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# Development of an *in situ* analysis system for methane dissolved in seawater based on cavity ringdown spectroscopy

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### ABSTRACT

This paper reports the development of a compact *in situ* real-time concentration analysis system for methane dissolved in seawater by using a continuous-wave cavity ringdown spectroscopy (CRDS) technique. The miniaturized design of the system, including optical resonance cavity and control and data acquisition-analysis electronics, has a cylindrical dimension of 550 mm in length and 100 mm in diameter. Ringdown signal generation, data acquisition and storage, current driver, and temperature controller of the diode laser are all integrated in the miniaturized system circuits, with an electrical power consumption of less than 12 W. Fitting algorithms of the ringdown signal and spectral line are implemented in a digital signal processor, which is the main control chip of the system circuit. The detection sensitivity for methane concentration can reach 0.4 ppbv with an approximate averaging time of 240 s (or 4 min). Comparing the system's measurement of ambient air against a high-quality commercial CRDS instrument has demonstrated a good agreement in results. In addition, as a "proof of concept" for measuring dissolved methane, the developed instrument was tested in an actual underwater environment. The results showed the potential of this miniaturized portable instrument for *in situ* gas sensing applications.

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## I. INTRODUCTION

The concentration of dissolved gases in seawater has a significant impact on marine ecology and is also an important parameter for observing the changes in ocean water environment. In particular, methane is an efficient and clean energy source, an important greenhouse gas, and an important part of the Earth's carbon cycle.<sup>1</sup> In recent decades, extensive research related to methane has been conducted through remote sensing and sampling of seawater.<sup>2–6</sup> However, advancements in measurement techniques are needed for future investigations of dissolved gases in seawater. This is because traditional methods are based on analysis of collected water samples, making it difficult to meet continuous long-term observation needs. Submarine sediments contain a large amount of methane, which are generally stored in deep sediments as hydrates, and are extremely sensitive to changes in temperature and pressure. Rising sea levels and seawater temperatures due to global warming have lowered the stability of methane hydrate in seafloor sediments, and the cleavage of hydrates releases a large amount of methane into seawater.<sup>2</sup>

*In situ* detection technology<sup>3–6</sup> is better than traditional methods as it has the advantage of providing real-time continuous monitoring measurements. In addition to monitoring methane dissolved in seawater, some other applications also urgently need *in situ*, fast, and accurate dissolved gas detection, for example, geochemistry, monitoring marine environments and water quality, exploration of submarine oil and gas resources, and leak inspections of natural gas pipelines.<sup>7</sup> In recent years, there have been some developments in *in situ* seawater-dissolved gas detection technologies, such as instruments based on semiconductor gas sensing devices, mass spectrometry,<sup>4,8</sup> and infrared absorption spectroscopy;<sup>5–7,9</sup> however, further development of the measurement technologies for gases dissolved in seawater is still required. In this work, we applied a laser cavity ringdown spectroscopy (CRDS) technique for optical detection of methane.<sup>3,10–12</sup>

CRDS is an ultra-sensitive cavity-enhanced direct absorption spectroscopy technique.<sup>11,13</sup> The sample of gas-phase molecules is contained in a high-finesse optical cavity into which a coherent laser light is introduced. This light is allowed to build up in intensity and then interrupted by one means or another.<sup>11,12,14</sup> The decay (i.e., "ringdown") of the intra-cavity light has a characteristic exponential time constant, which depends on the reflectivity of the cavity mirrors and additional intra-cavity optical losses. An optical absorption causes the ringdown rate constant to increase relative to that for an absorber-free cavity. Such cavity-enhanced techniques benefit from the fact that the equivalent effective absorption path length is significantly enhanced (up to tens of kilometers) due to multiple reflections by the highly reflective cavity mirrors.

Another advantage of CRD spectroscopy is that it measures the temporal decay of radiation inside the cavity, rather than transmitted optical power that is measured in conventional absorption spectroscopy. This allows the CRD approach to be insensitive to initial light intensity and its fluctuations. A further advantage of the CRDS method is that it measures the spectral absorption coefficient based on a change in the decay rate of the intra-cavity light. No calibrations during field deployments are required. Therefore, the CRDS technique is particularly well suited for making accurate long-term monitoring measurements.

