Identification of Non-Pertechnetate Species in Hanford Tank Waste, Their Synthesis, Characterization, and Fundamental Chemistry

(Project 81988)

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Ultimate objective: is to separate all of the technetium from Hanford tank waste

TcO_4^- no problem: 80% removal will get this

Non-pertechnetate (TcN) is hard to separate and oxidize, some tanks have >50% TcN

Concept: If we knew what the non-pertechnetate species were we could develop their separation and/or oxidation chemistry to solve this problem.

General Approach: Isolate the non-pertechnetate fractions from a waste sample by standard separation techniques

Analyzed the fraction by CE/MS to identify individual compounds

Synthesize and characterize workable quantities of the identified compounds

Study their redox and ligand substitution chemistry so that they may be oxidized to TcO_4^- and separated by Superlig 639 or removed be a alternative separation method.

Project Benefits

Identifying and understanding the chemistry of the non-pertechnetate species would:

- **Allow the development of efficient oxidation or separation methods for these species from Hanford waste**
- **Aid in the development of "Tc getters" for use around leaking Hanford tanks**
- **Benefit other DOE sites that have Tc environmental problems**
- **Add to the fundamental chemistry of technetium. Stable technetium complexes may be useful ^{99m}Tc radio-pharmaceuticals.**

The Non-Pertechnetate Problem, History, and Status

- ~2000 Kg of technetium are in the Hanford tanks.
- Technetium is a major contributor to the long-term risk associated with low-level waste disposal.
- 101-SY, 103-SY, and AN-107 (high organic waste) contain 60-70% non-pertechnetate (Schroeder 1995, 2001).
- Non-pertechnetate species are stable ($t_{1/2}$ ~8 months when heated and exposed to air) and hard to oxidize (Schroeder 1998, 2001).
- The stability and inability to separate these non-pertechnetate species presents a potential problem to Hanford's River Protection Project if the overall goal of 80% technetium removal can not be met.

The Non-Pertechnetate Problem and History (continued)

Current status:

XANES data show Tc(IV) and some Tc(V) complexes in these wastes. (Blanchard 1995)

Model studied on the radiolytic reduction of TcO_4^- show:

1. **Radiolytic reduction of TcO_4^- is attributed to NO_3^{2-}.**
2. **Organics are required to scavenge oxidizing O^- radicals to give a net reduction technetium.**
3. **Gem-diol and 1, 2 diol ligands are important for forming soluble reduced technetium species, $(RO)_8[Tc(IV)\mu\text{-}O]_2$.**
4. **The complexes oxidize in air within days.**

   (Shuh, Edelstein, and Lukens, 2000)

Tc(IV) and (V) gluconate complexes, formed in base, are stable in base and have complex structures. Complexes are air stable. (Schroeder 2000 and Chamberlin 2000)

1, 2-diols form stable complexes in base with Tc(V) and/or Tc(IV). The complexes are air stable. (Schroeder 2001-2003, current project)

Project Goals, General Workscope, and Specific Objectives

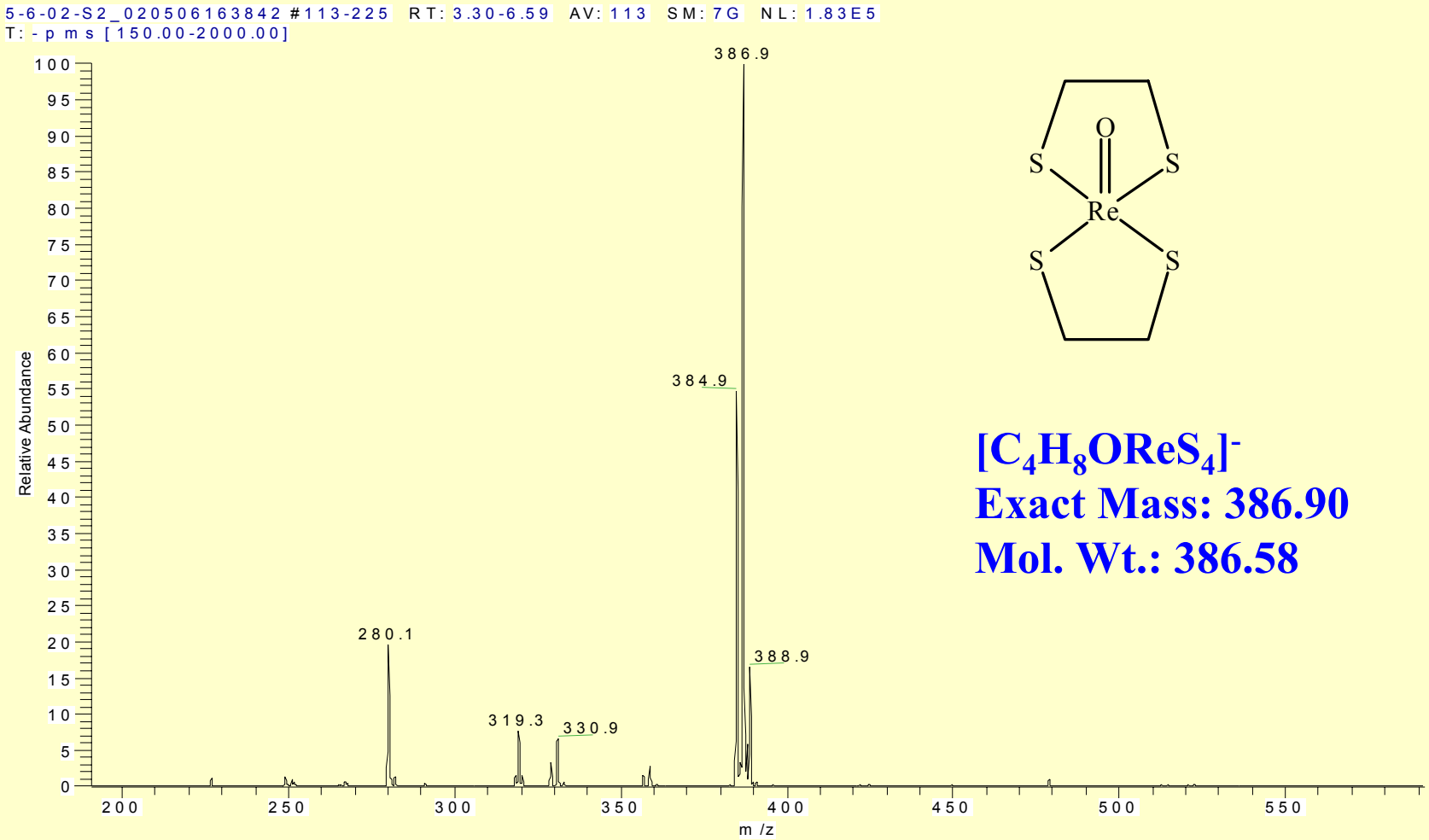
Workscope			
FY1 Objectives	**FY2 Objectives**	**FY3 Objectives**	**Goals**
Run model Re/Tc complexes on CE/MS	Run a non-TcO_4^- fraction from AN-107 on CE/MS	Run other non-TcO_4^- fractions from AN-107 on CE/MS	**Develop a Capillary Electrophoresis/Mass Spectrometry (CE/MS) technique for identifying non-TcO_4^- species**
Optimize the separation of a non-TcO_4^- fraction from AN-107	Separate other non-TcO_4^- fractions from AN-107	Other envelope C post-Superlig 639 effluents	**Develop a method to separate non-TcO_4^- fractions from Hanford waste samples**
Scoping chemistry on Re/Tc gluconate and alkoxide complexes	Synthesize and characterize ID'ed non-TcO_4^- compounds	Study the redox and ligand substitution chemistry of the compounds	**Synthesize, characterize, and develop the chemistry of the identified non-TcO_4^- species**

