

Report for 2004HI55B: Development of a New Technique for the Use of Dissolved Helium as an Environmental Groundwater Tracer

- Articles in Refereed Scientific Journals:
 - Richter, F.; R.B. Whittier; A.I. El-Kadi, Use of dissolved helium as an environmental open-water tracer, Journal of Contaminant Hydrology, to be submitted.

Report Follows

Problem and Research Objectives

Tracer tests are an important method for determining the flow characteristics and patterns of subsurface water (such as groundwater aquifers) and surface water bodies (such as streams and the ocean). In such tests, a constituent is added to the water. The constituent is either non-native to that water or high enough in concentration to be distinguished from the native component in that water. Many of the commonly used tracers have one or more limitations, such as being toxic, being esthetically objectionable, being difficult to be differentiated from the naturally occurring fraction, requiring complex laboratory analysis for their detection and quantification, requiring a high concentration, and reacting with the aquifer matrix. These limitations are not common to helium, however. Thus, if a field method can be developed to detect and quantify the concentration of dissolved helium in surface or groundwater in real time, then helium has great potential for use in certain tracer applications, including its use near drinking water sources or in environmentally sensitive areas such as wetlands and fish farms, its use in areas where esthetics are a concern (e.g., recreational beaches), and its use in conjunction with investigations of the diffusion characteristics of groundwater aquifers.

Helium was successfully tested as a reliable and economical tracer (S.K. Gupta, L.S. Lau, P.S. Moravcik, and A.I. El-Kadi, 1991, *Injected helium: A new hydrological tracer*, Special Report 06.01.90, Water Resources Research Center, University of Hawaii at Manoa, 94 pp.; L.S. Lau, and P.S. Moravcik, 1994, *Ground-water tracing with injected helium*, *Ground Water* 32(1):96–102). Its behavior in open tanks was identical to that of fluorescein dye. Although the system was simple and specific for helium, the small surface area and fragility of the thin quartz window limited its sensitivity and reliability. Moreover, the technique was only suitable for the analysis of discrete samples.

The objective of this project is to develop and demonstrate a new analytical system that substantially improves the precision and utility of the helium tracer analysis techniques for routine use in surface water and groundwater. The work proposed encompasses developing and calibrating the system, and testing the helium tracer in the laboratory against a commonly used tracer.

Methodology

Instrumentation

Compared to the above-mentioned design of Gupta and others, our system, consisting of a gas extraction system and a separate helium analyzer, is somewhat more complex but substantially more sensitive (Figure 1). The new design allows on-site, continuous, real-time monitoring in a completely automated structure. Results of the analysis are automatically recorded on a lap-top computer.

Our system is built around a permeable membrane contactor, which is used commercially to extract dissolved gases from liquids. This contactor is a shell-and-tube device containing thousands of microporous hydrophobic polypropylene hollow fibers woven into a fabric array. To extract dissolved helium, a steady flow of helium-tagged water is maintained through the wet side of the contactor. A constant flow of clean, dry nitrogen through the gas side of the contactor provides a helium concentration gradient and results in the diffusion of helium from water to the gas side of the membrane contactor. Our design includes the use of the 2.5 in. × 8 in. Extra-Flow Membrane from Liqui-Cel. Nitrogen gas is moved inside the hollow fibers at a specified pressure. The rate of helium extraction depends on the partial pressure difference and the flow rate of water. A trial-and-error approach was used to estimate a certain combination of the flow rate and pressure. For example, at 20 psi the optimal flow rate was 600 ml/min.

A vacuum leak detector probe is placed in the discharge path from the gas side of membrane contactor. The leak detector has a helium-based mass spectrometer which generates an electrical signal that is proportional to the helium concentration in the gas discharge from the membrane contactor. This electrical signal is displayed as a leak rate.

