

May 17, 2019 Version 1

Bubble strip aqueous gas sampling V.1

DOI

dx.doi.org/10.17504/protocols.io.2x5gfg6



Daniel B Nothaft¹

¹University of Colorado at Boulder

Chemistry Method Devel...



Daniel B Nothaft

University of Colorado at Boulder

OPEN  ACCESS



DOI: dx.doi.org/10.17504/protocols.io.2x5gfg6

Protocol Citation: Daniel B Nothaft 2019. Bubble strip aqueous gas sampling. **protocols.io**
<https://dx.doi.org/10.17504/protocols.io.2x5gfg6>

Manuscript citation:

License: This is an open access protocol distributed under the terms of the **Creative Commons Attribution License**, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited

Protocol status: Working

We use this protocol in our group and it is working. We are planning further tests to compare it against copper tube gas sampling, which is the standard in the noble gas community.

Created: May 16, 2019

Last Modified: May 17, 2019

Protocol Integer ID: 23261

Keywords: bubble strip aqueous gas methane hydrogen



Abstract

The "bubble strip" method has been shown to be an effective means for sampling a gas phase in equilibrium with water (Kampbell et al., 1998). Here, a method optimized for sampling large quantities of equilibrated gas (~60 mL) is demonstrated. This has applications for advanced isotopic analyses, which often require large sample sizes.

Kampbell D. H., Wilson J. T., Mcinnes D. M. (1998) Determining Dissolved Hydrogen, Methane, and Vinyl Chloride Concentrations in Aqueous Solution on a Nanomolar Scale With the Bubble Strip Method. In *Proceedings of the 1998 Conference on Hazardous Waste Research* pp. 176–190.



Materials

MATERIALS

✂ PYREX™ Reusable Media Storage Bottles 100 mL **Fisher Scientific Catalog #06-414-1A**

✂ BOTTLE CAP GASKET FOR GL45 CAPS VITON **COBERT ASSOCIATES LAB STORE Catalog #GS-014**

✂ Cole-Parmer™ VapLock™ Solvent Delivery Caps 304 SS Port Thread Inserts three 1/4 in.-28 **Fisher Scientific Catalog #13-311-001**

✂ Flangeless Nut Short PEEK 1/4-28 Flat-Bottom for 1/8 OD **IDEX Health & Science Catalog #LT-115X**

✂ Extreme-Pressure PEEK Tubing for Chemicals Opaque 0.062 ID 1/8 OD **McMaster-Carr Catalog #51085K49**

✂ Luer Adapter 1/4-28 Female to Female Luer PEEK **IDEX Health & Science Catalog #P-658**

Leap PAL PartsSupplier Diversity Partner VICI Valco MinInert Syringe Valve For Luer-Tip Syringe alLow
✂ Series C and D Syringes to store Samples up to 250 PSI Valve body is PTFE With Stainless Steel stem **Fisher Scientific Catalog #50-109-0255**

✂ BD General Use and PrecisionGlide Hypodermic Needles - 23g (0.064 cm x 2.5 cm) **Fisher Scientific Catalog #14-826A**

Assembling bubble strip apparatus:

This should be pretty straightforward, but here are a few things to keep in mind.

- It is important to replace the standard vaplock cap gasket with a viton gasket. This reduces gas leakage / diffusion out of the bottle.
- Make sure all the fittings for the PEEK tubing are secure. They don't need to be super tight, though.
- The inlet PEEK tubing should be ~1 cm from the top of the bottle, whereas the gas sampling PEEK tubing should be as near to the top of bottle as possible without getting water in it (when cap is on bottom and water is flowing). See photo.

Other things you will need:

