle since the hydride contribution changes during the course of a measurement.
- Ratios and Atom-percents are calculated on a single cycle basis.
- Average values and uncertainties are finally calculated.
- Measurements of a Uranium SRM (typically SRM U900) are made on the same day and used to correct for mass fractionation.
  - The standard measurements often “bracket” the measurements of the “unknowns”.
  - All isotopic fractionation corrections are “external” correction made with respect to SRM U900 measurements.

Key Components of Isotopic Ratio Measurements

- Stable primary and secondary ion currents.
- Suitable Mass Resolution with flat-topped peaks.
- High efficiency and sensitivity.
- Precise characterization of counting system behavior.
- Proper selection of homogeneous, well characterized standards.
- Reproducible sample extraction distance (Z-motion adjustment).
- High degree of reproducibility over a long period of time.
- Good agreement with TIMS measurements on the same particles.



Natural uranium peaks showing a typical hydride.



Peaks have extended flat tops at a MRP of ~2700. This is sufficient to exclude many isobaric interferences.

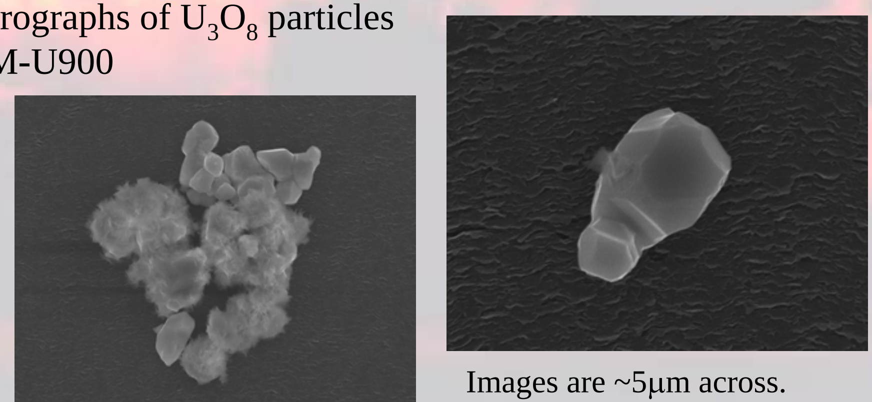
Efficiency Comparison among the Cameca Magnetic sector instruments (except the nanoSIMS).

	O^- ims-1270@10kV (MRP=2300)			O^- ims-4f@4.5kV (MRP=300)			O^- ims-6f @5kV (MRP=300)			O^- ims-6f @10kV (MRP=300)		
PNL-2 Clay Beads	^{235}U	^{238}U	^{239}Pu	^{235}U	^{238}U	^{239}Pu	^{235}U	^{238}U	^{239}Pu	^{235}U	^{238}U	^{239}Pu
Raw Mean:	2.08%	2.04%	5.16%	0.70%	0.65%	1.98%	1.14%	1.10%	2.95%	3.65%	3.53%	8.62%
Uncertainty‡:	0.40%	0.39%	1.16%	0.02%	0.04%	0.07%	0.10%	0.09%	0.27%	0.16%	0.17%	0.52%
Ratio to 4f	3.0	3.1	2.6	1.0	1.0	1.0	1.6	1.7	1.5	5.2	5.4	4.4
Particles:	8			20			5			6		
Corr. Mean:	2.19%	2.14%	5.41%	0.97%	0.90%	2.75%	2.08%	2.01%	5.38%	4.05%	3.93%	9.58%
Uncertainty:	0.42%	0.41%	1.22%	0.03%	0.06%	0.10%	0.17%	0.16%	0.48%	0.18%	0.19%	0.58%
U900		O^- ims-1270@10kV† (MRP=2300)			O^- ims-4f@4.5kV (MRP=300)						O^- ims-6f @10keV (MRP=300)	
		^{234}U			^{234}U						^{234}U	
Raw Mean:		0.33%			0.16%						0.84%	
Uncertainty:		0.05%			0.06%						0.13%	
Ratio to 4f		2.1			1.0						5.4	
Particles:	5			14						6		
Corr. Mean:		0.35%			0.22%						0.93%	
Uncertainty:		0.05%			0.08%						0.14%	

