Title
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Abstract

A new system has been developed to capture tritiated water vapor that normally would be released to the environment during glove-box operations. Columns of silica gel are connected to the exhaust lines, and essentially all the tritium released in the box is captured. The silica gel can initially be in equilibrium with atmospheric humidity without impairment of its capacity for absorbing tritiated water. This means that the silica gel can remain connected to the exhaust line for an indefinite period of time and still be ready for active operation.

In our application of the system we can use standard pipetting techniques for transferring tritiated water of very high specific activity without allowing any tritium to escape with the exhaust air. For convenience and economy, the silica gel columns are designed so we can easily empty and refill them without removing the columns from the system.

We also found that the silica gel can be used as a convenient room sampler for tritium.

Introduction

A need exists at Lawrence Berkeley Laboratory for tritiated water for use in biodynamic studies. To prevent any release of contaminant to the environment, a method has been developed for capturing tritiated water vapor from glove-box operations by using a filter containing silica gel. We have found this procedure to be both faster and more convenient than using the rather involved method of vacuum transfer.

Purpose of the Study

The need for tritiated water has steadily increased over the past few years. At the same time we have also been more concerned with lessening the environmental pollution. To meet the demand for tritium and also prevent any release of contaminant to the environment, some sort of method had to be developed that would stay within the limitations. In addition, the method or the system to be used had to be very flexible so we could carry out the many different types of operations involved in the transfer of a range of quantities of tritium, from very large to extremely small.

Tritiated water is shipped to us from the supplier in ampoules (Fig. 1) containing 20 ml T_2O, with a specific activity of approximately 40 Ci/ml, totaling approximately 800 Ci. For reasons of safety and convenience these large ampoules must be broken down to smaller quantities, such as approximately 2 ml or 80 Ci per container. Requests by the researchers needing the T_2O vary anywhere from a few λ to several ml. One can readily see that vacuum transfer would be rather difficult if some sort of accuracy is to be maintained. The situation called for the use of open or regular pipetting techniques in a glove box. Present box filters do not stop tritiated water vapor; this led us to the development of the silica gel filter.

Experimental Techniques

The experimental equipment is shown in Fig. 2. It consists of a T_2O source and an ion chamber to which a strip-chart recorder has been connected. Farther down the line is the test column. The column volume ranges from 40 ml to approximately 1 liter. Downstream from the test column are another T_2 sniffer and strip-chart recorder. The pump in the T_2 sniffer provides the air flow, which is in the range of 6 to 10 liters/minute.

Dehumidification of air streams by silica gel or other desiccants is a common practice. There is certainly nothing remarkable about removing tritiated water[1] (along with other water) by previously dehydrated silica gel. The remarkable thing we discovered is that it is not necessary to first dehydrate the silica gel. It can be saturated with water at ordinary room temperature and humidity, and still remove tritiated water vapor with 100% efficiency. The effectivenss is approximately the same as with dry desiccant. The reason is that a rapid exchange occurs between water in the adsorbed and vapor phases. The same amount of water is leaving as is entering the column, but it is not the same water. Thus, tritiated water enters, but only normal water leaves, until the column is finally saturated with the tritiated water.

Figure 3 compares the breakthrough curves for oven-dried silica gel and silica gel already in equilibrium with the ambient humidity. In either case, no significant amount of tritium shows up in the effluent for more than 25 hours.

The fact that the desiccant need not be dehydrated has important practical consequences. A bed of silica gel can be left in the exhaust stream continuously and yet will be effective in removing any sudden pulse of T_2O vapor. No fancy detection and valving systems are required.

As with other dynamic adsorption systems, this process can be considered a diffusional process. The equations worked out by Madey and colleagues[2, 3] can be applied in this situation to characterize the operation and allow the prediction of behavior.

Two parameters are sufficient to characterize an adsorption column: a dispersion number and the total adsorption capacity. The adsorption capacity is a property of the adsorbent, but the dispersion number depends on parameters such as column dimensions, flow rates, and particle size. Using Davisson Grade 40 silica gel (6-12 mesh) we found an effective adsorptivity of about 35 000. The dispersion number varied with different columns. For a column of convenient size, in which the diameter and length are about equal, and a superficial velocity of 10 cm/sec, we obtained a dispersion number of about 0.08. Longer columns and less velocity tend to decrease the dispersion, up to a point. The sharpest breakthrough curves (lowest dispersion numbers) were obtained with a column 23 cm long and 7 cm in diameter, and a superficial velocity of 4.3 cm/sec. This gave a dispersion number of 0.02.

If the log of the concentration is plotted against the log of the time, a symmetrical curve should be obtained. Its shape is a function only of the dispersion number, and its location on the x axis is a function only of the adsorption capacity. The curves we observed approximated this ideal, but in some cases the shape tended toward a double-humped curve.

During our measurements we used ordinary room air. No attempt was made to control temperature or humidity, which may well account for some variability in the data and the lack of symmetry mentioned above. A few log-log plots are shown in Fig. 4, covering a range of column sizes, shapes, and flow rates. In this plot, all curves have been normalized to an input pulse totaling 1 curie. Even with poorly designed columns, more than 1000 column volumes can pass through the adsorbent before breakthrough. Reasonably effective designs are good for about 10 000 column volumes.

Several other desiccants were tried. Activated alumina and $CaSO_4$ were found to be inferior for this application. Molecular sieve, grade 5A, was about equal to silica gel in effectiveness.

Practical Usage

To accommodate the air flow (10 ft^3/min)in our glove boxes, special silica gel filters were designed, Fig. 5. Calculations showed that with an air flow of 10 ft^3/min, 5 pounds of silica gel should hold the T_2O vapor for approximately 1 hour before breaking through. The filters have a volume of approximately 5 liters; this allows a plenum of approximately 1 in. between the air intake and the silica gel. The bottoms of the filters have an expanded-metal grid, covered with a glass-fiber mat, thus retaining the silica gel. For convenience and economy, the filters were also provided with a filling spout and a bag pass-out arrangement.

