Dual Separation of Krypton and Argon from Environmental Samples for Radioisotope Dating

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ABSTRACT: The noble gas radioisotopes ^{85}Kr, ^{81}Kr, and ^{39}Ar are nearly ideal environmental tracers because of their chemical inertness and simple transport mechanisms. Recent advances in Atom Trap Trace Analysis have enabled measurements of ^{85}Kr and ^{81}Kr using 10−20 kg of water or ice, and ^{39}Ar in only a few kilograms, making these tracers available to be applied in the earth sciences on a large-scale. To meet the resulting increase in demand, we have developed

an automated process for the dual separation of krypton and argon from environmental samples based on titanium gettering and gas chromatography. 0.5−4 L STP air samples have been purified, demonstrating purities and recoveries of >90% for krypton and >99% for argon within 90−120 min of processing time. Samples of high methane admixtures, a challenge regularly encountered in groundwater applications, have been purified by exploiting the full potential of titanium gettering at high temperatures (>1000 °C). Samples with 0.4−48 L STP of methane admixture are processed in 2−5 h without compromising purity or recovery. The applicability of the purification system is further demonstrated using actual groundwater samples with carbon dioxide and methane content in the extracted gas up to 16 L STP and 42 L STP, respectively.
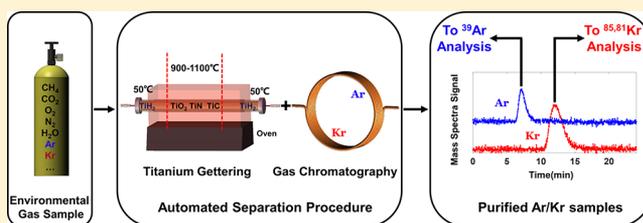
The noble gas radioisotopes ^{81}Kr (half-life $t_{1/2}$ = 229 ka), ^{85}Kr ($t_{1/2}$ = 11 a), and ^{39}Ar ($t_{1/2}$ = 269 a) are nearly ideal tracers for environmental processes owing to their chemical inertness and their gaseous properties.[1,2] Together with ^{14}C ($t_{1/2}$ = 5730 a), they cover a continuous dating range from a few years back to 1.3 million years. However, a decade ago the application of ^{81}Kr, ^{85}Kr, and ^{39}Ar in the earth sciences was hampered by their extremely low atmospheric abundances in the range of 10^{-15} to 10^{-11}.[1] The analytical method Atom Trap Trace Analysis (ATTA), which detects single atoms via their fluorescence in a magneto-optical trap, has made ^{81}Kr available to the earth science community at large.[3] Recently, the required sample size for ^{81}Kr and ^{85}Kr analysis has been lowered to 1 μL[4,5] (throughout the whole text, gas amounts are provided in the units of volume at the STP condition) of krypton, which is contained in about 10−20 kg of water or ice. This sample reduction allows radiokrypton dating to be performed not only on groundwater but also on glacier ice and ocean water. ATTA has also been realized for ^{39}Ar. Practical dating of groundwater, ocean, and ice samples was demonstrated using 0.5−2 mL of argon, corresponding to 1−4 kg of water or ice.[6−9]

These recent advances in ATTA have led to a significant increase in the demand for ^{85}Kr, ^{81}Kr, and ^{39}Ar analysis, particularly for applications in the earth and environmental sciences on the large-scale. For example, hundreds of ocean samples have already been obtained in recent voyages for ^{85}Kr as well as ^{39}Ar analysis while further sampling cruises are underway. In addition, about 1000 samples from the Atlantic ocean were collected for ^{39}Ar and ^{85}Kr analysis in the 1980s of which only

about 100 were analyzed by LLC at the University of Bern.[2] The remaining 900 samples are now accessible for ATTA analysis. This rising demand necessitates the development of an efficient, automated, and fast separation process that can extract both krypton and argon from the same sample.

