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# *Actinides at the Crossroads: ICP-MS or Alpha Spectrometry?*

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## Why turn to mass spectrometry for radiochemical measurements?

Radiochemical techniques, especially $\alpha$ and $\beta$ counting, suffer from:

1. High spectral bandpass (spectral interferences)

2. High radiation absorption in matter (self-absorption)

3. Long counting periods, primarily for long-lived radionuclides

***Ultimately, these requirements translate into high labor costs and low turnaround***

**What might be some advantages of using ICP mass spectrometry?**

1. Mass spectrometers analyze isobars, not decay energy

   *$^{239}Pu$ and $^{240}Pu$, $^{235}U$ and $^{236}U$ may be determined separately by MS*

2. Measurement speed is very high (minutes per sample)

   *Relative to decay counting, 100-fold improvements might be attained*

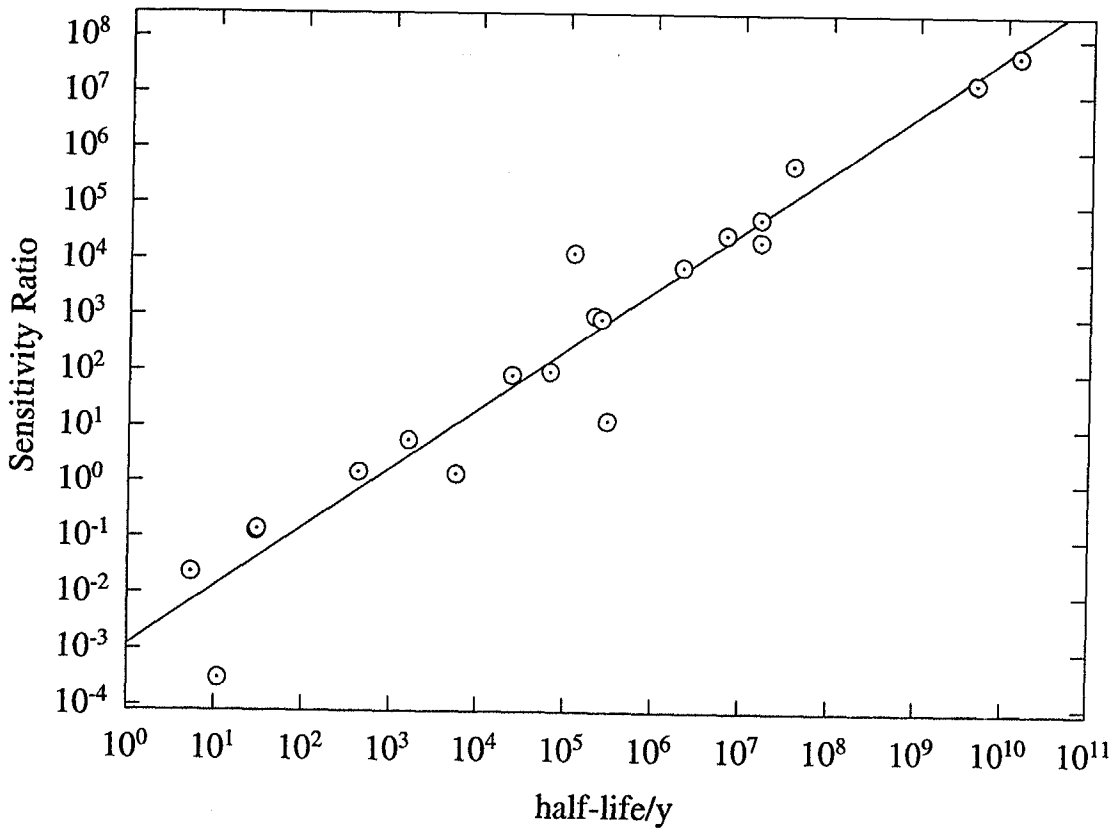
3. Samples may be introduced as solids, liquids, or gases

   *Different introduction options can be used to reduce preparative requirements and attain required detection limits*

