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Title: Separation of dissolved Kr from a water sample by means of a hollow fiber  
membrane

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## Abstract

We investigated extraction of the krypton (Kr) radioisotope  $^{85}\text{Kr}$  from groundwater having an ultra-low concentration with a Kr-extraction system using an external inflow type hollow fiber membrane. Our aim was to develop a system able to effectively extract Kr isotopes from a large volume of groundwater ( $10^4$  L) in field studies for measurement of  $^{85}\text{Kr}$  radioactivity. Before testing our Kr-extraction system in the field, we determined experimentally the conditions necessary for effective extraction of Kr isotopes from groundwater. We investigated the efficiency of Kr extraction from water by extracting trace amounts of Kr in the laboratory. With our system, we were able to extract 99% of Kr and  $\text{O}_2$  dissolved in water at water temperatures ranging from 11 to 29 °C and with a flow rate of less than 24 L/min, confirming that the separation efficiency of the system was sufficient for extraction of Kr isotopes from groundwater. We then used our method to extract  $^{85}\text{Kr}$  from groundwater at sites at Kyoto University in Osaka and on the Kumamoto Plain in central Kyushu, Japan. We showed that this technique for extracting  $^{85}\text{Kr}$  from the groundwater can be an effective tool for investigating the residence time of young groundwater.

## 1. Introduction

Ultra-low concentrations of the krypton (Kr) isotopes,  $^{78}\text{Kr}$ ,  $^{80}\text{Kr}$ ,  $^{82}\text{Kr}$ ,  $^{83}\text{Kr}$ ,  $^{84}\text{Kr}$ ,  $^{86}\text{Kr}$ ,  $^{85}\text{Kr}$ , and  $^{81}\text{Kr}$  are present in natural waters.  $^{85}\text{Kr}$  and  $^{81}\text{Kr}$  are radiogenic nuclides with very different half-lives;  $^{81}\text{Kr}$  has a half-life of  $2 \times 10^5$  years and is of cosmogenic origin, whereas  $^{85}\text{Kr}$ , with a half-life of 10 years, is dominantly a product of anthropogenic fission reactions. Moreover, as Kr is a rare gas, it is unnecessary to consider chemical reactions between Kr and other elements in groundwater. Therefore,

$^{81}\text{Kr}$  and  $^{85}\text{Kr}$  in groundwater should be an excellent tool for estimating groundwater residence time. In particular,  $^{85}\text{Kr}$  is expected to be useful for dating relatively young groundwater, with a residence time of several tens of years (Bauer et al., 2001; Cook and Solomon, 1997; Corcho et al., 2005, 2007; Oeschger et al., 1974; Rozanski and Florkowski, 1979; Sidle and Fischer, 2003, Sidle, 2006; Smethie et al., 1992), whereas  $^{81}\text{Kr}$  is expected to be applicable to the dating of water deep underground with a residence time on the order of  $10^4$ – $10^6$  years (Collon, 2004; Collon et al., 1997, 2000; Lehmann et al., 1991, 2003; Tolstikhin and Gröning, 2003).

Kr isotopes in natural waters originate from the atmosphere, where the concentration of Kr is 1.14 ppm (Aoki and Makide, 2005). The concentration of Kr in water at equilibrium with the atmosphere at 25 °C (standard temperature and pressure; STP) is  $6 \times 10^{-8}$  cm<sup>3</sup>/L. As the  $^{85}\text{Kr}$  concentration in the atmosphere is 1.5 Bq/m<sup>3</sup> and the  $^{81}\text{Kr}/\text{Kr}$  (atoms) ratio is on the order of  $5 \times 10^{-13}$ , the concentrations of  $^{85}\text{Kr}$  and  $^{81}\text{Kr}$  in water at equilibrium with the atmosphere are 0.1 Bq STP/m<sup>3</sup> and  $7 \times 10^{-8}$  cm<sup>3</sup> STP/g, respectively. Extraction techniques commonly used to extract  $^{85}\text{Kr}$  from groundwater include the following: (1) degassing by heating the water sample to 95 °C (Oeschger et al., 1974; Loosli, 1983, Loosli et al., 1987), (2) extraction of gases from water in the field by means of a container under lowered pressure (Salvarmoser, 1982), (3) a gas extraction method combining (1) and (2) (Schröder, 1975; Rozanski and Florkowski, 1979), (4) extraction by flushing the water sample with helium (Held et al., 1992; Sidle, 2003), and (5) degassing several liters of groundwater in the field and then compressing the extracted gas in an evacuated cylinder (Loosli et al., 1983, 1987).  $^{81}\text{Kr}$  can be measured by accelerator mass spectrometry (AMS; Lehman et al., 1991, 2003; Collon, 2004), and  $^{85}\text{Kr}$  can be measured with a liquid scintillation counter (LSC; Smethie et al.,

1986, 1992) or a low-level proportional counter (Smethie and Mathieu, 1986; Smethie et al. 1992; Held et al., 1992, Corcho et al., 2005, 2007). For measurement by LSC, the amount of  $^{85}\text{Kr}$  needs to be at least about 50 mBq. Because the concentrations of  $^{85}\text{Kr}$  and  $^{81}\text{Kr}$  in groundwater are ultra-low, they must be extracted from a large volume of sampled water (on the order of  $10^4$  L) to be measured by AMS or LSC. Therefore, it is difficult to collect enough water in the field to obtain sufficient amounts of  $^{85}\text{Kr}$  and  $^{81}\text{Kr}$  for use with the normal extraction techniques listed above.

Recently, Probst et al. (2007) developed an analytical method using a hollow fiber membrane to extract radioactive  $^{85}\text{Kr}$  from groundwater, with the aim of efficiently collecting  $^{85}\text{Kr}$  from a large volume of groundwater during field work. Probst et al. (2007) initially tested the extraction efficiency of their system on dissolved oxygen (DO) in Chicago tap water. There are two types of hollow fiber membrane: an internal pressure type and an external pressure type. Probst (2007) described a system, later applied by Probst et al. (2007), that is based on the internal pressure type of membrane to extract gas from water; in this system, water flows through the inner surface of the membrane when a vacuum is applied to its outer surface. With their system, Probst et al. (2007) achieved an extraction efficiency for DO from tap water of 67% at a flow rate of 4 L/min and of 88% at a flow rate of 5 L/min. The extraction efficiency for Kr gas by this system, calculated by Probst et al. (2007) as a function of Kr solubility, is expected to be 65%. This extraction method using a hollow fiber membrane should be suitable for use in the field, but a higher extraction efficiency than that achieved by Probst et al. (2007) would be preferable. Therefore, to increase the extraction efficiency for Kr from groundwater, we decided to use an external pressure type of hollow fiber membrane, in which the fluid (the groundwater) is in contact with the outside of the fibers, and a

vacuum is applied inside the hollow fibers. In an internal pressure type of membrane, the water flow on the inner surface of the fibers is laminar, producing a boundary layer between the surface of the hollow fiber membrane and the water. As a result, the gas permeation rate in the water across the hollow fiber membrane is slow. In the external pressure type, the water flow on the outer surface of the membrane is turbulent, so a boundary layer is usually not produced, thus improving the extraction efficiency by increasing the gas permeation rate. As the hollow fiber membrane of the external pressure type shows excellent dissolved gas extraction performance, it may be useful for effectively extracting Kr from a large volume of groundwater.

In this study, we developed a system for effectively extracting  $^{85}\text{Kr}$  from groundwater by using a hollow fiber membrane of the external pressure type and tested the system using a large volume of sample water ( $10^4$  L). In the laboratory, we experimentally determined the conditions necessary for efficient extraction of Kr isotopes from a large volume of groundwater. Subsequently, we tested the applicability of our system to the determination of groundwater residence time in the field.

