Technetium Chemistry in HLW: Role of Organic Complexants

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Problem Statement – *Background*

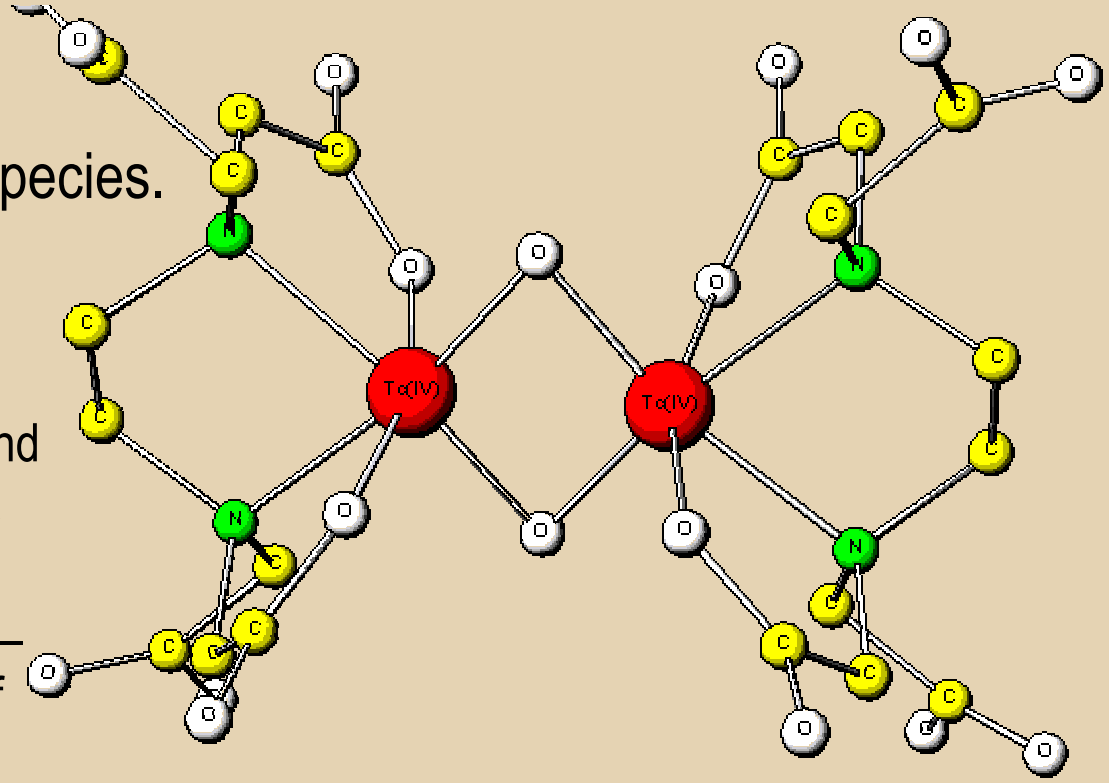
- HLW in Hanford's SST and DST contains 22.5 to 32.5 kCi of ^{99}Tc.
- Current feed specifications for ILAW requires an overall decontamination factor of 6 to 20.
- Tank Farm Closure requires removal of 99% of waste from tanks - fate of Tc in residual waste is unknown.

Problem Statement – *Background*

- Baseline assumption is that Tc is present as pertechnetate, TcO_4^- which is highly soluble.
- Sampling of SST and DST wastes indicates that reduced species of Tc are also present
- Presence of reduced Tc species complicates pretreatment strategies to remove Tc and the prediction of long-term risk of Tc in waste residuals.

Hypothesis

HLW tanks contain significant quantities of organic complexants that can stabilize reduced Tc species.



Implications:

Tc speciation in HLW sludge and supernatant – pretreatment strategies.

Tc speciation in tank residuals – necessary for calculation of release rates following closure

Approach *(original)*

Past approaches have been to study the effect of possible organic complexants on the solubility of Tc.

Our approach: Isolate and identify Tc species from actual tank waste using state of the art analytical organic chemistry, separations, and speciation techniques.

- Isolation: Electrophoresis and high performance liquid chromatography
- Identification: Electrospray ionization mass spectroscopy, Tc nuclear magnetic resonance, and X-ray absorption spectroscopy.

