

ARTICLE

Efficient Separation of Ar and Kr from Environmental Samples for Trace Radioactive Noble Gas Detection[†]

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Radioactive noble-gas isotopes, ⁸⁵Kr (half-life $t_{1/2}=10.8$ y), ³⁹Ar ($t_{1/2}=269$ y), and ⁸¹Kr ($t_{1/2}=229,000$ y), are ideal tracers and can be detected by atom trap trace analysis (ATTA), a laser-based technique, from environmental samples like air and groundwater. Prior to ATTA measurements, it is necessary to efficiently extract krypton and argon gases from samples. Using a combination of cryogenic distillation, titanium chemical reaction and gas chromatography, we demonstrate that we can recover both krypton and argon gases from 1–10 L “air-like” samples with yields in excess of 90% and 98%, respectively, which meet well the requirements for ATTA measurements. A group of testing samples are analyzed to verify the performance of the system, including two groundwater samples obtained from north China plain.

Key words: Atom trap trace analysis, Gas chromatography, Radioactive noble gas

I. INTRODUCTION

Owing to the unique properties of noble gases, three radioactive isotopes, ⁸⁵Kr (half-life $t_{1/2}=10.8$ y), ³⁹Ar ($t_{1/2}=269$ y) and ⁸¹Kr ($t_{1/2}=229$ ky), are homogeneously distributed in the atmosphere, and have simple mixing and transportation mechanisms in the environment. They are considered as ideal tracers in various studies, including groundwater dating, ocean ventilation, and nuclear safety. ⁸⁵Kr is a fission product emitted to the northern hemisphere since the nuclear age [1]. ⁸⁵Kr can be used to monitor anthropic nuclear activities and to calibrate atmospheric transport models [2, 3]. It can also be used as a tracer for dating young groundwater with an age range of 2–50 y [4–8]. ⁸¹Kr is a cosmogenic nuclide, and human nuclear activities have no detectable effect on the abundance of ⁸¹Kr. These outstanding characteristics make ⁸¹Kr a desired tracer for dating old groundwater [9–12] and ices [13] on the time scale of 50–1000 ky. ³⁹Ar in the atmosphere is also produced by cosmic-ray, which is particularly interested for studies of deep ocean mixing and circulation on a time scale of 50–1000 y, filling a time window inaccessible by other radioactive tracers [14–17].

The concentration of krypton in the earth's atmo-

sphere is 1.14 ppm (part per million) by volume [18]. The isotopic abundances of ⁸⁵Kr and ⁸¹Kr have been determined to be 2.2×10^{-11} and $(5.2\pm 0.6)\times 10^{-13}$, respectively [2, 19–21]. Argon constitutes 0.934% of the atmosphere by volume, larger than krypton by four orders of magnitude, but the isotopic abundance of ³⁹Ar is only 8×10^{-16} . ⁸⁵Kr and ³⁹Ar can be analyzed by low-level counting (LLC) of the decay. The minimal sample size of LLC analysis of ⁸⁵Kr is about 10 μ L krypton (STP, standard temperature and pressure), and several hundred milliliters argon (STP) for ³⁹Ar. The later one corresponds to a groundwater sample size of several tons [21]. Due to much longer half-life time of ⁸¹Kr, it is impractical to analyze ⁸¹Kr with LLC. Accelerator mass spectrometry (AMS) has been successfully applied for ⁸¹Kr-dating, but the sample size was huge: about 500 μ L krypton gas recovered from 16 ton groundwater [10]. Atom trap trace analysis (ATTA) [22] is a laser-based technique, utilizing a magneto-optical trap to selectively capture and count atoms. The minimum krypton sample size for ⁸⁵Kr/⁸¹Kr detection with ATTA has been reduced to a few microliter [23–25]. ATTA analysis of ³⁹Ar also becomes feasible [26, 27]. It has been concluded [28] that ATTA is currently the most practical method of dating environmental samples using radioactive krypton and argon isotopes.

