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Preliminary Tests for Development of a Non-pertechnetate Analysis Method

David P. Diprete
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Savannah River National Laboratory™

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EXECUTIVE SUMMARY

The Hanford site has approximately 56 million gallons of radioactive waste stored in 177 underground storage tanks. The Hanford Waste Treatment and Immobilization Plant (WTP) is being built to treat this waste. After decontamination in the Pretreatment Facility, the tank liquid waste will be vitrified in two Low Activity Waste (LAW) melters. The design production rate of these two melters is inadequate to disposition all of the LAW tank liquid in the current plan, so supplemental capacity will be needed in the future. The immobilized waste form selected for Supplemental LAW is presumed to be glass, but alternatives are also being investigated.

Over twenty years ago, some Hanford waste samples were found to contain a form of soluble ^{99}Tc species that is not pertechnetate ion, known as "non-pertechnetate". Although it is believed that non-pertechnetate will be converted to pertechnetate in the glass melter, if the Supplemental LAW immobilization method is not glass, the inventory and behavior of non-pertechnetate in that waste form needs to be known. Only ten tanks have ever been measured for the non-pertechnetate inventory, but it is up to 70% of the total soluble Tc inventory in four of those ten tanks. The inventory in the other six tanks is low (<~10%), but exact concentrations are not known because of conflicting data. The inventory in the other 167 tanks has never been measured. There is also a small amount of an element at mass 99 that may not be Tc (perhaps non-radioactive ^{99}Ru). No measurements of the amount of non-pertechnetate in waste tanks have been made in about fifteen years.

The potential presence of non-pertechnetate is currently relevant because if a low temperature waste form is selected for Supplemental LAW, it is not known how this species will perform in the waste form. When pertechnetate-containing waste is mixed with the grout-forming materials, the ^{99}Tc(VII) is reduced to insoluble ^{99}Tc(IV). However, non-pertechnetate is already reduced and therefore cannot undergo this redox chemistry, therefore, it is unlikely to undergo the redox reaction which would render it insoluble and retained in a waste form. This carries the risk that a low-temperature waste form would be rejected because it cannot retain the portion of Tc that is present as non-pertechnetate, assuming Tc is the key nuclide in the performance assessment. A key component of assessing this risk is to know the current inventory and distribution of non-pertechnetate in the tank farms. If a method of quantifying the forms of Tc was implemented in the analysis suite performed in the Hanford 222-S lab on routine tank samples, it would provide information on the inventory of Tc species so that future decisions can be made regarding potential disposition in a low-temperature waste form.

Further, it is important to know the inventory of non-pertechnetate for tank closure activities. Although the tank closure Performance Assessment (PA) has not been done for Hanford, the assumptions used in the closure PA for Savannah River Site (SRS) are based on using a reducing grout to fill the tanks to forestall migration of a key radionuclide, ^{99}Tc [SRR-CWDA-2010-00128, R1]. Assuming a similar basis is used for Hanford, the redox chemistry that is relied on for sequestering ^{99}Tc after tank closure would not exist for non-pertechnetate, impacting the mobility of that fraction of ^{99}Tc.

The objective of this task was to develop a non-pertechnetate analysis method that 222-S lab could easily implement. The initial scope involved working with 222-S laboratory personnel to

adapt the existing Tc analytical method to fractionate the non-pertechnetate and pertechnetate. SRNL then developed and tested amethod using commercial sorbents containing Aliquat® 336 to extract the pertechnetate (thereby separating it from non-pertechnetate), followed by oxidation, extraction, and stripping steps, and finally analysis by beta counting and Mass Spectroscopy. Several additional items were partially investigated, including impacts of a ^{137}Cs removal step. The method was initially tested on SRS tank waste samples to determine its viability. Although SRS tank waste does not contain non-pertechnetate, testing with it was useful to investigate the compatibility, separation efficiency, interference removal efficacy, and method sensitivity.

Initial testing involved identifying the oxidation method that is expected to oxidize all of the non-pertechnetate to pertechnetate. To demonstrate rigorous oxidation conditions, tests of ^{14}C-labeled benzoic acid were conducted using a sulfuric acid oxidation, catalyzed with hydrogen peroxide. Several experiments were conducted, successively raising the oxidation solution volume and temperature until optimum conditions were established. This oxidation technique was then coupled with a method to extract, and thereby separate, pertechnetate from the tank samples using a pair of TEVA®[a] cartridges. The TEVA® cartridge strip step was tested with a set of spiked blank samples and was found to quantitatively strip pertechnetate from the matrix. A series of stripping, ^{137}Cs removal, and oxidation steps were performed followed by loading the Tc onto a TEVA® disc. The TEVA® disc was then placed into liquid scintillation cocktail (Ultima Gold™ AB[b]) for beta counting. To further demonstrate the applicability of the method and examine matrix effects, an actual Savannah River Site waste tank sample was processed through the entire sequence for this analysis method. As expected, non-pertechnetate levels in the SRS supernate samples were found to be <0.1%.

This report summarizes the initial "proof of principal" testing. Additional testing is needed to fully optimize the procedure prior to deploying it in the 222-S lab. Additionally, testing and analyses are also needed to confirm that there is a small amount of a species at mass 99 that is not Tc.

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[a] TEVA® is a registered trademark of Eichrom Technologies, LLC, Lisle, Illinois, U.S.A.

[b] Ultima Gold™ AB is a registered trademark of Perkin Elmer, Waltham, Massachusetts, U.S.A.