A typical glove box used in T_2O transfer is shown in Fig. 6. As one can see, two filters are connected to the airtron; however, only one is used at any given time. This allows one to have steady, uninterrupted air flow all the time, plus a safe and convenient change from one filter to the other as needed.

The box arrangement shown in Fig. 6 usually contains a couple of hundred curies of T_2O, which is contained in an ampoule that is enclosed in a T_2 degassing unit shown in Fig. 7. The T_2O we receive, which has a rather high specific activity (40 Ci/ml), has a tendency to break down upon standing to form several gases, one of which is T_2. Since the silica gel does not capture or hold back the T_2, the degassing unit must be used in the following way. The unit is connected via a Tygon tube to a vacuum bottle located outside the box. (The volume of the bottle is optional, of course. We use a 5-liter bottle or cylinder pumped down to a gauge pressure of around 29 in.). With valve "A" open, the outside of the ampoule is now exposed to the vacuum; this should be for at least a couple of minutes. Next step is to open the ampoule screw cap stopper "B", using handle "C." The T_2O in the ampoule is now exposed to the vacuum for 10 to 15 minutes. After this has been completed, valve "D" is slowly opened, permitting enough air to flow through the unit; this should decrease the gauge pressure approximately 15 in. The valve on the vacuum bottle is closed and the Tygon tube at valve "A" is disconnected.

The top part of the T_2 degassing unit can now be removed.

To keep the T_2O contamination to a minimum, several sheets of absorbent paper have been placed in the box floor. The screw cap on the ampoule can now be completely removed, and pipetting or transferring should commence immediately. At this point, the glove box will be completely saturated with T_2O vapor. In our case the box reads approximately 5×10^3 to 1×10^5 $\mu Ci/m^3$; at the same time, the T_2O sniffer sampling downstream from the filter reads zero. A great amount of effort should be exercised in order not to contaminate the box more than absolutely necessary. If a spill should occur, however, it must be cleaned up as soon as possible, and the paper or whatever was used in the cleaning should be sealed in a plastic bag.

The time it takes the T_2O to work completely through the filter may vary anywhere from 1 to 4 hours. This is an interesting characteristic that we cannot quite explain. It appears to us that the longer the silica gel is connected to the exhaust stream (air flow 10 ft^3/min 24 hr/day) the longer it takes the T_2O vapor to "break through." We hope to get a reasonable answer for this in the near future.

When pipetting or transfer is completed (which usually takes 10 to 15 min) it is very important that the screw-cap on the ampoule be tightly secured before the ampoule is placed back in the T_2 degassing unit. Valves "A" and "B" are now closed. Residual amounts of T_2O vapor linger in the box for up to 3 to 6 hours after everything has been closed off. When the T_2O concentration downstream from the filter is increased by a factor of 2 over background, the T_2O sniffer sampling it sounds the alarm. At this time, the second filter is opened to the system and the first is shut off, emptied, and refilled. At the time of filter change, it is very important to know the concentration in the box. If there is any appreciable amount over background, the second filter must be emptied either when the box concentration goes to zero or upon T_2O breakthrough. As an example, in our case, where the filters are usually connected to the line for approximately 2 weeks, and we are to transfer approximately 2 curies of T_2O from the 200-Ci ampoule, the total time is approximately 4 hours. The first filter has

a breakthrough time of 2.5 to 3 hours, the second 1 to 1.5 hours--provided, of course, that no T_2O was sprayed around the box.

An excellent graphical example of practical usage of the silica gel filters can be seen in Fig. 8. This clearly shows the drop in concentration in the exhaust stream.

Acknowledgments

We are grateful to Robert M. Latimer, Health Chemistry Department Head, for supporting this project by reinforcing the Health Chemistry policy of minimum release to the environment, and James T. Haley for his many good suggestions and invaluable assistance. We thank Eilen Doyle for her drawings and Carol Legge for her secretarial assistance.

References

1. W. D. Chiswell and G. H. C. Dancer, Health Phys. 17, 331 (1969).
2. R. Madey, R. A. Fiore, E. Pflumm, and T. E. Stephenson, Transmission of a Pulse of Gas Through an Absorber Bed, ANS Trans. 5, 456 (1962).
3. K. G. Lee and Richard Madey, The Transport of a Fluid Through a Packed Bed, Trans. Faraday Soc. 67, 329 (1971).

FIGURE CAPTIONS

Fig. 1. Supplier's shipping ampoule is shown to the left and storage ampoule to the right.

Fig. 2. Schematic of experimental equipment.

Fig. 3. Comparison of the breakthrough curves for oven-dried silica gel and silica gel already in equilibrium with the ambient humidity.

Fig. 4. Log-log plots covering a range of column sizes, shapes, and flow rates.

Fig. 5. Silica gel filter.

Fig. 6. Typical glove box arrangement for T_2O transfer.

Fig. 7. Tritium degassing unit.

