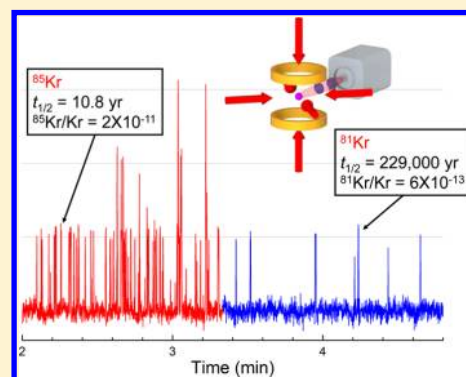


Analysis of Krypton-85 and Krypton-81 in a Few Liters of Air

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ABSTRACT: Long-lived radioactive krypton isotopes, ^{81}Kr ($t_{1/2} = 229\,000$ year) and ^{85}Kr ($t_{1/2} = 10.76$ year), are ideal tracers. ^{81}Kr is cosmogenic and can be used for dating groundwater beyond the ^{14}C age. ^{85}Kr is a fission product and can be applied in atmospheric studies, nuclear safety inspections, and dating young groundwater. It has long been a challenge to analyze radio-krypton in small samples, in which the total number of such isotopes can be as low as 1×10^5 . This work presents a system developed to analyze ^{81}Kr and ^{85}Kr from a few liters of air samples. A separation system based on cryogenic distillation and gas chromatographic separation is used to extract krypton gas with an efficiency of over 90% from air samples of 1–50 L. $^{85}\text{Kr}/\text{Kr}$ and $^{81}\text{Kr}/\text{Kr}$ ratios in krypton gases are determined from single-atom counting using a laser-based atom trap. In order to test the performance of the system, we have analyzed various samples collected from ambient air and extracted from groundwater, with a minimum size of 1 L. The system can be applied to analyze ^{81}Kr and ^{85}Kr in environmental samples including air, groundwater, and ices.



Noble gas isotopes are ideal tracers because of their chemically inert character and very simple mechanism of transportation and mixing in the environment. Two radioactive krypton isotopes, krypton-85 and krypton-81, have been of particular interest for decades in various studies. ^{81}Kr (half-life time $t_{1/2} = 229\,000$ year)¹ is cosmogenic in origin, spatially homogeneous, and temporally constant in the atmosphere. Anthropogenic and subsurface production of ^{81}Kr is negligible; therefore, it is ideal for dating groundwater and ices in the age range of 5×10^4 to 1×10^6 years. Extensive studies in this age range have been performed using ^{36}Cl which has a close half-life time ($t_{1/2} = 301\,000$ year). However, subsurface production and multiple transport processes complicate the interpretation of the ^{36}Cl data. ^{85}Kr (half-life time $t_{1/2} = 10.76$ year)² is a fission product and mainly released during the nuclear fuel reprocessing activities in the northern hemisphere.³ The interhemispheric exchange time has been estimated to be 1.1 years.⁴ Since 1945, the content of ^{85}Kr in the atmosphere has increased steadily by 6 orders of magnitude. ^{85}Kr has been used for validation and calibration of atmospheric transport models,⁵ dating groundwater in the age range of 2–50 years,⁶ and as an indicator for a clandestine plutonium separation.³

Krypton is present in the atmosphere with a concentration of 1.14 ppmv (part per million in volume) and about 0.1 $\mu\text{L}/\text{kg}$ in groundwater.⁷ The global atmospheric inventory of ^{85}Kr has been estimated to about 5.5×10^{18} Bq by the end of 2009,⁸ which corresponds to an atmospheric ratio of $^{85}\text{Kr}/\text{Kr} \approx 2.2 \times 10^{-11}$. The ratio of $^{81}\text{Kr}/\text{Kr}$ in the atmosphere has been determined to be $(6.2 \pm 0.7) \times 10^{-13}$ and $(4.9 \pm 0.3) \times 10^{-13}$ from low-level counting (LLC) measurements^{9,10} and $(5.3 \pm 1.2) \times 10^{-13}$ from an accelerator mass spectroscopy (AMS)

measurement.¹¹ There are about 700 000 ^{85}Kr atoms and 20 000 ^{81}Kr atoms in 1 L of modern air or in 10 kg of modern groundwater. Low abundances make it a challenge to detect ^{81}Kr and ^{85}Kr atoms, particularly when the sample size is limited.

