NOV 3 1999
Sta 15

ENGINEERING DATA TRANSMITTAL

S New Orig.

Page 1 of 1
1. EDT 626586

2. To: (Receiving Organization) SST Programs		3. From: (Originating Organization) Numatec Hanford Corporation		4. Related EDT No.: N/A	
5. Proj./Prog./Dept./Div.: RPP		6. Design Authority/ Design Agent/Cog. Engr.: G. L. Troyer 10/25/99		7. Purchase Order No.: N/A	
8. Originator Remarks: For Approval and Release				9. Equip./Component No.: N/A	
				10. System/Bldg./Facility: N/A	
11. Receiver Remarks: 11A. Design Baseline Document? ☐ Yes ☒ No				12. Major Assm. Dwg. No.: N/A	
				13. Permit/Permit Application No.: N/A	
				14. Required Response Date: 10/30/99	

15. DATA TRANSMITTED					(F)	(G)	(H)	(I)
(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	Approval Designator	Reason for Transmittal	Originator Disposition	Receiver Disposition
1	HNF-5309		0	Survey of Technetium Analytical Production Methods Supporting Hanford Nuclear Materials Processing	N/A	1	1	1

16. KEY					
Approval Designator (F)		Reason for Transmittal (G)		Disposition (H) & (I)	
E, S, Q, D or N/A (see WHC-CM-3-5, Sec. 12.7)		1. Approval 2. Release 3. Information	4. Review 5. Post-Review 6. Dist. (Receipt Acknow. Required)	1. Approved 2. Approved w/comment 3. Disapproved w/comment	4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged

17. SIGNATURE/DISTRIBUTION (See Approval Designator for required signatures)											
(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN
		Design Authority	N/A			1	1	WI Winters	<i>Will Winters</i>	10/26/99	T6-50
		Design Agent	N/A			2	1	LL Lockrem	<i>LL Lockrem</i>	10/26/99	T6-07
1	1	Cog. Eng.	GL Troyer	10/25/99	T6-50						
1	1	Cog. Mgr.	CC Haass	10/25/99	T6-89						
		QA	N/A								
		Safety	N/A			3		Central Files			B1-07
		Env.	N/A			3		RL Reading Room			H2-53

18. Signature of EPT Originator <i>[Signature]</i> 10/25/99		19. Authorized Representative for Receiving Organization <i>[Signature]</i> 10/27/99		20. Cognizant Manager <i>[Signature]</i> 10/27/99		21. DOE APPROVAL (if required) Ctrl. No. ☐ Approved ☐ Approved w/comments ☐ Disapproved w/comments	
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Survey of Technetium Analytical Production Methods Supporting Hanford Nuclear Materials Processing

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U.S. Department of Energy Contract DE-AC06-96RL13200

EDT/ECN: 626586 UC: 2000
Org Code: 88200 Charge Code: 102320/EH00 *HMLM0351*
B&R Code: EW02J1160 Total Pages: 26

Key Words: tank waste, sludge, technetium, analysis, pertechnetate, liquid scintillation

Abstract: This document provides a historical survey of analytical methods used for measuring ^{99}Tc in nuclear fuel reprocessing materials and wastes at Hanford. Method challenges including special sludge matrices tested are discussed. Special problems and recommendations are presented.

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Christine H. Hargrave 11-3-99
Release Approval Date

Approved for Public Release

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October 20, 1999

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Executive Summary

The nuclear fuels chemical reprocessing activities at Hanford went forward for many years with little attention about the presence or quantities of technetium in the systems. When needs changed, the analytical chemistry laboratories developed methods to isolate and measure technetium. It was found that if technetium could be oxidized, it could be readily and selectively extracted by organic based complexants. Over time, ever more efficient and lower cost methods were developed, mostly directed at aqueous solutions or simple sample matrices. With the change from production to waste cleanup, problematic sample matrices are causing unexpected discrepancies in the measurement of technetium.

This document traces the development of technetium analytical methods over the history of Hanford operations. The evolution of current issues and problems with the accepted analytical methods are described. Where possible and based on evidence, recommendations for improvements are described. A section on analytical directions is included which provides a rationale for the needed development and methodologies. Included are discussions about the effect of organic complexants in waste tank supernates or solutions and the observed problems with analyzing tank bottom sludges.

Survey of Technetium Analytical Production Methods Supporting Hanford Nuclear Materials Processing

1 Introduction

Interest in analytical measurement for technetium produced during the early chemical processing operations at Hanford was limited. No references to technetium analytical procedures for that period were identified during this study. However, by the mid 1950's there appeared to be a stronger interest in studying and recovering the by-products of the nuclear process as part of the Atoms for Peace program. References to technetium measurements were better documented. Hanford was involved in the recovery of technetium during that time and that work is summarized (Roberts, 1971). However, no Tc analytical methods were described in the document. The National Academy of Sciences Nuclear Science Series on The Radiochemistry of Technetium published in November 1960 summarizes several technetium analytical methods. Most of these focused on the separation of Tc from molybdenum. The methods in this NAS document for separation of Tc from the fission products used tetraphenylarsonium chloride to either precipitate or extract the technetium from other fission products. Distillation of Tc or precipitations were used to reduce interference from other beta emitting fission products. The predominant approaches then and now focus on the Tc(VII) or pertechnetate form of technetium as an isolatable species.

2 Summary of Hanford Technetium Analytical Methods

2.1 Hanford Technetium Analytical Methods

Six analytical methods have been identified as used to analyze technetium in Hanford chemical processing waste streams. There are five radiochemical separation methods and a method based on inductively coupled plasma mass spectrometry (ICP/MS). The radiochemical methods and their approximate chronological time of use are summarized in Table 1. A graph showing the correlation to nuclear fuel and waste reprocessing is shown in Figure 1.

