Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste

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Background

There are currently more than 65 million gallons of high-level nuclear waste stored in 177 underground tanks at the Hanford facility in Washington state. The separation of radioactive species from non-radioactive matrix elements will minimize the volume of high-level waste and the cost of its disposal. Numerous technologies have been developed for the separation of problematic radionuclides such as technetium, cesium, strontium, plutonium, and americium. However, these methods are typically ineffective in tanks containing significant amounts of organic complexants (ie. EDTA, NTA, citrate), as well as high concentrations of nitrates, hydroxides, etc. The effects of radiolytic and chemolytic aging complicates this problem, producing poorly characterized radionuclide complexes.

Specific DOE Problem Being Address: All methods of separating technetium from DOE waste streams require technetium to be present as pertechnetate (TcO_4^-). A large fraction of the technetium in the Hanford tanks is not TcO_4^-. Failure to understand the chemistry of these non-pertechnetate species may result in by applying a process that is incapable of removing technetium from the waste streams to the required decontamination factor. Within the high-level waste investment portfolio DOE has identified a specific need to investigate the fundamental chemistry of technetium and how this relates to potential technetium separation processes.

Significance of Project to the EMSP and Benefits: Understanding the chemistry of the non-pertechnetate species in Hanford tank waste would be of value to Environmental Management Science Program (EMSP) because it could either lead to oxidation methods that would convert these species to TcO_4^- that could make existing technetium separations workable or provide the necessary information to develop the separation chemistry for these unknown technetium species. EMSP should also be interested in this project because the synthesized compounds could be used to develop improved characterization methods (e.g. CE-MS) for the technetium species in Hanford waste and they serve as standards for other characterization techniques (EXAFS and XANES). Knowledge of the fundamental chemistry of these complexes will also be useful when it becomes necessary to remediate the soil and groundwater surrounding the leaking tanks. Separation of technetium from mixed waste may benefit from the information generated by this research because non-pertechnetate species may also exist in these wastes. Lastly, this work may benefit the medical community by discovery of new complexes that may have application as technetium radiopharmaceuticals.

Technetium Partitioning

History: ^{99}Tc is a major fission product resulting from the production of plutonium at Hanford; ~2000 Kg of ^{99}Tc are stored in the Hanford Tanks. Typical [Tc] = 5×10^{-5} M.

Risk: ^{99}Tc, because of its long half life (213000 years), and ability to migrate in the environment, contributes to the long-term risk associated with low-level waste disposal.

Goal: Remove ^{99}Tc from the low-level waste streams so that the final waste forms meet their performance criteria. Currently, this requires a separation factor of ~6.4 to meet the NRC Class "A" waste limit: 0.3 Ci/m^3, 18 g Tc/m^3, or 6000 ppb.

Problems: Current technetium separation technology assumes that it exists as pertechnetate (TcO_4^-). However, recent work indicates that the combination of chemical and radiolytic aging in the presence of complexants has produced unidentified, reduced technetium species that are difficult to separate oxidize.

Research: This project is aimed at understanding the technetium coordination chemistry that is found in the complex chemical environment of the Hanford tanks.

The Non-Pertechnetate Problem

- Treatment schemes assume technetium exists as TcO_4^-
- Some wastes contain non-pertechnetate species

  (N. C. Schroeder et al., Sci. and Tech. For Disp. of Rad. Tank Wastes, Plenum, 1998.)

  – Probably Tc(IV) or Tc(V) complexes
  – % non-pertechnetate roughly correlates with organic concentration
  – Reduced species are difficult to separate or oxidize

X-Ray Absorption Spectroscopy

Waste Samples

- XAS analysis of the Tc in samples of waste from Hanford tanks AN-107, AW-101, 101-SY, and 103-SY has been performed by David Blanchard, our collaborator from PNNL.

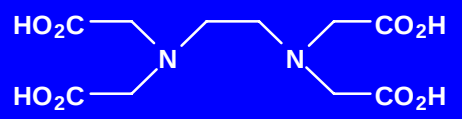
- Pertechnetate removed with Reillex™-HPQ anion exchanger prior to analysis.

- The highest concentration of non-pertechnetate species were found in waste with the highest organic complexant concentration.

- XANES (x-ray absorption near edge spectroscopy) consistent with a Tc(IV) species bound to complexants or complexant fragments through oxygen linkages.