## **2. Design and performance of our Kr extraction system**

Kr isotopes in sample waters were extracted using a system (Fig. 1) consisting of a water pump, a pre-filter with a pore size of  $5\ \mu\text{m}$  (FH-A-5 CW-5R, Nihon Filter Co. Ltd.), a hollow fiber membrane module ( $180\ \text{mm}\ \phi \times 675\ \text{mm}$  long, SEPAREL EF-040P, Dainippon Ink and Chemicals Co. Ltd.), a compressor (DOP-80SP), a dry pump (DOP-40D), and a gas cylinder. All tubing of this equipment was composed of SUS metal. The hollow fiber membrane was composed of poly-4-methylpentene, a polyolefin resin, and had an outside diameter of  $215 \pm 20\ \mu\text{m}$ , and an inside diameter of

135 ± 20 μm. The surface area of the membrane was 40 m<sup>2</sup>. Water flowed through the outer surface of the membrane when a vacuum was applied to the inner surface of the fibers. Table 1 lists the model numbers of the components of our Kr-extraction system. In this system, the sample water was first pumped through a 5-μm pore size membrane pre-filter and then through the hollow fiber membrane module to which a vacuum was applied (Fig. 1). The dissolved gas was extracted from the sample water through the inner surface membrane under vacuum, and the remaining water drained out. The vacuum was produced with a dry pump. The extracted gas was compressed by the compressor with an attainable pressure of 0.5 MPa (about 5 kg/cm<sup>2</sup>) and a dry pump (1.2 × 10<sup>3</sup> Pa, about 9 torr) and collected in a gas cylinder. The sample water volume was measured by an integrated flow meter (Fig. 1). This system can extract DO from water with a DO concentration of 1 μg/L, 0.025 mg/L, and 0.5 mg/L at water flow rates of less than 20 L/min, 2000 L/h (33 L/min), and 5000 L/h (83 L/min), respectively (brochure published by Dainihon Inc. Co. Ltd.), and at water temperatures ranging from 5 to 50 °C. According to the manufacturer (ULVAC Kiko, Inc., pers. comm.), air leaks into the system via the vacuum pumps at a rate of 100 ml/min or less. We estimated that the amount of <sup>85</sup>Kr contamination from the surrounding air would range from 4% to 15%. This possible source of <sup>85</sup>Kr contamination is discussed in greater detail later.

Using our system with (1) a hollow fiber membrane of the external pressure type (the inner surface of the membrane under vacuum), (2) a hollow fiber membrane composed of poly-4-methylpentene, and (3) attainable pressures of the pressure compressor and dry pump of 0.5 M Pa and 1.2 × 10<sup>3</sup> Pa, respectively, we tried to achieve a high collection efficiency for Kr and DO from water samples.

### **3. Kr tracer test**

#### **3. 1. System and extraction method**

A Kr tracer test performed by the Research Reactor Institute, Kyoto University, confirmed that a system using a hollow fiber membrane of the external inflow type (Fig. 2) was able to extract Kr from water. Sample water was prepared from tap water, originally derived from groundwater, and pure Kr gas (Iwatani Co. Ltd. Japan). The Kr gas was dissolved in the tap water in a container made of SUS under 2 atm of pressure. The concentration of Kr in the sample water was about 0.1 cm<sup>3</sup> STP/g, and the sample water volume ranged from 15 to 43 L. The sample water was pumped through the system with flow velocities of 0.5, 1.8, or 2.6 L/min. The time when the vacuum was applied to the inner surface of the hollow fiber membrane was defined as the starting time ( $t = 0$ ). Water samples with dissolved Kr were collected in a glass syringe.

In this tracer test, sample water was collected with an ordinary injector, which was connected to a stopcock, and a cap with a small plastic chip. Vacuum grease was used to lubricate the piston of the syringe. Two stopcocks (cocks 1 and 2) were installed in the Kr extraction system, and a syringe was used to collect initial sample water and drain water for measurement of Kr (Fig. 2.) via each stopcock. Each syringe could hold 20 ml of sample water. Three to five samples of the initial water were collected. After the syringe was filled with the sample water, it was capped. All syringes with the collected samples were put into a plastic box, which was also filled with sample water, and transported to the laboratory at Kyushu University, where the Kr in the water was measured by gas chromatography. The Kr extraction system was also equipped with two in-line DO meters, which measured DO in the initial sample water and in the drain water (Fig. 2). Calcium, chlorine, sodium, and silicate are typically major constituents



in groundwater. Therefore, we confirmed that only the gases, and not other ions, were separated from the water by the system. Sample water with dissolved Cl, Ca, Na, and Si was collected in glass vials to investigate the behavior of these ions in the system.

### **3. 2. Measurement of Kr, Cl, Ca, Si, Na, and DO**

The efficiency of Kr and DO separation from the sample waters is described by the following equations:

$$C_1 = C_0 \cdot \alpha$$

$$\alpha = 1 - (C_0 - C_1)/C_0,$$

where  $C_0$  is the amount of Kr or DO in the initial sample water,  $C_1$  is the amount of Kr collected from the initial water sample by the system, and  $\alpha$  is the collection efficiency.  $(C_0 - C_1)$  is the amount of Kr in the sample water after it has passed through the system. The concentrations of Kr and DO ( $C_0$  and  $(C_0 - C_1)$ ) were measured by gas chromatography and with a DO meter, respectively, to obtain the extraction efficiency,  $\alpha$ .

Sample water collected in each syringe was transferred to a glass washing bottle. The sample water with Kr was bubbled for 10–12 minutes with He, and the released Kr was collected in a molecular sieve in a liquid nitrogen trap after removal of the  $H_2O$  in a molecular sieve column. The temperature of the molecular sieve was increased to room temperature to liberate the Kr, which was then introduced into a gas chromatograph (GC-8A, Shimadzu Co. Ltd) with a stainless steel chromatographic column (6 m long, 3 mm in diameter, 30–60 mesh molecular sieves) and a thermal conductivity detector. The

chromatographic separation and determination of Kr were carried out at a He carrier gas flow rate of 60 ml/min at a column temperature of 56 °C.

The Cl concentration in the sample water was measured by ion chromatography (IC 7000, Yokogawa Co Ltd.) equipped with an autosampler (PS7000, Yokogawa Co Ltd.) and a negative ion column (ICS-A23) with polyvinyl alcohol exchange resins.

Na, Si, and Ca in the sample water were measured by ICP-AES (ICPS-AES 1000 and Shimadzu Co Ltd.) equipped with an autosampler (AS-6 and Shimadzu Co Ltd.).

DO in the water sample was measured with a DO meter (SG 6 -ELK, Mettler Toledo Co. Ltd.). The analytical conditions are summarized in Table 2.

### **3. 3. Extraction efficiency**

The extraction efficiency for Kr, DO, and ions at various flow rates was measured at several time points after the vacuum was applied to the hollow fiber membrane (Figs. 3 and 4). The amount of standard Kr gas in the sample water was calculated to be 0.5 mL or 1 mL of standard Kr gas. The initial concentration of Kr in the sample water ranged from 3.4 to 8.8 ml/L, and that in the drain water sample from 0.004 to 0.03 ml/L, suggesting that less than 1% of the initial total amount of Kr passed all the way through the system, for an extraction efficiency of 99%. The time required to reach 99% efficiency at flow rates from 0.5 to 2.6 L/min was less than 2 min. No difference in the collection efficiency between Kr and DO was observed in our system. However, the amounts of Cl, Na, Ca, and Si in the drain water sample were the same as in the initial sample water (Fig. 4); thus, the system did not extract dissolved ions from the water, confirming that our procedure efficiently extracted only gases from the sample water.

