Comparison of chromatographic methods for hydrogen isotope separation by Pd beds

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Abstract

Comparison among three chromatographic separation methods, i.e. hydrogen-displacement chromatography, self-displacement chromatography and frontal chromatography, is made in an experimental way using several gas mixtures of hydrogen and deuterium. There is small difference in the height equivalent to a theoretical plate (HETP) based on the plate theory among the three chromatographic techniques. The HETP value for the self-displacement chromatography is 3.9 cm, and that for the frontal or H_2-displacement chromatography is 3.0 cm at the same flow-rate. The self-displacement chromatography is more useful for the separation of a small amount of deuterium or tritium from other hydrogen isotopes under a moderate recovery ratio. Since the frontal chromatography uses no other gas than the sample, it is more convenient for the separation of deuterium from natural hydrogen even though a lower recovery ratio. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Separation of hydrogen isotopes as a fuel of a nuclear fusion reactor or for chemical or medical use as a tracer has been of great concern for years. Cryogenic distillation is considered the most promising way in a large scale, e.g. the isotope separation system of International Thermonuclear Experimental Reactor [1]. Thermal diffusion column [2] is also considered an alternative in a small scale. However, these two methods have disadvantages, e.g. they have to be operated under tough conditions of very low or very high temperature. As an alternative for the hydrogen isotope separation, there is a way to use hydrogen-absorbing metals or alloys which have a comparatively large isotope separation factor. The easiest method to separate hydrogen isotopes using a hydrogen-absorbing metal or alloy is a chromatographic way. Some methods investigated previously are: (1) the hydrogen-displacement chromatography [3–5]; (2) the self-displacement chromatography [6,7]; and (3) the frontal chromatography [8,9]. Although all of them are a batch process, good separation performance is expected by use of laboratory-scale apparatuses. However, any comparison among the methods has not been made from the viewpoint of which chromatographic technique is the

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most effective for a given gas sample. The elution chromatography was not investigated here because of poor separation performance [10].

In order to make clear the difference in characteristics of the three chromatographic separation techniques for hydrogen–deuterium mixtures, we here compare the hydrogen-displacement, self-displacement and frontal chromatographies in an experimental way in terms of the deuterium recovery ratio, the maximum deuterium atomic molar fraction and the height equivalent to a theoretical plate (HETP).

2. Experimental

2.1. Apparatus

Fig. 1 shows a schematic diagram of the experimental apparatus composing of four columns. Each column of 3.0 mm in inner diameter and 70.0 cm in length made of stainless steel is packed with Pd particles with an average diameter of 350 μm, and the packed amount per column is 10.00 g. The maximum hydrogen absorption capacity per column

is 720 ml (NTP)[1]. The columns are supplied with any of the following four hydrogen–deuterium gas mixtures (atomic molar fraction); (1) H_2 (0.451)–D_2 (0.549), (2) H_2 (0.950)–D_2 (0.050), (3) H_2 (0.990)–D_2 (0.00996), (4) natural hydrogen produced by water–vapor reforming of methanol, which includes the deuterium atomic molar fraction of 0.00015. Isotopic equilibrium between hydrogen and deuterium has not been reached in the feed gas mixtures except for the natural hydrogen. However, it was found that the outlet gas after passing through the Pd column reaches isotopic equilibrium completely. This result is consistent with Trentin et al. [11]. In the present experiment, therefore, the gas concentration in the product flow as well as in the feed flow are correlated in terms of the deuterium atomic molar fraction, which is denoted by $x_{D,out}$ or $x_{D,in}$.

The gas flow-rate of a hydrogen–deuterium mixture from the gas cylinder (1) is regulated by the mass-flow controller (3), and the mixture is introduced through a five-way valve into one of the four columns (C1–C4) from the bottom. When a single

