U.S. DEPARTMENT OF
ENERGY

PNNL-23180
EMSP-RPT-020

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Protocol for Identifying the Presence of and Understanding the Nature of Soluble, Non-pertechnetate Technetium in Hanford Tank Supernatants

BM Rapko

February 2014

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Acknowledgements

The author would like to thank R Robbins and co-workers at Washington River Protection Solutions for helpful discussions, SA Bryan (PNNL) for his technical review, and E Buck (PNNL) for information on the use of STEM-EDS on colloidal solids and of its potential use in solutions.

Executive Summary

The purpose of this report is twofold: first, to propose a test protocol for identifying the presence of soluble, non-pertechnetate Tc (n-Tc) in alkaline, high ionic strength, Hanford tank supernatants, and second, to evaluate various methods of obtaining information about the nature of the identified, non-pertechnetate species.

The proposed protocol addresses three questions: 1) is n-Tc present and what fraction of the total soluble Tc is present in this form, 2) is there an interference at m/e 99 in the inductively coupled plasma mass spectrometry (ICP-MS) that gives false positives in a test for n-Tc, and 3) is there another isotope that could act as an interference in a test for n-Tc by liquid scintillation counting.

For ALARA (as low as reasonably achievable) reasons, the protocol involves an initial Cs decontamination by contact with the Cs selective IE-911 ion exchanger. It is recommended that the Cs-depleted supernatant be spiked with a non-Tc-99 source (likely Tc-99m) of pertechnetate to allow an independent assessment of pertechnetate and total technetium behaviors during the test. The solution is then passed through a column containing a pertechnetate getter. Because of its extensive use with Hanford tank waste supernatants, SuperLig® 639 is recommended as the pertechnetate getter. The resulting effluent is sampled for analysis by gamma energy analysis, liquid scintillation counting for beta activity, and ICP-MS for its mass 99 concentration.

Should there be a significant difference in pertechnetate versus total technetium behavior, the effluent is exhaustively oxidized by a persulfate/microwave digestion, adjusted as needed in composition, passed again through an appropriate pertechnetate getter, and resampled. From analysis of these sample results, the questions posed above can be addressed.

The report concludes with an evaluation of a variety of spectroscopic methods that might be used either to identify n-Tc spectroscopically in Hanford tank waste supernatant or to gain insight into the chemical structure of n-Tc. It is concluded that most methods evaluated either are unsuitable, sufficiently insensitive to preclude use at the technetium concentrations present in Hanford tank waste supernatant, or would require significant methods development before they might be effective in n-Tc species analysis. The two methods currently available that can supply useful speciation information are X-ray absorption spectroscopy (of various types) and Tc-99 nuclear magnetic resonance spectroscopy.

Acronyms and Abbreviations

DOE	U.S. Department of Energy
EPR	electron paramagnetic resonance
ESR	electron spin resonance
GEA	gamma energy analysis
ICP-MS	inductively coupled plasma mass spectrometry
LSC	liquid scintillation counting
NMR	nuclear magnetic resonance
STEM-EDS	scanning transition electron microscopy - energy dispersive spectroscopy
XAFS	X-ray absorption fine structure
XANES	X-ray adsorption near edge structure
XAS	X-ray absorption spectroscopy

Contents

Figures

Tables

1.0 Introduction

The Technetium Management program represents an integrated effort that includes work funded directly by the Office of River Protection (ORP), U.S. Department of Energy (DOE) subcontractors, and the DOE Office of Environmental Management (EM). This report is part of this integrated effort.

The objective of this report is to propose a method to evaluate the presence and extent of soluble, non-pertechnetate Tc in Hanford tank supernatants as well as methods that might be used to gain insight as to the nature of the species that make up this fraction. This study will then provide a recommendation as to the preferred approach for identifying and quantifying the presence of Hanford tank supernatant-soluble, non-pertechnetate, technetium. The recommendation will also describe an approach to address the issue of whether inductively coupled plasma mass spectrometry (ICP-MS) analysis, which is useful as a monitoring tool for Tc, may be confounded by the presence of other mass 99 species.

