DISCUSSION

Of: **A gas chromatographic-based headspace biochemical oxygen demand test.** B.E. Logan, R. Patnaik, **69,** 206 (1997).

Reza Iranpour, Y.J. Shao, A. Magallanes, K. Flaig

The authors are to be commended for their efforts to develop a biochemical oxygen demand (BOD) test that overcomes the deficiencies of the standard 5-day BOD (BOD_5) test. We hope that the following comments are viewed as constructive criticism and that they will continue their efforts to find ways to improve on the present BOD_5 test.

The authors begin this paper by explaining that, like the Logan and Wagenseller (1993) study of testing BOD by fermentation in a sealed container in which the headspace acts as an oxygen reservoir, this research was inspired by the deficiencies of the standard BOD_5 test. The discussions of these deficiencies in both papers may be condensed into the following list:

1. It is too slow for a timely response to any abnormal condition;
2. It requires a large amount of laboratory personnel time;
3. It requires a large amount of incubator space;
4. The many dilutions increase the risk of error; and
5. The whole process is not a close simulation of fermentation in a wastewater treatment system.

Because they have discussed these deficiencies so clearly, it seems fair to consider how well these criteria would be satisfied by a 3-day gas chromatographic HBOD (GC-$HBOD_3$) test, as this paper recommends. Their description implies that the test satisfies criteria 2, 3, and 4 well for it requires no dilution, hence requires little incubator space. If laboratory space is a concern, we presume that the bulk of the GC is acceptable. Moreover, little technician time is needed during the sample preparation and measurement phases. None is needed while the vials are incubated on a shaker table.

We suggest that the authors might compare the costs and labor requirements of measuring oxygen concentrations with the GC to those using other dry oxygen detectors, such as the fuel cell detector provided by Columbus Instruments (1994). This device claims high accuracy and appears to be simpler to operate than the GC. It requires no supply of carrier gas such as helium used by the authors, and a direct reading is obtained instead of needing to integrate the area under the peak produced by the thermal conductivity detector. This device may also have a lower capital cost. Moreover, the same manufacturer also supplies infrared photometers capable of detecting carbon dioxide and several other gases. Comparing oxygen consumption and carbon dioxide production allows a respiratory quotient of these two quantities to be determined for a sample. This may provide a useful alternative to using a GC for the $HBOD_3$ test.

The authors were wise to verify that GC-$HBOD_3$ values are relatively stable despite substantial variations of the ratio between headspace and sample volume in the tubes, as shown in their Figure 4. Likewise, unresolved questions about the methods used in the Logan and Wagenseller (1993) study are answered by the portions of this paper, for example Figure 8, in which discrepancies in the 1993 calibration results are explained. It is reassuring that the low values from the diluted samples are explained by reduction of the amount of biomass available to metabolize the suspended nutrients.

However, it is not clear that the incubation conditions of the GC-$HBOD_3$ test are a realistic simulation of conditions in a treatment plant because, although there is no dilution, the GC-$HBOD_3$ test is like the BOD_5 test in taking samples of wastewater and allowing the indigenous microbial population to ferment it for a period of several days. This is different from using additional biomass and allowing fermentation for a few hours, as is done by an activated-sludge system. If one were interested in simulating a wastewater treatment process more closely, one would use a device such as the Anatel (1996) BioMonitor, which uses activated sludge to obtain BOD measurements in a few minutes.

As this last observation indicates, instruments are already on the market that provide BOD_5 measurements more rapidly than the GC-$HBOD_3$ test. Not only the Anatel BioMonitor, but the STIP BIOX-1010 of Cosa Instrument (1994), the Nissin Electric BOD-2000 series of Central Kagaku Corporation (1994), and the Lange ARAS SensorBOD instruments (Riedel, 1985) estimate wastewater BOD in periods ranging from a few minutes to nearly an hour, that is, a few hundred to a few thousand times faster than BOD_5 or GC-$HBOD_3$. Thus, replacing the BOD_5 test with a GC-$HBOD_3$ test does not compete with the speed of these instruments. Moreover, a 3-day test still does not provide a fast enough result to be used for process control; the sections at the end of the paper about savings lost on fines would be more appropriate for one of the fast instruments, discussed above. Under conditions in which the 3-day measurement time is acceptable, if the GC-HBOD test were preferred, it would have to be because of cost or accuracy.

However, the treatment in this paper of the accuracy of the GC-$HBOD_3$ test seems insufficient. Figure 2 suggests that the principal reason for recommending a GC-$HBOD_3$ test is that the authors observed occasions when their GC-$HBOD_3$ protocol produced oxygen demand results after 3 days that closely matched the BOD_5 values for other aliquots of the same sample. If they are serious in proposing the GC-$HBOD_3$ test as a replacement for the BOD_5 test they need to provide more information to show that the GC-BOD_5 test produces reliable results. Because the BOD_5 test is well established, there is a natural tendency for wastewater researchers to consider another BOD test to be reliable if it correlates well with BOD_5, and if it does not, then extensive work would be needed to show that it is right and BOD_5 is wrong. Tests should be conducted with laboratory calibration solutions over a range of concentrations, not just at 300 mg/L, and using other substrates such as acetic acid as well as glucose and glutamic acid, as was done by Karube *et al.* (1977) for the yeast biosensor in the BOD-2000. Also, many samples of natural wastewater should be tested so that a scatter plot of GC-$HBOD_3$ versus BOD_5 can be presented. A regression calculation with a correlation coefficient between BOD_5 and GC-$HBOD_3$ could then be performed to show the reliability, as was done by Iranpour *et al.* (1997a and b) for the BOD-2000.

