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I am submitting herewith a thesis written by Gerald A. Colman entitled "Systems Study for an Advanced Tritium Detector." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Electrical Engineering.

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2

SYSTEMS STUDY FOR AN ADVANCED TRITIUM DETECTOR

A Thesis

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Degree

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Gerald A. Colman

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ABSTRACT

This thesis describes a thorough and comprehensive systems study on the development of an advanced tritium-in-air monitor. Three technologies were investigated for possible use in a state-of-the-art tritium detector system: double-resonance laser-induced fluorescence spectroscopy, direct beta detection using a $\text{CaF}_2(\text{Eu})$ /bismuth germanate phosphor structure, and indirect beta detection using a closed-loop liquid scintillation system.

The concept of each of these technologies is discussed in this thesis. Various detector systems are proposed, and the numerous components making up each system are selected based on performance and cost. Calculations of sensitivity and estimated purchase price are included in the analysis of each proposed system. Each is also evaluated in terms of its time constant, portability, movability, ability to distinguish between the elemental (HT) and oxide (HTO) forms of tritium in air, and the ability to reject false signals from external alpha-, beta-, and gamma-emitting radionuclides.

This thesis is intended to be used as an aid in the selection of a conceptual system to be developed as an advanced tritium-in-air monitor; therefore, development costs and probabilities of successful implementation are given for each proposed system. It is concluded that two systems, a laser-induced fluorescence detector and a $\text{CaF}_2(\text{Eu})$ /bismuth germanate detector, should be considered for further development, and a development scenario is recommended.

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I. INTRODUCTION

This thesis describes a systems study undertaken for the development of an advanced tritium detector. This work was carried out at Oak Ridge National Laboratory under the auspices of the Department of the U.S. Navy's Naval Electronics Systems Command Nucleonics Branch, Code 81531.

The current state of the technology was first surveyed by comparing the various existing detection techniques. Following that, the different technologies were assessed with regard to potential improvements in tritium monitoring techniques. For example, a liquid scintillation system in which the scintillator is continuously cleaned of the sample and contained in a closed loop has been considered in this study as an improvement in an existing technology. Other techniques, such as tritium detection using ionization chambers, have also been investigated. However, it is believed that application of most of the current technologies would result in only minimal improvements unless a major breakthrough occurs.

This study was therefore directed toward the conceptual development of two promising new techniques for detecting tritium in air: laser spectroscopy and solid scintillation detection using a "phoswich" structure. It is anticipated that these new detection techniques might increase detection sensitivity at a minimal increase in cost.

The development of these new detection techniques followed the framework of a conventional systems study. The study was broken

down into three main phases--concept, selection, and analysis. The synthesis phase, normally included in a systems study, was not included here because it is anticipated that this phase will occur later based on a favorable evaluation of the proposed systems.

The primary function of the advanced tritium detector system is to measure airborne tritium isotope activity both on shipboard and at shore weapon facilities, and air samples shall be representative of the air normally inhaled by personnel located at these sites. The detector system shall repeatedly measure a specified concentration of tritium in air (sensitivity). A desirable level of sensitivity is $0.1 \mu\text{Ci}/\text{m}^3$. A feasibility and cost analysis was also made for each conceptual detector system to decide whether to include the capability of differentiating between and recording the activity levels of hydrogen tritium (HT) molecules and hydrogen tritium oxide (HTO) molecules. Consideration was also given to minimizing the sensitivity of each system to radiation-emitting nuclides other than tritium.

II. TECHNOLOGIES PRESENTLY EMPLOYED

This systems study began with a literature search which investigated the different detection techniques used in the past to measure airborne tritium levels. An effort was made to assess each technique in a qualitative manner. Table 1 lists the papers reviewed in the literature search and gives a description of the detection technique along with counting data, operating data, ability to compensate for gamma radiation and other external sources, and comments on good and bad points of the particular detection technique. Table 2 lists commercially available detectors according to model and gives data on detector type, sensitivity, range, response rate, temperature range, humidity range, compensation, and cost.

All detectors manufactured in the United States use flow-through ionization chambers. Some of the problems associated with the use of these detectors when counting tritium include their sensitivity to external gamma radiation, to other beta and alpha emitting radionuclides, to ions present in the air, to smoke and dust particles, and to temperature and humidity changes. Most of these problems can be solved, but in general the lower limit of detector sensitivity is imposed by its response to external gamma sources. Practical sensitivities for ionization chambers are about $5 \mu\text{Ci}/\text{m}^3$ ($1 \text{ Ci} = 3.7 \times 10^{10}$ disintegrations per second).

Table 3 is a comparison of the technologies employed in the past according to sensitivity. Each method is also evaluated

Table 1. Tritium detection instruments and methods described in literature.

Reference	Description	Counting data ^d	Operating data	Gamma compensation and other radionuclides	Comments	HT or HTO suitability
Colmanares et al., Nucl. Instrum. Methods 114, 277-289 (1974).	6.35-cm-diam $\times$ 0.37-cm CaF ₂ (Eu) Scintillator/ Low Noise PMT. Pulse shape discrimination employed to reject PMT thermal pulses.	Minimum detectable concentration = 48 $\mu\text{Ci}/\text{m}^3$ (STP).	0-100°C; light output changes: 1/172 over this temp. range. 30- to 60-s counting time.	Not demonstrated in paper. Could be used in flowwich arrangements to reject Compton interactions and energetic beta particles.	Low solubility. Available from Harshaw.	HT and HTO
Osborne et al., IEEE Trans. Nucl. Sci., NS-22, 676-680 (1975).	Air bubbled through flowing stream of water (98% of HTO removed). Water sent through array of plastic scintillator sheets in flow-through counter. NE102 (300-cm ² surface)	0.1 cps per $\mu\text{Ci}/\text{m}^3$ Background = 0.2 cps (no noble gas & <0.1 m/h). 1 $\mu\text{Ci}/\text{m}^3$ detectable in ~200 s.	31-s time constant for air-to-water system.	Most dissolved noble gases removed by bubbling clean N ₂ or air through stream. Count rate from noble gases <70% that of H ₂ at same concentration.	Used as a central tritium monitor for Canadian CANDU reactors. ^d	HTO
Gibson et al., J. Nucl. Energy Parts A/B 20, 185-190 (1966).	Water condensed continuously (10 g/h), subsequently counted in flow cell filled with anthracene crystals/PMT.	Range: 0.1 $\mu\text{Ci}/\text{m}^3$ to 10 ³ $\mu\text{Ci}/\text{m}^3$. ~50 cps per $\mu\text{Ci}/\text{m}^3$. Background = 6 cps.	Measurements made at 72°F, 58% relative humidity. (Dependent on humidity.)	Can be operated in high gamma fields and does not detect radioactive gas such as ⁴¹ Ar. Contained in a 3-in. lead pig. GM tubes used to measure and correct for background γ .	Instrument is large 3 $\times$ 4 $\times$ 6-1/2 ft high. Contamination of anthracene can be removed by flushing cell with distilled H ₂ O.	HTO
Singh et al., IEEE Trans. Nucl. Sci., NS-21, 188-193 (1974).	Flow cell packed with 250- 350 μm plastic scintillator powder. Active volume = 6 cm ³ . Uses single PMT-EMI 9514 S/A.	500 cps per $\mu\text{Ci}/\text{m}^3$. Background = 50 cps. Counting efficiency = 2.5%. Minimum detectable concentration = 0.01 $\mu\text{Ci}/\text{m}^3$.	Time constant $\approx$ 5 min at 1.6 cm ³ /min. Dependent on humidity. Dependence could be eliminated by saturating sample with inactive H ₂ O prior to condensation. At 25°C & 100 L/min of saturated air, condensation rate $\approx$ 1.6 cm ³ /min.	Low gamma response.	Does not show any background buildup over long period of time. Two PMTs in coincidence could reduce background significantly.	HTO
Howell et al., Nucl. Instrum. Methods 124, 579-583 (1975).	Separation of HT, noble gases, & HTO vapor with semipermeable membranes. Enhanced sample mixed with counting gas and counted in flow-through proportional counter.	Enhancement Data: Type: Con. HTO Con. HT Dimethyl/silicone 51 Silicone polymer 60 Formvar 70 Two-stage system yielded an enhance- ment factor of 1880.	Time constant $\approx$ 3 min at: 250 cm ³ /min flow rate, 250 cm ³ detector volume.		Sensitivity = 2.3 $\mu\text{Ci}/\text{m}^3$ in 10 s counting time.	HTO
Ogawa et al., Nucl. Instrum. Methods 176, 591-594 (1980).	Mixture of sample gas & pure air was fed to a large- volume ionization chamber. Mixing ratio was modulated by a sine function (1/120 Hz).	Sensitivity = 0.1 $\mu\text{Ci}/\text{m}^3$.	Modulation frequency = 1/120 s ⁻¹ . Counting time $\approx$ 40 min.		Correlation analysis used to recover signal where intensity is buried in strong back- ground.	HT and HTO

Table 1 (continued)

Reference	Description	Counting data ²	Operating data	Gamma compensation and other radionuclides	Comments	HT or HTO suitability
Beach et al., Nucl. Instrum. Methods 175, 369-377 (1980).	Sample gas is selectively filtered through a dimethyl silicon membrane. Throughput 400 times greater for HTO than for HT. Mixed with 10% methane, 90% argon and counted in flow-through proportional counter. (10 cm ³).	0.09 cps/μPC. Background = 1.0 cps. Can detect levels as low as 10 MPC in 60 s.	Response times for membrane (93% equilibrium): 9 s for HT, 5 min for HTO.	Pulse height analysis used for noise rejection.	Detector responds on an MPC level. MPC _{HTO} = 400 MPC _{HT}	HT and HTO
Osborn et al., IAEA-SM-265/57 Vienna, Feb. 18-22, 1980.	Nafion tubes used to separate HTO from HT. HT mixed with flowing liquid scintillator and subsequently counted.	Minimum detectable concentration = 7 nCi/m ³ . Scintillator flow rate = 0.1 cm ³ /min.		Premutation rate for radionuclides relative to HTO is 10 ⁻⁴ .	Nafion tube: Discrimination factors of 10 ³ can be obtained (Conc. HTO / Conc. HT). Tritium collection is enhanced when water is used in the liquid scintillator. Water alone allows 100% collection.	HTO
Hoy et al., Health Phys. 5, 203 (1961).	5l.5-liter Kanne chamber. 3 concentric cylinders, inner and outer electrodes at GND, intermediate cylinder at 200 V. Region between outer and intermediate cylinders acts as an ion trap. Inner region is the ion chamber. Electrometer measures current.	Under ideal conditions sensitivity = 5 μCi/m ³ . Sensitive area = 1.1 × 10 ⁶ cm ² . 2 × 10 ¹³ μCi/m ³ per amp.		Buildup of activity causes contamination. Heat or air purging can remove most contamination.		HTO and HT
Anderson et al., IAEA-SM-245/19, Vienna, Feb. 18-22, 1980; also CONF-800427, 274-277.	Improved Kanne chamber. HV electrode replaced by wire cylinder. Sensitive area = 266 cm ² . Electrometer sensitivity = 10 ⁻¹⁵ A.	1.8 × 10 ¹³ μCi/m ³ per amp. Sensitivity = 0.1 μCi/m ³ with contaminating environment.		Wire cylinder reduces area on which contaminants may collect.	Operated at LASL	HT and HTO
Jalbert, R. A., Trans. Am. Nucl. Soc. 22, 739-740 (1975).	Flow-through ionization chamber. Volume = 1.6 L.	Sensitivity = 1 μCi/m ³ .	Time constant = 3.5 s.	Second chamber used for compensation. Common wall: 0.25-in. mesh copper screen covered with 0.25-mil aluminized Mylar. Opaque to H ³ betas only.		HT and HTO

Table 1 (continued)

Reference	Description	Counting data ¹	Operating data	Gamma compensation and other radionuclides	Comments	HT or HTO suitability
Jalbert, R. A., LA-9382-MS, Aug. 1982.	Dual flow-through ion chamber. Outer used for compensation. Wall between inner and outer chamber is opaque to 10^5 d. Wall constructed of square mesh (6.3-mm spacing) copper screen covered with 0.064-mm double-aluminized Mylar.	Sensitivity $\approx 1\text{--}3 \mu\text{Ci}/\text{m}^3$ in absence of contami- nant gases. Electrometer sensi- tivity = $10\text{--}15$ A. Range: to 10^{10} A.	Time constant = 60 s. Temperature and pressure should remain constant.	Wall between inner and outer chambers allows higher energy betas to penetrate for current subtraction.	Operated at LASL HT and HTO for Tokamaks.	
Osborne, R. V., AFCL-4303, Sept. 1972.	Condenses HTO vapor to water. Uses plastic and liquid scintillator. Array of 0.13-mm-thick sheets.	Plastic scintillator sensitivity = $10 \text{ pCi}/\text{cm}^3$, with $1 \text{ nCi}/\text{cm}^3$ noble gas. For 240 cm^2 active area 5 cpm per $1 \text{ pCi}/\text{cm}^3$. Background = 14 cpm.	2% error in exchange due to variations in humidity. Flow rate $4000 \text{ cm}^3/\text{min}$. Time constant = 4 min.	Water/water vapor exchanger is a poor collector of noble gases. Discrimination of noble gases = factor of 40.		HTO
Sheehan et al., M2M-2205, Feb. 14, 1975; also Trans. Am. Nucl. Soc. 32, 142-143 (1979).	Freeze-out trap used to collect HTO. HT passed over hot palladium catalyst and condensed in the form of water in another freeze-out trap.	Sensitivity = $0.5 \mu\text{Ci}/\text{m}^3$. Background = 600 cpm at Mound Lab.	Not real-time monitoring.	Can be used in a gamma background up to $0.05 \text{ mR}/\text{h}$.	Palladium catalyst must operate in a tube furnace. Operated at Mound Lab. Ethylene glycol bubblers also used to collect water vapor.	Differen- tiates between HT and HTO
Tice et al., Johnston Labs. Presented at the meeting of the Health Physics Soc. June 20, 1973.	2.27-liter wall-less gas flow counter surrounded by an integral coaxial anti- coincidence shield counter. 87.5% methane + 12.5% sample air.	450 cpm per $\mu\text{Ci}/\text{m}^3$. Background = 5 cpm using 4.2-cm steel shield. Sensitivity = 0.01 $\mu\text{Ci}/\text{m}^3$.	Range: $0.01 \mu\text{Ci}/\text{m}^3$ to $600 \mu\text{Ci}/\text{m}^3$. Humidity = 0-99% RH. Max Temp = 38°C . Time constant = 4 min at methane flow = $1.12 \text{ L}/\text{min}$.	Gamma sensitive. Cannot discriminate noble gases.	Dryer used which typically removes 99.5% of HTO.	Differen- tiates between HT and HTO
Brown et al., M2M-2015 April 6, 1973.	Grab sampler. Silica gel strips HTO from airstream. Subsequently passed through silicon gel coated with palladium black to capture HT in the form of water. Analyzed by liquid scintillation counting.	Sensitivity = $1.6 \times 10^{-6} \mu\text{Ci}/\text{m}^3$.	Not real-time monitoring.			Differen- tiates between HT and HTO
Sudar et al., Nucl. Instrum. Methods 112, 399-404 (1973).	Pulse shape discrimination used with proportional counter. Non-flow-through CH_4 counting gas used.			5 cm Pb, 2 to 4 cm Fe, and 9 cm paraffin + H_2SO_4 shield was used. Meson guard ring used.	Rise times of γ HT and HTO vary more widely than rise times of β .	HT and HTO

Table 1 (continued)

Reference	Description	Counting data ^a	Operating data	Gamma compensation and other radionuclides	Comments	HT or HTO suitability
Osborne et. al., Nucl. Instrum. Methods 106, 131-187 (1973).	Dual ionization chambers, 1.2 L each. Coaxial arrangement.	Sensitivity = 5 $\mu\text{Ci}/\text{m}^3$. Accuracy better than 10%.	Portable & battery operat- ed. Time constant = 70 s at air flow rate = 30 cm^3/s . Range: 5 to 10 ⁴ $\mu\text{Ci}/\text{m}^3$. Sensitive to changes in humidity: $\pm 5\%$ over 15-65% RH range.	Compensation for γ background irradiation from any direction >95%. Sensitive to noble gases: ⁴¹ Ar sensitivity = 2.2 times that for ³ H at same concentration.	Used in the Canadian Atomic Energy Program.	HT and HTO
Block et al., UCRL-51131, Sept. 27, 1971.	Large area, thin window gas- flow proportional counter. 2 counters used, one with aluminized Mylar window (opaque to ³ H β^-) and other has a forward window.	Easily measures 5 $\mu\text{Ci}/\text{m}^3$ of HTO at 3 m/h uniform γ field.		Both detectors measure same background. Difference in outputs yields ³ H activity.	HTO has greater permeation rate through forward than HT.	HTO
Naghissi et al., Nucl. Instrum. Methods 68, 159 (1969); also CONF-680821, New York, Aug. 28, 1968.	100 3-mm-diam anthracene coated rods. Two PMTs connected in coincidence. Plexiglas rods used.	20 cps per $\mu\text{Ci}/\text{m}^3$. Background = 30 cps without shielding.			Memory effect often observed with plastic phosphors is minimized.	HTO and HT
Osborne, R. V., CRNL-593, Aug. 1971 also Nucl. Instrum. Methods 77, 170-172 (1970).	Tritium water monitor. 60 (5 cm $\times$ 5 cm) NE102, 125- μm - thick sheets stacked vertically. Two PMTs connected in coincidence. Surface area = 3045 cm^2 .	Measures down to 1 $\mu\text{Ci}/\text{L}$. 0.4 cps per $\mu\text{Ci}/\text{L}$. Background = 0.4 cps. Accuracy = $\pm 10\%$ at 1 $\mu\text{Ci}/\text{L}$, $\pm 3\%$ at 10 $\mu\text{Ci}/\text{L}$.	Response time = 1 min. Range: 1 - 1000 $\mu\text{Ci}/\text{L}$. Can operate at less than 40°C.	10-cm Pb shield surrounds chamber. Sensitivities: Low energy γ (Cs137): <0.025 cps per mR/h. High energy γ (Co60): 0.75 cps per mR/h. Low/Moderate energy β^- (<0.8 MeV): 60 cps per $\mu\text{Ci}/\text{L}$. High energy β^- (³² S): 270 cps per $\mu\text{Ci}/\text{L}$.	Used in the Canadian Atomic Energy Program.	³ H in water
Osborne, R. V., AECL-4034 Las Vegas, August 30, 1971; also Nucl. Instrum. Methods 77, 170-172 (1970).	60 (5 cm $\times$ 5 cm) NE102 125- μm -thick sheets stacked vertically. Two PMTs connected in coincidence. Surface area = 3045 cm^2 . Same as water monitor but used for air.	Sensitivity = 0.1 $\mu\text{Ci}/\text{m}^3$. 150 cps per $\mu\text{Ci}/\text{m}^3$. Background = 30 cps.	Response time = 1 min.	Gamma sensitivity = 80 cps per mR/h with 10-cm Pb shield.	Used as ³ H water monitor in CANDU program but can be used as air monitor.	HT and HTO
Prevo et al., UCRL-50882, May 26, 1970.	Measures ³ H in natural gas on-line. 1.732-in.-diam $\times$ 0.010 in. $\text{CaF}_2(\text{Eu})$ crystal.	Sensitivity = 20 $\mu\text{Ci}/\text{m}^3$ for counting time of 20 min.			Pulse shape discrimination may greatly reduce dark current. $\text{CaF}_2(\text{Eu})$ can be evaporated onto a disk.	HT and HTO

Table 1 (continued)

Reference	Description	Counting data ^a	Operating Data	Gamma compensation and other radionuclides	Comments	HT or HTO Suitability
Valentine, A. M., LA-3916, July 26, 1968.	Describes a bubbler consisting of a dry gas wash bottle with a fritted glass tip on the inlet and distilled water as the collecting medium.		Collection efficiency >90% at 8-10 L/min and 25-35°C using 30-50 cm ³ distilled H ₂ O.		Measurement made with liquid scintillator and compared to flow-through ionization chamber.	HTO
Osborne, R. V., AECL-2699, Nov. 1967; also AECL-2604, Oct. 1966. (Survey of various instruments)	40-L dual coaxial ionization chamber AEPI0101. 1.2-L dual coaxial ionization chamber AEPI498.	Most sensitive range: 0-7.5 $\mu\text{Ci}/\text{m}^3$. Least sensitive range: 0-0.25 Ci/m^3 . Most sensitive range: 0-50 $\mu\text{Ci}/\text{m}^3$. Least sensitive range: 0-5000 $\mu\text{Ci}/\text{m}^3$.	Flow rate = 36 L/min. Rise time = 2 min. Sensitive to humidity changes. Sensitive to humidity changes. Response time less than 1 min.	Inhomogeneities in gamma field can lead to over-compensation. Inhomogeneities in gamma field can lead to over-compensation.		HTO and HT
	NE102 wound into a double spiral. 192-cm ² active area. 0.005-in.-thick sheets. 2 PMTs connected in coincidence.	Sensitive range: 0.5-5 $\mu\text{Ci}/\text{m}^3$.		5/8-in. lead shield and pulse height analysis. Gamma compensation ~98%.	Portable model.	HTO and HT
Burt et al., AENE-R-4638 May 1964. (Survey of detectors for measuring ³ H in water.)	Liquid scintillation NE220. Single PMT. Scintillator Beads NE102A. 100- μm spheres. Single PMT.	Efficiency = 7.0%. Sensitivity = 0.154 $\mu\text{Ci}/\text{L}$. Limit of Detection = 0.019 $\mu\text{Ci}/\text{L}$. Efficiency = 0.2%. Sensitivity = 390 $\mu\text{Ci}/\text{L}$. Limit of Detection = 2.29 $\mu\text{Ci}/\text{L}$.			PMT was water cooled. PMT was water cooled. Beads strongly phosphorescent, need 24 h to decay.	H ³ in H ₂ O
	Scintillation Spiral NE801, 0.7-mm ID. Single PMT.	Efficiency = 0.06%. Sensitivity = 300 $\mu\text{Ci}/\text{L}$. Limit of Detection = 3.74 $\mu\text{Ci}/\text{L}$.			PMT at +5°C, refrigerated. Contaminated from H ³ .	H ³ in H ₂ O
	Anthracene Crystal Cell NE804 in 2-mm ID plastic tube. Single PMT.	Efficiency = 1.16%. Sensitivity = 13.3 $\mu\text{Ci}/\text{L}$. Limit of Detection = 0.306 $\mu\text{Ci}/\text{L}$.			PMT at +5°C, refrigerated. Contaminated from H ³ . Most suitable for continuous H ³ monitoring.	H ³ in H ₂ O

Table 1 (continued)

Reference	Description	Counting data	Operating data	Gamma compensation and other radionuclides	Comments	HT or HTO Suitability
Descours et al., Radioprotection 16(1), 15-23 (1981).	Ball plastic scintillator flow-through plastic cell. 2 PMTs in coincidence.	Sensitivity limit = 1 $\mu\text{Ci/L}$.	Response time below 30 min for 3×10^{-3} $\mu\text{Ci/mL}$.	5-cm Pb shield.		H ³ in H ₂ O
McElroy et al., CONF-800427, Dayton, Apr. 29, 1980, pp. 169-176. (Survey of various detectors from Canadian Atomic Program)	Hand-held monitor: 2 adjacent 80-cm ³ ionization chambers. Nafion membrane to separate HTO from HT. 100 parallel tubes, 0.65-mm ID, 0.9-mm OD. Effective length = 45 cm.	Sensitivity = 0.32 mV/ $\mu\text{Ci-m}^{-3}$. Resolution = 10 $\mu\text{Ci/m}^3$.	4-s electrical time constant. Measures up to 20 $\mu\text{Ci/m}^3$.	Dual ionization chambers for current subtraction.	Inexpensive electrical and mechanical components used.	HT and HTO
	Single Nafion tube and flowing liquid scintillator.	Sensitivity = 7 nCi/m ³ .		Ratio of permeation rates for HT and Xe with respect to HTO are 10^3 and 10^4 , respectively, for a practical monitor.		HTO
	Ethylene glycol bubblers with hot palladium sponge catalyst. Liquid scintilla- tion counting of ethylene glycol.	Lower detection limit = 10 ⁻⁴ $\mu\text{Ci/m}^3$.	No real-time measurement. No upper limit or satura- tion point.	Concentration of HTO relative to HT after passage through membrane dependent on type of scintillator.	Can be used to monitor total HT and HTO present over an extended time period.	Differen- tiates between HT and HTO
Hurley, J. D., CONF-800427, Dayton, Apr. 29, 1980, pp. 186-189.	Air drawn through type 4A molecular sieve (480°C). HTO collected in cold trap (-40°C). Air then passed through 1.82 palladium- impregnated type 4A molecu- lar sieve (480°C). Oxidized HT collected in cold trap (-40°C). Aqueous sample volumes (2-3 mL) decomposed by passage over hot magnesium turnings. Mixed with propane and counted in proportional counter.	Sensitivity = 0.01 pCi/m ³ of air.	1000 min counting time.			Differen- tiates between HT and HTO

^aMinimum detectable concentration:

$$\text{MDC} = \frac{1}{k} \left[1.29 \left(\frac{R_b}{t_s} \right)^{1/2} + \frac{2.7}{t_s} \right] (\mu\text{Ci/cm}^3)$$

where

R_b = background in cpm,

t_s = samples plus background counting time,

k = detector sensitivity in cpm/ $\mu\text{Ci-cm}^{-3}$ (STP).

$\therefore \text{MPC}_{\text{HT}} = 2000 \mu\text{Ci/m}^3$.

$\text{MPC}_{\text{HTO}} = 5 \mu\text{Ci/m}^3$.

^cNote: 1 pCi/cm³ = 1 $\mu\text{Ci/m}^3$.

^dCanadian: MPC = 10 $\mu\text{Ci/m}^3$ for HTO
USA: MPC = 5 $\mu\text{Ci/m}^3$ for HTO.

^eIn water 1 nCi/mL = 1 $\mu\text{Ci/L}$.

Table 2. Commercially available instruments for the detection of airborne tritium.

