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CHARACTERIZATION OF STACK EFFLUENTS FROM CERTAIN NUCLEAR FACILITIES

Final Report

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ABSTRACT

Nuclear power reactors produce copious quantities of several species of permanent gas radioactivity, some directly by fission and others by neutron activation of reactor materials and coolants. The gaseous effluents from a boiling-water reactor (BWR), two pressurized light-water reactors (PWR), a high-temperature gas-cooled reactor (HTGR) and a pressurized heavy-water research reactor (PHWR) have been analyzed for radioactive and stable constituents. In the case of the BWR, direct stack sampling has insured representative sampling. The PWRs, HTGR and PHWR do not provide for direct stack sampling, so analyses of hold-up tank gas, pressure-vessel gas, cover gas, primary-coolant strip-gas, and containment air were required to derive characteristic patterns of gas releases from these reactors.

Gamma-emitting gaseous species were measured spectrometrically using a Ge(Li) detector. Chromatographic separation of various gas fractions on a series of molecular sieve columns permitted the use of internal gas-proportional counting tubes for spectrometric resolution of beta-emitting gas species.

In addition to measurement of gamma-emitting noble gases, ^{3}H (as hydrogen gas and methane), ^{14}C (as methane and carbon dioxide), ^{37}Ar and ^{39}Ar have been quantitatively identified. Higher hydrocarbon, carbon monoxide and methyl iodide fractions in the gaseous effluents contained only very low quantities of radioactivity.

This report provides estimates of total annual release of the several species, relative release rates as compared to control requirements, and estimates of long-range transport of ^{37}Ar as compared to atmospheric measurements performed by other laboratories.

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Characterization of Stack Effluents from Certain Nuclear Facilities

1. INTRODUCTION

Noble gas releases from nuclear facilities are usually monitored routinely by the facility operator to insure against an excessive external (submersion) dose to the population living in the environs of the facility. Facility measurement systems are therefore designed to measure gamma-emitting radiogases. Some facilities also collect water vapor from the gas stream in order to measure releases of tritiated water.

The Radiological Sciences Laboratory of the New York State Department of Health has conducted a study of the gaseous effluents from various types of reactors, searching particularly for radiogases which would not be measured by normal plant effluent monitoring but which might contribute to the total off-site dose or to atmospheric permanent gas measurements. Gas samples were obtained from a boiling-water reactor (BWR), two pressurized light-water reactors (PWR), one high-temperature gas-cooled reactor (HTGR) and a pressurized heavy-water research reactor (PHWR) in order to determine the levels of noble gases, tritium, ^{14}C and other radionuclides normally not measured by routine reactor-monitoring techniques.

Certain noble and permanent gases, particularly ^{37}Ar and tritium, have found increasing use as atmospheric tracers [1-3]. A number of these gases are released by certain reactors in sufficient quantities to influence atmospheric measurements, particularly if the collection locations are near the release sites.

This report presents activity ratios for the several species in gaseous reactor effluents, the estimated annual release levels of the several nuclides of interest and projections of potential release levels for larger reactors.

The original program included an effort to study the gaseous effluents from a nuclear fuel reprocessing plant. Unfortunately, fuel reprocessing gases were not available due to a temporary shutdown of the only operating commercial fuel reprocessing plant in the United States during the time this study was conducted. There are no commercial fuel reprocessing plants operating in the United States at the time this report is being written.

The unavailability of convenient, operating nuclear fuel reprocessing facilities precluded meaningful measurements of $^{238,239}Pu$ and $^{235,238}U$ measurements or vapor phase collections. Analyses for these radionuclides were attempted on reactor samples, but release rates from the reactors proved too low for measurement for all but ^{131}I and the tritium species. Though HT releases from the reactors proved consistent, the HTO releases were highly variable.

Gas samples from a small research PHWR were added to the study. This reactor is hopefully of sufficient size to provide information on the permanent gas releases to be expected from heavy-water moderated power reactors. These results are included with the discussion concerning the U. S. power reactor releases.

Measurements for $^{14}CO_2$, ^{14}CO, $^{14}C_2H_6$, $^{14}C_3H_8$, C_2H_5T and C_3H_7T were also added, though they were not part of the proposed study. Only the $^{14}CO_2$ measurements provided any meaningful information.

The facility operating staffs have been very helpful in providing samples and information concerning plant operations.

2. EXPERIMENTAL PROGRAM

2.1 Sample Collection

Samples were collected directly from the stack of the BWR. The PWR samples, collected from a variety of locations, included pressure-tank or cover gas, dissolved gas in the primary coolant (strip gas), decay-tank gas and containment air.

Samples received from the HTGR have consisted of the off-gas from regeneration of two cryogenic charcoal beds used to purify the helium primary coolant.

The set of samples from the PHWR were collected from the pressure vessel.

Sample containers (Figure 1) used in this study varied according to the collection facilities available at each reactor. If flow-through samples could be collected, conventional 30-ml, 125-ml or 1,000-ml gas-sampling containers were filled to pressures from one to three atmospheres. Otherwise, the 14-ml or 125-ml, rubber-capped septum vials were filled through a hypodermic needle, as is conventionally done at most power reactor facilities. Containment air was collected in a 15-liter stainless steel container. To permit measurement of even minor constituents, the largest possible sample was collected, limited only by the activity level that the facility health physics staff would permit off site. The collection volumes corresponding to various activity levels were: 16-liter stainless steel vessel (least active gaseous radionuclide $<10^{-6}$ μCi/ml), 1-liter stainless steel vessels ($<10^{-4}$ μCi/ml), and 125-ml and 30-ml glass gas-collection bulbs ($>10^{-3}$ μCi/ml), and 125-ml or 14-ml septum bottles ($>10^{-3}$ μCi/ml). Collection in the rubber-capped septum vials was avoided as much as possible because leakage often caused large sample losses.

2.2 Sample Processing

Immediately upon receipt at the Laboratory, an aliquot of the sample was counted on a Ge(Li) spectrometry system for identification and measurement of gamma-emitting gaseous radionuclides.

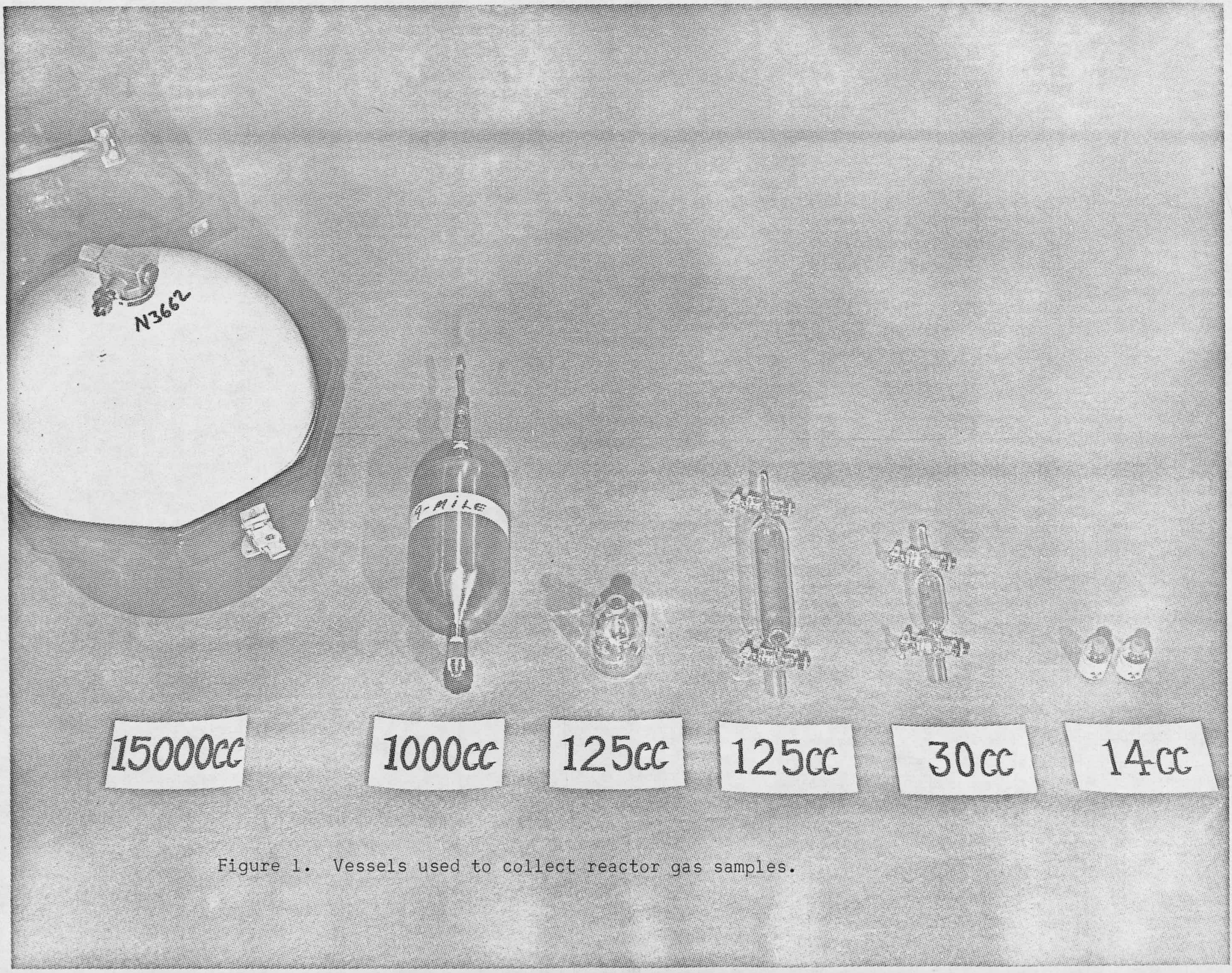

Figure 1. Vessels used to collect reactor gas samples.

An aliquot of the sample was also taken for mass spectrometric analysis to determine the composition of the gas. A few examples of such analyses of gases sampled from various locations in each of the reactors are shown in Table 1. The composition, which can vary considerably from sample to sample, influenced the choice of a separation procedure. The mass spectrometric analyses confirmed the presence of higher hydrocarbons, which were subsequently measured for possible ^{14}C or tritium activity. It was also necessary to insure that none of the gases being separated were present in sufficient amounts to affect chemical recovery.

The concentrations of most of the radioactive gases in the sample were far too low for the normal methods of chemical analysis. Measured amounts of carriers were therefore added. The radiochemical recovery of the separated gas was determined by comparing the volume finally loaded into a proportional tube for counting with the total amount of gas present before separation.

The range of the specific activity from sample to sample was greater than five orders of magnitude, depending on the reactor and sampling locations. The activities of various nuclides in individual samples differed in activity by approximately seven orders of magnitude. Consequently, precautions had to be taken to prevent cross-contamination from sample to sample and between different radioactive gases within a sample. Sample aliquots from about 0.1 ml to several liters were processed, depending on the activity of the gases being analyzed.

Sample volumes less than 10 ml were separated directly by chromatographic methods. Larger samples were processed using cryogenic-adsorption techniques for rough separation followed by chromatographic purification. Processing requirements imposed by gas composition were taken into consideration.

Table 1. Gas composition of samples from various reactors (vol %).

Gas	BWR stack gas	PWR(I) decay tank	PWR(II) decay tank	PWR(II) containment air	HTGR decay tank	PHWR cover gas
N_2	68.79	7.61	79.14	78.83	10.88	0.22
O_2	21.41	0.17	0.04	20.09	1.10	0.02
Ar	0.80	0.08	0.17	0.92	0.14	-----
CO_2	0.11	0.04	0.11	0.20	0.12	-----
H_2	8.89	91.82	18.76	-----	0.07	-----
He	-----	-----	-----	-----	87.69	99.76
CH_4	-----	0.14	0.19	-----	-----	-----
C_2H_6	-----	ID[a]	0.02	-----	-----	-----
C_3H_8	-----	ID[a]	-----	-----	-----	-----
H_2O	-----	0.07	0.87	-----	-----	-----

[a] Mass peak identified, but too low for quantification.

2.2.1 General Separation Procedure

Figure 2 indicates the general procedure for processing the samples. If a sample (such as cover gas or decay-tank gas) was relatively high in total specific activity and if the concentration of the lowest-activity gas fraction was higher than approximately 5 x 10^{-6} μCi/ml of sample, less than 10 ml of sample was processed. The sample was mixed with carriers and injected directly into a chromatograph reserved for high-activity samples. The separated fractions were trapped; those relatively high in activity were measured for chemical recovery and loaded into proportional tubes for counting. The trapped gases that were relatively low in activity (in general, <10^{-4} μCi in each separated fraction) were sent through another gas chromatograph for further purification and decontamination. The gases trapped from this intermediate-level chromatograph were measured for chemical recovery and loaded into gas-proportional counting tubes using a gas-handling rack reserved for the intermediate- to low-activity fractions. Segregation of systems was necessary to minimize cross-contamination.

Samples (such as containment air) that were relatively low in specific activity and contained gas fractions with activity less than approximately 5 x 10^{-6} μCi/ml had to be processed in aliquots of one or more liters. These samples underwent concentration and rough separation prior to chromatographic purification. Because of the volume reduction caused by the rough separation, some fractions developed high specific activity, though others remained relatively low. The high-activity fractions and the intermediate-activity fractions were chromatographically purified as described above prior to being loaded for counting.

2.2.2 High-Activity Samples

Figure 3 is a schematic drawing of the gas-handling vacuum rack used for processing samples of less than about 10 ml of gas having relatively high specific activity.