4. Sensitivity and interferences are independent of half-life

# Sensitivity of ETV-ICP-MS relative to decay counting (versus half-life)

M. Smith *et al.*, J. Radioanal. Nucl. Chem, **160**, 341 (1992).



# ICP-MS instrument detection limits (in mBq $L^{-1}$) for dissolved actinide isotopes

J. Crain *et al.*, J. Radioanal. Nucl. Chem., **194**, 133 (1995).

| | scanning | | multiple ion monitoring | | GRRASP |
|---|---|---|---|---|---|
| isotope | PN | USN | PN | USN | RDL [a] |
| $^{230}Th$ | 2000 | 50 | 500 | 8 | 37 |
| $^{232}Th$ | 0.04 | $4\times10^{-3}$ | 0.04 | $4\times10^{-3}$ | 37 |
| $^{233}U$ | 2000 | 40 | 200 | 4 | 22 |
| $^{234}U$ | 900 | 20 | 200 | 5 | |
| $^{235}U$ | 0.4 | $8\times10^{-3}$ | 0.06 | $2\times10^{-3}$ | 22 |
| $^{236}U$ | 10 | 0.2 | 2 | 0.05 | |
| $^{238}U$ | 0.1 | 0.01 | 0.1 | $9\times10^{-3}$ | 22 |
| $^{237}Np$ | 100 | 3 | 20 | 0.5 | 37 |
| $^{239}Pu$ | $1\times10^{4}$ | 200 | 2000 | 50 | 0.37 |

[a] General Radiochemistry and Routine Analytical Services Protocol, EG&G Rocky Flats Plant (1991).

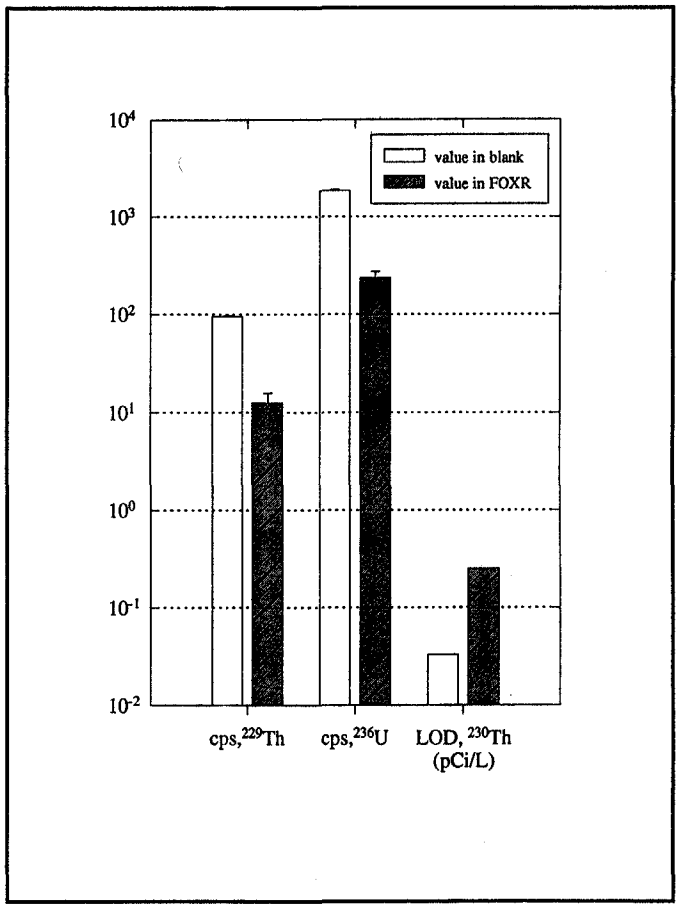
# Effect of dissolved solids on USN-ICP-MS analysis

*analysis of 5:2 Fox River water, spiked with $^{229}Th$ and $^{236}U$*

| Isotope | mBq $L^{-1}$, ICP-MS | mBq $L^{-1}$, α-spec |
|---|---|---|
| $^{226}Ra$ | ND [a] | 15 ± 4 |
| $^{230}Th$ | < 9 | 1.8 ± 0.3 |
| $^{232}Th$ | NA [b] | 1.1 ± 0.3 |
| $^{234}U$ | 12 ± 2 | 15.9 ± 0.7 |
| $^{238}U$ | 11.1 ± 0.7 | 11.5 ± 0.7 |

