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AMPEROMETRIC SENSORS FOR THE ANALYSIS OF THE OXYGEN CONTENT

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Abstract

The paper presents the using of amperometric sensors in measurements of the oxygen content in the organic solutions such as beer. The resulted data compared with spectrophotometric data.

Keywords: current sensors, statistical analysis, and oxygen content analysis

1. Introduction

Amperometric sensors monitor AC or DC current. Included are adjustable linear, null balance, digital, and linear current sensors.

Typical applications are variable speed motor, automotive diagnostics (battery drain detector), ground fault detectors, motor overload protection, current monitoring of electric welders, and protection of semiconductors power, Levices control system diagnostics and more.

In order to determine the oxygen in the beer and in the beer must, different methods are used: volumetric gas ones [1], photometric ones [2-7], electrochemical ones [8-10]. The electrochemical methods use galvanic oxygen sensors [11-15], current sensors, with a membrane [16-21] or sensors with optic fibers [22]. The functioning of the oxygen sensors is influenced by the presence of the carbon dioxide; namely, it modifies the pH of the basic electrolyte (by forming carbonates), or the oxygen reduction mechanism [19, 22].

We use a sensor for beer analysis. Beer is obtained by brewing the beer must, that is by transforming the fermentable sugars into alcohol and carbon dioxide with the aid of the enzyme complex of the beer yeast.

2. The experiment

Our sensor module (the brown cylindrical cartridge in the plastic part of the SBE 23) has a working life of at least 6 months if kept moist. If the sensor is stored in dry air, however, operating life may be appreciably shorter. When possible, store the sensor with a loop of Tygon tubing containing distilled or deionizer water. Care must be taken to avoid fouling the oxygen membrane with oil or grease. It is recommended that the oxygen sensor be flushed with distilled water after each use and be kept filled with distilled water between uses. An additional important benefit of keeping the sensor closed with Tygon is to keep air born contaminants (of which there is abundance on most research vessels) from entering the sensor.

If it is not practical to keep the sensor filled with distilled water between use (for example, in Arctic environments where freezing is a hazard), at least flush it with clean fresh water (preferably distilled) and close the cell with Tygon. Also, remember to keep the Tygon in a clean place (so that it does not pick up contaminants) while the instrument is in use.
For routine cleaning, fill the sensor with a 1% solution of Triton X-100 and let soak for 30 minutes. Using a length of 7/16” Tygon tubing to form a closed loop including the sensor most easily does this.

The Teflon membrane should be pointing up so that an air bubble does not block the cleaning solution. After the soak, drain and flush with warm (not hot) fresh water for 1 minute. Refill the sensor with distilled water until the next usage.

The determining of oxygen was carried out by means of the current sensor under strict thermostatic conditions t (^{o}C) = 20±0.2. As a basic electrolyte, a carbonate – bicarbonate solution was used (KCl 0.75M; K_2CO_3 0.5M; $KHCO_3$ 0.25 M).

The calibration mixtures were air-argon, air-carbon dioxide, and water saturated air [23]. The determinations were carried out with three different sensors, achieved according to the method described in [24]. Thus, the sensitivity values according to the oxygen concentration were determined (tables 1 and 2).

From the data in tables 1 and 2 it is noticed that the sensors have the same sensitivity for the different mixtures of air-argon and air-carbon dioxide, the standard deviation “s” is small, the value being s = $8.55\cdot10^{-2}$ [ppm]. The functioning of the sensors is not influenced by the presence of the carbon dioxide.

The amperometric sensors maintain their initial sensitivity ($S_{0,1}$ = 0.1164 μA/ppm, $S_{0,2}$ = 0.1604 μA/ppm, $S_{0,3}$ = 0.1733 μA/ppm), after their immersion for 24 hours in water saturated with air, or carbon dioxide, respectively ($S_{1,1}$ = 0.1160 μA/ppm, $S_{1,2}$ = 0.1600 μA/ppm, $S_{1,3}$ = 0.1126 μA/ppm). The relative error is also constant (0.34–0.40%).

