# TECHNICAL NOTE

# ESTIMATION OF BIOCHEMICAL OXYGEN DEMAND IN SLURRY AND EFFLUENTS USING ULTRA-VIOLET SPECTROPHOTOMETRY

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**Abstract**—The absorbance at 280 nm was determined for samples of dirty water, and pig and cow slurry effluents collected annually over a period of 3 years. Regression analysis showed an exponential relationship between absorbance and biochemical oxygen demand ($BOD_5$). Well fitted regressions of absorbance (280 nm) on $BOD_5$ were obtained for each year, especially for exponential regression analysis. Such regressions were then used to estimate $BOD_5$. Once a relationship is established between UV absorbance and BOD, UV absorbance measurements can be used to rapidly analyse large batches of samples, and also to improve the efficiency of the $BOD_5$ test by indicating dilution ranges. Copyright © 1996 Elsevier Science Ltd

## INTRODUCTION

Biochemical oxygen demand (BOD) is defined as the potential for removal of oxygen from water, by aerobic heterotrophic bacteria that utilise organic matter for the production of energy and for multiplication. BOD values of farm wastes and effluents are generally high but can vary markedly. For example, untreated domestic sewage has a $BOD_5$ of 300 mg $l^{-1}$ whilst milk has a $BOD_5$ of 120,000 mg $l^{-1}$. Values for slurry and silage effluent range from 10,000 to 80,000 mg $l^{-1}$ while those for dirty water range between 200 and 15,000 mg $l^{-1}$. BOD is widely used to detect and assess contamination of surface waters by organic wastes.

Methods for the determination of BOD include the use of a microbial sensor (Riedel *et al.*, 1990); potentiometric stripping analysis (Fayyad *et al.*, 1987); incubation in acidified N/80 permanganate for 4 h to give the permanganate value (Lowden, 1981); the Winkler titration method (Winkler, 1888) and the use of a scanning optical sensor based on the oxygen quenching of luminescence (Li *et al.*, 1994). The most commonly used standard method is $BOD_5$ where samples are incubated at 20°C for 5 days (DOE, Standing Committee of Analysts, 1989). The method is time consuming, needs prior estimation of BOD, and requires a 5-day period before results are available. Ultra-violet (UV) spectrophotometry has been used to determine dissolved organic matter in stream water (Grieve, 1985) and also to measure total organic carbon in waste water (Dobbs *et al.*, 1972),

as many pollutants in water and waste water strongly absorb UV radiation. This paper evaluates the potential use of the relationship between UV absorbance and BOD over a range of farm wastes.

Organic materials present in farm wastes include fats, carbohydrates, proteins and sometimes aromatic organic chemicals, such as phenols. Inorganic chemicals include chlorides, heavy metals and other toxic compounds. Compounds that contribute to the BOD of an effluent include carbonaceous organic matter, oxidizable nitrogen compounds and reduced inorganics, e.g. ferrous iron and sulphur compounds (Stafford *et al.*, 1980). Thus, the UV absorbance of an effluent may vary considerably according to its chemical composition. The ability of an organic compound to absorb UV radiation is dependant on its electronic structure (Silverstein *et al.*, 1974). The organic compounds present in an effluent each have a peak absorbance at a certain wavelength, termed $\lambda$max. For example, acetic acid has a $\lambda$max of 204 nm, whereas phenol has a $\lambda$max of 210 nm. Because effluents consist of many compounds in different proportions, $\lambda$max could vary according to the type of effluent and its pretreatment.

## MATERIALS AND METHODS

Samples of farm wastes were collected over a 3-year period to provide 82 dirty water samples in 1992, 107 dirty water samples in 1993 and 361 pig and cow slurry effluents in 1994. The dirty water comprised yard runoff, milking parlour washings, slurry and silage effluent. Initially, a

selection of samples were taken to determine the wavelength at which maximum absorbance occurred by taking measurements through the complete spectrum (190–900 nm) using a spectrophotometer (Pye Unicam SP8-100 UV). The maximum absorbance occurred at 280 nm for all samples and so absorbance at this wavelength was used in future work. Absorbance was measured using 10 mm silica spectrometer cuvettes. Samples were diluted where necessary.

