High-frequency, long-duration water sampling in acid mine drainage studies: a short review of current methods and recent advances in automated water samplers.

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Abstract

Hand-collected grab samples are the most common water sampling method but using grab sampling to monitor temporally variable aquatic processes such as diel metal cycling or episodic events is rarely feasible or cost-effective. Currently available automated samplers are a proven, widely used technology and typically collect up to 24 samples during a deployment. However, these automated samplers are not well suited for long-term sampling in remote areas or in freezing conditions. There is a critical need for low-cost, long-duration, high-frequency water sampling technology to improve our understanding of the geochemical response to temporally variable processes. This review article will examine recent developments in automated water sampler technology and utilize selected field data from acid mine drainage studies to illustrate the utility of high-frequency, long-duration water sampling.

1. Introduction

Hand-collected water samples, also known as “grab”, “spot” or “discrete” samples, are the most common type of water sample collected and well-developed protocols have been established to avoid sampling error and contamination (USGS, 2006). Grab sampling can be very labor intensive and expensive, with significant costs for salary, field vehicles and sampling equipment. For example, the U.S. Geological Survey (USGS) estimated that a single grab sample collected from the Mississippi River costs 4,000-6,000 USD before analytical costs are added in (Horowitz, 2013). If study sites are in areas that are difficult to access (remote, snowbound, large river, etc.) or dangerous (abandoned mines, flash flood or high current areas,

etc.) then sampling costs can increase significantly due to specialized vehicles and safety procedures.

The goal of water sampling is to collect a ‘representative’ water sample while maintaining sample integrity and sample accuracy. One of the greatest challenges in collecting a ‘representative’ water sample is addressing the issue of temporal changes in water chemistry (Madrid and Zayas, 2007). Long-term, high-frequency monitoring of more easily measured water quality parameters such as streamflow and conductivity clearly demonstrate that water chemistry changes can occur on timescales ranging from seconds to years. However, documenting temporally variable processes such as diel cycles or episodic events with traditional grab sampling is often very difficult, expensive and rarely feasible in remote areas.

Efforts to monitor high-frequency biogeochemical aquatic processes have primarily focused on the development of onsite sensors or analyzers for nutrients, gases, and some metals (Johnson et al., 2007, Lourião-Cabana et al., 2010; Namour et al., 2010, Superville et al., 2011). These onsite instruments tend to be relatively expensive (15,000 to >50,000 USD) and most instruments only measure a single analyte (Johnson et al., 2007). Onsite analyzers/sensors are rarely able to provide the multi-element detection capability and low detection limits of lab-based methods so there will always be value in collecting a water sample and taking it back to the laboratory for analysis.

Advances in high-sensitivity analytical instruments such as inductively coupled plasma mass spectrometry (ICP-MS) now provide routine sub-ppb detection of over 40 elements with only a few mLs of sample (Lamothe et al., 2002). Our understanding of biogeochemical processes is greatly enhanced when analytes with differing reaction pathways are detected. For example, in acid mine drainage locations where pH may fluctuate between acidic and neutral conditions, the

geochemical cycling and eco-toxicity of pH-sensitive metals (e.g. Al, Pb, Cu) may be completely different from less pH-sensitive metals (e.g. Zn, Cd) (Nordstrom, 2011).

Recent advances in water sampler design have primarily focused on development and application of passive diffusion samplers which collect a single time integrated sample. (Vrana et al., 2005; Kot-Wasik et al., 2007). In the simplest terms, passive water samplers rely on the diffusive transfer of analytes from the medium (water) through a semi-permeable barrier to a sample collection chamber (Allan et al., 2006; Vrana et al., 2005). Passive samplers have many attractive features including: small size; low-cost (10-100 USD); simple to deploy; require no power or electronics; provide analyte pre-concentration; no water depth limitations; and can be deployed for days to a few months at a time. Membrane composition determines what compounds will diffuse into the sample collection chamber and many different classes of compounds (organics, pesticides, pharmaceuticals, metals etc.) can be sampled with passive diffusion samplers (Vrana et al., 2005; Mills et al., 2007; Pesavento et al., 2009; Balistrieri et al., 2012). Analyte uptake depends on a number of environmental and physical factors that affect the diffusive transfer such as water temperature, turbulence, membrane/gel properties, bio-fouling, etc. and passive diffusion samplers require extensive laboratory and field calibration for proper use (Vrana et al., 2005). While diffusion-based samplers can provide information about time weighted average analyte concentrations, these water samplers are not well suited for examining the details of high-frequency aquatic processes and passive diffusion samplers will not be examined further (Shaw and Mueller, 2009).