### **3. 4 Investigations of applicable velocity and temperature**

We investigated the difference in the extraction efficiency between Kr and DO. The extraction efficiencies of Kr and DO were determined as described in section 3.3 (Fig. 5). No difference in the extraction efficiency was observed between Kr and DO at flow velocities from 0.5 to 2.6 L/min. Therefore, we inferred that DO in the water could be used as an index for the extraction of Kr from the sample water. We also investigated applicable water flow velocities and water temperatures for extraction of gas from water samples with the system.

For flow velocities of the sample water ranging from 0.5 to 24 L/min, the extraction efficiency was constant at 99% (Fig. 6). Thus, Kr could be quantitatively extracted from a water sample by the system at a flow velocity of up to 24 L/min, which is sufficient for use in field studies, because of practical limitations of using an AC generator in the field and considering the volume of water needed for detection of <sup>85</sup>Kr by a LSC and the coefficient of permeability of the aquifer. The extraction efficiency was also constant for water temperatures ranging from 11 to 29 °C (Fig. 7). When a gas is extracted by using fibers, a dependence on water temperature is observed. At high water temperatures, the extraction rate is high with a high flow rate of sample water (Patent JP 4-288710 report). For degassing, a hollow fiber membrane composed of poly-4-methylpentene is superior to polypropylene (PP), polyethylene (PE), Teflon, or PVDF membranes, because gases are able to pass only through surface pores of the latter polymers, but gases are able to pass through the surface of poly-4-methylpentene whether porous or not (Patent number: JP 4-288710). Thus, the heterogeneous poly-4-methylpentene membrane has a permeability coefficient as high as that of a nonporous homogenous membrane. The constant extraction efficiency of DO over a

range of water temperatures at a flow rate of less than 24 L/min suggests that the extraction efficiency did not decrease because of the high permeability of the poly-4-methylpentene membrane. At a flow velocity higher than 24 L/min, a dependence on water temperature might be expected, but at high water temperatures, gas extraction by the membrane is possible at high flow velocity (Patent number: JP 4-288710). The water temperature dependence might not be apparent at flow velocities of less than 24 L/min. In the future, the collecting efficiency of Kr at flow velocities higher than 24 L/min by this system should be investigated. Though the water temperature of shallow groundwater is low in winter, Kr should be sufficiently extracted from groundwater at a water temperature of about 10 °C with a flow velocity of less than 24 L/min by the system. Therefore, the present method should allow the quantitative extraction of Kr from a large volume of groundwater at typical groundwater temperatures.

A system withstand test was performed by using a water volume of about 5000 L and a testing period of about 6 hours. The DO in the sample water after passing through the system was about 0.2% of the initial concentration in the sample water. Thus, the system was able to quantitatively and continuously extract DO from 5000 L of sample water during continuous operation for about six hours. Therefore, this system should be able to extract Kr from several thousand liters of sample water.

Probst et al. (2007) described a degassing system based on an internal pressure type hollow fiber membrane. The difference in degassing efficiency between the system of Probst et al. (2007) and our system may result from the different type of membrane used, the internal pressure type versus the external pressure type, because of the boundary layer produced between the hollow fiber membrane and the water by laminar flow with

the internal pressure type, as explained above (DIC Co. Ltd., private communication). The excellent extraction efficiency of our system may also be due to the material used for the membrane filter, poly-4-methylpentene. Furthermore, the performance of the compressor and dry pump used by our system might be superior to that used by Probst et al. (2007). The collection efficiency for Kr and DO of our system of 99% is higher than that reported by Probst et al. (2007) using their system.

#### **4. Application of the Kr extraction system to a groundwater sample**

As the Kr extraction system with an external pressure type hollow fiber membrane was effective for collection of Kr from a large volume of water with a small Kr content in the laboratory, we applied the system to the collection of  $^{85}\text{Kr}$  from groundwaters in the southern Kansai district, western Japan, and in Kyushu district, southern Japan (Fig. 8). The sampling area in southern Kansai district was in the campus yard of the Research Reactor Institute, Kyoto University, in the southern district of Osaka, and Kr was extracted from groundwater from 230 m depth. The sampling sites in Kyushu district were near Edzu-ko lake, a groundwater discharge area, and Ohzu, a recharge area, in central Kumamoto. The groundwater near Edzu-ko lake flows under artesian pressure. The Kumamoto Plain is described in detail by Mahara (1995a).

The extraction system was installed on a small truck, and a groundwater-sampling pump (MP-1 Grundfos Co.) run by three parallel AC generators was used to collect the water. Kr isotopes were collected by the system into two gas cylinders, each with a volume of 47 L at 0.5 MPa, on 18 December 2007. The water volume sampled at Edzu-ko lake was 5179 L, and 6542 L was sampled at Ohzu. The flow velocity ranged from 8.8 to 13.5 L/min. The difference in DO between the input water and the drain

water was used as an indicator of the Kr extraction efficiency. Shallow groundwater contains a lot of oxygen, so DO is a suitable index of the extraction efficiency of Kr gas. In contrast, the DO in deep groundwater is usually ultra low, so DO may not be a suitable index of the extraction efficiency of Kr from deep groundwater. Instead, dissolved CO<sub>2</sub> and <sup>222</sup>Rn in deep groundwater may be a better indicator of the extraction efficiency of Kr.

The gas samples collected in the field were transported to a laboratory at Kyushu University. CO<sub>2</sub> collected with Kr and other gas in the gas cylinder was adsorbed with 3 M NaOH. Then Kr isotopes were separated from other gases, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>, collected in the cylinder by gas chromatography (Shimadzu Co. Ltd.). The Kr isotopes, after isolation from other major gases, were added to a *p*-xylene scintillator cocktail. The counting vial for <sup>85</sup>Kr was made of synthesized quartz with very low background and no leakage of Kr from the vial wall. The activity of <sup>85</sup>Kr in the cocktail was measured with a LSC (Aloka LB5, Aloka Co. Ltd.) for 500 min. The procedure for separating Kr isotopes from other gases and the <sup>85</sup>Kr results for the groundwater sample will be described elsewhere (Momoshima et al., in preparation). In brief, both <sup>85</sup>Kr and <sup>222</sup>Rn were present in the cocktail (<sup>222</sup>Rn radioactivity was shown by the pattern of decay). Therefore, we stored the cocktail for 1 month to allow the radioactivity of <sup>222</sup>Rn and its daughter isotopes to disappear and then measured the <sup>85</sup>Kr activity. Our system using a hollow fiber membrane of the external pressure type can extract O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> as well as <sup>222</sup>Rn and Kr from groundwater. The detection limit of the present analytical method was calculated by equation 1 with a 95% confidence level for paired (sample and background) measurements (Currie, 1968):

$$SD = 2.71 + 4.65Sb , \quad (1)$$

where SD is the detection limit, and Sb is the standard deviation of the background measurements. For a background count rate of 0.1597 cps, a counting time of 2500 min, and a counting efficiency of 72.1%, values obtained by analysis of 1.3 L of air, SD = 0.0015 Bq, which corresponds to a 74.6% recovery rate of Kr. However, the detection limit of Kr by gas chromatography is about 0.01 ml; thus, 12.2 L of air are required to identify Kr separation with a thermal conductivity detector (TCD). It should be noted that commercially available Kr contains  $^{85}\text{Kr}$  because it is produced from air, so it cannot be used as a stable tracer in a  $^{85}\text{Kr}$  analysis. A few tens of liters of air are therefore necessary to detect atmospheric  $^{85}\text{Kr}$  in the general environment by the present analytical method. The amounts of  $^{85}\text{Kr}$  in the samples collected for LSC measurement at Edzu-ko, Ohzu, and Kyoto University were 198, 398, and 265 mBq, respectively. Because the leakage rate of our system was at most 100 ml/min, as aforementioned 2., the amount of contaminating  $^{85}\text{Kr}$  from air would be small. For young groundwater with a residence time of several years, the contamination rate of  $^{85}\text{Kr}$  leaked from the equipment into the cylinder would be several percent, suggesting a negligible amount of contamination. However, for older groundwater with a residence time of several tens of years the contamination rate would be more than 10%, so correction for the amount of  $^{85}\text{Kr}$  contamination from air would be needed. Efforts should thus be made to decrease the amount of air leakage into the system.

