LA-UR- 97-2406
CONF-9706122--

Tritium Monitor Calibration at Los Alamos National Laboratory

by

Christopher W. Bjork, Douglas J Aikin, and Thomas W. Houlton
Health Physics Measurements Group, ESH-4
Mail Stop G761
Los Alamos National Laboratory
Los Alamos, NM 87545
E-mail to: cbjork@lanl.gov

ABSTRACT:

TRITIUM MONITOR CALIBRATION AT LOS ALAMOS NATIONAL LABORATORY. C.W. Bjork, D.J. Aikin, and T.W. Houlton (Health Physics Measurement Group, Mail Stop G761, Los Alamos National Laboratory, Los Alamos, NM 87545)

Tritium in air is monitored at Los Alamos National Laboratory (LANL) with air-breathing instruments based on ionization chambers. Stack emissions are continuously monitored from sample tubes which each connect to a "Tritium bubbler" which differentially collects HTO and HT. A set of glass vials of glycol capture the HTO. The HT is oxidized with a palladium catalyst and the resultant HTO is captured in a second set of vials of glycol. The glycol is counted with a liquid scintillation counter. All calibrations are performed with tritium-containing gas. The Radiation Instrumentation and Calibration (RIC) Team has constructed and maintains two closed-loop-gas-handling systems based on femtoTECH model U24 tritium ion-chamber monitors: a fixed system housed in a fume hood and a portable system mounted on two two-wheeled hand trucks. The U24 monitors are calibrated against tritium-in-nitrogen gas standards. They are used as standard transfer instruments to calibrate other ion-chamber monitors with tritium-in nitrogen, diluted with air. The gas-handling systems include a circulation pump which permits a closed-circulation loop to be established among the U24 monitor and typically two to four other monitors of a given model during calibration. Fixed and portable monitors can be calibrated. The stack bubblers are calibrated in the field by: blending a known concentration of tritium in air within the known volume of the two portable carts, coupled into a common loop; releasing that gas mixture into a ventilation intake to the stack; collecting oxidized tritium in the bubbler; counting the glycol; and using the stack and bubbler flow rates, computing the bubbler's efficiency. Gas calibration has become a convenient and quality tool in maintaining the tritium monitors at LANL.

Complete Paper Accompanying the Poster Presentation at the Health Physics Society Annual Meeting, San Antonio, Texas, June 29 - July 3, 1997:

Tritium in air is monitored at Los Alamos National Laboratory (LANL) with air-breathing instruments based on ionization chambers. Stack emissions are continuously monitored from sample tubes which each connect to a "tritium bubbler" which differentially collects HTO and HT. Calibrations are performed on the ion chambers and bubblers using tritium-in-nitrogen gas. The calibrations are traceable to the National Institute of Standards and Technology (NIST). The following describes the use of the tritium-in-nitrogen gas standards, the femto-TECH model U24 ion-chamber tritium monitors used in our calibration equipment, the EG&G model EL-700 differential tritium bubblers, and the techniques used in calibration.

Tritium-in-Nitrogen Gas Standards: Dilute tritium in air is measured by the air-breathing ion-chamber monitors, both portable and fixed, used for protection of the people who work in tritium facilities. Calibration of such instruments with gas requires dilute gas standards. To our knowledge standards have been produced in the range from 10 mCi/m^3 (370 Bq/cm^3) to 1000Ci/m^3 (3.7 x 10^7 Bq/cm^3), usually quoted at Standard Temperature and Pressure (STP). The tritium monitors typically display the readings in Curies per cubic meter (or with the usual prefixes of micro and milli). Therefore all of our work uses these traditional units. Good standards usually contain 0.1% hydrogen which assures that the gaseous tritium will be in the molecular form HT. The balance of the gas can be dry nitrogen, especially for tritium-in-air applications. Other carrier gases have been used. For appreciation of the dilution of the tritium, consider the high end of the range given above. There are 9619 Curies per gram of tritium. Therefore 1000 Ci would be 0.104 gram of tritium or 0.104/4 = 0.026 mole of HT in 1 cubic meter (1000 liters) of nitrogen at STP. There are 1000/22.4 = 44.6 moles of N_2 in 1 cubic meter at STP. Therefore the HT dilution in $_2$N is 0.026/44.6 = 0.00058, or 580 HT molecules per million N_2 molecules.

Our recent supplier of gas was Atomic Energy of Canada Limited (AECL) at Chalk River, Ontario. We sent them a "quantum-passivated" stainless-steel gas cylinder produced by Quantum Mechanics (QM) Corporation in Sonoma, California. The passivation is a proprietary process of QM Corp. Such cylinders can store dilute gas for several years with little degradation. Dilute gas, HT in N_2 with 0.1%H_2 and less than 0.1% HTO was put into our QM cylinder at AECL. This gas will be used to calibrate our transfer instruments used in our future calibrations. We also purchased a lecture bottle with high concentration HT in N_2 for our routine calibrations of ion chambers and bubblers.

Traceability to NIST is achieved by comparison of our work to the results of internal gas proportional counting of a gas sample at NIST which provides a certified value for the tritium concentration of the sample[1]. This is a proven technique whereby HT in a carrier which is freezeable with liquid helium, or a tritiated water sample (reduced to HT and H_2 by Zinc in a hot oven), can be counted directly with accompanying argon and methane counting gas in proportional counters. The current expert at NIST is Mike Unterweger. Contact him at e-mail: unterweg@micf.nist.gov.

femto-TECH Model U24 Ion-chamber Tritium Monitor: Los Alamos has standardized on the 2.4-liter femto-TECH U24 ion chamber as our transfer instrument for tritium-in-air calibration. The usual U24 has an auto-ranging chamber and electronics unit which automatically switches between the microCurie and milliCurie per cubic meter ranges, as required. Experiments at high concentrations (near 15 Ci/m^3) at Los Alamos atmospheric pressure, 580 Torr, showed that a larger chamber bias than the typical 24 volts was useful. Therefore, each of our two calibration systems have a low-range chamber, useful from 2 to 15000 microCuries/m^3, biased at 24 volts, and a high-range chamber, useful from 1 to 15000 milliCuries/m^3, biased at 300 volts by a battery. We manually switch from one chamber to the other with a common electronics box on each calibration system. Figures 1 and 2 show the good linearity of the chambers in a Cs-137 gamma-ray field. Figure 3 shows good linearity of response as dilute gas is added through a sequence of aliquots to our closed-loop system. Even the high-range chamber which has only one- and two-digit ouput display shows good linearity. Notice that the lines have slightly different slope and intercept. The precision resistors in the electronics are not perfectly matched in the two chambers. So the calibration process must include the approriate corrections to be absolutely accurate. Figure 4 shows the high-range chamber response as high-concentration gas is added as a sequence of aliquots to the closed-loop system. The response has some curvature which is due to the technique and not chamber response. Tests consisting of insertion of a lot of HT into the loop, followed by measured dilutions (partial evacuation, backfilling with