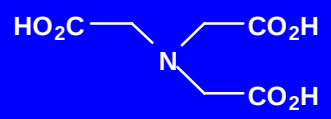
A Sampling of Known Complexants Found in Tank Wastes

Parent Complexants

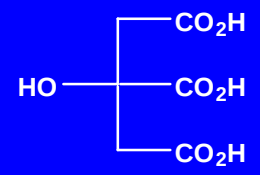


EDTA

HEDTA

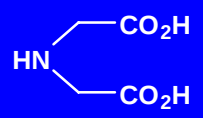


NTA

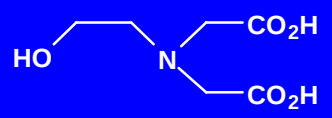


Citric Acid

Degradation Products

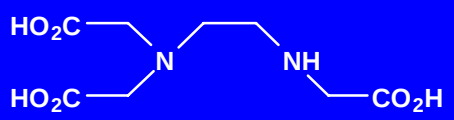


IDA

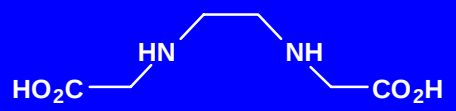


HEIDA

Glycolic Acid



ED3A



EDDA

Oxalic Acid

The Observed, True, and Calculated K_d Values for Unoxidized Waste Samples and the Percent Non-Pertechnetate in the Waste

Sample (Dilution)	Technetium K_d, (mL/g)[a] Observed K_d	True K_d	Calculated K_d	Non-Pertechnetate %
AN107 (1:3.8)	5.20	321 ± 84	318 ± 20	63
AN107 (1:3.8)	8.91	672 ± 206	746 ± 32	51
AN107 (1:4)	7.98	406 ±142	470 ± 12	53
101-SY (1:3.9)	3.99 ± 0.19	545 ± 154	643 ± 38	70
103-SY (1:2.9)	5.16 ± 0.44	543 ± 21	559 ± 32	64

[a]The uncertainties in these K_d values are due primarily to counting statistics.

Oxidative Treatment of Waste

	Sr-90	Tc-99
No treatment	**4**	**16**
UV Photolysis, 6 h	**8**	**110**
UV + ozone	**120**	**---**
UV + $K_2S_2O_8$	**210**	**290**

†Comparable treatment of SY-101 waste: N. C. Schroeder *et al.*, submitted to *Radiochim. Acta*

Tank AN-107 Waste

- "Alkali deficient" tank: unusually low pH ~ 11
- ^{137}Cs removed at PNNL for shipping
- High organic content: 40.4 g/L TOC

Nuclide	dpm/mL	Cation	M	Anion	M
^{90}Sr	1.3×10^{8}	Sodium	8.48	Nitrate	3.71
^{137}Cs	7.6×10^{4}	Potassium	0.046	Carbonate	1.40
^{99}Tc	1.4×10^{5}	Iron	0.030	Nitrite	1.33
^{60}Co	2.6×10^{5}	Calcium	0.015	Sulfate	0.086
^{154}Eu	1.1×10^{6}	Aluminum	0.014	Chloride	0.052
^{155}Eu	8.0×10^{5}	Manganese	0.010	Hydroxide	0.020
^{241}Am	8.8×10^{5}			Phosphate	0.018
Total α	6×10^{5}			Bromide	0.014
Total β,γ	2×10^{8}			Fluoride	0.007

Speculation on the Source of the Technetium Problem

Waste Tanks

$$TcO_4^- + \text{complexant} + \text{reductants} \xrightarrow[\text{70 °C, 30-50 years, pH = 14}]{\text{Radiolysis}} \text{Tc(IV) complex}$$

Our Synthetic Method

$$TcO_4^- + \text{complexant} + NaHSO_3 \xrightarrow[\text{RT, overnight, 0.1 M NaOH}]{} \text{Tc(IV) complex}$$

- Ligands studied include EDTA, NTA, oxalate, EDDA, IDA, glycolate, citrate, tetn, en, DTPA..

