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**EVALUATION OF THE INEL PASSIVE CRYOGENIC
WHOLE AIR SAMPLER**

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Abstract

This report documents the results of an evaluation of a portable, passive cryogenic sampler designed for the collection of whole air samples without loss or concentration of any atmospheric constituents. The design criteria included:

- a) Sample volume capacity greater than 100 liters STP.
- b) No concentration or loss of atmospheric constituents.
- c) No vertical dimension greater than 50 cm or horizontal dimension greater than 15 cm.
- d) Operation without electrical power.
- e) Sampling lifetime greater than two hours.
- f) Total gross weight less than 20 kg.
- g) Resistance to undetected tampering.

The sampler described in this report has been found to meet or exceed the design criteria once safety-related add-ons (rotameter, pressure relief valves, and base-plate) are either removed or redesigned for a smaller profile.

Introduction

This report documents the results of an evaluation of a portable, passive cryogenic sampler designed for the collection of whole air samples without loss or concentration of any atmospheric constituents. The principle of operation of the sampler is the collection of the whole air sample into a previously evacuated sample cylinder immersed in a liquid nitrogen filled reservoir. Design criteria for the portable, passive cryogenic whole air sampler include the following characteristics:

- 1) A total sample volume of 100 liters at STP.
- 2) No concentration or loss of any atmospheric constituents.
- 3) No vertical dimension greater than 50 cm or horizontal dimension greater than 15 cm.
- 4) Operation without electrical power.
- 5) A sampling lifetime greater than two hours.
- 6) A total gross weight less than 20 kgs.
- 7) Resistance to undetected tampering.

The cryogenic air sampler, constructed in-house of readily commercially available components, is shown in Figure 1. Specific components of the sampler, numbered in the same manner as Figure 1, are as follows:

- 1) A Matheson 24.75-cm tall x 3.2-cm wide rotameter equipped with a flow control valve, a 602 tube, and glass and stainless steel floats for measurement of sample flowrate.
- 2) A Whitey DK Series No. 14DKM4-S4 forged body stainless steel shutoff valve with a 4.0-mm orifice and dimensions of 5.4-cm x 5.8-cm for sample introduction and isolation. The valve is linked to the rotameter by 14.4-cm length of 0.63-cm stainless steel tubing.
- 3) A 5.4 x 2.7-cm female tee joint manufactured by CAJON (No. 4-T) with a pressure rating of 6900 psig.
- 4) A 15.2-cm long stainless steel hexagonal nipple manufactured by CAJON (No. 4-HLN) with a pressure rating of 7500 psig.

Figure 1. Passive Cryogenic Sampler.

- 5) A Cajon (No. 304L-HDF4-500) 500-cc internal volume stainless steel cylinder for the collection of the whole air sample. Dimensions of the sample cylinder are 35.6-cm long x 5.1-cm outside diameter x 0.277-cm wall thickness. The pressure rating of the cylinder is 1800 psig and the DOT classification is 3E-1800. The end of the cylinder near the base of the sampler is closed by a male stainless steel pipe plug.
- 6) An approximately 2.7 liter internal volume liquid nitrogen reservoir for cooling of the sampler cylinder. The reservoir is constructed of two sections of stainless steel pipe positioned concentrically and separated at the walls by a 0.95-cm thick layer of Rubatex insulation. The inner section is welded to a 12.7-cm diameter x 0.32-cm thick stainless steel plate; the outer section is welded to the base of the sampler, Item 7 below. Dimensions of the outer section are 12.7-cm outside diameter x 45.7-cm long x 0.32-cm thick. Dimensions of the inner section are 10.2-cm outside diameter x 44.5-cm long x 0.32-cm thick.
- 7) A 25.4-cm square by 0.64-cm thick stainless steel sampler base. The base is insulated from the liquid nitrogen reservoir by 2.54-cm of Rubatex insulation.
- 8) A 12.7-cm diameter by 1.27-cm thick stainless steel lid for the liquid nitrogen reservoir. The lid is secured to the liquid nitrogen reservoir by three steel spring loaded latches.
- 9) A section of 0.64-cm diameter stainless steel tubing for the addition of liquid nitrogen during sample collection. The tube is welded to the lid of the liquid nitrogen reservoir and extends 5.6-cm above and below the lid.
- 10) A NUPRO (No. 4C) fixed setpoint pressure relief valve for venting of the liquid nitrogen reservoir. The setpoint of the valve is 3 psi. The valve is 6.1-cm in length and is mounted on a 3.8-cm length of 0.64-cm stainless steel tubing. Overall, the valve assembly extends 15.2 cm above the lid of the liquid nitrogen reservoir.
- 11) A NUPRO (no. SS-4R3A-316) variable setpoint pressure relief valve for venting the sample cylinder. The setpoint range of the valve is 750-5000 psi. The valve is 10.5-cm in length and is mounted above the tee joint. The relief valve was incorporated as a safety precaution in the event of excessive pressure buildup in the sample cylinder. In the event of such an occurrence, the pressure relief valve only vents the pressure in excess of the setpoint prior to reclosure. As a result, only a small portion of a sample is lost. The loss may nonetheless result in a non-representative sample.

