

Hydrogen Isotope Separation by Advanced Gas Chromatography and Fractionation

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A new kind of gas chromatography and a tritium counting device were developed for the separation of hydrogen isotopes. The active materials examined for chromatography were Pd/Al₂O₃, Pd and Pd-Pt(8 at%) alloy powders. The Pd-Pt alloy showed the best separation efficiency among the three materials. It could separate a 50%H₂-50%D₂ mixture to H₂ and D₂ of 97.5 % purity with 80% recovery at 274K without using any replacement gas. The bremsstrahlung X-ray counting device developed for measuring high concentration tritium showed a good linearity between the counting rate and the tritium pressure, the specific counting rate being evaluated as 70.8 cps/Pa. The combined use of these two devices is expected to be applicable to the recovery of tritium from the flow of fuel gas in thermonuclear fusion reactor.

1. Introduction

Tritium as well as deuterium will be used in kg amounts for the International Thermonuclear Experimental Reactor, where only several percents of the fuel injected into the reactor will be burned. Consequently, most of the fuel gas will be exhausted from the core, and hence a mixture of deuterium and tritium should be purified and separated from each other for re-fueling.

Concerning isotope separation, several methods have been proposed for fuel processing and waste handling[1]. Among them, liquid hydrogen distillation has been considered to be the first candidate for isotope separation in fuel processing[2]. A cryogenic-wall thermal diffusion device attracts attention recent years as well[3, 4].

Gas chromatographic methods are also promising for the separation of hydrogen isotopes because they are based on simple principle, are of simple construction, and have a high separation efficiency as well as a small tritium inventory. Besides the conventional low temperature gas chromatography, a replacement chromatographic technique has been proposed[5]. Its operation procedures are, however, complicated and the tritium

inventory in the column is expected to be rather large, depending on operation conditions, in comparison with the low temperature gas chromatography[6]. In this respect, the present authors directed their effort to improve these features and to develop a new type of gas chromatography working near room temperature with low tritium inventory without using any replacement gas[7, 8, 9].

In connection with the isotope separation, simple and reliable tritium counting devices are indispensable to detect effluent tritium species (T₂, DT and others) and to lead them into appropriate storage devices or other unit for following operations such as refueling. The counting devices for this purpose should be of fast response and free from the effects of contamination, the gas composition, the total pressure and other variables of the flowing gas in the tritium processing system. From this viewpoint, the present authors developed a bremsstrahlung X-ray counting device, which is very attractive for process monitor[10, 11, 12].

In this work, a "self-developing chromatography" for hydrogen isotope separation and a bremsstrahlung X-ray counter as well as their combined operation are discussed.

2. Experimental

2.1 Gas chromatographic separation

Gases used for chromatographic measurements were deuterium, a mixture of 50% H_2 -50% D_2 and Ar. The active materials examined were Pd supported by alumina (2 wt%); and powders of Pd and Pd-Pt(8 at%) of less than 100 mesh. The latter two were mixed with copper powder of 40-80 mesh and packed into stainless steel tubes.

The chromatograms by Pd/ Al_2O_3 were obtained with a stainless steel tube of 0.42 inner diameter and 200 cm length. It was packed with 16 g of Pd/ Al_2O_3 . The chromatograms by Pd/Cu were measured using a stainless steel tube of 0.42 cm diameter, packed with 1.28g of Pd and 75.4g of Cu. As for Pd-Pt/Cu, the column was also prepared with a stainless steel tube of 0.3 cm diameter, which was packed with 1.5 g of Pd-Pt and 62.1 g of Cu.

Prior to chromatographic separation experiments, a given column was first processed by heating at 523K in a flow of Ar carrier gas at a rate of 10 cm³/min for 2 hours to remove adsorbed water and other adsorbates. Subsequently, the column was cooled to a given operation temperature with flowing the carrier gas before each run. A small fraction of the effluent gas was introduced into the vacuum chamber at a pressure of 2×10^{-4} Pa for analysis. Other experimental details have been described elsewhere[7, 8, 9].

2.2 Bremsstrahlung X-ray counting

The device for bremsstrahlung X-ray counting was provided with a window made of beryllium disc with 3.0 cm diameter and 0.013 cm thickness, whose inner surface was coated with a gold evaporated film of 80 nm thickness. It was attached to a ConFlat flange. To expose the Be-window to mixtures of tritium and deuterium under various conditions, it was installed to a vacuum system.

