Oxygen Mass-Transfer Coefficients for Different Sample Containers Used in the Headspace Biochemical Oxygen Demand Test

Bruce E. Logan, David Kohler

ABSTRACT: To accurately measure the oxygen demand of a wastewater sample in a headspace biochemical oxygen demand (HBOD) or other respirometric test, the rate of oxygen transfer to the aqueous phase must be greater than the oxygen exertion rate by the sample. Oxygen mass-transfer coefficients ($K_{aw}a$) measured for 28-, 55-, and 160-mL, partially full (18 to 89%) containers placed on their sides on a shaker table and mixed at 200 r/min averaged 8.0 h^{-1} (range 5.4 to 9.9 h^{-1}). For this mass-transfer coefficient, HBOD values as great as 1340 mg/L·d are possible at the start of an HBOD test, although the maximum daily HBOD declines to 192 mg/L·d at the end of the test because of oxygen depletion in the sample headspace. Mass-transfer coefficients for shaken samples decreased only at low shaking speeds (< 50 r/min). Oxygen mass-transfer coefficients for shaken samples were always larger than those (average of 1.8 h^{-1}) measured for samples in a 250-mL bottle mixed with a stir bar on a stir plate. These mass-transfer coefficients indicate that the oxygen demand of typical full-strength municipal wastewaters can be measured in HBOD tests without oxygen transfer limiting the reaction rate. *Water Environ. Res.*, **73,** 58 (2001).

KEYWORDS: headspace biochemical oxygen demand test, oxygen mass-transfer coefficient, oxygen uptake.

Introduction

For many years, respirometric tests have been used to determine the concentration of biodegradable organic matter in wastewater and the rate of oxygen use by batch cultures (Arthur, 1984; Caldwell and Langlier, 1948; Grady et al., 1999; and Rozich and Gaudy, 1992). Respirometric tests differ from conventional biochemical oxygen demand (BOD) tests because both gas and liquid phases are present in a respirometer sample, whereas in a BOD test bottle there is only a liquid phase. The BOD reaction is limited by the initial dissolved oxygen concentration present in the sample but, in the respirometric test, oxygen is continually transferred from the gas to the liquid phase. Oxygen use in the respirometer bottle is monitored either by measuring oxygen depletion in the headspace or by measuring the mass of oxygen that must be replenished in the headspace to maintain constant conditions. In both cases, the respirometer will only accurately model oxygen use if the oxygen-transfer rate to the liquid is faster than the oxygen use rate by the sample (Li and Zhang, 1996).

In most respirometric tests, the sample is stirred while the headspace is continually monitored to provide oxygen use rate data. Although continuous monitoring can provide extensive data on oxygen use rates, it also requires that each sample bottle contain its own monitoring system. Such monitoring can be expensive when a large number of samples must be analyzed. An alternative to continuous respirometric BOD (RBOD) tests is the headspace BOD (HBOD) test. In the HBOD test, samples are sealed in a test tube or other gastight container and placed on a shaker table to provide oxygen transfer during sample incubation (Logan and Patnaik, 1997, and Logan and Wagenseller, 1993). The HBOD tubes can then be sampled at any time by analyzing the oxygen in the headspace using a gas chromatograph (GC); therefore, only one monitoring device is necessary for all samples (Logan and Patnaik, 1997). Although the BOD and respirometric tests are fundamentally quite different, the 5-day BOD (BOD_5) test for domestic wastewater is typically exerted in an RBOD or HBOD test in only 2 to 3 days, providing a much faster measurement of comparable oxygen demand (Logan and Patnaik, 1997, and Young and Baumann, 1976).

For the HBOD test to work as well as other respirometric tests, oxygen transfer during incubation on the shaker table must not limit oxygen utilization rates. However, the rate of oxygen transfer in HBOD tubes and other gastight containers is not known. To measure oxygen-transfer rates in containers suitable for HBOD analysis, a standardized protocol for measuring oxygen transfer in a respirometric test was developed. Using this procedure, factors that could potentially affect oxygen-transfer rates were examined, such as shaking speed and liquid-to-gas volumetric ratios in the tubes, and mass-transfer coefficients were measured for several different containers.