DISCLAIMER

air, and thorough mixing with precise pressure monitoring) to lower concentrations shows linear ion-chamber response. Figure 5 shows the response of the low-range chamber as aliquots of nitrogen were sequentially added to the system, mixing the gas thorougly at each step. A monitor with no pressure effect would show a flat response. Figure 5 shows the well-behaved response of the U24. The response has only dropped by 1% at about 300 and 700 Torr with respect to its atmospheric response at Los Alamos at 580 Torr. The good linearity and flat pressure response can be exploited in the calibration of the transfer instrument by adding aliquots of gas of known concentration in a similar way as was done to generate the data in Figure 3. The change in concentration is proportional to the change in pressure at constant volume and constant temperature. The slope of the graph (as in Figure 3) for a calibrated instrument should equal the known concentration of the gas at STP at the date of the calibration procedure modified by the multiplicative factor: (273/760T) where T is the loop temperature in degrees Kelvin and the calibration slope is in units of concentration per Torr. A similar calibration scenario can be the addition of a single aliquot of gas of known concentration, C_{known}, to a closed system of air at absolute temperature T with a resulting increase in the pressure, ΔP, and a predicted tritium concentration, C_{loop}, given by:

$$C_{loop} = C_{known} (\Delta P/760) (273/T)$$

Tritium-in-Air Calibration Laboratory: The Radiation Instrumentation and Calibration (RIC) Team of ESH-4 has constructed and maintains two closed-loop-gas-handling systems based on femto-TECH model U24 tritium ion-chamber monitors: a fixed system housed in a fume hood and a portable system mounted on two two-wheeled hand trucks. Figure 6 is a schematic drawing of the fixed system showing the circulation pump, the evacuation pump, the MKS Baratron pressure gauge, the low- and high-range U24 ion chambers, several Nupro valves, and the lecture-size gas cylinder of tritium-in-nitrogen and regulator (to the right of valve V4). After construction, the volume of the fixed system was precisely measured for future use. The U24 chambers account for 4.8 of the 4.915 Liters of the closed-loop system. The fixed system is used to calibrate the tritium laboratory transfer instrument, which includes the 2 ion chambers shown. The portable system can be hooked to the fixed system to perform a transfer calibration of the portable system's U24 using tritium-in-air. Both the fixed system and the portable system can be used to perform a transfer calibration with tritium-in-air to any other ion-chamber tritium monitor. The laboratory also includes a helium leak detector to assist in fixing leaky systems.

Portable Calibration Apparatus: The portable system mounted on two hand trucks can be used for ion-chamber calibrations (U24 cart only) or for stack calibrations of tritium bubblers (U24 Cart coupled to the ballast cart). Figure 7 is a schematic drawing of the gas-handling system of the U24 cart. The cart includes a lecture bottle of calibration gas with its regulator, the U24 ion chambers, the U24 electronics, a circulation pump and associated stainless-steel tubing and Nupro valves. To calibrate an ion-chamber tritium monitor, the inlet and outlet of the U24 cart are connected to the inlet and outlet of the instrument under test (IUT), typically with tygon tubing. With valves V3 and V1 closed, and V2, V4 and V5 open, the circulation pump can establish an equillibrium background closed-loop condition between the U24 and the IUT. Usually a little purging with air by opening one joint in the closed loop is done to achieve a low background. The background readings of the U24 and the IUT are recorded. Next, the operator checks that the regulator is closed, and opens and closes the gas-bottle valve, VG. The regulator pressure is raised to some low value and V1 is opened and closed to admit tritium-in-nitrogen to the closed-loop system. The circulation pump continues to run to mix the gas and the equillibrium concentrations are observed for the U24 and the IUT. The operator will add sufficient tritium to achieve the highest desired concentration as required for the particular IUT and its use. Calibration adjustments are usually made to the IUT at the highest concentration

on a given range of that instrument. The operator records the readings of the U24 and the IUT. One connection between the IUT and the U24 is opened to the air, e.g. at the U24 cart inlet to dilute the tritium with air. The connection is closed and the operator records the U24 and IUT readings when equillibrium is established. The process is continued for several dilutions to a level of about 20 microCuries/m^3. Each range of the IUT will be checked at several concentrations. Later, the operator enters the data into a computer data base and a report of the calibration is generated. A sample report is included at the end of this paper. The mean correction factor and its relative standard deviation are calculated by the data base program from the data for each range of the IUT. Some instruments can be adjusted to a correction factor close to 1. Others may require the use of the correction factor by the user of the particular instrument. A copy of the report is attached to each instrument for the user. The user, usually a Radiological Control Technician (RCT), routinely irradiates the tritium monitor with a Cs-137 source at a reproducible position with respect to the ion chamber. The RCT records the quantitiative result of this performance test to insure accurate monitoring between tritium calibrations of the instrument.

Figure 8 is a schematic drawing of the gas-handling system when the U24 cart (at the top of Figure 8) is coupled to the ballast cart (at the bottom of Figure 8). The connections between the carts are from A to B and C to D in Figure 8 using stainless-steel bellows tubing. The ballast cart contains three stainless-steel cylinders with a total volume of nearly 20 liters. An electronic pressure gauge and a vacuum pump are also mounted on the ballast cart. Such a configuration is used for mixing a large quantitiy of tritium for stack bubbler calibrations as discussed below.

EG&G EL-700 Differential Tritium Bubblers: Tritium emissions from exhaust stacks at LANL are monitored by EG&G model EL-700 bubblers. Each tritium stack has a sample tube connected to the inlet of the bubbler. An internal pump and an electronic flow controller provide a continuous sample of the stack effluent at a flow rate of 150 cm^3/minute. The sampled air passes serially through six glass vials which contain 30 mL each of ethylene glycol. Water vapor will be trapped in the glycol. Glycol was chosen over water in Los Alamos because of our low relative humidity. No evaporative losses should occur. The inlet to each vial is via a stainless steel tube, welded to the sealed cap of the vial, with an opening near the bottom of the vial. The outlet of each vial is an opening in the cap which then becomes another length of tubing. The vials are connected in series, i.e. the outlet of a vial carries air to the inlet of the next vial. Therefore, as air is pulled through the instrument, it bubbles up in the glycol in each vial. The first three vials will trap tritium as HTO. The connection between vial #3 and vial #4 includes a U-tube filled with a palladium catalyst having large surface area and low average density. It is called palladium sponge. The U-tube is held in a solid stainless-steel clamp as is a heating element. The clamp is housed in a double-walled stainless steel box filled with fiberglass insulation. In operation, the catalyst assembly is kept at 475 degrees C. HT in the air will be oxidized on the catalyst and gradually released as HTO to the air stream. Vials #4, #5, and #6 will trap the HTO produced by oxidizing the HT in the catalyst. Therefore, HT and HTO are differentially removed from the air and trapped as HTO in the glycol.

