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^{99}Tc Process Monitoring System In-Lab Performance Characterization

MJ O'Hara
CM Niver

January 2014

Pacific Northwest
NATIONAL LABORATORY

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Executive Summary

A ^{99}Tc Process Monitoring (Tc-Mon) System has been designed and built for deployment at the recently constructed 200 West Pump & Treat (200W P&T) Plant in the 200 West Area ZP-1 Operable Unit of the Hanford Site. The plant is operated by CH2M Hill Plateau Remediation Company (CHPRC). The Tc-Mon system was created through collaboration between Pacific Northwest National Laboratory (PNNL) and Burge Environmental, Inc. The design of the new system has been optimized based on experience from an earlier field test (2011) of a prototype system at the 200W-ZP-1 Interim Pump & Treat Plant.[1]

A portion of the new 200W P&T Plant is dedicated to removal of ^{99}Tc from contaminated groundwater in the 200 West Area. ^{99}Tc, as the pertechnetate anion ($^{99}TcO_4^-$), is remediated through delivery of water into two trains (Trains A and B) of three tandem extraction columns filled with Purolite A530E resin. The resin columns cannot be regenerated; therefore, once they have reached their maximum useful capacity, the columns must be disposed of as radioactive waste. The primary use of the Tc-Mon system will be for on-demand sampling and analysis of effluents from the primary extraction columns to determine ^{99}Tc breakthrough levels. The system will supplement, not replace, CHPRC's established monthly grab sampling and analysis program.

This report contains the following information:

- The genesis of the ^{99}Tc sensor and the Tc-Mon analytical system.
- A description of the Tc-Mon system's major hardware and software components.
- A description of the operational principles behind the ^{99}Tc sensor.
- Results from the calibration of three components within the Tc-Mon system. The three systems requiring calibration are:
    1. Sampling Chamber
    2. Conductivity Sensor
    3. ^{99}Tc Sensor
- Presentation of analytical results obtained on the fully calibrated Tc-Mon system. This includes a determination of the precision and accuracy of each system defined above.
- Estimation of the ^{99}Tc sensor's minimum detectable activity and limit of quantification.
- A brief discussion of potential chemical and radiological influences on the ^{99}Tc sensor based on known contaminants in 200W P&T Plant water.
- Observations regarding ^{99}Tc sensor longevity.

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[1] O'Hara, M.J., et al., Radiochemical sensing systems for measurement of beta and x-ray emitting radionuclides in groundwater, in 242nd National ACS Conference. Aug. 30, 2011: Denver, CO.

Acronyms and Abbreviations

200W P&T	200 West Area Pump & Treat (System)
CHPRC	CH2M Hill Plateau Remediation Company
DOE-RL	U.S. Department of Energy Richland Operations Office
DWL	drinking water limit
EEProm	Electrically Erasable Programmable Read-Only Memory
FY	fiscal year
LOQ	limit of quantification
MDA	minimum detectable activity
NIST	National Institute of Standards and Technology
PMT	photomultiplier tube
PNNL	Pacific Northwest National Laboratory
RPL	Radiochemical Processing Laboratory
RTD	resistance temperature detector
Tc-Mon	^{99}Tc Process Monitoring (System)
WSCF	Waste Sampling and Characterization Facility

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1.0 Introduction

1.1 ^{99}Tc-Monitoring System History

The ^{99}Tc Process Monitoring (Tc-Mon) System is an autonomous analytical device capable of sampling, analyzing, and reporting water conductivity and ^{99}Tc activity concentration automatically. At the heart of the Tc-Mon system lies the equilibrium-based preconcentrating mini-column sensor, which enables quantification of ^{99}Tc via a combination of analyte concentration and scintillation-induced signal transduction. The operational principle behind this sensor was originally described by Egorov, O'Hara, and Grate in *Analytical Chemistry* [1]. Here, a chamber filled with a homogeneous mixture of sorbent and scintillator is observed by two photomultiplier tubes (PMTs) counting in coincidence. It was demonstrated to effectively target and measure β-emitting radionuclides (^{90}Sr and ^{99}Tc) out of groundwater.

The ^{99}Tc sensor showed promise for field-deployed monitoring of specific β-emitting radionuclides. The first attempt at engineering a deployable sensor was described in the *Journal of Radioanalytical and Nuclear Chemistry* [2]. Here, the sensor was configured for measurement of ^{99}Tc. The sensor was embedded in a down-well probe, designed to be compatible with a 4-inch well casing geometry. This system was constructed and tested, but never had the opportunity for deployment. One disadvantage of this down-well design was its lack of flexibility, as it was inherently only capable of monitoring a single location.

Later, Pacific Northwest National Laboratory (PNNL) had the opportunity to collaborate with Burge Environmental, Inc. Burge Environmental specializes in field-deployable analytical systems for chlorinated solvents [3, 4] and hexavalent chromium [5] in groundwater. Through a U.S. Department of Energy (DOE) funded Small Business Technology Transfer (STTR) research partnership, PNNL and Burge Environmental were able to design and engineer automated analytical systems that incorporated the mini-column sensor, enabling the measurement of ^{90}Sr [6] and ^{99}Tc [7] in nuclear waste contaminated groundwater. Additionally, the partnership enabled PNNL to further characterize the ^{99}Tc sensor's performance in a range of chemical and radiochemical co-contaminants, and elucidated the optimal method of sensor calibration, which was matrix spike addition [7]. Next, PNNL and Burge Environmental integrated the ^{99}Tc sensor into a fully functional analytical system prototype, which was vetted at PNNL and later field-tested at the 200W-ZP-1 Interim Pump & Treat Plant at Hanford. This system was recently described in the *Handbook of Radioactivity Analysis* [8]. Unlike the down-well probe described above, the Burge Environmental system was designed for above-ground use, whereby water samples from a variety of locations (e.g., wells or pipes) could be delivered to a centralized analytical platform.

A photo of the prototype system's exterior, as it was deployed to the 200W-ZP-1 Interim Pump & Treat Plant, is shown in Figure 1 (top). Although this plant did not remediate ^{99}Tc from the groundwater (it only removed chlorinated solvents), some of the influent wells contained ^{99}Tc to varying concentrations. These ^{99}Tc-bearing water streams enabled evaluation of the performance of the prototype in an industrial setting, and provided insight into design modifications that would be required prior to deployment at an active ^{99}Tc remediation plant.

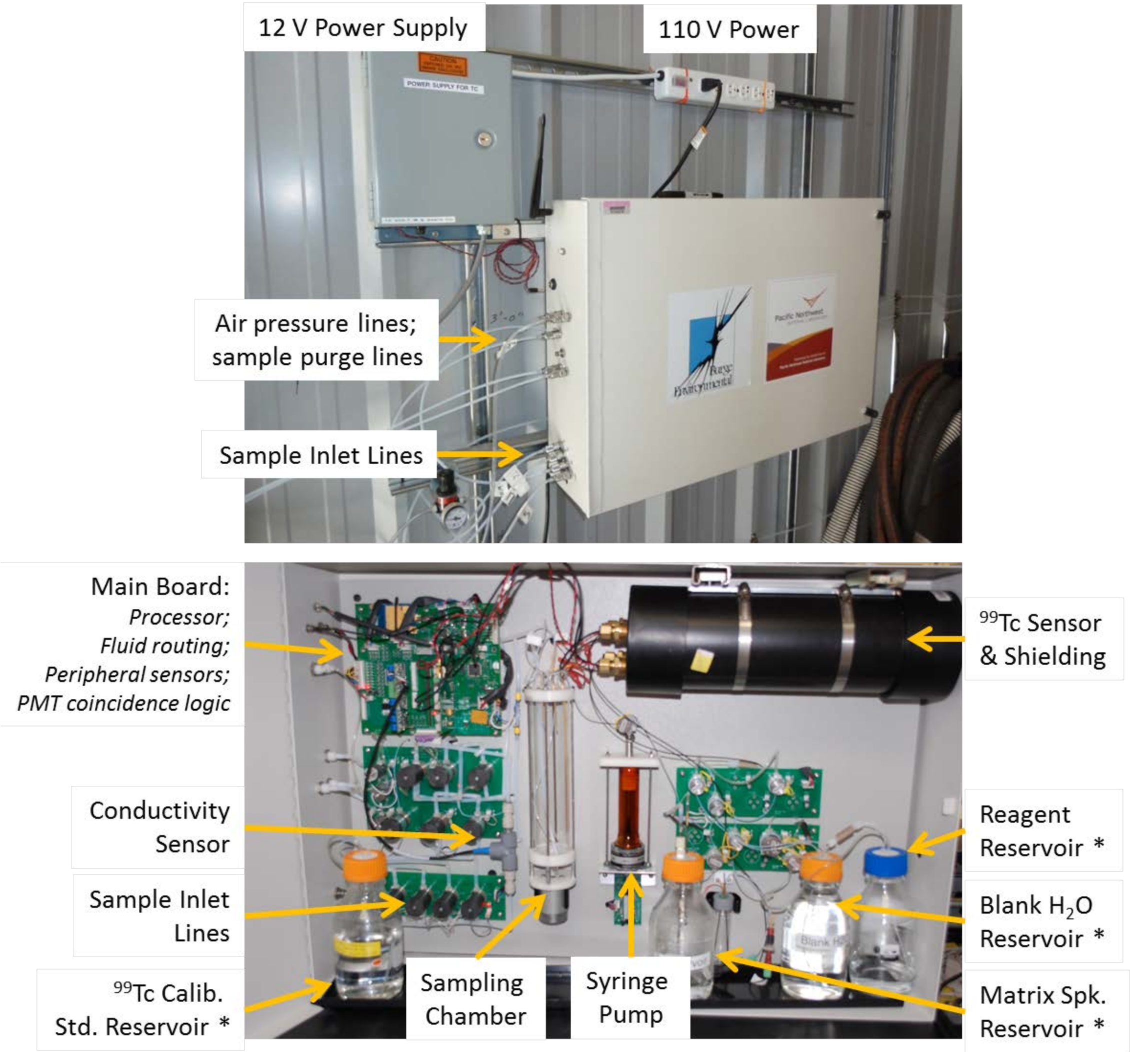

Figure 1. Photo of PNNL/Burge Environmental's prototype ^{99}Tc Process Monitor, as deployed at the 200W-ZP-1 Interim Pump & Treat Plant (top). Labeled components within the ^{99}Tc Process Monitor enclosure (bottom). (An asterisk (*) denotes solution reservoirs that will be housed in separate compartment.)

In fiscal year (FY) 2012, PNNL was tasked with developing a plan for eventual field deployment of a ^{99}Tc analytical system at the new 200 West Area Pump & Treat (200W P&T) Plant in the Hanford 200 West Area. The purpose of the system would be to monitor breakthrough of ^{99}Tc from the primary ^{99}Tc extraction columns on demand. PNNL prepared and submitted a report [9] to the DOE Richland Operations Office (RL) and CHRPC in September 2012. This report delineated the performance and installation requirements necessary for such a device to be effective.

In FY13, funding was received for construction of a Tc-Mon system for eventual deployment at the 200W P&T Plant. The system was built by Burge Environmental and incorporated PNNL's ^{99}Tc sensor design. Burge Environmental delivered the Tc-Mon system to PNNL's 325 Building in June 2013. Once laboratory set-up was complete, an in-lab performance characterization study commenced.

1.2 Report Objectives

This report documents the key features of the Tc-Mon system, the results of its in-lab calibrations, and the system performance over several weeks of testing. Performance testing included the analysis of actual 200W P&T Plant grab samples. *It should be noted, however, that the system performance in the radiochemistry laboratory environment has limitations.* Notably, the ^{99}Tc sensor's background count rate is likely higher, and the signal less stable, than can be expected once the system is deployed at the 200W P&T Plant (this was observed after deployment of the prototype system from the 325 Building to the 200W-ZP-1 Interim Pump & Treat Plant). The higher and less stable radiation background directly affects the results acquired during the in-lab performance testing. Nevertheless, this report is intended to provide DOE-RL and CHPRC with evidence of the system's overall analytical performance and reliability.

2.0 Overview of the Tc-Mon System

2.1 Hardware Overview

The Tc-Mon system prototype is shown in Figure 1 (top) as it was deployed at the 200W-ZP-1 Interim Pump & Treat Plant. Figure 2 shows a schematic of the system as it will look at the 200W P&T Plant. In this version, the lower box has been incorporated to safely contain supporting liquids, which include blank water, ^{99}Tc calibration standard, reagent, a check standard, and calibration solution reservoir. The interior of the current Tc-Mon system is shown at the bottom of Figure 1. The photo was taken during in-lab testing at PNNL. Note that the solution bottles shown in Figure 1 will be housed in the lower box (illustrated in Figure 2) once the Tc-Mon system is deployed at the 200W P&T Plant.

The Tc-Mon system has several important modules that are required to perform ^{99}Tc analyses. Briefly, these include the following:

1. Main board. This board is the central command. It contains an Electrically Erasable Programmable Read-Only Memory (EEProm) computer chip that uploads and executes operational program routines and reads and sends analytical results back to the laptop computer. The main board also houses the PMT coincidence counting board and telemetry (discussed in section 2.2).

2. Water sampling module. This includes four water sample inlet ports and valves that are capable of routing solutions through an on-board conductivity sensor and then out through a purge line. Once the conductivity sensor stabilizes and makes a reading, the water sample is routed to the sampling chamber, where a precisely measured sample volume is acquired. Note that all groundwater introduced to the system during this study was initially filtered to 0.45 μm prior to use (Millipore 47 mm dia., Type HA).

3. Water chemistry module. Includes an air line to initially sparge the water sample in order to remove radon gas. Additionally, fluidic pathways enable addition of precise volumes of reagent (e.g., acid) and ^{99}Tc standard to the sampling chamber. A magnetic stir bar coupled to a motor effectively homogenizes the input solutions with the water sample.

4. ^{99}Tc sensor module. This module consists of a syringe pump driven by a stepper motor to deliver prepared sample to the ^{99}Tc sensor inlet line. The ^{99}Tc sensor inlet line is affixed with a 13 mm diameter, 2.7 μm glass microfiber filter disc (Whatman) to ensure no particulate matter is transported to the inlet frit of the ^{99}Tc sensor. The ^{99}Tc sensor is housed in a light-tight canister. PMT power lines and signal output lines are routed to a board (connected to the main board) that processes PMT signals to produce coincidence counts.

5. Service lines. These include ports to receive pneumatic air pressure, which is used to drive solutions, induce sample sparging, and evacuate the sampling chamber at the end of the run. Additionally, a series of solution collection lines route post-analyzed solutions to waste.