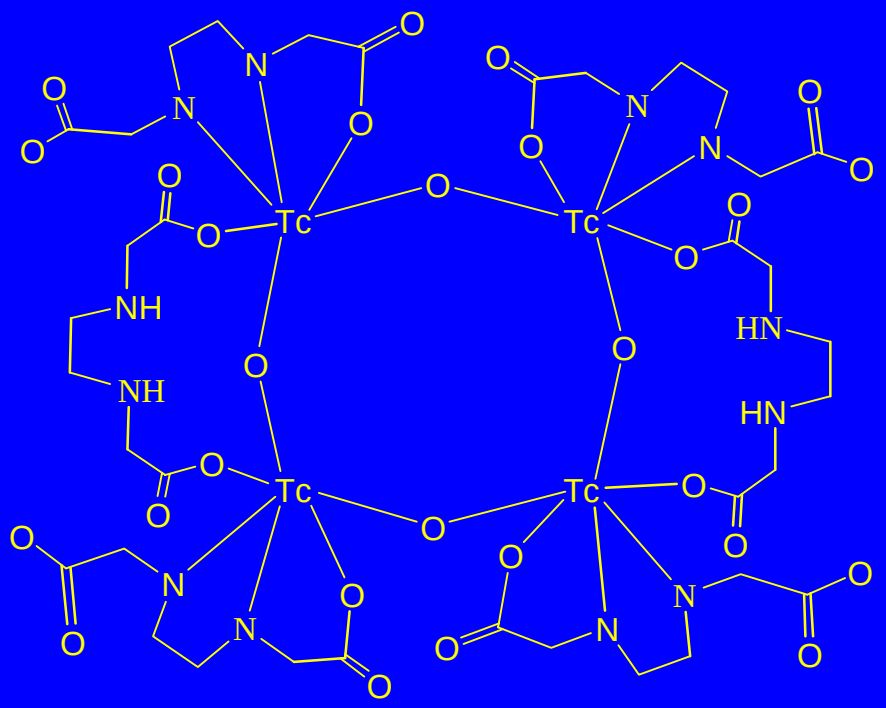
Project Goals

The proposed research will develop the complexation chemistry of aqueous pertechnetate under reducing conditions. The four major goals of this research are to:

- synthesize and characterize the major classes of technetium complexes formed under tank waste conditions
- study the ligand substitution and redox chemistry of these complexes
- use the complexes as standards for characterizing the non-pertechnetate species in actual waste using x-ray absorption spectroscopy (EXAFS and XANES)
- use the technetium complexes to develop efficient oxidation or separation methods for the non-pertechnetate species in actual wastes.