The sampler evaluation was performed in three phases. The first phase determined sample flowrate, sample size, resultant sample pressure, and sample collection lifetime as a function of the liquid nitrogen additions. The second phase analyzed simulated whole air samples for bulk composition, noble gases, selected chlorofluorocarbons, and tritium before and after collection in the cryogenic air sampler. The third phase collected actual field samples; direct analyses of the samples for bulk composition and chlorofluorocarbon content; and concentration, separation and analysis of noble gases in the samples. Also included in the third phase was the analysis of altered whole air samples, blindly and randomly introduced into the sample analysis scheme as a means of detecting of sample tampering.

Experimental Testing and Results

Sampler Operation: Operation of the sampler consists of preparation of the sampler, collection of the sample, direct sampling and analysis of the contents of the sampler, and transfer of the sample to a sample storage container for subsequent analysis.

The sampler is prepared by evacuating the cylinder. After pumping for 10 minutes, a heat gun is used to warm the sampler cylinder for 20 minutes. Pumping is continued for another 20-25 minutes after heating and the sample cylinder is isolated by closing the sample introduction valve. Then the liquid nitrogen reservoir is filled through the lid opening. The sample cylinder is immersed in the liquid nitrogen, and the liquid nitrogen reservoir is then topped off.

Sampling is begun by opening the sample inlet/sample isolation valve and adjusting the flowrate. The flowrate is periodically monitored. If the flowrate drops below the desired level, the liquid nitrogen reservoir is refilled to maintain the sample cylinder at a temperature of 77°K. Maintaining the sample cylinder at the temperature of liquid nitrogen is required to keep reduced pressure in the sample cylinder and to provide the driving force for collection of the whole air sample. The number of times the liquid nitrogen reservoir must be filled is dependent upon the desired sample flowrate, sample volume, and sample collection lifetime.

Following the collection of the desired size sample or the desired period of time, collection is terminated by closing the sample inlet/sample isolation valve. The sampler is then allowed to return to ambient temperature. The actual volume of the sample is determined by weight. Independently, the sample volume is determined by measurement of the final pressure within the sample cylinder with an external pressure gauge and a previously determined sample cylinder pressure versus sample volume curve. Dependent upon the desired analysis, the contents of the sample cylinder are sampled directly for analysis by the use of a pressure regulator and a small sample bulb or transferred for subsequent analysis to an 8 liter sample storage cylinder.

Sample Flowrate Measurements: A series of tests were conducted to measure the stability of the flowrate with time. For these tests, the sampler was prepared and sample collection was started as described above. During the test the flowrates were measured with the sampler rotameter and periodically recorded. Tests were conducted for both single and multiple additions of liquid nitrogen to the liquid reservoir.

For the first block of tests using single additions of liquid nitrogen to the reservoir, the initial flowrate was between 3.28 and 3.38 L/min. Within 2 to 4 minutes, the flowrate stabilized after a decrease to around 1.1 L/min. The flowrate remained near constant at a value of approximately 1 L/min for 35 minutes. The flowrate then gradually decreased to a value of 0.12 to 0.3 L/min after an hour or of sample collection. Individual test data are shown in Table 1.

For the second block of tests using 2 additions of liquid nitrogen to the reservoir, the flowrate increased to between 0.79 and 1.07 L/min after the second addition. The flowrate then decreased at a much slower rate to around 0.5 L/min at 20 minutes. The flowrate gradually decreased to a value near 0.2 L/min at the end of an hour. Individual test data are shown in Table 2.

For the third block of tests using 3 additions of liquid nitrogen to the reservoir, in general, the decrease in the flowrate is less pronounced. From an initial value of between 0.5 and 0.7 L/min after the third addition, the flowrate decreased to about 0.12 to 0.20 L/min over an hour. Individual test data are shown in Table 3.