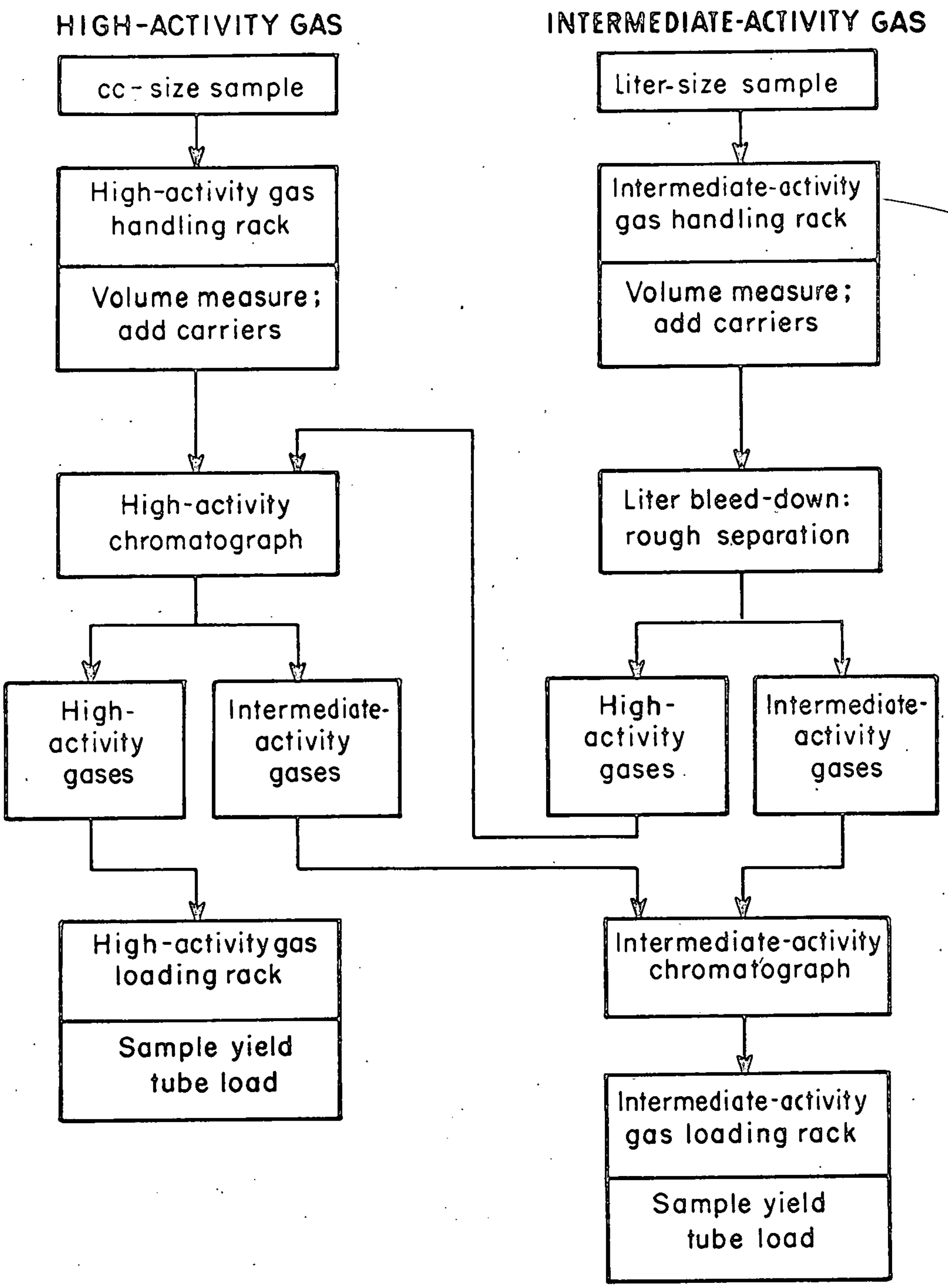

Figure 2. Processing procedure for high-activity and intermediate-activity gas samples.

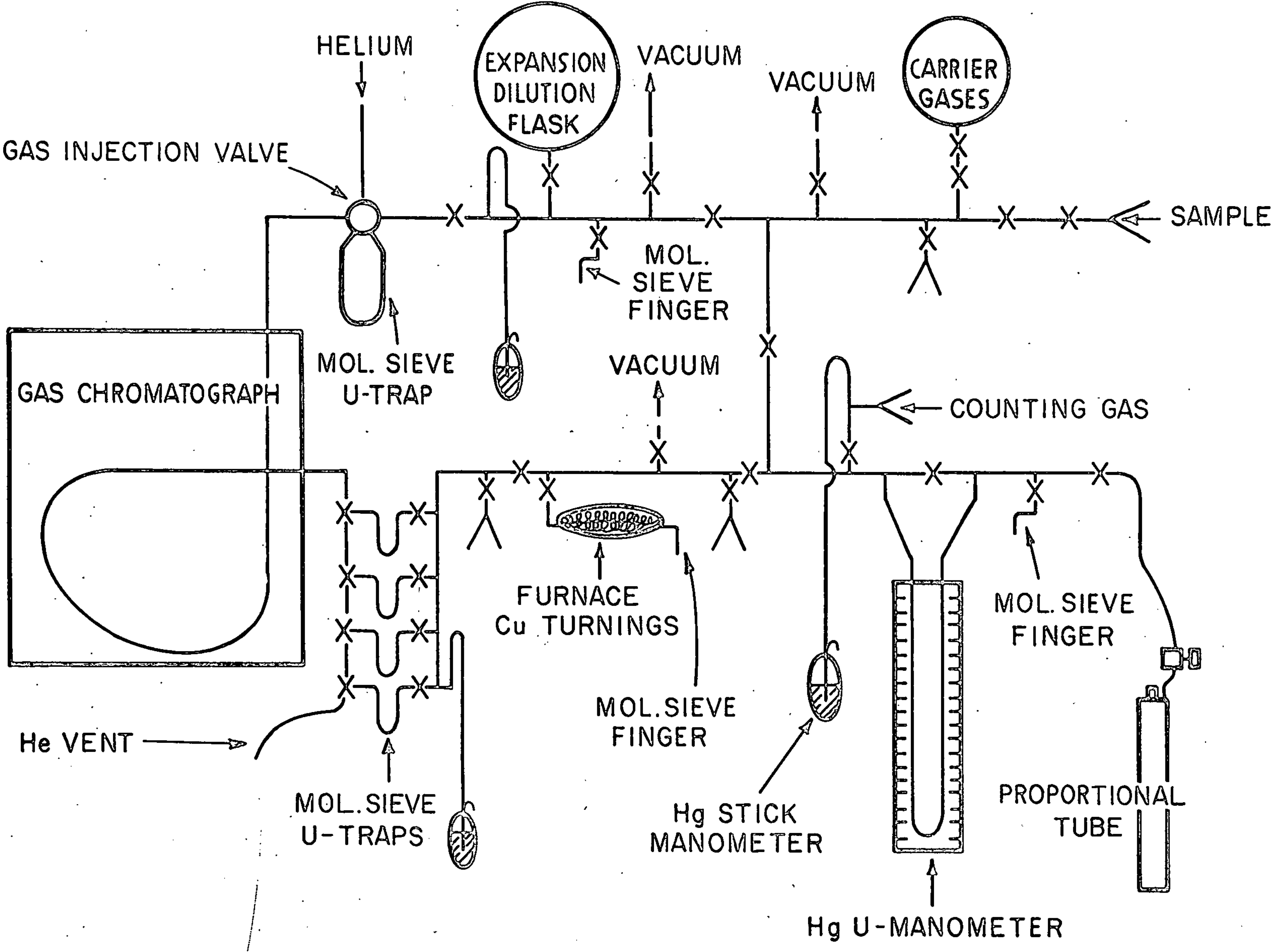

Figure 3. Schematic diagram of the high-activity gas separation system.

After the sample volume was determined, the sample was mixed with measured amounts of carriers for Ar, Kr, Xe, H_2, CH_4 and CO_2. (Later samples included carriers for C_2H_6 and C_3H_8, as well). About 0.5-1.5 ml of each carrier was found to be a convenient amount to process. The sample and carriers were then transferred to a molecular sieve U-trap connected to a gas injection valve on the chromatograph. The gases were transferred from section to section using molecular sieve fingers and U-traps. The molecular sieve was cooled with liquid nitrogen to adsorb the gases and heated with a nichrome wire wrap to desorb the gases. Using helium carrier gas, the sample was passed through the chromatograph. The eluted gas fractions (as observed with a thermal conductivity detector) were trapped on molecular sieve U-traps cooled with liquid nitrogen. The helium carrier was pumped off the cooled traps. The trapped gases that were relatively high in activity were volume-measured for chemical recovery and then loaded into gas-proportional counting tubes. The low-activity gases were transferred to the intermediate-activity system. There they were further purified through the intermediate-activity chromatograph, volume-measured and loaded into counting tubes.

Figure 4 is a more detailed drawing of the volume-measure and tube-load system. The gas to be measured was transferred to a molecular sieve finger. Stopcocks A and B were then closed, and the finger was heated to desorb the gas from the molecular sieve. When no more gas was being desorbed, stopcock C was closed, and the pressure of the gas contained in the previously calibrated volume contained between stopcocks A, B and C was measured. From these data the amount of gas present was calculated. The gas was loaded by expansion into an evacuated proportional-counting tube, which was then filled with counting gas to slightly more than atmospheric pressure.

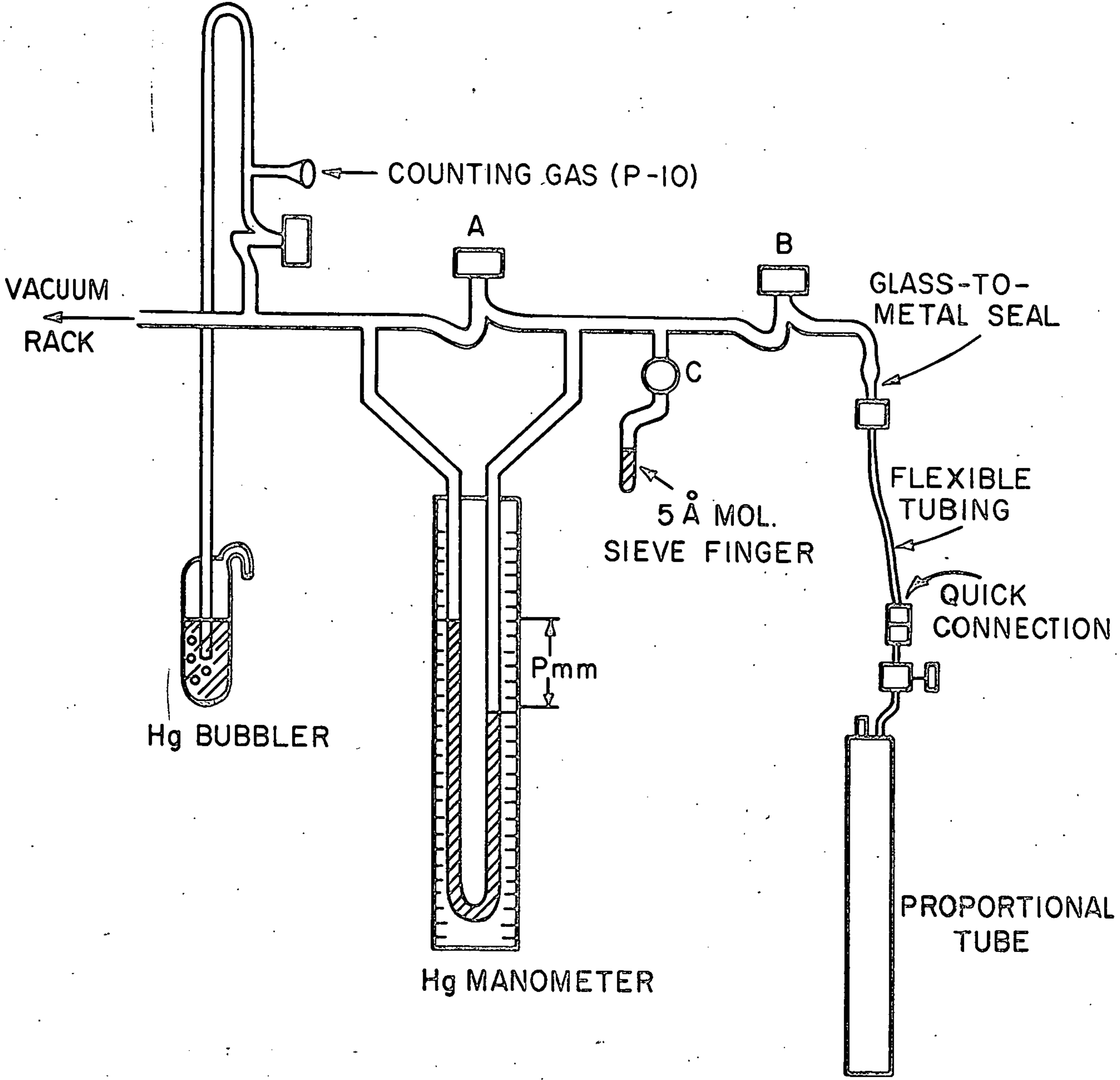

Figure 4. Volume-measure and tube-load sections of separation system.

Figure 5 shows typical chromatograms obtained with high-activity and intermediate-activity chromatographs. The high-activity chromatograph has a column of 10' x 0.25" molecular sieve 5A, 40-60 mesh, with helium carrier flowing at 60 ml/min. Normally the column was run at room temperature until the CH_4 fraction was off, then heated to 300°C to drive off the xenon and CO_2 fractions. There was very little separation between the krypton and CH_4 on the high-level chromatograph. However, on the intermediate-level chromatograph, which has a column of 20' x 0.25" molecular sieve 5A, 40-60 mesh, the separation was very good.

Very often the krypton in a sample had a much higher activity than the ^{14}C or tritium in methane. To determine the decontamination factor between krypton and CH_4, a ^{85}Kr source was mixed with carriers, and as the krypton and CH_4 were eluted from the high-level chromatograph, the gases were trapped separately and subsequently counted without further purification. The initial activity of the krypton was 3.5×10^{-3} μCi and that of krypton in the CH_4 fraction was 2.0×10^{-5} μCi, indicating a decontamination factor for krypton in the CH_4 fraction from the high-level chromatograph of about 175.

The same experiment was repeated with the intermediate-level chromatograph. In this case, to avoid possible contamination of the system, only 1.4×10^{-4} μCi of krypton was mixed with the carriers prior to injection. No measureable activity could be seen for krypton in the CH_4 fraction at a detection limit of 8.2×10^{-7} μCi, resulting in a decontamination factor greater than 170. There is over 10 min of baseline separation between these peaks, and the decontamination factor is certainly much higher than indicated from the low activity of krypton used. In normal processing of a sample, the CH_4 fraction trapped off the high-level chromatograph was reprocessed through the intermediate-level chromatograph prior to counting, with a combined decontamination from krypton considerably greater than 3×10^4. Decontamination factors for all other nuclide combinations were greater than 10^6.

