

TRITIUM INVENTORY MEASUREMENT BY BETA SCINTILLATION DETECTION

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ABSTRACT

A new design for a beta scintillation detector (BSD) has been developed for measurement of tritium partial pressure and total-tritium concentration in HDT-He process samples. The tritium beta energy deposited in the $\text{CaF}_2[\text{Eu}]$ scintillation crystal produces light that is measured by a photodiode and electrometer producing an output voltage linearly proportional to the partial pressure of tritium. Mole percentage of tritium in unknown and standard samples is calculated from the ratio of BSD tritium partial pressure to the total sample pressure measured by a capacitance diaphragm gauge. Daily calibration to determine a new sensitivity $S[\text{V}/\text{Torr-T}_2]$ using a single standard HDT-He mixture produces analyses with errors typically less than 1.3 percent of value as determined by analysis of other standard mixtures over a one year period. This error of tritium measurement is monitored with a measurement control program at Los Alamos to assure accuracy for all tritium inventory samples measured by this method.

I. INTRODUCTION

Tritium inventory measurement by PVT-gas analysis is a routine requirement for handling tritium[1]. Traditionally, the gas analysis and tritium composition measurement is made by mass spectrometry, gas chromatography or laser raman spectroscopy. All of these techniques require extensive calibration to produce a complete analysis of all peaks when all that is needed for an inventory measurement (and some processing decisions) is total tritium in any chemical form (including methane, water and ammonia impurities). Beta scintillation detection has been used for many years within the US-DOE complex as a means for measuring tritium partial pressure and concentration in HDT-He gas samples [2,3]. This paper presents a new design for BSD which features all-metal seals and UHV compatible hardware and a replaceable crystal.

II. THEORY OF OPERATION AND APPARATUS

A beta scintillation detector (BSD) has been built for measurement of tritium partial pressure by converting the energy that a beta particle deposits in a europium-doped

calcium fluoride scintillation crystal ($\text{CaF}_2[\text{Eu}]$) into light. This light produces a photocurrent in a vacuum photodiode that is measured with an electrometer as indicated in Fig. 1.

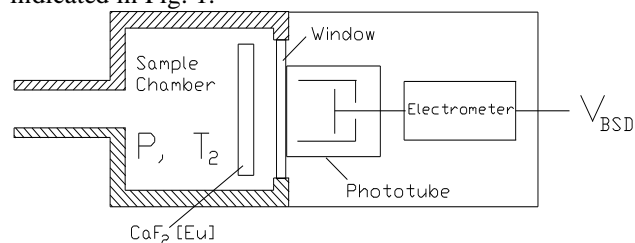


Fig. 1. A beta scintillation detector provides a voltage V_{BSD} proportional to tritium partial pressure .

The voltage output of the electrometer is linearly proportional to the partial pressure of the beta producing species. For tritium, the sensitivity calibration constant ($S[\text{V}/\text{torr-T}_2]$) relating BSD output voltage to the partial pressure of T_2 is determined by introducing known partial pressures of T_2 with standard gas mixtures at low pressures (< 10 Torr). If a low pressure sample of a gas containing tritium is introduced into the detection chamber of the BSD, the mean free path of the beta particle is long, so little energy is lost to collisions with other gas molecules, and thus the BSD has a linear response to the number density of tritium atoms in any chemical form. This means that tritium tied up as CT_4 or DTO can be measured as a T_2 equivalent concentration which, together with a moles measurement, allows calculation of tritium inventory in grams as

$$\text{Tritium}[\text{g}] = 6.032 [\text{PV}/\text{RT}] [T_2(\text{Mol-\%})/100] \quad (1)$$

where 6.032 is the grams per mole of T_2 , PV/RT gives the moles of gas in a storage volume V , and $T_2(\text{Mol-\%})$ is the T_2 equivalent mole percentage of the gas in volume V . The BSD response with a low pressure sample has little or no effect from the remaining composition of the gas sample so no matrix corrections are needed. Figure 2 shows the theoretical energy loss versus sample pressure which predicts less than 1 percent loss in beta energy for sample pressures less than 10 torr. Typically much smaller sample pressures are used to conserve tritium consumed in sampling.

