PNWD-3014
BNFL-RPT-020 Rev. 0

Automated ^{99}Tc Analysis in AW-101 and AN-107 "Diluted Feed" Matrixes

OB Egorov
DE Kurath

March 2000

Prepared for BNFL, Inc. under
Project 29953
Battelle, Richland, Washington, 99352

LEGAL NOTICE

This report was prepared by Battelle Memorial Institute (Battelle) as an account of sponsored research activities. Neither Client nor Battelle nor any person acting on behalf of either:

MAKES ANY WARRANTY OR REPRESENTATION, EXPRESS OR IMPLIED, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, process, or composition disclosed in this report may not infringe privately owned rights; or

Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, process, or composition disclosed in this report.

References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by Battelle. The views and opinions of authors expressed herein do not necessarily state or reflect those of Battelle.

SUMMARY

An on-line/at-line monitor is needed by British Nuclear Fuels Limited, Inc (BNFL Inc.) to monitor total ^{99}Tc in column effluents during technetium removal from the aqueous fraction of the Hanford high-level tank wastes. The monitor must achieve detection limits of 1×10^{-8}Ci/mL (0.6 μg/mL). Measurements must be done in near real time, with an analysis frequency of ~15 min or faster. The monitoring technology must be sufficiently simple and robust for unattended operation at the plant settings.

Recent work at Battelle has been directed at the development of the automated, computer-controlled instrumentation and analytical procedures for analyzing several important radionuclides in Hanford nuclear wastes.[a] Automated fluidic instrumentation is used to execute the required chemical separation steps using radionuclide-selective extraction chromatographic resins (Eichrom Industries). The separated radionuclide fractions are delivered to an on-line scintillation detector for quantification. Specifically, Battelle has recently developed an automated ^{99}Tc(VII) analyzer with stopped-flow radiometric detection. Pertechnetate separation was accomplished using TEVA-resin, which selectively retains pertechnetate from low-acidity solutions.[b] Interfering species are not retained and were removed with a short column wash. Separated ^{99}Tc(VII) was eluted using nitric acid solution and delivered to the flow cell of an on-line liquid scintillation detector. To enhance analysis sensitivity, quantification was carried out using stopped-flow detection. The method was validated using diluted AN-107 tank waste samples treated with crystalline silicotitanate for ^{137}Cs removal.

The work contained in this report describes initial scoping studies to determine the applicability of Battelle's automated radiochemical analyzer methodology for ^{99}Tc monitoring in the diluted feed matrixes. An automated radiochemical separation instrument with on-line radiometric detection was assembled and tested. Automated separation procedures for analyzing acidic and caustic samples were tested using on-line radiometric detection. The automated radiochemical analysis method requires that Tc be present in the sample as pertechnetate. Manual sample oxidation procedures to convert all Tc to Tc(VII) were therefore developed and tested. The AW-101 and AN-107 samples were oxidized, and the resulting solutions were analyzed using automated analyzer and inductively coupled plasma-mass spectrometry (ICP-MS) techniques. The analytical results obtained using the radiochemical analyzer technique were in excellent agreement with the total Tc concentrations as determined by ICP-MS. The detection limits that can be achieved using an automated radiochemical analyzer are a factor of 40 below the target detection limit of 1×10^{-8}Ci/mL. Given the development of rapid automated sample-oxidation procedures, automated radiochemical analyzer technology shows promise for developing a relatively straightforward process monitoring instrumentation.

---

[a] J. W. Grate and O. B. Egorov. 1998. "Automating Analytical Separations in Radiochemistry," *Analytical Chemistry* (A-pages report), 70,779A-788A.

[b] Egorov, O., M. J. O'Hara, J. Ruzicka, and J. W. Grate. 1998. "Sequential Injection System with Stopped Flow Radiometric Detection for Automated Analysis of ^{99}Tc in Nuclear Waste," *Analytical Chemistry*, 70, 977-984.

TERMS AND ABBREVIATIONS

BNFL	BNFL, Inc; subsidiary of British Nuclear Fuels, Ltd.
DI	deionized water
dpm	disintegrations per minute
ICP-MS	inductively coupled plasma/mass spectrometry
LS	liquid scintillation
RSD	relative standard deviation
std	standard deviation

CONTENTS

FIGURES

TABLES

1.0 INTRODUCTION

A process monitor is needed by British Nuclear Fuels Limited, Inc. (BNFL Inc.) to measure total ^{99}Tc levels in column effluents during technetium removal from the aqueous fraction of the Hanford high-level tank wastes. The monitor must achieve detection limits of 1×10^{-8}Ci/mL (0.6 μg/mL). Measurements must be done in near real time, with an analysis frequency of ~15 min. The monitoring technology must be sufficiently simple and robust for unattended continuous operation in the plant settings.

Recent work at Battelle has been directed at the development of computer-controlled instrumentation and analytical procedures for automated analysis of several important radionuclides in Hanford nuclear wastes. A separation-optimized sequential injection technique is used to execute required chemical separation steps using various radionuclide-selective extraction chromatographic resins (Eichrom Ind.). The separated radionuclide fractions are delivered to an on-line scintillation detector for quantification. Specifically, Battelle has recently developed an automated ^{99}Tc(VII) analyzer with stopped-flow radiometric detection. Pertechnetate separation was accomplished using TEVA-resin, which selectively retains pertechnetate from low-acidity solutions. Interfering species are not retained and were removed with a short column wash. Separated ^{99}Tc(VII) was eluted using nitric acid solution and delivered to the flow cell of an on-line liquid scintillation detector. To enhance analysis sensitivity, quantification was carried out using stopped-flow detection. The method was validated using diluted AN-107 tank waste samples treated with crystalline silicotitanate for ^{137}Cs and ^{90}Sr removal.

This report contains the results of initial scoping experiments to determine the applicability of the automated radiochemical analyzer methodology for monitoring ^{99}Tc in the diluted feed samples (AW-101 and AN-107). Similar to our previous work in automated radiochemistry (Egorov 1998), the overall approach was based on the sequential execution of the analyte separation and radiometric detection steps using automated fluidic instrumentation. Automated ^{99}Tc(VII) separation from the radioactive interferences and stable matrix was carried out using TEVA-resin (Eichrom). On-line detection of the pertechnetate eluted from the column was carried out using a flow-through scintillation detector. Sample treatment steps to convert all Tc to the pertechnetate form required by the analysis procedure were developed and carried out in a manual format.

The objectives of this study were to:

- assemble and test prototype analyzer instrument; develop and evaluate automated analytical procedures for analyzing ^{99}Tc (VII) in caustic and acidic sample matrixes; evaluate analytical characteristics using tracers and waste simulants
- develop and test manual procedures for sample oxidation
- analyze the oxidized AW-101 and AN-107 samples using an automated technique and compare the analysis results with the baseline ICP-MS data
- develop recommendations and establish needs for the future research (given the feasibility of the automated radiochemical analyzer technique).

2.0 EXPERIMENTAL

2.1 Automated Radiochemical Analysis System

The instrument was set up to perform automated solution handling steps required to separate ^{99}Tc(VII) from the sample matrix and deliver the separated pertechnetate fraction to a flow-through scintillation detector. A schematic diagram of the Tc analyzer system is shown in Figure 2.1. The instrument was configured with two high-precision 24000-step digital syringe pumps (Pump 1 and Pump 2, syringe volume 10 mL) (Alitea USA, Medina, WA), 10-port multiposition Cheminert valve (Valve 1), and two 4-port two-position Cheminert valves (Valve 2 and Valve 3) (Valco Instruments Co, Houston, TX). Pump 1 was used to deliver sample and reagent solutions to the separation column. Pump 2 was used for the cocktail delivery. Multiposition Valve 1 was used to select sample or reagent solution to be delivered to the column. The two-way Valve 2 was used to facilitate the flow reversal through the separation column during the pertechnetate elution step. The two-way Valve 3 was operated as a diverter valve used to direct the column effluents to waste (during column conditioning, sample loading , and column wash steps) or to the flow-through detector during the technetium elution step.

The holding coil was constructed from 1.6 mm i.d. FEP Teflon tubing (Upchurch Scientific, Oak Harbor, WA) of 6 m length (calculated volume 12 mL). All transport and reagent lines were made of 0.8 mm i.d. FEP Teflon tubing (Upchurch Scientific), and the sample inlet was made of 0.5 mm i.d. FEP tubing (Upchurch). The column was 4.6 × 50 mm (calculated volume 0.83 mL), constructed of parts from the OmegaChrom column system (Upchurch Scientific) and frits from the Quick-Snap column system (IsoLab, Inc., Akron, OH).

