



## **Development of a portable membrane contactor sampler for noble gas analyses of surface and groundwater samples**

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Noble gas isotopes dissolved in groundwater provide valuable information about climatic conditions during air–water exchange, as well as the residence time of groundwater and its renewal rate. The isotope composition of noble gases can also serve as geochemical fingerprints to decipher the origin of groundwater and its flow system. Conventionally, groundwater is sampled using a copper tube, which is subsequently degassed using a vacuum extraction system for isotope analysis by a mass spectrometer. Although this conventional and well-established way of sampling is widely recognised as being reliable and robust, a major drawback to this method is its size and weight. For example, our sampler consists of a copper tube of 10 mm diameter x 1000 mm length and a metal casing with pinch-off clamps with its total weight to be 2 kg each. A box of 24 samplers well exceeds 40 kg. Considering that sampling fields are not necessarily easily accessible by vehicle, taking hundreds of samples in the field is generally a tough task for everyone. There is a different type of sampler, which is comprised of a much smaller copper tube (6 mm in diameter and 100 mm long for our case) with clamps and a semi-permeable membrane filter. It is sunk into water and left there for dissolved gases to diffuse into the sampler until their concentrations in water become equilibrated with those in the tube. This diffusion sampler is small and easy to handle in the field; it has an advantage over conventional copper tubes, as the diffusion sampler collects gases so that there is no gas extraction process needed before isotope analysis. However, this method requires an equilibration time of 24 hours or more, which could result in lower time-efficiency for sampling work.

In order to enable time-efficient and less-painstaking sampling of noble gases dissolved in surface and groundwater, we have developed a portable and self-powered sampling device specified to noble gas analysis by mass spectrometer, following the design of a similar device reported in literatures. The sampling device uses a commercially available membrane contactor which can separate gas phase from continuous from of water. We have examined its extraction performance by preparing several samples for different time spans. We found that our membrane contactor can extract heavier noble gases (Ar, Kr, and Xe) more efficient than lighter noble gases (He and Ne), implying that sorption of gas atoms to the membrane contactor is controlling the transport of noble gases through the membrane. We confirmed that extraction of about 60 min is sufficient for all noble gases reach equilibrium with those dissolved in the water.  $^3\text{He}/^4\text{He}$  ratios and other noble gas isotope ratios showed no signs of isotope fractionation, suggesting that the device can be applicable for sampling of dissolved noble gases from the water aiming to the groundwater dating and paleo-climate reconstruction.