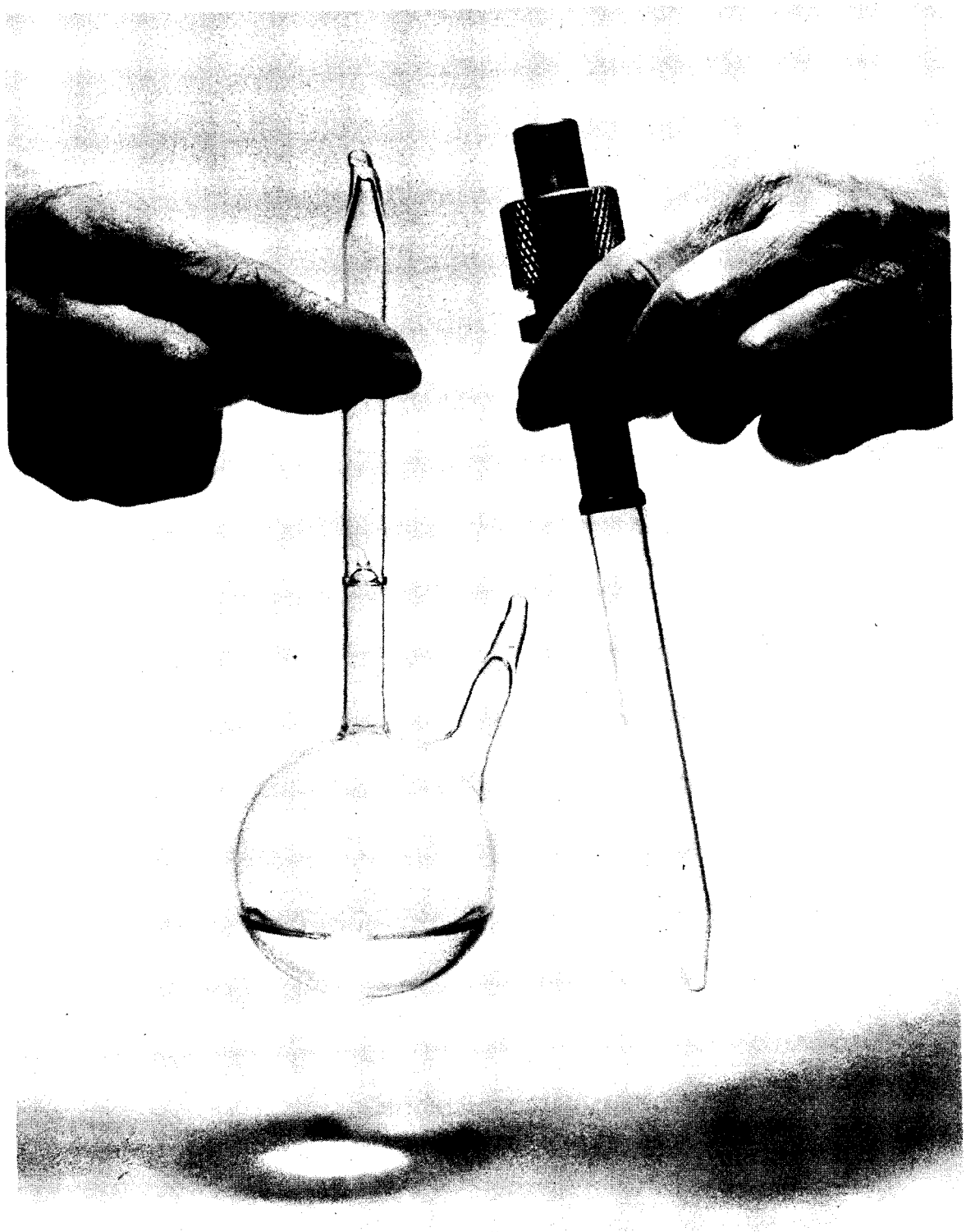
Fig. 8. Graph shows the amount discharged (millicuries/week) before and after the silica gel filters were used.

Fig. 9. Curves show concentration (microcuries/cubic meter) during a typical T_2O transfer. Solid line is the concentration before the silica gel filter; dotted line, the concentration after the filter in the exhaust line.

Fig. 10. Arrangement of storage ampoules in storage cylinder.

Fig. 11. Storage cylinder holding 10 storage ampoules under approximately 15 in. vacuum.

Fig. 12. Photo shows the earlier throw-away filters (top) and the new refillable filters (bottom) with the bag passout arrangement.