Goal 1: Develop a Capillary Electrophoresis/Mass Spectrometry (CE/MS) Technique for Identifying Non-Pertechnetate Species

Plan:

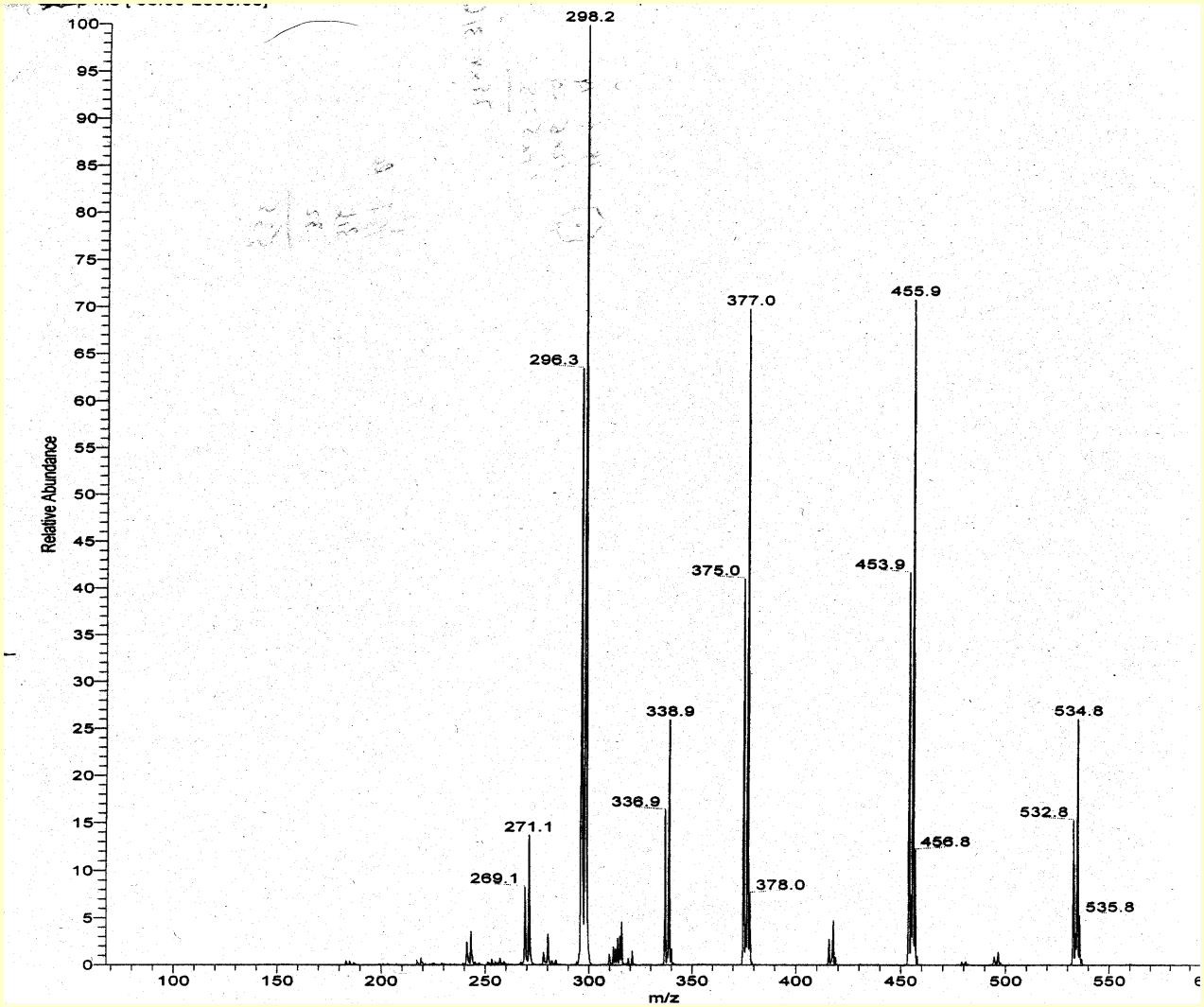
- **Develop the CE and MS techniques in parallel**
- **Prepare Re and Tc complexes (gluconate, alkoxides, etc.)**
- **Use Re complexes for CE and MS development work then test with Tc complexes**
- **Couple CE to MS and test with Re and Tc complexes**
- **Run TcN fractions from separations work**