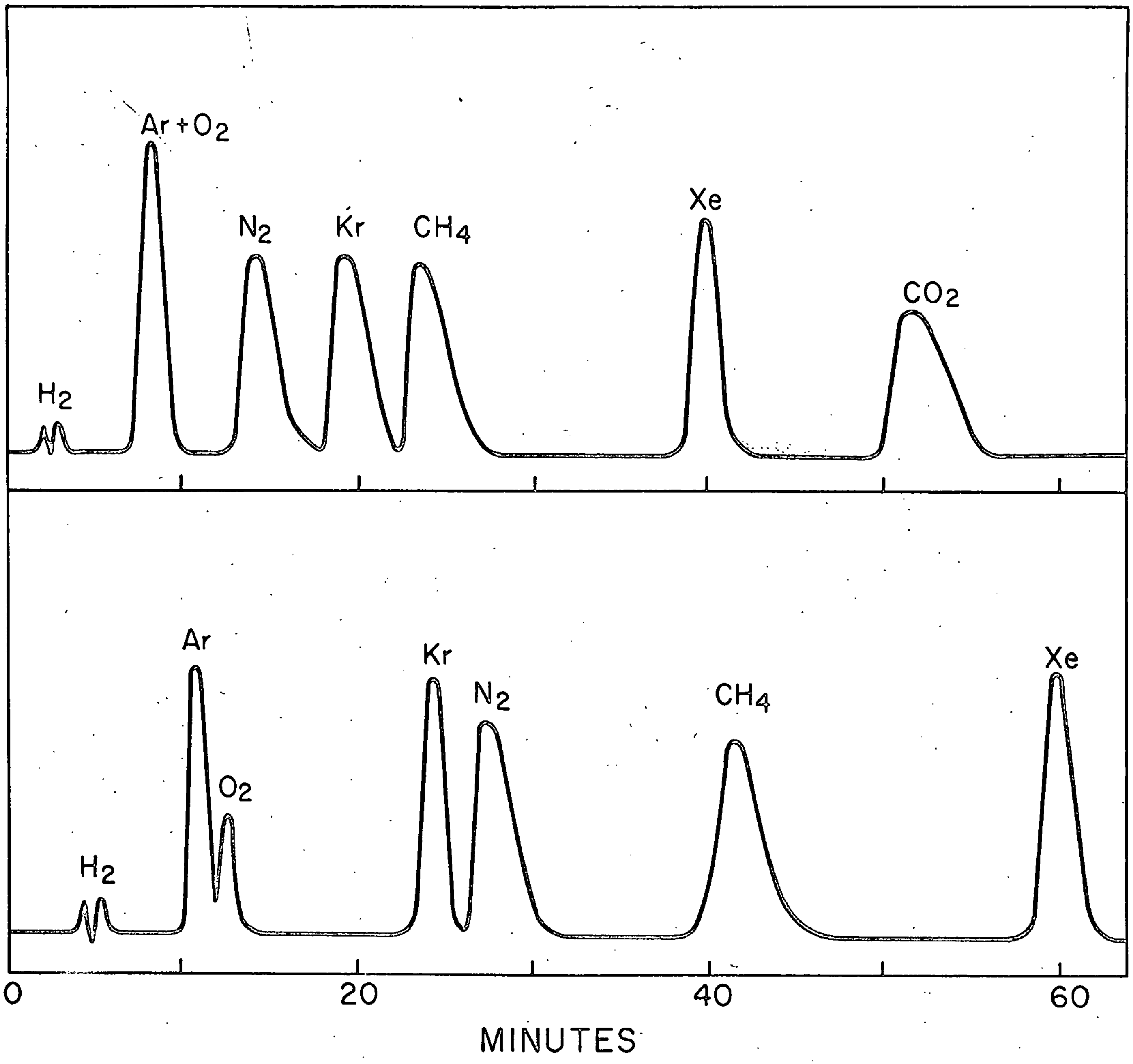

Figure 5. Chromatograms for permanent gases on molecular sieve 5A, 40-60 mesh; helium flow 60 ml/min. Top: High-activity column; 10' x 1/4". Bottom: Intermediate-activity column; 20' x 1/4".

The bulk of the CO_2 fraction eluted as a fairly sharp peak at about 300°C but left a small residue of adsorbed gas on the molecular sieve even when purged with helium at 400°C. The residual gas would then exchange with subsequent CO_2 fractions. To remove adsorbed $^{14}CO_2$, it was necessary to purge the molecular sieve after each run with CO_2 carrier at 400°C for several hours. Currently the separation system is being redesigned to use silica gel columns for gases condensable in liquid nitrogen such as Xe and CO_2. The more volatile gases would continue to be separated with molecular sieve columns.

Tritium, as water vapor or gas, also caused system contamination. Exchange with water molecules adsorbed on the molecular sieve, or on the walls of the gas handling system, produced cross-contamination. Measures such as purging with hydrogen and heating were necessary after processing samples containing high levels of tritium. System and counting-tube blanks were run between samples to determine possible residual activities.

2.2.3 Intermediate-Activity Samples

The separation system for liter-size, intermediate-activity samples is shown schematically in Figure 6. With this system the volume of each separated fraction was reduced to a few milliliters for subsequent chromatographic purification. The procedure involved adsorption followed by elution with helium carrier, similar to the methods described by Momyer [4] for krypton and xenon. The sample was mixed with carriers, bled at a rate of approximately 40 cc/min through two cold traps, and then adsorbed on a 4' x 0.5" glass coil of activated charcoal, cooled with liquid nitrogen. The first cold trap was cooled with dry ice-acetone and collected the water vapor; the second trap, cooled with liquid nitrogen, collected the xenon and CO_2.

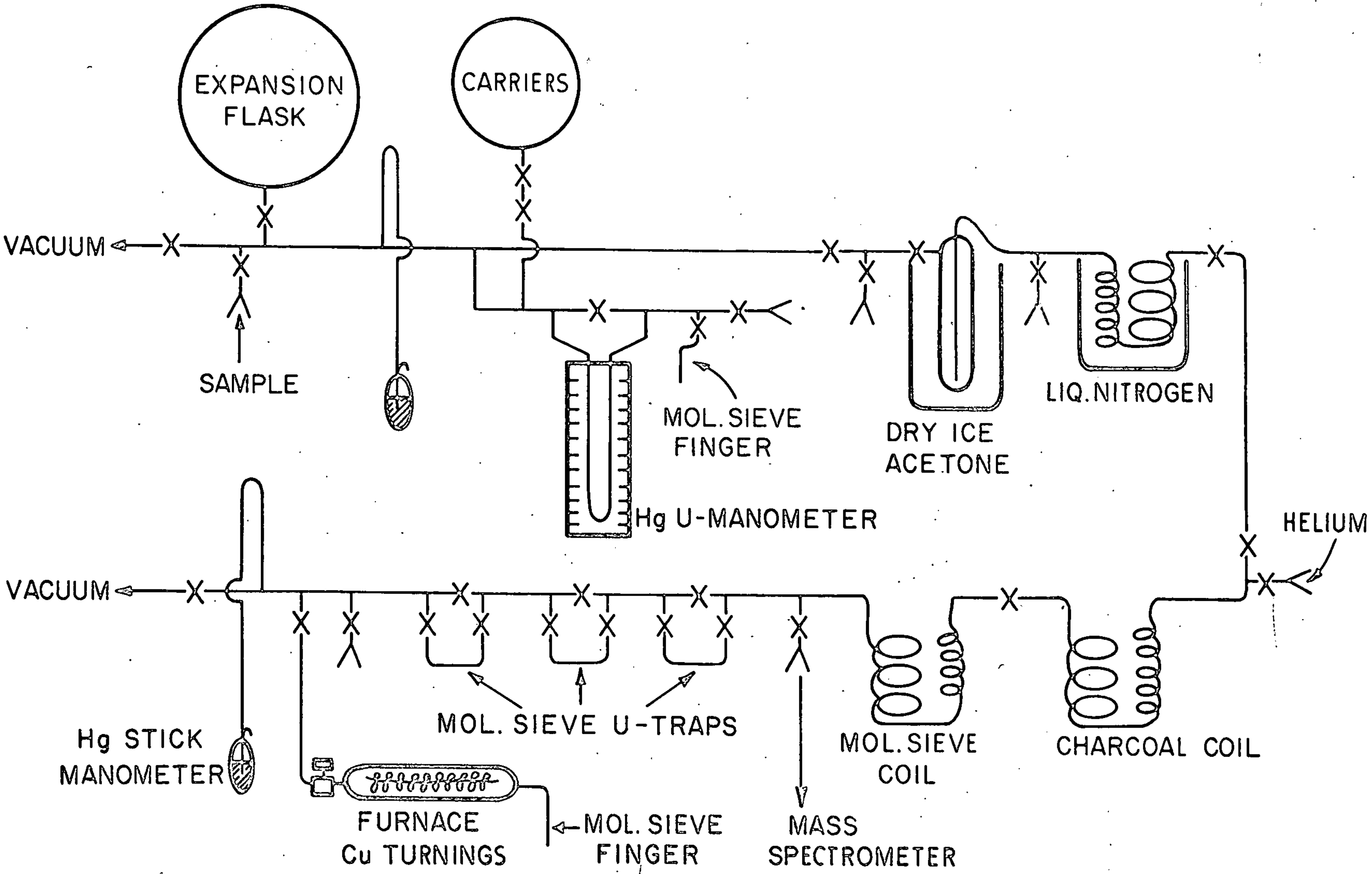

Figure 6. Bleed-down system for liter-size samples.

After the sample had been adsorbed onto the charcoal, which was maintained in a liquid nitrogen bath, a helium flow was initiated at about 500 ml/min, passing through the charcoal and molecular-sieve coils and out through a mercury stick manometer. The molecular-sieve coil was also 4' x 0.5".

Retention time for the gases of interest was determined by diverting a small fraction of the helium stream coming off the molecular-sieve coil into the Aero Vac 610 mass spectrometer. Once the retention times for the gases of interest had been determined, sampling was not generally necessary.

When dry ice-acetone slurries were placed around both the charcoal and molecular-sieve coils, hydrogen, argon, oxygen and nitrogen were rapidly eluted from the charcoal, while krypton and CH_4 were retained. The hydrogen fraction was observed coming off the molecular-sieve coil about 5 min after both coils had been cooled with dry ice-acetone, and it was entirely off approximately 3 min later. It was trapped in a molecular-sieve U-trap cooled with liquid nitrogen. Approximately 5 min after the hydrogen fraction was eluted, argon and oxygen were observed coming off the molecular-sieve coil. These gases were trapped together on a separate U-trap. At dry ice temperature, nitrogen was retained on the molecular-sieve coil, while argon and oxygen were eluted together and collected on a U-trap. The coil was warmed to room temperature to elute nitrogen. Both coils were then warmed to about 100°C to accelerate the elution of the krypton and CH_4, which were trapped together on a third molecular-sieve U-trap. Argon and oxygen are not easily separated by chromatographic methods. The mixed fraction was transferred to a furnace containing copper turnings heated to approximately 400°C to remove the oxygen by reduction to CuO.

All the separated fractions, which were now reduced in volume to a few cubic centimeters, were chromatographically purified as described in 2.2.2 for small-volume samples.

Between samples all the adsorbents used in separation of the gases were heated to 400°C while being evacuated or purged with helium. This removed any residual gases and reactivated the adsorbents for subsequent processing cycles. Additional system decontamination for $^{14}CO_2$ and tritium as described previously for high-level samples was required for this system.

2.3 Counting Methods

As mentioned previously, reactor gas samples were first analyzed by Ge(Li) gamma-ray spectroscopy. Separated gas fractions were then counted using internal gas-proportional spectrometry. Although gamma-ray spectroscopy is the simpler procedure, low-background beta-proportional counting offers greater sensitivity for all reactor-produced radioactive permanent gases, and it is a necessity for radionuclides which decay with little or no gamma emission. Although one might expect the activity of reactor samples to be so high that a low-background system is not needed, this is not the case. The range of activity ratios within a given sample may be 10^7 between nuclides requiring very sensitive measurements for the lowest activity fractions.

The use of multichannel analyzers for counting proportional tube output offers several advantages as compared to integral-bias counting. These include improvement in the figure of merit for some beta-emitters, a check on the purity of the sample after chromatographic separation, and simultaneous analysis of certain isotopic mixtures found in reactor gas effluents after chromatographic separation. These mixtures include $^{37}Ar/^{39}Ar$ in the radioargon fraction and ^{14}C/tritium in methane and other hydrocarbon fractions.

The gases routinely measured in reactor effluents by internal gas-proportional counting included the noble gases, ^{85}Kr, ^{131m}Xe, ^{133}Xe, ^{37}Ar and ^{39}Ar, and the permanent gases, HT, $^{14}CO_2$ and CH_4 (^{14}C and tritium). Beta spectrometry proved particularly desirable to insure against contamination of the argon fraction with HT, the methane fraction with ^{85}Kr, or the $^{14}CO_2$ fraction with the ^{133}Xe.

2.3.1 Ge(Li) Gamma Spectrometry System

The Ge(Li) gamma-spectrometry system consisted of a large volume Ge(Li) detector (10.0% of 3" x 3" NaI crystal at 1.33 MeV) with 2.15 keV resolution coupled through associated electronics to a Northern Scientific 8192-Analyzer system (NS 666). Background was reduced by shielding the detector with 15 cm of steel on each side and 10 cm of lead at the top and bottom.

2.3.2 Gas-Proportional Beta-Spectrometry System

The beta-spectrometry system is similar to those described by Curran [5]. The tubes used in the reactor sample measurements are commercial 100-ml stainless steel proportional tubes manufactured by LND, Inc. The active region of these tubes is a cylinder 2.3 cm in diameter and 24 cm long. For background reduction, plastic scintillator anticoincidence guard detectors were used, and the entire system was enclosed in a 14.4-cm-thick steel shield. Figure 7 shows a 1-liter proportional tube, two of the 100-ml tubes and two guard detectors. The smaller guard will accept the 100-ml tubes; the larger guard will accept tubes as large as a 2.6-liter tube manufactured by LND, Inc. A typical 100-ml tube with a P-10 (90% argon, 10% methane) fill has a 250-volt plateau beginning at 1,750 volts with a slope of less than 1% per 100 volts.

A block diagram of the system is shown in Figure 8. Pulses from the proportional tube are amplified and shaped before passing through a linear gate to the multichannel analyzer. If an event occurs in the guard detector, the linear gate is closed for 10 μsec. The system dead time due to such closing is less than 0.1%. All components shown in Figure 8, with the exception of the plastic guard detector, are commercial products. With new multichannel analyzers, one can use the built-in linear gate in anticoincidence mode and avoid the cost of an external gate.

