RESEARCH ARTICLE

Krypton Separation from Ambient Air for Application in Collinear Fast Beam Laser Spectroscopy

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Abstract

A portable apparatus for the separation of krypton from environmental air samples was tested. The apparatus is based on the cryogenic trapping of gases at liquid nitrogen temperature followed by controlled releases at higher temperatures. The setup consists of a liquid nitrogen trap for the removal of H_2O and CO_2, followed by charcoal-filled coils that sequentially collect and release krypton and other gases providing four stages of gas chromatography to achieve separation and purification of krypton from mainly N_2, O_2, and Ar. Residual reactive gases remaining after the final stage of chromatography are removed with a hot Ti sponge getter. A thermal conductivity detector is used to monitor the characteristic elution times of the various components of condensed gases in the traps during step-wise warming of the traps from liquid nitrogen temperatures to 0 °C, and then to 100 °C. This allows optimizing the switching times of the valves between the stages of gas chromatography so that mainly krypton is selected and loaded to the next stage while exhausting the other gases using a He carrier. A krypton separation efficiency of ~80 % was determined using a quadrupole mass spectrometer.

Key words: Fast beam laser spectroscopy, Krypton, Time-of-flight ion mass spectrometry

Introduction

Atmospheric krypton constitutes 1 ppm of the earth's atmosphere by volume. Krypton has six stable isotopes having the relative abundances: ^{78}Kr(0.355 %), ^{80}Kr (2.286 %), ^{82}Kr(11.59 %), ^{83}Kr(11.50 %), ^{84}Kr(56.99 %), and ^{86}Kr(17.28 %) [1]. Krypton also has two long-lived and extremely low-abundance radioactive isotopes, ^{81}Kr and ^{85}Kr. Kypton-81 ($\tau_{\frac{1}{2}} = 229000$ years) is produced in the atmosphere by cosmic ray-induced spallation and neutron activation of stable krypton. The atmosphere can be considered as the only major reservoir of ^{81}Kr on Earth. Due to its long half-life, short-term fluctuations in the cosmic ray intensities (hence, the production rates of ^{81}Kr)

are averaged, and consequently the ^{81}Kr/Kr ratio $(5.2\pm0.4)\times10^{-13}$ is constant [1]. In addition, ^{81}Kr is present in surface water and is expected to decrease in groundwater along a water flow line because of radioactive decay. Consequently, the measured ^{81}Kr/Kr ratio gives a direct measure of the mean age of the groundwater on a time scale from ~50,000 to a million years [2, 3]. The measurement of ^{81}Kr in a groundwater sample was first demonstrated using several isotopic enrichment steps followed by resonance ionization and time-of-flight (TOF) mass spectrometry [4]. Due to the very low abundance of ^{81}Kr in groundwater, namely about 1200 atoms/L in modern water, these first measurements employed static mass spectrometers, similar to the type of spectrometer used in this work, for all processing steps. Therefore, gas extracted from less than 50 L of water was sufficient, but systematic effects from the enrichment steps limited the accuracy [2–4]. Otherwise, large sample volumes

are required. After demonstrating measurement of the [81]Kr concentration in atmospheric Kr using an accelerator mass spectrometry (AMS) technique [5], Collon et al. [3] validated the method by dating very old groundwater from the Great Artesian Basin in Australia by extracting gas from 16,000 L of water. More recently, a laser-based atom trap method [6] was used to measure the age of groundwater from the Sahara using 2000 L of water per measurement [7].

Presently, and in contrast to [81]Kr, the majority of [85]Kr $\left({}^{85}\mathrm{Kr} / \mathrm{Kr} \approx 10^{-12}, \ \tau_{\frac{1}{2}} = 10.8 \ \text{years} \right)$ is manmade, and stems from nuclear testing and as an effluent from nuclear reactors, where it is a byproduct of fission processes involving [235]U and [239]P [8]. Its release into the atmosphere has also been identified with reprocessing of nuclear fuel. Monitoring atmospheric [85]Kr concentrations is of interest because it gives information on the degree of military and civil nuclear activities. It can be used to assess the amount of environmental contamination due to neighboring nuclear facilities, and it serves as an early indication of nuclear weapons activity [9, 10]. Also, [85]Kr is useful for dating relatively young reservoirs of groundwater with a residence time of several tens of years [2, 11–13]. In addition, since it does not occur naturally and is not subject to chemical or biological reactions, [85]Kr is being used as a tracer in several applications, which include exploring the structure of petroleum reservoirs [14], ventilation studies, flow rate measurements, and leak testing [15].