Methods

Sample Containers. In previous HBOD tests, oxygen demand was measured using 28-mL anaerobic test tubes (18 mm outside diameter × 150 mm long; Bellco Glass, Inc., Vineland, New Jersey) (Logan and Patnaik, 1997, and Logan and Wagenseller, 1993). These tubes, referred to here as HBOD tubes, were also used in this study. Other bottles tested included 55-mL tubes (25 mm × 152 mm, Kimble, Vineland, New Jersey), 160-mL serum vials (35 mm × 170 mm, Kimble), and 250-mL bottles (58 mm × 150 mm, Wheaton Scientific, Millville, New Jersey). The 28- and 160-mL containers were sealed with Teflon septa (West Company, Lititz, Pennsylvania) and aluminum crimp tops, the 250-mL bottles were sealed with Teflon septa and screw caps (Wheaton Scientific), and the 55-mL tubes were sealed with Mininert tops (Alltech, Deerfield, Illinois).

Determination of Mass-Transfer Coefficient. The overall rate of oxygen transfer from gas phase to liquid phase is limited by the

liquid-phase resistance. Therefore, the rate of oxygen transfer can be expressed in terms of an overall mass-transfer coefficient between the air and water phases, K_{aw}, as

$$\frac{dc_{Oa}}{dt} = -K_{aw}a(c_{Oa} - c_{Oa,i}) \quad (1)$$

Where

c_{Oa} = concentration of oxygen in the bulk air,
$c_{Oa,i}$ = oxygen concentration at the air–water interface, and
a = total interfacial area per volume.

Because the area depends on the mixing rate and is difficult to determine independently, only the product $K_{aw}a$ was measured here. When the dissolved oxygen concentration in the water is maintained at zero, $c_{Oa,i} \approx 0$ and equation 1 simplifies to

$$\frac{dc_{Oa}}{dt} = -K_{aw}ac_{Oa} \quad (2)$$

Separating variables and integrating from an initial concentration in the air of C_0 to a final air concentration C at any time t gives

$$\frac{C}{C_0} = \exp(-K_{aw}at) \quad (3)$$

Oxygen in the headspace was measured using 100-μL injections (Alltech gastight syringe with Mininert adapter) and a gas chromatograph (GC, 8610B, SRI Instruments, Torrance, California) equipped with a thermal conductivity detector and a molecular sieve column with helium as the carrier gas. Oven temperatures ranged from 40 to 60 °C, resulting in analysis times of 2 to 3 minutes. The GC was calibrated using laboratory air (20.9% oxygen). The ratio C/C_0 can be expressed directly as the ratio of the area of an oxygen peak at any time, A, to the initial oxygen peak, A_0. The initial oxygen concentration was assumed to be the same as that measured for laboratory air. The mass-transfer coefficient was calculated by linearizing equation 3 by a natural log–log transformation and by using oxygen peak areas directly as

$$\ln\frac{A}{A_0} = -(K_{aw}a)t \quad (4)$$

Therefore, $K_{aw}a$ is calculated as the negative of the slope in a plot of ln (A/A_0) versus time.

Oxygen was removed from water containing an added cobalt catalyst (1.5 mg/L cobaltous chloride) using sodium sulfite at a concentration sufficient to scavenge all of the oxygen in the headspace and maintain a concentration greater than 0.05 M sodium sulfite (Li and Zhang, 1996). From a mass balance of oxygen in the headspace, and neglecting the small concentration of dissolved oxygen initially in the tube, the mass of sodium sulfite added to each sample container to achieve less than 0.05 M sodium sulfite was calculated as

$$Na_2SO_3\,[mg] = \frac{0.03pV_a}{T} + 6.3V_L \quad (5)$$

Where

p = partial pressure of oxygen in air, Pa;
T = temperature, K;
V_a = volume of air, mL; and
V_L = volume of liquid, mL.

