

An Improved Method for the Determination of ^{235}U and ^{238}U in Urine by Inductively Coupled Plasma-Mass Spectrometry

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Intercomparison Studies Program

&

**RADIOBIOASSAY
LABORATORY
STAFF**



Alpha Spectrometry



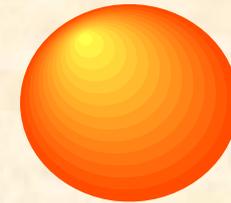
SAMPLE



CO-PRECIPIATION



ION EXCHANGE



ELECTRODEPOSITION



COUNTING

ADVANTAGES

✱ **ISOTOPIC**

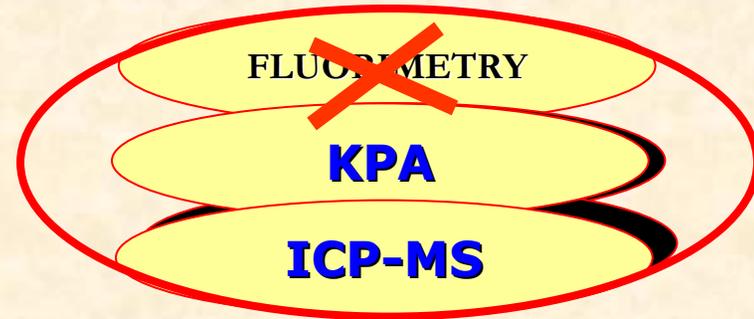
DISADVANTAGES

- ◆ **RESOLUTION**
- ◆ **RECOVERY**
- ◆ **ANALYSIS TIME**
- ◆ **LABOR-INTENSIVE**
- ◆ **WASTE**

ALTERNATE METHODS

DESIRED CHARACTERISTICS

- **FAST**
- **ACCURATE**
- **ISOTOPIC**
- **CHEMICAL SEPARATIONS NOT NEEDED**



KPA

ADVANTAGES

- Rapid and relatively simple
- Sensitive to low levels of uranium
- Chemical separations not needed

LIMITATIONS

- Uranium must be present as U(VI)
- Not isotopic
- Potential contamination from reagents
- Quenching
- Interferences
 - ❖ Chromate
 - ❖ Suspended particles

ICP-MS

ADVANTAGES

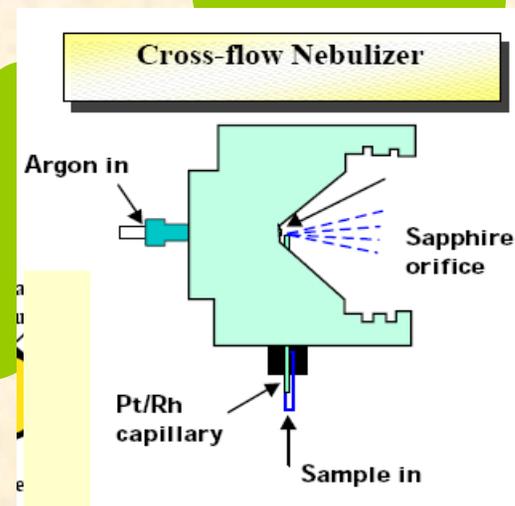
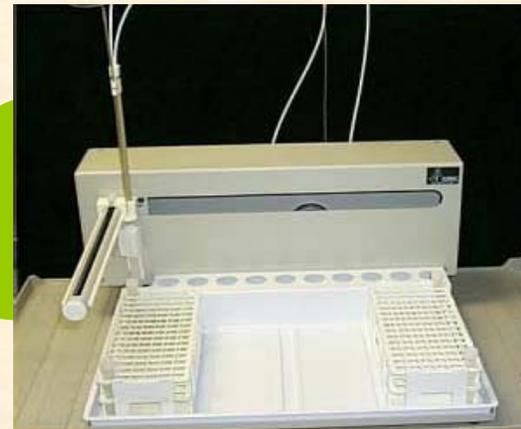
- Rapid
- Better than alpha spectrometry
- Isotopic
- Cost-effective
- Less labor
- Waste reduction

LIMITATIONS

- ^{235}U & ^{238}U only (bioassay)

Relative Detection Sensitivities

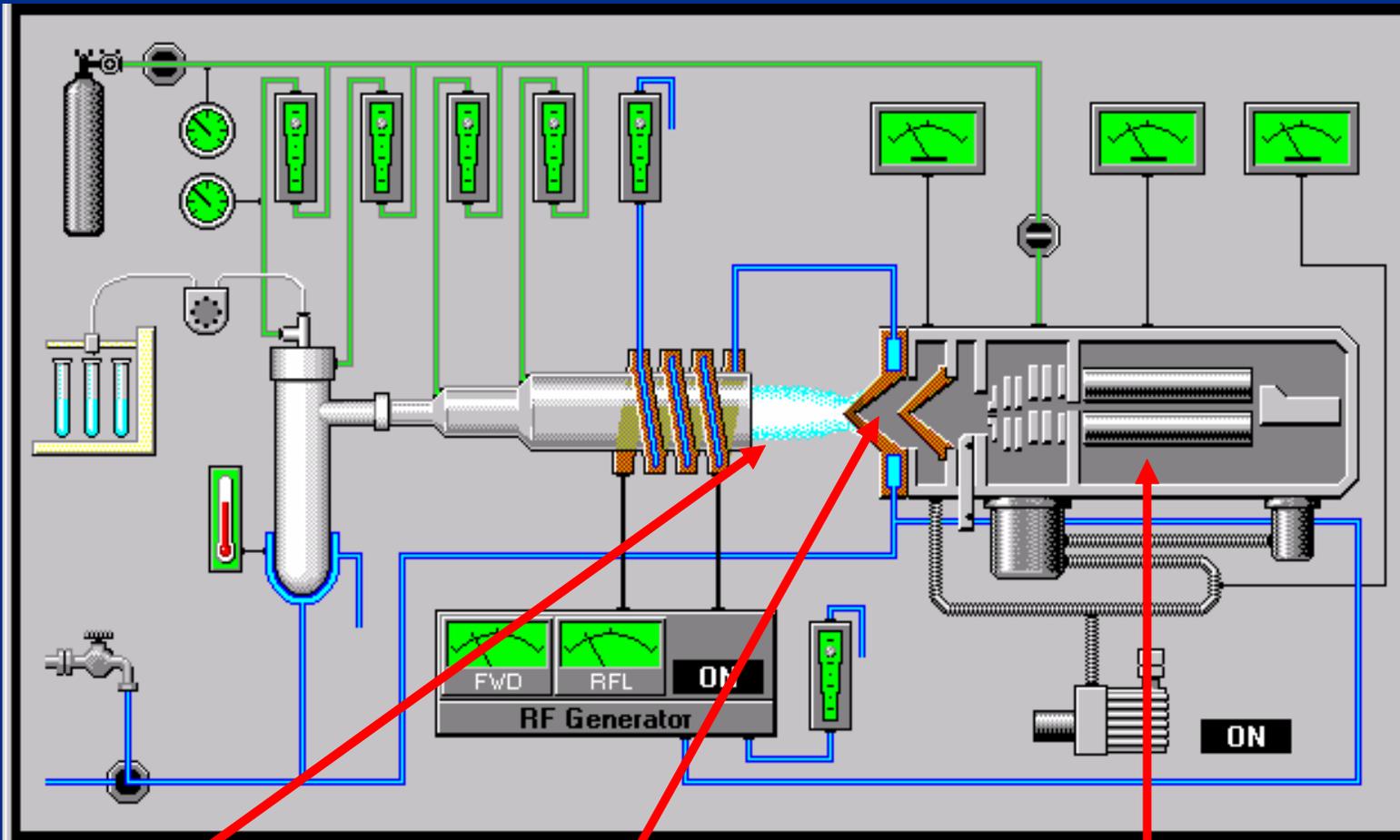
Nuclide	Specific Activity (dpm/g)	Relative Detection Sensitivities	
		Mass	Activity
^{238}Pu	3.8×10^{13}	1	5.1×10^7
^{238}U	7.4×10^5	1	1
^{236}U	1.4×10^8	1	1.9×10^2
^{235}U	4.8×10^6	1	6.5×10^0
^{234}U	1.4×10^{10}	1	1.9×10^4
^{233}U	2.1×10^{10}	1	2.8×10^4
^{232}u	4.9×10^{13}	1	6.6×10^7



- Perkin Elmer DRC-e
- 240-Sample CETAC ASX-510 Auto Sampler
- Cross Flow II Nebulizer – Ryton Scott Spray Chamber
- Quadrupole Mass Spectrometer

OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

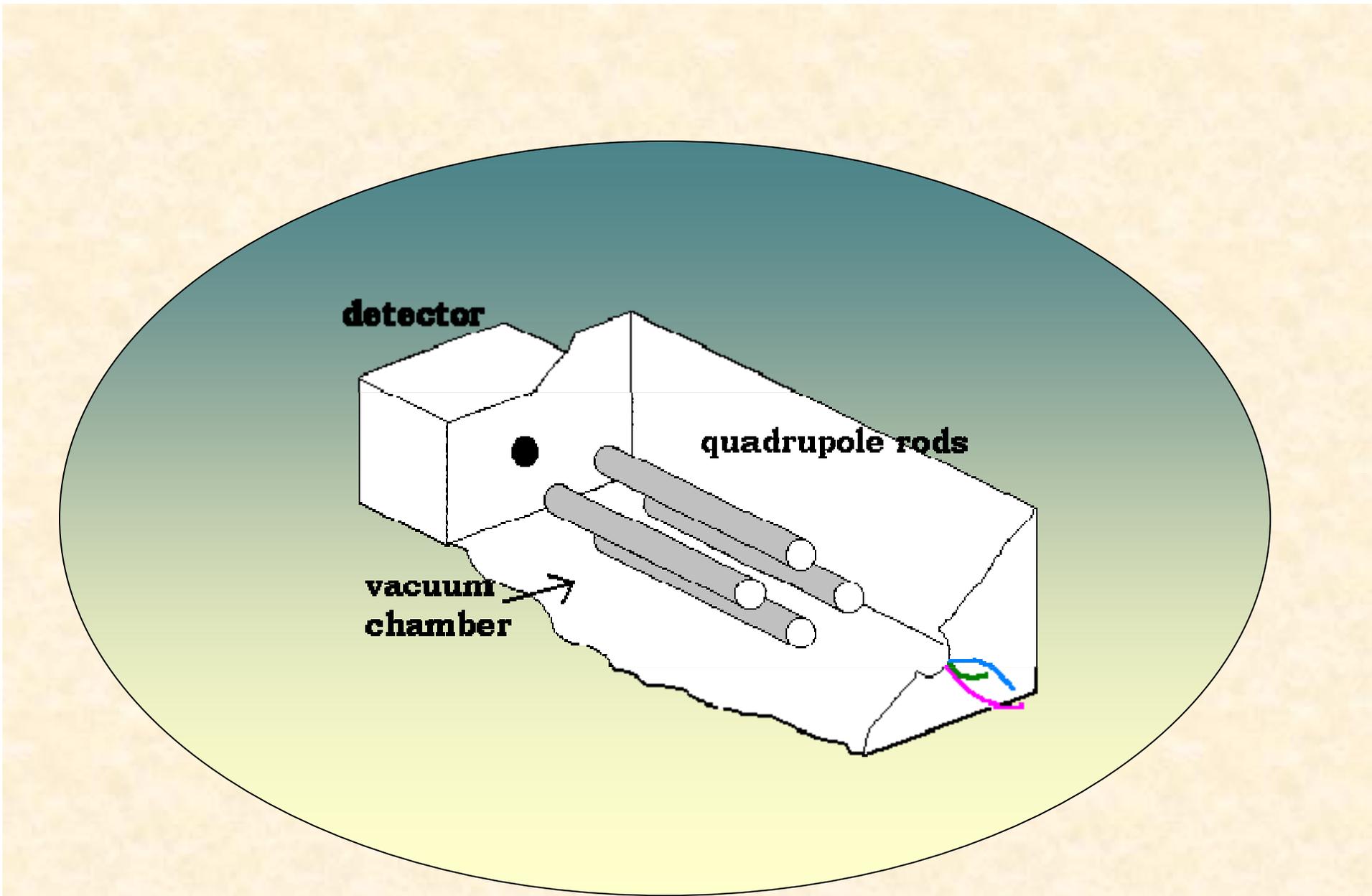
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Ionization