A krypton purification system for ATTA was developed by Yokochi et al.[10] for large gas amounts up to 125 L, employing cryogenic distillation, gas chromatography, and titanium gettering. Based on the same concepts, a modified setup for krypton purification for smaller samples between 1−20 L of air was developed by Tu et al.[11] By replacing the cryogenic distillation with a fractionating desorption on an activated charcoal column at 138 K, Yokochi et al.[12] purified krypton within 75 min for air samples of 1.2−26.8 L, tolerating methane admixtures up to 1.9 L.

None of the purification systems discussed above included the separation of argon. Riedman et al.[13] have reported an argon separation line for gas samples of 10−120 L based on chromatographic desorption on Li-LSX at 150 K. For smaller samples below 10 L, titanium gettering and cryogenic distillation on a nude stainless steel trap have been used.[14,15] An argon purification system for gas samples <10 L based on titanium gettering was developed by Beyersdorfer et al.[16] for ^{39}Ar dating of ocean water, glacier ice, and groundwater. To remove the large amounts of hydrogen that can be present for saltwater
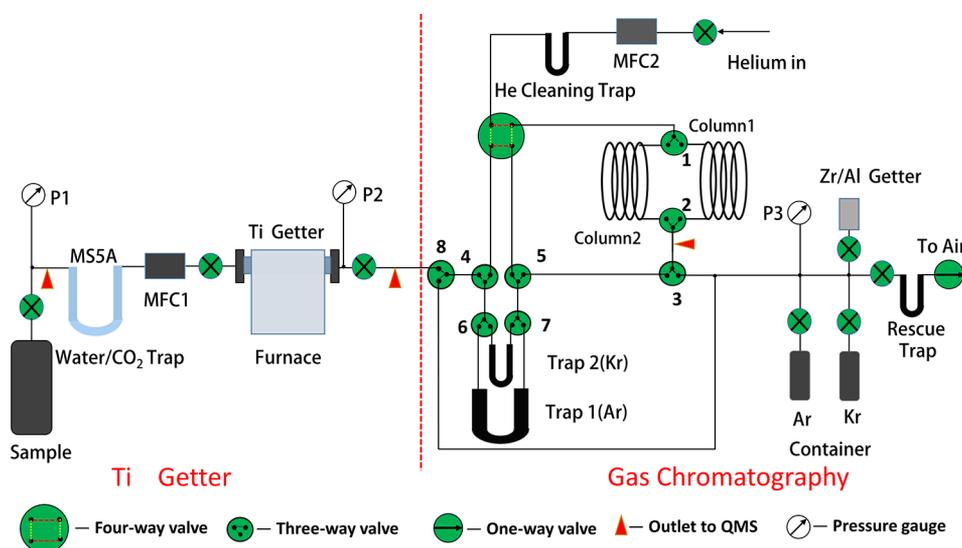
Figure 1. Schematic of the dual Kr/Ar separation system: MFC, mass flow controller; QMS, quadrupole mass spectrometer; trap, tube filled with activated charcoal or MS5A (molecular sieve); column, long tube filled with MS5A.

samples stored in steel containers, a second getter at room temperature was used as proposed in Stout et al.[17] Argon recoveries >97% and purities >99% were reached within 2 h of processing time. In Tu et al.[18] the purification of the argon fraction was integrated into the krypton purification system by gettering the effluent from the cryogenic distillation with a titanium sponge. For 5−10 L airlike samples, purity and recovery in excess of 90% for krypton and 95% for argon were obtained, tolerating methane admixture up to 1 L. However, the krypton purity which is a key requirement for ^{81}Kr and ^{85}Kr analysis particularly for small samples, dropped from 91.8% for 5 L air samples down to 56.2% for 1 L samples, and the time needed for purifying a sample exceeded 5 h. Moreover, the system was not capable of purifying samples with high (>5 L) methane content. Gas samples from groundwater can be highly (>90%) enriched in methane due to methanogenesis. Separation of krypton from such samples poses a major difficulty.

