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*Research Article*

# Comparison Study of Different BOD Tests in the Determination of $BOD_7$ Evaluated in a Model Domestic Sewage

**Katri Roppola,[1] Toivo Kuokkanen,[1] Jaakko Rämö,[2] Hanna Prokkola,[1] and Eeva Heiska[3]**

[1] *Department of Chemistry, Faculty of Science, University of Oulu, P.O. Box 3000, 90014 Oulu, Finland*
[2] *Water Resources and Environmental Engineering Laboratory, Department of Process and Environmental Engineering, Faculty of Technology, University of Oulu, P.O. Box 4300, 90014 Oulu, Finland*
[3] *Oulu Waterworks, Kasarmintie 29, Box 35, 90015 Oulu, Finland*

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The aim of this research was to study the suitability of a manometric respirometric test (OECD 301F) for the determination of biological oxygen demand (BOD) in domestic wastewater. This was done by comparing four different BOD tests (a manometric respirometric test, oxygen sensor determination, iodometric titration, and UV absorption measurement) and by evaluating the $BOD_7$ value after a short-term measurement applying the manometric respirometric test. Measurements were done in three different laboratories. The respirometric test was performed well on municipal sewage, and the precision of results was good. There were minor deviations between $BOD_7$ values as determined by the different methods, but the deviations were not essentially big enough to have a practical impact. Evaluation of the $BOD_7$ value after two or three days' incubation by the respirometric method was shown to work well; average deviations between measured and evaluated values after three days' incubation were 5–18%. Hence, the manometric respirometric test proved to be a rapid and suitable tool for process control purposes.



## 1. INTRODUCTION

Biological oxygen demand (BOD) is an important and widely used sum parameter to evaluate water quality. BOD is a measure for the quantity of oxygen required for the biodegradation of organic matter (carbonaceous demand) in water but it is affected by oxygen consumed for oxidising inorganic material such as sulphides and ferrous iron and by the amount of oxygen used to oxidise reduced forms of nitrogen (nitrogenous demand), unless their oxidation is prevented by an inhibitor [1]. However, conventional BOD measuring tests are problematically slow, typically intended to last five or seven days. Management of a wastewater treatment plant can be very difficult using these timeconsuming tests, because conditions in the plant will have been already changed during such test periods. Conventional tests are also affected by factors such as dilution and sample preparation. On the other hand, conventional BOD tests have some benefits as compared to new, rapid, automatic, analytical techniques. The classical methods are used universally and the results are therefore comparable. In addition, they do not require expensive equipment [2]. Nevertheless, due to the increasing demand considering, for example, biodegradability, it is very important to develop automatic, faster, and more precise ways for BOD determination. The new inventions must subsequently be compared with conventional methods in order to detect sources of error.

We recently studied the biological oxygen demand of wastewaters from the Stora Enso Oyj Veitsiluoto (Kemi, Finland) pulp and paper mills, using three methods: the manometric respirometric test (WTW Weilheim, Germany), oxygen sensor determination, as well as iodometric titration [3]. The results showed that the manometric respirometric method was suitable for the BOD determination of the wastewater of the pulp and paper mills. The main difference that was noticed between the results of the three different BOD tests was found to be a consequence of the mineral solution (dilution solution) used in conventional BOD tests. The paper mill samples did not contain a sufficient amount of nutrients. Hence, the results of the manometric respirometric test were much lower than results obtained by conventional tests. When the same mineral solution was used both in the respirometric test as well in conventional test, differences diminished remarkably and the results became similar. The manometric respirometric method also showed practically that shapes of the BOD curves were different for different wastewater types. We have also studied earlier the biodegradation of different oils in groundwater and standard

conditions described in OECD 301F, as well as in various soils using the manometric respirometric method [4–7]. This research still continues. In this study, we tested an automatic respirometric method for the determination of BOD in several stages of wastewater treatment at the activated sludge plant in Oulu, situated in Northern Finland, which treats over 16 million $m^3$ of wastewater per year. The aim was to compare the manometric respirometric test with conventional BOD tests. Additionally, we have included an online UV absorbance measurement as a comparison in the results. An additional objective was to estimate the seventh-day BOD value ($BOD_7$) after a short-term measuring period (1–3 days) by respirometric test. Predictability of the $BOD_7$ value will reduce the measurement time, improving, for example, the chemical adjustment of the sewage treatment process.

