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Project #42370. Radioanalytical Chemistry for Automated Nuclear Waste Process Monitoring

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Radioanalytical Chemistry for Automated Nuclear Waste Process Monitoring

- Research program directed toward rapid, sensitive and selective determination of β- and α- emitters in LAW processing streams:
  - specific targets ^{90}Sr, ^{99}Tc and TRU
- Automated radiochemical measurements via integration of A)*sample preparation/treatment*, B) *rapid selective separation*, and C)*on-line radiometric detection* steps within a single functional analytical instrument
- Knowledge gaps exist relative to designing chemistries for such instruments so that analytes can be quantitatively and rapidly separated and analyzed in challenging matrixes

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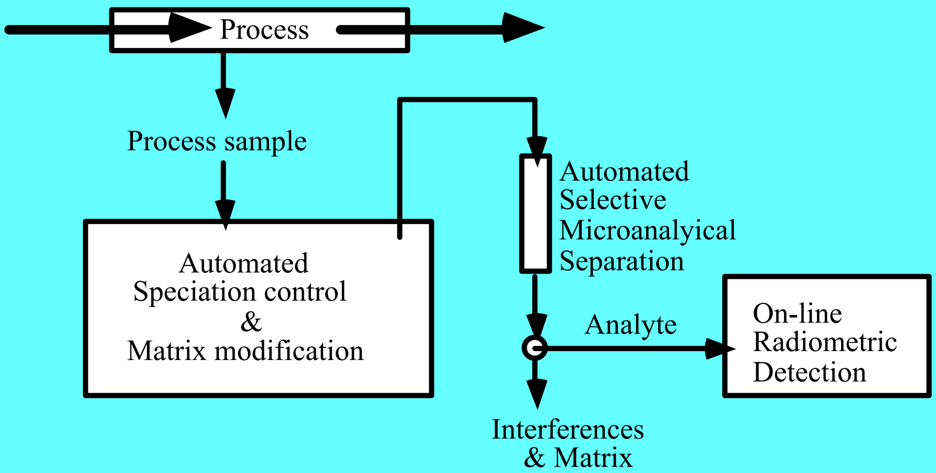
Project Objectives

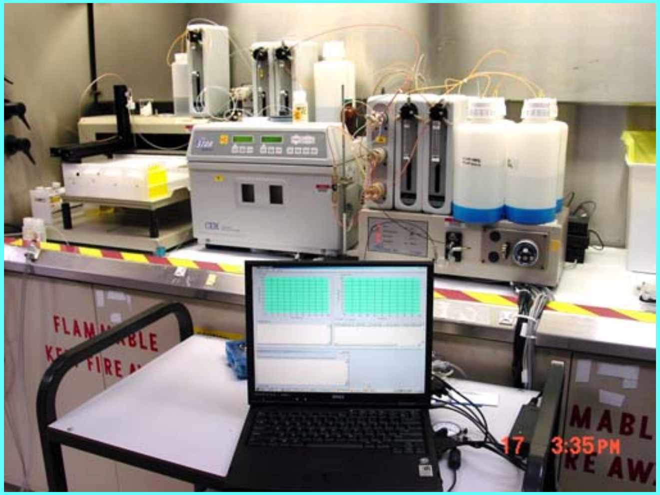
- Introduce automated radiochemistry to the field of process monitoring of LAW matrices
- Develop fundamental understanding of the chemical processes that must occur within the analyzer instrument (i.e., matrix modification/speciation control and selective separation chemistries)
- Investigate matrix modification chemistries for chemically complex, variable matrices
- Investigate separation chemistries suitable for rapid selective separation of target analytes
- Investigate a new flow-through radiometric detector concept based on solid state diode detectors for quantification of TRU in process solutions
- Investigate new data acquisition and signal processing techniques to enhance performance of scintillation and diode detectors for use in process monitoring
- Characterize candidate chemistries and instrument configurations with regard to detection limits,sensitivity, selectivity, analyses time
- Define the limitations and the potential of the proposed monitoring approach. New knowledge and expertise will provide information for designing effective instruments
- Educate students in modern radiochemistry and DOE cleanup challenges

Process Monitoring Challenges and Reality

- Generic Challenges:
  - Complex, high-ionic strength, caustic brine sample matrixes
  - Undefined or varying chemical speciation
  - Low mass concentrations, need for isotopic information
  - Radioactive and stable matrix interferences
  - Detection limits, robustness, sample turnaround time
- Challenges/requirements limit the choice of analytical approaches
- **Reality:** "Radiochemistry has always been and still is a crucial tool in the field of radionuclide determination, …particularly in the case of alpha and beta emitters".
- Current baseline: costly and lengthy laboratory analyses

Automated Radiochemistry:Approach





- ***Automated radiochemical measurements via integration of the following steps within a single functional instrument:***
  - *sample preparation/treatment*,
  - *rapid selective separation*,
  - *on-line radiometric detection*

Automated Radiochemistry:Research Focus

- Sample modification/ speciation control chemistries for ^{99}Tc, ^{90}Sr (TRU?) (acidification, digestion, oxidation, speciation control)
- Separation chemistries for ^{99}Tc and ^{90}Sr (hopefully not for TRU)
  - sorbent material selection and characterization (uptake selectivity, kinetics, elution chemistries, stability etc.
  - development of rapid, automated separation schemes
- On-line radiometric detection
  - solid state diode detection for in-situ alpha detection/spectroscopy
  - light detection, detector design and signal processing for beta scintillation detection (Clemson)
- Analytical and radiochemistry of the LAW waste matrices