There remain several significant uncertainties in the understanding and modeling of the fate and speciation of Tc-99 in tanks, glass, and low-temperature waste forms. As described below, a significant (2% to 25%) fraction of the ^{99}Tc in tank waste may be present as a supernatant-soluble, non-pertechnetate species that has only been partially identified and, based on experimentation to date, cannot be effectively separated from the soluble fraction of the tank waste. It remains undocumented whether alkaline tank conditions even support the formation of the proposed low-valent Tc-99 species for the supernatant-soluble, non-pertechnetate technetium, i.e., Tc(I) carbonyl compounds. The presence of these low-valent ^{99}Tc species affects both the ability to separate Tc-99 from low-activity waste and the performance of any alternative low-temperature waste forms. While there has been significant work on the removal of the pertechnetate anion from solution, there has been limited work in the area of removing the non-pertechnetate species and the redox chemistry necessary to convert these species to pertechnetate or some other form of Tc that can be removed. In addition, only preliminary tests have been started recently to explore separation of ^{99}Tc from the off-gas streams.

2.0 Background

Over the past two decades, considerable work has been done examining the effectiveness of anion exchange-like resins for their ability to remove soluble Tc from Hanford tank supernatants. As discussed in Rapko et al. (2013) and elsewhere, in most cases, excellent removal of Tc was observed. However, in several instances, there appeared to be a source of Tc that behaves differently than the Tc present as pertechnetate, $[TcO_4]^-$. The fraction of soluble Tc that is not pertechnetate appears to vary significantly between tanks as well, ranging from effectively none to being the majority of the soluble Tc present in the tank supernatant (see Table 1).

Table 1. Reported Distribution of Non-pertechnetate Technetium Present in Various Hanford Tank Supernatants (from Rapko et al. 2013)

Tank	Method	% Non-pertechnetate (Max)	% Non-pertechnetate (Min)
AN-102	SL-639 lag breakthrough	70	60
AN-102	SL-639 column	80	70
AN-102	SL-639 column	70	
AN-102	Multiple SL-639 contacts	63	
AN-102	MP-1 captured TcO_4^- before/after oxidation	57	
AN-102	SL-639 column	48	
AN-103	SL-639 lag breakthrough	8	7
AN-103	SL-639 column	8	3
AN-103	SL-639 column	2.4	2.4
AN-103	Multiple SL-639 contacts	1.6	
AN-107	XANES fit	62	
AN-107		78	75
AN-107	SL-639 column	80	
AN-107	Fit to Kd Reilley HPQ	63	48
AN-107	Fit to Kd Reilley HPQ	67	
AN-107	MP-1 captured TcO_4^- before/after oxidation	57	
AN-107	SL-639 column	50	
AP-104	MP-1 captured TcO_4^- before/after oxidation	72	
AP-104	SL-639 column	72	
AW-101		0.06	0
AW-101	Reillex HPQ column	15	
AW-101		2.9	
AW-101	% Tc in feed vs effluent	4.5	
AZ-101	SL-639 column	0	0
AZ-102	SL-639 column	0	0
AZ-102	Feed and Product Tc ratio	33	
AZ-102		0.04	0
AZ-102	Multiple SL-639 contacts	<0.1	
DSSF	Reillex HPQ batch Kd	7	
SY-101	Reillex HPQ batch Kd	53	
SY-101	Fit to Kd Reilley HPQ	70	
SY-101	Fit to Kd Reilley HPQ/TcO_4^- by NMR	70	63
SY-103	Reillex HPQ batch Kd	54	
SY-103	XANES fit	78	
SY-103	Fit to Kd Reilley HPQ	64	
SY-103	Fit to Kd Reilley HPQ/TcO_4^- by NMR	70	64

3.0 Approach/Discussion

For the most part, identification of the presence of soluble, non-pertechnetate technetium (hereafter abbreviated as n-Tc) has been phenomenological, that is, Tc has been identified as being present after being subjected to processes that remove Tc present as pertechnetate. In the absence of a full identification of the specie that make up n-Tc, this approach seems a reasonable basis for identifying problematic Tc; for if sequestration of n-Tc is possible by the same process that removes pertechnetate, then, from a processing standpoint, the presence of multiple species is not an issue.

A scheme summarizing the proposed protocol for identifying soluble n-Tc is shown in Figure 1.