## 2. EXPERIMENTAL

Samples were collected from a wastewater treatment plant (Oulu Waterworks, Taskila WTP) during five days. The samples were collected separately from three different stages of the sewage treatment process: after preclarification, after aeration basin (biologically treated), and after final clarification (outflowing water).

A manometric respirometric test was carried out with the OxiTop Control system (WTW Weilheim, Germany). According to preliminary data of the operation laboratory of the plant, the $BOD_7$ of preclarified water was known to vary between 70–150 mg/L, whereas the other two samples varied between 5–10 mg/L. In respirometric measurements, the measurement range of 0–200 mg/L was chosen for preclarified water and the measurement range of 0–40 mg/L for the other two sample types. Sample volumes were thus 250 mL and 432 mL, respectively. All the respirometric measurements were carried out with undiluted samples, because there were sufficient nutrient salts and suitable microorganisms present in domestic wastewater. The bottles were sealed with a rubber sleeve containing a $CO_2$ absorber immediately after the bottles were filled with the sample and the nitrification inhibitor *n*-allylthiourea was added. The measuring heads were screwed onto the bottles and the samples were stabilized in the incubation cabinet ($20.0 \pm 0.2^\circ C$) for two hours before measurements began [8]. The theory of the measurement is described in more detail in our earlier studies [3–7]. The computer programs used in the evaluation of $BOD_7$ values after a short-term measurement were Excel and TBL Curve.

The used chemical method was *Determination of biochemical oxygen demand after n-days ($BOD_n$)*. Part 1; *Dilution and seeding method with allylthiourea addition* (SFS-EN 1899-1) [9]. The residual oxygen after seven days' incubation was determined according to the standards of *Determination of dissolved oxygen, iodometric method* (SFS-EN 25813) [10], and *electrochemical probe method* (SFS-EN 25814) [11]. The analyses with an oxygen sensor (WTW, Stirrox G, WP3-ST) were carried out at the operation laboratory of the wastewater plant, at the Finland's Environmental Administration in Helsinki, and at the University of Oulu, which also performed all iodometric analysis. Some measurements by the chemical methods used in this study were carried out with diluted samples with a dilution factor from 2 to 50. Nutrient solution was prepared using $KH_2PO_4$, $K_2HPO_4$, $NaHPO_4 \cdot 2H_2O$, $NH_4Cl, CaCl_2$, $MgSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ [9]. The pH values of the wastewater samples were measured with a Consort P600 pH meter.

A UV absorption meter (Endress-Hauser, Stamosens CSM 750/CSS 70) continuously measured the biologically treated wastewater. Measurement is based on the spectral absorption of organic substances in the UV range (the wavelength of measurement $l = 254$ nm). Measured spectral absorption coefficient [1/m] was set in correlation to $BOD_7$ value [mg/L]. The UV absorption measurement is direct measurement of wastewater and does not require chemical addition or sample preparation [12].

## 3. RESULTS AND DISCUSSION

### 3.1. Comparison of different methods

Table 1 lists the results measured by the respirometric method, as well as by the conventional methods and UV absorption meter. The UV absorption meter gave the absorption value ($BOD_7$ value) at every hour (24 measuring data per day). The $BOD_7$ values of UV measurements presented in Table 1 are the mean values of one day's continuous measurements.

According to Table 1, there were no considerable differences between the results of the three separate BOD tests: respirometric, iodometric, and oxygen sensor. This is in accordance with our earlier results which we discovered in our study of the wastewater of a pulp mill [3]. Relative standard deviations (RSD) between the three tests were between 1–35%. These deviations can in part be explained to be due to the heterogeneity of the samples. Considering the UV technique, composition of wastewater must remain similar, as varying compositions in the organic matrix will have an effect on results [12], as can be seen in Table 1.