In this paper, we report the development of a compact CRDS system for *in situ* measurements of methane dissolved in seawater. The system was designed by a linear optical resonance cavity,

embedded with hardware and software. Section II will describe the design of the optical system, embedded hardware circuit system, and CRDS signal processing algorithm. Section III will cover the comparison measurement results and *in situ* tests.

### **II. DESIGN AND IMPLEMENTATION**

The diagram of our compact instrument for *in situ* analysis of  $CH_4$  dissolved in seawater is shown in Fig. 1. It comprises various function blocks and can be grouped as: (a) dissolved gas extraction, (b) mechanical and optical structure of the CRDS, and (c) electronics for laser control and data acquisition and analysis.

After a short description about the aspect (a) and the spectral absorption features used for  $CH_4$  detection, details for (b) and (c) will be reported in Secs. II A and II B, respectively. The spectral measurements and signal processing will be presented in Sec. II C.

The extraction of dissolved gases in seawater was achieved by using a membrane.<sup>2,3</sup> The membrane was made of Teflon with a dimension of 8 cm in diameter and 100  $\mu$ m in thickness. The membrane was supported by using a porous metal plate of 10 mm of thickness, providing mechanical strength for the membrane under high pressure differences. Part of the dissolved gas molecules in the liquid permeated through the membrane into the gas phase. The partial pressure of the gas was proportional to the molar concentration of the gas dissolved in the solution at equilibrium, as described by Henry's law.<sup>15,16</sup>

In our experimental setup, seawater was flushed over the surface of the membrane. The concentration on both sides of the membrane would gradually reach equilibrium. A mini gas pump (KNF model NMP09KPDC-S) circulated the permeated gases including methane near the membrane into the CRDS measurement cavity. In order to reduce the influence of water vapor on the target measurement spectral line of  $CH_4$ , the permeated gases were dried by



FIG. 1. Diagram of the instrument and its various function blocks, including dissolved gas extraction based on the membrane, optical cavity for spectroscopic detection of extracted gas, laser electronics, and data acquisition and processing. SOA: Semiconductor optical amplifier; TEC: thermal electrical cooler/heater; TIA: *trans*-impedance amplifier; TMS320C6748 is a digital signal processor.

Rev. Sci. Instrum. **91**, 083106 (2020); doi: 10.1063/5.0004742 Published under license by AIP Publishing passing through the silicone desiccant (Wisepac silica gel desiccant) and a particulate filter (Swagelok model SS-2F-2) before entering the optical cavity for spectroscopic measurements.

The detection and concentration measurement of the  $CH_4$  gas was by means of a sensitive optical spectroscopy in the near-infrared wavelength region around 1654 nm.  $CH_4$  has a strong absorption feature near 1653.7 nm (or frequency ~6047.0 cm<sup>-1</sup>) and a weak absorption feature near 1654.2 nm (or frequency ~6045.1 cm<sup>-1</sup>). In order to expand the measurement range of concentration, the strong absorption feature was used for low concentration measurements, whereas the weak absorption feature was used for high concentration measurements. A single diode laser can operate over the wavelength range by tuning its operation temperature. For our CRDS system, the 1654.2-nm feature became suitable for  $CH_4$  concentrations above ~20 ppmv, subject to empty-cavity ringdown time, photodetector gain, and laser output power.

In order to analyze the possible interference from other gas absorptions to the measurement of CH<sub>4</sub> between the frequency range of 6044 cm<sup>-1</sup>–6049 cm<sup>-1</sup> (or wavelength 1654.53 nm –1653.16 nm), the absorption line with the concentration of saturated water vapor, <sup>17,18</sup> CO<sub>2</sub>, and CH<sub>4</sub> in the atmosphere between the range of 6044 cm<sup>-1</sup>–6049 cm<sup>-1</sup> was simulated, as shown in Fig. 2. Simulation conditions were for an absorption path length of 1 cm, with respective concentrations of 2.86% H<sub>2</sub>O, 400 ppm CO<sub>2</sub>, and 2 ppm CH<sub>4</sub> in air at a pressure of 1 atm.

It was obvious that  $H_2O$  vapor absorptions at 6044.85 cm<sup>-1</sup> and 6047.78 cm<sup>-1</sup> had an influence on the target measurement CH<sub>4</sub> spectral features, as shown in Fig. 2. Therefore, it was necessary to reduce the effect of water vapor by a desiccant before the dissolved gas entered the measurement chamber. The absorption line of CO<sub>2</sub> had less effect on CH<sub>4</sub>, so no treatment was performed in measurement.