A Veeco MS-40 Portable Leak Detector manufactured by Vacuum Instrument Corporation was used in our design. The MS-40 detector is equipped with software that allows communicating with a computer to automatically record output signals. The test port of the MS-40 detector is connected to the gas outlet of the extraction system by polytetrafluoroethylene (PTFE) tubing, which is permeable in regard to the small helium molecules. It is not necessary to use a more gas-tight material, such as copper, considering that the residence time of the molecules is too short for major diffusion processes to occur. In addition, most applications are only concerned with relative concentrations, hence the introduced error can be ignored. The flexibility of PTFE-tubing is an advantage for field

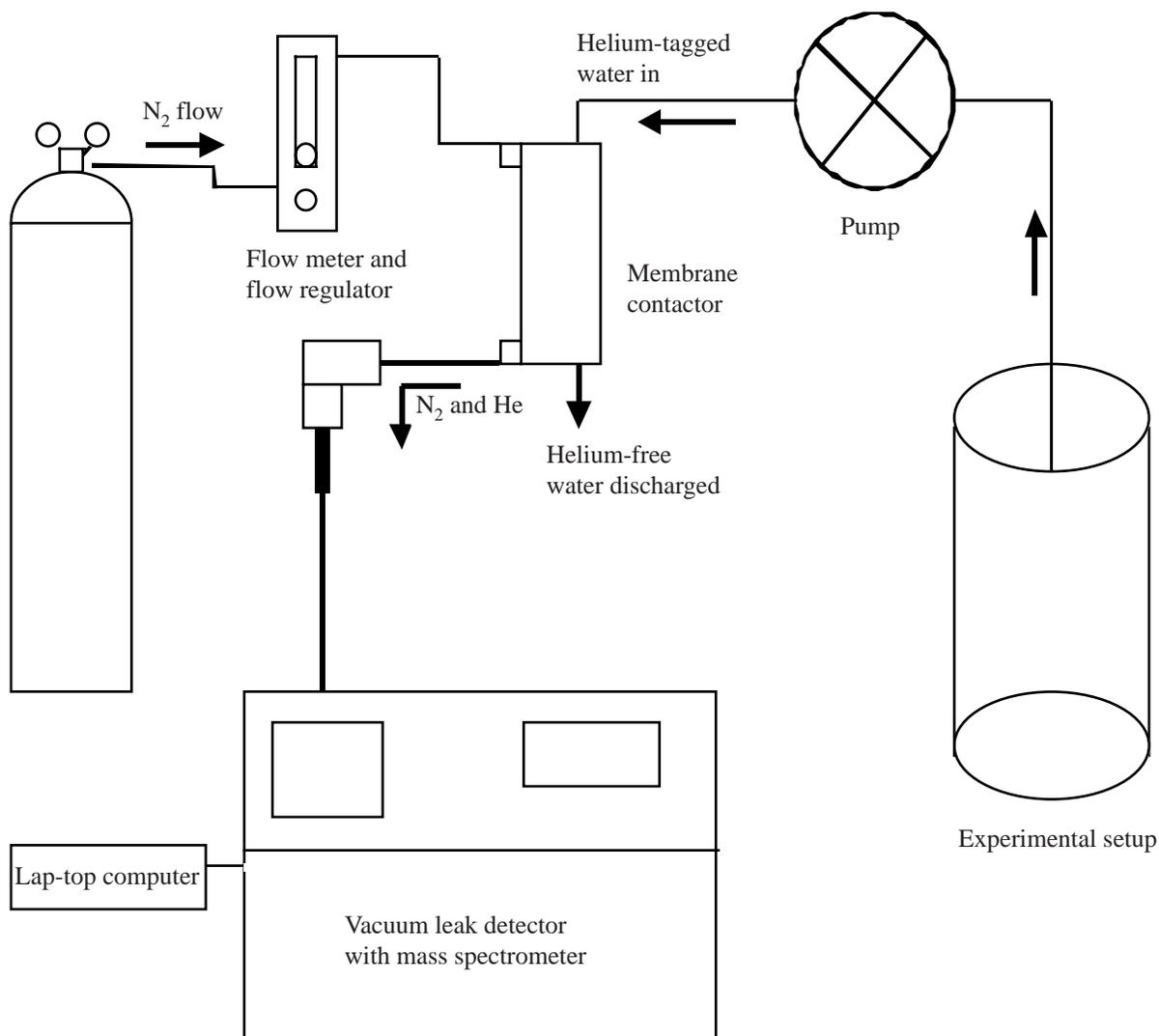


Figure 1. Schematic of the helium tracer system

work. To prevent water vapor from entering the mass spectrometer's high vacuum chamber, a 13 in. \times 1 in. PVC cylinder filled with Drierite desiccants (1/4-in. granules) is placed in the flow line between the extraction system outlet port and the mass spectrometer's inlet port.