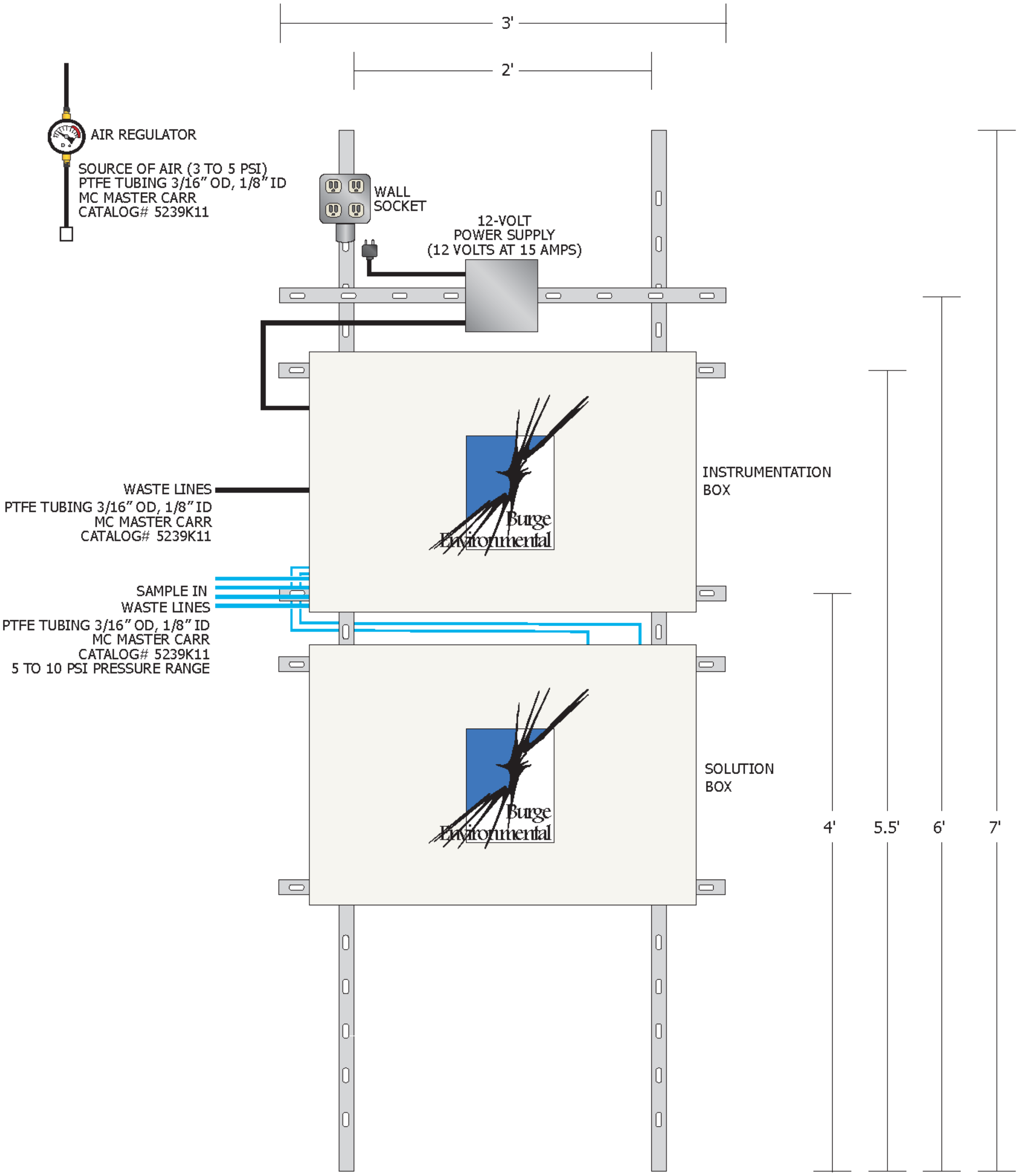

Figure 2. Schematic of Burge Environmental Tc-Mon system for installation at the 200W P&T Plant. Top box contains measurement components; bottom box is a container for housing blank solution, check standard, reagent, and ^{99}Tc standard.

The Tc-Mon system can perform a multitude of automated operations. However, the primary operational task is to measure ^{99}Tc in the primary ^{99}Tc extraction column effluents at the 200W P&T Plant. The sequence of steps involved in a routine ^{99}Tc analysis is outlined in Table 1.

Table 1. Sequential steps performed in the analysis of ^{99}Tc in groundwater using the Tc-Mon.

Step	Task
1	Selection of water source
2	Water purge to waste
3	Measurement of water conductivity(a)
4	Filling of a measured volume of sample into a sample chamber(b)
5	Air sparge of sample to eliminate radon gas
6	Addition of acid to normalize water sample pH to ~2(b)
7	Mixing of water sample / acid mixture(c)
8	Dispensing of water sample to mini-column sensor(d)
9	Measurement and charting of PMT coincidence signal
10	Calculation of average sensor count rate under equilibrium conditions(e)
11	Background subtraction of sensor signal(f)
12	Conversion of net sensor signal to ^{99}Tc activity(g)
13	Creation of summary file listing sampling time, water conductivity, and ^{99}Tc activity
14	Ability to export sample summary information to Microsoft Excel

(a) Conductivity sensor is calibrated via a manual routine.
(b) Sample chamber volumes are calibrated via a manual routine.
(c) Mixing of solution is accomplished with a magnetic stir bar coupled to a motor.
(d) Delivery of water sample from sampling chamber to sensor is performed via a syringe pump.
(e) Performed at the completion of the analysis.
(f) Sensor background is periodically determined via a special analysis using ^{99}Tc-free groundwater of similar composition to 200W P&T Plant water.
(g) Conversion of net count rate observed from sensor via matrix spike addition to periodically determine sensor calibration factor, E_m; the E_m is determined by periodically conducting a matrix spike addition calibration (defined in section 2.3).

2.2 Computer and Software Overview

The software that operates the Tc-Mon system was written by Burge Environmental using Microsoft Visual Basic (v. 6.0, SP5). The software is installed on a Dell Latitude D610 laptop computer running on Windows XP. Communication between the computer and the Tc-Mon system's main board is made via an RS-232 connection. Remote communication can alternatively be made possible with the configuration of radio-frequency based telemetry between the laptop and the Tc-Mon. This capability can be added later if needed (e.g., if plant operators wish to operate the system from the control room). Additionally, remote communications with the laptop computer are possible using the Microsoft Remote Desktop application (when the laptop computer is connected to the internet via Local Area Network or Wi-Fi). With a Remote Desktop application, the user can operate the Tc-Mon system and acquire analytical results from any networked computer.

The Burge Environmental software has a variety of tools and forms that enable the user to perform a variety of tasks, some of which are highlighted in Table 2. Figure 3 shows a screenshot of the Tc-Mon software main user interface page.[1]

Table 2. Overview of the primary operational tools and forms available in the Burge Environmental software.

Name	Function
Data Entry Forms	Program system operational parameters Set delay times prior to system error
Optimization Forms	Perform discreet sub-task routines Direct operation of syringe pump Perform direct PMT measurements
Run Monitoring Systems	Perform water conductivity and ^{99}Tc analysis Perform water conductivity analysis only
Data Review Forms	Extract data directly from EEProm chip View current calibration file Review sample results Review matrix spike results View archived calibration results
Calibration Forms	PMT standardization (^{99}Tc sensor calibration) Conductivity sensor calibration Sample chamber calibration

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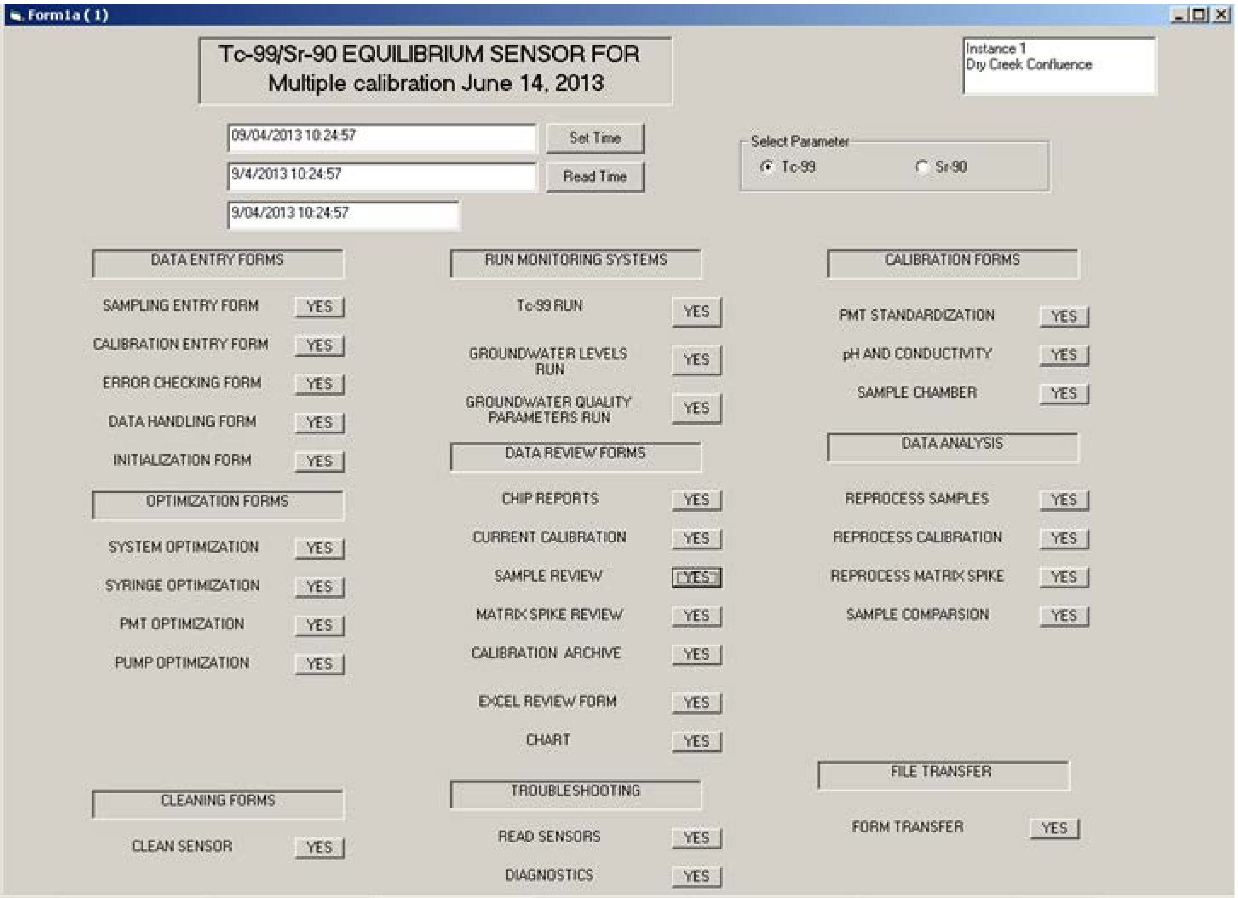
[1] Layout of main user interface page may be slightly modified in the deployed software version.



Form1a (1)

Tc-99/Sr-90 EQUILIBRIUM SENSOR FOR
Multiple calibration June 14, 2013

Instance 1
Dry Creek Confluence

09/04/2013 10:24:57
9/4/2013 10:24:57
9/04/2013 10:24:57

Select Parameter
● Tc-99 ○ Sr-90

Figure 3. Image of the Burge Environmental software main user interface page.

2.3 Mini-Column ^{99}Tc Sensor Overview

The mini-column sensor assembly (Figure 4) was conceptualized, designed, and manufactured at PNNL. Later, the engineering drawings were transferred to Burge Environmental, where replicate sensor assemblies were manufactured. Figure 4 (top left) illustrates the basic operational principles. Sample solution is pumped into a column body, which is composed of a heterogeneous mixture of selective sorbent media (orange dots) and organic scintillating particles (green dots). The two sides of the column are composed of quartz windows that are transparent to both visible and ultra-violet photons. The sensor column is observed by dual PMTs counting in coincidence.

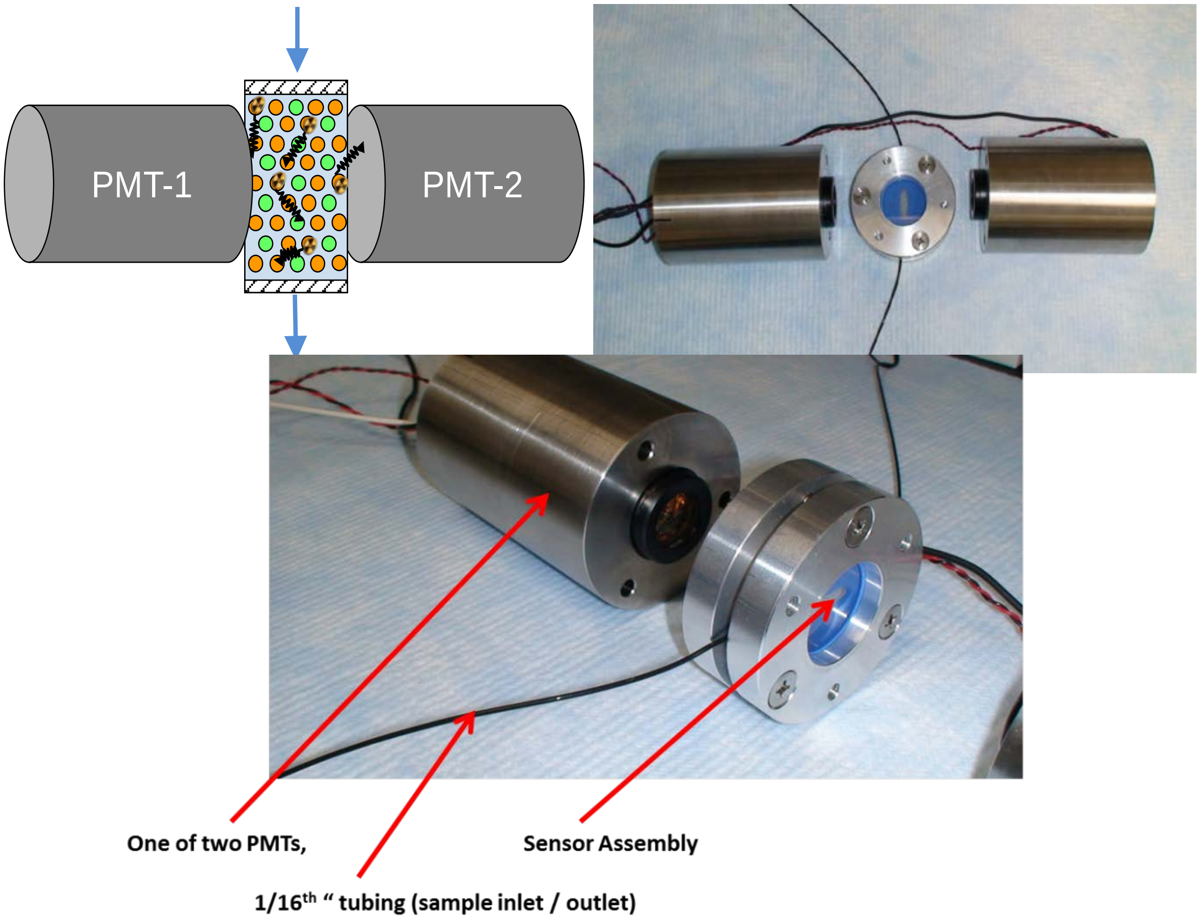


Figure 4. Schematic of mini-column sensor (top left). Photos of equilibrium sensor (partially disassembled) for ^{99}Tc monitoring are shown in top right and bottom.

As a sample is delivered (via a syringe pump) through the column body, the targeted radioactive analyte, ^{99}Tc as the pertechnetate anion ($^{99}TcO_4^-$), is sorbed onto the anion exchange particles. The concentration of reagent (acid) added to the sample has an inverse relationship to the ^{99}Tc sensor's ability to concentrate ^{99}Tc (e.g., as the concentration of HNO_3 increases, ^{99}Tc affinity to the sensor drops. Therefore, the acid concentration of the sample can be used to fine-tune the level of concentration of ^{99}Tc onto the sensor). The analyte accumulates within the sensor column as sample is delivered. When a beta emission occurs, there is a high probability that the beta particle will strike an adjacent scintillating bead. If the beta particle strikes a scintillating bead with sufficient energy, the scintillator will become excited by the radiation. The subsequent de-excitation of the scintillating media results in the emission of photons in the near-ultraviolet region of the visible spectrum (~400 nm).

Perpendicular to the dual-component column body are two PMTs. Each PMT observes the column through the quartz windows. The near-ultraviolet scintillation-induced photons are measurable by the PMTs. However, the number of photons produced by the β-decay emissions from environmental-level radionuclides is small, while the signal level produced by each PMT (via dark current, terrestrial and cosmic radiation events, etc.) is high.

To decrease the background of the PMTs and increase the sensitivity to scintillation events within the sensor column, Burge Environmental developed a coincidence logic within a compact computer board that enables the random individual PMT signal events to be discarded, while only scintillation events within the sensor, observable by both PMTs simultaneously, are counted. This method of coincidence counting decreases the PMT signal from several hundred hertz down to less than 1 Hz.

Figure 4 (top right and bottom) shows photographs of the actual mini-column sensor assembly, designed and built for the measurement of ^{99}Tc in groundwater. The two PMTs are embedded in stainless steel cylinders with a 2.54 cm wall thickness for shielding. The 2.54 cm thick stainless steel is equivalent to approximately 1.4 cm of lead, which provides adequate shielding from the majority of terrestrial and cosmic radiation. At this thickness, the stainless steel cylinders are capable of reducing the transmission of 1 MeV gamma photons to ~30%.