There is disagreement in the literature on the concentration of sulfite necessary to make oxygen transfer independent of the sulfite concentrations, with values of 0.05 M (Li and Zhang, 1996), 0.2 M (Phillips and Johnson, 1959), and 0.7 to 2 M (Yoshida et al., 1960) reported. Therefore, some experiments were run at greater than 0.2 M sodium sulfite, so that the coefficient of 6.3 in equation 5 is replaced by 25.2. Note that these sodium sulfite concentrations are chosen for final oxygen concentrations after all of the oxygen in the air has been consumed so that the initial concentration of sodium sufite is greater at the start of the experiment.

Experimental Procedure. Sodium sulfite was added to dry sample containers according to equation 5 and then the water containing the cobalt catalyst was added to the tubes. Samples were immediately sampled or transferred to a shaker table or stir plate. Tubes and serum vials (28, 55, and 160 mL) were placed on their sides in a box mounted on a shaker table (Lab Line Model 4626, Melrose Park, Illinois) set at 200 r/min except as otherwise noted. Respirometer bottles (250 mL) containing a Teflon-coated stir bar (9.2 mm diameter and 38 mm long) were placed on a Challenge respirometer plate (Fayetteville, Arkansas) set at a dial reading of 3 or 5, which was estimated by the manufacturer to be 450 to 500 r/min and 750 to 800 r/min, respectively. Each mass-transfer coefficient was based on three separate experiments. Experimental variables included container type, liquid volume, and agitation or stirring speed. For each experiment, tubes or bottles that were shaken were prepared in triplicate and each tube or bottle was analyzed only once (i.e., the sample was sacrificed) by GC analysis. Oxygen reaction rates were too rapid, and headspace volumes too small, in HBOD tubes and 160-mL bottles to permit oxygen concentrations to be based on duplicate injections. For larger bottles (250 mL) mixed by a stir bar, the same bottle was used and sampled several times.

Results

Oxygen depletion was very rapid in the test tubes and serum vials mixed on their sides on the shaker table (Figure 1). Because of the time necessary to analyze a GC sample, measurement of oxygen in the headspace of the tubes and serum vials required a minimum of 2 minutes. There was substantial oxygen use before the samples were placed on the shaker table, as demonstrated by a nonlinear oxygen depletion (expressed in terms of natural logarithm) for the first sample time compared with subsequent measurements. Therefore, the first interval was not used in mass-transfer coefficient calculations; only the intervals following the first measurement were used to calculate $K_{aw}a$ values as shown in Figure 1. Oxygen use rates were slower in the stirred 250-mL bottles than in the shaken tubes and smaller bottles, resulting in sampling times spanning 15 minutes for the bottles versus only 5 minutes for the tubes (Figure 1).

Mass-transfer coefficients measured for the 28-, 55-, and 160-mL containers shaken on their sides at 200 r/min ranged from 5.4 to 9.9 h^{-1}, with an average of 8.0 ± 1.5 h^{-1} (Figure 2). Containers were filled with different volumes of liquid, resulting in a range of liquid volumes of 18 to 89%. There was no apparent relationship between the mass-transfer coefficient and the liquid volume.

When samples were kept upright and mixed, overall mass-transfer coefficients were appreciably lower likely because of the smaller surface area for oxygen transfer. The $K_{aw}a$ measured for