The presence of ^{85}Kr atoms can be measured directly through counting the decay rays they emit. Typical sample size for LLC measurements of ^{85}Kr is 50 μL of krypton gas at the standard temperature and pressure (STP),¹² which corresponds to an air sample size of 50 L. Because ^{81}Kr has a much longer lifetime than ^{85}Kr , LLC measurement of ^{81}Kr is impractical. AMS has been applied to measure ^{81}Kr using 500 μL of krypton gas sample which was extracted from 16 ton of groundwater.^{11,13} The large sample size makes it difficult for wide applications using ^{81}Kr as a tracer. Some laser-based methods have been developed for trace isotope analysis, such as resonance ionization mass spectrometry (RIMS)^{14–17} and photon burst mass spectrometry (PBMS).¹⁸ Atom trap trace analysis (ATTA) is an emerging technique detecting rare isotopes by counting individual atoms in a magneto-optic trap.¹⁹ The necessary krypton sample size for ^{81}Kr and ^{85}Kr detection with ATTA has been recently reduced to a few microliters.^{20,21}

Prior to the measurement of ^{81}Kr or ^{85}Kr , it is essential to separate krypton gas from air samples. It should be of high efficiency to prevent any possible isotopic distillation during the separation. It should also be airtight avoiding contamination

Received: January 29, 2014

Accepted: March 19, 2014

Published: March 19, 2014

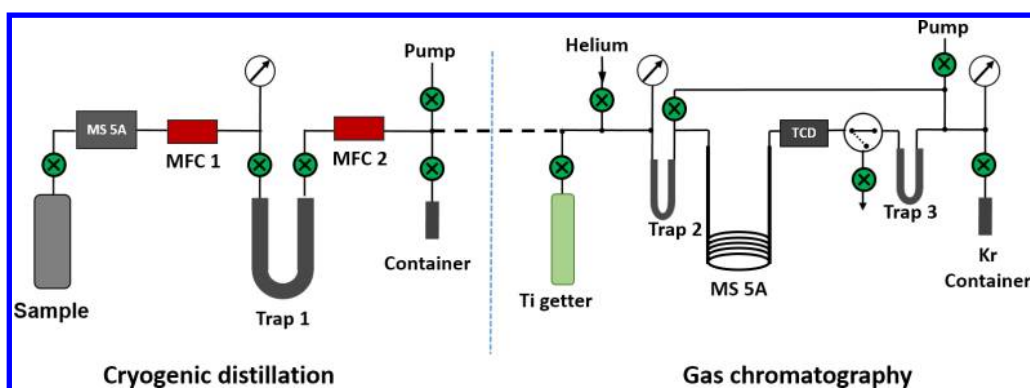


Figure 1. Diagram of the krypton purification system: MS, molecular sieve; MFC, mass flow controller; TCD, thermal conductivity detector; trap, liquid-nitrogen frozen trap filled with activated charcoal.

from ambient air. There have been reports on the separation systems for recovering krypton from gas samples using cryogenic distillation, titanium gettering, gas chromatographic separation, or a combination of these methods.^{13,22–27} The sample size varies from several hundred liters down to 5 L with a Kr recovering efficiency of about 80%.^{28,29} However, there is a need to recover krypton efficiently from smaller samples. The present ATTA instruments handle typically 5–10 μL of krypton gas which can be recovered from air samples of 5–10 L. By improving the detection efficiency and eliminating the cross-sample contamination effect in the ATTA measurements,^{20,21,30} the sample size can be potentially reduced to 1 L of air or even less.

Here we present a system developed in Hefei (China) to analyze radio-krypton in small air samples. A procedure combining cryogenic distillation and gas chromatography is applied to separate krypton gas of microliters from air samples of 1–50 L. A krypton recovering efficiency of over 90% has been achieved, which was tested with air samples of different sizes between 1 and 20 L. The concentrations of ^{81}Kr and ^{85}Kr in the samples are determined from single-atom counting by the ATTA apparatus built in Hefei. As a demonstration, the radio-krypton concentrations have been determined for a few samples, including ambient air and gases extracted from groundwater samples.

