

The Determination of Pertechnetate and Non-Pertechnetate Species in Hanford Tanks -- Phase 1

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EXECUTIVE SUMMARY

An analytical method is required to distinguish between the pertechnetate and non-pertechnetate forms of technetium; currently, the methods available only report the total technetium present in a sample. The overall objective of this effort is to develop a method for routinely analyzing Hanford tank waste for technetium in the pertechnetate and the non-pertechnetate forms. A phased approach will be deployed to accomplish this objective.

| | |
|-----------|--|
| Phase I | Comparison of existing technetium analysis methods with modification |
| Phase II | Demonstration of modified methods using non-pertechnetate spiked simulants |
| Phase III | Demonstration of chosen method on Hanford tank sample containing non-pertechnetate |

This report describes the Phase I work, providing a comparison of Aliquat 336 and TEVA^{®1} in the removal of pertechnetate and discussing the subsequent analysis for technetium in both alkaline and acidic environments without oxidation. The effort was executed under LAB-PLN-13-00004, *The Determination of Pertechnetate and Non-Pertechnetate Species in Hanford Tanks Phase I*.

The presence of non-pertechnetate species in Hanford tank waste has been postulated by several studies. Two procedures are routinely used for analysis of technetium in Hanford tank samples, neither of which provides a determination of the non-pertechnetate species; and due to incorporation of acidification and oxidation steps, the methods may actually convert any non-pertechnetate technetium present in the sample to pertechnetate.

One of the laboratory procedures LA-438-114, "Determination of Technetium-99 by Extraction with TEVA[®] Resin," adjusts the pH between 7 and 12 with 1M nitric acid prior to extraction with TEVA[®] Resin. The other procedure LA-438-101, "Determination of Technetium-99 by Solvent Extraction" uses solvent extraction prior to binding with Aliquat^{®2} 336. In this method, the sample undergoes oxidation with peroxide to convert any non-pertechnetate to pertechnetate followed by nitric acid and sodium hydroxide washes. In both methods, liquid scintillation is employed for radiological counting.

In Phase I of this effort, it appears that both Aliquat^{®2} 336 and TEVA[®] Resin extract pertechnetate either directly from the highly alkaline sample or from the sample after acidification. The TEVA[®] Resin exhibited less error than did the Aliquat[®] 336 extraction. In the extraction using TEVA[®] Resin in the highly alkaline solution, the sample was not subjected to oxidation as occurred with the Aliquat[®] 336. When using Aliquat[®] 336, the vortex step used to partition the pertechnetate into the organic will oxidize non-pertechnetate. It also appeared that the pertechnetate largely remained bound to the Aliquat[®] 336 and did not readily extract into the acid and base washes.

The relative percent difference between the Aliquat[®] 336 and the TEVA[®] Resin is 8.1%. If the spike is considered to be a true value (1.7447E04 dpm/mL), then the percent of error is 13.6%

¹ TEVA is a registered trademark of Eichrom Technologies, Inc., Lisle, Illinois.

² Aliquat 336 is a registered trademark of BASF, Ludwigshafen, Germany.

and 6.35%, respectively (Table ES-1). The TEVA[®] Resin exhibited less error than did the Aliquat[®] 336 extraction.

Table ES-1. Results of Aliquat[®] 336 Extraction and TEVA[®] Resin.

| Sample Number | Matrix | dpm/mL | Relative % Difference | Error (%) |
|---------------|--------------------------|--------|-----------------------|-----------|
| S13R000511 | Aliquat [®] 336 | 15,074 | 8.1 | 13.6 |
| S13R000511 | TEVA [®] Resin | 16,339 | | 6.35 |

The primary conclusion from this effort is that the TEVA[®] Resin works under very alkaline conditions and is a candidate for further study in the attempt to delineate non-pertechnetate technetium from pertechnetate technetium.

For a future effort, it is suggested that other valence states of technetium be employed along with pertechnetate in a simple simulant. For example, in alkaline pH, reducing sugars will auto reduce pertechnetate to Tc (IV/V) with the sugar as the ligand. The sugar D-threose will convert approximately 98% of Tc (VII) to the Tc (IV/V) state. (“The autoreduction of pertechnetate in aqueous, alkaline solutions,” [D. E. Berning et al. 2005]). A second method to reduce Tc (VII) to a lower valence state is mixing with hydroxylamine in an alkaline solution. The resulting reduced technetium species would be with and without an organic ligand.