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LIST OF ABBREVIATIONS

AMP	Ammonium Molybdophosphate
DFLAW	Direct Feed Low-Activity Waste
DI	Deionized (water)
DOE	Department of Energy
dpm	Disintegrations per minute
DST	Double Shell Tank
EMF	Effluent Management Facility
ETF	Effluent Treatment Facility
EXAFS	Extended X-ray Absorption Fine Structure
g	Grams
hr	hour
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
Kg	kilogram
L	Liter
LAW	Low-Activity Waste
M	Molar
mg	Milligram
mL	Milliliter
N	Normal
PA	Performance Assessment
SBS	Submerged Bed Scrubber
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
VSL	Vitreous State Laboratory
WESP	Wet Electrostatic Precipitator
WRPS	Washington River Protection Solutions
WTP	Waste Treatment Plant
XANES	X-ray Absorption Near Edge Structure

1.0 Introduction

1.1 Background

The Hanford site has approximately 56 million gallons of radioactive waste stored in 177 underground storage tanks. The Hanford Waste Treatment and Immobilization Plant (WTP) is being built to treat all of the waste in the tank farms. The Pretreatment Facility will separate the tank sludge from the tank liquid waste, and then decontaminate the liquid using ion exchange to remove ^{137}Cs. The tank sludge and eluate from the Cs ion exchange will be vitrified in the High Level Waste (HLW) facility. The decontaminated tank liquid waste will then be vitrified in two Low Activity Waste (LAW) melters in WTP. The design production rates of these two melters is inadequate to disposition all of the LAW tank liquid in the current plan schedule, so additional capacity will be needed in the future, and this is referred to as “Supplemental LAW”. The immobilized waste form selected for Supplemental LAW is presumed to be glass, but alternatives are also being investigated, including low-temperature waste forms.

Approximately twenty years ago, some Hanford Double Shell Tanks (DSTs) were found to contain a form of soluble Tc species that is not pertechnetate ion, known as “non-pertechnetate” [1]. The original flowsheet for the WTP included an ion exchange process to remove Tc, but this was eliminated in 2003. The amount of non-pertechnetate was important at that time because the ion exchange process only removed the pertechnetate form. Testing of Tc removal methods and non-pertechnetate measurements were continued until 2003, but the non-pertechnetate fraction has not been analyzed for again in the nearly fifteen years and it is once again important to know if it still exists so that its flowsheet impacts can be projected. No methods for removing non-pertechnetate have been developed. The exact identity of the soluble non-pertechnetate is uncertain. Based on the XANES analysis of samples from SY-101 and SY-103, the non-pertechnetate is most likely to be a Tc(I) carbonyl complex [2]. Although it is believed that non-pertechnetate will be converted to pertechnetate in the glass melter in WTP, if the Supplemental LAW immobilization method is not vitrification, the inventory and behavior of non-pertechnetate in that waste form needs to be known. The potential presence of non-pertechnetate is currently relevant because if a low temperature waste form is selected for Supplemental LAW, it is not known how this species will perform in the waste form. It should also be noted that it is possible that “non-pertechnetate” could be more than one species.

Of the ten tanks measured for non-pertechnetate inventory, it was found to be the predominant form in four tanks, SY-101, SY-103, AN-102 and AN-107 [3]. Tank AP-104 was also found to contain high non-pertechnetate, but that tank may have contained waste from SY tanks at the time, and transfers since then have subsequently mixed it with other wastes. The non-pertechnetate specie(s) is up to 70% of the total soluble Tc inventory in those four DSTs, and is usually, but not always, associated with Complex Concentrate wastes. The quantity of non-pertechnetate is low in the other six tanks that have been measured, but the exact concentrations are not known because there is conflicting data. It is only speculation to project the concentration of non-pertechnetate in other tanks, so an easy method is needed to analyze them. Only soluble forms of Tc are of significance here because of its impact on the Immobilized LAW (ILAW) and its disposal, but the vast majority of Tc is presumed to be soluble in either supernate or saltcake liquids [3]. Any insoluble Tc would be expected to either be converted to pertechnetate and dissolved during sludge retrieval and processing, or remain insoluble in WTP and partition to the HLW. Once in the HLW melter, a portion will vaporize into the offgas system and convert to the soluble pertechnetate form when it is scrubbed out, ultimately ending up in the LAW melter. Any insoluble Tc that does not vaporize will remain in the HLW glass, and shipped to the Repository. It is not known if the non-pertechnetate still exists in the tanks, but it is known that this species is unstable, decomposing to pertechnetate in samples removed from the tank and stored for ~2 years under aerated conditions [4].

As stated above, the potential presence of non-pertechnetate is currently relevant because if a grout waste form is selected for Supplemental LAW, it is not known how this species will react in the waste form. When pertechnetate-containing waste is mixed with the grout-forming materials, particularly Blast Furnace Slag (BFS), the Tc(VII) as soluble pertechnetate gets reduced to insoluble Tc(IV) as TcO_2 or TcS_2 [5, 6,]. XANES and EXAFS indicates that the Tc in Saltstone is first reduced and hydrolyzed, and eventually reacts to form a polymerized sulfide species [7]. However, non-pertechnetate (with a +1 oxidation state) has the risk of not undergoing this electrochemical reaction and thus not being retained in a waste form because it is already reduced and therefore cannot undergo this redox chemistry. This has not been tested, however, but it is logical that since non-pertechnetate is in the +1 oxidation state, reduction by grout constituents would not generate the insoluble Tc(IV) species. The Tc(I) would have to be oxidized to get to the insoluble Tc(IV) state; however, the grout is a reducing environment. This carries the risk that a low-temperature waste form would be rejected because it cannot retain the portion of Tc that is present as non-pertechnetate because it would be expected to remain soluble and quickly leach.

One component of assessing this risk is to know the current inventory and distribution of non-pertechnetate in the tank farms. If a method of quantifying the forms of Tc was implemented in the analysis suite performed in the Hanford 222-S lab on routine tank samples, it would provide information on the inventory of Tc species so that future decisions can be made regarding a low-temperature waste form. Although the 222-S lab currently uses a preparation procedure on some samples that includes oxidized and non-oxidized process steps, that procedure has not been shown to accurately distinguish between pertechnetate and non-pertechnetate. Further, the method is also not capable of quantifying amounts of non-pertechnetate that are <10% of the total. The development program that initiated performing that test procedure was intended to develop a method for quantifying Tc species but was never completed [8].

It is also important to know the inventory of non-pertechnetate for tank closure activities. Although the tank closure Performance Assessment (PA) has not been done for Hanford, the assumptions used in the closure PA for Savannah River Site are based on using a reducing grout to fill the tanks to forestall migration of ^{99}Tc, a key radionuclide [9]. Assuming a similar basis is used for Hanford, the redox chemistry that is relied on for sequestering ^{99}Tc after tank closure would not exist for non-pertechnetate, impacting the mobility of that fraction of ^{99}Tc.