It is well known that BOD_5 measurements have an uncertainty of approximately 30%, and the authors' other criticisms of its lack of similarity to wastewater treatment are valid. However, because it has been established for many years, there is now a vast body of experience with comparing it to the results of wastewater treatment, and with the aid of this experience, BOD_5 results have been found to be valuable and reliable.

If one takes a large enough perspective, one can see that the BOD of any wastewater is not a sharply defined concept, for there are many nutrients that are metabolized at varying rates, and any test that operates over at most a few days is somewhat arbitrary. This range of metabolizability is acknowledged in treatment plants that use secondary activated-sludge treatment that lasts a few hours and also sludge digestion lasting many days.

Table 1 in the paper shows the range of BODs that can be obtained with the 28-mL bottles used by the authors. With a large liquid volume and a small headspace, small BOD values can be observed. With a large headspace and a small liquid volume a larger BOD value can be determined. Overall, a range of BODs covering nearly two orders of magnitude can be observed, from 7 to 500. If larger bottles were used, it probably would be possible to cover a wider range of BOD values, especially at the high end, to determine values reached when a treatment plant is subject to shock loadings.

The discussion of cost is another good feature of this paper and is another improvement over Logan and Wagenseller (1993). However, there are some additional cost issues that eventually should be addressed in any effort to replace BOD_5. For example, faster BOD instruments discussed above are more expensive than the GC because they cost more than $20 000.00 (U.S.). However, these instruments can also be used for process control in a way that is not possible for a 3-day test.

Because they make a larger number of measurements than the GC, the cost per measurement is relatively low. Furthermore, when a device is fast enough to be used for process control, the financial picture changes because it now can include not only the direct costs of using the instrument and amortizing its purchase price but also possible savings of fines from regulatory agencies and costs of process upsets that are prevented by plant adjustments made possible by early detection of BOD variations.

We believe the ultimate goal of research of BOD measurement methods should be the development of durable and reliable on-line BOD monitoring instruments for process control and maintaining a healthy microecology in the treatment plant. If the work in this paper were developed until it could provide a headspace oxygen consumption test that worked in a few minutes or hours and was well correlated with other measures of treatability, this would be a viable alternative to the fast instruments that are presently available.

Acknowledgments

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Closure

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Iranpour and Shao raise several interesting topics in their comments, including alternate oxygen sensors for the HBOD test, the utility of on-line BOD systems, and the need for more data on the GC-HBOD test. There are several alternative techniques to the GC to measure oxygen in gases, and Iranpour and Shao suggest that dry detectors, such as the fuel cell detector provided by Columbus Instruments, might be more cost effective than a GC. This fuel cell detector currently costs approximately $7 500.00 (U.S.), which is more than the cost of GC used in our tests. More important, the use of this fuel cell detector currently requires gas flows (50 to 200 mL/min) that make its use impractical for measuring oxygen in small headspace volumes in the 28-mL tubes currently used in the HBOD test. Other detectors that Columbus Instruments sells cost slightly less for just oxygen (approximately $6 500.00), but they cost more if additional gases are added (approximately $3 000.00 more). Their complete respirometric system can cost $50 000.00 to $60 000.00 to continuously monitor approximately 20 chambers. If there are more cost-effective methods for measuring oxygen in the HBOD tubes than the GC in our paper, we would certainly be interested in learning more about them.

It is pointed out that on-line instruments such as the Anatel BioMonitor, the STIP BIOX-1010, and others can provide measurements of oxygen demand for a wastewater stream over a period of minutes to 1 hour. These instruments are used for different purposes than batch tests such as the BOD and HBOD tests; therefore, they were not considered in our paper. On-line instruments, if correctly designed and operated, can be used to measure variations in wastewater strength and test for the occurrence of toxic loads. Being able to rapidly measure oxygen demands can result in more efficient aeration strategies and plant operation. As the discussors are aware, however, the use of on-line systems in field applications has not always been successful (Iranpour *et al.*, 1997). On-line systems are also expensive to purchase, and while they can provide a low cost per sample (because they make frequent measurements), the location of the sampling point in the plant is typically fixed. In the future, the use of on-line systems could no doubt have a favorable effect on plant operation, but there will continue to be a need for grab measurements of BOD or HBOD at different locations in a wastewater treatment plant as well as a need for oxygen demand measurements of water and wastewater not in treatment plants.

Iranpour and Shao suggest that if the GC-HBOD test is seriously being proposed to replace the BOD_5 test, more research is necessary. Examples they cited were to define the success of the test with other substrates, such as acetic acid, over a wider range of concentrations, and make HBOD test measurements at different wastewater treatment plants. Such data are essentially already available, however, in the form of respirometric test data. The GC-HBOD test is a variation of respirometric techniques that have been around for some time now, and the usefulness of the respirometric tests has been well established. One of the primary advantages of the GC-HBOD test is that it is more cost effective for large numbers of samples than other respirometric tests. Thus, the type of data requested by the authors is essentially available, but it is agreed that results specific to the GC-HBOD would be helpful.

I thank Iranpour and Shao for their kind comments on the GC-HBOD test. It is hoped that they and other researchers and plant personnel will begin conducting the HBOD test on their wastewater and that such data could be used to help further establish the general applicability of the test. The BOD test has certainly been around for a long time, and its use is well entrenched in the wastewater treatment field, but that does not mean that it is not time to replace it with a faster and easier test based on modern technology.