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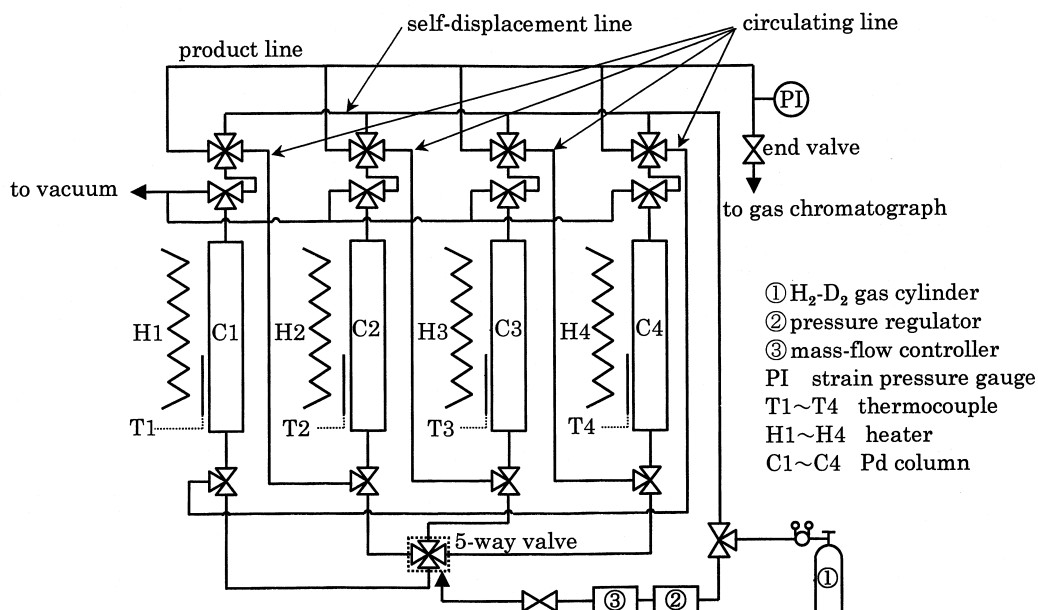[1] NTP = Normal temperature and pressure.

Fig. 1. A schematic diagram of the experimental apparatus.

column is used, an outlet gas mixture through a three-way valve and a four-way valve at the top end is withdrawn from a product line, and its deuterium concentration is detected by the gas chromatography. When plural columns are used, the outlet gas withdrawn from a column is introduced into another column through a circulating or self-displacement line. The absorption–desorption procedures are repeated until necessary operation times.

2.2. Procedures

In the self-displacement chromatography, one needs to prepare at least two Pd columns that have the same absorption capacity. At first, all of the columns to be used are sufficiently degassed at 493 K under Ar flow for about 1 h and then under vacuum for about 1 h, and they are cooled down to 303 K under vacuum. A proper volume of a hydrogen–deuterium mixture is introduced into one of the Pd columns with the end valve kept closed.

Since hydrogen is preferentially absorbed in Pd particles, a hydrogen-rich band is formed near the bed inlet, and a deuterium-rich band is downstream. After the Pd column has been filled with the gas mixture, hydrogen and deuterium in the solid-phase are desorbed by heating the column up to 493 K, and the three-way and four-way valves at the top of the column are connected to the self-displacement line. So, the desorbed gas is introduced into another Pd column maintained at 303 K through the mass-flow controller (3). Then the deuterium-rich band is eluted faster in the Pd bed, and the hydrogen-rich band is later. The maximum deuterium concentration is observed near the front of the deuterium-rich band. The two bands proceed downstream with different velocities. The procedures of the gas transport are repeated until necessary concentration of deuterium has been attained. There is no need to use carrier gas in the self-displacement chromatography.

In the H_2-displacement chromatography, a proper volume of a hydrogen–deuterium mixture is introduced into a single fresh Pd bed maintained at 303 K with the end valve closed in a similar way to the self-displacement chromatography. Then the mixture is displaced by natural hydrogen supplied from another gas cylinder under a constant flow-rate at 303 K. The column outlet is connected to the product

line. With an increase in displacement volume, the deuterium-rich band is eluted in the downstream direction of the Pd bed. When the front of the deuterium-rich band has arrived at the top end of the column, the pressure gauge at the end depicted by P1 in Fig. 1 starts rising, and at the same time the end valve is opened. There is possibility in that gas mixtures with the diluted deuterium concentration are generated in the H_2-displacement chromatography.

In the frontal chromatography, several Pd columns are degassed at 493 K under vacuum and Ar flow for 2 h before the sample gas supply. Then they are cooled down to 303 K, and one of the columns continues to be supplied with a constant concentration of a hydrogen–deuterium mixture. When the pressure starts rising, the outlet gas mixture is sent to the next column through the circulating line. In the frontal chromatography only the deuterium-rich band is formed in the Pd bed because the feed gas acts also as a carrier. The rest is a region where the concentration is near the feed gas composition. A specified volume of the deuterium-rich product is withdrawn through the end valve when the pressure difference between the inlet and the outlet becomes sufficiently small.