The primary way that non-pertechnetate was quantified in earlier experiments was by passing a large volume of liquid (~1 L) through an ion exchange column containing resin that selectively removed pertechnetate [10]. That work led to a recommended sample preparation method using an ion exchange column comparable to that used for WTP flowsheet testing with tank waste samples [11]. Although that method builds on prior methods shown successful, it requires a large amount of sample, special ion exchange media, equipment, and experience at handling the resin that would be burdensome to the 222-S personnel. This method is not practical for handling the small quantities of sample typically available (<100 mL), and takes considerable resources and expertise to perform routinely. The original method of identifying non-pertechnetate would also not determine small amounts of non-pertechnetate, and would require highly accurate data on the chemistry of competing ions in the sample [1]. It is desirable to develop a simple method that uses as much of the methodology and equipment that is already available in 222-S lab as possible and uses minimal sample volume, preferably <5 mL. The method also must quantify small amounts of non-pertechnetate (<10%) and measure the amount of the species at mass 99 that is thought to not be technetium. Further, if more than one non-pertechnetate species exists, it is important to quantify the entire amount of Tc that is not pertechnetate. As described above, a few tank samples that were rigorously oxidized and then had pertechnetate removed still exhibited a small amount of a species at mass 99 as identified by ICP-MS measurements [12]. It is speculated that this is not Tc, but may be non-radioactive ^{99}Ru. It is about 1-6% of the total mass 99 species in the initial samples, and it would be beneficial to identify it.

1.2 Method Development

The initial scope of this task was to work with personnel from the 222-S laboratory to establish a concept to adapt the existing Tc analytical method to quantify the non-pertechnetate and pertechnetate fractions. The preliminary concept was to use resin beads or discs containing Aliquat®[3] 336 to extract the pertechnetate from the initial tank sample. The pertechnetate-stripped sample would then be oxidized to convert all remaining Tc to pertechnetate, followed by extraction of pertechnetate with Aliquat® 336. Both extractions would then be back-stripped to remove the Tc, followed by beta counting and ICP-MS to quantify the Tc. The analyses would provide the quantity of pertechnetate and non-pertechnetate, separately from the same sample. There are several additional steps, including removal of ^{137}Cs, which would require investigation. The method was initially tested on SRS tank waste samples to determine its viability (SRS tank waste does not contain non-pertechnetate, but is useful to investigate several aspects of the separation and analysis method.)

Initial testing at SRNL involved identifying the oxidation method expected to oxidize all of the non-pertechnetate to pertechnetate. Literature reports [1, 4, 12] indicated that the complete oxidation of the non-pertechnetate is challenging. Oxidation with hydrogen peroxide, sodium hypochlorite/hydrogen peroxide, sodium bromate, sodium bismuthate, lead(IV) oxide and ammonium vanadate were unsuccessful. Sodium peroxydisulfate and sodium peroxydisulfate/silver(I) were found to be successful. Other methods were either only partially successful, or required unique equipment not currently available in 222-S lab (e.g. ozone generator). An automated Tc analyzer was developed and showed that peroxydisulfate was an effective oxidizer [13]. Electrochemical oxidation was also found to be mostly successful, and destruction of the soluble organic carbon species trended with oxidation of the non-pertechnetateTc [12]. But some mass 99 species remained non-extractable with an ion exchange resin even after complete electrochemical oxidation of organics. An alternate explanation for the conclusions in the report is that this may be due to ^{99}Ru interference in the ICP-MS analysis. No

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[3] Aliquat® is a trademark of the BASF, Germany

extraction and beta counting was performed that could have definitively shown that the residual non-extractable mass 99 species was actually Tc. The automated Tc analyzer method [13] used both extraction and beta counting and ICP-MS, but the criteria for agreement between the methods was ± 15%, which is too large to identify the potential for a small amount of non-Tc species at mass 99. This is another area of research that was planned for this task but was not completed due to termination of the program. To address oxidation of the organics and the corresponding impact on non-pertechnetate and the mass 99 species, SRNL performed tests to identify conditions that would be expected to fully oxidize organics, consistent with the observed comparable oxidation of non-pertechnetate when using electrochemical oxidation. Although peroxydisulfate is known to oxidize at least most of the non-pertechnetate also under certain conditions, hydrogen peroxide oxidation was already used in the technetium analysis procedure in 222-S laboratory, so it was selected for the initial test, although the peroxydisulfate could be investigated as an alternative as well if this program resumes. As no Hanford waste was available for testing at SRNL, the oxidation was tested using ^{14}C-labeled benzoic acid. Benzoic acid was chosen because aromatic hydrocarbons are particularly difficult to oxidize, so any method found to oxidize it should be more than sufficient to oxidize the straight-chain hydrocarbons expected in Hanford's Complex Concentrate waste. The balance of the organic load was simulated using ^{14}C-labeled oxalic acid. Several experiments were conducted to optimize the volume of the oxidation solution.

1.3 SRS Tank Sample Characterization

SRNL obtained an actual SRS waste tank sample for this test program. Although SRS waste is not expected to contain non-pertechnetate, it is still useful for comparison of many of the processing steps, such as ^{137}Cs removal. The sample was from SRS Tank 21 and was the "Salt Batch 7" prepared for treatment in the Actinide Removal Process/Modular Caustic Side Solvent Extraction Process (ARP/MCU). This sample had been fully characterized [14]. Partial results from the chemical analyses are shown in Table 1, and radiological analysis results are shown in Table 2. The Tc analysis results shown in Table 2 were obtained by separating the ^{99}Tc using 2 successive extractions with Eichrom TEVA® resin. The extractions were traced with ^{99m}Tc. The ^{99}Tc levels were measured with liquid scintillation counting. Additionally, Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) analysis [from laboratory notebook SRNL-NB-2013-00040] indicated 1.21 mg/L at mass 99, which is calculated to be 2.06E4 pCi/mL of ^{99}Tc. This is 23% more ^{99}Tc than the amount shown in Table 2. A positive bias is expected in the ICP-MS mass 99 result, likely because traces of ^{99}Ruare also probably present, and no separation was conducted prior to the ICP-MS analysis.