The column body is composed of a disc machined from polyether ether ketone (PEEK), which features threaded 10-32 inlet and outlet ports for the fluid delivery lines (1/16 inches OD). An embedded stainless steel 10-micron mesh disc at either end ensures that the packed media remains fixed within the column body. The assembly is made watertight through the use of a silicon rubber gasket (blue disc in Figure 4); everything is compressed through the use of two stainless steel rings secured with three screws. The entire assembly is held together with six screws that secure the sensor body to each PMT assembly (as shown in Figure 5).

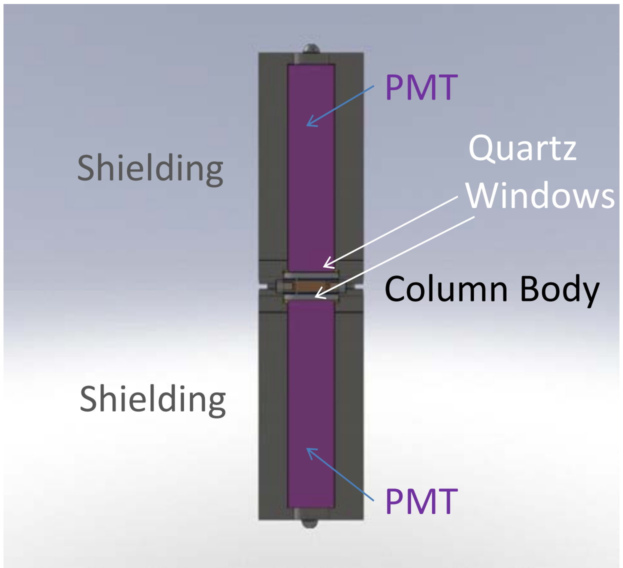


Figure 5. Schematic of fully assembled mini-column sensor system.

Figure 6 shows a close-up view of the ^{99}Tc mini-column sensor column, as packed with a mixture of Toyopearl QAE-550C Strong Anion Exchange Resin, 50 - 150 µm particle size and BC-400 scintillating beads (250 - 500 µm, Saint-Gobain Crystals) in a ~0.13:1, v/v ratio (dry QAE-550C:BC-400). A black light placed behind the sensor shows the strong scintillating properties of the BC-400 beads, as well as the high degree of light transmission through the packed bed.

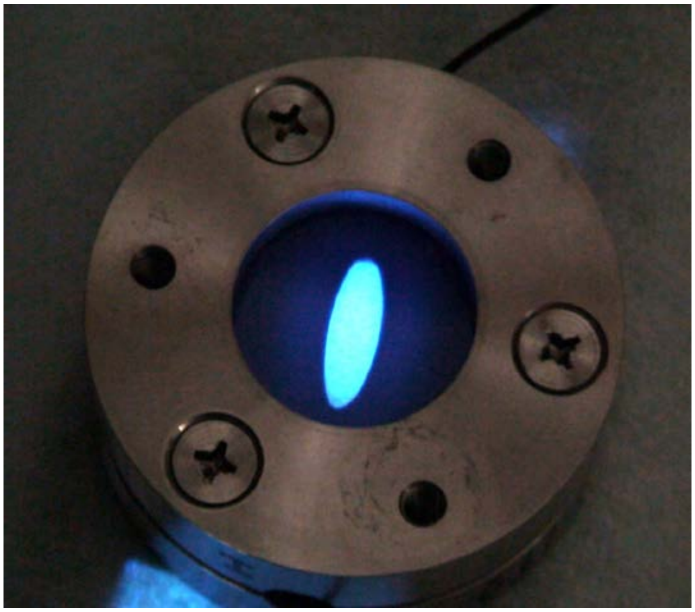


Figure 6. Close-up of ^{99}Tc mini-column sensor. A black light behind the sensor shows scintillating and light transmission properties of the packed bed.

A comprehensive description of the equilibrium-based preconcentrating mini-column radiochemical sensor operational principles can be found in Egorov, O'Hara, and Grate [1]. More recently, in O'Hara, Burge, and Grate [7], the method and calculations for matrix spike addition were defined. The basic sensor operation is described briefly using Table 3 and Figure 7. Sample containing the β-emitting analyte is delivered to the radiochemical sensor (step 2 in Table 3). As the analyte concentrates within the sensor packed bed, the PMT signal rises linearly until the sensor establishes chromatographic equilibrium with the radioactive analyte (step 3). At this point, the signal establishes a steady-state condition. When the radioactive analyte is not present in the groundwater solution, the analyte is reversibly removed from the sensor and the PMT signal drops (step 4) until all the analyte is eluted from the sensor, and the sensor once again establishes background condition (step 5).

Table 3. Description of sample delivery to mini-column chamber; results shown in Figure 7.

Step	Matrix	β-emitter Conc., Arbitrary
1	Groundwater	0
2	Spiked Groundwater	1
3	Spiked Groundwater	1
4	Groundwater	0
5	Groundwater	0

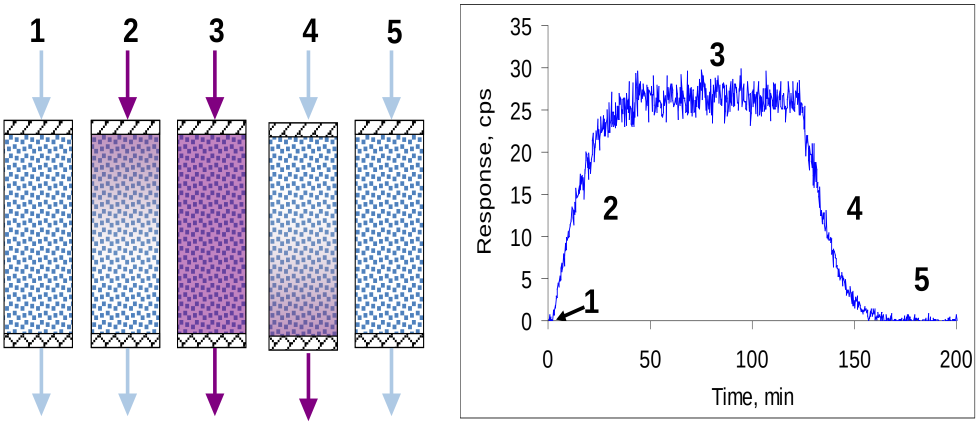


Figure 7. Equilibrium sensing conceptual schematic showing in-flow of a β-emitter in water (left), and simultaneous sensor response to β-decay events (right). See Table 3 for a description of experimental conditions.

Conversion of net sensor count rate to activity of ^{99}Tc per unit volume (A_{Tc}, Bq/mL) is calculated by Eq. (1) where R_{eq} is the net count rate (cps) of the sensor at equilibrium with ^{99}Tc, and E_m is the measurement efficiency (in units of cps/(Bq/mL)). Conversion of Bq/mL to pCi/L is accomplished via the conversion factor of 27,027 pCi/L per Bq/mL.

$$A_{Tc} = \frac{R_{eq}}{E_m} \tag{1}$$

For real-world applications, where the chemistry (e.g., distribution of anions) of the groundwater can change over time, the process of matrix spike addition to determine the E_m is necessary. Eq. (2) defines the E_m calculation for matrix spike addition,

$$E_m = \frac{R_{eq,sp} - (\frac{V_s - V_{sp}}{V_s})R_{eq}}{A_{matrixsp}} \tag{2}$$

where $R_{eq,\,sp}$ is the net count rate of the spiked sample at equilibrium, R_{eq} is the net count rate of the unspiked sample, V_s is the volume of the sample, V_{sp} is the volume of the ^{99}Tc spike, and $A_{matrixsp}$ is the activity of the ^{99}Tc matrix spike in the mixed sample.

Eq. (3) defines the calculation for the $A_{matrixsp}$, where A_{sp} is the activity of the ^{99}Tc on-board standard (in Bq/mL).

$$A_{matrixsp} = \frac{A_{sp}V_{sp}}{V_s} \tag{3}$$

3.0 Tc-Mon System Calibration

The Burge Environmental Tc-Mon system was fully calibrated during the in-lab performance characterization study. There are three components that require calibration on this unit: 1) sampling chamber, 2) conductivity sensor, and 3) ^{99}Tc sensor. The following sections describe each component and the results from the calibration activities.

3.1 Sampling Chamber Calibration

The sampling chamber is a container within the Tc-Mon main housing that enables collection of water sample and delivery of ^{99}Tc standard, and allows for chemistry to be performed on that sample. An image of the sampling chamber is shown in Figure 8. The chamber consists of a glass cylinder with Delrin caps on the top and bottom. A magnetic stir bar is placed at the bottom of the chamber. The stir bar is magnetically coupled to a stirring motor that lies underneath the chamber. The top cap has several machined ports that enable air and liquids (e.g., sample water, reagent, ^{99}Tc standard) to enter and exit the chamber. Additionally, four gold-plated steel rods protrude down from the cap. These are conductivity monitoring leads that act as liquid level sensors within the chamber. The longest rod (protruding deepest into the chamber) acts as a common ground. The rods are described in Table 4 and are labeled in Figure 8.

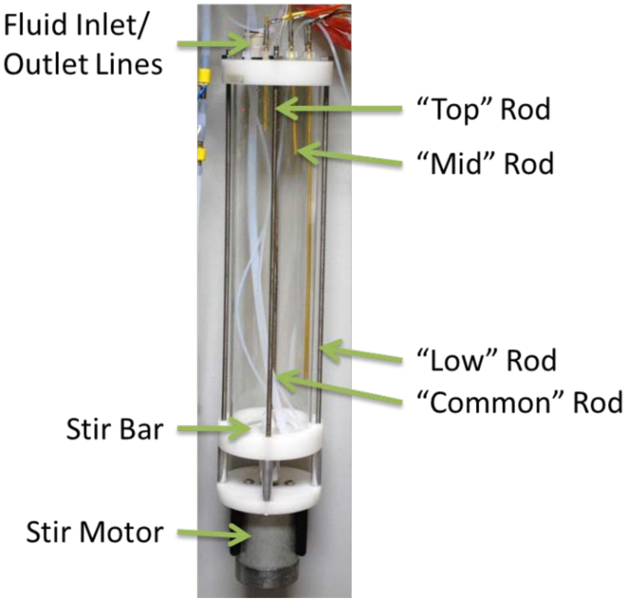
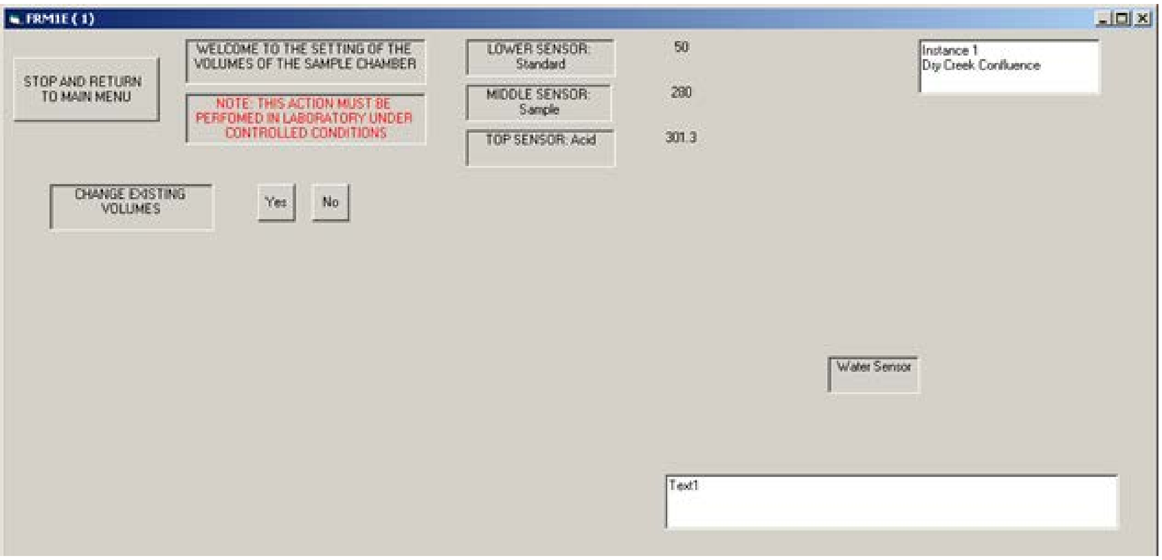


Figure 8. Close-up of sampling chamber.

Table 4. Description of each liquid level probe within the sampling chamber.

Rod Identification	Description/Purpose
Common	Common grounding rod that connects each conductivity monitoring lead
Low	Measures ^{99}Tc matrix spike addition volume
Mid	Measures groundwater sample volume (following matrix spike addition, if applicable)
Top	Measures acid volume (following sample addition)

The Burge Environmental software has a sampling chamber calibration page, labeled Sample Chamber, under the Calibration Forms main page header. Figure 9 shows the Sample Chamber form. This page enables the operator to systematically 1) load the sampling chamber to the desired level sensor (using a water source connected to Port 1), then 2) connect the sampling chamber drain to a tared liquid container (e.g., a volumetric cylinder), then 3) empty the contents of the sampling chamber into the container (via pneumatic pressure applied automatically by the program). Once this is complete, the operator can determine the volume within the container (volumetrically or gravimetrically). Finally, the operator programs the observed value into the sampling chamber calibration form. This is repeated for all three level sensors.



WELCOME TO THE SETTING OF THE VOLUMES OF THE SAMPLE CHAMBER

NOTE: THIS ACTION MUST BE PERFOMED IN LABORATORY UNDER CONTROLLED CONDITIONS

LOWER SENSOR: Standard 50
MIDDLE SENSOR: Sample 280
TOP SENSOR: Acid 301.3

Instance 1
Dry Creek Confluence

Figure 9. Sample Chamber programming page.

When the routine is completed, the program has stored all three volumes in memory, and uses two volumes (“Low” and “Mid”) in the calculation of V_{sp} and V_s, respectively (see Eq. (2) and Eq. (3)).

Additionally, the operator can determine the delivered reagent (e.g., acid) volume by taking the difference of the “Top” and “Mid” sensor volumes. Based on this known volume, the operator can prepare a reagent with a concentration that will form a desired final reagent concentration in the sampling chamber once the reagent has been added and mixed with the sample. Eq. (4) shows the calculation for determining the concentration of the stock reagent (C_{Stock}), given the desired final reagent concentration (C_{Final}), the volume of the “Top” level sensor (V_{Top}), and the volume of the “Mid” level sensor (V_{Mid}).

$$C_{stock} = \frac{C_{Final} \cdot V_{Top}}{(V_{Top} - V_{Mid})} \tag{4}$$

Table 5 summarizes the results of the calibration of the level sensors. Each level sensor volume was measured in quintuplet. Collected calibration samples were determined gravimetrically, then converted to volume units based on water density at the measured water temperature. The table lists the average and standard deviations of the five measurements. The relative standard deviations were very small, with the largest being for the "Low" level sensor, at ± 0.16%. The table also documents the actual value programmed into the Burge Environmental software water level calibration page (last column). Consistency in the volumes delivered into the sampling chamber is important, in that it dictates the quality of the ^{99}Tc measurements. Since the Burge Environmental software utilizes the programmed volumes in its calculation of E_m and ^{99}Tc activity concentration, these values must be reproducible.

For the in-lab performance characterization studies, we desired the final sample solution volume to be acidified to 0.01 M HNO_3. Therefore, using the volumes listed in Table 5 and Eq. (4), we determined that the concentration of the stock reagent bottle (C_{Stock}) needed to be 0.138 M HNO_3.

Table 5. Sampling chamber volume calibration.