The purpose of the holding-coil tubing is to accommodate aspirated solutions without their introduction into the syringe. An air segment is used to separate aspirated solutions from the carrier solution. Each solution is aspirated and dispensed before loading and dispensing the next solution. In this manner, the holding coil functions as a zero-dispersion volumetric extension of the syringe, and the syringe contacts only inert carrier solvent. Each solution delivery operation begins by aspirating a 100 μL air segment into the holding coil, followed by aspiration of the required volume of the solution plus an additional 50-μL portion of the same solution. Aspiration steps were performed at an 8 mL/min flow rate. Following the aspiration step, the main line of Valve 1, which contains the holding coil, is connected to the column line, and the solution is dispensed from the holding coil to the separation column (via two-way Valve 2) at a specified flow rate. After the required volume of solution has been dispensed, the main line of the Valve 1 is connected to waste. The remaining 50 μL of the solution and the 100-μL air segment are expelled to waste followed by 200 μL of water carrier. The system is ready for the delivery of the next solution. Specific experimental protocols used in the automated ^{99}Tc analysis are described in the Results and Discussion section of this report (Table 3.1, Table 3.2, Table 3.4, Table 3.5)

2.2 On-line Separation Column

TEVA-resin (Eichrom Industries, Inc.) extraction chromatographic material of particle-size 20 to 50 μm was slurried in DI water and packed into the column using a 5-mL hand-held plastic syringe. The packing syringe was connected to the frit-free column end fitting via the luer adapter.

The pressure was applied to the syringe until the column body was packed and the sorbent bed extended into the syringe.

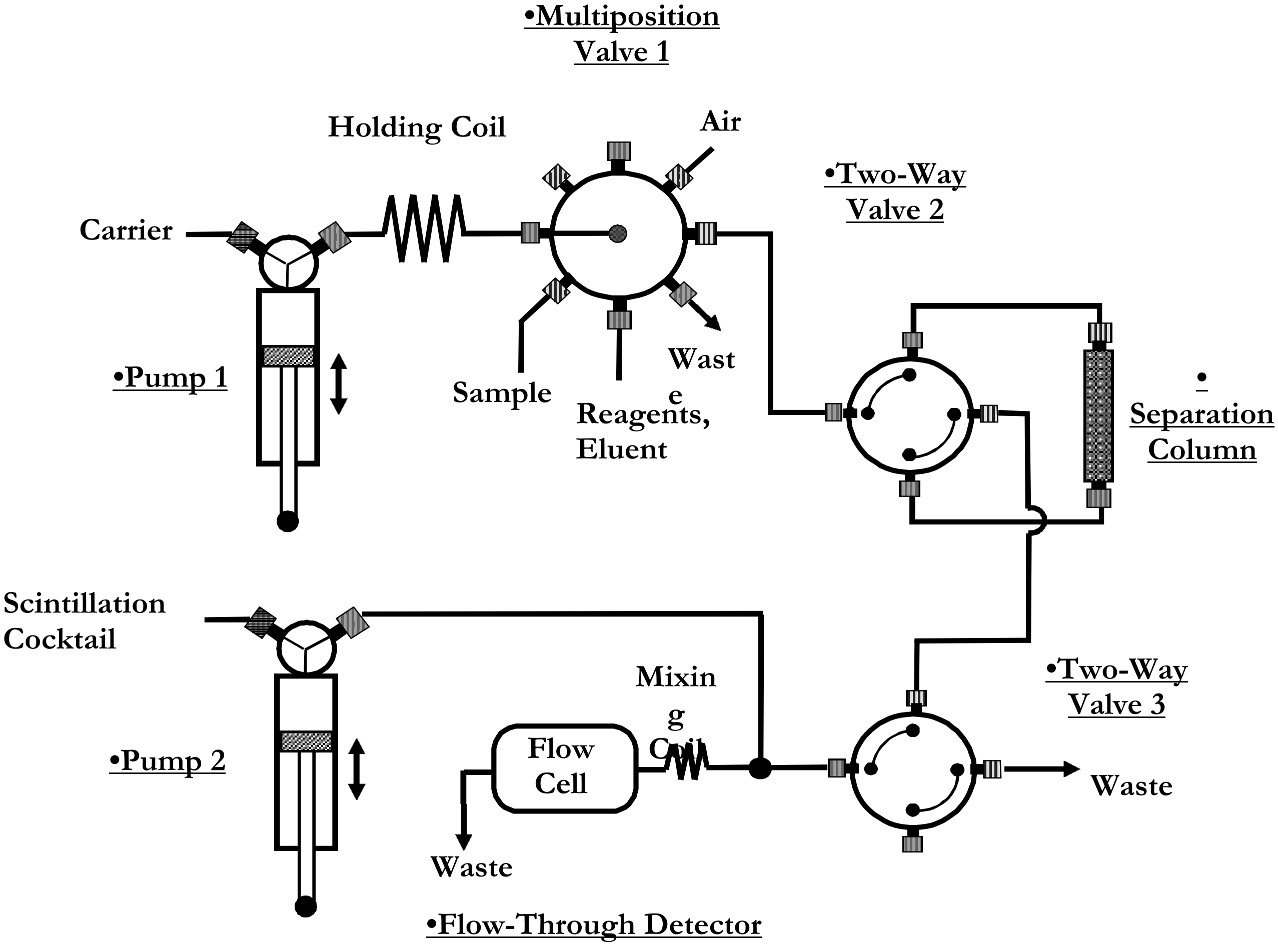


Figure 2.1. Schematic of the Tc Analyzer Instrument

Next, the frit-free end fitting was replaced with the fritted-end fitting. This packing procedure was found reliable and consistently provided uniformly packed void-free columns.

2.3 On-line Detector

The flow-through radioactivity detector was a β-Ram 2B (IN/US Systems, Inc., Tampa, FL) liquid scintillation counter. To improve the accuracy and reliability of the cocktail delivery and to eliminate the need for cocktail pump calibration, a second syringe pump (Pump 2, Figure 2.1) was used to deliver liquid scintillation (LS) cocktail to the mixing tee. A solid scintillator (Li glass) flow cell (void volume 0.5 mL) was evaluated in several initial experiments. A liquid flow cell of 0.5 mL volume was used throughout the rest of this study. In the majority analysis experiments, the cocktail flow rate was 0.5 mL/min, and the eluent flow rate was 2 mL/min (eluent-to-cocktail ratio 2:1).

2.4 Instrumentation Control

Pumps and valves were controlled using RS-232 serial communication protocol. Instrument devices were connected to the laptop PC serial port using a 5-port expandable serial switch (B&B Electronics Ottawa, IL). The software used for manual and automated device control was MicroFluidicLab, beta version. The software code was written in-house in C language using Lab Windows Instrument Development Environment (National Instruments, Austin, TX). The detector was operated by control software (IN/US) running on a separate laptop PC connected to the detector via a serial line. The detector data were acquired directly into the Excel software for data processing. The detection cycle was initiated externally by a TTL signal from the DAQ-516 (National Instruments) PCMCIA card placed in the laptop PC controlling the analyzer instrument.

2.5 Reagents, Standards, Simulants and Samples

All chemical s used were of analytical grade. The DI water was obtained from the MilliQ Plus system (18 mΩ/cm). An Ultima-Flo AP low-viscosity scintillation cocktail was used in all flow-through measurements with the liquid flow cell. The ^{99}Tc(VII) standards and spikes were prepared by diluting the certified traceble standard solution. The activity of the standard was verified by ICP-MS and LS counting measurements.

An AW-101 caustic feed simulant [Na$^+$]~ 5 M was obtained as a ready-to-use solution prepared for the prior IX studies. The actual AW-101 feed sample was an effluent from the Cs IX removal studies. An AN-107 feed sample was the AN-107 Archive Subsample.

The baseline total ^{99}Tc data on the oxidized samples and spiked oxidized samples were obtained using ICP-MS method. Standard analytical procedures and quality-control protocols were used. No correction for potential ^{99}Ru interference was carried out.

2.6 Sample Oxidation Procedures

Several oxidation procedures were evaluated with the objective of rapid conversion of non-pertechnetate species to pertechnetate before the automated separation/analysis procedure. Oxidative sample treatment steps were performed manually in a glass beaker heated on a hot plate. The oxidation procedures tested were **(A)** $KMnO_4$ treatment without acidification (in caustic), **(B)** H_2O_2 treatment without acidification, **(C)** $KMnO_4$ treatment after sample acidification, and **(D)** $Na_2S_2O_8$ treatment after sample acidification.

Procedure (**A**) involved mixing 3 mL of sample solution (AW-101 simulant) with 1 mL of saturated $KMnO_4$ solution in water, heating to near boiling, and filtration. Heating and filtration steps were carried out several times until the solution was colorless (free of K_2MnO_4). Procedure **B)** involved mixing 1 mL of the sample solution (AW-101 simulant) with 1 mL of 30% solution of

H_2O_2. The mixture was heated for several minutes until the effervescence ceased. Oxidation procedure **(C)**, using $KMnO_4$ treatment of the acidified sample, is summarized in Table 2.1.

Oxidation procedures using persulfate are summarized in Table 2.2 and Table 2.3 for AW-101 and AN-107 samples, respectively.