This review article will begin with an example of the challenges in remote water sample collection followed by a discussion of currently available high-frequency water sampling technology. Next, a brief look at recent USGS field applications of automated high-frequency

water sampling will be presented followed by a discussion of potential future directions for water sampling. Selected USGS data from acid mine drainage studies in Colorado will be used to illustrate the advantages of high-frequency water sampling for different scientific objectives. The goal of this review article is to illustrate the utility of new automated water sampling technology. A detailed discussion of sampling sites, analytical methods and interpretation of geochemical results are beyond the scope of this article and can be found in the cited literature.

1.1 Limitations of traditional water sampling methods

Figure 1 illustrates the basic problem of matching water sampling frequency with temporally changing water quality in a remote, difficult to access location. The Standard Mine is an abandoned precious metal mine site located at an elevation of 3,350 m near the town of Crested Butte in central Colorado, USA. The Standard Mine was listed as an US Environmental Protection Agency Superfund site in 2006 due to high levels of Zn, Cd, Pb, and Mn issuing from the mine adit (Manning et al., 2011). Access to the mine site is by 4WD vehicle from mid-June to late October. Deep snow from November to June requires snow machines and long backcountry ski trips through avalanche prone areas to access the Standard Mine in winter. Hand-collected samples were analyzed for over 40 elements by ICP-MS and results for Pb and Mn are presented here to demonstrate contrasting geochemical responses to temporally varying conditions (Manning et al., 2011).

Figure 1 shows data from automated daily monitoring of flow and conductivity out of the Standard mine adit and Pb and Mn data from hand-collected grab samples. Adit flow begins to increase in mid-April due to snowmelt runoff, peaks in early June, and decreases to low values

during the summer. Conductivity tends to decrease with increasing flow but there is a lot of variability (Figure 1).

During winter 2010, USGS personnel used 4WD vehicles, snow machines and skis to reach the mine site and collected four bi-monthly grab samples from late March to May (Manning et al., 2011). During the initial snowmelt runoff in mid-April, Pb concentrations spiked from < 0.1 ppm to over 1.5 ppm (Figure 1A), while Mn concentrations decreased from 11 ppm to 7 ppm (Figure 1B). In early May, flow out of the adit decreased, Pb levels decreased towards low baseline values and Mn concentrations increased towards winter high values. Increasing flows from mid-May through June showed elevated Pb levels (Figure 1A). Mn showed a minimum concentration during maximum flow from the adit (Figure 1B). The intensive field efforts during the deep winter demonstrated that early snowmelt changes in flow have a dramatic effect on Pb and Mn concentrations at the Standard Mine Superfund site (Manning et al., 2011). Estimated field costs for salary (3 scientists), vehicles (snow machines), travel and sampling equipment were 2,500 USD per sample for a total of 10,000 USD for four over-winter samples.

From June to September the Standard Mine is accessible by 4WD vehicle and four samples were collected (Figure 1). Pb concentrations were elevated during the peak snowmelt runoff in June and lower during the low flow summer period (Figure 1A). Mn had the opposite trend; lowest concentrations during maximum runoff in June and high concentrations during low flow periods (Figure 1B). Estimated field costs for salary, vehicles travel and sampling equipment were 1,000 USD per sample for a total of 4,000 USD for four samples.

Access to remote sites typically limits water sample collection to a few samples collected during the more accessible summer period and this low-frequency sampling rarely captures the details of transient events. Higher frequency water sampling with hand-collected grab sampling

is labor intensive and often cost prohibitive. The intense winter and summer water sampling at the Standard Mine provided 8 grab samples during a 7 month period with an overall estimated cost of 14,000 USD or 1,750 USD per sample. The need for reliable, low-cost automated water sampling is clear.