2.3. Maximum atomic molar fraction, recovery ratio and HETP

Three values on deuterium separation are used for comparison among the three chromatographic methods. The first one is the maximum deuterium atomic molar fraction in the product gas, $(x_{D,out})_{max}$. The maximum enrichment ratio $E_{D,max}$ defined as $(x_{D,out})_{max}/x_{D,in}$ is also used supplementary.

The next one is the deuterium recovery ratio, R_D, defined as follows:

$$R_D = \frac{\text{the deuterium volume withdrawn as the product}}{\text{the deuterium volume fed}}$$

(1)

The recovery ratio is calculated under the condition where the product is withdrawn as follows:

$$\frac{x_{D,out} - x_{D,in}}{(x_{D,out})_{max}} > 0.05$$

(2)

The value of HETP is determined by fitting the analytical deuterium concentration at the bed outlet on the basis of the plate theory [9] to the experimental deuterium concentration. The analytical profile of the deuterium concentration as a function of the plate number J is expressed as follows:

$$\frac{x_{D,J+1}}{\alpha_{H-D} - (\alpha_{H-D} - 1)x_{D,J+1}} = x_{D,J}$$

$$- \frac{(\alpha_{H-D,in} - 1)(1 - x_{D,in})x_{D,in}}{\alpha_{H-D,in} - (\alpha_{H-D,in} - 1)x_{D,in}} \qquad (3)$$

Here, α_{H-D} is the isotope separation factor depending on $x_{D,J}$ defined as follows:

$$\alpha_{H-D} = \frac{x_{D,J}(1 - y_{D,J})}{(1 - x_{D,J})y_{D,J}} \qquad (4)$$

$y_{D,J}$ is a deuterium atomic molar fraction in the solid-phase at the plate number J and $\alpha_{H-D,in}$ is the isotope separation factor at $x_D = x_{D,in}$. The value of α_{H-D} was given by the previous research as follows [12]:

$$\alpha_{H-D} = \frac{1 - y_{D,J} + 4y_{D,J}\alpha_{H_2-HD}/K_{H-D}}{1 - y_{D,J} + y_{D,J}\alpha_{H_2-HD}} \cdot \alpha_{H_2-HD} \qquad (5)$$

Here, K_{H-D} is the equilibrium constant of the reaction $H_2 + D_2 = 2HD$, and α_{H2-HD} is the isotope separation factor under the dilute deuterium concentration and is a function of temperature as follows [12]:

$$\alpha_{H_2-HD} = \exp(-0.121 + 228/T) \qquad (6)$$

3. Results and discussion

3.1. Self-displacement chromatography

Fig. 2 shows the results of the variations of the outlet deuterium concentration with time after the operation of the self-displacement chromatography. The time 0 on the horizontal axis is taken to be the breakthrough time of the total concentration of hydrogen and deuterium. Since the total outlet concentration normalized by the inlet one was almost unity after the breakthrough under the present experimental condition, the hydrogen atomic molar fraction at the outlet becomes $1 - x_{D,out}$. The number
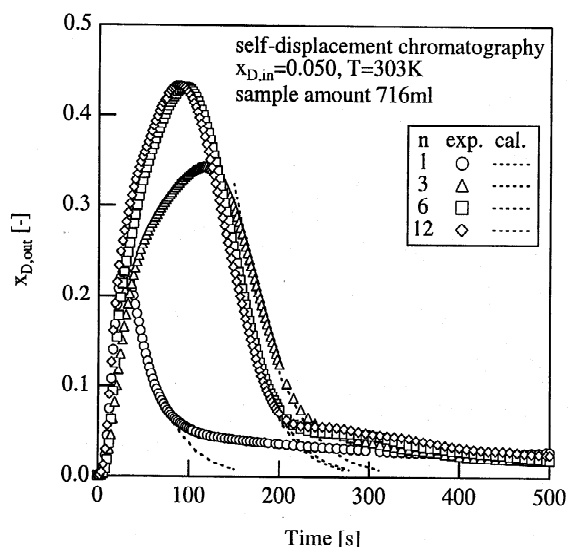