EXPERIMENTAL SECTION

Krypton Purification. The purification process is applied to recover krypton gas of microliters from liters of gas samples which have been collected from ambient air or extracted from air-solvated groundwater, seawater, or ices. The “air” samples extracted from groundwater may have reduced concentration of oxygen but sometimes excess CO_2 or CH_4 due to processes including biological activity and water–rock reactions. The schematic configuration of the krypton purification system is shown in Figure 1. It takes about 3–4 h to finish the whole process, which includes two steps as follows.

Cryogenic Distillation. The air sample first passes through a molecular sieve 5A to remove carbon dioxide and water vapor. The dried air is then trapped in a liquid-nitrogen frozen trap (trap 1, 200 cm^3 volume) filled with activated charcoal (grain size, no. 16-32; 4 g). A mass flow controller (MFC 1) is used to monitor the flow rate and therefore the total volume of the gas trapped in trap 1. It takes about half an hour to condense 10 L of air in trap 1. The residual gas above trap 1 is slowly pumped out through a 6 mm tube by a rotary pump, with a pumping

rate of about 0.2 L/min, also constrained by a mass flow controller (MFC 2). When most of the nitrogen and oxygen in trap 1 has been pumped out, there will be a drop on the readings given by MFC 2, which is illustrated in Figure 2. A gas

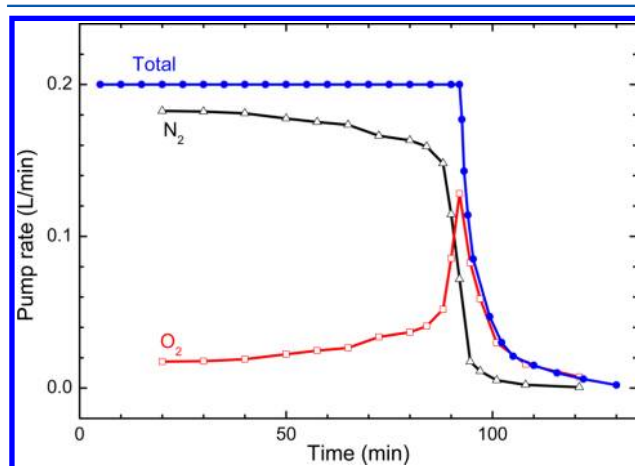


Figure 2. Typical pumping rates during the cryogenic distillation process. A 20 L air sample was used. The total pumping rate (solid circles) was constrained to be below 0.2 L/min by a mass flow controller. The open triangles and open squares stand for the pumping rates of N_2 and O_2 , respectively.

chromatographic analysis shows that the exhaust gas was mainly nitrogen at the beginning of the pumping. Then oxygen started to be pumped out from the trap, and after a few minutes, the total pumping rate dramatically decreased. We stop pumping at this moment.

The cryogenic distillation process applied here can reduce the size of residual gas to about 0.1 L without any detectable loss of krypton. The process presented here is considerably simpler than those given in refs 24–28. No precise temperature control except the liquid nitrogen is used. We have also tried to monitor the components in the exhaust gas using a quadrupole mass spectrometer (RGA 100, Stanford Research Systems), but using the drop of pumping rate as an indicator to finish the distillation process is considerably more convenient. From the readings given by the two mass flow controllers (MFC 1 and MFC 2), we can also estimate the size of the distillation residue condensed in trap 1, avoiding potential high pressure before removing liquid nitrogen from trap 1. Typical size of the distillation residue is 0.1 L. Note that CH_4 cannot be separated by cryogenic distillation. In case of CH_4 -rich samples, the size

of the distillation residue will be considerably larger. CH₄ in the residue can be removed following the method developed in University of Bern, by passing the gas through a furnace (840 °C) containing CuO.¹³

Gas Chromatography Separation. The distillation residue of 100 mL is released by heating trap 1 to about 300 °C. The gas is sent slowly at a flow rate of about 20 mL/min into a stainless steel chamber containing a Ti-getter pump (Nanjing Huadong Electronics Co.) working at about 500 °C. Residual active gases including O₂, hydrocarbon molecules, and most N₂ are removed. The size of the residual gas, mainly consisted of argon and N₂, has been reduced to about 10 mL. The gas is transferred to a liquid-nitrogen trap (trap 2, 10 cm³ volume) filled with activated charcoal (grain size, no. 16-32; 1 g), being ready for the chromatographic separation.