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Relevance

- ^{90}Sr, ^{99}Tc and TRU process measurements will be required at WTP at Hanford and Savannah River sites
  - Better process control, plant throughput and regulatory compliance
- Lack of analytical methodologies for these radionuclides
- Baseline is not significantly different from PUREX plant days
- Plants are being constructed: this research is timely
- This analytical methodology has dual use:
  - on-line/at-line measurements
  - automated tool for the analytical laboratory
- Significant cost savings over operational cycle of the waste treatment plants

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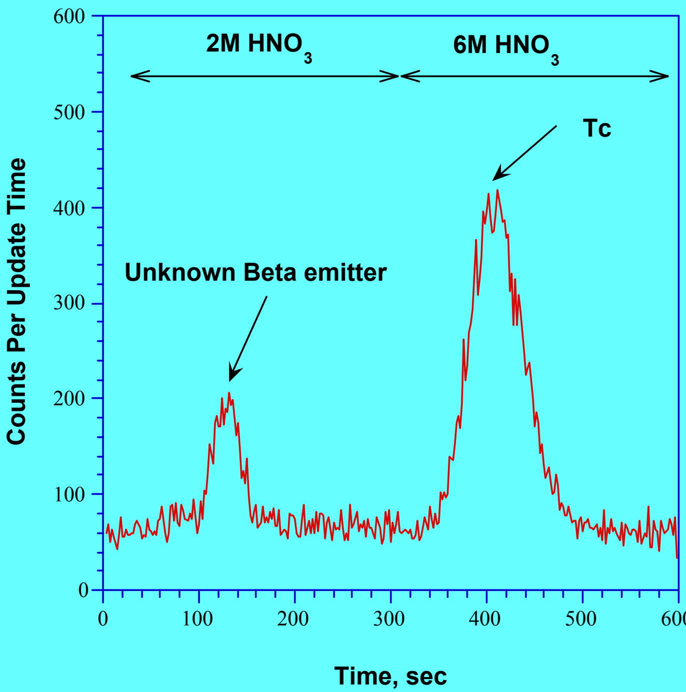
Automated Radiochemistry: Challenges

Tank AN-102 -Radiochemical interference issue in the automated Tc analysis.

Inventory in	uCi/mL
Gross alpha:	0.18
Gross beta:	590
Tc-99	8.23(ppm)
(at least 60% as non-pertechnetate)	
Cs-137	335
Cs-135	3.02
Sr-90	84
Co-60	0.12
Pu-239/240 0.01	
Am-241	0.15
Unknown Activity	158



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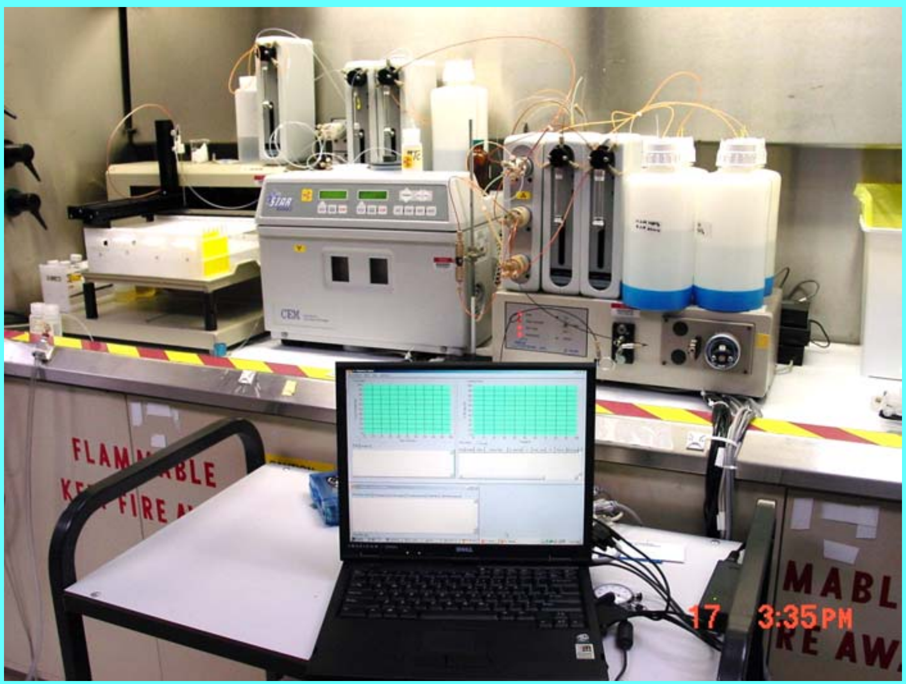
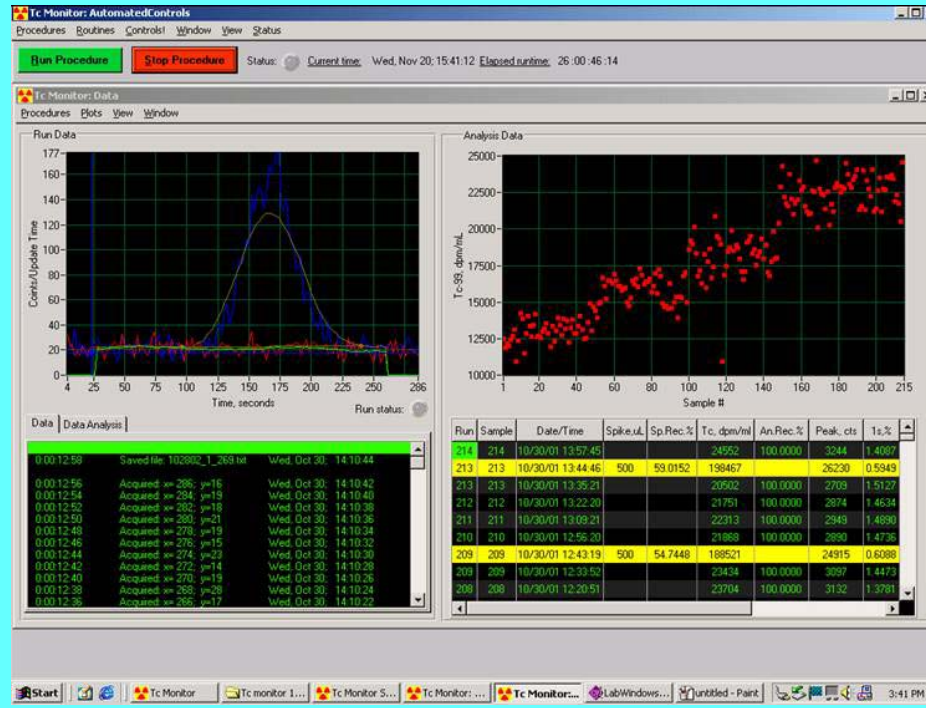
Automated Radiochemistry Example: Tc Process Monitoring