$[Me_4N][ReO(SCH_2CH_2S)_2]$ 1.6 mg in 1.6 ml $MeOH/H_2O/HAc$ (1.0/0.55/0.05), Negative Mode



$[C_4H_8OReS_4]^-$
Exact Mass: 386.90
Mol. Wt.: 386.58

Mass Spectrum of $[Re(O)_2(py)_4]^+$, Positive Mode



$[Re(O)_2(py)_4]^+$ (py = pyridine) give a parent peak (mass 534) and peaks (mass 455, 377, and 298) for the sequential loss of the py ligands

Tc Mass Spectrometry Status

With a good instrument, we can get a good spectra, in either positive or negative mode, for known stable compounds.

Two CE units have been built. One is being used by the chemist to develop separation parameters for Tc complexes, the other is for the MS instrument.

The instrument we originally used could not operate in negative mode.

We have purchased a complete electrospray ion source and source lens stack for the Finnigan LCQ instrument that is available for our use.

This source will allow us to switch the instrument to electrospray mode, use the negative ionization capability of the instrument, and allow us to run low level radioactive Tc samples.

The source and lens stack cost ~$15000 and is scheduled to arrive on May 9th.

Goal 2: Develop a Method to Separate Non-Pertechnetate Fractions from Hanford Waste Samples

Plan:

- **Separate the gross β and γ activity from ^{99}Tc using cation exchange: Dowex 50Wx8, 100-200 mesh, H^+ or Na^+ form, and elute with water.**

- **Clean up the technetium fractions from residual gross activity and separate the various technetium fractions using size exclusion chromatography (Sephadex G-10, a hydrolyzed starch) and water elution.**

AN-107 Waste Composition

Species	Concentration	Species	Concentration
Na	4.96 M	PO_4^{3-}	0.0076 M
Al	0.0245 M	CO_3^{2-}	0.25 M
K	0.0266 M	NO_2^-	0.756 ± 0.088 M[a]
Ca	0.010 M	NO_3^-	3.09 ± 0.51 M[a]
Fe	0.0094 M	TOC (g/L)	20.74
pH	12.4[a]	density (g/mL)	1.253 ± 0.003[a]
free OH^-	0.087 M[a]	^{241}Am (mCi/L)	0.40[a]
^{90}Sr (mCi/L)	56.8[a]	^{137}Cs (mCi/L)	0.034[a]
^{39}Pu (mCi/L)	0.07[a]	^{60}Co (mCi/L)	0.12[a]
^{99}Tc (mCi/L)	0.0569[a]	^{99}Tc (cpm/mL)	12,6447 ± 4655[a]
^{99}Tc	$(3.39 \pm 0.13) \times 10^{-5}$ M		

[a]determined at LANL

Technetium Solubility and %TcN

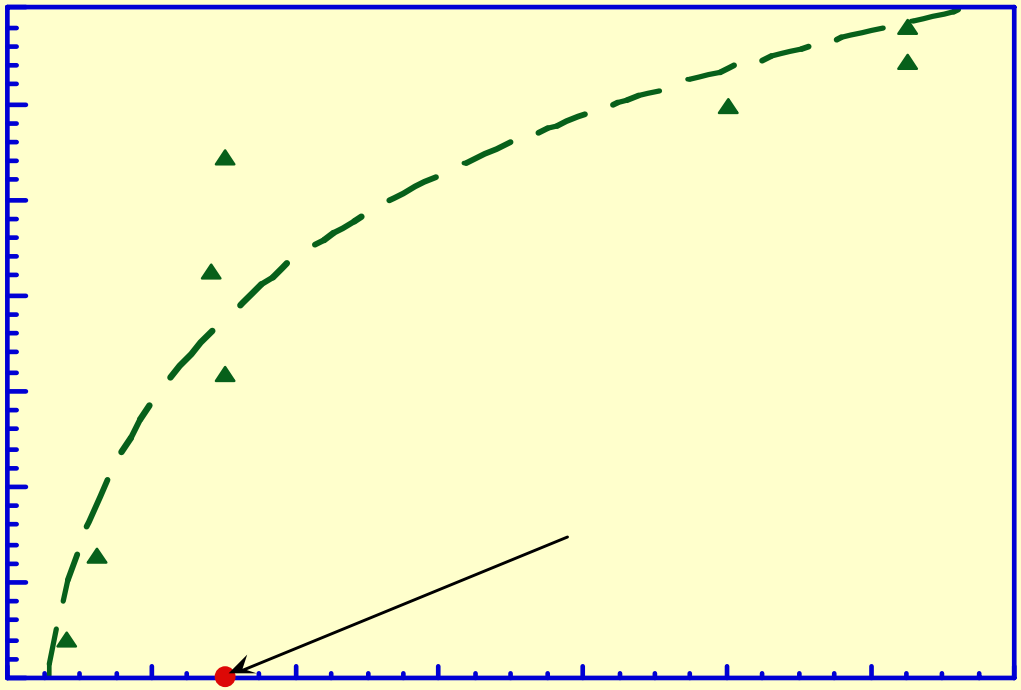
1999 122,045 ± 2,795 cpm/mL (stirred sample)
125,995 ± 2,885 cpm/mL (centrifuged sample)
All technetium species, TcO_4^- and TcN, are soluble.