The pertechnetate and reduced technetium species would then be subjected to extraction by Aliquat[®] 336 and TEVA[®] Resin and analysis using inductively coupled plasma-mass spectrometry. The effort would be focused on the partitioning of the technetium species and the total concentration of mass 99 using the inductively coupled plasma-mass spectrometry with a collision cell to ensure molecules are analyzed in their atomic units.

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List of Terms

Acronyms and Abbreviations

| | |
|--------|--|
| ATL | Advanced Technologies and Laboratories International, Inc. |
| ICP-MS | inductively coupled plasma-mass spectrometry |
| LSC | liquid scintillation count(ing) |
| SBD | sample breakdown diagram |
| RCRA | Resource Conservation and Recovery Act |

Units

| | |
|-----|----------------------------|
| dpm | disintegrations per minute |
| μCi | microcurie |
| M | molar |
| mL | milliliter |

1 INTRODUCTION

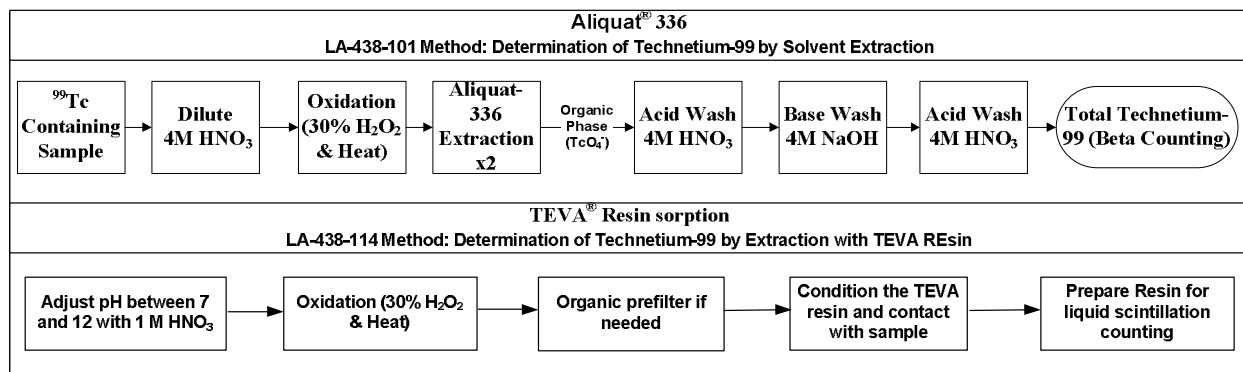
The presence of non-pertechnetate species in Hanford tank waste has been identified by several studies. For example, work by Schroeder, et al. (LA-UR-95-4440, *Technetium Partitioning for the Hanford Tank Waste Remediation System: Anion Exchange Studies for Partitioning Technetium from Synthetic DSSF and DSS Simulants and Actual Hanford Wastes (101-SY and 103-SY) Using Reillex-HPQ Resin*) indicated that tank 241-SY-101 and tank 241-SY-103 contained 37% and 30% of the technetium as the pertechnetate species, leaving 63% and 70% as non-pertechnetate species, respectively. The most mature technetium removal technologies (e.g., ion exchange) are specific for the pertechnetate anion, and any technetium present in a different form will not be removed. The ability to quantify the amount of non-pertechnetate present in Hanford Tank samples is essential to the development of an effective technetium removal process.

Notes are located in lab book HNF-274-3, page 43. All other records, such as the waste stream fact sheets, job hazard analysis, radiation control check sheet, and laboratory analytical data are contained in the project files.

This report contains information gathered in the first phase of a multi-phased approach to delineate a method or methods to yield an accurate estimate of the amount of non-pertechnetate in the Hanford tank waste.