While applications involving [85]Kr and [81]Kr are important and attractive, the task of analyzing isotopes at a relative abundance less than 10^{-9} is an experimental challenge. Low level counting (LLC) [16] and AMS [17, 18] were the only two practical methods for decades until the recent advancements and achievements in methods based upon laser spectroscopy techniques. Resonance ionization mass spectrometry (RIMS) [18–21] and photon burst mass spectrometry (PBMS) [22–24] are two such laser-based methods applied in the 1970s. A more recent laser-based method, atom trap trace analysis (ATTA) [25], was demonstrated and used to detect [81]Kr and [85]Kr in natural atmospheric samples at the isotopic abundance level of 10^{-12}. Moreover, collinear fast beam laser spectroscopy (CFBLS) [26, 27] has evolved into a powerful tool of ultrasensitive rare isotope detection [28, 29]. It offers high sensitivity and selectivity due to several main features [30]. First, mass separation of isotopes can be easily incorporated. Secondly, Doppler broadening of the spectral lines can be practically eliminated by velocity bunching. An artificial isotope shift introduced by accelerating the ions to a large energy further separates the spectral lines of different isotopes. Finally, the ions can be converted into neutral atoms by charge exchange collisions, readily allowing for optical excitation of an atomic beam in and around the visible region. This is easily implemented compared with the excitation necessary for ion beams or ground-state atoms, which require radiation in the UV or VUV spectral range.

The first step towards analyzing isotopes at the abundance level of 10^{-11} for [85]Kr and 10^{-12} for [81]Kr is the separation of all krypton isotopes from an air sample. A number of separation systems, which recover krypton from air, are known [31–38]. In earlier setups, the total number of krypton atoms was measured [31], while in the recent ones [33], radioactive decay counting was implemented. In these later experiments, beta rays emitted from [85]Kr were measured by using either liquid scintillation counting [35, 37] or proportional counting [36]. To isolate sufficient amount of [85]Kr requires processing of large sample volumes (i.e., in Reference [37] 1000 L were used).

In this paper, we present results of krypton separated from atmospheric gas samples using a portable krypton separation apparatus. The apparatus was obtained from the Institute for Rare Isotope Measurements at the University of Tennessee. This system had been modified and improved over many years, and was based on a design originating from the University of Bern [39]. The composition of the separated samples was determined with a quadrupole mass spectrometer. With this apparatus, we could separate the total krypton content from a 5 L air sample with 80 % efficiency in 3 h. This process is the initial step in our research, and subsequently it will be used to separate [85]Kr from well gas samples after it has been injected as a tracer in a petroleum reservoir. Analyzing the [85]Kr content will then be carried out with our collinear fast beam laser spectroscopy apparatus. Initial results of our tracer research have been published [14], and a more detailed paper on precision collinear fast beam laser spectroscopy of noble gases will be published elsewhere.

Experimental

Figure 1 shows a schematic of the krypton separation system. The device is built mostly using stainless steel tubing (6.3 mm o.d. and 4.6 mm i.d.) and connected by stainless steel VCR and Swagelok fittings. The method is based on cryogenically trapping gas constituents in air at liquid nitrogen temperature in charcoal traps. In particular, the apparatus starts with a stainless steel trap at liquid nitrogen temperature for the removal of H_2O and CO_2, followed by trap T1, which is filled with activated charcoal for the collection of krypton and other gases, and three additional stages of gas chromatography T2, T3, and T4. Each of the latter, having successively smaller volume, is filled with activated charcoal. This arrangement achieves separation and purification of krypton from mainly N_2, O_2, and Ar. Residual N_2 and other reactive gases remaining after the final stage of chromatography are removed with a hot Ti sponge getter.