The first three methods were applied to either Purex waste streams or high level waste in the tanks. Because these methods were used during fuel processing periods, the short lived fission products ($^{95}\text{ZrNb}$, $^{106}\text{RuRh}$, and $^{144}\text{CePr}$) were much higher than today and the methods more subject to positive interferences if very clean separations of the Tc were not obtained. The Aliquat-336 method was directly aimed at analyzing Tc in waste containing organic complexants. The tetraphenylarsonium method was used by PNNL during the early 1990's as part of the tank waste characterization program. The use of ICP/MS for the determination of Tc in the waste did not start until about 1995.

Table 1. Hanford Radiochemical Technetium Methods	
Date	Basis of Method
1963	Extraction with Tri-Butylphosphate
1966	Extraction with Cyclohexanone
1971	Extraction with Tetrapropylammonium Hydroxide
1984	Extraction with Aliquat-336
1993	Extraction with Tetraphenylarsonium Chloride and Hexone

Figure 1. Hanford chemical processing relationship to technetium analytical method development. TBP = Tributylphosphate extraction, CHO = Cyclohexanone extraction, TPA/OH = Tetrapropylammonium hydroxide extraction, 336 = Aliquat 336 extraction, TPA/Cl = Tetraphenylarsonium chloride extraction, ICP/MS = Inductively coupled plasma/mass spectrometer, TEVA = Eichrom Industries filter (aliquat 336N), 336+ = Aliquat 336 extraction with heated peroxide step

2.1.1 Tributyl Phosphate (TBP) Tc Method

This TBP method (Campbell 1963) was developed in the early 1960's to determine Tc in PUREX waste streams and existing alkaline waste tank supernates. The sample was diluted into a final acid mixture with a concentration of 1M H_2SO_4 and 0.025M NaF . One drop of concentrated H_2O_2 was added to oxidize the Tc to Tc(VII). After extracting the Tc into 45% TBP/Soltrol (kerosene mixture) the extracted Tc in the TBP was washed with the same acid mixture to remove residual fission products. The Tc was stripped from the TBP phase with water. Fission products and U and Pu isotopes in the water strip were removed by passing the aqueous phase through a Dowex 50X8 cation exchange resin. The effluent from the cation exchanger was collected on a beta mounting dish, dried and counted on a beta proportional detector.

This TBP method had reported Tc recoveries of about 92%. The NaF was added to reduce the extraction of $^{95}\text{ZrNb}$. Decontamination factors of about 10^4 were obtained for $^{95}\text{ZrNb}$ and $^{106}\text{RuRh}$. This method did not use tracers or spikes to correct for the extraction efficiency. Later reports indicated that the 92% recovery yield could not always be achieved.

2.1.2 Cyclohexanone Tc Method

The Tc cyclohexanone method (Campbell 1966) was also applied to Purex waste streams. One of the method's primary advantages was the ability to dilute the cyclohexanone directly into a liquid scintillation cocktail for counting. This eliminated the drying step required for beta proportional counting and also the possibility of Tc losses during drying.

The method extracts Tc from a 0.5M H_3PO_4 matrix. Phosphoric acid was found to provide the best decontamination from $^{106}\text{RuRh}$ and the best de-entrainment from the cyclohexanone. The potential for $^{106}\text{RuRh}$ contamination could still be a problem if the sample size was too large. Small amounts of $^{106}\text{RuRh}$ contamination could be corrected for by the liquid scintillation counting procedure. Hydrogen peroxide was used to oxidize Tc to Tc(VII). The Tc recovery for spikes with this procedure was 97.7%. The decontamination factor for $^{106}\text{RuRh}$ was about 10^3 . Even though this method was faster it does not appear to have as good as fission product decontamination factors as the TBP method.

2.1.3 Tetrapropylammonium Hydroxide (TPAOH) Tc Method

The tetrapropylammonium hydroxide Tc method was developed for the analysis of Purex acid waste solutions (Smith 1974). The method was tested on waste from the AX tank farm and the current acid waste (CAW) from Purex. It does not appear that this method was used extensively for any routine operations but was developed for a specific project that did not materialize. The Tc is oxidized to Tc(VII) with hydrogen peroxide. Diethylenetriaminepentaacetic acid (DTPA) is added to complex other metals or extractable radionuclides. The extraction of the Tc-TPAOH complex is made from about 3M NaOH with a 50:50 mixture of chloroform and methylisobutylketone. Decontamination from fission products is about 10^5 with the exception of a small amount of $^{110\text{m}}\text{Ag}$ which extracted from CAW. The spike recovery for the method was

$102.9 \pm 5.9\%$. The beta count was corrected by using gamma energy analysis of the mount for other beta emitting isotopes; these were normally small or non-existent.

2.1.4 Aliquat-336 Tc Method

The Aliquat-336 method (Metcalf 1984) has been the predominant Tc method used by the 222-S Laboratory since its development in 1984. The quaternary amine, Aliquat-336, essentially behaves as a liquid anion exchanger. The sample is diluted in $4M$ HNO_3 and the Tc oxidized to Tc(VII) with H_2O_2 and heat. As discussed later in this report, sometime in the historical use of this procedure the heating of the peroxide step was dropped from the procedure. This omission created problems in samples with high organic complexant content because of the incomplete oxidation of the Tc in these matrices. After oxidation, Tc is extracted into 30% Aliquat-336/xylene using two contacts. The organic phase is removed and washed once with $4M$ HNO_3 and once with $4M$ NaOH. The present method has been modified from the original study and a final $4M$ HNO_3 wash performed on the organic before transferring an aliquot to the liquid scintillation vial. This wash and a few drops of glacial acetic acid were added to reduce fluorescence of the Aliquat-336 in the scintillation vial.

The average spike recovery on waste from AY-101, AZ-102, AW-104 and AW-105 in the original study was $92.5 \pm 4.8\%$. All the results from this method are corrected for the spike recovery. Therefore, the results are sensitive to the reproducibility of the technologist. Standard recoveries for the method are typically $102.9 \pm 7.5\%$ at the 95% confidence level.