Sample → **Matrix Adjustment, Speciation Control Tc → Tc(VII)** → **Tc(VII) Separation** → **^{99}Tc Scintillation Detection**

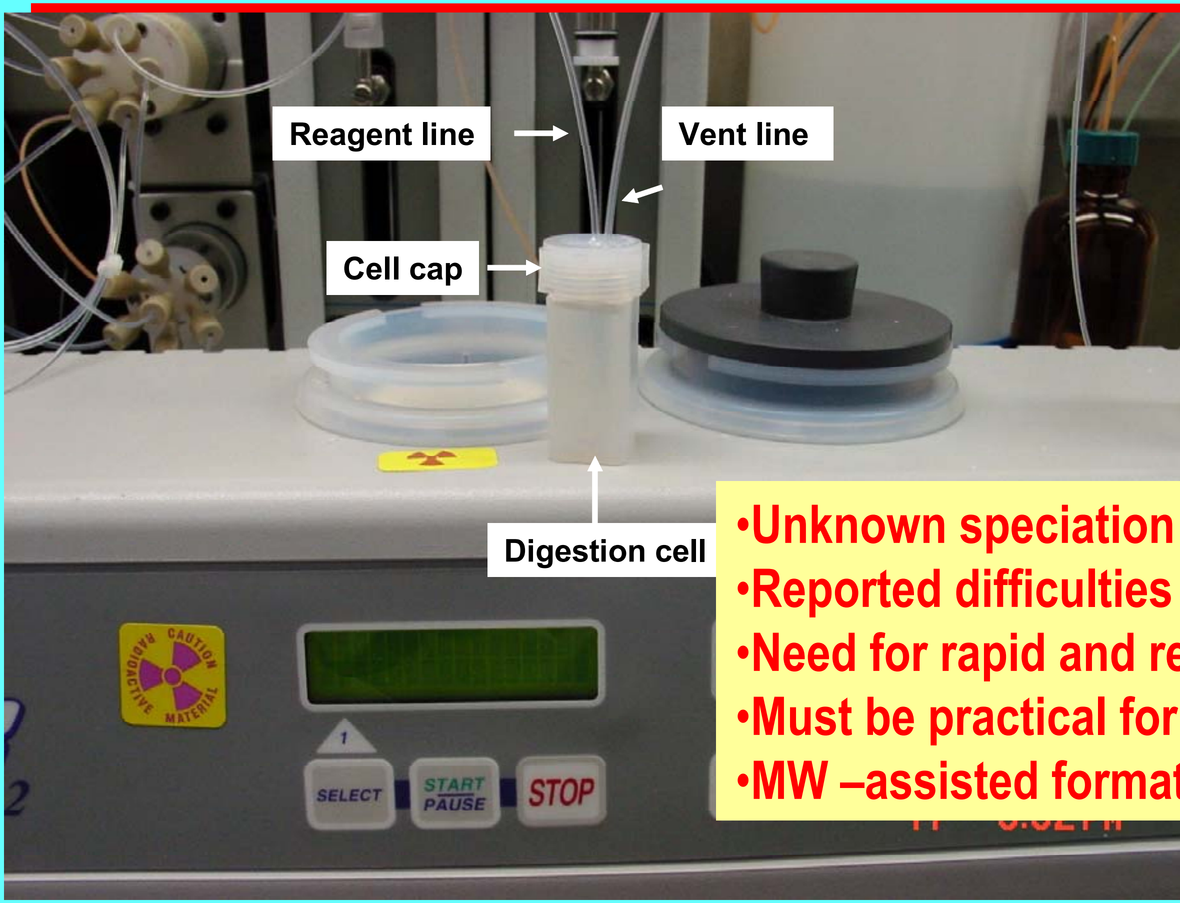
- **Flow-through scintillation detection of the beta-emitting ^{99}Tc**
(radiometric detection is sensitive to meet DL with short counting times)
    - Detection using glass scintillator flow cell
- **Automated, rapid radiochemical separation of the ^{99}Tc(VII) from sample matrix and radioactive interferences (e.g. ^{90}Sr/^{90}Y, ^{137}Cs, etc.)**
(separation is required to measure ^{99}Tc in the presence of other radionuclides)
    - Small column separation using anion exchange sorbent
- **Automated, rapid sample treatment/oxidation to control Tc speciation**
(oxidation is required to convert all ^{99}Tc to ^{99}Tc(VII) for total ^{99}Tc analysis)
    - Sample acidification and microwave assisted oxidation using persulfate
- **Automated, digital fluid handling for sample/solution delivery and system integration**
    - Computer-controlled valves and syringe pumps