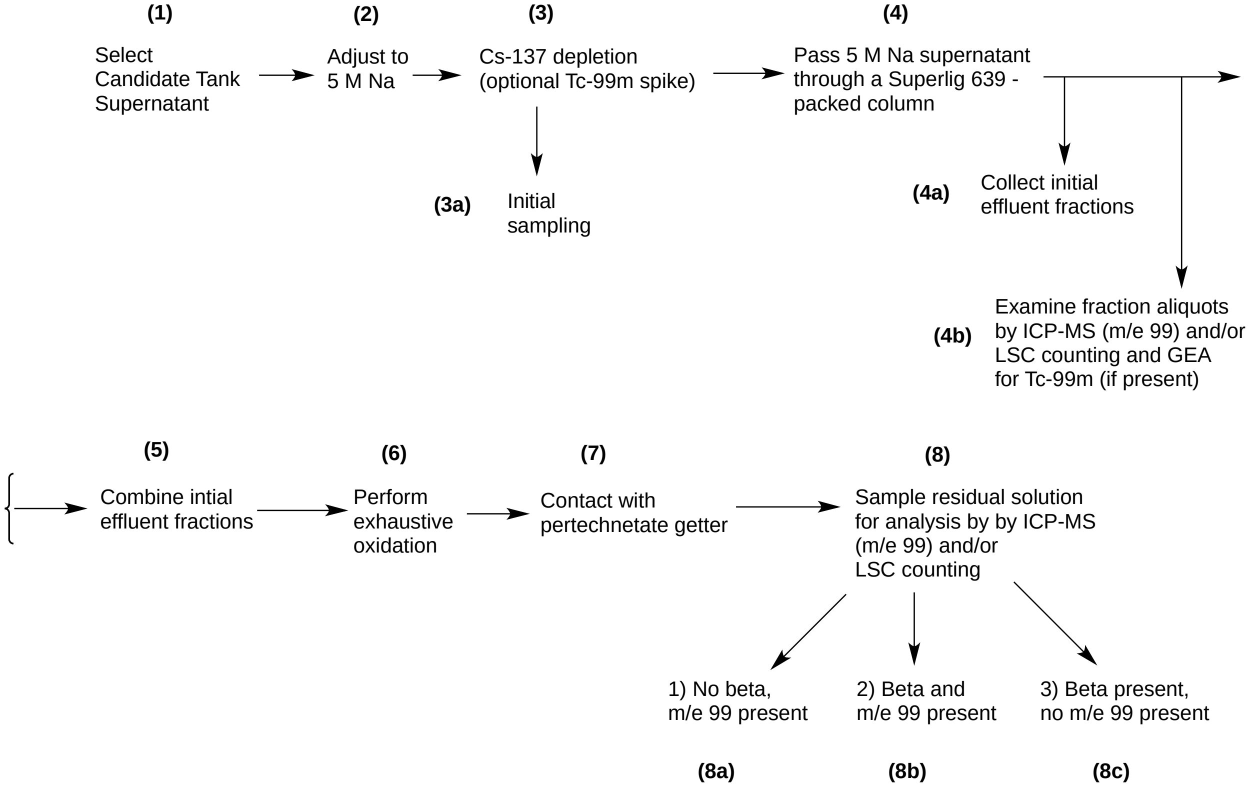

Figure 1. Protocol for n-Tc Identification in Candidate Hanford Tank Supernatant

Justification of the choices of reagents and conditions chosen in Figure 1 is provided as needed. However, an exhaustive review of the literature relevant to these choices is deemed to be outside the scope of the report and is not provided. Figure 1 starts with step 1, which involves selection of the candidate supernatant. Step 2 involves adjustment of the supernatant to 5 M in sodium. This of course requires either previous knowledge of the sodium concentration or a preliminary sampling and analysis for sodium.

The adjustment to 5 M sodium has two benefits. First, it provides a concentration range where SuperLig® 639 has been shown to perform well in removing pertechnetate (Duncan et al. 2011). Second, higher concentrations of sodium tend to create supernatants with densities greater than that of SuperLig®

639, which makes performing the column test in step 4 more problematic due to resin floating when exposed to the supernatant.

In step 3, one or two further adjustments are made to the tank supernatant to prepare it for the step 4 column test and subsequent sampling and analysis. First, it is recommended that the supernatant be contacted with IONSIV IE-911, a commercial material (UOP LLC, Des Plaines, Illinois) that is selective for Cs-137 in high sodium environments. The contact can be either in batch mode, with a subsequent solid/liquid separation, or, preferably, by passing the resin through a column packed with IE-911. The latter has been shown to be very efficient in removal of Cs from a Hanford tank supernatant with minimal perturbation of the other supernatant components (Rapko et al. 2005). Removal of Cs-137 is beneficial as the reduction in dose from the Cs-depleted supernatant allows the subsequent steps to be performed in a fume hood or glovebox rather than in the more cumbersome and expensive hot cell environment.