2.1.5 Tetraphenylarsonium Tc Method

The tetraphenylarsonium method is used by the PNNL laboratories to determine Tc in Hanford tank waste. Originally the method used dichromate to oxidize the Tc to Tc(VII). However, because of the oxidation problems identified in the high organic complexant waste, the oxidizing agent has been changed in 1997 to ceric ion and the oxidizing conditions made more rigorous. After the oxidation step the sample is passed through a cation exchange resin to remove other potential beta emitting isotopes. Tetraphenylarsonium chloride is then added to complex the pertechnetate anion in the ion exchange effluent. The technetium tetraphenylarsonium complex is extracted into hexone and an aliquot of the hexone dried and counted by a beta gas flow proportional counter to determine the technetium concentration. The results from this method are not normally corrected for spike recovery through the system utilizing a second aliquot of sample. However, PNNL laboratories have occasionally utilized ^{99m}Tc as a tracer and corrected the results based on the tracer recovery.

2.1.6 TEVA Resin Method for Tc

In recent time, innovative extraction media have become available for use in separating ^{99}Tc . As an example, Eichrome Industries perfected a technetium specific anionic resin for extracting low

levels of Tc from environmental waters. The TEVA¹ filter is a polyacrylic filter bed impregnated with a non-mobile form of Aliquat-336. As with other methods using the extractant, the technetium must be maintained at the Tc(VII) level for extraction to occur. Although clever in principle, application to directly prepared tank waste samples shows interference from ¹³⁷Cs. The problem arises from the relatively enormous concentration of ¹³⁷Cs over ⁹⁹Tc. Sample liquid is entrained in the filter clamp region of the filtration apparatus. Not all of the ¹³⁷Cs can be washed out and activity sufficient to overshadow the ⁹⁹Tc will remain for the counting step. Therefore, this method, although perfected for environmental samples, is not in use for tank samples. The TEVA exchange material may also be used in a column to separate Tc. However, the method has not been evaluated for high level waste at Hanford.

2.1.7 ICP/MS Method for Tc

The ICP/MS method used at Hanford does not utilize a chemical separation of Tc from the waste matrix. The sample is either 1) diluted in acid if liquid, 2) digested in HNO₃/H₂O₂/HCl as per EPA SW-846 method 3050² or 3) fused in KOH and dissolved in HCl. Because the mass spectrometer is more isotope selective than beta counting, the method is subject to fewer interferences. Isobaric interferences are possible from Ru. However, Ru has other isotopes that may be checked to determine if it is present in significant quantities. Ruthenium has not been a problem in samples examined to this date and the DOE Savannah River Plant has had similar experiences. The prepared waste samples are normally diluted by a factor of 10³ to 10⁴ to reduce the dissolved solids content of the samples. Larger dilutions are required for the KOH fusion preparations and this may lead to detection limit problems for some samples. The ICP/MS method is simpler than the radiochemical method because separations are not normally required. Therefore it is 1) faster and 2) less prone to technician errors and 3) less likely to have Tc losses. There have been instances for some sludge samples where the ICP/MS data suggest that the present acid digestion may not be as complete as the KOH fusion. Further comparisons between acid and fusion sample preparations are needed to confirm these observations. The ability to confirm the analysis for Tc by a second independent technique provides a high level of confidence in the data. Therefore, continued characterization of waste and comparison of the results using both ICP/MS and radiochemistry is recommended.

2.2 Speciation of Technetium

All of the present radiochemical methods are designed with oxidation steps to convert other Tc valence states to pertechnetate and provide total Tc results for the samples. If the procedures

¹TEVA is a trademark of Eichrome Industries.

²It is acknowledged that use of HCl is not strictly specified. This acid can conflict with the accepted use of ICP/MS. Other similar methods such as EPA method 200.8 include HCl and this acid is required for proper dissolution of Hanford high iron content tank samples.

were modified to eliminate the oxidation steps then the separations would reflect the concentration of pertechnetate, Tc(VII), in the samples. The affect of any sample preparation on the Tc valence must also be considered in the evaluation of the Tc species. For alkaline supernates, the acidification of the sample for extraction could result in valence changes and therefore not reflect the Tc valence in the actual tank wastes. For solid samples, analysis of water leaches may provide the best estimate of Tc(VII). Because the tetrapropylammonium hydroxide Tc separation is performed from an alkaline medium, it may be the preferred approach for Tc speciation with less chance of the method conditions changing the Tc valence. Evaluating the Tc speciation in waste with high concentrations of organic complexants becomes more difficult because anionic complexes of lower Tc valence states may be present. Because of the complex chemistry of the Hanford waste, additional testing and evaluation is recommended to assure accurate Tc speciation data is obtained.

3 Technetium Analyses for Sample Exchange and Evaluation (SEE) Program

In 1993, a sample exchange program was established between the 222-S laboratory in the 200-W processing area operated by Westinghouse Hanford Company and the 325 Laboratory in the 300 area operated by Pacific Northwest National Laboratory (PNNL). The objective of the SEE program was to compare and evaluate the different methods used to characterize the waste in Hanford's single shell and double shell tanks.

The program was carried out in several phases from 1993 to 1997. Initially the program focused on radionuclide analyses because of the different separation and measurement schemes used by the laboratories and because no nationally accepted standard radiochemical methods are available. As the program progressed, the sample preparation complexity increased from handling homogeneous liquids to homogenized solids with different dissolutions. Discussions here relate to solid samples as prepared by either KOH fusion or acid digest. Technetium was one of the analytes that was compared in the SEE program. Therefore, the SEE data can provide further insight into the reproducibility of these methods and associated potential problems.

3.1 SEE Technetium Methods

The 222-S and 325 laboratory ^{99}Tc methods used in this program were based on radiochemistry but used different oxidation, separation and counting technologies. Inductively coupled plasma mass spectrometry (ICP/MS) was available at the 325 laboratory and was run along with the radiochemical analyses on several occasions.