Instrument calibration

The instrument was calibrated to convert signals from the helium detector to helium concentrations. Helium solutions of known concentrations were prepared based on the solubility of helium in equilibrium with atmospheric air at sea level (i.e., 5.0×10^{-5} ppm) and the maximum solubility at 1 atm of helium (i.e., 8 ppm). The solution with the maximum helium concentration was prepared by bubbling pure helium through a diffuser into a few liters of water at room temperature for at least 15 minutes. This solution was diluted to helium solutions of 10%, 1%, and 0.1%. The helium signal detected by the mass spectrometer is the volume of helium gas that is extracted from the test water per second. In order to estimate the actual helium concentration in the sample, the measured gas volume was divided by the volume of water that passes through the membrane contactor per second, given by the constant water flow rate of 600 ml/min. Figure 2 shows the observed relationship between the concentration based on the helium signal recorded by the mass spectrometer and the directly measured helium concentrations in five helium solutions. A linear relationship exists between the two helium concentrations. However, the detected concentrations were lower than the measured values by an average of 3.13×10^{-3} ppm. The main reason for such an error is likely

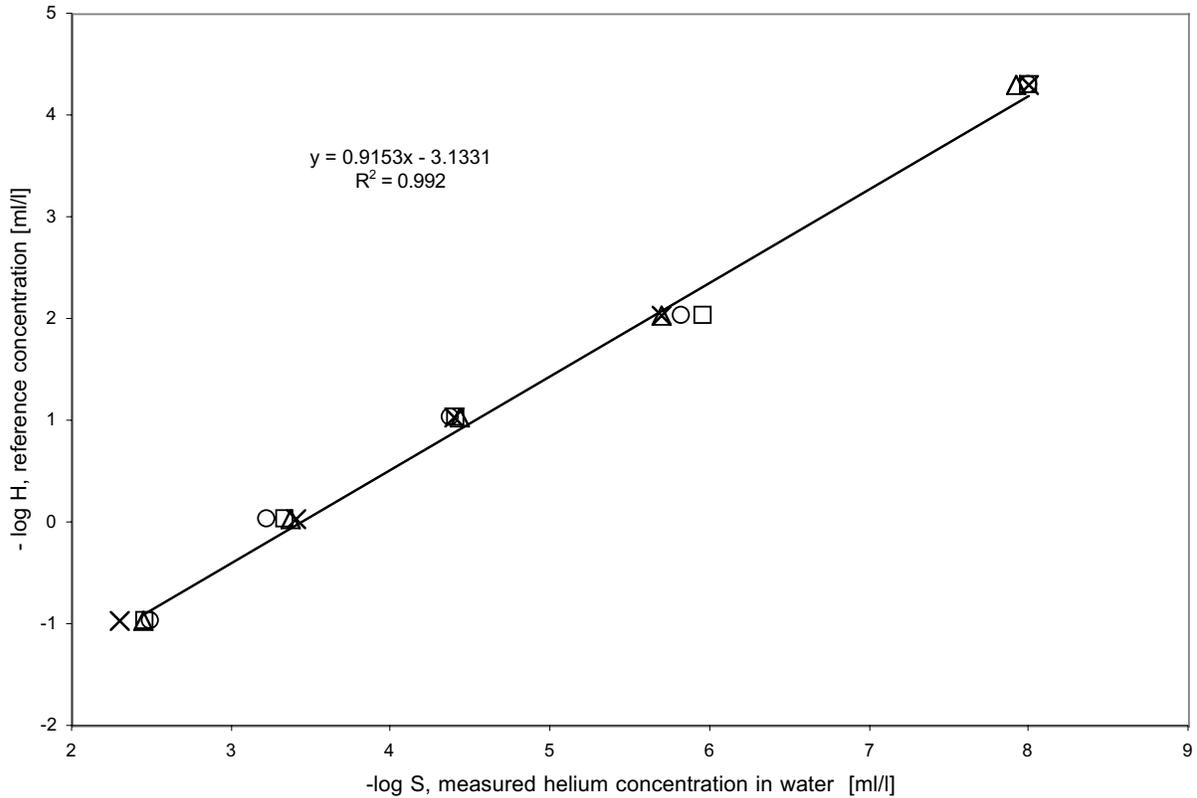


Figure 2. Instrument calibration curve using five different helium solutions. Four test samples were tested for each solution (shown by different symbols)