Prototype Instrument for Hanford WTP





Microwave Assisted Sample Oxidation



- Unknown speciation
- Reported difficulties for converting Tc to Tc(VII)
- Need for rapid and reliable methodology
- Must be practical for use in plant settings
- MW –assisted format using acidification and oxidation

Microwave Assisted Sample Oxidation for Tc Speciation Control

1) Sample acidification using nitric acid (nitrite removal)

- $Al(OH)_3$ precipitation/dissolution;
- Digested matrix must be compatible with subsequent separation approach

2) Tc oxidation using $Na_2S_2O_8$ as the oxidizing reagent

- Complete destruction of organic complexants is not necessary
- Ag catalyst is typically used but not necessary
- No Tc losses during digestion
- Rapid, reliable, automated process

Advantages of peroxidisulfate:

- strong oxidant (E^0=2.01 V)
- good shelf life
- excess reagent is readily destroyed by boiling

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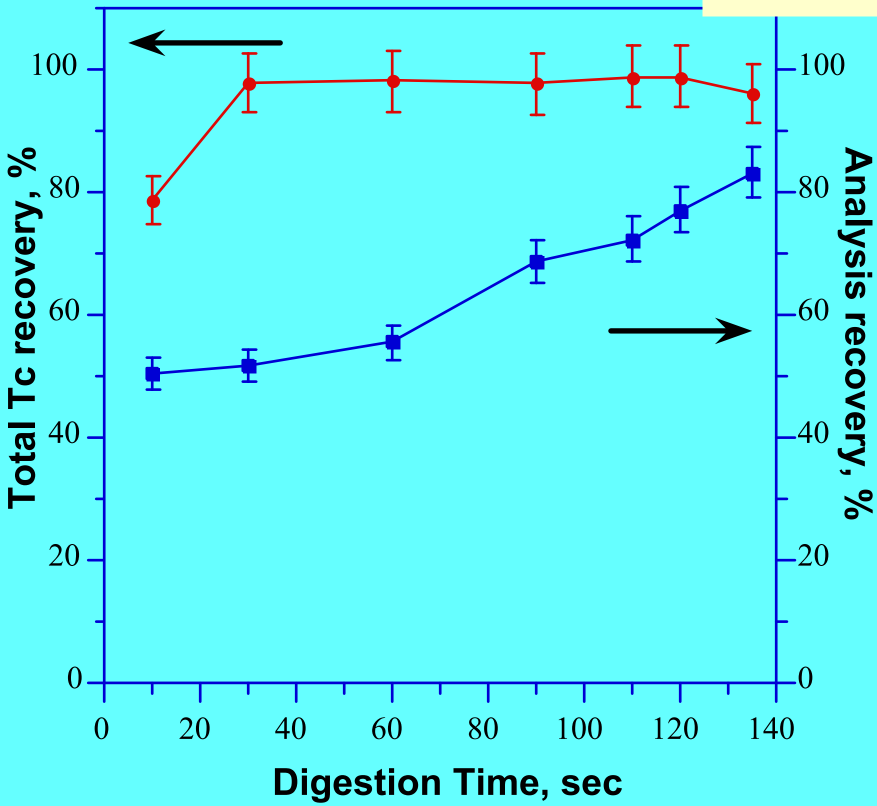
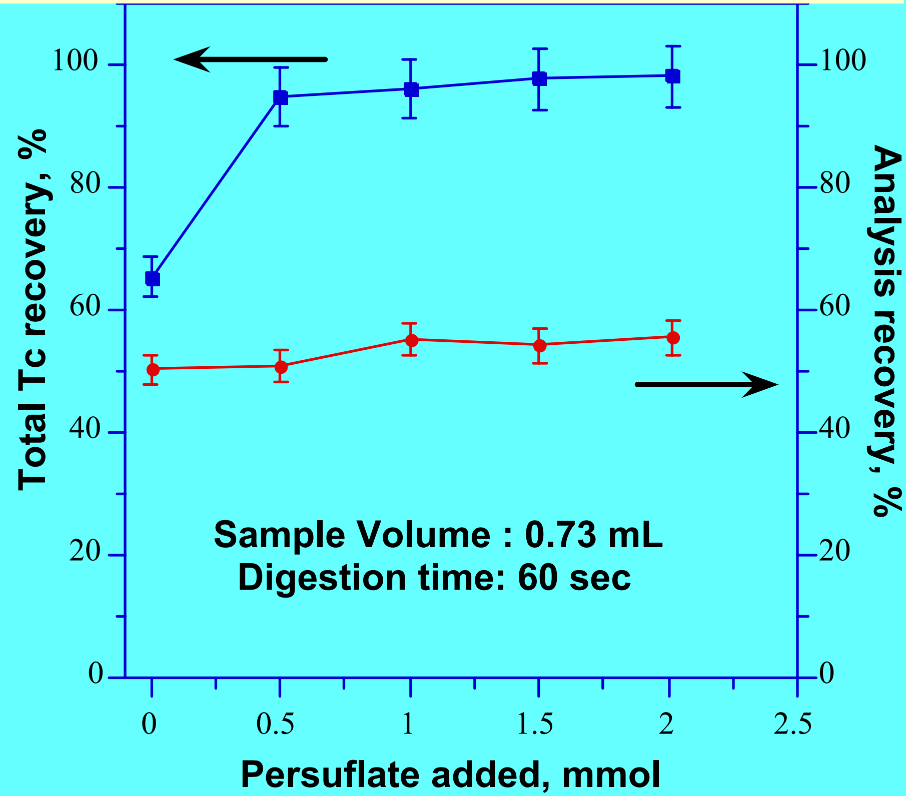
Microwave-Assisted Oxidation of Non-Pertechnetate

