A Handheld Sampler for Collecting Organic Samples from Shallow Hydrothermal Vents

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ABSTRACT

This study describes a new handheld sampler, specially designed to be deployed by scuba divers, to collect fluid samples from shallow hydrothermal vents. The new sampler utilizes a syringe-like titanium sampling bottle with a regulated filling rate to collect samples. The filling rate regulation mechanism of the new sampler was studied. Through theoretical analysis and simulation, it is found that the filling rate can be regulated by either an orifice or an annular gap on the sampler. Further study indicates that the orifice is superior to the annular gap, since the former has a much lower requirement of machining accuracy. Moreover, the filling rate regulated by the orifice is independent of temperature and ambient pressure. The new sampler also features a compact structure, simple operation, and gas-tight performance. Efforts were made to minimize the organic carbon blank of the sampler by careful selection of the materials that may come into contact with the fluid samples. The sampler has been tested at the shallow hydrothermal vents off northeastern Taiwan. High-purity organic samples were successfully collected.

1. Introduction

The dissolved organic matter (DOM) in hydrothermal fluids plays an important role in the biological processes in hydrothermal systems. The origin and cycling of dissolved organic carbon (DOC) in hydrothermal systems may have critical implications to understanding the origin and evolution of life on Earth (Lang et al. 2006; Martin et al. 2008). In recent years, the organic chemistry of both deep-sea and shallow hydrothermal systems has received more and more attention, although the studies are far from enough (e.g., Svensson et al. 2004; Skoog et al. 2007; Konn et al. 2009; Lang et al. 2010; Chen 2011; Mccarthy et al. 2011; Yang et al. 2012).

The methods for studying the chemistry of hydrothermal fluids are generally summarized into two kinds: 1) in situ measurement with chemical sensors and analyzers, which is confined to several specific species, such as H$_2$S, H$_2$, pH, nitrate, sulfide, dissolved iron, and so on (e.g., Le Bris et al. 2000; Ding et al. 2001; Ding and Seyfried 2007; Vuillemin et al. 2009; Tan et al. 2012); and 2) collection of fluid samples with suitable samplers and then completion of the analysis using the instruments on board ships or onshore (e.g., Edmond et al. 1992; Seewald et al. 2002; Wu et al. 2011). To date, the in situ chemical sensors and analyzers are mainly focused on the measurement of inorganic matter. The study of the organic chemistry of hydrothermal fluids largely relies on the sampling method. Samplers for collecting organic samples from deep-sea hydrothermal vents include the “major” samplers (Lang et al. 2006), the Hydrothermal Fluid and Particulate Sampler (HFPS) (Lang et al. 2010), a gas-tight titanium bottle, and the isobaric gas-tight sampler (Proskurowski et al. 2008). One common feature of these samplers is that they are all made of chemically inert materials. The samples collected only came into contact with titanium, Teflon, or Tedlar polyvinyl fluoride (PVF). These samplers have low organic carbon blanks when properly cleaned. However, they are not suitable for shallow hydrothermal vents. The main reason is that they were designed to be deployed by underwater...
vehicles, like manned submersibles and remotely operated vehicles (ROVs), and are not suited to be operated by scuba divers. In contrast to the deep-sea samplers, there is almost no sampler specially designed for shallow hydrothermal fluids.

In recent years, a number of shallow hydrothermal vents have been found and studied at the flanks of volcanic islands and on the tops of seamounts (Pichler et al. 1999; Chen et al. 2005a,b; Cardigos et al. 2005; Valsamis-Jones et al. 2005). In earlier studies, collection of fluid samples at these shallow sites was usually fulfilled by plastic bottles [e.g., polyvinyl chloride (PVC)] or medical syringes operated by scuba divers. These methods are simple and low cost; however, because of the lack of real-time measurement of temperature while sampling, it is difficult to obtain pure fluid samples, as the hydrothermal fluids usually have a steep temperature gradient when they erupt out of the vent and mix with seawater. Moreover, the plastic bottles and syringes are also not suitable for measurements of organic matter. Currently, organic samples of shallow hydrothermal vents are collected using evacuated glass bottles (Svensson et al. 2004; Skoog et al. 2007; Yang et al. 2012). One problem with this method is that the filling rate is very fast and cannot be regulated. In fact, as the hydrothermal fluid rushes in when the valve is opened, the sudden suction often entrains the surrounding seawater as well.

