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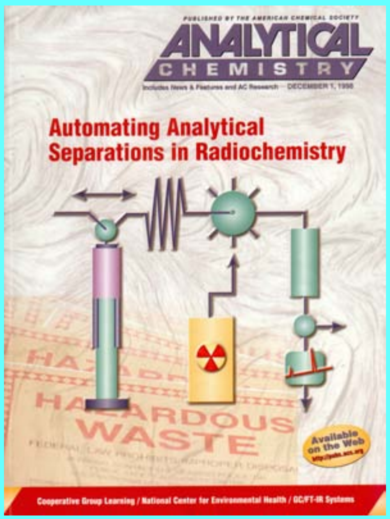
Project #42370. Radioanalytical Chemistry for Automated Nuclear Waste Process Monitoring



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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 ^{99}Tc (previous focus), ^{90}Sr, ^{137}Cs 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
- Significant knowledge gaps exist relative to designing chemistries for such instruments so that analytes can be quantitatively and rapidly separated and analyzed in challenging matrixes
- Specific focus for the renewal period: ^{90}Sr, TRU-gross alpha, ^{137}Cs

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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

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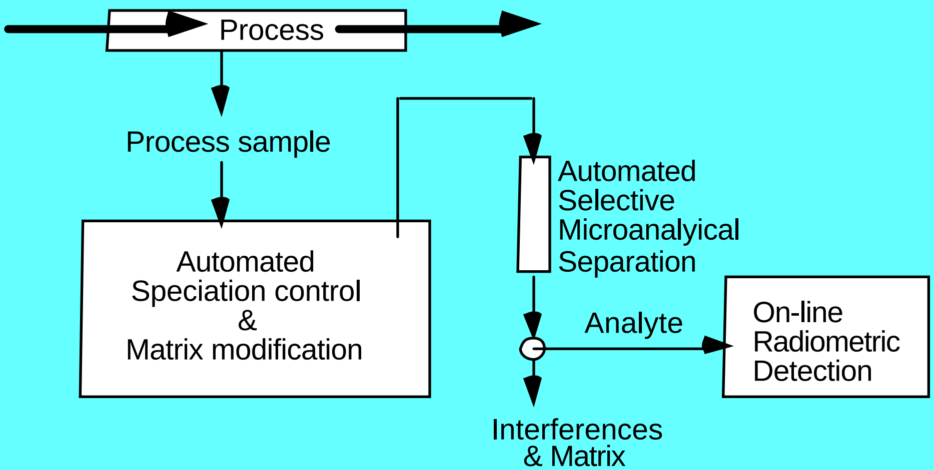
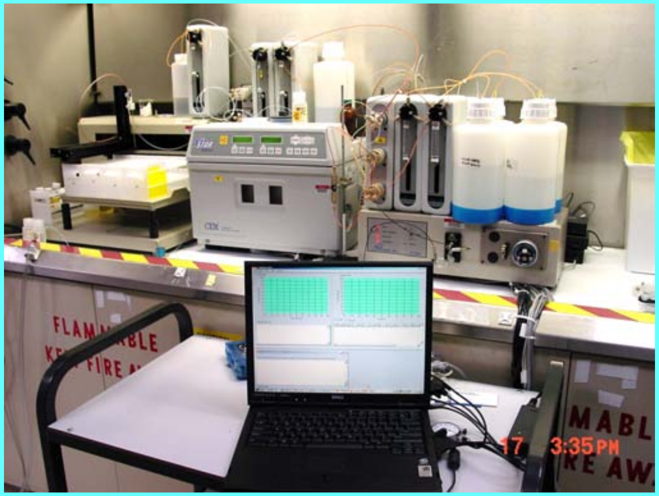
Process Monitoring Challenges and Reality

- 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 manual laboratory measurements

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

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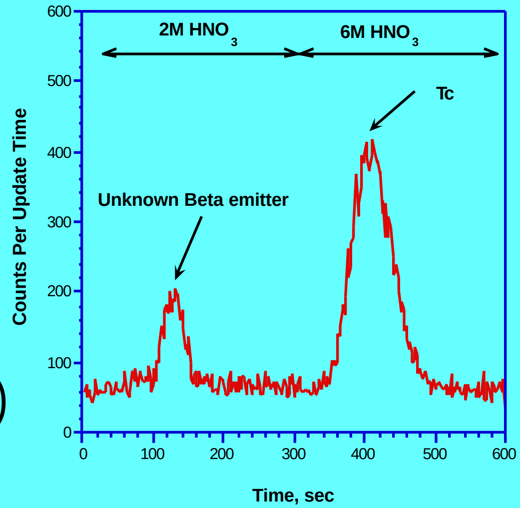
Automated Radiochemistry:Research Focus