One liter of modern groundwater at 10 °C contains about 58000 ⁸⁵Kr atoms, 1300 ⁸¹Kr atoms, and 8500 ³⁹Ar atoms [29, 30]. Currently, ATTA measurement of radio-krypton needs a typical groundwater sample size of about 100 L. Prior to the ATTA measurement, it is necessary to extract noble gases (mostly argon and

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krypton) from groundwater samples, and it can be accomplished in two steps: first to extract the solved gas from groundwater, and then to separate krypton/argon from the “air-like” gas sample. Taking into account the complicated transfer and mixing of groundwater, analysis with multiple tracers is preferred in groundwater dating. Therefore, it is desired to separate and recover both argon and krypton from different gas samples with high yields to prevent any possible isotopic fractionation.

There have been several reports on the systems of Kr separation from “air-like” gases [5, 10, 25, 31–33]. A method based on frozen charcoal trap and gas chromatography [5, 32] has been applied for several liters of gas samples extracted from groundwater. A special krypton purification system for more than 100 L of bulk gas was reported by using several gas chromatographic steps, which has been applied in ^{81}Kr dating with AMS [10]. Systems for recovering krypton from gases with a volume in the range of 1–100 liters have also been built based on cryogenic distillation, gas chromatography, and titanium reactions [25, 33], and they have been successfully applied in radio-krypton dating measurements using ATTA. Here we report on a new system developed to recover both krypton and argon from ATTA measurements using 1–10 L gas extracted from groundwater samples. Using a combined process of cryogenic distillation, gas chromatography and titanium reaction, yields in excess of 90% and 99% have been achieved for krypton and argon, respectively. As a demonstration, abundances of ^{85}Kr and ^{81}Kr in several environmental samples have been determined by the ATTA instrument in Hefei (China).

II. EXPERIMENTS

A. Sampling in the field: extract gases from groundwater

The configuration of the sampling system for field sampling is shown in Fig.1. A membrane contactor (Liquicel, 4×13 , type X40) is used to extract gases from groundwater. The hydrophobic hollow-fibre membrane contactor can efficiently separate gases from liquid [34], and has been widely used in different applications [35–38]. High efficiency and simple structure make it very suitable to be used in field. Groundwater sample first passes through two fine filters to remove particles in the sample, then is introduced into the membrane contactor with a flow rate of 5–20 L/min monitored by a water flow meter. The contactor allows gases to diffuse from the water into gas-filled contactor pores which contact with gas line directly. The gas line is first evacuated by a diaphragm pump and is further purged by the gas extracted from groundwater. When the size of the residual air is believed to be negligible, the extracted gas will be pumped into a sample cylinder by the diaphragm pump. Under a water flow rate of 10 L/min, about 5 L aqueous gas can be collected in

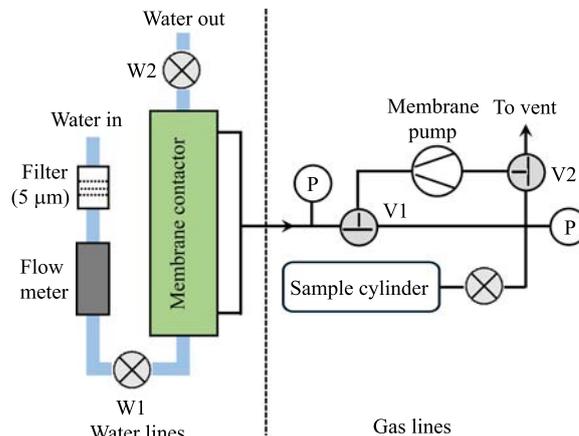


FIG. 1 Schematic of the system for groundwater degassing. Abbreviations: W1 and W2: water valve, V1 and V2: three-way valve, P: pressure gauge.

about 0.5 h, with an extraction efficiency of about 90% for Ar and O₂ and 70% for Kr. The exhaust end of the diaphragm pump connects with a sample cylinder, and the pressure of the final collected gas is limited to be about 1.2 bar. More gas can be collected in the same cylinder if a compressor pump is used, but it considerably increases the weight of the system and consumes more power in the field.

Gas samples extracted from groundwater are contained in cylinders in the field. Noble gases in the samples, mainly argon and krypton, will be extracted in the laboratories using cryogenic distillation and high-temperature Ti-reaction, followed by gas chromatographic separation. A schematic of the purification system is shown in Fig.2.