CBB 716-2746

Fig. 1

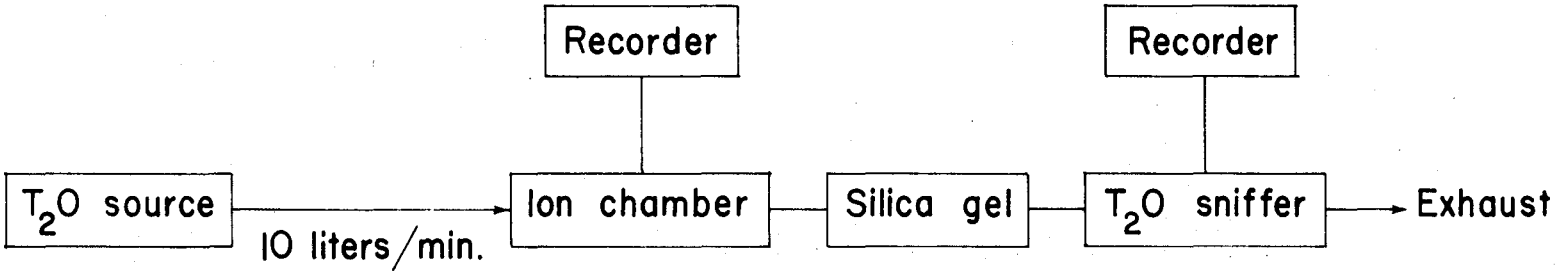
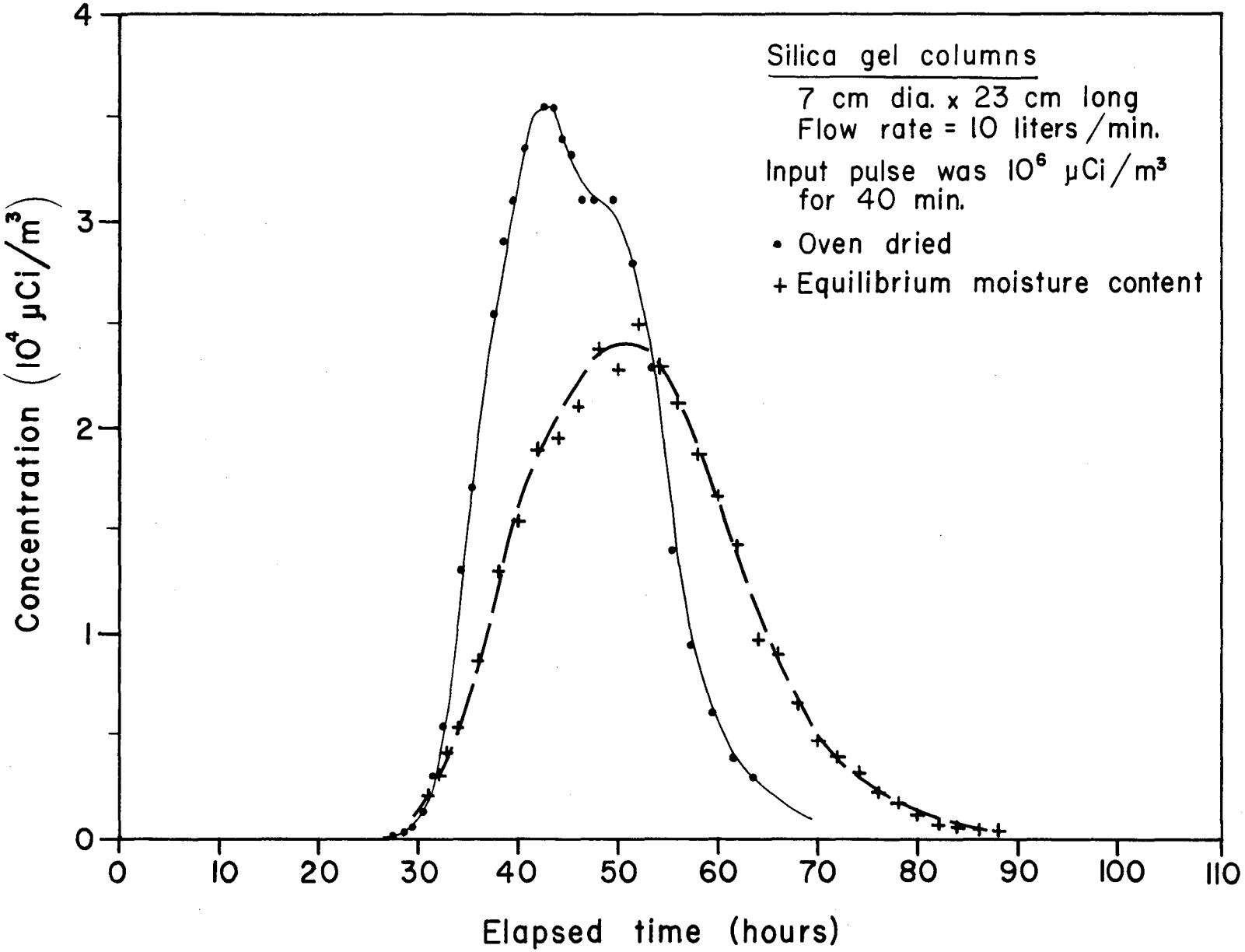
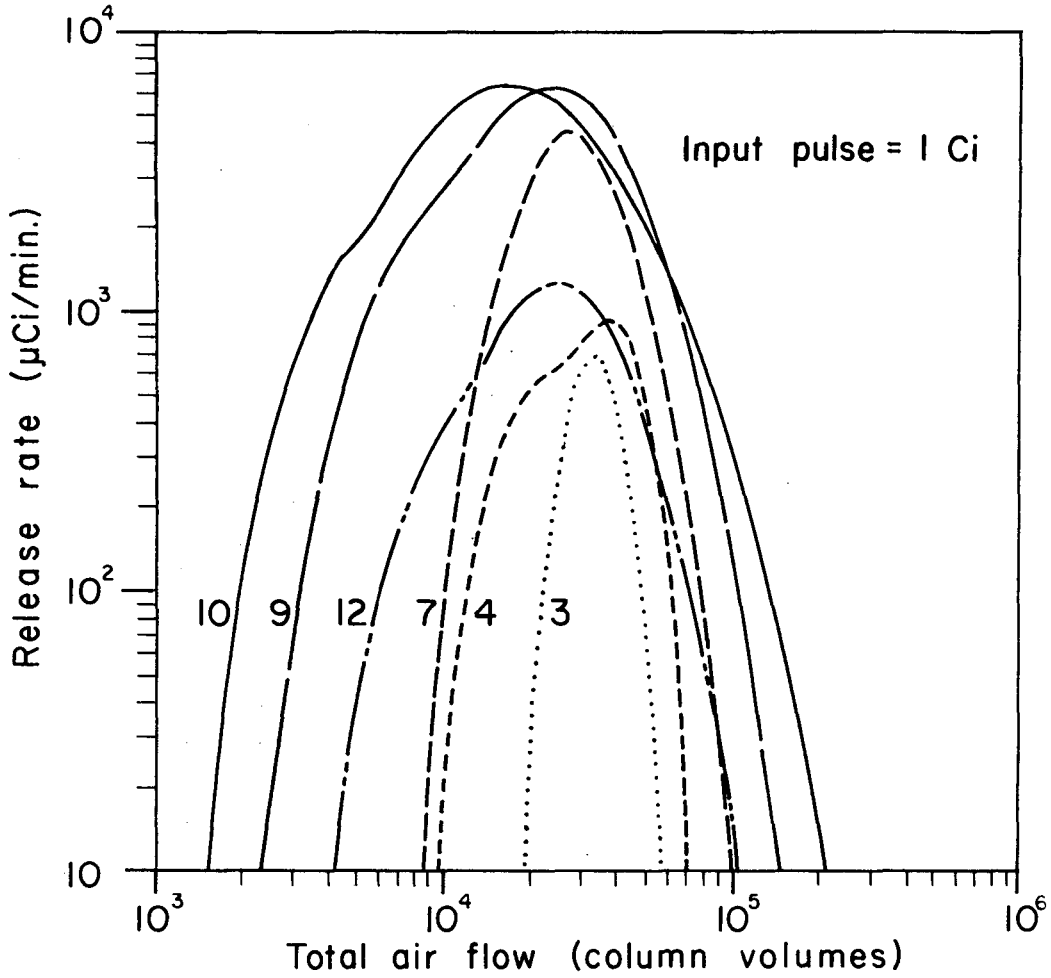