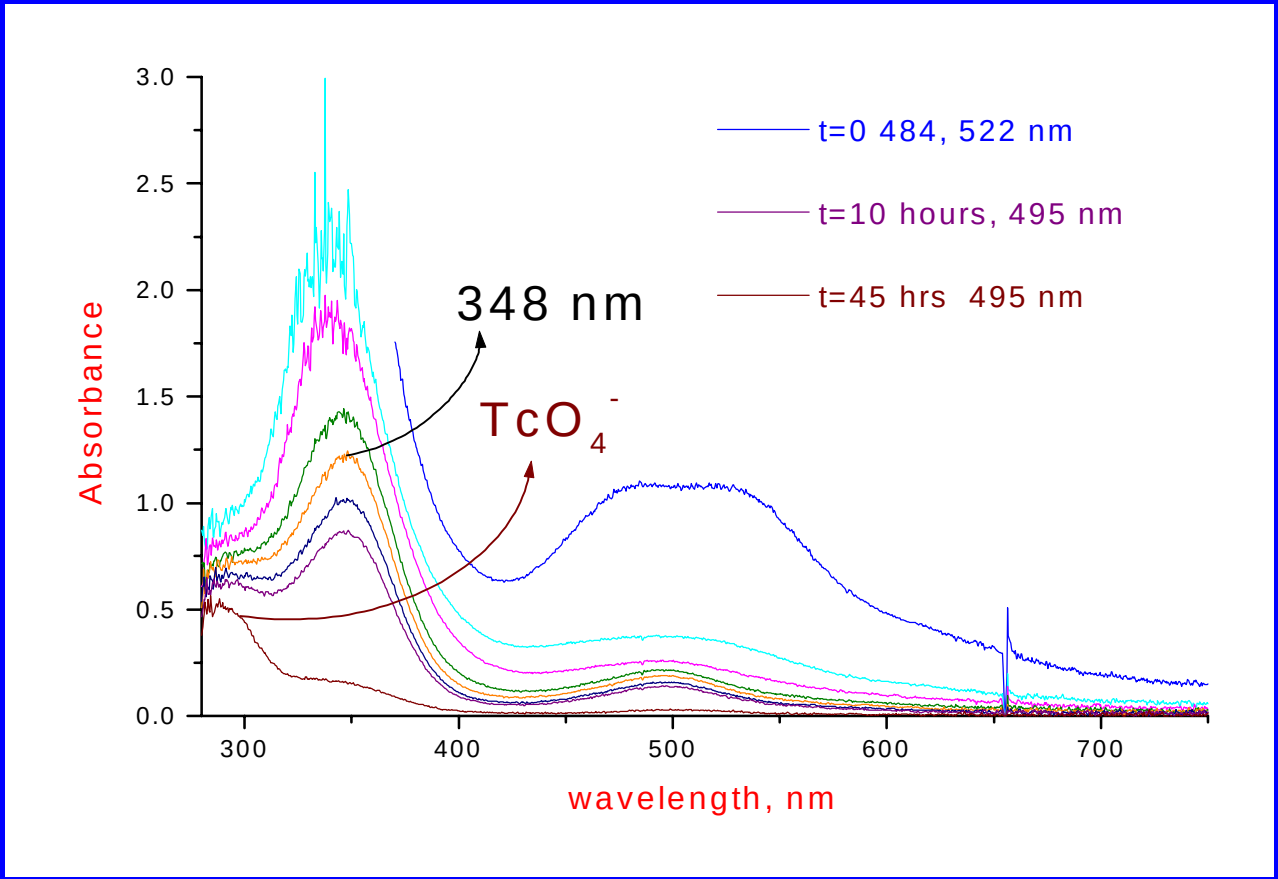
Tc-EDDA

- Elemental Analysis gives $Tc_1N_3C_9H_{14} \approx [Tc_2EDDA_3]_n$
- EXAFS - Suggests a polynuclear complex with Tc-Tc bond distance of 3.51 Å