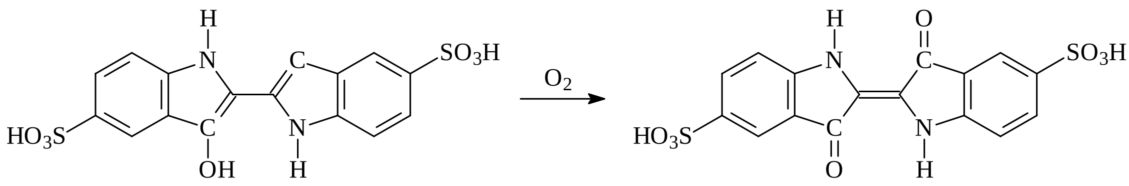
Table 1. The sensitivity values of some sensors for different argon mixtures

Concentration O_2 [ppm]	Sensor l		Sensor 2		Sensor 3	
	i[μA]	S [μA/ppm]	i[μA]	S [μA/ppm]	i[μA]	S [μA/ppm]
1.83	0.213	0.1163	0.294	0.1607	0.317	0.1732
4.30	0.504	0.1172	0.691	0.1607	0.745	0.1733
5.90	0.687	0.1164	0.947	0.1605	1.022	0.1732
8.47	0.986	0.1164	1.359	0.1604	1.466	0.1731

Table 2. The sensitivity values of some oxygen sensors for different air-CO_2 mixtures

Concentration O_2 [ppm]	Sensor l		Sensor 2		Sensor 3	
	i[μA]	S [μA/ppm]	i[μA]	S [μA/ppm]	i[μA]	S [μA/ppm]
1.98	0.231	0.1167	0.318	0.1606	0.343	0.1732
4.52	0.526	0.1164	0.724	0.1602	0.781	0.1728
6.08	0.707	0.1163	1.356	0.1602	1.050	0.1724
8.47	0.985	0.1163	1.356	0.1601	1.460	0.1724

Within the thermostatic cell, argon was stir up for 15 minutes. A volume of beer was siphoned, so that this should replace the volume of the cell, once. The tightness of the cell was ensured. The sample was stir up and the concentration of oxygen was determined by both the current and the spectrophotometric sensors [4], adapted to the given conditions. As a color indicator, carmine indigo was used. The reaction at the basis of this determination consists in the oxidation of the Leuco form of the carmine indigo, which is yellow, by the oxygen, to the oxidized form, which is blue, according to the chemical reaction:



The absorption curves were plotted for the carmine indigo solution in its reduced and oxidized form, in order to determine the λ optimum wavelength (see figure 1).

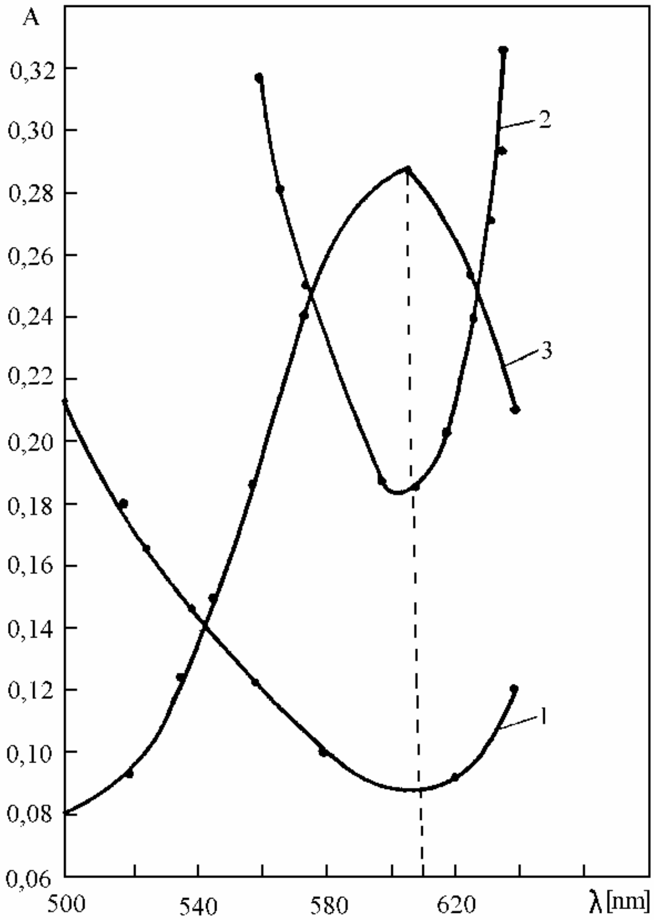


Fig. 1. The absorption curve in aqueous medium for beer (1), carmine indigo (CI) reduced form (2), CI oxidized form (3) with $C_{CI} = 10^{-3} mol \cdot l^{-1}$

For the spectrophotometric determining, the tightness of the vat was ensured, so that the oxygen in the air should not affect the oxygen quantity in the sample. The reduced form of the carmine indigo was obtained by hot treatment with glucose, in alkaline medium [4]. The processes taking place can be represented by the following scheme:

$$(IC)_{ox} \xrightarrow{\text{Glucose}} (IC)_{red} \xrightarrow{+O_2 \text{ in the sample}} (IC)_{ox}$$

blue *yellow* *blue*

The data obtained by the spectrophotometric method and those resulted by using the oxygen sensor was compared by means of the STAS 7688-84 method.