Fig. 2. Self-displacement chromatography of a hydrogen–deuterium gas mixture using a multi-column Pd bed system.

of the passed columns denoted by n in the figure varies from 1 to 12. The dotted lines are calculated using Eqs. (3)–(6). Fig. 3 shows variations of the gas flow-rate and the outlet pressure with time at $n = 3$. The gas flow-rate, w, is regulated to 28.7 ml (NTP)/min by the mass-flow controller as much as possible. The outlet pressure varies from 0.7 kg/cm^2 to atmospheric pressure. However, the gas flow-rate dropped steeply when almost all gas has been
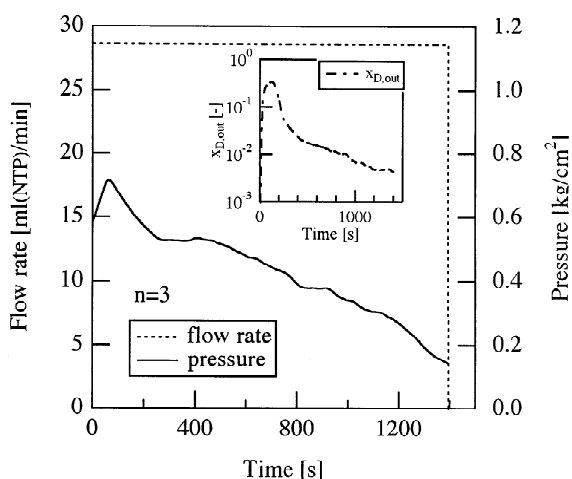

Fig. 3. Variations of the gas flow-rate and the outlet pressure with time for the self-displacement chromatography.

desorbed and the outlet pressure has become near atmospheric pressure, which corresponds to after around 1400 s. Table 1 summarizes the values of the maximum deuterium atomic molar fraction, $(x_{D,out})_{max}$, the deuterium recovery ratio, R_D, and HETP for the three chromatographic methods.

It is found that high enrichment has been attained when $n > 3$ as seen in Fig. 2. The concentration profile seems to approach to an asymptotic one when $n > 6$. Then the asymptotic value of $(x_{D,out})_{max}$ is 0.43, and that of R_D 0.73. The rest of deuterium is not diluted in a large amount because of no carrier gas. The HETP value was about 3.9 cm independent of n. Consequently, the self-displacement chromatography will be more useful for the separation of a small volume of deuterium from other hydrogen isotopes because of the moderate recovery ratio and the high enrichment. This may be true for tritium separation.

3.2. Hydrogen-displacement chromatography

Fig. 4 shows the results of the hydrogen-displacement chromatography using a single Pd column under different inlet gas compositions. The gas flow-rate is strictly regulated to constant throughout the operation of the H_2-displacement chromatography at 303 K (and also that of the frontal chromatography). The highest enrichment and highest recovery ratio among the three chromatographic techniques can be also attained judging from the values in Table 1. Thus, the H_2-displacement chromatography is also applicable to concentration of the diluted deuterium or tritium in a similar way to the self-displacement chromatography. The enrichment ratio for the H_2-displacement chromatography ($E_{D,max} = 13.0$) is still greater than that for the self-displacement chromatography ($E_{D,max} = 4.54$) under the same feed concentration at $x_{D,in} = 0.05$. This is because the flow-

Table 1
Values of $(x_{D,out})_{max}$, R_D and HETP of various chromatographic methods

	Total column number n	Flow rate, w [ml(NTP)/min]	Sample amount [ml(NTP)]	Feed D concentration, $X_{D,in}$ [−]	Maximum D concentration in product, $(x_{D,out})_{max}$ (−)	Recovery ratio, R_D (−)	HETP (cm)
Self-displacement	1	28.7	716	0.050	0.227	0.140	3.7
chromatography	3	28.7	716	0.050	0.344	0.692	4.3
(303 K absorption–	6	28.7	716	0.050	0.431	0.720	3.8
493 K desorption)	12	28.7	716	0.050	0.433	0.732	3.9
H_2-displacement	1	28.7	392	0.00996	0.134	0.825	3.4
chromatography	1	28.7	392	0.050	0.652	0.837	3.0
(303 K absorption– 303 K displacement)	1	28.7	392	0.549	1.0	≅1.0	3.0
Frontal	1	57.8	–	0.00015	0.00464	–	2.0
chromatography	1	57.8	–	0.00996	0.0716	0.314	3.0
(303 K absorption)	1	57.8	–	0.050	0.683	0.417	2.0
	1	57.8	–	0.549	0.992	0.722	[a]
	2	57.8	–	0.00996	0.213	0.419	3.0
	3	57.8	–	0.00996	0.322	0.449	2.8
	7	57.8	–	0.00996	0.425	0.427	[b]
	11	57.8	–	0.00996	0.531	0.454	[b]
	16	57.8	–	0.00996	0.728	0.458	[b]
	1	28.7	–	0.00015	0.0046	0.677	1.4
	3	28.7	–	0.00015	0.0126	0.563	1.4
	12	28.7	–	0.00015	0.0218	0.509	2.2
	16	28.7	–	0.00015	0.0508	0.639	2.0