A thermal conductivity detector (TCD) with electronics and software from the GOW-MAC Instrument Co. (Bethlehem, PA, USA) was used to monitor the characteristic elution times of the various components of condensed gases in the traps after quickly warming the traps from liquid nitrogen to 0 °C, which released N_2, O_2, and Ar, and then to boiling water temperature to release Kr. This requires optimizing of the switching times of valves between the gas chromatography stages, such that mainly krypton is selected and loaded to the next stage, while exhausting the other gases using He for transport. The TCD detector block is divided into two cells containing two filaments each. One cell holds the reference pair, while the
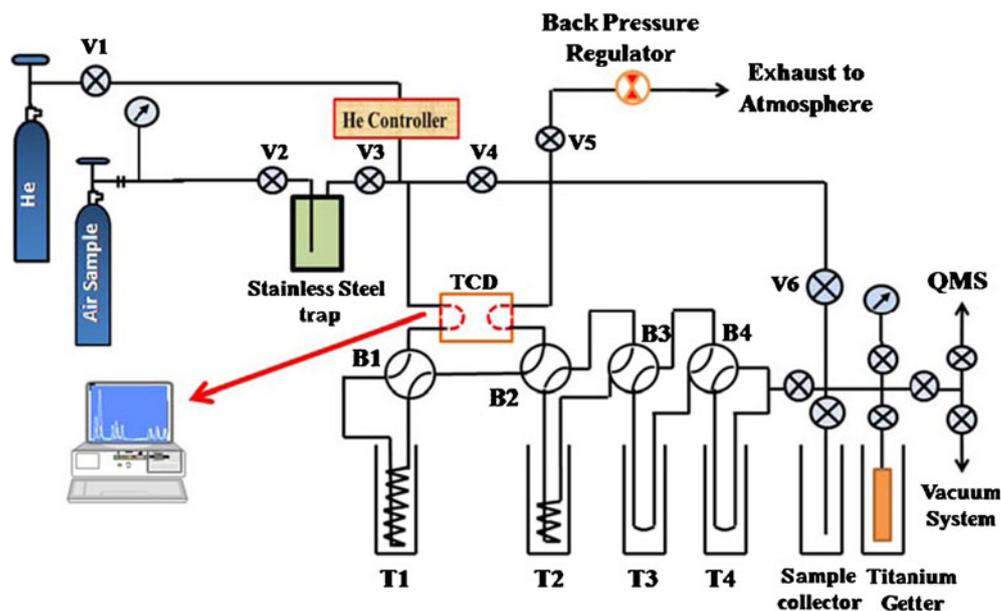
Figure 1. Schematic of the krypton separation system. QMS = quadrupole mass spectrometer; T1–T4 = gas traps; B1–B4 = 4-way valves; TCD = thermal conductivity detector. See text for details regarding the chromatographic procedure

other cell holds the sample pair. All four TCD filaments are physically identical except for their color-coding for identification. The filaments form a Wheatstone bridge, which is connected to a bridge control and DC power supply unit (model 40–200) that provides all necessary circuitry between the TCD and the readout. An advanced Chromatography Data Station (Clarity) (Bethlehem, PA, USA) with software was used for data acquisition, processing, instrument control, and evaluating data from the TCD.

A quadrupole mass spectrometer (RGA-300; Stanford Research System, Sunnyvale, CA, USA) with a resolution better than 1 Da was used to analyze the collected gases in the sample collector trap and to measure the efficiency of the gas separation. The RGA-300 was mounted in a vacuum chamber, which is connected through a valve to the separation system. The whole krypton separation system and the RGA-300 vacuum chamber were kept at $<10^{-7}$ Torr by using a turbo molecular and Scroll vacuum pumps from Oerlikon (Cologne, Germany).