The  $^{85}\text{Kr}$  activity in the groundwater at Kumamoto indicated a groundwater age of a few years near Edzu-ko lake and at Ohzu. Mahara (1995b) applied  $^3\text{H}/^3\text{He}$  age determination, which is based on the mixing rates of atmospheric He, mantle He, and

radiogenic He, to the same groundwater area and reported the age of young groundwater at Ohzu and near Edzu-ko lake to be 4.6 years and 10 years, respectively. Thus, the residence time obtained from the  $^{85}\text{Kr}$  in the groundwater at Kumamoto agreed with the young groundwater  $^3\text{H}/^3\text{He}$  age. Therefore, radioactive  $^{85}\text{Kr}$  can be quantitatively extracted from a large volume of groundwater in field studies.

At the Research Reactor Institute site at Kyoto University, Kr was extracted from 5789 L of groundwater at a flow velocity of 20 L/min into two gas cylinders on 18 December 2007. The obtained  $^{85}\text{Kr}$  radioactivity indicated a groundwater age of 12 years. This groundwater is pumped from a well that is screened at depths of 95–104, 113–119, 149–155, 167–176, and 230–236 m below the ground surface.  $^3\text{H}$  has been detected in this groundwater with a concentration is  $1.7 \pm 0.7$  T. U. It is possible that there is young water mixed with older water in this area. As the amount of mantle He in groundwater in this area is unknown, the  $^3\text{H}/^3\text{He}$  method cannot be used to estimate the groundwater residence time here. When young groundwater with a short residence time is mixed with groundwater including mantle origin He, the residence time estimated from  $^3\text{H}/^3\text{He}$  will be older than the actual residence time unless the mantle He is subtracted. As  $^3\text{H}/^3\text{He}$  can reflect He in both old and young groundwater, it is necessary to consider the mixing rate of water of mantle origin, young groundwater, and old groundwater. In contrast,  $^{85}\text{Kr}$  in young groundwater is derived from rainwater and is never of mantle origin. Therefore, the age of one end member, the young groundwater, can be determined from  $^{85}\text{Kr}$  radioactivity.

Age determination of young groundwater by each method,  $^3\text{H}/^3\text{He}$ ,  $^{85}\text{Kr}$ , and CFC, has both advantages and disadvantages, but the disadvantages of the individual methods can be offset by using multiple tracers. In particular, although it is difficult by other



methods to extract  $^{85}\text{Kr}$  from a large volume of groundwater having an ultralow concentration of  $^{85}\text{Kr}$ , with our extraction system, Kr in a large volume of groundwater can be extracted and accurately measured.

## Summary

We described the experimental conditions used for our separation technique, in which Kr-extracting equipment with a hollow fiber membrane of the external pressure type was used to determine the  $^{85}\text{Kr}$  radioactivity in groundwater. The method was designed to be applicable to field studies. The system was able to quantitatively extract 99% of Kr and dissolved  $\text{O}_2$  from water. This extraction method can be applied to 5000 L of groundwater at a flow rate of 24 L/min, though a flow velocity of less than 24 L/min is preferable for groundwater sampling. We used our system to extract Kr isotopes from groundwaters at the Research Reactor Institute, Kyoto University, and on the Kumamoto Plain. The residence time of  $^{85}\text{Kr}$  obtained from these young groundwaters was a few years. The residence time of young groundwater determined by the  $^3\text{H}/^3\text{He}$  method at Kumamoto was comparable to the  $^{85}\text{Kr}$  age, indicating that our system can extract  $^{85}\text{Kr}$  efficiently for accurate determination of its concentration in groundwater. Though several kinds of gas such as  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $^{222}\text{Rn}$ , can likely be extracted from groundwater samples using our system, we showed here that Kr isotopes, which reflect the residence time of groundwater, can easily be obtained by the system.

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#### Figure captions

Fig. 1 Krypton extraction system equipped with a microporous hollow fiber membrane.

Fig. 2 Krypton extraction system modified for the Kr tracer test.

Fig. 3 Extraction efficiencies for Kr and DO.

Fig. 4 Extraction efficiencies for Cl, Na, and Si.

Fig. 5 Extraction of Kr and DO at various flow velocities.

Fig. 6 Recovery of DO from a water sample in relation to water velocity.

Fig. 7 Recovery of DO from a sample water in relation to water temperature.

Fig. 8 Groundwater sampling sites.

