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DEMONSTRATION OF NOBLE GAS COLLECTION USING THE CRYOGENIC TECHNIQUE

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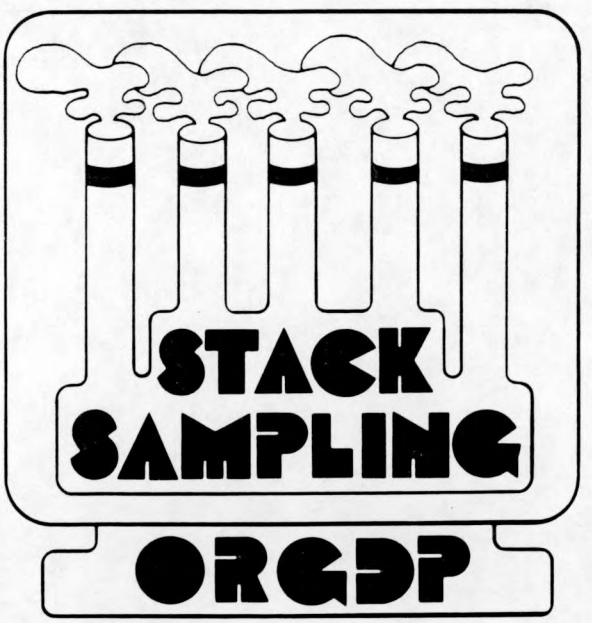

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DEMONSTRATION OF NOBLE GAS COLLECTION USING THE CRYOGENIC TECHNIQUE

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INTRODUCTION

Monitoring devices used for detecting and measuring airborne radioactive noble gases in stack emissions have been limited in their precision and detection capability. Cryogenic sampling is one method used for sampling gamma emitting radioactive gases in stack emissions. A cryogenic air sampler, originally developed at the Oak Ridge National Laboratory (ORNL) and further developed by the Systems Demonstration and Environmental Air Sampling Group (SDEASG) at the Oak Ridge Gaseous Diffusion Plant (ORGDP) is being tested. The cryogenic sampler will be used to study the off-gas from various emission points at ORNL after completion of the preliminary study by SDEASG. Work is currently under way to demonstrate the effectiveness of the sampler and the efficiency of the sampling method. Various tests have been and are being conducted to determine the sample collection techniques which will result in the greatest sample transfer efficiency, sampling precision, and gamma emission counting efficiencies.

PROCESS DESCRIPTION

During a sampling procedure, the stack gas passes through a probe, through a millipore filter to remove any particulates in the gas stream, through a transducer connected to a mass flow meter and

totalizer which measures the gas flow rate, through a needle valve followed by a 0.5 mm orifice to regulate the flow, then into the cryogenic sampling vessel which is immersed in a liquid nitrogen bath. Figure 1 shows the entire cryogenic sampling train, consisting of: (1) a filter and sampling probe assembly, (2) either a rotameter or a mass flow meter and transducer, (3) a 0.5 mm copper orifice, (4) an orifice holder, (5) a regulating valve, (6) a 20 liter liquid nitrogen refrigerator, and (7) a 1.6 liter stainless steel sampling vessel.

As a first step preparatory to sample collection, the manifold, consisting of a metering valve, an orifice holder, and a copper disk with a 0.5 mm orifice (items 3, 4, and 5, above), is assembled and checked for leaks. The manifold is mounted into the sampling vessel with a rubber stopper, serving two purposes: (1) it insures safety, since only a small positive pressure is required to force the stopper out; and (2) it provides insulation between the copper orifice and the sampling vessel. The orifice holder acts as a heat sink to prevent ice, which could plug the small orifice, from forming. Next, the liquid nitrogen refrigerator is filled and a small amount of liquid nitrogen is poured into the sampling vessel to cool it, thus eliminating an initial sharp drop in the sampling rate by ensuring rapid cooling of gas as it enters the sampler. The sampling vessel and manifold, with valve closed, are lowered into the refrigerator. With the system connected and leak-checked, the regulating valve is opened and the gas flowrate is adjusted to the predetermined setting.