- Sample modification/ speciation control chemistries for ^{90}Sr, TRU, ^{137}Cs (acidification, digestion, oxidation, speciation control)
- Separation chemistries for ^{99}Tc and ^{90}Sr, ^{137}Cs and TRU as necessary
  - 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
  - thin film scintillation detection for in-situ alpha detection in corrosive matrices
  - light detection, radiation detector design and signal processing for beta scintillation detection (Clemson)
- Analytical and radiochemistry of the LAW waste matrices

Automated Radiochemistry Challenges

Example: 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



^{90}Sr-high abundance of ^{137}Cs/^{137m}Ba (separation chemistry)
TRU- corrosive matrix, high β/γ backgrounds

•Knowledge gaps exist and are being filled as an outcome of this research

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Automated Radiochemistry Example: Tc Process Monitoring

Sample → **Matrix Adjustment, Speciation Control Tc à 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

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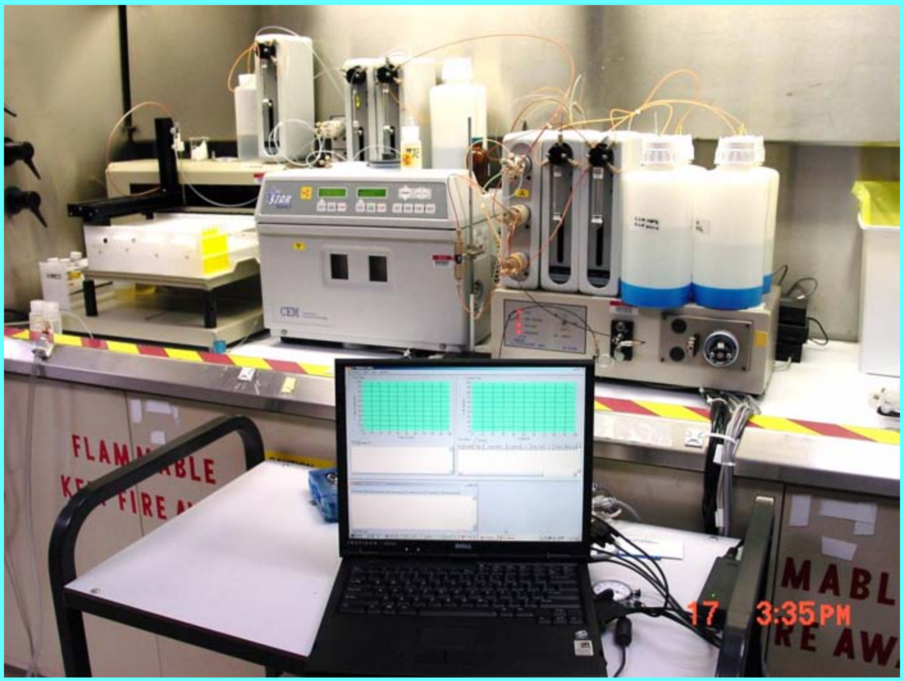
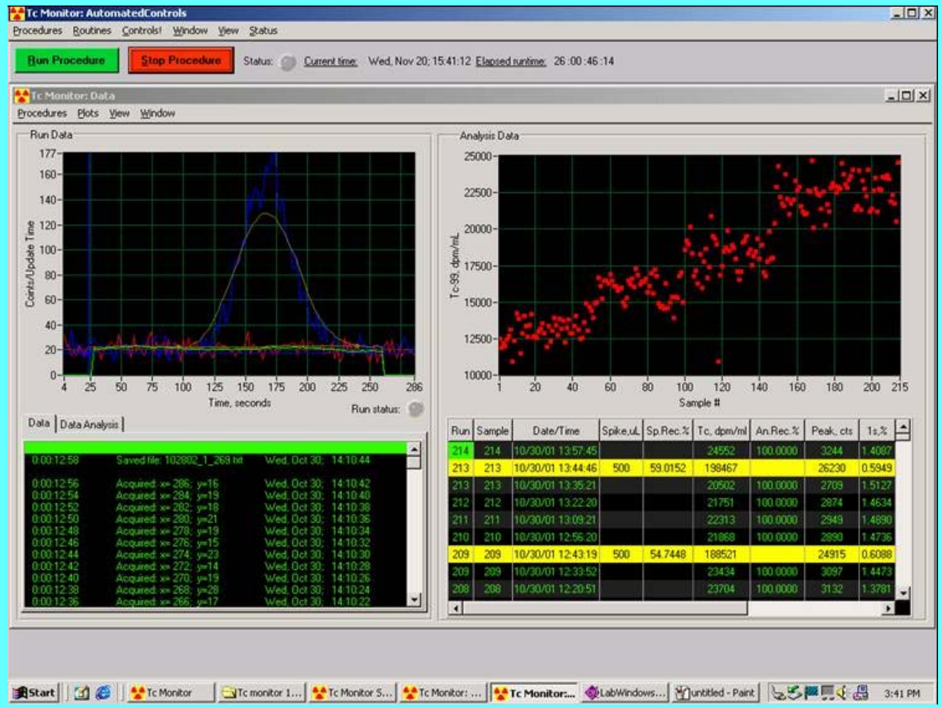
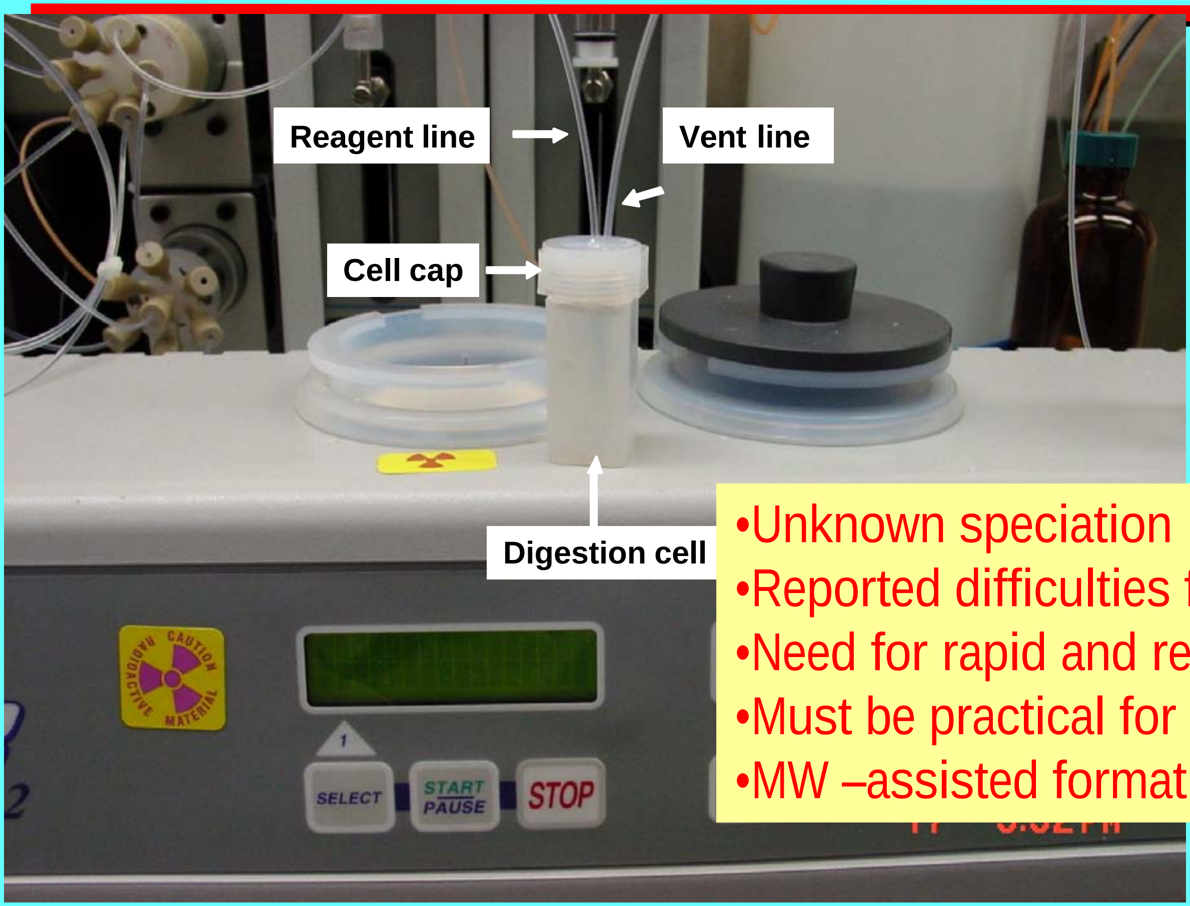
Prototype Instrument Built on EMSP Science: ^{99}Tc Analyzer for WTP