Table 2.1 Oxidation Procedure Using $KMnO_4$ Treatment with Sample Acidification

Step	**Solution/Reagent**
1	5 mL sample
2	3.25 mL 8 M HNO_3
3	2 mL sat $KMnO_4$
4	0.25 mL 30% H_2O_2
5	7 mL DI water
6	1 mL 2M NaOH
Sample Dilution Factor: 3.7	

Table 2.2 Oxidation Procedure Using $Na_2S_2O_8$ Treatment with Sample Acidification for the AW-101 sample

Step	**Solution/Reagent**
1	5 mL sample
2	3.25 mL 8 M HNO_3
3	3 mL 2 M $Na_2S_2O_8$
4	6.25 mL DI water
5	3.75 mL 2M NaOH
Sample Dilution Factor: 4.3	

Table 2.3 Oxidation Procedure Using $Na_2S_2O_8$ Treatment with Sample Acidification for the AN-107 Sample

Step	**Solution/Reagent**
1	5 mL sample
2	1.63 mL 8 M HNO_3
3	3 mL 2 M $Na_2S_2O_8$
4	6. mL DI water
5	8 mL 2M NaOH
Sample Dilution Factor: 4.7	

3.0 RESULTS AND DISCUSSION

3.1 Optimization of the Tc(VII) On-line Quantification. Separation from the Alkaline Sample Matrixes.

Initial experiments were directed at verifying an automated experimental set up. These experiments were conducted using ^{99}Tc(VII) standards in 0.2 M nitric acid as the sample and using the simplified experimental procedure described in Table 3.1. On-line detection was performed using a liquid flow cell. The cocktail flow rate was 0.5 mL/min. Six molar nitric acid was used as the eluent that compromises between Tc(VII) elution speed and provides an acceptable degree of quenching with on-line liquid scintillation detection. It was found that flow reversal during the Tc elution step resulted in more rapid Tc elution and sharper elution peaks. Typical elution profiles for the analysis of the ^{99}Tc(VII) standard with and without flow reversal are shown in Figure 3.1. With the flow reversal, the volume of Tc elution peak using 6 M HNO_3 was under 1 mL. On this basis, flow reversal during Tc elution was used in all subsequent experiments. Overall analysis efficiency (detection efficiency times separation recovery) was estimated to be 34±3% (±2 std). The detection limit of the radiometric detection procedure estimated as 3 std of the blank was 2.2×10^{-7} Ci/L. This value is a factor of 40 lower than required detection limit of 1×10^{-5} Ci/L.

Table 3.1. Analysis Procedure Used in the Initial Tc Elution/Detection Experiments (dilute acid sample matrix)

	Description	Reagent	Volume, mL	Flow Rate, mL/min
1.	Column conditioning	0.2 M HNO_3	3	3
2.	Sample load	^{99}Tc(VII) standard in 0.2 M HNO_3	0.5	3
3.	Column wash	0.2 M HNO_3	5	3
4.	Tc elution	6 M HNO_3	5	1

Experiments were conducted to evaluate the feasibility of ^{99}Tc(VII) separation and analysis from caustic sample matrixes. These experiments were performed using the ^{99}Tc(VII) standard in 2 M NaOH. The automated procedure developed for the analysis of caustic samples is given in Table 3.2. To speed up the analysis procedure involving multiple wash solutions, the flow rate during most of the column wash steps was increased to 5 mL/min. Sample loading was accomplished at 3 mL/min.

Using experimental conditions given in Table 3.2, the analysis efficiency for the ^{99}Tc(VII) standard in 2 M NaOH was found to be 33±3%. This is in excellent agreement with the efficiency obtained in the prior experiments using dilute acid sample matrix and slower flow rates (Table 3.1). In addition, both the position and shape of the Tc elution peaks remained unchanged relative to the separation experiments using acidic sample matrixes. On this basis, Tc(VII) separation can be accomplished directly from the caustic sample matrixes and using high flow rates (5 mL/min).

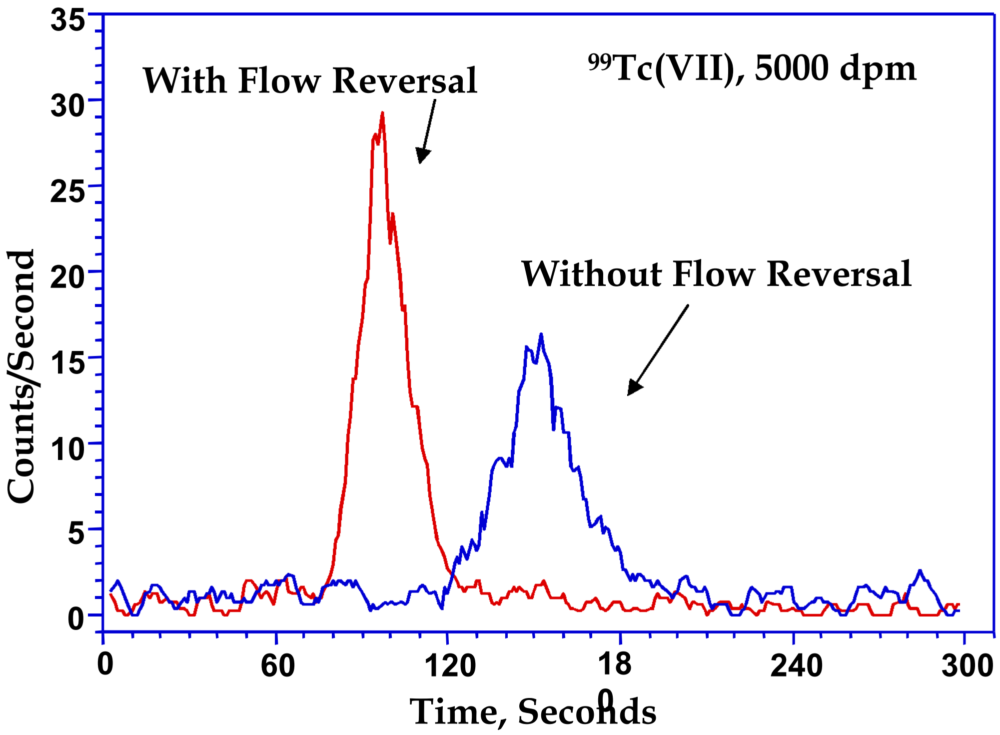


Figure 3.1. Tc Elution Profiles With and Without Flow Reversal. Eluent flow rate 1 mL/min. Cocktail flow rate 0.5 mL/min.

Table 3.2. Analysis Procedure for Caustic Sample Matrixes

	Description	Reagent	Volume, mL	Flow Rate, mL/min
1.	Column conditioning	2 M NaOH	3	5
2.	Sample load	^{99}Tc(VII) standard in 2 M NaOH	0.5	3
3.	Basic wash 1	2 M NaOH	1.5	3
4.	Basic wash 2	2 M NaOH	1	5
5.	Water wash 1	DI water	3	5
6.	Acid wash	0.2 M HNO_3	5	5
7.	Tc elution	6 M HNO_3	5	1 or 2
8.	Water wash 2	DI water	3	5

In subsequent experiments, on-line detection was evaluated using both solid scintillator and liquid flow cells. With the liquid cell, effects of the eluent flow rate and eluent-to-cocktail ratios on Tc quantification were examined. Experiments were conducted using the experimental procedure given in Table 3.2. Experimental results are summarized in Table 3.3. The experimental errors are given as propagated counting errors (±2 sigma). Analysis efficiency is assumed to be equal to detection efficiency (100% separation recovery). Detection limits are estimated as 3 sigma counting error of the blank run, assuming 0.5 mL sample volume

Table 3.3 Results of the Detection Optimization Experiments

Flow Cell	Eluent Flow Rate, mL/min	Cocktail Flow Rate, mL/min	Net Counts	Background, cpm	Residence Time, min	Efficiency, %	Detection Limit, Ci/L
solid	1	NA	2105±92	624±50	0.5	84±4	2.4×10^{-7}
liquid	1	1	581±48	50±14	0.25	46±4	2.0×10^{-7}
liquid	1	0.5	565±48	56±14	0.33	34±4	2.2×10^{-7}
liquid	2	1	356±38	57±15	0.17	43±5	3.7×10^{-7}
liquid	2	0.5	373±39	35±12	0.2	37±4	2.3×10^{-7}

A solid scintillator cell eliminates the need for the cocktail and eliminates mixed acidic/organic waste. In addition, it provides high detection efficiency for ^{99}Tc. Nevertheless, observed background levels with solid cell were unusually high. Furthermore, a 0.5-mL void volume solid cell provided significant back pressure; elution flow rates exceeding 1 mL/min were not possible with low pressure syringe pumps used in this study. In addition, solid cells can be subject to cross contamination, plugging, and detection efficiency degradation due to exposure to corrosive chemicals. Also, once exposed to light (i.e., during replacement), solid flow cells must be stored in dark for over 12 h to eliminate high backgrounds due to light-induced fluorescence.