Model	Type	Sensitivity	Range	Response rate	Temperature	Relative humidity	Compensation	Cost
BETATEC Monitors (off-the-shelf) ¹ available from Overhoff & Associates, Inc., P.O. Box 8091, Cincinnati, OH 45208								
110/2L	Remote, single 2-L ionization chamber.	$\pm 1 \mu\text{Ci}/\text{m}^3$, Noise & drift: $1 \mu\text{Ci}/\text{m}^3$, Accuracy = $\pm 10\%$ of reading.	0-2,000 $\mu\text{Ci}/\text{m}^3$, (0-20,000 $\mu\text{Ci}/\text{m}^3$ optional).	20 s (5 s with radon rejection circuitry).	0-75°C, Ion chamber. 0-50°C, Display cabinet.	0-90%	None	\$7,848.00 (12/31/81)
210/2L	Internal, single 2-L ionization chamber.	$\pm 1 \mu\text{Ci}/\text{m}^3$, Noise & drift: $1 \mu\text{Ci}/\text{m}^3$, Accuracy = $\pm 10\%$ of reading.	0-2,000 $\mu\text{Ci}/\text{m}^3$, (0-20,000 $\mu\text{Ci}/\text{m}^3$ optional).	20 s (5 s with radon rejection circuitry).	0-75°C, Ion chamber. 0-50°C, Display cabinet.	0-90%	None	\$7,438.00 (12/31/81)
120/2L	Remote, dual 2-L ionization chamber. Separate chambers side by side or end to end.	$\pm 1 \mu\text{Ci}/\text{m}^3$, Noise & drift: $1 \mu\text{Ci}/\text{m}^3$, Accuracy = $\pm 10\%$ of reading.	0-2,000 $\mu\text{Ci}/\text{m}^3$, (0-20,000 $\mu\text{Ci}/\text{m}^3$ optional).	20 s (5 s with radon rejection circuitry).	0-75°C, Ion chamber. 0-50°C, Display cabinet.	0-90%	Gamma-compensated version of Model 110/2L-data unavailable.	\$8,238.00 (12/31/81)
220/2L	Internal, dual 2-L ionization chamber.	$\pm 1 \mu\text{Ci}/\text{m}^3$, Noise & drift: $1 \mu\text{Ci}/\text{m}^3$, Accuracy = $\pm 10\%$ of reading.	0-2,000 $\mu\text{Ci}/\text{m}^3$, (0-20,000 $\mu\text{Ci}/\text{m}^3$ optional).	20 s (5 s with radon rejection circuitry).	0-75°C, Ion chamber. 0-50°C, Display cabinet.	0-90%	Gamma-compensated version of Model 210/2L-data unavailable.	\$7,815.00 (12/31/81)
Special Order Tritium Monitors available from Overhoff & Associates, Inc., P.O. Box 8091, Cincinnati, OH 45208								
Single-range model.	External, 6-L lead-lined ionization chamber.	$\pm 0.1 \mu\text{Ci}/\text{m}^3$, Noise & drift: $0.1 \mu\text{Ci}/\text{m}^3$, Accuracy = $\pm 10\%$ of reading.	0-2,000 $\mu\text{Ci}/\text{m}^3$ in one range.	10 s with radon rejection circuit.	0 to 40°C	0-98%	Data unavailable.	?
Military Model 57 meets MIL 184006, shipboard shock, 9015.	2-L chamber common.	$\pm 0.2 \mu\text{Ci}/\text{m}^3$, Noise and drift: $0.2 \mu\text{Ci}/\text{m}^3$, Accuracy = $\pm 10\%$ of reading.	0-10,000 $\mu\text{Ci}/\text{m}^3$ in 7 manually switched ranges.	20 s with radon rejection circuit.	-20°C to 50°C	0-98%	Data unavailable.	\$5,000.00 (6/13/83)
Lightweight, high-sensitivity portable Model 786.	Single or dual, 1-L ionization chamber.	$\pm 1 \mu\text{Ci}/\text{m}^3$, Noise and drift: $2 \mu\text{Ci}/\text{m}^3$, Accuracy = $\pm 10\%$ of reading.	Dual scales: 0-10,000 $\mu\text{Ci}/\text{m}^3$ 0-10,000 $\mu\text{Ci}/\text{m}^3$.	5 s with radon rejection circuit.	0 to 40°C	0-98%	Gamma compensated with dual chamber side by side or end to end.	\$3,500.00(7) (6/13/83)
Tritium Monitors available from Johnston Laboratories, Inc., Cockeysville, MD 21030								
Portable Model 111.	Dual 0.4-L each ionization chambers.	Accuracy: $\pm 10\%$ on linear range, $\pm 20\%$ on log ranges.	4 ranges: 2 linear-- 0-50 $\mu\text{Ci}/\text{m}^3$ 0-500 $\mu\text{Ci}/\text{m}^3$ 2 log-- 10^1 - 10^4 $\mu\text{Ci}/\text{m}^3$ 10^3 - 10^6 $\mu\text{Ci}/\text{m}^3$.	20 s on 0-50 $\mu\text{Ci}/\text{m}^3$ range.	0 to 50°C	0-90%	Gamma compensation up to 5 m/h for uniform gamma field. Square array of 4 cylindrical chambers for excellent gamma compensation in non-uniform fields.	\$6,500.00 (6/13/83)
High Sensitivity Model 955B.	Four 5-L ionization chambers.	Reproducible: $\pm 2\%$. Accuracy: $\pm 10\%$ FS.	4 ranges: 0-10 $\mu\text{Ci}/\text{m}^3$ 0-100 $\mu\text{Ci}/\text{m}^3$ 0-1,000 $\mu\text{Ci}/\text{m}^3$ 0-10,000 $\mu\text{Ci}/\text{m}^3$.	Switch selectable 15 and 45 s.	0 to 50°C	0-90%	Gamma compensation up to 5 m/h for uniform field.	\$5,600.00 (6/13/83)

Table 2 (continued)

Model	Type	Sensitivity	Range	Response rate	Temperature	Relative humidity	Compensation	Cost
Model 1125 meets MIL-1237528 Shock MIL-S-911C.	1.0-L ionization chamber. Equal-volume gamma chamber at ambient pressure.	Accuracy: $\pm 1\%$ FS.	3 ranges: 0-100 $\mu\text{Ci}/\text{m}^3$ 0-1,000 $\mu\text{Ci}/\text{m}^3$ 0-10,000 $\mu\text{Ci}/\text{m}^3$.	20 s	+40°F to 150°F with stated accuracy. -20°F to +180°F	0-90%	Gamma compensation up to 5 mR/h for uniform field.	Discontinued
Model 755 Continuous air pump.	Dual 1.2-L ionization chambers.	Reproducible: $\pm 2\%$. Accuracy: $\pm 10\%$ FS.	4 ranges: 0-100 $\mu\text{Ci}/\text{m}^3$ 0-1,000 $\mu\text{Ci}/\text{m}^3$ 0-10,000 $\mu\text{Ci}/\text{m}^3$ 0-1.0 Ci/m^3 .	30 s	0-50°C	0-90%	Gamma compensation up to 5 mR/h for uniform field.	Discontinued
Model 10559 Non-continuous air pump	Dual 1.2-L ionization chambers.	Reproducible: $\pm 2\%$. Accuracy: $\pm 10\%$ FS.	4 ranges: 0-50 $\mu\text{Ci}/\text{m}^3$ 0-500 $\mu\text{Ci}/\text{m}^3$ 0-5,000 $\mu\text{Ci}/\text{m}^3$ 0-50,000 $\mu\text{Ci}/\text{m}^3$.	20 s	0-50°C	0-90%	Gamma compensation up to 5 mR/h for uniform field.	Discontinued replaced by Model 111.
Tritium Monitors available from Munchener Apparatebau, Postfach 144, 8012 Ottobrunn, Federal Republic of Germany								
Tritium Monitor	Flow-through proportional counter. Sizes sample with methane or pure natural gas (30-L/h).	8.3 cps/ $\mu\text{Ci}/\text{m}^3$. Background = 0.08 cps. Measures $\sim 0.01 \mu\text{Ci}/\text{m}^3$ in ~ 100 s.	Saturation at $\sim 200 \mu\text{Ci}/\text{m}^3$.	?	?	?	Compensation factors: (percentage coincidence counts in anticoincidence channel): C ₁ : 182 X ₂ : 133; 72	?

BETATEC Monitor Options:

^a Extended Range 0-20,000 $\mu\text{Ci}/\text{m}^3$

Cost: \$269.00

Super sensitivity, radon alpha background discrimination, stability to $\pm 0.3 \mu\text{Ci}/\text{m}^3$. Cost: \$858.00

Chambers available in 1-L, 5-L, 20-L, 200 cc, 20 cc, and other sizes on special request. Prices on request.

Note:

Rack-mounted, benchtop, and battery-operated portable models are available. $1 \mu\text{Ci}/\text{m}^3 = 1 \text{ pCi}/\text{cm}^3$.

Table 3. Comparison of various detection methods.

Sensitivity ($\mu\text{Ci}/\text{m}^3$)					
100	10	1.0	0.1	0.01	10 ⁻³ 10 ⁻⁴ 10 ⁻⁵ 10 ⁻⁶
Method of measurement					
Real-time measurement					
Suitable for HT or HTO					
Time constant					
Gamma compensation and other radionuclides					
Dual chamber method reduces γ sensitivity, up to 5 mR/h typical.					
Improved version reduces contamination.					
Correlation analysis used to recover signal buried in noise.					
Count rate from 2 mR/h - $\bar{r} \pm$ count rate from 1 $\mu\text{Ci}/\text{m}^3$ - $\bar{r}^2$.					
Low gamma response.					
Low gamma response.					
Operates in high γ -field, insensitive to noble gases.					
Low sensitivity to noble gases.					
Bubbling N_2 through water removes most noble gases.					
Good noble gas rejection.					
Unaffected by radon and thoron daughters.					
Counting time: 1000 min.					

according to its ability to make real-time measurements; its suitability to differentiate between and separately measure the activities of HT and HTO; its time constant; and its ability to compensate for external gamma sources and other beta- and alpha-emitting radionuclides.

Notable technologies include liquid and solid scintillation counting, both of which achieve an acceptable degree of sensitivity. However, all liquid scintillators possess solvents that are toxic to individuals by either inhalation or absorption through the skin. Consequently, the liquid scintillator must be isolated in order for the liquid scintillation technique to be employed in a closed environment such as a submarine. A conceptual system would include some technique to continuously clean the liquid scintillator of the sample. For example, the scintillator could be contained in a closed loop which would constantly take in a sample, count it, and then extract the sample from the scintillator, making it possible to use the liquid scintillator over and over. The systems study has investigated just such a possibility. The technique will be discussed in detail later in this thesis.

Another interesting technology is the solid scintillator method, which in the past has used plastic scintillators to view a given sample of air. This method allows relatively large-area detectors to be built. The main disadvantage of using plastic scintillators is their "memory effects." Tritium, in the form of either HT or HTO, can readily diffuse through the plastic and become

attached to the scintillator's molecules by a chemical reaction. Hence, over a period of time the detector's background increases, causing its sensitivity to decrease. Eventually the plastic scintillator must be replaced with fresh material.

An alternate scintillator material investigated during this study is $\text{CaF}_2(\text{Eu})$, which is nonhygroscopic (water vapor does not diffuse well through it). Since it is a nonorganic material, attachment by molecular hydrogen through chemical means is a negligible occurrence as compared to organic plastic scintillators. This study has investigated $\text{CaF}_2(\text{Eu})$ by using it in a phoswich structure, a technique that reduces the response of the detector to external gamma radiation and hence increases sensitivity to tritium. A detailed discussion of this technique will follow later in this report.

Several methods have been developed to physically separate the two molecules HT and HTO in order to differentiate and separately count their activities. Two methods which may be incorporated into a portable instrument are separation by semipermeable membranes and separation by condensation. In the latter case HTO can be condensed readily by passing the air sample over a cold plate, mixing the condensate with a liquid scintillator, and subsequently counting it in a liquid scintillation detector. After condensing the water from the air sample, a hot palladium catalyst can be used to convert HT to HTO. After the air sample has passed over the catalyst a second condensation will take place in which the activity of the condensate

will be in direct proportion to the amount of HT in the sample. This second condensate can also be counted in the liquid scintillation counter. The effects of varying humidity levels in the air sample can be compensated by first saturating the air with water and then condensing the water. An attractive feature of this method is that radioactive noble gases are not condensed but remain in the gaseous form.

Another method of separating HT from HTO is by using semipermeable membranes. Separation factors on the order of 1000 and time constants on the order of 5 min are easily obtained using multiple cells. Other techniques for separating HTO from HT include bubblers in which the air sample is bubbled through a water sample. This method collects 90 to 98% of the HTO but only about 0.01% of the HT. The main problem with this method is its long time constant, which is the main reason that it has not been used in the past. Both the condensation method and the use of semipermeable membranes to separate HT and HTO will be discussed further as components of actual systems. The condensation method finds particular relevance in the liquid scintillation counting system, while semipermeable membranes are well suited to use in the solid scintillator flowthrough cell.

Various techniques have been used in the past to enrich a given sample. Of particular importance is electrolysis, in which an electrical current is passed through a water sample and molecular hydrogen and oxygen gas are evolved. The hydrogen gas can then be allowed to enter the counting cell. (The water sample may be the

condensate from the condensation system described above.) This technique is particularly attractive from a radiological viewpoint because the more hazardous HTO is converted to HT. Other enrichment techniques include thermal diffusion, gas chromatography, and distillation. These techniques require sophisticated and bulky laboratory apparatuses which would not be suitable for a portable instrument. The electrolysis method will be discussed further relative to the conceptual development of the laser spectroscopy system.

III. OVERVIEW OF ADVANCED TRITIUM DETECTION TECHNIQUES EXAMINED

A. Laser Spectroscopy Technique

Based on the experience of coworkers at ORNL, it was thought that laser spectroscopy would be a sensitive and viable means of detecting HT and HTO (Hurst, et al, 1980). It was anticipated that this method would be capable of separately measuring the concentration of HT and HTO without using any preparatory separation techniques such as condensation. Various laser spectroscopy techniques are compared in Table 4 (Radziemski, 1983). The molecular density of tritium in air equals 2.066×10^7 molecules/cm³ at an activity level of 1 $\mu\text{Ci}/\text{m}^3$. This compares to 2.689×10^{19} molecules of air per cm³ at 300°K and standard pressure. Therefore, tritium must be detected in concentrations of approximately 1:10¹⁴. Based on the comparisons given in Table 4, the two methods which seem most suitable for such a task are laser-induced fluorescence (LIF) and resonance ionization spectroscopy (RIS).

The basic physical concept of LIF is illustrated in Figure 1 (Steinfeld, 1974). A laser is used to selectively excite the molecule of interest from its ground state to a vibrational level of an excited electronic state. The molecule then decays to the lowest vibrational level of the excited electronic state via nonradiative collisions with surrounding molecules. (The time involved to decay to the lowest vibrational level is typically on the order of 1 ns.) After a period of time characteristic of the excited electronic state, the molecule decays further to a vibrational level of the

Table 4. Comparison of various laser spectroscopy techniques.

	Laser absorption spectroscopy	Laser-induced fluorescence (LIF)	Optoacoustic	Laser-Raman	Resonance ionization spectroscopy (RIS)
Selective	Yes	Yes	Yes	Yes	Yes
Quantitative	Yes	Yes	Yes	Yes	Yes
Limits of detection	Parts per billion	Less than parts per billion	Parts per billion	Parts per thousand	Parts per trillion
Number of lasers	1	1	1	2	1
Movable	Yes	Yes	Yes	Yes	Yes
Portable	Yes	Yes	Yes	Yes	No
Cost	Low	Low	Low	High	High
Capable of detecting low levels	No	Yes	No	No	Yes

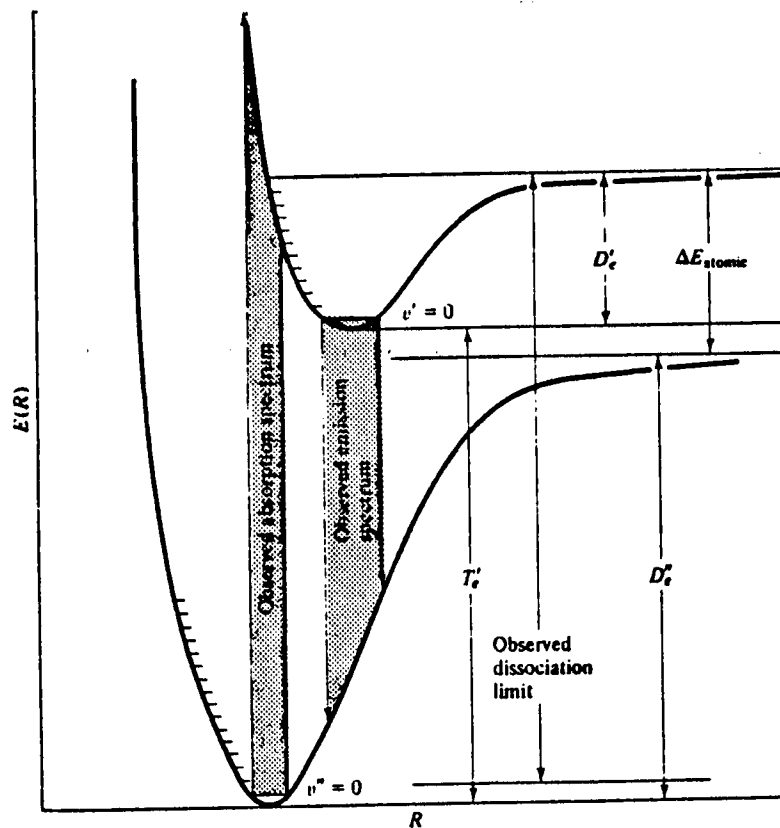


Figure 1. Electronic transitions in a molecule: illustration of laser-induced fluorescence.

ground state of the molecule. During this phase a photon is emitted, a process known as fluorescence. The molecule finally decays to the lowest vibrational level of the ground state via non-radiative collisions with neighboring molecules. Lasers are well suited as the excitation source in such a system because they are highly monochromatic, thus enabling selective excitation. The laser frequency can be tuned to a frequency exactly equal to a given transition energy in a molecule of interest. Since very few photons of an energy different from the excitation energy are mixed in the laser beam, other molecules in the sample are not excited. Also a laser is capable of directing its emitted energy in a very small collimated beam. Since the energy is concentrated in this beam, and diverges to such a small extent compared to other light sources, excitation of trace amounts of selected molecules can be achieved in a volume containing large amounts of other molecules.

The basic setup of a typical LIF system is shown in Figure 2. The laser beam is allowed to enter the cell containing the sample. Reflective coatings on the opposite wall allow multiple passes of the beam through the cell, which increases the volume of possible excitation and may therefore excite a larger number of the molecules of interest. The molecule then decays via fluorescence, and these emitted photons are present for detection. The detector's surface is placed at a 90° angle to the laser beam. Since the frequency of the photons emitted by the laser is higher than those given off in fluorescence, optical filtering can be used in front of the detector

ORNL DWG 83-17625

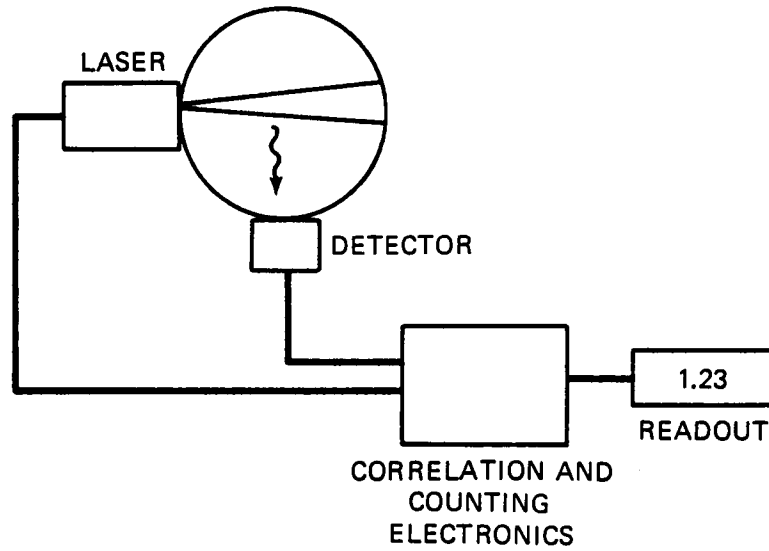


Figure 2. Basic laser-induced fluorescence (LIF) system.

to pass only the fluorescence photons. This greatly reduces background counts and hence makes the system very sensitive. The laser is pulsed, allowing a correlation analysis of the detector and the laser, a technique that allows signals buried in large amounts of noise to be extracted. The system therefore becomes even more sensitive. Because of the efficiency and selectivity of the system, LIF is capable of detecting very low concentrations of molecules. A system has been reported (Fairbank, et al, 1975) which can detect sodium vapor to concentrations of 100 atoms/cm^3 .

In resonance ionization spectroscopy the molecule is carried directly to ionization by the use of two or more laser photons of different wavelengths. Since the power output of lasers can be made relatively high, most of the molecules of interest are ionized. Once ionized, the molecules can be detected as they drift and are collected in an ionization chamber or proportional counter. Because efficiency of detecting the ions is very close to unity, the overall system can detect molecules of interest to a high degree of sensitivity. Theoretically, single atoms can be detected using this system. It is among the most sensitive techniques in spectroscopy. However, its main disadvantage is that high-power lasers are needed in order to ionize the molecules, which requires very expensive and bulky equipment. Consequently this technique is not suitable for use in a portable instrument, and it is therefore obvious that LIF is the technique most suitable for a portable tritium detector.

B. Solid Scintillation Technique

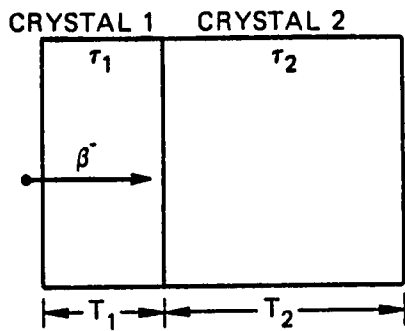
As mentioned earlier, solid scintillation detectors have been used in the past to detect tritium in real time. The two primary scintillators which have been used are NE102 and anthracene, both of which are low atomic number (Z) organic scintillators. This makes them relatively insensitive to gamma radiation since the gamma cross section increases monotonically with Z. Sensitivities on the order of $0.1 \mu\text{Ci}/\text{m}^3$ have been reported using such systems. As indicated before, however, organic scintillators suffer memory effects when detecting tritium. This is because HT and HTO diffuse easily into the scintillator and become attached to its molecules through chemical reactions. Various other solid scintillators have been compared in an effort to select a better material (see Table 5). Ideally, the scintillator should be of low Z material, which enables low energy charged particles to penetrate easily into the material. According to Table 5, $\text{CaF}_2(\text{Eu})$ has the lowest average Z of the scintillators listed. A particularly important feature of $\text{CaF}_2(\text{Eu})$ is that it is nonhygroscopic; its solubility is 0.0016 g/ml at 18°C . In comparison, hygroscopic $\text{NaI}(\text{Tl})$ has a solubility of 187 g/ml at 18°C . Hence, very little diffusion of HTO can be expected using $\text{CaF}_2(\text{Eu})$. It has been reported that $\text{CaF}_2(\text{Eu})$ can be evaporated as a thin film onto a substrate. A 0.0001-in. layer of $\text{CaF}_2(\text{Eu})$ has been vacuum deposited onto a 0.0625-in. pyrex disc and has successfully detected tritium (Prevo, et al, 1970). The range of the

Table 5. Comparison of various solid scintillators.

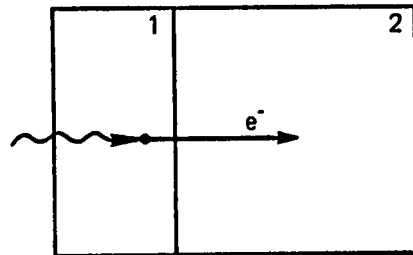
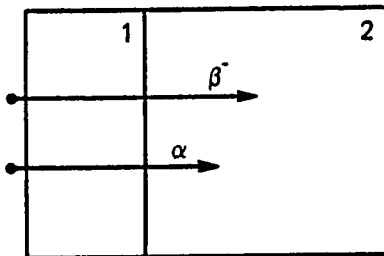
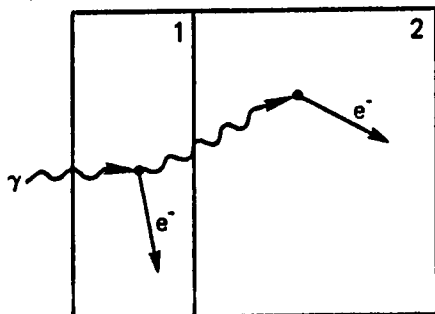
Scintillator	Type	Density (g/cm ³)	Refractive index	Light output (% Anthracene)	Decay constant, main component (s)	Wavelength of maximum emission (Å)	Ratio of H atoms to C atoms	Average atomic number Z
NE102	Plastic	1.032	1.581	65	2.2×10^{-9}	4250	1.105	
Anthracene	Crystal	1.25	1.62	100	30×10^{-9}	4470	0.715	
Stilbene	Crystal	1.16	1.626	50	4.5×10^{-9}	4100	0.858	
NaI(Tl)	Crystal	3.67	1.775	230	0.23×10^{-6}	4130		32
LiI(Eu)	Crystal	4.06		75	1.2×10^{-6}	4750		28
GdI(Tl)	Crystal	4.51	1.788	95	0.7×10^{-6}	4200-5900		54
CsF	Crystal	3.59	1.434	12	5×10^{-9}	3900		32
CaI ₂ (Eu)	Crystal	3.96		460	0.79×10^{-6}	4700		63
CaF ₂ (Eu)	Crystal	3.179	1.44	69-115	0.96×10^{-6}	4350		19
ZnS(Ag)	Multi- crystal	4.09	2.356	300	0.2×10^{-6}	4500		23
Bi ₄ Ge ₃ O ₁₂	Crystal	7.13	2.152	23	0.30×10^{-6}	4800		27.6

18.6-keV maximum energy beta particle emitted in tritium decay is 7.26×10^{-5} in $\text{CaF}_2(\text{Eu})$. Therefore, the 0.0001-in. evaporated $\text{CaF}_2(\text{Eu})$ layer would stop all tritium betas but would pass all other betas with higher energy. (Tritium is the lowest energy beta emitter of interest.) A phoswich structure could be employed, whereby a different scintillator could be placed directly behind the evaporated $\text{CaF}_2(\text{Eu})$ crystal. Here, the higher energy betas would deposit only a fraction of their energy in the $\text{CaF}_2(\text{Eu})$ crystal; most of their energy would be deposited in the other detection media. This method allows most all other beta emitters to be rejected.

The concept of a phoswich detector is illustrated in Figure 3. Two scintillator crystals with different light decay time constants are placed back-to-back. Different light decay time constants are used in order to identify the crystal in which a radiation event has occurred. Pulse shape discrimination is used to reject light pulses from crystal 2 and to accept light pulses from crystal 1. For tritium detection, the first crystal's thickness is made equal to the range of the maximum energy beta emitted in tritium decay. Crystal 1 is made of low Z material in order to efficiently detect tritium betas. Crystal 2 is made of high Z and high density material in order to efficiently detect Compton scattered photons, generated in crystal 1, and to stop all charged particles in a short range. The light decay time constant of crystal 2 is less than crystal 1. The pulse shape from tritium decay has a long rise time, while shorter rise-time pulses are generated for all higher energy beta emitters.