Extraction

Selection

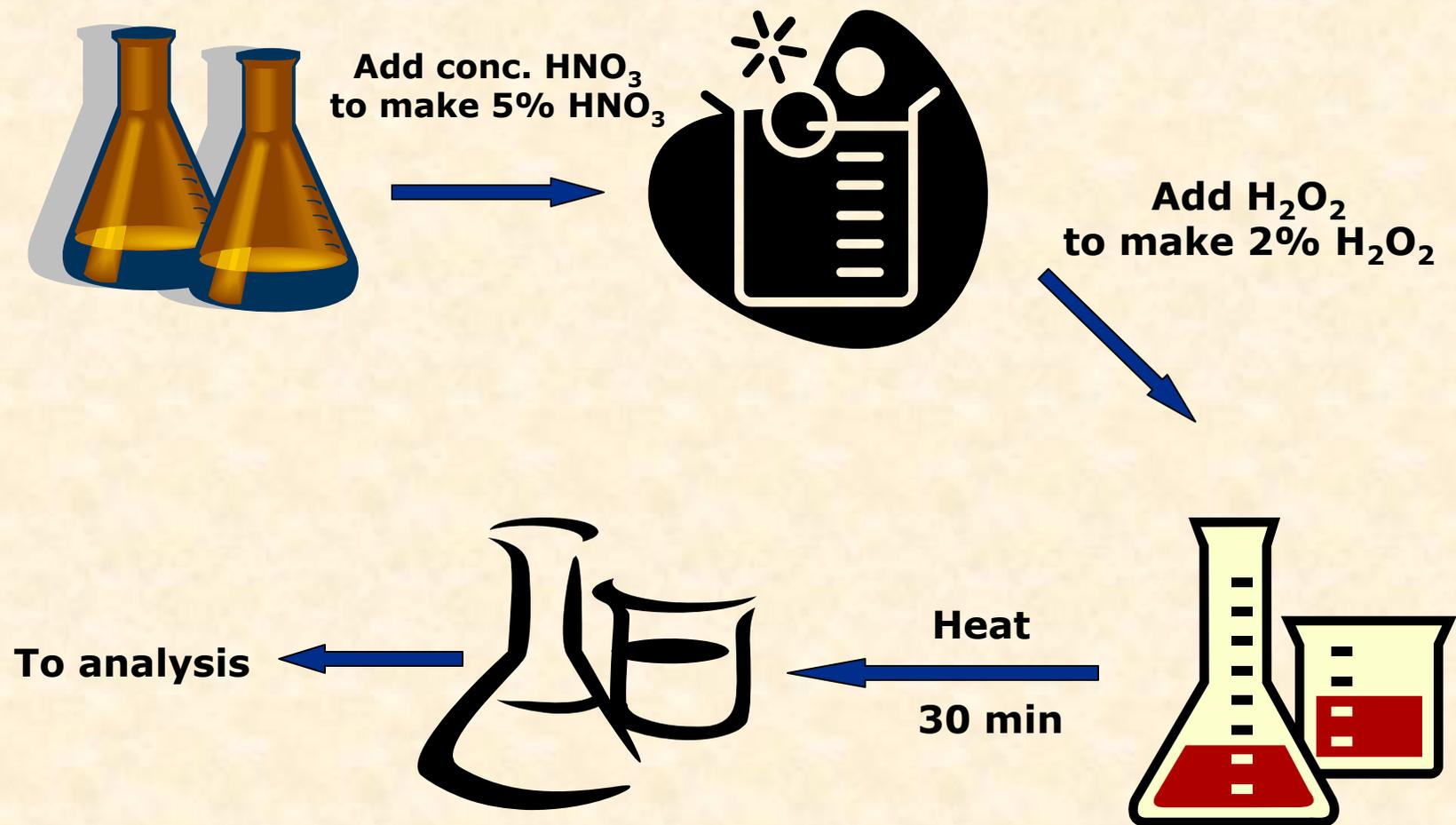


Instrumental Parameters

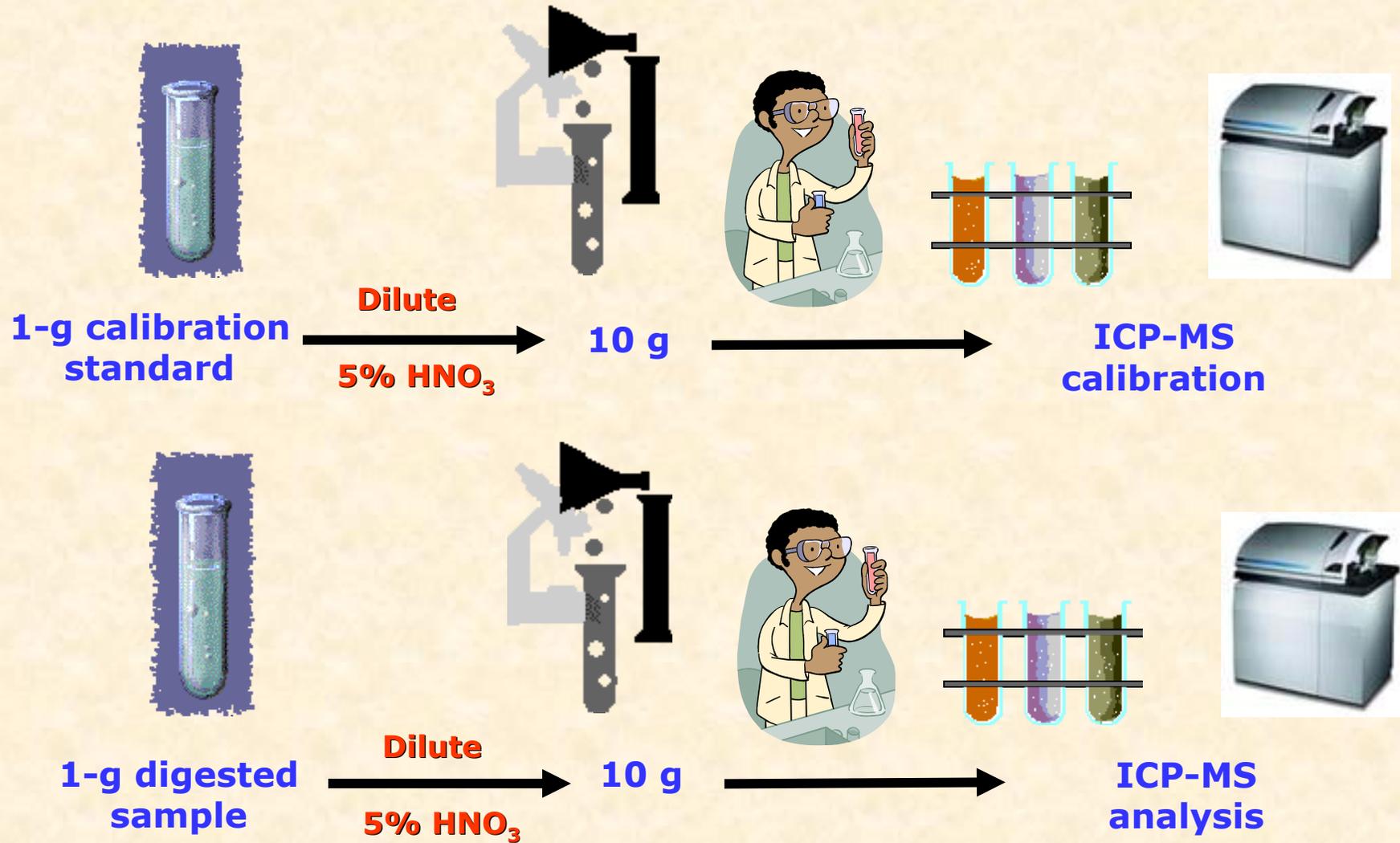
<i>Operating Parameters</i>	
RF power	1100 W
Plasma gas flow rate	15.0 L/min
Auxiliary gas	1.2 L/min
Carrier gas flow rate	0.92 L min
Nebulizer	Cross Flow II
Spray chamber	Ryton™ Scott-type
Sampling/skimmer cones	Nickel
Isotopes monitored	^{235}U , ^{236}U , ^{238}U
Scan mode	Peak hopping
Dwell time per AMU	400 ms
Integration time	4000 ms