Separation Procedures and Experimental Results

We recover krypton gas from air samples with a separation system based on gas chromatography. The resulting distillate was analyzed with a quadrupole mass spectrometer (QMS) having a sensitivity of 10^{-14} Torr. Typical background pressure in the separation system was 10^{-7} Torr, achieved by baking the system at 250 °C for about 2 h. To ensure the complete removal of contaminants from the getter, resulting from the oxidation of titanium, the getter was baked at 890 °C. To purge residual contaminants from the separation system, helium gas (99.995 %) was introduced into the system (valve V1) and then evacuated. Each trap was initially immersed in a liquid nitrogen bath. Sample gas from a 5 L gas cylinder was loaded

into the primary trap (Trap 1) using valves V2 and V3. Carbon dioxide and water were removed in this process by a stainless steel trap held at liquid nitrogen temperatures. Following the cold trap, the remaining gases, with the exception of helium, were condensed in trap T1, which was filled with activated charcoal. After loading trap T1, the liquid nitrogen bath on this trap was replaced with ice water to allow the trap to quickly warm up [40]. Figure 2 shows the elution times of Ar, O_2, N_2, and CH_4 as they were released from the trap. The gas removal was facilitated by establishing helium (acting as a carrier) flow
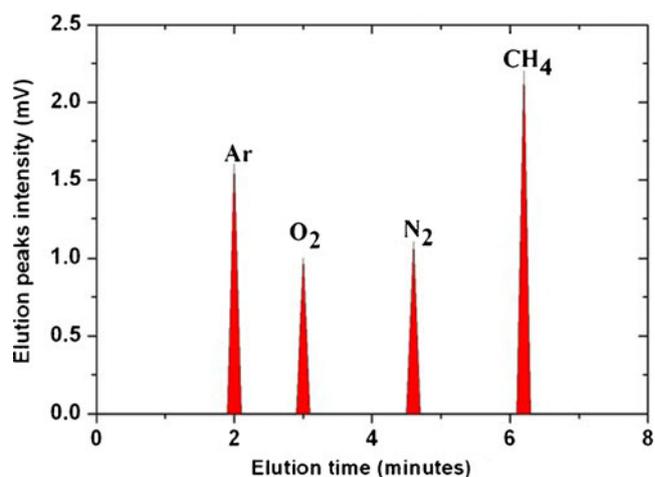

Figure 2. Characteristic elution times. Elution of trapped gases from trap T1 as a function of time. After switching the liquid nitrogen bath with an ice water bath, a sequence of released gases is observed in time. The first gas, argon, appears 2 min following the removal of the nitrogen bath. Krypton, the gas of interest, is released after 12 min, as was determined by a separate calibration experiments

through Trap T1 and out of the back pressure regulator to the atmosphere. Different gas peaks were monitored by the TCD. The calibration for each gas was determined by loading trap T1 with the particular gas and noting the elution time. Once the elution times are determined, the collection of krypton gas can be controlled by the four-way valve B2 in such a way that krypton is the major gas transferred to the second trap T2 with the other gases being flushed out of the back pressure regulator by helium. This occurs roughly 12 min after the removal of the liquid nitrogen bath. At this time, the trap was submerged in boiling water to expedite the elution process and assure that all Kr was released. The process of freezing, sequentially releasing, and separating transferred gas was repeated for Traps T2, T3, and T4. The excess He was pumped off and the remaining Kr gas was transferred to the sample collector. As the final purification step, the sample gas was allowed to flow through a Ti Getter. The highly reactive metal in the getter readily reacts at high temperature 950 °C with the remaining minute amounts of O_2 and N_2 to form titanium oxides and titanium nitrides. Consequently, small amounts of the active gases that remained trapped with krypton in the sample collector are removed by the Ti getter in this last stage of the separation process.

To check for the presence of Kr gas in the distilled sample, the sample collector was mounted to a separate vacuum chamber, where a QMS had been previously installed. A background TOF spectrum was obtained without admitting the sample gas into the vacuum chamber. The spectrum showed the absence of peaks in the mass spectrum where krypton is expected to appear. The main residual gas components at background pressure of about 10^{-7} Torr were observed in the scan range below 70 Da. The sample gas was then admitted into the vacuum chamber, and the mass spectrum of Figure 3 was obtained. In this spectrum, the stable isotopes of krypton were observed, and their relative abundance was found to be as expected [1]. No significant changes were observed in the partial pressures of the residual atmospheric gasses before and after admitting the distillate into the ionization chamber, which confirms that mainly krypton was collected in the sample collector trap.