(a) ^3H BETA DETECTION

T_1 = RANGE OF MAX. ^3H BETA
 τ_1 = LIGHT DECAY TIME OF CRYSTAL 1
 τ_2 = LIGHT DECAY TIME OF CRYSTAL 2
 ASSUME $T_1 > T_2$

(d) γ - PHOTOELECTRIC INTERACTION(b) OTHER β^- AND α DETECTION(c) γ - COMPTON INTERACTION

PULSE SHAPES

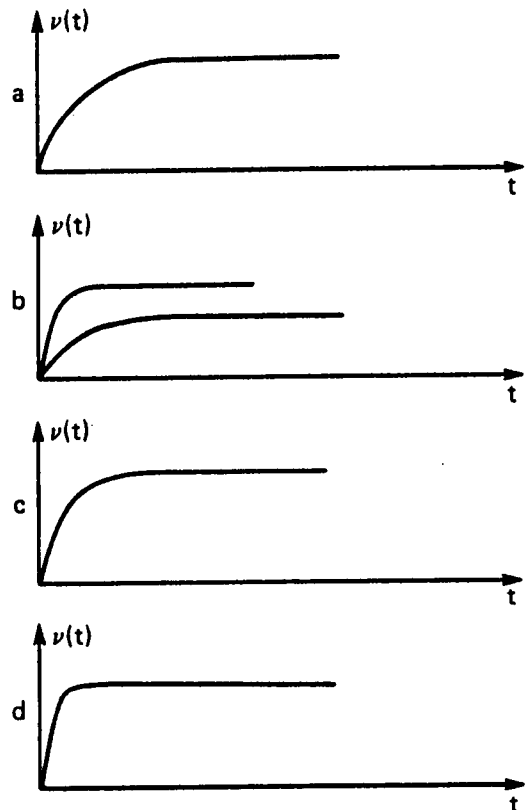


Figure 3. Phoswich detector concept.

Most of the higher energy beta emitters deposit nearly all of their energy in crystal 2. Therefore, the light pulse from the phoswich system is composed almost entirely of the light emitted in crystal 2. The same holds true for alpha particles, except that a comparatively small amount of energy is deposited in crystal 2. For alphas that decay further away from the window, the alpha may be completely stopped in crystal 1. This is due to the fact that energy is lost in the air between the point of decay and the window. Therefore, alpha discrimination may be a problem. Pulse height analysis may also be employed here to discriminate against alphas, since the relative pulse height of an alpha interaction is 0.2 times that of a beta interaction, where equal energies are deposited in the $\text{CaF}_2(\text{Eu})$ crystal. Most alpha energies range from 5.3 to 8.8 MeV. Calculations on possible pulse amplitudes for various particles will be given later in this report.

The phoswich detector is also useful in discriminating against gamma interactions. Again, Figure 3 illustrates this concept. Crystal 2 is made thick enough to stop all Compton scattered photons generated in crystal 1. The light pulse will be primarily dominated by the light generated in crystal 2, in which the scattered photon is stopped. In the case of a photoelectric interaction in crystal 1, the pulse is again dominated by the light from crystal 2. Most photoelectric interactions generate very high energy electrons whose energy is about equal to the gamma's energy. Also, since

crystal 1 is made of low Z material, the probability of a photoelectric interaction is low.

A very good detection system is one that uses $\text{CaF}_2(\text{Eu})$ as crystal 1 and bismuth germanate ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$) as crystal 2. From the data given in Table 5, it is seen that the light decay time of bismuth germanate is approximately three times smaller than that of $\text{CaF}_2(\text{Eu})$. Also, $\text{CaF}_2(\text{Eu})$ is a low Z material, making it efficient for low-energy beta detection and inefficient for gamma detection. Bismuth germanate has a high density and is a high Z material. These characteristics make it efficient for detecting Compton scattered photons generated in the $\text{CaF}_2(\text{Eu})$ crystal. Both scintillators are nonhygroscopic, which is particularly attractive because no special controlled environments are needed in either constructing or operating the detector. Since it has been reported that $\text{CaF}_2(\text{Eu})$ can be evaporated as a thin film, a conceptual detector could be one in which a 0.0001-in. thick layer of $\text{CaF}_2(\text{Eu})$ is evaporated onto a bismuth germanate crystal. The actual conceptual development of such a detector will be given later in this thesis.

C. Liquid Scintillation Technique

As indicated earlier, the method of liquid scintillation counting is a very sensitive technique for detecting tritium. A prototype model which detects aqueous tritium has been developed for the U.S. Navy (Colman, et al, 1982). Figure 4 illustrates the block diagram of the system. Coincidence circuits are used to reduce

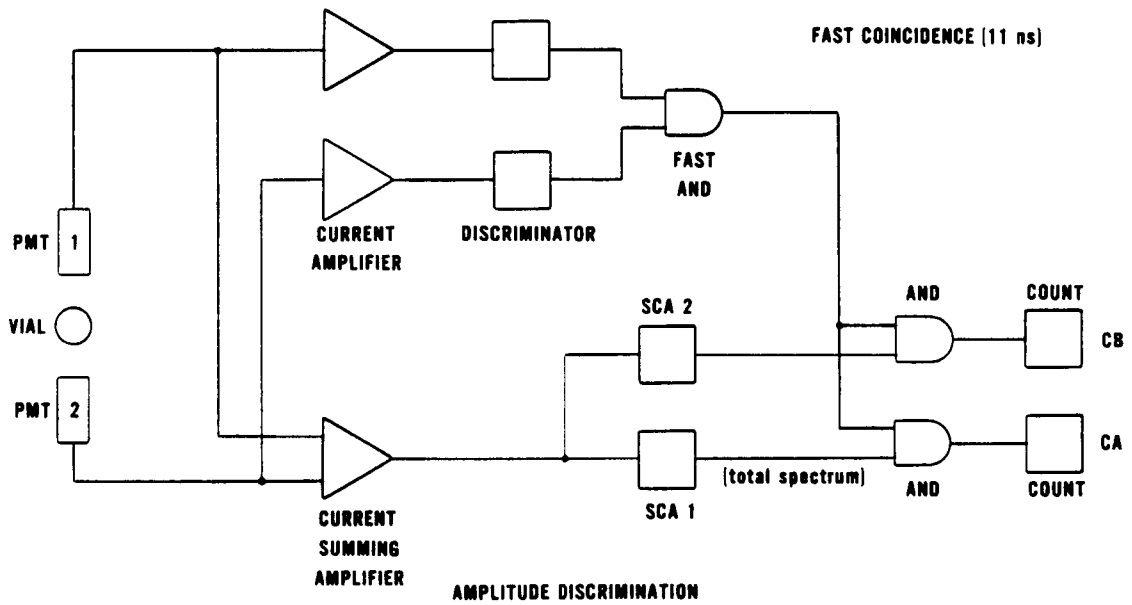


Figure 4. Liquid scintillation counting system.

phosphorescence, and the two single-channel analyzers (SCAs) are used to correct the measured count for quenching effects. A separate circuit has been developed in which the two photomultiplier tubes (PMTs) can be easily and quickly balanced in the field, which eliminates the need of stocking matched PMTs. A conceptual liquid scintillation system could be developed in which the above described detector could be modified to detect HT and HTO in air. In such a system air samples could be condensed, HT and HTO could be separated, and the condensates could be mixed with a liquid scintillator and counted.

As mentioned previously, liquid scintillators possess toxic solvents. Consequently, in order for such a system to be used in a closed environment such as a submarine, the liquid scintillator would have to be kept in a closed loop. A technology must therefore be developed whereby the scintillator can be continuously cleaned and reused. Investigations have shown that radioactive organic solvents can be separated from liquid scintillators by distillation (Mangravite, 1983). (Any radioactive water remaining in the liquid scintillator was reported to be removed with anhydrous CaCl_2 .) For the conceptual development of this system, the only sample present in the liquid scintillator is water. Therefore, distillation is not needed, and anhydrous CaCl_2 could be used to remove the sample. From a radiological viewpoint, this is an attractive way of removing HT and HTO from the environment. The CaCl_2 could be removed and disposed of periodically as low-level waste. Other improvements can

also be made to increase the sensitivity of the system. For example, a plastic scintillator could be placed around the sample cell and connected in anticoincidence. This would reduce the gamma sensitivity of the system since Compton scattered photons could be rejected. Further discussion of this system will be presented later in this thesis.

IV. LASER-INDUCED FLUORESCENCE DETECTOR

A. Overview of Conceptual System Development

This section describes the study of the conceptual development of a tritium detector using the technique of laser-induced fluorescence (LIF). In the concept phase of the study the molecular energy levels of HT and HTO were analyzed and compared with the molecular energy levels of H₂ and H₂O. While HT and H₂ can be readily distinguished using this method, HTO and H₂O cannot be so readily distinguished because of the close spacing of their molecular vibrational levels. It was therefore initially decided that it would be cost effective to develop a system that detects only HT. (HTO can be decomposed to HT by first condensing an air sample and then decomposing the condensate to molecular hydrogen by electrolysis, and the resultant hydrogen gas can be analyzed by the LIF method.)

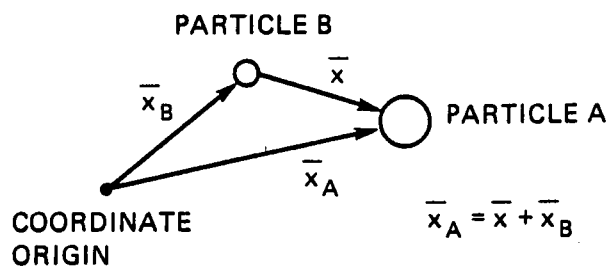
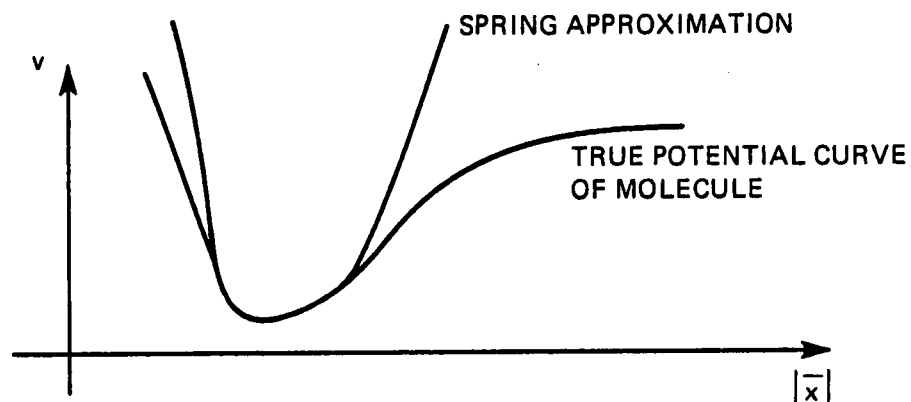
The next step of the study concentrated on selection of the various components that would be used in the system. The main components include a vacuum ultraviolet (VUV) source, a tunable infrared (IR) diode laser, and an IR detector. In order to detect HT a double resonance excitation was needed, which requires two sources that emit two different wavelengths of light. A VUV source is needed in order to excite all hydrogen molecules in the sample (HT and H₂). Once in the excited state, an IR diode laser is used to selectively excite HT. As HT decays via fluorescence a spectrum of IR photons is emitted, and the IR detector is used to count the number of HT molecules present in the sample. A particularly

attractive feature of this method is that an HT molecule can be re-excited many times. Therefore, efficiencies close to unity may be feasible since a great many photons can be detected from a single HT molecule. The theoretical efficiency of such a system could be much greater than a system which detects the beta particle since only one beta particle is given off per HT molecule, and its half-life is 12.262 years.

Based on a comparison of the different components of the system, the study relegates itself to configuring an entire system. Here, price versus sensitivity becomes a major factor. The final portion of the study is based on an analysis of the system. Sensitivity is calculated for the overall system, and the results of analyzing cost versus sensitivity for various components in the system are presented.

B. HT and H₂ Molecular Levels

Using the LIF technique, HT and H₂ are distinguished from each other by the fact that their molecular vibrational frequencies are different in a given electronic state. One can consider, as a first-order approximation, the two hydrogen atoms attached by a spring. The mass of tritium is three times greater than the mass of hydrogen. Therefore, it becomes intuitively apparent that the frequency of vibration for HT should be less than that for H₂. Figure 5 illustrates a classical calculation of the vibrational motion of a diatomic molecule. The mathematical analysis of a harmonic oscillator is included as an appendix. As can be seen, when



$m_A \equiv$ MASS OF PARTICLE A.
 $m_B \equiv$ MASS OF PARTICLE B.

Figure 5. Diatomic molecule and its potential energy curve.

comparing the potential energy curves the analogy of attaching the two atoms to a spring is a good one. Calculations indicate that the frequency of vibration is inversely proportional to the square root of the reduced mass of the system. The reduced mass is equal to 0.503913 u for the H_2 molecule and 0.755404 u for the HT molecule. Therefore, the frequency of vibration of the HT molecule is less than the frequency of vibration of the H_2 molecule by a factor of 0.816748. In order to completely analyze the vibrational motion of a diatomic molecule, a quantum mechanical analysis is required (Tipler, 1969). Schrodinger's Equation can be written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2M}{h^2} (E - V)\psi = 0 \quad , \quad (1)$$

where

ψ = wave function of diatomic molecule,

M = reduced mass of the molecule,

h = Planck's constant,

E = energy of the molecule, and

V = potential energy of the molecule.

Using Hooke's Law, the molecule's potential energy is assumed to be equivalent to that of a spring. Schrodinger's Equation, for a harmonic oscillator, then becomes

$$\frac{d^2\psi}{dx^2} - \frac{4\pi^2Mk}{h^2} x^2\psi + \frac{8\pi^2ME}{h^2} \psi = 0 \quad , \quad (2)$$

where k is Hooke's constant for the spring. The solution to Eq. (2) yields a quantitized set of values for the energy of the harmonic oscillator:

$$E = \omega_e \left(v + \frac{1}{2} \right) , \quad (3)$$

where v is the vibrational quantum number of the molecule. It is a constant and can have values of $0, 1, 2, 3, \dots$. The fundamental frequency of vibration of the system, ω_e , is equal to that obtained from the classical analysis of the harmonic oscillator and is given by

$$\omega_e = \frac{h}{2\pi} \sqrt{\frac{K}{M}} . \quad (4)$$

A better approximation of the potential energy function of the diatomic model is obtained from its Maclaurin series:

$$V(x) = V_0 + \left(\frac{dV}{dx} \right)_0 x + \frac{1}{2} \left(\frac{d^2V}{dx^2} \right)_0 x^2 + \frac{1}{6} \left(\frac{d^3V}{dx^3} \right)_0 x^3 + \dots, \quad (5)$$

where the constants are evaluated at the equilibrium position of the molecule. When Eq. (5) is substituted into Eq. (1) and solved, the vibrational energy levels are given by

$$E = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \omega_e y_e \left(v + \frac{1}{2} \right)^3 + \dots, \quad (6)$$

where x_e and y_e are anharmonicity constants. The energy levels can be calculated for an isotopically substituted molecule. Here, the reduced mass of the system is taken into account and the result is

$$E = \rho \omega_e \left(v + \frac{1}{2}\right) - \rho^2 \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \rho^3 \omega_e y_e \left(v + \frac{1}{2}\right)^3 + \dots, \quad (7)$$

where ρ is the square root of the ratio of the reduced mass of the two molecules and is equal to 0.816748 for the HT/H₂ molecules.

A molecule has many electronic states each of which is described by potential energy curves similar to those shown in Figure 1, p. 19. Imposed on each curve are discrete vibrational energies which the molecule can assume, as given in Eqs. (6) and (7). It is assumed that the gross electronic structure of a molecule remains the same for all isotopic combinations. It is also assumed that only the vibrational energies are changed. The gross electronic states of both HT and H₂ are shown, according to energy versus quantum states, in Figure 6. Quantum selection rules allow only certain transitions to take place. The allowed transitions are indicated by arrows. It must be kept in mind that Figure 6 does not show the vibrational levels for each state.

Table 6 lists the values of the dissociation energies of various electronic states of H₂, along with their fundamental vibrational frequencies and anharmonicity constants (Herzberg, 1957). Using Eq. (7) the values of the fundamental vibrational frequencies and anharmonicity constants of the same electronic states for HT

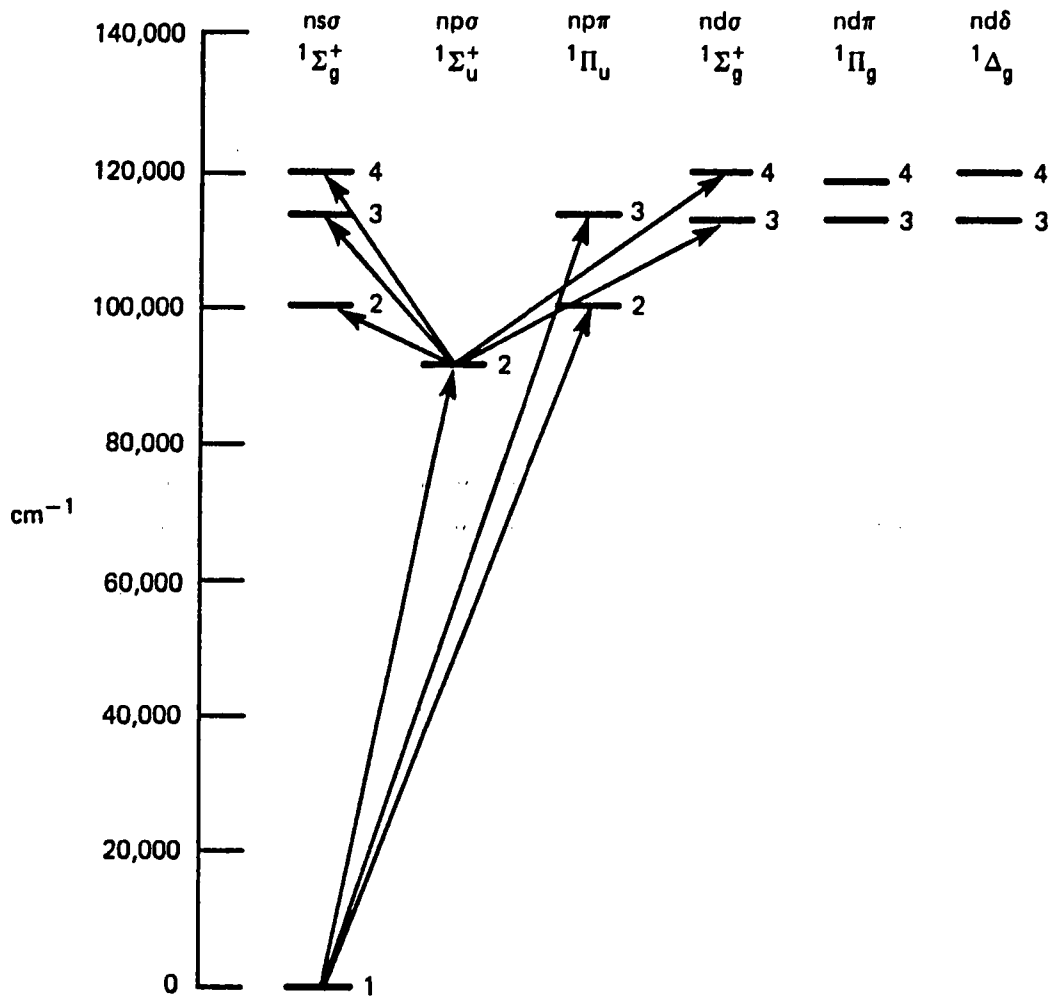


Figure 6. Gross electronic spectra of H_2 and HT .

Table 6. Singlet states.

State	T_e^*	ω_e^*	$\omega_e x_e^*$	$\omega_e y_e^*$	Remarks
<u>H₂ Experimental</u>					
X $^1\Sigma_g^+$	0	4 395.2	117.99	+0.29	1s σ ²
B $^1\Sigma_u^+$	91 689	1 356.90	19.932	+0.4029	1s σ 2p σ Lyman Bands
C $^1\Pi_u$	100 043.0	2 442.72	67.03		1s σ 2p π Werner Bands
E $^1\Sigma_g^+$	100 062.8	2 588.9	130.5		1s σ 2s σ
D $^1\Pi_u$	113 888	2 325.1	52.25		1s σ 3p π
H $^1\Sigma_g^+$	113 889	2 538	124		1s σ 3s σ
<u>HT Calculated (corrected with isotopic ratio)</u>					
X $^1\Sigma_g^+$	0	3 589.8	78.708	+0.16	1s σ ²
B $^1\Sigma_u^+$	91 689	1 108.25	13.296	+0.2195	1s σ 2p σ Lyman Bands
C $^1\Pi_u$	100 043.0	1 995.09	44.71		1s σ 2p π Werner Bands
E $^1\Sigma_g^+$	100 062.8	2 114.5	87.05		1s σ 2s σ
D $^1\Pi_u$	113 888	1 899.0	34.85		1s σ 3p π
H $^1\Sigma_g^+$	113 889	2 073	82.7		1s σ 3s σ

*Values given are in units of cm⁻¹.

were calculated. They are also shown in Table 6. The transitional wavelengths required to excite both H_2 and HT have been calculated and the results are presented in Table 7. Experimental values for the excitation of H_2 are also given (Suchard, et al, 1976). As can be seen, Eq. (6) agrees nicely with experimental values, particularly at the low vibrational quantum numbers of the excited B state. It is also apparent that different excitation wavelengths are needed to excite the HT molecule to the equivalent level. This level was chosen as the first excitation level in the double resonance scheme. Excitation to this level requires vacuum ultraviolet (VUV) sources with wavelengths that can be obtained easily and inexpensively. Excitation to any other electronic level would require shorter wavelength photons and would increase the cost of the system dramatically since exotic sources of VUV photons would be needed. A source which emits a continuum of required wavelengths can be used to populate the B state of both H_2 and HT. Selective excitation of only the B state of HT, using a laser, would be very difficult and costly. The source, which will be described later, will populate a number of the vibrational levels of the B state for both HT and H_2 . The lifetimes of the higher vibrational states are equal to 1 ± 0.2 ns (Suchard, et al, 1976). Collisions with nearby molecules will de-excite the B state to its lowest vibrational level ($v = 0$), nonradiatively.

Once in the lowest vibrational level of the B state, a laser is used to selectively excite the HT molecule to the first

Table 7. Transitional energies for H₂ and HT

$$(\dots (1s\sigma^2) X \ ^1\Sigma_g^+ |_{v''} = 0 \rightarrow$$

$$\dots (1s\sigma \ 2p\sigma) B \ ^1\Sigma_u^+ |_{v'}).$$

State B, vibrational quantum number, v'	Transition wavelength		
	H ₂		HT
	Calculated (Å)	Experimental (Å)	Calculated (Å)
1	1092.74	1092.6	1092.34
2	1077.65	1077.5	1079.86
3	1063.34	1063.3	1067.93
4	1049.76	1049.7	1056.51
5	1036.83	1036.9	1045.55
6	1024.49	1024.7	1035.03
7	1012.70	1013.1	1024.90
8	1001.38	1002.1	1015.15
9	990.51	991.6	1005.73
10	980.04	981.7	996.62
11	969.91	972.2	987.81
12	960.11	963.2	979.26
13	950.59	954.6	970.95

vibrational level of the E state. The wavelengths required to achieve this transition have been calculated for a number of vibrational quantum numbers of the E state, and the results are shown in Table 8. The transition to the first vibrational level of the E electronic state appears to be the best to excite selectively. This wavelength is at the limit of the tunable, inexpensive diode lasers. Excitation to higher vibrational levels would require expensive, tunable, bulky dye lasers. Selection of the laser will be discussed in a later section.

Once in the first vibrational level of the E state, collisions with nearby molecules will cause the HT molecule to quickly decay nonradiatively to the lowest vibrational level of the E state. No experimental data have been found for the lifetimes of the vibrational levels in the E state, but it is anticipated that they are on the order of a few nanoseconds. From the lowest vibrational level of the E state, the HT molecule will decay radiatively to various vibrational levels of the B state. These transitional wavelengths have been calculated for the HT molecule and are listed in Table 9. As can be seen, photons of different wavelengths are emitted. An infrared (IR) detector is used to detect and count the photons emitted in this transition of the HT molecule. The H_2 molecule does not emit IR photons because it has not been excited to the E state. (The laser is used to excite only the HT molecules in the sample.)

Table 8. Transitional energies for H₂ and HT

$$(\dots (1s\sigma \ 2 \ p\sigma) \ B \ ^1\Sigma_u^+ |_{v''} = 0 \rightarrow$$

$$\dots (1s\sigma \ 2s\sigma) \ E \ ^1\Sigma_g^+ |_{v'}).$$

State E, vibrational quantum number, v'	Transition wavelength	
	H ₂	HT
	Calculated (Å)	Calculated (Å)
1	8857.39	9260.24
2	7486.76	7958.51
3	6595.09	7063.46
4	5985.26	6420.36
5	5558.16	5945.49
6	5259.15	5589.91
7	5056.54	5323.35
8	4931.63	5126.40
9	4873.96	4986.42

Table 9. Emission spectrum of HT

$$(\dots (1s\sigma \ 2s\sigma) \ E \ ^1\Sigma_g^+ | v'' = 0 \rightarrow$$

$$\dots (1s\sigma \ 2p\sigma) \ B \ ^1\Sigma_u^+ | v').$$

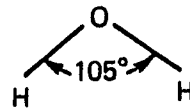
State B, vibrational quantum number, v'	Calculated transition wavelength (Å)
1	12 860
2	14 885
3	17 593
4	21 409
5	27 181

C. HTO and H₂O Molecular Levels

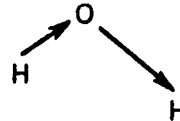
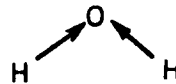
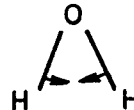
The next step in the systems study was an analysis of the H₂O and HTO molecules. In the analysis of the triatomic molecule the conventional assumption was made that the vibrational frequencies of a particular molecular bond were independent of any other properties of the molecule. Bond properties such as length or disassociation energy can also be assumed to be largely independent of the surrounding atoms in the molecule. Bonds for which this approximation is true are said to have "localized" molecular orbitals, i.e., orbitals in which only a pair of nuclei are contained. H₂O bonding is achieved when the molecule forms four sp^3 hybrid orbitals. Mutual repulsion causes the electrons in this orbital to form a tetrahedral bonding arrangement. The measured bond angle of 105 deg confirms that this is true. Since sp^3 bonding is a localized form of bonding, the assumption of separating the vibrations of the two O-H bonds is a valid one.