due to the inability of the contactor membrane to extract all the helium gas from the solution. As mentioned earlier, the helium removal performance of the contactor membranes depends on the water flow rate. The lower the flow rate the higher is the efficiency of the system to extract helium. The flow rate of 600 ml/min used was the lowest possible operable flow rate. Below that value, it was found that air bubbles form in the system due to insufficient water pressure. It is also likely that some helium gas molecules were lost due to diffusion during their passage through the system.

The helium concentration in the sample water can be calculated by the following equation of the least square fit line (Figure 2):

$$-\log(H) = 0.0153[-\log(S)] - 3.1331$$

where

H = helium concentration based on detector signal (ppm)

S = actual helium concentration (ppm)

The scatter of the measured data points for the different reference concentrations can be partly explained by the lack of precision in preparing the reference dilutions.

Principal Findings and Significance

A number of bench-scale experiments, including pipe and open-tank experiments, were done to test the instrument. The helium results were compared to a sodium chloride (NaCl) solution to evaluate the suitability of using helium as a tracer.

Pipe Experiment

Tracer experiments were conducted in PVC pipes to test the behavior of dissolved helium as a tracer to that for NaCl. Water was pumped from a reservoir through a 20-ft-long PVC pipe with a 2 in. diameter at a constant flow rate of 1,100 ml/min. Two 10-ft PVC pipes were connected by two 90-degree elbows to fit the experimental setup into the laboratory. An He (~ 66% saturation)/NaCl (66 g/l) solution was injected into the pipes through a 1/4-in. inlet at the same constant flow rate of 1,100 ml/min for one minute. After the tracer injection, pumping from the water reservoir resumed for the remainder of the experiment. The 1/4-in. PVC pipe outlet was connected to the helium extraction and detection unit by 1/4-in. flexible PVC tubing. At the outlet of this unit the conductivity was measured by a conductivity probe. The relative He and NaCl concentration was continuously recorded throughout the experiment.

The results of the helium concentration are compared against NaCl results in Figure 3. Excellent match can be seen regarding the rising limb of the breakthrough curve concerning the first arrival and the slope of the curve. However, fluctuations are evident near the peak concentrations, which are likely due to the high helium concentration in the injected solute. Probably for this reason, some disagreement also exists in the elution of helium. We are currently working on additional test cases to improve on the results and on applying the methodology to longer pipe systems.

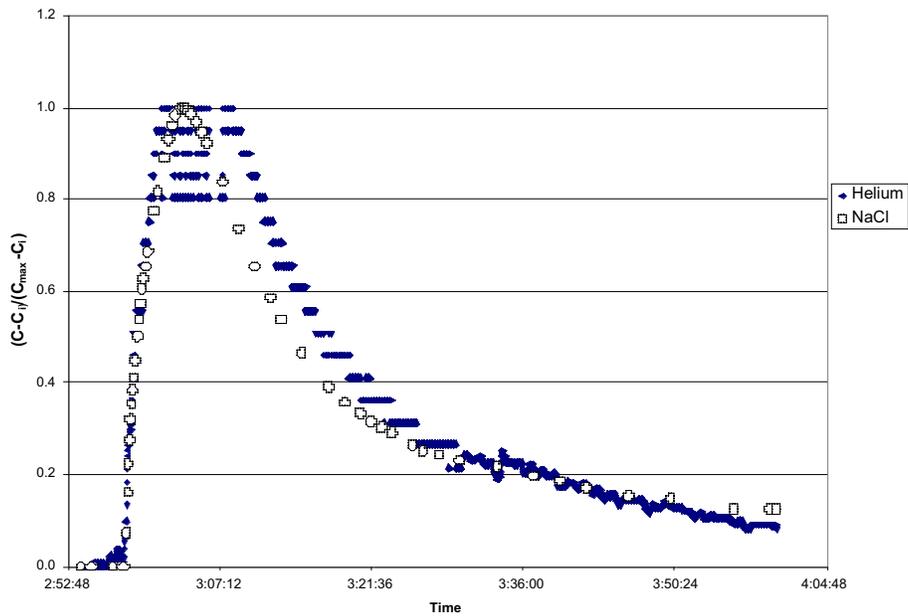


Figure 3. Breakthrough curves for the pipe experiment for NaCl and helium. C is the concentration, and C_o and C_i are the peak and initial concentrations, respectively.