The 222-S method was essentially the same as the radiochemical method described in section 2.1.4 (Metcalf 1984). The Tc is normally analyzed on a KOH fused waste sample that is dissolved in hydrochloric acid (HCl). An aliquot of the fused sample is adjusted to about 4M HNO_3 and the Tc oxidized to Tc (VII) with hydrogen peroxide. Recently a heating step was added to this oxidation to ensure that Tc is oxidized in the presence of organic complexants.

However, this was not done during the SEE program. The Tc (VII) is then extracted into Aliquat-336, a quaternary amine liquid anion exchanger. The Aliquat-336 is washed with 4M HNO₃ and NaOH to remove other beta emitting interferences. A aliquot of the Aliquat-336 is finally diluted into a liquid scintillation cocktail and counted. A second sample aliquot is spiked with a known amount of Tc-99 and carried through the same procedure. The final result is corrected for the chemical yield of the Tc-99 spike.

The 325 laboratory uses a similar KOH fusion and dissolution method as the 222-S lab. Technetium is oxidized to Tc(VII) using dichromate before removing potential beta emitting interferences via a cation ion exchange column. The Tc in the effluent is further purified by complexing it with tetraphenylarsenate and extracting the complex into hexone. An aliquot of the hexone is mounted in a 1" counting dish and counted on a gas flow proportional counter. The 325 laboratory results were not corrected for chemical yield based on a spike. Instead, ^{99m}Tc is used as a tracer to correct for chemical yield. The ^{99m}Tc tracer was not normally used in the SEE program.

3.2 SEE Phase I Technetium Results

The Tc-99 analyses in Phase I were performed on solid samples from tanks B-111 and T-107. The samples were all prepared by KOH fusion at the 325 laboratory and the dissolutions split for analysis at the two laboratories. In addition to the tank materials, QC standards for Tc were also analyzed. The results of these analyses are summarized in Table 2.

Table 2. SEE Phase I Technetium Results			
Tank/Standard	Average RPD - % (325-222S)/Average	Percent Recovery for Standards	
		325	222-S
B-111	11.4		
T-107	-19.3		
325 Lab Standard	-2.0	110.3	112.5
222-S Lab Standard	19.1	78.7	95.4

For the eight B-111 waste aliquots analyzed, the average relative percent difference (RPD) between the two laboratories was 11.4%. The 325 lab was higher in 7 of the 8 analyses for this tank. The average RPD between the labs for the four samples from tank T-107 waste was 19.3% with the 222-S lab having the highest value for all the samples. The 222-S lab utilized smaller samples which tended to increase counting errors.

3.3 SEE Phase II Technetium Results

Technetium was determined on waste from tanks B-201 and C-112 in Phase II of the SEE program. The Tc results on B-201 were too low for comparison. The RPD between the two lab Tc results for C-112 was 16.3% with the 222-S laboratory being higher. The average 222-S standard recovery was 100.9%. The 325 lab standard recovery was 84.6% with a RPD between labs of 17.6% similar to the RPD for C-112 samples. The estimated counting error for the analyses was about 10% for both laboratories. The ICP/MS technetium result on an acid digestion ($\text{HNO}_3/\text{H}_2\text{O}_2/\text{HCl}$) of the C-112 was 100 times less than the radiochemical analysis of the sample prepared by fusion. This could be an indication of a positive interference in the radiochemical method or possibly a difference in the effectiveness of the digestion procedures. A negative ICP/MS interference or a homogeneity difference of this magnitude seems less likely.

3.4 SEE Phase III Technetium Results

A homogenized sample of B-204 waste was split between the two laboratories and analyzed for Tc in Phase III. The 222-S lab reported a $<0.035 \mu\text{Ci/g}$ and the 325 lab reported $0.028 \mu\text{Ci/g}$. The results are consistent but are not comparable. Some problems were encountered with the Tc standards data. After the 222-S lab re-analyzed the standards, the results were about 19% higher than the 325 laboratory.

3.5 SEE Phase IV and V Technetium Results

No technetium analyses were performed in Phase IV of the program. In Phase V, Tc-99 analyses were performed on AW-101 and AN-107 double shell supernate wastes. The AW-101 supernate waste is low in organic complexants; whereas, the AN-107 waste has high organic complexant concentrations. The results for both labs were the same (RPD = 0.0%) for the AW-101 samples. The RPD between the radiochemical and ICP/MS results on AW-101 was 18.8% with the radiochemical result being the higher. The Tc results for the AN-107 sample are summarized in Table 2.

Table 3. Technetium Results for Tank AN-107 Supernate				
222-S Radchem $\mu\text{Ci/mL}$	RPD - % (325-222S)/Av	Radchem 325 $\mu\text{Ci/mL}$	RPD - % (Rad-ICP)/Av	325 ICP/MS $\mu\text{Ci/mL}$
0.052	65.0	0.10	22.6	0.13

The 325 Laboratory changed to a more vigorous oxidation procedure using ceric ion and heat in their radiochemical method for this high complexant matrix. This improved the conversion of Tc species to Tc(VII) and produced results similar to the ICP/MS. The 222-S lab was using the H_2O_2 oxidation without heat which fails to oxidize all the Tc to Tc(VII). As discussed in the

method section of this report, this oxidation step has been modified to include heat which has been shown to give comparable results with ICP/MS on high complexant waste samples.

3.6 SEE Program Conclusion

The SEE program data indicates that in most cases the radiochemical data between the labs are comparable (RPD<20%). The 222-S lab appears to produce higher radiochemical results than the 325 lab. This could be a result of applying the spike recovery correction factor to the data. The SEE program data shows the need for stronger oxidation conditions when analyzing high complexant waste. The independent ICP/MS technology is valuable for identifying potential problems in radiochemical analyses and in dissolution procedures as indicated in the C-112 results for acid and fusion prepared samples. Unfortunately the SEE data set is still relatively small to adequately explain some of the observed differences and make conclusive statements.