The prototype of the BSD concept shown in Fig. 1 was developed by the first author at EG&G Mound. It used a Hamamatsu 2060 photomultiplier tube with all dynodes

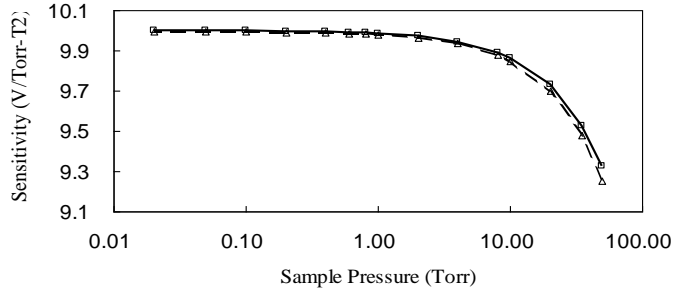


Fig. 2. BSD sensitivity versus sample pressure for HDT-He samples (■) and HDT-He with 10% N₂ (♦) samples. corrections are needed..

shorted together (effectively a phototube) with an Analog Devices 310J electrometer module to measure the photocurrent. Two additional units of this design were built for use at Princeton Plasma Physics Laboratory [4] and for this application (BSD-1) at Los Alamos National Laboratory. A commercial version of this prototype has recently been developed by *femto*-TECH, Inc. and their detector head is shown in Fig. 3; a unit like this is also used at LANL (BSD-2) for tritium inventory and process measurements. A separate chassis and readout display is used providing a 5 digit V_{BSD} display with 1 mV resolution.

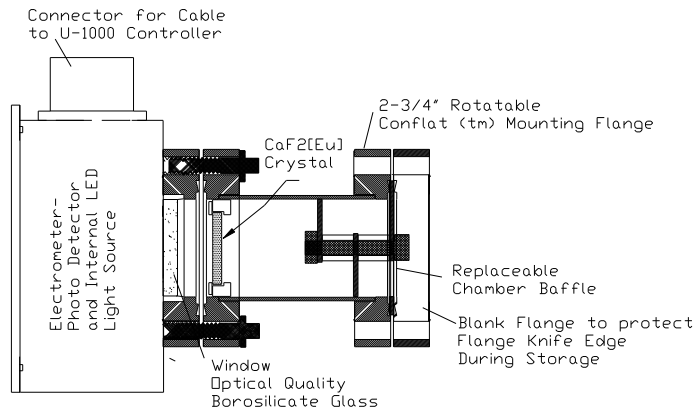


Fig. 3. *femto*-TECH Model BSD-1001 Detector Head.

The Mound units and the *femto*-TECH model BSD-1001 beta scintillation detector (BSD) head all use a 1.0" ϕ x 0.125" CaF₂(Eu) scintillation crystal spring mounted in a crystal holder on the non-rotatable end of a short UHV nipple. The region between a UHV window and the chamber baffle defines the volume of gas whose tritium betas can strike both sides of the crystal with a fixed geometry which makes the sensitivity of the BSD independent of the shape of the rest of the gas sampling system. A schematic of the LANL gas sampling and BSD tritium analysis system is shown in Fig. 4. HDT-He Standards or well-characterized mixtures

of T₂ in D₂, H₂ and/or ³He are used as a reference gases for calibration. The tritium content is known accurately by decay of initial composition to the date of analysis. Samples of standard mixtures are drawn through Vacuum Technology, Inc. sampling valves with 0.013 cm i.d. SS capillary sampling lines of 3 m length that produces a 0.5 T-L/s flow rate. Capillary lines for process samples have longer lengths to the process and larger i.d.'s [3]. Calibration of the BSD response is done by sampling gas from a known standard with tritium concentration T₂(Mol-%) and calculating a sensitivity, S(V/torr-T₂, T_{CAL}), at the recorded Kelvin temperature of the head, T_{CAL}, during calibration:

$$S(V/\text{torr-T}_2, T_{\text{CAL}}) = \frac{100 * [V_{\text{BSD}}(P) - V_{\text{BSD}}(0)]}{T_2(\text{Mol-\%}) * [P - P_0]} \quad (2)$$