Figure 7 illustrates the H₂O molecule and its three vibrational modes--the symmetric stretch, antisymmetric stretch, and bending modes. Each mode of vibration is assigned a separate and independent quantum number, v_i . The equation of vibrational energy states can be calculated in much the same manner as was the diatomic molecule (Herzberg, 1966). The results are given by

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VIBRATIONAL MODES:

SYMMETRIC STRETCH (ν_1)ANTISYMMETRIC STRETCH (ν_2)BENDING (ν_3)Figure 7. The H₂O molecule.

$$\begin{aligned}
E(v_1, v_2, v_3) = & \omega_1 \left(v_1 + \frac{1}{2}\right) + \omega_2 \left(v_2 + \frac{1}{2}\right) + \omega_3 \left(v_3 + \frac{1}{2}\right) \\
& + x_{11} \left(v_1 + \frac{1}{2}\right)^2 + x_{22} \left(v_2 + \frac{1}{2}\right)^2 + x_{33} \left(v_3 + \frac{1}{2}\right)^2 \\
& + x_{12} \left(v_1 + \frac{1}{2}\right)\left(v_2 + \frac{1}{2}\right) + x_{13} \left(v_1 + \frac{1}{2}\right)\left(v_3 + \frac{1}{2}\right) \\
& + x_{23} \left(v_2 + \frac{1}{2}\right)\left(v_3 + \frac{1}{2}\right) + \dots, \tag{8}
\end{aligned}$$

where

v_1 = quantum number of the symmetric stretch mode,

v_2 = quantum number of the antisymmetric stretch mode,

v_3 = quantum number of the bending mode,

ω_1 = zero-order frequency of the symmetric stretch,

ω_2 = zero-order frequency of the antisymmetric stretch,

ω_3 = zero-order frequency of the bending mode, and

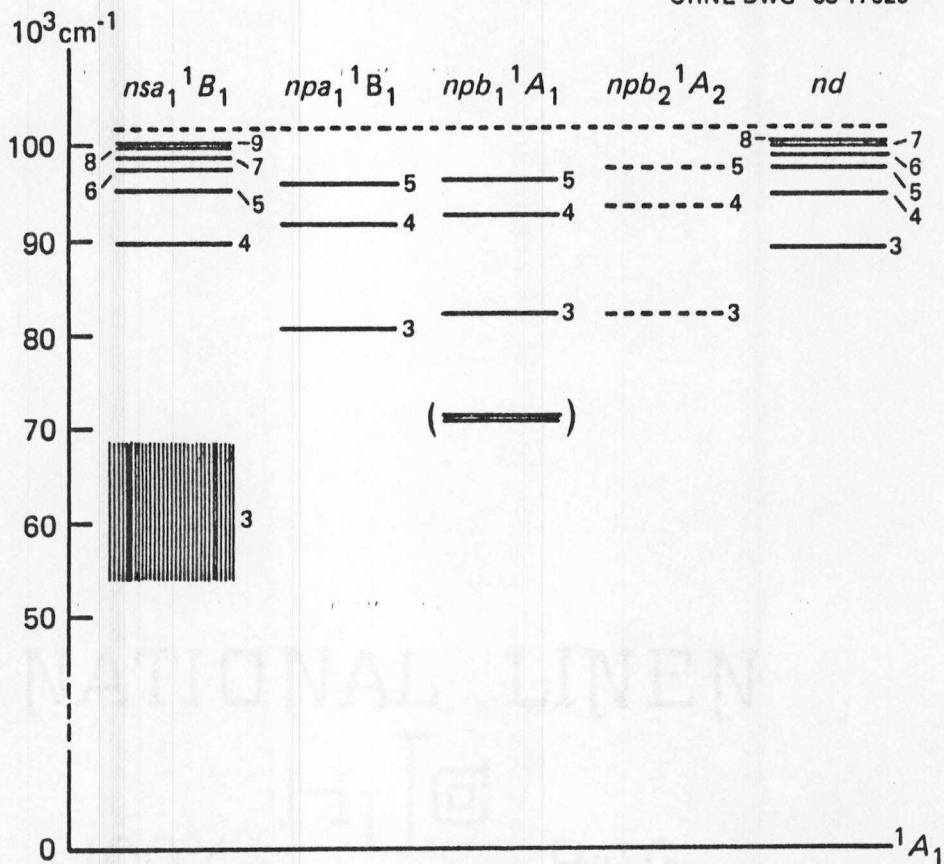
x_{ik} = anharmonicity constants.

A vibrating molecule can take on all possible combinations of vibrational quantum numbers. Isotopic variations of a given molecule can change the frequencies of vibration in a manner analogous to the diatomic molecule case. It is assumed, though, that the disassociation energies of the electronic states do not change with respect to isotopic variations.

The gross electronic structures of HTO and H₂O are shown in Figure 8, (Herzberg, 1966) and the allowed transitions of the C_{2v} point group are given in Figure 9. A calculation was made of the transition wavelengths that would be required to excite the HTO and H₂O molecules to the C state, and the results are shown in Figure 10 for the HTO molecule and in Figure 11 for the H₂O molecule. As can be seen, there is very little separation in wavelengths for the two molecules. This is due to the complicated nature of the possible combinations of vibrational modes in the molecule. It was next thought possible to use a double-resonance technique analogous to the method described earlier for the detection of HT. Calculations were made of the transition wavelengths from the C to the D states. The results are shown in Figures 12 and 13 for HTO and H₂O respectively. As can be seen, the required photons fall in the far-infrared region. The present state of technology does not allow very selective excitation at these frequencies. Higher energy states could be excited from the C state, but since little data is available for these electronic states, the transition wavelengths could not be analyzed.

D. Electrolysis of Hydrogen from Water

It is thought that it would be advantageous to separate H₂O and HTO molecules from a sample and count only HT molecules using the double-resonance LIF method. Water can be condensed from the air sample using a commercially available cold plate. The amount of water liberated from the condensation method can be made

Figure 8. Gross electronic structure of HTO and H₂O.

		Initial State			
		A ₁	A ₂	B ₁	B ₂
Final State	A ₁	M _z ^a	f ₁ ^b	M _x	M _y
	A ₂	f ₁	M _z	M _y	M _x
	B ₁	M _x	M _y	M _z	f ₁
	B ₂	M _y	M _x	f ₁	M _z

^aM_x, M_y, and M_z give the orientation for the dipole moment of the particular transition.

^bf₁ refers to a forbidden transition.

Figure 9. Transition moments of the C_{2v} point group for HTO and H₂O.

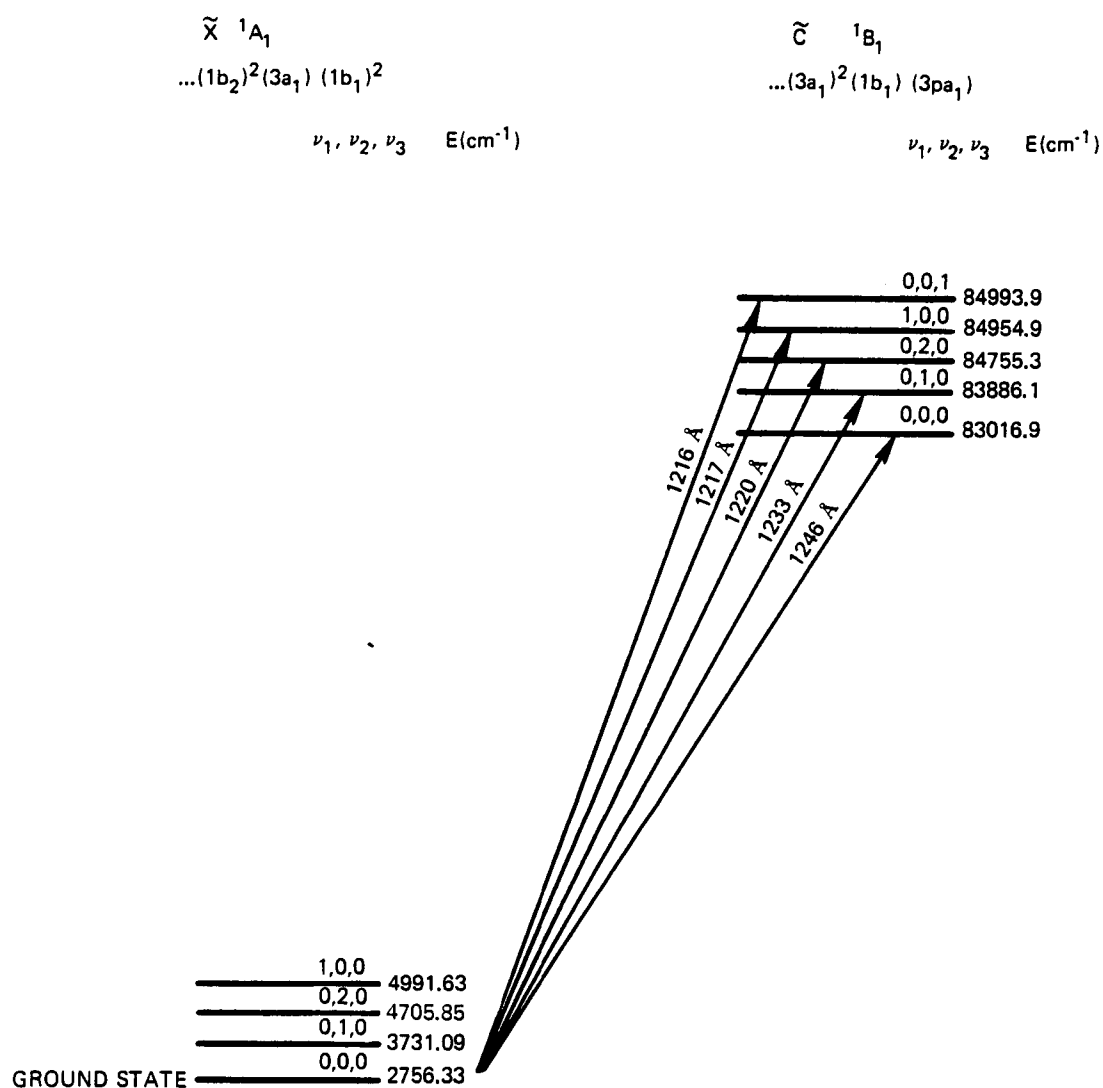
HTO O-T BOND

Figure 10. HTO molecular levels (O-T band).

H₂O O-H BOND

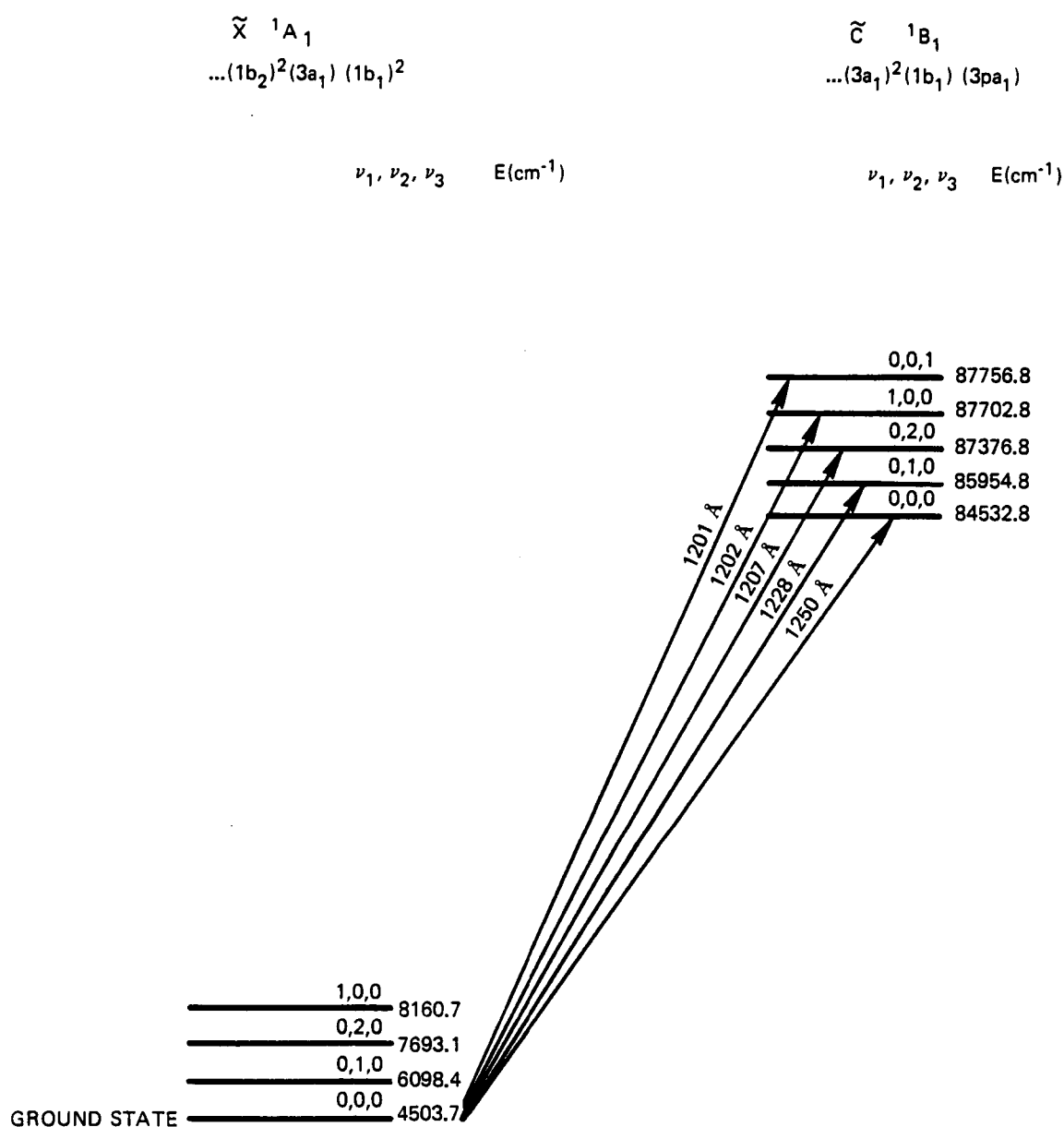


Figure 11. H₂O molecular levels (O-H band).

HTO O-T BOND

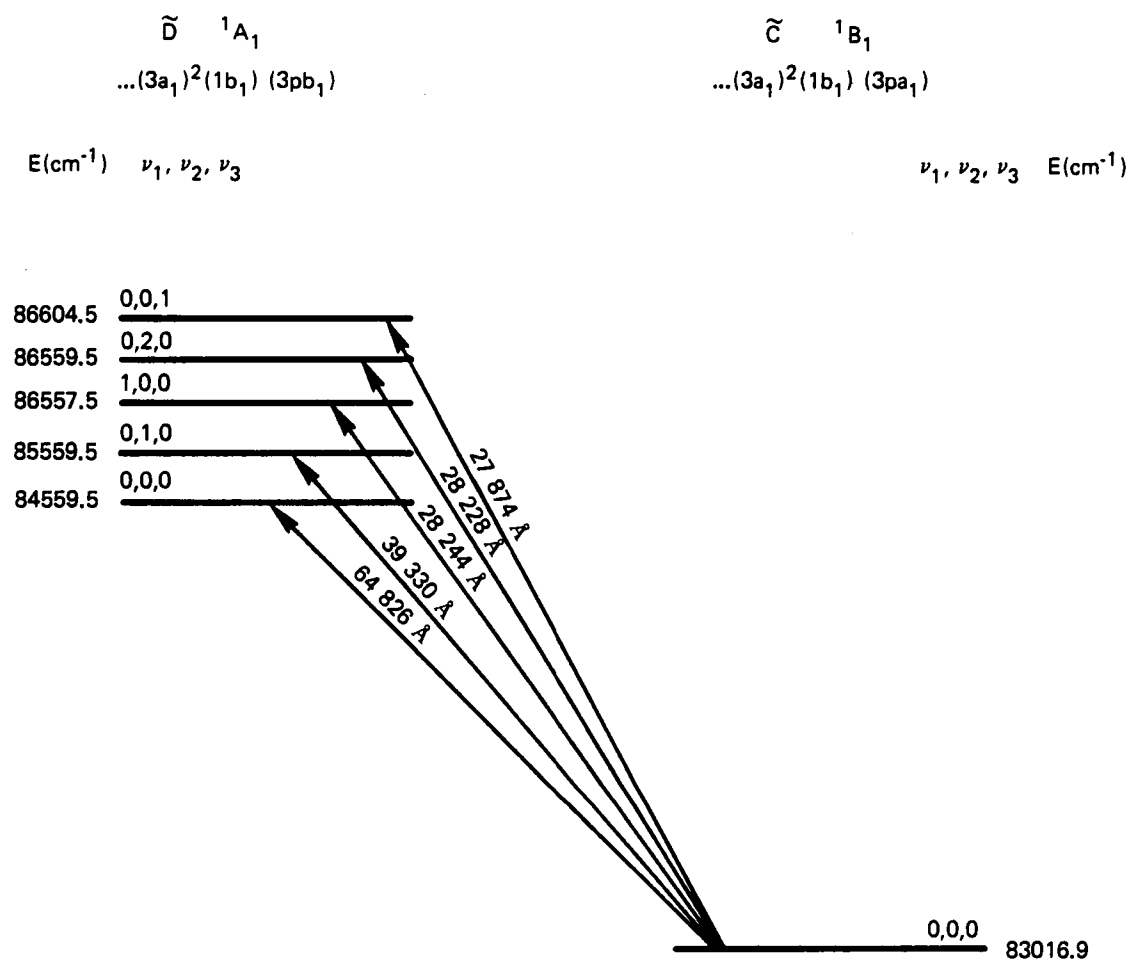
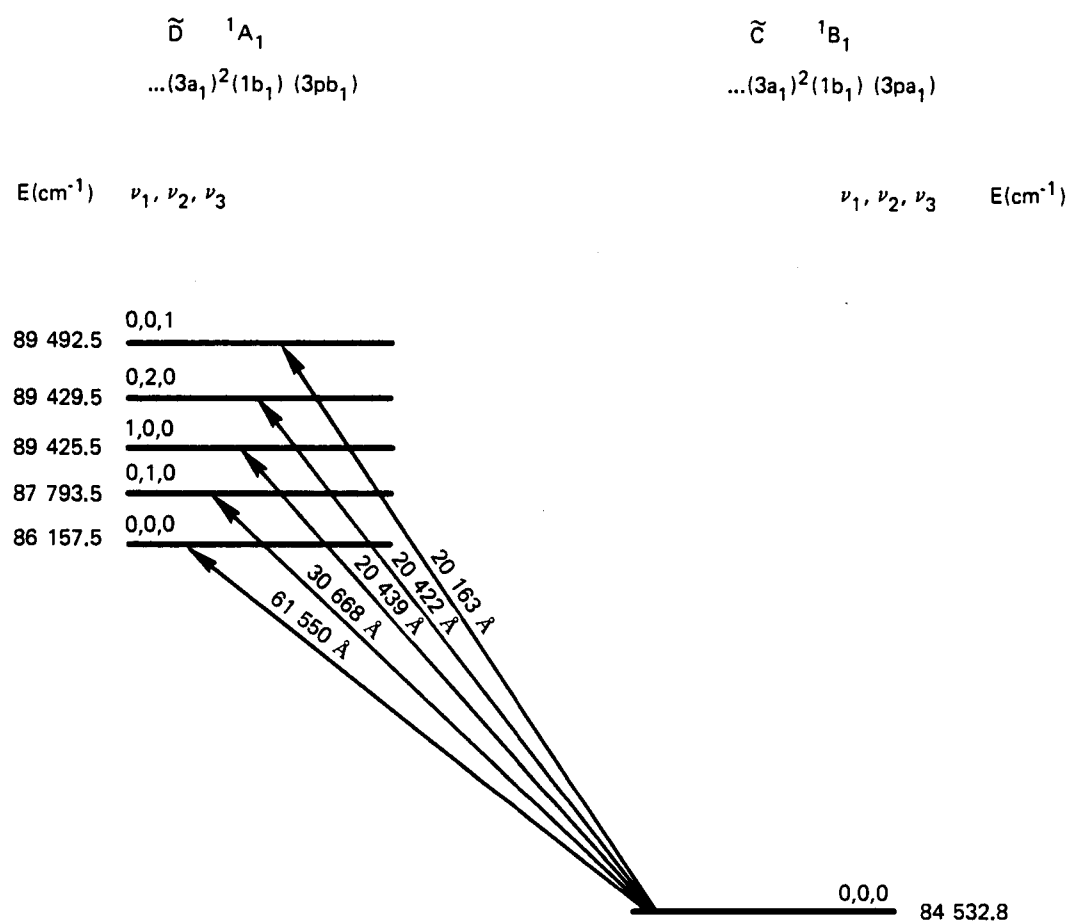


Figure 12. HTO molecular levels (O-T band).

H₂O

O-H BOND

Figure 13. H₂O molecular levels (O-H band).

independent of the humidity levels present in the sample of air by first saturating the air. This can be achieved by passing the air over a continuously wetted filter.

The reasons for removing water from the sample are threefold. First, as mentioned previously, selective excitation of HTO is unachievable from a practical viewpoint. Electrolysis of the condensation would liberate HT and H₂, and the evolved gas could then be counted using the double-resonance LIF method. Conversion from HTO to HT is the second reason for using this method, because from a radiological viewpoint HT is much less hazardous than HTO. The third reason for removing water from the sample is that water may provide a trapping center for the VUV photons that are intended to excite HT and H₂. The higher vibrational levels of the C electronic state of the water molecule could conceivably be excited when it is the intention to excite the hydrogen molecule.

A block diagram of a system that condenses water vapor from the air sample and converts the condensate to gaseous hydrogen is shown in Figure 14. The level indicators can be two simple contacts monitored by an on-board microprocessor. All valves can be solenoid operated, controlled by the microprocessor. The positive displacement pump is used to fill the LIF counting cell with either a dry air sample or a hydrogen sample. Because of isotopic effects, H₂O will be decomposed and liberated more rapidly as H₂ than HTO. The entire system is configured in such a way that the entire operation of taking air samples and separately

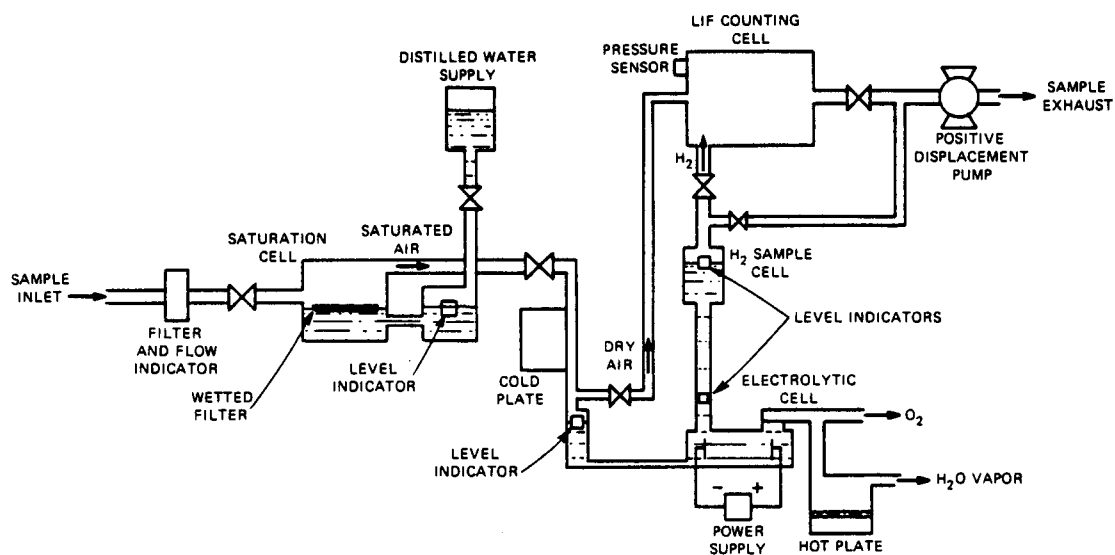


Figure 14. Block diagram of system for the conversion of HTO and H₂O molecules to HT and H₂.

monitoring for HT and HTO can be accomplished by an on-board microprocessor.

A typical thermoelectric cold plate costs \$550, while the cost of the vacuum pump and the hot plate are typically \$550 and \$200 respectively. The power supply used in the electrolysis of the condensate costs approximately \$200. All components of this system are readily available from most laboratory supply houses. The entire condensation and electrolysis system, including all other components, is estimated to cost about \$2000.

E. VUV Light Sources

The selection of a vacuum ultraviolet (VUV) light source for the excitation of the hydrogen molecule from the ground state to the B electronic state is not a trivial matter. A survey of various suppliers of UV light sources indicated that none were commercially available at the frequencies of interest. A survey of the emitted spectra of various low-pressure discharge sources is presented in Figure 15 (Price, 1959). As can be seen, Ne emits a continuum of wavelengths over the required range. The wavelength range needed to excite molecular hydrogen is 1100 to 970 Å. However, the Ne source could be filled to slightly higher pressures, which would cause the emission spectrum to shift to slightly longer wavelengths due to collisional broadening. Filling the source to higher pressures also increases the power output of the source. A simple high-voltage power supply and a discharge capacitor can be

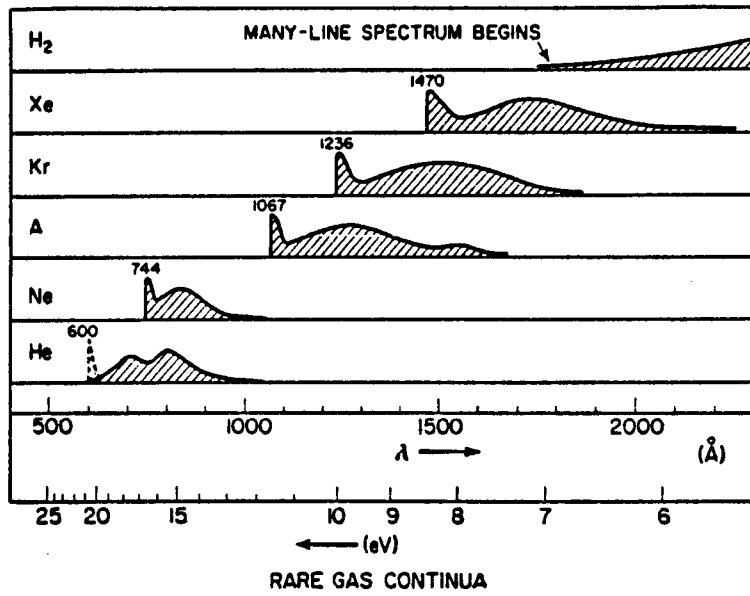


Figure 15. Continuous emission spectra of the inert gases.

used to operate the Ne source. The cost of such a power supply is estimated to be approximately \$100.

Various window materials that can transmit VUV light are listed in Table 10 (McNeeby, et al, 1964). It appears that LIF is the preferred window material for the VUV source. LIF can be sealed with black wax (Apiezon W) to Pyrex for use at room temperature. Therefore the construction of the VUV source is a simple and inexpensive matter. It is anticipated that such sources could be constructed at prices well under \$50.

F. IR Tunable Lasers

The wavelength required to excite the HT molecule from the lowest vibrational level of the B electronic state to the first vibrational level of the E electronic state is 9260 Å. Figure 16 compares the current technology of tunable laser sources according to the range of emitted wavelengths (Demtroder, 1981). As can be seen, semiconductor lasers and dye lasers offer two possible sources at the required wavelength. However, dye lasers are traditionally large and expensive, and therefore they would not be suitable for this application. On the other hand, semiconductor lasers are small and inexpensive, their only problem being their relatively low power output.

