Laser Based Chlorine Dioxide Concentration Sensor

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ABSTRACT

In this work a concept and a prototype of a compact optical sensor is presented. The sensor is designed for monitoring chlorine dioxide concentration in potable and industrial water at consumer side. The rapid and maintenance free device is working on the principle of direct photometry. The combination of single and multipath measurement arrangement provides a wide detectable concentration range. The sensor prototype consists mostly of 3D printed parts. For signal conditioning and data acquisition a dedicated module is built. The first experimental results are presented.

Keywords — water; chlorine dioxide; photometry; absorbance; 3D prototyping.

1 INTRODUCTION

Fresh water is essential to sustain human life [1]. Beside the physical and chemical water contamination, the most dangerous is biological one. “More than four million people die annually of illnesses caused by microorganisms, and in most cases caused by water contaminated by microorganisms” [2]. The appropriate water quality control alongside with water treatment may help to address this threat. One of the most important water purification techniques, addressing biologically hazardous contamination is water disinfection.

The chlorine dioxide (ClO_2) is one of the common widely used in Europe disinfectant [3]. It has advanced bactericidal characteristics [4]; moreover it is highly efficient in removing biofilms and preventing its re-growth [5].

In the systems for water disinfection the fast and reliable sensor is required in order to provide a closed loop operation for chlorine dioxide injection unit. The ClO_2 concentration should be kept in prescribed range. Following the DIN 12671:2014, drinkable water may contain 0.05-0.2 mg/l of chlorine dioxide whereas during disinfection it may reach up to 0.4 mg/l. Such sensor may take its place in standalone hotels equipped with own water supply. The water disinfection is also required in food industry for cleaning the technological vessels, pipelines, reactors, tools, etc.

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Nevertheless it is very often when microorganisms play the key role in food production [6]. A good example is the fermentation process taking place in breweries. The souring milk is another example. In order to prevent harm to these “good” microorganisms the processing water has to be examined before the use.

Among the other methods the direct measurement of the optical absorption of the ClO_2 dissolved in water is advantageous: it requires no chemical agents, the system can work in pipe system under the substantial pressure, and it has highest performance, low manufacturing and maintenance costs. Combining various optical path lengths, the measurement range can be extended up to 0.05 to 300 mg/l. As soon as the measurement arrangement has flat measuring surface [7], the sensor is expected to withstand natural fouling due to the properties of ClO_2 and self-cleaning of the optical windows during water circulation.

The prototype, presented in this work is designed and manufactured in order to provide a convenient measurement rig. It serves the purposes of testing and development of the sensor, which will be mounted in a water pipe system.

2 THE MEASUREMENT

The photometric sensor consists of three major components: a photometric cell containing the sample, a light source of known intensity and a photo sensor, monitoring light passed through the cell.

The light absorbed by substance in a photometric cell following Beer–Lambert–Bouguer law can be written as:

$$A = -log_{10}\left(\frac{I_t}{I_0}\right) = \varepsilon\ c\ l,$$

where I_0 and I_t are the radiant fluxes received and transmitted through the media, ε is an extinction coefficient or molar attenuation coefficient, c denotes the molar concentration of the ClO_2 in water and l is the length of optical path.

The range of measured substance concentration is defined by the wavelength of the light source and the length of the photometry cell. For example if the portion of light is reflected back to an additional photo sensor, the lower limit of detectable concentration will be extended by factor of 10. Figure 1. illustrates such measurement setup.

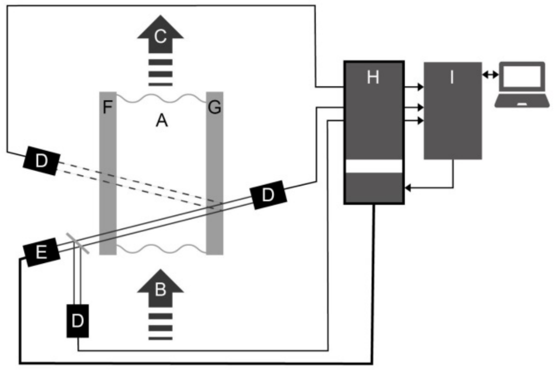

Fig. 1 Measurement arrangement: A) flow cell; B),C) in- and outlet; D) photodiodes; E) laser; F) window; G) semi-transparent mirror; H) signal conditioning module with laser driver; I) data acquisition device

During the experiment the intensity of the incident and transmitted light is controlled with photodiodes. Resulting transmittance is normalized over the one of the sample containing no ClO_2. Water containing controlled amount of chlorine dioxide is circulating through the flow cell. The ClO_2 concentration is controlled with industry standard DPD colorimetric method (DIN 7393). By adding controlled amount of concentrated ClO_2 solution in circulating water, the common chlorine dioxide concentration is changed stepwise. Thus the transmittance of the cell can be measured with respect to defined ClO_2 concentration.