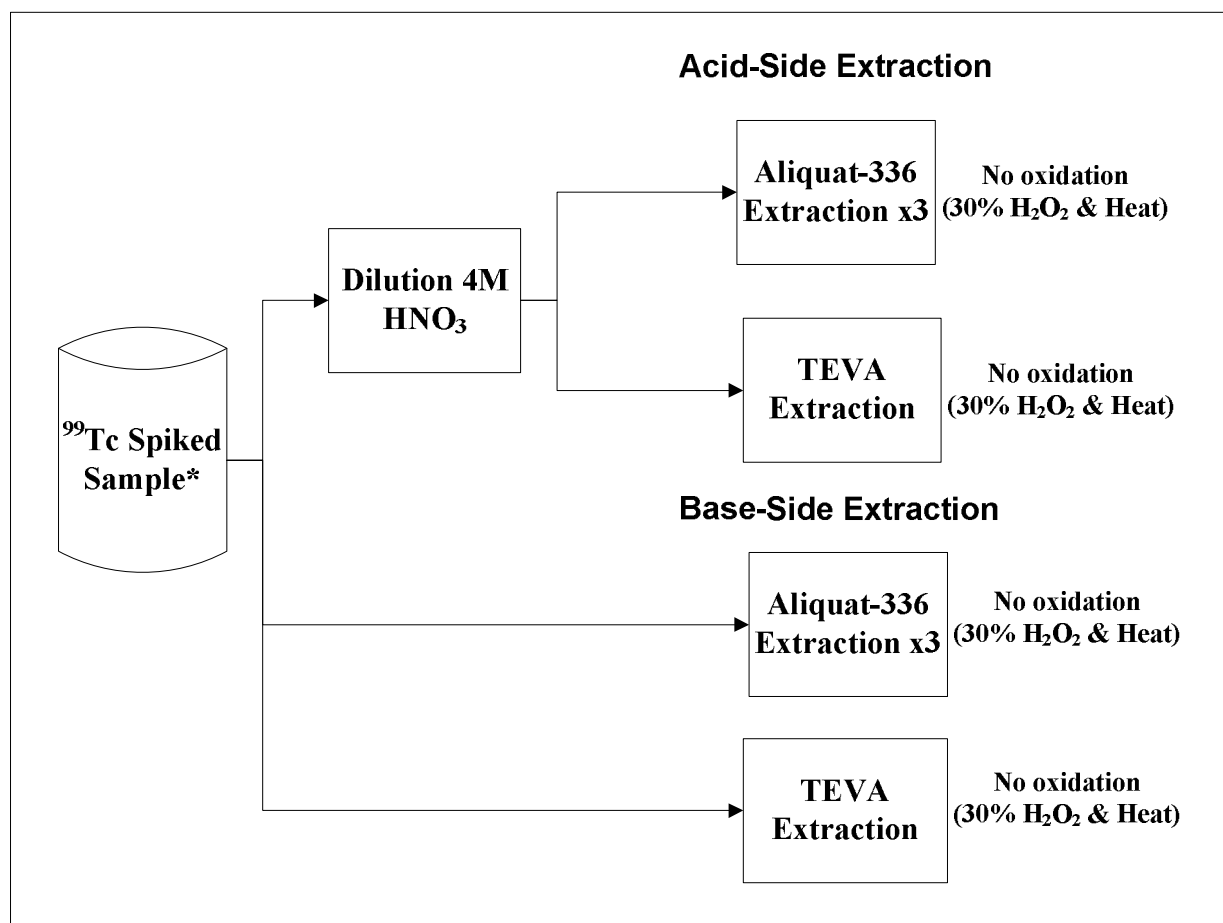
The objective of Phase 1 is to compare the effectiveness of Aliquat[®] 336 and TEVA[®] sorbent (solid phase with Aliquat[®] 336 coating) in their ability to remove pertechnetate from an acidic and basic simple simulant without oxidation. Aliquot 336[®] is tricapryl-methyl ammonium nitrate quaternary ammonium salt which extracts technetium with an anion exchange mechanism (“Extraction behaviour of technetium and actinides in the Aliquat-336/nitric acid system,” [Landgren and Lilgenzin 1999]).

To meet the objective of differentiating between pertechnetate and non-pertechnetate species, there are a number of issues associated with the current Advanced Technologies and Laboratories International, Inc. (ATL) methods for determining technetium (see Figure 1).

Figure 1. Current ATL Laboratory Methods for Technetium Determination.

1. The oxidation step (30% H₂O₂ and heat) is included specifically to convert any non-pertechnetate to the pertechnetate form.
2. The acidification with nitric acid may have an oxidizing effect and also convert some or all of the non-pertechnetate to pertechnetate.

The effect of omitting these steps from either method is not known. The first phase of development of a viable non-pertechnetate analysis method is to compare modified versions (no acidification or oxidation) of the current ATL technetium determination methods to ascertain the impact these changes may have on the recovery of technetium from a spiked simple simulant. The modified methods are shown in Figure 2.

