# A Multi-Channel Data Logger of In-situ Chemical Sensors for Cabled Seafloor Observatories

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***Abstract*—This paper describes the development of a multi-channel data logger for real-time in-situ monitoring. The data logger can connect various types of chemical sensors, including pH electrode, $Ca^{2+}$ electrode, $H_2S$ sensor, etc. It can process the signals of these chemical sensors with high input impedance, online communication, low power consumption, compact size and high reliability. The data logger consists of a preamplifier circuit for processing signals from the sensors, a micro controller unit (MCU), a flash memory, a RS-485 communication interface and a power module. A cylindrical pressure vessel ensures the security and reliability of the data logger when used under deep sea. The data logger with a novel pH sensor which consists of the all-solid-state reference and pH electrode based on poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) (PEDOT(PSS)) and plasticized polyvinyl chloride (PVC) membrane was tested to measure five tris(hydroxymethyl)aminomethane-HCl (Tris-HCl) buffer solutions at different pH values. And the results prove that the data logger works well and meets the requirements of cabled seafloor observatories.**

***Keywords—data logger; in-situ monitoring; deep sea; chemical sensors***

## I. INTRODUCTION

There are two ways to research the physical and chemical characteristics of deep sea environment. One is analyzing the sample which was obtained from the sea with high fidelity in the laboratory, the other is real-time in-situ monitoring. Obviously, the latter way is better than the former one [1]. Cabled seafloor observatories are widely used for in-situ monitoring. They can be utilized to explore and exploit marine resources which are of great significance for human beings. Data logger plays a key role in the cabled seafloor observatories for real-time in-situ monitoring. It is an essential component which connects sensors and scientific instrument interface module (SIIM).

In the past several years, marine scientific instruments have been in great demand, especially autonomous instruments with large capacity for a long term monitoring while performing continuous data acquisition and storage. A variety of data loggers have been developed to acquire the data of different sensors. A new low power data logger based on compact flash memory cards is capable of long term seismic data acquisition [2]. A small-sized data logger attached to a marine animal can obtain information about behavior and physiology of the animals directly [3].

Although various types of data loggers have been designed and utilized, the size, power consumption and input impedance cannot meet the demand for long term in-situ monitoring. We have studied a certain number of ion-selective electrodes (ISEs), including pH electrode, $Ca^{2+}$ electrode, oxidation-reduction potential (ORP) sensor, $H_2S$ sensor, etc. The ISE features high sensitivity, rapid response, reliable performance and compact size. As a common membrane matrix in ISEs, plasticized polyvinyl chloride (PVC) is often chosen as the membrane material. The dynamic response of an ISE is generated by selective complexation of the action of the target ions and the ionophores dispersed in the PVC matrix [4]. Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) (PEDOT(PSS)) is known as one of the most stable conducting polymers available today [5]. It has been shown that PEDOT(PSS) is particularly suitable as solid-contact material in ISEs due to its low sensitivity to $O_2$ and $CO_2$ (pH) [6]. This technology has attracted much interest because of its high stability and conductivity.

The novel all-solid state sensors, which are liquid junction free, pressure-resistant and easy to package and seal, are suitable for in-situ underwater measurement. However, these sensors also perform extremely high impedance and weak output signals compared with commercial sensors. In addition to ISEs, we also developed amperometric chemical sensors, including dissolved oxygen sensor. Therefore, this paper presents the development of a data logger which can process signals of both ISEs and amperometric chemical sensors with high input impedance, online communication, low power consumption, compact size and high reliability.

## II. DATALOGGER SYSTEM

### A. System Configuration

The data logger has a modular structure as shown in Fig. 1. It can connect various kinds of chemical sensors to measure the value of pH [7], $Ca^{2+}$, $H_2S$, ORP and dissolved oxygen in the sea. There are six ISEs channels, one amperometric sensor channel and one temperature sensor channel [8].

The data logger includes a preamplifier circuit for processing signals from the sensors, a micro controller unit

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(MCU) to control the circuit, a flash memory for data storage, a RS-485 communication interface and a power module.

*B. Hardware Description*

According to previous experience, the output potential difference of ISEs which are mentioned above will fall into the range of $\pm 800$ mV. All these weak output signals of the sensors are amplified to 0~2.5V by the preamplifier circuit and digitized by the A/D converter so that they are apt to be processed by MCU [9].