2002 129,480 ± 8,030 cpm/mL (centrifuged sample)
Technetium is remaining soluble.

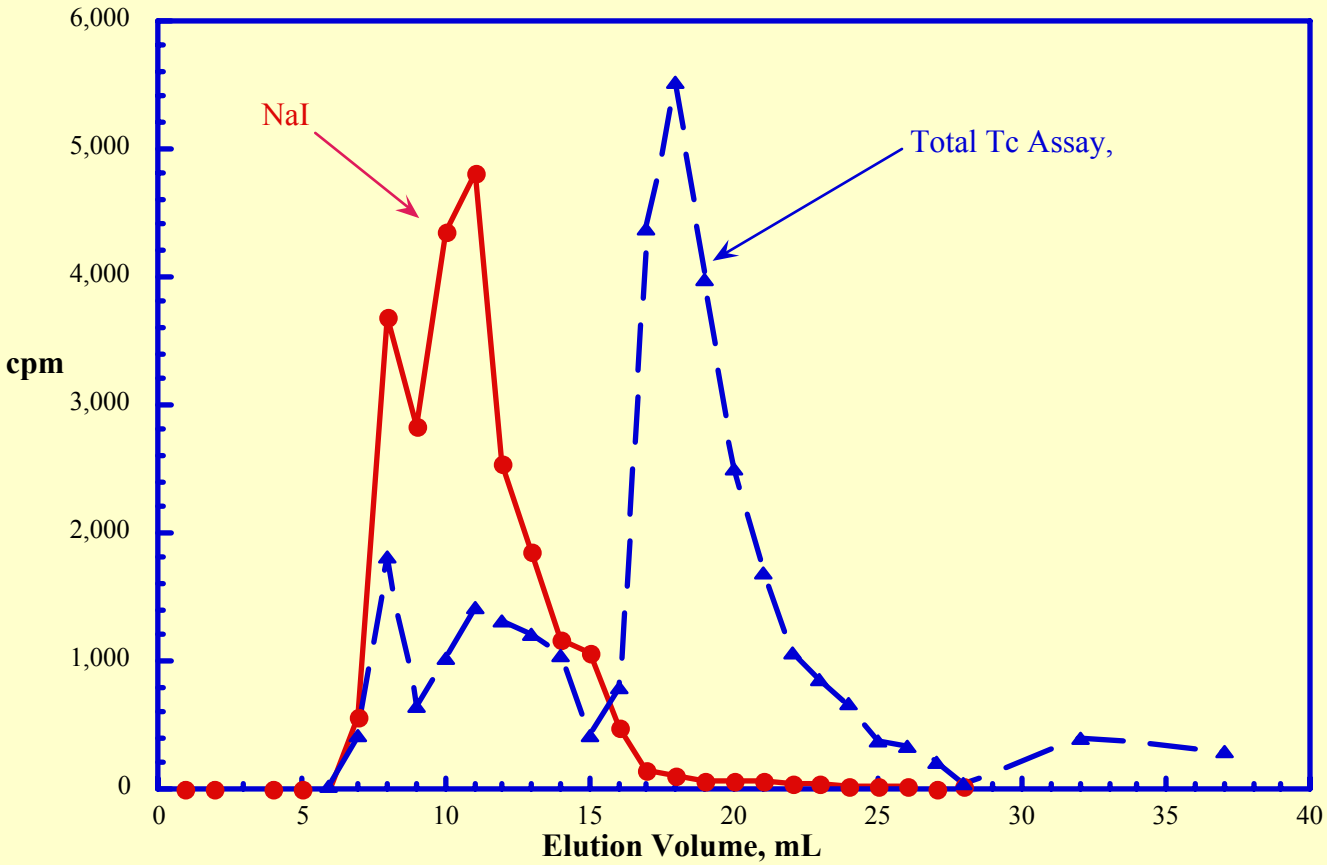
1998 ${}^{app}K_d = 4.42 \pm 0.70$ mL/g
${}^{True}K_d = 315 \pm 41$ mL/g
TcN = 66 ±10%

2002 ${}^{app}K_d = 5.82 \pm 0.30$ mL/g
TcN = 60 ± 8%
The sample is stable to oxidation

Gross Activity in the Cation Exchange Column Eluents as a Function of Sample pH



pH Adjusted Sample: 1 mL of AN-107 through two H^+ form cation exchange columns (@ pH ~ 3) and through a 1 x 40 G-10 column



pH Adjusted Samples: Results

- Gross activity was removed by the cation resin at low pH
- 8–24% sorption of technetium on the H^+ or Na^+ form cation columns
- TcO_4^- in a water solution or in a 1.50 M $NaNO_3$/1.0 M NaOH solution is not sorbed by a G-10 column (1 x 2 cm)
- 25% of the technetium in AN-107 sorbed by a G-10 column (1 x 2 cm), TcN is being sorbed
- Large separation had 55% accountability
- Did 2 cation columns and the high acidity cause 45% of the technetium to sorb? If so, is there a cationic Tc species?
- Does the low pH compromise the technetium speciation?