Figure 2. Technetium Determination Method Comparison Testing.

2 MATERIALS AND METHODS

A simple tank simulant was formulated as shown in Table 1.

Table 1. Simulant Composition.

| Reagent | Concentration |
|------------------|---------------|
| Sodium hydroxide | 1 M |
| Sodium nitrate | 2 M |
| Sodium nitrite | 1 M |

The simulant was spiked with a known amount of pertechnetate, 54,000 dpm or 0.0245 $\mu\text{Ci}/\text{mL}$. The spike was 5 mL of pertechnetate to 10 mL of simulant. The sample breakdown diagrams (SBD) are shown in Appendix A.

Since the stock simulant solution used to cascade each of the SBD sections was made from the same container of non-spiked composition, and since the pertechnetate spike was introduced at the same volume from the same source, it was decided to submit only S13R000499 for analysis. The expected count for the spiked simulant was 18,000 dpm.

For the acid-side extraction, the simulant was diluted in 10 mL of 4M nitric acid; an aliquot was extracted with TEVA[®] resin, and the remainder was extracted three times with Aliquat[®] 336. The organic phase was transferred to 10 mL of 4M nitric, mixed using a vortex mixer, and 1 mL of Aliquat[®] 336 was removed and placed in OPTIMA Gold^{™3} for liquid scintillation counting (LSC). These steps were carried out for the base wash in 4M sodium hydroxide and a second acid wash using 4M nitric acid (see acid-side extraction in Appendix A).

For the base-side extraction, the spiked simulant was subjected to TEVA[®] resin extraction as well as Aliquat[®] 336 extraction. For the Aliquat[®] 336 extraction samples (S13R000492, -493, and -494), duplicates were taken, and 0.5 mL of the 54,000 dpm pertechnetate solution was added as the technetium spike. Aliquots of the Aliquat[®] 336 and the TEVA[®] extractions were transferred to OPTIMA Gold^{™4} for LSC. Any sample not subjected to LSC was submitted for inductively coupled plasma-mass spectrometry (ICP-MS) analyses (see base-side extraction in Appendix A).

3 RESULTS

A sample of the simulant without the pertechnetate spike (S13R000510) was analyzed by ICP-MS, resulting in a less-than value for mass 99. Table 2 presents the results for the Aliquat[®] 336 cascade of acid and base washings.

Table 2. Results from the Analyses of Aliquat[®] 336 from Acid-Side Extraction.

| Sample Number | Wash | Matrix | dpm/mL |
|---------------|---------------------|---------------------------------|-----------------------------|
| S13R000491 | NA | Spiked Simulant | 17,447 (18,000 expected) |
| S13R000497 | NA | TEVA [®] Resin | 14,112 |
| S13R000496 | NA | Effluent from TEVA [®] | <2.26 |
| S13R000492 | 4M Nitric Acid | Aliquat [®] 336 | 18,521 |
| S13R000493 | 4M Sodium Hydroxide | Aliquat [®] 336 | 17,919 |
| S13R000494 | 4M Nitric Acid | Aliquat [®] 336 | 19,562 |
| S13R000512 | 4M Nitric Acid | 4M Nitric Acid | 177 |

Table 3 presents the results from the base-side extraction.

³ OPTIMA Gold is a trademark of PerkinElmer Inc., Waltham, MA.

Table 3. Results from the Analyses of Base-Side Extractions.

| Sample Number | Wash | Matrix | dpm/mL |
|---------------|--------------------------|---------------------------------|-----------------------------|
| S13R000499 | NA | Spiked Simulant | 17,447 (18,000 expected) |
| S13R000507 | NA | TEVA [®] Resin | 19,566 |
| S13R000506 | NA | Effluent from TEVA [®] | <2.26 |
| S13R000503 | 4M Nitric Acid | 4M Nitric Acid | 1,056 |
| S13R000504 | 4M Sodium Hydroxide | 4M Sodium Hydroxide | 7.4 |
| S13R000505 | 4M Nitric Acid | 4M Nitric Acid | 891 |
| S13R000508 | Aliquat [®] 336 | Aliquat [®] 336 | 23,913 |

An aliquot of the spiked simulant (S13R000499) was split and subjected to both Aliquat[®] 336 extraction and TEVA[®] Resin. Table 4 shows the results.