Tritium stored in a ZrNi getter was used after being mixed with deuterium. The concentration was varied from 0.39 to 3.4% at total pressures of $10 \sim 10^4$ Pa. All of the counting measurements were carried out with a Si-avalanche photodiode at room tempera-

ture. The signals obtained by the photodiode were recorded by a multichannel analyzer through a preamplifier and a shaping amplifier. The spectra were calibrated to the low energy X-rays (6.40 and 7.06 keV) and γ -rays (14.4 keV) of ^{57}Co . More experimental details have been described elsewhere [10, 11, 12]

2.3. Fractionation

A tritium flow simulator was fabricated. It consisted of a Si-avalanche photodiode to detect X-rays, a glass tube, a solid radioactive source and a reciprocative motion device. ^{57}Co was selected as an X-ray emitter for its low energy X-rays. Its activity was about 5 μCi . It was reciprocated back and forth in the glass tube at a given velocity by a DC motor and two micro switches.

The signal from the X-ray detector was accumulated by a scaler. The accumulated counts were converted to an electrical signal and sent to a comparator. The signal accumulation time was varied in a range between 0.5 and 2.0 seconds to examine the response of the changeover valves.

Electromagnetic valves were selected for the changeover valves. One will be used for the channel of tritium containing gas, and the another for the channel of tritium-free gas. They were designed to work oppositely. The changeover valves were controlled by a comparator, which gave signals to a relay circuit by comparing the signal intensity from the scaler with a predetermined cutoff level. On receiving the signals from the relay circuit, a power source for the changeover valves would be switched on or off. The opening and closing action of the changeover valves was examined with a flow of argon gas instead of tritium containing gas. The counting rate of X-rays and valve action have been recorded by a personal computer and a recorder. More experimental details have been described elsewhere [13].

3. Results and Discussion

3.1. Isotope Separation

3.3.1. Pd/ Al_2O_3

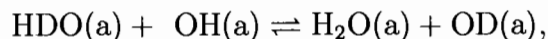
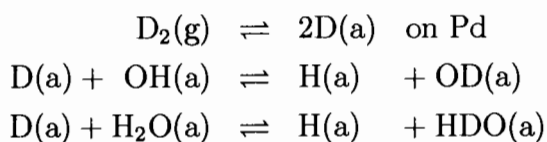
The Pd/ Al_2O_3 powder out-gassed at 1073K was packed into the stainless steel column.

After processing the column following the above mentioned conditions, 1.6 mmol of the 50%H₂-50%D₂ mixture was introduced as a pulse into the column at 343K. However, no hydrogen isotope efflux was detected initially. Hydrogen isotopes only appeared in the effluent gas after repeating four runs. This means that the sample gas amounting at least 6.4 mmol was captured by the Pd/Al₂O₃.

Successive addition of the sample gas amounting 1.6 mmol at a time caused D₂, HD and H₂ to appear in the effluent gas. However, hydrogen and deuterium were hardly separated under these conditions. Although the column could separate the three isotope molecules under other conditions, the separation efficiency was considerably poor. It should be mentioned that hydrogen isotopes were flowed out from the column without adding any replacement gas and that the ratio between the amounts of effluent deuterium and hydrogen was always below unity, for example, D/H ≈ 0.37 at the 18th run. This means that a fraction of deuterium was still trapped in the column.

Separate measurements of hydrogen adsorption on the Pd/Al₂O₃ sample showed over a 100 times greater amount of absorption than support-free Pd, suggesting that the spill-over of hydrogen took place on the present sample to form OQ(a) on the alumina surface, where Q denotes H or D and (a) an adsorbed state[14]. Apparently, this is why no hydrogen isotopes appeared during the initial runs in chromatographic measurements.

After saturation of the sites for OQ(a), isotope exchange or replacement reactions should be possible. Namely, when deuterium molecules are adsorbed by Pd-particles, they will spill-over to the alumina area to exchange with OH(a) to form OD(a). In addition, if there is adsorbed water, it should be also replaced by deuterium to form HDO(a). Since adsorbed water is rather mobile, it will act as deuterium carrier to distant OH(a) sites. These processes are described as



where (g) and (a) represent gaseous and adsorbed states. When the surface saturated with OQ(a) is exposed to a mixture of H₂ and D₂, deuterium atoms are replaced with hydrogen according to the above exchange reactions, because the O-D bond is more stable than the O-H. As a whole, deuterium will be captured preferentially by Pd/Al₂O₃ and cause to desorb hydrogen. This appears to be a reason that the isotope abundance ratio, [D]/[H], in the effluent gas was below unity for Pd/Al₂O₃.