Liquid flow cells require LS cocktail and generally have lower detection efficiency relative to the solid cells. Nevertheless, liquid cells are more robust and are not subjected to cross-contamination, plugging, and long-term performance degradation. Moreover, using 2 mL/min eluent and 0.5 mL/min cocktail flow rate Tc quantification can be accomplished rapidly. The detection step is complete in 2 min. The cocktail consumption is only 1 mL per analysis. Despite high flow rates and low cocktail-to-eluent ratios, no significant reduction in analysis sensitivity was observed (see Table 3.3). On this basis, all subsequent experiments in this study were performed with liquid flow cell using a 2 mL/min eluent flow rate and 0.5 mL/min LS cocktail flow rate.

In summary, we established that pertechnetate separation on TEVA-resin is possible directly from caustic sample matrix without the need for sample acidification. High flow rates can be used during column wash steps. Flow reversal during elution results in improved elution performance. On-line detection of the separated pertechnetate can be accomplished rapidly. The use of the liquid flow cell is generally preferred over the solid cell. On-line radiometric detection exceeds the detection-limit requirements (factor of ~40 lower than the target value). The LS cocktail consumption when using liquid flow cell for on-line detection can be as low as 1 mL per analysis.

3.2 Analysis of the Caustic AW-101 Simulant

An AW-101 simulant was treated using $KMnO_4$ oxidative treatment without sample acidification as described in the Experimental section. The resulting solutions were spiked with ^{99}Tc(VII) standard. Three spiked solutions were prepared with a ^{99}Tc(VII) content of 5,110 dpm/mL, 9794 dpm/mL, and 19,834 dpm/mL. Note that the detection-limit requirement of 1×10^{-5} Ci/L corresponds to the sample activity of 22,200 dpm/mL.

Caustic-spiked simulants were analyzed according to the experimental procedure given in Table 3.4. Note that HF was incorporated into the dilute nitric acid wash at this time. The use of HF complexant in the column wash results in efficient removal of any retained tetravalent actinides (e.g., Pu). The sample volume was 1 mL.

The samples were analyzed in duplicates, which were sandwiched between blank runs. The highest activity sample was analyzed in triplicate to evaluate the analysis reproducibility. To speed up the experimentation, the blank runs involved an abbreviated analysis procedure, which consisted of steps 6 through 8 in Table 3.4. Two approaches were used to calculate the count rate of the eluted ^{99}Tc(VII). In one approach, the net peak counts were calculated as the difference in the sum of counts between the analysis run and the blank run. In another approach, which is more suitable for on-line applications, the net counts were calculated by subtracting the baseline, which was established by summing counts before and after the Tc elution peak. Both methods yielded results indistinguishable within the counting errors. The later approach was adopted for data processing in all subsequent experiments.

The sample peak integral count rate gave a linear calibration curve when plotted against the sample activity (Figure 3.2). The slope of the calibration line corresponded to the 33% analysis efficiency. The average analysis efficiency of 7 runs was 33±2 %. These values are in good agreement with the results of the previous experiments using ^{99}Tc(VII) standards in 2 M NaOH. These results indicate that analysis is not affected by the complex sample matrix. Figure 3.3 shows Tc elution peaks for triplicate analyses of the highest activity sample. These data illustrate the reproducibility of an automated analysis technique. The relative standard deviation for the triplicate analyses of 19,834 dpm/mL sample was 4%.

Table 3.4. Procedure Used in the Analysis of the Spiked Treated AW-101 Simulant

	Description	Reagent	Volume, mL	Flow Rate, mL/min
1.	Column conditioning	2 M NaOH	3	5
2.	Sample load	AW-101 simulant spiked with ^{99}Tc(VII)	1	3
3.	Basic wash 1	2 M NaOH	1.5	3
4.	Basic wash 2	2 M NaOH	1	5
5.	Water wash 1	DI water	2	5
6.	Acid wash	0.2 M HNO_3-0.2 M HF	5	5
7.	Tc elution [1,2]	6 M HNO_3	5	2
8.	Water wash 2	DI water	3	5

[1] Detection cycle started simultaneously with the beginning of the Tc elution step.

[2] Cocktail flow rate 0.5 mL/min. Only the first 4 mL of the Tc eluent were mixed with cocktail for on-line detection.

3.3 Oxidative Treatments Using $KMnO_4$ in Caustic and Acidified Samples

When $KMnO_4$ was added to the caustic simulant and AW-101 sample, the solution was instantaneously turning green, indicating formation of K_2MnO_4 and incomplete reduction of $KMnO_4$. The MnO_2 formation was observed only with prolonged heating at near boiling temperatures. We speculate that these observations can be attributed to the copious amounts of nitrite present in the caustic samples. The nitrite would consume the oxidizer to be oxidized to NO_3^- (oxidation potential E=-0.01 V, with reaction favored in basic media). To enhance the effectiveness of the oxidative treatment, it was decided to perform sample acidification before oxidation.

The total base content (amount of acid necessary to make the sample solution neutral) was estimated by titration using phenolpthtalein as an indicator. The total base content for the AW 101 simulant and AW 101 samples was estimated to be 2.5 M and 2.8 M, respectively. A sample acidification/oxidation procedure was developed (see Table 2.1) and tested. When 8 M nitric acid was added to the sample, extensive foaming and NO_2 evolution was observed, but subsided rapidly. Formation of white precipitate (presumably $Al(OH)_3$) was evident. However, the precipitate was readily dissolved upon brief heating. When aliquots (1 mL) of $KMnO_4$ were added to the heated solution, immediate formation of an MnO_2 precipitate was observed. Amounts of $KMnO_4$ used in the oxidation procedure were in excess. A pink color persisted upon adding the last $KMnO_4$ aliquot.

The addition of 30% H_20_2 resulted in complete and rapid dissolution of the MnO_2 precipitate, and the resulting solution was clear. Formation of small quantities of $Al(OH)_3$ precipitate was evident when NaOH was added to reduce the solution acidity. Acidity of the samples after acidification/oxidation was determined by titration. The acidity was estimated to be ~0.5 M [H^+] for both simulant and the actual waste sample. Resulting sample solutions were filtered using 0. 45-µm filter before analysis.