Table 4. Results of Aliquat[®] 336 Extraction and TEVA[®] Resin.

| Sample Number | Matrix | dpm/mL |
|---------------|--------------------------|--------|
| S13R000511 | Aliquat [®] 336 | 15,074 |
| S13R000511 | TEVA [®] Resin | 16,399 |

4 CONCLUSIONS

In Phase 1 of this effort, it appears that both Aliquat[®] 336 and TEVA[®] Resin extract pertechnetate either directly from the highly alkaline sample or from the sample after acidification. In the extraction using TEVA[®] Resin, the sample is not subjected to oxidation as occurs with Aliquat[®] 336. When using Aliquat[®] 336, the vortex step used to partition the pertechnetate into the organic will oxidize non-pertechnetate technetium. It also appears that the pertechnetate largely remained with the Aliquat[®] 336 and did not readily partition in the acid and base washes.

The spiked simulant value of 1.39E-02 $\mu\text{Ci/mL}$, as reported by ICP-MS, converts to 17,447 dpm/mL. If this value is taken as a true value and used to calculate percent error by the following equation, the results are as presented in Table 5. The typical request from the Hanford tank farms is for results that are plus or minus 20% error, while the Resource Conservation and Recovery Act (RCRA) "J" Flag indicates an estimated value.

$$\% \text{Error} = (\text{Absolute}(\text{True value} - \text{Experimental value}) / \text{True Value}) * 100 \quad (4-1)$$

Table 5. Percent Error as a Function of Spike Concentration.

| Acid-Side Extraction | | | | |
|---|--------------------------|----------------------------|---------------|----------------|
| Sample Number | Wash | Matrix | dpm/mL | % Error |
| S13R000491 | NA | Spiked Simulant | 17,447 | NA |
| S13R000497 | NA | TEVA [®] Resin | 14,112 | 19.12 |
| S13R000496 | NA | TEVA [®] Effluent | <2.26 | - |
| S13R000492 | 4M Nitric Acid | Aliquat [®] 336 | 18,521 | 6.16 |
| S13R000493 | 4M Sodium Hydroxide | Aliquat [®] 336 | 17,919 | 2.71 |
| S13R000494 | 4M Nitric Acid | Aliquat [®] 336 | 19,562 | 12.12 |
| S13R000512 | 4M Nitric Acid | 4M Nitric Acid | 177 | 98.98 |
| Base-Side Extraction | | | | |
| Sample Number | Wash | Matrix | dpm/mL | % Error |
| S13R000499 | NA | Spiked Simulant | 17,447 | NA |
| S13R000507 | NA | TEVA [®] Resin | 19,566 | 12.14 |
| S13R000506 | NA | TEVA [®] Effluent | <2.26 | - |
| S13R000503 | 4M Nitric Acid | 4M Nitric Acid | 1,056 | 93.94 |
| S13R000504 | 4M Sodium Hydroxide | 4M Sodium Hydroxide | 7.4 | 99.96 |
| S13R000505 | 4M Nitric Acid | 4M Nitric Acid | 891 | 94.90 |
| S13R000508 | Aliquat [®] 336 | Aliquat [®] 336 | 23,913 | 37.06 |
| S13R000499 Subjected to TEVA[®] and Aliquat[®] 336 | | | | |
| Sample Number | Wash | Matrix | dpm/mL | % Error |
| S13R000511 | NA | Aliquat [®] 336 | 15,074 | 13.60 |
| S13R000511 | NA | TEVA [®] Resin | 16,399 | 6.35 |

Upon inspection of Table 5, several conclusions are readily drawn from the data:

- From the Acid-Side Extraction:
 - The pertechnetate did not readily partition into the acid and base washes, and largely remained with the Aliquat[®] 336.
 - The TEVA[®] Resin did capture pertechnetate, based on the effluent analyses which were below detection limits for technetium-99 by ICP-MS analysis. The higher percent error (19.12) was most probably a function of sampling error.
 - The high percent error associated with sample S13R000512 is merely an indication that a very small amount of pertechnetate was partitioned at the very last wash step.
- From the Base-Side Extraction:
 - The pertechnetate did not readily partition into the acid and base washes, albeit the acid wash was more amenable to partitioning.
 - The TEVA[®] Resin did capture pertechnetate based on the effluent analyses, which were below detection limits for technetium-99 by ICP-MS analysis. The higher percent error (12.14) was most probably a function of sampling error.
 - Sample S13R000508 was the LSC analysis of the Aliquat[®] 336 after all washings. The reason for the high percent error may be due to uncertainty

around the spike recovery (if the spike recovery number is less than the concentration, the sample number will increase), experimental error, operator error, etc.