Table 1. Tank 21 Sample chemical analysis results [14]

Analyte	Result (mg/L)	Analyte	Result (mg/L)
Ag	<1.12	Sb	<34.5
Al	3320 (0.21%)	Si	74.2 (0.76%)
B	56.6 (0.13%)	Sn	<11.8
Ba	<0.62	Sr	<0.05
Be	<0.12	Th	<5.12
Ca	1.18 (0.60%)	Ti	<0.58
Cd	<0.84	U	<28.2
Ce	<6.45	V	<0.63
Cr	38.0 (0.19%)	Zn	4.90 (0.29%)
Cu	<0.98	Zr	<0.49
Fe	1.51 (5.62%)	F^-	<100
Gd	<1.38	Cl^-	264 (0.81%)
K	288 (1.47%)	Br^-	<1000
La	<1.26	Formate	649 (0.55%)
Li	21.9 (0.00%)	Nitrite	33000 (0.86%)
Mg	0.183 (5.81%)	Nitrate	148,000 (1.44%)
Mn	<0.16	Phosphate	556 (0.13%)
Mo	<5.99	Sulfate	9080 (0.23%)
Na	137,000 (0.52%)	Oxalate	392 (0.54%)
Ni	<2.07	TIC	3590 (0.59%)
P	212 (1.00%)	TOC	327 (0.43%)
Pb	<8.18	Free Hydroxide	1.93 (1.10%) M
S	3140 (1.58%)		

Values in parentheses are the RSD.

Table 2. Tank 21 Sample radiological analysis results (pCi/mL) [14]

Analyte	Average Result	Analyte	Average Result
^{3}H	*5.28E+02 (14.1%)*	^{155}Eu	<4.73E+01
^{14}C	7.40E+02 (30.3%)	^{226}Ra	<6.71E+01
^{59}Ni	<2.03E+00	^{232}U	2.32E+00 (26.0%)
^{63}Ni	<3.15E+01	^{233}U	<9.68E+01
^{60}Co	<1.88E+00	^{234}U	9.66E+01 (18.8%)
^{90}Sr	2.61E+05 (7.33%)	^{235}U	4.19E-01 (0.00%)
^{90}Y	2.61E+05 (7.33%)	^{236}U	1.09E+00 (20.6%)
^{94}Nb	<1.03E+01	^{238}U	9.16E+00 (1.82%)
^{99}Tc	1.67E+04 (1.71%)	^{237}Np	<7.05E+00
^{106}Ru	<1.41E+02	^{238}Pu (unfiltered)	1.15E+04 (1.38%)
^{106}Rh	<1.41E+02	^{238}Pu (filtered)	1.20E+04 (3.18%)
^{125}Sb	<1.07E+02	^{239}Pu	*1.57E+03 (20%)*
^{125m}Te	<1.07E+02	^{240}Pu	<2.28E+03
^{126}Sn	1.32E+02 (9.88%)	$^{239/40}$Pu	6.62E+02 (4.81%)
^{129}I	1.21E+01 (6.86%)	^{241}Pu	2.21E+03 (3.02%)
^{134}Cs	<4.07E+03	^{242}Pu	<3.82E+01
^{135}Cs	2.47E+02 (12.9%)	^{244}Pu	<1.77E-01
^{137}Cs	4.61E+07 (2.07%)	^{241}Am	<2.53E+00
^{137m}Ba	4.37E+07 (2.07%)	^{243}Am	<7.16E-01
^{144}Ce	<1.16E+02	^{244}Cm	2.34E+00 (43.1%)
^{144}Pr	<1.16E+02	^{245}Cm	<1.87E+00
^{147}Pm	<2.71E+01	Total Alpha	<1.01E+05
^{151}Sm	<1.23E+01	Total Beta	9.18E+07 (0.69%)
^{154}Eu	<7.11E+00	Total Gamma	4.61E+07

Shaded results are calculated values. Values in parentheses are the RSD unless only a single result, then the value is the analytical uncertainty. Values in italics are single results.

2.0 Experimental Procedure

2.1 Oxidation tests

For the current SRNL scope, oxidation tests were conducted using a sulfuric acid oxidation, catalyzed with hydrogen peroxide. Five tests were conducted. As no Hanford waste was available for testing at SRNL, the oxidation was tested utilizing ^{14}C-labeled benzoic acid, with the balance of the organic load simulated with oxalic acid. The oxidation tests were all conducted with nominally 7 mg of carbon (0.1 mL of 3M oxalic acid and trace benzoic acid), which mimics a 1-mL aliquot of ~6% total organic carbon (TOC) Hanford supernate. The efficiency of the oxidation of the organic compounds was evaluated by measuring the ratio of the final ^{14}C concentrations to the initial ^{14}C concentrations. As the organic compounds were oxidized, it was expected the ^{14}C would be lost as carbon dioxide. The ^{14}C was measured by liquid scintillation counting (LSC).

The initial test evaluated the efficiency of the sulfuric acid/hydrogen peroxide oxidation/combustion with ^{14}C-labeled benzoic acid as well as ^{14}C-labeled carbonate. The labeled carbonate was used since it readily oxidizes to CO_2 and it was desirable to demonstrate any CO_2 produced could readily exit the matrix. A test sample of ^{99}Tc was also analyzed to verify no ^{99}Tc losses would occur from the oxidation process. A mixture of 0.1 mL of standard and 0.1 mL of 3 M oxalic acid added to 0.9 mL of 2 M NaOH were contacted with 0.9 mL of concentrated sulfuric acid and 0.3 mL of 30% hydrogen peroxide for 1 hour. The combustion solutions were then quenched with 13.7 mL of 2 M NaOH, and allowed to rest an additional hour, at which time 0.5 mL of the resulting solution was added to 19 mL Perkin Elmer Ultima Gold^{TM} AB liquid scintillation cocktail. While the carbonate sample was completely purged as carbon dioxide due to the acidification and did not remain in the solution, all of the benzoic acid remained in the solution, indicating no oxidation occurred. No losses were observed for the ^{99}Tc sample.

