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Determination of the Chemical Form of Tritium in Self-Luminous Signs

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EXECUTIVE SUMMARY

Building exit signs containing tritium self-luminous light sources were dismantled, and the light sources were tested to determine the chemical form of tritium in this study. The objective was to quantify the amounts of tritiated water (T_2O or TOH) present in the light sources. The light sources consist of sealed glass tubes coated internally with a phosphor (zinc sulfide) and filled with tritium gas (T_2).

The chemical form of tritium is an important consideration for assessing radiological health impacts. The radiotoxicity of tritium gas (T_2 or TH) is much lower than that of tritiated water (T_2O or TOH). The amount of tritiated water in self-luminous devices is limited to two percent of the total tritium inventory.

When the signs were dismantled, exterior and interior surfaces were wiped and the 'swipes' were tested for removable contamination. Four of the six signs examined had removable contamination on interior surfaces, ranging from less than 100 to more than 2,000 disintegrations per minute.

Quantitative measurements of total tritium and tritiated water were made by scintillation counting. Samples for counting were obtained by breaking the light source tubes in a gas flow system equipped with cold traps and a catalytic reactor. The system separated tritiated water from T_2 and converted T_2 to T_2O for subsequent trapping and counting. Qualitative tests conducted with a residual gas analyser verified the presence of tritiated water in one light source tube. More tubes could not be tested with this method because of equipment problems.

Light source tubes from four exit signs were tested. Two were new signs, one was six years old, and one was thirteen years old. In one of the new signs, the total tritium inventory included two percent tritiated water. Two of the other signs had higher amounts of tritiated water: 4.5% for the other new sign, and 14.5% for the six-year-old sign. In the oldest sign, an accurate inventory of the tritium content was not available, but tritiated water accounted for 12.2 percent of the total tritium collected for counting.

After individual experiments with the light source tubes, pieces of glass and phosphor powder remained. These residues were immersed in water, and the water was tested for tritium by scintillation counting. The residues all contained variable amounts of tritium which was released to the water. Tritium release was slow, and its concentration in the water increased with time for each sample, up to 78 days.

This scoping study has shown that tritiated water is present in all signs tested. Older signs appear to have higher percentages of tritiated water than new signs.

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1. INTRODUCTION

Tritium gas sealed in phosphor-coated glass tubes is one of the more common applications of radioactive materials in commercial and consumer goods. Beta radiation from the tritium excites the phosphor to produce visible light. Tritium light sources have been used in aircraft exit signs, airport landing lights, electronic devices, building exit signs, and watches.

Several incidents involving damage to building exit signs and breakage of individual light sources have occurred recently. The contamination resulting from these incidents was more extensive than had been expected by both the sign vendors and the Nuclear Regulatory Commission (NRC). The extensive contamination raised questions about the chemical form of the tritium, since the radiotoxicity of tritium is more than 10,000 times lower for tritium gas (T_2 or HT) than it is for tritiated water (T_2O or TOH).[a] The different radiotoxicities are reflected in the derived air concentration (DAC) limits for radiation workers calculated by the International Commission on Radiological Protection.(1) Workers exposed to tritium gas <u>or</u> tritiated water vapor for 2,000 hours per year will receive a 5 rem dose when the air concentrations are:

HT	$21.6\ \mu Ci/m^3$
HTO	$5.4 \times 10^4\ \mu Ci/m^3$.

The chemical form of tritium in the light sources is thus an important consideration for assessing their radiological health impacts. A study, conducted some years ago,(2) reported that five light sources, about 2.5 years old, had tritiated water contents ranging from 0.6% to 6.8% of the total tritium content.

In view of the recent contamination incidents and because of uncertainties about tritiated water contents in the light sources, the NRC contracted with Brookhaven National Laboratory (BNL) to determine the chemical forms of tritium and amounts of each in selected building exit signs. In addition to chemical analyses, the project also called for dismantling the exit signs and testing interior and exterior components and glass tube (light source) surfaces for tritium contamination.

The results of this scoping study are presented in the balance of this report. Section 2 describes the signs received and tested and additionally lists those signs with surface contamination. Section 3 describes the experiments conducted to identify the chemical species quantitatively. Two methods were used: quadrupole mass spectrometry and a "wet chemical" method involving separation of the different chemical species followed by scintillation counting. The latter method is a modification of the procedure used in the earlier study by Niemeyer.(2) Finally, the conclusions of this study are presented in Section 4, which also suggests topics for further investigation to determine more accurately the radiological health effects resulting from use of tritium light sources in commercial and consumer goods.

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[a] In this report, T is the chemical symbol for tritium. The two possible forms of tritiated water are sometimes referred to as tritium oxide (T_2O) and tritium hydroxide (TOH). Here the term tritiated water refers to both. The term tritium gas refers to T_2 and HT.

2. DESCRIPTION OF SIGNS AND SURFACE CONTAMINATION

BNL received six building exit signs made by the first four manufacturers listed in Table 1. The fifth, Safety Light Corporation, sent aircraft exit signs made in the 1960's, which were not examined for this study. The fourth manufacturer listed, American Atomics Corporation of Tucson, has apparently gone out of business. The sign made by that company was sent by the Atomic Energy Control Board (AECB) of Canada. Because of the sensitive issues raised and due to the fact that this work is scoping in nature, the identification of which test results correspond to which manufacturer's signs has been maintained as proprietary, except for the sign obtained from the AECB.

Table 2 provides information on the signs. Tubes from four of the signs, A, B, D and F, were tested in this study. The signs themselves had labels on them listing the manufacturer, model and serial number, date of manufacture, and nominal tritium content in curies. From telephone contacts with the manufacturers, it was learned that the signs usually contained significantly less than the quantity listed on the label. An exact figure for the tritium content of sign F could not be obtained because American Atomics Corporation, the company that made that sign, could not be reached. Of the four signs tested, two were brand new (A and D), and two were of older vintage (B and F).

All the signs were similar in design, with external dimensions of approximately 20 cm high by 33 cm wide by 2.5 cm deep (8 x 13 x 1 inch). Figure 1 shows one of the signs after being dismantled. The tritium light sources were contained inside a hard plastic outer shell. Behind the tritium-containing tubes was a reflector, and in front of the tubes a transparent plastic plate or a translucent diffuser. The glass tubes were fixed in place with an epoxy-type glue or potting material. Older signs had 7 mm outer diameter glass tubes: newer signs were equipped with 5 mm OD tubes.

It is worth noting that the signs were not easily disassembled; a hammer and wedge were necessary to break glued joints. None of the glass tubes inside the signs were broken when the signs were disassembled.

Table 3 lists dry smear test results. Four of the six signs had removable contamination from internal surfaces. Staff from the Health Physics Group (Safety & Environmental Protection Division, BNL) conducted the smear tests. Counts were obtained on a gas flow counter. The contamination levels (disintegrations per minute or dpm) shown in Table 3 were calculated from counts per minute after accounting for the detector's efficiency (20%) and a background of 30±6 counts per minute. Smears were taken of the exterior and interior surfaces of the signs, and of each letter individually.

None of the signs had tritium contamination on external surfaces. Four of the signs had some contamination on the glass tubes (inside the signs), the worst being sign A, which had more than 2,000 disintegrations per minute (dpm) on the letters 'E' and 'IT.' The latter were on a new sign, made in August, 1989.

Table 1

Manufacturers Providing Self-Luminous Building Exit Signs

1. SRB Technologies, Inc.
   P. O. Box 25267
   Winston-Salem, NC 27114

2. NRD
   2937 Alt Blvd. North
   Grand Island, NY 14072

3. Self-Powered Lighting, Inc.
   8 Westchester Plaza
   Elmsford, NY 10523

4. American Atomics Corp.
   Tucson, AZ
   (Sign supplied by Atomic Energy Control
   Board of Canada)

5. Safety Light Corporation
   4150-A Old Berwick Road
   Bloomsburg, PA 17815
   (Aircraft exit signs provided)

Table 2

Description of Exit Signs

BNL Designation	Date of Manufacture	Tritium Content (Curies)(1)		Total Length of Glass Tubes in Sign (cm)
		Nominal	Actual	
A	8/89	20	4.7	105.6
B	12/83	25	14.9	102.0
C	4/85	25	19.8	105.7
D	8/89	25	10.5	106.7
E	8/89	20	--	110.4
F	10/76	21	--	109.4

(1) Values shown are for the date of manufacture. Nominal amounts were listed on sign labels as the maximum content. Actual amounts were obtained by telephone contacts with the manufacturer.