4 Current Findings

4.1 Evolution of Issues

The 222-S Laboratory (222-S) at Hanford provides significant analytical support in the characterization of defense nuclear waste identified above. It was shown (Schroeder, 1995) that certain laboratory measurements did not provide complete measurement of the ^{99}Tc concentration in tank samples. In particular, aqueous liquid supernates from tanks with large quantities of organic complexants showed losses in excess of 50%. Evidence of these losses is shown in Table 4 from rigorous analysis at Los Alamos National Laboratory (LANL) (Schroeder, 1995) as compared to routine analysis results from 222-S Laboratory.

Table 4. [^{99}Tc] Analysis Comparison for Organic Complex Supernate Samples			
Sample	LANL*	222-S*	Ratio, LANL/222-S
SY-101	5.9E-05	1.7E-05	3.5
SY-103	6.6E-05	3.5E-05	1.8
*Values as Molar concentration			

These data and the associated evaluation created a need to investigate the performance of the primary ^{99}Tc procedure at 222-S. Correspondingly, Pacific Northwest National Laboratory (PNNL) made several reagent studies on the separation of ^{99}Tc using modifications of the LANL and PNNL procedures (Fadeff, 1996). These studies showed that the organic complexants are of concern in the ^{99}Tc measurement and that proper ^{99}Tc can be recovered if the organics are

properly processed. Investigation into this and further issues on aged sludges are summarized here.

4.2 Effects of Aged Organic Wastes

As tank characterization sampling moved to tanks with significant quantities of organics, the complex nature of ^{99}Tc chemistry and complexes was observed. As noted in section 3.1, the radchem method at 222-S generated results considerably lower than more rigorous oxidation methods and ICP/MS. This led to investigation of the 222-S method. The original work utilizing tricapryl methyl ammonium chloride (Aliquat-336) (Metcalf, 1984), on simulated organic complexes showed no effect from heating the sample during the oxidation step. Thus, the formal implementation omitted the heating step. It was found that the heating step is crucial in assuring that all entrained ^{99}Tc is released and/or oxidized to Tc(VII) for anionic removal by Aliquat-336 (Troyer, 1998). Evidence is presented in Table 5 in which a non-organic tank (AN-105) is compared to organic tanks (AN-107 and SY-101). Further evidence is shown in Figure 2 in which several combinations of oxidant and temperature levels were used with the Aliquat-336 extraction. A fallout of this work is that some speciation inference may be possible with proper use of the heat step. The base method at 222-S was modified to include the heating step in 1998 (Relyea, 1998).

Table 5. Results of Tank Supernate Sample Comparisons - ^{99}Tc $\mu\text{Ci/L}$				
Tank Sample	Total Organic Carbon, g/L	222-S No Heat	222-S With Heat	ICP/MS
AN-105	-	244	-	255
AN107	60	53.2	106	101
SY-101	15	288	604	634

4.3 Tank Sludges and Solids

4.3.1 AX-104 Sludge Heel

Samples were taken from the emptied tank AX-104 in support of Hanford Tank Initiative (HTI) for risk assessment of residual materials. The primary focus was the water leach rate of various components from the waste (Crawford, 1998a, 1998b). Technetium was a primary component of interest.

Blended samples from two tank riser access locations were analyzed for ^{99}Tc by ICP/MS, Laser Ablation Mass Spectrometry (LAMS), and radiochemical separation. Significant differences and poor replication were found among the data for core riser 9G as summarized in Table 6. It should be noted that results for individual 9G and 3A samples were from acid digest preparations. The 9G composite Tc samples were prepared by KOH fusion. Further work on AX-104 is dependent

Figure 2. Representative results of ^{99}Tc assay with excess oxidant and heating. Note that excess oxidant has insignificant impact on releasing or oxidizing the Tc to a species suitable for Aliquat-336 extraction.

on acquiring additional sample material.

Table 6. Tank AX-104 Sludge ⁹⁹ Tc Results						
Source Riser	ICP/MS μCi/gm	%RPD	LAMS μCi/gm	%RPD	RadChem μCi/gm	%RPD
9G	<.02	N/A	<.02	N/A	.8 to 3.0	<100%
3A	<.0002	N/A	<.02	N/A	<.02	N/A
9G Composite	.65	No Duplicate			.4	47%

4.3.2 C-104 Sludge

During FY1998, samples of Hanford high level waste tank 241-C-104 bottom sludge were analyzed for performance assessment of leaching and various component content. Initial radiochemistry (radchem) results were higher than expected and became important concerns regarding ⁹⁹Tc concentrations for decision criteria on retrieval/pre-treatment process flowsheets. Due to previous studies (Crawford, 1998a/b; Troyer, 1998), the opportunity to further assess the reliability between radchem and Inductively Coupled/Mass Spectrometry (ICP/MS) was exploited. As shown in Table 7, the initial analyses for C-104 showed that the ICP/MS produced results 50 times lower than the radchem, a direct inversion of previous experience with organic complexant waste (Troyer, 1998). This evidence initiated a study to resolve the difference.

Table 7. ⁹⁹ Tc Results for C-104 Sludge Sample S98T002049		
Method	μg/g	μCi/g
⁹⁹ Tc by ICP/MS LA-505-159	2.05	(.035)
⁹⁹ Tc by Liq. Scint	(99)	1.7
(Values) are calculated from italic measured results using specific activity for ⁹⁹ Tc.		

A test plan was developed to resolve the ⁹⁹Tc differences. A series of new sample preparations were defined: water leach, acid digest, and KOH fusion. The water leach was expected to provide inference as to the soluble pertechnetate (Tc(VII)) species. Duplicate aliquots were digested and submitted for ICP/MS and radchem analysis. A secondary, no-heat/oxidation step variation was also prescribed for further potential speciation. For the digest and fusions, a pre-digest spike with ⁹⁹Tc standard was also included. All of these aliquots were submitted for both ICP/MS and radchem.