**FIG. 2.** Simulation of two CH<sub>4</sub> absorption features (in blue) with very different absorption strengths at 6047.0 cm<sup>-1</sup> and 6045.1 cm<sup>-1</sup>, suitable for optical sensing at low and high concentration ranges, respectively. Interference absorptions of H<sub>2</sub>O vapor (in black) and CO<sub>2</sub> (in red) are also shown.

We applied a cavity ringdown spectroscopy (CRDS) technique for the spectroscopic detection and measurement of the extracted CH4. CRDS is a well-established technique for ultra-sensitive detection of gas concentrations.<sup>15,19,20</sup> Our research group has publications reporting details.<sup>21,22</sup> In this work, the 1654-nm tunable laser source was a distributed feedback (DFB) laser manufactured by NEL. We used a semiconductor optical amplifier (SOA, Thorlabs, 1082P series) as a fast optical switch between the laser output and the optical cavity. Alternatively, a nano-speed optical switch may be used.<sup>23</sup> A digital signal processor (DSP) (TI, TMS320C6748) managed most aspects of the instrument, including the scan of the laser wavelength, radiation detection of the optical cavity buildup and decay, switch of the SOA drive current, and the spectral data analysis. After a complete spectrum scan was completed, the process key parameters of the calculation and scanned spectral data were backed up in the secure digital (SD) memory card on the circuit board.

## A. Mechanical and optical structure of the compact instrument

The overall structure of the CRDS device is illustrated in Fig. 3. It integrated the optical cavity, diode laser, and electronics together into a compact design. The overall structure was columnar with an optical resonant cavity in the middle, and electronic circuit boards were mounted on two enclosure boxes on both sides of the optical cavity. This part was connected via two pipe lines to the separated part of dissolved gas extraction.

Resonance cavity of CRDS was primarily composed of two super-mirrors, two collimating lenses, and two optical fibers. The length of the cavity was determined to be 32.3 cm, which results in a cavity-free spectral range (FSR, the interval between successive cavity resonance frequencies) of 464.1 MHz or 0.01548 cm<sup>-1</sup>. This was determined by counting the number of cavity resonances between two spectral absorption lines of well-known transition frequencies. The empty-cavity ringdown time was about 65  $\mu$ s, which corresponded to an effective optical path length of about 20 km. The incident light beam was coupled through one optical fiber to a collimating lens that focused the beam onto the optical cavity.<sup>24</sup> In order to reduce the influence of high-order transverse modes of the



FIG. 3. Diagram of the mechanical and optical structure of the compact instrument for gas concentration measurements based on cavity ringdown spectroscopy. It comprises optical cavity, electronics for operation control, and data analysis.



FIG. 4. Diagram of the main system circuit board, showing various function blocks, including current driver and TEC controller of the DFB laser, matching the laser wavelength in the optical resonance with the optical cavity, SOA on/off switching control, cavity ringdown data acquisition, and ringdown decay rate analysis. PD: photodiode; TIA: *trans*-impedance amplifier. TMS320C6748 is a digital signal processor.

optical cavity, a single-mode fiber reception was used at the receiving end as a spatial filter to couple the cavity transmission and the ringdown signal to a fast photodiode detector. The diode laser and semiconductor optical amplifier were mounted on two electronic boards (see Fig. 5) inside two metal boxes. The temperature control of the optical cavity has not been implemented yet. For quantitative measurements in the future applications, either an active temperature control or a simultaneous recording of temperature for correcting the temperature dependence of spectral line strengths will be required.

#### B. Design of the electronic system of the instrument

The instrument hardware circuits were separated into two parts: main system circuit board and SOA drive circuit board. On the main system circuit board, there were data acquisition, signal generation, *trans*-impedance amplifier (TIA), current driver, and thermal–electrical cooler (TEC) controller of the DFB laser. The second board for the SOA included a current driver and a TEC controller, which are similar to those for the laser on the main system board and will not be described here explicitly. The function modules of the main system circuit are presented in Fig. 4.