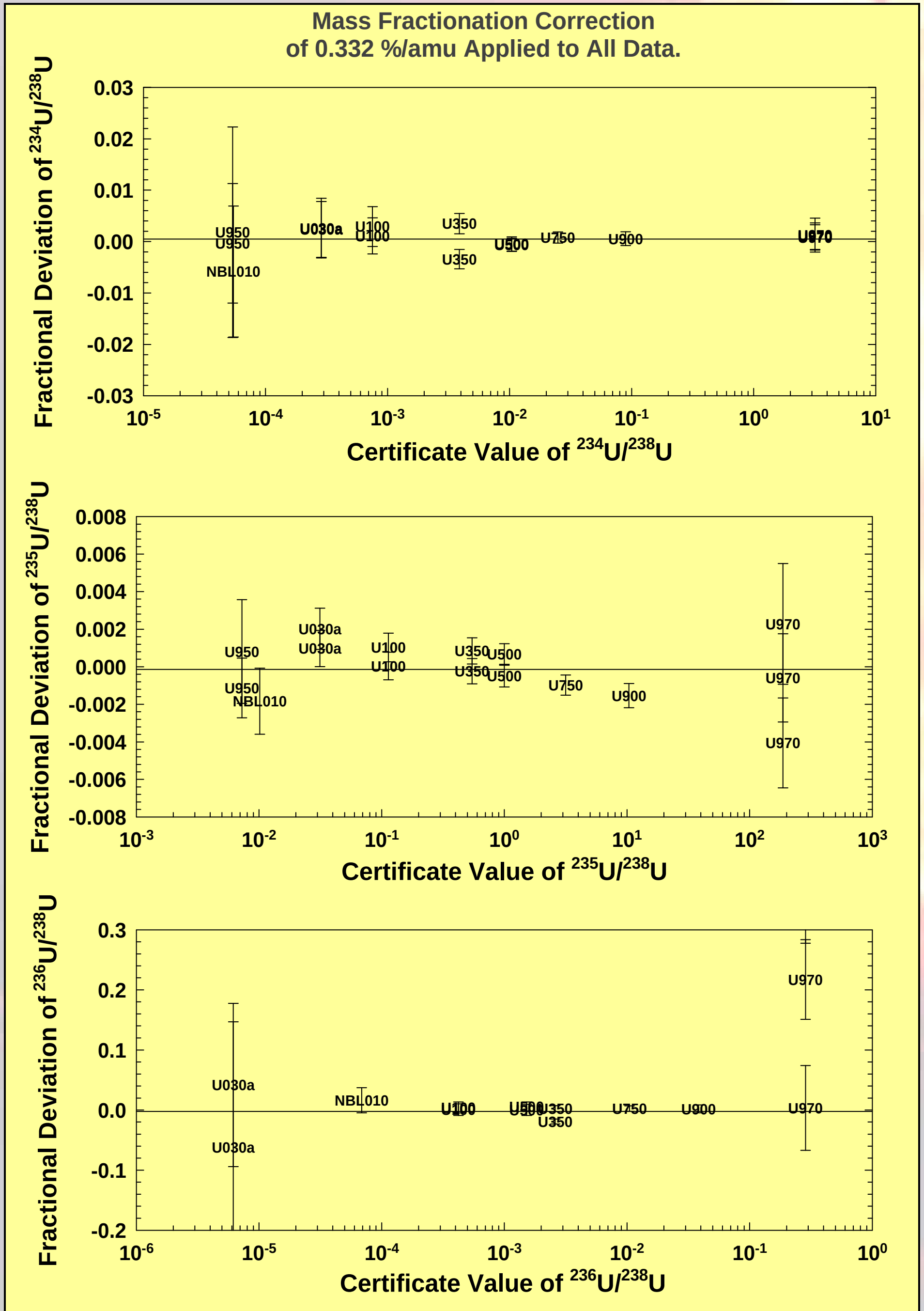
‡-Uncertainty, in all cases in this table, is one standard deviation since the measurements may contain a non-random variation; this represents a conservative "external" error on the measurements.

