

Site phone # at TMI is: (717) 782-3955
Office in Middletown # is: (717) 782-4014

March 5, 1980

Mr. John Collins
Three Mile Island Nuclear Power Plant
U.S. Nuclear Regulatory Commission
P.O. Box 311
Middletown, Pennsylvania 17057

Dear Mr. Collins:

As discussed on the phone we see an unique opportunity to make use of our sensitive measuring capabilities during the possible release of containment air at TMI in the summer. The following is an outline of what could be done with emphasis on two major points:

- 1) Immediate: Analysis of a sample of containment air for the radioactive noble gases ^{85}Kr , ^{37}Ar (and ^{39}Ar) and analysis for the ^{14}C and ^3H concentrations and their distribution among the chemical compounds CO_2 , CO , CH_4 , C_2H_6 and higher hydrocarbons. This would enable you to assess the ^{14}C inventory of the containment air.
- 2) During possible release: Based on the anticipated ^{85}Kr releases our sensitivity would allow us to make measurements of ^{85}Kr concentrations in air at 50 miles and beyond. Sets of continuously drawn samples for extended periods of time in a sector at these distances during a clear-cut meteorological situation would enable us to check the validity of presently accepted dispersion models. All details would have to be planned according to the specific release situation and in close cooperation with a meteorology group. We feel that from such a comparison of a few (2-3) selected events to calculated predictions one could obtain valuable information in a unique release situation.

I am at any time ready to discuss aspects and details. My telephone number is (518) 474-5719, or FTS564-5719.

Sincerely yours,

Martin Wahlen, Ph.D.
Research Scientist IV
Radiological Sciences Laboratory

MW/rz

8008080048

Reprint Series
8 February 1980, Volume 207, pp. 639-640

Radioactive Plume from the Three Mile Island Accident: Xenon-133 in Air at a Distance of 375 Kilometers

Abstract. *The transit of an air mass containing radioactive gas released from the Three Mile Island reactor was recorded in Albany, New York, by measuring xenon-133. These measurements provide an evaluation of Three Mile Island effluents to distances greater than 100 kilometers. Two independent techniques identified xenon-133 in ambient air at concentrations as high as 3900 picocuries per cubic meter. The local γ -ray whole-body dose from the passing radioactivity amounted to 0.004 millirem, or 0.004 percent of the annual dose from natural sources.*

We observed the passage of radioactive ^{133}Xe , released from the Three Mile Island reactor, through the Albany, New York, area from 29 March through 2 April 1979. After the announcement of the reactor accident and possible releases of fission products into the atmosphere, air samples were collected in Albany and were analyzed for ^{133}Xe , which has a half-life of 5.3 days. We also monitored ^{133}Xe directly in ambient air throughout the entire transit period by observing the 81-keV γ -ray line with a planar intrinsic Ge detector located in a low-background steel chamber. To our knowledge, these measurements provided the only evaluation of Three Mile Island effluents at distances greater than 100 km.

Gas analyses of 1- to 3- m^3 samples of air were performed in two stages: cryogenic and chromatographic separation of Xe, followed by analysis of the β -decay spectrum (maximum energy, 346 keV) by internal gas-proportional counting in low-background systems (1). Aged compressed-air samples were processed through the gas separation system as blanks between Albany air samples. A low residual activity found after the processing of the higher-activity samples did not substantially reduce the sensitivity.

Ambient laboratory air was monitored by an intrinsic Ge diode with an area of 500 mm^2 and a resolution of 630 eV (full width at half-maximum at 81 keV). This instrument was in a low-background steel chamber (3.3 m square; 2.4 m high; wall thickness, 14.5 cm) in which outside air was exchanged about ten times an hour. During the entire period when ^{133}Xe was recorded, the thin window was covered by a pressed pellet of lake sedi-

ments with a thickness of 0.76 g cm^{-2} , which reduced the counting efficiency for ^{133}Xe by about 15 percent. After the transit the detector was calibrated under the same conditions with a virtual point source of ^{133}Xe . The net count rate in the 81-keV photopeak was measured as a function of the angular and radial position of the source over the entire field of view. Integration yielded an overall efficiency of 1.03×10^{-4} cpm $\text{pCi}^{-1} \text{m}^3$. The air volume effectively seen by the detector was 10.2 m^3 .

Errors reported are ± 2 standard deviations from the root-mean-square counting statistics of sample measure-

ments and background determinations. An additional uncertainty of ± 5 percent is introduced by the calibration. Detection limits are three times the background standard deviation.

Air samples collected on 30 March showed high ^{133}Xe concentrations: 3120 ± 160 pCi m^{-3} at 1500 Eastern standard time (EST), 3530 ± 180 at 1900, and 3900 ± 200 in a 10-hour sample (from 1545 to 0145 the next morning). By 31 March at 0900 the concentration had fallen to 39 ± 4 pCi m^{-3} . Samples collected on 3 April at 1600 and on 4 April at 1500 contained 11 ± 4 and 5 ± 2 pCi m^{-3} , respectively.

Ambient air analyses showed the same pattern of ^{133}Xe concentrations: no counts above background (< 360 pCi m^{-3}) before 29 March, but 1390 ± 290 pCi m^{-3} in a sample spanning 29 March (1230 EST) to 30 March (1500) and 1060 ± 180 pCi m^{-3} in a sample spanning 30 March (1530) to 2 April (0830). No excess counts were recorded after 2 April. The peak concentrations were more than three orders of magnitude higher than those normally present in ambient air. In 1974 the concentration of ^{133}Xe from all sources including routine releases from nuclear reactors was 2.6 pCi m^{-3} for the Albany area (1).

The results (plotted in Fig. 1) indicate that the air mass containing ^{133}Xe arrived in the Albany area after 1230 on 29 March and before 1500 on 30 March. A more precise arrival time could not be determined, since the diode measurements were integrated over a 24-hour pe-

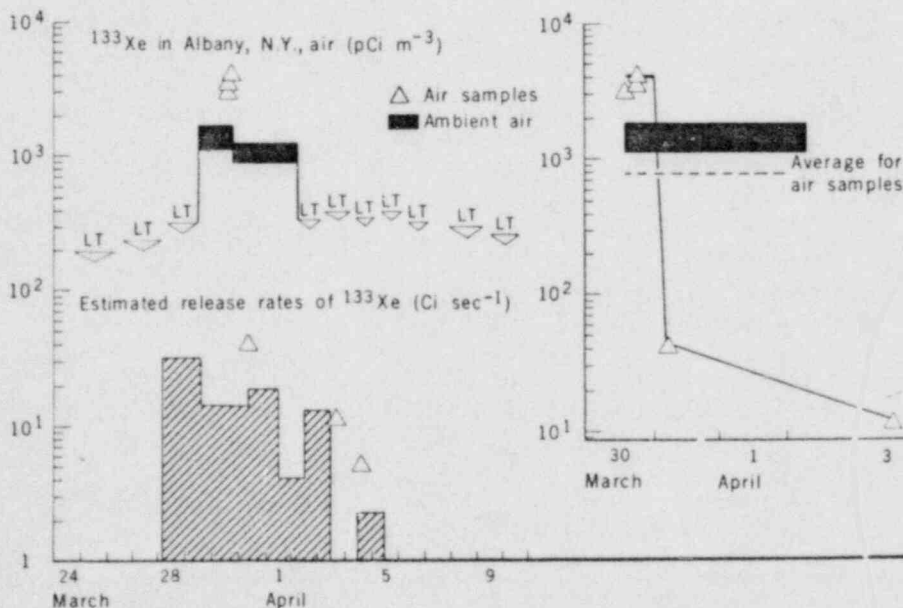


Fig. 1. Xenon-133 activity (picocuries per cubic meter of air) in Albany, New York, for the end of March and early April 1979. The lower trace shows the time-averaged estimates of releases (curies per second) from the Three Mile Island reactor (2). The inset shows detailed values for air samples (gas counting) and concurrent average values for ambient air (Ge diode). Abbreviation: LT, less than.

riod. The trailing edge is more sharply defined from the measurement of the air samples. The time behavior shown in the inset of Fig. 1 from the widely spaced air samples must closely represent the actual trailing edge of the passing air mass. This is evident from a comparison of the calculated time-averaged activity of 780 pCi m⁻³ for this period from air samples and the observed averaged activity of 1060 pCi m⁻³ from the diode measurement. The observed peak value for the ¹³³Xe activity at ground level was 3900 pCi m⁻³ for the air sample taken late on 30 March. Peak concentrations of ¹³³Xe for the period before 30 March could have been higher, depending on the actual arrival time of the air containing ¹³³Xe. The average value from the diode measurement for the 24-hour interval preceding 30 March was 1390 pCi m⁻³.

To describe the air mass transport in more detail, we collated the available data on release rates from the reactor and the regional meteorological conditions. Measured release rates for ¹³³Xe from the reactor were not available. Average release rates were estimated indirectly by the Nuclear Regulatory Commission, using thermoluminescence dosimeters in the vicinity of the reactor (2). These rates are plotted in Fig. 1. No releases occurred before 0400 EST on 28 March.

Regional meteorological conditions were examined by using forward (from Middletown, Pennsylvania) and backward (from Albany) air trajectories provided by the Air Resources Laboratory of the National Oceanic and Atmospheric Administration (3). The backward trajectories were calculated for a mean transport layer between 300 and 1500 m above the terrain. Forward trajectories were calculated for the same mean transport layer and also for transport at heights corresponding to 95, 90, and 85 kPa (10² kPa = 1 bar).

For the first release period on 28 March, the meteorological conditions at Middletown were rather stagnant, with medium- to low-speed winds gradually shifting from northwesterly to northeasterly to easterly and finally to southeasterly. From 29 to 31 March, southwesterly winds prevailed at increased speed. The mean transport layer forward trajectories for this period passed 80 to 160 km south of Albany. Backward trajectories for 29 to 31 March show that the mean transport through Albany originated predominantly from regions to the west and northwest of Harrisburg, Pennsylvania. Forward transport at the 95-

kPa level did, however, indicate a plume passage in the Albany area on 29 March.

In summary, the meteorology indicates that air arriving at Albany on 29 March contained radioactive gas released from the Three Mile Island reactor on 28 March, which had been dispersed rather widely around the point of origin and then moved northeastward at low levels. The most probable transit time appears to have been 18 to 24 hours for an approximate actual travel distance of about 500 km.

The whole-body dose to an individual in the Albany area from exposure to γ -rays and x-rays from the passing ¹³³Xe, calculated from the average activity values, was 0.004 mrem (4). This is about 0.004 percent of the annual whole-body dose from natural sources.

A search for airborne ¹³¹I showed no measurable activity, even though the air was analyzed by a highly sensitive β/γ coincidence counting method (5). Albany air processed through a charcoal cartridge impregnated with triethylenediamine during the 24-hour period of highest ¹³³Xe activity did not contain ¹³¹I at or above 8×10^{-4} pCi m⁻³.

Nor did we observe a measurable increase of ⁸⁵Kr in air. This is not surprising, considering the long half-life of ⁸⁵Kr (10 years), the lower fission yield, and the sizable atmospheric background concentration from atmospheric weapon testing and routine releases by the nuclear industry. The ⁸⁵Kr measured in the sample from 30 March (1500 EST)

amounted to 12.6 pCi m⁻³, which is within the range of 10.9 to 18.4 pCi m⁻³ encountered in samples of Albany air for the period 1975 to 1979.

In conclusion, the elevated ¹³³Xe concentrations observed in Albany on 29 and 30 March 1979 could be attributed to releases from the Three Mile Island reactor accident. The ¹³³Xe concentrations normally present in Albany air due to routine releases from nuclear reactors are lower by more than three orders of magnitude (1). The dose received from the passing radioactivity was found to be extremely small when compared to the dose from natural sources.

MARTIN WAHLEN
CHARLES O. KUNZ, JOHN M. MATUSZEK
WILLIAM E. MAHONEY
ROGER C. THOMPSON

*Division of Laboratories and Research,
New York State Department of Health,
Albany 12201*

References and Notes

1. C. O. Kunz, in *Noble Gases* (CONF-730915, ERDA, 1973), pp. 209-217; C. J. Paperiello, in *ibid.*, pp. 239-248; C. O. Kunz and C. J. Paperiello, *Science* **192**, 1235 (1974).
 2. L. Barret, Nuclear Regulatory Commission, Washington, D.C., personal communication.
 3. L. Machta, K. Telegadas, and J. Heffler from the Air Resources Laboratory of the National Oceanic and Atmospheric Administration, Silver Spring, Md., provided us with forward and backward trajectory calculations for the entire period of interest.
 4. 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* (revision 2, June 1974).
 5. C. J. Paperiello and J. M. Matuszek, *IEEE Trans. Nucl. Sci.* **22**, 642 (1975).
- 7 August 1979; revised 19 November 1979

Xenon-133: Ambient Activity from Nuclear Power Stations

Abstract. The average activity of xenon-133 within and at approximately 100 kilometers from Albany, New York, from April to July 1975 was 2.6 picocuries per cubic meter of air. The source was gaseous effluents from boiling water reactors located in the northeastern United States. Its 5.29-day half-life makes xenon-133 an appropriate isotope to observe for the study of regional and hemispheric dispersion of pollutants.

Although ^{133}Xe is an important gaseous radioactive fission product released in nuclear weapons tests and in the normal operation of the nuclear fuel cycle, it has usually been considered a local problem. With few exceptions, measurements of ^{133}Xe have been attempted primarily at the site boundaries of nuclear facilities. During 1964 and 1965, however, Scholch *et al.* (1) measured the activity of ^{133}Xe in atmospheric air samples taken from a location in West Germany. They observed an average activity of about 0.1 pc/m³. The source for this activity was not evident. However, a maximum was obtained in June 1965, possibly attributable to a Chinese nuclear bomb test.

In 1975 we undertook to measure the average ambient background of ^{133}Xe in northeastern New York State and to determine the source of this activity. From April to July we collected samples at various locations within and at approximately 100 km from Albany (Fig. 1). The pattern was designed to ensure that the activity we were measuring was not from a local source, such as a hospital or laboratory using ^{133}Xe , but was an ambient activity for this section of the state. Most of the sampling locations were 100 km or more from the nearest nuclear power reactor releasing ^{133}Xe . Whereas samples in the West German study were obtained from an air liquefaction plant, our sys-

tem permitted collection of grab samples at any desired location.

Air samples of 1 m³ were collected with a portable air compressor and 15-liter stainless steel vessels containing 1 to 5 cm³ of stable xenon carrier. The krypton and xenon fractions were separated from the samples by cryogenic adsorption and gas chromatography, as follows. The air sample in the high-pressure vessel was leaked at a reduced pressure of approximately 300 torr through a system containing three traps in series. The first trap, empty and at Dry Ice temperature, removed water vapor. The second trap, filled with glass beads and held at liquid nitrogen temperature, removed CO₂. The third trap, a column 1.5 m long and 1.25 cm in diameter filled with activated charcoal and maintained at liquid nitrogen temperature, retained the xenon and krypton. After the sample had been passed through, the charcoal-filled trap was warmed to 15°C, under vacuum, to remove most of the adsorbed nitrogen, oxygen, and argon. It was then heated to 200°C to drive off xenon and krypton, which were collected on a small molecular-sieve trap at liquid nitrogen temperature.

The krypton and xenon fractions are chromatographically separated and purified by using a column 4.6 m long and 0.63 cm in diameter filled with 94 percent type-5A molecular sieve and 6 percent

activated charcoal. Mass spectrometric analysis has shown that the separated fractions contained less than 1 percent N₂ and He impurities. The separated fractions are loaded into gas-proportional detectors, the specific volumes are measured, and the recovery fraction of each is determined from the known carrier volume of xenon added or from the known abundance of krypton in air. Recovery fractions averaged 70 percent for each.

The counting system for ^{85}Kr has been described (2). The counting system for ^{133}Xe is a beta-gamma coincidence system with a 45-cm³ gas-proportional detector with thin aluminum walls and a 7.6 by 17.8 cm NaI(Tl) well detector. It includes a plastic scintillation anticoincidence cosmic-ray guard, with all components enclosed in a 15.2-cm-thick steel shield. The purified xenon sample is mixed with P-10 counting gas and loaded. The counting rates in the ^{133}Cs x-ray region and the 81-keV gamma-ray region of the photon spectrum are used to quantify the ^{133}Xe . In the x-ray region the background is 0.018 count/min, and the efficiency is 0.26 count/min per disintegration per minute. Under the usual conditions of recovery and decay and for a 1-m³ sample volume, the detection limit, defined as 3 standard deviations over background (3), is 0.05 pc/m³.

Intermingled with the whole-air samples, 13 system blanks consisting of compressed, aged air were also processed. The results showed that the observed activities were not an artifact of the system. Spectral shapes and half-life measurements confirmed that the observed activity in the xenon fraction was due to ^{133}Xe . All sample spectra had the same shape as that of a National Bureau of

Fig. 1. Sampling area for ^{133}Xe survey. Marked sites are (●) sampling locations, (■) boiling water reactors, and (△) pressurized water reactors.

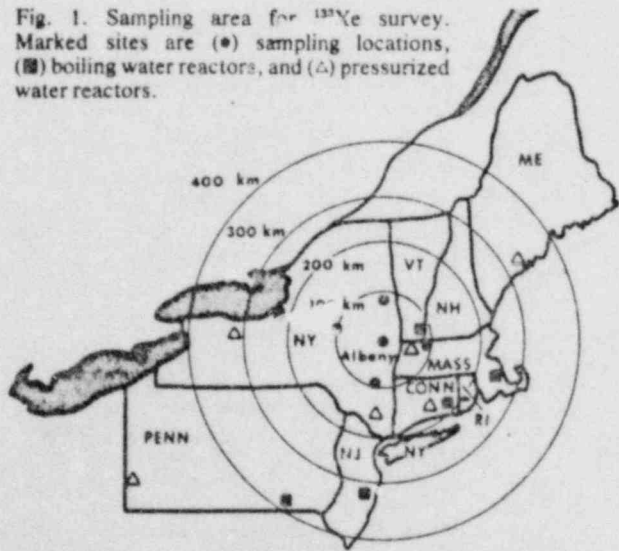


Table 1. Activity levels of ^{133}Xe and ^{85}Kr around Albany, New York, April to July 1975.

Date collected	Location	Activity (pc/m ³)	
		^{133}Xe	^{85}Kr
2 April	Albany	0.52 ± 0.09	
2 April	Albany	0.75 ± 0.11	16.7 ± 1.5
29 April	Albany	4.4 ± 0.3	16.2 ± 1.3
29 April	Albany	3.4 ± 0.3	16.3 ± 0.9
18 May	Albany	3.9 ± 0.2	17.8 ± 1.5
18 May	Albany	4.0 ± 0.2	18.4 ± 1.7
27 May	Little Falls	1.32 ± 0.08	14.3 ± 1.4
4 June	Kingston	3.18 ± 0.15	14.8 ± 1.2
11 June	Albany	7.5 ± 0.2	14.8 ± 1.2
18 June	Greenfield, Mass.	0.42 ± 0.05	17.2 ± 1.8
23 June	Albany	1.29 ± 0.13	16.5 ± 1.0
24 June	Albany	2.9 ± 0.3	16.5 ± 1.1
25 June	Albany	0.32 ± 0.07	16.1 ± 1.2
7 July	Lake George	2.37 ± 0.16	18.4 ± 1.0
Average		2.6	16.5

Standards ^{133}Xe standard, and the half-lives determined for several of the samples agreed with the 5.29-day half-life of ^{133}Xe . Samples collected in duplicate, then processed and counted several days apart, were also in agreement.