The system circuit was based on a digital signal processor (DSP, Texas instruments TMS320C6748), which ran at 456 MHz, and had an 8-stage pipeline structure and rich peripheral interfaces. The signal generation and data acquisition circuits were based on a DAC (Texas instruments DAC904, 14 bit, 165 MSPS) and an analog-todigital converter (ADC) (Analog devices LTC2203, 16 bit, 25 MSPS) controlled via the universal Parallel Port (uPP) of TMS320C6748. The RS232 communication circuit and SD card storage circuit were implemented with the TMS320C6748 UART and multimedia card (MMC)/secure digital (SD) card interfaces, respectively. The transmission CRD signal was detected by using a photodiode and amplified by a TIA based on a fast low-noise operation amplifier chip (Analog devices AD8065, 145 MHz bandwidth). The CRD signal threshold comparison input and SOA on/off control output were designed using the GPIO (general purpose input output) interface and the external interrupt function of the TMS320C6748. The operation temperature of the DFB laser was stabilized via an integrated TEC temperature control chip (Analog devices ADN8834).

An external computer can communicate with the DSP board via the RS232 port for debugging and downloading measurement results.

Photographs of the two circuit boards and the assembled instrument are displayed in Fig. 5. The size of the SOA circuit board is  $50 \times 80 \text{ mm}^2$ , whereas the size of the main system circuit board is  $50 \times 190 \text{ mm}^2$ . The total length of the assembled instrument is 500 mm with a maximum width of 100 mm for its middle section. The power consumption was about 12 W.

#### C. Developments for spectral measurements and signal processing

We have developed software for the operation of the instrument hardware circuits described in above Sec. II B. It managed all the aspects of the system operation and measurements, including laser operation and wavelength control, generation and acquisition of the ringdown signal, ringdown rate determination, and spectral and gas concentration analysis.

The software ran on a real-time operating system TI-RTOS from the DSP manufacturer Texas instruments. The flowchart of our software is shown in Fig. 6.

After the system was powered on, the real-time operating system TI-RTOS booted up and the main DSP chip TMS320C6748 configured the peripherals, based on their predetermined performance parameters. The temperatures of both the DFB laser and the SOA were stabilized to their set optimal operation temperatures via their TEC controllers. When the temperatures of both the DFB laser and the SOA become stabilized, the TEC controllers notify the DSP chip by its GPIOs and external interrupts.

At the beginning of the wavelength locking procedure, the SOA (as an optical switch) was activated via a logic signal of a GPIO pin of the DSP, so the diode laser output radiation could pass through the SOA and be directed to the optical cavity. The drive current of the diode laser was controlled by the DAC output signal, which was the superposition of an average bias value and a triangular



FIG. 5. Picture of instrument circuit boards and the assembled instrument. (a) Picture of an SOA drive circuit board (top) and the main system circuit board (bottom); (b) Picture of the assembled instrument, without the enclosure plate for the middle compartment.



**FIG. 6.** Flowchart of the software on the main system control board based on a digital signal processor. LD: laser diode; SOA: semiconductor optical amplifier; RD: ringdown; ADC: analog-to-digital converter.

waveform modulation with a small amplitude. Modulation of the laser diode current caused a small wavelength dithering, typically within a quarter of the wavelength (for ~half of the FSR). If the laser wavelength matches the optical cavity during the wavelength dithering, the photodetector would detect some optical transmission signal. A photodetector and a TIA converted the optical transmission radiation into a voltage signal. The voltage signal is compared against a preset threshold voltage. By making small adjustments to the bias voltage and monitoring the transmission signal of the photodetector, the laser wavelength will be centered to a nearby cavity resonance wavelength/frequency.

Afterward, when resonance occurs as detected by a signal voltage comparison against a preset threshold level, the DSP chip received this event via its external interrupt interface. Subsequently, the DSP stopped the wavelength dithering immediately and then turned off the SOA optical switch and the incident radiation to the cavity so that the optical radiation inside the cavity starts its exponential ringdown process. The ADC acquired a given number of the photodetector's ringdown signal. The DSP applied a nonlinear leastsquares fitting of a single exponential decay function to determine the decay rate of the ringdown event.

A typical temporal profile of recorded cavity ringdown signals and its modeling to an exponential decay function are shown in Fig. 7(a). The residuals between the measurement signal and modeling were very uniform, indicating the ringdown decay followed a single exponential decay. Based on the residual values of the modeling, we rejected about 10% ringdown events with larger deviations. This helped us to remove outliers caused by the fluctuations of laser frequency. At each laser wavelength position, cavity ringdown events were acquired and analyzed 40 times. The average of these 40 ringdown rates was used for spectral analysis in the next step.