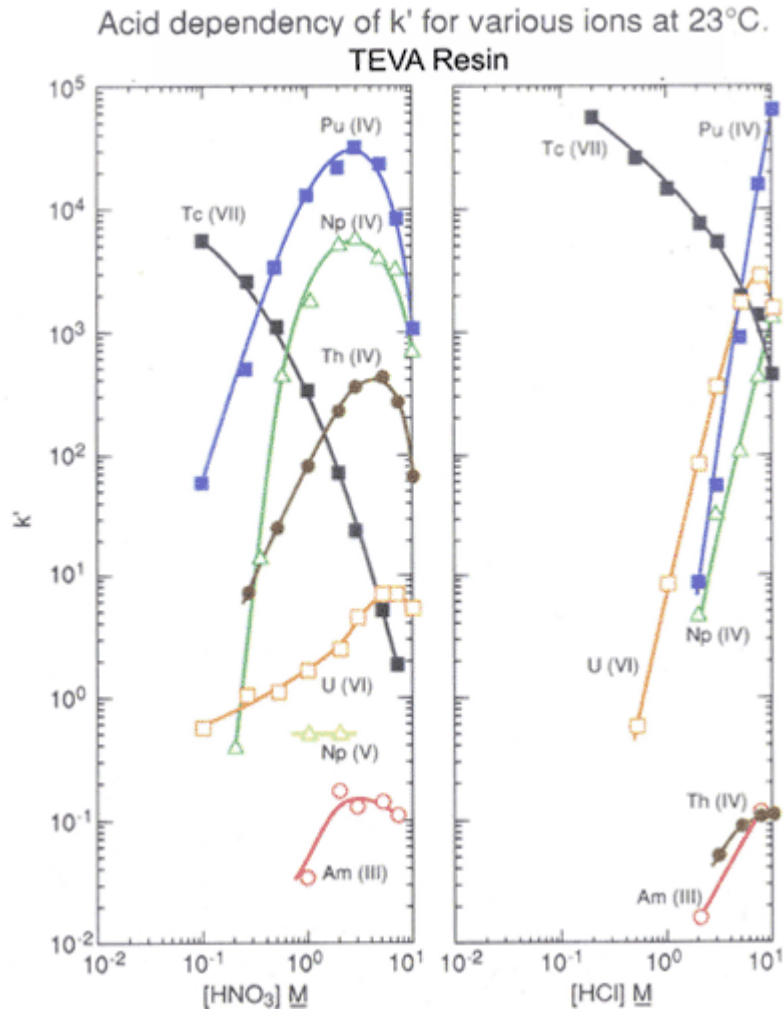
- Sample S13R000511, processed in duplicate and analyzed by both Aliquat[®] 336 and TEVA[®] Resin, yielded 13.60% and 6.35% error, respectively.

It would appear that the TEVA[®] Resin is a candidate for the uptake of pertechnetate; it remains to be determined how non-pertechnetate species will behave in the matrix. Figure 3 is a graph from Eichrom showing pertechnetate being fixed for an acidity range between 0.1 to 1M H⁺; the pertechnetate is eluted from the resin using 8M HNO₃ (TEVA Resin, [Eichrom 2006]).

Another possible candidate for a pertechnetate sorbent is Purolite^{®5} A530E resin. The resin has been shown to have a high specificity for pertechnetate, exhibiting a distribution coefficient of ~1150 at 250 minutes (LAB-RPT-12-00002, *Laboratory Report on the Removal of Pertechnetate from Tank 241-AN-105 Simulant using Purolite A530E*).

⁵ Purolite is a registered trademark of Brotech Corporation, Bala Cynwyd, Pennsylvania.