3 PROTOTYPE AND MANUFACTURING

3.1 MEASUREMENT FLOW CELL

The flow cell is a core unit of the setup. It is equipped with in- and outlet, optical window, semi-transparent mirror. All other optical components are attached to the cell via adjustable fasteners. (Fig. 2) The light source and photodiodes are slid into dedicated slots of the optical assembly attached to the sides of the flow cell. The probing light beam is tilted by 16 degrees to normal of the optical window. The intensity of the light reflected from the semi-transparent mirror is measured with the photodiode attached to the optical assembly along with the light source, beam splitter and the reference photodiode. The intensity of light transmitted through the cell is measured with another photodiode, mounted to the back side of the cell. Most of the prototype components are manufactured with Fused Deposition Modeling (FDM) 3D printing technique. The water tightness of the flow cell is provided through vacuum impregnation of the 3D prints with a two-component PDMS compound.

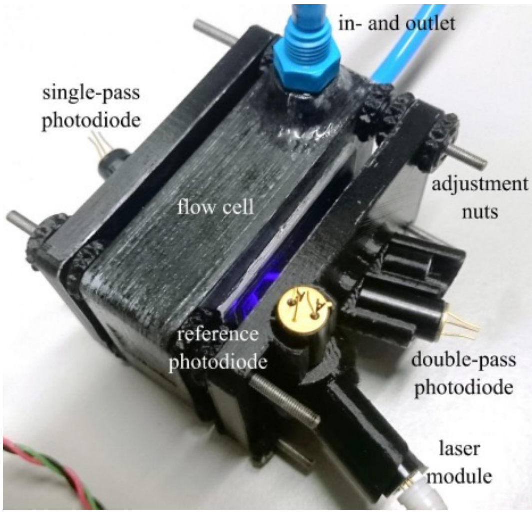

Fig. 2 The Sensor prototype assembled

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3.2 OPTICAL MODULES OF THE SENSOR

Most of the affordable photo sensors are sensitive to light in wide wavelength range. In order to provide high substance selectivity, the monochromatic light source is preferred. The maximal absorptivity of aqueous ClO_2 is detected in the 240-440 nm range with a maximum at 370 nm [8]. Such blue to near ultraviolet range is covered with number of light emitting diodes (LED). However the width of the emission spectra reaches up to 30 nm. From the other hand the effective focusing of the LEDs in a parallel beam is hindered by the étendue conservation principle. Thus an affordable laser diode is chosen. The diode emission peaks at 405 nm corresponding to 600 L/(mol·cm) [8] extinction coefficient of the ClO_2 aqueous solution. The emitting CW power of the diode is limited to 10 mW.

Photo sensors are silicon diodes in TO-5 package having 3.6 mm x 3.6 mm sensitive area. Both the laser diode and the photodiodes are mounted into 15 mm tubular holder of 10 mm diameter. The laser beam is focused with dual lens aspherical laser collimator (see Fig.3). Such unified tubular mounting simplifies the axial alignment of the optical system.

