MLM-2345(OP)

Conf-760579--1

DIFFERENTIAL MEASUREMENT OF LOW LEVEL HTO AND HT LEAK RATES

W. E. Sheehan and K. M. Muldoon
Monsanto Research Corporation
Mound Laboratory
Miamisburg, Ohio

Report presented at DAMSUL Committee Meeting, May 12-13, 1976

August 1976

EB

CONTRACT NO. E-33-1-GEN-53

DISCLAIMER

MLM-2345(OP)

DIFFERENTIAL MEASUREMENT OF LOW LEVEL HTO AND HT LEAK RATES

W. E. Sheehan and K. M. Muldoon
Monsanto Research Corporation
Mound Laboratory*
Miamisburg, Ohio

ABSTRACT

Leak rates of 5 x 10^{-17} cm^3/sec and greater can be measured by a very simple technique that will also differentiate tritium oxide (HTO) from tritium gas (HT). Because of the much greater health hazard of tritium oxide (200 to 1), the determination of chemical form is significant.

The method involves flushing a gas collection chamber, containing the item being measured, with dry air. The flushed air is passed through an ethylene glycol bubbler which removes only the HTO. The outlet of the ethylene glycol bubbler is connected to a heated (400°C) palladium sponge catalyst which converts the HT to HTO and then to a second ethylene glycol bubbler for collection of the oxidized tritium gas. Liquid scintillation (p-dioxane base) counting solution is added directly to the bubblers and counted for tritium in a Liquid Scintillation Spectrometer.

Advantages, method validation, operational experience, and data obtained by this technique are discussed. The sensitivity of the method is dependent on the time allowed between bubbler changes, the liquid scintillation spectrometer counting efficiency, background, and counting times employed.

INTRODUCTION

A former method used for leak rate measurements involved sealing the item in a methane atmosphere in an appropriate-sized gas collection chamber (1, 5, and 16 gal cans as shown in Figure 1), the interior of which had been coated with cellulose acetate (1). After approximately one week of standing static, a portion of the methane was expanded into a 2-liter proportional gas counting tube. Several gas aliquots were taken and counted prior to opening the gas collection chamber. After the item was removed from the collection chamber, the film of cellulose acetate was stripped from the entire inner surface of the gas collection chamber, dissolved in p-dioxane base liquid scintillation solution, and counted for tritium. The coating and stripping of the cellulose film was necessary because significant amounts of tritium had adsorbed to the

---

*Mound Laboratory is operated by Monsanto Research Corporation for the U. S. Energy Research and Development Administration under Contract No. E-33-1-GEN-53.

gas collection chamber and thus were not accounted for by the methane gas that was counted. This method was very tedious and time consuming. The static gas collection period enhanced the adsorption problem and made these low-level measurements more difficult.

LEAK TEST METHOD

As in the former method, the item to be tested is placed into either a 1, 5, or 16 gal test chamber. In contrast to the former method, a static period for tritium collection is not required. Immediately after the item is sealed in the collection chamber, it is placed onto the leak test system shown in Figure 2. Tritium is purged from the collection chamber with compressed air and not allowed to build up on the inner surfaces as in the former method. Tritium is continually flushed from the system and concentrated in the ethylene glycol bubblers, rather than in the gas collection chamber as in the former procedure. The sensitivity of the measurement can be increased or decreased by adjusting the time interval between bubbler changes and the counting time used in the liquid scintillation counting. It is normal procedure to seal the item and test the collection chamber for leaks prior to placing it on the leak test system. The bubblers are changed at the end of the first day and again the following morning and daily (except weekends) thereafter until the test is completed, usually at the end of one week.

During the initial flushing period, a noticeable drop in activity is observed. This is generally more apparent in the low-level tests (10^{-14} cm^3/sec) and below. It is believed that during the initial flush period the surface of the item is being decontaminated. When a constant rate for three successive bubbler changes had been observed, the leak rate is then calculated over that period of time. The leak rate, R, is calculated as follows:

$$R = \frac{T}{\tau A}$$

where T = total dis/min
τ = time (sec)
A = specific activity of ^3H STP
(5.26×10^{-12} dis/min/cm^3).

VALIDATION OF LEAK TEST PROCEDURES

This procedure was tested by introducing known amounts of HT and HTO into the collection chambers and allowing the test chambers to remain static for several days prior to flushing through a leak test system similar to that shown in Figure 2. The HT introduced into the cans was first standardized by proportional counting and the HTO by liquid scintillation counting. The accuracy of both standards is directly traceable to NBS standards (1). Results of these validation tests are listed in Tables 1 and 2. The general technique, that is, ethylene glycol collection and the use of a heated palladium catalyst, was developed (2) and tested for tritium air monitoring of stack gas effluents.