When the ringdown rate at one cavity resonance frequency was completed, the diode drive current will be advanced in small steps as discussed before, to turn the laser frequency into a successive cavity resonance frequency. Once the laser was locked to adjunct the resonance frequency, another 40 ringdown decay events would be acquired and analyzed to obtain an averaged ringdown rate for that spectral position. This process was repeated many times until a complete spectral profile of the absorption feature was completed. The corresponding absorption coefficient values (including empty-cavity baseline) were calculated based on the ringdown decay rates.

Figure 7(b) displays a complete spectral scan of the  $CH_4$  absorption feature at 6047.0 cm<sup>-1</sup>. The "step" in the spectrum is due to the fact that the laser frequency is step-scanned/locked to consecutive discrete cavity resonance frequencies. The measurements were



**FIG. 7.** (a) Example of one measurement ringdown signal and its modeling result and residual. (b) A step-scanned CH<sub>4</sub> absorption feature at 6047.0 cm<sup>-1</sup>. At each consecutive cavity resonance frequency step, 40 data points were obtained for 40 ringdown events recorded.

repeated 40 times at each consecutive cavity resonance frequency. The ringdown time of the empty cavity was about 65  $\mu$ s.

Measurements related to Figs. 7–10 were at a pressure of 1 atm. For field applications, our instrument did not actively regulate the total pressure inside the optical cavity. Although a lower pressure could reduce the interference and linewidth of the neighboring water vapor absorption line, regulating the cavity pressure would add complexity to the instrument. Instead, we included water vapor absorption contribution in the spectral fitting process.

The measurement data points in Fig. 8 are derived from similar measurements, as shown in Fig. 7(b). Each spectral data point in Fig. 8 was the average value of each set of the 40 individual measurements at each wavelength step. The measurement spectrum was modeled based on a Voigt profile by using a Levenberg-Marquartt (LM) least-squares algorithm. Four spectral parameters can be obtained after fitting: spectral-integrated absorption coefficient, Lorentzian linewidth, Gaussian linewidth, and the corresponding position of the laser scan at the spectral peak.<sup>25-28</sup> The Gaussian linewidth could be fixed and calculated based on the temperature of the optical cavity.

Figure 8(a) shows a fitting result without considering a nearby residual  $H_2O$  vapor absorption at 6046.8 cm<sup>-1</sup>. The deviation between the measurement and the fit was relatively large, in particular, around 6046.8 cm<sup>-1</sup>. This residual absorption could occur when



**FIG. 8**. Measurement spectrum of CH<sub>4</sub> with residual H<sub>2</sub>O vapor, fitted by singlepeak and dual-peak models. (a) With a single spectral peak of CH<sub>4</sub> at 6047.0 cm<sup>-1</sup>; (b) improved fitting with the inclusion of a residual water vapor absorption around 6046.8 cm<sup>-1</sup>.



**FIG. 9.** (a) Calibration measurements of the system by using reference gases of six different nominal CH<sub>4</sub> concentrations as indicated; (b) straight-line fit between the uncalibrated measurement values and the nominal reference gas concentrations.

the desiccant has been used for too long and needs to be replaced. Figure 8(b) shows an improved fitting result after including the  $H_2O$  vapor absorption at 6046.8 cm<sup>-1</sup>. Consequently, the fitting residual is more than  $10 \times$  reduced than that in Fig. 8(a).

In order to insure minimal interference by the potential residual  $H_2O$  vapor in the optical cavity, our software monitored the water vapor absorption and generated a warning signal sent through the RS232 interface when the residual water vapor absorption became above  $1 \times 10^{-8}$  cm<sup>-1</sup>. This warning signal prompted for a replacement of the desiccant. The concentration of the  $H_2O$  vapor



**FIG. 10**. (a) 3-h measurement results of the 2.3-ppmv  $CH_4$  reference gas sample; (b) Allan–Werle deviation analysis of measurement data.

After the spectral fitting, the methane concentration value was calculated based on the fitting result of the spectral-integrated absorption coefficient. The corresponding position of the laser scan at the spectral peak was used as a feedback for fine adjustment of the laser current scan range of the consecutive spectral scans. This is corrected for any drift away of the laser wavelength during long-term measurement applications.