The separation of krypton and methane via physical methods such as cryogenic distillation or gas chromatography is hampered due to their similar physical properties. Methane can be removed chemically, e.g., by oxidation on copper oxide.[19,20] However, the reaction rate is slow and an additional step has to be added to remove the reaction products water and carbon dioxide. In Yokochi et al.,[10,12] methane was separated from krypton by gas chromatography on MS5A at 163 K. For a sample containing 1.9 L of methane, four cycles of gas chromatography were needed to completely remove the methane fraction, with each cycle taking 0.5 h. The resulting krypton recovery dropped to 86% as compared to near 100% for methane-free samples. It seems that using this technique to purify krypton from a larger amount (5−50 L) of methane would take longer time and be less efficient. Titanium was employed as a getter for oxygen, nitrogen, carbon dioxide, water, and methane above 700 °C.[17,21] For hydrogen, titanium absorbs the gas in the range of 25−400 °C but releases it back out at a higher temperature. Stout et al.[17] observed that, at 1200 °C, titanium could decompose methane and sorb the carbon while the hydrogen is released. In combination with titanium at a temperature below 400 °C, also hydrogen can be sorbed.

Here we present an automated system for dual separation of krypton and argon from environmental samples based on titanium gettering for removing reactive gases and gas chromatography on MS5A at room temperature for separating krypton and argon. We obtain high purities and recoveries over a wide range of sample sizes for argon as well as for krypton while only needing short processing times. By using titanium sponge at temperatures beyond 1000 °C, we can omit cryogenic distillation for bulk separation and purify krypton and argon from samples with methane admixtures as high as 48 L.

■ EXPERIMENTAL SECTION

The purification system (Figure 1) can be divided into two main sections: Ti gettering and gas chromatography (GC). Upon entering the system, H_2O and CO_2 are removed from the sample gas in a column filled with MS5A. Then all of the reactive gases except H_2 are gettered by the Ti sponge at a temperature of 900−1100 °C while H_2 is removed at a lower temperature of 50−400 °C. The remaining Kr and Ar are subsequently separated via three consecutive cycles of gas chromatography on MS5A columns. Following gas chromatography, while the Ar fraction already meets the purity requirement, the Kr fraction still contains traces of reactive gases, which are then removed by a commercial Zr/Al getter. The entire separation procedure is monitored with a quadrupole mass spectrometer (QMS) and automated with computer control. The procedure is described below in more detail.

Ti Gettering. The sample gas flows through a U-shaped trap (25 mm inner diameter, 30 cm length) filled with MS5A (mesh 200) at room temperature where H_2O and CO_2 are removed. The flow rate is adjusted via a mass-flow controller (MFC1) to below the sorption rate of the Ti getter. It then passes through a heated pipe (quartz, 700 mm long, 50 mm inner diameter) filled with 1.4 kg of Ti sponge. The center of the pipe is heated inside a furnace to 900 °C for regular samples or to 1000−1100 °C for methane-rich samples. Near the edges of the furnace the temperature drops to around 50 °C. This temperature distribution is particularly important for removing CH_4. The high temperature near the center is needed for decomposing CH_4 while the low temperature at the edges is needed for Ti to absorb the released H_2. The remaining gas after Ti gettering
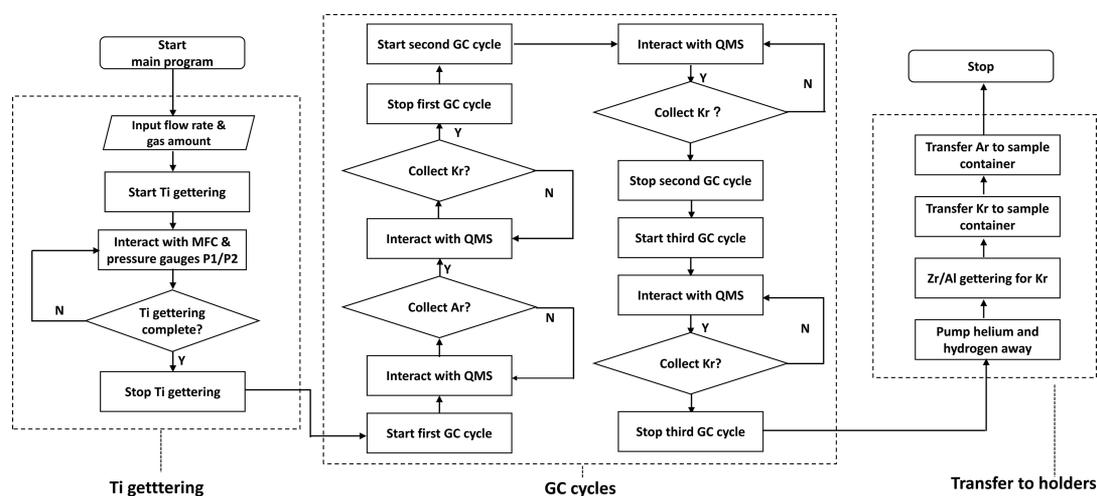
Figure 2. Flowchart of the automated separation procedure.