[a] The HETP value could not be determined by the plate theory.
[b] The HETP values could not be determined exactly because of the destortion of the effluent curves.
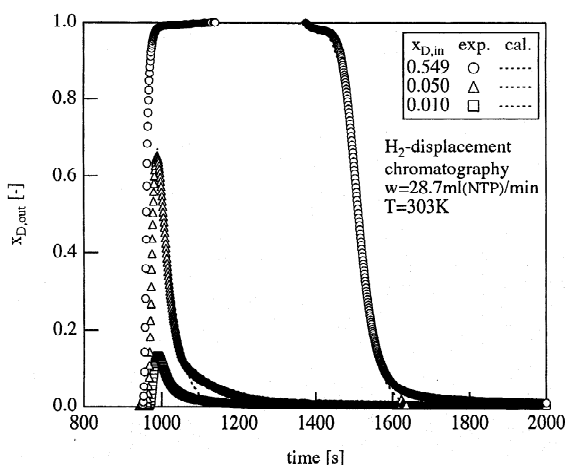
Fig. 4. Hydrogen-displacement chromatography of hydrogen–deuterium gas mixtures using a single Pd column.

Fig. 5. Frontal chromatography of hydrogen–deuterium gas mixtures using a single Pd column.

rate and the pressure in the bed is strictly controlled to constant throughout the operation. However, there is possibility in that a large amount of diluted deuterium is generated by the use of the hydrogen displacement gas. The HETP value was about 3 cm, and the value is a little smaller than that of the self-displacement chromatography. The cause for the difference is considered that less mixing occurred because of the conditions of the more stable pressure, temperature and flow in the H_2-displacement chromatography.

3.3. Frontal chromatography

Fig. 5 shows examples of the results of the frontal chromatography using a single Pd column under different inlet gas compositions. Very high enrichment similar to the H_2-displacement chromatography has been attained for any chromatogram regardless of the difference in inlet deuterium concentration. Judging from the values of the frontal chromatography in Table 1, it is considered that this method provides a way of very high enrichment using a single Pd column. It is a very simple operation, and there is no need to prepare any carrier except for the sample gas. One defect is a lower recovery ratio. The HETP value varied from 2.0 to 3.0 for different inlet concentration. The smallest HETP value was obtained only under the condition of the natural hydrogen. We could not define the reason for that. In addition, the HETP value at $x_{D,in} = 0.549$ was not
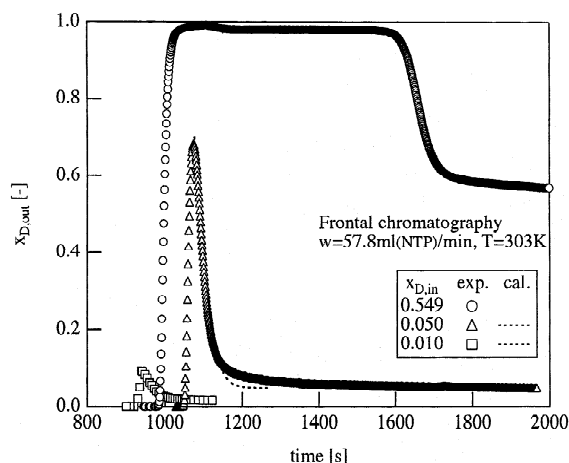
determined because a steady-state solution for the high $x_{D,in}$ could not be correlated by the plate theory.