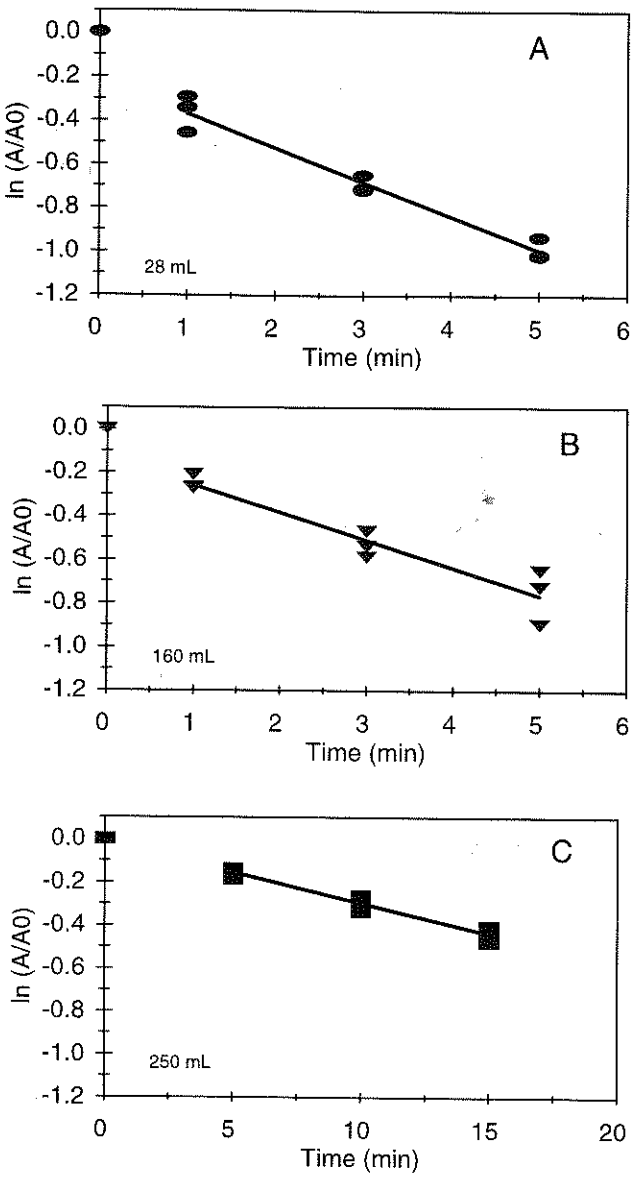

Figure 1—Oxygen depletion data (three separate runs; some points overlap) of (a) 28-mL tubes filled with 10 mL of water; (b) 160-mL bottles filled with 50 mL of water, both placed on their side on a shaker table at 200 r/min; and (c) 250-mL bottles filled with 150 mL of water and mixed with a magnetic stir bar (~750 to 800 r/min). The initial oxygen reading (A_0) is based on multiple measurements of laboratory air (n = 6; error bar is smaller than symbol size); all other values are single measurements. The sodium sulfite concentration was 0.05 M in the 160-mL bottles and 0.2 M in the other tests.

upright samples in the 160-mL tube was 3.9 ± 0.3 h^{-1}, or approximately one-half that obtained when samples were mixed on their sides.

Effect of Shaking Speed on Mass Transfer. The primary resistance to oxygen transfer from air to water is the liquid phase; therefore, if the liquid is not mixed, the oxygen-transfer rate should be slower (Logan, 1999). The speed of the mixing table had a measurable effect on the mass-transfer coefficient, but only at

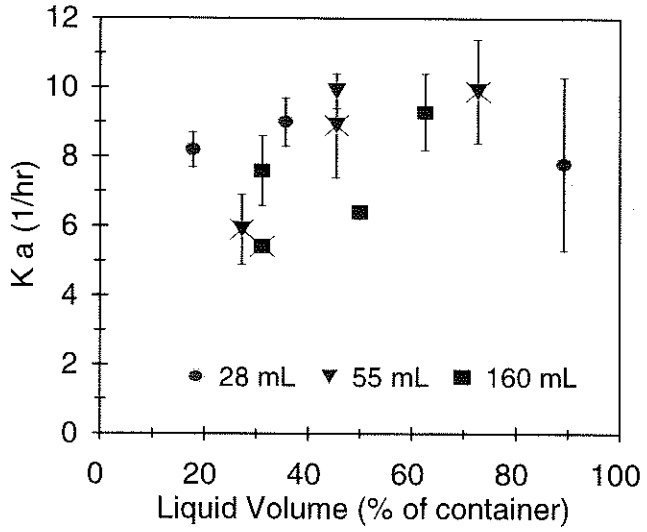

Figure 2—Mass-transfer coefficients measured in 28- and 55-mL test tubes and a 160-mL serum vial as a function of liquid volume (samples mixed on their side at 200 r/min). All points contain error bars indicating 1 standard deviation for triplicate measurements. Symbols with an additional × indicate tests with 0.05 M sodium sulfite; all others were with 0.02 M sodium sulfite.

mixing speeds (Figure 3). When the samples were mixed at 25 r/min, the $K_{aw}a$ value was 6.1 h^{-1}, or 75% of that measured at 100 r/min and higher mixing speeds.