In the presence of Q₂O(a) and OQ(a) on the material, chromatographic separation would arise from the isotope effects on not only H-Pd bonding but also O-H bonding. If the isotope exchange reaction between D₂ and H₂O(a) or OH(a) plays a predominant role, the separation should be poorer than the case that hydrogen absorption by Pd predominates, because the isotope effects on O-H bonding is much smaller than those on H-Pd bonding[15, 16].

3.1.2. Pd and Cu Mixture

The observations mentioned above indicate that hydrophobic supporting materials impair the isotope separation by this kind of chromatography. In other words, support free Pd is expected to show much better separation. In fact, this was observed for the Pd/Cu column as shown in **Fig. 1**. This column gave the outflow of hydrogen isotopes by the pulse-wise introduction of the sample gas amounting 2.35 mmol from the first run. A deuterium rich gas flowed out first and a hydrogen rich gas followed.

The chromatogram of D₂ made a sharp peak. That of HD showed a peak accompanied by a long tail. H₂ gave a peak with a shoulder and formed a broad band. In this case, a deuterium gas of 85.0% purity was obtained with 50% recovery of D₂ loaded into the column in the elapsed time of 11 min. At the end of the H₂ band, the ratio among the amount of effluent isotope molecules was H₂ : HD : D₂ = 1 : 0.41 : 1, which corresponds to the atomic ratio of the sample gas; H : D = 1 : 1.

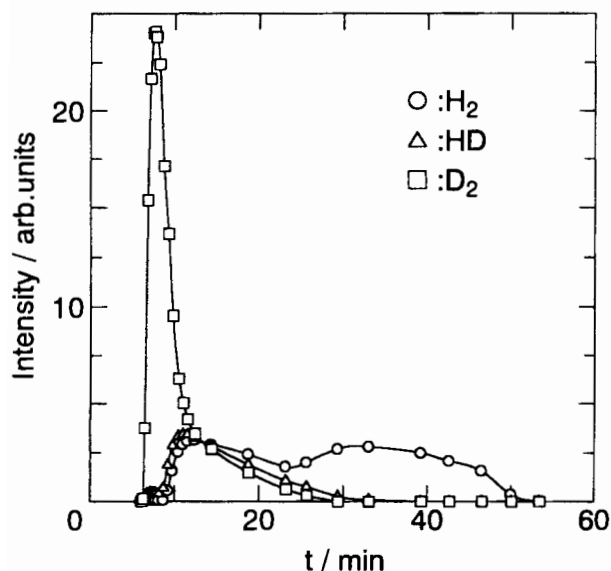


Fig. 1: Chromatograms for 50% H_2 -50% D_2 mixture by Pd/Cu: column temp. = 343K, carrier gas pressure = 1.3 atm., flow rate = $10\text{ cm}^3/\text{min}$, sample gas = 2.35 mmol

Although both hydrogen and deuterium flowed out from the column without adding replacement gas, the effluent isotopes were only 83% of the amount of injected gas. In addition, the operation temperature had to be rather high. This is principally due to the relatively large heat of hydrogen solution and/or hydride formation for Pd.

3.1.3. Pd-Pt and Cu Mixture

As mentioned above, the Pd/Cu column showed unsatisfactory results in terms of the separation efficiency, the deuterium recovery and the operation temperature. To lower the operation temperature without losing the self-developing property and the separation efficiency, it is necessary to use materials having lower heat of solution or hydride formation as well as large isotope effect. It has been reported that Pd-Pt alloys have lower heat of hydrogen absorption than Pd and show relatively large isotope effect[17]. **Figure 2** is an example of the chromatograms for 50% H_2 -50% D_2 mixture by Pd-Pt/Cu. Although the column was 400 cm in length in this case, it is apparent that the separation of hydrogen and deuterium was much better than that by Pd/Cu. It should be mentioned that the operation temperature was 274K, being much lower than that by Pd/Cu.

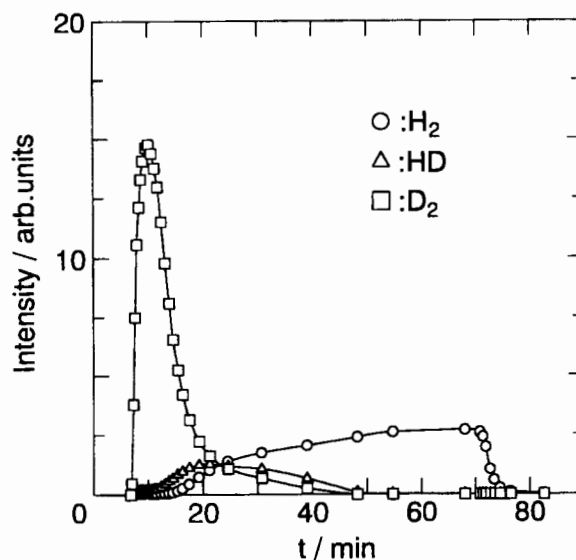


Figure 2: Chromatograms for 50% H_2 -50% D_2 mixture by Pd-Pt/Cu: column temp. = 274K, carrier gas pressure = 2.0 atm., flow rate = $10\text{ cm}^3/\text{min}$, sample gas = 2.35 mmol