Envelope C AN-107 waste: ~ 60% of non-pertechnetate
Chemical speciation is unknown

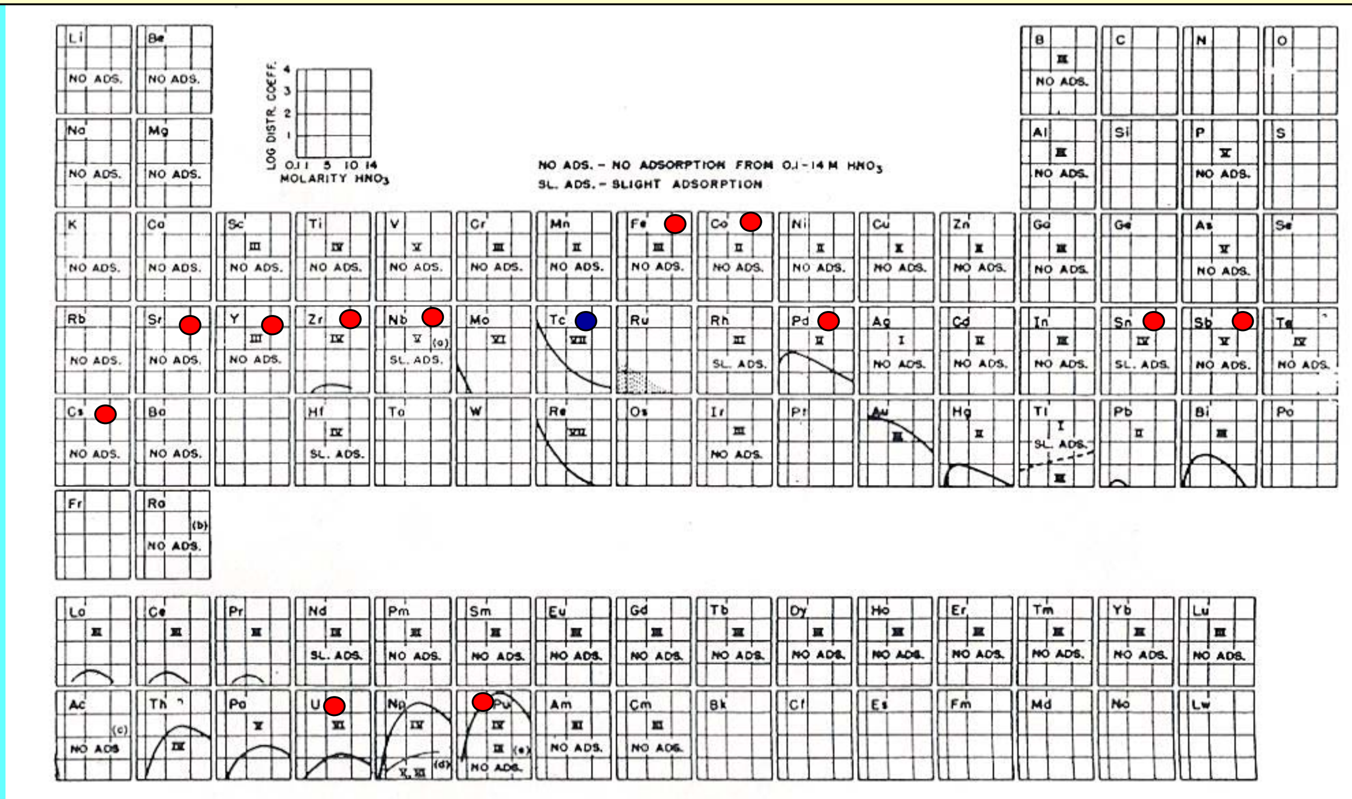




- **Rapid, reliable Tc oxidation is possible using MW-assisted $Na_2S_2O_8$ treatment**

Anion Exchange Separation of Tc

- Macroreticular strongly basic IX material (AGMP-1)
- Less straightforward in separating anionic species (Sb, Sn, Ru/Rh)



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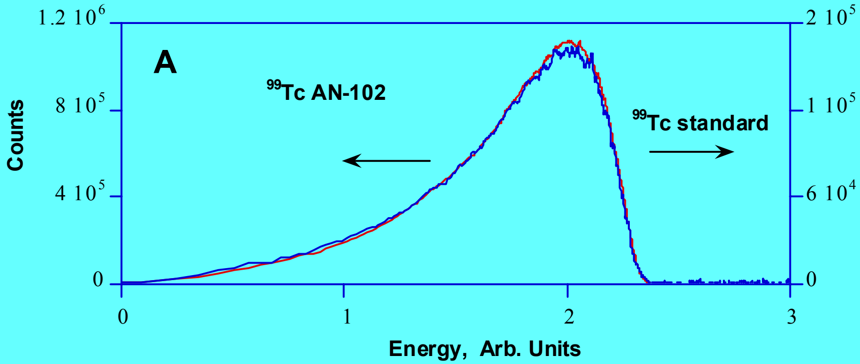
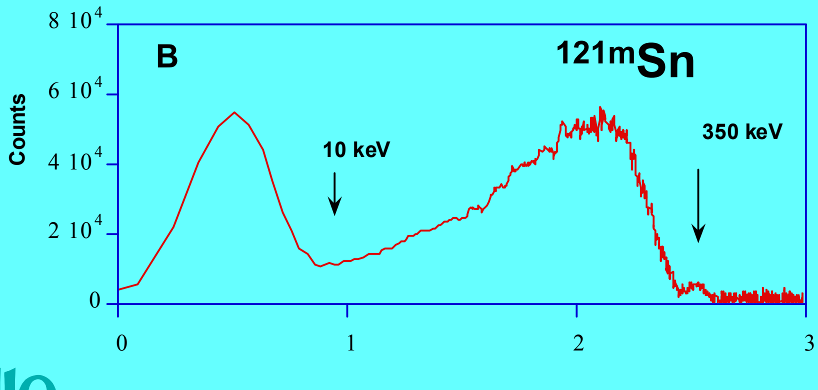
Identification of Initial Interferent in Automated Radiochemical Tc Measurement