Microwave Assisted Sample Oxidation/Digestion for Automated Measurements



- 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

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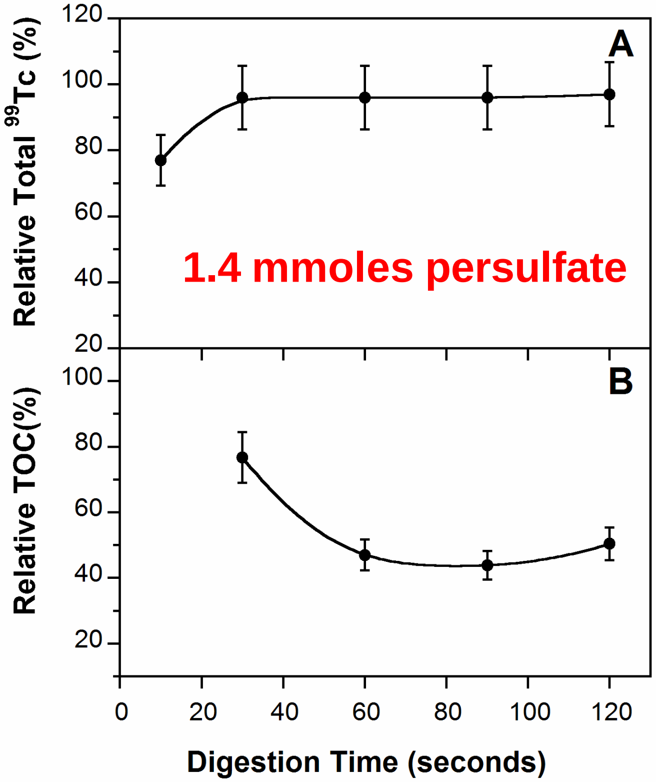
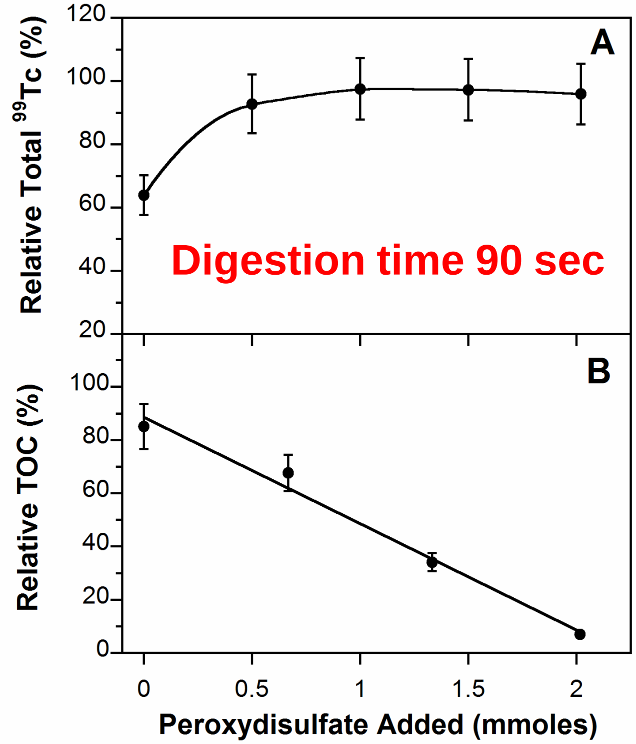
Microwave-Assisted Oxidation of Non-Pertechnetate

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**

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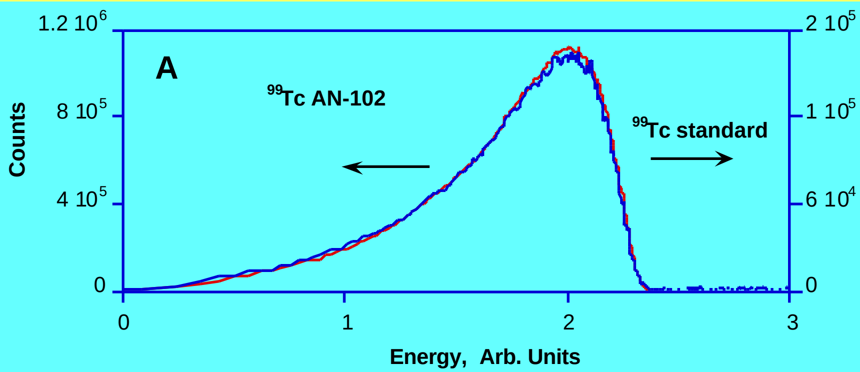
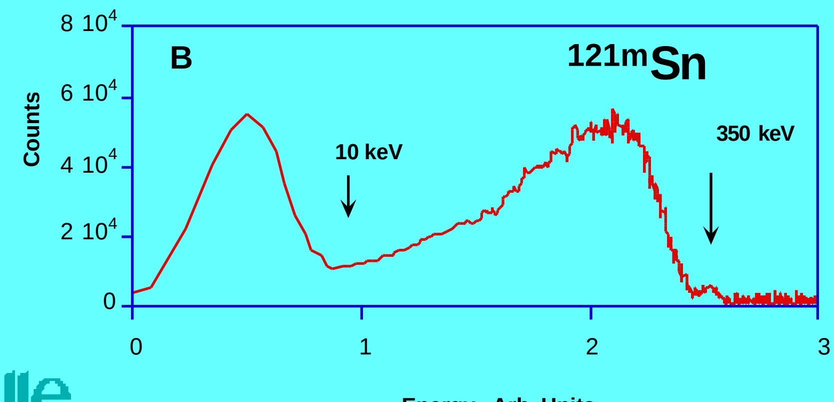
EMSP Program Enabled Identification of Interferent in the Tc Measurement