The next adjustment is optional but highly recommended. It involves introducing an alternative isotope of Tc as pertechnetate and monitoring its distribution independent of any Tc-99 analysis. This determines whether any early breakthrough of technetium or other mass 99 element (if ICP-MS is used as the analysis tool) is due to mechanical aspects of the separation (for example, breakthrough due to column channeling, which will allow Tc to pass through the column regardless of its speciation), or (if Tc-99 breakthrough is observed but not the alternative isotope) to alternative species of Tc being present in the supernatant. Two isotopes are convenient for this purpose. Technetium-95m is a relatively long-lived isotope (half-life of 61 days; major emissions at 204, 582, and 835 keV), but is no longer routinely available in the U.S. Technetium-99m has a short half-life (6.04 hours, 140.5 keV emission), but is readily available through a commercially available Mo-99/Tc-99m generator. If a non Tc-99 spike is added, particularly if Tc-99m is the isotope used, then an initial sampling of the spiked solution is recommended. Periodic analysis of the initial solution's Tc-99m activity can then be compared to later, post-pertechnetate removal samples, to account for isotope decay in evaluating pertechnetate removal performance. This proposed use of other Tc isotopes for this purpose is not novel; it has previously been used during testing of materials for Tc removal from Hanford tank supernatants for just this purpose.

Step 4 involves passing the (modified as per steps 2 and 3) candidate supernatant through a pertechnetate getter material. A variety of materials have been tested for this purpose, including SuperLig® 639 (IBC Advanced Technologies, American Fork, Utah), TEVA resin (Eichrom Technologies LLC, Lisle, Illinois), Reillex®-HPQ (Vertellus Specialties Inc., Indianapolis, Indiana), ABEC-2000 (Eichrom Technologies LLC, Lisle, Illinois), AG MP-1 (Bio-Rad, Hercules, California), and Purolite-A530E (Purolite Corporation, Bala Cynwyd, Pennsylvania), to name just a few of the most studied for this purpose (Duncan et al. 2011). Liquid-liquid systems are also available for such separations but are not recommended (Dyrkacz et al. 1979 and references therein).

Although many of these resins have been shown to be effective at pertechnetate removal from high sodium nitrate and nitrite solutions, SuperLig® 639 is the most studied of the successful resins with actual Hanford tank supernatants (Robbins and McCabe 2013) and therefore is the recommended material for this testing. From existing test results (for example AW-101 testing), well over 40 bed volumes of supernatant can be passed through a SuperLig® 639 column before significant breakthrough of pertechnetate is observed (Hassan et al. 2003).

In step 4a, the first few bed volumes of effluent from the SuperLig® 639 column are collected. In step 4b, 1) the beta activity is determined by liquid scintillation counting (LSC), 2) the concentration at m/e 99 by ICP-MS is measured, and 3) if Tc-95m or Tc-99m was added initially, the concentration of that isotope is determined by gamma energy analysis (GEA). If more than 99% of the Tc beta activity and/or m/e 99 material is removed by treatment of the supernatant with SuperLig® 639, then no further analysis is needed and it can be concluded that there are no significant quantities of n-Tc present in the supernatant.

If there is a significant amount of beta activity and/or m/e 99 material present in the first few volumes of effluent, then, if alternative Tc isotopes were added in step 3, the GEA results should be reviewed. Behavior in the pertechnetate-spike similar to the behavior described by LSC and ICP-MS results indicates a mechanical problem with the column run such as channeling (possibly as a result of resin floating). If little to none of the alternative Tc isotope is present, then the later steps of the protocol should be performed.

Step 5 involves simply collecting all of the effluent processed and mixing to provide a test solution for the subsequent steps. A composite sample should be collected for later comparison at this point.

Step 6 involves performing an exhaustive oxidation of the system to convert any soluble n-Tc to pertechnetate. The method of exhaustive oxidation consists of microwave digestion of an acidified solution in the presence of sodium persulfate as described by Egorov et al. (2004, 2012).