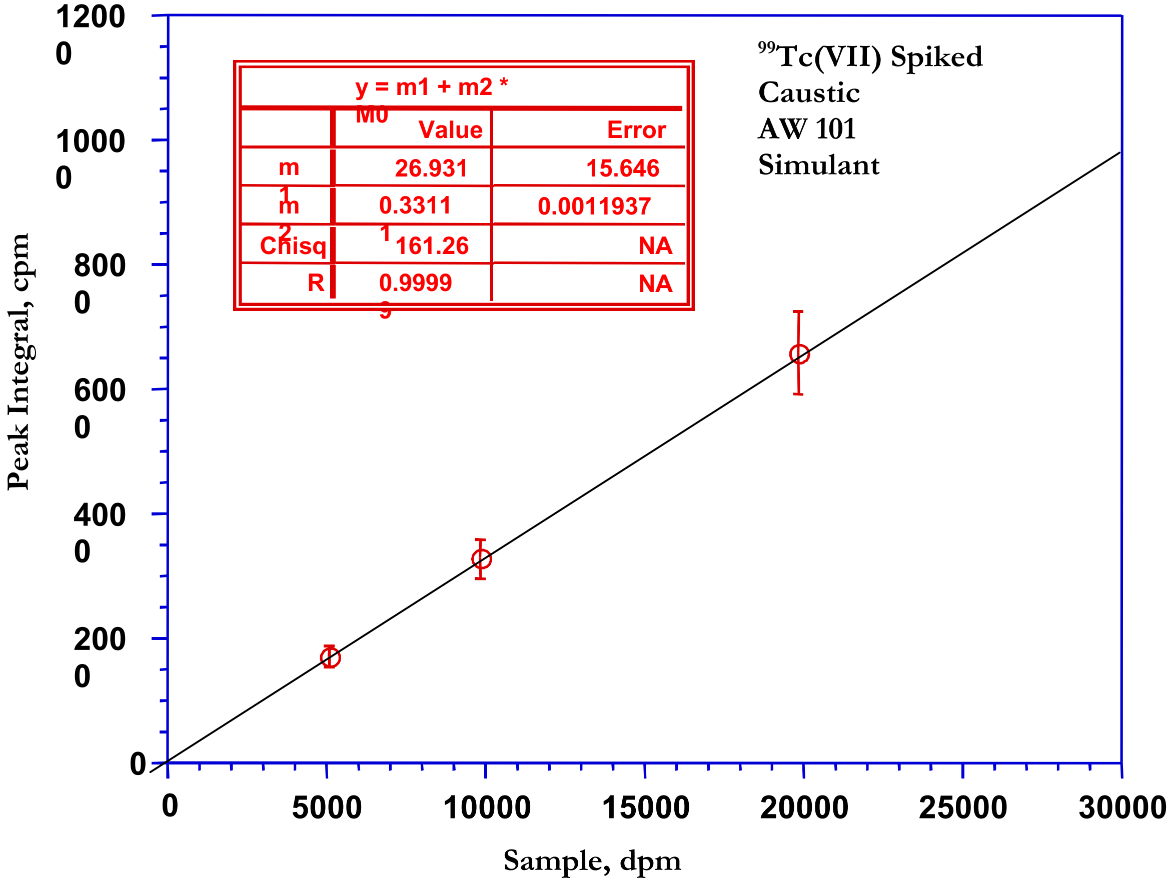


Figure 3.2. Calibration Plot for Analyzing Spiked Caustic Simulant

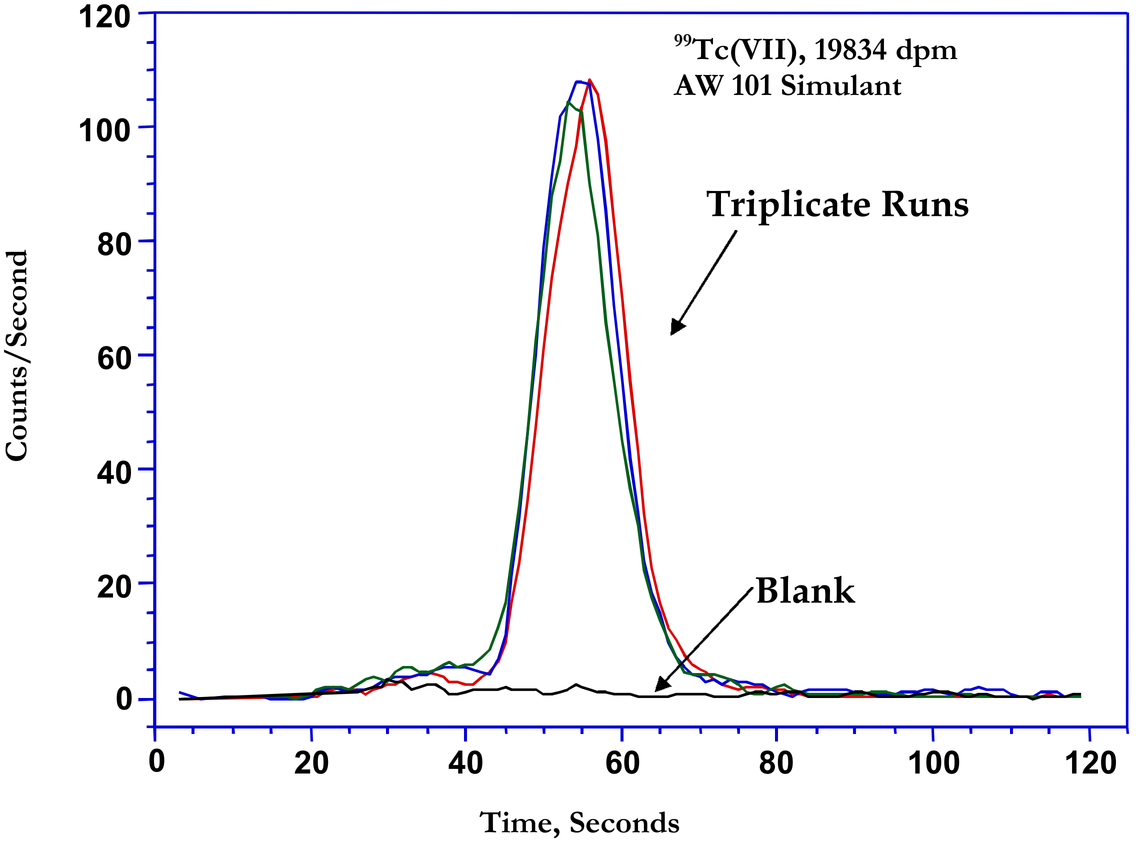


Figure 3.3. Detector Traces Corresponding to Triplicate Analyses of the Spiked Caustic Simulant. Eluent flow rate 2 mL/min. Cocktail flow rate 0.5 mL/min.

3.4 Analysis of the Acidified AW-101 Simulant Treated with $KMnO_4$

The AW-101 simulant was acidified and treated using the $KMnO_4$ oxidation procedure as described in the previous section. Resulting solutions were spiked with known amounts of ^{99}Tc(VII). Four samples were prepared. The ^{99}Tc(VII) activities were 1378 dpm/mL, 2757 dpm/mL, 5502 dpm/mL, and 10960 dpm/mL) (detection limit requirement of 1×10^{-5} Ci/L corresponds to the sample activity of 22200 dpm/mL).

Spiked acidic simulants were analyzed according to the experimental procedure given in Table 3.5. The sample volume was 1.75 mL. Each sample analysis was performed in triplicate. Blank runs were performed after analysis of each sample set.

Table 3.5. Experimental Procedure Used in Analyzing the Spiked AW-101 Simulant with Acidification and $KMnO_4$ Treatment

	Description	Reagent	Volume, mL	Flow Rate, mL/min
1.	Column conditioning	0.2 M HNO_3-0.2 M HF	3	5
2.	Sample load	AW-101 simulant spiked with ^{99}Tc(VII)	1.75	3
3.	Acid wash 1	0.2 M HNO_3-0.2 M HF	1	3
6.	Acid wash 2	0.2 M HNO_3-0.2 M HF	9	3
7.	Tc elution [1,2]	6 M HNO_3	5	2
8.	Water wash 2	DI water	3	5

[1] Detection cycle started simultaneously with the beginning of the Tc elution step.

[2] Cocktail flow rate 0.5 mL/min. Only the first 4 mL of the Tc eluent were mixed with cocktail for on-line detection.

The highest activity sample was analyzed 7 times to evaluate the reproducibility. The relative standard deviation of the peak area for the seven measurements was 4%. The sample peak integral count rate gave a linear calibration curve when plotted against the sample activity (Figure 3.4). The slope of the calibration line corresponded to the analysis efficiency of 33%. This is in excellent agreement with the analysis efficiency obtained in the prior experiments.

3.5 Analysis of the acidified AW-101 sample treated with permanganate

The AW-101 sample was prepared by acidification and by using the $KMnO_4$ oxidation procedure. An aliquot of the treated sample was spiked with a known amount of ^{99}Tc(VII) (3.89×10^4 dpm/mL). The sample and the spiked sample were analyzed by ICP-MS to obtain the baseline validation data. Sample solutions were analyzed in parallel by an automated analyzer instrument using the analytical procedure described in Table 3.5. The sample volume was 0.5 mL.

The analytical data for Tc content in the sample were obtained using standard addition methodology. The analysis results obtained by ICP-MS and automated radiochemical analyzer results are compared in Table 3.6 and are in good agreement.

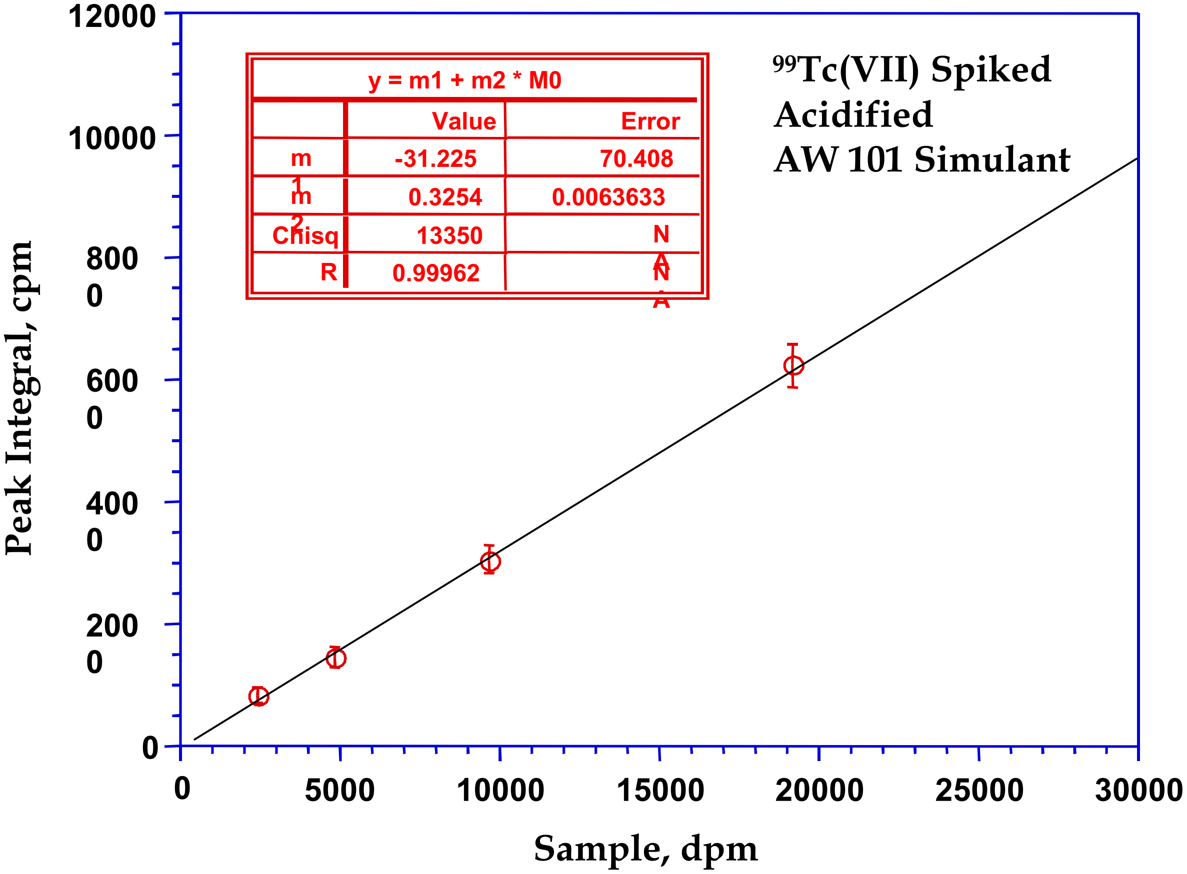


Figure 3.4. Calibration Plot for Analyzing Spiked Acidified Simulant Treated with $KMnO_4$