B. Cryogenic distillation and high-temperature Ti-reaction

Water vapor and carbon dioxide are first removed by a molecular sieve 5 Å trap (MS 5A), then the gas sample is introduced into a liquid-N₂ (77 K) cooled charcoal trap (trap 1, 200 cm³ volume, 4 g charcoal of 16–32 mesh). A vacuum compressor is used and typically it takes about 30 min to condense more than 95% of the gas sample into trap 1. The vapor above the condensed sample in trap 1 flows into a quartz tube with a flow rate of about 50 mL/min, which is constrained by a mass flow controller. The quartz tube (“burner”) is 34 mm in diameter, 70 cm long, and O-ring sealed at both ends. The tube has been filled with about 200 g titanium sponge, and slowly heated to 1000 °C by a furnace. At temperature of 1000 °C, titanium reacts with gaseous O₂ and N₂ to form titanium oxides and titanium nitrides, respectively. Titanium also consumes other chemically active gases, including CH₄ at such high temperature. Consequently, residual gases in the burner are mostly noble gases, together with little amounts of N₂ and CH₄. The flow rate of 50 mL/min is

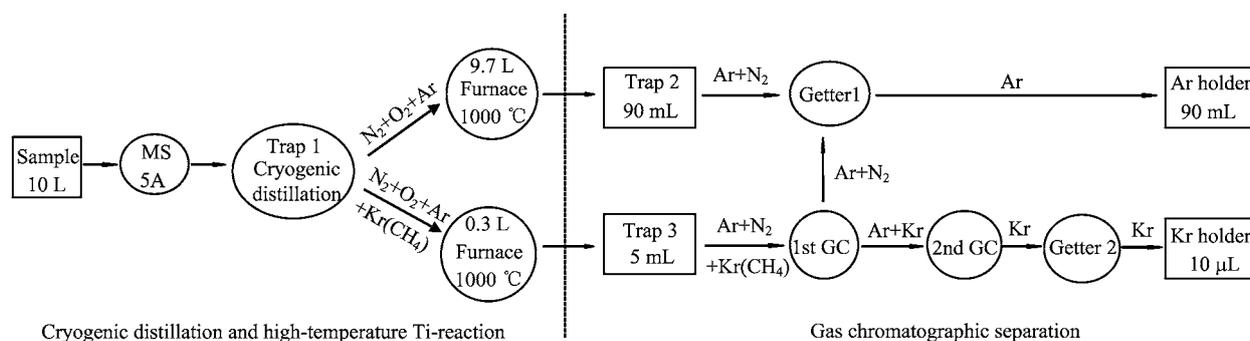


FIG. 2 Schematic of the system to separate krypton and argon from air-like samples. MS 5A: molecular sieve 5 Å trap. Trap: frozen trap with activated charcoal. Furnace: furnace for titanium-reaction. Getter: titanium getter pump. GC: gas chromatography.

selected to keep a mild reaction rate to avoid overheating the burner. During the process, the pressure in the quartz tube is monitored with a gauge (MKS Baratron 627B, relative accuracy of 0.12%). Because krypton has a lower vapor pressure in liquid-N₂ cooled charcoal trap, krypton is kept condensed in trap 1, while most Ar, O₂, and N₂ gases are released to the burner.

When the argon gas accumulates in the burner, the gas pressure gets higher and prevents the gas flow from trap 1 to the burner. At this point, we turn off the gas flow into the burner. The gas pressure in the burner will decrease since the Ti-reaction continues. It takes about 20 minutes to reach an equilibrium, which is illustrated in Fig.3(a). The residual gas (mostly argon) will be collected with another liquid-N₂ cooled charcoal trap (trap 2). Subsequently, we can turn on the gas flow from trap 1 to the burner again and restart the distillation. The procedure above can be repeated until most gas in Trap 1 is transferred, which is evidenced by a sudden drop of flow rate from trap 1 to the burner. Usually two iterations are needed for a sample with an original size of 10 L. We have investigated the composition of the gas flow during the process using gas chromatographic analysis, which is shown in Fig.3(b). At the beginning, the main composition is N₂. Later when N₂ depletes, O₂ and Ar become dominant in the flow. Finally, the flow stops when O₂ and Ar deplete.

When all the gas in the burner is collected in trap 2, the residual gas in trap 1 will be released by heating the trap to about 200 °C. It contains all the krypton in the original sample, but being still mostly N₂ and O₂, together with methane and some argon. The typical size is about 0.3 L (excluding methane). The gas released from trap 1 is also introduced to the burner with a flow rate controlled to be less than 50 mL/min.