The chromatographic column filled with molecular sieve (MS 5A, grain size, no. 60-80; diameter, 6 mm; length, 2 m) is operated at room temperature, and pure helium is used as the carrier gas. A thermal conductivity detector (TCD) is used to monitor the characteristic elution peaks of various gas components. A typical TCD signal of the gases released from the chromatography is shown in Figure 3. The O₂ peak

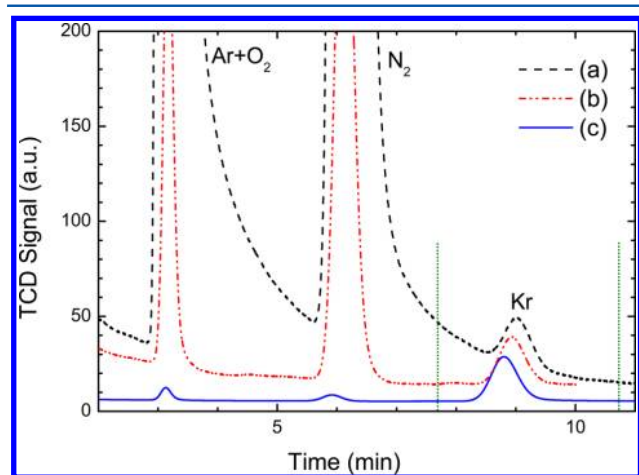


Figure 3. Example of the gas chromatography of a gas sample: (a) after the cryogenic distillation process but before GC separation; (b) after the first run of GC separation; (c) after the second run of GC separation. Two vertical dotted lines indicate the time range for krypton gas collection during the GC separation.

overlaps with the Ar peak, and the krypton peak emerges after the N₂ peak. Once the N₂ peak has passed the column completely (typically 8 min after the start), the gas is sent to the third liquid-nitrogen trap filled with activated charcoal (trap 3). A second run of chromatographic separation is applied to completely separate the krypton gas. The results after each GC process are illustrated by the TCD signals shown in Figure 3. After the GC separation, krypton becomes the dominant component in the collected gas, which is ready for the ATTA measurement.

ATTA Measurement. The configuration of the ATTA instrument has been presented in previous studies,^{21,31} and it will be only briefly described here. The sample gas is introduced to a liquid-nitrogen-cooled ceramic tube where an rf-driven discharge excites krypton atoms to the metastable state ($5s[3/2]_2$, denoted as Kr*). The typical sample size for ATTA measurements is 8 μ L (STP) of krypton gas. If only a smaller sample is available, the krypton gas will be premixed

with some pure xenon gas before the measurement, in order to sustain the discharge. The atomic beam is transversely cooled by a resonating 811 nm laser beam, and then slightly focused.³² Subsequently, Kr* atoms are slowed down in a Zeeman slower and then trapped in a magneto-optic trap (MOT) about 2 m downstream from the discharge. By tuning the laser frequency, we can selectively trap different isotopes in the MOT. Typically, about 10⁸ ⁸³Kr (isotopic abundance 11%) atoms can be trapped simultaneously in the MOT, and the fluorescence emitted by the trapped atoms can be detected by a photodiode. For rare radioactive isotopes, ⁸¹Kr and ⁸⁵Kr, only individual atoms will be trapped at a time, and the image of the trapped rare isotopes will be observed by an electron-multiplied charge-coupled device (EMCCD).