Table 3

Smearable Contamination Detected (disintegrations/minute above background)

Sign No.	Exterior	Interior	E	X	I	T
A	-	-	2,300	-	2,800[1]	
B	-	-	160	-	-	-
D	-	-	-	-	10	-
E	-	-	-	90	-	-

[1] Letters I and T were tested using one wiper.

Figure 1. Picture of Disassembled Building Exit Sign Containing Tritium Self-Luminous Light Source.

3. DETERMINATION OF THE CHEMICAL FORM OF TRITIUM

3.1 Analytical Methods

Two methods were used to determine the chemical form of tritium in self-luminous signs: mass spectrometry and chemical separation followed by scintillation counting. Mass spectrometry was preferred because it was considered a rapid and reliable method for distinguishing tritium gas from tritiated water. An additional advantage was generation of less tritium-contaminated waste, since the gas was vented to the exhaust stack used by the High Flux Beam Reactor (HFBR). However, because of equipment problems with the Residual Gas Analyzer (RGA) and its high-vacuum system, the chemical separation method was used to obtain quantitative measurements of the chemical form of tritium.

3.1.1 Chemical Separation and Trapping Experiments

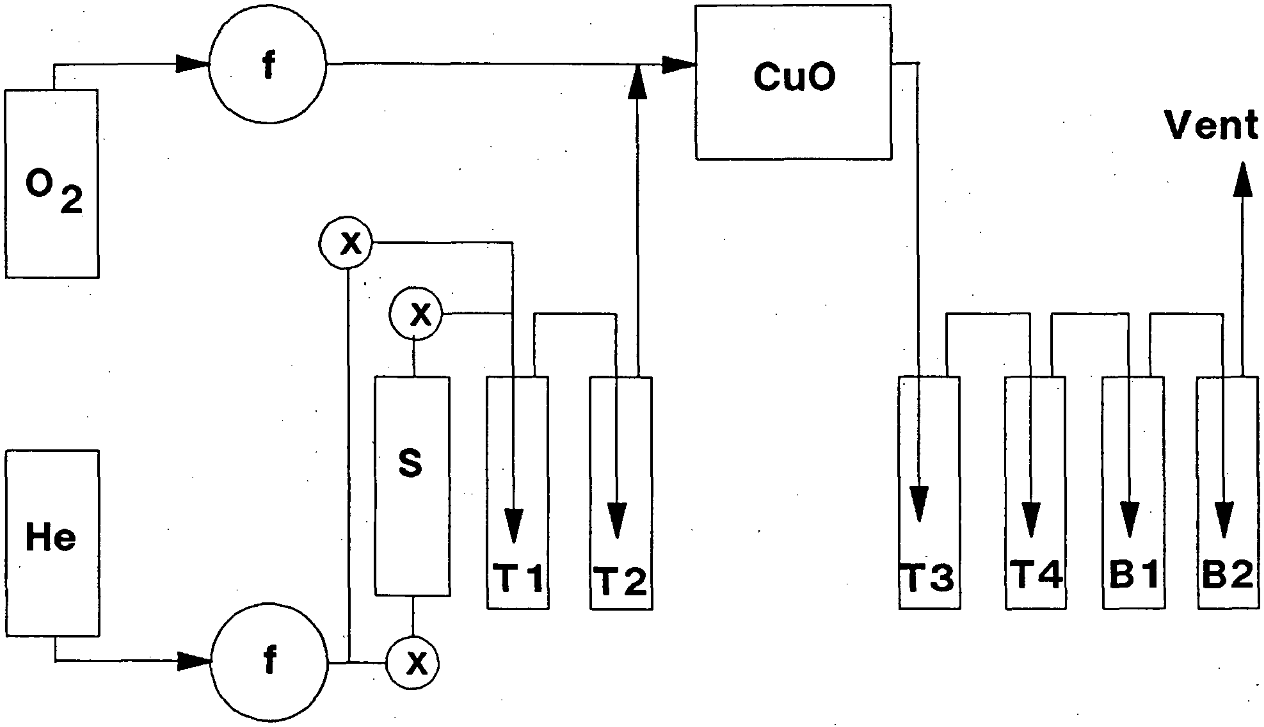
The chemical separation and trapping experiments were adapted from procedures described by Niemeyer.(2) The general principal involves breaking a glass tube containing phosphor and tritium in a metal container, and flushing the container with helium gas through a series of traps and a catalytic reactor. Figure 2 shows a schematic diagram of the system; a picture of the system, except for the gas supply cylinders, is shown in Figure 3.

The glass tubes were removed from several building exit signs. These are placed one at a time in a stainless steel tube (3/4" OD) with two ball bearings (3/8" dia.) on each end. Before valves were assembled on the ends of the metal tube, a porous filter material was packed in the tube ends to prevent glass pieces and phosphor from being carried by the gas flow into the rest of the apparatus. The metal "break tube" was evacuated for the first several runs to minimize reactions with air to form tritiated water. In the last three trapping experiments, the metal tube was flushed with helium to remove oxygen before breaking the glass tube.

After oxygen was removed from the metal break tube, the valves were closed off and the unit removed from the apparatus and shaken to break the glass tube with the ball bearings. The metal break tube was then reattached to the trapping apparatus, and the gas flow started. In the first three tests, the metal container was heated with a hot air gun to ensure that all tritiated water was driven into the trap apparatus. Heat was not applied in later tests to simulate accidental exit sign breakage.

While the break tube assembly was being prepared, the furnace for the catalytic reactor was turned on and warmed up. The reactor, consisting of a quartz tube packed with cupric oxide (CuO), was kept at 600° C to oxidize T_2 to T_2O.

The liquid nitrogen cooled traps (T1 to T4 in Figure 2) removed water and tritiated water (HOH, TOH, and TOT) from the gas phase. After the second trap, oxygen was added to the gas stream which then passed through the catalytic reactor. Tritium gas converted to tritiated water was collected in the third and fourth cold traps. Two gas bubblers containing deionized water were last in line to achieve more complete tritium removal before venting the gas to a fume hood connected to the HFBR exhaust stack.



KEY:

He	helium gas supply
O_2	oxygen gas supply
f	flowmeter
x	valve
CuO	copper oxide/furnace
T1 - T4	liquid nitrogen traps
B1, B2	gas bubblers

Figure 2. Schematic Diagram of Separation and Trapping Apparatus.

