

DEVELOPMENT OF A REAL-TIME IN-SITU TRITIUM SENSOR FOR VADOSE AND GROUNDWATER ZONES

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ABSTRACT

Tritium is an integral part of the nuclear weapons industry and has been released into the environment through both the production and testing of nuclear weapons. There are many sites across the U.S. Department of Energy (DOE) complex where tritium has been released into the subsurface through the disposal of radioactive waste, and at the Nevada Test Site (NTS) and a handful of other locations, through the underground testing of nuclear weapons. Numerous DOE facilities have an on-going regulatory need to monitor tritium concentrations in groundwater and in the vadose zone beneath waste disposal pits and shafts and other release sites. Typical access to groundwater is through deep monitoring wells and situated in remote locations. In response to this need, Science & Engineering Associates, Inc. (SEA) has conducted the applied research and engineering and produced a real-time, in-situ monitoring system for the detection and measurement of low levels of tritium in the groundwater and in the vadose zone. The prototype (Model 1) monitoring system has been field tested in both the vadose zone near a buried radioactive waste package and in the groundwater in a monitoring well at the NTS. In August 2002, SEA tested the tritium monitoring system in the vadose zone at GCD-05U within the Area 5 Radioactive Waste Management Site (RWMS) at the NTS, and in September 2002, in groundwater at the monitoring well UE-5n near the underground nuclear test Cambric. Results were within a factor of two of measurements provided by traditional sampling and analysis methods at GCD-05U, and within 23% of measurements provided by traditional sampling and analysis methods at UE-5n. During the 2002 field tests, SEA implemented an innovative sparge sampling method that eliminated the need for the sensor to be deployed downhole. Therefore, in 2003, SEA tested a new sensor design (Model 2) with a larger measurement chamber to reach lower detection limits than was found in 2002. Initial tests of the Model 2 indicate a stable response and a detection limit just less than 100,000 picocuries per liter (pCi/l). In 2004, a mixing mechanism will be engineered into the Model 2 sensor to eliminate stratification of gases, which should enable the inclusion of a hydrogen generator into the sensor design and a subsequent detection limit at or near federal drinking water standards (20,000 pCi/l). The development effort was funded through the DOE National Energy Technology Laboratory (NETL) and the DOE Nevada Operations Office, Advanced Monitoring Systems Initiative (AMSI) Program.

INTRODUCTION

SEA has developed and tested a real-time, in-situ down-hole sensor system for the measurement of tritium concentrations in the vadose and groundwater zones, in response to a DOE Site Need Statement [1]. The system uses a high sensitivity gas proportional counter to quantify the tritium in the vapor phase. For vadose zone measurements, soil gas is drawn directly into the system for

analysis, while for saturated zone sampling, tritiated water vapor evolves from the water through a sparge sampling process (Fig. 1).

In October 2001 SEA initiated a DOE NETL-funded Phase I effort to demonstrate the viability of integrating gas proportional sensing technology with sampling systems designed for the vadose and saturated zone applications. In the initial effort, a conceptual design was developed, basic sensing and sampling system components were acquired or developed and laboratory tests conducted to determine the viability of the conceptual design. During this effort design features evolved that resulted in a simpler fluid sampling system. Concurrent with this effort, an opportunity arose via DOE Nevada's AMSI program to perform field demonstrations at the NTS in both vadose and saturated zones. Although field testing of the sensor system was originally planned as a Phase II activity, it was felt that the simplified sampling systems could support field tests, and funding for two accelerated Phase I field deployments (one for the vadose zone and one for groundwater) was provided by the AMSI program. These two deployments were conducted in August and September 2002.

In August 2002, SEA and NTS staff deployed the sensor for the measurement of tritium concentrations in the vadose zone at the Greater Confinement Disposal (GCD) unit GCD-05U, within the Area 5 RWMS at the NTS. Tritium concentrations were measured from four vadose zone soil gas sampling ports (four different depths) at GCD-05U. Tritium concentrations in soil gas (in microcuries per cubic meter [$\mu\text{Ci}/\text{m}^3$]) at three of the four sampling ports were within 54, 42, and 17 percent difference of the concentrations provided by laboratory analysis, and in the fourth sample about 75% difference, suspected due to insufficient sample purge time. In September 2002, SEA deployed the sensor for the measurement of tritium concentrations in the groundwater at the groundwater monitoring well UE-5n, near the underground test shot Cambria in Area 5, at the NTS. Tritium concentrations measured using the sensor were within 13 and 23 percent (daily averages from two different days of measurements) of the decay-corrected concentration (in pCi/l) measured in 2001 by traditional sampling and analysis methods. These two successful field tests are noteworthy in that this marks the first field deployment of a down-hole real-time tritium sensor at the NTS for the vadose and groundwater zones.