(mainly consisting of Ar, Ne, and Kr) exits the heated pipe and flows to the next section to be captured in trap 1 (stainless steel U-shaped tube, 30 cm long, 9 mm inner diameter, ~3 g activated charcoal) at 77 K. Neon is not trapped due to its weak adsorption on activated charcoal (AC) at 77 K[22] and is therefore not detected during the GC cycles. At a typical flow rate of 200 mL/min, it takes 10 min to feed 2 L of air into the getter, during which the pressure P2 in the heated pipe increases to about 5 mbar. It takes another 10 min for Ar and Kr to be fully captured in trap 1. More than 99% of Ar and Kr are collected in trap 1 by the time the pressure P2 has dropped to 0.1 mbar.

Gas Chromatography. The Ar and Kr are separated via gas chromatography on MS5A at room temperature. He (99.999% purity) is used as a carrier gas with a flow rate into the system of about 67 mL/min (controlled with MFC2) and is further purified with AC at 77 K (He cleaning trap). The He consumption rate is typically 2000 L in 2−3 months and can be reduced by implementing He recirculation. The GC columns are made from 3 m long stainless steel tubes of 4 mm inner diameter, filled with MS5A mesh 60−80. If not collected, the effluent from the GC columns is exhausted via a one-way valve that opens when the internal pressure is 70 mbar higher than the ambient atmospheric pressure. This way it avoids atmospheric contamination due to back flow. The columns as well as trap 2 (stainless steel U-shaped tube, 15 cm long, 4 mm inner diameter, ~0.5 g AC) and trap 1 can be connected or bypassed via three-way valves. Moreover, a QMS port is located at the outlet of the columns to monitor the separation process. A trap of activated charcoal at 77 K (rescue trap) is connected at the end of the flow path to prevent inadvertent sample loss in case of incomplete collection or unexpected interruption.

After Ti gettering, the Ar fraction is 4 orders of magnitude larger than the Kr fraction. Three GC-cycles are necessary to reduce the Ar fraction in the Kr to a few percent level. The first GC-cycle starts with trap 1 heated to 150 °C to release the trapped Ar/Kr. Then the four-way valve is switched so that He carries Ar/Kr into column 1. When almost all the gas has flowed into column 1 after about 4 min, the four-way valve is switched again so that trap 2 and trap 1 can be used to collect the GC effluent. Having been used to store Ar and Kr earlier, trap 1 is not suitable for collecting Kr due to the remaining trace amounts of Ar. However, it is suitable for collecting Ar while the clean trap 2 is used to capture Kr. When the Ar peak appears on the QMS, valves 3, 5, 4, and 8 are switched sequentially such that the Ar

fraction is collected on trap 1 now held at 77 K. At this point, the argon purification is complete.