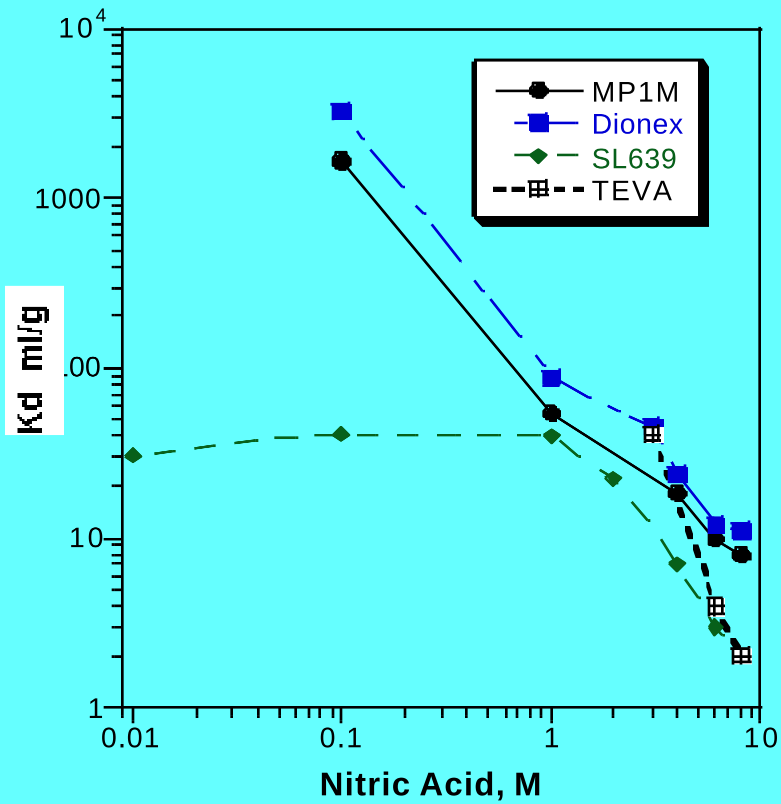
- **liquid scintillation spectrometry of the separated Tc fractions indicated good radiochemical purity for the analysis of radiochemically complex samples**