In 2003, a new sensor model (Model 2) was designed and built in which the volume of each of the measurement and background chambers was increased from 1 to 2.5 liters, and significant additional shielding was added. The new sensor also employed a hydrogen generator, referred to as a proton exchange membrane (PEM), in order to concentrate the hydrogen (and tritium) and thereby reduce the MDA. Work on this project is not yet complete, and future work includes the design of a mixing loop into the sensor setup in order to rapidly circulate gases through the sensor measurement chamber in order to eliminate stratification of gases.

METHODS

Sensor Design (Model 1)

The SEA tritium sensor is essentially an adaptation of an existing low-level tritium air monitoring system. The SEA adaptation was to design sample collection mechanisms that allowed the air monitoring system to be deployed down-hole, for measuring tritium

concentrations in groundwater and in the vadose zone. The Model 1 sensor design consists of two gas proportional chambers. The beta radiation (18.6 keV e-max) emitted by the tritium isotope of hydrogen causes ionizations within the fill gas. The electric field created by the high voltage difference between the anode wire and cathode shell induces ion movement, creating a current pulse with duration proportional to the energy of the original radiation event. Pulse shape discrimination only counts pulses generated by the radioactive decay characteristic of tritium. The second chamber is run without tritium and is used for background compensation. The combination of pulse shape discrimination and gamma compensation allow the low level measurements.

The SEA tritium monitoring system was manufactured by Overhoff Technologies Corporation (OTC) in the spring of 2002. The original system consists of two gas proportional chambers, 4.4 cm (1.75 in) in diameter, and 1.86 m (6.1 ft) long, and an electronics unit approximately 15 x 30 x 45 cm (6 x 12 x 18 in) in size. The chambers were designed such that they could be deployed into a 2-inch diameter monitoring well, as per the requirements in the DOE Site Need Statement [1]. Signal cables connect the electronics unit to the measurement and compensation chambers. The electronics unit operates on 110Vac electrical power.

Sensor Calibration (Model 1)

During the summer of 2002, bench-top experiments were conducted on the tritium sensor by personnel from the Harry Reid Center (HRC) Radiation Detection Laboratory (RDC) at the University of Nevada in Las Vegas (UNLV). Calibration of the instrument was conducted using several dilutions of tritiated deionized water in the range of 100K pCi/l to 100M pCi/l.

Experimental Setup for 2002 Vadose Zone Field Testing

A schematic of the instrument operating configuration for the field deployment at GCD-05U is shown in the top of Fig. 1. A slightly modified configuration was used for calibration in the laboratory due to the necessity of creating a saturated air stream. As shown in Fig. 1, P-10 fill gas was released at a constant flow rate through the compensation chamber. From the compensation chamber, the gas entered the permeation tube where it flowed counter-current to the sample air stream. The air stream was drawn through the permeation tube (counter-current to the fill gas) at a rate of 7 milliliters per minute (ml/min). The ratio of fill gas to the air flow was run at or in excess of 25:1 so that the removal of water vapor from the air stream to the fill gas stream was 100% efficient. The fill gas then exited the permeation tube and entered the measurement chamber. The activity of tritium in the water vapor removed from the soil gas was then measured. The permeation tube is essentially an air drier for process streams made by Perma Pure Inc. [2]. The water moves through the tube membrane wall, constructed of Nafion®, and evaporates into the surrounding air or gas in a process called “pervaporation”. This process is driven by the humidity gradient between the inner and outer tubing. The P-10 fill gas is extremely dry so a strong humidity gradient exists between the fill gas and the saturated air stream, and when the dry gas stream is run at a sufficiently higher flow rate in proportion to the wet air stream the process becomes 100% efficient.

During the week of August 26-30, 2002, the SEA prototype (Model 1) tritium sensor was deployed at the GCD-05U site at the NTS. GCD-05U consists of a 3-m (10-ft) diameter by 37-m (120-ft) deep borehole that contains a large tritium inventory (2.2 million Curies at time of disposal) located at the center of the RWMS, which is instrumented with two strings of nine soil-gas sampling ports buried at depths of 3 to 37 m (10 to 120 ft). Tritium sampling at GCD-05U provides a measure of tritium migration from waste packages with time due to degradation of waste containers and the natural transport processes of advection and diffusion.