Valves 6 and 7 are switched as soon as the Kr peak emerges on the QMS so that Kr is collected in trap 2, now held at 77 K. Following Kr collection, trap 2 is heated to 150 °C to start the second GC-cycle. Valves 1 and 2 are switched to feed the gases into the so-far unused, clean column 2. Column 1 is avoided here because trace amounts of Ar remain from the first GC-cycle. After the second GC-cycle, again trap 2 at 77 K is used to collect Kr. Similar operations are performed during the third and final GC-cycle to further purify the Kr fraction. Because more than 99% of the Ar fraction are already collected in trap 1 after the first GC-cycle, Ar is not collected on trap 1 in the second and third GC cycle but exhausted with the He flow to the rescue trap. The remaining He and H_2 are pumped away while trap 1 (containing Ar) and trap 2 (containing Kr) are held at 77 K. Then trap 2 is heated to 150 °C to release the Kr fraction to a commercial Zr/Al getter for removing the remaining traces of reactive gases. Finally, the purified krypton is collected in a small sample holder (~3 mL volume) containing activated charcoal (~0.1 g) at 77 K. The Ar fraction is already pure enough and is directly transferred from trap 1 to a sample holder (~10 mL volume, ~1 g of AC) without further gettering.

Automation. The system is automated to achieve a high sample throughput and reduce human errors. All valves in the system are pneumatic. Each trap is wrapped with an electric heater and equipped with a LN_2 cup on a pneumatic lift so that all traps can be held at 77 K or 150 °C. All valves, lifts, QMS, MFCs, heaters, and sensors (pressure gauges, thermometers) are readout and controlled by a Matlab program (Figure 2). At the start, the sample bottle as well as clean Kr/Ar containers are connected manually to the system. Before the main program starts, the amount and composition of the sample are determined manually via pressure gauge P1 and QMS, respectively. Based on the sample gas composition, a suitable flow rate and the desired amount of gas are used. From then on, the separation procedure runs automatically, including the final collection of Ar and Kr into the sample holders. Liquid nitrogen for cooling traps and holders is refilled manually, about five times per sample. Better insulation is being developed to reduce the need for refilling. A commercial system of automated LN_2 refilling is also under consideration. Cleaning the system between two samples includes heating and pumping of traps and holders while the GC columns are continuously flushed with
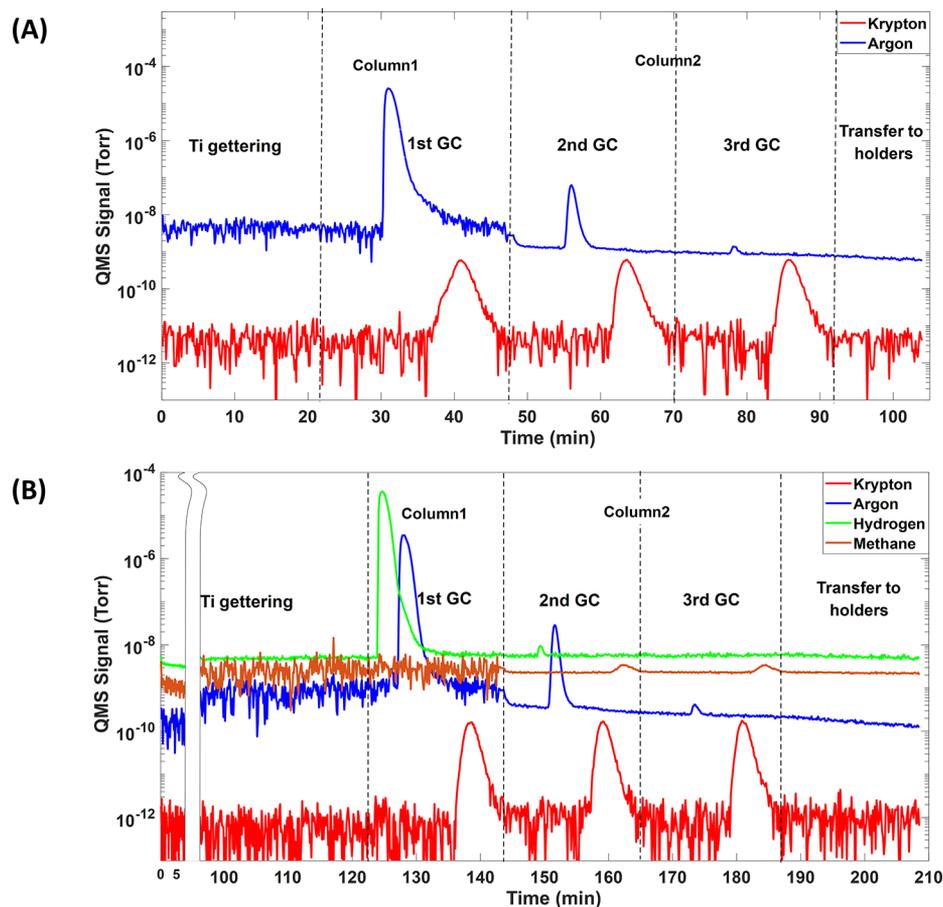
Figure 3. Chromatogram detected by the QMS port in the outlet of the columns for a typical separation of Ar and Kr from (A) 1.5 L of air and (B) 14.4 L of gas with 90% CH_4 and 10% air. The electron multiplier (EM) of the QMS is used for Kr detection all the time, whereas in the first GC-cycle all other gases are detected with the less sensitive Faraday cup due to the high partial pressure, especially of argon. After the first GC-cycle, the partial pressure of all gases except helium is low enough such that the electron multiplier can be used for higher sensitivity.