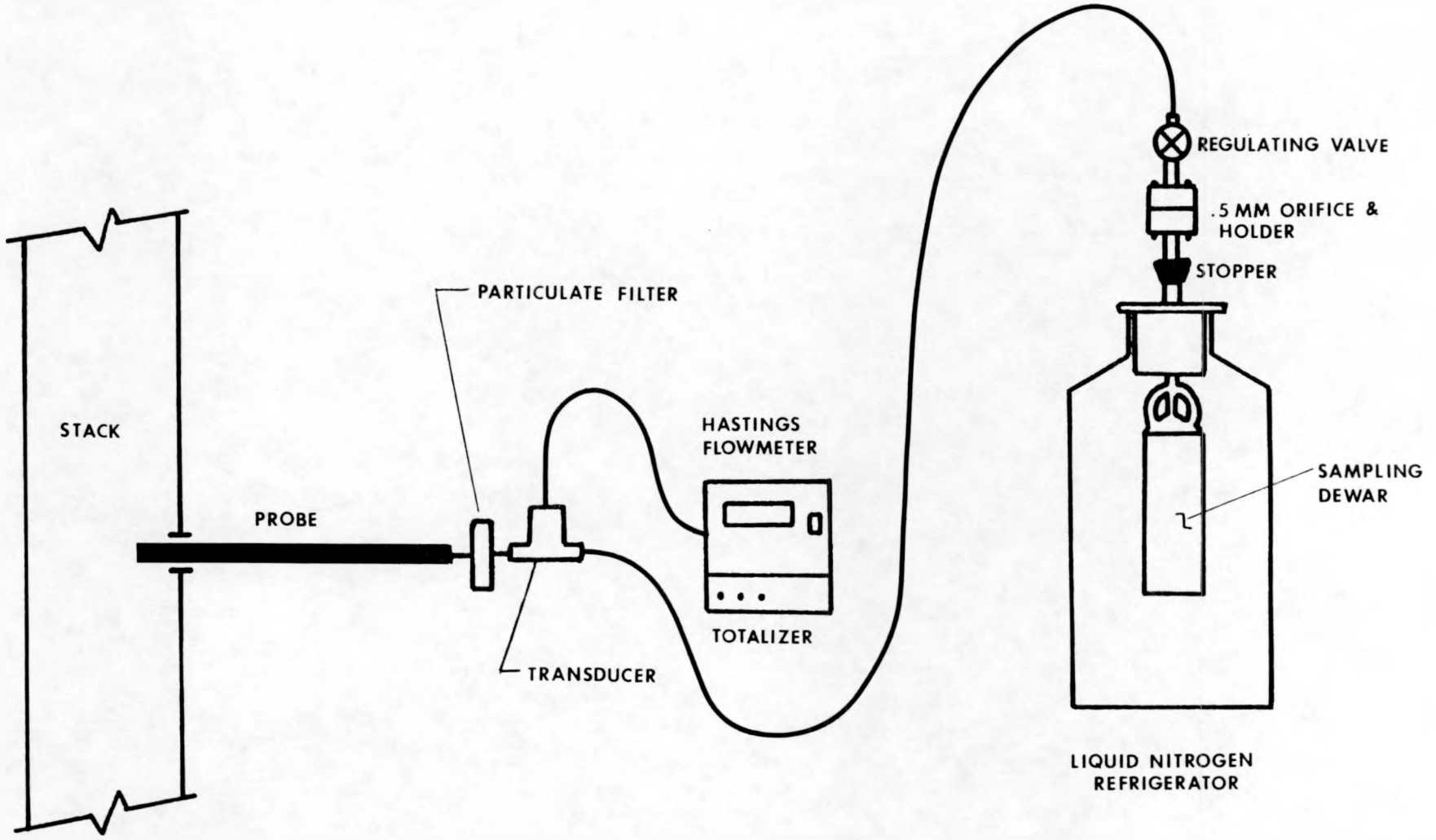

Fig. 1. Cryogenic sampling train

The cryogenic sampling vessel shown in Figure 2 is a 1.6 liter stainless steel container with a narrow neck which projects through an insulated cover. During sampling, the vessel is immersed to the neck in liquid nitrogen, contained in a liquid nitrogen refrigerator (Fig. 3). Liquefaction of gas within the sampler occurs as its temperature approaches that of the surrounding liquid nitrogen. The design of the sampler affords a large surface-area-to-volume ratio to enhance the cooling effect. The volume reduction accompanying liquefaction creates a negative pressure gradient between the outside gas and the gas inside the sampling vessel. This pressure gradient causes gas to be drawn through a 0.5 mm orifice into the sampling vessel where it is liquefied, a process that continues as long as the pressure gradient exists. This sampler is capable of collecting one liter of gas per minute at STP over a period of 10 to 12 hours.