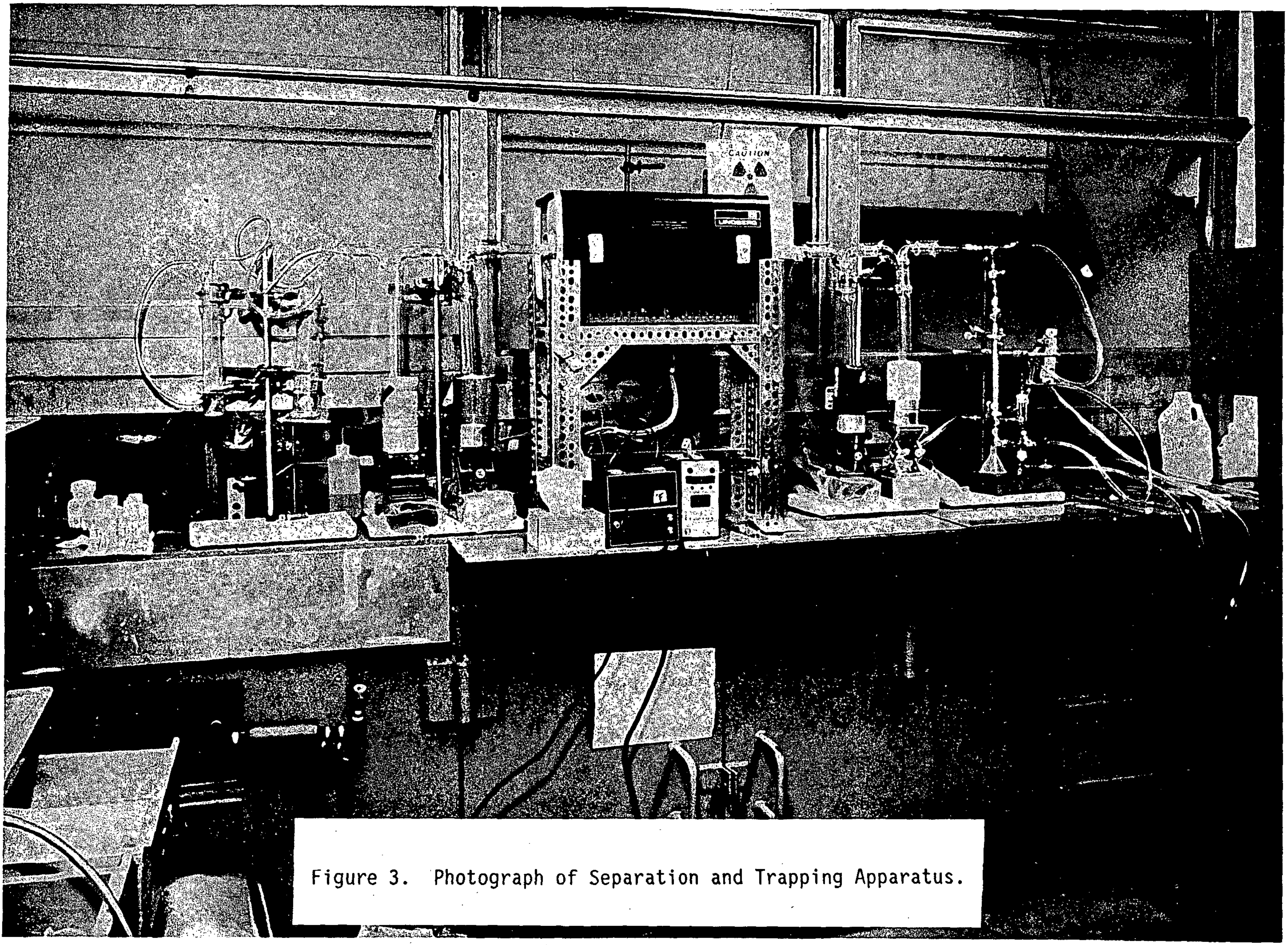


Figure 3. Photograph of Separation and Trapping Apparatus.

Gas flow rates were as follows:

Helium flow:	0.1 to 0.2 L/min
Oxygen flow:	0.1 L/min

For each tube broken (except the first), 18 samples were collected: one from each trap and bubbler collected after three trapping runs conducted over three days. The traps were rinsed with deionized water into 150 mL plastic bottles. The bottles were then analysed by liquid scintillation counting as described below. After rinsing, the traps were connected to the apparatus for subsequent experiments.

Experimental runs to generate a set of six samples lasted four to five hours. After three runs, the glass fragments and phosphor were collected and immersed in deionized water with the filter packing and assorted Kimwipes used to clean out the metal break tube. (The ball bearings were wiped and removed from this sample after the first test, because the water began to turn brown from the bearings rusting.) This nineteenth sample was also tested for residual tritium using liquid scintillation counting. Because not all of the tritium theoretically present in the tubes could be accounted for (see results, Section 3.3) additional scintillation counting measurements of the glass/ phosphor residues were made at later times to see if tritium bound to the phosphor or glass could be released into the water as time passed.

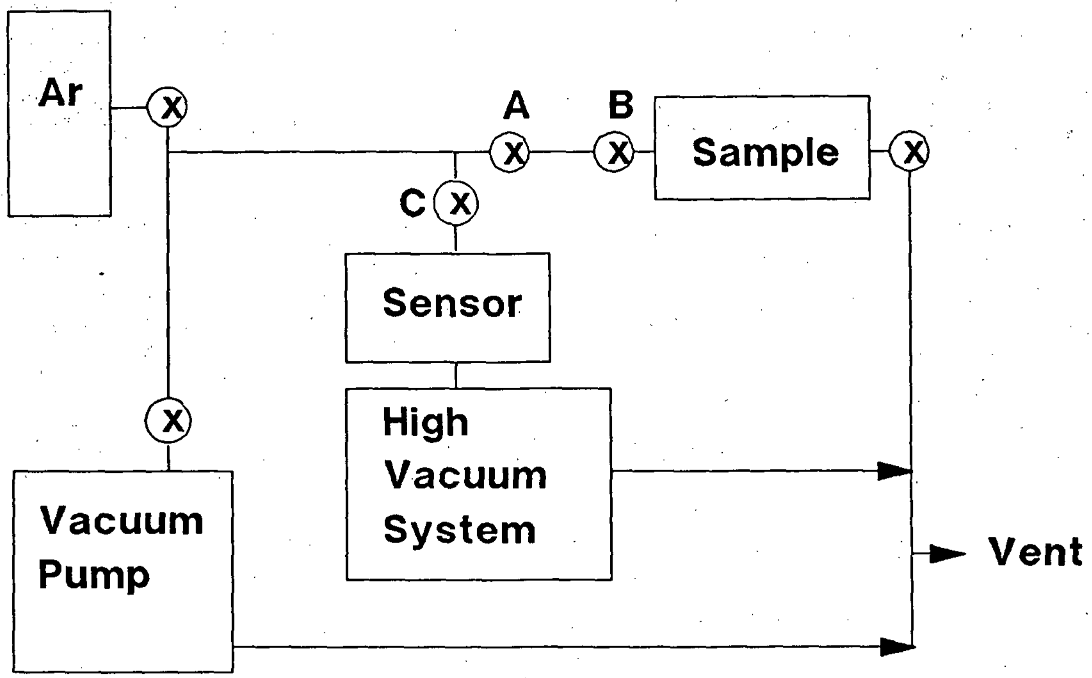
3.1.2 Procedures for Mass Spectrometer Experiments

The initial plan for this study was to analyse the chemical form of tritium using a residual gas analyser (RGA) containing a quadrupole mass spectrometer. An Inficon IQ 200 mass analyser system (Leybold-Heraeus) that was available was dedicated for use in this task. The handling procedure for glass tubes from the exit signs was similar to that described for the trapping apparatus in the previous section. In these experiments, the tritium was NOT completely converted to tritiated water, as was done earlier.

A schematic diagram of the apparatus is shown in Figure 4; Figure 5 is a picture of the system. The glass tubes containing tritium and phosphor were placed inside a stainless steel tube (3/4" OD) with two stainless steel ball bearings (3/8" diameter). The metal break tube was connected to the gas manifold, and evacuated. The evacuated tube was disconnected (between valves A and B) and shaken to break the glass tube, then reconnected to the manifold. After the system was evacuated again (with valve B closed), the analysis of the gas was accomplished by opening valve B and the variable leak valve (C) enough to let gas from the glass tube into the mass spectrometer's high vacuum system.

Two sets of mass spectrometer readings were taken, with the sample at room temperature and at 100°C. The higher temperature tests were conducted to ensure that all tritiated water in the system was in the gas phase.

After the measurements of gas composition, the variable leak valve was closed and the gas manifold system including the break tube was flushed with high-purity argon to a hood which vents to the HFBR and Hot Lab stack through a HEPA filter. The glass and phosphor residues were collected in a bottle and immersed in deionized water, together with Kimwipes that were used to clean out the metal break tube. The ball bearings were wiped clean and saved for later tests.



KEY:

Ar	Argon flush gas
x	valves

Figure 4. Schematic Diagram of Residual Gas Analyser System.