BSD response to light only is recorded as response to the internal LED light signal at the time of calibration:

$$\text{LED}_{\text{CAL}} = [V_{\text{BSD}}(P) - V_{\text{BSD}}(0)] \quad (3)$$

Mole percentage of tritium in unknown samples is calculated from the ratio of BSD tritium partial pressure to the total sample pressure measured by a capacitance diaphragm gauge (CDG). The photocurrent reading, V_{BSD}, is used with a sensitivity S(V/torr-T₂, T_{CAL}) to calculate a tritium partial pressure (Eq. 4) and then, in ratio to the total sample pressure, the mole percentage (Eq. 5) of total tritium can be computed:

$$\text{PP}[T_2](\text{torr}) = \frac{[V_{\text{BSD}}(P) - V_{\text{BSD}}(0)] * [T_{\text{Sample}}/T_{\text{CAL}}]}{S * [\text{LED}_{\text{Sample}} / \text{LED}_{\text{CAL}}]} \quad (4)$$

and

$$T_2(\text{Mol-\%}) = \frac{100 * [V_{\text{BSD}}(P) - V_{\text{BSD}}(0)] * [T_{\text{Sample}}/T_{\text{CAL}}]}{[P - P_0] * S * [\text{LED}_{\text{Sample}} / \text{LED}_{\text{CAL}}]} \quad (5)$$

where V_{BSD}(0) and P₀ are the most recently measured zero readings when the foreline is evacuated. The difference [P - P₀] gives the total sample pressure from CDG readings, and, T_{Sample}/T_{CAL} and LED_{Sample} / LED_{CAL} correction for temperature dependence of gas density and electronic response.

III. CALIBRATION AND PERFORMANCE TESTING

Daily single-point calibration of a tritium beta scintillation detector (BSD) at LANL is done using a tritium standard with 50 to 100 mol-% of tritium. Assurance of accuracy for lower tritium compositions is verified by analyzing other HDT-He mixtures before and after process measurements are made on unknown samples. The measurement control protocol to gather data for monitoring the daily performance of a BSD is given in Table I. With the first sample, a sensitivity for the day is determined using Eq. 2. A record of S(V/Torr-T₂) as a

function of time is shown in Fig. 5 along with the $V_{\text{BSD}}(0)$ value (shown multiplied by 10 to show variation). During the

Table I.
Daily analysis sequence for a LANL BSD operation.

Run No.	Standard Mixture	T ₂ (Mol-%)	Function
1	LANL-5	72.6	Calibration S(V/Torr-T ₂)
2	LANL-1	16.3	Accuracy Check
3	LANL-2A	5.02	Accuracy Check
[Analyze Unknown Samples for Total Tritium Concentration]			
4	LANL-2A	5.02	Accuracy Check
5	LANL-1	16.3	Accuracy Check
6	LANL-5	72.6	Accuracy Check

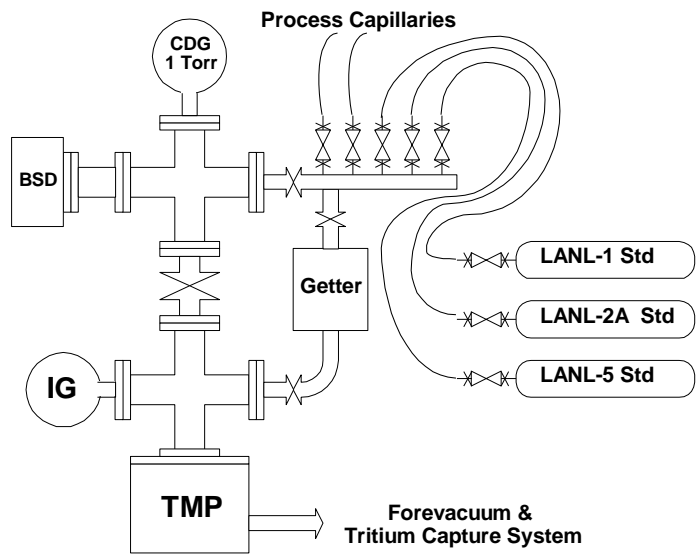


Fig. 4. LANL gas sampling and BSD tritium analysis apparatus which accesses multiple standard mixtures and process sampling points using capillary sampling lines.