2. Commercially available automated water samplers

The high expense of collecting water samples spurred the development of automated water samplers. Most commercially available automated samplers are active samplers which use a mechanical system, usually a pump, to transfer a water sample into a sample container. The primary advantage of active water samplers is that the sampling frequency and sample volume can be user controlled. Active water sampler design is often a balance between a number of competing factors including: cost; power requirements; deployment duration, sample capacity; sample preservation; required analytical volume; ease of deployment; and in situ vs. ex situ deployment. It should be noted that while this article will use examples from high-resolution sampling for toxic metals in acid mine drainage studies, automated water samplers can collect samples for other analytes of interest (nutrients, organics, pesticides, pharmaceuticals, etc.) if appropriate methods are used (Wilde et al., 2014).

The most commonly used active water samplers are siphon auto-samplers (e.g. Teledyne-Isco, Sigma, Hach, Sirco, etc.). These auto-samplers are located out of water on the streambank and use a peristaltic pump to pull water from the stream to fill sample bottles. Deployments typically collect 24 one liter samples but some auto-samplers can be configured to collect fewer larger volume samples (e.g. one 25 liter sample) and some samplers have the capability to collect forty-eight 500 mL samples. These auto-samplers are computer controlled and collect discrete or

time-integrated samples at pre-determined sampling times or in response to an event trigger (depth, conductivity, turbidity, telemetry signal, etc.). These instruments have moderate cost (~5,000 USD) and can be battery powered for field studies. Siphon auto-samplers are a mature sampling technology with well-developed protocols and high reliability (Wilde et al., 2014)).

Excellent high-frequency time series data for long-term toxic mine drainage studies (Fey et al., 2002; Kimball et al., 2010); episodic events (Canovas et al., 2010; Byrne et al., 2013); and diel cycling (Nimick et al., 2011; Gammons et al., 2014) have been obtained with siphon auto-samplers. For example, Nimick et al. (2011) has extensively used siphon auto-samplers for diel metal cycling studies in acid mine drainage areas. Water samples were collected every 1-2 hours for 48-96 hour deployments and demonstrated that diel fluctuations in a number of biogeochemical processes (photosynthesis-respiration, adsorption-desorption reactions, biological uptake, etc.) can regularly change metal concentrations in near neutral pH streams by a factor of 10 over the course of a day (Nimick et al., 2011, Gammons et al., 2014). Diel cycling of toxic metals has very important implications in water quality monitoring strategies and failure to account for changes in metal concentrations due to diel cycling “could lead to data that are potentially biased, inconclusive or misleading” (Gammons et al., 2014).

Siphon auto-samplers, however, do have a number of limitations. Siphon auto-samplers were originally designed for urban storm-water sampling and work best for short term deployments (days-weeks) at easily accessible locations. Longer-term deployments require careful attention to power (line power or large batteries with solar panel recharge), sample preservation issues, and frequent servicing to change out sample bottles. Siphon auto-samplers are also not well suited for remote or difficult to access field sites since they are large, heavy (>40 kg when full), subject to vandalism, and do not operate in freezing conditions without

insulated or heated environmental enclosures (Figure 2). Hand-collected water samples for metal analysis are often preserved by onsite sample filtration and acidification to ~pH 2 (USGS, 2006). However, commercially available auto-samplers do not provide an option for sample filtration and acidification and sample preservation is a major concern with long deployments of siphon auto-sampler deployments. In addition sample bottles in siphon auto-samplers are open to the atmosphere and allow gas exchange could affect sample pH and metal solubilities or introduce airborne contamination to samples. In order to address some of the limitations of siphon auto-samplers, Kim et al. (2012) added a custom built 0.45 μm filtration and acidification module to extend the deployment duration of commercially available auto-samplers.

3 Recent advances for in situ active water samplers

Advances in high-sensitivity, multi-element analytical instruments such as ICP-MS have greatly reduced the sample volume required and routine analysis can be performed on milliliter sized samples. Instead of 100-1000 mL samples collected by typical siphon auto-samplers, new water sampling technologies only need to collect a few milliliters of sample. An ideal active water sampler would have the following attributes: small and easy to transport; low-cost; low-power; provide filtration and sample preservation; be simple to deploy; capable of long-duration deployments and have a high sample capacity. Table 1 provides an overview of the costs and capabilities of the automated water samplers presented in this article.

