Carbon dioxide gas sensor based on optical control of color in liquid indicator

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Abstract. A new optical carbon dioxide sensor based on the change in glow intensity of the Europium-III complex, caused by CO₂ absorption to various pH-indicators (thymol blue, phenol red and cresol red) of carbon dioxide was developed, and its sensitive properties were studied.

1. Introduction

CO₂ is significant used in industry gas for various applications, which include the production of chemicals, it also acts as an inert agent for food packaging, used for the manufacture of beverages, refrigeration systems, welding systems, fire extinguishers, water purification systems, etc. [1,2].

In the agro-industry, CO₂ is widely used for packing in a modified atmosphere, where its purpose is to inhibit the growth of spoilage bacteria [3,4]. For example, in active packaging technologies, the CO₂-generating system could be considered as a supplementing method for oxygen cleaning [5]. High CO₂ level (10-80 vol.%) is desired for food products such as meat and poultry, in order to inhibit the growth of microorganisms on the surface and to extend shelf life. Maintenance of the CO₂ concentration in the packages with food [6], for example using nested sachets [7,8] should be carefully monitored, since CO₂ permeability is 3-5 times higher than the oxygen one for most plastic films, so CO₂ is absorbed by many products, such as meat and poultry.

Real-time processes monitoring is essential for effective process control. The rapid development of the biological processes use together with the agro-industry has led to an intensive search for new sensors, able to provide real-time information about the status of processes.

Conventional methods for determining the CO₂ include, among others, infrared spectrometry [9] or electrochemical sensors based on liquid or solid electrolytes [10,11]. The most popular sensors used for CO₂ gas sensing in biotechnological applications are based on electrochemical measurements that may be obtained from a variety of materials. Optical CO₂ sensors with low detection limits are used in various industrial processes, such as environmental monitoring, pollution control, biotechnology and food industries [12]. They are based on CO₂ Lewis acid properties; namely, by reaction with an aqueous Lewis donor, the pH change occurs and could be monitored using absorbance or the fluorescence of the pH values. Generally, acid-base indicators are immobilized in so-called membranes of the solids sensors [13], made of gas-permeable polymers such as ethyl cellulose [14], the sol-gel [15], silicone [16], composite materials [17], or they are directly attached to the tip at the end of the optical fiber or in its core [18]. In addition to the indicator, the membrane often comprises a quaternary ammonium hydroxide [19] and/or ionic liquids at room temperature [20] for an ion pair
with the basic form of the pH indicator, as well as to supply water required to form a hydrated ion pair for the absorption of CO₂ from the atmosphere by forming lipophilic carbonate buffer.

Gaseous CO₂ is measured by infrared absorptiometry as well as electrochemically, using the Severinghaus electrode [21]. Since the infrared absorption band at the wave carbon dioxide is in the range of 4200-4400 nm, infrared absorptiometry is used in optical sensors. On the other hand, the CO₂ sensor with the Severinghaus electrode consists of a glass electrode that detects changes in the pH-level in surrounding bicarbonate ionic solution after it enters and subsequent hydration of CO₂ through the thin film. However, a very sensitive IR absorptiometry-based sensor is influenced by water vapor, and by itself is a very expensive system. To overcome these issues, the study and improvement of the CO₂ sensor was made. In recent years the CO₂-sensors operating by colorimetric and fluorimetric pH-sensitive indicators changes or sensitive to CO₂ colored indicators were developed.

Optical CO₂ sensors come in two types. One of them is based on the change in color of pH-indicator: timolsulfonftalein (thymol blue), fenolsulfonftalein (phenol red), cresol red, etc. Another sensor based on the change of color CO₂-sensitive luminescent colored indicator, for example, 1-hydroxypyrene trisulfonate and ruthenium complexes. This method is simple and convenient. In the case of the fluorescent phenol-based CO₂ sensor the fluorescence intensity change with a shift of the fluorescent flow color from fluorescent (phenol anion) to not fluorescent (a neutral form of phenol) is used. However, the number of substances for which fluorescence level changes under the influence of CO₂, severely limited. To solve this problem, the CO₂ sensor that runs on a combination of color change technology and fluorescent flow was developed. The own glow should not be changed under the influence of CO₂. The principle of this sensor is based on the overlap of the wavelengths of the own inner glow range CO₂ absorption range when using the pH-indicator.

The study of the CO₂ sensor with two dyes, one of which is basic, was published. Ruthenium fluorescent complex is used as a basic indicator.