Liquid scintillation counting is used to analyze the glycol after a period of collection of tritium by a bubbler. Typically, 1 mL of glycol from each vial is mixed with 15 mL of "Ultima Gold" liquid scintillation fluor to produce each of the six scintillation cocktails.

Before a bubbler is put into service on a stack, we use the helium leak detector and repair all leaky joints. Then, a functional test of the bubbler is performed in the Tritum-in-Air Calibration Laboratory. The flow rate is adjusted and precisely determined by measuring the rate of rise of a soap bubble in a graduated glass

burette attached to the inlet of the bubbler. Next, a known quantity of tritium-in-air is mixed in our fixed closed-loop system. The known volume of the system multiplied by the calibrated concentration given by the transfer instrument is equal to the total activity of tritium in the closed loop. The bubbler is connected to the loop and pulls air from it at 150 cm^3/minute. Just after the start of the "bubbler run" (the collection of all the tritium in the loop) another valve of the loop must be opened to admit fresh air to the loop and maintain its pressure at atmospheric. The exhaust from the bubbler is monitored by an ion-chamber tritium monitor as insurance against loss of HT by a dirty catalyst. Figure 9 shows the tritium concentration in the closed loop versus time during a bubbler run. The bubbler started to draw upon the loop at time zero. After one hour only about 10% of the tritium remains in the loop. However, we have learned not to terminate a bubbler run sooner than four hours. A time delay of as much as two hours can occur in the catalyst for release of the HTO to the air stream. Four hours is a conservative choice which ensures complete tritium recovery in the glycol. Scintillation counting of the sampled glycol then verifies that all of the tritium is captured by the bubbler and the catalyst efficiency can be declared to be 100%.

After the bubbler installation on a stack and every six months thereafter, a stack calibration is performed on the bubbler/stack system. The coupled calibration carts (as seen in Figure 8) are used to prepare a mixture of high-concentration tritium in air, up to 15,000 mCi/m^3 in a total volume of 25.36 liters (precisely measured after construction of the carts). The coupled system is usually purged, evacuated to about two pounds per square inch (psi) below atmospheric pressure (to insure leaks go into the system rather than out), the tritum-in-air is well mixed, and the equillibrium concentration is recorded. A fresh set of glycol vials is mounted on the bubbler. The outlet of the U24 cart is coupled to an exhaust intake of the stack with a tygon tube. With the circulation pump on, outlet valve V4 is slowly opened to admit tritium to the stack. Later, inlet valve V2 is opened to let in fresh air as the "tritium stacking" contiunues. The tritium concentration in the stack is measured by the facility's ion-chamber monitor from a stack sample tube similar to the bubbler's sampler but using a pump flow of 20 liters/minute. The stack concentration usually rises and falls to background levels within 20 minutes. The coupled carts are left in this purging configuration and the bubbler run is terminated four hours after stacking. The six glycol vials from the tritium-stacking run are removed and replaced with fresh vials to record a background for the stack. The background run is typically twenty hours. The facility is required to be at a steady state with no deliberate tritium releases beyond the usual outgassing.

Table 1 shows a typical set of results from the liquid scintillation counting of a stack calibration. One mL of glycol was removed from each vial to prepare the cocktail. Each cocktail was counted for ten minutes. The tritium column shows the disintegrations per minute of each cocktail from the tritium-stacking run. Most of the signal is in Vial #4, which collects the HTO converted from HT just after the catalyst. The background column is normalized to the same amount of tritium accumulation time in the glycol as the tritium-stacking run. The original background results were about five times as large as in Table 1 because the background run was twenty hours and the tritium run was four hours. The net signal column is just the difference between the tritium column and the background column. Notice that some net HTO is observed in vials #1, #2, and #3. Also notice that Vial #4 contributes most of the signal. Only a small fraction of the HTO is trapped in vials #5 and #6. The stack calibration is basically a validation of the catalyst efficiency and of the stack flow rate.

Table 1

Stack Bubbler Scintillation Counting Results

Vial #	Tritium-Stacking Run (dpm)	Background Run (dpm)	Net Signal (dpm)
1	457	325	132
2	87	24	63
3	77	16	61
4	14114	107	14007
5	79	19	60
6	81	14	67

The analysis of such data is straight forward. In this example, the equillibrium tritium concentration in the coupled carts was 11759 mCi/m^3 in the 0.02536 m^3 volume for a total activity of 298.2 mCi to be stacked. The net HT collected as HTO in vials #4 through #6 showed 14134dpm/mL of glycol. Each vial had 30 mL glycol, so the total activity collected in vials #4, #5 and #6 is:

$$14134 \text{ dpm/mL} \times 30\text{mL} / 2.22 \times 10^6 \text{ dpm/}\mu\text{Ci} = 0.191 \ \mu\text{Ci}$$

The estimate of the HT which left during the stacking of tritium from the liquid scintillation counts is just the collected activity, 0.191 μCi above, multiplied by the ratio of the stack flow rate to the bubbler flow rate:

$$0.191 \ \mu\text{Ci} \times (10^{-3}\text{mCi/}\mu\text{Ci}) \times 233.0 \text{ m}^3\text{/minute} / (150 \text{ cm}^3\text{/minute} \times 1 \text{ m}^3\text{/ } 10^6 \text{ cm}^3) = 296.7 \text{ mCi}$$

The catalyst efficiency estimate is then the ratio of the collected estimate to the gas activity stacked:

$$296.7 / 298.2 = 0.995 \quad (\text{or } 99.5\%)$$

Such a result indicates a fully efficient bubbler and a good value for the stack flow rate. The flow rate of each stack is periodically measured independently.

The ratio of the net signal summed for vials #1 through #3 to the sum for all six vials is a measure of the HTO fraction in the stacked gas:

$$256/(256 + 14134) = 1.78\%$$

Conclusion: Tritium monitor and tritium bubbler calibration using tritium-in-nitrogen gas is a convenient and a quality technique in use at LANL. We welcome any requests for assistance or information.
We offer calibration services for any air-breathing ion-chamber tritium monitor. Please inquire at e-mail: cbjork@lanl.gov.