Figure 17 illustrates the spectral ranges of various semiconductor materials (Demtroder, 1981). Three materials would be suited for this application: $\text{In}_{1-x}\text{Ga}_x\text{P}$, $\text{Al}_x\text{Ga}_{1-x}\text{As}$, and $\text{GaAs}_{1-x}\text{P}_x$.

Table 10. Transmission of some window materials in the vacuum ultraviolet.

Window material	Wavelength above which a 1-mm-thick window has >10% transmission (Å)
LiF	1050
LiF (x-rayed)	1200
CaF ₂	1200
Sapphire	1450

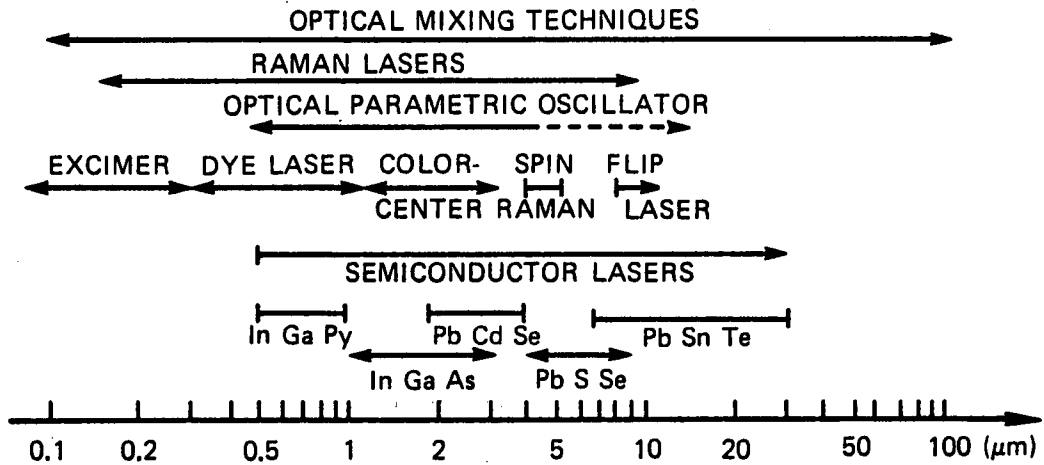


Figure 16. Spectral ranges of different tunable coherent sources.

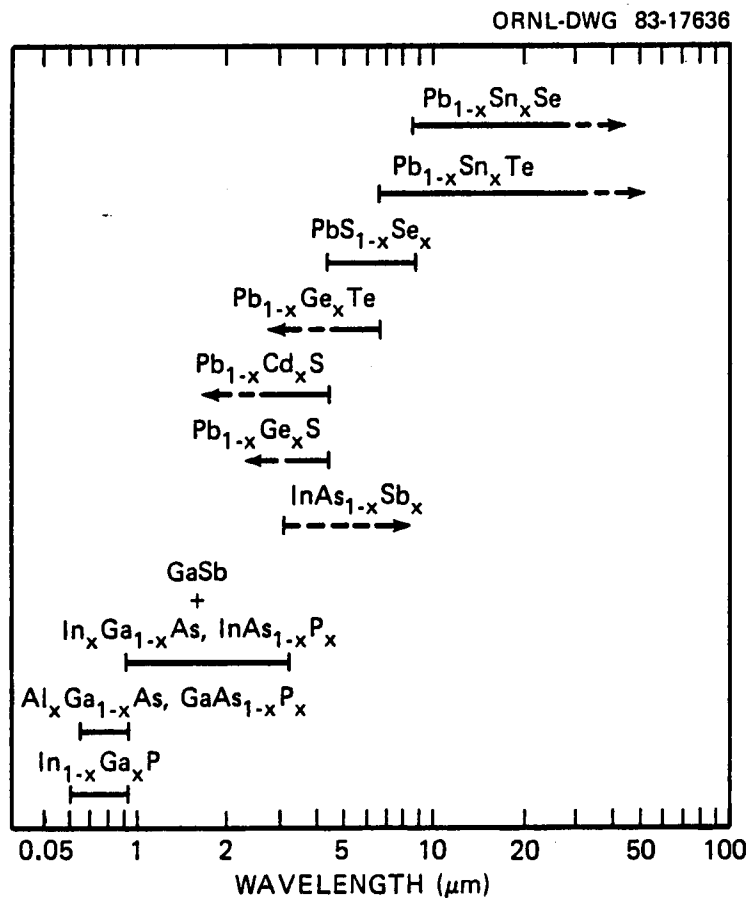


Figure 17. Spectral ranges of various semiconductor materials.

Semiconductor diode lasers can be tuned by varying the bias current of the device.

Tuning appears to be preferable from the viewpoint of calibration. Initially, a tritium sample of known concentration could be introduced into the LIF cell for calibration purposes, and the on-board microprocessor could automatically tune the laser to the right excitation frequency while monitoring the IR detector. The response from the IR detector is calibrated according to the concentration of tritium injected into the LIF counting cell, making calibration a simple and easy task which could be performed at various maintenance points such as ports of call or other labs.

A survey of various commercially available laser diodes indicates that the 926-nm wavelength is not available as an off-the-shelf item. Typical AlGaAs lasers have spectral emissions in the range of 795 to 905 nm, while the spectral emission range of InGaAs lasers is 1270 to 1330 nm. However, by changing the composition of the semiconductor material it would be possible to achieve the 926-nm wavelength. This is achieved by specifying a lower tolerance on the wavelength range of the laser. The cost of such a device is approximately \$2800, (Opto-Electronics, Inc.) its rise time is less than 55 ps, and its peak pulse power is stated to range from 100 to 600 mW.

It is also possible to make the transition to the lowest vibrational level of the E electronic state instead of exciting the first vibrational level of the E state. The required wavelengths for this

transition are 1129 nm and 1116 nm for HT and H₂, respectively. The required wavelengths are not as well separated as for the transition to the first vibrational level, but commercial laser sources are readily available at this wavelength.

An alternative IR source that could be used is a noncoherent, IR-emitting diode. Texas Instruments (Texas Instruments) manufactures an efficient high power GaAs IR diode with a peak output intensity of 925 nm. Its fwhm bandwidth is 45 nm, and the output power of this device can easily reach 50 mW. The only requirement for using such a device is that an optical bandpass filter must be used to pass only the 926-nm wavelength and stop the 886-nm wavelength. These filters are easily obtained and cost approximately \$100 each.

Dye lasers are commercially available in the range 400 to 800 nm, and the price and physical size of these devices have decreased recently. It may be possible to excite the third vibrational level of the E electronic state of the HT molecule. The wavelength required to make this transition is 706 nm, which is well separated from the transition wavelengths of 749 nm and 660 nm for H₂. Such units cost about \$3500, (Laser Science, Inc.) and their physical size is 12.25 × 4.62 × 2.06 in. The main problem with such a unit is that tuning must be done with an adjustable micrometer. Automatic tuning would be very difficult.

In order to efficiently operate both the laser and the noncoherent diodes, it is necessary to reduce the temperature of the

device. Temperature regulation is necessary also because the emitted spectra for both devices shift as temperature changes. A cold plate would provide a simple solution to this problem. Cold plates are readily available from laboratory supply houses and cost approximately \$550. They are capable of operation from an ac source and can maintain a temperature of 0°C. A servo-mechanism could be used in which thermocouples could be attached to various points in the instrument. The on-board microprocessor could then take periodic readings and make the necessary adjustments to the cold plate controls.

G. IR Detectors

The IR detector must be able to detect wavelengths ranging from 1286 nm (1.286 μm) to 2141 nm (2.141 μm). Figures 18 through 21 illustrate sensitivity versus wavelength for a variety of different IR detectors (McCormick, 1983). As can be seen, Ge, PbS, and HgCdTe detectors can be operated at or about room temperature. PbS and Ge have about equivalent sensitivities, depending on their temperature, while HgCdTe is the least sensitive of the three. A Ge detector sold by Opto-Electronics, Inc. (Opto-Electronics, Inc.) has a response range of 500 to 1800 nm, and its cost is \$3900. The rise time response of this device is less than 0.6 ns, which makes it ideal for photon counting.

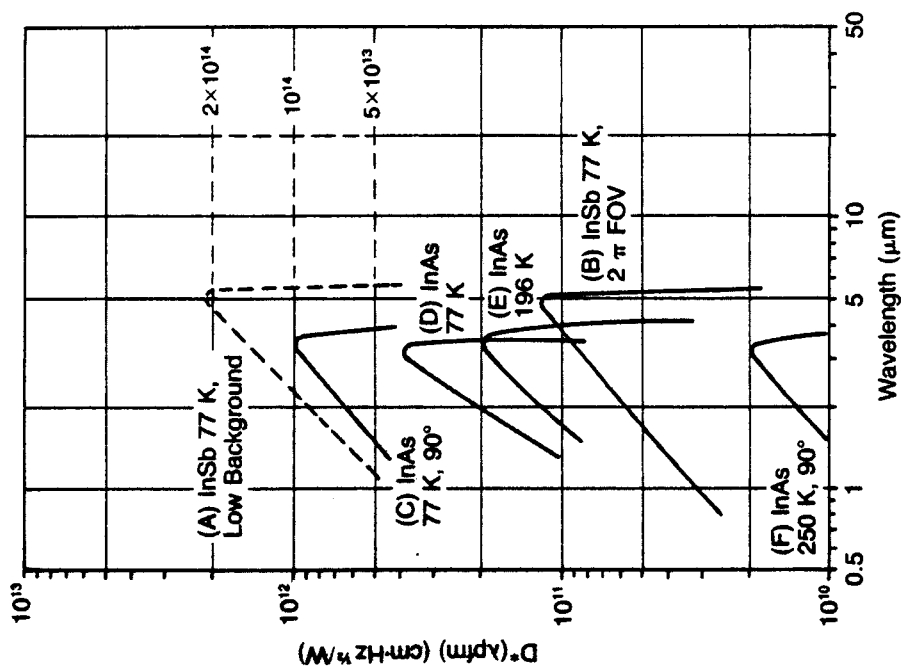


Figure 18. Germanium photodiodes.

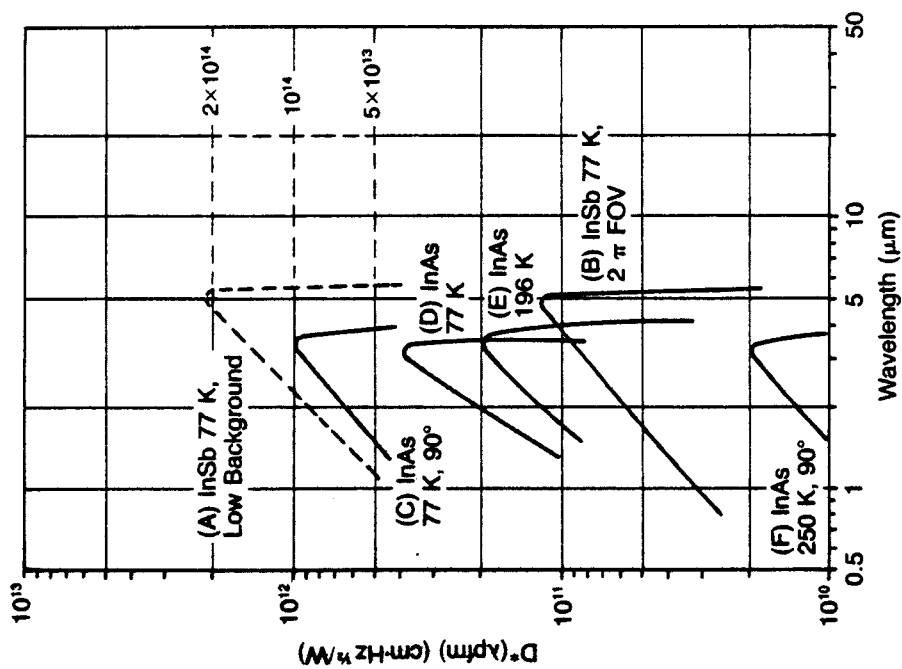


Figure 19. III-V compounds.

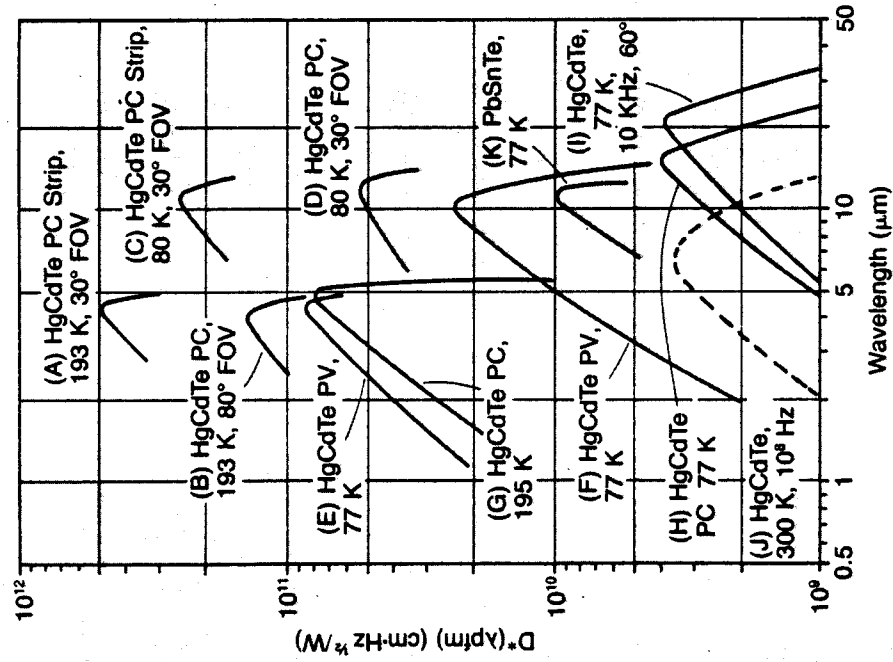


Figure 21. HgCdTe and PbSnTe detectors.

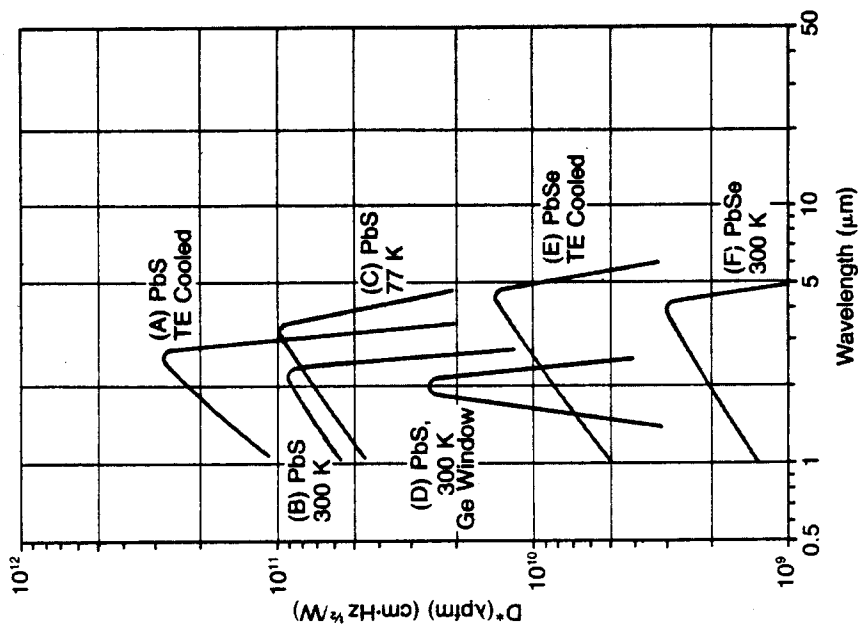


Figure 20. Lead salt detectors.

H. Calculations of Sensitivity

A brief discussion is presented here on the physics of the emission and absorption of electromagnetic radiation in atomic systems. Results are used to calculate the sensitivity of the double resonance LIF system for HT described earlier. A transition can take place in an atomic system with an initial energy, E_m , and final energy, E_n , if a photon of energy $(E_n - E_m)$ is absorbed. As mentioned previously, only certain discrete energy levels are present in the HT molecule.

Since each energy state has a finite lifetime, an absorption spectrum is associated with that state. The lineshape function, $g(\nu)$, determines the probability of absorption and emission of a given electronic state with respect to the frequency of the electromagnetic radiation (Yariv, 1976). It is normalized over the entire range of frequencies:

$$\int_{-\infty}^{\infty} g(\nu) d\nu = 1 \quad (9)$$

In the case of homogeneous broadening due to the lifetime of the atomic states, the lineshape assumes a Lorentzian function:

$$g(\nu) = \frac{\Delta\nu}{2\pi[(\nu - \nu_o)^2 + (\frac{\Delta\nu}{2})^2]} \quad (10)$$

where

$$\Delta\nu = \frac{1}{\pi\tau} \quad (11)$$

and τ is the lifetime of the emitting or absorbing state and ν_0 is the transition frequency. The transition probability for absorption, B_{mn} , is given by

$$B_{mn} = \frac{8\pi^3}{3h^2c} \left| \overline{R}^{nm} \right|^2, \quad (12)$$

and the transition probability for spontaneous emission, A_{nm} , is given by

$$A_{nm} = \frac{64\pi^4\nu_0^3}{3h} \left| \overline{R}^{nm} \right|^2. \quad (13)$$

The matrix element, $\overline{R}^{nm}$, is given by

$$\overline{R}^{nm} = \int \psi_m^* \overline{M}_e \psi_n d\tau, \quad (14)$$

where

$\overline{M}_e$ = dipole moment of the electron states

ψ_n, ψ_m = electronic eigenfunctions

$d\tau$ = volume element.

Normally, the transition probability is given in terms of oscillator strengths, f^{nm} :

$$f^{nm} = \frac{8\pi^2\mu_c\nu_0}{3h\epsilon^2} \left| \overline{R}^{nm} \right|^2, \quad (15)$$

where

μ = mass of electron,

ϵ = charge of electron, and

c = speed of light in vacuum.

The relationship between transition probabilities is given by

$$B_{mn} = \frac{1}{8\pi\hbar c \nu_o^3} A_{nm} \quad (16)$$

Oscillator strengths for the transitions to various vibrational levels of the B electronic state from the ground vibrational level of the X state, for the HT molecule, are given in Table 11. The radiative lifetimes of various vibrational levels of the B state have been calculated (Dalgarno, et al, 1970) and they are listed in Table 12. Experimentally, the intensity of a light source, I , falls as it travels through an absorbing gas according to the equation

$$I = I_0 e^{-k_v \Delta x}, \quad (17)$$

where

I_0 = initial intensity,

k_v = absorption coefficient, and

Δx = distance travelled through the gas.

Table 11. Oscillator strengths, f_{nm} , for the transition $B \ ^1\Sigma_u^+ | v = 0 \rightarrow X \ ^1\Sigma_g^+$ of the HT and H_2 molecules.

Band	f_{nm}
(0,0)	1.75×10^3
(1,0)	5.19×10^3
(2,0)	11.5×10^3
(3,0)	17.6×10^3
(4,0)	24.5×10^3
(5,0)	25.8×10^3

Table 12. Lifetimes of various vibrational levels in the $B \ ^1\Sigma_u^+$ electronic state for HT and H_2 .

Quantum vibrational number, v	Lifetime (ns)
0	0.53
1	0.57
2	0.61
3	0.65
4	0.69
5	0.73
6	0.77
7	0.83
8	0.88
9	0.93
10	0.97
11	1.01
12	1.05
13	1.10

The energy absorbed by the gas, per unit area and per unit time, is equal to

$$I_{\text{abs}}^{\text{nm}} = \int (I_0 - I) d\nu = I_0 \Delta x \int k_\nu d\nu \quad . \quad (18)$$

It can be shown that this is equal to

$$I_{\text{abs}}^{\text{nm}} = I_0 N_m B_{mn} h\nu_0 \Delta x \quad , \quad (19)$$

where N_m is equal to the concentration of molecules in the lower state. Setting Eqs. (18) and (19) equal, the value of the absorption coefficient is obtained:

$$\int k_\nu d\nu = \frac{8\pi^3 \nu_0}{3hc} N_m \left| \overline{R}^{\text{nm}} \right|^2 \quad . \quad (20)$$

In terms of oscillator strength, the absorbed intensity becomes

$$I_{\text{abs}}^{\text{nm}} = I \Delta x \frac{\pi N_m f^{\text{nm}} \epsilon^2}{\mu c^2} \quad . \quad (21)$$

It is assumed that the first five vibrational levels of the B state of HT are populated using the Ne source. The population, N_B , of the lowest vibrational level of the B state is given by

$$\frac{dN_B}{dt} = I_{\text{abs}}^{\text{nm}} - \frac{N_B}{\tau_B} \quad . \quad (22)$$

In steady state, the derivative is equal to zero and the population becomes

$$N_B = \tau_B I_{abs}^{nm} . \quad (23)$$

From the calculated lifetimes, (Dalgarno, 1970) $\tau_B = 0.53$ ns. In the calculations, the necessary conversions are made to convert from power to number photons/s. Also, various constants are employed, which may not be given in the equations, in order to keep units consistent.

It is assumed, for purposes of sensitivity calculations, that the VUV source emits 10 W of continuous power over the spectrum of interest. It is also assumed that the energy emitted per unit frequency of the source is constant. Hence, over the range of 744 to 1100 nm, the power emitted per unit frequency is 7.6679×10^{-14} W/Hz. The power emitted per unit frequency is integrated with Eq. (10) to yield the power absorbed at the various transition frequencies. This is easily converted to the photon rate involved in the transition ($\partial n / \partial t$). Table 13 lists the various values calculated in the VUV transition to the B state of HT. The value of the transition bandwidth, $\Delta\nu$, used in Eq. 10 is calculated from the Doppler-broadened case. Since the sample is at 0°C and 1 atm, Doppler absorption predominates (Dalgarno, 1970). This can be calculated by the equation

Table 13. Calculations of the VUV transitions to the B state of HT [10-W VUV neon source (LIF window)]

$$(\dots (1s\sigma^2) X \ ^1\Sigma_g^+ |_{v'''} = 0 \rightarrow$$

$$\dots (1s\sigma \ 2p\sigma) B \ ^1\Sigma_u^+ |_{v''}).$$

B state, vibrational quantum number, v	Transition wavelength ($\lambda_o = c/\nu_o$) (Å)	Lifetime of state (τ_v) (ns)	Oscillator strength ($f^{o,v}$)	Doppler-broadened bandwidth [$\Delta\nu_v$ (300°K)] (Hz)	Power delivered to transition (P_v) (mW)	Photon rate delivered to transition (dn/dt) (s ⁻¹)
0	1105.40	0.53	1.75×10^3	2.367×10^{10}	3.630	2.02×10^{15}
1	1092.34	0.57	5.19×10^3	2.396×10^{10}	3.674	2.02×10^{15}
2	1079.86	0.61	11.5×10^3	2.423×10^{10}	3.716	2.02×10^{15}
3	1067.93	0.65	17.6×10^3	2.450×10^{10}	3.757	2.02×10^{15}
4	1056.51	0.69	24.5×10^3	2.477×10^{10}	3.799	2.02×10^{15}
5	1045.55	0.73	25.8×10^3	2.503×10^{10}	3.839	2.02×10^{15}

$$\Delta\nu_v = \frac{2c}{\lambda_o} \sqrt{\frac{2kT}{Mc^2} \ln 2} . \quad (24)$$

The population of the lowest vibrational level of the B electronic state in the HT molecule is directly proportional to the concentration of HT in the sample and the power of the VUV source. This approximation is valid for low power levels of the VUV source where stimulated emission is negligible.

Using Eqs. (20), (21), and (24), the absorption coefficients are calculated for the passage of the various transition wavelengths through a concentration of $1 \mu\text{Ci}/\text{m}^3$ of HT gas:

$$K_v \cong N_m \frac{2\pi^2 \epsilon_f^2 f^{nm}}{\mu c \Delta\nu_v} \quad (25)$$

The power delivered to the transition is approximated by

$$P_v \cong 2 \frac{dP}{d\nu} \Delta\nu_v , \quad (26)$$

where $dP/d\nu$ is 7.6679×10^{-14} W/Hz and $\Delta\nu$ is the Doppler broadened bandwidth calculated for each transition. The values are given in Table 14. Again it is assumed that the transitions are dominated by Doppler broadening. A conceptual LIF cell is shown in Figure 22. The VUV source is placed on one of the large area walls. The population of the lowest vibrational level of the B electronic state, N_B , is approximated by

Table 14. VUV absorption coefficients for HT.

B State of HT, vibrational quantum number, v	Transition wavelength, λ_0 (Å)	Integrated absorption coefficient,* K (cm ⁻¹)
0	1105.40	0.255
1	1092.34	0.252
2	1079.86	0.249
3	1067.93	0.246
4	1056.51	0.243
5	1045.55	0.241

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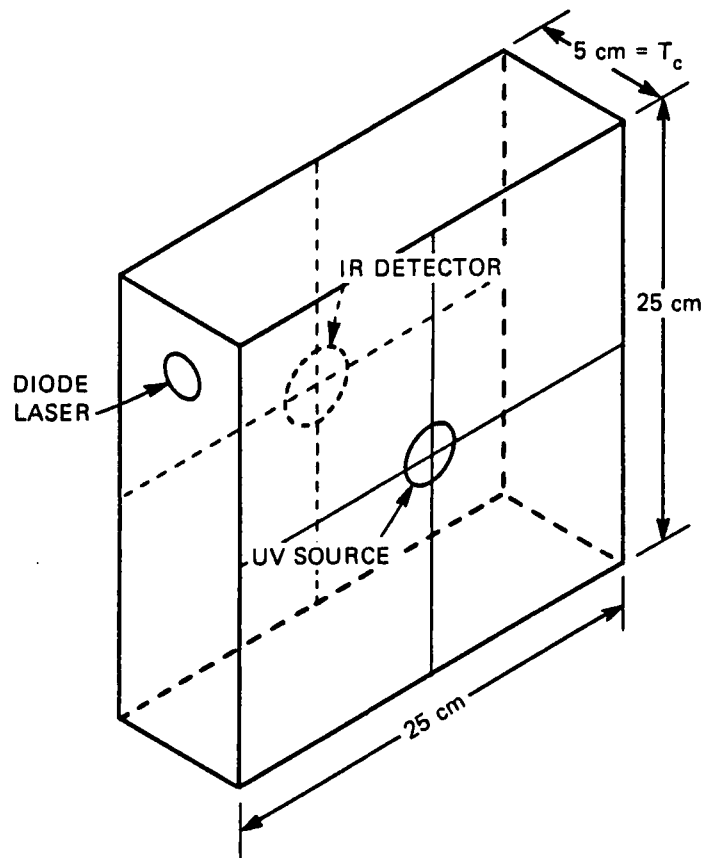


Figure 22. Laser-induced fluorescence (LIF) cell.

$$N_B \cong \frac{\tau_B T_w}{2} \sum_v \frac{dn_v}{dt} (1 - e^{-k_v T_c}) , \quad (27)$$

where the window attenuation is assumed to equal 0.10 for all VUV wavelengths. The factor of 1/2 approximates the geometrical factor of the LIF cell. The cell's thickness, T_C , is shown to equal 5 cm. The sum is taken over all five transition frequencies. Hence, for the 10-W VUV source, and a concentration of $1 \mu\text{Ci}/\text{m}^3$, the steady-state population of the lowest vibrational level of the B electronic state in HT is approximately equal to 2.28×10^5 .