A new optical carbon dioxide sensor was developed, and its sensitive properties were studied. The sensor is based on the change in glow intensity of the Europium-III complex, caused by CO₂ absorption to various pH-indicators (thymol blue, phenol red and cresol red) of carbon dioxide. For all CO₂ sensors operating on the pH-indicators the glow intensity at 612 nm was registered and increased with an increase in carbon dioxide concentration. The best results were obtained using the thymol blue indicator. In its case, the sensitive film response time to the carbon dioxide was 4 seconds, at the transition from 100% nitrogen atmosphere to 100% CO₂. The recovery time of the sensitive film in the reverse transition to a 100% nitrogen atmosphere was 36 seconds. The response time when using the indicator phenol red and cresol red was 4.4 seconds and 8.8 seconds respectively. The recovery times were 39.2 seconds and 56.6 seconds respectively. Currently, the research of the sensor behaviour in the air is conducted to improve the composition of the sensitive film [22].

2. Experiment

2.1. Reagents
As a chemical indicator responsive to the concentration of carbon dioxide, bromothymol blue indicator was chosen. The indicator allows determining a change in pH values in the range of 6.0 to 7.6 while changing its color from yellow to blue through green colors (Fig. 1) [23].

![Figure 1. pH-scale of the bromothymol blue indicator.](image)

2.2. Design of the reaction chamber
The reaction chamber of the installation is a camera for the reaction between the liquid indicator and the gas tested for the presence of carbon dioxide. Upon contact with carbon dioxide, the liquid in the
chamber changes its optical properties, namely the colors. This change must be captured electronically by optical sensors of the measuring system, and after the subsequent transformations are presented to the user in the digital form.

The reaction chamber is a container, which is made of an optically transparent in the visible range of light frequencies organic polymer (plexiglass). It consists of two parts and has inside a cuvette for placing the indicator fluid and channels for supplying the tested gas (Figure 2). The main problem of the chamber is the evaporation through the supply channels of the indicator fluid. In this regard, necessary to increase the hydrodynamic resistance of the channel. The balance between the free access of the tested gas into the chamber and minimal evaporation of the test liquid should be maintained. The dynamics of this indicator depends on the characteristics of the environment: atmospheric pressure, air temperature and the temperature of the cuvette. Necessary to consider that while increasing the temperature of the cuvette, the temperature of the indicator fluid increases as well, which in turn reduces the coefficients of its viscosity and increase volatility coefficient. This leads to an increase in fluid velocity in the channels and further to its evaporation, and to the throttled gas in the channels. The hydrophobic membrane structures were installed to reduce the flow rate (Figure 3). Their aim is to pass gas into the chamber and not let go of the camera the indicator fluid. At the ends of the camera the optocoupler (LED and photodiode) is set. The LED is a light source of constant intensity and a narrow frequency range [24]. The photodiode allows investigating changes in the intensity of light passing through the liquid indicator when painting indicator to a different color under the influence of carbon dioxide.

![Figure 2. 3D-model of the reaction chamber.](image)

![Figure 3. The composite camera with hydrophobic membranes for retaining the indicator liquid (the side view).](image)

2.3. **Measuring system design**

To analyze the changes in the CO₂ concentration and liquid color, the electro-optical method of inspection and measurement is applied. The color of the indicator fluid is directly dependent on the
level of carbon dioxide in the atmosphere that comes with this liquid contact. At low CO\textsubscript{2} concentrations liquid indicator changes its color, and the light radiation passing therethrough does not change in intensity. With an increase in CO\textsubscript{2} concentration in the atmosphere contacting with the liquid, the fluid color change from light blue to yellow. In consequence of this changes the intensity of light radiation passing through the liquid. It falls on the photodiode, which causes further signal enhancement, which is received in the system of measurement and digitization (Figure 4).

![Figure 4](image.png)

**Figure 4.** The scheme of the carbon dioxide concentration in the gas measuring apparatus.

As seen in Figure 4, the device scheme comprises seven constituents [23]. The emitting semiconductor diodes are used as a source of monochromatic radiation. They irradiate the sample with light of the desired frequency spectrum with specified intensity, which varies during the passage of the light beam through the test sample. The voltage regulator of the radiation system power supply is applied in the system. Its presence in the system is determined by the need to reduce current fluctuations and, as a result, fluctuations of the LED light intensity. DC stabilizer is built on the integrated high-precision linear regulators. The features of such linear regulators are: high load capacity; small change - subsidence of the output voltage of the regulator changes the load current; low noise; small temporal and thermal drift. The sample is placed between the emitting diode and photodiode. Outgoing from the emitting diode light passes the sample and reaches the photodiode or photodetector. The photodiode detects changes in the intensity of the radiation coming from it.

3. Conclusion
The paper describes the optical carbon dioxide sensor based on the change in light intensity Europium-III complex, caused by CO\textsubscript{2} absorption to various pH-indicators of carbon dioxide. To analyze the changes in the CO2 concentration and liquid color, the electro-optical method of inspection and measurement was applied. The best results were obtained using the thymol blue indicator. In its case, the sensitive film response time to the carbon dioxide was 4 seconds, at the transition from 100% nitrogen atmosphere to 100% CO\textsubscript{2}.

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