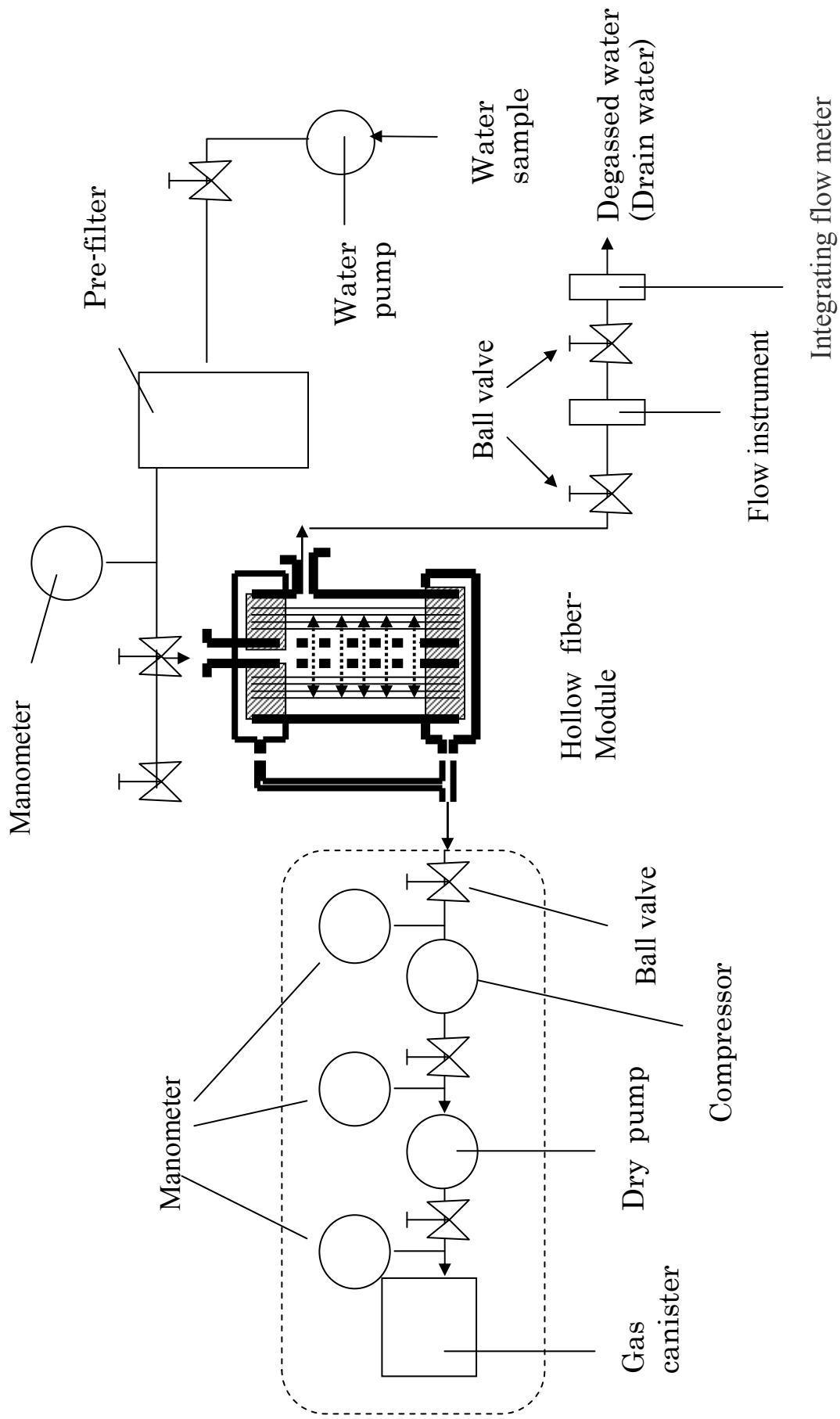


Fig. 1

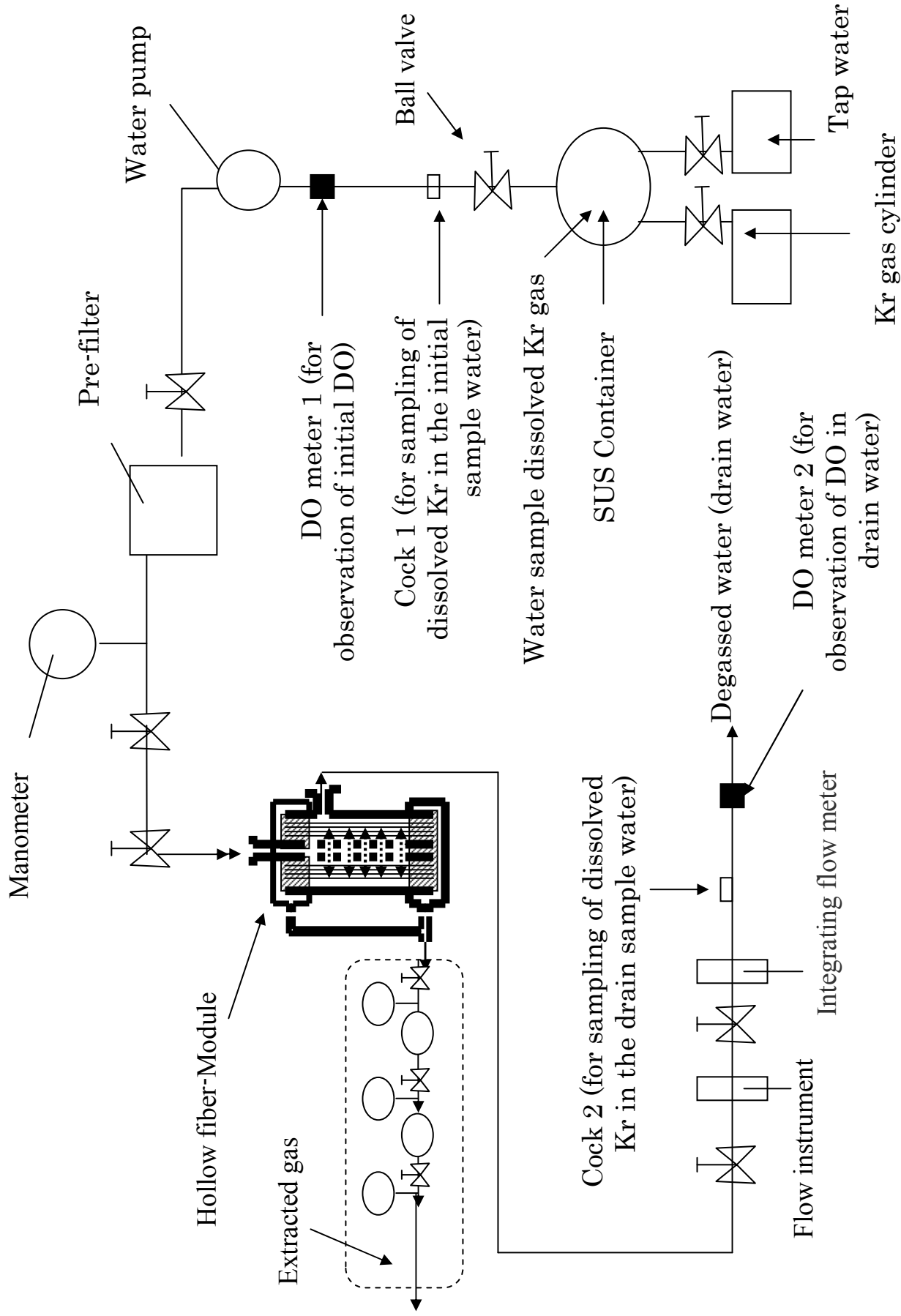


Fig. 2

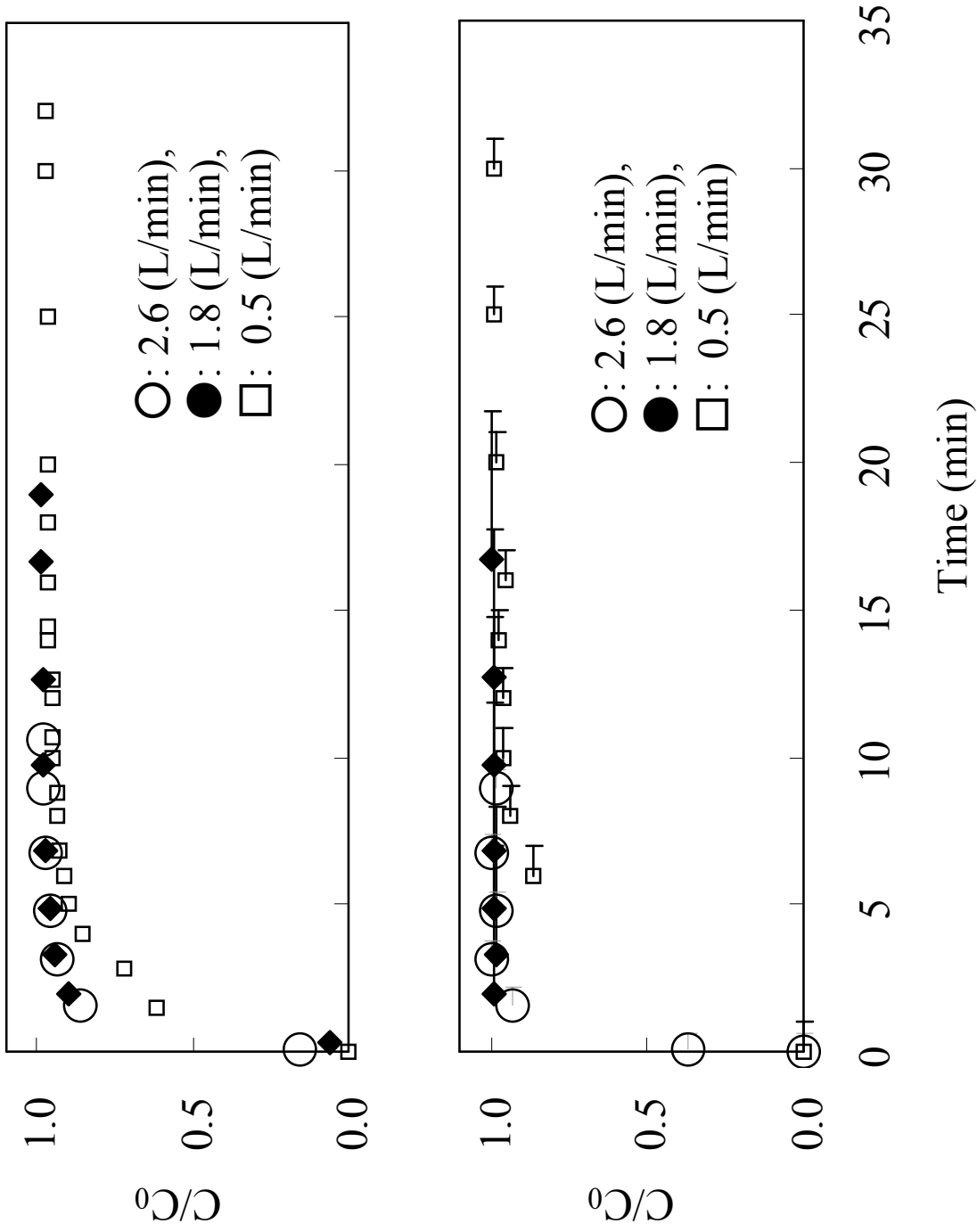