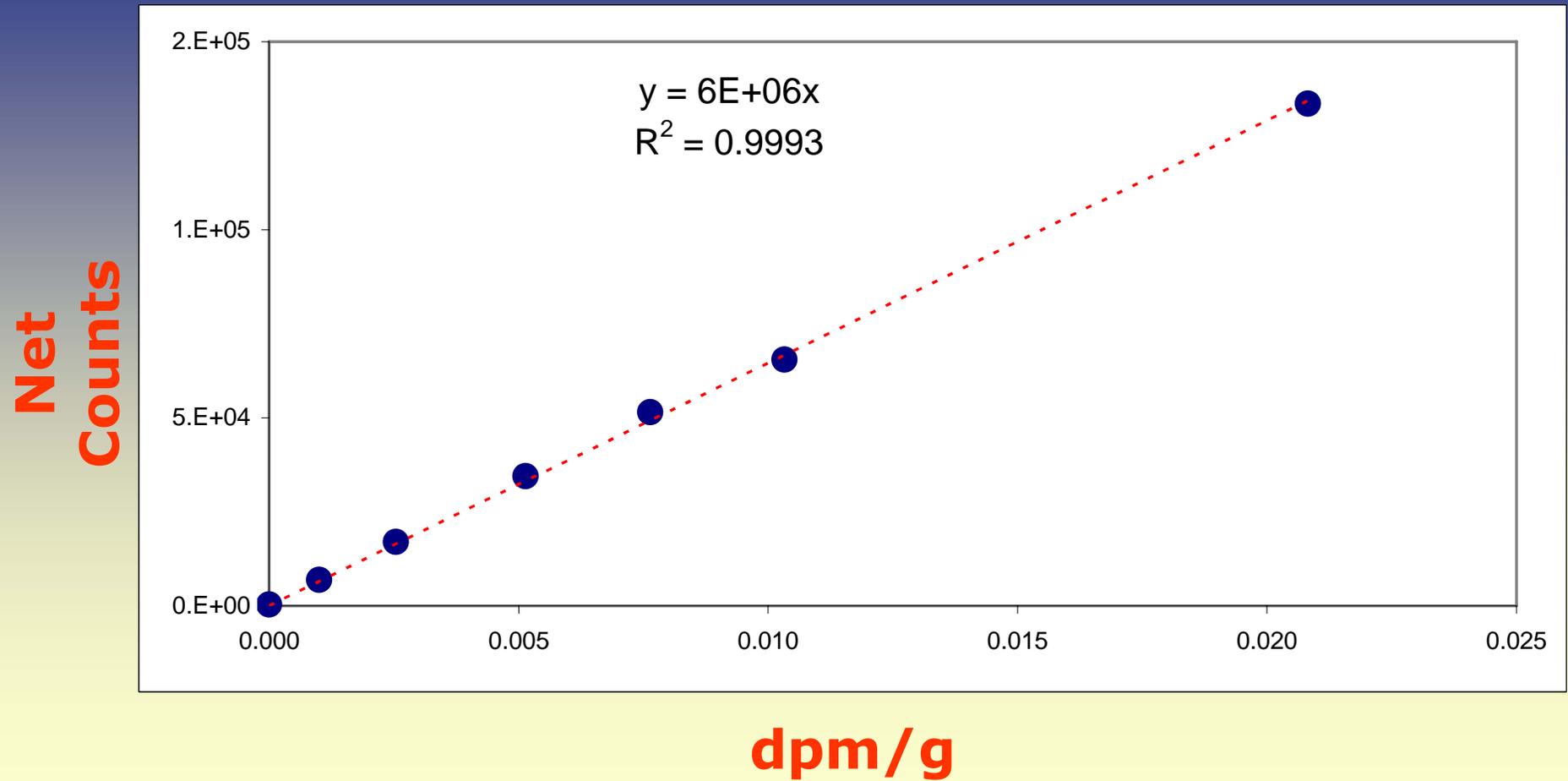
Sample Preparation



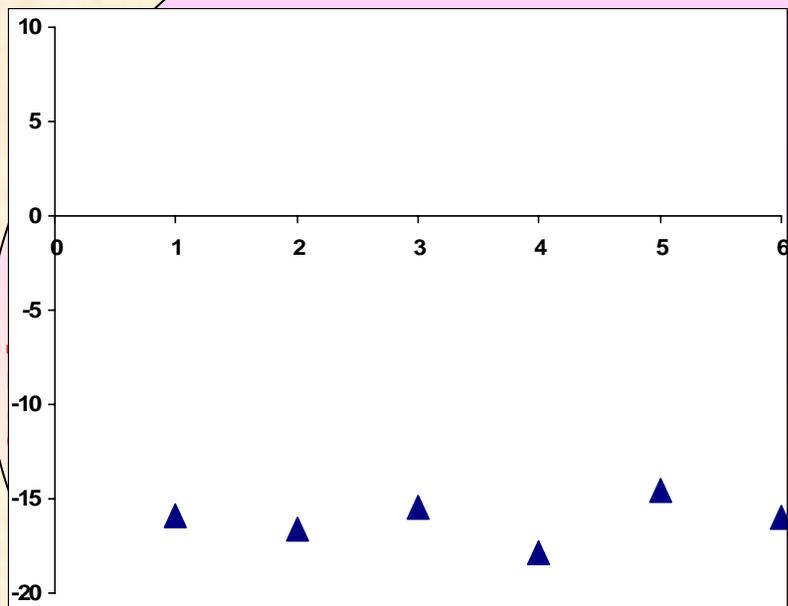
Analysis



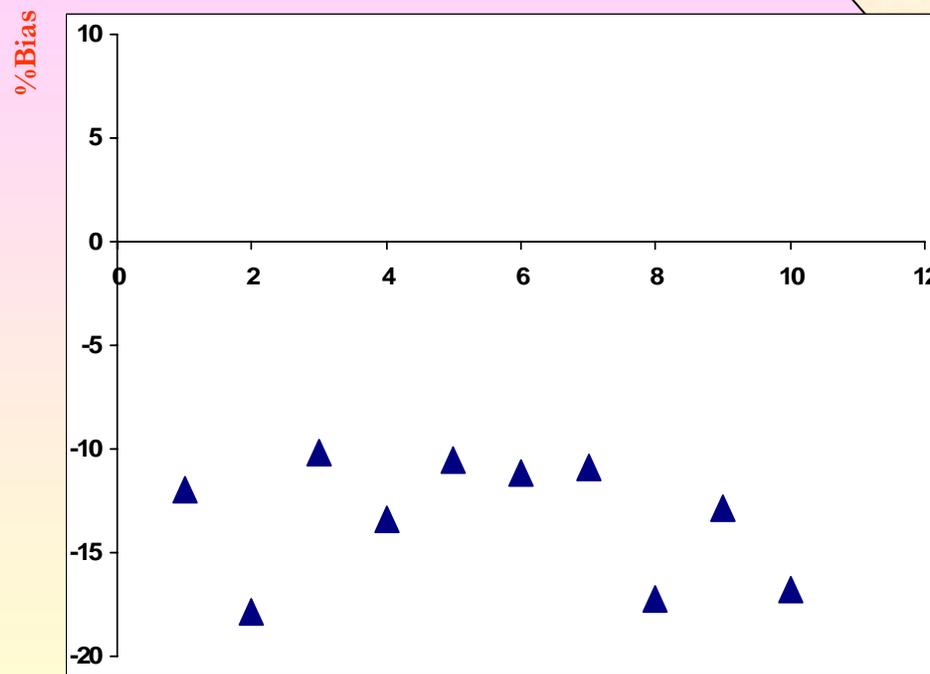
Calibration: ^{238}U



Initial Results



Synthetic urine



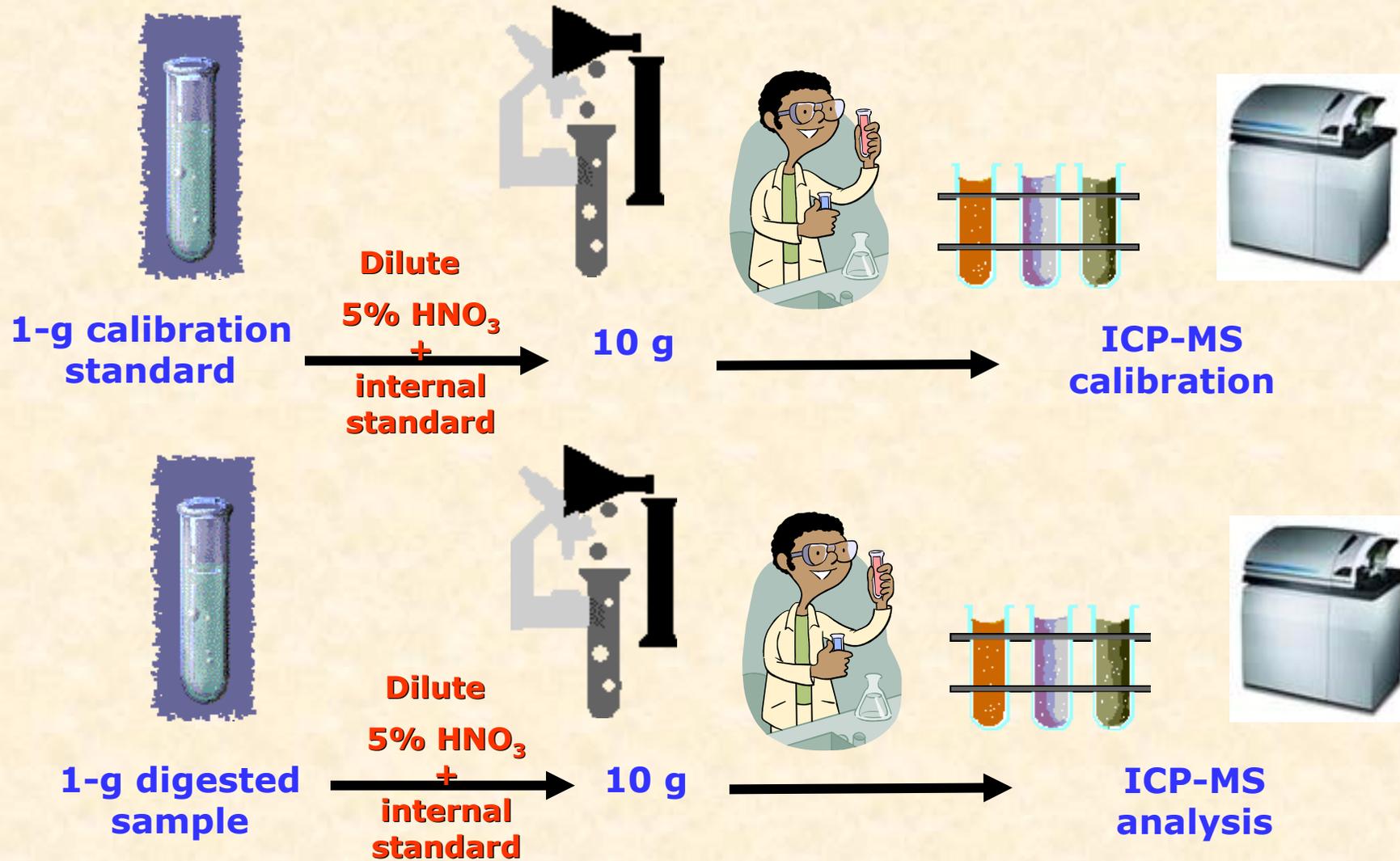
Natural urine

^{238}U

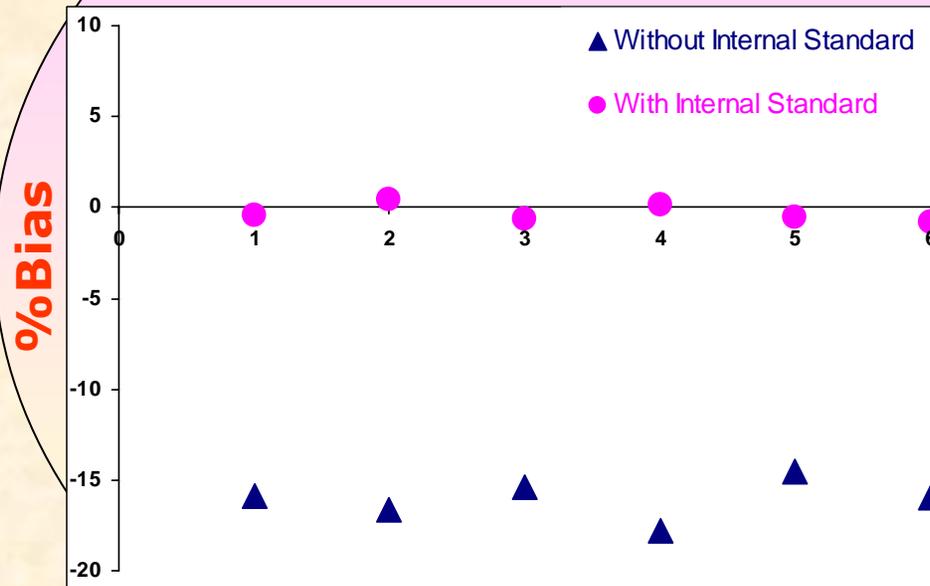
Internal Standard

- Surrogate element expected to mimic the behavior of the analyte of interest.
- Must not normally be present in the samples being analyzed.
- Must not interfere with the analyte of interest.
- Better accuracy if same internal standard solution is used in calibration and sample analysis.
- Ratio of analyte signal to internal standard signal is independent of variations in flow rates, sample introduction efficiency, plasma conditions, detector response, matrix effects, etc.
- Typical standards: Bi, Re, Rh, Ir, etc., used in uranium analysis.