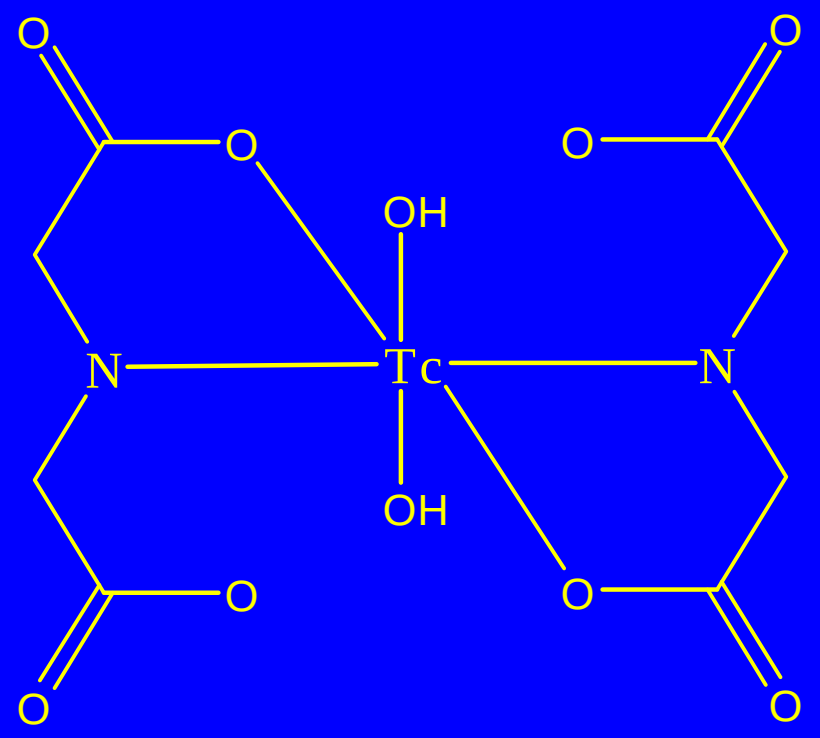
Tc-EDDA cont'd

- Decomposition in 0.67 M NaOH, in air



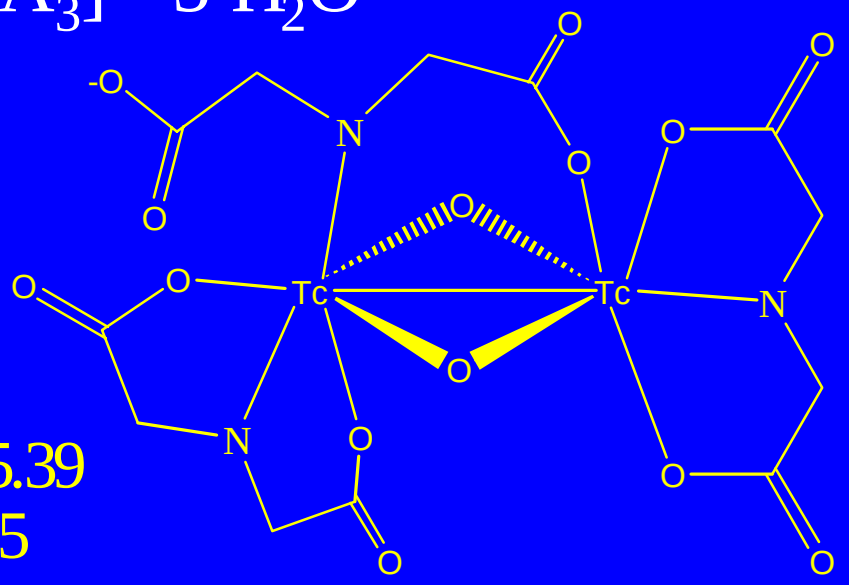
Red Tc-IDA Complex

- EXAFS suggests a monomer
- IR indicates carboxylate coordination (1638 cm^{-1}) with no evidence of a bis-(μ-oxo) bridge



Blue Tc-IDA Complex

- EXAFS suggests a dimer
- Blue color consistent with a III/IV dimer
- IR indicates carboxylate coordination (1615 cm^{-1}) and a bis-(μ-oxo) bridge (748 cm^{-1})
- EA consistent with $Na_3[Tc_2IDA_3] \cdot 5\ H_2O$



$C_{12}H_{22}N_3Na_3O_{19}Tc_2$

Calculated: C, 18.50; H, 2.85; N, 5.39; Tc, 25.39

Found: C, 18.45; H, 3.15; N, 5.46; Tc, 24.75

Citrate and Glycolate Tc Complexes

Tc-citrate

• Deep red complex (λ_{max} = 530 nm).

• IR indicates carboxylate coordination at 1583 cm^{-1}, a possibly Tc-OH band around 1108 cm^{-1}, a possible bridging Tc-O-Tc band at 718 cm^{-1}, and coordinated or lattice water.

• Decomposes to pertechnetate in 0.5 M NaOH overnight.

Tc-glycolate

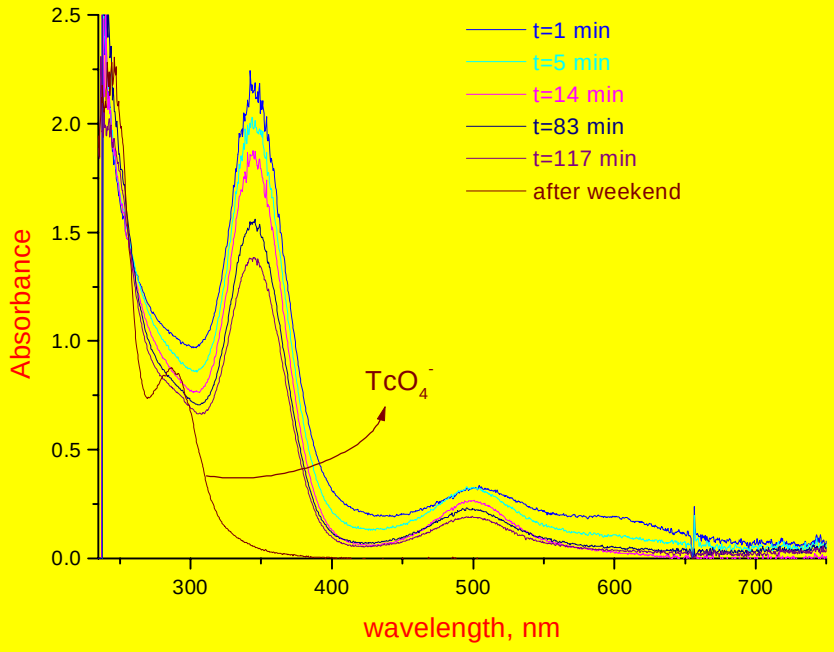
• Deep red complex (λ_{max} = 518 nm).