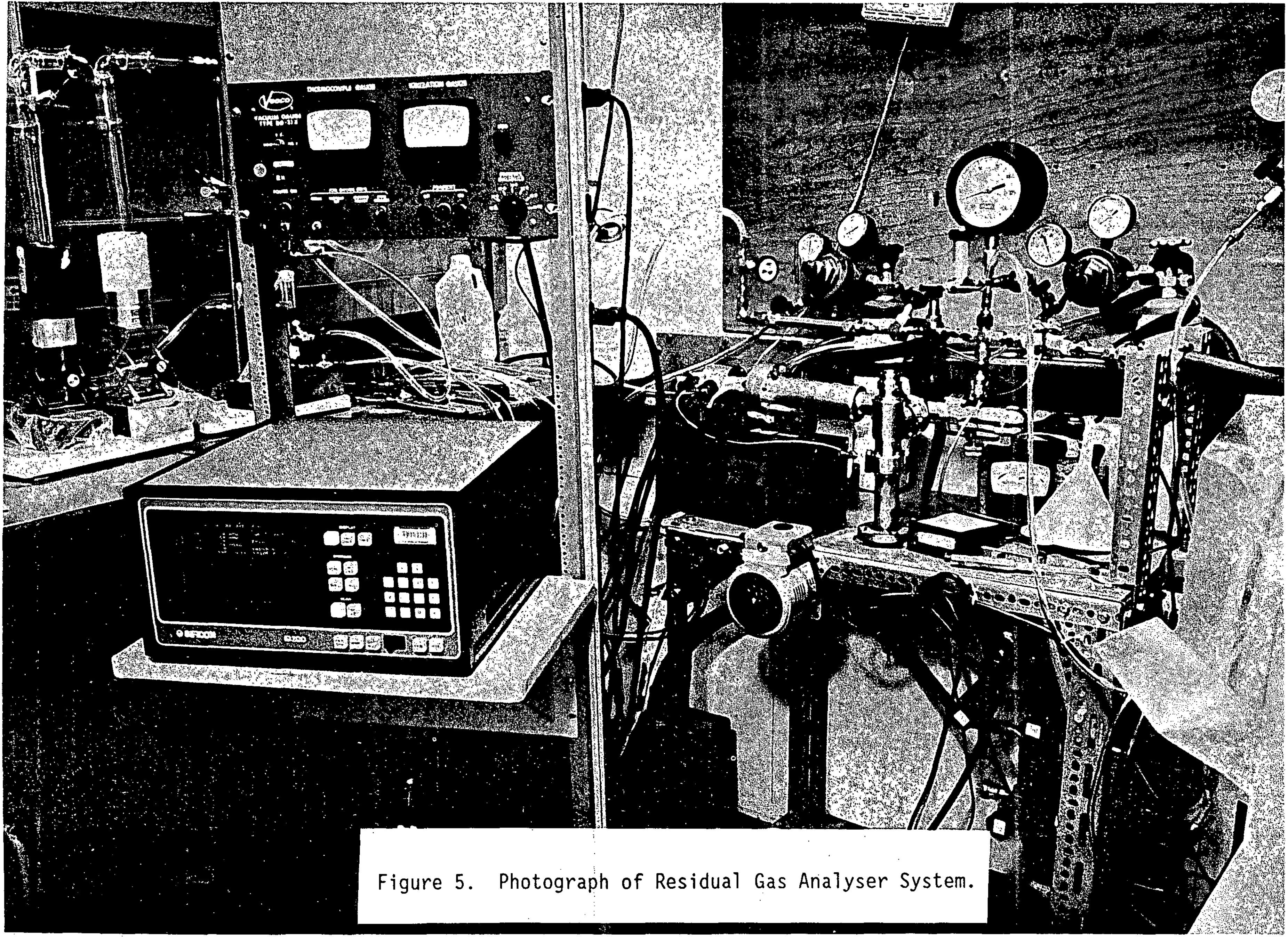


Figure 5. Photograph of Residual Gas Analyser System.

Samples of the water covering the residues were tested by scintillation counting for residual tritium after a few days immersion. The residues and associated water were tested at later times to see if the tritium bound to the phosphor or glass was released slowly after immersion in water.

As noted earlier (Section 3.1), equipment problems were encountered with the RGA and the high-vacuum system. As a result, reproducible quantitative data could not be obtained. Qualitative confirmation of the presence of tritiated water was achieved in one of the three tubes examined (see Section 3.2)

3.2 Scintillation Counting Procedures

Water samples from the tritium trapping apparatus and water samples containing glass tube and phosphor residues were analysed for tritium by scintillation counting. The Waste Management Research and Development Group (Radiological Sciences Division, BNL) performed the scintillation counting analysis. The procedure involved taking a 20 microliter (μL) aliquot from each bottle and mixing this with 10 mL of liquid scintillation cocktail. For those samples with too high a concentration of tritium, dilutions were necessary to obtain an accurate reading of counts per minute. Results for this study were reported as disintegrations per minute per milliliter (dpm/mL).

For each set of samples to be counted, blanks and standards were interspersed with the tritium samples. Blanks consisted of deionized water; calibration standards were prepared from a tritiated water standard purchased from Dupont NEN Research Products (Tritium Reference Source, NES-003, Lot No. NS 239-016, 1982). The scintillation counter system was a Searle Analytic 92 Liquid Scintillation System.

3.3 Results and Discussion

Table 4 lists the tubes which were tested for this study, as well as the sign from which they were obtained, the tritium content of each tube, and the method of testing. Six experiments were conducted using the trapping and scintillation counting method, and four tubes were examined with the RGA. Two of the tubes examined, one by each experimental method, contained tritium gas only (no phosphor) at the time of manufacture. These tubes are available commercially, and were tested because they contained a known quantity of tritium.

3.3.1 Calculation of Tritium Content of Tubes

For the older tubes tested, the amount of tritium originally present has decreased due to radioactive decay. A correction to the total tritium in the older samples was necessary for tubes taken from sign B (manufactured in December, 1983) and sign F (manufactured in October, 1976). Sign B contained 14.9 Curies of tritium when it was made, according to the manufacturer. Since the company that made sign F could not be reached, total original tritium content was assumed to be 21 Curies. This was the nominal amount listed on the sign's label, but this is believed to be higher than the amount actually in the sign.

Table 4

List of Tubes Tested

Sample No.	Sign	Length (cm)	Tritium Content in Tube[1] (mCi)	Experimental Method
a	B	15.7	1,650.963	Scintillation Counting
b	B	5.3	557.331	Scintillation Counting
c	A	4.2	186.932	Scintillation Counting
d	A	4.3	--[2]	Mass Spectrometer
e	[3]	--	--[2]	Mass Spectrometer
f	F	7.2	--[2]	Mass Spectrometer
g	F	7.2	655.042	Scintillation Counting
h	B	5.4	--[2]	Mass Spectrometer
i	D	4.7	462.380	Scintillation Counting
j	[4]	--	1,000.000	Scintillation Counting

[1] mCi amounts for signs B and F corrected to the month in which they were tested.

[2] Tritium content of tubes tested in RGA was not calculated because a quantitative mass balance of tritium was not attempted.

[3] Sample e was a glass tube of tritium gas obtained from Amersham in 1978 and kept in storage at BNL.

[4] Sample j was a glass tube containing nominal 1.0 Ci of tritium gas obtained from a commercial isotope supplier in 1990.

The current activity level (at the time of the experiment) is calculated using:(3)

$$A = A_0 \, e^{-(\ln 2)\Delta t/t1/2}$$

where

A = current Curie amount,

A_0 = original Curie amount,

Δt = time change, in years, and

$t_{1/2}$ = tritium's 12.3 year half-life.

Sign B was tested in October, 1989, and sign F in January, 1990. The current activity levels are 10.726 Ci and 9.953 Ci, respectively. Decay corrections for tubes from signs A and D were not made since these were both manufactured in August, 1989 and tested within six months of the date. Total tritium would thus have decreased at most by 3 %.

To calculate how much tritium was present in each tube, it was assumed that tritium was distributed uniformly among the pieces of glass tubing in each sign. Dividing tritium inventory by total length of tubing (both quantities are listed in Table 2) and then multiplying by the length of each tube (listed in Table 4) yields the number of millicuries for each tube listed in Table 4.

3.3.2 Summary of Trapping Experiment Data

The initial data obtained from the trapping experiments are listed in Tables 5 through 10, inclusive. To calculate the number of millicuries in each sample, the water volume was multiplied by the specific activity and then by the conversion factor 4.55×10^{-10} mCi/dpm.(3) For these experiments, tritiated water from the glass tubes was assumed to be trapped in the cold traps situated upstream of the catalytic reactor (T1 for tube a, T1 and T2 for the rest of the experiments). Tritiated water was also assumed to be present in samples containing the glass and phosphor residues (samples labeled BT_).