2.3.3 Beta-Spectrometer Operation and Characteristics

Spectra of tritium, ^{14}C and ^{85}Kr obtained with the beta-spectrometry system are shown in Figure 9. Using the X-ray fluorescence produced in the steel walls of the proportional tube with an external ^{125}I source, the gain of the system was set

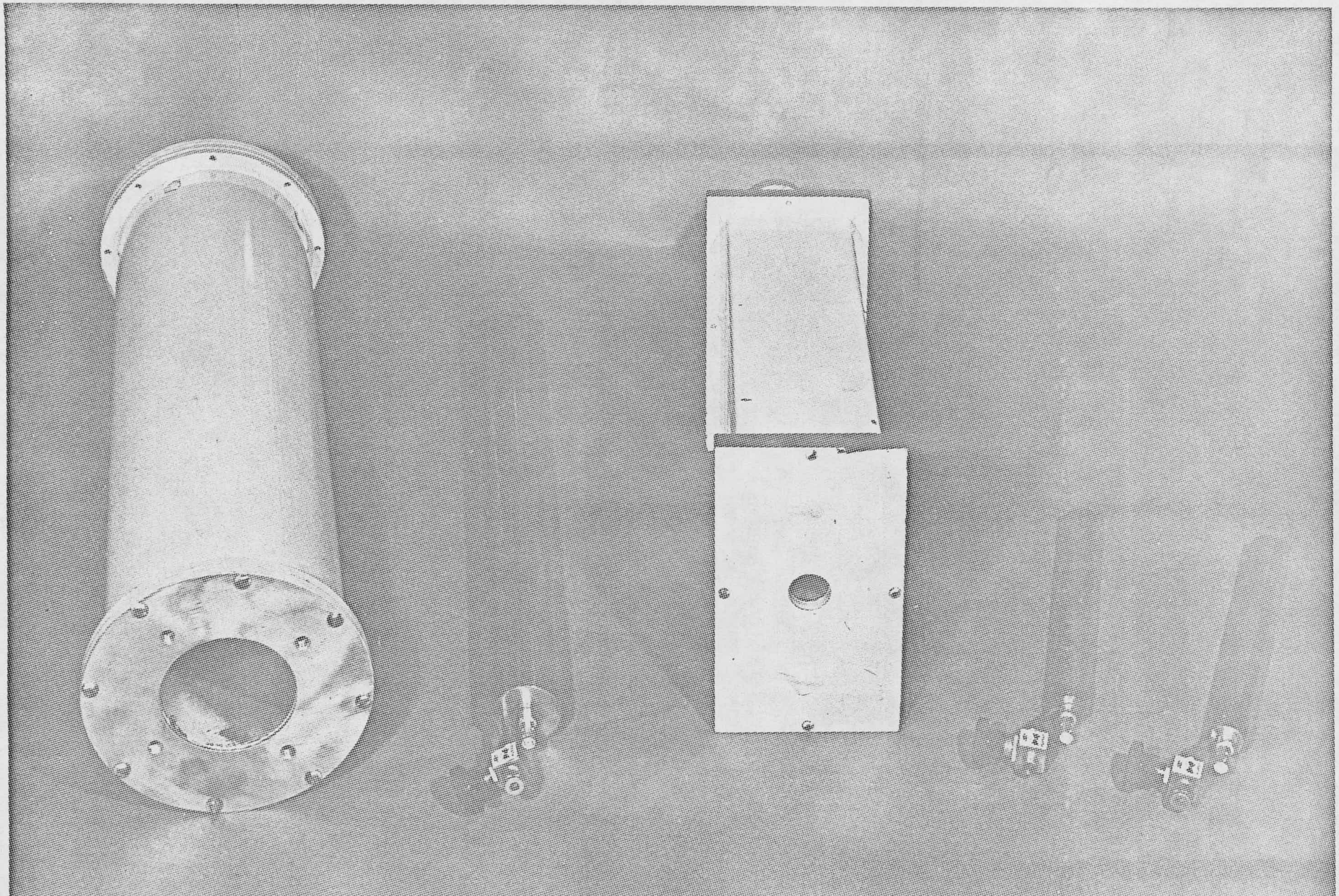

Figure 7. Proportional tubes, 1-liter and 100-ml, with plastic scintillator guard detectors.

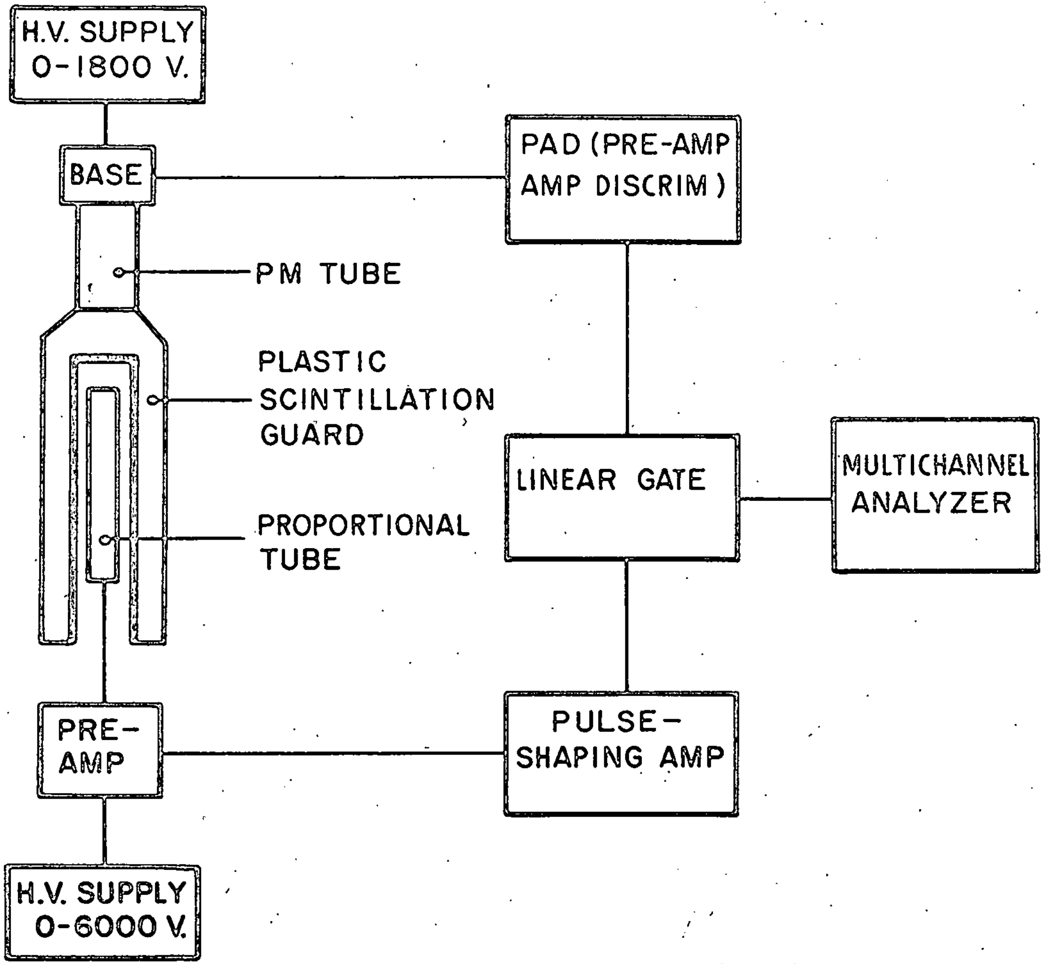

Figure 8. Block diagram of internal gas-proportional beta-spectrometer system.

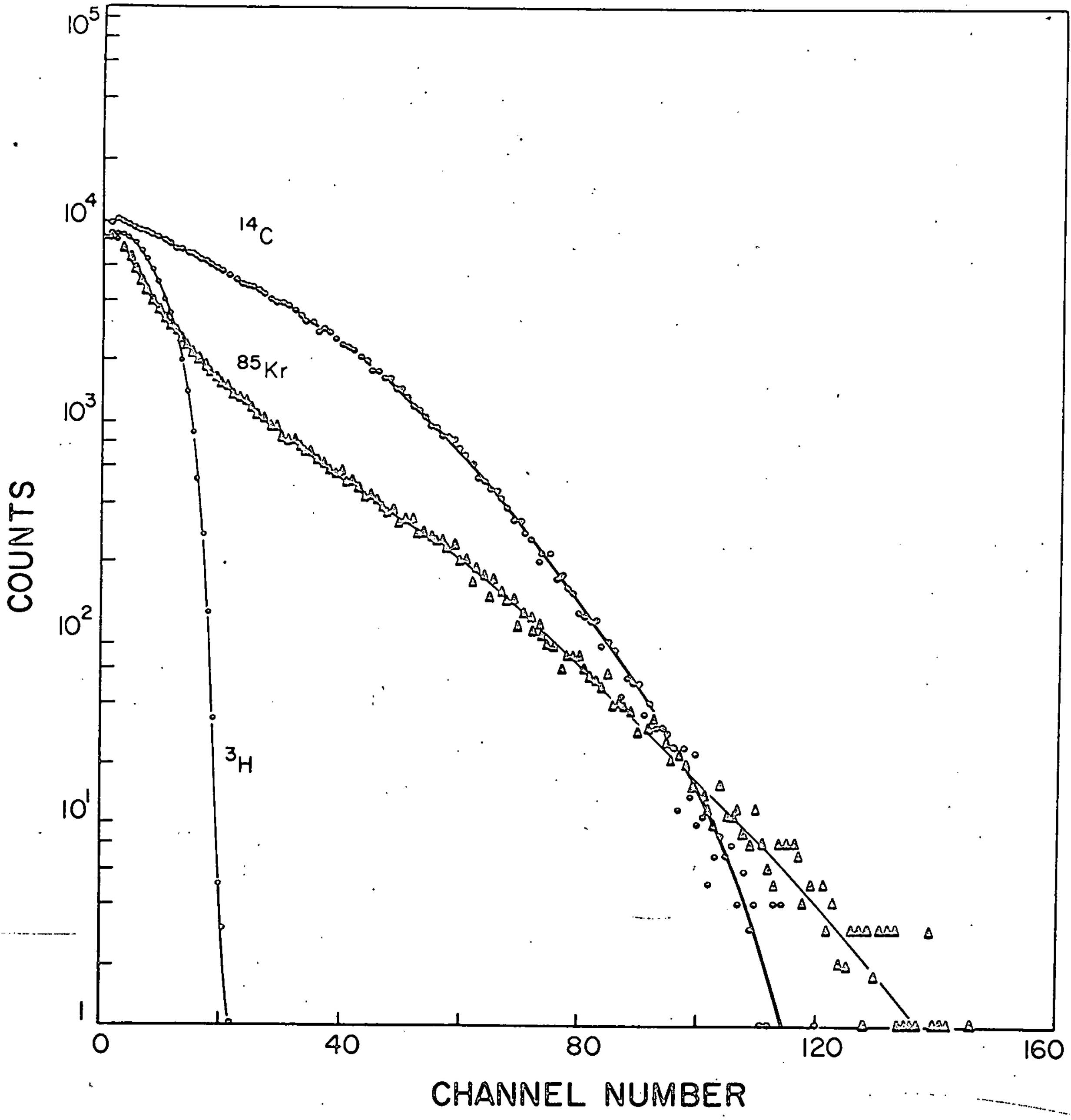

Figure 9. Beta-spectra of tritium, ^{14}C and ^{85}Kr. Gain of 0.83 keV/channel.

at 0.83 keV/channel. At this fixed gain there are clear differences in end points and shapes for these three isotopes.

Background spectra at a system gain of 0.42 keV/channel are shown in Figure 10. The integrated backgrounds were 104 cpm for the bare stainless steel detector, 53 cpm for the detector shielded by 14.4 cm of steel, and 4.9 cpm for the detector shielded by the steel and an anticoincidence guard. With a 100-ml copper tube, not presently used for these reactor samples, an integrated background as low as 1.25 cpm has been achieved with a background of 0.3 cpm under the ^{37}Ar peak.

Argon spectra were analyzed for both ^{37}Ar (from the Auger peak) and ^{39}Ar (from the continuous spectrum). In order to avoid possible pulse pileup from ^{37}Ar, only the spectral region above 6 keV was used for ^{39}Ar analysis. The system has been calibrated for ^{37}Ar efficiency using a standard obtained from the National Bureau of Standards, and a value of 0.63 cpm/dpm has been obtained for the Auger peak efficiency.

A major advantage of spectral analysis is shown by comparing the spectra of an NBS ^{37}Ar standard, a contaminated argon fraction after two passes through a gas chromatograph, and the same sample after an additional pass (Figure 11). The contaminated sample contains a very small amount of ^{3}H, which would not seriously affect the ^{37}Ar value (because of the large amount of ^{37}Ar in this sample) but which could have a serious effect on the ^{39}Ar value. Integral-bias counting would not show this contamination. Gross contamination can occur even with double chromatographic separation because of the large range of isotopic abundances in reactor gas effluents.

We occasionally observed tritium interferences in argon, ^{85}Kr in methane and ^{133}Xe and ^{131m}Xe in CO and CO_2 fractions. If great care was not taken in cleaning the separation system after a particularly high activity sample, tritium was apt to appear in any fraction.

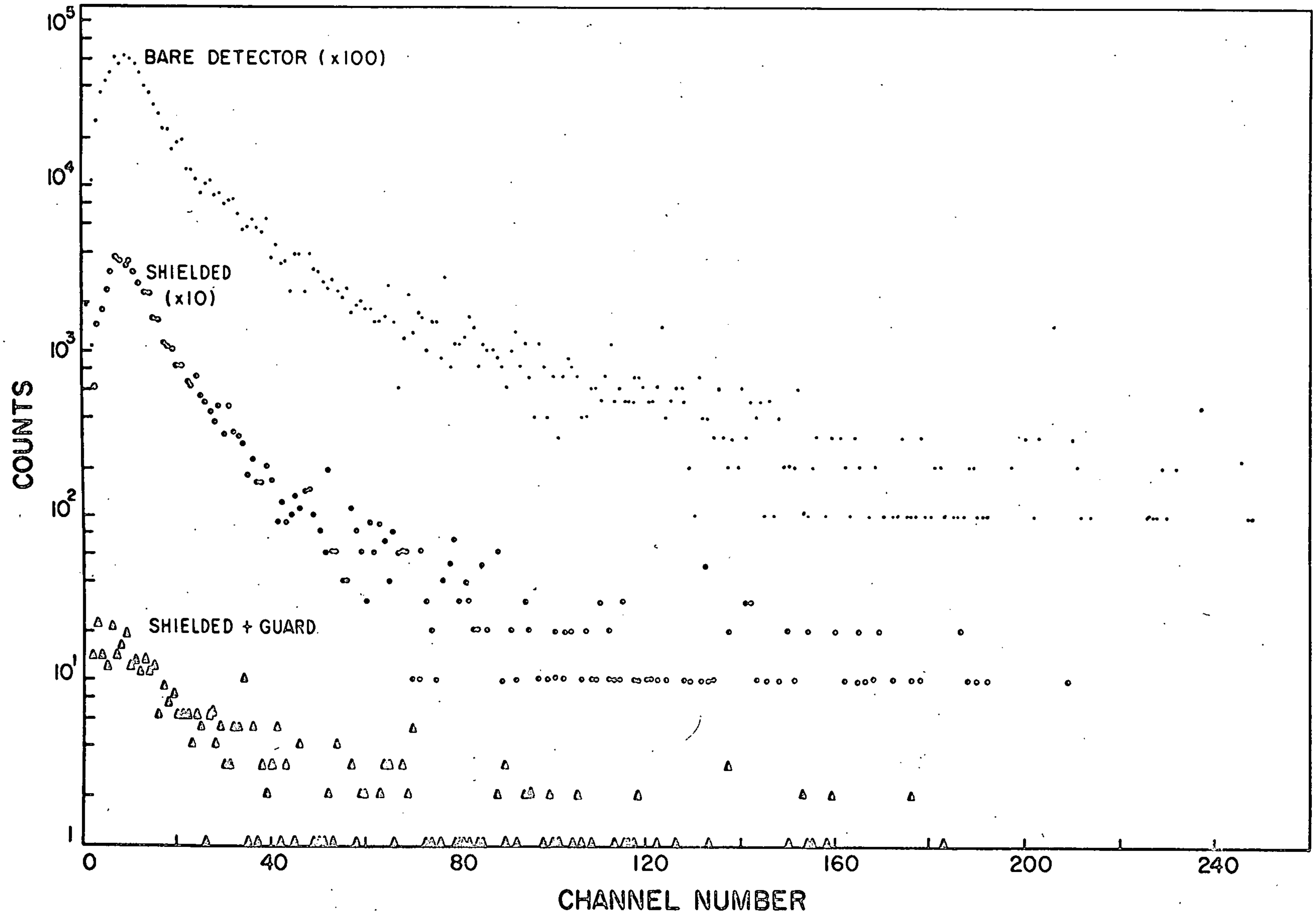

Figure 10. Background spectra for a 100-ml steel proportional tube. The spectra of the shielded and bare detectors have been shifted upward by factors of 10 and 100, respectively. Gain 0.42 keV/channel. 100 minute counting time.