The results of these tests essentially confirmed the initial results. The ICP/MS showed considerably lower results than the radchem. However, a significant instability also appeared in the radchem results. The primary indicator was loss of control of the internal analytical quality control. Several attempts were made to improve the results through analytical reruns. A summary of the data is shown in Table 8.

As shown in Table 8, the ICP/MS results were consistently lower than the radchem, in initial cases, by as much as 50 to 150 times. It is also shown that the radchem reported generally unstable results with an indication of downward trend over time. The less than detectable measurement by ICP/MS for the fusion is a factor of diluting the excess salts generated by the fusion process for proper operation in this instrument.

Several attempts were made to resolve the continuing discrepancy. The acid digest prepared stocks were conditioned with additional hydrogen peroxide and heat. Aliquots of these were again submitted to ICP/MS and radchem. The results are shown in Table 13 as the oxidation strike data row. As before, the ICP/MS showed consistent results while the radchem shows continued instability as reflected in the relative per cent difference (RPD) value.

Table 8. Tank C-104 Sludge 222-S ⁹⁹Tc Reanalysis*						
Preparation	ICP/MS, $\mu\text{Ci/gm}$			Radchem, $\mu\text{Ci/gm}$		
	Sample	Duplicate	RPD	Sample	Duplicate	RPD
Caustic Fusion	<0.043	.		3.2	3.0	6
				1.9	2.1	8
				0.15	0.25	50
				0.16	0.32	65
				0.54	1.30	82
Acid Digest	0.016	0.014	13	2.9	11.00	117
				2.0	1.8	12
				0.21	0.22	7
Acid Digest w/oxidation strike	.022	.018	20	1.36	0.31	125
Water Leach	0.0079	.0079	1	0.02	0.03	24
*Results presented in chronological order.						

Examination of the liquid scintillation spectra for this last set of radchem analyses showed that a significant contaminant was present. Further investigation with pure nuclide standards showed that the liquid scintillation spectra for ²⁴¹Pu are quite similar to the sample spectrum. Comparison of sample, sample+spike (tracer), and ⁹⁹Tc standard spectra (**Figure 3.**) indicate such a contaminant. Commonly, the ⁹⁹Tc liquid scintillation results are created by integrating an energy

region of interest from zero to the ^{99}Tc energy endpoint. As evidenced in the spectra in **Figure 3.**, this includes the significant low energy response from the suspect ^{241}Pu . No other beta/gamma emitting nuclides were detected with gamma assay³ of the separated materials. The mechanism for carryover of plutonium into the extractant is unknown. The discovery is likely due to a higher partitioning of plutonium into the sludges due to caustic matrix solubilities. To date, a minor concentration of plutonium in supernates has not been a significant confounding contaminant in the extraction procedure.

Figure 3. Liquid scintillation beta spectra of Aliquat 336 ^{99}Tc extraction from prepared C-104 sludge sample material. Spectra for sample and "sample+spike" are adjusted for dilution, ^{99}Tc standard is normalized to "sample+spike". Region of interest provides response of sample/spike ratio comparable to ICP/MS.

Based on these studies, it is evident that more information on the chemistry of aged nuclear waste sludges is needed. An immediate work around establishing a specific spectral region of interest for ^{99}Tc in the liquid scintillation counting is recommended. A proposed region of interest

³Confirmation of ^{241}Pu by ^{241}Am gamma assay is not likely due to liquid scintillation/HPGe detector relative efficiencies.

integration as shown in **Figure 3**, provides ratios between the sample and sample+spike comparable to the ratios found by ICP/MS. In addition, routine examination of the beta spectra is needed to assure that other contaminants are avoided. Finally, further investigations into improvements in decontamination and stability of the radchem method are needed.

4.3.3 Tank C-106 Slurry

During 1996, twenty grab samples were taken from the slurry portion of Tank C-106. These samples were used by PNNL to estimate effects of sludge washing and preparation for feed to vitrification processes. These samples underwent significant dilution, compositing, splitting, and washing operations. From these operations, two primary sample types are identifiable for ^{99}Tc comparisons (Esch, 1997). A summary of the ^{99}Tc results is shown in Table 9, all data generated by ICP/MS. The first is an Original Material (OM). This comprised a composite of all the samples and diluted by a ratio of 3:2 with water. Three aliquots of the OM were dried and portions processed by both acid digest and KOH fusion.

The second material was a Vendor Product (VP) developed by repeated washing of the OM with various caustic solutions. Resulting solids were separated by centrifugation and decanting. These solids were then dried and subjected to various tests.

Table 9. ^{99}Tc Analysis Summary of Envelope D Sampling of Tank C-106		
Sample Material	KOH Fusion, $\mu\text{Ci/gm}$	Acid Digest, $\mu\text{Ci/gm}$
Original Material, composited and dried.	9.6E-2	3.1E-2
Vendor Product, washed and dried solids.	N/A	5.7E-3

As has been generally noted, the ICP/MS results check internally quite well (Esch, 1997). Therefore the difference observable between the KOH and acid preparation are not suspect. It was noted that blending of samples produced magnetic particles on the stir bars and that these were included in the acid digest. No further comments on the condition of the digested samples were found. Finally, the results from the VP samples imply that a significant portion of the ^{99}Tc is in an unincorporated form, likely the pertechnetate species, as only about 10% remained in the VP.

4.3.4 Additional Sludge Washing Performance

The partitioning of tank waste materials continues to be evaluated through caustic washing and leaching. A recent report (Lumetta, 1998) identifies a number of tank materials processed similar

to the C-106 efforts (Esch, 1997). Prepared samples, washes, and residual solids were assayed for several components of interest including ^{99}Tc . Based on these results as shown in Table 10, a significant amount of the ^{99}Tc is soluble and can be removed from the solids by simple washing. All results were generated by ICP/MS.