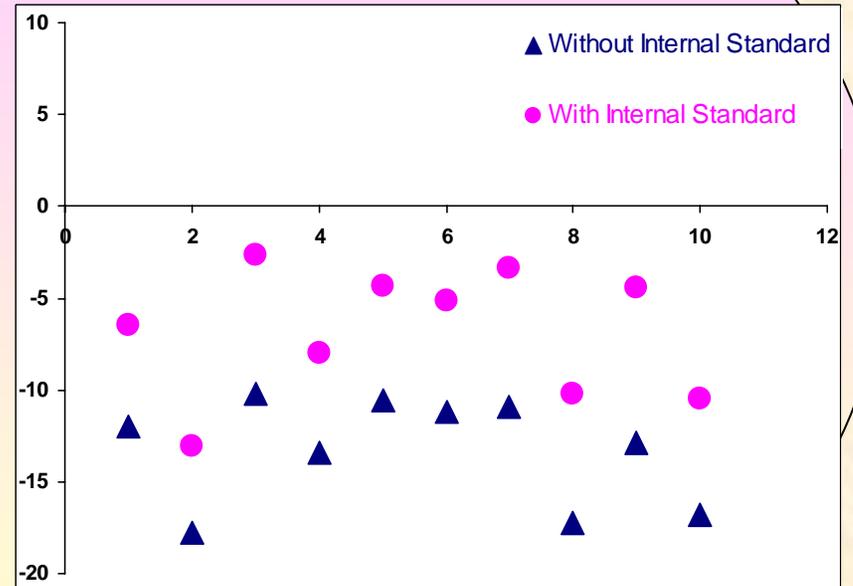
Analysis with Internal Standard



^{209}Bi Internal Standard Correction



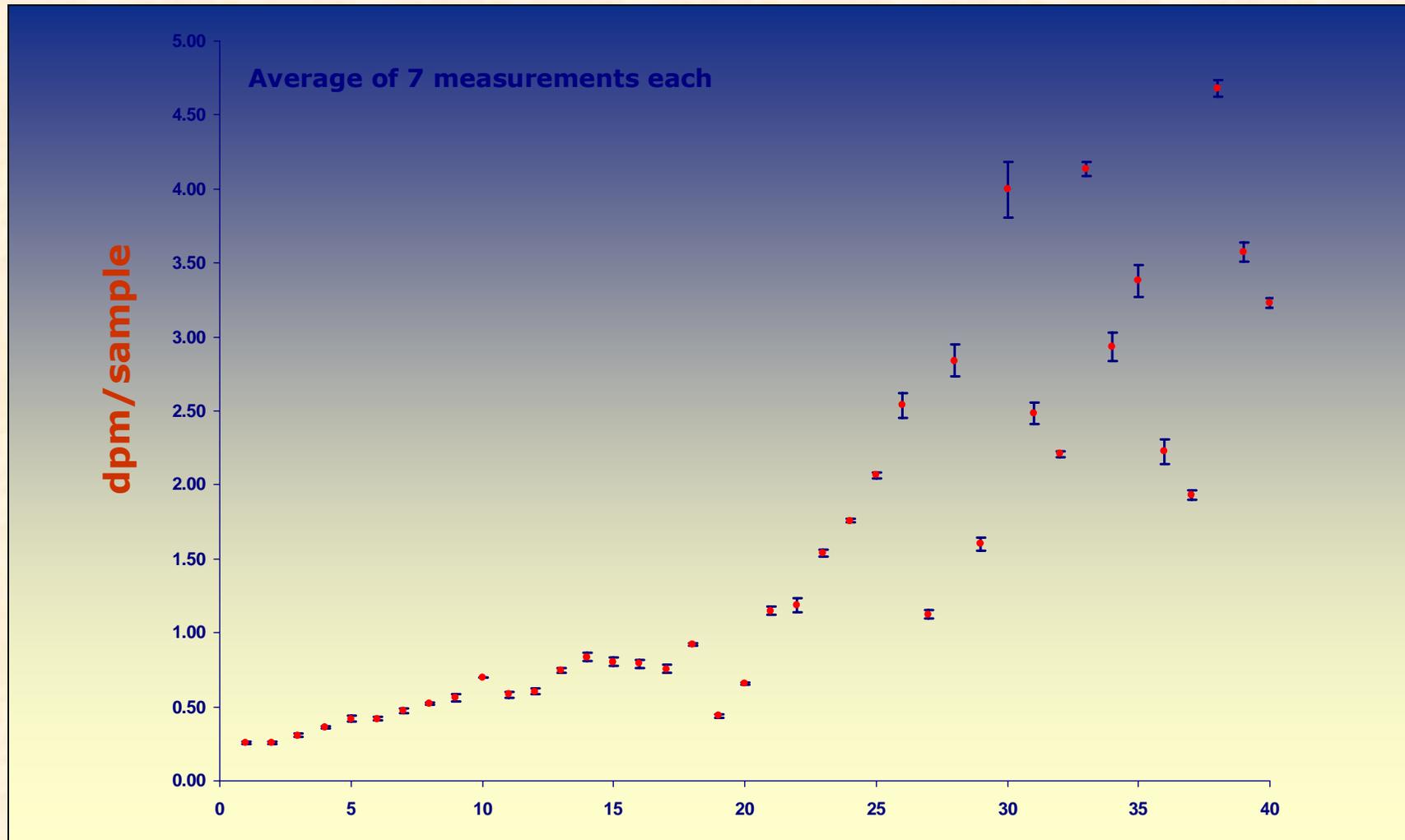
Synthetic urine

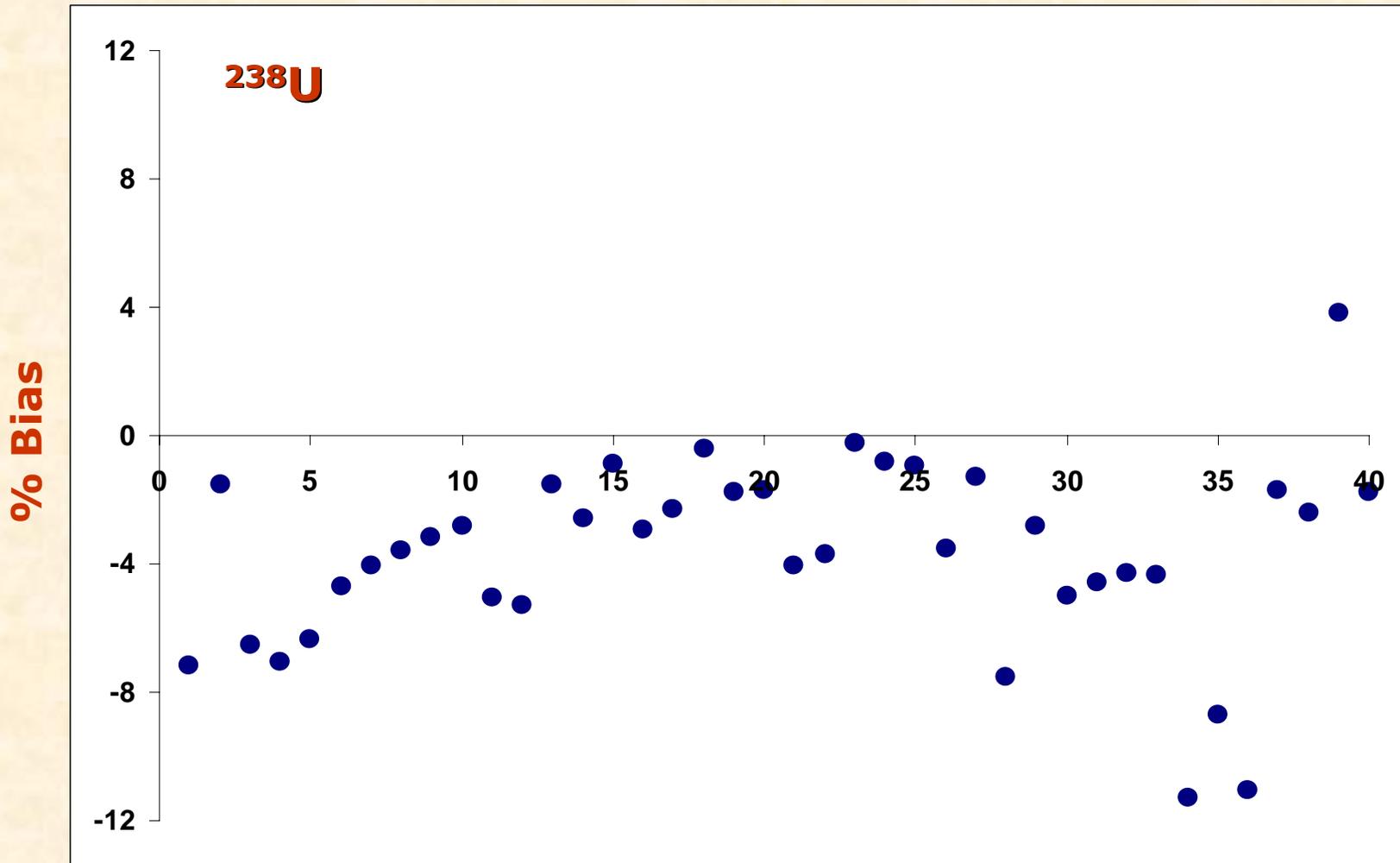


Natural urine

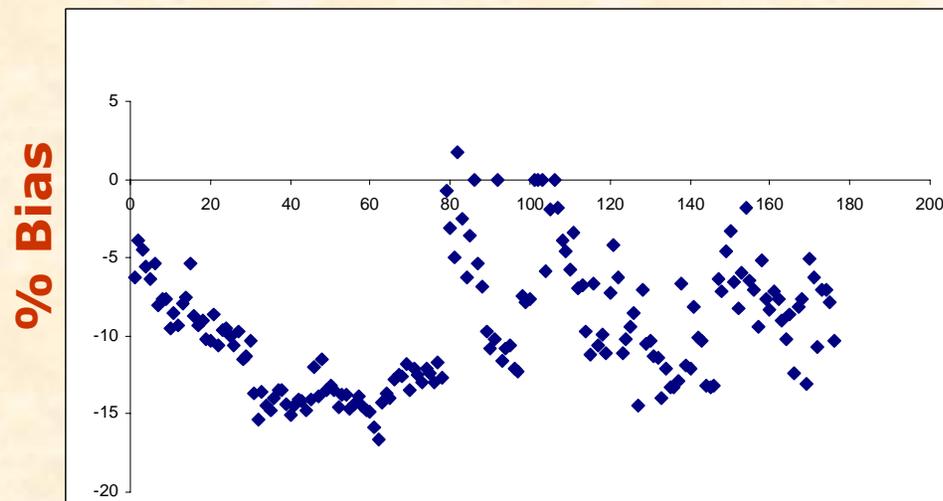