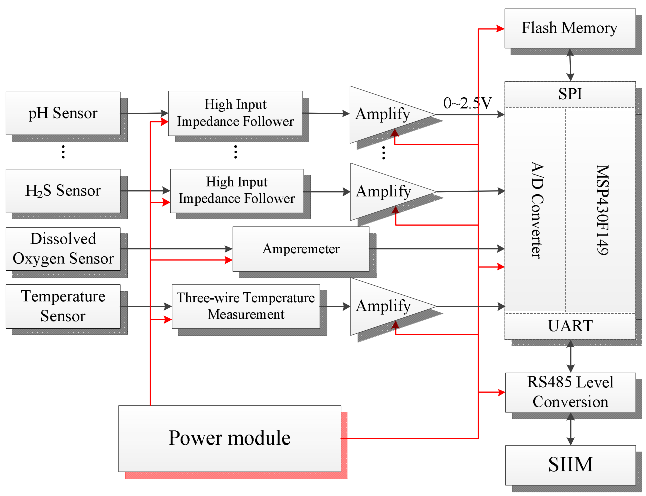


Fig. 1. Structure of the data logger

The signals of ISEs channels can be amplified as the following formula:

$$U_{out} = -R_5 \left( \frac{U_x}{R_1} + \frac{U_{in}}{R_7} \right) \quad (1)$$

in which $U_{in}$ and $U_{out}$ are the output voltage of the sensor and the preamplifier circuit, respectively. $U_x$ refers to the regulation voltage which is set to be 2.5V. $R_1$, $R_5$ and $R_7$ can be set according to the magnification which is determined by the range of input voltage.

The signals of amperometric sensor channel can be amplified as the following formula:

$$I_{op} = \frac{U_{out} - U_{op}}{R_4} \quad (2)$$

where $I_{op}$ and $U_{op}$ refer to the working current and voltage of the sensor, respectively. $U_{out}$ is the output voltage of the preamplifier circuit, $R_4$ can be determined by the magnification. And the other channels have corresponding formulas.

The data logger is an instrument whose power should be supplied by batteries, but it is impossible to replace batteries in the deep sea. Therefore, the power consumption plays a critical role in battery-driven instrument design. The power consumption of a circuit is defined as the following equation:

$$p(t) = i(t)\,v(t) \quad (3)$$

where $i(t)$ is the instantaneous current of the whole circuit, and $v(t)$ is the instantaneous supply voltage. The power consumption impacts battery life.

It takes the MSP430F149 microprocessor as the MCU. MSP430F149, which is a MCU of the Texas Instruments and has characteristics of ultra-low power consumption, low supply voltage and abundant on-chip peripheral modules, such as eight-channel twelve-bit AD converter and UART interfaces, is suitable for system miniaturization and low power consumption design.

Flash memories have been extensively used for data storage. Their high memory density and high power efficiency make them well suited for flexible design [10]. The data logger has a 1 GB flash memory which can communicate with MSP430F149 through serial peripheral interface (SPI). The high capacity of flash memory ensures a long term storage of data [11]. For example, it can save the data continuously for a month with 10 Hz, the highest sampling frequency. The storage is divided into 4096 blocks with 128 pages in each block. The program and read operations are executed on a page basis, while the erase operation is executed on a block basis. When reading, the system clock will switch to an integrated high-speed digitally controlled oscillator (DCO) to achieve high-speed data transmission. The flash memory provides cache program in a block. It is possible to write data into the cache registers while data stored in data registers are being programmed into memory cells in cache program mode. The program performance may be dramatically improved by cache program when there are lots of pages of data to be programmed.

To convert the transistor-transistor logic (TTL) signals to RS-485 signals and vice versa for data communication between the data logger and SIIM, a RS-485 communication interface for level conversion is used. The device can operate in two modes: transmit and receive, selected by the user. Therefore, the data logger can achieve real-time online measurement of chemical sensors data at more than 3000 m depth in the sea.