Recorder
Recorder
T_2O source
10 liters/min.
Ion chamber
Silica gel
T_2O sniffer
Exhaust
XBL 716-1146

Fig. 2



XBL 716-1169

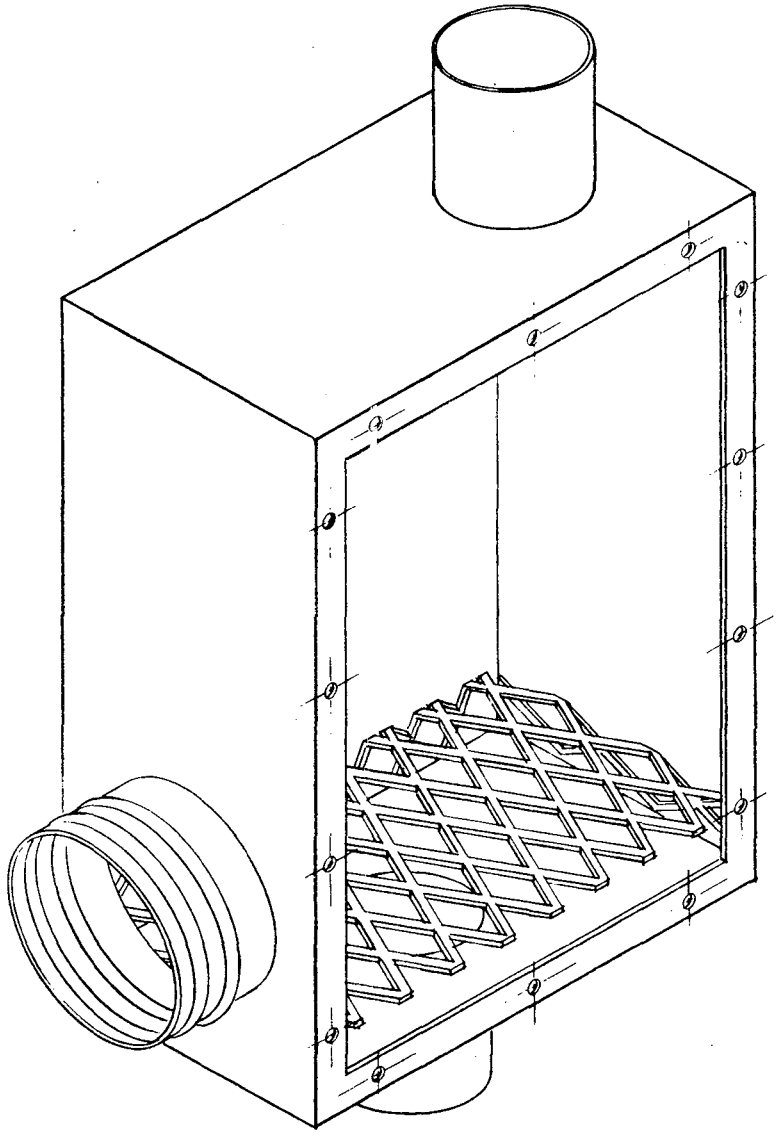
Fig. 3



Run no.	Dia. (cm)	L'gth (cm)	Vol. (cm^3)	Flow rate (ℓ/min.)	Superficial velocity (cm/min.)
3	7.0	23	880	10.0	261
4	8.9	3.8	236	6.7	108
7	4.4	5.1	79	9.5	614
9	1.6	20.	40.2	9.7	4824
10	4.4	2.6	39.5	9.8	633
12	8.9	3.8	236	10.0	161