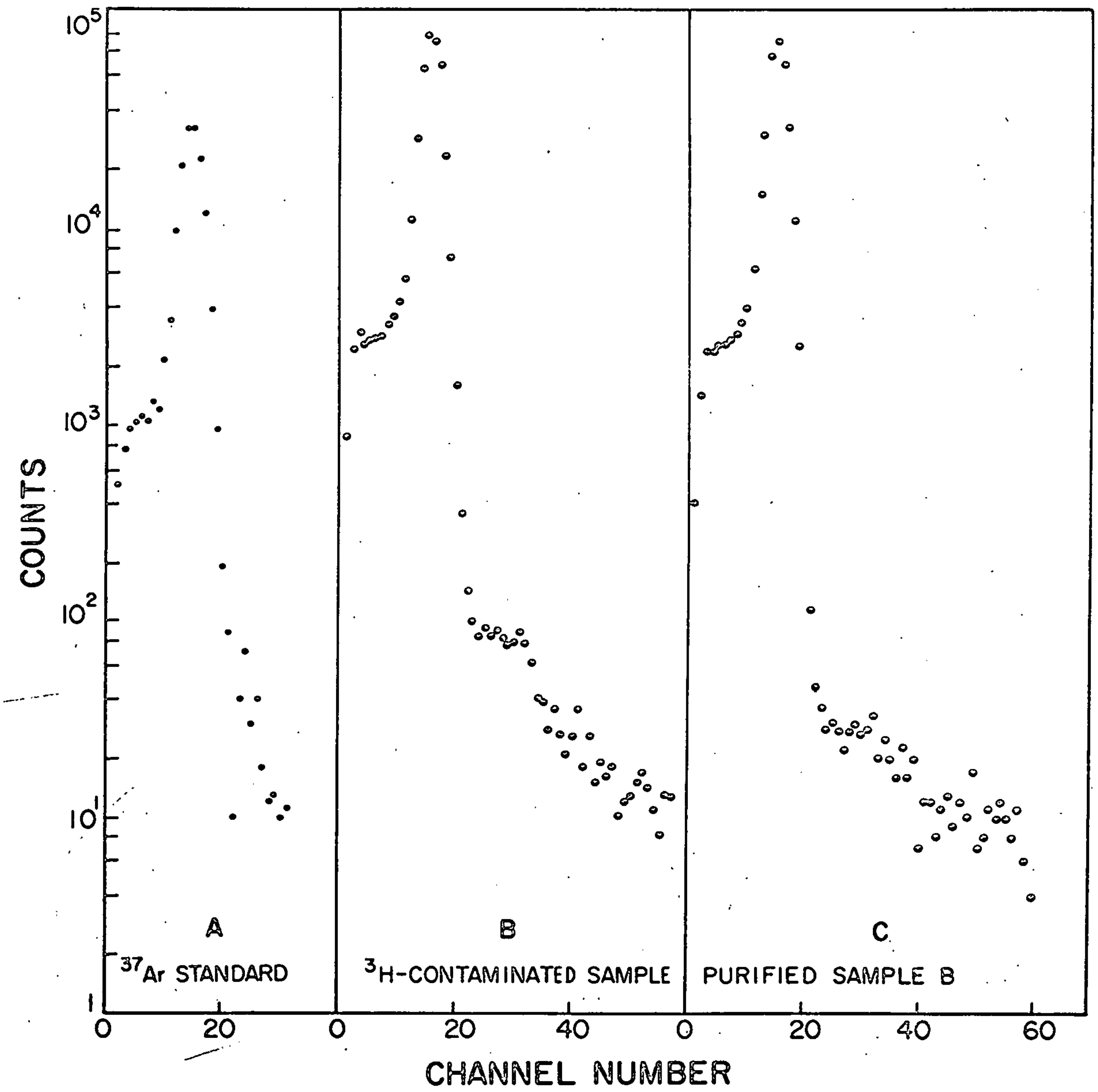

Figure 11. Argon spectra: A, NBS ^{37}Ar standard. B, argon fraction with tritium contamination. C, fraction shown in B after an extra purification step. Gain 0.21 keV/channel.

For sample spectra such as those for ^{85}Kr, tritium, $^{14}CO_2$ and ^{14}CO, the spectral shape and end point were first examined for radiochemical purity. The spectrum was then summed, the background subtracted, and the net counting rate corrected for counting efficiency, sample size, chemical recovery and radioactive decay. In the cases of ^{131m}Xe and ^{133}Xe this procedure was repeated for several counts, and the data were fitted by a least-squares method using a two-component decay curve.

At the present time, ^{37}Ar and ^{85}Kr are the only gas standards available from NBS. For ^{133}Xe, the method of beta-gamma coincidence counting [6] was used to determine efficiency. This procedure gave a value of 0.86 cpm/dpm, which was consistent with other measured efficiency values. The same efficiency factor is used for ^{131m}Xe . Since ^{39}Ar has a beta spectrum similar to that for ^{85}Kr, the ^{85}Kr efficiency factor for the appropriate spectral region was used for ^{39}Ar. In reactor gas samples where ^{85}Kr and ^{133}Xe were present in a sufficient concentration to permit analysis by Ge(Li) gamma counting of the sample in the sampling vessel, the ^{133}Xe proportional-counter efficiency from the coincidence calibration provided good agreement with the Ge(Li) diode measurements.

One of the more interesting gases present in reactor effluents is methane. It may contain tritium or ^{14}C, or both. Beta-spectrometry permits the simultaneous analysis of both nuclides. In Figure 12 the spectrum of the methane fraction from the PHWR is presented. The spectrum was run at a system gain of 0.42 keV/channel. The regions from channels 1 to 39 and from 40 to 255 were summed and the appropriate background values subtracted. The net counts in region 1 and 2, N_1 and N_2 are given by:

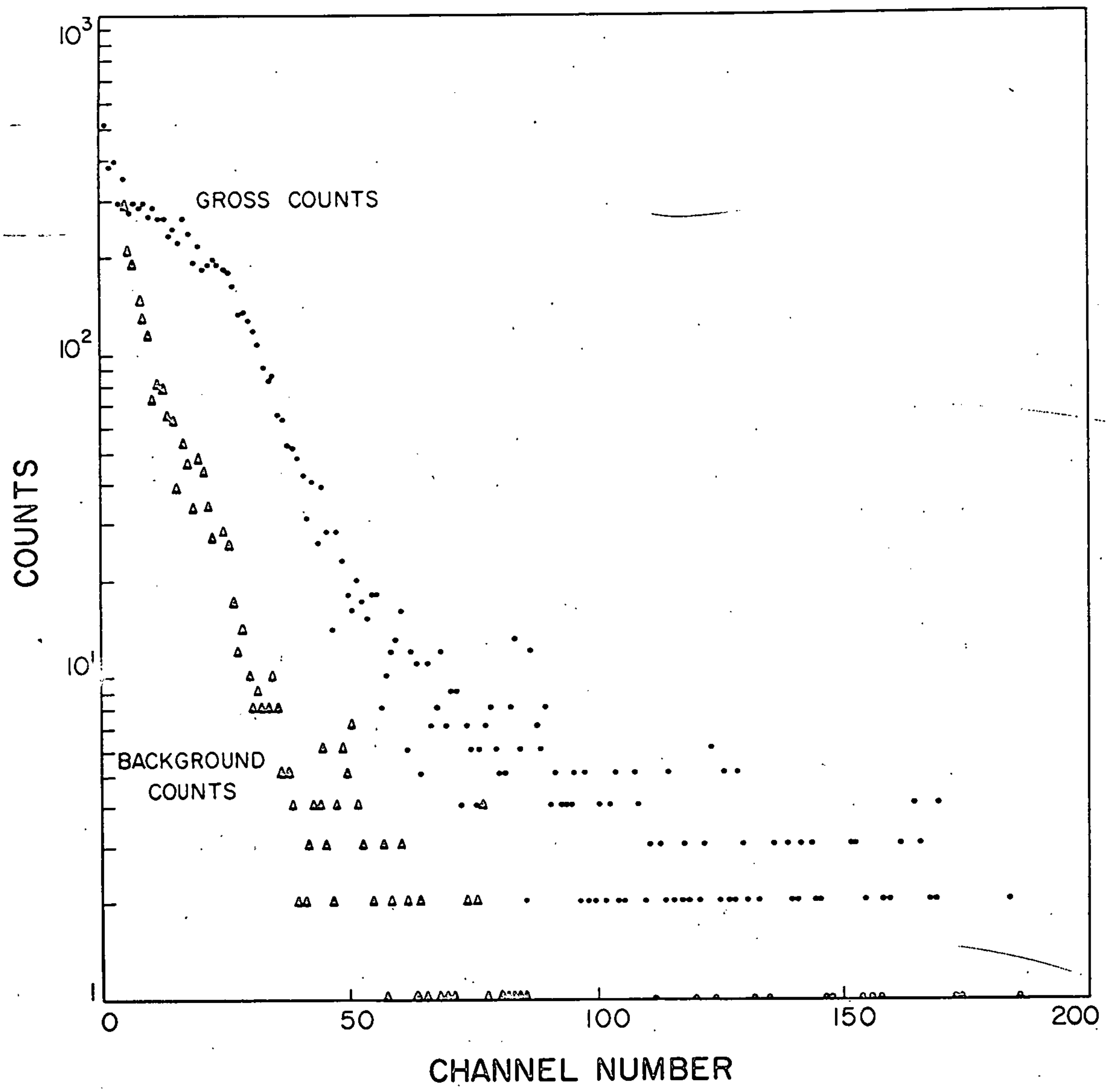

Figure 12. Gross spectrum of a methane fraction showing the presence of tritium and ^{14}C compared with background. Gain 0.42 keV/channel.

$$N_1 = f_1(T)N_T + f_1(C)N_C \quad (1)$$

$$N_2 = f_2(T)N_T + f_2(C)N_C \quad (2)$$

where

$f_1(T)$ = fraction of tritium spectrum in region 1,

$f_1(C)$ = fraction of ^{14}C spectrum in region 1,

$f_2(T)$ = fraction of tritium spectrum in region 2,

$f_2(C)$ = fraction of ^{14}C spectrum in region 2,

N_T = net tritium count in spectral region,

N_C = net ^{14}C count in spectral region.

For our tubes and gain range these equations are:

$$N_1 = 0.985\ N_T + 0.575\ N_C \quad (3)$$

$$N_2 = 0.015\ N_T + 0.425\ N_C \quad (4)$$

Using the measured values for N_1 and N_2, these equations were solved for N_T and N_C and the activities determined without combustion of the sample. By counting a series of twelve $^{14}CH_4$ samples it was shown that the gain could be set using an external ^{125}I source with sufficient reproducibility that the errors in the constant terms in Equations 3 and 4 are restricted to the third significant figure. The major drawback of this method is that the tritium sensitivity is limited by the amount of ^{14}C present. If the ^{14}C activity is one order of magnitude or more above the background, the detectable limit for tritium is about 7% of the ^{14}C activity. In Figure 13 the decomposition of the methane fraction into tritium and ^{14}C components is shown.

System performance is summarized in Table 2. The detectable limit can be influenced by poor chemical recovery and, for short-lived nuclides, by long delays between collection and counting. It can be enhanced by processing larger sample volumes.

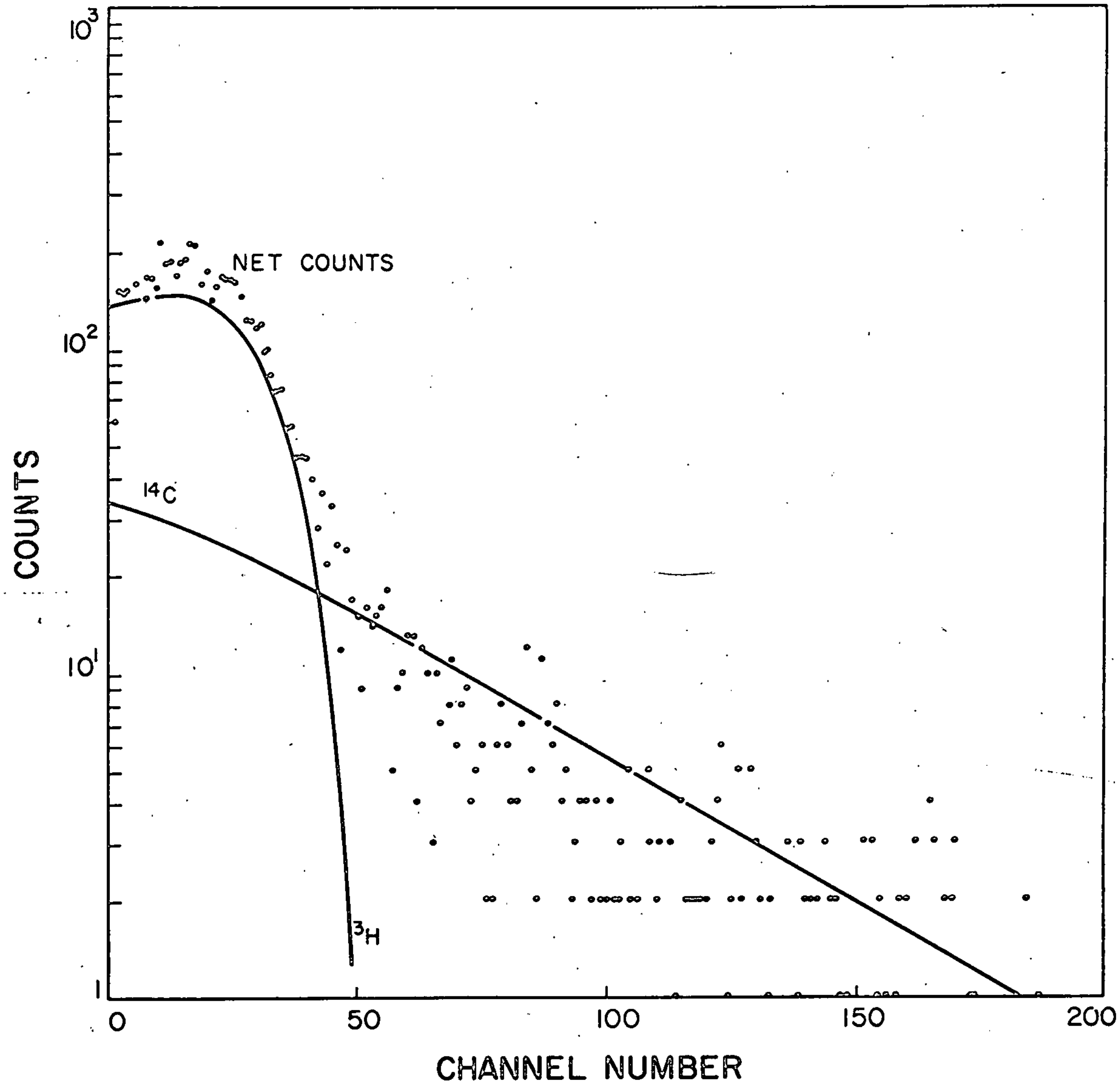

Figure 13. Spectrum of the methane fraction shown in Fig. 12 with background subtracted. The tritium and ^{14}C components are indicated. Gain 0.42 keV/channel.