Cation Exchange and Size Exclusion Chromatography Procedure and Results: Zn procedure

$Zn(EDTA)^{2-}$ log K= 16.5
$Sr(EDTA)^{2-}$ log K = 8.74

Zn^{2+} added to the waste solution could displace EDTA type ligands from Sr^{2+} and allow it to be sorbed by the Na^{+} form of the cation resin.

Little or no pH change would be expected from the metathesis reaction.

Amount of Zn^{2+} added was based on the TOC = 20.7 g/L (1.723 M carbon)

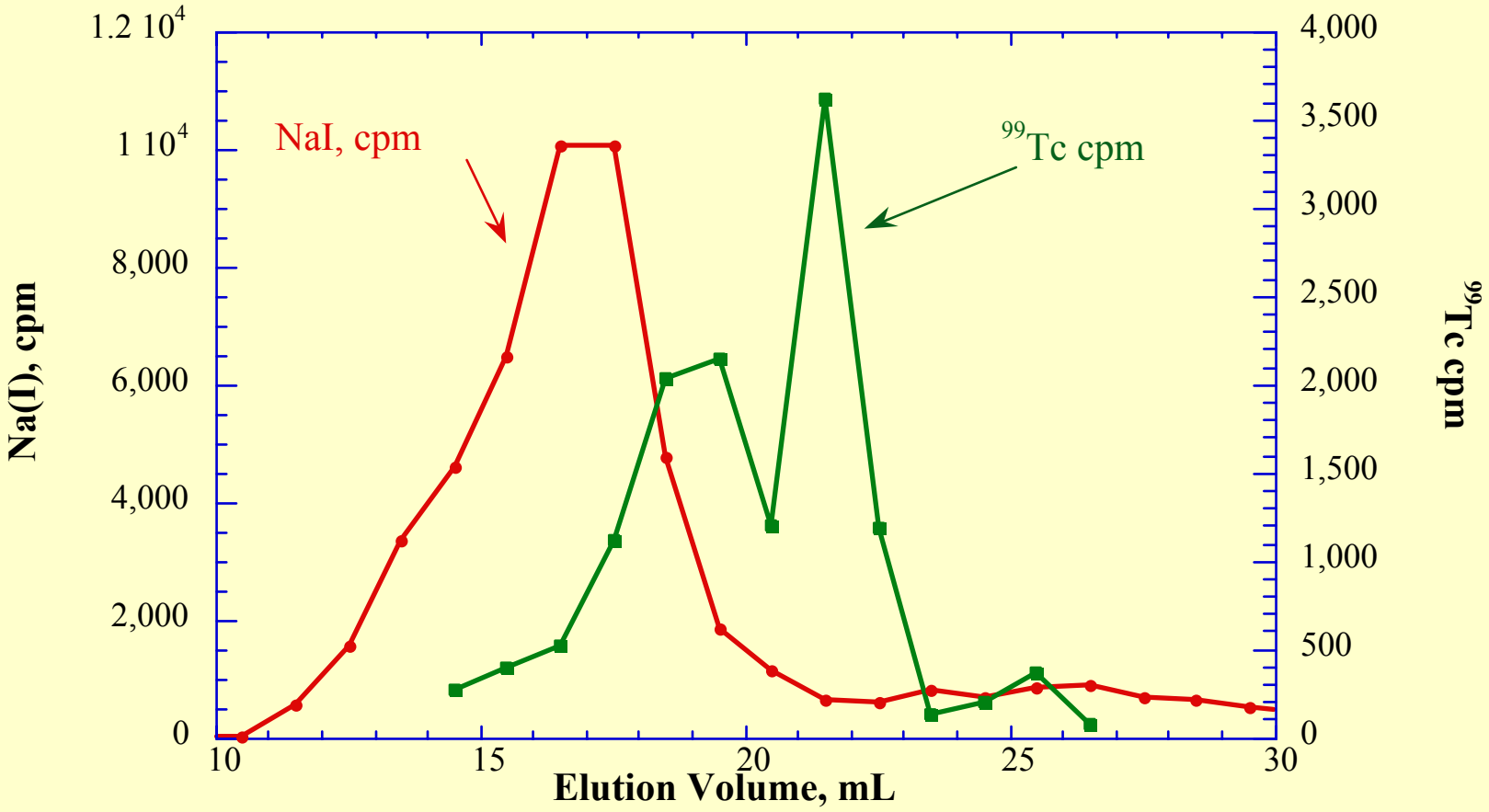
If there are 2C/chelating ligand ≅ 0.0862 mmole chelator/0.100 mL

A two-fold excess of Zn^{2+}(0.17 mmol) was added to the sample to insure formation of Zn^{2+}/chelator complex.

Technetium Accountability in the Zn^{2+} Metathesis Decontamination Procedure

Fraction #	Eluent Vol., mL	Fraction	^{99}Tc, cpm	% Recovered ^{99}Tc	NaI, cpm
1	H_2O	5	8,326	66	22,565
2	H_2O	8	586	4.6	20,314
3	H_2O	8	240	1.9	13,599
4	H_2O	8	38	0.3	7,142
5	1.0 M HNO_3	12	611	4.8	21,056
6	8.0 M HNO_3	16	573	4.5	441,854

Elution of the G-10 column after prior treatment with Zn^{2+} ion and cation exchange column separation



Separation Status

- The Zn/cation procedure needs to be optimized to reduce non-pertechnetate losses; NH_4^+ or K^+ forms of the resin may reduce sorption

- G-10 (dextran) has an affinity for the TcN species in AN-107 and removes ~30% of the technetium. A polyalcohol may be a better eluent to force TcN off the dextran

- Sephadex G-10 separated two different technetium fractions from AN-107.