The power module consists of a low dropout linear regulator and two lithium batteries which are both 2200 mAh. A DC-DC converter is more efficient than the low dropout linear regulator, but the ripple of DC-DC converter can interfere the weak output signals of the sensors. Low power consumption is not the only objective in real-time in-situ monitoring. Performance is also a critical factor. According to calculation, the power module ensures that the data logger operates for 283 days continuously with 2 Hz sampling frequency.

According to the characteristics of data logger, several methods are available in our design. In the preamplifier circuit, we adopt a high impedance amplifier with $10^{14}$ ohm to measure the sensor signals accurately. The operational amplifier features gate-protected positive channel metal oxide semiconductor (PMOS) transistors in the input circuit to provide very high input impedance, very low input currents (less than 1 pA). The internal bootstrapping network features a unique guardbanding technique for reducing the doubling of leakage current for every 10°C increase in temperature. This operational amplifier is internally phase compensated to achieve stable operation in the unity gain follower configuration. It operates at total supply voltages from 2V to 20V either single or dual supply. Considering the electromagnetic compatibility, anti-electromagnetic interference method is adopted throughout the circuit design. The selection of surface mounted devices (SMD) and high integration density of the circuit contribute to the compact of the mechanical structure to achieve miniaturization.

A cylindrical pressure vessel whose both sides can be open is used to seal the circuit board, as shown in Fig. 2. Its outer diameter, inner diameter and length are 90 mm, 65 mm and 300 mm, respectively. There is a water resistant connector interface in the end cover to ensure the safe introduction of the sensor signals. The pressure vessel has been designed to ensure its resistance to tremendous pressure when used under deep sea. It is connected to the chemical sensors and SIIM via water resistant connectors.

Fig. 2. The data logger inside the cylindrical pressure vessel (90 mm × 300 mm) with a water resistant connector

### C. *Software Description*

The data logger can achieve the functions of multi-channel data acquisition, mass data storage, real-time online communication and fast data transmission. In general, the data logger works in the sleep mode in which all the subsystems including the analog circuit are shut down to save power, and waits for timer interrupt signal. The sleep mode offers the largest power savings and consequently the lowest level of available functionality [12]. The current of subsystems and components in the sleep mode is as low as 6 µA. When an interrupt signal appears, the data logger will identify which kind of signal it is. Then the data logger turns on the correlative subsystems and executes the corresponding interrupt service routines. After completing the interrupt service, the data logger returns to the sleep mode. According to these manners, the working time of data logger can be prolonged considerably to match the requirement for long term in-situ monitoring in the deep sea.

## III. EXPERIMENTAL DETAILS

### A. *Reference Electrode Preparation*

Prior to polymerization, the carbon paste working electrode was rinsed with water. PEDOT(PSS) was synthesized by cyclic voltammetry (CV) electropolymerization from a deaerated aqueous solution (purged with $N_2$ for about 10 min) containing 20 mM 3,4-ethylenedioxythiophene monomer (EDOT) and 100 mM poly(sodium 4-styrenesulfonate) (NaPSS) as the supporting electrolyte. All experiments were performed under a nitrogen atmosphere at room temperature (20 ± 2℃). The process of electropolymerization was scanning the potential for ten cycles between –0.2 and 1.0 V at a scan rate of 50 mV $s^{-1}$, and the polymerization charge was about 190 mC, corresponding to a film thickness of about 7.5 µm [13]. The PEDOT(PSS) layer was covered by a PVC membrane, which contains the lipophilic anion-exchanger potassium tetrakis-(*p*-chlorophenyl)borate (KT*p*ClPB) and cation-exchanger tridodecylmethylammonium chloride (TDMA-Cl). Cyclohexanone (CHA) was used as solvent for the PVC membrane and the membrane consisted of bis(2-ethylhexyl) sebacate (DOS) (66.8%, w/w) as a plasticizer, PVC (32.0%, w/w) as a membrane matrix, KT*p*ClPB (0.6%, w/w) as a lipophilic anion and TDMA-Cl (0.6%, w/w) as a lipophilic cation. Exactly 28.0 mg of PVC was dissolved in 0.3 mL CHA and stored in a 4℃ refrigerator in seal for more than 2 h to prepare membrane solutions. 1 µL of the solutions of reference PVC membrane was then dipped to cover the PEDOT(PSS) layer on the carbon paste electrode. Dried in atmosphere at ambient temperature for 24 h without light, the thicknesses of the PVC membranes formed were approximately 10 µm. When the thickness of the PVC is larger than 10 µm, it takes a longer time for the reference electrode to reach a stable potential. However, if the PVC film is too thin, it can be broken easily [14].