An average ambient activity of 2.6 pc/m^3 was obtained for ^{133}Xe (Table I). The variation of the ^{133}Xe activities measured for all locations is consistent with values anticipated for regional sources, indicating that the levels obtained are not due to a local source but represent the ambient activity for this section of the Northeast. The observed average value of 16.5 pc/m^3 for ^{85}Kr (Table I) is in agreement with the values measured by the Environmental Radiation Ambient Monitoring System (4).

The observed levels of ^{133}Xe represent no significant health hazard at the present time. However, the genetically significant dose from ^{133}Xe is about three times greater than that from ambient ^{85}Kr .

Nuclear power reactors are apparently the source of the ^{133}Xe activity. The interaction of cosmic rays with stable xenon cannot account for the observed levels, and there were no atmospheric tests for nuclear weapons during the 4 months when our measurements were made. The Soviet Union conducted two underground tests on 28 April and 10 June 1975. However, our findings before and after these tests show no indication that gaseous venting following these tests made a significant contribution of ^{133}Xe to the ambient level in the Northeastern United States. The locations of the operating nuclear power reactors within a radius of about 500 km from the sampling area are included in Fig. 1. Six boiling water reactors of current design release about two or three orders of magnitude more ^{133}Xe than the pressurized water reactors, they are evidently the predominant source of activity.

A regional dispersion model proposed by Machta *et al.* (5) for estimating long-term air concentrations was used to cal-

culate an average expected value of ^{133}Xe from the six boiling water reactors shown in Fig. 1. We used their phase 2 equation, which estimates concentrations in the region at distances representing a few hours to several days' travel from the source, and assumed that the wind frequency is equal in all directions. In view of the geographic distribution of the sources relative to the sampling sites, we believe that any errors inherent in this assumption would tend to cancel out. We further assumed that each boiling water reactor releases ^{133}Xe at a rate of $6.4 \times 10^{-6} \text{ c/sec}$ per megawatt (electric) capacity (6) and that each plant operates at 80 percent capacity. We also corrected for decay during diffusion. The calculated value of 3.3 pc/m^3 is in good agreement with the observed average of 2.6 pc/m^3 , especially allowing for the approximations used in the calculation.

Models for estimating concentrations over a short period, such as a few hours, would require wind data monitored at a number of stations to determine wind trajectories, combined with measurements of the release rate of ^{133}Xe from all sources. This information was not available. The activity levels for 23, 24, and 25 June, however, do show the influence of weather patterns. On 23 and 24 June the Albany area was under an inversion layer that had originated to the southeast. During the night of 24 June a cold front moved through the area. On 25 June the area was under the influence of a high-pressure system which had moved in from the northwest. The activity level decreased from 2.9 to 0.32 pc/m^3 after the weather front moved through.

Almost all the nuclear reactors currently in operation are located in the middle latitudes of the Northern Hemisphere. Dispersion of the effluent from these reactors is fairly rapid latitudinally and also vertically up to the mean mixing height. It takes about 30 days (5) for the effluent to travel around the earth, but in a matter of hours it reaches its mean mix-

ing height, which varies from about 200 to 4000 m, depending on location, weather conditions, and season (7). Vertical dispersion above the mean mixing height and beyond the temperate latitudes proceeds more slowly, requiring 1 to 2 years for dispersion throughout the earth's atmosphere.

The half-life of 5.29 days for ^{133}Xe is such that dispersion on a regional and hemispheric scale can be followed. Isotopes with significantly longer half-lives, such as ^{85}Kr (10.76 years), accumulate throughout the atmosphere, making regional dispersion measurements difficult. Further measurements of ambient ^{133}Xe could be correlated with more detailed information on the amount of ^{133}Xe being discharged from the various sources and on the climatologic and geographic parameters. Such an approach would provide a more comprehensive model for estimating regional and hemispheric dispersion of all airborne pollutants, both radioactive and non-radioactive.

C. O. KUNZ
C. J. PAPERIELLO

Division of Laboratories and Research,
New York State Department of Health,
Albany 12201

References and Notes

1. J. Scholch, W. Stich, K. O. Munnich, *Tellus* **18**, 298 (1966).
2. C. J. Paperiello, paper presented at the Noble Gases Symposium, Las Vegas, Nev., 24 to 28 September 1973.
3. IUPAC Commission, *Spectrochemical and Other Optical Procedures of Analysis, Appendices on Tentative Nomenclature, Symbols, Units and Standards* (International Union of Pure and Applied Chemistry, Washington, D.C., 1972), vol. 4, No. 26, p. 17.
4. Office of Radiation Programs, Environmental Protection Agency, Washington, D.C., private communication.
5. L. Machta, G. J. Ferber, J. L. Heffter, in *Physical Behavior of Radioactive Contaminants in the Atmosphere* (International Atomic Energy Agency, Vienna, 1974), p. 411.
6. "The safety of nuclear power reactors and related facilities," *USAEC Rep. WASH-1250* (1973), pp. 4-15.
7. G. C. Holzworth, *Mon. Weather Rev.* **89**, 235 (1964).
8. We thank J. M. Matuzek for his valuable advice and T. W. Miller for technical assistance.

12 January 1976; revised 7 April 1976

The experimental procedures have been described.¹⁻⁴ The radioactive species in the sample are individually counted in gas proportional counters after chromatographic separation.

At all six BWRs, over 95% of the ¹⁴C activity in off-gas samples was in the form of ¹⁴CO₂, as would be expected from the oxidizing atmosphere within the reactor vessel of a BWR. Since the off-gas is continuously released at a rate proportional to the power level of the reactor, we derived estimates for ¹⁴C release rates by using the measured specific activities and the actual or assumed condenser off-gas flow rates (Table I). At the reactor A, which has been repetitively sampled over a period of 3 years, the average release rate was found to be 12.4 Ci/GW(e)-yr. Release rates calculated from individual samples from this reactor were within a factor of 2 of the long-term average. At this writing, the other five BWRs have been sampled only once.

From the extensive data for reactor A and from the results for three of the other BWRs, the release estimates appear to be in reasonable agreement with the rates calculated for the production of ¹⁴C in the coolant of a BWR.⁵⁻⁸ The calculated rates are based primarily on ¹⁷O activation and vary from 9.2 to 11.5 Ci/GW(e)-yr. The estimated releases for the two remaining BWRs demonstrate that substantially higher production rates of ¹⁴C are possible. We attribute these to excessive nitrogen in the coolant. An equivalent amount of ¹⁴C would be produced from an N₂ concentration of about 25 ppm.

Carbon-14 and radioactive noble gases in stack-gas samples were generally found to be diluted according to the ratio of the release volumes of off-gas and stack gas, indicating that the coolant is the major source term for ¹⁴C gaseous release.

To judge the relative importance of gaseous ¹⁴C releases from BWRs, we compared the resulting ¹⁴C activity levels in the vicinity of a reactor to the present-day ¹⁴C activity in tropospheric air. The current ambient level of ~1.5 × 10⁻¹² Ci/m³ air originates from cosmic-ray production (1.06 × 10⁻¹² Ci/m³ air) and residual ¹⁴C from atmospheric testing of nuclear weapons (+40%). Using a representative measured value of 1.0 × 10⁻⁸ for the dispersion at 5 km from the stack of the reactor A¹⁰

2. ¹⁴C Discharge from Boiling Water Reactors, M. Wahlen, C. O. Kunz (NY State Dept of Health)

Carbon-14 is an activation product present in light-water reactors, originating from neutron reactions with isotopes of oxygen and nitrogen (¹⁷O, ¹⁴N) in both the coolant and the fuel. Gaseous ¹⁴C released at the reactor appears to be predominantly formed in the coolant.

To assess this ¹⁴C production and release, we determined (a) the chemical form and specific activity of various ¹⁴C species in off-gas and stack-gas samples from a series of BWRs and PWRs, and (b) the ¹⁴C activity in the coolant and in a variety of liquid and solid reactor wastes. In this paper we discuss the results obtained for six BWRs. Results and assessments of nine PWRs are now being completed.

TABLE I
¹⁴C Activities in BWR Off-Gas

Reactor	Maximum power [MW(e)]	¹⁴ C in off-gas (μCi/cm ³)	Power level at time of sampling (% max)	Off-gas rate (cfm)	Estimated ¹⁴ C release rate	
					(Ci/yr) ^a	[Ci/GW(e)-yr]
A	620	5.1-9.8 × 10 ⁻⁶	70-100	80-105	7.7	12.4
B	520	3.6 × 10 ⁻⁶	97	52	2.9	5.5
C	650	2.3 × 10 ⁻⁶	69	96	4.8	7.3
D	820	8.5 × 10 ⁻⁶	61	125	26	32
E	650	4.2 × 10 ⁻⁵	100 ^b	65	41	63
F	310	3.2-5.6 × 10 ⁻⁵	100 ^b	7.0-8.2	4.3	13.7

^a For operation at maximum power

^b Assumed

^c Assumed to be 6.027 cfm/MW(e)

and an annual release of 12.4 Ci of ^{14}C , we calculated an activity concentration of 3.9×10^{-15} Ci/m³ air at that distance. This corresponds to an increase of 0.4% above the natural level. At 1 km from the stack, these values would be about an order of magnitude higher.

Carbon-14 activity levels in the coolant, evaporator concentrates, spent resins, and filter materials varied considerably. Carbon-14 is present in liquid and solid wastes held for eventual discharge to burial sites; however, it is very difficult to relate these activities to quantitative release estimates, which will require more extensive sampling and close cooperation with the reactor operators. Preliminary estimates show that the amount of ^{14}C discharged as liquid and solid waste is less than that in gaseous effluents.

In conclusion, the release estimates for gaseous ^{14}C obtained from measurements on four BWRs are compatible with the calculated production from ^{17}O in the coolant. The results from two BWRs show that considerably higher discharges are possible, originating most likely from activation of excessive ^{14}N in the coolant.

1. C. O. KUNZ, W. E. MAHONEY, and T. W. MILLER, *Proc. Health Phys. Soc. 8th Midyear Symp.*, Knoxville, TN, CONF-741018, pp. 229-234 (1974).
2. C. O. KUNZ, W. E. MAHONEY, and T. W. MILLER, *Trans. Am. Nucl. Soc.*, 21, 91 (1975).
3. C. O. KUNZ, *Proc. Noble Gas Symp.*, Las Vegas, NV, pp. 209-217 (1973).
4. C. J. PAPERIELLO, *Proc. Noble Gas Symp.*, Las Vegas, NV, pp. 239-248 (1973).
5. H. BONKA, K. BRUSSERMANN, and G. SCHWARZ, *Reaktortagung*, Berlin (1974).
6. P. J. MAGNO, C. B. NELSON, and W. H. ELLETT, 13th AEC Air Cleaning Conf., San Francisco (1974).
7. D. W. HAYES and K. W. MacMURDO, *Health Phys.*, 32, 215 (1977).
8. G. N. KELLY, J. A. JONES, P. M. BRYANT, and F. MORLEY, Doc. V/2676/75, Commission of the European Communities, Luxembourg (1975).
9. T. W. FOWLER, R. L. CLARK, J. M. BRUHLKE, and J. L. RUSSELL, EPA Technical Note, ORP/TAD-76-3 (1976).
10. Niagara Mohawk Power Corporation, Preliminary Hazards Summary Rept. Nine Mile Point, Vol. II, Appendices (1974).

3. ¹⁴C Activity and Distribution in Gaseous Effluents from Pressurized Water Reactors, M. Wahlen, C. O. Kunz (NY State Dept of Health)

Production calculations predict that ¹⁴C is formed in the coolant of a PWR at a rate of 3.3 to 11.1 Ci/GW(e)yr (Ref. 1). Most ¹⁴C activity has been presumed to be released in gaseous form.

We have measured ¹⁴C activity and its distribution among carbon compounds in samples of decay-tank gas, containment air, and ventilation air obtained from nine PWRs. The concentrations of radioactive noble gases and tritium in these samples were also measured. From these data we have derived preliminary release estimates for ¹⁴C. The experimental techniques (gas-chromatographic separation and internal gas-proportional counting) have been described earlier.^{2,3} The results are summarized in Table I.

TABLE I
 Total ¹⁴C Activities and Distributions Among Carbon Compounds in Gas Samples from Nine PWRs

PWR	Total ¹⁴ C activity ($\mu\text{Ci}/\text{cm}^3$)			¹⁴ CO ₂			¹⁴ CH ₄			¹⁴ C-hydrocarbons ^a		
	Decay $\times 10^{-4}$	Cont $\times 10^{-7}$	Vent $\times 10^{-9}$	%			%			%		
				Decay	Cont	Vent	Decay	Cont	Vent	Decay	Cont	Vent
A	2.3	2.0		10			70			19		
C	3.5	7.9	<2	9	20		80	80		10	-	
E	2.7	27	<0.6	11	3		74	94		15	3	
F	6.7	0.17		9	-		63	62		28	38	
G2	0.29			4			68			28		
B1	2.0	2.3	5.9	27	7	13	37	65	58	33	29	20
B2		43			3			50			47	
B3	1.6			28			45			19		
D	25	8.6	2.2	27	9	18	55	91	82	18	-	-

Decay: Decay tank gas
 Cont: Containment air
 Vent: Ventilation air
^aC₂H₆ + C₃H₈ + C₄H₁₀

The distribution of ^{14}C among the carbon compounds in PWR decay-tank gas suggests that the reactors fall into two groups. For the first group, 89 to 96% of the activity is found as hydrocarbons. These compounds are expected from the reducing conditions in the primary coolant (H_2 cover gas). In the second group, almost 30% of the ^{14}C is present as CO_2 , most likely formed by oxidation of the hydrocarbons in the decay tanks due to high radiation levels and excessive air inleakage from the vent header.⁴

For containment-air samples the ^{14}C activity of all nine reactors is predominantly in hydrocarbons, distributed much like the first group of decay-tank samples. The low $^{14}\text{CO}_2$ concentrations in containment air support the assumption that $^{14}\text{CO}_2$ is formed in the decay tanks and that the ^{14}C activity in containment is not likely to have been produced by activation of ^{14}N under the oxidizing conditions of containment air. It apparently originates from gases which are formed in the coolant under reducing conditions and then leak into the containment vessel. We estimate ^{14}C release rates of 0.3 to 1.9 Ci/GW(e)yr from containment purges, based on measured specific activities, containment volumes, and periods of isolation prior to sampling.

We have attempted to estimate total gaseous ^{14}C activity releases by applying the measured ratio of $^{14}\text{C}/^{85}\text{Kr}$ in the decay-tank samples to the reported ^{85}Kr release rate from all sources, averaged over the period of sampling. This approach assumes that the coolant is the common source for gaseous ^{14}C , which appears reasonable, given the similarity of $^{14}\text{C}/^{85}\text{Kr}$ ratios in containment air, ventilation air, and decay-tank gas of any one PWR. Unfortunately this approach relies on reported ^{85}Kr releases, which can vary considerably with time according to fuel-rod integrity and decay-tank gas release practices.

Since production of ^{14}C is likely to be proportional to the reactor power level, representative release estimates can be obtained by this method only for reactors with reasonably constant ^{85}Kr releases. This is the case for PWR A, B1-3, and D, with estimated ^{14}C releases of 9.8, 6.6, and 9.9 Ci/GW(e)yr, respectively, using reported ^{85}Kr releases for the 3 months prior to and 3 months after the sampling date. At reactor E most of the ^{85}Kr is released from decay tanks, which are vented about once a year. The ^{14}C release was estimated at 7.5 Ci/GW(e)yr, using a 4-yr average of the ^{85}Kr releases from these tanks. For the remaining reactors, C and F, highly variable ^{85}Kr releases are reported, so the ^{14}C release estimates also ranged widely [1 to 36 and 5 to 134 Ci/GW(e)yr, respectively, based on slightly different averaging periods].

At most reactors only one set of samples was obtained. However, the estimate of 9.8 Ci/GW(e)yr for PWR A is an average of six sets of samples taken over a period of 3 years. The release estimates for individual samples ranged from 3.8 to 23.3 Ci/GW(e)yr.

Apart from variations in ^{85}Kr release rates, the monitoring of ^{85}Kr releases may not be sufficiently accurate to measure all the ^{85}Kr discharged. ^{14}C releases can be determined more accurately by employing continuous stack-gas and ventilation-air samplers for CO_2 and hydrocarbons over extended periods, including all phases of the reactor operating cycle.

1. T. W. FOWLER, R. L. CLARK, J. M. BRUHLKE, and J. L. RUSSELL, ORP/TAD-76-3, EPA Technical Note (1976).
2. C. O. KUNZ, *Proc. Noble Gases Symp.*, Las Vegas, NV, pp. 209-217 (1973).

3. C. J. PAPERIELLO, *Proc. Noble Gases Symp.*, Las Vegas, NV, pp. 239-248 (1973).
4. C. T. YONGUE, Personal Communication.

SEPARATION TECHNIQUES FOR REACTOR-PRODUCED NOBLE GASES*

C. O. Kunz
Radiological Sciences Laboratory
Division of Laboratories and Research
New York State Department of Health
Albany, New York 12201

Abstract

Procedures for separating the permanent gases have been developed as part of a study to characterize the gaseous radioactive effluents released from nuclear facilities. The gases being separated for internal gas-proportional counting include Ar, Kr, Xe, H₂, CH₄, and CO₂. Water vapor is cryogenically separated for liquid scintillation counting. Samples taken for processing within each facility range from 0.1 ml to several liters in volume. Sample volumes less than 10 ml are separated directly by chromatographic methods. Larger samples are processed using cryogenic-adsorption techniques for rough separation followed by chromatographic purification. Procedures for preventing cross-contamination from sample to sample, and between different radioactive gases within a sample, are considered. Processing requirements imposed by gas composition are also discussed.

INTRODUCTION

The Radiological Sciences Laboratory of the New York State Department of Health is studying the gaseous radioactive effluents from nuclear facilities (Matuszek, *et al.*, 1973). Samples have been obtained from two pressurized water reactors (PWR), a boiling water reactor (BWR), a high-temperature gas-cooled reactor (HTGR), and a pressurized heavy-water-moderated research reactor. The samples, taken from a variety of locations at each reactor, include primary strip gas, cover gas, decay-tank gas, containment air from the PWRs, and stack gas from the BWR.

Procedures for separating the noble gases, in addition to other permanent gases, have been developed as part of this study. The gases currently being routinely separated include Ar, Kr, Xe, H₂, CH₄, and CO₂. The activity is measured using internal gas-proportional beta-spectrometry (Paperiello, 1973). Water vapor is cryogenically separated for liquid scintillation counting.

The range of specific activity from sample to sample has been greater than five orders of magnitude, depending on the reactor and sampling locations. We have measured activities of various nuclides in individual samples that differ in activity by approximately seven orders of magnitude. Consequently precautions have been 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 have been processed, depending on the activity of the gases being analyzed.

Sample volumes less than 10 ml are separated directly by chromatographic methods. Larger samples are processed using cryogenic-adsorption techniques for rough separation followed by chromatographic purification.