The separation efficiency depends on not only the material used but also on the column size, the packing state of the material, and operation conditions such as temperature, flow rate, pressure, amount of sample gas and so on. **Figure 3** shows an example of such dependence.

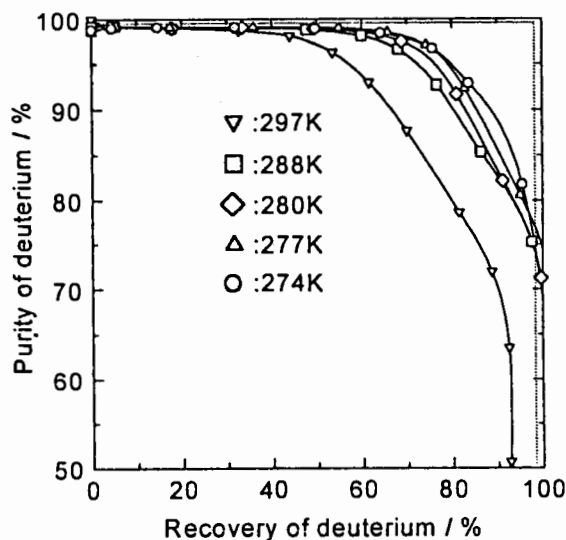


Fig. 3: Variation of separation efficiency at different temperatures for Pd-Pt/Cu: carrier gas pressure = 2 atm., flow rate = $10\text{ cm}^3/\text{min}$, sample gas = 2.35 mmol

The ordinate indicates the atomic fraction of D, in percent unit, to the sum of D and H atoms in the effluent gas, and the abscissa the

ratio of the number of D atoms flowed out in a given elapsed time to the total number of D atoms loaded. The bold dotted line shows the complete separation of D_2 from H_2 . This figure shows that the operation temperature is an important factor, as expected, to determine the separation efficiency; the lower the temperature is, the higher the efficiency. On the other hand, it is seen that the efficiency approaches a constant level with decreasing operation temperature, revealing that the extent of isotope effect is not the unique factor to determine the separation efficiency.

In fact, better separation was observed by higher pressures and/or slower flow rates of the carrier gas. Those observations suggest that the separation efficiency can be improved much more by suitable selection of operation conditions. It should be also mentioned that this column could decompose heteronuclear hydrogen molecules like HD and separate to H_2 and D_2 [18]. This feature is one of the important advantages of the present method.

3.2. Bremsstrahlung Counting

3.2.1. X-ray spectra and Sensitivity

Figure 4 shows an example of the X-ray spectra observed through the Be-window coated with Au-evaporated film, where the spectrum through a bare Be-window is also

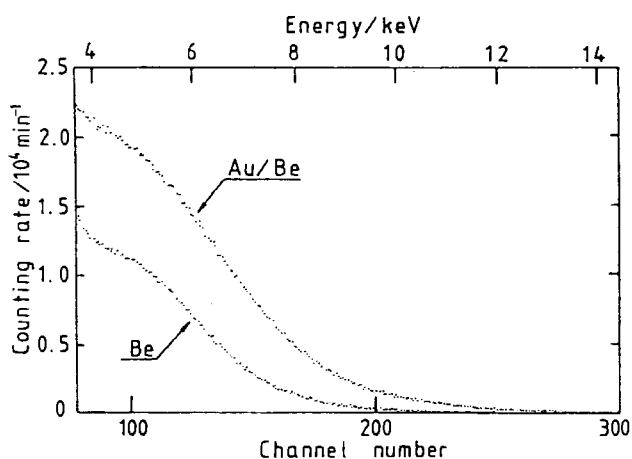


Fig. 4: An example of the observed bremsstrahlung X-ray spectra

shown for comparison. They were observed at 296 K for the tritium gas of 4.85 mCi/cm^3 . The integrated intensities were 2.41 and 1.17×10^4 cps for the Au-coated and the bare Be-window, respectively; that is to say, the

former showed about twice the counting rate than the latter.