During sampling, it is important that the flow be closely monitored and recorded, since the total volume of gas sampled is calculated as a product of flow rate and time sampled. To measure the amount of gas pulled into the sampling vessel, one of two devices can be used. If no power is available, flow is measured by a 0 to 2 liter per minute rotameter. When power is available, the more accurate thermal mass flowmeter is preferred. A totalizer may be used in place of manual recording; this will automatically record total flow for the duration of the run.

Fig. 2. Cryogenic sampler (left) with a 20-L liquid nitrogen refrigerator (right)

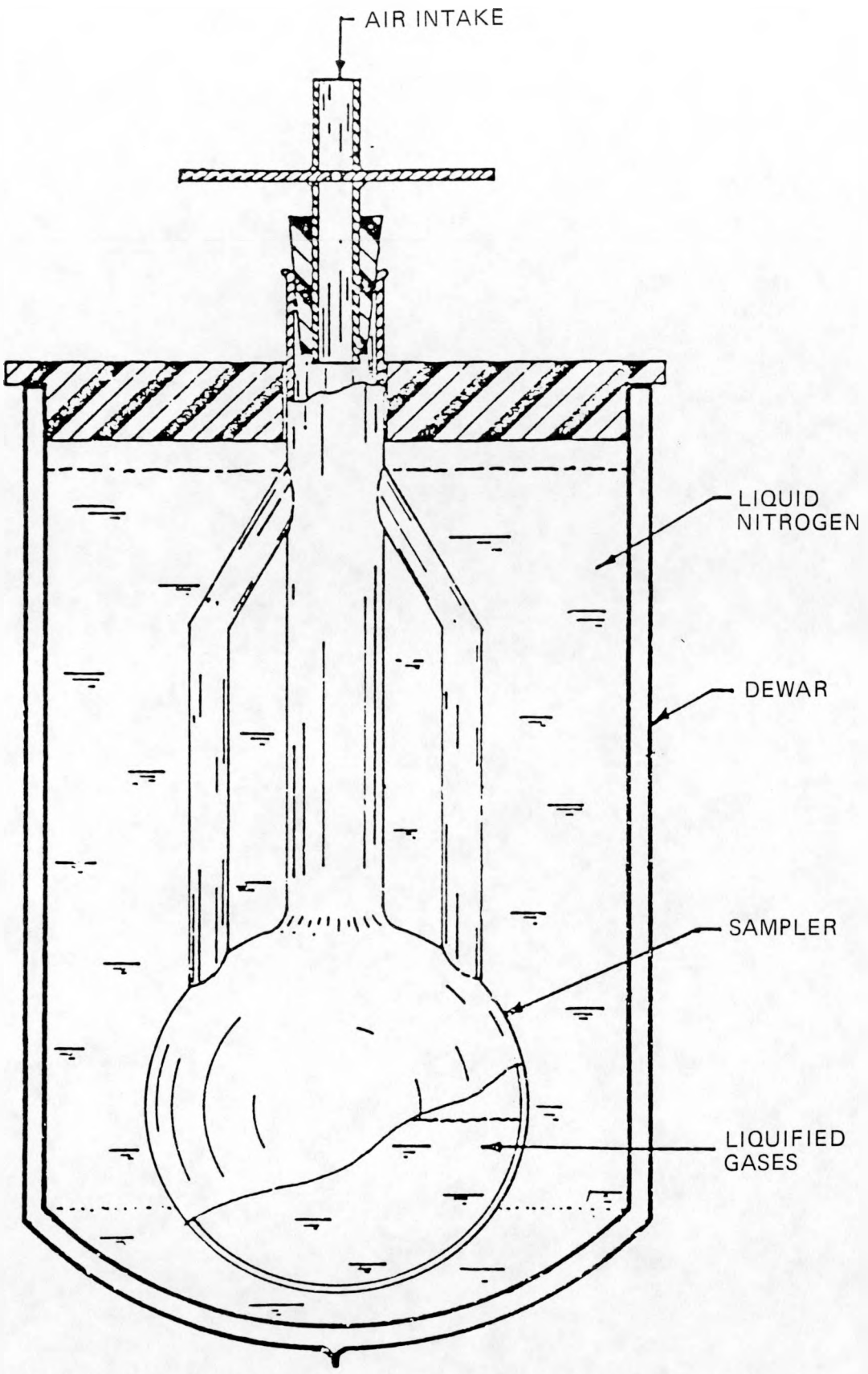

Fig. 3. Schematic of the cryogenic sampler during the sampling process

SAMPLE TRANSFER

After the stack gas has been collected in the sampling vessel, it is transferred into the 3.5 liter Marinelli Dewar (Fig. 4), which has been pre-cooled by adding liquid nitrogen to the Dewar. This eliminates most of the flash-off or boil-off of the liquid gas as it is poured into the Dewar.

Care must be taken during transfer. When the stopper is removed, the neck of the sampling vessel must be checked to make sure that no ice has formed. If that has occurred, the ice is chipped down into the liquid gas before the sampling vessel is removed from the liquid nitrogen refrigerator. After clearing the neck of the sampling vessel, the liquid gas is quickly but carefully poured into the pre-cooled Marinelli counting Dewar and filled to a consistent level with liquid nitrogen. The purpose of adding the liquid nitrogen to the flask is to provide a uniform sample counting geometry. The sample is now ready to be counted.

RESULTS

An empirical factor, to compensate for sample loss due to evaporation during transfer from the sampling vessel to the counting Dewar,