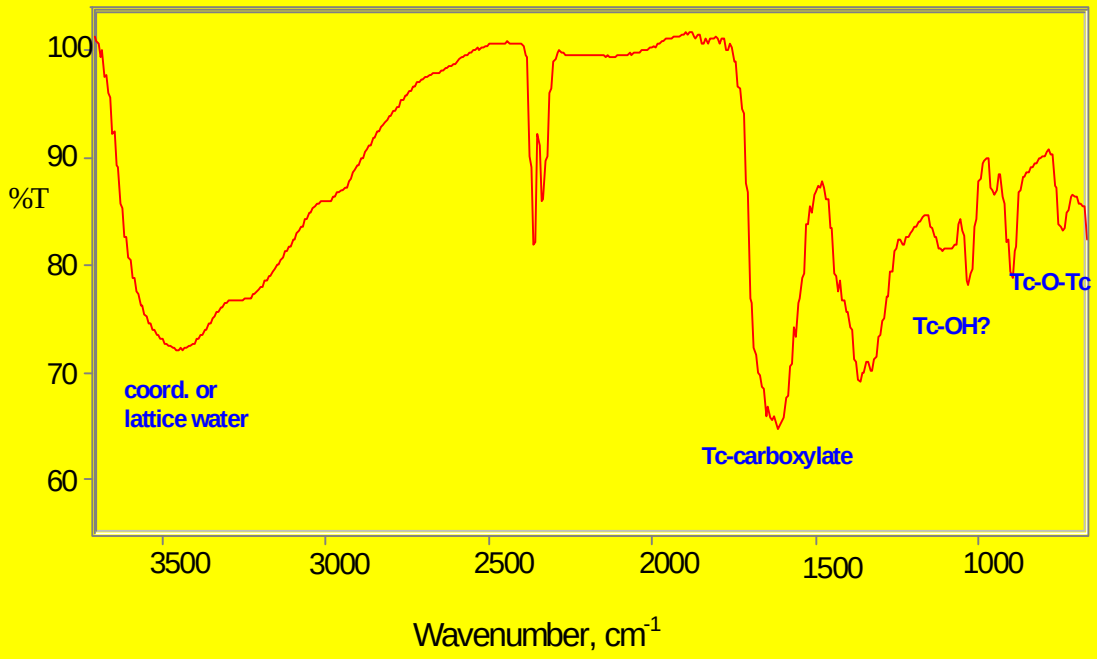
• IR shows carboxylate coordination at 1629 cm^{-1}, a possible Tc-OH stretch at 1142 cm^{-1}, and a bis-μ-oxo stretch at 718 cm^{-1}.

• This complex shows significant stability in 2 M NaOH but eventually decomposes to pertechnetate and a small amount of brown precipitate (See Figure on next slide).

Sample Spectra

Decomposition of Tc-glycolate in 2 M NaOH





IR Spectrum of Blue Tc-IDA

Tc-Nitrido Complexes

$$TcNCl_4^- + \text{Ligand} \xrightarrow[\text{0.5 M } HNO_3 \text{ or NaOH}]{\text{acetone/water}} \text{TcN complex}$$

Ligand = EDTA, oxalate, HEDTA, glycolate, citrate, IDA, EDDA

- A scarlet red complex, and a bright yellow complex form almost instantly in acid and base respectively
- IR shows the characteristic Tc-N stretch around 1050 cm^{-1}, carboxylate coordination (~1625 cm^{-1}), and the presence of a bis-(μ-oxo) core (~725 cm^{-1})
- These complexes also show significant stability in base

Structure of TcN complexes?

- Takayama et al. have reported dimeric technetium nitrido complexes of EDTA and EDDA.

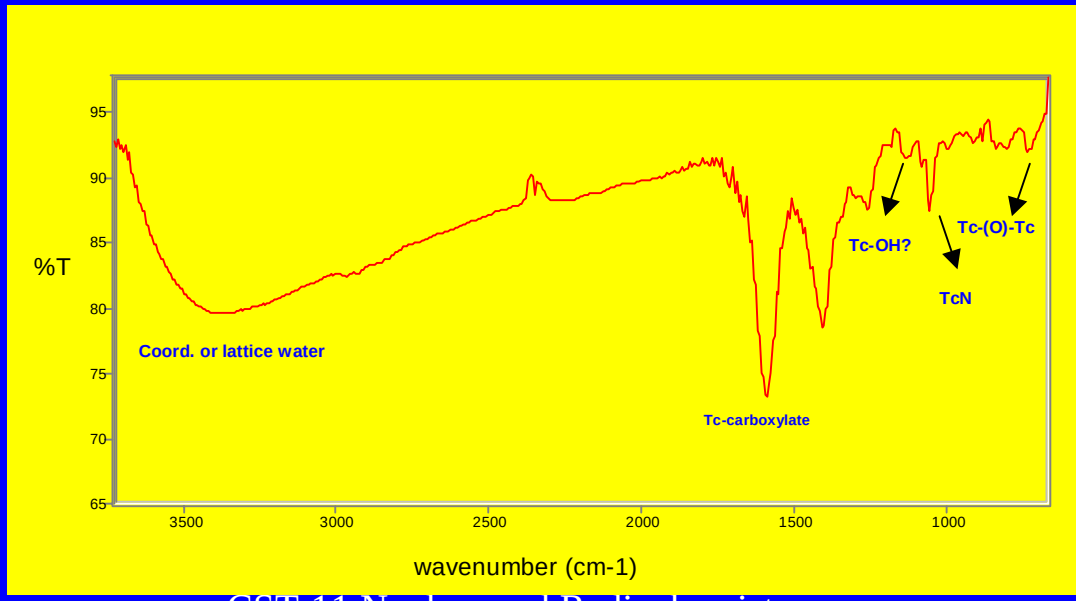
  J. Radioanal. Nucl. Chem., Letters 199 (3) 217-227.