In this paper, we present a new sampler specially designed to be operated by scuba divers to collect fluid samples from shallow hydrothermal vents. The new sampler employs a titanium syringe bottle and a Teflon fluorinated ethylene propylene (FEP)-encapsulated O-ring seal to achieve a good gas-tight performance while minimizing the organic carbon blank, so it is well suited for the study of organic chemistry of shallow hydrothermal fluids. A temperature logger is integrated into the new sampler to allow for real-time temperature measurement, temperature display, and storage temperature during sampling process. In addition, the filling rate of the new sampler can be regulated. The new sampler features a compact structure, easy operation, and the capability to obtain high-purity hydrothermal fluids.

2. Design of the handheld sampler

a. Instrument description

The schematic illustration of the new sampler is shown in Fig. 1. The major component of the sampler is a syringe-type titanium bottle that mainly consists of a sample chamber with a volume of 500 mL, a piston, and a compression spring. A commercially available needle valve is adopted here as the sampling valve. In addition, a temperature logger chamber is fixed above the sample chamber to allow the scuba diver to monitor the temperature. Without the snorkel and L-shaped handle, the new sampler is 42 cm long, 8.5 cm wide, and 24 cm high. It weighs approximately 4.5 kg in air and 3.9 kg in seawater.

Prior to deployment, the piston is positioned at the bottom of the chamber (as shown in Fig. 1). The snorkel, sampling valve (which is left open prior to deployment), and sample chamber on the back side of the piston are filled with ultrapure water. The total sampler dead volume is approximately 5 mL. The spring is compressed, while the snorkel and L-shaped handle, the new sampler is 42 cm long, 8.5 cm wide, and 24 cm high. It weighs approximately 4.5 kg in air and 3.9 kg in seawater.

In this paper, we present a new sampler specially designed to be operated by scuba divers to collect fluid samples from shallow hydrothermal vents. The new sampler employs a titanium syringe bottle and a Teflon fluorinated ethylene propylene (FEP)-encapsulated O-ring seal to achieve a good gas-tight performance while minimizing the organic carbon blank, so it is well suited for the study of organic chemistry of shallow hydrothermal fluids. A temperature logger is integrated into the new sampler to allow for real-time temperature measurement,
packing ring and FEP-encapsulated O-rings, respectively. The combination of the FEP exterior and elastic rubber core gives the FEP-encapsulated O-rings excellent chemical resistance (similar to Teflon) and good compressibility. This kind of O-ring is employed here to give the sampler good sealing performance and low organic carbon blank. As the sampler is triggered by the finger of the scuba diver, the trigger force must be as small as possible. Therefore, two linear bearings are applied to reduce the friction force on the shaft.

b. Temperature logger

High-temperature hydrothermal vent fluids usually have a steep temperature gradient, as they mix with seawater. During collection, the placement of the sampler snorkel into the hydrothermal vent orifice is critical to the collection of high-purity vent fluids. Temperature is used as the guide for snorkel placement, as the highest temperature indicates where the vent fluid is undergoing the smallest amount of mixing with the surrounding seawater (Fornari et al. 1997). Therefore, a temperature logger is integrated into the new sampler to allow for real-time temperature measurement, temperature display, and storage during the sampling process. As shown in Figs. 1 and 2, the temperature logger utilizes a thermocouple (type E), which is housed in a 1/8-in.-diameter titanium tube, to measure the temperature of hydrothermal fluids. The titanium tubing is connected to the electronics chamber via a Parker Autoclave Engineers fitting. Inside the chamber, a thermistor is used to measure the cold junction temperature of the thermocouple. The outputs of the thermocouple and thermistor are digitized by a circuit board, the results of which are then converted to temperature and displayed via a light-emitting diode (LED) display. In addition, the circuit board also integrates the real-time clock (PCF8563), flash memory (ATD45DB321), and RS232 serial communication (LTC1385) modules. When working at a time interval of 1 s, the temperature logger is able to record 8 days of temperature data.