Figure 3. Acid Dependency of k' for Various Ions at 23 °C on TEVA Resin.¹



¹Eichrom 2006

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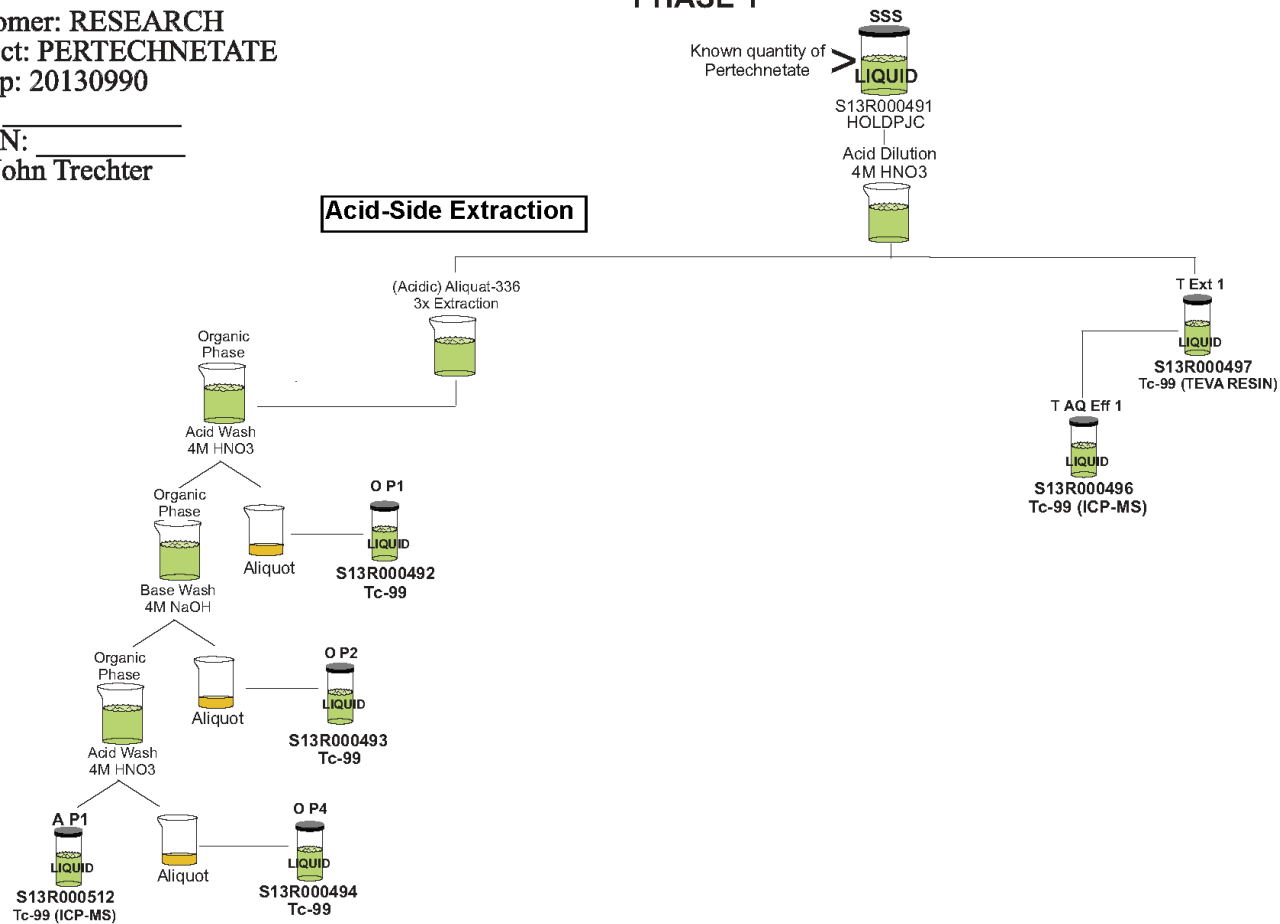
Attachment A