Figure 5 shows relations observed for two windows between the intensity of bremsstrahlung X-rays and the partial pressure of tritium gas of 3.4%. To evaluate the partial pressure of tritium, the chemical form was presumed to be DT because tritium used in the present study was highly diluted with deuterium and was stored in ZrNi alloy, by which the gas phase should be equilibrated. It was found that the intensities of the bremsstrahlung X-rays were proportional to the partial pressure of tritium.

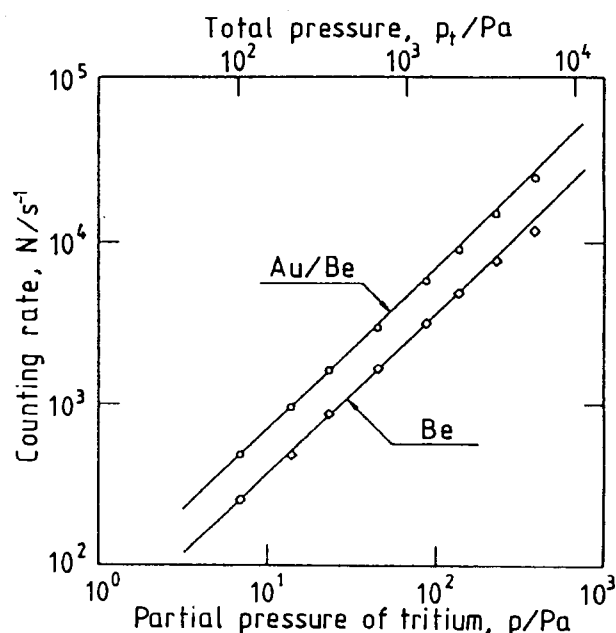


Fig. 5: Relations between the counting rate and partial pressure of tritium observed for Au-coated and bare Be-windows

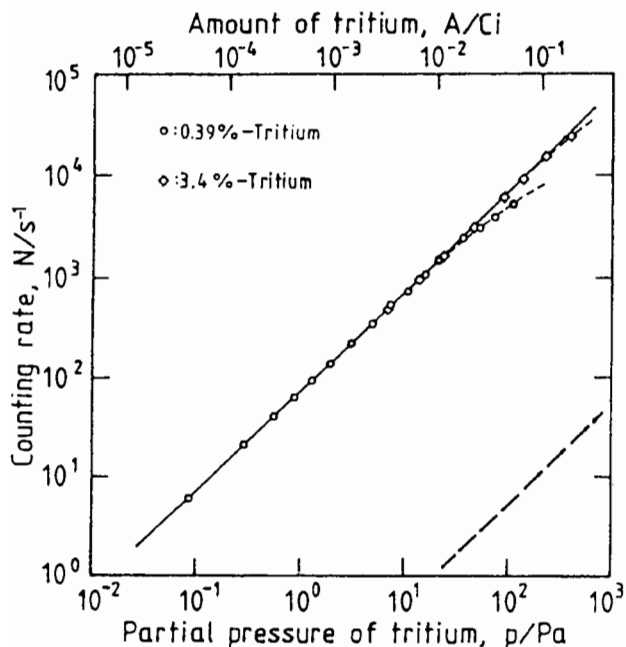
From the straight line for Au/Be, the sensitivity was evaluated as 70.8 cps/Pa, which corresponds to 5.95×10^3 cps/mCi/cm³. On the other hand, the bare Be-window gave 35 cps/Pa. Therefore, the Au-evaporated film acts as an efficient generator of bremsstrahlung X-rays.

3.3.2. Deviation from the Linearity

Figure 6 shows the comparison of the counting rate vs pressure relations between two different tritium mixtures, namely, 0.39 and 3.4%-T. The counting rates plotted in the figure were obtained from the Au/Be window. It is clear in this figure that the counting rate is proportional to the partial pressure over a

wide range. The linear broken line in the figure shows the relation observed for tritium enclosed in a glass container with use of a specially designed proportional counter [10], where the sensitivity was 5.26×10^{-2} cps/Pa.

This demonstrates clearly the advantage of the use of Au/Be window. The background



counting rate in the present system was found to be below 0.3 cps. Under the present experimental conditions, the lower detection limit is estimated to be about 10^{-2} Pa.

Above 15 Pa for 0.39% and 130 Pa for 3.4% mixture, on the other hand, downward deviations from the linear relation were observed. Although the deviation began at different partial pressures, it took place at the same total pressure of 2.0 kPa.