For the transition from state B to state E, a laser diode is used which is tuned to the wavelength of 926 nm. Since this is a strong transition, an oscillator strength of 1×10^3 is assumed. Data have not been found that could confirm this. From the above calculations, the B state is assumed to be uniformly populated in the cell at a calculated concentration of 72.96 cm^{-3} (population divided by cell volume). The Doppler-broadened bandwidth is equal to $2.837 \times 10^9 \text{ Hz}$ at this transition. It is assumed that the laser absorption is dominated by Doppler broadening since the sample is at 300°K and 1 atm. At the given concentration the attenuation coefficient, K , is calculated, from Eq. (25), to equal $4.289 \times 10^{-6} \text{ cm}^{-1}$. The laser diode available from Opto-Electronics, Inc., has a typical output of 300 mW at the transition frequency. This is equivalent to a photon emission rate, $\partial n/\partial t$, of $1.40 \times 10^{18} \text{ photons/s}$. The emitted light from the laser is allowed to pass through the cell many times by the use of mirrors placed on

the appropriate walls of the cell. A practical value of 10 reflections is assumed on one mirror, therefore the pathlength, χ , is equal to 500 cm. The steady-state deexcitation-transition rate of the lowest vibrational level of the E state to the B state is given by

$$\frac{\partial N_E}{\partial t} = \left(\frac{\partial n}{\partial t} \right) (1 - e^{-k\Delta\chi}) . \quad (28)$$

Therefore, the rate of detectable photons emitted, as the E state decays back to the B state via fluorescence, is equal to 2.99×10^{15} photons/s. For the same concentration of tritium in the same volume, the rate of detectable betas emitted is equal to 116 betas/s. Therefore, a great many more detectable photons than detectable betas are emitted.

The surface area of the IR photodetector available from Opto-Electronics, Inc., has a diameter of 20 cm. Therefore, it is assumed about half of the photons emitted in the sample, when the E state decays to the B state via fluorescence, falls onto the detector's surface. Therefore, about 1.49×10^{15} photons/s are detected by the photodetector. This is equivalent to a power of 1.98×10^{-4} W impinging on the detector. The noise of the detector is given at 5×10^{-6} W, and the minimum detectable concentration of tritium is therefore approximately $0.025 \mu\text{Ci/m}^3$. If the laser is pulsed and correlation analysis is used to recover the signal, it is not inconceivable that the sensitivity could approach

$1 \times 10^{-3} \mu\text{Ci}/\text{m}^3$. The equivalent counting time of such a system could conceivably be on the order of 1 min.

Since the laser provided a sensitivity close to the desired value, it was determined that the laser diode would be more suitable than the IR diode as an excitation source. Also, the power delivered to the transition by the IR diode would be many orders of magnitude less than that provided by the laser. Therefore, the laser diode is preferable as the source to excite HT from the B state to the E state.

I. Possibility of Detecting HTO Using LIF

A re-analysis of the molecular levels of the HTO molecule indicates that it may be possible to detect HTO by the LIF method, which would eliminate the need of a condensation and electrolysis system to separate HTO. Also, the same LIF cell could be used to measure both HT and HTO. There is very little data available on the molecular levels of HTO higher than the D state (Herzberg, 1966). What is known is presented in Table 15. It is thought that it may be possible to excite HTO from the C state to the F state with a diode laser. The C state could be populated with a VUV source using required wavelengths of about 120 nm and an argon discharge lamp as the source.

Once a steady-state population has been reached in the lowest vibrational level of the C state, a diode laser could be used to excite HTO from this level to the first vibrational level of the F state. Since the vibrational levels are well separated for the

Table 15. Available data on electronic states of H₂O.

State	Point group	T ₀ (cm ⁻¹)	Vibrational frequencies (cm ⁻¹)			Electron configuration	Observed transitions (Å)
			v ₁	v ₂	v ₃		
$\tilde{S}$		125820		(1700)			$\tilde{S} + \tilde{X}$ 795 - 750
$\tilde{X}$		116760		(900)			$\tilde{X} + \tilde{X}$ 857 - 815
$\tilde{F}$	C _{2v}	89680				... (3a ₁) ² (1b ₁)(3d)	$\tilde{F} + \tilde{X}$ 1115
$\tilde{E}$ (¹ B ₁)	C _{2v}	88660				... (3a ₁) ² (1b ₁)(4sa ₁)	$\tilde{E} + \tilde{X}$ 1128
$\tilde{D}$ ¹ A ₁	C _{2v}	82038	3268	1636	(3335)	... (3a ₁) ² (1b ₁)(3pb ₁)	$\tilde{D} + \tilde{X}$ 1219 - 1172
$\tilde{C}$ ¹ B ₁	C _{2v}	80624.8	3170	(1422)	(3224)	... (3a ₁) ² (1b ₁)(3pa ₁)	$\tilde{C} + \tilde{X}$ 1241 - 1194
$\tilde{B}$ (¹ A ₁)	(D _{∞h})	70870		(800)		... (3a ₁)(1b ₁) ² (3sa ₁)	$\tilde{B} + \tilde{X}$ 1411 - 1256
$\tilde{A}$ (¹ B ₁)	C _{2v}	(53800)	continuous absorption			... (1b ₂) ² (3a ₁) ² (1b ₁)(3sa ₁)	$\tilde{A} + \tilde{X}$ 1860 - 1450
$\tilde{X}$ (¹ A ₁)		0	3657.0	1594.7	3755.7	... (1b ₂) ² (3a ₁) ² (1b ₁) ²	Infrared spectrum

lowest vibrational quantum numbers, it is anticipated that a laser could selectively excite HTO and not H₂O.

No data are available on the vibrational constants for the F level. It is estimated, though, that the required transition wavelength is approximately 1181 nm. Since the fluorescence wavelength is estimated to be 1250 nm, the same laser could be used to excite both HT and HTO if the lowest vibrational level of the E state of HT is excited. The required wavelength for the HT transition is 1116 nm, and the laser could be tuned from one wavelength to another. Laser diodes are readily available in this frequency range. The light emitted from the fluorescence of the HTO molecule could also be detected with the same detector.

Therefore, the only required addition to the system would be a VUV source, which would cost about \$50, and the entire electrolysis and condensation system could be eliminated, which would save about \$2000. This system could separately measure HT and HTO levels at an anticipated sensitivity of $1 \times 10^{-3} \mu\text{Ci}/\text{m}^3$ for both molecules. It must be kept in mind, however, that it is not known if this is entirely feasible since little data are available on the vibrational levels of the F state. It may be necessary to eliminate water in the air sample when measuring HT. This can be easily done using anhydrous calcium chloride as the drying agent and passing the sample through the cell in which the calcium chloride is contained. The cell could be designed in such a way that it could be easily removed and discarded.

J. Cost Considerations

As mentioned above, two possible methods could be adapted to detect HT and HTO simultaneously. A block diagram of the first system, which detects only HT, is shown in Figure 23. An electrolysis and condensation system is employed to separate and count HTO from an air sample. This system would be movable but not portable, and it would cost about \$10,000. It is estimated that a sensitivity of $1 \times 10^{-3} \mu\text{Ci}/\text{m}^3$ could be achieved for HT. Although a laboratory analysis of the condensation and electrolysis system would be needed in order to estimate the sensitivity of detecting HTO, a sensitivity of $1 \times 10^{-3} \mu\text{Ci}/\text{m}^3$ is also anticipated for HTO. The main disadvantage of the condensation and electrolysis method is the inherently long time constant present in the conversion of water vapor to gaseous hydrogen. Again, a laboratory analysis would be needed in order to estimate this value.

The second possible system, which would detect both HT and HTO directly using the LIF method, is shown in Figure 24. It would cost approximately \$8,000, and it would be portable since there is no condensation or electrolysis involved. It is uncertain however, whether LIF could be used to separately and directly detect HTO because no data are available for the electronic level of interest. A laboratory analysis would be necessary to investigate the feasibility of such a scheme, although preliminary estimates indicate that such a method has a high probability of being feasible. A

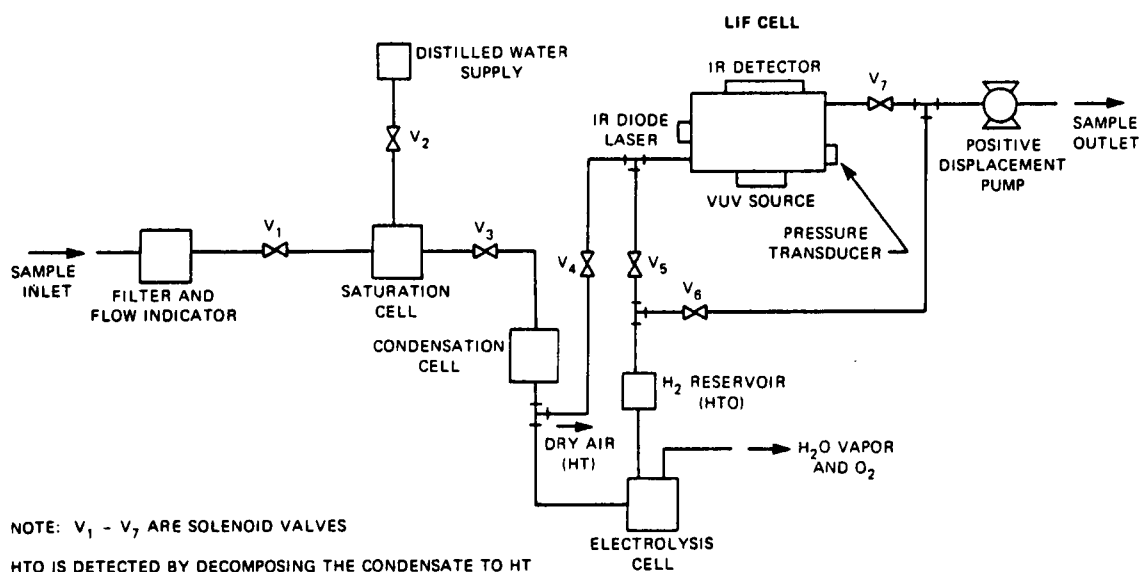


Figure 23. Laser-induced fluorescence (LIF) system for detecting HT.

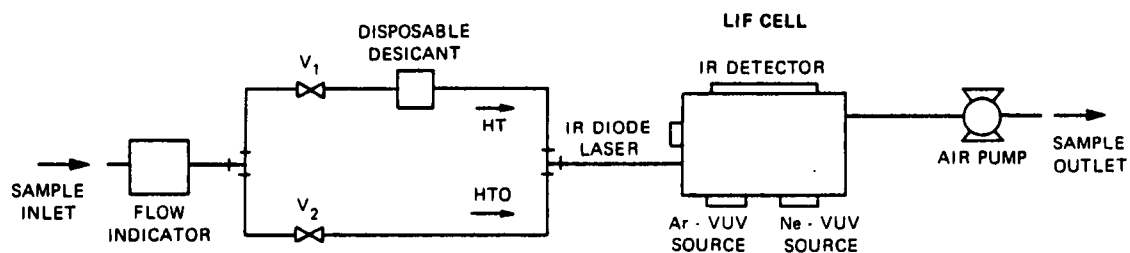


Figure 24. Laser-induced fluorescence (LIF) system for simultaneous detection and separate measurement of HT and HTO.

brief summary of the calculated operational characteristics of both LIF systems is given in Table 16.

Table 16. Calculated operational characteristics of two proposed laser-induced fluorescence (LIF) systems.

Characteristic	Direct excitation and measurement of HT. HTO detected by condensation and electrolysis	Direct excitation and measurement of both HT and HTO. No condensation or electrolysis
HT sensitivity	$1 \times 10^{-3} \mu\text{Ci}/\text{m}^3$	$1 \times 10^{-3} \mu\text{Ci}/\text{m}^3$
HTO sensitivity		
(est.)	$1 \times 10^{-3} \mu\text{Ci}/\text{m}^3$	$1 \times 10^{-3} \mu\text{Ci}/\text{m}^3$
Cost (est.)	\$10,000	\$8,000
HT time constant	~1 min	~1 - 5 min
HTO time constant	~10 min	~1 min
Movable	Yes	Yes
Portable	No	Yes

V. SOLID SCINTILLATION DETECTOR

A. Overview of Conceptual System Development

The basic concept of the solid scintillation scheme which would be used to detect molecular tritium has been discussed earlier in this thesis. Comparisons of various scintillator materials have been made, and the best appears to be $\text{CaF}_2(\text{Eu})$. It is a low-density, low-Z material, which makes it relatively insensitive to gamma radiation and sensitive to low energy beta radiation. Also, $\text{CaF}_2(\text{Eu})$ is a nonhygroscopic material, which makes it particularly attractive from the viewpoint of the manufacture and operation of the detector. Conceivably it would suffer from no memory effects as do organic plastic scintillators after they have been operated over a period of time in an environment containing tritium.

Ideally, the thickness of the scintillator should be equal to the maximum range of the most energetic beta particle emitted in the decay of tritium. This corresponds to a thickness of about 0.0001 in. in $\text{CaF}_2(\text{Eu})$. It has been reported that $\text{CaF}_2(\text{Eu})$ can be evaporated as a 0.0001-in. thin film capable of detecting beta particles. Since a substrate must be used, it was thought that a second scintillator may be used as the substrate in the evaporation of $\text{CaF}_2(\text{Eu})$. This would allow a phoswich detector to be constructed. (The concept of the phoswich detection system and the selection of the two scintillators was given earlier in this thesis.)

The phoswich detector would reduce the sensitivity of the detector for external gamma radiation and for beta- and alpha-emitting radionuclides. The best scintillator that could be used as the substrate would be bismuth germanate (BGO). It is felt that it is cost effective to use a second scintillator as the substrate and to employ the phoswich scheme since the price of nonscintillating substrates is similar to that of BGO. Traditionally, the cost of the analog electronics used in the phoswich scheme is relatively high, but a circuit scheme has been developed which would dramatically decrease the cost and complexity of the electronics. Therefore, the tritium sensitivity of the detector can be dramatically improved, for a given surface area, by employing the phoswich detector scheme at a comparatively small increase in cost. From the qualitative arguments given above it was decided to develop a phoswich detector system. An analysis was made of the developed system and of an equivalent system which did not employ the phoswich scheme. It will be shown that without the phoswich detector the sensitivity would be greatly diminished at a very little savings in cost.

B. Sensitivity Calculations

In calculating the sensitivity of a $\text{CaF}_2(\text{Eu})/\text{BGO}$ phoswich detector, it is assumed that the detector has no window since $\text{CaF}_2(\text{Eu})$ is nonhygroscopic. It can be shown that the count rate of

such a detector viewing a medium in which the tritium is uniformly distributed can be approximated by

$$\dot{C} = T_w \frac{\dot{S}A}{2\mu_m \rho}, \quad (29)$$

where

T_w = transmission factor due to surface scattering,

$\dot{S}$ = specific activity of the medium containing tritium,

A = area of detector,

μ_m = mass absorption coefficient, and

ρ = density of medium containing tritium.

The mass absorption coefficient (Price, 1958) can be approximated by

$$\mu_m = \frac{17}{E_m^{1.14}} \text{ (cm}^2\text{/g)}, \quad (30)$$

where E_m is the maximum energy of the beta emitter in MeV. The scattering transmission factor, T_w , at the detector's surface is dependent on the Z of the detector and the average energy of the beta emitter. For the case of tritium and a $\text{CaF}_2(\text{Eu})$ detector, T_w is equal to 0.957. Using Eq. (27) and various possible detector areas, it was possible to calculate the counting times necessary to achieve a given measurement uncertainty with no background present. The result of these calculations is shown in Figure 25.

These calculations were based on the assumption of $0.1 \mu\text{Ci/m}^3$ of tritium uniformly distributed in air. For example, the

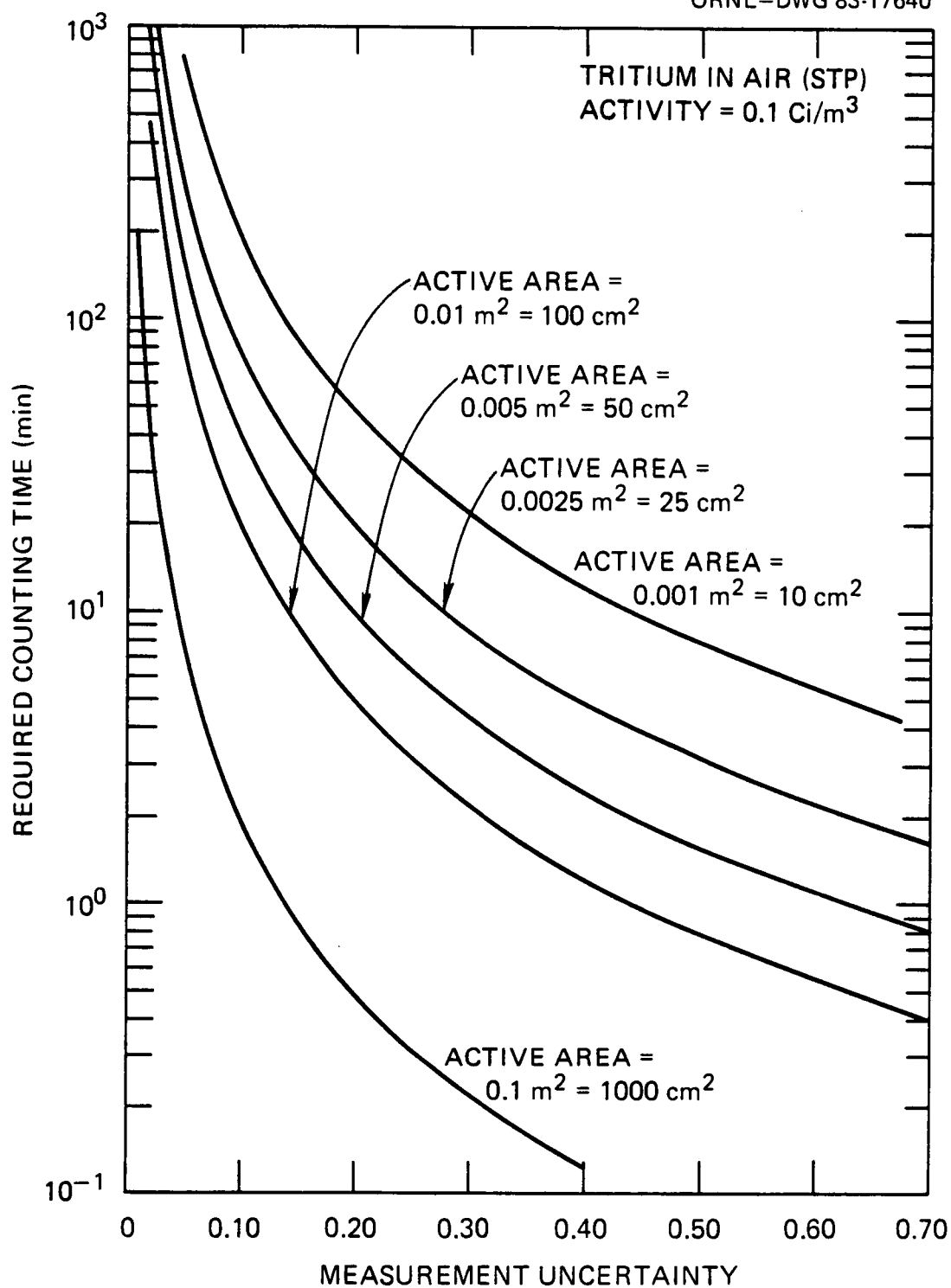
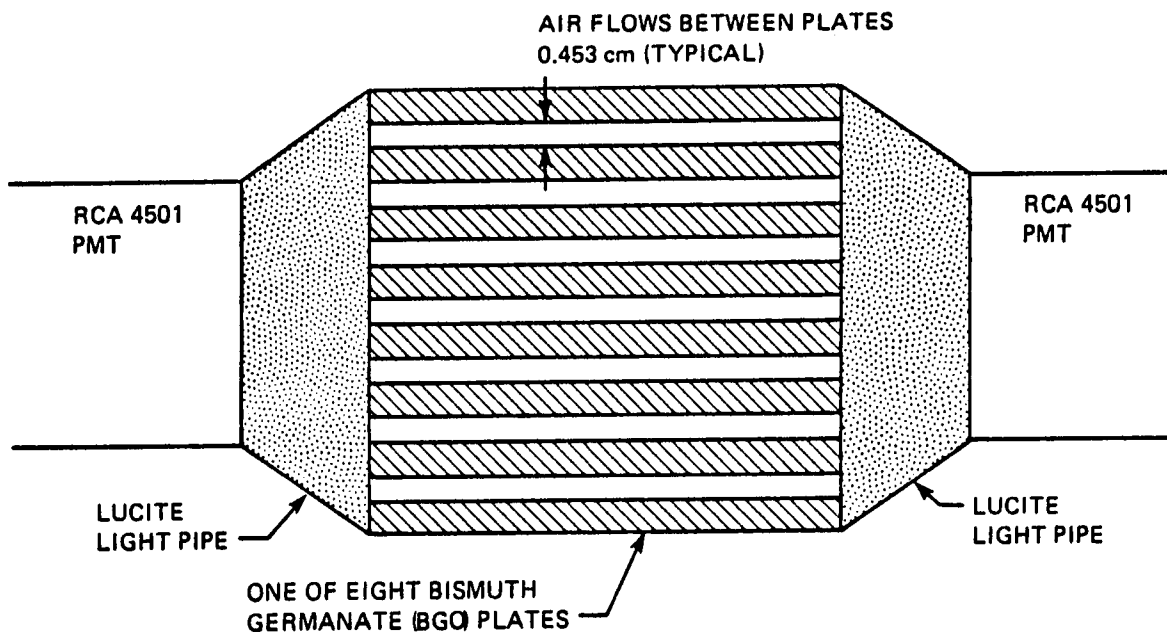


Figure 25. Measurement uncertainty for various active areas.

detector's active area must be about 1000 cm^2 in order to achieve a measurement uncertainty of 10% in a counting time less than 10 min when detecting tritium at a concentration of $0.1 \mu\text{Ci}/\text{m}^3$ with no background present. The range of the maximum energy tritium beta in air is 0.453 cm.

An eight-plate detector can be constructed as shown in Figure 26 using plates constructed of BGO and having a 0.0001-in. thin layer of $\text{CaF}_2(\text{Eu})$ evaporated on both sides. Two photomultiplier tubes are connected in a coincidence arrangement in order to reduce thermally generated counts. The active area of the device is 1396 cm^2 , and the count rate of such a device at an activity level of $0.1 \mu\text{Ci}/\text{m}^3$ is 1.20 counts/s. A counting time of 1.39 min would be needed to achieve an uncertainty of 10% if no background were present.

The response of the detector to external gamma radiation is shown in Figure 27. Calculations were made of a detector similar to that of Figure 26, and four configurations were analyzed: the detector in a phoswich arrangement with no lead shielding; the detector in a phoswich arrangement with 1 in. of lead shielding; the detector not in a phoswich arrangement with no lead shielding; and the detector not in a phoswich arrangement with 1 in. of lead shielding. A quartz or pyrex substrate could be used instead of BGO if the detector is not in a phoswich arrangement. Figure 27 plots calculated count rate versus gamma energy at an exposure rate of 1 mR/h for the four different configurations. As gamma energy



FULL SCALE

DIMENSIONS: 9.34 cm X 9.39 cm X 0.635 cm
 BOTH SIDES EVAPORATED WITH CaF_2 (0.0001 in.)
 TOTAL AREA = 1396 cm²

ORNL DWG 83-17624

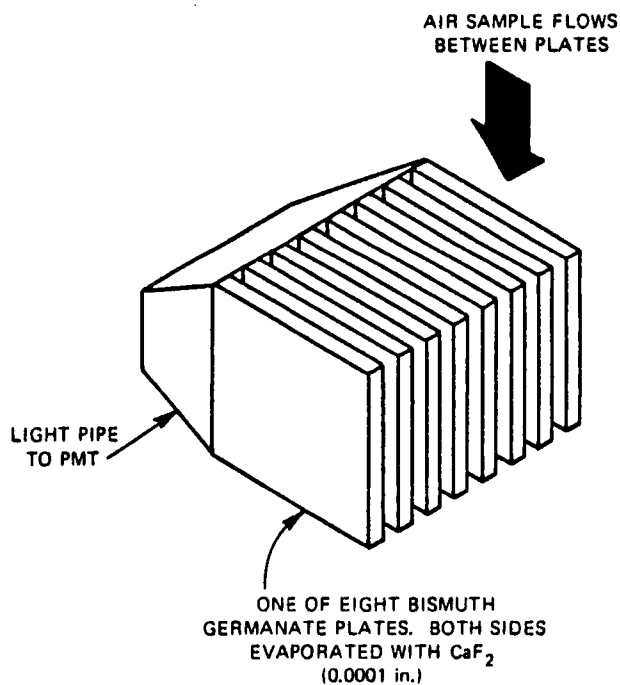


Figure 26. Solid scintillator flowthrough cell.