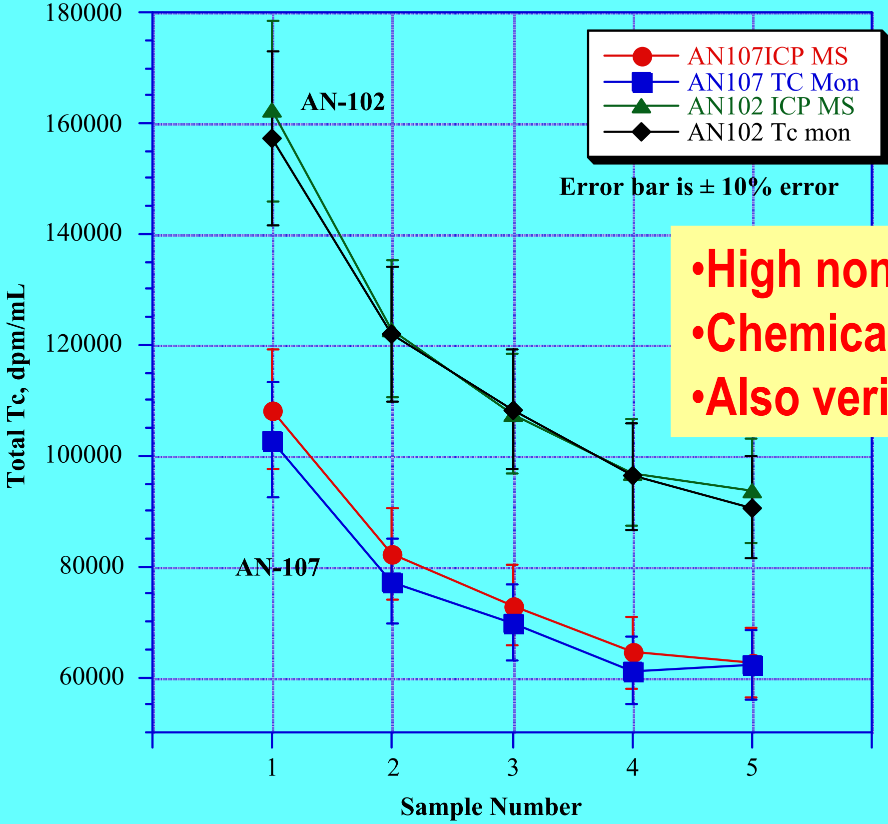
- **liquid scintillation spectrometry of the separated Tc fractions indicated good radiochemical purity for the analysis of radiochemically complex samples**





Additional verification:
- LEPS
- Gamma
- ICP MS

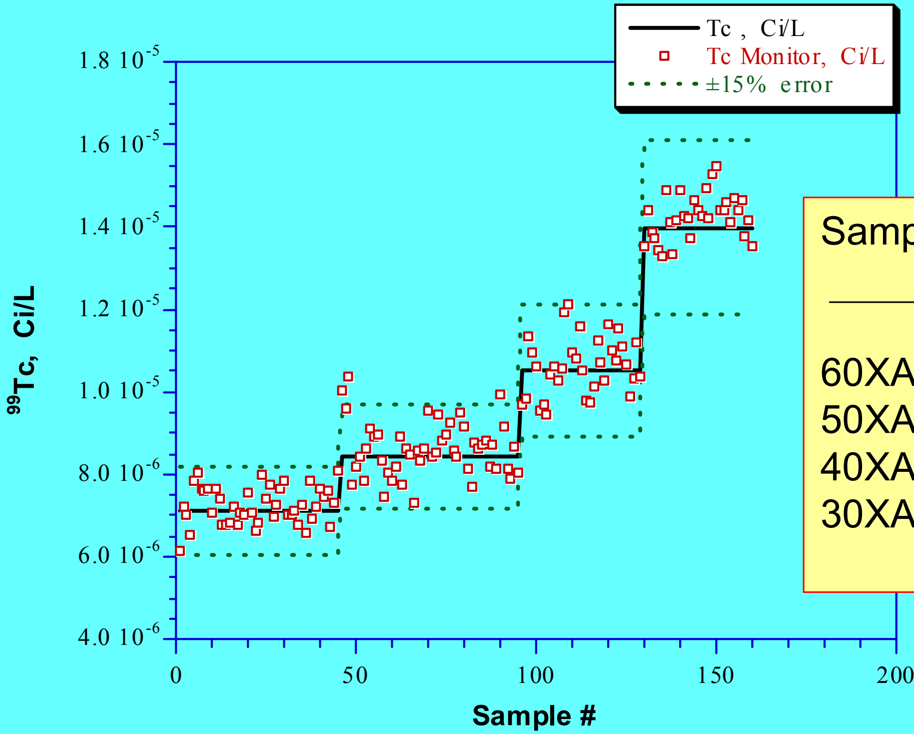
Automated Tc Measurements in Hanford Waste



- High non-pertechnetate content
- Chemically & radiochemically most challenging matrices
- Also verified for Envelope A, B, and C wastes

- Samples were batch contacted with SL639 Resin
- Better than 10% agreement for both matrixes
- No bias