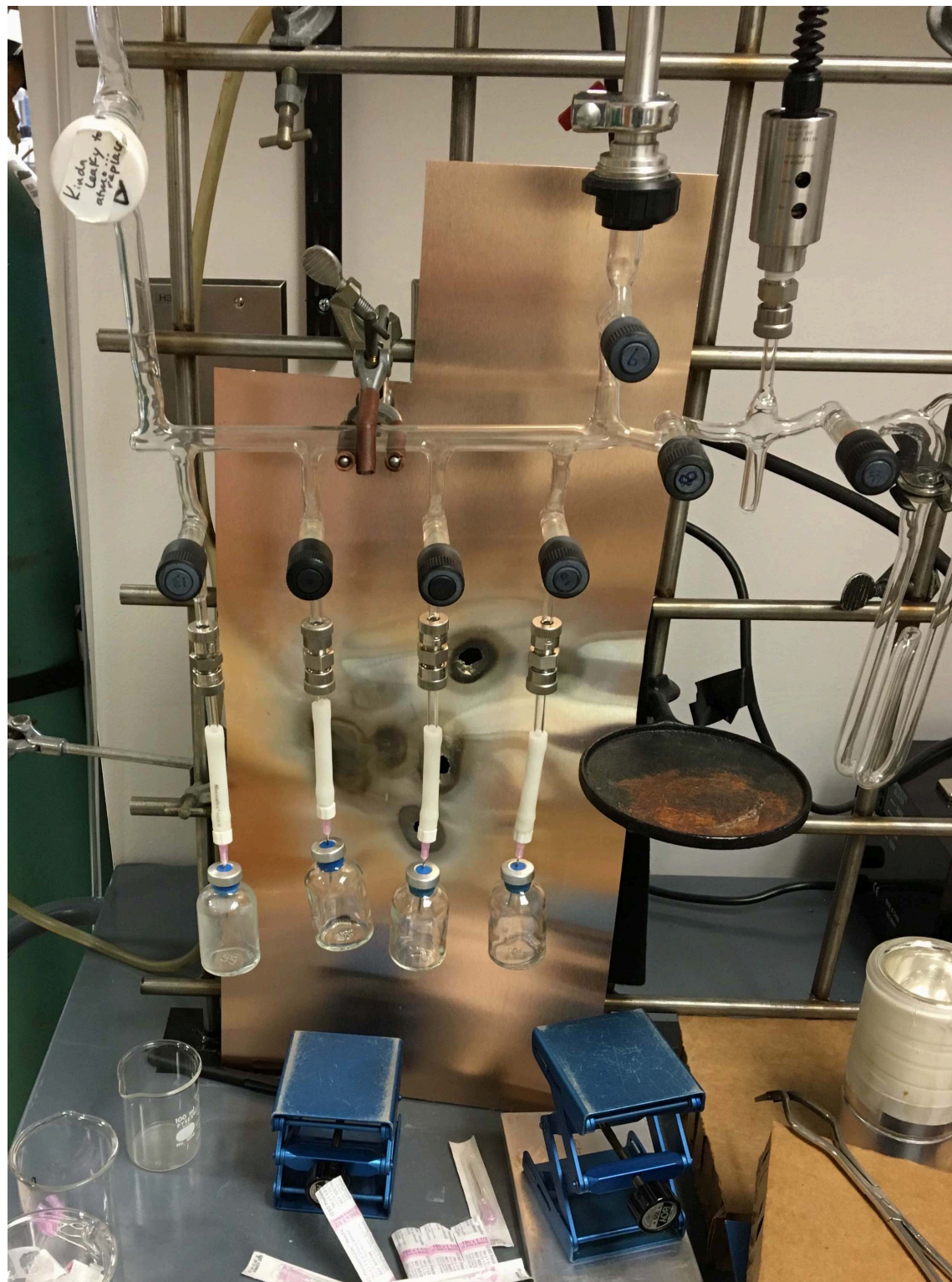
- Ring stand
- Sterile 60 mL syringe with luer lock tip
- Sterile 0.2 µm syringe filter
- Sterile needle (23g is good)

Prepping sample vials

- 1 Pre-treat blue chlorobutyl stoppers to reduce potential contaminants by boiling in 0.1 N NaOH for 45 min followed by immersion in distilled water for ~8 hours), according to procedure of Oremland et al. (1987).

Oremland R. S., Miller L. G. and Whiticar M. J. (1987) Sources and flux of natural gasses from Mono Lake, California. *Geochim. Cosmochim. Acta* 51, 2915–2929.

- 2 Insert stoppers into 37 mL borosilicate glass vials, and secure stoppers with aluminum crimp tops.
- 3 Autoclave sterilize vials (90 minutes at 125°C).
- 4 Evacuate vials. I do this on a glass line connected to turbo pump, about 5 minutes per vial. See photo. Sterile 18G needles are used.