Fig. 6 shows the results of the frontal chromatography using several connected Pd columns. The $(x_{D,out})_{max}$ values increase with an increase in n, while the slope is unchanged.

Fig. 7 shows $E_{D,max}$ values as a function of n for $x_{D,in} = 0.00997$ and 0.00015 (natural hydrogen). Even when $x_{D,in}$ is small, $x_{D,out}$ can become high. This is because $E_{D,max}$ increases with n unless $(x_{D,out})_{max}$ becomes unity. The $E_{D,max}$ value becomes over 400 after 16 repetitions. Thus the frontal
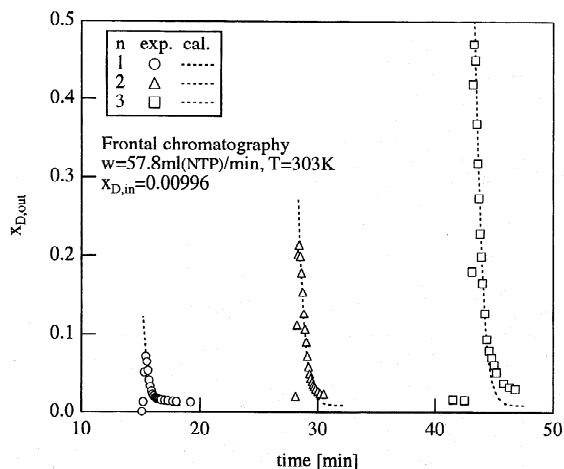

Fig. 6. Variations of the outlet deuterium concentration in frontal chromatography with the number of passed columns.
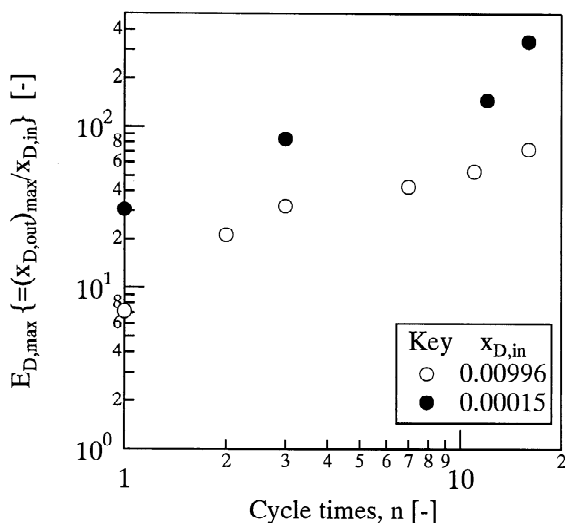
Fig. 7. The maximum enrichment ratio as a function of the number of cycle times.

chromatography is the most useful for the deuterium recovery from natural hydrogen. Even if the recovery ratio in the frontal chromatography is lower than that in the H_2-displacement chromatography, depleted natural hydrogen can be used as 'normal hydrogen' for usual chemical processes.

Some continuous techniques for chromatographic separation have been developed recently [13–16]. Although they perform complicated operation such as changing flow directions or use two or more columns packed with the same or different materials, basic scheme of separation occurring in columns seems to be similar to the present self-displacement or frontal chromatography that uses no carrier gas. Hydrogen isotopes themselves flow in columns without carrier gas in the continuous chromatography as well as the two chromatographic techniques. Judging from the comparison of the present results among the three chromatographic techniques, higher separation performance will be established by the stable conditions of the gas flow-rate, pressure and temperature.

4. Conclusions

Experimental comparison among three chromato-

graphic methods has been made using different deuterium concentration gases. The displacement chromatography was found to be more useful for the separation of a small amount of deuterium (or tritium) from hydrogen isotope gas mixtures. Especially, the self-displacement chromatography has some advantages of no carrier gas, a high enrichment ratio and a moderate recovery ratio. The present experiment showed that six times the absorption–desorption cycling concentrate the mixture of $x_{D,in} = 0.05$ to $(x_{D,out})_{max} = 0.43$. The H_2-displacement chromatography gave the highest enrichment ratio and recovery ratio of deuterium among the three chromatographies. The frontal chromatography was found to be more convenient for the recovery of deuterium from natural hydrogen. The deuterium recovery ratio from the natural hydrogen or the hydrogen–deuterium mixture of $x_{D,in} = 0.00996$ was about 60 or 45%. The maximum enrichment ratio was over 100.

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