ORNL-DWG 83-17641

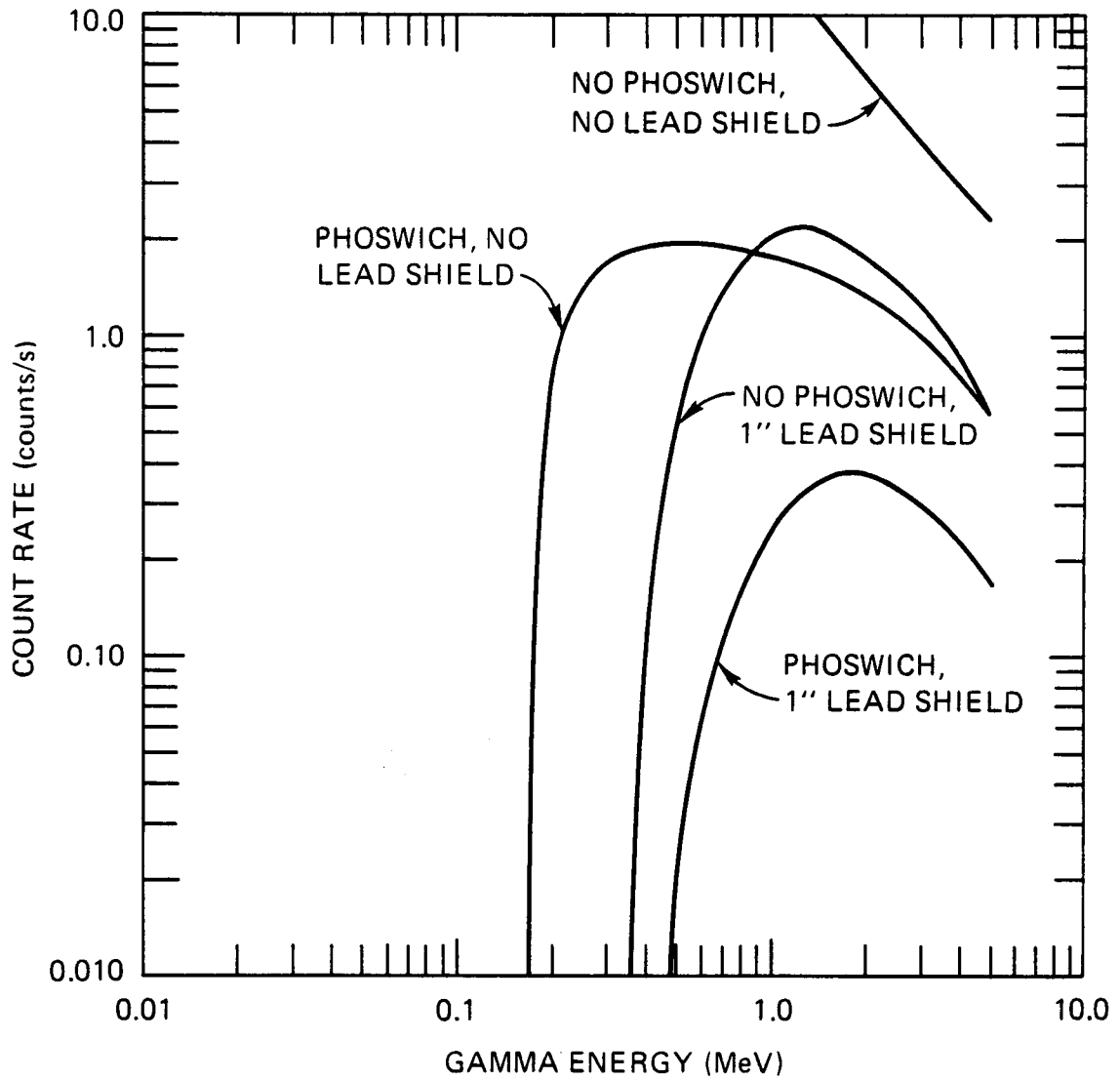


Figure 27. Calculated count rate for 1 mR/h external gamma exposure.

decreases, the count rate of the no phoswich/no shield configuration increases dramatically. At 0.6 MeV the calculated count rate would be 30.28 cps and would rise to 641.2 cps at 0.1 MeV. As can be seen in Figure 27, the count rate drops off dramatically, particularly at low energies, when the phoswich arrangement is employed. Its response is almost equivalent to that of the no phoswich 1-in. lead shield configuration. The maximum count rate of the phoswich 1-in. lead shield configuration occurs at about 1.85 MeV and is equal to about 0.38 cps. This compares to a count rate of 1.20 cps for tritium at an activity level of $0.1 \mu\text{Ci}/\text{m}^3$. The added weight of 1 in. of lead shielding around the detector configuration shown in Figure 26 would be about 38.3 lb.

As mentioned previously, most alpha energies range from 5.3 to 8.8 MeV. The range of a 5.3-MeV alpha particle in air is approximately equal to 3.65 cm, while the range of an 8.8-MeV alpha particle in air is equal to 8.27 cm. The spacing between plates of the configuration shown in Figure 26 is equal to 0.178 in. Calculations indicate that only a small fraction of the alpha's energy would be deposited in the 0.0001-in. $\text{CaF}_2(\text{Eu})$ layer, while almost all of it would be deposited in the BGO crystal, for a decay event occurring right on the face of the detector.

The light pulse will be predominantly the light generated by the BGO crystal making pulse shape discrimination of alpha events rather easy. Because alpha particles lose energy as they travel through air, pulse shape discrimination becomes more difficult for

alphas that have decayed farther away from the detector since more relative energy is deposited in the $\text{CaF}_2(\text{Eu})$ layer and less in the BGO layer. This problem is reduced since the effective distance an alpha particle can travel in air is less than its maximum range. The spacing between the plates, in which the air sample can flow, is kept purposely small in order to reduce the alpha sensitivity of the device.

Calculations were made in order to estimate the sensitivity of the detector for alpha particles above the 5.3- to 8.8-MeV energy range. It was assumed that pulse shape discrimination would be ineffective when the light emitted by $\text{CaF}_2(\text{Eu})$ equals the light emitted by BGO. At an activity of $0.1 \mu\text{Ci}/\text{m}^3$ the count rate was calculated to be about 4.06×10^{-4} cps over the 5.3- to 8.8-MeV energy range. The count rate for tritium at the same activity level was calculated to be 1.20 cps. Hence, at the same activity levels the detector has a tritium-to-alpha count rate ratio of about 3000.

Calculation of the sensitivity of the detector to other beta-emitting radionuclides is very difficult because beta particles are emitted over a spectrum of energies. It is believed, though, that discrimination factors on the order of about 3000 may be possible, particularly at higher energies. Since the spacing between the plates is made equal to the range of the tritium beta in air, the effective volume of higher energy betas is lower than with larger plate spacings. Air attenuates very little of the betas' energy and, since $\text{CaF}_2(\text{Eu})$ is of low density and low Z, little energy will

be lost in that layer. Hence, pulse shape discrimination would be very effective in rejecting many higher energy betas. In fact, the only betas that would be counted are those with energies approaching 18.6 keV.

C. Construction Techniques

Construction of a detector similar to the one shown in Figure 26 would be relatively simple and straightforward. Since both $\text{CaF}_2(\text{Eu})$ and BGO are nonhygroscopic, no special handling techniques would be required. The BGO substrates could be evaporated as single plates by either electron beam or thermal evaporation. [The vapor pressure of $\text{CaF}_2(\text{Eu})$ is 10^{-4} torr at 1000°C .] A quartz crucible can be used to contain the $\text{CaF}_2(\text{Eu})$ sample during evaporation, and it can be expected that variations in thickness along the plate would be less than 25%.

The lucite light pipes could be easily machined, and the BGO plates can be attached to the lucite light pipes with an optical grease in order to assure good light transmission through the interface. Since the evaporated layer of $\text{CaF}_2(\text{Eu})$ is very smooth, the air interface acts much like a mirror. Consequently, internal reflections cause most of the emitted light to be directed to the photomultiplier tubes.

D. Separation of HT and HTO

The literature survey of tritium detectors indicates that semi-permeable membranes could be used to separate HT and HTO. The time

constant through such a membrane would be on the order of 5 min, and therefore the total time response of the detector, including counting time, could be on the order of 10 min. A conceptual block diagram of such a system is shown in Figure 28. A simple air pump could be used, and the sample could count either HT or HTO by using a simple purge procedure when switching from HT to HTO or vice versa. The use of semipermeable membranes is also attractive from the standpoint of rejecting beta-emitting noble gases. Separation factors of 10^4 have been reported.

E. Electronics

As mentioned previously, pulse shape discrimination has traditionally required expensive and sophisticated pulse processing electronics. A block diagram of such a system is shown in Figure 29. The system uses an integrating network composed of a parallel resistor and capacitor, which causes the output pulse of the preamp to rise exponentially with a time constant equal to the light-decay time constant of the scintillator. [The light-decay time constants for $\text{CaF}_2(\text{Eu})$ and BGO are 0.94 and 0.30 μs respectively.] The output of the preamplifier is connected to a parallel pulse shaping network. Both sides of the network have double delay line filters, but the clipping time, T_1 , of one filter is less than the clipping time, T_2 , of the other. Zero crossing detectors are placed at the outputs of both double delay line filters. A logic pulse is generated at exactly the time the input pulse crosses the baseline. The interval from the time the short

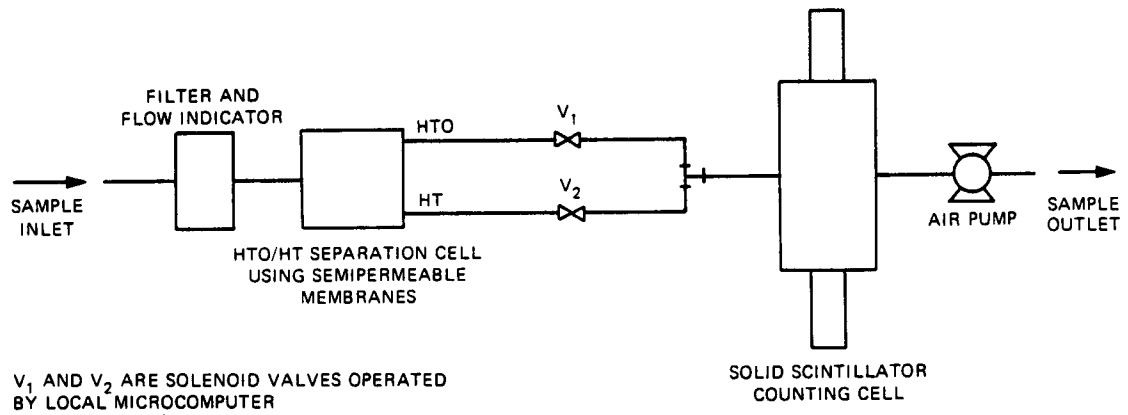


Figure 28. Solid scintillator counting system.

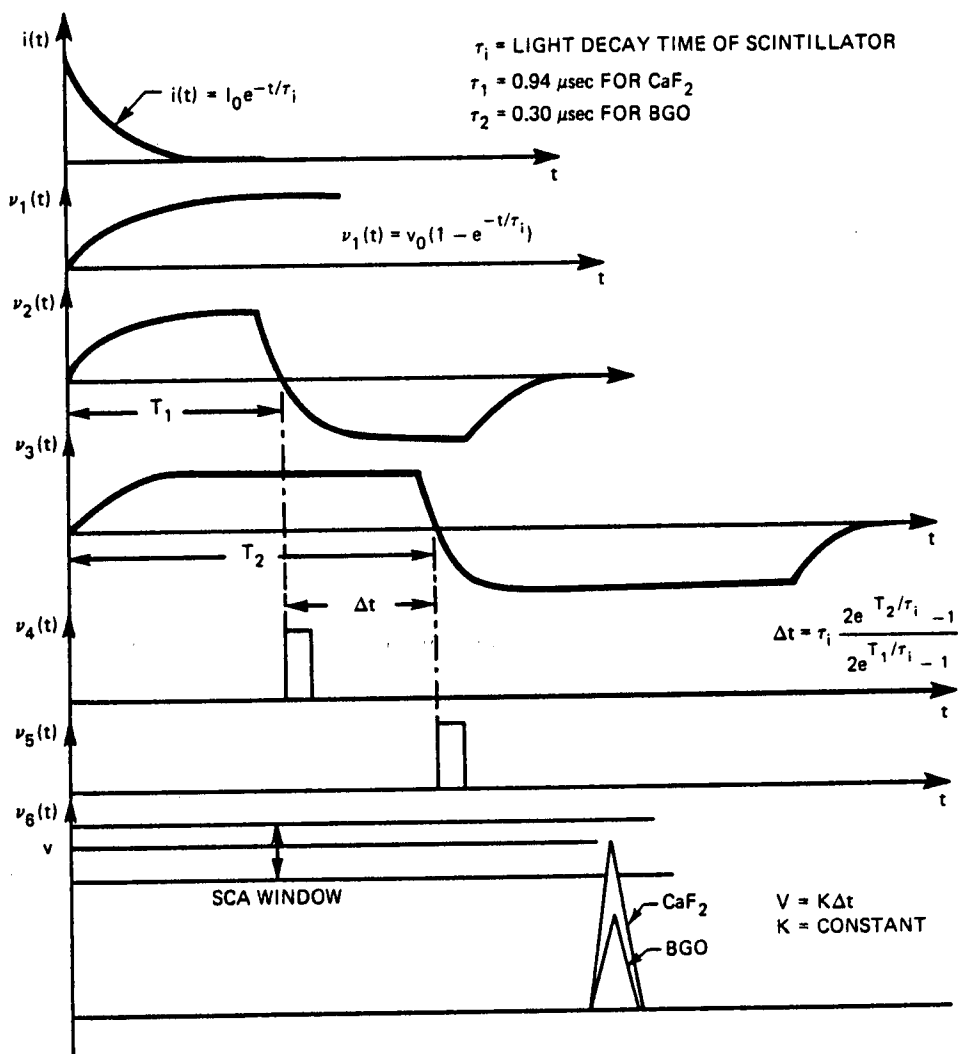
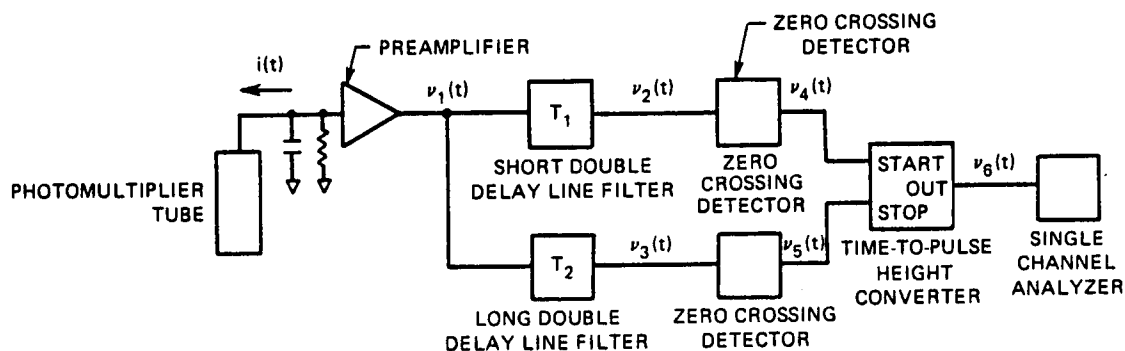


Figure 29. Traditional pulse shape discrimination system.

double delay line pulse crosses the baseline to the time the long double delay line pulse crosses the baseline is a direct indication of the light decay time of the scintillator. The time is less for the BGO scintillation pulse than for the $\text{CaF}_2(\text{Eu})$ pulse because the light decay time of BGO is smaller. The time-to-pulse height converter (TPHC) generates a pulse whose amplitude is directly proportional to this time duration. The amplitude of the output pulse from the TPHC is greater for a $\text{CaF}_2(\text{Eu})$ scintillation event than for a BGO scintillation event. The major drawback of this system is that the TPHC is a comparatively expensive and complicated circuit.

An alternative circuit is shown in Figure 30. Again the same preamplifier, double delay line filters, and zero crossing detectors are used. Instead of a TPHC, a simple combination of "one shots" (monostable multivibrators) and an edge-triggered D-type flip-flop logic element is used. The pulse duration of the one shot, which is connected to the D input of the flip-flop, is set so that only $\text{CaF}_2(\text{Eu})$ pulses are accepted. The timing is adjusted in such a way that a BGO scintillation event will not produce a pulse at the output of the flip-flop; only a $\text{CaF}_2(\text{Eu})$ scintillation event will produce an output pulse, and it can be directly counted by a simple counter.

A block diagram of the entire electronics system for the solid scintillation detector is shown in Figure 31. As can be seen, pulse processing electronics is broken down into three networks. The

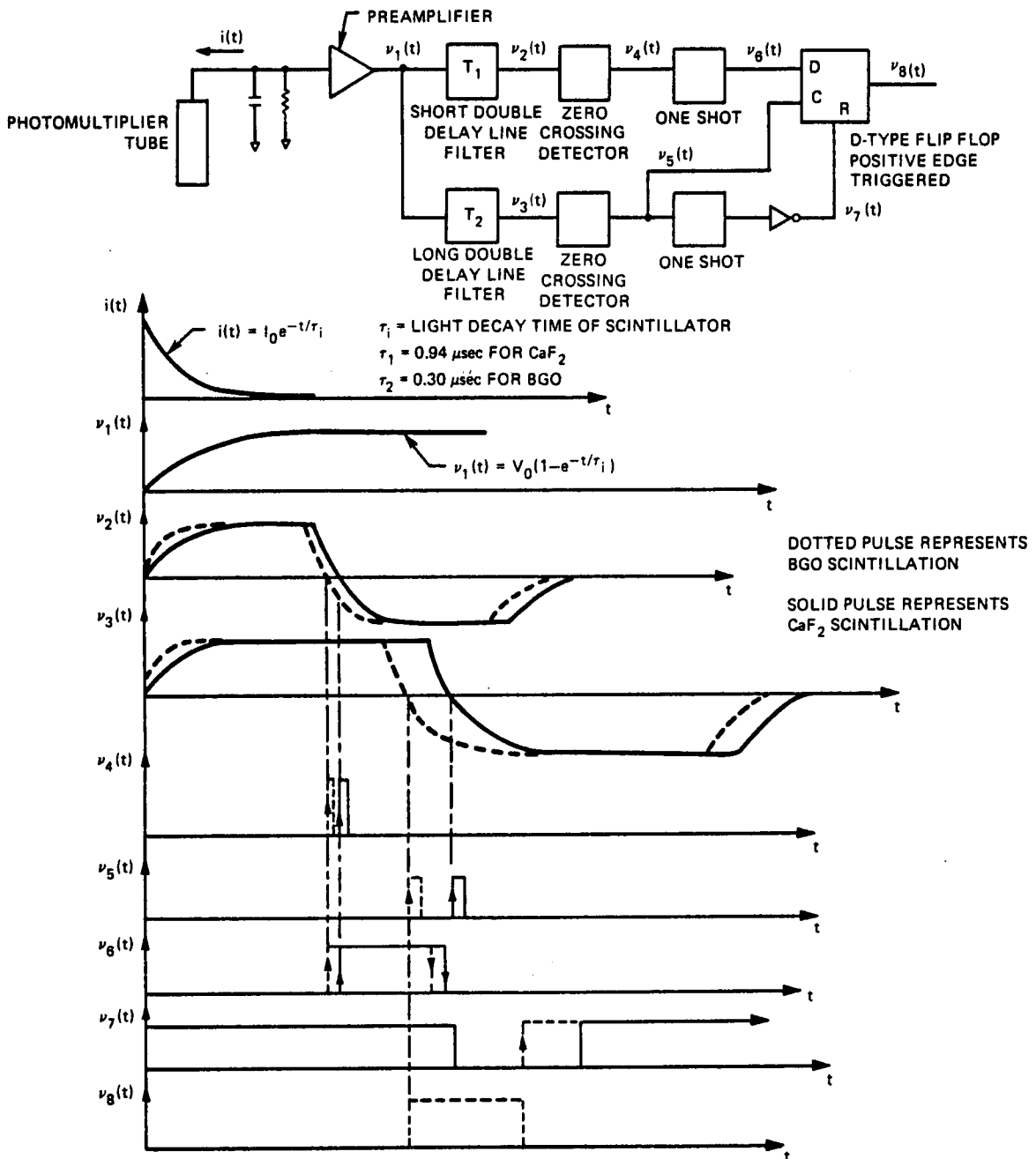


Figure 30. Alternative pulse shape discrimination system.

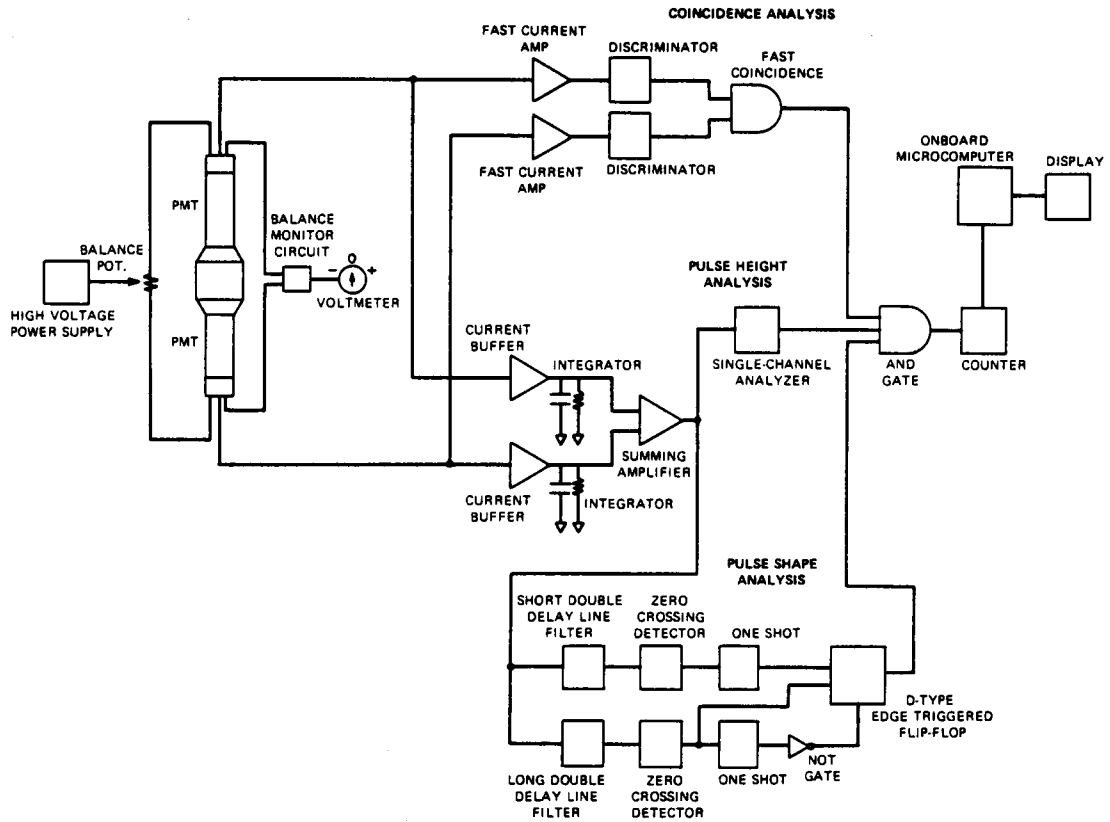


Figure 31. Diagram of the complete electronic system for a solid scintillation counter.

coincidence analysis network reduces unwanted counts from thermally generated noise pulses in the photomultiplier tubes (PMTs), which eliminates the necessity of cooling the PMTs. The pulse height analysis network counts only pulses whose height is in the range of tritium pulses. The pulse shape analysis network accepts pulses only from scintillation events occurring in $\text{CaF}_2(\text{Eu})$. If all three criteria are met, a count is registered. A balance monitor circuit, developed for a liquid scintillation counter, (Colman et al., 1982) would permit the use of tubes that are not matched in gain, thereby reducing the serious logistics problem of stocking matched pairs of PMTs.

F. Cost Considerations

It is estimated that the cost of the solid scintillation cell, including labor and material, would be about \$5,000. This is the price most commercial vendors charge for a specially constructed, large-area phoswich detector. The cost of the two PMTs would be about \$1,200, and the cost of any mechanical parts, including labor, would be about \$1,800. Finally, the estimated cost of the electronics would be about \$2,000. Therefore, the cost of the entire system would be approximately \$10,000.

VI. CLOSED LIQUID SCINTILLATOR SYSTEM

A. Scintillator Cleanup Material

The possibility of separating water samples from organic liquid scintillators has been reported just recently, (Tipler, 1969) and thus far anhydrous calcium chloride is the only material known to achieve the separation. Separation is accomplished by passing the scintillator, with the water sample incorporated in it, through a closed cell containing the calcium chloride. The water would be absorbed by the calcium chloride and remain in the cell. Large separation factors, in which nearly all the water has been removed, have been reported. The cell could be discarded periodically and replaced with a fresh cell. The cell can be disposed of as a low-level waste; anhydrous calcium chloride requires no hazard labeling, but exposure to it will burn skin and eyes.

B. Conceptual Liquid Scintillation System

A liquid scintillation system similar to one reported previously by this author (Colman et al., 1982) would be ideally suited for this application. Figure 32 contains plots of the counting times required to achieve a given measurement uncertainty with this system in the presence of various background exposure rates. A typical background exposure rate, measured in the lab, is about 0.016 mR/h, but this value may vary with the location of the detector.

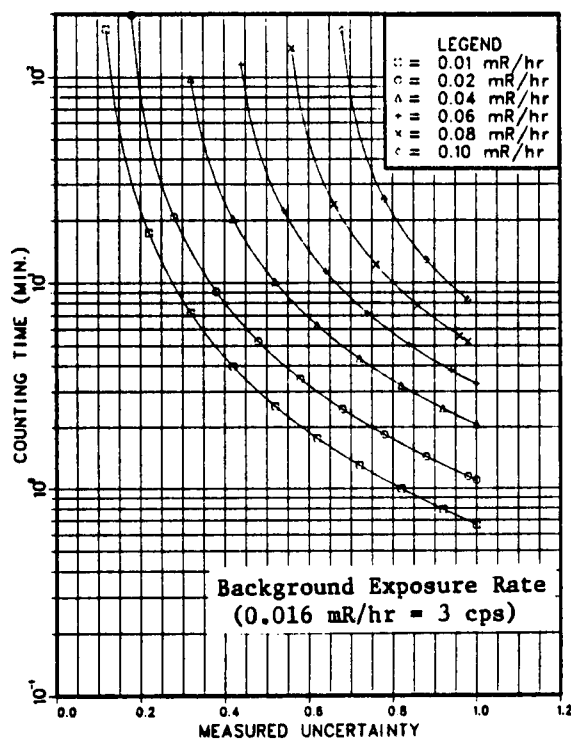
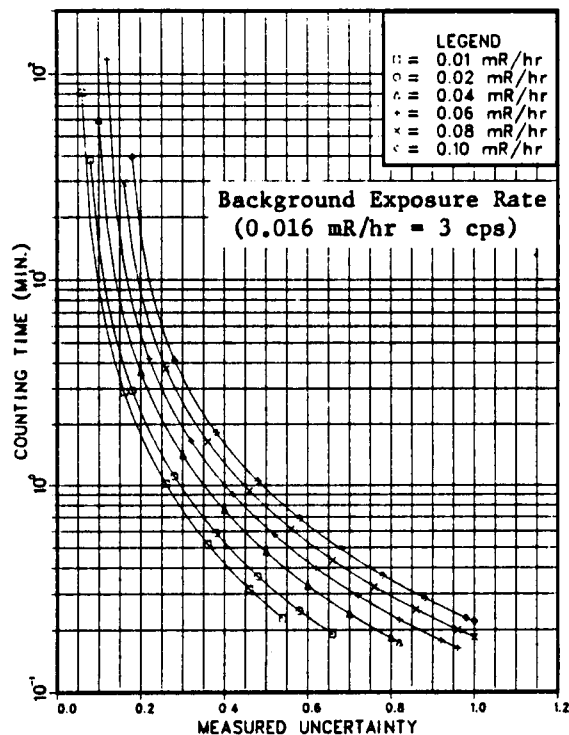
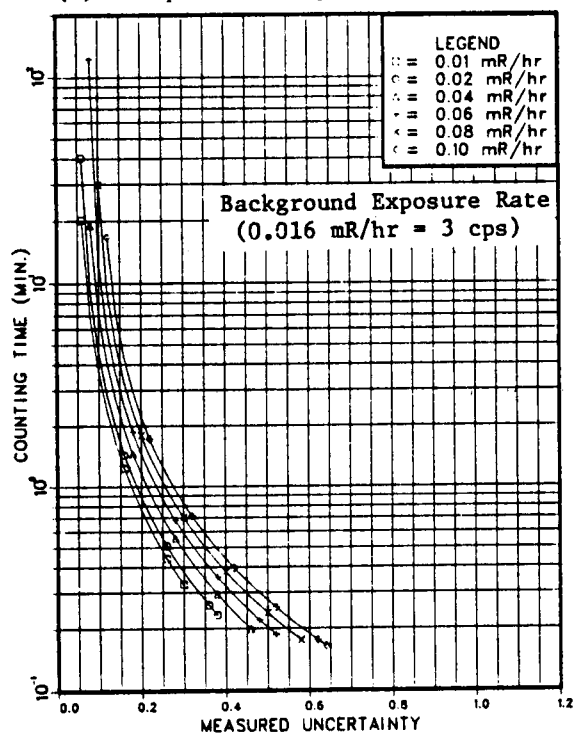
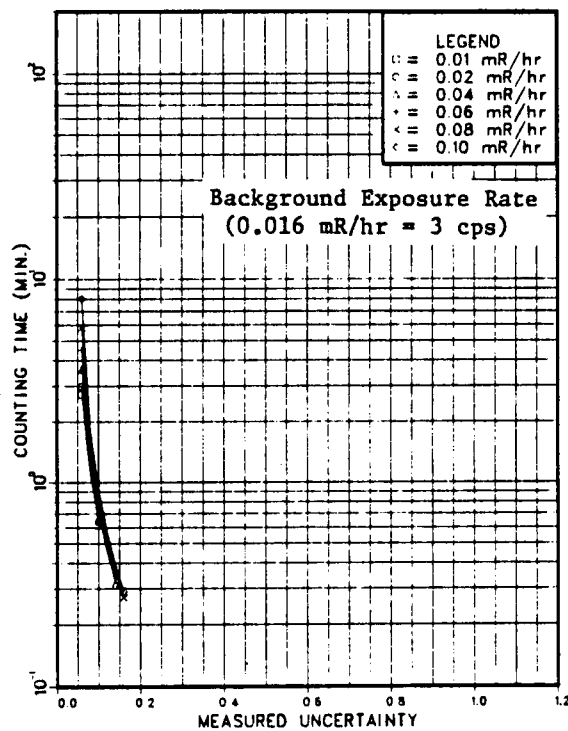
(a) Sample activity = 0.1 $\mu\text{Ci/L}$ (b) Sample activity = 0.5 $\mu\text{Ci/L}$ (c) Sample activity = 1 $\mu\text{Ci/L}$ (d) Sample activity = 5 $\mu\text{Ci/L}$

Figure 32. Plots of required sample counting times versus measured uncertainty at various background exposure rates for a water sample with no quench.