Level Sensor (equation aliases)	Delivered H_2O Mass, g	Delivered H_2O Vol., mL$^{(a)}$	Avg. H_2O Vol., mL (± 1σ)	Programmed H_2O Vol. into Burge Software$^{(b)}$
Low (V_{sp})	49.9	50.0	**50.0 ± 0.08**	**50**
	49.7	49.9		
	49.7	49.9		
	49.8	49.9		
	49.9	50.1		
Mid (V_{Mid}; V_s)	279.0	279.8	**279.5 ± 0.18**	**280**
	278.6	279.4		
	278.6	279.4		
	278.5	279.3		
	278.8	279.6		
Top (V_{Top})	300.5	301.4	**301.3 ± 0.04**	**301.3**
	300.4	301.3		
	300.4	301.3		
	300.4	301.3		
	300.4	301.3		

(a) H_2O temperature was 25 °C; corresponding density = 0.99705 g/mL.
(b) In the Burge Environmental software, "Low" and "Mid" values are coded as integers, while "Top" is coded as floating-point (hence, "Top" records the value as a decimal).

Additionally, we desired to know the final ^{99}Tc activity concentration in the matrix spiked samples. The "Low" level sensor volume of 50 mL is equivalent to V_{sp} in Eq. (3), and the "Mid" level sensor volume of 280 mL is equivalent to V_s. Therefore, given the on-board ^{99}Tc calibration standard activity concentration of 1.478 Bq/mL (39,950 pCi/L), the final matrix spike activity concentration was calculated to be 0.264 Bq/mL (7130 pCi/L).

3.2 Conductivity Sensor Calibration

The Tc-Mon system is equipped with a flow-through conductivity sensor (Figure 10). The sensor measures the conductivity of the influent water sample following a water purge interval that is set by the operator. It is manufactured by Eutech Instruments and is supplied by Cole-Parmer (Model 1921323-31-010T). The unit contains a glass cell with two platinum bands. It also contains a resistance temperature detector (RTD) sensor so that measured conductivity can be temperature compensated.

Upon the startup of a water measurement cycle (either a conductivity-only measurement or a full ^{99}Tc analysis), the sample water is sent through the conductivity sensor, via the water purge line, until the sensor signal stabilizes. At that point, the water conductivity is recorded, and a solenoid valve diverts the water to fill the sampling chamber. Note that a delay time can be programmed into the Burge Environmental software so that a desired purge volume can be achieved before the software engages active monitoring of the conductivity sensor.

The Burge Environmental software contains a conductivity sensor calibration programming page labeled pH and Conductivity under the Calibration Forms section of the main page. The pH and Conductivity form is shown in Figure 11, with the conductivity calibration portion located in the central portion of the form. The sensor is calibrated via two conductivity calibration standards, typically 100 and 1000 μS/cm.

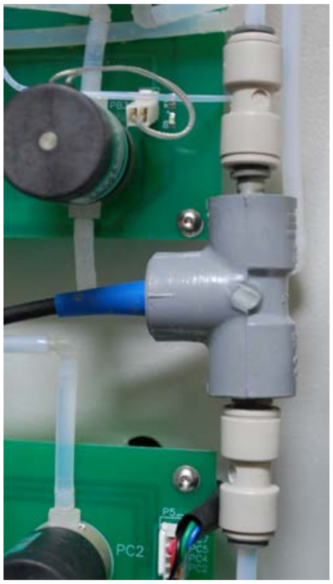
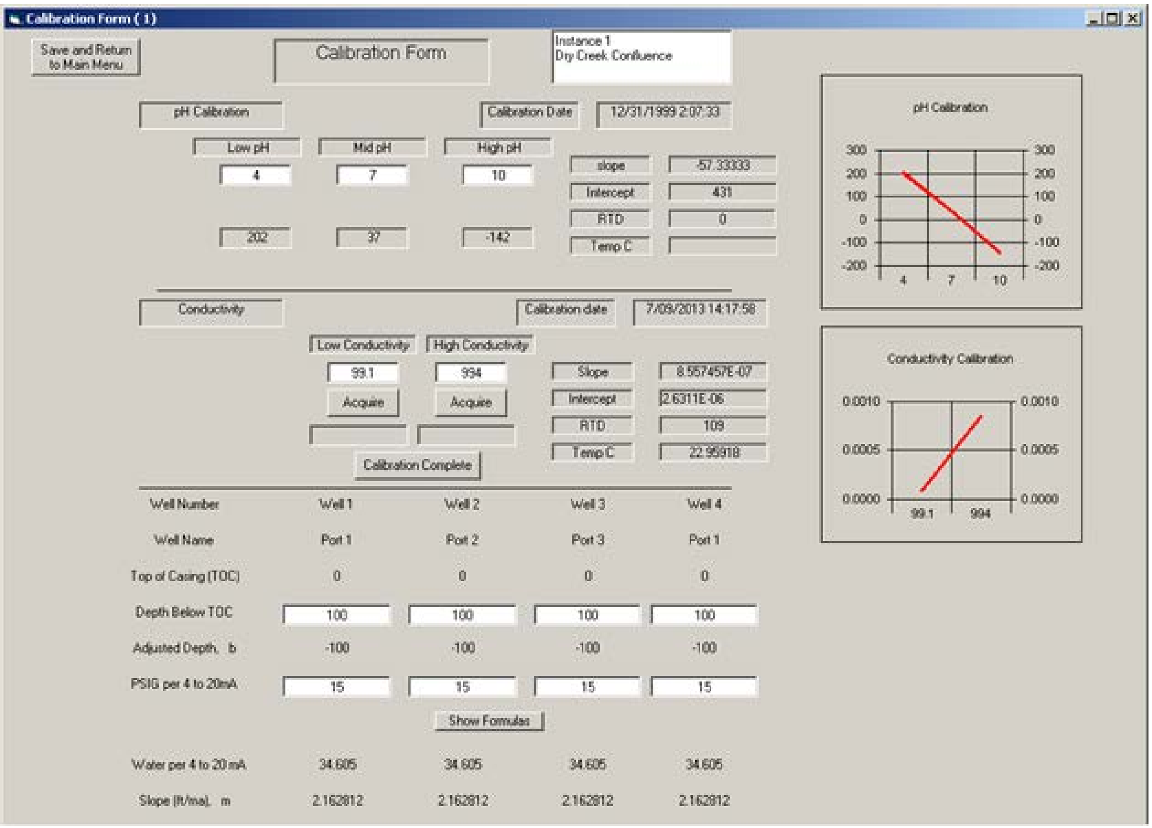


Figure 10. Close-up of conductivity sensor.



Instance 1
Dry Creek Confluence

Calibration Date: 12/31/1999 2:07:33

Low pH	Mid pH	High pH
4	7	10
202	37	-142

slope: -57.33333
Intercept: 431
RTD: 0
Temp C:

Calibration date: 7/09/2013 14:17:58

Low Conductivity	High Conductivity
99.1	994

Slope: 8.557457E-07
Intercept: 2.6311E-06
RTD: 109
Temp C: 22.95918

Well Number	Well 1	Well 2	Well 3	Well 4
Well Name	Port 1	Port 2	Port 3	Port 1
Top of Casing (TOC)	0	0	0	0
Depth Below TOC	100	100	100	100
Adjusted Depth, b	-100	-100	-100	-100
PSIG per 4 to 20mA	15	15	15	15
Water per 4 to 20 mA	34.605	34.605	34.605	34.605
Slope (ft/ma), m	2.162812	2.162812	2.162812	2.162812

Figure 11. Conductivity sensor calibration programming tool within the pH and Conductivity form.

The calibration routine is fast and simple. The operator loads the low conductivity standard into a ~20–30 mL syringe, and connects the syringe, via a tube, to the Port 1 sample inlet line. Next, the operator enters the low conductivity standard value into the input box labeled Low Conductivity, and then clicks the Calibrate Conductivity radio button to obtain sensor measurements while the operator slowly delivers conductivity standard through the sensor. When the sensor output values stabilize, that measurement is complete, as the program records the last sensor output value measured. The high conductivity standard output is subsequently measured and recorded in the same way.

The sensor was calibrated using Fisher Scientific National Institute of Standards and Technology (NIST)-traceable conductivity standards at 100 and 1000 µS/cm. Table 6 provides the input and output values for the conductivity sensor calibration that was performed during the in-lab performance characterization study. These parameters are recorded in memory, and are available for viewing on the conductivity sensor calibration programming tool in the pH and Conductivity form.

Table 6. Parameters from Tc-Mon conductivity sensor calibration.

Standard[(a)] µS/cm	Certified Conductivity, µS/cm[(b)]	Observed Signal	Slope	Intercept	RTD	Temp. °C
100	99.1	8.744E-05	8.558E-07	2.631E-06	109	23.0
1000	994	8.532E-04				

(a) Fisher Scientific NIST-traceable conductivity standards, Lots CC11665 and CC11642.
(b) At 25 °C.

Several conductivity check solutions (Table 7) were prepared via dilution of the 1000 µS/cm Fisher Scientific conductivity standard. The calibration of the conductivity sensor was verified by the delivery and measurement of 100, 250, 500, and 750 µS/cm solutions. These measurements were obtained via the Groundwater Quality Parameters Run form under the Run Monitoring Systems header on the main page. This routine first purges the Port 1 sample line with conductivity solution to flush through the conductivity sensor. The purge routine was programmed, by the operator, for a 5-second duration. Next, the conductivity sensor begins to monitor signal, and records a conductivity value once its signal has stabilized. Table 7 lists the measured conductivities of the four calibration verification solutions measured. Observed analytical bias, also listed in the table, was between 1.1% and 7.7%. The range of conductivity check solutions brackets the typically observed Hanford groundwater (~530 µS/cm) and 200W P&T Plant water (~640 µS/cm) conductivities.

Table 7. Results of Tc-Mon conductivity sensor calibration verification.

	Conductivity, µS/cm			
Standard ID	Certified Value[(a)] µS/cm	Tc-Mon Meas.	Bias, %	Comment
100	99.1	100	1.1	Fisher Calib. Std. Lot CC11665
250	250	269	7.7	Dilution of 1000 µS/cm Fisher Sci. Std., Lot CC11642
500	500	521	4.2	
750	750	772	2.9	

(a) At 25 °C.

3.3 ^{99}Tc Sensor Calibration

The ^{99}Tc sensor, as packed in the Tc-Mon main cabinet, is shown in Figure 12. The assembly lies within a black PVC tube, with black PVC end caps, to ensure that the sensor receives no external light. The assembly is hung from the top of the Tc-Mon system main box by two steel rails. The sample fluid inlet/outlet lines, along with PMT power and signal wires, are routed through light-shielded fittings in the left end cap.

Figure 12. ^{99}Tc sensor packaged and hanging in the Tc-Mon system cabinet.

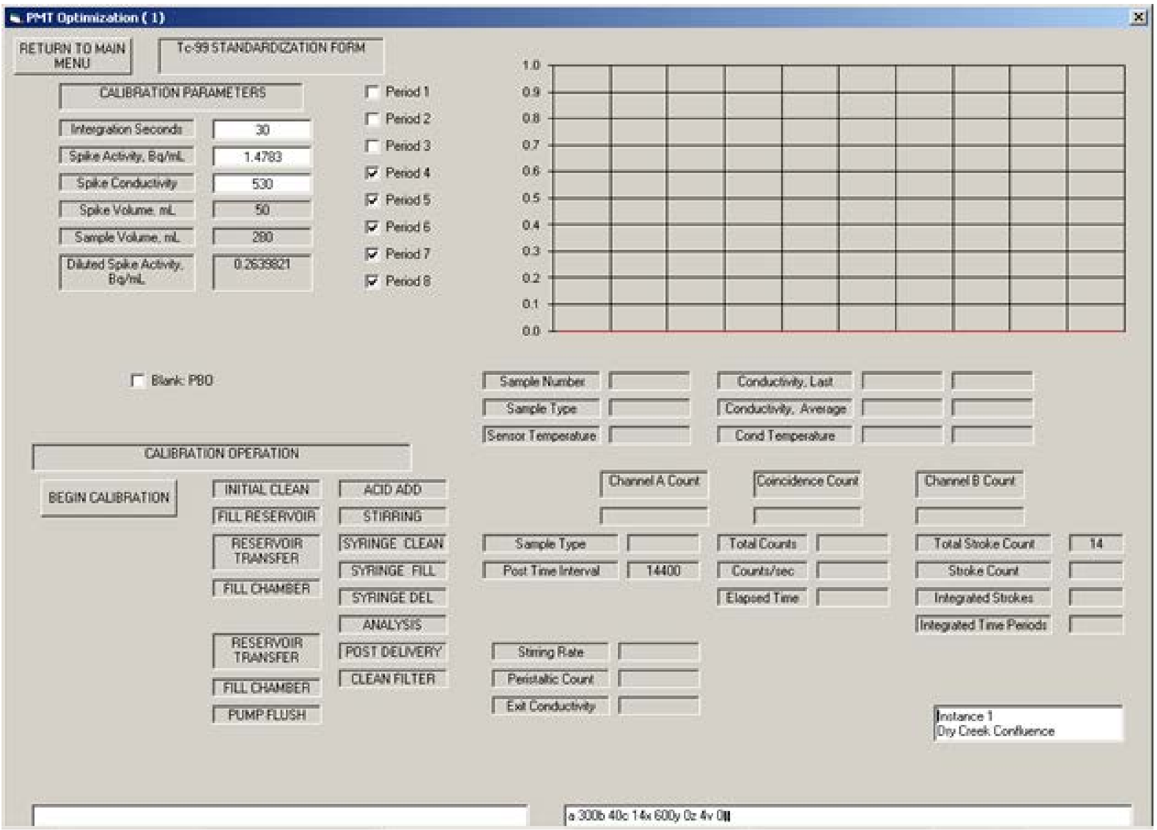
The ^{99}Tc sensor is calibrated via a four-step process. These four steps involve two interactions with the system operator. The operator first performs a blank run (step 1), and then a matrix spike addition run (steps 2‑4). The blank run utilizes a ^{99}Tc-free water sample (preferably uncontaminated groundwater, or simple tap water) to obtain the ^{99}Tc sensor's background count rate. The blank water resides in an on-board reservoir bottle connected to the sampling chamber via a valve/tube. All subsequently measured sample and standard count rates will be corrected by this background count rate in order to obtain the "net" sensor signal.

Table 8. Sequence of steps to perform calibration of ^{99}Tc sensor.

Step	Description	Objective
1	Blank run	Determine ^{99}Tc sensor background count rate
2	Unspiked sample delivery	Determine ^{99}Tc signal in sample (if present)
3	Spiked sample delivery	Determine sensor response to sample + known ^{99}Tc addition
4	Calculate E_m	Determine sensor efficiency for calculation of activity concentration of subsequent samples from net sensor count rate

The matrix spike addition run requires the operator to select a representative water sample that is closely matrix-matched to the samples that will be analyzed for ^{99}Tc (e.g., actual 200W P&T Plant Post-Resin treated plant water). This water sample will first be delivered to the sensor to obtain the ^{99}Tc count rate (unknown activity). Next, the system will perform a "spiked" measurement using the same water sample, but first adding a known volume of ^{99}Tc standard (V_{sp}) via the system's on-board ^{99}Tc standard reservoir. This "spiked" sample is then delivered through the ^{99}Tc sensor, and the new sensor response is recorded. The difference in count rate between the net spiked signal and the net unspiked signal is the sensor response to a known addition of ^{99}Tc. From this response, the measurement efficiency, E_m, can be calculated (see Eq. (1) through Eq. (3)).

The ^{99}Tc blank determination and matrix spike addition routines are accessed via the PMT Standardization form that resides under the Calibration Forms header of the main software page (Figure 13). This form allows the operator to specify the PMT data integration time (seconds), the activity concentration of the on-board ^{99}Tc standard (A_{sp}), and the conductivity of the on-board ^{99}Tc standard solution.[1] It also allows the operator to select which one of the eight data integration periods they would like to utilize in the final calculation of sensor response (upper left region of Figure 13). Periods 1–3 represent the count rates for the final three syringe deliveries to the sensor (counting under dynamic flow), and Periods 4–8 represent the post-delivery static count time, split into five even time segments. During all in-lab performance characterization studies, the operators have selected Periods 4–8 for data integration.