1. S.B. Garfinkel, W.B. Mann, F.J. Schima and M.P. Unterweger, NIM **112**, 59-67 (1973).

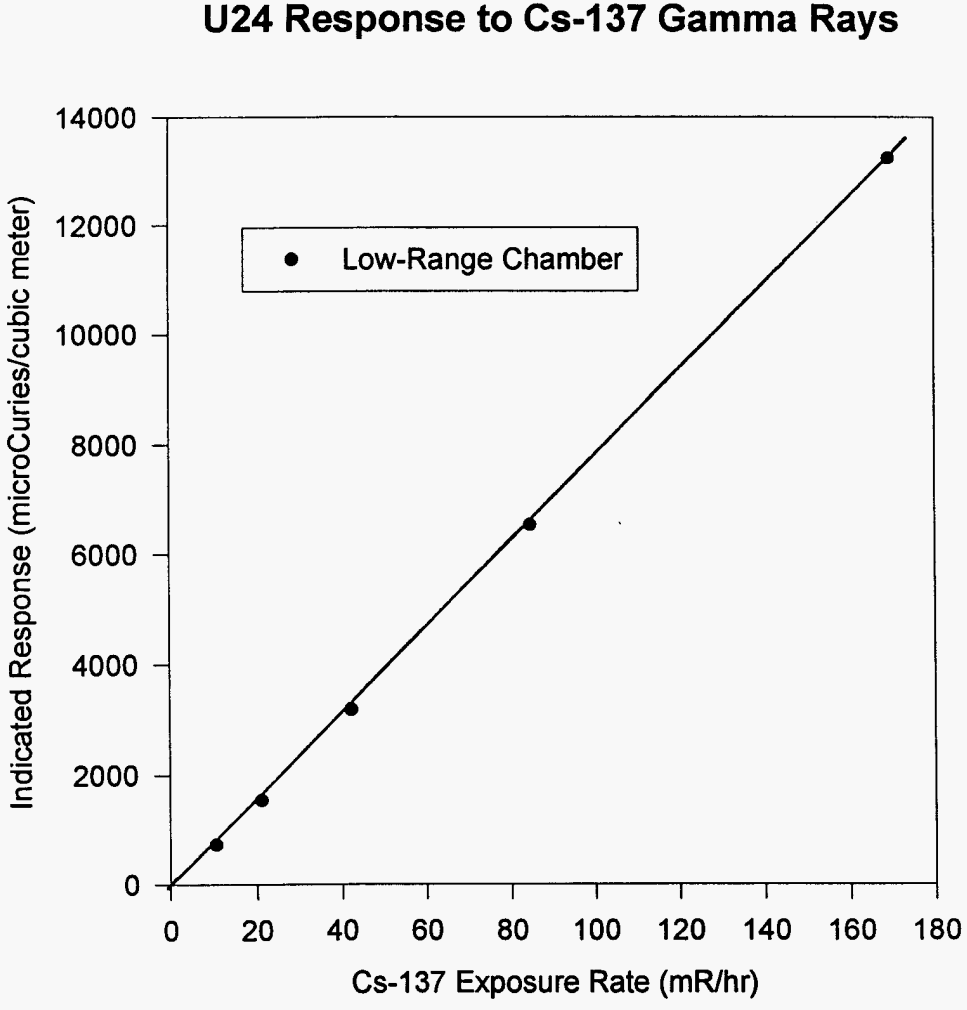

Figure 1

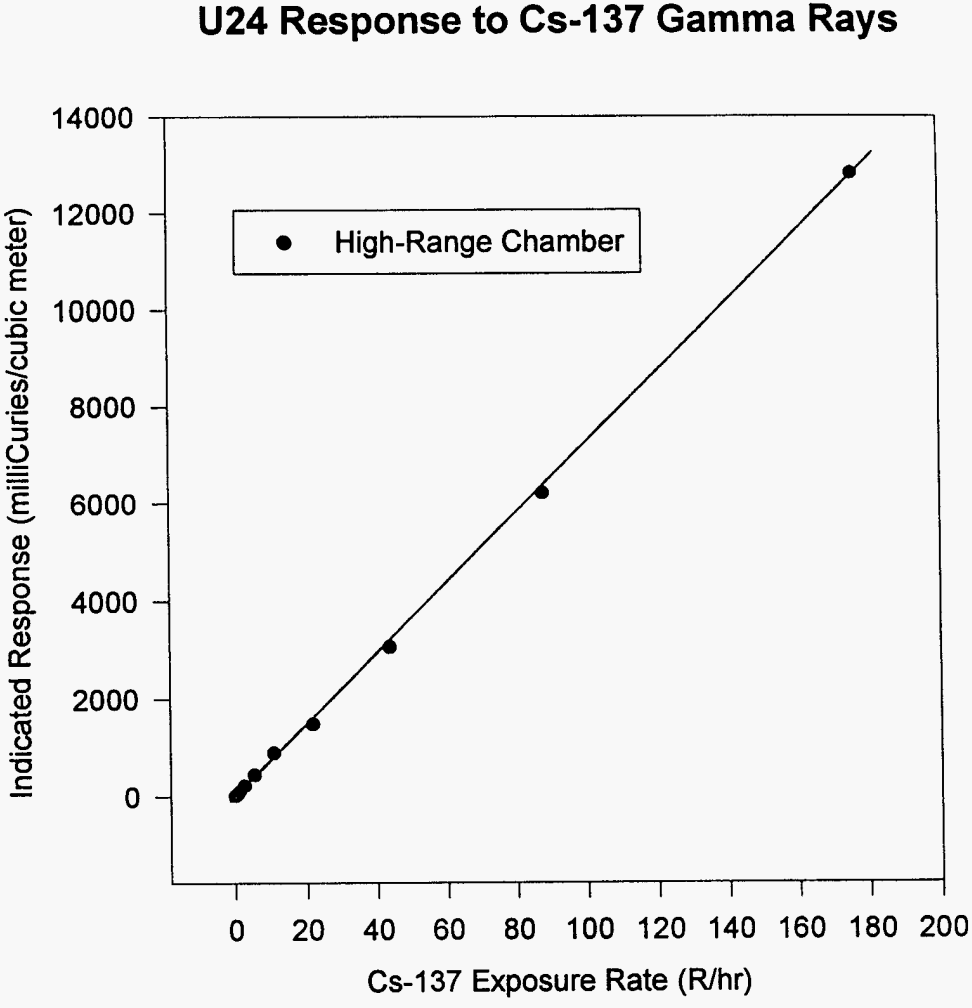

Figure 2

U24 Response vs. Loop Pressure (as low-concentration HT/N is added to the Closed Loop)