- Need to work on concentrating the post G-10 sample while maintaining the sample integrity

Goal 3: Synthesize, Characterize, and Develop the Chemistry of the Identified Non-Pertechnetate Species

Plan:

Our previous EMSP work and others have shown that EDTA, EDDA, NTA, IDA, and glycolate technetium complexes are not stable in base.

Technetium gluconate complexes can be formed in base and are stable for at least 6 months even in the presence of air. Similar observations have been noted for 1,2 diol type ligands.

Prepare and study the chemistry of technetium gluconate, diol, and polyol complexes to see how they may be related to the non-pertechnetate problem.

Reproduction of Radiolysis Work - Initial Studies

- **Initial Goal - Reproduce Lukens' work, isolate Tc-gluconate, analyze by ElectroSpray Mass Spectroscopy (ESMS)**
  - **Lukens used a 600 Ci ^{60}Co source for radiolysis**
  - **We had 1 mCi ^{137}Cs source**
  - **We saw reduction of TcO_4^- to form reduced, soluble Tc-gluconate**
  - **Surprised and questioned the results**
  - **Ran control - no external radiation source**
  - **We saw reduction of TcO_4^- to form reduced, soluble Tc-gluconate**
  - **Photolysis?**
  - **Ran control - wrapped rxn. vial in aluminum foil, no external radiation source**
  - **We saw reduction of TcO_4^- to form reduced, soluble Tc-gluconate**

Generality of the Reaction - Screen Organic Compounds

- Mono- and disaccharides
  - Used in Purex Solvent Extraction Plant at Hanford to reduce the nitric acid concentration before neutralization
  - Degradation products from sucrose - glucose, fructose, oxalic acid etc.
- Polyaminocarboxylates
  - Used in Purex plant for removal of metals
  - Degradation products - glyoxylate and formaldehyde
- Dibutyl Phosphate
  - Used in Purex plant for extraction of actinides
- Alcohols
  - Used in this study to model polyhydroxy compounds

Experimental Procedures

- **Reaction Conditions**

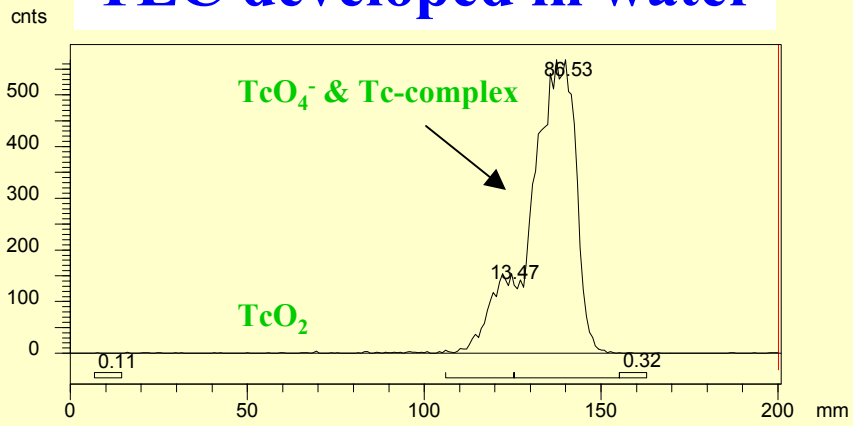
$$\underset{0.01\ M}{NaTcO_4} + \underset{1.0\ M}{100\ \text{sodium gluconate}} \xrightarrow{2M\ NaOH} \text{complex}$$

- **Analysis**
  - **Radiochemical Yield - Thin Layer Chromatography & Bioscan Imaging Scanner**
  - **UV-vis spectroscopy**

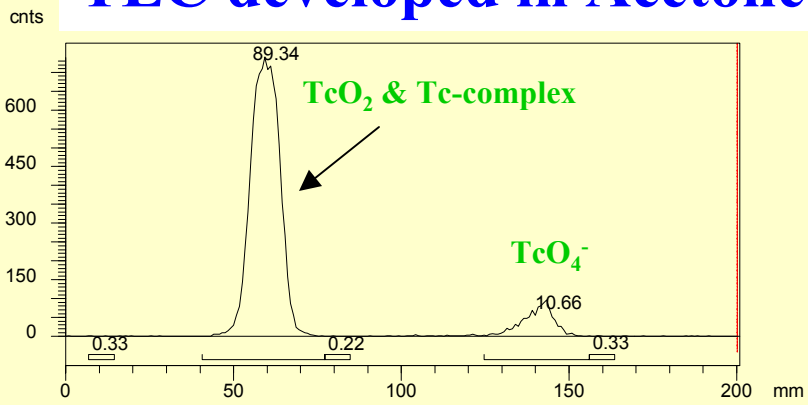
- **Controls**
  - **Reaction conditions - water vs. 2M NaOH**
  - **Analysis Controls - TLC of TcO_4^- and TcO_2**