Submerging an automated water sampler in the stream provides a number of advantages and a few disadvantages. In situ deployment provides more concealment from vandalism, more stable temperature, and the potential to operate under ice in freezing conditions. The disadvantages of in situ deployments are: increased cost/complexity to make the sampler waterproof and able to withstand harsh conditions (freezing conditions, corrosive water, etc.);

safety issues during in stream deployment, and increased risk of losing an instrument in episodic events (spring runoff, flash floods, debris flows, etc.).

A few automated water samplers for oceanographic applications have been developed but these instruments tend to be large, heavy, and very expensive. The McClane RAS sampler and the Envirotech AquaMonitor use a pump and multiport valve to collect 48-50 samples (Honda and Watanabe, 2007). Samples are collected in 50-500 mL collapsible polyethylene bags and onboard filtration and preservation are possible. These instruments cost ~50,000 USD and are not well suited for remote stream deployments. A high-frequency deep ocean water sampler capable of collecting 128 samples was recently developed by Okamura et al. (2013). This instrument uses low-power piezo electric pumps and small solenoid valves to fill one of 128 sample tubes with a 40 mL sample volume. As currently configured, this sampler is designed to collect samples every 3 minutes during a single deep ocean deployment lasting a few hours. The components of the Okumara sampler could be adapted to longer, lower frequency deployments, but this sampler is also large, heavy and expensive (estimated 40,000 USD) and therefore not cost-effective for remote stream water-sampling.

The following low-cost, in situ active samplers solve the design challenge in different ways. These instruments are not commercially available but can be made with standard machining techniques. A small, low cost (~500 USD) in situ water sampler developed by Martin et al. (2004) uses plastic syringes as the sample collection container. This instrument uses ten 60 mL plastic syringes with a powerful spring on the syringe plunger. The outlet of the syringe is connected to a solenoid valve in the closed position which prevents the spring from pulling water into the syringe. A micro-controller opens the solenoid valve at preset intervals and the spring extends the syringe plunger out drawing a water sample into the syringe barrel. Syringes can be

pre-loaded with preservative and common syringe filters can provide standard sample filtration and preservation protocols. To date, this multi-syringe sampler has not been used in field applications but the design concept is sound and deserves further exploration. Multiple samplers could provide increased sampling resolution or deployment duration.

A novel submersible water sampler, the OsmoSampler, utilizes osmotic pumps to collect small volume water samples over periods of months to years (Wheat et. al., 2003; Jannasch et al., 2004). Osmotic pumps require no electrical power, have no moving parts, have no water depth limitations, and use the osmotic gradient across a semi-permeable membrane to generate ultra-low flow rates in the 1 mL/day range (Figure 2). In contrast to passive diffusion samplers which continuously draw water into a sample collection bag and generate one integrated sample, OsmoSamplers slowly pull water into a very long continuous coil of small diameter (~ 1 mm I.D.) teflon tubing. The very low flow rates and small diameter of the sample tubing minimize sample dispersion (smearing) and temporal resolution is maintained as the water sample is pulled through the long coil (Jannasch et al., 2004). A flow rate of 1 mL/day fills 1-2 m of the sample coil depending on the tubing internal diameter and the total sample coil tubing length can be over 2,000 m for multi-year deployments (Wheat et. al., 2003). OsmoSamplers were originally designed for sampling deep ocean boreholes and hydrothermal sites where stable water temperature reduces fluctuation in osmotic flow rate due to temperature changes. Sample flow rate can be controlled by increasing/decreasing the area of the osmotic membrane but there is no user control of sample flow rate once the OsmoSampler is built. Inline filtration and acidification can provide sample preservation if needed (Jannasch et al., 2004). After the OsmoSampler is recovered, the sample coil tubing is cut into 1-2 m sections and the water sample within each cut tubing section is transferred into separate sample vials for later analysis. Hundreds of water

samples can be collected during long deployments and typically provide 1-2 day temporal resolution (Jannasch et al., 2004).

Deployment of osmotic samplers in locations with more variable temperature (i.e. rivers) has recently been demonstrated (Gkritzalis-Papadopoulos et al., 2012A, 2012B). Their key innovation was to add a battery powered micro-pump and temperature logger to the Jannasch OsmoSampler design. The micro-pump injected a visible dye marker into the intake of the osmotic samplers every 24 hours. The dye marker showed some dispersion in the sample coil but the center of the dye marker was clearly visible and represented the precise time of the dye injection. The osmotic sampler provided daily integrated water samples and results compared favorably to hand-collected grab samples for a 30 day deployment (Gkritzalis-Papadopoulos et al., 2012A, 2012B). The OsmoSampler design is flexible and instruments can be configured to fit different applications. For example a 5 or 10 cm diameter OsmoSampler would be ideal for borehole sampling in acid mine drainage monitoring.