When most N₂, O₂ and CH₄ are removed in the burner, the residual gas is transferred to another activated liquid-N₂ cooled charcoal trap (trap 3, 10 mL volume, 1 g charcoal of 16–32 mesh). Typical time needed for the whole distillation and titanium reaction process is about 4 h for an air sample of 10 L.

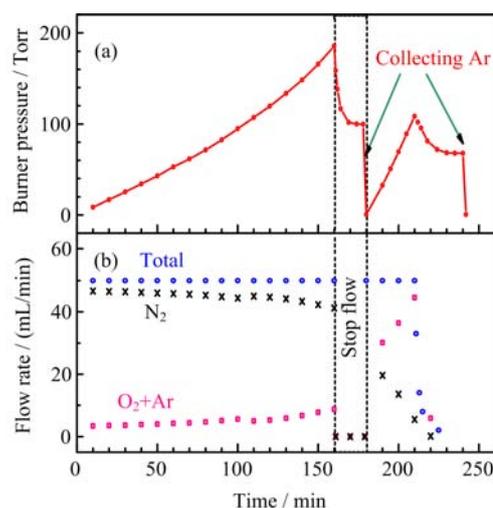


FIG. 3 (a) Observed residual gas pressure in the “burner” during cryogenic distillation of an air sample of 10 L. (b) The measured flow rates of different gases. The total flow rate was controlled to be 50 mL/min by a mass flow controller. The distillation process was separated into two stages as indicated with vertical dotted lines. When the gas pressure in the “burner” is high, the gas flow is stopped for 20 min also and restarted when the argon gas is transferred to a cold trap.

C. Chromatographic separation of krypton

A gas chromatographic (GC) separation process is applied to extract krypton gas from the sample. The residual gas in trap 3 is released by heating the trap to 200 °C and flushed into a chromatographic column. The column is filled with a molecular sieve (MS 5A, grain size of No.60–80, diameter of 6 mm, length of 2 m) and installed in a constant temperature bath at 30 °C. Pure helium (99.999% purity, 30 mL/min) is used as carrier gas. Characteristic elution peaks of various gas components are monitored with a thermal conductivity detector (TCD), and they are shown in Fig.4. Because several milliliters of argon and almost all krypton

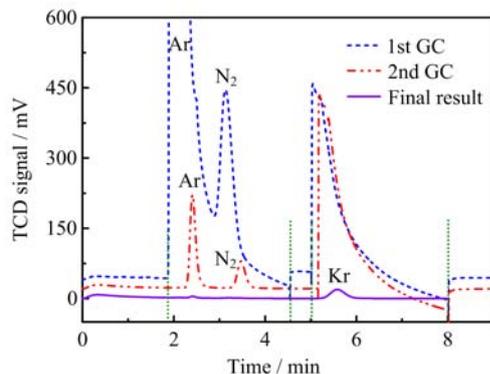


FIG. 4 Chromatograms of the elution times of various gases originally extracted from an air-like sample. Two pairs of vertical dotted lines indicate the time ranges for Ar and Kr gas collection during 1st GC separation. The solid line shows the final constituents of the Kr sample.

(micro-liters) are presented here, the chromatographic separation process includes a 2.5 min collection of argon and a 3 min collection of krypton, which is shown in Fig.4.

The collected argon gas, together with the gas previously stored in trap 2, is transferred into a chamber installed with a Ti-getter pump (Getter 1, 500 °C, Nanjing Huadong Electronics Co.) to get rid of residual N₂. After that, the argon gas is collected in a sample holder filled with activated charcoal at liquid-N₂ temperature, and then stored at room temperature. A second run of chromatographic separation is applied to extract the Kr gas, which is also shown in Fig.4. Then a getter process is applied to remove residual contaminants from the obtained krypton sample. Finally, the purified krypton gas is also collected in a sample holder filled with activated charcoal at liquid-N₂ temperature, being ready for ATTA measurement. The duration of the GC separation is about 1 h.

Note that the TCD signal in the GC process has been calibrated by using pure Ar, N₂, Kr, and CH₄ samples. The areas under the chromatographic peaks are used to determine the contents of various components in the obtained krypton gas. The quantity of extracted argon is derived from the pressure gauge and the volume of the sample holder. Typically 90 mL argon can be obtained from an ambient air sample of 10 L (STP).