SAMPLE COLLECTION AND MASS SPECTROMETRIC ANALYSIS

Samples are collected in a variety of vessels ranging in volume from 14 ml to 16 liters. Since vessels with septum caps tend to leak, those with stopcocks or valves are preferable.

Upon receipt of a sample, an aliquot is counted on a Ge(Li) spectrometry system to measure the activity of gamma-emitting gaseous radionuclides. These results are used as an aid in determining the subsequent separation procedures, and are compared with the results obtained by proportional counting.

An aliquot of the sample is 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 various types of reactors are shown in Table 1. The composition, which can vary considerably from sample, to sample, influences the choice of a separation procedure. In addition, species such as hydrocarbons that may contain ¹⁴C or tritium can be identified and subsequently measured for possible activity. Finally, it is necessary to determine whether a significant amount of any of the gases being separated is present in the sample. The concentrations of most of the radioactive gases in the sample are far too low for the normal methods of chemical analysis, and measured amounts of carriers for the gases being separated are added. The radiochemical recovery of the separated gas finally loaded into a proportional tube for counting is determined from the total amount of gas present before separation.

GENERAL SEPARATION PROCEDURE

Figure 1 indicates the general procedure for processing the samples. If a sample (such as cover gas or decay-tank gas) is relatively high in total specific activity, and if the concentration of the lowest-activity gas fraction

*Supported in part by USAEC contract AT(11-1)2222 and USEPA contracts 68-01-0522 and 68-01-LA 0505.

is higher than approximately 5 pCi/ml of sample, less than 10 ml of sample is processed. The sample is mixed with carriers and injected directly into a chromatograph for high-activity samples. The separated fractions are trapped, and those relatively high in activity are measured for percent yield, and loaded into proportional tubes for counting. The trapped gases that are relatively low in activity (in general, $< 10^{-1}$ μ Ci in the separated fraction) are sent through a separate chromatograph for further purification and decontamination. The gases trapped from this intermediate-level chromatograph are measured for chemical recovery, and loaded into gas-proportional counting tubes using a gas-handling rack reserved for the intermediate- to low-activity fractions. This separation of systems is necessary to minimize cross-contamination.

Samples (such as containment air) that are relatively low in specific activity and contain gas fractions with activity less than approximately 5 pCi/ml must be processed in aliquots of one or more liters. These undergo rough separation prior to chromatographic purification. Because of the volume reduction following this rough separation from such large sample volumes, some fractions have high specific activity, while others are relatively low. The high-activity fractions and the intermediate- to low-activity fractions are chromatographically purified on separate systems prior to being loaded for counting as described above.

HIGH-ACTIVITY SAMPLES

Figure 2 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. The sample is measured and mixed with measured amounts of carriers for Ar, Kr, Xe, H₂, CH₄, and CO₂. About 0.5-1.5 ml of each carrier is a convenient amount to process. The sample and carriers are then transferred to a molecular sieve U-trap connected to a gas injection valve on the chromatograph. The gases are transferred from section to section using molecular sieve fingers and U-traps. The molecular sieve is 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 is passed through the chromatograph. As the various gases are eluted (as observed with a thermal conductivity detector), the gases of interest are trapped on molecular sieve U-traps cooled with liquid nitrogen. The helium carrier is pumped off the cooled traps. The trapped gases that are relatively high in activity are volume-measured for chemical recovery and then loaded into gas-proportional counting tubes. The low-activity gases are transferred to a separate system used only for intermediate- to low-level gases. There they are further purified through the intermediate-activity chromatograph, volume-measured, and loaded into tubes.

Figure 3 is a more detailed drawing of the type of volume-measure and tube-load systems used. The gas to be measured is transferred to the molecular sieve finger. Stopcocks A and B are then closed, and the finger is heated to desorb the gas off the molecular sieve. When no more gas is being desorbed, stopcock C is closed, and the pressure of the gas contained between stopcocks A, B, and C is measured. The volume contained between these stopcocks has previously been determined, and from these data the amount of gas present is calculated. If the gas is to be loaded into a proportional-counting tube, it is expanded into the evacuated tube, which is then filled with counting gas to slightly more than atmospheric pressure.

Figure 4 shows typical chromatograms obtained with the high-activity and intermediate-activity chromatographs. The high-activity chromatograph has a column of 10' x 1/4" molecular sieve 5A, 40-60 mesh, with helium carrier flowing at 60 ml/min. Normally the column is run at room temperature until the CH₄ fraction is off, and then is heated to 300°C to drive off the xenon and CO₂ fractions. There is very little separation between the krypton and CH₄ on the high-level chromatograph. However, on the intermediate-level chromatograph, which has a column of 20' x 1/4" molecular sieve 5A, 40-60 mesh, the separation is very good.

Very often the krypton in a sample has a much higher activity than the ¹⁴C or tritium in methane. To determine the decontamination factor between krypton and CH₄, a ⁸⁵Kr source was mixed with the carriers, and as the krypton and CH₄ 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} μ Ci; the activity of krypton in the CH₄ fraction was 2.0×10^{-5} μ Ci. The decontamination factor for krypton in the CH₄ fraction was thus 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^{-1} μ Ci of krypton was mixed with the carriers prior to injection. No measurable activity could be seen for krypton in the CH₄ fraction, and a value of less than 8.2×10^{-7} μ Ci was obtained, resulting in a decontamination factor greater than 170. There is over 10 minutes of baseline separation between these peaks, and the decontamination factor is certainly much higher than indicated from the low activity of krypton used. In the normal processing of a sample, the CH₄ fraction trapped off the high-level chromatograph would be sent through the intermediate-level chromatograph prior to counting, with a combined decontamination of krypton considerably greater than 3×10^1 . This example illustrates the high decontamination factors obtainable with multiple GC purification.

Cross contamination is normally limited not by GC separation, but by system contamination. The problem of system contamination varies from gas to gas, and is most severe with tritium — either as gas or water vapor. To measure activities differing by more than six orders of magnitude, a separation of gas-handling systems and chromatographs as described above is required. In addition, system and proportional-tube blanks must be run between samples to determine possible residual activities.

INTERMEDIATE-ACTIVITY SAMPLES

The separation system used for liter-size, intermediate-activity samples is shown schematically in Figure 5. With this system, the volume of each separated fraction is reduced to several milliliters for subsequent chromatographic purification. The procedure involves adsorption followed by elution with helium carrier, similar to the methods described by Momyer (1960) for krypton and xenon. The sample is mixed with carriers, bled at a rate of approximately 40 ml/min through two cold traps, and then adsorbed on a 4' x 1/2" glass coil of activated charcoal cooled with liquid nitrogen. The trap cooled with dry ice-acetone collects the water vapor; the trap cooled with liquid nitrogen collects the xenon and CO₂.

After the sample has been adsorbed onto the charcoal, which is maintained in a liquid nitrogen bath, a helium flow is 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 is about 4' x 1/2". After the helium flow is established, a small fraction of the helium stream coming off the molecular sieve coil is continuously sampled with an Aero Vac 610 mass spectrometer. Various other methods, such as a thermal conductivity cell, could be used to monitor the gases eluted from the adsorbents.

Once the retention times for the gases of interest have been determined, sampling is not necessary. When dry ice-acetone slurries are placed around both the charcoal and molecular sieve coils, the hydrogen, argon, oxygen and nitrogen are rapidly eluted from the charcoal, while the krypton and CH₄ are retained. The hydrogen is observed coming off the molecular sieve coil about 5 minutes after both coils have been cooled with dry ice-acetone, and it is entirely off approximately 3 minutes later. It is trapped in a molecular sieve U-trap cooled with liquid nitrogen. Approximately 5 minutes after the hydrogen is off, argon and oxygen are observed coming off the molecular sieve coil. These gases are trapped together on a separate U-trap. At dry-ice temperature, the nitrogen is retained on the molecular sieve coil, while the argon and oxygen are eluted and trapped. The coil is then warmed to room temperature to elute the nitrogen. When the nitrogen is off, both coils are warmed to about 100°C to accelerate the elution of the krypton and CH₄, which are trapped together on the third molecular sieve U-trap. The argon and oxygen, which are not easily separated by chromatographic methods, are transferred to a furnace containing copper turnings which is heated to approximately 400°C to remove the oxygen by reduction to CuO.

All the separated fractions, which are now reduced in volume to several milliliters, are chromatographically purified as described for small-volume samples.

Between samples all the adsorbents used in separation of the gases are heated to 400°C while being purged with helium, or evacuated, in order to remove any residual gases and to reactivate the adsorbents for subsequent processing cycles.

SUMMARY

Methods of separation for Ar, Kr, Xe, H₂, CH₄, and CO₂ in reactor gas effluent samples up to several liters in size have been described. These general separation procedures are being extended to include other gases of interest, such as CO, C₂H₆, C₃H₈, SO₂, I₂, and CH₃I.

The counting techniques and interpretation of the effects of noble gas levels are described in the accompanying papers.

REFERENCES

Matuszek, J.M., C.J. Paperiello and C.O. Kutz, (1973), *Reactor Contributions to Atmospheric Noble-Gas Radioactivity Levels*, Proceedings of the Noble Gas Symposium, Las Vegas, Nevada, September 24-28, 1973.

Momyer, F.F., (1960), *The Radiochemistry of the Rare Gases*, Report NAS-NS 3025 (National Academy of Sciences, National Research Council).

Paperiello, C.J., (1973), *Internal Gas-Proportional Beta-Spectrometry for Measurement of Radioactive Noble Gases in Reactor Effluents*, Proceedings of the Noble Gas Symposium, Las Vegas, Nevada, September 24-28, 1973.

TABLE 1. The Gas Compositions 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	Heavy-water research reactor 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 ₂ H ₆	---	ID	0.02	---	---	---
C ₃ H ₈	---	ID	---	---	---	---
H ₂ O	---	0.07	0.87	---	---	---

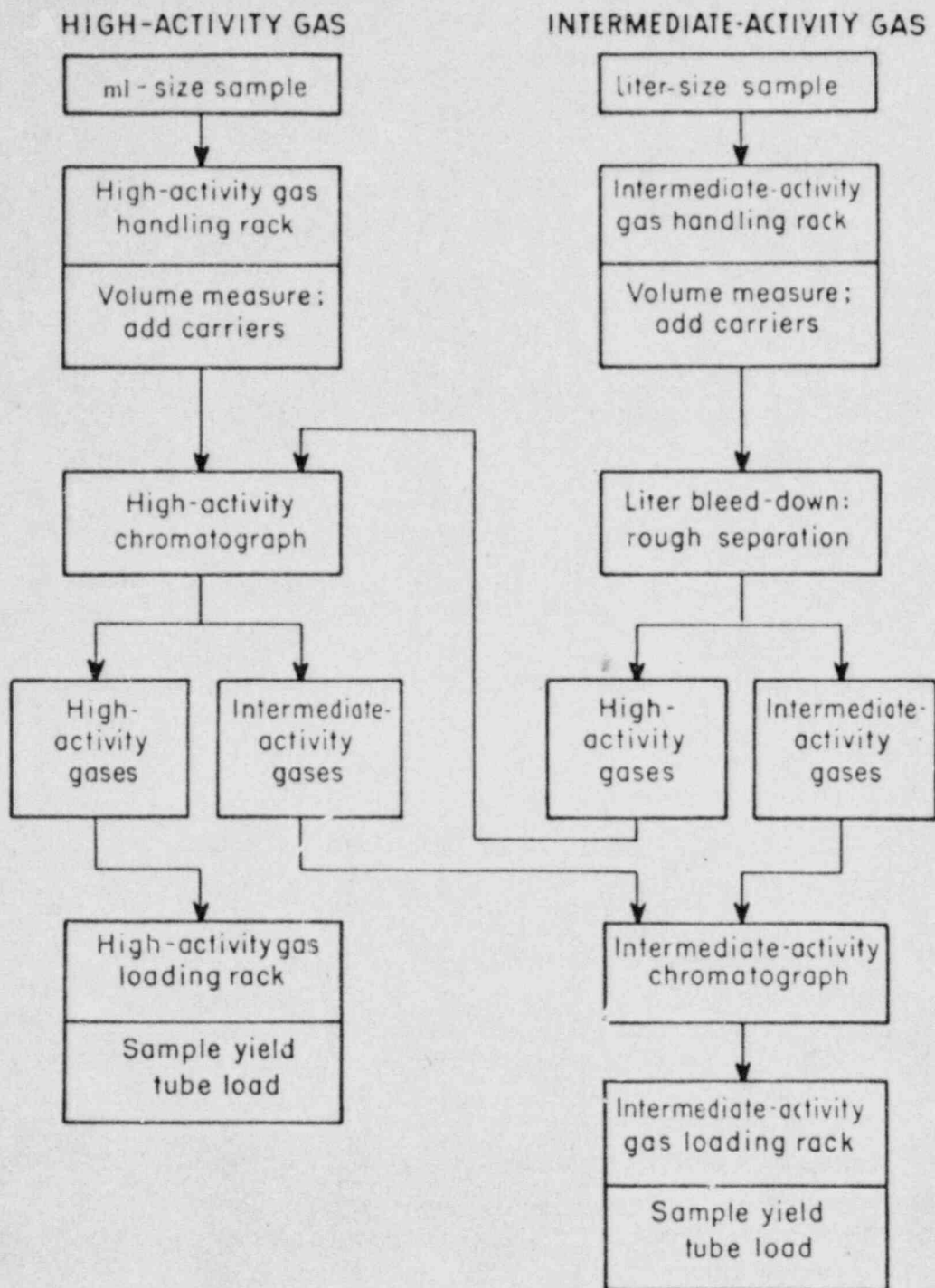


Figure 1. Processing procedure for high-activity and intermediate-activity gas samples.

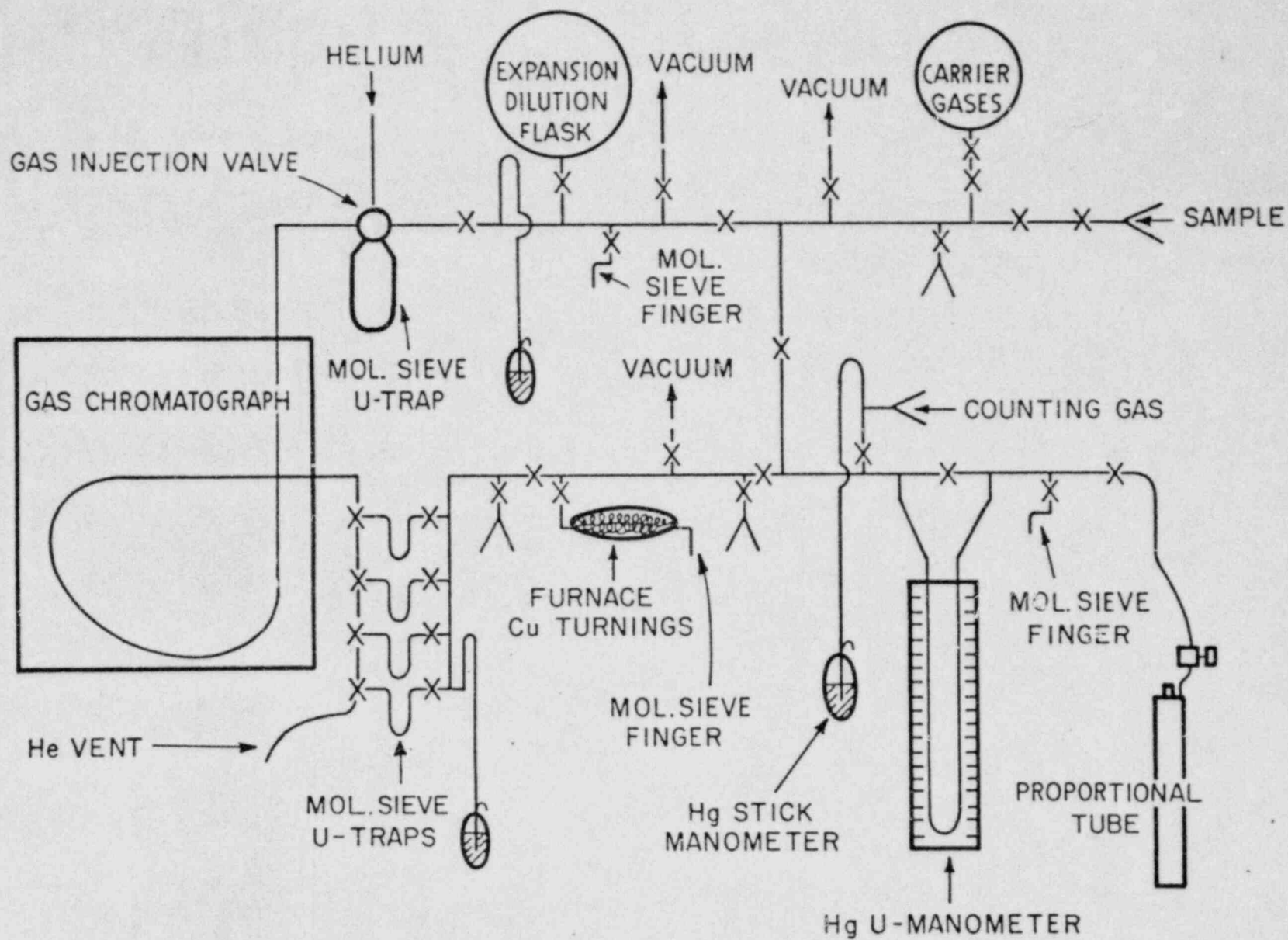


Figure 2. Schematic diagram of the high-activity gas separation system.