Approach *(current)*

I. **Characterization of model complexes**
   - *Electrospray ionization mass spectroscopy*
   - *EXAFS, NMR*

II. **Solubility studies → development of thermodynamic data**
   - *EDTA, citrate, gluconate, glycolate, formate,*
   - *Oxalate, DTP, D2HEP*

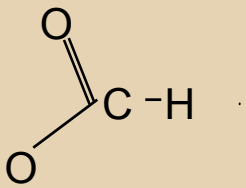
Electrospray Mass Spec Status

Studies using Re analogs:

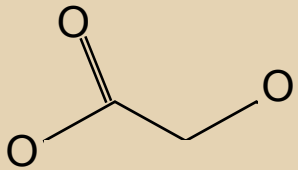
- Good results for Re vinyl pyridine compounds
- Poor results for Re NTA and oxalate compounds
  - High salt content suppressed signal?
  - Nature of Re bonding to these ligands?
- Other mass spec approaches are being explored.

Ligand Schematics

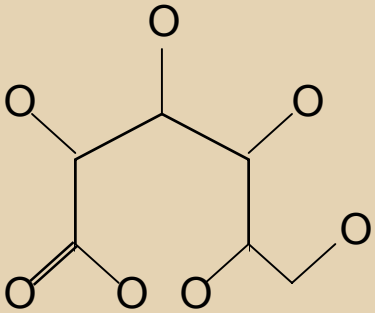
Formate
CH_2O_2



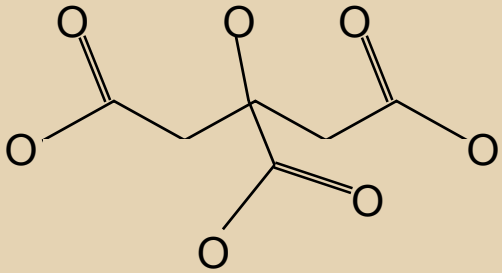
Glycolate
$C_2H_4O_7$



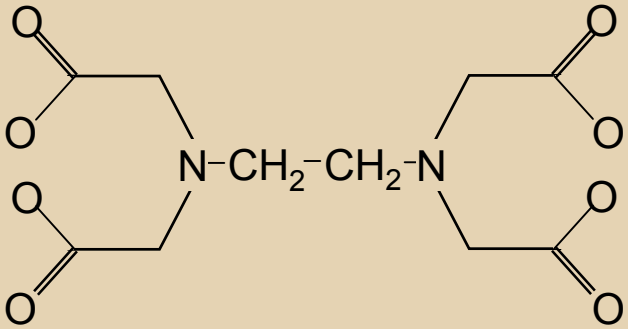
Gluconate
$C_6H_{12}O_7$



Citrate
$C_6H_8O_7$



EDTA
$C_{10}N_2H_{16}O_8$

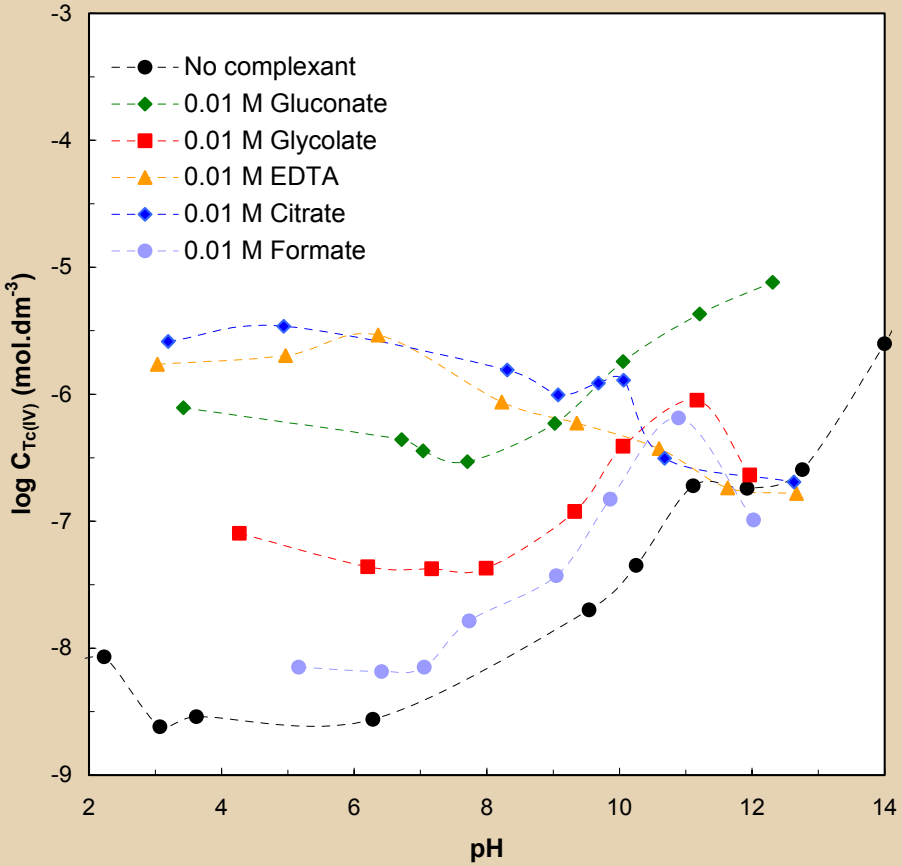


TcO_2(am) solubility in the presence of complexants

