COMPARISON OF METHODS FOR DETERMINING THE BIOLOGICAL OXYGEN DEMAND

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Abstract: Biochemical Oxygen Demand is one of the most commonly used group determination. The aim of work was to compare the selected methods used for determining the biological oxygen demand. For comparison respirometry and electrochemical methods for determining the biological oxygen demand were chosen. This article compares these methods when common matrices waste water and sludge from wastewater treatment plants were used. Furthermore, analysis duration, investment costs and operating requirements were evaluated for each method. The result is a comparison of the results of each method.

Key Words: biological oxygen demand, waste water, sludge, comparison of analytic methods

INTRODUCTION

Biological Oxygen Demand (BOD) is one of the parameter, which indicates the water quality. It is defined as a mass concentration of dissolved oxygen in solution, which is used during the biochemical oxidation of organic substances under specified conditions. Therefore it is an indirect indicator of the amount of biodegradable organic matter in the water. The standardized method in The Czech Republic is incubating of sample for five days, thus (BOD_5), when the BOD_5 is determined by dilution method, under aerobic conditions at 20 °C (Pitter, 1999).

According to the Czech standards, it is possible to determine BOD_5 by various analytic methods, the result obtained should be comparable. Our objective was to test this hypothesis, therefore, to compare the analytic methods on various matrices processed and detect any statistically significant differences in the results. Selected methods of determining BOD_5 were compared in terms of analysis duration, investment costs, operating requirements and repeatability, therefore to show the similar results in the same matrices.

THE MATERIAL AND METHOD

For the determination of BOD_5 two different samples were taken. Waste water without inorganic particles was taken at the wastewater treatment plant (WWTP) after mechanical treatment and sewage sludge was taken from the activation tank. Individual samples were collected from two different wastewater treatment plants, WWTP Moravany, Czech Republic (5500 PE) and WWTP Brno, Czech Republic (513,000 PE). For the purpose of the research, the origin of the samples was not important because the main task was not to determine BOD_5 of the samples to find out an amount of biodegradable organic substances in it. The task of the measurement was to compare the methods of BOD determination.

After transport of the samples to the laboratory the samples were tempered at 20 °C and aerated so the initial oxygen concentration ranged between 8.5–9.0 [mg/l].

Measuring of the dissolved oxygen by the electrochemical method with a membrane probe

We followed the Czech standard CSN EN ISO 5814 which specifies the electrochemical method for assessment of the dissolved oxygen in water with an electrochemical cell. The electrochemical cell is separated from the sample by a membrane permeable for gas (CSN EN ISO 5814).

The measuring was done on multi-parameter portable meter ProfiLine Multi 3320 (Figure 1) , Serial Number 15430032 manufacturer WTW, Germany in combination with a sensor CellOx® 325 which measures the concentration of the oxygen in milligrams per litres. It was necessary to dilute the samples before the measuring according to the Czech standard CSN EN 1899-1 and also aerate. Prepared samples were spilled into the Winkler flask. The first half of the samples was measured by the electrode, the second half of samples was put into the thermostat at 20 °C and measured after five days. The difference was calculated and expressed as BOD5 [mg/l].

Figure 1 Measuring device Multi 3320 and sensor 325 CellOx® in a calibration vessel OxiCal® SL

Respirometry determination

This method is based on the assumption that the microorganisms oxidising organic substrate, when use the oxygen dissolved in water and the oxygen in head space of the measuring bottle as oxygen source. Carbon dioxide (CO2) generated during this process is absorbed (the absorbent is NaOH). Due to the decrease of the oxygen concentration and adsorption of CO2 on NaOH the pressure in the bottle decreases. This change is detected by a pressure indicator (Figure 3) in the infrared head of a measuring bottle and saved into its memory. The data can be transferred to controller (Figure 2) which displays the exact BOD5 value. Thus, no other calculation is needed (Slevogt 2006).

Measuring bottles were filled according to the data visible at the display of controller (expected range of BOD and appropriate amount of sample). The device used in the laboratory is OxiTop® - the measuring head with inductive mixing system and OxiTop® OC 100 – a controller (Figure 2). Manufacturer WTW, Germany. No dilution of samples necessary (Slevogt, 2006).

The bottles were cleaned and dried prior of the measurement. The bottles were filled with an exact volume of sample which represents the presuming BOD5 value (The controller allows display the table with an amount of sample for individual ranges of BOD5, so it is essential to know the presuming range so that the pressure sensor could work correctly).

After the bottle is filled up, the stirrer is inserted into the bottle. The rubber plug is filled with NaOH (1-2 capsules) and put inside the neck of the bottle. The measuring head is screwed on the bottle and the controller is switched on to the mode of communication with measuring heads. The presumed range of BOD and corresponding volume should be chosen and then confirmed. The measurement starts after the temperature of sample reach 20 °C. The head detects the pressure every 20 minutes and converts it to BOD5. The result is a chart of oxygen consumption development (Slevogt, 2006).

Figure 2 OxiTop® set of 6 bottles with a controller

Figure 3 Bottom view of the sensor head and integrated in the pressure-sensitive membrane

RESULTS AND DISCUSSION

As is evident from Table 1, we performed four measurements in three weeks. The respirometry method included only three measurements because of the number of the measuring heads. It can be concluded that both methods have the same results for the same matrice.