^{238}U

Blind Spiked Samples (ISP) Internal Standard: ^{209}Bi

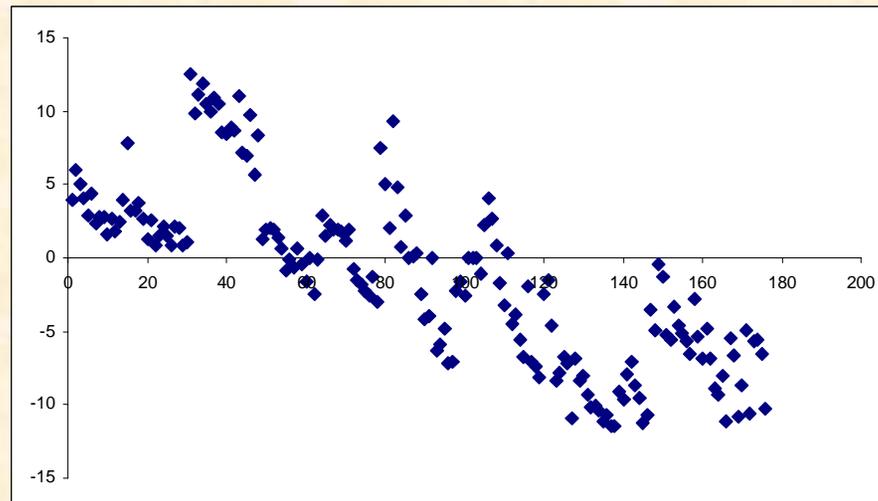




Other Internal Standards



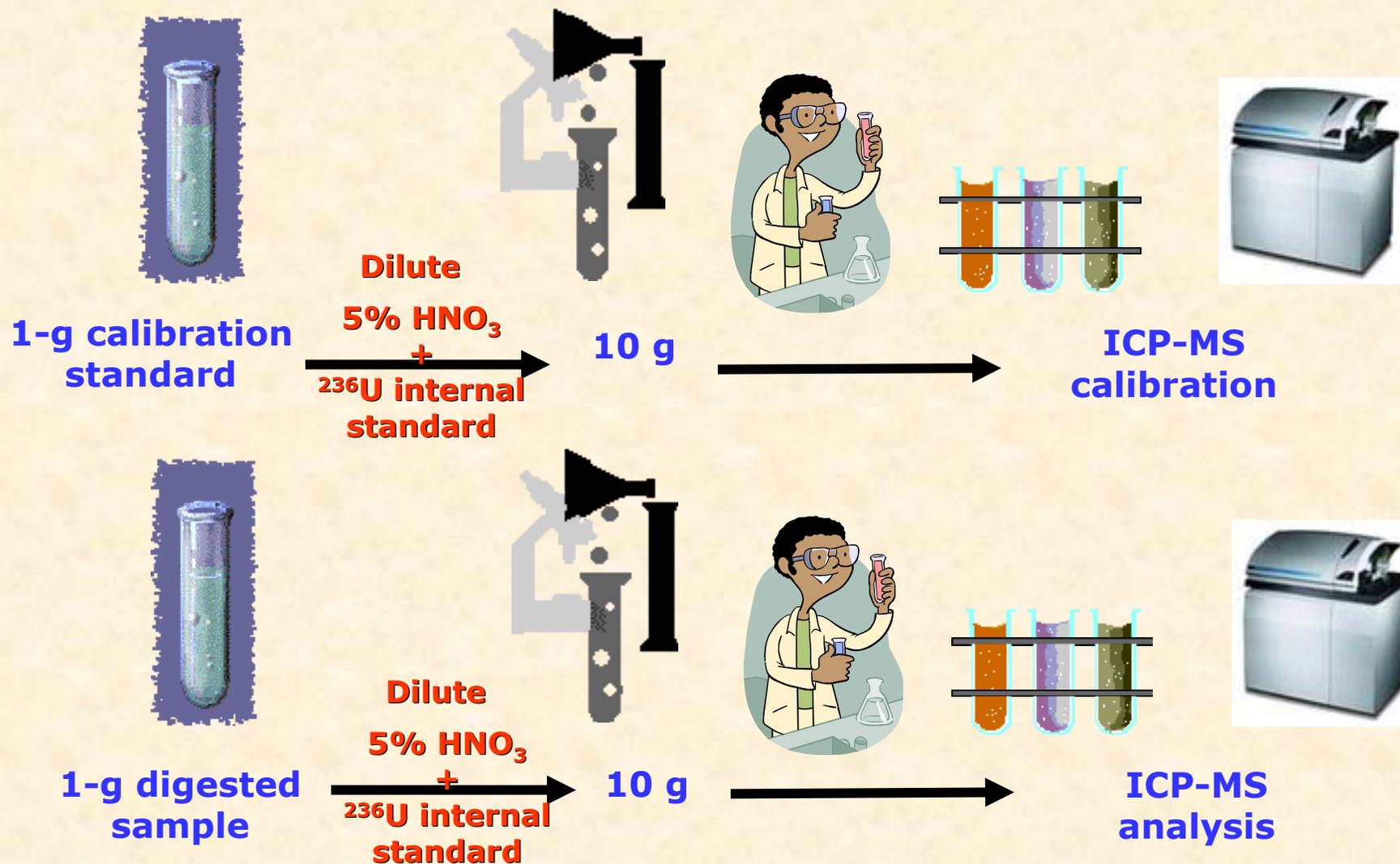
Re



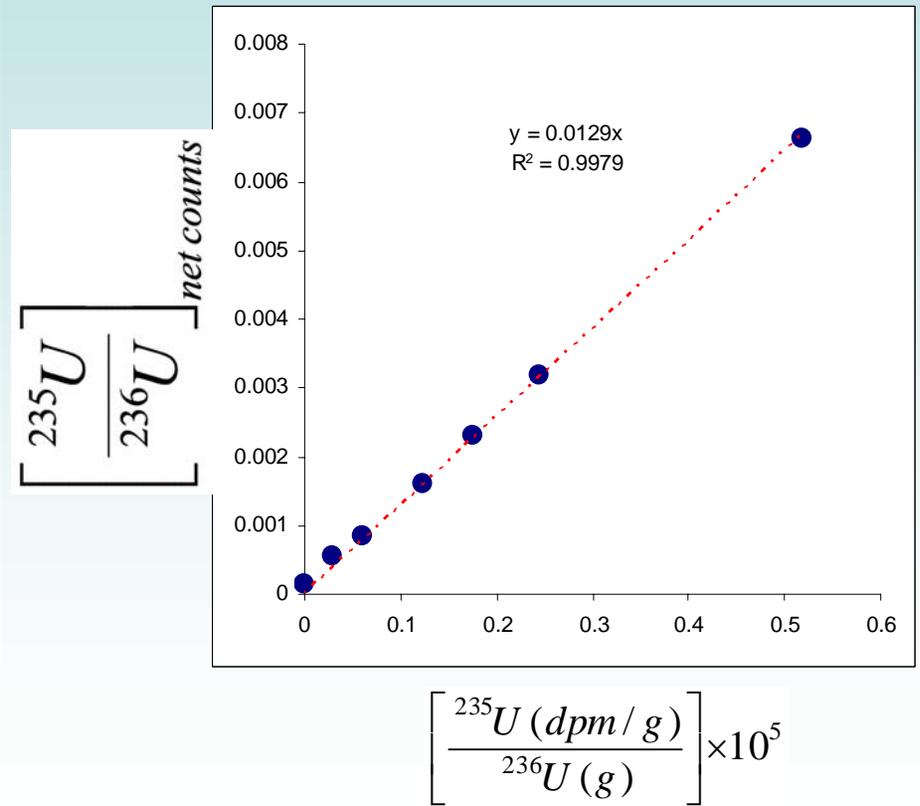
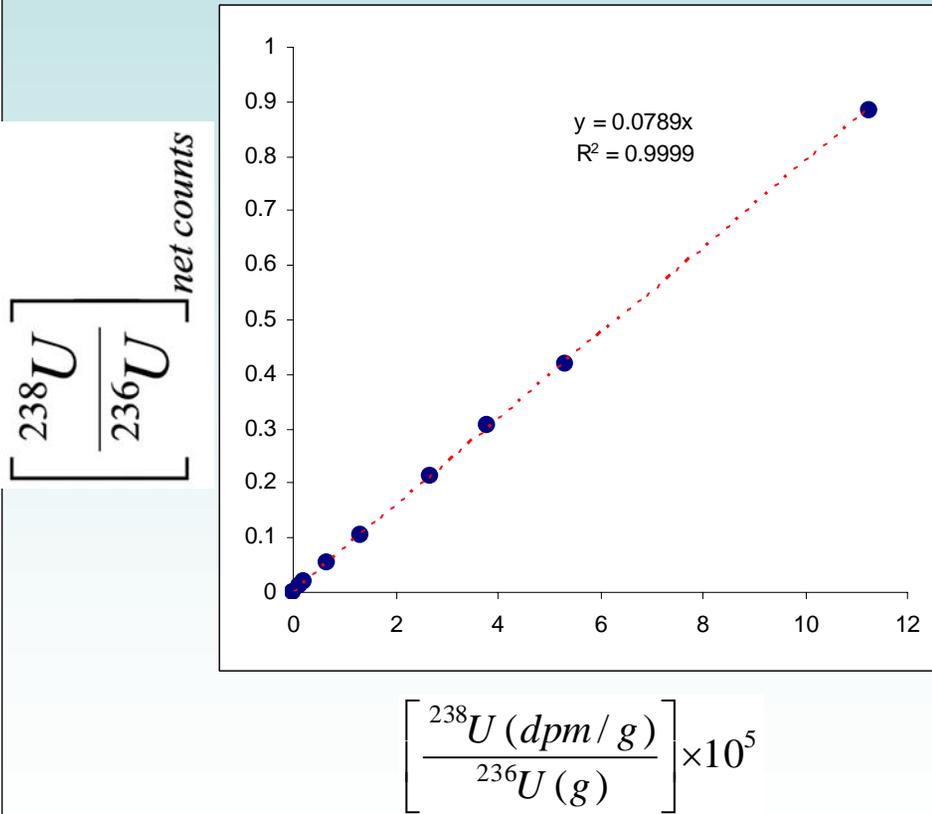
Rh