Tc Process Monitor Instrument Testing for WTP

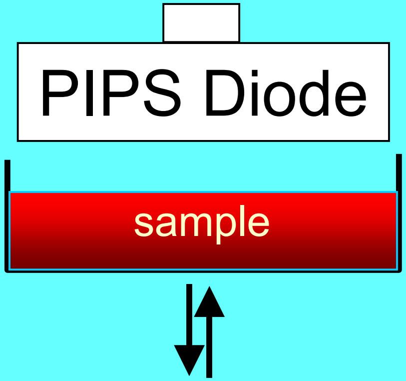


Sample	Accuracy (%)	Precision (%RSD)	N
60XAZ102	4.4	6.2	45
50XAZ102	2.0	7.6	50
40XAZ102	1.2	6.6	34
30XAZ102	2.0	3.8	31

- ***Analytical approach/instrument selected for Hanford WTP in peer reviewed, competitive selection process!!!***

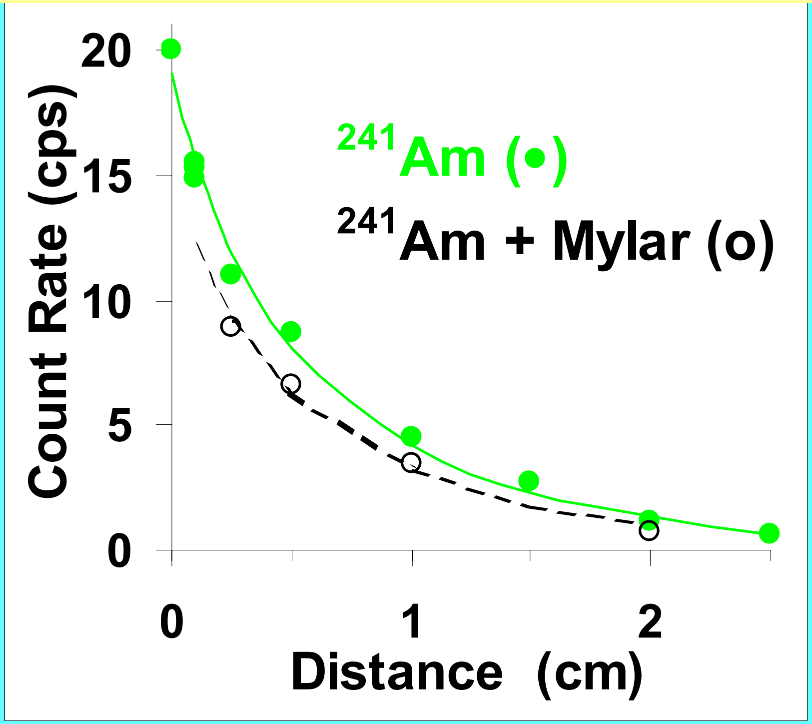
Direct Detection of Alpha Emitters In Solution Using PIPS Diodes

- **Low noise and good resolution**
- **Operation in ambient light**
- **Passivated surface w/o metal contacts**
  - **Rugged**
  - **Chemically resistant**
  - **Surface can be touched, cleaned--*modified***



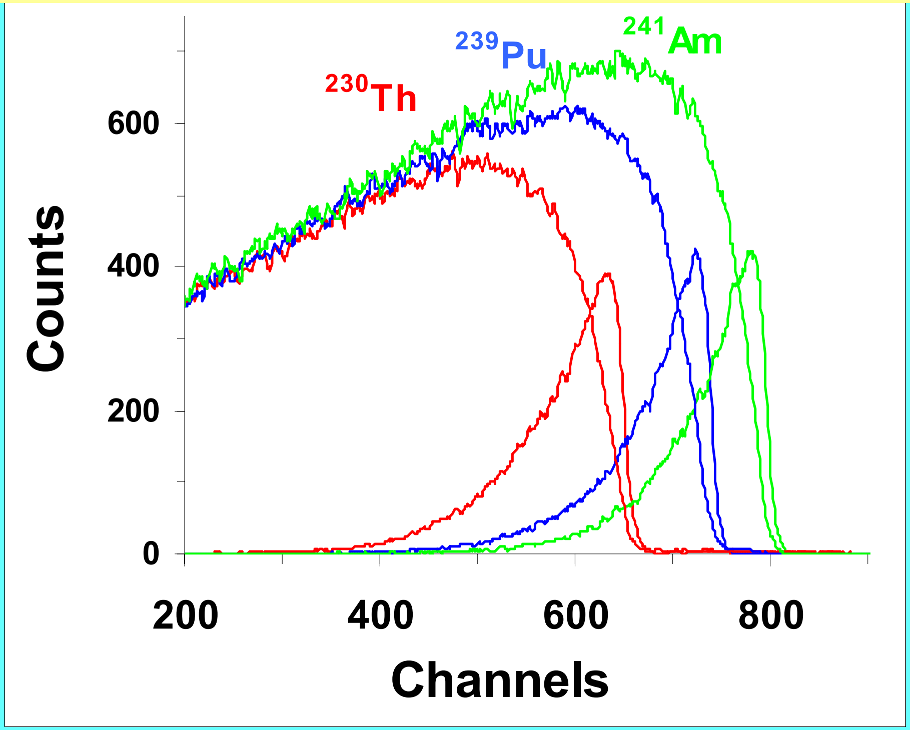
Direct Analysis of Alpha Emitters In Solution