3. Characteristics of the filling rate regulation

a. Modeling of the sampling process

The filling rate of the evacuated glass bottles used for the collection of organic samples from shallow hydrothermal vents in previous studies is very rapid. This may introduce excessive entrainment of ambient seawater. So, the capability of effective filling rate regulation is critical to the hydrothermal fluid sampler. As shown in Fig. 3, the filling rate of the new sampler can be regulated by two methods: 1) the orifice on the end cap and 2) the annular gap between the piston rod and end cap. In the first model (Fig. 3a), an O-ring seal is used to prevent water from flowing through the gap between the piston rod and end cap. The snorkel and sampling valve are not considered in both models, since they have relatively larger flow passages compared to the orifice and annular gap.

Mathematical models of the new sampler are established according to the simplified physical models. During the sampling process, the dynamic equation of the piston is

\[ k_s (l_0 - x) - f - B_p \frac{dx}{dt} - A_p \Delta p = m \frac{d^2x}{dt^2}, \]  

where \( k_s \) is the stiffness of spring; \( l_0 \) is the initial compression length of spring; \( x \) is the displacement of the piston; \( f \) is the dynamic friction force between the piston
and the chamber; \( B_p \) is the viscous friction coefficient; \( A_p \) is the effective area of the piston on the side with the piston rod; \( \Delta p \) is the pressure differential between the chamber interior (on the back side of the piston) and ambient seawater; and \( m \) is the total mass of the piston, piston rod, and spring seat. For the model with the orifice, the flow equation is expressed as follows:

\[
A_p \frac{dx}{dt} = C_q A_o \left( \frac{2\Delta p}{\rho} \right)^{1/2},
\]

where \( C_q \) is the flow coefficient, \( A_o \) is the cross-sectional area of the orifice, and \( \rho \) is the density of water. Based on Eqs. (1) and (2), the following equation is obtained:

\[
m \frac{d^2 x}{dt^2} + \frac{6\mu A_p (2A_p - \pi \delta)}{2C_q A_o} \left( \frac{dx}{dt} \right)^2 + B \frac{dx}{dt} + k_x x + f - k_s l_0 = 0.
\]

(3)

Since Eq. (3) is a second-order nonlinear differential equation, it is difficult to find the analytical solution. However, the numerical solution of Eq. (3) can be easily obtained using Matlab software algorithms.

For the model with concentric annulus, the flow equation is

\[
A_p \frac{dx}{dt} = \frac{\pi d^3}{12\mu l} \Delta p + \frac{1}{2} \frac{dx}{dt} \pi d \delta,
\]

where \( d \) is the diameter of the piston rod, \( \delta \) is the gap between the piston rod and the hole on the end cap, \( \mu \) is the kinetic viscosity, and \( l \) is the length of the annulus. As a result, the following equation is obtained:

\[
m \frac{d^2 x}{dt^2} + \frac{6\mu A_p (2A_p - \pi \delta)}{\pi \delta^3} \frac{dx}{dt} + B \frac{dx}{dt} + k_x x + f - k_s l_0 = 0.
\]

(5)

The analytical solution of Eq. (5) is given as follows:

\[
x(t) = \frac{k_s l_0}{k_s} - \frac{f}{k_s} \left( 1 - m\frac{a_1 - a_1 e^{-a_1 t} - a_1 - m\beta}{m\omega} e^{-\beta t} \right),
\]

(6)

**TABLE 1. Parameters of the sampler used for calculation and simulation.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stiffness of spring (( k_s ))</td>
<td>1550</td>
<td>N m(^{-1} )</td>
</tr>
<tr>
<td>Initial spring force (( k_s l_0 ))</td>
<td>298</td>
<td>N</td>
</tr>
<tr>
<td>Friction force (( f ))</td>
<td>80</td>
<td>N</td>
</tr>
<tr>
<td>Diameter of piston</td>
<td>70</td>
<td>mm</td>
</tr>
<tr>
<td>Diameter of piston rod (( d ))</td>
<td>10</td>
<td>mm</td>
</tr>
<tr>
<td>Effective area of piston (( A_p ))</td>
<td>( 3.77 \times 10^{-3} )</td>
<td>m(^2 )</td>
</tr>
<tr>
<td>Mass of piston, rod, and spring seat (( m ))</td>
<td>0.7</td>
<td>kg</td>
</tr>
<tr>
<td>Flow coefficient (( C_q ))</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Density of water (( \rho ))</td>
<td>1000</td>
<td>kg m(^{-3} )</td>
</tr>
<tr>
<td>Kinetic viscosity (( \mu ))</td>
<td>0.89</td>
<td>cP</td>
</tr>
<tr>
<td>Length of the annulus (( l ))</td>
<td>10</td>
<td>mm</td>
</tr>
<tr>
<td>Length of snorkel</td>
<td>500</td>
<td>mm</td>
</tr>
<tr>
<td>Inner diameter of snorkel</td>
<td>4</td>
<td>mm</td>
</tr>
</tbody>
</table>
where
\[ \alpha = \frac{a_1}{2m} + \frac{m \omega}{2m}, \quad \beta = \frac{a_1 - m \omega}{2m}, \quad \text{and} \quad \omega = \left[ \left( \frac{a_1}{m} \right)^2 - \frac{4k}{m} \right]^{1/2}. \]