Data Analysis for TLC/Bioscan

TLC developed in water



TLC developed in Acetone

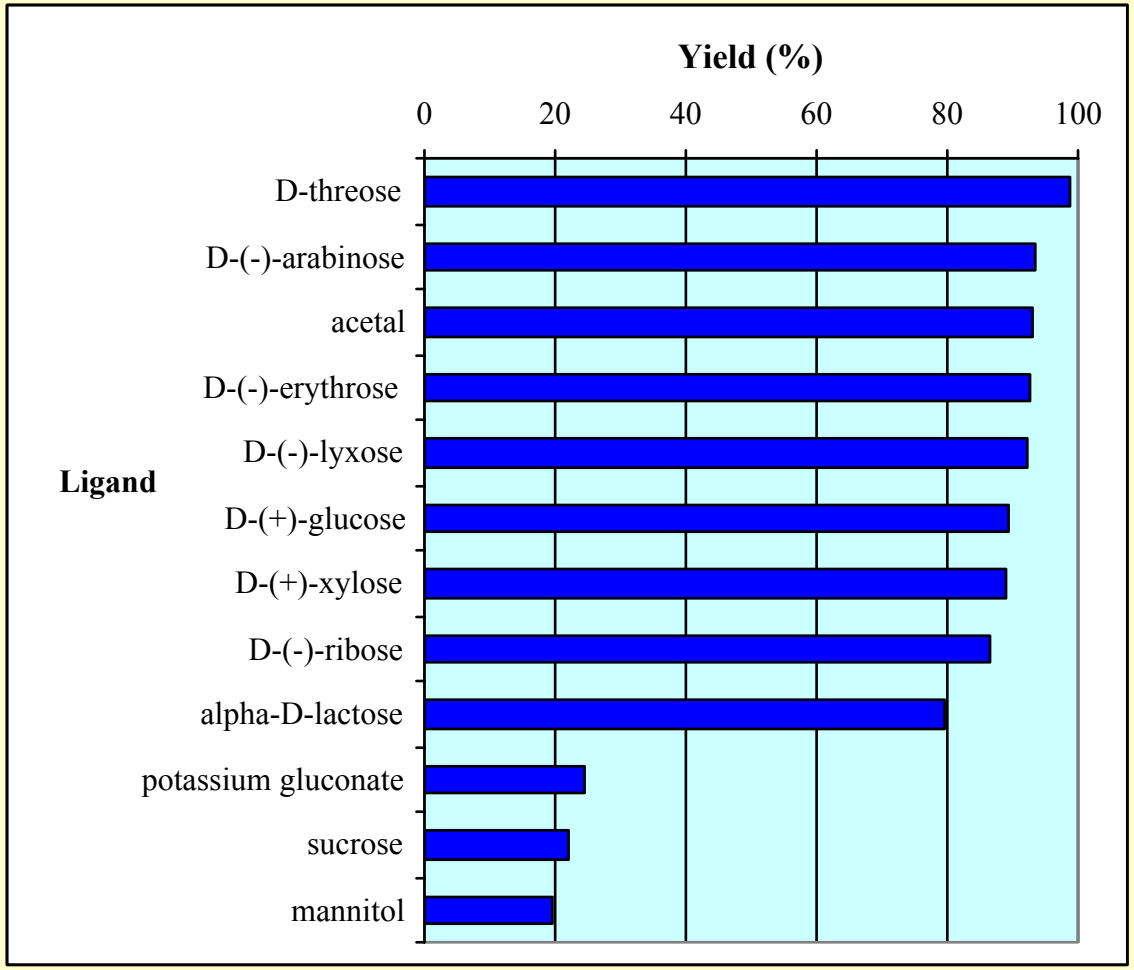


Interpretation

1) No TcO_2 in rxn. - TLC developed in water

2) All activity (89.34%) at origin of TLC developed in Acetone must be due to Tc-complex

Graph of High Reactivity Organic Compounds



No correlation of stereochemistry or carbon in sugar with yield

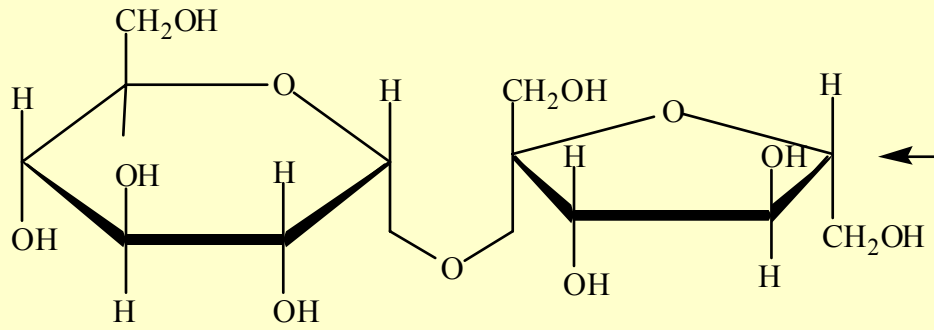
Table of Organic Compounds with Low or No Reactivity

Ligand	% Reduced, soluble complex	
hydroxyethyl(ethylenediaminetriacetic acid)	12	*
nitrilotriacetic acid	11	
malonic acid	9	
sodium oxalate	7	
EDTA, tetrasodium salt	7	*
polyethyleneimine polymer	3	
2,3-butanediol	2	
dibutylphosphate	0	
iminodiacetic acid	0	
succinic acid	0	
sodium citrate	0	

Ligand	% Reduced, soluble complex
sodium citrate	0
N-(2-hydroxyethyl)iminodiacetic acid	0
methyliminodiacetic acid	0
ethanol	0
ethylene glycol	0
formaldehyde	0
glycerol	0
cis-1,2-cyclohexanediol	0
1,3-propanediol	0
1,4-butanediol	0
2,3-dimethyl-2,3-butanediol	0

