Method for Extraction of Dissolved Gases From Groundwater for Radiokrypton Analysis

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Two radioactive isotopes of krypton (Kr) are valuable environmental tracers having powerful applications such as determining groundwater residence times, ocean circulation and mixing rates, and ages of glacial ice. ^{81}Kr ($t_{1/2}$ = 229,000 yr) is an ideal tracer on the 10^4 to 10^6 year time scale. ^{85}Kr ($t_{1/2}$ = 10.8 yr) is ideal for tracing processes in the <50 yr range. The isotopic analysis uses the Atom Trap Trace Analysis (ATTA) apparatus developed by Z.-T. Lu and colleagues at Argonne National Laboratory. This apparatus uses tuned diode lasers to hold and count individual Kr atoms of with complete isotopic selectivity in a magneto-optical trap ((Chen et al., 1999; Du et. al. 2003). ATTA analysis currently requires ~50 µL of Kr, which is the amount contained in ~700 L of air-saturated water. The object of this ^{81}Kr/Kr analysis has recently dated groundwater from a Nubian aquifer in the Western Desert of Egypt to be as old as 106 years. The results of the ATTA analysis showed agreement to ^{36}Cl data and marked the first time ATTA was used to determine groundwater residence time (Sturchio et al., 2004). We developed a new, high-volume gas-extraction system, EDGAR (Extraction of Dissolved Gases for Analysis of Radiokrypton) that provides a simple and rapid method for obtaining high-volume samples suitable for recovery of micromolar amounts of non-reactive trace gases for isotopic analysis.

Method

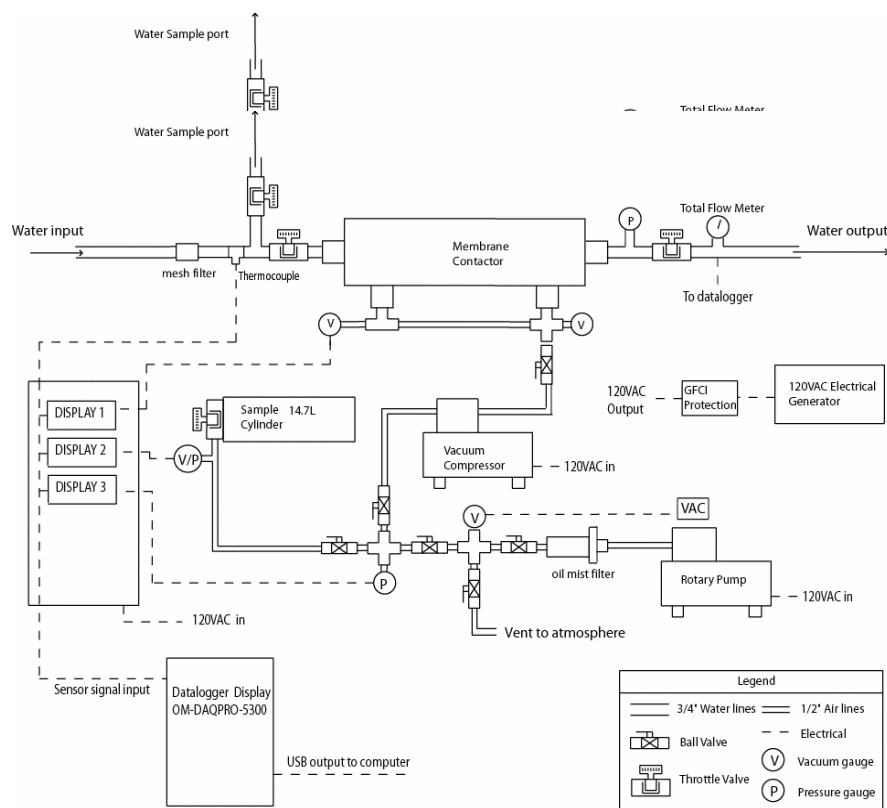The key component of EDGAR is a hydrophobic semi-permeable membrane contactor (Membrana Corp.). This extracts dissolved gases from water with efficiency approaching 90%. Water flows through the inner surface of the membrane and a vacuum is applied to the outer surface of the membrane. Vacuum is produced with the compressor that compresses the extracted gas into a standard gas cylinder. The extraction apparatus is contained in a rigid frame (Fig.1). EDGAR weighs about 180 kg and is powered by a 120VAC, 20-amp power source. Electronic sensors monitor the membrane vacuum, sample tank pressure, water temperature and total water flow. A data logger records the sensor signals. A schematic of EDGAR is shown in Fig. 2.

Figure 1. Picture of EDGAR being deployed in the field.

Testing

Initial testing of membrane extraction efficiency was conducted using Chicago tap water. Dissolved O_2 (DO) was measured in water before and after passing through the membrane at flow rates ranging from 4 to 34 L/min. DO dropped from 12 to 15 mg/L (before) to 1.6 to 3.7 mg/L (after),
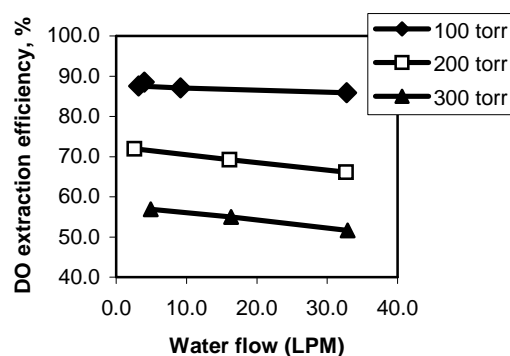
Figure 2. Schematic diagram of EDGAR.

According to this model, E_i values for N_2, CH_4, Ar, and Kr are expected to be 0.89, 0.78, 0.78 and 0.65 respectively for $E_{ox} = 0.8$ at ambient temperature (0 to $20^{\circ}C$). Nitrogen and Kr should then be fractionated relative to Ar by +14% and -17%, respectively, which is roughly in agreement with the observation. E_i values for Ar and O_2 are nearly equal.

indicating DO extraction efficiency of 67 to 88 % at a flow rate of 4 to 5 L/min.

The DO extraction efficiency decreased with membrane vacuum pressure and with flow rate (Fig. 3), but was insensitive to water pressure in the range 1,000 to 3,000 torr.

Field testing of EDGAR was performed on a groundwater well in Oswego, IL. The compositions of dissolved and extracted gases were measured using a quadrupole mass spectrometer. The concentration of O_2 was at blank level in these samples, indicating negligible atmospheric contamination. Nitrogen in extracted gas was enriched by ~15 % and Kr was depleted by ~ 21 % relative to Ar. The correlation between DO extraction efficiency (Eox) and membrane vacuum pressure suggests that water and gas phases across the membrane are in solubility equilibrium. Consequently, extraction efficiencies of other gas species i (E_i) can be estimated as a function of their solubilities (S_i) from:

$$\frac{S_i E_i}{(1 - E_i)} = \frac{S_{ox} E_{ox}}{(1 - E_{ox})}$$

Figure 3. DO extraction efficiency (%) vs. water flow rate as a function of pressure on the gas side of the membrane.

Acknowledgments

References

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