In absence of complexants solubility of TcO_2(am) increases under highly basic conditions.

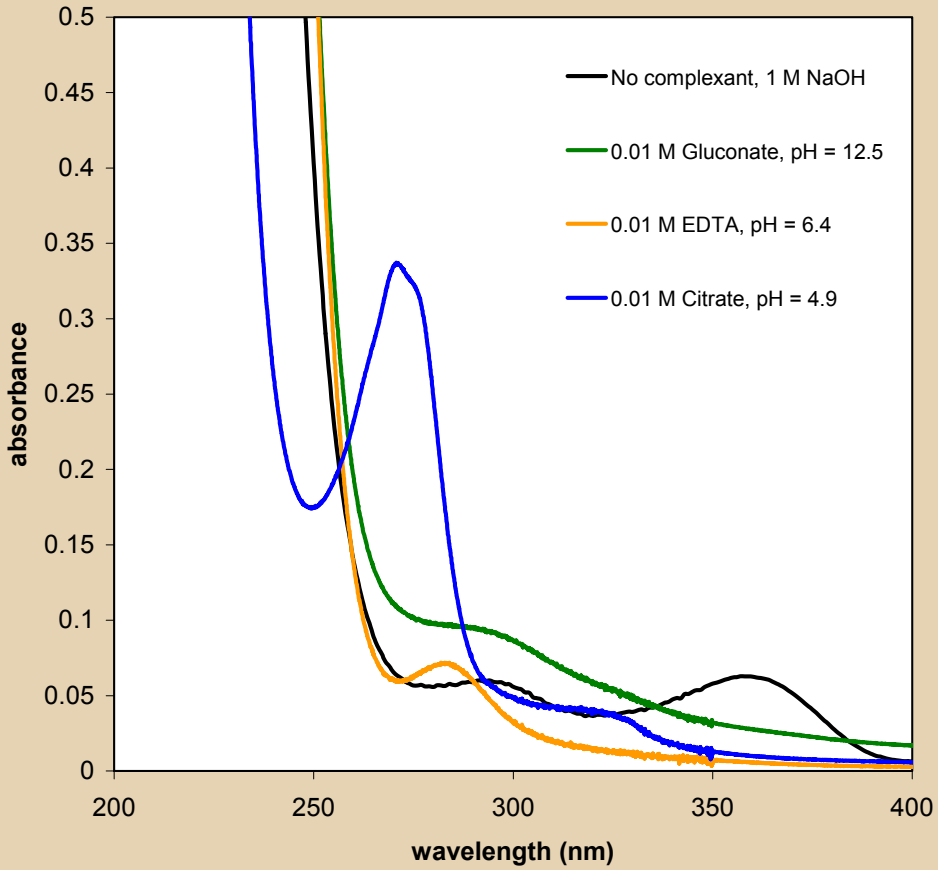
Gluconate is only complexant studied that forms a strong complex with Tc(IV) under highly basic conditions.

Formate forms the weakest complex with Tc(IV) aqueous species.



Spectroscopic characterization

- UV-Vis proven useful to characterize species
  - Unusually high molar extinction coefficients, ca. 10^4 mol^{-1} cm^{-1}
- NMR studies may be useful to characterize the Tc: ligand ratio.



Investigators

- Jim Campbell - separations and characterization of organic complexes
- Herman Cho and Bruce McNamara - NMR
- Yuanxian Xia – solubility studies
- Nancy Hess - UV-Vis, Raman, EXAFS
- Steve Conradson (LANL) – EXAFS

Research Integration

- Collaborate with other EMSP programs on Tc chemistry and the aging of organics complexants.
- Take advantage of Hanford tank sampling schedules to obtain sludge and supernatant samples.
- Disseminate the results to interested parties.