^{238}U

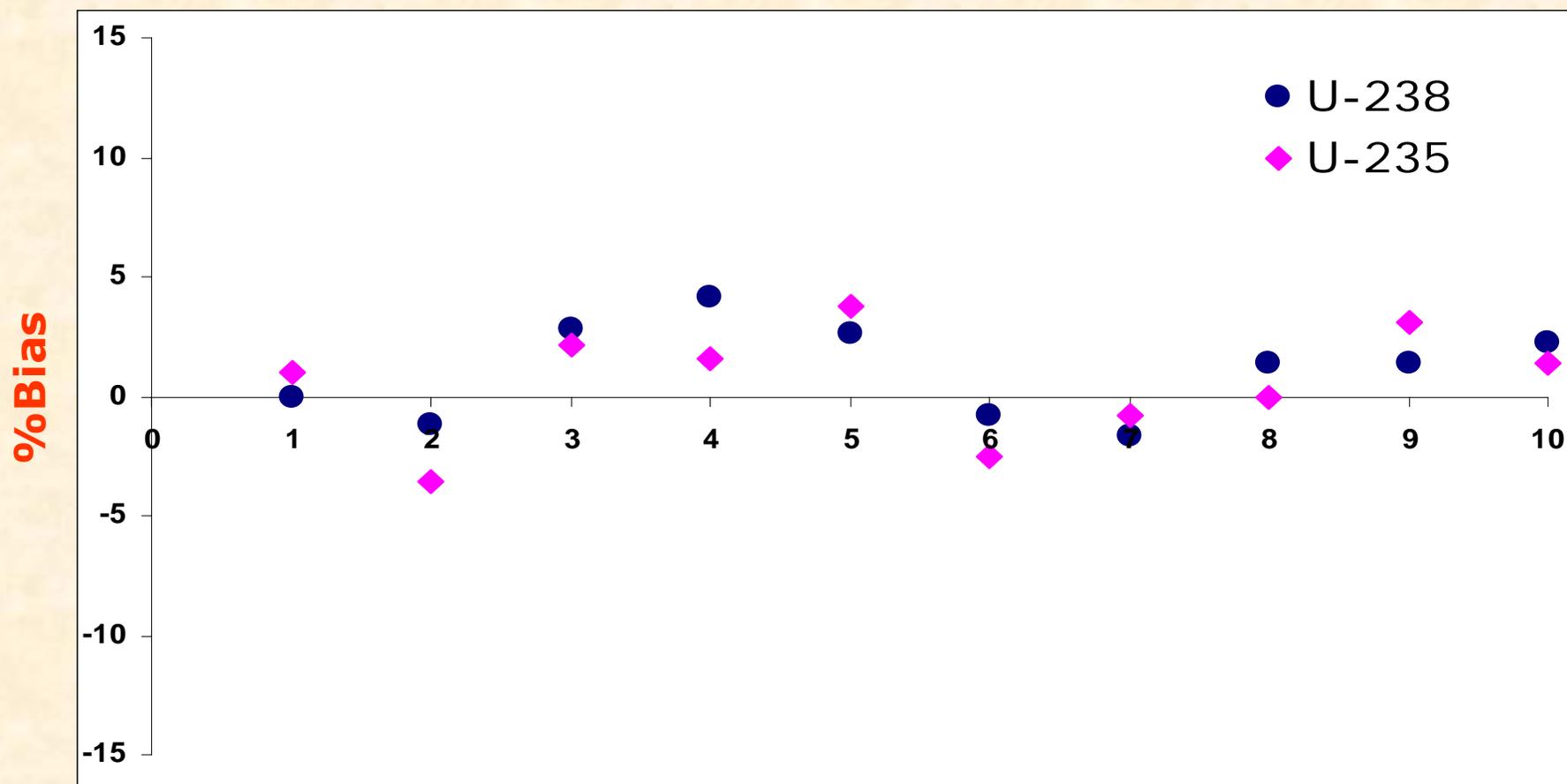
Analysis with Internal Standard



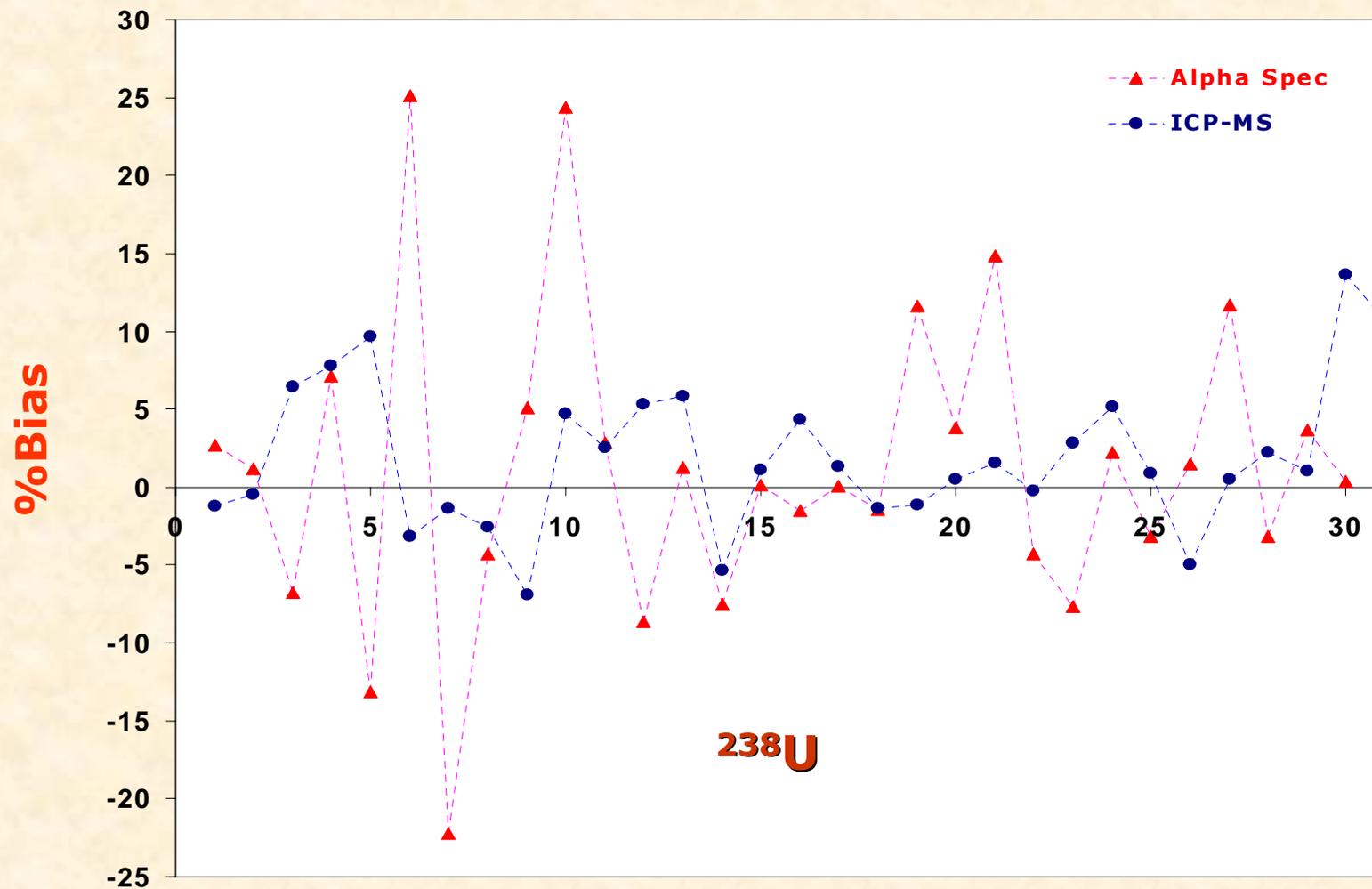
CALIBRATION WITH INTERNAL STANDARD ^{236}U