XBL 716-1170

Fig. 4



XBL 716-1091

Fig. 5

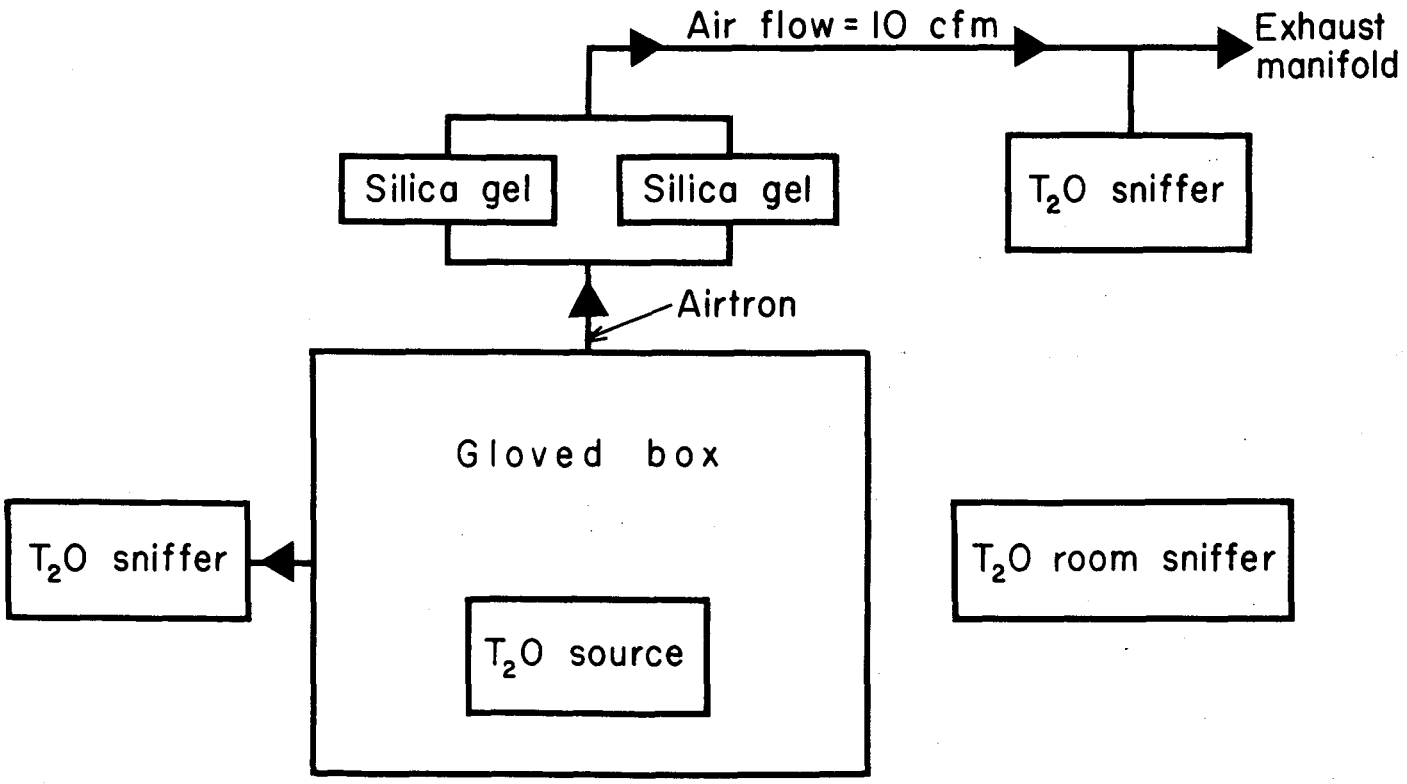

Air flow = 10 cfm
Exhaust manifold
Silica gel
Silica gel
T_2O sniffer
Airtron
Gloved box
T_2O sniffer
T_2O room sniffer
T_2O source
XBL 712-189