The experiment was repeated a second time for the benzoic acid to investigate the impact of the volume of reactants used as well as reaction duration on the difficult-to-digest organic matrix. Additional contact times and additional volumes of combustion solutions were evaluated using a mixture of 0.1 mL of the ^{14}C-labeled benzoic acid standard and 0.1 mL of the 3 M oxalic acid. One, 2, and 3 hour contacts were evaluated using 0.9 mL of concentrated sulfuric acid and 0.3 mL of 30% hydrogen peroxide (single combustion volume) as well as 1.8 mL of concentrated sulfuric acid and 0.6 mL of 30% hydrogen peroxide (double combustion volume). For the 1 hour contact, 19% of the single combustion volume test, and 59% of the double combustion volume test was oxidized. For the 2 hour contact, 22% of the single combustion volume test, and 65% of the double combustion volume test was oxidized. For the 3 hour contact, 27% of the single combustion volume test, and 60% of the double combustion volume test was oxidized. In summary, the results indicated additional contact time was not productive in increasing combustion efficiency, but additional combustion reagent volumes were.

The experiment was repeated a 3rd time, tripling and quadrupling the combustion solution volumes, maintaining the contact time at 1 hour, and using a mixture of 0.1 mL of the ^{14}C-labeled benzoic standard and 0.1 mL of the 3M oxalic acid. The results indicated 57% of the triple combustion volume case, and 51% of the quadruple combustion volume case was oxidized.

A 4th oxidation experiment was then conducted to again evaluate the usefulness of additional reaction time. Additional contact times (2 hour and 4 hour) for the triple and quadruple combustion solution volume cases were evaluated. For the 2 hour contact, 55% of the triple combustion volume case, and 58% of the quadruple combustion volume case was oxidized. For the 4 hour contact, 54% of the triple combustion volume case, and 58% of the quadruple combustion volume case was oxidized.

As a limit to the extent of oxidation achievable appeared to be reached for this methodology, heat was added in a 5th experiment to see if it would catalyze the oxidation. A mixture of 0.1mL of the benzoic acid standard and 0.1 mL of the 3 M oxalic acid were contacted with 1.8 mL of concentrated sulfuric acid and 0.6 mL of 30% hydrogen peroxide for 1 hour at 60 ºC. A second mixture was contacted with the same volumes for 2 hours at 60 ºC. A third mixture was contacted with the same volumes for 2 hours at 60 ºC, and 1 hour at 80 ºC, and a fourth was contacted for 2 hours at 60 ºC, and 2 hours at 80 ºC. The combustions for the various conditions were 96%, 97%, 99%, and 99% respectively. The results clearly indicate the improved oxidation with heat.

2.2 Evaluation of oxidation methodology on Technetium retention using a TEVA® Extraction

Once the methodology was proven to be effective for oxidizing organic compounds, the methodology was then evaluated to determine if the chemistry was compatible with a ^{99}Tc extraction using TEVA®. Four 2-mL aliquots of 2M NaOH were spiked with ^{99}Tc. Samples were pH-adjusted, reduced to dryness, and oxidized using 1.8mL concentrated sulfuric acid and 0.6 mL 30% hydrogen peroxide followed by heating for 1 hour at 80 ºC. ^{99}Tc recoveries for these oxidation steps were evaluated using LSC prior to continuing with the TEVA® extractions. For the 4 test samples, ^{99}Tc recoveries through the oxidation procedure were 81%, 89%, 96% and 99%, respectively. The samples were diluted, pH adjusted, added to TEVA® cartridges, and subjected to a rinse/elution profile that is typical for SRNL ^{99}Tc analyses. The flow rates through the cartridges were measured. Samples 1, 3, and 4 flowrates through the cartridges were ~2.6 mL/min, and sample 2 flowrate was ~2.2 mL/min. ^{99}Tc recoveries associated with only the TEVA® extraction process following the oxidation were 73%, 79%, 78% and 94%, respectively. Overall extraction recoveries were 59%, 70%, 75%, and 93%, respectively. Flow-rates through the cartridges were not evaluated prior to the programs termination, so these recoveries could likely be improved with additional testing.

2.3 Evaluation of pertechnetate recovery on TEVA® discs at various flow rates

As with any type of separation and analysis scheme, it is imperative to quantify the method recovery of the analyte of interest. SRNL accomplishes this for ^{99}Tc separations using a ^{99m}Tc tracer generated from the activation of molybdenum in the SRNL ^{252}Cf-based Neutron Activation Analysis Facility. Hanford does not currently have access to ^{99m}Tc because its ^{252}Cf-based neutron facility was decommissioned over a decade ago. An alternative could be obtaining a vendor-supplied *partially spent* ^{99m}Tc generator. The partially spent generators are typically too low for use as a medical isotope source, but could still supply enough ^{99m}Tc for for this method to last approximately 3 months before decaying to a point where it was no longer useful. Another option would be to investigate whether a university could provide activated molybdenum targets from their research reactors, from which ^{99m}Tc could be extracted at the 222-S laboratory.

If Hanford laboratories are not able to obtain ^{99m}Tc to trace separation yields for each individual analysis, it is critical to optimize and fully understand the expected yields from the analysis process. If the method will be yielded using a ^{99}Tc yield monitor sample versus tracing each sample with ^{99m}Tc, highly reproducible yields would be required. To this end, the impact of flow rate through TEVA® discs was investigated. It is proposed that the final steps of the analysis sequence involve extracting Tc onto the disks, at which time each disk is added to liquid scintillation cocktail and analyzed. Impacts to yield of flow-rates through the disks was investigated. A ^{99}Tc spike was added to 15 mL of 9M nitric acid. The acid concentration was reduced using 12 mL of 8M nitric acid. That solution was diluted with 18 mL of DI water, and

