AUTONOMOUS MICROFLUIDIC SYSTEM FOR SPECTROSCOPIC pH MEASUREMENTS

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ABSTRACT

The design and measurement results of an autonomous submersible instrument for pH measurements in fresh surface and ground water are presented. Miniaturization of the complete instrument is achieved a microfluidic system in combination with a pH-sensitive dye mixture, LEDs and spectroscopic detection. Pump, outlet filter, dye reservoir, mixer and optical path are all integrated in a single microfluidic chip. Results show good accuracy with the pH buffer solutions.

KEYWORDS: Microfluidics, Integration, pH, Autonomous, Optics, Spectroscopy

INTRODUCTION

pH is an important parameter in aqueous systems as it is used in the understanding of acid-base equilibriums of dissolved gases, the solubility of trace metals and as an indicator of biological activity. Current groundwater monitoring is based on sampling and is not able to resolve short-term variations. The sample might be compromised by CO_2 loss/gain due to biological alteration or gas exchange.

Glass electrodes and more recently ISFETs are commonly used for pH measurements. However, these electrodes require a reference electrode making them less suitable for some applications. For example, applications at higher pressures, such as in water or oil wells, and/or applications that require autonomous sensors, such as ground or surface water monitoring wells at remote locations, cannot be served with these electrodes.

Spectroscopic pH measurements have been very successful for seawater applications. Several papers have shown accuracies better than 0.005 pH unit [1]. Martz et al have reported the development of a submersible spectroscopic pH sensor [2] for fresh water applications. The instrument is fabricated using conventional pumps, valves and tubing. It is therefore large, requires sample volumes of several milliliters and has high power consumption. Furthermore, it uses a single dye, limiting its operation range to about 2.5 pH units.

The development of the instrument described in this paper has been focused on size, cost, autonomy, and low maintenance: the instrument must fit in 1.5-2 inch diameter groundwater monitoring wells and be able to obtain about 750 measurements over a six-month period (i.e. 4 measurements a day) without recalibration or other human intervention. The work has been based on the work of Salamitou et al. described in a US patent [3].

THEORY, CHIP AND INSTRUMENT DESIGN

The use of pH sensitive dyes to determine pH is well established but typically has a limited range of about 2 pH units. This range can be extended by using a mixture of dyes with similar color changes but different pK's. Raghuraman et al. [4] have reported a model to optimize the measurement range and to minimize the measurement error using a given dye mixture. The model shows that a mixture of three dyes, i.e. phenol red (pKa = 7.79), chlorophenol red (pKa = 6.11) and bromophenol blue (pKa = 4.11) can be used to achieve a pH range of more than 4 pH units with an error less than 0.1 pH unit. The model also shows that optimum performance is reached in case of almost equal weight of dye.

The above modeling is based on a ratiometric measurement of both the acid and the base peak. In principle, measurements at a single wavelength, either at the acid or at the base peak, are sufficient to obtain a pH measurement. However, such a system would be very sensitive to variations in the dye concentration. Measuring both the acid and the base peak and relating the ratio between these two peaks to the pH will allow the measurement to remain within certain limits insensitive to the dye concentration. Figure 1 shows the absorption spectra of the three dye mixture at various pH values. Ideally, one would prefer the dye concentration to be as high as possible, but a very high dye concentration will alter the pH of the sample and should therefore be avoided.

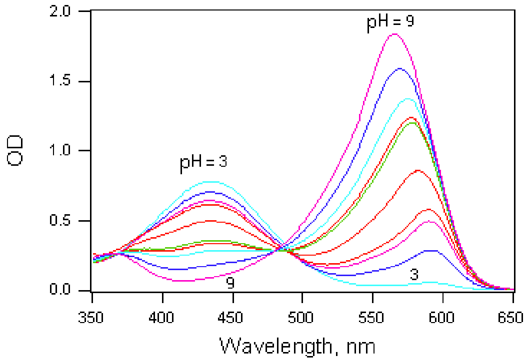

Figure 1: Spectra of the three-dye mixture in standard buffer solutions with pH varying from 3 to 9 at 293 K. Measurements done with Cary 500 Scan (Varian)