## **III. RESULTS**

#### A. Calibration experiment

Due to uncertainties such as spectral parameters and cavity length, the developed instrument was calibrated by using reference gas mixtures of six different (i.e., 1.5 ppmv, 2.3 ppmv, 2.7 ppmv, 3.1 ppmv, 4.2 ppmv, and 5.0 ppmv) CH<sub>4</sub> concentrations in the N<sub>2</sub> buffer gas. The nominal uncertainty of the reference mixtures was 5%. It will be desirable to use better calibrated gases with much less uncertainty in the future. Figure 9(a) shows the uncalibrated measurement results. The measurement time at each gas concentration was more than 40 min. The nominal concentrations are labeled in the figure. The statistical analysis for each measurement group is given in Table I. The straight-line relationship between the nominal value and measured mean values is described in Fig. 9(b). All of these measured values were within the nominal uncertainty of the reference gas concentrations. The slope value of the straight-line fit can be used to scale raw uncalibrated measurement concentrations. This empirical approach is very useful and reduces requirements on accurate details of spectral lines and optical cavity length.

#### **B.** Minimum detection limit

The minimum detection limit of the instrument was generally evaluated by the Allan–Werle deviation plot as a function of the measurement averaging time.<sup>20</sup> For this set of measurements, the optical cavity was first evacuated and then filled with a 2.3-ppmv CH<sub>4</sub> gas mixture up to the ambient atmosphere pressure. Afterward, a small inlet gas flow (controlled via a pinhole valve) was maintained and the outlet of the cavity was opened to the ambient atmosphere via another pinhole valve. The measurement started 20 min late allowing sufficient time for pipelines and cavity surfaces to be conditioned with the gas sample. Figure 10(a) shows such concentration measurement results for about 3 h, and the corresponding Allan–Werle deviation analysis is plotted in Fig. 10(b).

The measured data in Fig. 10(a) show a slow upward trend, presumably due to the drop of ambient temperature, as the experiment was carried out from 5 pm to 8 pm. A variation in temperature would lead to a change in the spectral line strengths of CH<sub>4</sub> molecules. For future field applications, simultaneous recordings of ambient temperature would help account for the temperature dependence of the spectral line strengths. In Fig. 10(b), it can be seen that the measurement resolution can reach 0.4 ppbv with an approximate averaging time of 240 s (or 4 min). This corresponds to an averaging of 30 measurement data points, which has a time interval of ~8 s. The detection uncertainty in terms of normalized absorption coefficient is  $2.4 \times 10^{-9}$  cm<sup>-1</sup> Hz<sup>-1/2</sup>. This detection uncertainty was for an application-expected CH<sub>4</sub> concentration of ~2.3 ppmv as in ambient air, whereas the traditional noise-limited minimal detection limit is based on the detection noise of an empty cavity. Generally speaking, the detection uncertainty increases when the ringdown time is reduced due to gas absorption.

## C. Atmospheric CH4 observation and comparison with Picarro G2131-i

The company Picarro has developed commercial CRDS instruments for atmospheric trace gas observations. The performance of its instruments has been widely recognized by users. Picarro G2131-*i* is one of its products, which can simultaneously measure CH<sub>4</sub>, H<sub>2</sub>O, CO<sub>2</sub>, and <sup>13</sup>CO<sub>2</sub> in the atmosphere. Its nominal measurement precision for methane is 50 ppbv (30 s averaging time). Therefore, measurement comparison between a Picarro instrument and our newly developed instrument (referred here as AIOFM instrument, Anhui Institute of Optics and Fine Mechanics) would serve as a performance check. In the comparison test, the air pipes of two instruments were connected in series, and ambient gas was pumped into our AIOFM instrument and then flowed to the Picarro instrument successively.

The comparison test was carried out continuously for about 20 h in total, as displayed in Fig. 11. There was a difference in the measurement data interval between the two instruments. The time interval between data points was 7 s for the Picarro instrument and

**TABLE I.** Calibration of the system based on six  $CH_4$  reference mixture measurements and statistical analysis.

Nominal CH <sub>4</sub> concentration (ppmv)	Measurement average (ppmv)	Measurement variance (ppmv)	Measurement minimum (ppmv)	Measurement maximum (ppmv)
1.5	1.5399	0.0022	1.5332	1.5459
2.3	2.3211	0.0020	2.3112	2.3265
2.7	2.6653	0.0017	2.6575	2.6712
3.1	3.0312	0.0021	3.0245	3.0365
4.2	4.3762	0.0041	4.3644	4.3863
5.0	5.1060	0.0061	5.0930	5.1213