- The red color attributed to a transition in a linear Tc-O-Tc three-center π-bond system.

- The yellow complexes were suggested to be either dimeric in nature with a bis-μ-oxo bridge, or monomeric.

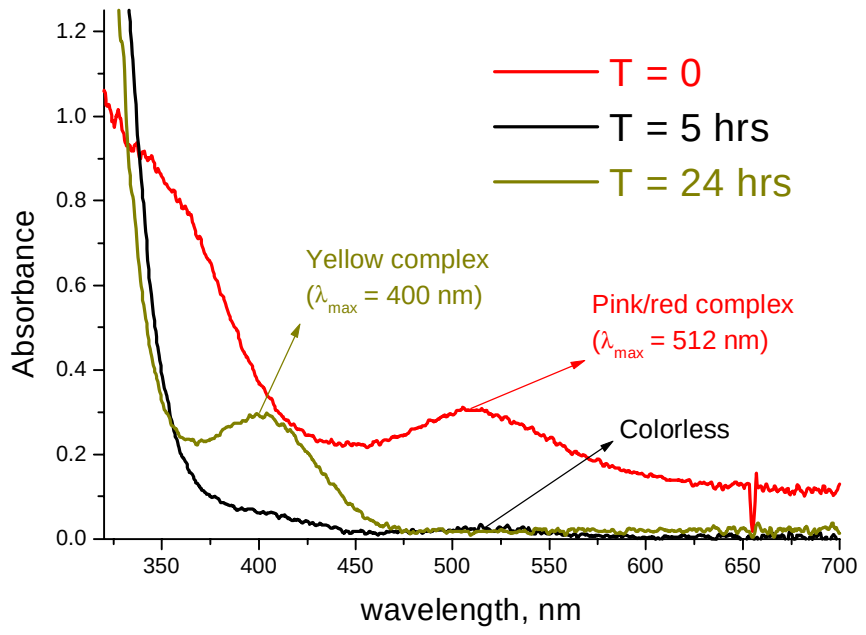
- IR analysis for several of these complexes suggests a dimeric structure. Carboxylate coordination, the TcN stretch, and a bridging Tc-O-Tc stretch are clearly visible.

IR of TcNglycolate



Tc-gluconate

- Stable pink/red Tc-gluconate complex readily forms in 2.5 M NaOH
- Appears the same as the commonly used radiopharmaceutical transfer ligand complex of the type $[TcO(gluconate)_2]^{1-}$
- Addition of H_2O_2 causes the pink color to slowly fade, then turns yellow (see figure)
- Unknown yellow species has been stable for at least two months



Possible transfer ligand complex in Hanford waste?

Relevance to Waste?

• Most of the complexes eventually decompose under caustic conditions in air. Stability is enhanced by the presence of excess ligand and reductant.

•This raises the question: Is the stability higher in the tanks?

•This may be true since real waste contains a large excess of ligand, has a reducing atmosphere, and has has the potential to reduce species through radiolysis and other complex chemistry.

•The Tc-gluconate has shown significant stability in base. This complex has been used as a precursor to form stable Tc complexes used in nuclear medicine.

•Gluconate was added to waste as a denitrating agent. Did Tc-gluconate form in the waste and act as a precursor to form reduced stable complexes in the waste?

Future Work

•Finish characterization of the complexes: elemental analysis, FT-Raman experiments, and XRD on powder samples and single crystals.

• Study the ligand substitution reactions and redox chemistry of the Tc-gluconate complex.