To quantitatively determine the number of krypton atoms separated from the air sample, the distillate was continually leaked into the vacuum chamber, while the partial pressure of ^{84}Kr was monitored as a function of time (Figure 4). Krypton-84 was chosen because it has the largest relative abundance of all the Kr isotopes. For an interval of time Δt in which the pressure in the chamber remains constant, the turbo pump displaces a volume of $V = \alpha \Delta t$. Here α is the pumping rate. Using the ideal gas law, the number of ^{84}Kr atoms measured in this time interval can be obtained from knowledge of the pumping rate and the measured partial pressure

$$N_{Kr84} = \frac{P}{kT}\alpha\Delta t. \qquad (1)$$

Here P is the partial pressure, k is the Boltzmann constant, and T is the temperature. Over time, the partial pressure of ^{84}Kr
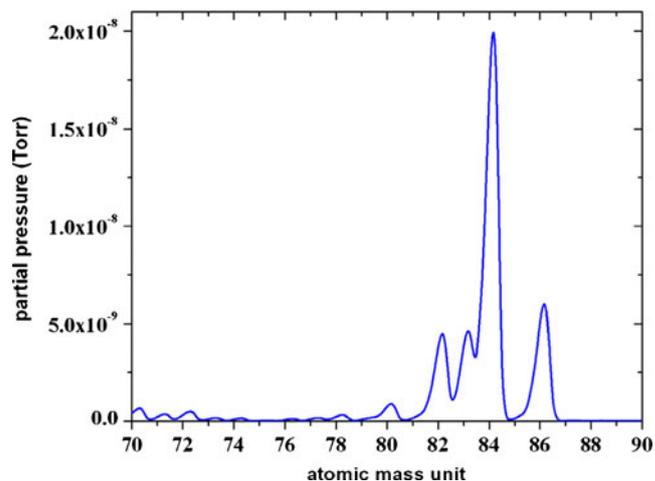

Figure 3. QMS mass spectrum of the distilled air sample from the sample collector trap measured as partial pressure dependent on the atomic mass to charge ratio M/Q ($m = Mu$, where u is 1 Da$\approx 1.67\times10^{-27}$ kg, and the charge is taken as $Q=1$). The mass spectrum shows stable isotopes of krypton, and their relative abundances were determined by taking the value of their peaks and comparing the result to that found for ^{84}Kr. From this analysis the isotope abundances were found to be within ~8 % of their expected values for ^{82}Kr, ^{83}Kr, ^{86}Kr, ~50 % for ^{80}Kr , and undetermined for ^{78}Kr

will not remain constant, and for each interval of time Δt the number of ^{84}Kr atoms displaced by the pump will change. The total number of atoms can be determined by summing (integrating) the contributions from each time interval

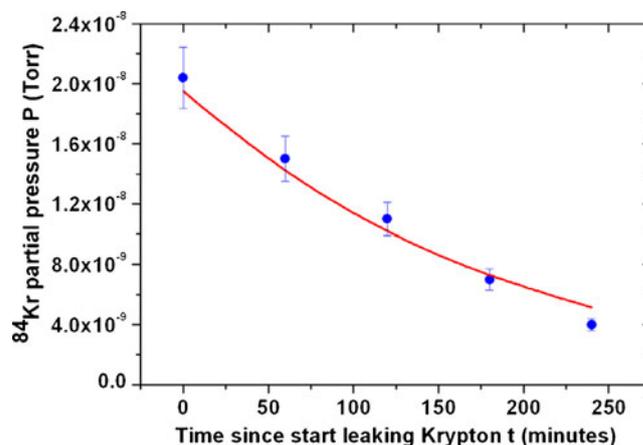$$N_{Kr84} = \frac{\alpha}{kT}\int_0^\infty P(t)dt. \qquad (2)$$

Figure 4. Time dependence of the partial pressure of ^{84}Kr as measured with the QMS: experimental data (solid circles), and exponential fitting curve (solid line). From the fit, the initial partial pressure of ^{84}Kr leaked into the chamber at time $t=0$ was found to be $P_0 \approx 2.1\times10^{-8}$ Torr, and the $1/e$ partial pressure was found to occur at the characteristic time $\tau = 200$ min

