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Development of krypton separation system for the application of ATTA in geochemistry

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Radiokrypton isotopes (^{81}Kr, $t_{1/2}$=229,000 years and ^{85}Kr, $t_{1/2}$=10.8 years) are ideal tracers of geochemical processes that involve atmospheric components (e.g. in groundwater, sea water, ice cores and the atmosphere, e.g. [1]). However, due to their low isotopic abundances (~10^{-12} for ^{81}Kr and ~10^{-11} for ^{85}Kr) only ^{85}Kr has been conventionally measured by low level counting. The recent application of Atom Trap Trace Analysis (ATTA) on Kr at Argonne National Laboratory now enables the quantification of both ^{81}Kr and ^{85}Kr [2,3].

Atmospheric components contain a few ppm of krypton. As ATTA analyses currently require ~50 μL of pure krypton, it needs to be purified from 50-100 L (at STP) of gas sample. The progress in development of the krypton separation procedure is reported herein.

Procedures and efficiency

Atmospheric components (atmosphere and gases extracted from air-saturated water) contain nitrogen (65-99 %), argon (1-2 %), oxygen (0-35 %) and a trace amount of krypton (2.5 ppm at most). Additionally, natural samples can contain water vapour, carbon dioxide, hydrogen sulphide and methane. Figure 1 shows the outline of the process under development to separate these gases; (i) H_2O and CO_2 removal using adsorbents, (ii) cryogenic distillation for a rough separation of krypton from other major atmospheric gases, (iii) gas chromatography for complete Ar-Kr and CH_4-Kr separation. A quadrupole mass spectrometer (RGA-200 by Stanford Instruments) is connected to the Kr separation line, and was used to examine the efficiency of gas separations.

At liquid nitrogen temperature, nitrogen, argon and oxygen have higher vapor pressures than krypton by factors of about 330, 100 and 110, respectively. Exploiting these physical property differences, the first stage of the purification is by cryogenic distillation. Sample gas (16 L tank, 5 bars) is condensed into a smaller container at liquid nitrogen temperature. Most of the condensation process occurs spontaneously within 5 minutes, and an additional 10 minutes' operation of a vacuum compressor condenses 98% of the total sample. The gas phase in equilibrium with this condensed liquid should be depleted in krypton by a factor of a few hundred, thus the removal of this gas phase results in an enrichment of Kr in the residual liquid phase. During this process, the $N_2/^{40}$Ar ratio of the gas phase is monitored to

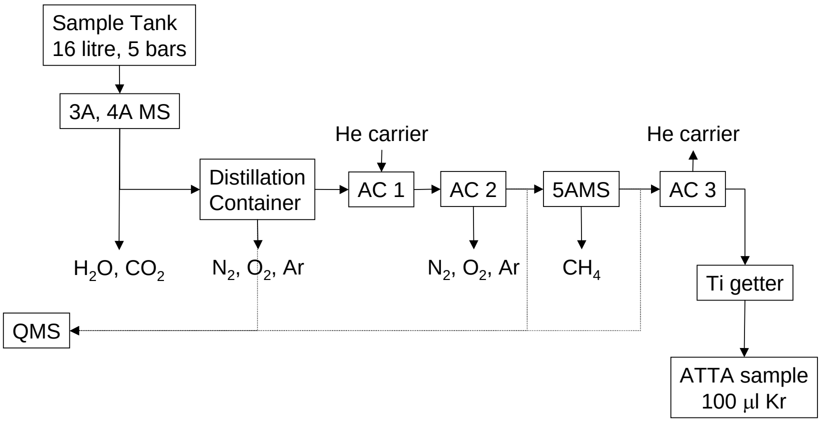

Figure 1: Flow chart of the Kr separation system. AC and MS represents activated charcoal and molecular sieve, respectively.

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evaluate whether the expected elemental fractionation actually takes place. Theoretically, the residual liquid (1-2 L at STP) is expected to represent a few percent of the initial sample while retaining 97% of the initial krypton inventory by the end of the distillation procedure. However, some of the processes do not occur in strict equilibrium, and the current estimate of the Kr yield through this procedure is >80% according to the observed $N_2/^{40}Ar$ ratios. The distillation residue is then entirely adsorbed on a cold activated charcoal trap (AC1). Subsequent packed column gas chromatography allows more complete purification. AC2 separates the residual nitrogen, oxygen and argon from krypton as shown in Figure 2. The molecular sieve 5A column (MS5A) selectively retains methane longer than krypton, which will be trapped at AC3 held at liquid nitrogen temperature.

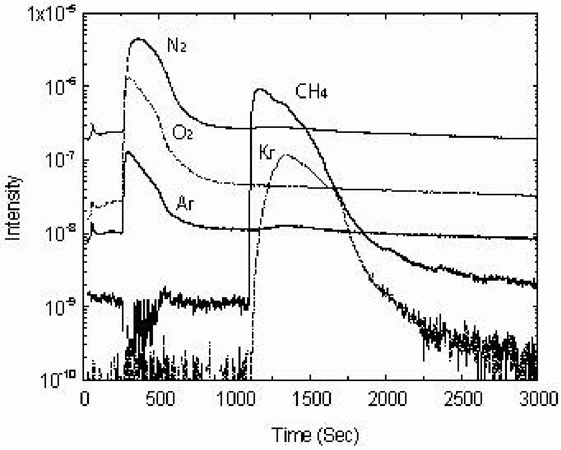

Figure 2: Results of gas chromatographic separation between $N_2/O_2/Ar$ and Kr by activated charcoal. Sample gas constitutes of 96 % air, 5% methane and 1% krypton. The quantity of gas used for this spectra was approximately 300ccSTP.

Finally, the carrier gas (He) is removed from the AC3 by pumping, and the trapped gas is subsequently desorbed and exposed to a hot titanium getter. Pure krypton is then collected in a sample cylinder containing activated charcoal held at liquid nitrogen temperature. Overall Kr yield of 70-80 % is expected through the entire separation process according to the available results.

Future developments

Chemical separation of H_2S is required before the distillation procedure to prevent vacuum line corrosion. This H_2S removal method is to be established before extending this procedure to high-H_2S samples.
Most of the valves in the purification line are air-actuated, and are controlled through the LabVIEW software, which will allow for future automation of the entire system. Temperature controls, gauges, and QMS software will be integrated to the LabVIEW system in the future.

Application to noble gas analysis

A complete separation of krypton from argo or xenon is a difficult task, while it is helpful for precise isotope analyses. It is possible to apply the above-mentioned gas chromatography separation for such purpose, to obtain large noble gas samples for high-precision mass spectrometry in dynamic mode, whereas a carrier gas-free procedure is desirable when dealing with small noble gas quantities. An attempt to separate noble gases by carrier-free chromatography is underway, and the uses and problems of this method may be discussed.

Acknowledgments

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