



# Separation of argon from environmental samples for Ar-37 and Ar-39 analyses



Robin A. Riedmann\*, Roland Purtschert

Climate & Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, 3011 Bern, Switzerland

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## ABSTRACT

High purity argon is required for ultra-low background measurements of  $^{37}\text{Ar}$  and  $^{39}\text{Ar}$ . Both short separation times and high argon recovery are required. Here we report the development of an argon separation line from gas samples of 10–120 l volume by a chromatographic desorption from Li-LSX at  $-120\text{ }^\circ\text{C}$ . Gases desorb in the order  $\text{Ar} < \text{O}_2 < \text{Kr} < \text{CH}_4 \approx \text{N}_2 < \text{CO}_2$ , in agreement with published heats of adsorption.

The optimum temperature of  $-120\text{ }^\circ\text{C}$  for Ar separation from atmospheric air is achieved by a combination of cryogenic cooling with liquid nitrogen and counter-heating. So far,  $\sim 16,500\text{ l}$  of sample gas have been processed on the separation line. The final purity of the argon is  $>99.99\%$  with a recovery of  $>94\%$ . The separation process for 80 l atmospheric air requires 3–4.5 h, which allows the purification of 2 samples per working day.

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## 1. Introduction

### 1.1. Application and motivation for large volume Ar separation

Due to its chemical inertness, the noble gas argon has a wide application as a tracer for environmental processes. Recently, the Comprehensive Test Ban Treaty (CTBT) considered measurements of  $^{37}\text{Ar}$  ( $t_{1/2} = 35.1$  days) an important technique e.g., [1,2]. In the atmosphere  $^{37}\text{Ar}$  is mainly produced by neutron activation of  $^{40}\text{Ar}$ ,  $^{40}\text{Ar}(n,4n)^{37}\text{Ar}$  and  $^{36}\text{Ar}(n,\gamma)^{37}\text{Ar}$ , and in the lithosphere due to spallation of calcium by the reaction  $^{40}\text{Ca}(n,\alpha)^{37}\text{Ar}$  [3,4].

$^{39}\text{Ar}$  ( $t_{1/2} = 269$  years), is produced by spallation in the upper atmosphere [5], and in the lithosphere by the nuclear reaction  $^{39}\text{K}(n, p)^{39}\text{Ar}$ . It can be used to date hydrological reservoirs for time scales of centuries [6] or longer [7].

Measurements of the radioactive argon isotopes  $^{37}\text{Ar}$  and  $^{39}\text{Ar}$  are performed with ultra-low  $\beta$ -counting in an underground laboratory [8–10]. These applications require the argon separation from atmospheric air, from soil-air or from gas extracted from groundwater. Typical gas sample volumes are 40–80 l of atmospheric composition. Underground  $\text{CO}_2$  can accumulate from different sources in the unsaturated (biogenic  $\text{CO}_2$ ) or the saturated soil zones (biogenic, chemogenic or thermogenic). Under reducing conditions  $\text{O}_2$  is consumed and  $\text{CH}_4$  can be produced by

methanogenesis or  $\text{CO}_2$  reduction [11].  $\text{N}_2$  as a result of denitrification of nitrates is another common subsurface gas source in many aquifers. Thus, an Ar purification system must be able to efficiently separate Ar from large quantities of gas with variable composition and Ar concentration (Fig. 1). Additionally, krypton must be trapped for further purification for radio Kr analyses [12].

One of the most important separation benchmarks is the recovery of argon. A high recovery reduces the air volumes to be sampled i.e., in the soil column or groundwater, which, in turn, decreases both the risk of atmospheric air contamination and the detection limit of  $^{37}\text{Ar}$  and  $^{39}\text{Ar}$ . Due to the relatively short half-life of  $^{37}\text{Ar}$ , a short processing time is also critical [3].