Sample Breakdown Diagrams

PERTECHNETATE AND NON-PERTECHNETATE SPECIES IN HANFORD TANKS PHASE 1

Rev3

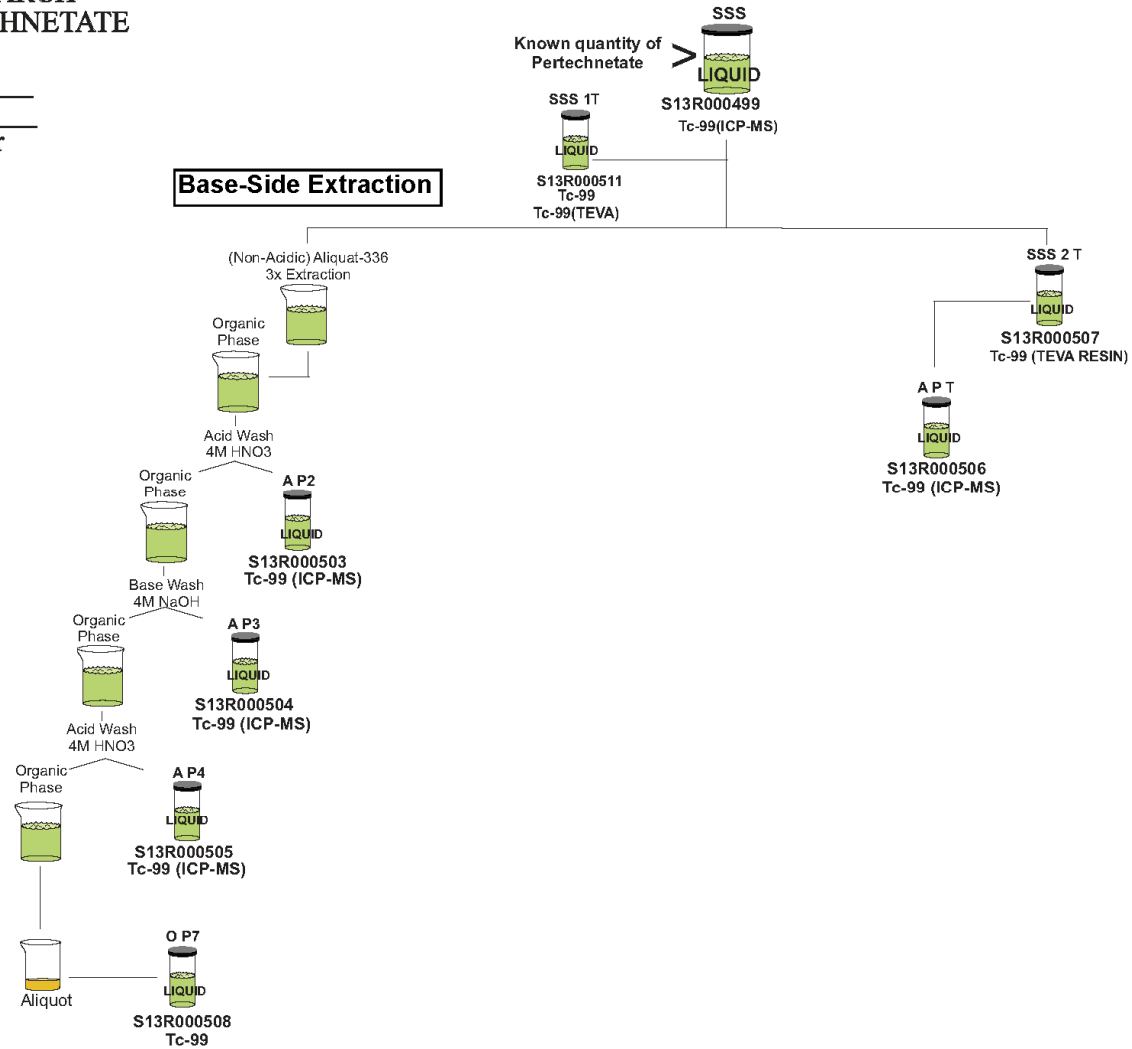
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CACN: _____
PC: John Trechter



**PERTECHNETATE AND NON-PERTECHNETATE SPECIES
IN HANFORD TANKS
PHASE 1**

Rev3

Customer: RESEARCH
Project: PERTECHNETATE
Group: 20130990
Due: _____
CACN: _____
PC: John Trechter



PERTECHNETATE AND NON-PERTECHNETATE SPECIES
IN HANFORD TANKS
PHASE 1

Rev3

Customer: RESEARCH
Project: PERTECHNETATE
Group: 20130990
Due: _____
CACN: _____
PC: John Trechter



ACRONYM KEY

OP-----ORGANIC PHASE
AP-----AQUEOUS PHASE
SSS-----STOCK SIMULANT SOLUTION
T EXT-----TEVA EXTRACTION
T AQ EFF----TEVA AQUEOUS EFFLUENT
BSSS-----BLANK STOCK SIMULANT SOLUTION
T-----TEVA

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