In an effort to address some of the limitations of currently available active water-sampling technologies, the USGS developed the MiniSipper to provide high-capacity, long-duration water-sampling in areas that are snowbound for many months or difficult/dangerous to access (Chapin and Todd, 2012). The MiniSipper expanded on the OsmoSampler concept of using a long continuous sample coil to hold multiple water samples. While osmotic samplers rely on very low flow rates in small diameter sample tubing to minimize dispersion, the MiniSipper utilizes low power micro-pumps to inject water samples, add an acid preservative, and inject N₂ bubbles to separate water samples in the long sample coil (Figure 2). A typical deployment collects ~250 acidified five mL discrete or composite water samples (e.g. 0.5 mL collected every 2 hours and composited into a daily 6 mL sample). The MiniSipper can be configured to change

sampling rate in response to an episodic event (e.g. daily sampling then hourly sampling during an event). MiniSipper filtration was initially provided by a 10 μm polyethylene solvent filter which closely tracks the 0.45 μm dissolved fraction (Chapin and Todd, 2012). Current MiniSipper deployments can use 0.45 μm filtration if required. The MiniSipper will operate unattended for 12 months and can sample flowing water under ice and snow for overwinter studies. After recovery, samples are pumped out of the MiniSipper coil into sample vials for analysis. Comparison of MiniSipper results with hand-collected grab samples show that metal results typically agree within 10% (Chapin and Todd, 2012).

3.1 Applications and modifications of MiniSipper technology

The following examples of MiniSipper deployments will illustrate the capabilities of high-frequency water samplers in acid mine drainage studies. It should be noted that MiniSipper technology should be applicable to high-frequency long-duration sampling of other analytes (organics, nutrients, pesticides, etc.) as long as issues of sample preservation are taken into consideration.

Figure 3 shows the results obtained from the MiniSipper for automated high-frequency water sampling at the Standard Mine during March-September 2010 which overlapped the intensive grab sampling presented in Figure 1. MiniSipper sampling provided much more detail of the changes in metal concentrations during snowmelt runoff and 125 samples were automatically collected, filtered and acid preserved during the March 1 to October 1, 2010 period. MiniSipper results provide assurance that the trends observed in the bi-monthly winter grab sampling were real (Figure 3). However, the MiniSipper results also point out the fortuitous timing of the winter

grab sampling. If the bi-monthly sampling had started a week earlier or later, the maximums and minimums in Pb and Mn concentrations may have been missed (Figure 3). The MiniSipper results also demonstrated that the highest Pb concentrations were missed by the grab sampling (Figure 3A). The cost for the MiniSipper deployments was 2,000 USD for the instrument and 2,000 USD for two field trips, yielding an estimated cost of 32 USD per MiniSipper sample, more than fifty times less costly than conventional grab sampling.

Figure 4A shows a direct comparison of hourly sampling with a MiniSipper and an Isco siphon auto-sampler for a diel cycling study in Leavenworth Creek in central Colorado. The MiniSipper was deployed unattended for 3 days and provided online filtration and acidification. The Isco samplers required personnel onsite for daily field processing of samples (filtration and acidification) and re-loading fresh sampling bottles into the auto-sampler. Both instruments show a diel cycle in Zn concentration at very low levels (< 25 ppb) with lowest Zn concentrations during late afternoon, the warmest part of the day (Figure 4A).

The small size, high sample capacity (250 samples or more), and long-duration capability of the MiniSipper provide tremendous flexibility for remote aquatic sampling. Figure 4B shows the results of an underground lithium tracer study in an abandoned mine in central Colorado. The tracer sampling site was located almost 2 km from the mine entrance and the small size of the MiniSipper allowed the instrument to be carried relatively easily to the deep underground site. The MiniSipper sampled every 2 hours for a week and recorded the Li tracer breakthrough on day 2 of the experiment (Figure 4B).