*unstable in air

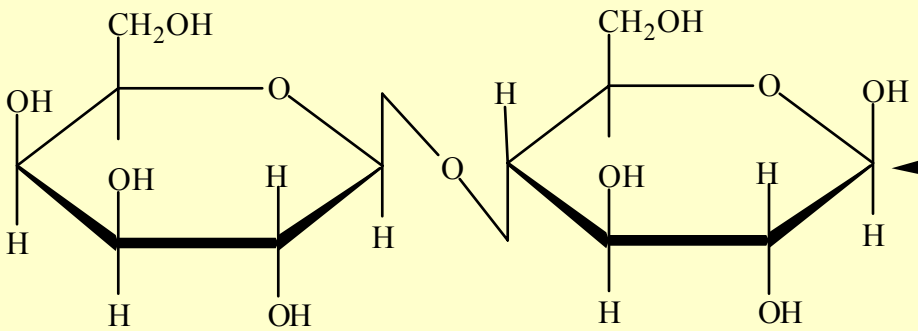
Structural/Activity Relationship - Reducing vs. Non-reducing Disaccharides



unreactive anomeric carbon
linear form cannot be oxidized

Sucrose - Non-reducing disaccharide
reduced, soluble Tc-complex - 22%

Slow base hydrolysis of sucrose generates glucose, a reducing sugar



reactive anomeric carbon
linear form can be oxidized

Lactose - Reducing disaccharide
reduced, soluble Tc-complex - 79%

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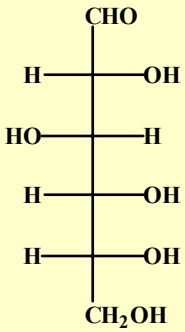
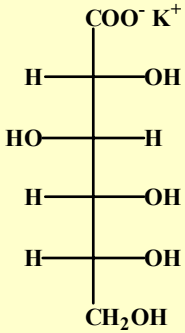
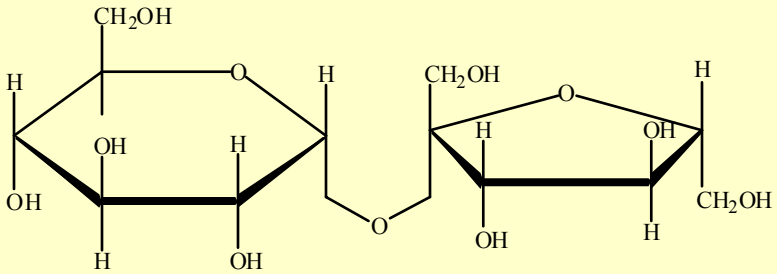
Structural/Activity Relationship - Effect of Chemical Form for Aldohexose



glucose 89%



potassium gluconate 24%



Glucose

Fructose

Sucrose 22%

Oxidation State of ^{99}Tc-complexes

- ^{99}Tc-gluconate rxns.
  - Tc(V) complex
  - $Na[^{99}Tc^{V}(\text{ethylene glycol})_2]$
    - $\lambda = 535$ nm, $\varepsilon = 60\ M^{-1}\ cm^{-1}$

Davison, A.; DePamphilis, B. V.; Jones, A. G.; Franklin, K. J.; Lock, C. J. L. *Inorganica Chimica Acta* **1987**, *128*, 161.

- ^{99}Tc-mono- and disaccharides
  - ^{99}Tc(IV) complexes
  - $K_2[^{99}Tc^{IV}(\text{ethylene glycol})_3]$
    - $\lambda = 270$ nm
    - Only stable at pH > 10 - 11

Alberto, R.; Anderegg, G.; May, K. *Polyhedron* **1986**, *5*, 2107.

Conclusions

- $^{99}TcO_4^-$ can be reduced to reduced, soluble ^{99}Tc-complexes without external radiation or catalytic metals
- Yields for mono- and disaccharides can be > 85%
- $^{99}Tc(IV)$ or $^{99}Tc(V)$ complexes are formed depending on the ligand - gluconate forms $^{99}Tc(V)$ complexes whereas, all other ligands form $^{99}Tc(IV)$ complexes

Sample needs: **We have 101-SY, 103-SY, and two AN-107 samples. These are enough to get us through this project.**

Collaborations:

Dr. Kenneth R. Ashley, Chemistry Department, Texas A&M-Commerce

Dr. Wayne Lukens, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley

Publications

Norman C. Schroeder, Susan D. Radzinski, Kenneth R. Ashley, Anh P. Truong, Glenn D. Whitener "Feed Adjustment Chemistry for Hanford 101-SY and 103-SY Tank Waste: Attempts to Oxidize the Non-Pertechnetate Species" *Journal of Radioanalytical and Nuclear Chemistry*, 250, 271 (2001).

Chamberlin, R. M.; Ashley, K. R.; Ball, J. R.; Bauer, E.; Bernard, J. G.; Berning, D. E.; Schroeder, N. C.; Sylvester, P. "Radioanalytical Methods in the Discovery and Characterization of Non-Pertechnetate (99Tc) Species in Hanford Tank Wastes." Submitted to *Radioanalytical Methods at the Frontier of Interdisciplinary Sciences,* C. A. Laue and K. L. Nash, eds. ACS Symposium Series book chapter (anticipated publication date 2003).

N. C. Schroeder and K. R. Ashley, "Separation of Non-Pertechnetate Species from Hanford AN-107 Tank Waste", submitted to the *Journal of Radioanalytical and Nuclear Chemistry,* 2003.

D. E. Berning, N. C. Schroeder, and R. M. Chamberlin, "The Auto-reduction of Pertechnetate in Aqueous, Alkaline Solutions", submitted to the *Journal of Radioanalytical and Nuclear Chemistry,* 2003.

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