During the ATTA measurement, the trap is iteratively switched between an abundant stable isotope (⁸³Kr) and the rare isotopes (⁸⁵Kr and ⁸¹Kr). Figure 4 shows a typical time

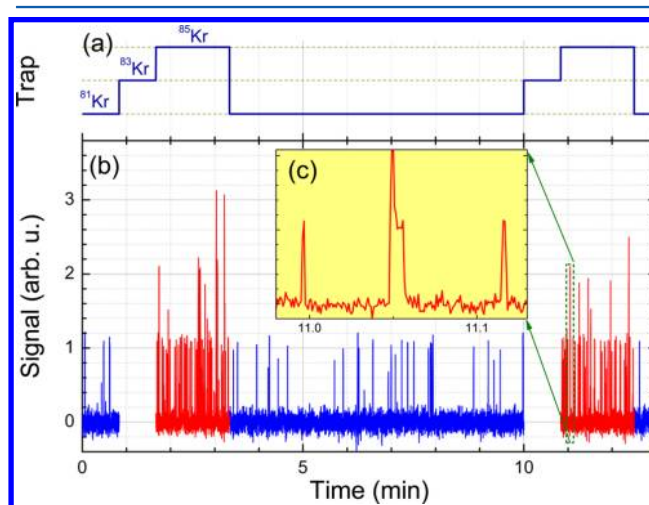


Figure 4. (a) Control sequence of the ATTA measurement. By tuning the laser frequency, one isotope will be trapped at a time. (b) The integrated fluorescence signal of trapped ⁸¹Kr (blue curve) and ⁸⁵Kr (red curve) atoms. In the blank region, ⁸³Kr is trapped and the loading rate of the abundant ⁸³Kr atoms is measured. The inset (C) shows a sample piece of the data recorded in several seconds. Four ⁸⁵Kr atoms were trapped during this time range.

sequence of the measurement and an example of the recorded signals of single-atom counting. Because the concentration of ⁸⁵Kr in the sample is much higher than ⁸¹Kr, quite often there are two (even three) ⁸⁵Kr atoms trapped simultaneously, while the situation is seldom for ⁸¹Kr. The counting rate of the rare isotopes, number of atom counts divided by the length of the time slot, will be further normalized by the measured loading rate of ⁸³Kr to eliminate the drift of the trapping efficiency. We have shown that the “normalized” single-atom counting rate is proportional to the isotopic abundance with an experimental uncertainty of about 3%.³¹ The uncertainty mainly comes from the statistical fluctuation due to limited counts of single atoms. The isotopic concentration (⁸⁵Kr/Kr or ⁸¹Kr/Kr) in the sample is expressed with the relative ratio between the studied sample and the “standard” krypton sample from a commercial gas bottle bought in 2007 (denoted as “2007 bottle”). The ⁸⁵Kr/Kr concentration of the “2007 bottle” sample has been determined to be 1.54(4) $\times 10^{-11}$ from a comparison between the ATTA measurements and LLC measurements.²¹ Note that the ⁸⁵Kr/Kr concentration of the “2007 bottle” sample is decreasing due

to the decay of ^{85}Kr ($t_{1/2} = 10.76$ year), and the value given above corresponds to the value in June 2013.

RESULTS AND DISCUSSION

Efficiency of Kr Extraction. The efficiency of the krypton extraction process was tested by using several air samples with volumes varying from 1 to 20 L (STP). The same process was applied for all the samples. The sizes of the Kr gases obtained from different samples were determined from the gas pressure measured by an absolute pressure gauge (MKS Baratron 627B, relative accuracy of 0.12%). The constituents in the obtained “purified” krypton gases were determined from GC measurements. The GC data are shown in Figure 5. Besides the krypton

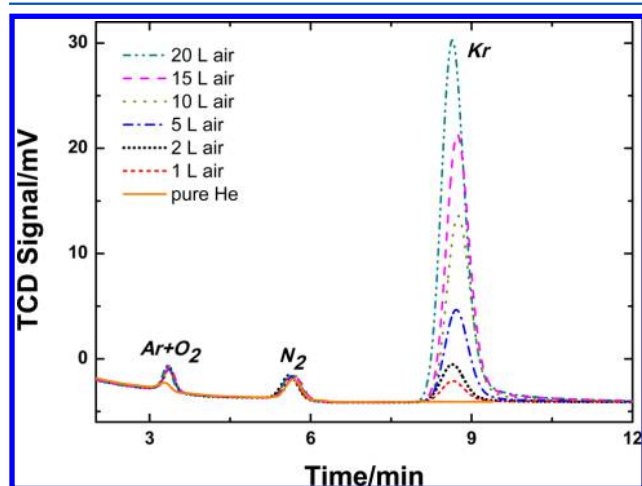


Figure 5. Gas chromatography of the krypton gases purified from air samples of different sizes. The curve at the bottom is from a blank sample (pure helium).