BOD was determined using the BOD$_5$ method (DOE, Standing Committee of Analysts, 1989) by the National Rivers Authority in 1992 and 1993 and at North Wyke Research Station in 1994. Briefly, samples were diluted with synthetic river water seeded with sewage outflow. The dissolved oxygen content was measured before and after incubating in the dark for 5 days at 20°C. The combined data for the 3 years and the data for each separate year were analysed by regression analyses (Genstat 5, 1993) using exponential ($y = a + br^x$) and linear equations ($y = bx + a$).

## RESULTS AND DISCUSSION

Data for the 3 years combined gave $R^2$ values of 0.74 and 0.76 for the linear and exponential regression of UV absorbance with BOD, respectively. The regressions for data collected in 1992 and 1994 were similar but those for 1993 were less steep (Fig. 1). Values of $R^2$ for individual years were slightly greater for the exponential regression (Table 1) compared with the linear regression, but both linear and exponential formulae showed a good within year fit. Mean square prediction error analysis was conducted on the data (Theil, 1966) to examine whether the regression formula derived from a particular year's data would be accurate in predicting BODs of effluents collected in other years. Analysis indicated unacceptably poor accuracy in predicting across years.

Generally the biochemical nature of the BOD$_5$ test makes it difficult to obtain reproducible results (Lowden, 1981). Results depend on type of bacteria present, time taken for them to acclimatise and presence of toxic materials. The year to year variability, where 1993 BOD values were lower than expected, could be explained by differences in silage effluent management. In 1993 the silage effluent entering the dirty water system collected in a large tank that overflowed through a pipe leading to the dirty water tank. But in the previous year silage effluent was pumped directly to the dirty water system. The presence of toxic substances such as toxic metals and aromatic compounds, e.g. phenol (present in slurries), and toxic organics such as formaldehydes or cyanides can inhibit the activity of the microbial seed, making the BOD test unreliable (Stafford et al., 1980). If chlorines or chloramines are present (from chemicals used for cleaning milking parlours), chlorine may combine with organic compounds to produce substances that inhibit biochemical oxidation or can be bacteriocidal. In this situation the BOD will be lower than indicated by methods of organic matter determination (DOE, Standing Committee of Analysts, 1989). The presence of hydrogen sulphide and or sulphur dioxide can

consume oxygen. Hydrogen sulphide can interfere in instrumental oxygen measurements causing reductions of dissolved oxygen values (DOE, Standing
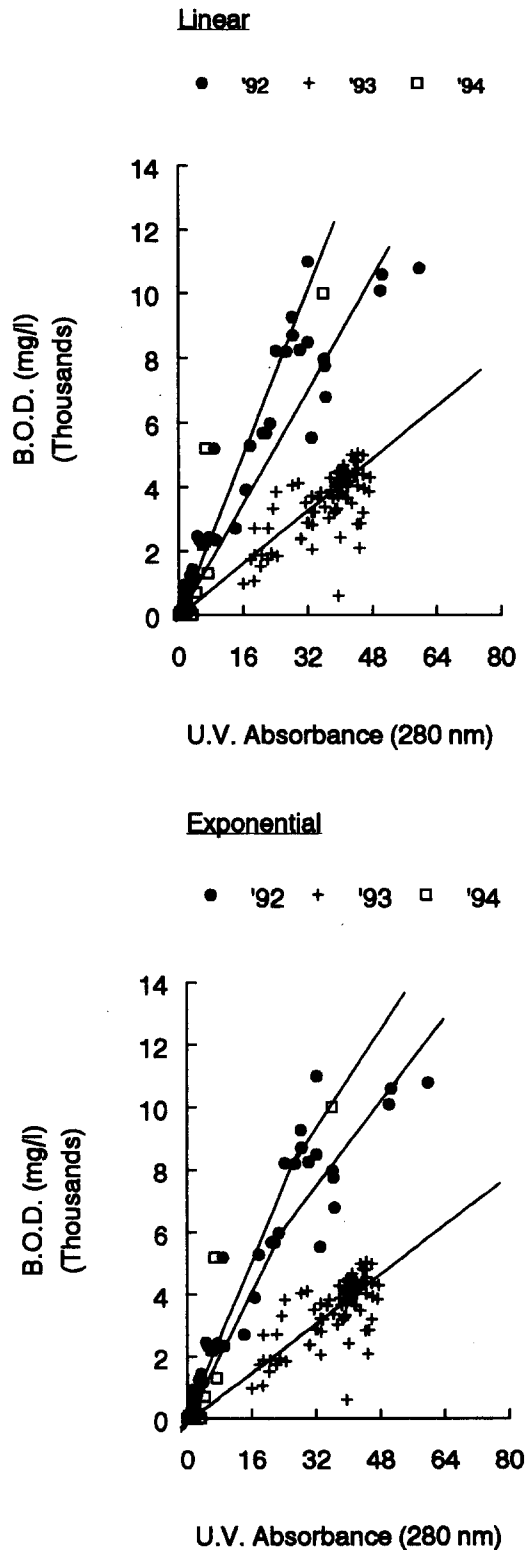