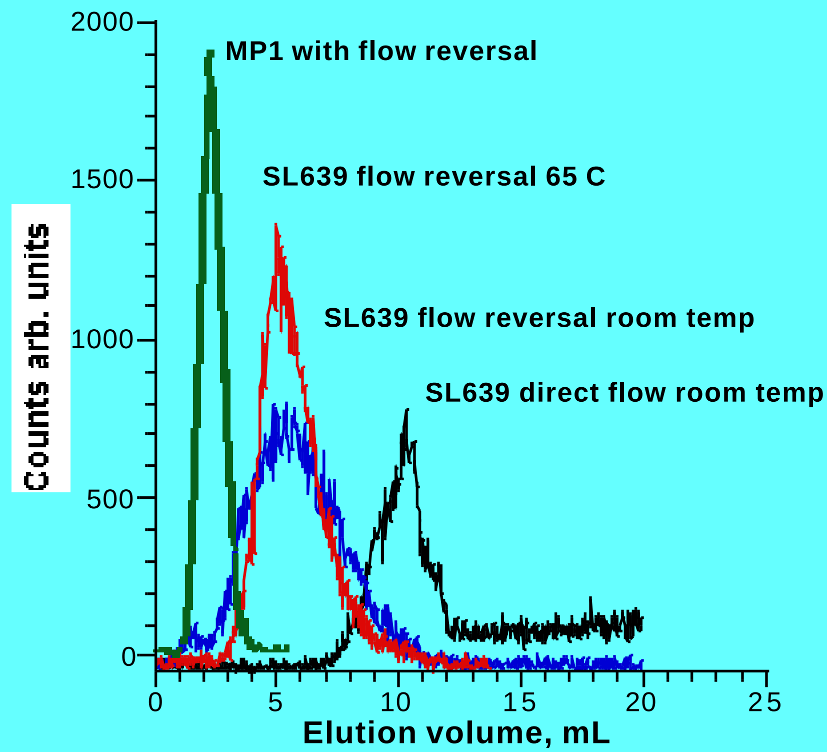


Additional verification:
LEPS
Gamma
ICP MS



Tc(VII) Separation Chemistries





- ***Strongly basic AnIX is a prefered material for Tc separation***

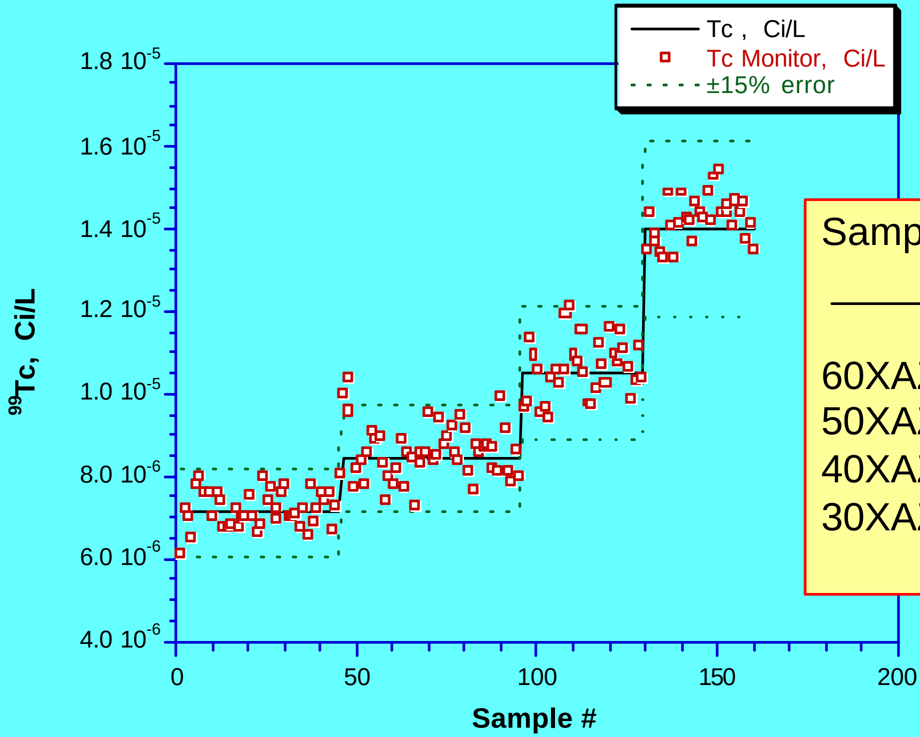
Separation of ^{99}Tc from Interferences in LAW

- Sequence of column scrub steps is required to remove interferences

Column: MP-1 resin 4.6 x 50 mm (0.83 mL bed volume)

Step/Description	Reagent	Volume	Flow Rate
1. Column Conditioning	0.2M HNO_3	2 mL	7.5 mL/min
2. Sample load	Digested sample	1.6 mL	5 mL/min
3. Column scrub I	0.2 M HNO_3	5 mL	7.5 mL/min
4. Column scrub II	1 M NaOH	6 mL	7.5 mL/min
5. Column scrub III	0.2 M HNO_3-0.5 M $H_2C_2O_4$	6 mL	7.5 mL/min
6. Column scrub IV	2 M HNO_3	5 mL	7.5 mL/min
7. Pertechnetate elution[a]	8 M HNO_3	5.6 mL	1.5 mL/min
a. Flow direction through the column is reversed during elution step.			

Tc Process Monitor Instrument Testing

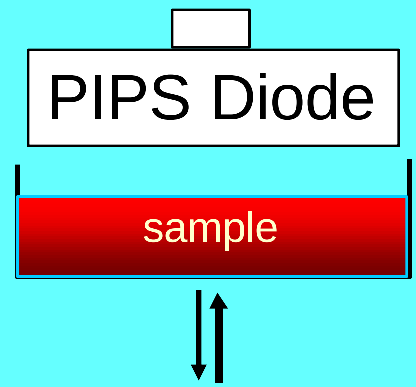


Sample	Accuracy (%)	Precision (%RSD)	N
60XAZ102	4.4	6.2	45
50XAZ102	2.0	7.6	50
40XAZ102	1.2	6.6	34
30XAZ102	2.0	3.8	31

•Instrument selected for Hanford WTP in peer reviewed, competitive selection process!!!