Activity vs. Distance*



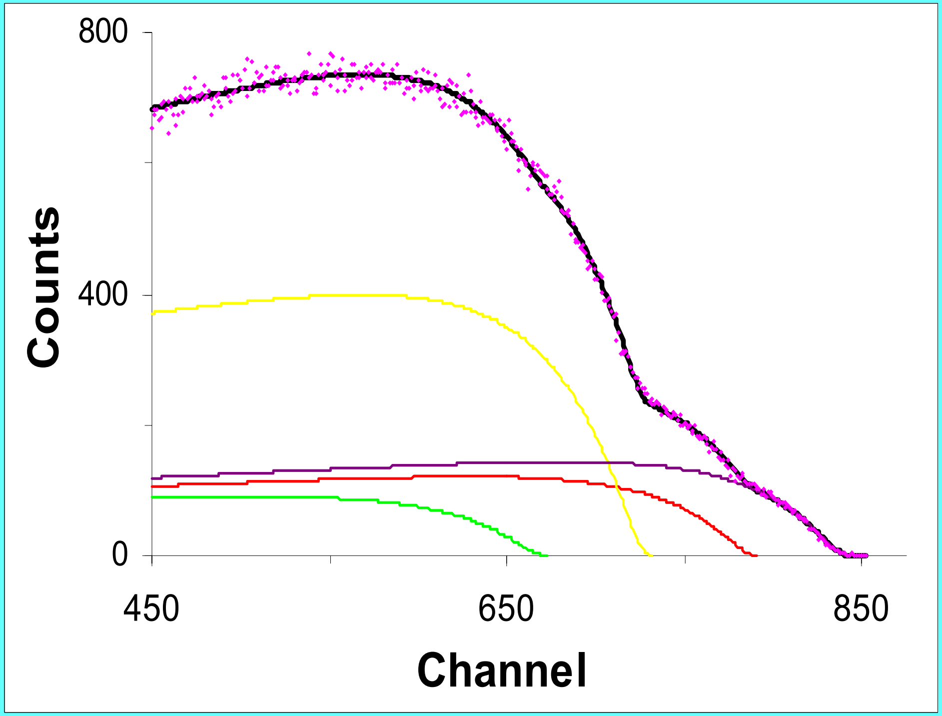
* Distance between solution surface and detector face. 125 nCi/ml ^{241}Am activity.

Alpha Energy "Spectra"†



† 125 nCi/ml, 10 hr counts, 0.5 cm standoff from surface.

Direct AEA in Liquids by Spectral Deconvolution



20% ^{244}Cm, 15% ^{241}Am, 50% ^{239}Pu, 15% ^{233}U
Total solution activity 125 nCi/mL

Isotope	Solution Activity [a]	Calculated Activity [b]
^{244}Cm	25.0	24.8
^{241}Am	18.8	20.2
^{239}Pu	62.5	60.9
^{233}U	18.8	19.3

a) nCi/mL, mixture of standards
b) nCi/mL, spectral deconvolution, least squares optimization

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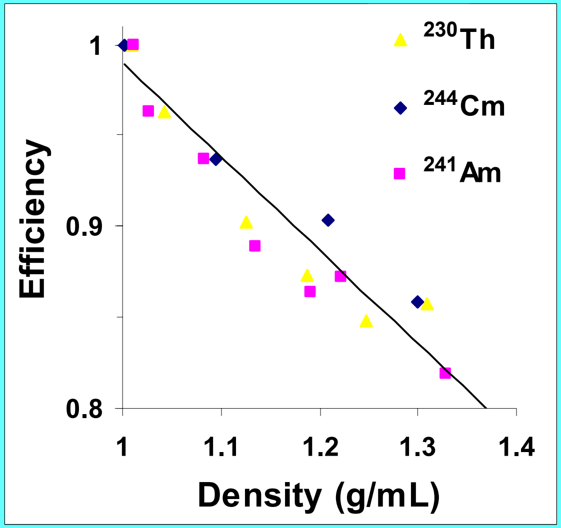
Analysis of Actual Samples

Sample Matrix	Density (g/mL)	PIPS Assay[a] (Bq/ml)	Lab Assay[b] (Bq/ml)	Difference (%)
Water[c]	1	4.6	4.0	-13.9
Water[c]	1	392.7	403.0	2.6
Hanford Tank AZ-101[c,d]	1.22	17.1	15.7	-9.2
Hanford Tank AN-107[d]	1.249	70.4	82.1	14.2
Hanford Tank AZ-102[d]	1.260	120.0	154.9	22.5
Savanna River Tank 23[c,d]	1.031	817.6	745.0	-9.7
Savanna River Tank 33[d]	1.171	6.6	8.6	22.7
Savanna River Tank 43[d]	1.204	224.8	205.5	-9.4



a) Based upon ^{241}Am, 10 min count, efficiency corrected
b) Precipitation plating and AES
c) Spiked with ^{241}Am
d) supernate

- Rapid total alpha assay
- Limited sensitivity ~5 Bq/mL
- Spectral information….

Implementation

- Hanford WTP:
  - On-line Tc monitoring is required for the operation of the Tc removal columns
  - Our technology was selected for the Hanford WTP
  - Sr and TRU monitoring: automated laboratory measurements on grab samples (so far no interest at Hanford)
- Salt processing facility at SRS
  - Need for rapid Sr and TRU analysis in the lab to support process control
  - Indication that such technology may be a preferred method for this need
  - Goal is to pursue prototype instrumentation development with SRS using **new scientific knowledge** developed under this EMSP program

Current Focus & Conclusions

- Alternative separation chemistries for Sr and Tc
  - Simplify separation protocols, Ba/Sr separation issues
- Diode detection and signal processing

- Radiochemistry represent a viable approach for process monitoring if successfully automated
- Tc monitor instrumentation/ approach was selected for use at the Hanford WTP
- Work with WTP contractors would have not been possible without the science base and knowledge developed under an on going EMSP program

Acknowledgements

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