Sample Volume and Lifetime Measurements: A series of 18 tests were conducted to establish the relationship of the volume of sample collected versus length of sampling time and number of liquid nitrogen additions to the reservoir. For these tests, the sampler was again prepared and sample collection was started as described above. The weight of sample collected was determined directly by weighing the cryogenic air sampler before and after collection. From the net weight of the sample, the volume of sample collected was then calculated from the density of air at standard conditions. In the 18 tests, the liquid nitrogen reservoir was filled 2 times in 11 of the tests, 3 times in 5 of the tests, and 4 times in 2 of the tests. Individual test data are shown in Table 4.

For tests of 2 additions to the liquid nitrogen reservoir, the volumes of samples collected in general increased with sample lifetime. Excluding samples of known sample venting, the volumes of samples increased from 68.8 liters (1.25 hour) to 119.2 liters (2.27 hour) and then decreased to 40.7 liters (3.00 hour). This data indicate the maximum sample lifetime with the current sampler configuration is on the order of 2 to 2.5 hours. A sample lifetime of this order will yield samples of the desired size, nominally 100 liters. A sample lifetime of greater duration will yield a smaller volume sample due to sample venting.

TABLE 1

Flowrate Measurements of Passive Cryogenic Sampler
- Single Liquid Nitrogen Refill -

<u>Block/Test Number</u>	<u>Flowrate (Liters/Minute)</u>	<u>Time In (Minutes)</u>
1/1	3.38	0
	1.51	1
	1.11	6
	1.01	12
	1.03	18
	0.97	34
	0.83	42
	0.68	50
	0.52	56
	0.34	61
1/2	3.34	0
	1.59	1
	1.18	7
	1.07	18
	1.03	37
	0.92	48
	0.72	58
	0.43	63
	0.17	65
1/3	3.32	0
	1.57	1
	1.15	3
	1.03	20
	0.75	55
	0.64	60
	0.47	65
	0.27	69
1/4	3.29	0
	1.01	25
	0.67	56
	0.50	63
	0.40	66
	0.26	69
	0.14	71

TABLE 1 (Continued)

Flowrate Measurements of Passive Cryogenic Sampler
- Single Liquid Nitrogen Refill -

<u>Block/Test Number</u>	<u>Flowrate (Liters/Minute)</u>	<u>Time In (Minutes)</u>
1/5	3.33	0
	1.22	3
	0.99	35
	0.56	56
	0.14	64
1/6	3.30	0
	1.13	4
	1.00	24
	0.35	60
	0.12	65
1/7	3.32	0
	1.30	2
	1.07	27
	0.94	48
	0.40	59
	0.18	63
1/8	3.28	0
	1.19	3
	1.07	6
	0.87	48
	0.19	66
1/9	3.38	0
	1.36	2
	1.13	10
	0.94	41
	0.27	57
1/10	3.33	0
	1.47	2
	1.19	13
	0.84	46
	0.2	61

TABLE 2

Flowrate Measurements of Passive Cryogenic Sampler
- Second Liquid Nitrogen Filling -

<u>Block/Test Number</u>	<u>Flowrate Liters/Minute</u>	<u>Time In Minutes</u>
2/1	0.96	0
	0.86	2
	0.58	19
	0.46	35
	0.35	50
	0.25	58
	0.16	62
2/2	1.01	0
	0.91	2
	0.82	7
	0.73	12
2/3	0.96	0
	0.91	2
	0.85	7
	0.58	40
	0.43	52
	0.33	58
	0.28	60
	0.21	62
2/4	0.79	0
	0.65	8
	0.57	16
	0.54	20
2/5	1.03	0
	0.73	26
	0.16	56
2/6	0.98	0
	0.82	9
	0.62	30

TABLE 2 (Continued)

Flowrate Measurements of Passive Cryogenic Sampler
- Second Liquid Nitrogen Filling -

<u>Block/Test Number</u>	<u>Flowrate Liters/Minute</u>	<u>Time In Minutes</u>
2/7	1.00	0
	0.95	5
	0.74	31
	0.46	52
	0.16	60
2/8	0.91	0
	0.75	13
	0.41	49
	0.24	63
2/9	1.07	0
	0.99	6
	0.89	27
	0.60	49
	0.56	51
2/10	1.04	0
	0.76	22
	0.13	59

TABLE 3

Flowrate Measurements of Passive Cryogenic Sampler
- Third Liquid Nitrogen Filling -