Table 10 shows the results of trapping experiments conducted using a nominal 1.0 Curie tritium gas source obtained from a commercial isotope supplier. The tritium was contained in a glass tube, but no phosphor was present. Surprisingly, more than four curies were collected in this experiment. Contacts with the supplier revealed that tritium packaged as gas in tubes is measured out using manometers. According to the supplier, 1.0 curie represents the lower limit for accurately metering tritium. Although the total tritium inventory was more than expected, the experiment demonstrated the method's validity in that even relatively small amounts of tritiated water were separated from the gas for subsequent analysis.

The important consideration for this study was to quantify how much tritium was present as T_2O or TOH. Table 11 lists the amounts of tritiated water for each tube as millicuries and as a percentage of the total tritium activity in the tubes. the percentages of tritiated water are calculated for the theoretical amount of tritium present in each tube and as a percentage of the amount trapped.

Table 5

Tritium Trapping Results, Sign B, Tube a (15.7 cm)

Sample No.*	Chemical Form of Tritium	Rinse Water Volume (mL)	Specific Activity (dpm/mL)	Total Activity (mCi)
BTa	T_2O	301.20	7.418×10^7	10.166
Tlao	T_2O	30.78	8.874×10^9	124.279
Tlal	T_2O	26.14	2.702×10^8	3.214
T2ao	T_2	60.93	1.255×10^{10}	347.926
T2al	T_2	42.87	1.898×10^7	0.370
T3ao	T_2	23.03	9.151×10^9	95.890
T3al	T_2	57.87	1.409×10^7	0.371
Blao	T_2	90.40	4.845×10^9	199.285
Blal	T_2	100.32	1.052×10^6	0.048
Bla2	T_2	100.22	1.012×10^6	0.046
			TOTAL	781.595

*T refers to traps, BTa is Break Tube residue, i.e., rinse water covering glass and phosphor residue from the metal break tube, and Bl is the gas bubbler.

Tritiated water was found to be present in each tube. The lowest percentages of tritiated water, i.e., 2 to about 5 %, were found in tubes removed from the two newest signs, A and D. From these limited data, it appears that older signs will have a higher percentage of tritium in the form of tritiated water. Although tube 'g' from sign F apparently had 1.2 % tritium of the theoretical amount, it is believed that this value is low, because the nominal total tritium was used for the calculation rather than an exact value from the manufacturer.

Table 6

Tritium Trapping Results, Sign B, Tube b (5.3 cm)

Sample No.*	Chemical Form of Tritium	Rinse Water Volume (mL)	Specific Activity (dpm/mL)	Total Activity (mCi)
BTb	T_2O	201.12	1.555×10^{8}	14.230
T1bo	T_2O	29.23	3.817×10^{9}	50.765
T1b1	T_2O	50.20	3.453×10^{8}	7.887
T1b2	T_2O	83.43	4.258×10^{7}	1.616
T2bo	T_2O	30.03	1.292×10^{8}	1.765
T2b1	T_2O	70.74	1.144×10^{8}	3.682
T2b2	T_2O	58.79	2.980×10^{7}	0.797
T3bo	T_2	41.93	9.871×10^{9}	188.320
T3b1	T_2	65.00	4.496×10^{8}	13.297
T3b2	T_2	58.06	1.039×10^{7}	0.274
T4bo	T_2	45.85	2.411×10^{9}	50.298
T4b1	T_2	66.45	1.442×10^{8}	4.360
T4b2	T_2	70.44	1.699×10^{6}	0.054
B1bo	T_2	130.06	3.229×10^{8}	19.108
B1bo-1	T_2	38.91	1.693×10^{6}	0.030
B1b1	T_2	131.24	1.446×10^{7}	0.863
B1b1-1	T_2	115.60	3.526×10^{7}	1.855
B1b2	T_2	113.32	5.265×10^{5}	0.027
B2b2	T_2	106.19	3.336×10^{3}	0.0002
			TOTAL	359.228

*T refers to traps, B to gas bubbler, BT to Break Tube residues.

Table 7

Tritium Trapping Results, Sign A, Tube c (4.2 cm)

Sample No.*	Chemical Form of Tritium	Rinse Water Volume (mL)	Specific Activity (dpm/mL)	Total Activity (mCi)
BTc	T_2O	163.53	1.755×10^7	1.306
T1co	T_2O	52.96	1.839×10^8	4.431
T1c1	T_2O	44.08	2.647×10^7	0.531
T1c2	T_2O	39.30	3.200×10^7	0.572
T2co	T_2O	74.19	9.530×10^6	0.322
T2c1	T_2O	49.20	4.079×10^7	0.913
T2c2	T_2O	41.15	1.500×10^7	0.281
T3co	T_2	56.37	4.137×10^9	106.107
T3c1	T_2	42.97	1.529×10^8	2.989
T3c2	T_2	42.12	9.361×10^6	0.179
T4co	T_2	49.41	1.111×10^8	2.498
T4c1	T_2	47.72	6.088×10^8	13.219
T4c2	T_2	73.85	3.712×10^6	0.125
B1co	T_2	127.39	1.016×10^8	5.889
B1c1	T_2	100.13	1.288×10^8	5.868
B1c2	T_2	94.93	7.973×10^5	0.034
B2co	T_2	87.45	1.972×10^7	0.785
B2c1	T_2	74.45	1.291×10^6	0.044
B2c2	T_2	69.71	8.905×10^4	0.003
Brc	T_2	149.91	9.681×10^4	0.007
			TOTAL	146.103

*T refers to traps, B to gas bubblers, BT to break tube residues.

Table 8

Tritium Trapping Results, Sign F, Tube g (7.2 cm)

Sample No.*	Chemical Form of Tritium	Rinse Water Volume (mL)	Specific Activity (dpm/mL)	Total Activity (mCi)
BTg	T_2O	128.72	9.845×10^7	5.766
T1go	T_2O	47.26	6.629×10^9	0.143
T1g1	T_2O	54.31	2.333×10^7	0.577
T1g2	T_2O	57.32	1.205×10^7	0.314
T2go	T_2O	42.24	2.084×10^5	0.004
T2g1	T_2O	54.69	3.366×10^7	0.838
T2g2	T_2O	50.00	1.626×10^6	0.037
T3go	T_2	51.27	1.054×10^9	24.588
T3g1	T_2	46.81	1.246×10^9	26.538
T3g2	T_2	59.52	3.692×10^6	0.100
T4go	T_2	56.14	5.718×10^6	0.146
T4g1	T_2	48.68	1.427×10^8	3.161
T4g2	T_2	49.22	6.835×10^6	0.153
B1go	T_2	98.22	1.086×10^6	0.049
B1g1	T_2	108.53	6.038×10^6	0.298
B1g2	T_2	105.07	2.792×10^5	0.013
B2go	T_2	77.35	8.971×10^2	0.00003
B2g1	T_2	91.59	9.868×10^3	0.0004
B2g2	T_2	75.15	2.587×10^4	0.0009
Brg	T_2	130.81	8.782×10^4	0.0052
			TOTAL	62.732

*T refers to traps, BTa is Break Tube residue, i.e., rinse water covering glass and phosphor residue from the metal break tube, and B1 is the gas bubbler.

Table 9

Tritium Trapping Results, Sign D, Tube i (4.7 cm)

Sample No.*	Chemical Form of Tritium	Rinse Water Volume (mL)	Specific Activity (dpm/mL)	Total Activity (mCi)
BTi	T_2O	141.53	8.740×10^{7}	5.628
T1io	T_2O	44.90	7.824×10^{7}	1.598
T1i1	T_2O	52.03	9.618×10^{6}	0.228
T1i2	T_2O	51.43	1.823×10^{7}	0.427
T2io	T_2O	60.15	5.248×10^{6}	0.144
T2i1	T_2O	56.33	2.294×10^{7}	0.588
T2i2	T_2O	42.72	6.725×10^{6}	0.131
T3io	T_2	45.67	1.661×10^{10}	345.153
T3i1	T_2	42.94	8.724×10^{7}	1.704
T3i2	T_2	56.20	4.564×10^{6}	0.117
T4io	T_2	56.40	1.565×10^{9}	40.161
T4i1	T_2	52.47	1.686×10^{8}	4.025
T4i2	T_2	41.09	1.783×10^{6}	0.033
B1io	T_2	108.23	1.670×10^{8}	8.224
B1i1	T_2	127.29	1.912×10^{7}	1.107
B1i2	T_2	121.98	2.637×10^{5}	0.015
B2io	T_2	96.79	1.092×10^{6}	0.048
B2i1	T_2	92.76	9.288×10^{5}	0.039
B2i2	T_2	87.21	9.414×10^{4}	0.004
			TOTAL	409.374

*T refers to traps, B to gas bubbler, BT to Break Tube residues.