PNL-2 Clay Beads

SEM micrographs of U_3O_8 particles from SRM-U900



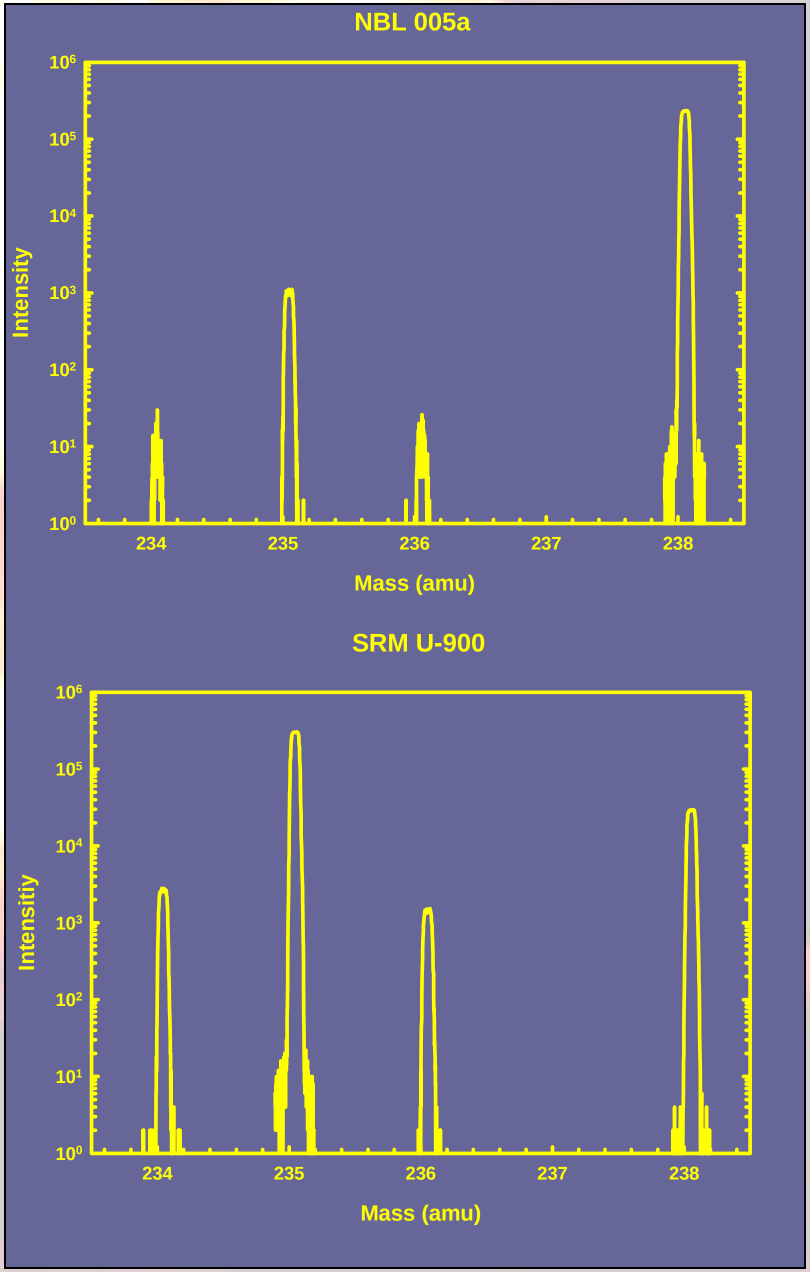
Images are ~5µm across.