<u>Block/Test Number</u>	<u>Flowrate Liters/Minute</u>	<u>Time In Minutes</u>
3/1	0.67	0
	0.55	4
	0.42	26
	0.25	46
	0.12	51
3/2	0.71	0
	0.60	14
	0.55	20
3/3	0.50	0
	0.42	12
	0.35	34
	0.28	50
	0.18	60
3/4	0.60	0
	0.48	9
	0.41	27

TABLE 4

Sample Volume and Lifetime versus Number
of Liquid Nitrogen Reservoir Additions

<u>Test Number</u>	<u>Sample Collection Time (Hours)</u>	<u>Liquid Nitrogen Fills</u>	<u>Air (Liters @ STP)</u>	<u>Net Mass (grams)</u>
1	1.25	2	68.8	89.0
2	1.35	2	78.9	102.0
3	1.43	2	107.2	138.5
4	1.48	2	83.9	108.5
5	1.52	2	77.7	100.5
6	1.60	2	85.1	110.0
7	1.97	2	107.2	138.5
8	2.15	2	79.3	102.5
9	2.27	2	119.2	154.0
10	2.33	2	105.3	136.2
11	3.00	2	40.7	52.6
12	2.20	3	97.1	125.5
13	2.50	3	85.9	111.0
14	2.58	3	78.4	101.5
15	2.62	3	75.4	97.5
16	3.42	3	89.2	115.4
17	2.73	4	57.3	74.0
18	3.00	4	70.3	90.8

Sample Pressure Measurements: The same series of 18 tests reported above was also used to determine the resultant pressure in the sample cylinder. Measurement of the final pressure within the sample cylinder was performed with an external pressure gauge. The pressure of the collected samples ranged from 900 to 3650 psi. The majority of the samples were in the 2050 to 2900 psi range. These data are shown in Table 5.

These pressure data allowed verification of the sample size data obtained from weights of the samples. In addition, the technique provides a convenient, rapid method for determining sample size in the field. The technique required calibration of the internal volume of the sampler using standard methods. Calculation of the weight of the sample from the known internal volume and temperature and the observed pressure of the sample can then be performed. Comparisons of sample volumes obtained both from the sample weight technique and the pressure technique are shown in Table 6. In most cases there is an excellent agreement between the calculated weight of the sample and the measured weight of the sample.

Laboratory Simulated Noble Gas Sample Measurements: A test was performed to evaluate possible alteration of bulk composition and noble gas content of laboratory prepared simulated noble gas samples during collection and analysis. The simulated sample was prepared by 10 fold dilution of a 5% krypton and 5% xenon in air commercial standard in an 8 liter cylinder. Following preparation, the standard was expanded into a Teflon sample bag. The sample was withdrawn from the bag into the cryogenic sampler and allowed to warm to ambient temperature. The collected sample was again transferred to a different Teflon bag. Small samples of the diluted mixture of the commercial standard were collected from the two Teflon bags and subsequently analyzed by gas mass spectrometry.

The results of the analysis are shown in Table 7. Presented are the bulk compositions, krypton isotopic ratios, and xenon isotopic ratios in the two samples before and after collection in the cryogenic sampler. As can be seen, agreement between the bulk composition is relatively good. The small differences are attributed to minor dilution of the sample during expansion into the Teflon bag. The agreement among isotopic measurements is excellent.

Actual Noble Gas Sample Measurements: A series of tests were performed to evaluate possible alteration of bulk composition and noble gas content of actual laboratory and field samples during collection and analysis. In these tests, the sampler was located either in the laboratory or at a field test site, the sampler was prepared as described previously, and the samples were collected for a predetermined period of time. The sampler was warmed to ambient temperature, returned directly to the laboratory for analysis, and expanded into an 8 liter sample storage cylinder prior to analysis.

TABLE 5

Sample Pressure Versus Liquid Nitrogen Additions

<u>Test Number</u>	<u>Time to Collect Sample (Hours)</u>	<u>Liquid Nitrogen Additions</u>	<u>Pressure (PSI)</u>
1	1.25	2	2200
2	1.35	2	3200
3	1.43	2	3500
4	1.48	2	2675
5	1.52	2	2475
6	1.60	2	2750
7	1.97	2	3600
8	2.15	2	2500
9	2.27	2	3650
10	2.33	2	2050
11	3.00	2	900
12	2.20	3	2550
13	2.50	3	2700
14	2.58	3	2500
15	2.62	3	2400
16	3.42	3	2800
17	2.73	4	1840
18	3.00	4	1680