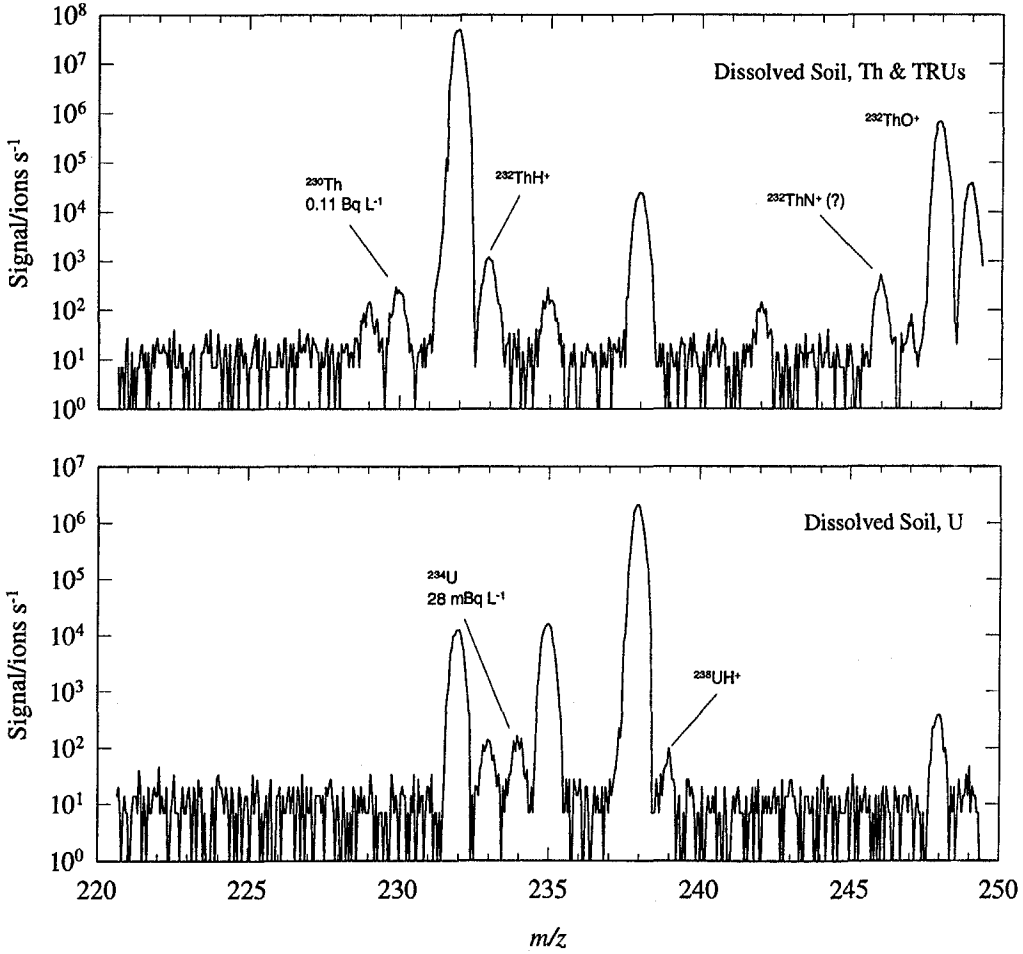
[a] radium was not detected

[b] $^{232}Th$ was not determined due to low $^{229}Th$ intensity




**Dissolved solids exert a strong negative influence upon ICP-MS figures of merit (esp. with ultrasonic nebulization)**

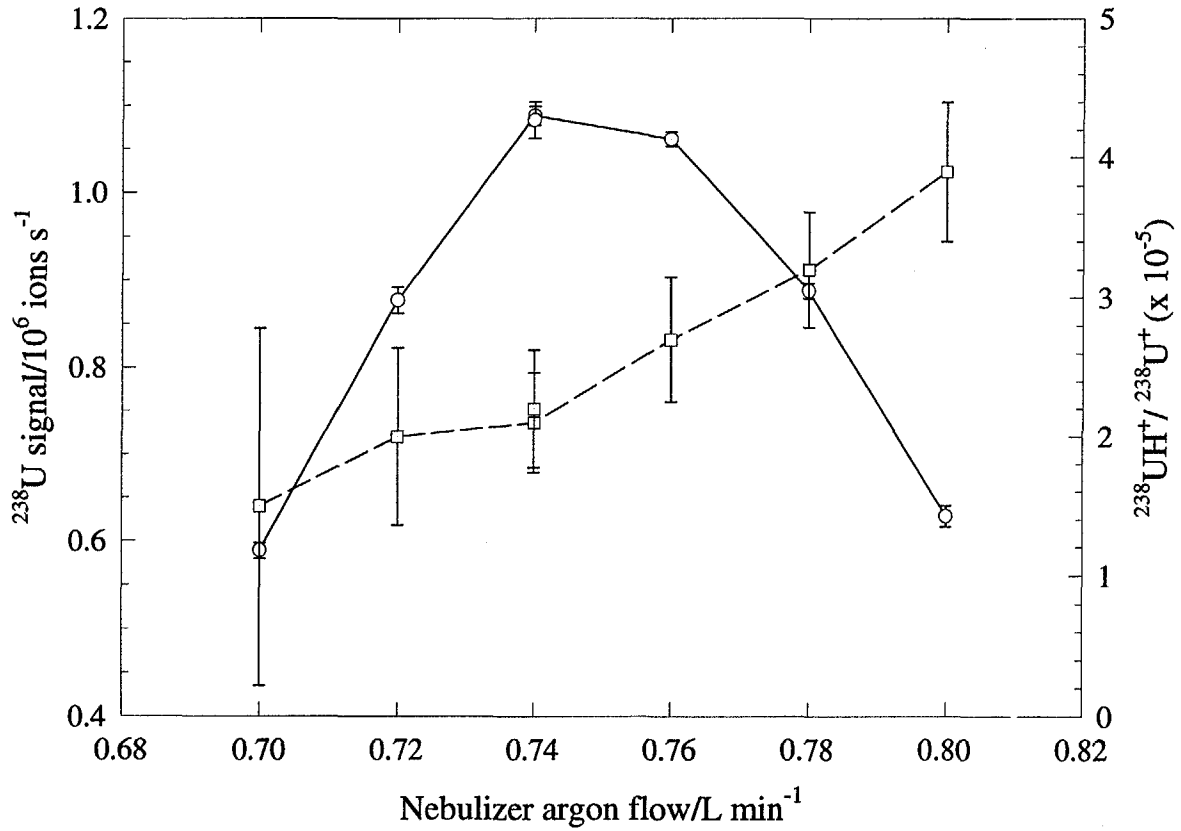
# Polyatomic ion interferences in ICP-MS actinide measurements




4th CIRMS Meeting, NIST-Gaithersburg, November, 28-30, 1995.

# Effect of operating conditions on uranium and protonated uranium signal

J. Crain and J. Alvarado, J. Anal. At. Spectrom., **9**, 1223 (1994).



## ICP mass spectrometry performance in actinide determinations

a comparative evaluation of benefits and drawbacks

| | Benefit | Concern |
|---|---|---|
| 1. | Isobaric selectivity | Spectral overlaps remain problematic (though less severe) |
| 2. | Flexible sample introduction | Sample is consumed |
| 3. | Low integration times | |
| 4. | Good sensitivity for $t_{1/2} \gtrsim 10^3$y (even better with HR-ICP-MS) | Sensitivity depends on sample matrix |