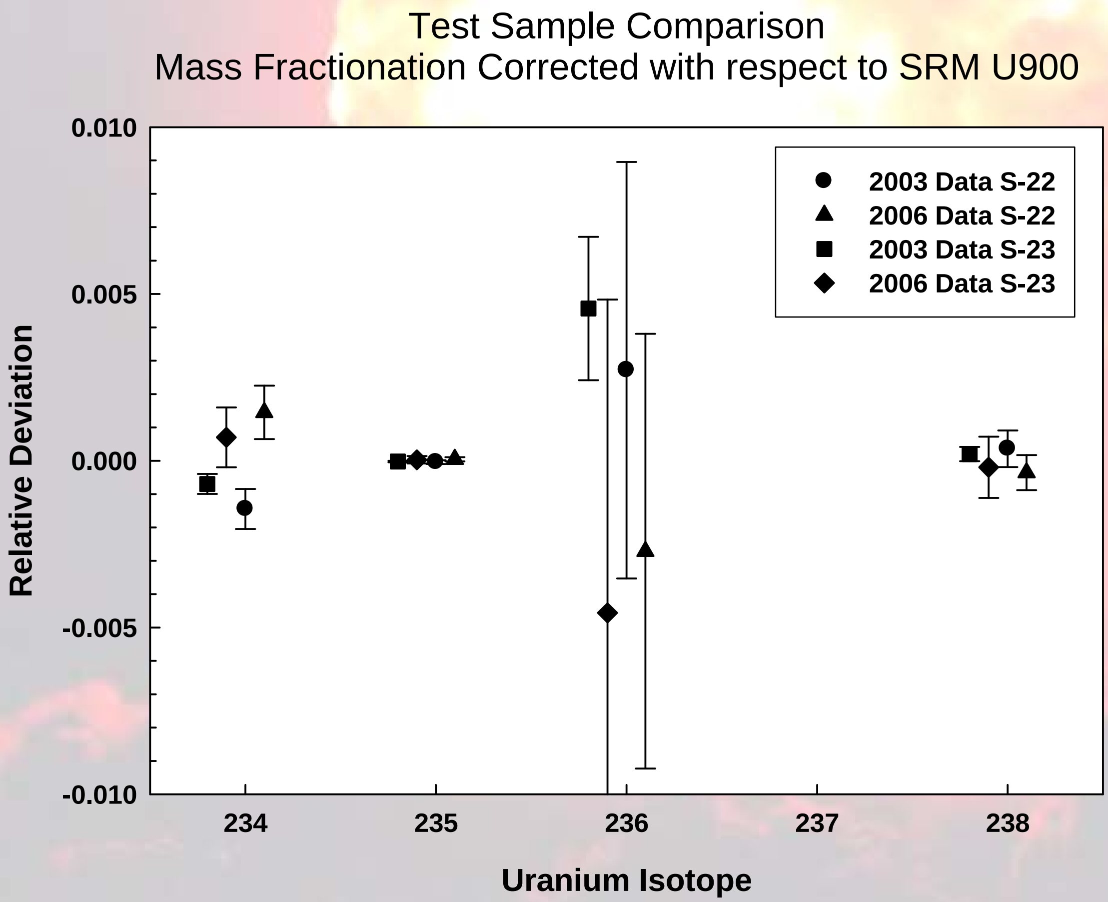
- 9 Uranium SRM’s were measured.
  - 8 isotopic
  - 1 SRM-950 isotopic composition is “natural” where ratios were obtained by TIMS.
- Linearity of counting system and mass spectrometer is very good
  - Deviation of 2-4 ‰ over more that 4 orders of magnitude.
  - Some difficulty evident for ^{236}U measurement at the highest ^{235}U enrichments.

- Particle standards used for U-isotopic measurements.
- Compositions ranged from DU to 97% enriched.
- Note the signal at 236.

Isotopic Composition of SRM U-900		
	Atom %	Ratio to ^{238}U
^{234}U	0.7777%	0.0895
^{235}U	90.1960%	10.3757
^{236}U	0.3327%	0.0383
^{238}U	8.6930%	1.0000



Long term reproducibility of Uranium isotopic measurements.