Considering that dye volume, size, and power consumption are limiting factors in the development of this instrument, utilizing the microfluidic approach becomes an attractive option. A single pump is used to pull both the sample and the reagent through the microfluidic chip. The pump is a self-priming micro diaphragm pump made out of the same material as the rest of the chip. The flow rate of each of the micro pumps is controlled by the frequency of the piezo actuator [5]. A porous Teflon inlet filter was used at the sample inlet to prevent particles from entering the microfluidic chip. The water channel is split into two channels of both 140 µm wide. The dye channel is 30 µm wide and joins both water channels in such a way that the dye is injected in the middle of the water flow. The mixing ratio is determined by the flow resistance of the fluid channels and set to be around 50:1. The fluids are mixed using a simplified version of the herringbone mixer as described by Stroock et al. [6], consisting of parallel grooves at the bottom of the fluid channel. The optical path length was optimized to obtain maximum absorbance and minimal optical losses due to stray light and was set at 1 cm. After optical interrogation the mixture is discharged through the outlet filter which contains charcoal to absorb the dye [7]. Together with the pump, the 2 ml dye reservoir and the outlet filter, all the microfluidic components are integrated on a single 1 by 3 inch chip, as shown in Figure 2. The chip was fabricated in Cyclic Olefin Copolymer (COC), a material often used to make lenses and thus optically transparent. All fluid connections are integrated within the chip except for the inlet filter which is screwed on to the chip and sealed with an O-ring.

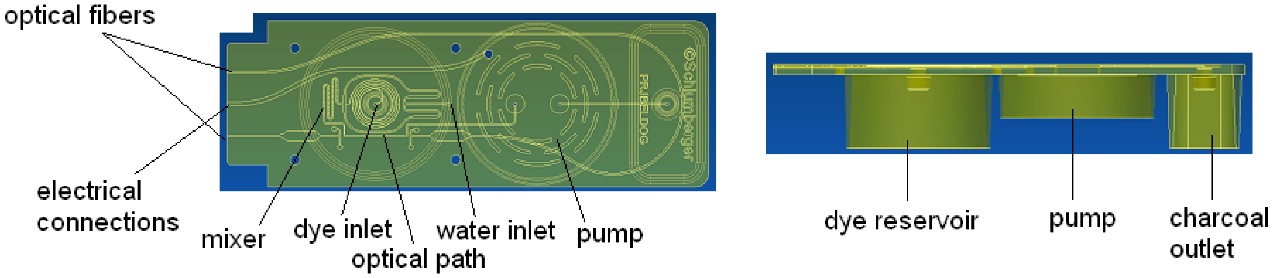

Figure 2: Schematic representation of the microfluidic chip

The optical interrogation is conducted using three wavelengths, i.e. 450 nm for the acid peak, 670 nm for the base peak and 950 nm as a reference to detect air bubbles and particles in the optical path. A custom designed optical holder was made to hold the LED, a 15 nm band filter and a ball lens to focus the light. The three LED's are connected to a three to two fiber beam splitter. One part of the light goes to the chip and is used for the measurement, whereas the second part of the light goes directly to a photodiode to act as a reference. The reference compensates for any fluctuations in the LED output due to aging of the LED, temperature variation and/or depletion of the battery used as a power supply. The optical fiber going to the chip is glued in place using an UV adhesive, which is optically clear and almost index matched to the COC and water. The fiber is not in direct contact with the sample but shines through a 500 µm-thick COC window, which is fully integrated in the chip. Each of the three LED's is powered in a pulse mode at 100 to 200 Hz and fired sequentially for each measurement.

The instrument needs to be capable of operating stand-alone in areas where there is no power supply available and therefore battery operation is preferred. For a typical 6-month operation, two ½AA size lithium thionyl batteries should be sufficient. The electronics include specific high voltage electronics for the pump, driving electronics for the LEDs and electronics for optical communication with the instrument. Furthermore, the instrument contains a datalogger to store the raw measurement data and the calculated pH. The pump electronics is calculated to be the major power consumer and pump usage should therefore be minimized to increase the life time of the batteries. The chip is molded to a specially designed bulk head that has three feed throughs for the optical fibers and the electrical connections to the pump. The bulk head is sealed with O-rings to the rest of the instrument which has a watertight stainless steel housing making the instrument fully submersible. Figure 3 shows a partially assembled tool with some of the key components.