Table 3.6. Method Validation Using Acidified AW-101 Sample Treated with $KMnO_4$

Sample ID	Description	ICP-MS, ^{99}Tc ppm	Radiometric Monitor, ^{99}Tc ppm[1]
AIR-P-TR	Processed AW-101 sample	1.323±0.062	1.36±0.05 (1.13±0.05)
AIR-P-TR-S	Spiked processed AW-101 sample	2.381±0.013	(1.96±0.05)

[1] Obtained using standard addition approach. The results in parenthesis were obtained using 33% analysis efficiency from the analyzer calibration. Sample volume 0.5 mL.
1 ppm=629 Bq/mL= 1.7×10^{-5} Ci/L

3.6 Persulfate Treatment of the Acidified AW-101 and AN-107 Samples

When the $KMnO_4$ treatment was applied to the AN-107 sample, the amount of $KMnO_4$ necessary to obtain reagent excess (pink color persists upon addition of the next aliquot of the oxidizing reagent) was approximately 6 times higher relative to the AW-101 sample. This resulted in the formation of copious quantities of MnO_2 precipitate. Large quantities of MnO_2 rendered this approach impractical.

To avoid this problem, a persulfate treatment was developed and tested with AW-101 and AN-107 samples (see Table 2.2 and Table 2.3 in Experimental section). No precipitate formation was evident when the persulfate treatment was applied to AN-107 and AW 101 samples; the filtration step was unnecessary. The acidity of the final solutions determined by titration was ~0.4 M $[H^+]$ for both types of samples.

3.7 Analysis of Acidified AW-101 and AN-107 Samples Using Persulfate Treatment

The AW-101 and AN-107 analytical samples were prepared by acidifying the diluted feed samples and using $Na_2S_2O_8$ oxidation procedures (Table 2.2-2.3). An aliquot of the treated sample was spiked with a known amount of ^{99}Tc(VII) (40,000 dpm/mL). The sample and spiked sample were analyzed by ICP-MS to obtain the baseline total ^{99}Tc data. Sample solutions were analyzed in parallel with an automated analyzer instrument. The analysis was performed using procedure described in Table 3.5. The sample volume was 0.25 mL. The analysis runs were performed in triplicate. Blank run was performed after triplicate analyses of each sample set. Analytical data for the ^{99}Tc content in the sample was obtained using standard addition methodology. Blank runs revealed no detectable carryover, indicating effective Tc removal during elution step. The analysis results obtained by ICP-MS and automated radiochemical analyzer results are compared in Table 3.7 and are in excellent agreement.

The overall analysis efficiency estimated from the standard addition data for the analysis of AW-101 and AN-107 samples was 34% and 30% respectively. These values are in good agreement with the analysis efficiency obtained in prior calibration experiments.

Table 3. 7. Method Validation Using Acidified AW-101 and AN-107 Samples Treated with $Na_2S_2O_8$

Sample ID	Description	ICP-MS, ^{99}Tc ppm	Radiometric Monitor, ^{99}Tc ppm[1]
AIR-PS-TR	processed AW-101 sample	1.66±0.17	1.65±0.05 (1.53±0.05)
AIR-PS-TR-S	spiked processed AW-101 sample	2.79±0.28	NA (2.57±0.13)
AN-107-PS-TR	processed AN-107 sample	0.706±0.07	0.610±0.06 (0.625±0.06)
AN-107-PS-TR-S	spiked processed AN-107 sample	1.81±0.18	NA (1.82±0.05)

[1] Obtained using standard addition approach. Results in parenthesis were obtained using 33% analysis efficiency from the previous analyzer calibration. Sample volume 0.25 mL.
1 ppm=629 Bq/mL= 1.7×10^{-5} Ci/L

In separate experiments, analyses of the AN-107-PS-TR sample were performed using sample volumes of 0.25 mL, 1 mL, and 7 mL. The analysis efficiency relative to the procedure using a 0.25-mL sample volume was 80% for 1-mL sample volume and 70% when using a 7-mL sample volume. These results indicate that sample preconcentration is possible. However, the analyte recovery is reduced when larger sample volumes are used in the analysis. The tradeoffs between larger sample volumes and smaller dilution factors during sample preparation (more concentrated sample matrix) remain to be investigated.

3.8 Separation Column Life

In the current study, no column degradation was evident after 35 analysis cycles. Longer term column stability using persulfate-containing samples remains to be evaluated. We have previously demonstrated that the column life of extraction chromatographic materials can be significantly improved using a column wash reagent pre-saturated with the organic extractant (Grate 1999). Automated column switching procedures were also demonstrated in our previous work (Grate 1999).

4.0 CONCLUSIONS AND RECOMMENDATIONS

- The radiometric detection approach is sufficiently sensitive for ^{99}Tc monitoring in column effluents. The detection limit of the automated analysis system is ~2.5×10^{-7} Ci/L.

- Using a liquid cell for on-line quantification is preferred over a solid scintillator cell. Using a liquid cell, the on-line quantification step can be accomplished rapidly using only 1 mL of the cocktail.

- The automated separation of Tc(VII) using TEVA-resin can be accomplished using both dilute acid and caustic sample matrixes.

- Flow reversal during the elution step improves the effectiveness of the Tc(VII) elution using 6 M nitric acid.

- Sample acidification was found to be necessary before sample oxidation. Potassium permanganate and persulfate oxidative treatments were effective in converting Tc to Tc(VII) in the envelope A samples.

- Persulfate treatment was effective in converting Tc species to Tc(VII) in the envelope C samples and eliminated the problem of excessive solids formation observed when using the $KMnO_4$ treatment.

- The results for the analysis of total ^{99}Tc in Envelop A and C samples obtained using an automated radiochemical analyzer were in excellent agreement with the baseline ICP-MS method.

- Analysis efficiency obtained by the standard addition technique (33%) in the analysis of actual samples was in good agreement with the analysis efficiency obtained in the instrument calibration experiments.

- The automated radiochemical analysis procedure has good reproducibility (better than 6% RSD). Separation columns can be reused multiple times without fouling and degradation.

- The automated radiochemical analyzer approach (automated separation/detection) shows promise for the development of the ^{99}Tc process monitor.

- The feasibility of a rapid automated sample oxidation procedure remains to be investigated.

..

5.0 REFERENCES

Egorov, O., M. J. O'Hara, J. Ruzicka, and J. W. Grate. 1998. "Sequential Injection System with Stopped Flow Radiometric Detection for Automated Analysis of ^{99}Tc in Nuclear Waste," *Analytical Chemistry*, 70, 977-984.

Grate, J. W., S. K. Fadeff, and O. Egorov. 1999. "Separation-Optimized Sequential Injection Method for Rapid Automated Separation and Determination of ^{90}Sr in Nuclear Waste," *Analyst,* 124, 203-210.

Appendix A

Poster Presentation Given to BNFL Inc.

APPENDIX A

Poster presentation given to BNFL Inc. representatives during the Laboratory tour on November 10, 1999.