The standard MiniSipper is not well suited for locations where water depth changes significantly due to seasonal flow changes or flash floods. MiniSippers can be deployed up to 1 m deep but if water depth (pressure) increases significantly then the small micro-pumps do not

pump effectively. A shore-based version of the MiniSipper designed for event-response sampling in flash flood areas is currently undergoing field testing. This instrument places the MiniSipper well above expected flash flood height and uses separate peristaltic pumps to draw water out of the stream and push it up to the MiniSipper. The MiniSipper draws samples weekly during normal conditions and a water contact trigger sends the MiniSipper into a high-frequency sampling mode during a flash flood event. The high sample capacity (250 samples) allows long duration deployments and multiple flash flood events can be sampled automatically.

4. Future directions and conclusion

Future developments in automated water sampling could utilize recent advances in micro-fluidics. Micro-fluidic sensors/analyzers have the potential to offer significant cost-savings through mass production and a few instruments have been successfully deployed for aquatic monitoring conductivity, pH, nutrients and metals (Johnson et al., 2007, Namour et al., 2010). A literature search for applications of micro-fluidics technology to create a high-capacity, long-duration micro water samplers did not produce any references. One possible approach would be coupling a micro-pump to a multi-port valve manifold with numerous 1-2 mL sample channels. Stacking sample channels horizontally and vertically could create a sample manifold that could hold 500 samples in a cube ~15 cm on a side. Micro-fluidic pumps are commercially available but multi-port valve manifolds are not yet commercially available and adapting this micro-fluidics technology for long-term in situ water samplers will be a challenge.

The high expense incurred by traditional water collection methods has spurred development of new automated water samplers. The development and application of passive

water samplers for water quality monitoring has far outpaced the development of active water-sampling technology. However, new water-sampling technology such as MiniSippers and OsmoSamplers have greatly enhanced our ability to examine high-frequency and episodic processes in aquatic systems. In the future, low-cost, high-capacity, long-duration water-sampling instruments could have a major impact on water quality monitoring programs.

Table1. Available automated sampler technology

Instrument	Sample Type Discrete Integrated	# Samples	Sample size (mL)	Typical Duration	Sample control Adjustable Fixed	Event Capable	Sample Preservation	Approx Cost (USD)	Ref
Siphon Auto-samplers	D, I	1-24	500-1000	days-weeks	A	Yes	No	5,000	Wilde (2014)
McLane RAS	D	48	50-500	Months years	A	No	Yes	50,000	Honda (2007)
Okamura	D	128	40	hours	A	No	Possible	40,000?	Okamura (2014)
Syringe Sampler	D	10	60	weeks-months	A	No	Possible	500	Martin (2004)
Osmotic Samplers	I	10s-100s	~1 mL	months-years	F	No	Yes	2,000	Jannasch (2004)
MiniSipper	D, I	100-500	2-10	months-years	A	Yes	Yes	2000	Chapin (2012)

Figure 1: Standard Mine March to September 2010 data for conductivity (—), flow (---), Pb (A) and Mn (B). Summer 4WD access provided 4 grab samples (●). Winter snow-mobile and backcountry ski access provided 4 additional grab samples (○). Snowmelt runoff beginning in April lead to dramatic changes in Pb and Mn concentrations.

ISCO samplers in
winter insulated shack

OsmoSampler

MiniSipper

Figure 2. Automated water sampler options for overwinter sample collection.

Figure 3. Field comparison of Standard Mine MiniSipper and grab sample results for Pb (A) and Mn (B). MiniSipper was deployed in October 2009 and recovered in July 2010 when the Standard Mine was accessible by 4WD. Winter access for hand-collected grab samples required snow mobiles and backcountry skiing. MiniSipper results agree with hand-collected grab samples but the MiniSipper captured details of higher Pb fluctuations during snowmelt runoff from April to June that were missed by grab sampling.

Figure 4. Field applications of MiniSipper high-frequency water sampling. Comparison of Zn diel cycling in Leavenworth Creek, CO captured by MiniSipppe and ISCO siphon auto-samplers (A). MiniSipppe operated unattended for the 3 day diel study while the Isco sampler required sample bottle replacement every 24 hours. Underground deployment of MiniSipper for Li tracer study (B). Deployment site was over 1.5 km from mine entrance in a partially flooded mine. The high-frequency automated water sampling over the 7 day tracer study was only possible due to the small size and portability of the MiniSipper instrument.

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