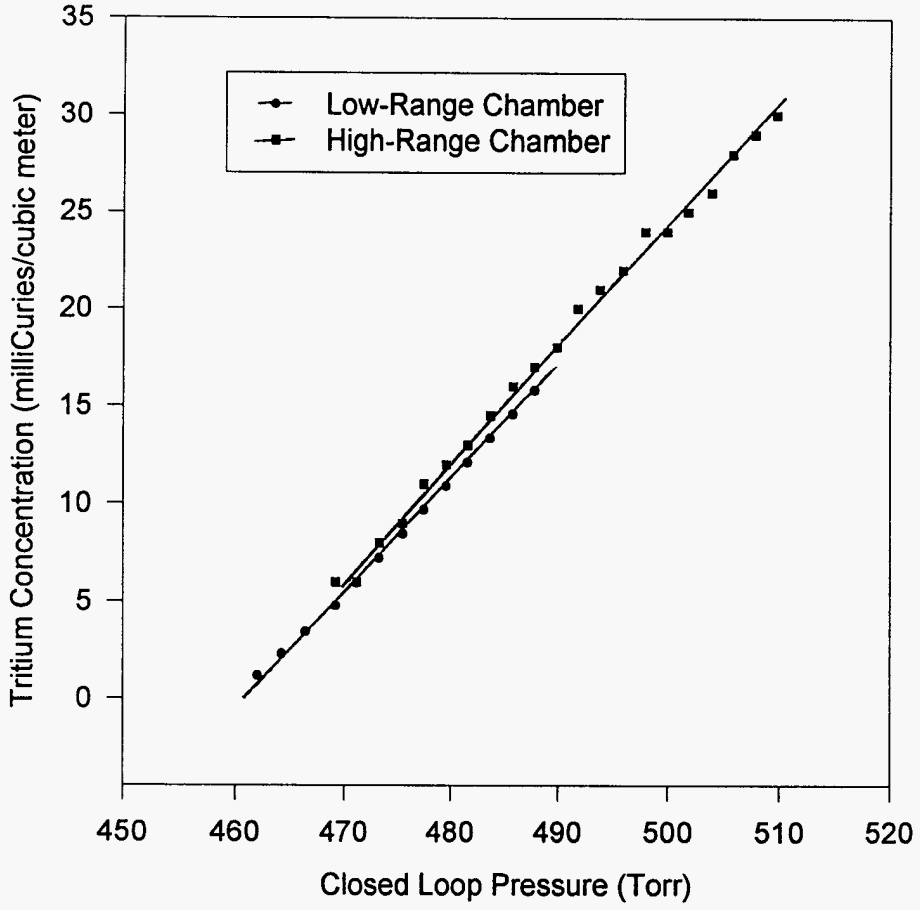

Figure 3

U24 Response vs. Loop Pressure (as high-concentration HT/N is added to the Closed Loop)