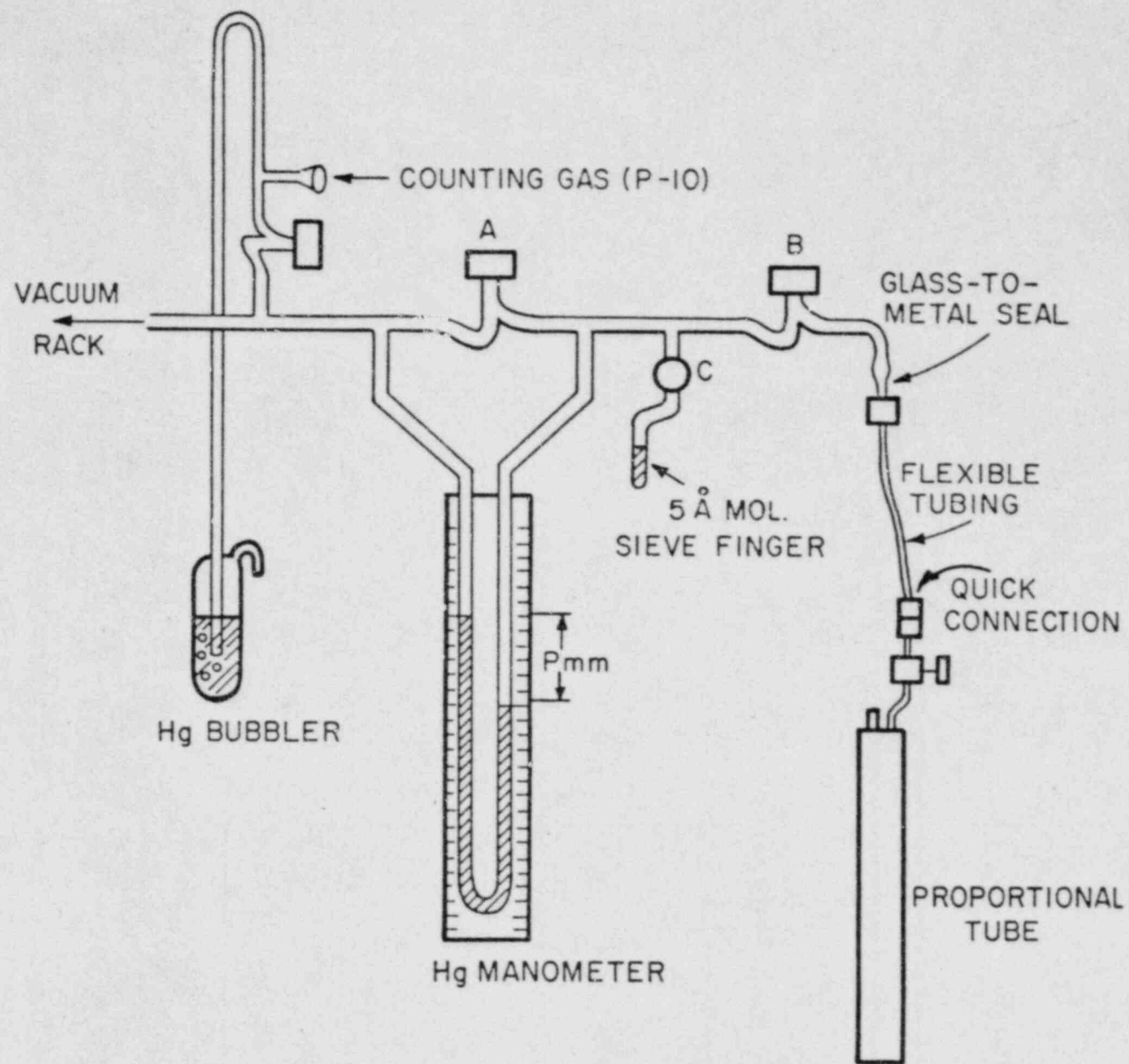


Figure 3. Volume-measure and tube-load sections of separation system.

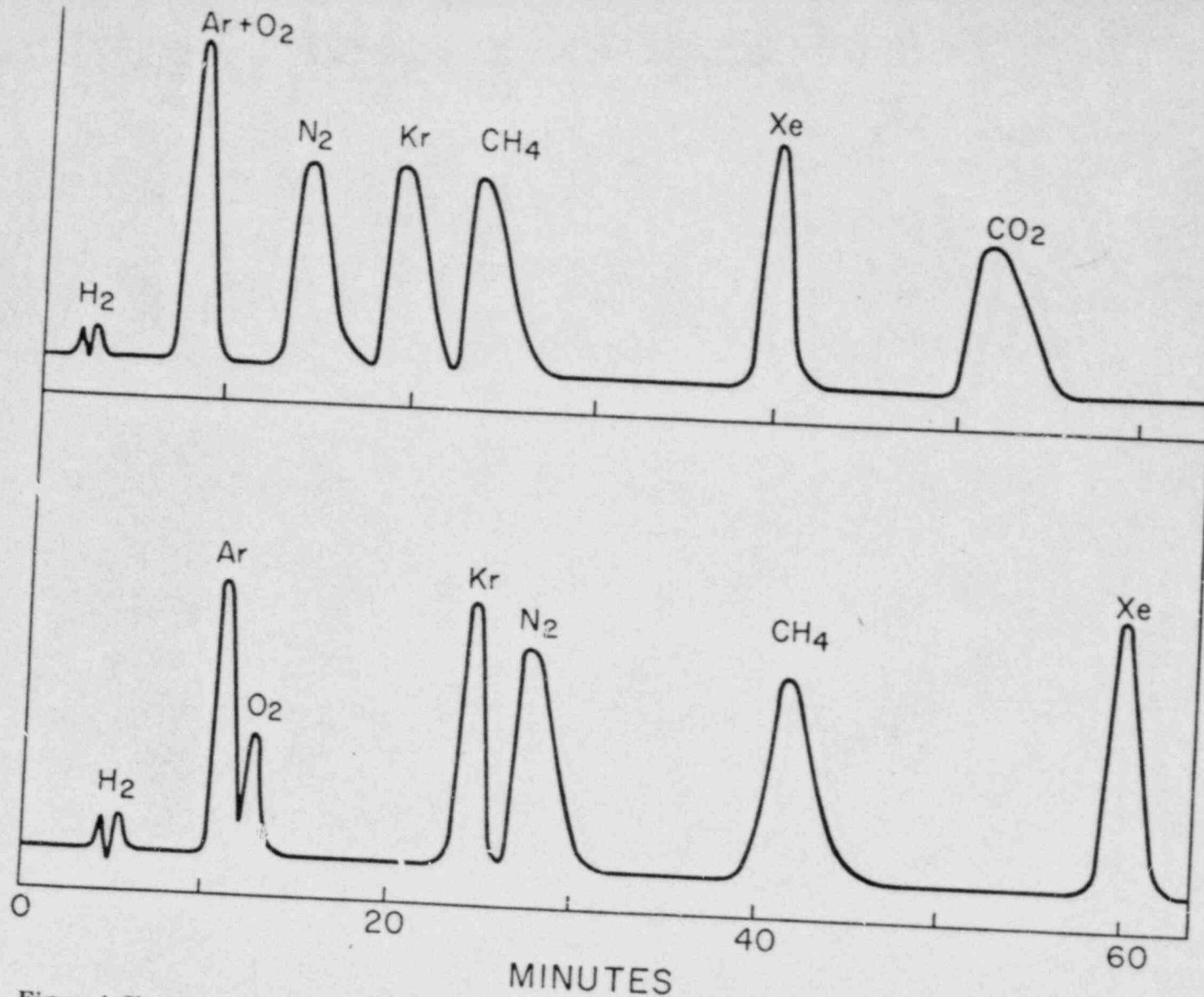


Figure 4. Chromatograms for permanent gases on molecular sieve 5A, 40-60 mesh; helium flow 60 ml/min. (Top: High-activity column; 10' x 1/4". Bottom: Intermediate-activity column; 20' x 1/4".)

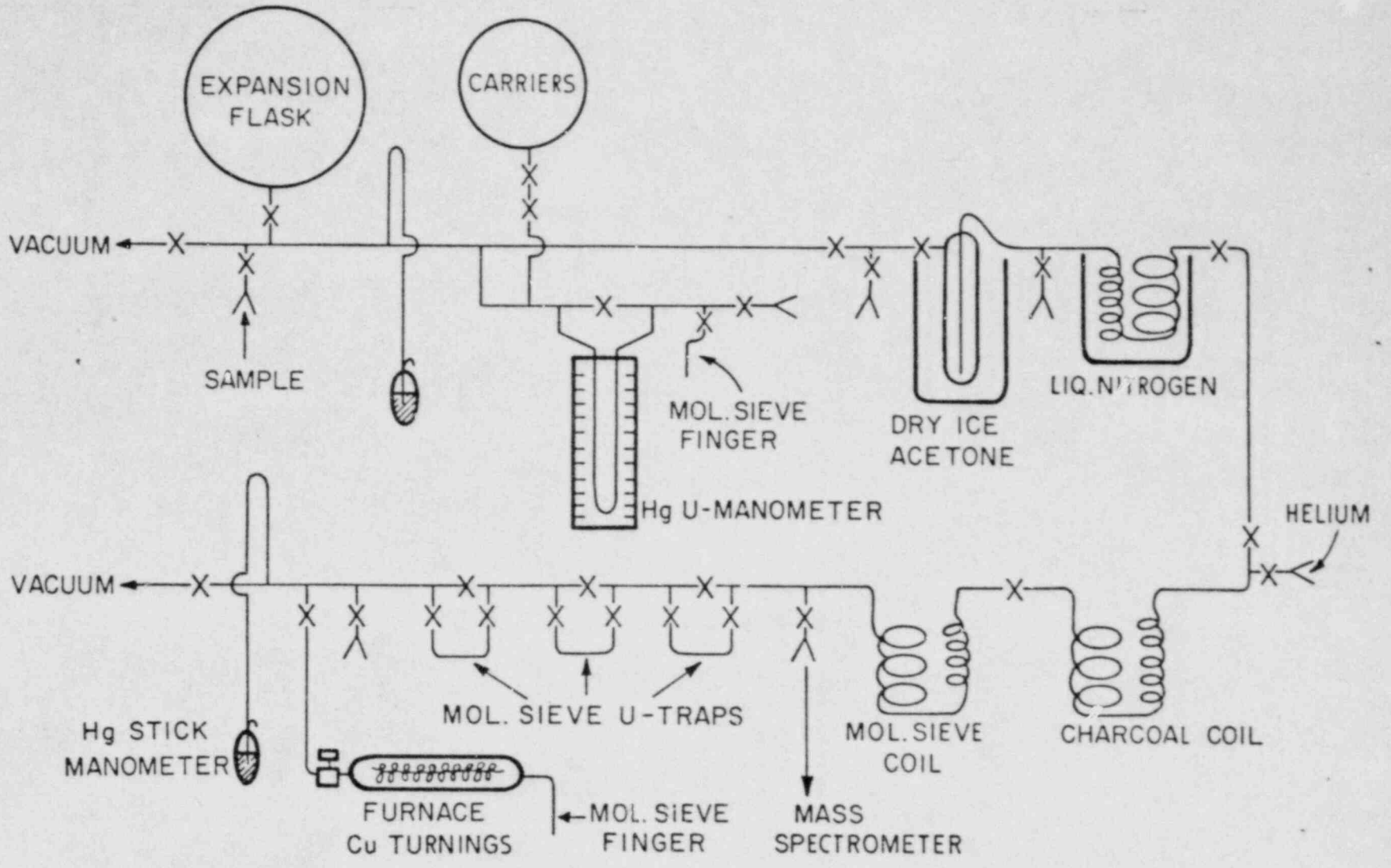


Figure 5. Bleed down system for liter-size samples.

INTERNAL GAS-PROPORTIONAL BETA-SPECTROMETRY FOR MEASUREMENT OF RADIOACTIVE NOBLE GASES IN REACTOR EFFLUENTS*

C.J. Paperiello
Radiological Sciences Laboratory
Division of Laboratories and Research
New York State Department of Health
Albany, New York 12201

Abstract

At the Radiological Sciences Laboratory of the New York State Department of Health, gas fractions separated by gas chromatography are analyzed by internal gas-proportional spectrometry systems. These systems include gas-proportional detectors, plastic anticoincidence detectors, multichannel analyzers, and associated electronics. Detector systems are enclosed in 6-inch thick steel shields.

Internal proportional counting with multichannel analysis offers several advantages, particularly improved sensitivity and specificity. Gas counting efficiencies are greater than 60% for ^{37}Ar and 90% for ^{85}Kr . Detector background with 100-ml copper proportional tubes and plastic anticoincidence guards is on the order of 0.3 cpm for ^{37}Ar and 1.5 cpm for ^{85}Kr . Shielded and guarded steel tubes have backgrounds approximately four times higher, but are acceptable for high-level reactor samples.

By examining the spectra with a multichannel analyzer, the figure of merit for low-energy beta-emitters is greatly improved over integral bias counting. The purity of the sample following chromatographic separation can also be checked. Within certain abundance ratios, the levels of ^3H and ^{14}C in hydrocarbon fractions can be determined without combustion. Similarly, direct ^{37}Ar and ^{39}Ar measurements are possible.

The application of spectrometric techniques for analysis of several types of reactor gas effluents is discussed.

INTRODUCTION

At the Radiological Sciences Laboratory of the New York State Department of Health, reactor gas effluents are analyzed by Ge(Li) gamma-ray spectroscopy and internal gas-proportional spectrometric systems. Although gamma-ray spectroscopy is the simpler procedure, low-background beta-proportional counting offers greater sensitivity for all gaseous radioactive fission products, and for those which decay with little or no gamma emission it is an absolute necessity. Although one might expect the activity of reactor samples to be so high a low-background system is not needed, this is not the case. The range of activity ratios for a given sample may be 10^7 between nuclides, and the range of activity may be greater than 10^5 between samples, resulting in an overall range of about 10^{12} in activity in these studies.

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 in the radiargon fraction, $^{14}\text{C}/^3\text{H}$ in methane, and other hydrocarbon fractions.

The gases routinely measured in reactor effluents by internal gas-proportional counting include the noble gases ^{85}Kr , ^{133}mXe , ^{133}Xe , ^{37}Ar , and ^{39}Ar and the permanent gases ^3H , $^{14}\text{CO}_2$, and CH_4 (^{14}C and ^3H). The latter group is important in noble gas measurements because during chromatographic separation, contamination of the argon fraction with $^3\text{H}_2$, the methane fraction with ^{85}Kr , and the CO_2 fraction with the ^{133}Xe can occur.

SPECTROMETER SYSTEM

The spectrometer system is similar to those described by Curran (1958). The proportional 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 are used, and the entire detection system is enclosed in a 14.4-cm thick steel shield. Figure 1 shows two of the 100-ml proportional tubes along with a 1-liter tube and two of the guard detectors. The smaller guard will accept the 100-ml tubes, while the larger guard will accept tubes as large as the 2.6-liter tube manufactured by LND, Inc. A typical 100-ml tube with a P-10 (90% argon, 10% methane) fill has a plateau 250 volts long, 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 2. 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 for 10 μsec . The system dead-time, due to guard events closing the linear gate, is less than 0.1%. All of the units shown in Figure 2, with the exception of the plastic guard detector, are commercial products. With new multichannel analyzers, one can use the built-in linear gate in the anticoincidence mode, thereby avoiding the cost of an external gate.

*Supported in part by USAEC contract AT(11-1)2222 and USEPA contracts 68-01-0522 and 68-01-LA-0505.

OPERATION AND CHARACTERISTICS OF SPECTROMETER SYSTEM

Spectra of ^3H , ^{14}C , and ^{85}Kr obtained with this spectrometer system are shown in Figure 3. 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 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 4. The integrated backgrounds were: for the bare stainless-steel detector, 104 cpm; for the detector shielded by 14.4 cm of steel, 53 cpm; and for the detector shielded by the steel and an anticoincidence guard, 4.9 cpm. 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 are 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 about 6 keV is 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 5). The contaminated sample contains a very small amount of ^3H , which would not affect the ^{37}Ar value, but 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. The chromatographic separation sequence leads to decontamination factors of 10^3 to 10^4 (Kunz, 1973). One may occasionally observe ^3H interferences in argon, ^{85}Kr in methane, and ^{133}Xe and ^{135}Xe in CO and CO_2 fractions. If great care is not taken in cleaning the separation system after a particularly high activity sample, ^3H can show up anywhere.

For sample spectra such as ^{85}Kr , ^3H , $^{14}\text{CO}_2$, and ^{14}CO , the spectral shape and end point are first examined for radiochemical purity. The spectrum is then summed; the background is subtracted; and the net counting rate is corrected for counting efficiency, sample size, chemical recovery, and radioactive decay. In the cases of ^{135}Xe and ^{133}Xe , this procedure is repeated for several counts, and the data are fitted by a least squares method to 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 (Allen, 1965) was used to determine efficiency. While this procedure gave a value of 0.86 cpm/dpm, which seems consistent with other measured efficiency values, the presence of a conversion electron branch in ^{133}Xe has been ignored. The result should be a somewhat greater value for this factor. The same factor is used for ^{135}Xe . Since ^{39}Ar has a beta spectrum similar to ^{85}Kr , the ^{85}Kr efficiency factor for that spectral region is used for ^{39}Ar . In many reactor gas samples ^{85}Kr and ^{133}Xe are 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 coincidence calibration provides good agreement with the Ge(Li) diode measurements.

One of the more interesting gases present in reactor effluents is methane. It may be composed of ^3H or ^{14}C , or both, and beta-spectrometry permits the simultaneous analysis of both nuclides. In Figure 6 the spectrum of the methane fraction from a heavy-water-moderated reactor is presented. The spectrum is run at a system gain of 0.42 keV/channel. The regions from channels 1 to 39, and from 40 to 255, are summed, and the background subtracted. The net counts in region 1 and 2, N_1 and N_2 are given by:

$$N_1 = f_1(\text{T})N_{\text{T}} + f_1(\text{C})N_{\text{C}} \quad (1)$$

$$N_2 = f_2(\text{T})N_{\text{T}} + f_2(\text{C})N_{\text{C}} \quad (2)$$

where $f_1(\text{T})$ = fraction of ^3H spectrum in region 1,

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

$f_2(\text{T})$ = fraction of ^3H spectrum in region 2,

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

N_{T} = net ^3H count in spectral region,

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

For our tubes and gain range these equations are:

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

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

Since N_1 and N_2 have been measured, these equations can be solved for N_T and N_C and the activities determined without combustion of the sample. By counting a series of twelve ^{14}C methane samples, it has been determined that the gain can be set with ^{125}I 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 ^3H 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 ^3H is about 7% of the ^{14}C activity. In Figure 7 the decomposition of the methane fraction into ^3H and ^{14}C components is shown. A summary of system performance appears in Table 1.

The detectable limit is reduced by poor chemical recovery and, for short-lived nuclides, long delays between collection and counting. It is enhanced by processing larger samples. Samples as large as 2 liters have been processed in our laboratory. The major uncertainty in our work at the present time is the accuracy of the efficiency factors. Those given in Table 1 for ^{39}Ar , ^3H , and ^{14}C are estimates for ^{85}Kr and ^{37}Ar , and that for ^{133}Xe has been determined by a method which is somewhat lacking in technical justification.

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.

REFERENCES

- Allen, R.A., (1965), *Measurement of Source Strength. In Alpha-, Beta- and Gamma-Ray Spectroscopy* Vol. 1. K. Siegbahn, Ed., p. 425. (Amsterdam, North-Holland).
- Curran, S.C., (1958), *The Proportional Counter as Detector and Spectrometer*, in *Handbuch der Physik*, Vol. 45, 174 (Berlin:Springer).
- Kunz, C.O., (1973), *Separation Techniques for Reactor-Produced Noble Gases*, Proceedings of the Noble Gas Symposium, Las Vegas, Nevada, Sept. 24-28, 1973.

TABLE 1. Spectrometer Performance.