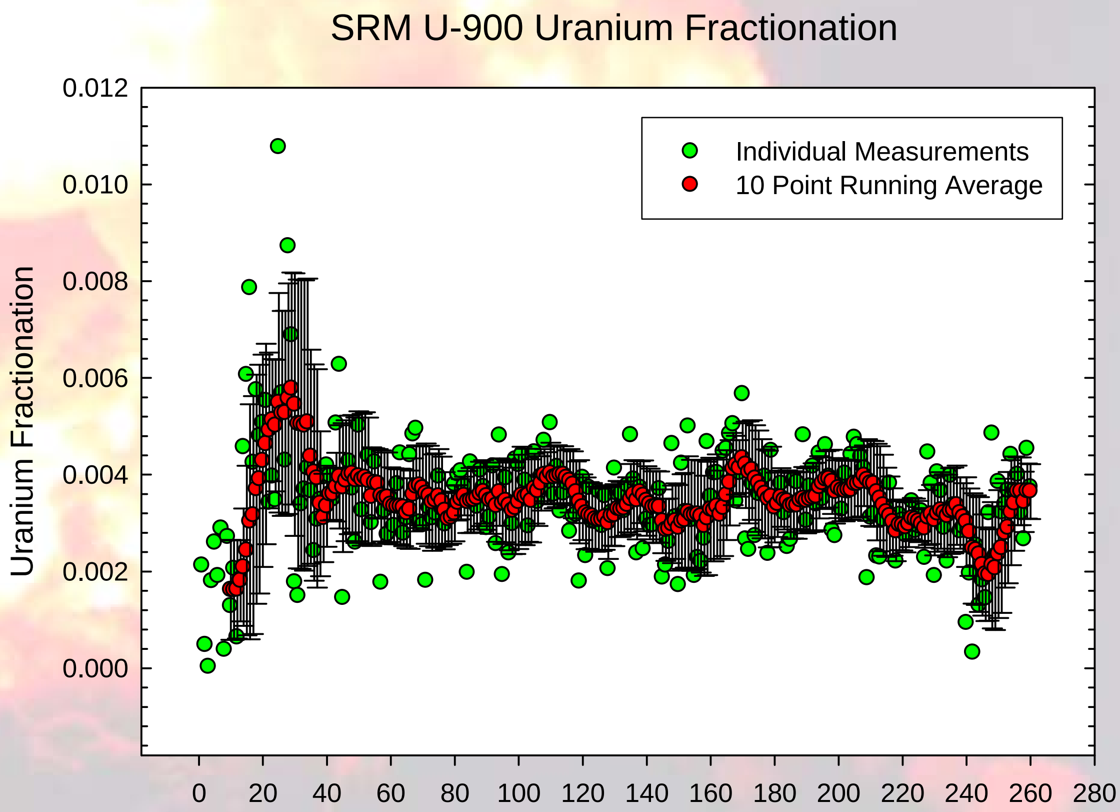


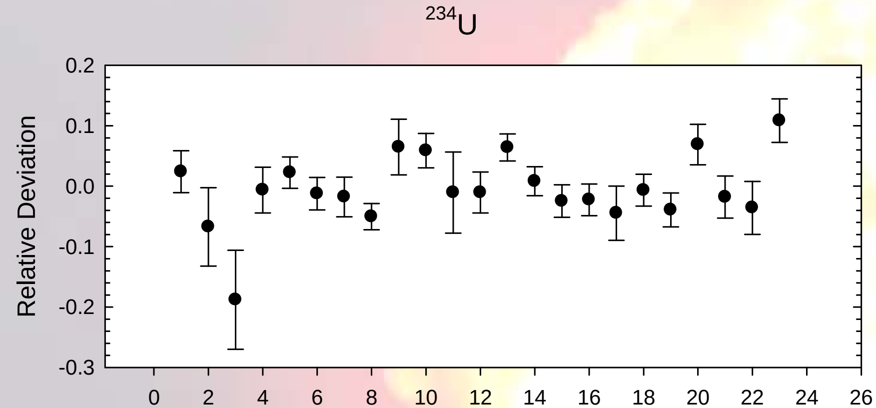
- Same sample measured ~2 ½ years apart.
  - 2003 data measured by A. Fahey
  - 2006 data measured by D. Simons and J. Fassett.
  - Measurements are averages of 4-15 particles.