3. Results and discussion

The obtained data are presented in the following tables. The data in table 3 show a good concordance of the results obtained by the oxygen sensor compared to the STAS method, and compared to the spectrophotometric method.

The two methods, the spectrophotometric, and the oxygen sensor one were applied to samples of bottled beer, produced at “Ursus” Factory (table 3). The oxygen concentration in the beer has a value of about 1 ppm O_2.

Table 3. Oxygen content with spectrophotometer (Sp), sensor (Se) and STAS method for water (STAS)

No Crt	Water			Beer		Aired Beer Must	
	STAS	Sp	Se	Sp	Se	Sp	Se
1	1.83	1.83	1.83	0.53	0.52	7.02	6.95
2	1	1.15	0.98	1.15	1.04	7.1	7
3	1.65	1.76	1.64	1.08	1.02	7.3	7.2
4	1.12	1.2	1.12	0.96	0.9	7.2	7.16
5	2.4	2.46	2.42	0.83	0.79	7.1	7.04
6	2.82	2.82	2.82	0.65	0.63	7.05	6.95
7	2.97	3.07	2.97	0.94	0.9	7.11	7.06
8	0.5	0.49	0.49	1.26	1.22	7.19	7.11
9	0.48	0.5	0.47	0.76	0.72	7.1	7.04
10	2.15	2.11	2.15	0.88	0.81	7	6.98

In the aired beer must, the oxygen concentrations are of about 7 times greater (~ 7 ppm), but the sensor/spectrophotometric measurements remain accurate (table 3).

Using the homemade oxygen sensor the content of oxygen was determined in different stages of the beer production process and table 4, presents inverse values as an average of 5 determinations.

Table 4. The dissolved oxygen, in the different stages of the beer brewing process

No. crt.	Place of sampling	Average values (stationary conditions) [ppm O_2]
1.	Must cooling	7.0
2.	Must lowering	0.2
3.	Tanking	1.0
4.	28 day beer	0.6
5.	35 day beer	0.4
6.	Mixing platform input	0.6
7.	Plate filter input	0.7
8.	Plate filter output	0.8
9.	Tank input	1.0
10.	Tank output	1.6
11.	Bottled beer	2.0

The regression analysis of the measured data is represented in figure 2.

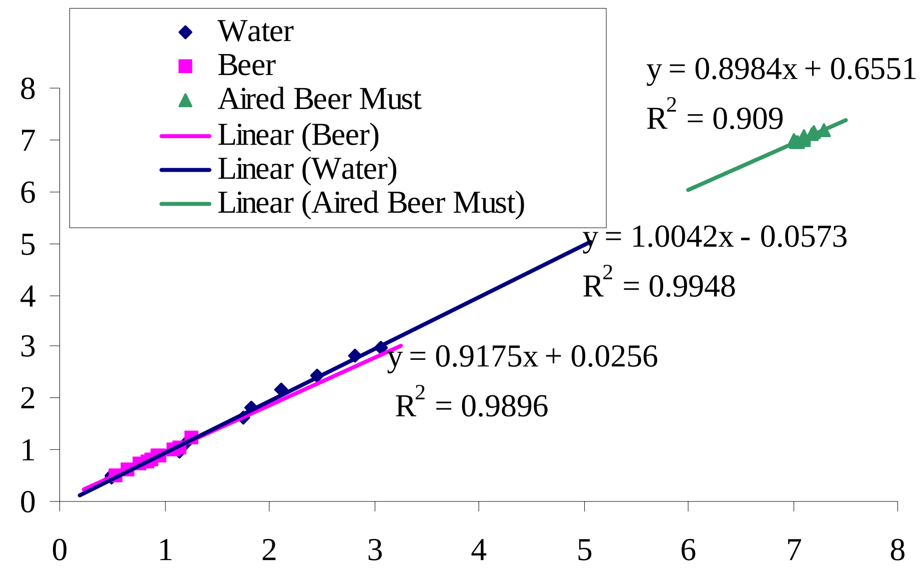


Fig. 2. Data plots of water, beer and aired beer must
(spectrophotometric vs. sensor measurements)

4. Conclusions

The oxygen sensor can be used for determining the oxygen content along the production process, namely for controlling it (correlation coefficients ~ 0.9 and relative error ~ 0.34%).

The method employing the amperometric sensor allows for the on-line control and the automation of the process.

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