Isotope	Gain keV/channel	Channels used	Gas detector efficiency (cpm/dpm)	Ave bkgd (cpm)	Detectable limit 1-ml sample 1,000-min count ($\mu\text{Ci/ml}$)
^{85}Kr	0.83	1-255	0.90	5.0	1.1×10^{-7}
^{37}Ar	0.21	10-19	0.63	0.8	6.0×10^{-8}
^{39}Ar	0.21	32-255	0.45	1.5	1.2×10^{-7}
^{133}Xe	0.83	1-255	0.86	5.0	1.1×10^{-7}
^3H	0.42	1-39	0.75	5.0	1.3×10^{-7}
^{14}C	0.42	1-255	0.85	5.0	1.1×10^{-7}
^{14}C	0.42	40-255	0.36	0.13	4.0×10^{-8}

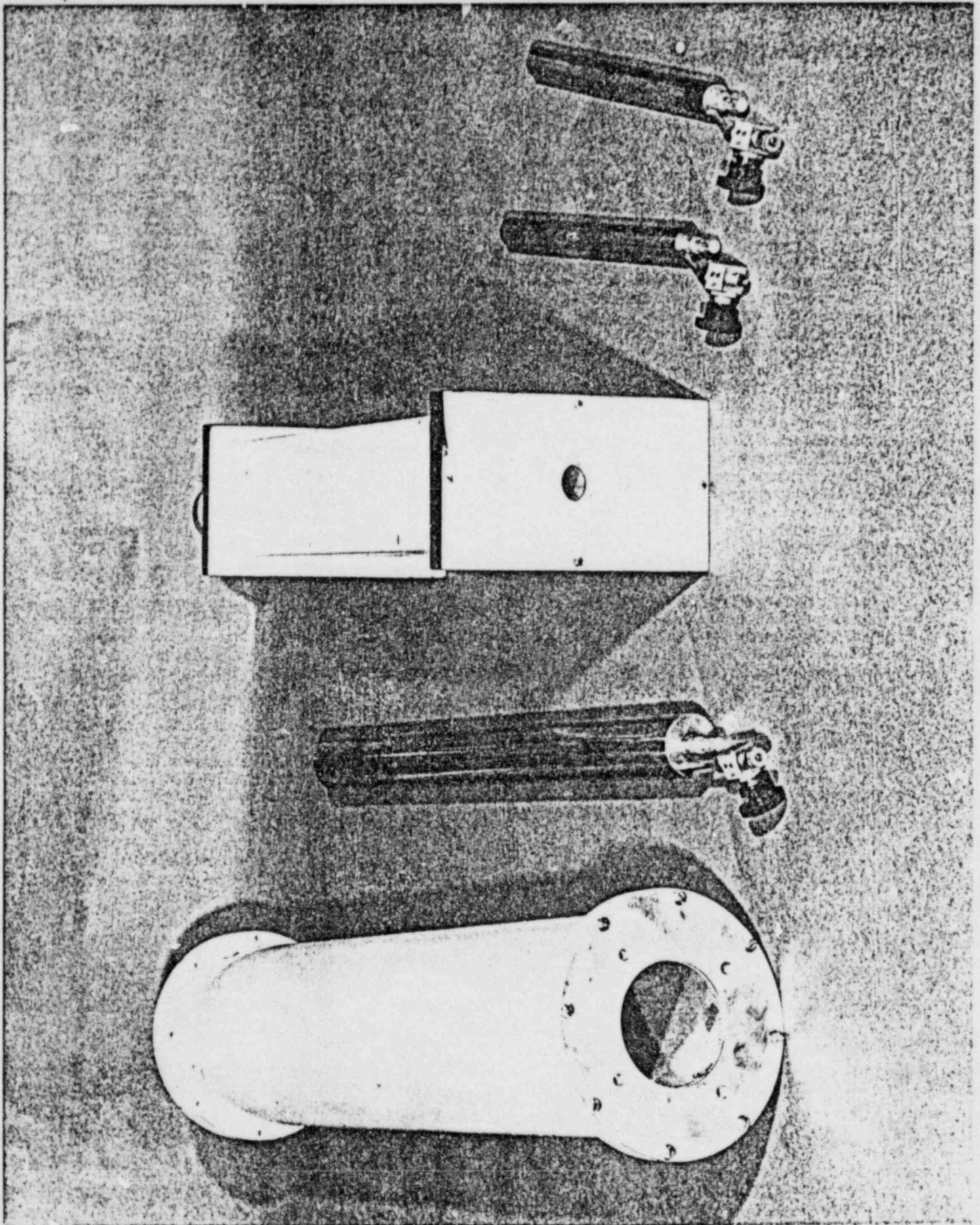


Figure 1 Proportional tubes, 100 ml and 1 liter, with plastic scintillator guard detectors.

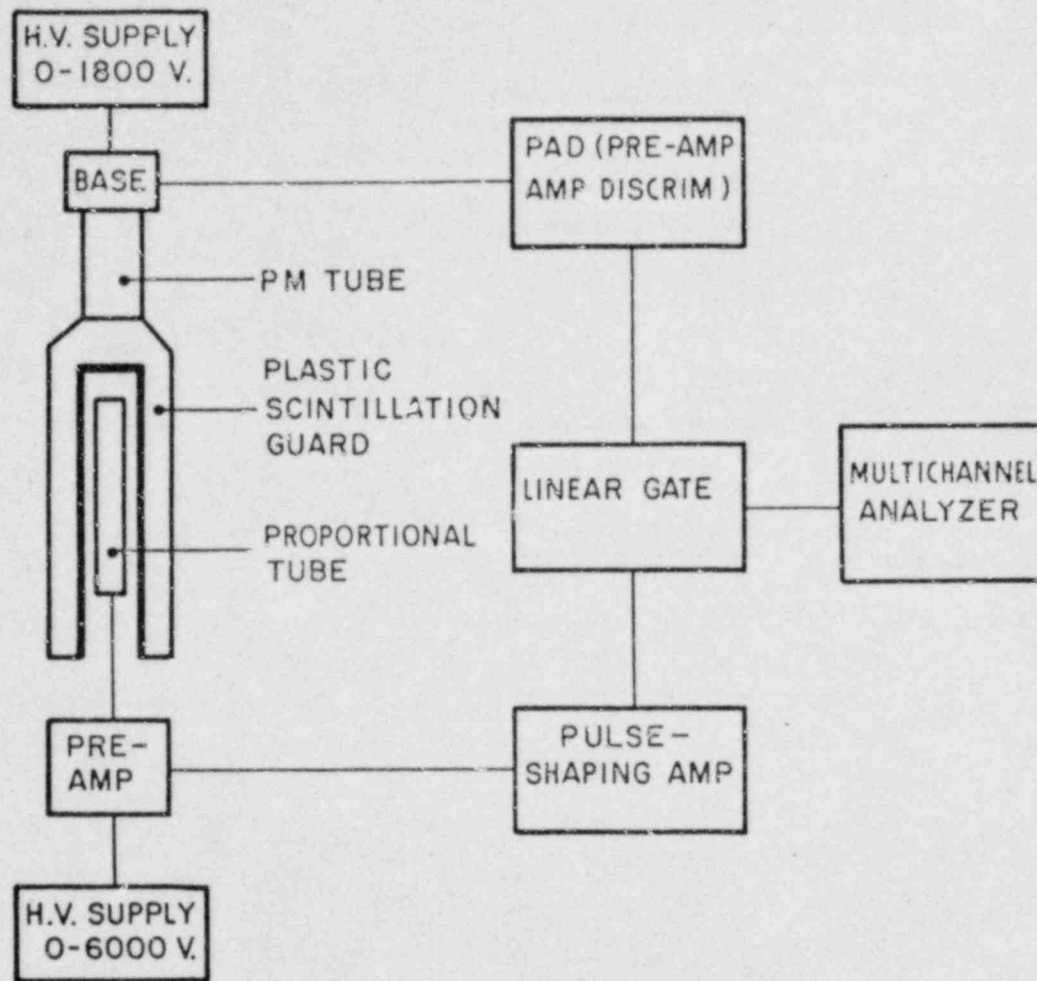


Figure 2. Block diagram of internal gas-proportional beta-spectrometer system.

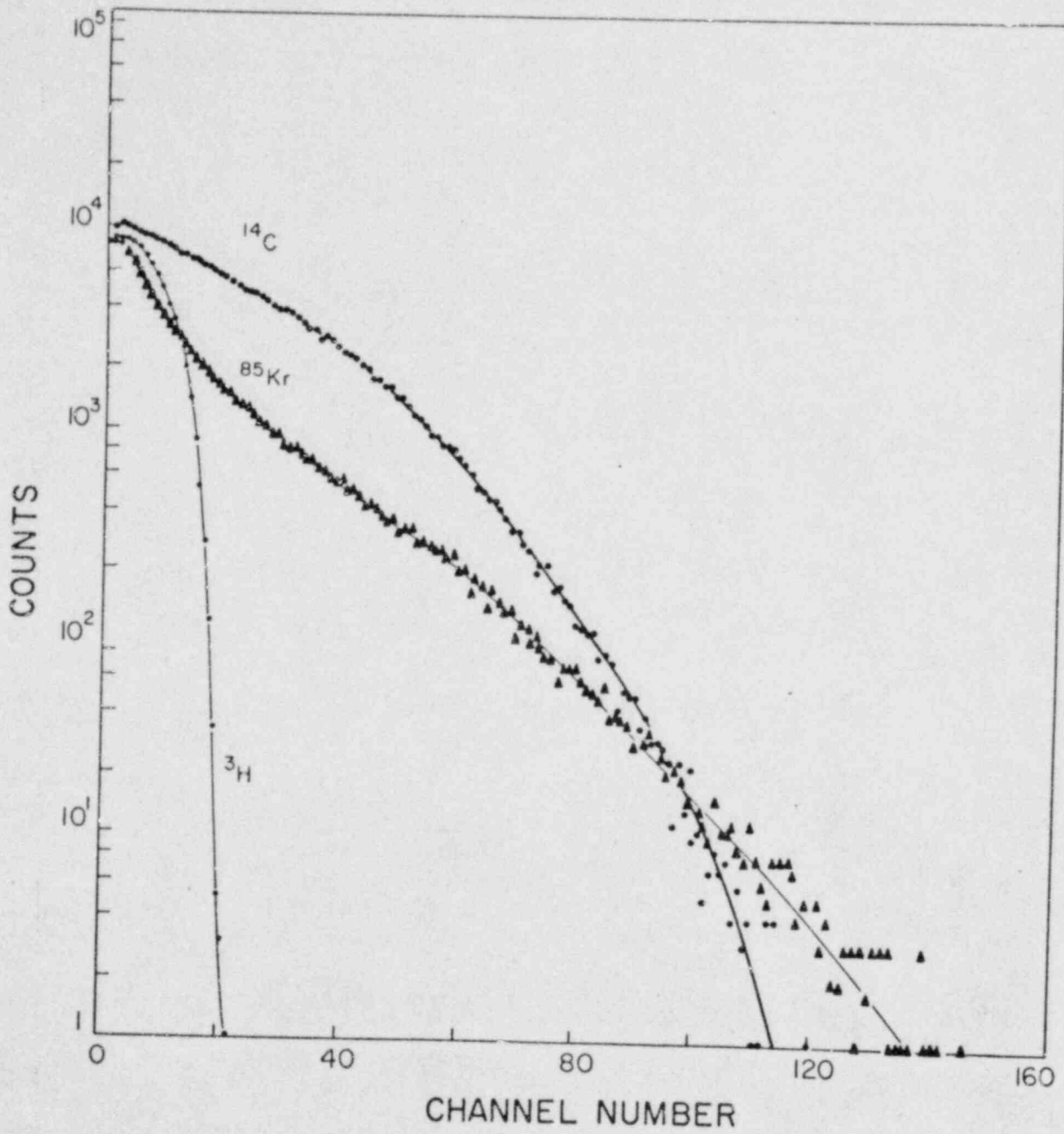


Figure 3. Spectra of ³H, ¹⁴C, and ⁸⁵Kr. (Gain 0.83 keV/channel.)

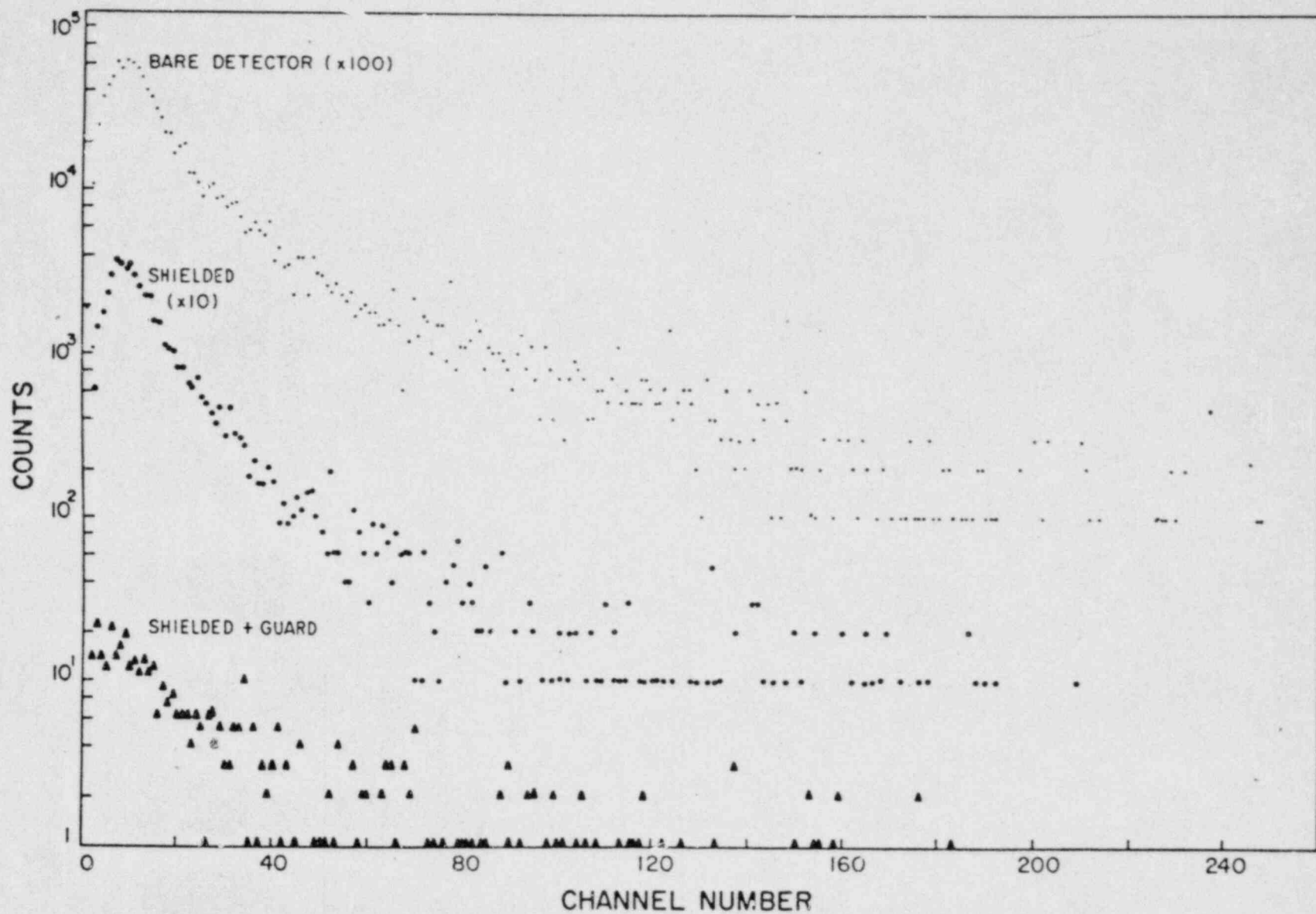


Figure 4. Background spectra for a 100-ml steel proportional tube. The spectra of the shielded and bare detectors have been shifted upward by factors of 10 and 100, respectively. (Gain 0.42 keV/channel.)

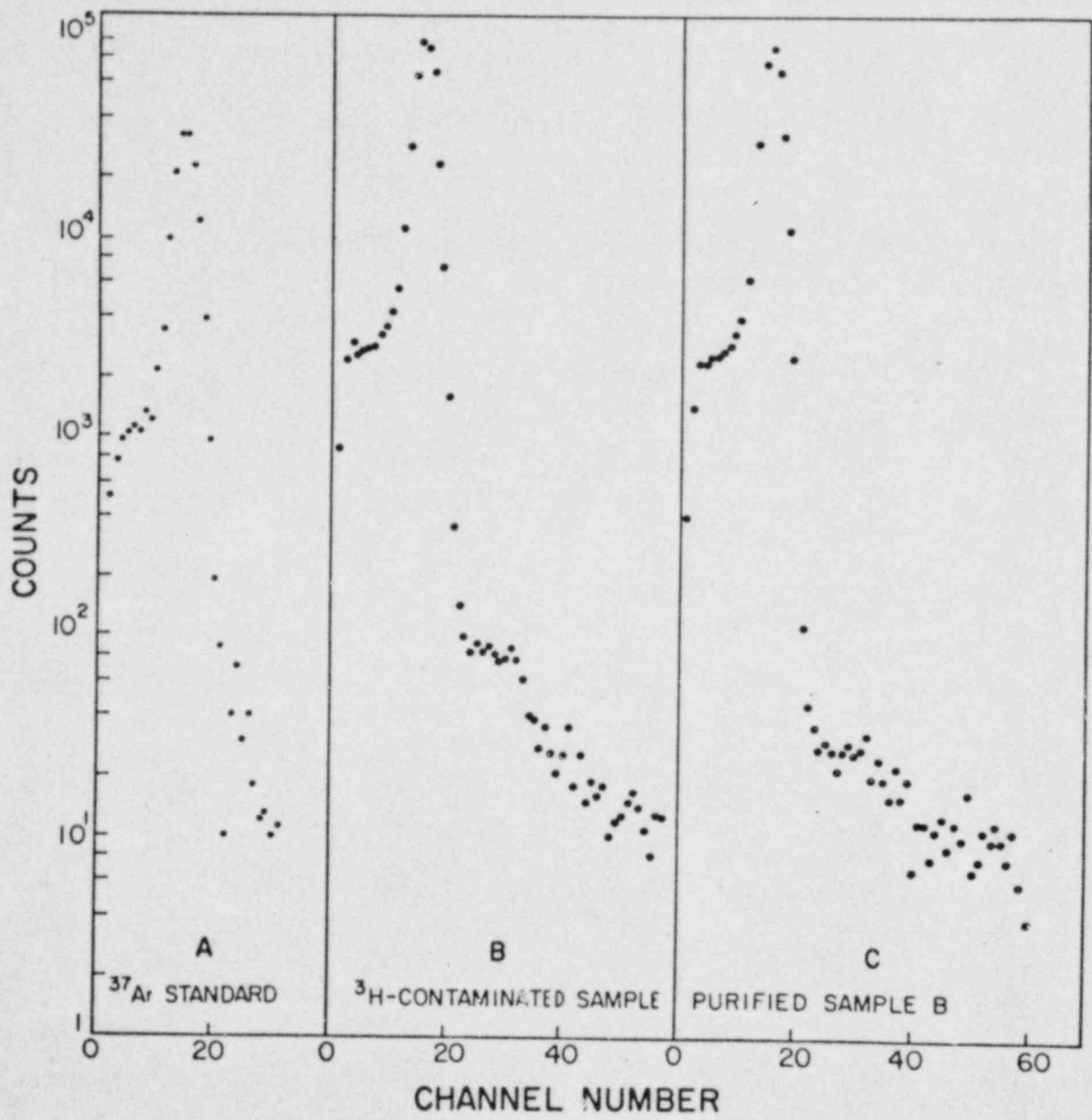


Figure 5. Argon spectra: A. NBS ³⁷Ar standard; B. Argon fraction with ³H contamination; and C. Fraction shown in B with an extra purification step. (Gain 0.21 keV/channel.)