peak, a peak of N_2 and an overlapping peak due to argon and O_2 (noted as “Ar + O_2 ” in the figure) are also present in the spectra. Since the same N_2 peak and a smaller Ar + O_2 peak present in the “zero” sample (pure helium), they are attributed to the air leaking during the chromatography measurements. The larger Ar + O_2 peaks in the spectrum of air samples indicate the presence of argon in the “purified” Kr samples. There are possibly two sources of the argon in the sample: One is due to the long tail of the Ar peak in the chromatography; thus a small amount of argon has been collected during GC separation. The other one is due to the air leaking during the collection. Since the concentration of krypton in ambient air is only about 1/10000 of that of argon, the concentration of the “contaminated” krypton due to air leaking can be neglected in the final “purified” krypton samples (<0.01%).

After the calibration of the chromatography data, the relative purity of krypton in a sample can be derived from the integrated areas under the peaks shown in Figure 5. The purity of the obtained Kr gas and overall extraction yield ratio for each sample are given in Table 1. The mean concentration of krypton in the earth’s atmosphere, 1.14 ppmv, was used to calculate the total Kr in original air samples. For all the six test samples, the yield ratios are over 90%. The yield ratio decreases with a few percent for an increasing sample size, probably because of the cutoff loss due to the limited collection time (3 min for the samples of 1–15 L and 5 min for the one of 20 L) in the GC separation. It is likely the only source of krypton loss in our purification system, since we could not detect any

Table 1. Constituents in the Extracted Gases from Air Samples of Different Sizes^a

air (L)	Kr content (μL) ^b	extracted gas (μL)		
		Kr	Ar	Kr yield (%)
1	1.14	1.1	0.4	97
2	2.28	2.2	0.5	97
5	5.70	5.5	0.4	96
10	11.4	10.8	0.5	94
15	17.1	15.6	0.5	91
20	22.8	21.2	0.6	93

^aThere is a 2% uncertainty in the given experimental values.

^bCalculated values, using the krypton concentration value of 1.14 ppmv in the atmosphere.

krypton in the exhaust gas pumped out during the cryogenic distillation process. We note that there is an almost constant constituent of argon (0.4–0.6 μL) in the obtained purified krypton gases. Using a longer collection time in GC separation will reduce the loss of krypton, but it may also leave more argon in the collected gas. Since the residual argon does not change the relative ratio between the radio-krypton and the stable krypton, therefore no influence on the ATTA measurements, we do not apply further efforts to remove the argon impurities.

Radio-Krypton in Ambient Air and Groundwater Samples. The concentrations of ^{85}Kr and ^{81}Kr in different samples were analyzed by ATTA, and the results are given in Table 2. The “2007 bottle” sample is taken as a relative standard, and the corresponding values are set to be 1.00. Note that about 32% of the ^{85}Kr atoms in the “2007 bottle” gas have decayed in last 6 years. Three ambient air samples, including two from Hefei (inside and outside the laboratory) and one from a field campaign (Gansu, China), were analyzed. The derived $^{85}\text{Kr}/\text{Kr}$ ratios are very close to each other but about 40% higher than the “2007 bottle” sample. Note that the size of the Gansu air sample is very small (0.95 L air), which results with less single-atom counts and relatively larger uncertainty in the obtained abundances of rare isotopes.

Two samples extracted from groundwater have also been analyzed. One was from a shallow groundwater, and the other one was from a deep groundwater. Gases solved in the groundwater samples were extracted by spraying the water into a vacuum chamber, using an apparatus similar to that presented by Smethie and Mathieu.²² Sizes of the extracted “air” and krypton gases are given in Table 2. The “air” samples extracted from groundwater contain about 98% nitrogen and 2% argon, while oxygen was completely depleted. Note that the relative ratios between the obtained krypton and the whole “air” extracted from groundwater samples are 3.3 and 3.9 ppmv, respectively, considerably higher than that in the ambient air. The numbers agree with the relative ratio of the water solubilities between krypton and nitrogen, which is roughly 4:1 at a temperature of about 15 °C,³³ indicating that most krypton in the samples should have been recovered.