Experimental Setup for 2002 Groundwater Field Testing

During the week of September 9-13, 2002, the SEA prototype (Model 1) tritium sensor was deployed at the groundwater monitoring well UE-5n. UE-5n is an open monitoring well with a casing diameter of 25 cm (10 in), a total depth of 514 m (1687 ft), and a depth to groundwater of 215 m (705 ft).

The SEA tritium sensor was deployed down-hole but not under water. Instead, an innovative experimental setup was used in which a stainless steel can was deployed to the sampling depth of interest (221 m [725 ft] below ground surface). A counting gas (P-10) consisting of 90% argon and 10% methane was then bubbled into the submerged can. This process is known as sparging. The gas stream then changed from 0% to 100% relative humidity, and was saturated with groundwater vapor (and tritium). This saturated air stream was then in turn diluted by an additional stream of P-10 gas because no more than 1 percent by volume of water can be run through the tritium sensor measurement chamber without causing the Corona effect (electrical shorting). The P-10 gas stream used for the sparging was run through a compensation chamber before reaching the groundwater in order to measure the background radiation conditions of the measurement environment. The saturated gas stream then flowed through the measurement chamber and tritium concentrations in saturated air were measured. Mass flow meters measured the total mass balance of the system, to back-calculate tritium concentrations in groundwater. A schematic diagram of the groundwater sampling setup is shown in the bottom of Fig. 1.

Sensor Design (Model 2)

The new sensor design (Model 2) that was manufactured by OTC was built in the summer of 2003. The proportional chamber volume was increased to 2.5 liters, with an outside diameter of 11.4 cm (4.5 inches) and a length of 65 cm (25.5 inches). The original (Model 1) electronics package was used with Model 2, but with some modifications such as improved voltage controllers. Benchtop testing and calibration of the Model 2 design was conducted at SEA, in July through October 2003.

The sensor setup was the same as that used for the Model 1, except only one chamber was used for both measurement and background measurements with the Model 2 design. As previously discussed, the purpose of the compensation or "background" chamber is to obtain a measure of the background count rate that would exist in the measurement chamber if no tritium were present. For any given set of operating conditions (high voltage level and gas flow rates) of these two chambers, the resulting count rates were noted to be slightly different; typically the measurement chamber reported a count rate 7.5% above that from the compensation chamber. It

is suspected that the count rate differences result from small differences in the “as-built” dimensions and geometry of the two chambers, as well as small differences in the operating characteristics of the pulse shape analysis circuitry for the two independent signal processing trains.

In order to use the count rate results from the compensation chamber to correct the count rate results from the measurement chamber for contribution from background it was, therefore, necessary to compute an empirical correction factor. It is the uncertainty in this empirically derived correction factor that limits a two-chamber system’s ability to accurately measure low levels of tritium activity.

In addition to developing an accurate measure of such a correction factor, it was also necessary to ensure that this correction factor would maintain a constant value with changes in the background conditions of the measurement environment, such as might be attributable to changes in the cosmic ray flux, and/or differences in terrestrial sources (i.e. radon exhalation). Empirical measurements of the stability of the correction factor with an artificial increase in the background activity level revealed a dependency of the correction factor on the background activity level. Further laboratory measurements revealed that a better estimate of the true background count rate from the measurement chamber could be obtained by alternating the gas flow into the measurement chamber between a distilled water blank (i.e. background conditions) and the tritium bearing water sample using a period of approximately 6 to 8 hours in each configuration.

A variety of tests were conducted on the Model 2 sensor, including tests with and without the PEM hydrogen generator, and tests in which the measurement chamber was placed in horizontal versus vertical orientations to evaluate the effects of sensor orientation on the apparent stratification of gases (P-10 gas and hydrogen) when using the PEM.

RESULTS

Vadose Zone Measurements (Model 1)

Tritium concentrations measured at GCD-05U from four soil gas sampling ports using the tritium sensor and from traditional sampling and laboratory analysis (2001 results) are compared in Table I and in the top of Fig. 2. Tritium concentrations at three of the four sampling ports were within 53, 42, and 17 percent error of the historic 2001 concentrations. The tritium concentration measured in port 119A using the tritium sensor was about 25 percent of the concentration provided by lab analysis results, suspected due to insufficient purge time before this reading was taken.