Fig. 3



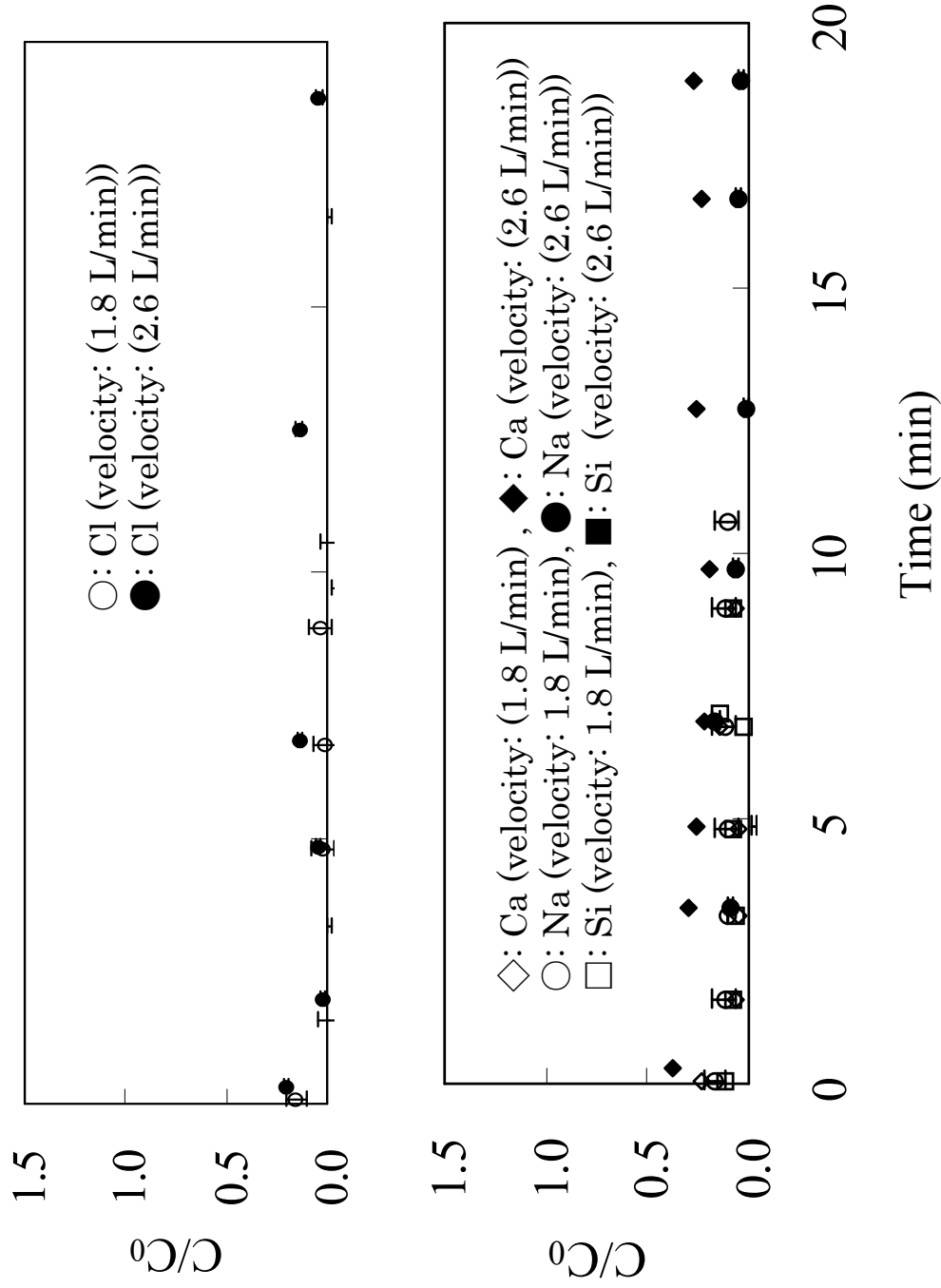


Fig. 4

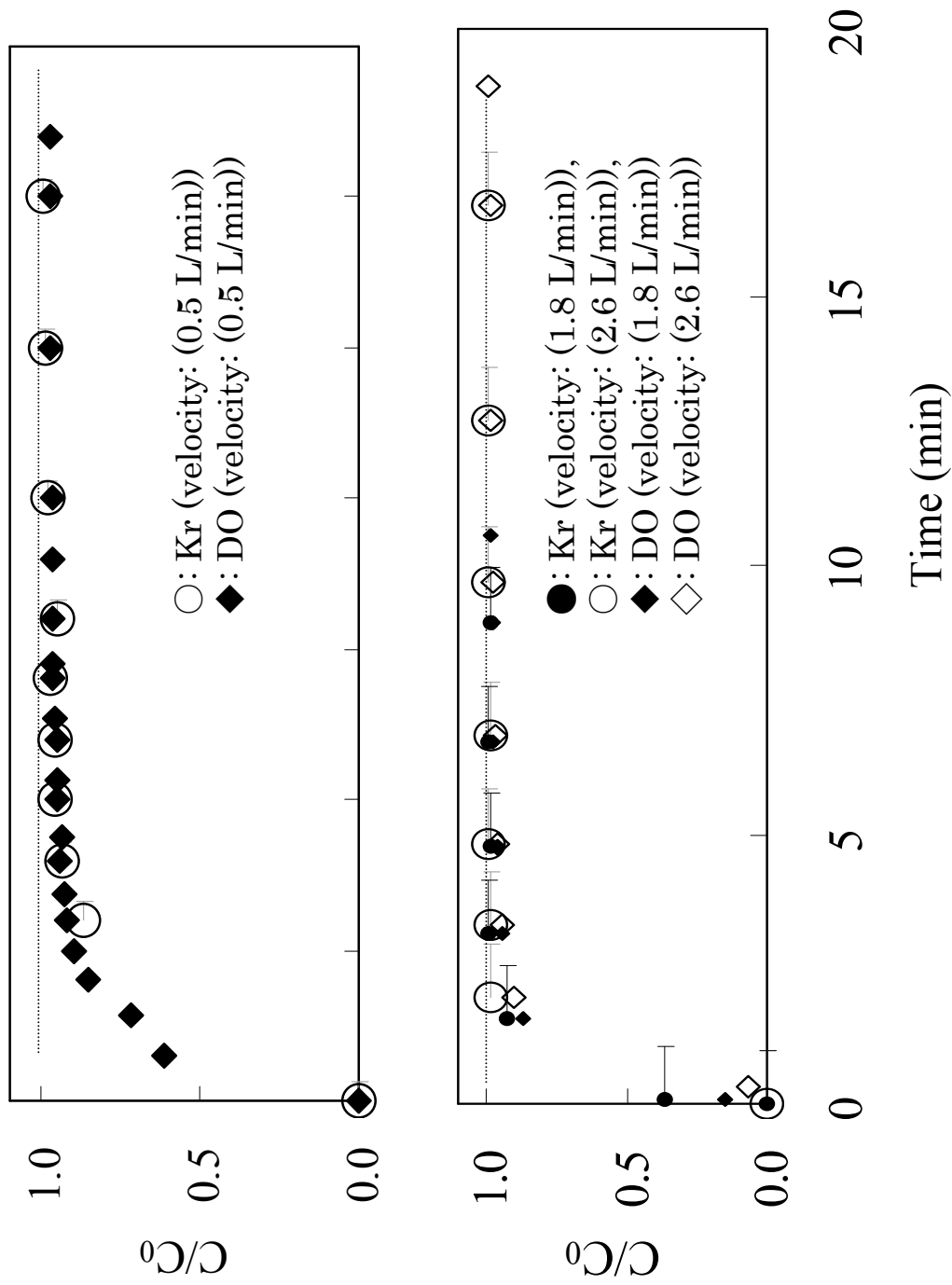


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