Table 2. Spectrometer performance.

Isotope	Gain (keV/ch)	Channels used	Gas detector efficiency (cpm/dpm)	Avg bkg (cpm)	Detectable limit 1-ml sample 1000-min count (μCi/ml)
^{85}Kr	0.83	1-255	0.90	5.0	1.1 E-7[a]
^{37}Ar	0.21	10-19	0.63	0.8	6.0 E-8
^{39}Ar	0.21	32-255	0.45	1.5	1.2 E-7
^{133}Xe	0.83	1-255	0.86	5.0	1.1 E-7
^{3}H	0.42	1-39	0.75	5.0	1.3 E-7
^{14}C	0.42	1-255	0.85	5.0	1.1 E-7
^{14}C	0.42	40-255	0.36	0.13	4.0 E-8

[a] In this and all subsequent tables, the number following the "E" is the power of 10 to which preceding number is raised. For example, 1.1 E-7 equals 1.1 x 10^{-7}.

Some uncertainty must be attributed to the accuracy of most of the efficiency factors. Only those for ^{85}Kr and ^{37}Ar have been determined from primary standards. That for ^{133}Xe was determined using the aforementioned beta-gamma coincidence system. Efficiency factors for ^{39}Ar, tritium and ^{14}C were estimated from those for ^{85}Kr and ^{37}Ar.

Standards for these and other gases will presumably become available in the future. Proportional tube efficiency, however, unlike that of most other radiation detectors, varies slowly over a wide range of energies. Extrapolation of detector efficiency for beta-emitting isotopes is not especially difficult, but isotopes which decay by electron capture or by decay of metastable states present problems which require direct comparison to standards.

Calibration of the Ge(Li) gamma-spectrometry system was also complicated by the lack of adequate gas standards.

A primary ^{85}Kr standard was transferred to a rubber-capped septum vial to fix the system efficiency at 514 keV. A solution standard of ^{85}Sr was then counted in the same geometry to obtain geometry and self-absorption factors. A calibration curve for solution standards was adjusted from the ^{85}Kr/^{85}Sr ratio, using additional corrections for self-absorption changes as a function of gamma energy. The efficiency factor obtained using a ^{133}Ba standard (81 keV) agreed within acceptable counting limits with the efficiency factor obtained using the secondary ^{133}Xe standard prepared by beta-gamma coincidence counting on the gas-proportional system.

3. RESULTS AND DISCUSSION

3.1 Activity Levels

Transit time to the Laboratory for most samples was at least 3 hr from time of collection. Often the first gamma-spectral measurements were made after 20 hr had passed, so data for noble gas activities with half-lives <10 hr are limited. The results presented here are therefore confined primarily to nuclides with half-lives >1 day.

Sample activities are initially calculated in μCi/ml, then reported as ratios of one of the noble gases present. In Table 3 all values are normalized on ^{85}Kr, and values for the PWRs [subsequently identified as PWR(I) and PWR(II)] and HTGR are weighted averages of the values for the several types of samples collected. All ratios have been corrected for decay from time of sample collection to time of release. Concentration values for all samples, corrected to day of sample collection only, are included in Appendices A through E.

The "less than" values (<) in Table 3 indicate activity levels below the limit of detection of the system. The detection limit is the level at which the error at the 95% confidence level equals the numerical value obtained.

The total number of samples processed and the number of replicates at each site are evident from the data in Appendices A through E.

The CO_2 ratios for the PWR samples are listed in Table 3 as minimum values (>) because the standard collection procedure at the PWRs for cover-gas, strip-gas and decay tank samples involves contact with water. The $^{14}CO_2$ values for containment air, which is sampled directly, were too low to obtain real values, but maximum levels produced $^{14}CO_2/^{85}Kr$ ratios consistent with those for other types of PWR samples.

The $^{14}CH_4/^{85}Kr$ ratio in containment air from PWR(I) is similar to ratios for cover and strip gas. The containment-air ratio for the new core in PWR(II) is approximately 10 times greater than the ratio for decay-tank samples. Though containment-air release contributes only a small fraction of the total gaseous activity released, its high $^{14}CH_4/^{85}Kr$ ratio in

Table 3. Average activity ratios (nuclide/^{85}Kr) of long-lived permanent-gas reactor effluents at time of release.

Reactor	^{37}Ar	^{39}Ar	^{85}Kr	^{131m}Xe	^{133m}Xe	^{133}Xe	HT	CH_3T	$^{14}CH_4$	$^{14}CO_2$
BWR	8.5 E-2	1.1 E-4	1.0	9	9.5 E 1	2.1 E 3	8 E-3	<2 E-5	<5 E-3	1.2 E-2
PWR(I)	3.1 E-3	<4 E-6	1.0	4 E-1	1	3.2 E 1	7 E-4	<3 E-4	3 E-3	>2 E-4
PWR(II)[a]	3.1 E-3	<1 E-6	1.0			6	<7 E-6	<2 E-5	1.7 E-4	>4 E-5
PWR(II)[b]	8 E-2	6 E-5	1.0	8 E-2	1.1 E-2	5	5 E-4	<5 E-4	1 E-2	>6 E-5
PHWR	1.9 E 4	3 E-1	1.0			1.4 E 4	2.2 E 4	2.8	1.4	8.6
HTGR[c]	5 E 1	<2 E-2	1.0			<3 E-2	>1 E-1	4 E-1	<9 E-4	2 E-3
	8	1.4 E-3	1.0				1.6	1.1 E-1	<4 E-4	<8 E-4

[a] Old core.
[b] New core.
[c] Two sets of samples, 7 months apart, differed too widely for averaging (see text).

the PWR(II) makes the average $^{14}CH_4$ activity ratio in Table 3 significantly higher for that reactor.

The gaseous tritium values for the HTGR are also thought to be minimum values. In the HTGR the helium primary coolant is purified by passage through two charcoal beds, one at and one slightly above liquid nitrogen temperature. Charcoal under these conditions has poor H_2 retention, so a scaling factor of at least 10 may be required for representative values of the gaseous tritium from the HTGR.

The two samples received 8 months apart from the HTGR showed markedly differing ratios which may be due to build-up of long-lived gases as the core ages.

3.2 Annual Release Levels

3.2.1 Noble Fission Gases

Multiplication of the normalized activity ratio (Table 3) by the operator's published release levels (Table 4) of ^{85}Kr or "total noble gas" provides an estimate of the amount of each noble gas released annually (Table 5) for the two PWRs and the HTGR. Since ^{85}Kr is not measured by the BWR operator and the total noble gas includes many short-lived activities, annual release estimates were made from reported ^{133}Xe levels. The PHWR operator reports only the amount of HTO released annually, so all noble gas release estimates were calculated from the operator's estimates of total pressure-vessel volume and from the radionuclide concentrations measured by the Radiological Sciences Laboratory.

Reported values for BWR fission-gas releases normally include ^{133}Xe as the longest-lived noble gas constituent. The calculated amounts of ^{85}Kr released appear low when compared to the values for other reactors. Radioargon releases from the BWR are lower than those from the other reactors with the exception of PWR(I).

Long-lived noble gas releases from PWR(I) are also low. Radioargon releases are lower than those for any other reactor studied.

Table 4. Reported annual releases of long-lived noble gases.

		Reported releases (Ci)		
Reactor	Year	Total	^{85}Kr	^{133}Xe
BWR	1970	9.5 E 3		
(1538 MWt)	1971	2.5 E 5	—	4.3 E 4
	1972	5.2 E 5		6.5 E 4
PWR(I)	1970	1.7 E 3		
(615 MWt)	1971	3.6 E 2		
	1972	5.4 E 2		
PWR(II)	1970[a]	1.0 E 4		
(1300 MWt)	1971[a]	3.2 E 4		
	1972[a]	1.2 E 4	1.2 E 3	1.0 E 4
	1973[b]	5.8 E 2	6.0 E 1	4.4 E 2
PHWR	1970	NA[c]		
(40 MWt)	1971			
	1972			
HTGR	1970	5.7		
(116 MWt)	1971	1.2 E 2		
	1972	5.8 E 1		

[a] Old core.
[b] New core.
[c] Not applicable; facility operator does not measure any noble gas or permanent gas releases.

Fuel elements used in PWR(II) during 1970-1972 were of a type which experienced cladding cracks due to fuel densification [7]. Fission gas releases were high during these years, and releases of ^{85}Kr were higher than those from the other light-water reactors studied. Installation of pressurized fuel elements appears to have reduced the amount of fission gases released in 1973 by a factor of 20 for ^{85}Kr and ^{133}Xe. The amounts of permanent gases apparently produced by activation outside the fuel elements do not appear to be appreciably reduced, however. Releases of ^{37}Ar from PWR(II) remain the highest from the light-water reactors. The change in fuel element design has

Table 5. Estimated annual release of long-lived permenent gas effluents.

		Estimated releases (Ci)									
Reactor	Year	^{37}Ar	^{39}Ar	^{85}Kr	^{131m}Xe	^{133m}Xe	^{133}Xe	HT	CH_3T	$^{14}CH_4$	$^{14}CO_2$
BWR	1970	6 E-2	8 E-5	7 E-1	6	7.0 E 1	1.5 E 3	6 E-3	<1.4 E-5	<4 E-5	8 E-3
	1971	2	2 E-3	2.0 E 1	1.7 E 2	1.9 E 3	4.3 E 4	1.6 E-1	<4 E-4	<1.0 E-3	2 E-1
	1972	3	3 E-3	3.1 E 1	2.6 E 2	2.9 E 3	6.5 E 4	3 E-1	<6 E-4	<1.6 E-3	4 E-1
PWR(I)	1970	1.7 E-1	<2 E-4	5.3 E 1	2.0 E 1	5.0 E 1	1.7 E 3	4 E-2	<1.6 E-2	1.6 E-1	>1.1 E-2
	1971	4 E-2	<5 E-5	1.1 E 1	4	2.0 E 1	3.5 E 2	8 E-3	<3 E-3	3 E-2	>2 E-3
	1972	5 E-2	<7 E-5	1.7 E 1	7	3.5 E 1	5.4 E 2	1.2 E-2	<5 E-3	5 E-2	>4 E-3
PWR(II)	1970[a]	4	1.2 E-3	1.2 E 3			7.7 E 3	<8 E-3	<2 E-2	2 E-1	>5 E-2
	1971[a]	1.2 E 1	<4 E-3	3.7 E 3			2.3 E 4	<3 E-2	<7 E-2	6 E-1	>1.5 E-1
	1972[a]	5	<1.4 E-3	1.4 E 3			9.0 E 3	<1 E-2	<3 E-2	2 E-1	>6 E-2
	1973[b]	5	3 E-3	6 E 1	5	7 E-1	3.0 E 2	3 E-2	<3 E-2	7 E-1	>3 E-3
PHWR	1970 1971 1972	1.9 E-1	3 E-6	9 E-6			1.0 E-1	2 E-1	3 E-5	1.3 E-4	8 E-5
HTGR	1970	2.9 E 2	9 E-2	5.7			<2 E-1	>6 E-1	2	<5 E-3	5 E-3
	1971	6.0 E 3	2	1.22 E 2			<4	>1.2 E 1	5.0 E 1	<1.1 E-1	1.1 E-1
	1972	2.9 E 3	9 E-1	5.8 E 1			<2	>6	2.0 E 1	<5 E-2	5 E-2

[a] Old core.

[b] New core.

not significantly reduced them, indicating that ^{37}Ar production occurs outside the fuel elements.

Fission gas releases from the PHWR are also low and appear to consist predominantly of ^{133}Xe and other short-lived noble gases. However, only a single sample has been analyzed to date. This research reactor has a 4-week operating cycle, and build-up factors may be more sensitively related to the time of sampling within the cycle, so the present data must be considered somewhat tenuous. Plans have been made to collect a series of samples at different times during the operating cycle.

3.2.2 Other Permanent Gases

The highest single-year releases of tritium, ^{14}C and ^{37}Ar are listed in Table 6. The tritium values are the sum of HT and CH_3T; the ^{14}C values are the sum of $^{14}CH_4$ and $^{14}CO_2$.

Table 6. Highest single-year releases of permanent-gas radioactivity.

Reactor	Year	^{3}H (Ci)	^{14}C (Ci)	^{37}Ar (Ci)
BWR (1538 MWt)	1971	2 E-1	2.4 E-1	2
PWR(I) (615 MWt)	1970	<6 E-2	>1.8 E-1	1.7 E-1
PWR(II)[a] (1300 MWt)	1971	<1 E-1	>8 E-1	1.2 E 1
PWR(II)[b] (1300 MWt)	1973	<1 E-1	7 E-1	5
PHWR (40 MWt)		2 E-1	2 E-4	1.9 E-1
HTGR (116 MWt)	1971	>6 E 1	<2 E-1	6.0 E 3

[a] Old core.
[b] New core.

Although the HTGR operator has reported a maximum annual release of only 14 Ci/yr of HTO in liquid effluents, the total tritium released may be well over 60 Ci/year, a value more consistent with the 700 Ci/yr available for release from an HTGR of this size [8].

Projections are shown in Table 7 of permanent gas releases for large reactors of similar thermal power now under construction or on order. Because of the difficulties in insuring against $^{14}CO_2$ losses during sample collection, total gaseous ^{14}C releases from a PWR may exceed the values in the table. Releases from a large HTGR could exceed 1,300 Ci/yr of HT and could approach 2 x 10^6 Ci/yr of ^{37}Ar if hold-up times are significantly less than 120 days.

Table 7. Projected annual release and boundary dose (1 km) of permanent-gas radioactivity from new reactors.