100 mL of 0.01M nitric acid. Ten solutions were created and introduced to TEVA® discs. Vacuum settings were altered to change flow rates, which were measured by determining the amount of time required for solutions to completely flow through each disk. The following flow rates were measured: 8, 9, 48, 174, 193, 212, and 290 mL/min, and three at maximum vacuum, resulting in a 348 mL/min flow rate. The discs were rinsed with 40 mL of 0.1M nitric acid and added to Perkin Elmer Ultima Gold™ AB LSC cocktail. Each sample was counted immediately after the separation for 10 minutes by LSC. They were counted again the following day and results showed significant increases in count rate, indicating time was needed to fully incorporate the ^{99}Tc into the LSC cocktail. The samples were subsequently counted over a number of days to establish when the count rates would stabilize, at which point the separation recoveries could be determined. Each sample was counted five times, the same day as the extraction, the following morning, the following evening, after a two-day delay, and after a five-day delay. The count rates appeared to become fairly stable following the two-day delay. Recoveries for the various flow rates follow: 8 mL/min (96%), 9 mL/min (51%), 48 mL/min (86%), 174 mL/min (68%), 193 mL/min (54%), 212 mL/min (63%), 290 mL/min (60%), and three at 348 mL/min flow rate (50%, 52%, 49%). The data from this experiment clearly indicate flow rate has an impact upon extraction efficiency, and further studies are needed in order to optimize the flow rate as well as the counting protocol. An experiment was planned to evaluate the effects of vortexing the LSC vial containing the ^{99}Tc-loaded TEVA® disk to shorten the time required to maximize counting efficiency, but the experimental work was terminated prior to the execution of that test. The kinetics of extraction and counting protocols need further optimization.

2.4 Evaluation of pertechnetate removal using two TEVA® cartridges

This project required the development of a method to measure the non-pertechnetate species present in Hanford supernate, so a process at the beginning of the method was required to remove the pertechnetate portion of the ^{99}Tc sample inventory. An experiment was conducted to evaluate the effectiveness of pertechnetate removal under conditions that would not have an effect on the oxidation state of the ^{99}Tc. A tracer of ^{99}Tc as pertechnetate was prepared by adding 0.2 mL of tracer to 2 mL of 2M NaOH, followed by 18mL of deionized water. Ten of these samples were prepared. Two TEVA® cartridges were connected in series, and an assembly of the cartridges was set up for each sample. Cartridges were conditioned with 10 mL of DI water, samples were added to their respective cartridges, and then the cartridges were rinsed with an additional 10 mL of DI water. The solutions produced by these steps were quantified by LSC. The samples were processed in batches of two, and for each batch the vacuum was varied to enable evaluation of the effect of flow rate on pertechnetate removal. Aliquots of solution that passed through the cartridges were assayed to evaluate the breakthrough of pertechnetate through two TEVA® cartridges that were connected in series. The cartridges were attached to a manifold box, and vacuum on the box was run at maximum suction for the 1st batch of two and subsequently decreased for each successive batch of two. The caustic liquid samples flowed very slowly through the cartridges, and there was variability in flow rates, even sometimes among the two in each batchs at the same vacuum. The flow rates measured for the ten samples were, respectively; 1.3, 1.1, 1.4, 1.3, 0.6, 0.6, 0.4, 0.4, 0.4, and 0.3 mL/min. No correlation was observed between breakthrough and flowrate, however. Eight of the ten samples had no measureable levels of technetium (<0.78% of the total) in the solutions that had flowed through the columns, indicating good extractions of ^{99}Tc. One sample in the third batch had a measureable level of technetium, which was 1.6% of the total. One sample in the 4th batch was an outlier, with 11.6% of the total technetium measured in the solutions that flowed through the TEVA® cartridges.

2.5 Evaluation of pertechnetate removal using two TEVA® columns

The experiment conducted using TEVA® cartridges was repeated using TEVA® columns. Columns contain the same resin as cartridges, but are commercially packed with a coarser grade of the resin bead. Pertechnetate removal was evaluated using two columns compared to two cartridges, as faster flowrates could be achieved through the columns, and faster flow-times were desirable to shorten the overall method duration. The maximum flow rate obtainable through the cartridges had been ~1 mL/min. The experimental conditions of the cartridge experiment were repeated. Since columns can not be connected together in series, the solutions were run through one column and collected, and the collected solutions were run through a second column. The flow rates measured for the ten samples were, respectively; 14.2, 14.6, 11.5, 11.0, 7.1, 7.3, 1.7, 1.7, 1.1, and 1.1 mL/min. Again, almost no breakthrough was observed, so no correlation was observed between breakthrough and flowrate, indicating extraction kinetics are very fast. Nine of the ten samples had no measureable levels of technetium (<0.79% of the total) in the solutions that passed through the columns. One sample in the fourth batch had a measureable level of technetium, which was 1.2% of the total.

2.6 SRS Tank Sample Tests Evaluating ^{137}Cs removal

The presence of ^{137}Cs is an interference for ^{99}Tc analysis by LSC, so ^{137}Cs removal must be performed when analyzing for ^{99}Tc in Hanford samples. An experiment was designed to test the robustness of the ^{137}Cs removal process for the proposed non-pertechnetate analysis methodology. Two 2-mL aliquots of SRS Tank 21 Salt Batch 7 (Table 2) and a sample blank were run through the analysis. Total ^{137}Cs activity in 2 mL of this matrix is 2.05E8 dpm. The samples were initially diluted to 20 mL using DI water. The pertechnetate was extracted from each sample using 2 TEVA® cartridges stacked together on a vacuum box and pre-conditioned with 10 mL DI water. The cartridges were rinsed with 10 mL of DI water. The TEVA® cartridges, which contained the pertechnetate inventory from each sample, were then discarded. One of the two sample solutions that were collected below the cartridges was spiked with ^{99}Tc to evaluate its behavior through the remainder of this procedure. The solutions were acidified with the addition of 2 mL of 8M nitric acid. Bio-Rad ammonium molybdophosphate (AMP) (~0.2 g) was added to each solution. Solution vials were capped and shaken for 20 seconds. The AMP resin was filtered off, and the sample bottles and subsequently the filters were rinsed with 10 mL of DI water.