Table I. Results of tritium sensor results compared to historical results at GCD-05U.

Sample Port	Depth (m)	Measured Tritium Activity in Soil Gas ($\mu\text{Ci}/\text{m}^3$)	Historic 2001 Tritium Activity ($\mu\text{Ci}/\text{m}^3$)	Activity of Tritium in Pore Water (pCi/l)	Historic 2001 Tritium Activity in Pore Water (pCi/l)
10A	3.0	0.046	0.03	2.80E+06	1.84E+06
40A	12.2	0.085	0.06	5.15E+06	4.40E+06
50A	15.2	0.15	0.18	9.35E+06	8.69E+06
119A	36.3	0.75*	2.24	4.54E+07*	1.77E+08

* This result is suspected low due to insufficient purge time.

Groundwater Measurements (Model 1)

The tritium concentrations measured using the sensor were within 13 percent on September 11, 2002, and within 23 percent on September 12, 2002, of the decay-corrected concentration measured in 2001 by traditional sampling and analysis methods. Tritium concentrations measured at UE-5n using the SEA tritium sensor and from traditional sampling and laboratory analysis from 2001 are compared in Table II and in the bottom of Fig 2.

Table II. Results of tritium sensor results compared to historical results at UE-5n.

Date	Time	Tritium Concentration (pCi/l)	Date	Time	Tritium Concentration (pCi/l)
9/11/2002	1300	117,954	9/12/2002	840	94,950
9/11/2002	1310	113,549	9/12/2002	850	101,313
9/11/2002	1320	115,017	9/12/2002	900	96,419
9/11/2002	1330	115,996	9/12/2002	910	98,866
9/11/2002	1340	111,591	9/12/2002	920	103,271
9/11/2002	1350	112,081	9/12/2002	930	102,292
9/11/2002	1400	113,549	9/12/2002	940	99,355
9/11/2002	1410	108,655	9/12/2002	950	95,440
9/11/2002	1420	115,507	9/12/2002	1000	99,355
9/11/2002	1430	111,102			
9/11/2002	1440	109,633			
9/11/2002	1450	117,954			
9/11/2002	1500	114,038			
9/11/2002	1510	115,996			
9/11/2002	1520	106,697			
9/11/2002	1530	108,655			
9/11/2002	1540	110,123			
9/11/2002	1550	103,760			
9/11/2002	1600	110,612			
9/11/2002	1610	116,486			
Average tritium measurement over 3-hour sampling time		112,448	Average tritium measurement over 1.5-hour sampling time		99,029
Average tritium analytical result from 2001 (decay corrected)		128,846	Average tritium analytical result from 2001 (decay corrected)		128,846
% error between average real time measurement and average analytical result		13%	% error between average real time measurement and average analytical result		23%

Benchtop Testing (Model 2)

Preliminary results using the Model 2 sensor in a vertical orientation and with a PEM indicate that the new MDA should approach or reach federal drinking water standards (20,000 pCi/l). Further testing is required in order to confirm these preliminary results. If the PEM is not included in the Model 2 sensor setup, results indicate that the sensor response is stable and extremely linear, as shown in the sensor calibration in Fig. 3. However, this sensor configuration only yields an MDA of approximately 100,000 pCi/l.

CONCLUSIONS

SEA has developed and tested a real-time sensor for the measurement of tritium concentrations in the vadose and groundwater zones through funding provided by DOE NETL and the DOE Nevada AMSI program. The SEA tritium sensing system is essentially an adaptation of a gas proportional tritium air monitor, reconfigured for deployment with media-specific sampling

systems. In August and September 2002, the tritium sensor was deployed for vadose zone and groundwater measurements at the NTS. These two successful field deployments are noteworthy in that this marks the first field deployment of a down-hole real-time tritium sensor at the NTS for the vadose and groundwater zones.

Many lessons were learned during the development and two field deployments of this sensor. The most significant innovation during Phase I of the project was the application of the sparge sampling process. The benefits of this approach are significant:

- Because the tritium instrumentation can be located above ground, it can be of any size needed to achieve the desired detection limit. In general, the larger the detector volume (especially for gas proportional counters) and the more substantial the shielding, the lower the detection limit.
- The tubing and sample assembly (including the inverted can at the sample point) are relatively inexpensive components and can be fabricated for, and installed to whatever depth is desired, and dedicated to a given well. The instrumentation trailer can either be stationary or moved from well to well.
- The tritium instrumentation and water treatment system does not need to be designed for the high hydrostatic pressures present at depth.
- Sparge sampling allows the sampling of virtually any groundwater well for tritium, regardless of well diameter, depth, or head.