TABLE 6
Calculated Versus Measured Sample Weights

<u>Test Number</u>	<u>Calculated Mass (grams)</u>	<u>Actual Mass (grams)</u>
1	90.4	89.
2	101.5	102.0
3	143.4	138.5
4	110.8	108.5
5	102.6	100.5
6	112.0	110.0
7	147.5	138.5
8	102.6	102.5
9	117.2	154.0
10	84.2	136.2
11	41.4	52.6
12	104.6	125.5
13	110.8	111.0
14	102.6	101.5
15	98.5	97.5
16	114.8	115.4
17	76.1	74
18	70.0	90.8

TABLE 7

Bulk Composition, Krypton Isotopic Ratios,
and Xenon Isotopic Ratios of Simulated Laboratory Samples
Before and After Collection

	<u>Prior To Collection</u>	<u>Following Collection</u>
Composition (%)		
Hydrogen	0.001	0.017
Nitrogen	77.401	78.719
Oxygen	21.548	20.321
Argon	0.076	0.093
Carbon Dioxide	0.017	0.020
Krypton	0.477	0.412
Xenon	0.480	0.412
Krypton Isotopic		
82/83	1.009	1.007
82/84	0.203	0.203
82/86	0.670	0.670
84/86	3.299	3.309
Xenon Isotopic		
129/130	6.490	6.555
129/131	1.245	1.246
129/132	0.982	0.983
129/134	2.525	2.536
129/136	2.973	2.988
131/132	0.789	0.789
131/134	2.028	2.035
131/136	2.388	2.398
132/134	2.570	2.579
132/136	3.027	3.040
134/136	1.178	1.178

In the laboratory, the noble gases are separated and concentrated prior to the measurement of their isotopic composition.

The separation system is prepared for sample introduction by regenerating the charcoal bed and the two molecular sieve columns at a temperature of 350°C for a period of 50-60 minutes. Then the three thermistors and their associated electronics are balanced at nominal helium flows.

Before introducing the sample, the system is evacuated and the precooler and charcoal bed are cooled with liquid nitrogen. Sample introduction takes approximately 80 minutes. The sample flowrate is controlled at 15 to 20 liters/minute and the pressure within the precooler and charcoal bed is maintained at 370-380 mm of mercury to avoid the formation of liquid oxygen. A strip recorder is used to monitor the elution, which typically takes 25-30 minutes. The recorder pen returns to the baseline when the elution is complete.

The transfer of the sample from the charcoal bed to the first molecular sieve column is accomplished by removing the methanol bath and replacing it with a clam shell heater (that has been preheated to 350°C). The first molecular sieve column is cooled with liquid nitrogen. Completion of the transfer takes 15-20 minutes and is indicated by the return of the recorder pen to baseline.

Separation takes place on the two molecular sieve columns. The separation entails sequential, temperature selective transfer of the krypton and xenon from the first to the second molecular sieve column, and then onto the small charcoal bed. The chart recorder indicates elution of the gases.

The transfer of the krypton from the first molecular sieve is accomplished by replacing the liquid with a methanol bath that is -7°C and decreases to -31°C. Argon and oxygen are released within 3 minutes and vented. Krypton elutes between 8 and 11 minutes and is transferred to the second molecular sieve. Nitrogen and methane elute between 14 to 19 minutes and are vented.

The transfer of the xenon is accomplished by replacing the methanol bath with a warm water bath that is 26°C and decreases to 23°C. Several gases are released and vented during the first 5 minutes. Xenon elutes in 9-12 minutes and is transferred to the second molecular sieve column. Shortly after the xenon elutes the carbon monoxide is released and vented. The transfer of the krypton and xenon from the second molecular sieve column to the small charcoal bed is accomplished in a similar manner. The liquid nitrogen on the second molecular sieve column is replaced with a methanol bath that is -7°C and decreases to -31°C. Liquid nitrogen is placed on the small charcoal bed. As before, argon and oxygen are released in 3 minutes and are vented. Krypton elutes in 8-11 minutes and is transferred to the small charcoal bed. The small charcoal bed is heated with a heat gun to transfer the krypton to the sample bulb, that is cooled with liquid nitrogen. The small charcoal bed must now be regenerated before the xenon can be collected.

For the transfer of xenon the methanol bath is replaced with a warm water bath that is 26°C and decreases to 23°C. Xenon elutes in 9-12 minutes and is transferred to the small charcoal bed. The small charcoal bed is heated with a heat gun to transfer the xenon to a sample bulb that is cooled with liquid nitrogen.