### 3.2. Evaluation of the $BOD_7$ values

The precision of the respirometric test was determined by measuring the BOD values of the wastewater samples twice. Figure 1 shows the typical results of the duplication tests for the preclarified, biologically treated, and outflowing wastewaters.

The evaluation of the $BOD_7$ values was calculated with the Excel or TBL curve programs. In accordance with our earlier study [3], the result showed that the BOD values are mathematically regular in shape. The TBL curve program calculated dozens of different equations from which the most applicable were selected by substituting the time values to equations. Also, the earlier results were used as a suggestive [3]. The evaluation results are represented in Table 2. The BOD graphs formed in the respirometric measurements of biologically treated and outflowing wastewaters were quite linear in shape, whereas the curves of preclarified

Table 1: The $BOD_7$ results at 20°C determined by respirometric test, iodometric titration, oxygen sensor, and UV absorption test for wastewaters from Taskila's WTP, Oulu Waterworks.

| Sample | | Respirometric test [mg/L] | Iodometric test [mg/L] | Oxygen sensor [mg/L] | UV absorption[(a)] [mg/L] |
|---|---|---|---|---|---|
| *18.05.* | Preclarified | 65 | 56 | — | — |
| | Biol.treated | 4.5 | 4.8 | — | 5.7 |
| | Outflowing | 5.6 | 5.6 | 5.0 | — |
| *15.06.* | Preclarified | 106 | 108 | — | — |
| | Biol.treated | 4.0 | 6.7 | — | 4.9 |
| | Outflowing | 4.2 | 5.8 | 4.0 | — |
| *24.08.* | Biol.treated | 6.2 | 4.5 | 5.0 | 10.6 |
| | Outflowing | 7.0 | 6.0 | 8.0 | — |
| *07.09.* | Preclarified | 86 | 66 | — | — |
| | Biol.treated | 5.3 | 6.0 | 4.0 | 2.1 |
| | Outflowing | 6.0 | 7.3 | 6.0 | — |

[(a)] Results of the UV measurements (correlated to $BOD_7$ value) are the mean values of one-day measurement.

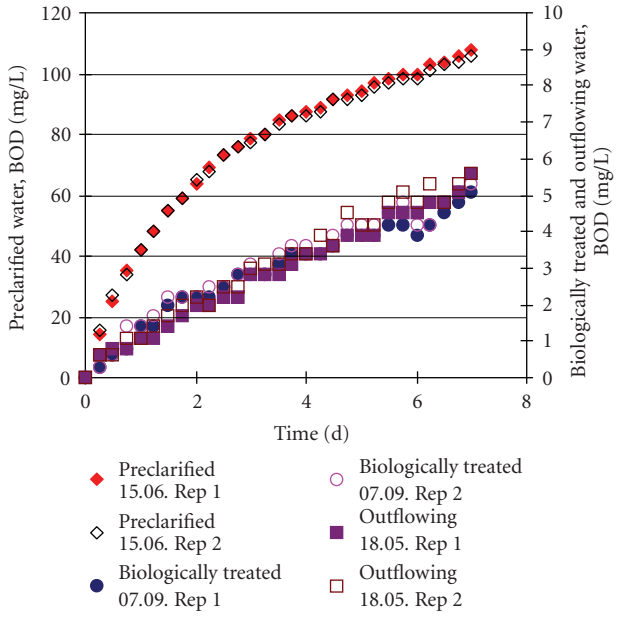


Figure 1: BOD results of duplication tests for pre-clarified, biologically treated and outflowing wastewaters from Oulu Waterworks, Taskila WTP at 20°C.

wastewaters were nonlinear (Figure 1). It was noticed that the BOD graph of the preclarified wastewater curved exactly like BOD curves of paper mill samples in our earlier research [3]. The curving of the BOD graphs could be due to a coagulation/flocculation chemical (polyaluminium chloride, PAC) used in the preclarification of both the treatment plants.