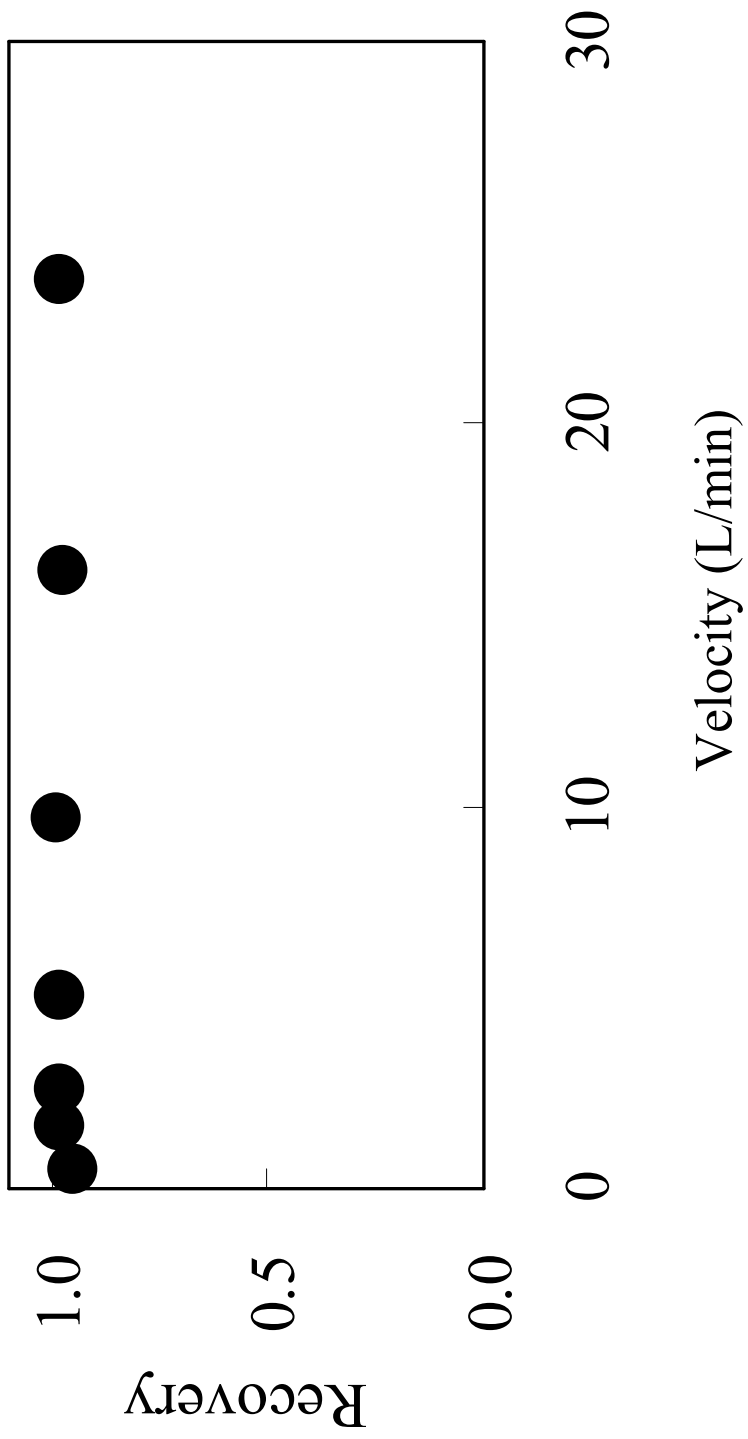


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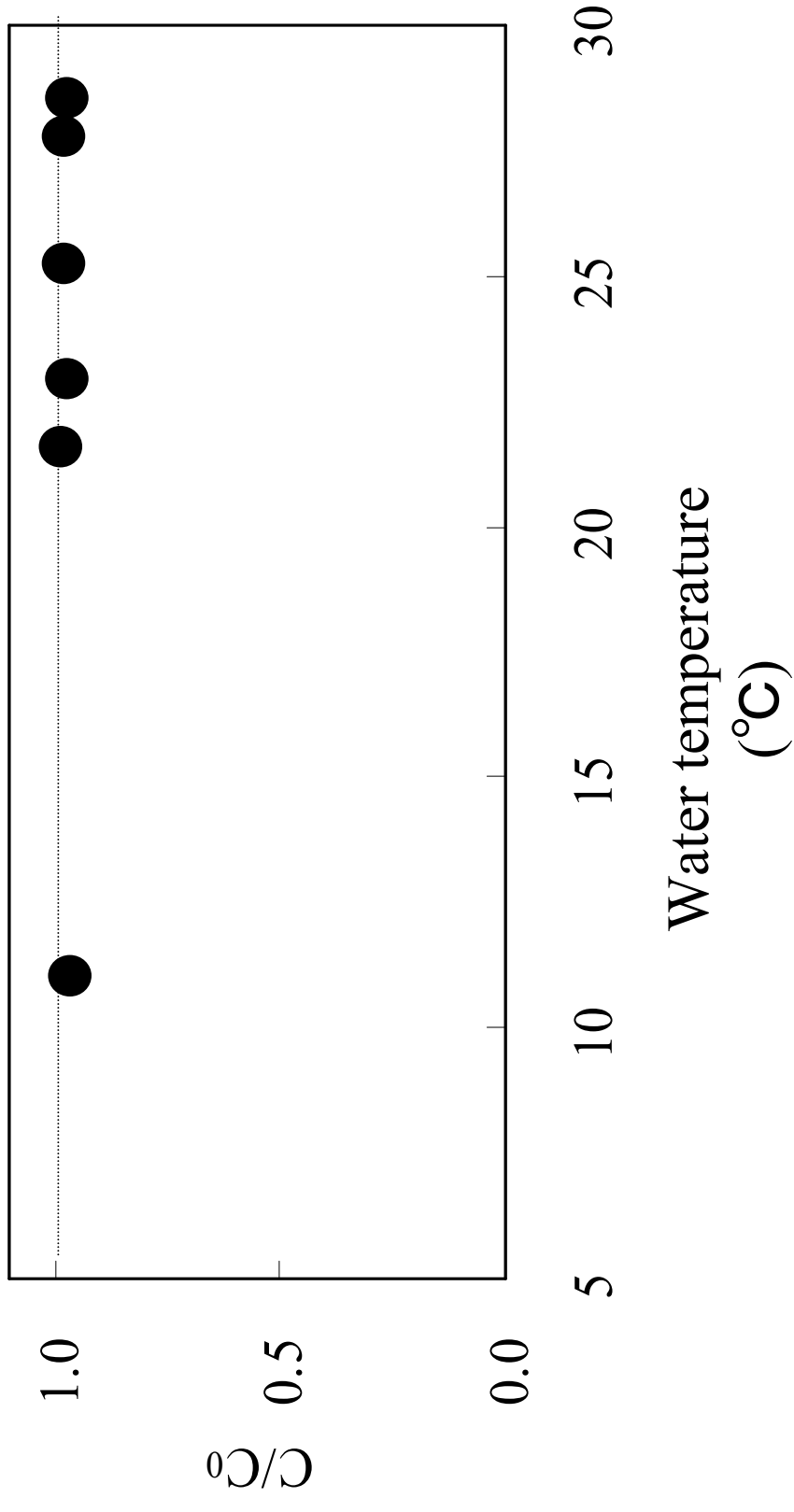