The noble gas isotopic composition of air samples collected in the laboratory with the passive cryogenic sampler have been measured. These data are shown in Table 8 and show excellent agreement.

In order to ensure that the numbers are indicative of noble gas values, two control samples were analyzed. These samples had spikes of 5% krypton and 5% xenon. The results obtained agree closely with the samples measured and are shown in Table 9.

Chlorofluorocarbons

The chlorofluorocarbons (CFCs) are analyzed by gas chromatography with electron capture detectors (ECD) with constant current electronics. ECD technology is extremely sensitive to polychlorinated molecules.

The system used was a J&W Scientific GS-Q column in a Varian 3700 GC equipped with an ECD. A HP-3390A reporting integrator was used to record the chromatograms. The calculated detection limit for the GC is 0.4 ppb Freon 11 and 4 ppb Freon 12. Nitrogen was used as the carrier gas. All CFCs were analyzed at a column temperature of 160°C (column flowrate of 6.80 53 mL/min and splits = 7.34 and 5.74). The detector temperature was set at 260°C. Syringe injections were made direct via the use of the splinter. The on-column method of injection was used. Runs were made for 5 minute time intervals. Uncertainties in the data were propagated to 95% confidence levels. Two CFCs of widely differing boiling points, chlorotrifluoromethane Freon 11 (23.8°C) and dichlorodifluoromethane Freon 12 (-29.8°C), were used in this test. A mixture was prepared by adding the CFCs to about 60 liters of instrument air in a Teflon bag and gently mixing the contents. Measurements established the concentration as being 1.43 ppm of Freon 11 and 27.1 ppm Freon 12. Syringe samples were taken over a several hour period and analyzed to ensure the concentration did not significantly decrease. In this manner it was possible to demonstrate that the CFCs remain stable for a time period of sufficient length to be accurately sampled and analyzed.

The tests samples gathered in the laboratory to evaluate CFC techniques were collected in a manner identical to that used for the noble gases. The sample cylinder was evacuated for 10 minutes. A heat gun was used to warm the sample cylinder while pumping was continued. After heating, pumping was continued for an additional 20 minutes before closing the inlet valve. The sample cylinder was then placed in the liquid nitrogen reservoir.

The sample was then drawn into the cryogenic sampler from the bag during a 2 hour interval. While the contents of the bag were being collected, 6 to 8 syringe samples were withdrawn from the bag and analyzed. The collected sample was allowed to warm to ambient temperature for at least 2 hours, expanded into a different clean 100 L bag, and analyzed by GC/ECD 6 to 8 times. This sequence was repeated three times. The results are shown in Tables 10 and 11. The recovery of Freon 11 was $96\% \pm 4\%$. The recovery of Freon 12 was $97\% \pm 4\%$.

TABLE 8
Noble Gas Isotopic Ratio Data

<u>Test Number</u>	<u>Krypton</u>	<u>Xenon</u>
1	82/83 = 1.009 82/84 = 0.204 82/85 = 13607 82/86 = 0.673 84/86 = 3.302	129/130 = 6.255 129/131 = 1.206 129/132 = 0.954 129/134 = 2.469 129/136 = 2.927 131/132 = 0.791 131/134 = 2.048 131/136 = 2.428 132/134 = 2.588 132/136 = 3.069 134/136 = 1.186
2	N/A	129/130 = 6.528 129/131 = 1.257 129/132 = 0.996 129/134 = 2.587 129/136 = 3.071 131/132 = 0.792 131/134 = 2.058 131/136 = 2.444 132/134 = 2.598 132/136 = 3.084 134/136 = 1.187
3	82/83 = 1.008 82/84 = 0.203 82/85 = 3863 82/86 = 0.671 84/86 = 3.297	129/130 = 6.508 129/131 = 1.255 129/132 = 0.994 129/134 = 2.578 129/136 = 3.059 131/132 = 0.792 131/134 = 2.054 131/136 = 2.437 132/134 = 2.593 132/136 = 3.077 134/136 = 1.187
4	82/83 = 1.008 82/84 = 0.203 82/85 = 3863 82/86 = 0.671 84/86 = 3.297	129/130 = 6.382 129/131 = 1.254 129/132 = 0.006 129/134 = 2.574 129/136 = 3.050 131/132 = 0.794 131/134 = 2.052 131/136 = 2.431 132/134 = 2.584 132/136 = 3.062 134/136 = 1.185