To evaluate in detail the total pressure dependence of the counting rate, correlations between the specific counting rate and the total pressure were examined for the 0.39% mixture. As seen in Fig. 7, the specific counting rate was kept at an almost constant level of 70.8 cps/Pa below 2.0 kPa. Above this pressure, the specific counting rate decreased gradually with the total pressure.

Such behavior could be interpreted in terms of the self-absorption of β -rays in gas phase; i.e., the kinetic energy of β -particles is partially consumed by collisions with molecules in gas phase before reaching at the window.

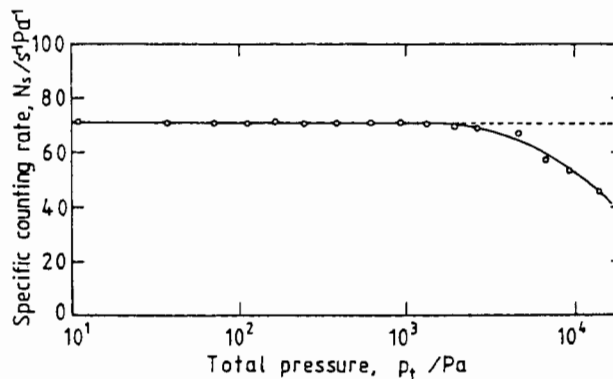


Fig. 7: Total pressure dependence of the sensitivity

The energy loss should increase with the total pressure, resulting in an increase in the fraction of low energy β -particles reaching the window. This gives a larger fraction of low energy bremsstrahlung X-rays in comparison with the intrinsic β -rays of tritium. The low energy photons of less than about 3 keV are expected to be absorbed in the Au/Be disc, because the absorption coefficient is greater for low energy photons than for high energy ones. Consequently, the total counting rate decreases with increasing total pressure. The effect can be approximated with a simple exponential function as

$$C = 70.8 \exp(-3.12 \times 10^{-5} P_t),$$

where C is the counting rate and P_t represents the total pressure in Pa unit. It could be possible to determine the tritium pressure upto 10^5 Pa by applying this relation.

On account of the low background counting rate and the above approximation, it is expected that the present device is valid to in-situ and real time measurements of the partial pressure of tritium in the wide pressure range from 10^{-2} to 10^5 Pa. Because the absorption coefficients of β -particles for tritium and helium are approximately the same, the equation above should also be applicable to the mixture of these gases.

3.3. Fractionation

3.3.1. Signals from Flow Simulator

Figure 8 shows an example of a simulated bremsstrahlung X-ray signal for a tritium flow, which was obtained by the reciprocal motion of the ^{57}Co source at a constant

velocity of 0.8 cm/sec. The signal accumulation time of the scaler was set to one second. In this peak profile, the average value of the counting rate up to 20 s was about 2 cps, whereas the peak gave the total count of 393. Similar peak profiles were observed for differ-

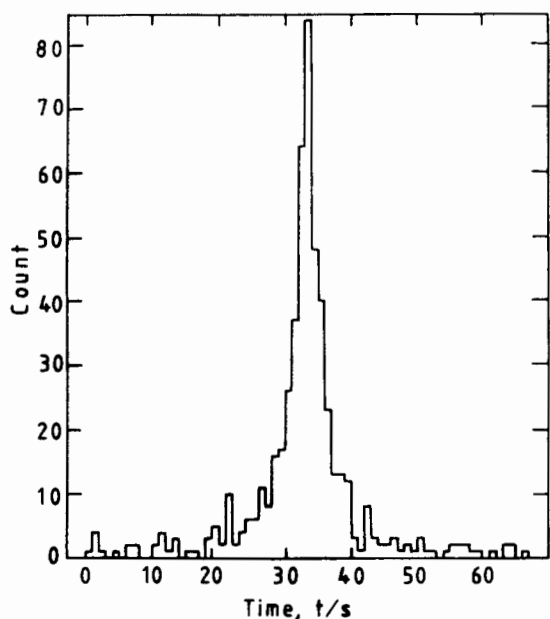


Fig. 8: An artificial signal from tritium flow simulator

ent motion velocities of the source, although the total count differed from each other.

Figure 9 shows the correlation between the total count and the accumulation time in a range from 0.5 to 2 s at various motion velocities of the source. As seen in the figure, the total count was almost constant irrespective of the varying accumulation time, whereas it decreased with increasing motion velocity. The motion speed was varied in a range from 0.8 to 6 cm/s, corresponding to the flow rate of tritium gas in a range from 7.2 to 54 cm³/min, assuming that the tritium gas flowed in a tube with 1/4 inch in inner diameter.