Integration Seconds 30
Spike Activity, Bq/mL 1.4783
Spike Conductivity 530
Spike Volume, mL 50
Sample Volume, mL 280
Diluted Spike Activity, Bq/mL 0.2639821

☐ Period 1
☐ Period 2
☐ Period 3
☑ Period 4
☑ Period 5
☑ Period 6
☑ Period 7
☑ Period 8

☐ Blank: PBO

Post Time Interval 14400
Total Stroke Count 14

Instance 1
Dry Creek Confluence

a 300b 40c 14x 600y 0z 4v 0

Figure 13. ^{99}Tc sensor calibration tool within the PMT Standardization form.

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[1] It is important to ensure that the water conductivity of the on-board ^{99}Tc standard approximates the typical water sample chemistry. This ensures similar sensor affinity to ^{99}Tc during calibration and sample analysis (i.e., E_m values are not biased due to more dilute ionic strength during calibration versus during routine measurements).

3.3.1 ^{99}Tc Sensor Calibration Using Water from the 699-49-100C Well

The Tc-Mon system's ^{99}Tc sensor was first blanked using City of Richland tap water, and subsequently calibrated using a matrix of uncontaminated Hanford groundwater (well 699-49-100C). The on-board ^{99}Tc calibration standard (1.478 Bq/mL; 39,950 pCi/L) was prepared in 699-49-100C water. Figure 14 (black trace) shows the PMT data output for the blank run. The dashed grey trace shows the sensor response to the unspiked water (0–475 min) followed by the matrix spiked water (475–950 min). There is virtually no difference in the ^{99}Tc sensor's response between the blank and the unspiked 699-49-100C groundwater, because neither of these samples contains ^{99}Tc.

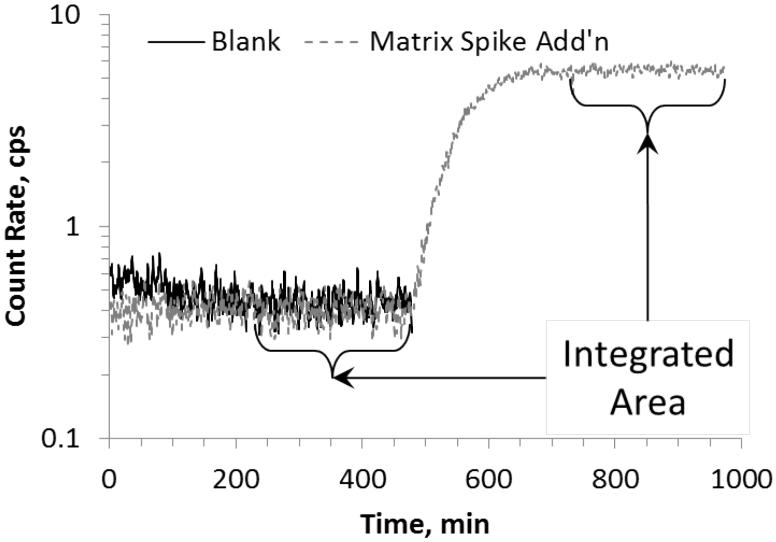

Figure 14. PMT trace of blank run and matrix spike addition runs for calibration performed in Hanford groundwater from well 699-49-100C. (5-pt smooth)

The ^{99}Tc sensor responses, as determined by the software, are shown in Table 9. Only count rate values 4–8 were utilized in the calculation of E_m, and the average sensor response is shown on the last line. Hand calculations of the average sensor response confirmed the proper treatment of the values via the Burge Environmental software. The equivalent sensor signal for count rate values 4–8 are indicated in Figure 14 as "Integrated Area."

The resulting E_m from this calibration was recorded as 19.1207 cps/(Bq/mL) by the software. Table 10 lists all the values involved in the determination of E_m. Hand calculations of all input values (via Eq. (1) through Eq. (3)) confirmed correct calculation of the E_m term.

Table 9. PMT count results of Tc-Mon system calibration using Hanford groundwater from well 699-49-100C.

Acquisition Interval	Pump Operation	Data Used in Final Calcs?	Blank (Tap H_2O) File 2050	699-49-100C File 2051	699-49-100C Matrix Spike File 2051
1	Dynamic	No	0.458	0.422	5.310
2			0.405	0.429	5.132
3			0.438	0.440	5.280
4	Static	Yes	0.449	0.397	5.435
5			0.425	0.400	5.435
6			0.445	0.416	5.498
7			0.445	0.412	5.510
8			0.449	0.412	5.428
		Average ± 1σ	**0.443 ± 0.010**	**0.407 ± 0.008**	**5.461 ± 0.039**

Table 10. Calculation of Tc-Mon sensor measurement efficiency (E_m) for Hanford groundwater matrix (well 699-49-100C).

Term	Equation Representation	Value	Units
Sample Vol.	V_s	280	mL
Spike Vol.	V_{sp}	50	mL
Spike Activity	A_{sp}	1.4783	Bq/mL
Post-Spiked Activity	$A_{matrixsp}$	0.2640	Bq/mL
Background Signal	---	0.4426	cps
Gross Sample Signal	---	0.4074	cps
Gross Spike Signal	---	5.4612	cps
Net Sample Signal	R_{eq}	-0.0352	cps
Net Spike Signal	$R_{eq,\ sp}$	5.0186	cps
Measurement Efficiency	E_m	19.1207	cps/(Bq/mL)

3.3.2 ^{99}Tc Sensor Calibration Using 200W P&T Plant Post-Resin Grab Sample Water

The ^{99}Tc sensor was also calibrated using actual 200W P&T Plant grab sample water (5/8/13 Post-Resin, sample B2PD59). The on-board ^{99}Tc calibration standard was the same as that described above. Figure 15, black trace, shows the PMT data output for the blank run (City of Richland tap water). The dashed grey trace shows the sensor response to the unspiked water (0–475 min) followed by the matrix spiked water (475–950 min). The ^{99}Tc sensor response to the 200W P&T Plant groundwater sample, which contained 0.0113 Bq/mL (306 pCi/L) ^{99}Tc,[1] is shown as a rise in sensor signal between 0 and ~180 min, followed by a plateau at that level.

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[1] As per analytical results provided by the Waste Sampling and Characterization Facility.

The software-summarized ^{99}Tc sensor responses are shown in Table 11. Again, only count rate values 4–8 were utilized in the calculation of E_m, and the average sensor response is shown on the last line. Hand calculations of the average sensor response confirmed the proper treatment of the values via the Burge Environmental software.

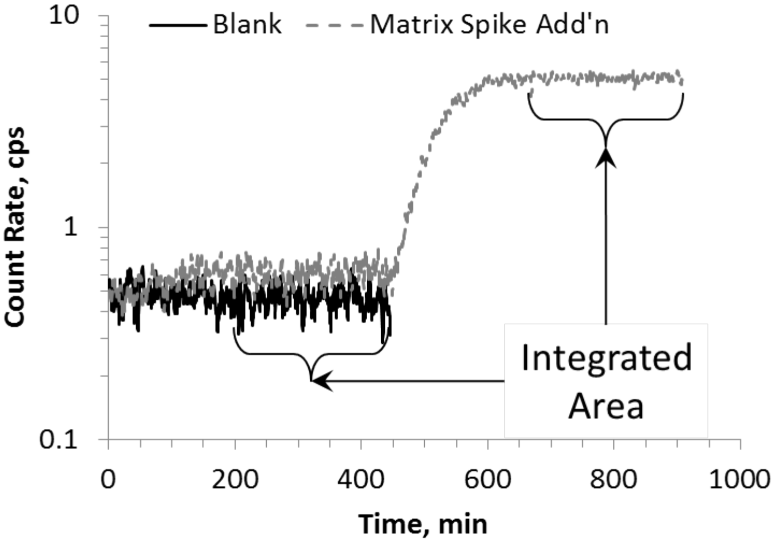

Figure 15. PMT trace of blank run and matrix spike addition runs for 200W P&T Plant 5/8/13 Post-Treat grab sample water.

The resulting software-generated E_m from this calibration was determined to be 17.067 cps/(Bq/mL). Table 12 lists all the values involved in the determination of E_m. Hand calculations of all input values (via Eq. (1) through Eq. (3)) confirmed correct calculation of the E_m term. Note that it is expected that the ^{99}Tc sensor will have a lower E_m for the 200W P&T Plant water than for the pristine groundwater. This is because the pristine groundwater from well 699-49-100C contains a lower level of dissolved solids than the contaminated 200W P&T Plant water. The pertechnetate anion's affinity to the sensor will be generally diminished when there is a higher concentration of anions (e.g., NO_3^-) in the groundwater [7]. Additionally, the 200W P&T Plant water contains ~50 μg/L hexavalent chromium, which has been shown to quench scintillation photons induced within the ^{99}Tc sensor [7]. Groundwater composition effects on the ^{99}Tc sensor are more thoroughly explored in section 4.3.2.

Table 11. Results of initial Tc-Mon system calibration using 200W P&T Plant 5/8/13 Post-Treat grab sample water (8/9/2013).

Acquisition Interval	Pump Operation	Data Used in Final Calcs?	Blank (Tap H_2O) File 2030	5/8/13 Post-Treat File 2031	5/8/13 Post-Treat Matrix Spike File 2031
1	Dynamic	No	0.451	0.585	4.971
2			0.445	0.622	4.958
3			0.455	0.615	5.064
4	Static	Yes	0.456	0.610	5.097
5			0.480	0.581	5.063
6			0.468	0.616	5.083
7			0.487	0.625	5.081
8			0.439	0.626	5.131
		Average	**0.466**	**0.612**	**5.091**
		± 1σ	**± 0.019**	**± 0.018**	**± 0.025**

Table 12. Calculation of Tc-Mon sensor measurement efficiency (E_m) for 200W P&T Plant 5/8/13 Post-Resin grab sample water.

Term	Equation Representation	Value	Units
Sample Vol.	V_s	280	mL
Spike Vol.	V_{sp}	50	mL
Spike Activity	A_{sp}	1.4783	Bq/mL
Post-Spiked Activity	$A_{matrixsp}$	0.2640	Bq/mL
Background Signal	---	0.466	cps
Gross Sample Signal	---	0.612	cps
Gross Spike Signal	---	5.091	cps
Net Sample Signal	R_{eq}	0.146	cps
Net Spike Signal	$R_{eq, sp}$	4.625	cps
Measurement Efficiency	E_m	17.067	cps/(Bq/mL)

3.3.3 ^{99}Tc Sensor Calibration Reproducibility

Fifteen days after the initial ^{99}Tc sensor calibration using the 200W P&T Plant Post-Resin grab sample was performed, a second matrix spike addition was performed on the same Post-Resin grab sample. This was to determine how consistent the E_m had remained over ~2 weeks and ~4 liters of sample passed through the sensor. The traces in Figure 16 show the similarity in sensor response between the two matrix spike additions. The two E_m determinations came within 1% of each other.

This performance comparison confirms several important points: 1) the Tc-Mon system is capable of highly reproducible volume deliveries in the on-board preparation of calibration solutions (spike delivery and acidification level); 2) the PMT coincidence detectors maintain stable sensitivities over time; and 3) the sensor packing media appears to be sufficiently rugged to resist fouling from filtered groundwater at the multi-liter scale.

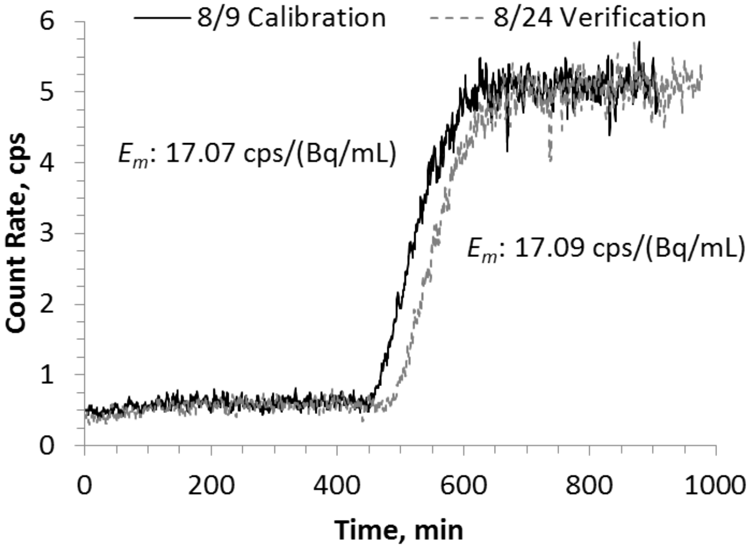

Figure 16. Comparison of PMT sensor traces between initial calibration (8/9/13) and follow-on matrix spike addition (8/24/13). Resulting E_m values are indicated. Spike additions performed on 200W P&T Plant 5-8-13 Post-Resin grab sample. (5-pt smooth)

4.0 Tc-Mon System Performance Characterization

Following calibration of the systems described above (Sampling Chamber, Conductivity Sensor, and ^{99}Tc Sensor), the Tc-Mon system was operated in a series of experiments to confirm calibration integrity and determine performance. The results of these performance characterization activities are presented below.

4.1 Sampling Chamber Characterization

Port 1 of the Tc-Mon system was connected to a container filled with Richland tap water. Next, the Sample Chamber form, under the Calibration Forms section of the main software page, was utilized to systematically fill the sampling chamber to each of the three level sensors and then purge the contents into a tared container. The water in the container was then gravimetrically determined and converted to volume via water density correction. The results of these triplicate measurements are listed in Table 13. This exercise illustrates that the Tc-Mon system's sampling chamber calibration tool is viable, and that the three level sensors are capable of accurate and precise delivery of solution.

Table 13. Evaluation of sampling chamber volume deliveries.

Level Sensor	Delivered H_2O Mass g	Delivered H_2O Volume mL$^{(a)}$	Ave. H_2O Vol., mL (± 1σ)	Programmed H_2O Vol., mL	Bias, %
Low	50.5	50.6	50.5 ± 0.1	**50**	1.2
	50.5	50.6			1.2
	50.3	50.4			0.8
Mid	278.7	279.4	279.2 ± 0.2	**280**	-0.2
	278.4	279.1			-0.3
	278.3	279.0			-0.4
Top	300.2	300.9	300.9 ± 0.0	**301.3**	-0.1
	300.2	300.9			-0.1
	300.2	300.9			-0.1

(a) H_2O temperature was 23.5 °C; corresponding density = 0.9975 g/mL.

4.2 Conductivity Sensor Characterization

Once calibrated, the Tc-Mon system's in-line conductivity sensor was evaluated against a series of conductivity solutions in an effort to determine the accuracy of the sensor, given the two-point calibration that was performed on it using NIST-traceable ~100 and 1000 µS/cm standards supplied by Fisher Scientific (see Table 6). The sensor's calibration was evaluated between the range of ~100 and 750 µS/cm (see Table 7). Solutions of 250, 500, and 750 µS/cm were prepared as dilutions of the 1000 µS/cm Fisher Scientific calibration standard; the 100 µS/cm standard was used as-is from Fisher Scientific. The results show that the in-line conductivity sensor is capable of accurate measurements within the calibration range.

4.2.1 Confirmation of Standard and 200W P&T Plant Sample Conductivities via Independent Conductivity Analyzer

The integrity of the Fisher Scientific NIST-traceable conductivity standards needed to be verified against an independent set of NIST-traceable conductivity standards in order to rigorously ensure its accuracy. Therefore, we obtained an independent set of NIST-traceable standards from Inorganic Ventures. Next, we calibrated an independent conductivity analyzer (GE Healthcare) using the 100 and 1000 μS/cm Fisher Scientific standards. The results of the calibration are shown in Table 14.

Table 14. Calibration of GE Healthcare benchtop conductivity analyzer.(a)

Certified Conductivity Value(b) μS/cm	Measured Value μS/cm	Slope	Intercept	R^2
0.0	11	1.0582	15.4746	0.9999
92.2	118			
945.0	1015			

(a) Calibration standards provided by Fisher Scientific, Lots CC11665 and CC11642.
(b) At 22.5 °C, certified values used from certificate at indicated temperature were used.

The Inorganic Ventures standards (100 and 1000 μS/cm) were then run against this calibration. The results are shown in the first two rows of Table 15. Agreement between the two standard sets was within 10%, confirming the integrity of the Fisher Scientific standards.