Table 10. Technetium Response to Caustic Washing and Leaching								
Tank Sample	0.1M NaOH Wash				Solids Washing			
	Original Sample uCi	Combined Wash uCi	Washed Solids uCi	% Decontamination	1M NaOH @70°C uCi/ml	3M NaOH @70°C uCi/ml	1M NaOH @95°C uCi/ml	3M NaOH @95°C uCi/ml
B-101	n/d	n/d	n/d		nm	nm	nm	nm
BX-110	1.64	1.41	2.3E-01	86	nm	nm	nm	nm
BX-112	12.8	14.4	0.6	96	nm	nm	nm	nm
S-101	13.7	n/d	13.8	99	4.4E-05	n/d	1.6E-04	n/d
n/d = not detected, nm = not measured.								

5 Analytical Directions

Based on the evidence of studies presented above, it is apparent that more effort is required for sample preparation, method reliability, inter-comparisons of methods, and potentially other analytical techniques. Some of the Hanford waste sample matrix types to date have challenged the reliability of existing 222-S methods. In general, the methods are sufficient for aqueous and aqueous/organic supernate matrices, provided that current oxidation steps are followed. However, reliability and inter-method agreement has not been robust for solids and sludges from the high level aged wastes. There are chemistry concerns ranging from the initial sample preparation to the final isolated material measurement. Some of the key issues are discussed here.

5.1 Dissolution Methods

Several methods are in use at 222-S laboratory for general preparation of samples. For water soluble species, a simple water leach is used (Anastos, 1999). For more complete dissolution of solid matrices, two options are available, an acid digest with HNO_3 , HCl , and H_2O_2 (Anastos, 1999 and EPA, 1996), and a potassium hydroxide (KOH) fusion (Fitzgerald, 1998).

Recognizing the limited utility of the water leach, the focus on solids dissolution is for acid digest or KOH fusion. The acid digest is visually successful, but generates a new matrix which is not always desirable. For example, the use of hydrochloric acid introduces high chloride ion concentration which may conflict with many other methods based on a nitric acid matrix. However, HCl is needed for effective dissolution of iron based sludges. This is evidenced by visual inspection of the process for C-104 sludge which showed that the HCl was required to

obtain a clear solution. In the case of Tc, it has been reported (Cotton, 1962) that HCl can cause Tc to reduce from the pertechnetate form. This affect is currently uncertain, but could be a factor with the time instability shown for the C-104 sludge analysis. In support of acid digest, the detection limits and ease of use for ICP/MS are positive factors. However, for the sludge material, the intercomparison for the two main methods has not been successful on the limited number of samples to date (AX-104 and C-104). Based on the observation that plutonium contamination can be found in the Aliquat 336 extractant, these methods should become consistent with further improvement in the radchem method.

The KOH fusion provides a robust but destructive process for bringing the tank sludges into solution. This type of preparation is designed for solid materials, in particular soils. The KOH fusion has typically been used for dissolving silicate rocks and minerals. In tank waste, it will attack silicate materials and metathesize acid insoluble metal fluorides, sulphates and phosphates into more acid soluble hydroxides. The typical fusion uses 5 g of KOH which results in a final potassium concentration of about 20 g/l. For ICP/MS, the resulting prepared sample must be significantly diluted to less than 0.1 g/l in order to avoid over driving the instrument's sensitivity due to the added salts. The required degree of dilution causes reduction in sensitivity. The processing of the C-104 sludges by KOH fusion made ⁹⁹Tc undetectable in comparison to radchem for the same stock. With regard to the C-104 sludge, radchem fusion results exhibited instability in results comparable to the acid digest. The cause of the instability is not understood and should be investigated further for these types of samples.

5.2 Environmental Samples

Environmental samples typically do not have the radionuclide interference challenges of the high level nuclear wastes. Technetium preparation methods using modern filter and ion exchange media such as TEVA resin (Kaye, 1995) or Rad Disk⁴ (Iwatate, 1997) filters are currently used. To date, the Waste Sampling and Characterization Facility (WSCF) has shown good success on direct analysis of environmental aqueous samples. For various environmental solids, only acid leach preparation procedures are in use. This is based on an assumption that the ⁹⁹Tc should be deposited on surfaces rather than incorporated into the solid matrix. In all cases, matrix spikes are the primary quality control which may be questionable based on the more extreme situations discovered in high level nuclear wastes. Only limited consideration is given for the possibility that a soluble non-extractable complex form may be present. As more is understood regarding the behavior of environmental Tc, investigations into the robustness of environmental methods may be required.

⁴Rad Disk is a trademark of 3M Corporation.

5.3 High Level Tank Supernates

5.3.1 Aqueous Supernates

Measurements of ^{99}Tc have been in aqueous supernates for most of the Hanford chemical processing history. Indeed, analytical development was dominated by work on these fresh materials, including later development for supernates with organic complexes (Metcalf, 1984). The cited literature shows good analytical performance with ever improving separation factors. The Hanford process support laboratories relied then and now on ^{99}Tc spike and standards performance to assure correct results. Since all the methods use oxidation steps to measure total Tc as Tc(VII) , little evaluation in the context of speciation can be made. Only recently has an alternative technology, ICP/MS, become available for confirming radchem analyses. Even though comparison data for non-complexed supernates are generally good, these materials should be included in any attempts to confirm inter-method and inter-laboratory consistency.

5.3.2 Organic Supernates

The inter-comparison work performed on aged Hanford high level wastes containing organic complexants showed discrepancies in results (Table 4; Schroeder, 1995; Fadeff, 1996). A key confirmation was that the aged complexed waste contains species that do not readily release Tc for extraction as the free pertechnetate (Troyer, 1998). While the solution was to simply apply heated hydrogen peroxide in the 222-S procedure (Relyea, 1999), little effort has been made to fully understand the mechanisms of the process. Additional work in this area is needed such that the chemical forms and potential problems are understood as more requests for these measurements are made. Knowledge about the species is expected to assist in development of treatment processes and risk models.