The product of the total count and the corresponding motion velocity, however, showed an almost constant value of 305 ± 56 count.cm/s. The relatively large standard deviation of the product appears to be due to the low total count in each peak. The average value of the products corresponds to a pulsed flow of tritium amounting to 20-30 μ Ci in a 1/4 inch tube. On account of this fact, the ⁵⁷Co source could simulate well a tritium flow. Namely, this device should be applicable

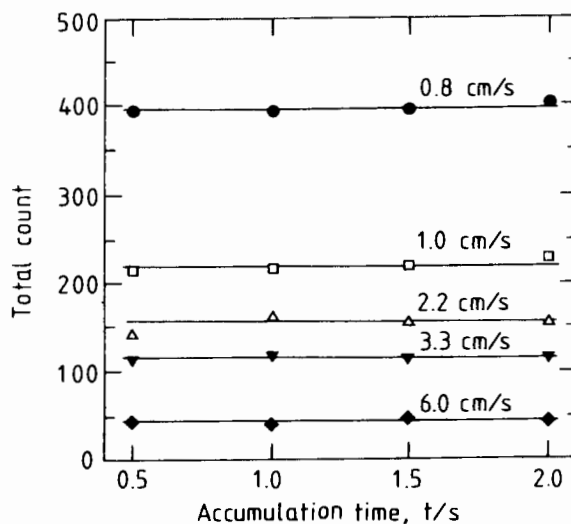


Fig. 9: Changes in the total count with accumulation time and moving velocity of ⁵⁷Co

to examine the response of a bremsstrahlung counter for changing over the tritium flow channel, because the energy range of X-rays from ⁵⁷Co source is fairly close to that of the bremsstrahlung X-rays stimulated by tritium β -rays.

3.3.2. Response of the Changeover Valves

Figure 10 shows an example of the valve action by reciprocal motion of the ⁵⁷Co source with 1 cm/s, where the accumulation time was set to one second. The dotted line indicated as LL was a discrimination level of the background noise, which was set to 7 counts in this measurement. The opening and closing action of the two valves was observed as shown by the upper inset in the figure, which indicates that two valves worked alternatively quite well. Similar valve action was observed for different accumulation times and moving velocities.

Figure 11 shows an example of the effect of the accumulation time on the valve action. The accumulation time was varied in the range from 0.5 to 2.0 s, whereas the moving velocity of the radioactive source and the LL level were fixed at 2.2 cm/s and 5 counts, respectively. The total count of each peak was almost the same irrespective to the accumulation time as shown in Fig. 11. On the other hand, the peak became wider with increasing

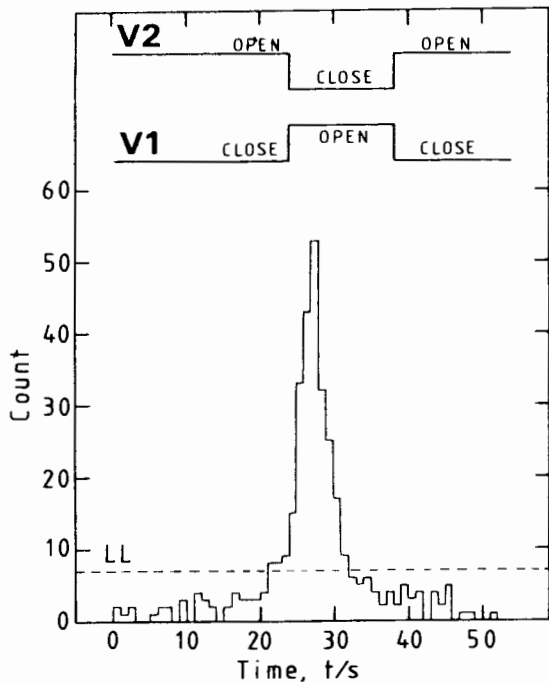


Fig. 10: An example of valve response to simulated tritium flow

accumulation time. On account of the difference in the accumulation time, this tendency is reasonable.

In addition, it is evident that such a feature will not impede the changeover of tritium flow channel, because the radioactivity of tritium corresponding to the simulated peaks should be very low as mentioned above and hence the flow of tritium of substantial amount will merely enlarge the peak height and width. Namely, the variation of peak width owing to different accumulation time should be negligibly small. Therefore, the valve action observed above is acceptable for the changeover of the tritium flow channel.