Oxygen mass-transfer coefficients for the tubes and serum vials placed on their sides and not mixed were 1.7 ± 0.3 h^{-1} for 28-mL tubes, 0.9 ± 0.1 h^{-1} for 55-mL tubes, and 0.16 ± 0.06 h^{-1} for 160-mL vials. These values are lower by 1 order of magnitude or more than the average mass-transfer coefficient of 8.0 h^{-1} obtained when these containers were mixed at 200 r/min.

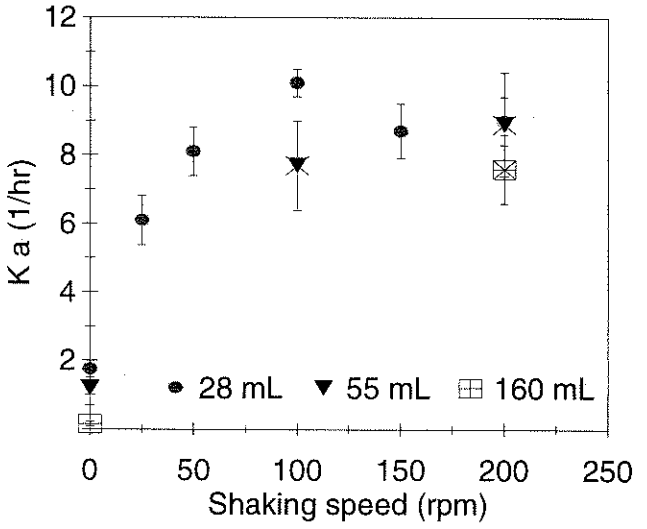

Figure 3—Mass-transfer coefficients measured in 28- and 55-mL test tubes and a 160-mL serum vial as a function of mixing speed (all samples on their sides). Notation is as in Figure 2.

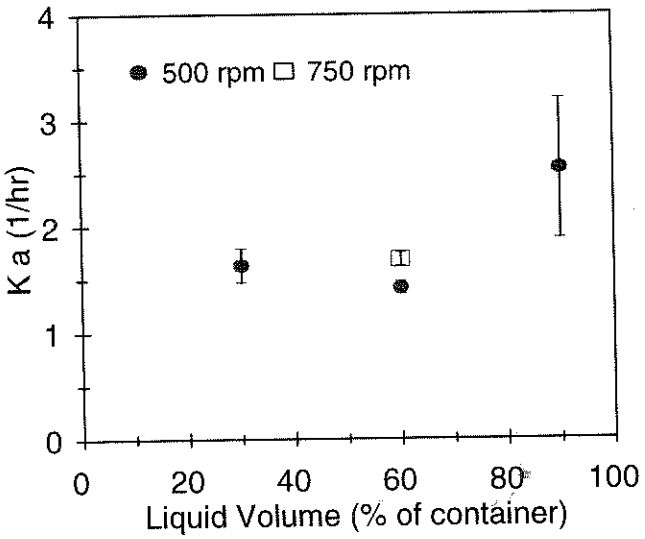

Figure 4—Mass-transfer coefficients measured in 250-mL bottles as a function of volume and stirring speed. Notation is as in Figure 2.

Mass-Transfer Coefficients in Stirred Samples. To compare the effects of sample mixing and shaking, a few oxygen mass-transfer coefficients were measured in 250-mL bottles typically used in respirometer tests (Figure 4). Mixing speeds were all relatively rapid in these bottles and, although extensive tests of the effect of mixing speed were not conducted, the average mass-transfer coefficient for all four experiments was 1.8 h^{-1}, or a value approximately one-fifth of that measured for the samples shaken at 200 r/min.