**b. Simulation results**

Beside the above-mentioned mathematical modeling, a simulation of the sampling process was also conducted using AMESim software. As shown in Fig. 4, the simulation models are similar to the simplified physical models, except that the snorkel was considered during the simulation. A hydraulic annular pipe was used to simulate the concentric annulus in the second sampler model. The main parameters of the sampler are shown in Table 1. The dynamic friction force of the piston was measured to be about 80 N. The viscosity of water at 25°C was selected in this study (Kestin et al. 1978). Since the viscosity of water is very low, the viscous friction was ignored during simulation.

A parameter study was carried out to investigate the influence of different orifice and annular gap sizes on the filling rate using the constants in Table 1. As shown in Fig. 5, for both sampler models, the filling rate (illustrated as the displacement of piston) is well regulated by the orifice (Fig. 5a) and annular gap (Fig. 5b). However, when the sizes of the orifice and annular gap are greater than 5 and 0.3 mm, respectively, the filling rate becomes almost constant and is predominantly controlled by the sampler snorkel. Usually, it is better to use a sampler with a slow filling rate to collect hydrothermal fluids from diffuse vent areas characterized by low flow rates and low temperatures. When sampling high-temperature hydrothermal vents characterized by high flow rates, the filling rate of sampler can be faster.

From Fig. 5 one may obtain the filling time when the piston moves to the end of sample chamber (when the piston displacement is 130 mm). It may be seen that the filling time has a good proportional relationship with the inverse square of the orifice diameter and the inverse cube of the gap size. Obviously, the filling rate is more sensitive to the change in gap size. Meanwhile, one may see that the size of the gap is an order of magnitude smaller than that of the orifice at the same filling time.
From the viewpoint of machining, the orifice is better than the concentric annulus in regulating the filling rate of the sampler. Moreover, the filling rate of the sampler with concentric annulus is influenced by the viscosity of water, which changes dramatically with temperature (Kestin et al. 1978). As the hydrothermal vents and diffuse flow areas have different temperature gradients, the temperature of the sampler chamber may vary from several degrees Celsius to tens of degrees Celsius when collecting hydrothermal fluids. As shown in Fig. 6, the filling time increased by 1.5 times when the temperature changes from 50° to 5°C. On the contrary, the filling rate regulated by the orifice will not change with temperature. Another feature of this type of sampler is that the filling rate will not change with ambient pressure, which is certainly in contrast to the previous gas-tight samplers (Chen et al. 2007).

c. Experimental results

To verify the accuracy of the simulation results, the filling times of both sampler models with three sizes of orifices (1.7, 2, and 2.5 mm) and one size of annular gap (0.12 mm) were measured in the laboratory. Each filling time was measured three times. As shown in Table 2, the measured filling times agree well with the simulation results. It should be pointed out that the water temperature during the experiments was 9°C. So, the simulation results in Table 2 were based on this temperature and the water viscosity of 1.35 cP (Kestin et al. 1978).

Table 2. Comparison of the filling times between experiments and simulations.