It should be mentioned here, however, that the valve action happened to be lagged behind the point of intersection of the counting curve with the LL level. This appears mainly due to the setting of a rather large time constant of a comparator. Although this delayed valve action should be improved by a smaller time constant, hunting around the base line should induce undesirable valve actions. Similar erroneous actions are expected by setting inadequately low LL level. On the other hand, although a larger time constant as well as a higher LL level should improve the hunting, non-negligible amount of tritium will

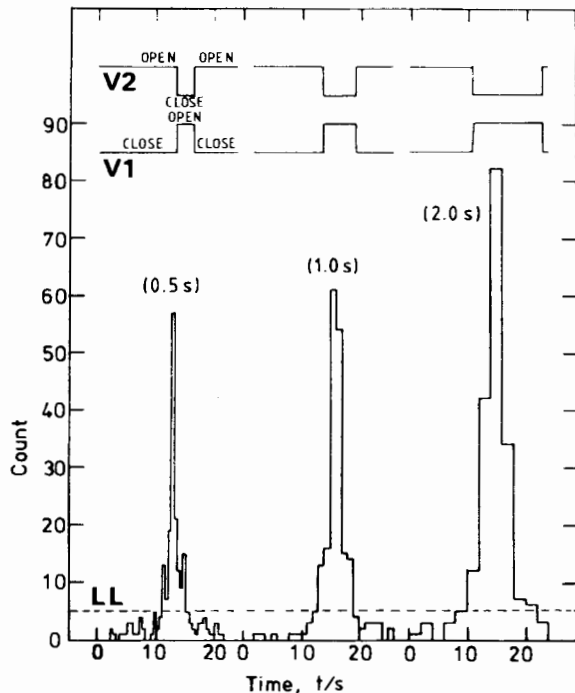


Fig. 11: Valve response to varying accumulation time

pass through the valve owing to the lagging of valve response. Therefore, an adequate time constant and LL level should be set to avoid undesirable actions by the valve by lagging and hunting in order to switch adequately the flow channel of tritium.

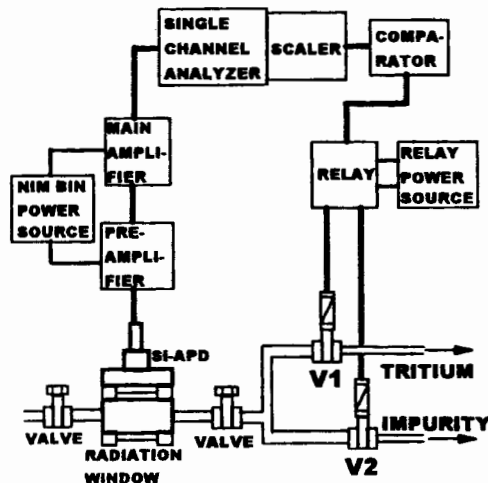


Fig. 12: Device for changing over the flow channel of tritium

Figure 12 illustrates the schematic diagram of a simple device to change over a tritium flow, designed on the basis of the above observations. In the present design, the role of the changeover device was restricted to discriminate tritium efflux and tritium free one in tritium processing such as hydrogen isotope

separation by gas chromatography. Accordingly, only two valves are equipped with the changeover system, and the bremsstrahlung counting device was attached to the upstream side of the two valves. The most favorable distance from the valves to the bremsstrahlung counting device must be determined by taking account of flow rate, accumulation time and the time constant of a comparator. The potential of the system will be evaluated by using tritium gas in the near future.

5. Conclusions

An advanced gas chromatography having the self-developing property was developed by use of active materials such as Pd-Pt alloys. It was found that a Pd-Pt (8 at%) alloy has very good properties for this purpose. The material allowed operation near room temperature without use of any replacement gas. It was observed that supporting materials play a very important role. Hydrophobic supporting materials significantly interfere with the self-developing chromatographic separation of hydrogen isotopes through trapping of hydrogen isotopes as $Q_2O(a)$ and/or $OQ(a)$.

To fractionate tritium species from the effluent gas of a chromatographic separation system, a bremsstrahlung X-ray counter was developed. The counter is provided with a Be-window coated with an Au evaporated film. A good linear relationship between the counting rate and the tritium partial pressure was obtained. The sensitivity of the counter was found to be high, i.e. 70.8 cps/Pa, and the wide working range was $10^{-2} \sim 10^5$ Pa. In addition, it was free from contamination effect and impurity gases, and showed fast response.

The fractionation of tritium effluents from the self-developed chromatography were simulated with a tritium flow simulator using ^{57}Co and the bremsstrahlung counting device. It was demonstrated that the fractionation of tritium effluent can be done fairly easily by the changeover valves controlled by the signals from the X-ray counter. One important advantage of this coupling lies in the fact that there is no need of high or cold temperatures.

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