Direct Detection of Alpha Emitters 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



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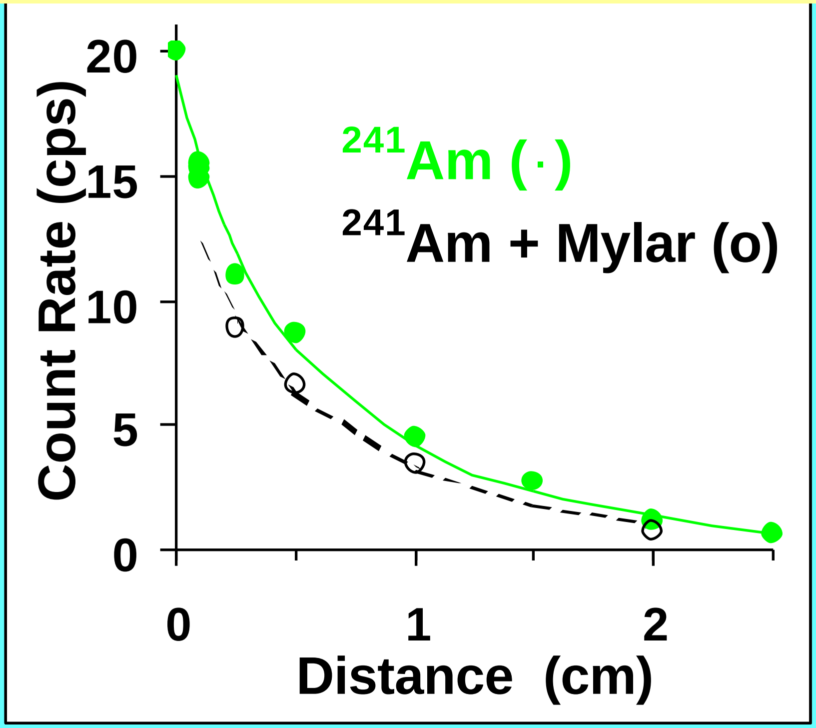
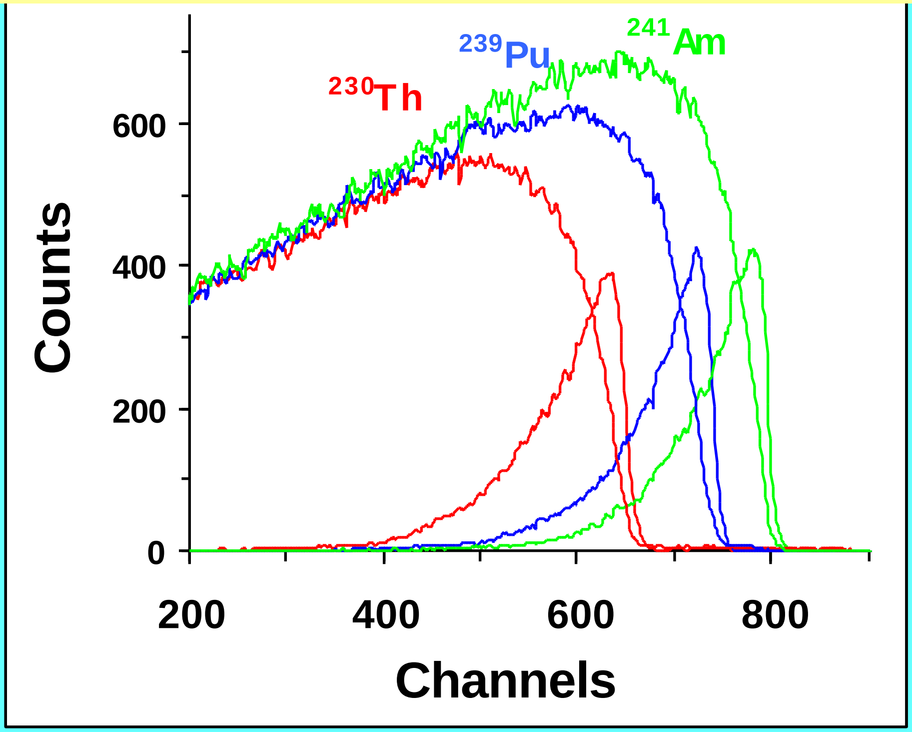
Direct Analysis of Alpha Emitters In Solution

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.