III. RESULTS AND DISCUSSION

A. Yield and purity of products

The efficiency and purity of the extraction process were tested by several samples: ambient air samples with volumes varying from 1 L to 10 L (STP), two air samples of 10 L and mixed with 1% CH₄, and two groundwater samples. The GC data of recovered krypton and argon gases are shown in Fig.5. The sizes of

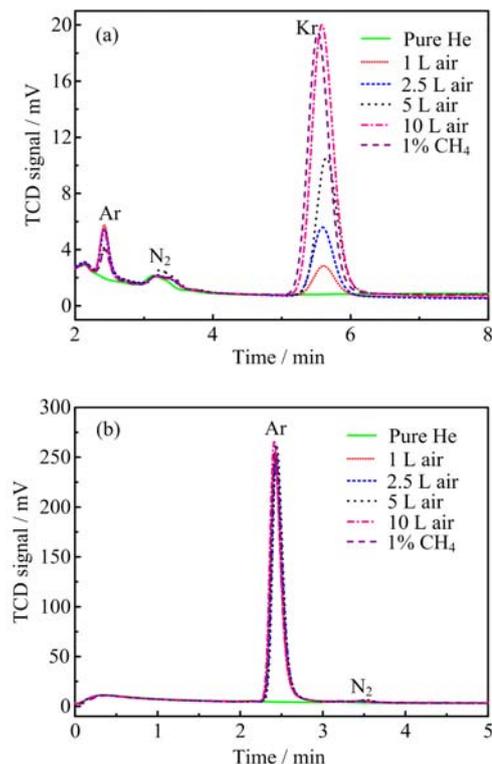


FIG. 5 Chromatograms of the final components of (a) Kr and (b) Ar gases recovered from air samples of different sizes. The curve at the bottom of each panel is from a blank sample (pure helium).

original samples and recovered Kr/Ar gases are presented in Table I.

Although Ar and N₂ contents are observed from the chromatography spectra (Fig.5(a)), which may result from air leak during the collection process. The size of “impurities” in obtained Kr samples becomes relatively larger when the original sample size gets smaller. Since only 1 ppm of ambient air is krypton, even at the worst case (1 L air sample, Fig.5(a)), the content of contaminated krypton relative to the whole krypton sample size is less than 0.1% and therefore negligible.

A small N₂ peak also presents in the TCD spectra of the recovered argon sample (Fig.5(b)). It indicates that the Ti-reaction and getter cannot completely remove N₂ from the argon sample. But the content of N₂ is below 1%. In addition, we cannot detect any loss of krypton (<0.1%) in the distillation process. Since the residual small impurities have no influence on ATTA measurements, there is no need of further efforts to remove the impurities from the obtained krypton and argon samples.

For ambient air gases and CH₄-rich samples, the yields of Kr and Ar are more than 85% and 90%, respectively. The O₂-poor samples were extracted in field from groundwater, and their initial constituents were analyzed by gas chromatography. Although original krypton contents in these two samples are too small

TABLE I The quality of processed gas (content of Kr in μL , content of Ar in mL), extraction yield (in %) and purity (in %) of Kr and Ar^a.

Gas type	Total gas/L	Chemical composition/%				Kr				Ar			
		N ₂	O ₂	Ar	CH ₄	Content ^b	Extracted	Yield	Purity	Content ^c	Extracted	Yield	Purity
Air	1	78.1	20.8	0.93	<0.01	1.14	1.1	97.0	56.2	9.34	8.50	91.0	99.5
Air	2.5	78.1	20.8	0.93	<0.01	2.85	2.63	92.1	77.0	23.4	23.1	99.0	99.2
Air	5	78.1	20.8	0.93	<0.01	5.7	5.2	90.3	91.8	46.7	44.9	96.2	99.1
Air	10	78.1	20.8	0.93	<0.01	11.4	10.5	91.8	92.8	93.4	90.6	97.0	99.7
CH ₄ -rich ^d	10.1	77.3	20.6	0.92	0.99	11.4	9.8	86.3	95.9	93.4	92.2	98.7	99.8
CH ₄ -rich ^d	10.1	77.3	20.6	0.92	1.01	11.4	9.9	87.1	95.8	93.4	92.3	98.8	99.7
O ₂ -poor ^e	4.45	97.7	<0.1	2.00	0.35		16.4			89.0	86.2	96.9	99.9
O ₂ -poor ^e	4.25	98.1	<0.1	1.90	<0.01		14.5			80.8	77.4	95.8	99.9

^a There is an uncertainty of 2.5% in the given yields of krypton and argon.