The previously prepared set of dilutions of the 1000 μS/cm Fisher Scientific standard (250, 500, and 750 μS/cm) were utilized. These solutions, as well as the 100 μS/cm Fisher Scientific standard, were analyzed using the GE Healthcare benchtop conductivity analyzer to verify solution conductivity. The results are shown in Table 15. The dilutions resulted in as-expected conductivity values, with agreement within 3% of the anticipated values. These are the same solutions used in the Tc-Mon conductivity sensor performance characterization study described above (Table 7).

The GE Healthcare conductivity analyzer was also used to determine the conductivities of the 200W P&T Plant grab samples that had been delivered to PNNL, as no other reference values were available (e.g., from the Waste Sampling and Characterization Facility (WSCF)). Table 16 provides the measured conductivities for 200W P&T Plant grab samples collected between May and August 2013 (plus Hanford groundwater from well 699-49-100C). The determined conductivity values in this table were subsequently used to determine the accuracy of the Tc-Mon's in-line sensor.

Table 15. Results of water conductivity check standards measured by GE Healthcare benchtop conductivity analyzer.

Standard ID µS/cm[a]	Conductivity, µS/cm		Bias, %	Comment
	Expected	Measured		
Independent[b] 100	96.8	92.2	-4.8	
Independent[b] 1000	953	961	0.8	
100	92.2	90.3	-2.1	Fisher Calib. Std.
250	250	252	0.7	Dil. Fisher Std.
500	500	497	-0.7	Dil. Fisher Std.
750	750	731	-2.5	Dil. Fisher Std.
1000	945	944	0.0	Fisher Calib. Std.

(a) At 22.5 °C
(b) Inorganic Ventures conductivity standards, Lots F2-COND01063 and E2-COND01012

Table 16. Conductivities of pristine Hanford groundwater from well 699-49-100C and 200W P&T Plant grab samples measured by GE Healthcare benchtop conductivity analyzer.

Sample ID	Measured Conductivity, µS/cm	Comment
699-49-100C	533 – 541[a]	Hanford Groundwater
5-8-13 Pre-Resin	637	B2PD56
6-4-13 Pre-Resin	635	B2PDH6
7-10-13 Pre-Resin	631	B2PT99
8-5-13 Pre-Resin	624	B2R1B7
5-8-13 Post-Resin	643	B2PD59
6-4-13 Post-Resin	646	B2PDJ0
7-10-13 Post-Resin	640	B2PTB3
8-5-13 Post-Resin	627	B2R1C0

(a) n = 4; Average ± 1σ = 535 ± 4 µS/cm.

4.2.2 Determination of Sample Conductivities via Tc-Mon Conductivity Sensor

The Tc-Mon's on-board conductivity sensor was evaluated for accuracy using a set of conductivity standards shown in Table 7. These standards enabled us to check the calibration of the sensor within a range of 100–750 µS/cm. The analytical bias between the certified values and the Tc-Mon's measured output was under 8%.

Between the dates of 7/12/13 and 9/18/13, the Tc-Mon conductivity sensor was utilized with its original calibration for all measurements. Each time the Tc-Mon performs a ^{99}Tc measurement, the conductivity of the water sample is measured and recorded by the Burge Environmental software. Table 17 lists the results from a series of Hanford groundwater (well 699-49-100C) sample conductivity measurements performed by the Tc-Mon sensor.[1] Here, it is observed that accuracy is excellent, with a maximum analytical bias of 8.1%.

Table 17. Results of Hanford groundwater 699-49-100C samples measured by the Tc-Mon system's conductivity sensor. Values obtained during ^{99}Tc measurement routines.

		Conductivity, µS/cm		
File ID	^{99}Tc Conc. pCi/L	Independent Meas.	Tc-Mon Meas.	Bias, %
2052	0	535 ± 4[(a)]	553	3.3
2053	90		545	1.8
2054	180		519	-3.1
2055	540		568	6.2
2056	900		547	2.1
2057	1800		575	7.5
2058	2700		572	6.8
2059	270		545	1.7
2060	0		579	8.1

(a) Value determined by GE Healthcare conductivity analyzer using unspiked groundwater (see Table 16).

Table 18. Results of 200W P&T Plant grab samples measured by the Tc-Mon system's conductivity sensor. Values obtained during ^{99}Tc measurement routines.

	Conductivity, µS/cm				
Sample ID	Independent Meas.[(a)]	Tc-Mon Meas.	n[(b)]	Bias, %	Comment
699-49-100C	535 ± 4	569 ± 16	6	6.2	Hanford groundwater
5-8-13 Pre-Resin	637	671	1	5.4	B2PD56
6-4-13 Pre-Resin	635	659	1	3.8	B2PDH6
7-10-13 Pre-Resin	631	655 ± 23	2	3.9	B2PT99
8-5-13 Pre-Resin	624	657 ± 1	2	5.4	B2R1B7
5-8-13 Post-Resin	643	683 ± 15	3	6.2	B2PD59
6-4-13 Post-Resin	646	695 ± 3	3	7.6	B2PDJ0
7-10-13 Post-Resin	640	666 ± 17	3	4.0	B2PTB3
8-5-13 Post-Resin	627	670 ± 4	3	6.7	B2R1C0

(a) GE Healthcare conductivity analyzer result (see Table 16).
(b) When n = 2, deviation is the absolute difference between the two measurements.

PNNL researchers received four sets of Pre-Resin and Post-Resin samples from monthly sampling events at the 200W P&T Plant between the dates of 5/8/13 and 8/5/13. Next, the Tc-Mon's conductivity sensor results were evaluated against 200W P&T Plant grab samples, whose conductivity values were determined by the independent conductivity analyzer (see Table 16). The results of the Tc-Mon analyses

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[1] Groundwater samples were spiked with ^{99}Tc to the indicated activity concentration. Independent conductivity measurements confirmed that the ^{99}Tc spike did not significantly affect the sample conductivity (< 6.5%).

are shown in Table 18. Replicate measurements (when obtained) indicated good precision, and the analytical bias, as compared to the independently determined conductivity values, were all within 8%.

4.3 ^{99}Tc Sensor Characterization

4.3.1 ^{99}Tc Sensor Evaluation with Hanford Groundwater (Well 699-49-100C) Matrix Calibration

The ^{99}Tc sensor was calibrated using Hanford groundwater from well 699-49-100C, as described in section 3.3.1. Next, a series of ^{99}Tc standards, prepared in the same groundwater matrix, were systematically processed through the Tc-Mon system's ^{99}Tc measurement routine. The time-based data traces from the sensor are shown in Figure 17. The traces are listed in the order in which they were processed through the sensor. For example, the blue "0" pCi/L sample began immediately following the matrix spike addition calibration run, so the data trace begins at the ^{99}Tc spike signal (~5 cps) and then drops to the baseline level as the ^{99}Tc sensor re-equilibrates to the non-^{99}Tc bearing solution. Subsequently, the sensor signals steadily rise as the ^{99}Tc standards delivered through it increase in activity concentration. Then, after 2700 pCi/L, the ^{99}Tc standard drops 10x to 270 pCi/L, which is observable by the drop in the mauve trace.

Figure 17 also indicates approximately which time zone is involved in active delivery of sample to the sensor (dynamic), and which zone is involved in static counting of the ^{99}Tc sensor. For this series of analyses, the static count time was configured to be 4 hours (same as the blank and calibration static time periods).

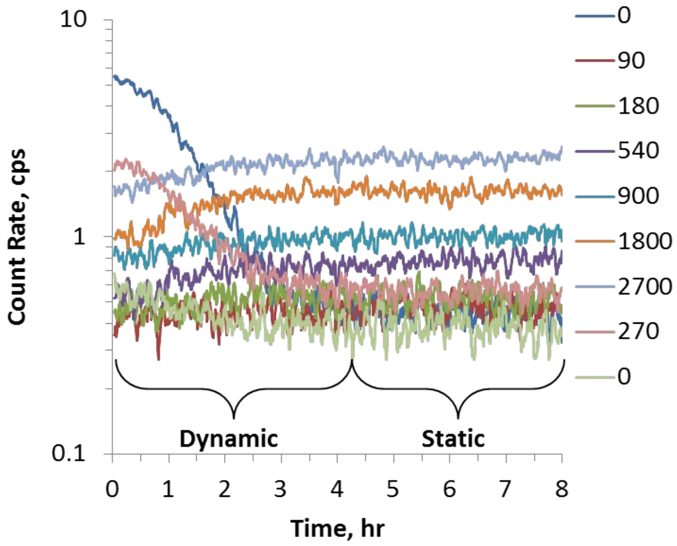

Figure 17. PMT traces of a series of ^{99}Tc standards processed in the Tc-Mon system's ^{99}Tc sensor. Legend indicates ^{99}Tc activity concentration (pCi/L) and is listed in run order. Braces indicate approximate times between active (dynamic) flow of sample to the sensor, and stopped-flow (static) counting conditions. (7-pt smooth)

Figure 18 provides a clearer view, with cumulative detector time, of the sensor response to the final three ^{99}Tc standards, shown in Figure 17, that were processed in this experimental set. Here, it is clear that the ^{99}Tc sensor is capable of full re-equilibration between each delivered sample, even when the decrease in ^{99}Tc concentration drops ten-fold.

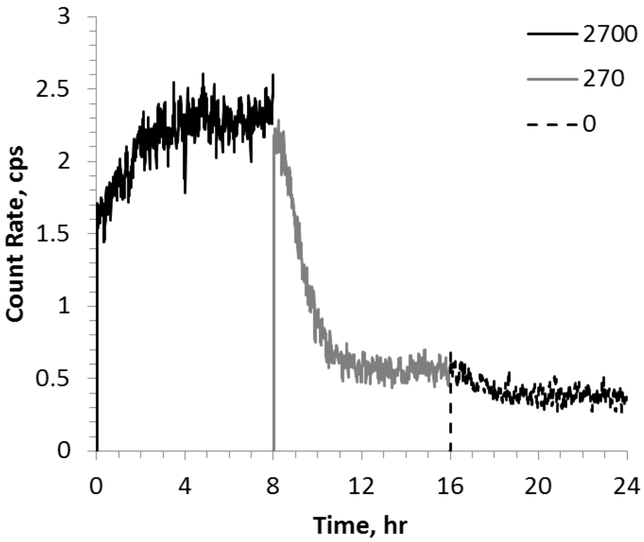

Figure 18. PMT traces of three ^{99}Tc standards delivered through the ^{99}Tc sensor in run order: 2700→270→0 pCi/L. (7-pt smooth)

The Burge Environmental software determines ^{99}Tc activity concentration, as Bq/mL, via Eq. (1), which is simply the net count rate of the sensor (integrated during the static counting interval) divided by the E_m. Figure 19 plots the net count rates of the ^{99}Tc sensor across all samples analyzed in this set. The slope of the linear regression, 18.671 cps/(Bq/mL), is in excellent agreement with the originally determined E_m value of 19.121 cps/(Bq/mL) (see Table 10).

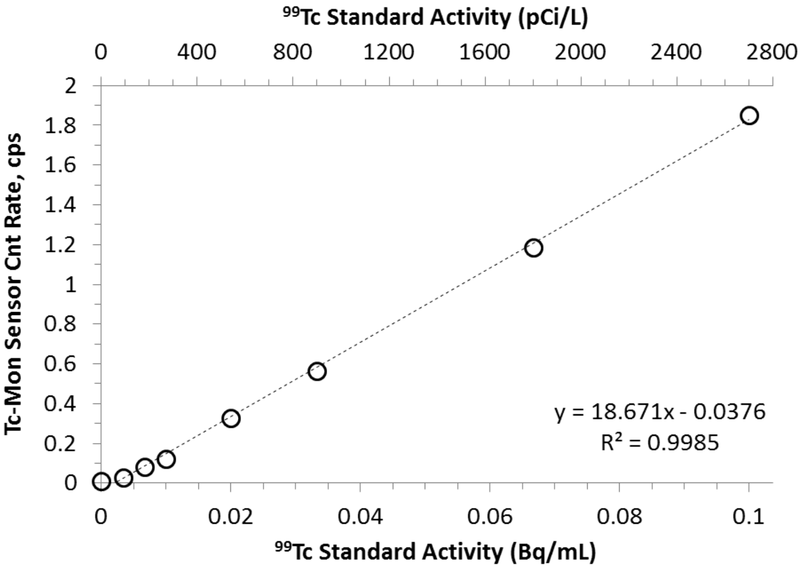

Figure 19. Net ^{99}Tc sensor count rates of blank and ^{99}Tc check standards prepared in Hanford groundwater 699-49-100C.

The ^{99}Tc activity concentrations determined by the Tc-Mon for this sample set are listed in Table 19, in units of both Bq/mL and pCi/L. This table also lists analytical bias for all samples, which is the percent difference between the Tc-Mon reported values and the known ^{99}Tc concentrations as per the PNNL Radiochemical Processing Laboratory (RPL) standards laboratory documented values.

Table 19. Results of ^{99}Tc standards in 699-49-100C groundwater, measured by the Tc-Mon system's ^{99}Tc sensor, calibrated using Hanford groundwater from well 699-49-100C.

	^{99}Tc, Bq/mL		^{99}Tc, pCi/L		
File ID	^{99}Tc Std Value$^{(a)}$	Tc-Mon Meas.	^{99}Tc Std Value$^{(a)}$	Tc-Mon Meas.	Bias, %
2052	0	0.0007	0	18	---
2053	0.0033	0.0015	90	40	-55.1
2054	0.0067	0.0042	180	114	-36.9
2055	0.0200	0.0172	540	465	-13.9
2056	0.0333	0.0296	900	799	-11.2
2057	0.0666	0.0620	1800	1674	-7.0
2058	0.0999	0.0969	2700	2618	-3.0
2059	0.0100	0.0064	270	174	-35.6
2060	0	-0.0031	0	-85	---

(a) ^{99}Tc standards prepared from NIST-traceable solution; prepared by RPL standards laboratory.

Based on the negative blank reading from the final groundwater sample listed in Table 19 (-0.0031 Bq/mL, or -85 pCi/L), it was suspected that there was a drop in the background count rate of the ^{99}Tc sensor during the analysis of the ^{99}Tc standard set. Baseline drift has been a noted problem during the in-lab study, as can be observed in Figure 20. It is suspected that the ever-changing radiation environment within the 325 Building research facility is responsible. During prior studies, it was observed that the sensor baseline count rate was ~1 cps in RPL, and dropped to ~0.2 cps when the same system was deployed at the 200W-ZP-1 Interim Pump & Treat Plant. Therefore, it is suspected that our analytical results are being adversely impacted from other radiological activities ongoing in the 325 Building. However, during these in-lab studies, it is impossible to attribute the baseline float to either the background radiation environment or some instability in the sensor PMTs. Absolute determination of PMT signal stability will need to be determined once the Tc-Mon system has been deployed at the 200W P&T Plant.

Utilizing the same ^{99}Tc calibration parameters (baseline count rate and E_m), the Tc-Mon ^{99}Tc standard analysis set (from Table 19) was continued for several additional runs. Table 20 shows the follow-on ^{99}Tc analysis results, with a continuation of large negative analytical bias (see "^{99}Tc" columns). The results include four new blank groundwater runs (shown in right circle of Figure 20), each of which has a closely clustered background analysis result that is lower than the initial background cluster of 0.4422 ± 0.0109 cps (left circle). The new background count rates average to 0.3865 ± 0.0042 (n = 4). If this new background count rate is applied to the results in Table 20, then the analytical biases become substantially lower (see "Bkgd Adjusted ^{99}Tc" columns). This is further exemplified graphically in Figure 21, where (○) represents the analytical biases in Table 19, while (□) indicates the background-adjusted results in Table 20.