**In environmental applications, chemical preparation remains important!**

*(resolve isobars, remove matrix)*

## Determination of Actinide Elements in Soil

J. Crain and L. Smith *et al.*, J. Radioanal. Nucl. Chem., **194**, 133 and 151 (1995).

1. Leach or Fuse/Dissolve Soil

2. Add $^{229}Th$, $^{232,233\text{ or }236}U$, $^{242}Pu$ and equilibrate

3. Eliminate matrix by co-ppt'n or ion exchange

4. Separate U from Th and TRUs on EIChroM TRU™ resin
   - ☞ Elute Th/TRUs with tetrahydrofuran tetracarboxylic acid (THFTCA)
   - ☞ Elute U with ammonium binoxalate, $NH_4(HC_2O_4)$

5. Determine radionuclides by isotope dilution

# Leachable $^{230}$Th and $^{239}$Pu in soil as determined by ICP-MS and α spectrometry

| | | $^{230}$Th/Bq kg$^{-1}$ | | $^{239}$Pu/Bq kg$^{-1}$ | | ICP-MS/α-spec. | |
|---|---|---|---|---|---|---|---|
| sample | mass/g | ICP-MS | α-spec. | ICP-MS | α-spec. | $^{230}$Th | $^{239}$Pu |
| SRM 4350B | 2.02 | 18 | 18.1 | < 4 | 0.7 | 0.99 | - |
| | 1.9 | 17 | 19.6 | < 3 | 0.7 | 0.87 | - |
| SRM 4353 | 2.05 | 26 | 32 | 6 | 6.8 | 0.81 | 0.88 |
| | 1.84 | 30 | 27 | 7.2 | 7.2 | 1.11 | 1.00 |
| SRM 4354 | 1.43 | 12 | 11.8 | 5 | 4.0 | 1.02 | 1.25 |
| | 1.49 | 11 | 13.3 | 3.9 | 3.3 | 0.83 | 1.18 |
| QAP 37 | 3.397 | 10.6 | 10.7 | 7 | 6.1 | 0.99 | 1.15 |
| QAP 38 | 2.89 | 33 | 34.4 | 8 | 9.6 | 0.96 | 0.83 |
| QAP 39 | 3.08 | 9 | 9.3 | 2.0 | 1.1 | 0.97 | 1.82 |
| | | | | | $\bar{x} \pm s$ | 0.95 ± 0.10 | 1.16 ± 0.33 |
| | | | | | t (μ=1) | 1.50 | 1.30 |

# Leachable $^{234}U$ and $^{238}U$ in soil as determined by ICP-MS and α spectrometry

| | $^{234}U$/Bq kg$^{-1}$ | | $^{238}U$/Bq kg$^{-1}$ | | ICP-MS/α-spec. | | |
|---|---|---|---|---|---|---|---|
| Sample | ICP-MS | α-spec. | ICP-MS | α-spec. | $^{234}U$ | $^{238}U$ | $^{234}U/^{238}U$ |
| SRM 4350B | 16 | 18 | 13 | 14.2 | 0.89 | 0.92 | 0.97 |
| | 16 | 19 | 13 | 14.8 | 0.84 | 0.88 | 0.96 |
| SRM 4353 | 20 | 20 | 18 | 20 | 1.00 | 0.90 | 1.11 |
| | 19 | 22 | 18 | 22 | 0.86 | 0.82 | 1.06 |
| SRM 4354 | 14 | 13.6 | 14 | 13.1 | 1.03 | 1.07 | 0.96 |
| | 14 | 14.4 | 14 | 14.2 | 0.97 | 0.99 | 0.99 |
| QAP 37 | 12.1 | 13.8 | 11.0 | 12.9 | 0.88 | 0.85 | 1.03 |
| QAP 38 | 15.8 | 17.9 | 16 | 17.0 | 0.88 | 0.94 | 0.94 |
| QAP 39 | 8.5 | 9.4 | 8.1 | 9.4 | 0.90 | 0.86 | 1.05 |
| | | | | $\bar{x} \pm s$ | 0.92 ± 0.07 | 0.91 ± 0.08 | 1.01 ± 0.06 |
| | | | | t (μ=1) | 3.80 | 3.40 | 0.42 |