Table 10

Tritium Trapping Results, Commercial T_2 Sample, Tube j

Sample No.*	Chemical Form of Tritium	Rinse Water Volume (mL)	Specific Activity (dpm/mL)	Total Activity (mCi)
BTj	T_2O	171.68	1.356×10^8	10.592
T1jo	T_2O	41.11	1.423×10^8	2.662
T1j1	T_2O	34.68	5.678×10^7	0.896
T1j2	T_2O	45.42	7.611×10^7	1.573
T2jo	T_2O	51.32	3.041×10^7	0.710
T2j1	T_2O	32.19	1.835×10^8	2.688
T2j2	T_2O	40.69	1.692×10^7	0.313
T3jo	T_2	51.21	1.863×10^{11}	4,340.892
T3j1	T_2	38.99	5.260×10^8	9.331
T3j2	T_2	42.47	1.949×10^7	0.377
T4jo	T_2	40.37	2.545×10^9	46.747
T4j1	T_2	38.82	7.027×10^8	12.412
T4j2	T_2	43.05	4.624×10^6	0.091
B1jo	T_2	103.03	1.783×10^8	8.358
B1j1	T_2	103.83	4.354×10^7	2.057
B1j2	T_2	122.39	2.058×10^6	0.115
B2jo	T_2	88.36	5.996×10^5	0.024
B2j1	T_2	94.90	5.835×10^5	0.025
B2j2	T_2	99.58	1.059×10^5	0.005
			TOTAL	4,439.868

*T refers to traps, B to gas bubbler, BT to Break Tube residues.

Table 11

Trapping Efficiency and Amount of T_2O

Test Sample	Total Tritium (mCi)		Trapping Efficiency (%)	Tritiated Water		
				Total (mCi)	Percent	
	Theoretical	Trapped			Theoretical	Trapped
Sign B:						
a(15.7 cm tube)	1,650.963	781.595	47.3	137.659	8.3	17.6
b(5.3 cm tube)	557.331	359.228	64.5	80.742	14.5	22.5
Sign A:						
c(4.2 cm tube)	186.932	146.103	78.2	8.356	4.5	5.7
Sign F:						
g(7.2 cm tube)	655.019	62.732	9.6	7.679	1.2	12.2
Sign D:						
i(4.7 cm tube)	462.380	409.374	88.5	8.744	1.9	2.1
Commercial T_2 Sample:						
j (no phosphor)	1,000.00	4,439.868	--[a]	19.434	--[a]	0.4

[a] More than 100% trapping efficiency. Theoretical amount of tritiated water was not calculated.

An important parameter for measuring total tritiated water is the determination of how much tritium is bound to the phosphor or glass tube residues. Significant revisions to the initial data were necessary when follow-up measurements of tritium in the solutions covering the glass and phosphor residues were made. Second measurements were made when it was found that all tritium theoretically present in the tubes was not accounted for. It was thought that tritium might be released more slowly from the phosphor and glass. When increased levels of tritium were measured in a second count of the residues for tubes 'a' and 'b,' it was decided to monitor all the residues until the end of the study.

Table 12 shows the time-dependent releases of tritium from the residues into the water covering them. For all the tubes, tritium release continued over the time that the materials were measured. The slow release of tritium appears to level off after 30 days, in those cases where data are available. In all cases, the deficit in accounting for the total amount of tritium theoretically present in the tubes is not made up by tritium present in the residues. Assuming that the tubes contained the theoretical amount of tritium, then some of the tritium passed through the trapping apparatus as T_2 without being converted to T_2O. This was confirmed by placing a borrowed Triton tritium gas monitor and passing the exit gas from the apparatus through the monitor while tube 'c' was being tested. A quantitative estimate of the amount of tritium passing through the traps was not possible, however.

The data shown in Tables 5 through 11 for the break tube samples (sample no. BT_) reflect only the initial measurement of tritium associated with the residues, because of some uncertainties about the chemical form of the tritium. At first, it was assumed that all tritium associated with the residues was tritiated water, and that subsequent releases of tritium from the residues into the water covering them should be added to total tritiated water. However, it is likely that some of the tritium is the gas (T_2) adsorbed onto the glass and phophor surfaces and/or absorbed in the bulk materials. In this case, as the T_2 is desorbed from the materials, it probably will exchange with the water covering the materials. The important point is that the percentages of tritiated water listed in Table 11 will be higher if it is assumed that all the tritium associated with the residues is T_2O or TOH. The increases in percent tritiated water range from less than one percent to about two percent if the highest values from Table 12 are incorporated into Tables 5 through 11.

One significant result from the residue immersion tests is tube 'e,' which was a tritium gas sample which had been purchased from Amersham in 1978 and stored at BNL until it was used in this study in one of the mass spectrometer experiments. The tritium was contained in a glass breakseal tube that had no other material inside. A label glued to the outside of the tube was left on the tube when it was tested, because attempts to remove the label threatened to break the tube. Tritium was released from the glass residues and label, doubling over the first 21 days, as shown in Table 12. This was initially surprising, and suggests that a significant amount of tritium diffuses into the glass over 11-plus years.

Table 12

Phosphor/Glass Residues Water Immersion Tests[1]

Tube	Days	mCi
a	0	10.278
	15	25.792
	57	28.053
	78	30.589
b	0	14.230
	32	17.268
	53	17.661
c	0	1.306
	21	2.054
d	0	9.169
	21	11.160
e	0	7.580
	21	14.807
f	0	18.494
	14	23.624
g	0	5.766
	7	7.602

[1] These represent repeated measurements of the BT_ samples listed in Tables 5 through 10.

The greatest and most rapid adsorption of T_2 after the time of sign manufacture can be expected on the surface of the phosphor, since this is a powder with a large surface area. The phophor used is zinc sulfide, a hydrated material ($ZnS \cdot H_2O$). When they are made, zinc sulfide phosphors are mixed with 2% sodium chloride and and 0.005% copper, manganese, or other activators and fired in a non-oxidising atmosphere.(4) If the water of hydration remains with the phosphor after it is made, or if the dehydrated phosphor becomes hydrated during handling before being put in the glass tubes, adsorbed T_2 will probably undergo exchange with the water of hydration to some degree as time passes. It should be noted that one supplier was contacted for information about the phosphor. According to the supplier, they provide two particle sizes: 20 and 40 microns. The phosphor they supply is not hydrated, and has a small amount of zinc oxide. Except for the zinc oxide, the material is 100 % zinc sulfide.

These considerations about the presence of water in the phosphor present the possibility that the amounts of tritiated water in the glass tubes might be minimized by changing quality control procedures during manufacture of the light sources. The generation of tritiated water from tritium gas can only occur if oxygen is present to react with T_2 or if water is present to undergo exchange reactions. The strict exclusion of oxygen and the water of hydration from the glass tubes while they are being made would thus minimize the amounts of T_2O and TOH that would appear over the long term.

To illustrate the need to reduce, if not completely eliminate, water in the light sources, one can calculate the minimum amount of water necessary to exchange with 1 Curie of tritium gas. The reaction to consider is

$$T_2 + H_2O = TH + TOH.$$

The specific activity of 100% tritium gas is 9.64×10^3 Ci/g. Using this and the molecular weights of T_2 and H_2O (6 and 18 g/mol, respectively) one can calculate that 0.3 milligrams of water are needed to react with 1 Curie of T_2 following the above reaction.

3.3.3 Summary of Mass Spectrometer Experiments

As noted earlier, equipment problems were encountered with the residual gas analyser (RGA) system. Three tritium light source tubes and an old tritium gas sample (Amersham, 1978) were examined. After each experiment, adjustments were made to the instrument to increase sensitivity and improve resolution. For the first two light sources and the tritium gas sample, peaks at masses 6 and 3 confirmed the presence of tritium gas and helium-3 ions. Tube 'h,' the last examined with the RGA, exhibited peaks at masses 19, 20 and 22 in addition to those at 6 and 3. Masses 22, 20 and 19 correspond to T_2O, TOH, and TO ions, respectively.