TABLE 9**Noble Gas Natural Standard Data**

<u>Test Number</u>	<u>Krypton</u>	<u>Xenon</u>
1	82/83 = 1.001	129/130 = 6.500
(5% Spike Kr, Xe)	82/84 = 0.201	129/131 = 1.249
	82/86 = 0.654	129/132 = 0.986
	84/86 = 3.256	129/134 = 2.545
		129/136 = 3.008
		131/132 = 0.790
		131/134 = 2.038
		131/136 = 2.049
		132/134 = 2.580
		132/136 = 3.049
		134/136 = 1.182
2	82/83 = 1.004	129/130 = 6.496
(5% Spike Kr, Xe)	82/84 = 0.202	129/131 = 1.248
	82/86 = 0.659	129/132 = 0.985
	84/86 = 3.267	129/134 = 2.541
		129/136 = 3.001
		131/132 = 0.790
		131/134 = 2.036
		131/136 = 2.405
		132/134 = 2.578
		132/136 = 3.046
		134/136 = 1.181

A mass balance was performed on the total gas sample during the third run. The total volume of mixture prepared was 57.089 liters. After cryogenic sampling, 6.494 liters remained in the bag. The quantity of gas expanded from the 0.494 liter cryogenic sampler was 50.745 liters. This yields a volume recovery of approximately 100%. The results of these tests suggest that CFCs which are nonreactive can be collected successfully by the cryogenic sampler with a recovery of $95\% \pm 4\%$.

Tritium

A series of 4 tests were performed to evaluate the recovery of tritium from laboratory samples following collection in the cryogenic sampler. The test tritium samples were prepared by the addition of tritium in the form of HT to a Teflon sample bag to a known concentration. During the tests, the tritium concentration in the sample bag was verified by measurements at two minute intervals for a period of 20-30 minutes by means of an ionization chamber. The cryogenic sampler was then prepared as described previously and the tritium mixture was transferred to the cryogenic sampler. The cryogenic sampler was then allowed to return to ambient temperature and the tritium mixture was transferred back to the Teflon sample bag for remeasurement of the tritium concentration in the same manner. The results for the 4 tests are listed in Table 12.

TABLE 10

Fractionation of CFC-11

Run	Concentration		Recovery (%)
	Before (ppm)	After (ppm)	
1	4.01 ± 0.30	4.23 ± 0.23	105.5 ± 9.8
2	2.59 ± 0.13	2.48 ± 0.12	95.8 ± 6.7
3	1.81 ± 0.05	1.64 ± 0.07	90.6 ± 4.6
MEAN			97.3 ± 4.2

TABLE 11

Fractionation of CFC-12

Run	Concentration		Recovery (%)
	Before (ppm)	After (ppm)	
1	24.5 ± 1.5	24.5 ± 0.8	100.0 ± 6.9
2	16.3 ± 0.9	16.0 ± 0.7	98.2 ± 6.9
3	19.0 ± 0.7	17.3 ± 0.5	91.1 ± 4.3
MEAN			96.4 ± 3.6

Uncertainties are propagated to 95% Confidence Level.

TABLE 12
Tritium Recovery Experiments

<u>Experiment 1</u>			
<u>Before Collection</u>		<u>After Collection</u>	
<u>Elapsed Time</u>	<u>Concentration</u>	<u>Elapsed Time</u>	<u>Concentration</u>
<u>(min)</u>	<u>($\mu\text{Ci}/\text{m}^3$)</u>	<u>(min)</u>	<u>($\mu\text{Ci}/\text{m}^3$)</u>
0	22.8	0	19.3
1	22.7	2	18.6
5	21.1	4	19.4
7	22.1	6	19.3
9	21.8	8	18.5
12	22.0	10	19.0
14	22.6	12	19.0
16	22.4		
18	22.5	Mean	19.0
19	21.2	Std. Dev.	0.35
21	21.3		
23	22.6		
25	21.4		
27	22.2		
28	22.0		
30	22.4		
Mean	22.1		
Std. Dev.	0.56		

TABLE 12 (Continued)
Tritium Recovery Experiments

<u>Experiment 2</u>			
<u>Before Collection</u>		<u>After Collection</u>	
<u>Elapsed Time</u> <u>(min)</u>	<u>Concentration</u> <u>($\mu\text{Ci}/\text{m}^3$)</u>	<u>Elapsed Time</u> <u>(min)</u>	<u>Concentration</u> <u>($\mu\text{Ci}/\text{m}^3$)</u>
0	51.1	0	45.9
2	50.6	2	46.0
4	51.2	4	46.1
6	50.9	6	45.2
8	50.8	8	44.9
10	50.8	10	45.2
12	50.7	12	44.8
14	50.1	14	45.3
16	51.0	16	45.2
18	50.3	20	45.5
20	50.7	22	45.9
22	50.3	24	45.3
24	<u>50.8</u>	26	44.8
		28	<u>44.8</u>
Mean	50.70	Mean	45.40
Std. Dev.	0.32	Std. Dev.	0.46