The primary technical challenge remaining for this tritium sensor is to reduce the MDA. The MDA using the Model 1 sensor configuration for measuring tritium in both the vadose zone (using a permeation tube setup) and saturated zone (using P-10 sparging and direct analysis of the P-10/water vapor stream) is approximately 100,000 pCi/l. Although this MDA is adequate for groundwater sampling at UE-5n, and most other tritium-contaminated groundwater wells at the NTS and other DOE sites, it is not generally low enough for all vadose zone and groundwater applications of a tritium sensor.

The MDA can be reduced significantly if the tritiated water is separated into its hydrogen and oxygen components using a PEM. This increases the volume fraction of tritium in the detector by approximately a factor of 3 or 4. Eliminating water vapor is also beneficial to the detector operation. These components can be readily implemented in a trailer configuration. Refer to Fig. 1 (bottom) for a schematic diagram of the sensor configuration using a PEM.

Benchtop testing during the initial Model 2 testing period suggest that inclusion of two PEMs (one for tritiated water, one for pure water) into the sensor setup (refer to Fig. 4) will yield an MDA of approximately 20,000 pCi/l. However, stratification of P-10 and hydrogen gases remains one last problem to be resolved. Preliminary work utilizing a rapid-flow mixing loop into the sensor setup shows great promise toward resolving this problem (Fig. 4).

REFERENCES

- 1 Department of Energy (DOE). 2001. DOE Nevada Site Need Statement "Down-Hole, Real-Time Monitoring of Radiation (Mainly Tritium) in Boreholes".

- 2 <http://www.nv.doe.gov/programs/envmgmt/blackmtn/PDFs/NV01-0200-01S.pdf>
- 3 PERMAPURE™. <http://www.permapure.com/newweb/ME/ME-Series.htm>

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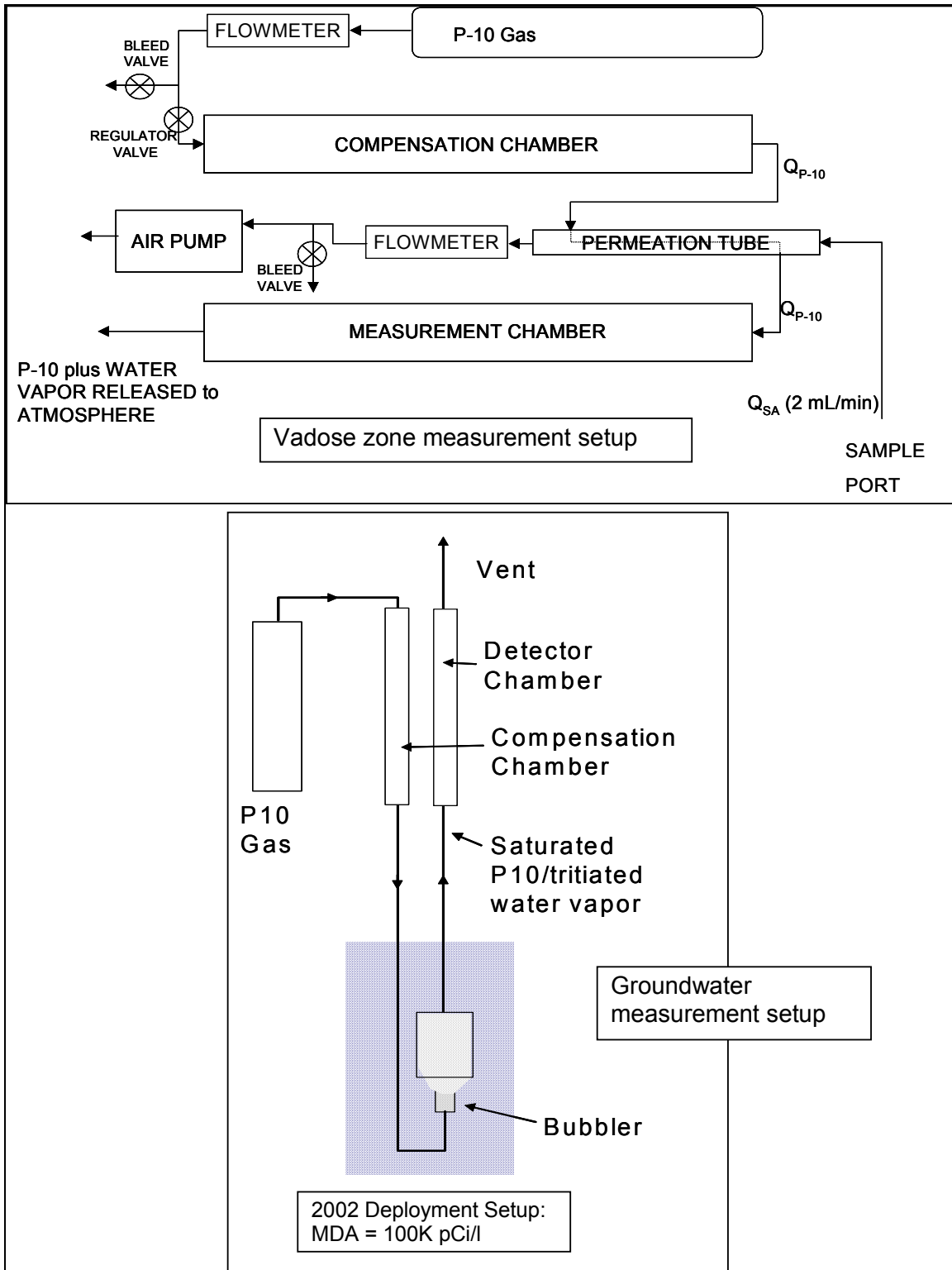