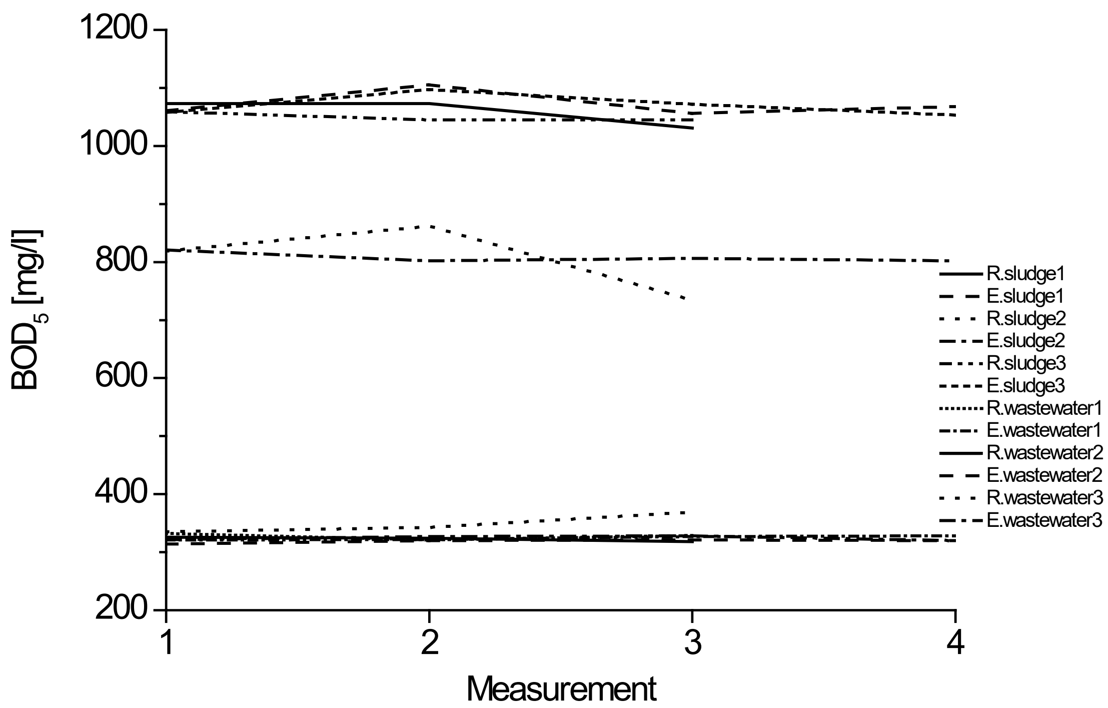
Table 1 Overview of measurement results BOD_5 particular methods and substrates.

Date	Measure	BOD_5 [mg/l]			
		R. waste water	E. waste water	E. sludge	R. sludge
30. 3. 2016	1	332	321.44	1061.07	1073
	2	321	321.81	1105.07	1073
	3	329	326.81	1056.20	1031
	4		328.15	1068.43	
6. 4. 2016	1	326	314.33	821.10	819
	2	324	320.11	801.77	862
	3	318	321.44	806.43	734
	4		320.11	802.38	
18. 5. 2016	1	335	321.81	1058.19	1059
	2	343	326.81	1096.86	1045
	3	369	328.15	1071.52	1045
	4		319.52	1053.07	

Legend: R. – Respirometry method of determining, E - Electrochemical method for determination

Progress of BOD value during the measurement is shown in figure 4. The results indicate that the differences between the results are not statistically significant at a significance level of $p = 0.05$.

Figure 4 Results of comparison of methods for determination of BOD_5



Legend:R. – Respirometry method of determining, E - Electrochemical method for determination, 1, 2, 3, are days of measurement

Investment costs of equipment for electrochemical method for the determination of BOD_5. Price of Winkler flask is around € 17.6. For 3 measurements 6 bottles is needed. Altogether it is € 105.6. The

MultiMeter 3320 is € 1246.2, CellOx® 325 probe with calibration container € 775.5. Chemicals for preparation of diluted solution € 53.8. Altogether it is € 2181.1. Investment costs for the respirometry method. OxiTop® set with 6 bottles and measuring heads, induction stirrer, controller and software, total € 4965.1, (WTW 2016) (P-LAB 2016) (VWR 2016). For both methods purchase of thermostat and access to distilled water was not considered,

During BOD determination, we found that the least demanding on operation is respirometry method, since it is not necessary to dilute the sample and after sampling sample can be just fill up into the measuring bottles. The BOD determination by respirometry method is fully automatic, after five days data from controller are transferred to the computer. Electrochemical method is much more time-consuming. It is necessary tempered and aerate the dilution water and then dilute samples and fill it into the bottles. After that the samples are ready for measurement by immersing the electrode to the samples and writing the value of dissolved oxygen in sample. The same needs to be done after five days.

CONCLUSION

The aim of the paper was to compare the respirometry method and the electrochemical method of BOD_5 determination. It is clear from the results that the data obtained from the individual methods varies according to the different days of the measurement which is caused by diverse kinds of samples. Within a single measurement, the results are comparable. Both methods give very similar results but their investment costs are different. The electrochemical method is € 2181.1 and the respirometry method is € 4965.1, which is two times more.

The electrochemical method is applicable for quick measuring of the dissolved oxygen in the solution. Its convenience is a mobility, which means possibility of in situ measurement, for instance, inflow to the wastewater treatment plant. The problem is the necessary of calibration and degradation of permeable membrane which can cause errors in the measurement. This method is also more time demanding in comparison with the respirometry method.

On the other side, the respirometry method is easy and time undemanding. The samples do not have to be diluted and the electronic sensor with memory allows deducting the results even after 5 days. The disadvantage of this method is a necessity of preliminary knowledge of the BOD_5 range. Consequently, knowledge of the matrice analysed, and environment influence is needed. It is also essential to take care about airtight tightening of the heads on the bottle. This method is two times more expensive than the electrochemical method.

Measuring of BOD_5 in the laboratory is still in process together with measuring the matrices of drinking water and the standard solution. It is also planned to measure the methods volumetrically and spectrophotometry.

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