Following the exhaustive oxidation, the all-Tc-as-pertechnetate is now present as an acidic solution approximately 1.5 M in sodium. In step 7, contact with a medium suitable for removing pertechnetate is needed. To return the sodium molarity to a point where SuperLig® 639 has been shown to be effective, concentration of the system back to 5 M sodium, could be performed, followed by passing the oxidized supernatant back through a SuperLig® 639 column as described in step 4. It should be noted that SuperLig® 639 has not been tested under acidic conditions from a 5 M sodium solution, but there appears to be no obvious reason why it shouldn't work. Of course, some testing to validate this belief is needed before implementation. A recommended alternative is to add concentrated sodium hydroxide until 5 M sodium is obtained, thus returning to the high sodium alkaline conditions where SuperLig® 639 has been shown to be effective. Alternatively, contact of the acidified, oxidized, approximately 1.5 M in sodium can be performed with a strongly basic anion exchange resin followed by selected washes and elution. Egorov et al. (2012) have demonstrated a protocol using both simulants and actual Hanford tank wastes containing significant fractions of n-Tc that converts the n-Tc to pertechnetate and then complexes pertechnetate with AG MP-1 strongly basic anion exchange resin. Several types of washes are performed and then the pertechnetate is eluted with 6–8 M nitric acid (Egorov et al. 2004, 2012). The purpose of the washings is to selectively remove tetra-valent actinides and Sn-121m, which interfere in the evaluation of the Tc-99 concentration by LSC.

Finally in step 8, the effluent/eluate(s) are sampled and analyzed by ICP-MS and LSC. There are three sets of possible results—each allows a different conclusion to be drawn. For outcome 8a, the final sample shows no beta activity but does indicate the presence of a m/e 99 material. From this, we can conclude that there is a m/e 99 isotope that is not Tc, and so is almost certainly ruthenium-99. Furthermore, this compound tracks with pertechnetate throughout processing, and therefore is likely an anionic species like RuO_4^-; note that in this example, ruthenium, like technetium in pertechnetate, is in the +7 oxidation state.

Outcome 8b shows both beta activity and the presence of a mass 99 isotope by ICP-MS. The most likely interpretation of this result is a failure to oxidize n-Tc back to pertechnetate. This result would be surprising given the documented success of Egorov et al. (2012) in oxidizing n-Tc in five different Hanford tank waste supernatants. An alternative explanation would be assignment of the beta activity to another species such as Sn-121m and the mass 99 result to a non-technetium isotope such as ruthenium-99. Repeating steps 6 through 8 and obtaining the same 8b result would lend credence to the latter explanation.

Outcome 8c, the detection of no beta activity and no mass 99 isotope by ICP-MS, is the expected outcome for supernatants where n-Tc species were present initially but were subsequently oxidized by the microwave/chemical oxidation treatment.

This analysis of outcomes 8a–c relies on a SuperLig® 639-type of pertechnetate getter in step 7. In the case of a strongly basic anion exchange resin being used in step 7, the sampling must be performed of the high nitric acid strip solution to achieve case 8c. If the 2 M nitric acid wash is sampled, outcome 8c for the wash solution would be characteristic of the presence of radioactive tin in the eluate. Outcome 8a from the initial effluent would be indicative of Ru-99 as before and outcome 8b would be indicative of the presence of unoxidized n-Tc as before. Avoiding this added complexity is one reason for choosing SuperLig® 639 as the pertechnetate-getter.

Protocol Recommendations: The use of the protocol described in Figure 1 addresses important questions concerning the removal of technetium from alkaline tank supernatants. First, a problematic form of technetium is defined as one that breaks through a column of the known pertechnetate getter at high concentrations of sodium, SuperLig® 639. It is recommended that a different isotope of technetium, likely Tc-99m, be spiked into the supernatant initially to document the performance of pertechnetate in the supernatant. The technetium that passes through the column eluent quickly is accepted to be in a valence state lower than the +7 of pertechnetate. The technetium present in the eluent is then extensively oxidized and converted to pertechnetate. Literature results indicate that the use of an acidic persulfate-containing solution, concomitant with microwave digestion, is capable of re-oxidizing n-Tc back to pertechnetate. Following the exhaustive oxidation, pertechnetate is now in an acidic nitrate/sulfate-containing solution. It can either be returned to a high sodium alkaline form by addition of concentrated sodium hydroxide to again return it to an environment in which SuperLig® 639 is demonstrated to be effective or it can turn to a typical strongly basic anion exchange resin as done previously by Egorov et al. (2012). Either way, re-contact with a suitable pertechnetate getter for the environment should be performed. Samples should be taken for GEA analysis, LSC analysis of beta activity, and for measurement of the mass 99 concentration in the solution by ICP-MS.