Fig. 6

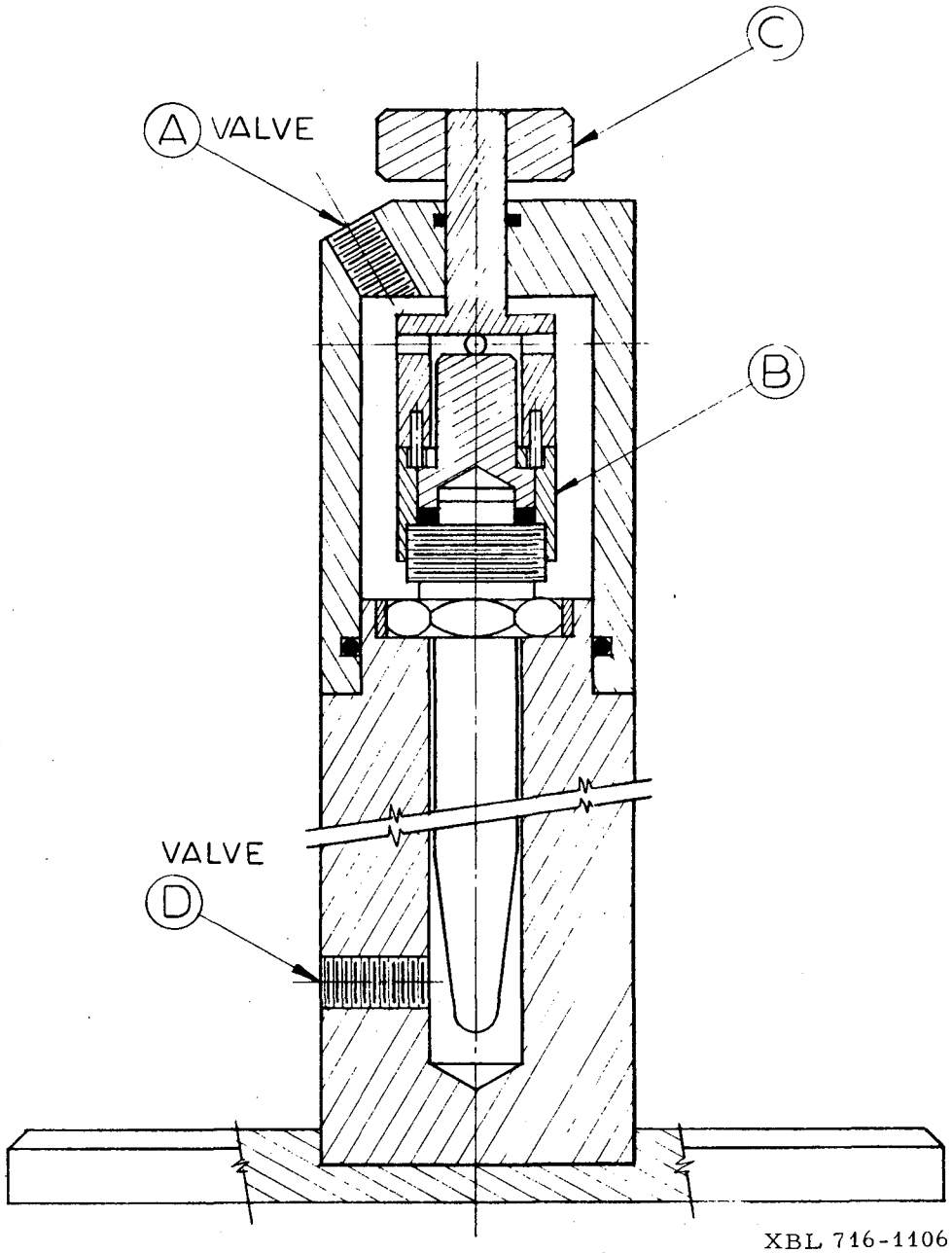


Fig. 7

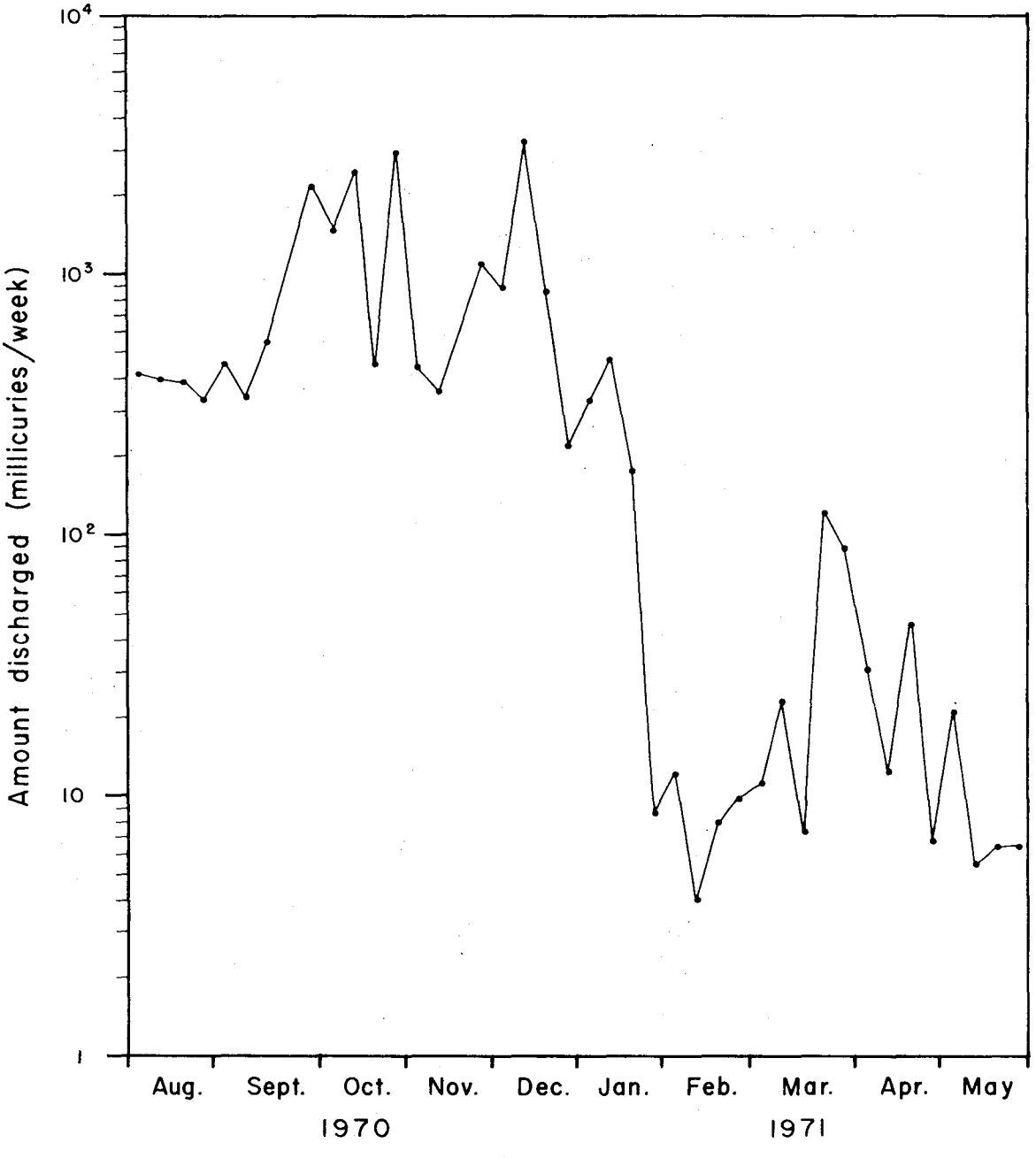

Amount discharged (millicuries/week)
10⁴
10³
10²
10
1
Aug.
Sept.
Oct.
Nov.
Dec.
Jan.
Feb.
Mar.
Apr.
May
1970
1971
XBL 716-1171