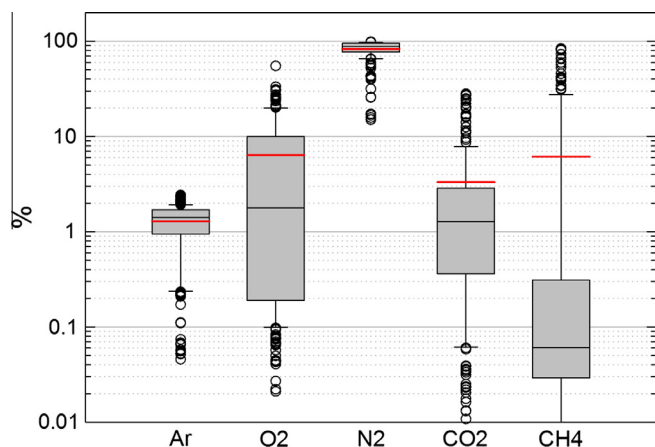
Here we report the development of an argon separation line from gas samples of  $<120\text{ l}$  volume by a chromatographic desorption from Li-LSX at  $-120\text{ }^\circ\text{C}$ .

### 1.2. Review of existing methods and materials

Due to their similar physical properties, separation of argon and oxygen is more difficult than the separation of argon from nitrogen [13,14]. Currently four methods are commercially used for  $\text{O}_2$  and Ar separation: (1) cryogenic distillation in a sidearm argon column with multiple rectification stages [15–20]; (2) catalytic hydrogenation of the  $\text{O}_2$  from a crude Ar stream to form water (i.e. a chemisorption process); (3) cryogenic adsorption with zeolites at low temperatures in the range of  $-157\text{ }^\circ\text{C}$  to  $-179\text{ }^\circ\text{C}$ ; (4) In order to decrease economic costs (especially regarding the operating

\* Corresponding author.

E-mail address: [riedmann@climate.unibe.ch](mailto:riedmann@climate.unibe.ch) (R.A. Riedmann).



**Fig. 1.** Box plot of composition of 277 gas samples, extracted from groundwater. Gray areas correspond to inter-quartiles, the black line is the median and the solid red line is the average. Atmospheric air samples and gas extracted from soil air show smaller variations and were not included in this plot. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

temperature), pressure swing adsorption (PSA), vacuum swing adsorption (VSA) or a combination of both at room temperature have also been increasingly investigated [21].

In PSA or VSA systems separation of nitrogen is based on selective  $N_2$  adsorption on zeolites. A vast literature on the separation of nitrogen and oxygen e.g., [22–24] and on simulations and modeling of PSA e.g., [25–27] can be found. Separation of air by adsorption of the less abundant component is usually more desirable [28]. Separated argon is the primary product in some experiments in the search of dark matter, but their quantities exceed the ones used here by orders of magnitude e.g., [29–31].

Although some sorbents such as mordenite, calcium chabazite, and Ag-mordenite showed a small adsorptive preference for Ar compared to  $O_2$ , the equilibrium selectivity was not sufficient to enable efficient separation [13]. This is in agreement with Jin, Malek and Farooq [32] who reported that an equilibrium-based PSA process is not suitable to separate oxygen and argon at ambient temperature. Their kinetic-based PSA produced argon with a purity <50% and a recovery <67% mostly because of similar kinetic diameters of Ar and  $O_2$  [33].

The effectiveness of a particular zeolite for gas separation depends on the pores size distribution and location, and charge of any cations present [22]. Jia and Murad [26] reported that for mixtures of components with similar molecular size and adsorption characteristics, such as  $O_2/N_2$ , small-pore size zeolites (such as chabazite) are not appropriate. This is because molecules cannot easily pass each other in the narrow pore system.

Due to the structural configuration and charge distribution the low-silica version of the X-type zeolite has a 1.5 times higher adsorption capacity for Nitrogen compared with the “regular” version [22]. The best sorbent in industrial use for the separation of air components by adsorption processes is therefore the low silica form of the Li-cation exchanged faujasite zeolite (Li-LSX) since the pore diameter is 7.4 Å and leads into a larger cavity of 12 Å [28,34–37]. The difference in adsorption strength between argon and oxygen is relatively large [38,39] and it is commercially available. An alternative to Li- would be Ca-exchanged zeolites [40]. However, Ca is the most likely contamination source for  $^{37}Ar$  and therefore not suitable in the context of the work presented here.