From the test results, several questions can be addressed: First, if all the Tc is sequestered by SuperLig® 639, then by definition there is no problematic technetium present. If n-Tc is suspected (by having both beta activity in the LSC data and a mass 99 peak in the ICP-MS), then exhaustive oxidation is performed. Contact with an appropriate pertechnetate getter then provides a means to evaluate three questions: one, does the beta activity now behave like pertechnetate? Second, is there another source of beta activity, in particular tin-121m, in the supernatant? Finally, is there an interfering mass 99 species, likely ruthenium, in the supernatant? As further supernatants are examined with this protocol, re-interpretation of earlier data becomes easier and an increased understanding of the extent of n-Tc in the Hanford tank supernatants can occur.

4.0 Characterization of Discovered n-Tc in Hanford Tank Supernatants

Any proposed characterization of n-Tc is Hanford tank waste supernatants must consider that no means of isolating or concentrating (aside from evaporation—which also concentrates all other species present except water) n-Tc has been discovered, although efforts in this area have been made (Schroeder and Ashley 2005). Therefore, any characterization must be made on the actual supernatant solution and its maximum concentration of around 10^{-5} M technetium.

In this section, various types of classic spectroscopies and other types of measurements are briefly evaluated for the applicability to n-Tc, particularly for soluble Tc(IV) compounds, and the proposed Tc(I) species for n-Tc (Lukens et al. 2004), $[Tc(CO)_3L_3]^+$. A qualitative consideration as to time, unusual costs, and any peculiarities specific to the measurement will be noted.

Electronic Absorbance Spectroscopy: Spectral features in the visible to ultraviolet region often map the movement of electrons between ligands and metals and between metal orbitals within a metal. Such transitions are often characteristic for a particular species and provide a fingerprint as to its presence. In addition, routine collection of such data in solution is relatively simple and inexpensive. UV-vis spectra for the Tc(I) compound, $[Tc(CO)_3(H_2O)_3]^+$, and the Tc(VII) compound, pertechnetate, TcO_4^-, have been compared (Rapko et al. 2013) but show almost identical spectra in the UV-vis region and so do not provide a signature distinct enough to be used to identify the presence of the n-Tc candidate Tc(I) compounds.

Vibrational Spectroscopy: Like electronic spectroscopy, spectral features characteristic of bond vibrations are often characteristic for a particular type of bond and can provide a fingerprint as to its presence. The Tc-carbonyl region is particularly attractive functionality that can be identified by vibrational spectroscopy as it occurs in a spectral region where few potential interferences exist. Again, as with electronic spectroscopy, routine collection of such data in solution is relatively simple and inexpensive. Two types of vibrational spectroscopy, infrared and Raman, have been used to examine solutions of the Tc-tricarbonyl moiety in aqueous solution at Tc concentrations similar to those observed in Hanford tank waste supernatants. No signatures were observed, presumably due to the relatively small extinction coefficients associated with these absorptions.

X-ray and Neutron Crystallography: From these measurements, one can derive the type of atom and its location relative to other atoms, and assign bonding between atoms. However, these measurements can only be made on crystalline solids and therefore are not suitable to the solution conditions found here.

Polarography: Numerous electrochemical techniques could conceivably be applied towards identification of n-Tc. However, only the venerable polarography with a mercury electrode is considered here. Polarography measures the flow of current as a function of the applied voltage at the working electrode. It will respond then to any electrochemically active species in solution with an increase in current at a characteristic voltage. There are several features, however, that argue against applying this technique for this application: first, the workable range of concentrations detectable by this method appears to be above the typical soluble Tc concentrations in Hanford tank waste supernatants (Bard and Faulkner 1980); second, the multiple electroactive components likely present in Hanford tank supernatants may make a response difficult to interpret; third, this is a new technique for examination of Hanford tank supernatants and that likely will need considerable developmental work to implement.