TABLE 12 (Continued)
Tritium Recovery Experiments

<u>Experiment 3</u>			
<u>Before Collection</u>		<u>After Collection</u>	
<u>Elapsed Time</u> <u>(min)</u>	<u>Concentration</u> <u>(uCi/m³)</u>	<u>Elapsed Time</u> <u>(min)</u>	<u>Concentration</u> <u>(uCi/m³)</u>
0	112.6	0	111.2
2	112.0	2	110.5
4	112.0	4	110.8
6	112.4	6	110.0
8	112.7	8	109.9
10	112.4	10	109.3
12	112.2	12	109.1
14	112.9	14	108.9
16	112.8	16	109.4
18	112.7	18	109.4
20	<u>111.9</u>		
Mean	112.40	Mean	109.85
Std. Dev.	0.35	Std. Dev.	0.77

TABLE 12 (Concluded)
Tritium Recovery Experiments

<u>Experiment 4</u>			
<u>Before Collection</u>		<u>After Collection</u>	
<u>Elapsed Time</u> <u>(min)</u>	<u>Concentration</u> <u>(uCi/m³)</u>	<u>Elapsed Time</u> <u>(min)</u>	<u>Concentration</u> <u>(uCi/m³)</u>
0	48.4	0	45.3
2	48.1	2	45.6
4	47.8	4	45.8
6	47.0	6	44.9
8	47.1	8	45.4
10	46.9	10	45.5
12	46.9	12	45.3
14	47.1	14	44.9
16	46.7	16	45.2
18	46.4	18	45.7
20	46.8	20	45.5
22	46.6	22	45.0
24	46.1	24	45.3
26	46.8	26	45.1
28	46.0	28	45.3
30	46.3	30	44.9
Mean	112.40	Mean	45.30
Std. Dev.	0.35	Std. Dev.	0.28

Recommendations and Conclusions

In this study we evaluated a portable, passive cryogenic sampler for atmospheric monitoring. We have found the sampler to meet or exceed all of the design specifications.

The sampler is capable of the collection of samples without concentration or loss of any sample constituents regardless of boiling point. A summary of the conclusions are as follows.

- 1) The sample volume of 100 L at STP has been successfully achieved. Samples as large as 131.2 L have been collected. Most samples are between 70 and 90 L. The volume of sample collected is dependent upon the sample duration and flowrate. By selection of the proper combination of sample duration and flowrate, samples of accurately known size from a few to nominally 100 liters may be collected unattended within 30 minutes or over a period of time of 2 hours.
- 2) All sampler components utilized in this work are rated for 1800 PSI or greater pressure. The maximum pressure within the sampler is limited by adjustment of a variable setpoint sample cylinder pressure relief valve. In the event of the release of the pressure relief valve, typically, only a small portion of the sample is lost, as the pressure relief valve is set to vent only pressures in excess of 3200 psig prior to reclosure. The loss may nonetheless result in a nonrepresentative sample.
- 3) Laboratory tests on known standards demonstrate that no concentration or loss of atmospheric constituents occurs.
- 4) No electrical power is required for operation of the sampler, which would enable it to operate in hazardous environments such as where potentially explosive mixtures of hydrogen and oxygen are found.
- 5) The sampling lifetime can extend to 4 hours with refilling of the liquid nitrogen reservoir. In practice 2 or 3 fillings of the reservoir are necessary in the field for a collection over 2 hours. Our field sampling program has found through repeated collections that a 30 minute sampling time is sufficient to collect approximately 2400 PSI in the sample cylinder. This represents a sample in excess of 75 liters which is adequate for most analysis.

A summary of the recommendations are as follows.

- 1) A recommendation is made that the sampler be redesigned with a 5000 PSI sample cylinder. This would reduce the risk of reaching the bursting pressure of the cylinder during sample collection. The strengthened sample cylinder would also allow a larger volume (STP) sample to be collected.
- 2) During the redesign, efforts could be made to decrease the maximum vertical and horizontal dimensions of the sampler, resulting in a more compact, field portable package.

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