^b Calculated values from krypton concentration of 1.14 ppm by volume in the earth's atmosphere.

^c Calculated values from argon concentration of 0.934%.

^d Gas mixture with enriched CH₄.

^e Dissolved gas samples extracted from groundwater.

to be determined by conventional chromatography, the sizes of recovered krypton gases agree reasonably with the estimated values according to the solubility of krypton and the temperature of the groundwater.

B. Isotopic fractionation and environmental samples

The extracted krypton gas is ready for ATTA measurements. Figure 6 shows the fluorescence signal of the trapped stable krypton isotopes when scanning the laser frequency. Two krypton samples were tested, one is a commercial pure krypton gas sample bought in 2007 (denoted as "2007 bottle"), and the other one is from a groundwater sample (the last sample shown in Table I). As shown in the figure, relative intensities of respective isotopes remain the same in both samples, indicating no detectable isotopic fractionation effect in the gas extraction and purification process. When the laser frequency is set on resonance with the rare isotope ⁸⁵Kr or ⁸¹Kr, image of single atoms will be detected by a sensitive EMCCD camera and counts of individual atoms will be used to derive the isotopic abundances [24]. Two "O₂-poor" samples extracted from deep groundwater obtained in north China plain are presented in Table I as application examples of the system. For the first sample, 5 counts of ⁸⁵Kr and 228 counts of ⁸¹Kr have been obtained in 4 h. The isotopic abundances of ⁸⁵Kr and ⁸¹Kr, relative to the modern values, are determined to be 0.3% and 71±5%, respectively, which leads to a ⁸¹Kr age of about 113±23 ky. For the second sample, 18 counts of ⁸⁵Kr and 411 counts of ⁸¹Kr have been recorded in 4 h. The relative-to-modern isotopic abundances of ⁸⁵Kr and ⁸¹Kr are 0.6% and 106±6%, respectively. It indicates that the age of this groundwater sample is beyond both detection ranges of ⁸⁵Kr and ⁸¹Kr, and should be older than 50 y. The very low ⁸⁵Kr counts also indicate that air contamination throughout

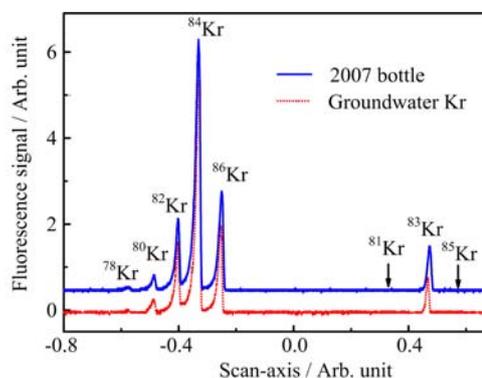


FIG. 6 The fluorescence spectra of krypton recovered from one groundwater sample and the "standard" krypton from a commercial gas bottle in 2007. The spectra show stable isotopes of krypton (⁷⁸Kr, ⁸⁰Kr, ⁸²Kr, ⁸³Kr, ⁸⁴Kr and ⁸⁶Kr) and their relative abundances, and demonstrates that there is no significant isotopic fractionation throughout the whole krypton separation process. Two arrows mark the position of the two rare isotopes ⁸¹Kr and ⁸⁵Kr.

the sample extraction and purification process is negligible.

IV. CONCLUSION

we have developed an apparatus to extract krypton and argon gases from air-like gas samples using a combination of cryogenic distillation, chemical absorption by titanium, and gas chromatography. A portable sampling instrument has also been developed to extract solved air from groundwater samples in the field. The system has been tested by applying several different gas samples, including ambient air samples with a size of 1–10 L, synthesized CH₄ enriched samples which mimic gases extracted from groundwater, and also two samples

obtained from real groundwater in the field. Krypton and argon gases can be separated with an efficiency better than 90%. The system fulfills present needs of the ATTA measurement of the rare noble-gas isotopes including ^{85}Kr , ^{81}Kr and ^{39}Ar .

V. ACKNOWLEDGMENTS

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