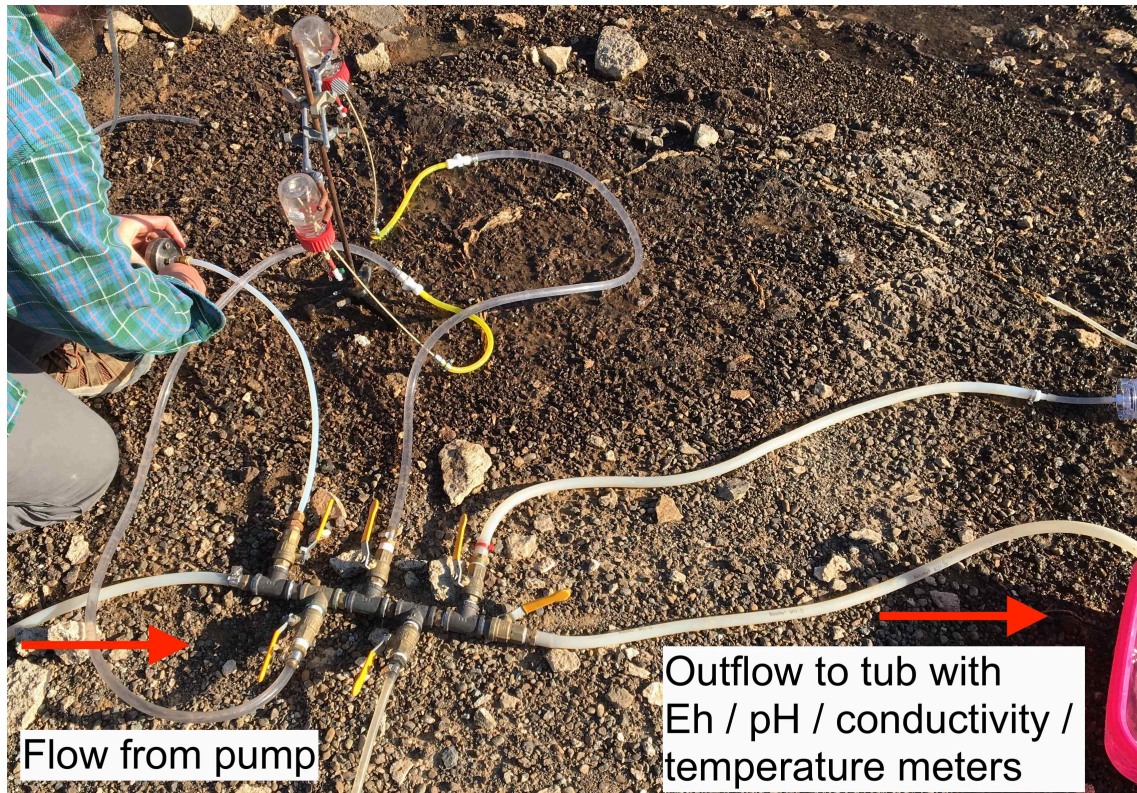
Field sampling

- 5 Attach a 100 mL borosilicate glass bottle (with appropriate fittings installed - see materials) to a ring stand, cap facing up. Connect inlet tubing of bubble strip to pumped water source (i.e. manifold).
- 6 Slowly open water flow valve on manifold. Let bottle fill up with water.
- 7 Flip bottle 180° such that the cap faces downwards.
- 8 Attach a mininert stopcock to a 60 mL plastic syringe. Fill syringe with 60 mL of air.

Note

In Oman sampling in 2017, 60 mL air was used as headspace gas. In 2018, 50 mL high-purity helium was used instead. Choice of the volume and type of headspace gas depends on the application. My primary objective was to obtain large quantities of CH₄ for advanced isotopologue analyses, which is why I used relatively large headspace volumes. Larger headspaces require longer equilibration times and/or higher flow rates. I do not report N₂, O₂, Ar, CO₂, or He measurements on these samples, so the choice of headspace gas (air/He/N₂, and their potential to contaminate the sample if equilibration was not fully obtained) is irrelevant. I used dissolved inorganic carbon analyses on water samples, in addition to pH measurements, to quantify pCO₂. I observed good correlation between the dissolved inorganic carbon analyses and CO₂ measured on bubble strip gas samples, indicating that water/gas equilibrium was obtained, or closely approached.

- 9 Attach syringe to sampling port on bottle cap.
- 10 Inject 60 mL air through the sampling port into the glass bottle. Close mininert valve. The setup should look like this picture. In this example (from 2018 Oman sampling), 2 bubble strip gas samples are equilibrating simultaneously. Other tubes connected to biomass filters and/or water sampling ports are unrelated to the bubble strip.



- 11 Measure flow rate by timing the filling of a 500 mL graduated cylinder from outlet tube. Flow rate should be at least 300 mL/min.
- 12 Periodically monitor flow rate and water temperature. If flow remains at least 300 mL/min, the headspace gas should equilibrate within 30 minutes of flow, and then can be sampled. The water temperature is good to note so that Henry's constants can be adjusted for temperature.
- 13 After sufficient flow has been allowed for gas equilibration, re-attach syringe to bubble strip apparatus if it has been removed (although typically it is best to just leave syringe connected). Then, open mininert valve, and withdraw 60 mL of headspace gas. Close mininert valve.
- 14 Remove syringe and mininert valve from sampling apparatus. Connect a sterile 0.2 μm syringe filter and sterile 23G needle (BD precisionglide) to the mininert valve.
- 15 Open mininert valve on syringe. Inject gas through the filter and needle until the syringe reads 50 mL. Immediately inject the remaining 50 mL of gas into an evacuated 37 mL vial. Holding needle securely, remove syringe from vial.