Fig 1. Schematic diagram of deployment configurations for vadose zone (top) and groundwater (bottom) field measurements using Model 1.

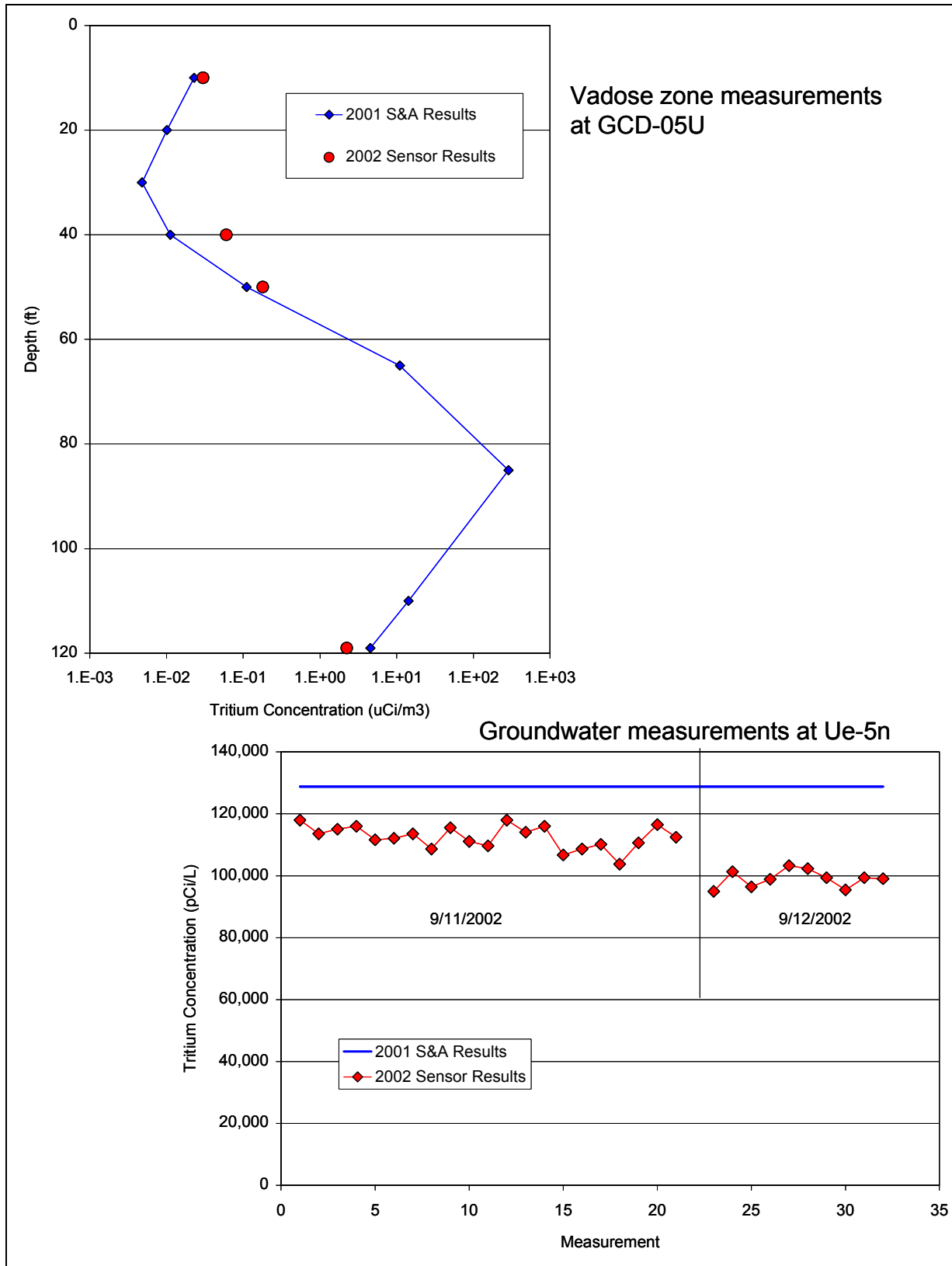


Fig 2. Results of the 2002 vadose zone (top) and groundwater (bottom) measurements taken at the NTS using Model 1.