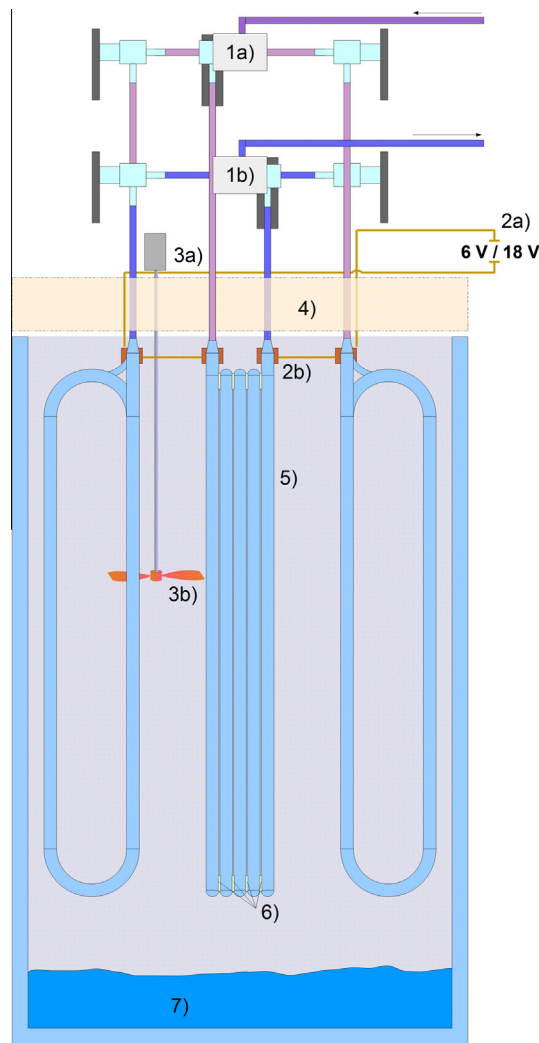
In general, the adsorption strength of major atmospheric air constituents on Li-LSX increases in the order  $Ar < O_2 < Kr < CH_4 \approx N_2 < CO_2$  [25,28,38,41–53]. This total physical adsorption

capacity can be expressed in terms of a Langmuir isotherm and is an Arrhenius activated process e.g., [41].

## 2. Materials and methods

The volume range of the gas samples (10–120 l) requires a total mass of Li-LSX of 1.7 kg ( $3200 \text{ cm}^3$ ) for separation at temperatures  $< -100 \text{ }^\circ\text{C}$  [54]. This separation volume is subdivided into nine equal columns operating in parallel. Each column can be added individually. This allows for a flexible processing depending on gas composition and samples sizes. The columns (inner diameter 1 cm, length 43 cm) were cut from stainless steel, packed with Li-LSX (Zeox Z12, 0.2–0.8 mm diameter, Zeochem AG) and bent to an elliptical coil. The major axis is placed in vertical direction and the in- & outlet pointing in upward direction (Fig. 2). The columns were placed in a circular arrangement for a synchronized gas flow.

The effect of axial dispersion was assessed in preliminary tests with columns of identical volume but different geometries. Larger radius, but shorter column was observed to be detrimental. Smaller diameters of granules (from an American vendor) showed



**Fig. 2.** Schematic of design and temperature control of the separation columns (only 3 shown for simplicity). (1a) gas inlet, (1b) gas outlet made from Polyetheretherketone (PEEK), (2a) electric circuit for heating, (2b) copper clamps for electric current, (3a) motor and (3b) rotor for swirling, (4) top insulation, (5), separation column, (6) Teflon insulation, (7) liquid nitrogen. All parts are in scale.

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