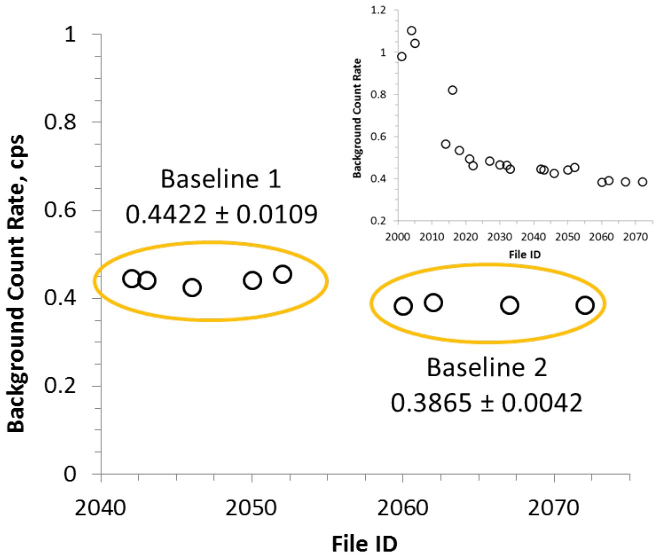

Figure 20. Observed ^{99}Tc sensor background count rates across all blank runs during in-lab studies on ^{99}Tc standards in Hanford groundwater. Inset: All background count rates observed during entire in-lab study.

Table 20. Continuation of ^{99}Tc sensor measurements. Impact of drifting sensor background count rate (initial background count rate = 0.4426 cps).

			^{99}Tc, pCi/L		Bkgd Adjusted ^{99}Tc, pCi/L[(b)]	
File ID	^{99}Tc Std Value, pCi/L[(a)]	Background Count Rate, cps	Tc-Mon Meas.	Bias, %	Tc-Mon Meas.	Bias, %
2060	0	0.3828	-85	---	-5	
2061	270		162	-40.0	241	-10.6
2062	0	0.3924	-71	---	8	---
2063	180		77	-57.0	157	-12.9
2064	270		138	-48.8	218	-19.4
2065	540		366	-32.2	446	-17.5
2067	0	0.3862	-80	---	0	---
2068	900		705	-21.7	784	-12.9
2069	90		-1	-101	78	-13.2
2070	180		54	-70.2	133	-26.1
2071	270		142	-47.5	221	-18.2
2072	0	0.3846	-82	---	-3	---

(a) ^{99}Tc standards prepared from NIST-traceable solution; prepared by RPL standards laboratory.

(b) Samples corrected for sensor baseline count rate drop to 0.3865 cps.

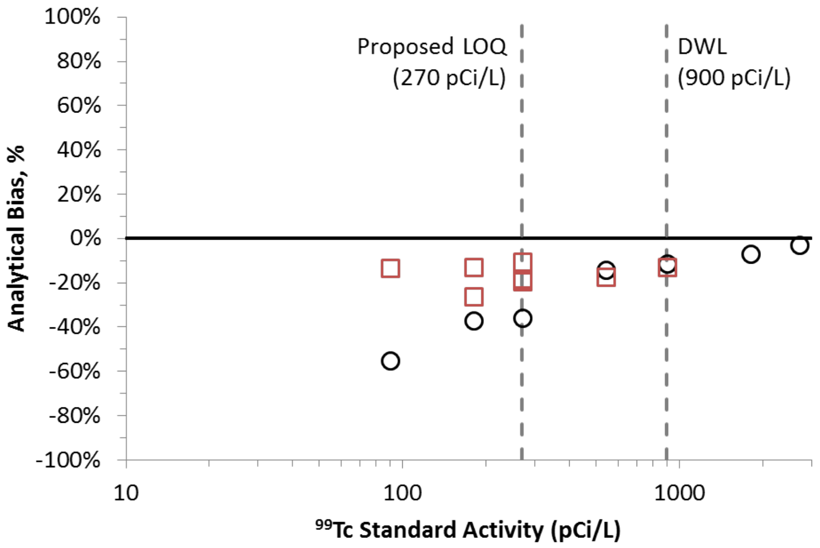

Figure 21. Analytical biases for ^{99}Tc sensor as a function of ^{99}Tc standard activity concentration. Original ^{99}Tc standard analysis series results (○); follow-on analysis series, background-adjusted results (□). The suggested LOQ[1] and ^{99}Tc drinking water limit (DWL) are shown.

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[1] Limit of quantification (LOQ) is defined in section 5.0.

Table 21 summarizes the overall performance of the ^{99}Tc sensor for the entire ^{99}Tc standard analysis set, considering the revised background count rate corrections discussed above. The precision and accuracy of the analytical results indicated in this table forms the basis of the determination of the ^{99}Tc sensor LOQ, as is discussed in section 5.0.

Table 21. Overall precision and accuracy of ^{99}Tc sensor following background drift and subsequent correction.

			Bkgd Adjusted ^{99}Tc, pCi/L	
^{99}Tc Std Value[(a)]	n[(b)]	Background Count Rate, cps (± %)	Tc-Mon Meas. (± %)	Bias, %
0	4	0.3828 ± 0.0042 (± 1.1%)	---	---
90	1		78	-13.1
180	2		145 ± 24 (± 16.6%)	-19.5
270	3		227 ± 13 (± 5.7%)	-16.1
540	2		455 ± 19 (± 4.2%)	-15.7
900	2		791 ± 15 (± 1.9%)	-12.1
1800[(c)]	1		1674	-7.0
2700[(c)]	1		2618	-3.0

(a) ^{99}Tc standards prepared from NIST-traceable solution; prepared by RPL standards laboratory.
(b) When n = 2, deviation is the absolute difference between the two measurements. Otherwise, deviation is reported as ± 1σ.
(c) Values not affected by background drift.

4.3.2 200W P&T Plant Grab Sample Contaminants

PNNL researchers received four sets of Pre-Resin and Post-Resin samples from monthly sampling events at the 200W P&T Plant between the dates of 5/8/13 and 8/5/13. ^{99}Tc activity concentrations for each grab sample were provided by CHPRC.[1] The WSCF analytical results were used as the ^{99}Tc reference values in the present study. *It is therefore important to note that any bias in the ^{99}Tc analytical results from WSCF will directly affect the reported ^{99}Tc sensor analytical biases.*

Table 22 summarizes the radionuclides measured in each sample, as reported by WSCF. The analytical procedure utilized by WSCF for determining total ^{99}Tc is listed as Document LA-438-402 [10].

Table 22. Groundwater radionuclide concentrations, as reported by WSCF.

Sample ID	Activity Conc., pCi/L			Mass Conc., µg/L	
	^{3}H	^{99}Tc	^{129}I	U	Cr(VI)
5-8-13 Pre-Resin	8500	1496	< 0.226	2	57.9
6-4-13 Pre-Resin	8000	1500	0.317	1.93	56.6
7-10-13 Pre-Resin	7700	1500	0.232	1.79	56.1
8-5-13 Pre-Resin	8800	1700	< 0.238	1.6	54.1
5-8-13 Post-Resin	8200	306	< 0.195	1.89	48.8
6-4-13 Post-Resin	7800	230	< 0.240	2.01	49.8
7-10-13 Post-Resin	7400	330	< 0.221	1.83	47.7
8-5-13 Post-Resin	8200	400	< 0.210	1.61	35.9

As can be seen in Table 22, these samples contain ~8000 pCi/L tritium (^{3}H). This activity level is of no concern, as the ^{99}Tc sensor can neither concentrate ^{3}H onto its sorbent, nor can it measure the low energy β-emissions from ^{3}H. Previously, PNNL confirmed the lack of sensor response to ^{3}H by delivering a solution containing ~15 Bq/mL (~400,000 pCi/L) ^{3}H through the sensor. The sensor did not respond to this activity concentration [7].

Iodine-129 exists at < 1 pCi/L in the 200W P&T Plant water. ^{129}I, likely found at least partially as the iodide anion (^{129}I^{-}) [11], is concentrated onto the ^{99}Tc sensor, but is retained to a lesser degree than pertechnetate. Additionally, ^{129}I has a significantly lower energy β emission than ^{99}Tc. PNNL previously established that the sensitivity of the ^{99}Tc sensor to ^{129}I^{-} (i.e., the relative E_m for ^{129}I^{-}) was ~30 times lower than that observed for ^{99}Tc [7]. Therefore, the trace level of ^{129}I in the 200W P&T Plant water is of little concern.

Uranium is present in 200W P&T Plant water at ~2 µg/L. No isotopic data was provided; we will assume here that it is predominantly natural U. Assuming it is natural U, this is equivalent to only ~2 pCi/L of alpha activity (excluding progeny). Due to the short range of α particles in aqueous media, no measurable interaction between the α particles and scintillating particles is expected. It was previously observed that U caused no sensor response when it was present at activities exceeding that of ^{99}Tc in groundwater [7].

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[1] Each month, duplicate grab samples were collected and analyzed at WSCF. CHPRC then provided the ^{99}Tc analytical results to PNNL.

Hexavalent chromium, likely found as the divalent chromate anion (CrO_4^{-2}), is present in 200W P&T Plant waters at levels exceeding 50 µg/L. As was documented in [7], chromate has an affinity for the anion exchange component in the ^{99}Tc sensor (originally measured at ~4x the affinity of pertechnetate). As chromate concentrates onto the sensor, it is possible that the sensor's scintillation signal will be quenched due to the absorption of scintillation-induced photons by the metal anion (chromate absorbs at ~375 nm). PNNL demonstrated that quench of the ^{99}Tc sensor was proportional to the concentration of chromate in the sample. It was determined that a solution containing 300 µg/L chromate (~5 - 6x higher than is present in 200W P&T Plant water) resulted in a 37% decrease in ^{99}Tc E_m. Therefore, at the present 200W P&T Plant water chromate concentrations, it can be anticipated that the ^{99}Tc sensor loses an estimated 5 - 10% sensitivity due to the presence of this contaminant. At this time, it does not appear that this would represent a significant loss in ^{99}Tc sensor performance.

One radioactive element of concern regarding the ^{99}Tc sensor that is not reported by WSCF is radon. It has been reported that groundwater from deep wells drilled into the Priest Rapids Formation below the Hanford Site contain between 108 and 225 pCi/L ^{222}Rn [12]. With a half-life of 3.8 days, ^{222}Rn is the daughter of ^{226}Rn and progeny of ^{238}U. Given the short duration of time between groundwater extraction and delivery to the 200W P&T Plant, the groundwater is expected to still contain radon gas that has emanated from both the upper and lower aquifers under the 200 West Area. During evaluation of the ^{99}Tc sensor performance on the prototype Tc-Mon system at the 200W-ZP-1 Interim Pump & Treat Plant, we observed that radon gas caused a positive bias on the ^{99}Tc sensor output. It was hypothesized that the ^{222}Rn was adsorbing onto the organic scintillator within the ^{99}Tc sensor, thus producing excess scintillation events. To solve the problem with radon, PNNL researchers retrofitted the prototype system to produce an air sparge of the sample immediately following delivery of the water to the sampling chamber. We found that sparging for 20 minutes, immediately prior to delivery of the water sample to the ^{99}Tc sensor, eliminated the radon-induced positive bias. The current Tc-Mon system has been fitted with a sparging system to ensure that radon gas does not affect ^{99}Tc analysis quality.

4.3.3 ^{99}Tc Sensor Evaluation with 200W P&T Plant Post-Resin Grab Sample Matrix Calibration

The ^{99}Tc sensor was originally calibrated using 200W P&T Plant Post-Resin grab sample that was collected on 5/8/13 (E_m = 17.07 cps/(Bq/mL), Table 12). Later, a second analysis set was performed using a matrix spike calibration on a Post-Resin grab sample that was collected on 8/5/13 (E_m = 14.81 cps/(Bq/mL). Between these two calibration dates, approximately 60 samples were processed through the sensor, which represented approximately 15 liters of groundwater. The observed drop in E_m between the two calibrations is due to gradual sensor fouling that occurred between these dates. Sensor fouling is described further in section 6.0.

In two analysis campaigns, 200W P&T Plant grab samples were analyzed randomly by the ^{99}Tc sensor. The net ^{99}Tc sensor count rate results for each sample (Pre-Resin and Post-Resin samples plus a series of Hanford groundwater "blanks") are shown in Figure 22. Count rates of the first analysis campaign are indicated as (**○**), while those of the second analysis campaign are indicated as (**□**). A linear regression of the first set of measurements results in the line y = 15.833x - 0.0215 (R^2 = 0.996). The slope of the line should agree with the calibration factor, E_m, for that set of measurements (17.07 cps/(Bq/mL)). Indeed, the regression slope is 7.3% lower than the E_m. A linear regression of the second set of measurements results in the line y = 14.392x - 0.0002 (R^2 = 0.999). Once again, the slope of the line should agree with the calibration factor, E_m, for that set of measurements (14.81 cps/(Bq/mL)). For this set of measurements, the regression slope is 2.8% lower than the E_m. This indicates that the ^{99}Tc sensor is responding to the 200W P&T Plant groundwater samples in a linear fashion through the full range of ^{99}Tc concentrations present in these samples.

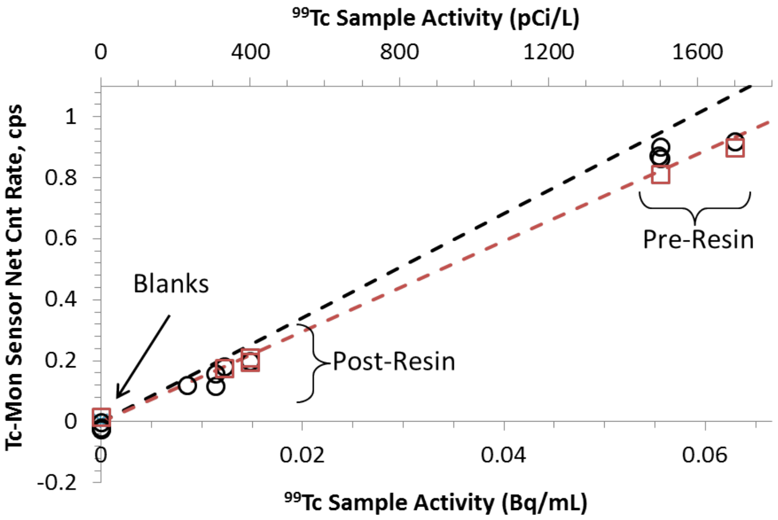

Figure 22. Net ^{99}Tc sensor count rates of blank and 200W P&T Plant grab samples (Pre- and Post-Resin) collected between May and August 2013. Black and red lines indicate the calibration parameters (E_m) for the first and second analysis campaigns (E_m = 17.07 and 14.81 cps/(Bq/mL), respectively). Groundwater measurement results following the first and second calibrations are indicated as (○) and (□), respectively.

The Tc-Mon-generated ^{99}Tc analytical results for the two analysis sets are shown in Table 23. Additionally, Figure 23 plots the ^{99}Tc analytical bias for each measured 200W P&T Plant grab sample. The mean analytical biases for all Pre-Resin and Post-Resin sample analyses (as compared to WSCF reported results) were observed to be -6.7 ± 4.6% and -14.3 ± 11.2%, respectively. Note that the Post-Resin analysis set contains a distinct “flyer” of -39%. This result corresponds to the final analysis of the 5/8/13 Post-Resin grab sample in the first analysis series; the result was likely caused by a change in the ambient radiation field in the laboratory. Unfortunately, a sensor background run was not performed immediately following this analysis to confirm the hypothesis. Excluding this point, the mean 200W P&T Plant Post-Resin sample analytical bias is reduced to -11.3 ± 7.0%.

Table 23. Results of 200W P&T Plant grab samples measured by the Tc-Mon system's ^{99}Tc sensor, calibrated using the 5/8/2013 Post-Resin grab sample.