one year of operation shown in Fig. 5, BSD-1 shows a loss in sensitivity and a corresponding increase in baseline reading, $V_{\text{BSD}}(0)$. The loss of sensitivity is attributed to beta-induced growth of a (hydrocarbon) film of 100 to 300 nm on the scintillation crystal while the increase of $V_{\text{BSD}}(0)$ is due to increased background on the walls of the BSD sample chamber. However, in spite of the loss in sensitivity and increased background, the use of the Table I protocol with a new sensitivity measured each day results in uniform small errors in the analysis of the check standards (2 -6 in Table I) as indicated in Fig. 6. In Fig. 6 the two-sigma (95 % confidence level) deviation for any single measurement is 1.3 % of value over the broad range of tritium compositions

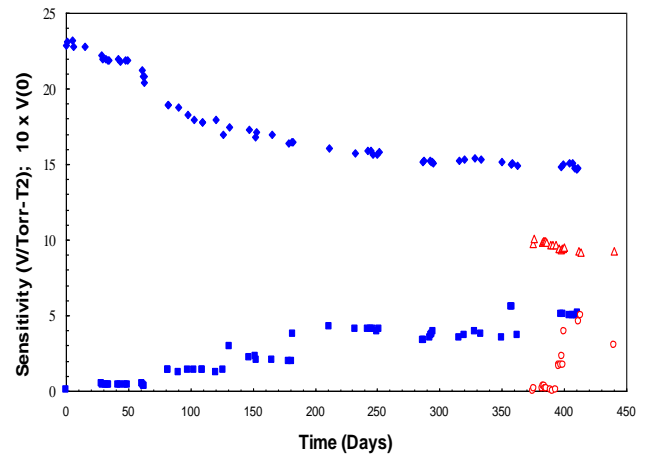


Fig. 5. BSD-1 Sensitivity (\blacklozenge) decrease with time for one year of operation and the corresponding increase in background BSD voltage $V_{\text{BSD}}(0)$ (\blacksquare) plotted here times 10. Similar data for BSD-2 are sensitivity (\triangle) and $V_{\text{BSD}}(0)$ (\circ) times 10.

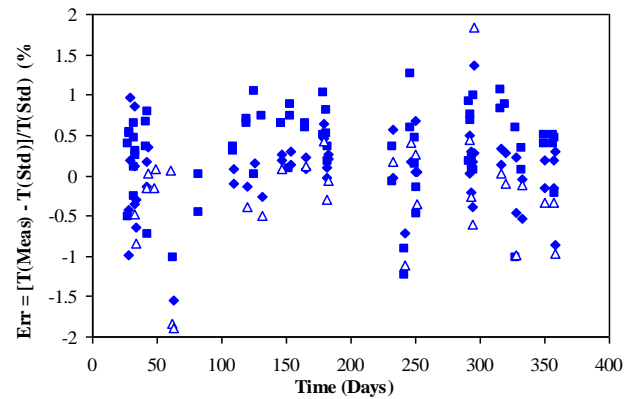


Fig. 6. Percent deviations of BSD-1 measured tritium value for three standard mixtures based on the single-point calibration each day (Fig. 5 Sensitivity data). Tritium values of HDT-He standards are nominally (\blacklozenge) 25 mol-%, (\triangle) 16 mol-% and (\blacksquare) 75 mol-%.

measured. The sensitivity for BSD-2, was adjusted to 10 V/Torr-T₂ initially to accommodate samples with up to 1 Torr of T₂. Figure 5 shows that BSD-2 sensitivity has decreased by 8 percent in 50 days due to film formation from tritium exposure. The $V_{\text{BSD}}(0)$ also increased due to tritium exchange with hydrocarbons and water on internal surfaces of the sample chamber. The largest increase in $V_{\text{BSD}}(0)$ occurred during an analysis of a sample that had significant HTO content, some of which adsorbed on the surface. But the daily calibration protocol accounts for these changes, and the errors in the analyses of standard mixtures are again small as shown in Fig. 7. The two-sigma (95 % confidence level) deviation for any single measurement is 1.2 % of value over the broad range of tritium compositions measured.