$^{85}\text{Kr}/\text{Kr}$ and $^{81}\text{Kr}/\text{Kr}$ concentrations in the groundwater samples were determined, and they are given in Table 2. Compared with the respective $^{85}\text{Kr}/\text{Kr}$ and $^{81}\text{Kr}/\text{Kr}$ ratios in ambient air samples, the shallow groundwater sample has lower (about 1/5) $^{85}\text{Kr}/\text{Kr}$ but a same $^{81}\text{Kr}/\text{Kr}$ ratio, while the deep groundwater sample has almost no ^{85}Kr but very low $^{81}\text{Kr}/\text{Kr}$. The information can be applied to derive the ^{85}Kr (or ^{81}Kr) age of the groundwater. The last example also indicates that a good airtight seal has been maintained during the whole process of

Table 2. ^{85}Kr Isotopic Abundances in Different Samples Measured by ATTA

sample ID	note	date	total gas (L)	extracted Kr (μL)	$^{85}\text{Kr}/\text{Kr}$ arb. unit ^a	$^{81}\text{Kr}/\text{Kr}$ arb. unit ^a
10000	2007 bottle	June 2013			1.00	1.00
10016	air (Hefei)	Aug 26, 2013	10	10.6	1.42 \pm 0.06	
10018	air (in lab)	Oct 14, 2013	10	10.9	1.41 \pm 0.07	1.06 \pm 0.07
10021	air (Gansu)	Nov 04, 2013	0.95	1.0	1.33 \pm 0.11	0.87 \pm 0.14
10020	groundwater ^b	Oct 30, 2013	1.8	6.0	0.25 \pm 0.03	1.08 \pm 0.09
10023	groundwater ^c	Dec 05, 2013	4.7	18.4	<0.01	0.12 \pm 0.02

^aTaking the value of the "2007 bottle" sample as 1.00. ^bAir sample extracted from 90 L of shallow groundwater. ^cAir sample extracted from 300 L of deep groundwater.

sample extraction and ATTA measurement, since a small contamination from the ambient air will result with an evident ^{85}Kr concentration. Analysis of the groundwater samples obtained in the field campaigns will be presented in separate studies.

CONCLUSIONS

We present a system for analysis of the radio-krypton, ^{81}Kr ($t_{1/2} = 229\,000$ year) and ^{85}Kr ($t_{1/2} = 10.76$ year), in environmental samples. Krypton gas of microliters can be extracted from air samples of 1–50 L, using a purification system based on cryogenic distillation and gas chromatographic separation. The cryogenic distillation procedure reduces the sample size from several tens of liters to about 100 mL. A following gas chromatography separation process removes residual impurities from the sample. Tests with air samples show that over 90% of krypton can be recovered. Note that the cryogenic distillation step can be processed in a guest institute or even in the field if liquid nitrogen is available. An obvious advantage is that a small krypton-enriched sample (0.1 L) will be considerably easier to transport, since no pressure container is needed. Using an atom trap system, individual radio-krypton atoms (^{81}Kr and ^{85}Kr) in the extracted krypton gas are counted to derive the relative abundances in the gas. A series of gas samples including ambient air and gases extracted from shallow and deep groundwater have been analyzed to test the whole system. ^{81}Kr and ^{85}Kr concentrations in these samples were determined, and the results confirm the quantitative reliability of the system. The system is ready for radio-krypton analysis of environmental samples, such as air, groundwater, and ices.

The present typical sample size for ATTA measurements is several microliters of krypton (STP), which is equivalent to the air samples of several liters. We have also demonstrated to measure smaller air samples down to 1 L. At present, the sample size is mainly limited by the cross-sample contamination effect.²⁰ The method to prepare metastable krypton atoms using all-optical excitations, which is under development in various laboratories,^{34,35} may potentially eliminates cross-sample contamination and dramatically increases the single-atom counting efficiency of the ATTA instruments. Therefore, the necessary sample size can be further reduced, which will create more applications in geosciences.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is jointly supported by the NSFC (91221304, 21225314, and 41102151) and by the NBRPC (2013BAK12B00 and 2013CB834602). Zong-Yu Chen from CAGS is acknowledged for providing the groundwater samples.

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