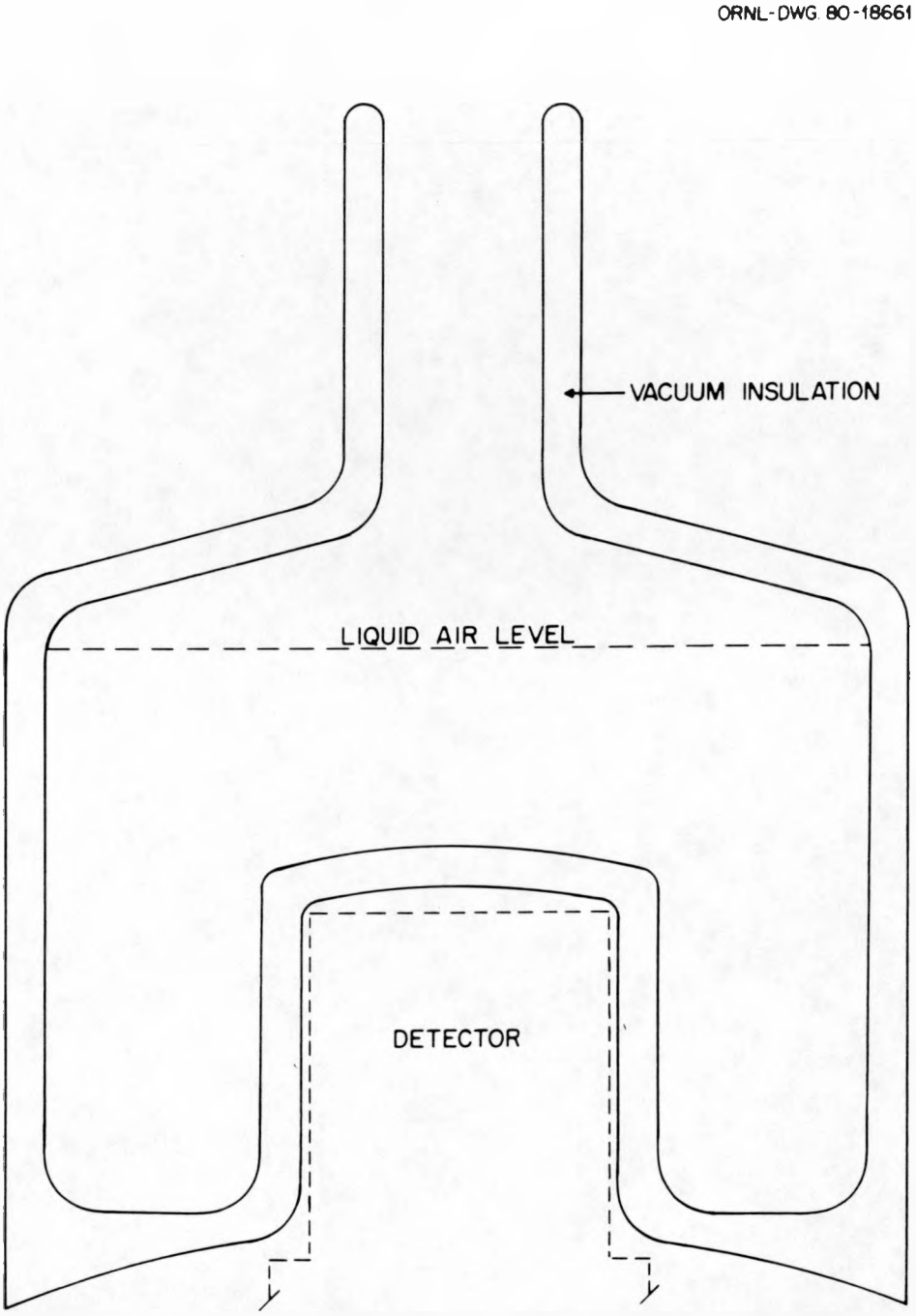

Fig. 4. Cross-sectional view of Marinelli counting dewar.

was calculated. The procedure, conducted over a total of fifteen tests, was performed as follows: 300 to 600 mL of liquid nitrogen was poured into a sampling vessel, which had been submerged in a liquid nitrogen refrigerator. The counting Dewar, containing approximately 2 liters of liquid nitrogen, was weighed; the sampling vessel was then removed from the liquid nitrogen refrigerator, immediately weighed, and the contents poured into the counting Dewar. The sampling vessel and counting Dewar were re-weighed to establish a net weight loss, calculated as the difference between the weight gain of the counting Dewar and the weight loss of the sampling vessel. The mean net weight loss was 20.8 mg, an average of 5.5% of the total weight of the contents. The results are shown in Table 1.

Because the sampling vessel is uninsulated, there is constant evaporation and subsequent weight loss whenever the vessel is removed from the liquid nitrogen to warmer surroundings. It was necessary to determine the amount of the weight loss as a function of time for use in routine sampling, since weight determinations will not normally be performed. The sampling vessel was again submerged in the liquid nitrogen refrigerator and approximately 300 grams of liquid nitrogen was poured into the sampling vessel (nitrogen has the lowest boiling point of gasses normally found in the samples, and is the first to evaporate). The sampling vessel was then removed from the nitrogen refrigerator and weighed. The weight was recorded every 30 seconds for