The solutions, which had had cesium removal steps completed, were processed using the proposed non-pertechnetate method as follows: The solutions were evaporated to dryness at 130 ºC in a drying oven. The residues were allowed to cool for 20 minutes. Deionized water (0.5 mL) was added to each sample, followed by 1.8 mL of concentrated sulfuric acid. After brief mixing, 0.6 mL of 30% hydrogen peroxide was added, and the samples were heated at 80 ºC for 1 hour. The samples were allowed to cool for 20 minutes and the sample solutions were diluted with 30 mL DI water. Eleven milliliters of 6M NaOH were added to the samples to reduce the acid concentration. A TEVA® cartridge was set up for each sample and the blank on a vacuum box. The cartridges were conditioned with 20 mL of 1 M NaOH. The cartridges were then rinsed with 10 mL of 1M NaOH, 20 mL of 0.1 M nitric acid, another 20 mL of 0.1M nitric acid, and lastly 20 mL of 1.0 M nitric acid. The samples and the caustic rinses went through the cartridges very slowly, follow-up studies should be run using a TEVA® packed column, and/or reduce the concentrations of NaOH. Tc-99 was eluted from the cartridges with 5 mL of 9 M nitric acid followed by an additional 10 mL of 9 M nitric acid. The acid concentrations were reduced by the addition of 12 mL 8M NaOH. The solutions were diluted with 100 mL of 0.01M nitric acid. A TEVA® disc (conditioned with 10mL 0.01M nitric acid) was set up for each sample and the samples were added to their TEVA® discs at a flow rate of 10 mL/min. The discs were rinsed with 40 mL of 0.1 M nitric, and then rinsed again with 20 mL of 1.0 M nitric acid. The discs were then removed from their manifolds, added to 20 mL Ultima Gold™ AB, and analyzed.

The results indicated a ^{137}Cs decontamination factor greater than 8.67E6. Although this experiment was designed to evaluate ^{137}Cs removal efficacy, it also provided information about ^{99}Tc in the tank sample. Results indicate ~0.08% of the ^{99}Tc in the Tank 21 sample passed through the discs. This could be attributed to several factors, most likely as minor bleed-through of ^{99}Tc or cross-contamination. Regardless of the cause, it shows that <0.1% of the ^{99}Tc in the SRS sample could be present as non-pertechnetate.

2.7 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Results are recorded in Electronic Laboratory Notebook # F7480-00185-10. This report documents partial completion of scope in Task 3.7 in the Task Technical and Quality Assurance Plan SRNL-RP-2015-01038, Rev. 0 [15].

3.0 Results and Discussion

3.1 Oxidation Tests

For the current SRNL scope, tests were performed to optimize the oxidation of organic species. Oxidation studies were conducted using a sulfuric acid oxidation, catalyzed with hydrogen peroxide. During initial testing, the maximum oxidation of ^{14}C-containing organic material was only ~60%. Subsequent testing included heating, and a short heating step (1 hour at 80 ºC) succeeded in oxidizing 99% of the ^{14}C-containing organic material. Four ^{99}Tc-spiked blanks were subjected to the oxidation procedure and their recoveries were 81%, 89%, 96% and 99%. The oxidized solutions were diluted with DI water and neutralized with NaOH. At this point, the solutions were loaded and subsequently eluted from TEVA® resin systems to determine whether the sulfuric/peroxide matrix would adversely impact the TEVA® based ^{99}Tc extraction. Recoveries for this portion of the extraction procedure were 73%, 79%, 78% and 94%. Overall recoveries for the oxidation and extraction procedures were 59%, 70%, 75% and 93%. Because this task was terminated prior to completion, it was not possible to determine if these conditions would oxidize a real waste sample containing non-pertechnetate.

A method to extract pertechnetate from the Hanford matrices was developed based on this oxidation technique. The initial step involved diluting 2 mL of supernate sample with 18 mL of DI water. The pertechnetate in the matrix was then removed using a pair of TEVA® cartridges. The TEVA® cartridge strip step was tested with a set of spiked blank samples and was found to quantitatively strip pertechnetate from the matrix. Flow rates were also studied, but liquid flow through the cartridges is so restrictive that even with continuous vacuum, it took about 20 minutes to pull the samples through the cartridges. No adverse effects were observed on ^{99}Tc removal on flow rate, even at the maximum achievable flow rate.

The solution that had been stripped of pertechnetate was then subjected to a ^{137}Cs removal technique based on an ammonium phosphomolybdate extraction. The Cs-removed solution was then oxidized as previously described. The oxidized ^{99}Tc solution was then processed through a ^{99}Tc extraction, using typical conditions for the SRNL Analytical Development laboratory. To accomplish this, the solution was pH-adjusted, and ^{99}Tc was extracted using a TEVA® cartridge. The cartridge was washed numerous times, and ^{99}Tc was then eluted with 9M nitric acid. The eluate was neutralized, and loaded onto a TEVA® disc. The TEVA® disc was then placed into LSC cocktail (Ultima Gold™ AB). A set of experiments were carried out to evaluate this TEVA® disc step explicitly. It was found that the liquid flow rates did have an effect on this step. Also, it was observed at a 1-day delay was required to allow the ^{99}Tc to diffuse off the disc and into the cocktail before LSC counting.

3.2 Procedural Steps

The steps for the non-pertechnetate procedure developed, thus far, are provided. This procedure is not considered final or optimized, but work was halted while experimentation was incomplete. Due to the lack of optimization, it is highly recommended the sample steps be traced using ^{99m}Tc counted in a well-type gamma system. SRNL has experienced that measuring the ^{99m}Tc yields is best done with a well geometry gamma spectrometer because, initially, the ^{99m}Tc has not entirely diffused from the TEVA filter, so the sample is not completely homogeneous and a gamma spectrometer looking upward or to the side of the LSC vial may not be accurate.