A block diagram of a conceptual closed-loop liquid scintillation detector is shown in Figure 33. In this system an air sample is bubbled through a given volume of distilled water. It has been reported that 90 to 98% HTO is collected and about 0.01% of HT is collected using this method. Air is not bubbled directly through the liquid scintillator, since this would release toxic scintillator gases into the environment. Periodically, the water sample is mixed with the scintillator and transferred to the counting cell. When the count is completed, the scintillator containing the water sample is passed through the anhydrous calcium chloride cleanup cell, removing the water sample from the scintillator. The clean scintillator is then stored in a reservoir until another cycle is started.

Typical circulating air pumps have a flow rate of 30 liters per minute. For example, consider a 1-mL water sample through which the air is bubbled. From Figure 32, it is apparent that a sample with an activity of $5 \mu\text{Ci/L}$ would be desirable from the standpoint of short counting times. Therefore, an air sample containing a tritium concentration of $0.1 \mu\text{Ci/m}^3$, would require a bubbling time of 1.67 min in order to achieve a measurement uncertainty of 10% in a 1-min counting time. Therefore, the total time constant of the system would be about 5 min, including the time for mixing the sample with the scintillator and transferring the scintillator to the counting cell. Assuming an intrinsic efficiency of 0.30 for the liquid scintillator counting system, the expected sensitivity of the

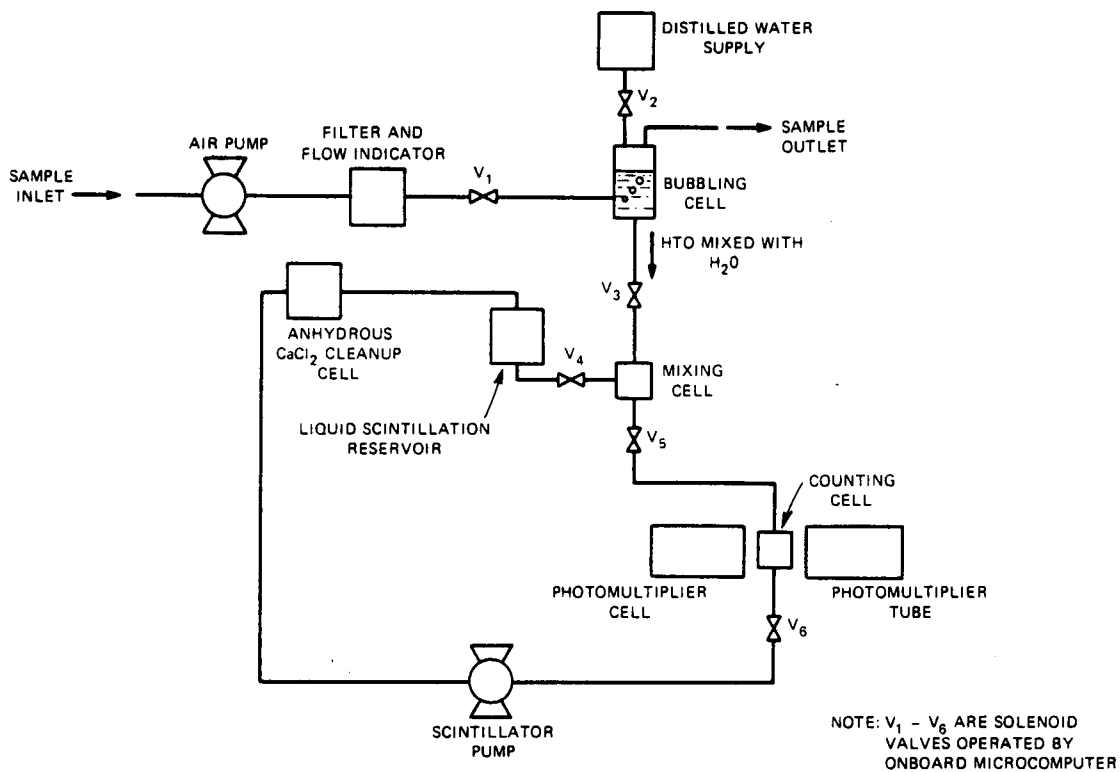


Figure 33. Conceptual liquid scintillation HTO detector.

detector would be 560 cps per $\mu\text{Ci}/\text{m}^3$. The bubbling technique contributes to this high sensitivity because it is very effective in removing beta-emitting noble gases and alpha-emitting radionuclides, thereby reducing the background count rate.

The system shown in Figure 33 is incapable of measuring HT, but an alternative system, which can detect HT, is shown in Figure 34. In the alternative system HTO is directly condensed using a cold plate, and the condensate is mixed with the liquid scintillator. The dried air sample is then passed through a hot palladium catalyst cell where HT is converted to HTO. The cell requires a tube furnace because the palladium catalyst must be kept at 400°C . Another cold plate is used to condense the HTO vapor present at the output of the hot palladium cell.

C. Cost Considerations

The approximate cost of the first system would be: two PMTs, \$1,200; electronics, \$2,000; circulating air pumps (which can be purchased from most laboratory supply houses), \$400; and all mechanical parts (including the filters), \$5,000. Hence, the total cost of the HTO system would be about \$8,600. The alternative system, which can detect HT and HTO, would cost about \$11,000 since the additional cost of the cold plates and hot palladium catalyst cell would add an additional \$2,400 (less the insignificant cost of the bubbling cell).

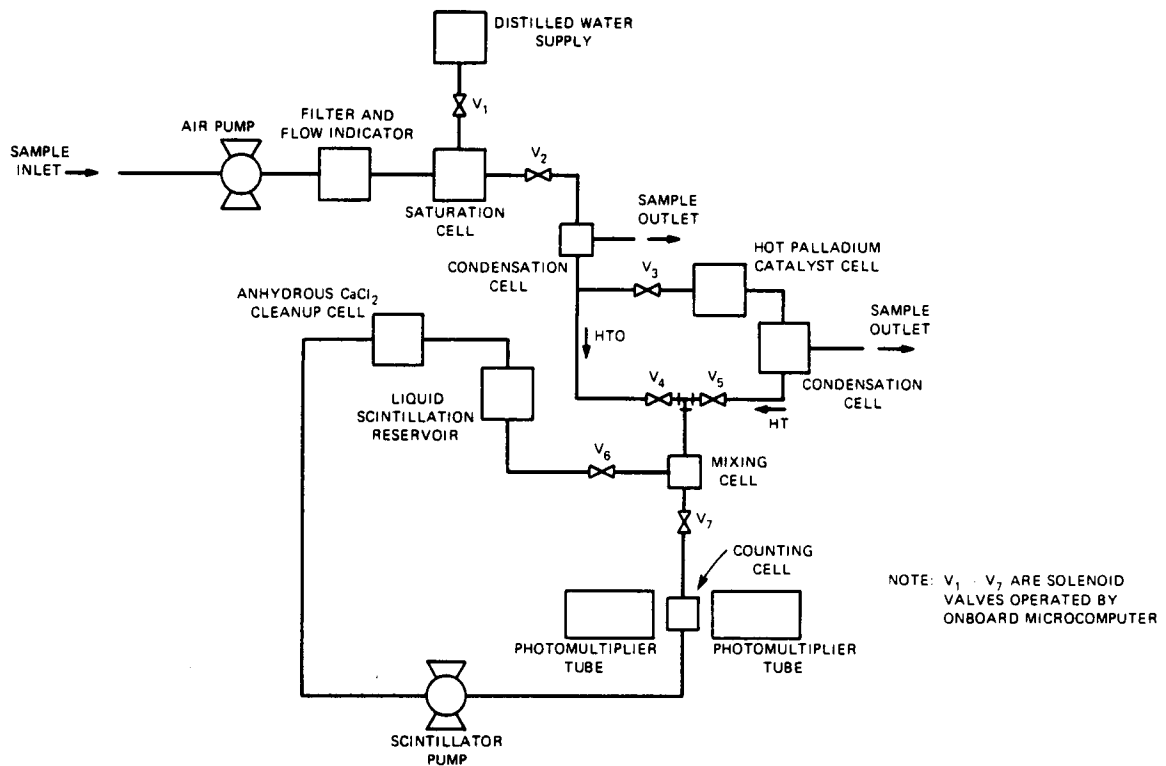


Figure 34. Conceptual liquid scintillation HT/HTO detector.

VII. CONCLUSIONS AND RECOMMENDATIONS

A. Comparison of Proposed Detector Systems

Three advanced tritium detector concepts (laser-induced fluorescence, solid scintillator, and closed-loop liquid scintillator) were analyzed. Based on a study of each of these, further evaluation of various detection systems is proposed. A comparison of the detector systems proposed for evaluation is given in Table 17. Two of the proposed systems use the LIF concept, three use the solid scintillator concept, and two use the closed-loop liquid scintillator concept.

One LIF system proposed for further evaluation employs a double-resonance scheme to detect and measure HT directly. HTO is converted to HT using a condensation and electrolysis scheme. It is estimated that this detector can reliably measure a minimum detectable concentration of $10^{-3} \mu\text{Ci}/\text{m}^3$. The main disadvantage of this system is that it is not portable; the condensation and electrolysis system make the detector bulky and heavy. The second LIF system would eliminate the condensation and electrolysis system by directly exciting and measuring both HT and HTO. Automatically tuning the laser source would make possible independent measurements of both molecules, and it is estimated that the minimum detectable concentration for this system would also be $10^{-3} \mu\text{Ci}/\text{m}^3$. However, the probability of implementing this system, as opposed to the other LIF system, is small because there are no available data on the molecular levels that would need to be excited in the HTO molecule. This

Table 17. Comparison of proposed advanced real-time tritium detectors.

	LIF system for HT, / HTO decomposed to HT and counted	LIF system for direct measurement of HT and HTO	CaF ₂ /MCO phoswich, no lead shielding	CaF ₂ /MCO phoswich, with lead shielding	CaF ₂ with lead shielding	Closed-loop liquid scintillation counter for HTO	Closed-loop liquid scintillation counter for HT and HTO
Sensitivity	$10^{-3} \mu\text{Ci}/\text{m}^3$ at $N = 1$	$10^{-3} \mu\text{Ci}/\text{m}^3$ at $N = 1$	12 cps per $\mu\text{Ci}/\text{m}^3$	12 cps per $\mu\text{Ci}/\text{m}^3$	12 cps per $\mu\text{Ci}/\text{m}^3$	560 cps per $\mu\text{Ci}/\text{m}^3$	560 cps per $\mu\text{Ci}/\text{m}^3$
Cost	\$10,000	\$8,000	\$9,000	\$10,000	\$8,000	\$8,600	\$11,000
Gamma response	None	None	2 cps per mR/h	0.38 cps per mR/h	2.2 cps per mR/h	188 cps per mR/h	188 cps per mR/h
Response to alpha and other beta	None	None	$\frac{C_{\beta}}{C_{\alpha, \beta}} = 3000$	$\frac{C_{\beta}}{C_{\alpha}} = 3000$	$\frac{C_{\beta}}{C_{\alpha}} = 1$	Good rejection of α and other beta	Good rejection of α and other beta
Time constant	~10 min	~1 min	~10 min	~10 min	~10 min	~5 min	~15 min
Portable	No	Yes	Yes	No	No	No	No
Movable	Yes	Yes	Yes	Yes	Yes	Yes	Yes
HTO and HT	Direct measurement of HT, HTO converted to HT	Direct measurement of HT and HTO	HT and HTO separated by membranes	HT and HTO separated by membranes	HT and HTO separated by membranes	HTO	HT and HTO
Minimum detectable activity	$10^{-3} \mu\text{Ci}/\text{m}^3$	$10^{-3} \mu\text{Ci}/\text{m}^3$	$3 \times 10^{-3} \mu\text{Ci}/\text{m}^3$	$5 \times 10^{-4} \mu\text{Ci}/\text{m}^3$	$0.1 \mu\text{Ci}/\text{m}^3$	$5 \times 10^{-3} \mu\text{Ci}/\text{m}^3$	$5 \times 10^{-3} \mu\text{Ci}/\text{m}^3$

system appears, though, to be the best possible candidate for further development since it meets or exceeds all U.S. Navy requirements. The particularly attractive feature of both LIF detectors is that neither of them is sensitive to other forms of radiation, and therefore no counts would be measured from gamma, alpha, or other beta sources.

Three systems using the $\text{CaF}_2(\text{Eu})$ solid scintillator technology, two phoswich detectors and one nonphoswich detector, are proposed for further study. The first phoswich detector system uses one inch of lead shielding, as does the nonphoswich detector. The shielded detectors are not portable, because the lead shielding probably would weigh about 38 lbs. The phoswich detector with no shielding appears to meet or exceed most of the required specifications except the time constant, which is equal to approximately 10 min. Although this could be reduced to about 3 min if the semipermeable membranes were not used, that change would render the detector incapable of separately measuring HT and HTO.

Two systems using a closed-loop liquid scintillation counter are recommended for further study. One system is capable of detecting only HTO by bubbling an air sample through distilled water, while the other system is capable of independently measuring HT and HTO by using a condensation and catalyst system. Neither system is portable due to the liquid scintillation cleanup system and the sample preparation system, which make the detectors bulky and heavy. The main disadvantage of closed-loop liquid scintillation systems is

that the liquid scintillator may be exposed to the environment in the event of an accident. Also, no supportive data are available in the literature on using anhydrous calcium chloride to remove water samples from liquid scintillators.

B. Cost/Benefit Analysis

Each of the three proposed technologies was analyzed in terms of development costs and time. The cost of development is given in terms of work-years of funding. Currently at ORNL, one work-year is equal to about \$95,000. The results of this analysis are summarized in Table 18. Also, a qualitative analysis was made for each proposed system with regard to the probability of its successful implementation. The element of risk involved in the development of a proposed system is also discussed.

It is estimated that approximately two work-years of funding would be needed for the proof-of-principle portion of LIF concept development. Because this technology is entirely new, basic measurements would be needed to identify the possible excitation levels of HT and HTO. Further theoretical analysis would be needed which would take into account all possible interactions between the molecules and the stimulating photons. If the proof-of-principle portion proves to be successful, it is estimated that one-half work-year of funding would be needed for a bench-scale demonstration of the device. Finally, it is estimated that one work-year of funding would be needed for breadboarding a portable instrument and one work-year for transferring the technology to a private manufacturing

Table 18. Costs and probabilities of success for the development of proposed advanced real-time tritium detectors.

	LIV system for HT, HTO decomposed to HT and counted	LIV system for direct measurement of HT and HTO	CaF ₂ /BCO phosphor, no lead shielding	CaF ₂ /BCO with phosphor, with lead shielding	CaF ₂ with lead shielding	Closed loop liquid scintillation counter for HT and HTO	Closed loop liquid scintillation counter for HT and HTO
Per unit purchase price	\$10,000	\$8,000	\$9,000	\$10,000	\$8,000	\$8,600	\$11,000
Development costs:							
Proof-of-principle	2 work-years	2 work-years	1 work-year	1 work-year	1 work-year	1½ work-year	1½ work-year
Bench scale demonstration	½ work-year	½ work-year	½ work-year	½ work-year	½ work-year	1 work year	1 work-year
Breadboarding portable instrument	1 work-year	1 work-year	1 work-year	1 work-year	1 work-year	1 work-year	1 work-year
Technology transfer	1 work-year	1 work-year	1 work-year	1 work-year	1 work-year	1 work-year	1 work-year
Probability of successful development	Low	Low	High	High	High	Low	Low

firm. Therefore, it is estimated that about 4 1/2 work-years of funding would be needed in order to develop the LIF concept to a point where a portable working instrument could be produced. Both proposed LIF systems have the highest element of risk for successful development as compared to the other proposed systems.

It is estimated that the development of the solid scintillation concept would require a total of 3 1/2 work-years of funding: One work-year would be needed for proof-of-principle, one-half work-year for bench-scale demonstration, one work-year for breadboarding a portable instrument, and one work-year for technology transfer. The best of the solid scintillation instruments appears to be the phosphor detector with no lead shielding. The technology of the components of the instrument, including electronics and detector, are well established. It appears that this proposed system has the greatest probability of successful implementation compared to all other proposed systems.

It is estimated that 4 1/2 work-years of funding would be required to develop the closed-loop liquid scintillation concept. A funding level of 1 1/2 work-years would be needed for proof-of-principle of this system, primarily because of the time needed to investigate the feasibility of the new concept of cleaning an organic liquid scintillator of its water sample using anhydrous calcium chloride. The technology of the other components used in both proposed liquid scintillation systems is well known because it has been developed by the author. It is estimated that it would

require one work-year each of funding for a bench-scale demonstration, for breadboarding a portable instrument, and for technology transfer. It is estimated that the probability of successful implementation for both proposed systems is less than for the phoswich detector with no lead shielding, but greater than for the two proposed LIF systems.

C. Recommendations

The proposed LIF system that directly measures HT and HTO meets all requirements, has the lowest estimated cost, and is the most selective of the proposed systems. Its sensitivity is the highest of all proposed systems and, based on information gathered from the literature search, it would achieve the state-of-the-art in tritium detection. Although it has the highest risk of development among the proposed systems, it is recommended that ORNL pursue its development. The fact that ORNL has direct access to suitable laboratory facilities and to personnel familiar with this technology would make it cost effective to design and develop this proposed system at ORNL. The other portable instrument concept recommended for further development is the $\text{CaF}_2(\text{Eu})/\text{BGO}$ phoswich detector with no lead shielding. This system meets many of the criteria established for it, and the probability of its successful implementation is very high because the technology for all of its components is already established. Much of the electronic technology has been developed for the proposed detector at ORNL by the author, and it is therefore recommended that ORNL design the system. The proof-of-principle

phase of development could be contracted to an outside firm under the supervision of ORNL, which would allow a parallel development effort to be undertaken in conjunction with the LIF system. Based on the results of the proof-of-principle phase for both systems, one system can be selected for final bench-scale demonstration and breadboarding.

Neither of the proposed closed-loop liquid scintillation systems is portable, and the estimated purchase price of the system that could simultaneously detect HT and HTO is the highest of all proposed systems. Furthermore, the estimated development cost of both systems is estimated to equal that of the phoswich system. Also, the risk of successful implementation of this concept is greater than for the solid scintillation concept. Therefore, it is recommended that concept not be carried into the development phase. However, it could be used as a backup if the other two proposed systems were to fail.

REFERENCES

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1. G. S. Hurst, M. G. Payne, S. D. Kramer, and C. H. Chen, "Counting the Atoms," Phys. Today 33, 24 (1980).
2. L. J. Radziemski, Applications of Lasers and Spectroscopy, Second Edition (Toledo, Ohio: Laser Institute of America, Professional Advancement Series, May 1983).
3. J. I. Steinfeld, Molecules and Radiation, An Introduction to Modern Molecular Spectroscopy (New York: Harper and Row, 1974).
4. W. M. Fairbank, Jr., T. W. Hansch, and A. L. Schawlow, J. Opt. Soc. Am. 65, 199 (1975).
5. C. T. Prevo and V. C. Santomassimo, "Introduction for Monitoring of ^{85}Kr and ^3H in Natural Gas," Report UCRL-50882 (May 26, 1970).
6. G. A. Colman, G. W. Allin, J. T. De Lorenzo, and J. E. Phelps, "Development Report: A RADIAC System for Measuring Aqueous Tritium Concentration by the Liquid Scintillation Method," Draft Report, November 1982.
7. J. A. Mangravite, D. Gallis, and R. Foery, Am. Lab. 27, 24-34 (July 1983).
8. P. A. Tipler, Foundations of Modern Physics, (New York: Worth Publ. Inc., 1969).
9. G. Herzberg, Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules, Second Edition (Princeton, New Jersey: D. Van Nostrand Co., Inc., 1957).
10. S. N. Suchard and J. E. Melzer, Eds., Spectroscopic Data, Volume 2 (New York: Plenum, 1976).
11. G. Herzberg, Molecular Spectra and Molecular Structure, III. Electronic Spectra and Electronic Structure of Polyatomic Molecules (New York: D. Van Nostrand Reinhold Co., 1966).
12. W. C. Price, "Spectroscopy in the Vacuum Ultra-Violet," in Advances in Spectroscopy, Volume 1, H. W. Thompson, Editor (New York: Interscience Publ. Inc., 1959).
13. J. R. McNeeby and H. Okabe, "Vacuum Ultraviolet Photochemistry," in Advances in Photochemistry, Volume 3, W. Noyes et al., Editors (New York: John Wiley and Sons, 1964).

14. W. Demtroder, Laser Spectroscopy, Basic Concepts and Instrumentation (New York: Springer Verlag, 1981).
15. Opto-Electronics, Inc. Unit 9, 2538 Speers Road, Oakville, Ontario, Canada L6L 5K9.
16. Texas Instruments, Inc., P.O. Box 225012, Dallas, TX 75265.
17. Laser Science, Inc., 80 Prospect Street, Cambridge, MA 02139.
18. M. McCormick, "Infrared Detector Update," Electro-Op., 62-69 (June 1983).
19. A. Yariv, Introduction to Optical Electronics, Second Edition (New York: Holt, Rinehart and Winston, 1976).
20. A. Dalgarno and T. L. Stephens, Astrophys. J., 160, L107-L109 (May 1970).
21. W. J. Price, Nuclear Radiation Detection (New York: McGraw-Hill, 1958).

APPENDIX

APPENDIX

MATHEMATICAL ANALYSIS OF A HARMONIC OSCILLATOR

Lagrange equation of motion for the molecule:

$$\frac{d}{dt} \frac{dT}{dx} + \frac{dv}{dx} = 0 \quad (\text{A-1})$$

where

$T \equiv$ Kinetic energy of the molecule

$v \equiv$ Potential energy of the molecule

$$\dot{x} \equiv \frac{dx}{dt} .$$

$$T = \frac{1}{2} M_A \dot{x}_A^2 + \frac{1}{2} M_B \dot{x}_B^2 . \quad (\text{A-2})$$

The molecule is assumed to have no translational momentum:

$$\overline{P} = M_A \dot{x}_A + M_B \dot{x}_B = 0 \quad (\text{A-3})$$

Therefore,

$$\dot{x}_A = \frac{M_B}{M_A + M_B} \dot{x}$$

$$\dot{x}_B = - \frac{M_A}{M_A + M_B} \dot{x} . \quad (\text{A-5})$$

Kinetic energy becomes:

$$T = \frac{1}{2} \frac{M_A M_B}{M_A + M_B} \dot{x}^2 \quad (\text{A-6})$$

$$\frac{dT}{dx} = \frac{M_A M_B}{M_A + M_B} \dot{x} \quad (A-7)$$

$$\frac{d}{dt} \frac{dT}{dx} = \frac{M_A M_B}{M_A + M_B} \ddot{x} \quad (A-8)$$

Minimum of potential curve approximated by Hooke's Law

$$F \equiv - \frac{dv}{dx} = -Kx \quad (A-9)$$

Therefore,

$$\frac{dv}{dx} = Kx \quad (A-10)$$

where $K \equiv$ spring constant.

Substitution into the Lagrange equation of motion:

$$\frac{M_A M_B}{M_A + M_B} \ddot{x} + Kx = 0 \quad (A-11)$$

$$\text{Let } M = \text{reduced mass} = \frac{M_A M_B}{M_A + M_B}$$

The equation of motion becomes

$$\frac{d^2x}{dt^2} + \frac{K}{M} x = 0 \quad (A-12)$$

Solution of the form,

$$x = C_1 \cos (2\pi vt) + C_2 \sin (2\pi vt) \quad (A-13)$$

where $v \equiv$ frequency

$$v = \frac{1}{2\pi} \sqrt{\frac{K}{M}} \quad (A-14)$$

where C_1 and C_2 are arbitrary constants.

VITA

Gerald A. Colman was born in Toledo, Ohio, on March 17, 1956. He attended elementary and high schools in Temperance, Michigan, where he graduated from Bedford Senior High School in June 1974. The following fall he entered the University of Toledo. He was named outstanding engineering student by the Technical Society of Toledo in May 1979. After graduating cum laude with a Bachelor of Science degree in Engineering Physics, he accepted a staff position at Oak Ridge National Laboratory, where he is presently employed.

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