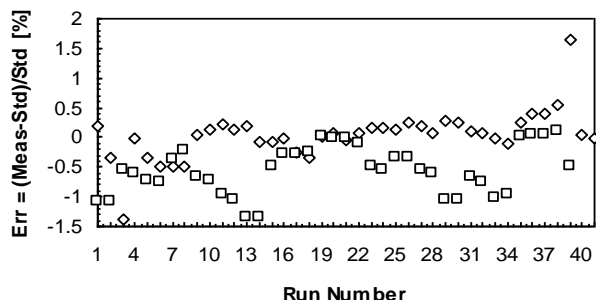


Fig. 7. BSD-2 analysis errors for two different standard tritium mixtures: Tritium values are (◆) 59.5 mol and (■) 28.0 mol-%.

IV. RESULTS AND DISCUSSION

The data in Fig. 5 on absolute sensitivity for BSD-1 shows a marked decrease of 30 percent over the year with notable decrease between day 55 and 80. During this time period, a failure of a diaphragm forepump introduced hydrocarbons into the BSD sample chamber by backstreaming producing a film on the crystal and surface contamination on the chamber walls that increases in tritium background by isotopic exchange. The film creates a dead layer on the crystal surfaces in which tritium betas lose energy but generate no light thus decreasing the sensitivity. Keeping the BSD sample chamber clean results in a stable sensitivity and low background readings as seen with BSD-2 (*femto*-TECH unit) data in Fig. 5. The importance of a local calibration method defined in Table I using some consistent standard to determine daily sensitivity is seen by examining the analyses of other standards each day in Fig. 6. Although the absolute sensitivity decreased by 30 percent, the error of daily measurements was within 1.3 percent at the 95 percent confidence interval. The accuracies of the standard mixtures is calculated to be about 0.3 percent of component value for tritium at preparation time. Care has been taken to preserve the purity and integrity of the mixtures by dedicating a sampling capillary line to each specific standard as seen in Fig. 4. The data in Fig. 6 gives no evidence of contamination (e.g. a shift in bias) of any standard during the year of use.

Since beta flux is related to the number density of tritium atoms in the sample chamber, and composition of tritium mole fraction is determined as ratio of tritium partial pressure to total pressure, the absolute sensitivity is inversely dependent on the Kelvin temperature of the gas as indicated in Eq. 4 and 5. The laboratory temperature for BSD-1 was stable at 23 ± 1 °C such that no temperature corrections in Eq. 5 were needed to account for changing gas density. However, the effect of changing temperature of the BSD sample chamber and crystal was

seen on BSD-2 data where glovebox temperatures and thus the head temperature increased by 4 °C from morning calibration to the final analysis taken late in the afternoon of a normal summer workday. This temperature change causes a 1.3 percent change in gas density by itself. The temperature dependence for light production by the scintillation crystal and light measurement by the electronics is determined by measuring the response to a stable LED internal light source. Measurements at calibration using Eq. 3 give a value LED_{CAL} , and similar measurements for each sample give LED_{Sample} which can be used in Eq 4 and 5. Both temperature and LED corrections were made for all measurements with BSD-2, which experienced the large temperature changes. No temperature corrections were made with BSD-1 data because temperature deviations were small and are part of the 1.2 % error measured.

V. SUMMARY

A method for measurement of total tritium by beta scintillation detection has been developed and implemented for tritium inventory and process measurements. Accuracy is measured daily with a suite of tritium standards and found to be ≤ 1.3 percent of component over a one year period for one BSD and similar performance for a second system over a 50 day period independent of loss of sensitivity due to buildup of a thin hydrocarbon dead layer on each scintillation crystal.

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