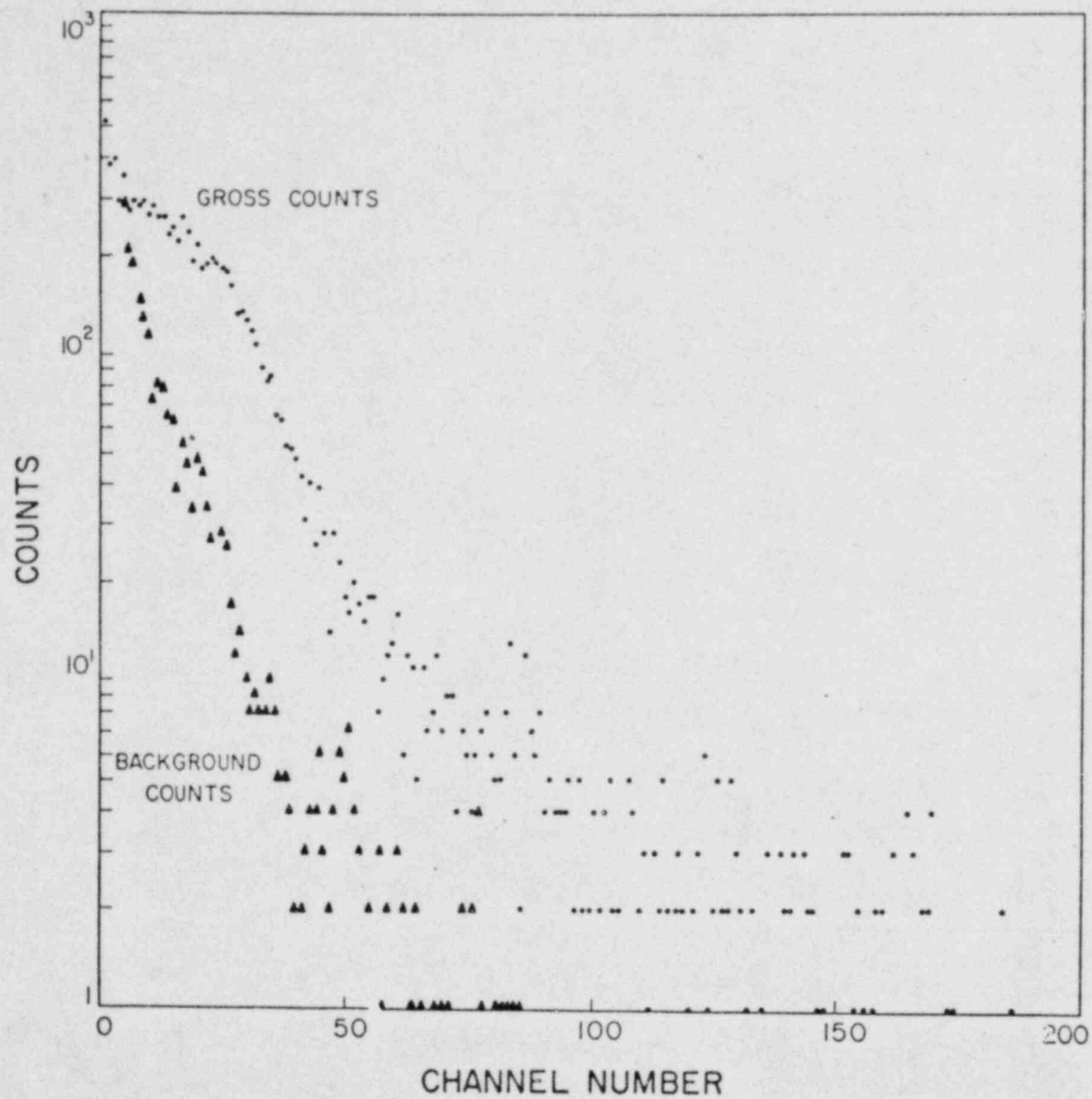


Figure 6. Gross spectrum of a methane fraction showing the presence of ^3H and ^{13}C compared with background. (Gain 0.42 keV/channel.)

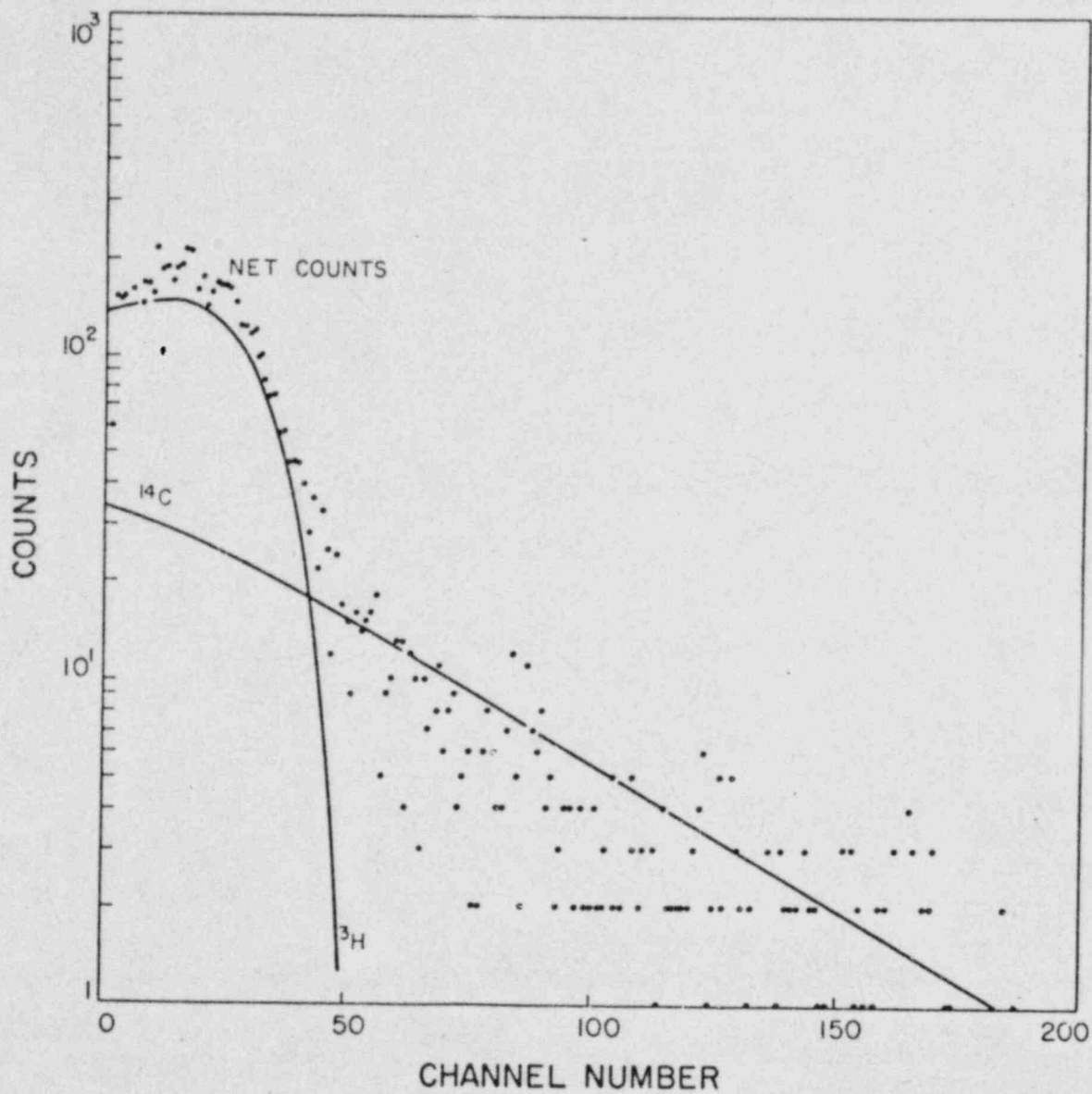


Figure 7. Spectrum of the methane fraction shown in Figure 6 with background subtracted. The ³H and ¹⁴C components are indicated. (Gain 0.42 keV/channel.)

ENVIRONMENTAL MONITORING FOR KRYPTON-85*

D. E. Barber
School of Public Health
University of Minnesota
Minneapolis, Minnesota 55455

Abstract

⁸⁵Kr presents unique environmental monitoring problems because it does not react with other elements and compounds at normal ambient temperatures and pressures. However, elaborate means are available to manage the ⁸⁵Kr problem, but a simpler, inexpensive approach is required if monitoring is to be accomplished at many sampling locations. This work shows that environmental monitoring for ⁸⁵Kr is possible by collecting air samples in thin plastic bags, and counting the bags for beta particle activity. The direct counting of contained samples of this type makes it possible to detect concentrations less than the public MPC for ⁸⁵Kr. The bagged-sample technique is readily adaptable to any environmental monitoring station with power to run a low-volume air pump. The idea of counting the bagged-sample directly is a new, low-cost, approach to environmental gas monitoring which may have application in environmental, clinical, and industrial situations.

INTRODUCTION

⁸⁵Kr is a fission product which escapes or is released to the environment primarily as a byproduct of reprocessing nuclear fuel. In fuel reprocessing, ⁸⁵Kr, ¹³¹I, ¹²⁹I, ^{133m}Xe, ¹³³Xe, and ³H are released, but only ⁸⁵Kr and ³H are released in sufficient quantities, and have long enough half-lives, to produce significant concentrations in extensive environmental air volumes (Kirk, 1972). The present atmospheric inventory of ⁸⁵Kr is estimated to be 60 MCi — more than twice the inventory in 1962 (Kirk, 1972). If projections with respect to population, demand for electric power, use of nuclear power plants, and release of ⁸⁵Kr to the environment are correct, concentrations of ⁸⁵Kr in the atmosphere may reach 3×10^{-7} μ Ci/ml (the public MPC) about the year 2050 (Hollanu, 1969; Cowser and Morgan, 1967; and Coleman and Liberace, 1966). Treatment of effluents to remove up to 98 percent of the noble gases from fuel reprocessing is possible, and methods have been tested on a pilot plant scale (Slansky, 1971). The cost of treating the effluent has been estimated at about 1 percent of the total reprocessing cost (Slansky, *et al.*, 1969), and treatment will probably be used extensively in the near future. Consequently, present projections with respect to anticipated atmospheric concentrations in the 21st century are probably much too high. However, effluent treatment or not, ⁸⁵Kr releases to the atmosphere will require environmental monitoring for the gas because:

(1) A removal efficiency of 98 percent reduces released concentrations to only 0.02 times their original values.

(2) The atmosphere cannot be used exclusively for ⁸⁵Kr dilution.

(3) It will be necessary to assure compliance with regulatory standards.

Although this paper addresses itself to the problems of monitoring ⁸⁵Kr, the results are more generally useful. There are situations which arise when one would like to know the response to be expected from ordinary radiation detectors when they are presented to clouds of beta particles or low-energy gamma ray emitters with dimensions less than those of infinite volume.

There are a number of possibilities for monitoring ⁸⁵Kr in the atmosphere given unlimited financial resources. Any of the methods for removal of noble gases on a large scale from fuel reprocessing effluents might be used on a smaller scale; but, these methods involve elaborate pretreatment of the intake gases and/or cryogenic temperatures (Slansky, 1971). When adsorbing media such as molecular sieves or charcoal beds are used, the operating temperature must be matched to the sampling rate and sample size (Kirk, 1972). In liquid scintillation counting, the lowest concentration of ⁸⁵Kr that can be analyzed without preconcentration is about 3 pCi/ml, and the poor solubility of air in liquid scintillation cocktail presents a problem for sampling air mixtures of gases (Kirk, 1972). So, sophisticated sampling for ⁸⁵Kr in the environment presents severe practical limitations for both technical and financial reasons, especially in those situations where numerous monitoring stations may be involved. Simple, inexpensive methods must be found.

Direct counting of gas samples in vinylidene chloride (Saran) is the approach taken here. The sampling approach is similar to one already reported for ²²²Rn (Sill, 1969). But, the idea of counting beta particle emitters directly, without removing the sample from the bag for the purpose of gas monitoring, is believed to be new. It has been noted recently that ¹³³Xe contamination in the air should probably be done by counting the air sample directly rather than attempting to collect the Xe in aqueous solution (LeBlanc, 1972). LeBlanc points out that there is a misunderstanding concerning the best methods to monitor for ¹³³Xe because of erroneous solubilities for ¹³³Xe given by the Hbk. of Chm. and Phys. (1966). Similar uncertainties may also apply to krypton.

*The data on ⁸⁵Kr reported here resulted from work completed in the Faculty Research Participation Program of Associated Western Universities at the Health Services Laboratory, USAEC, Idaho Falls, Idaho. The author also gratefully acknowledges the cooperation of Aerojet Nuclear Company.

PROPERTIES OF ^{85}Kr AND INTERFERENCE PROBLEMS

Some properties of ^{85}Kr are given in Table 1. ^{85}Kr is nearly a pure beta emitter from the dosimetry viewpoint, but the gamma ray is useful for calibration purposes for activities greater than $10^{-2}\mu\text{Ci}$. Monitoring for ^{85}Kr by gamma ray spectrometry can be accomplished provided the concentration is high enough, and is sustained for a period of time at least equal to the measurement period. At concentrations approaching the maximum permissible concentrations, however, the branching ratio (0.004) of gamma ray disintegration to beta particle disintegration makes beta particle measurements far more attractive.

Iodine impregnated, activated charcoal can be used to eliminate interference from iodine-131. Silica gel can be used to keep the sample dry. Storage can be used to eliminate interference from radon-daughter product activity, and filters can be used to reduce interference from particulate activity. There remain, then, ^{133}Xe and ^{133m}Xe . This technique might be biased against these nuclides by storage, careful selection of detector window thickness, and detector design. Interference from ^{133}Xe is not expected to be significant at present because the ratio of ^{133}Xe to ^{85}Kr activity for aged nuclear fuel is typically less than 10^{-4} percent (Smith, *et al.*, 1970). However, as use of nuclear fuels increases, the used fuel will be less and less aged before reprocessing, in which case it will be necessary to cope with the ^{133}Xe problem. This should be relatively easy to do because of the large differences in modes of decay, and beta energies between those for ^{133}Xe and ^{85}Kr .

If ^{133}Xe is produced as a fission product, ^{133m}Xe will also be present (Martin and Blichert-Toft, 1970). The ^{133m}Xe could present severe beta particle detection interference problems if fuel is stored for less than 10 days prior to reprocessing. The conversion electron energies from ^{133m}Xe are only slightly lower than the average energy of beta particles from ^{85}Kr . However, advantage might be taken of the 0.233 MeV gamma ray from ^{133m}Xe to distinguish it from both ^{85}Kr and ^{133}Xe .

METHODS

1. ^{85}Kr Chamber.

A chamber approximating an infinite volume of air for ^{85}Kr beta particles was constructed of 4' x 8' x 3/4" plywood on a 2" x 4" wood superstructure. The resultant chamber was an 8' cube equipped with feed-throughs provided for power, sampling inlets, outlets, and a G.M. detector lead. The chamber was kept outside at ambient temperature and pressure.

Chamber concentrations were measured and monitored by a 30 mg/cm² metal-walled Amperex G.M. tube (1/2" dia. x 7" long) operated at 960 volts. Pulses from this detector were counted with a Baird-Atomic Mod. 530 scaler.

Serial dilutions from ^{85}Kr stock to glass vials, to the chamber, and ultimately to polyethylene and Saran bags, were made to produce various concentrations of ^{85}Kr ranging from $2 \times 10^{-8}\mu\text{Ci/ml}$ to $7 \times 10^{-4}\mu\text{Ci/ml}$.

2. Calibrations.

Unfortunately, the detection limit by gamma ray spectrometry for ^{85}Kr is on the order of $10^{-2}\mu\text{Ci}$. As a result, chamber concentrations could not be confirmed by this method over the range of concentrations of interest. To enable measurements of concentration in the chamber over the entire range of interest, the G.M. tube in the chamber was calibrated as follows. A sample from ^{85}Kr stock was counted on a 65 ml GeLi detector in the standard geometry. The GeLi detector was calibrated with a ^{85}Kr source from the National Bureau of Standards. The sample was then transferred to a 4.2-liter Saran bag to calibrate an 8" x 4" NaI detector for this geometry. A 4.2-liter sample taken from the chamber was then counted on the same crystal yielding the true concentration in the chamber, $1.05 \pm 0.15 \times 10^{-4}\mu\text{Ci/ml}$. This concentration provided the primary calibration factor, $3.82 \times 10^{-9}\mu\text{Ci/ml}$ per cpm, for the chamber G.M. tube. The G.M. tube count rate was then used as the reference for the concentration in all samples taken from the chamber. The G.M. tube calibration factor agrees well with the $2.1 \times 10^{-9}\mu\text{Ci/ml}$ per cpm previously reported for a similar, but longer, G.M. tube (Smith, *et al.*, 1970).

The rotameter was calibrated with a wet-test meter, and was found to be in calibration within ± 20 percent. The uncertainties in visually setting the rotameter are large. Consequently, the rotameter reading was taken to be the true flow rate at ambient temperature and pressure.

3. Sampling and Instrumentation.

A diagram of the dilution and sampling system is given in Figure 1. The sampling line was prepared as it might be used in the field to pretreat samples taken from the chamber. Components of the sampling line were connected with plastic tubing ranging from 1/4 to 3/8 inch inside diameter. The input to the rotameter from the chamber was at ambient pressure, and consisted of 3/8 inch plastic tubing suspended at the center of the ^{85}Kr chamber close to the G.M. tube. Samples were collected at various flow rates and various sampling times as indicated in the results.

Except for a few measurements with the 5-liter Saran bag filled to capacity, bags were filled to less than capacity to minimize leakage, if any should occur, and to provide a flexible bag geometry. In this way, it was possible to achieve 2π counting geometry when samples were placed on the detectors, and to reduce the error which might be introduced as a result of pressure build-up in the bag.

The instruments used to analyze the bagged-samples were as follows:

- (1) Ludlum Instrument Co., Model 14A Gieger Counter with LND Inc. G.M. tube, 30 mg/cm² metal wall.
- (2) Eberline Instrument Co., Model HP-210 G.M. probe with LND 731-1 G.M. tube, 2" diameter thin window, connected to Baird-Atomic, Model 530 scaler, operated at 800 V.
- (3) A sheet of plastic scintillator, 4.1" diameter by 0.19" thick, attached with Dow Corning QC-2-0057 silicone compound to a DuMont 6364 photomultiplier tube (5" diameter face). The scintillator was covered with two layers of doubly aluminized Mylar to make a total window thickness of 2.06 mg/cm². The detector signal was fed through a preamplifier into a Baird-Atomic, Model 530 scaler with input sensitivity set at approximately 50 mV. The high-voltage to the detector was 1,000 V.

The first and second instruments were used outside, immediately adjacent to the chamber, to examine their response to samples taken from the chamber. The third detector was used inside a vault with 10" thick steel walls.

Measurements with the first two instruments were made in the presence of radon-daughter product activity. Measurements with the third instrument were made on samples stored overnight.

4. Sample Containers.

Two types of plastic bags were used to collect, store, and count samples. One bag was Saran type 18-100 (manufactured by Analytical Specialties, Inc., and distributed by the Anspec Co., Ann Arbor, Michigan). This Saran has a density thickness of 8.0 mg/cm². Saran is known to contain ²²²Rn with losses of less than 0.12 percent per day up to at least 14 days (Percival, 1971). It, therefore, seemed a suitable choice for ⁸⁵Kr. Saran of this thickness is also very durable and easy to handle.

