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Instruments and Methods

Combined sample collection and gas extraction for the measurement of helium isotopes and neon in natural waters

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ABSTRACT

We present a new method to obtain samples for the measurement of helium isotopes and neon in water, to replace the classical sampling procedure using clamped-off Cu tubing containers that we have been using so far. The new method saves the gas extraction step prior to admission to the mass spectrometer, which the classical method requires. Water is drawn into evacuated glass ampoules with subsequent flame sealing. Approximately 50% headspace is left, from which admission into the mass spectrometer occurs without further treatment. Extensive testing has shown that, with due care and with small corrections applied, the samples represent the gas concentrations in the water within $\pm 0.07\%$ (95% confidence level; $\pm 0.05\%$ with special handling). Fast evacuation is achieved by pumping on a small charge of water placed in the ampoule. The new method was successfully tested at sea in comparison with Cu-tubing sampling. We found that the ampoule samples were superior in data precision and that a lower percentage of samples were lost prior to measurement. Further measurements revealed agreement between the two methods in helium, ^{3}He and neon within $\pm 0.1\%$. The new method facilitates the dealing with large sample sets and minimizes the delay between sampling and measurement. The method is applicable also for gases other than helium and neon.

1. Introduction

Since the Bremen He laboratory became operative in 1989, it has collected numerous observations of the helium isotopes (^{3}He, ^{4}He) and of neon, and applied them in oceanic and groundwater studies (e.g., Roether and Putzka, 1996; Roether et al., 1998a, 2001; Rüth et al., 2000; Well et al., 2001, 2003; Huhn et al., 2008; Massmann et al., 2009; Rhein et al., 2010; Walter et al., 2010; Roether and Lupton, 2011; Sültenfuß et al., 2011). Especially oceanic studies often require several hundred measurements and the concentrations range over a few percent only, so that convenient sampling under accurate representation of the water body sampled is an issue. Determining helium (He) and neon (Ne) concentrations in environmental waters consists of collecting water into leak-tight containers in the field and transferring the contained permanent gases into the measurement system (mass spectrometer, MS) in the home laboratory. We have been using the classical clamped-off copper tubing containers (Weiss, 1968), from which the permanent gases are extracted at Bremen into glass ampoules for inlet into the MS (Sültenfuß et al., 2009). While that technique is mechanically robust, the extraction is cumbersome and enforces an extra delay between sampling and measurement. Proven alternatives are limited to Cu-tubing with cold-welded ends (Young and Lupton, 1983) and the at-sea extraction of Lott and Jenkins (1998). The method of Emerson et al. (1999) is restricted to gases heavier than Ne, and further ones, such as the diffusion sampler of Gardner and Solomon (2009), only serve special applications.

We present a new method that combines sample collection and gas extraction in one step, using glass ampoules that are flame-sealed. It employs a device that we denote by Ampoule-based Water Sampler (AWS). We describe the technical design and performance of the device. We address all steps of the handling, the corrections that have to be applied, and their uncertainty margins. We have employed the AWS method at sea, comparing the He and Ne results with ones obtained using Cu-tubing containers. We show that the new method is superior in precision, suffers a lower loss of samples and is well suited for field work. We also demonstrate agreement in the measurement of AWS and Cu-tubing samples. A further, special use will be sampling in the context of a redetermination of He and Ne solubilities (in progress). For this application, the lowest possible deviation from the water being sampled has been aimed at.

2. Design and construction of the AWS

2.1. Design

The new method uses glass ampoules that are evacuated in the field, filled with water about half and then flame-sealed.

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The ampoules' head space is subsequently transferred into the MS in the home laboratory without further treatment. Flame-sealed glass ampoules are well-proven for safe sample storage, but for the evacuation and filling of an ampoule, a separating valve is needed. Consequently, a small part of the sample is lost in the flame-sealing. Furthermore, some He and Ne remain dissolved in the contained water upon inlet into the MS. Blanks are also a concern, especially for He. For continuity, the sample masses were chosen to be similar to those of our Cu-tubing containers (~42 g). The AWS method builds on a previous approach that used a similar setup, but with the ampoules being evacuated in the home laboratory; for sampling water in the field, they were filled (with head-space left free) by breaking the ampoules' end tubing, whereupon the ampoule was flame-sealed (Roether et al., 1998b). Being found to be prone to air contamination, that approach had to be abandoned.

Fig. 1a shows the device that we have developed. The ampoules (90 ml volume) are made of soda-lime glass, which in our view offers the best combination of He tightness and comparatively easy bake-out (Appendix A). They are connected to a valve via a 3 mm glass end tube and a 1/8″ Swagelok® connector with nylon ferrule.