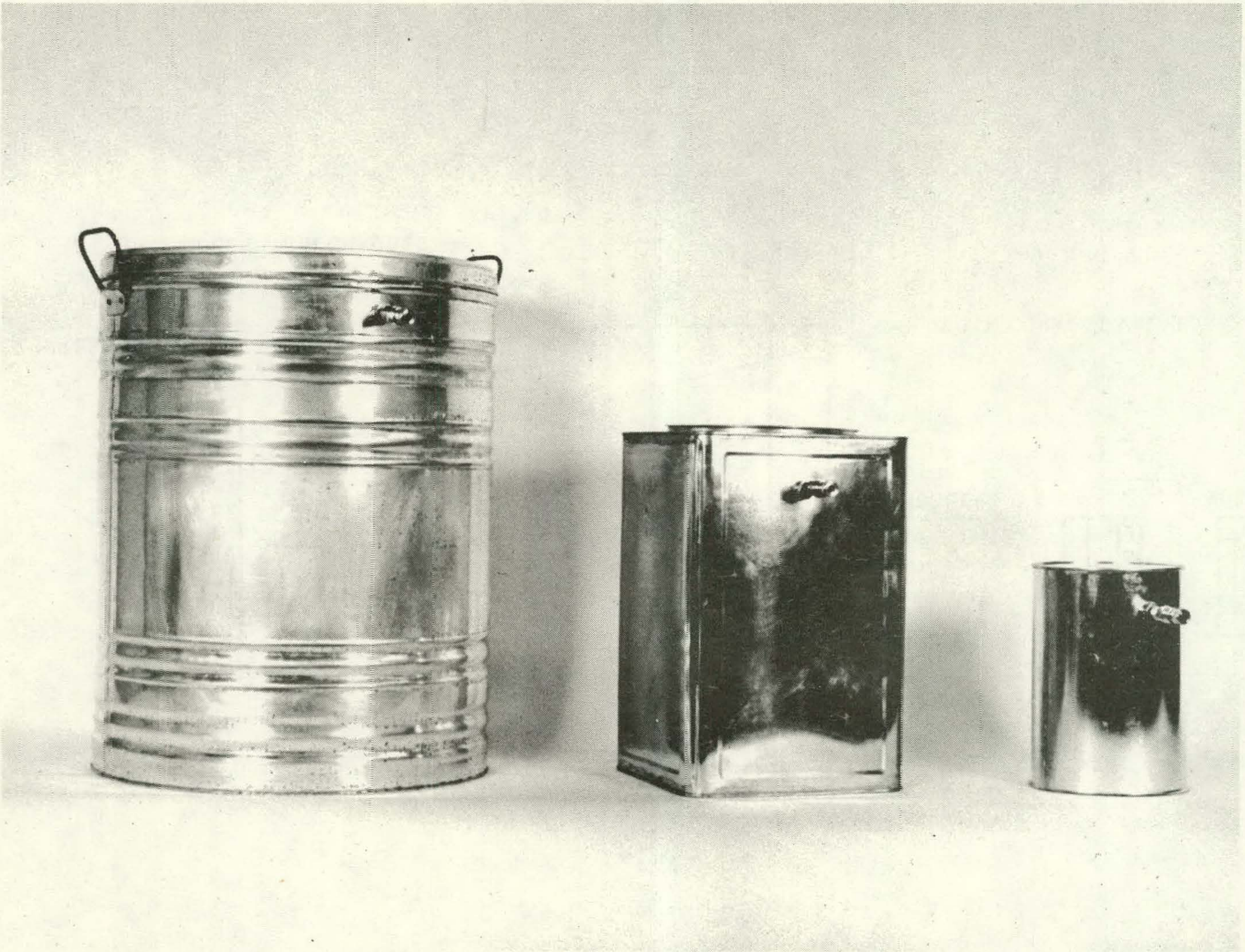

Figure 1. Disposable Collection Chambers

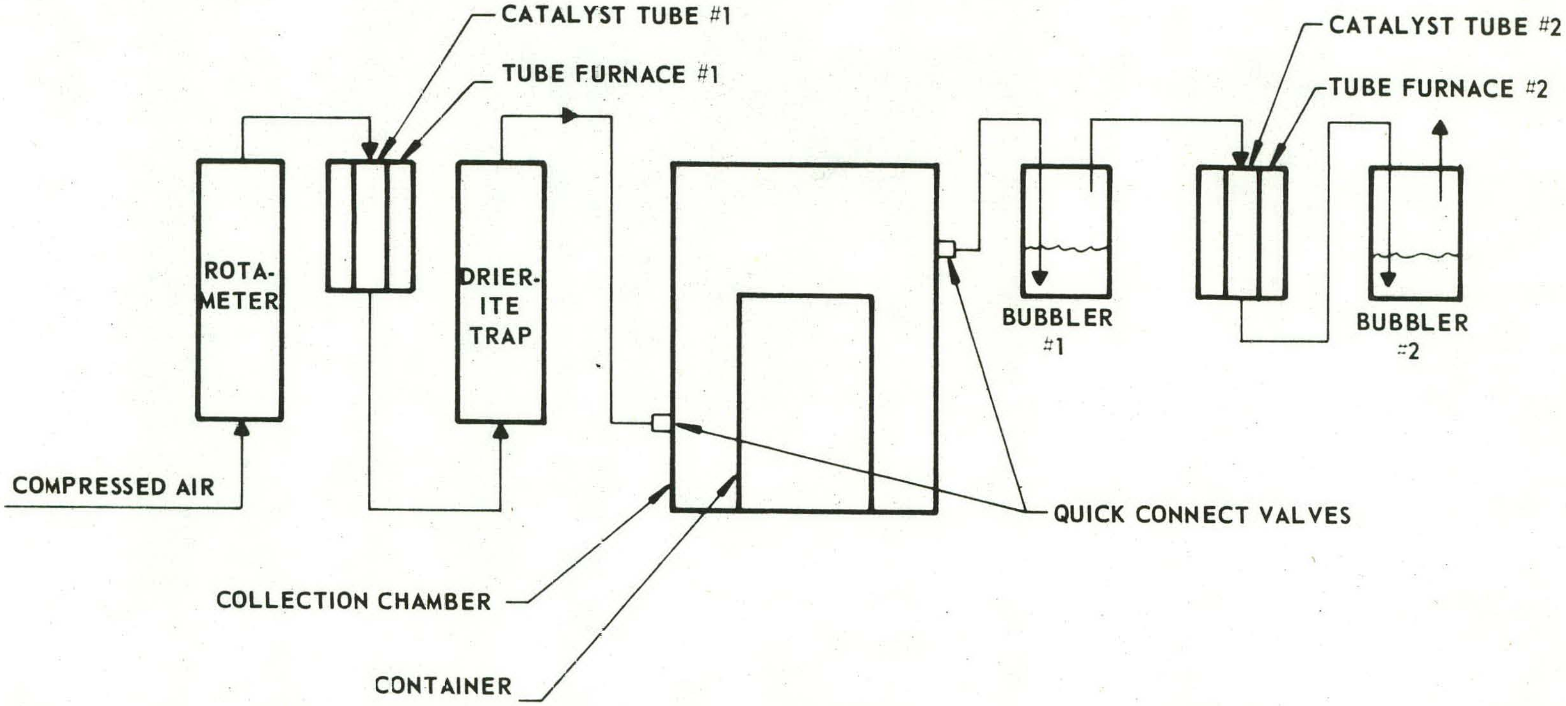

Figure 2. Leak Detection System

Table 1

Validation of Palladium Catalyst Ethylene Glycol Leak Test Method

Std. No.	Test Chamber Size (gal)	Std. Value (dis/min x 10^3)	Percent Recovery
1	1	349	99.1
2	1	185	100.0
3	1	119	90.7
4	1	4.08	102.3
5	1	8.53	104.5
6	1	350	96.5
7	1	274	97.8
8	5	82.1	99.1
9	16	249	93.4
10	1	336	99.8
			98.3 ave
			± 4.0 Rel. Std. Dev.

Table 2

Validation of HTO vs. HT Differential Analysis in Leak Test Method

Std. Value (dis/min)	Form	HTO Bubbler	HT Bubbler	Total % Recovered
6.56 x 10^6	HTO	6.34 x 10^6	0.13 x 10^6	98.6
3.21 x 10^5	HT	0.01 x 10^5	3.08 x 10^5	96.3

OPERATIONAL EXPERIENCE WITH LEAK TEST SYSTEM

A four-position leak test station has been in operation for over two years. House compressed air is passed through a heated palladium catalyst and a Drierite desiccant to remove any tritium in the air supply. The manifold system and bubbler fixtures are made of stainless steel. Tygon tubing and Quick Connect fittings are used to connect the test chambers to the leak test system.