The partial pressure of ^{84}Kr as a function of time can be well-approximated by $P = P_0 e^{-t/\tau}$, here P_0 is the initial partial pressure of ^{84}Kr at $t=0$, and τ is the time it takes for the partial pressure to drop to the $1/e$ level from the initial partial pressure, i.e. $P(t = \tau) = P_0 e^{-1}$. This approximation is justified because the background partial pressure of krypton in the vacuum chamber was estimated to be $P_{Kr} = (N_{Kr}/N_B)P_B \approx 10^{-13}$ Torr, which is close to the sensitivity limit of the QMS 10^{-14} Torr. For our experimental parameters, this background partial pressure is much less than the measured initial partial pressure of krypton (10^{-8} Torr) from the sample collector, which is a difference of 5 orders of magnitude. Performing the integration in Equation (2) yields the convenient expression for the total number of ^{84}Kr atoms in the sample collector,

$$N_{\mathrm{Kr84}} = \frac{P_0}{kT}\alpha\tau. \qquad (3)$$

The measured data was fitted exponentially (see Figure 4) giving a value of the initial partial pressure to be $P_0 = 2.1 \times 10^{-8}$ Torr and a characteristic time τ of 200 min. Using these experimentally obtained parameters with $\alpha = 160$ l/s in Equation (3), the total number of collected krypton atoms was found to be $N_{\mathrm{Kr84}} = 1.2 \times 10^{18}$. Since the relative abundance of ^{84}Kr in atmospheric air is 56.99 %, the total number of collected krypton atoms from the air sample with our krypton separation system is $N_{\mathrm{Kr}} = 2.2 \times 10^{18}$ atoms. The error in the measured partial pressure values is estimated to be ± 10 % due to the variation of the measured partial pressure values by the QMS.

For comparison, the total number of krypton atoms in the gas sample distilled from our sample cylinder of air was estimated using the ideal gas law. The volume of sample cylinder was 4790 cm^3 and the pressure was $\sim 18.75 \times 10^3$ Torr, giving the total number of molecules in the air sample to be $N = 2.8 \times 10^{24}$. Taking into account that atmospheric krypton gas constitutes 1 ppm of the earth atmosphere in fractional volume, the total number of krypton atoms in our air sample is therefore $N_{\mathrm{Kr}} = 2.8 \times 10^{24}$, which is slightly higher than the experimentally obtained number of krypton atoms. From this the separation efficiency of the separation system, which is defined as the ratio of the number of collected krypton atoms from the air sample using the separation system to the calculated number of krypton atoms in the sample, was found to be about 80 %.

Outlook for ^{85}Kr Measurements

As previously mentioned, we will employ such pre-separated samples in our collinear fast beam laser spectroscopy apparatus [30] to optimize the experimental detection procedures with stable krypton atoms. An improved Colutron (Colutron Research Corporation, Boulder, CO, USA) ion source [41] will be used and has ionization efficiency of about 10^{-3} for krypton gas. In it, close tolerance fitting of the Boron Nitride cylinder and lid and feedthroughs ensured gas tight confinement. The krypton ions created at the ion source are accelerated to about 15 keV and go collinear with the laser beam through the beam line. Taking into account the ionization efficiency of the ion source and the transmission efficiency of the krypton ion beam through the beam line of about 50 %, we have about an 18 nA krypton ion beam for 3 h at the interaction region. After further characterization and development of the system, which will include collecting statistics of isotope abundances and purging techniques to remove residue contaminations between successive runs, the next step is to detect ^{85}Kr in gas samples from oil/gas reservoirs, where it has been injected as a tracer. In particular, we are planning to determine the reservoir structure of the largest gas field in the world (Northfield, Qatar) [42], using ^{85}Kr as a tracer. The ^{85}Kr will be injected through a central injection well and the appearance of the ^{85}Kr in the surrounding production wells as a function of time will be observed.

Conclusion

A portable apparatus was tested for the rapid separation of krypton from environmental air samples. This apparatus extracts all krypton isotopes together. For trace detection of the long-lived isotopes ^{85,81}Kr collinear fast beam laser spectroscopy (CFBLS) will need to be implemented. With our separation apparatus, krypton can be collected from 5 L of air with 80 % recovery efficiency in about 3 h. The krypton separation efficiency was determined using a quadrupole mass spectrometer (RGA-300). Future work with this setup will be focused on using tracers to study oil/gas reservoirs, and aquifers.

Acknowledgment

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