**FIG. 11**. Comparison of 20-h atmosphere measurement results between Picarro G2131-*i* and our AIOFM instrument. The measurement was started at 12:00 noon. At the beginning of operation, the responses of two instruments to the initial start of the air circulation pump were slightly different.

was ~8 s for our AIOFM instrument. At the beginning of the test, the responses of two instruments to the initial start of the air circulation pump are slightly different. After a stable air flow was established in a short time, the concentrations measured by the two instruments had very good consistency, as shown in Fig. 11. The measurement noise of the AIOFM instrument was 1.3 ppbv, whereas the G2131-*i* instrument was of 8.5 ppbv. We noted also that G2131-*i* provided simultaneous measurements for four gas species, not just for CH<sub>4</sub>. The data rates vary among the four gas species, with a specified average measurement time interval of ~2 s.

#### D. In situ dissolved methane measurement

In order to verify the developed analysis system for dissolved methane application, we conducted an *in situ* underwater measurement experiment. The experiment was carried out for about 14.5 h (from 18:09 pm to 8:40 am). The instrument was powered by a 24-V lithium battery pack. The dissolved methane measurement system was placed in seawater near the Institute of Deep-sea Science and Engineering of the Chinese Academy of Sciences. Figure 12 shows a measured curve of dissolved methane concentration.

One hour after the instrument was placed into seawater, the methane concentration in the optical cavity rose from about 2 ppmv to about 3.5 ppmv and then rose to 3.8 ppmv at about 2 h. At about 21:00, we went to the site and checked the working status of the instrument via its RS232 communication interface. The methane concentration value measured at this moment just had a descending process. In general, the concentration fluctuated larger before 24 o'clock in the night and became smaller from 24 o'clock to 8 o'clock of the next morning, which may be mainly due to more human activities near the measurement location before 24 o'clock and the decrease in human activities after 24 o'clock in the night. This field deployment was more a "proof of concept" than a proper determination of seawater methane concentrations.



FIG. 12. (a) Photograph of the developed instrument placed under coastal seawater during a field deployment. (b) Result of field *in situ* measurements of methane dissolved in seawater.

#### **IV. SUMMARY AND DISCUSSION**

We have developed a compact system-including hardware and embedded software-for in situ concentration analysis of methane dissolved in seawater by using a highly sensitive optical cavity ringdown spectroscopy (CRDS) technique. The dissolved methane molecules were extracted via 100-µm thin Teflon membrane permeability from seawater into the optical cavity for spectral measurements. The linear structure of the cavity provided high mechanical stability. The optical cavity, DFB laser source, optical switcher, gas circulation pump, and all the associated control and data processing electronics were packaged into a cylindrical form measuring 550 mm in length and 100 mm in diameter. The power consumption of the system was about 12 W. The optical gas concentration measurement was calibrated by using reference gas mixtures with 5% accuracy in the laboratory. The minimum detection limit was analyzed by the Allan-Werle variance method to be 0.4 ppbv with an averaging time of 4 min. Measurements of our instrument were also compared and found to be in very good agreement with those of a commercial Picarro's CRDS instrument. Finally, a field measurement experiment was carried out successfully to demonstrate and verify the operation and performance of the developed system.

The embedded measurement system realized the generation, acquisition, analysis of cavity ringdown signals, and fitting of spectral profiles. The extracted spectral parameters were then used to calculate the gas concentration. The developed instrument can be extended for measurements of other gas species by replacing the laser and cavity mirrors for the wavelength of the targeted gas absorption lines. We believe that this compact instrument will be suitable for various *in situ* gas sensing applications.

The main goal of this work was to develop the hardware and software. However, there will be a few further investigations in the future that could improve the system. First, the reference gases used in this work had a large concentration uncertainty of 5% due to availability at the time. Use of reference gases with less uncertainty can improve the accuracy of the instrument calibration in the future. Second, the gas temperature was taken as constant in this work, but should be better managed in the future development. As the strengths of absorption lines are temperature dependent, a detailed characterization of the temperature dependence would be helpful for correcting the temperature impact on concentration estimation. Alternatively, the temperature of the optical cavity may be actively maintained at a fixed temperature. Furthermore, the knowledge of the equilibrium conditions of seawater gas extraction as a function of temperature and salinity would also be generally required to predict the dissolved gas concentrations in seawater.

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