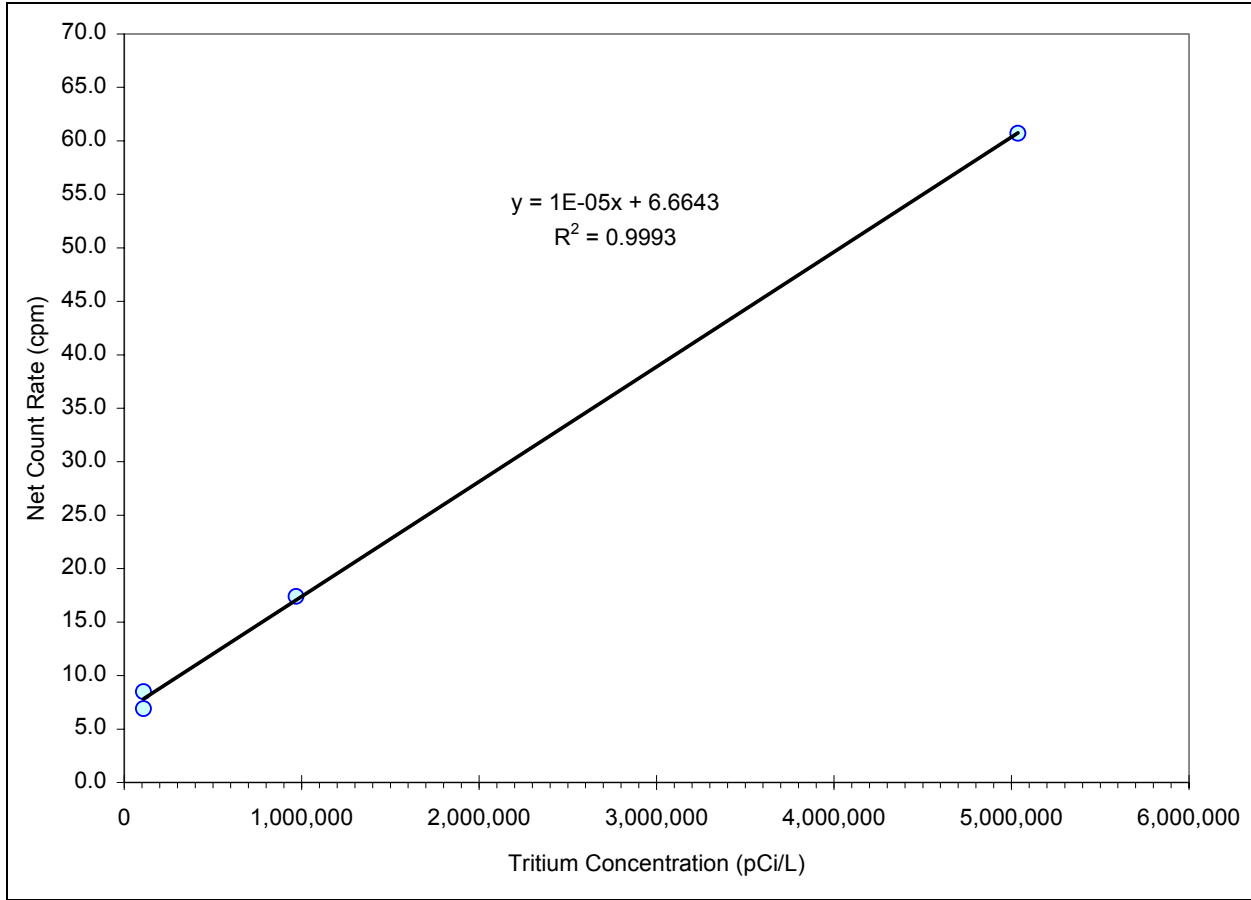


Fig 3. 2003 Calibration of SEA tritium sensor (Model 2) using P-10 gas and water vapor (without a PEM hydrogen generator).