He. The titanium getter is cleaned during the gas chromatography step. The cleaning step between two samples is also automated and takes about 0.5 h.

■ RESULTS AND DISCUSSION

Titanium Gettering. Tests have been carried out to determine the performance of the Ti sponge at high temperature for gettering of air and of CH_4. Air samples with CH_4 admixtures less than 10% can be fed into the Ti getter at 900 °C with a rate up to 400 mL/min. Starting with a sample of 2 L of air, less than 1 μL of N_2 remains after the Ti getter. For a single load of 1.4 kg of Ti sponge, the getter capacity for air is measured to be 90 L, i.e., 45 standard-size (2 L) air samples. For CH_4-rich samples, i.e., when CH_4 concentrations in the bulk gas are higher than 10%, CH_4 and other reactive gases can be thoroughly absorbed at a flow rate less than 300 mL/min when operating the getter at 1000−1100 °C. Starting with a 13.2 L sample containing 90% CH_4, less than 1 μL of CH_4 remains after gettering at a temperature of 1050 °C and a flow rate of 170 mL/min. During gettering, CH_4 is decomposed into C and H_2. While the C is sorbed by the Ti sponge in the high temperature zone at the center of the pipe, the bulk of the released H_2 is absorbed below 400 °C at the margins of the pipe. The remaining H_2 leads to a pressure in the pipe of about 50 mbar, whereas the pressure would be more than 60 bar for a 30 L methane sample if no titanium sponge with a temperature <400 °C were present. After

processing a sample with >30 L of CH_4 admixture, H_2 needs to be removed from the Ti sponge, a process that takes about 1 day if performed by pumping. Alternatively, the Ti sponge can be replaced which allows for processing the next sample a few hours later. At a flow rate of 300 mL/min and a Ti temperature of 1100 °C, the capacity for pure CH_4 is determined to be 70 L.