Nuclear Magnetic Resonance (NMR) Spectroscopy: NMR spectroscopy looks at the transition of a nuclear spin in a magnetic field from a low energy state in line with the magnetic field to a high energy state opposing the magnetic field. Tc-99, in its low spin +1 (d^6) and in its +7 (d^0) oxidation states, is diamagnetic and therefore is particularly suitable for Tc-99 NMR spectroscopy. The measurement is typically made in solution, and therefore tank supernatant is an acceptable medium for this type of measurement. Pertechnetate has been observed by Tc-99 in Hanford tank wastes (Rapko et al. 2003). The Tc-tricarbonyl moiety has also been prepared and various derivatives prepared. It has been shown that the derivatives possess significant differences in their chemical shifts and line widths. However, the presence of paramagnetic species or viscous solutions often associated with Hanford tank waste supernatants can broaden the signals, with a corresponding deleterious impact on sensitivity.

Electron Paramagnetic Resonance (EPR)/Electron Spin Resonance (ESR): ESR measures the transition of an unpaired electron spin in a magnetic field from a low energy state to a high energy state as noted above for NMR spectroscopy. ESR also shows shifts that are responsive to its environment. ESR can be performed in solution as well as with NMR spectroscopy. Technetium ESR spectroscopy is most suited for the paramagnetic oxidation states of Tc that are poorly suited for NMR; in this sense, NMR spectroscopy and ESP spectroscopy complement each other. However, no work has been done applying ESR spectroscopy to Hanford tank supernatants; therefore, some (and perhaps considerable) developmental work would be required to address questions about potential interferences and to identify the detectable concentrations of various Tc species.

X-ray Absorption Spectroscopy (XAS): XAS is a method, suitable for solutions or solids, that provides elemental specific information on oxidation states and can provide structural parameters of its nearest neighbor's type and environment. Subclasses of this method, such as X-ray adsorption near edge structure (XANES) and X-ray absorption fine structure (XAFS) spectra have been the major spectroscopic methods for providing the information known to date about the nature of n-Tc in actual Hanford tank waste supernatants (Blanchard et al. 1997; Lukens et al. 2004, 2006). The major drawbacks to these methods are, first, these methods require a source of synchrotron radiation. This effectively limits measurements to places like Brookhaven National Laboratory in New York, Stanford University in California, or the Advanced Photo Source at Argonne National Laboratory in Illinois. In addition, because of the heavy demand for these systems, there will be long lead times between the time of detection of the presence of n-Tc and XAS sample measurement. Finally, the collected data requires extensive processing and analysis, which adds to the expense of the measurement.

Mass Spectroscopy: The use of mass spectroscopy to identify the presence of specific isotopes has been mentioned previously but it can also be used to identify molecular species if "soft" ionization methods are used such as electrospray ionization, matrix-assisted laser desorption ionization, secondary ion mass spectrometry, and fast atom bombardment. Measurements can be made on both solids and solutions. Instruments with these ionization methods and the infrastructure to perform such measurements are available at the national laboratories. Measurements and data analysis are much less time- and labor-intensive than XAS. However, soft ionization mass spectroscopy has not been tried for identification of n-Tc. Because of the complex matrix that is Hanford tank waste supernatant and the lack of prior relevant work, developmental work would be required before this method would be useful.

Scanning Transition Electron Microscopy (STEM) - Energy Dispersive Spectroscopy (EDS): The STEM-EDS analysis is both element and oxidation/chemical state sensitive and has been used for analysis of technetium in solids (Lear et al. 2010). The instrumentation is available at sites such as national laboratories (Pacific Northwest National Laboratory) and universities (University of Nevada, Las Vegas) that are capable of handling such radioactive materials. The disadvantages are, first, it is difficult to measure solutions—the analysis is typically performed under vacuum. Specialized sample holders for liquids are available but are expensive (estimated \$60–\$100K). This would be a new area of investigation, so some developmental time is likely. Finally, like X-ray photoelectron spectroscopy, significant analysis time is required, so results would take typically two months or more from the time a sample of interest is identified.

5.0 Characterization of Discovered n-Tc in Hanford Tank Supernatants - Recommendations

Unfortunately, there is no clear method to characterize n-Tc species in Hanford tank sludge supernatants. Of the commonly used methods for inorganic compounds, UV-vis and vibrational spectroscopy are perhaps the most routine, but to date, have not provided any useful information or any characteristic signal that can be associated with the presence of n-Tc. To date, the only method that has given information as to the oxidation state and structural features of n-Tc is XAS of one form or another. Unfortunately, this type of analysis is both time- and labor-intensive. Still, to the extent possible, continued analysis of new sources of n-Tc by XANES and/or XAFS is recommended.

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