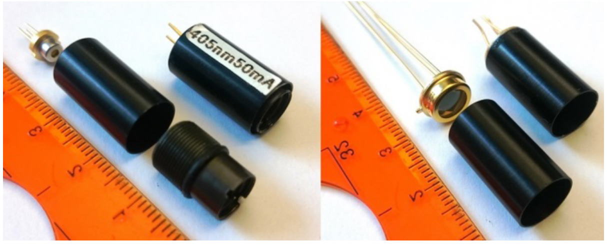

Fig. 3 laser module; photodiode module

3.3 OPTICAL WINDOWS

Most of optical grade glasses have good (within 90%) transmissivity above 300-400 nm. However the maximum light absorption of ClO_2 aqueous solution is 370 nm which defines the better window material – UV grade fuse silica. It is 90-95% transparent at wavelengths starting from 200 nm [9]. The sheets of UV grade fused silica (approx. 2 mm thin) are widely used as substrates for the photolithography masks. This material is rigid, durable; the flat faces are of optical grade (smooth, flat and parallel). The sheets were cut by a dicing machine to 50x30 mm. Before the metal mirror deposition of the windows were boiled in fresh piranha solution (H_2SO_4 to H_2O_2 as 2:1). The aluminum reflecting coatings in blue - to near ultraviolet range outperform all the other metallic reflective coatings [10]. The aluminum film is deposited with electron beam evaporation. Transmittance and reflectance of the semi-transparent mirrors are controlled with direct photometric test. At 10 nm thickness of aluminum film the transmittance of the semitransparent mirror is 20 % whereas the reflectance is 70 %. The film of the best surface quality is manufactured at 12 Å/second deposition rate. Despite the self-passivation of the aluminum surface it is subjected to aging. It is protected with 250 nm thin SiO_2 protective film by means of PECVD. The window and the mirror are fixed to the flow cell with two components adhesive. The estimated critical excess pressure of the 2 mm thin glass window is $2*10^5$ Pa.

3.4 OPTICAL HOLDER

Laser and photodiode sensors are clamped in the 3D printed holder. The optical holder is secured to the flow cell with a set of threaded rods. The focused laser beam is 6 mm wide; however the sensitive area of the silicon diode is smaller than the beam cross section. When a slightest non-controllable mechanically, thermally or hydraulically induced misalignment takes place, a strong deviation of intensity occurs, reducing accuracy of the measurement. This effect is mitigated by shaping the beam down to 2 mm diameter with the set of the diaphragms integrated into the optical holder. The holder is equipped with sliding sockets for optical modules and a beam sampler which splits a portion of the incident optical signal to the reference diode. The probe beam is s-polarized with respect to the sampler plate and p-polarized with respect to the cell windows system. Thus the reference diode is well lit and the reflection losses at the cell windows are minimized.

3.5 SIGNAL CONDITIONING AND DATA ACQUISITION

A photodiode converts absorbed light in the photocurrent proportional to the light intensity. The photocurrent is transformed and amplified with transimpedance amplifier. The signal corresponding to dark current is subtracted from the measured optical signal. Later it is normalized to the reference signal. Thus the transmittance value of the photometric cell is derived. The dedicated signal conditioning module is combining 3 transimpedance amplifiers, power supply and a laser driver providing secure laser modulation and current stabilization. The amplified signal is than sent to a data acquisition device LabJack U6 equipped with a USB interface, multichannel ADCs and digital outputs which are used for laser modulation. The device is automated with a Python script running on a PC.

4 RESULTS AND DISCUSSION

The first calibration tests are performed at Dr. Küke GmbH laboratory (Mellendorf, Germany).

The extinction coefficient of aqueous ClO_2 at 405 nm is corrected to 545 L/(mol·cm) and concentration independent dissipation factor of the tested water sample is 0.04 cm-1 (Fig. 4). The results of the measurements demonstrate comparable results to commercially available sensor systems, but with a faster response time and higher long-term stability, due to the fact, that no degeneration of agents or components occurs. Further measurements are now in ongoing phase.

In this paper a concept and the sensor prototype are presented. The sensor monitors the concentration of ClO_2 in water in real time via direct light absorptivity measurement at 405 nm.

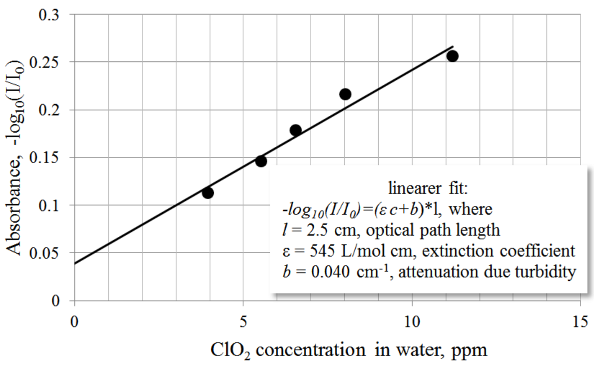

Fig. 4 Linear approximation of experimental results in terms of Beer–Lambert–Bouguer law.

5 ACKNOWLEDGMENT

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