several minutes. The average weight loss was found to be 12 mg. per 30 seconds, or 0.4 mg. per second.

Transferring the sampling vessel from the liquid nitrogen refrigerator to the scale and then pouring its contents into the counting Dewar together took an average time of 15 seconds. During sampling, the weighing step is eliminated; transferring the gas sample directly to the counting Dewar from the liquid nitrogen refrigerator takes an average of 8 seconds. Therefore, the seven seconds of extra time required to weigh the sample is subtracted from the combined weigh and transfer time of 15 seconds. This would account for 2.8 mg. of weight loss (7 sec. X 0.4 mg.) which, subtracted from the experimentally found mean weight loss of 20.8 mg. (Table 2), projects an average weight loss during routine testing of approximately 18 mg. or 4.7%. From previous work[1], a 3%-5% weight loss during sample transfer was consistently recorded. The 4.7% weight loss in this study compares favorably with those results.

Other tests were performed to check the precision of concentration measurements in repeated sampling. A sample of pure Kr^{85} was introduced into a large cylinder and diluted with nitrogen to a concentration that could be counted using a Canberra Series 30 Multi-Channel

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[1]Perdue, P.T., and F. F. Haywood, "The Use of Cryogenic Air Sampling in the Spectroscopy of Airborne Gamma-Ray Emitters," Second International Conference on Low-Level Counting, 24-28 November, 1980, High Tatras, Strbske Pleso, Czechoslovakia.