Open-Tank Experiment

The experiment involves tracing a plume of dissolved helium and saltwater in an open tank (wedge shape of 244 cm length \times 60 cm in the widest part \times 25 cm depth). The flow field in this experiment mimics a steady-state radial flow situation. NaCl dissolved in 3 liters of a saturated helium solution was injected instantly at the wider end of the tank. At the opposite end water was continuously pumped out of the tank and into the helium extraction/detection system at a rate of 600 ml/min. At the outlet of the extraction unit the conductivity of the sample water was continuously measured. Purified tap water was continuously injected into the tank at a recharge rate of 600 ml/min to maintain a steady state between inflow and outflow.

The results of the open-tank experiments (Figure 4) clearly show that the helium-measuring instrument responds instantly to a change of helium concentration in water. The arrival and peak of the NaCl breakthrough curve is delayed by 15 seconds. This can be explained by the different methods used to measure the two solutes. The conductivity probe is mounted in line at the helium extraction unit water outlet. In this case, it seems it takes 15 seconds for a water molecule to travel from the contactor membrane to the conductivity probe.

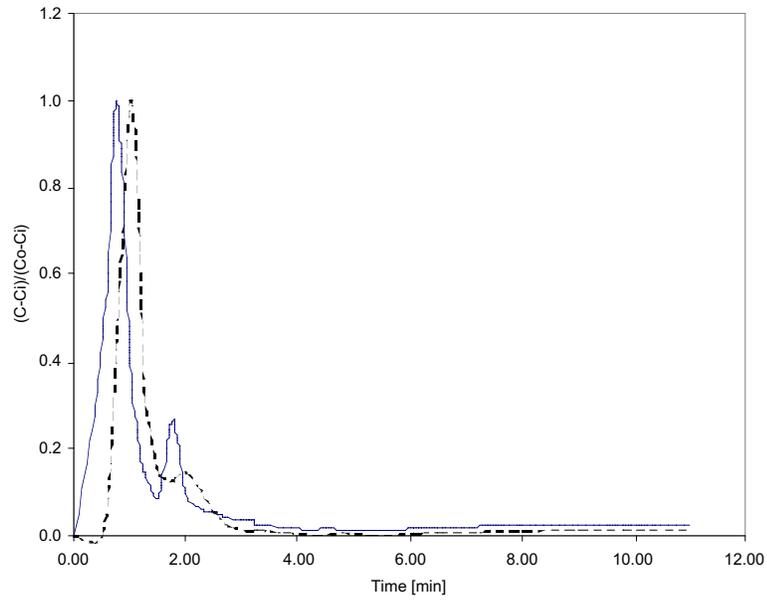


Figure 4. Breakthrough curves for the open-tank experiment for NaCl and helium. C is the concentration, and C_o and C_i are the peak and initial concentrations, respectively.

The different transport properties of the two tracers can provide another explanation for the lag of the NaCl breakthrough curve. Advection is presumably the main solute transport process for NaCl, whereas the helium molecules might travel at a higher transport velocity than the water molecules due to molecular diffusion. In larger-scale applications over a long travel time, this lag should not be a serious limitation of the method. As evidence, such an error did not occur in the pipe experiment discussed above due to the longer travel time.

The second peak, which is smaller and which occurs after about 2 minutes, is likely due to the flow condition created by the instant injection of the tracer. Such behavior was confirmed during a second experiment. However, the similar behavior of the two solutes proves the potential success of the helium detection system in responding to multiple injection episodes.

The work completed has demonstrated the success of the new technology in allowing continuous, real-time monitoring in a completely automated structure. Results favorably compare helium as tracer to sodium chloride. The instrument has been successfully calibrated. The drawback of the methodology includes sensitivity of the results to the flow rate and the initial helium concentration of the injected solution. A number of groundwater runs for a sand column and sand tank were completed, but improvements are needed. Groundwater applications will be further addressed in the second year of the project.