Gas Chromatography. During the three cycles of gas chromatography, mass spectra are taken by the QMS (Figure 3). Ar is reduced by about 2 orders of magnitude with each GC-cycle, reaching a final fraction of a few percent of Kr after three cycles. There is a clear drop in the Ar baseline when switching from column 1 to column 2 following the first GC-cycle. As discussed above, this is because of the remaining argon in column 1 after the argon bulk has passed it. During the gas chromatography, no N_2 and O_2 are detected by QMS even when using the electron multiplier (i.e., their amount is less than about 1 μL), which demonstrates that the titanium getter absorbs nearly all of the reactive gases. The purification procedures start at time zero in Figure 3. For normal air samples (Figure 3(a)), the Ti-gettering step as well as one GC-cycle each take about 20 min. Adding the time for connecting the sample, evacuating the system, and sample transfer, the total time for Ar and Kr purification is 90−120 min. If only Ar separation is required, no GC-cycles are needed and then the operation time can be reduced to about 30 min.

A separation spectrum of a 13.2 L sample with 90% CH_4 and 10% air is shown in Figure 3(b). At a flow rate of about 170 mL/

Table 1. Results for Dual Separation of Kr and Ar from Pure Air Samples, Air Samples with CH$_4$ Admixture, and Gases Extracted from Groundwater (GW)^a

Gas type	Total gas	Ar				Kr			
		Content^a	Extracted	Recovery	Purity	Content^b	Extracted	Recovery	Purity
	(LSTP)	(mLSTP)	(mLSTP)	%	%	(μLSTP)	(μLSTP)	%	%
Air	0.0	0.0	<0.001	—	—	0.00	<0.01	—	—
Air	0.5	4.7	4.7	>99	>99	0.55	0.52	95	91
Air	0.9	8.4	8.4	>99	>99	0.99	0.94	95	92
Air	1.8	16.8	16.7	>99	>99	1.98	1.89	95	96
Air	2.7	25.2	25.0	>99	>99	2.97	2.81	95	99
Air	3.7	34.6	34.4	>99	>99	4.07	3.84	94	97
20% CH$_4$	2.1	15.7	15.6	>99	>99	1.85	1.73	94	94
50% CH$_4$	2.7	12.6	12.6	>99	>99	1.49	1.40	94	96
90% CH$_4$	13.2	12.3	12.3	>99	>99	1.45	1.37	94	94
95% CH$_4$	50.8	23.7	23.5	>99	>99	2.79	2.66	95	91
GW1^{cd}	2.3		38.7		>99		7.51		98
GW2^e	40.1	—	21.3	—	>99	—	2.35	—	91
GW3^f	46.4		17.0		>99		1.83		97

^{a}The uncertainty for the recovery and purity is 4% for Kr and 2% for Ar. ^{b}Values calculated using the Ar concentration of 0.934% in the atmosphere. ^{c}Values calculated using the Kr concentration of 1.10 ppmv in the atmosphere. ^{d}For the gas extracted from groundwater, the recovery for Ar and Kr cannot be determined, as the initial amount is not known. ^{e}Gas composition: 70% N$_2$, 20% CO$_2$, 10% CH$_4$. ^{f}Gas composition: 6% N$_2$, 41% CO$_2$, 53% CH$_4$. ^{g}Gas composition: 2% N$_2$, 8% CO$_2$, 90% CH$_4$.

min for Ti gettering, almost all of the CH$_4$ is removed, but a small amount of the H$_2$ remains. After two GC-cycles, the H$_2$ fraction is removed and it has no effect on the recovery or purity of Ar and Kr. A few microliters of CH$_4$ are detected with the electron multiplier during the second and third GC-cycle. Due to the overlap of Kr and CH$_4$ after passing the MS5A column, these trace amounts of CH$_4$ cannot be separated from Kr via gas chromatography but can later be removed by a Zr/Al getter.