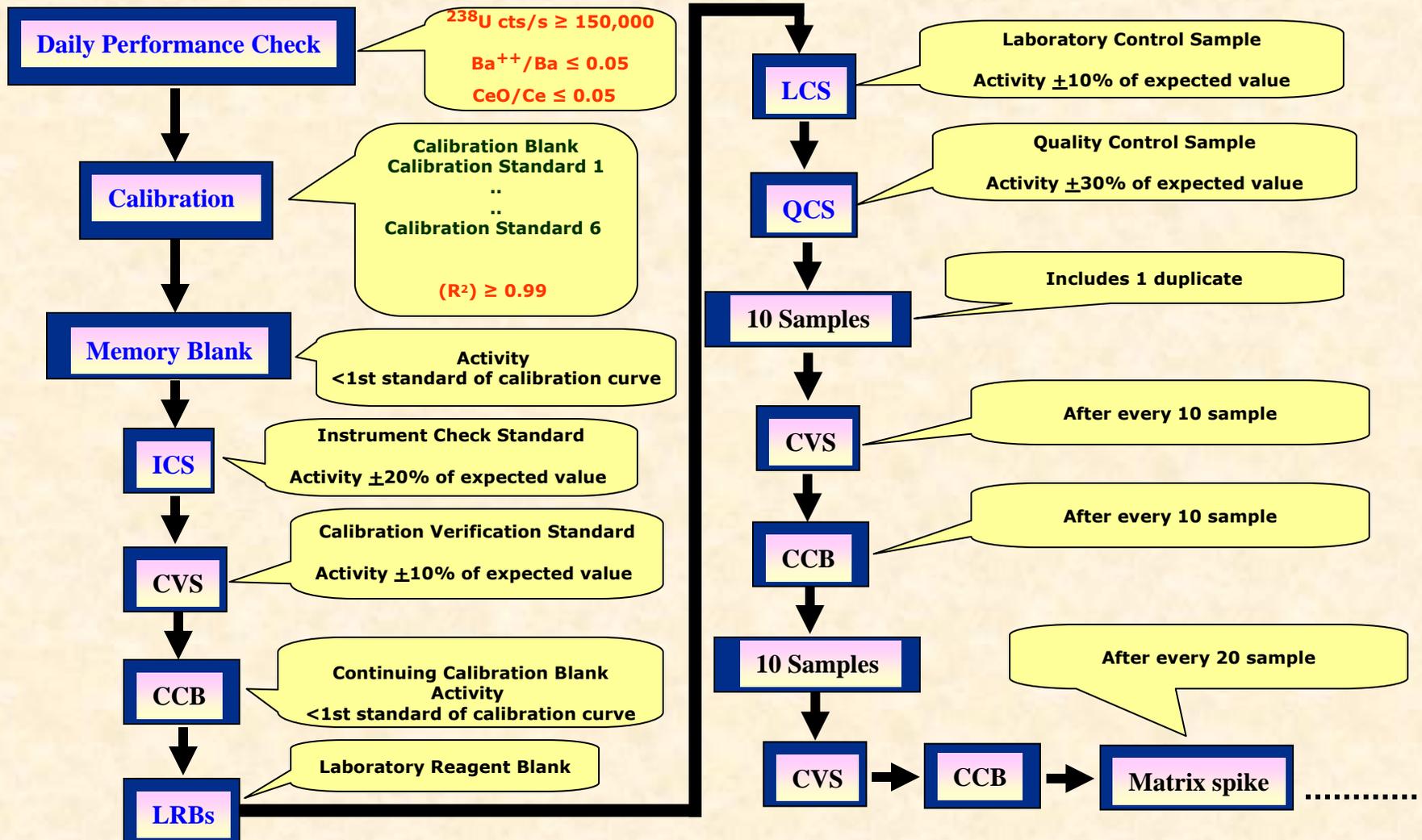
Blind Spiked Samples (ISP) Internal Standard: ^{236}U



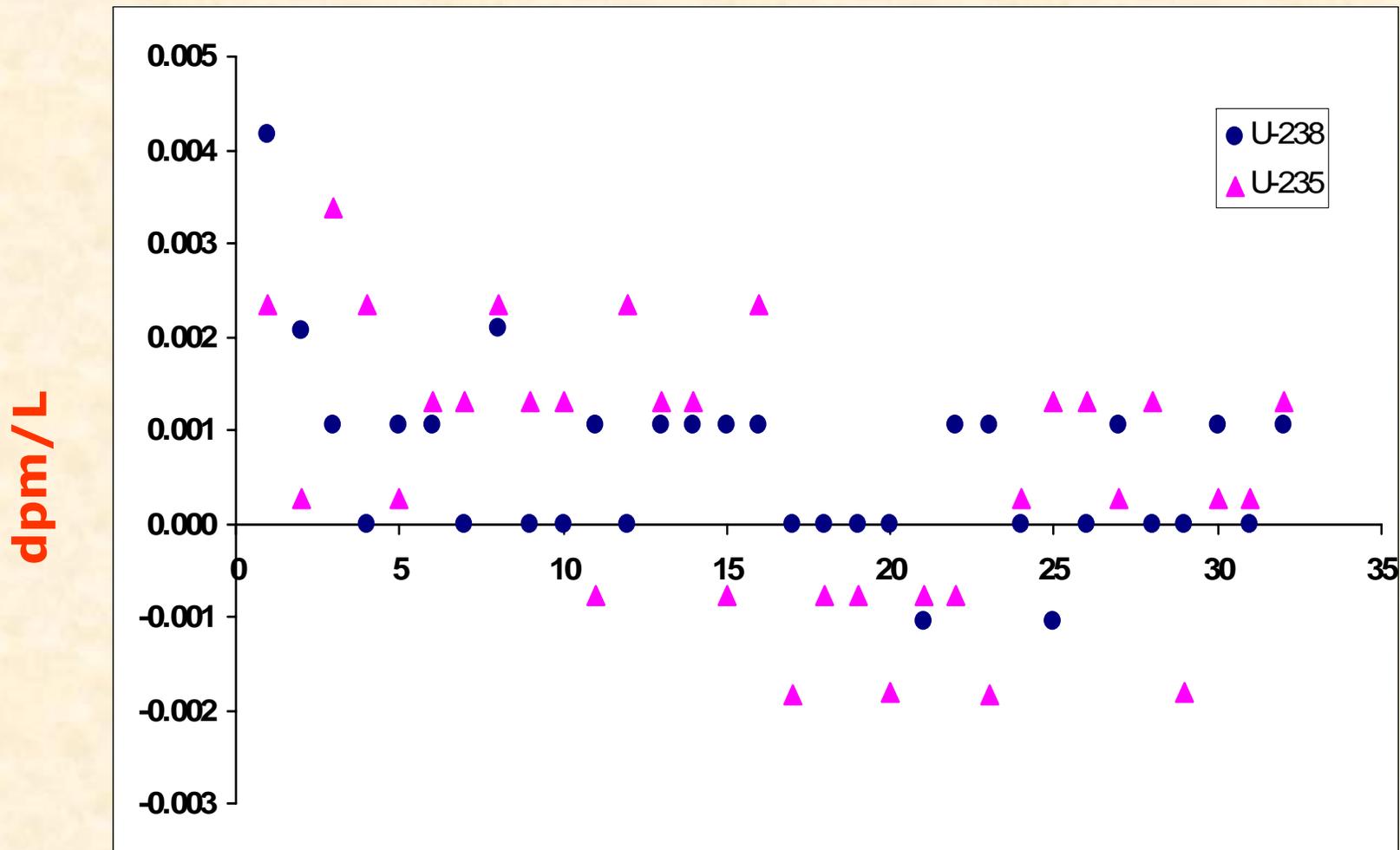
ICP-MS vs Alpha Spectrometry



Analysis Protocol



Laboratory Reagent Blank (LRB)



Calculations

$$A_{U-238} = k \times DF \times \left(\frac{C_{U-238}}{C_{U-236}} - \frac{B_{U-238}}{B_{U-236}} \right) \times 10^{-5} - LRB$$

k: Calibration Constant

DF: Dilution Factor

C: Sample Counts

B: Calibration Blank Counts

$$MDA (dpm / L) = 4.65 \times S_{LRB}$$

$$^{238}\text{U} : 0.005 \text{ dpm} / \text{L} (1.5 \text{ ng} / \text{L})$$

$$^{235}\text{U} : 0.007 \text{ dpm} / \text{L} (6.8 \text{ ng} / \text{L})$$

Final Words

Use of ^{236}U as an internal standard has improved reproducibility.

Granted Technical Equivalency by DOELAP.

Additional ideas being explored:

- **Improve MDA for ^{235}U by clean-up chemistry.**
- **Fecal samples?**
- **^{232}Th ?**

Alpha spectrometry continues to be used for other uranium isotopes.