The mass spectrum scans for tube 'h' are shown in Figures 6a, b, and c. Figure 6a is for masses 0 to 10. The peak at mass 4 represents residual helium-4 in the system. Peaks for tritiated water are evident in Figure 6b which covers masses 15 to 25. Also present are peaks at 18 and 17, due to water, and one at 16, which corresponds to doubly ionized O_2. An additional contribution to the peak at mass 20 is doubly ionized argon. Argon is present because it was used to flush the system. Figure 6c covers the mass range 33 to 43. This was looked at to examine the remote possibility that T_2 could react or exchange with the zinc sulfide phosphor to form tritiated hydrogen sulfide (T_2S or THS). Ions from tritiated hydrogen sulfide would appear at masses 35, 36, and 38; none was detected.

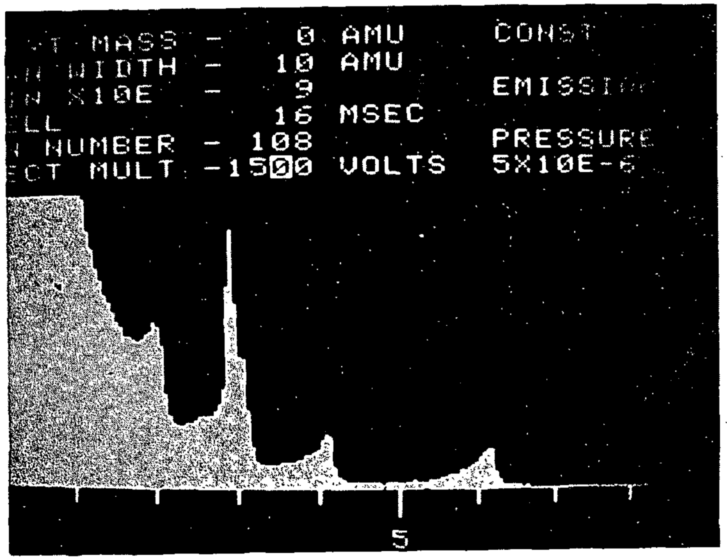


Figure 6a. Mass spectrum scan, 0 to 10 amu.

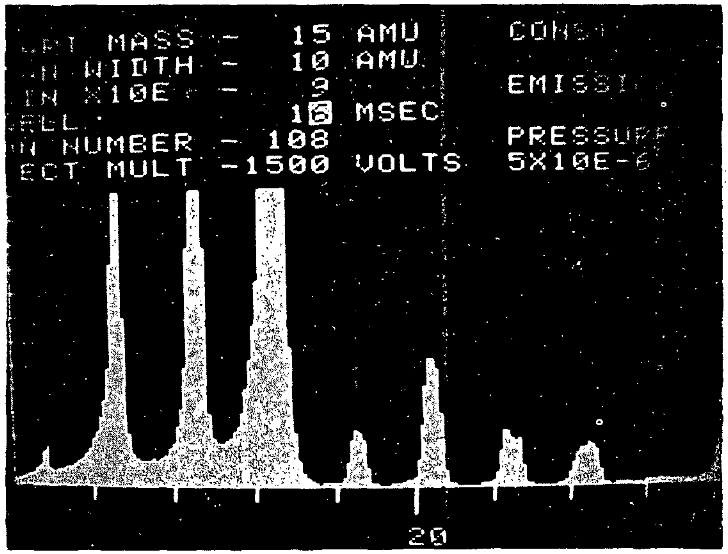


Figure 6b. Mass spectrum scan, 15 to 25 amu.

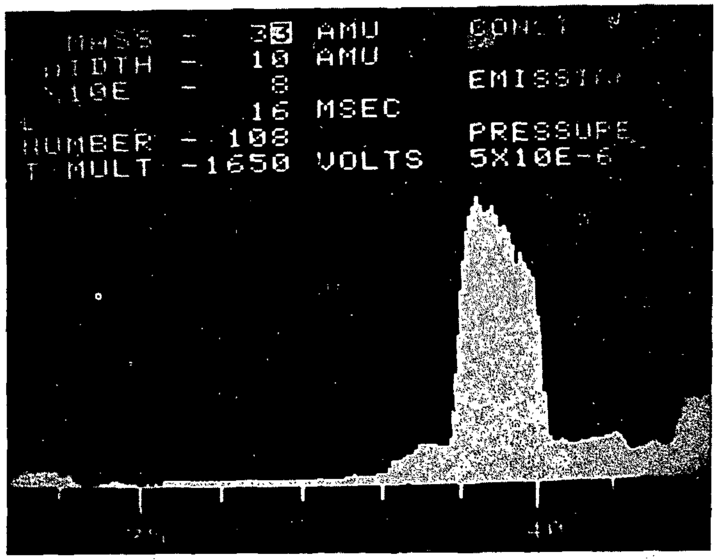


Figure 6c. Mass spectrum scan, 33 to 43 amu.

Mass	Ion
3	T^+, T_2^{++}, $^3He^+$
6	T_2^+
19	TO^+
20	THO^+, Ar^{++}
22	T_2O^+
35	TS^+
36	THS^+
38	T_2S^+

3.3.4 Phosphor Particle Size Measurements

While discussing the preliminary findings of this investigation, the USNRC expressed an interest in determining the particle size distribution of the zinc sulfide phosphor.

A sample of zinc sulfide powder was obtained from the USNRC. This was sprinkled onto a piece of filter paper which had already been wetted with a mixture of graphite and isopropanol. The choice of this method for grounding the powder is due to the fact that insulating or non-conductive particles build up a space charge region by accumulation of absorbed electrons which deflects the incident beam of a scanning electron microscope (SEM). This deflection produces intense image distortions.

The filter paper (containing the grounded zinc sulfide powder) was loaded into and then examined by electron microscopy. Figures 7a and 7b are typical scans showing the size distribution of the powder. The largest particle observed was approximately 36 microns and the smallest seen was 1 micron.

Energy dispersive spectroscopy (EDS)[b] was performed on the phosphor which verified that zinc and sulfur were the primary constituents of the powder (Figure 7c).

3.3.5 Laboratory Surface and Personnel Contamination

During the experimental studies, the laboratory area and staff conducting the work were monitored for contamination. The greatest amounts of contamination were associated with sample changes after experiments were completed, transferring glass and phosphor residues to containers for immersion in water. At least twice during the project, the experimentor had about 100 dpm contamination on his head and neck; showering removed the contamination. Bioassays were taken within 24 hours of the two worst contamination incidents and on a monthly basis otherwise. No tritium was detected in the bioassays.

After one sample change in which contamination was found on the experimentor, a survey of laboratory surfaces was made as shown in Table 13. The worst contamination was on the ledge work area within 12 inches around the spot where the metal break tube assembly was dismantled to transfer the glass and phosphor residues to a plastic bottle. An exact reading was not taken because the Health Physics technician did not wish to contaminate his counting equipment. The measurement was terminated when more than 1,000 counts were reached in less than 5 seconds.

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[b] EDS is an analytical technique, capable of performing elemental analysis of microvolumes, typically on the order of a few cubic microns in bulk samples and considerably less in thinner sections. Analysis of X-rays emitted from a sample is accomplished by crystal spectrometers which use energy dispersive spectrometers and permit analysis by discriminating among X-ray energies.

The feature of electron beam microanalysis that best describes this technique is its mass sensitivity. For example, it is often possible to detect less than 10^{-16} grams of an element present in a specific microvolume of a sample. The minimum detectable quantity of a given element or its detectability limit varies with many factors, and in most cases is less than 10^{-16} grams/microvolume.

For purposes of this report, EDS was considered to be a satisfactory method of chemical analysis. EDS will only discern elements with atomic numbers greater than 11 (sodium) so certain light elements such as oxygen will not be detected.