Fig. 8

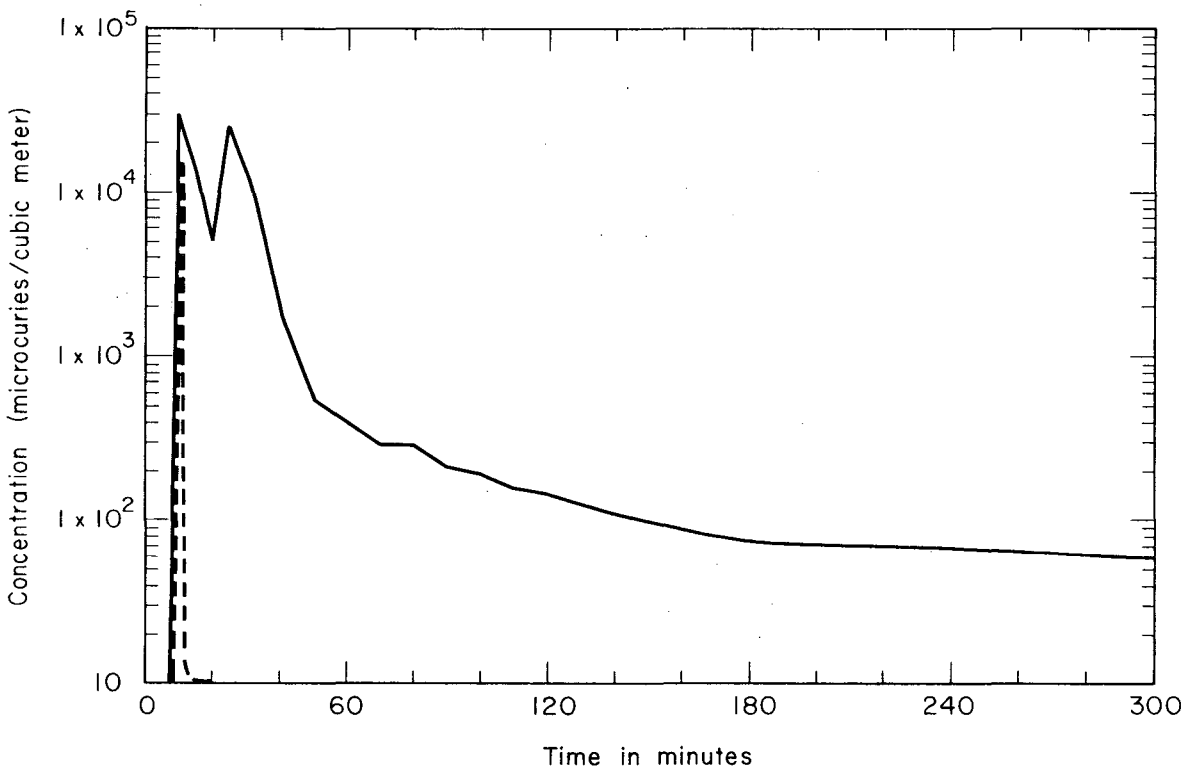

1 x 10^5
1 x 10^4
1 x 10^3
1 x 10^2
10
Concentration (microcuries/cubic meter)
0
60
120
180
240
300
Time in minutes

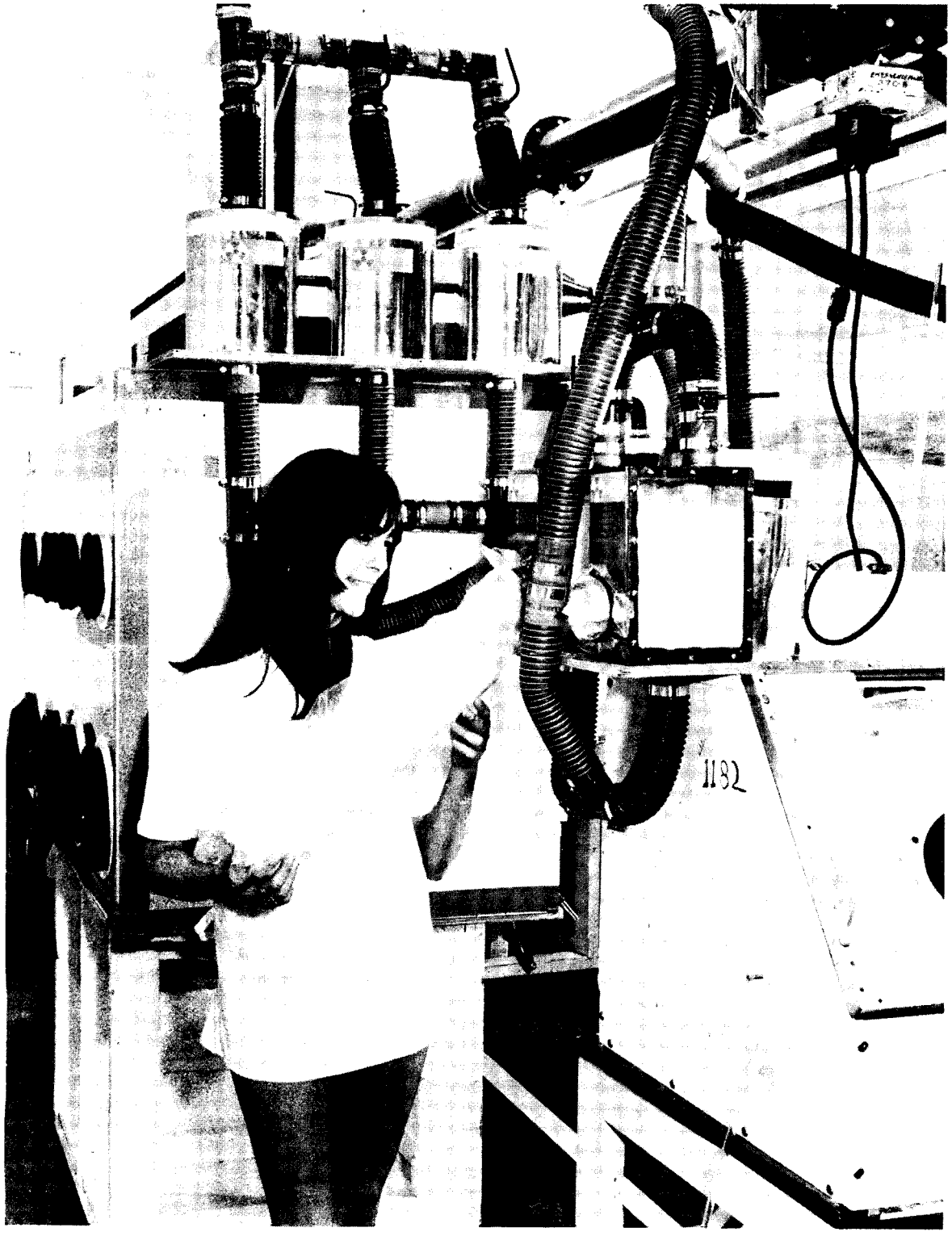
Fig. 9

CBB 716-2748

Fig. 10

CBB 716-2750

Fig. 11



CBB 712-525

Fig. 12