### B. *pH Ion Selective Electrode Preparation*

The all-solid-state pH ISE prepared in this research was a thick-film electrode using the same screen printing technology as the reference electrode, and it was also present in a structure of a PEDOT(PSS) layer on a carbon paste thick-film electrode covered by a hydrogen sensitive PVC membrane, the composition of which was DOS (65.9%, w/w) as the plasticizer, PVC (33.0%, w/w) as the membrane matrix, tridecylamine (1.0%, w/w) as the hydrogen ionophore and KT*p*ClPB (0.1%, w/w) as the lipophilic anion. The fabrication process of the layers of pH ISE was similar to that of the reference electrode mentioned before. The thickness of the $H^+$ selective PVC membrane was approximately 20 µm.

### C. *Electromotive Force Measurements*

The data logger with a novel pH sensor which consists of the all-solid-state reference and pH ISE based on PEDOT(PSS) and PVC membrane, was tested to measure five tris(hydroxymethyl)aminomethane-HCl (Tris-HCl) buffer solutions at different pH values and each buffer solution was tested three times at 19℃. After the all-solid-state reference and pH ISE were immersed in the testing solution, the potential between them at 15 s was recorded. Then they were washed with deionized water and wiped with the filter paper, ready for the next measurement.

## IV. RESULTS AND DISCUSSION

Plasticized PVC membrane, not containing any ionophore except lipophilic anion and cation, was coated over the solid contact to protect the vulnerable PEDOT(PSS) layer and maintained the stable potential of the reference electrode. The pH electrode was also based on PEDOT(PSS) as the solid contact, but with a hydrogen ion selective PVC membrane containing the hydrogen ionophore and lipophilic cation. The structural similarity between the reference and pH electrodes eliminates systematic error and improves the response time.

The typical calibration curve is shown in Fig. 3 with error bars, and illustrates a near-Nernstian response of −55.671 ± 0.8 mV/pH over 6 to 10 pH ($R^2$ = 0.9998). Note that all error bars are extremely narrow, which indicates that the repeatability of such a data logger with the pH sensor is practically acceptable. The data logger operated for twenty hours continuously with no communication error, and the repeatability of the data logger is 0.1 μV (ISE sensor) and 10 nA (amperometric sensor).

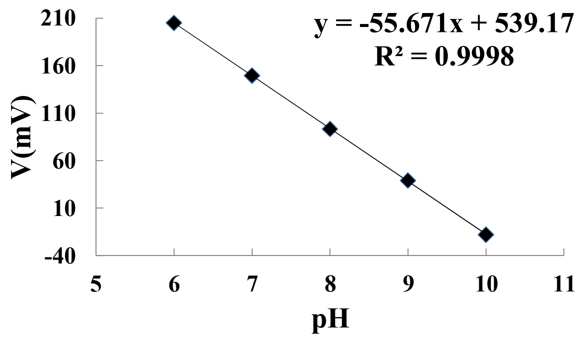


Fig. 3. The calibration curve of pH sensor. Note that error bars are very narrow.

The experiments prove that the data logger works well and the design of signal processing is reliable. All these meet the requirements of cabled seafloor observatories. The procedure for operating the data logger is simple and requires no special training, allowing the data logger to be used directly by any research scientist.

In the future, the data logger should be tested with more types of sensors, including ORP sensor, $H_2S$ sensor, etc. According to the advantages mentioned in this paper, the data logger can be used to detect the environment variables in the river or the lake. And it can be easily used for exploring marine resources by various submersibles, such as remotely operate vehicle (ROV) and autonomous underwater vehicle (AUV).

## Acknowledgment


The work is supported by the Program for Zhejiang Leading Team of S&T Innovation (Grant No. 2010R50036), Natural Science Foundation of China (Grant No. 61004132 and 61128003), the Fundamental Research Funds for the Central Universities and Zhejiang Key Discipline of Marine Technology and Systems.


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