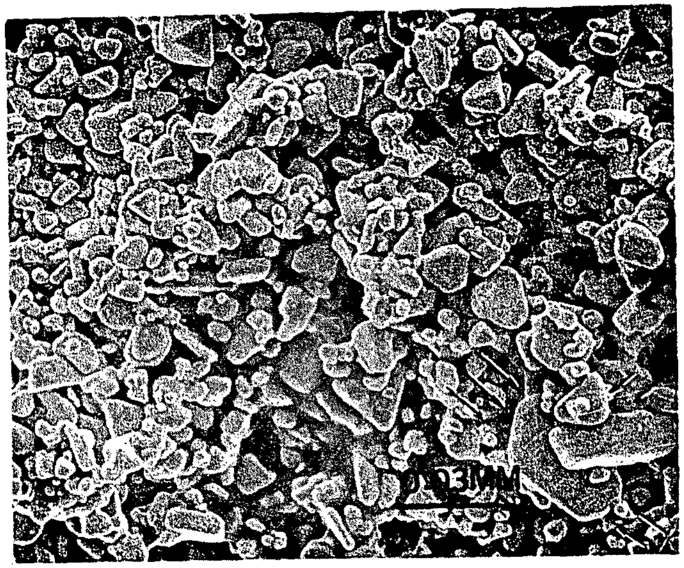

Figure 7a. Photomicrograph of zinc sulfide particles (arrows point out largest particle).

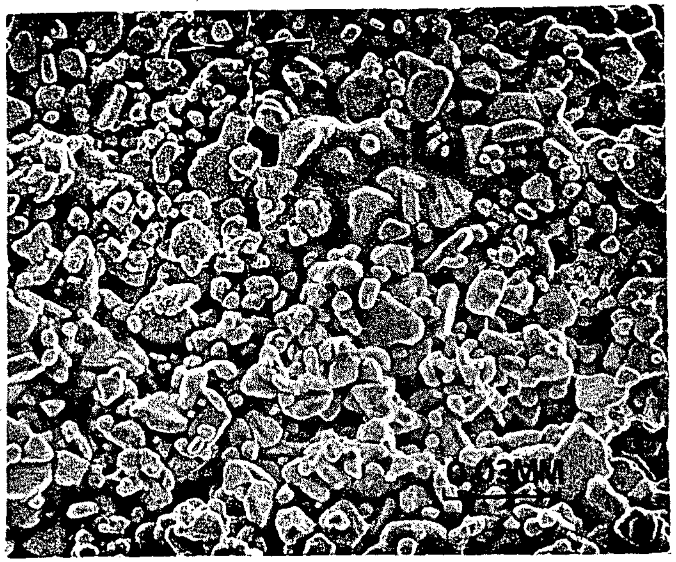

Figure 7b. SEM photograph of ZnS particles (arrows surround smallest particle seen).

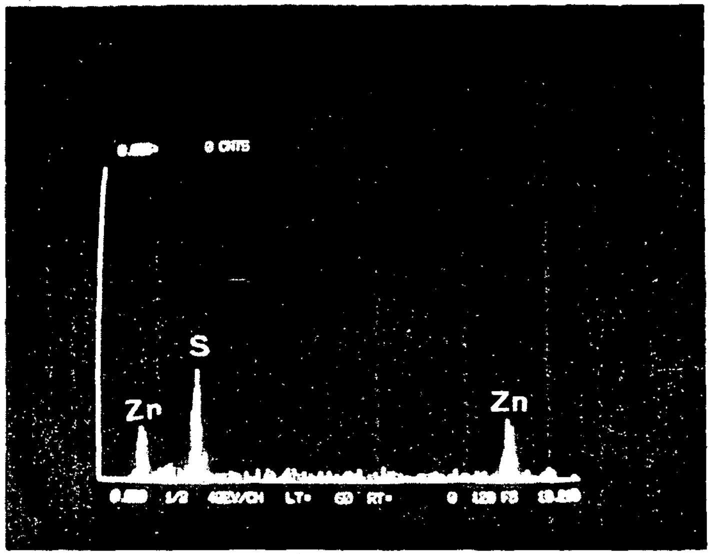

Figure 7c. EDS scan of ZnS powder.

The contamination on the RGA system components may have occurred when disconnecting the metal break tube assembly, even though all valves to the system were closed. The IQ 200 RF source and sensor were just under the break tube assembly. During sample changeout, these components were situated directly behind the experimentor and about 3 feet from the ledge work area.

Immediately after the survey was taken, all surfaces were wiped several times with a damp towel. There was a gritty feel to the ledge work area, indicating that some of the phophor and smaller glass fragments had been spilled during the sample transfer. Two days later, some of the surfaces were tested again; the results are given in Table 13.

Table 13

Laboratory Surface Contamination After Tritium Sample Change

Surface Tested	Contamination (dpm) First Survey	Second Survey*
Ledge Work Area	>>10,000	7,500
Floor Under Ledge	> 1,000	--
Wrenches	> 1,000	--
IQ200 RF Source	1,500	100
IQ200 Sensor	> 1,000	100

*Surfaces were wiped with a damp paper towels within an hour after the first measurements were made. "--" means no measurement was made.

4. CONCLUSIONS AND RECOMMENDATIONS

A preliminary study to determine the chemical form of tritium in self-luminous light sources has been completed. The light sources tested were obtained from commercial building exit signs. The quantitative analysis experiments were designed to separate tritium gas from tritiated water for subsequent analysis by scintillation counting. Qualitative analyses with a residual gas analyser confirmed the presence of tritiated water in one self-luminous source.

All self-luminous tubes tested in the quantitative experiments contained tritiated water. For the two newest signs tested, about 2 % and 5 % of the total tritium present was tritiated water. In the older signs, the percentage of tritiated water was significantly higher, ranging above 10 % of the total tritium trapped.

In order to test the sources, it was necessary to break the glass tubes containing the tritium and phosphor materials. After the experiments, the glass and phosphor residues were collected and placed in water to collect and account for residual tritium (assumed to be tritiated water). Tritium concentrations in the water increased for every sample over the time the samples were tested. For the samples immersed for more than 30 days, the tritium releases were leveling off.

Because this was a scoping study, only four signs were tested. The results obtained suggest that more signs should be tested in order to ascertain whether the presence of tritiated water is an inherent property of the design, or whether better controls in the manufacturing process could minimize or possibly eliminate tritiated water. Differences in the amounts of tritiated water from two new signs suggest that manufacturing quality control could reduce the amounts of tritiated water in the light sources. Since all the older signs had higher levels of tritiated water, it would appear that, given enough time, tritiated water will appear in the signs. The results from the older signs thus indicate that the presence of more than 2 % tritiated water is an inherent property of the design of the system.

Tests with more signs should be conducted to provide a statistical basis for determining how many signs have significant (more than 2 %) amounts of tritiated water. A follow-up study of this type should include new and old signs from all the manufacturers now supplying the signs. In addition, other consumer goods, such as watches with self-luminous dial lights should be examined for tritiated water in the light sources.

To quantify the role of the phosphor in the appearance of tritiated water, studies of tritium absorption by and reactivity with the phosphor material should be carried out. Such a study could be conducted with hydrogen or deuterium to assess the chemical reactivity of the phosphor.

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10. SUPPLEMENTARY NOTES

11. ABSTRACT *(200 words or less)*

Building exit signs containing tritium self-luminous light sources were dismantled, and the light sources were tested to determine the chemical form of tritium in this study. The objective was to quantify the amounts of tritiated water (T_2O or TOH) present in the light sources. The light sources consist of sealed glass tubes coated internally with a phosphor (zinc sulfide) and filled with tritium gas (T_2).

Light source tubes from four exit signs were tested. Two were new signs, one was six years old, and one was thirteen years old. In one of the new signs, the total tritium inventory included two percent tritiated water. Two signs had higher amounts of tritiated water: 4.5% for the other new sign, and 14.5% for the six-year-old sign. In the oldest sign, an accurate inventory of the tritium content was not available, but tritiated water accounted for 12.2% of the total tritium collected for counting.

12. KEY WORDS/DESCRIPTORS *(List words or phrases that will assist researchers in locating the report.)* Tritium compounds; Tritium oxides; Isotopes; Inspection; Zinc Sulfides; Luminescence; Phosphorescence;	13. AVAILABILITY STATEMENT Unlimited 14. SECURITY CLASSIFICATION *(This Page)* Unclassified *(This Report)* Unclassified 15. NUMBER OF PAGES 16. PRICE