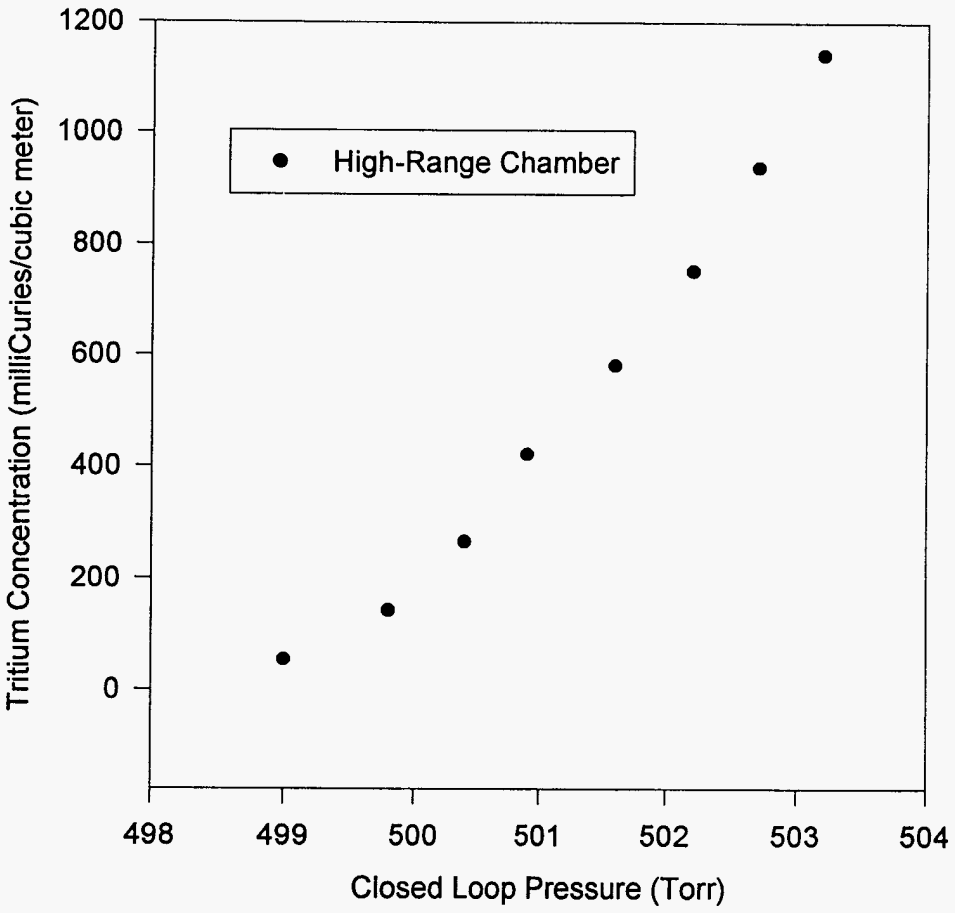

Figure 4

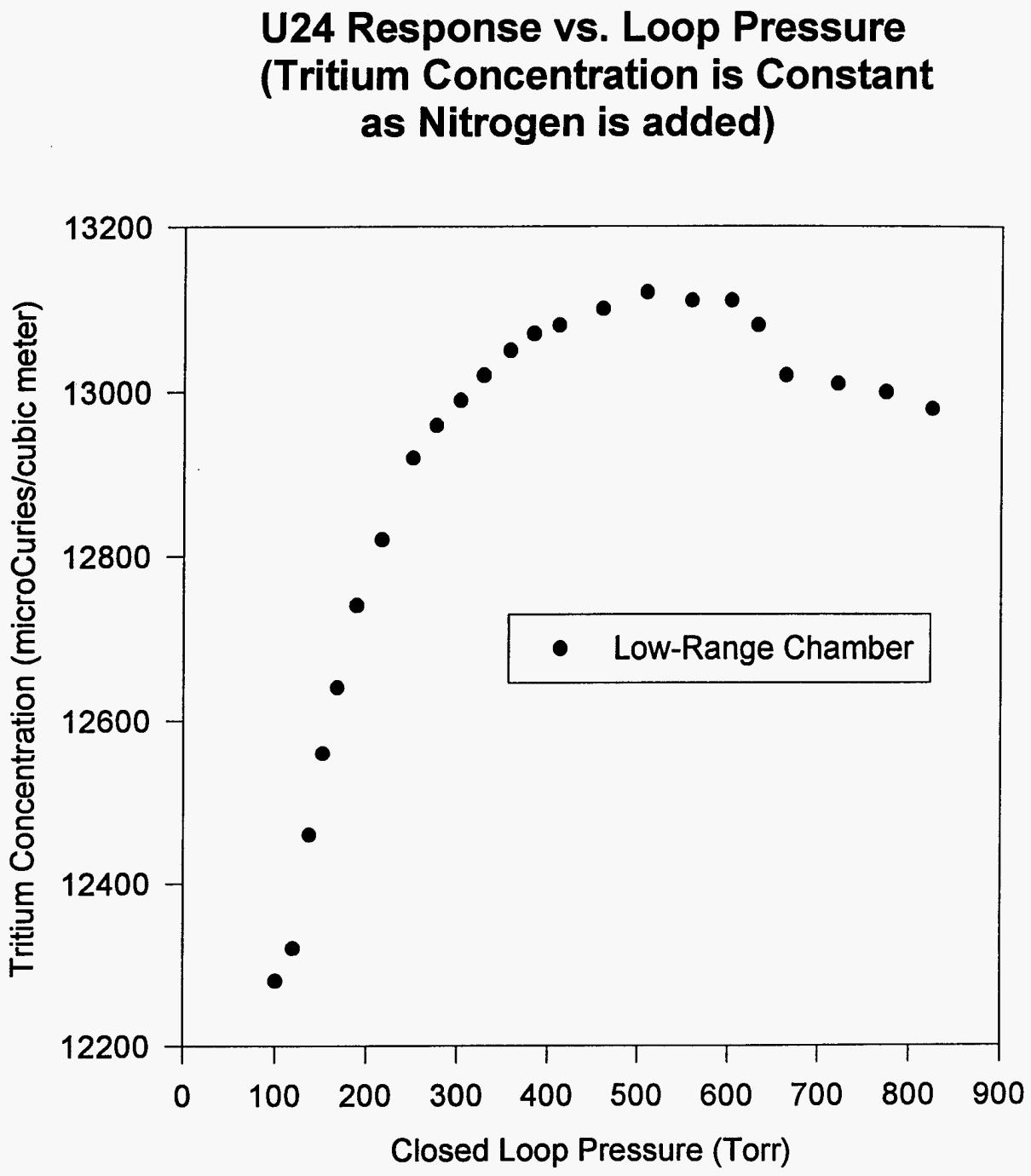
U24 Response vs. Loop Pressure
(Tritium Concentration is Constant
as Nitrogen is added)
Tritium Concentration (microCuries/cubic meter)
13200
13000
12800
12600
12400
12200
0
100
200
300
400
500
600
700
800
900
Closed Loop Pressure (Torr)
Low-Range Chamber

Figure 5

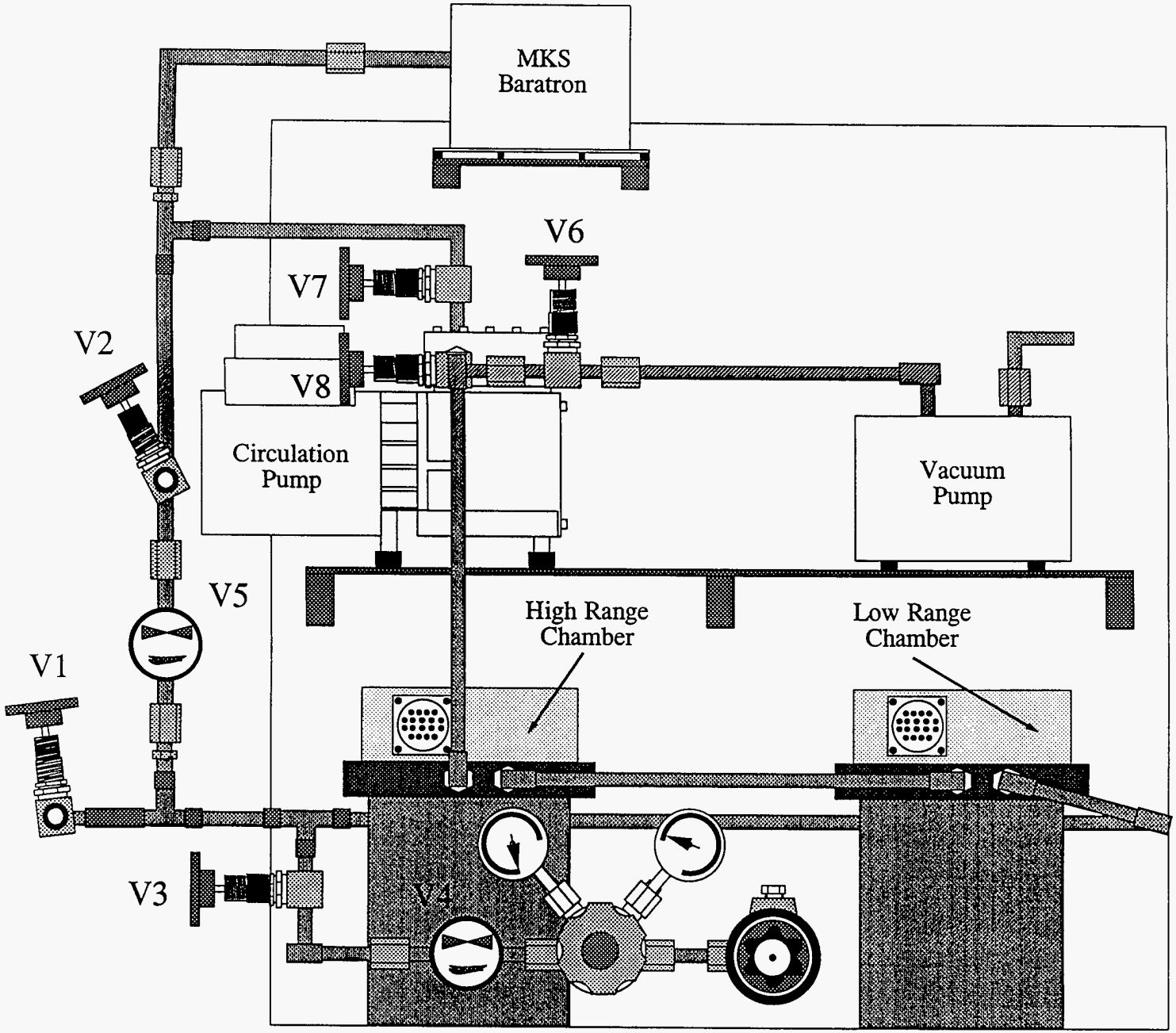
MKS
Baratron
V6
V7
V2
V8
Circulation
Pump
Vacuum
Pump
V5
High Range
Chamber
Low Range
Chamber
V1
V3
V4