Recovery and Purity of Ar and Kr. Air samples of 0.5−4 L, samples with CH$_4$ content of 20%, 50%, 90%, and 95%, as well as gas samples extracted from groundwater have been processed to test and demonstrate the performance of the system. The Kr recovery and purity have been determined by measuring the final Kr amount in a calibrated vacuum system with a QMS while the total gas amount is determined with a pressure gauge in a calibrated volume. The initial Kr amount has been calculated given the atmospheric Kr concentration of 1.10 ppmv.[23] The impurity in the separated Kr is almost entirely caused by Ar, as other impurities were not detected. Thus, the Kr purity can also be determined by measuring the Ar fraction. The two methods yield similar Kr purities within ±5% uncertainty. The purity of the recovered Ar has been determined with a QMS. Because the obtained purities are all >99%, the Ar recovery is determined barometrically with a calibrated volume and the given atmospheric Ar concentration of 0.934%. Besides the prepared test samples, three gas samples extracted from groundwater have also been purified (Table 1). Sample GW1 contains only small amounts of CO$_2$ and CH$_4$ (20% and 10%, respectively) with a total gas amount of 2.3 L. GW2 and GW3 have large gas amounts of 40.1 and 46.4 L, respectively. GW2 mainly consists of CO$_2$ (41%) and CH$_4$ (53%) while containing only 6% N$_2$. GW3 mainly consists of CH$_4$ with a concentration of 90%. All of these groundwater samples have been processed following the same procedure as the test samples.

The purification results for all samples are compiled in Table 1. For the prepared samples, both purity and recovery are >90%

for Kr and >99% for Ar, even for the test sample with a gas amount of 50.8 L and a CH$_4$ concentration of 95%. The total separation time is about 2 h for all of the samples except the 90% CH$_4$ test sample (13.2 L) and the 95% CH$_4$ test sample (50.8 L), for which the separation times are 3.5 and 5 h, respectively. To measure the contamination of the separation system, the purification procedure has been carried out without feeding air into the system (first row in Table 1). The obtained argon and krypton amounts are below the detection limit and thus demonstrate that contamination is negligible. This result has been confirmed by numerous samples that were measured by ATTA to be free of ^{85}Kr (i.e., smaller than the detection limit of around 1 dpm/cc) since the commissioning of the purification system in December 2018. For the groundwater samples, the initial amounts of argon and krypton are not known so the recovery cannot be determined. The purity is >90% for Kr and >99% for Ar, similar to the test samples. Apart from 20 L of CH$_4$, sample GW2 also contains 16 L of CO$_2$, which does not seem to influence the purification. This is expected because the titanium-gettering speed for CO$_2$ at 900−1100 °C is a factor 2−24 higher than for N$_2$.[17]

■ CONCLUSIONS

An automated system for the dual separation of krypton and argon from environmental samples based on titanium gettering and gas chromatography has been realized. Atmospheric samples of 0.5−4 L STP have been processed to test the performance of the system, reaching both purities and recoveries of >90% for krypton and >99% for argon within 90−120 min of processing time. Samples with methane admixtures of 0.4−48 L STP have been processed within 2−5 h without compromising recovery or purity. Up to 46 L STP gas samples extracted from groundwater with up to 90% methane content were purified similarly. The present system allows processing of at least three airlike samples within a regular 8 h working day. For samples

with extraordinarily high methane content of more than 30 L STP, only one sample can be processed per day due to the time needed for removing hydrogen from the titanium, which can be shortened significantly by providing additional pumping. A single load of 1.4 kg of titanium sponge has a capacity for at least 90 L of air at a flow speed of 400 mL STP/min and a temperature of 900 °C. In practice, this means that the titanium needs to be replaced after processing about 45 standard 2 L STP samples. For pure methane gas, the capacity has been determined to be at least 70 L STP at a flow speed of 300 mL STP/min and 1100 °C.

This purification system represents an essential contribution to enable the coming large-scale applications of radio-krypton and radio-argon dating of environmental samples. The high methane tolerance greatly simplifies the application on ground-water rich in methane, a case often encountered especially in paleo-groundwater studies. Moreover, the high recovery over the entire sample range including small samples (<1 L STP) is of crucial importance for applications such as dating of deep ice cores.

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Notes
The authors declare no competing financial interest.

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