Tests ranging from 10^{-12} to 10^{-15} cm^3/sec are being routinely run with no special effort required to maintain a low background. The Tygon tubing is replaced after the higher rate tests are completed. A recent evaluation of the system background on two of the four positions is shown in Table 3. These data represent 14 and 10 changes of the bubblers on systems A and B. The total time per run ranged from 19 to 120 hr. On each system a routine leak test was conducted within the period of this data collection. Only the initial run following the leak test was eliminated from the background evaluation. There was no trend in the data other than the contamination observed in the initial purge of the system upon completion of a routine test.

A reusable test chamber which will accommodate a plastic bag liner was designed for use on this system. To date it has not been necessary to use the plastic liner as the memory of the chamber has not been a problem. Background of the chamber for two successive 24-hr periods following a routine test near the 10^{-14} cm^3/sec range is shown in Table 4. A period of 24 to 48 hr appears sufficient to purge the system following tests in the range of 10^{-14} cm^3/ sec and lower. More frequent changes of the bubblers may indicate that a shorter time is required than was observed in this test case.

Table 3

System Background

cm^3/sec x 10^{-17}

System	Changes	Total Time (hr)	HTO	HT
A	14	554	2.9 ± 0.7	0.8 ± 0.6
B	10	508	3.2 ± 0.7	0.8 ± 0.6

Table 4

Reusable Chamber After 10^{-14} cm^3/sec Test

Hr	dis/min	cm^3/sec x 10^{-15}
24	1133	2.5
24	344	0.8

Table 5

1.6×10^{-12} Rate

Hr	dis/min $\times 10^{5}$	cm^{3}/sec $\times 10^{-12}$
3	2.1	3.6
17	4.3	1.3
7	2.2	1.6
113	33.5	1.6
5	2.2	2.4
18	6.2	1.8
160	48.4	1.60

Table 6

2.9×10^{-14} Rate

Hr	dis/min $\times 10^{4}$	cm^{3}/sec $\times 10^{-14}$
5.5	2.1	20.0
24	1.8	4.0
24	1.0	2.2
24	1.2	2.7
24	1.2	2.7
96	5.2	2.86

Table 7

7.2×10^{-15} Rate

Hr	dis/min $\times 10^{3}$	cm^{3}/sec $\times 10^{-15}$
16	64.2	211
24	9.7	21
24	5.3	11.7
26	3.4	6.9
63	6.6	5.5
113	15.3	7.2

DATA OBTAINED WITH LEAK TEST SYSTEM

Examples of typical data are listed in Tables 5, 6, and 7. Several observations can be made concerning data obtained by this technique.

1. In most cases more than 95% of the activity is collected in the HTO bubbler. Only total tritium (HTO + HT) is listed in tables.

2. Rates that are in the 10^{-13} cm^3/sec and higher range stabilize quickly.

3. Rates that are in the 10^{-14} cm^3/sec and lower range usually show a rapid initial decline in rate.

4. There has been some indication that changes in room temperature will result in a change in the observed rate.

5. A variable that can affect the observed rate is the flush rate. These data were obtained using a flush rate of 200 cm^3/sec.

Most of these observations suggest that the source of the tritium is on the outer surfaces of the item and that initial flushing tends to remove or decontaminate the item to a point before a constant rate is observed. The leak rate is based upon that data obtained beyond the initial decontamination period.

CONCLUSIONS

This method of leak testing has significantly reduced the "hands on" time per test and in addition it has resolved the very serious absorption problem associated with the former method. Additional information is now being obtained as to chemical form (HTO vs. HT) which is significant to health hazard analysis and may be a clue to the source of the material. Successive leak rate measurements taken initially suggest that the items are contaminated on the surface and the true rate is significantly reduced once the surface contamination is removed.

REFERENCES

1. M. L. Curtis, C. T. Bishop, M. M. Bolton, and R. L. Ryan, "Determination of Tritium Leak Rates from Waste Processing Equipment," in Tritium, A. A. Moghissi and M. U. Carter (ed.), Messenger Graphics, Las Vegas, Nevada, 1973, pp. 784-791.

2. W. E. Sheehan, M. L. Curtis and D. C. Carter, Development of a Low Cost Versatile Method of Measurement of HTO and HT in Air, MLM-2205, February 14, 1975.