Analyzer. A total of five samples were then pulled, using a 3:1 ratio of ambient air and the $K^{r}8^{5}$ and N2 mixture, at flow rates from 0.8 to 1.0 liters per minute for a period of 30 minutes per test. Flow rates during the first test drifted from 1.0 to 0.81 liters per minute, for an average of 0.91 LPM. Total gas collected during this first test was 24.3 liters over a period of 30 minutes, yielding 134 counts per minute or 5.5 counts per liter of gas. The other 4 tests were conducted using the same sampling ratios. Results are shown in Table 2.

DISCUSSION AND CONTINUING DEVELOPMENTS

Some advantages of cryogenic sampling are that: (1) the cryogenic sampler is portable, (2) the sampler requires no electrical power for operation under ambient conditions, (3) the sampler can collect a constant, continuous gas sample for up to 10 hours, (4) the sampler collects a "complete" gas sample (all the gases in the sample are collected), (5) development and operation of the sampler is relatively inexpensive, and (6) this method is capable of measuring noble gas concentrations in off-gas streams at a factor of 30 or more below the maximum permissible concentrations.[2]

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[2]Perdue, P.T., and F. F. Haywood, "The Use of Cryogenic Air Sampling in the Spectroscopy of Airborne Gamma-Ray Emitters," Second International Conference on Low-Level Counting, 24-28 November, 1980, High Tatras, Strbske Pleso, Czechoslovakia.

It should be noted that as a liquified gas sample evaporates the concentration of oxygen in the sample increases. This increased oxygen may create a potentially explosive atmosphere. Another problem inherent to the use of this equipment is formation of ice in the neck of the sampling vessel which, if left unchecked, might completely close the opening and cause a buildup of pressure sufficient to burst the vessel.

TABLE 1: LOSSES ON TRANSFER OF LIQUID GAS FROM SAMPLER TO DEWAR

	Counting Dewar		Wt.	Sampling Vessel		Wt.	Net	Wt.
	Pre. Wt.	Post Wt.	Gain	Pre. Wt.	Post Wt.	Loss	Loss	Loss
	mg	mg	mg	mg	mg	mg	mg	%
1.	2753	3055	302	746	1062	316	14	4.4
2.	2680	3022	342	746	1106	360	18	5.0
3.	2632	2980	348	746	1117	371	23	6.2
4.	2367	2858	491	746	1262	516	25	4.8
5.	2302	2762	460	746	1232	486	26	5.4
6.	2329	2695	366	746	1133	387	21	5.4
7.	2168	2592	424	746	1192	446	22	4.9
8.	2140	2532	392	746	1159	413	21	5.1
9.	2481	2806	325	746	1088	342	17	5.0
10.	2502	2764	262	746	1025	279	17	6.1
11.	2423	2728	305	746	1068	322	17	5.3
12.	2440	2687	247	746	1008	262	15	5.7
13.	1856	2389	533	746	1314	568	35	6.2
14.	2389	2728	339	746	1106	360	21	5.8
15.	2728	3005	277	746	1043	297	20	6.7

Average Wt. Loss = 20.8 mg

Average % Wt. Loss = 5.5%

TABLE 2: RESULTS OF REPEATABILITY TESTS

Test No.	Average Flow Rate, lpm	Total Liters of Gas	Counts per Minute	Counts per Liter per Min.
1	.905	24.3	134	5.5
2	.97	29.1	150	5.2
3	.80	24.0	132	5.5
4	.80	24.0	130	5.4
5	.80	26.3	142	5.4

the vessel if it is removed from the liquid nitrogen bath; and the potential radiation hazard due to the concentration in the sampling vessel of any radioactive gas by a factor of about 700.

Work is progressing to establish counting efficiencies for the Marinelli Dewar geometry, to be used with the high resolution gamma-ray spectrometer (GeLi). These counting efficiencies will be used to convert counts per minute to total isotopic activity in the sample. Upon the successful completion of the aforementioned work, cryogenic sampling will commence at ORNL.