## Determination of uranium isotopic composition on smears

L. Smith and J. Crain *et al.*, unpublished data

1. Dry ash and dissolve smear in $HF/HNO_3$
2. Digest sample and reconstitute in 8M $HNO_3$
3. Remove Pu by anion exchange
4. Isolate U by extraction chromatography (EIChroM TRU™ resin)
5. Electroplate and determine U activity ratios by $\alpha$ spectrometry
6. Leach uranium from planchet and determine U isotope ratios by ICP-MS and TIMS

## Activity ratios ($^{234}U/^{238}U$) as determined by mass spectrometry and α spectrometry

$^{235+236}U$ not tabulated due to interference in α spectrum

| | Activity Ratio | | | | |
|---|---|---|---|---|---|
| Smear | α-spec | TIMS | ICP-MS | TIMS/α-spec | ICP-MS/α-spec |
| 1 | 4.29 | 3.18 | 4.56 | 0.741 | 1.063 |
| 2 | 6.70 | 4.89 | 5.95 | 0.730 | 0.888 |
| 3 | 8.77 | 8.34 | 8.88 | 0.951 | 1.012 |
| 5 | 8.37 | 9.87 | 8.82 | 1.179 | 1.054 |
| 6 | 0.59 | 0.60 | 0.60 | 1.008 | 1.017 |
| 8 | 11.2 | 10.50 | 8.38 | 0.934 | 0.748 |
| | | | $\bar{x} \pm s$ | 0.92 ± 0.17 | 0.982 ± 0.097 |
| | | | t (μ=1) | 1.15 | 0.45 |

## Uranium isotopic abundances (in atom percent) as determined by TIMS and ICP-MS

| | % $^{234}$U | | % $^{235}$U | | % $^{236}$U | | % $^{238}$U | |
|---|---|---|---|---|---|---|---|---|
| Smear | TIMS | ICP-MS | TIMS | ICP-MS | TIMS | ICP-MS | TIMS | ICP-MS |
| 1 | 0.0169 | 0.0242 | 3.596 | 3.56 | 0.0235 | 0.0236 | 96.364 | 96.4 |
| 2 | 0.0257 | 0.0313 | 4.555 | 4.55 | 0.0265 | 0.0307 | 95.393 | 95.4 |
| 3 | 0.0428 | 0.0456 | 6.627 | 6.61 | 0.0433 | 0.0426 | 93.287 | 93.3 |
| 5 | 0.0511 | 0.0457 | 5.862 | 5.80 | 0.0371 | 0.0299 | 94.050 | 94.1 |
| 6 | 0.0033 | 0.0033 | 0.632 | 0.624 | 0.0083 | 0.0069 | 99.356 | 99 |
| 8 | 0.0536 | 0.0428 | 7.188 | 7.04 | 0.0433 | 0.0370 | 92.715 | 92.9 |

## Comparison of uranium atom percentages determined by TIMS and ICP-MS

| | TIMS/ICP-MS | | | |
|---|---|---|---|---|
| Smear | % $^{234}$U | % $^{235}$U | % $^{236}$U | % $^{238}$U |
| 1 | 0.70 | 1.0098 | 0.99 | 0.99971 |
| 2 | 0.82 | 1.0010 | 0.86 | 1.00005 |
| 3 | 0.94 | 1.0023 | 1.02 | 0.99986 |
| 5 | 1.12 | 1.0107 | 1.24 | 0.99921 |
| 6 | 0.99 | 1.0129 | 1.20 | 0.99990 |
| 8 | 1.25 | 1.0203 | 1.17 | 0.99827 |
| $\bar{x}$ | 0.97 | 1.0095 | 1.08 | 0.99950 |
| s | 0.20 | 0.0071 | 0.15 | 0.00067 |
| t ($\mu$=1) | 0.37 | 3.28 | 1.36 | 1.83 |

## Conclusions

1. Isotope dilution and radiochemical preparative techniques work well in "radioanalytical" applications of ICP-MS. Analytical "problems" can be mitigated.

2. "Radioanalytical" ICP-MS data are equivalent to data from standard methods (TIMS, α-spec).

3. Applications in radiation protection and earth sciences are certain to expand further. (especially as the cost of quadrupole and high resolution ICP mass spectrometers drop)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