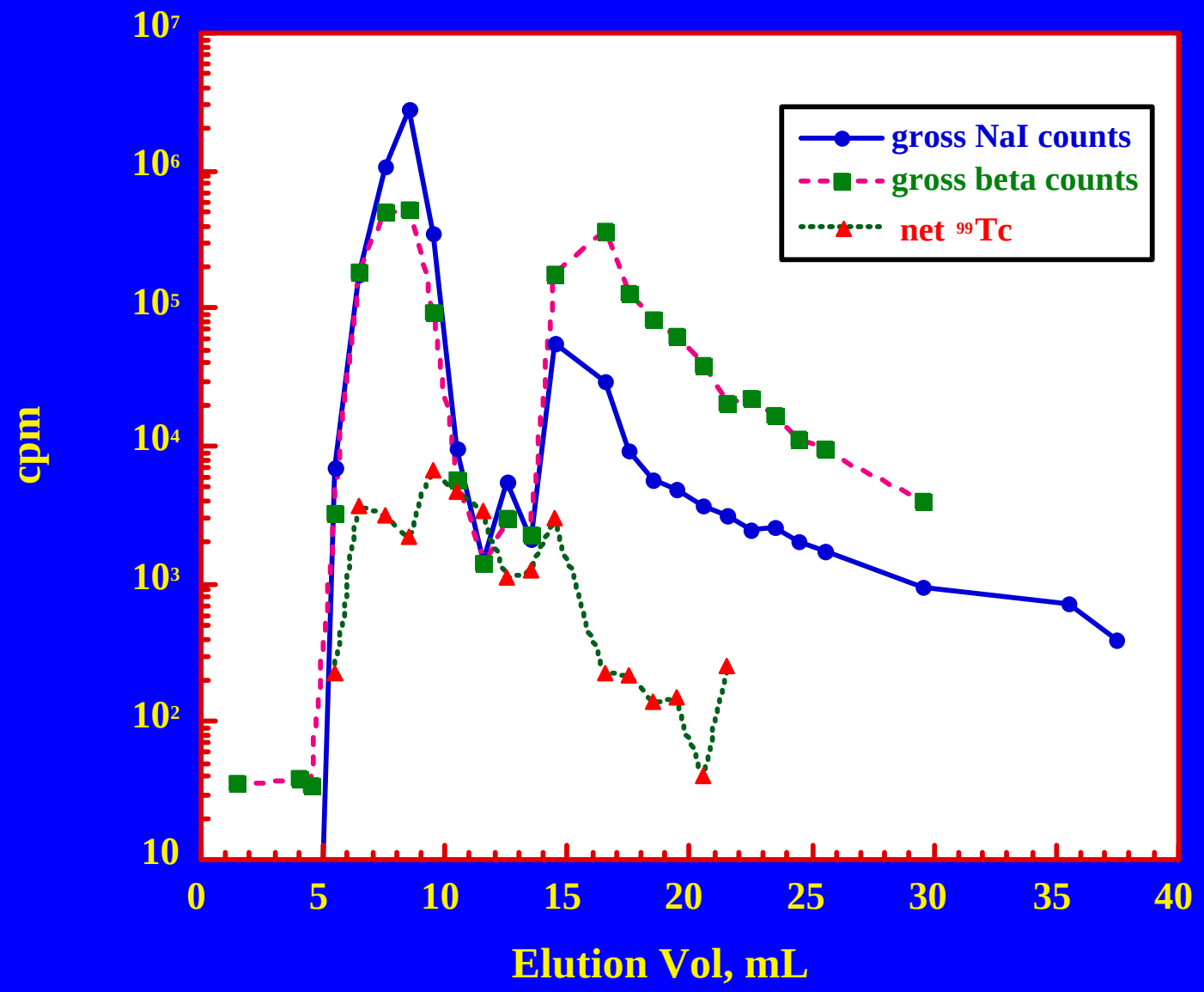
•Determine the stability of these complexes under the reducing conditions of a real waste sample.

• Use the complexes as XAS standards to characterize the non-pertechnetate species in real waste and as standards for calibrating a CE/MS (electrospray) instrument .

• Use the purification methods developed for isolating the Tc complexes to separate the non-pertechnetate fraction from AN-107 (see below).

•Use CE-MS (electrospray) to ID the non-pertechnetate species in this fraction.

• Prepared and characterize the ID species.



Separation of the Non-Pertechnetate Fraction from AN-107 on Sephadex® G10 Size Exclusion Gel; 60% Non-Pertechnetate. Note: TcO_4^- Sticks to the Top of the Column.

Acknowledgment

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