Fig. 7

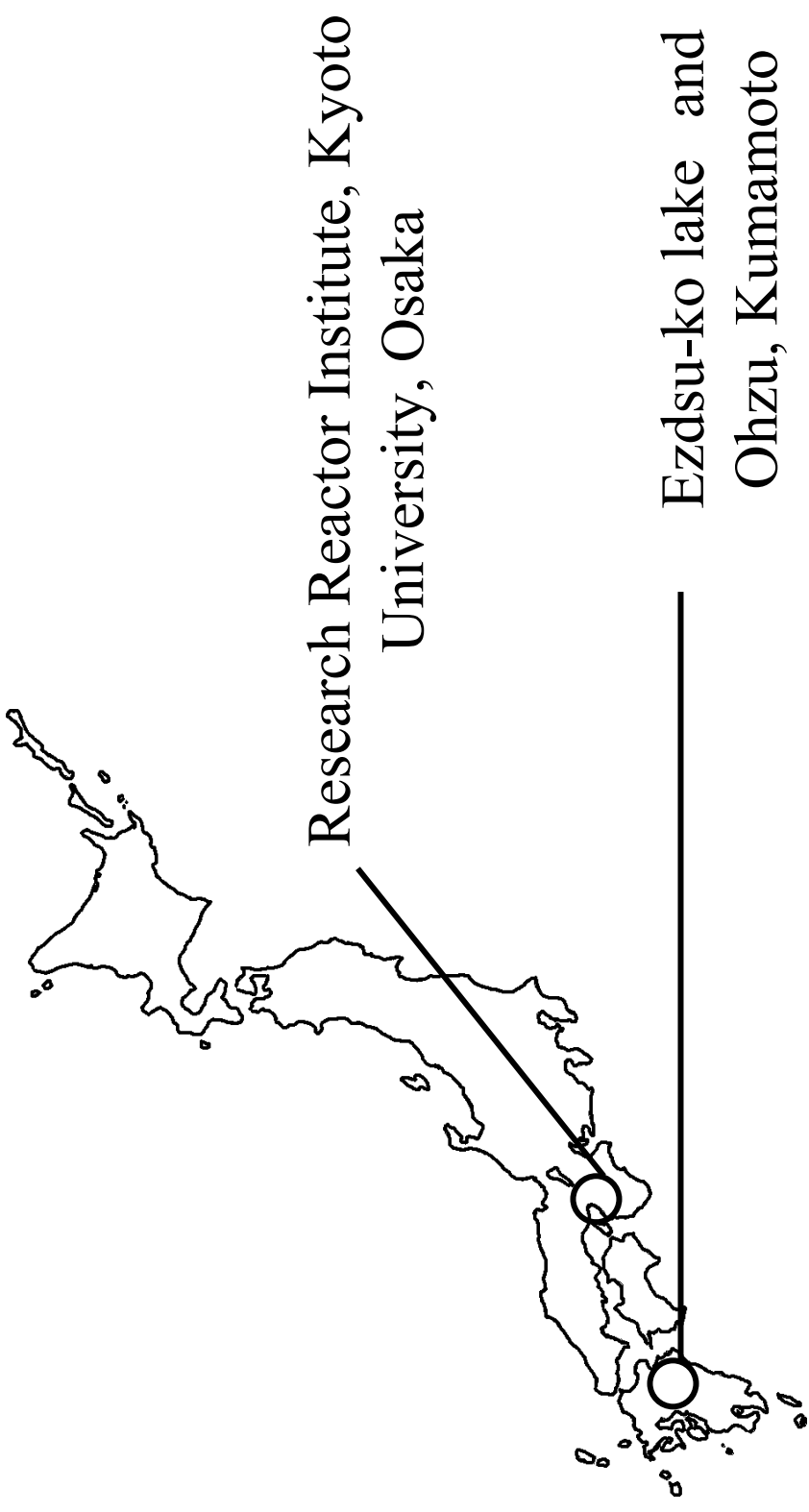


Fig. 8

Table 1 Kr extraction system

Instrument		
Water pump	HP-50	Terada Co. Ltd.
Pre-filter (5 $\mu\text{m}$ )	FH-A-5, CW-SR	Nihon filter Co. Ltd.
Hollow fiber module	EF-040P	Dainippon Co. Ltd. (DIC Co. Ltd.)
Flow meter	FLTN15A9-40	Nihon flow cell Co. Ltd.
Dry vacuum pump 1	DOP-40D	ULVAC Kiko, Inc.
Dry vacuum pump 2	DOP-80SP	ULVAC Kiko, Inc.
Ball valve	UTK15A	KITZ
Ball valve	SS63TS8	Swagelok
Monometer	A1.5TPF1/4	Daiichi Keiki Seisakisho Co, Ltd.

Table 2 Analytical conditions

	Instrument	Conditions
Cl	Ion Chromatography (IC 7000, Yokogawa Co. Ltd.)	Column (ICS-A23) Eluent: 3 mM Na <sub>2</sub> CO <sub>3</sub> , (1.0 ml/min) Regeneration solution: 15 mM H <sub>2</sub> SO <sub>4</sub> (1.0 ml/min) Amount of sample solution: 50 µl
Na	ICP-AES (ICPS-1000TR, Shimadzu Co. Ltd.)	1.2 kW
Ca		Coolant gas: 14.0 L/min
Si		Plasma gas: 1.20 L/min Carrier gas: 0.70 L/min Wavelengths: Na 588.995 nm, Ca 393.366 nm, Si 251.612nm
O <sub>2</sub>	DO meter (SG 6 -ELK, Mettler Toledo Co. Ltd.)	
Kr	Gas Chromatography (Shimadzu Co. Ltd.)	