Figure 6

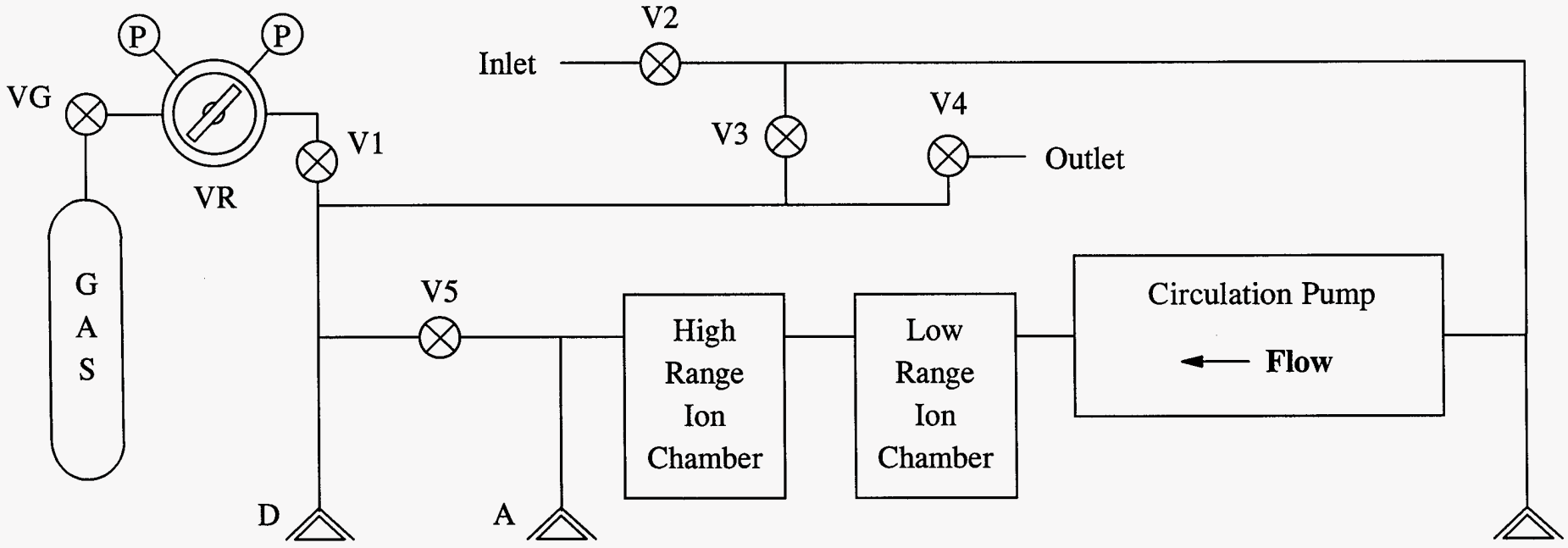
P
P
VG
VR
V1
V2
Inlet
V3
V4
Outlet
G
A
S
V5
High
Range
Ion
Chamber
Low
Range
Ion
Chamber
Circulation Pump
Flow
D
A

Figure 7

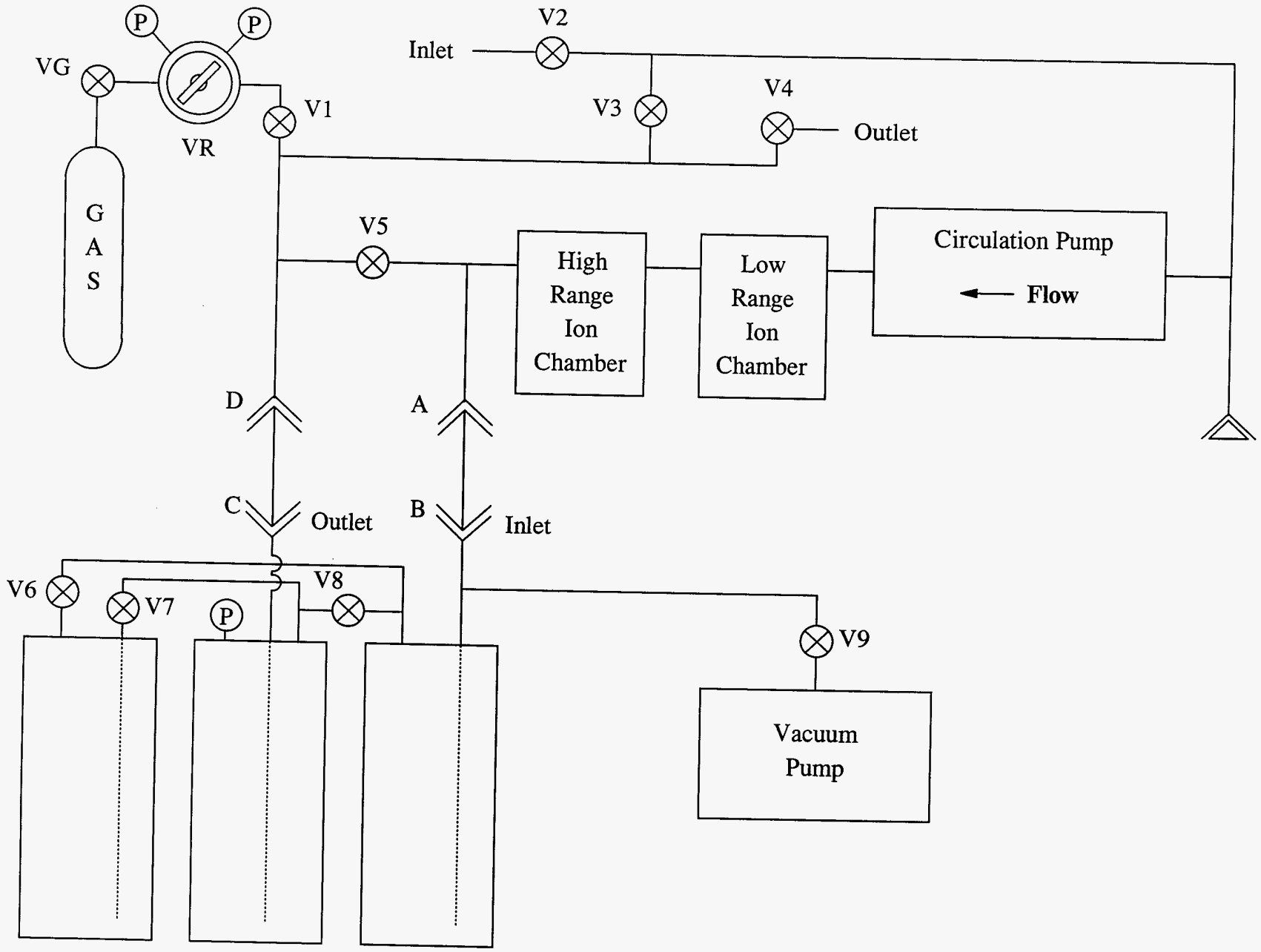
P
P
VG
V1
VR
GAS
V2
Inlet
V3
V4
Outlet
V5
High Range Ion Chamber
Low Range Ion Chamber
Circulation Pump
Flow
D
A
C
Outlet
B
Inlet
V6
V7
P
V8
V9
Vacuum Pump