5.4 Tank Sludges

As noted, only a limited amount of data has been generated on the performance of Tc analysis for aged tank sludges. These materials by nature are precipitates with high iron or aluminum content. The sample preparations are difficult, resulting in matrices that either have high salt (KOH fusion) or high acid mix. All that has been confirmed to date is that data between methods do not correlate, and reliability of the 222-S chemical separation is suspect. Significant additional effort is required to determine what is causing the bias between methods. Accurate analyses of these sludges will be important to evaluating the Privatization HLW treatment process.

5.5 Method Support

A process support or production based laboratory such as 222-S requires methods that are low cost and reliable. Exhaustive procedures to assure conditioning and isolation of Tc for reference basis are necessary and have been shown to be of great benefit (Schroeder, 1995; Fadeff, 1996).

However, the quicker methods based on simple preparation and extraction or ICP/MS are more desirable provided reliability is assured. The ICP/MS is a very attractive method due to its rapid response. The radchem separation methods provide large dynamic range and good sensitivity for unusual matrices. It is recommended that development continue in these areas with particular emphasis on matrix issues and inter-comparison support.

5.6 Tracers and Spikes

It is noted above that most of the development and performance check work is based on using ^{99}Tc as a spike or tracer. Since this material is an external performance monitor of the same analyte, analytical technique within a single aliquot is not completely tracked. A better choice would be the use of ^{99}Tc as a true and non-confounding tracer. The number of chemical manipulations would be reduced with the elimination of a spike-duplicate. Drawbacks are that the half life is short (61 d) and additional gamma measurements on the isolated Tc are required. The short half life makes supply a challenge, and for this reason, it has not been used at 222-S.

6 References

- Anastos, H. L., *Water Leach Sample Preparation*, LA-504-101, Rev. G1, Waste Management Hanford Co., Richland WA, January 25, 1999.
- Anastos, H. L., *Acid Digestion of Waste Tank Samples for Inductively Coupled Plasma (ICP)*, LA-50505-163, Rev. B1, Waste Management Hanford Co., Richland WA, June 26, 1999.
- Campbell M. H., 1963, *Separation of Technetium from Mixed Fission Products by Solvent Extraction with Tributyl Phosphate*, Analytical Chemistry, Vol.35, page 2052, December 1963.
- Campbell M. H. 1966, Internal Letter to J. V. Panesko, December 12, 1966, *Analysis for Technetium-99*, Isochem Inc., Richland, Washington.
- Cotton, F. A., and G. Wilkinson, *Advanced Inorganic Chemistry - A Comprehensive Text*, Interscience Publishers, John Wiley & Sons, 1962, p. 806.
- Crawford, B. A., 1998a, *Tank 241-AX-104 Residual Solids Leach Test Results*, TWR-3548, Rev. 0., Numatec Hanford Corporation for Fluor Daniel Hanford Inc., Richland, Washington.
- Crawford, B. A., 1998b, *Completion of Waste Minimization Database for LQA/MS Screening*, internal memorandum 8C520-AT98-009 to S. C. Howald and D. S. Merry, Numatec Hanford Corporation for Fluor Daniel Hanford Inc., Richland, Washington.

- EPA, 1996, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*, SW-846, Rev. 3, U.S. Environmental Protection Agency, Washington, D.C.
- Esch, R. A., *Tank Waste Remediation System (TWRS) Privatization Contractor Samples Waste Envelope D Material 241-C-106*, HNF-SD-WM-DP-225, Rev. 1, Rust Federal Services of Hanford, Inc., April 1997.
- Fadoff, S. K., letter report to D Blanchard, "Technetium Oxidation Comparisons", Pacific Northwest National Laboratory, Richland WA, April 1996.
- Fitzgerald, S. L., *Fusion by Alkali Metal Hydroxide*, LA-549-141, Rev. G0, Waste Management Hanford Co., Richland WA, March 3, 1998.
- Iwatate, K., *Determination of Technetium-99 by Rad Disk Filtration and Liquid Scintillation Counting*, LA-438-402, Rev. A0, Waste Management Hanford Co., Richland WA, September 30, 1997.
- Lumetta, G. J., et al, *Washing and Caustic Leaching of Hanford Tank Sludge: Results of FY 1998 Studies*, PNNL-12026, Pacific Northwest National Laboratory, Richland WA, December 1998.
- Kaye, J. H., *⁹⁹Technetium Analysis by Extraction Chromatography Using TEVA-Resin*, LA-433-401, Rev. A0, Waste Management Hanford Co., Richland WA, October 10, 1995.
- Metcalf, S. G., 1984, *Determination of Technetium-99 in Complexed Hanford Defense Waste*, SD-RE-LB-001, Rockwell Hanford Operations, Richland Washington.
- Relyea, J. A., "Determination of Technetium-99 Solvent Extraction and Liquid Scintillation Counting", LA-438-101, Rev. E2, Waste Management Hanford Co., Richland WA, January 1998.
- Roberts, F.P., "Summary of Research on Tc, Rh, and Pd by Battelle Northwest", USAEC Report, BNWL-B-49, 1971.
- Schroeder, N. C., et al, "Technetium Partitioning for the Hanford Tank Waste Remediation System: Anion Exchange Studies for Partitioning Technetium from Synthetic DSSF and DSS Simulants and Actual Hanford Wastes (101-SY and 103-SY) Using Reillex™-HPQ Resin", Los Alamos National Laboratory, LA-UR-95-4440, 1995.
- Smith H. E., 1974, Internal Letter to A. L. Case, November 14, 1974, *Technetium Determination in Boiling Waste – 1970 Analytical Work*, Atlantic Richfield Hanford Company, Richland, Washington.

Troyer, G. L., Internal Letter *C520-AT98-012 to C. M. Seidel, *The Analysis of ^{99}Tc in Aged Organic Complexants in Hanford Defense Nuclear Waste Tanks*, September 29, 1998.

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