<table>
<thead>
<tr>
<th>Sampler</th>
<th>Diam or gap size (mm)</th>
<th>Expt filling time (s)</th>
<th>Avg expt filling time (s)</th>
<th>Simulation filling time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orifice 1.7</td>
<td>45.9, 45.8, and 45.3</td>
<td>45.7</td>
<td>46.7</td>
<td></td>
</tr>
<tr>
<td>Orifice 2</td>
<td>35.9, 36.0, and 34.9</td>
<td>35.6</td>
<td>34.8</td>
<td></td>
</tr>
<tr>
<td>Orifice 2.5</td>
<td>20.9, 21.5, and 21.7</td>
<td>21.4</td>
<td>24.1</td>
<td></td>
</tr>
<tr>
<td>Annular gap</td>
<td>73.2, 74.7, and 72.9</td>
<td>73.6</td>
<td>72.0</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7. Collecting hydrothermal fluid samples using the new sampler at shallow hydrothermal vents off Kueishantao islet. Collecting samples at (a) a yellow vent and (b) a white vent. Temperature display at (c) the yellow vent and (d) the white vent.
4. Field test and results

The new handheld sampler was tested at the shallow hydrothermal vent site near Kueishantao islet (24°51′N, 121°55′E), which is located offshore of northeastern Taiwan. The known hydrothermal vents in this area, distributed at a water depth less than 30 m, fall into two typical kinds of vents: 1) yellow vents that discharge yellowish fluids with temperatures of 78°–116°C and 2) white vents that discharge whitish fluids with lower temperatures of 30°–65°C (Chen et al. 2005a,b). Hydrothermal fluids from both a yellow vent and a white vent were collected by using the new sampler during a cruise on 25 May 2011 (Fig. 7). In addition, hydrothermal fluids from the yellow vent were also collected by using traditional evacuated glass bottles during the same cruise. Water samples above the white vent were collected with PVC bottles.

The temperature logger worked very well during the sea trial. The highest temperature of the yellow vent was measured to be 116°C, which is consistent with previous observations. The temperature of the yellow vent was stable at 115°–116°C during sampling, indicating the successful collection of a high-purity fluid sample (Fig. 8a). In contrast, the temperature of the white vent varied approximately between 36° and 50°C (Fig. 8b). This phenomenon is typical of diffuse hydrothermal vents characterized by low flow rates and low temperatures.

Chemical analysis results of the samples are shown in Tables 3 and 4. In general, the DOC concentrations are lower than those reported in the previous study (Yang et al. 2012). The DOC concentration of the sample collected using the evacuated glass bottle is higher than that of the sample collected at the same time using the new sampler. This might be due to the entrainment of excessive seawater of a higher DOC concentration during sampling using the evacuated glass bottle, which on the other hand proved the capability of the new sampler to collect high-purity hydrothermal fluids. From Table 4, it may be seen that the sample collected at the white vent is of the lowest salinity and density, which agrees with the explanation that phase separation might have happened before the hydrothermal fluids erupted out of the vent (Chen et al. 2005b). So, lower salinity and density indicate higher purity of the collected hydrothermal fluid sample. The salinity of the white vent sampled during this cruise is very close to the lowest salinity (33.1) that was measured previously (Chen et al. 2005b), thus suggesting this was a high-purity hydrothermal fluid sample.

5. Conclusions

A new sampler for the collection of shallow hydrothermal fluids has been successfully designed and constructed. Since the samples collected only make contact with titanium, Teflon, and FEP, the sampler is well suited for the measurement of organic matter. The dynamic characteristic of the sampler has been studied. The filling rate can be regulated by either an orifice or the annular gap between the piston rod and the end cap. Results of theoretical analysis and simulation show that the orifice is better than the annular gap in regulating the filling rate, as the machining accuracy of the former can be much lower than the latter and the filling rate is independent of temperature. With the integration of in
site temperature measurement and filling rate regulation, this sampler is able to collect high-purity hydrothermal fluids from both high-temperature vents and low-temperature diffuse flow vents.

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REFERENCES


TABLE 4. Salinities and densities of the samples collected from white vent and the water column above white vent.

<table>
<thead>
<tr>
<th>Station</th>
<th>Salinity</th>
<th>Density (g cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>White vent</td>
<td>33.23</td>
<td>1.02200</td>
</tr>
<tr>
<td>2 m above vent</td>
<td>33.69</td>
<td>1.02242</td>
</tr>
<tr>
<td>7 m above vent</td>
<td>34.06</td>
<td>1.02266</td>
</tr>
<tr>
<td>10 m above vent</td>
<td>33.79</td>
<td>1.02250</td>
</tr>
</tbody>
</table>