The estimation of $BOD_7$ value of wastewater from Oulu Waterworks sewage treatment plant worked well and the results show that there is an acceptable correlation between the estimated results and the analysed iodometric $BOD_7$ results. Furthermore, in our previous study concerning wastewaters of pulp and paper mills [3], we noticed that the shape of the BOD curve is individual for each wastewater type. Therefore, fitting and selecting the equation used in evaluation of BOD values is case specific. Eventually, the two best fitting equations for outflowing wastewater and biologically treated water were tested; equation number 2 was noticed to work better after three days' incubation. The average deviation for equation number 2 after two days' incubation was 27%; and after three days' incubation 10%, whereas for the linear equation, average deviations were 29% and 18%, respectively. In spite of that, the linear shape would be simpler to use in a wastewater treatment plant. Equation number 3 was found to work best for preclarified sewage. The average deviation was 13% after two days, and only 5% after three days' incubation.

As can be seen from Table 2, the $BOD_7$ values of preclarified wastewaters collected at different times ranging between 65–108 mg/L. It would be helpful to have an estimation of the $BOD_7$ value beforehand to get the BOD : N : P relationship and aeration to right levels. Those factors have a major influence in order to maintain a suitable microbial population, affecting, for example, BOD reduction, nitrification, precipitation, and flotation. The rapid respirometric test could be a useful tool for process control purposes.

## 4. CONCLUSION

The respirometric test was found to be suitable for the purpose of BOD measurements in domestic sewage plant; the precision of the test was acceptable. There were only minor deviations between $BOD_7$ values as determined by the different methods studied. The RSD between the respirometric test, iodometric method, and oxygen sensor were 1–35%. The estimation of seventh-day BOD value worked well. The results revealed that the $BOD_7$ value of the domestic wastewater investigated could be estimated from the respirometric data as early as after two days' incubation, for example, for process control purposes.

Table 2: Evaluation results of wastewater examined in this research (equation number 1: $y = ax + b$; equation number 2: $y = (a + bx + c\sqrt{x})$; equation number 3: $y = [(a + cx)/(1 + bx)]$).

| Sample | | Equation number | Evaluation of $BOD_7$ after 2 days' incubation [mg/L] | Evaluation of $BOD_7$ after 3 days' incubation [mg/L] | Evaluation of $BOD_7$ after 4 days' incubation [mg/L] | $BOD_7$ value [mg/L] |
|---|---|---|---|---|---|---|
| | Preclarified | 3 | 67 | 64 | 64 | 65 |
| | Biol.treated | 1 | 4.5 | 4.5 | 4.1 | 4.5 |
| *18.05.* | Biol.treated | 2 | 4.3 | 4.1 | 4.4 | 4.5 |
| | Outflowing | 1 | 6.2 | 5.8 | 5.7 | 5.6 |
| | Outflowing | 2 | 5.2 | 5.6 | 5.3 | 5.6 |
| | Preclarified | 3 | 98 | 106 | 104 | 108 |
| | Biol.treated | 1 | 3.7 | 4.1 | 4.0 | 4.0 |
| *15.06.* | Biol.treated | 2 | — | 3.3 | 3.4 | 4.0 |
| | Outflowing | 1 | 3.8 | 4.8 | 4.7 | 4.2 |
| | Outflowing | 2 | 2.2 | 4.4 | 4.6 | 4.2 |
| | Preclarified | 3 | 92 | 93 | 93 | 100 |
| | Biol.treated | 1 | 8.3 | 8.0 | 7.2 | 6.2 |
| *24.08.* | Biol.treated | 2 | 8.3 | 7.1 | 6.3 | 6.2 |
| | Outflowing | 1 | 9.7 | 9.2 | 8.8 | 7.0 |
| | Outflowing | 2 | 8.4 | 8.4 | 8.0 | 7.0 |
| | Preclarified | 3 | 113 | 94 | 88 | 86 |
| *07.09.* | Biol.treated | 2 | 7.2 | 6.0 | 5.6 | 5.3 |
| | Outflowing | 2 | 8.1 | 6.0 | 6.1 | 5.9 |

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