Reactor type	Power level MW(th)	Total release (Ci/yr)			Boundary dose (mrad/yr)		
		Tritium	^{14}C	^{37}Ar	Tritium	^{14}C	^{37}Ar
BWR	2760	4 E-1	4 E-1	4	4 E-3	6 E-2	4 E-3
PWR[a]	2440	1.3 E-1	>1.3	1.0 E 1	1.3 E-3	>3 E-1	7 E-3
PHWR	2600	1.3 E 1	1.3 E-2	1.2 E 1	1 E-1	2 E-3	1 E-2
HTGR	2500	>1.3 E 3	<5	1.3 E 5[b]	1.2 E 2	<1	1.4 E 2[b]

[a] Projected from PWR(II), new core.

[b] With a short holdup, ^{37}Ar from the HTGR could approach 2 E 6 Ci/yr and 2 E 3 mrad/yr.

The highest annual release values are not necessarily the maximum possible release rates. For PWR(I) and PWR(II) the values represent only about 60% of plant operating capacity. We have no estimate of the operating time for the HTGR, but it seems reasonable to assume a 60% to 70% operating capacity for this reactor as well. As plant capacity improves with new reactor designs, scaling factors for annual noble gas release might show an increase greater than that based on thermal power levels alone.

3.3 Boundary Doses

Doses at a boundary (1 km from the reactor) were estimated on the basis of effluent projections for new reactors. These were used to facilitate direct comparison of dose without the complication of differing power levels (Table 7).

The submersion dose for ^{37}Ar was calculated using USAEC regulatory guides [9,10]. If the measurements obtained for the HTGR to date are representative over the long term, the release of ^{37}Ar from the HTGR is doubly significant. Though ^{85}Kr is the dose-limiting nuclide during release, ^{37}Ar can contribute 20% additional submersion dose. If the gas effluents from other HTGRs are held for less than 120 days, ^{37}Ar may become dose-limiting. With no holdup it approaches a value 3 times that for ^{85}Kr. The second HTGR sample, which was held for a longer time prior to release, exhibits a lower ^{37}Ar ratio.

Dose estimates for ^{14}C require consideration of local exchange and uptake as well as submersion dose. Pasquill diffusion graphs [9,10] were used to calculate ^{14}C concentrations at 1 km. Dose estimates were then made by direct comparison to doses from atmospheric ^{14}C concentrations [11]. Similar calculations were performed for ^{3}H. The Pasquill graphs provided concentration estimates. Cosmic ray production rates from Lal and Peters [1] were used with UNSCEAR values [11] to make the dose calculations.

The boundary dose of each effluent not normally measured by the reactor operators will apparently be 1 mrad/yr or less, with the possible exception of ^{37}Ar and ^{3}H from the HTGR.

Boundary doses from ^{14}C in gas effluents from liquid-metal cooled (LMFBR) and gas-cooled (GCBR) breeder reactors should be low as well. The breeder reactors should present less nitrogen or carbon for activation to ^{14}C. Gaseous tritium, however, may be produced in the LMFBR at twice the HTGR production rate, and its retention by fuel cladding is expected to be poorer than in light-water reactors [8]. Unless specific control steps are taken, the size of the breeders and their siting density may create significant dose levels, particularly in more heavily populated areas.

3.4 ^{37}Ar and ^{39}Ar Production Mechanisms

The mechanism for production of ^{37}Ar and ^{39}Ar reactors is a matter of conjecture. Activity ratios of ^{37}Ar/^{39}Ar for the light-water reactor effluents are reasonably similar (Table 8), but they are different from the air activation ratio calculated for each duty cycle. A likely source of ^{37}Ar would be the ^{40}Ca(n,α)^{37}Ar reaction on calcium impurities in such reactor materials. Particularly in the case of the HTGR with its massive carbon moderator, the ^{40}Ca(n,α)^{37}Ar reaction may predominate. Lack of ^{41}Ar data for these samples limits the comparison to the one ratio.

Table 8. Comparison of radioargon production ratios to air activation ratios.

Source	^{37}Ar/^{39}Ar	^{41}Ar/^{37}Ar
Annual duty cycle		
Air activation	1.5 E 4	
BWR	9 E 2	
PWR(I)	>1.6 E 3	
PWR(II)[a]	>8 E 3	
HTGR	9 E 4	
Monthly duty cycle		
Air activation	9 E 4	6 E 1
PHWR	5 E 4	5 E 1
PWR(II)[b]	1.7 E 3	

[a] Old core.
[b] New core; sample collected one month after start-up.

A ^{37}Ar/^{39}Ar ratio lower than that calculated for air activation could be due to inadequate accounting of ^{37}Ar decay. Except for the new-core PWR(II) and the PHWR, the calculations were made for continuous irradiation over the annual operating cycle. The power reactors actually make brief, periodic shutdowns, permitting some ^{37}Ar decay; but to explain the low ratio in this way, one would have to postulate the equivalent of approximately 100 days of unaccounted ^{37}Ar decay, which seems unreasonably long. A possible explanation in the light-water reactors is that the reaction ^{39}K(n,p)^{39}Ar leads to a greater abundance of ^{39}Ar, thus decreasing the value of the ratio below that for air activation. On the other hand, the very low abundance of ^{39}Ar relative to ^{133}Xe and ^{85}Kr may have resulted in contamination of the ^{39}Ar fraction by these nuclides, thus lowering the ^{37}Ar/^{39}Ar ratio. This possible source of error is being studied more closely.

The ^{37}Ar/^{39}Ar ratio for the PHWR effluents is within a factor of two of the calculated air activation ratio. The ^{41}Ar/^{37}Ar ratio is also similar to the air activation value.

The ^{37}Ar/^{39}Ar ratio for HTGR effluents is greater than the air activation value by a factor of approximately 6 when corrected for decay during holdup. Such a ratio would most likely occur from a combination of calcium activation and air activation.

Future reactor design appears oriented toward the development of breeder reactors, either LMFBR or GCBR. Since ^{37}Ar is most likely produced outside the fuel elements, emissions from the LMFBR or GCBR are difficult to predict. If calcium impurity concentrations are high, ^{37}Ar releases may be as large as those from the HTGR, again producing a significant immersion dose unless sufficient decay is permitted prior to release.

3.5 Influence of ^{37}Ar Releases on Atmospheric Measurements

The ^{37}Ar reactor release levels have an important relationship to atmospheric studies being conducted by several laboratories in the U.S. and Europe. Lal and Peters [1] estimated that the average tropospheric specific activity of ^{37}Ar would be 2.1 x 10^{-2} dpm per kg of air, which is equal to 3 x 10^{-3} dpm per liter of argon or 1 x 10^{-14} μCi/ml of air.

Using atmospheric dispersion coefficients suggested by the U.S. Atomic Energy Commission in recently published regulatory guides [9,10], the ^{37}Ar concentrations at 100 and 1,000 km from the stack can be estimated (Table 9).

Table 9. ^{37}Ar concentrations (μCi/ml) at 100 and 1,000 km from the stack.

Reactor	Decay Time	Release period	At stack	100 km distant	1,000 km distant
BWR	30 m	Continuous	1 E-8	2 E-16	2 E-17
PWR(I)	45 d	≈1 week	5 E-9	1 E-16	1 E-17
PWR(II)	45 d	≈8 hours	1 E-7	7 E-13	7 E-14
HWPWR	None	1 hour	5 E-7	1 E-12	1 E-13
HTGR	120 d	≈8 hours	5 E-4	3 E-10	3 E-11
	None	≈8 hours	5 E-3	3 E-9	3 E-10

The maximum release rate of ^{37}Ar from the BWR could be as high as 1 μCi/sec at a concentration of 1 x 10^{-8} μCi/ml. Since the total release rate can vary downward from the maximum value as much as one order of magnitude at any specific time, BWR releases are not continuous in the strictest sense. The mean release rate for ^{37}Ar is 0.3 μCi/sec.

The maximum release rate of ^{37}Ar from PWR(I) could be as high as 2 μCi/sec at a concentration of 5 x 10^{-9} μCi/ml.

Although ^{37}Ar releases from PWR(II) are too low to contribute to the submersion dose, they may be sufficiently large to affect atmospheric ^{37}Ar measurements. At a PWR of this type, ^{37}Ar activity could be released for a few hours at a rate of 12 μCi/sec and a concentration of about 2 x 10^{-7} μCi/ml with a periodicity of 4 to 8 weeks, depending on operating conditions.

Puffs could therefore appear periodically at locations where atmospheric ^{37}Ar samples are being collected.

The ^{37}Ar release levels from the PHWR are comparatively high relative to its size. Puff releases of approximately 1-hr duration would occur monthly at the rate of approximately 5 μCi/sec and a concentration of 5 x 10^{-7} μCi/ml.

Releases of ^{37}Ar from the HTGR could have a pronounced effect on atmospheric studies. Not only are copious quantities of ^{37}Ar released annually, but the releases occur as puffs of a few hours duration every 3 to 6 weeks. The release rate, calculated from the highest annual release level in Table 5, could be 4,000 μCi/sec at a concentration up to 5 x 10^{-4} μCi/ml. Furthermore, the ^{85}Kr release limit in the plant's technical specifications is 6,000 μCi/sec. The corresponding ^{37}Ar release level could be as high as 300,000 μCi/sec at a concentration of 3 x 10^{-2} μCi/ml.

It is apparent that the BWR and PWR(I) would have only a nominal effect, if any, on ^{37}Ar measurements such as those being carried out at approximately 10^{-14} μCi/ml [3]. The short-term puffs exemplified by PWR(II) could contribute to low-level ^{37}Ar measurements at the University of Bern because samples are being collected within 150 km of a reactor identical in design to PWR(II).

The influence of the PHWR on any of the atmospheric physics laboratories is less pronounced. To our knowledge, no samples of atmospheric ^{37}Ar are being collected near the facility in which this reactor is located. What influence other research reactors of similar design might have is a matter of conjecture. The 40-MWt power level of this PHWR is also very small compared to approximately 2,800 MWt for heavy-water power reactors distributed globally. The influence of these reactors on the global inventory of ^{37}Ar requires further examination.

The HTGR would apparently contribute significantly to atmospheric ^{37}Ar measurements at distances up to a few thousand kilometers. Furthermore, if ^{37}Ar is released at the technical specifications limit, an 80-fold increase would result for the

HTGR concentrations in Table 9. Since the HTGR is about 110 km from the National Bureau of Standards laboratory which is conducting atmospheric ^{37}Ar measurements, its impact there must be considered. The HTGR is relatively small compared to other gas-cooled reactors. The newest U.S. HTGR, due to start operations soon, could contribute up to 44,000 Ci/year of ^{37}Ar with 120-day holdup and 480,000 Ci/year with no holdup. Four HTGRs now on order in the U.S. could each release up to 130,000 Ci/year of ^{37}Ar when finally operational. If gas hold-up times are significantly less than 120 days, ^{37}Ar releases from each of the new reactors could approach 1 x 10^6 Ci/year.

Extrapolation of noble gas releases for reactors of different design - or even for different reactors of the same design - cannot be quantitatively exact. It seems fair to expect, however, that with a scaling factor of approximately 300 for total thermal power and decay, there is a reasonable probability of significant perturbations on atmospheric ^{37}Ar levels by the several HTGRs being constructed in the U.S.

A number of carbon-moderated, gas-cooled reactors in Europe, particularly in France (total of 2,700 MWt) and the United Kingdom (total of 18,200 MWt), could also contribute large quantities of ^{37}Ar to the global inventory and create a significant impact on atmospheric ^{37}Ar studies. Gas-cooled reactors in Japan (580 MWt) and Italy (700 MWt) could cause local perturbations of ^{37}Ar levels in air.

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[10] U.S. Atomic Energy Commission Regulatory Guide 1.4, Assumptions used for evaluating the potential radiological consequences of a loss of coolant accident for pressurized water reactors, 1973.

[11] Report of the United Nations Scientific Committee on the Effects of Atomic Radiation, Ionizing radiation: Levels and Effects, Volume 1: "Levels," United Nations, New York, 1972, p. 29.

5. PRESENTATIONS

No journal publications were prepared under the auspices of the contract. However, six papers describing work partially funded by this contract were presented at two international symposia, one societal meeting and the University of Bern, Switzerland. The presentations were:

1. "Characterization of Radiogases from Nuclear Facilities," John M. Matuszek, Charles O. Kunz, Carl J. Paperiello and James C. Daly. Presented by J. M. Matuszek at the 18th Annual Meeting of the Health Physics Society, Miami Beach, Florida, June 17-21, 1973.
2. "Separation Techniques for Reactor-Produced Noble Gases," Charles O. Kunz. Presented at the Noble Gases Symposium, Las Vegas, Nevada, September 24-28, 1973.
3. "International Gas-Proportional Beta-Spectrometry for Measurement of Radioactive Noble Gases in Reactor Effluents," Carl J. Paperiello. Presented at the Noble Gases Symposium, Las Vegas, Nevada, September 24-28, 1973.
4. "Reactor Contributions to Atmospheric Noble Gas Radioactivity Levels," J. M. Matuszek, C. J. Paperiello and C. O. Kunz. Presented by J. M. Matuszek at the Noble Gases Symposium, Las Vegas, Nevada, September 24-28, 1973.
5. "Permanent Gas Measurements as Part of an Environmental Surveillance Program," J. M. Matuszek, C. J. Paperiello, C. O. Kunz, J. A. Hutchinson and J. C. Daly. Presented by J. M. Matuszek at the Symposium on Environmental Surveillance around Nuclear Installations, Warsaw, Poland, November 5-9, 1973.
6. "Permanent Gas Effluents from Nuclear Power Reactors," J. M. Matuszek. Presented at the University of Bern, Switzerland, November 14, 1973.

6. APPENDICES

The following tables summarize the concentration values obtained for the variety of reactor samples collected.

Measurements obtained by Ge(Li) γ-ray spectrometry are identified in all the appendices by the notation (γ) following the data entry. All other measurements which were obtained by gas-proportional β-spectrometry have no distinguishing marks.

Appendix A. BWR data.

Sample number	Sample type	Collection date	Radionuclide concentration (μCi/ml)	
			^{37}Ar	^{39}Ar
820107	Stack gas	6/22/72		
820215	"	10/2/72		
820219	"	"		
820219A	"	"	(1.88±0.04)E-6	
820219B	"	"		
820219C	"	"		
820219D	"	"		
630001	"	1/8/73	(1.39±0.01)E-5	(1.67±0.10)E-8
630001A	"	"		
630001B	"	"		
630001C	"	"		
630001D	"	"		
330004	"	"		
330004A	"	"		
330034	"	9/27/73		

Appendix A. BWR data (continued).