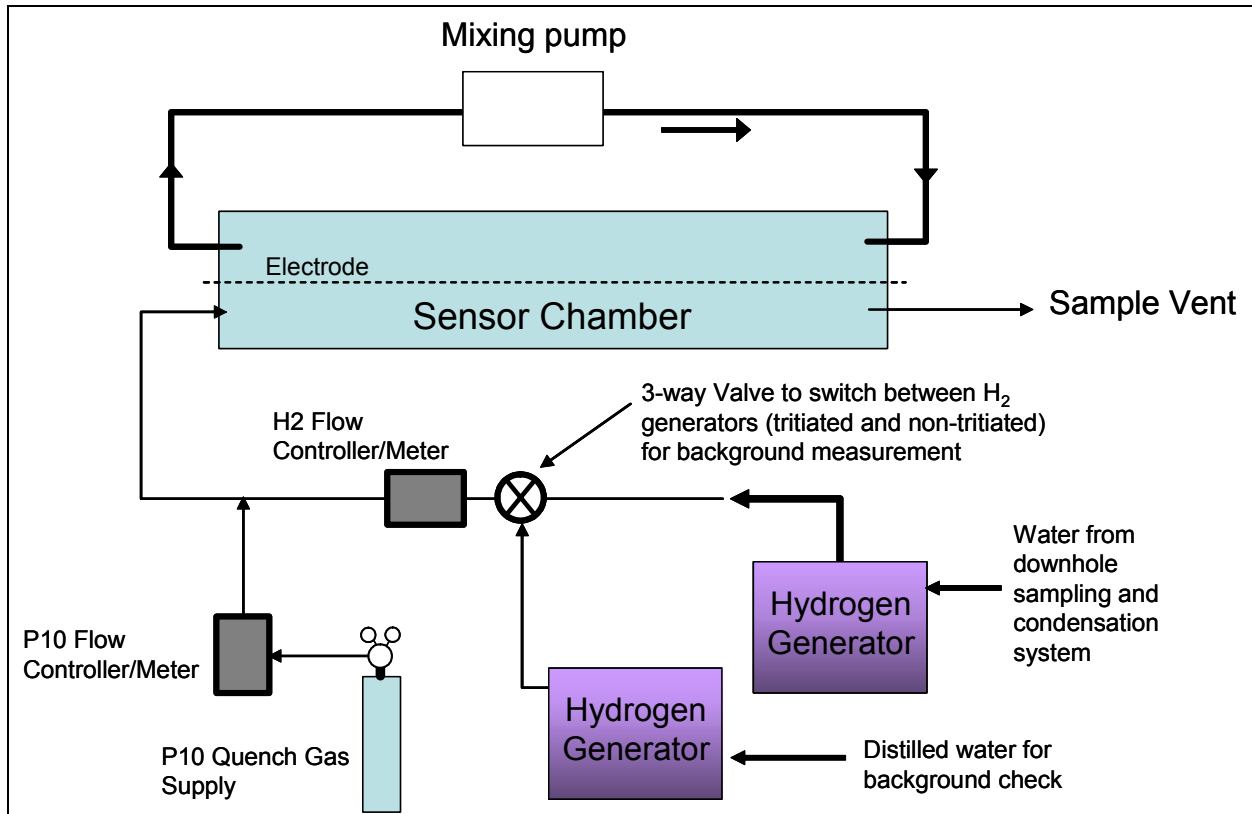


Fig 4. Schematic diagram of proposed Model 2 sensor setup using hydrogen generators and a mixing loop.