Fig. 1. Regression of UV absorbance on BOD$_5$ using linear and exponential equations.

Table 1. Parameter estimates from regression analysis, $y$ = BOD, $x$ = UV absorbance

| Exponential | Formula $y = a + br^x$ | | |
|---|---|---|---|
| | Estimates | s.e. | $R^2$ |
| 1992 | | | |
| $r$ | 0.9682 | 0.0050 | 0.95 |
| $b$ | −12,647 | 1098 | |
| $a$ | 12,590 | 1126 | |
| 1993 | | | |
| $r$ | 0.9867 | 0.0080 | 0.86 |
| $b$ | −9520 | 4182 | |
| $a$ | 9361 | 4242 | |
| 1994 | | | |
| $r$ | 0.9569 | 0.0033 | 0.85 |
| $b$ | −9684 | 334 | |
| $a$ | 9443 | 339 | |

| Linear | Formula $y = bx + a$ | | |
|---|---|---|---|
| | Estimates | s.e. | $R^2$ |
| 1992 | | | |
| $a$ | 275 | 124 | 0.92 |
| $b$ | 226.63 | 7.58 | |
| 1993 | | | |
| $a$ | −34 | 128 | 0.85 |
| $b$ | 95.81 | 3.87 | |
| 1994 | | | |
| $a$ | −40 | 25.7 | 0.69 |
| $b$ | 130.07 | 4.97 | |

s.e. = standard error.

Committee of Analysts, 1989). It is probable that the low BOD values in 1993 were caused by the reasons previously described in differences in silage effluent management. However, variability in the relative concentrations of the major UV absorbing substances, due to both source and storage, could also be contributary.

It is therefore necessary to produce regressions of UV absorbance with BOD for different materials. This study indicated that this method was suitable for BODs ranging between 100–10,000 mg $l^{-1}$ with poor sensitivity for values of less than 100 mg $l^{-1}$. It is possible that inaccuracies below 100 mg $l^{-1}$ were due to interference of UV absorbance by the presence of other materials, such as soil particles. It would be advantageous to be able to determine BODs of less than 100 mg $l^{-1}$ but further experimentation will be required in order to examine whether this is feasible. Estimation of high BODs (greater than 15,000 mg $l^{-1}$) was not studied in this experiment.

UV absorbance can also be used to improve the efficiency of the $BOD_5$ test by indicating dilution ranges because samples being analysed for BOD often require dilution to be within the range measureable by a dissolved oxygen meter. An estimation of $BOD_5$ would enable dilutions to be made within the correct range. This is important as ideally $BOD_5$ analysis should be conducted within 48 h of sampling. If incorrect dilutions are made, only to be discovered after a 5-day incubation, results may be lost. UV absorbance could also be used in the development of field equipment to provide a rapid, easy to use test to predict BOD for field officers and farmers to indicate the degree of pollution on the spot.

In order to construct a portable field instrument for estimating BOD by UV absorbance, a radiation source, a monochromator, a photometer, sample area and detector area are required (Silverstein et al., 1974). This would be feasible with a low energy, broad band width UV source and simple photo-diode amplifier.

## CONCLUSIONS

A good exponential relationship was achieved between absorbance and $BOD_5$ for each year, showing that this method could be used to predict $BOD_5$. Lower than expected BODs can occur if the samples contain certain chemicals, such as toxic metals. Improving the technique to estimate BODs of less than 100 mg $l^{-1}$ could be valuable because of the U.K. national threshold value of 20 mg $l^{-1}$. Finally, it may be feasible to develop a portable meter to measure UV absorbance in order to provide an indication of BOD in the field.

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