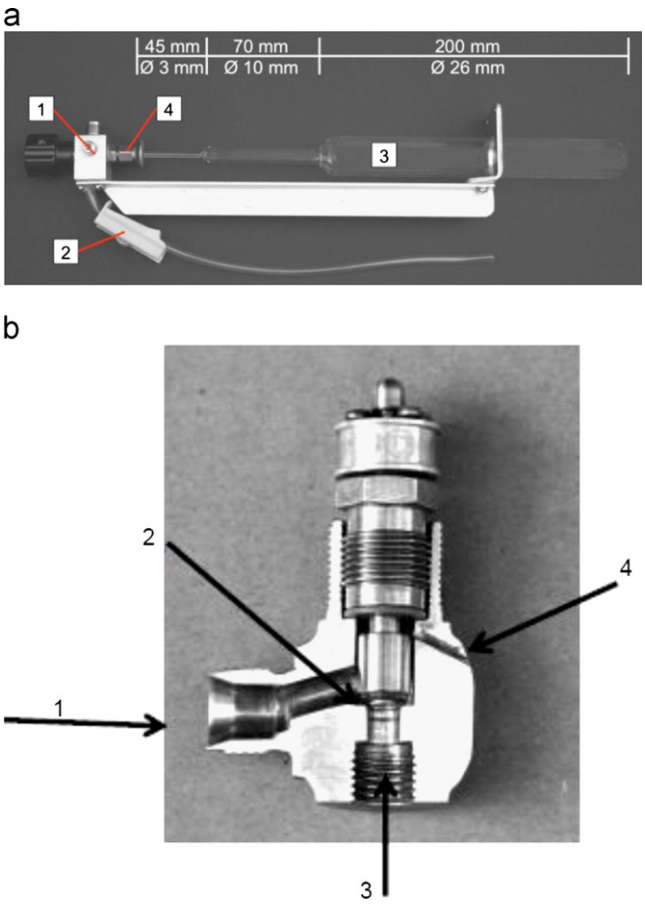

Fig. 1. (a) Photographic view of the Ampoule-based Water Sampler (AWS) in horizontal position (operational position is vertical with the valve on top). The valve (Swagelok® D-series) sits in a U-shaped block (1) to which it is fixed by a screw. The inlet port is on top, and below the rail is the flushing hose with clamp (2). The ampoule (3) is made of soda-lime glass. The middle tubing has 10 mm diameter to fit to our MS inlet ports. The 1/8″ connector (4) to the ampoule carries a temperature shield to protect the nylon ferrules in the flame sealing. (b): Photographic view of a section through the separating valve. (1) inlet port, 1/4″ Swagelok; (2) valve seal; (3) opening to be machined to accept a 1/8″ to 1/4″ Swagelok tube fitting reducer, and (4) position of exit channel for the flushing, connecting to the hose shown in (a). The inner volume below the valve seal is minimized by a custom-made insert with a 1 mm bore; a fed-in 0.5 mm wire raises the flow resistance of the insert about four-fold.

That connection was chosen because the ferrule offers a lower He permeation than an O ring-based connection would (Appendix A). The ampoules' 3 mm far end (Fig. 1a) has sufficient strength that the ampoule can be held in place by merely the Swagelok connector and a loose circular opening in the bracket near to the sample's center of mass. The valve is originally equipped with two 1/4″ Swagelok connectors in a 90° angle pattern. The straight connector is replaced by a 1/8″ connector, with an insert to fill the entire volume between the valve seal and the ferrule except for a narrow bore (Fig. 1b). To enable flushing of the valve head when sampling, the valve is further modified by adding a port that is in permanent connection with the port of water inlet, positioned to optimize the flushing. The added port carries a plastic hose with a clamp for close-off. The valve is mounted on a piece of metal rail to allow safe handling.

For removal of the air prior to sampling, the ampoules are charged with a small amount of water. Pumping sustains a flow of vapor, which flushes out the permanent gases while suppressing any backflow into the ampoules. Therefore, only moderate vacuum (~1 mbar) is needed, and even a small leak of the flushing outlet (plastic hose plus clamp) would not matter. The pumping and water loss rates depend on the vapor pressure and hence on the water's temperature, which in turn, is affected by the consumed heat of vaporization. Another cause of varying rates is differing inner diameters of the ampoules' end tubing, but such variation is counteracted by the additional flow resistance of the 1/8″ connector with insert and fed-in wire, which is designed to raise the combined resistance typically about 4-fold over that of the glass tubing alone.

For sampling water, the inlet line and the valve head of an AWS (that carries a previously evacuated ampoule) are flushed by opening the added port for about 20 s. This is followed by gently opening the separating valve to admit the desired amount of water (within roughly 20 s). Flame-sealing is next, whereupon the samples are ready for measurement. Our regular sample size of 42 g of water fills the ampoule nearly half. Consequently, no more than approximately 1% of the He and Ne remain in the water phase. Blank samples are obtained by simply omitting the filling step. The water charge is 0.2 ml, enough for safe transfer into the MS for the blanks.

Introducing the AWS samples into our MS system is identical to that for Cu-tubing samples (Sültenfuß et al., 2009). Our inlet ports accept glass ampoules with 10 mm end tubing and a short glass tip from the flame sealing. Breaking the tip, the sample enters together with water vapor, which acts as a carrier gas. A cooled surface between capillaries restricts vapor transfer into the MS and regulates the flow. Further downstream, cold traps of decreasing temperature (down to 25 K) reduce water vapor and permanent gases other than He, Ne and hydrogen such that only traces remain. The sample inlet is disconnected after 60 s. To allow one to determine the sample weight after the measurement (Section 3.2), slight heating is applied to transfer the water collected on the cooled surface back into the ampoule.

2.2. Construction details

The ampoules are made of soda-lime glass and their volume is 90 ml, somewhat more than twice the sample volume of about 42 ml. They are custom-made using commercial test tubes of appropriate size, with glass tubing of 10 and 3 mm diameter attached (dimensions see Fig. 1a). The 10 mm middle tubing is required by our MS inlet ports (see above) and thus specific to our system. The 3 mm (or 1/8″) end tubing is originally 9 cm long, to allow the ampoules to be pumped and flame-sealed twice (Section 3.3). The hose is silicon rubber of 5 mm outer diameter and 3 mm inner width and the clamp for close-off and for