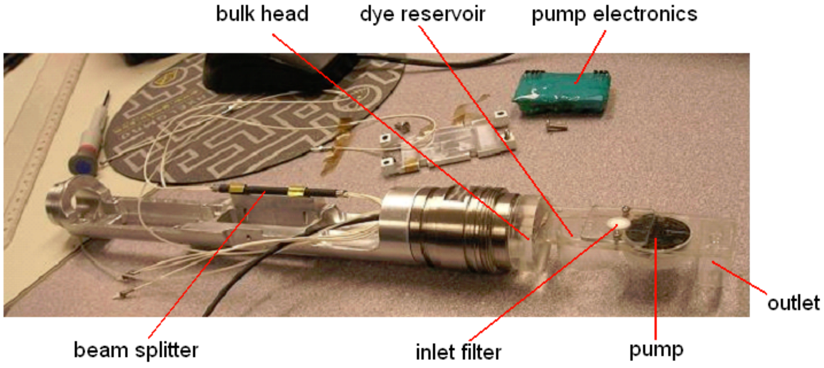

Figure 3 partially assembled tool with some of the key components

EXPERIMENTAL

Equal weight fractions are used for the dye mixture resulting in 0.88 mmol phenol red, 0.75 mmol chlorophenol red and 0.48 mmol bromophenol blue. All molar absorption coefficients of the dyes were taken with any new bottle of dye, due to variations between the bottles. Standard buffers from Acros were used as a reference. The optics was calibrated with buffer 7 in the dye reservoir and in the solution. The instrument was placed in the solution in such a way that the chip was always fully submersed. Pump duration of one minute was sufficient to replace five times the volume of the fluid in the chip up to the optical interrogation zone and including the inlet filter. Measurements were taken after the pumping was stopped for one second at each wavelength.

Battery lifetime was tested by running the instrument at a frequency of one measurement per two hours until the batteries died. Dye consumption was tested by connecting the instrument with a power supply, bypassing the batteries, and run a single measurement every 15 minutes in buffer 7.

RESULTS AND DISCUSSION

Table 1 shows the results of our instrument in standard buffer solutions. It can be seen that the results obtained with our instrument are in good agreement with the pH value of the buffer and well within our accuracy goal of 0.1 pH unit. The results show that a mixture of dyes is very well suitable to extend the measurement range from about 2 pH units to more than 4 pH units. Measurements at pH 3 and pH 9 are becoming less accurate due to the low absolute absorbance of respectively the base peak and the acid peak (Figure 1). Small variations, due to noise or other origins, in these values have a large influence on the ratio and thus on the calculated pH value. However, the pH range of 4 to 8 is sufficient for most ground and surface water sources. If values outside of this range are expected, then alternative dye mixtures can be used to extend the measurement range.

Table 1: Results of the measurement of standard buffer solutions with the new microfluidic chip.

Buffer pH	Chip pH
4.00	3.97
5.00	5.01
6.00	5.98
6.86	6.84
7.00	6.97
7.70	7.67
8.00	7.97

Battery lifetime was determined to be 589 measurements on two ½AA batteries. This is slightly less than the minimum requirement of 4 measurements a day for 6 months. However, the use of two full size AA batteries will double the battery lifetime and hardly change the length of the total instrument. After two thousand measurements the dye test was stopped and the intensity of the absorbance was still more than 50 % of the original value which is more than sufficient for good measurements.

CONCLUSION

The microfluidic chip is successfully integrated in a complete instrument and capable to measuring the pH within the required accuracy of 0.1 pH unit. The dimensions of the dye reservoir and the battery capacity are sufficient for 6 months of unattended operation with a measurement frequency of four measurements per day.

ACKNOWLEDGEMENT

The authors would like to thank Patrick Tabeling and Philippe Salamitou for their guidance during the project. Emilie Dressaire and Oleg Zhdaneev are thanked for their technical support and experimental efforts.

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