Sample number	Radionuclide concentration (μCi/ml)			
	^{85m}Kr	^{85}Kr	^{87}Kr	^{88}Kr
820107	(1.5±0.1)E-2(γ)[a]		<1.7 E-1 (γ)	(2.4±0.1)E-2(γ)
820215	(2.8±0.2)E-2(γ)	<5 E-4 (γ)		(5.0±0.9)E-2(γ)
820219		(2.38±0.09)E-5		
820219A		(1.95±0.02)E-5		
820219B		(5.0±0.8)E-6		
820219C				
820219D		(2.25±0.04)E-5		
630001		(1.53±0.01)E-4		
630001A		(1.61±0.08)E-4		
630001B		(1.88±0.01)E-4		
630001C		(1.84±0.01)E-4		
630001D		(1.68±0.03)E-4		
330004	(9.5±0.9)E-2(γ)		(2.6±0.3)E-1(γ)	(1.6±0.2)E-1(γ)
330004A				
330034	(6.9±0.7)E-3(γ)	<7 E-3 (γ)		(6.7±1.9)E-3(γ)

[a] Measurements obtained by Ge(Li) γ-ray spectrometry are indicated in this and all subsequent appendices by (γ).

Appendix A. BWR data (continued).

Sample number	Radionuclide concentration (μCi/ml)			
	^{131m}Xe	^{133m}Xe	^{133}Xe	^{135}Xe
820107		(2.4±0.3)E-3(γ)	(5.2±0.3)E-2(γ)	(5.2±0.3)E-2(γ)
820215		(5.1±0.5)E-3(γ)	(1.10±0.14)E-1(γ) (1.9±1.5)E-2(γ)	(1.07±0.06)E-1(γ)
820219			(4.0±1.5)E-2	
820219A			(5.04±0.07)E-2	
820219B				
820219C				
820219D				
630001	(1.3±0.2)E-3(γ)		(2.0±0.3)E-1(γ) (5.43±0.01)E-1	
630001A				
630001B				
630001C				
630001D				
330004			(2.1±0.3)E-1(γ)	(4.4±0.3)E-1(γ)
330004A		(1.01±0.09)E-1(γ)	(2.2±0.3)E-1(γ)	(4.5±0.3)E-1(γ)
330034	(1.9±0.9)E-3(γ)		(7.9±1.0)E-2(γ)	(7.6±0.5)E-2(γ)

Appendix A. BWR data (continued).

Sample number	Radionuclide concentration (µCi/ml)			
	HT	CH_3T	$^{14}CH_4$	$^{14}CO_2$
820107				
820215				
820219				
820219A	(2.15±0.11)E-7			(9.4±3.8)E-9
820219B				
820219C				
820219D	(2.7±1.5)E-7		<1.3 E-7	
630001		<2 E-9		(8.0±0.4)E-9
630001A	(6.00±0.04)E-7			
630001B				(4.9±0.2)E-6
630001C				(2.2±0.1)E-6
630001D				
330004				
330004A				
330034				

Appendix B. PWR(I) data.

Sample number	Sample type	Collection date	Radionuclide concentration (µCi/ml) ^{37}Ar	^{39}Ar
820223	Primary strip gas	10/18/72	(2.2±0.2)E-5	
820223A	Primary strip gas	10/18/72		
820225	Cover gas	10/18/72	(3.92±0.05)E-5	<4 E-7
820225A	Cover gas	10/18/72		
820225B	Cover gas	10/18/72		
820228	Containment air	10/18/72	(1.14±0.02)E-8	
820237	Cover gas	12/11/72		
820237A	Cover gas	12/11/72		
820237B	Cover gas	12/11/72	(1.96±0.02)E-4	

Appendix B. PWR(I) data (continued).

Sample number	Radionuclide concentration (µCi/ml) ^{85m}Kr	^{85}Kr	^{87}Kr	^{88}Kr
820223	(5.0±0.4)E-2(γ)[a]	(5.45±0.02)E-3	(1.4±0.1)E-2(γ)	(7.7±1.1)E-2(γ)
820223A		(6.4±0.3)E-3(γ)		
820225		(1.05±0.09)E-1(γ) (1.12±0.01)E-1		
820225A				
820225B		(3.93±0.02)E-3		
820228		(4.82±0.03)E-6 (3.74±0.03)E-6		
820237	(1.9±0.6)E-2(γ)	(6.7±1.1)E-2(γ)		
820237A		(4.61±0.02)E-2		
820237B		(6.61±0.03)E-2		

[a] See note for Appendix A.

Appendix B. PWR(I) data (continued).

Sample number	Radionuclide concentration (μCi/ml)			
	^{131m}Xe	^{133m}Xe	^{133}Xe	^{135}Xe
820223		(1.2±0.1)E-2(γ)	(4.2±0.5)E-1(γ) (3.58±0.03)E-1	(1.9±0.1)E-1(γ)
820223A	(3.0±0.3)E-3(γ)		(2.8±0.8)E-1(γ)	
820225	(3.3±0.5)E-2(γ)		2.4±0.3 (γ)	
820225A	(2.9±0.1)E-2(γ)		2.11±0.03	
820225B				
820228			(2.0±0.4)E-4(γ)	
820237		(2.4±0.2)E-2(γ)	1.33±0.17 (γ)	(7.3±0.4)E-2(γ)
820237A	(1.14±0.10)E-2		(9.2±1.0)E-1	
820237B				

Appendix B. PWR(I) data (continued).

Sample number	Radionuclide concentration (μCi/ml)			
	HT	CH_3T	$^{14}CH_4$	$^{14}CO_2$
820223	(5.2±0.6)E-6		(1.33±0.01)E-5	<2 E-6
820223A			(2.03±0.10)E-5	
820225				(2.3±0.4)E-6
820225A				
820225B	(3.6±0.2)E-6	<1.7 E-6	(1.69±0.02)E-5	
820228	(1.6±0.2)E-9		(8.9±0.3)E-9 (1.34±0.14)E-8	<3 E-10
820237		<4 E-5	(4.10±0.01)E-4	(7.6±0.2)E-6
820237A	(1.00±0.03)E-5			
820237B				

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Appendix C. PWR(II) data.

Sample number	Sample type	Collection date	Radionuclide concentration (μCi/ml)	
			^{37}Ar	^{39}Ar
820112[a]	Decay tank gas	6/23/72		
820207[a]	Decay tank gas	8/29/72	(4.52±0.06)E-5	
820220[a]	Burp gas	10/10/72	(3.01±0.01)E-4	<9 E-8
630005	Containment air	2/5/73	(1.41±0.07)E-5	
630005A	Containment air	2/5/73		
630005B	Containment air	2/5/73	(1.20±0.06)E-5	(6.0±1.0)E-9
330005	Primary strip gas	2/5/73		
330006	Primary strip gas	2/5/73	(6.5±0.4)E-4	
630002	In-service decay tank gas	2/5/73		
630003	In-service decay tank gas	2/5/73	(1.85±0.09)E-3	(1.41±0.12)E-6
630004	Decay tank gas	2/5/73	(2.8±0.01)E-3 (3.0±0.01)E-3	(2.0±0.1)E-6 (2.1±0.1)E-6
330018	Decay tank gas	5/11/73	(2.2±0.1)E-4	
330019	Decay tank gas	5/11/73		
330037	Decay tank gas	10/3/73		

[a] Samples 820112, 820207 and 820220 were taken from the old core; all others are from the new core.

Appendix C. PWR(II) data (continued).

Sample number	Radionuclide concentration (μCi/ml)			
	^{85m}Kr	^{85}Kr	^{87}Kr	^{88}Kr
820112[a]		1.18±0.05 (γ)[b]		
820207[a]		1.0±0.5 (γ) (7.07±0.03)E-1		
820220[a]		(7.7±0.7)E-2(γ)		
630005		(4±3)E-4(γ) (6.7±0.3)E-6		
630005A		(8.7±0.4)E-6		
630005B		(7.7±0.4)E-6		
330005	(3.1±0.2)E-2(γ)	(5.1±0.3)E-5	(4.6±1.1)E-2(γ)	(5.0±0.5)E-2(γ)
330006	(3.1±0.3)E-2(γ)	(8.7±0.5)E-5		
630002		(6.7±0.6)E-2(γ)		
630003		(6.9±0.6)E-2(γ) (4.7±0.2)E-2		
630004		(2.5±0.2)E-1(γ) (9.3±0.5)E-2		
330018	<2 E-1(γ)	(5.6±0.6)E-2(γ) (8.91±0.03)E-3		
330019		(5.1±0.4)E-2(γ)		
330037		(1.18±0.11)E-2(γ)		

[a] Samples 820112, 820207 and 820220 were taken from the old core; all others are from the new core.

[b] See note from Appendix A.

Appendix C. PWR(II) data (continued).

Sample number	Radionuclide concentration (μCi/ml)			
	^{131m}Xe	^{133m}Xe	^{133}Xe	^{135}Xe
820112[a]	(2.9±0.2)E-2(γ)		(1.8±0.1)E-2(γ)	
820207[a]			(2.2±0.1)E-2(γ) (1.90±0.02)E-2	(3.8±0.6)E-4(γ)
820220[a]		(1.2±0.1)E-2(γ)	(8.6±1.1)E-1(γ) (3.06±0.02)E-1	(4.9±1.5)E-4(γ)
630005			(7.6±1.0)E-4(γ)	
630005A			(5.9±0.3)E-4	
630005B				
330005		(1.0±0.1)E-2(γ)	(2.9±0.4)E-1(γ)	(1.90±0.10)E-1(γ)
330006		(1.0±0.1)E-2(γ)	(2.8±0.4)E-1(γ)	(1.85±0.11)E-1(γ)
630002		(1.60±0.14)E-2(γ)	(7.92±0.10)E-1(γ)	(4.6±0.3)E-2(γ)
630003	(6.0±0.3)E-3	(1.68±0.15)E-2(γ)	(8.04±0.10)E-1(γ) (3.7±0.3)E-1	(4.6±0.3)E-2(γ)
630004	(1.6±0.1)E-2		1.5±0.2 (γ) 1.4±0.1	
330018	(1.2±0.3)E-3(γ)		(3.3±0.4)E-2(γ)	(1.7±0.8)E-3(γ)
330019	(9.9±1.4)E-4(γ)	(4.0±0.6)E-4(γ)	(2.8±0.4)E-2(γ)	(1.5±0.5)E-2(γ)
330037	(5.9±0.9)E-4(γ)		(9±4)E-3(γ)	(1.2±0.8)E-5(γ)

[a] Samples 820112, 820207 and 820220 were taken from the old core; all others are from the new core.

Appendix C. PWR(II) data (continued).

Sample number	Radionuclide concentration (μCi/ml) HT	CH_3T	$^{14}CH_4$	$^{14}CO_2$
820112[a]				
820207[a]				
820220[a]	<5 E-7		(1.29±0.02)E-5	(3.0±0.4)E-6
630005	(8.0±0.4)E-8			
630005A	(6.0±0.3)E-8	<2 E-8	(2.65±0.15)E-7	(1.40±0.07)E-7
630005B				
330005				
330006				
630002				
630003	(5.4±0.8)E-6	<2 E-5	(1.9±0.1)E-4	(7±5)E-7
630004	(1.6±0.1)E-5	<5 E-5	(5.2±0.2)E-4	(5.7±1.1)E-6
330018	(2.79±0.18)E-6	<1.1 E-5	(1.08±0.06)E-4	
330019				
330037				

[a] Samples 820112, 820207 and 820220 were taken from the old core; all others are from the new core.

Appendix D. PHWR data.

Sample number	Sample type	Collection date	Radionuclide concentration (µCi/ml)		
			^{37}Ar	^{39}Ar	^{41}Ar
630007	Analyzer gas	3/21/73			(5.9±0.6)E-2(γ)
630008	Analyzer gas	3/21/73	(9.6±0.5)E-4		(5.6±1.7)E-2(γ)
630008A	Analyzer gas	3/21/73	(1.10±0.10)E-3 (1.17±0.10)E-3		
630008B	Analyzer gas	3/21/73	(1.10±0.10)E-3		
630008D	Analyzer gas	3/21/73		(2.38±0.15)E-8	
630008E	Analyzer gas	3/21/73		(2.12±0.18)E-8	

Appendix D. PHWR data (continued).

nple number	Radionuclide concentration (µCi/ml)				
	^{85m}Kr	^{85}Kr	^{88}Kr	^{133}Xe	^{135}Xe
630007	(9.0±1.0)E-5(γ)[a]		(1.1±0.3)E-4(γ)	(5.2±0.6)E-4(γ)	(1.59±0.12)E-4(γ)
630008				(5.6±0.7)E-4(γ) (7.9±0.4)E-4	(1.57±0.15)E-4(γ)
630008A		(5.8±0.3)E-8			

[a] See note for Appendix A.

Appendix D. PHWR data (continued).

Sample number	Radionuclide concentration (µCi/ml)			
	HT	CH_3T	$^{14}CH_4$	$^{14}CO_2$
630008A				(5.0±0.2)E-7
630008B	(1.30±0.10)E-3	(1.6±0.3)E-7	(8±2)E-8	

Appendix E. HTGR data.

Sample number	Sample type	Collection date	Radionuclide concentration (µCi/ml)		
			^{37}Ar	^{39}Ar	^{85}Kr
820235	Kr off-gas	11/5/72	4.53±0.03		(6.7±0.1)E-2(γ) (8.2±0.1)E-2
820235A	Kr off-gas	11/5/72			(1.19±0.01)E-2
820235B	Kr off-gas	11/5/72	1.83±0.06	(6.5±0.7)E-4	
820236	N$_2$-Ar off-gas	11/5/72	(2.12±0.02)E-2		(8.5±0.1)E-4(γ) (1.03±0.02)E-3
820236A	N$_2$-Ar off-gas	11/5/72	(2.43±0.01)E-2		(8.82±0.02)E-4
630011	Kr off-gas	6/28/73	1.06±0.05	(1.83±0.09)E-4	(1.09±0.05)E-1
630014	N$_2$-Ar off-gas	6/28/73	(1.79±0.09)E-2	(4.6±0.2)E-6	(2.0±0.2)E-2(γ) (1.94±0.10)E-2

Appendix E. HTGR data (continued).

Sample number	Radionuclide concentration (µCi/ml)				
	^{133}Xe	HT	CH$_3$T	^{14}CH$_4$	^{14}CO$_2$
820235	<3 E-3	<4 E-4	(4.55±0.04)E-2	<8 E-5	(3.5±0.6)E-4
820235A		(3.31±0.01)E-3	(3.96±0.01)E-2		(6.6±0.4)E-5
820235B					
820236	<3 E-5	(6.32±0.04)E-4	(1.49±0.03)E-4	<6 E-6	
820236A		(1.09±0.01)E-3	(5.68±0.02)E-5		(2.23±0.10)E-6
630011		(1.53±0.08)E-1	(1.22±0.12)E-2	<3 E-5	(9.3±0.6)E-6
630014		(4.5±0.2)E-2	(1.6±0.2)E-3	<1.6 E-5	(8.0±0.7)E-7