Figure 8

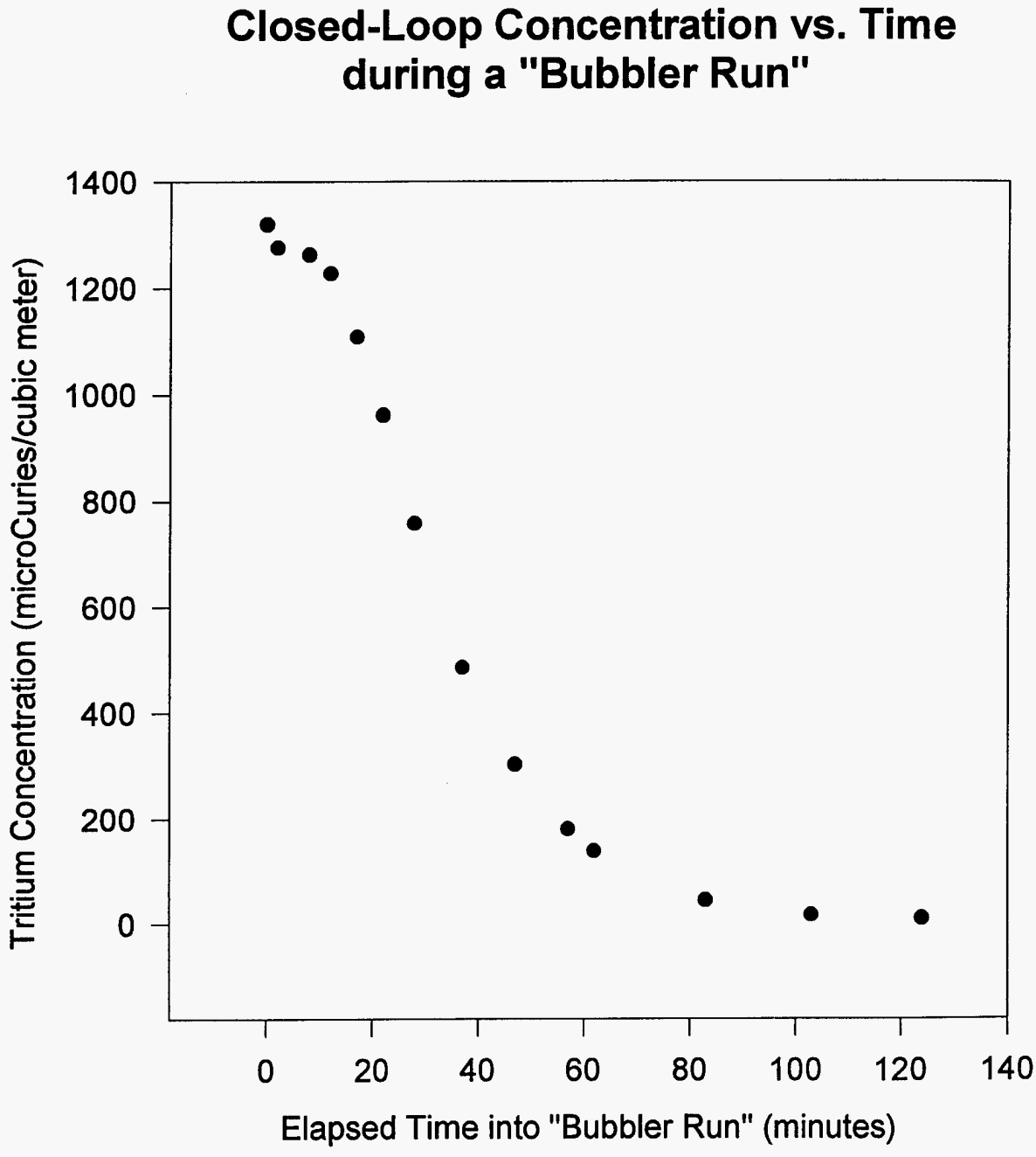
Closed-Loop Concentration vs. Time
during a "Bubbler Run"
Tritium Concentration (microCuries/cubic meter)
1400
1200
1000
800
600
400
200
0
0
20
40
60
80
100
120
140
Elapsed Time into "Bubbler Run" (minutes)

Figure 9

ESH-4 Radiation Instrumentation and Calibration Team
TA-3-40 Calibration and Evaluation Facility

Tritium-In-Air Monitor Calibration

Record #:	24	ESH #:	005191	Standard Transfer Inst.	
Cal. Date:	02/21/96	Manufacturer:	JOHNSTON	ESH#:	007175
Ref. Temp. (°C):	21.0	Model:	J-111	Model:	U-24
Ref. Press. ("Hg):	22.70	SN:	1137	CF:	1.00

Instrument Test Checks: Gamma Comp. Check: Y Alarm Check: Y Pump Check: Y

Calibration Data Tables

Instrument Backgrounds

Standard Inst. Background:	5 μCi/m3
IUT Background:	0 μCi/m3

Statistics for Each Range

Inst. Range Span	Normal. Response	Correction Factor	Std. Dev. (%)
50	1.090	0.919	4.651
500	0.951	1.053	3.421
10000	1.137	0.880	3.885
1000000	1.116	0.896	.586

Note: ALL Calibration Data Converted to μCi/m3

Std. Inst. (μCi/m3)	Std. Inst. Net (μCi/m3)	IUT Range Span	IUT (μCi/m3)	IUT Net (μCi/m3)	Normalized Response	Correction Factor
14	9	50	10	10	1.111	0.900
28	23	50	26	26	1.130	0.885
40	35	50	36	36	1.029	0.972
129	124	500	115	115	0.927	1.079
234	229	500	215	215	0.939	1.065
352	347	500	342	342	0.986	1.014
66	61	10000	70	70	1.148	0.871
513	508	10000	600	600	1.181	0.847
3700	3695	10000	4000	4000	1.083	0.923
3560	3555	1000000	4000	4000	1.125	0.889
9081	9076	1000000	10100	10100	1.113	0.898
63000	62995	1000000	70000	70000	1.111	0.900

Reject Comments:

Comments:

Does This Instrument Meet All Calibration Requirements? **YES** **(See Comments for exceptions)**

Calibrated By: _____ **Calibration Due:** 8-26-96

Report Number (14) LA-UR--97-2406
CONF-9706122--

Publ. Date (11) 199708
Sponsor Code (18) DOE/MA, XF
UC Category (19) UC-907, DOE/ER

DOE