Development of the Automated ^{99}Tc Monitor

Oleg Egorov
Environmental Molecular Sciences Laboratory
Pacific Northwest National Laboratory
Richland, WA 99352

PROJECT OBJECTIVE

- **Investigate the feasibility of automated ^{99}Tc analysis using sequential injection radiometric analyzer methodology**
- **Validate automated analyzer method in the analysis of AW-101 (Envelope A) and AN-107(Envelope C) samples**

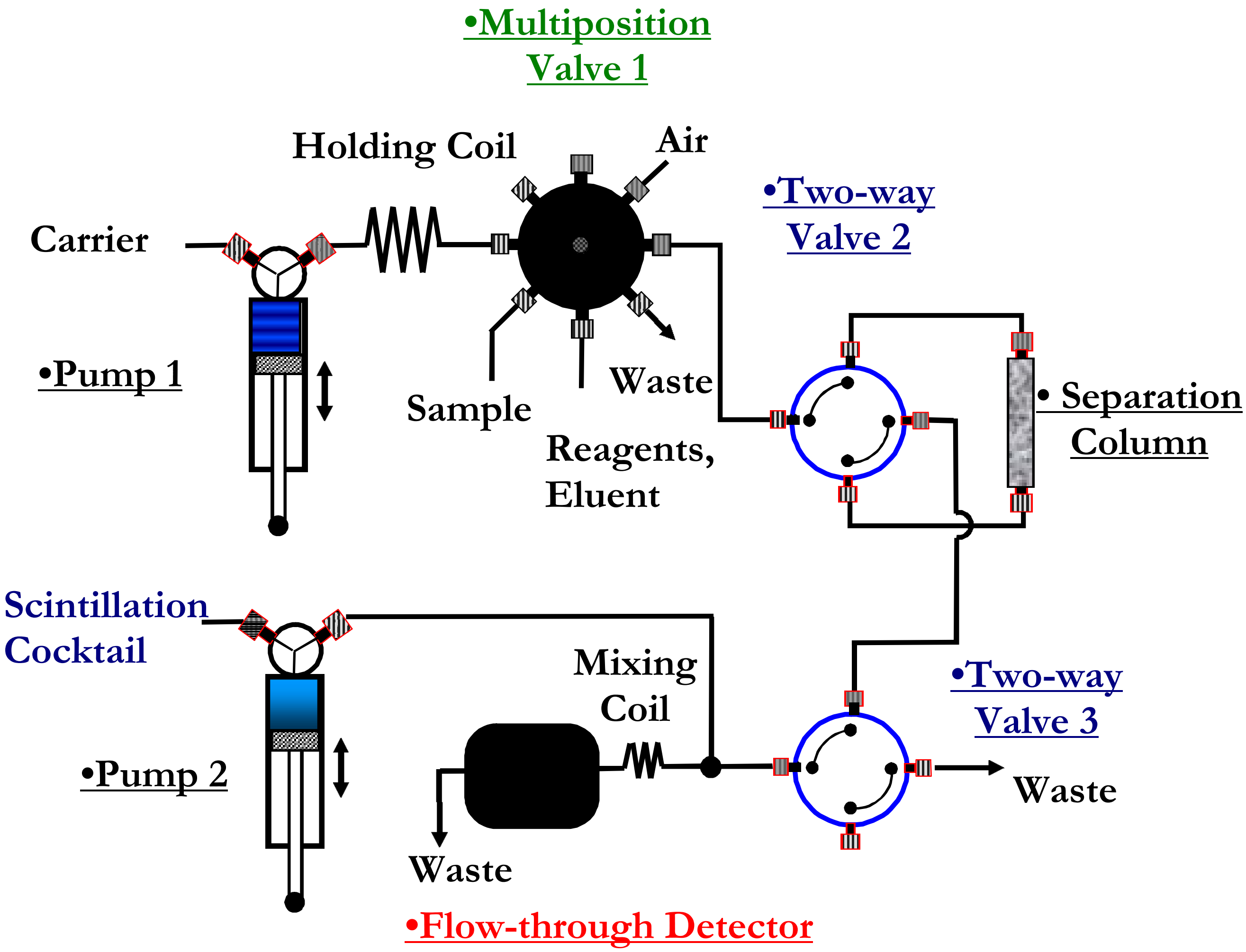
APROACH

- **Automated fluidics for solution handling**
- **Tc(VII) separation using on-line TEVA-resin column**
- **On-line radiometric detection (flow-through scintillation counter)**

ISSUES

- **Automated instrumentation**
- **Sensitivity of the on-line detection**
- **Separation of the caustic samples**
- **Effect of the complex sample matrixes**
    - **recovery, reproducibility, column reuse**
- **Sample oxidation for total Tc measurements (currently done in the manual format)**
- **Comparison with the baseline method (ICP-MS) for the analysis of AW-101 and AN-107 samples**
- **Future directions (if methodology is proven feasible)**

ANALYZER INSTRUMENT DESIGN



OXIDATION PROCEDURES

- ***Oxidation procedure using $KMnO_4$ treatment with sample acidification***

Step	Solution/Reagent
1	5 mL sample
2	3.25 mL 8 M HNO_3
3	2 mL sat $KMnO_4$
4	0.25 mL 30% H_2O_2
5	7 mL DI water
6	1 mL 2M NaOH
sample dilution factor: 3.7	

- ***Oxidation procedure using $Na_2S_2O_8$ treatment with sample acidification for AW101 sample.***

Step	Solution/Reagent
1	5 mL sample
2	3.25 mL 8 M HNO_3
3	3 mL 2 M $Na_2S_2O_8$
4	6.25 mL DI water
5	3.75 mL 2M NaOH
sample dilution factor: 4.3	

- ***Oxidation procedure using $Na_2S_2O_8$ treatment with sample acidification for AN107 sample.***

Step	Solution/Reagent
1	5 mL sample
2	1.63 mL 8 M HNO_3
3	3 mL 2 M $Na_2S_2O_8$
4	6. mL DI water
5	8 mL 2M NaOH
sample dilution factor: 4.7	

AUTOMATED ANALYSIS PROCEDURES

Caustic Sample

	Description	Reagent	Volume, mL	Flow rate, mL/min
1.	Column conditioning	2 M NaOH	3	5
2.	Sample load	AW101 simulant spiked with ^{99}Tc(VII)	1	3
3.	Basic wash 1	2 M NaOH	1.5	3
4.	Basic wash 2	2 M NaOH	1	5
5.	Water wash 1	DI water	2	5
6.	Acid wash	0.2 M HNO_3-0.2 M HF	5	5
7.	Tc elution [1,2]	6 M HNO_3	5	2
8.	Water wash 2	DI water	3	5

[1] Detection cycle started simultaneously with the beginning of the Tc elution step.

[2] Cocktail flow rate 0.5 mL/min. Only the first 4 mL of the Tc eluent were mixed with cocktail for on-line detection.

Acidified Sample

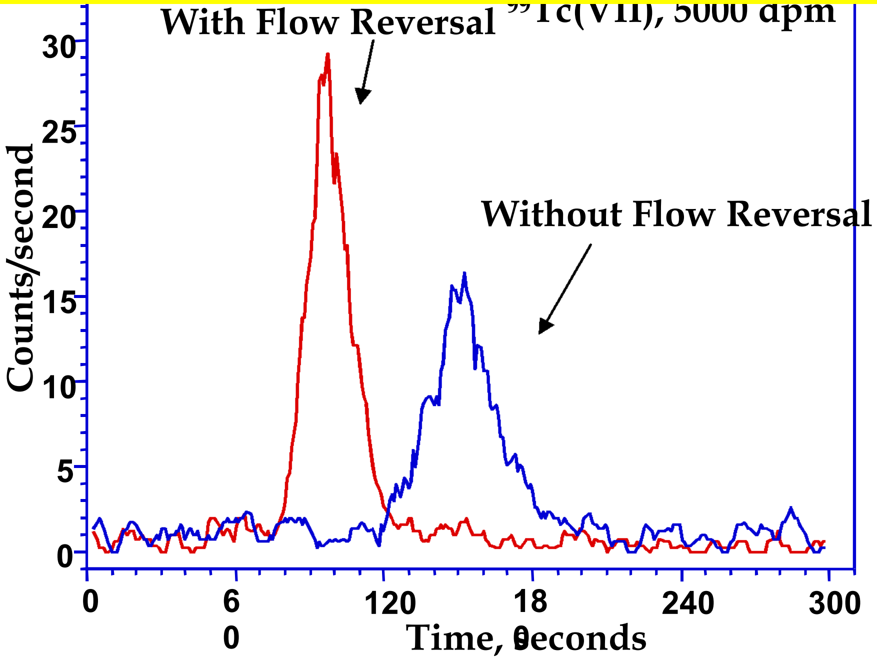
	Description	Reagent	Volume, mL	Flow rate, mL/min
1.	Column conditioning	0.2 M HNO_3-0.2 M HF	3	5
2.	Sample load	Sample solution (~ 0.5 M acid)	1.75	3
3.	Acid wash 1	0.2 M HNO_3-0.2 M HF	1	3
6.	Acid wash 2	0.2 M HNO_3-0.2 M HF	9	3
7.	Tc elution [1,2]	6 M HNO_3	5	2
8.	Water wash 2	DI water	3	5

[1] Detection cycle started simultaneously with the beginning of the Tc elution step.