The second type of plastic bag used in this work was a simple polyethylene bag. The bag was 20" square with a wall thickness of 4.7 mg/cm². The open end of the bag was heat-sealed, and the center of one side was cut out to a diameter of about 7" to accommodate a thin Saran window. The Saran used for this window was the ordinary household type. Its thickness was 2.2 mg/cm². The Saran window was attached to the bag with a translucent silicone rubber adhesive sealant (RTV-108, General Electric Co., Waterford, New York). This made a satisfactory seal for the purpose of this experiment, but it does not provide a permanent seal. Further, polyethylene is generally known to be permeable to many compounds, including water vapor, and probably is unsuitable for ⁸⁵Kr containment for more than a few days. The purpose in using these homemade bags was to provide a large-volume container with a very thin window to provide maximum beta particle transmission with essentially a 2 π geometry when placed on the plastic scintillation detector.

RESULTS

1. ⁸⁵Kr Chamber.

With the chamber containing 3×10^{-4} μ Ci/ml of ⁸⁵Kr, the count rate of the chamber G.M. tube dropped from 7.43×10^4 cpm to 7.30×10^4 cpm over a 150-minute period. This amounts to a leakage rate of 0.8 percent per hour at the highest concentrations used in the chamber.

Rate meter measurements showed that the gas dispersed in the chamber within two seconds, and remained dispersed even without the benefit of the fans in the chamber. No significant reduction in chamber concentration occurred which could not be explained on the basis of the chamber leakage rate. The chamber concentrations were remarkably stable and reproducible. With the access door fully open, and with the fans running as usual in the chamber, it required 2 to 3 minutes to reduce the chamber concentration to 1/2 of its original value.

2. Chamber G.M. Tube.

The count rate of the ⁸⁵Kr chamber G.M. tube as a function of ⁸⁵Kr concentration is given in Figure 2 for both input to the scaler and to the Ludlum rate meter. Each observation involved a 3-minute count. The first observation was made at the lowest concentration. Two subsequent additions of ⁸⁵Kr provided the three concentrations in the figure. The tube was used bare, and was supported with its coaxial cable at the center of the chamber. The practical lower limit of detection for the Ludlum rate meter with the chamber G.M. tube is about 6×10^{-7} μ Ci/ml; this provides a net meter reading of 0.04 mR/h in an infinite cloud. When the tube is connected to a scaler, the lower limit of sensitivity is a function of the background and counting time. For the conditions of Figure 2, the limit for detecting ⁸⁵Kr with the scaler is much lower than with the rate meter.

3. Ludlum G.M. Survey Meter.

With a chamber concentration of 7.0×10^{-4} μ Ci/ml samples were taken in the 5-liter Saran bag for time intervals ranging from 5 to 25 seconds at 12.5 lpm. When the Ludlum probe, with beta shield open, was laid on each sample the response was found to be linear with respect to activity — irrespective of bag geometry (see Figure 3).

The lowest activity was distributed in a volume of only 1 liter, but the highest activity was distributed in 5 liters. There are large uncertainties in reading this meter, but the linear relation over a factor of five change in volume is clear.

The minimum reliable net reading for the Ludlum survey meter is 0.04 mR/hr. This corresponds to about 0.05 μ Ci which, according to the figure, might be distributed in as much as 5 liters. Hence, the minimum detectable concentration for this meter under these conditions of measurement becomes 10^{-5} μ Ci/ml. This is much too high for environmental monitoring purposes.

4. Eberline G.M. Probe.

This probe was used to measure ^{85}Kr activity in the 5-liter Saran bag containing various volumes of gas at a constant concentration of 6.3×10^{-4} μ Ci/ml. The results are shown in Figure 4. The statistical counting errors are large; but, again the linear relation between activity and different geometries is obvious. One observation was made at low-activity (therefore, low-volume) by rolling the bag to about 1/4 of its maximum volume to show the importance of widely different geometries.

In this case the minimum detectable activity appears to be about 0.5 μ Ci. When expanded to 5 liters, this yields a minimum detectable concentration of 10^{-4} μ Ci/ml. But, measurements at maximum volume and various concentrations show the minimum detectable concentration to be much lower than this (See Figure 5).

When 5 liters of ^{85}Kr are taken from the chamber in the 5-liter Saran bag, the response of the probe is as indicated in Figure 5. The probe was lightly pressed against the side of the sample bag for each measurement. The highest concentration was measured first. Subsequent lower concentrations were produced by opening the chamber between samples. All counts were for three minutes.

The figure shows that this detector is capable of detecting as low as 3×10^{-7} μ Ci/ml of ^{85}Kr under the condition of measurement. But, it is not likely to detect 3×10^{-8} μ Ci/ml even for long counting times. A more sensitive detector is required.

5. Plastic Scintillation Detector.

Samples were taken from the chamber, diluted to the desired concentration with ambient air through the sampling chain into the polyethylene bags, and stored overnight to permit the decay of radon-daughter product activity. The ^{85}Kr concentration for all these samples was 2×10^{-7} μ Ci/ml. Ambient air samples taken through the sampling chain also were found to contain activity. This activity had an effective half-life of 33 minutes, which is typical for radon-daughter product activity. The filters do not eliminate interference from radon-daughter products at these low ^{85}Kr concentrations.

When stored samples of ^{85}Kr are counted, Figure 6 shows that it is possible to detect concentrations less than 3×10^{-8} μ Ci/ml using the polyethylene bags containing 23 liters of sample. Two 13-liter samples in commercial Saran bags showed that it may be possible to measure these low-concentrations in a lesser volume and in a more durable bag than provided by the polyethylene.

DISCUSSION

^{85}Kr has been measured at a variety of concentrations, in several different sample volumes, and with several different sample containers. In this work, the best combination was a 23-liter sample, stored overnight in a polyethylene bag with a 2.2 mg/cm² Saran window, and counted on a plastic scintillation counter. This combination provides minimum detectable concentrations of less than 3×10^{-8} μ Ci/ml for ^{85}Kr . The method is suitable for environmental monitoring provided pretreatment of the sample removes other beta emitters, such as ^{131}I , which would interfere with the analysis, and provided the sample container used in the field is reasonably durable and impermeable to ^{85}Kr .

The commercially available, 8.0 mg/cm² density thickness Saran bag, in the size advertised as 12 liters, is a good possibility for field sampling. One of the difficulties will be finding a metering pump with a low enough flow rate, and sufficient flow rate stability, to accurately pump a 12-liter volume into the bag over a long period of time. A much larger sample may be necessary for the sake of obtaining an accurately known volume of sample.

Common G.M. rate meters can detect ^{85}Kr in bagged, 5-liter samples containing concentrations as low as 10^{-4} to 10^{-5} μ Ci/ml. Common G.M. probes connected to scalars can detect ^{85}Kr in bagged, 5-liter samples containing concentrations as low as 3×10^{-7} μ Ci/ml — without benefit of shielding and in the presence of radon-daughter product activity. Under the conditions of an infinite cloud, bare G.M. detectors connected to scalars are capable of detecting concentrations below 3×10^{-8} μ Ci/ml, depending upon counting time. Detecting these low-concentrations with 12- or 23-liter bagged-samples requires a well-shielded, large area plastic scintillation counter or its equivalent. If the background count of the plastic scintillator doubled, and if the true concentrations in the samples were twice those reported here, it should still be possible to measure ^{85}Kr concentrations as small as 3×10^{-8} μ Ci/ml using the technique described here with slight modifications.

The variations in data points for bagged-samples are due primarily to inaccuracies in reproducing rotameter settings. Construction variations in polyethylene bags also contribute to the variation in observations where these bags were used. Observations in Figures 2 through 5 were made immediately after the samples were taken. Variations in radon-daughter product activity over short periods of time contribute to the variation in observation for these samples.

With the detector on the sample bag, the geometry is essentially constant at 2π . So, the detector response is expected to be linear with increasing volume (therefore activity) for a fixed concentration in the sample as shown in Figures 3 and 4. This should be true for volumes and geometries for which self-absorption in the sample is negligible. So, if one is on the edge of a cloud, detector response will be proportional to the total activity in the cloud, irrespective of cloud dimensions within broad geometric limits. The linear relation must begin to level off and reach saturation as the dimensions of the cloud approach those of an infinite volume. Figure 4 yields an efficiency of 0.003 cpm/dpm at all different volumes and geometries at a fixed concentration of $6.3 \times 10^{-4} \mu\text{Ci/ml}$.

There is some variation in counting efficiency with concentration of activity at a fixed volume. Figure 5 has a slope of 1.04, and shows an efficiency of 0.003 cpm/dpm at $10^{-6} \mu\text{Ci/ml}$ and 0.004 cpm/dpm at $6.3 \times 10^{-4} \mu\text{Ci/ml}$ (the concentration used in Figure 4). An increase in efficiency accompanying an increase in concentration is to be expected because of the larger number of maximum energy beta particles contained in the samples at higher concentrations. This increase in efficiency with increases in concentration is not apparent at concentrations on the order of $10^{-7} \mu\text{Ci/ml}$ as Figure 6 shows. The slope shown in Figure 6 is 1.00.

Figure 6 yields an efficiency of 0.014 cpm/dpm for 23-liter samples, and 0.024 cpm/dpm for 13-liter samples. The smaller, thicker bag yields higher efficiency probably because it keeps more activity in the solid angle of the detector. The 23-liter bags drooped somewhat below the 2π solid angle of the scintillation detector. The optimum geometry is probably a hemisphere with its flat plane centered on the detector surface. The optimum geometry and volume of the sample for this technique is still open to question and deserves additional study. Careful attention to this question would probably reduce further the minimum detectable concentration for ^{85}Kr .

Bagged-samples provide several advantages over "in situ" measurements of ^{85}Kr .

(1) When multiple sampling stations are required, "in situ" measurements require multiple detectors and recorders or a telemetering system. This approach is considerably more expensive.

(2) "In situ" measurements must also include pretreatment of the air to eliminate interference from other beta particle emitters. Accumulation of activity in the sampling chain may interfere with detection sensitivity to ^{85}Kr beta particles.

(3) Both sample geometry and detector geometry are always known, and are reproducible with bagged-samples.

(4) Provided sufficient activity is collected, the average concentration during the sampling period will be measured with bagged-samples, irrespective of either the dimensions or the concentrations of the contaminated air. This may yield a sensitivity greater than that provided by "in situ" measurements.

The disadvantages of bagged-samples are:

(1) They are incapable of identifying either the time or the magnitude of changes in air concentrations, and are not suitable for an alarm system.

(2) In large volumes they are awkward to handle, and require that precautions against leakage be taken.

SUMMARY AND CONCLUSIONS

An inexpensive method to monitor atmospheric ^{85}Kr at or below $3 \times 10^{-8} \mu\text{Ci/ml}$ (0.1 MPC), with minor modifications to existing environmental air sampling stations, has been described. But the method needs further development and testing with mixtures of radioactive gases and aerosols likely to be found where ^{85}Kr is emitted. The method does not require volumes which are infinite with respect to the beta particle energy of ^{85}Kr . Neither does it require concentrations of activity which are stable with respect to time. Therefore, it is a realistic method from the viewpoint of conditions likely to be experienced in the field. One rarely encounters a truly infinite cloud sustained over a period of time long enough to make infinite cloud measurements realistic.

The ultimate test of the technique should involve mixtures of ^{131}I , ^{133}Xe , ^3H , and ^{85}Kr in concentrations likely to be encountered in the environment of reactors and fuel reprocessing plants. If the technique should fail this test of mixtures, it may still be useful as a screening technique for radioactive gases released to the environment by man.

REFERENCES

- Berger, M. J., (1971), *J. of Nucl. Med.*, Sup. No. 5, Vol. 12.
Code of Federal Regulations (1965), Title 10, Part 20.
Coleman, J. R., and R. Liberace, (1966), *Radiolog. Health Data Reports*, 7, 615.
Cowler, K. E., and K. Z. Morgan, (1967), *Health Physics Division Annual Report*, ORNL-4168, 39-45.
Handbook of Chemistry and Physics, (1966), Cleveland: The Chemical Rubber Company.
Holland, J. A., (1969), *Proceedings of the AEC Symposium, Biological Implications of the Nuclear Age*, USAEC Division of Technical Information.
Kirk, W. P., (1972), Environmental Protection Agency, Office of Research and Monitoring, Washington, D.C.: U.S. Government Printing Office, 484-482/46.
LeBlanc, A. D., (1972), *Phys. Med. Biol.*, 17, 585-589.
Lederer, C. M., J. M. Hollander, and I. Perlman, (1967), *Table of Isotopes*, 6th Ed. (New York: John Wiley and Sons, Inc.).
Martin, M. J. and P. H. Blichert-Toft, (1970), *Nuclear Data Tables*, 8A, 108.

- Percival, D. R., (1971), Personal Communication, Analytical Chemistry Branch, Health Services Laboratory, USAEC, Idaho Falls, Idaho.
- Radiological Health Handbook, (1970), Washington: Public Health Service.
- Sill, C. W., (1969), Health Physics, 16, 371-377.
- Slansky, C. M., (1971), Atomic Energy Review, 9, 423-440.
- Slansky, C. M., H. K. Peterson, and V. G. Johnson, (1969), Environmental Science and Technology, 3, 446-451.
- Smith, D. G., J. A. Cochran, and B. Shleien, (1970), PHS, BRH/NERHL 70-4, Rockville, Maryland.
- Voilleque, P. G., D. R. Adams, and J. B. Echo, (1970), Health Physics, 19, 835.

TABLE 1. Properties of ^{85}Kr .

Property	^{85}Kr	Reference
Density, mg/ml	3.74	Hbk. of Chem. & Phys., (1966)
Density/Density Air	2.9	Hbk. of Chem. & Phys., (1966)
Maximum Beta Energy, MeV and Abundancy (%)	0.67 (99.6) 0.160 (0.4)	Lederer, <i>et al.</i> , (1967); Rad. Health Hbk., (1970); and Martin and Blichert-Toft, (1970)
Average Beta Energy, MeV	0.2464	Berger (1971)
Range of Maximum Energy Beta in: Aluminum, mg/cm ²	235	Rad. Health Hbk. (1970)
Air, cm	182	Rad. Health Hbk. (1970)
Range of Average Energy Beta in: Aluminum, mg/cm ²	59	Rad. Health Hbk. (1970)
Air, cm	46	Rad. Health Hbk. (1970)
Specific Gamma Ray Constant, $\frac{R}{\text{Ci-hr}}$ at 1 meter	2.34×10^{-4}	The Author
Deposition Velocity on Grass, cm/sec	2.3×10^{-11}	Voilleque, <i>et al.</i> , (1970)
Max. Permissible Concentrations, $\mu\text{Ci/ml}$;		
Occupational	1×10^{-5}	10 CFR20 (1965)
Public	3×10^{-7}	10 CFR20 (1965)
Half-life, years	10.76	Rad. Health Hbk. (1970)
Gamma-Ray Energy, MeV and Abundancy (%)	0.517 (0.4)	Martin and Blichert-Toft (1970)

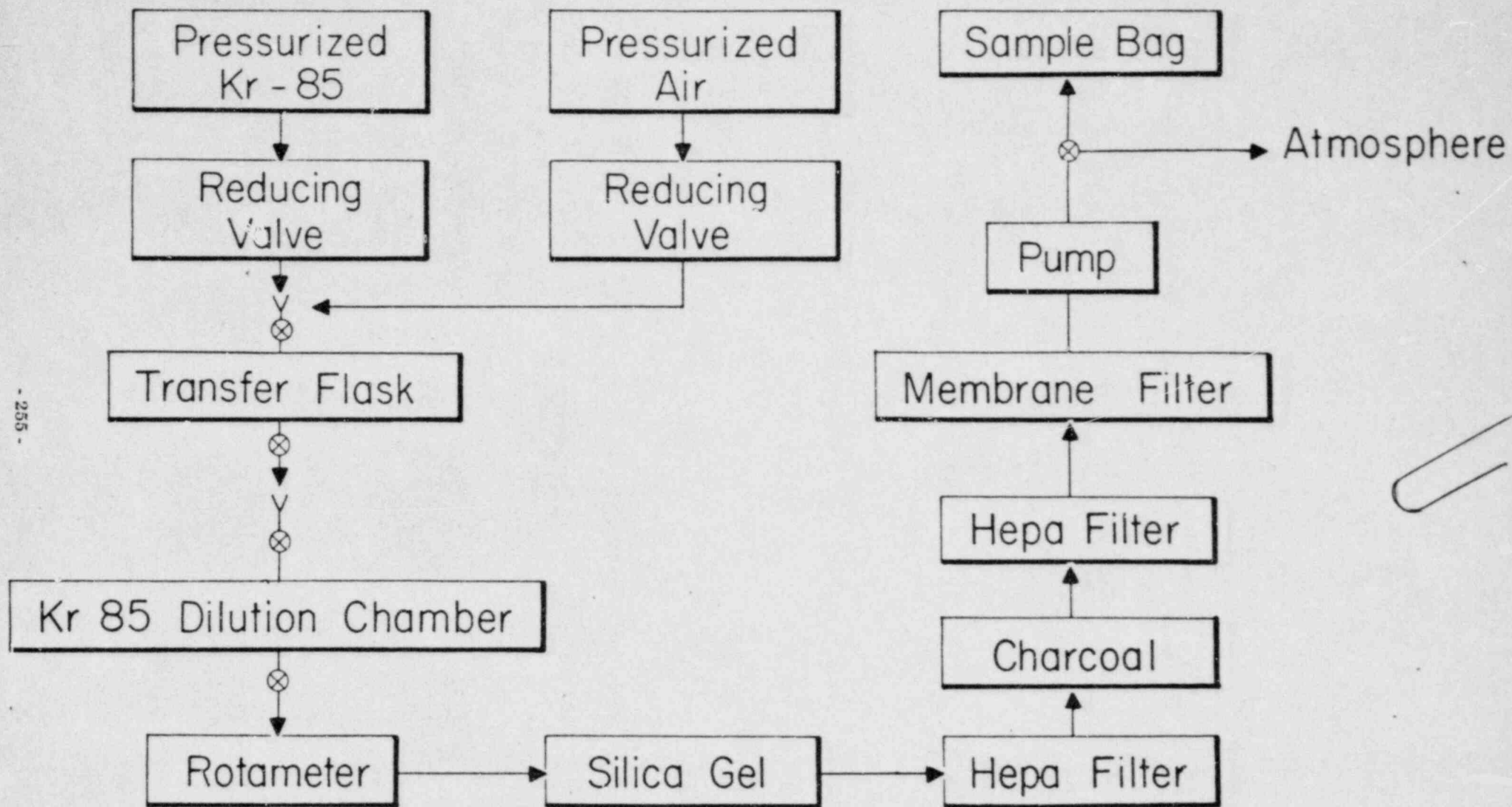


Figure 1. Krypton dilution and sampling system.