	^{99}Tc, Bq/mL		^{99}Tc, pCi/L				
Sample ID	WSCF Meas.	Tc-Mon Meas.	WSCF Meas.	Tc-Mon Meas.	n[(a)]	Bias, %	Comment
699-49-100C	---	-0.0013 ± 0.0007	---	-35 ± 19	6	---	Hanford Groundwater
5-8-13 Pre-Resin	0.0554	0.0512	1496	1383	1	-7.5	B2PD56
6-4-13 Pre-Resin	0.0555	0.0529	1500	1429	1	-4.7	B2PDH6
7-10-13 Pre-Resin	0.0555	0.0527 ± 0.0043	1500	1424 ± 115	2	-5.1	B2PT99
8-5-13 Pre-Resin	0.0629	0.0573 ± 0.0048	1700	1549 ± 130	2	-8.9	B2R1B7
5-8-13 Post-Resin	0.0113	0.0081 ± 0.0024	306	220 ± 64	2	-28.2	B2PD59
6-4-13 Post-Resin	0.0085	0.0071	230	192	1	-16.6	B2PDJ0
7-10-13 Post-Resin	0.0122	0.0113 ± 0.0013	330	304 ± 35	2	-7.8	B2PTB3
8-5-13 Post-Resin	0.0148	0.0133 ± 0.0012	400	360 ± 32	4	-10.1	B2R1C0

(a) When n = 2, deviation is the absolute difference between the two measurements.

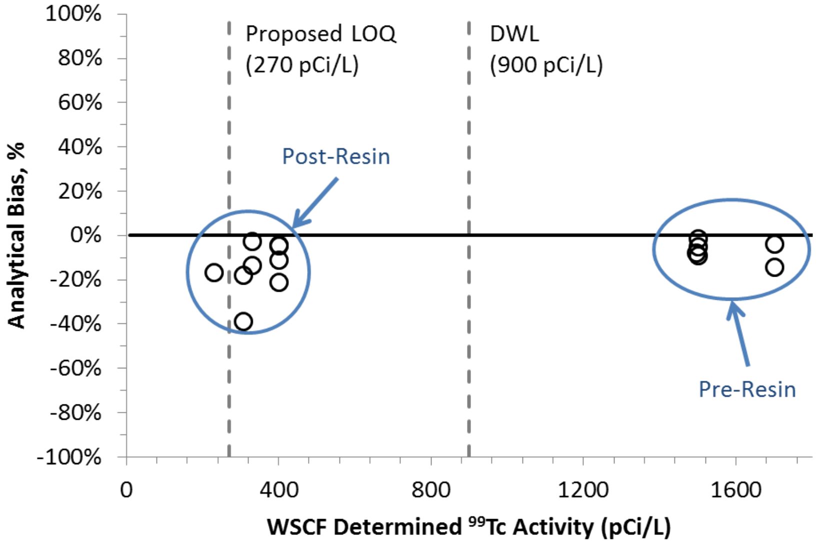

Figure 23. Analytical biases for ^{99}Tc sensor measurements as compared to WSCF reported ^{99}Tc activity concentrations. The suggested LOQ[1] and ^{99}Tc DWL are shown.

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[1] LOQ is defined in section 5.0.

5.0 Minimum Detectable Activity and Limit of Quantification

The ^{99}Tc analytical system minimum detectable activity (MDA) is determined by a number of parameters: 1) equilibrium sensor data integration time (t, sec), 2) background count rate (C_b, cps), and 3) equilibrium sensor measurement efficiency (E_m). In radioactivity measurements, the detection limit in counts, L_d, for the 95% confidence level is given by the Currie Equation [13]:

$$L_d = 4.653\sqrt{C_b \cdot t} + 2.706 \tag{5}$$

where C_b is the background count rate (cps) of the detector and t is the signal acquisition (count) time. The MDA of the analytical system, Eq. (6), is almost identical in form to Eq. (1); the only difference is that the L_d per count time, t, is substituted for the net count rate from a sample at equilibrium, R_{eq}:

$$MDA_{(Bq/mL)} = \frac{\left(\frac{L_d}{t}\right)}{E_m} \tag{6}$$

Figure 24 illustrates an MDA curve generated from the results of a Tc-Mon ^{99}Tc calibration routine performed on the 200W P&T Plant grab sample (see Table 12 for parameters utilized in this calculation). Given the observed background count rate (C_b) of 0.466 cps and measurement efficiency (E_m) of 17.07 cps/(Bq/mL), the MDA curve can be generated as a function of detector acquisition time.

For reasons discussed above, the MDA curve shown in Figure 24 is unique to the in-laboratory validation study at PNNL, and will not be the same once the Tc-Mon system is installed at the 200W P&T Plant. Some of the important factors that influence the C_b, E_m, and, subsequently, the MDA are as follows:

- Sensor packing composition
- Sample water acidification level
- Sensor packing density
- PMT background count rate
- Sensor age
- PMT temperature
- Sample water chemistry
- Detector acquisition time

The MDA for ^{99}Tc detection can be most easily decreased by 1) increasing the count time, t; 2) decreasing the PMT background signal, C_b (e.g., via additional sensor shielding); and 3) adjusting the equilibrium sensor column volume or altering the sorbent/scintillator ratio to ensure a higher degree of concentration of ^{99}Tc within the sensor column. Data integration time, t, greatly affects the MDA over relatively short count times, but the advantages are asymptotically decreased as count times are increased.

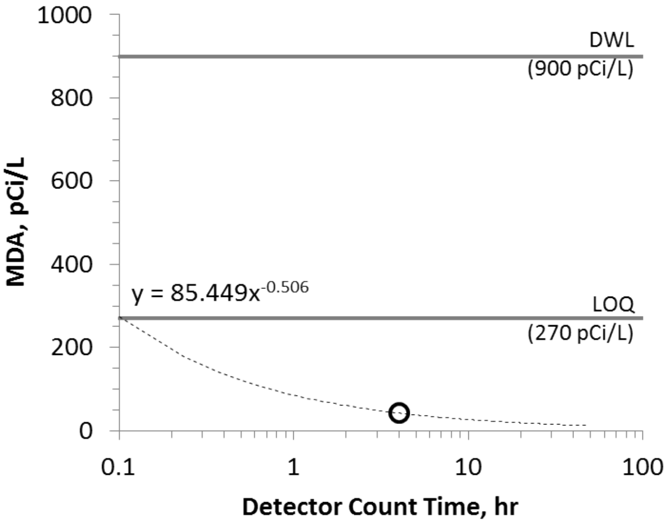

Figure 24. MDA curve for Tc-Mon calibration performed 8/9/13, using 200W P&T Plant Post-Resin water. Black circle indicates the MDA (42 pCi/L) achieved at a 4-hour static count time. The horizontal lines indicate ^{99}Tc activity concentrations of the DWL (900 pCi/L) and the estimated LOQ.

In PNNL-90778 [9], the estimated LOQ for the ^{99}Tc sensor was approximated as 270 pCi/L. It was defined as being three times the MDA, where the MDA would be a maximum of 90 pCi/L ^{99}Tc. Here, we determined an MDA of 42 pCi/L,[1] approximately 50% lower than was originally estimated. However, the instability of the sensor's background signal during in-lab studies causes us to maintain the conservative 90 pCi/L MDA value for the time being.

Based on the analytical biases documented in Figure 21 and Figure 23, 270 pCi/L appears to be a fairly accurate estimation of LOQ, at least for the in-lab studies. At this level, the average analytical bias is within 20%, and the measurement precision is < 6% (Table 21). The next lower activity ^{99}Tc standard evaluated was 180 pCi/L. At this lower level, the analytical bias averaged right at 20%, and the precision was significantly degraded, to ± ~17%. The LOQ will be re-determined once the Tc-Mon is deployed and operated at the 200W P&T Plant. If the ^{99}Tc sensor PMTs produce a lower and more stable background count rate, as is currently anticipated, it is possible that the LOQ of the deployed system will be lowered.

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[1] Based on a 4-hour static detector count time.

6.0 Chemical and Radiological Influences on the ^{99}Tc Sensor

The chemical and radiological influences that affect the ^{99}Tc sensor performance are described in PNNL-90778 [9]. Section 4.3.2 of this report also discusses the likelihood that the radiological and chemical groundwater constituents present in 200W P&T Plant waters will adversely affect the ^{99}Tc sensor.

The prior PNNL report likewise describes sensor fouling and anticipated lifetime, as per prior experience in the 200W-ZP-1 Interim Pump & Treat Plant. The originally determined sensor fouling rate was -0.22 E_m units per ^{99}Tc measurement. During the current in-lab testing of ^{99}Tc standards (in water from well 699-49-100C) and 200W P&T Plant grab samples, degradation of the sensor was observed to be very gradual, as can be seen in Figure 25, where E_m values are plotted as a function of the cumulative number of measurement cycles delivered through the sensor. Eighty analysis cycles (equivalent to ~20 liters of sample volume) were performed on a single ^{99}Tc sensor packing over the course of this study. The (○) represent calibrations using pristine Hanford groundwater, and the (□) represent calibrations made on 200W P&T Plant grab samples. For comparison, the dashed line overlay represents the previously observed sensor degradation rate (y = -0.22x) when the prototype Tc-Mon system was deployed at the 200W-ZP-1 Interim Pump & Treat Plant.

Clearly, the in-lab performance characterization study resulted in sensor degradation rates that are far more gradual than what was previously observed during the in-plant setting. The exact reason for this is not known. The prior deployment utilized 5 μm cartridge filters (Pentek GS-10 SED/5) at the water source, and a 13 mm diameter 0.45 μm polyethersulfone membrane filter (Thermo Scientific) was installed immediately prior to the ^{99}Tc sensor fluid inlet line. It should be reiterated that in the present study, all solutions were filtered to 0.45 μm prior to use, and a 13 mm diameter 2.7 μm glass fiber filter disc was installed immediately prior to the ^{99}Tc sensor fluid inlet line. This highly filtered water may have substantially decreased the sensor fouling rate. Additionally, the presence of the secondary glass fiber filter immediately prior to the ^{99}Tc sensor inlet may have removed trace organic contaminants that are the likely cause of sensor fouling (the glass fiber filter turned yellow-brown over time).

The true sensor fouling rate will need to be determined once the Tc-Mon system is deployed at the 200W P&T Plant and has operated for a period of time.

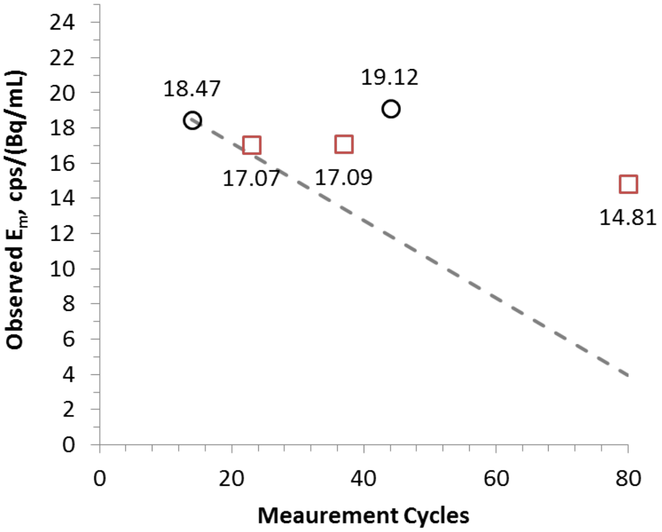

Figure 25. Observed E_m values from the ^{99}Tc sensor as a function of the number of measurements through the system. Hanford groundwater from well 699-49-100C calibration (○); 200W P&T Plant grab sample calibration (□). Dashed line represents previously observed sensor fouling rate of -0.22 E_m per measurement cycle.

7.0 Conclusions

A ^{99}Tc Process Monitoring System has been designed and constructed for deployment at the 200W P&T Plant. The system will be ultimately utilized by CHPRC to periodically monitor the breakthrough of ^{99}Tc from the Plant's primary extraction columns. The system was delivered to PNNL for an in-lab performance evaluation during the summer months of 2013. During this period, PNNL evaluated the performance of the Tc-Mon system against ^{99}Tc spiked groundwater standards and contaminated groundwater samples from the 200W P&T Plant. The in-lab Tc-Mon performance characterization results for the three calibrated components (Sampling Chamber, Conductivity Sensor, and ^{99}Tc Sensor) are briefly summarized below.

7.1 Sampling Chamber

The Sampling Chamber contains three conductivity-based level sensors that enable pre-determined volumes of ^{99}Tc spike, groundwater sample, and reagent (e.g., acid) to be added and subsequently mixed prior to delivery of the prepared sample to the ^{99}Tc sensor. The results indicate that delivered solution volumes to the Sampling Chamber are highly precise and accurate; this indicates that run-to-run variation of groundwater sample preparation (sample volume, acidification level) and calibration standard preparation (^{99}Tc standard addition) is small. These observations result from triplicate tests at each level sensor. Measurement precision for the Low, Mid, and Top level sensors were 0.20%, 0.07%, and < 0.01%, respectively. Accuracy for the Low, Mid, and Top level sensors were 1.2%, -0.4%, and -0.1%, respectively.

7.2 Conductivity Sensor

The Tc-Mon system records the conductivity of a water sample either on demand or at the onset of each ^{99}Tc analysis. The conductivity sensor was calibrated using NIST-traceable standards. A series of check standards were subsequently analyzed by the calibrated sensor, and excellent measurement accuracy was observed. Throughout the course of the in-lab study, the recorded conductivities for all analyzed groundwater samples were tracked. This included 1-gallon monthly grab samples for pre-treated (Pre-Resin) and post-treated (Post-Resin) 200W P&T Plant waters for May through August 2013. The complete results are listed in Table 7 (conductivity check standards), Table 17 (uncontaminated Hanford groundwater, from well 699-49-10C), and Table 18 (200W P&T Plant grab samples). The precision and accuracy of the conductivity sensor for the range of aqueous solutions is excellent, with the analytical biases all < 10%.

7.3 ^{99}Tc Sensor

The Pre-Resin and Post-Resin samples sent to PNNL were splits from samples that were submitted to WSCF for chemical and radiochemical analysis. A summary of the important inorganic and radioactive contaminants in the grab samples over this period, as reported by WSCF, is provided in Table 22. Pre-Resin grab samples contained between 1500 and 1700 pCi/L ^{99}Tc, while Post-Resin samples contained between 230 and 400 pCi/L ^{99}Tc. Additionally, all grab samples contained ^{3}H, ^{129}I, U, and hexavalent chromium. The evaluation described in this report examined the potential for each of these contaminants to affect the quality of the ^{99}Tc sensor results. Of these, it was determined that hexavalent chromium could potentially adversely affect the sensitivity of the ^{99}Tc sensor due to color quench, but that the effect would likely be < 10%.

This report demonstrates ^{99}Tc sensor calibration, via matrix spike addition, for uncontaminated Hanford groundwater (well 699-49-100C) and then for 200W P&T Plant Post-Resin water. The sensor's calibration parameter, E_m, was determined to be ~19 cps/(Bq/mL) for clean groundwater and between ~17 and ~15 cps/(Bq/mL) for 200W P&T Plant water (see Figure 25). The slightly lower sensitivity to 200W P&T Plant water matrix is due to either the contaminated groundwater's higher concentration of dissolved solids (as indicated by ~20% higher conductivity values as compared to clean Hanford groundwater) or the presence of hexavalent chromium (or a combination of both).

At 270 pCi/L ^{99}Tc activity concentration, for ^{99}Tc standards prepared in uncontaminated Hanford groundwater, the ^{99}Tc measurement precision was observed to be ± ~6% and the accuracy was observed to be -16.1%. Both precision and accuracy improved with ^{99}Tc concentrations above 270 pCi/L. Similar analytical performance was observed with 200W P&T Plant samples. When compared to the analytical results reported by WSCF, the overall Pre-Resin Tc-Mon analysis set resulted in an analytical bias of -6.7 ± 4.6%, and the overall Post-Resin analysis set resulted in a bias of -11.3 ± 7.0%.

7.4 MDA and LOQ

The MDA for ^{99}Tc has been estimated at 42 pCi/L (Figure 24). This is approximately one-half of the originally estimated 90 pCi/L MDA, as reported in PNNL-90778 [9]. The same report predicted a LOQ of 3x the 90 pCi/L MDA, 270 pCi/L. The present in-lab ^{99}Tc analysis results for ^{99}Tc standards in Hanford groundwater and 200W P&T Plant grab samples reaffirms the LOQ being set at or near 270 pCi/L. However, MDA and LOQ for the sensor will need to be reevaluated upon deployment of the Tc-Mon system to the 200W P&T Plant, based on an anticipated drop in the ambient radiation background.

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