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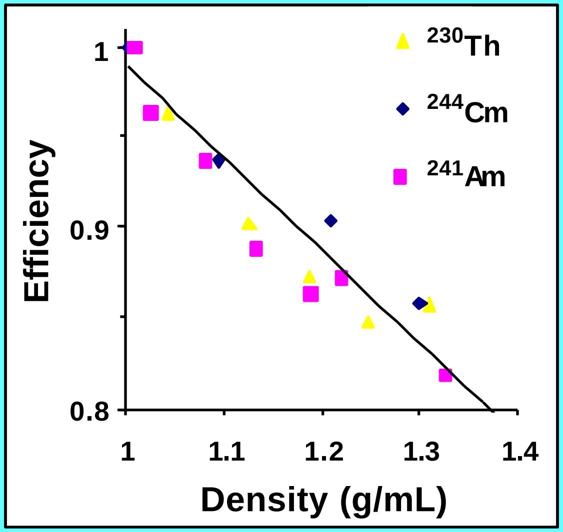
Analysis of Actual Samples

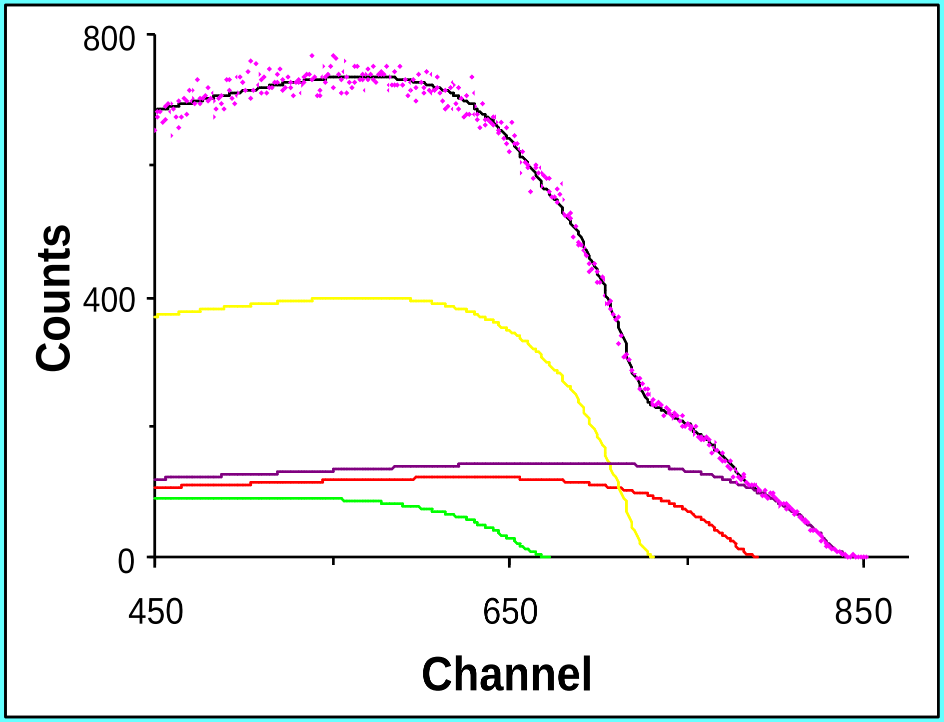
Sample Matrix	Density (g/mL)	PIPS Assay[a] (Bq/ml)	Lab Assay[b] (Bq/ml)	Difference (%)
Water[c]	1	4.6	4.0	-13.9
Water[c]	1	392.7	403.0	2.6
Hanford Tank AZ-101[c,d]	1.22	17.1	15.7	-9.2
Hanford Tank AN-107[d]	1.249	70.4	82.1	14.2
Hanford Tank AZ-102[d]	1.260	120.0	154.9	22.5
Savanna River Tank 23[c,d]	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….

Direct AEA in Liquids Using Diodes: 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

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
- Potential for significant cost savings over operational cycle of the waste treatment plants

Implementation/Relevance

- Hanford WTP:
  - On-line Tc monitoring is required for the operation of the Tc removal columns (if process is implemented)
  - Our technology was selected for the Hanford WTP
  - Sr and TRU monitoring: automated laboratory measurements on grab samples 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

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Conclusions

- EMSP support enabled development of the scientific knowledge lacking for the development of process analyzers based on automated radiochemistry
- Tc monitor instrumentation/ approach developed and characterized in detail and was selected for use at the Hanford WTP
- Work with WTP would have not been possible without the science and knowledge base developed under EMSP support
- The ongoing research is directed at ^{90}Sr, TRU and ^{137}Cs monitoring
- Invaluable opportunity for young investigators to develop scientific career while working on relevant problems