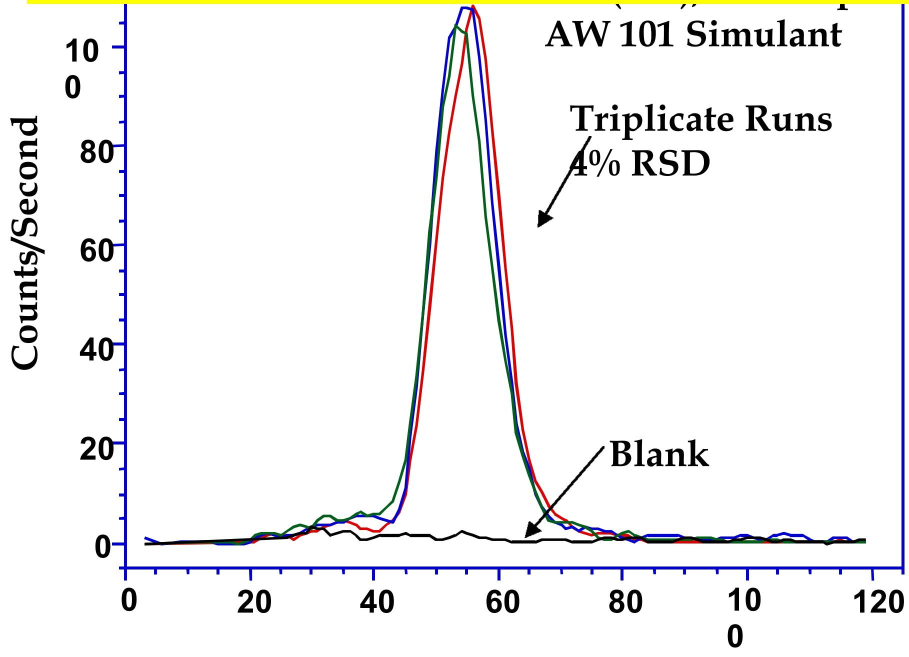
[2] Cocktail flowrate 0.5mL/min. Only the first 4 mL of the Tc eluent were mixed with cocktail for on-line detection.

ON-LINE ^{99}Tc QUANTIFICATION

Effect of the flow reversal during elution step.
Flow rates:eluent: 1 mL/min; cocktail 1 mL/min

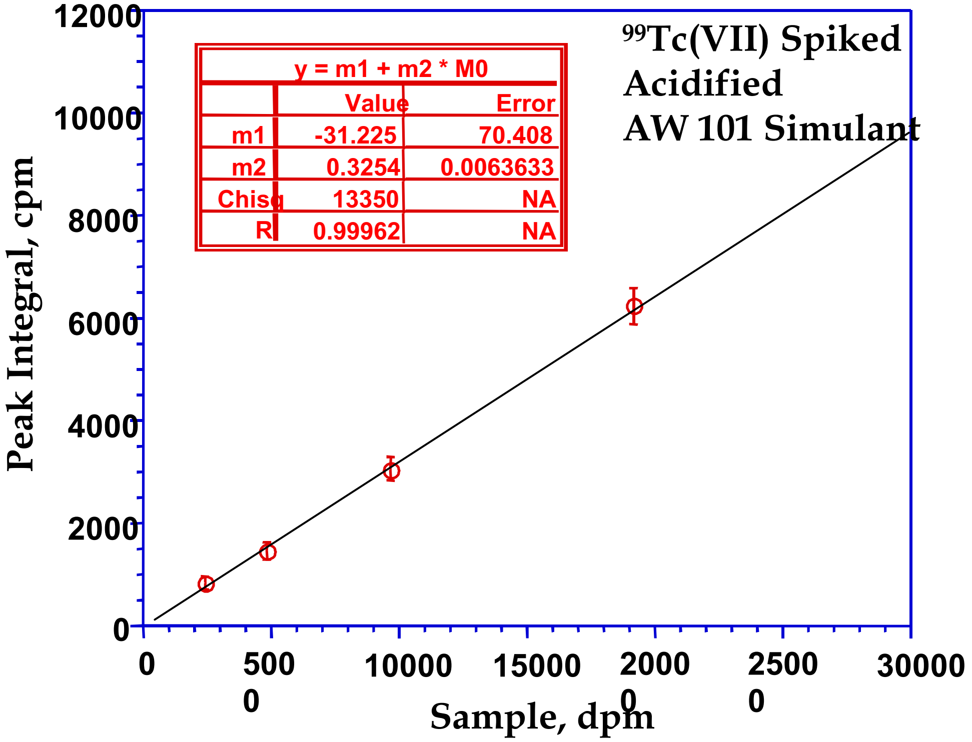


Analysis reproducibility.
Flow rates:eluent: 2 mL/min; cocktail 0.5 mL/min



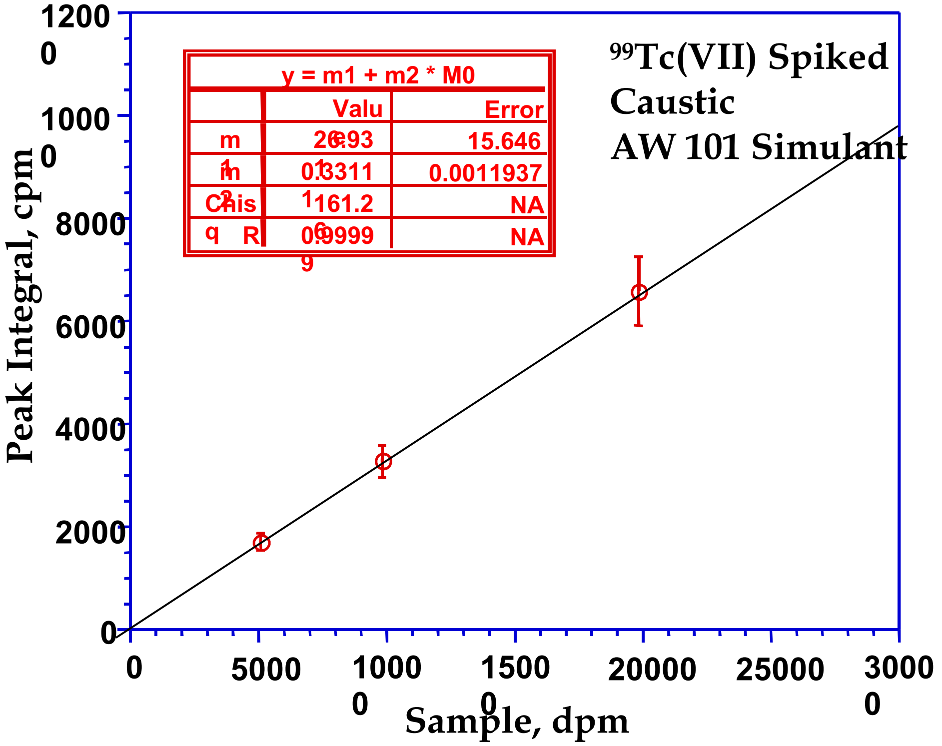
CALIBRATION

Time, Seconds



y = m1 + m2 * M0

	Value	Error
m1	-31.225	70.408
m2	0.3254	0.0063633
Chisq	13350	NA
R	0.99962	NA



y = m1 + m2 * M0

	Value	Error
m1	26.93	15.646
m2	0.3311	0.0011937
Chisq	1161.2	NA
R	0.9999	NA

Detection limits: ~2.5E-7 Ci/L
3 sigma blank, 1 mL sample volume & no dilution

VALIDATION BY ICP MS

Method validation using acidified AW101 sample with $KMnO_4$ treatment

Sample ID	Description	ICP MS result, ppm	Radiometric Monitor, ppm[1]
AIR-P-TR	processed AW101 sample	**1.323±0.062**	**1.36±0.05 (1.13±0.05)**
AIR-P-TR-S	spiked processed AW101 sample	**2.381±13**	**(1.96±0.05)**

[1]Obtained using standard addition approach. Results in parenthesis were obtained using 33% analysis efficiency from the analyzer calibration.
Sample volume 0.5 mL.
1 ppm=629 Bq/mL= 1.7 x 10^{-5} Ci/L

Method validation using acidified AW101 and AN107 samples with $Na_2S_2O_8$ treatment

Sample ID	Description	ICP MS result, ppm	Radiometric Monitor, ppm[1]
AIR-PS-TR	processed AW101 sample	**1.66±0.17**	**1.65±0.05 (1.53±0.05)**
AIR-PS-TR-S	spiked processed AW101 sample	**2.79±0.28**	**NA (2.57±0.13)**
AN107-PS-TR	processed AN107 sample	**0.706±0.07**	**0.610±0.06 (0.625±0.06)**
AN107-PS-TR-S	spiked processed AN107 sample	**1.81±0.18**	**NA (1.82±0.05)**

[1]Obtained using standard addition approach. Results in parenthesis were obtained using 33% analysis efficiency from the previous analyzer calibration.
Sample volume 0.25 mL.
1 ppm=629 Bq/mL= 1.7 x 10^{-5} Ci/L

CONCLUSIONS:

- **Automated radiochemical approach is feasible for Tc monitoring**
- **Further work is needed to build an operational monitor**

PROPOSED FUTURE RESEARCH

- **Goal: *Develop and test integrated analyzer instrument prototype* (6–9 month study)**
- **Improved fluidics hardware**
  - **automated fluidics can be utilized for other monitoring approaches (i.e. ICP-AES or MS)**
- **Develop on-line sample oxidation module using focused microwave reactor (Prolabo)**
- **Integrate sampling, oxidation, and analysis in a single instrument**
- **Develop dedicated user- friendly control software**
- **Develop analysis procedures for various scenarios**
- **Validate instrument under various monitoring scenarios**
  - **-total Tc analysis vs. Tc(VII), etc.**
  - **-on-line vs. at-line**