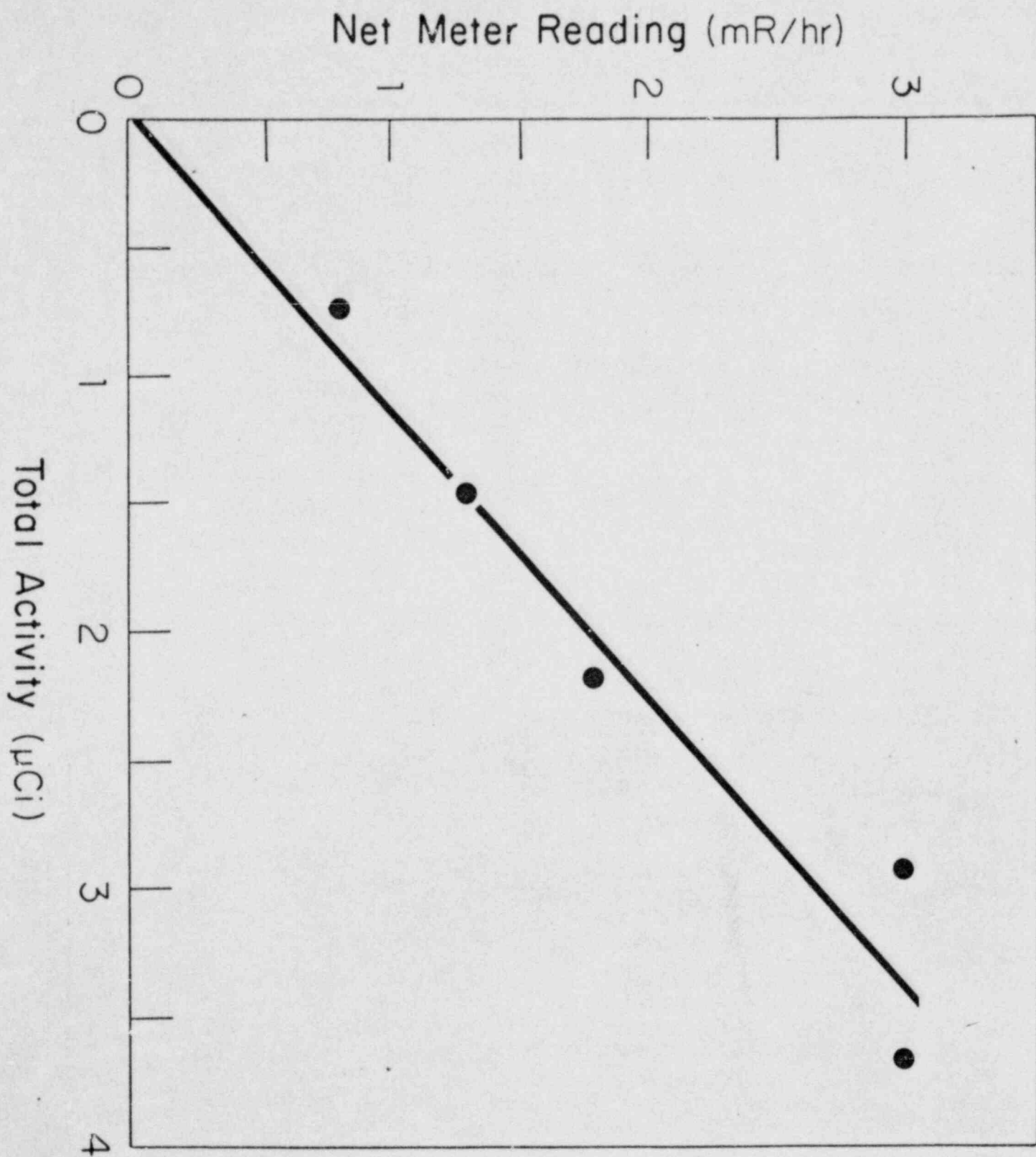


Figure 3. Ludlum G.M. survey meter response to a fixed concentration of ^{85}Kr in a 5-liter Saran bag at different volumes.

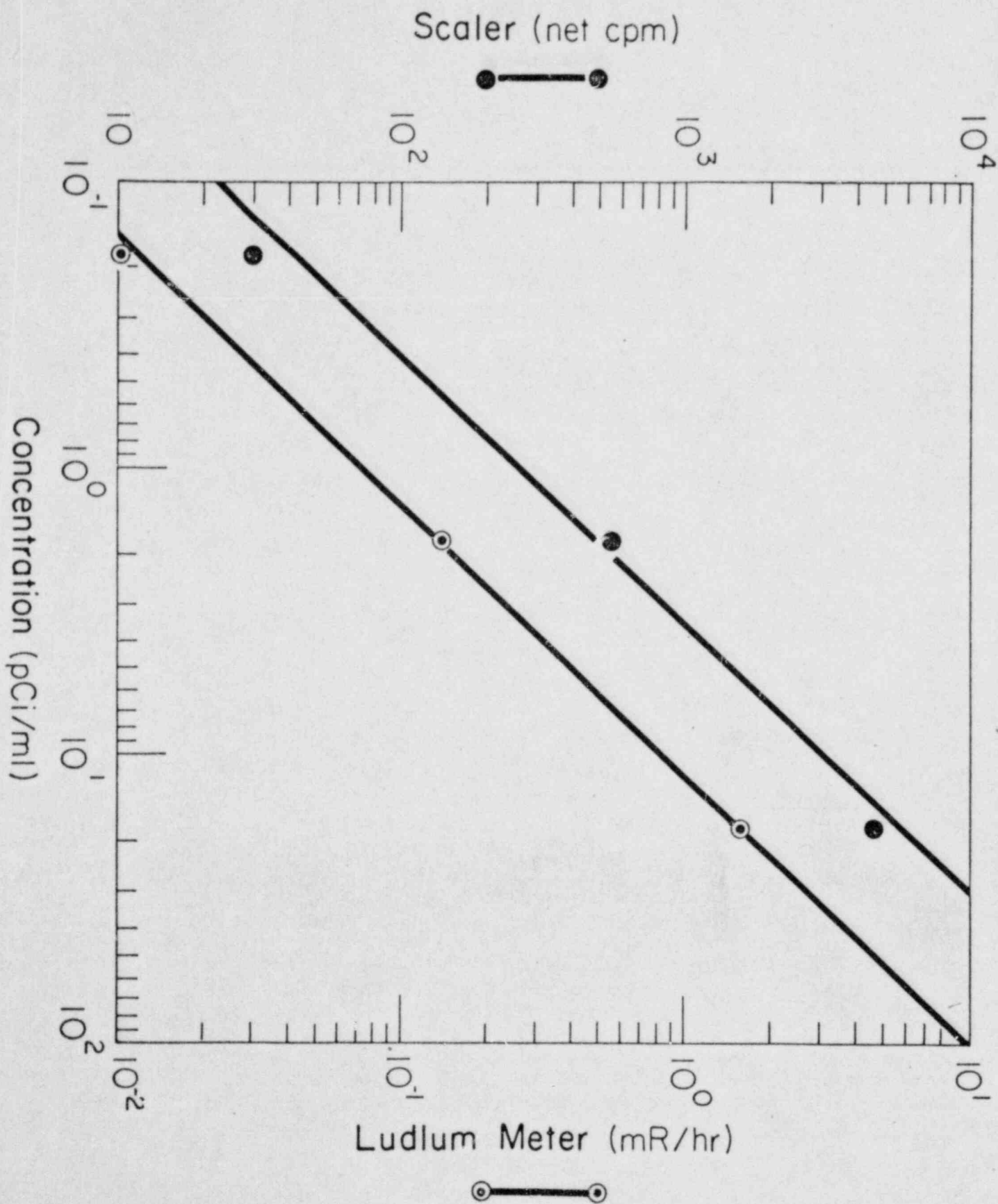


Figure 2. Response of the Amperex G.M. tube in the exposure chamber as a function of ^{85}Kr concentration. (The counting time for each observation with the scaler was 3 minutes.)

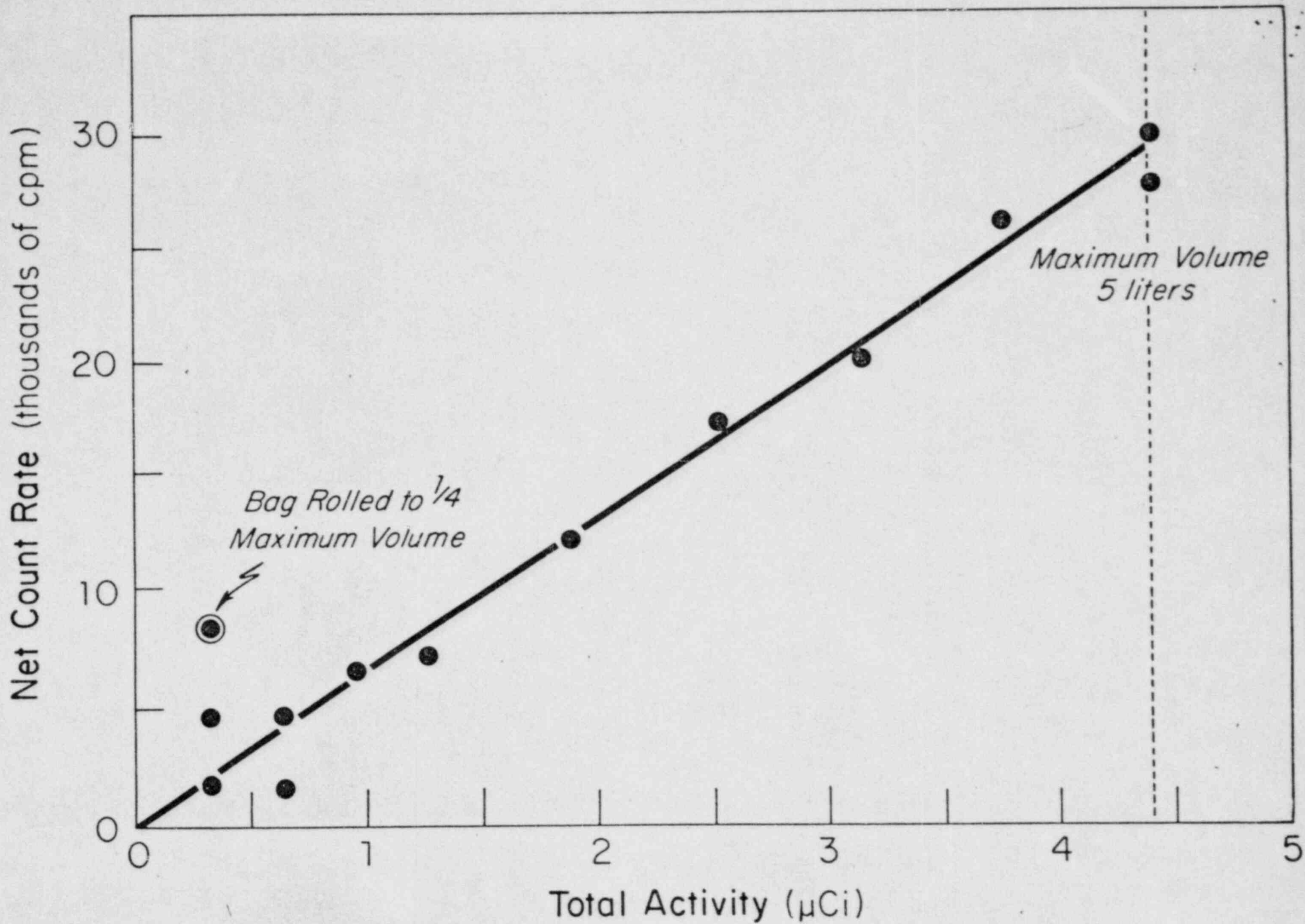


Figure 4. Response of the Eberline HP-210 G.M. probe to a fixed concentration of ^{85}Kr in a 5-liter Saran at different volumes. (The counting time for each observation was 1 minute.)

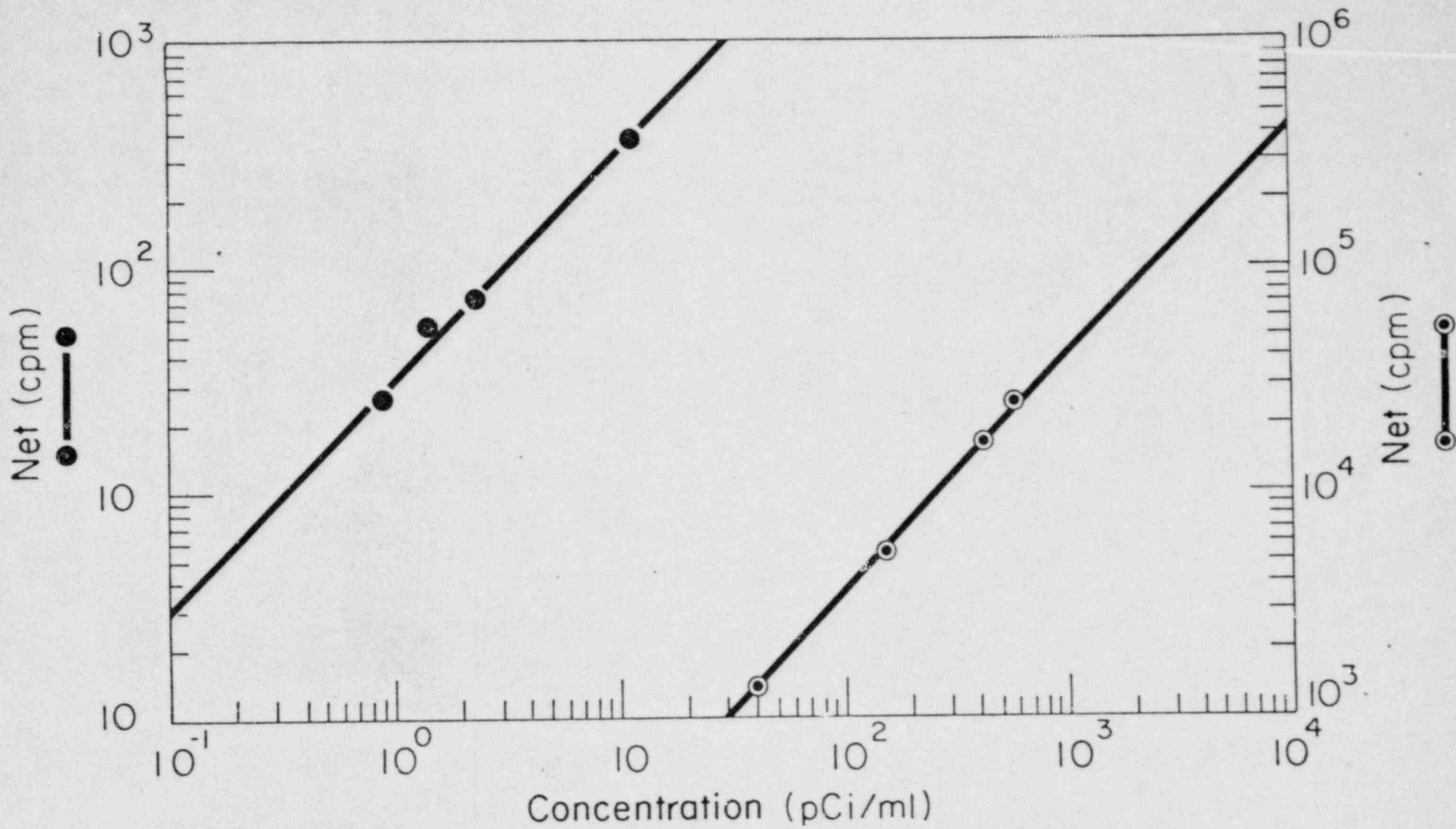


Figure 5. Response of the Eberline HP-210 G.M. probe to 5 liters of ^{85}Kr in the 5-liter Saran bag containing various concentrations. (The counting time for each observation was 3 minutes.)

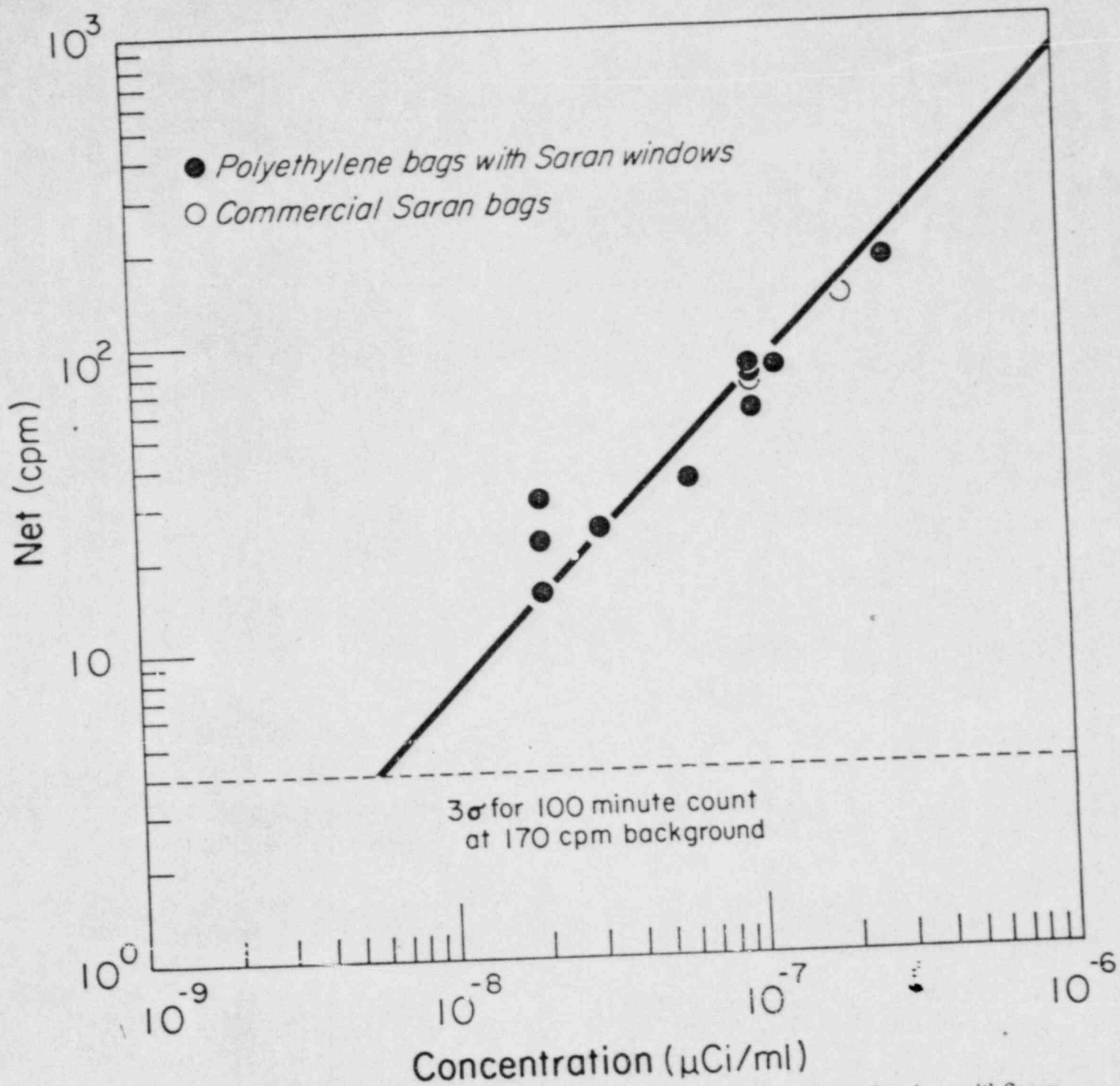


Figure 6. Response of plastic scintillation detector to 23-liter samples of ^{85}Kr in polyethylene bags with Saran windows and in commercial Saran bags. (All samples were stored overnight and counted to