Tc-99 Separation

1. Pipette 2 mL of sample into 18 mL of DI water**.**
    - Adding ^{99m}Tc tracer is recommended, or else a multiple matrix spike ^{99}Tc tracing methodology would need to be employed if pertechnetate must be measured
    - Adding a method blank is also recommended
2. Attach 2 TEVA® cartridges in series together on a vacuum box for each sample.
    - Experimental data indicated 2 TEVA® columns in series can be used here at very high flow rates
3. Condition each cartridge assembly with 5mL of DI water
4. Add each sample to its cartridge
    - Flow rates are very slow for cartridges
    - Flow rates up to 14.6 mL/min were evaluated to be acceptable
5. Add 10 mL of DI water to each cartridge for a rinse
6. Decant solution from centrifuge tube into a 60-mL polyethylene bottle

  - Discard the TEVA® cartridges or elute the Tc-99 using steps 30-39 if pertechnetate concentrations are desired
7. Add 2 mL of 8 M nitric acid
    - Adding ^{99m}Tc tracer is recommended, or else a multiple matrix spike ^{99}Tc tracing methodology would need to be employed to provide chemical yields for the non-pertechnetate analyses
8. Add ~0.2 g Bio-Rad AMP
9. Cap and shake for 20 seconds
10. Filter off the AMP with a self-contained Nalgene 0.45 micron filter assembly, decant the filtrate into a 100-mL beaker
11. Add 10 mL of DI water to the sample polyethylene bottle for rinse, add to self-contained Nalgene filter, decant that rinse filtrate into the 10-mL beaker
12. Evaporate to dryness in a drying oven at 130 ºC
13. Remove from the drying oven, reduce oven heat to 80 ºC
14. Let beaker cool 20 minutes
15. Add 0.5 mL of DI water to beaker, swirl around bottom of beaker
16. Add 1.8 mL of concentrated sulfuric acid (**Beware of splatter, use splash protection**)
17. Add 0.6 mL of 30% hydrogen peroxide (**Always add hydrogen peroxide after sulfuric acid**)
18. Put beaker back in the oven for 1 hour (80 ºC)
19. Let the beaker cool 20 minutes
20. Add 30 mL of DI water
21. Slowly add 11 mL of 6M NaOH to reduce the acid concentration (**Beware of splatter, use splash protection**)
    - This step was not optimized prior to terminating the program. The volume of NaOH could likely be reduced but testing was not performed.
22. Set up a TEVA® cartridge for the samples
    - This step was not optimized prior to terminating the program. Columns could possibly be used rather than cartridges to reduce flow time, but testing was not performed.
23. Condition each cartridge with 5 mL of 0.1M nitric acid.
24. Add each sample to its cartridge.
25. Add 10 mL of 1M NaOH to each cartridge for a rinse.
    - This step was not optimized prior to terminating the program. Volume of NaOH could likely be reduced but testing was not performed.Columns could likely be used, but was not tested.
26. Add 20 mL of 0.1M nitric to each cartridge for a second rinse.
27. Add 20 mL of 0.1M nitric to each cartridge for a third rinse.
28. Add 20 mL of 1.0M nitric to each cartridge for a fourth rinse
29. Replace the centrifuge tubes in the vacuum box.
30. Add 5 mL of 9M nitric acid to the cartridges to elute the ^{99}Tc.
31. Add 10 mL of 9M nitric acid to the cartridges to continue the elution, decant elutions into labeled beakers or bottles.
32. Slowly add 12 mL of 8M NaOH to the beakers containing the elutions (**Beware of splatter, use splash protection**)
33. Add 100 mL of 0.01M nitric acid to the beakers.

34. Set up a TEVA® disc for each sample on a vacuum manifold.
35. Condition each disc with 10 mL of 0.1M nitric acid
    - Solution flow-rate is not critical if ^{99m}Tc is being used. However, if separation is being yielded using a ^{99}Tc matrix spike, 8mL/min or slower flow rate is recommend
36. Add each sample to its disc.
37. Rinse the disc with 40 mL of 0.1M nitric acid
38. Rinse the disc again with 20 mL of 1.0M nitric acid
39. Remove the discs from their manifolds, place them into 20mL Ultima Gold™ AB for liquid scintillation counting (and gamma analysis if ^{99m}Tc being used)
    - This step was not optimized prior to terminating the program. Wait at least one day to count by LSC, or investigate whether vortexing the LSC vial facilitates faster equilibration of ^{99}Tc in the cocktail.

SRNL processed a sample of the Salt Batch 7 supernate through the entire sequence for this analysis method. It was found that this sequence was successful at removing ~7E6-fold (>99.99998) of ^{137}Cs, eliminating it as an interference. As expected, non-pertectnetate levels in the SRS supernate samples were found to be <0.1%.

4.0 Conclusions

This testing demonstrated the initial “proof of principal” that this is a viable approach to quantify non-pertechnetate versus pertechnetate in Hanford tank waste samples. This method is expected have a much improved detection limit for samples with low fractions of non-pertechnetate versus the current practice of analyzing oxidized and non-oxidized samples separately. It should also quantify all non-pertechnetate species, if more than one exists. The new method is compatible with commonly available equipment, instruments, and supplies, and does not require large amounts of sample. However, further testing is needed to fully optimize the procedure details, detection limits, and prepare it for deployment in 222-S lab. Additionally, no work was done to examine if a small amount of a species at mass 99 is present that is not Tc, and further testing and analyses are needed to resolve this. This is needed to finally establish if some of the “non-pertechnetate” that was not oxidized in the electrochemical oxidation tests [12] was actually ^{99}Ru, and if the small amount of early breakthrough of mass 99 species during ion exchange column tests was actually ^{99}Ru. If the concentration of pertechnetate and non-pertechnetate currently in the tanks can be accurately quantified, then that information can be used in future decision about a low temperature waste form and tank closure.

5.0 Future Work

Further testing is needed to finalize this analysis method and to deploy it for 222-S laboratory. This program was terminated prior to the completion of planned studies, so the scope of the work was interrupted, leaving optimization and demonstration of the oxidation and extractions with actual Hanford samples incomplete. A series of ^{99m}Tc traced analyses are needed to evaluate ^{99}Tc behavior throughout the entire process and, therefore, optimize the method. A number of notes for areas recommended for optimization are included in Section 3. This optimized procedure must then be tested with actual waste tank samples so that it can be determined if there are additional interferences and if the oxidation step works. Some of these should be freshly acquired samples from tanks that historically had high non-pertechnetate. Almost all of these steps are already included in routine 222-S procedures, so performing this analysis should cause minimal disruption or training changes, and utilizes existing equipment, standards, and chemicals, other than the Tc-99m source. A comparison of ICP-MS analyses to liquid scintillation analyses was planned, and is needed. It is highly recommended that the 222-S laboratory establish a means of obtaining a source of ^{99m}Tc tracer, either through a vendor, or perhaps by collaboration with a university with a nuclear reactor if this program resumes.

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