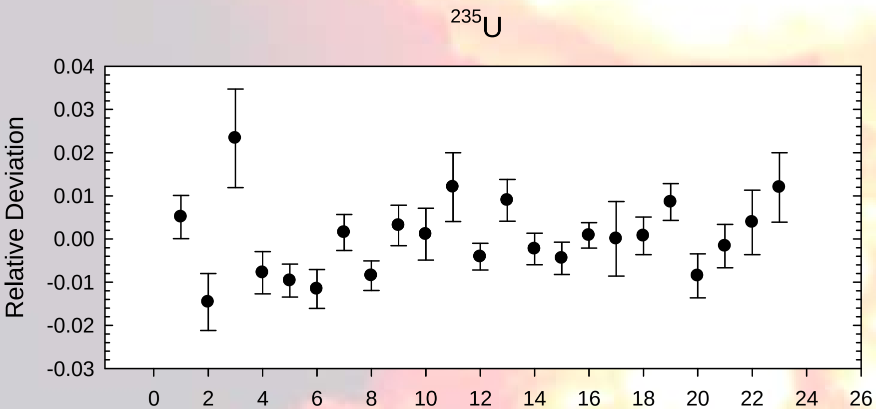
Variations in the Measured Uranium Isotopic Fractionation over Time.

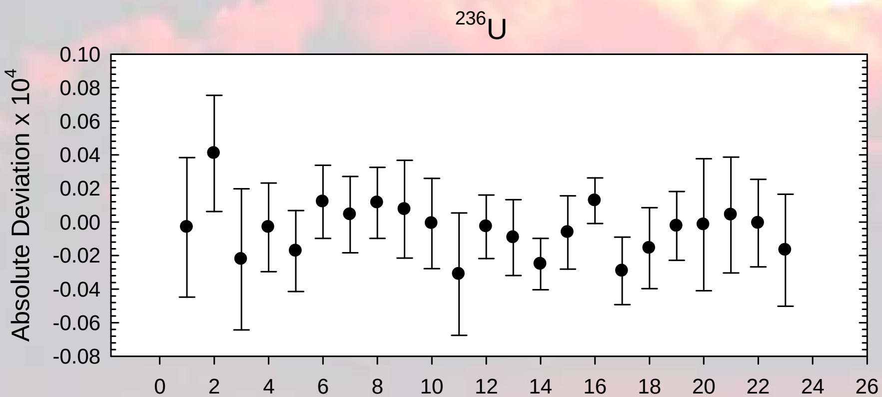
Approximately 6 months of measurements on SRM U900 show:

1. Relatively small variations in the uranium isotopic fractionation.
2. Relatively slow variations in the measured fractionation.









Comparison of Measured Abundances between SIMS and TIMS data on the same set of particles.

SIMS/TIMS Relative Deviations			
	Δ		Δ/σ
^{234}U	0.193%	0.653%	0.30
^{235}U	-0.242%	0.094%	2.56
^{236}U	-0.425%	0.489%	0.87

Summary and Conclusions

- The ims-1270 has been shown to be capable of reproducibility of ~4 ‰ for ^{234}U abundance measurements measured 2 ½ years apart.
- Comparison with TIMS measurements of the same particles show excellent agreement within the uncertainty.
- Long term reproducibility of mass fractionation is small and varies slowly with time.
- The ims-1270 clearly can be used to determine absolute uranium isotopic compositions to within a few permil.

August 6, 1945, 8:16 a.m.

Manhattan, 2016?