Discussion

Mixing samples in sealed tubes and serum vials on a shaker table on their sides is an effective method for achieving the high rates of oxygen transfer necessary in respirometric tests. Test tubes and serum vials mixed on their sides on a shaker table produced an average oxygen mass-transfer coefficient of 8.0 h^{-1}, or a value approximately 5 times larger than that obtained for samples in a 250-mL bottle mixed with a magnetic stir bar. Mixing sample containers upright on a shaker table reduced oxygen transfer but resulted in acceptable values that compared favorably to those measured here and in another study. In stirred respirometer tests using 500-mL bottles, Li and Zhang (1996) determined $K_{aw}a$ to be 1.8 h^{-1}, which is the same average value measured for stirred samples here.

Because the rate of oxygen transfer to the tubes is relatively higher than that typical of stirred respirometer systems, shaken HBOD tubes can be used for samples with much greater oxygen use rates than stirred reactors. For example, Li and Zhang (1996) recommended, for municipal wastewater, a rate criterion of less than 9613 (mg volatile suspended solids [VSS]/L)/(mg BOD/L) to avoid oxygen-transfer limitations in a respirometer. Using this criterion and the mass-transfer coefficient for the stirred respirometer in Li and Zhang's study ($K_{aw}a$ = 1.8 h^{-1}), a stirred vessel test should have a biomass concentration of less than 32 mg VSS/L for a wastewater BOD of 300 mg/L. For a shaken HBOD tube with a $K_{aw}a$ of 8.0 h^{-1}, this criterion translates to a greater allowable biomass concentration of less than 142 mg VSS/L. However, this analysis assumes that the partial pressure of oxygen in the atmosphere remains constant during the test.

An alternative approach to determining the useful range of the HBOD test is to compare oxygen-transfer and oxygen use rates on a daily basis. The daily HBOD exertion rate in a shaken HBOD tube should be less than the rate of oxygen transfer, or $B < 1$, where B is defined as

$$B = \frac{\text{HBOD}}{K_{aw}a(c_{ow,eq} - c_{ow})} \tag{6}$$

Where

$c_{o,w,eq}$ = oxygen concentration in the water in equilibrium with the gas phase, mg/L, and
$c_{o,w}$ = bulk oxygen concentration in the water, mg/L.

With $K_{aw}a$ = 8.0 h^{-1}, this relationship implies that the maximum daily HBOD exerted in a tube can be estimated as

$$\text{HBOD}\left[\frac{\text{mg}}{\text{L}\cdot\text{d}}\right] < 192(c_{ow,eq} - c_{ow})\left[\frac{\text{mg}}{\text{L}}\right] \tag{7}$$

It is recommended in a BOD test (APHA et al., 1995) that the bulk dissolved oxygen concentration be maintained at a concentration greater than 1 mg/L to avoid limiting the rate of reaction. In the HBOD test, it was recommended, for the same reason, that data only be used where the headspace oxygen concentration was greater than that necessary to produce a concentration of 2 mg/L dissolved oxygen (Logan and Patnaik, 1997). Thus, using equation 7 and allowing for a bulk c_{ow} of 2 mg/L dissolved oxygen and a maximum $c_{ow,eq}$ of 9.0 mg/L dissolved oxygen, the HBOD used in the first day of a test should be less than 1340 mg/L. By the end of the test, when oxygen has been consumed in the tube and the maximum possible $c_{ow,eq}$ is 3 mg/L dissolved oxygen and the bulk c_{ow} is 2 mg/L dissolved oxygen, the daily HBOD should be less than 192 mg/L. This rate estimated for the end of the test is conservative because a bulk dissolved oxygen concentration of 2 mg/L is much larger than that expected to limit oxygen use rate (< 1 mg/L) in a standard BOD test (APHA et al., 1995). These values are all well within the range of BODs expected for municipal wastewater but could require the dilution of some higher strength industrial wastewaters.

Conclusions

It is found that the rate of oxygen transfer to shaken tubes and serum vials is large enough to avoid oxygen-transfer limitations to wastewater samples analyzed and that mass-transfer coefficients are greater than those typical of stirred respirometers. It is recommended, however, that mass-transfer coefficients be determined on a case-by-case basis for specific laboratory shakers and bottles so that the useful range of HBOD at a site can be determined.

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